

# Highly soluble perylene dye: tetrabenzyl 3,4,9,10-perylenetetracarboxylate

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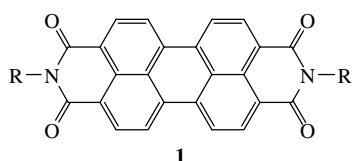
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We report on the preparation and spectroscopic characterization of a highly soluble perylene dye; the photophysical and electrochemical properties of this compound make promising its application in organic light-emitting devices.

Perylene-3,4,9,10-tetracarboxydiimides [perylene bis(imides)] **1** (Scheme 1) exhibit a unique combination of electrooptical and redox properties. Perylene bis(imides) are highly stable and widely used *n*-type materials for organic electronic devices such as solar cells, field-effect transistors and light-emitting diodes.<sup>1–6</sup> Perylene derivatives may also be used in liquid crystal displays<sup>7</sup> and in biomolecular chemistry as fluorescent labels.<sup>8,9</sup>



Scheme 1

The preparation and investigation of symmetrically and unsymmetrically substituted perylene bis(imides) was described previously.<sup>10–14</sup> However, most of the synthesised dyes possess low solubility in organic solvents; this is a serious drawback for their processing and material science applications.<sup>15</sup> To solve the solubility problem, bulky substituents can be introduced into the dye molecular framework. At the same time, bulky groups can prevent the  $\pi$ – $\pi$  stacking of dye molecules to result in improved solid-state fluorescence, which is an important prerequisite for the use of the material in organic light-emitting diodes (OLEDs).

The esters of 3,4,9,10-perylenetetracarboxylic acid can be an important class of highly soluble perylene dyes. However, just a low soluble methyl and few other simple alkyl esters of

this acid were synthesised and applied as materials in OLEDs so far, though their compositions and structures were not confirmed spectroscopically.<sup>16</sup> Here, we propose a simple method for the preparation of highly soluble perylene dyes starting from the potassium salt of 3,4,9,10-perylenetetracarboxylic acid **3**. In particular, tetrabenzyl 3,4,9,10-perylenetetracarboxylate **4** was synthesised (Scheme 2).

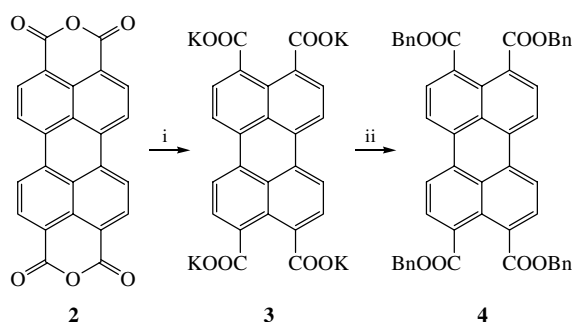
The crude potassium salt of 3,4,9,10-perylenetetracarboxylic acid **3** was prepared from dianhydride **2** (4 g, 10 mmol), which was dissolved in a 20% aqueous solution of potassium hydroxide (50 ml) with stirring at room temperature for 30 min. The addition of an acetone–isopropanol mixture (*ca.* 1:1 by volume, 1000 ml) resulted in the precipitation of a tetrapotassium salt, which was filtered off, dried in air and used without further purification.

The attempted synthesis of tetrabenzyl ester **4** by treatment of **3** with benzyl bromide and dry potassium carbonate under reflux in DMF resulted in the formation of an inseparable mixture of products. However, the use of chlorobenzene as a solvent improved the selectivity of the reaction and allowed for the preparation of compound **4**. According to an optimised procedure, a mixture of **3** (500 mg, 0.86 mmol), an excess of benzyl bromide (8 ml) and potassium carbonate (1.0 g) was heated at reflux in chlorobenzene (100 ml) for three days. The following chromatographic separation using toluene as an eluent afforded **4** as a bright orange solid in 57% yield.

