SUPPORTING INFORMATION

Luminescent assemblies of pyrene containing bent-core mesogens: liquid crystals, π-gels and nanotubes

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1. Materials and Methods

Chemical reagents used in this study were purchased from Aldrich and were used without further purification. ^{1}H NMR spectra were recorded on spectrometers operating at 300.13 MHz (ARX-300 and AV-300) and 400.17 MHz (AV-400), whereas ^{13}C NMR spectra were recorded at 75.47 MHz and 100.62 MHz, respectively, on the same spectrometers. The chemical structure of the synthesized compounds was determined by elemental analysis performed on a Perkin-Elmer 240C CHNS elemental analyzer. FT-IR spectra were performed in a ThermoNicolet Avatar 360 using KBr pellets. Mass spectral data (MALDI+) were obtained using a Microflex (MALDI-ToF). The preliminary mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. Nikon and Olympus BH-2 polarizing microscopes equipped with a Linkam THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements with DSC TA Instrument Q-20 system. Molecular dimensions were estimated by molecular modeling (ChemSketch3D). The X-ray investigations on non-oriented samples were carried out in Lindemann capillary tubes (diameter 0.9 mm) using a Pinhole (Anton-Paar) film camera. Synthetic procedures and characterization data of the novel compounds are reported in the Supporting Information.

- **General procedure for the preparation of gel materials**: into shell vials with polyethylene plug (40 mm length × 8.2 mm diameter, 1.00 mL capacity), variable amounts (1-7 mg) of the corresponding gelator and increasing amounts of solvent were placed. Then, these vials were gently heated with a heat gun until the solid material was completely dissolved, (additional use of the ultrasound was necessary at high concentrations). The resulting isotropic solution was then cooled down in air to room temperature. No control over temperature rate during the heating-cooling process was applied. By the inversion vial method, the materials were classified as "gel" if it did not exhibit gravitational flow upon turning the vial upside-down at room temperature.

The maximum concentration of these studies was 10% w/w and the continuous addition of solvent to explore lower concentrations allowed the determination of the critical gelation concentration (CGC, minimum concentration in which the compound is able to form a gel) by performing the mentioned typical protocol for gel formation.

In order to determine the thermal gel-to-sol transition temperature (T_{gs}) the vials were placed into a mold of an alumina block and heated up at approximately 1 °C min^{-1} using an electric heating plate equipped with a temperature control. T_{gs} was defined as the temperature at which the gel started to breakdown. Each measurement was made at least by duplicate and the average value was reported.

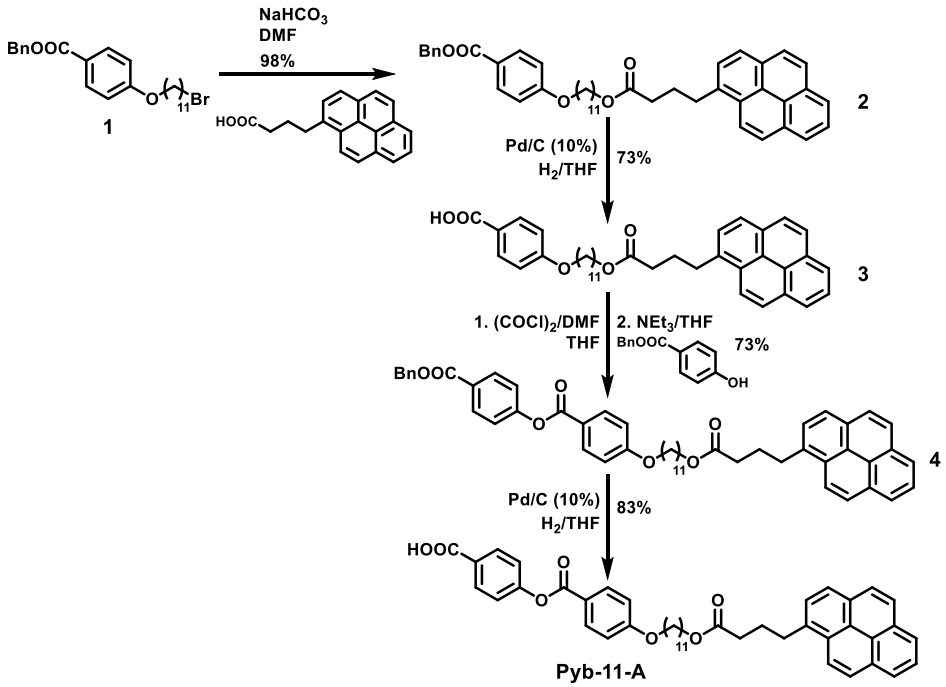
- The **morphological characterization** of gels and aggregates was carried out by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM): (i) FESEM images were obtained with a QUANTA FEG 250 field emission scanning electron microscope (LMA, Universidad de Zaragoza). The samples were prepared by depositing drops of the sol state on a glass slide and, when the gel was formed on the surface the solvent, it was dried first with a piece of paper and later under vacuum overnight at room temperature. Finally, the samples were sputtered with gold. (ii) TEM images were recorded using a TECNAI G2 20 (FEI COMPANY) (LMA, Universidad de Zaragoza) operating at 200 kV (accelerating voltage). The samples were prepared by depositing one drop of a dispersion (lower concentrations than CGC) on a carbon film copper grid. The solvent was dried, first, with a piece of paper and, then, one drop of an aqueous solution of 1% uranyl acetate was added. After 30 seconds, it was dried again with a piece of paper without damaging the surface and finally, with a vacuum pump for 24 hours.

2. Photophysical Measurements.

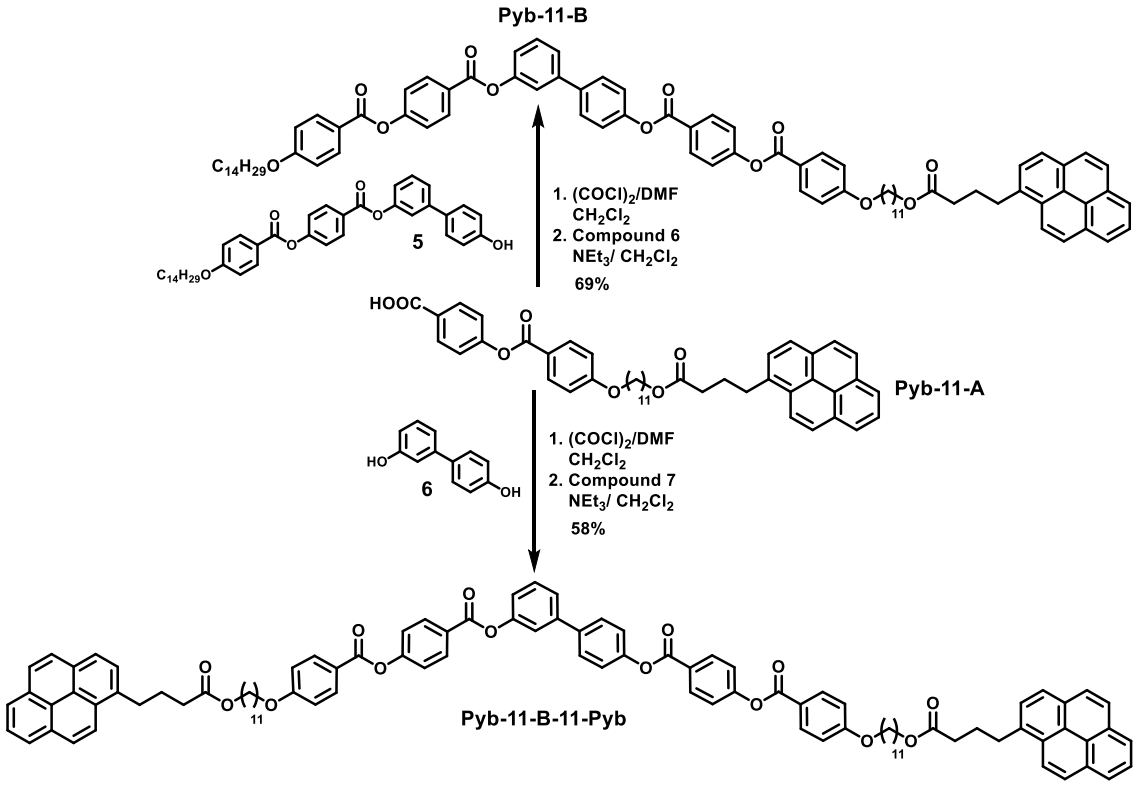
Absorption and fluorescence measurements in solution were carried out using ATI-Unicam UV4-200 and PERKIN-ELMER LS50B instrument, respectively. Fluorescence emission in solid state was measured in

Horiba FluoroLog 3 Spectrophotometer, equipped with double monochromators at the emission and excitation sides. Fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique. The excitation source was a 405 nm picosecond pulsed diode laser (LDH-D-C-405, PicoQuant) driven by a PDL828 driver (PicoQuant) with FWHM < 70ps. The emission was dispersed in wavelength using an Acton SP2500 spectrometer (as mentioned above) and detected by a blue sensitive, low dark current photomultiplier (PMA 06, PicoQuant), which covers a spectral range from 220 to 650 nm (transit time spread < 50 ps, FWHM). A HydraHarp-400 TCSPC event timer with 1 ps time resolution was used to measure the fluorescence decays. The PL quantum efficiencies of solutions and in condensed phases were measured in an absolute quantum yield measurement system (Hamamatsu C9920) with a detection range from 300 nm to 950 nm and bandwidth from 2 nm to 5 nm (FWHM).

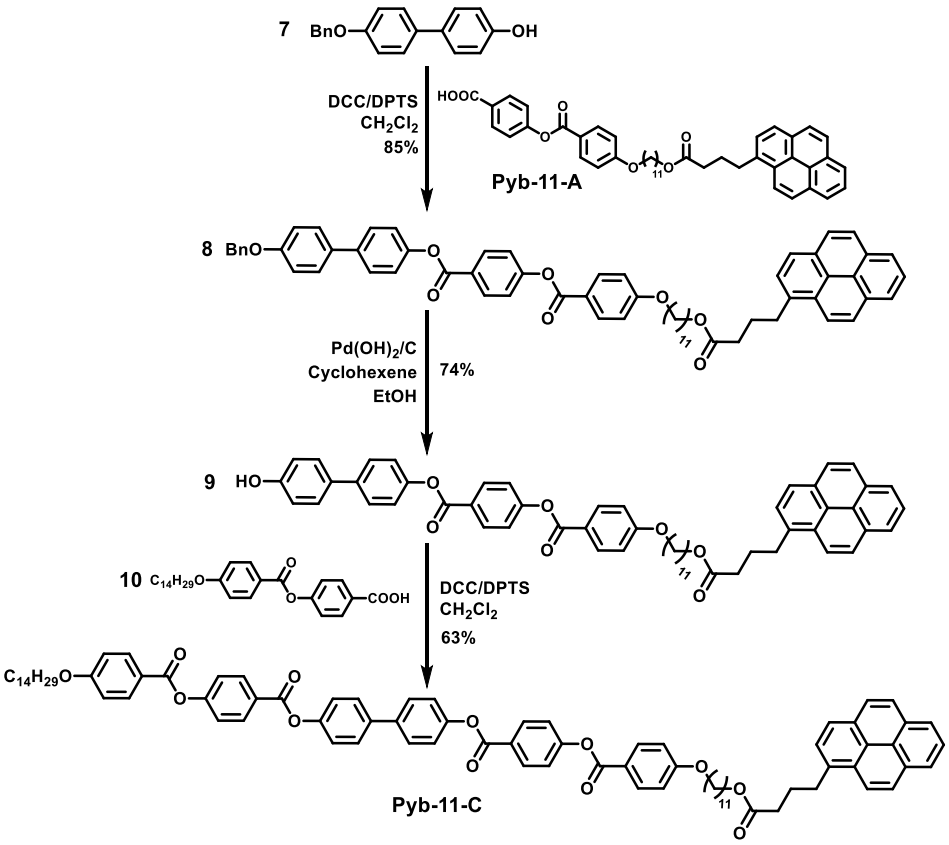
3. Synthetic schemes and synthesis of compounds



