

# One-dimensional luminescent nanoaggregates of perylene bisimides†‡

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A new perylene bisimide dye has been synthesized which self-assembles into columnar nanoaggregates and liquid crystalline mesophases with striking photoluminescent properties.

Among functional  $\pi$ -systems, perylene tetracarboxylic acid derivatives have attracted considerable attention on the account of their intense luminescence, light fastness, and n-type semiconductor properties.<sup>1,2</sup> These compounds have been widely applied in organic electronic devices, e.g., xerographic photoreceptors,<sup>3</sup> thin-film transistors<sup>4</sup> and solar cells.<sup>5</sup> In particular, the parent compound, perylene tetracarboxylic acid dianhydride (PTCDA), is regarded as the archetype molecular semiconductor because its crystals contain one-dimensional  $\pi$ - $\pi$  stacks of unusually tightly packed chromophores (distance of only 3.2 Å) that facilitate a high degree of  $\pi$ -orbital overlap between adjacent molecules along the stack. Novel properties emanate from such packing features, which are otherwise only observed in inorganic semiconductors, i.e., the formation of photoluminescent charge transfer (CT) excitons.<sup>6</sup> The latter enabled the construction of the first multiple quantum well structures and the confirmation of quantum size effects in organic solid state materials by Forrest and co-workers.<sup>6</sup> Noteworthy, such interesting features have not been observed yet for structurally related perylene tetracarboxylic acid diimides (PTCDI); an important class of colour pigments that rarely pack in such a way so as to provide highly photoluminescent materials.<sup>2,7</sup>

During recent years, our group has elaborated strategies to derive PTCDI derivatives containing specific receptor units that direct their self-assembly into predetermined supramolecular architectures.<sup>2</sup> Recently, we and other groups have reported that tridodecyloxyaryl-substituted PTCDI derivatives form liquid crystalline phases with a high charge carrier mobility.<sup>8</sup> However, supramolecular stacks of tridodecyloxyphenyl-substituted PTCDI are not luminescent, apparently due to photoinduced electron transfer from the electron rich trialkoxyphenyl group to the electron deficient PTCDI unit.<sup>8a,9</sup>

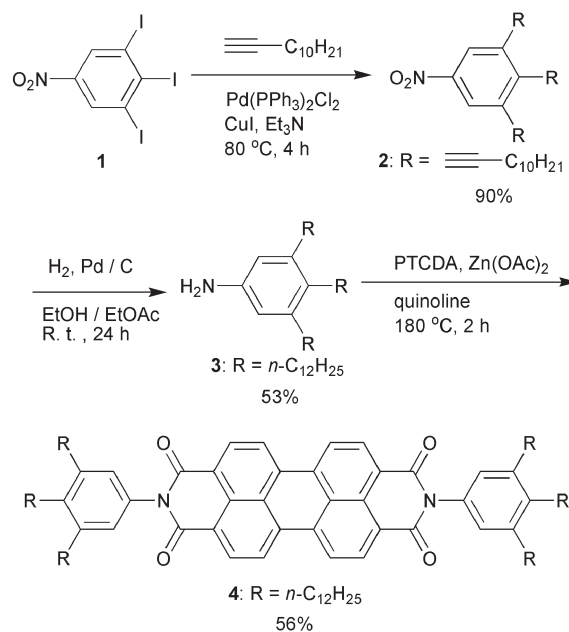
Here we present a new, highly photoluminescent PTCDI derivative **4** ( $\Phi_f = 0.65$  in methylcyclohexane (MCH)) which self-assembles into well defined one-dimensional columnar stacks that exhibit similar spectacular optical features to those reported by Forrest and co-workers for archetype organic crystals of PTCDA.<sup>6</sup>

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† Dedicated to Prof. Wolfgang Kiefer on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details including the synthesis and spectroscopic data of **4**. See DOI: 10.1039/b517020f



Scheme 1 Synthesis of PTCDI **4**.

As shown in Scheme 1, perylene bisimide **4** was synthesized by imidization of PTCDA with tridodecylaniline **3** using  $Zn(OAc)_2$  as catalyst. Aniline derivative **3** was obtained by Pd-catalysed hydrogenation of the triple bonds and nitro group of compound **2**, the latter being prepared by a Sonogashira coupling<sup>10</sup> reaction between dodec-1-yne and 3,4,5-triiodonitrobenzene.