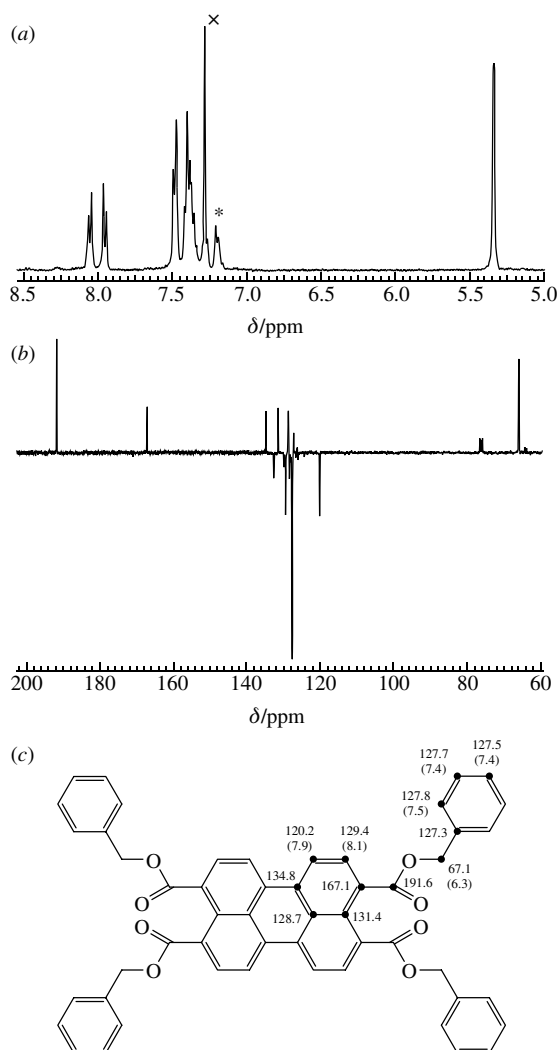
A modified synthetic procedure was used to shorten the synthesis time. The above mixture of reagents (salt **3**, benzyl bromide and  $K_2CO_3$ ) was initially stirred at room temperature in DMF (50 ml) for 5 h. Then, chlorobenzene (100 ml) was added, and the mixture was heated at reflux for 3 h. The chromatographic separation afforded compound **4** in 42% yield.

The tetrabenzyl 3,4,9,10-perylenetetracarboxylate **4** is readily soluble in low polarity organic solvents, such as toluene, chloroform and dichloromethane.<sup>†</sup> The  $^1H$  NMR spectrum of **4** consists of three sets of signals [Figure 1(a)]: a singlet from the benzyl  $CH_2$  group at 5.34 ppm, a typical set of two doublets due to the perylene core (8.05 and 7.95 ppm) and resonances corresponding to the phenyl protons (7.3–7.5 ppm). This spectrum proves  $D_{2h}$  symmetry of the molecule of **4**.

<sup>†</sup>  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 8.05 (d, 4H), 7.95 (d, 4H), 7.48 (d, 8H), 7.40 (m, 12H), 5.34 (s, 8H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$ : 191.65, 167.07, 134.8, 131.45, 129.44, 128.72, 127.76, 127.66, 127.54, 127.28, 120.23, 66.08.



Scheme 2 Reagents and conditions: i, 20% aq. KOH, room temperature, 30 min; ii,  $PhCH_2Br$ ,  $PhCl$ , reflux, 3 days.

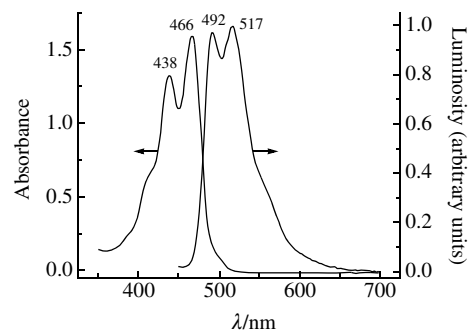


**Figure 1** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of **4** ('x' denotes the signals of  $\text{CHCl}_3$  in  $\text{CDCl}_3$ ; '\*' denotes the signals of residual toluene). (c) The assignment of the signals; bold circles point to carbon atoms and CH groups for which  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR shifts are given.

The  $^{13}\text{C}$  NMR spectrum of **4** recorded in APT regime demonstrates all signals expected for the suggested  $D_{2h}$  symmetrical structure of this compound [Figure 1(b)]. The assignment of the signals is given in Figure 1(c).

The solutions and solid powders of compound **4** are stable towards oxidation under ambient conditions. No degradation was observed by NMR in a dilute solution of **4** in toluene stored in air for six months. However, the compound is sensitive to hydrolysis at heating above  $50^\circ\text{C}$ ; therefore, the drying of solvents before use is desired.

