**Electronic Supplementary Information for:**

# Metal ion templated self-assembly of crown ether functionalized perylene bisimide dyes

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## 1. Materials and methods

All solvents and reagents were purchased from commercial sources and used as received. The racemic 2-hydroxymethyl-15-crown-5 (**4a**) and 2-hydroxymethyl-18-crown-6 (**4b**) were obtained from commercial supplier. The starting compound **2** was prepared according to the literature.[1] Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040-0.063 mm) and alumina (EcoChrom Alumina B, Akt. I). The melting points (mp) of compounds were determined with an Olympus BX-41 polarization microscope equipped with a Linkam THMS 600 hot stage and a temperature controller unit. $^1$H and $^{13}$C spectra were recorded in $CDCl_3$, $CD_3CN$ and DMSO-$d_6$ at 298 K on a Bruker Avance 400 or DMX 600 spectrometer. High-resolution ESI-TOF mass spectrometry was carried out on a micro-TOF focus instrument (BrukerDaltronik GmbH).

Solvents for spectroscopic studies were of spectroscopic grade and used as received. UV/Vis spectra were measured in cells with pathlengths of 1 mm and 1 cm on a Perkin Elmer Lambda

40P spectrometer equipped with a Peltier system as the temperature controller. The steady state fluorescence spectra were measured on a PTI QM4/2003 spectrofluorometer. The fluorescence quantum yields were determined by the optically dilute method ($A < 0.05$) by using *N*,*N*′-bis(2,6-diisopropylphenyl) perylene-3,4:9,10-tetracarboxylic acid bisimide ($\Phi_{\text{fl}} = 1.00$ in $CHCl_3$) as standard.[2] The reported quantum yields are averaged values obtained at four different excitation wavelengths for each PBI.

ITC spectra were measured at 293 K on a MicroCal VP-iTC instrument.

## 2. Synthetic procedures and product characterization data

***N*,*N*′-Bis(2-(dimethylamino)-ethyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (3).** 1,7-Dibromoperylene-3,4:9,10-tetracarboxylic acid bisanhydride (**2**) (350 mg, 0.64 mmol) was placed under argon in 5.30 ml dry DMF and 3.60 ml dioxane. *N*,*N*-dimethylethylenediamine (124 mg, 154 µl, 1.41 mmol) was added and the reaction mixture was stirred at 85 °C for 2 h. After cooling down to room temperature water was added and the precipitated solid was separated by filtration and dried under reduced pressure. The crude product was purified by column chromatography (dichloromethane/methanol/triethylamine 93:6.5:0.5 as eluent) yielding **3** as a dark red solid (368 mg, 84%). mp > 300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 9.48$ (d, 2H, $^3J = 8.2$ Hz), 8.92 (s, 2H), 8.70 (d, 2H, $^3J = 8.2$ Hz), 4.36 (m, 4H), 2.68 (m, 4H), 2.36 (s, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta = 163.0$ (C), 162.5 (C), 138.2 (CH), 133.1 (C), 133.0 (C), 130.2 (CH), 129.4 (C), 128.6 (CH), 127.1 (C), 123.3 (C), 122.8 (C), 120.9 (C), 57.1 ($CH_2$), 45.9 ($CH_3$), 38.6 ($CH_2$). HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 691.037 $[M+H]^+$, calculated for $C_{32}H_{27}Br_2N_4O_4$ 691.030. UV/Vis ($CHCl_3$/MeOH 4:1): $\lambda$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$) = 526 (40600), 490 (27600), 459 (11000). Fluorescence ($CHCl_3$/MeOH 4:1, $\lambda_{\text{ex}} = 480$ nm): $\lambda_{\text{max}}$ / nm = 551; fluorescence quantum yield $\Phi_{\text{fl}} = 0.03$.

***N*,*N*′-Bis(2-(dimethylamino)-ethyl)-1,7-di(oxymethyl-15-crown-5)perylene-3,4:9,10-tetracarboxylic acid bisimide (5a).** A solution of racemic 2-hydroxymethyl-15-crown-5 (**4a**) (182 mg, 0.73 mmol) in 2 ml dry THF was added dropwise to a flask under argon containing NaH (20.3 mg of 60% dispersion in mineral oil, 0.85 mmol). The mixture was stirred for 5 min at room temperature and a solution of perylene bisimide **3** (100 mg, 0.15 mmol) in 7.5 ml dry THF was added dropwise over a 15 min period. The mixture was stirred for ca. 20 h at room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over basic alumina (activity grade III) using chloroform/methanol 99.5:0.5 as an eluent and subsequently over deactivated silica gel (dichloromethane/methanol/triethylamine 96:3.5:0.5). Additionally, a column filtration over basic alumina (dichloromethane/methanol 99:1) was performed. After removal of solvent under reduced pressure obtained solid was freeze-dried to get pure **5a** as a violet solid (58.0 mg, 39%). mp 237 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.73 (d, 2H, $^3J$ = 8.3 Hz), 8.57 (d, 2H, $^3J$ = 8.4 Hz), 8.54 (s, 2H), 4.66 (m, 2H), 4.51 (m, 2H), 4.38 (m, 4H), 4.25 (m, 2H), 4.10-3.67 (m, 36H), 2.72 (m, 4H), 2.40 (s, 12H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 163.7 (C), 163.6 (C), 156.8 (C), 134.0 (C), 129.2 (C), 129.2 (CH), 129.0 (CH), 123.6 (C), 123.1 (C), 121.8 (C), 121.1 (C), 117.7 (CH), 78.35 (CH), 78.33 (CH), 71.7-70.4 (10 x $CH_2$), 56.7 ($CH_2$), 45.4 ($CH_3$), 37.8 ($CH_2$). HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 1029.471 $[M+H]^+$, calculated for 1029.471. UV/Vis ($CH_3CN$): $\lambda$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$) = 560 (35700), 524 (26100), 485 (9600). Fluorescence ($CH_3CN$, $\lambda_{ex}$ = 500 nm): $\lambda_{max}$ / nm = 591; fluorescence quantum yield $\Phi_{fl}$ = 0.10.

***N,N´*-Bis(2-(dimethylamino)-ethyl)-1,7-di(oxymethyl-18-crown-6)perylene-3,4:9,10-tetracarboxylic acid bisimide (5b).** A solution of racemic 2-hydroxymethyl-18-crown-6 (**4b**) (214 mg, 0.73 mmol) in 2.50 ml dry THF was added dropwise to a flask under argon containing NaH (20.3 mg of 60% dispersion in mineral oil, 0.85 mmol). The mixture was stirred for 5 min at room temperature and a solution of perylene bisimide **3** (100 mg, 0.15 mmol) in 7.00 ml dry THF was added dropwise over a 15 min period. The mixture was stirred for 24 h at room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over basic alumina (activity grade III) using chloroform/methanol 99.5:0.5 and subsequently over deactivated silica gel (dichloromethane/methanol/triethylamine 95:4.5:0.5). Additionally, a column filtration over basic alumina (dichloromethane/methanol 98:2) was performed. After removal of solvent under reduced pressure obtained solid was freeze-dried to get pure **5b** as a violet solid (90.0 mg, 55%). mp 110 °C. $^1$H NMR (400 MHz, $CDCl_3/CD_3OD$): $\delta$ = 9.71 (d, 2H, $^3J$ = 8.4 Hz), 8.57 (d, 2H, $^3J$ = 8.4 Hz), 8.54 (s, 2H), 4.65 (m, 2H), 4.58 (m, 2H), 4.38 (m, 4H), 4.24 (m, 2H), 3.66-4.00 (m, 44H), 2.70 (m, 4H), 2.38 (s, 12H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 163.8 (C), 163.7 (C), 156.9 (C), 134.1 (C), 129.5 (C), 129.4 (CH), 129.1 (CH), 123.9 (C), 123.4 (C), 122.1 (C), 121.5 (C), 118.0 (CH), 77.74 (CH), 77.75 (CH), 71.5-70.3 (8 x $CH_2$), 57.1 ($CH_2$), 45.9 ($CH_3$), 38.4 ($CH_2$). HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 1117.524

$[M+H]^+$, calculated for 1117.523. UV/Vis ($CH_3CN$): $\lambda$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$) = 560 (35600), 524 (26000), 485 (9500). Fluorescence ($CH_3CN$, $\lambda_{ex}$ = 510 nm): $\lambda_{max}$ / nm = 590; fluorescence quantum yield $\Phi_{fl}$ = 0.12.

***N,N´*-Bis(2-(trimethylammonium)-ethyl)-1,7-di(oxymethyl-15-crown-5)perylene-3,4:9,10-tetra-carboxylic acid bisimide (1a).** Perylene bisimide **5a** (20.0 mg, 0.02 mmol) was placed in 845 µl toluene. Methyl iodide (22.1 mg, 9.68 µl, 0.16 mmol) was added and the reaction mixture was stirred at 128 °C for 2.5 h. After cooling down to room temperature, the precipitate was filtered off and washed with diethyl ether. The solvent was removed under reduced pressure to obtain **1a** as a dark violet solid (25.0 mg, 98%). mp 296 °C (decomp.). $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.73 (d, 2H, $^3J$ = 8.3 Hz), 8.52 (d, 2H, $^3J$ = 8.4 Hz), 8.48 (s, 2H), 4.70 (m, 2H), 4.53 (m, 6H), 4.20 (m, 2H), 3.93-3.56 (m, 40H, overlapping of protons of crown ether and $CH_2$-group $(N(CH_3)_3)^+$), 3.25 (s, 18H). $^{13}C$ NMR (151 MHz, DMSO-$d_6$): 162.8 (C), 162.7 (C), 156.6 (C), 133.1 (C), 128.6 (CH), 128.5 (C), 123.2 (C), 123.1 (C), 121.1 (C), 120.7 (C), 117.9 (CH), 77.2 (CH), 70.6-69.6 (9 x $CH_2$), 61.9 ($CH_2$), 52.5 ($CH_3$), 33.8 ($CH_2$). HRMS (ESI, positive mode, methanol): *m/z* found 529.254 $[M]^{2+}$, calculated for $C_{56}H_{74}N_4O_{16}{}^{2+}$ 529.254. UV/Vis ($CH_3CN$): $\lambda$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$) = 566 (46600), 528 (29800), 490 (10800). Fluorescence ($CH_3CN$, $\lambda_{ex}$ = 505 nm): $\lambda_{max}$ / nm = 598; fluorescence quantum yield $\Phi_{fl}$ = 0.73.

