Thermodynamics of the Self-Assembly of *N*-Annulated Perylene Bisimides in Water. Disentangling the Enthalpic and Entropic Contributions

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# Experimental Procedures

1.- Materials and methods

General methods. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 MHz (^{1}H: 300 MHz; ^{13}C: 75 MHz) spectrometer at 298 K and a Bruker Avance 500 MHz (^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometer at 323 K using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts (*δ*) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 250 and 750 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm, by using a 1 cm quartz cuvette (Hellma). Thermal experiments were performed at constant heating rates of 1 °C min^{-1} from 10 to 95 °C in water. Emission spectra were registered on a Jasco FP-6300 spectrofluorometer.. High resolution mass spectra (HRMS) were recorded on a MALDI Bruker daltonics Ultraflex TOF/TOF spectrometer.

Computational details. Molecular dynamics (MD) simulations in water as solvent were performed with GROMACS 2021.3 using periodic boundary conditions.[S1] For *N*-PBIs, we used the OPLS-AA force field with atom type selection as assigned by the PolyParGen tool[S2] for an initial structure with lateral chains totally extended and previously optimized at semiempirical level (GFN2-xTB).[S3] The initial structure for monomers, dimers and tetramers were centered in a box large enough so the minimum distance between the box boundary and the closest atom was of 1.0 nm to avoid spurious interactions due to the periodic boundary conditions. Point charges were calculated by following the RESP procedure with Antechamber at the B3LYP/6-31G** level. For water molecules, we selected the widely-used TIP4P model.[S1] The standard protocol for MD simulations was followed: i) energy minimization, ii) solvent equilibration around the solute, and iii) production.

For energy minimization, we used a steepest descent algorithm with 0.01 nm step size until all forces were below 1000 kJ·mol^{-1}·nm^{-1}. The equilibration of the solvent consisted of two stages of 0.1 ps in steps of 2 fs in which the solute was kept frozen: an initial NVT scheme fixing volume and temperature (300 K), and, subsequently, an NPT scheme where pressure (1 bar) and temperature (300 K) were kept constant. Finally, the production run (NPT scheme) consisted of 2 ns calculations in steps of 2 fs. In all cases, we used a V-rescale thermostat with damping constant of 0.1 ps and a Parrinello-Rahman pressure coupling with damping constant of 2 ps. C-H bonds in **1** and **3** and O-H bonds in water were constrained with a 4th order LINCS algorithm. The cutoff radius for short-range electrostatic and van der Waals interactions was set to 1.0 nm and we used an order 4 Particle Mesh Ewald for long-range electrostatics.

Thermodynamic properties were computed by averaging the values obtained for 2001 structures extracted from the production MD trajectory, one every each ps. For this step, we prepared a new set of calculations for dimers and tetramers keeping constant the concentration by fixing the PBI:H$_2$O ratio to 1:3466 for **1** and 1:5406 for **3**. Aggregation enthalpies ($\Delta\bar{H}_{aggr}$) were estimated as the difference of the average enthalpy on the bonded state $\bar{H}_b$ of n *N*-PBIs (n = 2 for dimer and n = 4 for tetramer) minus n times the average enthalpy of the non-bonded state $\bar{H}_{nb}$ (monomer); namely, $\Delta\bar{H}_{aggr} = \bar{H}_b - n \cdot \bar{H}_{nb}$. Changes in the intermolecular interactions between bonded and non-bonded structures were analyzed by decomposing the potential energy of the full system *N*-PBI/H$_2$O ($\bar{E}_{pot}$) into three average terms: potential energy of the *N*-PBIs compounds ($\bar{E}_{pot}^{N-PBI}$), potential energy of the water molecules ($\bar{E}_{pot}^{H_2O}$), and *N*-PBI/H$_2$O interaction of the *N*-PBIs with water ($\bar{E}_{int}^{N-PBI-H_2O}$). The two first terms were calculated by extracting separately the *N*-PBIs and the water molecules from the MD trajectory of the full system and re-computing the average potential energy for the corresponding subsystem, whereas $\bar{E}_{int}^{N-PBI-H_2O}$ was computed as the difference between the two first terms and the average potential energy of the complete system $\bar{E}_{pot}$; i.e., $\bar{E}_{int}^{N-PBI-H_2O} = \bar{E}_{pot} - \bar{E}_{pot}^{N-PBI} - \bar{E}_{pot}^{H_2O}$.

2.- Synthesis and Characterization
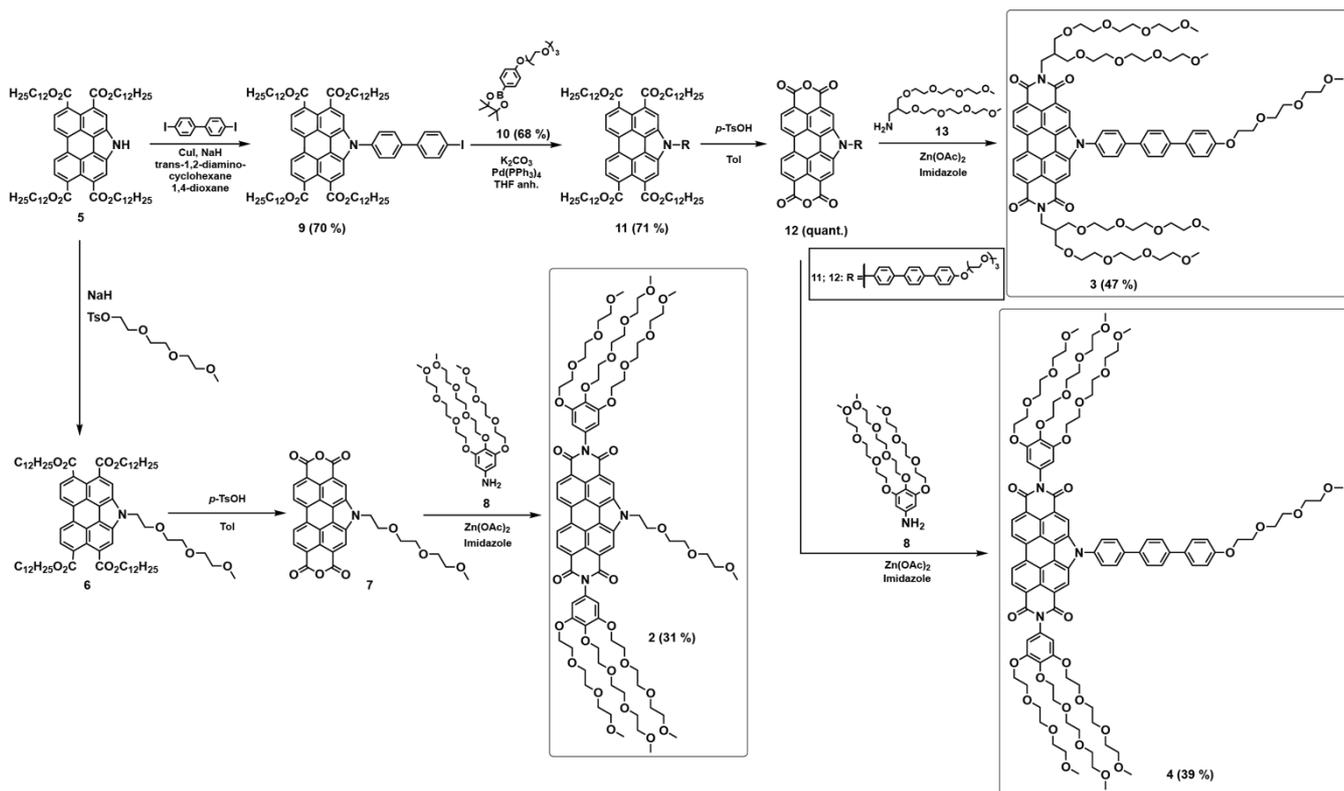
Scheme S1. Synthesis of amphiphilic *N*-PBIs **2**–**4**.

Compounds **1**,[S5] **5**,[S6] **6**,[S5] **7**,[S5] **8**,[S7] **10**,[S8] and **13**[S9] were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

Tetradodecyl 1-(4'-iodo-[1,1'-biphenyl]-4-yl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,4,9,10-tetracarboxylate (9)
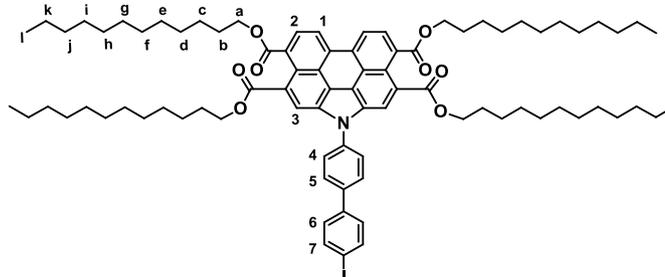
$C_{84}H_{114}INO_8$
Exact Mass: 1391.7589
Mol. Wt.: 1392.7103

NaH (36 mg, 0.90 mmol) was slowly added to a mixture of compound **5** (200 mg, 0.18 mmol), 4,4'-diiodobiphenyl (405 mg, 0.90 mmol), copper iodide (17 mg, 0.09 mmol), and trans-1,2-diaminocyclohexane (105 mg, 0.90 mmol) in dry 1,4-dioxane (20 mL). The resulting mixture was refluxed overnight under argon atmosphere. After cooling to room temperature, the reaction mixture was poured into cold water and extracted with CH_2Cl_2. The resulting organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The obtained product was purified by column chromatography (silica gel, Hex/CH_2Cl_2 1/4) affording compound **9** as a yellow solid (175 mg, 70 %). ^{1}H NMR (CDCl$_3$, 300 MHz) δ/ppm 8.78 (2H, H$_1$, d, J = 8.0 Hz), 8.57 (2H, H$_3$, s), 8.35 (2H, H$_2$, d, J = 7.9 Hz), 8.02 – 7.80 (6H, H$_{4+5+7}$, m), 7.46 (2H, H$_6$, d, J = 8.4 Hz), 4.44 – 4.33 (8H, H$_a$, m), 1.89 – 1.72 (8H, H$_b$, m), 1.50 – 1.16 (72H, H$_{c-k}$, m), 0.90 – 0.82 (12H, H$_l$, m). ^{13}C NMR (CDCl$_3$, 75 MHz) δ/ppm 169.4, 169.0, 139.6, 138.3, 137.7, 132.7, 132.0, 129.8, 129.5, 129.1, 129.0, 128.6, 125.4, 125.0, 124.4, 122.3, 119.7, 119.0, 93.9, 66.0, 65.9, 32.1, 29.8(3), 29.8(0), 29.7(7), 29.7(5), 29.7(1), 29.5, 28.8, 28.7, 26.2, 22.8, 14.3. FTIR (neat) 667, 727, 752, 799, 838, 874, 935, 1001, 1018, 1044, 1099, 1120, 1153, 1187, 1262, 1340, 1373, 1409, 1456, 1481, 1505, 1521, 1580, 1589, 1608, 1721, 2853, 2923, 2955 cm^{-1}. HRMS (MALDI-TOF) calcd. for $C_{84}H_{114}INO_8$ [M]$^+$, 1391.759; found, 1391.636.

Tetradodecyl 1-(4''-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1':4',1''-terphenyl]-4-yl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole-3,4,9,10-tetracarboxylate (11)
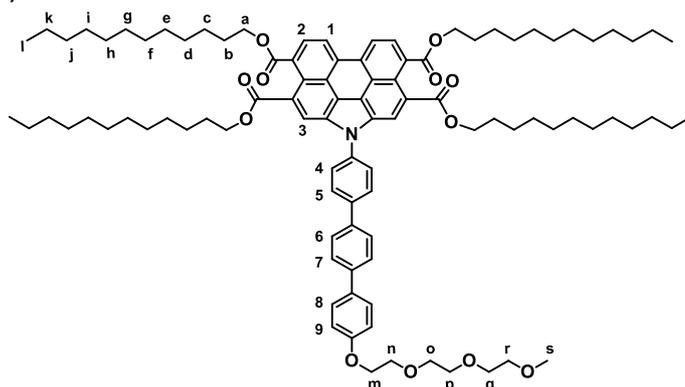
C$_{97}$H$_{133}$NO$_{12}$
Exact Mass: 1503.9828
Mol. Wt.: 1505.0934

Compound **9** (391 mg, 0.28 mmol), compound **10** (308 mg, 0.84 mmol), and tetrakis(triphenylphosphine)palladium(0) (71 mg, 0.06 mmol) were dissolved in dried THF (60 mL). K$_2$CO$_3$ (194 mg, 1.40 mmol) was dissolved in water (1 mL) and added to the solution under argon atmosphere. The reaction mixture was heated to reflux overnight. After that, the solvent was evaporated under reduced pressure and the residue was then redissolved in CH$_2$Cl$_2$ and washed with water. The organic layer was dried over MgSO$_4$, filtered, and the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography (silica gel, CHCl$_3$/MeOH 10/0.1) affording compound **11** as a light orange solid (302 mg, 71 %). ^{1}H NMR (CDCl$_3$, 300 MHz) δ/ppm 8.62 (2H, H$_1$, d, *J* = 8.0 Hz), 8.54 (2H, H$_3$, s), 8.28 (2H, H$_2$, d, *J* = 8.0 Hz), 7.99 (2H, H$_5$, d, *J* = 8.6 Hz), 7.94 (2H, H$_4$, d, *J* = 8.6 Hz), 7.79 (2H, H$_6$, d, *J* = 8.5 Hz), 7.71 (2H, H$_7$, d, *J* = 8.5 Hz), 7.60 (2H, H$_8$, d, *J* = 8.8 Hz), 7.03 (2H, H$_9$, d, *J* = 8.8 Hz), 4.39 (8H, H$_a$, m), 4.24 – 4.17 (2H, H$_m$, m), 3.94 – 3.88 (2H, H$_n$, m), 3.81 – 3.76 (2H, H$_o$, m), 3.75 – 3.70 (2H, H$_p$, m), 3.70 – 3.66 (2H, H$_q$, m), 3.61 – 3.55 (2H, H$_r$, m), 3.40 (3H, H$_s$, s), 1.91 – 1.72 (8H, H$_b$, m), 1.54 – 1.14 (72H, H$_{c-k}$, m), 0.92 – 0.78 (12H, H$_l$, m). ^{13}C NMR (75 MHz, CDCl$_3$) δ/ppm 169.3, 168.9, 158.7, 140.4, 140.1, 138.2, 137.2, 133.2, 132.4, 131.9, 129.5, 129.2, 128.8, 128.4, 128.1, 127.5, 127.3, 125.2, 124.8, 124.2, 122.0, 119.4, 119.1, 115.1, 72.1, 71.0, 70.8, 70.7, 69.9, 67.7, 65.9, 65.8, 59.2, 32.0, 29.8, 29.7(7), 29.7(5), 29.7(1), 29.5, 29.4, 28.8, 28.7, 26.2, 26.2, 22.8, 22.7, 14.2. FTIR (neat) 621, 670, 721, 751, 765, 800, 820, 839, 890, 952, 1003, 1015, 1047, 1153, 1187, 1209, 1258, 1317, 1351, 1378, 1423, 1467, 1492, 1534, 1590, 1608, 1668, 1715, 2853, 2922 cm^{-1}. HRMS (MALDI-TOF) calcd. for C$_{97}$H$_{133}$NO$_{12}$ [M]$^+$, 1503.982; found, 1503.549.

