Electronic Supplementary Material (ESI) for Chemical Science
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Supporting Information for:

Conjugated Macrocycles of Phenanthrene: a New Segment of [6,6]-Carbon Nanotube and Solution-Processed Organic Semiconductors

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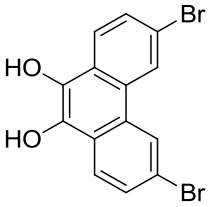
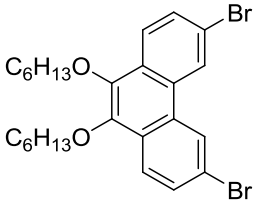
General: The reagents and starting materials employed were commercially available and used without any further purification if not specified elsewhere. Anhydrous and oxygen-free THF and toluene were purified by an Advanced Technology Pure-Solv PS-MD-4 system. Dry DMF was distilled over P_2O_5. ^{1}H-NMR or ^{13}C-NMR spectra were recorded on a Brucker ADVANCE III 400MHz spectrometer. Mass spectra were recorded on a Bruker Daltonics Autoflex MALDI-TOF Mass Spectrometer. UV-Vis and steady-state fluorescence spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer and a Hitachi F-4500 spectrofluorometer respectively. Melting points, without correction, were measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage.

1. Synthesis



3, 6-dibromophenanthrene-9, 10-diol were synthesized following the reported procedure.[1]



3, 6-dibromo-9, 10-bis(hexyloxy)phenanthrene (5)
To a mixture of 3, 6-dibromophenanthrene-9, 10-diol (4.208 g, 11.43 mmol) and K_2CO_3 (11.801 g, 85.51 mmol) in 24 ml DMF, which was purged with nitrogen for 30 minutes, was added 1-bromohexane (24.0 ml, 182.88 mmol) via a syringe under a nitrogen atmosphere at room temperature. The resulting solution was stirred under a N_2 atmosphere at room temperature overnight. The solution was then poured into water and extracted with CH_2Cl_2 for three times. The organic layers were combined, washed with brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to remove the CH_2Cl_2 and excessive 1-bromohexane. The pure product was recrystallized from ethanol to yield 3.378 g of 3, 6-dibromo-9, 10-bis(hexyloxy)phenanthrene (52%). ^{1}H-NMR($CDCl_3$) δ(ppm): 8.64 (s, 2H), 8.10 (d, J=9.0 Hz, 2H), 7.71 (dd, J_1=6.15 Hz, J_2=1.8 Hz, 2H), 4.18 (t, J=6.6 Hz, 4H), 1.88 (m, 4H), 1.38 (m,8H), 0.92 (t, J=6.9 Hz, 6H). ^{13}C-NMR($CDCl_3$) δ(ppm): 14.1, 22.6, 25.9, 30.4, 31.7, 73.7, 120.3, 124.2, 125.4, 128.7, 128.8, 130.4, 143.1. The NMR data are consistent with the reported.1

(1) B. N. Boden, J. K.-H. Hui, M. J. Maclachlan, *J. Org. Chem.* **2008,** *73,* 8069 – 8072.

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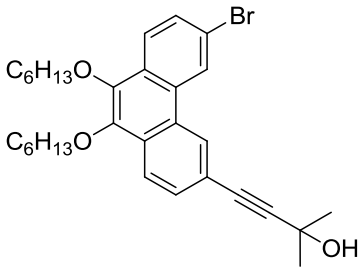
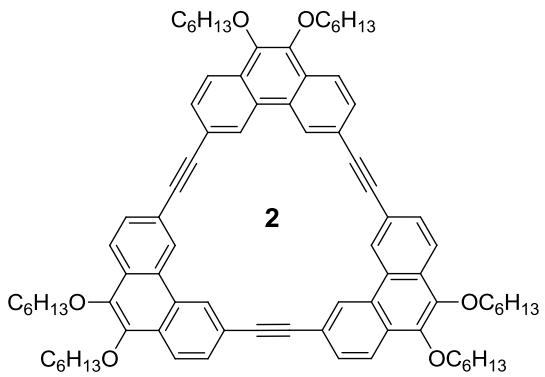
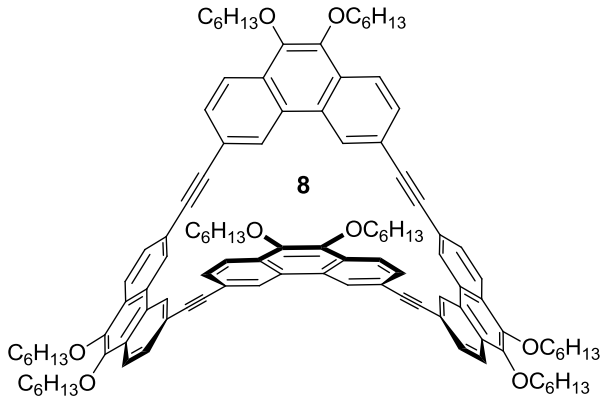


3-(2'-methyl-2'-ol-but-3'-nyl)-6-bromo-9, 10-bis(hexyloxy)-phenanthrene (6)

To a mixture of 3,6-dibromo-9, 10-bis(hexyloxy)phenanthrene (1.731 g, 3.23 mmol), CuI (123.0 mg, 0.65 mmol), PPh_3 (169.4 mg, 0.65 mmol), $Pd(PPh_3)_2Cl_2$ (72.5 mg, 0.10 mmol) and 1.35 ml of triethylamine in 40 ml of anhydrous and oxygen-free THF was added 2-methylbut-3-yn-2-ol (0.31 ml, 3.23 mmol) via a syringe under a nitrogen atmosphere at room temperature. The resulting solution was stirred under a nitrogen atmosphere at room temperature overnight. The reaction mixture was then extracted with diethyl ether for three times. The organic layers were combined, washed with water and brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel using dichloromethane as eluent yielded 979 mg (65%) of 3-(2'-methyl-2'-ol-but-3'-nyl)-6-bromo-9, 10-bis(hexyloxy) phenanthrene as a light yellow oil. ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.60 (d, J=1.2 Hz, 1H), 8.48 (s, 1H), 8.06 (d, J=8.8Hz, 1H), 8.03 (d, J=8.8 Hz, 1H), 7.65 (dd, J_1=8.8 Hz, J_2=1.6 Hz, 1H), 7.55 (d, J=8.4 Hz, 1H), 4.14 (t, J=6.8 Hz, 4H), 2.87 (s, 1H), 1.87 (m, 4H), 1.74 (s, 6H), 1.54 (m, 4H), 1.38 (m, 8H), 0.94(m, 6H). ^{13}C-NMR ($CDCl_3$) δ(ppm): 143.5, 143.0, 130.0, 129.8, 129.3, 129.2, 128.3, 126.9, 126.1, 125.2, 124.0, 122.1, 120.2, 120.0, 94.5, 82.4, 73.7, 73.6, 65.6, 31.6, 31.5, 30.3, 25.8, 22.6, 14.0. HRMS (MALDI-TOF): calcd. for $C_{31}H_{39}{}^{79}BrO_3$ ($[M]^+$): 538.2083, found: 538.1006.





To a mixture of 3-(2'-methyl-2'-ol-but-3'-nyl)-6-bromo-9, 10-bis(hexyloxy)-phenanthrene (760 mg, 1.4 mmol), CuI (13.5 mg, 0.07 mmol), *n*Bu_4NBr (22.5 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (81 mg, 0.07 mmol) were added 30 ml of benzene and 5 ml of 5 M NaOH aqueous solution, both of which were purged with nitrogen before use. The reaction mixture was heated at 90 ℃ under a nitrogen atmosphere for 24 hours, and then cooled to room temperature. The crude product was then extracted with diethyl ether for three times. The organic layers were combined, washed with water and brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel using dichloromethane:hexane 1:4 (V:V) as eluent yielded 150 mg (27%) of **2** as yellow solids and 40 mg (7%) of **8** as off-white solids.

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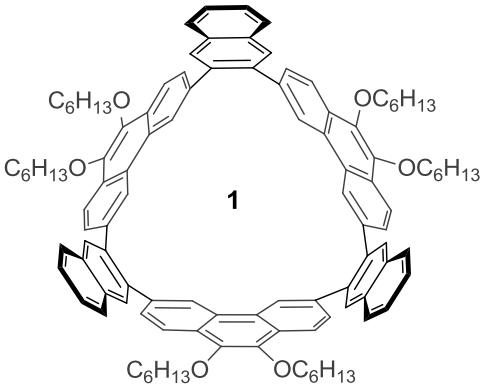
2 Melting point: 178 ℃. ^{1}H-NMR ($CDCl_3$, 1mg/ml) δ(ppm): 9.2 8(s, 6H), 8.24 (d, J=8.8 Hz, 6H), 7.81 (d, J=8.8 Hz, 6H), 4.25 (t, J=6.8 Hz, 12H), 1.95 (m, 12H), 1.61 (m, 12H), 1.43 (m, 24H), 0.96 (t, J=6.8 Hz, 18H). ^{13}C-NMR($CDCl_3$) δ(ppm): 14.3, 22.9, 26.1, 30.7, 31.9, 73.9, 91.2, 120.9, 122.5, 127.2, 128.2, 129.4, 129.5, 144.1. HRMS (MALDI-TOF): calcd. for $C_{84}H_{96}O_6$ ($[M]^+$): 1200.7207, found: 1200.7151.

8 ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.86 (s, 8H), 8.24 (d, J=8.4 Hz, 8H), 7.80 (dd, J_1=8.4 Hz, J_2=1.2Hz, 8H), 4.24 (t, J=6.8 Hz, 16H), 1.95 (m, 16H), 1.59 (m, 16H), 1.39 (m, 32H), 0.95 (t, J=6.8 Hz, 24H). ^{13}C-NMR($CDCl_3$) δ(ppm): 14.2, 22.8, 26.1, 30.6, 31.9, 73.9, 90.2, 120.8, 122.6, 126.2, 128.0, 129.7, 130.1, 144.0. HRMS (MALDI-TOF): calcd. for $C_{112}H_{128}O_8$ ($[M]^+$): 1601.9643, found: 1601.9590.



To a mixture of cyclic-tri(3-ethynyl-9,10-bis(hexyloxy)phenanthrene) (48 mg, 0.04 mmol) and $Cu(OTf)_2$ (9.0 mg, 0.024mmol) in 1,2-dichloroethane (10 mL) were added 2-phenylethynyl-benzaldehyde (50mg, 0.24 mmol) and CF_3COOH (20 uL, 0.264 mmol) successively at room temperature under a N_2 atmosphere. The resulting mixture was stirred at 100 ℃ for 3 hours and then cooled to room temperature. After addition of a saturated aqueous solution of $NaHCO_3$, the mixture was extracted with ether for three times. The combined extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane:hexane 1:5 (V:V) as eluent yielding 45 mg (75%) of **1** as off-white solids. Melting point: 143-144 ℃. ^{1}H-NMR (CD_2Cl_2) δ (ppm): 8.29 (s, 6H), 8.01 (d, J=8.4Hz, 6H), 7.88 (m, 12H), 7.70 (dd, J_1=8.4Hz, J_2=1.2Hz, 6H), 7.51 (dd, J_1=8.4Hz, J_2=1.2Hz, 6H), 4.05 (t, J=7.2Hz, 12H), 1.85 (m, 12H), 1.53 (m, 12H), 1.36 (m, 24H), 0,93 (t, J=7.2Hz, 18H). ^{13}C-NMR (CD_2Cl_2) δ (ppm): 14.3, 23.1, 26.3, 30.8, 32.2, 73.8, 121.2, 124.1, 126.7, 128.0, 128.5, 128.7, 129.7, 129.7, 132.7, 139.5, 140.9, 143.4. HRMS (MALDI-TOF): calcd. for $C_{108}H_{114}O_6$ ($[M]^+$): 1507.8649, found: 1507.8585.

Lewis acid-catalyzed [4+2] benzannulation of 8

To a mixture of **8** (40 mg, 0.025 mmol) and $Cu(OTf)_2$ (9.0 mg, 0.024mmol) in 1,2-dichloroethane (10 mL) were added 2-phenylethynyl-benzaldehyde (50mg, 0.24 mmol) and CF_3COOH (20 uL, 0.264 mmol) successively at room temperature under a N_2 atmosphere. The resulting mixture was stirred at 100 ℃ for 3 hours and then cooled to room temperature. After addition of a saturated aqueous solution of $NaHCO_3$, the mixture was extracted with diethyl ether for three times. The combined extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was a complex mixture as found from ^{1}H NMR spectrum. HRMS (ESI): calcd. for $C_{144}H_{152}O_8Na$ ($[M+Na]^+$): 2033.1413, found: 2033.1406. HRMS (MALDI-TOF): calcd. for $C_{144}H_{152}O_8$ ($[M]^+$): 2010.1521, found: 2010.1541.

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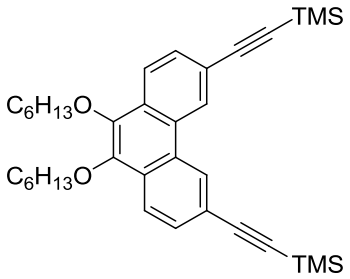
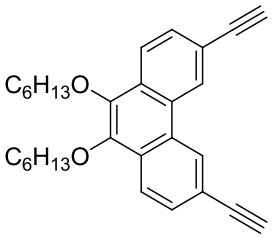


3, 6-bis(trimethylsilylethynyl)-9, 10-bis(hexyloxy)-phenanthrene

To a mixture of 3, 6-dibromo-9, 10-bis(hexyloxy)phenanthrene (1.072 g, 2.00 mmol), CuI (70.3 mg, 36.91 mmol), PPh_3 (120.7 mg, 0.46 mmol) and $Pd(PPh_3)_2Cl_2$ (75.0 mg, 0.10 mmol) in 20.0 ml anhydrous and oxygen-free toluene and 1.12 ml triethylamine was added (trimethylsilyl)acetylene (3.6 ml, 16.0 mmol) via a syringe under a nitrogen atmosphere at room temperature. The resulting solution was stirred under a nitrogen atmosphere and refluxed overnight. The reaction mixture was then extracted with diethyl ether for three times. The organic layers were combined, washed with water and brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane:hexane 1:10 (V:V) yielding 882 mg (77%) of 3, 6-bis(trimethylsilylethynyl)-9, 10-bis(hexyloxy)-phenanthrene. ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.76 (s, 2H), 8.15 (d, J=8.48 Hz, 2H), 7.68 (d, J=8.48 Hz, 2H), 4.19 (t, J=6.68 Hz, 4H), 1.90 (m, 4H), 1.56 (m, 4H), 1.39 (m, 8H), 0.95 (t, J=6.84 Hz, 6H), 0.35 (s, 18H). ^{13}C-NMR ($CDCl_3$) δ(ppm): 0.1, 14.1, 22.7, 25.9, 30.4, 31.7, 73.7, 94.8, 105.6, 120.5, 122.3, 126.7, 127.7, 129.6, 130.0, 143.8. These data are consistent with the reported literature.[2]



3, 6-diethynyl-9, 10-bis(hexyloxy)phenanthrene (**7**)

To a solution of 3, 6-bis(trimethylsilylethynyl)-9, 10-bis(hexyloxy)-phenanthrene (0.882 g, 1.55 mmol) in 10.0 ml THF was added 3.0 ml (6.0 mmol) of 2M KOH aqueous solution. The resulting solution was stirred under air at room temperature overnight. After reaction, saturated 3ml NH_4Cl was added and the solution was extracted with CH_2Cl_2 for three times. The organic layer was combined and washed with brine, dried with anhydrous Na_2SO_4 and removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane: hexane 1:10 (V:V) as eluent yielding 576 mg (88.0%) of 3, 6-diethynyl-9, 10-bis(hexyloxy) phenanthrene. ^{1}H-NMR ($CDCl_3$) δ(ppm): 8.76 (s, 2H), 8.18 (d, J=8.44 Hz, 2H), 7.70 (dd, J_1=8.44 Hz, J_2=1.24 Hz, 2H), 4.20 (t, J=6.72 Hz, 4H), 3.22 (s, 2H), 1.90 (m, 4H), 1.56 (m, 4H), 1.38 (m, 8H), 0.93 (t, J=2.48 Hz, 6H). ^{13}C-NMR ($CDCl_3$) δ(ppm): 143.9, 130.1, 129.9, 127.6, 126.9, 122.5, 119.5, 84.1, 77.8, 73.8, 31.7, 30.4, 25.9, 22.7, 14.1. These data are consistent with the reported literature.[2]

(2) B. L. Merner, L. N. Dawe, G. J. Bodwell, *Angew. Chem. Int. Ed.* **2009**, *48*, 5487 –5491.

