

Electronic Supplementary Information (ESI) for:

Perylene bisimide macrocycles and their self-assembly on HOPG surfaces

Felix Schlosser, Vladimir Stepanenko and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany.

Fax: +49 31 84756; Tel: +49 31 85340; E-mail: wuerthner@chemie.uni-wuerzburg.de

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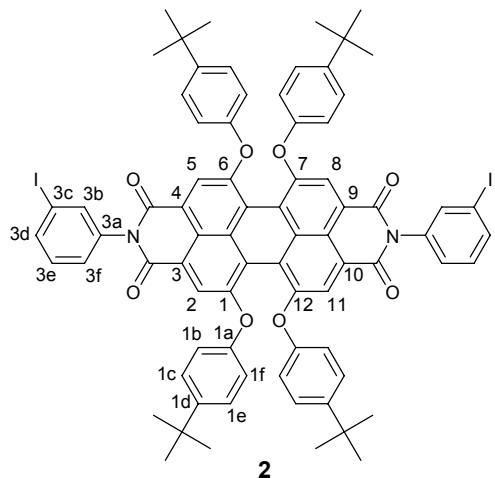
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1. General methods

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Solvents for spectroscopic studies were of spectroscopic grade and used as received. ^1H NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer and calibrated against the residual solvent peak. For the separation of the macrocycles, preparative recycling GPC LC-9105, Japan Analytical Industry Co., Ltd. (JAI) with JAIGEL 2H+2.5H columns was used. UV-vis spectra were measured on a Perkin-Elmer Lambda 950 spectrometer. AFM investigations were performed under ambient conditions using a MultiModeTM 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 and spring constant of ~ 42 N/m were used. Samples were prepared by spin-coating of the respective solution at 4000 rpm onto highly ordered pyrolytic graphite (HOPG).

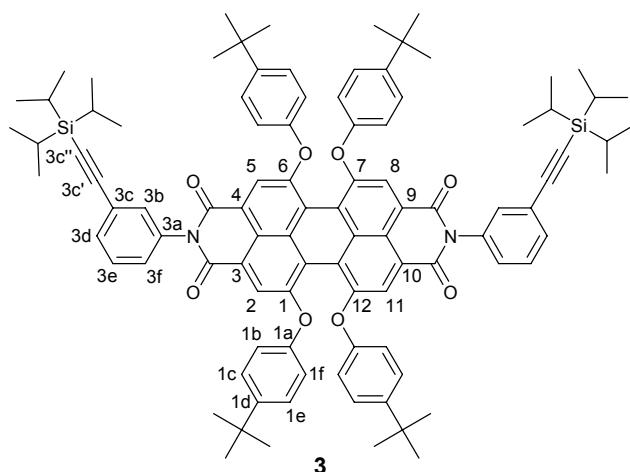
2. Experimental procedures, analytical and spectroscopic data

Perylene bisimide 2:



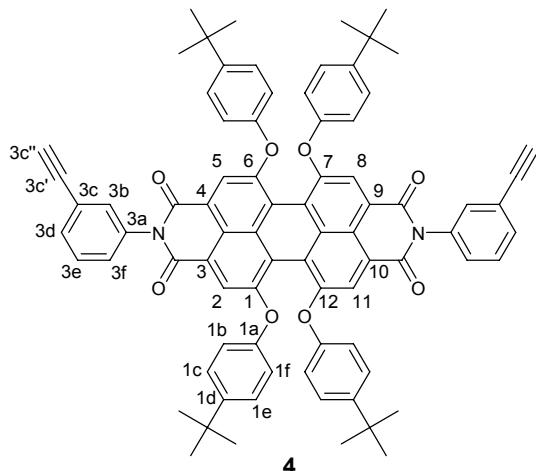
A mixture of perylene tetracarboxylic acid bisanhydride **1** (0.50 g, 0.51 mmol), the latter compound was prepared according to literature procedure,¹ 3-iodoaniline (2.45 g, 11.2 mmol) and 2.5 g imidazole was stirred at 120 °C for 30 min under an argon gas atmosphere. After being cooled to room temperature, the reaction mixture was dissolved in 200 mL distilled CH₂Cl₂, extracted with dilute HCl (2 x 200 mL) and H₂O (2 x 200 mL) and dried over MgSO₄. The desiccant was filtered off and the solvent was removed at a rotary evaporator. Then the crude product was slowly precipitated from CH₂Cl₂ solution by addition of methanol to give perylene bisimide **2** as a dark red powder (0.70 g, 0.50 mmol, 99%). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 8.16 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.82–7.80 (m, 2H; 3d-H), 7.65–7.64 (m, 2H; 3b-H), 7.28–7.25 (m, 12H; 3e-H, 3f-H, 1c-H, 1e-H), 6.84–6.82 (m, 8H; 1b-H, 1f-H), 1.29 (s, 36H; C(CH₃)₃). ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): δ 163.7 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 148.0 (1d-C), 138.2 (3b-C, 3d-C), 137.2 (3a-C), 133.7 (Per-C), 131.2 (3e-C), 128.9 (3f-C), 127.2 (1c-C, 1e-C), 123.0 (Per-C), 121.6 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 94.0 (3c-C), 34.9 (C(CH₃)₃), 31.8 (C(CH₃)₃). HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): *m/z* 1387.2826 [M+H]⁺ (calcd for C₇₆H₆₅I₂N₂O₈ 1387.2830).

Perylene bisimide 3:



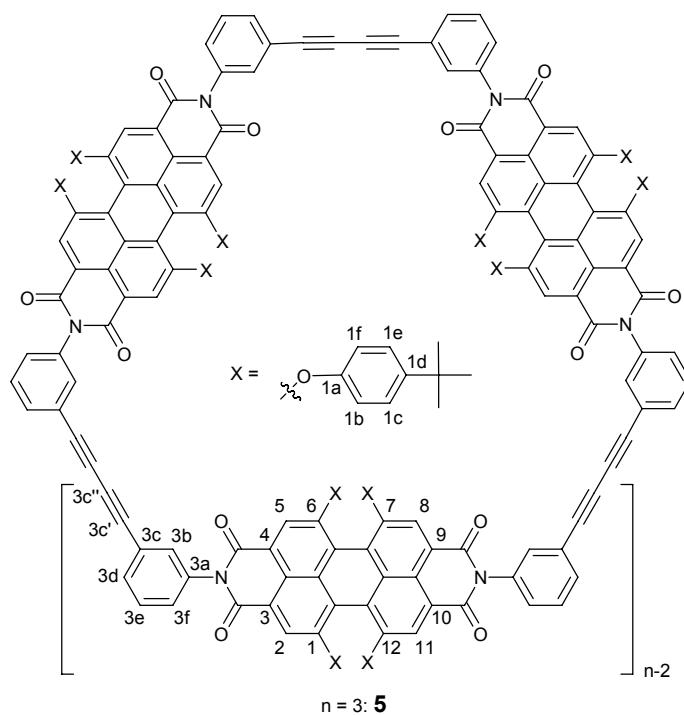
A mixture of compound **2** (0.70 g, 0.50 mmol), Pd(PPh₃)₂Cl₂ (35 mg, 50 μmol) and copper iodide (10 mg, 50 μmol) was dissolved in 30 mL of a degassed and distilled THF/HN*i*Pr₂ mixture (1:1) under an argon gas atmosphere. The reaction mixture was heated to 50 °C and triisopropylsilylacetylene (0.9 mL, 0.74 g, 4.0 mmol) was added. After stirring for one hour at this temperature, the solvent was removed at a rotary evaporator. The crude product was purified by silica gel column chromatography (CH₂Cl₂/n-Hexane = 50:50 as eluent) and then slowly precipitated from CH₂Cl₂ solution by addition of methanol to give perylene bisimide **3** as a dark red powder (0.74 g, 0.49 mmol, 99%). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 8.19 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.58–7.55 (m, 2H; 3d-H), 7.48–7.44 (m, 2H; 3e-H), 7.38–7.37 (m, 2H; 3b-H), 7.29–7.23 (m, 10H; 3f-H, 1c-H, 1e-H), 6.88–6.84 (m, 8H; 1b-H, 1f-H), 1.29 (s, 36H; C(CH₃)₃), 1.12 (s, 42H; SiCH(CH₃)₂). ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): δ 163.8 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.7 (1a-C), 148.0 (1d-C), 136.2 (3a-C), 133.7 (Per-C), 132.7 (3b-C), 132.6 (3d-C), 129.7 (3e-C), 129.5 (3f-C), 127.2 (1c-C, 1e-C), 125.3 (3c-C), 123.2 (Per-C), 121.5 (Per-C), 120.9 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 106.3 (3c'-C), 92.6 (3c''-C), 34.8 (C(CH₃)₃), 31.8 (C(CH₃)₃), 19.0 (SiCH(CH₃)₂), 11.9 (SiCH). HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): *m/z* 1496.7590 [M+H]⁺ (calcd for C₉₈H₁₀₇N₂O₈Si₂ 1496.7600).

