Russian Chemical Reviews **82** (6) 511 – 537 (2013) © 2013 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2013v082n06ABEH004339

Fluorescent photochromes of diarylethene series: synthesis and properties

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Abstract. The research data in the field of fluorescent photochromic di(het)arylethenes published over the last decade are summarized. The characteristics of these compounds significant for their application in the design of molecular optical memory systems and photocontrolled switches are considered. The main types of diarylethenes and methods for their synthesis are described, and the correlations between structure and spectral properties, in particular, fluorescence characteristics are analyzed. Considerable attention is given to the means for endowing diarylethenes with fluorescence properties as one of the most promising methods for data readout from molecular information carriers. The bibliography includes 203 references.

I. Introduction

In recent years, the chemistry of photochromic diarylethenes has developed rapidly, since these compounds are considered as promising photosensitive and photocontrolled materials for various practical applications. In particular, they can be used to devise a new generation of molecular systems for information storage and molecular switches. These systems feature high fatigue resistance (light resistance), thermal stability of photoinduced forms, fast response, and good sensitivity. Of special interest are fluorescent diarylethenes, which are widely studied, in particular, for the development of optical memory devices with non-destructive information readout. Among other methods, fluorescence readout seems to be most attractive, since it is characterized by particularly high sensitivity, it is optical and allows for the application of the same equipment for both information recording and reading.

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Received 7 June 2012
Uspekhi Khimii **81** (6) 511 – 537 (2013); translated by D V Aleksanyan

II. Photochromic diarylethenes: main methods for synthesis and physicochemical properties

Photochromes are the compounds that undergo, on exposure to electromagnetic radiation, reversible transformations between forms **A** and **B** [reaction (1)], which possess different absorption spectra (Fig. 1).[1]

$$\mathbf{A} \rightleftharpoons \mathbf{B} \qquad (1)$$

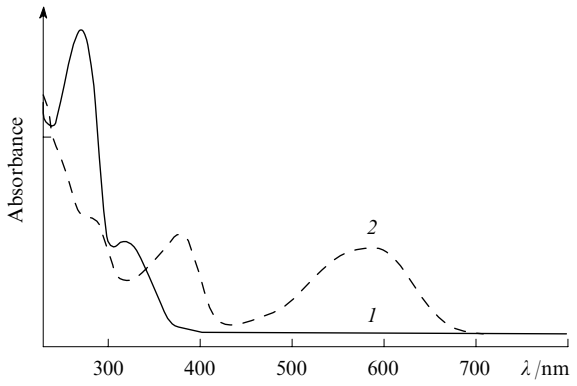


Figure 1. Typical change of the absorption spectrum of photochromic compound before (form **A**, curve *1*) and after irradiation (form **B**, curve *2*).[1]

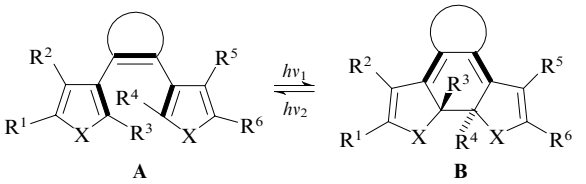
The most popular photochromes have a colourless or pale yellow form **A** and deeper coloured form **B**, *i.e.*, $\lambda_{max}(\mathbf{A}) < \lambda_{max}(\mathbf{B})$. In the event that $\lambda_{max}(\mathbf{A}) > \lambda_{max}(\mathbf{B})$, photochromism is called negative.

Form **B** arising under irradiation differs from the initial form **A** not only by wavelength of the absorbed light but also by other physicochemical characteristics: refractive index, dielectric permittivity, redox potential, spatial structure and so on. The changes in these properties can be

employed to develop information media and optical switches based on these systems.[2]

Among organic photochromic compounds, dihetarylethenes seem to be most promising. This is caused by their fatigue resistance,† thermal stability of a photoinduced form, fast response, and high sensitivity. The photochromic properties of di(het)arylethenes stem from the presence of a hexatriene system (three conjugated double bonds) in their molecules, which is capable of cyclization. Upon irradiation with UV light, the colourless open-ring dihetarylethene form **A** transforms into the coloured closed-ring form **B** (Scheme 1).

Scheme 1



X = NR^7, O, S, CH=CH

1. Main practically valuable characteristics of photochromic diarylethenes

To date, a great number of photochromic diarylethenes have been obtained but some or other drawbacks make them unsuitable for large-scale production of molecular optical memory systems and optical switches for various applications. For a diarylethene to be really applicable for these purposes, it must combine certain performance characteristics. These include [3]

— thermal stability of both isomers, which provides for the opportunity of the long-term data storage (or long switch operation);

— high fatigue resistance: the ability to undergo many colouration – decolouration cycles, which will allow for the multiple information recording or enable long service life of the switch;

— fast response and high sensitivity, which require, in turn, high values of the molar extinction coefficient of di(het)arylethene photoinduced forms and high quantum yields of the forward and reverse reactions;

— the possibility of non-destructive readout of the information data, *i.e.*, exclusion of data erasing upon its reading;

— sensitivity to particular wavelengths of laser radiation; in view of technical requirements, it is desirable that an absorption band of the coloured form lie in the wavelength range from 650 to 830 nm or at ~532 nm at generation of the YAG-laser second harmonic (1064 nm).

Among these requirements, the first two are the key ones.

a. Thermal stability

The history of photochromic diarylethenes originated from the mid-1980s when Japanese scientists Irie and Mohri,[4] who investigated transformations of substituted stilbenes on exposure to UV light, revealed that some of them are photochromic, *i.e.*, are amenable to multiple reversible photochemical transformations. However, the systems based on stilbenes appeared to be thermally unstable, and the reverse reaction proceeded even in the dark. (Later, thermally reversible photochromes came to be regarded as T-type compounds.) The subsequent quantum chemical studies showed [5] that only compounds for which the energy difference between the open and closed forms (ΔE) is not high can be thermally irreversible (P-type compounds), since, in this case, the enegy barrier to both forward (E_A) and reverse (E_B) reaction is high enough (Fig. 2).

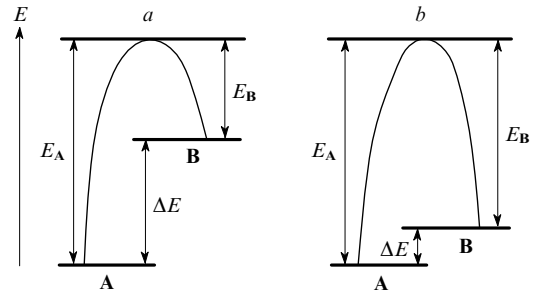


Figure 2. Energy diagram of thermally reversible (*a*) and irreversible (*b*) photochromic reactions of diarylethenes.[3]

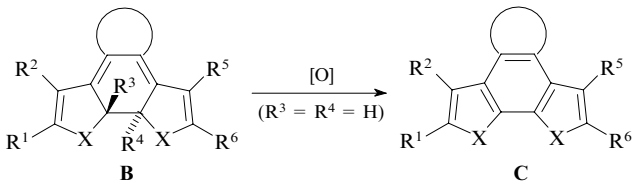
The calculations showed that the energy difference decreases from diphenylethenes to dipyrrolylethenes and further to difurylethenes, the lowest ΔE being inherent in dithienylethenes. Therefore, the lower the energy of stabilization of an aromatic system of the aryl fragments, the lower the energy difference and, as a result, the higher the thermal stability of compounds. It is the aromaticity of the aryl groups that serves as a key factor controlling the energy barrier to the forward and reverse reactions and, consequently, the stability of isomers. Hence, among the known diarylethenes, most promising are photochromic compounds based on thiophene, benzothiophene and thiazole.[3]

Moreover, a reduction in the thermal stability was found to be facilitated by weakening of the central C–C bond in the diarylethene molecules. This weakening may be due, for example, to the presence of bulky substituents at the 2-position of the benzothiophene aryl moiety [6] or highly electron-withdrawing substituents in the thiophene rings.[7]

b. Fatigue resistance

Photochromic reactions are reversible, and, theoretically, an infinite number of interconversions of forms **A** and **B** can be carried out. However, irradiation induces also side reactions, in particular, destruction which leads to ageing, *i.e.*, change in the material properties. These by-products can be *endo*-peroxides,[8] which form in the presence of air

Scheme 2

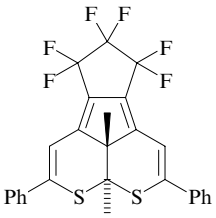


X = NR^7, O, S, CH=CH

† The number of cycles [3] of interconversion between forms **A** and **B** corresponding to the decomposition of 20% of a sample is called fatigue resistance.

oxygen, or heterocyclic analogues of phenanthrene (compounds **C**)[9] (Scheme 2).

The formation of six-membered fused rings (*e.g.*, compound **1**) was also detected.[10]



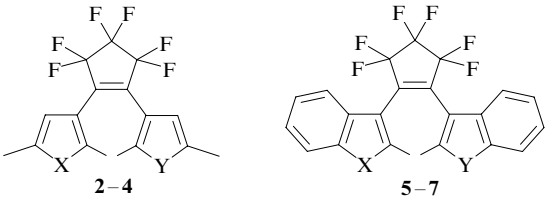
1

Monograph[11] describes in detail the calculation procedure and formula for the number of cycles of photoswitchings of photochromic diarylethenes. The importance of the absence of side reactions can be illustrated by the following example. Let the yield of a side reaction, in which a photochromic compound is spent irreversibly, be equal only to 0.1%. Then, in 100 cycles of irradiation, 9.5% of the initial compound will decompose, and 20% degradation of the sample will come after 223 cycles. In the case of the yield of a by-product of only 0.01%, the fatigue resistance of the photochrome will exceed 2200.‡

Like the thermal stability, the fatigue resistance strongly depends on the structure of molecules and, in particular, on the nature of the aryl groups at the double bond. Thus, it was found that a necessary condition for the high fatigue resistance of photochromic systems based on dihetarylethenes is the presence of substituents at the α-positions of heterocycles (R^3, $R^4 \neq H$, see Scheme 2). This structure completely rules out the route to give phenanthrene analogues **C**. Furthermore, the fatigue resistance can be increased by the replacement of thiophene aryl moieties by thiazole or benzothiophene moieties, which is caused by the lower reactivity of these aryl groups towards air oxygen.

The application of crystalline compounds also leads to an increase in the possible number of colouration–decolouration cycles: in this case, there are no rearrangements, and oxygen diffusion is suppressed. The fatigue resistance of diarylethenes may increase more than 100-fold on going from their solutions to the crystalline state.[10]

The fatigue resistance also increases considerably on going from thiophene derivatives (compounds **2**–**4**) to benzothiophenes (compounds **5**–**7**).

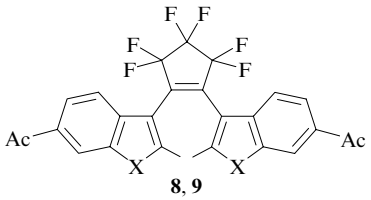


2–**4** **5**–**7**

X = Y = S (**2**, **5**), SO_2 (**3**, **6**); X = S, Y = SO_2 (**4**, **7**)

‡ Such a strong dependence of fatigue resistance on the presence of side reactions is a direct consequence of the repeatability of irradiation process. At the degree of consumption of the compound in one cycle x, in n cycles only $y = (1-x)^n$ part of the compound will be active. At low x and very high n, this formula is written as $y = 1-nx$. Taking logarithm of the first equality, one can obtain $\log y = n\log(1-x)$ or for fatigue resistance:[12] $n = \log 0.8/\log(1-x)$.

A considerable increase in the fatigue resistance of disulfones is faciliated by the introduction of acetyl groups into the benzothiophene moieties (compounds **8** and **9**).[13]



8, **9**

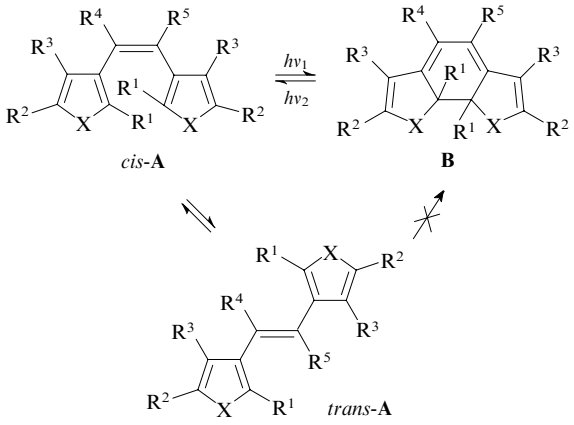
X = S (**8**), SO_2 (**9**)

Special mention should be made of the fatigue resistance of S-oxidized dithienylethenes.[14] Monosulfones **3** and **6** appeared to be more stable and disulfones **4** and **7** were less stable than non-oxidized diarylethenes **2** and **5**. The most promising photochrome is the product of oxidation at one of the sulfur atoms, namely, compound **6**.

2. Key types of photochromic diarylethenes and methods for their synthesis

The photochemistry of 1,2-diarylethenes is well studied. There are three main types of photochemical reactions: geometric (*cis*–*trans*) isomerization, intermolecular [2+2]-photocyclization and intramolecular cyclization of a hexatriene system (Scheme 3).[15–20] Of most interest are diarylethenes in which the ethene fragment (bridge) is a part of a (hetero)cycle.[3] This preference is explained by the fact that geometric isomerization and intermolecular cyclization are ruled out; moreover, the ethene bridge fixes *cis*-isomer **A**, thus facilitating an increase in the quantum yield of photochemical reactions.

Scheme 3



cis-**A** **B** *trans*-**A**

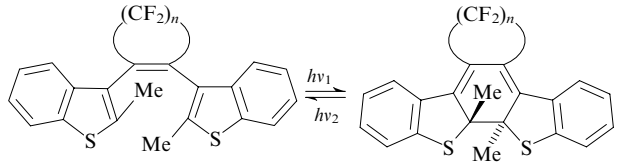
X = CH=CH, O, S, NR^6

It was shown[21] that in the series of diarylethenes **5**, **10** and **11** bearing fluorine-substituted carbocycles as bridges (Scheme 4), the absorption maximum of the photoinduced form depends on the ring size and shifts hypsochromically as the ring size increases. Thus, compound **10B** (see§) absorbs at 532 nm, compound **5B** has an absorption maximum at 526 nm, and compound **11B** absorbs at 510 nm. It was found that the quantum yield of the photochemical

§ Capital letters **A** and **B** after the compound number denote its open and closed forms, respectively.

reaction decreases upon decrease in the size of the ring containing the double bond.[22] Taking into account the requirement of that the absorption band of the coloured forms should shift to wavelengths of 650 – 830 nm, the most promising diarylethenes are compounds in which the central double bond is incorporated in a five-membered ring.

Scheme 4



5A, **10A**, **11A** **5B**, **10B**, **11B**

n = 2 (**10**), 3 (**5**), 4 (**11**)

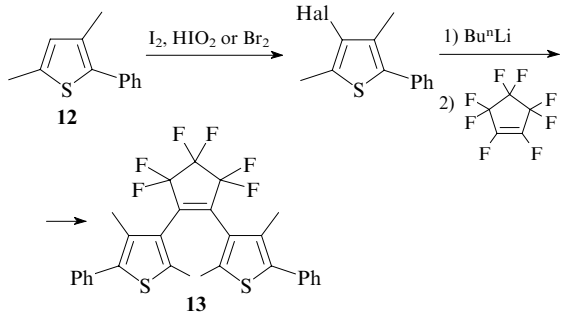
Most of the synthesized photochromic dihetarylethenes are dithienyl derivatives of the perfluorocyclopentene series. 3,4-Dihetaryl-substituted furan-[23–30] and pyrrole-2,5-diones[25,26,28,29,31–36] and 1,2-dihetarylcyclopentenes[37–45] were also described. Moreover, a wide range of dihetarylethenes with different carbocyclic and heterocyclic moieties as the ethene bridge were synthesized, and their spectral properties were studied. The photochromic compounds based on cyclobutene-[24,27,46–51] and cyclopentenedione,[52] cyclopentenone,[53–55] cyclohexenedione,[56,57] dihydrothiophene,[58–64] dihydropyrrole,[65,66] oxazole,[67,68] thiazole,[68–73] imidazole,[68,74–78] furanone,[30,79–81] furan,[82] thiophene[72,83–86] and pyrrole[87,88] derivatives and other heterocyclic systems were obtained.

The methods for synthesis of photochromic diarylethenes are described in detail in the above-mentioned papers and in recent reviews;[89,90] therefore, the present review deals with the general approaches to the synthesis of main classes of these compounds and their peculiarities.

a. Perfluorocyclopentene diarylethenes

One of the first photochromic diarylethenes which gained wide use are the compounds that contain a perfluorocyclopentene bridge. There are two main approaches to the synthesis of diarylperfluorocyclopentenes (Schemes 5, 6). The first one is based on the reaction of octafluorocyclopentenes with aryllithium and is used in the synthesis of both symmetrical and unsymmetrical photochromic diarylethenes of the fluorocyclopentene series. This method was used, for example, to obtain dithienylhexafluorocyclopentene **13** from 2,4-dimethyl-5-phenylthiophene (**12**) (see Scheme 5).

