

Modular Engineering of H-bonded Supramolecular Polymers for Reversible Functionalization of Carbon Nanotubes

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EXPERIMENTAL SECTION

Photophysical Characterization. The stock solutions were prepared by dissolving the purified MWCNTs•[X•Y]_n in 10 ml of CHCl₃. The samples for photophysical measurements were prepared by injecting microliter quantities (~50 μl) of this solution into 3 ml of CHCl₃. Electronic absorption and emission spectra were recorded, respectively, on a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin Elmer) and on a Edinburgh FLS920 spectrofluorimeter (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). Fluorescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed NanoLED excitation source (331 nm). Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. Emission quantum yields were determined according to the approach described by Demas and Crosby using Quinine sulfate ($\Phi_{em} = 0.546$ in air-equilibrated acid water solution, 1 N H₂SO₄)³⁸ as standard. The temperature of the solutions was varied with HAAKE F3-C digital heated/refrigerated water bath (Haake Mess-Technik GmbH u.Co., Germany) which can be manually connected to cuvette holder and controlled externally. All the solvents (CHCl₃, DMSO, MeOH) are spectroscopic grade Carlo Erba, (99.8 %) and were used as received.

X-ray Photoelectron Spectroscopy (XPS). Studies were performed to investigate the chemical composition of the functionalized MWCNT. For each analysis, 2 mg of material was deposited on a copper thin film, which was then fixed on an XPS sample holder using a double side adhesive conductive carbon tap (SPI supplies). For each compound, the analyses were performed on three different spots using ESCA SPECTROMETER where the photon source was a monochromatised Al K α line ($h\nu = 1486.6$ eV) applied with a takeoff angle of 35°. The survey

spectra are the result of the accumulation of 10 scans where the EV/Step is 0.08. The C 1s core level peak was taken as reference at 284.7 eV.

Microscopic Characterization.

Transmission Electron Microscopy (TEM). All the low resolution TEM images were obtained from the deposition onto Nickel grids (with carbon layer coating, 200 mesh) of dispersions (approximately $1 \text{ mg}\cdot\text{ml}^{-1}$) of hybrids **MWCNTs•[X•Y]_n** in CHCl_3 ; these grids were analyzed with a *Philips 208* electron microscope at a 100 kV voltage, and the resulting images were collected with an *AMT* high-resolution digital imaging camera.

Tapping-mode Atomic Force Microscopy (TM-AFM). TM-AFM measurements were carried out in air at 298 K, using a *Nanoscope IIIa* (Digital instruments Metrology Group, USA) instrument, model: MMAFMLN. The tips used in all measurements were phosphorous-doped silicon cantilevers ($T = 20\text{--}80 \text{ nm}$, $L = 115.135 \text{ mm}$, $f_0 = 200\text{--}400 \text{ kHz}$, $k = 20\text{--}80 \text{ N}\cdot\text{m}^{-1}$, *VEECO*, USA) at a resonance frequency of *ca.* 316 kHz. 1–2 Drops from dispersions in CHCl_3 (less than $1 \text{ mg}\cdot\text{ml}^{-1}$) of hybrids **MWCNTs•[X•Y]_n** were spin-coated (spinning rate: 2000 rpm) on clean Si(111) surfaces; the silicon substrates were previously cleaned using boiling 1,1',2,2'-tetrachloroethane for 10 minutes, copiously rinsed with acetone, then dried with a N_2 stream.

Scanning tunnelling microscopy (STM). STM measurements were performed in constant current mode using W tips electrochemically etched in a KOH solution and flashed under ultra high vacuum (UHV). In a classical experiment, one mg of hybrid **MWCNTs•[X•Y]_n** is dispersed in a CHCl_3 solution and sonicated during 5 minutes before being spin-coated onto an Au/mica substrate (ScienTec). All samples have been analysed by AFM prior to be subjected to STM.

Thermogravimetric analysis (TGA). All the TGAs were performed with a *TGA Q500* instrument manufactured by TA instruments (Italy), under a N_2 flow of $50 \text{ ml}\cdot\text{min}^{-1}$ following this method: equilibration from room temperature to $100 \text{ }^\circ\text{C}$ in 6 minutes, isothermal heating at $100 \text{ }^\circ\text{C}$ for 30 minutes, then thermal ramp from $100 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$ in 90 minutes (heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

1. Synthesis

Compounds were fully characterized (m.p., IR, ^1H and ^{13}C NMR, ES-MS). NMR spectra were obtained on a Jeol JNM-EX400 (400 MHz ^1H -NMR) and on a Varian Gemini 200 spectrometer (200 MHz ^1H -NMR and 50 MHz ^{13}C -NMR). Chemical shifts are reported in ppm using the

solvent residual signal as an internal reference (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublets), *m* (multiplet), *br* (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectrometer. Mass spectrometry measurements: Electron Impact (EI) performed on a Ion trap GCQ Finnigan Thermoquest at 70 eV were recorded at Università degli Studi di Trieste by Dr. Fabio Hollan. Melting Point (m.p.) was measured on a Büchi SMP-20. THF and NEt_3 were distilled from Na/benzophenone and CaH_2 respectively.

1,4-Bis(dodecyloxy)benzene (6). To a solution of hydroquinone (4 g, 36.33 mmol) in DMF (60 mL), K_2CO_3 (50.1 g, 0.363 mol) was added and the reaction mixture was allowed to stir at r.t. for 30 minutes. Following this, 1-bromododecane (26 mL, 108.98 mmol) was added to the mixture and the whole was stirred overnight at 60 °C. The suspension was diluted with CHCl_3 , washed with H_2O (40 mL \times 4), brine (40 mL \times 2), and dried over Na_2SO_4 . Concentration of the organic layer under vacuum and purification of the crude by CC (cyclohexane) yielded **6** (10.4 g, 64%) as a pale yellow crystalline solid. m.p. 72–73 °C; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 6.8 (*s*, 4H; Ar-*H*), 3.9 (*t*, 4H; Ar- $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 1.7 (*m*, 4H; Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H; Ar- $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H; Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ 153.35, 115.58, 68.91, 32.19, 29.94, 29.91, 29.86, 29.69, 29.58, 29.63, 26.34, 22.97, 14.40; IR (cm^{-1}): ν 2918.4, 2850.0, 1514.7, 1474.3, 1396.6, 1293.4, 1285.2, 1243.2, 1111.5, 1036.6, 826.1, 772.6, 728.7, 719.9, 538.2; MS (70 eV, EI): Found 446 (M^+), $\text{C}_{30}\text{H}_{54}\text{O}_2$ requires = 446.75.

1,4-Bis(dodecyloxy)-2,5-diiodobenzene (7). To a solution of **6** (2 g, 4.48 mmol) in CH_2Cl_2 (50 mL), $\text{Hg}(\text{OAc})_2$ (3.56 g, 11.19 mmol) and I_2 (2.8 g, 11.19 mmol) were added and the mixture was allowed to stir overnight at r.t. The reaction colour turned pink–purple and a white precipitate appeared. The precipitate was filtered over celite and the purple filtrate was washed with an aq. solution of $\text{Na}_2\text{S}_2\text{O}_5$ (50 mL \times 1), sat. aq. solution of NaHCO_3 (50 mL \times 1), H_2O (20 mL \times 2), brine (20 mL \times 2), and dried over Na_2SO_4 . Concentration of the organic layer and recrystallisation with hot EtOH yielded **7** (2.5 g, 80%) as a white crystalline solid. m.p. 65–67 °C; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.2 (*s*, 2H; Ar-*H*), 3.9 (*t*, 4H; Ar- $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 1.8 (*m*, 4H; Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H; Ar- $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H; Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ 152.92, 122.88, 86.43, 70.51, 32.10, 29.83, 29.76, 29.54, 29.73, 29.46, 29.32, 26.21, 22.89, 14.33; IR (cm^{-1}): ν 2919.3, 2848.3, 1487.8,

1460.0, 1389.0, 1353.3, 1263.1, 1216.3, 1071.2, 1053.2, 995.0, 846.7, 721.8; MS (70 eV, EI): Found 698 (M^+), $C_{30}H_{52}I_2O_2$ requires = 698.54.

1,4-Bis(dodecyloxy)-2,5-bis[(2,6-di(acetylamino)pyridin-4-yl)ethynyl]benzene (1a). To a degassed solution of dry Et_3N (4 mL) and THF (4 mL), **7** (0.2 g, 0.29 mmol), $[Pd(PPh_3)_4]$ (0.014 g, 0.012 mmol), and CuI (4 mg, 0.023 mmol) were added and the mixture degassed a second time. 2,6-Diacetylamino-4-ethynylpyridine⁵⁴ (0.16 g, 0.73 mmol) was then added, the reaction mixture degassed one last time, and refluxed overnight at 85 °C under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (cyclohexane/AcOEt, 5:5, then AcOEt) yielding **1a** (0.171 g, 68%) as a bright yellow solid. m.p. > 240 °C; 1H -NMR (200 MHz, $CDCl_3$): δ 8.1 (*s*, 4H; Py-*H*), 7.6 (*s*, 4H; CH_3CONH -Py), 7.0 (*s*, 2H; Ar-*H*), 4.1 (*t*, 4H; Ar- $OCH_2(CH_2)_{10}CH_3$), 2.2 (*s*, 12H; CH_3CONH -Py), 1.9 (*m*, 4H; Ar- $OCH_2CH_2(CH_2)_9CH_3$), 1.3 (*br*, 36H; Ar- $O(CH_2)_2(CH_2)_9CH_3$), 0.9 (*t*, 6H; Ar- $O(CH_2)_{11}CH_3$); ^{13}C -NMR (50 MHz, $CDCl_3$): δ 168.28, 153.66, 149.45, 136.13, 117.33, 113.62, 111.49, 92.95, 90.57, 69.83, 32.11, 29.83, 29.56, 29.51, 29.29, 26.14, 24.97, 22.88, 14.32; IR (cm^{-1}): ν 3285.3, 2959.1, 2925.6, 2220.3, 2162.1, 1708.1, 1685.4, 1612.1, 1554.9, 1419.2, 1249.8, 869.7, 843.0, 759.1, 642.1; MS (70 eV, EI): Found 877 (M^+), $C_{52}H_{72}N_6O_6$ requires = 877.16.

1,4-Bis(dodecyloxy)-2,5-bis[(trimethylsilyl)ethynyl]benzene (11). To a degassed solution of dry Et_3N (2.4 mL) and THF (2.4 mL), **7** (0.3 g, 0.43 mmol), $[Pd(PPh_3)_4]$ (0.02 g, 0.017 mmol), and CuI (6 mg, 0.034 mmol) were added and the mixture degassed a second time. TMSA (0.18 mL, 1.29 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was then filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane/AcOEt 7:3) yielding **11** (0.212 g, 40%) as a pale yellow crystalline solid. m.p. 70–73 °C; 1H -NMR (200 MHz, $CDCl_3$): δ 6.9 (*s*, 2H; Ar-*H*), 3.9 (*t*, 4H; Ar- $OCH_2(CH_2)_{10}CH_3$), 1.8 (*m*, 4H; Ar- $OCH_2CH_2(CH_2)_9CH_3$), 1.5 (*br*, 4H; Ar- $O(CH_2)_2CH_2(CH_2)_8CH_3$), 1.3 (*br*, 32H; Ar- $O(CH_2)_3(CH_2)_8CH_3$), 0.9 (*t*, 6; Ar- $O(CH_2)_{11}CH_3$), 0.2 (*s*, 18H; $Si(CH_3)_3$); ^{13}C -NMR (50 MHz, $CDCl_3$): δ 154.06, 117.22, 114.03, 101.16, 100.12, 69.53, 32.10, 29.86, 29.82, 29.61, 29.54, 26.21, 22.88, 14.32, 0.15; some peaks in the aliphatic region are missing probably due to overlap; IR (cm^{-1}): ν 2851.0, 2870.6, 2157.0, 1500.1, 1470.7, 1407.5, 1387.6, 1249.4, 1223.8, 1204.0, 1046.4, 1033.8, 894.9, 842.3, 759.5, 723.2, 626.8; MS (70 eV, EI): Found 639 (M^+), $C_{40}H_{70}O_2Si_2$ requires = 639.15.

1,4-Bis(dodecyloxy)-2,5-di(ethynyl)benzene (12). To a solution of **11** (0.2 g, 0.31 mmol) in 6 mL of THF/MeOH (1:1), 1 mL of 1 M KOH aq. solution was added and the whole was stirred 1 h at r.t. H₂O (10 mL) was then added and the organic phase extracted with CHCl₃ (10 mL × 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded **12** as brown crystalline solid in a quantitative yield. m.p. 69–72 °C; ¹H-NMR (200 MHz, CDCl₃): δ 7.0 (*s*, 2H; Ar-*H*), 4.0 (*t*, 4H; Ar-OCH₂(CH₂)₁₀CH₃), 3.35 (*s*, 2H; acetylene-*H*), 1.8 (*m*, 4H; Ar-OCH₂CH₂(CH₂)₉CH₃), 1.4 (*br*, 36H; Ar-O(CH₂)₂(CH₂)₉CH₃), 0.9 (*t*, 6H; Ar-O(CH₂)₁₁CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 154.00, 117.75, 113.31, 82.51, 79.88, 69.73, 32.08, 29.83, 29.82, 29.75, 29.73, 29.53, 29.49, 29.28, 26.06, 22.86, 14.29; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3457.1, 3286.5, 2923.4, 2849.2, 1500.7, 1466.2, 1385.0, 1218.2, 1199.9, 1029.7, 864.8, 645.2; MS (70 eV, EI): Found 494 (M⁺), C₃₄H₅₄O₂ requires = 494.79.

1,4-Bis(dodecyloxy)-2,5-bis[(1-hexylurac-6-yl)-ethynyl]benzene (4). To a degassed solution of dry Et₃N (6 mL) and THF (6 mL), 1-hexyl-6-iodouracil⁵⁴ (0.16 g, 0.5 mmol), [Pd(PPh₃)₄] (9 mg, 0.008 mmol) and CuI (3 mg, 0.016 mmol) were added and the mixture degassed a second time. **12** (0.1 g, 0.2 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was then filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane/AcOEt 7:3, 5:5, then CHCl₃) yielding **4** (0.14 g, 77%) as a bright yellow solid. m.p. 70–73 °C; ¹H-NMR (200 MHz, CDCl₃): δ 9.2 (*s*, 2H; CONHCO), 7.0 (*s*, 2H; Ar-*H*), 6.0 (*s*, 2H; COCH), 4.11 (*t*, 4H; Ar-OCH₂(CH₂)₁₀CH₃), 4.00 (*t*, 4H; NCH₂(CH₂)₄CH₃), 1.8 (*m*, 8H, Ar-OCH₂CH₂(CH₂)₉CH₃ and NCH₂CH₂(CH₂)₃CH₃), 1.3 (*br*, 48H, Ar-O(CH₂)₂(CH₂)₉CH₃ and N(CH₂)₂(CH₂)₃CH₃), 0.9 (*t*, 12H, Ar-O(CH₂)₁₁CH₃ and N(CH₂)₅CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 163.40, 154.06, 150.86, 138.69, 116.22, 112.74, 106.42, 96.67, 85.88, 69.37, 46.54, 31.78, 31.34, 29.50, 29.46, 29.20, 29.02, 28.69, 26.22, 25.77, 22.54, 22.45, 13.85, 13.73; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3434.8, 2924.1, 2854.3, 2214.3, 1671.1, 1588.9, 1459.2, 1413.6, 1284.4, 1220.8, 812.7; MS (70 eV, EI): Found 883 (M⁺), C₅₄H₈₂N₄O₆ requires = 883.25.

1,4-Bis(dodecyloxy)-2-[(trimethylsilyl)ethynyl]-5-iodobenzene (8). To a degassed solution of dry Et₃N (14 mL) and THF (14 mL), **7** (1.8 g, 2.57 mmol), [Pd(PPh₃)₄] (0.119 g, 0.103 mmol), and CuI (0.04 g, 0.206 mmol) were added and the mixture degassed a second time. TMSA (0.36

mL, 2.57 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (first cyclohexane, then cyclohexane/AcOEt 8:2) yielding **8** (0.623 g, 37%) as a yellow solid. m.p. 37–39 °C; ¹H-NMR (200 MHz, CDCl₃): δ 7.3 (*s*, 1H; Ar-*H*), 6.8 (*s*, 1H; Ar-*H*), 4.0 (*t*, 4H; Ar-OCH₂(CH₂)₁₀CH₃), 1.8 (*m*, 4H; Ar-OCH₂CH₂(CH₂)₉CH₃), 1.3 (*br*, 36H; Ar-O(CH₂)₂(CH₂)₉CH₃), 0.9 (*t*, 6H; Ar-O(CH₂)₁₁CH₃), 0.2 (*s*, 9H, Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 154.69, 151.69, 123.76, 116.27, 113.42, 100.877, 96.48, 87.99, 70.15, 69.83, 32.12, 29.87, 29.85, 29.83, 29.78, 29.76, 29.61, 29.56, 29.50, 29.35, 27.09, 27.06, 26.24, 26.17, 22.90, 14.33, 0.14; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 2921.9, 2850.7, 2161.5, 1485.1, 1468.4, 1374.1, 1249.4, 1214.3, 1163.1, 1032.7, 859.7, 842.3, 758.9, 723.0; MS (70 eV, EI): Found 668 (M⁺), C₃₅H₆₁IO₂Si requires = 668.85.

1,4-Bis(dodecyloxy)-2-[(trimethylsilyl)ethynyl]-5-[(2,6-di(acetylamino)pyridine-4-yl)ethynyl]benzene (9). To a degassed solution of dry Et₃N (12 mL) and THF (12 mL), **8** (0.6 g, 0.897 mmol), [Pd(PPh₃)₄] (0.042 g, 0.036 mmol), and CuI (0.014 g, 0.072 mmol) were added and the mixture degassed a second time. 2,6-Diacetylamino-4-ethynylpyridine (**76**) (0.290 g, 1.07 mmol) was then added, the reaction mixture degassed one last time, and stirred at r.t. for 48 h under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (CH₂Cl₂/AcOEt 9.5:0.5) yielding **9** (0.431 g, 63%) as a yellow fluorescent solid. m.p. 86–90 °C; ¹H-NMR (200 MHz, CDCl₃): δ 8.0 (*s*, 2H; Py-*H*), 7.9 (*s*, 2H; CH₃CONH-Py), 6.96 (*s*, 1H, Ar-*H*), 6.95 (*s*, 1H; Ar-*H*), 3.9 (*t*, 4H; Ar-OCH₂(CH₂)₁₀CH₃), 2.1 (*s*, 6H; CH₃CONH-Py), 1.8 (*m*, 4H; Ar-OCH₂CH₂(CH₂)₉CH₃), 1.5 (*m*, 4H; Ar-O(CH₂)₂CH₂(CH₂)₈CH₃), 1.3 (*br*, 32H; Ar-O(CH₂)₃(CH₂)₈CH₃), 0.9 (*t*, 6H; Ar-O(CH₂)₁₁CH₃), 0.2 (*s*, 9H; Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 168.62, 154.05, 153.69, 149.58, 135.83, 117.29, 117.09, 114.77, 112.93, 111.39, 100.97, 100.72, 92.59, 90.54, 69.73, 69.51, 32.02, 29.75, 29.56, 29.46, 29.38, 29.19, 26.14, 26.02, 24.71, 22.78, 14.23, 0.05; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3426.4, 2921.6, 2851.7, 2156.8, 1717.3, 1610.6, 1561.6, 1502.1, 1418.7, 1274.8, 1222.5, 1209.8, 1031.9, 865.7, 842.7, 623.5, 567.7; MS (70 eV, EI): Found 758 (M⁺), C₄₆H₇₁N₃O₄Si requires = 758.16.

1,4-Bis(dodecyloxy)-2-ethynyl-5-[(2,6-Di(acetylamino)pyridine-4-yl)ethynyl]benzene (10).