Perylene bisimide building block 4:



Perylene bisimide **3** (0.36 g, 0.24 mmol) was dissolved in 30 mL distilled THF and 3 mL of a *n*Bu₄NF solution (1 M in THF) was added. The reaction was stopped after two minutes by pouring the mixture into 200 mL of a dilute HCl/CH₂Cl₂ mixture (1:1), was then extracted with dilute HCl (2 x 100 mL) and H₂O (2 x 100 mL) and dried over MgSO₄. The crude product was purified by silica gel column chromatography (CH₂Cl₂ as an eluent) and afterwards slowly precipitated from CH₂Cl₂ solution by addition of methanol to give perylene bisimide **4** as a dark red powder (0.26 g, 0.22 mmol, 90%). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 8.19 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.59–7.56 (m, 2H; 3d-H), 7.50–7.46 (m, 2H; 3e-H), 7.40–7.39 (m, 2H; 3b-H), 7.30–7.26 (m, 10H; 3f-H, 1c-H, 1e-H), 6.89–6.85 (m, 8H; 1b-H, 1f-H), 3.18 (s, 2H; 3c''-H), 1.29 (s, 36H; C(CH₃)₃). ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): 163.7 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.7 (1a-C), 148.0 (1d-C), 136.2 (3a-C), 133.7 (Per-C), 133.0 (3b-C), 132.8 (3d-C), 130.0 (3f-C), 129.9 (3e-C), 127.2 (1c-C, 1e-C), 123.9 (3c-C), 123.1 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 82.9 (3c'-C), 78.8 (3c''-C), 34.9 (C(CH₃)₃), 31.8 (C(CH₃)₃). HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): *m/z* 1183.4892 [M+H]⁺ (calcd for C₈₀H₆₇N₂O₈ 1183.4897). UV-vis (CH₂Cl₂): λ_{max} (ϵ) 582 nm (49200 M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{\text{max}} = 611$ nm (λ_{ex} = 550 nm), Φ_{FI} = 0.95.

Macrocyclic trimer **5:**



PBI building block **4** (200 mg, 0.169 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (50 mg, 71 μmol) and copper iodide (20 mg, 0.11 mmol) were dissolved in 1 L mixture of distilled CH_2Cl_2 and HN^iPr_2 (9:1 vol%) at ambient atmosphere and stored in the freezer at -30 °C for three days. The solvent was removed at a rotary evaporator and the reaction mixture was filtered through a silica gel pad with CH_2Cl_2 to remove residual reagents and polymeric side products, and 92 mg (46 %) of a product mixture was obtained. The product mixture was further purified by recycling GPC (JAIGEL 2H+2.5H columns; CHCl_3 , 3.5 mL/min) and the trimer **5** (36 mg, 10.2 μmol , 18%) could be isolated after six cycles in pure form. ^1H NMR (600 MHz, CD_2Cl_2 , 298 K): δ 8.16 (s, 12H; 2-H, 5-H, 8-H, 11-H), 7.62–7.60 (m, 6H; 3d-H), 7.52–7.49 (m, 6H; 3e-H), 7.41–7.40 (m, 6H; 3b-H), 7.33–7.31 (m, 6H; 3f-H), 7.26–7.24 (m, 24H; 1c-H, 1e-H), 6.83–6.81 (m, 24H; 1b-H, 1f-H), 1.27 (s, 108H; $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (150 MHz, CD_2Cl_2 , 298 K): δ 163.6 ($\text{C}=\text{O}$), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 147.9 (1d-C), 136.3 (3a-C), 133.6 (Per-C), 133.5 (3b-C), 132.9 (3d-C), 130.6 (3f-C), 130.0 (3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.0 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C) 119.6 (1b-C, 1f-C), 81.1 (3c'-C), 75.0 (3c''-C), 34.8 ($\text{C}(\text{CH}_3)_3$), 31.7 ($\text{C}(\text{CH}_3)_3$). HRMS (ESI, CHCl_3 /acetonitrile 1:1, pos. mode): m/z 1772.7022 [$\text{M}+2\text{H}]^{2+}$ (calcd for $\text{C}_{240}\text{H}_{194}\text{N}_6\text{O}_{24}$ 1772.7106). UV-vis (CH_2Cl_2): λ_{\max} (ϵ) 582 nm ($139500 \text{ M}^{-1} \text{ cm}^{-1}$); fluorescence (CH_2Cl_2): $\lambda_{\max} = 614 \text{ nm}$ ($\lambda_{\text{ex}} = 550 \text{ nm}$), $\Phi_{\text{Fl}} = 0.91$.