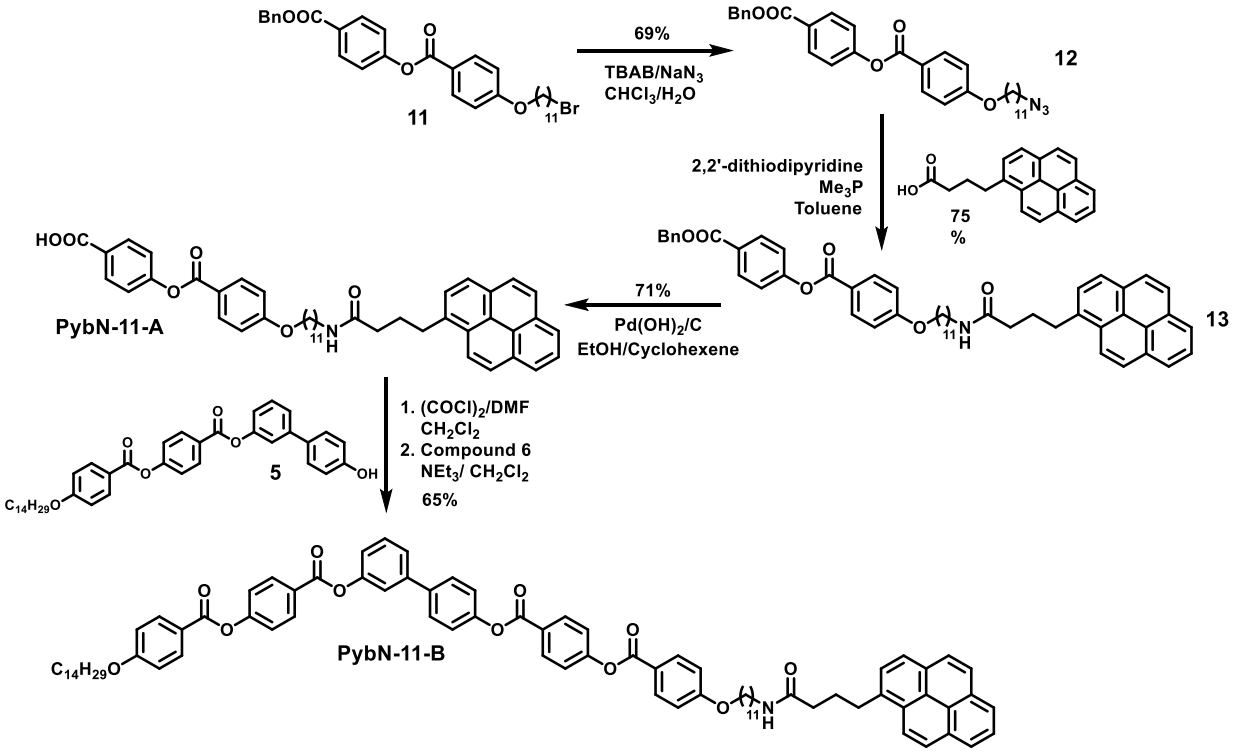
Scheme S1. Synthetic routes for the preparation of the 1-pyrenebutyrate (Pyb) precursors with spacer.



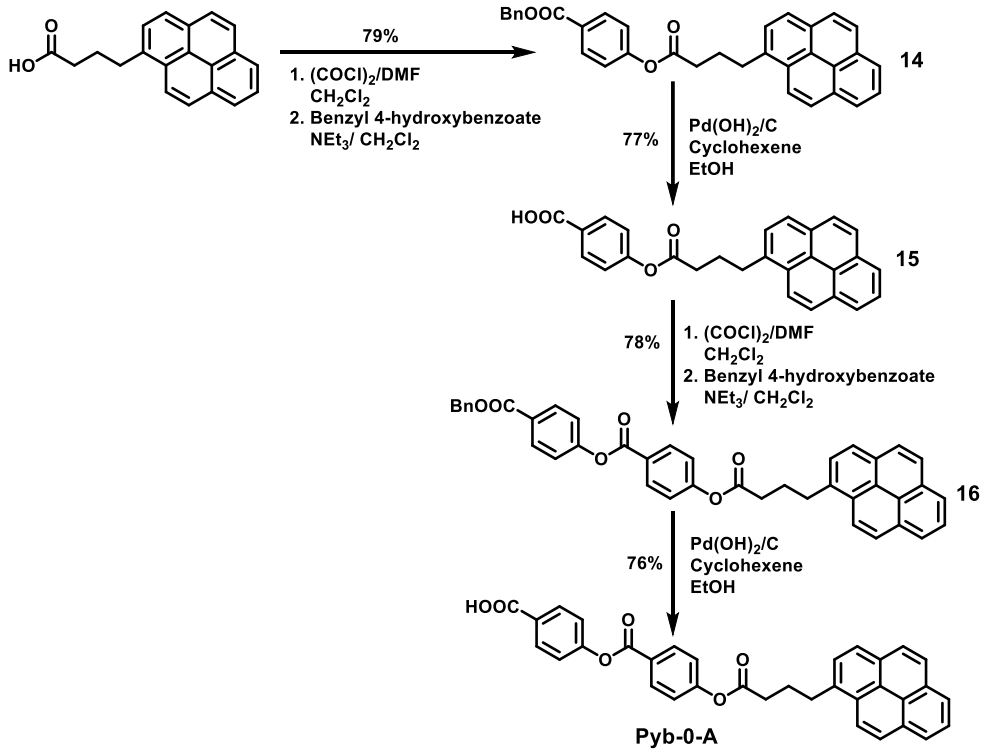
Scheme S2. Synthetic routes for the preparation of **Pyb-11-B** and **Pyb-11-B-11-Pyb**.



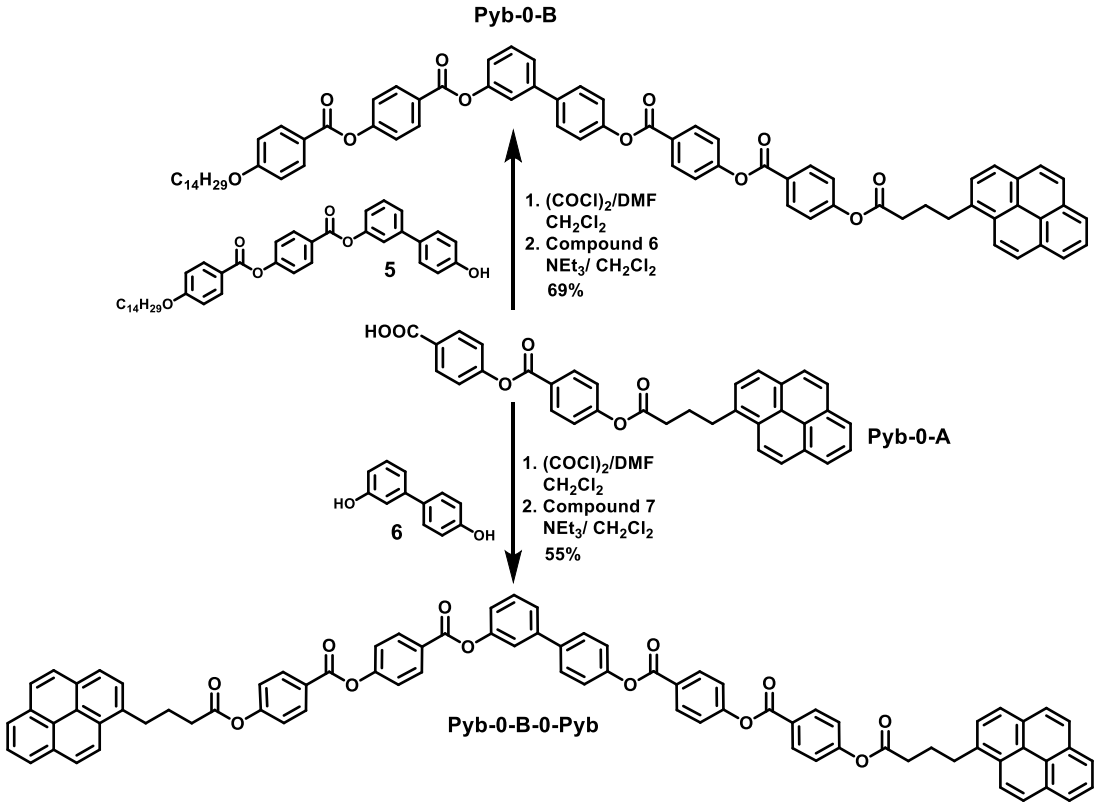
Scheme S3. Synthesis of **Pyb-11-C**.



Scheme S4. Synthesis of the bent-core compound **PybN-11-B**.



Scheme S5. Synthetic routes for the preparation of the1-pyrenebutyrate precursors without spacer.



Scheme S6. Synthesis of the bent-core compounds without spacer **Pyb-0-B** and **Pyb-0-B-0-Pyb**.

Compounds **1**, **5, 6, 7**, **10** and **11** were prepared according to procedures already reported in the literature[1] and the characterization data agree with those previously reported, so the experimental details are not included.

Compound 2: Pyrenebutyric acid (1.00 g, 3.46 mmol) was dissolved in DMF (30 ml), and then sodium hydrogen carbonate (0.86 g, 10.24 mmol) was added. The mixture was heated at 70 °C for 1 hour and then, compound **1** (1.30 g, 2.82 mmol) was added. After 7 hours, the mixture was poured onto 200 mL of water and extracted twice with hexane/ethyl acetate 1:1 (50/50 mL), washed with water and dried with magnesium sulfate. The solvent was evaporated and the product purified by column chromatography using hexane/ethyl acetate (8:2) as eluent (98% yield); **M.p. (°C):** 73-75; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.31 (d, *J* = 9.3 Hz, 1H), 8.22-8.08 (m, 4H), 8.08-7.93 (m, 5H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.51-7.30 (m, 5H), 6.95-6.83 (m, 2H), 5.34 (s, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.46-3.34 (m, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.27-2.13 (m, 2H), 1.82-1.70 (m, 2H), 1.69-1.56 (m, 2H), 1.50-1.19 (m, 14H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 166.4, 163.2, 136.5, 135.9, 131.85, 131.6, 131.1, 130.1, 128.9, 128.7, 128.3, 128.2, 127.6, 127.5, 127.5, 126.9, 126.0, 125.1, 124.9, 124.9, 123.5, 122.4, 114.2, 68.3, 66.5, 64.8, 34.1, 33.0, 29.6, 29.6, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 2928, 2916, 2851, 1730, 1709, 1605, 1510, 1417, 1276, 1250, 1175.

Compound 3: Compound **2** (1.00 g, 1.50 mmol) was dissolved in anhydrous THF (45 mL) and Pd/C (10% wt) (0.13 g) was added under an argon atmosphere. Three vacuum-argon cycles were performed, and after three of vacuum-hydrogen cycles the reaction was stirred at room temperature under hydrogen atmosphere for 30 hours. The reaction was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the compound was recrystallized from ethanol (73% yield); **M.p. (°C):** Cr 103 I; I 82 N 76 SmC 61 Cr; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.31 (d, *J* = 9.3 Hz, 1H), 8.23-7.92 (m, 9H), 7.86 (d, *J* = 7.8 Hz, 1H), 6.99-6.86 (m, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.47-3.32 (m, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.29-2.13 (m, 2H), 1.84-1.70 (m, 2H), 1.69-1.55 (m, 2H), 1.51-1.18 (m, 14H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 171.5, 163.8, 135.9, 132.4, 131.6, 131.0, 130.1, 128.9, 127.6, 127.5, 127.5, 126.8, 126.0, 125.2, 125.1, 125.0, 124.9, 124.9, 123.5, 121.5, 121.5, 114.3, 68.4, 64.8, 34.1, 33.0, 29.6, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 3200-2500, 2919, 2853, 1733, 1673, 1607, 1512, 1435, 1305, 1253, 1171.

