Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Determination of association constants and FRET in hydrazide-based molecular duplex strands

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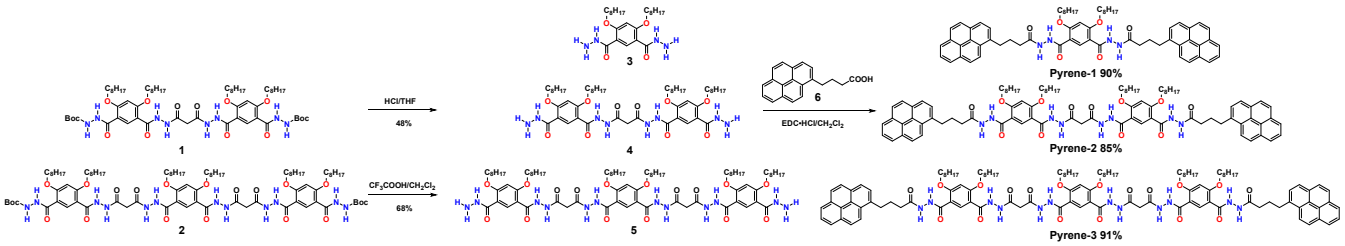
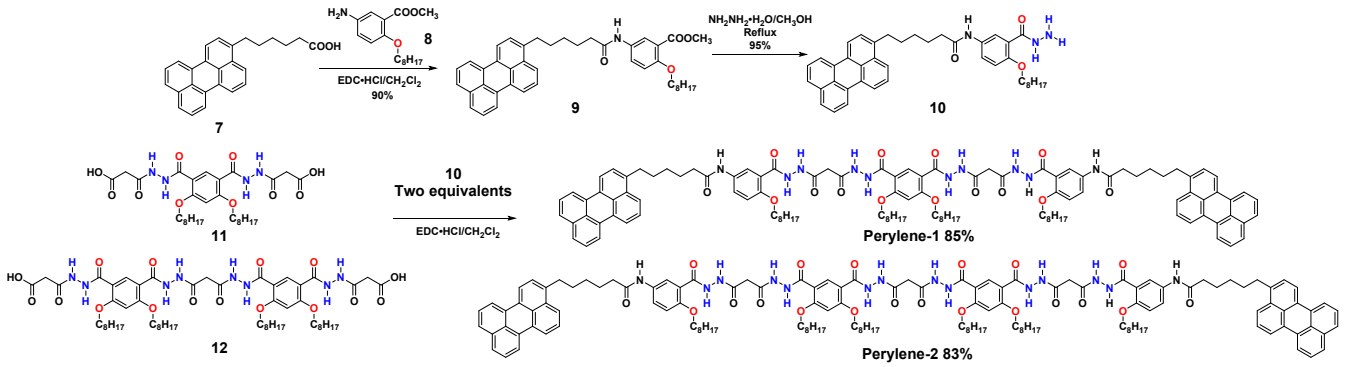
General Information for Synthesis and Characterization of New Compounds

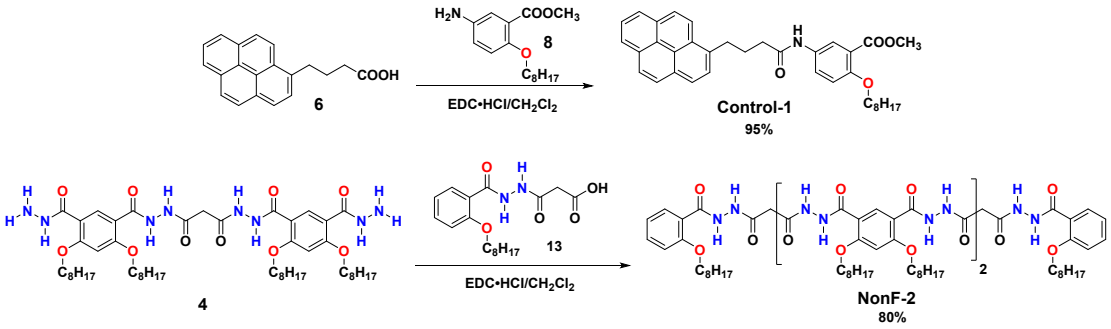
All solvents for reactions and column chromatography were used directly as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz or 300 MHz instruments. Chemical shifts were expressed in parts per million (δ: ppm) using residual solvent protons or TMS as internal standards. Chloroform (δ = 7.26 ppm) was used as an internal standard for chloroform-*d*. DMSO (δ = 2.50 ppm) was used as an internal standard for DMSO-d_6. Coupling constants (*J* values) were given in hertz (Hz). HRMS analysis was performed using a MALDI-TOF or ESI or APCI mass spectrometer.



Scheme 1 Synthetic route for pyrene labelled oligomers **Pyrene-1** ~ **Pyrene-3**.

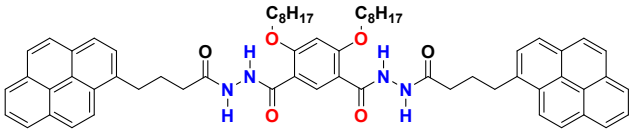


Scheme 2 Synthetic route for perylene labelled oligomers **Perylene-1** and **Perylene-2**.



Scheme S3 Synthetic routes for **Control-1** and **NonF-2**.

Compounds **1**[S1], **2**[S1], **3**[S2], **11**[S1], **12**[S1], **13**[S2], and **NonF-1**[S3] were synthesized previously in our group. Compound **6** is commercially available. Compound **7**[S4] and compound **8**[S5] were prepared according to reported literature procedures. Compound **8** was used directly for the next step without characterization after efficient catalytic hydrogenation reaction.



Pyrene-1

Pyrene-1: A mixture of compound **3**[S2] (67.5 mg, 0.15 mmol), 1-pyrenebutyric acid **6** (115 mg, 0.4 mmol), and EDC·HCl (192 mg, 1 mmol) in 10 mL CH_2Cl_2 was stirred at room temperature for 8 hours. The solvent was evaporated under reduced pressure. The residue was triturated with hot acetonitrile to give the pure product (134 mg, 90%) as a grey solid.

m. p.: 185.3-187.0 ℃.

^{1}H NMR (400 MHz, $CDCl_3$ & CF_3COOH, TMS, 298 K, ppm): δ 10.75 (s, 2H, N*H*^{c}), 10.41 (s, 2H, N*H*^{d}), 8.51 (s, 1H, Ar*H*^{b}), 8.24-7.83 (m, 18H, Pyrene-*H*), 6.15 (s, 1H, Ar*H*^{a}), 4.00 (t, *J* = 6.8 Hz, 4H, OC*H*$_2$), 3.44 (t, *J* = 7.4 Hz, 4H, Pyrene-C*H*$_2$), 2.67 (t, *J* = 7.2 Hz, 4H, COC*H*$_2$CH$_2$), 2.38 (m, 4H, COCH$_2$C*H*$_2$), 1.97 (m, 4H, OCH$_2$C*H*$_2$), 1.46 (br, 20H, C*H*$_2$), 0.87 (br, 6H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$ & CF_3COOH, TMS, 298 K, ppm): δ 169.4, 161.0, 159.7, 135.0, 129.4, 127.4, 116.2, 110.4, 95.6, 70.4, 31.74, 29.3, 29.1, 25.9, 22.6, 14.1.

HRMS (ESI$^+$) calcd. for $[C_{64}H_{70}N_4O_6 + Na]^+$ 1013.5188, found: 1013.5168.

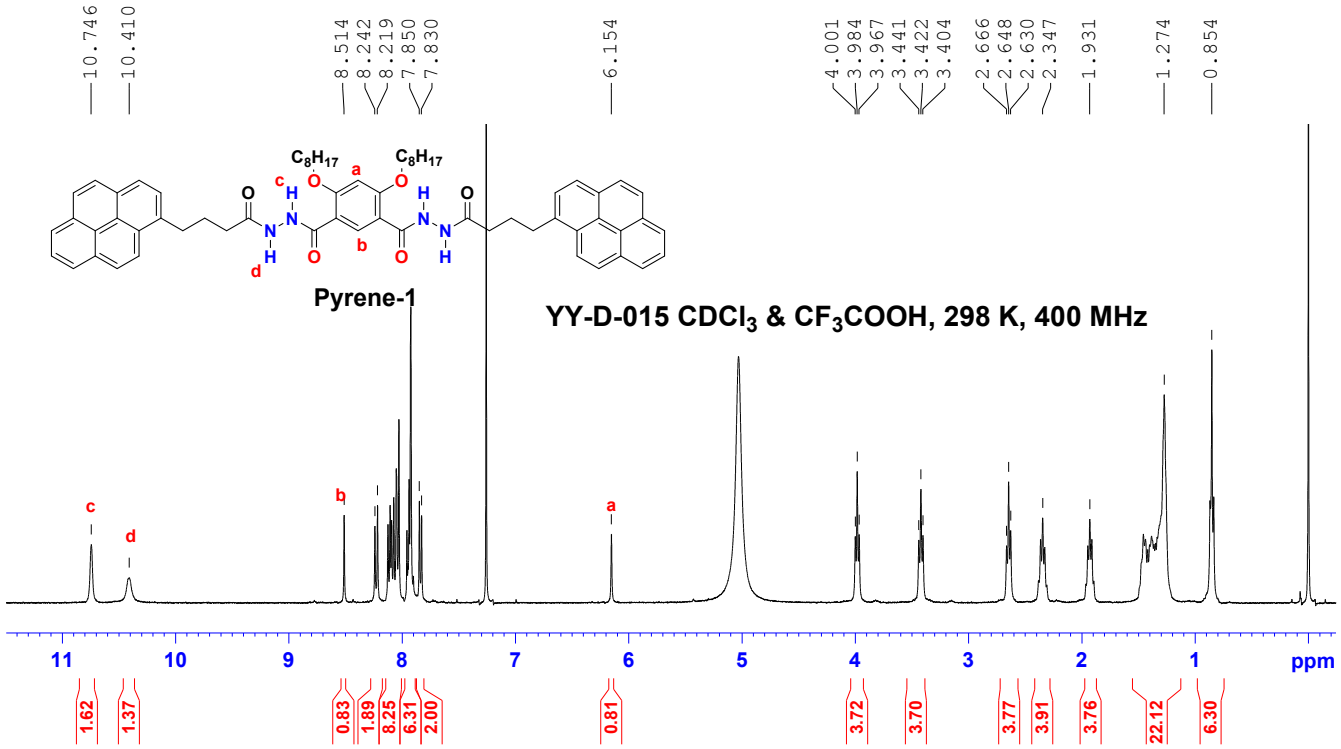


Figure S1 ^{1}H NMR spectrum for **Pyrene-1**, in $CDCl_3$ with a little CF_3COOH, 298 K, 400 MHz.

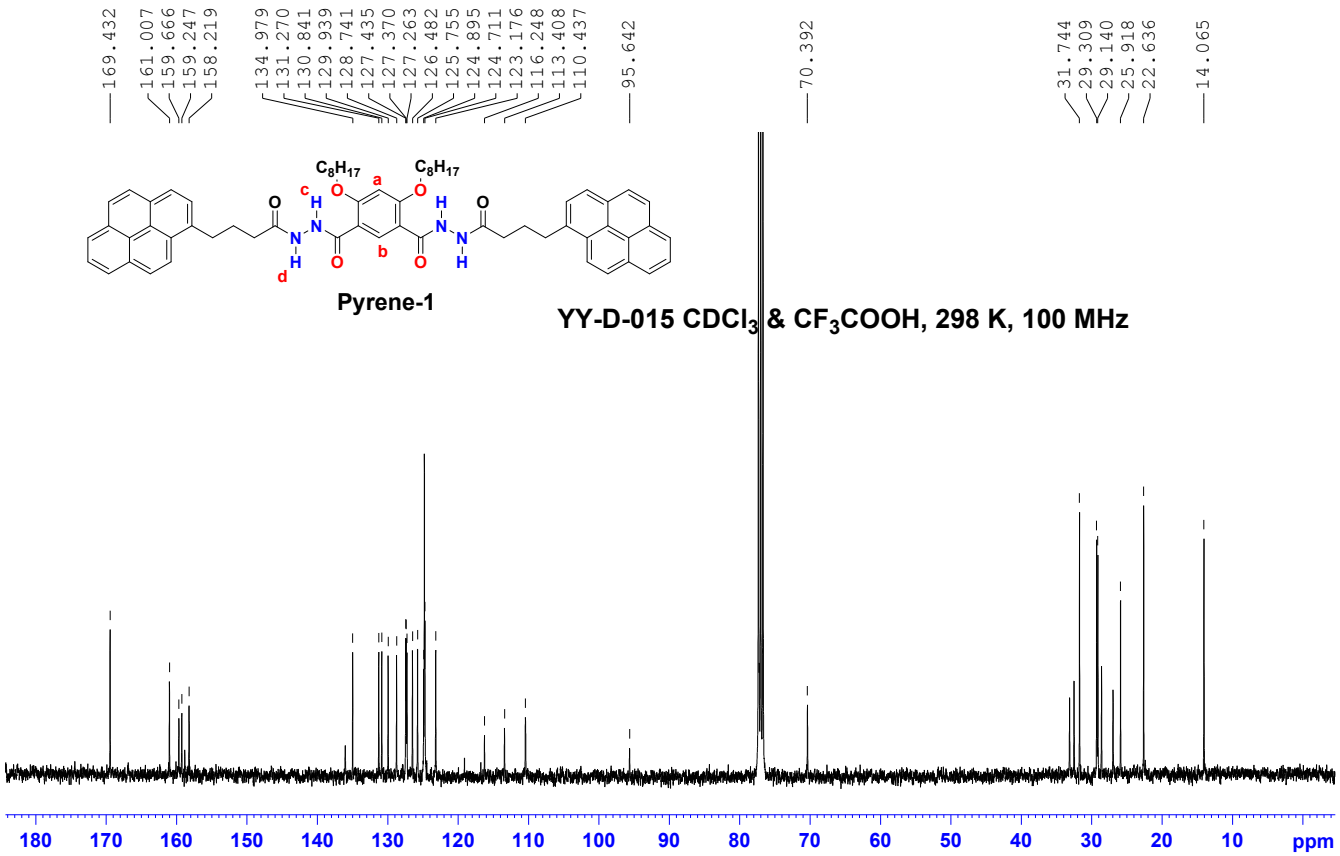
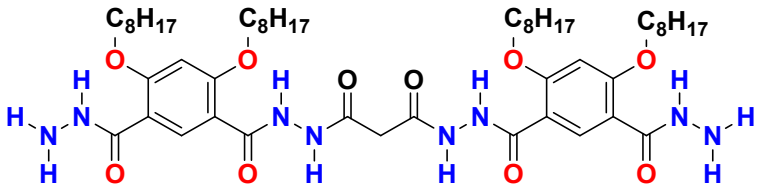


