Electronic Supplementary Information for

# Foldamer with spiral perylene bisimide staircase aggregate structure

**Volker Dehm,[a] Michael Büchner,[a] Joachim Seibt,[b] Volker Engel,[b] and Frank Würthner*[a]**

**[a] Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg (Germany); E-mail: wuerthner@chemie.uni-wuerzburg.de**
**[b] Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Am Hubland, 97074 Würzburg (Germany)**

## Table of contents:

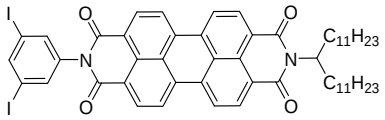
## 1. Materials and methods

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Diisopropylamine (99%) was purchased from Sigma-Aldrich and used as obtained. Toluene was purified according to literature procedures.[S1] *N*-(1-Undecyldodecyl)perylene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (**2**),[S2] 1,2-diethynyl-4,5-dihexylbenzene[S3] and 3,5-diiodoaniline[S4] were synthesized according to literature procedures. Column chromatography was performed using silica gel Si60 (0.035–0.070 mm). Melting points were determined on an Olympus BX41 polarization microscope and are uncorrected. $^1$H NMR and DOSY NMR spectra were recorded on Bruker Advance 400 and Bruker Advance DMX 600 spectrometers, respectively, and calibrated to the internal standard TMS. The APCI mass spectra were performed with a micrOTOF focus mass spectrometer (Bruker Daltonics, Bremen), equipped with an APCI ion source (Agilent G1947-60101). A stainless steel spraying capillary and as transfer capillary a nickel-coated glass capillary with an inner diameter of 500 µm was used. The ions were generated continuously by introducing a 10 µM solution in acetonitrile/chloroform (v/v 1:1) by using a syringe pump (Cole Palmer Instruments 789100C) and a flow rate of 200 µl min$^{-1}$ into the ion source. A 1:500 dilution of APCI/APPI Tuning Mix (G2432A; Agilent) in acetonitrile was used as internal calibration. The MALDI mass spectra were performed with an autoflex II mass spectrometer (Bruker Daltonics, Bremen), equipped with a 337 nm MidiNitrogen laser MNL (LTB Lasertechnik, Berlin). All MALDI-TOF spectra were acquired in the linear negative mode. Calibration was performed externally with 1 µl of a solution of protein calibration standard I (Bruker Daltonics, Bremen) in 0.1% trifluoroacetic acid, a saturated solution of sinapinic acid (Bruker Daltonics, Bremen) in a mixture of acetonitrile and 0.1% trifluoroacetic acid (v/v 1:1). 1 µl of the sample solutions (10 mg ml$^{-1}$ in tetrahydrofuran) and 1 µl of a 60 mg ml$^{-1}$ matrix solution (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile, DCTB in THF) were mixed and 0.5 µl were dropped onto the stainless steel target (MTP 384 massive target T; Bruker Daltonics 26755). Six spectra of 30 laser shots were accumulated. The spectrum was smoothed using Savitzky–Golay smoothing filter (1 cycle, width *m*/*z* = 5) and baseline subtracted (tangential, flatness = 5). Elemental analyses were performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany). Analytical GPC was performed at 20 °C on a system (PU-2080 Plus) with a multi-wavelength detector (MD-2015 Plus) and a RI detector (RI-2031 Plus) from JASCO, equipped with a ternary gradient unit (LG-2080-02) and line degasser (DG-2080-53). Semi-preparative GPC was performed at 20 °C on a system (PU-2080-Plus) with a diode array detector (UV-2077 Plus) and line degasser (DG-2080-53) from JASCO. HPLC grade THF (Rectapur) from VWR (Darmstadt, Germany) was used as eluent. GPC columns were obtained from PSS (Mainz, Germany). Analytical column: SDA083005LIM (PSS SDV linear M), pre-column SDA080505; semi-preparative column: SDP203005LIM (PSS SDV preparative linear M), pre-column SDP200505. Polystyrene standards from PSS were used for calibration. Lyophilization was carried out at –90 °C and 0.35 mbar using a Christ alpha 1-4 LD dry freezer and distilled