Compound 4: The carboxylic acid **3** (1.00 g, 1.73 mmol) was dissolved in dry DCM (80 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.30 mL, 0.44 g, 3.46 mmol) and two drops of DMF were added. After 12 hours the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (60 mL) and the solution was added over a solution of benzyl 4-hydroxybenzoate (0.33 g, 1.44 mmol) and trimethylamine (0.32 mL, 2.08 mmol) in dry DCM (40 mL) under an argon atmosphere. After stirring for 24 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane (8:2) as eluent (73% yield); **M.p. (°C):** 80-81; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.31 (d, *J* = 9.3 Hz, 1H), 8.21-8.08 (m, 8H), 8.04-7.92 (m, 3H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.50-7.33 (m, 5H), 7.32-7.26 (m, 2H), 6.99-6.91 (m, 2H), 5.38 (s, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.48-3.34 (m, 2H), 2.46 (t, *J* = 7.2Hz, 2H), 2.28-2.10 (m, 2H), 1.87-1.72 (m, 2H), 1.70-1.56 (m, 2H), 1.51-1.17 (m, 14H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 166.5, 163.9, 155.0, 136.1, 135.9, 132.5, 131.6, 131.5, 131.1, 130.1, 128.9, 128.7, 128.4, 128.3, 127.7, 127.6, 127.5, 126.9, 126.0, 125.1, 125.0, 124.9, 123.5, 122.0, 121.2, 114.5, 68.5, 66.9, 64.7, 34.1, 33.0, 29.6, 29.5,

1. (a) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C., Molecular design of nonchiral bent-core liquid crystals with antiferroelectric properties. *Journal of the American Chemical Society* **2000,** *122*, 1593-1601, (b) Gimeno, N.; Ros, M. B.; Serrano, J. L.; de la Fuente, M. R., Hydrogen-bonded banana liquid crystals. *Angewandte Chemie-International Edition* **2004,** *43*, 5235-5238 , (c) Gimeno, N.; Pintre, I.; Martinez-Abadia, M.; Serrano, J. L.; Ros, M. B., Bent-core liquid crystal phases promoted by azo-containing molecules: from monomers to side-chain polymers. *RSC Advances* **2014,** *4*, 19694-19702, (d) Wang, W.; Li, R.; Gokel, G. W., Membrane-Length Amphiphiles Exhibiting Structural Simplicity and Ion Channel Activity. *Chem. Eur. J.* **2009,** *15*, 10543-10553.

29.4, 29.2, 28.8, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 2919, 2851, 1737, 1726,1602, 1510, 1248, 1200, 1163.

Compound Pyb-11-A: Compound **4** (0.70 g, 0.87 mmol) was dissolved in anhydrous THF (30 mL) and Pd/C (10% wt) (0.10 g) was added under an argon atmosphere. Three vacuum-argon cycles were performed and, after three of vacuum-H_2 cycles, the reaction was stirred at room temperature under hydrogen atmosphere for 28 hours. The reaction was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the compound was recrystallized from ethanol and the obtained solid washed with DCM (83% yield); **M.p. (°C):** Cr 114 SmC 135 N 163 I; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.31 (d, *J* = 9.3 Hz, 1H), 8.22-8.08 (m, 8H), 8.06-7.94 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.37-7.30 (m, 2H), 7.00-6.92 (m, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.47-3.34 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.30-2.12 (m, 2H), 1.85-1.70 (m, 2H), 1.70-1.54 (m, 2H), 1.54-1.15 (m, 14H); **^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm):** 172.8, 163.8, 163.3, 154.1, 136.1, 132.1, 130.9, 130.4, 129.4, 128.1, 127.5, 127.4, 127.3, 126.5, 126.1, 125.0, 124.9, 124.8, 124.2, 124.1, 123.3, 122.1, 120.4, 114.7, 67.9, 63.8, 33.2, 31.9, 28.9, 28.8, 28.8, 28.6, 28.5, 28.4, 26.8, 25.4, 25.3; **IR, ν (KBr, cm^{-1}):** 3200-2500, 2920, 2851, 1728, 1685, 1602, 1511, 1422, 1258, 1210, 1160.

Compound Pyb-11-B: Pyb-11-A (0.20 g, 0.29 mmol) was dissolved in dry DCM (40 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.05 mL, 0.07 g, 0.58 mmol) and two drops of DMF were added. After 12 hours the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (30 mL) and the solution was added over a solution of compound **5** (0.15 g, 0.24 mmol) and trimethylamine (0.05 mL, 0.34 mmol) in dry DCM (30 mL) under an argon atmosphere. After stirring for 24 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane (8:2) as eluent, followed by recrystallization from ethyl acetate and toluene (69% yield); **M.p. (°C):** see Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.36-8.26 (m, 5H), 8.21-8.08 (m, 8H), 8.06-7.94 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.72-7.63 (m, 2H), 7.52 (d, *J* = 5.0 Hz, 2H), 7.49-7.43 (m, 1H), 7.43-7.35 (m, 4H), 7.35-7.28 (m, 2H), 7.26-7.20 (m, 1H), 7.04-6.93 (m, 4H), 4.16-3.96 (m, 6H), 3.45-3.33 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.29-2.13 (m, 2H), 1.92-1.71 (m, 4H), 1.68-1.56 (m, 2H),1.52-1.14 (m, 36H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 164.6, 164.6, 164.5, 164.5, 164.0, 163.9, 155.6, 151.5, 150.8, 142.2, 138.2, 132.6, 132.0, 131.6, 131.0, 130.1, 128.9, 128.5, 127.6, 127.5, 127.0, 126.9, 126.0, 125.1, 124.9, 124.9, 123.5, 122.3, 122.2, 121.1, 120.8, 120.6, 114.6, 68.6, 68.5, 64.8, 34.1, 33.0, 32.1, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1, 26.1, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2921, 2851, 1736, 1603, 1511, 1468, 1257, 1209, 1162; **MS (MALDI$^+$) m/z:** 1325.7 $[M + Na]^+$; **Elemental analysis:** Calcd. for $C_{85}H_{90}O_{12}$: C 78.31, H 6.96; found C 78.18, H 7.10.

Compound Pyb-11-B-11-Pyb: The carboxylic acid **Pyb-11A** (0.40 g, 0.57 mmol) was dissolved in dry DCM (60 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.10 mL, 0.14 g, 1.41 mmol) and two drops of DMF were added. After 12 hours, the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (60 mL) and the solution was added over a solution of compound **6** (0.05 g, 0.24 mmol) and trimethylamine (0.10 mL, 0.67 mmol) in dry DCM (20 mL) under an argon atmosphere. After stirring for 24 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane (8:2) as eluent, followed by recrystallization from ethyl acetate and toluene (58% yield); **M.p. (°C):** see Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.35-8.27 (m, 6H), 8.20-8.08 (m, 12H), 8.06-7.95 (m, 6H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.71-7.63 (m, 2H), 7.52 (d, *J* = 5.3 Hz, 2H), 7.49-7.45 (m, 1H), 7.43-7.36 (m, 4H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 7.01-6.93 (m, 4H), 4.10 (t, *J* = 6.7 Hz, 4H), 4.02 (t, *J* = 6.5 Hz, 4H), 3.46-3.35 (m, 4H), 2.47 (t, *J* = 7.1 Hz, 4H), 2.28-2.14 (m, 4H), 1.87-1.71 (m, 4H), 1.71-1.58 (m, 4H), 1.50-1.21 (m, 28H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 164.6, 164.6, 164.5, 163.9, 155.6, 151.5, 150.8, 142.2, 138.2, 135.9, 132.6, 132.0, 131.6, 131.0, 130.1, 130.0, 128.9, 128.5, 127.6, 127.5, 127.5, 127.5, 127.0, 127.0, 126.9, 126.0, 125.2, 125.1, 125.1, 124.9, 124.9, 123.5, 122.3, 122.3, 122.2, 121.1, 120.8, 120.6, 114.5, 68.5, 64.7, 34.1, 33.0, 29.6, 29.6, 29.6, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1, 26.1; **IR, ν**

(KBr, cm^{-1}): 2921, 2851, 1733, 1603, 1511, 1258, 1208, 1160; **MS (MALDI$^+$) m/z:** 1570.9 [M + Na]$^+$; **Elemental analysis:** Calcd. for $C_{102}H_{98}O_{14}$: C 79.15, H 6.38; found C 78.86, H 6.14.

Compound 8: Compound **Pyb-11-A** (0.60 g, 0.83 mmol), compound **7** (0.26 g, 0.94 mmol), DPTS (0.10 g, 0.34 mmol) and DCC (0.20 g, 1.00 mmol) were dissolved in dichloromethane (100 mL). After stirring at room temperature for 26 hours the mixture was filtered through a pad of Celite®, the solvent was evaporated and the resulting solid was purified by column chromatography using dichloromethane/hexane 9:1 as eluent (85% yield); **M.p. (°C):** 237 Dec; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.34-8.26 (m, 3H), 8.22-8.08 (m, 6H), 8.05-7.95 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.65-7.57 (m, 2H), 7.57-7.50 (m, 2H), 7.51-7.31 (m, 7H), 7.31-7.24 (m, 2H), 7.12-7.03 (m, 2H), 7.02-6.93 (m, 2H), 5.12 (s, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.45-3.34 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.27-2.13 (m, 2H), 1.87-1.72 (m, 2H), 1.70-1.57 (m, 2H), 1.51-1.16 (m, 14H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 164.7, 164.5, 164.0, 158.6, 155.6, 150.0, 138.8, 137.1, 135.9, 133.4, 132.6, 132.0, 131.6, 131.1, 130.1, 128.8, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.1, 126.9, 126.0, 125.1, 125.0, 125.0, 123.5, 122.2, 122.0, 121.1, 115.4, 114.6, 70.3, 68.5, 64.8, 34.1, 33.0, 29.6, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 2920, 2848, 1741, 1607, 1500, 1471, 1276, 1216, 1164.

Compound 9: Compound **8** (0.60 g, 0.62 mmol) was dissolved in ethanol (80 mL) and cyclohexene (40 mL) and $Pd(OH)_2/C$ (20% wt) (0.12 g) was added. The mixture was stirred at 80 ºC for 48 h under an argon atmosphere. The reaction mixture was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the compound was recrystallized from ethanol (74% yield); **M.p. (°C):** Cr 134 N 237 Dec; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.36-8.25 (m, 3H), 8.23-8.08 (m, 6H), 8.06-7.94 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.64-7.53 (m, 2H), 7.50-7.42 (m, 2H), 7.42-7.34 (m, 2H), 7.28-7.23 (m, 2H), 7.02-6.93 (m, 2H), 6.93-6.83 (m, 2H), 5.14 (s, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.47-3.34 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.29-2.11 (m, 2H), 1.89-1.71 (m, 2H), 1.72-1.53 (m, 2H), 1.51-1.15 (m, 14H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.8, 164.8, 164.6, 164.0, 155.5, 155.4, 150.0, 138.9, 135.9, 133.2, 132.6, 132.0, 131.6, 131.0, 130.1, 128.9, 128.5, 127.9, 127.6, 127.5, 127.5, 127.1, 126.9, 126.0, 125.2, 125.1, 124.9, 124.9, 123.5, 122.3, 122.0, 121.1, 115.8, 114.6, 68.5, 64.8, 34.1, 33.0, 29.6, 29.5, 29.4, 29.2, 28.8, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 3500-3100, 2927, 2849, 1739, 1718, 1701, 1606, 1500, 1464, 1366, 1272, 1212, 1175.

