Dyes and Pigments 91 (2011) 332–339

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Design and synthesis of novel fluorescence sensing perylene diimides based on photoinduced electron transfer

Nikolai I. Georgiev[a], Alaa R. Sakr[a,b], Vladimir B. Bojinov[a,*]

[a] Department of Organic Synthesis, University of Chemical Technology and Metallurgy, 8 Kliment Ohridsky Str., 1756 Sofia, Bulgaria
[b] Department of Chemistry, Faculty of Science, Zagazig University, Zagazig City, Egypt

ARTICLE INFO

Article history:
Received 21 March 2011
Received in revised form
25 April 2011
Accepted 28 April 2011
Available online 5 May 2011

Keywords:
Perylene-3,4,9,10-tetracarboxylic diimide (PDI)
Polyamidoamine (PAMAM)
Fluorescence
pH sensors
Metal ion sensors
Photoinduced electron transfer (PET)

ABSTRACT

Two novel tetraester- and PAMAM-branched perylene diimides were synthesized and configured as “fluorophore-spacer-receptor” systems based on photoinduced electron transfer. Due to their long alkylester and alkylamine terminal groups the examined compounds were well soluble in organic solvents. Photophysical characteristics of the dyes were investigated in DMF and water/DMF (1:1, v/v) solution. The ability of the synthesized perylene diimides to detect cations was evaluated by the changes in their fluorescence intensity in the presence of metal ions (Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Ag^{+} and Ni^{2+}) and protons. The dyes under study displayed “off–on” switching in its fluorescence as a function of pH, which is attributed to disallowing photoinduced electron transfer from the receptor moiety to the fluorophore. PAMAM-branched dye displayed a good pH sensor activity (FE = 6.4), however the pH sensing ability of tetraester was substantially higher (FE = 184). In the presence of Cu^{2+} and Pb^{2+} ions tetraester quenched its fluorescence intensity (FQ = 22 and 12 respectively), while PAMAM-branched dye enhanced its fluorescence intensity with pronounced selectivity to Cu^{2+} and Fe^{3+} (FE = 3.2 and 4.9, respectively). The results obtained indicate the potential of the novel compounds as fluorescent detectors for metal ions with pronounced selectivity towards Cu^{2+}, Pb^{2+} and Fe^{3+} ions and highly efficient “*off–on*” pH switches, especially a tetraester-branched perylene diimide.

1. Introduction

Perylene-3,4,9,10-tetracarboxylic diimides exhibit a unique combination of electrooptical and redox properties. They are highly stable and widely used n-type materials for organic electronic devices such as solar cells [1–3], field-effect transistors [4–6], light-emitting diodes [7–9], in liquid crystal displays [10,11], as chemosensing materials [12–14], light-harvesting materials [15,16] and as dyes in photodynamic therapy [17]. However, most of the synthesised dyes possess low solubility in organic solvents; this is a serious drawback for their processing and material science applications [18,19]. Usually the solubility is improved with the long-tail or swallow-tail conformation that is obtained by long alkyl substitutions in *N*-position of the dye [20–22].

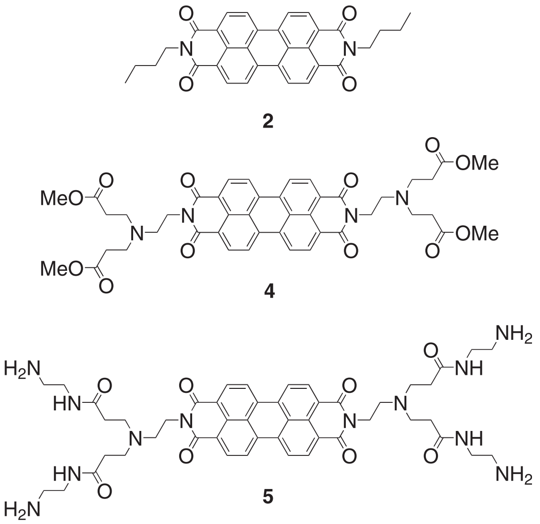
Dendrimers are well defined macromolecules exhibiting a three-dimensional structure that is roughly spherical or globular. A characteristic of dendritic macromolecules is the presence of numerous peripheral chain ends that all surround a single core [23,24]. The usage of perylene diimides as dendrimer core would increase their solubility in organic solvents due to the dendritic swallow-tail conformation [25,26]. The polyamidoamine (PAMAM) is a class of commercial dendrimers. Considerable interest in polyamidoamine (PAMAM) dendritic macromolecules has arisen because of their novel structural properties and wide range of potential applications [27–31]. Constructing a PAMAM dendrimer around a luminescent group could profitably alter the luminescence signals in the macromolecular structure and amplify the signals for sensing purposes [32–36].

Development of new sensors with improved characteristics (selectivity, sensitivity etc.) is a challenging and necessary task in the 21st century, marked by the technological booms consequences [37–41]. Because of the high sensitivity, high speed, and safety the fluorescent chemosensors and switches have been actively investigated in the recent years. The photoinduced electron transfer (PET) using the “*fluorophore-spacer-receptor*” format is the most commonly exploited approach for the design of the fluorescent sensors and switchers [42]. The components are chosen so that PET from the receptor (usually an amino group) to the fluorophore quenches the fluorescence of the system. However, in the presence of a guest, PET communication between the receptor and the fluorophore gets cut off

---

[*] Corresponding author. Tel.: + 359 2 8163169.
E-mail address: vlbojin@uctm.edu (V.B. Bojinov).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.04.015



Scheme 1.

and the fluorescence of the system is recovered. In other words, the presence of a guest is signaled by fluorescence enhancement of the system [43–46].

In this work we were focused on the divergent construction of a novel perylene diimide core functionalized PAMAM dendrimer **5** and tetraester **4** together with their photophysical and fluorescence chemosensing properties. Hence, compounds **4** and **5** (Scheme 1) were synthesized and investigated by electronic absorption and emission spectroscopy as potential PET sensors for protons and transition metal ions.

In order to receive a more complete comparative picture for the influence of the polyamidoamine backbone to the perylene diimide fluorophore, perylene diimide **2**, not containing tertiary amine in its molecule, was involved in the present study (Scheme 1).

