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Functionalized benzazines as luminescent materials and components for optoelectronics

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Extensive research on the synthesis and application of benzazine derivatives for electronic devices, luminescent elements, photoelectric conversion elements, and image sensors has been published recently. This review covers article data obtained within the period 2012 – 2018 on the synthesis and optical properties of functionalized quinolines, quinoxalines and quinazolines. Arylvinyl, arylethynyl and (het)aryl derivatives of these benzazines, their photoluminescence and photoisomerization are discussed. Examples of photosensitive annelated, oligo- and polymeric benzazines and also coordination compounds with benzazine ligands are reviewed.
The bibliography includes 267 references.

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1. Introduction

Organic photosensitive materials have attracted much attention during the past two decades due to their applications in electronic and optoelectronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic solar cells (OSCs), sensors and many other, as indicated by numerous publications, including recent monographs.[1–5] In themed issue of Journal of Materials Chemistry dedicated to novel organic optoelectronic materials,[6] it is noted that the research and development of these materials belong to the cross-disciplinary science uniting chemistry, physics, materials science, electronics, nanotechnology and biology. Numerous reviews are devoted to particular aspects in the field of creation and use of new photosensitive materials. So, research of luminescent materials, including organic, for semiconductor lighting have been presented in recent review article.[7] Pushkarev and Bochkarev[8] analyzed organic electroluminescent materials, including organometallic and coordination compounds, and also the devices emitting in UV and IR ranges. Data on coordination compounds of lanthanides with the organic ligands applied in design of electroluminescent diodes are systematized in another work of the same group of authors.[9] Recent advances in creation of the white light-emitting diodes (WOLEDs) having a number of advantages are presented.[10,11] New design of WOLEDs which decreases the number of photolithographic cycles and reduces the production cost has been discussed.[12] Materials for highly effective phosphorescent OLEDs with low working voltage are described in a review.[13] Organic materials with nonlinear optical properties are presented.[14] Fundamental processes in organic photo cells are discussed.[15] Data on the physical mechanisms defining optoelectronic properties of high-performance organic materials, materials for organic solar cells and semiconductors are summarized.[16]

Organic compounds with expanded π-electronic system represent the basis of photosensitive materials. Among them the important place is taken by the structures including the electron donating and electron withdrawing groups connected through π-conjugated spacer, so-called push-pull systems. Molecular properties of such chromophores are defined by the ability of both donating and withdrawing fragments to participate in intramolecular charge transfer (ICT). Aromatic nitrogen-containing π-deficient heterocycles, such as pyridine, quinoline and their aza-analogues, are widely used as electron withdrawing part in the systems with ICT.[13] The capacity of these heterocycles to protonation and complexation at nitrogen atoms, as well as incorporation of groups capable to polymerization expands the application of such compounds for the creation of light sensitive materials.[10]

Six-membered heterocycles with two nitrogen atoms — diazines (pyridazine, pyrimidine and pyrazine) and their benzoanalogues (quinazoline and quinoxaline) — have already proved to be the key structural fragments in functionalized π-conjugated systems, and they are presented in a number of reviews.[17–22] Aryl, arylvinyl and arylethenyl derivatives of pyrimidines and coordination compounds based on them are most studied, optical, electrochemical properties, photoluminescence, scopes of application are discussed.[17–19] As for similar derivatives of quinoxaline and quinazoline, some data are provided in reviews,[19,20,22,23] mainly such compounds are described in articles and patents. Taking into account that intensive research of organic compounds as key components for OLEDs has begun with derivatives of quinoline,[24] the properties of which are close to those of quinoxaline and quinazoline, it was of interest to carry out the comparative analysis of derivatives of these three heterocycles. Other benzo(di)azines such as isoquinoline, cinnoline and phthalazine have been much less used in the field of chromophores for optoelectronic.

In the present review we tried to summarize the data on the synthesis and optical properties of functionalized benzazines (quinolines, quinoxalines and quinazolines) as luminescent materials and components of optoelectronic devices. This review focuses on arylvinyl- arylethynyl- and aryl(hetaryl)benzazines, their metal complexes, annulated derivatives as well are oligomer and polymer structures bearing these moieties for the period of 2012 – 2018. Non aromatic benzazinones and structures bearing extra rings will not be discussed here.

The following abbreviations are used in the current review:

AACC — activtion – alkynylation – cyclocendensation,
acac — acetylacetonate,
AIE — aggregation-induced emission,
Alq_3 — complex of aluminium with 8-hydroxyquinoline,
BAZnP — butylaminozirconium phosphate,
biimquin — bis(imidazol-1-yl)quinoxaline,
bpy — 2,2-bipyridine,
Bz — benzoyl,
bzq — benzo[*h*]quinoline,
cd — candela,
CPDT — cyclopentadithiophene,
CPL — circularly polarized luminescence,
Cy — cyclohexyl,
D – A – D — donor – acceptor – donor,
dbm — dibenzoylmethane,
DBU — 1,8-diazabicyclo[5.4.0]undec-7-ene,
dca — dicyanamide,
DCM — dichloromethane,
dfppy — difluorophenylpyridine,
DFT — density functional theory,
dmp — dipivaloylmethane,
DNA — deoxyribonucleic acid,
DPEPO — [bis(2-diphenylphosphoryl)]phenyl ester,
dpquin — dipyrido[3,2-*f*:2,3-*h*]quinoxaline,
dpquin$(COOH)_2$ — 6,7-dicarboxypyrido[3,2-*f*:2,3-*h*]quinoxaline,
DSSC — dye-sensitized solar cell,
EFISH — electric field induced second harmonic,
ESIPT — excited state intramolecular proton transfer,
EQE — external quantum efficiency,
FRET — Förster resonance energy transfer,
FTO — fluorine-doped tin oxide,
GM — units of Goeppert-Mayer, characterizing two-photon absorption ($1GM = 1 \times 10^{-50}$ cm^4 s photon^{-1}),
HEPES — 4-(2-hydroxyethyl)-1-piperazine ethanesulphonic acid,
hip — deprotonated 5-hydroxyisophthalic acid,
HOMO — highest occupied molecular orbital,
H_2qldc — quinoline-2,3-dicarboxylic acid,
3-Hqlc — quinoline-3-carboxylic acid,
ICT — intramolecular charge transfer,
ITO — indium tin oxide,

^{3}LC — triplet ligand-centred,
LLCT — ligand – ligand charge transfer,
LUMO — lowest unoccupied molecular orbital,
^{3}MLCT — triplet metal-to-ligand charge transfer,
MTPP-Br — methyltriphenylphosphonium bromide,
MW — microwave irradiation,
Naph — naphthyl,
NLO — non-linear optics,
OFET — organic field-effect transistor,
OLED — organic light-emitting diode,
OPV — organic photovoltaics,
OSC — organic solar cell,
OTFT — organic thin film transistor,
P3HT — poly(3-hexylthiophene),
PBS — sodium phosphate buffer,
PCE — power conversion efficiency,
PEDOT — poly(3,4-ethylenedioxythiophene),
phen — 1,10-phenanthroline,
PhOLED — phosphorescent light-emitting diode,
PMMA — polymethyl methacrylate,
PPi — pyrophosphate,
ppq1 — 2,4-diphenylquinoline,
PSC — polymer solar cell,
PSS — polystyrenesulfonate,
Py — pyridyl,
PVC — photovoltaic cell,
q — 8-hydroxyquinoline,
ql — quinolone,
qnz — quinazoline,
qox — quinoline *N*-oxide,
quin — quinoxaline,
RISC — reverse intersystem crossing,
rt — room temperature,
SMM — single molecule magnet,
TADF — thermally activated delayed fluorescence,
TCE — 1,1,1-trichloroethane,
TDDFT — time-dependent DFT,
Th — thienyl,
TFA — trifluoroacetic acid,
TIPS — triisopropylsilyl,
TMS — trimethylsilyl,
TPA — two-photon absorption,
TPEF — two-photon-excited fluorescence,
Vs — volatile solids,
WOLED — white organic light-emitting diode,
Φ_F — luminescence quantum yield.

2. Arylvinyl-, arylethynyl- and (het)arylbenzazines

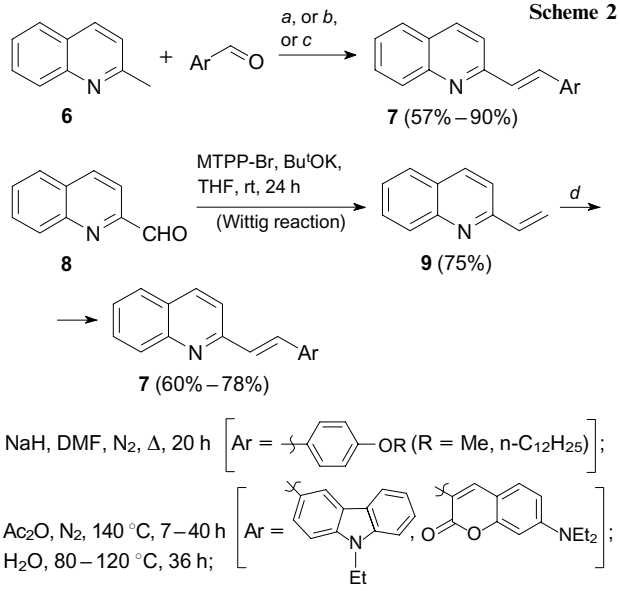
2.1. Synthesis, photoluminescence and photoisomerization of arylvinylbenzazines

Condensation of 2-methyl-substituted benzazines **1** with arylcarboxaldehydes **2** or arylcarboxdialdehydes **4** under basic or acidic conditions represents traditional synthetic approaches to arylvinylbenzazines **3**, **5** (Scheme 1) (see †).[22]

2.1.1. Arylvinylquinolines

2-Arylvinylquinoline chromophores are generally obtained exclusively as their *E* stereoisomers. Most of the time, they are obtained by functionalization of already formed quinoline fragment. 2-Arylvinylquinoline derivatives **7** can be easily prepared by condensation of arylcarboxaldehydes and 2-methylquinoline derivatives (**6**) (Scheme 2, top reaction). This reaction can be performed in basic media,[25] in acetic anhydride[26–28] or even in water without the presence of any catalyst.[29] These derivatives can also be obtained in two steps from 2-quinolinecarboxaldehyde (**8**) (Scheme 2, bottom reaction).[30] The first step consists in a Wittig reaction with methyltriphenylphosphonium bromide (MTPP-Br) to obtain 2-vinylquinoline **9**. This intermediate can be involved in a palladium catalyzed Heck cross-coupling reaction with aryl iodides to yield (*E*)-2-arylvinylquinolines **7**.

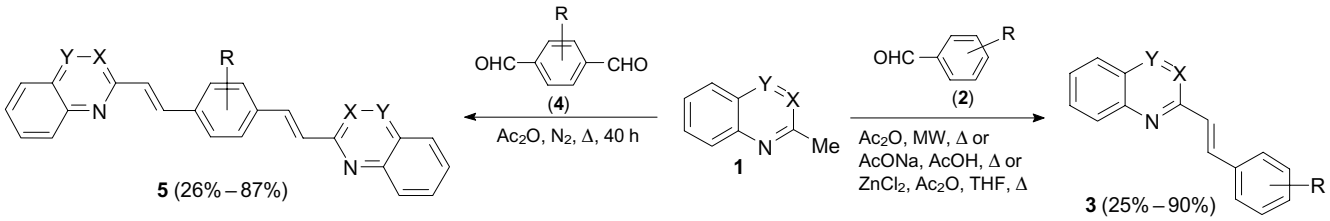
Scheme 2



2-Styrylquinoline derivatives **12** can also be obtained from *ortho*-iodoanilines **10** and 2-*trans*-styryl propargyl alcohols **11** by domino synthesis initiated by a Sonogashira

† In this review the numbering order of compounds corresponds to the sequence of images of structural formulas.

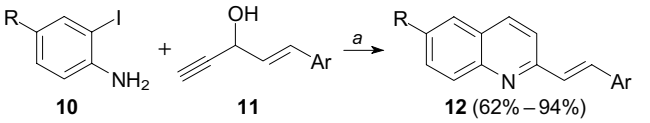
Scheme 1



1, **3**, **5**: X = CH, N; Y = N, CH; R = H, OMe

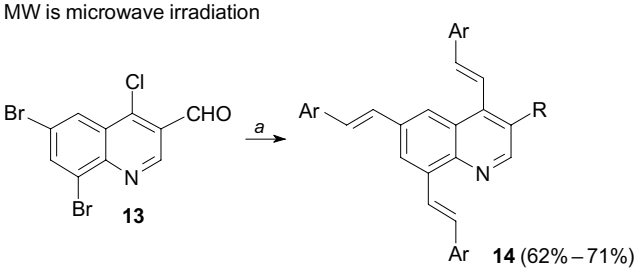
coupling and concluded by a base catalyzed propargyl alcohol – enone isomerization (Scheme 3, top reaction).[31] Sukuzi cross-coupling reaction with styrylboronic acids on 6,8-dibromo-4-chloroquinoline derivative **13** affords 4,6,8-tristyrylquinoline chromophores **14** (Scheme 3, bottom reaction).[32]

Scheme 3



10 **11** **12** (62% – 94%)

(*a*) $Pd(PPh_3)_2Cl_2$ (2 mol.%), CuI (1 mol.%), DBU (2 equiv.), THF, MW, 120 – 150 °C, 30 min; R = H, CF_3, CN; Ar = $C_6H_4NMe_2$-4; MW is microwave irradiation

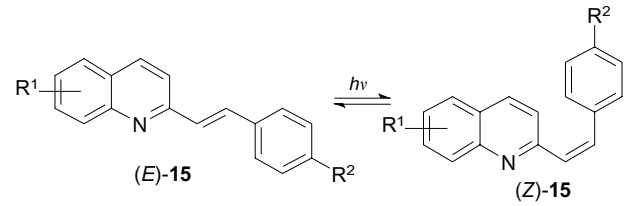


13 **14** (62% – 71%)

(*a*) ArCH=CHB(OH)$_2$ (3.5 eqiuv.), $Pd(PPh_3)_2Cl_2$, PCy_3, K_2CO_3, dioxane – water (4 : 1 vol.%), 90 °C, 3 h; Ar = Ph, C_6H_4F-4, C_6H_4OMe-4; Cy is cyclohexyl

As shown before, the majority of synthetic routes to 2-arylvinylquinoline lead to the *E* isomer. However reversible $E \rightarrow Z$ photoisomerization of compounds **15** is generally possible (Scheme 4).[33 – 35] The photoisomerizable 2-styrylquinoline fragment can be incorporated into methacrylic polymers as side chain with potential photonic applications.[36, 37]

Scheme 4

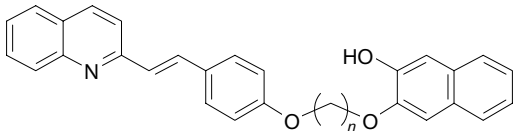


(*E*)-**15** (*Z*)-**15**

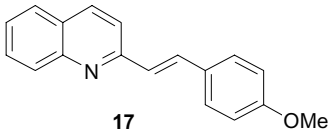
R^1 = 6-OMe, 4-OH, 8-  ; R^2 = H, NO_2, Me

Budyka *et al.*[38] have designed bichromophoric dyads **16** bearing 2-styrylquinoline and 2-naphthol chromophoric groups as photonic molecular switches. Whereas no significant interactions between chromophores are observed in ground state, Förster resonance energy transfer (FRET) occurs from the naphthol to the styrylquinoline fragment, quenching the emission of the naphthol fragment. In this structure, the *E*/*Z* photoisomerization of the styrylquinoline fragment in the dyads **16** occurs with the same quantum yield (~0.5) as in model methoxystyrylquinoline **17** irrespective of the methylene bridge length. The photoisomerization into the non-emissive *Z* isomer leads to enhancement of the naphthol fragment emission.

Structures 16, 17



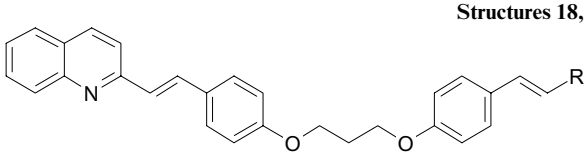
n = 2 – 5 **16**



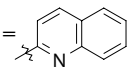
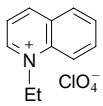
17

The same team[39] has designed also a monochromophoric dyad **18** bearing two 2-styrylquinoline fragments leading to possible isomers of **19**: *EE*, *EZ*, *ZE* and *ZZ*. When the polyethylene linker incorporates an *o*-xylylene bridge (compound **20**), along with photoisomerization, [2 + 2]-photocycloaddition occurs affording tetrasubstituted cyclobutane (Scheme 5).[40] When one of the two 2-styrylquinolines is replaced by a styrylquinolinium fragment (dyad **19**),[41 – 43] photoisomerization of the styrylquinoline fragment occurs only one way: it goes in *cis* → *trans* direction whereas *trans* → *cis* isomerization is quenched because of competing FRET to the styrylquinolinium fragment. Nevertheless, *trans* → *cis* photoisomerization can be observed upon protonation of the styrylquinoline fragment. Therefore, the cycle protonation → *trans* – *cis* photoisomerization (reversible) → deprotonation → *cis* – *trans* photoisomerization (one-way) — can be repeated and used for design of controlled molecular photoswitches.

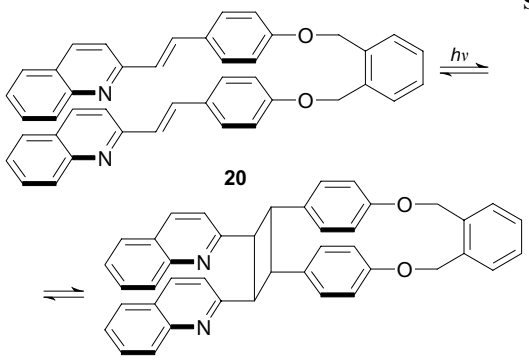
Structures 18, 19



18, **19**

R =  (**18**),  (**19**)

Scheme 5



The particular attention was paid to heterogeneous catalysis when styrylquinolinium fragment has been grafted on quantum dot *via* isothiouronium anchor (compound **21**, Figure 1).[44, 45] Compared to the free fragment, *E* – *Z* photo-

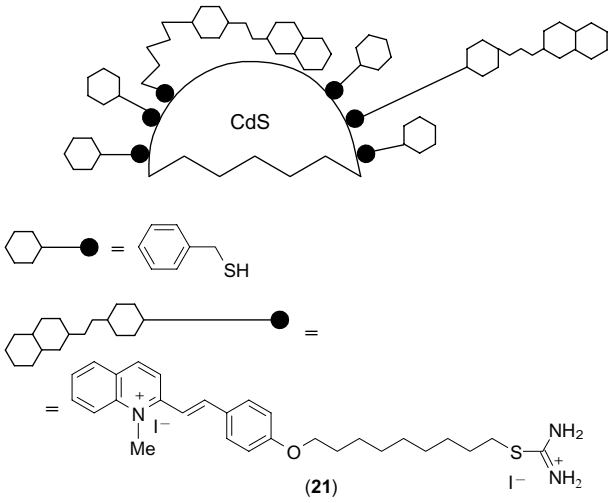


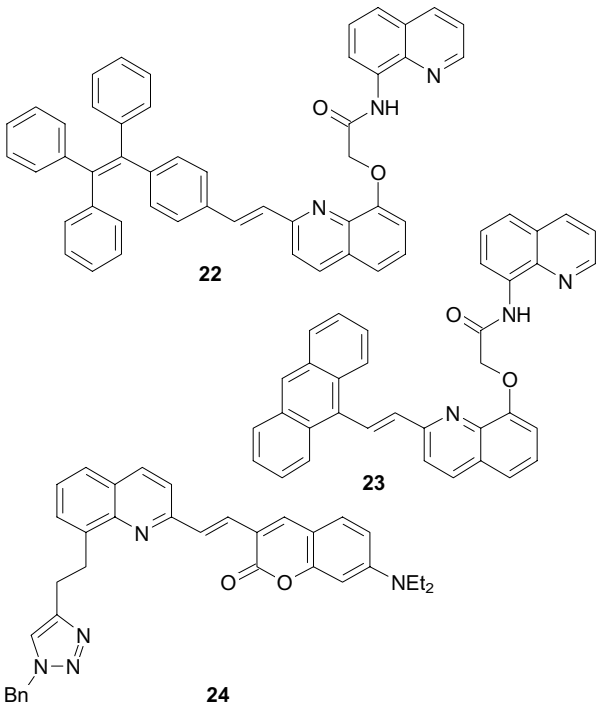
Figure 1. Styrylquinoline **21** grafted on quantum dot.[45]

isomerization of the styrylquinolinium fragment grafted on quantum dot was suppressed and its photodestruction was accelerated.

Xiong *et al.*[26] have designed two styrylquinoline chromophores **22** and **23** bearing tetraphenylethene and anthracene fragments. These compounds, nearly non emissive in DMSO/water system with low water content (f_w < 30%), exhibit aggregation induced emission (AIE). These compounds have been used as selective fluorescent probes of Cu^{2+} in aqueous solution and test strips (ON-OFF probe).

Wu *et al.*[46] have designed a styrylquinoline chromophore **24** bearing a coumarin fragment. This compound exhibits an emission at 516 nm in MeCN/water mixture and

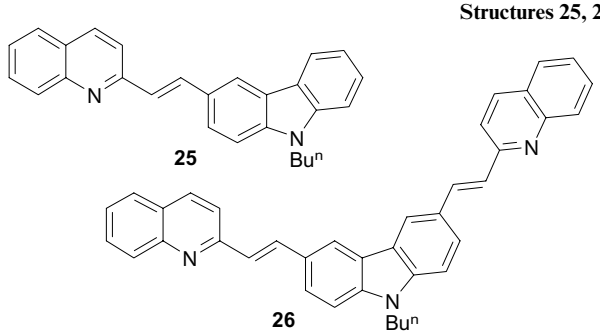
Structures 22 – 24



was used as selective ratiometric probe for Zn^{2+} in living cells.

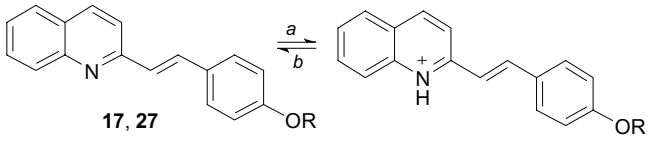
Li *et al.*[28] have designed carbazole derivatives **25** and **26**. These compounds exhibit two-photon absorption in DMF solution [**25**: σ_{TPA} = 81 GM (units of Goeppert-Mayer), **26**: σ_{TPA} = 364 GM measured by the two-photon excitation fluorescence (TPEF) method] and in doped polymethyl methacrylate (PMMA) thin film (**25**: σ_{TPA} = 470 GM, **26**: σ_{TPA} = 621 GM measured by the Z-Scan method).[47] Three-dimensional optical data storage experiments have been performed proving that these chromophores are well-suited as high-density optical information storage.

Structures 25, 26



Yuang *et al.*[25] have reported the solid state emission of alkoxy substituted styrylquinoline derivatives **17** and **27** (Scheme 6). These compounds remain emissive upon reversible protonation with a remarkable red shift (λ_{em} = 570 – 574 nm). Whereas the neutral forms exhibit negligible emission change upon mechanical force, remarkable piezochromism is observed for the protonated chromophores.

Scheme 6

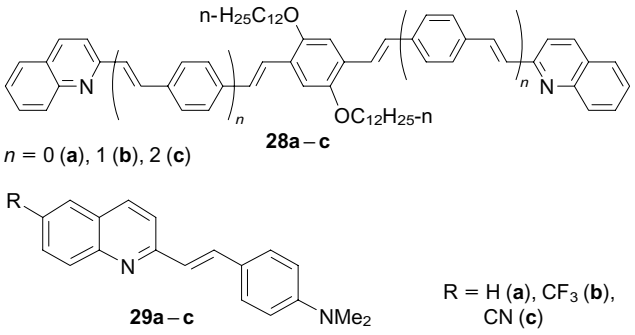


(*a*) H^+; (*b*) base ; R = Me (**17**), n-$C_{12}H_{25}$ (**27**)

Flores-Noria *et al.*[30] have designed phenylenevinylenequinoline derivatives **28a – c**. These compounds are highly luminescent in $CHCl_3$, THF and toluene. A push-pull effect is only observed for compound **28a,** whereas for **28b** and **28c** no significant effects of the quinoline fragment are observed either spectroscopically, or electrochemically, or theoretically. Compound **28a** is the most emissive (in $CHCl_3$ λ_{em} = 499 nm, luminescence quantum yield Φ_F = 0.64) making it suitable for optoelectronic devices.

Cinar *et al.*[31] have designed dimethylamino substituted styrylquinoline chromophores **29a – c**. In addition to strong emission solvatochromism characteristic of push-pull luminophores, these compounds exhibit a pH-sensitivity and 'ON-OFF-ON' emission profiles. Indeed the emission of these compounds can be quenched by addition of one proton (protonation of the quinoline ring) and blue shifted with respect to the free base upon a second protonation (amino group).

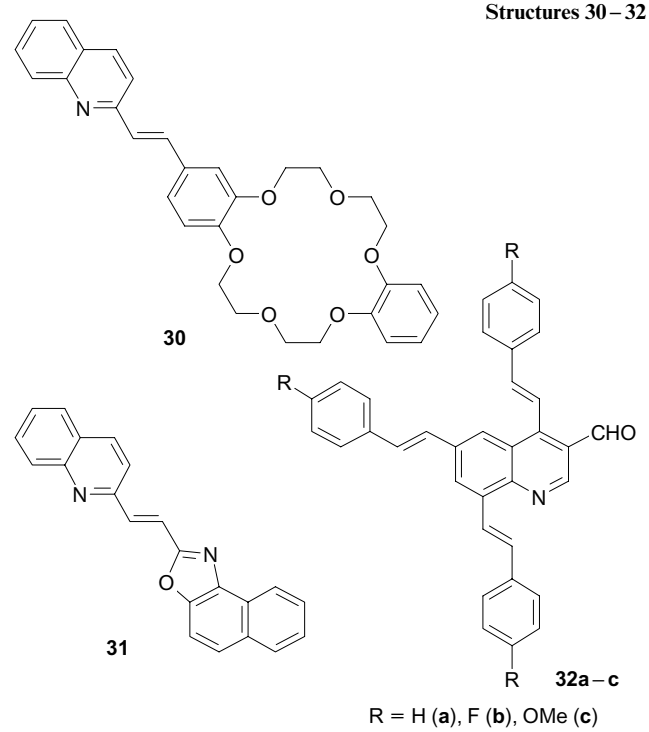
Structures 28, 29



Tzeli *et al.*[48] have designed theoretically a styrylquinoline derivative **30** bearing a benzo-18-crown-6-ether fragment. Due to the reversible sensitivity of photophysical properties (absorption and emission) to the presence of H^+, Ca^{2+} and the possibility of reversible photoisomerization, the authors propose the use of this chromophore to build logic gates.

R.P.Zanocco *et al.*[49] have designed chromophore **31**. This compound exhibits intense white light emission based on proton transfer in solvent mixture including at least a strong hydrogen-bonding solvent such as MeOH (for 17% of DMSO, the chromacity coordinates are 0.33, 0.35 and quantum yield is 0.31).

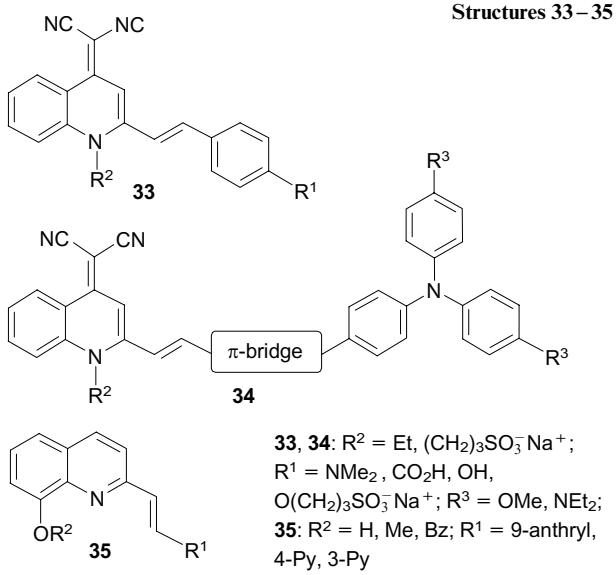
Structures 30 – 32



Mphahlele *et al.*[32] have reported 4,6,8-tristyrylquinoline derivatives **32a – c**. Whereas chromophore **32a** exhibits yellow-green luminescence (λ_{em} = 529 nm, Φ_F = 0.06) in DCM solutions, the substitution by electron-donating fluorine or methoxy group leads to blue shifted emission with enhanced quantum yield (**32b**: λ_{em} = 420, 430 nm, Φ_F = 0.17 and **32c**: λ_{em} = 370, 470 nm, Φ_F = 0.21).

Styrylquinolines **33** and **34** with expanded π-electronic system, bearing quinoline – malonodinitrile as new building block were synthesized and studied as fluorophores with aggregation-induced emission (AIE) in red and near IR ranges.[50] The authors summarized recent advances and discussed potential application of such derivatives containing donating groups as agents for optical biovisualization *in vivo*. Incorporation of different substituents (R, R^1, R^2), including sulfonate groups, makes compounds **33**, **34** suitable both for preparation of AIE-active nanoparticles, and for drug delivery using nanoparticles. New strategy of molecular design for generation of nanoagregates of different forms of these compounds possessing longwave emission was presented.

Structures 33 – 35

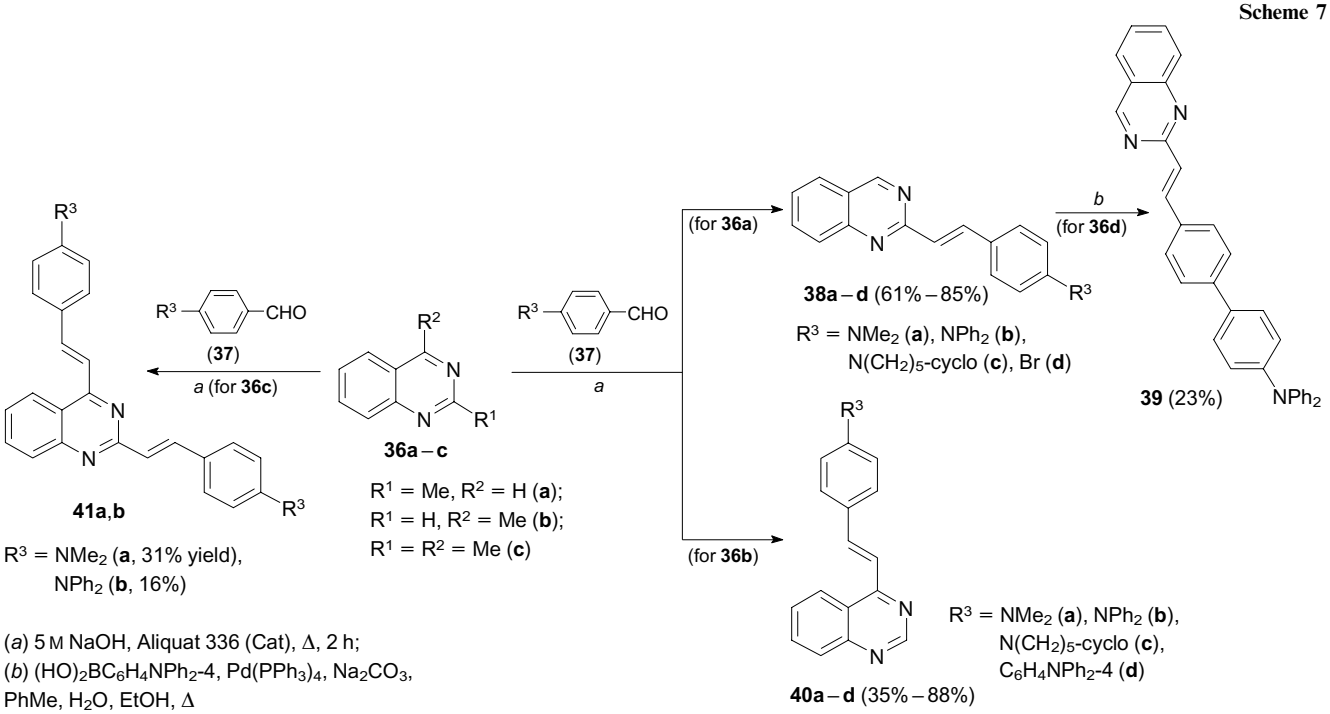


In continuation of research on 8-hydroxyquinoline derivatives, the synthesis and photoluminescence of styrylquinolines **35**, bearing ether groups at position 8 of quinoline unit and anthracene or pyridine fragments (R^1) was described.[51 – 53] It was shown that replacement of phenol hydrogen with methoxy group leads to the increase in fluorescence quantum yield from 0.067 to 0.25 for **35** (R^1 = 9-anthryl), to 0.41 for **35** (R^1 = 4-Py) and to 0.37 for **35** (R^1 = 3-Py).

2.1.2. Arylvinylquinazolines

Only few examples of arylvinylquinazoline chromophores have been described so far in the literature. 2- and 4-Arylvinylquinazolines **38a – d** and **40a – d** as well as 2,4-diarylvinylquinazoline **41a**,**b** can be obtained by Knoevenagel condensation from the corresponding methylquinazoline and benzaldehyde derivatives exclusively as *E* isomers (Scheme 7).[54] The reaction can be performed with electron-donating substituted benzaldehyde and it should be noted that 4-bromobenzaldehyde reacts only with 2-methylquinazoline. Bromo derivative **38d** can be involved in a Suzuki cross-coupling reaction to obtain biphenylenevinylene derivative **39**. The methylquinazoline intermediates **36** are not commercially available but can be obtained either from chloro derivatives by palladium catalyzed coupling with trimethylaluminium [4-methylquinazoline (**36b**) and 2,4-dichloroquinazoline (**36c**)][55] or by cyclization reaction

Scheme 7

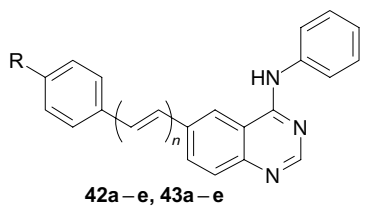


from 2-bromobenzaldehyde and acetamidine hydrochloride [2-methylquinazoline (**36a**)].[56]

2-Arylvinylquinazolines **38a – c** and **39** exhibit green emission in CH_2Cl_2 (λ_{em} = 520 – 545 nm), diphenylamino derivatives exhibit the highest fluorescence quantum yield (**38b**: Φ_F = 0.61, **39**: $\mathbf{F}_F$ = 0.65). It should be noted that biphenylenevinylene derivative **39** shows a significantly increased Stokes shifts ($\Delta\nu$ = 7796 cm^{-1}) relative to its phenylenevinylene analogue **38**. 4-Arylvinylquinazoline analogues **40a – d** exhibit significantly red-shifted emission (λ_{em} = 548 – 610 nm) but reduced quantum yield (up to 0.25 for **40b**). 4,6-Diarylvinylquinazolines **41a**,**b** exhibit emission maxima red-shifted with respect to their 2-arylvinylquinazoline analogues and blue-shifted in comparison with their 4-arylvinylquinazoline analogues but with low emission quantum yield (Φ_F = 0.02 – 0.09). All of these compounds exhibit strong emission solvatochromism, halochromism and are potential NLOphores.

Dhuguru and coworkers have described 6-arylvinyl- and 6-arylbutadienylquinazoline chromophores **42a – e** and **43a – e** obtained by Heck cross-coupling reaction from 6-iodoquinazoline precursors.[57] Bromopyridines were involved into Suzuki cross-coupling reaction for the arylalkenylation of the ring.[58] All the compounds are luminescent in $CHCl_3$ with good to moderate quantum yield (Φ_F = 0.02 – 0.57). In the arylvinylquinazoline series **42a – e**, the most red shifted absorption and emission are observed for the dimethylamino derivative **42a** (λ_{abs} = 381 nm and λ_{em} = 495 nm) and the nitro chromophore **42e** (λ_{abs} = 372 nm and λ_{em} = 539 nm). A red shift in absorption and emission is observed for butadiene derivatives **43a – e** with respect to their vinyl analogues **42a – e**. For all these compounds emission is attributed to ICT (from electron donating group to the quinazoline fragment in case of **42a – c** and **43a – c** and from the amino group to the electron-withdrawing substituent for **42d**,**e** and **43d**,**e** where the quinazoline fragment acts as a π-conjugated linker).