3. ^1H and ^{13}C NMR spectra

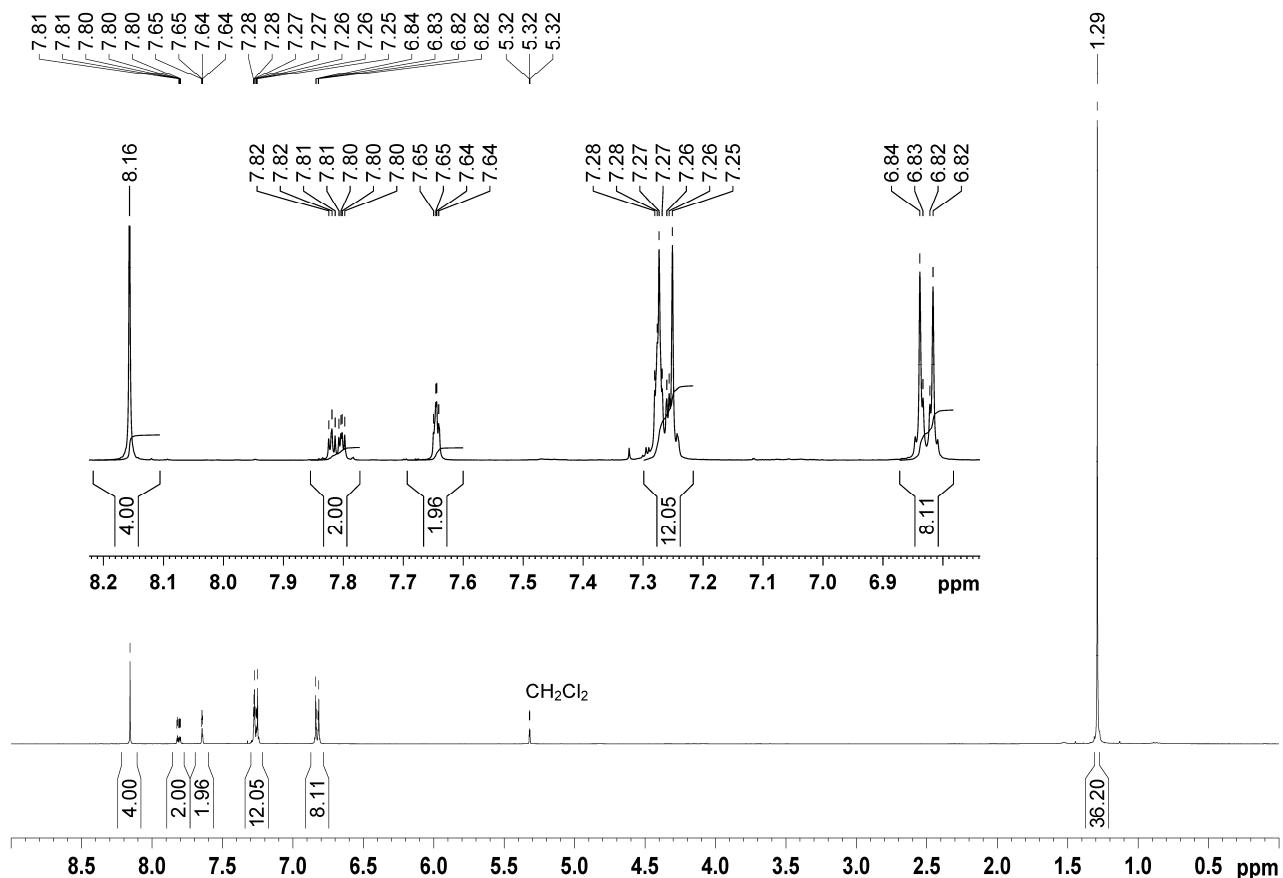


Fig. S1 ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of perylene bisimide **2**; inset: an expanded aromatic region.

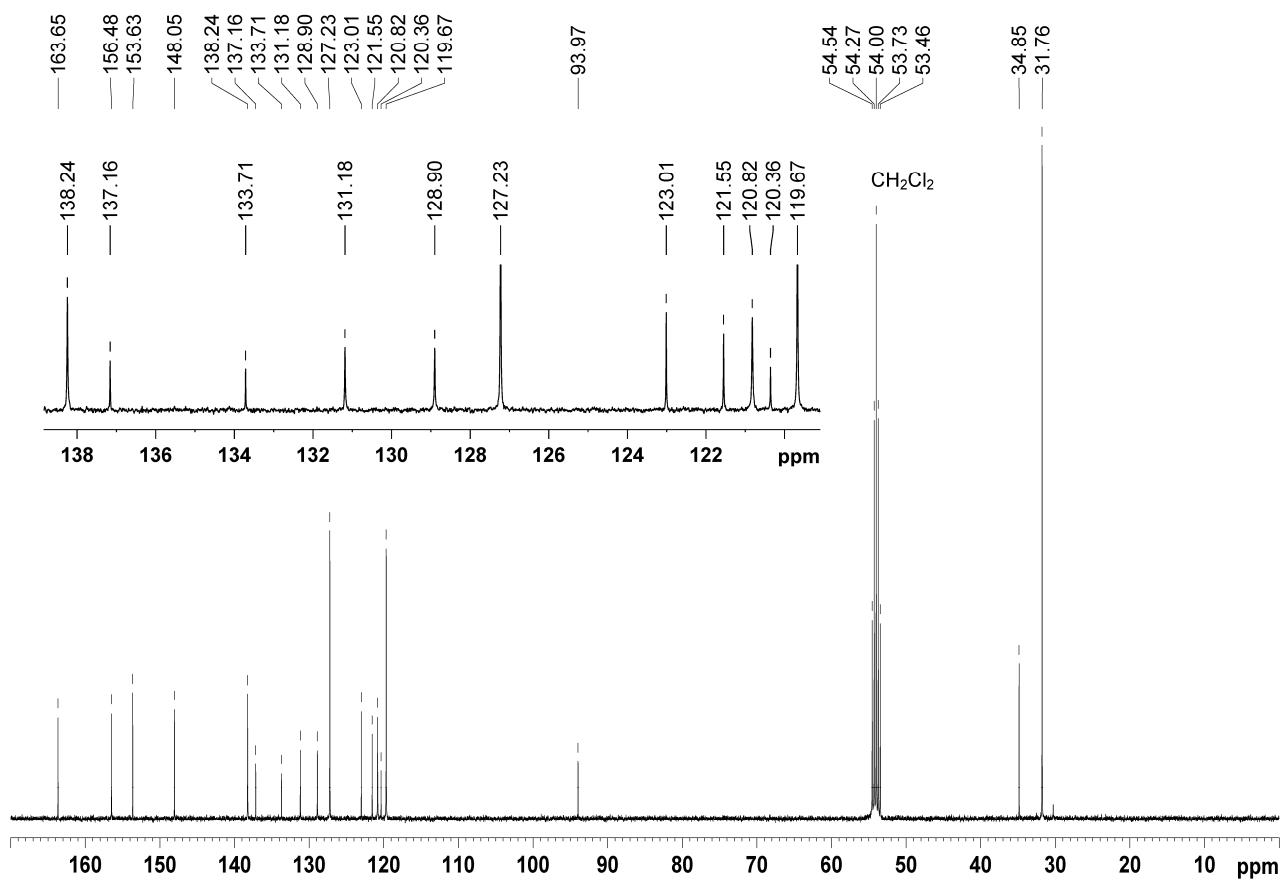


Fig. S2 ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of perylene bisimide **2**; inset: an expanded low field region.

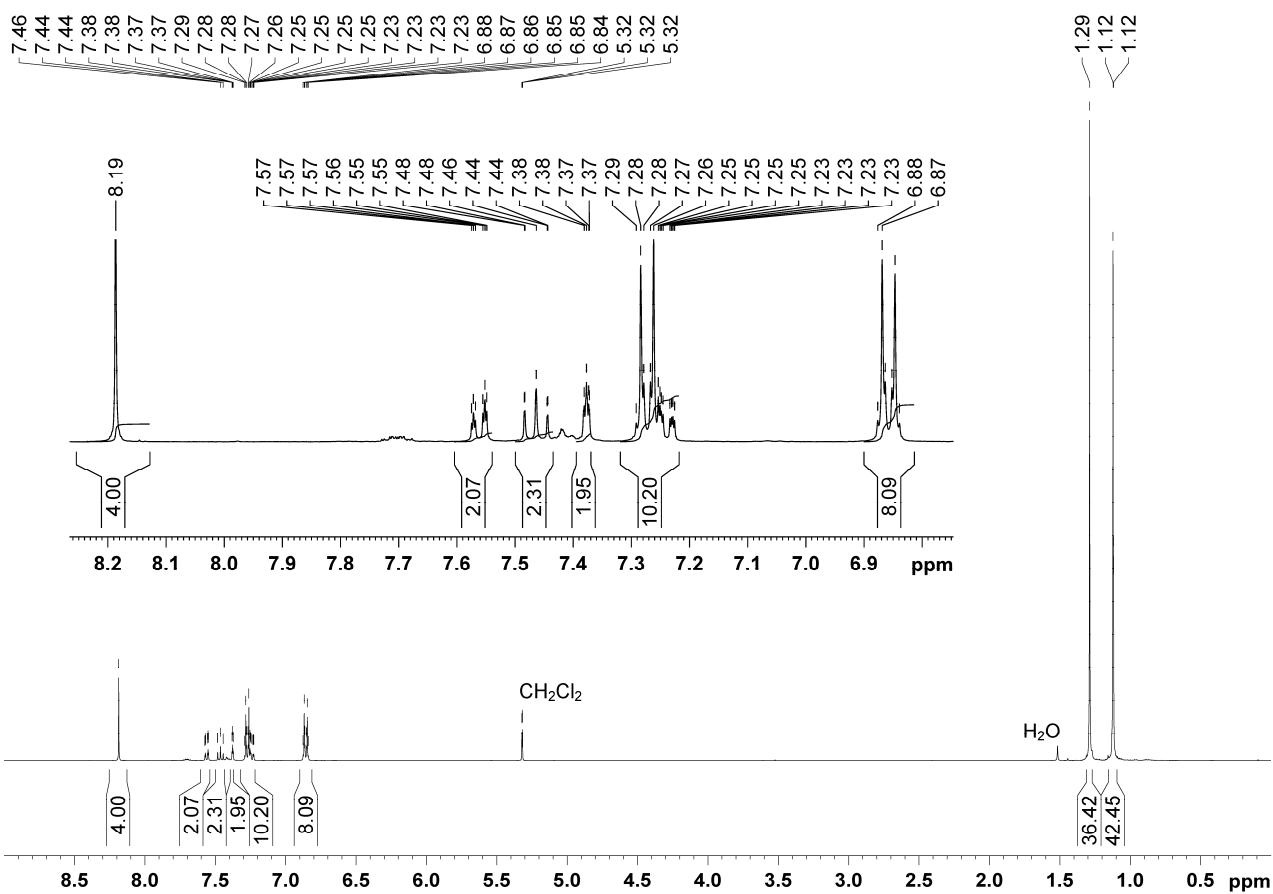


Fig. S3 ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of perylene bisimide **3**; inset: an expanded aromatic region.

