Supplementary Material (ESI) for:

Functional organogels from highly efficient organogelator based on perylene bisimide semiconductor

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Synthesis and Characterization of compound 3.

N,N'-Di[3,4,5-tris(dodecyloxy)benzoylaminoethyl]-perylene-3,4:9,10-tetracarboxylic acid bisimide

Perylene-3,4:9,10-tetracarboxylic acid bisanhydride (39 mg, 0.1 mmol), benzamide **2** (150 mg, 0.21 mmol) and zinc acetate (40 mg, 0.22 mmol) were mixed in 3 g of imidazole. The reaction mixture was stirred at 130 °C for 24 h. After cooling to room temperature, 100 ml MeOH was added and the precipitate was collected and washed with additional MeOH. After drying in vacuum, the crude product was purified by silica gel column chromatography (20/1 $CHCl_3$/MeOH) to give a red solid. Yield: 48%. Mp: 233 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K, TMS): δ = 8.50 (d, 4H, J = 7.6 Hz, H_{pery}), 8.36 (d, 4H, J = 8.0 Hz, H_{pery}), 7.08 (s, 2H, NH), 7.00 (s, 4H, Ar-H), 4.53 (m, 4H, CH_2), 3.98 (m, 12H, Ar-OCH_2), 3.88 (m, 4H, CH_2), 1.80-1.15 (m, 120H, CH_2), 0.88 (m, 18H, CH_3). MS (MALDI-TOF, matrix: DCTB): calculated for $C_{114}H_{172}N_4O_{12}$ (m/z) 1789.30, found 1790.28 $[M+H]^+$; elemental analysis (%) calculated for $C_{114}H_{172}N_4O_{12}$ (1790.6): C 76.47, H 9.68, N 3.13; found: C 76.58, H 9.92, N 2.97. UV/vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 528 (85300), 491 (51600), 460 (18500 M^{-1} cm^{-1}).

Gelation test of 3 in various organic solvents.

The gelation property of perylene bisimide **3** was assessed in 20 different organic solvents. For this purpose, the gelator and the solvent were put together in a screw-capped sample vial and it was heated until everything was dissolved. After leaving the sample over night at ambient temperature, the formation of gel was defined by the "stable-to-inversion of a vial" method. Transparent gels were formed in methylcyclohexane, cyclohexane, n-hexane, n-pentane, benzene, thiophene and toluene. In dioxane, THF, dibutylether and triethylamine opaque gels were formed. For the solvents chloroform, dichloromethane, acetone, ethanol, methanol, 1-octanol, diethylether, DMF and DMSO no gel was observed. The gels formed already at the concentration ≤ 2 mM. The critical gelation concentration (CGC) was determined in MCH, benzene and cyclohexane, which was 0.8 – 1.1 mM (< 0.2 wt%).

General methods. All solvents and reagents were purchased from commercial sources and used as received without further purification. The solvents for spectroscopic studies were of spectroscopic grade and used as received. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and all the spectra were calibrated against TMS. UV/vis spectra were measured on a Perkin-Elmer Lambda 40P spectrometer equipped with a Peltier system as temperature controller. FT-IR spectra were measured on a Jasco FT/IR-410 instrument. Differential scanning calorimetry (DSC) measurements were performed by using a TA Q1000 calorimeter. Optical textures at crossed polarizers were obtained with an Olympus BX-41 polarization microscope equipped with a Linkam THMS 600 hot stage and a temperature controller unit.

Atomic force microscopy (AFM). AFM measurements were performed under ambient conditions using a MultiMode Nanoscope IV system operating in tapping mode in air. Silicon cantilevers (OMCL-AC160TS) with a resonance frequency of ~300 kHz were used. Solutions of perylene bisimide **3** were spin-coated onto HOPG (highly oriented pyrolytic graphite) and mica under 7000 rpm.