dioxane. For spectroscopic measurements, 1 cm quartz glass cuvettes and spectroscopic grade solvents were used. UV/vis spectra were recorded on a Perkin Elmer UV/vis spectrometer Lamda 950 equipped with a PTP-1 Peltier system from Perkin Elmer as temperature controller. For the studies in solvent mixtures (Figure 4 in the main text), two stock solutions of identical concentration ($c$ = 4.08 mg $l^{-1}$) of oligomer **1** were prepared in spectrophotometric grade chloroform ($OD_{max} \approx 0.1$) and MCH ($OD_{max} \approx 0.07$), respectively. Mixed solvent compositions with varying fractions of chloroform in MCH were prepared by adding the respective amount of chloroform solution to a given volume of MCH solution. Fluorescence spectra[S5] were taken on a PTI QM-4/2003 spectrofluorometer and the spectra were corrected against photomultiplier and lamp intensity. The helical geometry (see Figure 1 in the main text) of the octameric PBI oligomer **1** was optimized by applying the MM+ force field method in HyperChem™ 7.03.

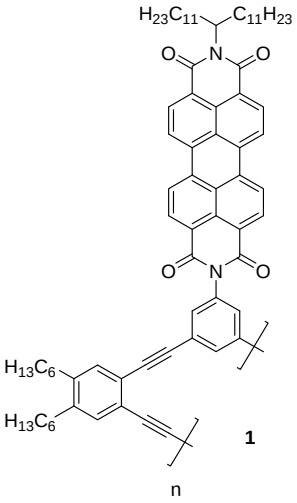
## 2. Synthesis and characterization

**_N_-(3,5-Diiodophenyl)-_N'_-(1-undecyldodecyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (3)**



A mixture of _N_-(1-undecyldodecyl)perylene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (**2**) (152 mg, 213 µmol) and 3,5-diiodoaniline (96.0 mg, 278 µmol) in 1 g imidazole and 1 ml pyridine were stirred in a sealed flask under an argon atmosphere at 150 °C for 2 h. After cooling down to room temperature, the mixture was diluted with dichloromethane (30 ml) and washed twice with 2N HCl (aq) (30 ml) and finally with $H_2O$ (30 ml). The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The raw product was purified by column chromatography (dichloromethane, silica gel). Subsequently, the resulting material was reprecipitated from dichloromethane by slow addition of methanol. The precipitate was isolated by centrifugation and washed twice with methanol (10 ml). After drying in vaccum (< $10^{-3}$ mbar) at 70 °C for 5 h, 162 mg (156 µmol, 73%) of a red powder was obtained. M.p. > 400 °C. $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 8.75–8.66 (m, 8H, perylene-H), 8.20 (t, $^4J$(H,H)=1.5 Hz, 1H; Ph-H), 7.69 (d, $^4J$(H,H)=1.4 Hz, 2H; Ph-H), 5.19 (m, 1H, N-C*H*), 2.30–2.20 (m, 2H, CH-C$H_2$), 1.95–1.80 (m, 2H, CH-C$H_2$), 1.45–1.15 (m, 36H, $CH_2$), 0.84 (t, $^3J$(H,H)=7.0 Hz, 6H; $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): $\delta$ = 148.4, 140.0, 139.5, 138.3, 134.8, 132.6, 132.3, 129.5, 129.1, 126.3, 125.8, 125.5, 97.1, 35.1, 34.7, 32.4, 32.32, 32.29, 32.1, 29.7, 25.4, 16.8. HRMS (APCI, positive) (chloroform / acetonitrile v/v 1:1) (*m*/*z*): $[M+H]^+$; calcd. for $C_{53}H_{59}I_2N_2O_4$: 1041.25587; found 1041.25514. Elemental analysis: calcd. (%) for $C_{53}H_{58}I_2N_2O_4$ (1040.87): C 61.16, H 5.62, N 2.69; found C 61.26, H 5.79, N 2.92.

**Co-polymerisation of *N*-(3,5-diiodophenyl)-*N'*-(1-undecyldodecyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (3) and 1,2-diethynyl-4,5-dihexylbenzene into oligomer 1.**