To a solution of **9** (0.4 g, 0.54 mmol) in 20 mL of CH₂Cl₂:MeOH (1:1), 6 mL of 1 M KOH aq. solution was added and the whole was stirred overnight at r.t. Following this, H₂O (10 mL) was added to the mixture and the organic phase was extracted with CHCl₃ (10 mL × 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded **10** as a yellow solid in a quantitative yield. m.p. 93–95 °C; ¹H-NMR (200 MHz, CDCl₃): δ 8.0 (*s*, 2H; Py-*H*), 7.9 (*s*, 2H; CH₃CONH-Py), 6.96 (*s*, 1H; Ar-*H*), 6.95 (*s*, 1H; Ar-*H*), 3.9 (*t*, 4H; Ar-OCH₂(CH₂)₁₀CH₃), 3.35 (*s*, 1H; acetylene-*H*), 2.18 (*s*, 6H; CH₃CONH-Py), 1.8 (*m*, 4H; Ar-OCH₂CH₂(CH₂)₉CH₃), 1.5 (*m*, 4H; Ar-O(CH₂)₂CH₂(CH₂)₈CH₃), 1.3 (*br*, 32H; Ar-O(CH₂)₃(CH₂)₈CH₃), 0.9 (*t*, 6H; Ar-O(CH₂)₁₁CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 168.59, 168.54, 154.04, 153.67, 149.59, 135.80, 117.84, 117.12, 113.64, 113.36, 111.42, 92.61, 90.31, 82.83, 79.94, 69.78, 69.69, 32.01, 31.98, 29.78, 29.75, 29.73, 29.71, 29.59, 29.56, 29.53, 29.47, 29.45, 29.39, 29.34, 29.25, 29.17, 26.02, 24.72, 22.83, 22.79, 22.76, 14.28, 14.23; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3290.7, 2921.6, 2852.8, 2214.1, 1679.5, 1611.7, 1558.2, 1503.6, 1418.4, 1277.2, 1207.5, 1033.3, 862.3, 636.3; MS (70 eV, EI): Found 685 (M⁺), C₄₃H₆₃N₃O₄ requires = 685.98.

1,4-Bis[[1,4-Bis(dodecyloxy)-2,5-Bis[(2,6-Di(acetylamino)pyridine-4-yl-ethynyl]benzenyl] benzene (1b). To a degassed solution of dry Et₃N (4 mL) and THF (4 mL), 1,4-diiodobenzene (0.036 g, 0.11 mmol), [Pd(PPh₃)₄] (5 mg, 0.004 mmol), and CuI (2 mg, 0.008 mmol) were added and the mixture degassed a second time. **10** (0.2 g, 0.29 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (cyclohexane/AcOEt 5:5) yielding **1b** (0.157 g, 46.5%) as a yellow fluorescent solid. m.p. 180–200 °C; ¹H-NMR (200 MHz, CDCl₃): δ 8.0 (*s*, 4H; Py-*H*₄), 7.7 (*s*, 4H; CH₃CONH-Py), 7.5 (*s*, 4H; Ar-*H*₁), 7.05 (*s*, 2H; Ar-*H*₂), 7.00 (*s*, 2H; Ar-*H*₃), 3.9 (*t*, 8H; Ar-OCH₂(CH₂)₁₀CH₃), 2.2 (*s*, 12H; CH₃CONH-Py), 1.85 (*m*, 8H; Ar-OCH₂CH₂(CH₂)₉CH₃), 1.55 (*m*, 8H; Ar-O(CH₂)₂CH₂(CH₂)₈CH₃), 1.3 (*br*, 64H; Ar-O(CH₂)₃(CH₂)₈CH₃), 0.9 (*t*, 12H; Ar-O(CH₂)₁₁CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 168.66, 154.95, 154.09, 154.85, 153.849, 153.68, 149.24, 132.25, 132.06, 131.58, 128.80, 128.56, 123.37, 117.32, 117.08, 114.97, 112.99, 111.37, 96.221, 92.66, 88.04, 79.94, 69.93, 69.77, 32.10, 29.84, 29.62, 29.55, 29.50, 29.33, 26.25, 26.16, 24.92, 22.87, 14.32; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3171.7, 2921.8, 2851.6, 2215.6, 1709.8, 1682.8, 1612.4, 1557.8, 1417.0, 1276.5, 1206.8,

1027.3, 996.6; MS (5600 eV, ESI): Found 1468.9 ($M + Na$)⁺, $C_{92}H_{128}N_6O_8Na$ requires = 1469.04.

1,2-Bis(dodecyloxy)benzene (14). To a solution of pyrocatechol (4 g, 36.33 mmol) in DMF (60 mL), K_2CO_3 (35 g, 0.25 mol) was added and the reaction mixture was allowed to stir at r.t. for 30 minutes. Following this, 1-bromododecane (26 mL, 0.11 mol) was added to the mixture and the whole stirred overnight at 60 °C. The suspension was diluted with $CHCl_3$, washed with H_2O (40 mL \times 4), brine (40 mL \times 2) and dried over Na_2SO_4 . Concentration of the organic layer under vacuum and purification by recrystallisation with EtOH, yielded **14** (11.27 g, 70%) as a white solid. m.p. 45 °C; 1H -NMR (200 MHz, $CDCl_3$): δ 6.9 (*s*, 4H; Ar-*H*), 3.9 (*t*, 4H; Ar- $OCH_2(CH_2)_{10}CH_3$), 1.8 (*m*, 4H; Ar- $OCH_2CH_2(CH_2)_9CH_3$), 1.3 (*br*, 36H; Ar- $O(CH_2)_2(CH_2)_9CH_3$), 0.9 (*t*, 6H; Ar- $O(CH_2)_{11}CH_3$); ^{13}C -NMR (50 MHz, $CDCl_3$): δ 149.31, 121.08, 114.21, 69.42, 32.12, 29.89, 29.86, 29.83, 29.64, 29.56, 29.54, 26.25, 22.89, 14.32; some peaks in the aliphatic region are missing probably due to overlap; IR (cm^{-1}): ν 2918.1, 2849.0, 1594.4, 1519.4, 1509.0, 1467.1, 1390.1, 1332.0, 1258.0, 1222.2, 1122.4, 997.7, 732.7; MS (70 eV, EI): Found 446 (M^+), $C_{30}H_{54}O_2$ requires = 446.75. Spectral data agree with that previously reported.⁵⁹

1,2-Bis(dodecyloxy)-4,5-diiodobenzene (15). To a solution of **14** (2 g, 4.48 mmol) in CH_2Cl_2 (50 mL), $Hg(OAc)_2$ (3.56 g, 11.19 mmol) and I_2 (2.8 g, 11.19 mmol) were added and the mixture allowed to stir overnight at r.t. The reaction colour turned pink-purple and a white precipitate appeared. The precipitate was filtered over celite and the purple filtrate washed with an aq. solution of $Na_2S_2O_5$ (50 mL), sat. aq. solution of $NaHCO_3$ (50 mL), H_2O (20 mL \times 2), brine (20 mL \times 2), and dried over Na_2SO_4 . Concentration of the organic layer and recrystallisation in hot EtOH yielded **15** (3.12 g, 85%) as a pale yellow crystalline solid. m.p. 57–60 °C; 1H -NMR (200 MHz, $CDCl_3$): δ 7.24 (*s*, 2H; Ar-*H*), 3.9 (*t*, 4H; Ar- $OCH_2(CH_2)_{10}CH_3$), 1.8 (*m*, 4H; Ar- $OCH_2CH_2(CH_2)_9CH_3$), 1.3 (*br*, 36H; Ar- $O(CH_2)_2(CH_2)_9CH_3$), 0.9 (*t*, 6H; Ar- $O(CH_2)_{11}CH_3$); ^{13}C -NMR (50 MHz, $CDCl_3$): δ 149.78, 123.79, 96.02, 69.56, 32.06, 29.62, 29.79, 29.73, 29.49, 29.47, 29.17, 26.05, 22.83, 14.27; some peaks in the aliphatic region are missing probably due to overlap; IR (cm^{-1}): ν 2918.1, 1850.1, 1471.3, 1245.7, 1196.0, 856.9; MS (70 eV, EI): Found 698 (M^+), $C_{30}H_{52}I_2O_2$ requires = 698.54.

1,2-Bis(dodecyloxy)-4,5-bis[(trimethylsilyl)ethynyl]benzene (16). To a degassed solution of dry Et_3N (8 mL) and THF (8 mL), **15** (1 g, 1.43 mmol), $[Pd(PPh_3)_4]$ (0.067 g, 0.058 mmol), and

CuI (0.021 g, 0.11 mmol) were added and the mixture degassed a second time. Trimethylsilylacetylene (0.59 mL, 4.29 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. Following this, the crude mixture was filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane/AcOEt 9:1, then 7:3) yielding **16** (0.320 g, 35.6%) as a yellow oil. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 6.9 (*s*, 2H; Ar-*H*), 3.9 (*t*, 4H; Ar- $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 1.8 (*m*, 4H; Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H; Ar- $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H; Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$), 0.2 (*s*, 18H; $\text{Si}(\text{CH}_3)_3$); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ 149.07, 118.75, 116.22, 103.69, 96.46, 69.17, 32.06, 29.83, 29.79, 29.74, 29.51, 29.20, 26.09, 22.84, 14.27, 0.31; some peaks in the aliphatic region are missing probably due to overlap; IR (cm^{-1}): ν 3433.2, 2925.6, 2854.7, 2154.9, 1508.8, 1467.9, 1249.2, 1206.7, 843.2, 759.5; MS (70 eV, EI): Found 639 (M^+), $\text{C}_{40}\text{H}_{70}\text{O}_2\text{Si}_2$ requires = 639.15.

1,2-Bis(dodecyloxy)-4,5-bis(ethynyl)benzene (17). To a solution of **16** (0.3 g, 0.47 mmol) in 6 mL of THF/MeOH (1:1), 1 mL of 1 M KOH aq. solution was added and the whole stirred 1 h at r.t. H_2O (10 mL) was added and the organic phase extracted with CHCl_3 (10 mL \times 5) and dried over Na_2SO_4 . Evaporation of the solvent under vacuum yielded **17** as brown crystalline solid in a quantitative yield. m.p. 48–50 °C; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 6.9 (*s*, 2H; Ar-*H*), 4.0 (*t*, 4H; Ar- $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 3.2 (*s*, 2H; acetylene-*H*), 1.8 (*m*, 4H; Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.3 (*br*, 36H; Ar- $\text{O}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 0.9 (*t*, 6H; Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): δ 149.39, 117.81, 116.56, 82.27, 79.46, 69.25, 32.06, 29.83, 29.79, 29.74, 29.50, 29.16, 26.08, 22.84, 14.27; some peaks in the aliphatic region are missing probably due to overlap; IR (cm^{-1}): ν 3292.6, 2929.3, 2850.3, 1595.1, 1509.3, 1470.9, 1338.2, 1265.0, 1216.3, 1093.5, 619.6; MS (70 eV, EI): Found 494 (M^+), $\text{C}_{34}\text{H}_{54}\text{O}_2$ requires = 494.79.

1,2-Bis(dodecyloxy)-4,5-bis[(1-hexylurac-6-yl)ethynyl]benzene (2). To a degassed solution of dry Et_3N (10 mL) and THF (10 mL), 1-hexyl-6-iodouracil⁵⁴ (0.096 g, 0.3 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (6 mg, 0.005 mmol), and CuI (2 mg, 0.01 mmol) were added and the mixture degassed a second time. **17** (0.06 g, 0.12 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. Following this, the crude mixture was filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane/AcOEt 5:5) yielding **2** (0.06g, 51%) as a yellow solid. m.p. 137 °C the compound burnt; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 8.9 (*s*, 2H; CONHCO), 6.9 (*s*, 2H; Ar-*H*), 6.0 (*s*, 2H; COCH), 4.0 (*m*, 8H; Ar-

OCH₂(CH₂)₁₀CH₃ and NCH₂(CH₂)₄CH₃), 1.8 (*m*, 4H; Ar–OCH₂CH₂(CH₂)₉CH₃), 1.7 (*m*, 4H; NCH₂CH₂(CH₂)₃CH₃), 1.3 (*br*, 48H; Ar–O(CH₂)₂(CH₂)₉CH₃ and N(CH₂)₂(CH₂)₃CH₃), 0.9 (*t*, 12H; Ar–O(CH₂)₁₁CH₃ and N(CH₂)₅CH₃); ¹³C–NMR (50 MHz, CDCl₃): δ 162.26, 151.07, 150.59, 138.25, 116.04, 107.07, 98.28, 83.13, 69.56, 46.80, 32.08, 31.57, 29.86, 29.82, 29.76, 29.53, 29.11, 28.99, 26.53, 26.10, 22.86, 22.71, 14.29, 14.13; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 2926.7, 2854.8, 2210.6, 1707.1, 1683.4, 1580.4, 1513.4, 1466.7, 1400.9, 1246.2, 1091.7, 837.0, 775.2; MS (70 eV, EI): Found 883 (M⁺), C₅₄H₈₂N₄O₆ requires = 883.25.

3,5–Dibromo–1–octadecyloxybenzene (19). To a solution of 3,5–dibromophenol (1 g, 3.9 mmol) in DMF (15 mL), K₂CO₃ (5.3 g, 39 mmol) was added. The reaction mixture was stirred at r.t. for 30 minutes. Iodoctadecene (2.24 g, 5.9 mmol) was added to the reaction mixture and the whole was allowed to stir overnight at 60 °C. After cooling to r.t., the organic phase was diluted with CHCl₃, washed with H₂O (20 mL × 4), brine (20 mL × 2), and dried over Na₂SO₄. Concentration of the organic layer under vacuum and purification by CC (heptane), yielded **19** (1.6 g, 80%) as a white crystalline solid. m.p. 50–53 °C; ¹H–NMR (200 MHz, CDCl₃): δ 7.2 (*s*, 1H; Ar–*H*), 6.9 (*s*, 2H; Ar–*H*), 3.9 (*t*, 2H; Ar–OCH₂(CH₂)₁₆CH₃), 1.7 (*m*, 2H; Ar–OCH₂CH₂(CH₂)₁₅CH₃), 1.3 (*br*, 30H; Ar–O(CH₂)₂(CH₂)₁₅CH₃), 0.9 (*t*, 3H; Ar–O(CH₂)₁₇CH₃); ¹³C–NMR (50 MHz, CDCl₃): δ 160.39, 126.21, 123.13, 116.99, 68.75, 32.13, 29.90, 29.87, 29.77, 29.73, 29.57, 29.49, 29.18, 26.1, 22.91, 14.34; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3081.4, 2922.1, 2848.9, 1707.5, 1679.7, 1583.1, 1557.6, 1468.5, 1439.2, 1417.6, 1389.1, 1297.3, 1254.6, 1230.3, 1035.5, 889.3, 889.3, 831.6, 742.0, 721.5, 666.7; MS (70 eV, EI): Found 504 (M⁺), C₂₄H₄₀Br₂O requires = 504.38.

3,5–Bis[(trimethylsilyl)ethynyl]–1–octadecyloxybenzene (21). To a degassed solution of dry *i*Pr₂NH (12 mL) and DMF (8 mL), **19** (1.1 g, 2.2 mmol), [PdCl₂(PPh₃)₂] (0.077 g, 0.1 mmol), CuI (0.042 g, 0.22 mmol) and trimethylsilylacetylene (0.9 mL, 6.5 mmol) were added, and the reaction mixture irradiated through microwaves during 5 minutes at 120 °C. The crude mixture was filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane) yielding **21** (0.9 g, 77%) as a pale yellow solid. m.p. 53–54 °C; ¹H–NMR (200 MHz, CDCl₃): δ 7.2 (*s*, 1H; Ar–*H*), 6.9 (*s*, 2H; Ar–*H*), 3.9 (*t*, 2H; Ar–OCH₂(CH₂)₁₆CH₃), 1.7 (*m*, 2H; Ar–OCH₂CH₂(CH₂)₁₅CH₃), 1.3 (*br*, 30H; Ar–O(CH₂)₂(CH₂)₁₅CH₃), 0.9 (*t*, 3H; Ar–O(CH₂)₁₇CH₃), 0.2 (*s*, 18H, Si(CH₃)₃); ¹³C–NMR (50 MHz, CDCl₃): δ 158.64, 126.07, 124.22,

118.37, 104.24, 94.6, 68.36, 32.13, 29.89, 29.86, 29.79, 29.77, 29.57, 29.53, 29.31, 26.16, 22.91, 14.35, 0.12; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3446.6, 2917.8, 2166.3, 1579.0, 1472.0, 1417.3, 1297.2, 1251.3, 1167.0, 1049.0, 989.6, 846.0, 760.1; MS (70 eV, EI): Found 538, C₃₄H₅₈OSi₂ requires = 538.99.

3,5-Bis(ethynyl)-1-octadecyloxybenzene (22). To a solution of **21** (0.781 g, 1.44 mmol) in 12 mL of THF/MeOH (1:1), 5 mL of 1 M KOH aq. solution was added and the whole stirred 2 h at r.t. H₂O (10 mL) was added to the mixture and the organic phase extracted with CHCl₃ (10 mL \times 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded **22** in a quantitative yield. m.p. 56–59 °C; ¹H-NMR (200 MHz, CDCl₃): δ 7.2 (*s*, 1H; Ar-*H*), 7.0 (*s*, 2H; Ar-*H*), 3.9 (*t*, 2H; Ar-OCH₂(CH₂)₁₆CH₃), 3.05 (*s*, 2H; acetylene-*H*), 1.8 (*m*, 2H; Ar-OCH₂CH₂(CH₂)₁₅CH₃), 1.3 (*br*, 30H; Ar-O(CH₂)₂(CH₂)₁₅CH₃), 0.9 (*t*, 3H; Ar-O(CH₂)₁₇CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 158.76, 128.13, 123.39, 118.95, 82.78, 77.63, 68.43, 32.11, 29.89, 29.77, 29.75, 29.56, 29.52, 29.27, 26.14, 22.89, 14.31; some peaks in the aliphatic region are missing probably due to overlap; IR (cm⁻¹): ν 3282.1, 2920.2, 2850.3, 1582.0, 1466.8, 1420.6, 1323.7, 1295.9, 1162.6, 1144.4, 1054.9, 854.1; MS (70 eV, EI): Found 394, C₂₈H₄₂O requires = 394.63.

3,5-Bis[(1-hexylurac-6-yl)ethynyl]-1-octadecyloxybenzene (3). To a degassed solution of dry Et₃N (10 mL) and THF (10 mL), 1-hexyl-6-iodouracil⁵⁴ (0.37 g, 1.15 mmol), [Pd(PPh₃)₄] (0.021 g, 0.018 mmol), and CuI (0.018 g, 0.092 mmol) were added and the mixture degassed a second time. **22** (0.18 g, 0.46 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was filtered over celite, the solvent concentrated under vacuum and the precipitate purified by CC (cyclohexane/AcOEt 5:5) yielding **3** (0.16 g, 46%) as a white solid. m.p. 175 °C the compound burnt; ¹H-NMR (400 MHz, CDCl₃): δ 8.2 (*s*, 2H; CONHCO), 7.2 (*s*, 1H; Ar-*H*), 7.1 (*s*, 2H; Ar-*H*), 6.0 (*s*, 2H; COCH), 4.0 (*m*, 6H; Ar-OCH₂(CH₂)₁₆CH₃ and NCH₂(CH₂)₄CH₃), 1.6 (*m*, 6H; Ar-OCH₂CH₂(CH₂)₁₅CH₃ and NCH₂CH₂(CH₂)₃CH₃), 1.3 (*br*, 42H; Ar-O(CH₂)₂(CH₂)₁₅CH₃ and N(CH₂)₂(CH₂)₃CH₃), 0.9 (*t*, 9H; Ar-O(CH₂)₁₇CH₃ and N(CH₂)₅CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 162.47, 159.36, 150.69, 138.13, 127.23, 122.14, 120.04, 107.51, 98.28, 81.04, 68.86, 46.85, 32.08, 31.61, 29.85, 29.75, 29.51, 29.19, 28.96, 26.54, 26.11, 22.85, 22.73, 14.29, 14.17; some peaks in the aliphatic region

are missing probably due to overlap; IR (cm^{-1}): ν 2924.1, 2853.4, 1718.8, 1702.1, 1597.5, 1459.2, 1153.2, 863.5; MS (70 eV, EI): Found 783, $\text{C}_{48}\text{H}_{70}\text{N}_4\text{O}_5$ requires = 783.09.

Preparation of the Supramolecular composites

1st Solubilization Cycle. To a dispersion of MWCNTs (6 mg) in CHCl_3 (15 mL), 5 ml of a CHCl_3 solution containing **X** (3×10^{-3} M) and **Y** (3×10^{-3} M) were added. {NOTE: X = 1a or 1b and Y = 2, 3, or 4. } The solution was then allowed to stir overnight at room temperature. After centrifugation (12000 rpm, 15 min) all the non-dispersed tubes were removed from each solution. The solutions were then filtered through a Teflon (JH) Millipore® filter (pore size = $0.45 \mu\text{m}$) and the solid black precipitate copiously washed with CHCl_3 in order to completely remove the unbound molecules (which were recovered for subsequent experiments). The tubes were then allowed to dry overnight under vacuum. *2nd Solubilization Cycle.* The recovered CHCl_3 solution containing the excess of unbound molecules after the first wrapping, was then used to perform a new reaction cycle using the same conditions as described for the first solubilization cycle.

