Functional organogels from highly efficient organogelator based on perylene bisimide semiconductor†

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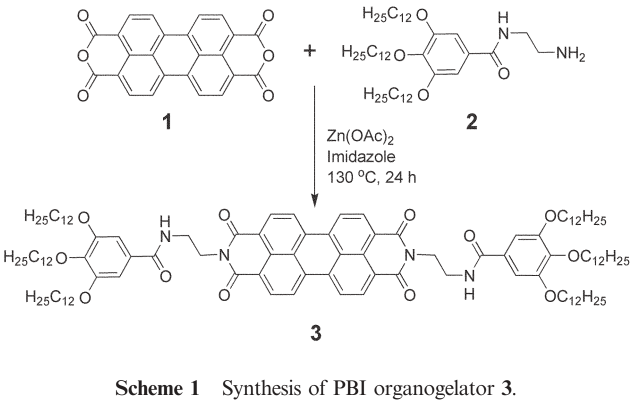
A new n-type semiconducting perylene bisimide dye has been synthesized that gelates a broad variety of organic solvents to afford well-defined nano- and mesoscopic helical fibers and bundles.

In recent years, significant efforts have been devoted toward well-organized π-conjugated organic materials because proper ordering of the functional molecular building blocks is essential for the realization of organic electronic and photonic materials with performance competitive to that of their inorganic counterparts.[1–3] Among the diverse areas of applications, those that seem to be particularly attractive for π-functional organic compounds rely on multifunctionality emerging from mixtures of molecular building blocks, which provide different functionalities. Typical examples are photofunctional composites as applied in xerographic photoreceptors,[4] photorefractive materials,[5] bulk p–n-heterojunction solar cells[6] as well as light-responsive sensory systems.[7] From the conceptual point of view, dye-based organogels[8] should be highly promising materials for all of these photofunctional applications if one or even more desired functionalities could be provided by the organogelator and additional ones are embedded in the gelated material.[9]

However, to progress towards this goal, robust organogelators are needed that are able to gelate a broad variety of media (*e.g.*, solvents, liquid crystals, *etc.*) and exhibit favourable functional properties. In recent years such versatile organogelators have been derived from several strongly absorbing as well as p-type semiconducting π-systems, including porphyrins, phthalocyanines, oligophenylenevinylenes and oligothiophenes.[10,11] However, for their n-type counterparts no organogelators have been obtained to date that can gelate a broad range of solvents of different polarity. Perylene bisimide (PBI) based organogelators appear to be the most promising candidates for this purpose due to their unrivalled combination of absorption, emission and n-type semiconducting properties.[12] However, all of the recently reported PBI organogelators can only gelate a few solvents or optimized solvent mixtures and, accordingly, lack the desired versatility.[13] In this work, we will introduce the first PBI organogelator with extended gelation capabilities and communicate our first results with regard to its optical and semiconducting properties.

As shown in Scheme 1, perylene bisimide **3** was synthesized by imidisation of perylene tetracarboxylic acid bisanhydride **1** with aminoethylbenzamide **2**[14] in imidazole using $Zn(OAc)_2$ as catalyst and isolated as a red powder in 48% yield. Interestingly, this dye is able to gelate a multitude of organic solvents at rather low concentration (< 0.2 wt%, *e.g.*, in benzene and methylcyclohexane) giving transparent gels for all investigated aliphatic solvents (n-pentane, n-hexane, cyclohexane, and methylcyclohexane) and aromatic solvents (benzene, toluene, and thiophene) as well as opaque gels for the ethers dioxane, tetrahydrofuran, dibutyl ether and for triethylamine. For the more polar solvents DMF, DMSO, and alcohols no gelation could be achieved. The observed gelation properties of PBI **3** can be attributed to the presence of hydrogen bonds between the benzamide functional groups that enforce the strong π–π stacking interactions which occur between PBI dyes (FT-IR data for NH and CO vibrations are given in the ESI†).[15,16]

The optical properties of dye **3** in the monomeric and aggregated state were investigated by temperature-dependent UV/vis spectroscopy (Fig. 1). At high temperature (non-aggregated state), the spectrum displayed an absorption band between 400 and 550 nm of the $S_0 \rightarrow S_1$ transition of the perylene bisimide with well-resolved vibronic structure that can be attributed to a breathing vibration of the perylene skeleton. Upon cooling, aggregation took place and the absorption coefficients decreased drastically with a concomitant blue-shift (*ca.* 30 nm) of the absorption maximum as well as a pronounced shoulder at longer wavelength. These spectral features are characteristic of perylene bisimide aggregates and indicative of a close face-to-face stacking of rotationally displaced chromophores.[17] However, in contrast to PBIs lacking additional functional groups, for dye **3** aggregation



Scheme 1 Synthesis of PBI organogelator **3**.