Under an argon atmosphere, perylene bisimide **3** (70.6 mg, 67.8 µmol), $(allylPdCl)_2$ (21.0 mg, 78.3 µmol), CuI (0.9 mg, 4.7 µmol) and P*t*$Bu_3$ (10.0 mg, 5.0 µmol) were treated with dry toluene (30 ml) and HN*i*$Pr_2$ (3 ml). The mixture was degassed by three freeze-pump-thaw cycles and then heated to 70 °C. A solution of 1,2-diethynyl-4,5-dihexylbenzene (20.0 mg, 67.4 µmol) in toluene (1 ml) was added in 30 min under argon atmosphere, and the mixture was stirred under light exclusion for 3 d at 70 °C. After cooling to room temperature, 2N HCl (aq) (20 ml) was added and the mixture was extracted twice with dichloromethane (50 ml). The combined organic layers were washed twice with 2N HCl (aq) (20 ml) and finally with $H_2O$ (50 ml). The organic phase was dried over $MgSO_4$ and the crude product was purified by column chromatography (silica gel). Impurities were removed by eluting with dichloromethane/methanol (98:2) and, subsequently, the product was eluted by increasing the vol% of methanol to 20%. The crude product was further purified by performing two successive semi-preparative gel permeation chromatographies. After submitting the resulting oily red product to lyophilization from dioxane, **1** was isolated as a voluminous red solid (7 mg, 19%). $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 8.7 (bm, 8H; perylene-H), 8.5–6.9 (bm, 3H; Ar-H), 5.2 (bm, 1H; N-C*H*), 2.9–2.4 (bm, 4H; Ar-C$H_2$), 2.4–2.2 (bm, 2H; N-CH-C$H_2$), 2.1–1.9 (bm, 2H; N-CH-C$H_2$), 1.9–1.0 (m, 52H; $CH_2$), 1.0–0.8 (m, 12H; $CH_3$). UV/vis ($CHCl_3$): $\lambda_{max}$ = 493, 529 nm. MS (MALDI, DCTB, negative): (*m*/*z*): $[A_4B_3H_2]^-$ calcd. 4027.65; found 4026.04; $[A_4B_4H_2]^-$ calcd. 4320.11; found 4318.04; $[A_2B_2H_2]^-$, calcd. 2161.06; found 2155.10; $[A_5B_4H_2]^-$ calcd. 5107.17; found 5107.19; $[A_4B_4H_2 + HCl]^-$ calcd. 4356.11; found 4356.38; $[A_5B_5H_2 + HCl]^-$ calcd. 5436.11; found 5436.81; $[A_3B_3H_2 + HCl]^-$ calcd. 3277.06; found 3275.16; $[A_5B_4H_2 + HCl]^-$ calcd. 5143.64; found 5144.33; $[A_3B_3H_2]^-$ calcd., 3240.59; found 3238.27; $[A_4B_3H_2 + HCl]^-$ calcd. 4064.12; found 4062.64; $[A_4B_4H_2 + 2\ HCl]^-$ calcd. 4393.10; found 4392.64; $[A_5B_5H_2]^-$ calcd. 5399.64; found 5399.80; $[A_6B_5H_2 + HCl]^-$ calcd. 6223.16; found 6225.63; $[A_6B_5H_2]^-$ calcd. 6186.70; found 6188.12; $[A_3B_4H_2 + HCl]^-$ calcd. 3569.52; found 3570.41; $[A_5B_5H_2 + 2\ HCl]^-$ calcd. 5472.58; found 5474.12; $[A_3B_2H_2 + 2HCl]^-$ calcd. 3021.06; found 3015.99; $[A_5B_4H_2 + 2\ HCl]^-$ calcd. 5180.11; found 5180.67; $[A_4B_3H_2 + 2\ HCl]^-$ calcd. 4100.58; found 4099.76; $[A_3B_3H_2 + 2\ HCl]^-$ calcd. 3313.53; found 3312.22;

$[A_2B_3H_2 + HCl]^-$ calcd. 2490.00; found 2485.83; $[A_6B_6H_2 + HCl]^-$ calcd. 6515.63; found 6519.01; $[A_4B_5H_2 + HCl]^-$ calcd. 4649.05; found 4649.83; $[A_6B_5H_2 + 2\ HCl]^-$ calcd. 6259.63; found 6261.54; $[A_6B_6H_2]^-$ calcd. 6479.16; found 6480.45; $[A_3B_4H_2]^-$ calcd. 3533.05; found 3531.53; $[A_6B_6H_2 + 2\ HCl]^-$ calcd. 6552.10; found 6556.21; $[A_7B_6H_2 + HCl]^-$ calcd. 7302.69; found 7307.85; $[A_4B_5H_2 + 2\ HCl]^-$ calcd. 4685.52; found 4686.30; $[A_7B_6H_2]^-$ calcd. 7266.22; found 7269.35; $[A_5B_6H_2 + HCl]^-$ calcd. 5728.57; found 5731.97; $[A_4B_5H_2]^-$ calcd. 4612.58; found 4613.75; $[A_3B_4H_2 + 2\ HCl]^-$ calcd. 3605.99; found 3605.10; $[A_5B_6H_2 + 2\ HCl]^-$ calcd. 5765.04; found 5768.76; $[A_7B_6H_2 + 2\ HCl]^-$ calcd. 7339.16; found 7342.98; $[A_7B_7H_2 + HCl]^-$ calcd. 7595.15; found 7600.62; $[A_5B_6H_2]^-$ calcd. 5692.10, found 5694.48. GPC analysis (column: PSS SDV linear M, solvent: tetrahydrofuran, 20 °C): $M_w$ = 8490 Da; $M_p$ = 7970 Da; D = 1.10.