2. ^1H and ^{13}C NMR characterization.

^1H and ^{13}C NMR spectra of molecule **1a**

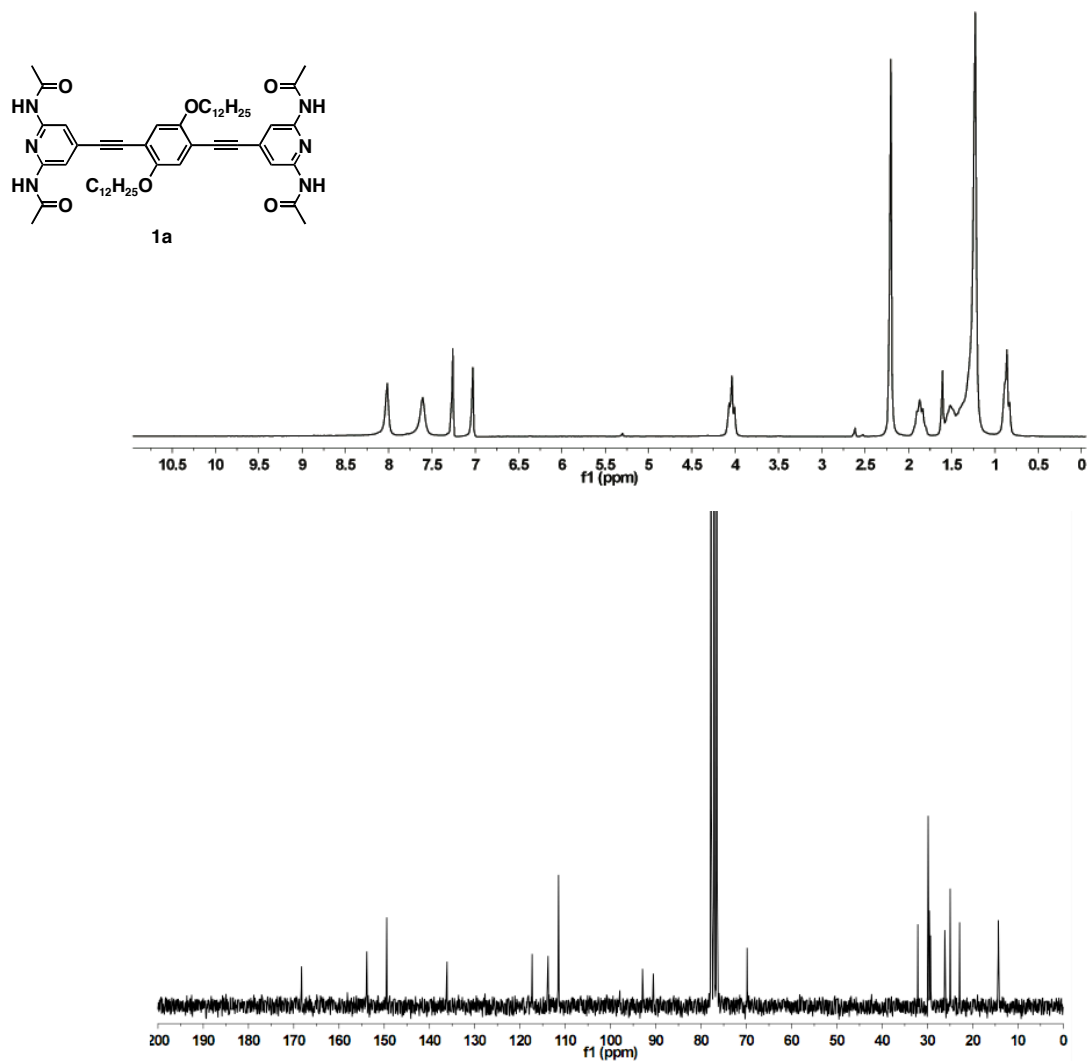


Figure S1. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule **1a** in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule **1b**

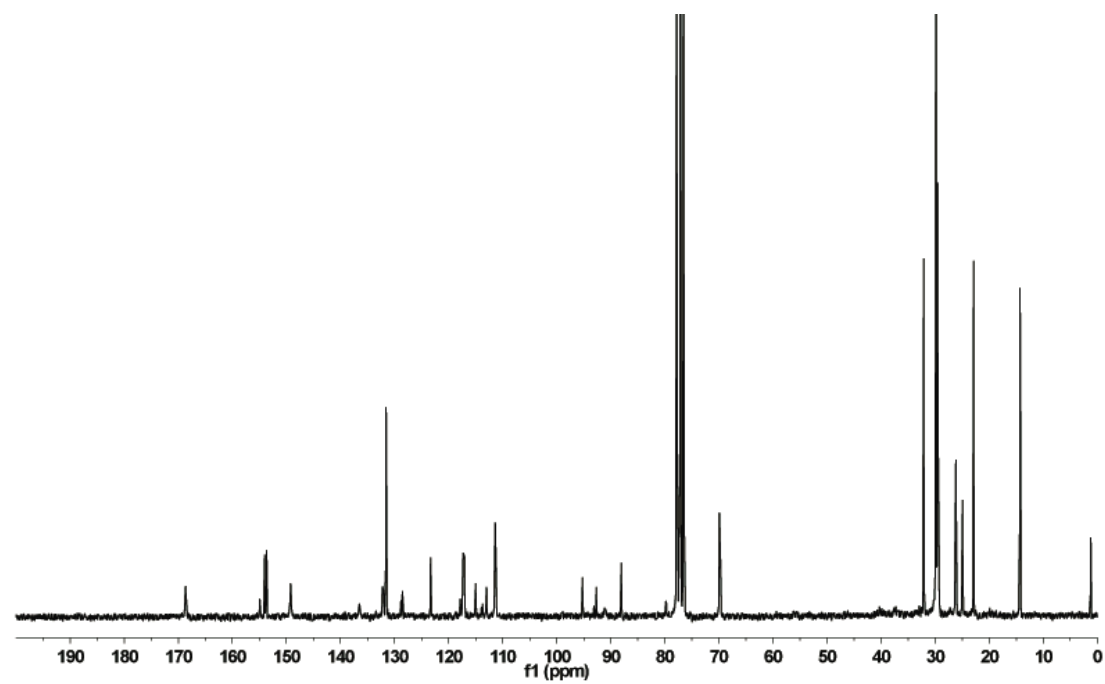
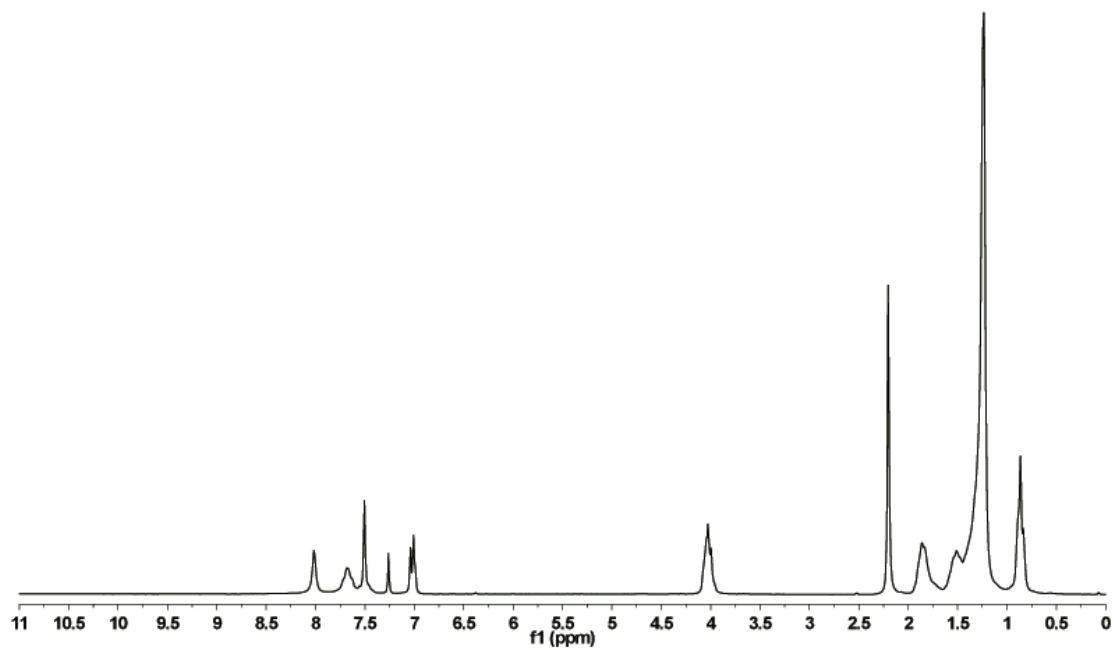
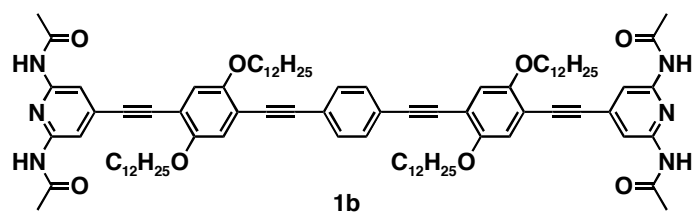


Figure S2. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule **1b** in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 2

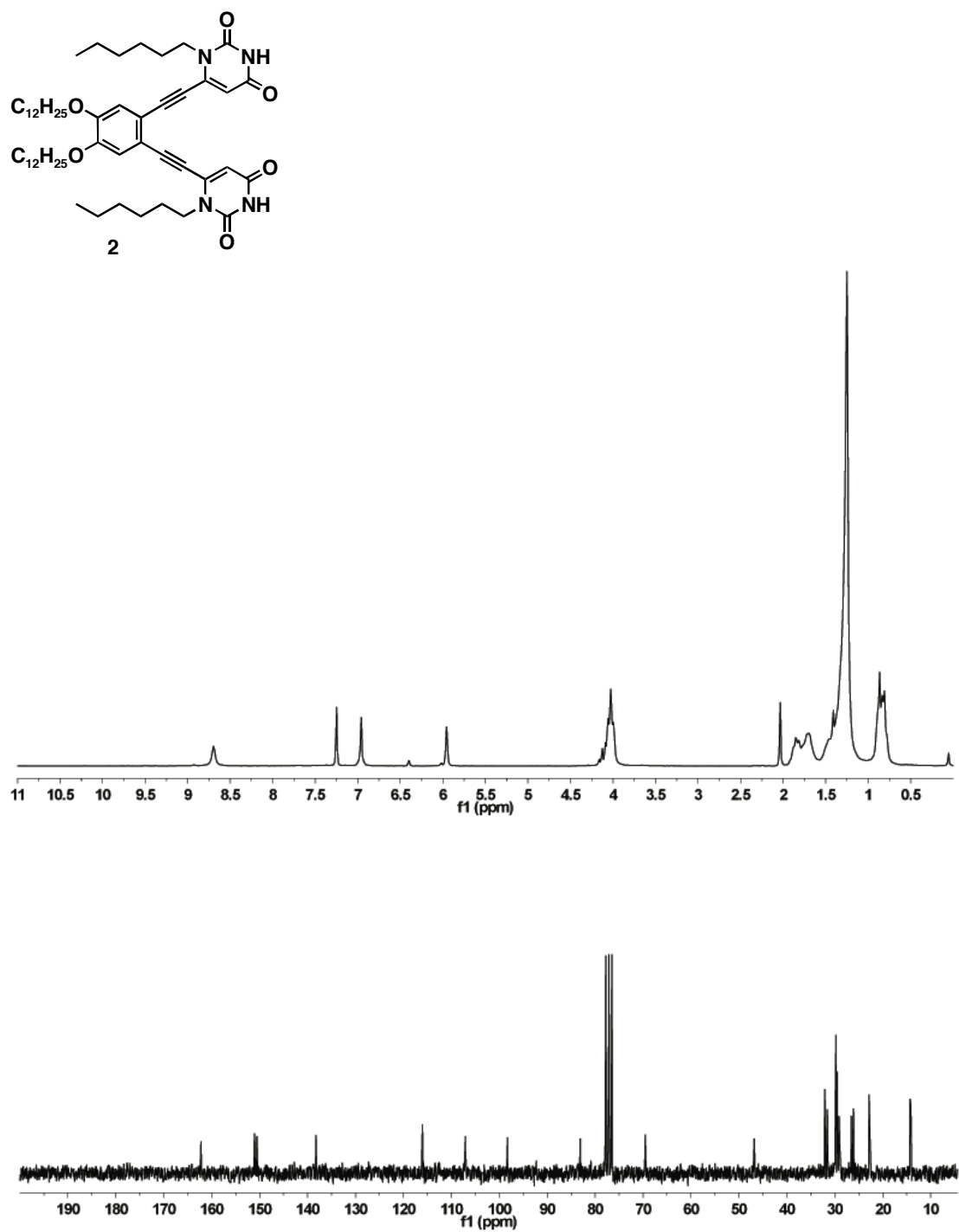


Figure S3. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 2 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 3

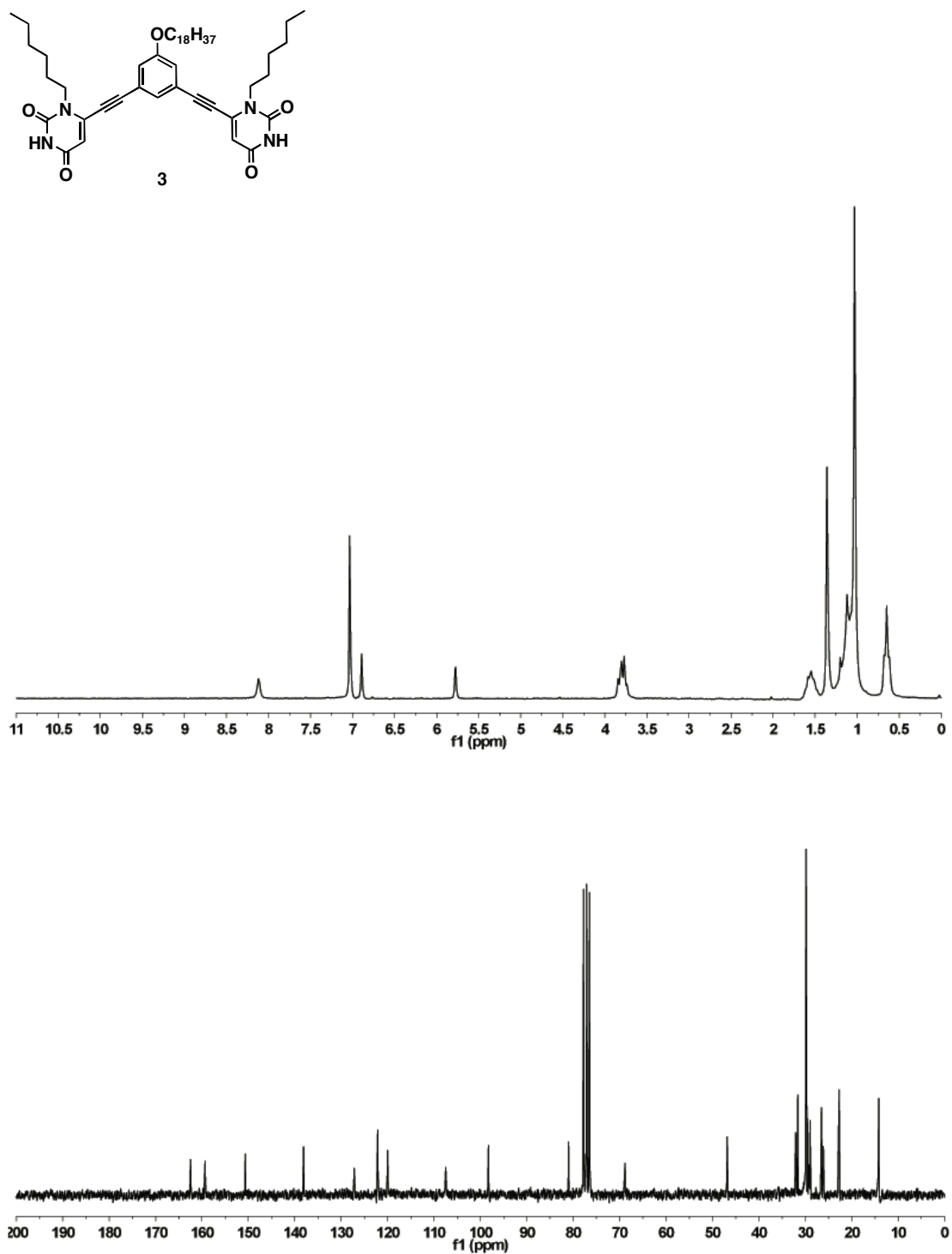


Figure S4. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 3 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 4

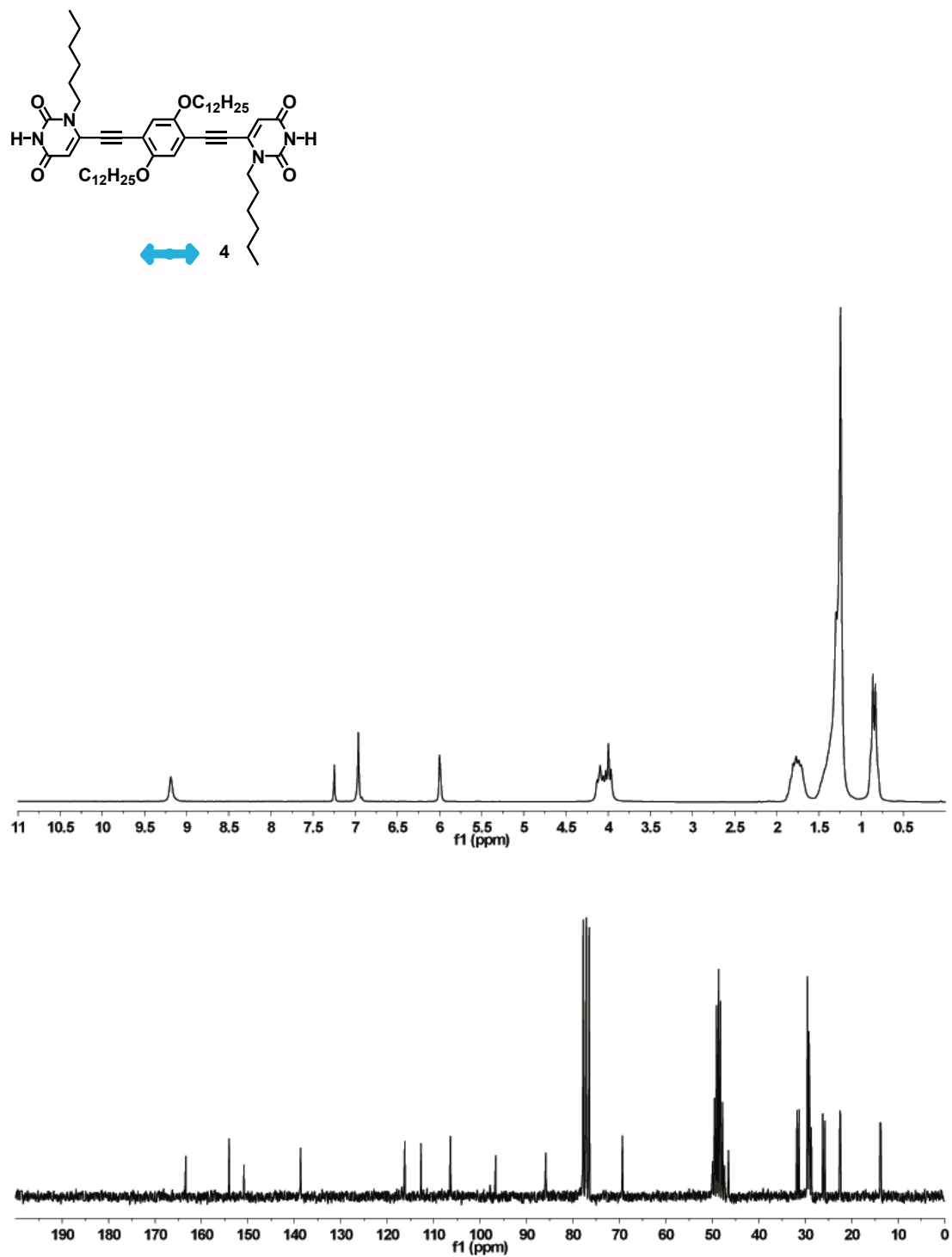
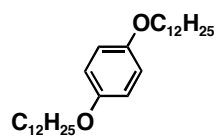