Compound Pyb-11-C: Compound **9** (0.20 g, 0.23 mmol), compound **10** (0.14 g, 0.30 mmol), DPTS (0.07 g, 0.23 mmol) and DCC (0.11 g, 0.55 mmol) were dissolved in dichloromethane (50 mL). After stirring at room temperature for 48 hours, the reaction mixture was filtered through a pad of Celite®, the solvent was evaporated and the resulting solid was purified by column chromatography using dichloromethane/hexane 9:1 as eluent, followed by recrystallization from ethyl acetate (63% yield); **M.p. (°C):** see Table 1; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.37-8.26 (m, 5H), 8.23-8.09 (m, 8H), 8.08-7.96 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.71-7.61 (m, 4H), 7.43-7.36 (m, 4H), 7.37-7.30 (m, 4H), 7.04-6.92 (m, 4H), 4.16-3.95 (m, 6H), 3.49-3.36 (m, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.28-2.11 (m, 2H), 1.90-1.72 (m, 4H), 1.73-1.58 (m, 4H), 1.55-1.15 (m, 36H), 0.88 (t, *J* = 6.5 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 173.7, 164.7, 164.5, 164.0, 164.0, 155.6, 150.6, 138.4, 135.9, 132.6, 132.0, 131.6, 131.1, 130.1, 128.9, 128.4, 127.6, 127.5, 127.5, 127.0, 126.9, 126.0, 125.1, 124.9, 124.9, 123.5, 122.3, 122.2, 121.1, 114.6, 114.6, 110.1, 68.5, 64.7, 34.1, 33.0, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.2, 29.2, 28.8, 27.0, 26.1, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2919, 2850, 1739, 1601, 1511, 1468, 1258, 1204; **MS (MALDI$^+$) m/z:** 1325.3 [M + Na]$^+$; **Elemental analysis:** Calcd. for $C_{85}H_{90}O_{12}$: C 78.31, H 6.96; found C 78.64, H 7.42.

Compound 12: Compound **11** (1.60 g, 2.90 mmol) and tetrabutylammonium bromide (TBAB) (1.86 g, 5.80 mmol) were dissolved in chloroform (6 mL) and water (3 mL). Then sodium azide (0.56 g, 8.70 mmol) was added and the reaction mixture was heated to reflux is. After 5 hours the reaction was stopped to prevent decomposition of esters caused by the basic medium. The crude reaction was extracted with DCM and the organic phase was washed twice with water. The organic phase was dried with anhydrous magnesium sulfate, filtered and the solvent was evaporated. The product was

purified by column chromatography using dichloromethane/hexane 7:3 as eluent (69% yield); **M.p. (°C):** 50-51; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.21-8.08 (m, 4H), 7.51-7.21 (m, 7H), 7.03-6.93 (m, 2H), 5.38 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 1.94-1.74 (m, 2H), 1.71-1.19 (m, 16H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 165.8, 164.5, 163.9, 155.0, 136.1, 132.5, 131.4, 128.7, 128.4, 128.3, 127.7, 122.0, 121.2, 114.5, 68.5, 66.9, 51.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.0, 26.8, 26.1; **IR, ν (KBr, cm^{-1}):** 2928, 2854, 2094, 1736, 1603, 1510, 1466, 1376, 1256, 1204, 1160.

Compound 13 [2]**:** To a mixture of 1-pyrene butyric acid (0.41 g, 1.43 mmol), compound **12** (0.80 g, 1.43 mmol) and 2,2'-dithiodipyridine (0.07 g, 0.29 mmol) in toluene (20 mL) at 0 °C under an atmosphere argon, was added trimethylphosphine (1.0 M in toluene, 3.43 mL, 3.43 mmol). After 10 minutes, the ice bath was removed and the reaction was allowed to proceed at room temperature with stirring for three hours, monitoring the reaction by TLC. Then 2 mL of water were added and the mixture was stirred for 10 minutes. The solid formed was filtered and washed with cold hydrochloric acid solution (5 mL, 1M) and water Finally, the solid was purified by column chromatography using DCM/ethyl acetate 9.75:0.25 as eluent (75% yield); **M.p. (°C):** 124; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 7.30 (d, *J* = 9.3 Hz, 1H), 8.05-7.94 (m, 3H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.50-7.34 (m, 5H), 7.34-7.26 (m, 2H), 7.00-6.91 (m, 2H), 5.38 (s, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.40 (t, *J* = 7.0 Hz, 2H), 3.29-3.19 (m, 2H), 2.35-2.18 (m, 4H), 1.88-1.70 (m, 2H), 1.54-1.12 (m, 16H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 172.6, 165.9, 164.5, 163.9, 155.1, 136.1, 136.0, 132.5, 131.6, 131.4, 131.1, 130.3, 130.1, 128.9, 128.8, 128.4, 128.3, 127.7, 127.6, 127.5, 126.9, 126.0, 125.1, 124.9, 123.5, 122.0, 121.2, 114.5, 68.5, 66.9, 39.7, 36.3, 32.9, 29.8, 29.6, 29.4, 29.4, 29.2, 27.6, 27.0, 26.1; **IR, ν (KBr, cm^{-1}):** 3315, 2926, 2853, 1718, 1642, 1536, 1510, 1475, 1413, 1375, 1271, 1203, 1110.

Compound PybN-11-A: An experimental procedure similar to that used for the synthesis of compound **9** was followed, using in this case compound **13** (0.50 g, 0.63 mmol), $Pd(OH)_2/C$ (20% wt) (0.09 g), ethanol (60 mL) and cyclohexene (30 mL). After 45 hours, the reaction mixture was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the compound was recrystallized from ethanol (71% yield); **M.p. (°C):** 195-197; **^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm):** 8.37 (d, *J* = 9.3 Hz, 1H), 8.32-8.17 (m, 4H), 8.17-7.98 (m, 7H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 5.6 Hz, 1H), 7.44-7.34 (m, 2H), 7.14-7.02 (m, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.38-3.23 (m, 2H), 3.14-3.00 (m, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 2.08-1.94 (m, 2H), 1.72-1.58 (m, 2H), 1.49-1.16 (m, 16H); **^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm):** 171.8, 166.6, 163.4, 162.8, 153.6, 135.6, 131.4, 130.4, 130.3, 129.9, 128.8, 127.8, 127.6, 126.7, 126.4, 125.7, 125.1, 124.0, 123.9, 122.8, 120.9, 120.0, 113.6, 67.4, 34.9, 32.0, 28.7, 28.6, 28.5, 28.4, 28.4, 28.1, 26.9, 26.1, 25.0; **IR, ν (KBr, cm^{-1}):** 3500-2400, 3306, 2927, 2852, 1731, 1685, 1641, 1604, 1538, 1511, 1466, 1422, 1314, 1258, 1204.

Compound PybN-11-B: The carboxylic acid **PybN-11-A** (0.15 g, 0.22 mmol) was dissolved in dry DCM (60 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.04 mL, 0.06 g, 0.48 mmol) and two drops of DMF were added. After 12 hours, the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (50 mL) and the solution was added over a solution of compound **5** (0.134 g, 0.22 mmol) and trimethylamine (0.05 mL, 0.30 mmol) in dry DCM (30 mL) under an argon atmosphere. After stirring for 28 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/ethyl acetate 9.75:0.25 as eluent and after increasing the polarity until 8:2. Finally, the product was recrystallized from ethyl acetate (67% yield); **M.p. (°C):** 165; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.35-8.27 (m, 5H), 8.20-8.09 (m, 8H), 8.05-7.96 (m, 3H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.70-7.65 (m, 2H), 7.52 (d, *J* = 4.9 Hz, 2H), 7.49-7.43 (m, 1H), 7.41-7.35 (m, 4H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 7.03-6.93 (m, 4H), 4.06 (t, *J* = 6.5 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.45-3.35 (t, 2H), 3.30-3.20 (m, 2H), 2.32-2.20 (m, 4H), 1.89-1.72 (m, 4H), 1.52-1.16 (m, 38H), 0.87 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 172.6, 164.6, 164.5, 164.0, 155.6, 151.5,

2. Burés, J.; Martín, M.; Urpí, F.; Vilarrasa, J., Catalytic Staudinger-Vilarrasa Reaction for the Direct Ligation of Carboxylic Acids and Azides. *J. Org. Chem.* **2009,** *74*, 2203-2206.

150.8, 142.2, 138.2, 136.0, 132.6, 132.0, 131.6, 131.1, 130.0, 130.0, 128.5, 127.6, 127.5, 127.0, 126.9, 126.0, 125.1, 124.9, 123.6, 122.3, 122.2, 121.1, 120.8, 120.6, 114.6, 68.6, 68.5, 39.7, 36.3, 32.9, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.2, 29.2, 27.6, 27.1, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):):** 3302, 2921, 2851, 1735, 1639, 1604, 1511, 1468, 1257, 1207, 1162; **MS (MALDI^{+}) m/z:** 1324.3 $[M + Na]^{+}$; **Elemental analysis:** Calcd. for $C_{85}H_{90}NO_{11}$: C 78.37, H 7.04, N 1.08; found C 78.18, H 7.10, N 1.05.

Compound 14: An experimental procedure similar to that used for the synthesis of compound **4** was followed, using in the first step 1-pyrenebutyric acid (3.00 g, 10.40 mmol), oxalyl chloride (1.96 mL, 3.05 g, 23.21 mmol), two drops of DMF and DCM (120 mL). After 14 hours, the solvent was evaporated and the freshly synthesized acid chloride was dissolved in DCM (90 mL). The solution was added over a solution of benzyl 4-hydroxybenzoate (2.00 g, 8.76 mmol) and trimethylamine (1.72 mL, 12.18 mmol) in dry DCM (50 mL) under an argon atmosphere. After stirring for 21 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane 9:1 as eluent (79% yield); **M.p. (°C):** 94-96; **^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm):** 8.33 (d, *J* = 9.3 Hz, 1H), 8.22-8.08 (m, 6H), 8.08-7.95 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.51-7.31 (m, 5H), 7.19-7.11 (m, 2H), 5.38 (s, 2H), 3.54-3.43 (m, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.40-2.26 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm):** 171.5, 165.7, 154.5, 136.1, 135.4, 131.5, 131.4, 131.0, 130.2, 128.9, 128.7, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 127.0, 126.0, 125.3, 125.1, 125.0, 123.3, 121.7, 66.9, 34.0, 32.7, 26.7; **IR, ν (KBr, cm^{-1}):** 2926, 2850, 1756, 1714, 1601, 1497, 1405, 1273, 1207, 1096.

Compound 15: An experimental procedure similar to that used for the synthesis of compound **9** was followed, using in this case compound **14** (3.00 g, 6.02 mmol), $Pd(OH)_2$/C (20% wt) (0.50 g), ethanol (150 mL) and cyclohexene (75 mL). After 32 hours, the reaction mixture was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the compound was recrystallized from ethanol (77% yield); **M.p. (°C):** 221-223 Dec; **^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm):** 8.42 (d, *J* = 9.3 Hz, 1H), 8.34-8.19 (m, 4H), 8.19-7.92 (m, 6H), 7.28-717 (m, 2H), 3.53-3.43 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.26-2.13 (m, 2H); **^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm):** 171.4, 166.7, 153.9, 136.0, 130.9, 130.9, 130.5, 129.5, 128.4, 128.3, 127.7, 127.5, 127.4, 126.7, 126.2, 125.1, 124.9, 124.3, 124.2, 123.5, 122.1, 39.5, 33.8, 31.8, 26.5; **IR, ν (KBr, cm^{-1}):** 3200-2400, 2926, 1753, 1684, 1604, 1508, 1430, 1319, 1294, 1294, 1252, 1123.

