

# Synthesis and properties of the bifunctional luminophors 3-[4-(4'-*N,N*-dimethylaminophenyl)butyl]perylene and 3-(4'-*N,N*-dimethylaminophenyl)perylene

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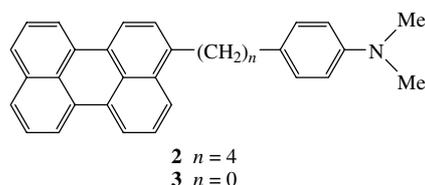
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DOI: 10.1070/MC2006v016n04ABEH002299

Luminophors of the perylene series containing the *N,N*-dimethylaniline residue in their molecules have been synthesised for the first time; spectral and luminescent properties of these compounds have been studied.

Bimolecular electron transfer (ET) reactions have been investigated very intensively for the last 40 years.<sup>1–6</sup> However, some problems in this area still remain unsolved. In particular, the rate constant of charge separation (CS) becomes inaccessible when the process of ET is diffusion-controlled. Yoshihara and co-workers<sup>7</sup> proposed to study the CS dynamics above the diffusion limit using a quencher as a solvent. This approach was used by Vauthey's group to investigate the ET quenching of perylene **1** and its derivatives in substituted anilines as a solvent.<sup>6,8,9</sup> The quenching dynamics was rationalised in assumption of three types of donor solvent molecules (D, substituted aniline) surrounding the acceptor (A, perylene or its derivatives).

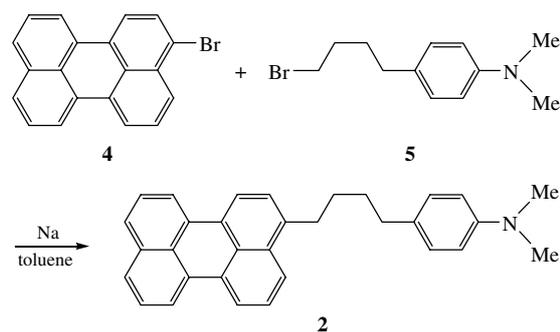


One could obtain supplementary information studying intramolecular CS reaction in bifunctional systems (D–X–A). For this purpose, we have carried out a directed synthesis of 3-[4-(4'-*N,N*-dimethylaminophenyl)butyl]perylene **2** [ $X = (\text{CH}_2)_4$ ] and 3-(4'-*N,N*-dimethylaminophenyl)perylene **3**.

3-Bromoperylene **4** was chosen as a key intermediate for target compounds **2** and **3**. Aryl halide **4** was obtained by selective bromination of perylene **1** with *N*-bromosuccinimide (NBS) in DMF.<sup>10,11</sup>

Alkyl derivative **2** was synthesised from bromoperylene **4** in one stage by the Wurtz–Fittig reaction. For this purpose, **4** was coupled with 4-(4'-*N,N*-dimethylaminophenyl)butyl bromide **5**<sup>12</sup> under the action of Na in toluene at a high temperature (Scheme 1). The reaction was accompanied by side processes, and the yield of **2** did not exceed 12%.<sup>†</sup> High solubility of **2** in concentrated

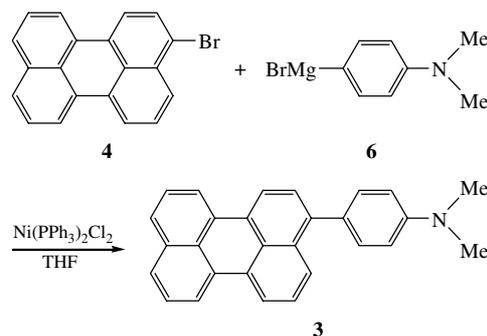
hydrochloric acid helped us to identify **2** in the reaction mixture. This identification facilitated the subsequent chromatographic isolation of the product.



Direct bonding between perylene and dimethylaniline residues was achieved by catalytic cross-coupling of bromoperylene **4** with 4-*N,N*-dimethylaminophenylmagnesium bromide **6** using a well-known synthetic procedure.<sup>13</sup> It was found that **4** reacts vigorously with an excess of **6** in THF at 65 °C, Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> being used as a catalyst (Scheme 2). According to TLC monitoring, this reaction accomplished quantitatively. The yield of arylperylene **3** after chromatographic purification and subsequent crystallization amounted to 34.2%.<sup>‡</sup> Grignard reagent **6** was obtained by the interaction of Mg with 4-bromo-*N,N*-dimethylaniline in THF.<sup>14</sup>