5-(4''-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1':4',1''-terphenyl]-4-yl)-1*H*-pyrano[3',4',5':4,5]naphtha[2,1,8-*cde*]-pyrano-[3',4',5':4,5]naphtho[8,1,2-*ghi*]isoindole-1,3,7,9(5*H*)-tetraone (12)
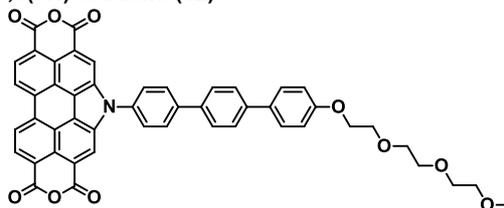

C$_{49}$H$_{33}$NO$_{10}$
Exact Mass: 795.2104
Mol. Wt.: 795.7870

A mixture of compound **11** (292 mg, 0.194 mmol) and *p*-toluene sulphonic acid monohydrate (185 mg, 0.97 mmol) in toluene (5 mL) was heated to reflux overnight. Still warm, MeOH was added to precipitate it. The mixture was filtered and washed with MeOH affording, without any further purification, compound **12** as a dark purple solid (154 mg, quant.). FTIR (neat) 685, 727, 744, 752, 798, 821, 903, 944, 999, 1023, 1041, 1066, 1121, 1175, 1209, 1267, 1325, 1385, 1413, 1458, 1494, 1539, 1561, 1601, 1752, 2854, 2924 cm^{-1}. HRMS (MALDI-TOF) calcd. for C$_{49}$H$_{33}$NO$_{10}$ [M]$^+$, 795.210; found, 795.145.

**Synthesis of PBIs 2–4. General procedure.**

A mixture of compound **7** or **12** (0.063 mmol), amines **8** or **13** (0.148 mmol), zinc acetate (46 mg, 0.251 mmol) and imidazole (2.0 g) was heated to 110 ºC overnight under argon atmosphere. After cooling at room temperature, the reaction mixture was extracted with CH_2Cl_2 and washed with a saturated NaCl solution, the organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. After that, the residue obtained was purified by column chromatography.

2,8-bis(13-(2,5,8,11-tetraoxadodecyl)-2,5,8,11-tetraoxatetradecan-14-yl)-5-(4''-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1':4', 1''-terphenyl]-4-yl)-1*H*-pyrido[3',4',5':4,5]naphtho[2,1,8-*cde*]pyrido[3',4',5':4,5]naphtho[8,1,2-*ghi*]isoindole1,3,7,9-(2*H*,5*H*,8*H*)-tetraone (2)

$C_{85}H_{107}N_3O_{24}$
Exact Mass: 1553.7245
Mol. Wt.: 1554.7648
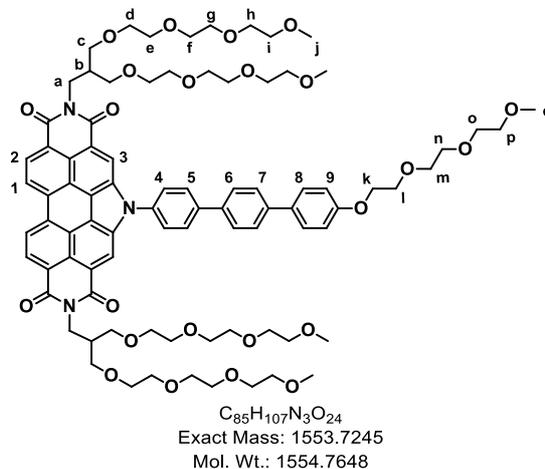
Compound **2** was obtained after column chromatography purification (silica gel, CHCl₃/MeOH 10/0.1) as a viscous red solid (46 mg, 47 %). ¹H NMR (CDCl₃, 300 MHz) δ/ppm 8.99 (2H, H₃, s), 8.80 (2H, H₁, d, J = 8.0 Hz), 8.71 (2H, H₂, d, J = 8.0 Hz), 8.03 (2H, H₅, d, J = 8.4 Hz), 7.97 (2H, H₄, d, J = 8.4 Hz), 7.80 (2H, H₆, d, J = 8.4 Hz), 7.73 (2H, H₇, d, J = 8.4 Hz), 7.60 (2H, H₈, d, J = 8.8 Hz), 7.03 (2H, H₉, d, J = 8.8 Hz), 4.36 (4H, Hₐ, d, J = 6.9 Hz), 4.25 – 4.19 (2H, Hₖ, m), 3.95 – 3.89 (2H, Hₗ, m), 3.82 – 3.77 (2H, ₘ, m), 3.75 – 3.72 (2H, Hₙ, m), 3.71 – 3.66 (2H, Hₒ, m), 3.65 – 3.44 (62H, H_{p+(c-i)}, m), 3.40 (3H, H_q, s), 3.31 (12H, H_j, s), 2.56 (2H, H_b, m). ¹³C NMR (CDCl₃, 75 MHz) δ/ppm 165.0, 163.9, 158.7, 140.9, 140.6, 137.9, 136.7, 134.3, 133.1, 132.8, 129.2, 128.2, 127.6, 127.5, 125.0, 124.8, 124.1, 122., 121.8, 120.2, 119.9, 115.2, 72.1, 72.0, 71.0, 70.9, 70.8, 70.7, 70.6(4), 70.6(2), 70.5(4), 70.5(2), 69.9, 67.7, 59.2, 59.1. FTIR (neat) 624, 655, 666, 709, 741, 805, 821, 844, 877, 940, 1003, 1042, 1106, 1182, 1200, 1258, 1314, 1351, 1368, 1393, 1425, 1446, 1457, 1473, 1494, 1534, 1560, 1604, 1656, 1692, 2871 cm⁻¹. HRMS (MALDI-TOF, exact mass) calcd. for $C_{85}H_{107}N_3O_{24}$ [M+Na]⁺, 1576.7245; found, 1576.7217.

5-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2,8-bis(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1*H*-pyrido-[3',4',5':4, 5]naphtho[2,1,8-*cde*]pyrido[3',4',5':4,5]naphtho[8,1,2-*ghi*]isoindole-1,3,7,9(2*H*, 5*H*,8*H*)-tetraone (3)

