Electronic Supporting Information for

Bay-substituted perylene bisimide dye with undistorted planar scaffold and outstanding solid state fluorescence properties

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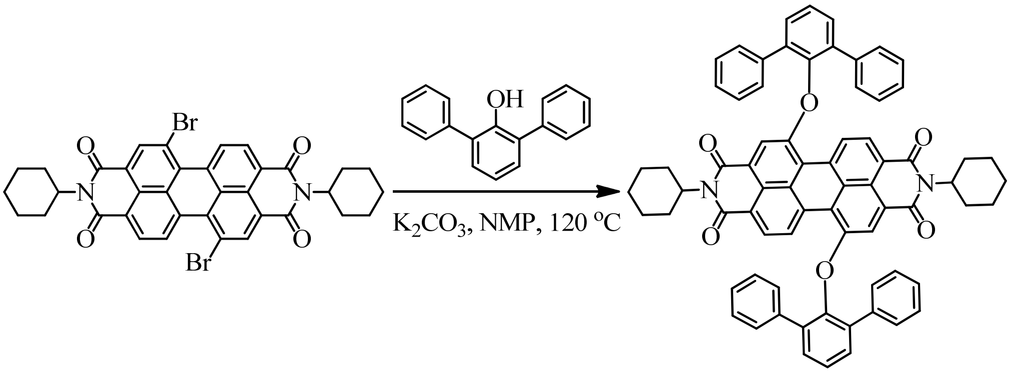
1. Materials and methods

Phenol, 2,6-diphenylphenol, potassium carbonate (≥ 99%) and *N*-methyl-2-pyrrolidone (NMP, 99.5%) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. NMP was fractionally distilled prior to use and potassium carbonate was dried in vacuo at 100 °C for 24 h. The starting material *N*,*N′*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide and reference compound *N*,*N′*-dicyclohexyl-3,4:9,10-tetracarboxylic acid bisimide (**3**) were prepared according to literature procedures.[S1] Flash column chromatography was performed using silica gel (Si60, mesh size 40-63 µm) from Merck. NMR spectra were recorded with a Bruker Avance 400 MHz instrument. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^{1}H coupling constants J are given in Hertz (Hz). MALDI-TOF mass spectra were recorded on an Autoflex II from Bruker Daltonics spectrometer. ESI-TOF mass spectra were recorded on a Bruker Daltonics micrOTOF focus instrument.

All the solvents used for the spectroscopic measurements were of spectroscopic grade (Uvasol®) and were used without further purification. The UV/Vis spectra were recorded on a Perkin Elmer PE 950 spectrometer equipped with a PTP-1 peltier element for temperature control, and corrected against the reference solution. The fluorescence spectra were recorded with a PTI QM-4/2003 instrument. All fluorescence measurements were performed under ambient conditions and corrected against photomultiplier and lamp intensity. The fluorescence quantum yields were determined as the average value for three different excitation wavelengths using *N*,*N*'-di(2,6-di-isopropylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide as reference (Φ_{fl} = 1.00 in dichloromethane[S2]) by applying high dilution conditions ($A < 0.05$). Solid state absorption spectra of PBI **1**-**3** were determined by applying the Kubelka-Munk theory to reflectance spectra of trituration of PBIs in $BaSO_4$ measured with a Lambda 950 UV/Vis/NIR spectrometer of Perkin Elmer equipped with an integrating sphere. Absolute fluorescence quantum yields were determined on a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02. The system is made up of an excitation source that uses a 150 W CW Xenon light source, a monochromator (250-700 nm, FWHM 10 nm), an integrating sphere, and a multi-channel spectrometer capable of simultaneously measuring multiple wavelengths between 300 and 950 nm and counting the number of absorbed and emitted photons.