***N,N´*-Bis(2-(trimethylammonium)-ethyl)-1,7-di(oxymethyl-18-crown-6)perylene-3,4:9,10-tetra-carboxylic acid bisimide (1b).** Perylene bisimide **5b** (10.0 mg, 0.01 mmol) was placed in 400 µl toluene. Methyl iodide (10.3 mg, 4.50 µl, 0.07 mmol) was added and the reaction mixture was stirred at 129 °C for 2 h. After cooling down to room temperature, the precipitate was filtered off and washed with diethyl ether. The solvent was removed under reduced pressure to obtain **1b** as a dark violet solid (10.0 mg, 80%). mp 286 °C (decomp.). $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.75 (d, 2H, $^3J$ = 8.4 Hz), 8.55 (d, 2H, $^3J$ = 8.4 Hz), 8.52 (s, 2H), 4.74 (m, 2H), 4.60 (m, 2H), 4.53 (m, 4H), 4.19 (m, 2H), 3.55-3.90 (m, 48H, overlapping of protons of crown ether and $CH_2$-group $(N(CH_3)_3)^+$), 3.24 (s, 18H). $^{13}C$ NMR (151 MHz, DMSO-$d_6$): $\delta$ = 162.7 (C), 162.6 (C), 156.4 (C), 132.9 (C), 128.5 (CH), 128.3 (C), 123.0 (C), 122.9 (C), 120.9 (C), 120.6 (C), 117.6 (CH), 76.7 (CH), 70.3-69.2 (9 x $CH_2$), 62.0 ($CH_2$), 52.5 ($CH_3$), 33.8 ($CH_2$). HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 573.280 $[M]^{2+}$, calculated for $C_{60}H_{82}N_4O_{18}{}^{2+}$ 573.280. UV/Vis ($CH_3CN$): $\lambda$ / nm ($\varepsilon$ / $M^{-1}$ $cm^{-1}$)

= 566 (38700), 528 (25000), 490 (9300). Fluorescence ($CH_3CN$, $\lambda_{ex}$ = 520 nm): $\lambda_{max}$ / nm = 595; fluorescence quantum yield $\Phi_{fl}$ = 0.82.

## 3. UV/Vis and fluorescence titration of 1a and Hill plot

For the investigation of metal ion templated self-assembly of PBI **1a**, UV/Vis and fluorescence titration experiments were performed in the presence of different metal ions. These experiments were carried out on 3.3 ml sample solutions of PBI **1a** ($c$ = 1.06 x $10^{-5}$ or 1.01 x $10^{-4}$ M) in acetonitrile by microadditions of metal salts stock solutions ($c$ = 5.00 x $10^{-3}$or 2.00 x $10^{-2}$ M) in acetonitrile.

Only the addition of $Ba^{2+}$ to PBI **1a** solutions leads to a decrease of the absorption maximum with hypsochromic shift and an emission intensity decrease. The changes in absorption maximum are plotted against the concentration of barium ion and the data points are fitted to the Hill equation[3] (S2). The Hill equation is derived from a binding reaction scheme (S1) in which $n$ molecules of guest (G), in the present case $Ba^{2+}$ bind to a receptor (R), in the present case PBI **1a**:

$$\mathrm{R} + n\mathrm{G} \rightleftharpoons \mathrm{RG}_n \quad \text{(S1)}$$

At equilibrium, the ratio of bound to total receptors ($y$) is:

$$y = \frac{[\mathrm{G}]^n \, {K_1}^n}{(1+{K_1}^n \, [\mathrm{G}]^n)} \qquad \text{(S2)}$$

Here $n$ is the Hill coefficient and $K_1$ is the association constant. From the fitting curve the $n$ and $K_1$ values can be derived.

The fitting of absorption data to Hill equation for PBI **1a** concentration of $c$ = 1.06 x $10^{-5}$ M is shown in the main text (Fig. 4) and for higher concentrations of PBI **1a** ($c$ = 1.01 x $10^{-4}$ M) in Fig. S1d.

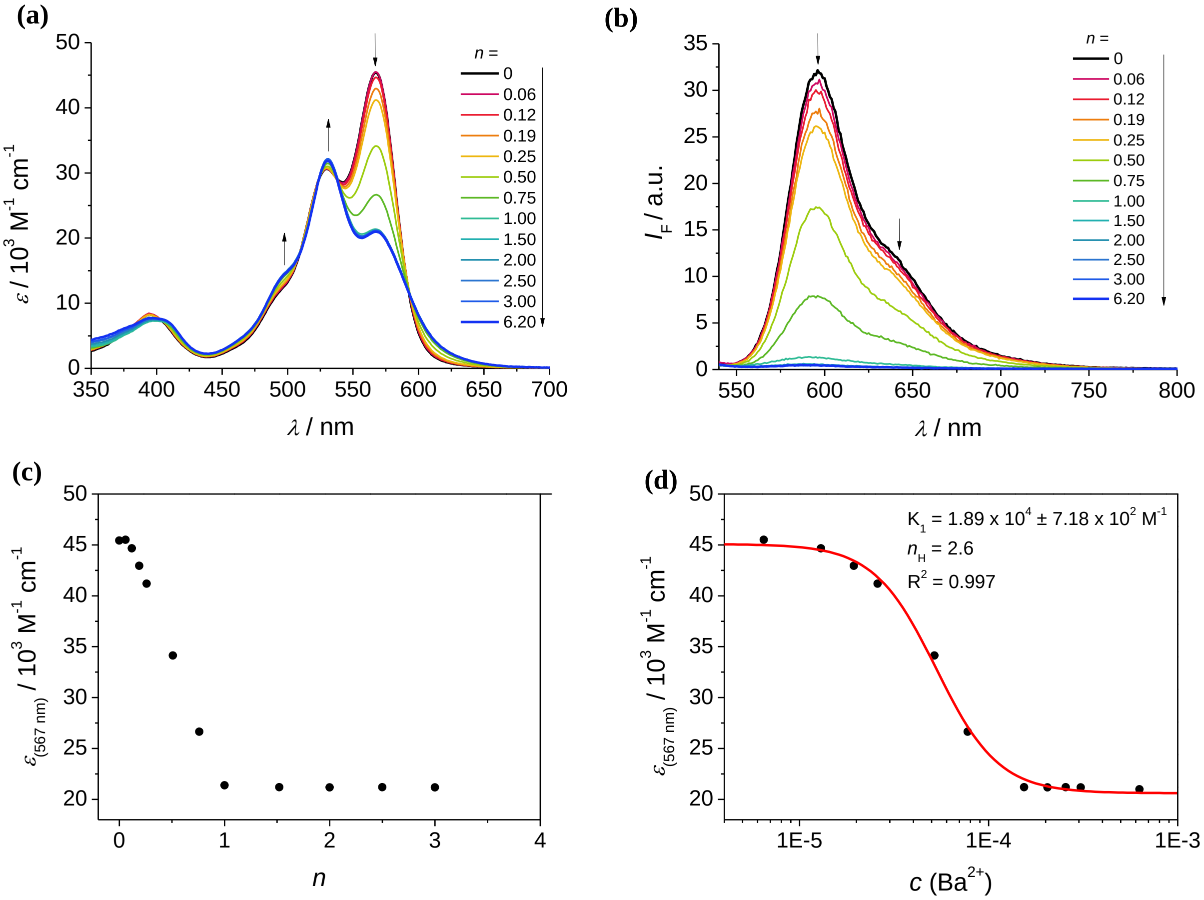


**Fig. S1** (a) UV/Vis absorption and (b) emission ($\lambda_{ex}$ = 505 nm) spectra of PBI **1a** in acetonitrile ($c$ = 1.01 x $10^{-4}$ M) on addition of Ba(ClO$_4$)$_2$ in acetonitrile (0 – 6.28 x $10^{-4}$ M, 0 – 6.2 equiv). (c) Plot of absorption at 567 nm against the molar ratio of $Ba^{2+}$/PBI **1a** ($n$). (d) Plot of $\varepsilon$ (at 567 nm) of PBI **1a** versus concentration of $Ba^{2+}$ and fit of the data points to the Hill equation. Black circles represent the experimental data obtained from UV/Vis spectra and the red line is the fitting curve.

## 4. UV/Vis and fluorescence titration of PBI 1b

For the investigation of the metal ion templated self-assembly of PBI **1b**, UV/Vis and fluorescence titration experiments were performed in the presence of different metal ions. The titration experiments were carried out on 3.3 ml sample solutions of PBI **1b** ($c$ = 1.01 x $10^{-5}$ M) in acetonitrile by microadditions of metal salts stock solutions in acetonitrile. The addition of different metal ions showed no or very little spectral changes in the absorption and emission spectra of PBI **1b**.