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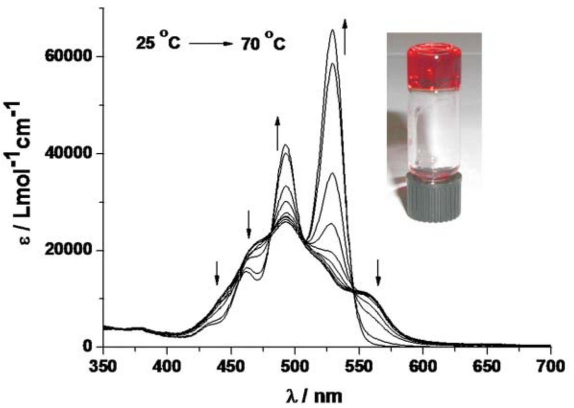

Fig. 1 Variable-temperature UV/vis absorption spectra of **3** (5.1×10^{-5} M, in toluene) and toluene organogel (inset) formed at 1.5 mM concentration. The arrows indicate spectral changes with increasing temperature.

occurs at significantly lower concentration, pinpointing the decisive contribution of additional hydrogen bonds.

Whilst the IR and UV/vis spectroscopic studies provided information on the local interactions between the individual molecules, atomic force microscopy (AFM) is the method of choice to explore the morphology on the nano- and mesoscopic scale that directs the network formation and the concomitant gelation capabilities. Remarkably, quite similar well-defined fibrous structures could be observed upon spin-coating of diluted gel solutions from different solvents (see ESI†). In addition, the structures are insignificantly influenced by the substrate.

As shown in Fig. 2, these fibers adopt both left-handed (*M*) and right-handed (*P*) helicities in the present gel matrix. The observed helicities of gel obtained from achiral **PBI 3** molecules can be explained by the hydrogen-bond directed π–π stacking (Fig. 2F). Gel fibers arise upon a strong preference for anisotropic unidirectional growth. As a consequence, long range chiral order can originate from nucleation from a small chiral supramolecular unit, *e.g.*, a hydrogen-bonded dimeric or oligomeric π-stack of *M* or *P* helicity.[18] On both highly oriented pyrolytic graphite (HOPG) and mica, the mean height of the helical fibers was 3.1 ± 0.3 nm with the width of 8.0 ± 2.0 nm, helical pitch of 15.0 ± 2.0 nm and several micrometers in length. There are few fibers without helicity on HOPG which might be created by a template effect of HOPG due to the well-known strong interactions between alkyl chains with this substrate. On the other hand, an impressive structural homogeneity of the helical fibers also on a large scale (see ESI†) is observed on the less strongly interacting mica substrate. Similar well-defined helical fibers, however from chiral precursors, have recently been observed for p-type semiconductive oligophenylene-vinylene organogelators[19] but are unprecedented for achiral perylene bisimides.

For the efficient entrapment of the solvent, it is of importance that these initially formed fibers interconnect to establish a continuous network. In the given system this happens most likely by interpenetration of the extended alkyl chains[20] because the height of the fibers does not change upon further self-assembly into larger structures (Fig. 2E). As shown by high-resolution AFM in Fig. 2D, there is little or no preference for the interpenetration of the alkyl chains of *M*- or *P*-configured helical fibers.