2. Synthesis



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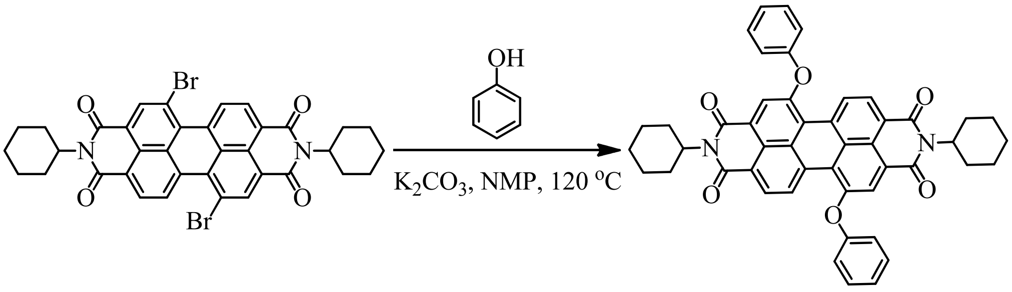
PBI 1. Under argon, to a degassed solution of *N*,*N'*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (350 mg, 0.49 mmol) and potassium carbonate (200 mg, 2.30 mmol) in dry NMP (20 mL), excess 2,6-diphenylphenol (0.30 g, 1.20 mmol) was added and the mixture was stirred at 120 °C for 3 h. After being cooled to room temperature, the reaction mixture was slowly dropped into 250 mL of 1 *N* HCl under stirring. The solid material was separated by filtration, and then washed successively with water (3 × 30 mL) and methanol (3 × 30 mL). The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent and afforded 402 mg of PBI **1** as a red solid. Yield: 79%, m.p. 216 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): $\delta = 9.22$ (d, $J = 8.0$ Hz, 2H), 8.33 (d, $J = 8.0$ Hz, 2H), 7.74 (s, 2H), 7.48-7.47 (m, 6H), 7.35-7.32(m, 8H), 6.94-6.82 (m, 12H), 4.87-4.79 (m, 2H), 2.43-2.34 (m, 4H), 1.81-1.78 (d, $J = 12.0$ Hz, 4H), 1.66-1.56(m, 6H), 1.39-1.16 (m, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2, ppm): $\delta = 164.2$, 163.6, 155.6, 148.1, 137.7, 136.8, 133.4, 131.5, 129.3, 129.2, 128.9, 128.7, 128.3, 127.8, 127.1, 124.2, 123.8, 122.5, 121.2, 119.8, 29.4, 26.9, 25.9. ESI-TOF-MS, calculated for $C_{72}H_{55}N_2O_6$: 1043.40601; found: $m/z = 1043.40546$.



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PBI 2. A mixture of *N*,*N'*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (220 mg, 0.31 mmol) was mixed with anhydrous potassium carbonate (425 mg), phenol (116 mg, 1.23 mmol), and dry NMP (10 mL). The mixture was heated at 120 °C under argon for 3 h. The reaction mixture was cooled to room temperature and poured into HCl 1M (50 mL). The resulting precipitate was filtered off and washed with water and methanol. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent to obtain 276 mg of PBI **2** as a red solid. Yield: 83%, m.p. 376 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.53 (d, *J* = 8.0 Hz, 2H), 8.56 (d, J = 8.0 Hz, 2H), 7.27 (s, 2H), 7.45 (t, *J* = 8.0 Hz, 4H), 7.2-7.1 (m, 2H), 7.15 (t, *J* = 8 Hz, 4H), 5.0-4.9 (m, 2H), 2.5-2.4 (m, 4H), 1.87 (d, *J* = 16 Hz, 4H), 1.7-1.6 (m, 6H), 1.4-1.2 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.74, 163.31 (C=O), 155.14, 155.14, 155.12, 133.23, 130.56, 130.20, 129.19, 128.77, 125.20, 125.07, 124.42, 124.03, 123.84, 122.78, 119.19, 29.08, 26.49, 25.41. MS (MALDI-TOF, DCTB): *m/z* = 738.27 $[M]^+$.

3. Single Crystal X-ray Analysis

Single crystals of PBIs 1 suitable for X-ray diffraction analysis were obtained by dissolving PBI 1 in a solvent mixture of CH_2Cl_2/EtOH = 90:10, followed by slow evaporation of the solvents. The crystal data of PBI 1 were collected on a Bruker X8APEX-II diffractometer with a CCD area detector and multi-layer mirror monochromated $\mathrm{Mo}_{\mathrm{K}□}$ radiation. The structure was solved using direct methods, expanded using Fourier techniques and refined with the Shelx software package [S3]. Hydrogen atoms were included in structure factors calculations at idealized positions and refined using a riding model.