$C_{85}H_{115}N_3O_{31}$
Exact Mass: 1673.7515
Mol. Wt.: 1674.8241
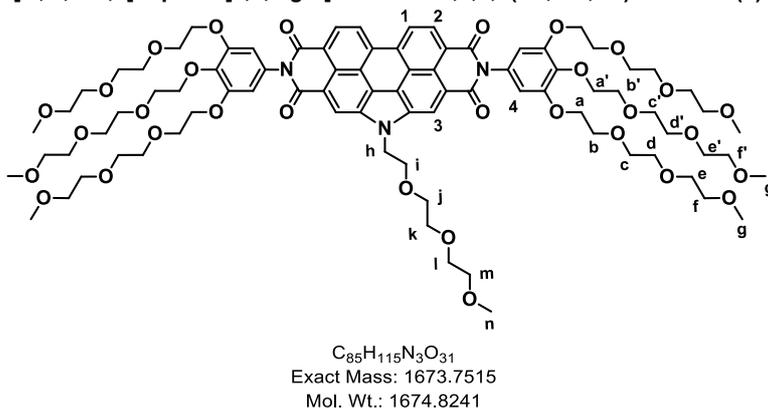
Compound **3** was obtained after column chromatography purification (silica gel, CHCl₃/MeOH 10/0.3) as a viscous red solid (52 mg, 31 %). ¹H NMR (CDCl₃, 500 MHz) δ/ppm 8.80 (2H, H₃, s), 8.59 (2H, H₁, d, J = 7.8 Hz), 8.44 (2H, H₂, br), 6.79 (4H, H₄, s), 4.97 (2H, H_h, br), 4.28 (4H, H_{a'}, t, J = 5.2 Hz), 4.13 (8H, Hₐ, t, J = 5.0 Hz), 4.10 (2H, Hᵢ, br), 3.90 (4H, H_{b'}, t, J = 5.2 Hz), 3.84 – 3.79 (12H, H_{b+c'}, m), 3.74 – 3.69 (16H, H_{c+d'+e'}, m), 3.67 – 3.62 (16H, H_{d+e}, m), 3.62 – 3.58 (6H, H_{f'+j}, m), 3.56 – 3.54 (2H, Hₖ, m), 3.54 – 3.51 (8H, H_f, m), 3.44 – 3.42 (2H, Hₗ, m), 3.41 (6H, H_{g'}, s), 3.34 (12H, H_g, s), 3.28 – 3.25 (2H, Hₘ, m), 3.12 (3H, Hₙ, s). ¹³C NMR (CDCl₃, 125 MHz) δ/ppm 164.7, 163.5, 153.0, 138.6, 134.8, 132.1, 131.2, 127.3, 124.0, 123.4, 122.1, 121.5, 120.9, 119.0, 118.8, 109.0, 72.5, 72.1, 72.0, 71.8, 71.1, 70.7, 70.6(8), 70.6(1), 70.5(5), 70.4(9), 70.4(1), 69.7, 69.1, 58.9, 58.8, 58.7. FTIR (neat) 635, 684, 710, 741, 769, 803, 849, 940, 1109, 1199 1243, 1303, 1352, 1377, 1399, 1425, 1504, 1558, 1600, 1662, 1697, 2874, 2923 cm⁻¹. HRMS (MALDI-TOF, exact mass) calcd. for $C_{85}H_{115}N_3O_{31}$ [M+Na]⁺, 1696.7412; found, 1696.7373.
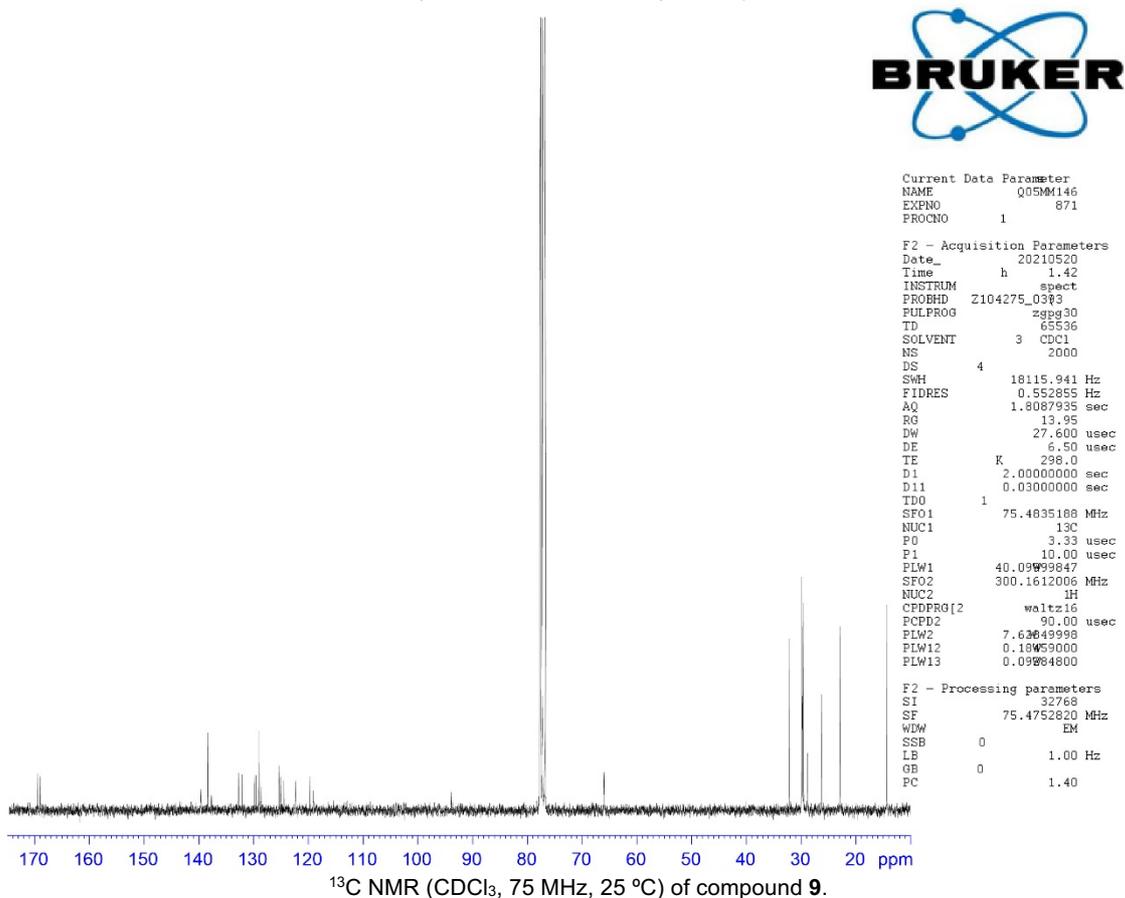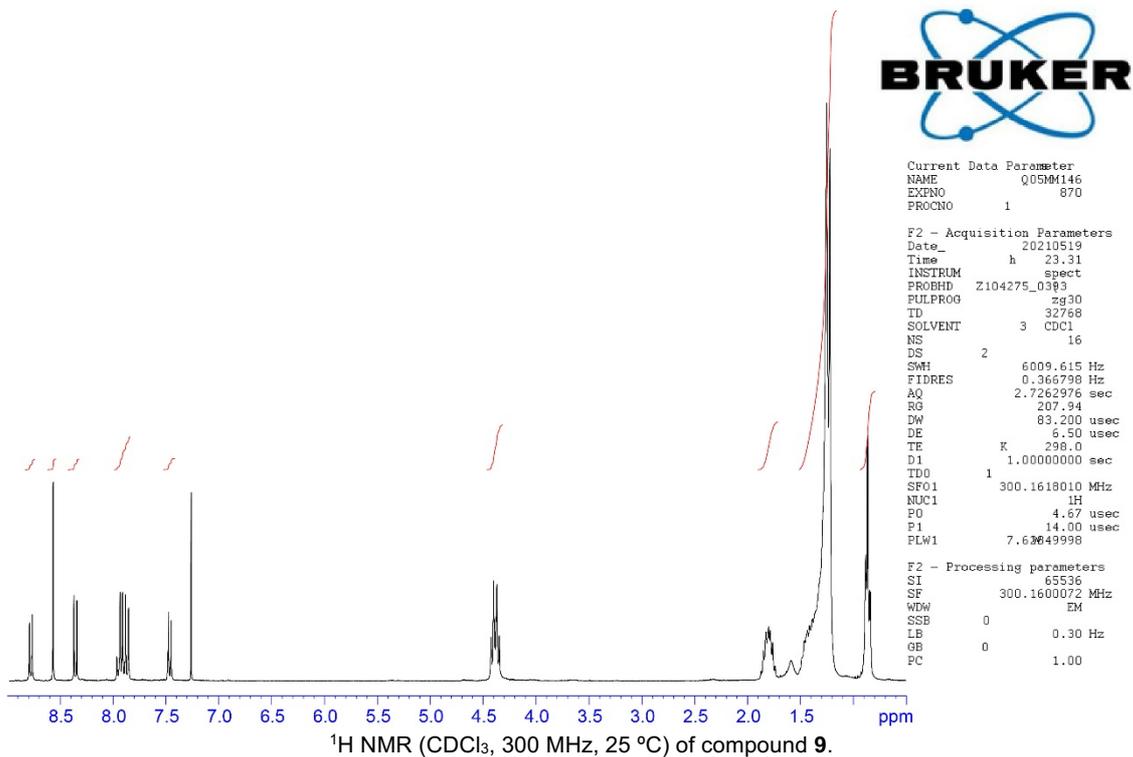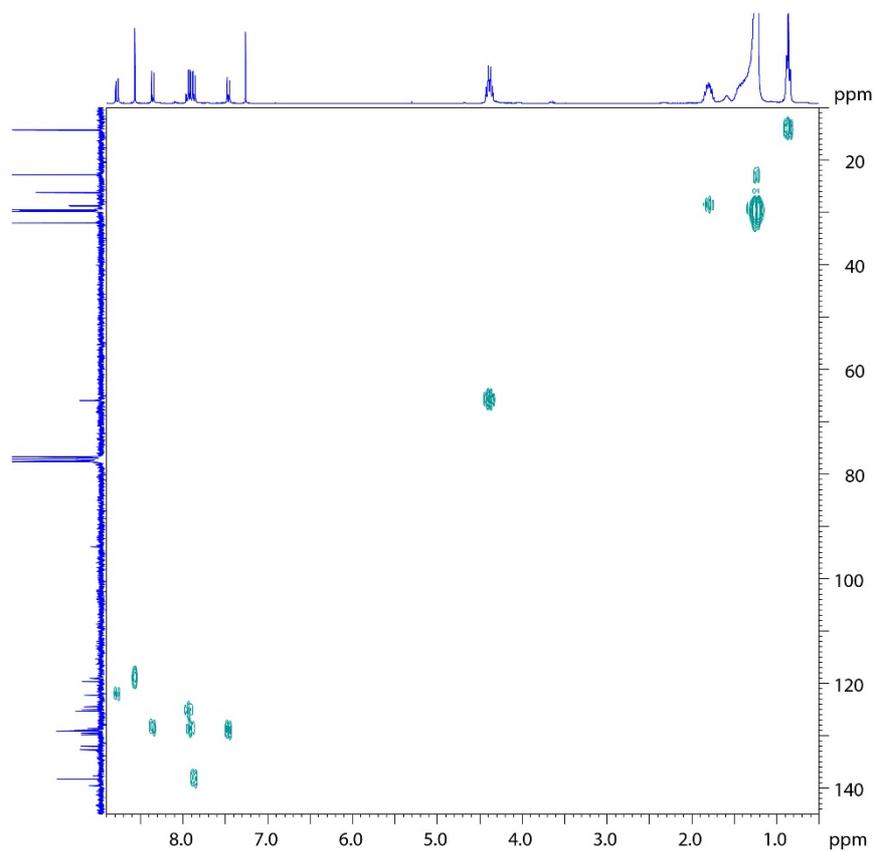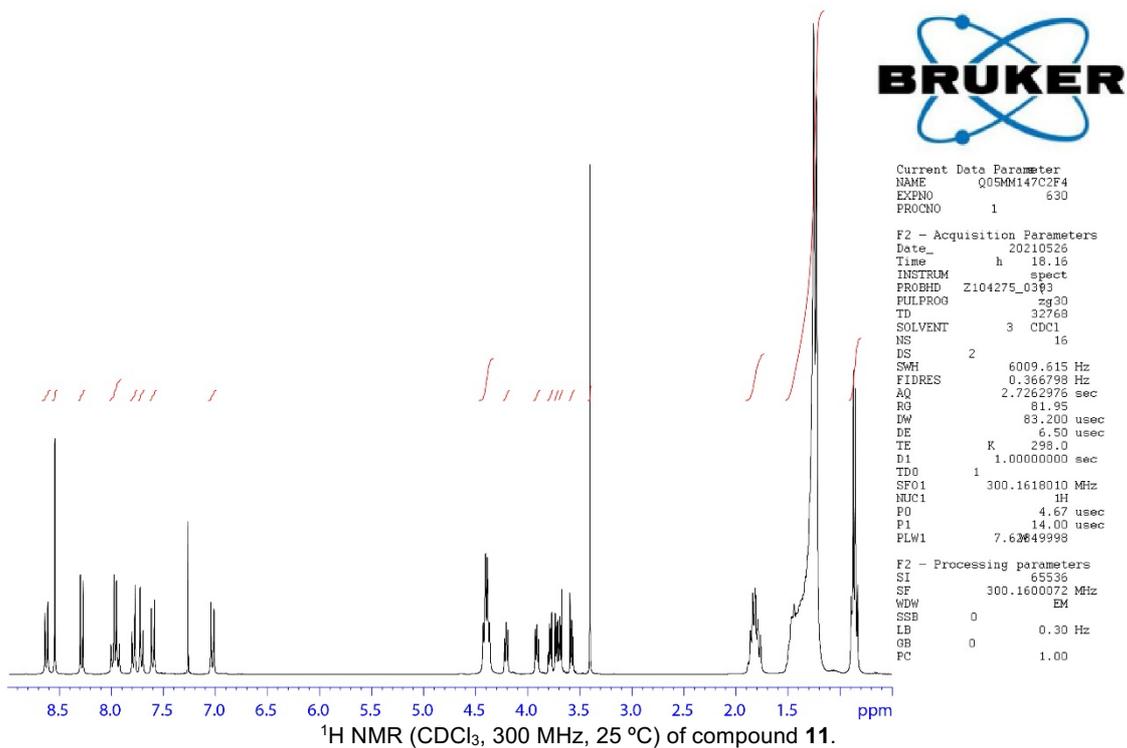
5-(4''-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1':4',1''-terphenyl]-4-yl)-2,8-bis(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)phenyl)-1*H*-pyrido[3',4',5':4,5]naphtho[2,1,8-*cde*]pyrido[3',4',5':4,5]naphtho[8,1,2-*ghi*]isoindole-1,3,7,9(2*H*,5*H*,8*H*)-tetraone (4)
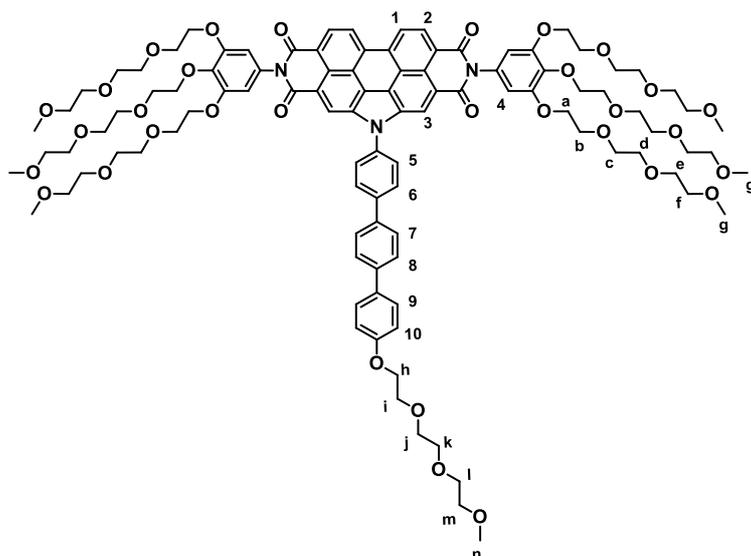
$C_{103}H_{127}N_3O_{32}$
Exact Mass: 1917.8403
Mol. Wt.: 1919.1114

Compound **4** was obtained after column chromatography purification (silica gel, CHCl₃/MeOH 10/0.3) as a viscous red solid (49 mg, 39 %). ^{1}H NMR (CDCl₃, 500 MHz) δ/ppm 8.83 (2H, H₃, s), 8.63 (2H, H₁, d, J = 8.0 Hz), 8.51 (2H, H₂, d, J = 8.0 Hz), 8.02 (2H, H₆, d, J = 8.4 Hz), 7.82 (2H, H₅, d, J = 8.4 Hz), 7.78 (2H, H₇, d, J = 8.4 Hz), 7.70 (2H, H₈, d, J = 8.4 Hz), 7.59 (2H, H₉, d, J = 8.8 Hz), 7.03 (2H, H₁₀, d, J = 8.8 Hz), 6.79 (4H, H₄, s), 4.28 (4H, H$_{a'}$, t, J = 5.2 Hz), 4.22 (2H, H$_h$, t, J = 5.0 Hz), 4.09 (8H, H$_a$, br), 3.93 − 3.87 (6H, H$_{b'+i}$, m), 3.82 − 3.76 (10H, H$_{b+j}$, m), 3.75 − 3.67 (22H, H$_{c+c'+d+k}$, m), 3.66 − 3.55 (22H, H$_{d'+e+e'+f'+l}$, m), 3.54 − 3.52 (2H, H$_m$, m), 3.52 − 3.48 (8H, H$_f$, m), 3.40 (6H, H$_{g'}$, s), 3.39 (3H, H$_n$, s), 3.32 (12H, H$_g$, s). ^{13}C NMR (CDCl₃, 125 MHz) δ/ppm 164.6, 163.4, 158.8, 153.2, 141.0, 140.7, 138.2, 137.5, 136.2, 133.6, 133.1, 132.3, 131.2, 129.4, 128.2, 127.6, 1274, 125.1, 124.3, 123.9, 122.6, 121.6, 121.0, 119.6, 115.2, 108.4, 72.6, 72.0(9), 72.0(7), 72.0(3), 72.0(0), 71.0, 70.8(1), 70.8(0), 70.7(9), 70.7(5), 70.7(1), 70.6(7), 70.6(5), 70.5(8), 69.9, 69.7, 68.9, 67.7, 59.2, 59.1(4), 59.0(7). FTIR (neat) 628, 667, 698, 711, 725, 740, 804, 822, 849, 945, 1004, 1109, 1182, 1199, 1245, 1303, 1363, 1391, 1422, 1436, 1455, 1472, 1493, 1532, 1559, 1602, 1663, 1698, 2873, 2922 cm$^{−1}$. HRMS (MALDI-TOF, exact mass) calcd. for $C_{103}H_{127}N_3O_{32}$ [M+Na]$^+$, 1940.8300; found, 1940.8279.
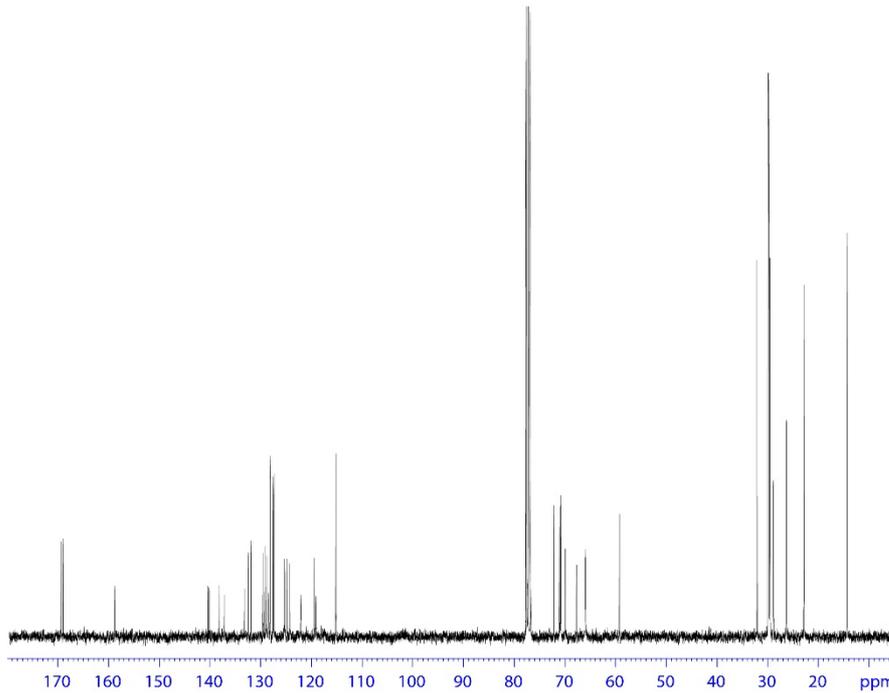
3.- Collection of spectra

S-7

^{1}H NMR (CDCl$_3$, 300 MHz, 25 ºC) of compound **9**.