Structures 42, 43



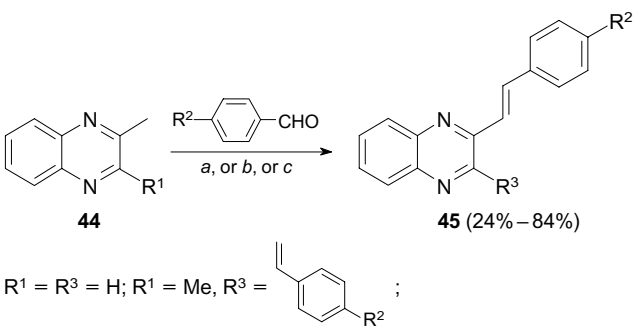
42a – e, 43a – e

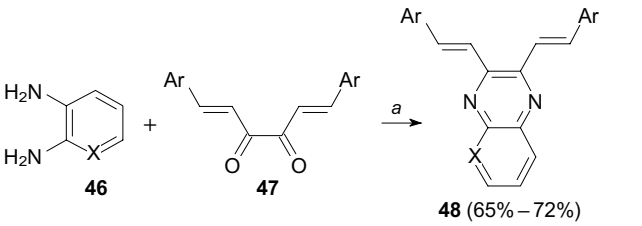
R = NMe_2 (**a**), OMe (**b**), H (**c**), CN (**d**), NO_2 (**e**); *n* = 1 (**42**), 2 (**43**)

2.1.3. Arylvinylquinoxalines

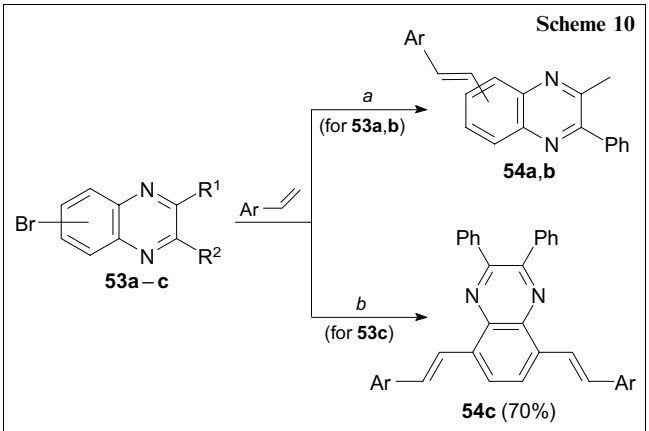
Various methods can be used to obtain 2-arylvinyl- and 2,3-diarylvinylquinoxaline derivatives, all leading exclusively to the *E*-isomers. The first one consists in Knoevenagel condensation between commercially available 2-methyl or 2,4-dimethylquinoxaline **44** and the corresponding arylcarboxaldehyde (Scheme 8, top reaction). Various conditions have been described; aqueous sodium hydroxide with Aliquat 336 as phase transfer catalyst,[59] NaH (Ref. 60) or Bu^tOK (Ref. 61) in THF. Another strategy consists in the condensation of a butanedione **47** bearing two arylvinyl substituents with an *o*-phenylenediamine derivative **46** (Scheme 8, bottom reaction).[62] Recently arylvinylquinoxalines **52** have been obtained by palladium-catalyzed C – H alkenylation of quinoxaline *N*-oxide intermediates **50** and subsequent reduction of derivatives **51**.[63,64] Compound **52** was synthesized from *N*-oxide **50** by iodine-catalyzed direct alkenylation with styrene (Scheme 9). Direct arylalkenylation of furazan[3,4-*b*]pyrazines was presented as new approach to CH-functionalization.[65] Synthesis of 6-styryl-substituted 1,6-dihydropyrazine derivatives by reaction of 6-hydroxy adducts with styrylboronic acid was presented.[66]

Scheme 8





Scheme 10



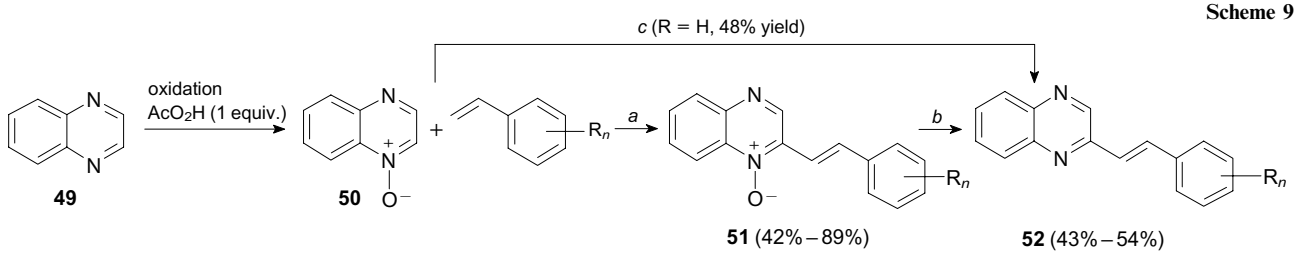
6-Bromo-, 7-bromo- and 5,8-dibromoquinoxaline derivatives **53a – c** can be involved in Heck cross-coupling reaction to yield the corresponding arylvinylquinoxalines **54a – c** (Scheme 10).[67, 68]

Achelle *et al.*[59, 69, 70] have described a series of 2-arylvinyl quinoxalines **55 – 59**. Compounds **58a – c** and **59a – d** have been obtained respectively by Suzuki and Sonogashira cross-coupling reactions from compound **55b**. Amino derivatives **55d – f** exhibit yellow emission with high fluorescence quantum yield ($\Phi_F = 0.59 - 0.70$) in DCM with strong positive emission solvatochromism in aprotic solvent of increasing polarity. Upon addition of trifluoroacetic acid to solutions of **55d**,**e**, a dramatic hypsochromic shift of the emission band is observed due to the protonation of the amino electron-donating group. In the case of compounds **56**, **58a** and **59b**, on the other hand, a progressive emission quenching attributed to the protonation of the quinoxaline fragment is observed. Biphenylenevinylene derivatives **58b**,**c** exhibit orange luminescence in DCM with lower fluorescence quantum yield ($\Phi_F = 0.14 - 0.35$) but extended emission solvatochromic range relative to their phenylenevinylene analogues **55d**,**e**. Compound **58a** exhibits blue luminescence with high fluorescence quantum yield ($\Phi_F = 0.42$). In compounds **59b – d** the addition of a triple bond between the two phenylene linkers leads to a red shift of absorption and emission relative to their analogues **58a**,**b**, and red emission was observed for **59c** ($\lambda_{em} = 647$ nm, $\Phi_F = 0.07$). The second order NLO response of compounds **55b** and **59c**,**d** has been measured by the electric field induced second harmonic generation method (EFISH) and moderate $\mu\beta$ values (respectively 300, 280 and 200×10^{-48} esu) have been measured in $CHCl_3$. The NLO response of compound **55d** has been also calculated theoretically by means of quantum chemical first principles calculations and calculated NLO response reproduce well the experimental value.[71]

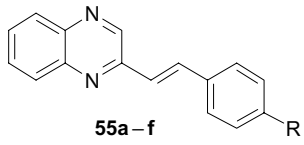
When comparing the photophysical properties of quinolin-2-yl, quinoxalin-2-yl, quinoxalin-4-yl and quinazolin-2-yl derivatives **29a**, **38a**, **40a** and **55d**, all bearing *N*,*N*-dimethylaminostyryl fragments (Table 1), it appears that the quinazoline derivarive **55d** exhibits the most red-shifted emission and the highest fluorescence quantum yield in CH_2Cl_2.

On the other hand, comparing the photophysical properties of *N*,*N*-diphenylamino substituted quinoxaline derivatives (**55f**, **58c** and **59d**), the extension of the conjugation by adding a second phenylene fragment in the π-conjugated fragment results in a significant blue shift of absorption and

Scheme 9

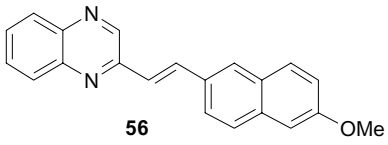


Structures 55 – 60

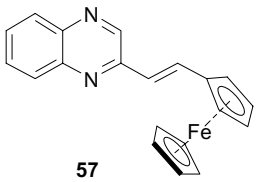


55a – f

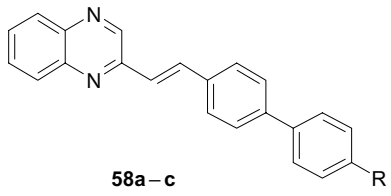
R = Cl (**a**), Br (**b**), SMe (**c**), NMe_2 (**d**), $N(CH_2)_5$-cyclo (**e**), NPh_2 (**f**)



56

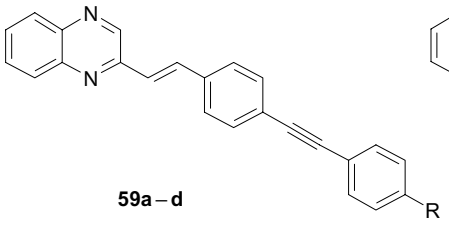


57



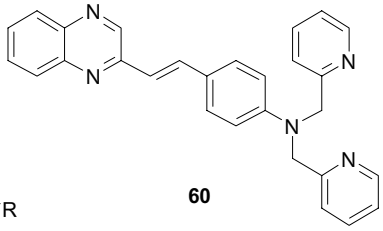
58a – c

R = OMe (**a**), NMe_2 (**b**), NPh_2 (**c**)



59a – d

R = H (**a**), OMe (**b**), NMe_2 (**c**), NPh_2 (**d**)



60

Table 1. Photophysical properties of *N*,*N*-dimethylamino- and *N*,*N*-diphenylaminostyrylbenzo(di)azine derivatives in CH_2Cl_2.

Compound	λ_{abs} /nm	ε /mM^{-1} cm^{-1}	λ_{em} /nm	Φ_F	Ref.
29a	392	27.0	512	0.12	31
38a	395	26.6	536	0.21	54
40a	433	18.0	548	0.07	54
55d	427	22.4	570	0.59	59
55f	421	25.4	565	0.67	59
58c	393	36.4	632	0.35	59
59d	403	35.7	630	0.37	68

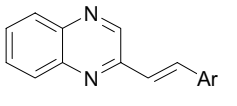
red shift in emission associated with a reduction of quantum yield. The incorporation of a triple bond between the two phenylene fragments (compounds **58c**, **59d**) does not significantly modify the photophysical properties.

The same group has designed dipicolylamine fluorophore **60**. This compound exhibits yellow emission in MeCN (λ_{em} = 593 nm, Φ_F = 0.15).[55] As shown by the previous series of compounds positive emission solvatochromism is observed in aprotic solvents as well as pH sensitivity with a dramatic red shift of absorption band and emission quenching. Moreover a significant blue shift of the emission has been observed in the presence of Zn^{2+} (and to a lesser extend with Cd^{2+}) due to complexation of the dipicolylamine fragment reducing its electron-donating character and consequently the ICT to the chromophore.

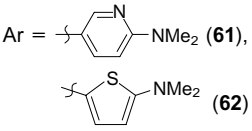
Zhu *et al.*[72] have designed 2-arylvinylquinazolines **61**, **62** and arylbutadienequinoxaline **64**. In EtOH, **61** exhibits green luminescence with moderate fluorescence quantum yield (λ_{em} = 568 nm, Φ_F = 0.22). In the same solvent, the emission quantum yield is much lower for **55d**, **62** and **63**. As far as **62** and **63** are compared, a significant red shift is observed for the butadiene derivative **63** (λ_{em} = 583 nm). These compounds have been used for *in vivo* florescence detection of cerebral tau protein in Alzheimer's models.

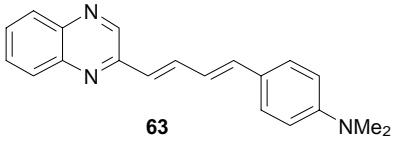
Zhao *et al.*[60] have described aminostyrylquinoxaline chromophores **64**, **65** exhibiting yellow emission in DCM with a bathochromic shift of around 20 nm for disubstituted compounds **65** relative to their monosubstituted analogues **64**. As shown in other series of compounds, strong emission solvatochromsim and pH sensitivity have been described. In addition, the chromophore **65b** exhibits reversible mechanofluorochromism: crystals exhibit yellow emission at 542 nm, red shifted to carmine emission at 592 nm upon grinding. Yellow emission can be recovered after fuming with DCM vapours.

Structures 61 – 65

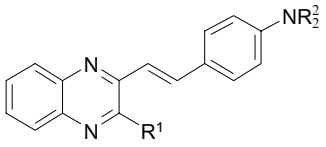


61, **62**

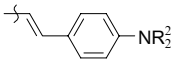
Ar =  (**62**)



63

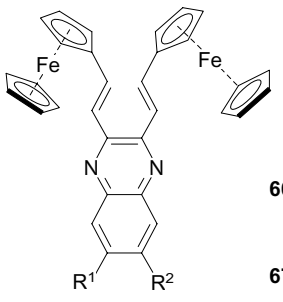


64a,**b**; **65a**,**b**

R^2 = Me (**a**), Ph (**b**);
64: R^1 = H;
65: R^1 = 

Independently, Chauhan *et al.*[73] and Senthilkumar *et al.*[74] have described a series of 2,3-di(ferrocenylstyryl)-quinoxalines **66**, **67**. Compounds **66a**,**c**,**f**,**g** were exploited as photosensitizers in TiO_2-based dye-sensitized solar cells and compounds **66c**,**g** were revealed to be the most efficient with overall conversion efficiency of 3.38% and 4.42% respec-

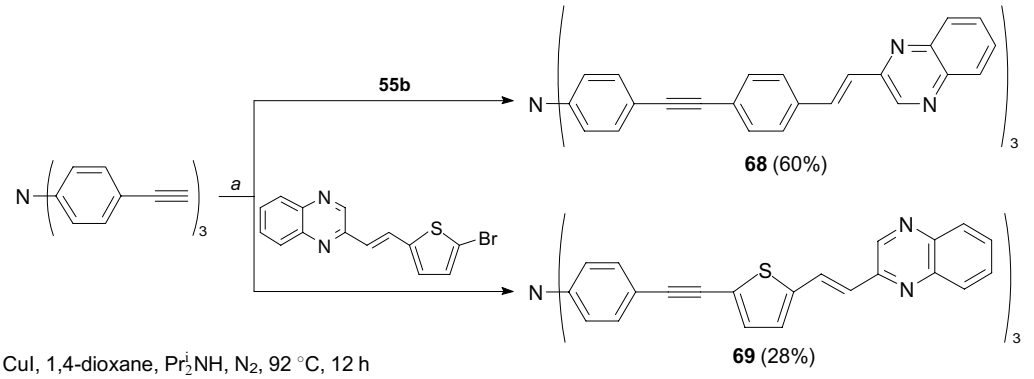
Structures 66, 67



66a – g, **67**

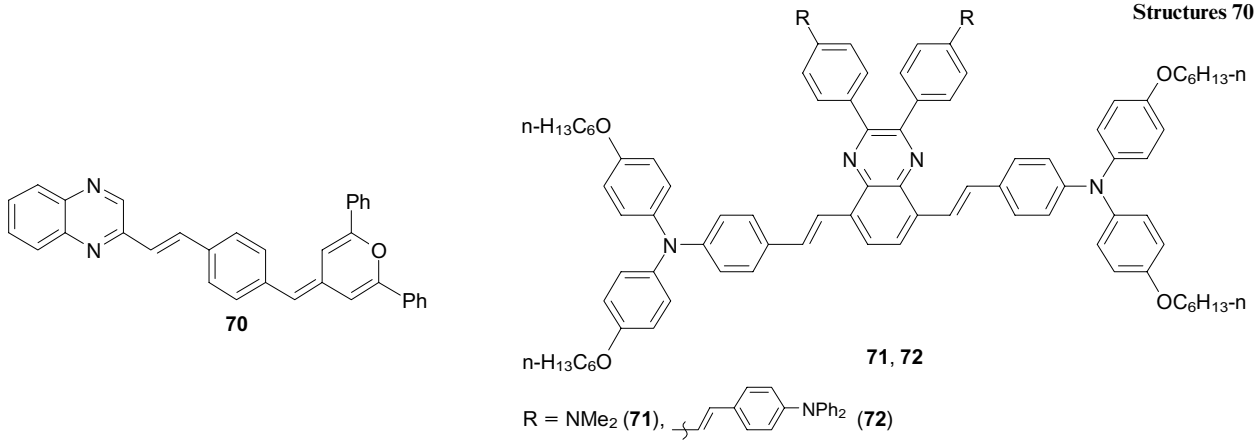
66: R^2 = H: R^1 = H (**a**), CF_3 (**b**), NO_2 (**c**), CN (**d**), OMe (**e**), Cl (**f**), CO_2H (**g**);
67: R^1 = R^2 = OMe

Scheme 11



(*a*) $Pd(PPh_3)_4$, CuI, 1,4-dioxane, Pr^i_2NH, N_2, 92 °C, 12 h

Structures 70 – 72



tively. The second order NLO properties of chromophores **66a – e** and **67** have been also studied by the EFISH method and negative $\mu\beta$ values up to -960×10^{-48} esu have been measured. Surprisingly high and stable second harmonic generation response in composite polymeric film has been also reported for **66b** (d_{33} = 5.27 pm V^{-1} in PMMA).

Cvejn *et al.*[75] have designed the tripodal chromophores **68** and **69** with peripherical vinylquinazoline fragments (Scheme 11). These compounds have been obtained in moderate yield by triple Sonogashira cross-coupling reaction between tris(4-ethynylphenyl)amine and bromoarylvinylquinoxaline intermediates. Compounds **68**, **69** exhibit orange-red photoluminescence with high Stokes shifts (> 6700 cm^{-1}) in DCM (**68**: λ_{em} = 630 nm, Φ_F = 0.37, **69**: λ_{em} = 617 nm, Φ_F = 0.38), strong emission solvatochromism and two-photon absorption properties with interesting two photon cross section (**68**: σ = 239 GM at 780 nm, **69**: σ = 416 GM at 760 nm).

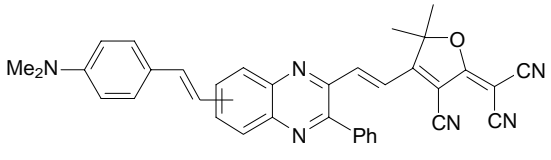
Achelle *et al.*[76] have described the pyranylidene derivative **70**. This compound described as a potential 2nd order NLO chromophore exhibits a significantly enhanced blue shifted emission upon protonation (λ_{em} = 479 nm, Φ_F = 0.25).

Chang *et al.*[68] have designed multisubstituted quinoxaline chromophores **71** and **72**; chloroform solutions and thin films of these compounds exhibit yellow photoluminescence. Photovoltaic cells (PVCs) and OLEDs were fabricated from **71** and **72** by solution processing. While PVCs with a structure of ITO/PEDOT : PSS/**71** or **72** : $PC_{71}BM$/Al ($PC_{71}BM$ is [6,6]-phenyl C_{71} butyric acid methyl ester) show power conversion efficiencies of 0.31% and 0.45%, respectively, OLEDs with a structure of ITO/PEDOT : PSS/**71** or **72**/LiF/Al exhibit a maximum luminance (efficiency) of 7.42 cd m^{-2} (0.034 cd A^{-1}) and 48.84 cd m^{-2} (0.032 cd A^{-1}) with a turn-on voltage of 3.6 and 2.4 V, respectively.

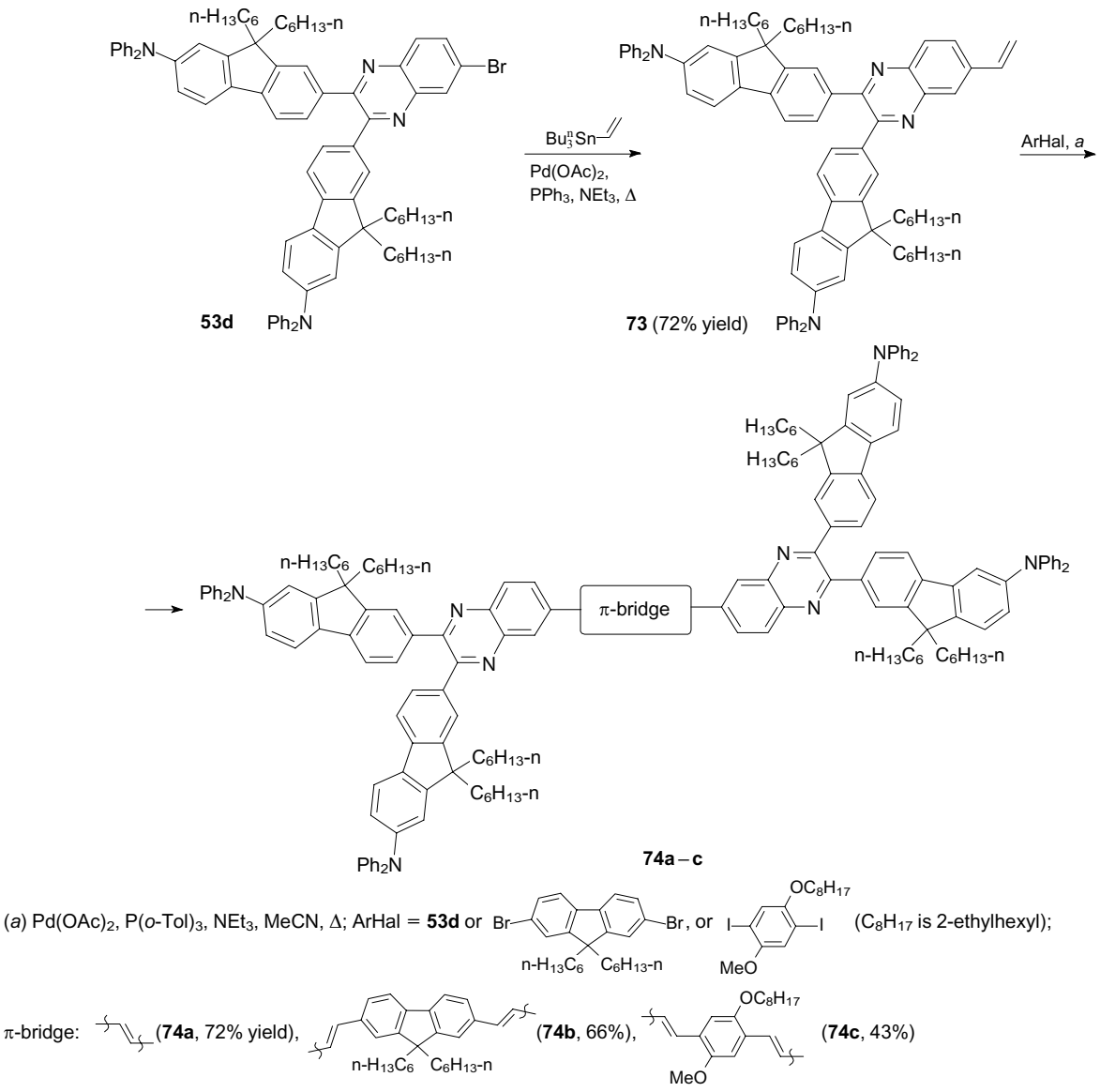
Lin *et al.*[77] have described three other multibranched quinoxaline chromophores **74a – c**. 6-Bromoquinoxaline **53d** is able to react with tributylvinyltin under conditions of Stille cross-coupling reaction leading to 6-vinylquinoline **73**, which was used in Heck cross-coupling with aryl bromides for the synthesis of styryl derivatives **74a – c** (Scheme 12). These compounds exhibit cyan luminescence in toluene as well as two-photon absorption with high cross section (**74a**: $\sigma \approx 1250$ GM, **74b**: $\sigma \approx 1680$ GM, **74c**: $\sigma \approx 2300$ GM). Optical power limiting properties of compound **74b** have been also demonstrated.

Kalinin *et al.*[67] have proposed two push-pull chromophores **75** and **76** in which the quinoxaline linker plays the role of π-conjugated linker. Red shifted absorption is observed for the isomer **76** (λ_{abs} = 600 nm). DFT calculation has shown that this chromophore can be considered as

Structures 75, 76



Scheme 12



a promising candidate for the development of 2nd order NLO materials.

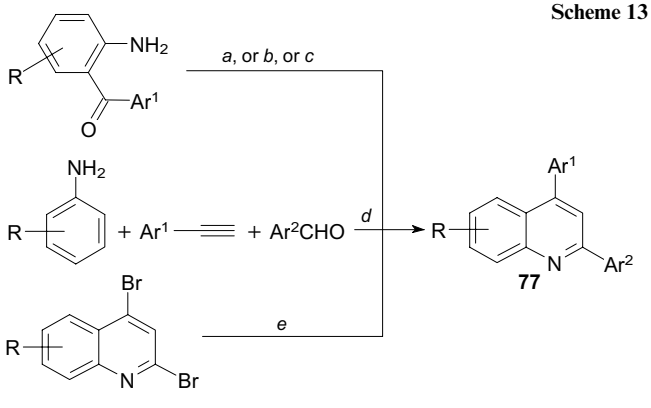
As shown with these examples, arylvinylbenzo(di)azine derivatives have been extensively studied for their luminescence, NLO and photovoltaic properties.

2.2. Synthesis and photoluminescence of arylethynyl- and aryl(hetaryl)benzazines

2.2.1. (Het)arylquinolines

2,4-Diarylquinoline chromophores **77** are generally obtained by condensation reaction leading to the construction of the quinoline core. Various methods have been proposed including Friedländer condensation,[78] condensation of arylalkynes and *o*-aminobenzophenone derivatives,[79] or multicomponent reaction between arylaldehyde, anilines and arylalkynes (Scheme 13).[80] The Suzuki cross-coupling reaction has been commonly used to afford 2-aryl-, 2,4-diaryl- or 4,6,8-triarylquinolines from 2-bromo, 2,4-dibromo and 6,8-dibromo-4-chloroquinoline derivatives, respectively.[32, 78, 81] Quinoline boronic ester have been also involved in Suzuki cross-coupling to obtain 5(6)-arylquinoline chromophores.[82]

Scheme 13

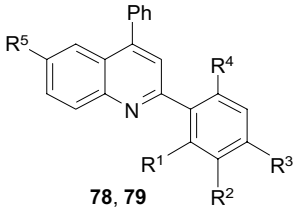


(*a*) $AcAr^2$, *m*-cresol, Ar, 145 °C, DPP (DPP = $(PhO)_2P(O)OH$), 68% – 99% yield (Friedländer reaction); (*b*) $Ar^2C{\equiv}CH$, $Ru_3(CO)_{12}$, HBF_4 (1.5 mol.%), PhMe, 150 °C, 2 h (50% – 63%); (*c*) $Ar^2C{\equiv}C$, $In(OTf)_3$, MW, 110 °C, 5 min (30% – 46%); (*d*) $NbCl_5$ (0.5 equiv.), MeCN, rt, 96 h (54% – 98%); (*e*) $Ar^1B(OH)_2$, $Pd(PPh_3)_2Cl_2$, PCy_3, K_2CO_3, dioxane – H_2O (4 : 1) (60% – 70%)

Carvalho dos Santos *et al.*[83] have described a series of 6-nitro- and 6-aminoquinolines **78** and **79**. In EtOH, nitro derivatives **78** exhibit purple emission with low fluorescence quantum yield ($\Phi_F < 0.03$) whereas amino analogues **79** exhibit blue emission with much stronger quantum yield ($\Phi_F = 0.14 - 0.83$). As expected, nitro substituents on the C2 phenyl ring of 6-aminoquinolines significantly reduce emission quantum yield.

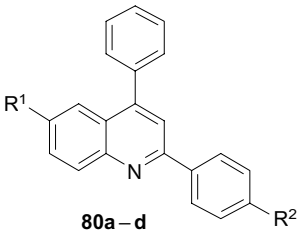
Kumar *et al.*[84] have studied the solid state (powder) emission of 2,4-diphenylquinoline **80a – c**. For **80a**,**b** emission peak appears at 492 nm together with a weak shoulder at 536 nm; in the case of **80c**, emission maximun is observed at 478 nm with a shoulder at 536 nm. For compounds **80a**,**b** the emission spectra are significantly broad due to $\pi - \pi^*$ interaction and(or) conformational rigidity in the solid state, leading to chromacity coordinates not far from white light (0.28, 0.35).

Structures 78 – 80



78, **79**

$R^5 = NO_2$ (**78**), NH_2 (**79**): R^1, R^2, R^3, R^4 = H, F, Cl, Br, Me, Bu^t, OMe, NMe_2, SMe, NO_2



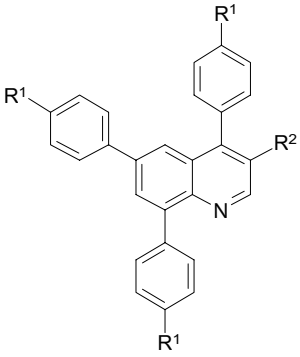
80a – d

R^1 = H (**a**), Cl (**b – d**);
R^2 = H (**a**, **b**), Cl (**c**), CN (**d**)

Ghate *et al.*[85] have synthesized cyano substituted quinoline derivative **80d**. This compound exhibits purple luminescence ($\lambda_{em} = 374 - 376$ nm with a shoulder at 395 nm) in various solvents (THF, DCM, $CHCl_3$) with high emission quantum yield ($\Phi_F = 0.69 - 0.75$) and blue emission ($\lambda_{em} = 434$ nm) in solid state (powder).

Mphahlele and Adeloye[32] have described a series of 4,6,8-triarylquinoline derivatives **81 – 83**. These compounds exhibit purple-blue luminescence in $CHCl_3$. Imines **82a – c** and methanol derivatives **83a – c** exhibit reduced emission intensity compared to the carbaldehyde analogues **81a – c**.

Structures 81 – 83



81a – c – 83a – c

R^2 = CHO (**81**),



(**82**),

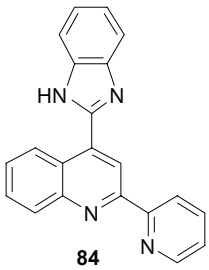
CH_2OH (**83**);

R^1 = H (**a**), F (**b**), OMe (**c**)

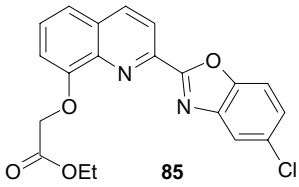
The presence of methoxy substituents in compounds **81** and **83** leads to a significantly red-shifted emission (**81c**: $\lambda_{em} = 470$ nm and **83c**: $\lambda_{em} = 461$ nm).

More and Shankarling[86] and Han *et al.*[87] have described the quinoline chromophores **84** and **85**, respectively, as Cu^{2+} fluorescent sensors. Both compounds exhibit blue photoluminescence in solution (**84** in MeCN/HEPES buffer, **85** in the mixture EtOH – H_2O). The presence of Cu^{2+} ion caused selectively a great fluorescence quenching of this compound (ON-OFF probe), whereas the addition of Cd^{2+} caused a slight reduction of emission intensity with a red shift ($\lambda_{em} = 380$ nm).

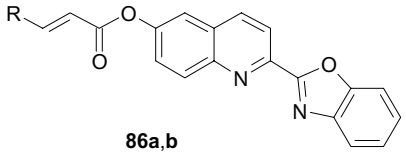
Structures 84 – 86



84



85



86a,**b**

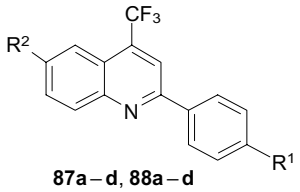
R = H (**a**), 2-Py (**b**)

Wu *et al.*[88] have designed chromophores **86a**,**b** as selective probes for cysteine for bioimaging in living cell. These probes can discriminate cysteine over other biothiols. Compound **86a** exhibits emission at 383 nm and quantum yield of 0.41 in EtOH – PBS (1 : 3). A ratiometric fluorescence response of **86a** toward cysteine with big peak-shifting to 518 nm is observed leading to detection limit below 1 μM. Compound **86b** acts as an OFF-ON probe for cysteine.

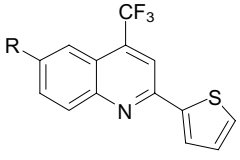
Bonacorso *et al.*[89] have designed a series of amine-substituted 2-aryl-4-trifluoromethylquinolines **87 – 89**. These compounds, which show blue luminescence ($\lambda_{em} = 468 - 482$ nm) with moderate emission quantum yield ($\Phi_F = 0.05 - 0.18$) in chloroform, exhibit strong interaction with ct-DNA and can be used for DNA titration.

Tran *et al.*[82] have described 8-dimethylaminoquinoline-derived quadrupolar two-photon absorption chromophores **90** and **91**. These compounds, which exhibit low luminescence ($\Phi_F = 0.04 - 0.12$) and moderate two-photon cross section (**90**: $\sigma = 25$ GM at 680 nm and **91**: $\sigma = 10$ GM at

Structures 87 – 89



87a – d, **88a – d**

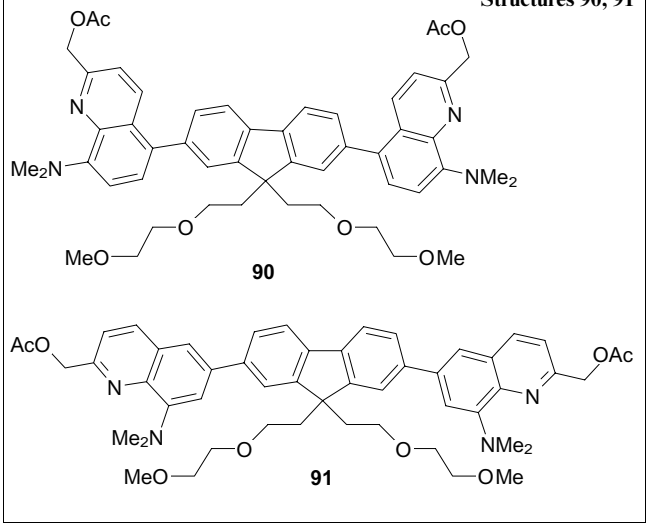


89a,**b**

R is morpholino (**87**), pyrrolidino (**88**);
R^1 = H (**a**), Me (**b**), F (**c**), CF_3 (**d**)

R is morpholino (**a**), pyrrolidino (**b**)

Structures 90, 91



700 nm), have been designed for two-photon acetyl uncaging application.

Cao *et al.*[81] have designed chromophore **92**. This compound forms organogel in various solvents. When self-assembled into organogel in MeCN, **92** exhibits two emission peaks at 385 nm and 495 nm due to π – π stacking interactions in the gel state. Solution and organogel of **92** in MeCN selectively and reversibly respond to volatile acid and organic amine vapours.