2. Experimental

2.1. Material

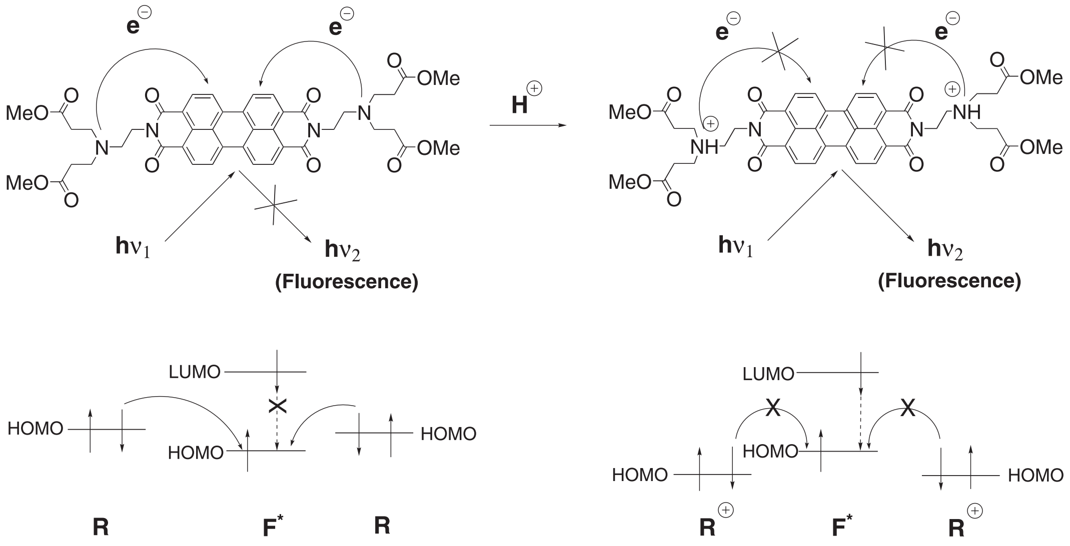
Reference perylene-3,4,9,10-tetracarboxylic diimide **2** was synthesized according to the procedure described before [47]. Ethylenediamine, methyl acrylate and perylene-3,4,9,10-tetracarboxylic acid dianhydride **1** (Aldrich), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade. $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Hg(NO_3)_2$ and $AgNO_3$ salts were the sources for metal cations.

2.2. Methods

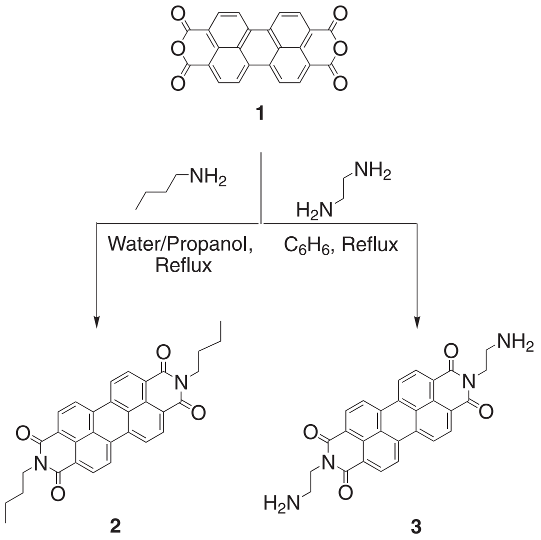
FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^{1}H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. TLC was performed on silica-gel, Fluka F60 254, 20 × 20, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–VIS absorption spectra were recorded on a spectrophotometer Hewlett Packard 8452A. The corrected fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter at room temperature (25 °C). To adjust the pH values very small volumes of hydrochloric acid and sodium hydroxide solution were used. The pH was determined with a pH meter Metrohm 704, which was standardized with Aldrich buffers. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding 30 μl portions of the metal cations stock solution (2.0×10^{-6} mol L^{-1}) to a known volume of the fluorophore solution (3 ml).

2.3. Synthesis of amino functionalized perylene-3,4,9,10-tetracarboxylic diimide (3)

To a suspension of 2 g (5 mmol) perylene-3,4,9,10-tetracarboxylic acid dianhydride in 25 ml of benzene, 6 ml ethylenediamine (90 mmol) was added and the resulting mixture was heated under reflux for 5 h. After cooling to room temperature the precipitate was collected by filtration, washed with benzene and dried. Then the crude solid was treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration, washing with water and drying 2.04 g (84%) of pure diimide **3** (m.p. > 250 °C). IR (KBr) cm^{-1}: 3368 (νNH_2); 1684 (ν^{as}N-$\underline{C}$=$\underline{O}$); 1658 (ν^{s}N-$\underline{C}$=$\underline{O}$). ^{1}H NMR (CF_3COOD-*d*, 250.13 MHz) ppm: 8.41 (m, 8H, perylene H); 4.39 (m, 4H, 2 × $\underline{CH_2}N(CO)_2$); 3.41 (m, 4H, 2 × $\underline{CH_2}NH_2$). Elemental analysis: Calculated for $C_{28}H_{20}N_4O_4$ (MW 476,5) C 70.58, H 4.23, N 11.76%; Found C 70.49, H 4.36, N 11.55%.



Scheme 2.



Scheme 3.

2.4. *Synthesis of perylene-3,4,9,10-tetracarboxylic diimide tetraester (4)*

A mixture of methyl acrylate (2.7 ml, 32 mmol) and 1.5 g of **3** (3.2 mmol) in 30 ml of methanol was stirred for 4 days at room temperature, then the precipitate was collected by filtration, washed with water and dried. The crude solid was extracted with boiling chloroform to give after vacuum evaporation of the solvent and silica-gel chromatography (methylene chloride) 0.74 g (28%) pure tetraester **4** as dark-red crystals (m.p. 206–209 °C). IR (KBr) cm^{-1}: 1730 ($\nu\underline{\text{COO}}\text{CH}_3$); 1688 ($\nu^{as}$N-$\underline{\text{C}}$=$\underline{\text{O}}$); 1660 ($\nu^{s}$N-$\underline{\text{C}}$=$\underline{\text{O}}$). ^{1}H NMR (CDCl$_3$-*d*, 250.13 MHz) ppm: 8.50 (d, 4H, *J* = 8.0 Hz, perylene H-3, H-4, H-9, H-10); 8.36 (d, 4H, *J* = 8.2 Hz, perylene H-5, H-6, H-7, H-8); 4.27 (t, 4H, *J* = 6.9 Hz, 2 × $\underline{\text{CH}_2}$N(CO)$_2$); 3.56 (s, 12H, 4 × O$\underline{\text{CH}_3}$); 2.91 (t, 8H, *J* = 7.0 Hz, 2 × CH$_2$N($\underline{\text{CH}_2}$)$_2$); 2.83 (t, 4H, *J* = 6.9 Hz, 2 × $\underline{\text{CH}_2}$N(CH$_2$)$_2$); 2.48 (t, 8H, *J* = 7.1 Hz, 4 × $\underline{\text{CH}_2}$COOCH$_3$). Elemental analysis: Calculated for $C_{44}H_{44}N_4O_{12}$ (MW 820.9) C 64.38, H 5.40, N 6.83%; Found C 64.19, H 5.29, N 6.70%.