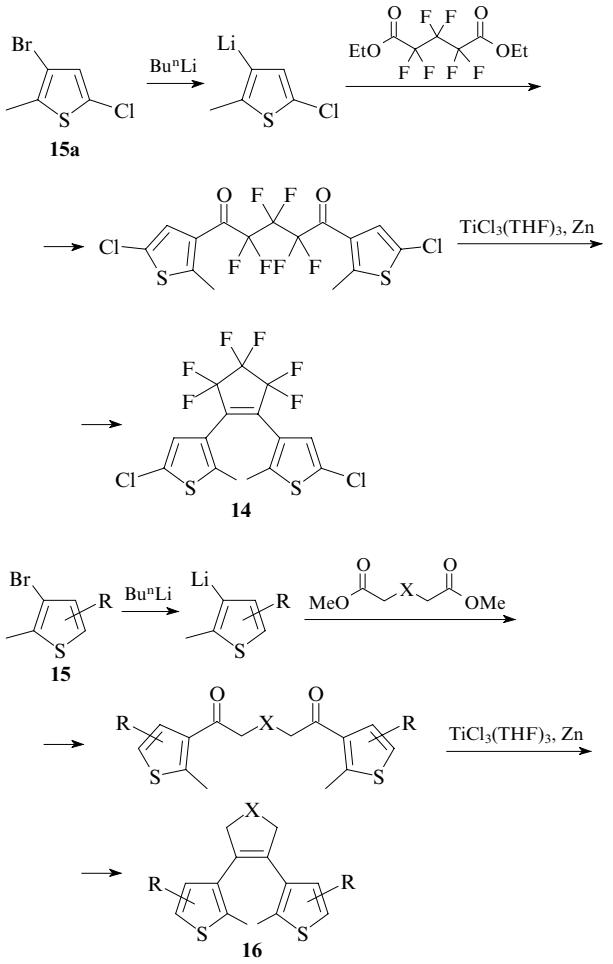
Scheme 5



The drawbacks of this method are very high volatility of the alkene (octafluorocyclopentene) and low yileds of the target products.

The second synthetic approach (see Scheme 6) includes two steps, the key step being the McMurry reaction.[91] However, this method is rarely used to prepare perfluorocyclopentene derivatives (*e.g.*, dithienylethene **14** from thiophene **15a**) but is practically the main method for production of diaryl derivatives of cyclopentene, tetrahydrothiophene, pyrrolidine and some other photochromic diarylethenes **16**.

Scheme 6

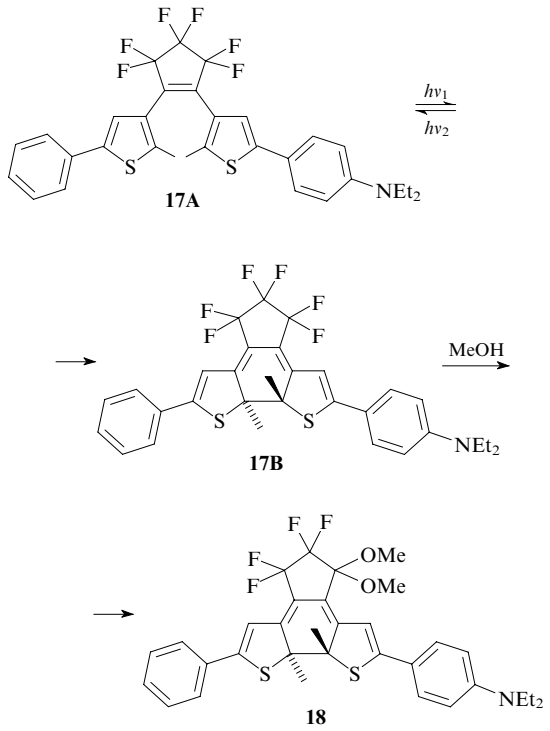


X = O, S, NAlk, CH_2

An important feature of perfluorocyclopentene diarylethenes is the chemical inertness of the ethene bridge. This causes, on the one hand, their significant advanatge over compounds containing other bridging groups, namely, high stability. On the other hand, an important drawback of these derivatives consists in the complexity of chemical modification of perfluorocyclopentene, which is important for the search of correlations between the properties of compounds and structure of the ethene bridge.

To date, there are two known works[92,93] that deal with the modification of a perfluorocyclopentene moiety by nucleophilic substitution of methoxy groups for the fluorine atoms. This method was used to obtain compound **18**, also possessing photochromic properties, by UV irradiation of diarylethene **17A** in methanol (Scheme 7).

Scheme 7

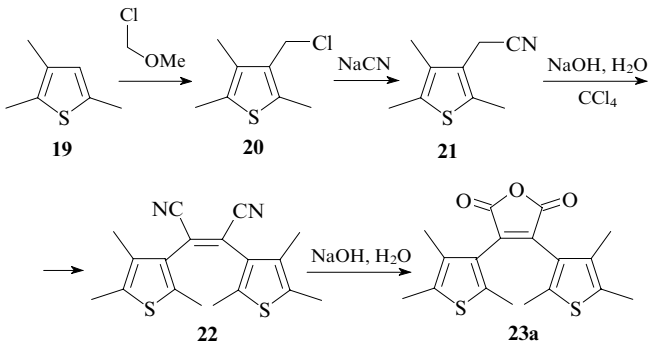


b. Diarylethenes with bridges based on maleic acid anhydride

Another promising class of diarylethenes is formed by structures based on cyclic anhydrides, namely, maleic acid anhydride. Schemes 8 – 12 show the possible methods for their synthesis.

Irie and Mohri[4] used 2,3,5-trimethylthiophene (**19**) as the initial compound, which was treated with chloromethyl methyl ether to be converted to chloromethyl derivative **20**, wich was converted to cyanomethylthiophene **21** by treatment with sodium cyanide (Scheme 8). In an aqueous solution of an alkali, diarylethene **22** was transformed into compound **21** in 47% yield, which was hydrolyzed in the presence of the alkali, giving rise to dihetarylethene **23a** containing a maleic anhydride moiety (yield 20%). When 2-methylbenzothiophene was used as the aryl component, the yield of the corresponding target product was only 14%.

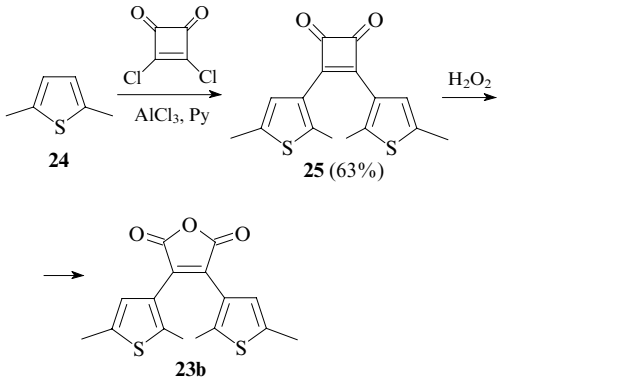
Scheme 8



The main drawback of this approach, besides labour intensity and low overall yield of the product (not more than 4% – 5% relative to the initial thiophene), is the fact that the dimerization step affords two dinitrile isomers, namely, *cis*-**22** and *trans*-**22.** Only the *cis*-isomer is able to give maleic anhydride **23a** upon hydrolysis. In some cases, an increase in the yield is achieved by the photochemical *cis* – *trans*-isomerization of dinitrile **22** prior to the hydrolysis.[4] This method can be used to obtain only symmetrical derivatives of maleic anhydride, which severely restricts its scope.

Subsequently, an alternative synthetic route to these photochromic dithienylketenes, *e.g.*, compound **23b**, was suggested (Scheme 9).[47, 51]

Scheme 9

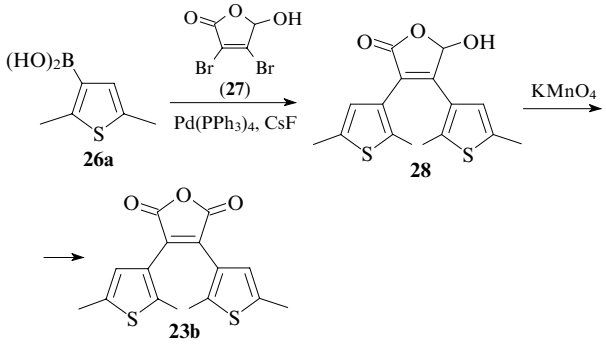


Py is pyridine

2,5-Dimethylthiophene (**24**) was first acylated with 3,4-dichlorobut-3-enedione, then the resulting diketone **25** was efficiently oxidized with hydrogen peroxide by the Baeyer – Villiger reaction (yield ~90%). Unlike the above-mentioned approach, this method allows one to obtain unsymmetrical derivatives of maleic anhydride.

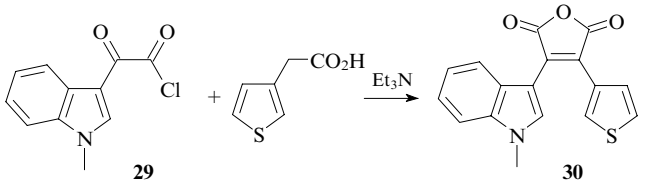
Another approach to the synthesis of compound **23b** is based on the use of boronic acid derivatives (Scheme 10).[36] It is somewhat less efficient but is based on the cheap and readily available reagents and rather simple reactions. Thus, the interaction of boronic acid **26a** with compound **27** catalyzed by palladium complex and caesium fluoride affords intermediate dithienylethene **28** in 32% yield, which is subsequently oxidized to target anhydride **23b**; at this stage, the product yield reaches 92%.

Scheme 10



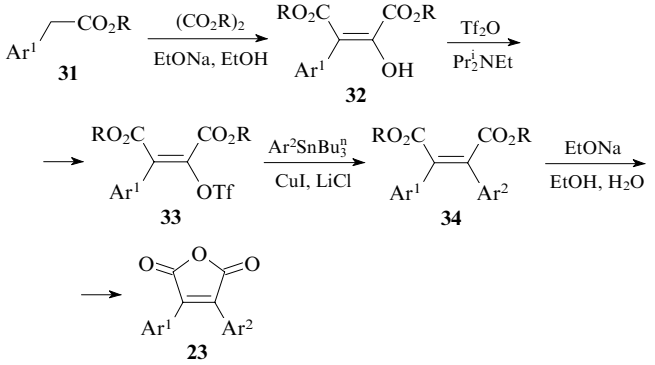
In the reaction of indolylglyoxylic acid chloride **29** with 3-thienylacetic acid (**30**) in the presence of triethylamine, the product yield varies within 20% – 35% relative to the initial chloride.[94]

Scheme 11



Another method for the synthesis of diarylfurandiones **23** is based on the application of tin compounds (Scheme 12).[95] The initial compounds are in this case arylacetic acids **31**, which condense with alkyl oxalates to form enols **32**. A key step is the Stille cross-coupling of triflate derivative **33** with an organotin aromatic compound. Esters **34** are further hydrolyzed to anhydrides **23**. The yields of the compounds in all steps of this scheme are high, but due to the great number of steps, the overall yield of the product is not high.

Scheme 12



Tf = CF_3SO_2

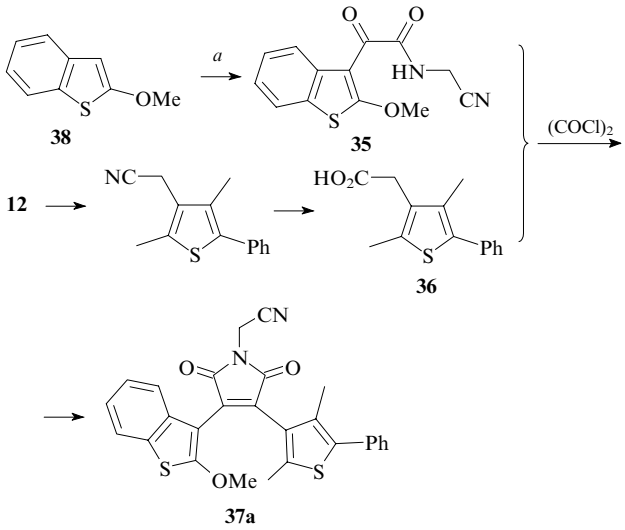
c. Diarylethenes based on maleimide

The simplest route to maleimides is the reaction of maleic anhydrides with amines. This approach, being widely used in the case of unsubstituted maleic anhydride, has received little application in the generation of dihetaryl derivatives, which is connected mainly with the inaccessibility of the corresponding anhydrides. However, in the case of furandione derivatives, this approach was found to be rather useful. Thus, this method was applied[24, 96] to synthesize a wide range of dihetarylmaleimides with various substituents at the nitrogen atoms from the corresponding maleic anhydride derivatives.

The condensation of 2-methoxy-3-[*N*-(cyanomethyl)-oxamoyl]benzothiophene **35** and thienylacetic acid **36** in the presence of oxalyl chloride leads to dihetaryl-substituted maleimide **37a** (Scheme 13). Benzothiophene **35** is synthesized by treatment of 2-methoxybenzothiophene **38** with aminoacetonitrile hydrogen sulfate and oxalyl chloride, and acid **36** is prepared from thiophene **12**. The yield of compound **37** relative to 2,4-dimethyl-5-phenylthiophene is $< 10\%$.

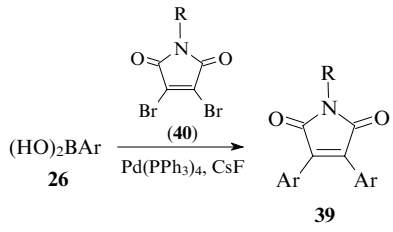
As in the case of dihetarylethenes with an anhydride bridge, a maleimide fragment can be introduced into the molecule by the reaction of arylboronic acids **26** with bromine-containing derivatives of maleimide **40** (Scheme 14). This method can also be used to obtain unsymmetrical ethenes **39**.

Scheme 13



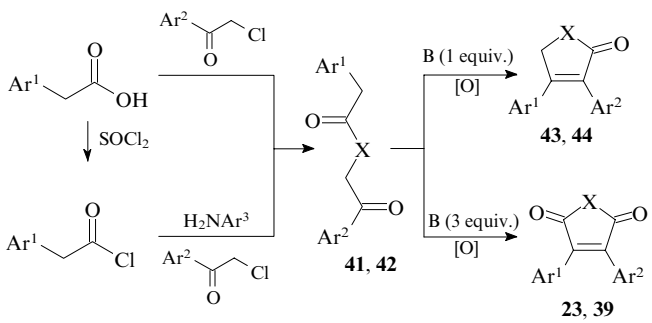
(*a*) $(COCl)_2$, $H_2NCH_2CN \cdot H_2SO_4$

Scheme 14



A general method was suggested[97] for the synthesis of 3,4-diaryl derivatives of furandione (**23**) and pyrrolidone (**39**) by the sequential transformations including cyclization and oxidation of phenacyl arylacetates (**41**, X = O) or arylacetic acid amides (**42**, X = NAr) (Scheme 15). In the presence of a base and air oxygen, compounds **41**, **42** undergo oxidative cyclization, giving anhydrides **43** and imides **44** in high yields. In the reaction under inert atmosphere, the corresponding lactones **23** or lactams **39** are formed. However, the overall yields in this multistep process are also not high.

Scheme 15

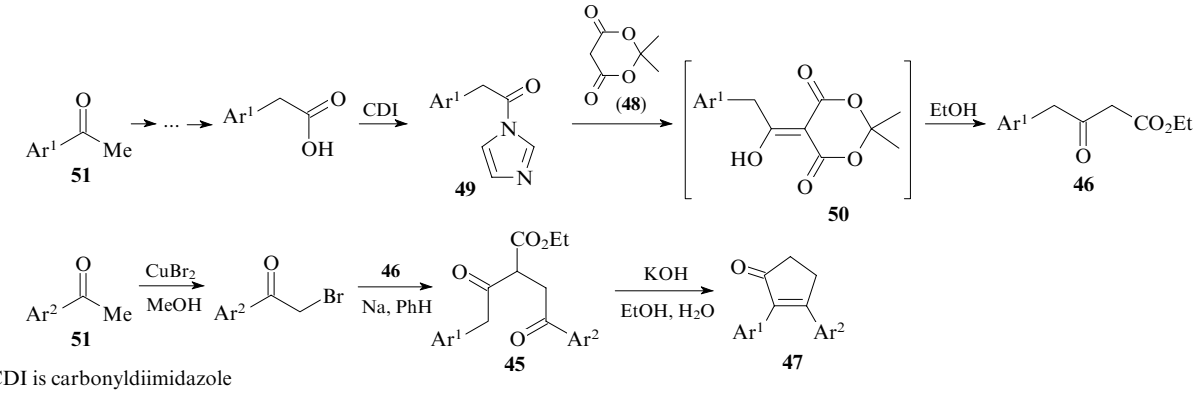


X = O (**23**, **41**, **43**), NAr (**39**, **42**, **44**); B is base

d. Diarylcyclopentenones as diarylethenes with readily modified ethene bridge

The main disadvantage of the above-mentioned diarylethenes is the chemical inertness of the ethene bridge. Due to this fact, all the chemical transformations of diarylethenes were carried out previously with the participation of the aryl moieties and directly and often strongly affected

Scheme 16



CDI is carbonyldiimidazole

the hexatriene π-system responsible for the photochromic properties. Although some correlations between the properties of diarylethenes and structure of the aryl groups can be pointed out (see Section III.2), the modification of the ethene bridge seems to be more promising. In the latter case, the variation of the spectral properties of compounds will be indirect and, therefore, more gentle, *i.e.*, so-called fine tuning of the properties of diarylethenes and preparation of compounds with required characteristics will be possible.