Charge carrier mobility measurement. The conductive properties were studied with the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique. Pressed pellets (25 mg, fill factor 0.75) of the material were irradiated with 10 nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator, which results in the creation of a uniform micromolar concentration of electron-hole pairs. The resulting change in conductivity was monitored as the microwave power absorbed by the mobile charge carriers in the material at an electro-magnetic field frequency of 33 GHz. The mobility values are determined from the conductivity at the end of the electron pulse. The lower limit to the mobility is obtained by assuming that all generated charges contribute to the conductivity (survival parameter $W_{eop} = 1$) and a pair formation energy of 16 eV as described elsewhere.[S1]

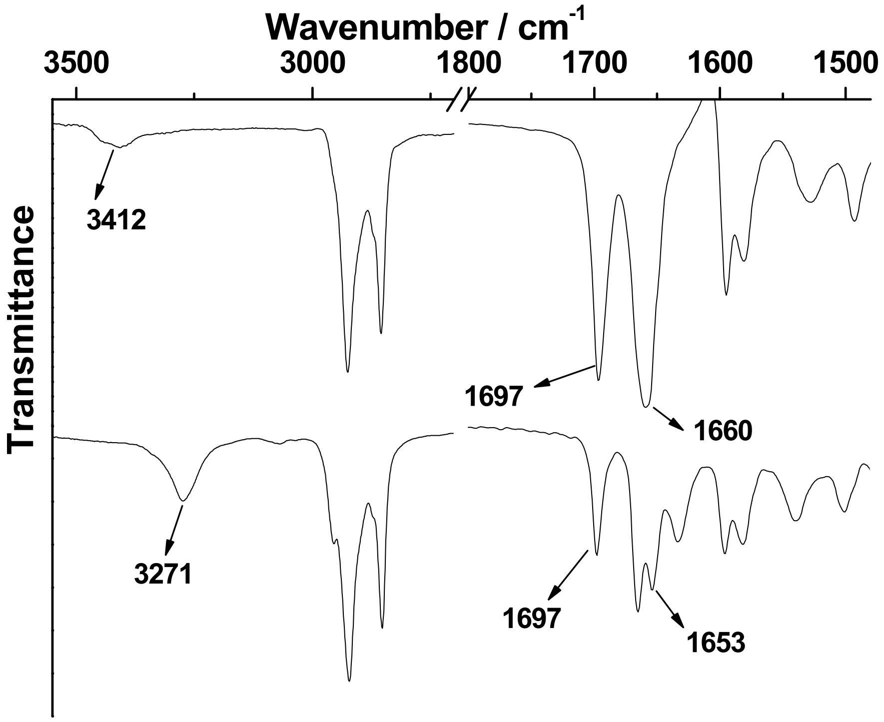

Fig. S1 IR spectra of **3**: (top) In CH_2Cl_2 solution (ca. 1 mM) and (bottom) for a xerogel of **3** prepared from MCH.

TOP: The FT-IR spectra of **3** in CH_2Cl_2 solution show a broad N-H stretching band at 3412 cm^{-1} that indicates the absence of hydrogen-bonding. The benzamide carbonyl group vibration band overlaps with the carbonyl group vibration of the perylene imide groups at 1660 cm^{-1}.

BOTTOM: In the gel phase, **3** shows a sharp N-H stretching band at 3271 cm^{-1} and a benzamide carbonyl group vibration at 1653 cm^{-1}. Both displacements to lower frequency are indicative for hydrogen-bonding interactions among the amide moieties that contribute to the formation of the gel. In contrast, the symmetrical carbonyl group vibration of the perylene imide groups remain located at 1697 cm^{-1}. This indicates that the imide carbonyl groups are not involved in hydrogen-bond formation.