Since the molecule lies about a centre of symmetry, the asymmetric unit comprises only one half of the molecule. With the current space group $P2_1/c$ this results in two molecules per unit cell. Contrary to the atoms of the bay area we found the atoms of the imide substituent and parts of the bulk substituent disordered about two sites, where the occupation factor of the main part is 84% and 77%, respectively. To keep the parts with minor occupation (16% and 23%, respectively) in chemically reasonable shape and their temperature factors at physically reasonable values 54 restraints had to be introduced in the least squares refinement (4 x ISOR , 14 x EADP, 1 EXYZ, SAME over 2 x 12 atoms) thus avoiding obvious correlations. 428 parameters were refined using 4560 reflections with Fo > 4sig(Fo).

Crystal data for PBI **1**: $C_{72}H_{54}N_2O_6$; $M_r = 1043.17$, red plate, $0.31 \times 0.29 \times 0.08$ mm^3, monoclinic space group $P2_1/c$ (No. 14), $a = 12.3452(15)$ Å, $b = 17.876(2)$ Å, $c = 12.6550(15)$ Å, $\beta = 104.209(5)°$, $V = 2707.4(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.280$ g·cm^{-3}, $\mu = 0.081$ mm^{-1}, $F(000) = 1096$, $T = 100(2)$ K, $GooF(F^2) = 1.018$, $R_1 = 0.0485$, $wR^2 = 0.1164$ for $I > 2\sigma(I)$, $R_1 = 0.0637$, $wR^2 = 0.1270$ for all data, 5769 independent reflections [$2\theta \leq 5$ 2.84°] and 428 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 901365. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4. Absorption and Fluorescence Spectra in Solution and Solid State

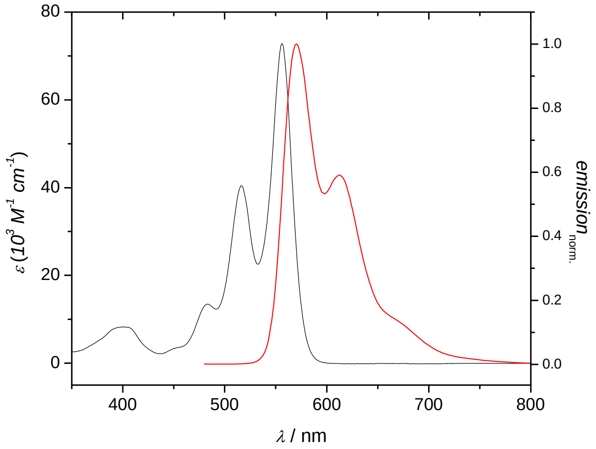

Fig. S1 UV/Vis absorption (4.0 × 10^{-6} mol/L) and emission spectra (4.0 × 10^{-6} mol/L) of PBI **1** in dichloromethane at room temperature.

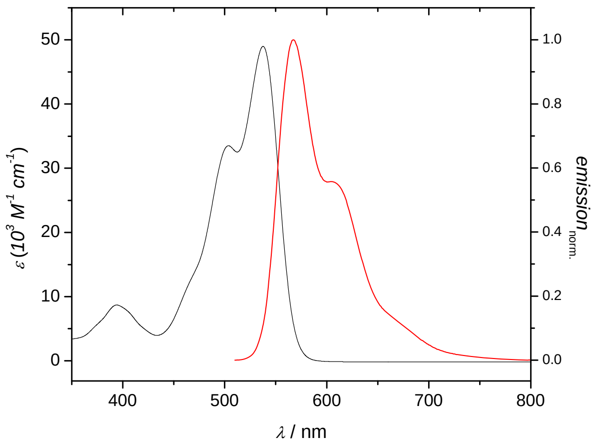

Fig. S2 UV/Vis absorption (2.0 × 10^{-5} mol/L) and emission spectra (2.0 × 10^{-5} mol/L) of PBI **2** in dichloromethane at room temperature.