Figure S2 ^{13}C NMR spectrum for **Pyrene-1**, in $CDCl_3$ with a little CF_3COOH, 298 K, 100 MHz.



4

Compound **4**: Into a solution of compound **1**[S1] (200 mg) in 5 mL THF was added dropwise a mixture of 5 mL THF and 5 mL HCl. Then the mixture was stirred at room temperature for 7 hours. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was nutralized with saturated K_2CO_3 solution. The aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine and water successively and then dried over anhydrous Na_2SO_4. After evaporation of CH_2Cl_2, the residue was recrystallized from hot methanol to give the pure product (75 mg, 48%) as a white solid.

m. p.: 164.2-165.3 ℃.

^1H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 11.5 (br, 2H, N*H*), 10.73 (s, 2H, N*H*), 8.99 (s, 2H, N*H*), 8.77 (s, 2H, Ar*H*^{c}), 6.45 (s, 2H, Ar*H*^{b}), 4.33 (br, 4H, N*H*), 4.16 (br, 8H, OC*H*$_2$), 3.95 (s, 2H, COC*H*$_2^a$), 2.07 (m, 4H, OCH$_2$C*H*$_2$), 1.94 (m, 4H, OCH$_2$C*H*$_2$), 1.37 (br, 40H, C*H*$_2$), 0.89 (br, 12H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 165.7, 161.3, 160.7, 160.5, 136.8, 113.4, 112.3, 96.3, 70.1, 69.8, 31.75, 29.2, 26.0, 22.6, 14.1.

HRMS (ESI$^+$) calcd. for $[C_{51}H_{84}N_8O_{10} + Na]^+$ 991.6203, found: 991.6187.

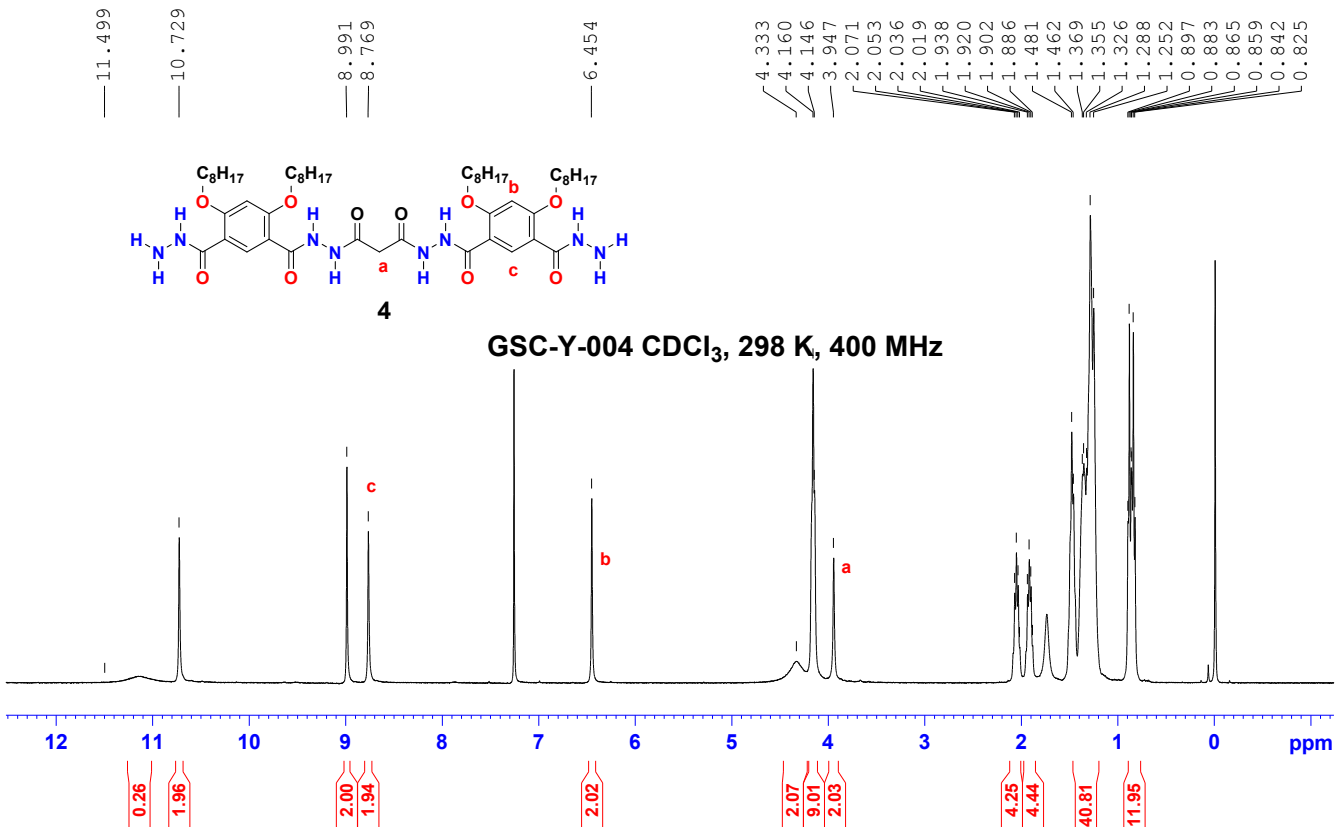


Figure S3 ^{1}H NMR spectrum for compound **4**, $CDCl_3$, 298 K, 400 MHz.

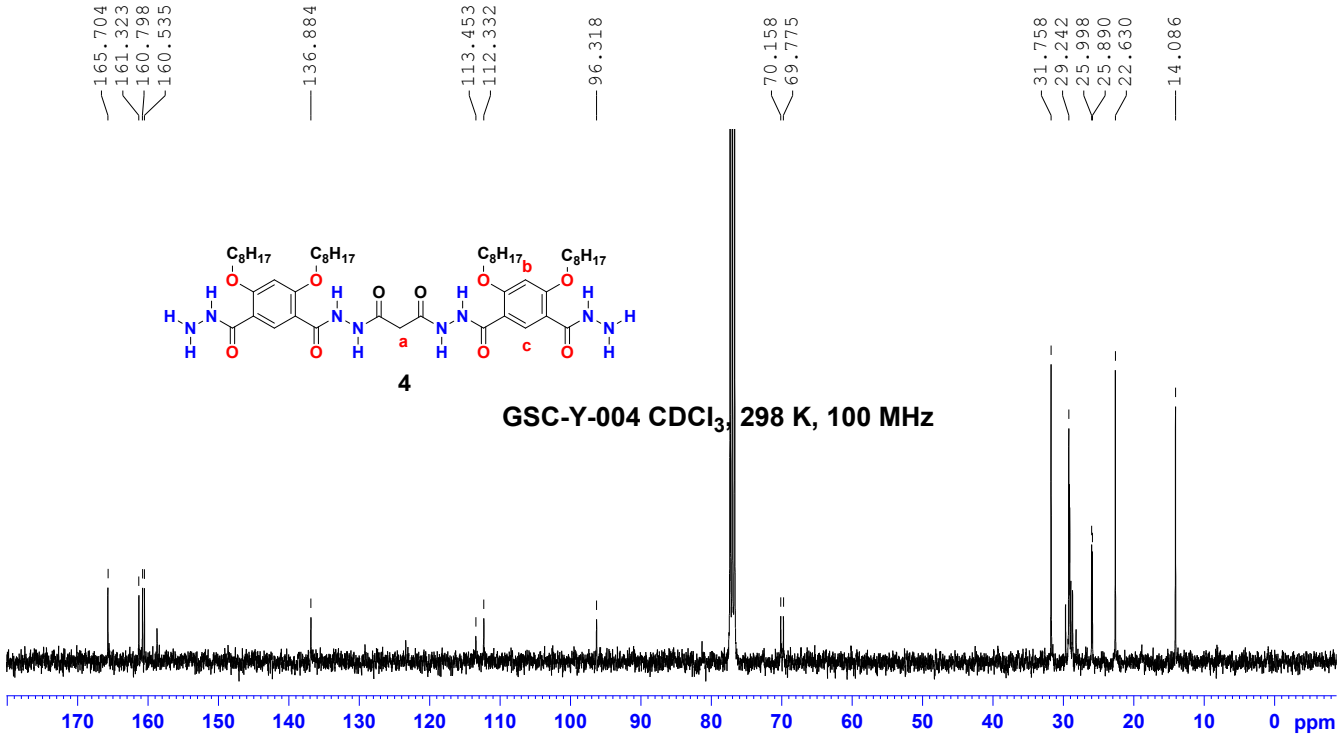
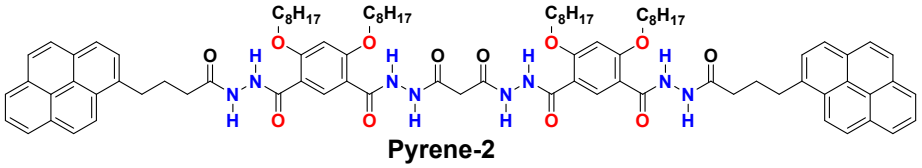


Figure S4 ^{13}C NMR spectrum for compound **4**, $CDCl_3$, 298 K, 100 MHz.



Pyrene-2: This compound was synthesized from coupling reaction of compound **4** and compound **6** according to a similar procedure as described for **Pyrene-1**.

Yield: 85%.

m. p.: 179.6-180.8 ℃.

^{1}H NMR (400 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.89 (d, J = 4.5 Hz, 2H, NH^d), 10.56 (d, J = 4 Hz, 2H, NH^c), 10.19 (d, J = 4.8 Hz, 2H, NH^b), 9.99 (d, J = 4 Hz, 2H, NH^a), 8.46-8.02 (m, 20H, ArH^f & Pyrene-H), 6.87 (s, 2H, ArH^e), 4.26 (br, 8H, OCH_2CH$_2$), 3.37 (br, 6H, COCH_2CO & Pyrene-CH_2), 2.41 (br, 4H, COCH_2CH$_2$), 2.13 (br, 4H, Pyrene-CH$_2$CH_2), 1.88 (br, 8H, OCH$_2$CH_2), 1.26 (br, 40H, CH_2), 0.85 (dt, J = 6.6 Hz, 12H, CH_3).

HRMS (ESI$^+$) calcd. for [$C_{91}H_{112}N_8O_{12}$ + H]$^+$ 1509.8472, found: 1509.8412, calcd.for [$C_{91}H_{112}N_8O_{12}$ + Na]$^+$ 1531.8292, found: 1531.8655.