Compound 16: An experimental procedure similar to that used for the synthesis of compound **4** was followed, using in the first step compound **15** (1.59 g, 3.89 mmol), oxalyl chloride (0.65 mL, 1.00 g, 7.69 mmol), two drops of DMF and DCM (80 mL). After 14 hours, the solvent was evaporated and the freshly synthesized acid chloride was dissolved in DCM (70 mL). The solution was added over a solution of benzyl 4-hydroxybenzoate (0.75 g, 3.24 mmol) and trimethylamine (0.64 mL, 4.54 mmol) in dry DCM (30 mL) under an argon atmosphere. After stirring for 21 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane 9:1 as eluent (78% yield); **M.p. (°C):** 138; **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 8.34 (d, *J* = 9.3 Hz, 1H), 8.25-8.11 (m, 8H), 8.07-7.97 (m, 3H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.49-7.33 (m, 5H), 7.33-7.27 (m, 2H), 7.24-7.19 (m, 2H), 5.38 (s, 2H), 3.58-3.47 (m, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.41-2.30 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):** 171.4, 165.8, 163.9, 155.2, 154.7, 136.1, 135.3, 132.0, 131.6, 131.5, 131.0, 130.3, 128.9, 128.8, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.0, 126.7, 126.1, 125.3, 125.2, 125.1, 125.0, 123.3, 122.0, 121.9, 67.0, 34.0, 32.8, 26.7; **IR, ν (KBr, cm^{-1}):** 2937, 2870, 1755, 1736, 1714, 1601, 1507, 1456, 1413, 1274, 1197.

Compound Pyb-0-A: An experimental procedure similar to that used for the synthesis of compound **9** was followed, using in this case compound **16** (1.30 g, 2.10 mmol), $Pd(OH)_2$/C (20% wt) (0.35 g), ethanol (100 mL) and cyclohexene (50 mL). After 36 hours, the reaction mixture was filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the product was recrystallized from ethanol (76% yield); **M.p. (°C):** Cr 225 I; I 202 N 163 Cr; **^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm):** 8.44 (d, *J* = 9.3 Hz, 1H), 8.34-8.11 (m, 8H), 8.10-7.96 (m, 4H), 7.49-7.40 (m,

2H), 7.41-7.31 (m, 2H), 3.53-3.40 (m, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.26-2.11 (m, 2H); **^{13}C NMR (75 MHz, DMSO-d$_6$), δ (ppm):** 171.3, 166.6, 163.5, 154.9, 154.0, 135.9, 131.6, 130.9, 130.9, 130.4, 129.4, 128.6, 128.2, 127.6, 127.4, 127.3, 126.6, 126.1, 126.1, 125.0, 124.8, 124.3, 124.1, 123.4, 122.5, 122.2, 33.2, 31.8, 26.4; **IR, ν (KBr, cm^{-1}):** 3200-2450, 2937, 2870, 1760, 1739, 1695, 1507, 1425, 1263, 1203, 1186.

Compound Pyb-0-B: The carboxylic acid **Pyb-0-A** (0.22 g, 0.42 mmol) was dissolved in dry DCM (40 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.07 mL, 0.11 g, 0.82 mmol) and two drops of DMF were added. After 14 hours, the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (35 mL) and the solution was added over a solution of compound **5** (0.22 g, 0.35 mmol) and trimethylamine (0.07 mL, 0.45 mmol) in dry DCM (25 mL) under an argon atmosphere. After stirring for 27 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane (8:2) as eluent, followed by two recrystallizations from ethyl acetate (69% yield); **M.p. (°C):** 146; **^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm):** 88.37-8.29 (m, 5H), 8.28-8.21 (m, 2H), 8.21-8.10 (m, 6H), 8.07-7.97 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.72-7.63 (m, 2H), 7.52 (d, *J* = 5.1 Hz, 2H), 7.48-7.45 (m, 1H), 7.43-7.36 (m, 4H), 7.36-7.28 (m, 2H), 7.27-7.20 (m, 3H), 7.05-6.95 (m, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.58-3.45 (m, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.43-2.29 (m, 2H), 1.91-1.76 (m, 2H), 1.54-1.17 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm):** 171.5, 164.6, 164.5, 164.5, 164.0, 163.9, 155.6, 155.3, 155.3, 151.5, 150.8, 142.2, 138.2, 135.3, 132.6, 132.1, 132.0, 131.6, 131.0, 130.3, 130.0, 129.0, 128.5, 127.7, 127.6, 127.6, 127.3, 127.0, 127.0, 126.6, 126.1, 125.3, 125.2, 125.1, 125.0, 124.9, 123.3, 122.3, 122.2, 122.2, 122.1, 121.1, 120.8, 120.6, 114.6, 68.6, 34.0, 32.8, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.2, 26.7, 26.1, 22.8, 14.3; **IR, ν (KBr, cm^{-1}):** 2919, 2849, 1733, 1603, 1507, 1257, 1203, 1159; **MS (MALDI$^+$) m/z:** 1155.5 [M + Na]$^+$; **Elemental analysis:** Calcd. for $C_{74}H_{68}O_{11}$: C 78.42, H 6.05; found C 78.31, H 6.40.

Compound Pyb-0-B-0-Pyb: The carboxylic acid **Pyb-0-A** (0.50 g, 0.95 mmol) was dissolved in dry DCM (80 mL) under an argon atmosphere at room temperature. Then, oxalyl chloride (0.16 mL, 0.25 g, 1.90 mmol) and two drops of DMF were added. After 14 hours, the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (80 mL) and the solution was added over a solution of compound **6** (0.07 g, 0.39 mmol) and trimethylamine (0.19 mL, 1.23 mmol) in dry DCM (20 mL) under an argon atmosphere. After stirring for 26 hours, the reaction was filtered through a pad of Celite®. The solvent was evaporated and the product purified by column chromatography using DCM/hexane (8:2) as eluent, followed by two recrystallizations from ethyl acetate (55% yield); **M.p. (°C):** 168; **^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm):** 8.38-8.28 (m, 6H), 8.29-8.21 (m, 4H), 8.21-8.10 (m, 8H), 8.08-7.97 (m, 6H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.71-7.64 (m, 2H), 7.52 (d, *J* = 5.0 Hz, 2H), 7.48-7.45 (m, 1H), 7.43-7.35 (m, 4H), 7.35-7.29 (m, 2H), 7.27-7.20 (m, 5H), 3.60-3.43 (m, 4H), 2.76 (t, *J* = 7.2 Hz, 4H), 2.44-2.28 (m, 4H); **^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm):** 171.5, 164.5, 163.9, 155.3, 151.4, 150.8, 142.2, 138.2, 135.3, 132.1, 131.6, 131.0, 130.3, 130.0, 129.0, 128.5, 127.7, 127.6, 127.6, 127.3, 127.3, 127.0, 126.6, 126.1, 125.3, 125.2, 125.1, 125.0, 124.9, 123.3, 120.8, 34.0, 32.8, 26.7; **IR, ν (KBr, cm^{-1}):** 2918, 2849, 1734, 1601, 1506, 1260, 1200, 1158; **MS (MALDI$^+$) m/z:** 1229.1 [M + Na]$^+$; **Elemental analysis:** Calcd. for $C_{80}H_{54}O_{12}$: C 79.59, H 4.51; found C 79.34, H 4.83.

4. NMR spectra

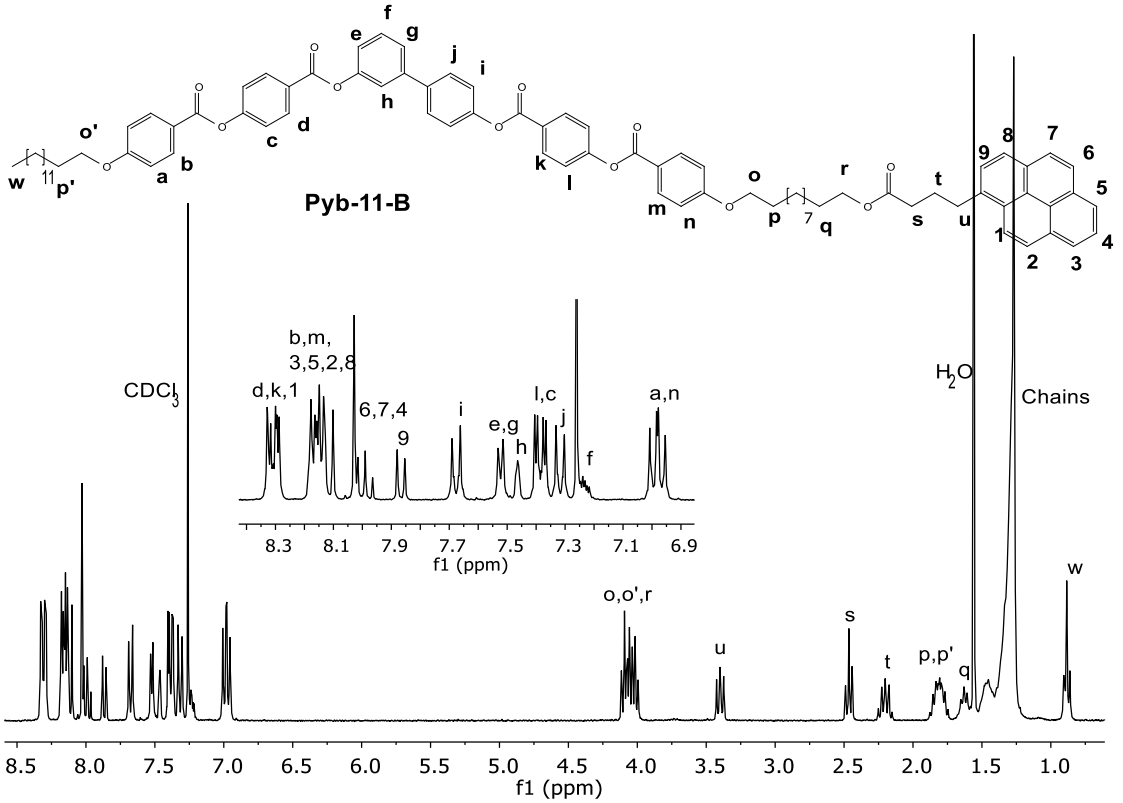


Figure S1. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **Pyb-11-B**.

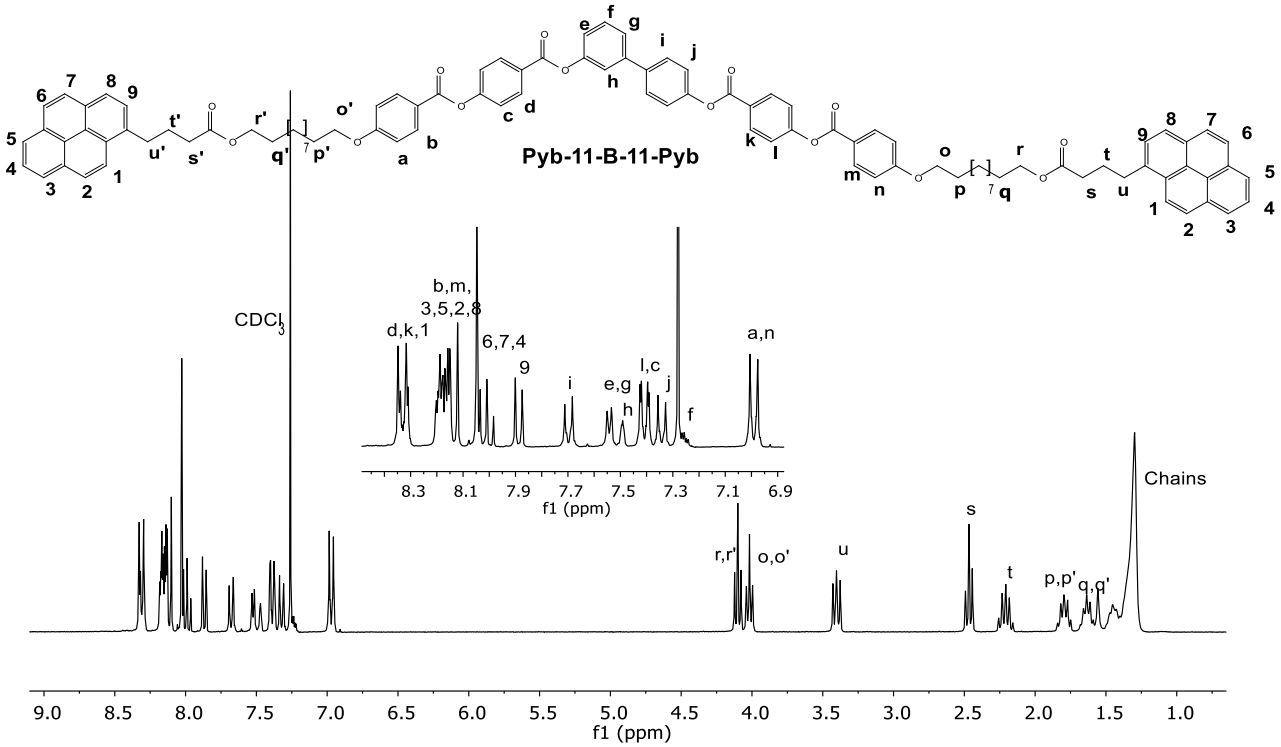


Figure S2. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **Pyb-11-B-11-Pyb**.

