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Synthesis and electropolymerization of novel oligothiophene-functionalized perylene bisimides†

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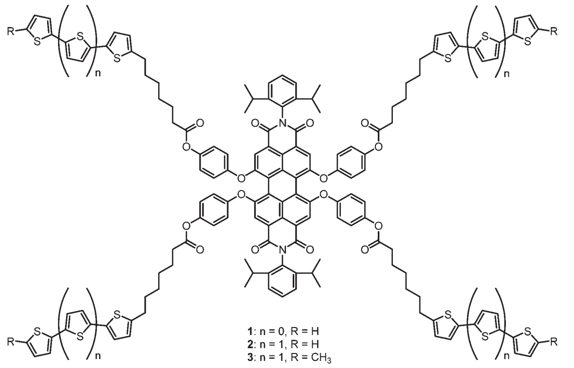
Fourfold oligothiophene-functionalized perylene bisimides have been synthesized by esterification of hydroxyphenoxy-substituted perylene bisimides and their optical properties as well as electrochemical polymerization properties have been investigated.

Incorporation of electron-rich and electron-poor dye molecules within a bulk material may lead to valuable electronic and photonic materials,[1–5] especially if one or both of the dye manifolds form an interpenetrating network in which photogenerated charge carriers exhibit high mobility. For example, in photorefractive materials a laser generates charge carriers which migrate in the presence of an external electric field to create holographic gratings.[4] On the other hand, in organic photovoltaics upon illumination by sunlight charge carriers are generated which have to migrate to the electrodes to provide a voltage.[5] Most currently applied materials are based on simple mixing of the required functional components and novel approaches by molecular and supramolecular engineering are just starting to emerge.[6,7] In this paper, we introduce molecules which contain four electron-rich oligothiophene units tethered to an electron-poor perylene bisimide dye and demonstrate that the oligothiophene units can be cross-linked by electrochemical means to give a polymeric network. This approach seems to be quite promising as it allows incorporation of those two classes of dyes that possess the highest p-type charge carrier mobility (*i.e.* oligothiophene)[8,9] and n-type charge carrier mobility (*i.e.* perylene bisimide)[9,10] within a single easily accessible material.

Oligothiophene-functionalized perylene bisimides **1–3** were synthesized by esterification of *N*,*N*′-bis(2,6-diisopropylphenyl)-1,6,7,12-tetra(4-hydroxyphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide[11] with ω-carboxyhexyl-α-bi- and terthiophenes[12] in the presence of DCC and DMAP as coupling reagents. The purification was achieved by conventional column chromatography (SiO_2) and the isolated yields of target compounds were around 50%.‡



The optical properties of oligothiophene-functionalized perylene bisimides **1–3** were investigated in dichloromethane (CH_2Cl_2) by UV/vis absorption as well as steady-state and time-resolved fluorescence spectroscopy. The representative spectra of terthiophene derivative **2** are depicted in Fig. 1. As can be seen, compound **2** shows two major absorption bands with maxima at 573 and 362 nm, respectively. The former is ascribed to the $S_0 \rightarrow S_1$ transition of perylene bisimide, while the latter is attributable to the $S_0 \rightarrow S_1$ transition of terthiophene moieties. The presence of oligothiophene units does not influence the absorption behaviour of the perylene chromophore and *vice versa*, implying negligible ground-state electronic interaction between these two chromophores. Steady-state fluorescence spectra show that all three oligothiophene-functionalized perylene bisimides **1–3** exhibit an intense perylene bisimide emission around 605 nm irrespective of the excitation wavelength. Upon irradiation at 360 nm, concomitant weak emission of the terthiophene units around 430 nm was also detected for compounds **2** and **3**.

Compared with 2,2′:5′,2″-terthiophene, the fluorescence of the terthiophene moieties in **2** is quenched by more than 85%. Fluorescence excitation spectra reveal an efficient fluorescence–resonance energy transfer (FRET) from the terthiophene functionalities to the perylene core. Because of the electron-richness of the oligothiophene groups, it is not surprising that photoinduced electron transfer (PET) processes reduce the luminescence of the perylene bisimide, leading to moderate quantum yields (Φ_F) of 0.26 for **1**, 0.25 for **2** and 0.21 for **3**, compared to > 0.90 for the parent chromophore.[13] Additional support for PET processes was obtained from time-resolved emission spectroscopy which showed a significant decrease in the fluorescence lifetime of the perylene bisimide chromophore for compound **2** ($\tau = 1.6$ ns in CH_2Cl_2) compared to the parent dye without oligothiophene substituents ($\tau = 5.5$ ns in CH_2Cl_2).

The redox behaviour of these oligothiophene-functionalized perylene bisimides has been investigated by cyclic voltammetry using a platinum disk ($\phi = 4$ mm) as working electrode. Fig. 2 illustrates the cyclic voltammograms of **2** and its polymerization in dichloromethane with 0.1 M $[Bu_4N][PF_6]$ as supporting electrolyte. The cyclic voltammogram of **2** (Fig. 2a) shows two reversible reduction waves at $E_{1/2} = -1.10$ and -1.31 V (*versus* Fc/Fc^+),

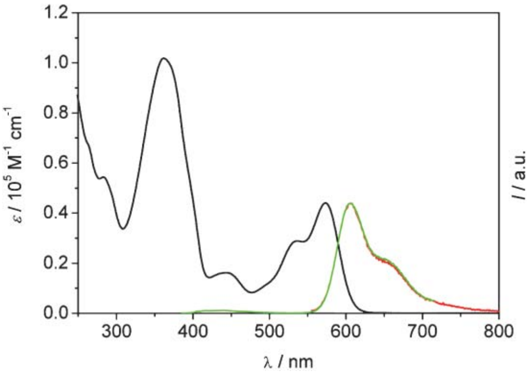


Fig. 1 UV/vis absorption and emission spectra of **2** in CH_2Cl_2. Emission spectra were recorded by irradiation at 360 nm (green line) and 545 nm (red line), respectively.