Recently, 2,3-diarylcyclopent-2-en-1-ones were suggested as photochromic diarylethenes.[53 – 55] These compounds contain reactive carbonyl and methylene groups in the ethene bridge, these groups being capable of various reactions (Scheme 16).

Although earlier works[98, 99] devoted to the synthesis of biologically active diarylcyclopentenones described some methods for the construction of a cyclopentenone ring, another, more convenient and efficient approach was proposed.[53 – 55] It is based on the formation of diketone **45** upon the alkylation of 4-aryl-3-oxobutanoates **46** with α-bromoketones in benzene in the presence of metallic sodium (see Scheme 16). This synthetic strategy allows for the preparation of diarylethenes **47** with the most diverse aryl fragments. Compared to symmetrical diaryl derivatives of perfluorocyclopentene, maleic anhydride and maleimide, the number of synthesized compounds **47** with one and the same hetaryl moiety can be twice greater, which provides variation of their properties over a wide range.

To obtain ketoesters **46**, a preparative method was developed[100] based on the acylation of the Meldrum's acid (**48**) with imidazoles **49** followed by the alcoholysis of intermediate products **50**. Compounds **49** and α-bromoketones were synthesized from acetophenones **51**: the first one was obtained through the formation of carboxylic acids and the second one was obtained by the bromination of the starting ketones with copper(II) bromides in methanol. An additional advantage of this method is that both arylacetic acids and bromoketones can be prepared from one and the same easily available acetophenones **51**.

III. Methods for endowing diarylethenes with fluorescence properties

1. Fluorescent method as a promising way of non-destructive readout in molecular optical memory devices

One of the main causes precluding practical use of currently known photochromic compounds for the creation of molecular optical memory systems is that they do not allow for reading of the recorded data without their erasure. Light photons which are used for readout can induce a photochromic reaction that leads to the partial loss of the recorded information.

Therefore, in the design of novel materials for optical data storage, it is important to develop a non-destructive readout method. In recent years, several methods for solving this problem have been suggested:

— data recording and erasure using UV and visible light and readout by the IR light, which cannot cause the photochromic molecular rearrangements;[101 – 103]

— non-destructive readout using polarized light, which implies the introduction of optically active substituents into the molecules of photochromic diarylethenes;[33, 104]

— application of fluorescence for readout, which forms the basis for an optical memory system.[3, 105 – 110]

Nowadays, the most developed method is the non-destructive readout of information based on the measurement of intensity of fluorescence emitted by diarylethenes. First of all, this method is optical, and, hence, a single device can be used for both data recording and readout. Second, readout is carried out using the wavelengths which do not lead to the information erasure. Finally, this method possesses extremely high sensitivity, which minimizes the possible negative consequences of irradiation owing to its low power.[105]

This method for information readout imposes two requirements on photochromic compounds, *viz.*,

— the fluorescence recording must not lead to a change in the molecule structure, *i.e.*, it must be non-destructive;

— there must be a significant difference between fluorescence of the photoinduced and initial diarylethene forms.

To fulfill the second requirement, two cases are possible

1) fluorescence must be characteristic of only one photochromic form (as a rule, the initial one, although there are examples of a reverse change of fluorescence);

2) both isomers must fluoresce but at different wavelengths.

A typical change in the absorption and fluorescence spectra during photochromic reaction (1) is shown in Fig. 3. Upon UV irradiation of diarylethene **A**, a photochromic reaction occurs and photoproduct **B** is formed; as this takes place, fluorescence intensity drastically changes. The irradiation of isomer **B** with a visible light (Vis) leads to a reverse transformation, which allows one to control fluorescence using light.

In the case of a pronounced difference between the wavelengths of the absorption and fluorescence bands, it is

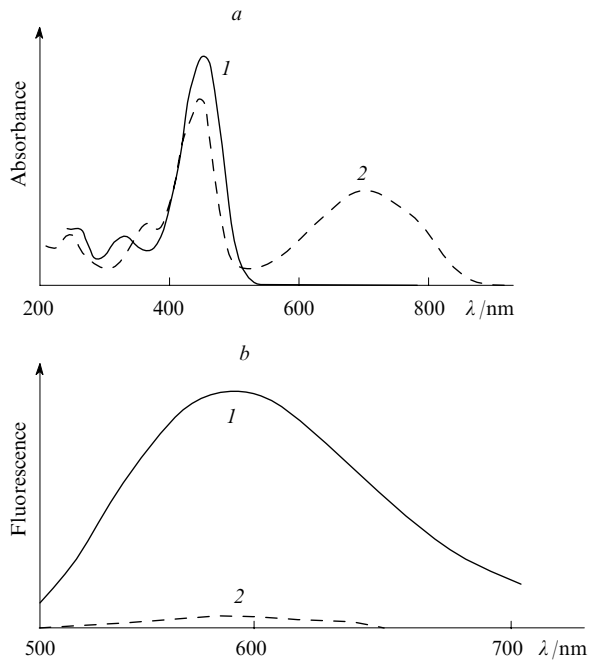


Figure 3. Typical changes in of the absorption (*a*) and fluorescence (*b*) spectra upon photochromic reaction (1) before (*1*) and after irradiation (*2*).

possible to choose such an excitation wavelength at which the photochromic transition will not occur in any of directions. Then, non-destructive readout of the recorded information using light can be implemented.[111]

2. The approaches to creation of fluorescent diarylethenes

There are several approaches to endow diarylethenes with fluorescence properties. Main ability of diarylethenes to emit radiation can be caused by the molecule structure, in particular, by the presence of certain aryl residues (and substituents in them) or ethene bridges. Moreover, fluorescence properties of diarylethenes can appear upon introduction of different fluorophores into the molecule. This can be accomplished by several methods:

1) fluorophore is attached to the diarylethene molecule either directly (to the aryl moiety or ethene bridge) or *via* a spacer (conjugated or unconjugated fragment);

2) mechanical mixtures of a photochrome and fluorophore are used, *i.e.*, the fluorescent compounds are added to diarylethene as dopants.

It is also possible to introduce the complexing substituents into the molecule structure (as a rule, into the aryl groups), the coordination of which with particular metals leads to emission.

One must also remember that the fluorescence parameters of diarylethenes strongly depend not only on their structure (in particular, the molecule charge[64]) but also on some external factors such as the nature of the environment (solvent or polymer)[112, 113] and the compound concentration in a solution. The concentration dependence of the fluorescence intensity is also associated with aggregation processes.[114 – 116]

The principles of production of photochromic fluorescent diarylethenes and their properties are described in detail below.

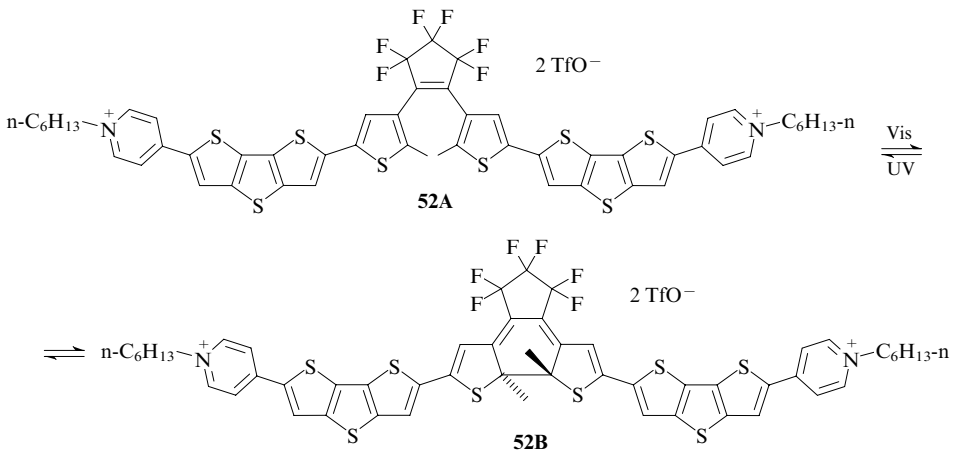
a. Fluorophoric diarylethenes

Many diarylethenes possess fluorescence (usually in the open form[117 – 119]); its intensity is often not very high and its change during photochemical reaction is insignificant.[120 – 122] More intense fluorescence is usually observed for compounds with the elongated conjugation chain, namely, 2-arylthiophene,[114, 115, 122, 123] 2-phenyloxazole,[124] and benzothiophene derivatives.[13, 125] The nature of substituents in the (hetero)aromatic systems also plays an important role: some groups quench fluorescence, the presence of other groups, in contrast, leads to enhanced emission.

The main method for production of fluorescent diarylethene photochromes is the use of fluorescent heterocycles as aryl fragments: oxazole, thiazole, indole, oligothiophene derivatives, fused thiophenes, and other heteroaromatic compounds.

One of the first fluorescent photochromes based on diarylethenes was obtained in the mid-1990s by the group of Prof. J-M Lehn, the Nobel Prize winner in chemistry (1987).[126, 127] Photochrome **52** exhibits fluorescence properties only in the open form (Scheme 17). The authors showed that the irradiation of a methanol solution of compound **52**

Scheme 17



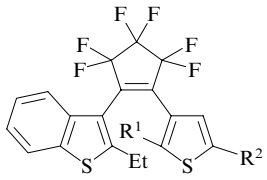
with a visible light at 400 – 500 nm leads only to emission with a maximum of 589 nm, the accompanying photochromic transformations being insignificant. Cyclic form **52B** is formed upon UV irradiation (λ_{max} = 330 – 365 nm) and is characterized by an absorption maximum at 704 nm, the intensity of residual fluorescence is less than 3% of the fluorescence intensity of the initial form. The residual fluorescence can be caused by incomplete conversion of the initial isomer during the photocyclization. The reverse transformation of the cyclic form into the open one becomes possible upon irradiation with a visible light at $\lambda > 600$ nm.

As noted above, it is the principle consiting in the information recording, readout and erasure with light at different wavelengths that serves as a necessary condition for the creation of devices suitable for non-destructive data readout using fluorescence.

A drawback of photochromic diarylethene **52** is that, upon fluorescence excitation (*i.e.*, upon information readout), the photocyclization proceeds by 10%, which leads to information loss. Most of the later works were concerned with the creation of novel fluorescent photochromes with the improved characteristics, first of all, deprived of this disadvantage.

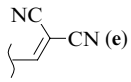
Over the last decade, the intense research into the effect of substituents in the aryl moieties on the spectral, in particular, fluorescence properties of photochromic diarylethenes was carried out by the group of Chinese researcher S Pu.[125] The authors obtained a wide range of compounds with the most diverse aryl groups bearing various donor and acceptor substituents.

Thus, it was found that in the series of compounds **53a** – **e** having thiophene and benzothiophene rings



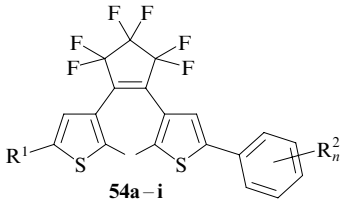
53a – **e**

R^1 = n-C_5H_{11}:

R^2 = CH_2OH (**a**),  (**b**),  (**c**), CHO (**d**),  (**e**)

a correlation between the substituent nature in the thiophene ring and the absorption maximum of the closed form is observed: the introduction of strongly electron-withdrawing substituents leads to a considerable bathochromic shift of absorption bands of the coloured forms.[125] Another important result is the dependence of the decolouration quantum yield on the conjugation chain of the coloured isomer: its elongation leads to a decrease in the quantum yield (*cf.* $\varphi = 0.32$ for compound **53a** and $\varphi = 0.11$ for compound **53e**). The fluorescence of dihetarylethenes **53** is reversibly quenched under the action of UV light to the value of ~15% of the initial emission. Compounds **53d**,**e** with electron-withdrawing groups have low-intensity fluorescence.

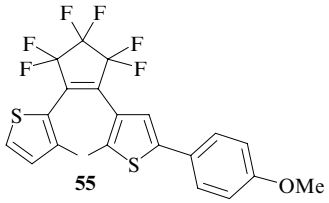
By comparing the properties of perfluorocyclopentenes **54** bearing aryl groups in one of the thiophene rings,[120, 122, 128 – 133] some regularities can also be elucidated; the position of substituents in the benzene ring plays a significant role.¶



54a – **i**

R^1 = Me: R_n^2 = 3,5-F_2 (**a**), CN (**b**), F (**c**); R^1 = Ph: R_n^2 = H (**d**), OMe (**e**); R^1 = XC_6H_4 [X = R_n^2 = 3-CF_3 (**f**), CN (**g**), F (**h**), Cl (**i**)]

Thus, in the case of derivatives **54e**, it was established that for compounds with the *ortho*-methoxy group, an absorption band of the closed form (583 nm) is shifted bathochromically by 10 nm relative to the *para*- and *meta*-isomers; as compared to unsubstituted analogue **54d**, the position of the absorption band of the coloured form (~580 nm) does not change considerably. Of note also is the blue shift of an absorption band of the photoinduced isomer on going from the *para*-isomer of diarylethene **54c** to compound **55**[134] containing a 3-methyl-2-thienyl moiety: after its irradiation, the absorption band is recorded at 497 nm.



55

For compounds **54g** with cyano groups in the *ortho*- and *meta*-positions, the absorption bands of closed forms are detected at the same wavelength as for unsusbtituted compound **54d** (580 nm), whereas for the *para*-substituted analogue, a 15 nm red shift is observed, which is explained by more efficient conjugation of the electron-withdrawing cyano groups with the molecule π-system. However, just owing to the elongation of the conjugation chain of this isomer, almost a 10-fold reduction in the quantum yield of the reverse reaction (compared to the *ortho*- and *meta*-derivatives and diarylethene **54d**) occurs. This conclusion is also supported by the results of comparison of mono- (**54b**) and di(cyanophenyl)-containing (**54g**) diarylethenes: on going to compounds **54b**, owing to shortening of the conjugation chain along with a 10-fold increase in the quantum yield of the decolouration reaction, a strong blue shift of the absorption band of the photoinduced isomer is observed (to ~540 nm for the *ortho*- and *meta*-derivatives and to 552 nm for the *para*-isomer). The effect of electron-withdrawing substituents on the quantum yields of the cyclization reactions is ambiguous: in the case of cyano groups (isomers **54b**,**g**), its value decreases relative to that for compound **54d**, whereas in the case of trifluoromethyl substituents (compound **54f**), φ increases to reach rather high value of 0.71.

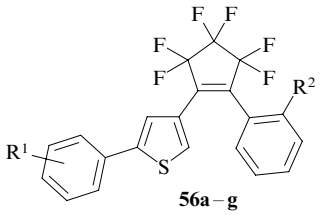
¶ If the substituent position is not mentioned, then all three isomers were obtained.

In the series of compounds **54**, despite the significant effect of substituents on the spectra of the photoinduced forms and on the quantum yields of the forward and reverse photochemical reactions, it is difficult to point out any clear-cut dependence of the fluorescence properties on the structure. A common feature of all these compounds is the presence of emission (in the range of 350 – 450 nm) for the open isomers and its reversible quenching during the photocyclization. In the case of cyano derivatives **54b**, only the *ortho*-isomer fluoresces in solutions, although in poly(methyl methacrylate) (PMMA) films, the emission is manifested by all three photochromes. At the same time, in the case of symmetrical cyano derivative **54g**, all three isomers are fluorescent in solutions, the emission maximum being shifted from 370 nm for the *meta*-derivative to 400 and 420 nm for the *para*- and *ortho*-isomers, respectively. In the case of fluorinated derivatives **54h**, the fluorescence emission band shifts to longer wavelengths on going from the *ortho*-isomers to the *meta*- and *para*-derivatives; for *para*-substituted compounds **54h**, the emission intensity is approximately 1.5 times higher than for the *meta*-isomers and 7 times higher than for the *ortho*-isomers. The same is also true for chloro derivatives **54i**: the *ortho*-isomer is the most intensively light-emitting.

The fluorescence properties are also typical of all isomers (*ortho*, *meta*, and *para*) of compounds **54b**,**c**,**e** both in solutions and in films. An increase in the electron-withdrawing properties of the benzene ring obviously leads to a shift in the emission band by 50 – 60 nm to longer wavelengths, which can be demonstrated by the example of diarylethenes **54c** ($\sim$350 nm) and **54a**,**b** ($\sim$400 nm).