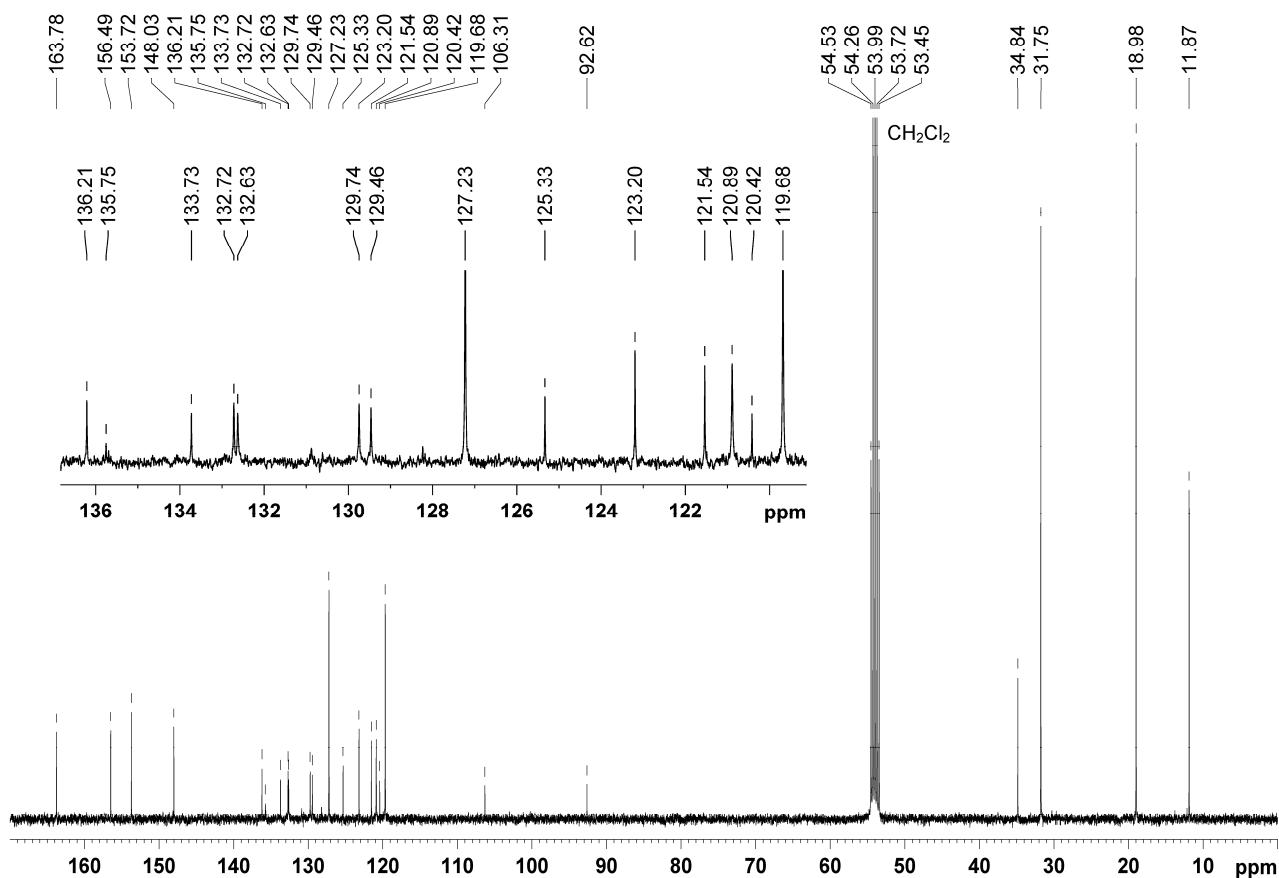


Fig. S4 ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of perylene bisimide **3**; inset: an expanded low field region.

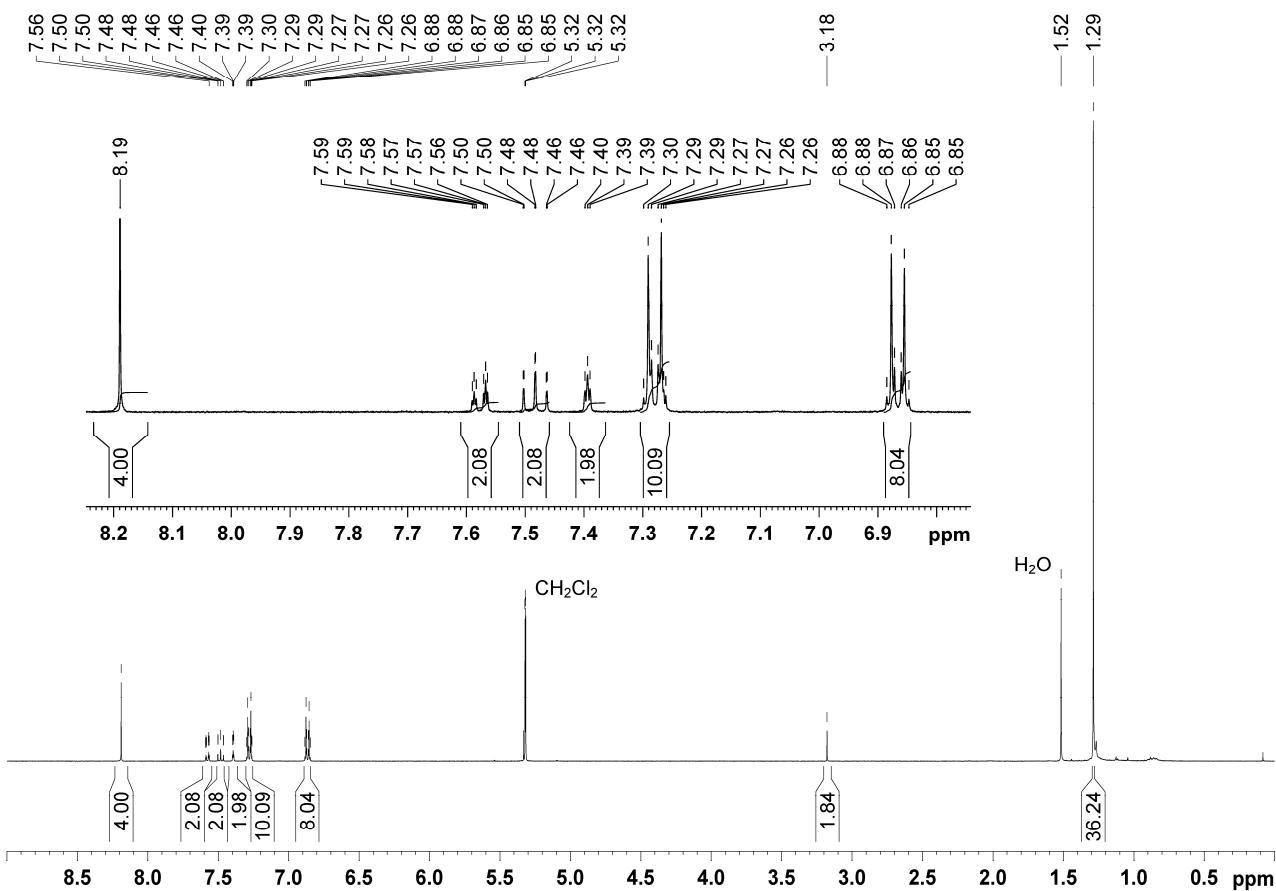


Fig. S5 ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of perylene bisimide building block **4**; inset: an expanded aromatic region.

