Anisotropic fluorescent materials *via* self-organization of perylenedicarboximide†

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In this communication, we report the self-organization of a perylenedicarboximide to produce materials that exhibit dichroic (direction-dependent) absorption and anisotropic fluorescence emission of visible light.

Organic materials have potential applications as optical and electronic materials, and in organic electroluminescent devices and microelectronic fields.[1] The intermolecular interaction and orientation of molecules in the solid state often have significant effects on the properties of organic molecular-base materials and the performance of devices based on these materials.[2] For instance, materials in which the organic molecules are oriented in a preferred direction will possess useful anisotropic (direction-dependent) properties that are not attainable from materials in which organic molecules are randomly oriented.[1,3] Molecular self-assembly and self-organization processes are important approaches to the construction of devices and materials.[4] Our research group is interested in the design and synthesis of organic compounds that self-organize to liquid crystals or crystals with anisotropic (direction-dependent) properties.[5] In this communication, we report the self-organization of perylenedicarboximide **1** to give solid-state materials that exhibit dichroic (direction-dependent) absorption and anisotropic fluorescence emission of visible light. The optical properties of **1** in the solid state are compared to those in the solution phase.

Compound **1** is very soluble in chloroform and methylene chloride but insoluble in methanol, ethanol, or water. Long crystals of variable dimensions (as long as 2–3 cm in length) were obtained by the addition of ethanol to a solution of **1** in chloroform.

The packing of **1** in the crystals was determined by single-crystal X-ray diffraction analysis (Fig. 1). The anisotropic stacking of molecules into columns was presumably caused by favorable electronic interactions among the planar aromatic rings. The presence of the flexible *N*,*N*-diethylaminoethyl chain helps to increase the solubility of the compound in organic solvents and yet is not too bulky to prevent stacking of the aromatic rings in the solid state. Furthermore, the span of the *N*,*N*-diethylamino group is about the same as the width of the perylenemonoimide ring allowing close packing of the columns in either parallel or antiparallel fashion in the solid phase.

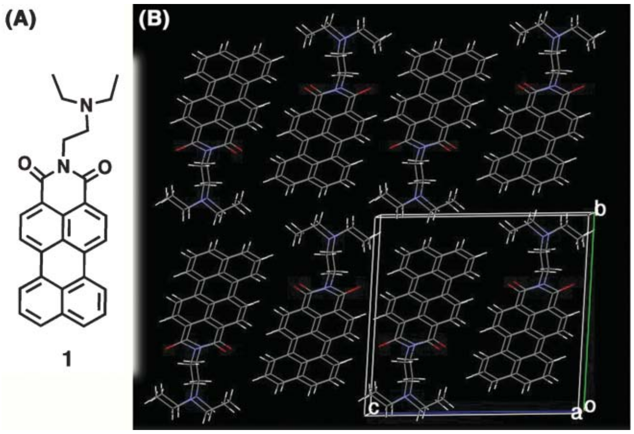

Fig. 1 (A) Molecular formula of **1**. (B) The crystal packing of **1** (16 molecules shown) determined by X-ray diffraction.‡

Studies of the long crystals of **1** under a polarizing microscope revealed that these solids exhibited direction-dependent absorption of light. As shown in Fig. 2, when the polarization axis of polarized light was in the vertical direction (perpendicular to the long axis of the crystal), intense absorption of light of most colors (except red) occurred resulting in the intense red color of the crystal observed. When the polarization axis of the polarized light was turned to the horizontal direction, parallel to the long axis of the crystals, the absorption was lower at all wavelengths and a peach color was observed for the crystals. The observed polarized absorption of visible light by these crystals indicate that the

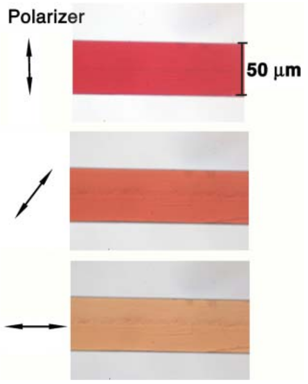

Fig. 2 Optical micrographs showing part of a crystal of **1** examined under an optical microscope equipped with a single polarizer between the incident light source and the crystal of **1**.