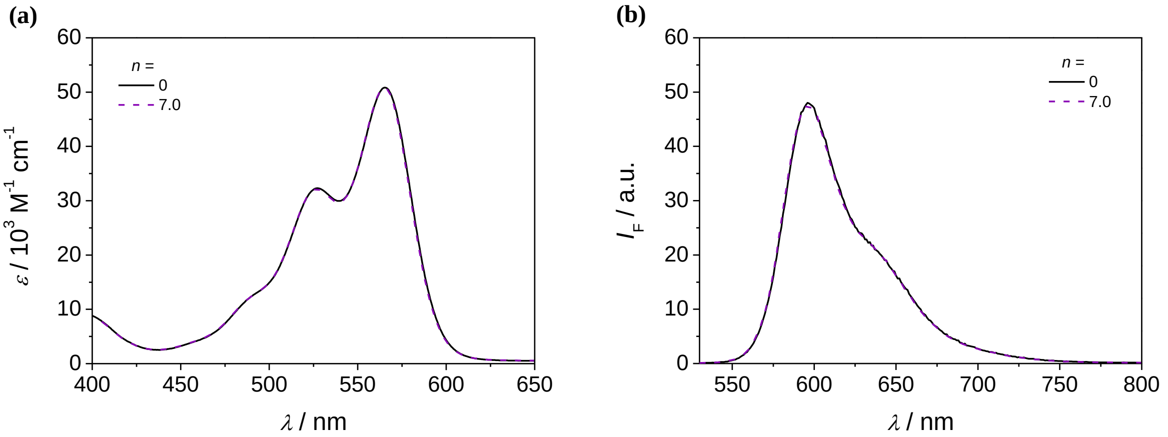


**Fig. S2** (a) UV/Vis absorption and (b) emission ($\lambda_{ex}$ = 520 nm) spectra of PBI **1b** in acetonitrile ($c$ = 1.01 x $10^{-5}$ M) on addition of NaClO$_4$ in acetonitrile (0 – 7.11 x $10^{-5}$ M); $n$ = molar ratio of Na$^+$/PBI **1b**. Spectra in the absence of Na$^+$ (black line) and with 7 equivalents of Na$^+$ (purple dashed line) are shown.

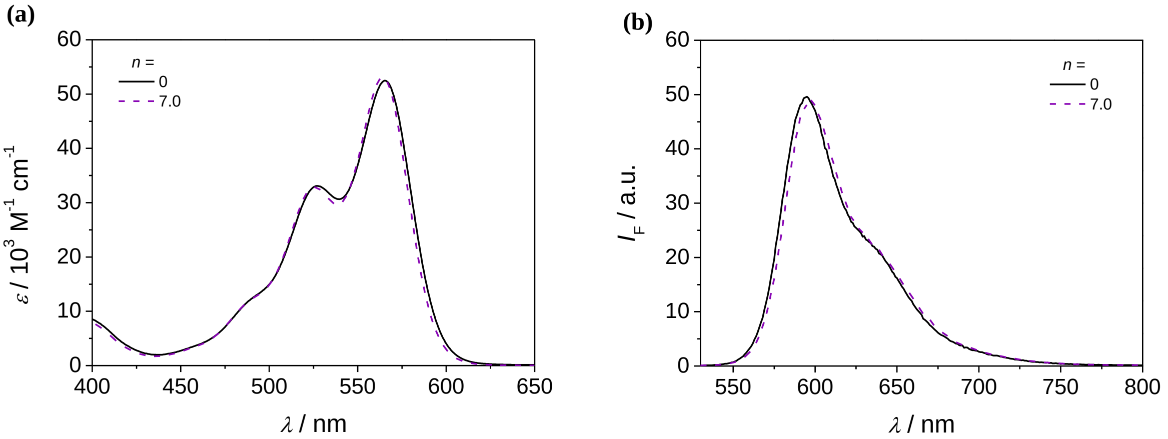


**Fig. S3** (a) UV/Vis absorption and (b) emission ($\lambda_{ex}$ = 520 nm) spectra of PBI **1b** in acetonitrile ($c$ = 1.01 x $10^{-5}$ M) on addition of KClO$_4$ in acetonitrile (0 – 7.08 x $10^{-5}$ M); $n$ = molar ratio of K$^+$/PBI **1b**. Spectra in the absence of K$^+$ (black line) and with 7 equivalents of K$^+$ (purple dashed line) are shown.

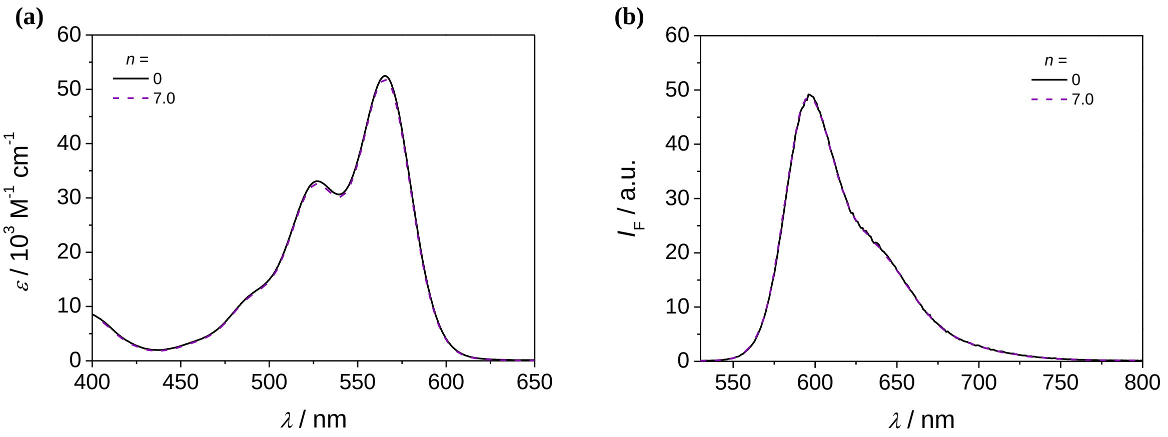


**Fig. S4** (a) UV/Vis absorption and (b) emission ($\lambda_{ex}$ = 520 nm) spectra of PBI **1b** in acetonitrile ($c$ = 1.01 x $10^{-5}$ M) on addition of $CsClO_4$ in acetonitrile (0 – 7.10 x $10^{-5}$ M); $n$ = molar ratio of $Cs^+$/PBI **1b**. Spectra in the absence of $Cs^+$ (black line) and with 7 equivalents of $Cs^+$ (purple dashed line) are shown.

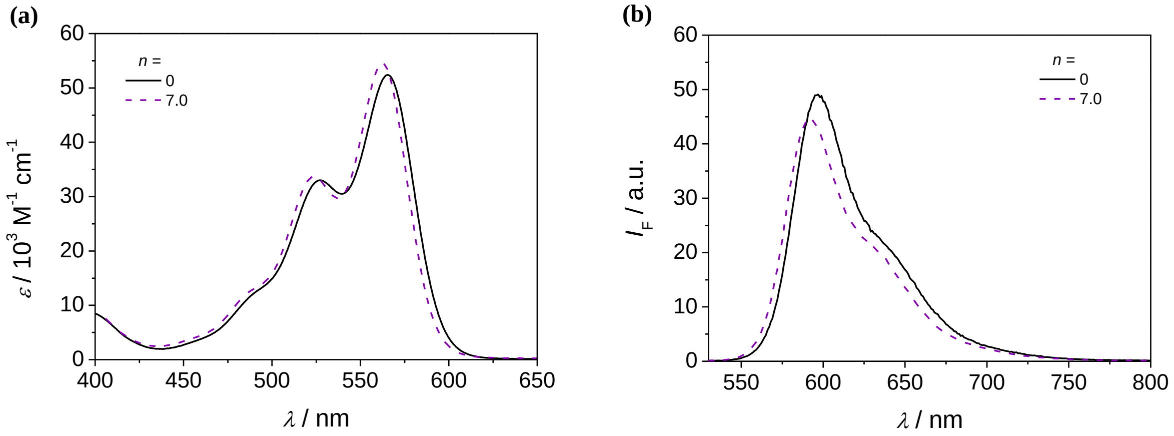


**Fig. S5** (a) UV/Vis absorption and (b) emission ($\lambda_{ex}$ = 520 nm) spectra of PBI **1b** in acetonitrile ($c$ = 1.01 x $10^{-5}$ M) on addition of $Ba(ClO_4)_2$ in acetonitrile (0 – 7.10 x $10^{-5}$ M); $n$ = molar ratio of $Ba^{2+}$/PBI **1b**. Spectra in the absence of $Ba^{2+}$ (black line) and with 7 equivalents of $Ba^{2+}$ (purple dashed line) are shown.

## 5. Isothermal titration calorimetry studies

In isothermal titration calorimetry (ITC) experiments, a solution of $Ba(ClO_4)_2$ in acetonitrile was injected stepwise at a rate of 0.5 µl/s to a solution of PBI **1a** ($c$ = 1.06 x $10^{-5}$ or 1.00 x $10^{-4}$ M) in the same solvent. A $Ba(ClO_4)_2$ concentration of 1.01 x $10^{-3}$ M was used for the experiments with PBI **1a** concentration of 1.06 x $10^{-5}$ M (Fig. S6a) and 1.00 x $10^{-2}$ M in the case of **1a** concentration of 1.00 x $10^{-4}$ M (Fig. S6b). Measurements were conducted at 293 K and the added volume of $Ba(ClO_4)_2$ solution was 1 µl per injection. Each new injection was started after reaching chemical and thermal equilibrium. The measured heat flows were recorded as a function of time and the area of each peak is then integrated and plotted versus the molar ratio of $Ba^{2+}$ to PBI **1a**. The center of the resulted binding isotherm gives the reaction stoichiometry. The enthalpy ($\Delta H$) is derived directly from the isotherm and provides the amount of heat released per mole of $Ba^{2+}$ bound.