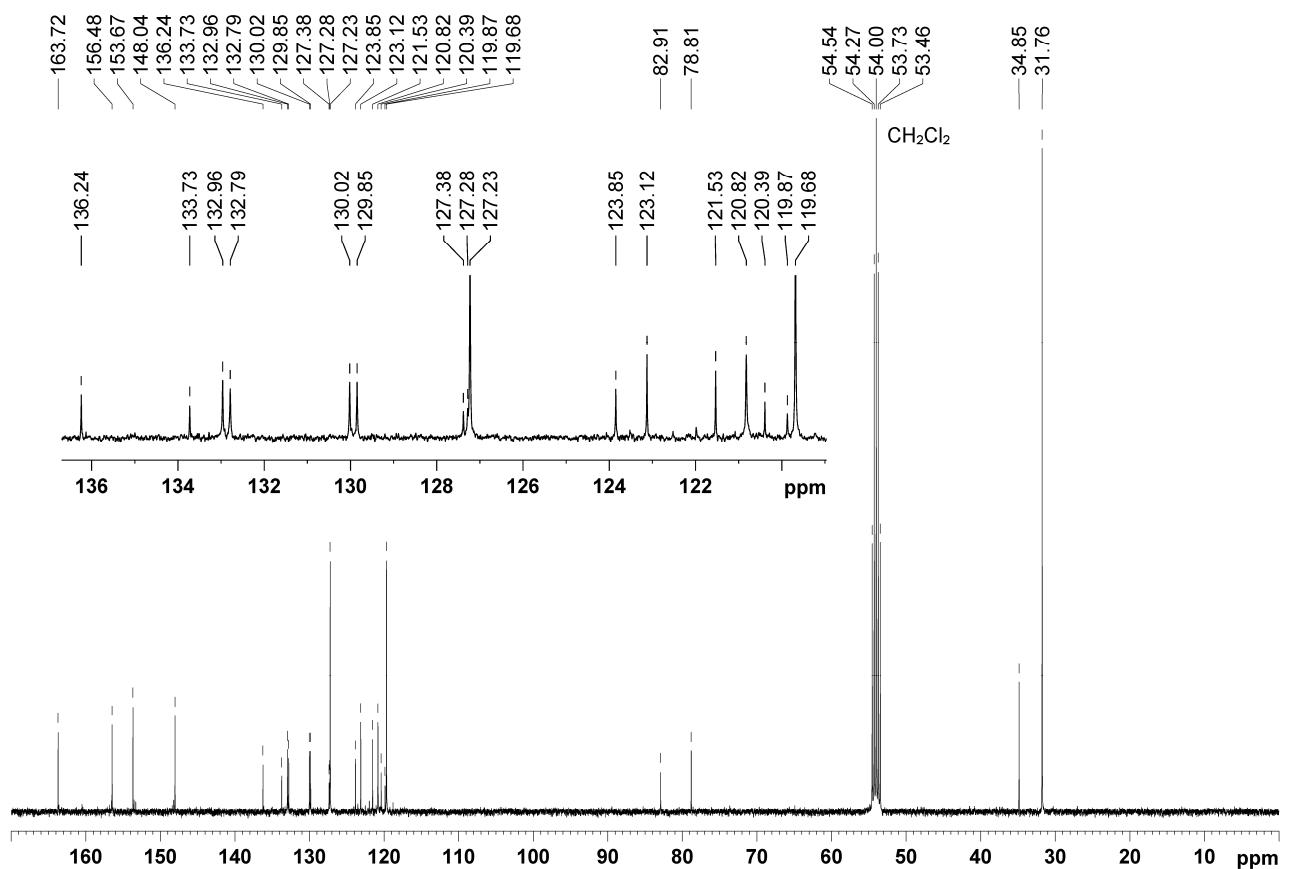


Fig. S6 ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of perylene bisimide building block 4; inset: an expanded low field region.

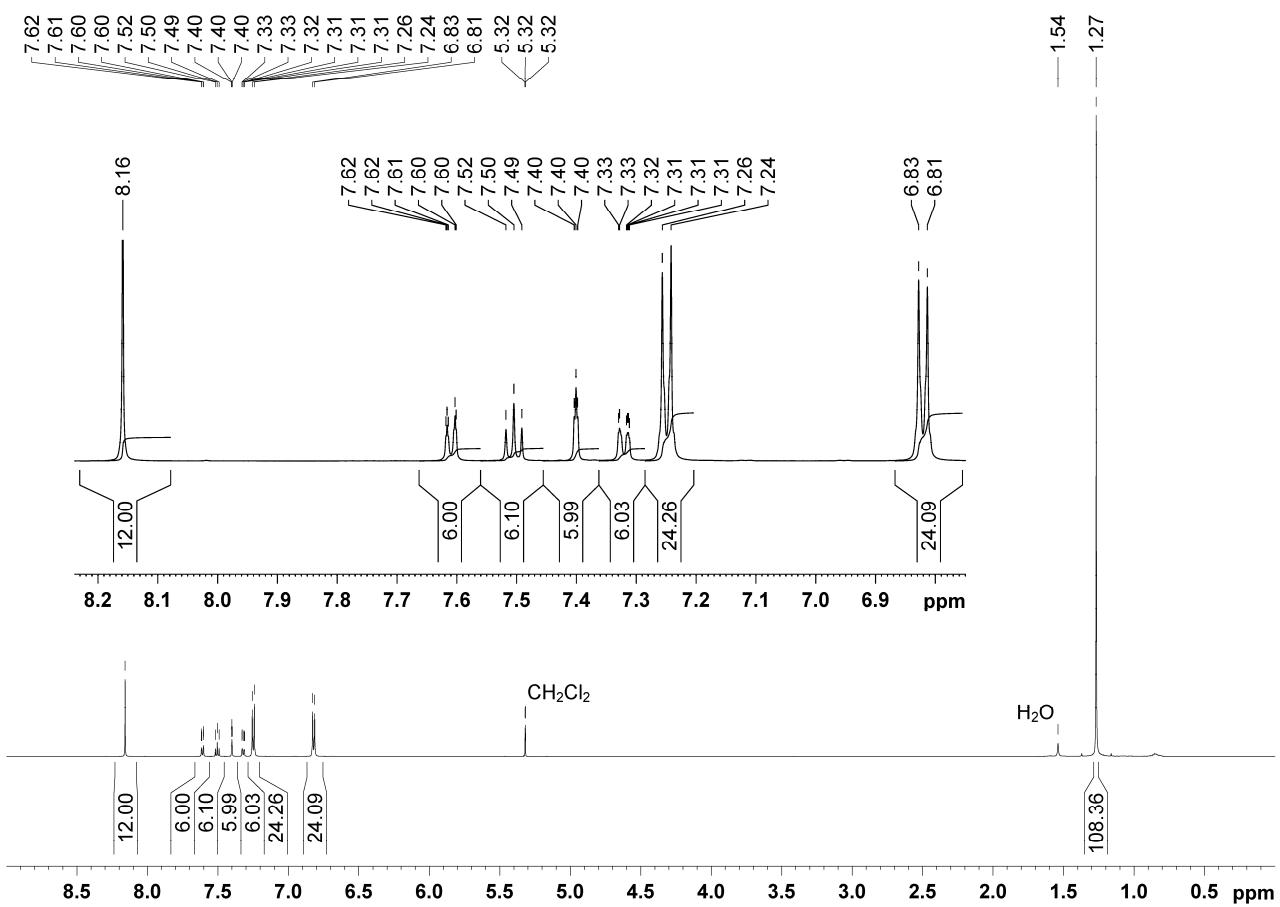


Fig. S7 ^1H NMR spectrum (600 MHz, CD_2Cl_2 , 298 K) of trimer **5**; inset: an expanded aromatic region.