Figure S5. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 4 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 6



6

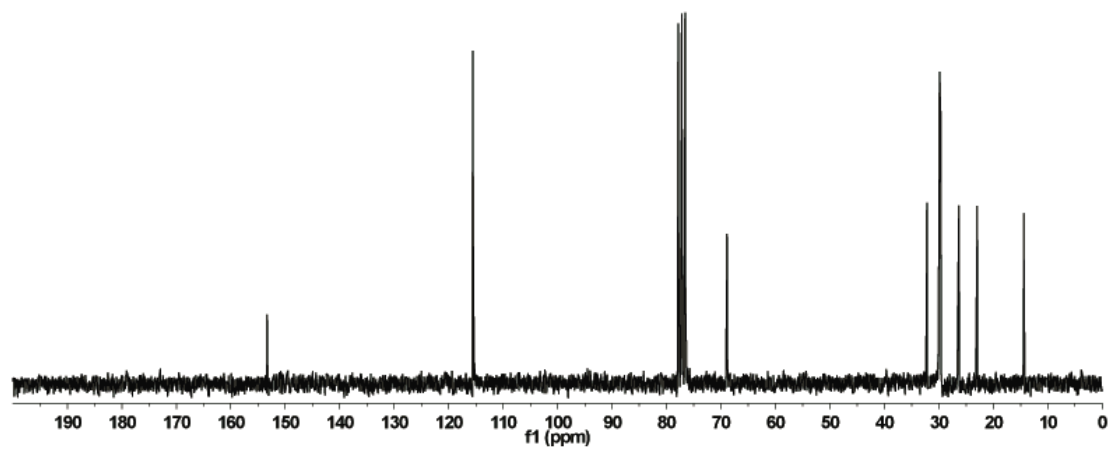
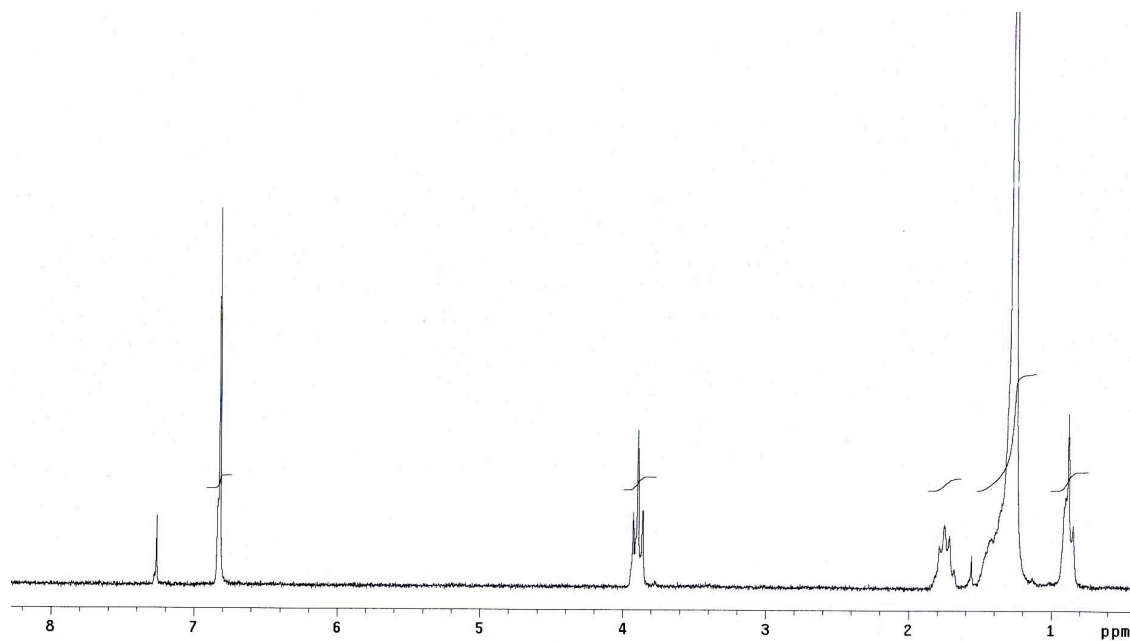
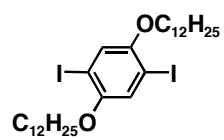


Figure S6. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 6 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 7



7

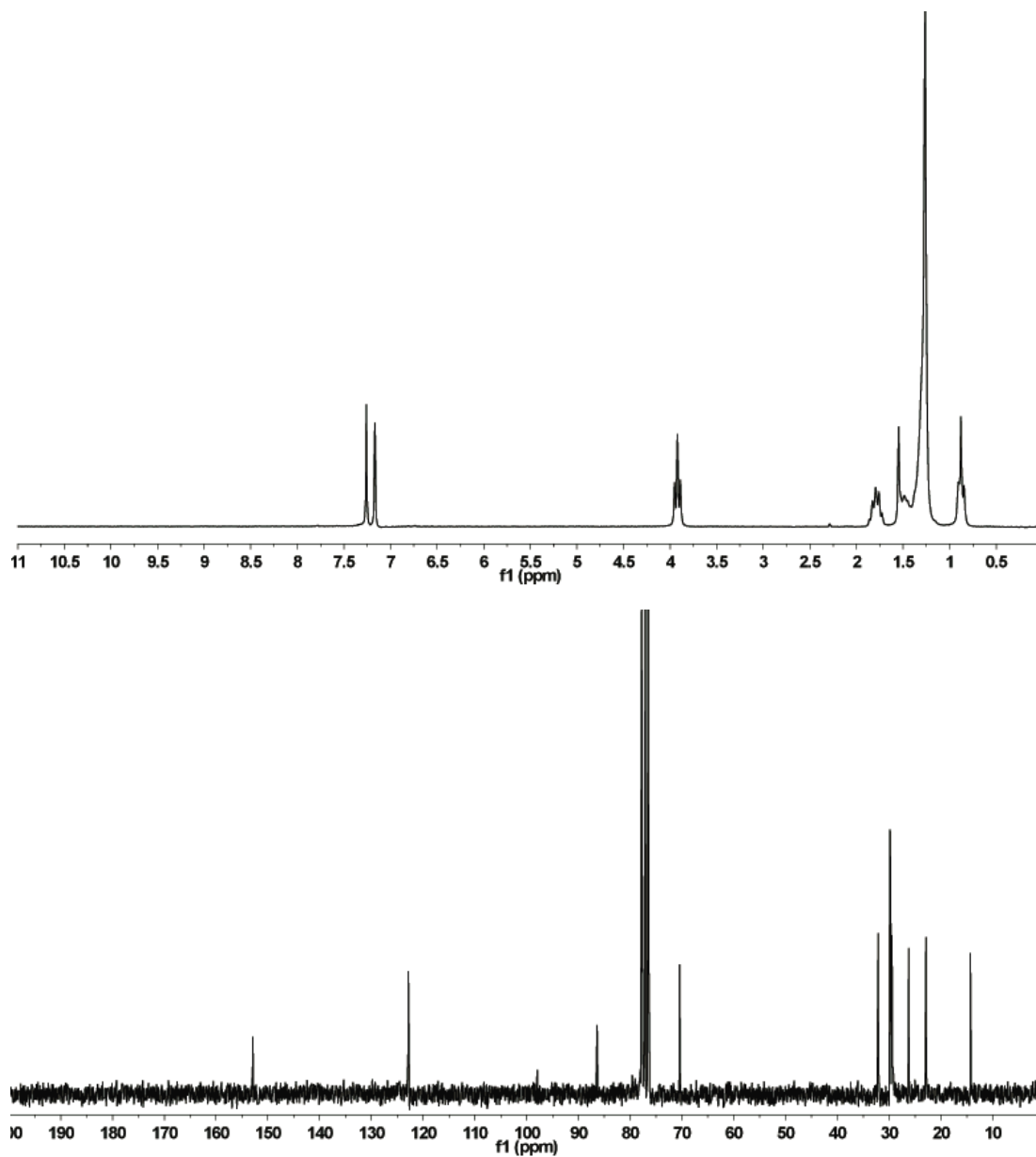
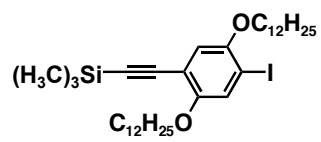


Figure S7. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 7 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 8



8

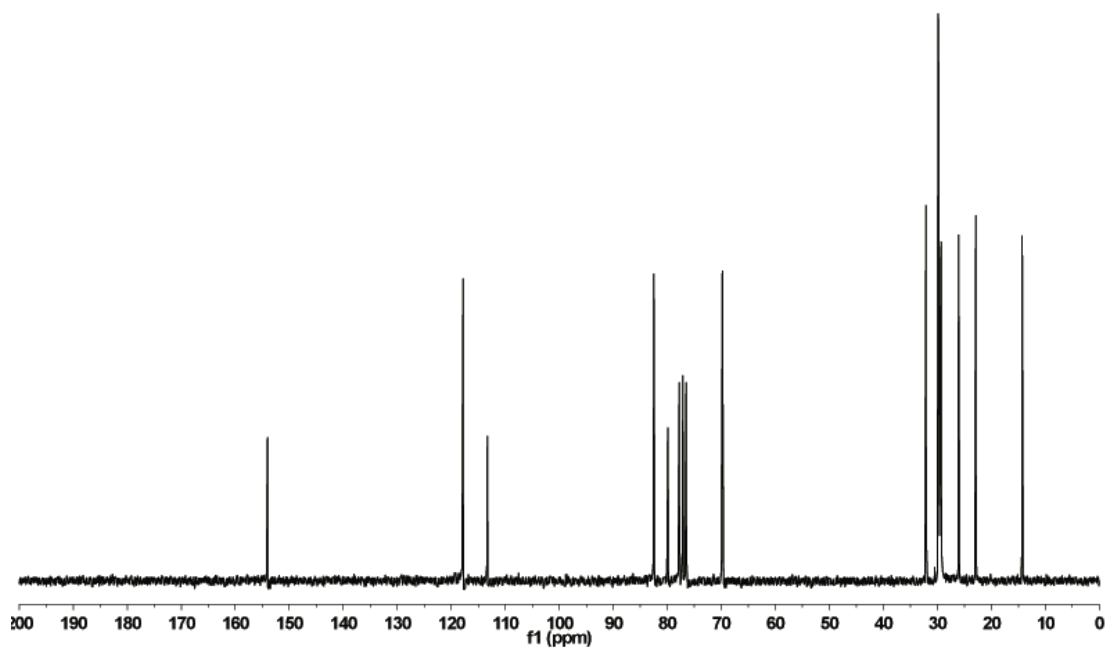
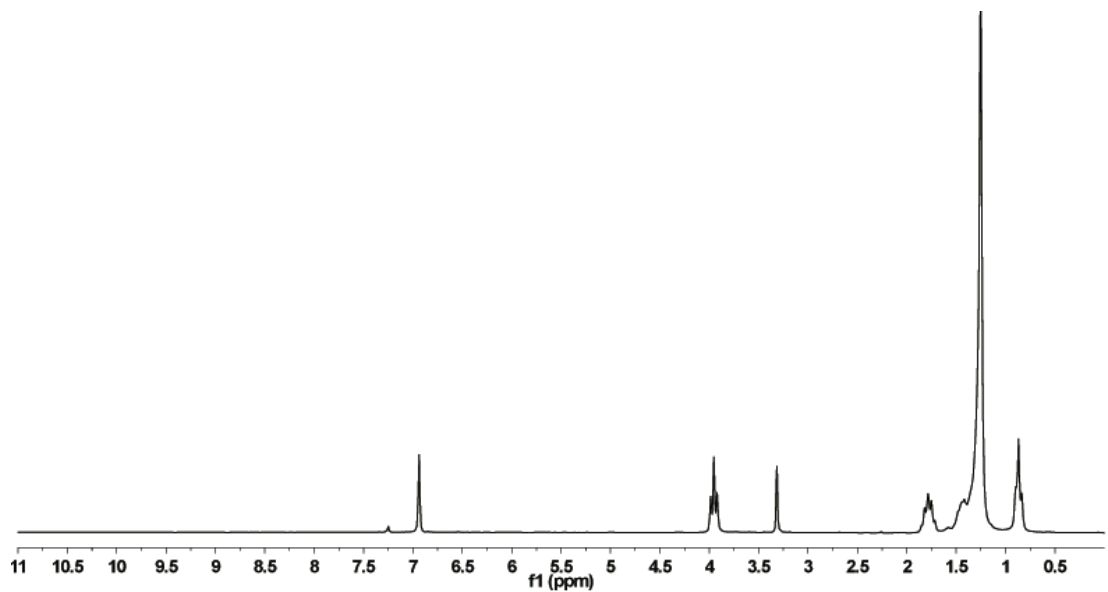


Figure S8. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 8 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 9

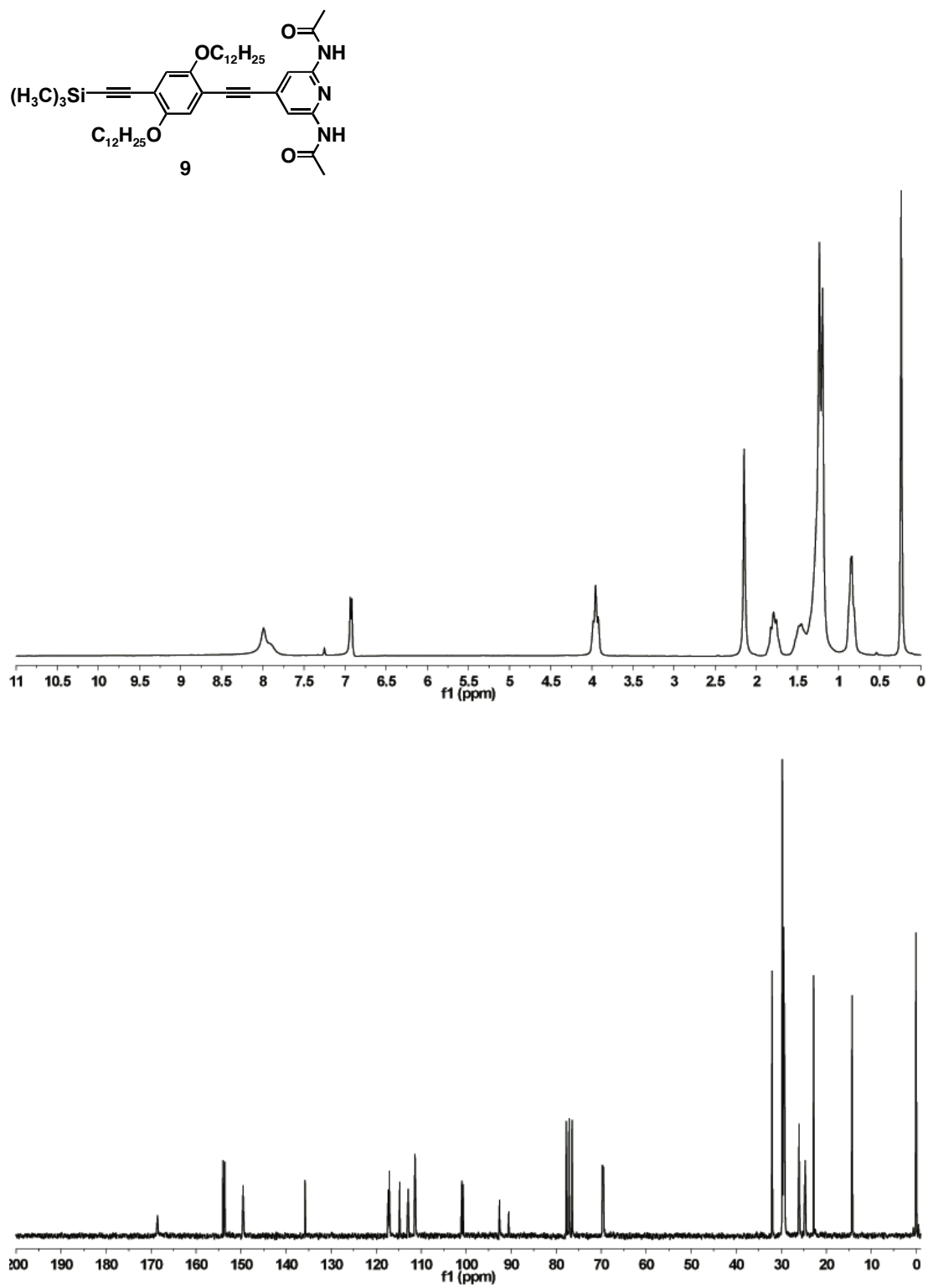


Figure S9. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 9 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 10

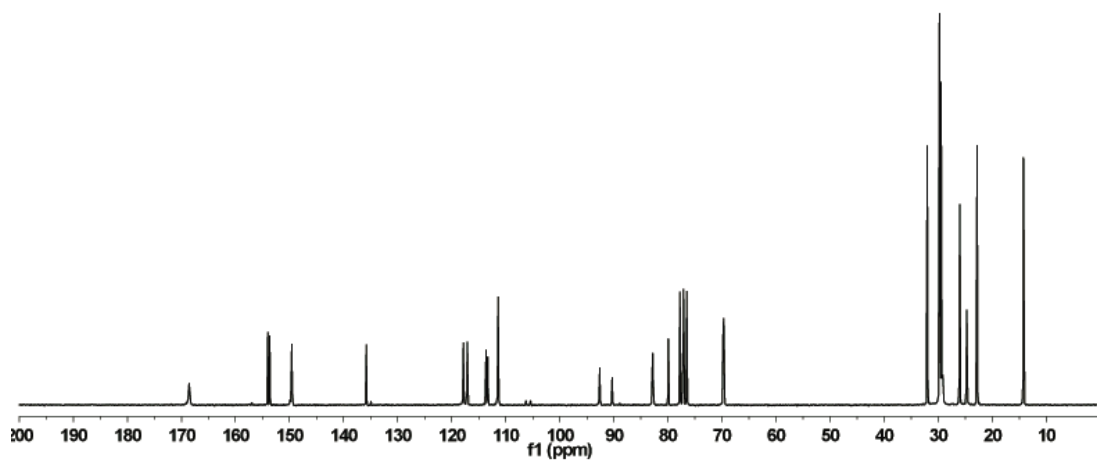
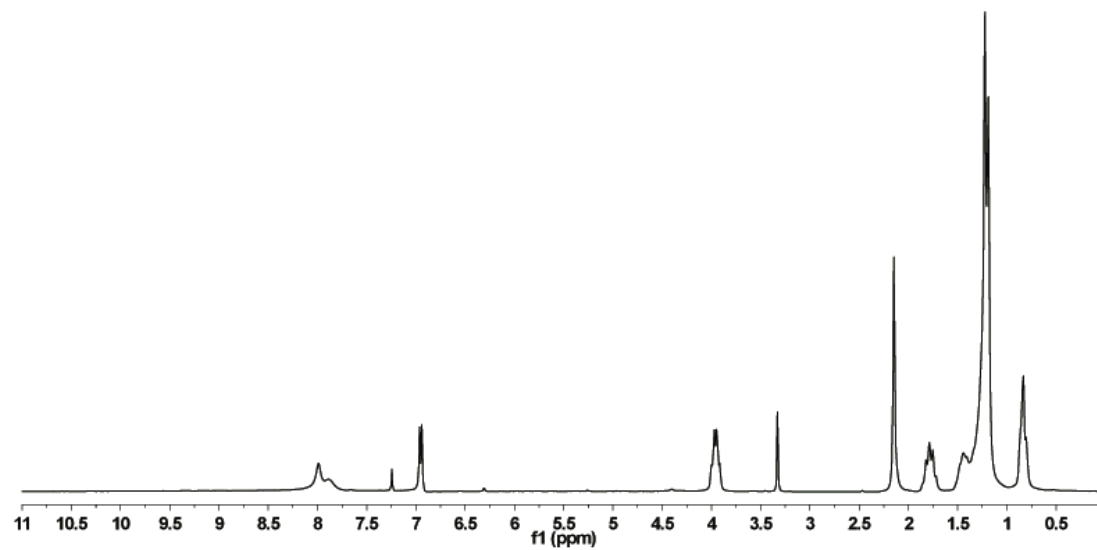
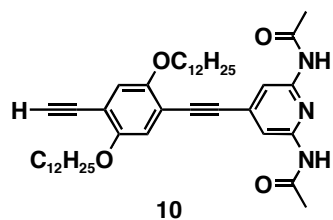
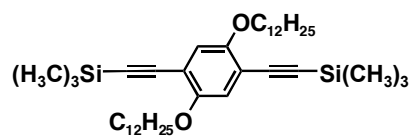


Figure S10. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 10 in CDCl₃.