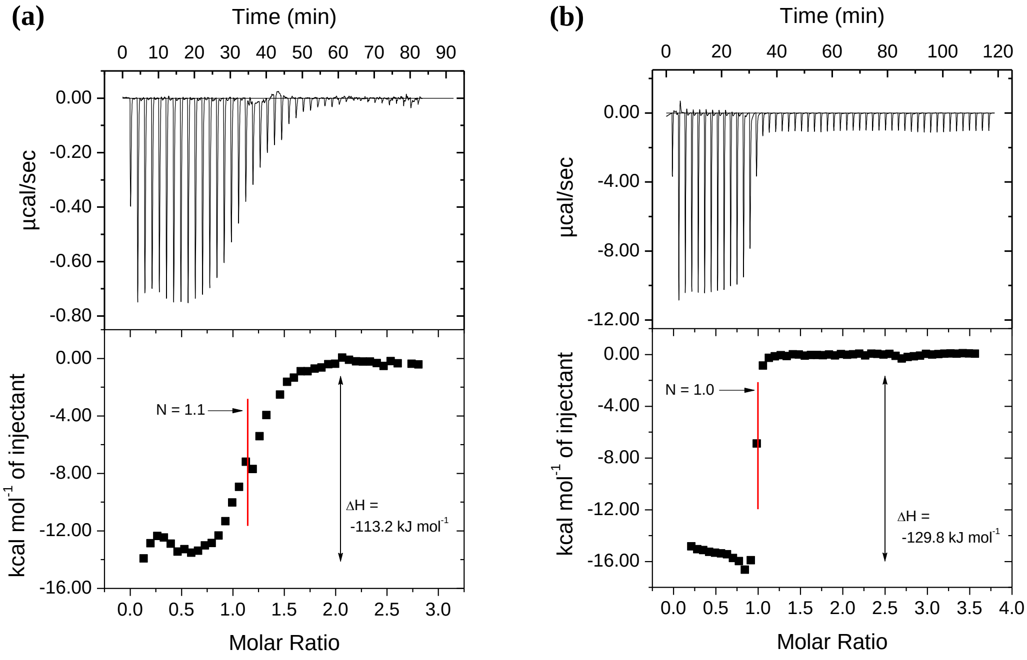


**Fig. S6** Calorimetric titration of $Ba(ClO_4)_2$ into 1.06 x $10^{-5}$ M (a) and 1.0 x $10^{-4}$ M (b) solution of PBI **1a** in acetonitrile at 293 K. Top: data obtained after periodic injections of $Ba(ClO_4)_2$ solution; bottom: released heat/mole of injectant $Ba^{2+}$ plotted against the molar ratio of $Ba^{2+}$ to PBI **1a**.

# 6. $^1$H NMR titration experiments of 1a with Ba$^{2+}$ ion

The $^1$H NMR titration experiments were performed in a NMR tube with 0.7 ml solution. Aliquots of a barium perchlorate solution ($c$ = 2.00 x 10$^{-2}$ M) in deuterated acetonitrile were added to a solution of **1a** ($c$ = 1.01 x 10$^{-4}$ M) in the same solvent.

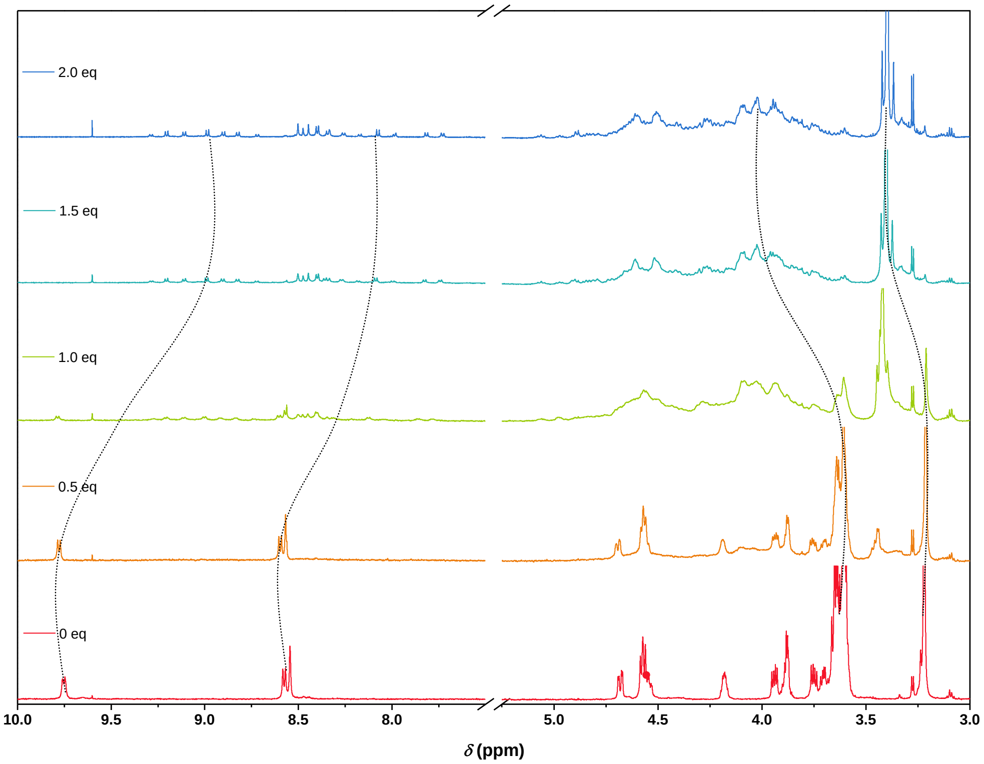


**Fig. S7** $^1$H NMR (600 MHz) spectra of PBI **1a** ($c$ = 1.0 x 10$^{-4}$ M) in $d_3$-acetonitrile on addition of 0 – 2.0 equivalents of Ba$^{2+}$ ions at 298 K.

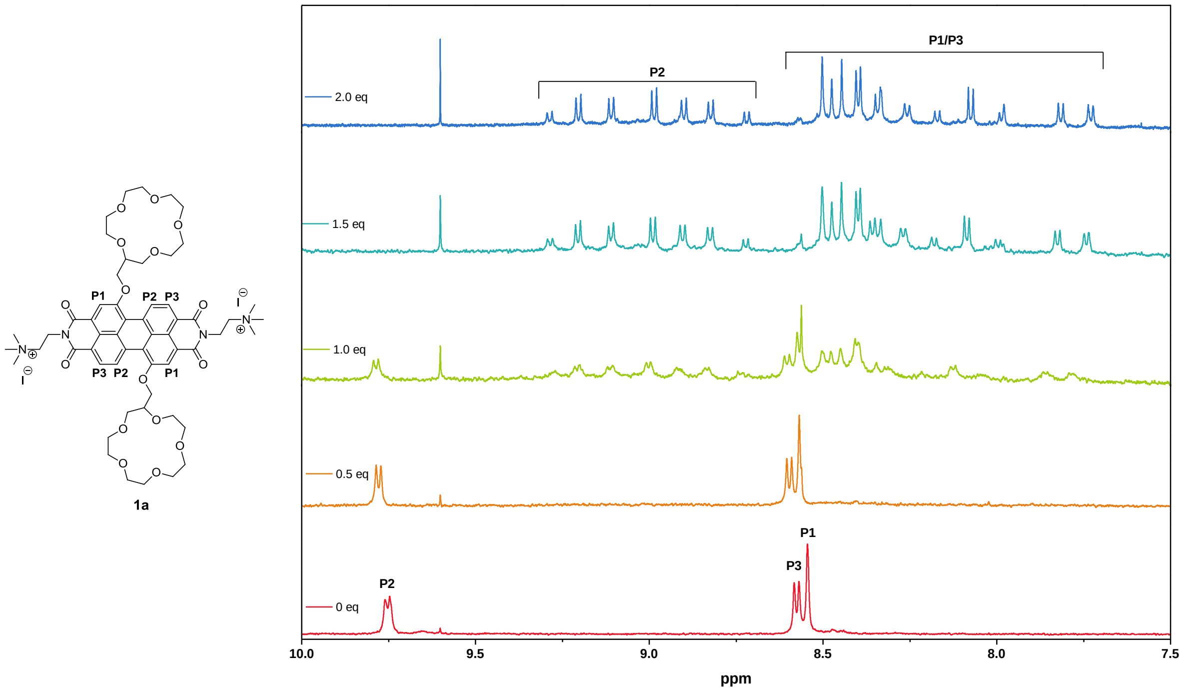
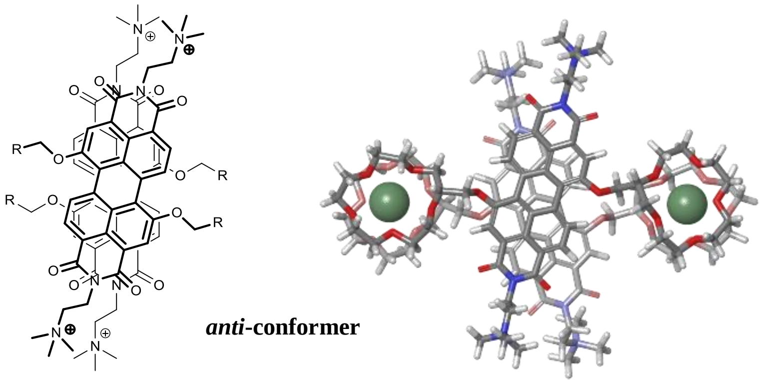
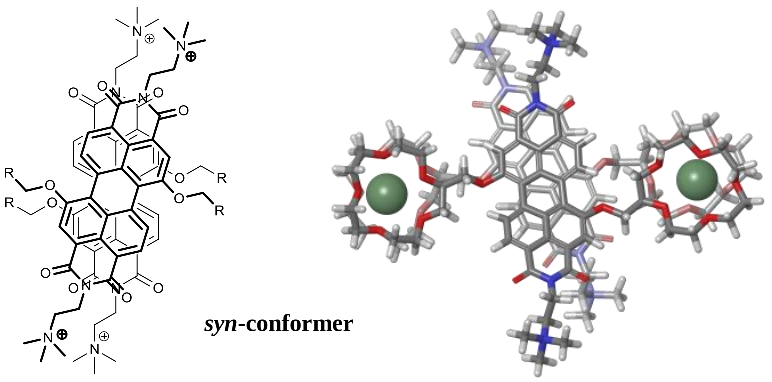


**Fig. S8** Left: Chemical structure of PBI **1a** with the assignment of perylene core protons. Right: Aromatic regions of $^1$H NMR spectra (600 MHz) of PBI **1a** ($c$ = 1.0 x $10^{-4}$ M) in $d_3$-acetonitrile on addition of 0 – 2.0 equivalents of $Ba^{2+}$ ions at 298 K. The signal at 9.60 ppm is due to impurity from the solvent.



