

Electronic Supplementary Information (ESI) for:

Perylene bisimide J-aggregates with absorption maxima in the NIR

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General Methods.

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. The solvents for spectroscopic studies were of spectroscopic grade and used as received. ¹H NMR spectra were recorded on a 400 MHz spectrometer and calibrated against TMS or residual solvent peak. UV-Vis spectra were measured on a Perkin-Elmer Lambda 950 spectrometer and for temperature dependent measurements 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. The IR spectra of the solutions were obtained by subtracting the spectra of blank solvents.

Synthesis and Characterisation of Green Perylene Bisimide 3.

Regioisomeric mixture of *N,N'*-bis(α -methylbenzyl)-1,7-dibromoperylene-3,4:9,10-tetra-carboxylic acid bisimide and *N,N'*-bis(α -methylbenzyl)-1,6-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide

A mixture of dibromoperylene bisanhydride **1** (1,7- and 1,6-regioisomer, 1.1 g, 2.0 mmol), α -methylbenzylamine (0.48 g, 4.0 mmol) and zinc acetate (20 mg, 0.09 mmol) in 10 mL freshly distilled quinoline was stirred at 140 °C for 6 h. After being

cooled to room temperature, the reaction mixture was poured into 30 mL methanol. The precipitate was collected by filtration, washed with methanol (3 × 20 mL), and then dried in vacuum. The crude product was first purified by silica gel column chromatography (CH₂Cl₂ as eluent) and then slowly precipitated from CH₂Cl₂ by addition of methanol to give the regioisomeric dibromoperylene bisimide as a red powder (1.0 g, 67 %). ¹H NMR (400 MHz, CDCl₃, 300 K): δ 9.47 (d, ³J = 8.1, 2H), 8.89 (s, 2H), 8.67 (d, ³J = 8.2, 2H), 7.53-7.49 (m, 4H), 7.36-7.31 (m, 4H), 7.28-7.23 (m, 2H), 6.54 (q, ³J = 7.1, 2H), 2.02 ppm (d, ³J = 7.2 Hz, 6H). MS (MALDI-TOF, pos. mode, DCTB): *m/z* 754.00 (calculated 754.01) [M]⁺. Elemental analysis (%) calculated for C₄₀H₂₄N₂O₄Br₂ (754.01): C 63.51, H 3.20, N 3.70; found C 63.07, H 3.41, N 3.82.

***N,N'*-Bis(α-methylbenzyl)-1,7-bis(tricosan-12-amine)perylene-3,4:9,10-tetracarboxylic acid bisimide (2)**

A regioisomeric mixture (ca. 85:15) of *N,N'*-bis(α-methylbenzyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide and *N,N'*-bis(α-methylbenzyl)-1,6-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (75 mg, 0.1 mmol) and tricosan-12-amine (1.02 g, 3.0 mmol) were heated at 150 °C for 6 h under an argon gas atmosphere; during this time the colour of the solution turned from red to green. The hot reaction mixture was poured into a solution of methanol/ 2N HCl (90/10 mL). The precipitate was collected by filtration, washed 3 times with methanol, and dried under vacuum at room temperature overnight to give a green solid. The crude product was purified by silica gel column chromatography (*n*-hexane/CH₂Cl₂ = 7:3 as eluent), and then slowly precipitated from CH₂Cl₂ by

addition of methanol to give 22 mg of the regioisomerically pure perylene bisimide **2** (17 % yield).

^1H NMR (400 MHz, CDCl_3 , 300 K): δ 8.80-8.73 (m, 2H), 8.38-8.735 (m, 2H), 8.16-8.15 (m, 2H), 7.58-7.48 (m, 4H), 7.35-7.30 (m, 4H), 7.24-7.22 (m, 2H), 6.57 (q, $^3J = 7.0$, 2H), 6.26-6.24 (m, 2H), 4.25-4.21 (m, 2H), 2.01 (d, $^3J = 7.2$ Hz, 6H), 1.84-1.71 (m, 8H), 1.42-1.23 (m, 72H), 0.88-0.85 ppm (m, 12H). HRMS (ESI, $\text{CHCl}_3/\text{acetonitrile}$ 1:1, pos. mode): m/z 1273.9382 $[\text{M}+\text{H}]^+$ (calcd for $\text{C}_{86}\text{H}_{121}\text{N}_4\text{O}_4$ 1273.9387).