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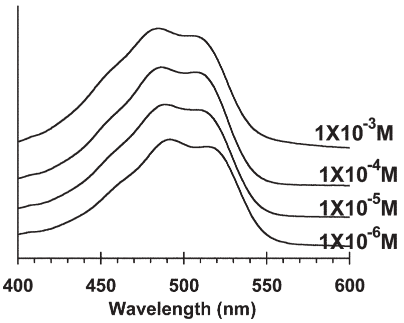

Fig. 3 Off-set visible absorption spectra of **1** (10^{-6} M to 10^{-3} M) in chloroform.

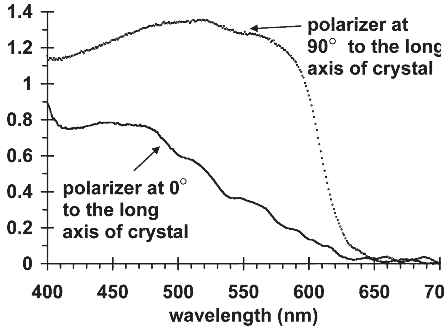

Fig. 4 Visible absorption spectra of a crystal of **1**. (●) The polarization axis of incident light was perpendicular (90°) to the long axis of the crystal. (—) The polarization axis of incident light was parallel (0°) to the long axis of the crystal.

molecules of **1** are anisotropically oriented in the crystals and the principal axis of the electronic transition of **1** was oriented at ~90° relative to the long axis of the crystals. These conclusions are consistent with the anisotropic packing of **1** in crystals (as shown in Fig. 1) determined by X-ray diffraction analysis. The orientation of the plane of stacked molecules in the crystals resulted in the unidirectional orientation of the principal axis of electronic transition of the molecules.

Further analysis of the electronic transition properties of **1** in solution and solid state were performed using visible spectroscopy. As shown in Fig. 3, **1** in chloroform showed intense absorption of green light (λ_{max} at ~490 nm and 520 nm). A blue shift in the λ_{max} with increasing concentrations of organic compounds generally results from the formation of H-aggregates. However, no significant change in the spectral shape was observed as the concentration was increased from 10^{-6} M to 10^{-3} M suggesting that no significant change in the extent of aggregation occurs in this concentration range.

The polarized visible absorption spectra of **1** in the solid state (Fig. 4) differ significantly from those of **1** in chloroform. Significant broadening of the spectra was observed in the solid state compared to the solution phase. As shown in Fig. 4, when the polarization axis of polarized light was 90° to the long axis of the crystal, intense absorption of visible light at wavelengths less than 630 nm occurred accounting for the intense red color of the crystal observed. When the polarization axis of the polarized light was parallel (0°) to the long axis of the crystals, the absorption was lower at all wavelengths, especially at wavelengths longer than 500 nm, resulting in a more orange/peach color of the crystals.

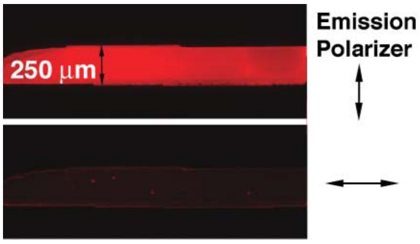

Fig. 5 Optical micrographs of fluorescence emission from an anisotropic crystal of **1**. The sample was viewed under a fluorescence microscope equipped with a filter block that transmitted incident light of wavelengths 530–560 nm and emission light of 573–648 nm, and with a single polarizer between the sample and the CCD camera. The polarization axis of the polarizer is at 90° (top) and 0° (bottom) to the long axis of the crystal.