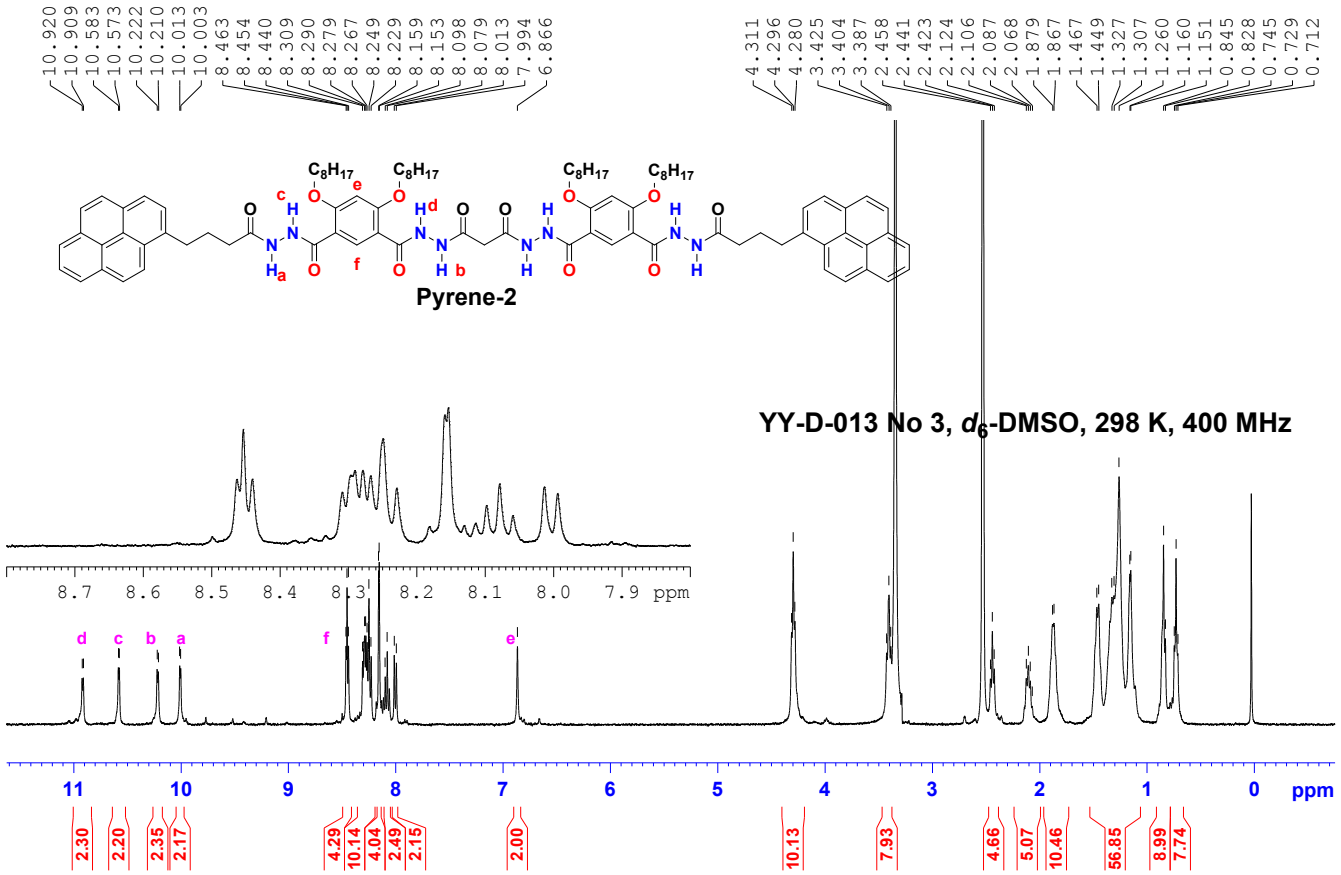
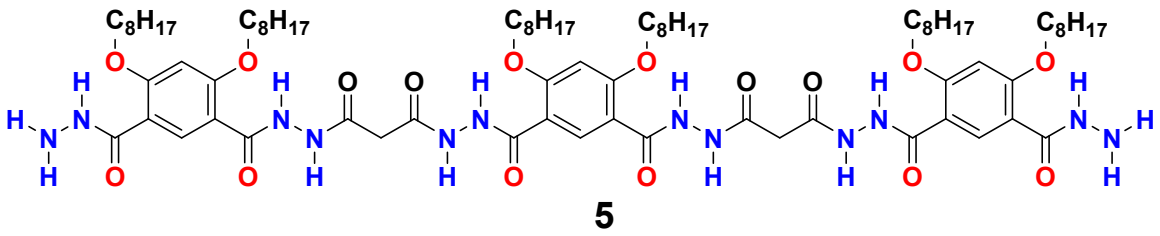


Figure S5 ^{1}H NMR spectrum for **Pyrene-2**, d_6-DMSO, 298 K, 400 MHz.



5

Compound **5**: Into a solution of compound **2**[S1] (100 mg) in 2 mL of CH_2Cl_2 was added 1.5 mL CF_3COOH cooling in an ice-water bath. The mixture was stirred at room temperature for 3 hours. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was nutralized with saturated K_2CO_3 solution. The aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine and water successively and then dried over anhydrous Na_2SO_4. After evaporation of CH_2Cl_2, the crude product was recrystallized from hot methanol to give the pure product (60 mg, 68%) as a pink solid.

m. p.: 117.6-118.3 ℃.

^{1}H NMR (400 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.92 (br, 4H, N*H*^{e}), 10.22 (d, *J* = 8.8 Hz, 4H, N*H*^{f}), 8.97 (br, 2H, N*H*^{i}), 8.45 (s, 1H, Ar*H*^{d}), 8.39 (s, 2H, Ar*H*^{c}), 6.88 (s, 1H, Ar*H*^{a}), 6.82 (s, 2H, Ar*H*^{b}), 4.59 (br, 4H, N*H*), 4.30 (br, 16H, OCH_2 & COCH_2CO), 1.88 (m, 12H, OCH$_2$CH_2), 1.46 (br, 60H, CH_2), 0.89 (br, 18H, CH_3).

^{13}C NMR (100 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 164.5, 163.4, 161.3, 160.8, 160.6, 160.2, 134.4, 114.9, 113.4, 112.8, 98.4, 70.2, 69.6, 31.7, 29.1, 25.9, 22.6, 14.4.

HRMS (ESI^{+}) calcd. for [$C_{78}H_{126}N_{12}O_{16}$ + H]$^{+}$ 1487.9488, found: 1487.9410.

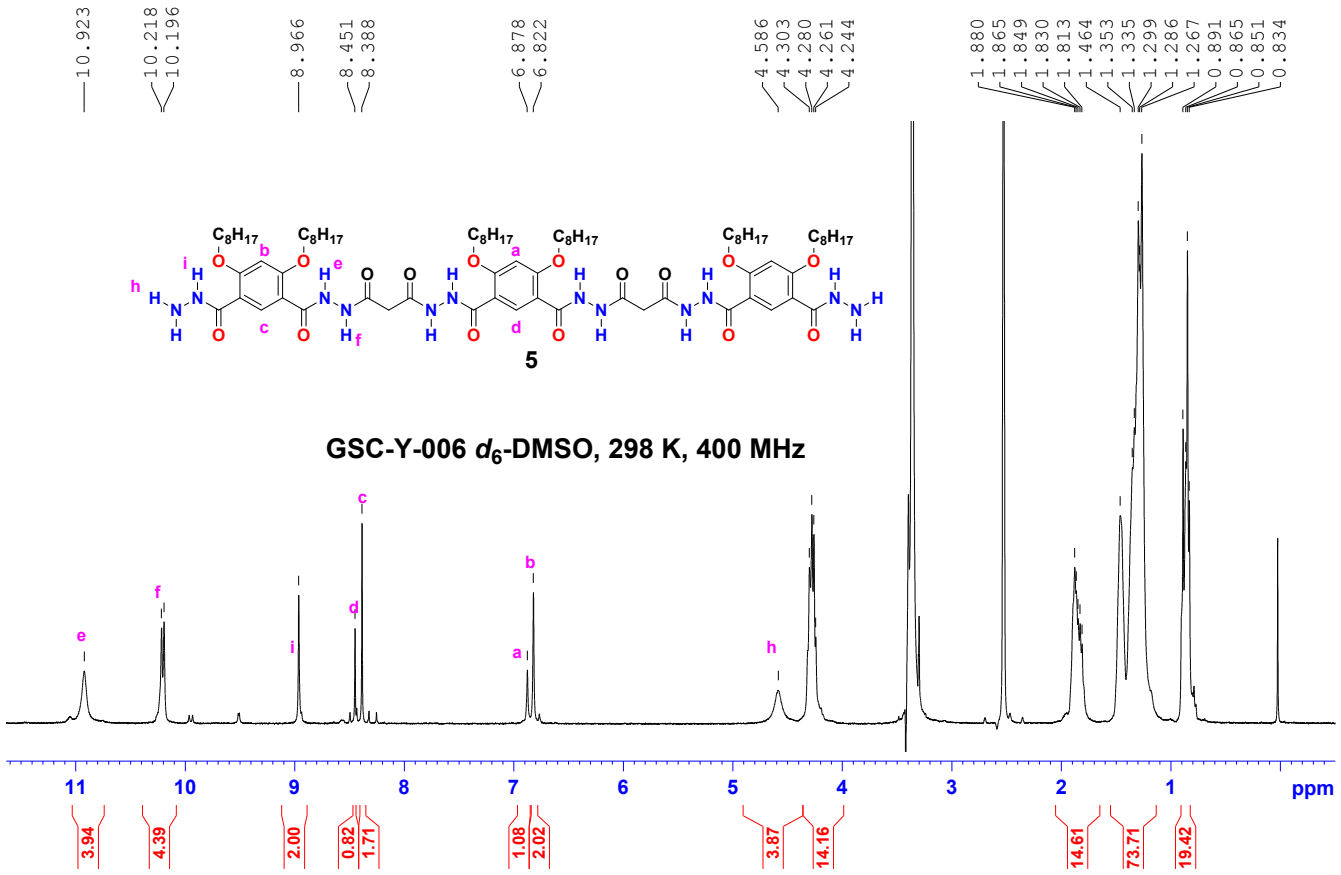


Figure S6 ^{1}H NMR spectrum for compound **5**, d_6-DMSO, 298 K, 400 MHz.

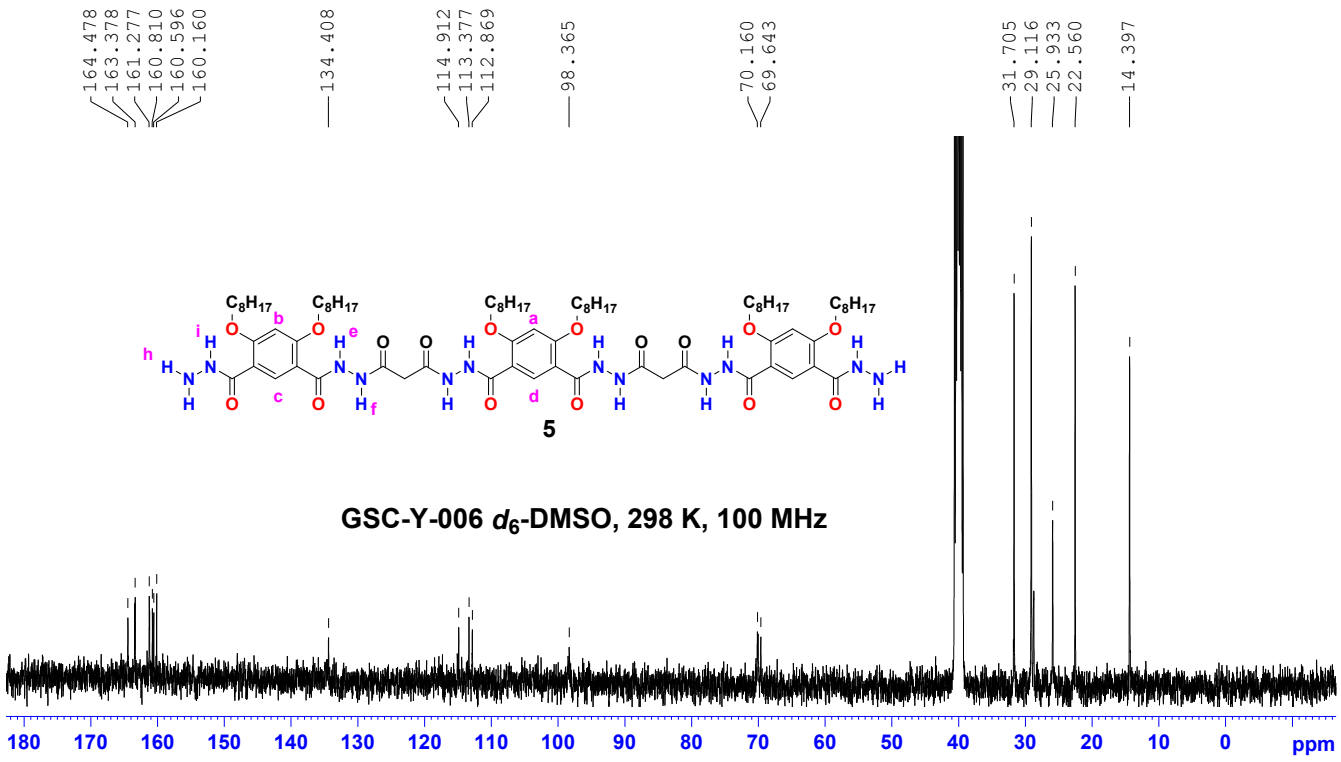
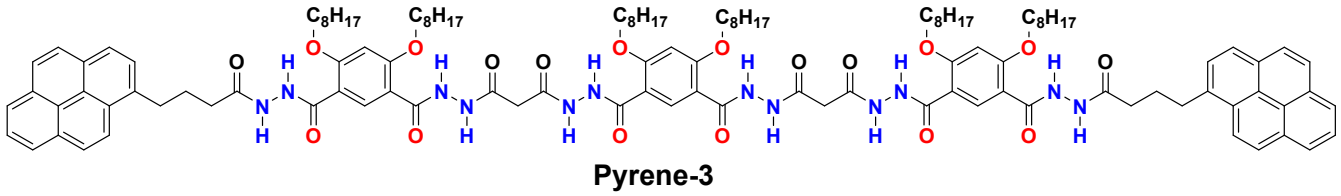


Figure S7 ^{13}C NMR spectrum for compound **5**, d_6-DMSO, 298 K, 100 MHz.