2.5. *Synthesis of core functionalized 3,4,9,10-perylenebis(dicarboximide) PAMAM dendrimer (5)*

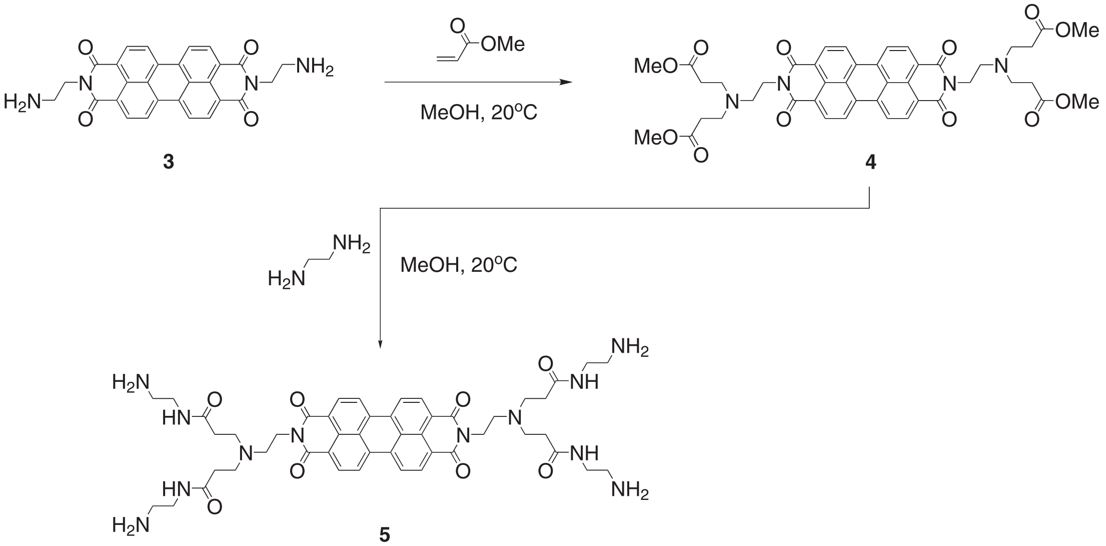
To a solution of ethylenediamine (4 ml, 60 mmol) in 5 ml of methanol, a suspension of perylene diimide **4** (0.82 g, 1 mmol) in 25 ml of methanol was added dropwise at 5 °C for a period of 30 min. The reaction mixture was stirred for 168 h at room temperature. Then the solvent and the ethylenediamine excess were distilled under vacuum. Final traces of ethylenediamine were removed azeotropically using a 9:1 toluene/methanol (v/v) solution. The aminofunctionalized dendrimer **5** was obtained as dark-red crystals (0.86 g, 92%, m.p. 163–166 °C). IR (KBr) cm^{-1}: (νNH and νNH$_2$); 2943–2842 (νCH); 1668 (ν^{as}N-$\underline{\text{C}}$=$\underline{\text{O}}$); 1646 (ν^{s}N-$\underline{\text{C}}$=$\underline{\text{O}}$). ^{1}H NMR (DMSO-*d*$_6$, 250.13 MHz) ppm: 8.72 (d, 4H, *J* = 8.0 Hz, perylene H-3, H-4, H-9, H-10); 8.54 (d, 4H, *J* = 8.2 Hz, perylene H-5, H-6, H-7, H-8); 7.96 (br.s, 4H, 4 × $\underline{\text{NH}}$CO); 4.14 (m, 4H, 2 × (CO)$_2$N$\underline{\text{CH}_2}$); 3.12 (m, 8H, 4 × NH$\underline{\text{CH}_2}$CH$_2$NH$_2$); 2.79 (m, 12H, 6 × N$\underline{\text{CH}_2}$); 2.55 (m, 8H, 4 × $\underline{\text{CH}_2}$CO); 2.31 (m, 8H, 4 × NHCH$_2\underline{\text{CH}_2}NH_2$). Elemental analysis: Calculated for $C_{48}H_{60}N_{12}O_8$ (MW 933.1) C 61.79, H 6.48, N 18.01%; Found C 61.58, H 6.25, N 17.77%.

3. Results and discussion

3.1. *Design of the dyes*

The dyes under study were designed as fluorescent core functionalized tetraester and PAMAM dendrimer, respectively, for determining transition metal cations and pH changes over a wider pH scale. We chose perylene diimide chromophore as a fluorescent core of the synthesized compounds, because of its chemical stability, high fluorescent efficiency and high electron-accepting ability.

The branching perylene diimides **4** and **5** were configured on the "*fluorophore-spacer-receptor*" model, where the perylene diimides core is the fluorophore and the tertiary amines are the proton receptors. The ethylene part between fluorophore and the branching amines serves as spacer that covalently separates the two units. In these particular cases, it was predicted that a PET process (an electron transfer from the receptors to the excited state



Scheme 4.

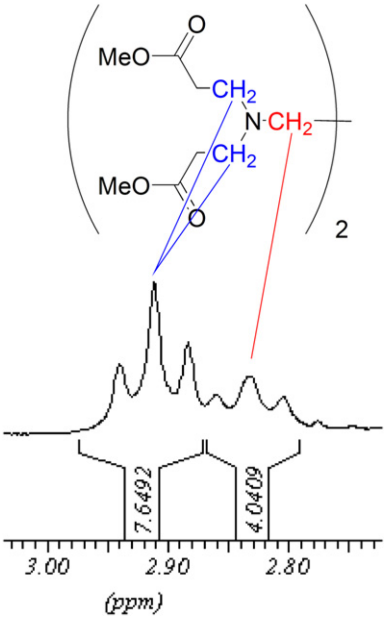


Fig. 1. ^{1}H NMR (CDCl$_3$-*d*, 250.13 MHz) spectrum of tetraester 4 in range of about 3.00–2.80 ppm.

of the fluorophore) would quench fluorescence emission of the perylene diimide unit. This would represent the "*off-state*" of the system. The protonation or the respective metal coordination of the amine receptors would increase their oxidation potential, and as such, thermodynamically disallows the electron transfer [48]. Consequently the emission would be "*switched on*". Thus we expect the fluorescence to be amplified in acidic media (Scheme 2).