1,7-Bis(tricosan-12-amine)perylene-3,4,9,10-tetracarboxylic acid bisimide (3)

Perylene bisimide **2** (13 mg, 0.01 mmol) was dissolved in 5 mL dry CH_2Cl_2 under an argon gas atmosphere. A solution of BBr_3 (0.05 mL, 3.34 mmol) in 3 mL dry CH_2Cl_2 was added dropwise to this solution at 0 °C within 10 min. The colour of the reaction mixture changed from green to red immediately after addition of BBr_3 . The solution was stirred at 0 °C for 30 min and an additional 2 h at room temperature. The solvent and excess BBr_3 was distilled off under vacuum and the residue was cooled to 0 °C. Then 10 mL of a mixture of methanol/water (1:4) was added to the solid and the suspension was treated for 30 min at 50 °C in an ultrasonic bath. The product was filtered off and dried under vacuum to obtain a green solid. The crude product was purified by silica gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{methanol} = 99.5:0.5$ as eluent). The obtained green product was further purified by preparative TLC, and then slowly precipitated from CH_2Cl_2 by addition of methanol to give the green perylene bisimide **3** (9.9 mg, 93 %). Mp: 250 °C (decomposition). ^1H NMR (400 MHz, CDCl_3 , 300 K): δ 8.89-8.81 (m, 2H), 8.41 (s, 2H), 8.40-8.37 (m, 2H), 8.19-8.18 (m, 2H), 6.35-6.31 (m, 2H), 4.27-4.25 (m, 1H), 4.11-4.09 (m, 1H), 2.03-1.63 (m, 8H),

1.26-1.21 (m, 72H), 0.86-0.85 (m, 12H). MS (MALDI-TOF, pos. mode, DCTB): m/z 1064.813 (calculated 1064.806) $[M]^+$. Elemental analysis (%) calculated for $C_{70}H_{104}N_4O_4 \cdot 0.5 H_2O$ (1073.82): C 78.24, H 9.85, N 5.21; found C 78.55, H 10.45, N 4.99. UV-Vis ($CHCl_3$): λ_{max} (ϵ) 702 (34900), 421 nm ($17100 M^{-1}cm^{-1}$); fluorescence ($CHCl_3$): $\lambda_{max} = 760$ nm ($\lambda_{ex} = 630$ nm), $\Phi_{Fl} = 0.10$.

AFM and STM Experiments.

AFM investigations were performed under ambient conditions using a MultiMode™ Nanoscope IV system (Veeco Metrology, Santa Barbara, CA) operating in tapping mode in air. Silicon cantilevers (Olympus, Japan) with a resonance frequency of ~ 300 kHz were used. Samples were prepared by spin-coating of the respective solution at 2000 rpm onto silicon wafer.

STM measurements at the liquid–solid interface were performed with a Nanoscope IV system using a low-current module. Mechanically cut Pt/Ir (90:10) wires were used as the tunnelling tips. A droplet of 5×10^{-5} M solution of perylene bisimide **3** in a mixture of octanoic acid/tetradecane (1:1) was applied onto freshly cleaved highly oriented pyrolytic graphite (HOPG). The tunnelling tip was then immersed directly into the droplet and STM measurement was carried out at room temperature. All images presented in this work were collected in constant current mode using a sample bias.

Calculation of the Transition Dipole Moment.

The transition dipole moment of the dye monomer is calculated from the integral of the reduced UV absorption band according to the equation 1^{S1}

$$|\mu_{eg}|^2 = \frac{3hc\varepsilon_0 \ln 10}{2\pi^2 N_A} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} \quad (1)$$

with the molar extinction coefficient $\varepsilon(\tilde{\nu})$, speed of light $c = 2.9979 \times 10^8 \text{ m s}^{-1}$, Planck's constant $h = 6.6262 \times 10^{-34} \text{ Js}$, permittivity $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$, and Avogadro's number $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$) to give a transition dipole moment $|\mu_{eg}| = 7.5 \text{ D}$ for the monomeric PBI **3** in MCH.

Supporting Figures.