Pyrene-3: This compound was synthesized from compound **5** and compound **6** according to a similar procedure as described for compound **Pyrene-1**.

Yield: 91%.

m. p.: 208.7-210.2 ℃.

^1H NMR (400 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.92 (br, 4H, N*H*^{d}), 10.59 (br, 2H, N*H*^{c}), 10.22 (br, 4H, N*H*^{b}), 10.01 (br, 2H, N*H*^{a}), 8.57-7.94 (m, 21H, Ar*H*$^{h\ \&\ i}$ & Pyrene-*H*), 6.87 (s, 3H, Ar*H*$^{e\ \&\ f}$), 4.30 (m, 12H, OC*H*$_2$CH$_2$), 3.43 (br, 8H, COC*H*$_2$CO & Pyrene-C*H*$_2$ in the water peak), 2.44 (br, 4H, COC*H*$_2$CH$_2$), 2.17 (m, 4H, Pyrene-CH$_2$C*H*$_2$), 1.88 (m, 12H, OCH$_2$C*H*$_2$), 1.47 (br, 60H, C*H*$_2$), 0.85 (br, 18*H*, C*H*$_3$).

HRMS (ESI$^+$) calcd. for [$C_{118}H_{154}N_{12}O_{18}$ + H]$^+$ 2028.1577, found: 2028.1854.

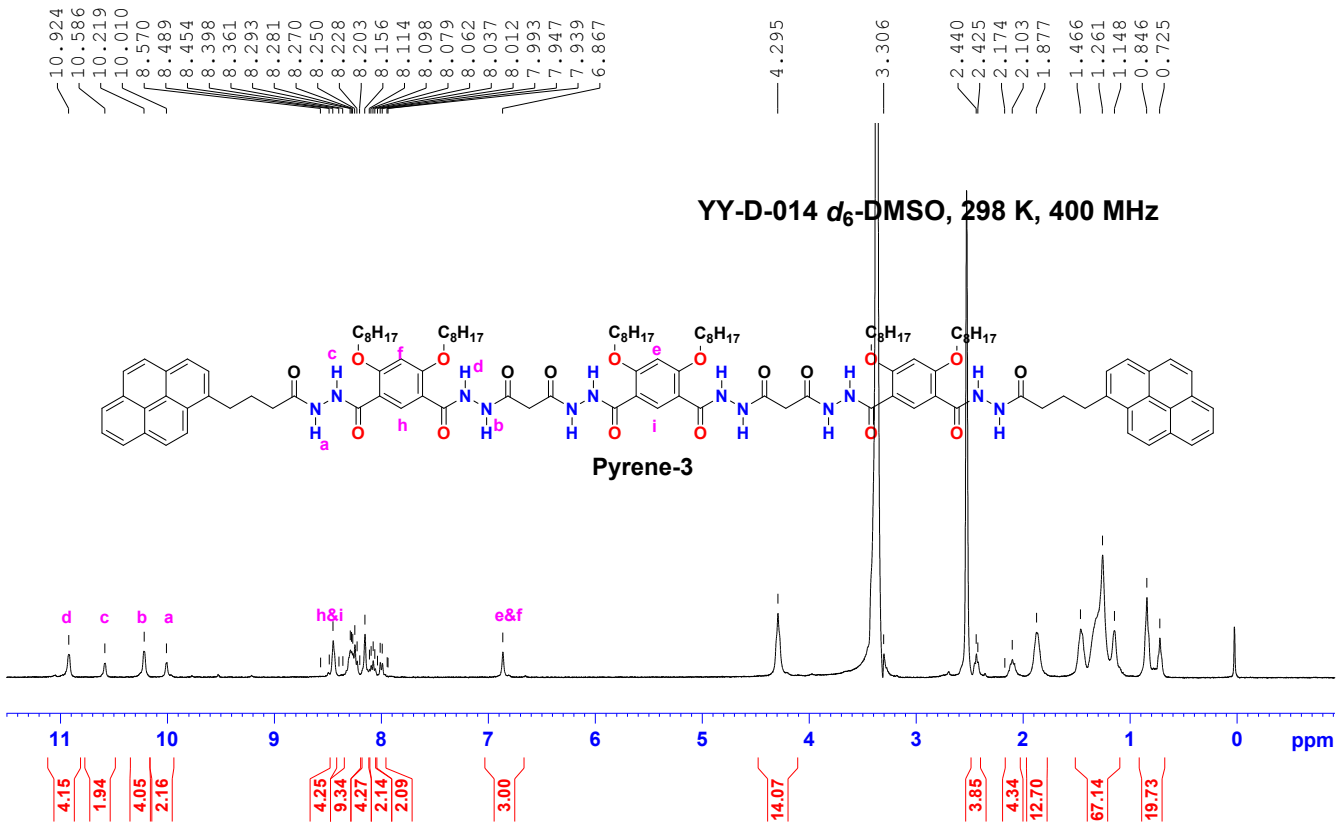
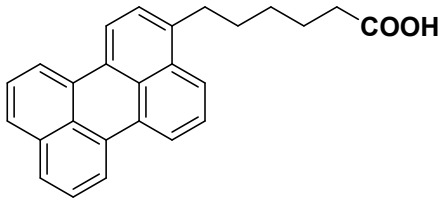


Figure S8 ^{1}H NMR spectrum for **Pyrene-3**, d_6-DMSO, 298 K, 400 MHz.



7

Compound **7**: This compound was prepared according to a previously reported literature procedure.[S4]

^{1}H NMR (400 MHz, d_6-DMSO, ppm): δ 12.0 (br, 1H, COO*H*^{a}), 8.39-7.41 (m, 11H, Perylene-*H*), 3.09 (t, J = 7.6 Hz, 2H, Perylene-CH_2^b), 2.53 (t, J = 7.2 Hz, 2H, COCH_2^c), 1.71-1.44 (m, 6H, CH_2).

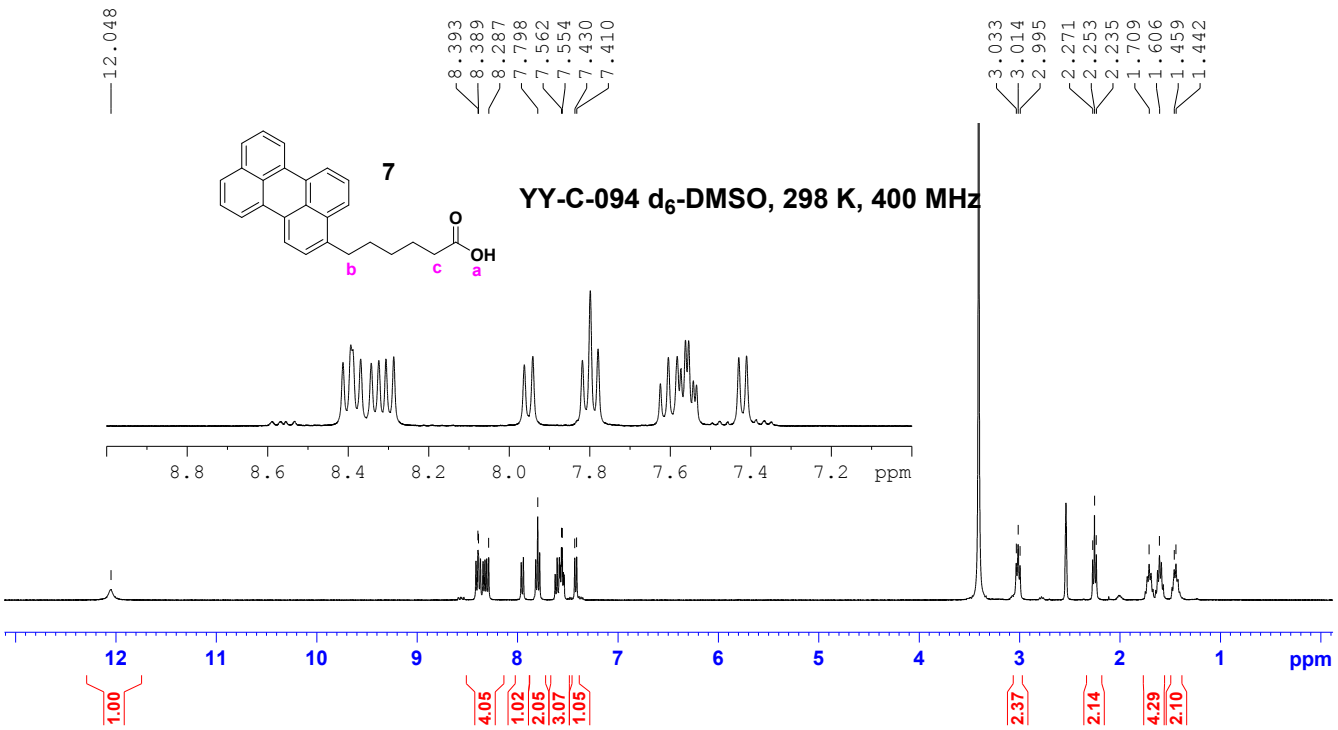
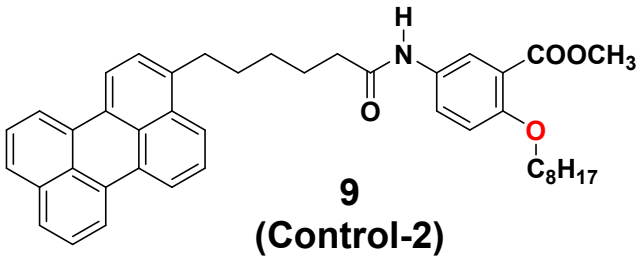


Figure S9 ^{1}H NMR spectrum for compound **7**, d_6-DMSO, 298 K, 400 MHz.



9
(Control-2)

Compound **9** (**Control-2**): This compound was synthesized from compound **7** and compound **8**[S5] according to a similar procedure as described for **Pyrene-1**.

Yield: 90%.

m. p.: 131.6-132.0 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.21-7.44 (m, 12H, Perylene-*H* & Ar*H)*, 7.34 (d, *J* = 7.7 Hz, 1H, ArH^{b}), 7.06 (s, 1H, N*H*), 6.87 (d, *J* = 8.9 Hz, 1H, ArH^{a}), 3.96 (t, *J* = 6.6 Hz, 2H, OCH_2), 3.86 (s, 3H, COOCH_3^{c}), 3.04 (t, *J* = 7.8 Hz, 2H, Perylene-CH_2), 2.33 (t, *J* = 7.3 Hz, 2H, COCH_2), 1.81 (m, 6H, $COCH_2C_3H_6$), 1.52 (m, 2H, OCH_2CH_2), 1.28 (br, 10H, CH_2), 0.88 (br, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 171.2, 166.4, 155.5, 138.5, 123.8, 120.1, 114.0, 69.4, 52.0, 37.4, 29.2, 25.9, 22.7, 14.1.

HRMS (ESI$^+$) calcd. for $[C_{42}H_{45}NO_4 + Na]^+$ 650.3241, found: 650.3246.