^1H and ^{13}C NMR spectra of molecule **11**



11

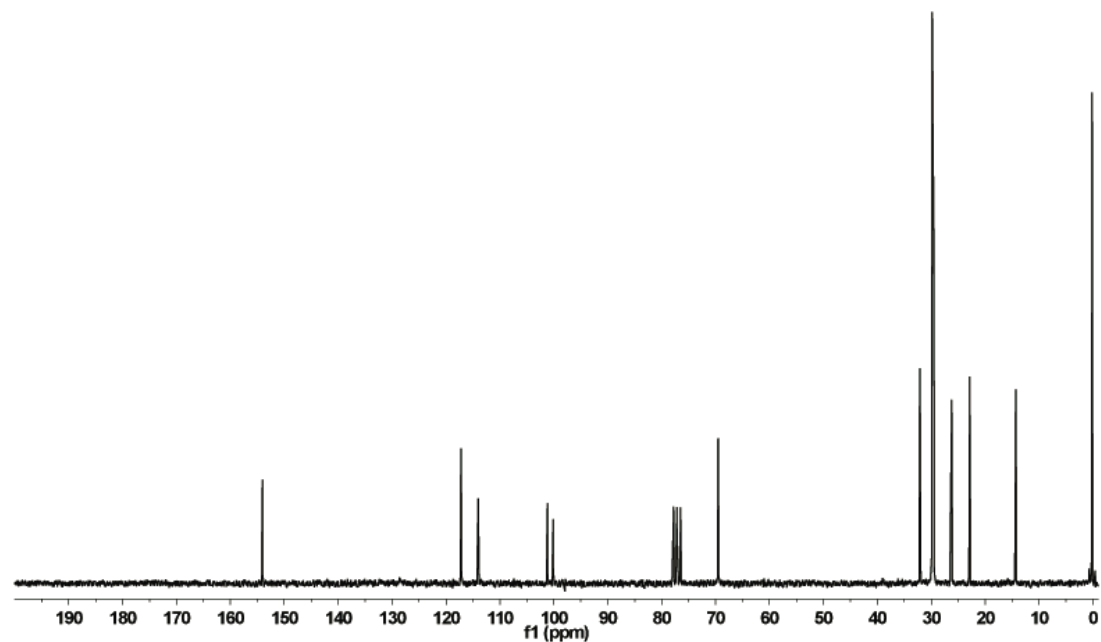
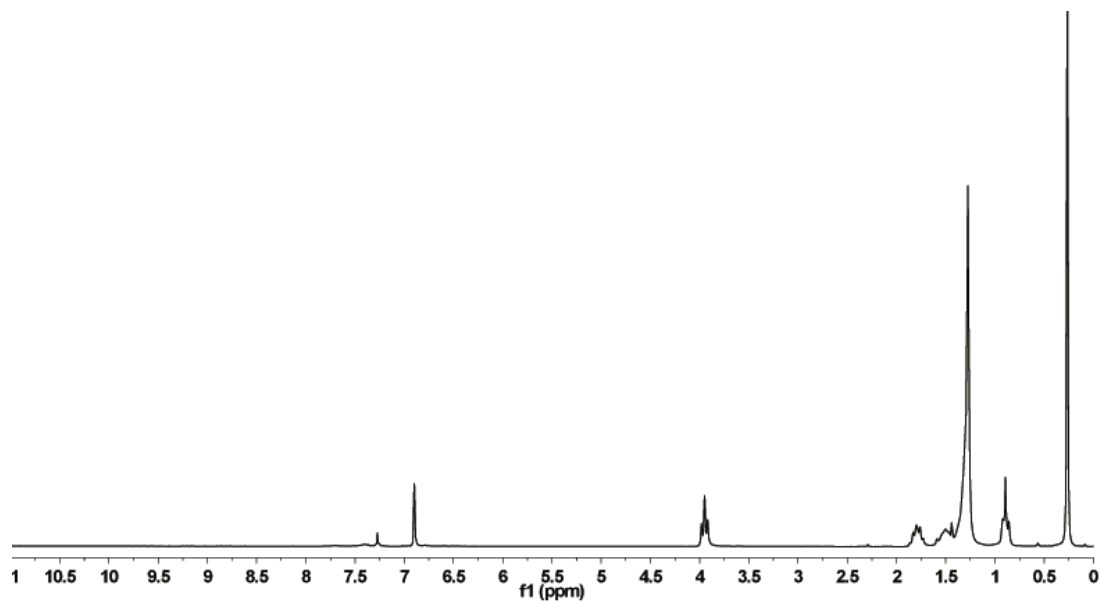
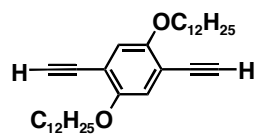


Figure S11. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule **11** in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule **12**



12

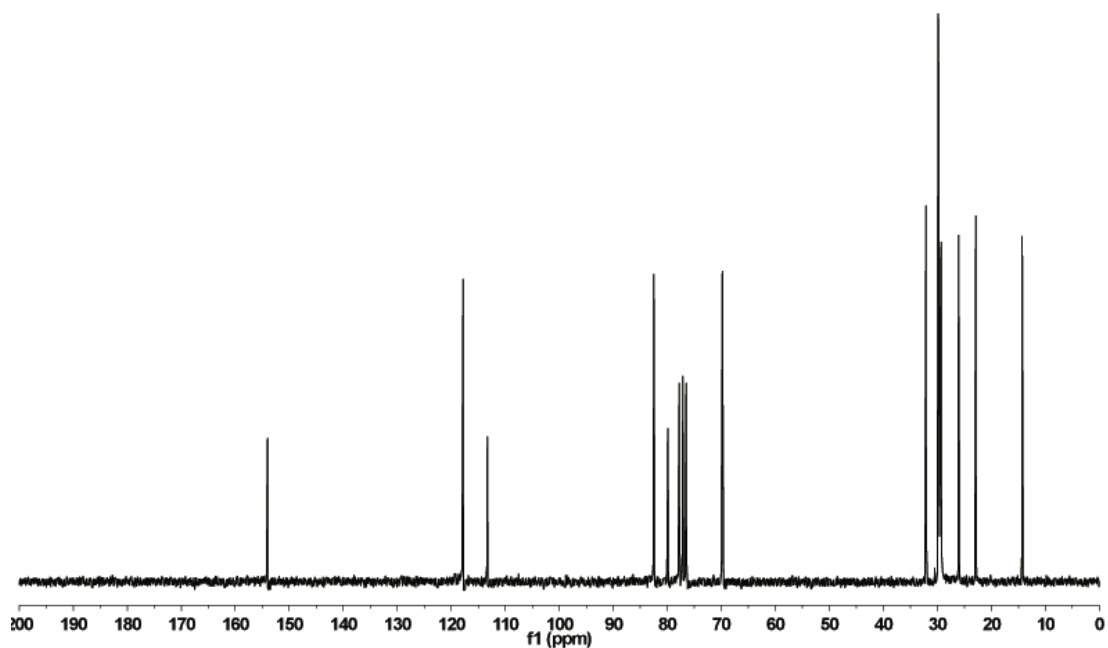
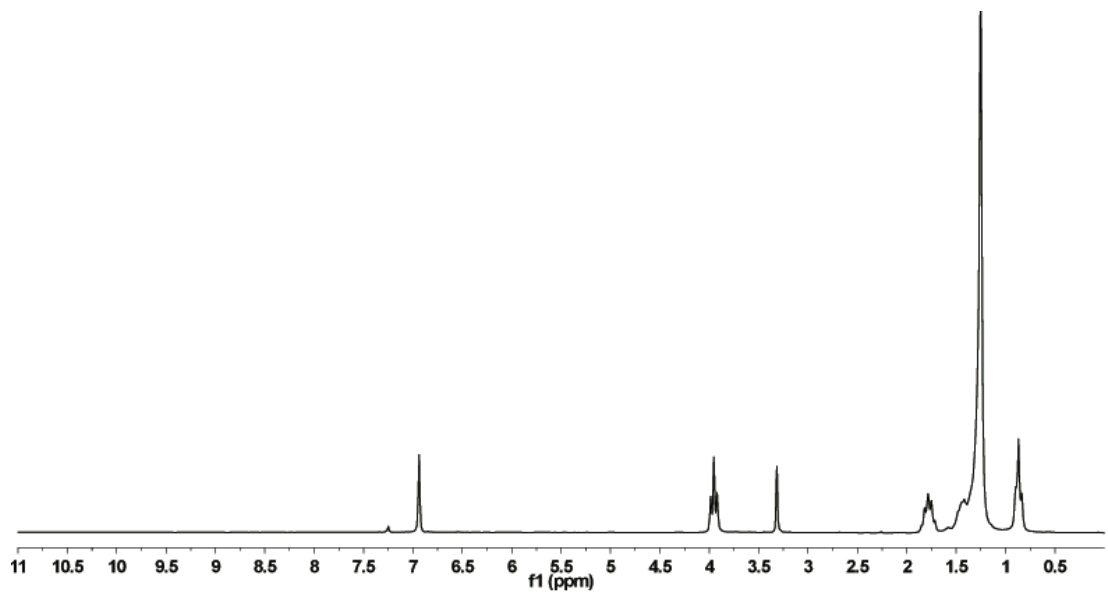


Figure S12. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule **12** in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 14

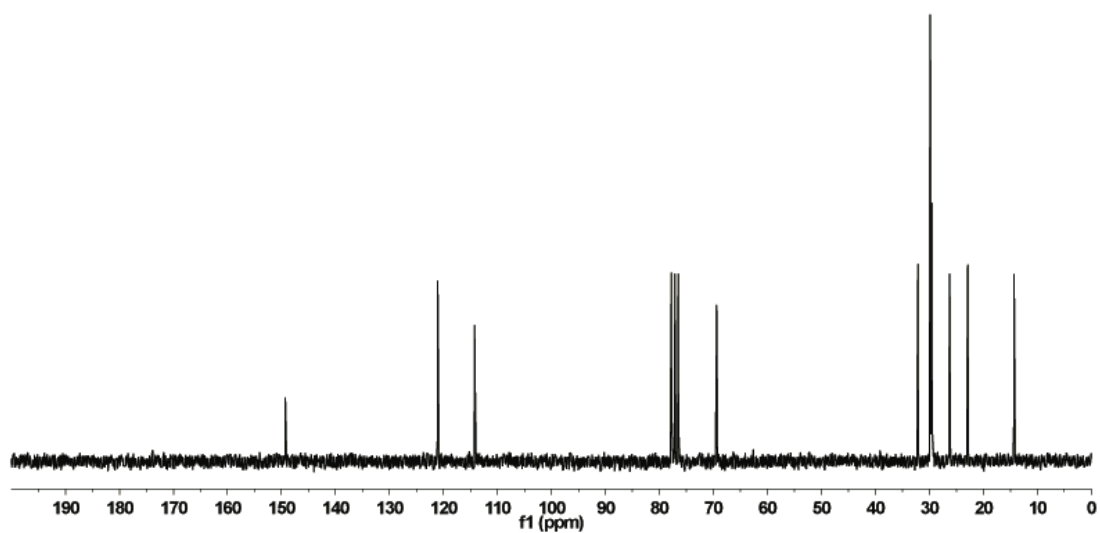
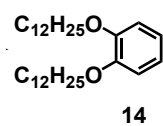
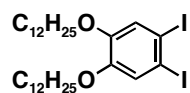


Figure S13. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 14 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 15



15

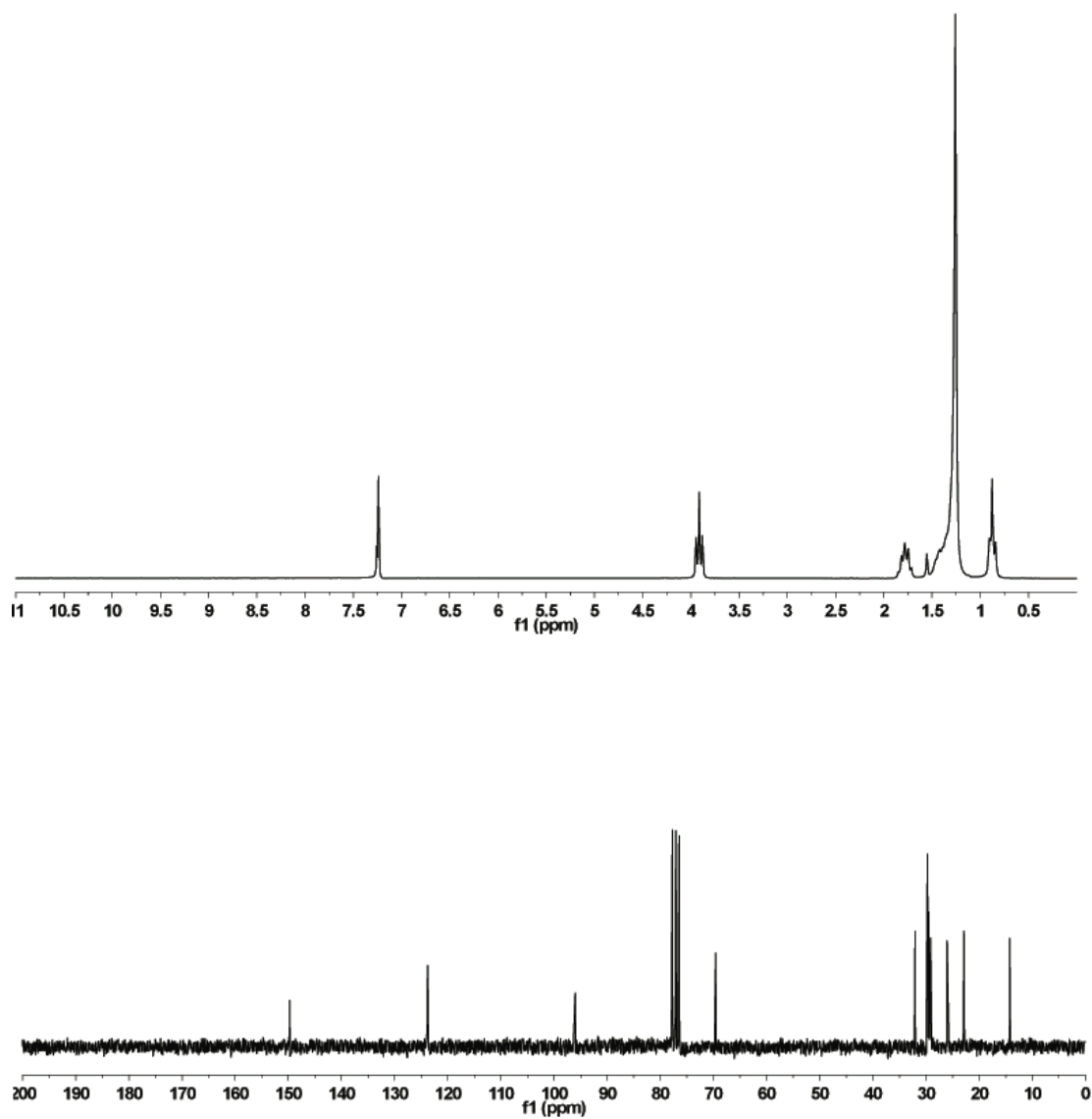


Figure S14. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 15 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 16

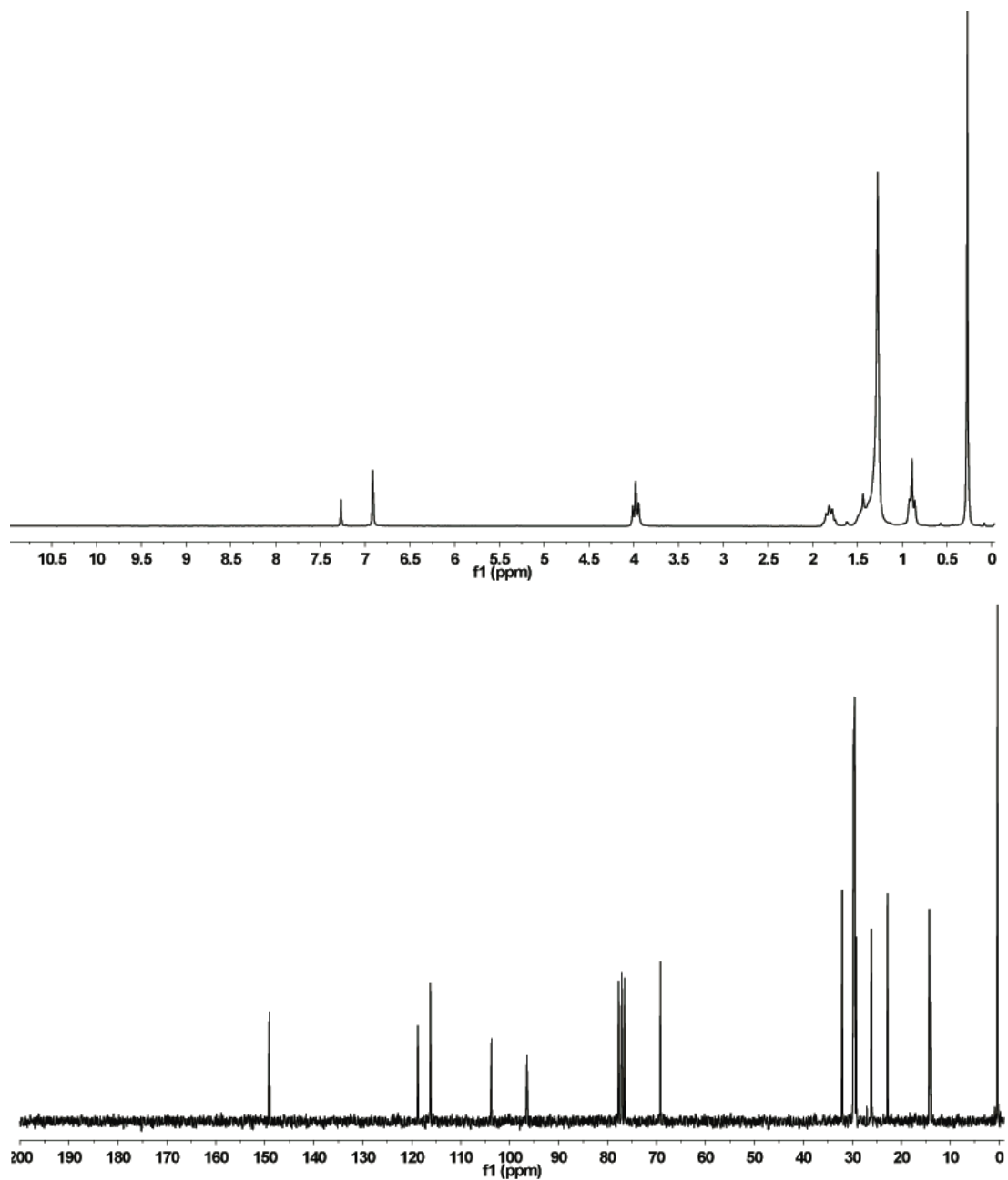
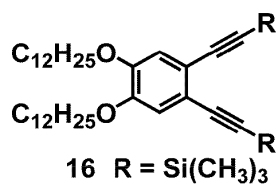
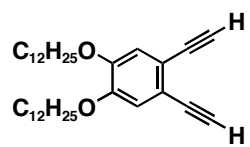


Figure S15. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 16 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 17