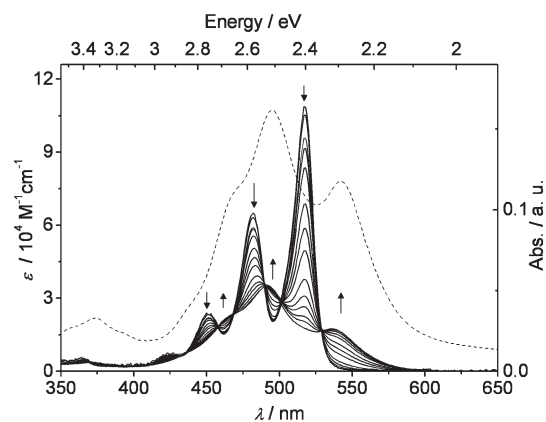
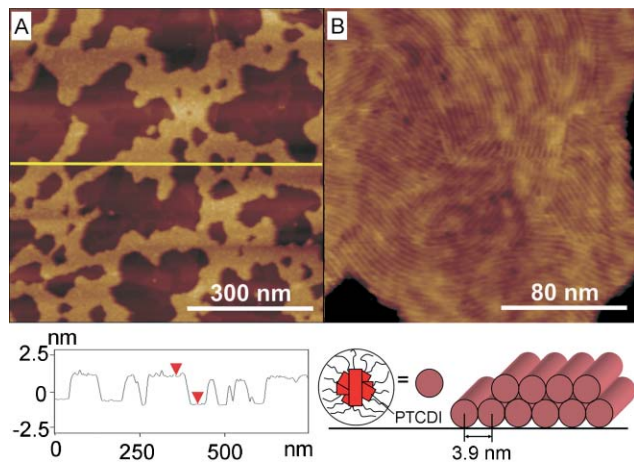


Fig. 1 Concentration-dependent UV/vis absorption spectra of PTCDI **4** ( $2.0 \times 10^{-7}$  M to  $1.0 \times 10^{-3}$  M) in MCH. Arrows indicate the changes upon increasing the concentration. Dashed line: UV/vis spectrum of the spin-coated film of **4** after annealing at 150 °C for 3 h.

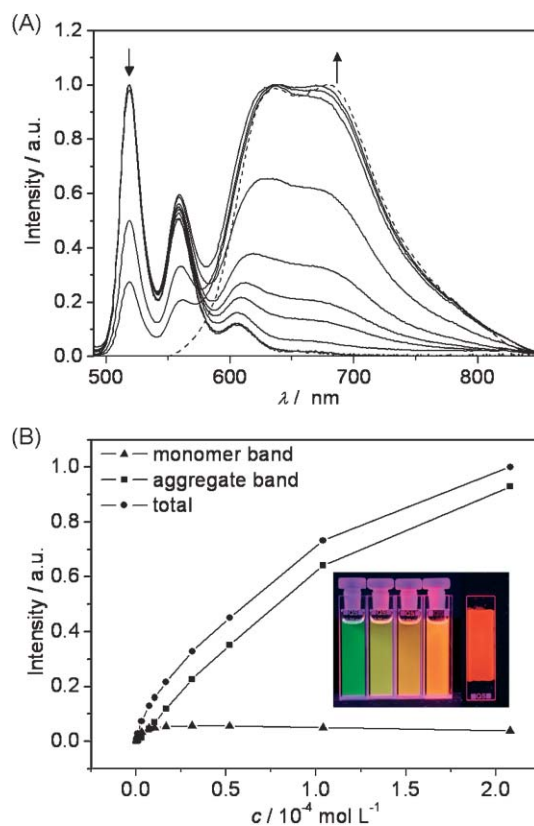
The spectroscopic properties of dye **4** and its aggregates were investigated in solution and in the condensed state (Fig. 1). At very low concentrations (non-aggregated state), the spectrum displayed an absorption band between 400 and 530 nm for the  $S_0 \rightarrow S_1$  transition of the perylene bisimide, with a well-resolved vibronic structure that can be attributed to breathing vibrations of the perylene skeleton. Upon aggregation, the absorption coefficients decreased drastically and a blue shift (*ca.* 30 nm) of the absorption maximum was observed. Both spectral features are indicative of a close face-to-face stacking of the chromophores.<sup>8a,11</sup> In addition, upon aggregation, a new broad band arose at 540 nm with an absorption coefficient of about  $1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ . A similar band was observed for a liquid crystalline thin-film<sup>12</sup> of this compound (543 nm, 2.29 eV). Remarkably, the spectral position and intensity of this long wavelength absorption band is highly comparable to the CT exciton state reported by Forrest *et al.* for PTCDA crystals.<sup>6</sup>

In contrast to crystalline PTCDA and PTCDI materials, the growth of PTCDI **4** aggregate is confined to one dimension due to the bulky alkyl chains. This was confirmed by temperature-dependent vapour pressure osmometry (VPO) and NMR studies, which revealed the reversible formation of extended aggregates of **4** in solution. Such oligomeric aggregates are generally polydisperse and can be described by the equal  $K$  model.<sup>13</sup> Non-linear least-square regression analysis of temperature-dependent UV/vis spectra at different concentrations provided enthalpy and entropy values of  $\Delta H^\circ = -56.3 \pm 1.1 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -95.8 \pm 3.6 \text{ J mol}^{-1}\text{K}^{-1}$  for the  $\pi$ - $\pi$  stacking of **4** in MCH. The average number of  $\pi$ - $\pi$ -stacked molecules at a concentration of  $5.0 \times 10^{-3} \text{ M}$  was determined as 11, 8 and 6 at temperatures of 40, 50 and 60 °C, respectively, which is in good agreement with the VPO data (Table S2 in ESI†).