In the series of arylthienylethenes **56a** – **g** bearing different *ortho*-substituents in one of the aryl groups, a clear dependence of the spectral kinetic characteristics on the electronic nature of these substituents is observed.[135 – 137]

First of all, replacement of the electron-donating groups by the electron-withdrawing ones leads to an essential shift in the absorption band of the ring isomers to shorter wavelengths comprising (nm): 581 (**56e**), 552 (**56d**), 548 (**56f**) and 539 (**56g**). In the same series, the quantum yield of the decolouration reaction decreases almost 10-fold, while the quantum yield of the forward reaction, in contrast, is maximum for diarylethenes with electron-withdrawing groups ($\varphi = 0.65$ for compound **56g**). The introduction into the thienyl moiety of *meta*-trifluoromethyl substituent (comparison of the spectra of compounds **56e** and **56a**) and *para*-methyl groups (comparison of the spectra of compounds **56g** and **56b**) does not affect significantly the position of the absorption maximum of the coloured isomers. Moreover, the absorption spectra of these compounds in PMMA films, as for diarylethenes **54**, show red shifts of the absorption bands by 10 – 15 nm relative to the values obatined in hexane solutions. It was also established that, except for cyano-substituted diarylethene **56f**, all other derivatives do not exhibit photochromic properties in crystals, although, according to X-ray diffraction data, in crystals all the molecules exist in the antiparallel conformation and the distance between the reaction centres does not exceed 4.0 Å. Based on the studies of a series of di(thienyl)-perfluorocyclopentenes, previously, Japanese researchers[138, 139] suggested that for the photocyclization in crystals of diarylethenes to be possible, this distance must not exceed 4.2 Å.

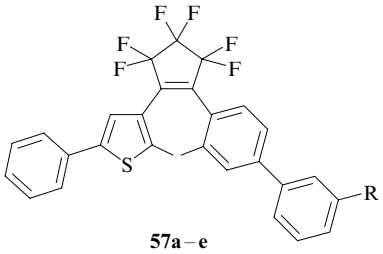


56a – **g**

R^1 = 3-CF_3, R^2 = OMe (**a**); R^1 = 4-Me, R^2 = CF_3 (**b**); R^1 = H: R^2 = H (*c*), Me (*d*), OMe (*e*), CN (f), CF_3 (**g**)

The effect of substituents in the *ortho*-position of the benzene ring on the fluorescence properties of arylthienylethenes **56** was studied.[135] Among compounds **56d** – **g**, the emission is characteristic only of methoxy derivative **56e**, while in PMMA films all diarylethenes are light-emitting. The intensity of fluorescence of compounds **56** decreases under the action of UV radiation, and, since the process is reversible, under the action of visible light, the intensity increases. It was also revealed that the solvent polarity is of high importance for the manifestation of fluorescence properties:[136] the emission of perfluorocyclopentene **56b** in dimethyl sulfoxide is 2 times more intense than in dichloromethane and is 4 times more intense than in hexane. Moreover, on going to a less polar solvent (from DMSO to hexane), a maximum of the emission band undergoes a substantial bathochromic shift (by more than 100 nm).

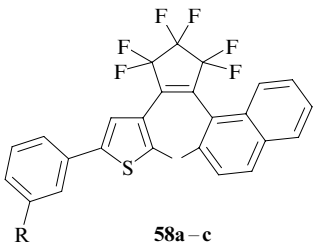
Biphenyl derivatives **57a** – **e** demonstrate good photochromic and fluorescence properties both in solutions and in PMMA films.[140]



57a – **e**

R = H (**a**), Me (**b**), OMe (**c**), CN (**d**), CF_3 (**e**)

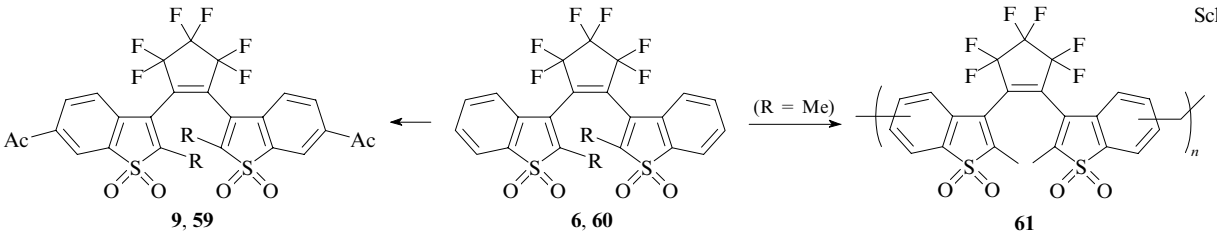
The electron-donating substituents in compounds **57b**,**c** displace the absorption maxima of the open and closed forms to the red range relative to the bands of diarylethene **57a**; the quantum yields of the forward reaction decrease, while those of the reverse reaction do not change. At the same time, the introduction of electron-withdrawing substituents (compounds **57d**,**e**) has a considerable influence only on the quantum yields of the decolouration reactions, which increase. As for fluorescence properties of diarylethenes **57**, it can be noted that upon introduction of electron-withdrawing groups into the molecule, a bath-



58a – **c**

R = H (**a**), OMe (**b**), CF_3 (**c**)

Scheme 18



9, **59** **6**, **60** **61**

R = Me (**6**, **9**), n-C_7H_{15} (**59**, **60**)

ochromic shift of the emission band is observed (415 and 431 nm for compounds **57c** and **57e**, respectively).

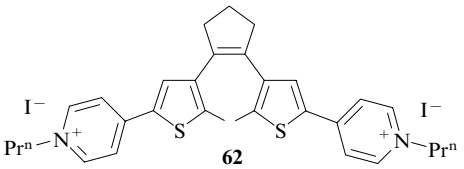
The replacement of one of the phenylthienyl moieties of compounds **54** by 2-methylnaphthyl moieties (diarylethenes **58a–c**)[141] leads to a hypsochromic shift of the absorption band of the diarylethene coloured form by 70 nm (for methoxy derivative **58b**).

Fluorescence of the initial form of compound **58c** (fluorescence intensity decreases upon irradiation with UV light) is 3 times more intense than for methoxy derivative **58b** and 4.5 times more intense than for their unsubstituted analogue **58a**.

Fluorescent diarylethenes **6**, **9**, **59–61** with oxidized sulfur atoms were reported (Scheme 18).[13,142–144] During the photocyclization, the intensity of their fluorescence considerably increases, whereas that for the non-oxidized precursors, conversely, decreases. Polymeric photochromic compound **61**[144] differs from monomer **6** by a sixfold increase in the fluorescence quantum yield and high fatigue resistance. Of note is also the appearance of a bathochromic shift of the fluorescence band of the closed forms upon introduction of acetyl and heptyl groups into the molecule: from 492 nm (for compound **6**) to 506, 520, and 502 nm for compounds **9**, **59**, and **60**, respectively.

Of these four compounds, most promising are diarylethenes **9** and **59** with acetyl functions in the benzothiophene moieties: the emission of their closed forms is 5 times more intense and the quantum yield is 3 times higher than those for diarylethenes **6** and **60**, respectively. Fluorescence of the closed form along with the above-mentioned high fatigue resistance of compounds **9** and **59** make these photochromes attractive for the design of optical memory elements and molecular switches based on them.[13]

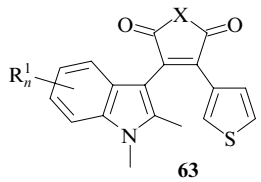
Interesting results were obtained upon application of a charged particle as a fluorophore.[112] Compound **62** demonstrated a 340-fold increase in fluorescence upon irradiation with light, which exceeds this value for other compounds of this class by a large factor.



62

Besides thienyl and substituted phenyl rings, diverse nitrogen-, oxygen-, and sulfur-containing heterocyclic moieties were also introduced in the diarylethene molecules.

In recent years, the intense research on the development of methods for synthesis and study of spectral kinetic characteristics of dihetarylethenes with various ethene bridges, in particular, with furan and pyrrolidone rings have been carried out by Russian scientists at the Southern Federal University (Rostov-on-Don).[145–150] The authors synthesized a wide range of new unsymmetrical photochromic dihetarylethenes in which one of the aryls is indole or benzindole derivative and studied the effect of substituents in the ethene bridge on the photochromic and fluorescence properties. In particular, it was shown[149] that, unlike furandione derivative **63** (X = O), pyrroldiones **63** (X = NR, where N = Alk, Ar) exhibit photochromic and fluorescence properties in hexane solutions. The quantum yields of the photocolouration of pyrroldiones are 4–5 times lower than analogous parameters of the decolouration reactions, and the quantum yields of fluorescence strongly depend on the nature of substituents at the nitrogen atoms.

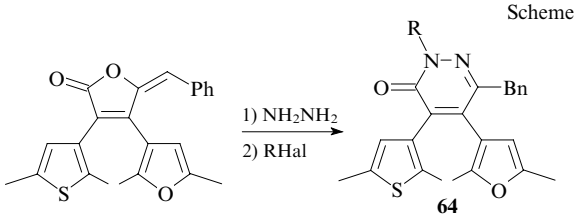


63

R^1_n = 5-OMe, 6,7-benzo; X = O, NBu^i, NBn, NPh, *etc.*

The modification of a five-membered ring acting as the ethene bridge afforded a series of substituted pyridazinones **64** (Scheme 19).[146] The investigation of spectral properties of these unsymmetrical dihetarylethenes showed that they are characterized by high efficiency of the photocolouration and thermal stability of the photoinduced forms. Moreover, it was found that the decelerated rotation of thiophene and furan rings around single bonds in solutions gives rise to a mixture of chiral diastereomers with a lifetime not more than 0.2 s.

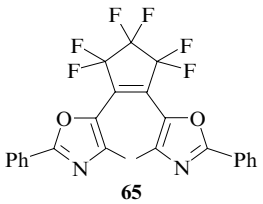
Scheme 19



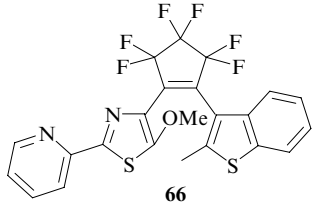
64

R = Me, Et, 4-$ClC_6H_4CH_2$, 4-$NCC_6H_4CH_2$

Photochromic diarylperfluorocyclopentene **65** containing oxazole rings as the aryl moieties were reported.[124]



65

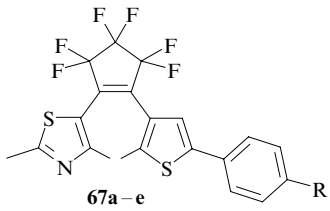


66

The quantum yield of fluorescence of photochrome **65** proved to be much higher than that of the known diarylethenes and to strongly depend on the excitation wavelength. A maximum of the fluorescence band is observed at 470 nm; the maximum value of the quantum yield is achieved at $\lambda = 365$ nm ($\varphi = 0.19$), while at $\lambda = 380$ nm, this value is already reduced by 38%.

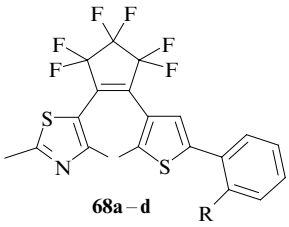
Chinese researchers [151] synthesized unsymmetrical diarylethene **66** with 2-pyridine-substituted thiazole as one of the aryl moieties. The authors studied in detail the spectral properties of this photochrome and the effect of protonation and coordination to divalent copper ion on them. It was shown that the protonation of the closed-ring form leads to a bathochromic shift of the emission maximum, and the addition of divalent copper ions quenches fluorescence. The fluorescent compounds with these polyfunctional characteristics are important for the design of multilayer switches.

The results of publications [123, 152, 153] which deal with the behaviour of diarylethenes **67a – e** and **68a – d** with a thiazole ring as aryl moieties in hexane solutions and PMMA films imply that the position of substituents in the benzene ring strongly affects the spectral properties of the compounds.



67a – e

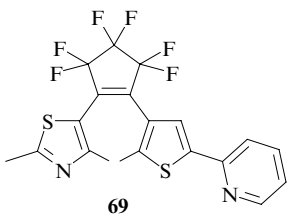
R = H (**a**), Me (**b**), OMe (**c**), CN (**d**), CF_3 (**e**)



68a – d

R = Me (**a**), OMe (**b**), CN (**c**), CF_3 (**d**)

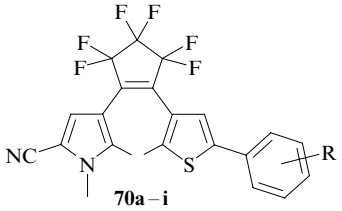
It was found that compared to diarylethene **67a** ($\lambda_{max} = 469$ nm) bearing unsubstituted benzene ring, the introduction of substituents in the *ortho*-position (compounds **68a – d**) leads to a hypsochromic shift of the absorption band of closed forms. In the case of electron-withdrawing substituents, this shift is greater than that for electron-donating groups (~440 and ~450 – 460 nm, respectively). The substituents at the *para*-position (compounds **67b – e**) have an opposite effect irrespective of their electronic properties: the absorption band of the photoinduced form is red-shifted. However, inrespective of the position of substituents in the benzene ring, the increase in the quantum yield of cyclization in the presence of donor groups and the decrease in the yield in the case of acceptor groups are observed. The replacement of phenyl group by 2-pyridyl group (dihetarylethene **69**) causes a considerable (to 497 nm) red shift of the absorption band of the closed form. There is no significant effect on the quantum yields of the forward and reverse reactions.



69

As in the case of absorption spectra, the position of substituents in the benzene ring plays a key role for the emission spectrum of the thiazole-containing dihetarylethenes: compared to unsubstituted diarylethene **67a** ($\lambda_{fl} = 440$ nm), the *para*-substitution (compounds **67b – e**) does not lead to a large shift of the fluorescence band, whereas for the *ortho*-isomers (compounds **68a – d**), the bands are shifted bathochromically by 30 nm on average. The effect of the nature of these substituents is less essential; however, it can be noted that the electron-donating groups shift the emission bands to longer wavelengths, while electron-withdrawing groups shift the bands to shorter wavelengths. These compounds are characterized by rather high quantum yields of the emission in polymer films (~50%) compared to a hexane solution (35%); fluorescence is reversibly quenched by UV light. Perfluorocyclopentene **67a** and its pyridine-containing analogue **69** differ insignificantly in their light-emitting properties.

Diarylethenes with N-heterocycles as the aryl fragments were also studied in detail. The spectral properties of photochromes **70a – i**



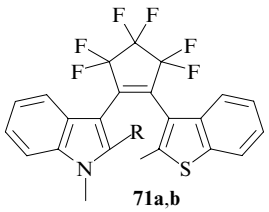
70a – i

R = H (**a**), 4-F (**b**), 4-CN (**c**), 2-CN (**d**), 3-CN (**e**), 4-Me (**f**), 4-OMe (**g**), 2-OMe (**h**), 3-OMe (**i**)

which contain a substituted pyrrole ring, were reported.[115, 154, 155] It was found that only in the case of cyano (**70c – e**) and methoxy groups (**70g**), an increase in the quantum yield of the forward reaction is observed (compared to diarylethene **70a** with the unsubstituted phenyl fragment); the positions of absorption maxima of the photoinduced forms are not affected by the presence of these substituents.

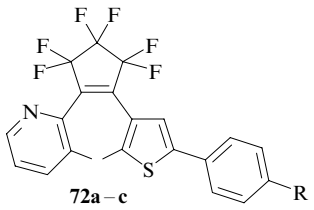
The intensity of fluorescence, which becomes stronger upon irradiation with visible light, decreases almost twofold upon introduction of a substituent into the *para*-position of the phenyl ring; however, the nature of substituent is not important. Furthermore, it was found that the effect of the methoxy group does not depend on its position. For the *para*- (**70g**), *ortho*- (**70h**) or *meta*-isomers (**70i**), an increase in the quantum yields of the forward reaction and increase in the fluorescene of the open form compared to those of unsubstituted analogue **70a** are observed, but at the same time, the fluorescence intensity decreases. The position of the fluorescence maxima of these compounds is strongly affected by the solution concentration: thus, in a 10^{-6} M solution they emit in the range of 401 – 427 nm, while increase in the concentration induces a bathochromic shift of the emission maximum by 29 nm. In a series of cyano derivatives **70c – e**, the values of quantum yields also depend on the position of the substituent, but its effect on the fluorescence properties can also be followed: the emission intensity of *ortho*-isomer **70d** and unsubstituted analogue **70a** is the same, whereas the emission of the *meta*- (**70e**) and *para*-isomers (**70c**) is almost twice lower.

The introduction of the fluorescent indole ring as the aryl moiety significantly influences the spectral characteristics of compounds **71a**,**b**.[156] Here, as in the case of most other dihetarylethenes, the fluorescence properties are characteristic of only the open form. An increase in the quantum yield of cyclization leads to a reduction in the emission intensity.



71a,**b**

R = Me (**a**), Ph (**b**)

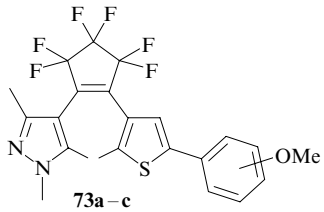


72a–**c**

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

A dramatic effect of substituents on the spectral properties is also observed in the series of pyridine-substituted diarylethenes **72a**–**c**.[157] Diarylethenes **72a** unsusbtituted at the phenyl group and methoxy derivative **72b** demonstrate relatively weak fluorescence in the range of 425–475 nm. The introduction of the cyano group (compound **72c**) leads to almost a 5-fold increase in the emission intensity and a 375 nm hypsochromic shift of the emission maximum.

The presence of a pyrazole ring provides for a profound enhancement of spectral characteristics of the corresponding dihetarylethenes.[113, 158] Thus, the quantum yields of the forward and reverse reactions of photoisomerization for compound **73c** having the methoxy group in the *para*-position of the benzene ring reach very high values (up to 0.57).