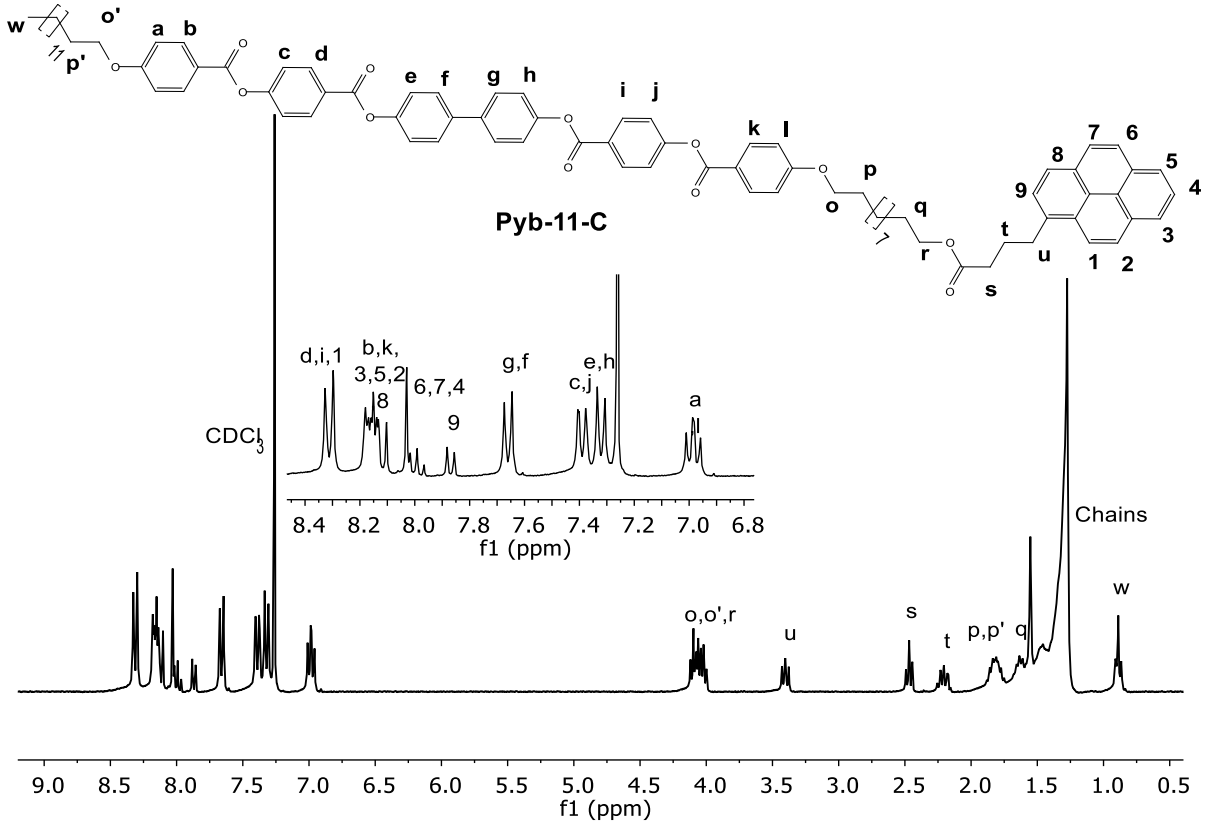


Figure S3. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **Pyb-11-C**.

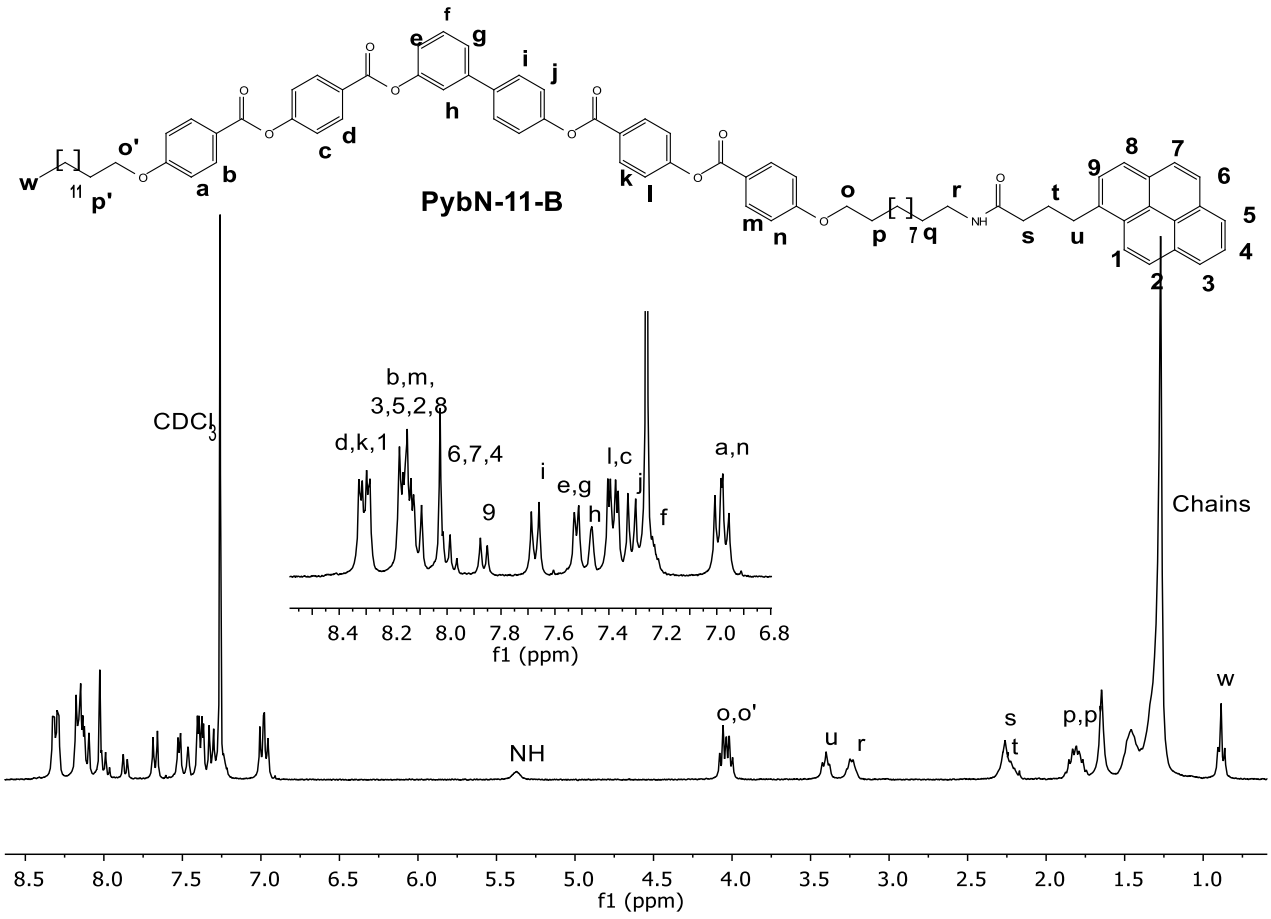


Figure S4. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **PybN-11-B**.

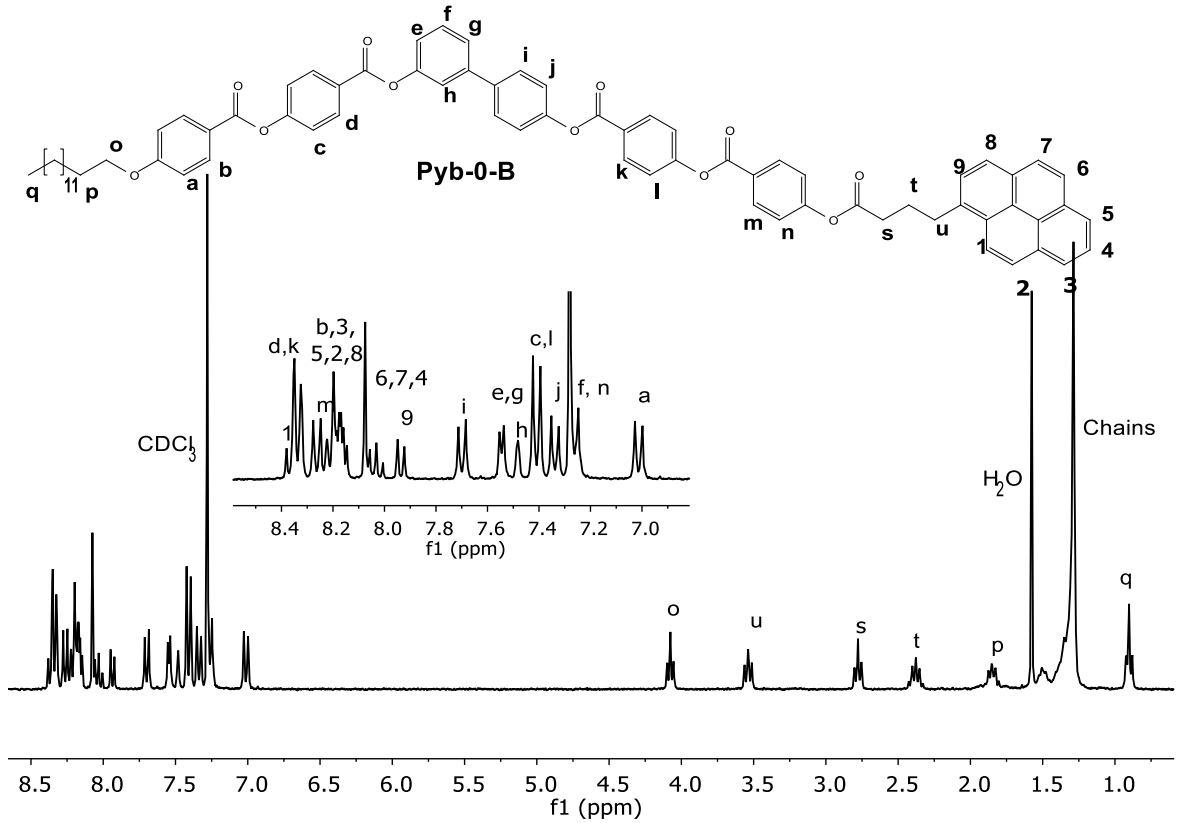


Figure S5. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **Pyb-0-B**.