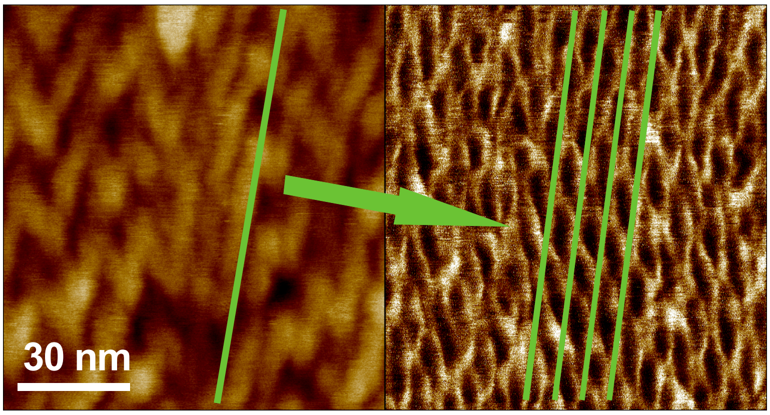

Fig. S2 High resolution AFM topography (left) and phase (right) images of a spin-coated film prepared from a diluted gel solution of **3** in toluene (1 × 10^{-4} M) onto a freshly cleaved HOPG surface.

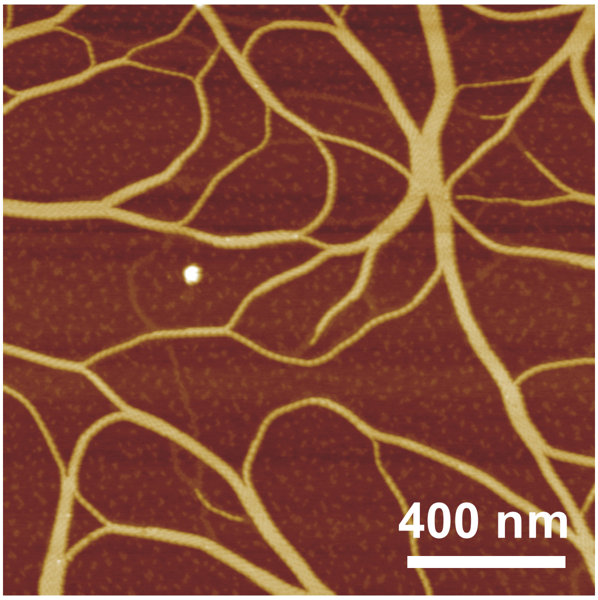

Fig. S3 AFM image of a spin-coated film from a diluted gel solution of **3** in toluene (1 × 10^{-4} M) onto freshly cleaved mica.

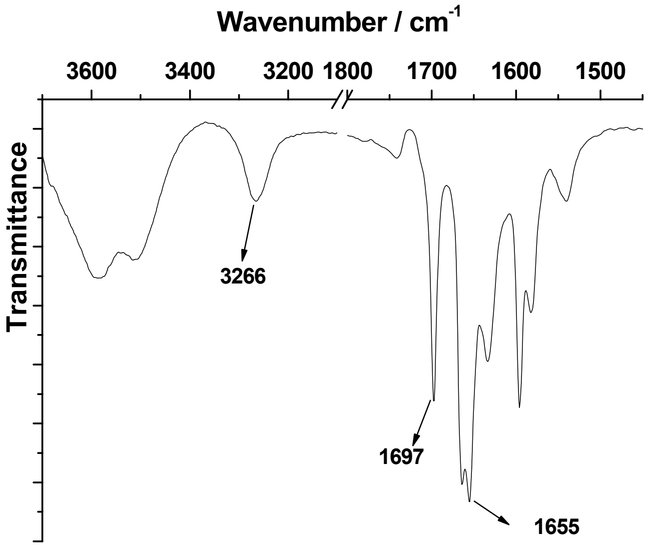

Fig. S4 IR spectrum of a gel of **3** in THF (1mM). The spectrum was obtained by subtracting the spectrum of blank THF. The FT-IR spectrum shows a sharp N-H stretching band at 3266 cm^{-1} and a benzamide carbonyl group vibration at 1655 cm^{-1}. The latter is indicative for the formation of hydrogen bonds between the individual gelator molecules even in the hydrogen bond acceptor solvent THF.