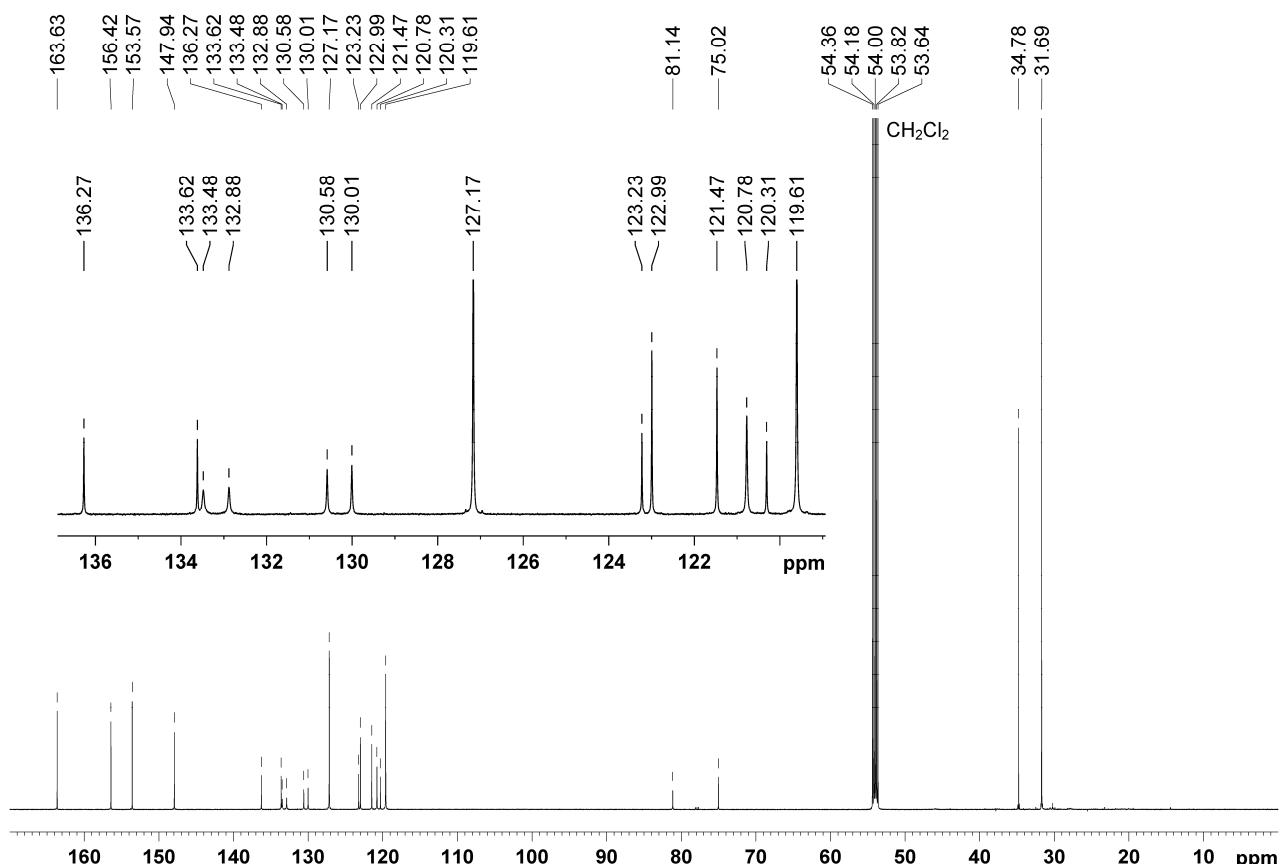


Fig. S8 ^{13}C NMR spectrum (150 MHz, CD_2Cl_2 , 298 K) of trimer 5; inset: an expanded low field region.

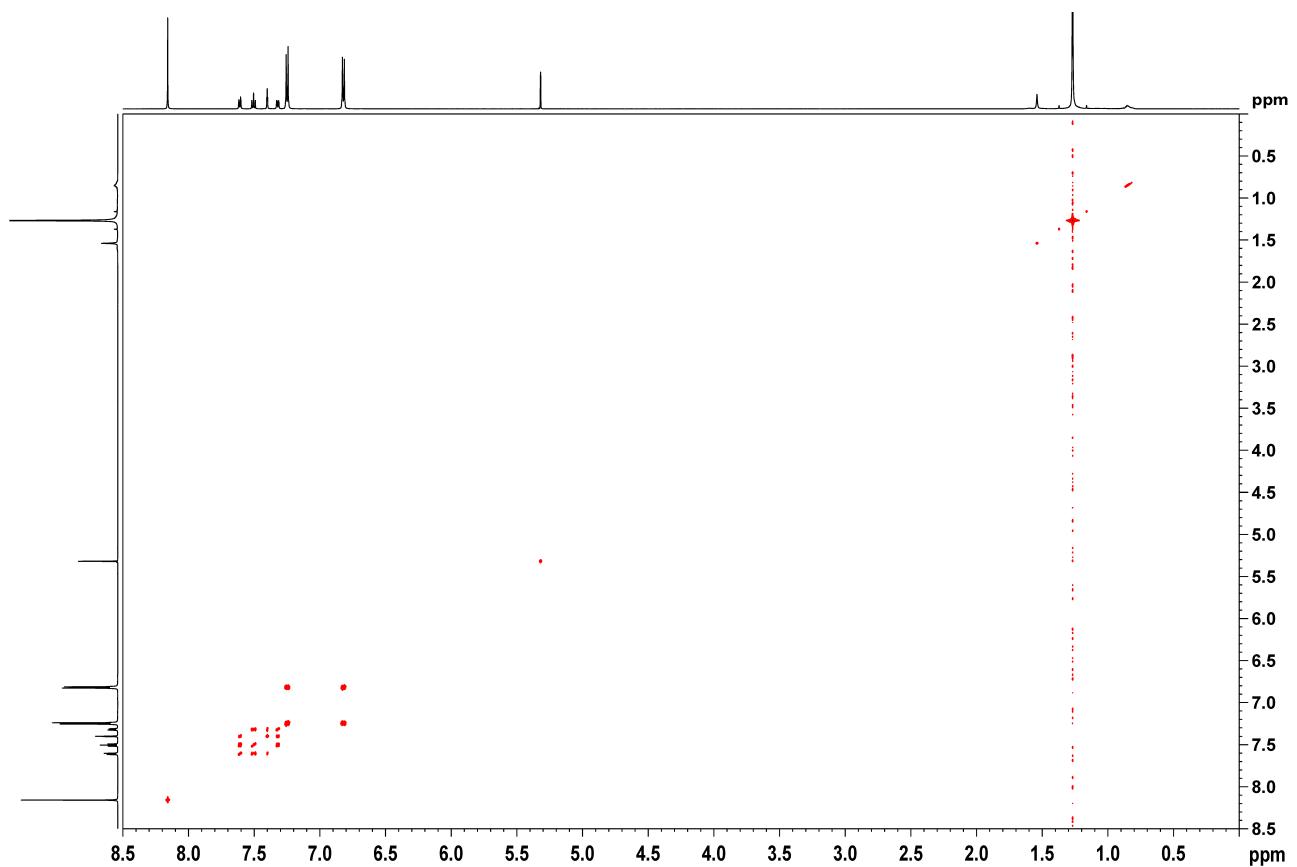


Fig. S9 (¹H, ¹H)-COSY NMR spectrum of trimer 5.