***anti*-conformer**



***syn*-conformer**

**Fig. S9** Left: Proposed chemical structures of *anti*- and *syn*-conformer of PBI **1a** dimer. For simplicity the crown ether units with $Ba^{2+}$ ions are left out. Right: Energy minimized structures (Macro Model) of both conformers of PBI **1a**/$Ba^{2+}$ dimer complex.

## 7. $^1$H and $^{13}$C NMR spectra of compounds 1a/1b, 5a/5b and 3

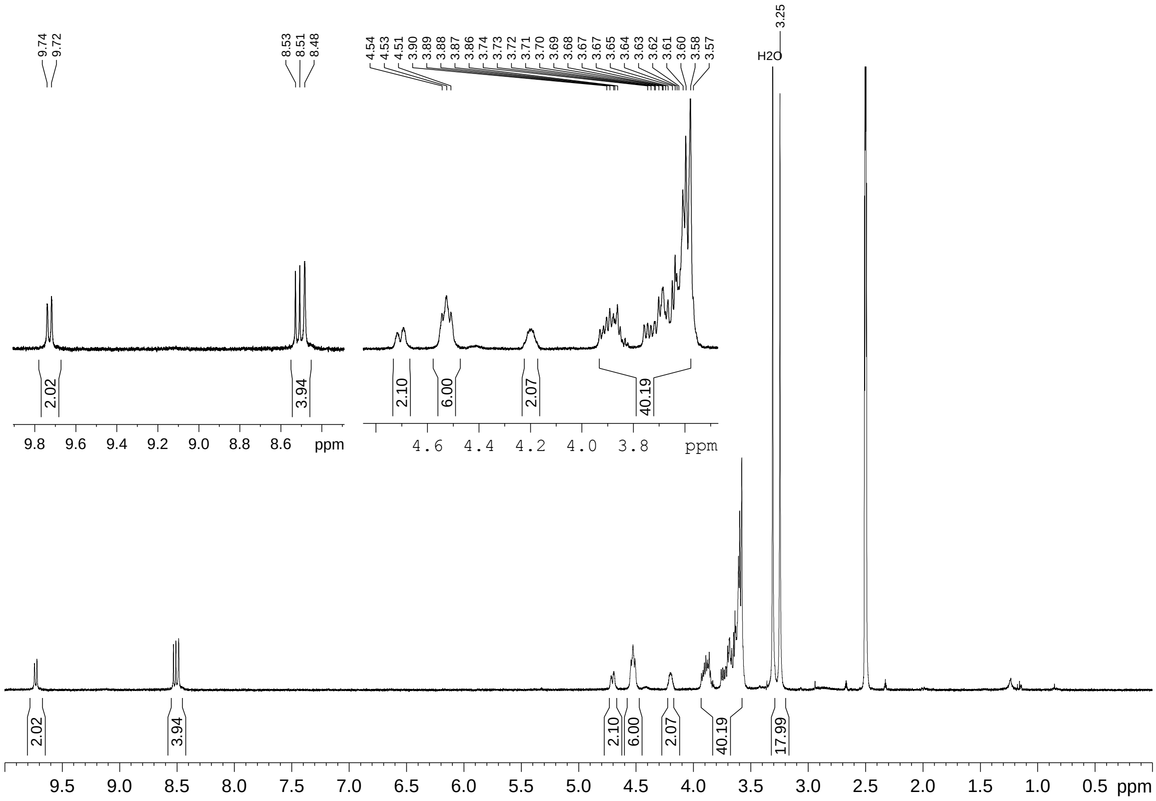


**Fig. S10** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of perylene bisimide **1a**.

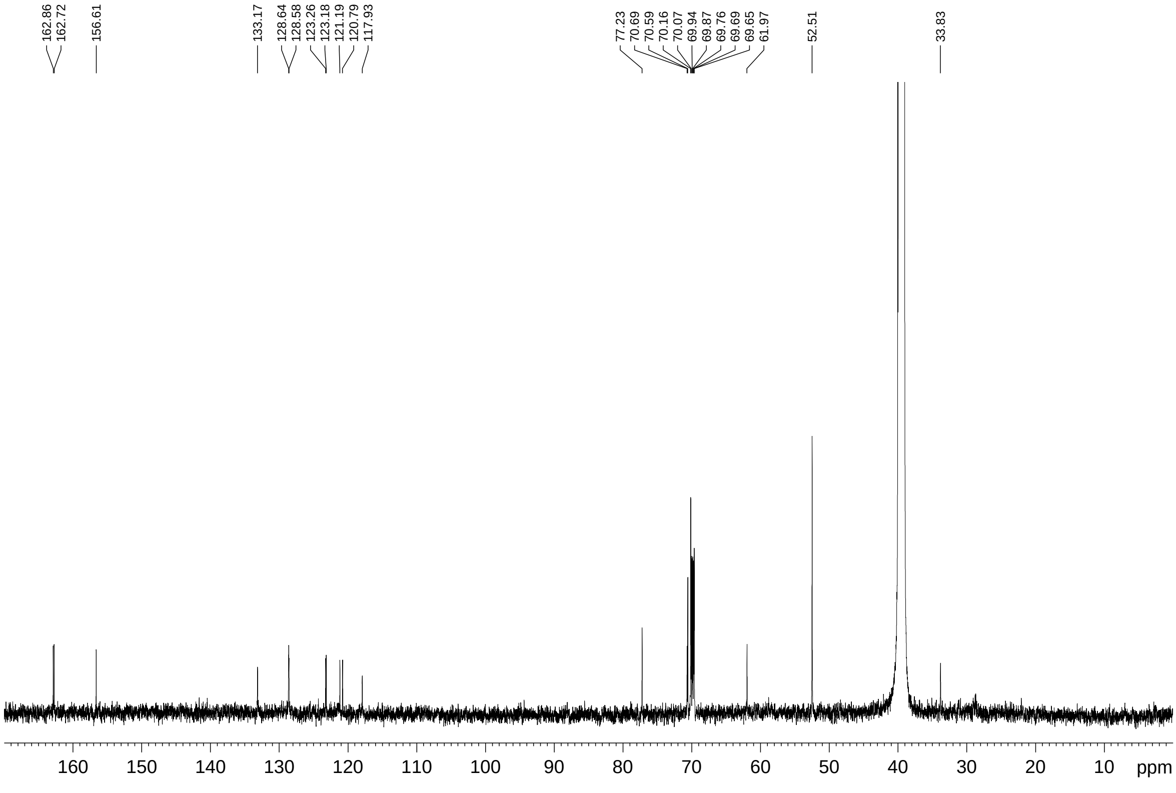