## 3. Mass spectrometry of foldamer 1

**Table S1** Calculated and observed molecular mass for oligomers **1**. A denotes the PBI part and B the diethynylphenyl counterpart of the respective oligomer **1**. The observed mass peaks were taken from the MALDI-TOF mass spectrum shown in Figure 2 in the main text.

| Oligomer | Calculated molecular mass $[M]^-$ / Da | Observed molecular mass $[M]^-$ / Da[a] | Observed molecular mass $[M+HCl]^-$ / Da[a] | Observed molecular mass $[M+2HCl]^-$ / Da[a] |
|---|---|---|---|---|
| $A_1H_2$ | 789.1 | - | - | - |
| $A_1B_1H_2$ | 1081.5 | - | - | - |
| $A_1B_2H_2$ | 1374.0 | - | - | - |
| $A_2B_1H_2$ | 1867.1 | - | - | - |
| $A_2B_2H_2$ | 2161.1 | 2155.1 | - | - |
| $A_2B_3H_2$ | 2453.5 | - | 2485.8 | - |
| $A_3B_2H_2$ | 2948.1 | - | - | 3016.0 |
| $A_3B_3H_2$ | 3240.6 | 3238.3 | 3275.2 | 3312.2 |
| $A_3B_4H_2$ | 3533.1 | 3531.5 | 3570.4 | 3605.1 |
| $A_4B_3H_2$ | 4027.7 | 4026.0 | 4062.6 | 4099.8 |
| $A_4B_4H_2$ | 4320.1 | 4318.0 | 4356.4 | 4392.6 |
| $A_4B_5H_2$ | 4612.6 | 4613.8 | 4649.8 | 4686.3 |
| $A_5B_4H_2$ | 5107.2 | 5107.2 | 5144.3 | 5180.7 |
| $A_5B_5H_2$ | 5399.6 | 5399.8 | 5436.8 | 5474.1 |
| $A_5B_6H_2$ | 5692.1 | 5694.5 | 5732.0 | 5768.8 |
| $A_6B_5H_2$ | 6186.7 | 6188.1 | 6225.6 | 6261.5 |
| $A_6B_6H_2$ | 6479.2 | 6480.5 | 6519.0 | 6556.2 |
| $A_6B_7H_2$ | 6771.6 | - | - | - |
| $A_7B_6H_2$ | 7266.2 | 7269.4 | 7307.9 | 7343.0 |
| $A_7B_7H_2$ | 7558.7 | - | 7600.6 | - |
| $A_7B_8H_2$ | 7851.2 | - | - | - |
| $A_8B_7H_2$ | 8345.7 | - | - | - |
| $A_8B_8H_2$ | 8638.2 | - | - | - |
| $A_8B_9H_2$ | 8930.7 | - | - | - |
| $A_9B_8H_2$ | 9425.3 | - | - | - |
| $A_9B_9H_2$ | 9717.7 | - | - | - |
| $A_9B_{10}H_2$ | 10010.2 | - | - | |

a The MALDI-TOF mass spectrum was smoothed (Savitzky–Golay, 1 cycle; smoothing width: 5 *m*/*z*).