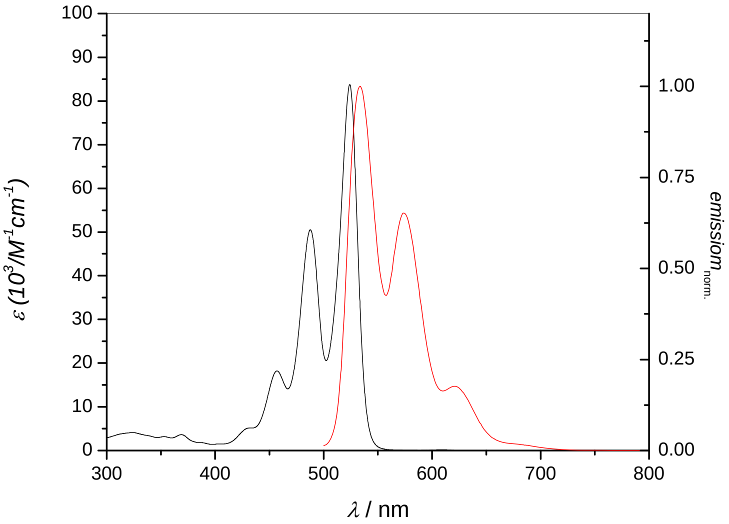

Fig. S3 UV/Vis absorption (7.0 × 10^{-6} mol/L) and emission spectra (7.0 × 10^{-6} mol/L) of PBI **3** in dichloromethane at room temperature.

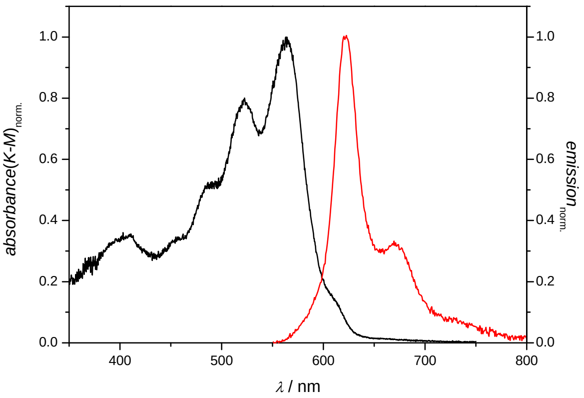

Fig. S4 Solid state absorption and emission spectra of PBI **1** at room temperature.

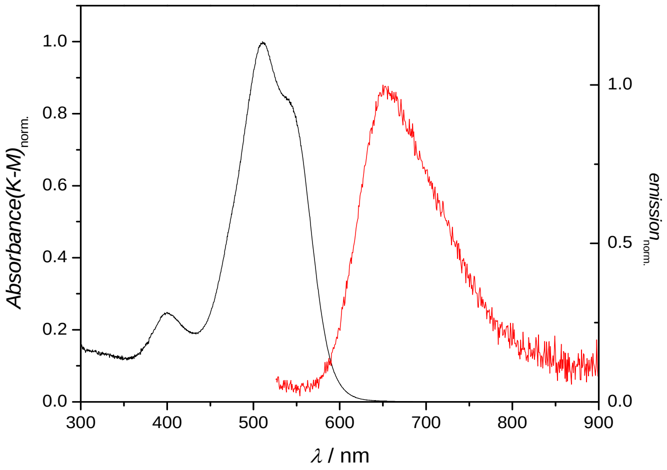

Fig. S5 Solid state absorption and emission spectra of PBI **2** at room temperature.

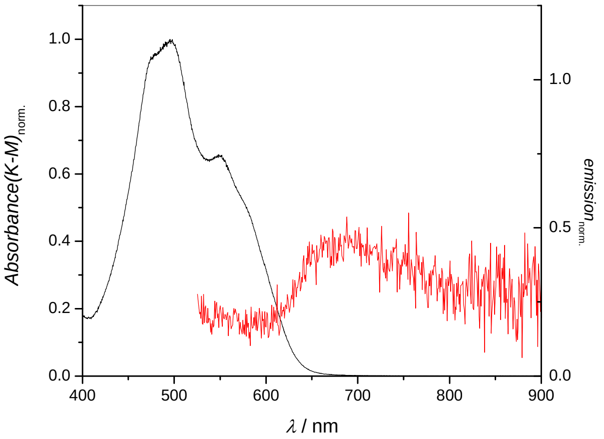

Fig. S6 Solid state absorption and emission spectra of PBI **3** at room temperature.

Table S1 Photophysical Properties of PBIs **1-3** in Solid State at Room Temperature

	λ_{max} (abs) (nm)	λ_{max} (em) (nm)	Stokes shift (nm)	Φ_{PL} (%)
1	563	622	59	37
2	510	653	143	13
3	495	672	177	3

5. References

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[S2] a) R. Gvishi, R. Reisfeld and Z. Burshtein, *Chem. Phys. Lett.,* 1993, **213**, 338-344; b) R. Sens and K. H. Drexhage, *J. Luminescence* 1981, **24**, 709-710.

[S3] G. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112-122.