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# Luminescent materials for modern light sources

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The studies dealing with luminescent materials for semiconductor lighting are surveyed. The luminescent materials are classified in terms of the class of chemical compounds they belong to and in terms of the way they are used in luminescent converters of light from the primary light source. The use of inorganic phosphors, organic luminescent materials and materials based on complex compounds, quantum dots and metal-organic frameworks are considered. Sequential and parallel luminescent converters are defined. The key problems are identified and the possible ways of addressing them are outlined. Particular attention is paid to the problem of photodegradation of luminescent converters.
The bibliography includes 101 references.

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## I. Introduction

Luminescent materials are widely used in electronics and optoelectronics. From the beginning of manufacturing of high-performance light-emitting diodes (LEDs) for blue spectral region,† the idea appeared to modify them to design LEDs with another emission color and white light-emitting LEDs suitable for lighting. A possible way to solve these

† In 2014, I.Akasaki, H.Amano and S.Nakamura were awarded the Nobel Prize in Physics for the discovery of blue LEDs.

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problems is to use luminophores that absorb blue light quanta and convert them to quanta with lower energy.

A similar way has been made in the development of luminescent lamps using mercury vapour in which the supplied electric power is first converted to UV radiation with 66% efficiency. This is followed by conversion of the emission at 254 and 185 nm to visible light by means of luminophores. The conversion stage is accompanied by considerable energy loss. This is mainly caused by the Stokes shift. If the excitation frequency is $\nu_{ex}$ and the emission frequency is $\nu_{em}$, then $\nu_{em} < \nu_{ex}$, and the difference $(h\nu_{ex} - h\nu_{em})$ is converted to heat. The excitation frequencies at wavelengths of 254 and 185 nm differ several-fold from the visible light frequency. As a result, only 21% of the supplied electric power is emitted as light (see p. 96 in the book [1]).

The luminescence conversion of the light from blue light-emitting diodes (BLEDs) at 450–460 nm is not accompanied by this sharp decrease in the energy efficiency caused by the Stokes shift, because both the excitation and emission frequencies belong to the visible range and differ by a factor of less than 1.5. The generation of white light based on blue light-emitting diodes is also facilitated by the human color perception: the light from a light source is perceived as white not only upon mixing of three colors, but also upon mixing of two complementary colors in a definite proportion, for example, mixing of the LED blue light with the yellow light from a luminescent converter (LUCO).

The features of human vision, first of all, the non-equivalence of different wavelengths in the formation of light perception are taken into account in lighting engineering,[2,3] where the luminous flux is expressed in lumens (lm), the density of luminous flux (luminous intensity) is measured in candelas ($cd = lm\ sr^{-1}$) and illuminance is expressed in luxes (lx). The luminous efficiency of light sources is characterized by the light output ratio (LOR), *i.e.*, the ratio of the luminous flux to the consumed electric power ($lm\ W^{-1}$). The color coordinates (CCs) and the correlated color temperature ($T_c$) are used as the spectral characteristics of the light source in lighting engineering. They are calculated on the basis of the color space model adopted by the International Commission on Illumination (CIE) in 1931. The CC and $T_c$ values are convenient for transmitting information about characteristics of light emitted by a particular source. To make use of this information, it is sufficient to employ the CIE (color triangle). The color rendering index (CRI) is used to evaluate how well one can perceive the multicolor image upon illumination by a light source.

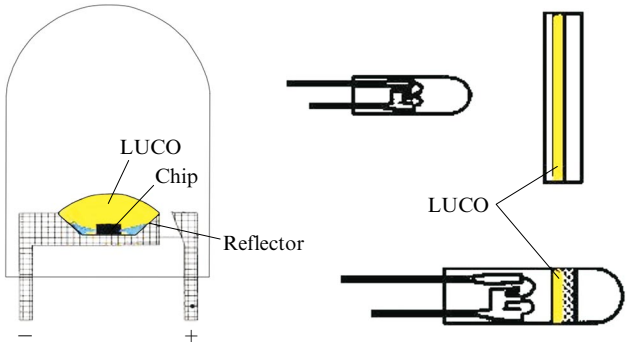
In the general case, a LUCO is an optical device that is placed in the path of light from a primary source of electromagnetic radiation, absorbs this light and emits light *via* luminescence. Since both light absorption and emission are quantum phenomena, the quantum efficiency ($\eta_{con}$) is a key value characterizing the efficiency of conversion.

$$\eta_{con} = f_{abs}\Phi_{lum} + (1 - f_{abs}) = 1 - f_{abs}(1 - \Phi_{lum}) \qquad (1)$$

where $f_{abs}$ is the ratio of the number of quanta absorbed by the converter to the number of quanta emitted by the primary source; $\Phi_{lum}$ is the quantum yield of luminescence, *i.e.*, the ratio of the number of quanta emitted by the converter to the number of absorbed quanta. If the light from the primary source is not involved in the optical flux at the LUCO exit, then $f_{abs} = 1$ and $\eta_{con} = \Phi_{lum}$. If $\Phi_{lum}$ tends to 1, then $\eta_{con}$ also tends to 1. In many cases that are considered below, $0 < f_{abs} < 1$, *i.e.*, the light from the primary source is involved in the optical flux at the LUCO exit. Relation (1) gives the upper limit of the converter quantum efficiency, because it takes into account only the absorption and luminescence of the converter, but neglects the light reflection and refraction at the boundaries of optical media and the change in the light propagation direction after the conversion, which depends on the converter design rather than on the converter material. The LUCO can be arranged in different ways relative to the primary source. In the case where the primary light source is LED, there are two possible configurations of the device (Fig. 1): the converter either adjoins the LED chip (crystal) (configuration 1) or is remote from the LED chip (configuration 2).

The first advances on the way towards the design of luminescence conversion LEDs were reported in 1997. Schlotter, Schmidt and Schneider[4] (Fraunhofer-Institut für Angewandte Festkörperphysik, Germany) embedded luminescent dyes (green, yellow or red perylene dye) or yellow inorganic phosphor, $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce), into the epoxy resin adjoining a blue light-emitting diode crystal. This gave white light-emitting diodes upon three-color process in the former case and upon mixing of two complementary colors in the latter case. In the same year of 1997, a similar result was obtained by Heeger‡ and co-workers[5] (University of California). They used a LUCO based on a luminescent polymer that emitted yellow luminescence upon excitation with blue light from InGaN LED. Finally, also in 1997 a book was published[6] giving an account of works on the design of BLEDs and later engineering works that were performed for many years by Nakamura and co-workers in the Nichia company, including the design of white light-emitting diodes. The LUCOs for these light-emitting diodes were based on the phosphor $(Y_{1-a}Gd_a)_3(Al_{1-b}Ga_b)_5O_{12}:Ce$ ($a$, $b$ = 0–0.5), and it was shown how white light of various

‡ Nobel Prize winner of 2000 in chemistry, together with A.G.MacDiarmid and H.Shirakawa for the discovery and development of conductive polymers.




Configuration 1
LUCO adjoins the LED chip

Configuration 2
LUCO is remote from the LED chip

**Figure 1.** Positions of the luminescent converter relative to the light-emitting diode chip.[4,5]

hues can be generated by mixing blue light with the light emitted by the luminophore with variable phosphor composition.

The authors cited above[4–6] correctly evaluated the prospects of luminescence conversion LEDs as light sources for illumination. An important reason for subsequent development of lighting engineering towards the use of phosphors was apparently the fact that inorganic phosphors have already long been used in vacuum color displays and manufacturing processes have been developed for them, whereas Heeger and co-workers[5] proposed a luminescent material unfamiliar to manufacturers.

The emission spectra of the first white LEDs[4–6] are shown in Fig. 2. The color coordinates of the white light obtained in the cited work[4] (spectra *1* and *2*) are unknown; the CCs of the light obtained in the other work[5] (spectra *3*–*5*) are as follows: (0.34, 0.29), (0.41, 0.32) and (0.55, 0.38). The Nakamura's light-emitting diode had CCs of (0.29, 0.30) and luminous efficiency of 5 lm $W^{-1}$ (Ref. 6). The trends of the design of LUCO LEDs outlined in the cited publications[4–6] have persisted until now and are being vigorously pursued.