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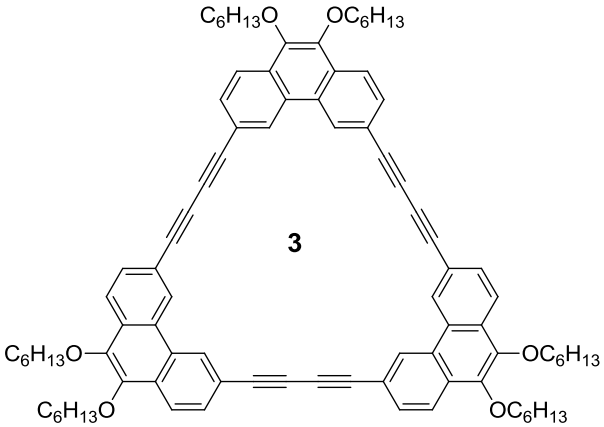
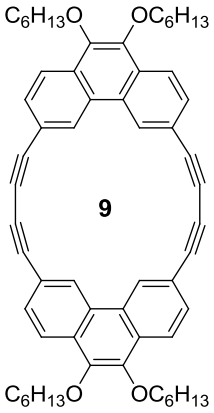
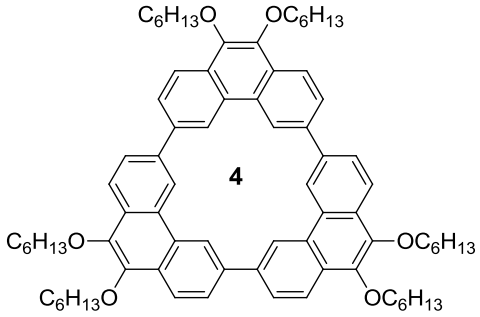




To a solution of 31.700 g (174.0 mmol) of $Cu(OAc)_2$ in 200 ml of pyridine and 20 ml CH_3OH was added a solution of 2.470 g (5.8 mmol) of 3,6-diethynyl-9,10 -bis(hexyloxy)phenanthrene in 150.0 ml pyridine dropwise over 2 hours. The resulting mixture was stirred at 55 ℃ overnight. Then the reaction mixture was cooled to room temperature and 200 ml methanol was added into the solution. The mixture was filtered and the resulting solid was washed thoroughly with water and methanol successively. The solid was purified with column chromatography on silica gel using dichloromethane: hexane (=1:3) as eluent yielding cyclic-tri(3, 6-diethynyl-9, 10-bis(hexyloxy)phenanthrene) and cyclic-bis(3, 6-diethynyl-9,10-bis(hexyloxy)phenanthrene) in two separate portions. Recrystallization from CH_2Cl_2 yielded 238.2 mg (9.7%) of **9** as yellow crystals. Precipitation from ethanol yielded 1.132 g (46%) of **3** as yellow solids.

3: Melting point: 244 ℃. ^{1}H-NMR ($CDCl_3$, 1mg/ml) δ(ppm): 8.71 (s, 6H), 8.10 (d, J=8.8 Hz, 6H), 7.67 (d, J=8.8 Hz, 6H), 4.20 (t, J=6.8 Hz, 12H), 1.94 (m, 12H), 1.60 (m, 12H), 1.43 (m, 24H), 0.97 (t, J=6.8 Hz, 18H). ^{13}C-NMR($CDCl_3$) δ(ppm): 14.2, 22.8, 26.0, 30.6, 31.9, 73.4, 75.4, 82.7, 119.2, 121.7, 126.9, 127.3, 128.9, 129.2, 143.6. HRMS (MALDI-TOF): calcd. for $C_{90}H_{97}O_6$ ($[M+H]^+$): 1273.7285, found: 1273.7358.

9: ^{1}H-NMR ($CDCl_3$) δ(ppm): 9.94 (s, 4H), 8.00 (d, J=8.44 Hz, 4H), 7.37 (d, J=8.36 Hz, 4H), 4.17 (t, J=6.68 Hz, 8H), 1.88 (m, 8H), 1.55 (m, 8H), 1.38 (m, 16H), 0.93 (t, J=6.84 Hz, 12H). ^{13}C-NMR($CDCl_3$) δ(ppm): 14.1, 22.6, 25.8, 30.4, 31.7, 73.8, 90.9, 119.9, 122.5, 125.8, 127.9, 130.2, 133.9, 144.7. HRMS (MALDI-TOF): calcd. for $C_{60}H_{64}O_4$ ($[M]^+$): 848.4805, found: 848.4807.



Cyclo-3,6-tris(9, 10-di(hexyloxy)phenanthrene) (4)

Bis(cyclooctadiene)nickel (660.2 mg, 2.4 mmol, 2.4 equiv), cyclooctadiene (0.295 ml, 2.4 mmol, 2.4 equiv), and 2,2′-bipyridine (374.9 mg, 2.4 mmol, 2.4 equiv) were dissolved in 10.0 ml dry N,N-dimethylformamide (DMF) in a Schlenk tube reactor. The mixture was heated at

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60 ℃ under a nitrogen atmosphere for 45 minutes with stirring to produce the catalyst, and then a solution of 3,6-dibromo-9,10-bis(hexyloxy)phenanthrene (536 mg, 1.0 mmol) in dry DMF (12.0 ml) was added. After being heated to 75 ℃ with stirring for 2 days, the resulting mixture was poured into a mixture of methanol (50.0 ml) and concentrated hydrochloric acid (25.0 ml) and stirred overnight. The brown precipitates were filtered off and washed with water and methanol. The crude product was purified by column chromatography on silica gel using hexane:CH_2Cl_2 3:1 (V:V) as eluent yielding a colorless oil, which was made into a slurry with methanol. The slurry was filtered and washed with methanol yielding 110 mg (30%) of cyclo-3,6-tris(9, 10-di(hexyloxy)phenanthrene (**4**) as white solids. Melting point: decomposed at 320 ℃. ^{1}H-NMR ($CDCl_3$, 10mg/ml) δ (ppm): 9.43(s, 6H), 8.31(d, J=8.8Hz, 6H), 8.25(d, J=8.8Hz, 6H), 4.30(t, J=7.2Hz, 12H), 2.01(m, 12H), 1.68(m, 12H), 1.47(m, 24H), 1.00(t, J=7.2Hz, 18H). ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.1, 22.7, 26.0, 30.6, 31.8, 73.9, 119.1, 123.3, 124.0, 128.9, 129.5, 135.0, 143.5. HRMS (MALDI-TOF): calcd. for $C_{78}H_{96}O_6$ ($[M]^+$): 1128.7207, found: 1128.7208.

2. Density functional theory calculation

2.1 Frontier molecular orbitals

The frontier molecular orbitals of **1-4** were calculated using simplified model molecules **1'-4'** (shown in the Supporting Information), which have smaller methyl groups replacing the hexyl groups in **1-4**, with the Gaussian 09 software package.[3] The geometries of these model molecules were first optimized at the B3LYP level of density functional theory (DFT) with the 6-31G(d, p) basis set, and the HOMO and LUMO were then calculated with the 6-311++G(d, p) basis set.

(3) Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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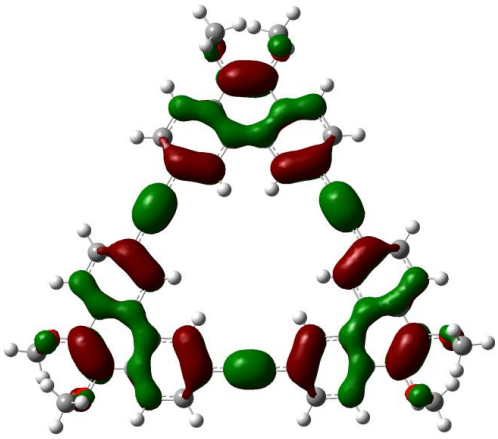
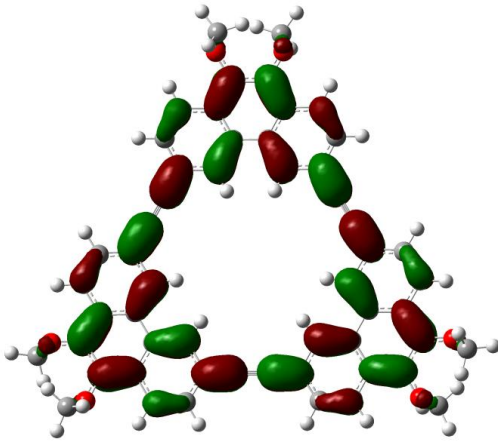
2'

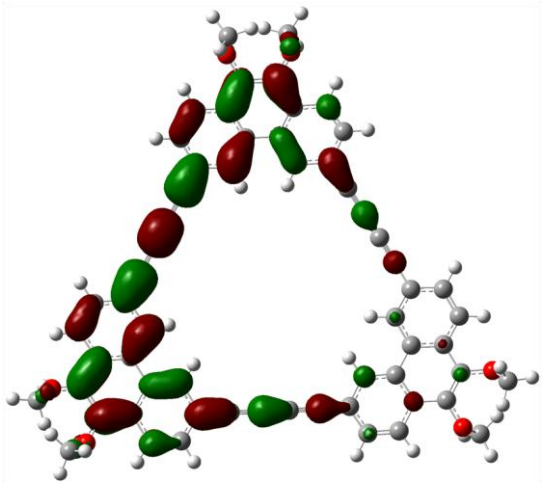


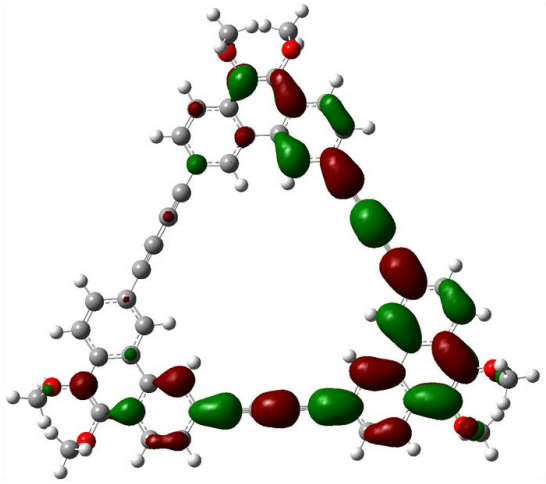
HOMO: −5.32 eV



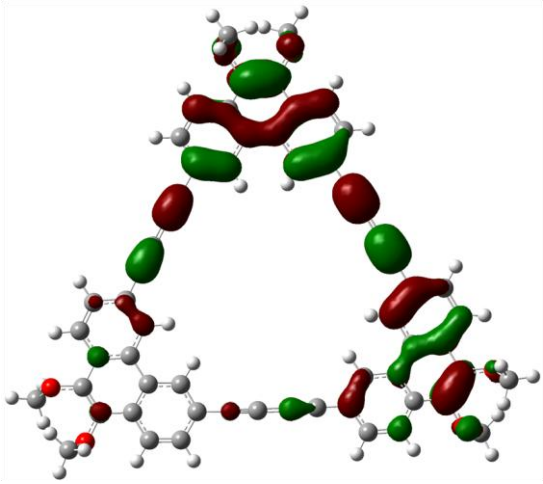
LUMO: −2.31 eV

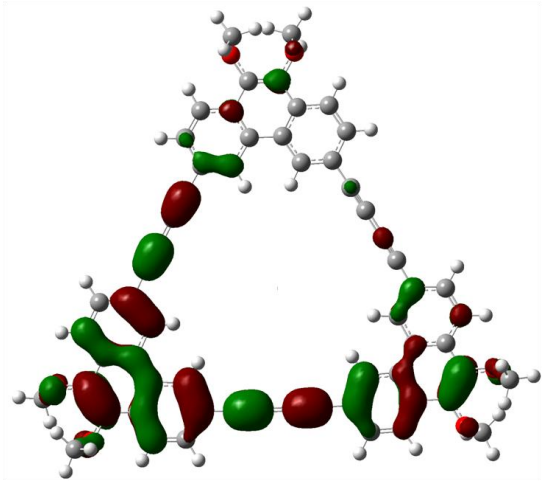
3'





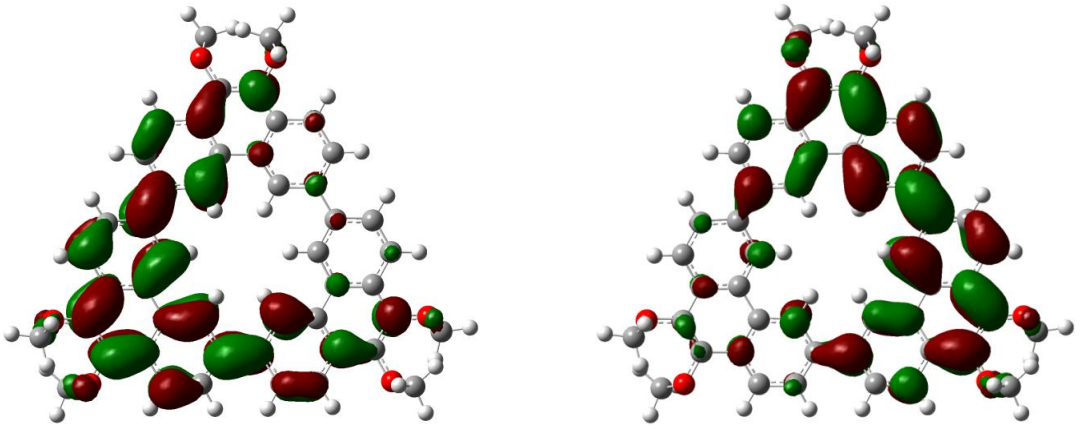
LUMO (doubly degenerate): −2.42 eV



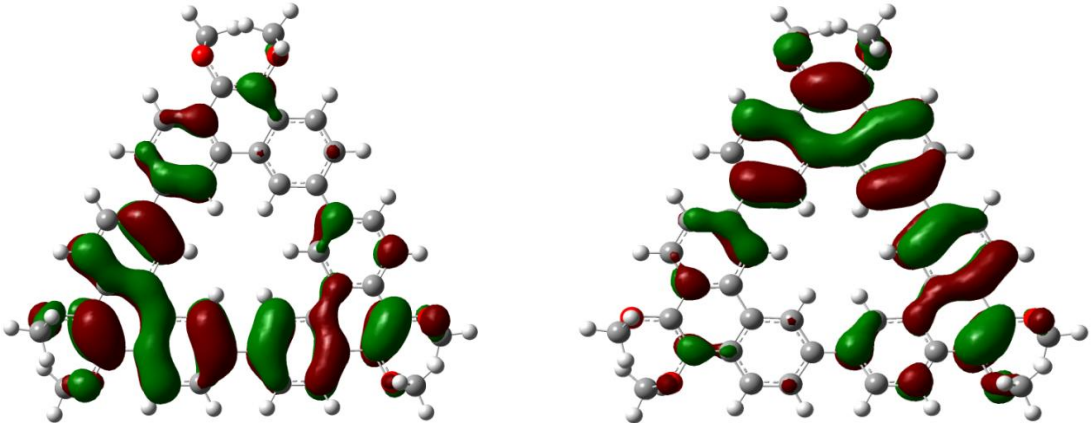


HOMO (doubly degenerate): −5.54 eV

4'



LUMO (doubly degenerate): −1.92 eV

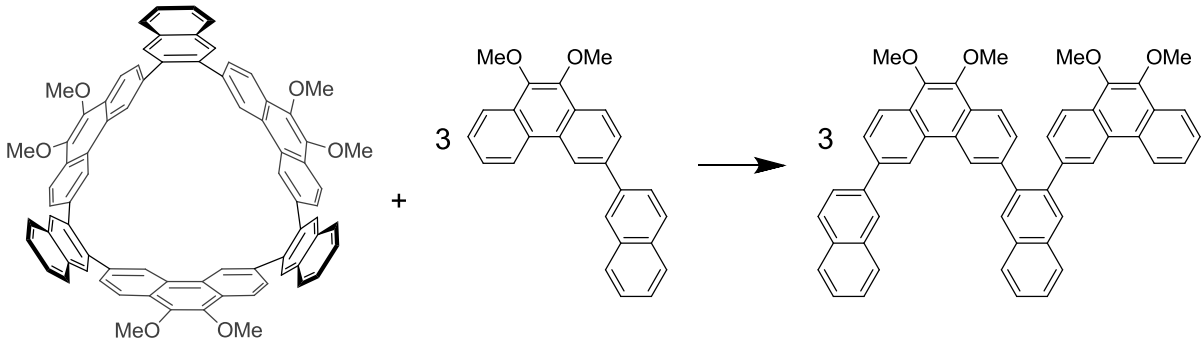


HOMO (doubly degenerate): −5.45 eV

Figure S1 Calculated frontier molecular orbitals of **2'**-**4'** with the energy levels.

2.2 Strain Energy of 1

The strain energy of **1** was estimated from the following hypothetical homodesmotic reaction. Molecules structures were optimized at the B3LYP level of DFT with the 6-31G(d, p) basis set, and the single-point energy was calculated at the B3LYP level with the 6-311++G(d, p) basis set.



E = –3457.05036696 a.u. E = –1153.55951397 a.u. E = –2305.91354733 a.u.

Scheme S1 Hypothetical homodesmotic reaction with calculated energies.

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$\Delta H = 3\times(-2305.91354733) - 3\times(-1153.55951397) - (-3457.05036696)$
$= -0.01173312$ a.u.
$= -7.362644$ kcal/mol

Therefore the strain energy of **1** is estimated as 7.4 kcal/mol, which is much smaller than those of [n]cycloparaphenylenes and [n]cycloparaphenyleneacetylenes.[4]

2.3 C2-Isomer of 1'

Benzannulation on the three alkyne moieties of **2** can in principle lead to two isomers depending on whether the benzannulation occurs on the same side of the flat macrocycle **2**. A simplified model with hexyl groups replaced by methyl group was optimized optimized at the B3LYP level of DFT with the 6-31G(d,p) basis set. As shown in Figure S2, the isomer of **1'** has a screwed structure with C2 symmetry. The single-point energy is calculated at the B3LYP level of DFT with 6-311++G(d, p) basis set.