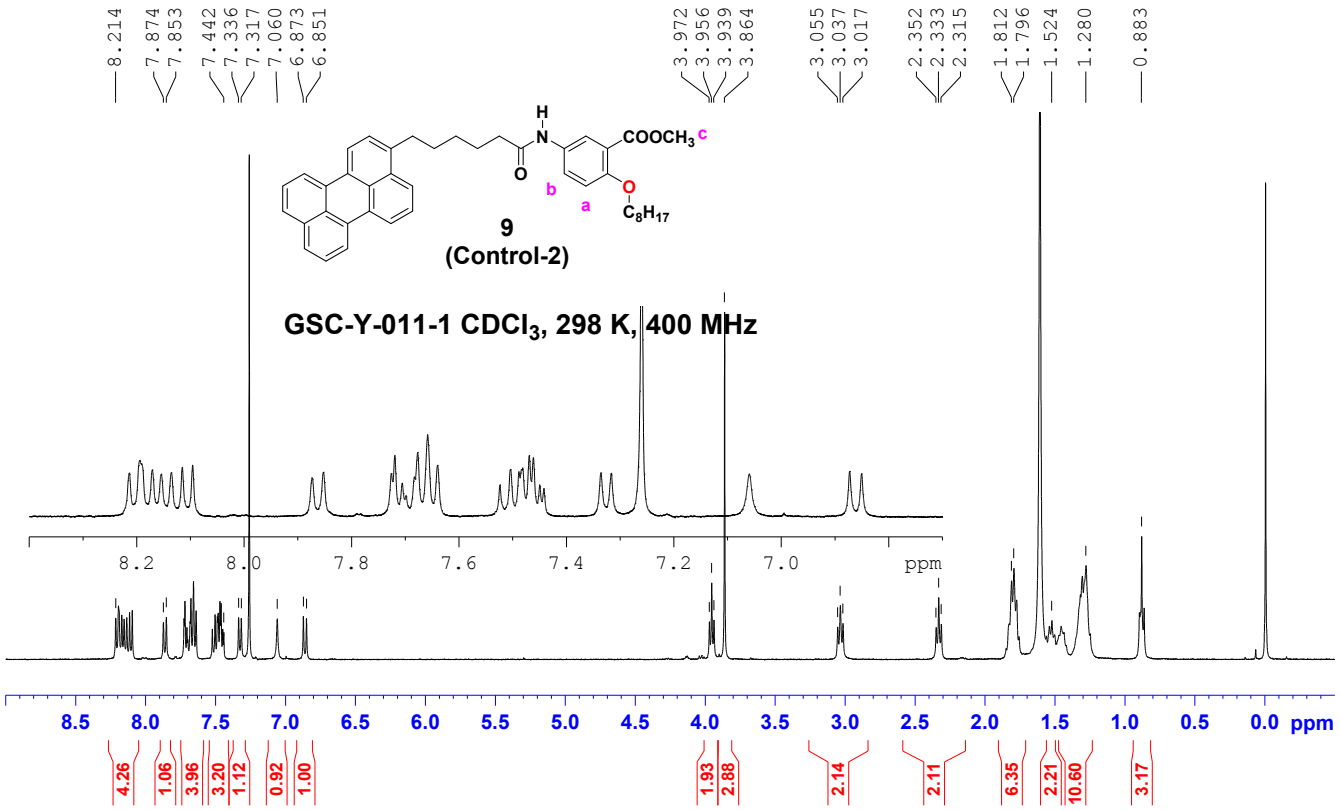


Figure S10 ^{1}H NMR spectrum for compound **9** (**Control-2**) $CDCl_3$, 298 K, 400 MHz.

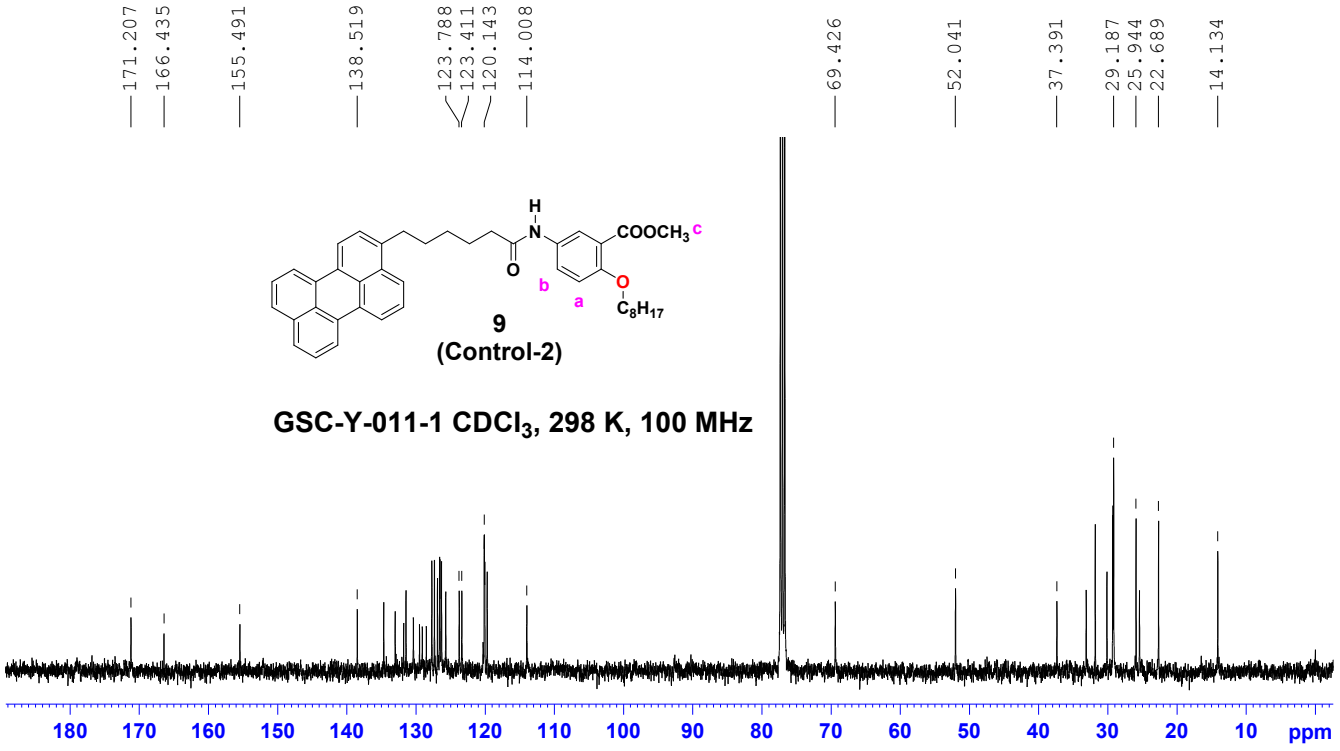
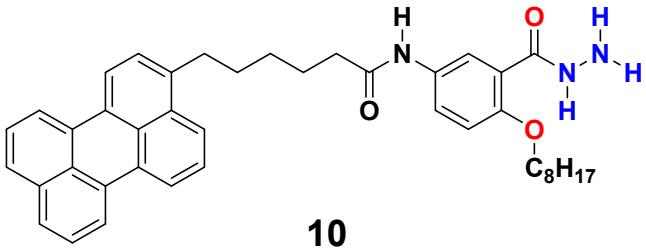


Figure S11 ^{13}C NMR spectrum for compound **9** (**Control-2**), $CDCl_3$, 298 K, 100 MHz.



10

Compound **10**: A mixture of compound **9** (100 mg) and 0.5 mL of $NH_2NH_2 \cdot H_2O$ (80%) in 10 mL CH_3OH was heated to reflux for 8 hours. After completion of the reaction, a yellow solid precipitated from the solution and was collected by filtration. After washing with CH_3OH, a light yellow solid (95 mg, 95%) was obtain.

m. p.: 155.2-156.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 9.09 (br, 1H, N*H*), 8.22-7.69 (m, 12H, Perylene-*H* & Ar*H)*, 7.37 (br, 2H, ArH^b & N*H*), 6.84 (d, *J* = 9.0 Hz, 1H, ArH^c), 4.18 (br, 2H, NH_2^a), 4.06 (t, *J* = 6.0 Hz, 2H, OCH_2), 3.07 (t, *J* = 6.8 Hz, 2H, Perylene-CH_2), 2.39 (t, *J* = 6.8 Hz, 2H, $COCH_2$), 1.85 (m, 6H, $COCH_2C_3H_6$), 1.56 (m, 2H, OCH_2CH_2), 1.33 (br, 10H, CH_2), 0.94 (br, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 171.3, 166.0, 153.4, 138.5, 120.1, 113.0, 69.5, 37.4, 33.1, 30.1, 26.0, 25.4, 22.6, 14.1.

HRMS (ESI$^+$) calcd. for $[C_{41}H_{45}N_3O_3 + H]^+$ 628.3534, found: 628.3527.

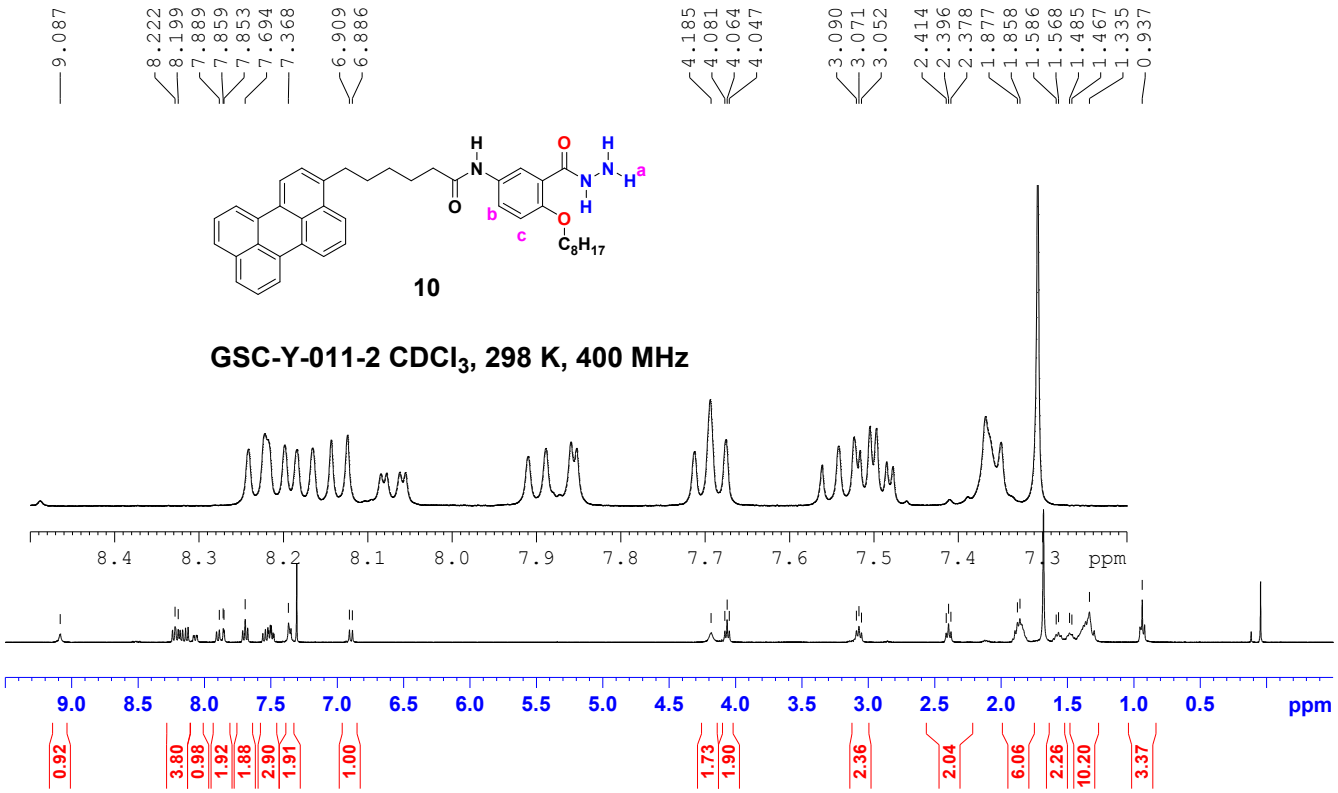


Figure S12 ^{1}H NMR spectrum for compound **10**, $CDCl_3$, 298 K, 400 MHz.

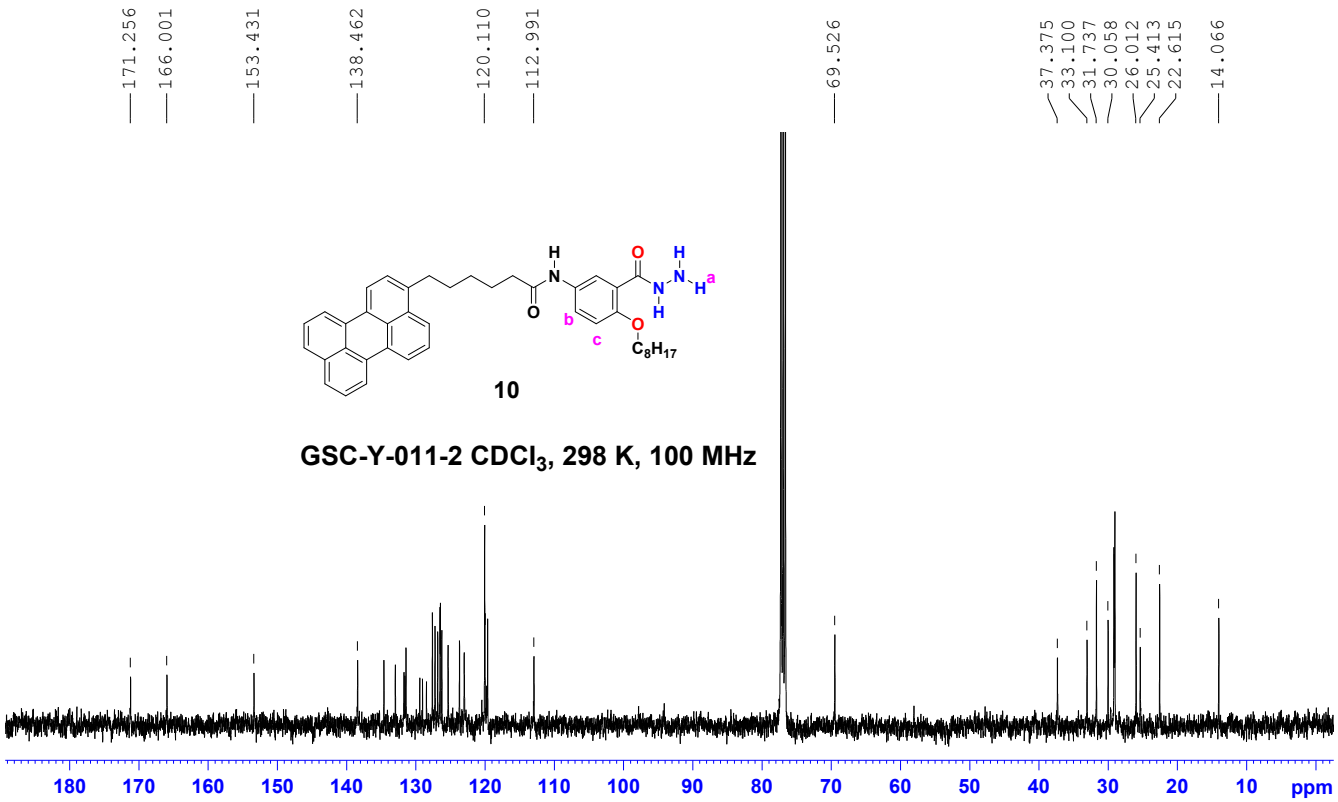
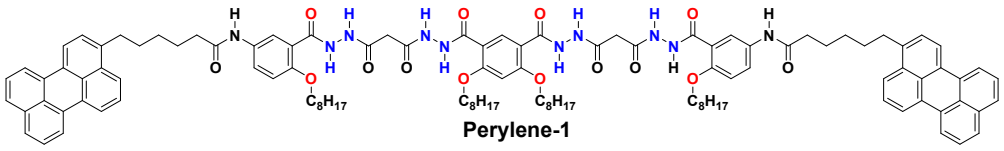