^{13}C NMR (CDCl$_3$, 75 MHz, 25 ºC) of compound **9**.

^{1}H,^{13}C-HMQC spectrum (CDCl$_3$, 25 ºC) of compound **9**.

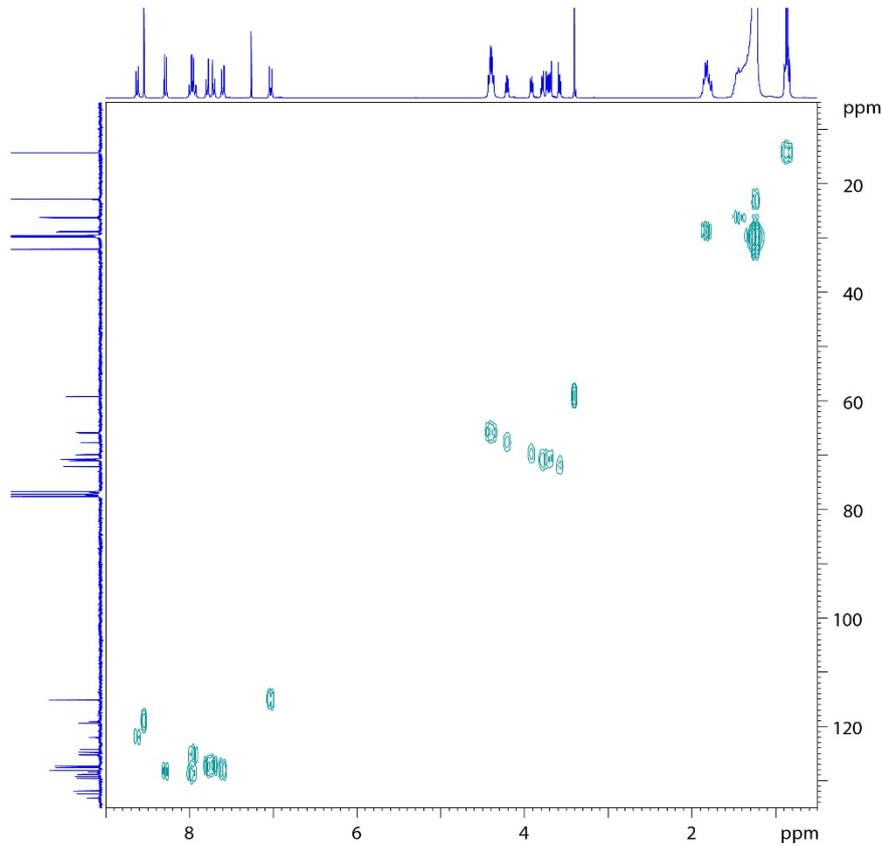Current Data Parameter
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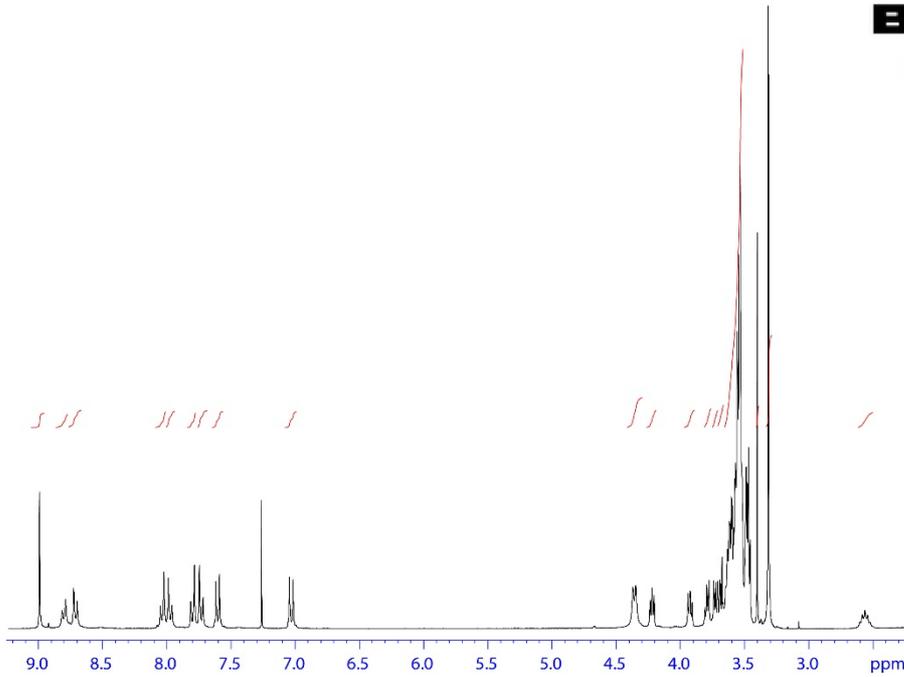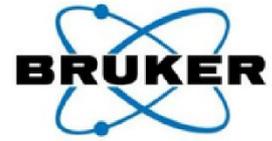EXPNO   630
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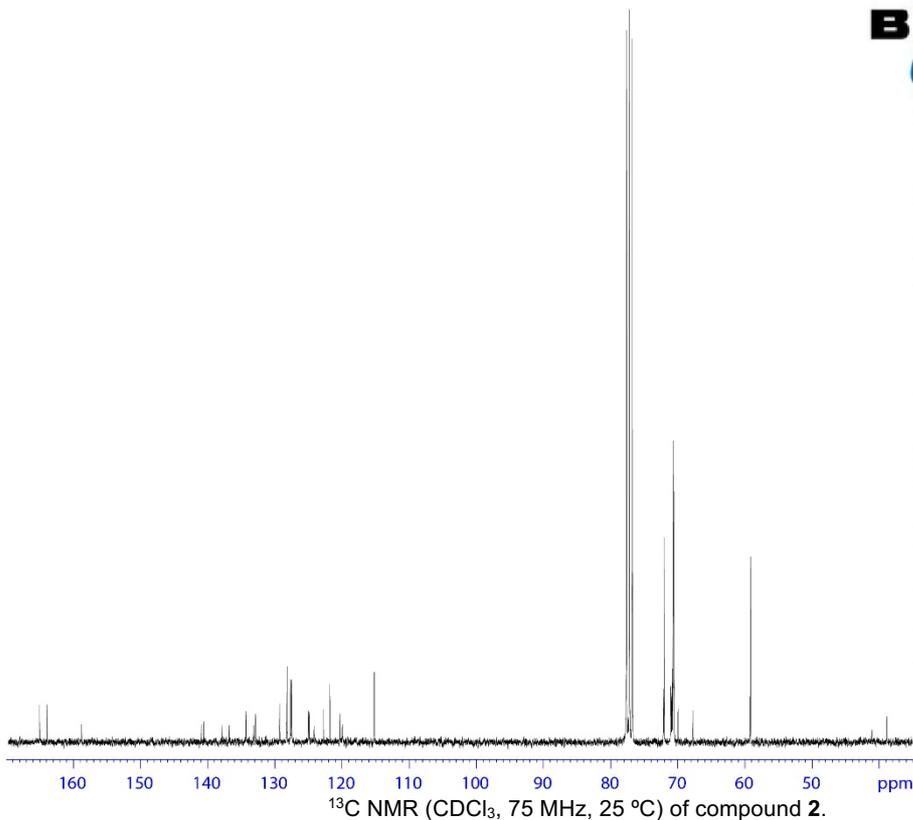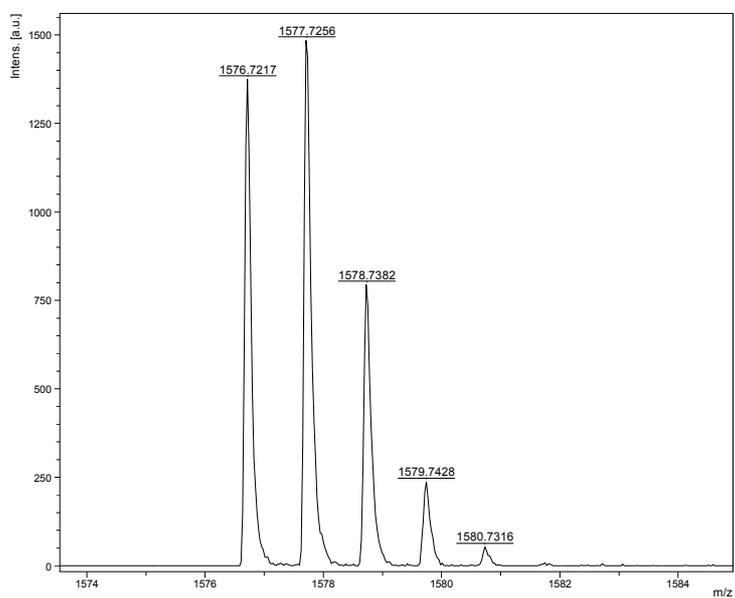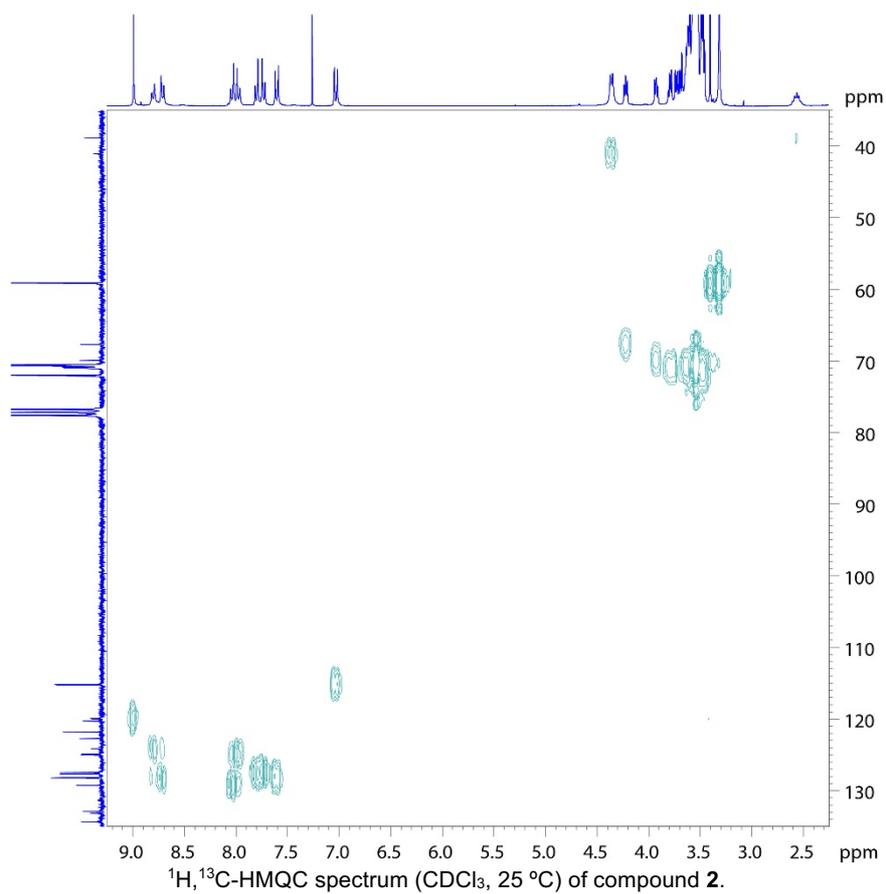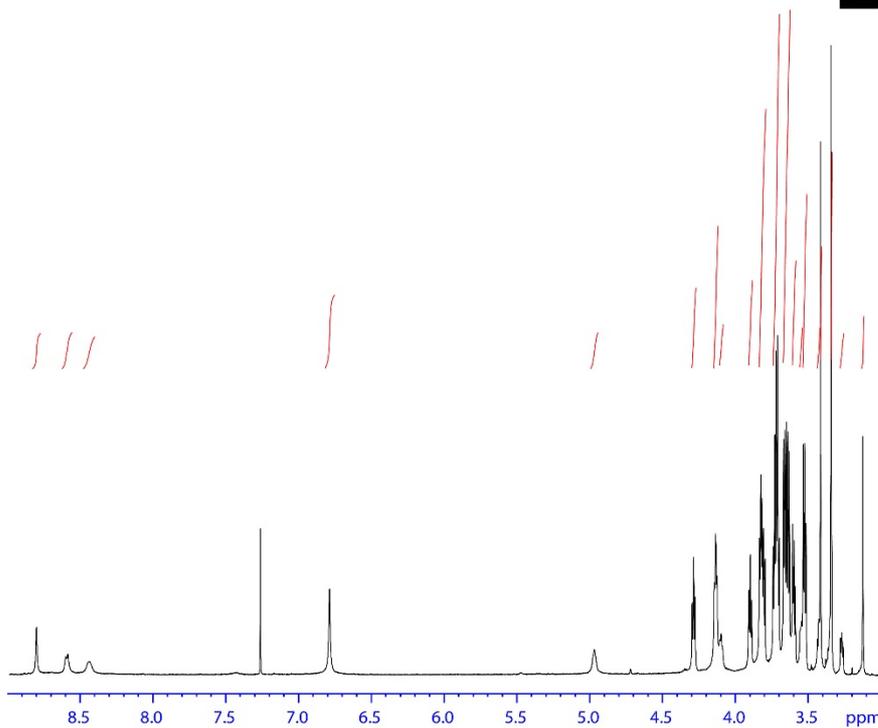
^{1}H NMR (CDCl$_3$, 300 MHz, 25 ºC) of compound **11**.