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† Electronic supplementary information (ESI) available: cyclic voltammograms of **1** and **3**; excitation and time-resolved emission spectra of **2**. See http://www.rsc.org/suppdata/cc/b4/b407551j/

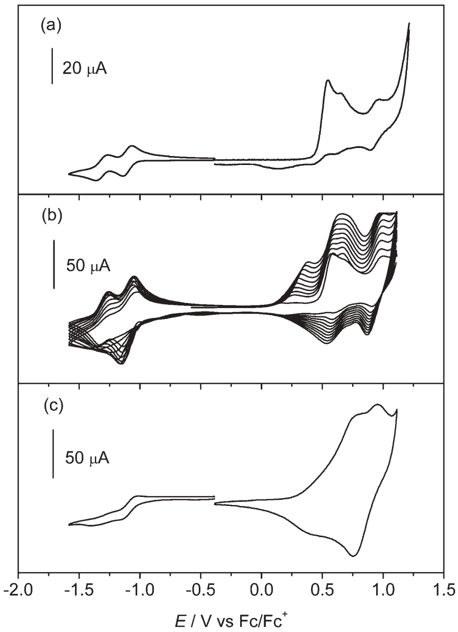

Fig. 2 Cyclic voltammograms of (a) terthiophene-functionalized perylene bisimide **2** (0.5 mM), (b) the potentiodynamic polymerization of **2** and (c) the polymer of **2** in monomer-free solution at room temperature (20 °C): 0.1 M $[Bu_4N][PF_6]$ in CH_2Cl_2, scan rate 100 mV s^{-1}.

which are typical for the reduction of perylene bisimides to radical anionic and dianionic species, respectively.[11,14] These two reduction waves are comparable to the perylene bisimides without terthiophene substituents, suggesting that the presence of terthiophene moieties does not affect the reduction process of the perylene bisimide core. The oxidation wave of terthiophene moieties appears at $E_{ox} = +0.55$ V, whose current intensity is almost four times that of the reduction current, confirming the electroactivity of all four terthiophene substituents. The oxidation wave at $E_{ox} = +0.97$ V should be ascribed again to the oxidation of the perylene bisimide moiety.

While the oxidation of methylterthiophene moieties in compound **3** is partially reversible (see ESI), the oxidation of terthiophene-functionalized perylene bisimide **2** leads to an electroactive film that is deposited on the working electrode. As shown in Fig. 2b, in the second cycle a new oxidation wave at +0.27 V appeared which should be assigned to the oxidation of α-sexithiophene (α-sexithiophene has an oxidation potential of 0.65 V *versus* Ag/AgCl,[15] which is recalculable to +0.29 V *versus* Fc/Fc^+), a follow-up product of the oxidative dimerization between radical cations of terthiophene. During the subsequent sweeps the current of the oxidation waves between 0 and 1.0 V increased substantially, indicating the formation of an electroactive polymeric network on the electrode. The current for the reduction waves of perylene bisimides, however, gradually decreased upon growth of the polymeric film. A similar polymerization process has also been observed for bithiophene-functionalized perylene bisimide **1**.

The polymer-doped electrode was investigated in a monomer-free CH_2Cl_2 solution with $[Bu_4N][PF_6]$ as supporting electrolyte. As can be seen from Fig. 2c, the film obtained is highly electroactive in the p-doping process, while less pronounced in the n-doping process. No significant changes in the features of the cyclic voltammograms were observed during repeated scanning, indicating the considerable stability of the film formed. One plausible explanation for the unsymmetric p-doping and n-doping processes is that the growth of the film leads to a regular arrangement of p-conducting oligothiophene aggregates on the electrode, while the perylene bisimide cores are embedded in the film structure in a disordered manner. Therefore, the ordered oligothiophene functions facilitate the charging and discharging in the p-doping process. Inversely, the n-doping process is unfavoured owing to the disordered perylene bisimides. Preliminary *in-situ* conductivity measurements of the polymer of **2** confirmed that the conductivity of the p-doped film is considerably higher than that of the n-doped film.[16]

In summary, we have presented herein a series of readily available oligothiophene-functionalized perylene bisimides, which exhibit promising optical and electrochemical properties. The electrochemical behaviour of these perylene bisimides was studied by cyclic voltammetry, showing that perylene bisimide-oligothiophene polymeric networks were formed which exhibit p-type conductivity. Further investigation of these and related oligothiophene-functionalized perylene bisimide materials is still underway.

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Notes and references

‡ Full synthetic details will be reported elsewhere. Selected data for **2**: ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.28 (s, 4H), 7.43 (t, 2H), 7.28 (d, 4H), 7.18 (d, 4H), 7.13 (d, 4H), 6.98 (m, 32H), 6.68 (d, 4H), 2.80 (t, 8H), 2.70 (m, 4H), 2.53 (t, 8H), 1.73 (m, 16H), 1.44 (m, 16H), 1.12 (d, 24H); MS (MALDI-TOF, dithranol): *m/z* 2578.0 $[M + H]^+$ (calcd for $C_{148}H_{130}N_2O_{16}S_{12}$: 2576.6); Anal. Calcd (%) for $C_{148}H_{130}N_2O_{16}S_{12}$: C 68.97, H 5.08, N 1.09, S 14.93; found C 68.51, H 5.21, N 1.25, S 14.97%.

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