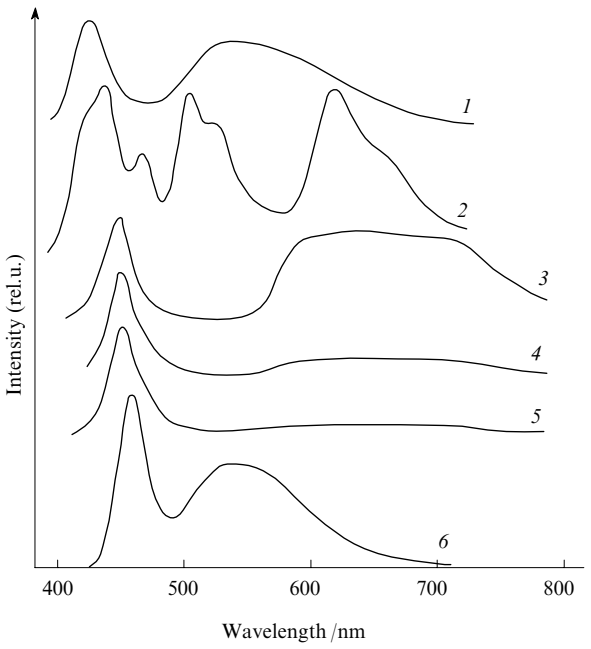



**Figure 2.** Spectra of the first white light-emitting diodes based on BLED and luminescent converter: spectra *1*, *2* are from Ref. 4; spectra *3*–*5* are from Ref. 5; spectrum *6* is from Ref. 6.
The primary source is LED with $\lambda_{max}$ = 430 (*1*–*2*), 450 (*3*–*5*) and 460 nm (*6*). The spectra are separated along the ordinate axis.

## II. Inorganic phosphors

The use of cerium-doped yttrium aluminium garnet for luminescence conversion for the generation of while light was a lucky idea proposed in several studies.[4,6,7] The issues of phosphor crystal growth and the forms in which it is used in white LEDs (moulding material, powder nanocomposite, single crystal) remain the subjects of numerous studies.[8–18] A detailed review (> 220 references) surveys studies published up to 2014 dealing with the use of phosphors in luminescence conversion.[19] It is not an exaggeration to say that the whole range of available white light-emitting diode lamps is the practical outcome of the research in this area.

Cerium-doped yttrium aluminium garnet has become the basic material for the luminescence conversion of LED blue light. This material absorbs in the blue spectral region and tolerates elevated temperature and dense light fluxes.[8] The best samples provide luminescence quantum yield > 0.81,[15] while the quantum yields for commercial samples (in 2006) vary from 0.61 to 0.70.[16] A drawback of the cerium-doped yttrium aluminium garnet is the overlap of the emission and absorption spectra in the 475 – 520 nm range.

Several studies address the materials in which yttrium and cerium atoms are replaced by other lanthanide ions. The $Tb_3Al_5O_{12}:Ce^{3+}$ system provides a light output ratio of 34 lm $W^{-1}$ and the emitted light has CRI = 79; a mixture of $Y_3Al_5O_{12}:Ce^{3+}$ with $Sr_3SiO_5:Eu^{2+}$ provides a lumunous efficiency of 40.9 lm $W^{-1}$ and the emitted light has CRI = 76, $T_c$ = 5716 K.[20] The phosphors $Y_3Al_5O_{12}:Ce^{3+}/Lu_2O_3$, $Sr_6(Y_{1-x}Ce_x)_2Al_4O_{15}$ ($0.005 \leqslant x \leqslant 0.20$) emitting orange-red luminescence (the emission peak is at about 600 nm) upon excitation with blue light have been reported.[21,22] The phosphors $Sr_9Sc(PO_4)_7:Eu^{2+},Mn^{2+}$ exhibit broad emission spectra with a flat top extended from 510 to 625 nm and are suitable for conversion of light from short-wavelength (< 450 nm) LEDs.[23]

Among the sorts of the phosphor YAG:Ce, noteworthy is Gd-YAG:Ce in which some of the yttrium ions have been replaced by gadolinium ions.[24–26] Cerium-doped Gd-YAG has an enhanced thermal stability. Whereas the luminescence of YAG:Ce decreases by more than 60% as the temperature rises from 25 to 205 °C, in the case of Gd-YAG:Ce it decreases only by 20%. The Gd-YAG:Ce phosphor ensures a high luminous efficiency: 144 lm $W^{-1}$ at $T_c$ = 5639 K and 127 lm $W^{-1}$ at $T_c$ = 4490 K.

Zhu *et al.*[27] manufactured a thermally stable phosphor, $K_2TiF_6:Mn^{4+}$, which emits red light with a quantum yield of 0.98 on excitation with blue light and does not contain lanthanides. LUCO samples based on the yellow phosphor YAG:Ce and the red phosphor $K_2TiF_6:Mn^{4+}$ coupled with BLED (455 nm) produced light with $T_c$ = 2700 – 2800 K, CRI = 83 – 85 and luminous efficiency of 99 – 124 lm $W^{-1}$.

For simplifying the manufacturing process of lighting devices based on blue LEDs, a popular idea is to utilize a remote position of the LUCO. Grushko and Bobkova[28] developed a slurry consisting of a low-melting glass powder, finely crystalline YAG:Ce, light-scattering material and a solvent for the deposition on the glass substrate followed by fusion to give a remotely arranged LUCO. Davydova *et al.*[29] described a process of manufacturing LUCO as a glass-ceramic disc filled with an ultradisperse luminescent YAG:Ce powder.

In the long view, the use of rare earth elements in white light sources may be restricted, to a certain extent, by availability of resources of these elements; this already affects the ultimate cost of 1 lm of luminous flux.§ However,

§ In 2014 the demands of mankind were 80 tonnes for Ga, 500 tonnes for Eu, 200 tonnes for Tb and 6000 tonnes for Y (almost 1 g per person) (author's estimate based on Internet sources).

for some applications such as manned spacecrafts, submersible vehicles and other autonomous machines, the cost of light sources is far from being the primary factor, quality of the emitted light and the operating life, energy efficiency and safety of the source being more important.

## III. Organic luminescent materials

### III.1. Polymeric luminophores

The applicability of organic luminophores for blue light converters was demonstrated by Schlotter *et al.*,[4,7] who used luminescent dyes, and by Heeger and co-workers,[5,30] who employed a polymeric luminescent material as the converter. Currently it is evident that the converters based on perylene dyes reported by Schlotter *et al.*[4,7] were only for demonstration purposes, because later it was shown that integrating converters made of organic luminophores with a LED crystal inevitably results in their fast degradation.

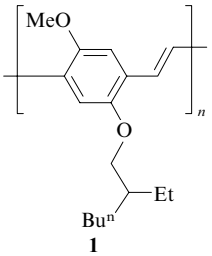
The polymeric LUCO developed by Heeger and co-workers[5,30] is made of conjugated polymers such as poly(phenylene vinylene) derivatives: poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (**1**), poly[2-methoxy-5- (2-ethylhexyloxy)-1,4-phenylene vinylene)-co-[2-n-butyl-5-(2-ethylhexyl)-1,4-phenylene vinylene] (**2**) and so on. These polymers luminesce in the visible spectral range and strongly absorb light in the blue range in which the absorption coefficients reach $\sim 10^5$ cm$^{-1}$. Polymeric converter samples were manufactured from submicrometre-thick layers of conjugated polymers, which were protected from the environmental impact by glass layers or by encapsulation. The best layered samples had luminescence quantum yields at a level of 0.6;[30,31] the spectra of polymers **1** and **2** and converters based on them are shown in Table 1 at the end of Section III. From the very beginning, the polymeric LUCOs were designed to be arranged remotely from the primary source. The use of polymeric LUCOs with various blue LEDs gave light with color coordinates very close to those of white color. The study of the polymeric LUCOs by Andersson *et al.*[31] included not only determination of lighting characteristics of the device, but also stability testing for >4000 h. During this testing, the luminosity of LED was monitored separately and was found to decrease by 25% after 4000 h. The samples of polymeric LUCO withstood the tests, their stability being not inferior to that of LED.