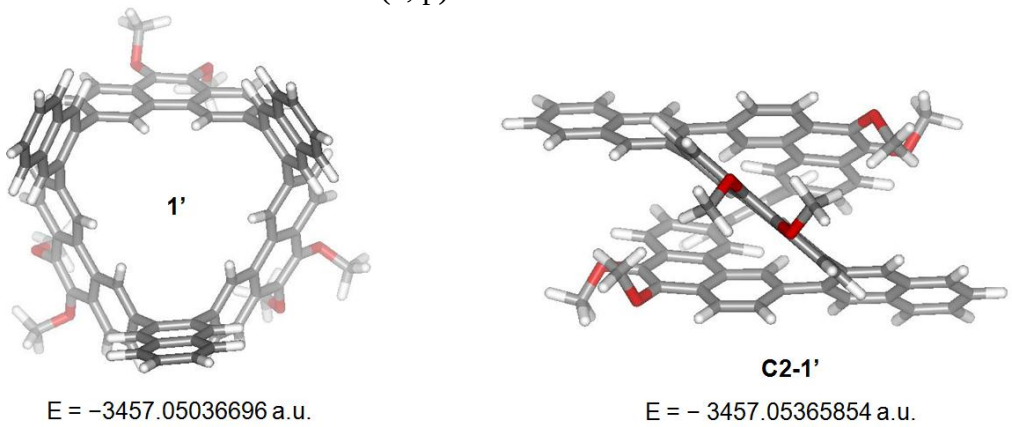

Figure S2 Stick models of **1'** and its isomer **C2-1'**.

2.3 Cartesian coordinates for optimized molecular structures

Cartesian coordinates for optimized structure of **1'**

C	-4.027362	2.513320	-1.914059
C	-3.120313	2.508206	-0.814826
C	-1.984476	3.420179	-0.825960
C	-1.768529	4.245110	-1.967370
C	-2.682035	4.187576	-3.078427
C	-3.787571	3.380220	-3.038144
C	-5.157675	1.665962	-1.888121
C	-5.385614	0.821043	-0.821692
C	-4.481923	0.772369	0.263243
C	-3.379300	1.616842	0.250428
C	-1.081170	3.537107	0.254853
C	0.000000	4.409793	0.230921
C	0.197453	5.210368	-0.917524
C	-0.666837	5.129487	-1.988705

4. Y. Segawa, H. Omachi, K. Itami, K. *Org. Lett.* **2010**, *12*, 2262–2265.

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C	-3.818993	-2.204896	0.230921
C	-4.611038	-2.434185	-0.917524
C	-4.108848	-3.142241	-1.988705
C	-2.792108	-3.654146	-1.967370
C	-1.969724	-3.428696	-0.825960
C	-2.522640	-2.704874	0.254853
C	-2.285530	-4.416498	-3.078427
C	-1.033571	-4.970242	-3.038144
C	-0.162918	-4.744457	-1.914059
C	-0.612014	-3.956374	-0.814826
C	1.136072	-5.299659	-1.888121
C	1.981763	-5.074600	-0.821692
C	1.572070	-4.267644	0.263243
C	0.289424	-3.734981	0.250428
C	3.818993	-2.204896	0.230921
C	4.413585	-2.776183	-0.917524
C	4.775684	-1.987246	-1.988705
C	4.560638	-0.590964	-1.967370
C	3.954200	0.008517	-0.825960
C	3.603809	-0.832233	0.254853
C	4.967565	0.228922	-3.078427
C	4.821142	1.590023	-3.038144
C	4.190279	2.231138	-1.914059
C	3.732327	1.448168	-0.814826
C	4.021603	3.633696	-1.888121
C	3.403851	4.253557	-0.821692
C	2.909853	3.495275	0.263243
C	3.089876	2.118139	0.250428
O	-3.124138	-4.613416	-4.155989
C	-2.724791	-3.934023	-5.354538
O	-2.433266	5.012290	-4.155989
C	-2.044569	4.326750	-5.354538
O	-4.681721	3.329179	-4.087331
C	-5.465438	4.516931	-4.266732
O	-0.542293	-5.719079	-4.087331
C	-1.179058	-6.991674	-4.266732
O	5.224014	2.389900	-4.087331
C	6.644497	2.474743	-4.266732
O	5.557404	-0.398875	-4.155989
C	4.769360	-0.392726	-5.354538
C	-5.059958	-1.689708	3.788002
C	-5.405558	-0.302697	3.793447
C	-5.209619	0.446232	2.605188
C	-4.715116	-0.118638	1.444329

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C	-4.376734	-1.515745	1.434892
C	-4.546050	-2.253693	2.593089
C	2.218361	-4.734779	2.605188
C	2.460301	-4.024091	1.444329
C	3.501040	-3.032490	1.434892
C	4.224780	-2.810148	2.593089
C	1.066649	5.226907	3.788002
C	2.440635	4.832699	3.793447
C	2.991258	4.288547	2.605188
C	2.254814	4.142729	1.444329
C	0.875693	4.548235	1.434892
C	0.321270	5.063841	2.593089
H	-5.840181	1.692554	-2.729488
H	-6.272186	0.195191	-0.808397
H	-2.697762	1.572548	1.092037
H	-1.225751	2.934673	1.144251
H	1.018902	5.917821	-0.941236
H	-0.530411	5.760638	-2.858956
H	-5.634434	-2.076516	-0.941236
H	-4.723653	-3.339668	-2.858956
H	-1.928626	-2.528868	1.144251
H	1.454296	-5.904022	-2.729488
H	2.967053	-5.529468	-0.808397
H	-0.012986	-3.122605	1.092037
H	4.615532	-3.841305	-0.941236
H	5.254064	-2.420969	-2.858956
H	3.154377	-0.405805	1.144251
H	4.385885	4.211468	-2.729488
H	3.305134	5.334277	-0.808397
H	2.710748	1.550056	1.092037
H	-3.490322	-4.157468	-6.100424
H	-2.682757	-2.850789	-5.190460
H	-1.750958	-4.289785	-5.703516
H	-1.855312	5.101441	-6.100424
H	-1.127478	3.748730	-5.190460
H	-2.839584	3.661266	-5.703516
H	-6.136144	4.314958	-5.104417
H	-6.059435	4.728690	-3.369589
H	-4.831683	5.378017	-4.497188
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H	-1.065448	-7.611969	-3.369589
H	-2.241658	-6.873368	-4.497188
H	6.804935	3.156578	-5.104417
H	7.073340	1.495351	-4.497188

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H	7.124883	2.883279	-3.369589
H	5.345634	-0.943974	-6.100424
H	4.590542	0.628519	-5.703516
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H	-5.452615	1.505659	2.612347
H	-4.285903	-3.308955	2.586578
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H	4.030247	3.969274	2.612347
H	-0.722687	5.366178	2.586578
C	3.993310	-3.537198	3.788002
C	2.964922	-4.530002	3.793447
C	4.744750	-3.317359	4.973853
C	2.724064	-5.266253	4.984400
H	5.526415	-2.562175	4.966285
H	1.940515	-6.019552	4.985444
C	3.198677	4.992235	4.984400
C	0.500542	5.767753	4.973853
H	4.242828	4.690311	4.985444
H	-0.544299	6.067103	4.966285
C	-5.922741	0.274018	4.984400
C	-5.245292	-2.450395	4.973853
H	-6.183342	1.329241	4.985444
H	-4.982116	-3.504928	4.966285
C	1.260408	5.910728	6.112559
C	2.622441	5.519321	6.117931
H	0.818073	6.324984	7.013814
H	3.210641	5.637380	7.023260
C	-5.749045	-1.863819	6.112559
C	-6.091093	-0.488560	6.117931
C	4.488637	-4.046909	6.112559
C	3.468652	-5.030761	6.117931
H	3.276794	-5.599186	7.023260
H	5.068560	-3.870964	7.013814
H	-5.886634	-2.454020	7.013814
H	-6.487435	-0.038194	7.023260

Cartesian coordinates for optimized structure of **C2-1'**

C	-4.027362	2.513320	-1.914059
C	-3.120313	2.508206	-0.814826
C	-1.984476	3.420179	-0.825960
C	-1.768529	4.245110	-1.967370
C	-2.682035	4.187576	-3.078427
C	-3.787571	3.380220	-3.038144

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C	-5.157675	1.665962	-1.888121
C	-5.385614	0.821043	-0.821692
C	-4.481923	0.772369	0.263243
C	-3.379300	1.616842	0.250428
C	-1.081170	3.537107	0.254853
C	0.000000	4.409793	0.230921
C	0.197453	5.210368	-0.917524
C	-0.666837	5.129487	-1.988705
C	-3.818993	-2.204896	0.230921
C	-4.611038	-2.434185	-0.917524
C	-4.108848	-3.142241	-1.988705
C	-2.792108	-3.654146	-1.967370
C	-1.969724	-3.428696	-0.825960
C	-2.522640	-2.704874	0.254853
C	-2.285530	-4.416498	-3.078427
C	-1.033571	-4.970242	-3.038144
C	-0.162918	-4.744457	-1.914059
C	-0.612014	-3.956374	-0.814826
C	1.136072	-5.299659	-1.888121
C	1.981763	-5.074600	-0.821692
C	1.572070	-4.267644	0.263243
C	0.289424	-3.734981	0.250428
C	3.818993	-2.204896	0.230921
C	4.413585	-2.776183	-0.917524
C	4.775684	-1.987246	-1.988705
C	4.560638	-0.590964	-1.967370
C	3.954200	0.008517	-0.825960
C	3.603809	-0.832233	0.254853
C	4.967565	0.228922	-3.078427
C	4.821142	1.590023	-3.038144
C	4.190279	2.231138	-1.914059
C	3.732327	1.448168	-0.814826
C	4.021603	3.633696	-1.888121
C	3.403851	4.253557	-0.821692
C	2.909853	3.495275	0.263243
C	3.089876	2.118139	0.250428
O	-3.124138	-4.613416	-4.155989
C	-2.724791	-3.934023	-5.354538
O	-2.433266	5.012290	-4.155989
C	-2.044569	4.326750	-5.354538
O	-4.681721	3.329179	-4.087331
C	-5.465438	4.516931	-4.266732
O	-0.542293	-5.719079	-4.087331
C	-1.179058	-6.991674	-4.266732

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O	5.224014	2.389900	-4.087331
C	6.644497	2.474743	-4.266732
O	5.557404	-0.398875	-4.155989
C	4.769360	-0.392726	-5.354538
C	-5.059958	-1.689708	3.788002
C	-5.405558	-0.302697	3.793447
C	-5.209619	0.446232	2.605188
C	-4.715116	-0.118638	1.444329
C	-4.376734	-1.515745	1.434892
C	-4.546050	-2.253693	2.593089
C	2.218361	-4.734779	2.605188
C	2.460301	-4.024091	1.444329
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C	1.066649	5.226907	3.788002
C	2.440635	4.832699	3.793447
C	2.991258	4.288547	2.605188
C	2.254814	4.142729	1.444329
C	0.875693	4.548235	1.434892
C	0.321270	5.063841	2.593089
H	-5.840181	1.692554	-2.729488
H	-6.272186	0.195191	-0.808397
H	-2.697762	1.572548	1.092037
H	-1.225751	2.934673	1.144251
H	1.018902	5.917821	-0.941236
H	-0.530411	5.760638	-2.858956
H	-5.634434	-2.076516	-0.941236
H	-4.723653	-3.339668	-2.858956
H	-1.928626	-2.528868	1.144251
H	1.454296	-5.904022	-2.729488
H	2.967053	-5.529468	-0.808397
H	-0.012986	-3.122605	1.092037
H	4.615532	-3.841305	-0.941236
H	5.254064	-2.420969	-2.858956
H	3.154377	-0.405805	1.144251
H	4.385885	4.211468	-2.729488
H	3.305134	5.334277	-0.808397
H	2.710748	1.550056	1.092037
H	-3.490322	-4.157468	-6.100424
H	-2.682757	-2.850789	-5.190460
H	-1.750958	-4.289785	-5.703516
H	-1.855312	5.101441	-6.100424
H	-1.127478	3.748730	-5.190460
H	-2.839584	3.661266	-5.703516

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H	-6.136144	4.314958	-5.104417
H	-6.059435	4.728690	-3.369589
H	-4.831683	5.378017	-4.497188
H	-0.668791	-7.471535	-5.104417
H	-1.065448	-7.611969	-3.369589
H	-2.241658	-6.873368	-4.497188
H	6.804935	3.156578	-5.104417
H	7.073340	1.495351	-4.497188
H	7.124883	2.883279	-3.369589
H	5.345634	-0.943974	-6.100424
H	4.590542	0.628519	-5.703516
H	3.810234	-0.897941	-5.190460
H	-5.452615	1.505659	2.612347
H	-4.285903	-3.308955	2.586578
H	1.422368	-5.474933	2.612347
H	5.008590	-2.057224	2.586578
H	4.030247	3.969274	2.612347
H	-0.722687	5.366178	2.586578
C	3.993310	-3.537198	3.788002
C	2.964922	-4.530002	3.793447
C	4.744750	-3.317359	4.973853
C	2.724064	-5.266253	4.984400
H	5.526415	-2.562175	4.966285
H	1.940515	-6.019552	4.985444
C	3.198677	4.992235	4.984400
C	0.500542	5.767753	4.973853
H	4.242828	4.690311	4.985444
H	-0.544299	6.067103	4.966285
C	-5.922741	0.274018	4.984400
C	-5.245292	-2.450395	4.973853
H	-6.183342	1.329241	4.985444
H	-4.982116	-3.504928	4.966285
C	1.260408	5.910728	6.112559
C	2.622441	5.519321	6.117931
H	0.818073	6.324984	7.013814
H	3.210641	5.637380	7.023260
C	-5.749045	-1.863819	6.112559
C	-6.091093	-0.488560	6.117931
C	4.488637	-4.046909	6.112559
C	3.468652	-5.030761	6.117931
H	3.276794	-5.599186	7.023260
H	5.068560	-3.870964	7.013814
H	-5.886634	-2.454020	7.013814
H	-6.487435	-0.038194	7.023260

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Cartesian coordinates for optimized structure of **2'**

C	-3.303237	-5.692393	0.019424
C	-2.971588	-4.304954	0.000968
C	-4.045193	-3.317170	-0.002962
C	-5.400299	-3.762636	-0.022701
C	-5.691456	-5.170477	-0.026811
C	-4.682208	-6.099168	0.022236
C	-2.268845	-6.658478	0.031787
C	-0.945014	-6.282464	0.027165
C	-0.593140	-4.906999	0.008792
C	-1.609721	-3.948965	-0.004512
C	-3.803614	-1.930487	0.004188
C	-4.842718	-0.996921	-0.008473
C	-6.184264	-1.461552	-0.028287
C	-6.448979	-2.812057	-0.034783
C	0.771449	-4.503584	0.002980
C	1.933633	-4.141423	-0.001464
C	3.285039	-3.695786	-0.006883
C	4.358362	-4.625183	-0.020333
C	5.660317	-4.179080	-0.024577
C	5.959225	-2.795639	-0.016758
C	4.895623	-1.844912	-0.002676
C	3.573943	-2.329061	0.002249
C	7.324060	-2.343448	-0.019744
C	7.623450	-1.004874	0.023834
C	6.581342	-0.014408	0.016145
C	5.214233	-0.421329	-0.002100
C	6.900882	1.364493	0.024338
C	5.913325	2.322913	0.016864
C	4.546334	1.939452	-0.000206
C	4.224985	0.580006	-0.010164
C	3.514462	2.919317	-0.007312
C	2.619227	3.744163	-0.012052
C	1.557678	4.691815	-0.016862
C	1.826312	6.085835	-0.035655
C	0.789149	6.990444	-0.038101
C	-0.558424	6.557787	-0.022778
C	-0.850488	5.161647	-0.003975
C	0.229540	4.258957	-0.001061
C	-1.632172	7.513969	-0.023096
C	-2.941012	7.104521	0.028609
C	-3.278456	5.706857	0.025852
C	-2.242775	4.726072	0.003521

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C	-4.632298	5.294371	0.042186
C	-4.969034	3.959984	0.036857
C	-3.953888	2.967601	0.013982
C	-2.615870	3.368821	-0.002363
C	-4.286658	1.584055	0.006313
C	-4.553238	0.396316	-0.000302
O	8.314401	-3.301463	-0.020187
C	9.090102	-3.366348	-1.226385
O	-7.016578	-5.547868	-0.033582
C	-7.455091	-6.192163	-1.239237
O	-4.949005	-7.450943	0.029669
C	-5.553766	-7.939798	1.236414
O	8.927414	-0.559648	0.029460
C	9.652665	-0.831572	1.238128
O	-3.978225	8.011621	0.037360
C	-4.098010	8.780142	1.244028
O	-1.296661	8.850325	-0.030638
C	-1.635578	9.550824	-1.236968
H	-2.545508	-7.706096	0.035395
H	-0.158511	-7.029636	0.034678
H	-1.318122	-2.906331	-0.021682
H	-2.788915	-1.553098	0.022449
H	-6.994077	-0.739720	-0.035505
H	-7.469982	-3.174737	-0.039539
H	4.138385	-5.687491	-0.024500
H	6.485086	-4.881771	-0.024301
H	2.739655	-1.638938	0.015329
H	7.946528	1.648293	0.027319
H	6.166783	3.377723	0.021581
H	3.176211	0.311347	-0.026032
H	2.856366	6.426101	-0.045134
H	0.985442	8.056028	-0.042069
H	0.049163	3.191412	0.016294
H	-5.400657	6.058301	0.049481
H	-6.009354	3.652597	0.047291
H	-1.859178	2.594516	-0.022419
H	9.805468	-4.178490	-1.083235
H	9.622837	-2.427993	-1.404189
H	8.449498	-3.593745	-2.086526
H	-8.517792	-6.400818	-1.101643
H	-6.911231	-7.125609	-1.408940
H	-7.323828	-5.528676	-2.102061
H	-5.675302	-9.016078	1.099845
H	-6.528291	-7.473667	1.406753