**Fig. S11** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$, 298 K) of perylene bisimide **1a.**

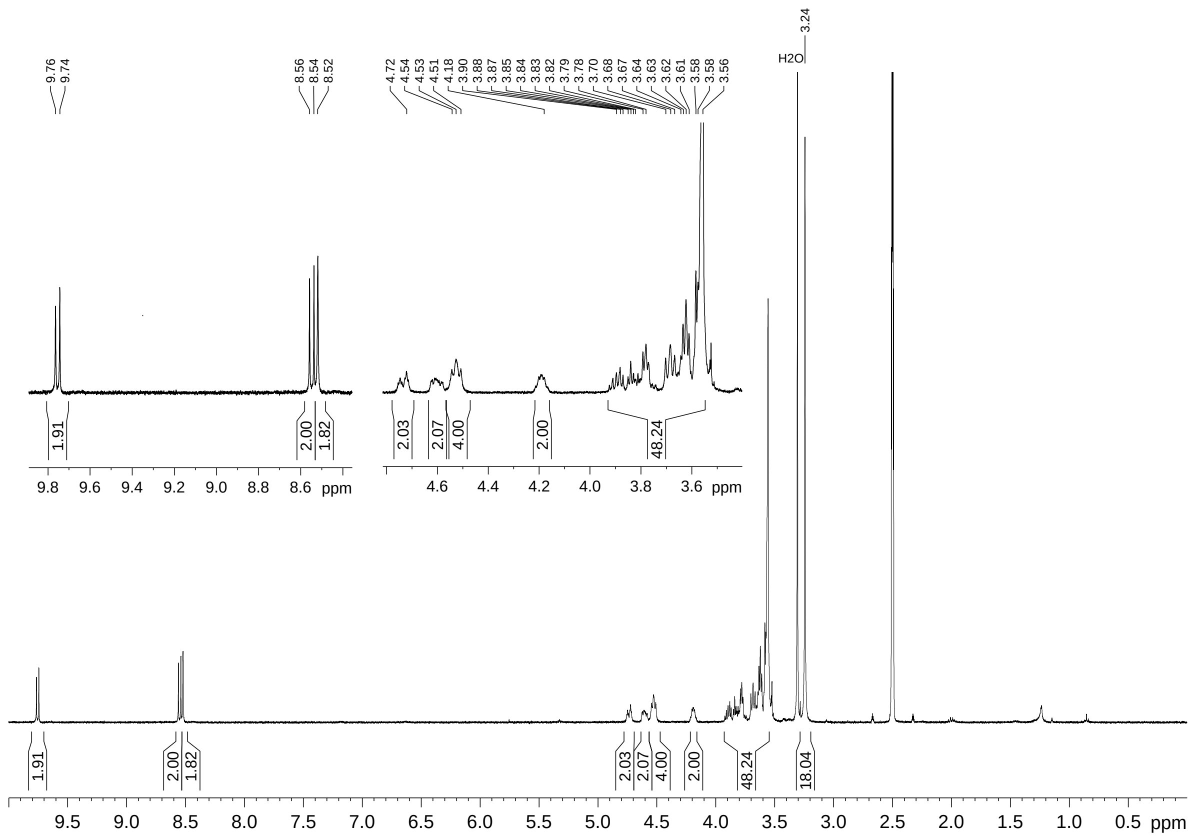


**Fig. S12** $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of perylene bisimide **1b**.

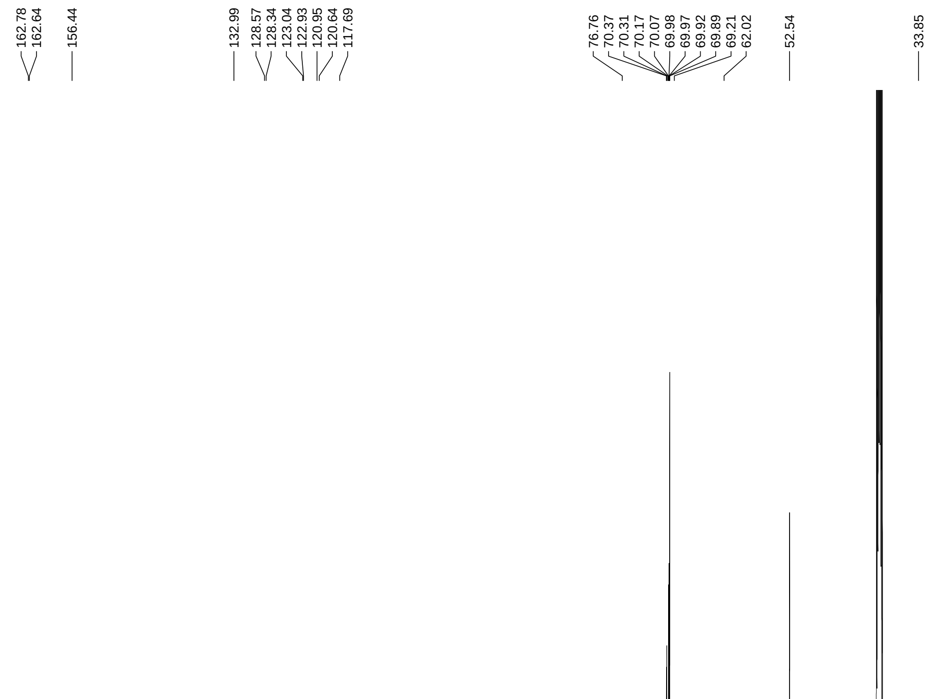


**Fig. S13** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$, 298 K) of perylene bisimide **1b.**

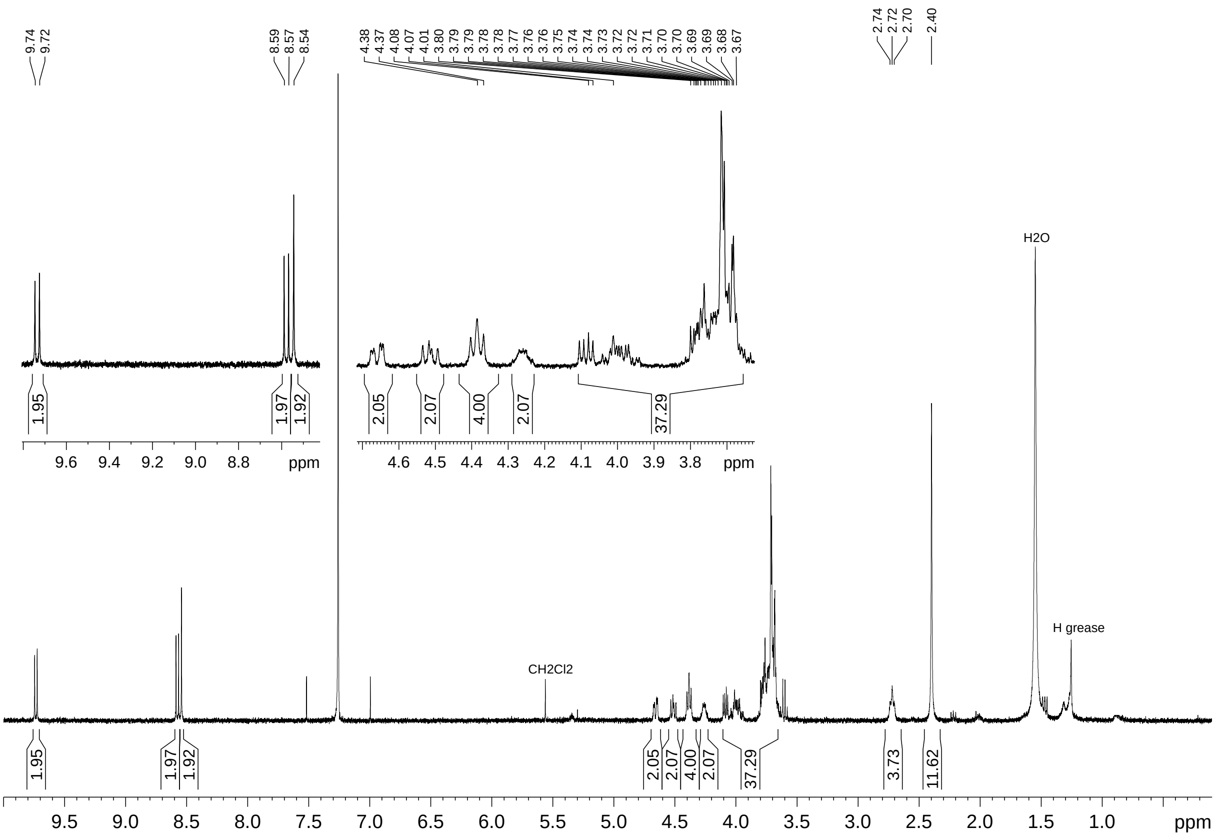


**Fig. S14** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of perylene bisimide **5a**.

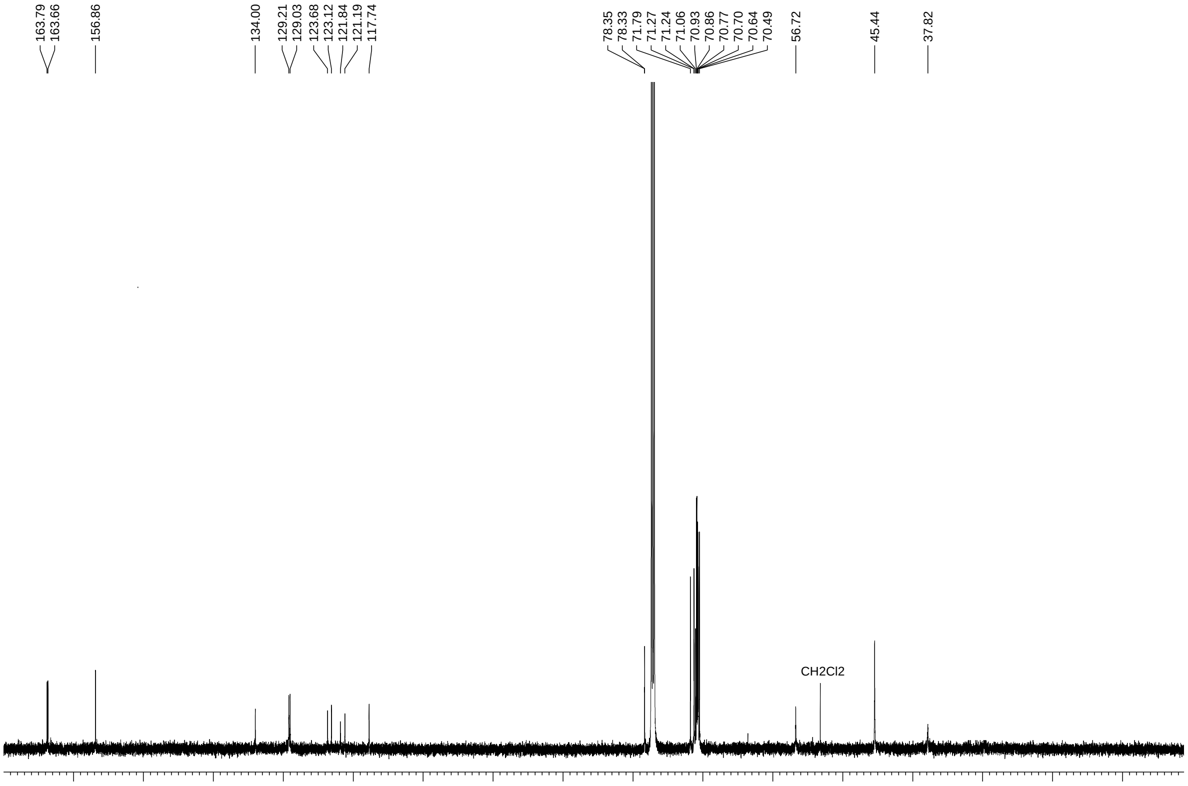


**Fig. S15** $^{13}$C NMR spectrum (151 MHz, $CDCl_3$, 298 K) of perylene bisimide **5a**.

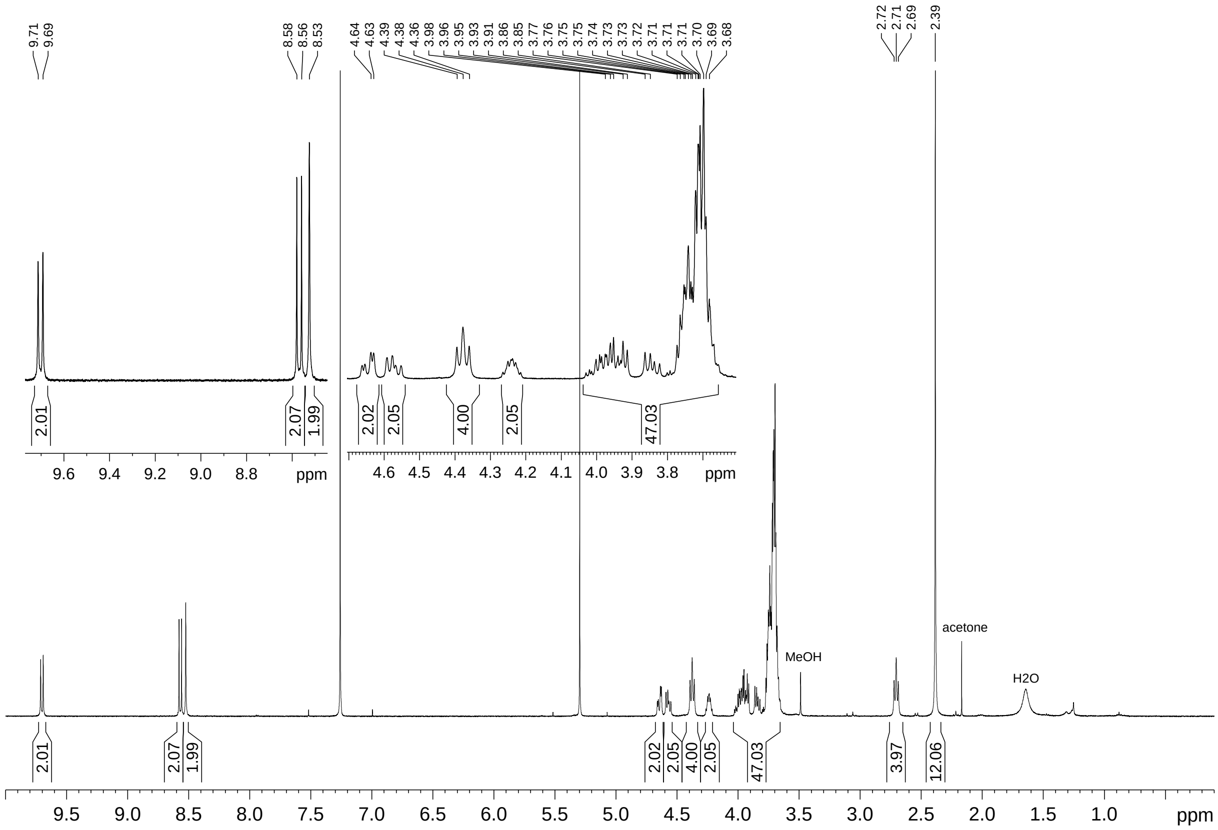