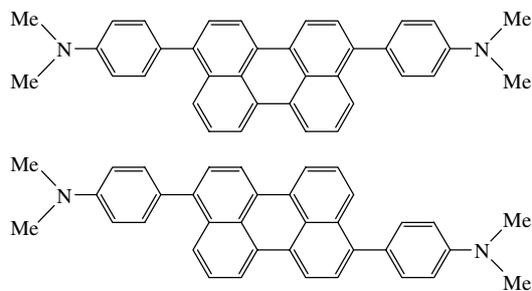
It had been found that insertion of two dimethylaniline substituents into a perylene residue may occur under analogous conditions. Investigating chemical behaviour of the mixture of 3,9- and 3,10-dibromoperylene **7**<sup>15</sup> (molar ratio between isomers being ~ 1:1) under conditions of arylperylene **3** synthesis, we obtained bis(dimethylaniline) perylene derivatives **8** in 22.1% yield.<sup>§</sup>

The product was identified by TLC as an individual compound. In the course of chromatographic purification, it behaves in a similar way. However, the <sup>1</sup>H NMR data allow one to assume that **8** is a mixture of two isomers, 3,9-bis(4'-*N,N*-dimethylaminophenyl)- and 3,10-bis(4'-*N,N*-dimethylaminophenyl)perylene, in a molar ratio of ~1:1. Attempts to separate these isomers were unsuccessful. Dihaloperylene **7** was synthesised



<sup>†</sup> <sup>1</sup>H NMR spectra of the synthesised compounds were measured using a Bruker AV300M spectrometer in CDCl<sub>3</sub> at room temperature. Mass spectra were recorded using a VG7070e spectrometer. The course of reactions and the purity of the products were controlled using TLC monitoring.

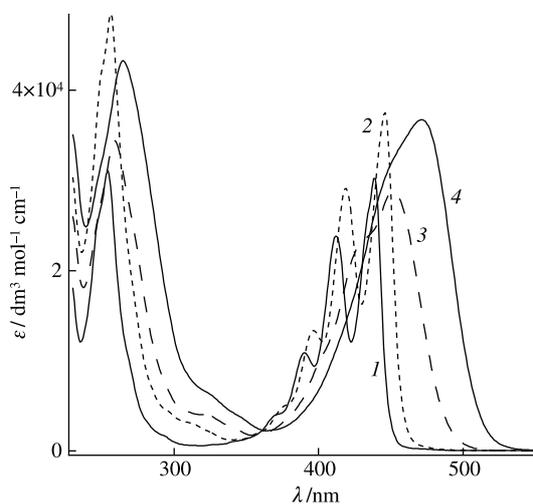
**Synthesis of 3-[4-(4'-*N,N*-dimethylaminophenyl)butyl]perylene **2**.** 0.793 g (2.40 mmol) of 3-bromoperylene **4**<sup>10</sup> and 1.360 g (5.31 mmol) of 4-(4'-*N,N*-dimethylaminophenyl)butyl bromide **5**<sup>12</sup> in 30 ml of anhydrous toluene was stirred under argon atmosphere at 110 °C, while an excess amount of Na as small pieces (up to 1 g) was added. The transformation of **4** into **2** was monitored using TLC (total time of stirring was 30 min). Then, the reaction mixture was cooled and filtered, and the precipitate was washed with a large amount of benzene. The solvent was removed in a vacuum, and the residue was chromatographed on silica gel in benzene. 0.120 g (11.7%) of **2** was obtained, mp 130–132 °C (from benzene). <sup>1</sup>H NMR,  $\delta$ : 1.68–1.89 [m, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>], 2.59 [t, 2H, CH<sub>2</sub>-C(1'),  $J$  7.2 Hz], 2.90 [s, 6H, NMe<sub>2</sub>], 3.03 [t, 2H, C(3)-CH<sub>2</sub>,  $J$  7.1 Hz], 6.70 [d, 2H, H(3'), H(5')],  $J$  8.3 Hz], 7.07 [d, 2H, H(2'), H(6')],  $J$  8.3 Hz], 7.31 [d, 1H, H(2)],  $J$  7.7 Hz], 7.42–7.54 [m, 3H, H(5), H(8), H(11)], 7.61–7.69 [m, 2H, H(9), H(10)], 7.85 [d, 1H, H(4)],  $J$  8.4 Hz], 8.07–8.24 [m, 4H, H(1), H(6), H(7), H(12)]. MS,  $m/z$  (%): 427 (80, M<sup>+</sup>), 265 (42), 134 (100).



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by the interaction of perylene **1** with two molar equivalents of NBS in DMF.