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H	-4.902201	-7.753983	2.098292
H	10.645487	-0.399316	1.099339
H	9.736426	-1.907513	1.414963
H	9.165610	-0.355097	2.097015
H	-4.968565	9.424566	1.107444
H	-3.206372	9.389999	1.414280
H	-4.263691	8.123382	2.106081
H	-1.286228	10.576041	-1.100251
H	-2.715859	9.545012	-1.406938
H	-1.125850	9.105087	-2.099195

Cartesian coordinates for optimized structure of **3'**

C	-5.309425	-4.100252	-0.001918
C	-7.342156	-2.125871	-0.023227
C	-4.989008	-2.730083	0.004918
C	-6.688350	-4.467551	-0.019345
C	-7.682076	-3.459176	-0.029207
C	-5.975163	-1.739210	-0.006012
C	-4.294154	-5.148246	-0.000524
C	-2.386226	-7.242734	0.019839
C	-4.705564	-6.514514	0.017043
C	-2.914271	-4.871380	-0.007585
C	-1.955645	-5.888932	0.002988
C	-3.729587	-7.540077	0.026183
C	-6.105304	-6.841519	0.022192
C	-7.060113	-5.855983	-0.024023
C	1.936616	-4.967097	-0.012062
C	3.121121	-4.665777	-0.015009
C	-5.609529	-0.367588	0.001088
C	-5.279657	0.809297	0.006374
C	5.509212	-5.290645	-0.029889
C	6.207133	-2.544532	-0.007543
C	6.834557	-4.920661	-0.030495
C	4.492304	-4.298599	-0.017738
C	4.859440	-2.949760	-0.006375
C	7.213186	-3.556542	-0.020015
C	6.609397	-1.142055	-0.004022
C	7.473463	1.556616	0.022949
C	7.998710	-0.817012	0.020298
C	5.681634	-0.083975	-0.014170
C	6.085434	1.254358	0.000058
C	8.400961	0.540351	0.032275
C	8.602225	-3.186124	-0.017555
C	8.980192	-1.867079	0.030942

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C	5.118682	2.293746	-0.008058
C	4.278916	3.181805	-0.012834
C	1.827206	7.411926	-0.042446
C	-0.900270	6.644429	-0.004873
C	0.844477	8.374995	-0.043678
C	1.476079	6.035523	-0.022171
C	0.124216	5.679629	-0.003145
C	-0.526345	8.021330	-0.025943
C	-2.316304	6.292123	0.005962
C	-5.085376	5.691933	0.047063
C	-3.292004	7.333221	0.030173
C	-2.769176	4.959682	0.001862
C	-4.130155	4.640573	0.022261
C	-4.668618	7.003193	0.050258
C	-1.541230	9.039082	-0.025760
C	-2.872513	8.708121	0.030248
O	-1.128256	10.352723	-0.037761
O	-3.853171	9.674461	0.040045
C	-1.415534	11.064698	-1.250492
C	-3.926019	10.451998	1.244461
O	-8.403962	-6.156430	-0.028971
O	-6.448453	-8.174980	0.027990
C	-8.882596	-6.769507	-1.235441
C	-7.071336	-8.634487	1.236707
O	9.532495	-4.201085	-0.016136
O	10.307632	-1.500250	0.045716
C	10.311735	-4.310604	-1.216570
C	11.005280	-1.808748	1.261594
C	3.336177	4.159703	-0.016573
C	2.479826	5.031793	-0.019339
C	0.617361	-5.290488	-0.008075
C	-0.572358	-5.570491	-0.003602
C	-4.547906	3.283921	0.016719
C	-4.900651	2.113688	0.011956
H	-8.109579	-1.358487	-0.028823
H	-3.954372	-2.409590	0.021000
H	-8.722463	-3.763158	-0.032009
H	-1.643796	-8.034339	0.024959
H	-2.561344	-3.847380	-0.023300
H	-4.066215	-8.570420	0.028585
H	5.226733	-6.338530	-0.035592
H	7.616494	-5.671256	-0.028670
H	4.065740	-2.212640	0.005871
H	7.789158	2.594945	0.030565

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H	4.618037	-0.288296	-0.034546
H	9.461977	0.761612	0.039499
H	2.875989	7.690800	-0.053897
H	1.104309	9.427366	-0.048087
H	-0.117538	4.623836	0.015625
H	-6.142503	5.446745	0.060414
H	-2.060645	4.140481	-0.019786
H	-5.390855	7.811431	0.058629
H	-0.925665	10.582816	-2.105492
H	-1.005759	12.067971	-1.114277
H	-2.493492	11.122496	-1.428313
H	-4.759405	11.144082	1.104949
H	-3.000180	11.010557	1.410478
H	-4.127656	9.806738	2.108284
H	-8.713678	-6.110743	-2.096090
H	-9.955822	-6.914268	-1.093276
H	-8.395136	-7.733405	-1.408746
H	-6.404020	-8.486992	2.094707
H	-7.250882	-9.702495	1.094834
H	-8.018652	-8.116879	1.414299
H	10.904768	-3.407089	-1.385897
H	9.663096	-4.493824	-2.081959
H	10.971940	-5.168084	-1.068785
H	12.023478	-1.437325	1.126311
H	11.022216	-2.887305	1.444091
H	10.539928	-1.297471	2.113219

Cartesian coordinates for optimized structure of **4'**

C	4.705738	2.120215	-0.216564
C	3.315018	1.900906	-0.044314
C	2.339025	3.022153	0.036378
C	2.747656	4.368982	0.212231
C	5.600373	1.069070	-0.236843
C	5.160747	-0.269771	-0.125552
C	3.764551	-0.523152	-0.024027
C	2.891137	0.576139	0.054517
C	0.968662	2.784872	-0.064290
C	0.000000	3.800932	0.017007
C	0.442989	5.148851	0.122472
C	1.829632	5.399771	0.234564
C	3.291704	-1.900466	0.017007
C	-1.429213	3.521773	-0.024027
C	-1.944520	2.215729	0.054517

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C	-3.303742	1.920437	-0.044314
C	-4.189029	3.015181	-0.216564
C	-3.726029	4.315530	-0.236843
C	-2.346745	4.604224	-0.125552
C	4.237542	-2.958065	0.122472
C	3.761523	-4.284393	0.234564
C	2.409822	-4.564031	0.212231
C	1.447749	-3.536731	0.036378
C	1.927439	-2.231322	-0.064290
C	-0.516709	-5.135396	-0.216564
C	-0.011276	-3.821343	-0.044314
C	-1.874344	-5.384600	-0.236843
C	-2.814002	-4.334452	-0.125552
C	-2.335339	-2.998621	-0.024027
C	-0.946618	-2.791868	0.054517
C	-3.786774	0.514578	0.036378
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C	-3.291704	-1.900466	0.017007
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C	5.644674	-2.658762	0.090093
C	6.087381	-1.370234	-0.088422
C	-4.230348	-4.586710	-0.088422
C	-5.124892	-3.559050	0.090093
C	-1.857033	5.956944	-0.088422
C	-0.519782	6.217812	0.090093
O	6.522044	-3.718677	0.175953
O	7.430819	-1.072035	-0.167601
O	-4.643820	-5.899261	-0.167601
O	-6.481491	-3.788917	0.175953
O	-2.787000	6.971296	-0.167601
O	-0.040553	7.507595	0.175953
C	-5.391305	-6.226361	-1.347932
C	-6.901635	-4.476085	1.363423
C	-2.696534	7.782187	-1.347932
C	-0.425586	8.215034	1.363423
C	8.087839	-1.555827	-1.347932
C	7.327221	-3.738949	1.363423
H	5.087107	3.128731	-0.332617
H	3.799029	4.607120	0.330016
H	6.663827	1.255976	-0.331538
H	1.845665	0.375742	0.241421
H	0.626319	1.777565	-0.254650

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H	2.161058	6.427141	0.332321
H	-1.248234	1.410522	0.241421
H	-5.253114	2.841198	-0.332617
H	-4.419621	5.143055	-0.331538
H	4.485539	-5.085102	0.332321
H	2.090368	-5.593615	0.330016
H	1.226257	-1.431190	-0.254650
H	0.166007	-5.969930	-0.332617
H	-2.244206	-6.399032	-0.331538
H	-0.597431	-1.786263	0.241421
H	-5.889397	0.986496	0.330016
H	-1.852575	-0.346374	-0.254650
H	-6.646597	-1.342039	0.332321
H	-6.322321	-5.654656	-1.398664
H	-4.795431	-6.035998	-2.248356
H	-5.613539	-7.293145	-1.280073
H	-6.628631	-3.904385	2.258241
H	-7.988948	-4.552835	1.300920
H	-6.460518	-5.475319	1.419708
H	-2.829612	7.170964	-2.248356
H	-1.735915	8.302619	-1.398664
H	-3.509279	8.508039	-1.280073
H	-0.066981	7.692755	2.258241
H	0.051603	9.195050	1.300920
H	-1.511506	8.332632	1.419708
H	7.625043	-1.134966	-2.248356
H	9.122818	-1.214895	-1.280073
H	8.058236	-2.647963	-1.398664
H	7.972024	-2.857313	1.419708
H	6.695612	-3.788370	2.258241
H	7.937345	-4.642215	1.300920

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3. Calculation of association constants based on variable-concentration ^{1}H NMR spectroscopy

The method described here is based on that developed by Horman and Dreux. [5] For dimerization of M, the following equilibrium is assumed:

$$2M \overset{K_{assoc}}{\rightleftharpoons} M_2$$

$$K_{assoc} = \frac{[M_2]}{[M]^2} \quad \text{..... (1)}$$

It is assumed that the measured chemical shift (δ) is the weighted average that of the monomer (δ_0) and dimer (δ_2):

$$\delta = f_0\delta_0 + f_2\delta_2;\ (f_0 + f_2 = 1) \quad \text{..... (2)}$$

Total concentration of monomer (c):

$$c = [M] + 2[M_2] = [M] + 2K_{assoc}[M]^2 \quad \text{..... (3)}$$

From (1) and (2), K_{assoc}, δ, δ_0, δ_2 and c are related by the following expression:

$$\delta = f_0\delta_0 + f_2\delta_2 = f_0\delta_0 + (1\text{-}f_0)\,\delta_2 = f_0(\delta_0\text{-}\delta_2) + \delta_2 = \frac{[M]}{c}(\delta_0\text{-}\delta_2) + \delta_2 \quad \text{.....(4)}$$

From (3), $[M] = \frac{-1+\sqrt{1^2-4\times 2K_{assoc}(-c)}}{2\times 2K_{assoc}} = \frac{-1+\sqrt{1+8cK_{assoc}}}{4K_{assoc}}$ .....(5)

Combine (4) and (5):

$$\delta = \delta_0 + \frac{1+4K_{assoc}c-\sqrt{1+8K_{assoc}c}}{4K_{assoc}c}(\delta_2 - \delta_0) \quad \text{..... (6)}$$

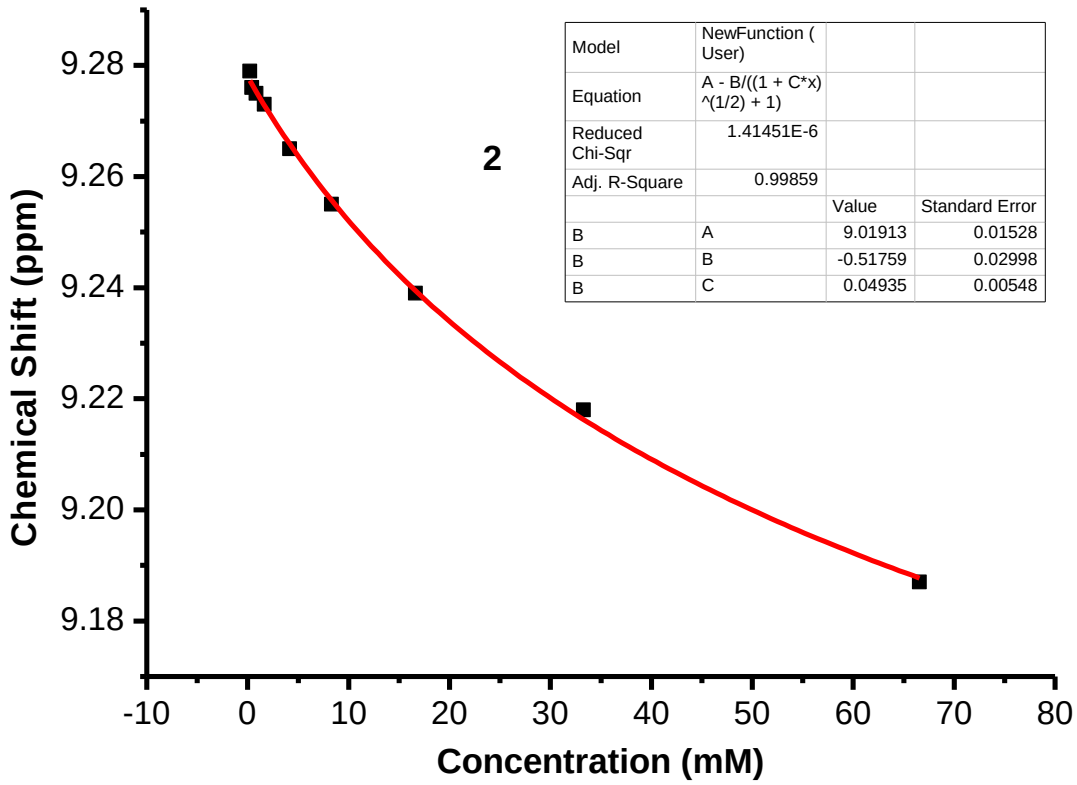
For each system, weighted-average chemical shift (δ) was measured at different total concentration of monomer (c). Chemical shifts of the monomer (δ_0) and dimer (δ_2) and the association constant K_{assoc} need to be calculated.

When $A=\delta_2$; $B=2(\delta_2-\delta_0)$; $C=8\,K_{assoc}$, the equation (6) is of the following form:

$$\delta = A - \frac{B}{1+\sqrt{1+Cc}} \quad \text{..... (7)}$$

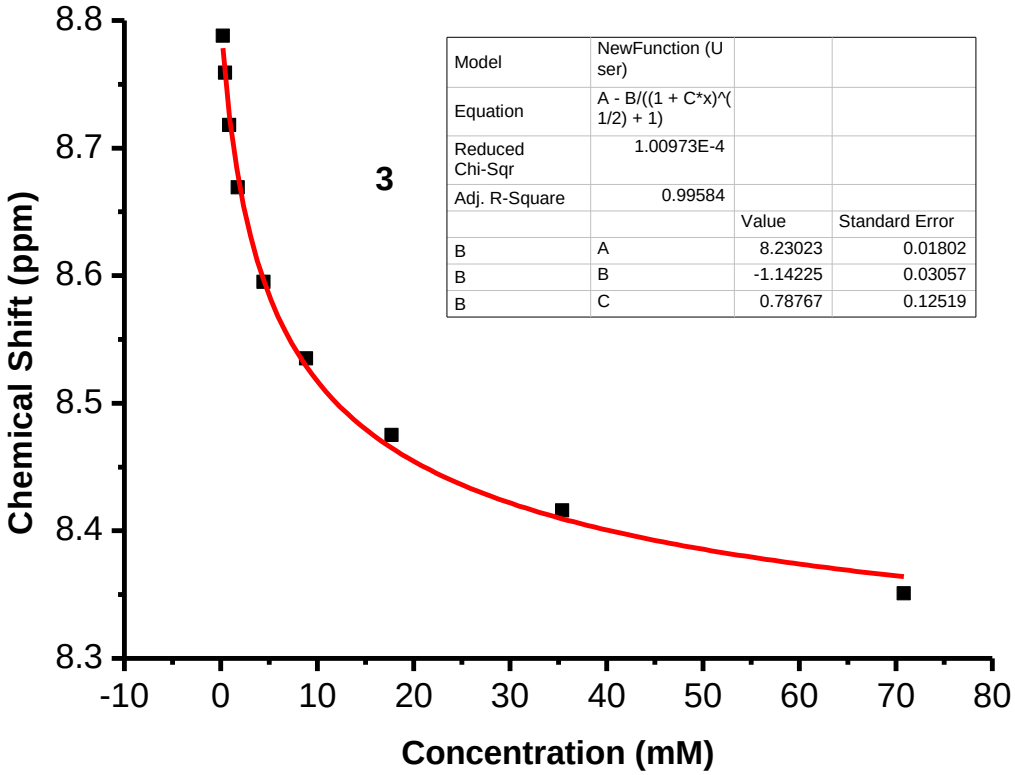
The curve fitting was then performed using Origin 8.5 to give A, B and C as shown here.