Figure S13 ^{13}C NMR spectrum for compound **10**, $CDCl_3$, 298 K, 100 MHz.



Perylene-1: This compound was synthesized from compound **10** and compound **11**[S1] according to a similar procedure as described for **Pyrene-1**.

Yield: 85%.

m. p.: 174.8-176.1 ℃.

^{1}H NMR (400 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.80 (br, 4H, NH^g), 10.33 (br, 2H, NH^m), 10.13 (br, 2H, NH^n), 9.82 (s, 2H, NH^i), 8.44 (s, 1H, ArH^b), 8.33-7.52 (m, 24H, Perylene-*H* & ArH), 7.41 (br, 2H, ArH^f), 7.11 (d, J = 8.4 Hz, 2H, ArH^e), 6.83 (s, 1H, ArH^c), 4.26 (br, 4H, OCH_2), 4.08 (br, 4H, OCH_2), 3.39 (s, 4H, COCH_2^{a}CO), 3.01 (br, 4H, Perylene-CH_2), 2.30 (br, 4H, COCH_2CH$_2$), 1.80 (m, 16H, COCH$_2$C$_3$$H_6$ & OCH$_2$CH_2), 1.43 (m, 4H, OCH$_2$CH_2), 1.23 (br, 40H, CH_2), 0.82 (br, 12H, CH_3).

^{13}C NMR (100 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 171.5, 163.5, 161.7, 160.8, 152.6, 139.1, 134.8, 127.2, 124.4, 120.6, 113.3, 111.0, 71.4, 68.4, 31.7, 29.1, 26.2, 25.9, 22.5, 14.4.

HRMS (MALDI$^+$) calcd. for [$C_{112}H_{132}N_{10}O_{14}$ + H]$^+$ 1841.9997, found: 1841.9914.

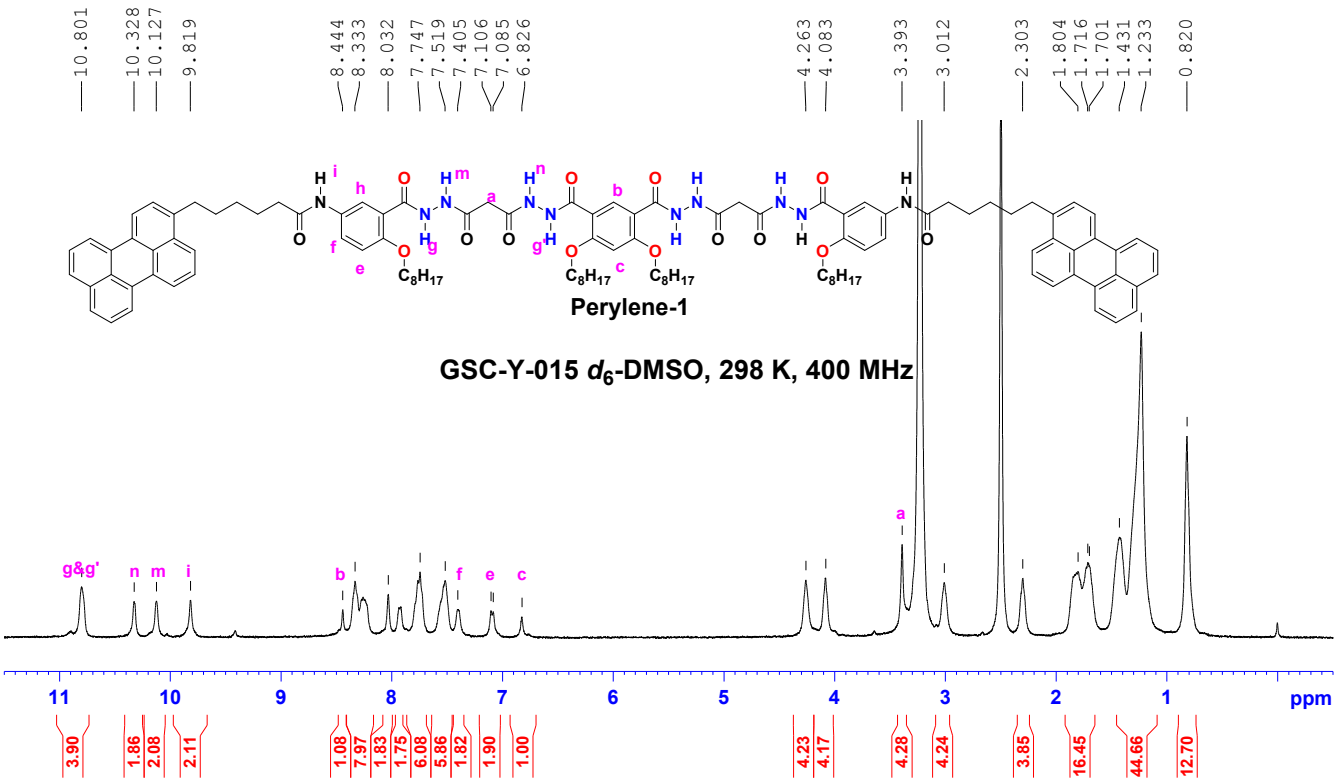


Figure S14 ^{1}H NMR spectrum for **Perylene-1**, d_6-DMSO, 298 K, 400 MHz

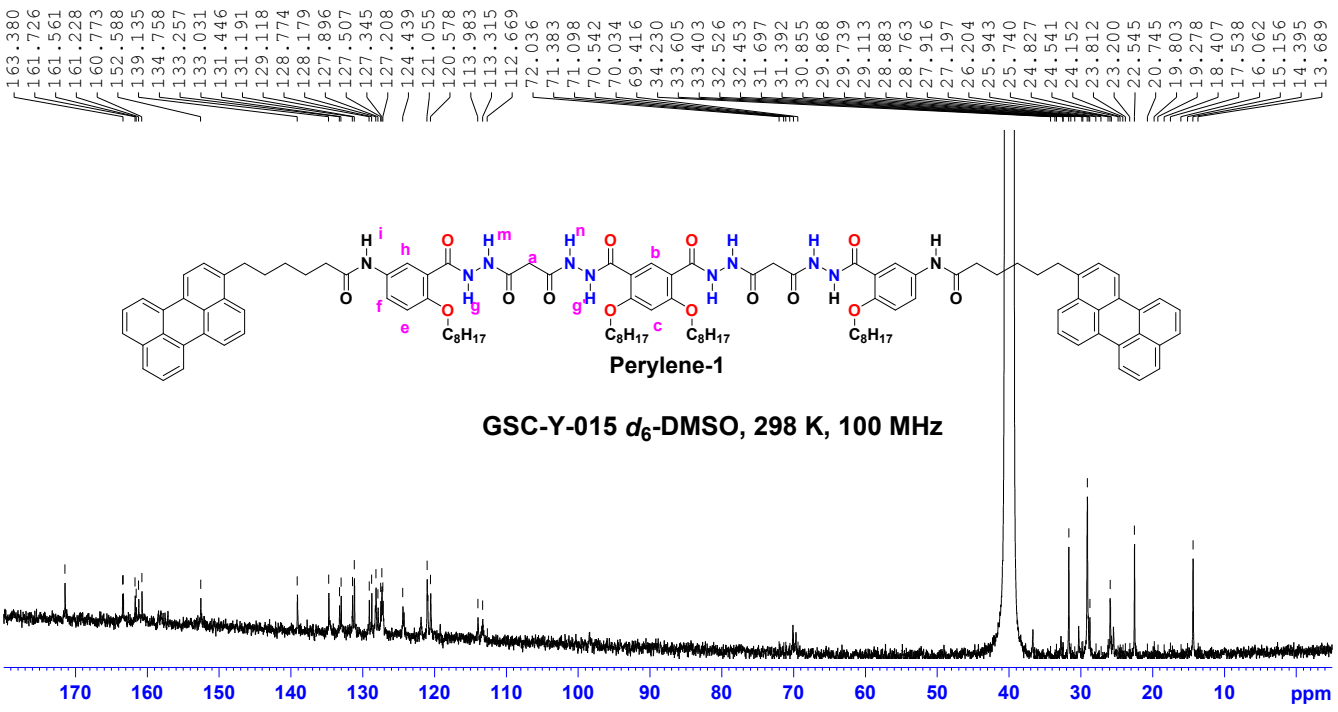
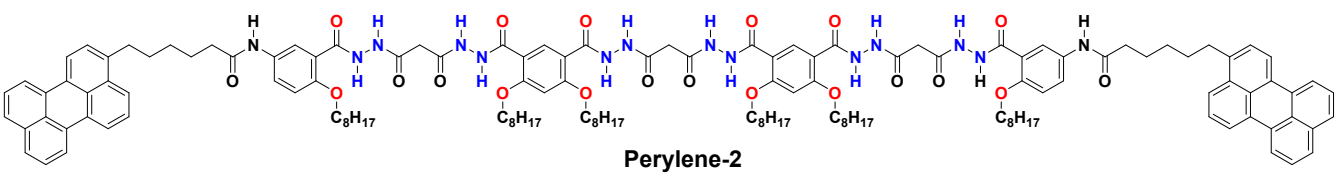


Figure S15 ^{13}C NMR spectrum for **Perylene-1**, d_6-DMSO, 298 K, 100 MHz



Perylene-2: This compound was synthesized from compound **10** and compound **12**[S1] according to a similar procedure as described for **Pyrene-1**.

Yield: 83%.

m. p.: 211.9-213.0 ℃.

^{1}H NMR (400 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.93 (br, 6H, N$H^{i\&i'\&i''}$), 10.39 (br, 2H, N$H^{f''}$), 10.19 (br, 4H, N$H^{f\&f'}$), 9.92 (s, 2H, NH^{e}), 8.42 (s, 2H, ArH^{d}), 8.32-7.51 (m, 24H, Perylene-*H* & Ar*H*), 7.40 (d, *J* = 6.7 Hz, 2H, ArH^{c}), 7.10 (d, *J* = 8.8 Hz, 2H, ArH^{b}), 6.81 (s, 2H, ArH^{a}), 4.24 (br, 8H, OCH_2), 4.06 (br, 4H, OCH_2), 3.39 (s, 4H, COCH_2CO in the water peak), 3.00 (br, 4H, Perylene-CH_2), 2.29 (br, 4H, COCH_2CH$_2$), 1.83 (m, 16H, COCH$_2$C$_3H_6$), 1.69 (m, 8H, OCH$_2$CH_2), 1.67 (m, 4H, OCH$_2$CH_2), 1.21 (br, 60H, CH_2), 0.80 (br, 18H, CH_3).

^{13}C NMR (100 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 171.5, 163.4, 160.7, 139.1, 134.7, 121.0, 113.3, 98.4, 70.1, 31.7, 29.1, 22.6, 14.4.

HRMS (MALDI$^+$) calcd. for [$C_{139}H_{174}N_{14}O_{20}$ + H]$^+$ 2360.3102, found: 2360.2982.