Heeger and co-workers[5,30] presented a thorough scientific and engineering study of the problem of semiconductor sources of white light; however, perhaps, the proposed solution was too revolutionary to be accepted by industry. The investigations of conjugated polymers for light-emitting devices were continued in the 21st century. Particular attention was concentrated on chemically, thermally and photochemically stable polyfluorenes, their derivatives[32–36] and composite materials based on polyfluorenes and oligoarylsilane dendrimers.[37,38]

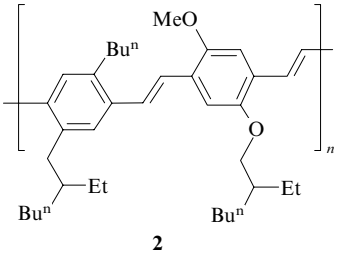
A study of Belton *et al.*[32] addressed the mechanisms of polyfluorene luminescence and, like the works of Luponosov *et al*.[37] and Uekert *et al.*,[38] it was rather devoted to their possible use in organic light-emitting diodes (OLEDs) and in displays, but not in light sources. The application of polyfluorenes in white light sources has been considered in several other studies.[33–35] The authors[33,34] obtained polyfluorene **3** with a molecular weight of $\sim$20 000 ($n \approx 40$) and with azide side groups, which provided cross-linking of polymer chains on heat treatment or on exposure to UV light. After this treatment, the polymer is a hetero-fluorophore with an unusually broad emission band. Polyfluorene **3** exhibits white luminescence with a quantum yield of 0.86 on excitation with long-wavelength UV light (see Table 1). The luminescence of polyfluorene **3** in converter samples was excited by UV LED (378 nm). Note that the light spectrum emitted by the hybrid device is completely determined by the converter. The quality of light emitted by the converter is as follows: CRI = 91, CCs are (0.2554, 0.2426) and $T_c$ = 32 400 K. The data on the converter stability were not reported.

A polymer composite was also used as the converter material;[35] polyfluorene **4** exhibiting blue luminescence and quantum dots (QDs) based on CdSe/ZnS with blue and yellow luminescence were embedded in poly(methyl methacrylate) (PMMA). This material was applied in specified amounts directly onto the UV LED (380 nm). The converter samples based on polyfluorene **4** and yellow-emitting QDs produced white light with $T_c$ from 3000 to 9000 K and CRI = 85–90. Although the luminescence quantum efficiencies of polymer **4** and QDs in solution were high (0.9 and 0.52, respectively), the quantum efficiency of the

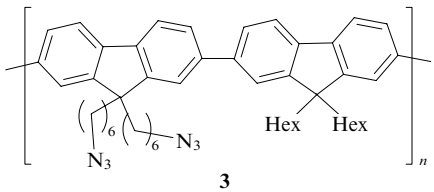
**Structures 1–5**




**1**

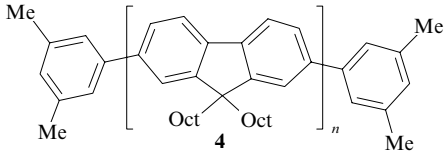



**2**



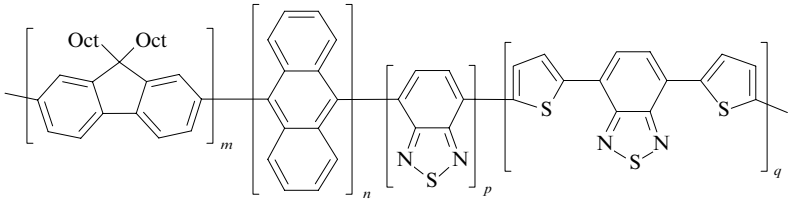

**3**

Hex = n-C$_6$H$_{13}$




**4**

Oct = n-C$_8$H$_{17}$




**5**

converter did not exceed 0.17, which was reflected in the luminous efficiency value of 13 lm $W^{-1}$.

Lai *et al.*[39] utilized the polymer converter to solve a specific problem of manufacturing a red light-emitting diode using a BLED for excitation. Polymer **5** served as the fluorophore; it was introduced into the UV-light cured organosilicon formulation containing 2,4-di-*tert*-butylphenol as an antioxidant. The resulting samples had enhanced (as compared with the AlGaInP red LED) luminous efficiency, but the lifetime was only 11 h.

### III.2. Molecular luminophores

The ideas of remote arrangement of the converter and flexible tuning of the emission spectra by means of organic luminophores expressed in the cited studies[5,30] have also been developed in the subsequent works devoted to the possibility of using organic luminophores, especially molecular luminescent dyes, for the LUCO. This is due to the facts that luminescent dyes are commercially available products and that LUCOs are of interest not only for lighting engineering, but for photovoltaics for converting the blue part of the solar spectrum to longer-wavelength light. The requirements to LUCOs are very similar for both applications, especially as regards the stability and tolerance to heat treatment and exposure to light. Also, the data on materials for photovoltaic LUCOs (most often, called concentrators) are useful for lighting engineering because they are of the same type and, in some cases, just identical to the LUCO materials for LEDs.[40] Below we consider the results of application of various organic molecular luminophores for LUCOs.

Ermakov *et al.*[41] reported the use of 4-dimethylaminochalcones (**6**) and Nile red (7-diethylamino-1,2-benzophenoxazin-3-one, **7**), which are representatives of chalcones and phenoxazines, respectively. The spectral luminescence properties of chalcone **6** substantially depend on the matrix; this compound shows solvatochromism and solvatofluorochromism and is used as a fluorescent probe in biophysical studies. In polar solvents, the emission peak is located at about 550 nm, with the quantum yield reaching 0.22.[42] For phenoxazine **7**, $\lambda_{abs} \approx 500$ nm and $\lambda_{em} \approx 625$ nm.[43] Ermakov *et al.*[41] used epoxy resin as the matrix. The arrangement of the converter in the hybrid LED corresponded to configuration 1 (see Fig. 1). Four types of converters were manufactured. The first two materials contained chalcone **6** in different concentrations, while the other two had a two-layer structure with the dye **7** layer covering the chalcone **6** layer and, conversely, chalcone **6** covering phenoxazine derivative **7**. The light emitted by the samples was visually perceived as blue-green with CCs of (0.197, 0.420), yellow-green with CCs of (0.400, 0.590), nearly white with CCs of (0.268, 0.357) and orange-red with CCs of (0.580, 0.435). The stability of the obtained samples was not reported.

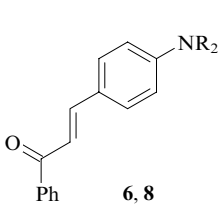
The application of 4-diphenylaminochalcone (**8**), which has yellow luminescence with a quantum yield of 0.44, for luminescence conversion has been reported.[44] Poly(ethylene glycol) with an average molecular weight of 6000 (PEG-6000) was used as the matrix. Stability testing demonstrated that the operation of the LUCO BLED is accompanied by a 30% decrease in the luminescence intensity after 2 h of operation.

Kim *et al.*[45] studied the use of naphthalimide and triarylmethane luminescent dyes, namely, 9-(4-*tert*-butylphenyl)-4-*N*,*N*-diphenylamino-1,8-naphthalimide (**9**) and fluorescein (as uranine). Both dyes have high luminescence quantum yields (0.96 for compound **9** in PMMA). The fluorescein-based converter was completely bleached in less than 1 h. The material based on naphthalimide **9** dispersed in epoxy resin was rapidly bleached, while that dispersed in PMMA was bleached considerably more slowly, by 50% within 200 h.

The understanding that the arrangement of LUCO in the close vicinity of the LED crystal is associated with high (and, perhaps, unreachable) requirements to the thermal and photochemical stability of luminophores has come from experiments performed by Kim *et al.*[46] It was shown that transition from configuration 1 to configuration 2 for luminescence conversion is accompanied by a decrease in the converter degradation rate by a factor of almost 100. It is obvious that in the cases where luminophore degradation is associated with photochemical processes, the increase in the distance between the primary source and the converter from fractions of a millimetre to several millimetres results in a decrease in the light density by hundreds of times with the corresponding decrease in the degradation rate.

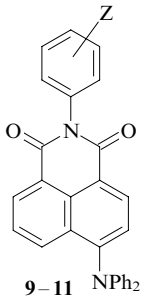
It is noteworthy that the remotely arranged LUCO based on copolymer of naphthalimide **10** with PMMA (copolymer **11** ) located remotely had stable characteristics during 12 days of continuous operation.[47] However, the luminescence quantum yields of compounds **10** and **11** were markedly lower than that of naphthalimide **9** in PMMA (0.65, 0.36 and 0.96, respectively).