## 4. DOSY NMR analysis of foldamer 1

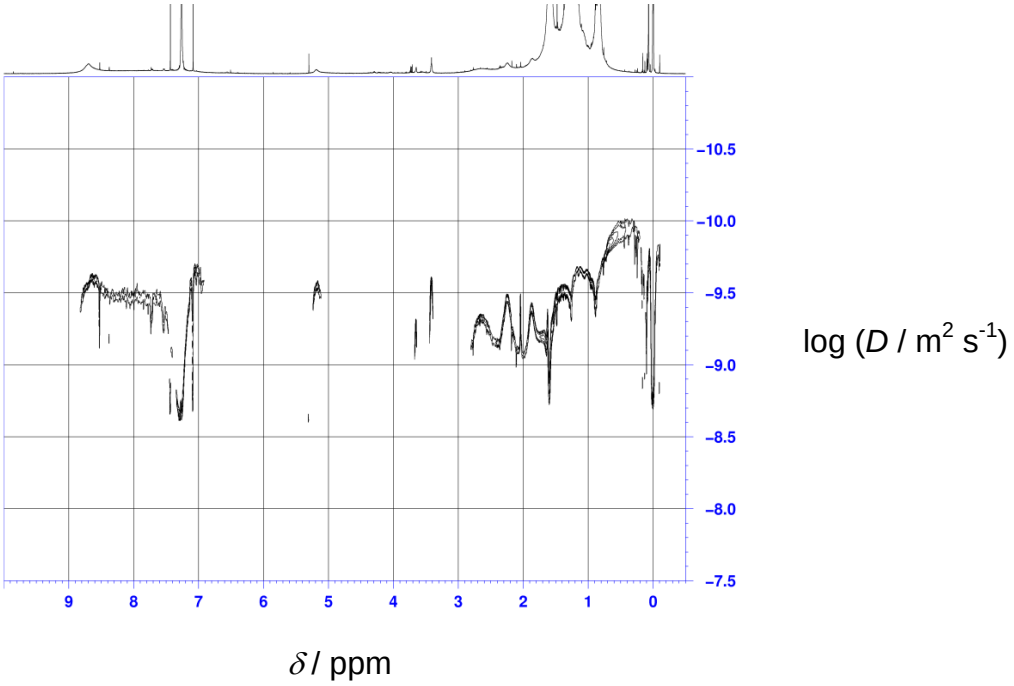
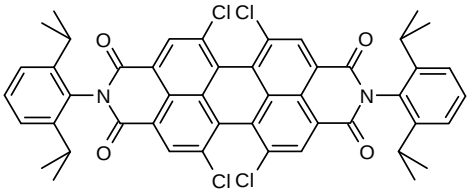



**Fig. S1** DOSY NMR (600 MHz) spectrum of **1** in $CDCl_3$ at 20 °C. The diffusion coefficients $D$ (in $m^2\ s^{-1}$) are plotted on a logarithmic scale against the chemical shift $\delta$.

Determination of the oligomer size of **1** by DOSY NMR spectroscopy:




**PBI-S1**

Comparative DOSY NMR experiments with **1** and reference compound **PBI-S1** in $CDCl_3$ were conducted, and the Stokes-Einstein equation (eqn S1) for spherical particles was applied to estimate the size of **1**.

$$D = \frac{k_B T}{6\pi \cdot \eta \cdot r}, \qquad \text{(S1)}$$

where $D$ is the diffusion coefficient of the compound, $k_B$ the Boltzmann constant, $T$ the temperature, $\eta$ the viscosity of the solvent, and $r$

the hydrodynamic radius of the molecule.

For the reference compound **PBI-S1** and oligomer **1**, the diffusion coefficients $5.86 \times 10^{-10}$ $m^2$ $s^{-1}$ and $2.56 \times 10^{-10}$ $m^2$ $s^{-1}$ were found, respectively. Regarding the Stokes-Einstein equation (S1), it is obvious that $r \sim 1 / D$, and hence, for the hydrodynamic volumes ($V$) for both compounds, a ratio of 1:12 was determined. By assuming the relation $V \sim M$ (molecular mass), from the molecular weights 847 g $mol^{-1}$ and 1080 g $mol^{-1}$ for **PBI-S1** and the repeating unit AB of **1**, respectively, an average oligomer size of 9.4, i.e., a nonamer for **1** can be approximated. This finding is in good agreement with the size obtained from GPC analysis (Figure 2a in main text), which yields a weight- average molecular mass $M_w$ = 8500 Da, corresponding to an octameric species.