Figure 2 shows the absorption and photoluminescence spectra of **4** in toluene. The absorption spectrum exhibits two major bands at 438 and 466 nm; the molar absorption coefficient at 466 nm is about  $2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The photoluminescence spectrum of **4** is a virtually accurate mirror image of the absorption spectrum and is represented by two main bands at 492 and 517 nm. It is remarkable that compound **4** demonstrates quite efficient photoluminescence from solid films in contrast to other perylene dyes. For example, reference  $N,N'$ -di(*n*-dodecyl)-perylene-3,4,9,10-tetracarboxylic diimide exhibited no fluorescence in the solid state. Emission from the solid films of **4** was observed at 600–650 nm, that is, ca. 100–150 nm red shifted in comparison with the solution-state photoluminescence spectrum. Most probably, this shift is a consequence of intermolecular interactions of dye molecules in columnar  $\pi$ -stuck aggregates formed in the solid



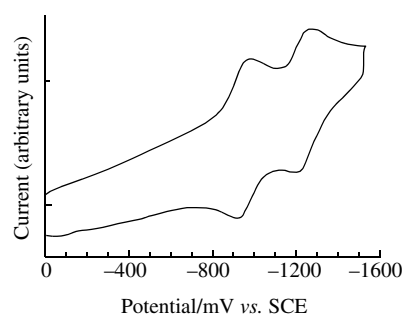
**Figure 2** Absorption (left) and photoluminescence (right) spectra of **4** in toluene.

phase.<sup>15,16</sup> The emission properties of compound **4** point to the possibility of its application as an emissive material or dopant in OLED structures.

The reduction potentials of compound **4** were investigated using cyclic voltammetry (CVA).<sup>‡</sup> The CVA curve (Figure 3) shows two reversible one-electron reduction peaks at  $E_{1/2 \text{ red } 1} = -0.95 \text{ V}$  and  $E_{1/2 \text{ red } 2} = -1.25 \text{ V}$  (in DMF, vs. SCE). These values are considerably more negative than the reduction potentials of perylene bis(imides); for example,  $N,N'$ -diphenylperylene-diimide undergoes one electron reductions at  $-0.51$  and  $-0.725 \text{ V}$  vs. SCE (in DMF).<sup>17</sup> Thus, compound **4** is a weaker electron acceptor than perylene bis(imides) because of the lack of the electron-withdrawing bis(imide) fragment in the molecule of ester **4**.

Compound **4** was tested as an acceptor material in model organic bulk heterojunction solar cells.<sup>18</sup> For this purpose, 26 mg of **4** and 5 mg of polyconjugated polymer MDMO-PPV (2-methoxy-5-[3',7'-dimethyloctyloxy]-*p*-phenylene vinylene) were dissolved in 1 ml of chlorobenzene. The resulting solution was spin-coated on an ITO substrate covered with PEDOT-PSS [hole transporting layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] and then aluminium was evaporated in a high vacuum ( $10^{-6} \text{ mbar}$ ) to give the top electrode. The photovoltaic devices exhibited very low performance; the best cells yielded an open circuit voltage of 520 mV, short circuit current densities of  $5 \times 10^{-3} \text{ mA cm}^{-2}$ , a fill factor of 26% and a calculated power conversion efficiency of  $\sim 7 \times 10^{-4}\%$ . For comparison, the best bulk heterojunction solar cells where perylene bis(imides) are acceptor materials give power conversion efficiencies as high as 1–1.9%;<sup>19</sup> thus, the use of **4** in photovoltaic devices can be considered low promising.

Our subsequent studies will be focused on the application of compound **4** and similar esters of 3,4,9,10-perylenetetracarboxylic acid as emitting materials or dopants in OLEDs.



**Figure 3** Cyclic voltammogram of **4** in DMF.

<sup>‡</sup> The cyclic voltammetry measurements were performed for ca.  $1 \times 10^{-3} \text{ M}$  solution of **4** in DMF in a cell equipped with glassy carbon working electrode ( $d = 2 \text{ mm}^2$ ), platinum wires as counter electrode, SCE as a reference electrode. Scan rate was  $200 \text{ mV s}^{-1}$ . The  $0.1 \text{ M}$  solution of  $\text{Bu}_4\text{NPF}_6$  was used as supporting electrolyte.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2007.05.008.

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