**Structures 6 – 11**

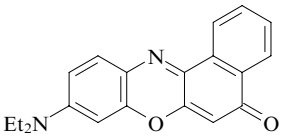



**6**, **8**

R = Me (**6**), Ph (**8**)

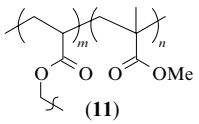



**9** – **11**




**7**

Z = 4-Bu$^t$ (**9**),
3-$CH_2OC(O)CH{=}CH_2$ (**10**),

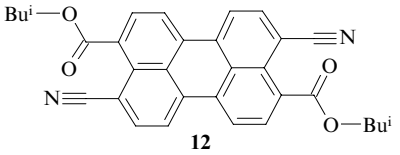



(**11**)

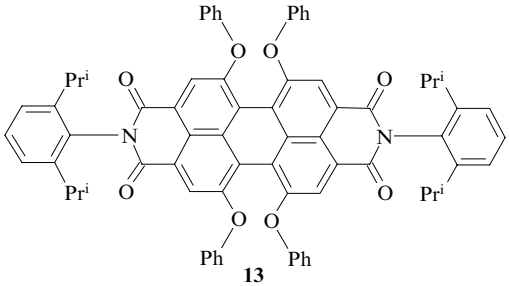
The history of application of perylene dyes for luminescence conversion was started by Schlotter *et al.*[4,7] In the dye chemistry, perylene-3,4,9,10-tetracarboxylic acid derivatives are among the most thermally and photochemically stable pigments. The LUCOs were based on the yellow luminescent dye Lumogen F 083 (bis-isobutyl 4,10-dicyanoperylene-3,9-dicarboxylate, **12**)¶ and red Lumogen F 305 (**13**). The spectra of ester **12** have a vibrational structure that is manifested most clearly in solid matrices based on epoxy resin and PMMA. In toluene, $\lambda_{abs} \approx 510$ nm, $\lambda_{lum} \approx 530$; in dichloromethane, $\lambda_{abs} \approx 476$ nm, $\lambda_{lum} \approx 490$ nm.[48,49] The luminescence quantum yield in toluene is $0.78 \pm 0.05$.[40] The application of ester **12** in the BLED (450 nm) convert-

¶ Lumogen is a BASF trademark.

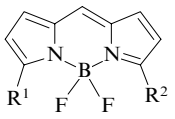
**Structures 12 – 15**



**12**

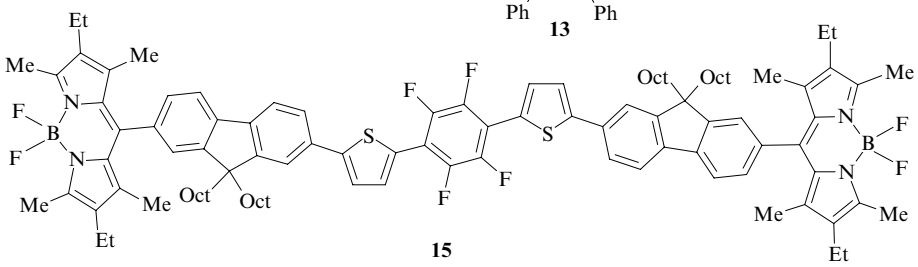


**13**



**14**

$R^1$, $R^2$ = Alk, Ar, *etc.*



**15**

ers to obtain white light upon mixing of two complementary colors has been investigated.[50] The dye was deposited from a solution of PMMA in ethyl acetate directly on the LED crystal (configuration 1). A considerable degradation of the conversion effect occurred as soon as after 3.5 h of operation. The authors suggested that the degradation is caused by dye decomposition under the action of high temperature. The use of a remotely arranged converter based on ester **12** with addition of dye **13** for enhancing the red component gave a warm white color.[51, 52] No stability data were reported, although it was noted that the stability is higher in the case of confuguration 2. Finally, it was shown [53] that the luminophore degradation is caused by light rather than temperature. It was suggested that primary photodestruction processes involve the PMMA matrix material.

The attempted use of dye **12** in photovoltaic concentrators revealed analogous stability problems. It was shown [54] that the stability of luminophores (in particular, ester **12**) in PMMA depends on the PMMA brand and manufacturer, *i.e.*, it depends on the presence of particular impurities and admixtures in the polymer, with the highest stability being noted for (chemically) pure PMMA. It was ascertained [55] that the photochemical processes in PMMA are due to ketone impurities, for example, the presence of methyl pyruvate, MeOC(O)C(O)Me. A detailed review of new polymeric materials to be used as matrices that increase the luminophore stability has been reported.[56]

The $BF_2$-dipyrromethane derivatives with structure **14**, known under the BODIPY trade name, represent a new class of luminophores, characterized by a high luminescence quantum yield and high absorption coefficients ($\sim$80 000 litre mol$^{-1}$ cm$^{-1}$). The variation of substituents gives rise to BODIPY luminophores with narrow emission spectra from 500 to 700 nm. Luminophore **15**, which showed yellow luminescence on excitation at 440 nm, was prepared.[57] The authors used this compound to design a converter as a cover glass coated by the luminophore in a curable polymer matrix. While operating with blue LED, the converter emitted white light. When the converter was remote from the LED by a 5 mm distance, the luminosity decreased by 10% after 200 h of continuous operation.

The BODIPY luminophores have small Stokes shifts (40 – 50 nm); they are characterized by inductive resonance energy transfer from the excited molecule to the neighbouring one. The Förster radius of BODIPY is 5.7 nm; as a consequence, the luminescence of BODIPY is subject to pronounced concentration quenching.† Strange as it may seem, there are known luminophores the luminescence of which is considerably enhanced only after aggregation (aggregation induced emission).[58] An example of such luminophores is 4,7-bis[4-(1,2,2-triphenylvinyl)phenyl]-benzo-2,1,3-thiadiazole (**16**). This luminophore with yellow luminescence was used for luminescence conversion BLED.[59] For this purpose, a drop of a solution of compound **16** in toluene with 20 g litre$^{-1}$ concentration was deposited on the BLED surface followed by solvent evaporation. The samples produced in this way had a good luminous efficiency, but the luminosity decreased by 20% after 10 min.

The study of Kim *et al.*[46] has already been mentioned above in the discussion of increase in the stability on going from configuration 1 to configuration 2 of the device. In this study, the converter represented a layered plastic in which the luminophore layer (40 – 80 μm thick) is sandwiched between the high-density polyethylene layers. The authors manufactured two types of converters. In one type, coumarin-6 (**17**) with a yellow-green luminescence was used as the luminescent material, and in the other type, CdSe/ZnS quantum dots with red luminescence were used. The luminophore layer contained also the polymeric base — PMMA or polystyrene — and α-terpineol as a viscosity controller; by varying the concentration of the latter agent, the layer thickness during lamination was varied. White light was generated from the emission of blue LED with a remotely arranged converter or two converters. When only the coumarin converter was used, the emitted light had CRI $<$65 due to low contribution in the orange and red spectral regions. The use of the composite converter increased the CRI to 85 (the emission spectrum for this case is shown in Table 1), the CCs of emitted light being (0.304, 0.366). Stability testing demonstrated that the luminous flux decreases by 10% – 12% within 1 h.

A converter operating with UV LED (395 or 405 nm) was designed using coumarin-30 (**18**) and N-alkylated pyrrolopyrrole-2,5-dione with thiophene substituents **19**.[60] The structure and spectra of compounds **18** and **17** are similar: the benzothiazole substituent in coumarin **17** is

† This underlies the application of BODIPY as a fluorescent probe.

replaced by the *N*-methylbenzimidazolyl group in coumarin **18**; coumarin **18** in PMMA has $\lambda_{lum} = 470$ nm, quantum yield of 0.92 and $\lambda_{abs} = 400$ nm. The absorption spectrum of compound **19** occurs in the emission band of coumarin **18**; in PMMA, $\lambda_{lum} = 580$ nm and the quantum yield is $\sim 1$. The emission spectra of the samples are shown in Table 1. The color coordinates of light emitted by dyes **18** and **19** are (0.16, 0.32) and (0.56, 0.43), respectively. By varying the concentration of the luminophores, it is possible to obtain various colors, including white. Since absorption at UV LED wavelengths is very low for compound **19** and very high for coumarin **18**, luminescent dye **19** can be excited *via* absorption of light emitted by coumarin **18** and *via* nonradiative transfer of excitation from molecule **18** by the inductive resonance mechanism. The radiative mechanism of excitation transfer predominates for this converter, because the excitation efficiency of compound **19** depends on the optical path length. The quantum efficiency of UV light conversion to the visible light for the best samples was 0.9 and CRI reached 90. Short-term stability was tested and it was found that the emitted light intensity decreases by 5% after 72 h of continuous operation.