(5) I. Horman, B. Dreux, *Helv. Chim. Acta.* **1984**, *67*, 754.



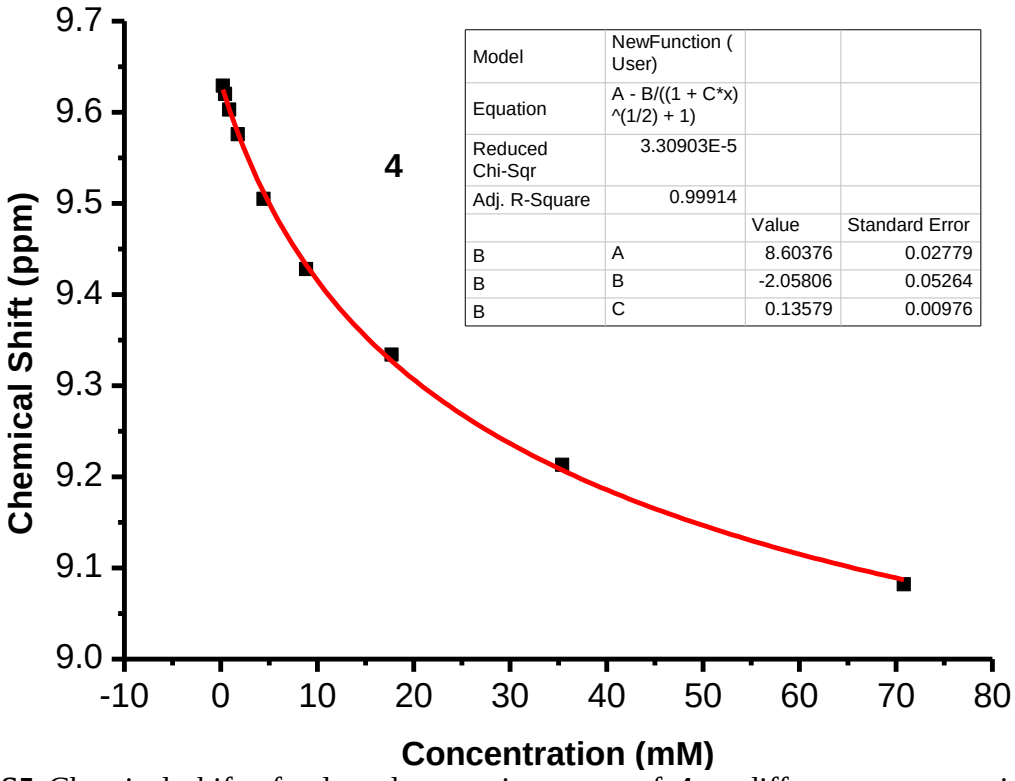
Model	NewFunction (User)		
Equation	A - B/((1 + C*x) ^(1/2) + 1)		
Reduced Chi-Sqr	1.41451E-6		
Adj. R-Square	0.99859		
		Value	Standard Error
B	A	9.01913	0.01528
B	B	-0.51759	0.02998
B	C	0.04935	0.00548

Figure S3 Chemical shift of selected aromatic proton of **2** at different concentration and curve fitting results.



Model	NewFunction (User)		
Equation	A - B/((1 + C*x)^(1/2) + 1)		
Reduced Chi-Sqr	1.00973E-4		
Adj. R-Square	0.99584		
		Value	Standard Error
B	A	8.23023	0.01802
B	B	-1.14225	0.03057
B	C	0.78767	0.12519

Figure S4 Chemical shift of selected aromatic proton of **3** at different concentration and curve fitting results.



Model	NewFunction (User)		
Equation	A - B/((1 + C*x) ^(1/2) + 1)		
Reduced Chi-Sqr	3.30903E-5		
Adj. R-Square	0.99914		
		Value	Standard Error
B	A	8.60376	0.02779
B	B	-2.05806	0.05264
B	C	0.13579	0.00976

Figure S5 Chemical shift of selected aromatic proton of **4** at different concentration and curve fitting results.

Table S1 Summary of chemical shifts of selected proton Hα at different concentration and curve fitting results.

Concentration for 1 and 3 (mM in $CDCl_3$)	**Chemical Shift (ppm)** **3**	**4**	**Concentration for 2 (mM in $CDCl_3$)**	**Chemical Shift (ppm)** **2**
0.22	8.788	9.629	0.21	9.279
0.44	8.759	9.62	0.41	9.276
0.89	8.718	9.603	0.84	9.275
1.77	8.669	9.576	1.66	9.273
4.43	8.595	9.505	4.16	9.265
8.85	8.535	9.428	8.32	9.255
17.71	8.475	9.334	16.65	9.239
35.41	8.416	9.213	33.29	9.218
70.82	8.351	9.082	66.57	9.187
Curve Fitting Results				
δ_2 (ppm)	8.230	8.604		9.019
δ_0 (ppm)	8.801	9.633		9.278
K_{assoc} (M^{-1})	98	17		6

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4. Variable-temperature ^{1}H NMR spectra of 1

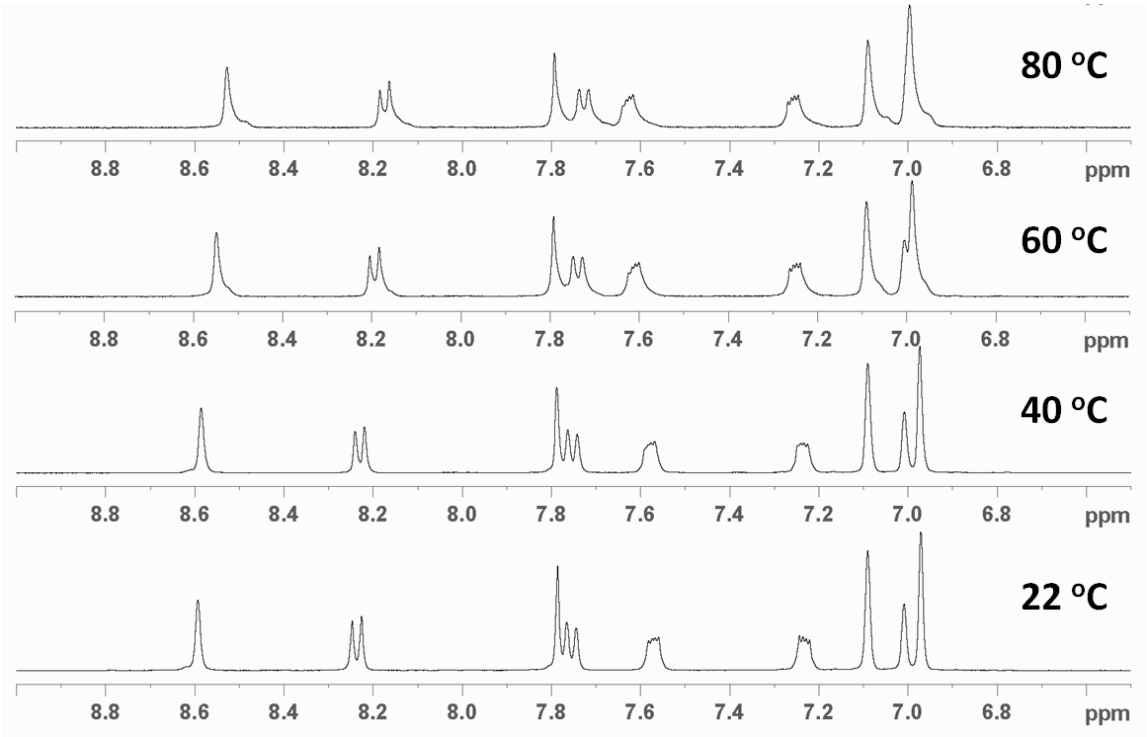

Figure S6 Partial ^{1}H NMR spectra of **1** in toluene-d_8 at different temperature. (22 ℃ to 80 ℃)

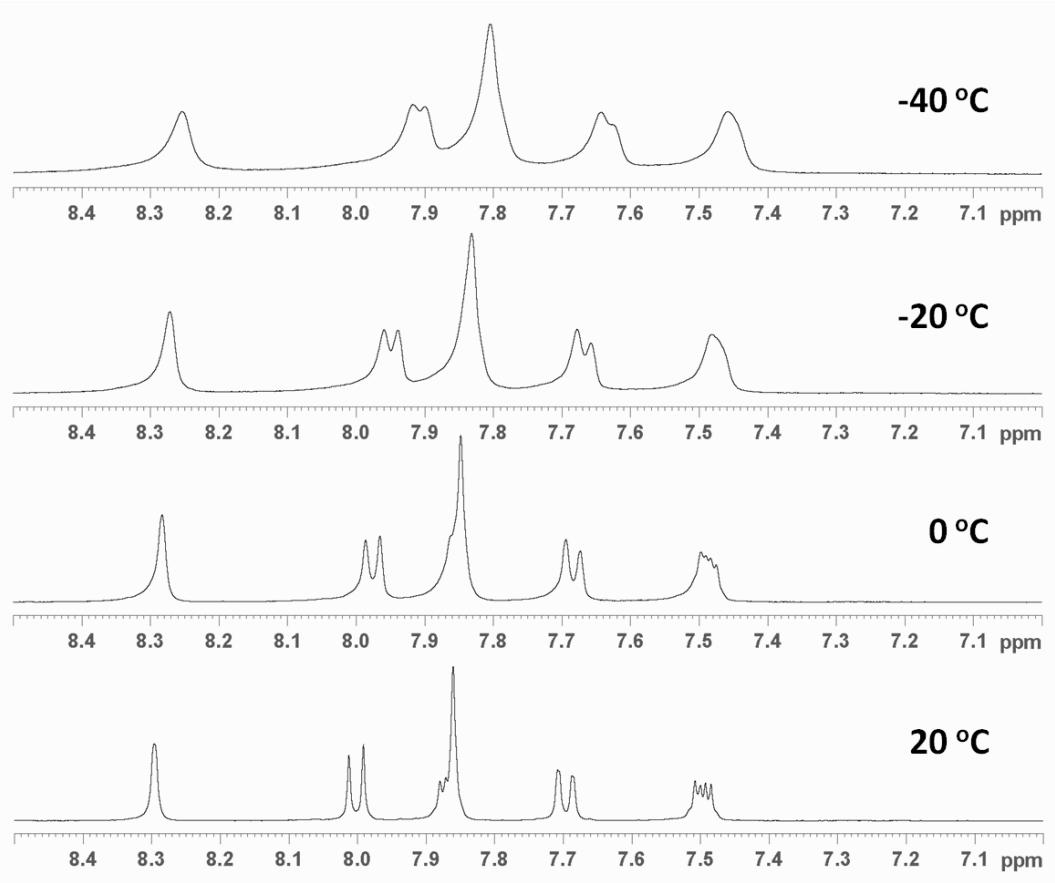

Figure S7 Partial ^{1}H NMR spectra for **1** in CD_2Cl_2 at different temperature. (22 ℃ to -40 ℃)

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5. Differential Scanning Calorimetry of 2

Differential Scanning Calorimetry (DSC) was performed on Perkin Elmer Differential Scanning Calorimeter Pyris 1.

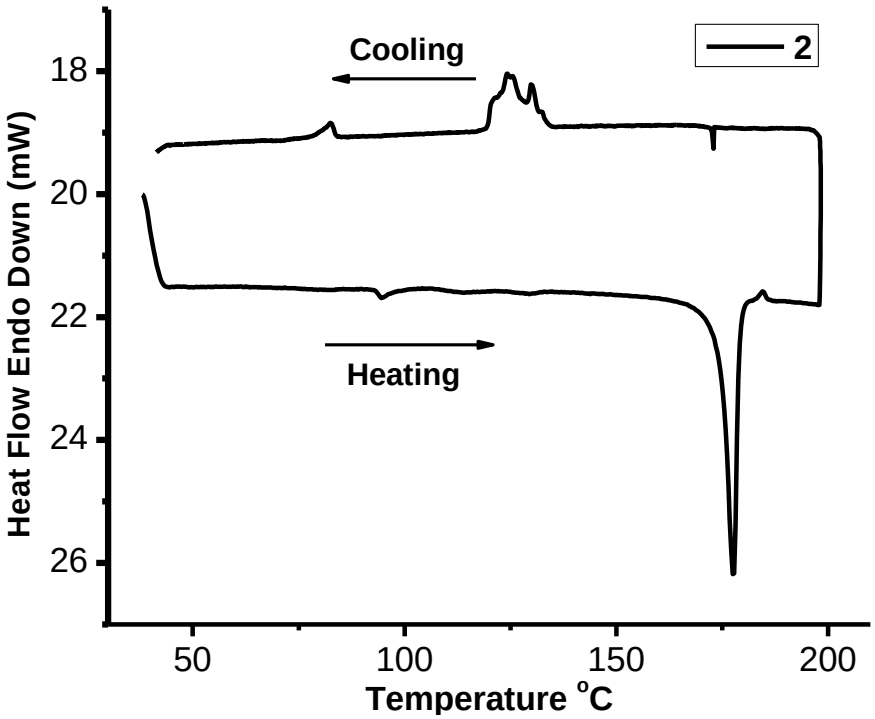

Figure S8 DSC trace of **2** for the first heating/cooling cycle with a heating rate of 10 ℃/min and a cooling rate of 5 ℃/min.

6. Fabrication and Characterization of Solution-Processed Thin Films and Transistors of 2-4

Deposition of thin films and fabrication of transistors

Organic thin films of **2-4** were deposited by drop-casting solutions onto octadecyltrimethoxysilane (OTMS) modified SiO_2/Si wafers [6] at room temperature in air ambient. To perform thermal annealing, the drop-cast films were heated at 120 ℃ for 10 minutes and then cooled in air to room temperature. Thin film devices of **2** with best performance were deposited by drop-casting a solution (1 mg in 0.6 mL toluene) onto a phenyltrichlorosilane (PTS)-modified SiO_2/Si wafer [7] at a substrate temperature of 120 ℃.

The devices were then placed in a vacuum oven at room temperature overnight to totally remove the organic solvents. Using an Edwards Auto 306 vacuum coater with a Turbomolecular pump at a pressure of 2.0×10^{-6} torr or lower, gold was vacuum-deposited through a shadow mask onto the organic films to form top contact drain and source electrodes, and the resulting semiconducting channels were 50μm(L)×1mm(W), 100μm(L)×1mm(W), 150μm(L)×1mm(W), 50μm(L)×2mm(W) and 100μm(L)×2mm(W).

(6) Y. Ito, A. A.Virkar, S. Mannsfeld, J. H. Oh, M. Toney, A. Locklin, Z. Bao, *J. Am. Chem. Soc*. **2009**, 131, 9396–9404.

(7) G. Giri, E. Verploegen, S. C. B. Mannsfeld, S. Atahan-Evrenk, D. H. Kim, S. Y. Lee, H. A. Becerril, A. Aspuru-Guzik, M. F. Toney, Z. Bao, *Nature*, **2011**, *480*, 504-508.

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Characterization of Thin Films

Reflection polarized light microscopy

Polarized optical images of the thin films were obtained using Nikon 50IPOL microscope.

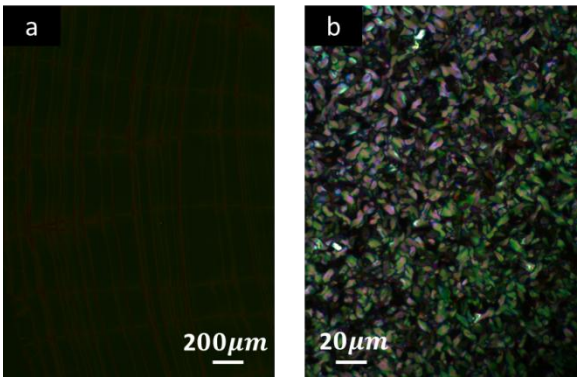

Figure S9 Reflected polarized-light micrographs for the films of **2** as deposited by drop-casting a 0.17 wt% solution in THF onto OTMS-modified SiO_2: (a) without thermal annealing; (b) with thermal annealing at 120 ℃.

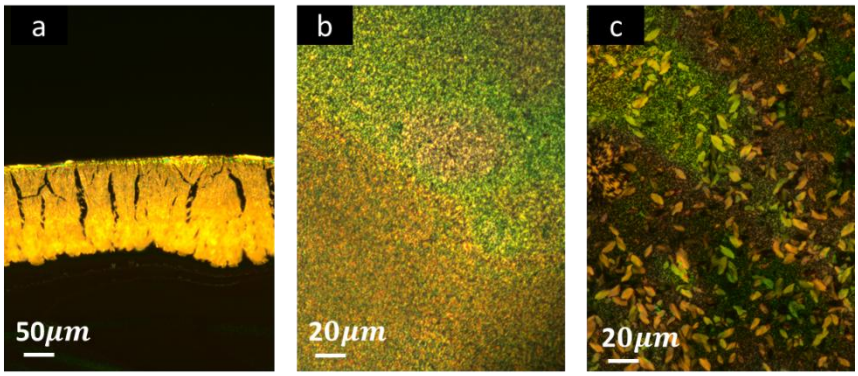

Figure S10 Reflected polarized-light micrographs for the films of **3** as deposited (a) by drop-casting a 0.2 wt% solution in cyclohexane onto a bare SiO_2 surface; (b) by drop-casting a 0.17 wt% solution in THF onto OTMS-modified SiO_2 surface without annealing; and (c) by drop-casting a 0.17 wt% solution in THF onto OTMS-modified SiO_2 surface followed by thermal annealing at 120 ℃.