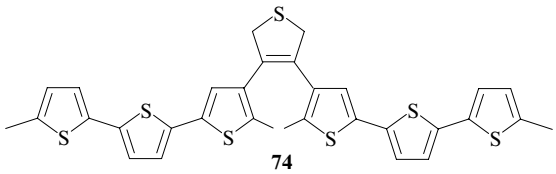


73a–**c**

Isomers: *ortho* (**a**), *meta* (**b**), *para* (**c**)

As compared with diarylethenes containing other heterocycles instead of pyrazole, the fluorescence intensity considerably increases in the series of *ortho*-, *meta*-, *para*-isomers **73a**–**c**, reaching the maximum value for *para*-methoxy derivative **73c**.

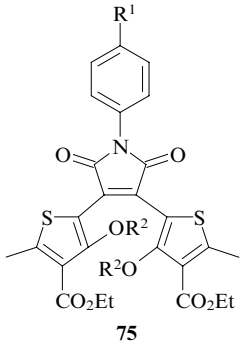
Of particular interest from the practical standpoint are dihetarylethenes with fluorescent oligothiophenes, *e.g.*, compound **74**.[159]



74

The oligothiophene moiety possesses electrochromic properties along with the photochromic and fluorescent characteristics. These compounds are used in the design of multifunctional switches.

The lack of photochromic properties in the presence of emission was reported for diarylethenes **75** with the maleimide bridge.[31]



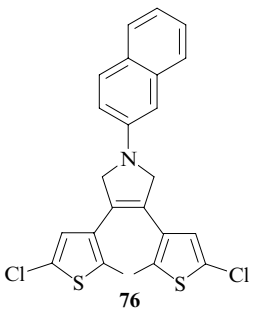
75

R^1 = H, Cl, OMe; R^2, Me, Ac, CH_2CO_2Et

It was shown that the properties of these compounds strongly depend on the substituents both in the ethene bridge and in the aryl moiety. For example, the most intense fluorescence is typical of the compounds with hydroxyl groups (R^2 = H). The alkylation of these compounds (R^2 = Me, CH_2CO_2Et) leads to a hypsochromic shift of the emission band by 15 nm, on average, and alsost tenfold decrease in the emission intensity. At the same time, the acyl-containing analogues (R^2 = Ac) do not fluoresce at all. As for the maleimide fragment, upon the introduction of a substituent into the phenyl group at the nitrogen atom (R^1 = 4-OMe), the fluorescence quenching is also observed.

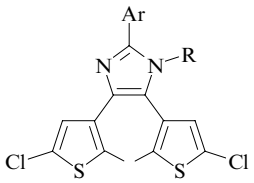
The effect of the solution pH on the properties of hydroxyl-containing diarylethenes **75** (R^2 = H) was studied. It was shown that in the presence of bases, the compound emission is quenched, and the stronger the base, the more pronounced is quenching. Thus, in the presence of pyridine, the quenching is not very strong (approximately 1.2-fold), whereas the application of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) induces almost complete disappearance of fluorescence behaviour of these compounds.

Various heterocycles possessing fluorescence properties can be used not only as the aryl moieties, but also as the ethene bridge. Xie and Chen[66] studied the photochromic and luminescence properties of dithienylethene **76**, which contains a fluorescent fluorophore as the ethene bridge. The pyrrole ring of diarylethene **76** is sensitive not only to light but also to acids. Upon addition of an acid, the fluorescence properties are retained, but a 10 nm hypsochromic shift of the emission maximum of the protonated form is observed.



76

The spectral properties of fluorescent diarylethenes **77**–**86** bearing imidazole derivatives as the ethene bridge were described.[160, 161]



77 – 86

R = H (**77 – 82**), Me (**83 – 86**); Ar = 2-Fu (**77**, **83**), 2-Th (**78**, **84**), 2-Pyr (**79**, **85**), Ph (**80**, **86**), 4-ClC_6H_4 (**81**), 4-$MeOC_6H_4$ (**82**); Fu is furyl, Th is thienyl, Pyr is pyrrolyl

The authors found clear-cut correlations between the structure of these compounds and their spectral properties. Thus, it was noted that the alkylation of the nitrogen atom of the imidazole ring (compounds **83 – 86**) results in a hypsochromic shift of the absorption maxima of the open forms, on average, by 15 nm compared to those for compounds **77 – 80**. The absorption bands of the photoinduced isomers, conversely, undergo a red shift by 10 – 60 nm, depending on the nature of the aryl group [the greatest differences are observed between diarylethenes **80** (λ = 516 nm) and **86** (λ = 574 nm)].

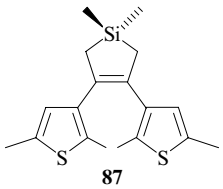
Moreover, alkylated derivatives **83 – 86** feature high quantum yields of the photocyclization reactions (maximum value φ = 0.71 is observed for compounds **83** and **84**); the quantum yields of the reverse reactions do not depend on the nature of substituent at the nitrogen atom. The substituents in the imidazole ring also affect the spectral properties of these compounds. It can be noted that the absorption band of the coloured form of phenyl derivative **80** is substantially blue-shifted (to 520 nm) compared to its heterocyclic analogues **77 – 79** (540 – 560 nm). The introduction of the chlorine atom in the *para*-position of the benzene ring (diarylethene **81**) leads to a blue shift, and the introduction of the donor methoxy group (diarylethene **82**) induces a red shift of the absorption bands of the closed form.

The emission intensity of the imidazole-containing diarylethenes during the photocyclization of a hexatriene system under UV irradiation increases by 98%. The alkylation at the nitrogen atom in the ethene bridge does not affect the fluorescence wavelengths of these compounds, but the quantum yields of emission increase as a result of this modification. It should also be noted that for pyrrole derivatives **79**, **85**, the emission band (λ = 550 nm) is characterized by a significant bathochromic shift compared to those for other compounds (λ = 450 – 470 nm); the most intense emission is observed for diarylethene **85** (approximately 4 times higher than for the other imidazole derivatives).

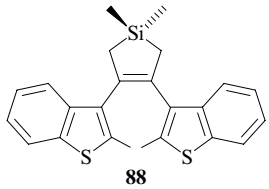
Interesting results were obtained in investigations of the fluorescence properties of compounds **81 – 82** and **86** containing phenyl groups at the carbon atom of the imidazole ring: the fluorescence is characteristic of both the acyclic (381 nm, φ_{fl} = 0.017) and photoinduced (452 nm, φ_{fl} = 0.014) isomers of compound **80**, *i.e.*, upon photocyclization, the emission band shifts by 71 nm. The introduction of the chlorine atoms into the phenyl group (compound **81**) leads to the essential quenching of fluorescence for the closed isomer, while increasing the quantum yield of emission of the open form to 0.114. For methoxy derivative **82**, in contrast, fluorescence is observed only for the closed form (φ_{fl} = 0.130).

The addition of metal ions to an acetonitrile solution of diarylethene **79** strongly affects the spectral properties of this compound (see below).

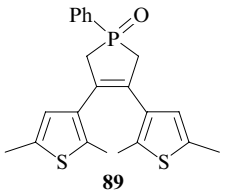
Unusual diarylethenes with silicon- (**87**, **88**) and phosphorus-containing heterocycles as the ethene bridges (**89**, **90**) were reported.[162]



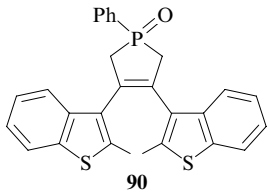
87



88



89



90

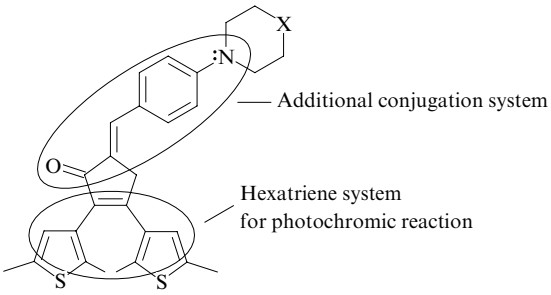
Compared to perfluorocyclopentene analogues **2** and **5**, the absorption bands of the coloured forms of diarylethenes **87 – 90** are hypsochromically shifted to ~450 nm (those of perfluorocyclopentene derivatives are λ = 520 nm). A similar shift is also observed for the emission maxima of the closed forms: from 625 nm for di(benzothienyl)perfluorocyclopentene **5** to ~570 nm for compounds **87 – 90**. Moreover, unlike perfluorocyclopentene **5** the fluorescence intensity of which diminishes under the action of UV light, in the case of these compounds UV light leads to enhanced fluorescence.

b. Covalent attachment of a fluorophore

Dithienylethenes with a cyclopentenone bridge can be endowed with fluorescence properties by modification of their structure. According to Shirinian *et al.*,[53] one of the approaches is the introduction of a merocyanine system into the molecule, *i.e.*, an extension of the conjugation chain between the donor nitrogen and acceptor oxygen atoms (Fig. 4). The strengthening of fluorescence properties is also facilitated by the inversion of the nitrogen lone electron pair.

To endow dihetarylethenes having the perfluorinated cyclopentene bridge with fluorescence properties, the fragments prone to fluorescence are introduced into the molecule. One can point out two main methods for such a functionalization. In the first case, the fluorophoric fragment is in the conjugation with the π-system of the compound responsible for the photochromic transformations: it is either directly attached to the aryl moiety or connected with it by the conjugated (rigid) spacers such as the vinyl or acetylene groups, aromatic or heteroaromatic rings. The second method implies the addition of a fluorophore to the photochromic molecule through the unconjugated (flexible) spacers, which are often methylene chains, ether, sulfide and other analogous groups. These linkers practically do not affect the π-system responsible for the photochromic transformations.

The approach based on flexible spacers as a route to functionlization of diarylethenes is most convenient, since it is possible to prepare the photochrome and fluorophore molecules separately and then connect them *via* various



91 (X = CH_2, O)

Figure 4. Fluorescent 2,3-diarylcyclopent-2-en-1-ones **91** with merocyanine system in the ethene bridge.

spacers.[163–166] (note that the attachment of a fluorescent fragment can also be carried out at the earlier stages of the synthesis.[66]) This provides easy variation of fluorophoric components, the constant ratio of a photochrome and fluorophore in the resulting compositions, and the absence of eletcronic interaction between the photochromic fragment and the fluorophore, which decreases the possibility of energy transfer from one molecule part to the other.

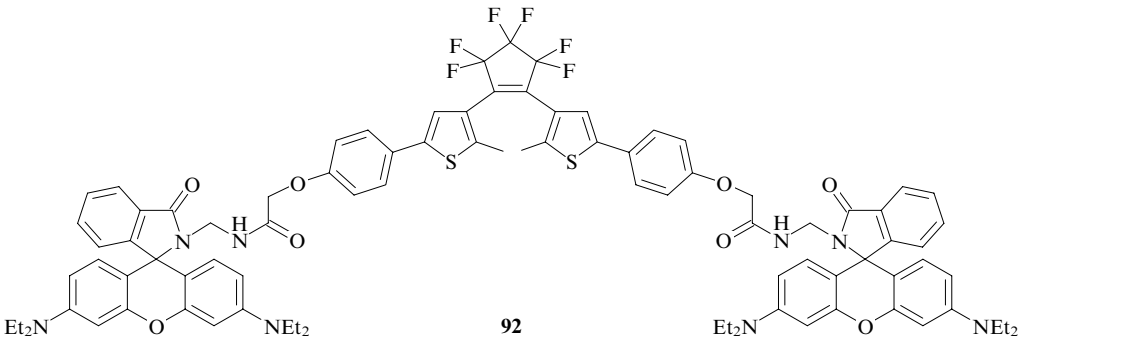
The rhodamine fragment was used as a fluorophore to obtain hybrid photochrome **92**.[167] This compound can be used as a photo- and acid-sensitive switch. Its action is based on the fluorescence modulation upon addition of trifluoroacetic acid to a solution of the open form. The addition of triethylamine or UV irradiation leads to the reverse transformation and fluorescence dissapears almost completely.

Fluorescent molecular switches **93a**,**b** based on di(thienyl)cyclopentene, which is linked to one or two terpyridine fragments *via* a phenylene-ethylene spacer, were synthesized by Chinese researchers.[168]

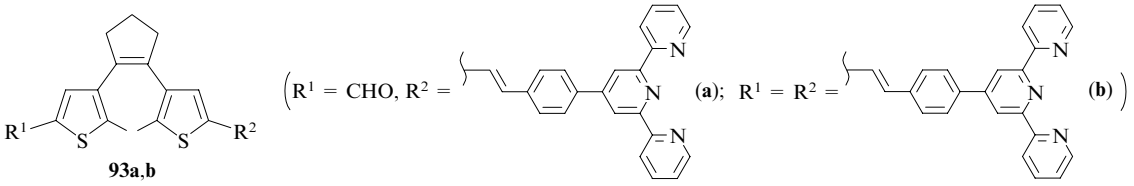
The terpyridine system not only has fluorescence properties but can also be coordinated to metal ions to give stable complexes. The spectral properties of these compounds, in particular, in the presence of transition metal ions were studied.[168] The emission of the open forms of diarylethenes **93a**,**b** is observed at the wavelengths of 467 and 458 nm, respectively. The irradiation with UV light leads to a considerable quenching of fluorescence; this indirectly confirms that the photoinduced form does not possess emission.

Fluorescent photochrome **94** bearing perylenetetracarboxylic acid bis(imide) as a fluorophore was studied both in solutions and in polymer matrices, namely, poly(methyl methacrylate) and poly(n-butyl methacrylate).[166, 169] Harnessing adamantane ring as a linker gave a fairly rigid structure. Owing to the presence of a perylene fragment, the quantum yields of fluorescence of compound **94** are very high both in solutions and in polymer matrices and reach 95%–98%.

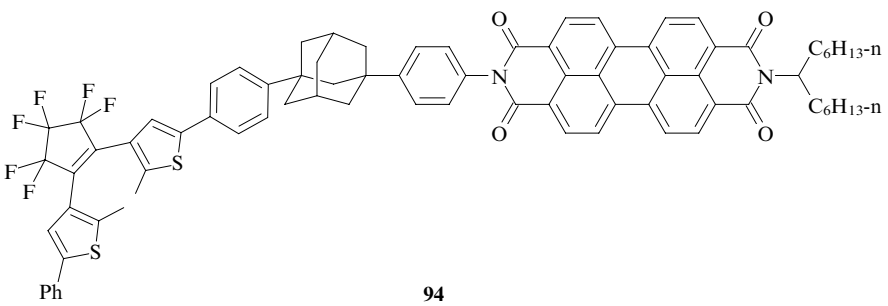
Meijere *et al.*[164] considered hybrid photochromic dithienylperfluorocyclopentenes **95a**,**b** bearing the anthracene system as a fluorophore. The photosensitive fragments were connected *via* bicyclo[1.1.1]pentane. The photoinduced forms of these compounds with the methoxy group at the 2-position of the thiophene ring were less stable to photo-



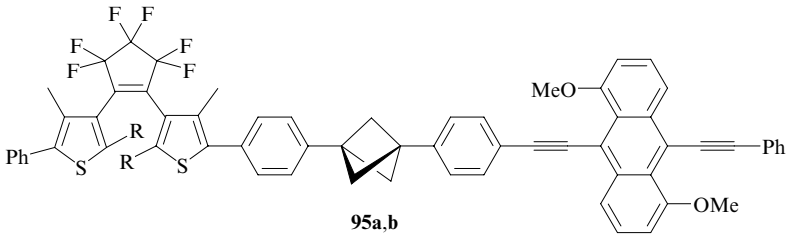
92



93a,**b**

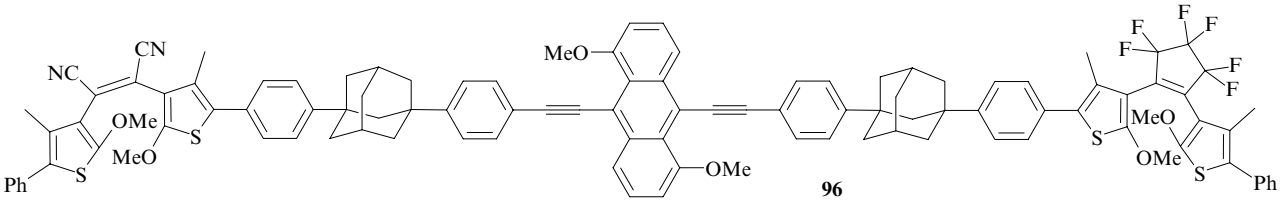


94

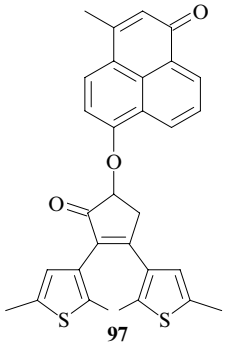


95a,**b**

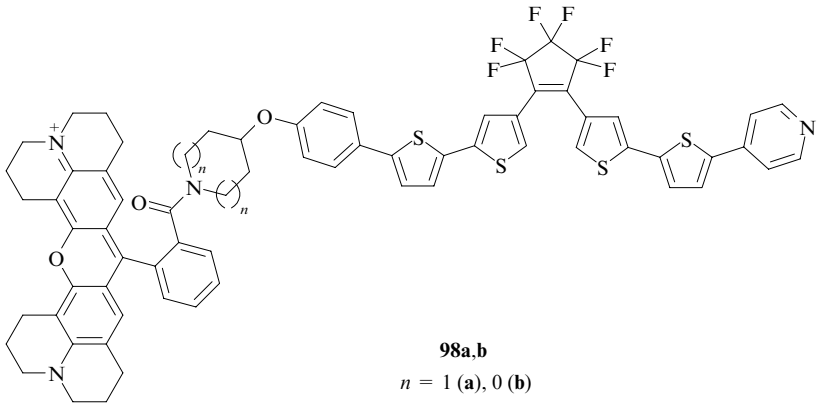
R = Me (**a**), OMe (**b**)



96



97



98a,**b**

n = 1 (**a**), 0 (**b**)

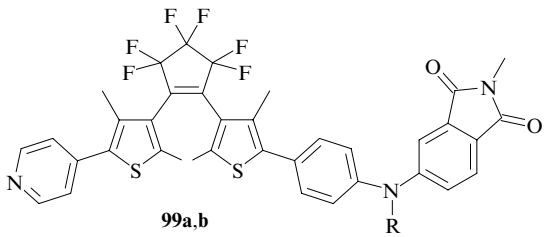
degradation compared to the methyl derivatives. The authors revealed that, upon irradiation, the quantitative resonant transfer of fluorescnece energy from the fluorophore (donor) to the photochrome (acceptor) takes place.