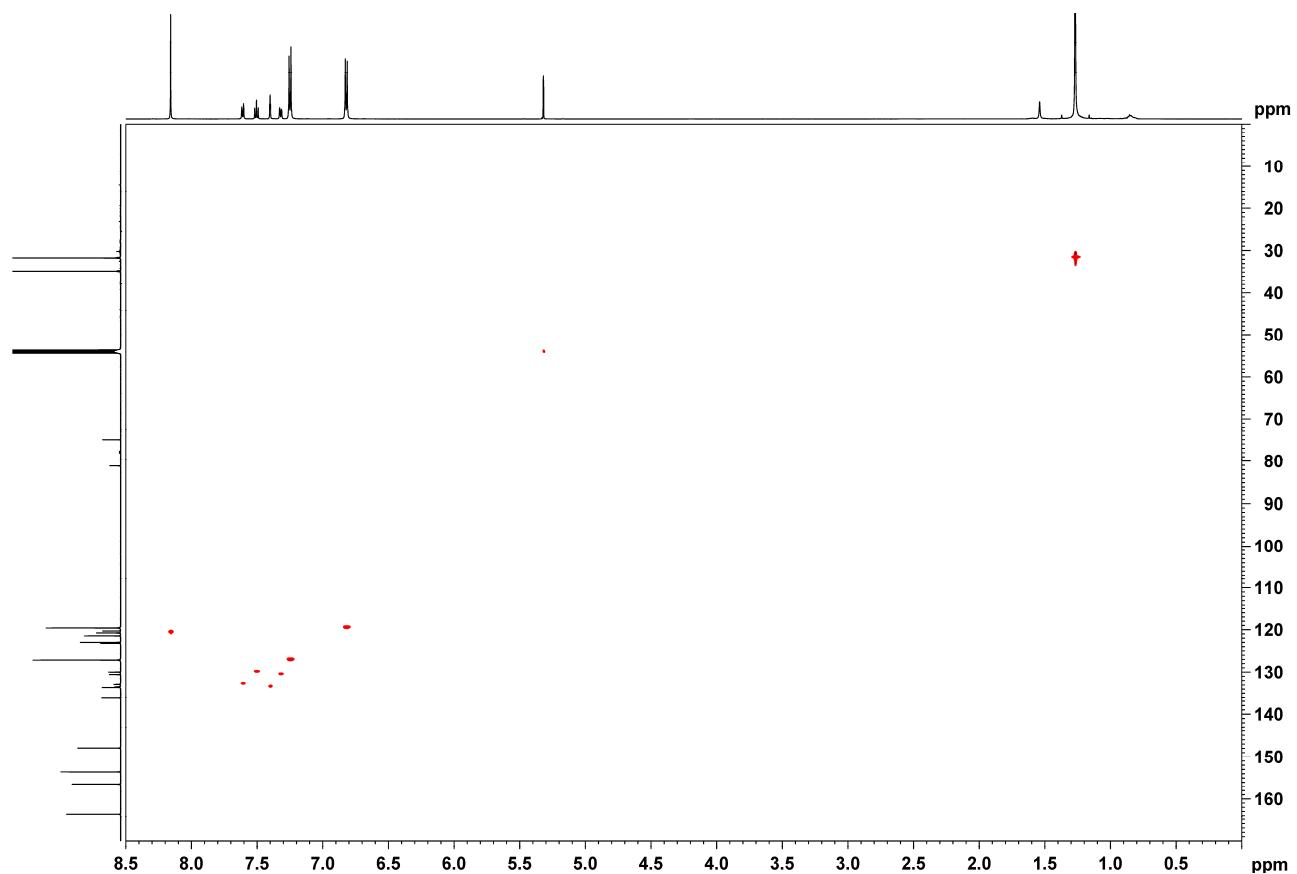


Fig. S10 (¹H, ¹³C)-HSQC NMR spectrum of trimer 5.

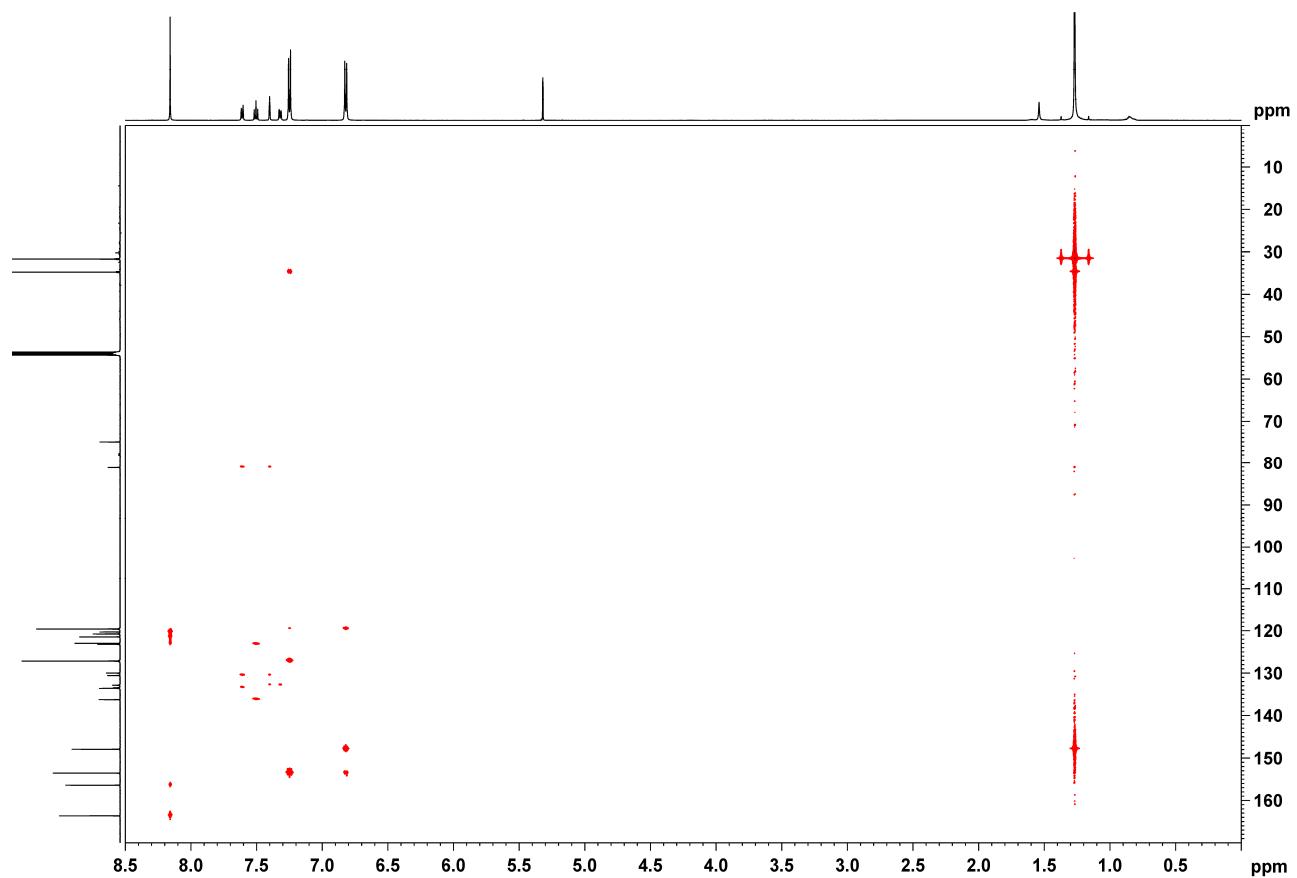


Fig. S11 (${}^1\text{H}, {}^{13}\text{C}$)-HMBC NMR spectrum of trimer **5**.