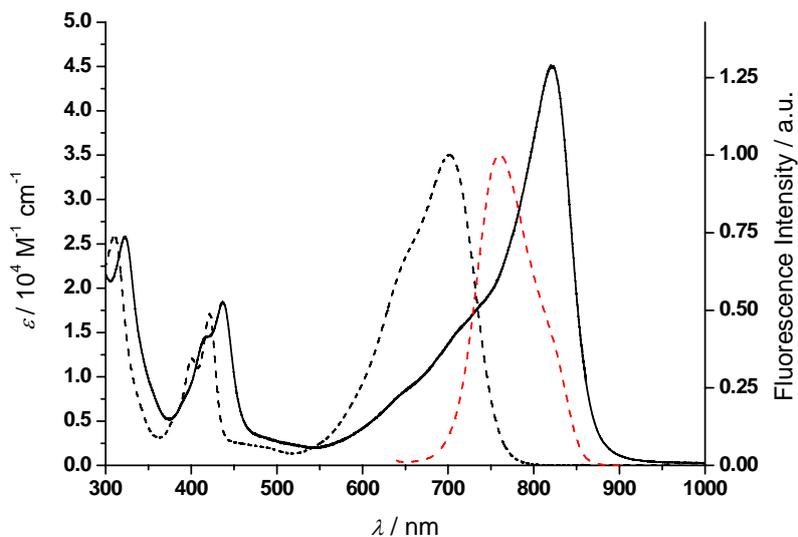


Fig. S1 UV-Vis (black lines) and fluorescence (red line) spectra of PBI **3** (10^{-5} M) in CHCl_3 (dashed lines) and in MCH (solid line).

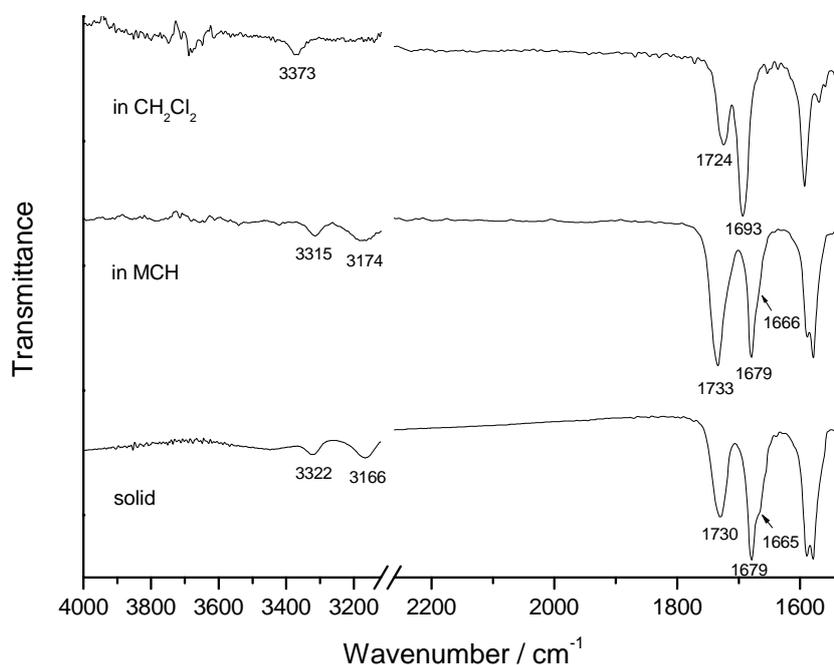


Fig. S2 FT-IR spectra of **3** in CH_2Cl_2 (10^{-4} M), MCH (10^{-3} M), and in solid state.

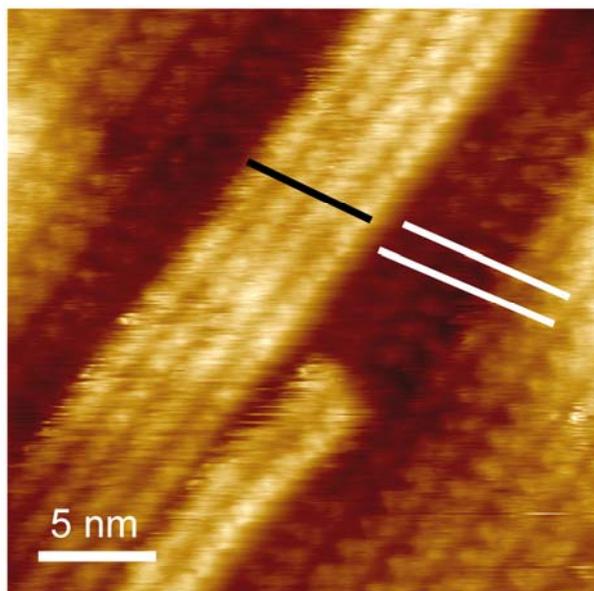


Fig. S3 STM image of assemblies of dye **3** at the octanoic acid/tetradecane (1:1) solution – HOPG interface. $V_{\text{bias}} = -1.5$ V, $I = 4$ pA. The black line is along the centres of PBI cores of the second layer, and white lines are along the centres of PBI cores of the first layer.

Additional Reference.

- S1 W. Liptay, R. Wortmann, H. Schaffrin, O. Burkhard, W. Reitingger and N. Detzer, *Chem. Phys.* 1988, **120**, 429.