Current Data Parameter
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EXPNO   631
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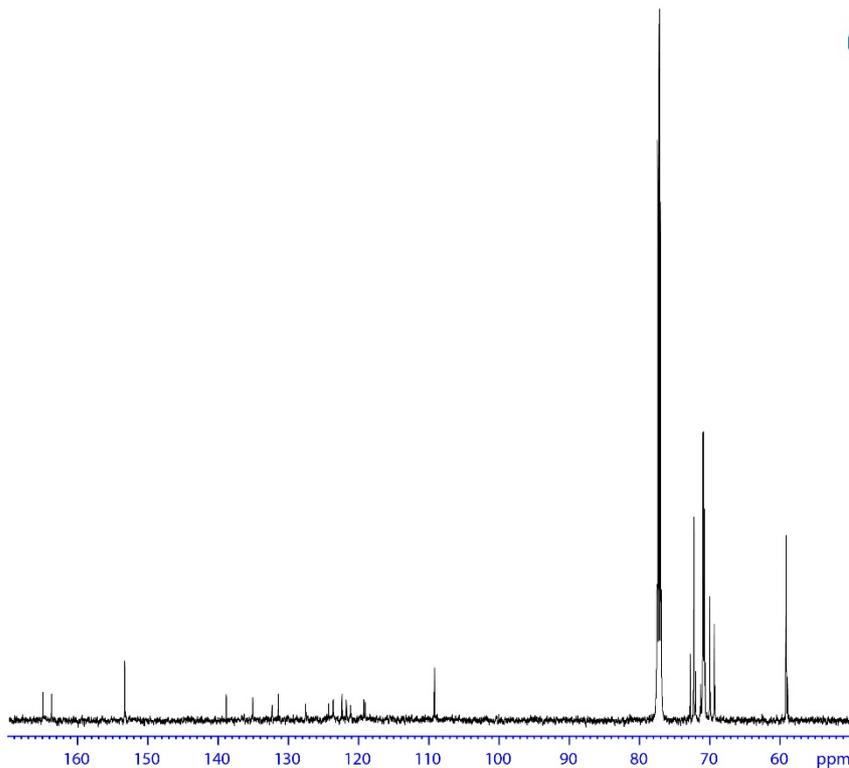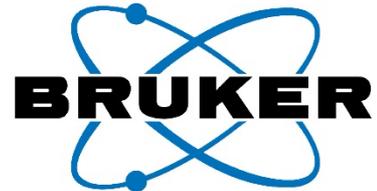WDW   EM
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^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C) of compound **11**.

^{1}H,^{13}C-HMQC spectrum (CDCl$_3$, 25 °C) of compound **11**.

^{1}H NMR (CDCl$_3$, 300 MHz, 25 ºC) of compound **2**.

^{13}C NMR (CDCl$_3$, 75 MHz, 25 ºC) of compound **2**.

^{1}H,^{13}C-HMQC spectrum (CDCl$_3$, 25 ºC) of compound **2**.

Mass spectrum of compound **2**.

¹H NMR (CDCl₃, 500 MHz, 50 ºC) of compound **3**.

¹³C NMR (CDCl₃, 125 MHz, 50 ºC) of compound **3**.

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^{1}H,^{13}C-HMQC spectrum (CDCl$_3$, 50 ºC) of compound **3**.

Mass spectrum of compound **3**.

^{1}H NMR (CDCl$_3$, 500 MHz, 50 ºC) of compound **4**.

^{13}C NMR (CDCl$_3$, 125 MHz, 50 ºC) of compound **4**.
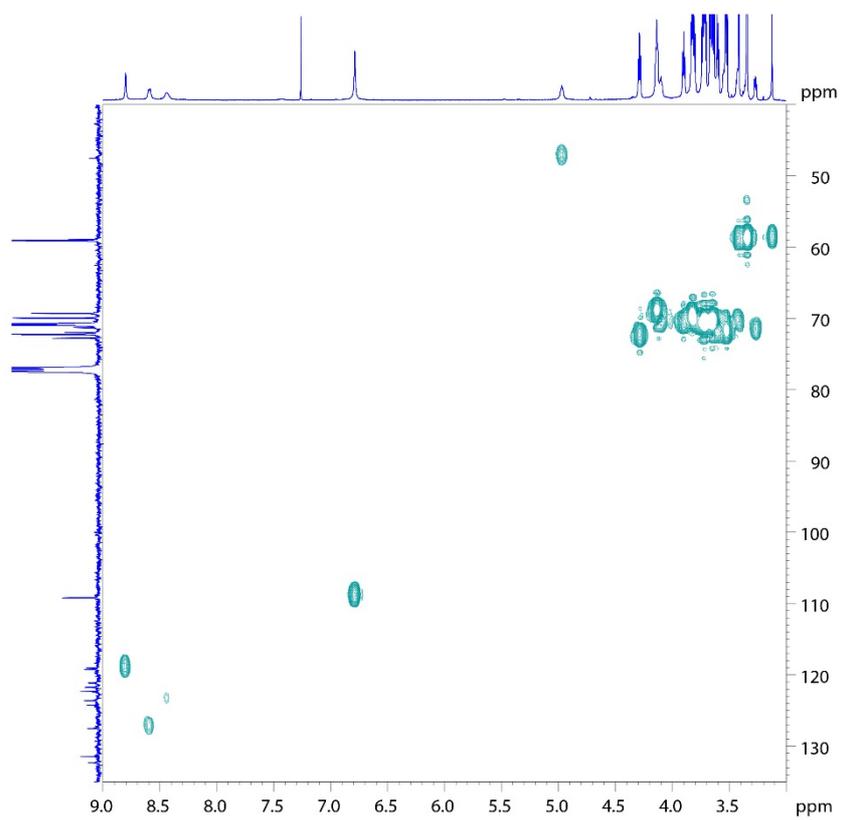
^{1}H,^{13}C-HMQC spectrum (CDCl$_3$, 50 °C) of compound **4**.

Mass spectrum of compound **4**.

4.- Supplementary Figures and Tables
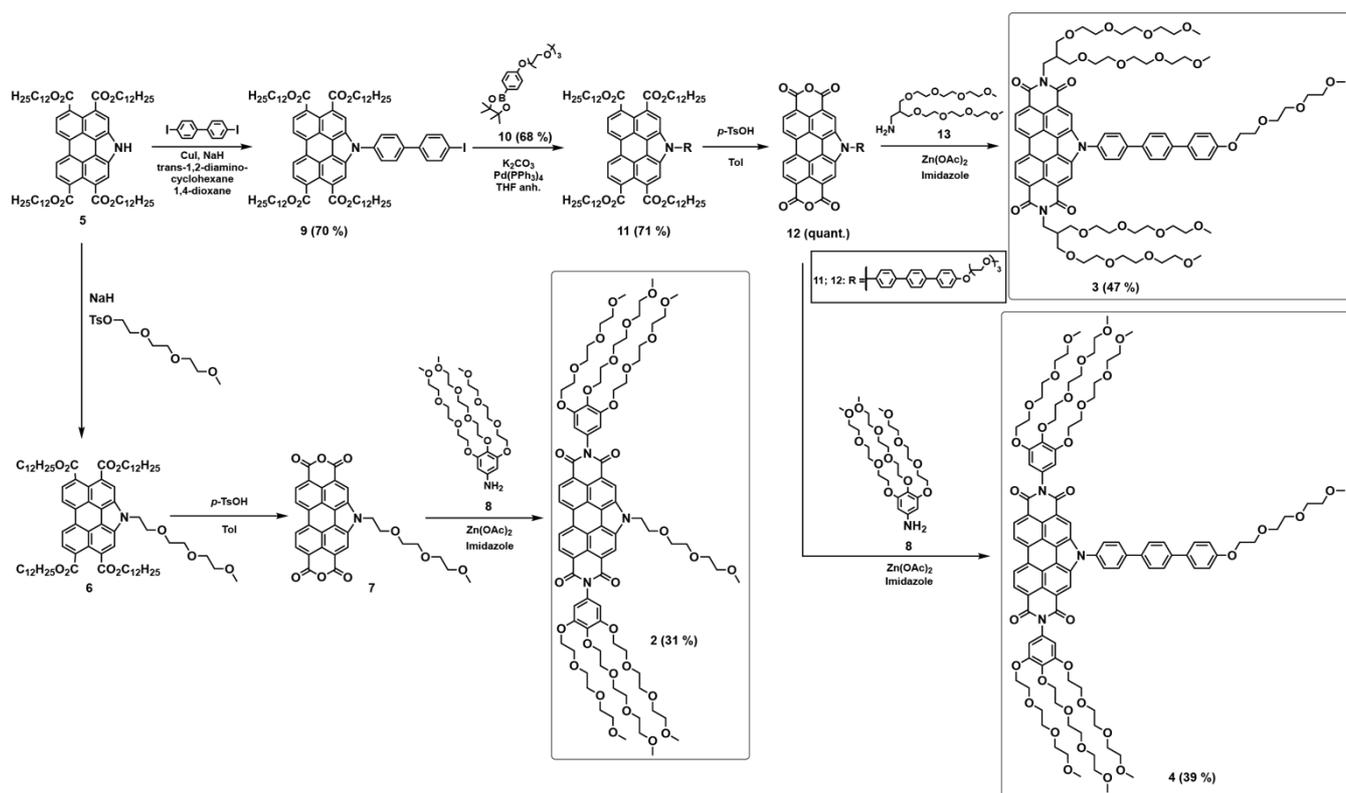
Scheme S1. Synthesis of amphiphilic *N*-annulated PBIs **2-4**.
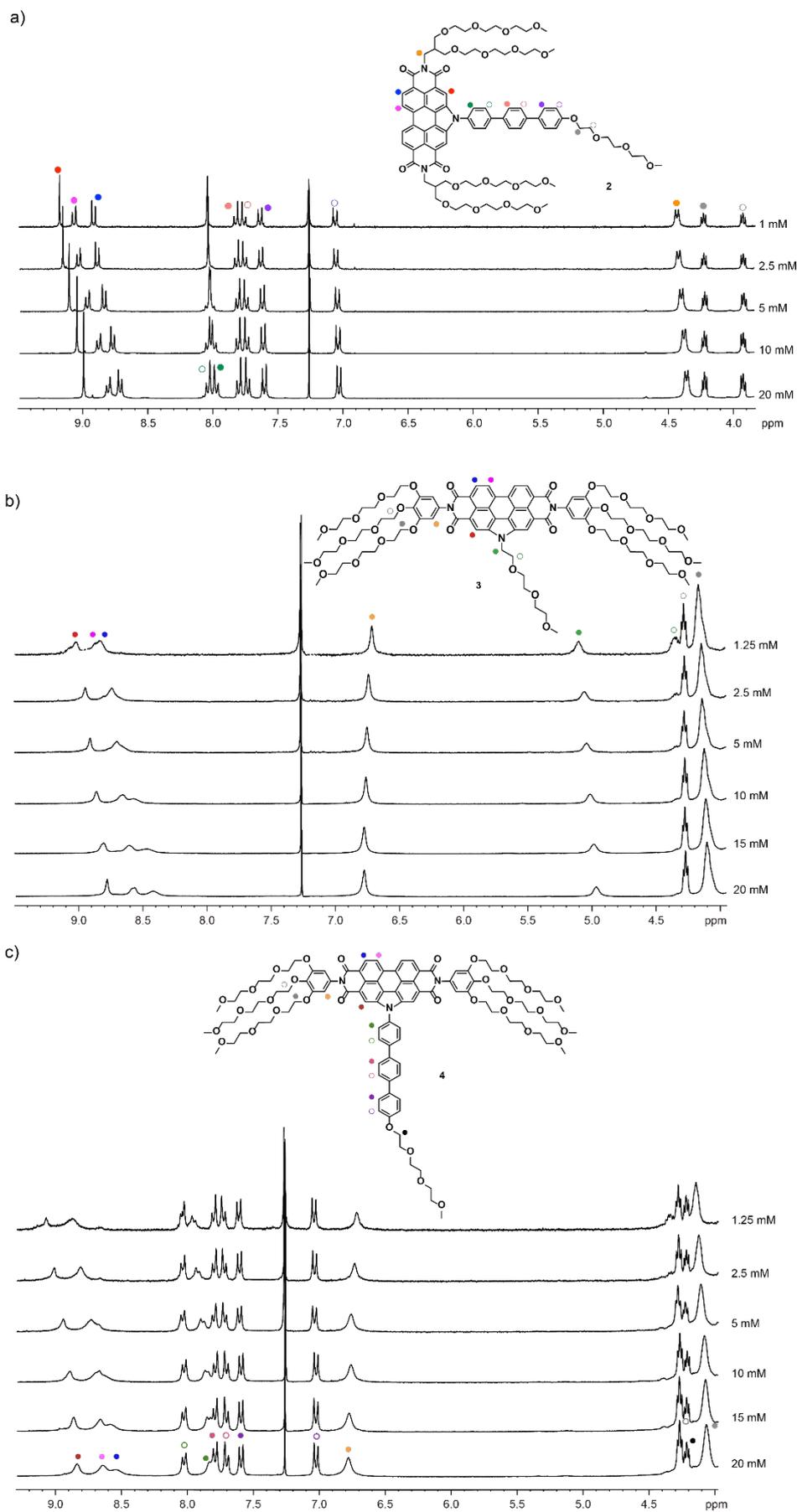
Figure S1. Partial ^{1}H NMR spectra of amphiphiles **2**–**4** (300 MHz; 298 K; CDCl$_3$).

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Table S1. Thermodynamic parameters associated to the self-assembly of **1** in water ($X_{dioxane}$ = 0).