3.2. Synthesis

The synthesis of perylene diimides **2** and **3** was achieved as shown in Scheme 3. The reference compound **2** was synthesized as described before [47] by refluxing perylene-3,4,9,10-tetracarboxy anhydride **1** and n-butylamine in water/propanol. The amino functionalized core **3** was prepared by analogy with the previously reported procedure [49] by refluxing perylene-3,4,9,10-tetracarboxy anhydride **1** with ethylenediamine in benzene media. The pure dye **3** was obtained after removing the unreacted anhydride **1** under boiling the crude solid in 5% aqueous sodium hydroxide.

The novel PAMAM perylene tetracarboxydiimide **5** was synthesized via PAMAM divergent strategy, involves initial Michael addition of amino functionalized core **3** with methyl acrylate followed by exhaustive amidation of the resulting tetraester **4** with a large excess of ethylenediamine to afford the fluorescent dendrimer **5** with amine ending groups of its periphery (Scheme 4).

The structure and purity of the desired products were confirmed by conventional techniques (elemental analysis data, UV–VIS, fluorescence, FT-IR and ^{1}H NMR spectroscopy). For instance, the FT-IR spectra of the synthesized perylene diimides **2** and **3** showed absorption bands at 1690–1680 cm^{-1} and 1660–1650 cm^{-1} resulting from the imide ring formation. At the same time absorption maxima in range of 1750–1800 cm^{-1} corresponding to the anhydride carbonyl functions are absent. This is solid evidence that the starting perylene anhydride **1** was completely converted in 1,8-naphthalimides **2** and **3**. Analogously, in the FT-IR spectra of **4** a typical for the ester compounds absorption band at 1730 cm^{-1} appears and no absorption above 3000 cm^{-1} corresponding to N-H primary and secondary amine groups were observed. Furthermore in the ^{1}H NMR (250.13 MHz) spectrum of compound **4** resonance triplets at 2.91 ppm for 8 protons and 2.83 ppm for 4 protons were observed (Fig. 1), suggesting that the two primary amine groups of **3** were completely branched to tetraester **4**. The structure of compound **5** was confirmed using the same logic. In the FT-IR spectrum of **5** the lack of ester absorption at 1730 cm^{-1} was accompanied with the appearance of novel bands in range of 3187–3268 cm^{-1} for amine groups that is well correlated with the ^{1}H NMR spectrum of the compound.

Table 1
Solubility of **3**, **4** and **5** in different organic solvents and water.

Compound	DMF	DMSO	Water	ROH	R-X
3	−	−	−	−	−
4	+	+	−	−	+
5	+	+	+	+	−

+ Soluble; − Insoluble; ROH = Methanol, Ethanol; R-X = Chloroform, Dichloromethane, Dichloroethane.

Table 2
Photophysical characteristics of **2**, **4** and **5** in DMF solution at concentration 10^{-5} mol L^{-1} (λ_{ex} = 460 nm).

Compound	DMF				
	λ_A (nm)	ε (L mol^{-1} cm^{-1})	λ_F (nm)	ν_A–ν_F (cm^{-1})	Φ_F[a]
2	524	85,497	540	565	1
4	524	81,280	539	531	0.04
5	524	78,846	542	634	0.03

[a] Φ_F is relative quantum yield of fluorescence calculated using compound **2** as standard.

3.3. Photophysical characterization of the dyes

The solubility of the perylene derivatives in different solvents was tested at concentration 0.1 mg mL^{-1} at room temperature (see Table 1). As can be seen from the data in Table 1 the starting perylene diimide **3** is insoluble in common organic solvents while the novel compounds **4** and **5** are well soluble. The improved solubility of the perylene derivatives **4** and **5** may be attributed to the introduction of swallow-tail branches that reduced the interaction between perylene rings with the solvent. Furthermore, as can be seen from the data presented in Table 1, the different terminal groups gave strong influence on the solubility of novel compounds **4** and **5**. The tetraester **4** was well soluble in chlorinated hydrocarbons (chloroform,

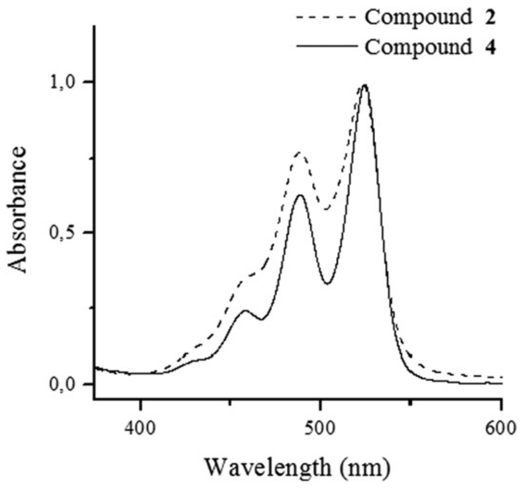


Fig. 2. Normalized absorption spectra of compounds 2 and 4 in DMF solution.

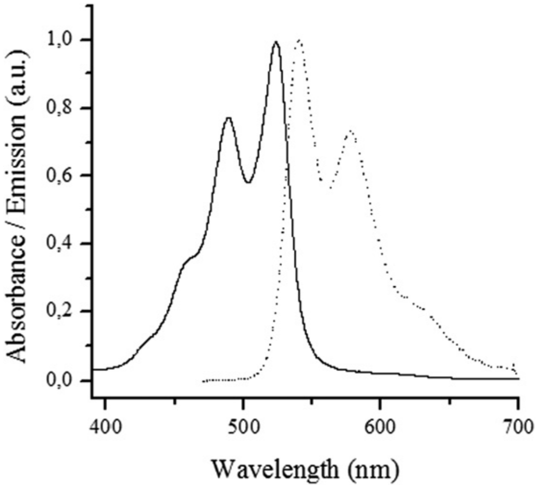


Fig. 3. Normalized absorption and fluorescence spectra of compound 2 in DMF solution.

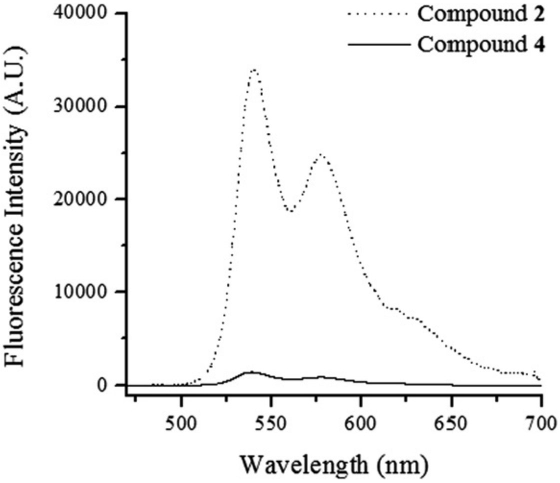


Fig. 4. Normalized to the optical density fluorescence spectra of compounds 2 and 4 in DMF solution.

dichloromethane and dichloroethane), while the amine terminated compound **5** was insoluble in these solvents. Also, unlike compound **5**, tetraester **4** was not soluble in water and alcohols.