One-dimensional columnar stacking of compound **4** was also observed in the bulk sample as well as in thin films cast from solution. Atomic force microscopy (AFM) revealed a fingerprint-like structure composed of long and bending columns of PTCDI aggregates. The width of the column was about 3.9 nm and the



**Fig. 2** Top: AFM image of a thin-film spin-coated from solution of **4** in MCH ( $4 \times 10^{-4} \text{ M}$ ) onto highly-ordered pyrolytic graphite (HOPG). (A) Topography image and (B) higher resolution image. Bottom: Cross-section analysis corresponding to the yellow line of (A) and proposed model for the packing of columnar stacks on HOPG.



**Fig. 3** (A) Normalized concentration-dependent fluorescence spectra (excitation at 469 nm) of **4** ( $2.1 \times 10^{-7} \text{ M}$  to  $2.1 \times 10^{-4} \text{ M}$ ) in MCH solution and of a spin-coated thin-film (dashed line). (B) Fluorescence intensity changes to the monomer band, aggregate band and whole spectra upon increasing the concentration. Inset: Colour photographs of MCH solutions of **4** with increasing concentration (left to right) and a thin-film of **4**.

height was 2.3 nm (Fig. 2). Both values are in good agreement with molecular modelling studies, which suggest a length of 4 nm for **4** along its long axis for fully extended alkyl chains.

Even more interesting than the changes to the UV/vis absorption spectra upon increasing the concentration are those of the emission spectra and the concomitant colour changes of this strongly luminescent dye (Fig. 3). Depending on the ratio of aggregated *vs.* total dye molecules,  $\alpha_{\text{agg}}$ , the colour of the emitted light changes from green ( $\alpha_{\text{agg}} < 0.3$ ) to yellow ( $\alpha_{\text{agg}} \approx 0.7$ ), orange ( $\alpha_{\text{agg}} \approx 0.8$ ) and red ( $\alpha_{\text{agg}} > 0.9$ ). As the spectra revealed, this tremendous colour change can be attributed to the occurrence of a broad aggregate emission band at 600 to 850 nm. Time-resolved fluorescence measurements indicate a substantial increase in fluorescence lifetime upon aggregation from  $\tau_f = 3.2 \text{ ns}$  for the monomeric dyes to  $\tau_f = 33 \text{ ns}$  for the aggregated dyes. Such increased lifetimes of an excited singlet state can be attributed to a reduced transition probability for the radiative  $S_1 \rightarrow S_0$  transition in H-type aggregates, but has rarely been observed for aggregated fluorophores owing to the presence of competitive non-radiative deactivation pathways.<sup>14</sup> Concomitant with aggregate formation, the fluorescence anisotropy becomes fully depolarized. For thin films, only the broad emission band was observed at even longer wavelengths, which already approach the value observed for crystalline PTCDA.<sup>6</sup>

Most of the spectral observations made for the present perylene bisimide derivative can be rationalized by molecular exciton theory<sup>15</sup> if we assume rotational displacements in the  $\pi$ - $\pi$  stacking of this dye with displacement angles of 70–80°.<sup>16</sup> At such large angles, the optical transition from the ground state to the lower energy excitonic state is no longer forbidden and, thus, photoluminescence can be observed even for H-type dye aggregates.<sup>15</sup> Likewise, the increase in fluorescence lifetime and fluorescence depolarization by exciton diffusion<sup>17</sup> are logical implications of such rotationally-displaced dyes. However, the most impressive feature, *i.e.*, the unusually large Stokes shift, is indicative of a profound structural and energetic relaxation process for the dye aggregates in their excited state. We suggest that the  $\pi$ -faces come to a closer proximity (possibly as close as the distance of 3.2 Å observed by Forrest *et al.* in PTCDA crystals)<sup>6</sup> to provide a stronger coupled excitonic state.<sup>18</sup> For such a relaxed excited state, a CT contribution by orbital interactions might be feasible if the electron rich perylene core of one dye slipped over the top of the electron poor imide moiety of a neighboring dye.<sup>19</sup> In our future studies we intend to shed light on this exciting possibility, which is not available for the majority of other photoluminescent  $\pi$ -conjugated materials.

Taken together, it can be concluded that the remarkable spectroscopic features reported for PTCDA crystals are also observable in highly-defined PTCDI aggregates in solution and thin films, as demonstrated for PTCDI **4**. Consequently, these columnar aggregates are highly promising analogues of archetype crystalline PTCDA organic semiconductors. Possible applications of such aggregates as semiconducting nanowires and in (nano-scopic) light-emitting devices are anticipated.

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