Note that it is virtually impossible to compare the stability data obtained in different studies, because the authors do not report the data on the energy flux or the density of light flux through a particular converter. Martino *et al.*[60] indicated the type of UV LED used for stability testing — LE-0503-03UV. The UV radiation flux of this LED is 210 μW. After the converter, the luminous flux was 0.06 lm. The internal and external surfaces of the converter are hemispheres of diameters 1 and 1.92 cm, respectively. Thus, the irradiance of the internal surface was 1.3 W $m^{-2}$ and the illuminance of the external surface of the converter was 50 lux. This is relatively small value: for example, the illuminance of the surface of the LED lamp bulb with an electric power of 7 W is 54 000 lux.

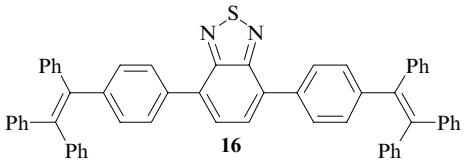
The converters described in the studies cited above[46, 60] can be called sequential. In a sequential converter, light emitted by the LED is absorbed by luminophore L1, which is thus excited. The luminescence of L1 partly passes through the LUCO and is partly absorbed by luminophore L2, thus exciting its luminescence. The quantum efficiency of a sequential converter is expressed as

$$\eta_{con} = f_{abs1}\Phi_{lum1} - f_{abs1}f_{abs2}\,\Phi_{lum1} + \\ + f_{abs1}f_{abs2}\Phi_{lum1}\Phi_{lum2} \quad (2)$$

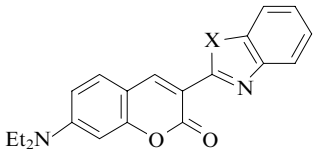
where $f_{abs1}$, $f_{abs2}$ are fractions of the numbers of quanta absorbed by luminophores L1 and L2; $\Phi_{lum1}$, $\Phi_{lum2}$ are the L1 and L2 luminescence quantum yields.

One more example of a sequential converter for UV LED was reported by Luridiana *et al.*[61] In this case, the converter is based on luminescence of ethyl 7-(diethylamino)coumarin-3-carboxylate (**20**) and 6-(4-dimethylaminostyryl)-4-(dicyanomethylene)-2-methyl-4*H*-pyran (**21**). The researchers[61] investigated in detail the spectral luminescence properties of luminophore **20** in various solvents and the dynamic and static concentration luminescence quenching. The converter proposed by the authors was a film cast from a solution that contained compounds **20** and **21** and a chloroform dispersion of polycarbonate. In the prototype devices, the converter was deposited on the surface of a commercial LED. The lighting parameters for three samples differing in the concentration of luminophores in the converter were the following: CCs of (0.4670, 0.4820), $T_c = 2779$ K, CRI = 65; CCs of (0.4150, 0.3670), $T_c = 3100$ K, CRI = 75; and CCs of (0.3216, 0.3447), $T_c = 5980$ K, CRI = 81. The operation stability of the converter was tested during 10 days of continuous operation. By the end of measurements, the intensity decreased by 4% – 5%. The UV LED used was Bivar UV5TZ-405-15 of 5 mm size with an UV light flux of 20 mW according to manufacturer's data. According to estimates, the irradiance of the internal surface of the converter was 510 W $m^{-2}$, that is, this value is not so low as in the study by Martino *et al.*[60] However, since the LED operation time is up to 1000 days, it is reasonable to consider that a converter passes the stability tests only if the testing interval is of the same order or if the testing duration is shorter, but the illumination conditions are more drastic.

**Structures 16 – 21**

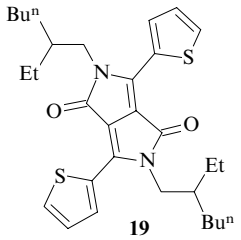



**16**

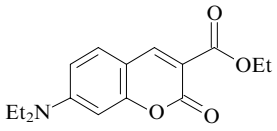



**17**, **18**

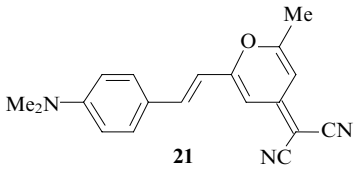
X = S (**17**), NMe (**18**)




**19**




**20**




**21**

The spectra of the considered luminophores and light-emitting diodes with luminescent converters based on them are summarized in Table 1.

## IV. Complex compounds

Metal porphyrins and other metal complexes are promising materials for optoelectronics. It is not surprising that they have attracted attention as possible LUCO components. Xiang *et al.*[62] used platinum(II) *meso*-tetrakis(pentafluorophenyl)porphyrin complex (**22**) and aluminium tris(8-hydroxyquinolinate) (**23**).

Compound **22** possesses red luminescence with a quantum yield of 0.12. The luminescence of complex **22** in polycarbonate does not change for 1000 h at 120 °C in air. The luminescence intensity decreases by one-third after exposure to UV light flux of 10 W $m^{-2}$ for 100 h. Hydroxyquinolinate **23** emits green luminescence. At definite concentrations of compounds **22** and **23**, the UV LED