Temperature (ºC)	ΔG (kJ mol^{-1})	m (kJ mol^{-1})	σ (-)
20	−37.7 ± 8	16.3	1
40	−38.5 ± 1	16.8	1
60	−40.3 ± 2	19.5	1
80	−41.7 ± 3	20.7	1

a)
1
y = 2142.2x + 8.1108
R² = 0.9855

b)
2
y = 2527x + 9.5073
R² = 0.93

c)
3
y = -2453.3x + 22.154
R² = 0.9273

d)
4
y = -4377.8x + 29.361
R² = 0.9548
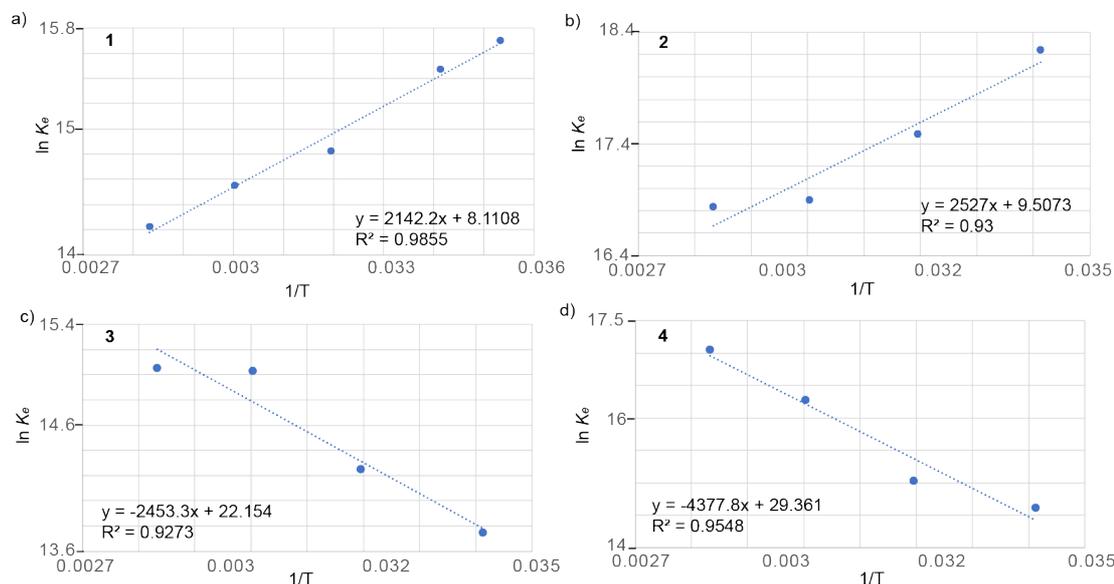
Figure S2. Van't Hoff plots for compounds **1**–**4** in water and at c_T = 10 μM. The inset in each panel collects the straight-line equation used to derive the values of ΔH and ΔS.
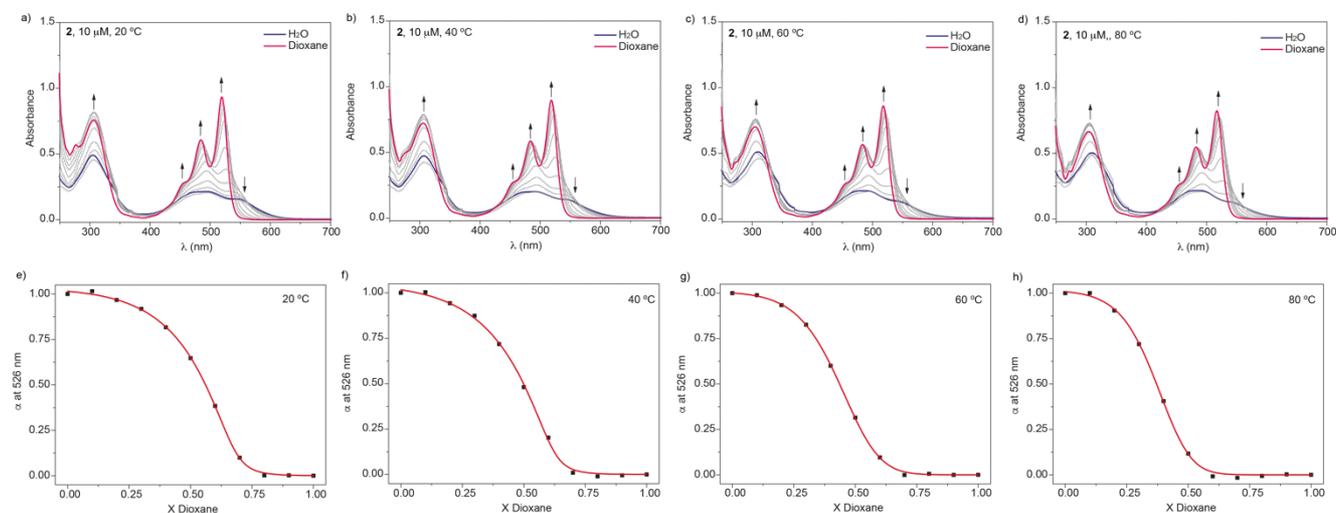
Figure S3. (a-d) UV-Vis spectra of amphiphile **2** in water/dioxane mixtures at different temperatures and a c_T = 10 μM. Arrows in panels (a-d) indicate the changes in the UV-Vis spectra upon adding increasing amounts of dioxane. (e-h) Denaturation curves of **2** in water/dioxane mixtures at different temperatures. Red lines in panels (e-h) depict the fitting to the SD model.

Table S2. Thermodynamic parameters associated to the self-assembly of **2** in water ($X_{dioxane}$ = 0).

Temperature (ºC)	ΔG (kJ mol^{-1})	m (kJ mol^{-1})	σ (-)
20	−37.6 ± 6	14.7	1.5×10^{-2}
40	−38.6 ± 1	14.5	1.0×10^{-2}
60	−47.9 ± 2	32.5	1
80	−50.6 ± 5	40.1	1
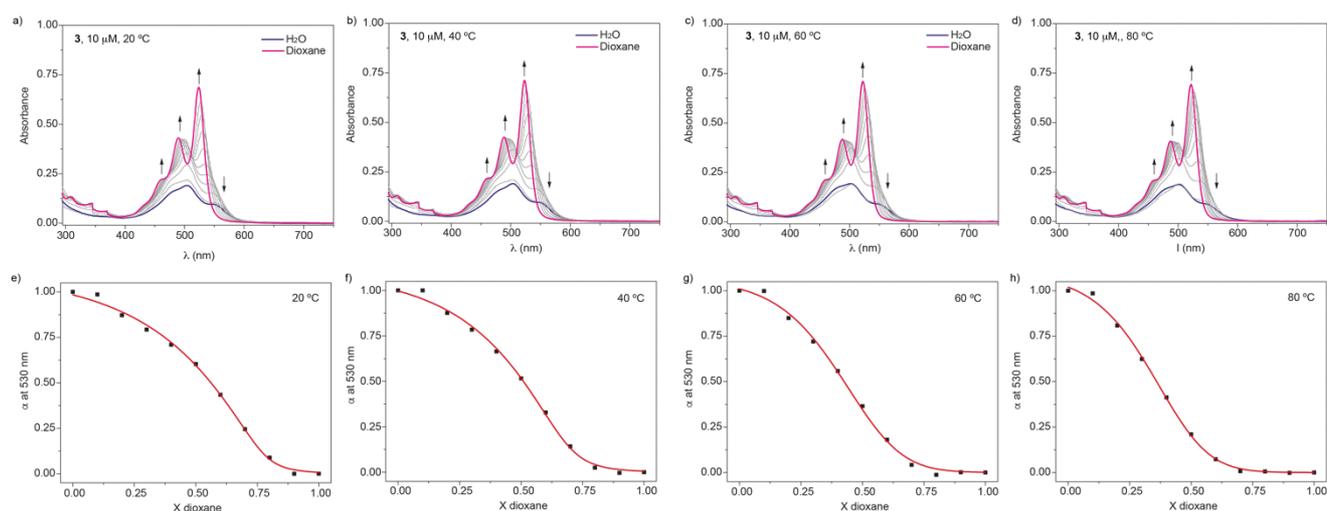
Figure S4. (a-d) UV-Vis spectra of amphiphile **3** in water/dioxane mixtures at different temperatures and a c_T = 10 μM. Arrows in panels (a-d) indicate the changes in the UV-Vis spectra upon adding increasing amounts of dioxane. (e-h) Denaturation curves of **3** in water/dioxane mixtures at different temperatures. Red lines in panels (e-h) depict the fitting to the SD model.

Table S3. Thermodynamic parameters associated to the self-assembly of **3** in water ($X_{dioxane}$ = 0).

Temperature (ºC)	ΔG (kJ mol^{-1})	m (kJ mol^{-1})	σ (-)
20	−33.5 ± 1	7.3	4.9×10^{-3}
40	−37.1 ± 2	9.5	1.6×10^{-2}
60	−41.6 ± 3	21.5	1
80	−44.1 ± 8	24.5	1

Figure S5. (a-d) UV-Vis spectra of amphiphile **4** in water/dioxane mixtures at different temperatures and a c_T = 10 μM. Arrows in panels (a-d) indicate the changes in the UV-Vis spectra upon adding increasing amounts of dioxane. (e-h) Denaturation curves of **4** in water/dioxane mixtures at different temperatures. Red lines in panels (e-h) depict the fitting to the SD model.

Table S4. Thermodynamic parameters associated to the self-assembly of **4** in water ($X_{dioxane}$ = 0).

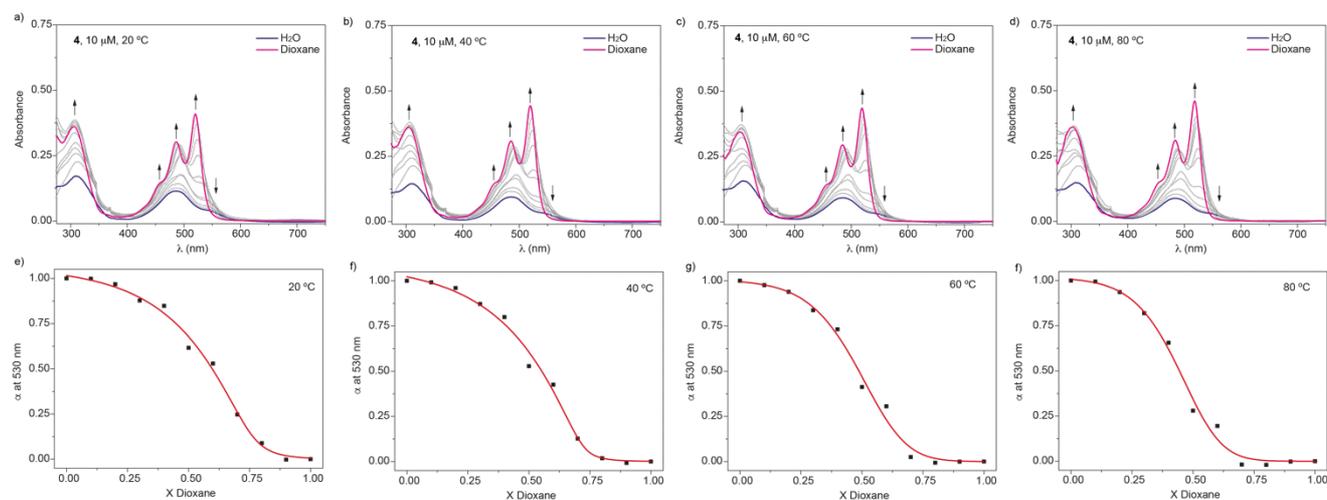| Temperature (ºC)	ΔG (kJ mol^{-1})	m (kJ mol^{-1})	σ (-)
20	−33.6 ± 1	10.4	1.3×10^{-2}
40	−39.1 ± 1	10.3	3.2×10^{-3}
60	−45.8 ± 14	27.2	1
80	−50.0 ± 16	32.2	1
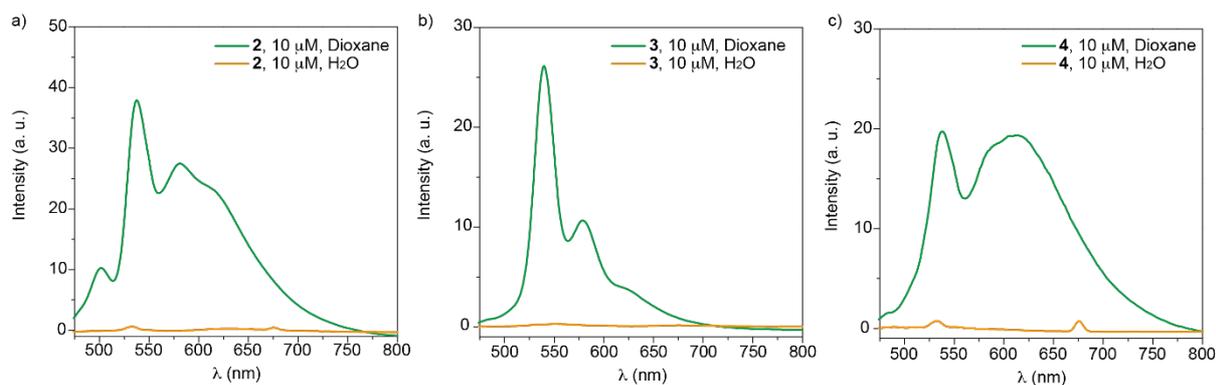
Figure S6. (a-c) Emission spectra of **2-3** in water (orange line) and dioxane (green line) (λ_{exc} = 493 nm; c_T = 10 µM).
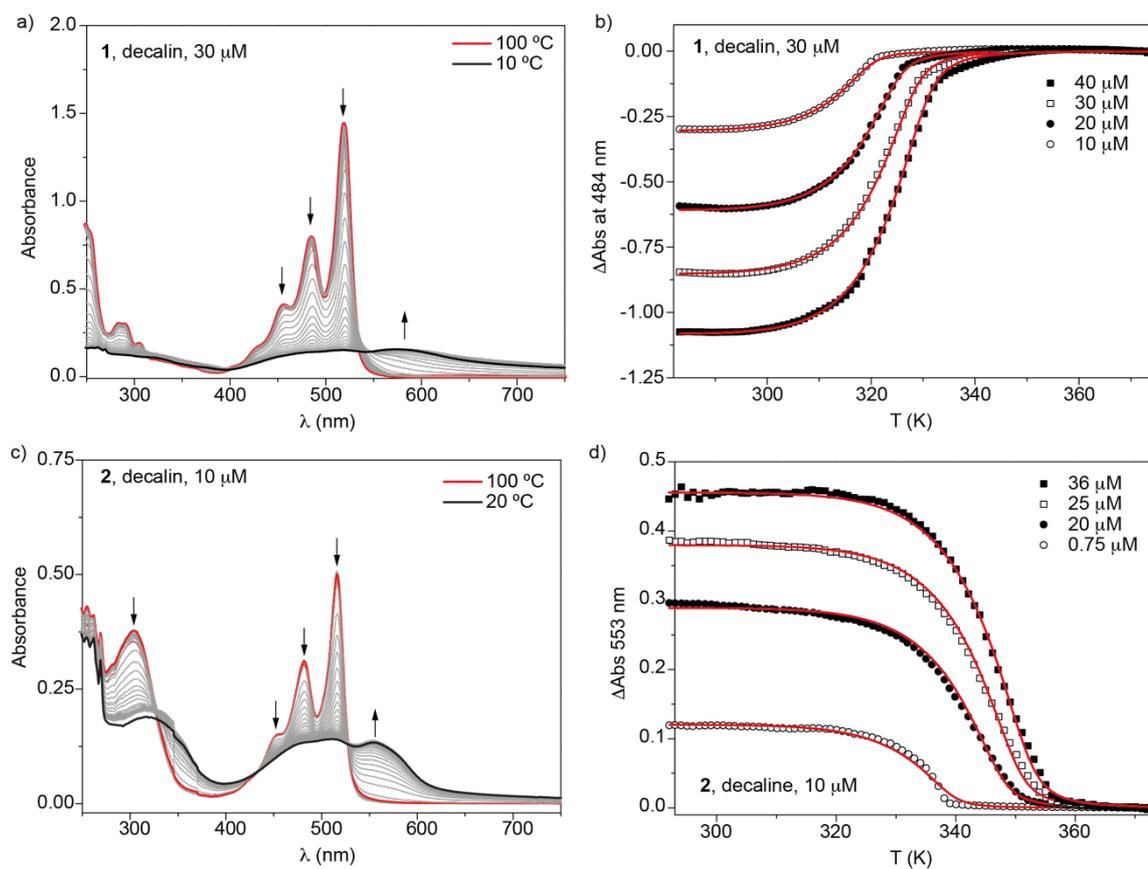
Figure S7. UV-Vis spectra of **1** (a) and **2** (c) at different temperatures in decalin as solvent. Arrows indicate the changes in the absorption bands upon decreasing the temperature. Cooling curves (1 K min⁻¹) of **1** (b) and **2** (d) in decalin at different concentrations. Red lines in (b) and (d) depict the fitting to the one-component EQ model.