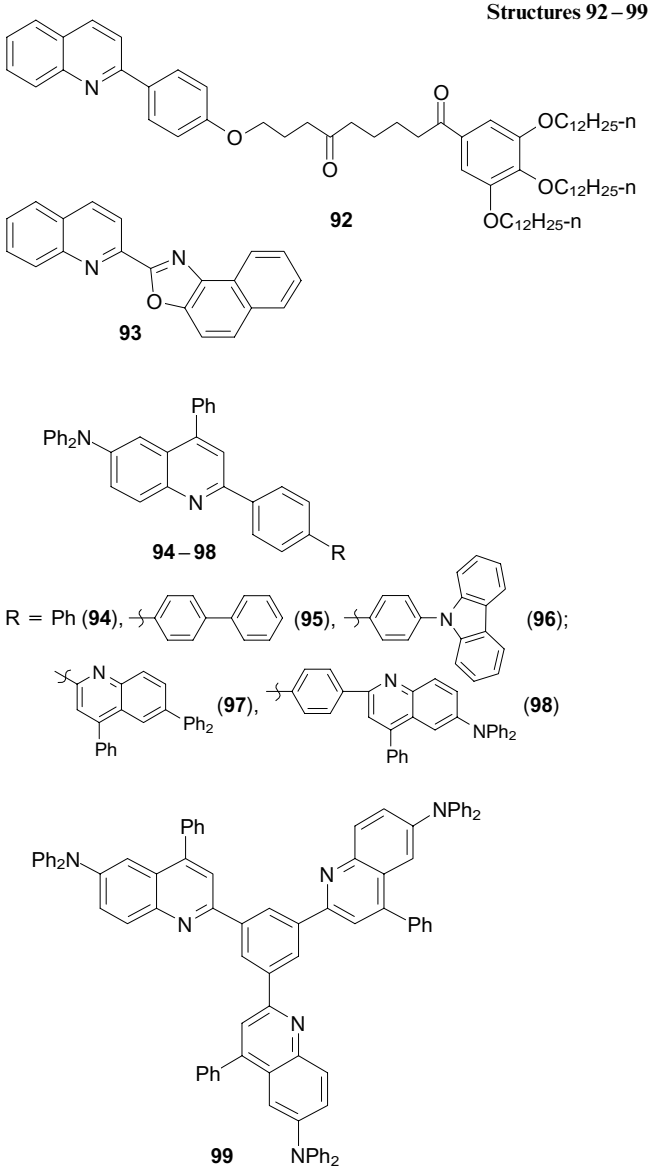
In addition to compound **31**, R.P.Zanocco *et al.*[49] have described an analogue **93** without vinyl linker. As expected, **93** exhibits blue shifted emission relative to **31** (410 nm for **93** and 450 nm for **31**) but the quantum yield remains close to 1 in benzene. Like **31**, compound **93** exhibits intense white light emission in MeOH (for 15% of DMSO, the chromacity coordinates are 0.28, 0.35) with higher emission quantum yield than **31** (0.42 *vs* 0.31).

Lee and co-workers have designed diphenylamino substituted quinoline chromophores **94** – **99**.[78] These compounds exhibit blue photoluminescence in toluene with high quantum yield (> 90%) attributed to charge transfer from the diphenylamino group to the quinoline ring. OLEDs have been fabricated with these chromophores with external quantum efficiency in the range of 1.2% – 2.3%.

Slodek *et al.*[79] have designed quinoline chromophores with a 2,2′-bithiophene fragment **100a** – **e**, **101**. Compounds **100** and **101** exhibit blue-green emission in DCM (λ_{em} = 444 – 479 nm) with moderate Stokes shifts and microsecond lifetime whereas orange-red fluorescence is observed for **100c** (λ_{em} = 595 nm) with a larger Stokes shift (7465 cm^{-1}). Starting from **100d**, the same team has described a series of Schiff bases **102a** – **c**.[90] The compounds **102** exhibit moderately strong blue emission in solution as well as in PMMA blend whereas green emission is observed in polyvinylcarbazole matrix. When mixed with silver nanowires, these compounds exhibit strong electroluminescence due to plasmonic enhancement.

The same team[91] has also compared bithiophene quinoline chromophores **100** with their carbazyl analogues **103a**. Stronger ICT occurs in carbazyl substituted quinoline **103a** than in **100**, and the carbazyl substituent leads to higher quantum yield and lifetime (respectively up to 0.7 and

Structures 92 – 99



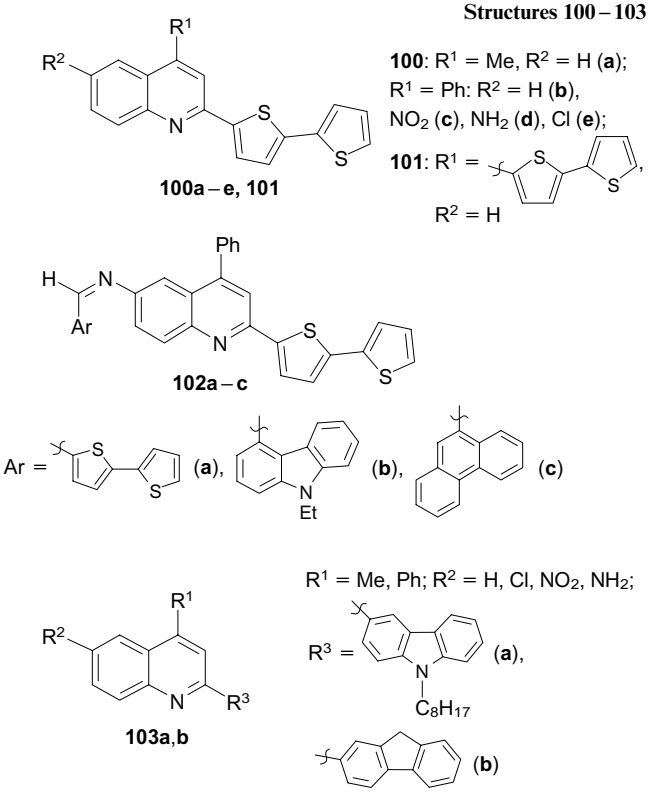
5.72 ns for **103a**). Applications as fluorescent cellular probes have been proposed.

Also the same group described the series of quinolines **103b**, bearing fluorenyl fragment at position 2.[92] These compounds exhibit emission with λ_{em} in the range of 400 – 560 nm, the presence of nitro group leads to the red shift; the luminescence quantum yield varies from 0.6 to 0.30. Fluorenyl derivative **103b** possesses glass-forming properties; the obtained films as well as solid samples exhibit fluorescence. The cyclic voltammetry showed that these compounds undergo multistep oxidation and reduction. Their semiconductor properties were studied, the derivative **103b** (R^1 = Me, R^2 = H) was tested as a component of the active layer for the solar cell.

Chen *et al.*[93] have designed carbazole – quinoline hybrids **104** – **106** as hosts for orange and deep-red phosphorescent OLEDs. The optimized orange phosphorescent OLEDs based on **104** exhibit an external quantum efficiency of 25.6% and a power efficiency of 68.1 lm W^{-1}.

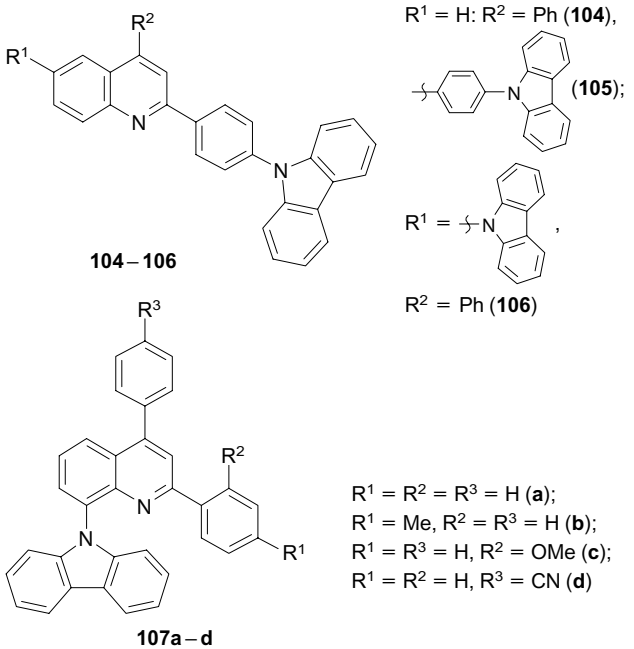
Bhattacharjee *et al.*[94] have designed carbazole – quinoline conjugates **107a** – **d** exhibiting dual emission resulting

Structures 100 – 103



from thermally activated delayed fluorescence and room temperature phosphorescence. The authors stated that these compounds have great promise for high-efficiency white OLEDs.

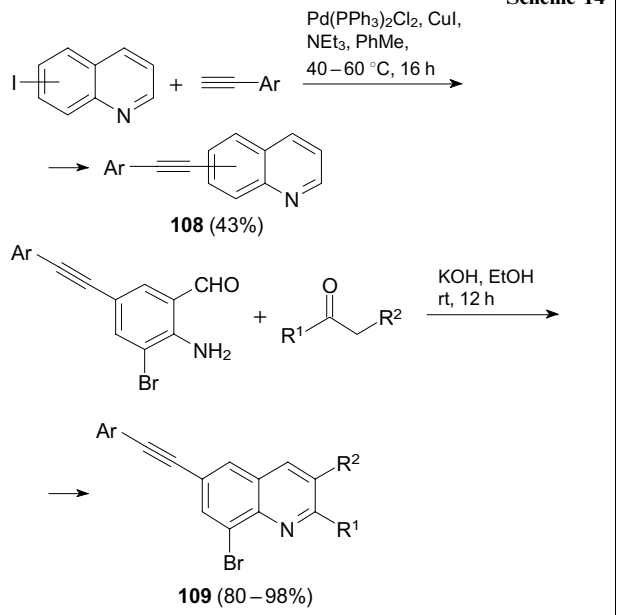
Structures 104 – 107



2.2.2. Arylethynylquinolines

5-, 6- and 8-Arylethynylquinolines **108** can be easily obtained by Sonogashira cross-coupling reaction from the corresponding iodoquinolines (Scheme 14, top reaction).[82,95] The same strategy can be used to obtain 4-arylethynylquinoline from the corresponding chloro intermediate.[96] 6-Arylethynylquinolines **109** have also been obtained by Friedländer condensation from arylethynyl substituted aminobenzaldehyde (Scheme 14, bottom reaction).[97]

Scheme 14



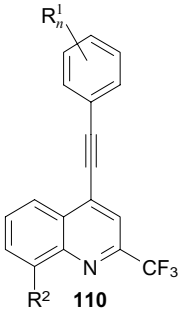
Alapour *et al.*[96] have designed a series of trifluoromethyl substituted 4-arylethynylquinoline chromophores **110**. These compounds exhibit blue luminescence in MeCN solution and in solid state. In solid state, the addition of CF_3 substituents was found to result in increased flexibility of the structure with a decrease in the number of intermolecular interactions and the authors stated that it could result in enhancement of their emission in solid state.

In addition to arylquinolines **90** and **91**, Tran *et al.*[82] have designed their arylethynyl analogues **111** and **112** as two-photon absorption chromophores for acetyl uncaging. In comparison with their analogues **90**, **91**, compounds **111**, **112** exhibit enhanced two-photon cross section (**111**: σ = 160 GM at 720 nm and **112**: σ = 70 GM at 710 nm).

Picard *et al.*[95] have also developed the chromophores **113** – **117** for the same application. These compounds exhibit blue emission in THF with high emission quantum yield (Φ_F = 0.59 – 0.68). Quadripolar compound **117** exhibits the lowest two-photon cross section (σ = 75 GM at λ = 710 nm) whereas the higher value is observed for **116** (σ = 480 GM at λ = 730 nm).

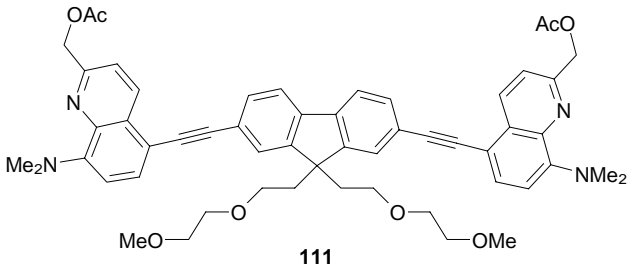
Picard *et al.*[97] have designed a series of diphenylamino-substituted 6-arylethynyl-8-bromoquinolines **118**. These chromophores combine (in toluene) significant two photon absorption cross section (σ = 116 – 265 GM) in the NIR region, good photosensitization ability (Φ_Δ = 0.4 – 0.6) and fluorescence properties (Φ_F = 0.2 – 0.6). The authors described these compounds as promising dyes for combining two-photon imaging and photodynamic therapy. Compound **118c** has been used as precursor to obtain **119**, which can be grafted on mesoporous silica nanoparticles *via* click chemistry for two-photon photodynamic therapy.[98]

Structures 110 – 117

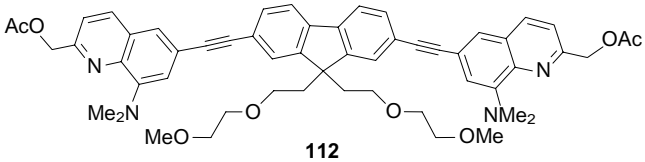


$R^2 = CF_3$: R^1_n = H, 4-Me, 4-Bu^t, 4-CF_3, 2-CF_3, 2-F, 4-F, 3,5-F_2;
R^2 = Me: R^1_n = H, 4-Me, 4-Bu^t, 4-CF_3;
R^2 = H: R^1_n = H, 4-Me, 4-Bu^t

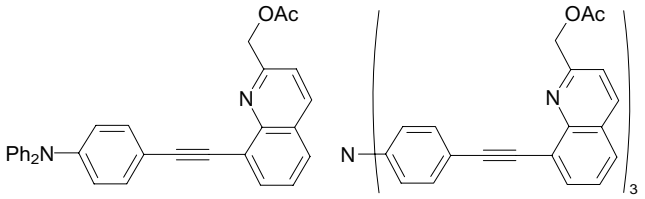
110



111

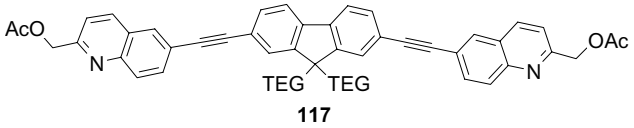


112



113 (8-isomer), **114** (6-isomer)

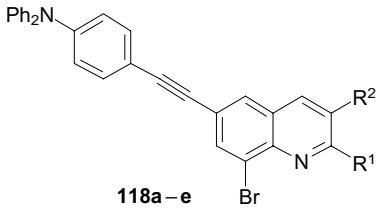
115 (6-isomer), **116** (8-isomer)



117

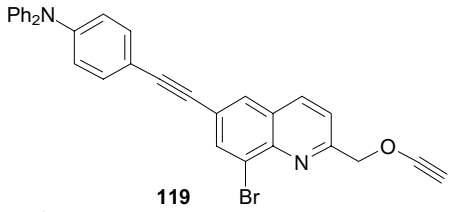
TEG = $[(CH_2)_2O]_3Me$

Structures 118 – 120

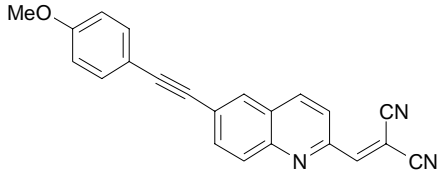


R^1 = Me (**a**), CHO (**b**), CH_2OH (**c**, **e**), Me (**d**);
R^2 = H (**a** – **c**), OH (**d**,**e**)

118a – e

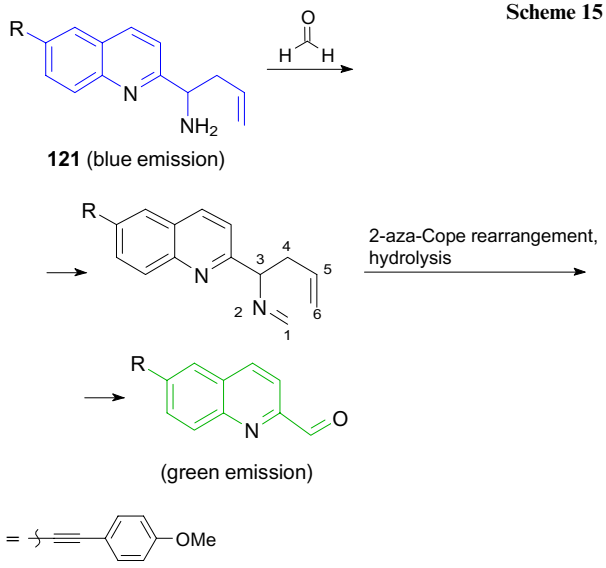


119



120

Scheme 15



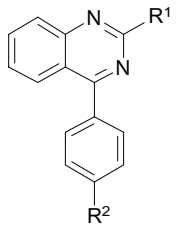
Ning and coworkers have designed chromophore **120** as two-photon viscosity probe.[99] It was shown that increasing the water – glycerol mixture viscosity, which blocks the rotation of the dicyanovinyl group, leads to strong enhancement of emission intensity of compound **120** upon two-photon excitation. Efficiency of application of this compound as fluorescent probe depending on the environment viscosity was shown *in vivo* on cervical tumour cells HeLa.

Yang *et al.*[100] have designed a two-photon fluorescent probe **121** for selective detection of endogenous formaldehyde *via* aza-Cope reaction (Scheme 15). In PBS buffer, compound **121** shows an emisison maximum at 405 nm (Φ_F = 0.03, σ = 185 GM), upon addition of formaldehyde, the emission maximum is red shifted to 490 nm (Φ_F = 0.10, σ = 275 GM).

2.2.3. (Het)arylquinazolines

Two main methods have been used to synthesize arylquinazoline derivatives. The first one consists in condensation reactions to build the quinazoline core and the second one is Suzuki cross-coupling reaction of haloquinazolines. 2-Arylquinazolines can be obtained by reaction of 2-aminobenzamide with arylcarboxaldehyde.[101] 4-Arylquinazoline can be obtained by Suzuki cross-coupling reaction from chlorine intermediates[54] or by iodine-catalyzed oxidative C – H amination from *ortho*-carbonyl-substituted anilines and ammonia.[102] 2,4-Diarylquinazolines can be obtained either by double Suzuki cross-coupling (the C4 position being more reactive than the C2 one),[54] by condensation reaction from 2-cyanoaniline[103] or by condensation of 2-aminobenzophenone with arylcarboxaldehyde.[104] 6-Arylquinazoline can also be obtained from 6-bromo or 6-iodoaniline by Suzuki cross-coupling.[57, 101]

Structures 122, 123



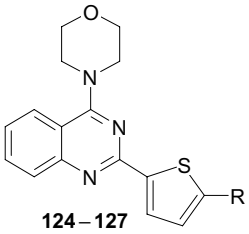
122a – c, **123a**,**b**

122: R^1 = H: R^2 = NMe_2 (**a**), NPh_2 (**b**), $C_6H_4NMe_2$-4 (**c**);
123: R^1 = $C_6H_4R^2$-4: R^2 = NMe_2 (**a**), NPh_2 (**b**)

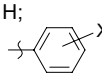
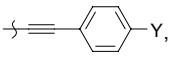
Achelle *et al.*[54, 105] have synthesized 4-aryl and 2,4-diarylquinazolines **122**, **123**. In DCM, compound **122a** exhibits blue photoluminescence, whereas compounds **122b** and **123a**,**b** exhibit green luminescence, and **122c** emits yellow-orange light. 4-Arylquinazolines **123a**,**b** have significantly higher quantum yield (Φ_F = 0.8 – 0.93) than their 2,4-diarylquinazoline **123** (Φ_F = 0.30 – 0.34) and 4-arylvinylquinazoline (Φ_F = 0.02 – 0.25) analogues. As expected compared to their arylvinyl analogues **40** and **41**, compounds **122**, **123** show blue shifted emission.[54]

Nosova and coworkers have designed a series of 4-morpholin-4-yl substituted quinazolines **124** – **127**. These compounds have been obtained by bromination of **124** followed by palladium catalyzed Suzuki/Sonogashira cross-coupling reaction.[106] Compounds **125d**,**e** exhibit green photoluminescence in MeCN whereas compounds **125b**,**c** and **126**, **127** show blue photoluminescence. pH sensitivity with significant red-shifted emission has been demonstrated. Cyano analogue **125e** is poorly emissive (λ_{em} = 471 nm, Φ_F < 0.01).[107]

Structures 124 – 127



124 – 127

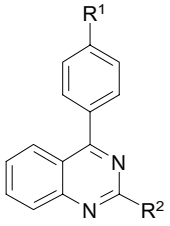
124: R = H;
125: R =  (X_n = H (**a**), 4-OMe (**b**), 3,4,5-$(OMe)_3$ (**c**), 4-NEt_2 (**d**), 4-NPh_2 (**e**), 4-(9*H*-carbazol-9-yl) (**f**);
126: R = 2-Th (Th is thienyl);
127: R = , [Y = H (**a**), OMe (**b**)]

The same research group has described a series of 2,4-diarylquinazoline derivatives **128** – **130**.[108] These compounds exhibit blue luminescence in toluene (λ_{em} = 431 – 459 nm) with emission quantum yield up to 0.82 for **128a** whereas orange emission is observed for the same compounds in MeCN with lower quantum yield (Φ_F = 0.05 – 0.28).

Wang *et al.*[109] have designed a series of 2-arylquinazoline-substituted ethene derivatives including chromophores **131a-d**. These compounds exhibit typical aggregation induced emission properties. As a typical example, compound **131b** exhibits green emission (λ_{em} = 530 nm) in thin film with high quantum yield (Φ_F = 0.52).

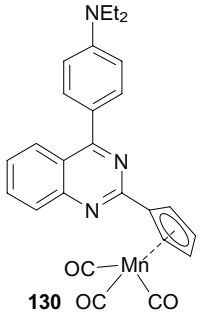
In addition to 6-arylvinylquinazoline derivatives **42** and their butadiene analogues **43**, Dhuguru *et al.*[57] have obtained 6-arylquinazoline chromophores **132a** – **e**. Except dimethylamino derivative **132a** (λ_{em} = 435 nm, Φ_F = 0.37 in $CHCl_3$), these compounds are poorly emissive (Φ_F < 0.03) with blue shifted emission relative to their vinyl or butadiene analogues **40** – **42**.

Structures 128 – 132

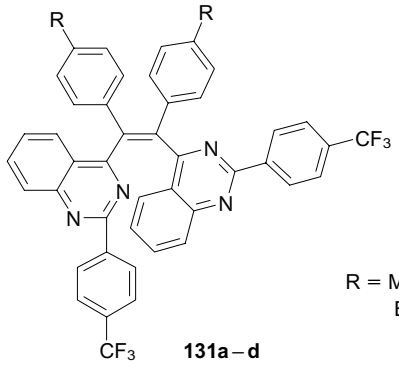


128a,**b**; **129a**,**b**

R^1 = NEt_2 (**a**), 9*H*-carbazol-9-yl (**b**): R^2 = Ph (**128**), fluoren-2-yl (**129**)

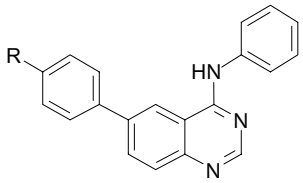


130



131a – d

R = Me (**a**), OMe (**b**), Bu^t (**c**), F (**d**)

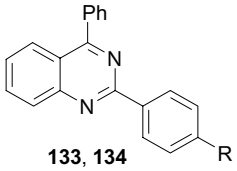


132a – e

R = NMe_2 (**a**), OMe (**b**), H (**c**), CN (**d**), NO_2 (**e**)

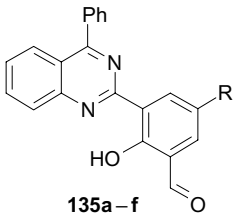
Liu *et al.*[103] have designed chromophores **133** and **134**. These compounds can be used for white photoluminescence and electroluminescence combining the blue-emitting neutral form and orange-emiting protonated form. Indeed, the protonation of the quinazoline ring greatly enhances its electron-withdrawing character and strengthens the ICT leading to bathochromically shifted emission.

Structures 133 – 135



133, **134**

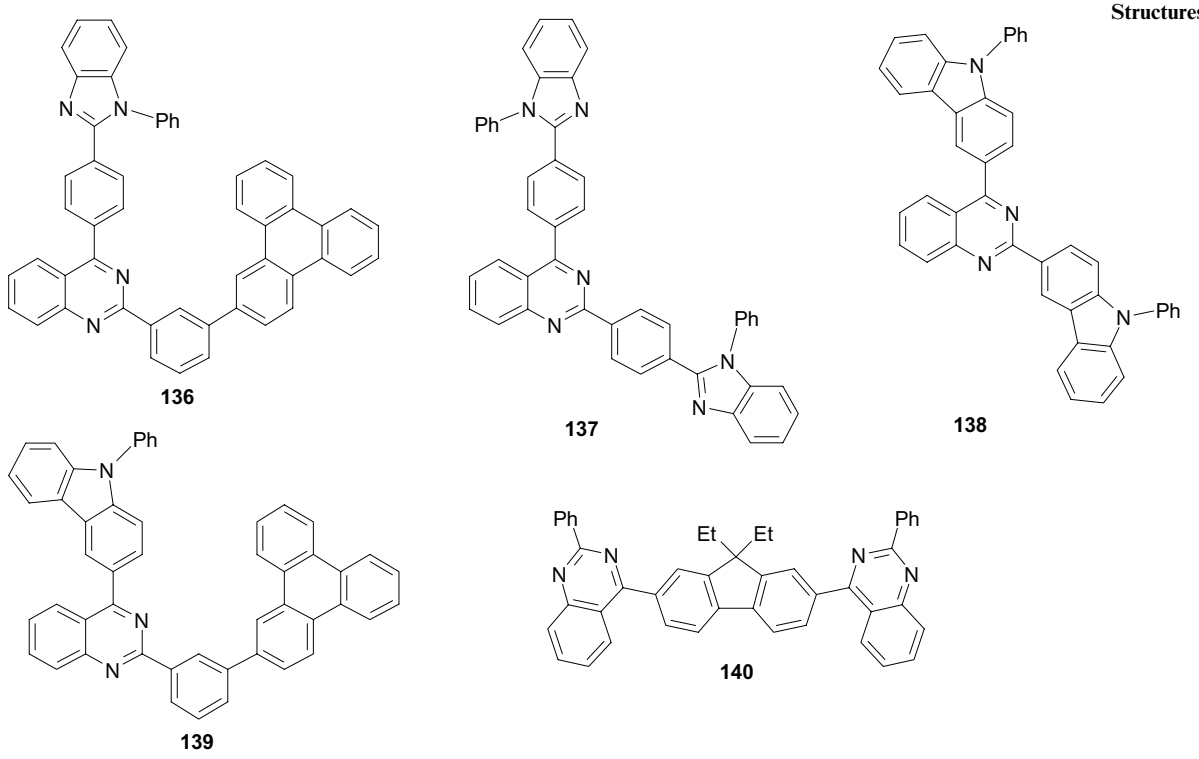
R = fluoren-2-yl (**133**), NPh_2 (**134**)



135a – f

R = CHO (**a**), Cl (**b**), Br (**c**), H (**d**), Me (**e**), OMe (**f**)

Structures 136 – 140



136 **137** **138** **139** **140**

Dwivedi *et al.*[104] have designed a series of quinazoline-based excited state intramolecular proton transfer (ESIPT) active systems **135a – f**. The ESIPT emission, completely quenched in solution, can be restored *via* aggregation-induced emission. In solid state, these compounds exhibit various emission bands corresponding to the enol (λ_{em} = 465 – 513 nm) and keto forms (λ_{em} = 560 – 704 nm). The authors claim that these tunable ESIPT emissive materials have potential applications in optoelectronic devices.

Zhang *et al.*[110] have described a series of 2,4-diarylquinazoline derivatives with benzoimidazole, carbazole and triphenylene substituents **136 – 139**. These compounds can be used as host materials for red phosphorescent organic light-emitting diodes. The best device was obtained with **136** with external quantum efficiency of 19.2%, current efficiency of 18.3 cd A^{-1} and 21.3 lm W^{-1}.

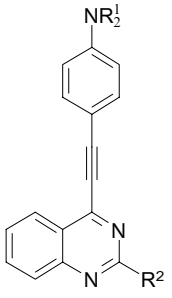
Kim *et al.*[111] have designed fluorene-bridged quinazoline derivative **140**. This compound shows luminescence in DCM solution and thin film. A blue OLED with external quantum efficiency of 1.58% at 20 mA cm^{-2} has been obtained with this compound.

2.2.4. Arylethynylquinazolines

Arylethynylquinazoline chromophores have been synthesized exclusively by Sonogashira cross-coupling reactions.[54] 4-Arylethynylquinazolines can be obtained from the corresponding chloro derivatives, whereas 6- and 8-arylethynylquinazolines are derived from 6-bromo- and 8-iodoquinazolines, respectively.[112, 113] To the best of our knowledge, no 2-ethynylarylquinazoline chromophores have been designed so far.

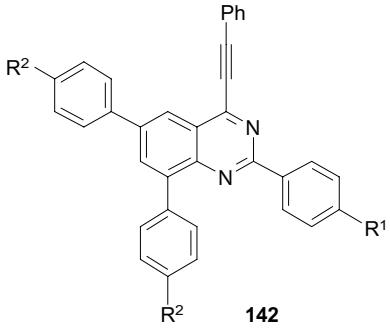
Achelle *et al.*[54] have proposed 4-arylethynylquiazolines **141a – c**. In DCM solution, these compounds exhibit green emission (λ_{em} = 551 – 565 nm) with low quantum yield, except the diphenylamino derivative **141b** (Φ_F = 0.41). As

Structures 141, 142



141a – c

R^2 = H: R^1 = Me (**a**), Ph (**b**); R^1 = Me, R^2 = Ph (**c**)



142

R^1 = H, F, Cl, OMe; R^2 = H, F, OMe

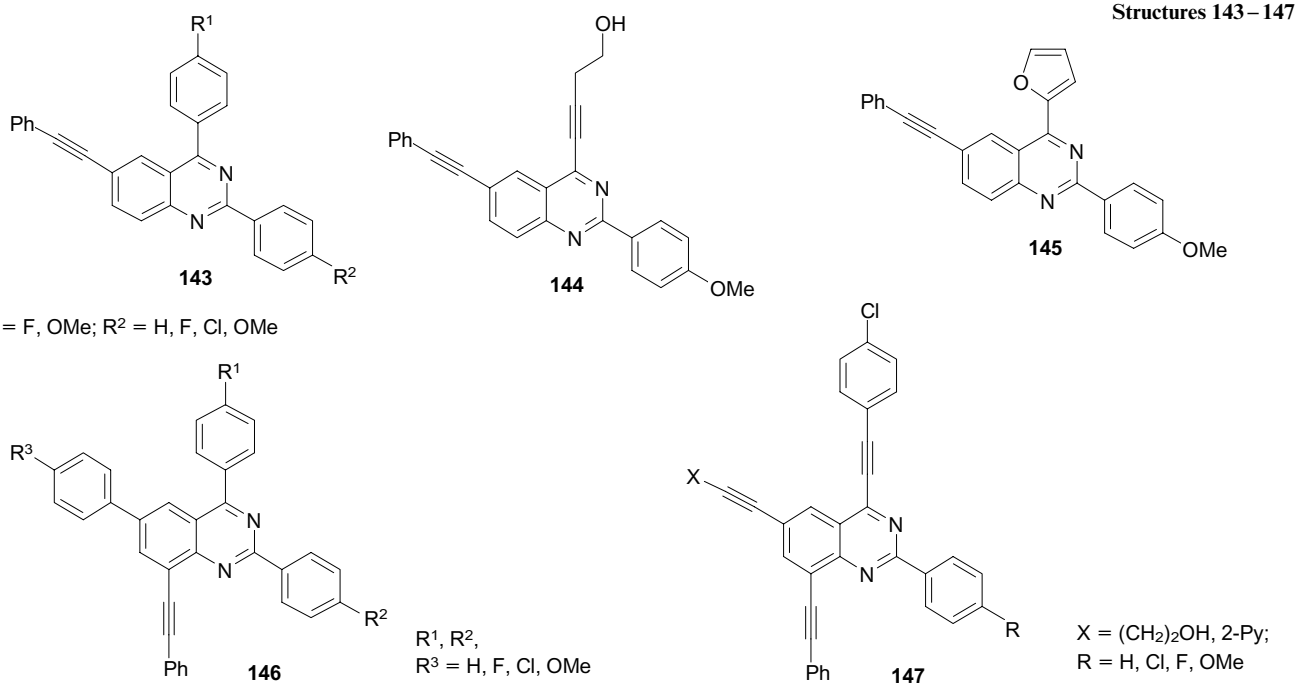
shown in Table 2, 4-arylethynylquinazolines **141** and 4-arylvinylquinazolines **40** exhibit red-shifted emission and lower quantum yield than their 4-arylquinazoline analogues **122**.

Mphahlele *et al.*[114] have designed a series of 2,6,8-triaryl-4-arylethynylquinazoline derivatives **142**. In $CHCl_3$,

Table 2. Comparison of photophysical properties of 4-arylethynylquinazolines **141**, 4-arylvinylquinazolines **40** and 4-arylquinazoline analogues **122** in CH_2Cl_2.[54]

Compound	λ_{abs}/nm	ε/mM^{-1} cm^{-1}	λ_{em}/nm	Φ_F
141a	411	27.5	560	0.03
40a	433	18.0	548	0.07
122a	380	16.4	490	0.93
141b	414	29.2	565	0.41
40b	429	16.9	571	0.25
122b	384	16.6	528	0.80

Structures 143 – 147



these compounds exhibit blue luminescence (λ_{em} = 454 – 480 nm) with low quantum yield (Φ_F = 0.10 – 0.07).

Mphahlele and co-workers [112, 113] have designed a series of 6-phenylethynylquinazoline derivatives **143** – **145** and the same research groups have also synthesized 8-phenylethynylquinazolines **146**, as well as 4,8-biarylethynyl- and 4,6,8-triarylethynylquinazolines **147**. These compounds exhibit also blue emission in $CHCl_3$ with low to moderate quantum yield.

2.2.5. (Het)arylquinoxalines

2,4-Diarylquinoxalines **150** are generally obtained by condensation of *o*-phenylenediamine **148** and diaryl 1,2-diketone derivatives **149** (Scheme 16 *a*).[115 – 117] 2-Arylquinoxalines **152** can be obtained by condensation reaction between *o*-phenylenediamine **148** and α-bromo-arylketone (*b*),[117,118] α-hydroxy-arylketone (*c*),[119,120] phenylethane-1,2-diol (*d* or *e*)[121, 122] or 2-arylethylamines (*f*).[123] Other strategies consist in Suzuki cross-coupling reaction of 2-chloroquinoxaline **151**,[105] as well as nucleophilic substitution of hydrogen in quinoxaline-N-oxides.[124]

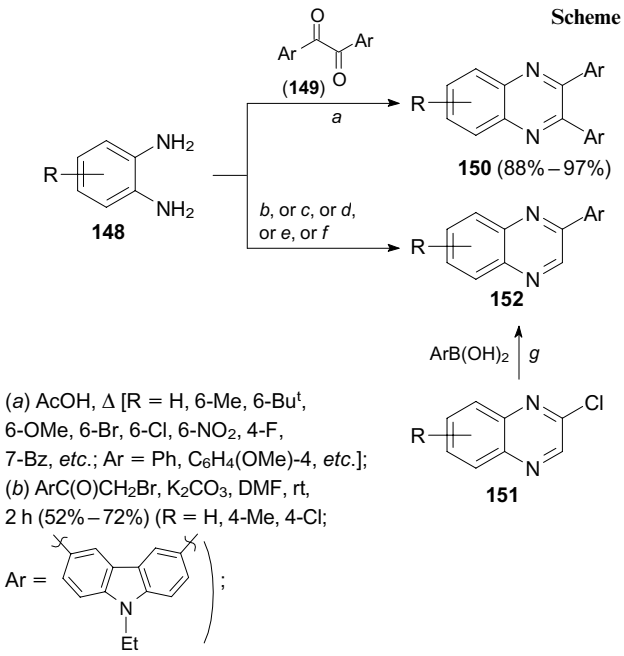
5-Aryl-, 6-aryl- and 5,8-diarylquinoxalines can be easily obtained by Suzuki or Stille cross-coupling reactions from the corresponding bromo or iodo derivatives.[111, 125, 126]

Nafe and coworkers have synthesized chromophore **153**, which exhibits blue luminescence in solution (unspecified solvent, λ_{em} = 467 nm, Φ_F = 0.6).[127]

Achelle and Robin-le Guen [105] have synthesized chromophore **154**. This compound exhibits green-yellow luminescence (λ_{em} = 539 nm) with high fluorescence quantum yield (Φ_F = 0.90) in DCM. Design of experimental methodology combined with ANOVA method have shown that compared with diazine fragment, the benzodiazine part led to a significant red shift in absorption and emission.