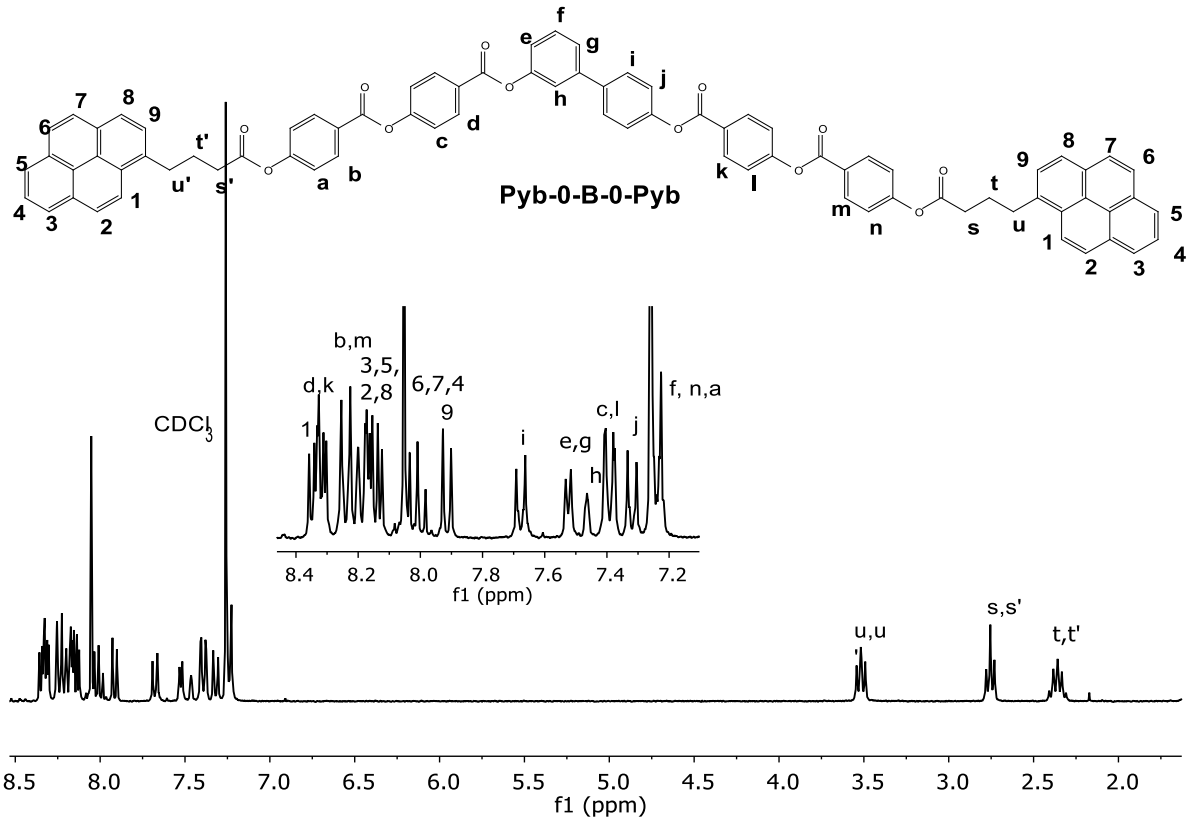


Figure S6. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **Pyb-0-B-0-Pyb**.

5. Thermal and Liquid Crystal Properties of the Compounds

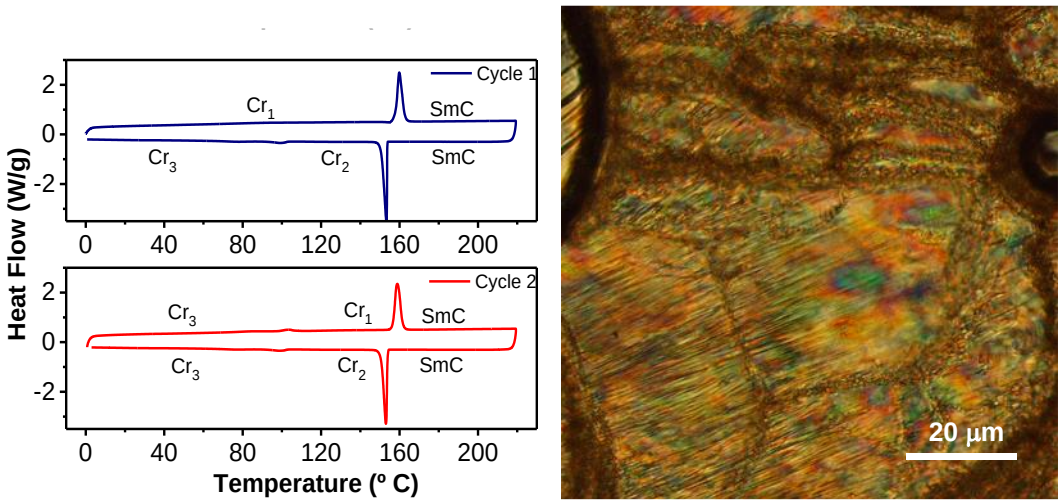


Figure S7. DSC thermogram (first and second heating/cooling cycle) and POM texture at 155 ºC (SmC phase) for compound **Pyb-11-C**.

6. Photophysics in Solution and in the Solid State

Table S1. UV-Vis and fluorescence data in dichloromethane (DCM) solution and as-obtained solid (*pristine*): Absorption and emission maxima (λ_{abs}, λ_{em}), fluorescence quantum yields (ϕ_F), and lifetimes (τ_F), radiative and non-radiative rates (k_r, k_{nr}).

Compound	DCM solution				As-obtained solid (*Pristine*)				
	λ_{abs} (nm)	ε_m (10^4 l mol^{-1}cm^{-1})	λ_{em} (nm)	ϕ_F[a]	λ_{em} (nm)	ϕ_F[b]	τ_F[c] (ns)	K_r[d] (s^{-1})	K_{nr}[d] (s^{-1})
Pyb-0-B-0-Pyb	245, 256, 266, 277, 314, 328, 345	21.2, 10.4, 11.3, 14.1, 2.5, 6.0, 8.9	377 397 418	0.16	478	0.58	94.4	$6.1\cdot10^6$	$4.4\cdot10^6$
Pyb-11-B-11-Pyb	245, 258, 266, 277, 315, 329, 345	17.8, 10.3, 15.0, 19.2, 2.7, 5.9, 8.7	377 397 418	0.13	475	0.55	57.0	$9.6\cdot10^6$	$7.9\cdot10^6$
Pyb-0-B	245, 257, 266, 277, 314, 328, 345	12.2, 8.1, 9.4, 10.5, 1.2, 2.9, 4.3	377 397 418	0.13	476	0.60	42.9	$1.4\cdot10^7$	$9.3\cdot10^6$
Pyb-11-B	245, 258, 267, 278, 314, 329, 345	11.3, 8.0, 11.0, 13.0, 1.3, 2.9, 4.4	377 397 418	0.14	377 391 397 412	0.59	53.1	$1.1\cdot10^7$	$7.3\cdot10^6$
PybN-11-B	245, 258, 267, 278, 315, 329, 345	11.3, 7.9, 10.9, 12.9, 1.3, 3.0, 4.5	377 397 418	0.14	449	0.19	16.2	$1.2\cdot10^7$	$5.0\cdot10^7$
Pyb-11-C	245, 258, 266, 277, 315, 329, 345	10.0, 7.0, 10.1, 12.6, 1.2, 2.7, 4.1	377 397 418	0.15	470	-	-	-	-

[a] From relative measurements using 9,10-diphenylanthracene in cyclohexane as reference (ϕ_F = 0.9). [b] From absolute measurements in an integrating sphere. [c] Intensity averages from bi and tri-exponential fits. [d] From $\tau_F = 1/(k_r + k_{nr})$, $\phi_F = k_r \cdot \tau_F$.

Table S2. Content of excimer emission (in %) of the total fluorescence intensity, as determined by spectral decomposition, utilizing pure monomer and excimer spectra.

Compound	Pristine	scf	Col	Gel
Pyb-0-B-0-Pyb	100	100	—	—
Pyb-11-B-11-Pyb	92	100	100	—
Pyb-0-B	100	99	—	94
Pyb-11-B	35	94	100	17
PybN-11-B	100	100	—	93
Pyb-11-C	100	100	100	95

Pristine (as-obtained powder), scf (slow cooled film at 10 °C min^{-1}), Col (mesophase Col_r); Gel: physical gel in 1-octanol)

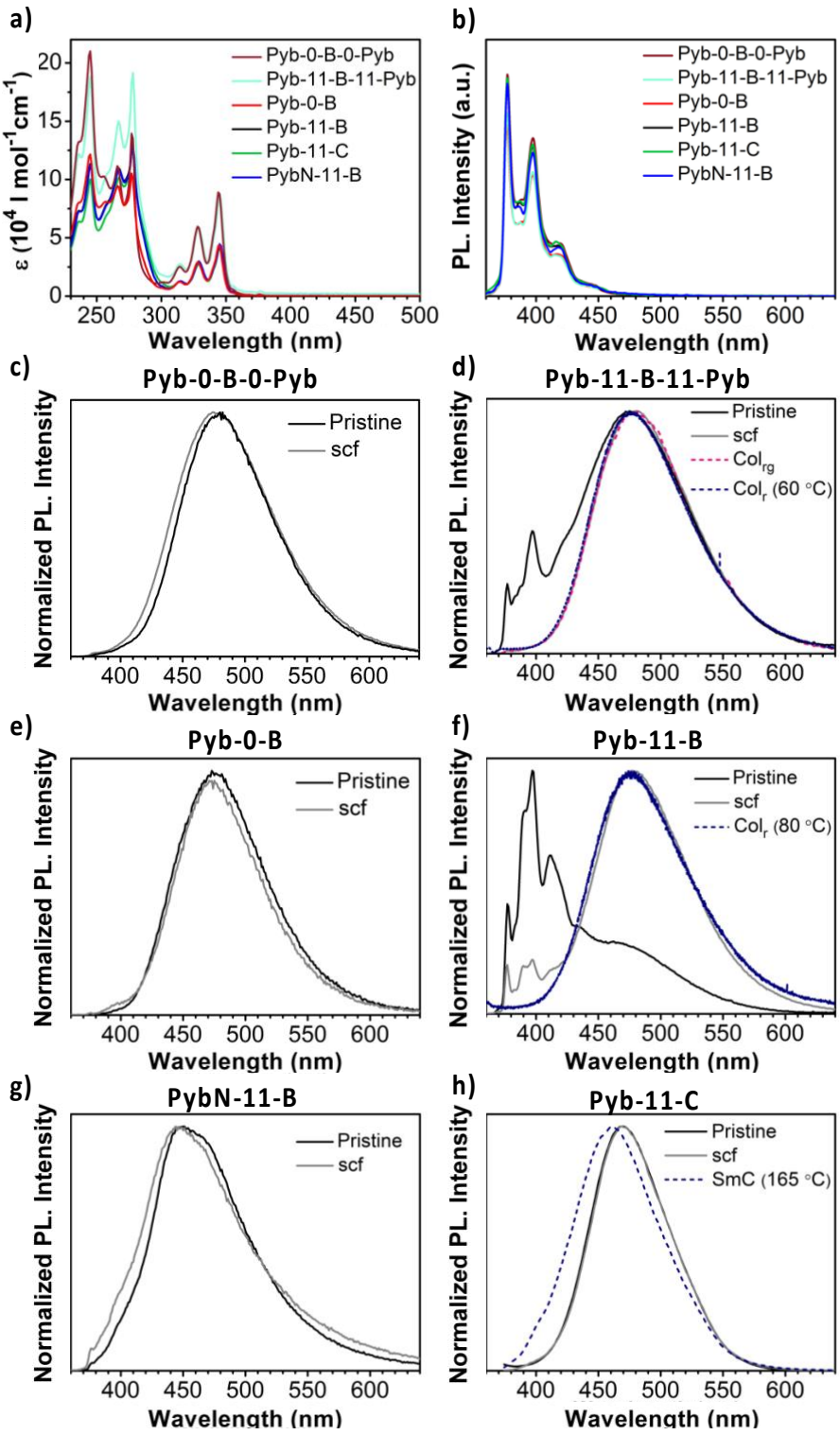


Figure S8. a, b) Absorption and fluorescence spectra, respectively, of final compounds in dichloromethane (DCM) solutions. The original fluorescence spectra have been divided by absorbance at the excitation wavelength for better comparison. c, d, e, f, g, h) Fluorescence spectra in different neat samples of **Pyb-0-B-0-Pyb**, **Pyb-11-B-11-Pyb**, **Pyb-0-B**, **Pyb-11-B**, **PybN-11-B** and **Pyb-11-C**, respectively. Pristine powder (black), scf: slow cooled film at 10 °C min^{-1} (grey), CL: mesophase (Col_r or SmC) (dark blue); CL_g: glassy mesophase (Col_{rg}) (pink).