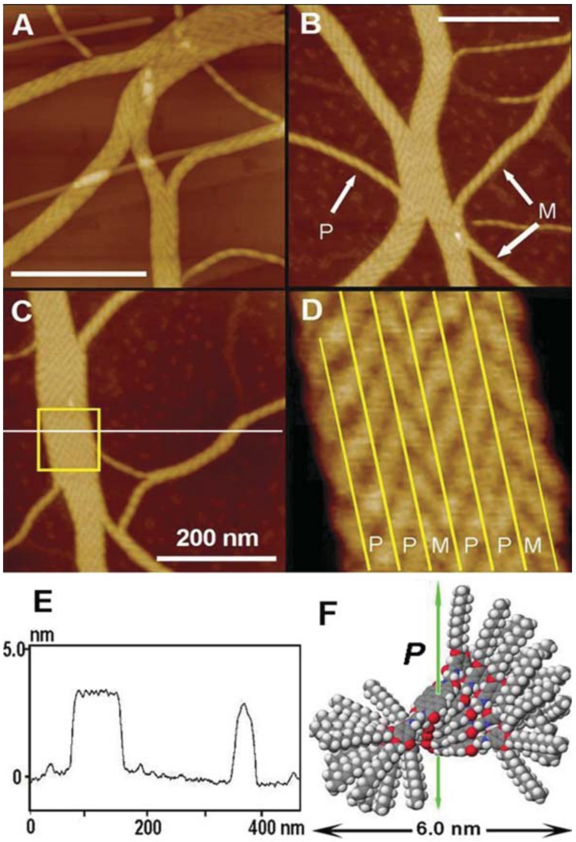

Fig. 2 AFM height images of films spin-coated from diluted gel solutions of **3** in toluene (1×10^{-4} M) onto HOPG (A) and mica (B and C); (D) is zoomed region image from (C). In images (A), (B) and (C) the scale bar corresponds to 200 nm and the z scale is 10 nm. (E) shows the cross-section analysis corresponding to the white line of (C) and (F) depicts a suggested packing model for self-assembled *P*-configured hydrogen-bonded aggregate with a diameter of 6.0 nm.

Differential scanning calorimetry (DSC, see ESI†) of PBI dye **3** reveals several enantiotropic phase transitions in the heating and cooling cycles. First, a crystal-to-crystal phase transition takes place at 96 °C. Subsequently the compound enters into a soft plastic crystalline phase at 126 °C and finally an isotropic liquid is formed at 235 °C with a melting enthalpy of ΔH = 47.3 kJ mol^{-1}. Remarkably, well-defined macroscopic fibers can be observed upon slow cooling from the isotropic liquid (Fig. 3) under the polarized optical microscope (POM). These structures even remain intact upon cooling to room temperature. They adopt a uniform diameter of 3.8 ± 0.2 μm and can extend to beyond 1 mm in length.

Such well-organized fibers and bundles which are composed of extended π-stacks of the electron poor dye **3** should provide efficient pathways for mobile n-type charge carriers. Therefore, the semiconducting properties of **3** in the solid state were investigated by using the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique, which offers the intrinsic charge carrier mobility of the material with minimized effects of grain boundaries as shown for a large number of organic materials in the past.[21] At room temperature, the sum of the isotropic electron and hole mobility is $\Sigma\mu_{\mathrm{TRMC}} = 0.052$ cm^2 V^{-1} s^{-1} for dye **3**.[22] This value is significantly higher than the values measured with the same

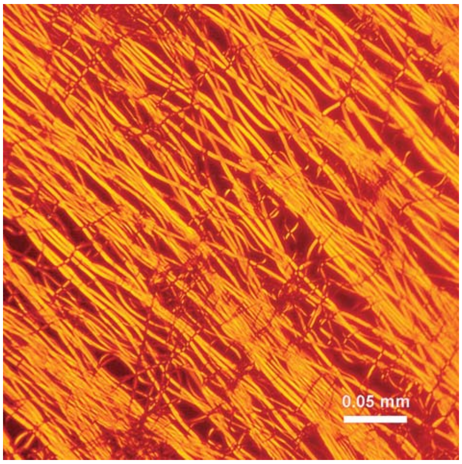

Fig. 3 Polarized optical microscopy image (crossed polarizers) of **3** after cooling from the melt at a temperature of 228 °C.

method for liquid crystalline phases of related PBIs with tridodecyloxyphenyl[17a] (0.008 $cm^2 V^{-1} s^{-1}$)[23a] or with tridodecyloxybenzyl[24] substituents at imide positions (0.011 $cm^2 V^{-1} s^{-1}$).[23a] Likewise, this charge carrier mobility is about one order of magnitude higher than the mobility measured for p-type semiconductive hydrogen-bond directed oligothiophene organogelators.[11]

In summary, the results presented here show that PBI organogelator **3** exhibits pronounced gelation capabilities leading to interpenetrating networks of PBI stacks in a broad variety of solvents, including electron-rich aromatic solvents such as thiophene. Based on the remarkably high n-type charge carrier mobility[22] and the broad absorption range from 400–600 nm, we are tempted to suggest that this gelator could provide efficient organic solar cells upon mixing with p-type organic semiconductors such as pentacene or polythiophene. Our current efforts are directed along this line.

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