**Fig. S16** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$/$CD_3OD$, 298 K) of perylene bisimide **5b**.

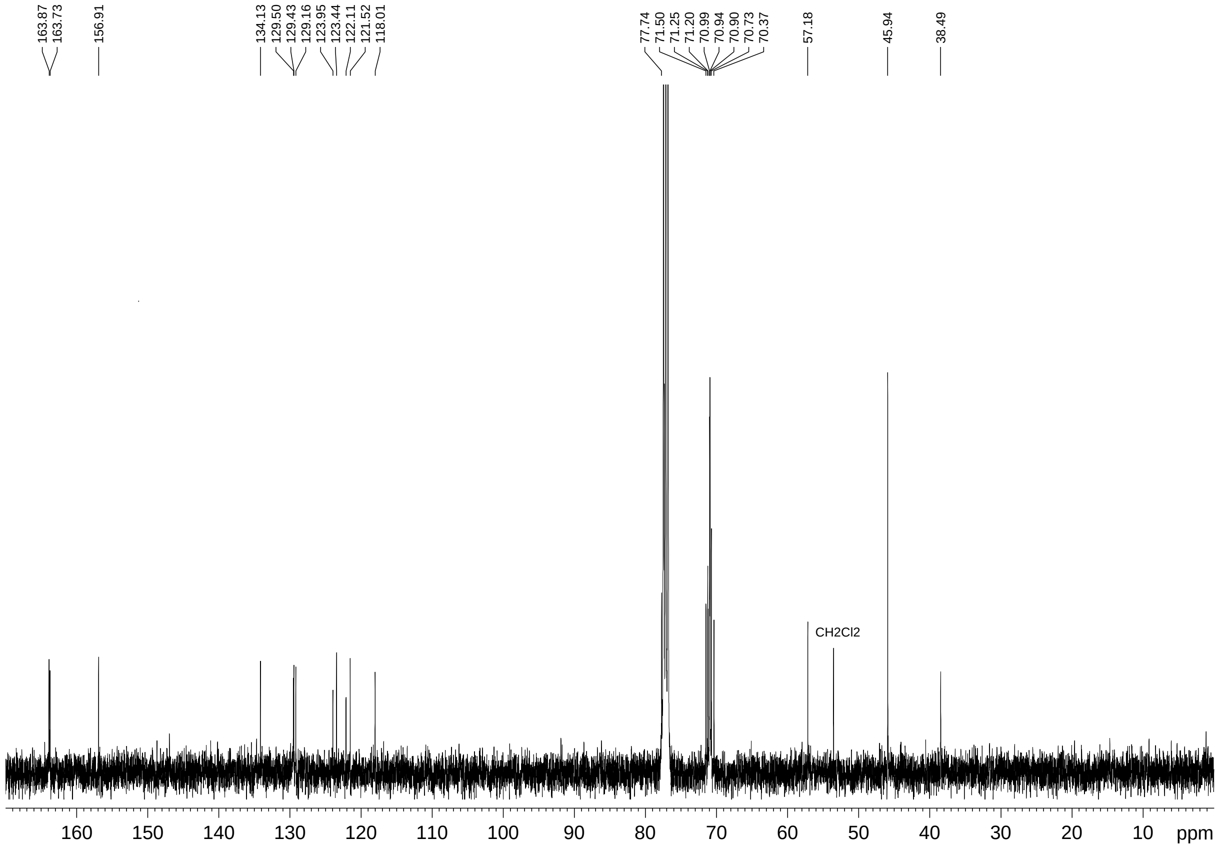


**Fig. S17** $^{13}$C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of perylene bisimide **5b**.

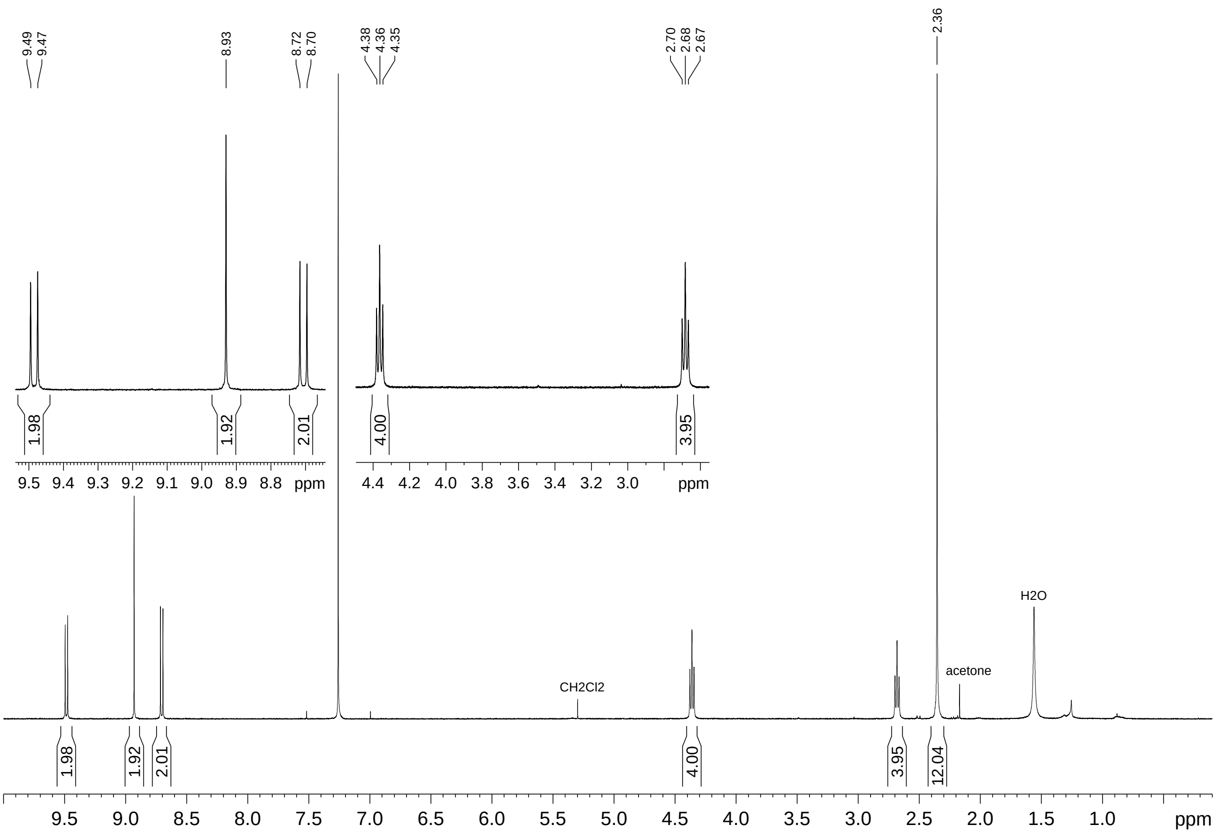


**Fig. S18** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of perylene bisimide **3**.

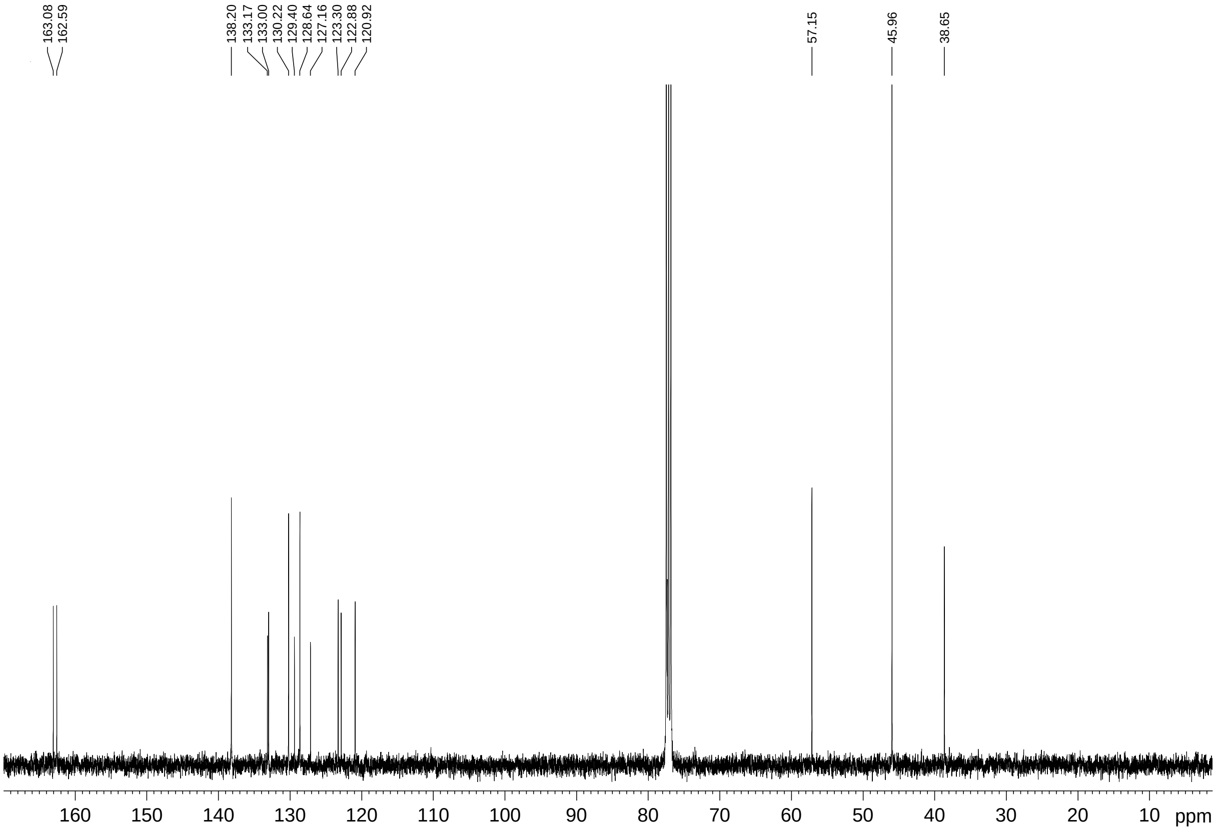


**Fig. S19** $^{13}$C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of perylene bisimide **3**.

## 8. High-resolution mass spectra of compounds 1a/1b, 5a/5b and 3

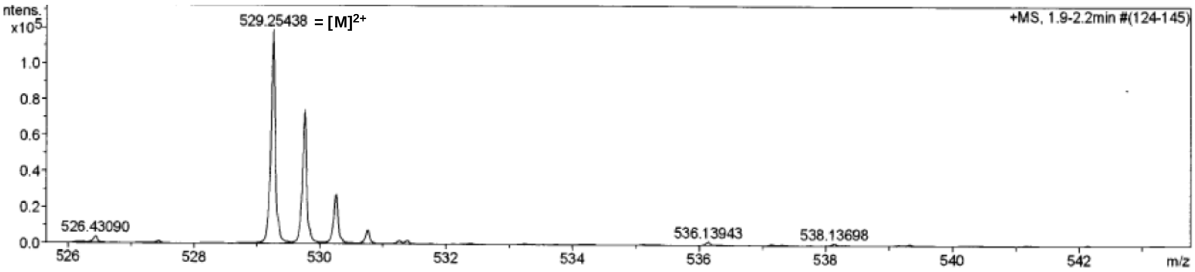