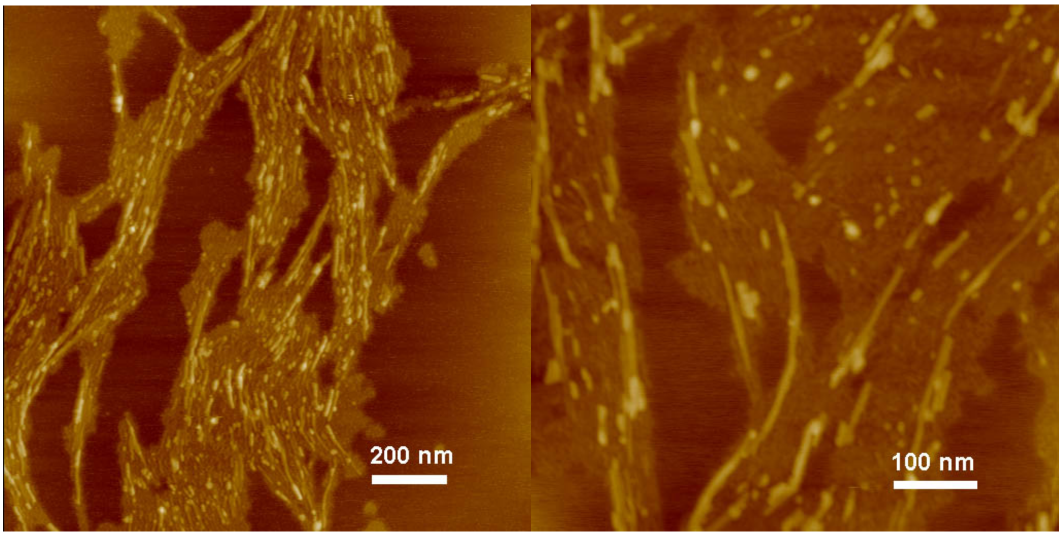

Fig. S5 AFM images of a spin-coated film from a diluted gel solution of **3** in THF (2 × 10^{-4} M) onto freshly cleaved mica. Although the fibers are shorter and less defined (no helicity could be resolved) in the hydrogen acceptor solvent bundle formation as a prerequisite for gel formation is still present.

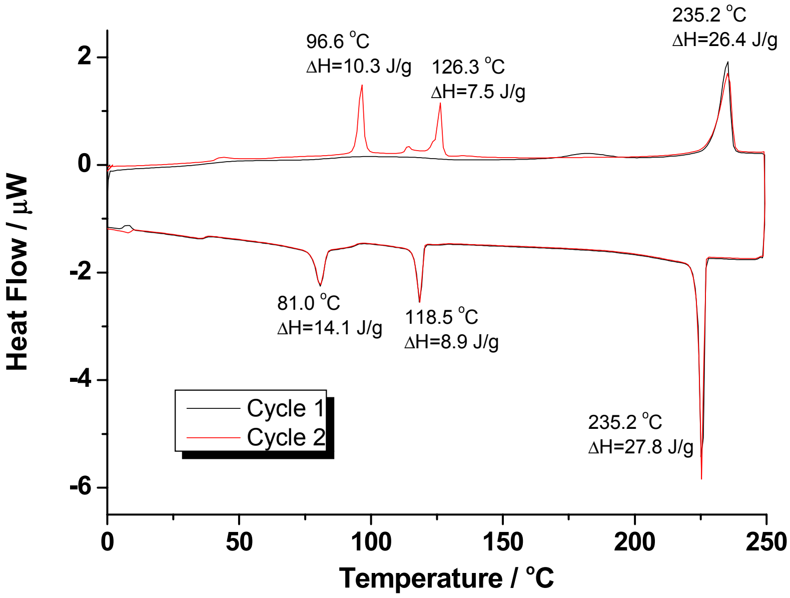

Fig. S6 Differential scanning calorimetry (DSC) traces of compound **3**. The black line indicates the first and the red line the second cycle of the DSC measurement, which were performed at heating and cooling rates of 10 °C / min.

Additional Reference.

[S1] (a) P. G. Schouten, J. M. Warman and M. P. de Haas, *J. Phys. Chem.,* 1993, **97**, 9863-9870; b) P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, Mc. K. Engel, M. Hanack, Y. H. Chang and W. T. Fords, *J. Am. Chem. Soc.,* 1994, **116**, 6880-6894.