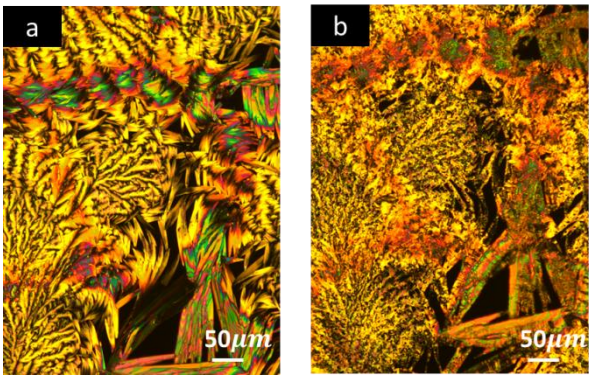

Figure S11 Reflected polarized-light micrographs for a film of **4** as drop-cast from a 0.17 wt% solution in mixed THF and acetone (1:1) onto OTMS-modified SiO_2 surface: (a) without thermal annealing; (b) followed by thermal annealing at 120 ℃.

Atomic Force Microscopy (AFM)

Thin films deposited through solution process were used for AFM studies. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments, with tapping mode and under ambient condition. The topographic images were collected from multiple samples, and for each sample, different regions were scanned to ensure reproducibility.

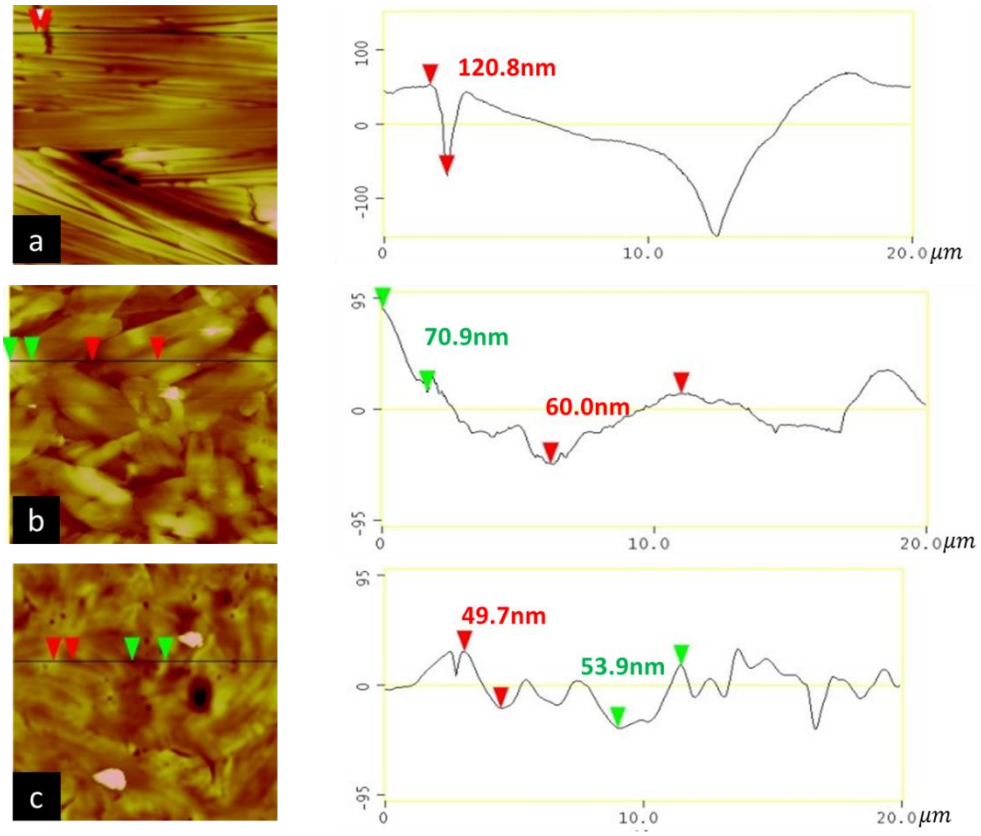

Figure S12 AFM section analysis for thin films of: (a) **2** as deposited by drop-casting a 0.17 wt% toluene solution onto PTS-modified SiO_2 surface at 120 ℃; (b) **3** as deposited by drop-casting a 0.17 wt% THF solution onto OTMS-modified SiO_2 surface; (d) **4** as deposited by drop-casting a 0.17 wt% solution in mixed THF and acetone (1:1) onto OTMS-modified SiO_2 surface.

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X-ray diffraction (XRD)

XRD data were collected on a SmartLab X-Ray Refractometer from powders or solution-processed films.

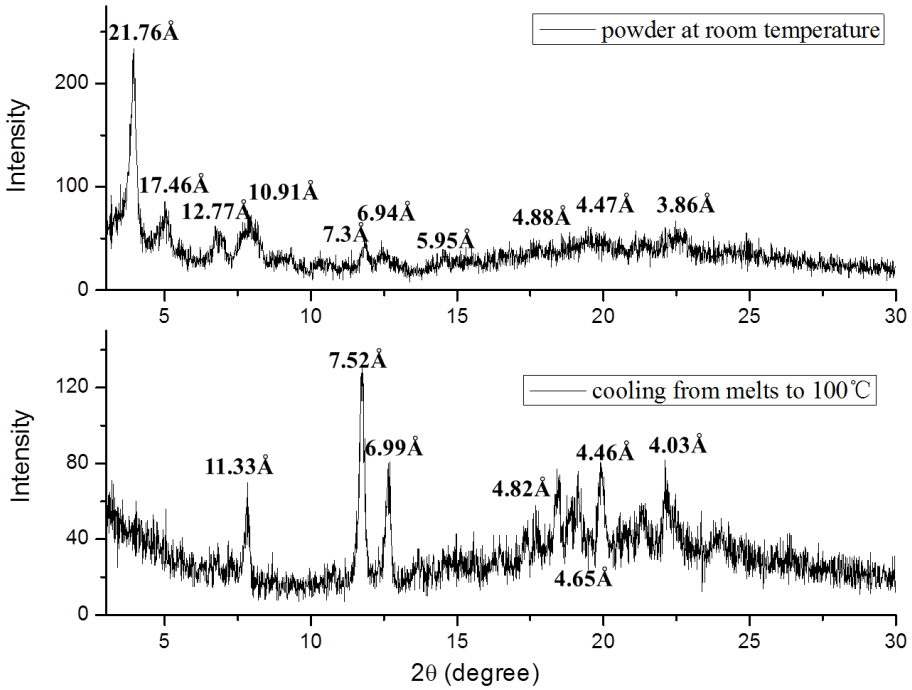

Figure S13 X-ray diffraction from powders of **2** at room temperature (above), and when cooling from melts to 100 ℃ (below).

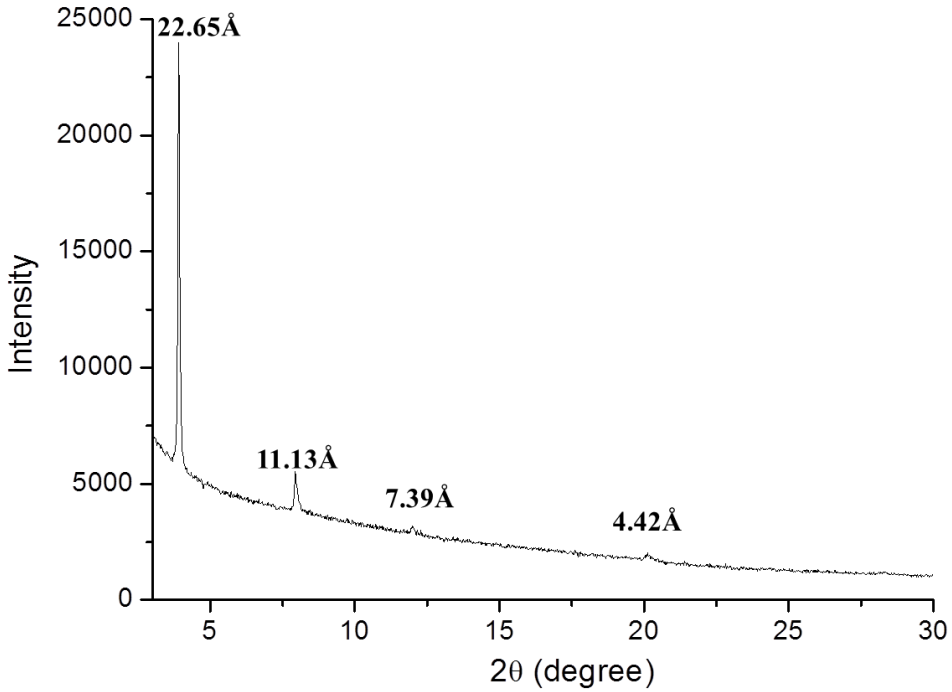

Figure S14 X-ray diffraction from thin films of **2** as drop-cast from a 0.17 wt% toluene solution onto PTS-modified SiO_2 surface at a substrate temperature of 120 ℃.

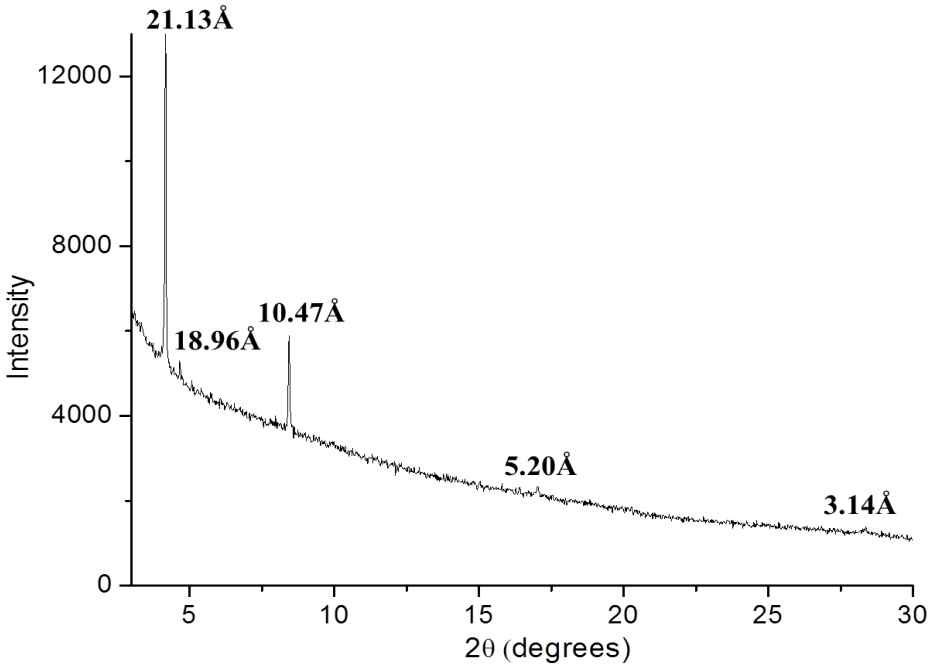

Figure S15 X-ray diffraction from a thin film of **4**, which was deposited by drop-casting a 0.17wt% solution in mixed THF and acetone (1:1) onto a OTMS-modified SiO_2/Si wafer.

Electrical Characterization of Thin Film Transistors

The current-voltage measurement was carried out on a JANIS ST-500-20-4TX probe station with a Keithley 4200 Semiconductor Characterization System at room temperature in ambient air.

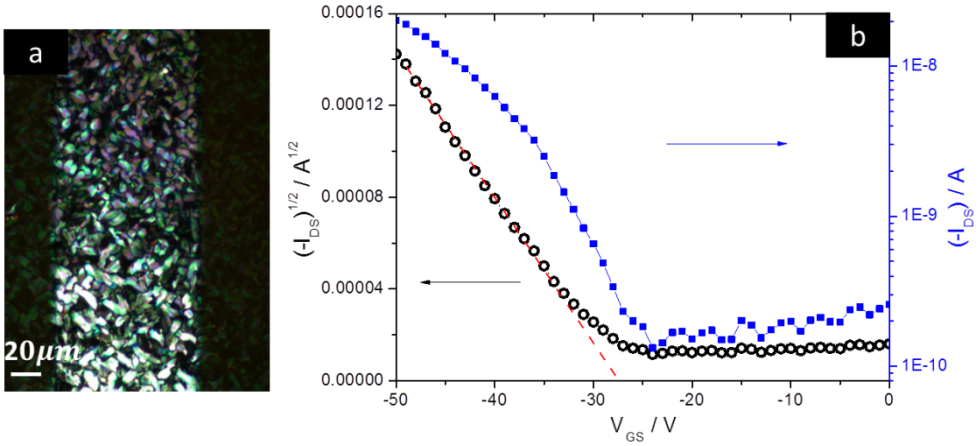

Figure S16 (a) Reflection polarized light micrograph for an OTFT of **2** (with an active channel of W = 1 mm and L = 100 μm), which was fabricated by drop-casting a 0.17 wt% solution in THF onto OTMS-modified SiO_2 and thermal annealing at 120 ℃; (b) transfer I-V curves for the device shown in (a) exhibiting a field effect mobility of 7.0×10^{-4} cm^2/V s.

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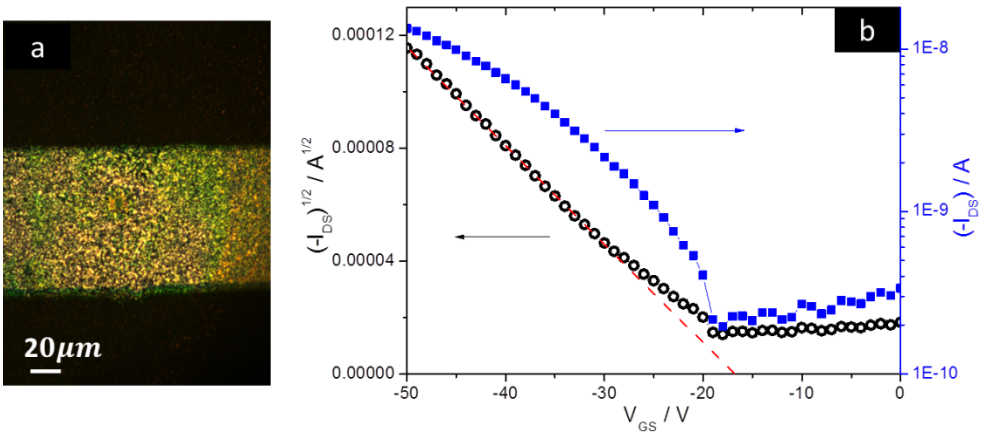


Figure S17 (a) Reflection polarized light micrograph for an OTFT of **3** (with an active channel of W = 1 mm and L = 100 μm), which was fabricated by drop-casting a 0.17 wt% solution in THF onto OTMS-modified SiO_2 at room temperature; (b) transfer I-V curves for the device shown in (a) exhibiting a field effect mobility of 2.4×10^{-4} cm^2/V s.