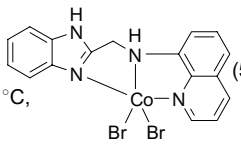
Telore *et al.*[118] have synthesized carbazole derivatives **155a** – **c**. These compounds exhibit blue luminescence in

Scheme 16



(*a*) AcOH, Δ [R = H, 6-Me, 6-Bu^t, 6-OMe, 6-Br, 6-Cl, 6-NO_2, 4-F, 7-Bz, *etc.*; Ar = Ph, C_6H_4(OMe)-4, *etc.*];
(*b*) ArC(O)CH_2Br, K_2CO_3, DMF, rt, 2 h (52% – 72%) (R = H, 4-Me, 4-Cl;

);
(*c*) ArC(O)CH_2OH, Cu-Mn/HT (HT is hydrotalcite), EtOH, O_2, 70 °C, 12 h (65% – 90%) (R = H, 4-Cl; Ar = Ph, C_6H_4Br-4, C_6H_4OMe-4, C_6H_4Cl-3, 3-Th, 2-Naph);
(*d*) ArCH(OH)CH_2OH, [2-Py-CH_2NH$(CH_2)_2$SBu^t]Mn(CO)$_3$ (4 mol.%), KOH, neat, 140 °C, 20 h (65% – 78%) (R = H, 6-Me, 7-Me, 6,7-Me_2, 6,7-Cl_2; Ar = Ph);
(*e*) PhCH(OH)CH_2OH, CsOH·H_2O, PhMe, 150 °C, 24 h (85%);

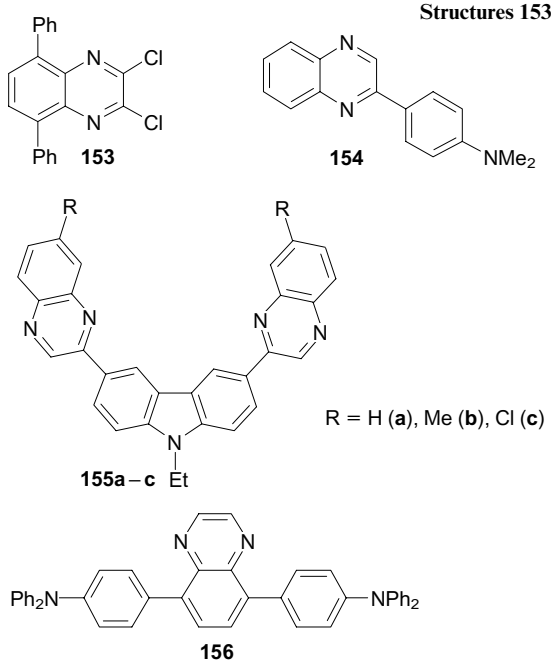


(5 mol.%),
(*f*) Ar$(CH_2)_2NH_2$, CuBr (10 mol.%), PhCl, O_2, rt, 6 h (78% – 97%); (R = H: Ar = Ph, C_6H_4Cl-2, C_6H_4Br-4, $C_6H_4CF_3$-4, C_6H_4OMe-4, C_6H_4OMe-3, C_6H_4OH-4, 1-Naph, 2-Py, 2-Th, *etc.*);
(*g*) Pd$(PPh_3)_4$, Na_2CO_3, EtOH, PhMe, N_2, Δ, 15 h (93% – 95%); (R = H: Ar = 4-$C_6H_4C_6H_4NMe_2$-4, $C_6H_4NMe_2$-4

DCM and emission solvatochromism attributed to ICT and are therefore potential NLO chromophores.

Lu *et al.*[128] have designed D – A – D chromophore **156**. This compound exhibits yellow-green emission (λ_{em} = 557 nm) in DCM due to ICT from diphenylamino groups to the central quinoxaline core. Bulk heterojunction solar cell application has been also proposed for this compound.[129]

Structures 153 – 156



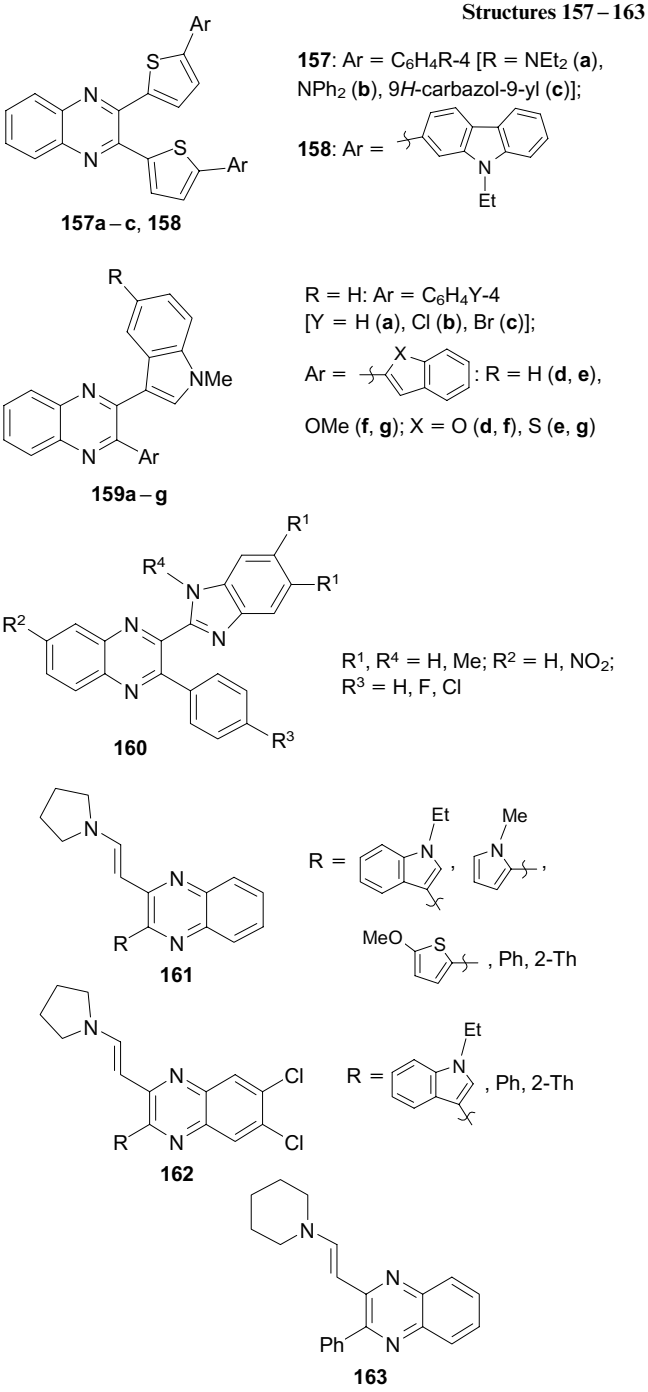
Moshkina *et al.*[115] have described a series of V-shaped 2,3-bis(5-arylthiophen-2-yl)quinoxaline derivatives **157a** – **c**, **158**. These compounds exhibit blue-green emission (λ_{em} = 498 – 557 nm) in toluene with moderate quantum yield (Φ_F = 0.14 – 0.07). The highest quantum yield is observed for the diphenylamino derivative **157b**. These compounds exhibit halochromism; and the ability of **157a** to function as colorimetric and luminescent pH sensor has been demonstrated. The addition of TFA (up to 135 equiv.) led to a blue shifted emission (from 547 nm to 461 nm) attributed to the protonation of the diethylaminophenyl moieties.

Zhang *et al.*[130] have designed chromophores **159a** – **g**. These compounds exhibit blue-green luminescence in DCM (494 – 530 nm) as well as emission solvatochromism.

Burdanov *et al.*[131] designed benzimidazolylquinoxalines **160** as novel fluorophores with tunable sensitivity to solvent effects. The wavelengths of lowest-energy absorptions in the spectra of various solutions of **160** vary in the range 352 – 396 nm, whereas the wavelengths of emission maxima vary in the rather broad range 440 – 519 nm (Φ_F = 0.03 – 0.29). It was found that the addition of small amounts of DMF or DMSO in the solution of **160** ($R^2 = NO_2$, R^3 = Cl, $R^4 = R^1$ = H) in DCM results in a dramatic quenching of the fluorescence.

Gers-Panters *et al.*[132] have designed a series of 2-aryl-3-aminovinylquinoxalines **161** – **163**. These compounds exhibit intense yellow emission in DCM (Φ_F up to 0.61) with prononced emission solvatochromsim and protochromic fluorescence quenching.

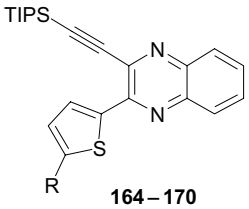
Structures 157 – 163



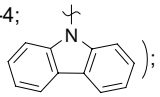
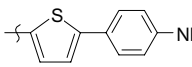
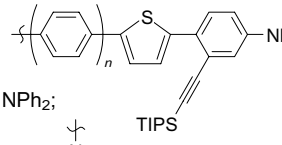
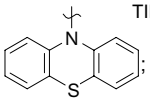
Merkt *et al.*[133, 134] have described a series of 2-thiophen-2-yl-3-ethynylquinoxalines **164** – **176**. These compounds exhibit blue to yellow emission in DCM depending of the substituent with emission quantum yield up to 0.75 for **164a** and **164j**. Aggregation induced emission phenomena have been found for compounds **165** and **169**: whereas methanol solutions of these compounds are non-emissive, the addition of water leads to yellow/pink emission. Compounds **165** and **170** are also emissive in solid state (powder and doped thin film of PMMA).

Wang *et al.*[135] have synthesized chromophores **177a**,**b**, which exhibit aggregation-enhanced emission in MeCN – water mixture and selective fluorescent quenching in the presence of picric acid.

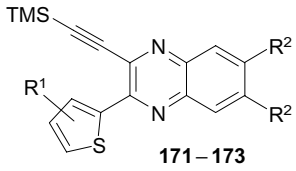
Structures 164 – 176



164 – 170

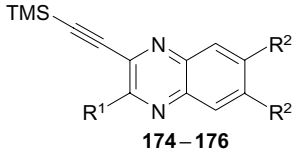
164: R = $C_6H_4X_n$ [X_n = H (**a**), 4-NMe_2 (**b**), 4-OMe (**c**), 4-Me (**d**), 4-CH_2OH (**e**), 4-Cl (**f**), 4-CN (**g**), 4-NO_2 (**h**), 4-CHO (**i**), 2,6-$(OMe)_2$ (**j**)];
165: R = $C_6H_4[N(C_6H_4OMe\text{-}4)_2]\text{-}4$;
166: R = $C_6H_4-CH{=}CY_2$ (Y = );
167: R = ;
168: R = ;
169: R = NPh_2;
170: R = ;

TIPS = $SiPr^i_3$

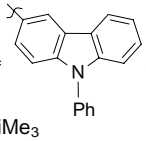


171 – 173

171: R^2 = H, R^1 = H, Me, Bu^t, SMe, OMe, NMe_2;
172: R^2 = H, R^1 = *o*-C_6H_4;
173: R^2 = Cl, R^1 = H



174 – 176

174: R^2 = H, R^1 = C_6H_4X-4 (X = H, Me, Bu^t, SMe, OMe, NMe_2);
175: R^1 = $C_6H_4NMe_2$-4; R^2 = Cl, CN;
176: R^1 = : R^2 = H, Cl;

TMS = $SiMe_3$

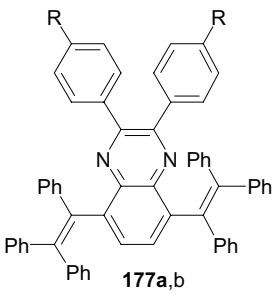
Lin *et al.*[116] have designed star-shaped chromophore **178**. This compound exhibits emission at 498 nm in toluene (Φ_F = 0.42) and TPA properties with TPA cross section as high as 8950 GM at 790 nm.

Kim *et al.*[111] have designed fluorene-bridged quinoxaline derivative **179**. Like its quinazoline analogue **140**, this compound exhibits blue luminescence in DCM solution and thin film. A blue OLED with external quantum efficiency of 1.30% (slightly lower than with **140**) has been obtained with this compound.

Yu *et al.*[136] have described two fluorine substituted quinoxaline chromophores **180a**,**b**, which exhibit aggregation-induced emission (AIE) and thermally activated delayed fluorescence (TADF). Compound **180a** has 23.5% efficiency (EQE) in doped OLEDs and 10% efficiency in non-doped orange OLEDs.

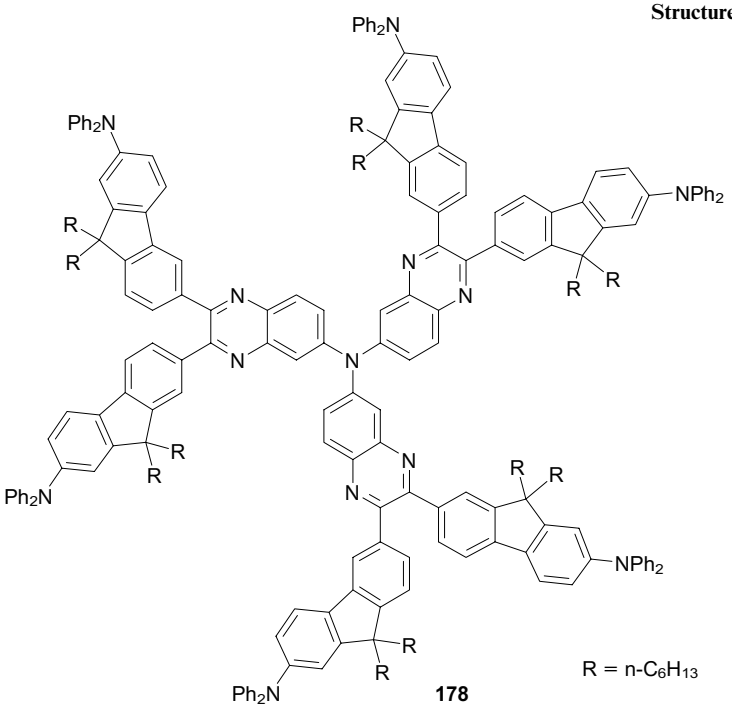
Nowadays much attention is paid to 2,3-diphenylquinoxaline derivatives as electron-acceptors for emitters exhibiting TADF effect; such materials are particularly promising for OLEDs due to their theoretical ability to reach 100% of internal quantum efficiency *via* reverse

Structures 177, 178



177a,b

R = H (**a**), OMe (**b**)



178

R = n-C_6H_{13}

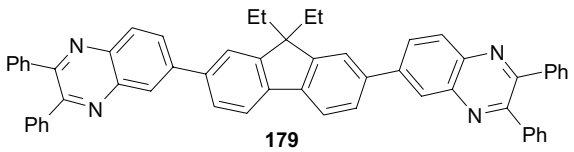
intersystem crossing (RISC) between singlet and triplet states. Compound **181**, which contains a fluorine-substituted quinoxaline as an electron acceptor and phenoxazine with good hole-transporting ability as an electron donor, was described.[137] Synthesis of **181** was realized by Pd-catalyzed C – N coupling reaction of 6,7-difluoro-2,3-diphenylquinoxaline with phenoxazine. The product **181** demonstrated good thermal stability with a high decomposition temperature of 348 °C and a broad and weak absorption around 400 – 500 nm. The neat film of **181** exhibited a bright orange-red emission peak at 606 nm; phosphorescence spectra with a maximum peak at 616 nm were recorded in the neat film at 77 K. According to the fluorescence and phosphorescence spectra, the energy gap (ΔE_{ST}) between first singlet excited state S_1 and first triplet excited state T_1 of **181** is estimated to be 0.04 eV, which is favourable for efficient RISC. Phenoxazine-containing quinoxaline **181** proved to be long-wave TADF emitter, OLED based on **181** achieved a maximum EQE of 13.9% or 9.0% depending on the way of its fabrication.

A series of new butterfly-shaped D – A – D type compounds **182** – **184** with quinoxaline as an electron acceptor and carbazole or dihydroacridine residues as electron donors was presented by the same Yu's scientific group.[138] These derivatives were synthesized form 5,8-diphenylquinoxaline using Pd-catalyzed C – N cross-coupling reaction, Suzuki process or copper-catalyzed Ullmann coupling reaction. All compounds exhibit excellent thermal stability with 5% weight loss decomposition temperatures (T_d) in the range of 394 – 471 °C. Electrochemical and photophysical properties of **182** – **184** were studied. It was shown that with the increasing electron-donating ability from phenyl to carbazole and dihydroacridine, the ICT absorption bands gradually red-shift from 370 nm (**182**) to 482 nm (**184**). In films all compounds exhibit luminescence from green to orange with λ_{em} from 502 mn (**182**) to 603 nm (**184**). Phosphorescence spectra were recorded at 77 K in order to estimate ΔE_{ST} value, which ranges from 0.07 eV (**184**) to 0.33 eV (**182**) and was found to be in agreement with results of the theoretical analysis. The authors successfully tuned the emission type from local excited-state (LE) to charge-transfer state (CT) transition to acquire a TADF molecule. Although the **184**-based orange TADF device exhibited an EQE of only 7.4%, the contribution from the delayed fluorescence to the overall EQE can reach up to 97%.

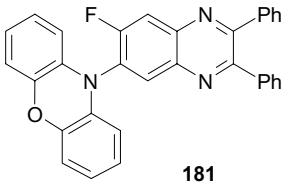
Two novel quinoxaline derivatives **185a**,**b** bearing di-substituted carbazole fragment also exhibit TADF emitter properties.[139] The authors demonstrated that the degree of planarity of emitter molecule has a decisive influence on its electroluminescence properties. The influence of structure of compounds **185** on molecular orientation in films and mixtures containing bis[2-(diphenylphosphino)phenyl] ester (DPEPO) and the electroluminescence properties in TADF OLEDs has been studied. Compounds **185** were found to possess green fluorescence in films at room temperature with λ_{em} = 517 nm (**185a**) and 546 nm (**185b**), luminescence quantum yield 60.4% and 50.2%, respectively, and the ΔE_{ST} value of 0.10 (**185a**), 0.12 (**185b**). More horizontal molecular orientation of **185** was observed in the mixtures of compounds (in 6 mass % concentrations) and DPEPO in comparison with neat films that influence positively OLED performances. The maximum electroluminescence external quantum efficiency measured in the device based on **185b** was found to be 15.4%.

Kim *et al.*[140] have incorporated compounds **186**, **187** as organic semiconductors in top-contact/bottom-gate organic

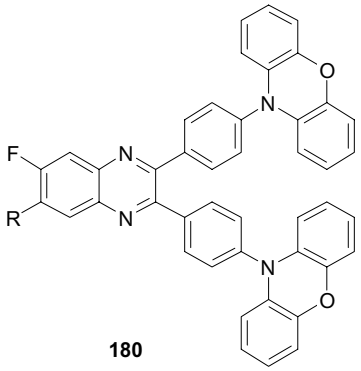
Structures 179 – 187



179

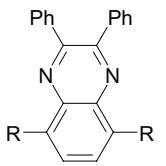


181

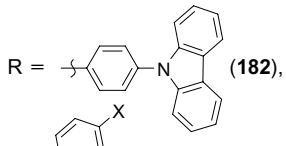


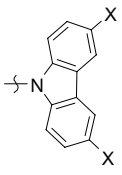
180

R = H (**a**), F (**b**)

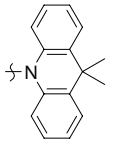


182 – **184**

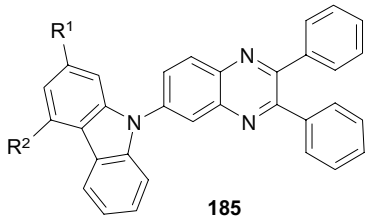




[X = H (**183a**), Bu^t (**183b**)],

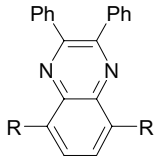


(**184**)



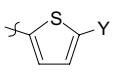
185

R^1 = H, R^2 is di(biphenyl-4yl)amine (**a**);
R^1 is di(biphenyl-4yl)amine, R^2 = H (**b**)



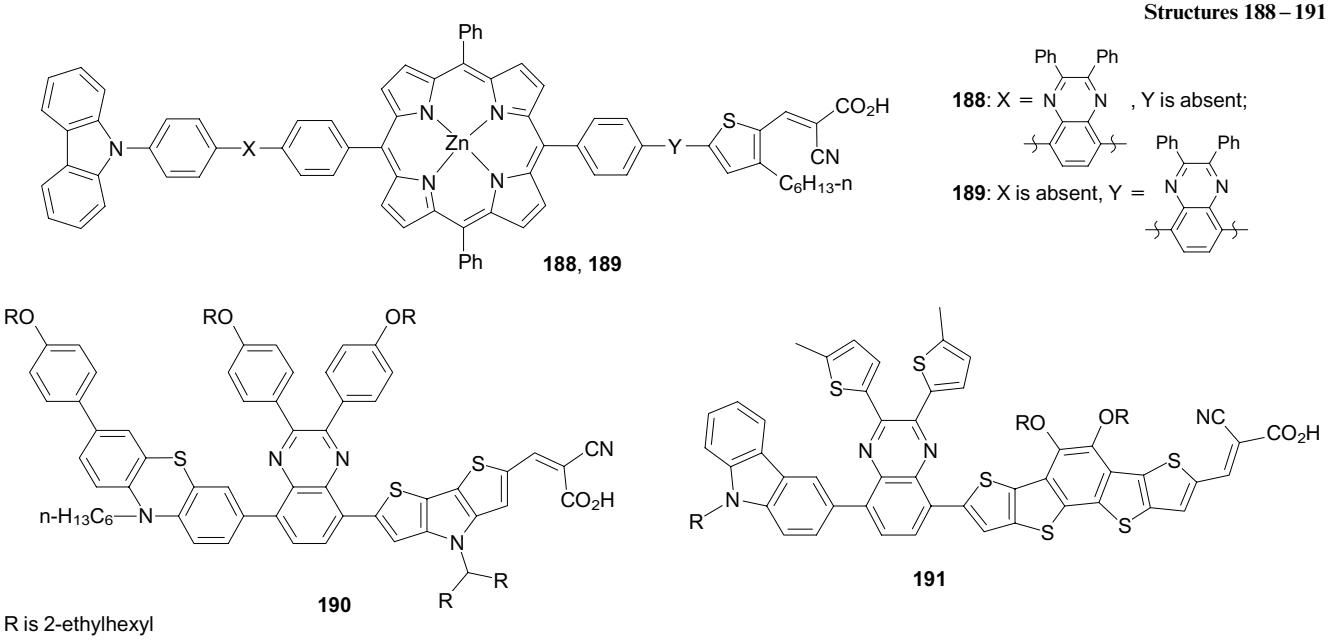
186, **187a**,**b**

R = Ph (**186**),



[Y = H (**187a**), Ph (**187b**)]

Structures 188 – 191



thin-film transistors (OTFTs). Thin film of **187b** showed p-channel characteristics with hole mobilities as high as 2.6×10^{-5} cm^2 (V s)$^{-1}$ and current on/off ratio of 3.5×10^6 *via* vacuum deposition.

The quinoxaline fragment has been extensively used in organic photovoltaics (OPV). In particular, the diphenylquinoxaline unit has shown a great potential in anti-aggregation and extension of spectral response.[141] The recent developments of quinoxaline derivatives for photovoltaics have been reviewed [142 – 144] and structures presented in these reviews will not be discussed here.

Fan *et al.*[145] have designed sensitizers **188** and **189**. In these structures, the 2,3-diphenylquinoxaline fragment acts as an auxiliary acceptor. Whereas the incorporation of this fragment between the donor and porphyrin unit (**188**) has negligible influence on the absorption property, its incorporation between the porphyrin unit and acceptor (**189**) significantly increases the absorbance for the Soret band and valley between Soret (corresponding to the transition S0 → S2) and Q bands (due to transition S0 → S2). The quasi solid state DSSC with **189** displays a PCE of 6.02%, 51% higher than those for **188**.

Han *et al.*[146] have designed phenothiazine chromophore **190**. DSSC based on this compound exhibits an excellent PCE of 10.06%. Zhang *et al.*[147] have designed dye **191** for DSSC application. DSSC device with PCE of 4.63% was obtained.

Pei *et al.*[125] and Wang *et al.*[148] have described D – A – π-A chromophores **192a**,**b**, **193a** to be used as solar cell sensitizers. The two phenyl groups grafted onto the quinoxaline core may prove to be efficient building blocks to improve photostability and thermal stability and antiaggregation functional units and appear as an alternative to stability deleterious alkyl chain grafted thienyl bridge. Dyes **192b** and **193a** exhibit conversion efficiency as high as 9.24% and 8.76% respectively. Compound **193b** with methoxy substituent on the phenyl fragment was designed by Xu *et al.*[149] and DSSC with this sensitizer exhibits a PCE of 9.83%.

Ji *et al.*[15] have shown that the addition of a 2,3-di-*p*-pentylquinoxaline as auxiliary acceptor in sensitizer **194** significantly enhances photovoltaic performance with PCE of 7.98%.

Godfroy *et al.*[151] have synthesized D – π-A – π-A organic sensitizer **195a**. DSSC based on **195a** shows a PCE of 6.36%. DSSCs obtained from similar structures **195b** and **196** designed by Ma *et al.*[152] exhibit PCE of 7.29% and 7.78%, respectively.

Lu *et al.*[153] have described a series of quinoxaline chromophores **197a** – **d** for DSSCs. When the alkyl substituent is removed from the spacer part in **197a** to the donor part in **197b** and **197c**, a more conjugated system and a red shifted absorption maximum can be realized. A quasi-solid state DSSC based on **197d** exhibits a power conversion efficiency of 7.14% (8.27% with liquid electrolyte). This sensitizer can be combined with another phenazine-based sensitizer with complimentary absorption profile and PCE of 8.04% in quasi solid state DSSC has been achieved.[154]

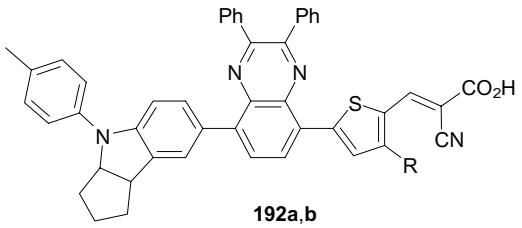
The incorporation of fluorine atom has also been tested on similar structures **198b** and **198c**.[155] When compared with unsubstituted analogue **198a**, the quasi-solid state DSSC based on **198c** exhibits a 37% higher efficiency (PCE of 8.2% for **198a**).

The same team has also designed sensitizers **199** and **200**.[156] A broader and more intense charge transfer band is observed for **199** with a single anchoring group that exhibits a power conversion efficiency of 5.2% for a quasi-solid-state DSSC (6.2% with liquid electrolyte) with good stability.

Shen *et al.*[157] have designed sensitizers **201a** – **c**. They have demonstrated that the incorporation of electron-deficient quinoxaline into the π-chain significantly enhances the PCE (20% increase) and DSSC based on **201a** exhibits the best performance (PCE of 8.05%).

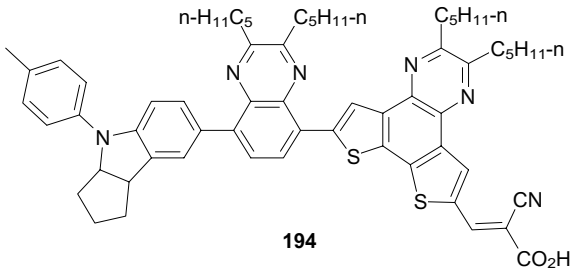
Li *et al.*[158] have designed two D – A – π-D sensitizers **202** and **203a** employing 3,4-ethylenedioxythiophene and cyclopentadithiophene as π-linkers, respectively. Compounds **202**, **203a** were obtained from 5,8-dibromo-2,3-diphenylquinoxaline *via* sequenced reactions of Stille cross-coupling,

Structures 192 – 200

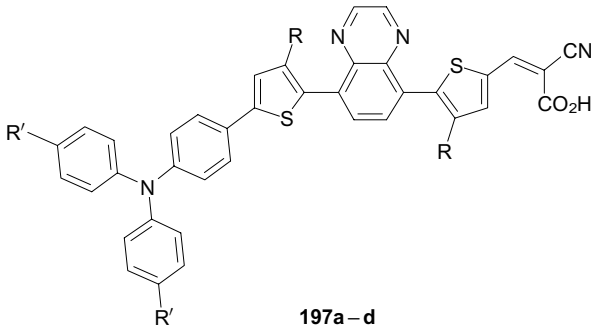


192a,**b**

R = H (**a**), n-$C_{10}H_{21}$ (**b**)

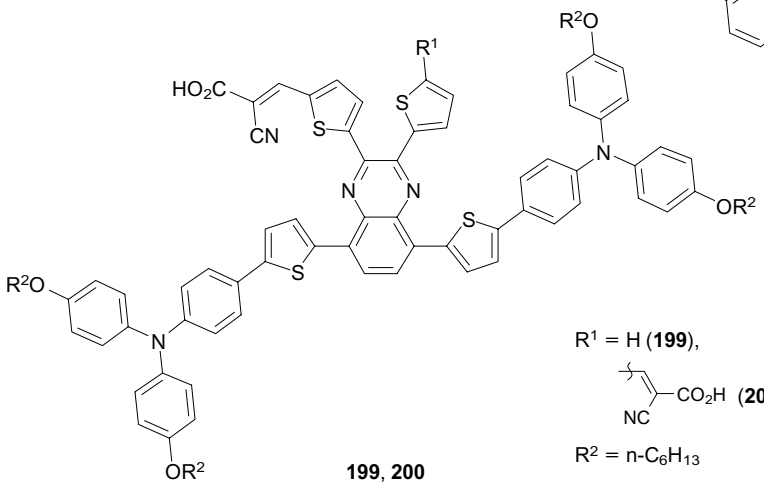


194



197a – d

R = n-C_6H_{13}, R′ = H (**a**); R = H, R′ = OC_6H_{13}-n (**b**);
R = H, R′ = OC_8H_{17}-n (**c**); R = n-C_6H_{13}, R′ = OC_8H_{17}-n (**d**)

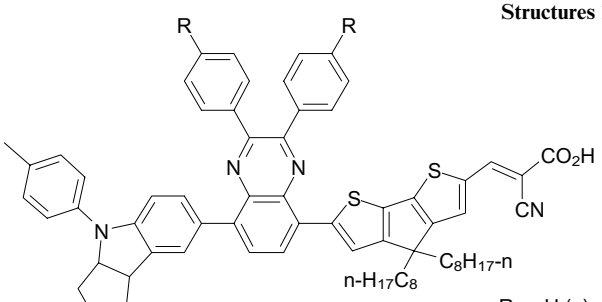


199, **200**

R^1 = H (**199**),

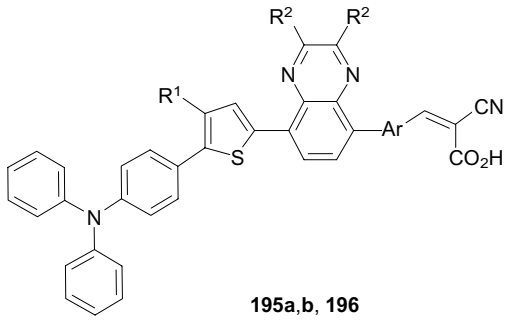
(**200**);

R^2 = n-C_6H_{13}

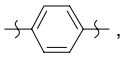
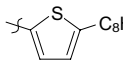


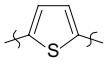
193a,**b**

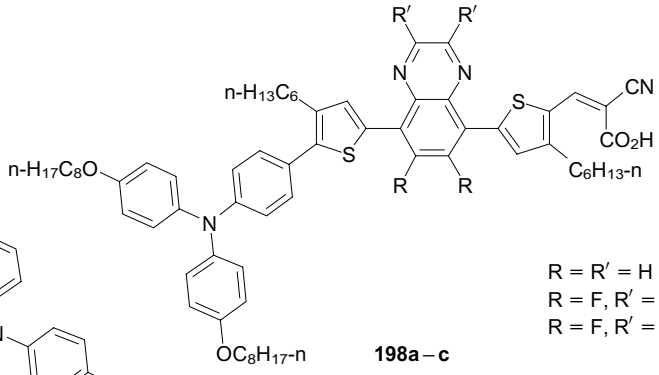
R = H (**a**), OMe (**b**)



195a,**b**, **196**

195: Ar = , R^2 = : R^1 = C_8H_{17} (**a**), H (**b**)

196: Ar = , R^1 = H, R^2 = n-C_8H_{17}



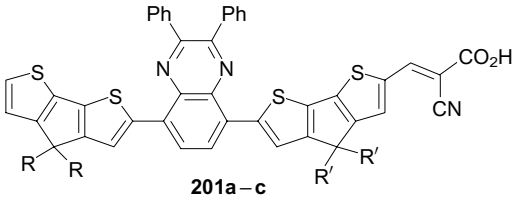
198a – c

R = R′ = H (**a**);
R = F, R′ = H (**b**);
R = F, R′ = Ph (**c**)

New blue dye **203b**, bearing 2,3-diphenylquinoxaline as acceptor, indeno[1,2-*b*]thiophene-functionalized triethylamine as donor and cyclopentadithiophene as π-linker, was synthesized by the same method as quinoxalines **202**, **203a**. Compound **203b** exhibits wide absorption band with λ_{abs} = 600 nm and high extinction coefficient ($\varepsilon = 6.3 \times 10^4$ M^{-1} cm^{-1}). DSSC device fabricated on the basis of **203b** demonstrated high efficiency (PCE = 7.81%).[159]

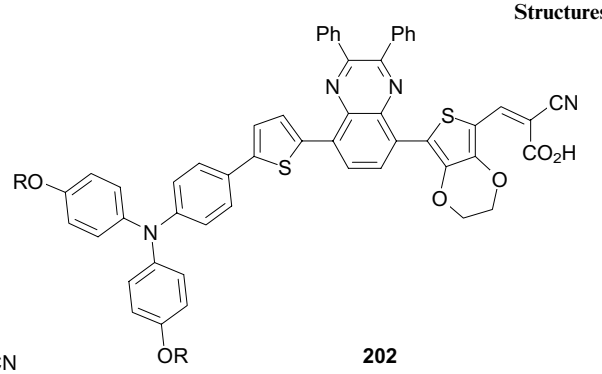
formylation, substitution of second bromine with (diarylaminophenyl)thiophene fragment and condensation with 2-cyanoacetic acid. 2,3-Diphenyl-5,8-dithienylquinoxalines **202**, **203a** possess intense absorption in DCM in visible range (λ_{abs} = 553 nm, $\varepsilon = 1.75 \times 10^4$ M^{-1} cm^{-1} for **202** and λ_{abs} = 569 nm, $\varepsilon = 4.12 \times 10^4$ M^{-1} cm^{-1} for **203a**). When grafted on TiO_2, blue shift of absorption band was observed with maxima λ_{abs} = 534 and 537 nm, respectively, for **202** and **203a**. An all-solid state DSSC with **203a** has been obtained with an impressive PCE of 8.0%.