## 5. UV/vis absorption studies

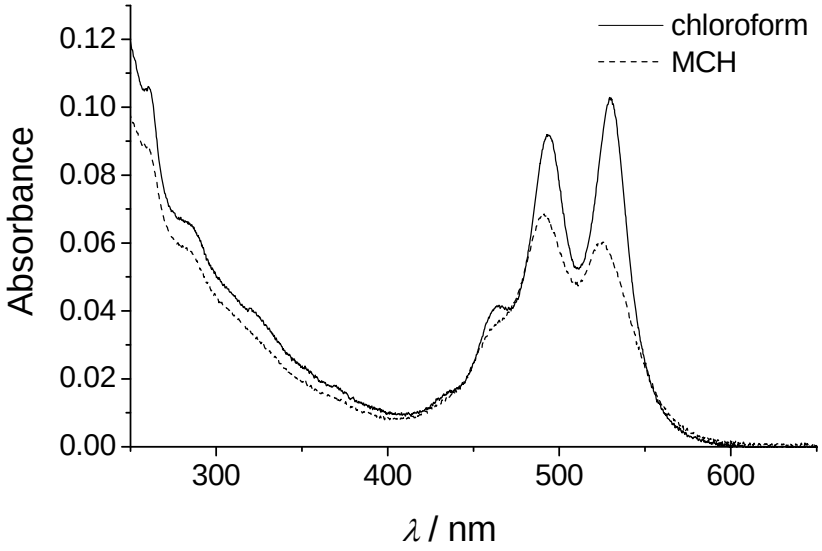



***Fig. S2.*** UV/vis absorption spectra of n-mer **1** (4.08 mg $l^{-1}$ at 20 °C) in chloroform (solid line) and MCH (dashed line).

***Table S2.*** Absorption maxima ($\lambda_{max1}$ and $\lambda_{max2}$) and the ratios $A_{max1}/A_{max2}$ of the absorption spectra of n-mer **1** for different solvents (see Fig. 3 in the manuscript). The dielectric constants ($\varepsilon_r$) and refractive indices ($n$) are given for the respective solvents.[S6]

| Solvent | $\lambda_{max1}$ (nm) | $\lambda_{max2}$ (nm) | $A_{max1}/A_{max2}$ | $\varepsilon_r$ | $n$ |
|---|---|---|---|---|---|
| PhCN | 496 | 533 | 1.05 | 25.20 | 1.527 |
| toluene | 494 | 530 | 1.07 | 2.38 | 1.494 |
| chloroform | 493 | 530 | 1.12 | 4.81 | 1.446 |
| $CH_2Cl_2$ | 493 | 529 | 1.08 | 8.93 | 1.424 |
| $CCl_4$ | 491 | 526 | 1.05 | 2.24 | 1.458 |
| di-*n*butylether | 491 | 524 | 0.94 | 3.08 | 1.397 |
| MCH | 491 | 524 | 0.88 | 2.02 | 1.420 |