**Table 1**. Spectra [a] of luminophores and light-emitting diodes with luminescent converters.

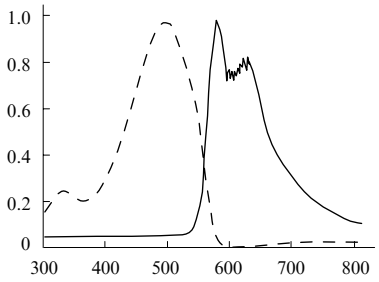
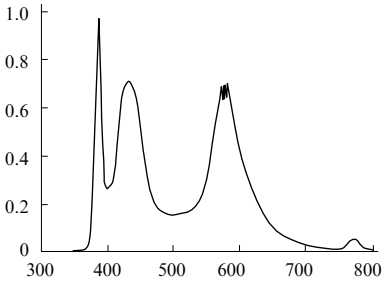
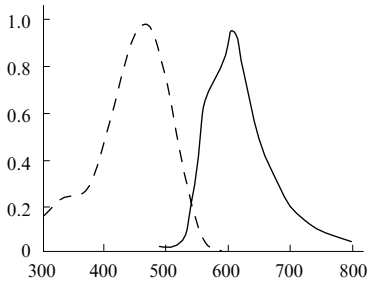
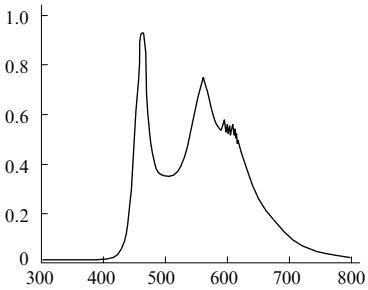
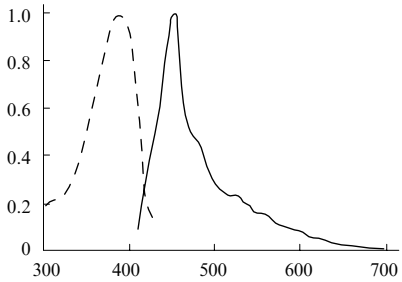
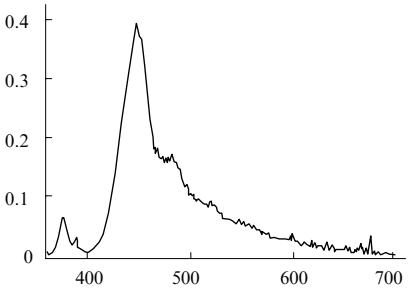
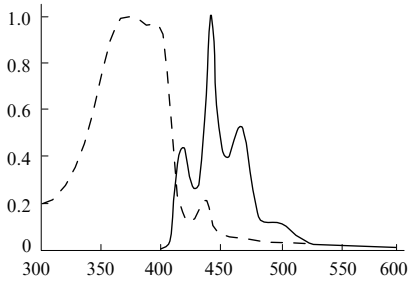
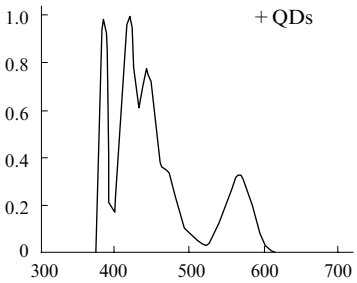
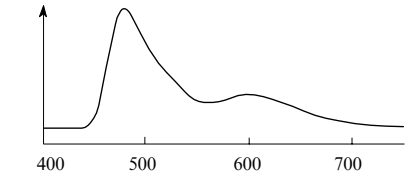
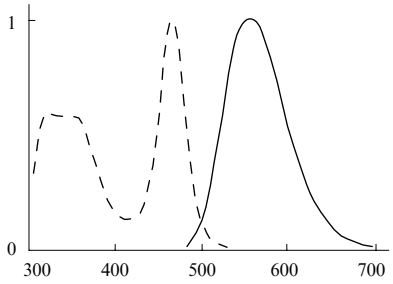
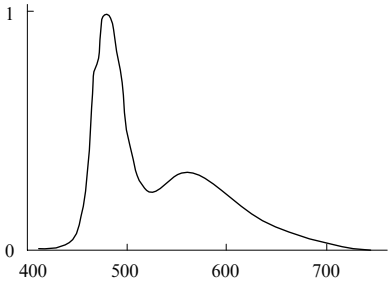
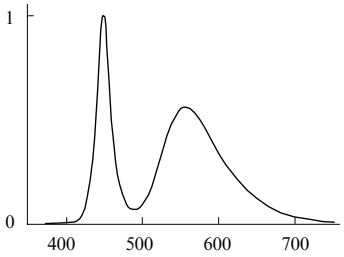
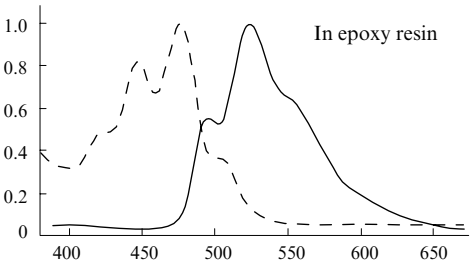
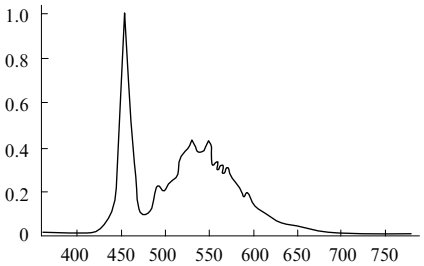
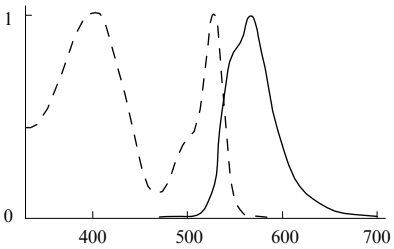
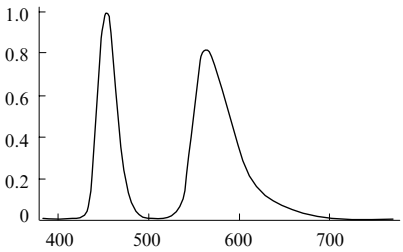
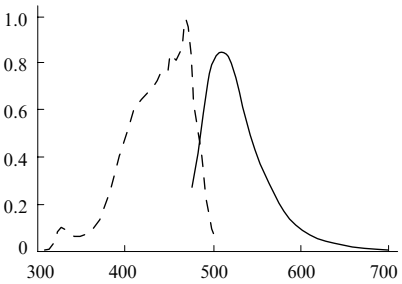
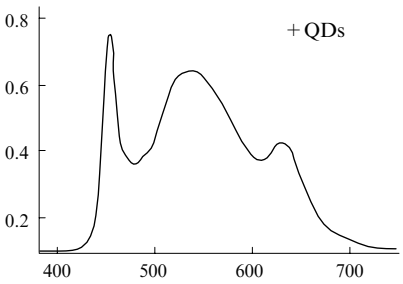
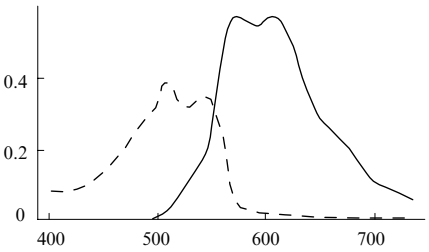
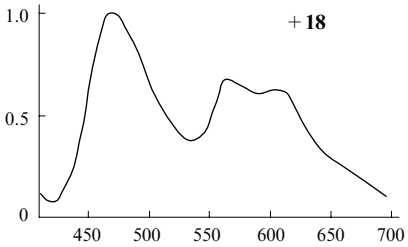
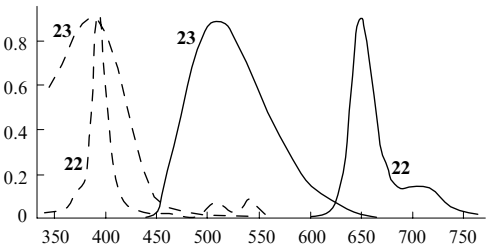
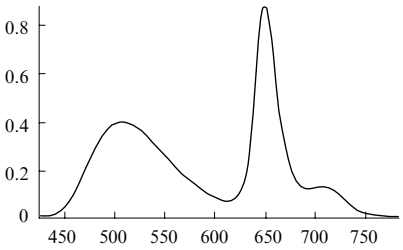
| Luminophore | Absorption (– – –) and emission (——) spectra of luminophores | Emission spectrum of LUCO LED | LED type | Ref. |
|---|---|---|---|---|
| **1** |  |  | B | 30 |
| **2** |  |  | B | 30 |
| **3** |  |  | UV | 33 |
| **4** |  |   | UV | 35 |
| **7**/**6** | – |  | B | 41 |
| **8** |  |  | B | 44 |

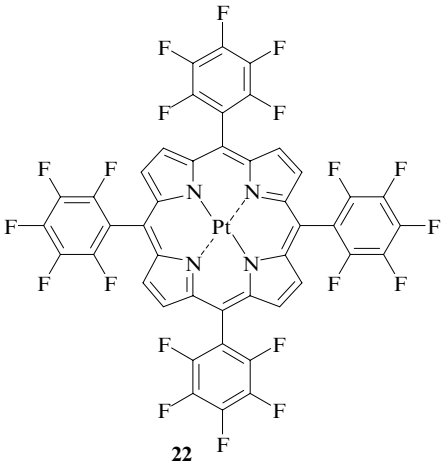
**Table 1** (continued).

| Luminophore | Absorption (– – –) and emission (——) spectra of luminophores | Emission spectrum of LUCO LED | LED type | Ref. |
|---|---|---|---|---|
| **9** | – |  | B | 45 |
| **12** |   |  | B | 50 |
| **15** |  |  | B | 57 |
| **17** |  |   | B | 46 |
| **19** |  |   | UV | 60 |
| **22**, **23** |   |  | UV | 62 |

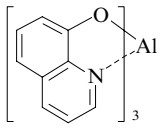
[a] The abscissa shows the wavelength in nm and the ordinate shows the intensity in rel.u.

light (394 nm) is converted to white light with CCs of (0.32, 0.31), CRI = 90.6, $T_c$ = 6800 K, LOR = 10 lm $W^{-1}$.