The basic photophysical characteristics of the examined compounds **2**, **4** and **5** such as absorption (λ_A) and fluorescence (λ_F) maxima, Stokes shift (ν_A–ν_F) and quantum yield of fluorescence (Φ_F) were measured in DMF and presented in Table 2.

Data presented in Table 2 and Fig. 2 showed that the different alkyl substituents at the perylene tetracarboxydiimide *N*-position (compounds **2**–**5**) did not affect the energy and the shape of the dyes' absorption bands.

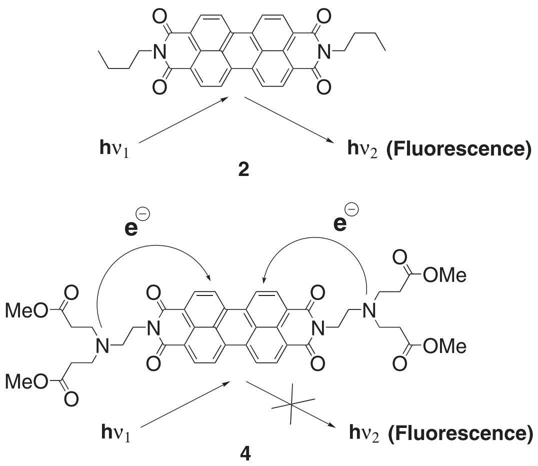
The compounds under study showed typical for the perylene tetracarboxydiimides fluorescence spectra (λ_{ex} = 460 nm) with three bands at about 540, 578 and 620 nm, as the highest intensity was observed at the lowest wavelength band (λ_F = 540 nm) [50]. The substituents at the *N*-position did not affect the energy of the dyes' fluorescence maximum. In all cases the shape and the maximum of the fluorescence band did not depend on the excitation wavelength. Fig. 3 presents the normalized absorption and emission spectra of perylene diimide **2** in DMF solution as a typical example for the spectra of all compounds under study. The fluorescence band is the mirror image of the absorption and no concentration effects on the shape of the fluorescence bands were observed for $C < 10^{-5}$ mol L^{-1}.

The Stoke's shift (ν_A–ν_F) is important parameter for the fluorescent compounds that indicates the differences in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1. The Stoke's shifts (cm^{-1}) were calculated by Eq. (1).

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \qquad (1)$$

The Stoke's shift values are between 531 and 634 cm^{-1}, which corresponds to the results for other perylene tetracarboxydiimide derivatives [50] and these values do not indicate remarkable changes in the geometry of the first singlet excited state due to the excitation.

As can be seen from the data in Table 2, the quantum yield of fluorescence of perylene diimides **4** and **5** are lower in comparison with the data for compound **2**, not containing tertiary amine moiety. This phenomenon might be caused by the possible PET process from the amine receptor to the perylene diimide fluorophore through the ethylene spacer. Thus the fluorescence of the perylene diimide fluorophores **4** and **5** is quenched (Scheme 5, Fig. 4), which was the reason to investigate their photophysical



Scheme 5.

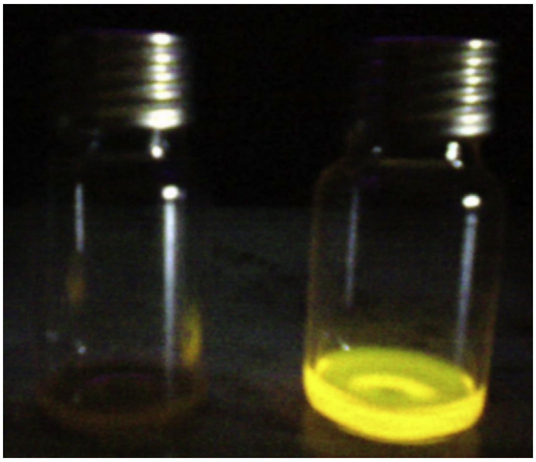


Fig. 5. Compound 4 in DMF solution (left sample) and in DMF after addition of HCl (right sample).

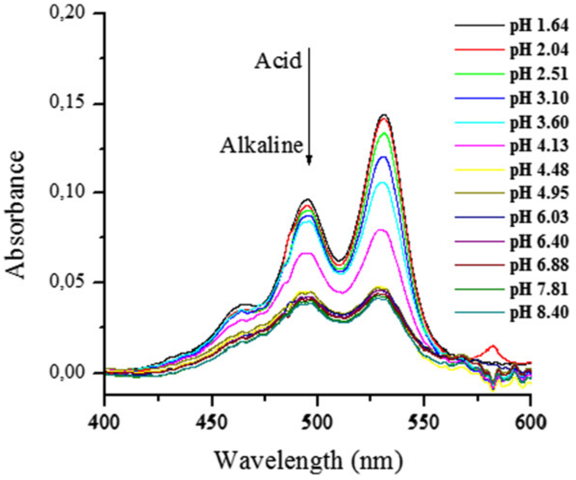


Fig. 6. Changes in the absorption intensity of 4 in water/DMF (1:1, v/v) as a function of pH.

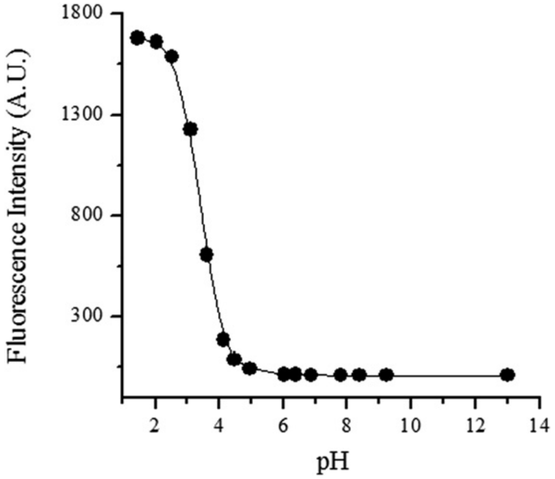


Fig. 8. Changes in the fluorescence intensity ($\lambda_F = 545$ nm) of 4 in water/DMF (1:1, v/v) as a function of pH.

behaviour at different pH values and in the presence of transition metal ions.