An analogue of diarylethene **95**, compound **96**, contains two diarylethene fragments: perfluorocyclopentene and dicyanoethene.[165] The diarylethene moieties in compound **96** act independently, which allows for the creation of a device which implements the logical functions AND, OR, NOT in one molecule (see below).

Based on 2,3-diarylcyclopent-2-en-1-one **47a** (Ar^1 = Ar^2 = 2,5-dimethylthien-3-yl), hybrid compound **97** was also obtained in which 6-hydroxy-3-methyl-1*H*-phenalen-1-one (fluorescent fragment) was connected with the photochromic diarylethene through the ether linker.[170] The introduction of the fluorophore into the photochromic molecule reduced the quantum yields of the photocyclization and photodecolouration reactions almost 10-fold compared to these parameters for the initial cyclopentenone **47a**. Such an effect is explained by the competition between the photochromism and fluorescence: the energy of light absorbed by the substance is spent both for emission and for the photochromic reaction, which leads to a considerable suppression of the latter compared to nonfluorescent diarylethene **47a**. As for the fluorescence properties of compound **97**, it was shown that emission of its open form is reversibly quenched under the action of UV light owing to the intermolecular transfer of the energy from the fluorophoric part to the photochromic part of the molecule. The mechanical mixtures based on diarylcyclopentenones **47** were also obtained (see below).[170] It was shown that the covalent attachment of a fluorophore to diarylethene (compound **97**) is a more promising approach to the creation of a photoswitch rather than the application of mechanical mixtures, since to achieve the same effect of fluorescence quenching in the latter case, a greater excess of diarylethenes **47** is required (up to 200-fold).

The most diverse saturated rings can serve as spacers, the ring size being significant. Thus, the quantum yield of fluorescence of compound **98a** with a stable piperidine ring as a spacer is 2.5 times higher than the analogous parameter for azetidine **98b**.[171]

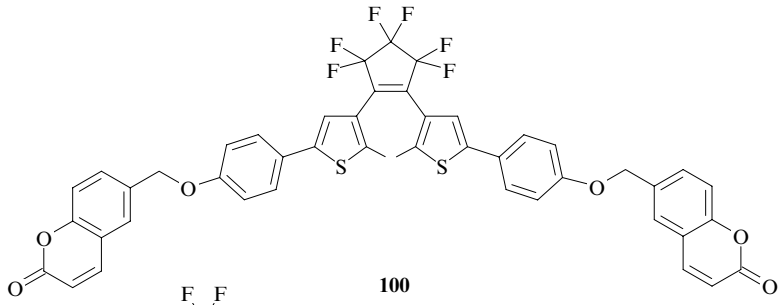
Novel fluorescent photochromes **99a** – **b** containing phthalimide fragment as a fluorophore were synthesized by Yan *et al.*[172]



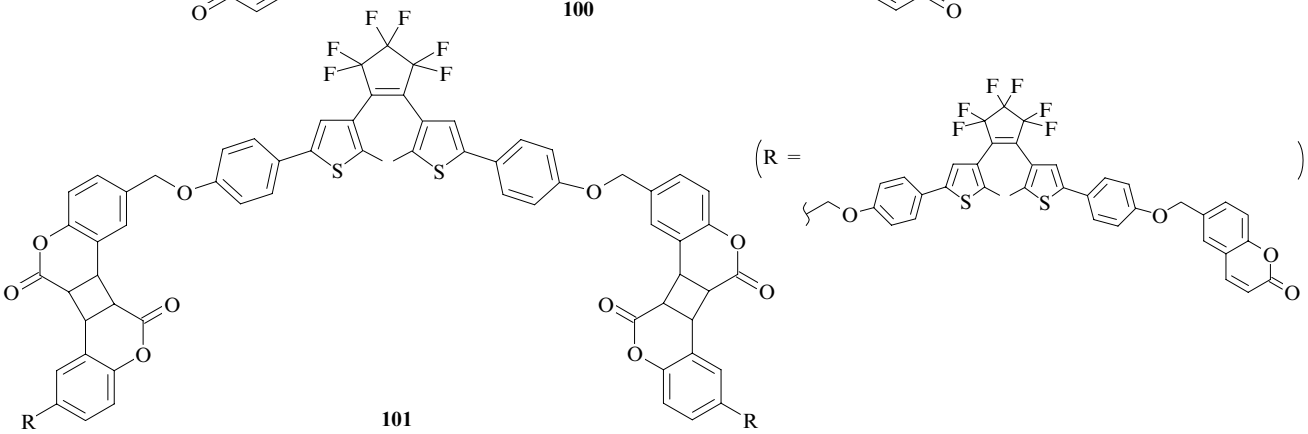
99a,**b**

R = H (**a**), Boc (**b**) (Boc is *tert*-butyloxycarbonyl)

The spectral properties of these compounds were studied in different solvents. It was found that at a maximum of the emission band, a positive solvatochromic effect is observed, and the fluorescence quantum yield decreases as the solvent polarity increases.



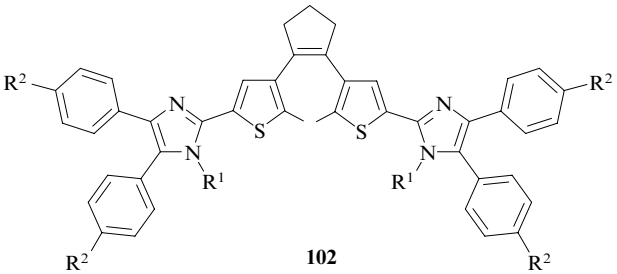
100



101

Interesting results were obtained for diarylethene **100** incorporating a coumarin moiety and dithienylperfluorocyclopentene system, which are connected *via* the ether bond.[173] It was found that the photochromic transformations under the action of light are accompnaied by the dimerization at the double bonds of the coumarin moieties in the presence of the Lewis acid, resulting in the formation of trimeric adduct **101**. The fluorescence properties of the system change both upon photocyclization and upon chemical dimerization.

The introduction of a fluorophore as the aryl substituent or through a rigid spacer is a rather labourious approach and implies more complicated synthetic protocols than the application of a flexible spacer. The spectral, in particular, fluorescence properties of di(thienyl)cyclopentenes **102** with diarylimidazole moieties were studied.[174]

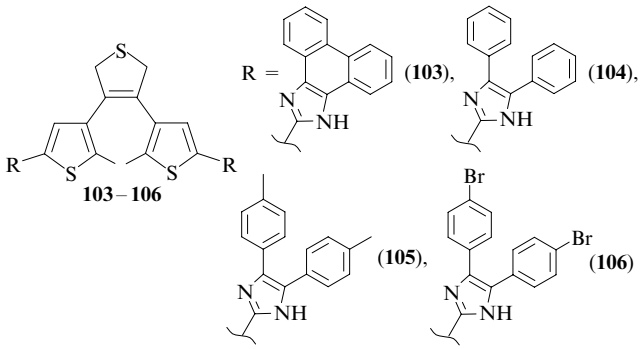


102

R^1 = H, Me; R^2 = H, Me, OMe, NMe_2

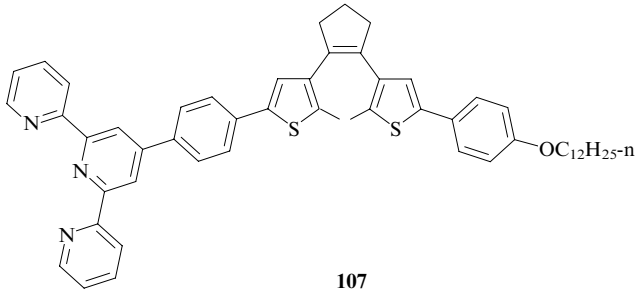
It was found that the fluorescence properties of these compounds strongly depend on the substituents both in the benzene ring and at the nitrogen atom. The strengthening of the donor properties of substituents in the benzene ring results in an increase in the intensity and quantum yield of fluorescence, whereas the methylation at the nitrogen atom leads to deterioration of the fluorescent characteristics.

Similar results were obtained for 3,4-dithienyl-2,5-dihydrothiophenes **103** – **106** containing imidazole fragments.[175] Upon investigation of their photochromic and fluorescence properties, it was found that the spectral characteristics are strongly affected by the nature of substituents in the benzene ring. The authors state that fluorescence is characteristic of both compound forms (open and photoinduced), and the fluorescence intensity of the open form is 3 times higher than that for the closed form.

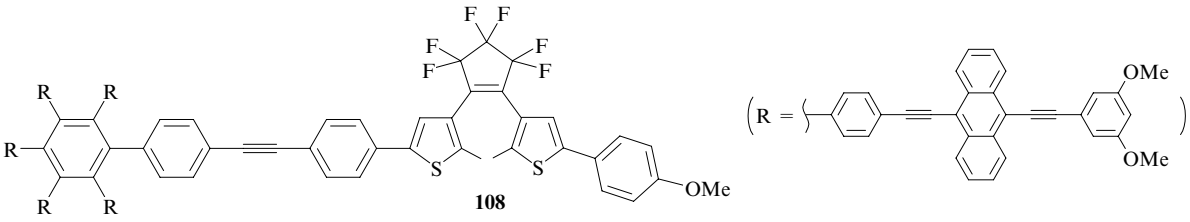


103 – **106**

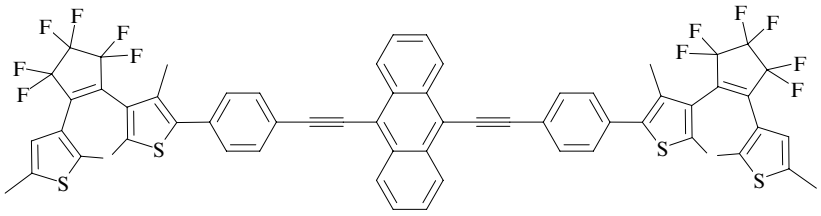
The above terpyridine fragment can also be linked with the photochromic molecule through a conjugated spacer.[176] Fluorescence of compound **107** (λ_{max} = 330 – 365 nm, φ_{fl} = 0.041) is quenched by 95% in the course of photocyclization. However, of particular interest are the spectral properties of this dihetarylethene and their switching upon complexation with zinc, which are discussed in more detail below (see Section III.2.d).



107



108



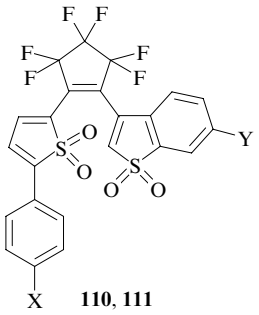
109

Keirstead *et al.*[177] synthesized compound **108**, which combines a photochromic diarylethene fragment with five bis(phenyl)ethynylanthracene fluorophores. A number of spectral properties including fluorescent characteristics of photochrome **108** were studied. It was shown that the fluorescence intensity can be controlled by irradiation wavelength: the irradiation at $\lambda = 610$ nm leads to a strong increase in the fluorescence intensity, and UV irradiation ($\lambda = 350$ nm) effectively quenches the emission.

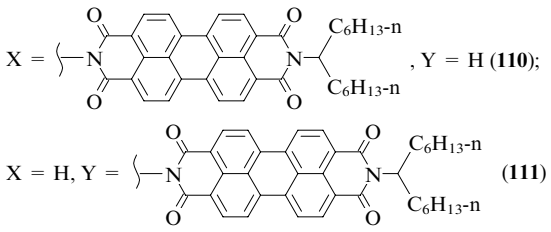
Compound **109** with two diarylethene moieties includes di(thienyl)anthracene as a spacer. Perfluorocyclopentene **109** features high value of fluorescence quantum yiled ($\varphi_{fl} = 0.83$).[178]

A wide range of perylene-containing diarylethenes with rigid spacers were described.[179–181] The irradiation of the open forms of compounds **110**–**112** with UV light gives rise to an absorption band at 350 nm, and this process is reversible.

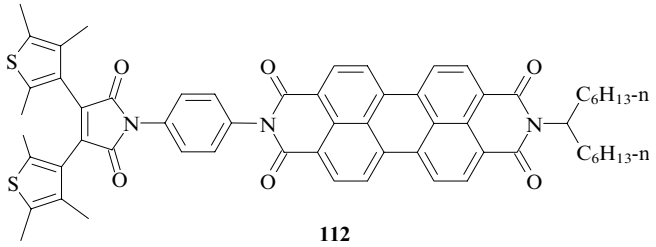
It was shown that in the coloured forms of these compounds, there is no energy transfer from the perylene fragment to the diarylethene, and fluorescence can be controlled by the solvent polarity. Thus, the dielectric constant of a solvent strongly affects the fluorescence properties of only closed form of compound **111**. The intense emission ($\varphi_{fl} = 0.8–0.9$) which is characteristic of the initial isomers upon irradiation in a dioxane solution, almost does not change and is efficiently quenched upon addition of more polar methanol to the solution.



110, **111**

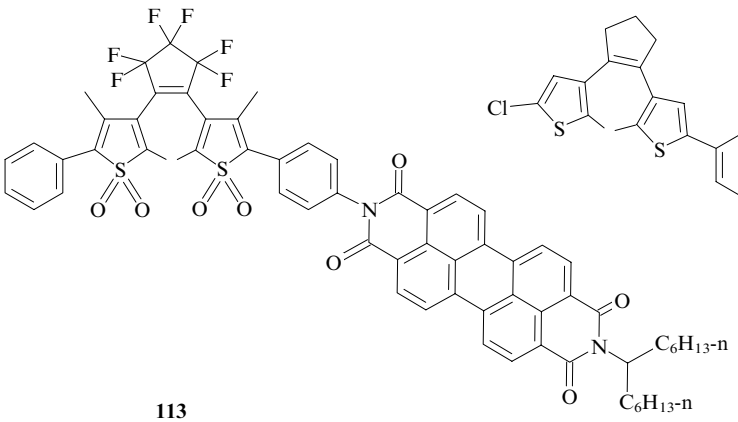


(**111**)

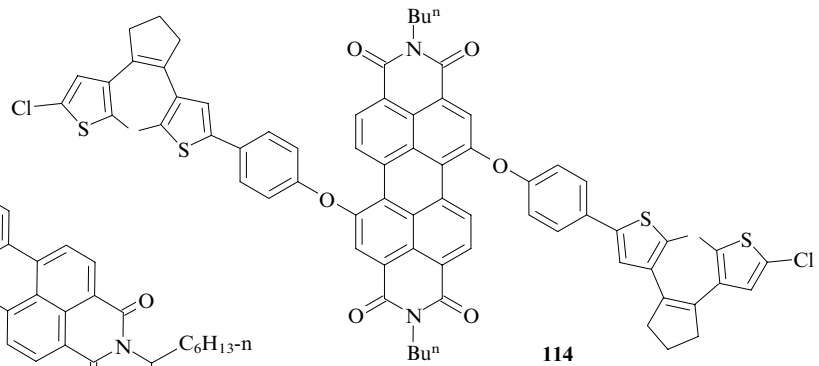


112

The spectral properties of photochromic compound **113** strongly depend on the solvent polarity. Thus, the fluorescence spectrum of its toluene solution does not change on exposue to UV light, whereas in acetonitrile, fluorescence is quenched by 50% despite the fact that in both of the solvents the photoswitching is observed.[182] Diarylethene