Structures 201 – 208

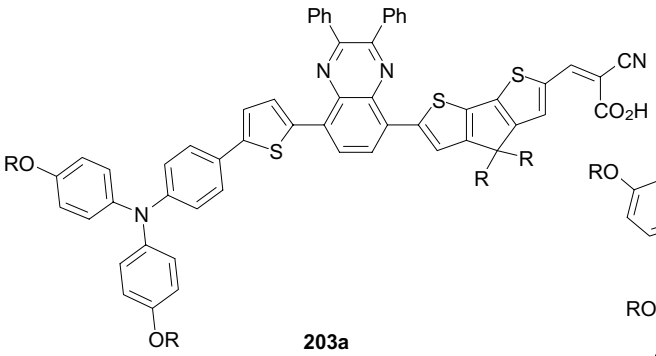


201a – c

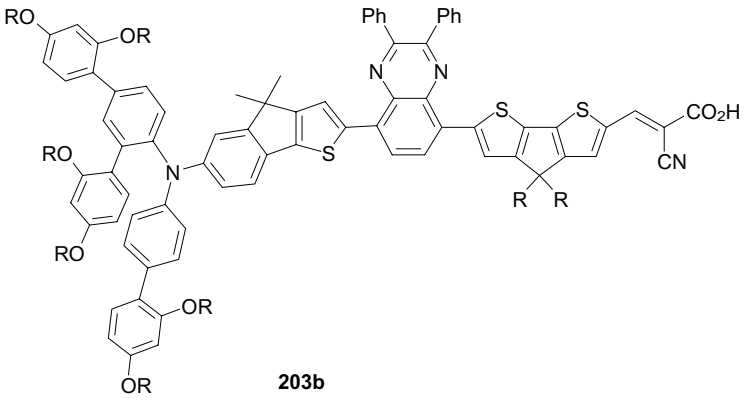
R = n-C_8H_{17}, R′ = Me (**a**); R = Me, R′ = n-C_8H_{17} (**b**),
R = R′ = n-C_8H_{17} (**c**)



202

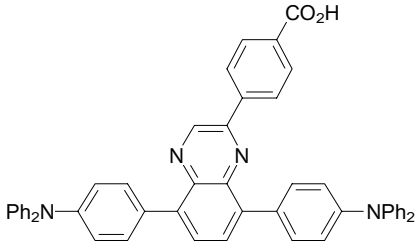


203a

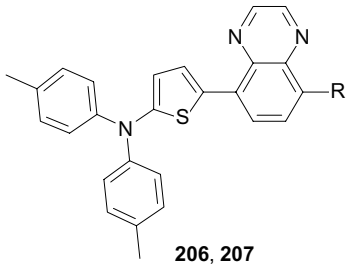


203b

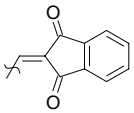
202, **203**: R is 2-ethylhexyl

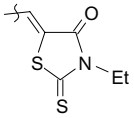


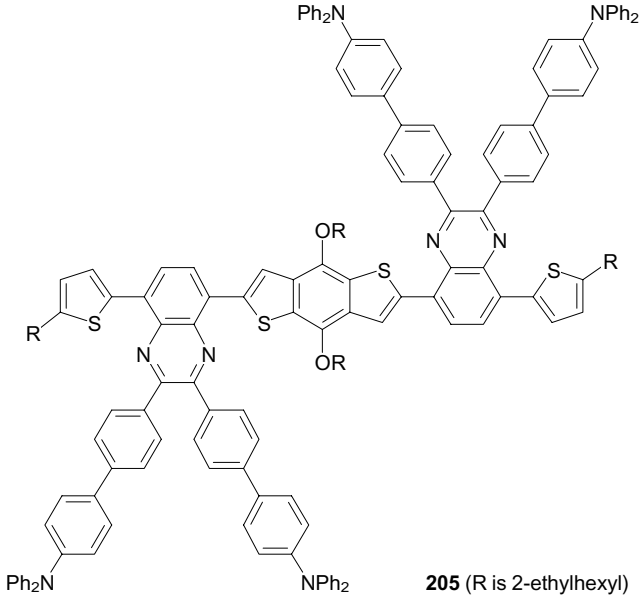
204



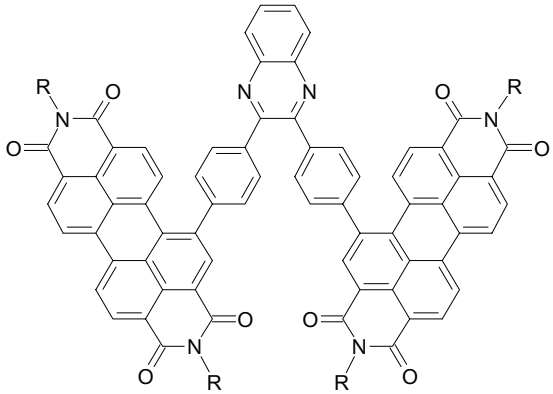
206, **207**

R =  (**206**),

 (**207**)

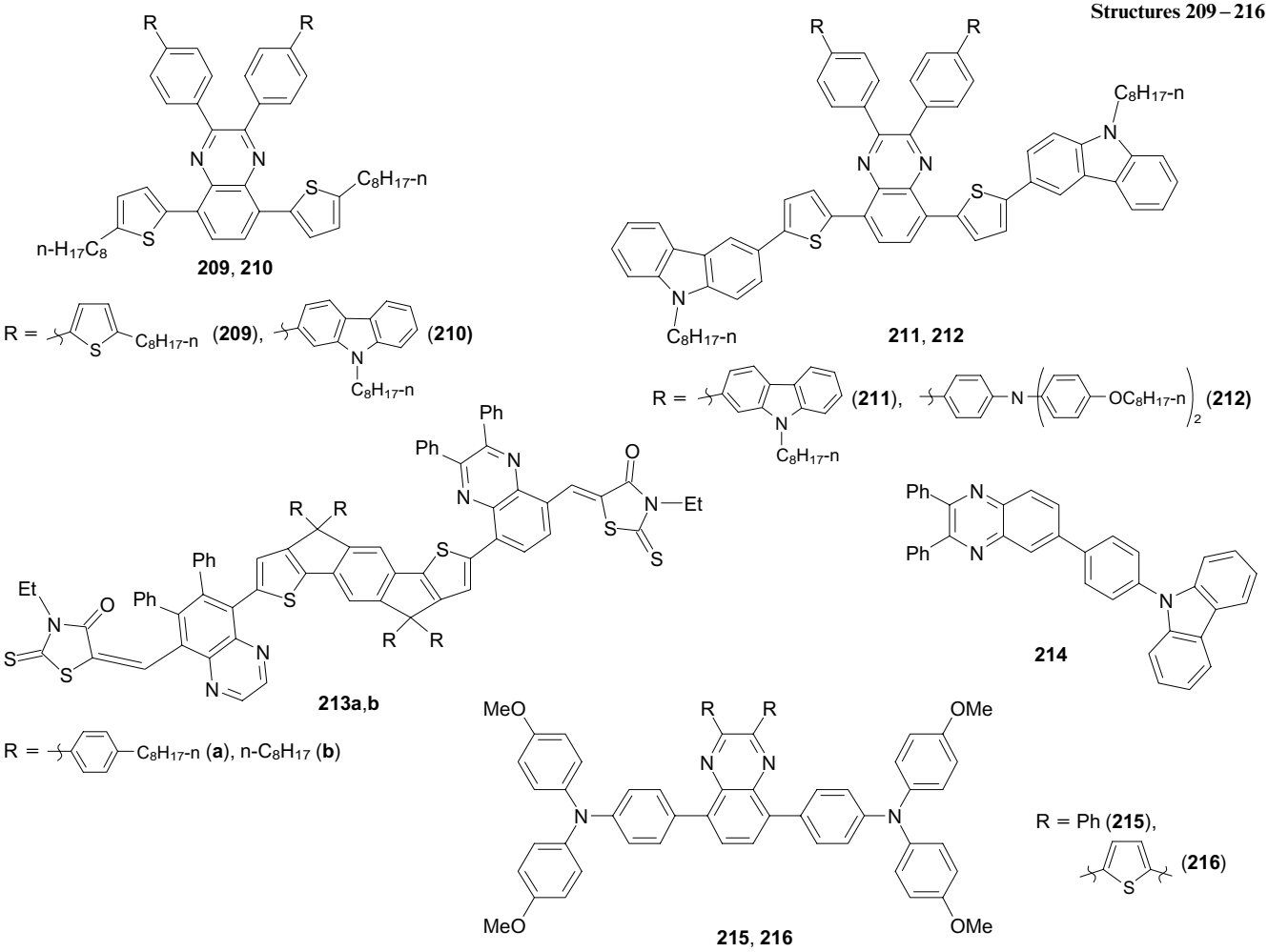


205 (R is 2-ethylhexyl)



208 [R = $CH(C_5H_{11}\text{-}n)_2$]

Structures 209 – 216



Kono *et al.*[160] have designed sensitizer **204**. DSSCs with **204** showed PCE of 3.2%. To improve the device performances, thienopyrazine analogue was used as a co-adsorbent and PCE of 6.2% was achieved.

Yu *et al.*[161] have designed sensitizer **205**, which can be used in solution-processed organic photovoltaic devices with PCE of 1.22%.

Qi *et al.*[162] have designed chromophores **206** and **207** as donors for bulk-heterojunction solar cells. With the configuration FTO/c-TiO_2/**206** or **207**: C_{70}/MoO_3/Ag, bulk-heterojunction solar cells with PCE of 1.44% and 1.70%, respectively, were obtained.

Liu *et al.*[163] have studied perylenediimide acceptor **208**. Based on **208** non-fullerene photovoltaic device has been obtained and showed PCE of 3.86%.

Deng *et al.*[164] have designed chromophores **209** – **212** based on quinoxaline as potential donor for bulk-heterojunction organic solar cells.

Xiao *et al.*[165] have described $A_2-A_1-D-A_1-A_2$ chromophores **213a**,**b** where the quinoxaline is used a bridge acceptor (A_1) fragment. These sensitizers exhibit the complementary absorption spectra with poly(3-hexylthiophene) (P3HT) and polymer solar cells based on P3HT : **213a** and P3HT : **213b** showed power conversion efficiency of 4.03% and 4.81%, respectively.

9-[4-(2,3-Diphenylquinoxalin-6-yl)phenyl]-9H-carbazole (**214**) was designed as host material for red phosphorescence OLED, which demonstrated outstanding electroluminescence performance with maximum current efficiency 21.9 cd A^{-1}, power efficiency 15.4 lm W^{-1} and external quantum efficiency 12.2%.[166]

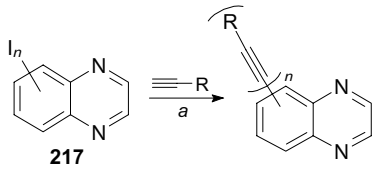
Zhang *et al.*[167] have designed D – A – D hole transporting materials **215** and **216** based on quinoxaline central core for perovskite solar cells. Perovskite solar cells based on **216** exhibit a maximum efficiency of 19.62% outperforming the spirobifluorene derivative generally used as hole transporting material.

2.2.6. Arylethynylquinoxalines

Arylethynylquinoxaline derivatives are generally obtained by Sonogashira cross-coupling reaction. 2-Arylethynylquinoxalines and 2,3-diarylethynylquinoxalines can be obtained from chloro derivatives.[168] On the other hand, 6-arylethynylquinoxalines and 5,8-diarylethynylquinoxalines **218** have been obtained from iodo derivatives **217** (Scheme 17, top reaction).[127, 169] Another strategy to obtain 2-aryl-3-ethynylquinoxaline **219** based on three-component activtion – alkynylation – cyclocendensation (AACC) process has been recently proposed (Scheme 17, bottom reaction).[134]

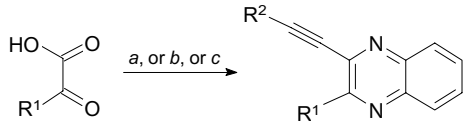
Nafe *et al.*[127] have synthesized 5,8-di(phenylethynyl)quinoxaline **220**. This compound exhibits red-shifted emission (λ_{em} = 483 nm) and increased fluorescence quantum yield (Φ_F = 0.85) relative to diphenyl analogue **153**.

Scheme 17

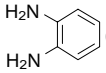


217 **218** (51% – 72%)

(*a*) $Pd(PPh_3)_2Cl_2$, CuI, Pr^i_2NH, PhMe, rt, 1.5 h; R = Ar, TMS; *n* = 1, 2



219 (28% – 100%)

(*a*) $(COCl)_2$, 1,4-dioxane, 50 °C, 4 h;
(*b*) R^2—≡, CuI (5 mol.%), NEt_3 (2 equiv.), rt, 15 h;
(*c*)  (**148**), AcOH, MeOH, 50 °C, 1 h;

R^1 = 2-Th, 5-bromo-2-thienyl, Ph, $C_6H_4NMe_2$-4, *etc.*; R^2 = TIPS, TMS

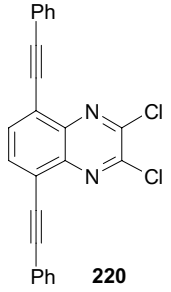
Nguyen *et al.*[168] have studied the photophysical properties of compounds **221**, **222**. Whereas 2-phenylethynylquinoxalines **221a**,**b** exhibit UV-emission (λ_{em} = 386 – 395 nm), disubstituted quinoxalines **222a**,**b** show purple emission (λ_{em} = 425 – 445 nm).

Merkt *et al.*[134] have designed 2-aryl-3-arylethynylquinoxalines **223**. These compounds exhibit yellow-orange emission (Φ_F = 0.23 – 0.42) in DCM with blue shifted emission when the electron-donating strength of the substituent of the phenylethynyl fragment is increased (**223a**: λ_{em} = 596 nm, **223b**: λ_{em} = 586 nm, **223c**: λ_{em} = 574 nm).

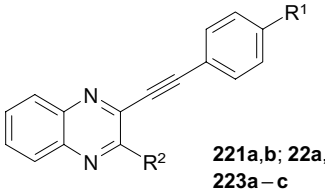
Lin *et al.*[169] have designed bisarylacetylene derivative **224** as two-photon absorption chromophore. A two photon cross section of ~2000 GM at 730 nm, higher than that of vinylene analogue **74a**, has been observed in toluene.

As shown by these numerous examples, the design of (het)aryl- and (het)arylethynylbenzo(di)azine has been a really active field of reseach during the last seven years. These chromophores have found applications in various fields such as bioimaging, OLEDs, photovoltaics.

Structures 220 – 223



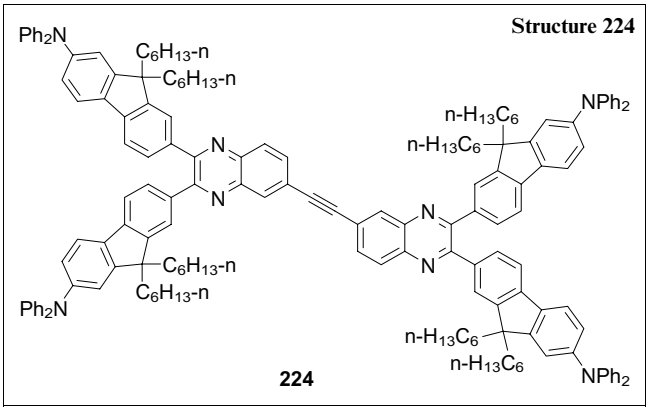
220



221a,**b**; **22a**,**b**; **223a – c**

221: R^2 = Cl: R^1 = H (**a**), NO_2 (**b**);
222: R^2 = C≡C--R^1:
R^1 = H (**a**), OMe (**b**);
223: R^2 = $C_6H_4NMe_2$-4: R^1 = H (**a**), OMe (**b**), NMe_2 (**c**)

Structure 224



224

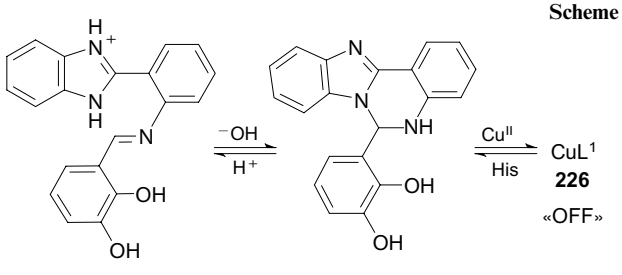
3. Annelated benzazines

Different annelated derivatives of quinazolines and quinoxalines are presented in reviews.[23, 170] Many derivatives of annelated benzazines found application as ligands for the synthesis of metal complexes. For example, benzo[*h*]quinoline[171, 172] and 4-arylthieno[3,2-*c*]quinoline[173] are used as cyclometallating ligands with expanded π-conjugated system. Derivatives of dipyrido[3,2-*f*:2,3-*h*]quinoxaline (dpquin) are applied for the complexation with wide range of metals,[174 – 176] in particular, for obtaining complexes with rare-earth elements in which ligand acts as effective antenna.[177]

Wang *et al.*[178] described 6-(2,3-dihydroxyphenyl)-5,6-dihydrobenzimidazo[1,2-*c*]quinoline **225**, obtained from 2-(2-aminophenyl)benzimidazole and 2,3-dihydroxybenzaldehyde by refluxing in methanol for 24 h. The structure of compound **225** was confirmed by X-ray diffraction method. This ligand (H_2L^1) exhibited strong emission at 434 nm in the mixture DMSO – water. Mixing of **225** with different metal ions demonstrated that only addition of Cu(II) ions leads to luminescence quenching in the ratio H_2L : Cu(II) = 1 : 1. The authors showed that complex **226** forms as azomethine intermediate (H_3L^1) into which ligand **225** transforms at pH below 5 (Scheme 18). The addition of histidine to complex **226** led to considerable increase of emission at 434 nm due to ligand substitution. Thus, authors presented compound **225** as fluorescent chemosensor for selective detection of Cu(II), including in physiological media, and complex **226** can be applied for the detection of histidine.

Acosta *et al.*[179] reported the new series of pyrazolo[1,5-*c*]pyrrolo[1,2-*a*]quinazolines and pyrazolo[1,5-*c*]-pyrido[1,2-*a*]quinazolines **229**, synthesized by the cascade reaction of anilines **227** and ω-chloroketones **228**

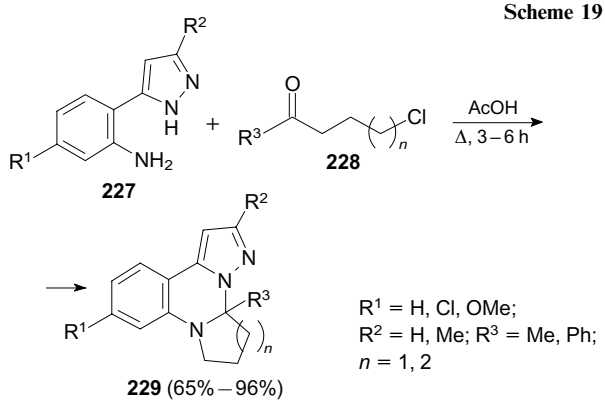
Scheme 18



$(H_3L^1)^+$ **225** (H_2L^1) «ON» **226** CuL^1 «OFF»

His is histamine

Scheme 19



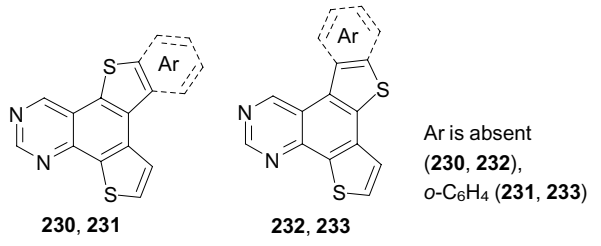
229 (65% – 96%)

(Scheme 19). These compounds demonstrated mainly blue or green luminescence. Emission spectra of **229** in chloroform exhibited two bands at 358 – 448 nm and 386 – 482 nm, attributed to associated and non-associated compounds in non-polar solvent. In ethanol, polar hydrogen-bonding solvent, emission spectra have one band at 382 – 409 nm, atributed to non-associated compounds. Notably, the luminescence quantum yields for these compounds are rather high (Φ_F = 0.63 – 0.13). Studying of electrochemical properties of compounds **229** showed that they can be oxidized chemically into completely π-conjugated systems.

Annelated dibenzo and phenanthroline quinazoline derivatives were described in patents[180, 181] as emitting, electron-transport and hole-transport layers for OLEDs. Derivatives of dibenzo[*f*,*h*]quinoxaline were patented as emitting elements in light-emitting materials and devices.[182]

Synthesis and photophysical properties of new dithienylquinazolines **230** – **233** are described.[183, 184] Compounds were obtained by oxidative cyclization of the corresponding 4,5-dithienylpyrimidines, they exhibit blue fluorescence (λ_{em} = 388 – 417 nm) with quantum yield in the range of 1.8% – 4.1%.

Structures 230 – 233

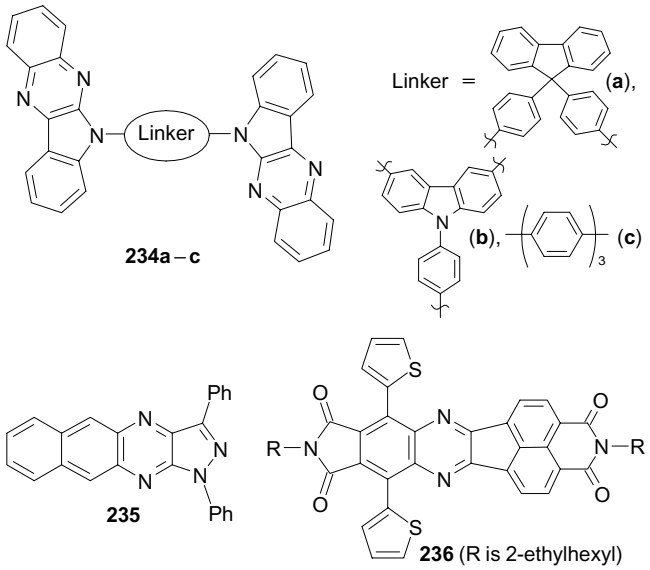


230, **231** **232**, **233**

Three novel bis(6*H*-indolo[2,3-*b*]quinoxalinyl) derivatives **234a** – **c** containing fluorenyl, terphenyl or carbazole bridge were described as emitters for phosphorescent OLEDs.[185] In toluene solution at room temperature these compounds exhibit fluorescence with λ_{em} = 470 – 500 nm, while in thin film, emission maxima were observed at 487 – 525 nm. At 77 K in thin film, phosphorescence with λ_{em} = 543 – 594 nm was noted. Electroluminescent devices based on these materials and iridium additives demonstrated deep red emission and showed EQE > 20%.

1,3-Diphenyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]quinoxaline **235**, obtained from 2,3-diaminonaphthalene and 2,5-diphenylpyrazole-3,4-dione, exhibited photoluminescence in THF solution with λ_{em} ~ 580 nm.[186] The electronic device fab-

Structures 234 – 236



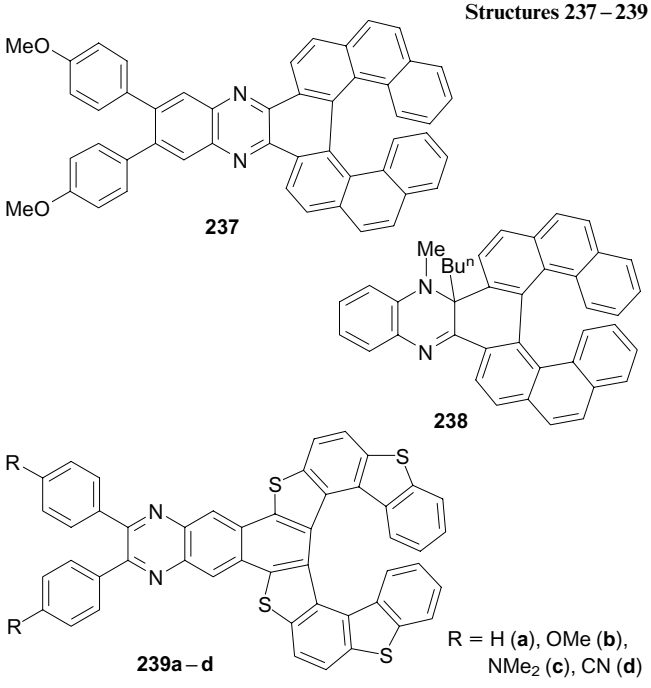
234a – **c** **235** **236** (R is 2-ethylhexyl)

ricated on the basis of **235** demonstrated yellow emission with λ_{em} = 548 nm and brightness 800 cd m^{-2}.

Lan *et al.*[187] reported acenaphtho[1,2-*b*]quinoxaline-diimide **236** as potential non-fullerene component for organic solar cells. This compound demonstrated relatively wide absorption band (from 300 to 650 nm) with moderately low-lying LUMO level (−3.64 eV) and average optical gap ~2 eV.

Sakai *et al.*[188, 189] reported quinoxaline[7]carbohelicene derivatives **237**, **238** as quinoxaline-containing nonplanar molecular systems possessing luminescent properties. Compound **237** and unsubstituted quinoxaline[7]carbohelicene were synthesized from carbohelicene diketone and the corresponding 1,2-diaminobenzene. In order to obtain 1,2-dialkyl-substituted **238**, the quinoxaline fragment was reduced with dithionite, then reaction with butyllithium

Structures 237 – 239



237 **238** **239a** – **d**

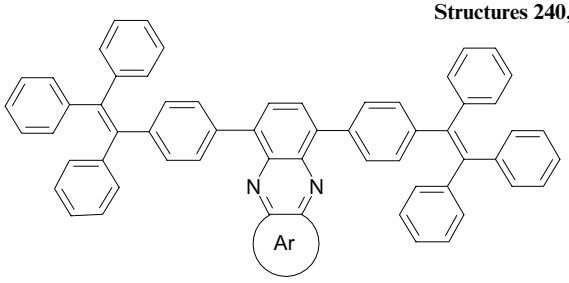
and methyl iodide was performed.[187] Both structures were characterized by spectral methods and X-ray diffraction. Compound **237** exhibited fluorescence in THF solution with $\lambda_{em} = 550$ nm and $\Phi_F = 0.05$.[188] In crystals the second band was also observed at 590 nm which can be attributed, according to the authors, to the excimer-like delocalized excited state.

Compound **238** demonstrated red shift of emission band in comparison with quinoxalin[7]carbohelicene by approximately 100 nm (yellow fluorescence) and five-fold increase in quantum yield ($\Phi_F = 0.25$) relatively to **237.** Circularly polarized luminescent (CPL) properties were studied, OLED based on derivative **238** as emitting layer was successfully fabricated.

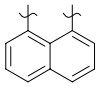
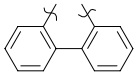
The same group of authors[190] obtained the series of fluorescent push-pull tetrathia[9]helicenes **239**, bearing quinoxaline as acceptor fragment. Compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as MALDI-TOF and ESI-QTOF mass-spectrometry data. Compounds **239** exhibit strong fluorescence in THF solution with $\lambda_{em} = 600 - 660$ nm depending on the nature of substituent R, higher quantum yield ($\Phi_F = 0.43$ for **239c** and 0.30 for **239d**) and large Stokes shift. Increased value of Φ_F for compound **239d** provided information on CPL properties, the degree of anisotropic factor was estimated ($g_{CPL} = 3.0 \times 10^{-3}$). Incorporation of quinoxaline into tetrathia[9]helicene core promotes the push-pull nature of thiahelicene derivatives.

New T-shaped tetraphenylethylene-substituted derivatives of acenaphthene- and phenanthrene-quinoxaline **240**, **241** with D – A – D structure were reported.[191] Both luminophores were synthesized by Suzuki cross-coupling reaction from quinoxaline dibromo derivative and boronic acids. Compounds exhibit fluorescence in solution, which is sensitive to solvent polarity: derivative **240** demonstrates blue emission in toluene with $\Phi_F = 0.18$ and green emission in dichloromethane with $\Phi_F = 0.33$, whereas its counterpart

Structures 240, 241



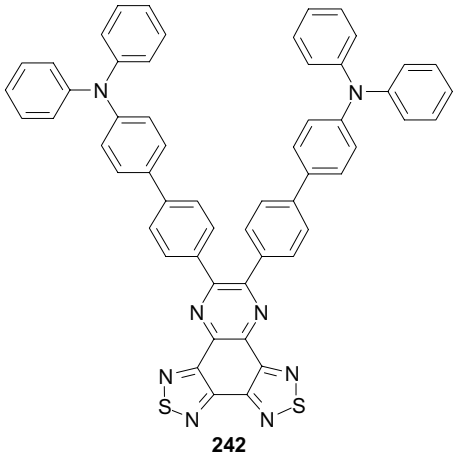
240, **241**

Ar =  (**240**),  (**241**)

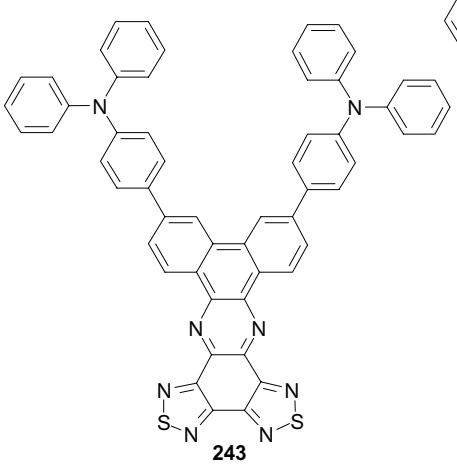
241 demonstrates green emission in toluene with $\Phi_F = 0.21$ and yellow emission in dichloromethane with $\Phi_F = 0.55$. Studying fluorescent properties of these compounds in a THF – water mixture showed that **240**, **241** exhibit aggregation induced emission. In solid state luminophores **240**, **241** demonstrated reversible mechanochromism with good colour contrast due to morphological change from crystal to amorphous state.

V-Shaped fluorescent dyes of D – A type **242** – **244** bearing bis(thiadiazole)quinoxaline and bis(thiadiazole)phenanthroquinoxaline were described.[192] In solution, the luminescence and red shift of emission band as well as decrease in intensity were observed with the growth of solvent polarity (for compound **242** λ_{em} changed from 474 nm in cyclohexane to 652 nm in DCM, Φ_F from 0.36 to 0.03; for compound **243** λ_{em} changed from 484 nm to 678 nm, Φ_F from 0.51 to 0.11). Derivative **244** with lack of donor fragment did not show the dependence of emission on solvent polarity. In solid state orange emission was observed for compound **243** with $\Phi_F = 0.17$, for **242** emission was weaker ($\Phi_F = 0.03$) and for **244** it was practically

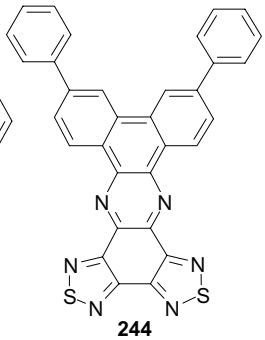
Structures 242 – 248



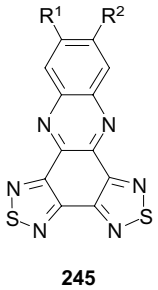
242



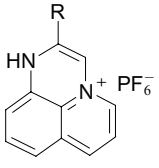
243



244

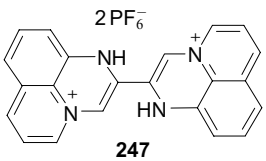


245

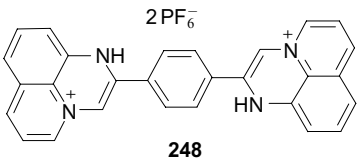


246a – f

R = Ph (**a**), 4-BrC_6H_4 (**b**), 2-Py (**c**), 2-Th (**d**), 1-Naph (**e**), 2-Naph (**f**)



247



248

absent. Emission behaviour of compounds **242** – **244** was studied in a THF – water mixture, the most distinct changes were observed for compound **243**. At 0% of water fraction this derivative emitted red light with $\lambda_{em} = 654$ nm and $\Phi_F = 0.23$, when increasing the water fraction up to 30% the intensity considerably decreased down to $\Phi_F = 0.002$. However, beginning from 40% of water the intensity of emission increased with the final value $\Phi_F = 0.18$ at 90% and hypsochromic shift to orange range is observed. At the high content of water compound **243** formed agregates due to hydrophobic interaction which create the hydrophobic space limiting polarization of the excited state and, as a result, quenching of emission. Transition from initial condition of emission to final through intermediate quenching, reached in V-shaped structure of compound **243**, was shown as an example of creation of emission system in the polar water medium. According to the authors, unusual double change of emission is caused by the combined aggregation effect and twisted ICT.

Derivatives of bis(thiadiazole)quinoxaline of general formula **245** were patented as organic light emitting elements and materials.[193] It is worth noting that organic dyes emitting in red and near IR range are most important for biovisualization and biological studies.

Laramee-Milette *et al.*[194] obtained the series of 1*H*-pyrido[1,2,3-*de*]quinoxaline cationic dyes **246** – **248** by the reaction of 8-aminoquinoline with α-bromoketone. The structure of compounds **246a**,**b** was confirmed by X-ray diffraction data. The majority of derivatives exhibit luminescent properties in solution and solid state with $\lambda_{em} = 500 - 700$ nm and low quantum yield ($\Phi_F = 0.005 - 0.017$ in MeOH). Compound **247**, which proved to be non-emissive in solid state, was an exception. On the basis of the conducted research authors came to the conclusion that the observed luminescence in solid state for compounds **246**, **248** can be caused by strong intermolecular π – π interaction leading to aggregation induced emission.

4. Polymer benzazines

Functionalized benzazines are included into various π-conjugated polymers which are promising for application in different spheres as photoactive materials. Among them quinoxaline and its derivatives have been widely used as building blocks because they can be easily modified by varying the side chains, which promotes the creation of polymeric products. Thus, recent reviews [142 – 144] are devoted to the development of quinoxaline based polymers for organic photovoltaics (OPV).

Gedefaw *et al.*[142] collected data on the basic structure of monomer qunoxalines and their incorporation into the conjugated polymers of D – A type, special attention was paid to a combination of quinoxaline and benzothiophene fragments in polymeric chain. A broad range of structures and devices considered in this work showed a possibility of precise control of the properties of quinoxaline-containing polymers for the creation of highly effective OPV devices due to high stability, versatility, smooth and inexpensive synthesis, and peculiar optical, chemical and electronic properties of quinoxaline as acceptor building-block in D – A polymers.

Yuan *et al.*[143] focused on design and synthesis of photovoltaic polymers, including quinoxaline fragment with flexible alkoxy, fluoro and conjugated side chains. It was shown that incorporation of the latter has a positive impact not only on absorption spectra, but also on charge conductivity, energy levels and a microstructure of active layers in polymeric solar cells (PSCs), which leads to considerable improvement of productivity of photovoltaic devices.

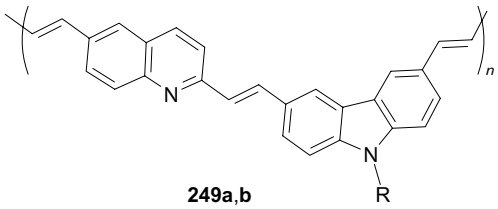
Liu *et al.*[144] generalized data on quinoxaline-based D – A conjugated polymers, classifying them by the donor unit incorporated into the quinoxaline moiety. Variously replaced fluorenes, carbazoles, indacetonodithiophenes, benzodithiophenes, thiophenes and other co-monomers were considered as such donor units. Modifications of chemical structure by two-dimensional side chains or fluorine substituents targeted to maximizing the productivity of solar cells were described.

Despite a large number and a variety of synthesized and studied π-conjugated polymers bearing acceptor quinoxaline fragments as well as some established structure – property correlations, the search for new photoactive polymers with improved characteristics is continued.

Upadhyay *et al.*[195, 196] synthesized novel series of donor-acceptor combined quinoline-carbazole oligomers **249**, using Wittig methodology. Compounds were characterized by IR, ^{1}H and ^{13}C NMR, cyclic voltammetry, atom microscopy and TGA. Oligomers demonstrated thermostability up to 200 °C, good solubility in common organic solvents. Oligomer **249a** possesses luminescence with $\lambda_{em} = 420 - 451$ nm depending on the solvent polarity and $\Phi_F = 0.23$ in chloroform. Oligomer **249b** also exhibited fluorescence with $\lambda_{em} = 385 - 441$ nm in solution and 473 nm in film. The luminescence of these compounds can be quenched by the addition of dimethylaniline or dimethyl terephthalate to the solution of oligomer. Optical data indicate that strong intramolecular π – π*-interaction between carbazole and quinoline takes place in oligomers.