3.4. Influence of pH on the fluorescence properties of the dyes

The PET process can be disallowed after protonation of the electron donating tertiary amine receptor in acid media. Because of this, compound **4** shows weak fluorescence emission in DMF solution (Fig. 5, left sample) and strong emission after acidification of the solution (Fig. 5, right sample). The last experiment clearly illustrates the potential of compound **4** as highly efficient "*off–on*" pH chemosensing material.

Photophysical characteristics of perylene diimides **4** and **5** as a function of pH were investigated in water/DMF (1:1, v/v) solution. In order to receive a more complete comparative picture for the influence of the nitrogen donor (amine receptor) to the perylene diimide fluorophore, the reference compound **2**, not containing amine receptor in its molecule, was involved in the present study.

The absorption spectra of **2**, **4** and **5** did not show any pH-dependent band shifts as the perylene-3,4,9,10-tetracarboxydiimide fluorophore does not give rise to ICT excited states. However, in the case of **4** and **5**, significant pH-dependent changes in absorption band intensities were observed (Fig. 6), which suggest reversible aggregation processes at alkaline pH values.

Due to the aggregation the absorption in alkaline media was decreased 4 times for **4** and 1.3 times for **5**, in comparison with their absorptions in acid media. Analysis of these absorbance (A) changes according to Eq. (2) [12] gives the pK_a values 3.1 and 1.9, respectively.

$$\log[(A_{\max} - A)/(A - A_{\min})] = \mathrm{pH} - EK_a \qquad (2)$$

The fluorescence spectra of compounds **2**, **4** and **5** were also recorded in water/DMF (4:1, v/v) solution at different pH values. *N,N'*-(*n*-Butyl)-perylene diimide **2**, which lacks the amine receptor, did not show any changes in emission properties as a function of pH. In contrast to the above result, in alkaline solution for compounds **4** and **5** only a weak emission was observed between 500 and 700 nm, with λ_F at 545 nm. However, upon acidification the emission was gradually increased as demonstrated in Figs. 7 and 8. After careful titration to pH *ca.* 2.0, the emission intensity of perylene diimides had enhanced more than hundred times (FE = 184). This fact is due to the two effects – reversible aggregation and PET quenching at alkaline pH values, which do not take

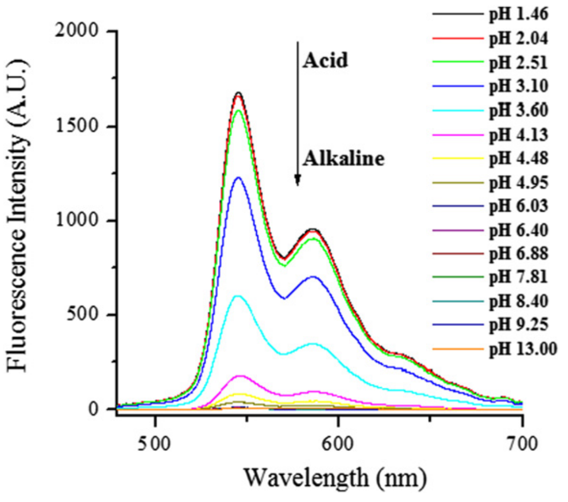


Fig. 7. Fluorescence spectra of 4 in water/DMF (1:1, v/v) in pH range *ca.* 1.5–13.0 ($\lambda_{ex} = 460$ nm).

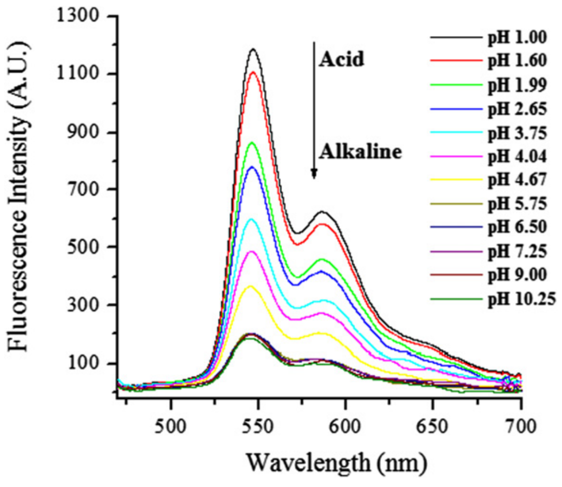


Fig. 9. Fluorescence spectra of 5 in water/DMF (1:1, v/v) in pH range *ca.* 1.0–10.0 ($\lambda_{ex} = 465$ nm).

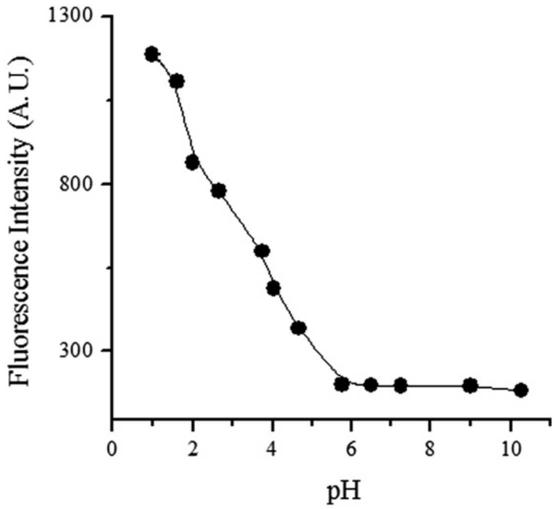


Fig. 10. Changes in the fluorescence intensity ($\lambda_F = 546$ nm) of 5 in water/DMF (1:1, v/v) as a function of pH.

place in acid media. As the aggregation quenches 4 times the fluorescence of **4** in alkaline media (Fig. 6), consequently the PET quenching effect is 46 times.

The pH dependence of the fluorescence properties of dendrimer **5** as a function of pH in water/DMF (1:1, v/v) is illustrated in Figs. 9 and 10. As can be seen in acid media the fluorescence intensity of dendrimer **5** is 6.4 times higher than in alkaline media. These changes are of such magnitude that they can be considered as representing two different "*states*", where the fluorescence emission is "*switched off*" in alkaline solution and "*switched on*" in acidic solution. The lower value of FE for compound **5** as compared to that for **4** probably is due to the conformational differences, which could be related to the increase the distance between the tertiary amine (receptor) and fluorophore in **5**. Also, the more flexible PAMAM scaffold is able to induce energy loses thus reducing the quantum yield of fluorescence in "on-state" of PAMAM compound **5**, which results in lower FE value.