**Fig. S20** High-resolution mass spectrum (ESI) of PBI **1a**.

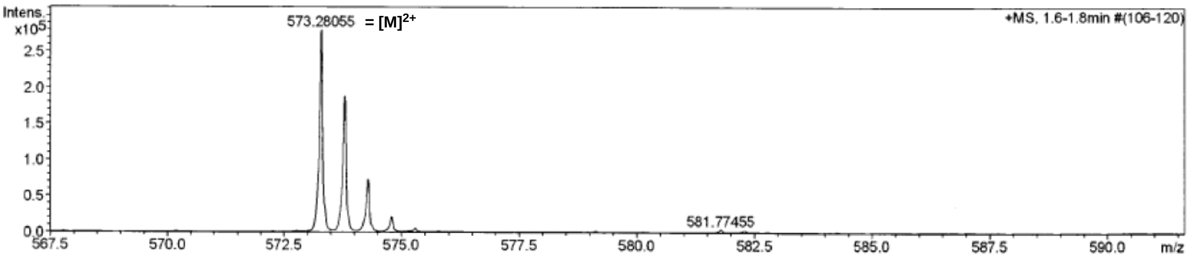


**Fig. S21** High-resolution mass spectrum (ESI) of PBI **1b**.

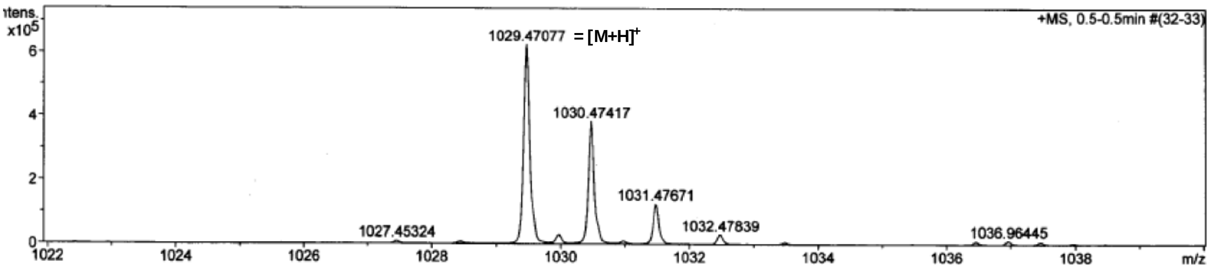


**Fig. S22** High-resolution mass spectrum (ESI) of PBI **5a**.

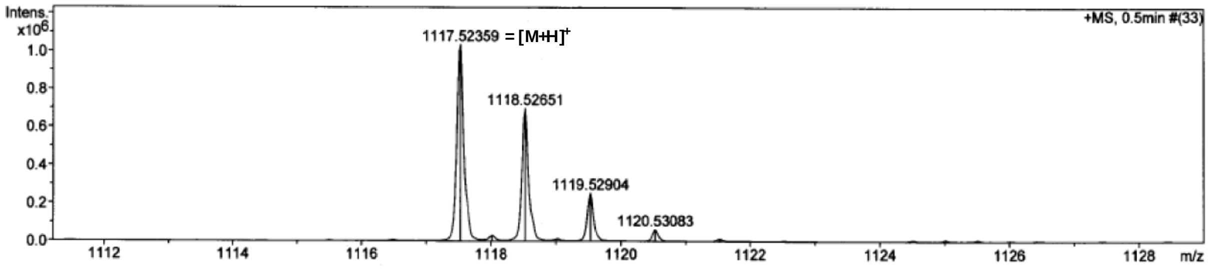


**Fig. S23** High-resolution mass spectrum (ESI) of PBI **5b**.

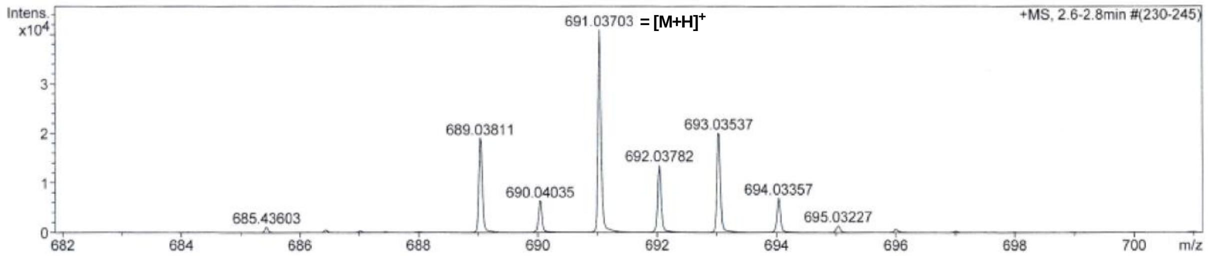


**Fig. S24** High-resolution mass spectrum (ESI) of PBI **3**.

## 9. References

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