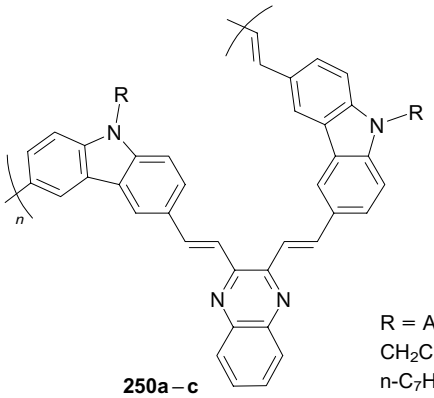
In another work the same authors [197] described synthesis and properties of oligomers **250a** – **c**, bearing quinoxaline ring as an acceptor. Compounds are well soluble in organic

Structures 249, 250



249a,**b**

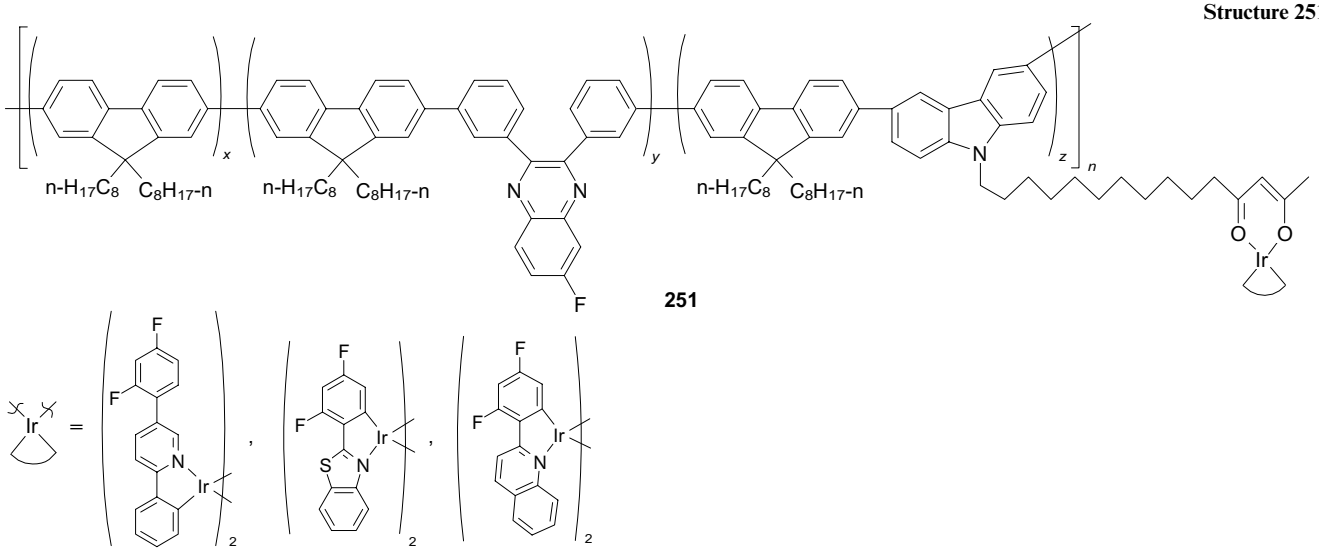
R = n-C_7H_{15} (**a**), All (**b**); $n = 6 - 9$



250a – **c**

R = All (**a**),
$CH_2CH{=}CMe_2$ (**b**),
n-C_7H_{15} (**c**); $n = 3 - 10$

Structure 251



251

solvents; decomposition temperatures exceeded 300 °C with 5% weight loss. Oligomers exhibited fluorescence in solution, red shift of emission band was observed with increasing the solvent polarity. Thus, for compound **250a**: λ_{em} = 471 ($CHCl_3$), 521 nm (DMF), Φ_F = 0.41 (DMF); for **250b**: λ_{em} = 529 nm, Φ_F = 0.49 (DMF); for **250c**: λ_{em} = 545 nm, Φ_F = 0.61 (DMF). In solid state the emission peak underwent red shift up to 550, 562 and 574 nm for **250a** – **c**, respectively. As in the case of oligomer **249**, luminescence of compounds **250** can be quenched by the same quenchers. The behaviour of oligomer **250** in relation to a wide range of metal cations was studied and it was shown that only the addition of a Ni^{2+} cation leads to strong decrease in fluorescence intensity. These compounds can be applied as selective probes for Ni^{2+} ions in the presence of other metals. According to the authors, these oligomers have potential application in OLEDs.

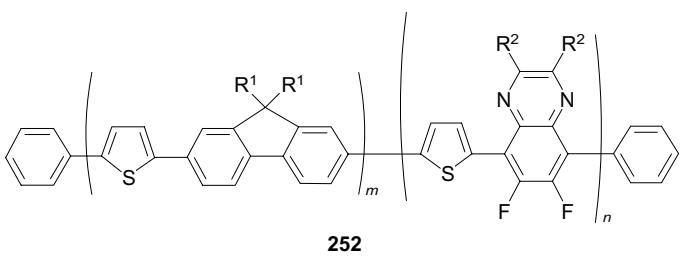
Guo *et al.*[198] described white light emitting polymers **251** based on polyfluorene derivative, bearing electron-deficient 2,3-biphenyl-6-fluoroquinoxaline in the main chain, and imparted iridium complexes in side chain. It is shown that the combination of blue fluorescence of the main chain and yellow phosphorescence of iridium complex resulted in effective white emission in this unique polymer.

In a number of works the improvement of polymer properties was reached by the modification of quinoxaline fragment. Kang *et al.*[199] prepared five new co-polymers **252**, containing 2,3-dialkyl-6,7-difluoroquinoxaline and 9,9-di-n-octylfluorene with their different ratio in the main chain. All polymers demonstrated high M_w, good solubility in chlorine-containing solvents and high termostability. These copolymers are characterized by rather low value of optical gap (1.93 – 2.08 eV) and deep level of HOMO energy (from −5.67 to 5.59 eV). PSCs based on co-polymers **252** were designed; these devices demonstrated maximum values of PCE in the range 2.91% – 3.98%.

Wang *et al.*[200] reported novel π-conjugated co-polymer of D – A type **253**, including 4-alkyl-3,5-difluorophenyl-substituted quinoxaline as acceptor, disubstituted benzodithiophene fragment as donor and thiophene as spacer in the main chain. Organic solar cells (OSCs) based on **253** exhibited excellent efficiencies both in fullerene (PCE = 9.2%) and non-fullerene devices (PCE = 9.6%). The authors demonstrated that incorporation of two weak electron-donating groups into position 4 of phenyl substituent of quinoxaline led to the improvement of photovoltaic properties.

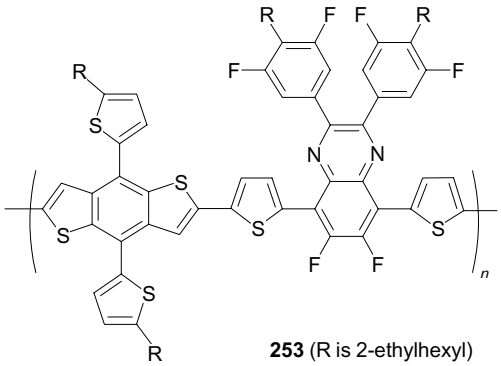
Yang *et al.*[201] described new polymers **254** for effective non-fullerene OSCs, containing 3,4-dialkoxyphenyl-substituted quinoxaline and dithiophenearyl fragment. It was shown that incorporation of 1 to 4 fluorine atoms into aryl fragment allows effective adjusting of the levels of polymer frontal molecular orbitals, molecular packing and the morphology of films. According to calculations, poly-

Structures 252, 253



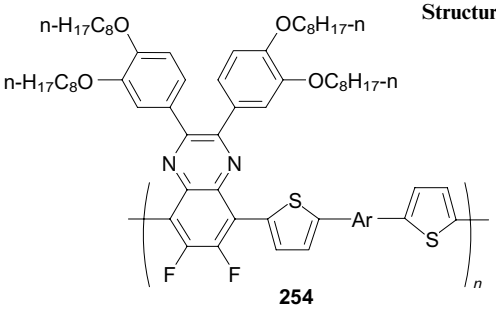
252

R^1 = n-C_8H_{17}, R^2 = n-$C_{12}H_{25}$



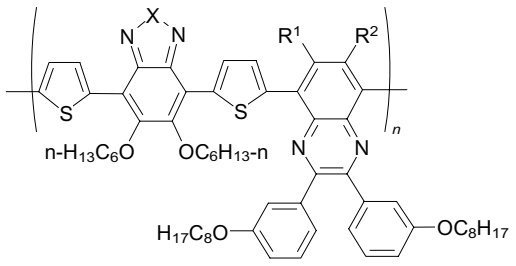
253 (R is 2-ethylhexyl)

Structures 254, 255



254

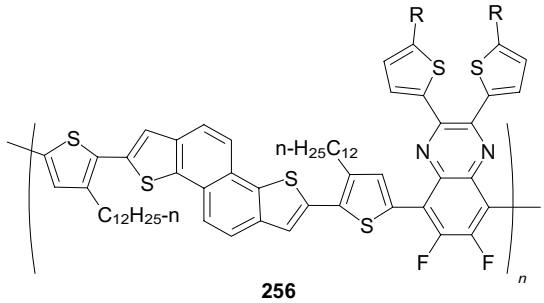
Ar = 1,4-C_6H_4 (**a**), 1,4-(2-FC_6H_3) (**b**), 1,4-(2,5-$F_2C_6H_2$) (**c**), 2,3,4,5-F_4C_6 (**d**)



255

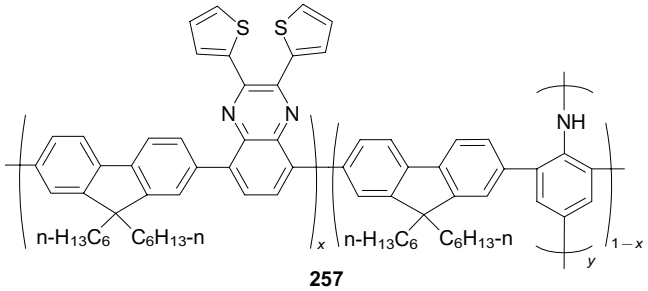
$R^1 = R^2$ = H, F; X = O, S

Structures 256, 257



256

R is 2-ethylhexylthio (**a**), 2-ethylhexyl (**b**)



257

mer **254c** is characterized by the greatest planarity due to intramolecular non-covalent S···F and H···F interactions. All polymers showed wide optical gap (E_g > 1.8 eV) and the great value of switching voltage (1.00 V) in non-fullerene OSCs. The device based on polymer **254c** exhibited PCE = 9.7%.

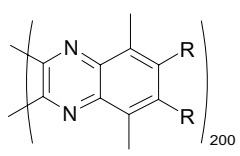
Wang *et al.*[202] obtained terpolymers **255** of $D-A_1-D-A_2$ structure by the combination of the simplest thiophene donor and two simple acceptors: alkoxy-containing benzoxadiazole (benzothiadiazole) and quinoxaline. Studying of optical, electrochemical properties of these polymers, characteristics of the PSCs samples fabricated on the basis of **255** showed that variation of the structure of A_2 moiety allows adjustment of the specified properties of the final polymer. The polymers absorbed in visible range with maximum at 565 – 630 nm in solution, an optical gap within 1.70 – 1.73 eV and the deep level of HOMO energy (from −5.60 to −5.34 eV). The maximum value of PCE = 5.84% was obtained for the device on the basis of terpolymer **255** (X = O, R^1 = H, R^2 = F), and it is much higher than for polymers of $D-A_1$ or $D-A_2$ type.

Lin *et al.*[203] described new D – A polymers **256**, containing naphtodithiophene as donor and quinoxaline bearing alkylthio and alkylthiophene side chains. Comparative studying of the influence of flexibility of such chains on polymer properties showed that alkylthio residues lead to the red shift of absorption bands, lowering of the HOMO and LUMO energy level, improvement of intermolecular π···π interactions and the morphology of films. It was found that PSC based on polymer **256a** possessed higher PCE (5.03%), whereas for PSC using **256b** PCE was only 1.93%. Results of research confirm an important role of substituents in quinoxaline acceptor in the tuning of properties of polymers and devices.

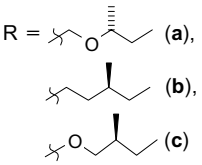
In the work of Jessop *et al.*[204] the two-dimensional conjugated polymer **257** based on aniline and 9,9-di-n-hexylfluorene as donor fragments and 2,3-dithienylquinoxaline as acceptor was synthesized. Comparison of the properties of this polymer with its one-dimensional precursor showed that the effect of perpendicular polyaniline branches resulted, mainly, in considerable reduction of molecular weight, whereas such characteristics as absorption and emission maxima, HOMO and LUMO energy level, size of optical gap practically do not change. OLED fabricated on the basis of polymer **257** as emissive layer, shows the low efficiency of the device, the electroluminescence arises at high value of switching voltage.

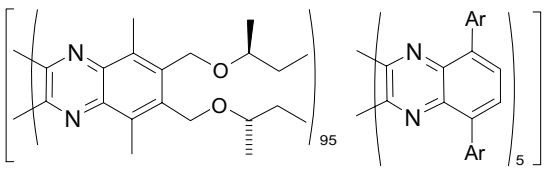
Nagata *et al.*[205] synthesized and studied properties of polymers **258**, bearing quinoxalin-2,3-diyl with different chiral side chains. These compounds were obtained by polymerization of 1,2-diisocyano-4,5-R-benzenes in the

Structures 258, 259

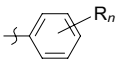


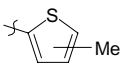
258a – c





259a – g

Ar =  [R_n = 4-CF_3 (**a**), 4-Me (**b**), 4-OMe (**c**), 4-NMe_2 (**d**), 3,4,5-$(OMe)_3$ (**e**)];

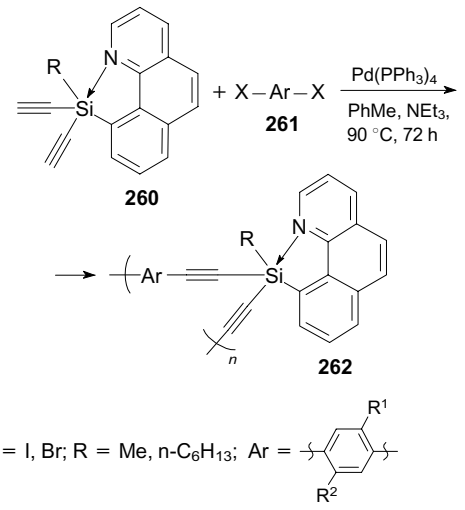
 : 3-isomer (**f**), 5-isomer (**g**)

presence of transition metal complexes, they possess spiral-like main chain caused by steric pushing of two substituents at positions 5 and 8 of quinoxaline.[206] Polymers **258** exhibited blue fluorescence in solution, the luminescence intensity for **258c** was mich higher than for **258a**,**b**. The dependence of spiral inversion of polymers **258a** – **c** on the solvent was studied and it was shown that all of them possess *M*-spiral structure in $CHCl_3$ and *P*-spiral in 1,1,1-trichloroethane (TCE). Circular polarized luminescence (CPL) spectra of polymer **258c** in dilute solutions of several solvents, including $CHCl_3$ and 1,1,1-TCE were recorded, and it was shown that observed signals are due to spiral conformation of quinoxaline rings. CD spectra in $CHCl_3$ and 1,1,1-TCE were almost mirror display of each other. Thus, polymers demonstrated the chiral-switched CPL in dilute solution and can be considered as new class of CPL materials.

In another work the same group of authors[207] described co-polymers **259**, containing achiral luminescent 5,8-diaryl-quinoxalines and poly(quinoxaline-2,3-diyl) as main chain with chiral side chains in the ratio 95 : 5. These co-polymers possess miltcolour emission; the colour depends on substituent Ar, red shift of λ_{em} was observed at the increase of electron-donating ability of Ar. Thus, compounds **255a**,**b** exhibit blue emission, **259c**,**d** — green, **259e**,**f**,**g** — orange or red. Like polymers **258**, co-polymers **259** possess *M*-spiral structure in $CHCl_3$. Copolymers **259** showed circular polarized luminescence and CPL spectra in 1,1,1-TCE were almost mirror display of the spectra recorded in $CHCl_3$, demonstrating that in 1,1,1-TCE they get *P*-spiral conformation. Having replaced (*S*)-2-butoxymethyl of side chain with (*S*)-3-octyloxymethyl one, the authors obtained copolymers exhibiting significant correlation between CPL and the nature of solvent (n-octane or cyclooctane) while maintaining the wavelength of the CPL. These results showed that in such chiral co-polymers the luminophore and chiral component can be independent of each other. In this case poly(quinoxaline-2,3-diyl) is a multifunctional chiral framework for CPL materials.

Tokoro *et al.*[208] reported the synthesis and optical properties of conjugated polymers **262**, including pentacoordinated organosilicon complex based on benzo[*h*]quinoline.

Scheme 20

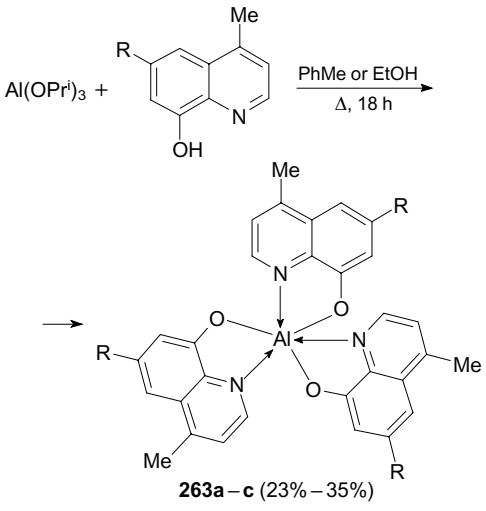


Compounds **262** were obtained from diethynyl monomers **260** and *para*-dihalogenated co-monomers **261** by Sonogashira – Hagihara cross-coupling reaction in 75% – 95% yield (Scheme 20). Polymers were characterized by ^1H, ^{13}C, ^{29}Si NMR and IR spectral data, possess good solubility in organic solvents. In THF these polymers possess intensive tunable luminescence with λ_{em} = 417 – 474 nm depending on the nature of aryl substituent and quantum yield up to 0.24. This is the first example of the luminescent polymers containing pentacoordinate silicon.

5. Coordination compounds of benzazines

Since the first data on the OLED based on aluminium complex of 8-hydroxyquinoline (Alq_3) possessing green fluorescence were published,[24] this compound has been widely studied as an electron-transport and luminescent material. Numerous researches were also focused on optimization of Alq_3 structure for achievement of blue emission. Thus, Pérez-Bolívar *et al.*[209] synthesized derivatives **263** bearing electron-donating or electron-withdrawing groups at quinoline core in order to tune the value of HOMO – LUMO gap. Complexes **263** were obtained through the reaction of tri(isopropoxide)aluminium with 4-methyl-6-R-quinolines (Scheme 21), the structure of **263a** was confirmed by X-ray diffraction. In DCM solution complexes **263** exhibit blue fluorescence with λ_{max} = 478 – 482 nm and Φ_F = 0.46 – 0.57, which exceeds the value for Alq_3 (Φ_F = 0.15). Simple devices using compounds **263** as an electron-transport and emitting material were created, the best value EQE (4.6%) was observed for OLED based on **263a**.

Scheme 21



R = F (**a**), CF_3 (**b**), CN (**c**)

Triplet energies of derivatives **263** were determined from the phosphorescence spectra recorded at 77 K, these data also showed blue shift in comparison with Alq_3 and higher values in comparison with the Ir complexes on the basis of quinoline derivatives. Such characteristics allowed applying compounds **263** for the creation of OLEDs emitting white light (WOLEDs). The device based on the derivative **263a** showed EQE up to 19% and high purity of white light (colour rendering index, CRI) ~80.[209]

Another approach for increasing the intensity of fluorescence of Alq_3 was developed.[210] The authors obtained organic – inorganic hybrid material in which Alq_3 chromophore is intercalated into zirconium phosphate modified with butylamine (BAZrP). This hybrid (Alq_3/BAZrP) showed very intense green-blue fluorescence with shift of λ_{em} up to 505 nm (λ_{em} = 515 nm for Alq_3). Besides, the hybrid showed prolonged lifetime of the excited state that allows applying it in other areas, such as conversion and storage of solar energy.

In the last decades, many researches on coordination compounds of benzazines for optoelectronic materials have been related to application of transition elements, in which electronic d- and f-sublevels are filled. Transition elements are divided into d-elements, lanthanides (4f-elements) and actinides (5f-elements), there are significant differences between these groups. d-Elements have filling of nd-orbitals: 3d-, 4d-, 5d- (three rows or three decades), d-elements of which differ in chemical properties. Examples of 3d-metals are Mn, Fe, Co, Ni, Cu, Zn; 4d-metals include Ru, Pd, Ag, Cd; and 5d-metals are Os, Ir, Pt. Any d-orbitals are located in space far beyond the atom or an ion; therefore, electrons in them are exposed to strong influence of a coordination environment. At the same time d-electrons strongly influence the adjacent atoms and ions. Existence of incomplete configurations of d-orbitals of transition metal atoms provides features of magnetic behaviour of their compounds. The main feature of almost any d-element is the variable valency of its atoms.

The review published by Katkova *et al.*[9] is devoted to complexes of rare-earth elements with quinoline ligands, and a number of Os, Ir, Pt complexes with azine ligands are presented.[8,211]

5.1. Complexes of benzazines with d-metals

5.1.1. Complexes with Zn^{II}, Cd^{II}, Co^{II}, Cu^{I}, AgI, Pd^{II}

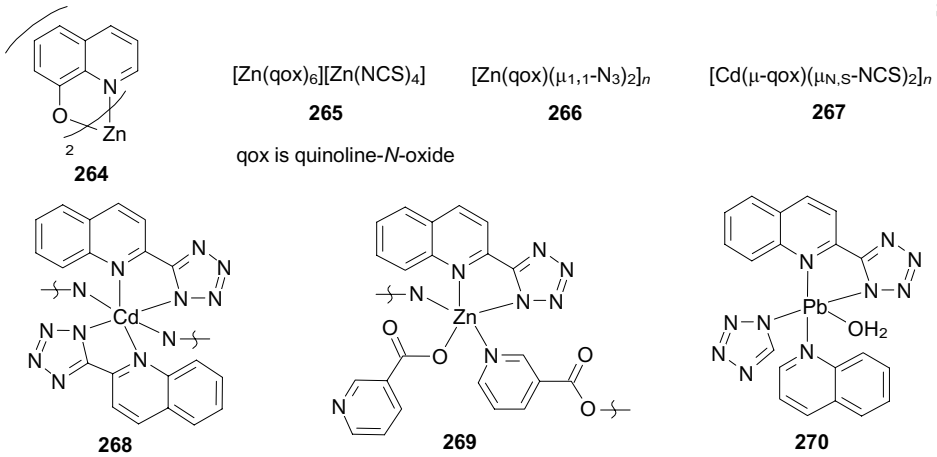
Quinoline derivatives containing coordinating group at positions 8 or 2 remain the most promising ligands for obtaining complexes with luminescent properties. Photophysical, thermal and electronic properties of polyaniline (PA) composite with zinc bis(8-hydroxyquinolate) **264**, obtained by oxidative polymerization, are compared with properties of free Zn complex.[212] It was shown that doping of PA with zinc complex led to the increase in termostability and conductivity. The intensity of fluorescence of composite increased considerably, and it can show purple emission with λ_{em} = 423 nm under excitation at λ_{exc} = 340 nm, or blue emission with λ_{em} = 468 nm under excitation at λ_{exc} = 360 nm. This polymeric composite represents potential material for electronic and optoelectronic application.

Quinoline N-oxide (qox) was used as O-ligand for the synthesis of Zn^{II} and Cd^{II} complexes **265** – **267**.[213] The structures of these compounds were determined by X-ray diffraction. Complex **265** consists of octahedral cation $[Zn(qox)_6]^{2+}$ and tetrahedral anion $[Zn(NCS)_4]^{2-}$. In complex **266** the Zn^{II} centres with coordination number 5 are connected with azide groups in a polymeric chain. Octahedral Cd^{II} centres in complex **267** are connected in a polymeric chain with ligand molecules and isothiocyanate anions. In solid state, Zn complexes **265** and **266** exhibit luminescence with broad emission band, aligned at 621 and 614 nm, respectively, whereas complex **267** shows two emission maxima, at 618 and 654 nm.

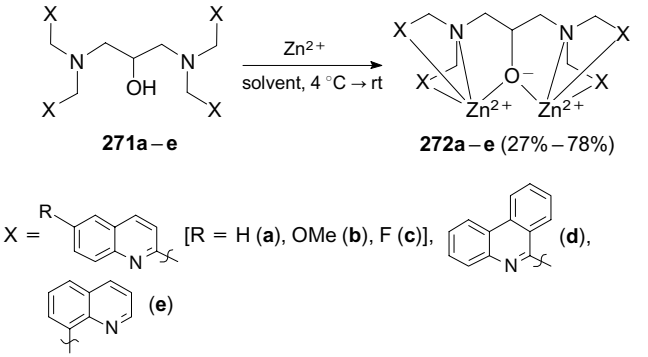
Complexes of Cd^{II} (**268**), Zn^{II} (**269**) and Pb^{II} (**270**), synthesized by solvothermal reaction of quinoline-2-carbonitrile, sodium azide and metal chloride in the presence of NH_4Cl (for **268**) or nicotinic acid (for **269**), were presented.[214] According to X-ray diffraction data, complex **268** represents linear polymer in which Cd ion has an octahedral environment formed by six nitrogen atoms of four quinoline tetrazole ligands. Zinc atom in complex **269** is also surrounded in octahedral way with four nitrogen atoms and two oxygen atoms of nicotinic acid. In compound **270**, the square-pyramidal environment of Pb ion takes place. All complexes possess strong luminescence in solid state. Compound **268** exhibited blue emission with λ_{em} = 494 nm, the spectrum of complex **269** contains two bands with maxima at 464 nm and 580 nm, in both cases emission is short-lived (10 – 12 nsec). Unlike them, the Pb complex **270** showed yellow emission with λ_{em} = 550 nm and longer lifetime (125 μs).

Binuclear Zn^{II} complexes (**272**) were obtained on the basis of tetrakis-quinoline ligands **271** (Scheme 22); compounds **272** were investigated for fluorescent sounding of phosphate anions.[215] The formation of complexes **272** with ligand : Zn^{2+} = 1 : 2 in solutions was controlled by monitoring of changes in absorption and fluorescence spectra upon addition of Zn^{2+} ions to a ligand. The composition and structure of complexes [(**272c** – **e**)(AcO^- or ClO_4^-)$_2$], obtained from ligands **271c**,**d**,**e** and acetate or perchlorate, were confirmed by X-ray diffraction. Each zinc ion in these

Structures 264 – 270



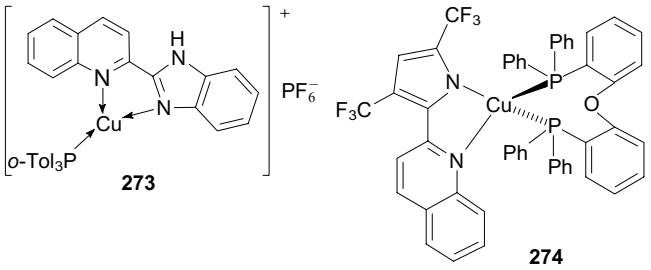
Scheme 22



complexes is pentacoordinated with three nitrogen atoms, one oxygen atom from a ligand and another oxygen atom from acetate anion. Complexes **272a**,**c**,**e** demonstrated weak fluorescence with λ_{em} = 450 nm, addition of pyrophosphate (PPi) up to 1 equiv. led to the increase of intensity, and further addition of PPi resulted in an intensity decrease. Such changes are due to the formation of ternary complex ligand – Zn^{2+} – PPi (1 : 2 : 1) corresponding to the emission maximum, and then removal of Zn under the excess of pyrophosphate takes place. Zn_2-Complex **272a** showed the best results in experiments with pyrophosphates and was used for determination of enzymatic activity of pyrophosphatase.

Complex **273**, obtained on the basis of 2-(benzimidazol-2-yl)quinoline and tri(*o*-tolyl)phosphine also contains tricoordinated Cu^{I} atom, according to X-ray data.[216] Compound **273** possesses strong yellow phosphorescence are proved to be promising for OLED.

Structures 273, 274



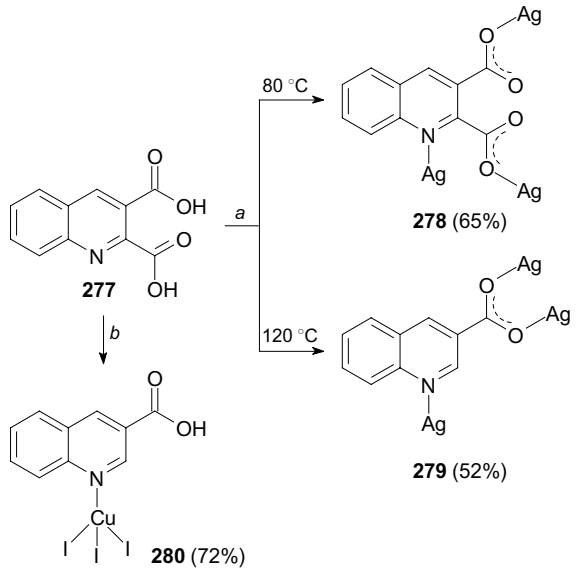
Neutral Cu^{I} complex **274** was synthesized using 3,5-bis(trifluoromethyl)-2-(quinolin-2-yl)pyrrole as N,N-ligand and bidentate phosphine auxiliary ligand.[217] In DCM solution at room temperature, compound **274** possesses orange-red luminescence with λ_{em} = 603 nm and Φ_F = 0.12. In a solid matrix (77 K) the blue shift of a maximum of emission > 50 nm and the increase in Φ_F up to 51% (total on fluorescence and phosphorescence bands) take place, thus, the complex shows rigidochromism.

The design of coordination polymers drew special attention due to their some interesting physical and optical properties and the possibility of use as multifunctional materials. Polymeric Zn^{II}, Cd^{II} and Hg^{II} complexes with general formula $[M(dca)_2(quin)_2]_n$ (**275a**–**c**) were obtained by the reaction of quinoxaline (quin), metal acetate and subsequent addition of dicyanamide (dca) in the ratio 1 : 1 : 2 in methanol.[218] According to X-ray diffraction data, complexes are isostructural and represent 1D coordination polymers. Complexes exhibit strong blue fluorescence both in methanol and solid state (λ_{em} = 407 – 445 nm, Φ_F = 0.21 – 0.70). Zinc complex **275a** possesses the highest intensity with Φ_F = 0.70, possibly, because of stronger π – π interactions between quinoxaline fragments.

Mixed Cd^{II} complexes based on quinazoline (qnz) and second co-ligand with compositions $[Cd(qnz)_2(SCN)_2]_n$ (**276a**), $[Cd(qnz)_2(dca)_2]_n$ (**276b**), $[Cd(qnz)_2(N_3)_2]_n$ (**276c**) were synthesized and characterized.[219] Polymeric structures of compounds **276a**,**b** were confirmed by X-ray diffraction. All three complexes exhibit strong fluorescence in solid state with λ_{em} = 397 nm and the type of spectra is close to a spectrum of initial quinazoline ligand.

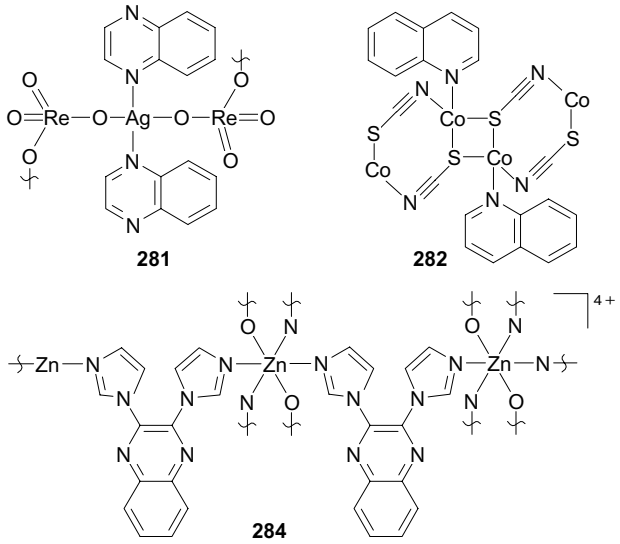
Coordination Cu^{I}, Ag^{I} polymers with some azine ligands exhibit interesting luminescent properties and already find application for obtaining the emitting layers in polymeric LEDs.[220] Complexes of Ag^{I} (**278**, **279**) and Cu^{I} (**280**), synthesized on the basis of 2,3-quinolinedicarboxylic acid (H_2qldc) (**277**) in the conditions of hydrothermal reaction, were presented.[221] It is established that temperature has an impact on the structure of final product (Scheme 23). Thus, at 80 °C complex **278** with preservation of both carboxyl groups is formed, and at 120 °C decarboxylation takes place, and complexes of both silver and copper (**279**, **280**) are formed with 3-quinolinecarboxylic acid (3-Hqlc). According to X-ray diffraction data, in structures **278**, **279** silver atom is coordinated with one nitrogen atom and two oxygen atoms from other quinoline molecules; copper atom in the structure **280** is coordinated with three iodine atoms and one nitrogen atom.

Scheme 23



Both Ag^{I} complexes exhibit stable blue luminescence in solid state and solution with intensive emission band at 404 – 427 nm depending on solvent nature at 298 K; at 77 K red shift of emission band was observed. Cu^{I} complex demonstrates tunable luminescence at 298 K and 77 K from yellow to red, demonstrating thermochromic behaviour. Polymethyl methacrylate doped by complex **280** shows

Structures 281 – 285



higher intensity of yellow luminescence, improved thermostability and longer lifetime of the excited state than initial coordination polymer **280**.[221]

Coordination polymer based on Ag^{I} with composition $[Ag(quin)](ReO_4)_n$ (**281**) was obtained by reaction of $AgReO_4$ with quinoxaline (quin) in acetonitrile at room temperature.[222] According to X-ray diffraction data, structure **281** includes cationic polymer chains built from $[Ag(quin)]^+$, in which silver ion possesses almost linear geometry. Two oxygen atoms of anion (ReO_4^-) act as bidentate bridges, connecting chains into 3D supramolecular structure. The obtained complex showed luminescence with emission bands at ~615 nm, 550 nm (as in initial quinoxaline) and an additional band at 445 nm.

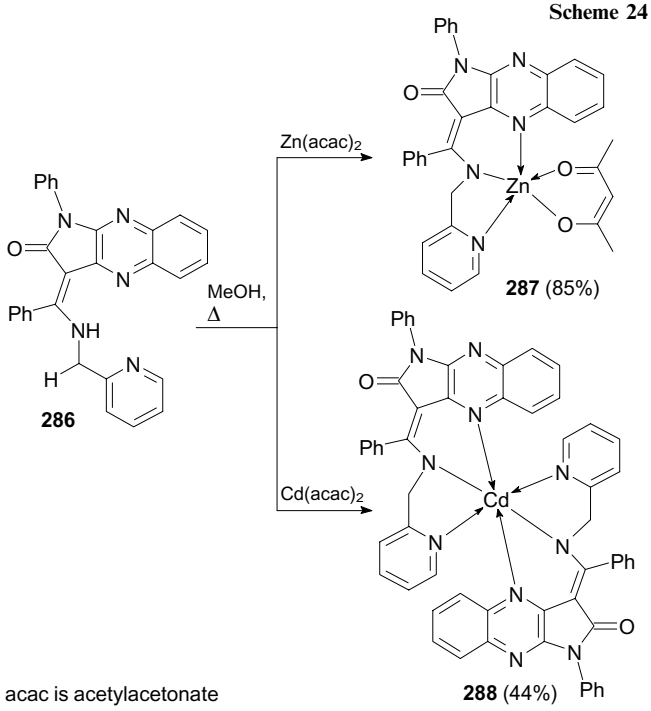
New one-dimentional coordination polymer based on Co^{I} with composition $[Co(SCN)(ql)]_n$ (**282**) was synthesized by reaction of $Co(NO_3)_2 \cdot 6H_2O$ with KSCN with quinoline (ql) in a water/MeCN mixture at room temperature.[223] According to X-ray diffraction data, Co^{I} atom possesses distorted trigonal-pyramidal environment N_2S_2 with two S atoms and one N atom from the third thiocyanate anion and N atom from quinoline ligand. Polymer shows blue luminescence with λ_{em} = 415 and 435 nm in solid state at ambient temperature.

Quinoxaline derivatives including annelated ones also often act as ligands for metal complexes. Thus reaction of 2,3-bis(imidazol-1-yl)quinoxaline (biimquin) with zinc acetate led to polymeric complex $[Zn(\mu_2\text{-biimquin})(OAc)_2] \cdot H_2O$ (**283**), whereas in the case of zinc chloride $[Zn(\mu_2\text{-biimquin})_2(H_2O)_2] \cdot 4Cl^- \cdot H_2O$ (**284**) was formed.[224] Composition and structure of complexes were determined by X-ray diffraction. In a one-dimensional zigzag chain of complex **283** Zn^{II} atoms are connected with ligands by the bridge through imidazole nitrogen atoms. In the complex **284** ligands are connected in the same way, but the structure represents a one-dimensional sphere-like double chain. Both complexes in solid state at room temperature show an intensive blue luminescence with λ_{em} = 387 nm (**283**) and 426 nm (**284**).