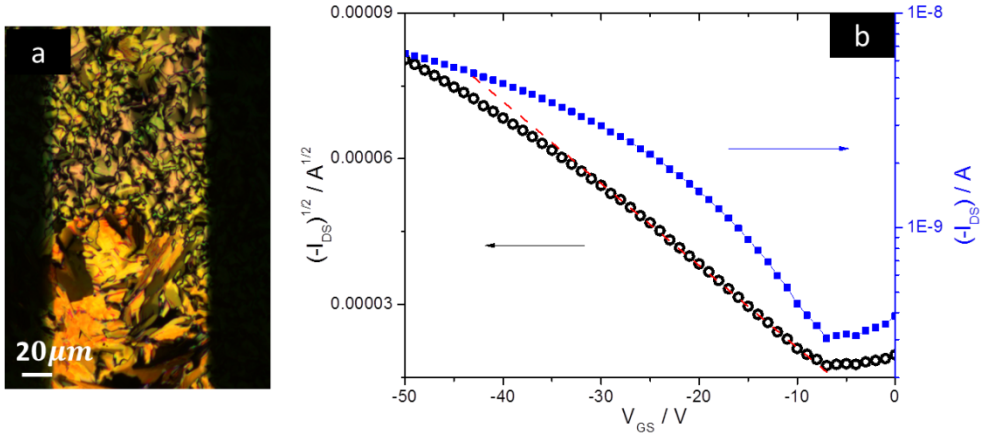
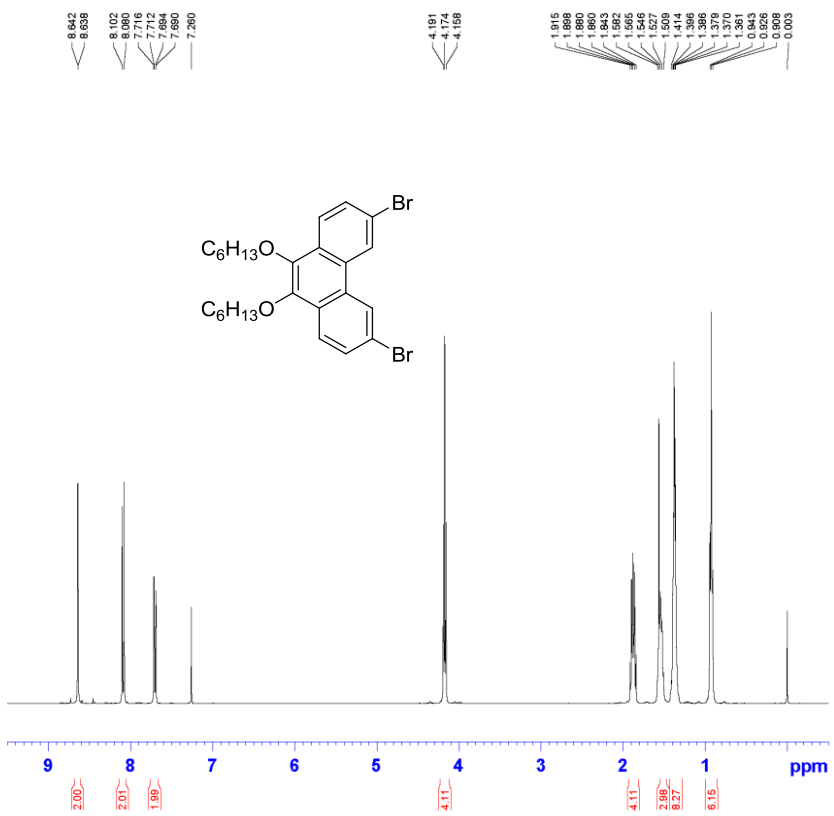
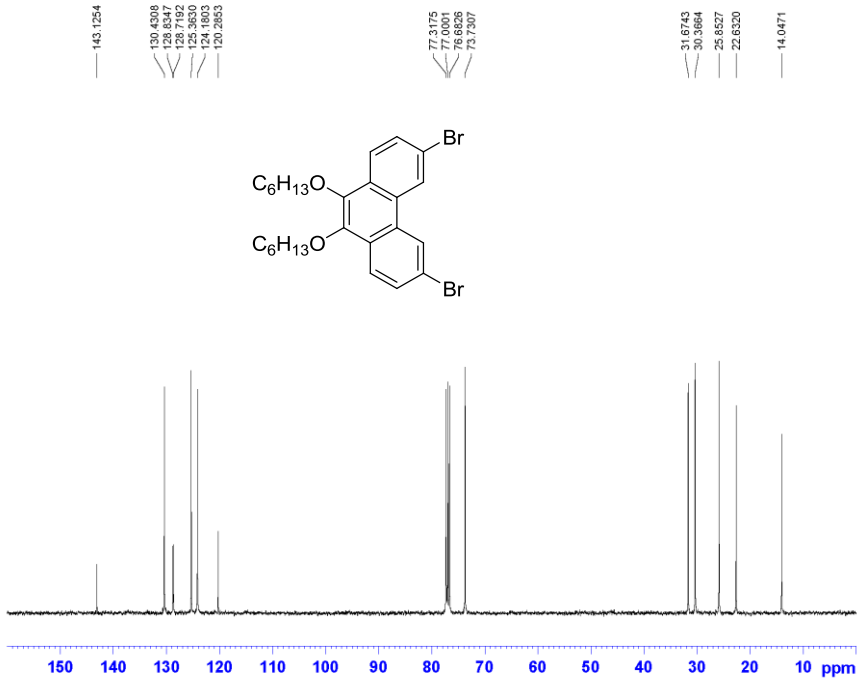


Figure S18 (a) Reflection polarized light micrograph for an OTFT of **4** (with an active channel of W = 1 mm and L = 100 μm), which was fabricated by drop-casting a 0.17 wt% solution in mixed THF and acetone (1:1) onto OTMS-modified SiO_2 at room temperature; (b) transfer I-V curves for the device shown in (a) exhibiting a field effect mobility of 4.4×10^{-5} cm^2/V s.

7. NMR spectra



^{1}H-NMR of 3, 6-dibromo-9, 10-bis(hexyloxy)phenanthrene in $CDCl_3$.



^{13}C-NMR of 3, 6-dibromo-9, 10-bis(hexyloxy)phenanthrene in $CDCl_3$.

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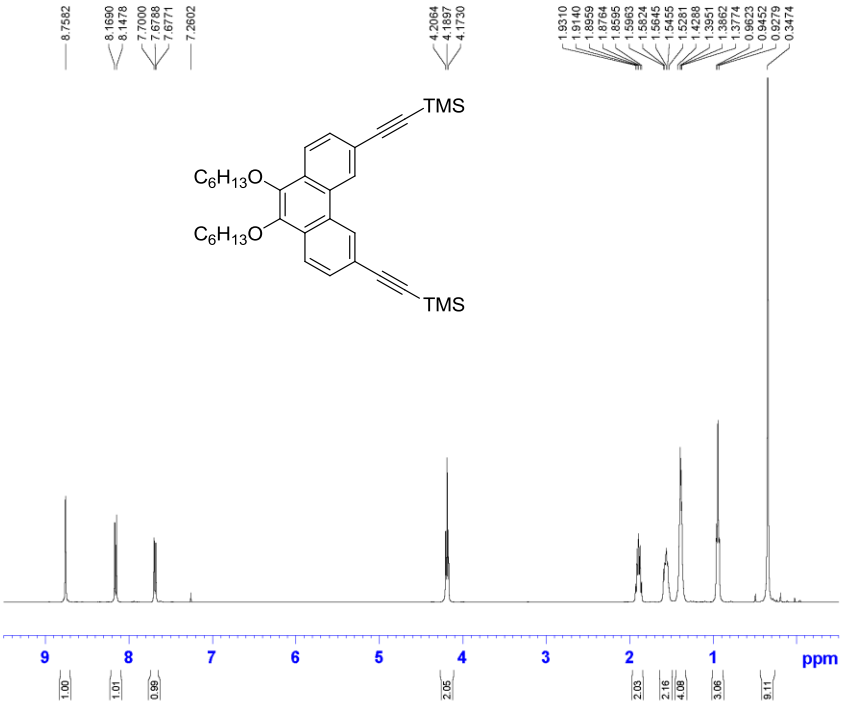
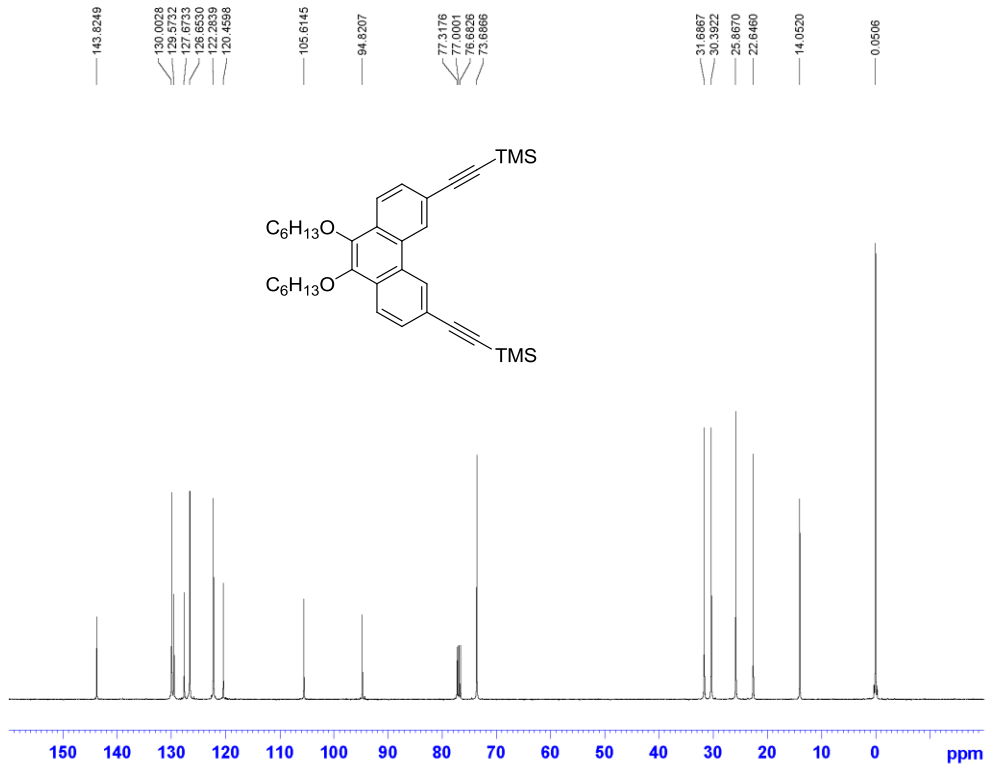


^{1}H-NMR of 3, 6-bis(trimethylsilylethynyl)-9, 10-bis(hexyloxy)-phenanthrene in $CDCl_3$.



^{13}C-NMR of 3, 6-bis(trimethylsilylethynyl)-9, 10-bis(hexyloxy)-phenanthrene in $CDCl_3$.

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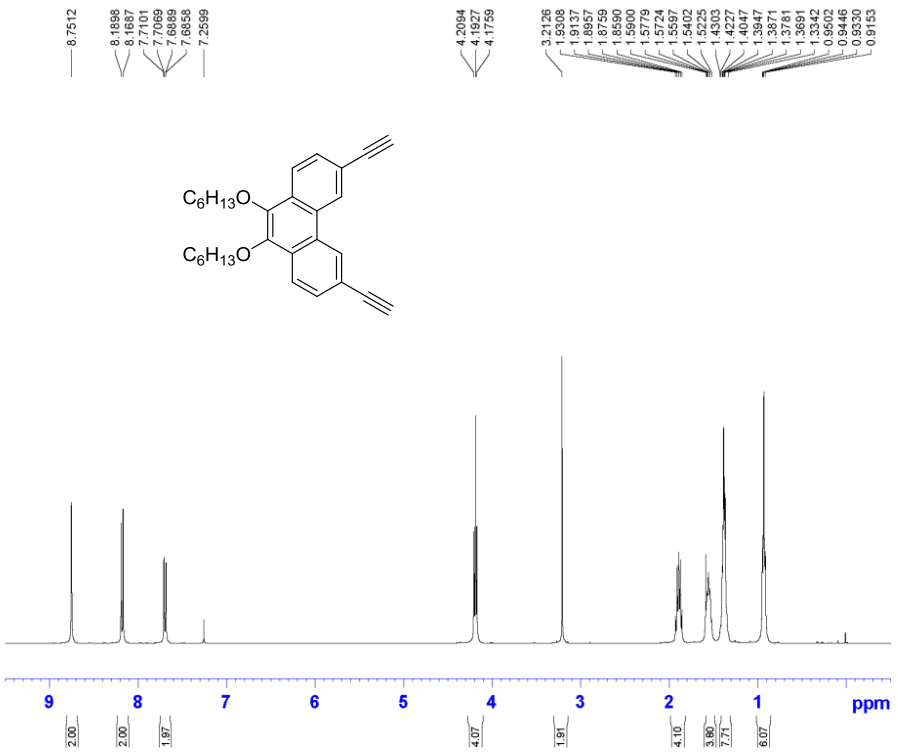
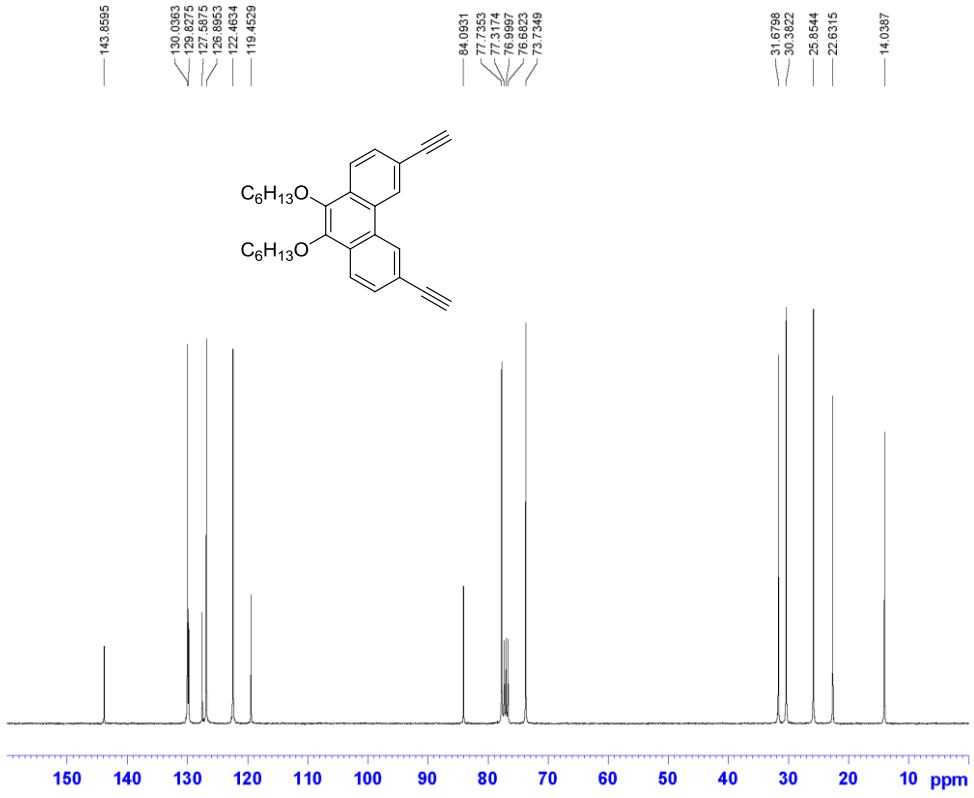
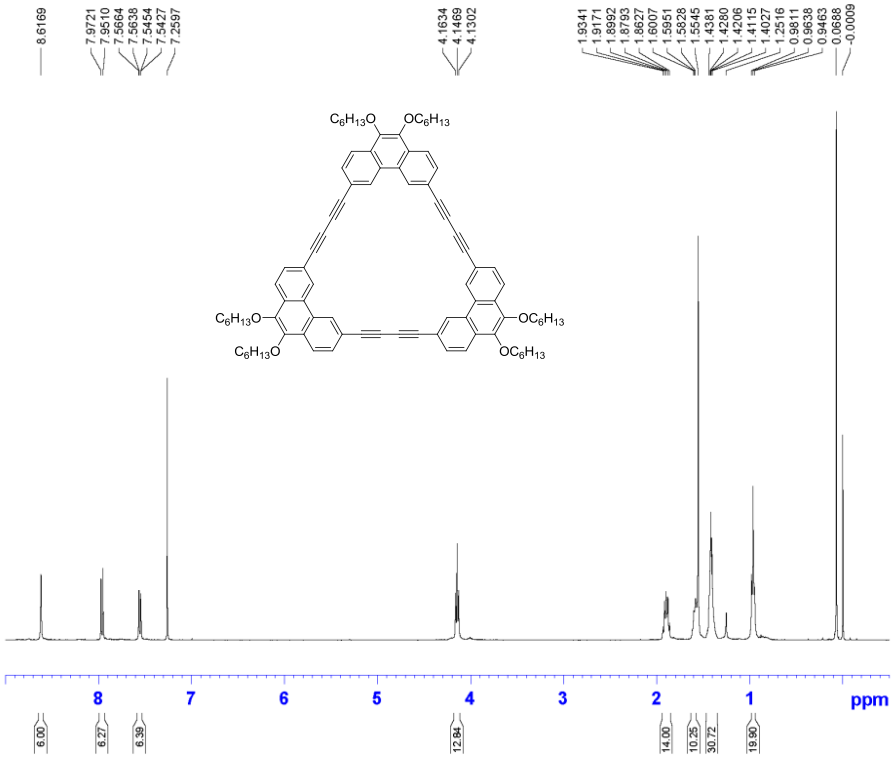


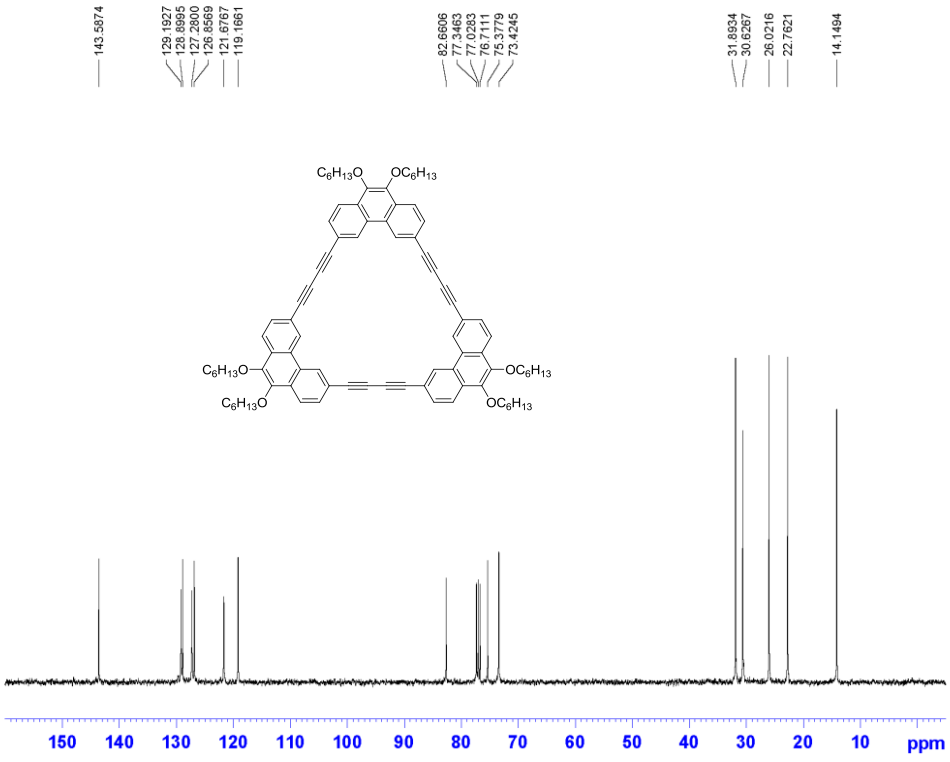
^{1}H-NMR of 3, 6-diethynyl-9, 10-bis(hexyloxy)-phenanthrene in $CDCl_3$.