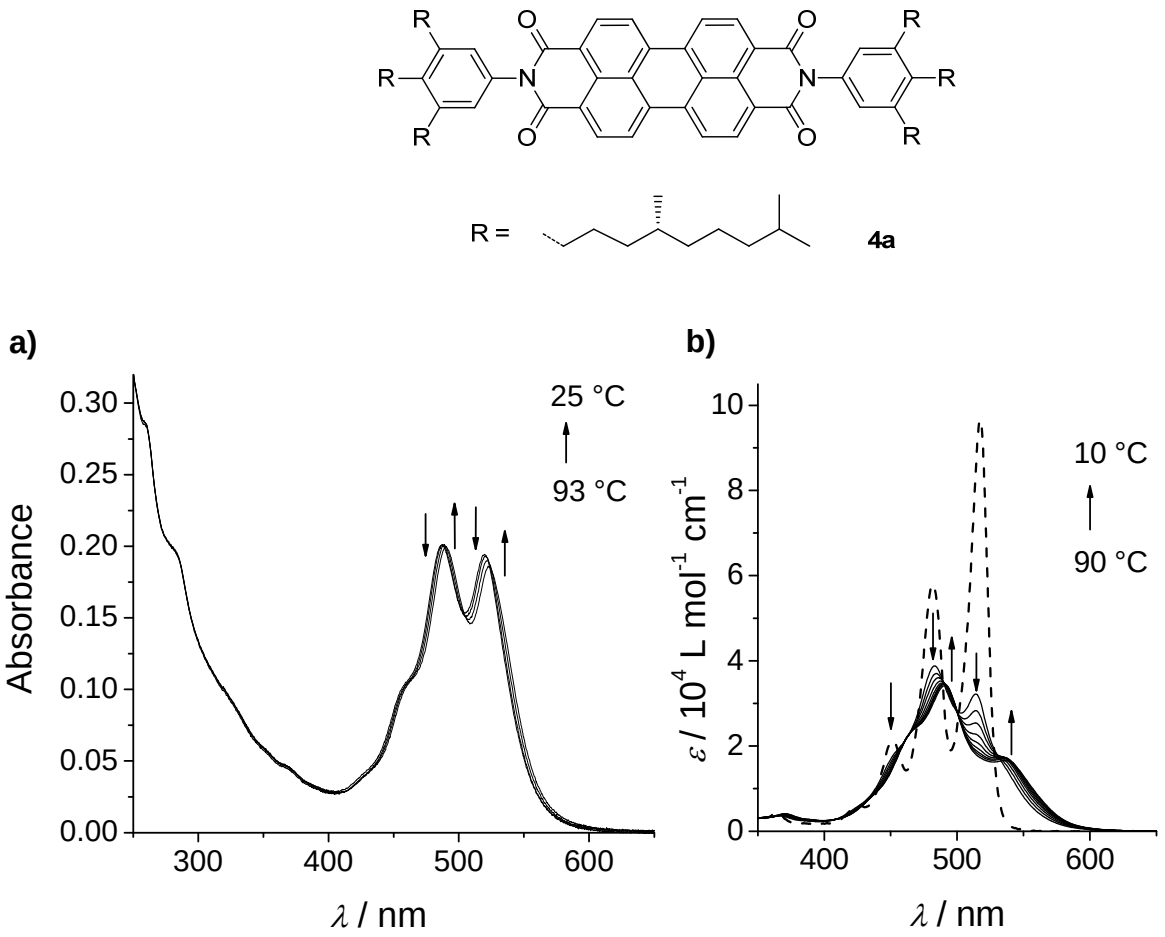



***Fig. S3.*** Temperature-dependent UV/vis spectra of (a) n-mer **1** in MCH (c = 11 mg $l^{-1}$) and (b) of a $2 \cdot 10^{-3}$ M (2.9 g $l^{-1}$) solution of **4a** in MCH (solid lines). Arrows indicate changes upon decrease of temperature. The dashed line is a monomer absorption spectrum of **4a** in MCH solution at $c = 1.5 \cdot 10^{-6}$ M (2.2 mg $l^{-1}$) and 25 °C.

## 6. $K_{eq}$ and $\Delta G$ values for folding

***Table S3.*** Thermodynamic data for the solvent-dependent folding of PBI **1**.

| Vol% of chloroform in MCH | $K_{eq}$(530 nm) | $K_{eq}$(495 nm) | $\Delta G$(530 nm) / kJ mol$^{-1}$ | $\Delta G$(495 nm) / kJ mol$^{-1}$ |
|---|---|---|---|---|
| 0 | - | - | - | - |
| 5 | 22.6 | 39.1 | -7.7 | -9.1 |
| 10 | 7.13 | 6.57 | -4.9 | -4.7 |
| 20 | 1.68 | 1.48 | -1.3 | -0.9 |
| 30 | 1.00 | 1.18 | 0 | -0.4 |
| 40 | 0.56 | 0.61 | 1.4 | 1.2 |
| 50 | 0.32 | 0.32 | 2.8 | 2.9 |
| 60 | 0.23 | 0.19 | 3.7 | 4.1 |
| 70 | 0.12 | 0.10 | 5.3 | 5.8 |
| 80 | 0.04 | 0.02 | 7.6 | 9.3 |
| 90 | - | - | - | - |
| 100 | - | - | - | - |

## 7. Additional references


S1 D. D. Perrin, W. L. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals – Second Edition*, Pergamon Press Ltd., Oxford, 1980.

S2 J. M. Tauber, F. R. Kelly, J. M. Giaimo, B. Rybtchinski, M. R. Wasielewski, *J. Am. Chem. Soc.* 2006, **128**, 1782.

S3 Q. Zhou, P. Carroll, T. M. Swager, *J. Org. Chem.* 1994, **59**, 1294.

S4 M. Berubé, D. Poirier, *Org. Lett.* 2004, **6**, 3127.

S5 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/ Plenum Publishers, New York, 1999.

S6 Solvent polarities were taken from: J. A. Riddik, W. B. Bunger, T. K. Sakano, *Organic Solvents – Physical Properties and Methods of Purification*, 4th Edition, VCH, New York, 1986.