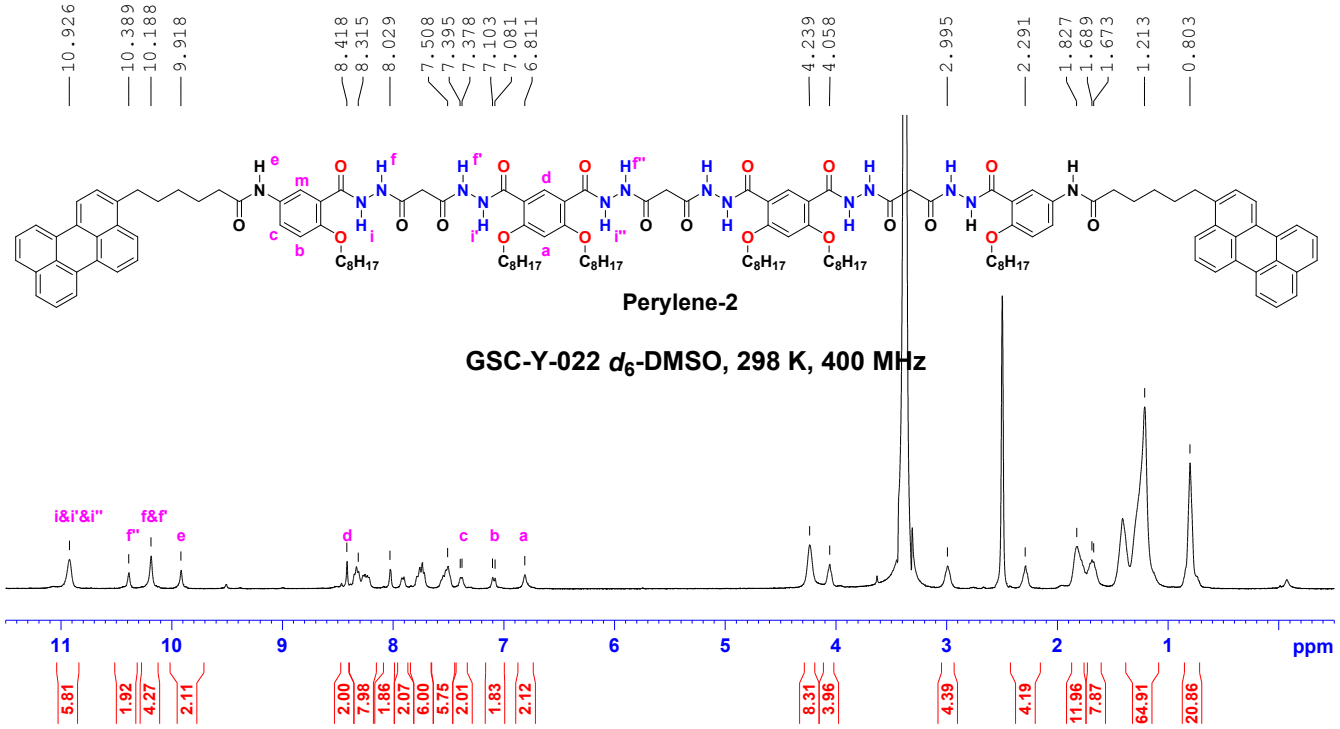


Figure S16 ^{1}H NMR spectrum for **Perylene-2**, d_6-DMSO, 298 K, 400 MHz.

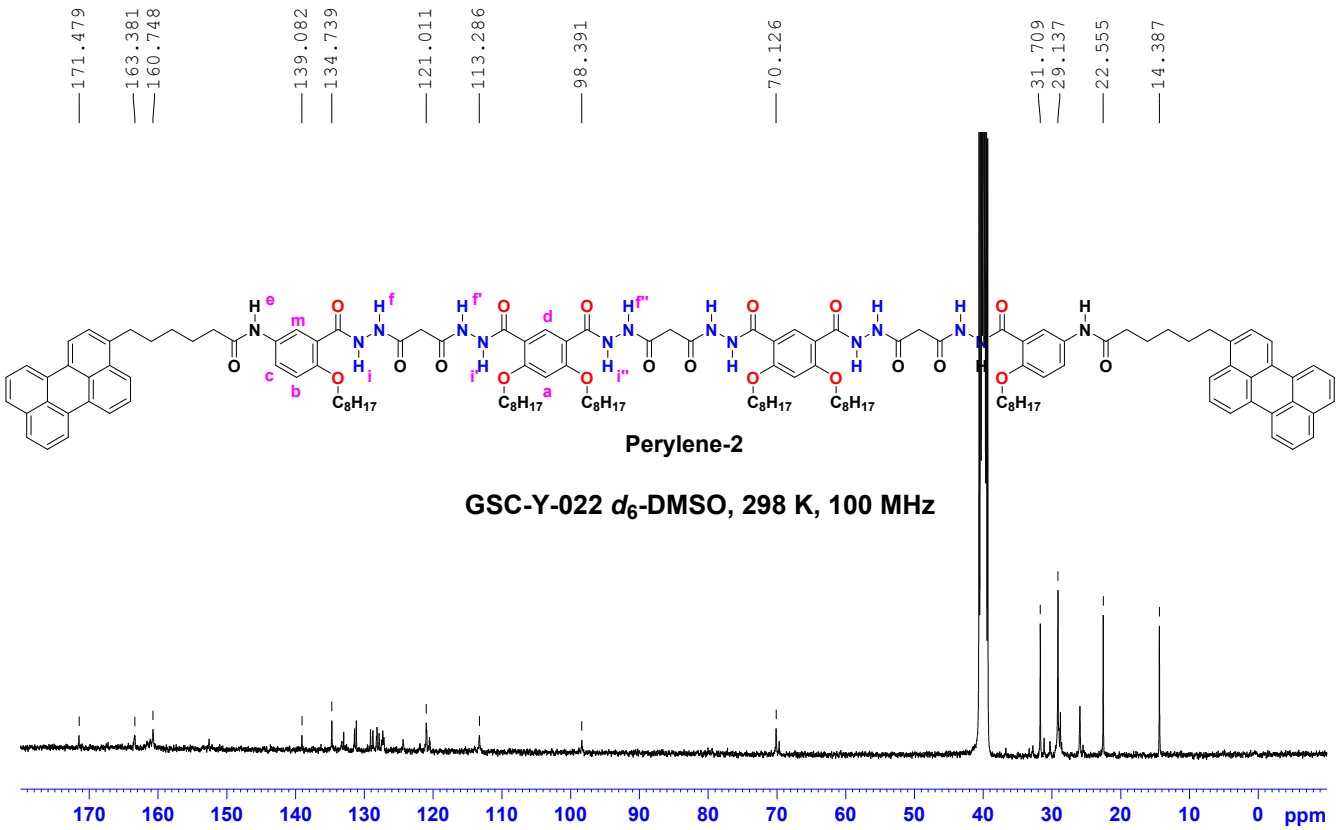
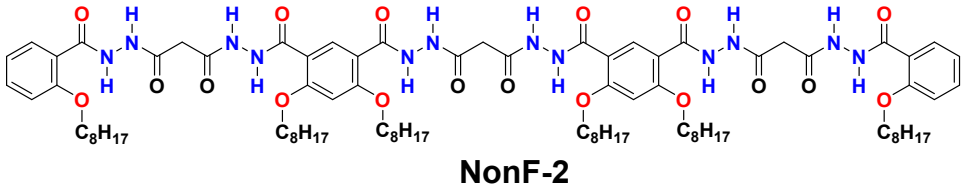


Figure S17 ^{13}C NMR spectrum for **Perylene-2**, d_6-DMSO, 298 K, 100 MHz.



NonF-2: This compound was synthesized from compound **4** and compound **13**[S2] according to a similar procedure as described for **Pyrene-1**.

Yield: 80%.

m. p.: 156.3-157.1 ℃.

^{1}H NMR (300 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 10.92 (d, J = 3.5 Hz, 4H, N$H^{f\&f'}$), 10.84 (d, J = 3.5 Hz, 2H, NH^{e}), 10.32 (d, J = 4.2 Hz, 2H, NH^{d}), 10.21 (d, J = 4.1 Hz, 4H, N$H^{c\&c'}$), 8.43 (s, 2H, ArH^{b}), 7.85 (d, J = 7.1 Hz, 2H, ArH^{g}), 7.54 (t, J = 7.9 Hz, 2H, ArH^{j}), 7.20 (d, J = 8.4 Hz, 2H, ArH^{h}), 7.10 (t, J = 7.5 Hz, 2H, ArH^{i}), 6.86 (s, 2H, ArH^{a}), 4.28 (br, 8H, OC$H_2^{m\&m'}$), 4.16 (t, J = 6.4 Hz, 4H, OCH_2^{n}), 3.38 (s, 6H, COCH_2CO), 1.86 (m, 12H, COCH_2CH_2), 1.24 (br, 60H, CH_2), 0.824 (br, 18H, CH_3).

^{13}C NMR (75 MHz, d_6-DMSO, TMS, 298 K, ppm): δ 162.9, 162.8, 161.6, 160.5, 160.3, 156.5, 133.0, 133.6, 120.6, 120.3, 113.1, 112.8, 98.0, 69.7, 68.9, 31.2, 28.6, 25.4, 22.0, 13.8.

HRMS (ESI$^+$) calcd. for [$C_{87}H_{132}N_{12}O_{18}$ + Na]$^+$ 1655.9675, found: 1655.9607.

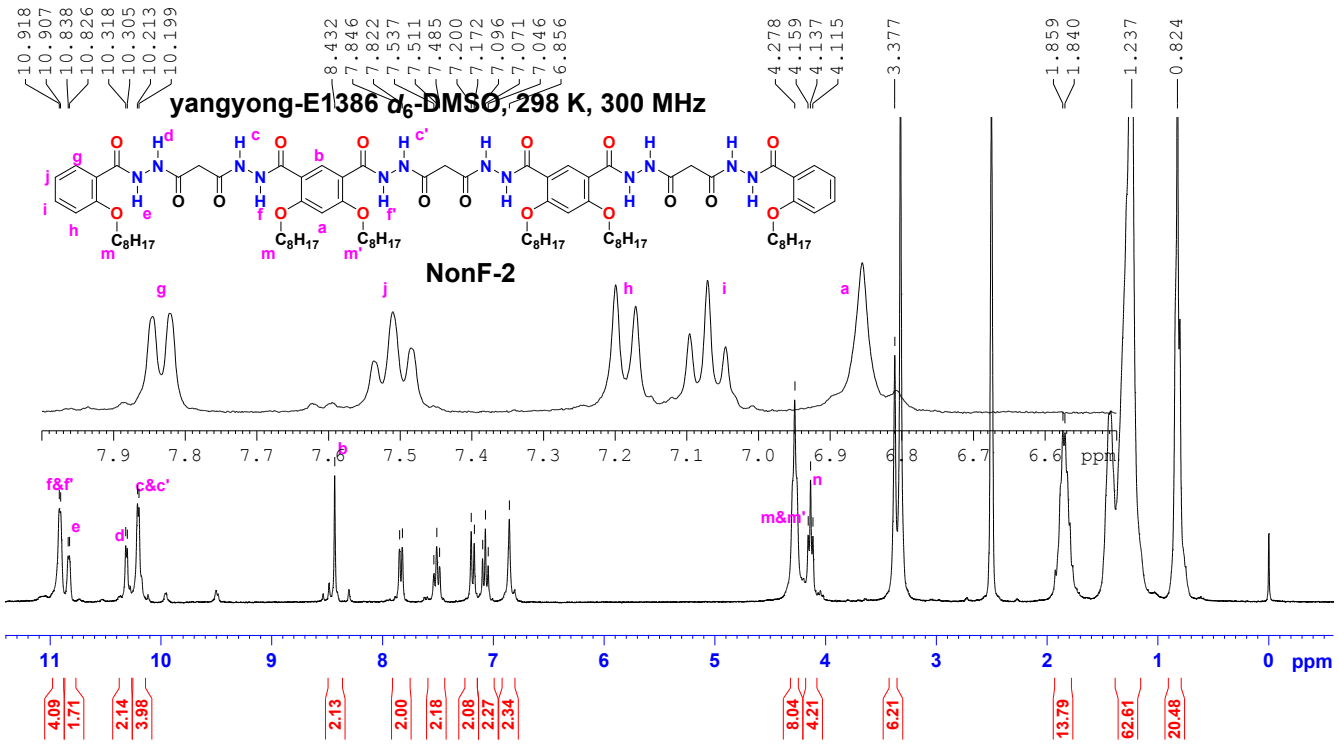


Figure S18 ^{1}H NMR spectrum for **NonF-2**, d_6-DMSO, 298 K, 300 MHz.