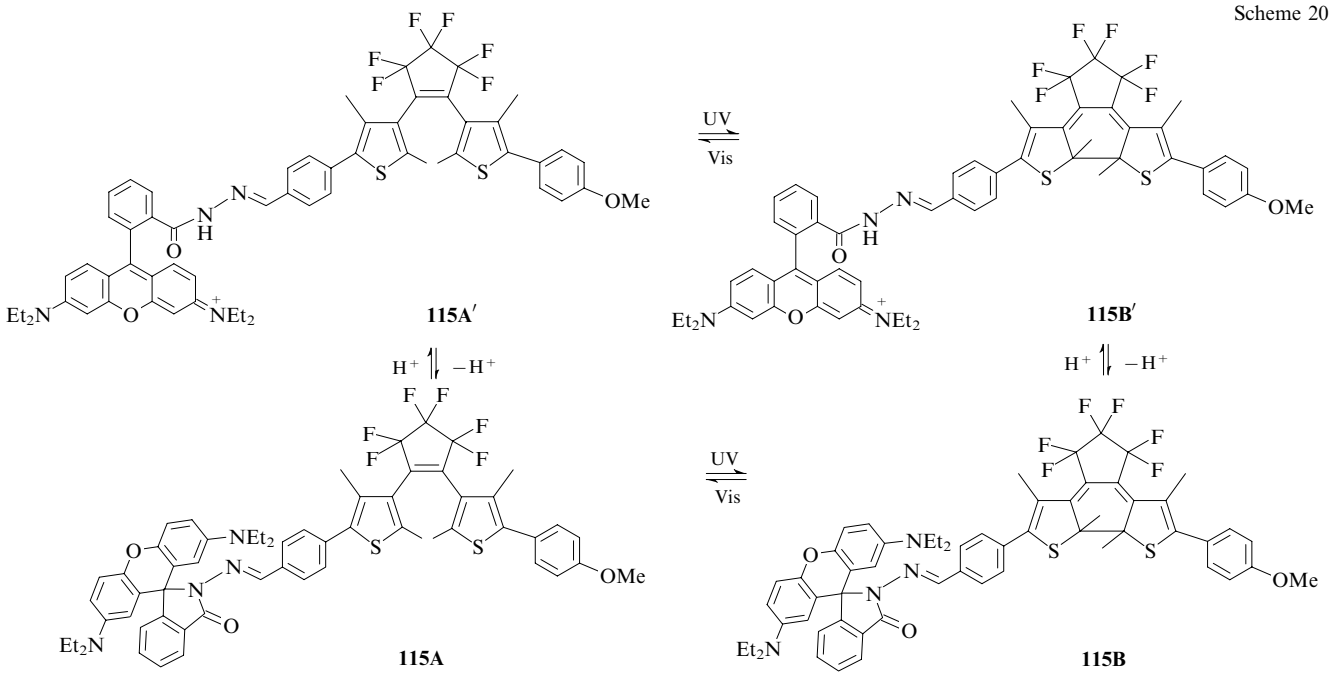


113



114

Scheme 20



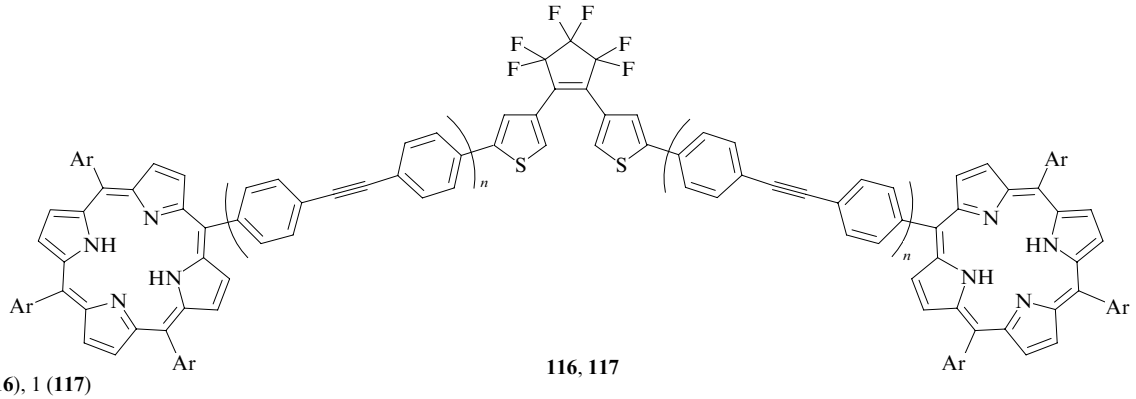
114 in which two photochromic fragments are connected to the perylene core through ether spacers appeared to be more sensitive to the action of UV light.[183] The changes in the absorption and emission spectra (increase in intensity) of this compound under irradiation at 254 nm were demonstrated.[183]

Recently described rhodamine derivative **115** can serve as a basis for photo- and pH-sensitive switches (Scheme 20).[184] The initial colourless form **115A** is not prone to emission in DMSO, while upon addition of trifluoroacetic acid to its solution, fluorescence is observed (λ_{max} = 586 nm, φ_{fl} = 0.103). This is caused by the protonation of diethylamino group of rhodamine and opening of the rhodamine ring, leading to form **115A′**. This phenomenon is reversible: upon addition of triethylamine, the spiro form of rhodamine **115A** is formed again, and fluorescence is quenched. The quenching of emission of the protonated form is also observed upon irradaition of a sample of **115** with UV light due to the energy transfer from the open rhodamine moiety to the closed form of diarylethene **115B′**. This compound possesses high fatigue resistance, which makes it especially promising for the design of molecular switches.

Porphyrin-containing diarylethenes deserve particular attention. As it was found, in this case, not only the structures of fluorophore and photochrome but also the spacer length are significant. Thus, in compound **116**, a rapid energy transfer from the photochromic fragment to the fluorophore is observed, which leads to the disappearance of photochromism. At the same time, compound **117** in which these fragments are far from each other is also photochromic.[185] The photochromic properties of this type of compounds also strongly depend on the character of substituents in the porphyrin system: on going from 3,5-di-*tert*-butylphenyl substituents to 3,5-di-n-octyloxyphenyl, the degree of the photochromic transition drops from 75% to 20%.

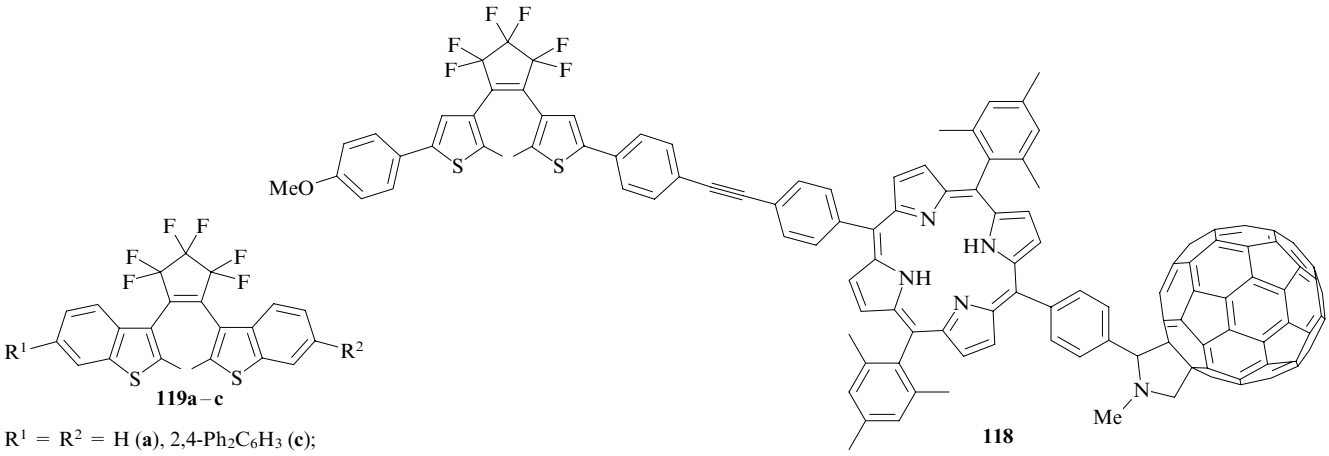
Compound **118**, which contains a fullerene core bound to the porphyrin moiety, was synthesized. However, this compound is not fluorescent in either the open or closed form, which can be explained by the rapid energy transfer from the porphyrin moiety to the fullerene part.[186]

A valuable feature of porphyrin-containing diarylethenes is their ability to form complexes with metal ions. It should be noted that the complexing moieties are often attached to the diarylethene molecules through various



116, **117**

n = 0 (**116**), 1 (**117**)



119a – c

$R^1 = R^2 = H$ (**a**), 2,4-$Ph_2C_6H_3$ (**c**);
R^1 = 2,4-$Ph_2C_6H_3$, $R^2 = H$ (**b**)

118

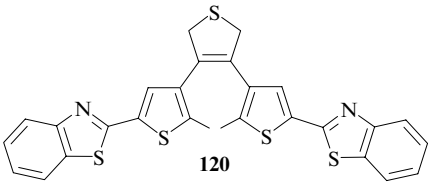
linkers. The properties of these complexes will be considered in detail below.

An important condition for the practical application of diarylethenes is the presence of photochromic properties in the solid phase — in crystals, in the amorphous phase or in polymeric matrices. In order to produce amorphous diarylethenes, a terphenyl substituent was introduced into the benzene ring of di(benzothienyl)ethene **119a**.[187] It was found that both mono- (**119b**) and disubstituted (**119c**) analogues convert to the amorphous state even at room temperature. Moreover, the introduction of the terphenyl moiety gives rise to fluorescence properties; compound **119c** is light-emitting in both forms: the emission maximum of the open form is observed at about 450 nm and that of the closed form is at 650 nm.

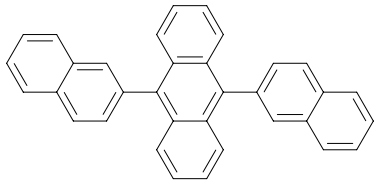
c. Diarylethene – fluorophore mechanical mixtures

Another approach which can be highly useful in a number of cases is the application of fluorophores as dopants to di(het)arylethene compounds.

The fluorescent and photochromic properties of a mixture of diarylethene **120** with fluorescent dye **121** were studied in solution and in polymeric matrix.[188]



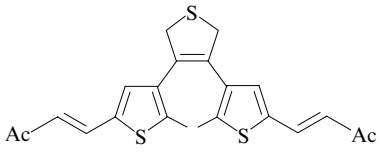
120



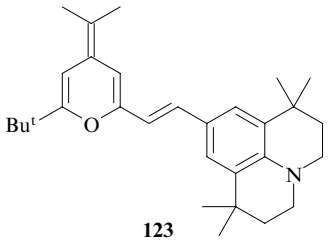
121

It was found that the irradiation of such a mixture with UV light leads to the photocyclization of the photochromic diarylethene. At the same time, a reduction in the emission intensity is observed, since the photoinduced form of photochrome **120**, unlike the initial one, has an absorption band in the same region in which the excitation of fluorescence of fluorophore **121** occurs. There is no energy transfer between the molecules of the photochrome and fluorophore, and the photochromic additive plays a role of the internal light filter with the controlled degree of light filtration. The optimal ratio of compounds **120** and **121** in a mixture provides for 10-fold fluorescence quenching. It was established that this system bears over 20 cycles of the photocyclization and recyclization reactions of photochromic diarylethene **120** in solution and 10 cycles in polymeric film; the fluorescence intensity of fluorophore **121** does not undergo any significant changes.

A simple and controlled fluorescent switch was obtained upon application of a mixture of photochrome **122** and fluorophore **123**.[63]



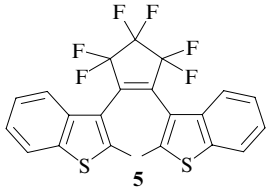
122



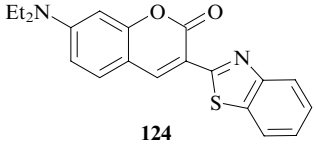
123

Dye **123** emits at 610 nm (excitaion at λ = 550 nm), and the photoinduced form of diarylethene **122** absorbs without isomerization at 615 nm. These mixtures are promising for the creation of polyfunctional optical memory systems and molecular switches.

One more example of switches featuring fluorescence properties is a mixture of coumarin-6 (compound **124**) with perfluorocyclopentene **5** in 1 : 500 ratio.[189]



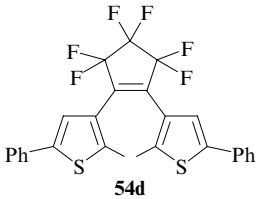
5



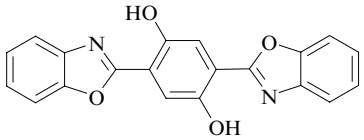
124

The investigation of the spectral properties of this mixture was carried out both in an acetonitrile solution and in PMMA films. The efficient and reversible quenching of fluorescence of coumarin-6 was detected (the quantum yield of the emission reduced from 0.74 to 0.05), which was caused by the intermolecular energy transfer to the coloured form of diarylethene **5**.

The system consisting of diarylethene **54d** and compound **125**, which is prone to intramolecular proton transfer in the excited state, was also studied.[190, 191]



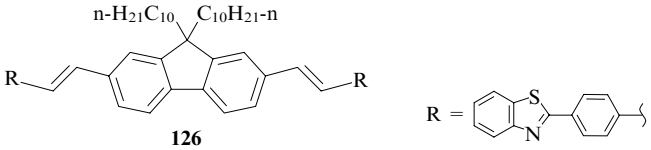
54d



125

This feature is responsible for the impressive difference (almost 300-fold) in the intensity of fluorescence between the states when a mixture contains the open and closed forms of diarylethene **54d** (emission of the open form is observed at λ_{max} = 590 nm).

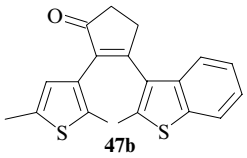
A mixture of photochrome **5** and fluorophore **126** was used to demonstrate a possibility of the creation of a three-dimensional multilayer optical memory based on a two-photon scheme.[192]



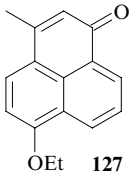
126

This system possesses very high fatigue resistance and allows for the application of one and the same laser both for information recording and reading.

The switches based on mixtures of diarylcyclopentenone **47b** with 3-methyl-6-ethoxy-1*H*-phenalen-1-one were obtained (**127**).[170]



47b



127

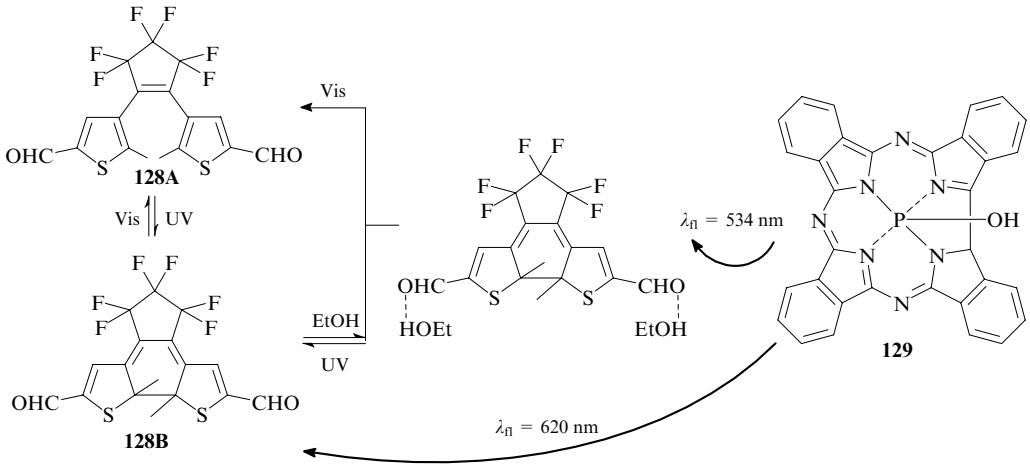
The spectral properties of this system were studied at different ratios of fluorophore **127** and photochrome **47b**. It was found that rather efficient quenching of emission of these switches under the action of UV light requires at least a 100-fold excess of fluorophore **127**.

A complex light- and solvatosensitive switch was suggested by Chinese scientists based on dihetarylethene **128**.[193] The fluorescence properties of this system are provided by the phosphorus derivative of tetrabenzotriazacorrole **129** (λ_{max} = 659 nm); the photochromism is due to dialdehyde-containing perfluorocyclopentene **128**, which does not possess fluorescence (Scheme 21, the emission is shown with the bold arrows).

Closed form **128B** absorbs in tetrahydrofuran with a maximum at 620 nm (the band largely overlaps with the emission band of fluorophore **129**), and upon addition of 20 equivalents of ethanol to this solution, the absorption band shifts to 534 nm (the band largely overlaps with the emission band of fluorophore **129**). Therefore, upon irradiation of a mixture of these compounds in THF, the fluorescence quenching is observed and reaches up to 20% of the initial value, and upon addition of ethanol to the irradiated mixture, the fluorescence intensity increases up to 50% of the initial value. Hence, the switch has two inputs, namely, UV radiation and ethanol, and one output, intensity of fluorophore **129** emission (Fig. 5). This is the so-called logical inhibitory gate combining the logical functions AND and NO; the output is inhibited by one of the inputs.