17

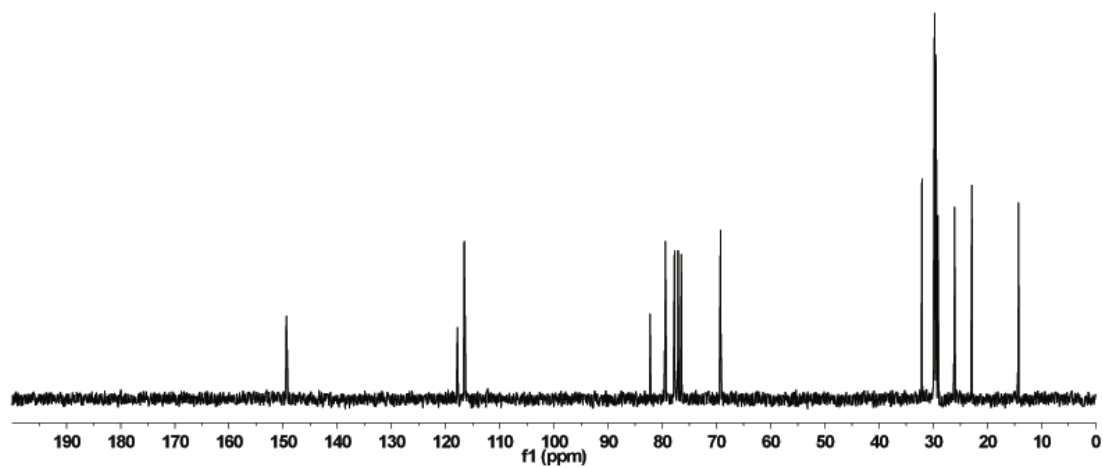
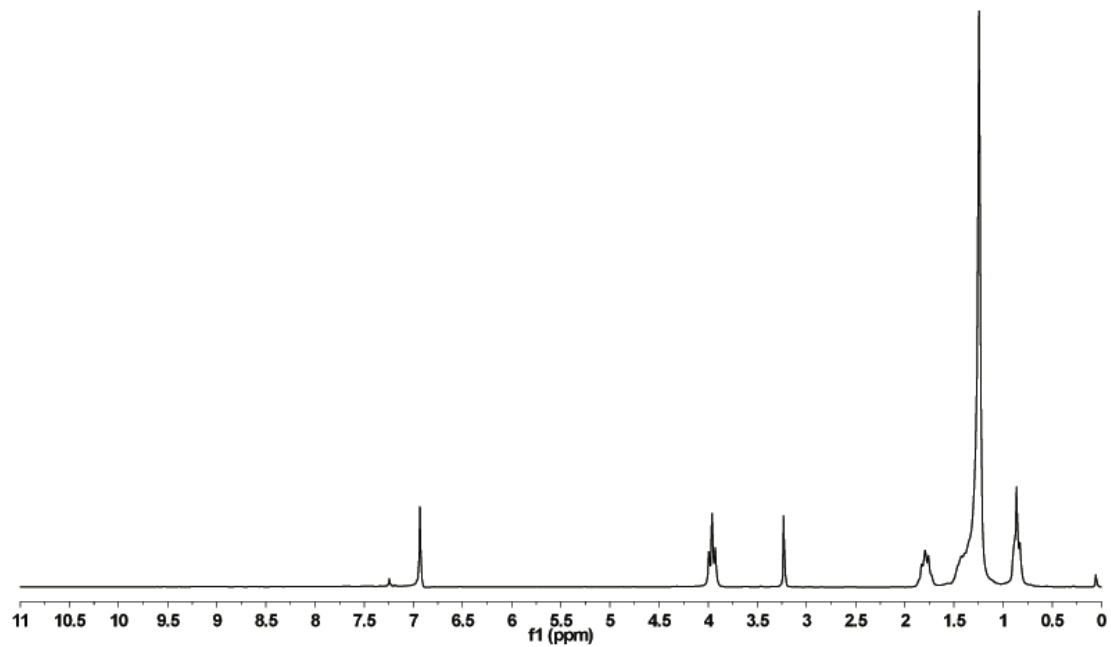
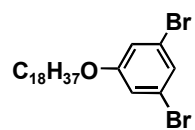


Figure S16. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 17 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 19



19

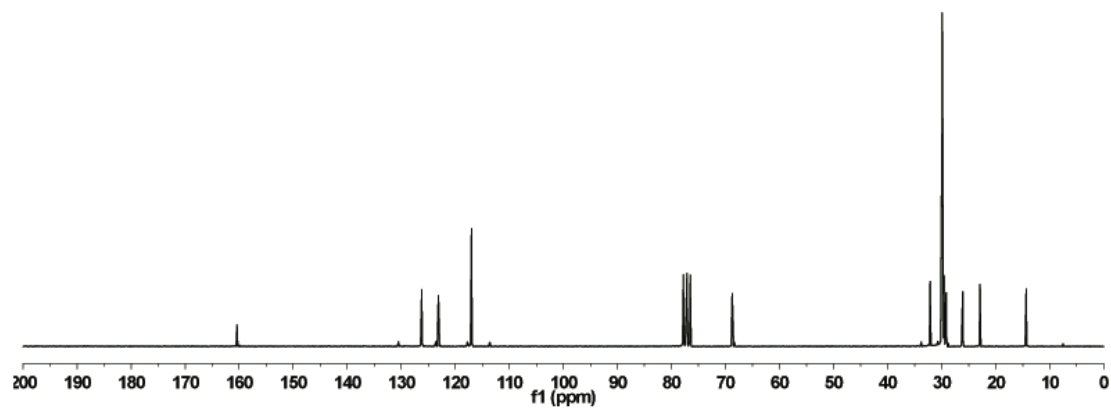
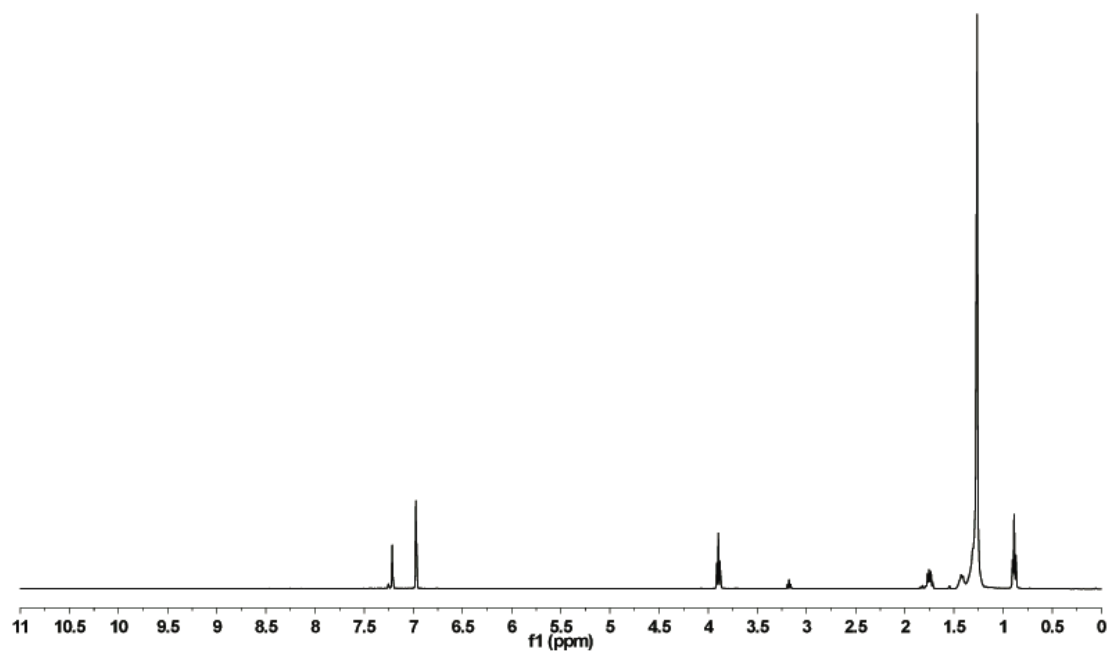


Figure S17. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 19 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 21

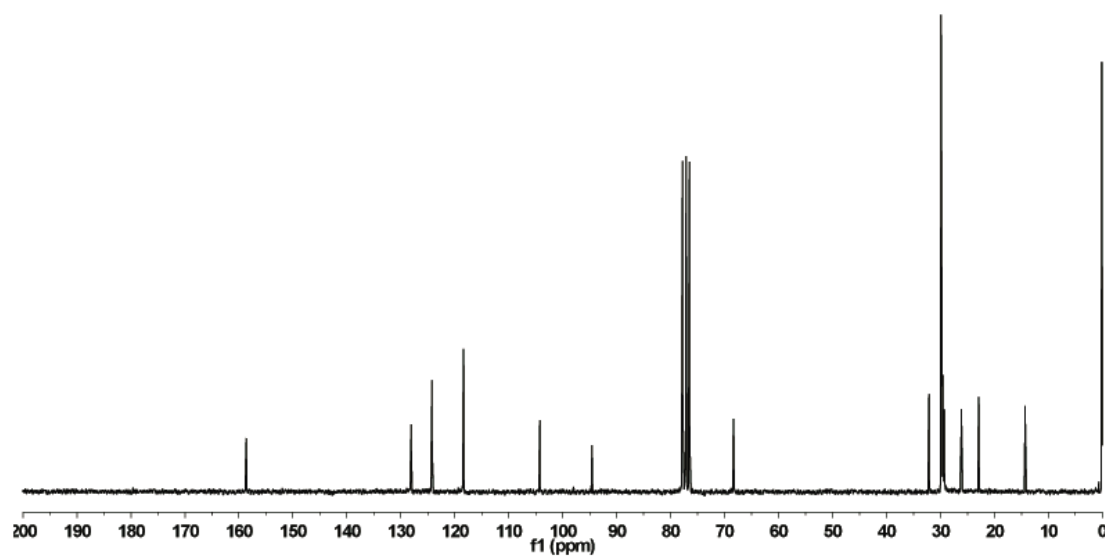
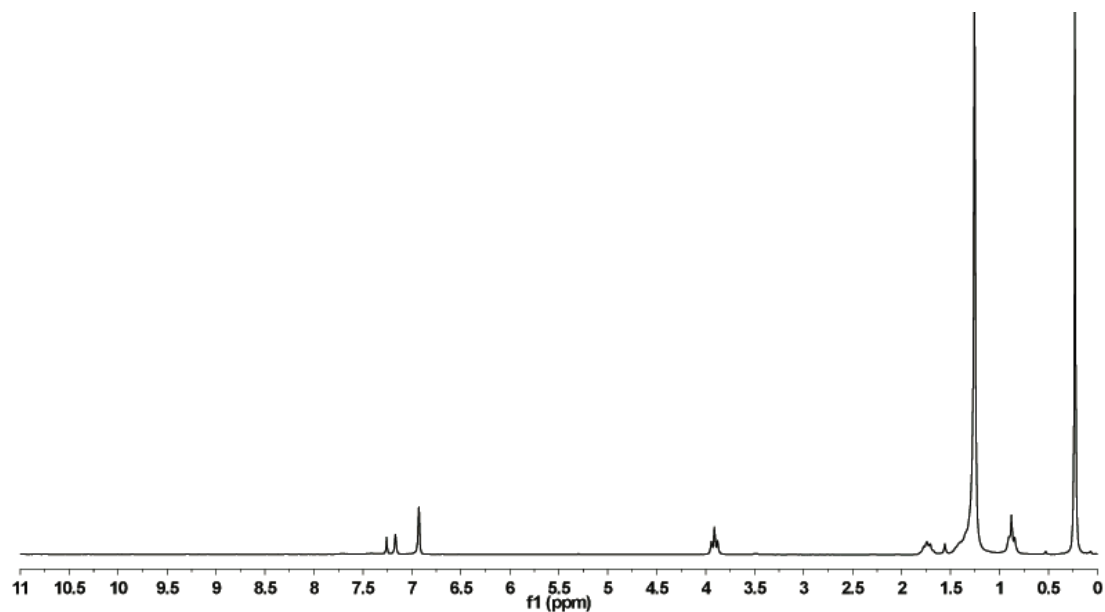
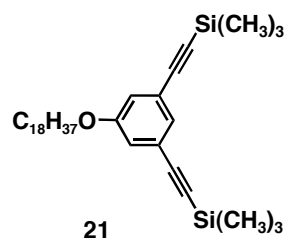


Figure S18. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 21 in CDCl_3 .

^1H and ^{13}C NMR spectra of molecule 22

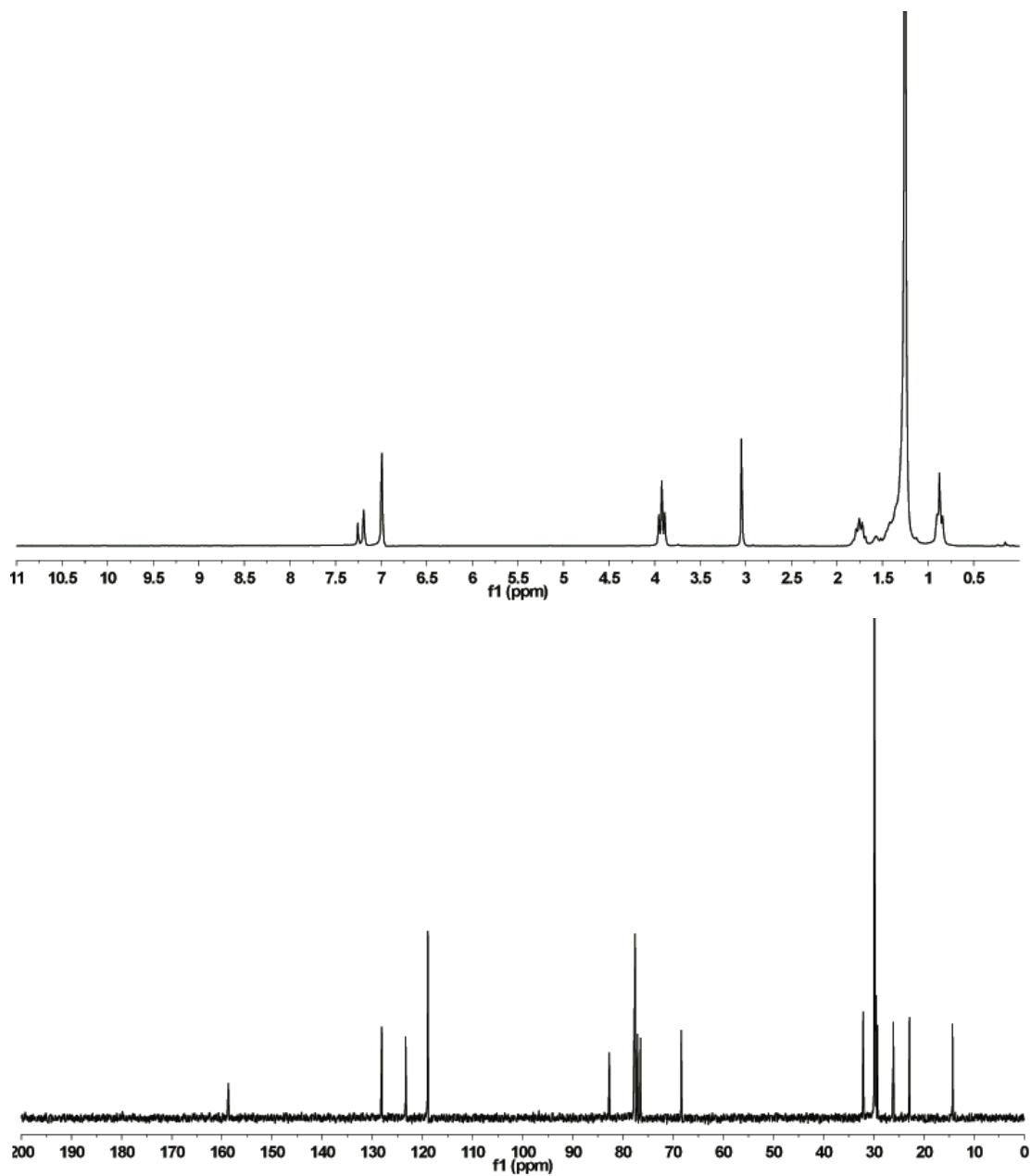
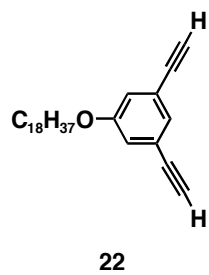


Figure S19. ^1H -NMR (up) and ^{13}C -NMR (bottom) of molecule 22 in CDCl_3 .

¹H-NMR Characterization of supramolecular polymers [1a•3]_n

The ¹H-NMR spectra in CDCl₃ of the supramolecular system composed by [1a•3]_n did not reveal any characteristic peak from the assembly as it can be distinguished from figure S20b. Figure S20a shows the spectrum of **1a** alone and figure S20c shows the spectrum of **3** alone, however when they are combined (figure S20b), most of the peaks disappear and only the signals in the alkylic region (the most intense signals) remain in the spectrum.

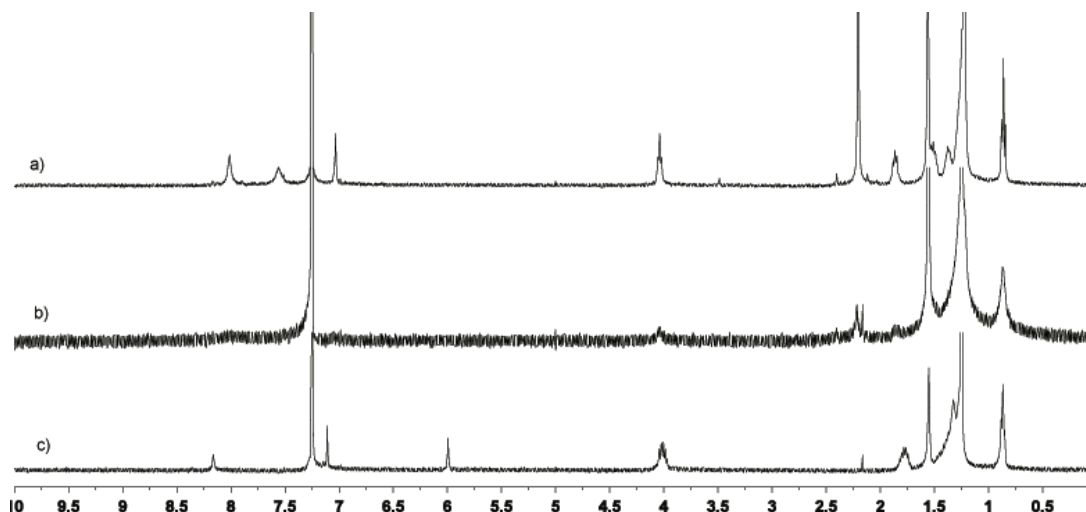


Figure S20. ¹H NMR spectra in CDCl₃ of a) **1a**; b) [1a•3]_n (1:1); c) **3**.

These results support the formation of a supramolecular polymer as represented in Figure S21.

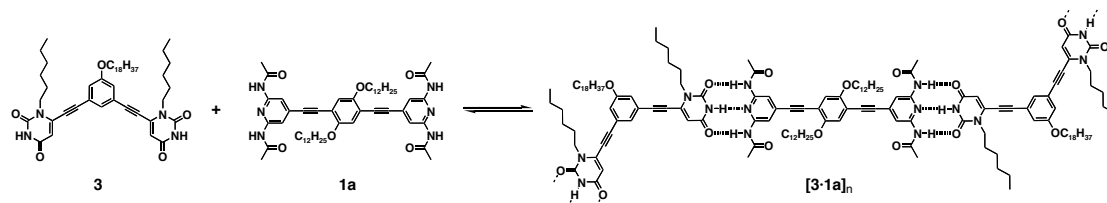


Figure S21. Molecular representation of the complementary H-bonding interaction of **1a** with **3** leading to the formation of supramolecular polymer [1a•3]_n.

In fact, when some drops of CD₃OD were added to a CDCl₃ solution containing a 1:1 mixture of **1a** and **3**, the spectrum of the initial components is completely recovered as it can be appreciated in Figure S22b. In such conditions, all the characteristic signals of both components (except the NH peaks) can be identified.

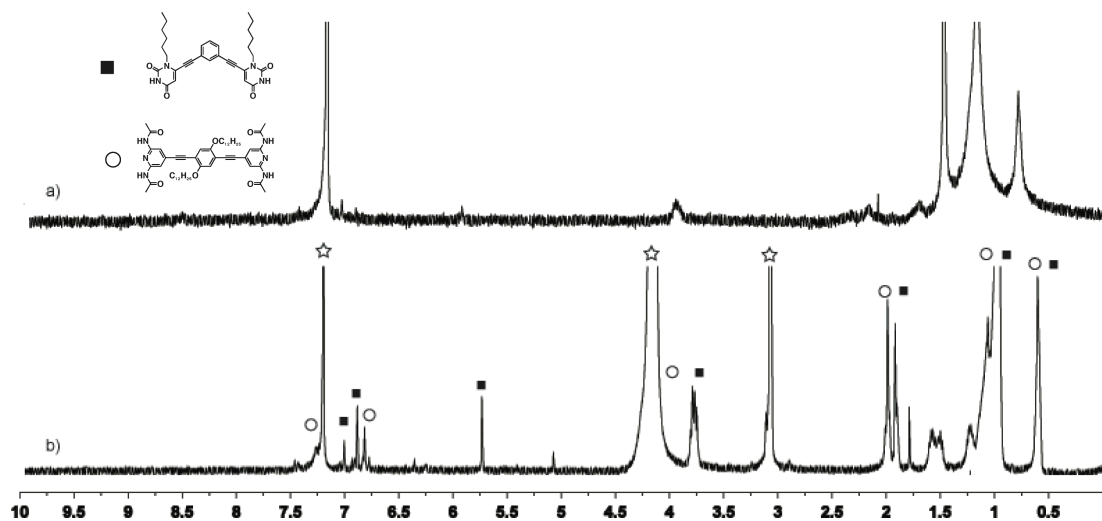


Figure S22. ^1H NMR spectrum of $[\mathbf{1a}\cdot\mathbf{3}]_n$ (1:1) in a) CDCl_3 and b) $\text{CDCl}_3+\text{CD}_3\text{OD}$. ☆ = residual solvent peaks. ■ = **3**, ○ = **1a**.