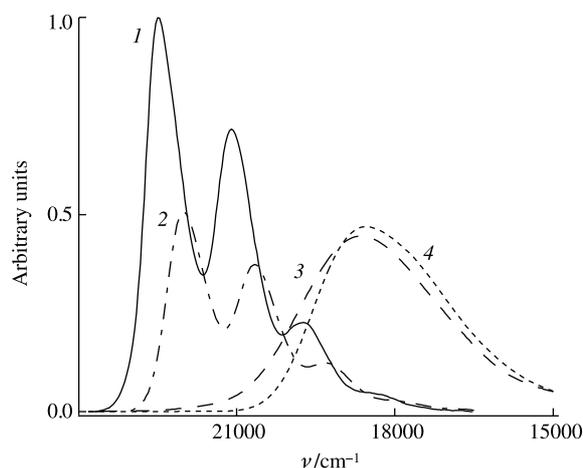
Crystalline compounds **2** and **3** are light yellow and red-orange, respectively. Deep colour of **3**, as well as **8**, is due to the direct bonding of perylene and dimethylaniline residues resulting in electronic interaction between them. It is indicative that  $^1\text{H NMR}$  signals from protons of dimethylaniline substituent in **3** (doublets) lie in a weaker field as compared to the analogous signals of the same protons in **2**: this difference exceeds to 0.3 ppm for protons, which are close to the perylene nucleus, whereas for further protons it equals 0.17 ppm. At the same time,  $^1\text{H NMR}$  spectra of **2** and **3** do not show any significant difference in the positions of the signals from the perylene residue protons.



**Figure 1** Electronic absorption spectra of perylenes (1) **1**, (2) **2**, (3) **3** and (4) **8** in  $\text{CHCl}_3$  at room temperature.

‡ *Synthesis of 3-(4'-N,N-dimethylaminophenyl)perylene 3.* 4-*N,N*-Dimethylaminomagnesium bromide **6**<sup>14</sup> was obtained in anhydrous THF by interaction of 2.033 g (10.17 mmol) of 4-bromo-*N,N*-dimethylaniline and 0.245 g (10.21 mmol) of disperse Mg shavings. Newly prepared and filtered solution of **6** in 15 ml of anhydrous THF was added to 0.540 g (1.63 mmol) of 3-bromoperylene **4**<sup>10</sup> in 25 ml of anhydrous THF in the presence of 0.068 g (0.10 mmol) of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ . Reaction mixture was stirred under Ar atmosphere at 65 °C for 30 min, cooled and diluted with water to 220 ml volume. The precipitate was filtered off, washed with water and dried. After chromatography on silica gel in benzene and vacuum evaporation, 0.207 g (34.2%) of crystalline **3** was isolated, mp 277–278 °C (from benzene).  $^1\text{H NMR}$ ,  $\delta$ : 3.04 (s, 6H,  $\text{NMe}_2$ ), 6.87 [d, 2H, H(3'), H(5')],  $J$  8.2 Hz], 7.35–7.52 [m, 6H, H(2), H(5), H(8), H(11), H(2'), H(6')], 7.67 [d, 2H, H(9), H(10)],  $J$  7.9 Hz], 7.88 [d, 1H, H(4),  $J$  8.5 Hz], 8.15–8.26 [m, 4H, H(1), H(6), H(7), H(12)]. MS,  $m/z$  (%): 371 (100,  $\text{M}^+$ ), 355 (18), 326 (17), 186 (20), 163 (26).

§ *Mixture of 3,9-bis(4'-N,N-dimethylaminophenyl)perylene and 3,10-bis(4'-N,N-dimethylaminophenyl)perylene (molar ratio ~1:1) 8.* This mixture was prepared by the interaction of a mixture of 3,9- and 3,10-bromoperlenes **7**<sup>15</sup> (molar ratio of ~1:1) with 4-*N,N*-dimethylaminomagnesium bromide **6** in the presence of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  in THF at 65 °C, mp > 300 °C (decomp.).  $^1\text{H NMR}$ ,  $\delta$ : 3.04 (s, 12H,  $\text{NMe}_2$ ), 6.87 [d, 4H, H(3'), H(5')],  $J$  8.7 Hz], 7.31–7.49 [m, 8H, H(2), H(5), H(8), H(11), 2H(2'), 2H(6')], 7.82–7.92 [m, 2H, H(4), H(9) and H(4), H(10)], 8.14–8.26 [m, 4H, H(1), H(6), H(7), H(12)].