Another group of Chinese researchers[116] suggested a mixture of compounds **130** and **131** in which the self-assembling of fluorescent complex **132** through the formation of hydrogen bonds is realized (Scheme 22). Diarylethene **130** and benzoic acid **131** separately possess

Scheme 21



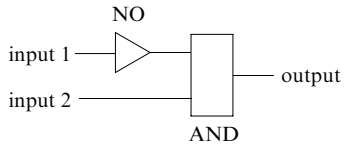
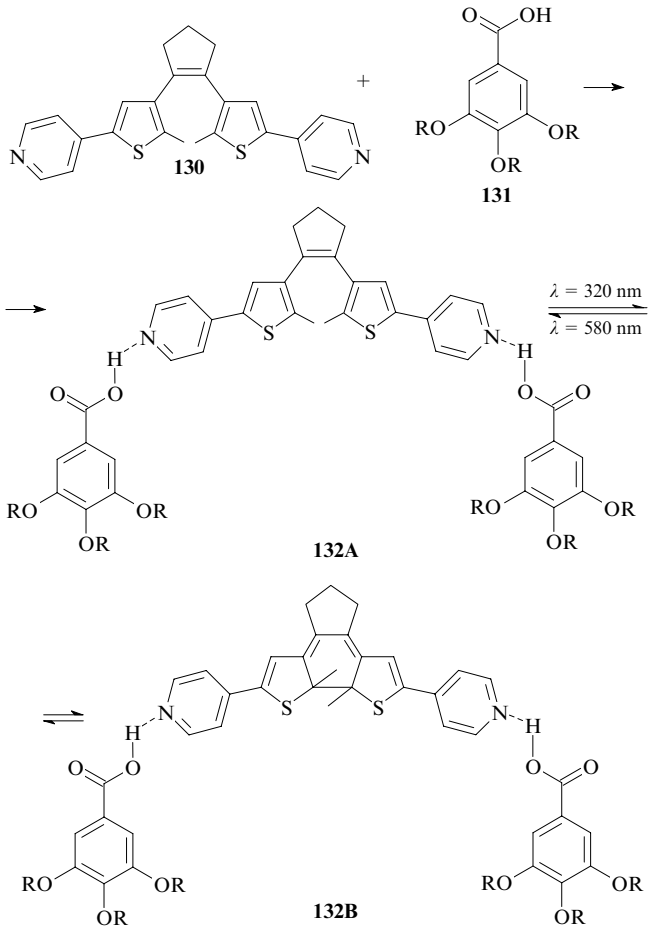


Figure 5. Diagram of photo- and solvato-switching of fluorescence (see text).

Scheme 22



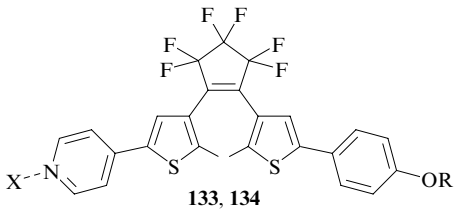
insignificant fluorescence in a tetrahydrofuran solution ($\varphi_{fl} \leqslant 0.02$), but the fluorescence of spontaneously formed complex **132** is 5 times higher.

The authors explain such an increase in the emission by the presence of hydrogen bonds which hamper the energy transfer. Furthermore, the paper discusses the effect of the solution concentration on the fluorescence properties: its increase leads to a red shift of the emission band maximum and a slight increase in its intensity.

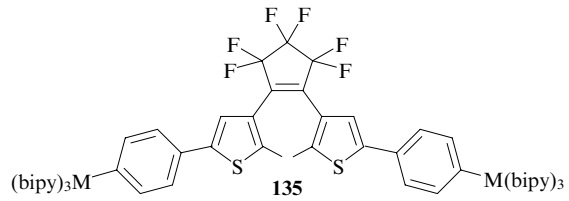
d. Fluorescent metal complexes of diarylethenes

Another route to considerable effect on the properties of diarylethenes in order to create photocontrolled fluorophores is the preparation of fluorescent metal complexes. These complexes can include one or several diarylethene fragments, and the complexing groups can be both in the aryl moiety and in the bridge. Moreover, metal complexes can be attached to diarylethenes using different spacers. The advances in this field of chemistry are described in detail in the recent reveiws.[194–196]

Over the last decade, the pyridine-containing ligands as parts of dithienylethenes, *e.g.*, compounds **133**, **134** have received wide application. Upon comparison of their properties, it was found that in tungsten complex **133**, fluorescence is strengthened during the photocyclization, whereas in the case of 2,2′-bipyridine (bipy) rhenium complex **134**, a reverse pattern is observed.[197] Binuclear complexes **135** were also obtained that demonstrate that the acceptor effect of a metal leads to a bathochromic shift of the absorption band of the closed forms of these compounds.



X = $W(CO)_5$, R = H (**133**);
X = [Re(bipy)$(CO)_3$]OTf, R = Me (**134**)



M = Ru, Os

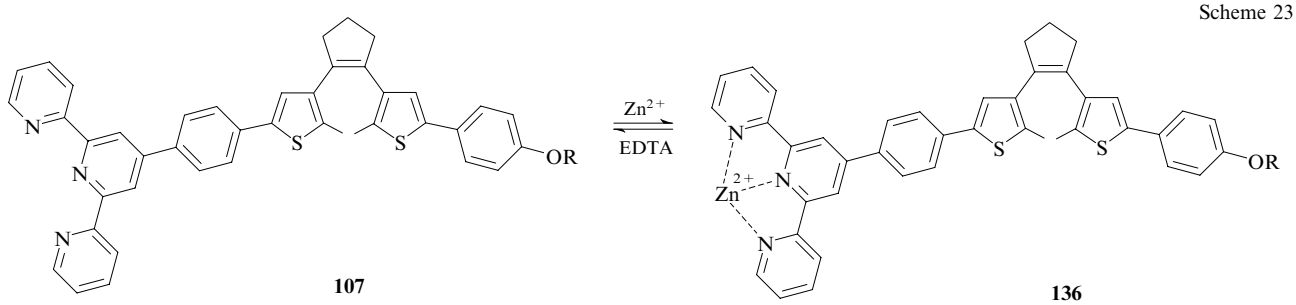
The above-mentioned compound **107** containing dithienylcyclopentene and terpyridine fragments can be coordinated to transition metal ions, forming stable complexes **136** (Scheme 23).[176] These complexes with zinc serve as a glowing example of controlled switches. An intensity of fluorescence of compound **107** can be reversibly controlled using zinc ions and ethylenediaminetetraacetic acid (EDTA): the former switch off the fluorescence, the latter, in contrast, switch on the emission.

A series of dithienylethenes bearing 1,10-phenanthroline group was described. The latter can be a part of the aryl moiety (compounds **137**, **138**) or a part of the ethene bridge (compounds **139**, **140**). The third modification is also possible when the ligand itself serves as the ethene bridge (compounds **141**, **142**).

Owing to the basicity of the nitrogen atoms, imidazophenanthroline derivatives **137** and **138** exhibit, along with the photochromism, acidochromic properties and can be used as versatile switches.[195] The detailed investigation of the excited states of photochromic compounds **139**, **140** was performed,[26] and it was shown that the molecules participate in the photochromic reaction in the triplet state. In compound **141**, no quenching of fluorescence is observed, but a red shift of the emission band during the photocyclization occurs (by $\sim$100 nm). Despite a similarity of structures of **141** and **142**, their spectral properties markedly differ. Unlike 2,5-dimethylthiophene derivative, diarylethene ligand of complex **142** does not possess the photochromic properties either in the free state or in the complex.

Fluorescent diarylethene **79** (see the above formula) bearing two different heterocyclic systems, imidazole and

Scheme 23



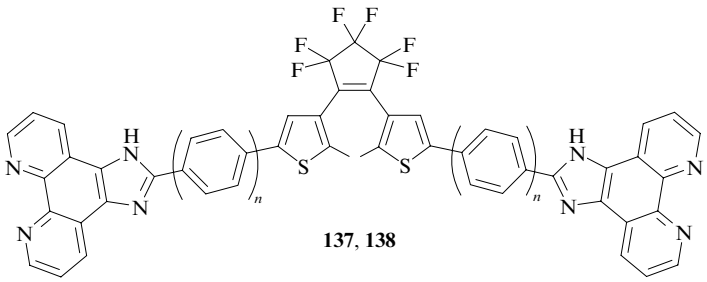
107 **136**

R = n-$C_{12}H_{25}$

pyrrole, in the ethene bridge is sensitive to copper, iron, and mercury ions.[160, 161] Thus, the addition of Fe^{3+} and Hg^{2+} ions results in a 2-fold reduction in the fluorescence intensity, and Cu^{2+} ions ensure complete quenching. Moreover, Hg^{2+} ions cause a hypsochromic shift of the emission band by ~100 nm: from 550 nm in the absence of mercury ions to 470 nm in their presence in a solution.

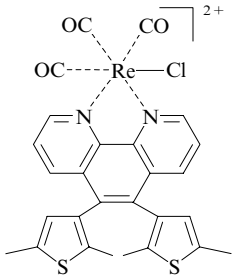
At present, there is a multitude of diarylethenes with ruthenium, osmium, and magnesium porphyrin complexes.[105] In particular, ruthenium complex **143** was described the open form of which has phosphorescence (emission maximum at 730 nm).[198, 199] The photocyclization of this complex can be carried out by 95%; moreover, the emission of the initial diarylethene reversibly reduces.

Of particular practical use is compound **144** with 1-aza-15-crown-5 ether ligands obtained by Korean researchers.[200] Fluorescence of this compound in the mercury complex is 4.5 times more intense than in the cadmium complex and 5.5 times more intense than in the case of zinc complex. Hence, diarylethene **144** can be used as a chemosensor for mercury ions to control the environment pollution with mercury.

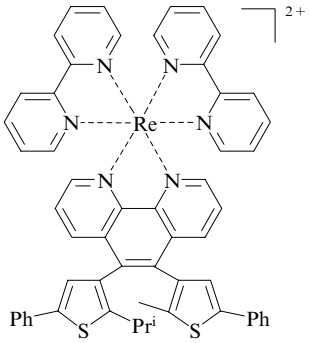


137, **138**

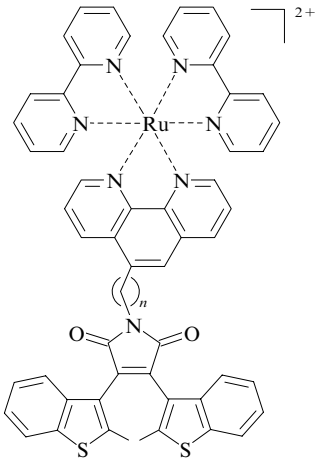
n = 0 (**137**), 1 (**138**)



141

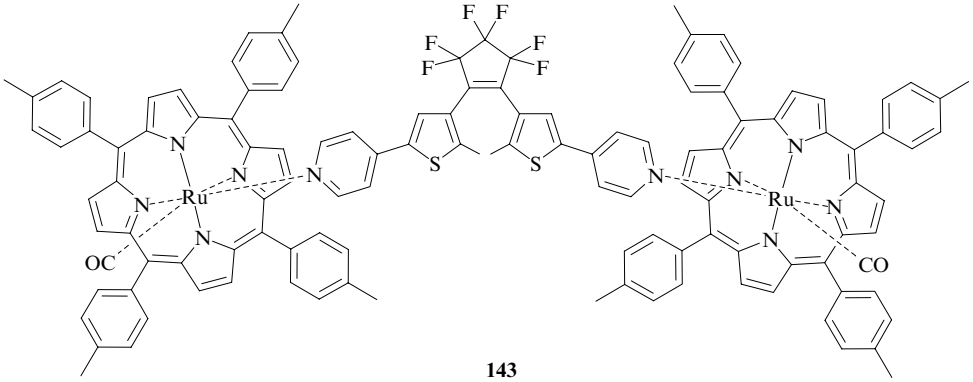


142

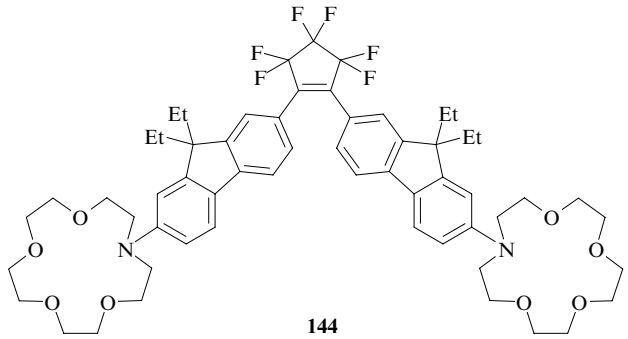


139, **140**

n = 0 (**139**), 1 (**140**)



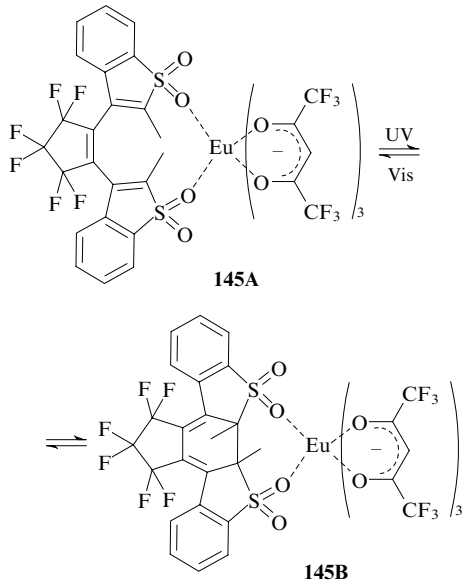
143



144

Complexes **145** obtained upon coordination of sulfone derivatives of diarylethenes **6** with europium were studied (Scheme 24).[143, 201, 202] It was shown that the fluorescence intensity decreases upon irradiation of the complex with UV light. However, the spectra of both initial form **145A** and photoinduced form **145B** do not show overlap of the absorption and emission bands, which excludes the quenching of fluorescence due to its absorption by the compound itself. The reduction in emission is likely to be caused by the structural changes occurring in the ligand during the photocyclization.

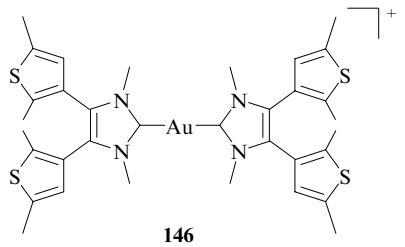
Scheme 24



145A

145B

Complexes that contain two and more diarylethene fragments were reported. In compound **146**, as well as in many related complexes with several photochromic groups, the cyclization of only one diarylethene fragment is observed.[78] At the same time, only one closed form is light-emitting.



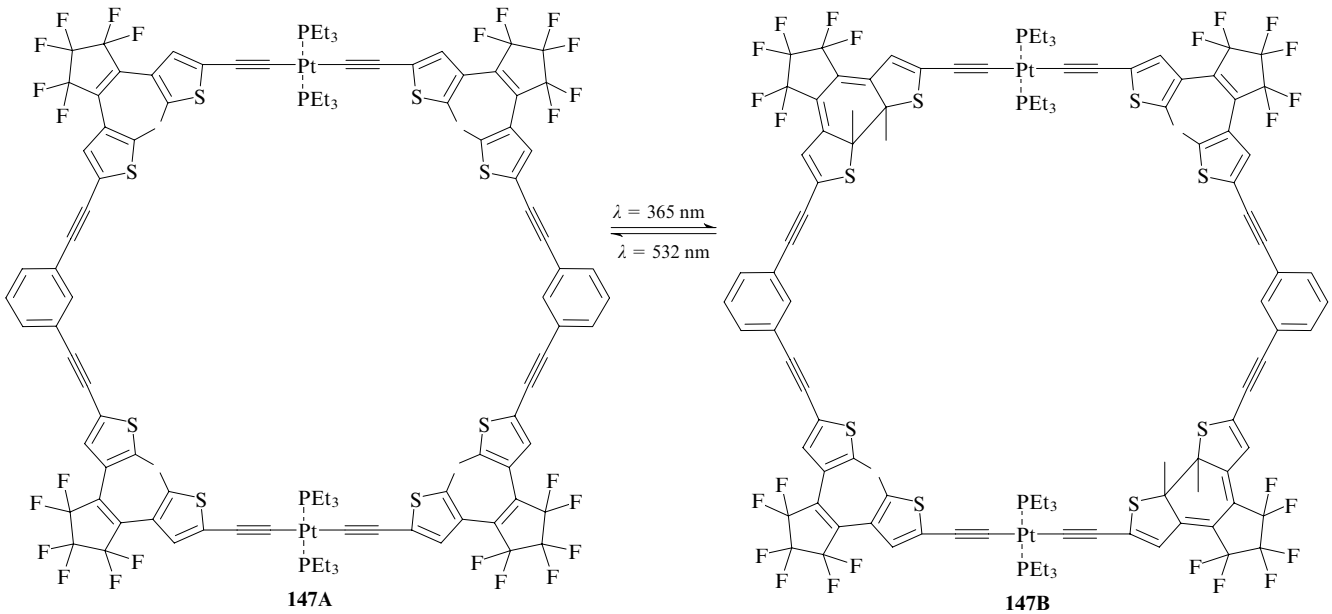
146

In macrocyclic compound **147** having four perfluorocyclopentene fragments, the simultaneous cyclization of two of them occurs as shown in Scheme 25. This complex features also high yield of the photocyclization reaction ($\varphi = 0.64$), which is caused by the rigid fixation of the antiparallel conformation of diarylethenes.[203]

* * *

Thus, the present review summarizes the data on the synthesis and spectral kinetic characteristics of fluorescent diarylethenes obtained over the last decade. A goal of most investigations is the creation of multifunctional materials for various applications. In the above text, the fluorescent diarylethenes are classified according to the principles of endowing the photochromic molecule with fluorescence properties, their spectral properties are analyzed, and the data on correlations between the compound fluorescent characteristics and structure are generalized.

Scheme 25



147A **147B**

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