Table S5. Thermodynamic parameters associated to the self-assembly of **1** and **2** in decalin at 293 K.

	ΔH_e (kJ·mol⁻¹)	ΔH_n (kJ mol⁻¹)	ΔS (J K⁻¹ mol⁻¹)	ΔG (kJ mol⁻¹)	K_e (M⁻¹)	K_n (M⁻¹)	σ (-)
1	−113.9 ± 1	−9.9 ± 1	−262 ± 2	−37.1 ± 1	1.9×10^6	3.6×10^4	1.8×10^{-2}
2	−122.5 ± 2	−12.0 ± 1	−264 ± 3	−45.1 ± 2	4.9×10^7	3.7×10^5	7.6×10^{-3}

Additional results for monomers
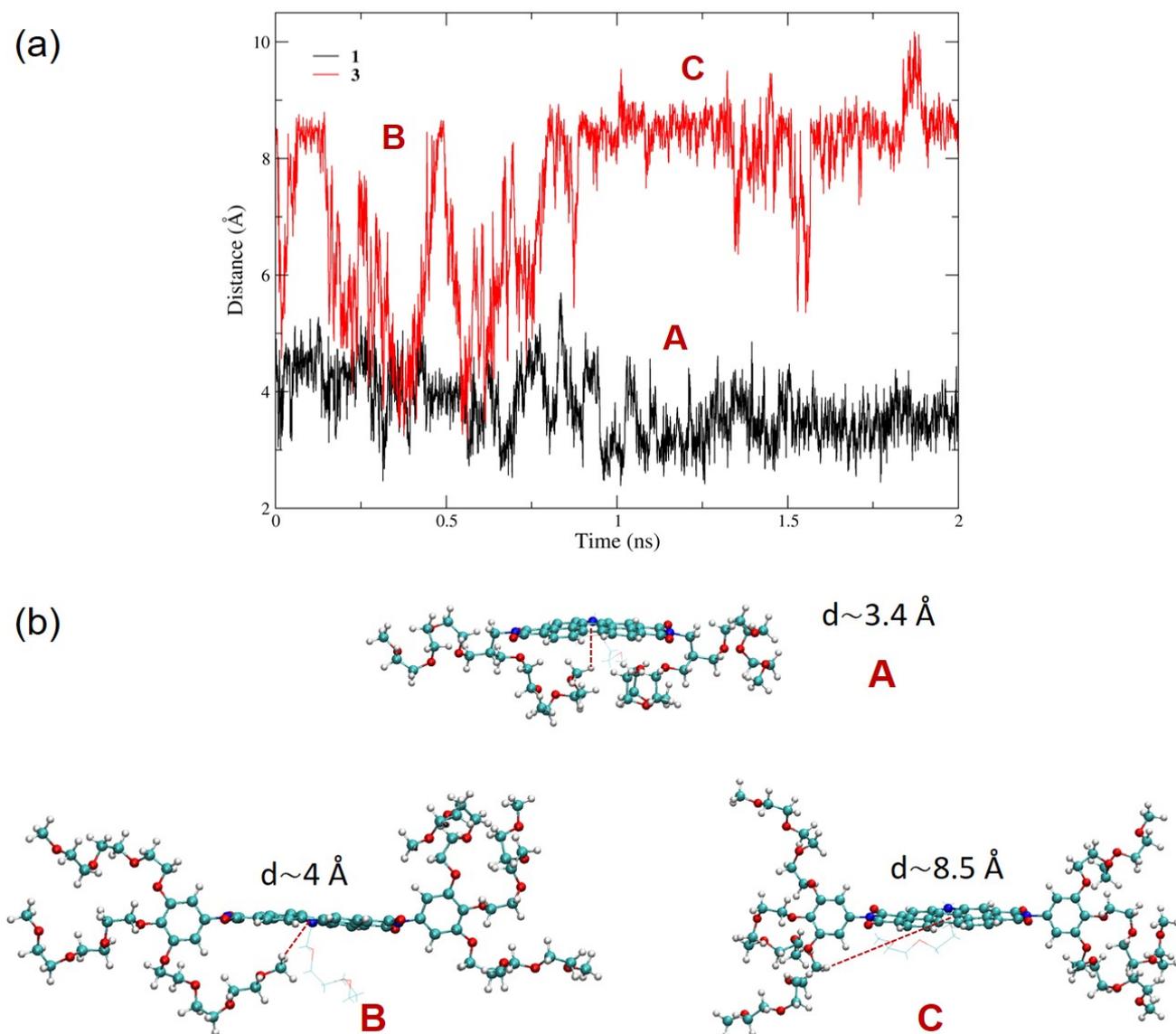
Figure S8. a) Minimum distance between the centroid of the central benzene ring of the *N*-PBI core and any atom of the terminal OEG chains on the imide positions along the MD trajectories of monomers **1** (black) and **3** (red) in water. b) Representative structures of **1** (A) and **3** (B and C) along the MD trajectories.

Discussion on the monomer energetics

As discussed on the main text, the chain-core, core-solvent and chain-solvent interactions ($\bar{E}_{pot}^{c-ch}$, $\bar{E}_{pot}^{c-solv}$ and $\bar{E}_{pot}^{ch-solv}$) for monomers of **1** and **3** have been evaluated and their values are shown in Table S6. Table S6 reveals that the chain-core interactions are stronger for **1** (−53 kJ/mol) compared to **3** (−12 kJ/mol), which is in line with the more rigidity of the side chains in **3** where the OEG segments cannot effectively cover and protect the hydrophobic *N*-PBI core with chain-core distances larger than those found for **1** along the MD trajectories (Figure S8). The hydrophobic *N*-PBI skeleton of **3** is therefore more exposed to the solvent with an average of 24 water molecules in close contact with the *N*-PBI core (Table S6). This is the reason why the $\bar{E}_{pot}^{c-solv}$ term for **3** (−239 kJ/mol) is slightly higher than that computed for **1** (−195 kJ/mol). Finally, the most important interaction is the chain-solvent contribution with a significant difference between **1** and **3** (−831 and −1192 kJ/mol, respectively) in concordance with the larger number of stabilizing water-OEG chain contacts for **3** compared to **1** (i.e., larger number of H-bonds between OEG chains and water, see Table S8). The self-assembly of **3** would therefore require the rupture of a larger number of stabilizing water-OEG chain and water-core interactions and it can explain the origin of the enthalpically unfavourable self-assembly process for **3** compared to **1**.

Table S6. Average chain-core, core-solvent and chain-solvent interactions ($\bar{E}_{pot}^{c-ch}$, $\bar{E}_{pot}^{c-solv}$ and $\bar{E}_{pot}^{ch-solv}$) in kJ/mol computed for *N*-PBI **1** and **3** from the MD run. Last column includes the average number of water molecules within a distance of 4 Å with respect to the *N*-PBI cores during the MD trajectory.

| Compound	$\bar{E}_{pot}^{c-ch}$	$\bar{E}_{pot}^{c-solv}$	$\bar{E}_{pot}^{ch-solv}$	Number of H_2O
N-PBI **1**	−53	−195	−831	19
N-PBI **3**	−12	−239	−1192	24

MD of dimers and tetramers

Table S7. Average length and estimated error of the cubic box edge used along the production stage of the MD simulation for energy calculations of the tetratmer, dimer, and monomer. All quantites are expressed in nm.

Compound	Tetramer	Dimer	Monomer
N-PBI **1**	7.4975 ± 0.0003	5.95034 ± 0.00012	4.72358 ± 0.00016
N-PBI **3**	8.69045 ± 0.00011	6.89793 ± 0.00018	5.47445 ± 0.00018

Table S8. Average kinetic (T), and pV energy terms (in kJ/mol) and their estimated errors calculated for the whole system from the trajectory of *N*-PBIs **1** and **3** dimers and monomers. The energy difference (ΔE) with respect to the equivalent number of monomers is also shown.

	N-PBI **1**		
Energy	Dimer	Monomer	ΔE
T	61691 ± 4	30847 ± 3	-2.7
pV	12.6876 ± 0.0008	6.34697 ± 0.0007	-0.0063
	N-PBI **3**		
Energy	Dimer	Monomer	ΔE
T	95866 ± 7	47923 ± 2	19.5
pV	19.7655 ± 0.0016	9.8804 ± 0.0010	0.0047
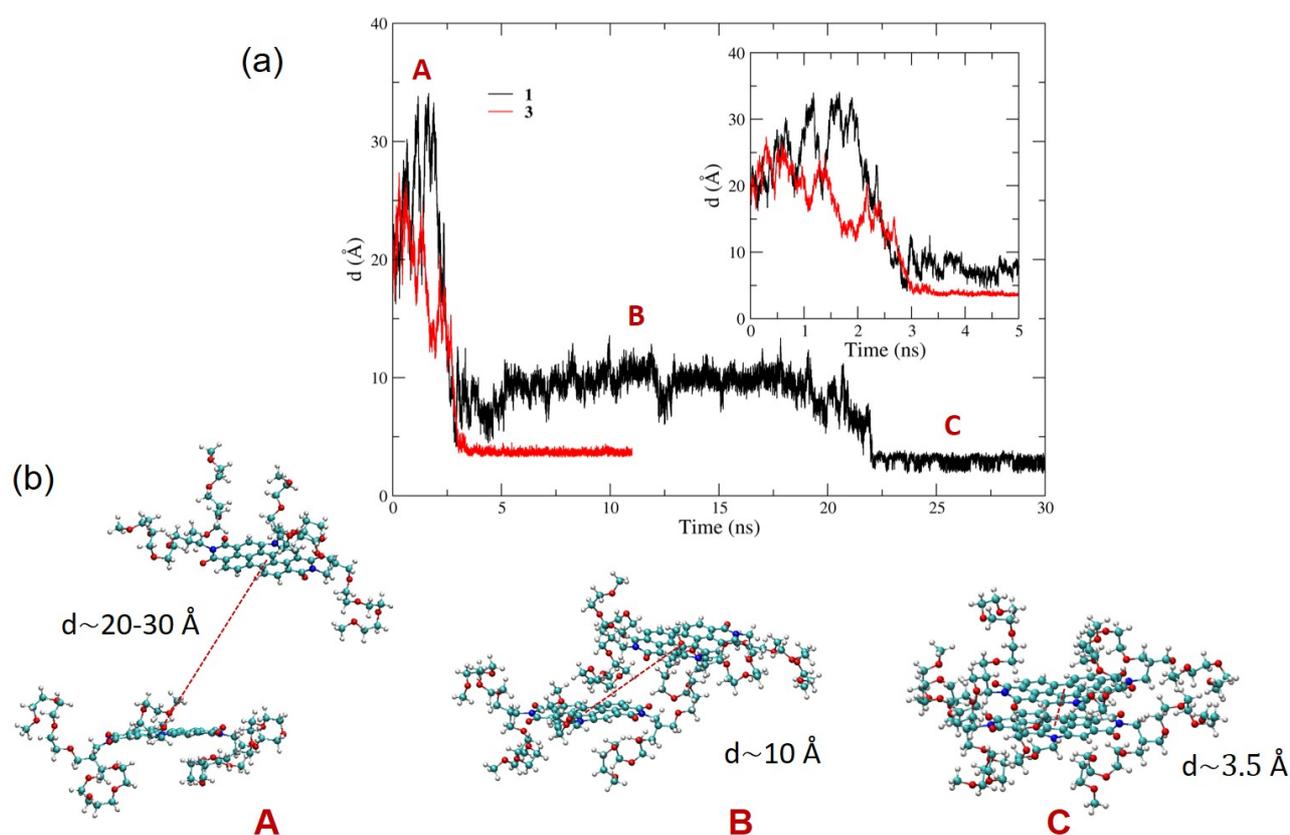
Figure S9. a) Distance between the centroids of the central benzene rings of the *N*-PBI cores (d) along the MD trajectories for *N*-PBI dimers of **1** (black) and **3** (red) in water. The two monomers were initially separated by 20 Å. The inset highlights the first 5 ns of the simulations. b) Structures A, B, and C correspond to representative dispositions of the two monomers in the *N*-PBI dimer of **1** along the MD trajectory.