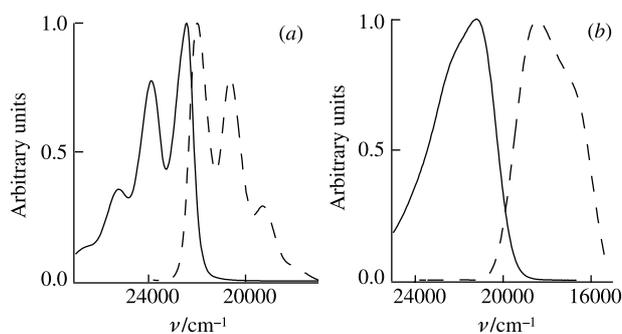


**Figure 2** Fluorescence spectra of perylenes (1) **1**, (2) **2**, (3) **3** and (4) **8** in  $\text{CHCl}_3$  ( $C = 10^{-6}$  mol  $\text{dm}^{-3}$ ) at room temperature detected upon 406 nm excitation and corrected for the spectral sensitivity of setup.

The structures of **2** and **3** were corroborated by mass-spectrometric data. There are signals of corresponding molecular ions in the mass spectra of these compounds,  $M = 427$  and  $M = 371$ . This signal is a primary one (100%) in the spectrum of **3**, while in the spectrum of **2** the most intense signal (100%) corresponds to an ion with a mass of 134.

Compounds **2**, **3**, **8** are highly photosensitive and decompose under irradiation with UV and visible light in a crystalline state, as well as being solvated in organic solvents or adsorbed on silica gel.

The absorption and fluorescence spectra of the synthesised compounds in  $\text{CHCl}_3$  and their comparison with the perylene spectra are displayed in Figures 1 and 2.¶ As one should expect, the absorption and fluorescence spectra of butyl derivative **2** are close to the spectra of perylene **1**, but shifted slightly (by about 400  $\text{cm}^{-1}$ ) to the red. The progressions with the average intervals of ~1430 and ~1360  $\text{cm}^{-1}$  were discerned in the absorption and fluorescence spectra of **1** and **2**, respectively. The only noticeable difference between **1** and **2** is the reduced quantum yield of the fluorescence of **2** (Table 1), most probably due to the intramolecular ET quenching. This assumption is very reasonable



**Figure 3** Absorption (solid lines) and fluorescence (dash lines) spectra of perylenes (a) **2** and (b) **3**.

¶ Electronic absorption spectra were obtained on a HP8453 spectrometer (200–800 nm). Fluorescence spectra were recorded as described elsewhere<sup>16</sup> using a 406 nm line of a high-pressure Hg lamp for excitation. The optical densities of the samples at 406 nm were 0.05–0.09, which correspond to very low concentrations of luminophores ( $\sim 10^{-6}$  mol  $\text{dm}^{-3}$ ).  $\text{CHCl}_3$  of analytical grade, which was purified additionally by fractional distillation, was used as a solvent. To remove oxygen, argon was bubbled through the samples for 20 min. Fluorescence spectra were corrected taking into account spectral sensitivity of the setup, which was determined in the range 390–650 nm using quinine bisulfate as a luminescent standard.<sup>17,18</sup> Fluorescence quantum yields of substituted perylenes **2–4** in  $\text{CHCl}_3$  ( $\varphi_F$ ) were determined from the formula  $\varphi_F = FA_0 n^2 \varphi_F^0 / AF_0 n_0^2$ , where the subscript 0 refers to perylene in cyclohexane ( $\varphi_F^0 = 0.94$ ),<sup>19</sup>  $A$  is the absorbance at the excitation wavelength,  $F$  is the integrated corrected fluorescence, and  $n$  is the refractive index of the solvent.

**Table 1** Maxima in the absorption ( $\nu_A$ ) and fluorescence ( $\nu_F$ ) spectra, 0–0 transitions ( $\nu_{0-0}$ ) and fluorescence quantum yields ( $\varphi_F$ ) of perylene **1** and its derivatives **2**, **3**, **8** in  $\text{CHCl}_3$ .

Compound	$\nu_A/\text{cm}^{-1}$	$\nu_F/\text{cm}^{-1}$	$\nu_{0-0}/\text{cm}^{-1}$	$\varphi_F$
<b>1</b>	22800	22470	22640	0.80±0.05
<b>2</b>	22440	21990	22230	0.45±0.03
<b>3</b>	22170	18630	20600	0.8±0.1
<b>8<sup>a</sup></b>	21230	18540	19900	0.8±0.1

<sup>a</sup>Mixture (~1:1) of isomers: 3,9- and 3,10-bis(4'-N,N-dimethylamino-phenyl)perylene.

since the intermolecular ET from dimethylaniline to the excited perylene was found to be very efficient.<sup>6,8,9</sup>