Despite the close packing of the molecules in the solid state which often leads to quenching of fluorescence emission, intense fluorescence emission was observed for the crystals of **1**. More importantly, the emission intensity is highly direction-dependent (Fig. 5). The maximum emission intensity was observed when the polarization axis of the emission polarizer was at 90° to the long axis of the crystal. The emission intensity decreased dramatically when the polarization axis of the emission polarizer was at 0° to the long axis of the crystal. The observed polarized emission of visible light by these crystals is consistent with the conclusion that the molecules of **1** are anisotropically oriented in the crystals and the principal axis of the electronic transition of **1** was oriented at ~90° relative to the long axis of the crystals.

Studies by fluorescence spectroscopy showed that excitation of **1** (1×10^{-7} M) in chloroform at 491 nm resulted in intense fluorescence emission at 548 nm and a shoulder at ~590 nm (Fig. 6). In the crystal phase, the λ_{max} of fluorescence emission of **1** was red-shifted by about 100 nm compared to the λ_{max} of **1** in chloroform. The emission in the direction perpendicular to the long axis of the crystal (Fig. 7b) was over 5 times more intense than the emission along the long axis (Fig. 7d).

In summary, this work shows that perylenemonoimide **1** self-organizes to form crystals with anisotropic absorption and fluorescence properties. The absorbance and the intensity of

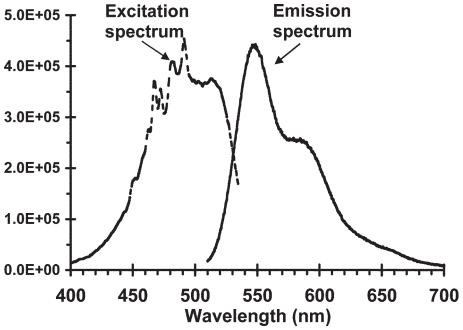

Fig. 6 Excitation and emission spectra of **1** (1×10^{-7} M) in $CHCl_3$. The excitation spectrum was acquired when the emission was observed at 548 nm. The emission spectrum was acquired when the solution was excited at 491 nm.

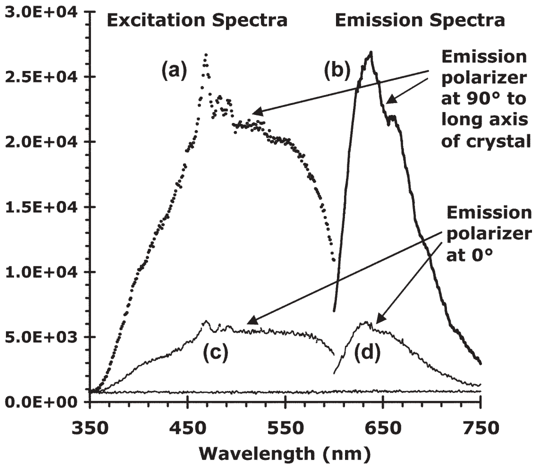

Fig. 7 Polarized fluorescence excitation and emission spectra of the crystal of **1** shown in Fig. 5. Excitation spectra (a and c) were acquired at an emission wavelength of 630 nm. Emission spectra (b and d) were acquired at an excitation wavelength of 467 nm.

fluorescence emission along the long axis of the crystals were substantially lower than in the perpendicular direction. In addition to the planar structure of the aromatic ring, the ethyl side chains on the amine function appear to be important for packing between the aromatic stacks to promote anisotropic packing of the molecules. Future studies will entail the preparation of anisotropic materials of **1** in micro- and nano-patterns, the determination of the semiconducting properties of **1** in the solid state, and the studies of the effect of substituents on the electronic transition and fluorescence properties of **1**.

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Notes and references

‡ $C_{28}H_{24}N_2O_2$; M_r 420.49; crystal system: triclinic; space group $P\bar{1}$; unit cell dimensions: a = 4.6959(7) Å, b = 14.281(2) Å, c = 15.472(2) Å, α = 93.424(4)°, β = 92.917(4)°, γ = 94.217(4)°; Z = 2; μ(Mo Kα) = 0.086 mm^{-1}; 17152 reflections measured (R_{int} = 0.0303); the final $R1$ and $wR2$ were 0.0472 and 0.0963 ($I > 2\sigma(I)$). CCDC 632620. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615802a

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