3. Conditions tested for the Sonogashira coupling reaction

Table S1. Conditions tested for the Sonogashira coupling between **19** and TMSA

Entry	Catalyst	Base ^[a]	Solvent ^[a]	T (°C) ^[b]	Compound
1	$[\text{Pd}(\text{PhCN})_2\text{Cl}_2]/\text{CuI}/\text{P}(t\text{-Bu})_3$	$i\text{Pr}_2\text{NH}$	dioxane	r.t.	-
2	$[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]\text{CuI}$	Et_3N	THF	60	20 (79%)
3	$[\text{Pd}(\text{PPh}_3)_4]/\text{CuI}$	Et_3N	THF	70	20 (63%)
4	$[\text{Pd}(\text{PPh}_3)\text{Cl}_2]/\text{CuI}$	Et_3N	THF	85	20 (55%)
5	$[\text{Pd}(\text{PPh}_3)\text{Cl}_2]/\text{CuI}$	$i\text{Pr}_2\text{NH}$	THF/DMF	MW, 120	21 (79%)

^[a] anhydrous and deoxygenated; ^[b] stirred overnight except entry 5, which was microwave irradiated for 5 minutes.

4. XPS analysis

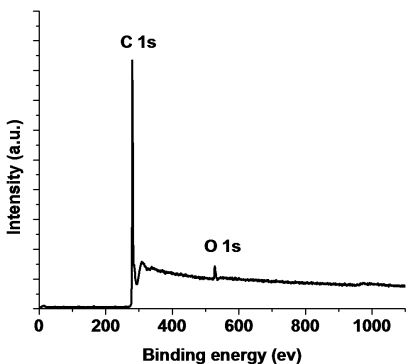


Figure S23.1 : XPS survey spectrum

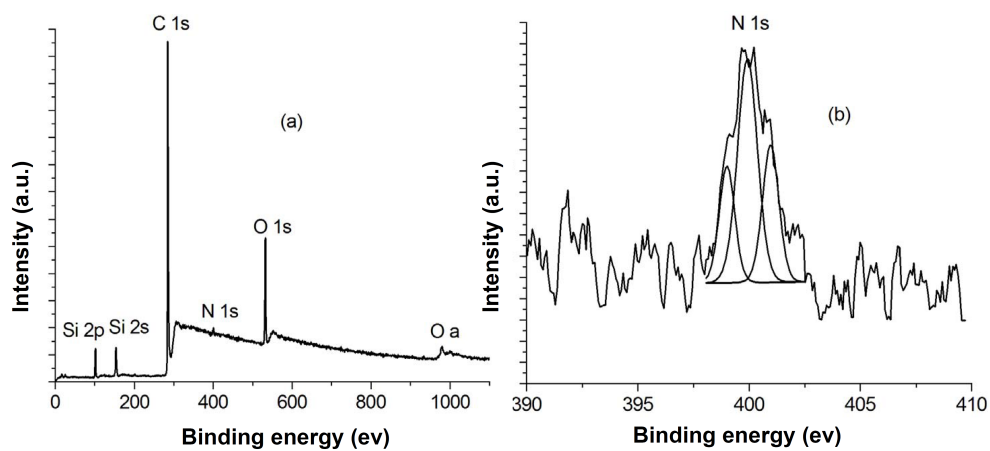


Figure S23 : XPS survey spectrum (a) and the XPS high resolution (b) on N 1s of the material $\text{MWCNTs}\cdot[1\mathbf{a}\cdot\mathbf{2}]_n$

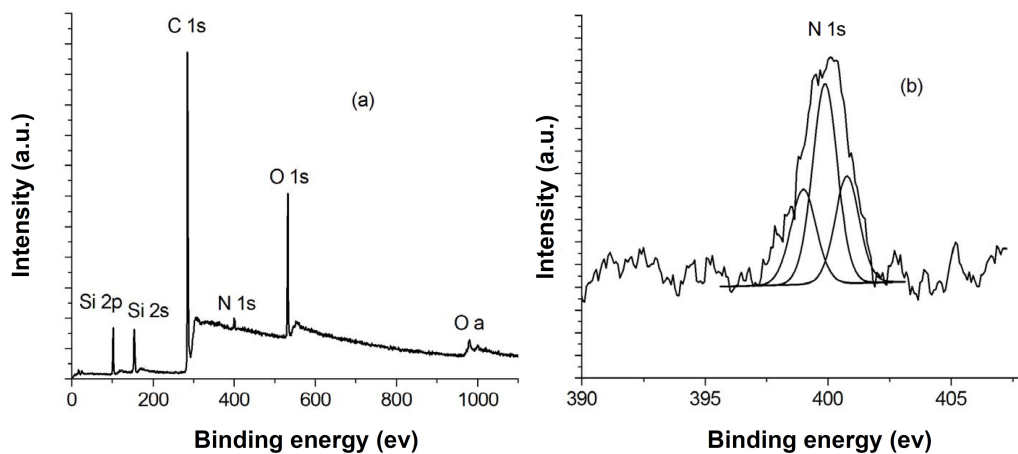


Figure S24 : XPS survey spectrum (a) and the XPS high resolution (b) on N 1s of the material $\text{MWCNTs}\cdot[1\mathbf{a}\cdot\mathbf{3}]_n$

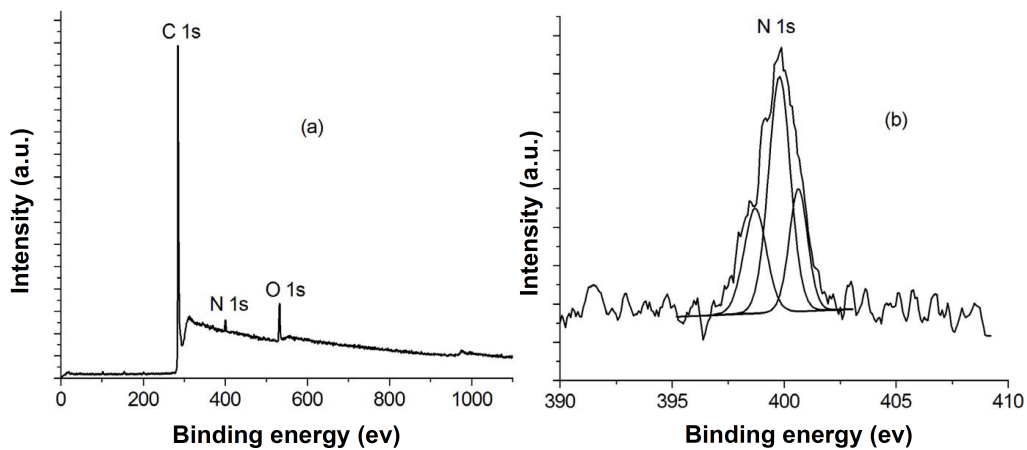


Figure S25 : XPS survey spectrum (a) and the XPS high resolution (b) on N 1s of the material MWCNTs•[1a•4]_n.

5. TGA analysis

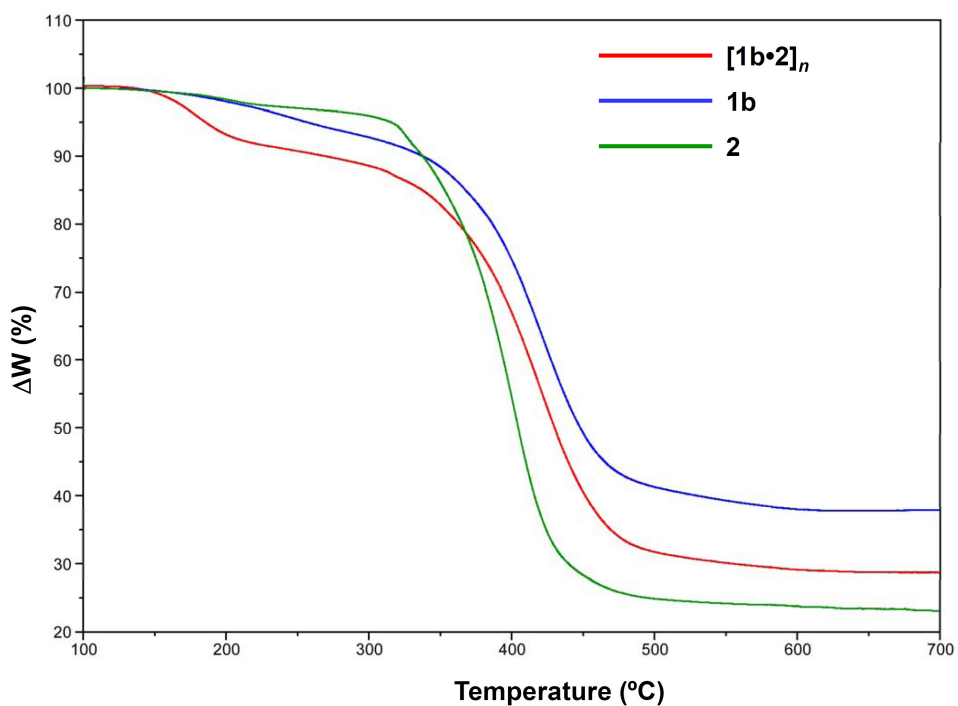


Figure S26. TGA traces of the supramolecular polymer [1b•2]_n (red), molecule 1b (blue) and molecule 2 (green).

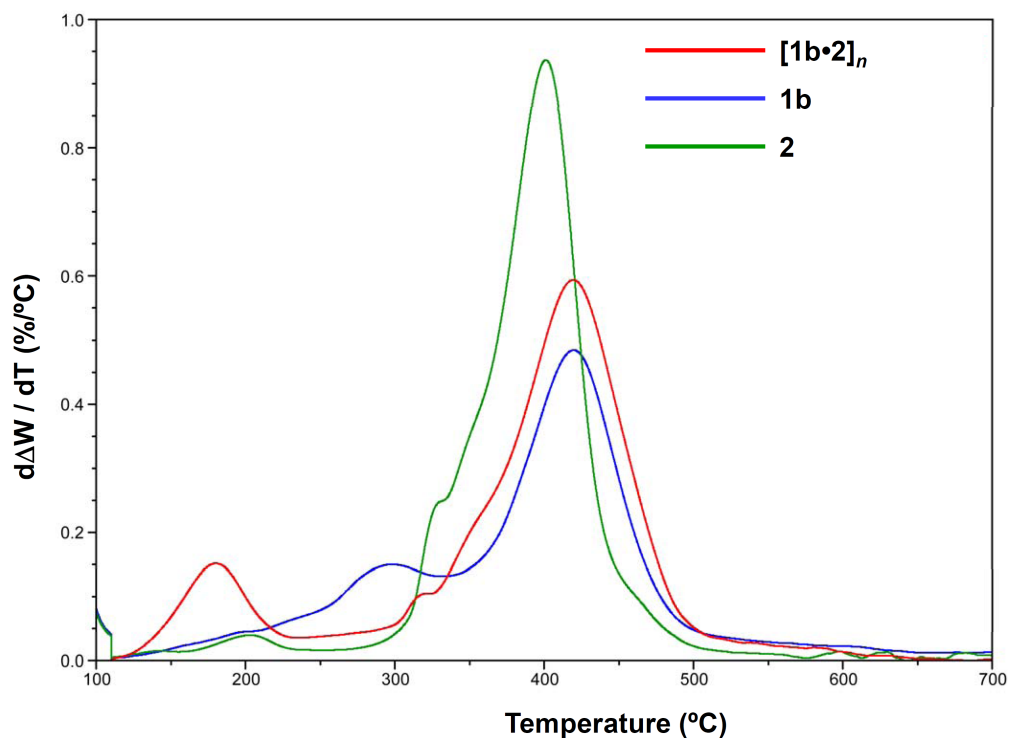


Figure S27. TGA weight derivate traces of the supramolecular polymer $[1b \cdot 2]_n$ (red), molecule **1b** (blue) and molecule **2** (green).

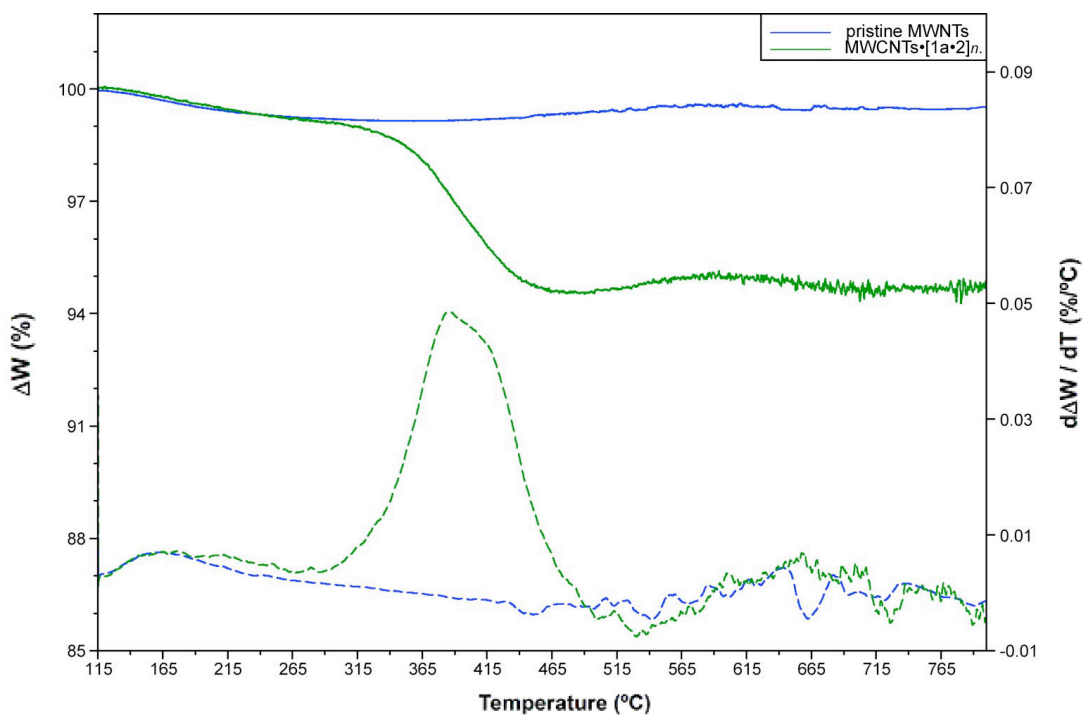


Figure S28. TGA traces (solid line) and their derivatives (---) of pristine MWCNTs (blue) and MWCNTs $\cdot[1a \cdot 2]_n$ (green). The temperature interval (310-510 $^\circ C$) represents the steepest weight loss due to organic decomposition

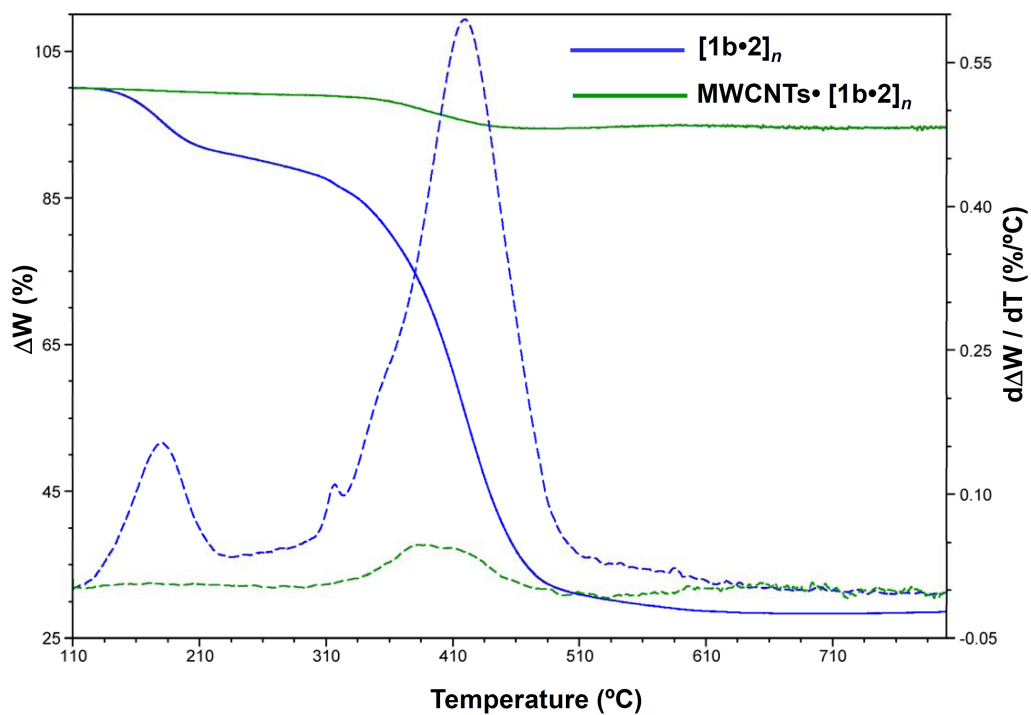


Figure S29. TGA traces of polymer $[1b\cdot 2]_n$ (blue) and $MWCNTs\cdot [1b\cdot 2]_n$ (green) and their weight derivatives (---). The temperature interval (310-510°C) represents the steepest weight loss due to organic decomposition.

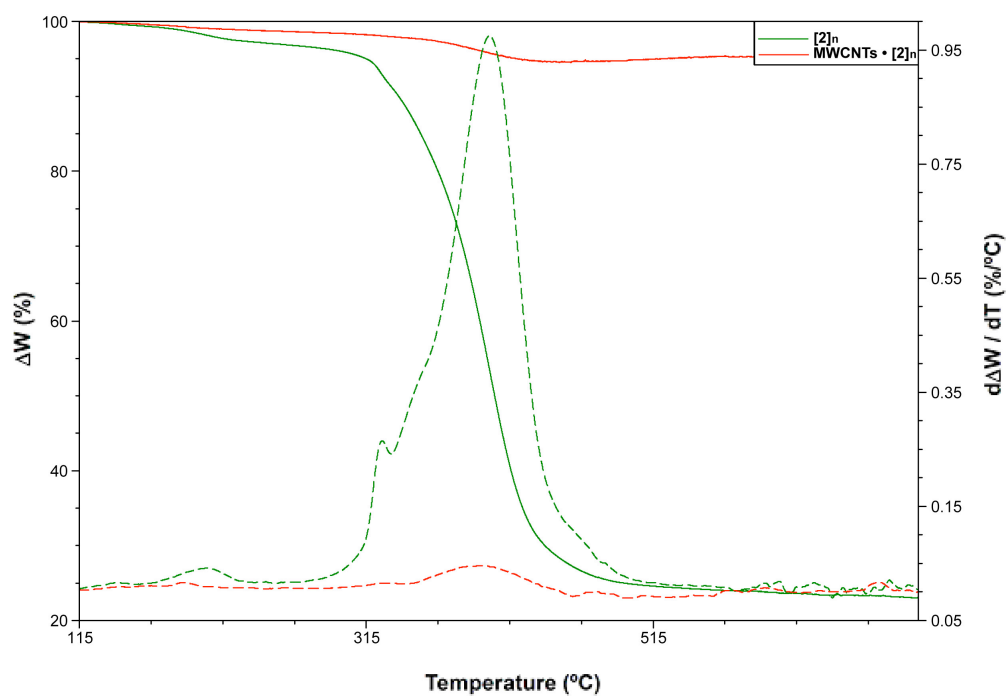


Figure S30. TGA traces of polymer $[2]_n$ (green) and $MWCNTs\cdot [2]_n$ (red) and their weight derivatives (---). The temperature interval (310-510°C) represents a steep weight loss due to organic decomposition.