Unlike substituted perylene **2**, characterised by a significant overlap between the fluorescence and absorption spectra and a very small Stokes shift (~400  $\text{cm}^{-1}$ ) similar to the case of perylene, 3-aryl-substituted analogue **3** is characterised by a large Stokes shift of about 3500  $\text{cm}^{-1}$  (Figure 3). In addition, the spectra of **3**, as well as those of a mixture of disubstituted isomers **8**, have no noticeable vibrational structure. The quantum yield of fluorescence of **3**, as well as the effective quantum yield of a mixture of **8**, are close to unity (Table 1). Therefore, the insertion of an aniline substituent directly into the perylene residue leads to considerable changes in its electron structure and, in turn, to significant changes in spectral characteristics. The local fluorescence of perylene is totally absent and the new structureless fluorescence band can be assigned to a charge transfer state. A detailed investigation of the photophysics of these compounds will be published elsewhere.

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Received: 30th December 2005; Com. 05/2642

## Transformations of cyanoacetylenic alcohols in the presence of the cyanide ion

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DOI: 10.1070/MC2006v016n04ABEH002250

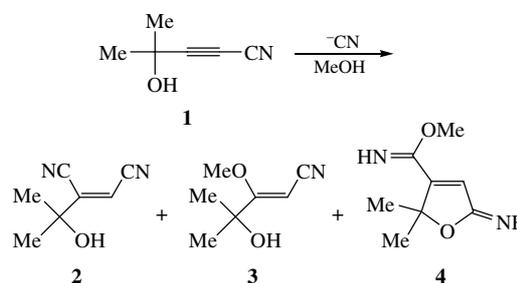
The transformation of 4-hydroxy-4-methylpent-2-ynenitrile in the presence of KCN in methanol (20–25 °C, 1 h) leads to (Z)-2-(1-hydroxy-1-methyl)but-2-enedinitrile, 4-hydroxy-3-methoxy-4-alkylalk-2-enenitrile and 2-imino-5,5-dimethyl-4-methoxy-carbimide-2,5-dihydrofuran. In dioxane at room temperature, KCN catalyses the auto-transformation of cyanoacetylene to 2,2-dimethyl-3,4-di(cyanomethylene)oxetane and 2,5-di(cyanomethylene)-3,3,6,6-tetramethyl-1,4-dioxane; in aqueous dioxane (20–25 °C, 4 h), the reaction affords 5-amino-2,2-dimethyl-3(2H)-furanone.

Cyanoacetylenes belong to the organic compounds found in space, and they are likely involved in the origination of life.<sup>1</sup> In turn, the cyanide ion in water tends to form complex molecules, such as amino acids and purine bases,<sup>2</sup> which play a key role in the functioning of living organisms. The reactions of cyanoacetylenes with the cyanide ion in water may also be expected to give functionalised nitrogen-containing compounds, such as aspartic acid, asparagine, cytosine *etc.*<sup>2</sup> Therefore, a systematic study of cyanoacetylene transformation in the presence of cyanides under biomimetic conditions may extend our knowledge of the organonitrogen matter evolution under prebiotic conditions.

Cyanoacetylenic alcohols,  $\text{R}^1\text{R}^2\text{C}(\text{OH})\text{C}\equiv\text{C}-\text{CN}$ , are simple Favorsky adducts of cyanoacetylene to aldehydes and ketones. They are the precursors of biologically important compounds related to ascorbic, penicillic, tetrionic acids and their thiol analogues.<sup>3,4</sup>

Here, the transformations of cyanoacetylenic alcohols in the presence of the cyanide ion observed on the example of 4-hydroxy-4-methylpent-2-ynenitrile **1** are discussed.

In methanol (20–25 °C, 1 h), cyanoacetylene **1** reacts with the cyanide ion to afford (Z)-dinitrile **2**, (Z)-3-methoxypentene-



Scheme 1

nitrile **3** and iminodihydrofuran **4** in a ratio of 2:2:1 (<sup>1</sup>H NMR, GC/MS) (Scheme 1).<sup>†</sup>

Dinitrile **2** is the expected adduct of  $-\text{CN}$  to the triple bond of **1**, while nitrile **3** results from similar addition of the methoxide ion to cyanoacetylene **1**.<sup>5</sup> The <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) spectrum of dinitrile **2** shows one olefin proton at 6.42 ppm, which is indicative of the formation of a single isomer. The latter has probably (Z)-configuration, if the reaction proceeds as normal concerted nucleophilic addition.<sup>6</sup> Iminodihydrofuran **4** is a product