Taking the part of the graphs located between pH 2 and 6, the pK_a values of compounds **4** and **5** have been calculated by the Eq. (3) [12].

$$\log[(I_{F\max} - I_F)/(I_F - I_{F\min})] = \mathrm{pH} - \mathrm{p}K_a \quad (3)$$

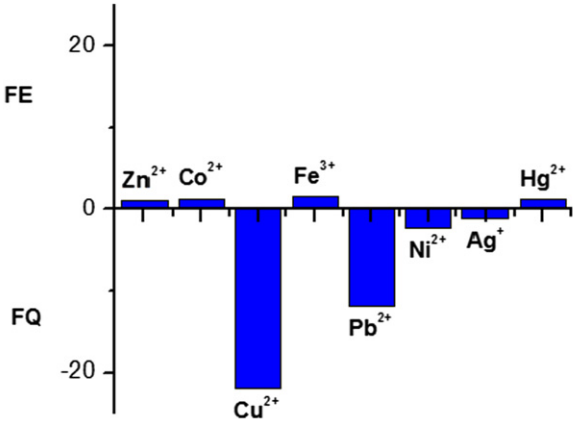


Fig. 11. Effect of the metal cations at concentration $c = 2 \times 10^{-6}$ mol L^{-1} on the fluorescence of 4 ($c = 10^{-6}$ mol L^{-1}) in DMF solution.

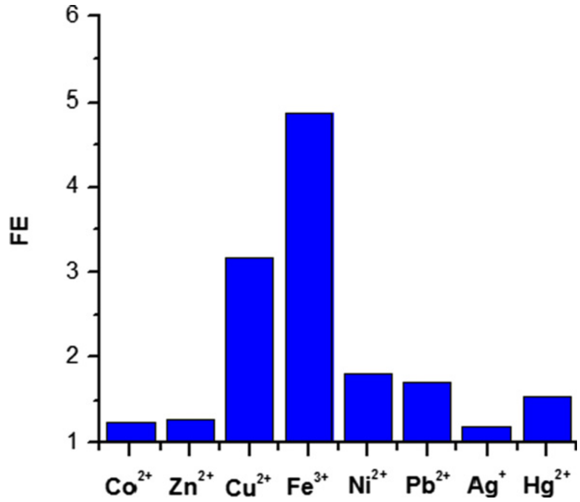


Fig. 12. Effect of the metal cations at concentration $c = 2 \times 10^{-6}$ mol L^{-1} on the fluorescence of 5 ($c = 10^{-6}$ mol L^{-1}) in DMF solution.

The determined pK_a values of 1.8 and 4.1 for **5** and 3.4 for **4** indicate that the amine branching perylene diimides would be able to act as efficient "*off–on*" switchers for pH. The lower pK_a value of 1.8 detected for **5** is similar to the value calculated using Eq. (2) and probably is characteristic of the aggregation.

3.5. *Influence of metal cations on the fluorescence intensity of the dyes*

The signaling fluorescent properties of novel perylene diimides **4** and **5** in the presence of transition metal ions have been investigated spectrophotometrically in DMF with regard to their potential application as PET sensors. DMF has been chosen in all measurements since it is able as a polar solvent to stabilize the dye charge separated state thus favouring the fluorescence switching by PET process. Also DMF guarantees a good solubility of the dye ligands, used metal salts and the respective complexes. Experiments have been performed in the presence of different metal cations: Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Ag^{+} and Ni^{2+}.

The above metal cations induced negligible changes in the absorption spectra of **4** and **5**. The enhancement (FE) and the quenching (FQ) of the fluorescence emission have been used as a qualitative parameter. The FE = I/I_o is determined as a ratio between the maximum fluorescence intensity (I - after the metal ion addition) and the minimum fluorescence intensity (I_o - free of metal cations solution). The FQ = I_o/I has been determined from the ratio between the maximum fluorescence intensity (I_o - solution free of metal cations) and the fluorescence intensity in the presence of metal cations (I). Figs. 11 and 12 present the calculated FE and FQ values for perylene diimides **4** and **5**.

As can be seen the novel perylene diimides **4** and **5** exhibit sensor selectivity. In DMF solution of tetraester **4**, the fluorescence quenching was observed only upon the addition of Cu^{2+} and Pb^{2+} (FQ = 22 and 12 respectively), while the other metal ions produced a negligible effect (Fig. 11). In contrast of the fluorescence behaviour of tetraester **4**, after addition of metal ions to the DMF solution of PAMAM dendrimer **5** (Fig. 12), the fluorescence of the latter was enhanced with pronounced selectivity to Cu^{2+} and Fe^{3+} (FE = 3.2 and 4.9, respectively).

The quenching effect of Cu^{2+}, Pb^{2+} and Ni^{2+} in DMF solution of **4** suggests that the tertiary amine is not involved in the coordination with metal ions in contrast to **5** at the same conditions. This is probably due to that the ester groups in **4** hindered the tertiary amine and in the presence of metal ions the PET quenching process from the amine receptor to the fluorophore core is still there. Also, the specific interaction between fluorophore **4** and Cu^{2+}, Pb^{2+}, Ni^{2+} causes an additional quenching process with well pronounced efficiency toward Cu^{2+} ions. Most likely the coordination occurring in the ester branches of **4** with Cu^{2+}, Pb^{2+} and Ni^{2+} ions is followed by an electron transfer or energy transfer from the fluorophore excited state to the metal complex, which quenches the fluorescence without any change in the maxima of the fluorescence and absorption spectra.

4. Conclusions

In this paper, we have given a comprehensive account of the design and synthesis of two new PET perylene diimide sensors for protons and transition metal ions. The novel compounds are based of branched perylene diimide core, containing tetraester and PAMAM wedges. Due to their long alkylester and alkilamine terminal groups the synthesized compounds show good solubility in organic solvents. Their photophysical properties were studied in both DMF and water/DMF (4:1, v/v) solution. The core emission intensity of novel systems had enhanced in the pH range from 10 to 2 − FE = 6.4 for PAMAM-branched dye **5** and FE = 184 for tetraester compound **4**. The determined pK_a values of 3.1 for **4** and 4.1 for **5** indicate that they would be able to act as highly efficient "off–on" switches for pH. Novel perylene diimides **4** and **5** showed sufficient sensor selectivity towards metal ions. In the presence of Cu^{2+} and Pb^{2+} tetraester quenched its fluorescence intensity (FQ = 22 and 12 respectively), while PAMAM-branched dye enhanced its fluorescence intensity with pronounced selectivity to Cu^{2+} and Fe^{3+} (FE = 3.2 and 4.9, respectively). The quenching effect of Cu^{2+}, Pb^{2+} and Ni^{2+} in DMF solution for dye **4** probably is due to that the ester groups hindered the tertiary amine and in the presence of metal ions the PET quenching process from the amine receptor to the fluorophore core is still there. The other reason for fluorescence quenching in compound **4** would be the electron or energy transfer from the fluorophore excited state to the metal complex. These results demonstrate the potential of the novel perylene diimides to detect metal ions with pronounced selectivity towards Cu^{2+}, Pb^{2+} and Fe^{3+}.