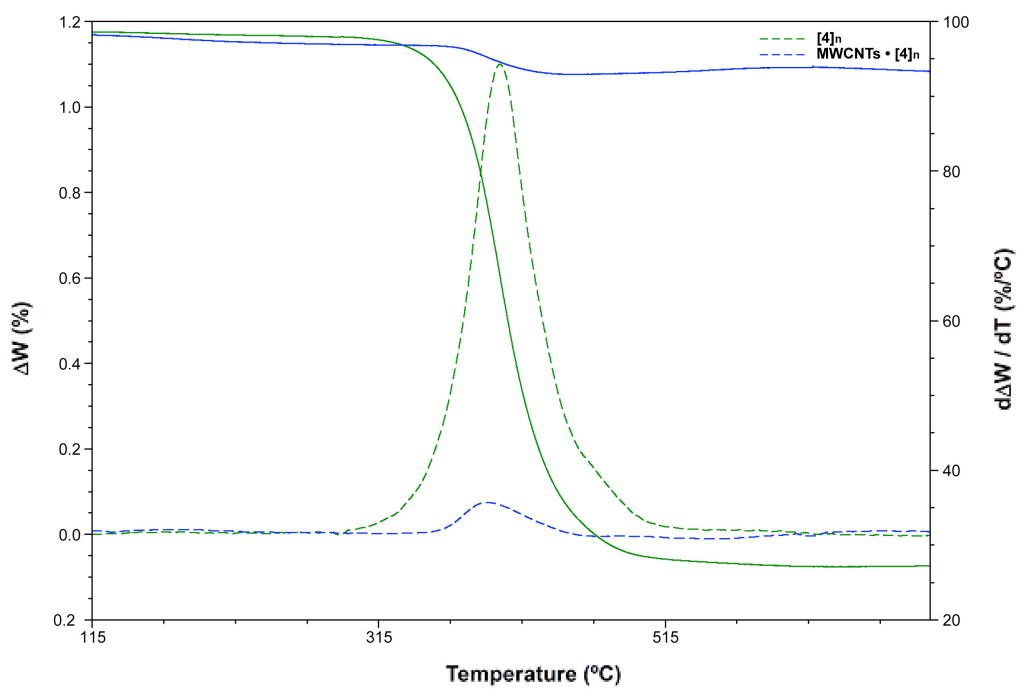
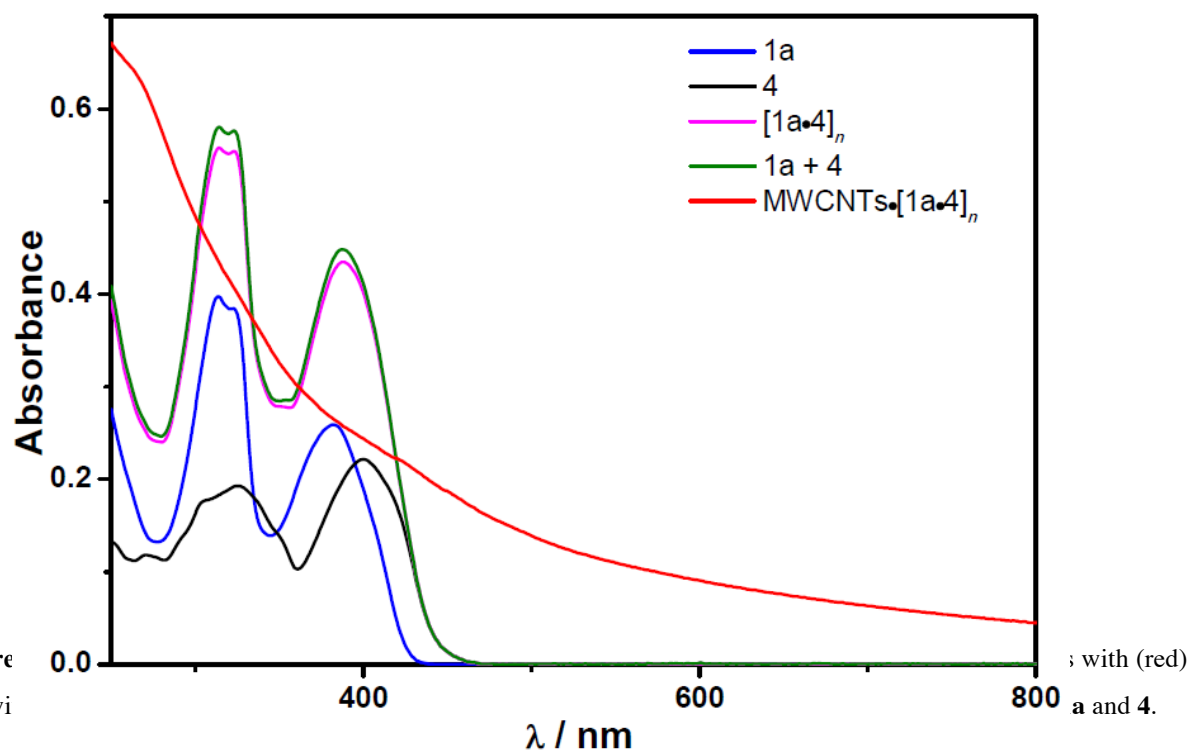


Figure S31. TGA traces of polymer $[4]_n$ (green) and $\text{MWCNTs}\cdot[4]_n$ (blue) and their weight derivatives (---). The temperature interval (310-510°C) represents a steep weight loss due to organic decomposition.

6. Photophysical investigations



7. TEM and AFM investigations

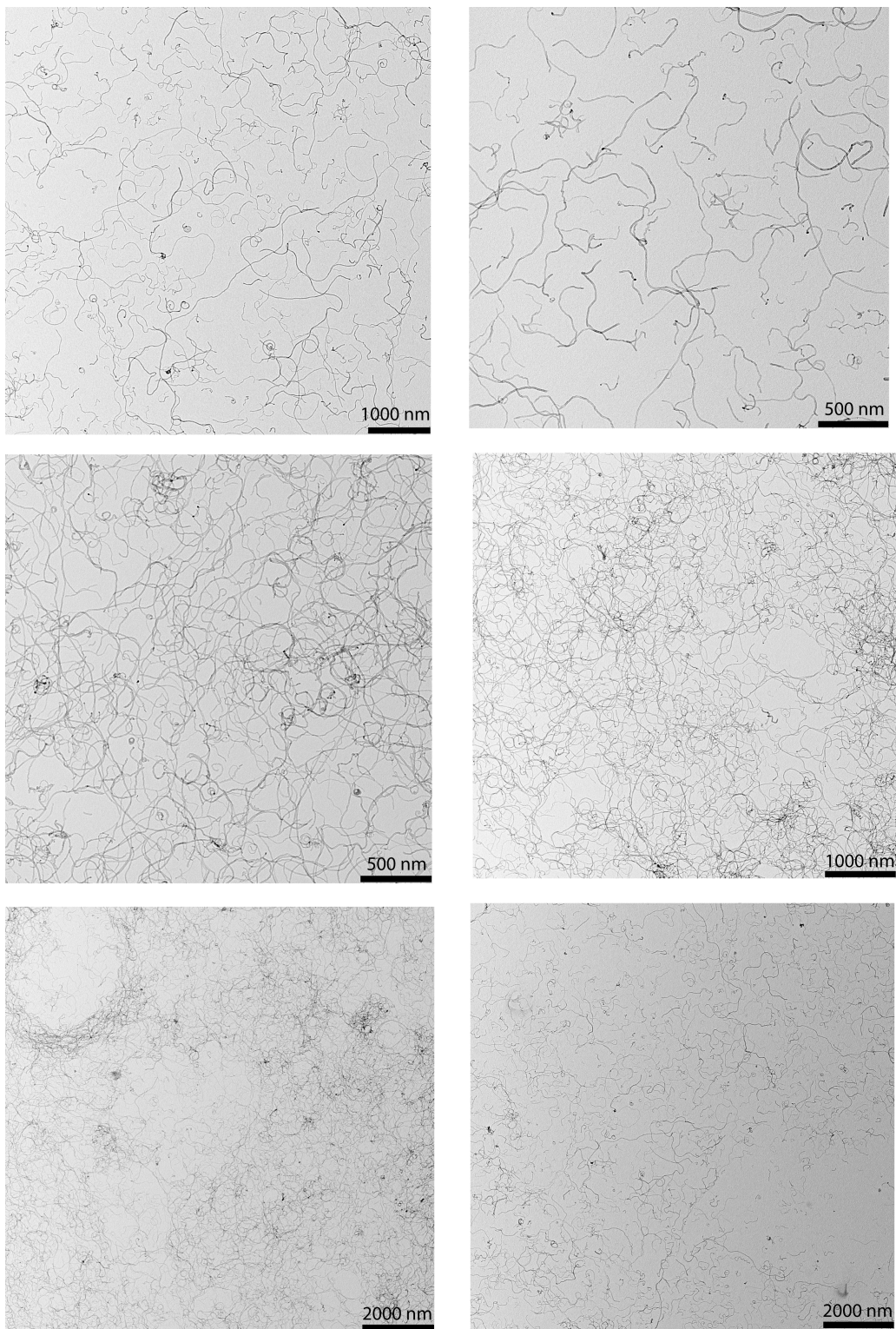


Figure S33. TEM images of hybrids MWCNTs•[1b•2]_n materials after filtration and extensive washing.

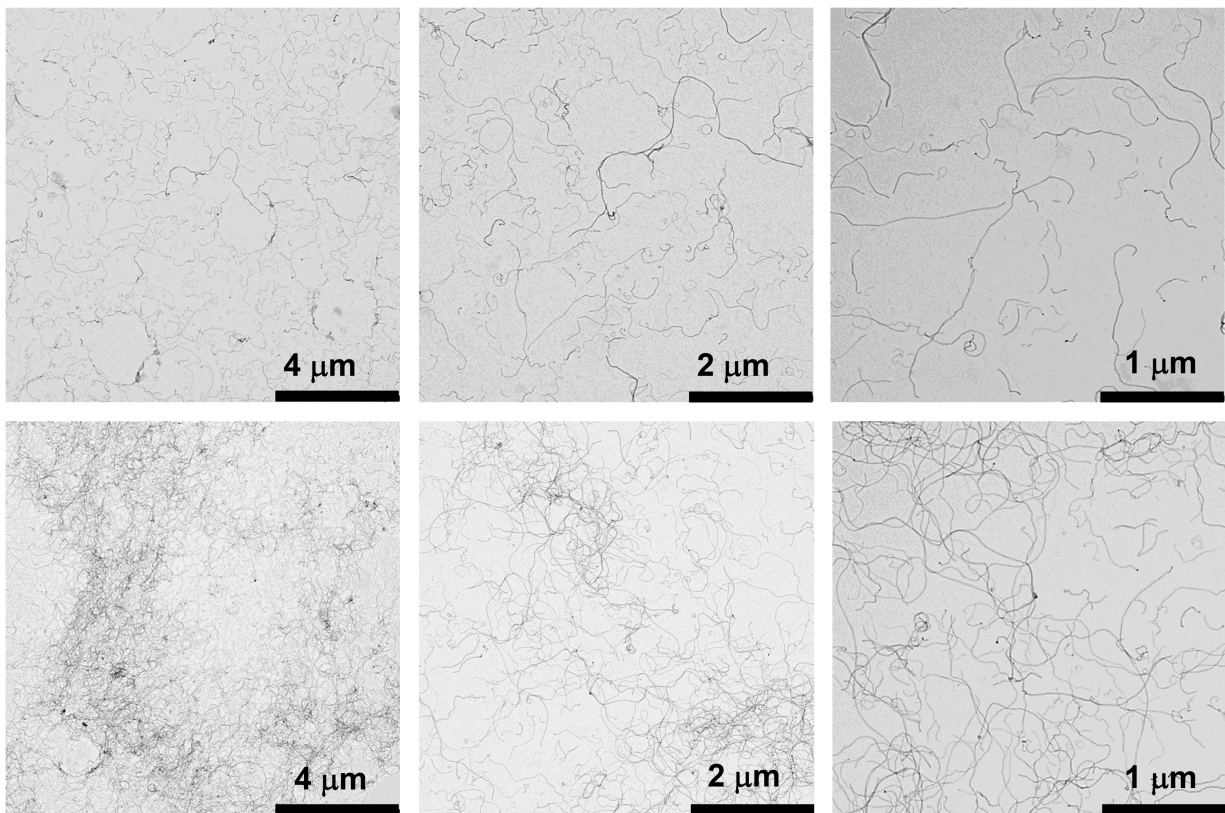


Figure S34. TEM images of hybrids $\text{MWCNTs}\cdot[1\mathbf{a}\cdot\mathbf{2}]_n$ materials after filtration and extensive washing.

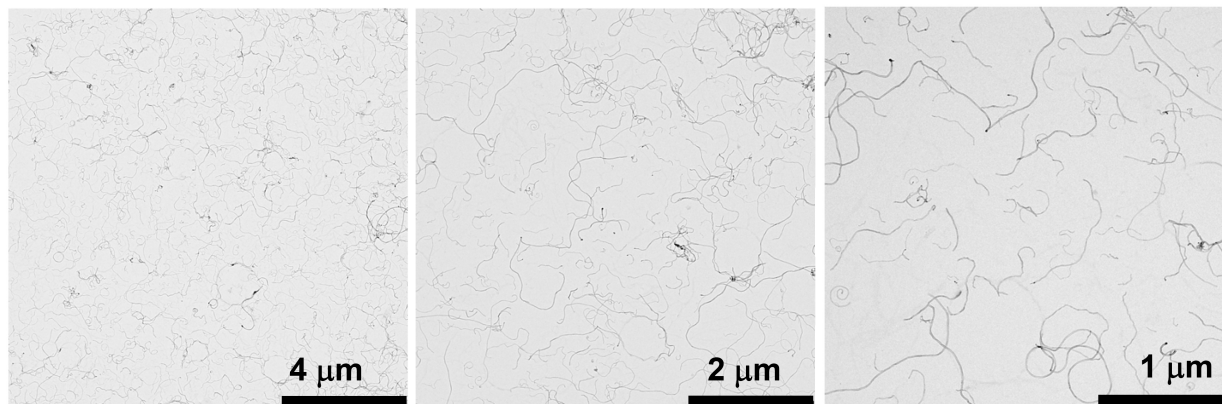


Figure S35. TEM images of hybrids $\text{MWCNTs}\cdot[1\mathbf{a}\cdot\mathbf{3}]_n$ materials after filtration and extensive washing.

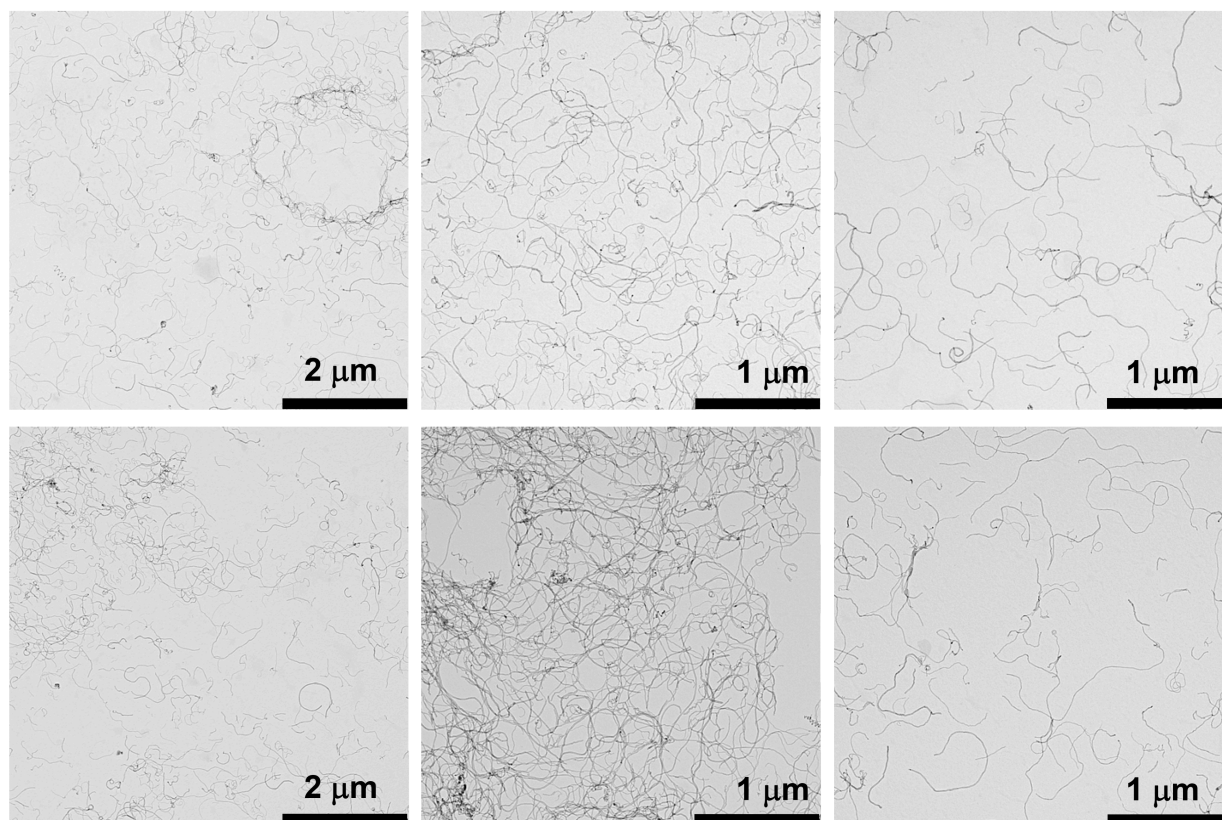


Figure S36. TEM images of hybrids $\text{MWCNTs}\cdot[1\mathbf{a}\cdot\mathbf{4}]_n$ materials after filtration and extensive washing.

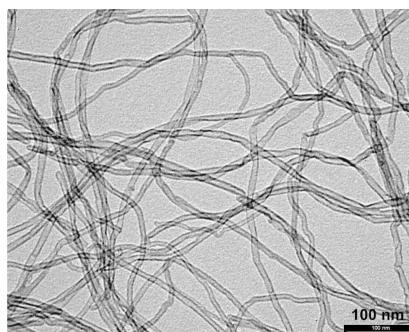


Figure S37. TEM image of raw Nanocyl MWCNTs.

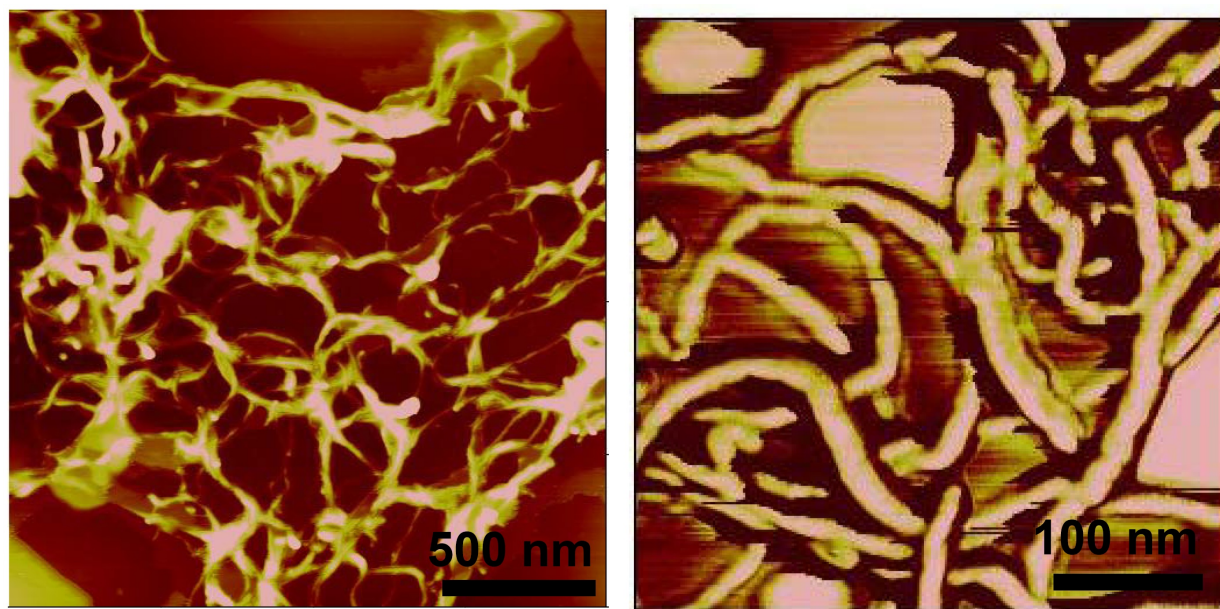


Figure S38. TM-AFM images of hybrids $\text{MWCNTs}\cdot[1\mathbf{b}\cdot\mathbf{4}]_n$