Cd^{II} complex on the basis of 5,8-di(1*H*-imidazol-1-yl)quinoxaline (biimquix) (**285**) was obtained by solvothermal reaction, and ligand was formed *in situ* from 3,6-di(4H-imidazol-4-yl)benzene-1,2-diamine and glyoxal.[225] According to X-ray diffraction data, the composition of **285** is $\{[Cd(biimquix)(hip)] \cdot 2H_2O\}_n$, where hip is deprotonated 5-hydroxyisophthalic acid. Each Cd^{II} centre is hexacoordinated with two nitrogen atoms from different biimquix ligands and with four carboxylate oxygen atoms from two different hip ligands. In solid state at room temperature complex exhibited intense wide emission band at λ_{em} = 454 nm. The sensitivity of this complex towards different metal ions was studied and it was shown that under addition of $Fe(NO_3)_3$ solution in DMF the intensity of emission of the complex is quenched by 82.5%, which considerably surpasses the sensitivity to other ions. It allowed recommending the complex **285** for luminescent detecting of Fe^{3+}.

New (N,N,N)-tridentate ligand **286**, bearing 2-aminomethylpyridyl group at enaminopyrrolo[2,3-*b*]quinoxalin-2-one, formed complex **287** under reaction with Zn^{II} acetyl-

Scheme 24



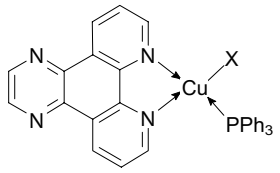
acetonate and complex **288** on treatment with $Cd(acac)_2$ (Scheme 24).[226] Structure and composition of complexes were determined by X-ray diffraction. Both complexes in solid state exhibit green luminescence with emission maximum at 472 nm (**287**) and 473 nm (**288**).

Cu^I complexes **289a**,**b** were synthesized on the basis of dipyrido[3,2-*f*:2,3-*h*]quinoxaline (dpquin) and triphenylphosphine.[227] According to X-ray diffraction data, the complexes are polynuclear and isostructural; in crystals, favourable paired π···π-stacking takes place. These complexes possess intense luminescence in ethanol solution at room temperature with λ_{em} at 451, 470 nm, the observed red shift relative to dpq (λ_{em} = 419 nm) is caused by the coordination of ligand with copper atom.

CN-Substituted complex **289c** in DMF solution demonstrates blue luminescence with λ_{em} = 417 nm, blue shifted relative to ligand emission band (λ_{em} = 430 nm).[228]

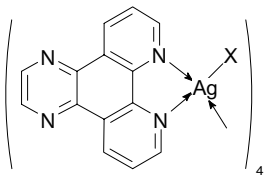
Complexes of Ag^I **290a**,**b** with composition $[AgX(dpquin)]_4$ were obtained by slow diffusion method for the first time.[229] According to X-ray diffraction data, **290a**,**b** are isostructural and tetranuclear**.** Structure **290a** includes four symmetrically equivalent cations $[Ag(dpquin)]^+$ connected into a square by four μ-bridged iodine anions. Ag atom is in tetrahedral environment formed by two nitrogen atoms of dpq and two I^-. In crystals of **290a**,**b** complexes, π···π-stacking interaction and Ag—Ag interaction take place. Both complexes possess an intense photoluminescence in ethanol solution at room temperature with emission maxima at 450, 470 and 480 nm.

Structures 289, 290



289a – c

X = I (**a**), Br (**b**), CN (**c**)



290a,**b**

X = I (**a**), Br (**b**)

Ability of numerous benzazine derivatives to be easily coordinated to metal ions is often used for their studying as sensors for metal ions. So, the Schiff base obtained from 8-aminoquinoline and 2-imidazolecarboxaldexyde was investigated as the selective and reversible luminescent chemosensor for Zn^{2+} ions in the mixture water – methanol with a limit of detection 5.81×10^{-6} M.[230] Another Schiff base synthesized from 1-aminopyrene and 8-hydroxyquinoline-2-carboxaldehyde proved to be selective reversible luminescent chemosensor for Fe^{3+} ions in aqueous medium with a limit of detection 2.52×10^{-8} M.[231]

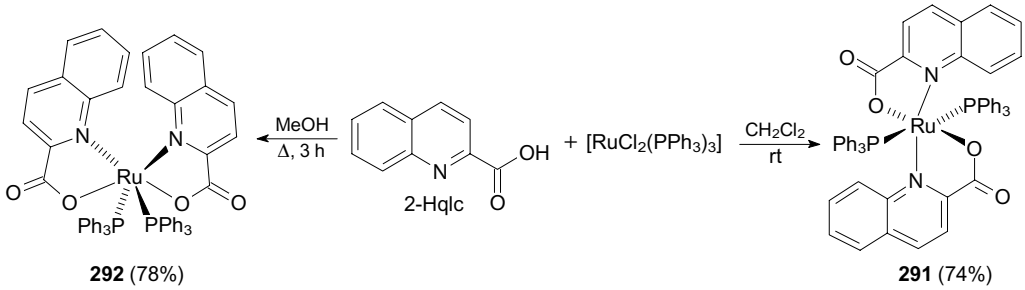
5.1.2. Complexes with Ru^{II}

Among transition metals, Ru^{II} drew close attention in coordination chemistry due to its stability, structural novelty and a number of interesting photophysical and photochemical properties, including ability to adjust colour scale of luminescence in a wide spectral interval. Complexes of Ru^{II} represent one of the most studied classes of phosphorescent materials as they often emit in red region, though with a small quantum yield, such as complexes of Ru^{II} with azine ligands.[232] Ru^{II} complexes of general formula *cis*,*trans*-$[Ru(PPh_3)_2(2\text{-Hqlc})_2]$ (**291**, **292**) with 2-quinolinecarboxylic acid (2-Hqlc) as co-ligand (Scheme 25) were synthesized and studied.[233] *trans*-Isomer **291** was obtained in DCM at room temperature, whereas *cis*-isomer **292** formed under reflux in methanol. The structure of complexes was confirmed by X-ray diffraction, the ruthenium atom geometry in both isomers represents distorted octahedron. It is interesting that *cis*-isomer **292** exhibited strong luminescence in DCM with λ_{em} = 324 nm and low-intense emission in methanol (λ_{em} = 343 nm) under irradiation at λ = 281 nm, at the same time *trans*-isomer **291** is non-emissive. For these complexes, luminescence properties are determined by both metal environment geometry, and polarity of solvent.

Three novel Ru^{II} complexes **293a – c** with expanded π-conjugated system in the second ligand (imidazoquinoline) were obtained and studied by spectral methods.[234] Solutions of complexes in DMF demonstrate red or orange luminescence with emission maxima at 621 nm (**293a**), 607 nm (**293b**) and 603 nm (**293c**). The authors demonstrated that substitution of anthracene with pyrene or perylene in auxiliary ligand allows tuning the quantum yield and lifetime of emission.

Ru^{II} complexes with dipyrido[3,2-*f*:2,3-*h*]quinoxaline (dpq) derivatives as main ligand were described.[174, 175] Thus, complexes with composition $\{Ru[dpquin(COOH)_2]_x(L)_{3-x}\}^{2+}$ (**294**), where $dpquin(COOH)_2$ is 6,7-dicarboxydipyrido[3,2-*f*:2,3-*h*]quinoxaline, L = bpy or phen, were synthesized.[174] 6,7-Dicyano derivative (dpquin) was used as starting compound, its refluxing with $[Ru(bpy)_2Cl_2]$ in the ratio 1 : 1 in acetonitrile and subsequent addition of $NaBF_4$ led to the formation of complex $\{Ru[dpquin(COOH)_2](bpy)_2\}(BF_4)_2$ (**294a**). By varying conditions, type of an auxiliary ligand and a ratio of ligands, the authors obtained complexes $\{Ru[dpquin(COOH)_2]_2(bpy)\}(BF_4)_2$ (**294b**), $\{Ru[dpquin(COOH)_2](phen)_2\}(BF_4)_2$ (**294c**), $\{Ru[dpquin(COOH)_2]_2(phen)\}(BF_4)_2$ (**294d**), $\{Ru[dpquin(COOH)_2]_3\}(BF_4)_2$ (**294e**). All compounds **294**

Scheme 25



292 (78%) **291** (74%)

Structures 293

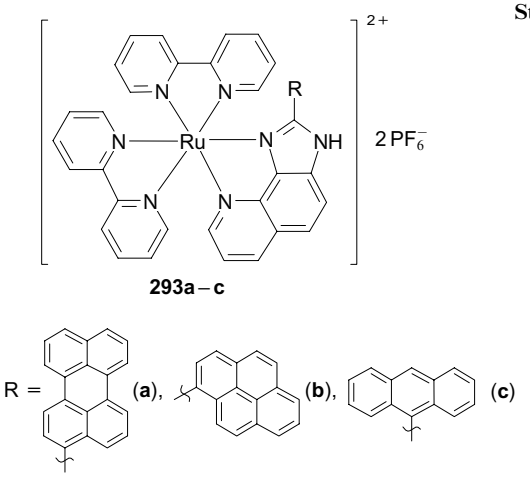


exhibit luminescent properties with red shift of emission maximum in acetonitrile from 513 nm (**294a**) to 646 nm (**294e**). LEDs created on the basis of these complexes demonstrated a possibility of tuning of electroluminescence colour from blue-green to orange through nearly white [λ_{em} changed from 485 nm (**294a**) up to 572 nm (**294e**)]. The best characteristics were shown by the device on the basis of complex **294a**.

Ru^{II} complex **295**, containing two dpquin ligands and [1,2,5]-thiadiazolo-[3,4-*f*][1,10]-phenantroline as auxiliary ligand, was presented.[175] Compound exhibits intense red luminescence with wide emission band with maximum at 637 nm (in DMF and water).

The new family of the luminophores based on Ru^{II} complexes is represented by compound **296** in which only one diimine ligand (dpquin) and four different auxiliary ligands are present.[176] The complex was synthesized by ligand-substitution reaction of precursor $[Ru(CO)(H)_2(PPh_3)_3]$ with dpquin in ethanol under reflux. The structure **296** was confirmed by X-ray diffraction. This complex exhibits orange luminescence with emission maximum at 592 nm in DCM at room temperature. In the vitrified environment at 77 K, blue shifted emission (λ_{em} up to 531 nm) and increase in excited state lifetime from 2.16 μs (in solution) up to 188.3 μs take place. Comparison of characteristics of complex **296** with other compounds of this group allowed the authors to conclude that increase in the rigidity and π-conjugation in diimine ligand leads to the increase in luminescence effectiveness.

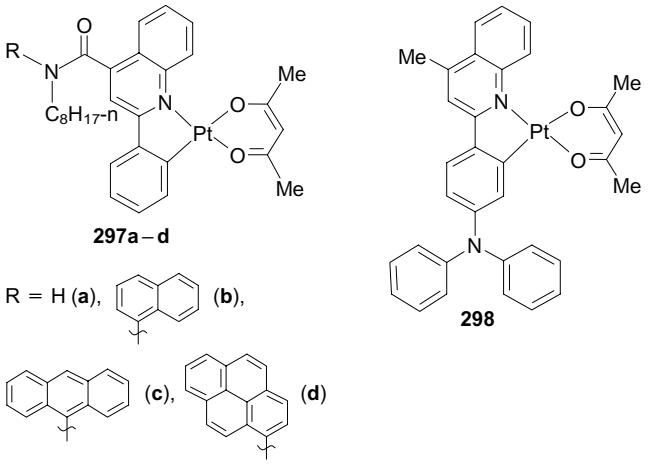
5.1.3. Complexes with Pt^{II}

Cyclometallated Pt^{II} complexes represent compounds containing five-membered metallocycle with covalent C – Pt bond. Such complexes attracted considerable interest in the last decades and already found various applications due to tunability of their photophysical properties and possibility to apply both singlet and triplet excitons for the increase of electroluminescence efficiency.[209] Complexes of such type are mixed liganded, and along with a bidentate cyclometallating (C,N) ligand, they contain N,O-, N,S-, O,O-, N,X- and other bi- and monodentate co-ligands.

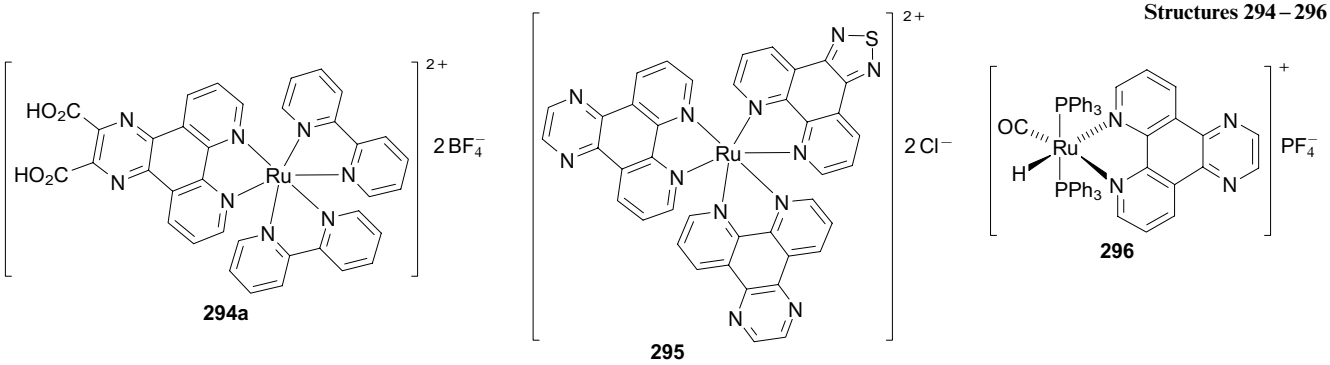
For tuning the emission of platinum complexes the introduction of chromophore groups in the structure of (C,N) ligand or changing the nature of co-ligand are used. The functionalized complexes **297**, containing *N*-octylcarboxamide residue with chromophore group R in quinoline fragment and acetylacetonate (acac) as co-ligand, were synthesized.[235] The structure of compounds **297c**,**d** was confirmed by X-ray diffraction data. Studying of luminescence of these complexes in aerobic and degassed solutions at ambient temperature and at 77 K showed that chromophore-containing compounds **297b** – **d** exhibit double emission: fluorescence due to chromophore with $\lambda_{em} < 500$ nm and phosphorescence with $\lambda_{em} = 605$ nm. In case of a pyrenyl derivative **297d**, sharp increase in emission lifetime ^{3}MLCT (up to 42 μs) was noticed; this could be due to a proximity of ^{3}MLCT and ^{3}LC energies in excited states and the possibility of energy transmission process between them.

On the basis of quinoline (C,N) ligand, bearing a strong electron-donating substituent such as triphenylamine and acac as co-ligand, cyclometallated complex **298** was

Structures 297, 298



Structures 294 – 296



obtained.[211] Compound **298** demonstrated red phosphorescence with λ_{em} = 593 nm and high quantum yield (0.99), it was used as a dopant for the creation of highly effective OLEDs.

New Pt^{II} complexes of dendrimer structure **299** – **301**, in which emitting base (ppq)Pt(acac/dmp) (ppq is 2,4-diphenylquinoline, acac is acetylacetone and dmp is dipyvaloylmethane) and carbazole dendron are connected with flexible n-butylene chain (**300**, **301**) or rigid *p*-phenylene bridge (**299**), were synthesized.[236] All compounds were characterized by ^1H and ^{13}C NMR and mass-spectrometry, and the structures of complexes **299b**, **301a** were confirmed by X-ray diffraction. The influence of dendrons and the linker on photophysical properties and packing of complexes were studied. The intense bands in absorption spectra at 409 – 415 nm coresponding to dp(Pt) π*(L) metal – ligand charge transfer (MLCT) mixed with the triplet LC transition were noted. All complexes exhibit bright red phosphorescence in DCM at room temperature with $\lambda_{em} \sim 608$ nm. In films, emission spectra are widened and shifted to the long-wave range. It is shown that flexible n-butylene linker practically does not affect photoluminescent properties, but changes the molecular packing, leading to the emergence of host material function. Compounds **299** – **301** possess also electroluminescence, and were used to fabricate OLED devices; the device based on complex **301a** demonstrated the best characteristics.

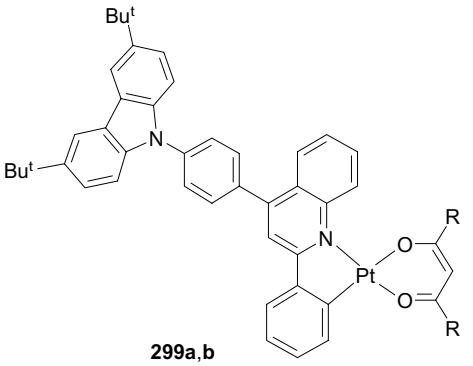
In some works [171, 172, 237] benzo[*h*]quinoline was used as (C,N) ligand for the synthesis of cyclometallated Pt^{II} complexes **302**, **303**.

Platinum(II) complex with benzo[*h*]quinoline (bzql) (**302**) was synthesized by the reaction of activating precursor [*cis*-$Pt(Ph)_2(thf)_2$] with benzoquinoline in boiling acetone during 2.5 h.[171] This compound was characterized with only spectral data. Reactions of complex **302** with equimolar amount of terminal alkynes or diphenylacetylene led to the formation of the correspomding η^2-alkyne-containing complexes [Pt(bzq)(C_6F_5)(η^2-HC≡CR)] (R = Ph, Bu^t, ferrocenyl) or [Pt(bzq)(C_6F_5)(η^2-PhC≡CPh)]. Complex **302** exhibits luminescence in solid state and in solution at room temperature and 77 K, arising mainly from intraligand (bzq) excited state with some mixing of ^{3}MLCT. In emission spectra, bands at 477 – 482 nm and 553 – 595 nm are observed, their ratio depends on excitation wavelength, temperature and physical state. It should be noted that this complex demonstrates considerable luminescent thermochromism (green at 77 K, orange at 298 K). The alkyne-containing complexes obtained from **302** also possess luminescent properties.

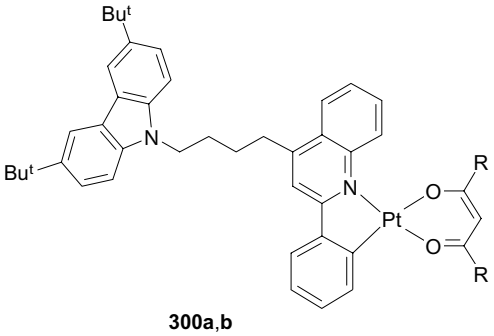
Binuclear cyclometallated complexes of methylplatinum(II), containing benzo[*h*]quinoline (**303**) or 2-phenylpyridine (**304**) as (C,N) ligand, were described.[237] Compounds were obtained by the substitution of SMe_2 coligands in the complex [PtMe(SMe_2)(C,N)] with bis(diphenylphosphino)methane in acetone at room temperature. The structures of **303** and **304** were confirmed by X-ray diffraction. Both complexes exhibit bright red luminescence in solid state with λ_{em} = 638 nm (**303**) and 655 nm (**304**). The authors demonstrated that complex **304** easily transfoms into binuclear Pt^{IV} complex with composition [$Pt_2Me_4(bzql)_2(\mu\text{-}I)_2$] under the action of the excess of MeI in acetone at 0 °C during 1 h; the structure of obtained product was confirmed by X-ray diffraction data.

Novel cyclometallated Pt^{II} complexes **306** – **308**, bearing the same (C,N) ligand, benzo[*h*]quinoline, were synthesized, and the effect of modification of an auxiliary ligand on

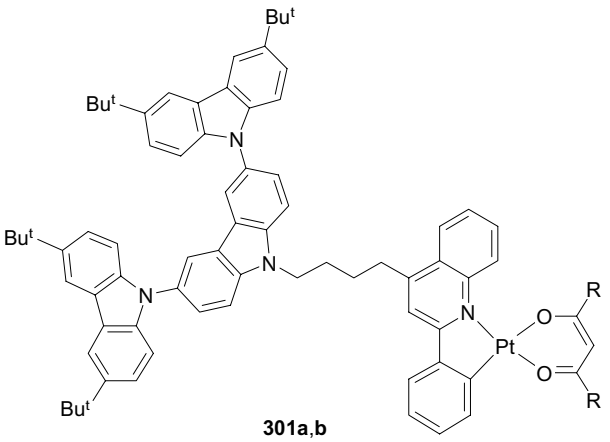
Structures 299 – 304



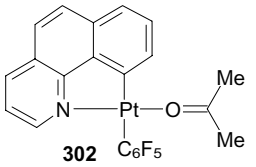
299a,**b**



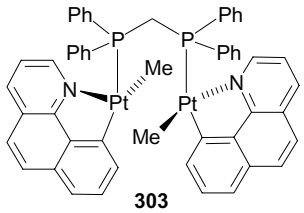
300a,**b**



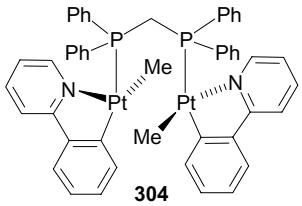
301a,**b**



302



303



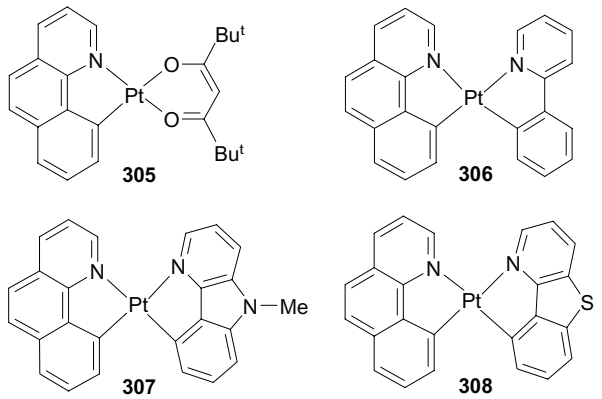
304

299 – **301**: R = Me (**a**), Bu^t (**b**)

phosphorescence efficiency in comparison with the earlier synthesized complex **305** was described.[172] The structure of compound **305** was confirmed by X-ray diffraction analysis;[238] the complex exhibits intense luminescence with $\lambda_{em} = 550$ nm in hexane at room temperature. It was shown that the complex emits from metal-perturbed ligand-centred triplet state with a rate constant 1.4×10^5 s^{-1}.

The authors performed calculations for structures **306** – **308** by means of DFT and TDDFT methods: geometry in the basic and the low-lying triplet excited state, frontal molecular orbitals, charge transfer, phosphorescence, rate constants of radiation and non-radiation processes.[172] The obtained results indicated that the replacement of dipivaloylmethane with other ligands in these structures led to the improvement of rigidity which can weaken non-emissive ways. Complex **307** showed the balanced electronic and hole conductivity, which is important for OLED materials. Complexes **306** and **308** could be regarded as excellent phosphorescent materials for devices with high phosphorescence quantum efficiency.

Structures 305 – 308



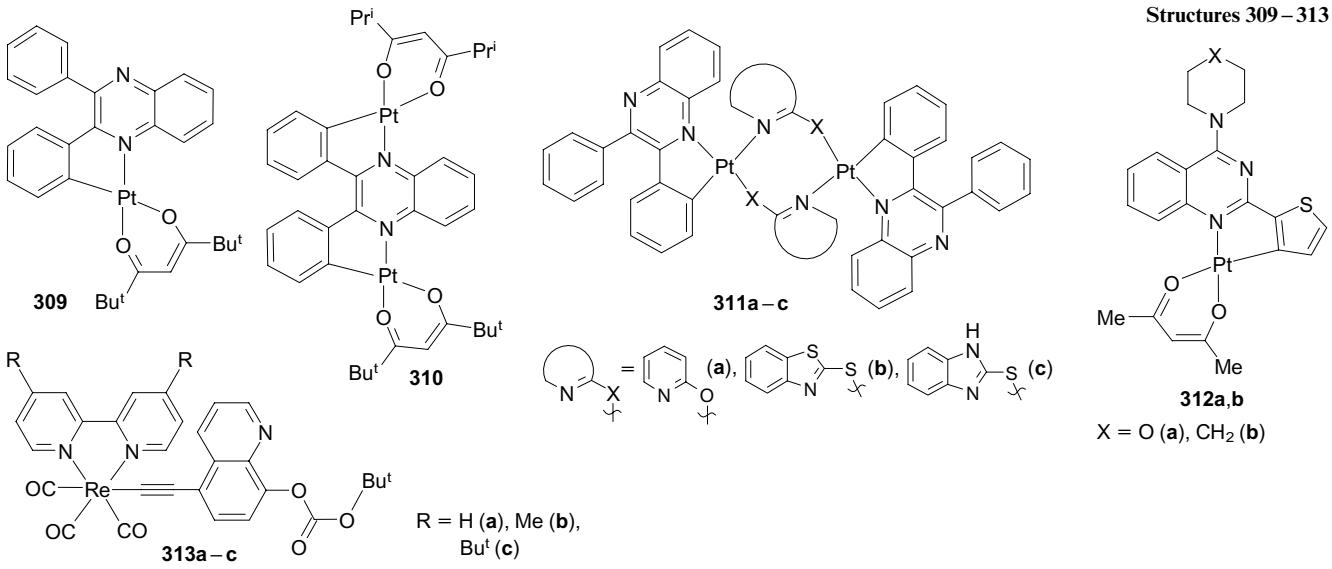
2,3-Diphenylquinoxaline represents a convenient C,N-ligand for the synthesis of mono- and binuclear cyclometallated Pt^{II} complexes.[239] So, the reaction of this ligand with K_2PtCl_4 (1.5 equiv.) in acetic acid led to a mixture of dichlorinated mono- and binuclear intermediates, which transformed into the mixture of mono- (**309**) and binuclear (**310**) complexes under the action of dipivaloylmethane.[237] Products were separated by column chromatography and characterized by ^1H NMR and mass spectra. Both complexes possess fluorescence in degassed DCM at room temperature with $\lambda_{em} = 668$ nm ($\Phi_F = 0.14$) (**309**) and $\lambda_{em} = 749$ nm ($\Phi_F = 0.025$) (**310**). At 77 K emission spectra are structured and exhibit maxima in red or near IR range at 625, 677, 747 nm (**309**) and 694, 760 nm (**310**). The authors noted that binuclear complexes based on 2,3-diphenylquinoxaline are potential phosphorescent materials which strongly absorb and brightly emit with extraordinarily low energy.

2,3-Diphenylquinoxaline was used for the synthesis of Pt^{II} complexes **311a** – **c** with a different structure.[240] The method includes the formation of dichloro-containing intermediate $(2,3\text{-}Ph_2quin)_2Pt_2Cl_2$, which interacts with auxillary ligand (2-hydroxypyridine, 2-mercaptothiazole, 2-mercaptobenzimidazole) in THF in the presence of sodium hydride leading to complexes **311**. The structure of **311a** was confirmed by X-ray diffraction. Complexes **311b**,**c** exhibit luminescence in DCM at 25 °C in red range with $\lambda_{em} = 744$ nm and 745 nm, respectively. At 77 K the blue shift of emission band took place by 37 nm (**311b**) and 17 nm (**311c**). A larger shift was observed in the PMMA film (up to 665 nm and 626 nm respectively). The authors reported that emission spectra of complex **311a** could not be measured.

We synthesized complexes **312a**,**b** on the basis of 2-(thiophen-2-yl)-4-(morpholin-4-yl) and 2-(thiophen-2-yl)-4-(piperidin-1-yl)quinazolines as (C,N) ligands.[241] The structure of **312a** was confirmed by X-ray diffraction. Both complexes exhibit orange luminescence in acetonitrile with emission maximum at 584 nm (**312a**) and 579 nm (**312b**).

Unlike well-known Pt^{II} complexes, exhibiting luminescent properties and widely presented in scientific literature, there are only few compounds of other d-elements such as Re, tricarbonyl-diimine complexes of which containing azine or benzazine fragment with the formation of Re – C bond, also possess luminescence. Recently[242] new class of complexes Re^I **313a** – **c** including 5-alkynyl-8-hydroxyquinoline derivative in the structure was reported. Compounds

Structures 309 – 313



were obtained by the reaction of $[Re(CO)_3(bpy)Cl]$ with 8-*tert*-butyloxycarbonyloxy-5-ethynylquinoline in THF in the presence of AgOTf and TEA under reflux in nitrogen atmosphere in the dark during 24 h. The structures of compounds were determined by ^{1}H NMR, IR and mass-spectral data as well as by X-ray diffraction data for the complex **313c**.

Complexes **313** demonstrated red luminescence in DCM; emission spectra exhibit broad bands with maxima at 643 – 632 nm; in solid state the bands were blue-shifted to 595 – 575 nm. Rather long luminescence lifetime measured at low and ambient temperature suggests the triplet nature of emission.

5.1.4. Complexes with Ir^{III}

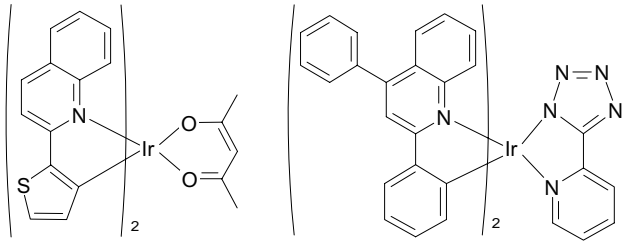
Cyclometallated Ir^{III} complexes represent the most studied class of the compounds used for the creation of the phosphorescent materials emitting in red or near IR range, which was outlined in recent reviews.[211,243] Ho *et al.* reported [243] a number of Ir^{III} complexes based on 2-phenylquinoline and 2,4-diphenylquinoline. 2-Thienylquinoline was used as one more C,N-ligand for the synthesis of Ir^{III} complex (**314**), and acetylacetone acted as an auxiliary ligand.[244] Compound exhibits red photoluminescence with λ_{em} = 629 nm in DCM. Values of HOMO and LUMO levels and energy gap were calculated from the data of cyclic voltammetry. OLEDs fabricated on the basis of the complex **314** demonstrated clear red phosphorescence with narrow value of full width at half maximum (46 nm), the maximum brightness of 24 000 cd m^{-2} and EQE = 11.1%.

The incorporation of 2-(*1H*-tetrazol-5-yl)pyridine as an auxiliary ligand into iridium complex **315** based on 2,4-diphenylquinoline gave a new thermostable phosphorescent emitter.[245] Photophysical characteristics demonstrated the mixing of singlet and triplet excited states. This complex exhibits orange luminescence in DCM with λ_{em} = 578 nm, quantum yield 0.87. Phosphorescence lifetime at room temperature is 1.34 μs. OLEDs fabricated with complex **315** as dopant-emitter possessed high efficiency, brightness and a yellow-orange emission.

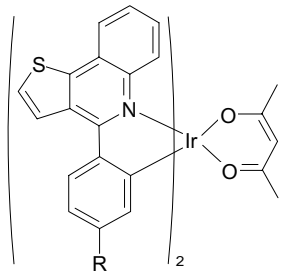
4-Arylthieno[3,2-*c*]quinoline was used as cyclometallating ligand with expanded π-conjugation system for the synthesis of Ir^{III} complexes **316**.[173] The obtained complexes are thermostable (5% of weight lose was observed at a temperature more than 340 °C). All complexes demonstrated red luminescence in DCM solution (λ_{em} = 612 – 617 nm). Photoluminescence quantum yields for complexes **316** doped into 4,4′-*N*,*N*′-dicarbazolebiphenyl films at concentration of 4 wt.% in air proved to be 0.46 – 0.47. The luminescence lifetime of compounds **316** measured in degassed DCM at ambient temperature is within 1.58 – 1.71 μs, which confirms their triplet-emitting nature. Red phosphorescent OLEDs were fabricated on the basis of these complexes, the device based on complex **316a** demonstrated the best characteristics with EQE = 22.9%.

Quinoline containing benzimidazole at position 2 was used as an auxiliary N,N-ligand in the synthesis of Ir^{III} complexes **317**, **318**.[246] The structure of compounds was confirmed by X-ray diffraction. It is shown that in complexes **317** the cyclometallated fragment $[Ir(dfppy)_2]^+$ (dfppy is difluorophenylpyridine) is coordinated with neutral benzimidazole molecule, forming the cationic Ir^{III} complex. In compound **318**, the fragment $[Ir(dfppy)_2]^+$ is coordinated with benzimidazole anion forming neutral Ir^{III}

Structures 314 – 316



314 **315**

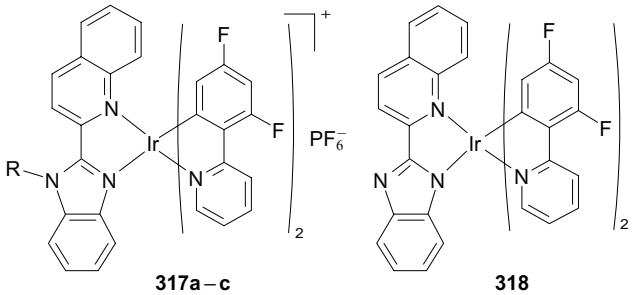


R = H (**a**), Me (**b**), Bu^t (**c**)

316a – c

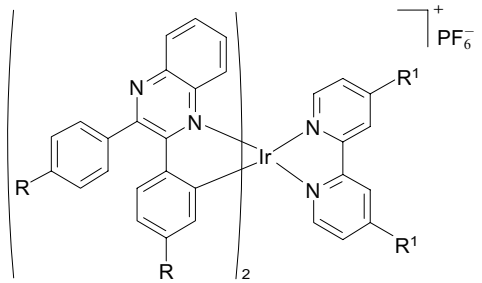
complex. All complexes differ in their molecular packing. Both types of complexes exhibited luminescence in DCM at ambient temperature; while compounds **317a – c** demonstrated strong emission bands with λ_{em} = 558, 572 and 573 nm, respectively, and wide shoulder at 585 nm (**317a**), 600 nm (**317b**,**c**); complex **318** exhibited rather weak emission at 546 nm. The luminescence quantum yields in DCM were 0.14 – 0.18 (**317a – c**) and 0.032 (**318**). At 77 K all complexes demonstrated rigidochromism with the shift of

Structures 317 – 319



317a – c **318**

R = H (**a**), Me (**b**), n-C_8H_{17} (**c**)



319a – e

R^1 = H, R^2 = Me (**a**);
R^1 = C(O)NHC$_8$H$_{17}$-n: R^2 = H (**b**), Br (**c**), Me (**d**), OMe (**e**)

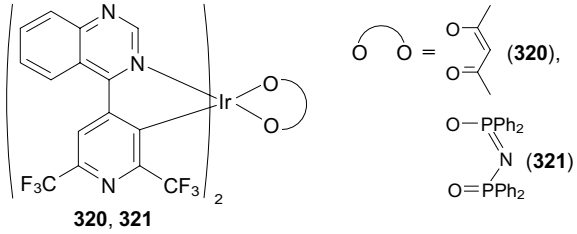
emission bands to the short-wave range. In solid state at ambient temperature all complexes demonstrated intense luminescence, yellow (**317a** – **c**) or orange (**318**), with the red-shifted emission maxima in comparison with solutions, the shifts being different for compounds **317** and **318**. The authors noted distinct influence of molecular structure of these complexes on their photophysical properties. It is interesting to note that complexes **317a** and **318**, which differ in hybridization of the imidazole nitrogen involved in the complexation, are able to switch the luminescence between the strong (λ_{em} = 558 nm) and weak (λ_{em} = 546 nm) luminescent states upon addition of NEt_3/TFA, which is attributed to their structural interconversion.

Substituted quinoxalines are also used as cyclomatellating ligands in the synthesis of Ir^{III} complexes, for example, for precise tuning of luminescent properties. Langdon-Jones *et al.*[247] synthesized a number of Ir^{III} complexes (**319a** – **e**) based on *para*-substituted 2,3-diphenylquinoxalines as (C,N) ligands and 2,2′-bipyridine or its 4,4′-di-n-octylamido derivatives as auxiliary ligands. Structures of compounds are characterized by spectral data and X-ray diffraction for complexes **319a** and **319d**. These complexes demonstrated luminescence with emission maximum at 619 – 640 nm depending on the nature of substituents and solvent, quantum yields were low (0.018 – 0.027). On the basis of experimental and theoretical studies of complexes **319** the authors came to the conclusion that the impact of ^{3}MLCT in excited state is significant, and mixing ^{3}MLCT – ^{3}LLCT in the most low-energy absorption and emission bands takes place.