4. High resolution mass spectrum

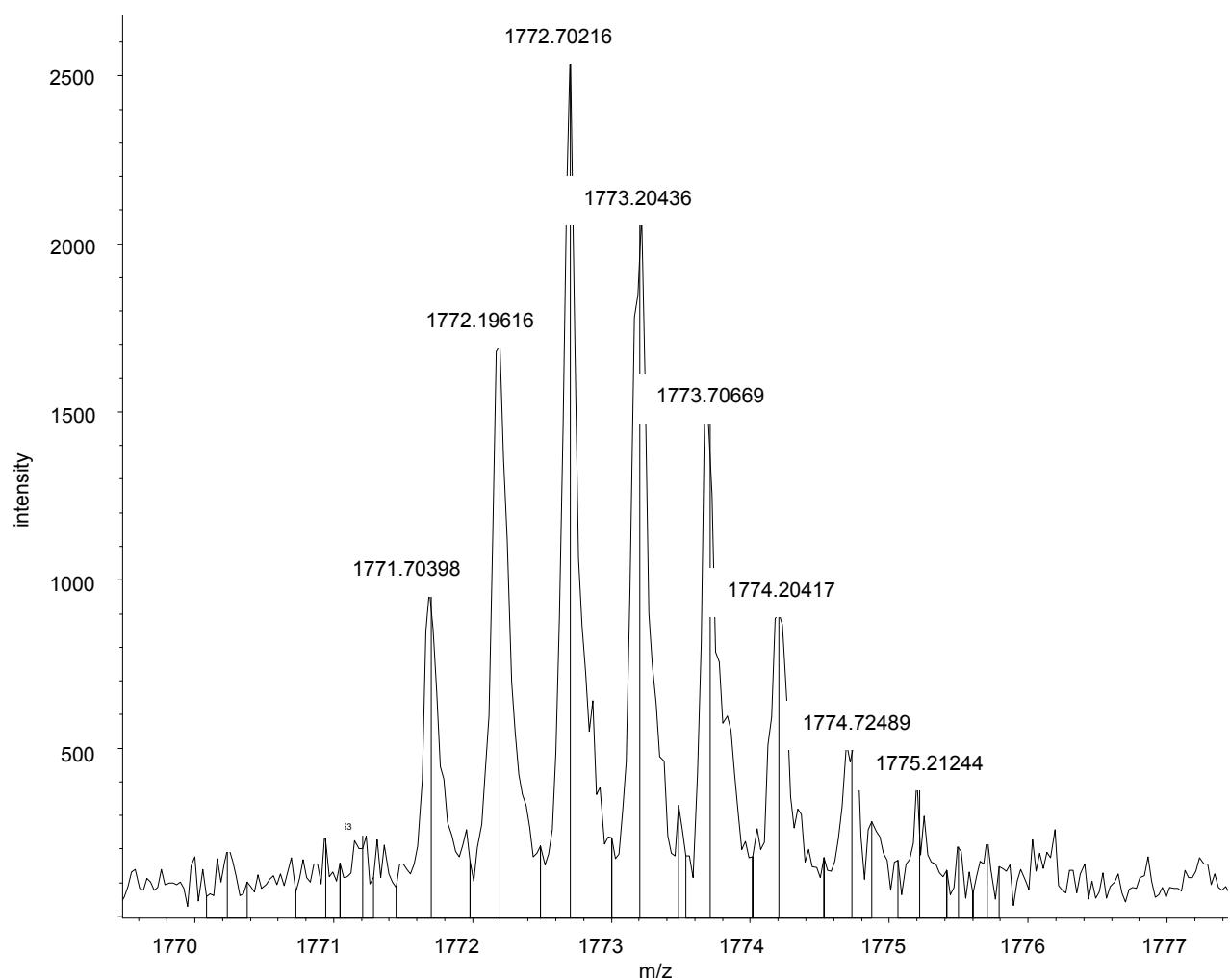


Fig. S12 High resolution mass spectrum (ESI) of macrocycle **5**.

5. UV-vis and fluorescence spectra

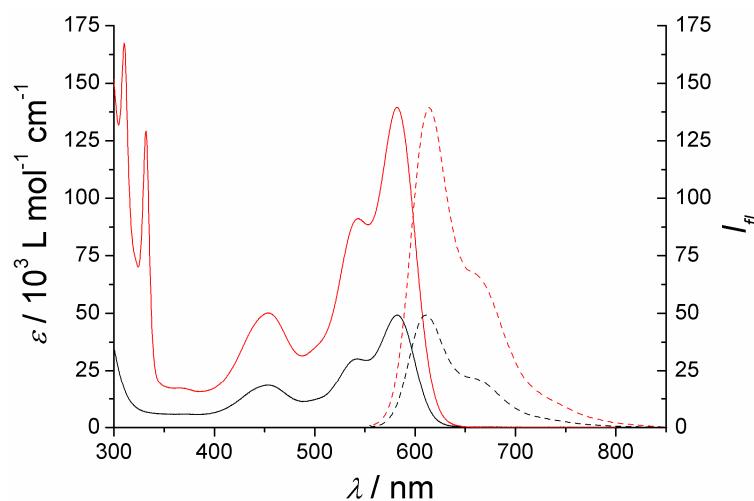


Fig. S13 UV-vis absorption spectra of monomer **4** (black solid line) and cyclic trimer **5** (red solid line) and the corresponding fluorescence spectra (dashed lines; $\lambda_{\text{ex}} = 550 \text{ nm}$); all measurements were performed at room temperature in CH_2Cl_2 at a concentration of $7.50 \times 10^{-6} \text{ M}$.

6. Cyclic voltammetry

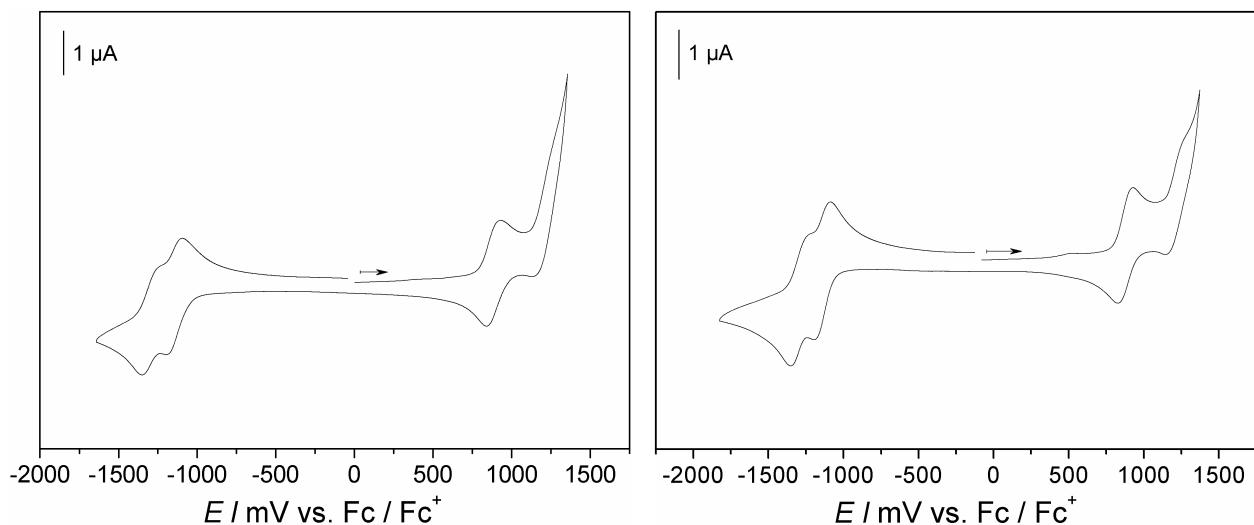


Fig. S14 Cyclic voltammograms of monomer **4** (left) and cyclic trimer **5** (right) in CH_2Cl_2 (vs. Fc/Fc^+). Scan rate 100 mV s^{-1} ; working electrode: Pt disc, $\varnothing 1 \text{ mm}$; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl ; electrolyte: TBAHFP (0.1 M); concentration ca. $2 \times 10^{-4} \text{ M}^{-1}$.

Tab. S1 Redox properties of the compounds **4** and **5** in CH₂Cl₂ (vs. Fc/Fc⁺).^a

compound	$E_{1/2}^{\text{red}}/\text{V}$ (PBI/PBI ²⁻)	$E_{1/2}^{\text{red}}/\text{V}$ (PBI/PBI ⁻)	$E_{1/2}^{\text{ox}}/\text{V}$ (PBI/PBI ⁺)
4	-1.29	-1.15	+0.87
5	-1.28	-1.15	+0.87

^a Scan rate 100 mV s⁻¹; working electrode: Pt disc, Ø 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: TBAHFP (0.1 M); concentration ca. 2 × 10⁻⁴ mol L⁻¹.

7. References

- 1 F. Würthner, A. Sautter, J. Schilling, *J. Org. Chem.*, 2002, **67**, 3037; F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach, O. Hollricher, *Chem. Eur. J.*, 2000, **6**, 3871.