Acknowledgements

This work was supported by the National Science Foundation of Bulgaria (project DVU-10-0195). Authors also acknowledge the Science Foundation at the University of Chemical Technology and Metallurgy (Sofia, Bulgaria).

References

[1] Tian H, Liu P-H, Zhu W, Gao E, Wu D-J, Cai S. J Mater Chem 2000;10:2708.
[2] Zafer C, Karapire C, Sariciftci N, Icli S. Sol Energy Mater Sol Cells 2005;88:11.
[3] Fortage J, Sèverac M, Houarner-Rassin C, Pellegrin Y, Blart E, Odobel F. J Photochem Photobiol A Chem 2008;197:156.
[4] Singh T, Erten S, GuËnes S, Zafer C, Turkmen G, Kuban B, et al. Org Electron 2006;7:480.
[5] Hosoi Y, Tsunami D, Ishii H, Furukawa Y. Chem Phys Lett 2007;436:139.
[6] Zhang Y, Seo H-S, An M-J, Choi J-H. Org Electron 2009;10:895.
[7] Zhang X, Wu Y, Li J, Li Fan, Li M. Dyes Pigm 2008;76:810.
[8] Angadi M, Gosztola D, Wasielewski M. Mater Sci Eng B 1999;63:191.
[9] Pan J, Zhu W, Li S, Zeng W, Cao Y, Tian H. Polymer 2005;46:7658.
[10] Sakong C, Kim Y, Choi J, Yoon C, Kim J. Dyes Pigm 2011;88:166.
[11] Choi J, Sakong C, Choi J-H, Yoon C, Kim J. Dyes Pigm 2011;90:82.
[12] Daffy L, de Silva A, Gunaratne H, Huber C, Lynch P, Werner T, et al. Chem A Eur J 1998;4:1810.
[13] Feng L, Chen Z. Sensors Actuators B 2007;26:600.
[14] Yan L, Yang L, Lan J, You J. Sci China Ser B Chem 2009;52:518.
[15] Cotlet M, Vosch T, Habuchi S, Weil T, Müllen K, Hofkens J, et al. J Am Chem Soc 2005;127:9760.
[16] Pan J, Zhu W, Li S, Xu J, Tian H. Eur J Org Chem 2006;4:986.
[17] Yukruk F, Dogan A, Canpinar H, Guc D, Akkaya E. Org Lett 2005;7:2885.
[18] Würthner F. Chem Commun; 2004:1564.
[19] Yang L, Shi M, Wang M, Chen H. Tetrahedron 2008;64:5404.
[20] Sun R, Xue C, Owak M, Peetz R, Jin S. Tetrahedron Lett 2007;48:6696.
[21] Mayorova J, Troshin P, Peregudov A, Peregudova S, Kaplunova M, Lyubovskaya R. Mendeleev Commun 2007;17:156.
[22] Zhang Y, Xu Z, Cai L, Lai G, Qiu H, Shen Y. J Photochem Photobiol A Chem 2008;200:334.
[23] Gillies E, Frèchet J. DDT 2005;10:35.
[24] Wurm F, Frey H. Prog Polym Sci 2011;36:1.
[25] Qu J, Pschirer N, Liu D, Stefan A, De Schryver F, Müllen K. Chem A Eur J 2004; 10:528.
[26] Dirksen A, De Cola L. C R Chim 2003;6:873.
[27] Betley T, Hessler J, Mecke A, Holl M, Orr B, Uppuluri S, et al. Langmuir 2002; 18:3127.
[28] Ghosh S, Banthia A, Chen Z. Tetrahedron 2005;61:2889.
[29] Lee D, Kim J, Park H, Jun Y, Hwang R, Lee W-Y, et al. Synth Met 2005;150:93.
[30] Grabchev I, Chovelon J-M, Bojinov V, Ivanova G. Tetrahedron 2003;59:9591.
[31] Staneva D, McKena M, Bosch P, Grabchev I. Spectrochim Acta Part A 2010;76: 150.
[32] Bojinov V, Georgiev N, Nikolov P. J Photochem Photobiol A Chem 2008;193: 129.
[33] Georgiev N, Bojinov V, Nikolov P. Dyes Pigm 2009;81:18.
[34] Georgiev N, Bojinov V. Dyes Pigm 2010;84:249.
[35] Georgiev N, Bojinov V, Nikolov P. Dyes Pigm 2011;88:350.
[36] Georgiev N, Bojinov V, Marinova N. Sensors Actuators B Chem 2010;150:655.
[37] Mohr G. Sensors Actuators B Chem 2005;107:2.
[38] de Silva A, McCaughan B, McKinney B, Querol M. Dalton Trans; 2003:1902.
[39] Callan J, de Silva A, Magri D. Tetrahedron 2005;61:8551.
[40] Magri D, Vance T, de Silva A. Inorg Chim Acta 2007;360:751.
[41] de Silva A, Vance T, West M, Wright G. Org Biomol Chem 2008;6:2468.
[42] de Silva A, Uchiyama S. Top Curr Chem; 2010. doi:10.1007/128_2010_96.
[43] Tian H, Gan J, Chen K, He J, Song Q, Hou X. J Mater Chem 2002;12:1262.
[44] Ramachandram B. J Fluoresc 2005;15:71.
[45] Xu Y, Zheng L, Huang X, Cheng Y, Zhu C. Polymer 2010;51:994.
[46] Lu X, Zhu W, Xie Y, Li X, Gao Y, Li F, et al. Chem Eur J 2010;16:8355.
[47] Lee H, Moon B, Ko H, Choi W, Kim S- H. Pyrrole derivative and photosensitive film using the same; 2008, Nov 4. US 7446166.
[48] de Silva A, Gunaratne H, Habib-Jiwan J-L, McCoy C, Rice T, Soumillion J-P. Angew Chem Int Ed Engl 1995;34:1728.
[49] Lukáč I, Langhals H. Chem Ber 1983;116:3524.
[50] Pasaogullari N, Icil H, Demuth M. Dyes Pigm 2006;69:118.