As it was already mentioned, quinazoline derivatives are actively used as ligands for the synthesis of metal complexes including cyclometallated ones.[23] Incorporation into the position 4 of quinazoline of 2,6-bis(trifluoromethyl)pyridyl substituent, able to affect molecular packing and electronic mobility due to CF_3 groups, gave Ir^{III} complexes **320**, **321** demonstrating highly effective orange-red electroluminescence.[248,249] Compounds include different auxiliary ligands, they were characterized by spectral data, and the structure of complex **321** was confirmed by X-ray diffraction. Thermal, electrochemical and photophysical properties of these compounds were studied.

Both complexes possess strong phosphorescence in DCM solution with emission maximum at 588 nm and quantum yield 0.91 (**320**), 0.98 (**321**). Using these complexes as emitters, devices with one and two emitting layers (EML) were created. Comparison of their characteristics showed that for double-EML devices they were much better. Also the nature of auxiliary ligand, the replacement of acetylacetonate with tetraphenylimidodiphosphinate (complex **321**) has great influence on electroluminescent efficiency. Higher characteristics were obtained for double-EML devices based on emitter **321** with addition of Eu^{III} complex [Eu(dbm)$_3$phen] as sensitizer: the maximum brightness was 129466 cd m^{-2}, maximum energy efficiency was 62.96 cd A^{-1}, 53.43 lm W^{-1} and EQE = 20.2%. The obtained results demonstrate that Ir^{III} complexes with qunazoline C,N ligand represent promising orange-red phosphorescent materials for OLEDs.

Structures 320, 321



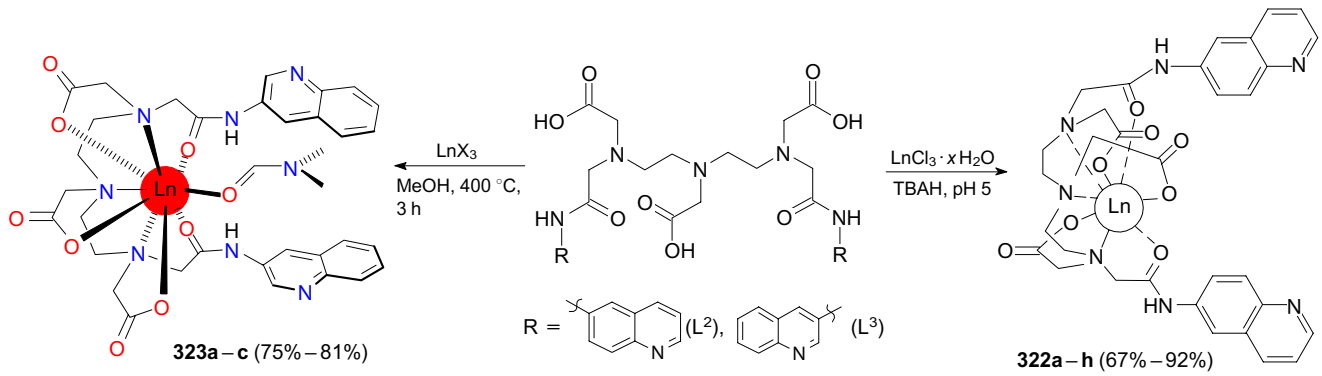
320, **321**

5.2. Complexes with rare earth elements

Luminescent complexes of rare earths (REE) with organic ligands are well-known and found rather broad application due to excellent optical properties owing to the specificities of the electronic structure of these metals, effective intramolecular energy transfer from ligand to metal atom (antenna effect), adjustable structure of complexes.[9] However REE complexes have also the drawbacks, related to low chemical, optical and thermal stability. For the improvement of properties of complexes, study of new organic ligands continues.

Bisamides of diethylenetriamino-*N*,*N*′,*N*″-pentaacetic acid (DTPA), containing quinoline derivatives as amino component functioning as light harvesting fluorophore antennas, were used as polydentate ligands of H_3L^2 and H_3L^3 types for the synthesis of complexes with a number of Ln^{III} ions.[250,251] Complexes with composition LnL^2 (**322a** – **h**) were obtained on the basis of ligands H_3L^2 (Scheme 26) and is was shown that 6-aminoquinoline acts

Scheme 26



Ln = Pr (**a**), Eu (**b**), Tb (**c**)

TBAN = $Bu_4^nN^+OH^-$

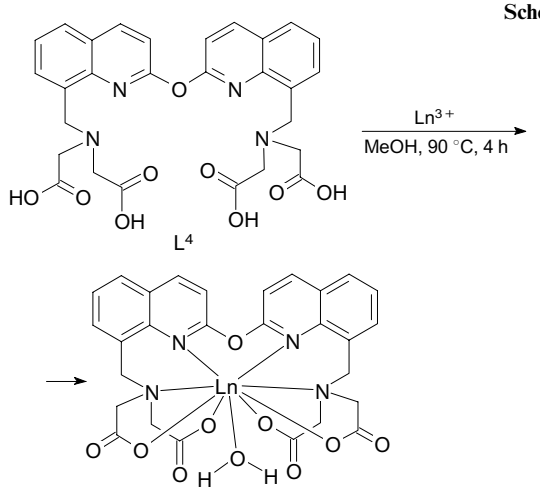
Ln = Y (**a**), Eu (**b**), Sm (**c**), Tb (**d**), Er (**e**), Yb (**f**), Nd (**g**), Gd (**h**)

as a remote sensitizer for Ln-ions.[250] All compounds were characterized by mass spectra, and diamagnetic complex **322a** was studied by ^{1}H NMR spectroscopy. The photophysical analysis of complexes showed that Eu (**322b**) and Sm (**322c**) compounds possess red emission and Er, Yb, Nd (**322e** – **g**) complexes emit in near IR range (900 – 1500 nm) in powders and solutions. It should be noted that among compounds **322**, complex Eu showed the considerable quantum yield (0.04) with emission in the visible range, and complex Yb demonstrated the most intense emission in IR range in non-deuterated solvent.

Lanthanide complexes **323** with ions of Pr (**a**), Eu (**b**), Tb (**c**) were synthesized on the basis of ligand H_3L^3.[251] The structures were confirmed by X-ray diffraction, nine-coordinated geometry of Ln^{3+} ion (LnN_3O_6) was revealed. Complexes of Eu^{III} and Tb^{III} exhibit strong red and green emission in solutions upon excitation with light at the absorption peak of quinoline chromophore. The experiments on DNA- and protein binding, DNA-splitting and cytotoxic study showed that complexes **323b**,**c** have potential applications in biomedicine as the probing or therapeutic agents or potential transporters of chemotherapeutic drugs.

One more polydentate ligand containing quinoline fragments connected by O-bridge and carboxyl groups (L^4) was synthesized and stable lanthanide complexes **324a**,**b** [Ln = Eu (**a**), Tb (**b**)] of structure $LnL^4(H_2O)$ were obtained in aqueous medium (Scheme 27).[252] The presence of water molecule in the coordination sphere was shown by mass spectrometry. Compounds exhibited red and green emission in water with rather high quantum yield: 0.095 for Eu complex **324a** and 0.02 for Tb complex **324b**.

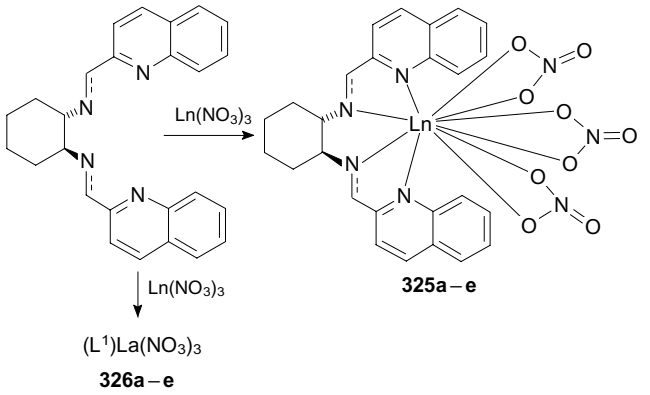
Scheme 27



324 (78%)

Lanthanide complexes **325**, **326** with new chiral ligands containing two quinoline fragments connected with rigid 1,2-cyclohexane diamine fragment were synthesized (Scheme 28).[253] According to X-ray diffraction data, the composition of complex **325a** is $(L^5)La(NO_3)_3$, the similarity of X-ray diffractions in powder for all complexes suggests the same structure for the whole series. Reflection and emission spectra of compounds **325**, **326** at ambient temperature in powders were analyzed and the possibility to obtain three different colour emissions (blue, green and red) depending on the nature of chelated ion was shown.

Scheme 28



$(L^1)La(NO_3)_3$

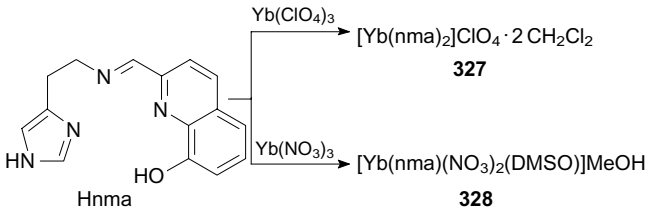
326a – **e** **325a** – **e**

L^5 (–N=CH–), L^6 (–N–CH_2–)
325, **326**: Ln = La (**a**), Eu (**b**), Gd (**c**), Tb (**d**), Lu (**e**)

According to the authors, the obtained complexes have potential application in the field of luminescent devices.

Ytterbium complexes **327**, **328** were obtained on the basis of *N*-{2-(8-hydroxyquinolinyl)methane[2-(4-imidazolyl)ethanamine]} (Hnma) (Scheme 29).[254] It should be noted that Hnma was formed *in situ* through the reaction of 8-hydroxyquinolin-2-aldehyde, histamine and ytterbium salt in the mixture MeOH – CH_2Cl_2 in the case of perchlorate and MeOH – CH_2Cl_2 – DMSO in the case of nitrate. The structures of complexes were determined by X-ray diffraction, it was shown that the anion plays an important role in the type of complexation. In complex **327**, the Yb^{3+} ion is completely encapsulated by two ligand molecules, and perchlorate anion is not coordinated, counterbalancing the positive charge, whereas in the complex **328**, the Yb^{3+} ion is coordinated by one ligand molecule and nitrate and DMSO oxygen atoms. The ligand nma works as antenna in complexes, activating luminescence in near IR range (900 – 1100 nm) with the bands characteristic of Yb^{3+} (Fig. 2).

Scheme 29



Complexes of some lanthanides with organic ligands continue to draw much attention also as single molecule magnets (SMM) demonstrating superparamagnetic behaviour below particular blocking temperature on a molecular scale. Thus, new binuclear lanthanide complexes with composition $[Ln_2(dbm)_4q_2(MeOH)_2]$ [**329**: Ln = Nd (**a**), Tb (**b**), Dy (**c**), Ho (**d**)] and $[Er_2(dbm)_4q_2(MeOH)]\cdot MeCOMe$ (**330**), containing 8-hydroxyquinoline (q) and dibenzoylmethane (dbm) ligands were synthesized.[255] The structures of compounds **329**, **330** were confirmed by X-ray diffraction; it was shown that Ln^{3+} ions are connected with μ-phenol bridges of quinoline ligands. In complexes **329** each Ln^{3+} ion is coordinated with two bidentate dbm molecules, two q ligands and one MeOH molecule. Luminescent properties

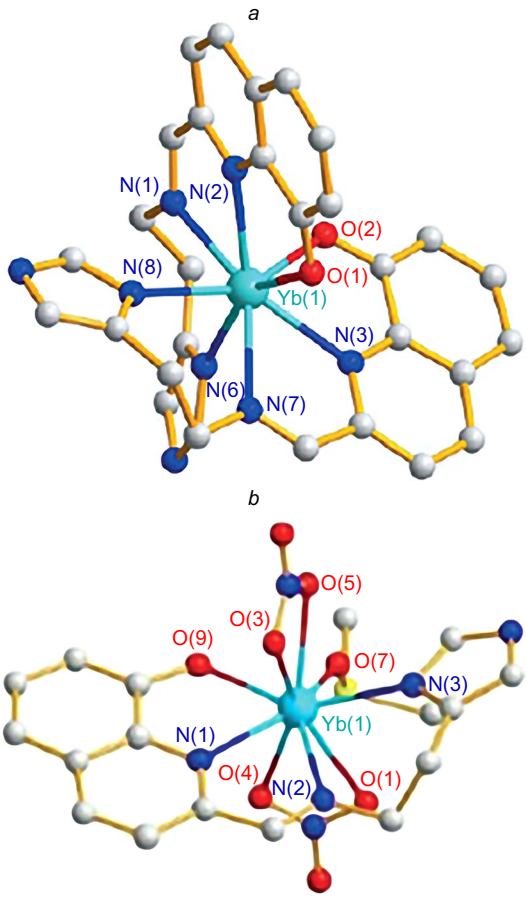
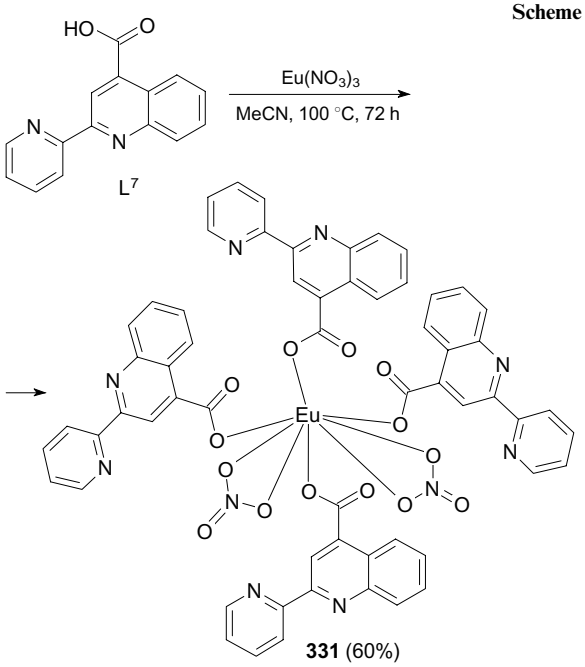


Figure 2. Molecular structure of complexes **327** (*a*), **328** (*b*).[254]

of obtained compounds were studied. Complex **329a** in solid state exhibits the typical emission of Nd^3 ion in near IR range with the most intense band at 1060 nm. Magnetic properties of polycrystalline samples of complexes **329**, **330** in the temperature range 300 – 2 K were studied. The research of magnetism dynamics revealed that complex **329c** (with Dy^{3+}) demonstrated single molecule magnet behaviour.

Coordination polymer **331** was synthesized by reaction of 2-(pyridin-2-yl)quinoline-4-carboxylic acid (L^7) with europium nitrate under solvothermal conditions (Scheme 30).[256] The structure of polymer was confirmed by X-ray diffraction; europium ion proved to be octacoordinated with four oxygen atoms from two nitrate ions and four oxygen atoms from four ligands. Each ligand binds two Eu^{3+} centres as a bridge; as a result 1D structure forms. All nitrogen atoms are not coordinated. Polymer **331** exhibited luminescence typical of Eu^{3+} ion with emission bands at 592, 616, 652 and 696 nm, the most intense was one at 616 nm. Under the action of HCl vapour on the polymer the luminescence quenched by more than 90% during 120 s. After the action of NH_3 vapour the luminescence was quickly restored (within ~ 90 s). After 5 cycles polymer retained about 50% of luminescent intensity, which attests to the possibility of its application as the sensor for fast visual detection of HCl. It was shown that protonation proceeds at pyridine nitrogen atom, changes energy of ligand excited state and makes it incapable to act as the antenna for Eu^{3+} ion.

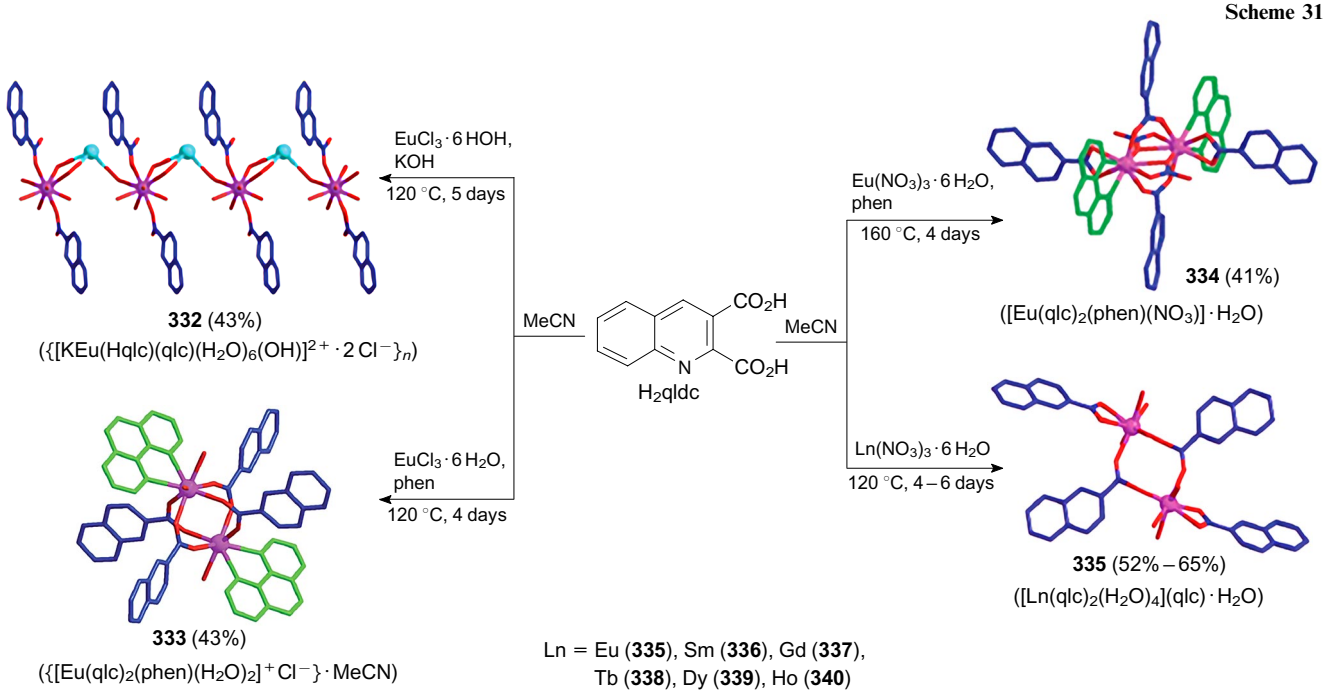
Scheme 30



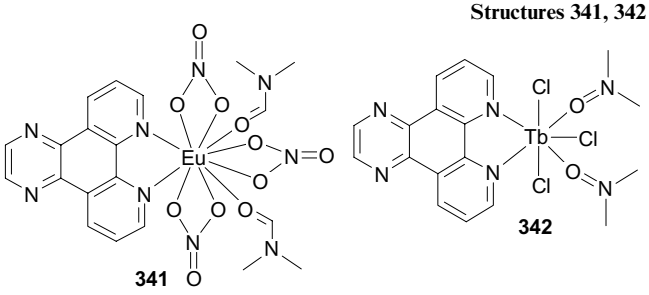
The series of lanthanide complexes **332** – **340** based on 2,3-quinolinedicarboxylic acid (H_2gldc) in solvo(hydro)thermal conditions was reported (Scheme 31).[257] As it was mentioned, this acid is decarboxylated into 3-Hglc under heating above 120 °C and participates in the formation of complexes.[221] All complexes were characterized by IR spectra and single crystal and powder X-ray diffraction. In the structure **332** K^+ ions act as structure-directing agents for the resulting crystal. Incorporation of phenanhtroline (phen) led to the increase of system rigidity, the dimeric structures of complexes **333** – **335** are different, and complexes **335** – **340** are isostructural. Luminescent properties of all compounds were studied in solid state at 298 K or 77 K. Compounds **332** – **335** exhibit red emission typical of Eu^{3+}, with the most intense band being located at 613 nm. Complexes **333, 334**, containing phen, possess higher luminescence lifetimes than **332** due to sensitization of not only Hglc, but also phen. Other complexes (**336** – **340**) exhibited luminescence typical of Ln ion. Hybrid materials demonstrating strong red luminescence at concentration of 8% were obtained by doping of complexes **333**, **334** in PMMA.

Luminescent complexes of Eu and Tb (**341**), (**342**) were obtained on the basis of dipyridoquinoxaline (dpquin).[177] According to X-ray diffraction data, complexes are mononuclear. The Eu ion is located in a dodecahedral surrounding in the structure **341,** coordinated with nitrogen atoms of dpquin ligand, two DMF molecules and three NO_3^- anions. The Tb complex has heptacoordinated structure of octaedral type; the nitrogen atoms of dpquin ligand and two DMF molecules and three Cl^- anions participate in the metal coordination. Both complexes are highly emissive, dpquin ligand acting as effective antenna; the emission spectra exhibit narrow intense bands typical of Eu and Tb ions. The authors showed prospects for application of these compounds for biomedicine.

Scheme 31



Structures 341, 342

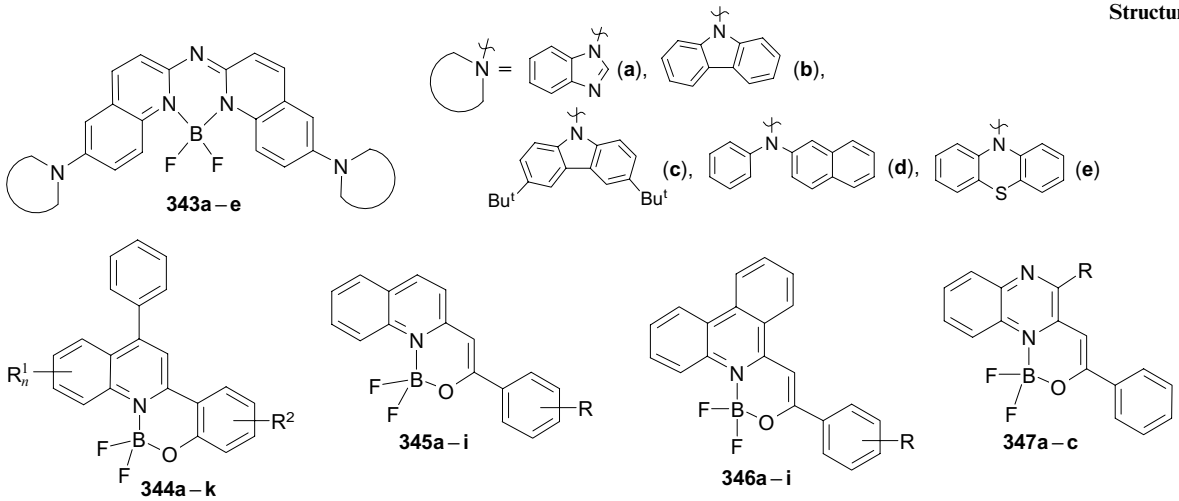


5.3. Complexes with boron(III)

Tetracoordinated B^{III} complexes with N,N- and N,O-heterocyclic ligands continue to draw much attention as bright emitting materials with a blue, green and orange luminescence. Some benzazine derivatives were reviewed [253] as such ligands.

A series of BF_2-complexes **343a – e** was synthesized on the basis of bis(6-bromoquinolin-2-yl)amine as N,N-ligand with subsequent substitution of bromine with N-aryl residue.[259] All compounds were characterized by multinuclear spectroscopy; X-ray diffraction data were obtained for complexes **343b**,**c**,**e**. Complexes **343** proved to be thermostable, they exhibit intense luminescence in DCM solution and in solid state in the visible range. Depending on the nature of N-aryl substituent, the emission maximum was observed at 440 – 505 nm; the quantum yield was rather high (0.24 – 0.78), with the highest quantum yield being observed for complex **343b**. The influence of protonation on luminescence of complex **343c** was studied, and it was shown that both in solution and in solid state (on filter

Structures 343 – 347



344: R^2 = H: R^1_n = 7-Cl (**a**), 6-Cl (**b**), 6-F (**c**), 6-Br (**d**), 6-OMe (**e**), 6-Me (**f**), 6,7-Me_2 (**g**); R^1 = H: R^2 = H (**h**), 2-OMe (**i**), 2-OEt (**j**), 4-Br (**k**);
345, **346**: R = 4-NMe_2 (**a**), 4-OMe (**b**), 4-Me (**c**), 3-Me (**d**), H (**e**), 4-Br (**f**), 3-Br (**g**), 3-F (**h**), 4-CF_3 (**i**); **347**: R = H (**a**), Me (**b**), Ph (**c**)

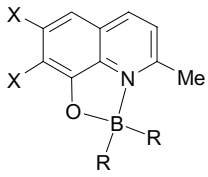
paper), the luminescence changed from green to red and back upon pH change from 1 to 12. The obtained results demonstrated that these complexes, the emission of which can be tuned by protonation, may be regarded as good candidates for pH sensors, biological tests and OLEDs.

Quinoline derivatives were used as N,O-ligands for the synthesis of BF_2-complexes **344**, **345**.[260–262] Compounds **344** were synthesized from 2-(4-phenylquinolin-2-yl)phenols.[260] Incorporation of a phenyl residue into position 4 of quinoline could improve luminescent properties in solid state due to a decrease in the π – π-interaction between the chromophores. The structure of complexes was confirmed by ^1H, ^{13}C, ^{19}F and ^{11}B NMR, mass spectrometry; X-ray diffraction study was performed for **344i**. All complexes exhibited luminescence in a chloroform solution with emission maximum at 467 – 538 nm and large Stokes shift (up to 10231 cm^{-1} for **344j**) and low quantum yield (0.03 – 0.12). Emission maxima of complexes in solid state are red shifted relative to those in solution (5 – 20 nm shift) and luminescence is more intense. Electrochemical properties of complexes were studied by CV method. The values of HOMO (−5.32 to −6.10 eV) and LUMO (−2.64 to −3.46 eV) energies and the energy gap (2.14 – 2.77 eV) were calculated; they were close to the values for the Alq_3 complex.[260] The obtained results demonstrate the existence of electron transport properties of BF_2 complexes **344**.

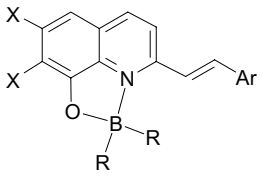
Difluoroborates based on 2-benzoylmethylenequinolines **345a – i** were characterized by ^1H, ^{13}C, ^{15}N, ^{19}F and ^{11}B NMR, powder X-ray difraction, quantum chemistry, and, for compounds **345b – f,i**, by X-ray diffraction.[261] In solutions of these complexes, through-space spin–spin coupling constants (^{TS}J) were observed between ^{19}F and $^1H(8)$ or $^{13}C(8)$ nuclei. The nature of bond in NBF_2O fragment was studied, and it was shown that the B – N contact is dative, while B – O and B – F are polar covalent bonds. The clear dependence between the nature of the substituent R and the constant $^1J(^{11}B, ^{19}F)$ was revealed. Complexes **345a – i** exhibit strong luminescence in chloroform with λ_{em} = 435 – 520 nm and quantum yield 0.37 – 0.94 depending on the nature of substituent.[262] The highest quantum yields were found for compounds **345a,b** (0.86, 0.94) with electron donor substituent R; the largest red shift in the absorption and emission spectra was observed for compound **345a** (with 4-NMe_2). The authors demonstrated that absorption and emission spectra of such complexes can be well simulated by quantum chemistry methods.

Recently,[263] BF_2-complexes **346a – i** were obtained using phenacylphenantridine with the same substituents R as in compounds **345**. Phenantridine can be regarded as an analogue of benzoannelated quinoline or isoquinoline. The authors studied the effect of substituent and double benzoannelation on photophysical properties of complexes **346** in comparison with quinoline complexes **345** obtained earlier[262] by experimental and quantum methods. It was shown that the substituent R has the same effect as in compounds **345**. Due to 4-NMe_2 groups present in **346a**, considerable red shifts take place in absorption and emission spectra, which is due to charge transfer in the excited state for this compound. The quinoid structure arising in the course of this process limits the mobility in excited state and explains high fluorescence quantum yield for complex **346a** (0.81). However, in general, complexes **346** show less intense luminescence (Φ_F = 0.67 – 0.09 for **346b – i**) than analogues **345** (Φ_F = 0.94 – 0.37 for **345b – i**).

Structures 348 – 351



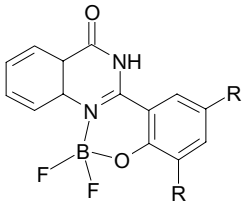
348a – d



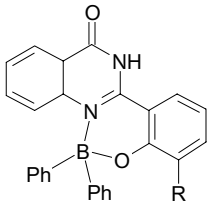
349a – d

R = Ph: X = H (**a**), F(**b**);
R = F: X = H (**c**), F (**d**)

R = Ph: X = H (**a**), F(**b**);
R = F: X = H (**c**), F (**d**);
Ar = 4-$MeOC_6H_4$



350a,b



351

R = H (**a**), Bu^t (**b**)

New quinoxaline-β-ketoiminate boron difluoride complexes **347a – c** possessing tunable and fascinating photophysical properties (λ_{em} = 467 – 482 nm, Φ_F = 0.78 – 0.92) have been developed.[264] Compounds **347** demonstrated unusual acidochromic behaviour triggered by acid vapour.

We synthesized BF_2 and BPh_2 complexes **348a – d, 349a – d** with five-membered chelate rings on the basis of 2-methyl-8-hydroxyquinoline and its 6,7-difluoro derivative.[265] Another ligand, 2-(2-hydroxyphenyl)-3H-quinazolin-4-one, was used for the preparation of complexes **350a,b**, **351** with six-membered boron-containing rings.

All complexes were characterized by ^1H, ^{19}F and ^{11}B NMR spectroscopy and mass spectrometry data; X-ray diffraction analysis was performed for compound **349a**. Compounds exhibit luminescent properties with emission maximum at 390 – 502 nm and large Stokes shift, the colour and intensity are dependent on the nature of substituents both in the ligand and at the boron atom. Thus, the presence of fluorine atoms in the benzene ring of complexes **348** led to a significant red shift of the emission band and to increase in the quantum yield from 0.005 to 0.025. Diphenylboron complexes **349a,b** have higher quantum yields than difluoroboron ones (0.18 and 0.29, respectively). The incorporation of *tert*-butyl group into phenol fragment of compound **350b** led to a long-wave shift of the emission band and an increase in Φ_F from 0.09 to 0.36.[265,266] In the case of complexes with five-membered chelate rings **348**, **349**, the luminescence of diphenylboron derivatives (**348a,b**, **349a,b**) exceedes the luminescence of difluoroboron complexes (**348c,d**, **349c,d**).

6. Conclusion

During the last years there has been a growing interest in the investigation of organic and organometallic push-pull chromophores for their futher applications in luminescent, photovoltaic and other optoelectronic devices. Indeed, in the context of green energy and reducing energy consumption, the development of new solar storage materials and the creation of energy-efficient lighting devices play a key role.

In the field of new technologies, data storage and optical processing are important, and highly efficient materials with nonlinear optical properties are required. regarding these applications, more preference is now given to organic and organometallic materials containing π-conjugated cores than to inorganic materials due to lower cost, easier tunability and low toxicity.

In this context, the incorporation of benzazine fragments into the structure is of interest: being electron-deficient heterocycles, benzazines exhibit electron-acceptor character and can be used as acceptor parts in push-pull structures, leading to ICT. Benzazine derivatives have a stronger electron-withdrawing effect on the system than their pyridine and diazine counterparts. Benzazines can also be used as π-conjugated linkers. A lone electron pair of nitrogen atom can easily interact with a proton or metal cation, allowing for tuning of photophysical and electronic properties of target compound.

Analysis of the literature shows that various quinoline derivatives and their aza-analogues continue to attract attention as promising luminescent materials and components for optoelectronics. The review presents the main approaches to the synthesis and functionalization of π-conjugated benzazine chromophores. Traditional methodologies include the formation of benzazine ring using different condensation reactions. More modern methods consist in functionalization of already formed benzazine core with application of Knoevenagel condensation and cross-coupling of different types from commercially available methyl- and halogen-substituted benzazines.

Many quinoline chromophores have found widespread use or appear promising. For example, ways of modifying structure **19** to provide a molecular switch and logic gates for processing information are discussed.[267] This review does not reveal any clear trends in the main uses of quinoline dyes. While for many quinoxaline chromophores, especially for 5,8-diarylquinoxaline derivatives, there is a clear trend — their design is implemented for photovoltaic devices as small molecules or polymers. The quinoxaline backbone is commonly used in these systems as the π-conjugated linker or the auxiliary electron-withdrawing group. Quinoxaline-containing polymers with different chiral side chains demonstrate a new class of materials with circularly polarized luminescence. According to our knowledge, such dyes are not yet used in industry, but they are closest to commercial adoption among all the structures mentioned in this review. Another promising application of quinoxaline chromophores is related to nonlinear optical properties: recently interesting structures with 2nd order nonlinear optical properties, in which the quinoxaline fragment acts as π-conjugated linker or electron-acceptor part, have been obtained.

The development of quinazoline chromophores has started relatively recently, and so far a limited number of molecules have been developed, possibly due to the small amount of commercially available quinazoline-type reagents. However, recently a promising application of these heterocycles has been proposed, namely, creation of pure organic chromophores for white OLEDs by partially protonating one of several nitrogen atoms of heterocyclic molecule and selecting a certain ratio of protonated to unprotonated forms of the benzazine derivative.

Annelation of benzazines with various fragments leads to new properties and applications. Dibenzo- and phenanthrolinequinazoline derivatives already find use as electron-transport and hole-transport layers; bis(indoloquinoxalinyl) derivatives with various bridges represent promising emitters for phosphorescence OLEDs; derivatives of acenaphthoquinoxalinediimide are of interest as non-fullerene components for organic solar cells.

New properties of annelated benzazines were also revealed. The modification of quinoxaline with carbohelicene or tetrathiahelicene allowed the creation of non-planar molecular systems exhibiting circular-polarized luminescence (CPL). The V-shaped thiadiazole annelated quinoxaline molecules demonstrated an example of creating an emission system in a polar aqueous environment with double emission change. The novel T-shaped tetraphenylethylene substituted derivatives of acenaphthene- and phenanthrenequinoxaline showed aggregation-induced emission and mechanochromism as cyclometallating ligands with an extended π-conjugated system.

Much attention is paid to obtaining coordination compounds of benzazines with various metals: mono- and binuclear, cyclometallated, possessing dendrimer or polymer structure, exhibiting luminescent properties in a wide spectral range. Pure organic benzazine derivatives are used in promising areas associated with the design of fluorophores for controlled molecular photoswitches; emitters exhibiting white emission; fluorophores with aggregation-induced emission in the red and near IR regions, which is important for biovisualization and biological research. Complexes of benzazines with such metals as Pt, Ir are already used or presented as promising high-performance phosphorescence emitters for OLEDs with tunable emission. Complexes of benzazine ligands with rare-earth elements possess unique chemical and photophysical properties; these structures are promising for biomedicine as probing and therapeutic agents. Compounds of lanthanides with functionalized benzazines also attracted attention as single-molecule magnets showing superparamagnetic behaviour.

Despite the progress made in synthesizing and investigating functionalized benzazines, there are still challenges to be solved. One of them is related to the development of atom-economic and low-stage synthetic approaches using metal-non-catalyzed reactions, which will bring the processes closer to the basic principles of green chemistry, reduce the adverse impact on the environment and economic costs.

Another problem is related to the design of highly rigid benzazine ligand structures to produce metal complexes capable of exhibiting the effect of thermally activated delayed fluorescence (TADF). In such compounds, the energy of both singlet and triplet excitons can be realized as emission through the singlet state, resulting in high quantum yields. TADF materials present an alternative to triplet emitters in OLEDs, which are characterized by low quantum phosphorescence yield.

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Figure 1 is courtesy of the Royal Society of Chemistry Publishing, and Figure 2 is courtesy of Wiley Publishing.

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