Table S3. Fluorescence decay parameters from bi and tri-exponential fits for the as-obtained solid of **Pyb-0-B-0-Pyb**, **Pyb-11-B-11-Pyb**, **Pyb-0-B**, **Pyb-11-B** and **PybN-11-B**; fluorescence maximum λ_{em}, intensity-average lifetime $\tau_F = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, individual lifetimes τ_i and amplitudes A_i.

Compound	As-obtained solid (*Pristine*)							
	λ_{em} (nm)	τ_F (ns)	A_1	A_2	A_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
Pyb-0-B-0-Pyb	478	94.4	0.62	0.38	-	107.3	46.9	-
Pyb-11-B-11-Pyb	475	57.0	0.69	0.31	-	62.1	17.7	-
Pyb-0-B	476	42.9	0.52	0.34	0.14	38.4	10.9	65.8
Pyb-11-B	377	53.1	0.68	0.32	-	58.2	18.2	-
PybN-11-B	449	16.2	0.25	0.72	0.03	18.9	5.4	44.3

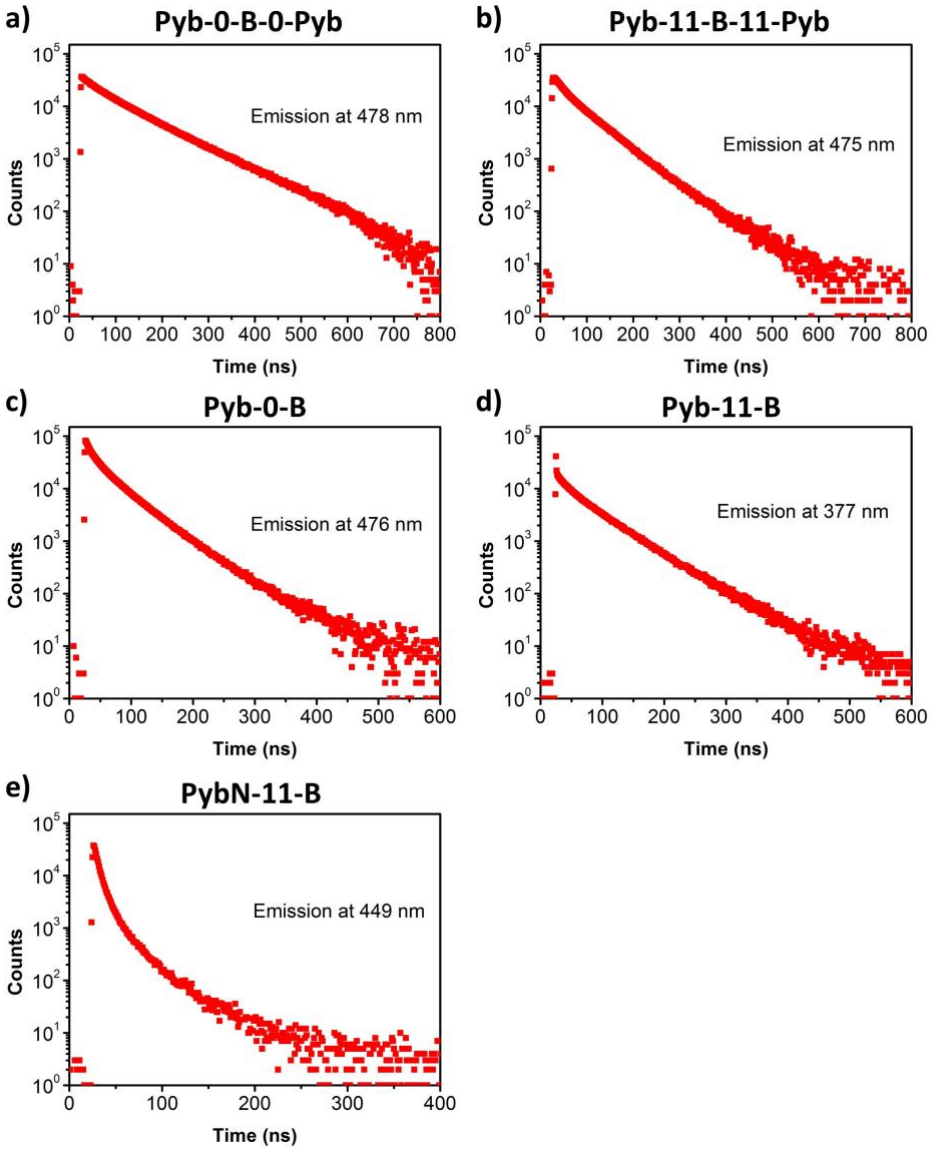


Figure S9. Fluorescence lifetime decays for the as-obtained solid of: a) **Pyb-0-B-0-Pyb** , b) **Pyb-11-B-11-Pyb**, c) **Pyb-0-B**, d) **Pyb-11-B**, and e) **PybN-11-B**.

7. Gelation Properties and Photophysics in the Gel State

Table S4: Gelation properties.[a, b, c]

Solvent	Pyb-11-B	Pyb-11-C	PybN-11-B	Pyb-0-B
1-Butanol	G (2.5-0.5) [91-84]	I	I	P[d]
1-Octanol	G (10-0.3) [107-77]	G (5-0.8) [99-74]	G (10) [121]	G (10-2.5) [128-115]
Toluene	P[d]	I	P[d]	I
Nitrobenzene	S[d]	I	G (2.4) [49]	I
Chlorobenzene	S[d]	I	G (10-1.8) [59-51]	I

[a] I= Insoluble, P= Precipitate, S= Solution, G= Gel; [b] The values in brackets show the concentrations (% w/w) that induce gelation. The studied values were 10, 5, 2.5 and 1% w/w. [c] The values in staples indicate transition temperatures (°C) from gel to sol (T_{gs}) for the maximum and minimum concentration that induce gelation. [d] Evaluated at 2.5 and 1% (w/w).

Table S5: Photophysical properties and fluorescence decay parameters from bi and tri-exponential fits in the gel state; fluorescence maximum λ_{em}, intensity-averaged lifetime $\tau_F = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, individual lifetimes τ_i and amplitudes A_i.

Compound	Solvent	λ_{em} (nm)	τ_F (ns)	A_1	A_2	A_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
Pyb-0-B	1-Octanol	474	72.3	0.15	0.85	-	102.7	63.6	-
Pyb-11-B	1-Octanol	377	60.5	0.77	0.23	-	64.5	23.4	-
PybN-11-B	1-Octanol	446	13.1	0.67	0.28	0.05	3.1	7.6	33.5

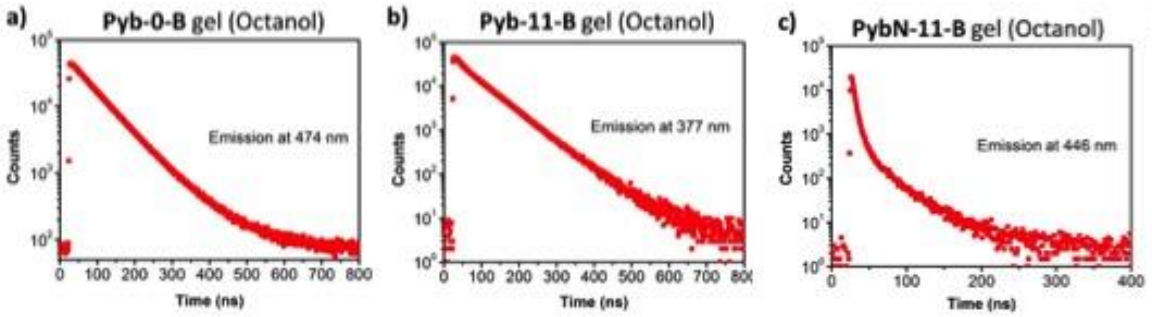


Figure S10. Fluorescence lifetime decays for the gels of **Pyb-0-B**, **Pyb-11-B** and **PybN-11-B** in 1-octanol (10% w/w)

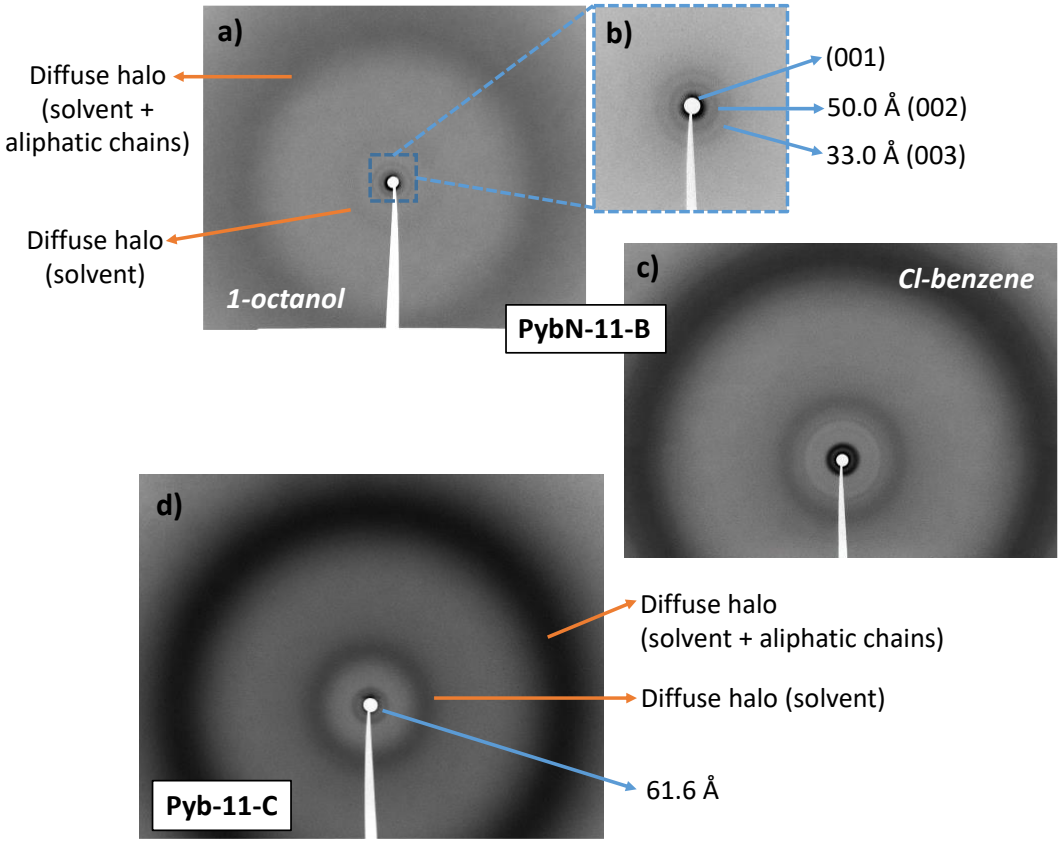


Figure S11. XRD pattern of **PybN-11-B** gel in 1-octanol (10% w/w) (a, b) and of **PybN-11-B** gel in chlorobenzene (10% w/w) (c). XRD pattern of **Pyb-11-C** gel in 1-octanol (5% w/w) (d).