**Structures 22, 23**



**22**



**23**

The above-considered converter, like that reported by Chen *et al.*,[35] is an example of parallel converter in which the light emitted by LED is absorbed by luminophores L1 and L2 and excites their luminescence. Note that in the parallel converter, the excitation light can be completely absorbed by the converter. The quantum efficiency of the parallel converter is expressed as

$$\eta_{con} = f_{abs1}\Phi_{lum1} + f_{abs2}\Phi_{lum2}$$

where $f_{abs1}$, $f_{abs2}$ are fractions of the numbers of quanta absorbed by luminophores L1 and L2; $\Phi_{lum1}$, $\Phi_{lum2}$ are the L1 and L2 luminescence quantum yields. Taking that $f_{abs1} + f_{abs2} = 1$, this expression can be written in the form

$$\eta_{con} = f_{abs1}\Phi_{lum1} + (1-f_{abs1})\Phi_{lum2} = \quad (3)$$

$$= f_{abs1}(\Phi_{lum1}-\Phi_{lum2}) + \Phi_{lum2}$$

## V. Quantum dots

Quantum dots as a new luminescent material have already been mentioned above.[63] Two publications report the first attempts at using QDs in LEDs.[64, 65] Park *et al.*[64] generated the white light by combining the blue luminescence of an organic polymer with the green and red luminescence of two sorts of CdSe quantum dots (3 and 7 nm in size). Bowers II *et al.*[65] generated the white light by using one sort of CdSe QDs (1.5 nm in size). These QDs had a broad emission spectrum (half-width ~200 nm). The deposition of QD-bearing polyurethane lacquer on the UV LED (400 nm) gave rise to white luminescence. The operating stability of the device was found to be 10 days. The quantum dots synthesized in the study cited[65] had a broad emission spectrum, strong band edge absorption and relatively large Stokes shift. The luminescence quantum yield was very low — ~0.02. In the books devoted to nanotechnology, just the opposite is called remarkable features of QD luminescence, namely, a narrow emission spectrum, a broad absorption band and a high quantum yield. An analogy with a tuned circuit is here appropriate: this circuit has a high Q-factor and a very narrow resonance curve at small losses and a low Q-factor and a broad resonance curve at high losses. Probably, narrow-band QDs will soon become luminescent materials that are going to replace the OLED technology in color displays. Meanwhile, for broad-band QDs the quantum yield has never been increased to an acceptable level.

An example of successful use of yellow-emitting QDs (that is, narrow-band QDs) for the blue LED conversion has been reported by Jang *et al.*[66] The authors used colloid QDs with the Cu-In-S core (Cu : In = 1 : 4) and two ZnS protecting shells. The QD core size was 2.72 nm. The QDs had a high luminescence quantum yield (0.92 – 0.97) and an emission peak at 559 nm. Two types of samples were prepared, one with QDs embedded in PMMA and the other with a QD-loaded PMMA layer being sandwiched between $SiO_2$ layers. Upon variation of the diode current from 20 to 300 mA, the lighting parameters of the hybrid LEDs with samples of the former type occurred in the following ranges: CCs were (0.32 – 0.322, 0.285 – 0.290); CRI = 70 – 72; $T_c$ = 6200 – 6500 K; the luminous efficiency was 68.6 lm $W^{-1}$ at a 20 mA current. The luminous efficiency sharply decreases with increasing current, but this is a typical feature of BLEDs rather than the hybrid device. Testing of the operating stability of the hybrid LED revealed that converters of the first type completely degraded within 20 h. The authors[66] thoroughly investigated the consequences of the photodegradation of QDs and concluded that the ZnS shells degrade *via* the reaction

$$ZnS + 2O_2 \xrightarrow{h\nu} ZnSO_4$$

and subsequent penetration of the oxygen molecule towards the QD core. The degradation of the converter in the second type of samples (with $SiO_2$ protecting layers) after 20 h of continuous operation was insignificant. However, the luminous efficiency decreased to 61 lm $W^{-1}$ and CRI decreased to 53 – 55. The reason is that in this case, the converter was a layered structure composed of material with different optical properties.

## VI. Metal-organic frameworks

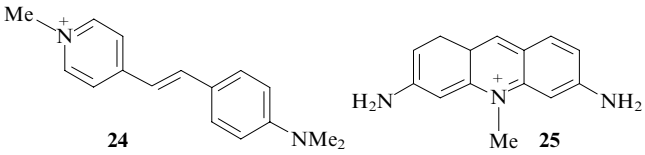
At the end of the 20th century, chemistry switched from studying clathrates and zeolites to the design and investigation of coordination polymers[67] and then metal-organic frameworks (MOFs). Metal-organic frameworks are crystalline materials consisting of transition metal cations and polydentate organic ligands. A typical feature of the crystal structure of MOFs is the presence of microscopic pores or channels, which can accommodate guest molecules.[68, 69]

As luminescent materials, MOFs are attractive because of the possibility to use both inorganic and organic blocks in luminescence centres or embed luminophore molecules into MOF as guests, which are accommodated in the pores. This provides for fine tuning of the emission spectra. The results of studying the applicability of MOFs for LUCO have been reported.[70 – 74] To date, the highest quantum yield of white luminescence of MOF, equal to 0.2, was attained by Sun *et al.*[73] White luminescence observed on UV excitation is here the result of summation of blue luminescence of the matrix and yellow luminescence of the iridium complex $[Ir(ppy)_2(bpy)]^+$ (ppy is 2-phenylpyridine, bpy is 2,2′-bipyridine) located in the host pores. The luminescence quantum yield of the material decreased by 10% at 150 °C, which is

indicative of its high thermal stability. The photostability of the material was not studied.

Cui *et al.*[74] placed luminophore cations with red and green luminescence, 4-(*p*-dimethylaminostyryl)-1-methylpyridine (**24**) and acriflavine (**25**), into the pores of anionic MOFs with the intrinsic blue luminescence. The embedding of luminophore **24** in MOF pores induced the increase in the luminescence quantum yield from 0.07 (solution in DMF) to 0.61.

**Structures 24, 25**




Using the obtained material as the LUCO for the UV LED (365 nm), the researchers[74] generated white light with CCs of (0.34, 0.32), CRI = 92 and $T_c$ = 5327 K.

## VII. Anti-Stokes shift luminescent materials

The conversion of long-wavelength optical radiation to short-wavelength radiation *via* interaction of the radiation with complex systems, *e.g.*, crystals with two types of activating ions, was discovered by Ovsyankin and Feofilov;[75–77] it was entered in the State Register of Discoveries of the USSR in 1966 under number 166. The summary of the discovery was as follows: 'A phenomenon of conversion of photoluminescence wavelengths, according to which the excitation of complex systems, for example, crystals activated by rare earth elements, with optical radiation gives rise to an optical radiation with markedly shorter wavelengths, which is caused by cooperative summation of the electronic excitation energy of particles of one subsystem on particles of another subsystem with higher energy states (cooperative sensitization of luminescence)'.

A modern review of achievements along this line has been reported.[78] The luminescent materials that exhibit cooperative luminescence are commonly called Anti-Stokes shift luminophores (ASLs).‡

The idea of obtaining white light upon the conversion of IR radiation to visible light by means of ASLs started to be actively developed[79–84] after the advent of high-performance (efficiency > 50%) high-power laser diodes of the near-IR range. Fluoride, lead fluoride, borate or other glass ceramics were used as matrices for encapsulating rare earth metal fluoride molecules or nanocrystals. The white light was obtained by three-color synthesis from narrow-band blue, green and red luminescence of $Tm^{3+}$ and $Er^{3+}$ ions[79,81] or $Tm^{3+}$ and $Ho^{3+}$ ions,[80,82,83] the excitation of which was collected from excited $Yb^{3+}$ ions. Doping of the perovskite type $KZnF_3$ crystal with $Yb^{3+}$, $Tm^{3+}$ and $Mn^{2+}$ ions produced white light with broadened spectral components upon laser diode excitation at 976 nm wavelength.[84]

The white luminescence of the crystal on exposure to an invisible IR beam is a spectacular experiment, which is, however, quite far from the prototype of a future lighting device. The absorption coefficients of rare earth ions are low; therefore, ASL-based converters of IR radiation should be extended to efficiently absorb this radiation. The technology of IR radiation transfer over long distances by means of optical fibres is well-developed. The optical fibre with incorporated ASL could be considered as a prototype of the extended light source. Potentially this approach could bring about a basically new method of lighting in which one IR laser illuminates the indoor spaces of a whole building.

‡ Lately, these materials have been called upconversion materials.

## VIII. Matrix

A considerable increase in the stability of luminophores was expected[85] as a result of using a rubber-like matrix. This matrix is obtained by drying a gel that is formed from a mixture of branched and linear polyethylene oxide in water or acetonitrile after vigorous stirring at 750 – 1500 rpm for many hours. The authors state that their matrix increases the stability of the luminophore up to 1000 h, irrespective of its nature, and that the matrix is also suited for green fluorescent protein and for quantum dots. However, acquaintance with the information that accompanies the study cited[85] shows that the obtained data are far from being as promising as it is stated in the paper.