Table S9. Average number of H-bonds per monomeric unit between the side OEG chains and the water molecules calculated along the MD trajectory for supramolecular aggregates (dimer and tetramers) of *N*-PBIs **1** and **3** compared to the monomer.

	N-PBI **1**		*N*-PBI **3**	
Species	H-bonds	Lost H-bonds	H-bonds	Lost H-bonds
Monomer	20.0	–	27.9	–
Dimer	18.5	1.5	25.2	2.7
Tetramer	16.9	3.1	23.2	4.8
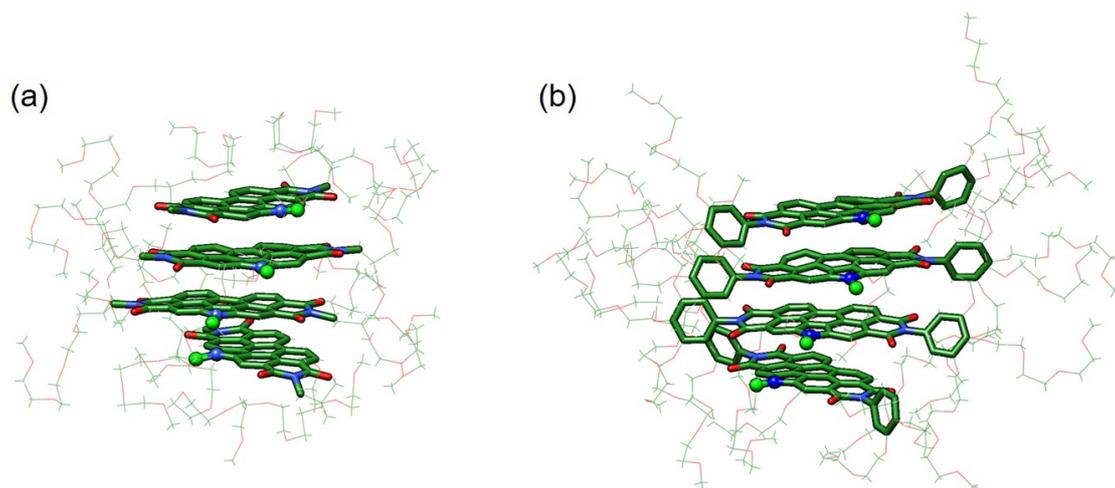
**Figure S10.** Detail of the helical-like supramolecular structure obtained for tetramers of *N*-PBIs **1** (a) and **3** (b) along the MD simulation. Some atoms are shown as spheres to highlight the helicity of the aggregate.

Table S10. Average values estimated for the electrostatic (Coulomb) and Lennard-Jones (LJ) energy terms along the MD trajectory of monomers and dimers of *N*-PBI **1** and **3**. The specific Coulomb interaction between the O atoms in the OEG chains and water is also shown for the same radius cutoff used during the dynamics and for a cutoff of 3.5 Å to isolate the contribution of hydrogen bonds. Finally, the average energy for a single hydrogen bond ($E_{\text{H-bond}}$), obtained from the Coulomb (3.5 Å, OEG O) energy and the average number of hydrogen bonds given in Table S9, is also reported. All values are in kJ/mol.

N-PBI **1**	Coulomb	LJ	Coulomb (only $H_2O\cdots O$)	Coulomb (3.5 Å, OEG O)	$E_{\text{H-bond}}$
Monomer	−506.5	−187.1	−834.7	−55.1	−2.8
Dimer	−967.0	−325.9	−1586.3	−106.8	−2.9
N-PBI **3**	Coulomb	LJ	Coulomb (only $H_2O\cdots O$)	Coulomb (3.5 Å, OEG O)	$E_{\text{H-bond}}$
Monomer	−757.8	−299.7	−1235.3	−85.1	−3.1
Dimer	−1466.0	−501.8	−2382.3	−166.0	−3.3

Calculations for related PBI and NBI systems

To extract more general structure-property relationships than those obtained for *N*-PBI **1** and **3**, we have also performed MD simulations for related PBI and NBI systems (PBI 1, NBI 3 and NBI 2 shown in Figure S11 and reported in Refs. 17a, 17b and 17c in the main text, respectively). Similar to *N*-PBIs **1** and **3**, our simulations are able to reproduce the experimental exothermic/endothermic character of the aggregation enthalpy for the related PBI and NBI systems; an endothermic aggregation enthalpy $\Delta \bar{H}_{aggr}$ of 62 and 14 kJ/mol is predicted for those systems in which the extended OEG chains are attached to the core through a benzene bridge (PBI 1 and NBI 3, respectively). These findings are in line with the enthalpically disfavoured self-assembly process of *N*-PBI **3** reported in this study. Unlike PBI 1 and NBI 3, NBI 2, in which the trialkoxyphenyl moieties are connected to the NBI core via a methylene spacer, exhibits a enthalpically favoured self-assembly process with a $\Delta \bar{H}_{aggr}$ value of −67 kJ/mol. The origin at the molecular level of these different exothermic/endothermic enthalpy behaviour for the self-assembly of PBI 1, NBI 3 and NBI 2 is similar to that found for *N*-PBIs **1** and **3**; that is, the flexibility of the OEG side chains to reach the hydrophobic core and protect it from the solvent. Figure S12 displays the distance computed between the centroids of the π-core and the terminal segment of an OEG side chain (i.e., last –OCH$_2$CH$_2$OCH$_3$) along the MD trajectory for all OEG side chains of PBI 1, NBI 3 and NBI 2. The comparison between PBI 1 (enthalpically disfavoured self-assembly) and NBI 2 (enthalpically favoured self-assembly) reveals that for PBI 1 only two side chains can effectively reach the central PBI core with close distances whereas all the side chains for NBI 2 can access to the NBI core with close and intermediate distances. This comes from the larger flexibility of the side chains in NBI 2 compared to PBI 1 due to the methylene spacer between the terminal trialkoxyphenyl units and the NBI core.
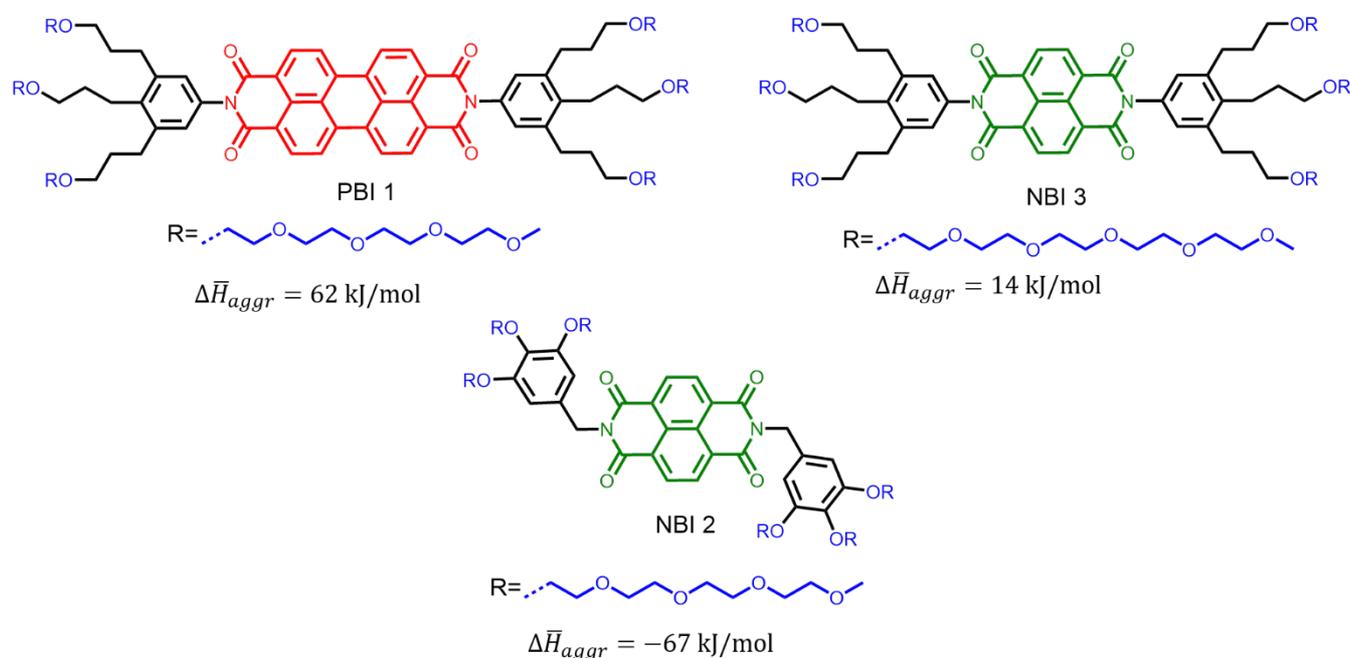
Figure S11. Chemical structures and aggregation enthalpies computed for related PBI and NBI systems (in particular, PBI 1, NBI 3 and NBI 2 from Refs 17a, 17b and 17c of the main text, respectively).
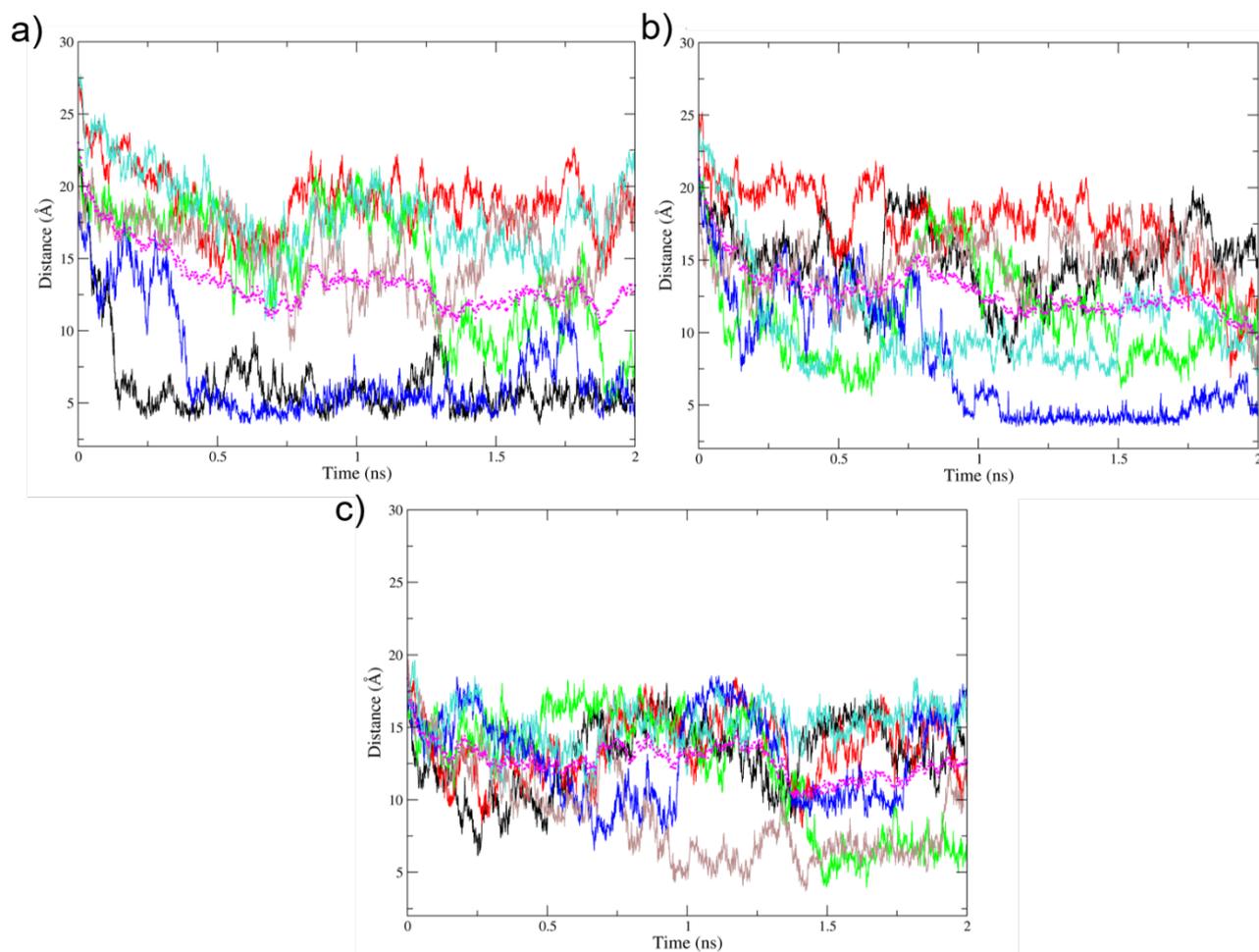
Figure S12. Distance between the centroids of the central π-core (PBI and NBI) and the terminal segment of an OEG side chain (i.e., last $–OCH_2CH_2OCH_3$) along the MD trajectory for all OEG side chains (solid colours) of PBI 1 (a), NBI 3 (b) and NBI 2 (c) in water. The average value of this distance for all OEG side chains is represented in magenta.

5.- References

S1   M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, *SoftwareX* **2015**, *1–2*, 19.

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S4   W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, *J. Chem.* Phys. **1983***, 79*, 926.

S5   M. A. Martínez, E. E. Greciano, J. Cuéllar, J. M. Valpuesta and L. Sánchez, *Nanomaterials* **2021**, *11*, 1457.

S6   R. K. Gupta, D. D. S. Rao, S. K. Prasad and A. S. Achalkumar, *Chem. Eur. J.* **2018**, *24*, 3566.

S7   T. N. B. Truong, S. Savagatrup, I. Jeon and T. M. Swager, *Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1133.

S8   S. Yamaguchi, A. Fukazawa and E. Yamaguchi, C. Wang WO2015111647 A1, **2015**.

S9   J. Buendía, F. García, B. Yélamos and L. Sánchez, *Chem. Commun.* **2016**, *52*, 8830.