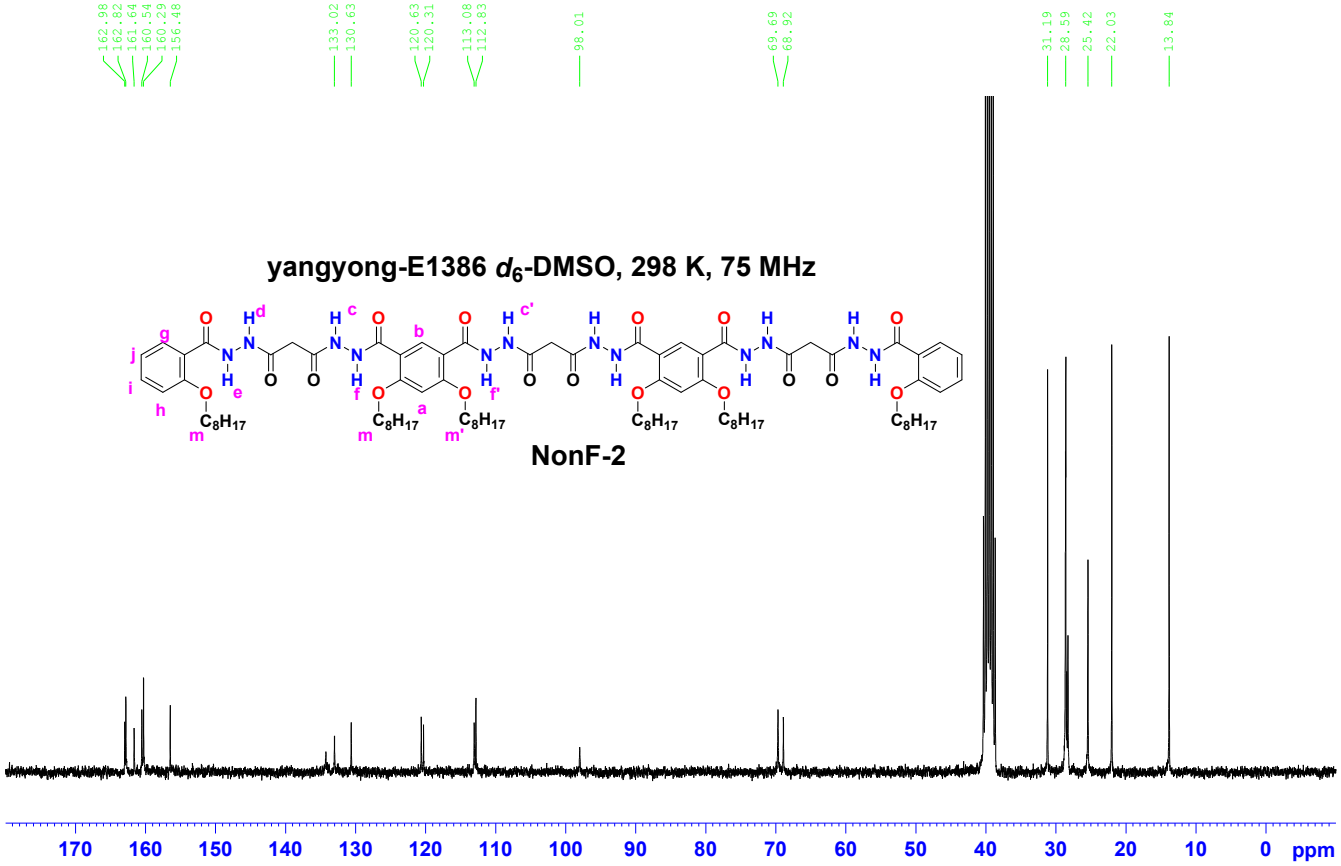
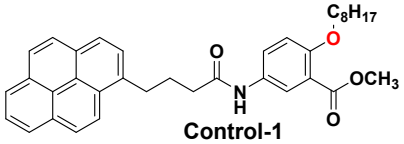


Figure S19 ^{13}C NMR spectrum for **NonF-2**, d_6-DMSO, 298 K, 75 MHz.



Control-1: This compound was synthesized from compound **8** and compound **6** according to a similar procedure as described for **Pyrene-1**.

Yield: 95%.

m. p.: 126.0-127.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 8.31-7.69 (m, 11H, Pyrene-*H* & Ar*H* & N*H)*, 7.02 (d, *J* = 10.4 Hz, 1H, Ar*H*^{b}), 6.90 (d, *J* = 9.2 Hz, 1H, Ar*H*^{a}), 4.00 (t, *J* = 6.4 Hz, 2H, OC*H*$_2$), 3.86 (s, 3H, COOC*H*$_3$^{c}), 3.47 (t, *J* = 7.2 Hz, 2H, Pyrene-C*H*$_2$), 2.40 (t, *J* = 6.4 Hz, 2H, COC*H*$_2$CH$_2$), 2.30 (m, 2H, COCH$_2$C*H*$_2$), 1.82 (m, 2H, OCH$_2$C*H*$_2$), 1.28 (br, 10H, C*H*$_2$), 0.88 (t, *J* = 7.0 Hz, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, TMS, 298 K, ppm): δ 170.8, 166.3, 161.6, 155.4, 160.3, 135.4, 123.3, 114.1, 69.5, 52.0, 32.5, 31.8, 29.3, 27.1, 25.9, 22.6, 14.1.

HRMS (ESI$^+$) calcd. for $[C_{36}H_{39}NO_4 + H]^+$ 550.2952, found: 550.2950.

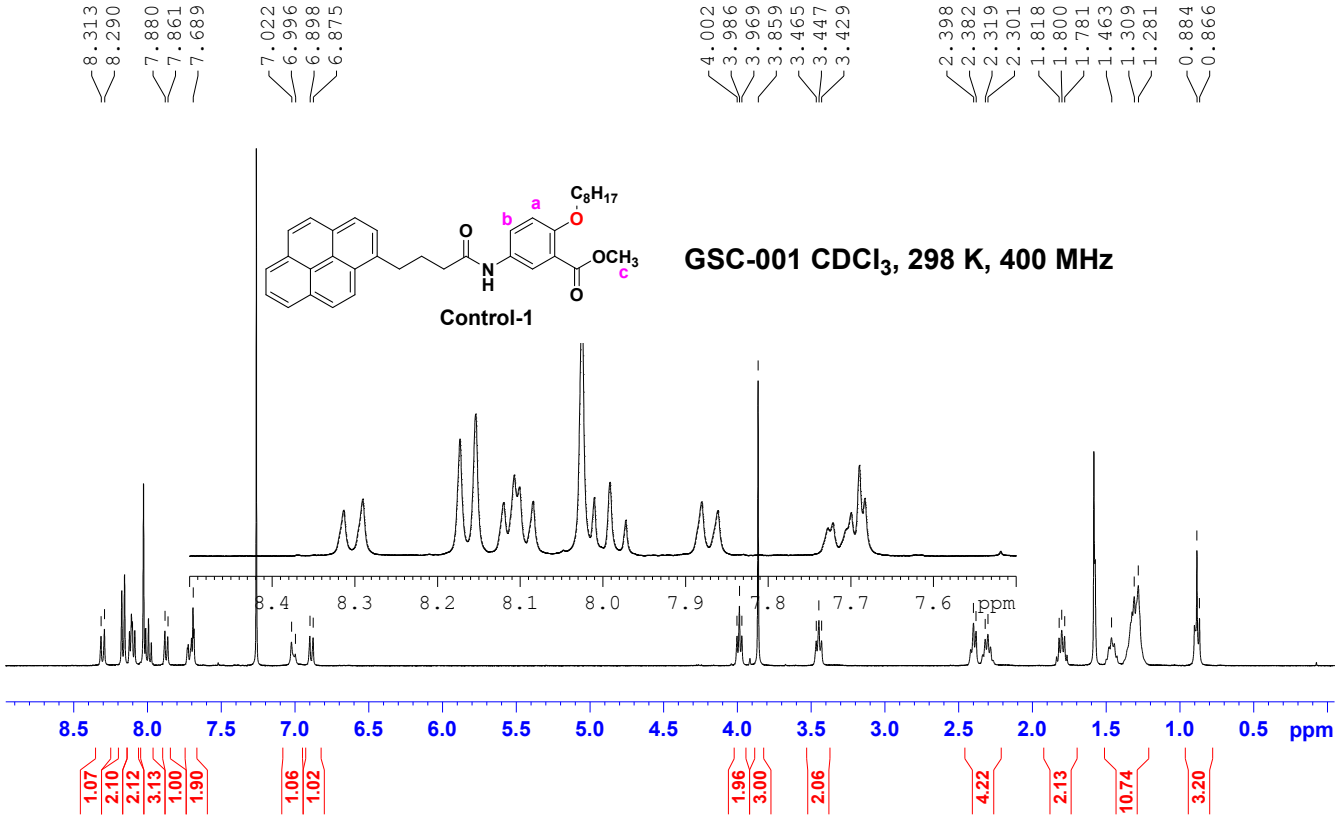


Figure S20 ^{1}H NMR spectrum for **Control-1**, $CDCl_3$, 298 K, 400 MHz.

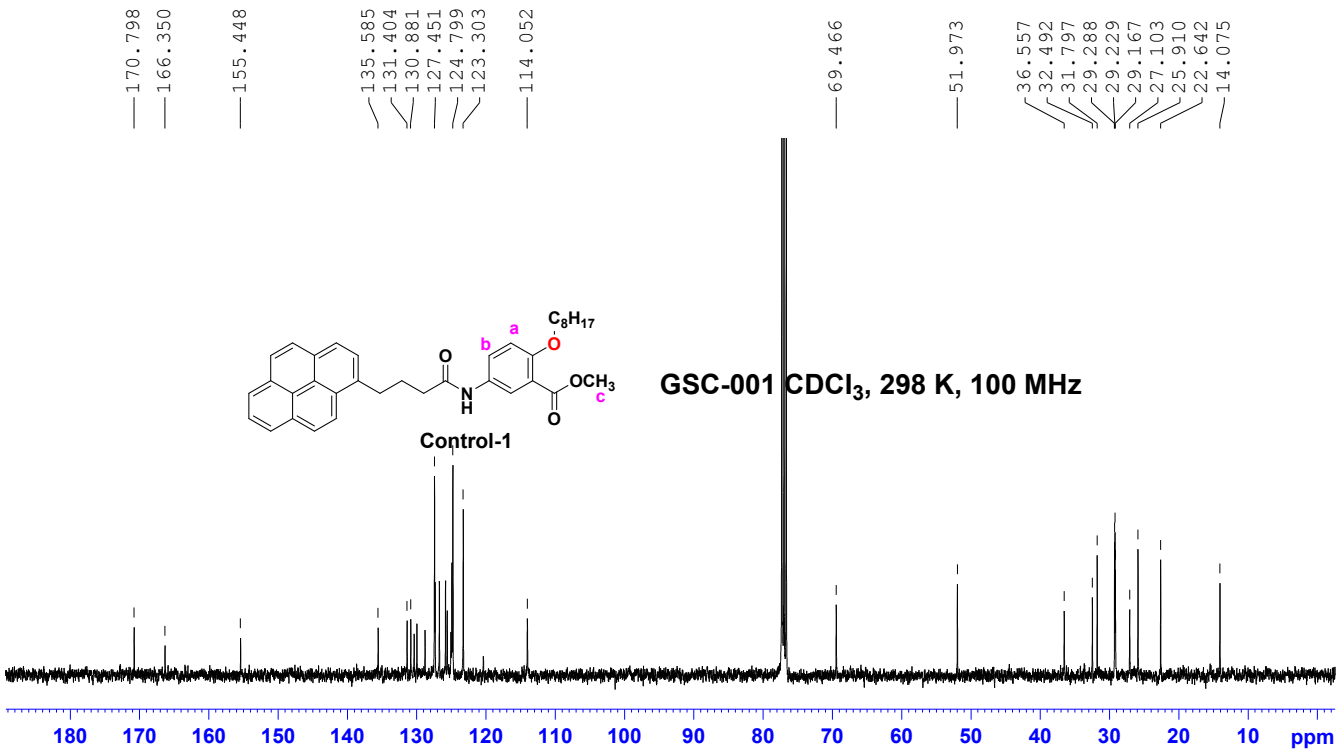


Figure S21 ^{13}C NMR spectrum for **Control-1**, $CDCl_3$, 298 K, 100 MHz.

References:

S1 Y. Yang, J. F. Xiang and C. F. Chen, Dynamic decomposition/recombination of hydrogen bonds in molecular duplex strands, *Org. Lett.*, 2007, **9**, 4355-4357.

S2 Y. Yang, Z. Y. Yang, Y. P. Yi, J. F. Xiang, C. F. Chen, L. J. Wan and Z. G. Shuai, Helical molecular duplex strands: Multiple hydrogen-bond-mediated assembly of self-complementary oligomeric hydrazide derivatives, *J. Org. Chem.*, 2007, **72**, 4936-4946.

S3 Y. Yang, J. F. Xiang, M. Xue, H. Y. Hu and C. F. Chen, Supramolecular substitution reactions between hydrazide-based molecular duplex strands: Complexation induced nonsymmetry and dynamic behavior, *J. Org. Chem.*, 2008, **73**, 6369-6377.

S4 P. Schlichting, U. Rohr and K. Müllen, *Liebigs Ann. Recl.*, 1997, 395-407.

S5 J. Zeng, W. Wang, P. Deng, W. Feng, J. Zhou, Y. Yang, L. Yuan, K. Yamato and B. Gong, Interplay of olefin metathesis and multiple hydrogen bonding interactions: Covalently cross-linked zippers, *Org. Lett.*, 2011, **13**, 3798-3801.