The photostability testing (UV 310 nm) for 1000 h was carried out only for the sample containing iridium complexes. The results indicated an almost two-fold decrease in the luminescence after exposure to UV light for 1000 h. The samples with a polymer (Super Yellow) as the luminophore, samples based on QDs and samples based on a mixture of coumarin, fluorescein and metal porphyrin lost 60% – 80% of their efficiency within a period of 15 to 286 h.[85] These results, together with the lack of stability data for the same luminophores in other matrices, mean only that these luminophores degrade also in this matrix. The effect of the composition of the atmospheric medium on the luminescence intensity was also considered. In an $N_2$ atmosphere, the luminescence was relatively stable, but as $N_2$ was replaced by $O_2$, the luminescence intensity considerably decreased within several hours. This behaviour is inherent in all samples listed above. These data confirm the results obtained by Jang *et al.*[66]

## IX. Problems and approaches to their solution

The luminescent materials that are suitable, according to their spectral parameters, for the conversion of light emitted by BLEDs and UV-LEDs to white light are quite diverse. White light can be generated by summing the light of two complementary colors (blue + yellow, blue-green + red) or by summing many colors. This summation may either include (only for BLEDs) or not include the primary source light.

The most important problem is the photostability of the luminescent converter material. This is true for both the luminophore constituent and the matrix. The photochemical stability of the luminophore itself is the key issue in the photodegradation of the converter, because particularly the luminophore absorbs the light from the primary source, the absorption of the matrix being negligibly small in comparison with the luminophore absorption. The vivid indication of the photodegradation of the luminophore in the converter is photobleaching.

In order to estimate the acceptable level of the quantum yield of photobleaching ($\varphi$), we will proceed from the fact that a small fraction of luminophore molecules present initially in the converter are degraded during operation time $t$. The initial number of the molecules is given by

$$\frac{N_A DS}{2300\,\varepsilon}$$

where $N_A$ is Avogadro's number, $D$ is the optical density of the converter at the absorption band, $S$ is the area of a converter unit, $\varepsilon$ is the absorption coefficient of the luminescent material. The number of quanta absorbed over time $t$ by unit $S$ amounts to

$$I(1-e^{-D})St$$

where $I$ is the density of the quantum flux entering the converter at its absorption band. The number of bleaching events is

$$\varphi I(1-e^{-D})St$$

Since the condition

$$\varphi I(1-e^{-D})St \ll \frac{N_A DS}{2300\,\varepsilon}$$

should hold, then

$$\varphi \ll \frac{N_A D}{2300\,\varepsilon\, I(1-e^{-D})t}$$

For $t = 1.8\times10^8$ s (corresponds to the usual BLED service life), $I = 7\times10^{16}$ quantum $s^{-1}$ $cm^{-2}$ (corresponding to the irradiance of 30 mW $cm^{-2}$ for quanta with the energy of $4.4\times10^{-19}$ J), $D = 1.4$ and $\varepsilon = 50\,000$ litre $mol^{-1}$ $cm^{-1}$, one has $\varphi \ll 10^{-9}$. For comparison, the photobleaching quantum yield for the most photostable fluorescent dye for laser spectroscopy — tetramethylrhodamine[86] — is $3.3\times10^{-7}$, *i.e.*, it is several orders of magnitude higher.

The photodegradation involves oxygen. For this reason, the removal of oxygen from the matrix during its formation and deposition of a coating that would hamper the entry of oxygen into the matrix are adequate measures for retarding the onset of photodegradation. However, oxygen will still enter the matrix with time. The oxidation of solid substrates with oxygen in the dark is very slow. However, it is accelerated by many orders of magnitude in the reactions of singlet oxygen, the formation of which accompanies luminescence (see Chapter 14 in the book[87]):

$^1L + h\nu_{ex} \longrightarrow {}^1L^*$ (L excitation)

$^1L^* \longrightarrow {}^1L + h\nu_{em}$ (L luminescence)

$^1L^* + {}^3O_2 \longrightarrow {}^3L + {}^1O_2$ (formation of singlet oxygen)

$^3L^* + {}^3O_2 \longrightarrow {}^1L + {}^1O_2$ (formation of singlet oxygen)

$^1L^* \rightsquigarrow {}^1L$ (non-radiative deactivation)

$^1L^* \rightsquigarrow {}^3L$ (intersystem crossing)

$^1L + {}^1O_2 \longrightarrow$ oxidation products

The lifetime of the singlet oxygen in water is rather short:[88] $3.3\pm0.5$ μs.§ The singlet oxygen is quenched by the hydroxyl groups with a rate constant of 2900 litre $mol^{-1}$ $s^{-1}$ (Ref. 89); therefore, it is better to use matrices with high concentrations of hydroxyl groups (*e.g.*, polyvinyl alcohol). The preferable luminophores should have short excited state lifetimes (this decreases the probability that an oxygen molecule will encounter an excited luminophore molecule) and high luminescence quantum yields (in this case, the proportion of molecules that undergo non-radiative deactivation and intersystem crossing is smaller).

The photostability of luminescent materials increases when molecules are isolated in cyclodextrin cavities[90] or in the presence of singlet oxygen scavengers or quenchers.[91,92] These compounds are able to retard photodegradation several-fold. However, it is necessary to increase the photostability by several orders of magnitude. This calls for basically new approaches.

The luminophore photobleaching, which depends on the presence of oxygen in the matrix, takes place inevitably. This raises the question of what sort of converter would be stable and would preserve its parameters under these conditions. We believe that the fundamental solution of the stability problem is in the use of a 'thick' converter, which completely absorbs the light emitted by the primary source. As a result, a change in the converter absorbance cannot be observed. The converter would degrade one layer after another throughout the primary source lifetime. The application of the 'thick' converter means that the light from the primary source is not utilized in the synthesis of white light and that the spectrum of the emitted light is determined by the converter. Therefore, a topical task is the search for luminophores that emit white light with high quantum efficiency upon UV excitation (400 nm).

Comparison of relations (2) and (3) for the quantum efficiency of a converter consisting of two luminophores makes clear that the manufacture of a thick sequential converter is impracticable, as opposed to a thick parallel converter. Indeed, the condition

$$\frac{\partial\eta_{con}}{\partial f_{abs}} = 0$$

in expression (2) can be fulfilled only at quite definite $f_{abs}$ values, while in expression (3), this requires only the equality $\Phi_{lum1} = \Phi_{lum2}$.

It should not go unmentioned that the strange emission spectra of LUCO LED, which are presented in Table 1, are in most cases perceived by the human eye as white light. The spectra of this white light considerably differ from the spectra of solar light or incandescent lamp light, which are similar to the emission spectrum of the ideal black body. The spectra of BLED-bases lamps (especially lamps with the color temperature of 6500 K) are overloaded with the blue component, which, in the opinion of physiologists, can affect the rhythms of sleep and awakening and have adverse consequences for eyes.[93–100] A possible way out from the 'blue crisis' is to reject the two-color (blue + yellow) technology of white light synthesis. However, this way will have

§ See also the book[88] for the summary of singlet oxygen lifetimes in solvents and polymers.

its cost. For example, such light sources would be inferior in the luminous efficiency to the BLED-based light sources. For information, the luminous efficiency of the Sun is 93 lm $W^{-1}$ (Ref. 101), while the Cree company has been manufacturing light emitting diodes with luminous efficiency $>160$ lm $W^{-1}$ since 2010.

## X. Conclusion

The use of LED lamps considerably enhances the energy efficiency of lighting and eliminates the environmentally hazardous and unsafe luminescent lamps operating with mercury vapour. Unfortunately, we perceive the light emitted by modern LED lamps as white only owing to the metameric effect, so that the design of energy-efficient light sources with a spectrum close to natural light is a relevant issue. Generally, the design of energy-efficient lighting should be treated as an interdisciplinary scientific problem having engineering, economic and humanitarian aspects.

Luminescent materials are necessary components of semiconductor light sources based on high-performance blue light-emitting diodes. Despite the broad variety of these materials, only a small range of compounds have found practical use. The use of known and newly synthesized luminescent materials for the LUCO had, as a rule, a negative outcome, because of the photodegradation of materials. One can predict more extensive research into the photochemistry of solids, which is now dealing with photochromes, dyes and optical bleaching agents. The photostability requirements imposed on LUCO materials are much more stringent than the requirements to the mentioned materials, because a converter should absorb a much higher amount of light energy during the service life.

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