^{13}C-NMR of 3, 6-diethynyl-9, 10-bis(hexyloxy)-phenanthrene in $CDCl_3$.



^{1}H-NMR of **3** in $CDCl_3$.



^{13}C-NMR of **3** in $CDCl_3$.

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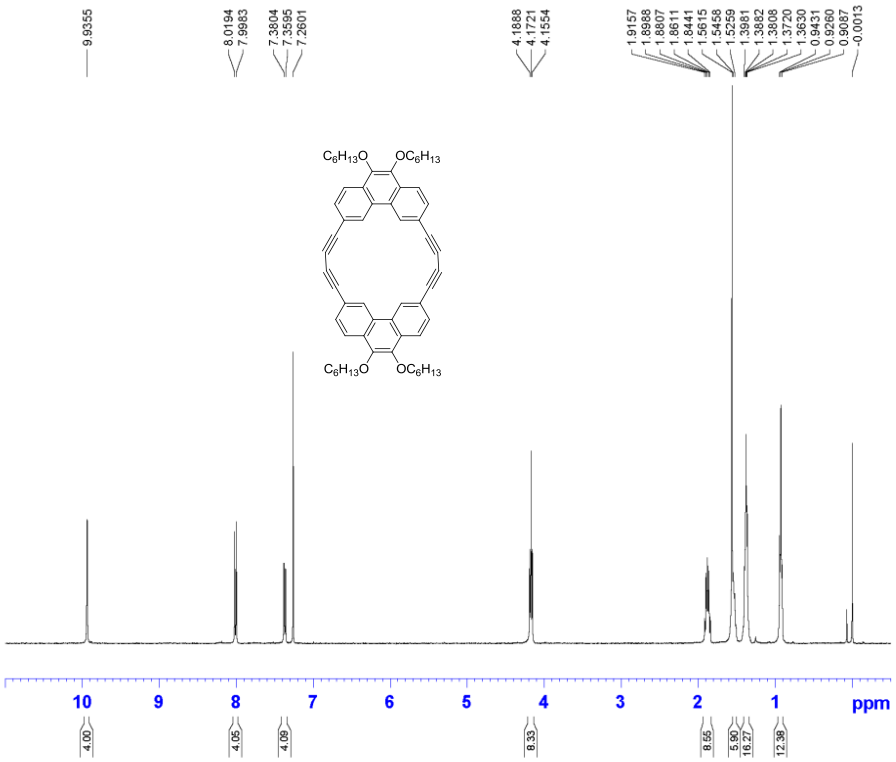
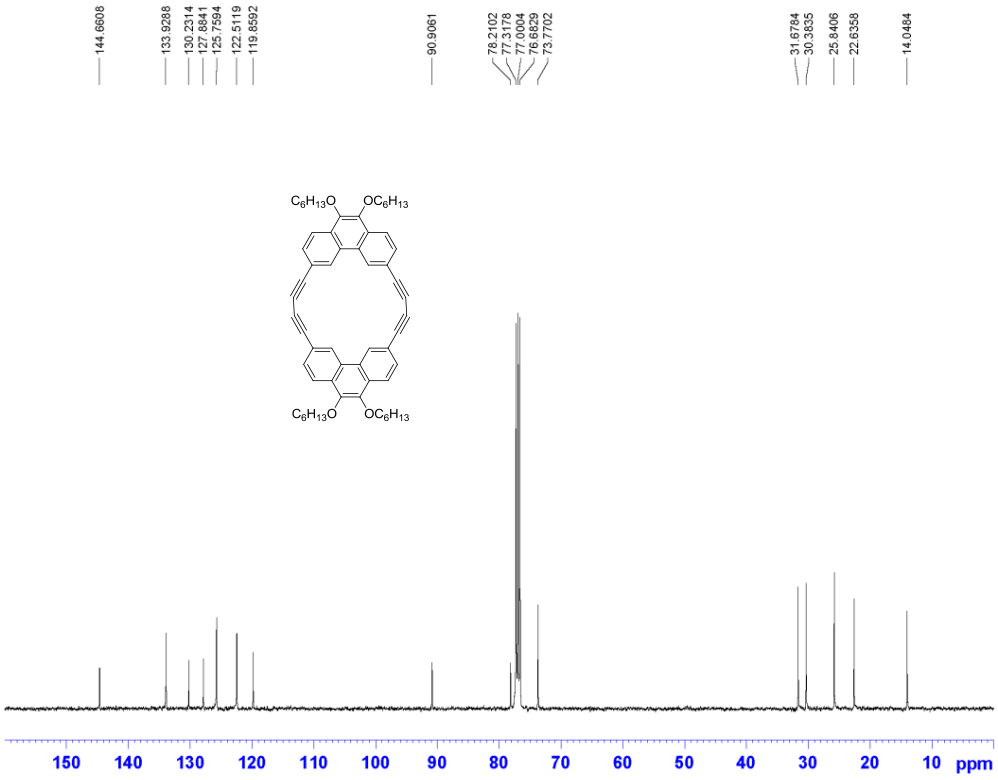


^{1}H-NMR of **9** in $CDCl_3$.



^{13}C-NMR of **9** in $CDCl_3$.

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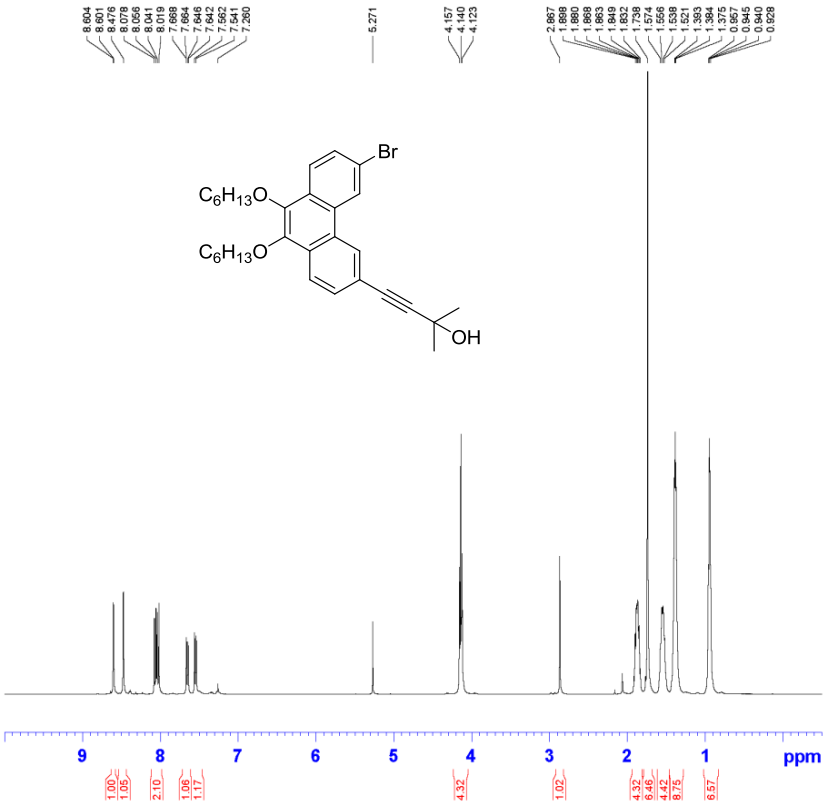
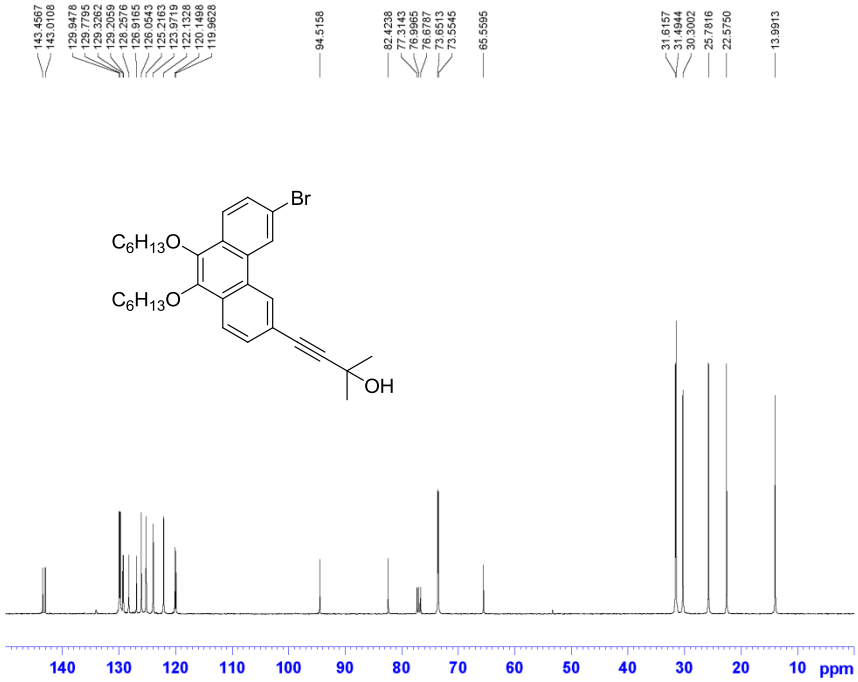


^{1}H-NMR of 3-(2'-methyl-2'-ol-but-3'-ynl)-6-bromo-9, 10-bis(hexyloxy)phenanthrene in $CDCl_3$.



^{13}C-NMR of 3-(2'-methyl-2'-ol-but-3'-ynl)-6-bromo-9, 10-bis(hexyloxy)phenanthrene in $CDCl_3$.

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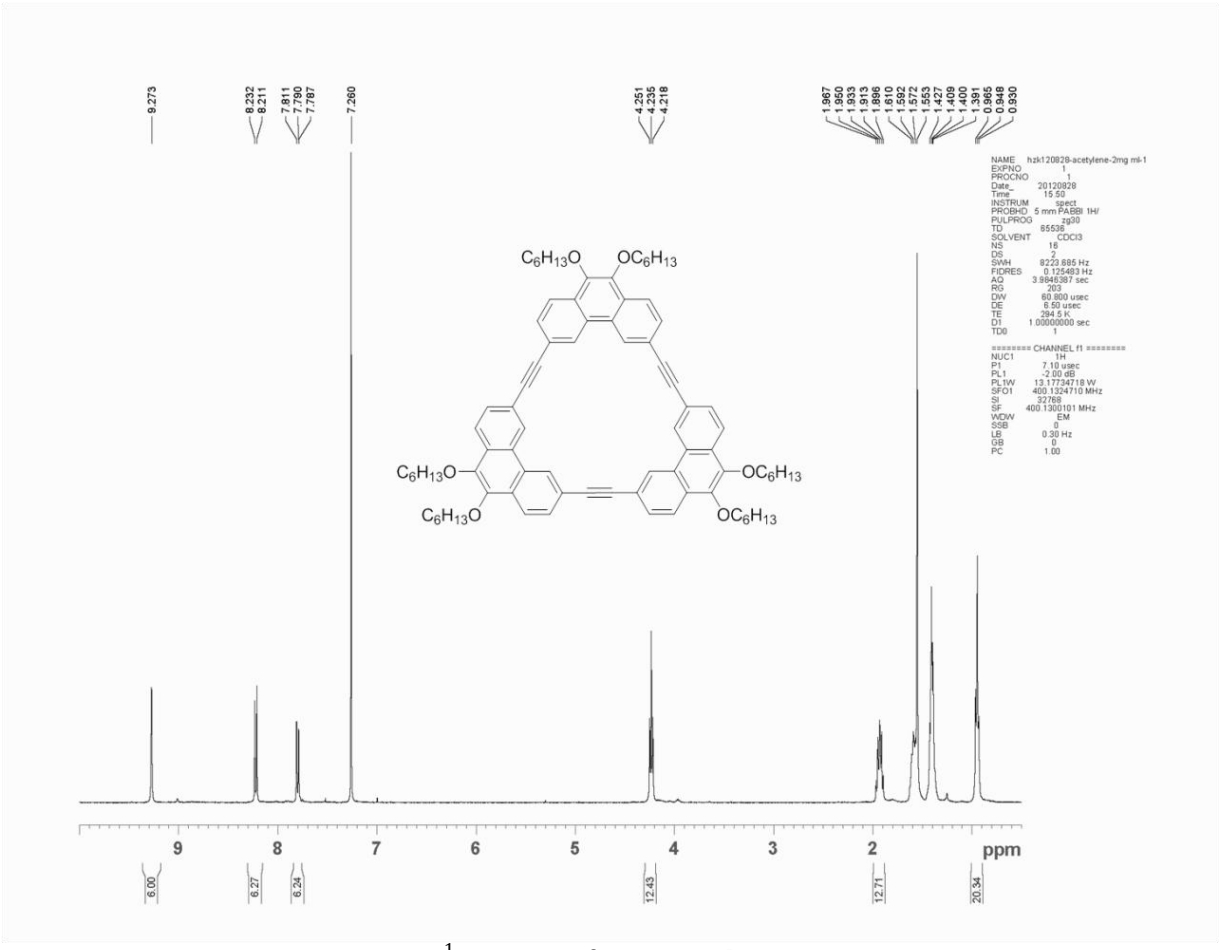
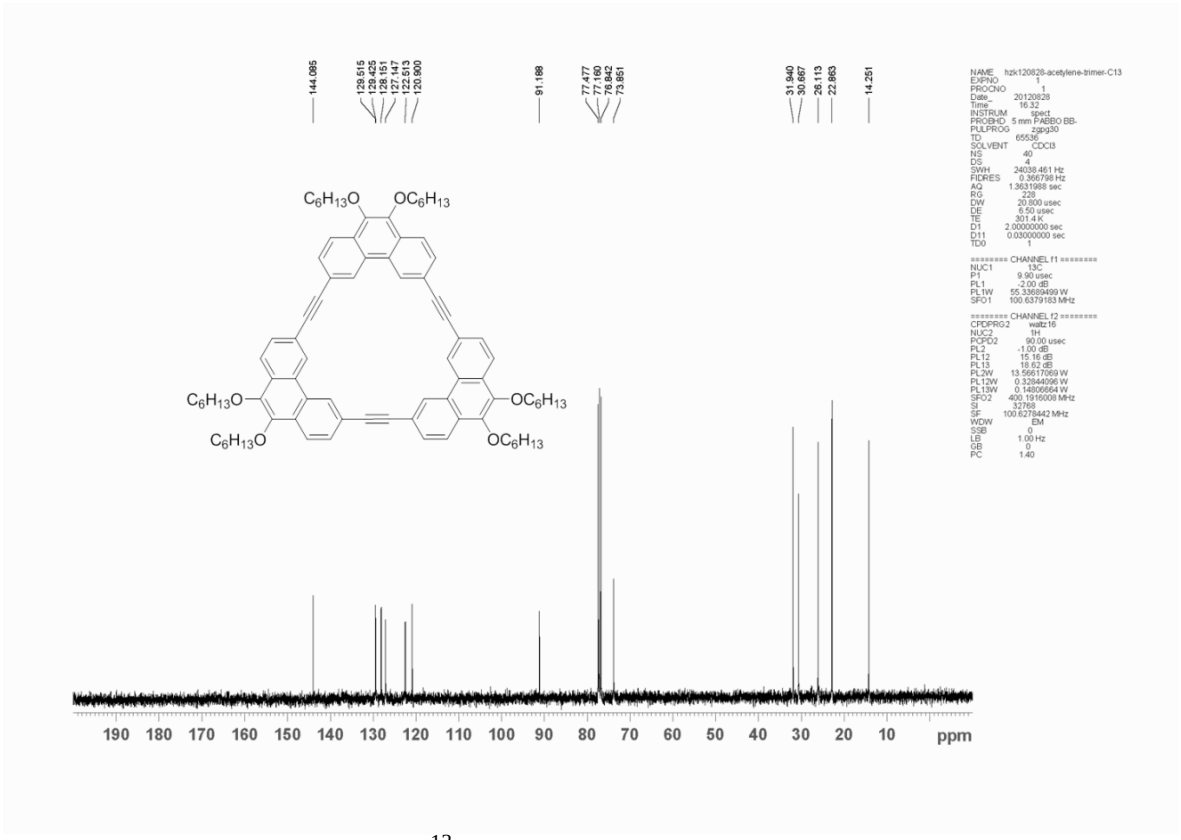


^{1}H-NMR of **2** in $CDCl_3$.



^{13}C-NMR of **2** in $CDCl_3$.

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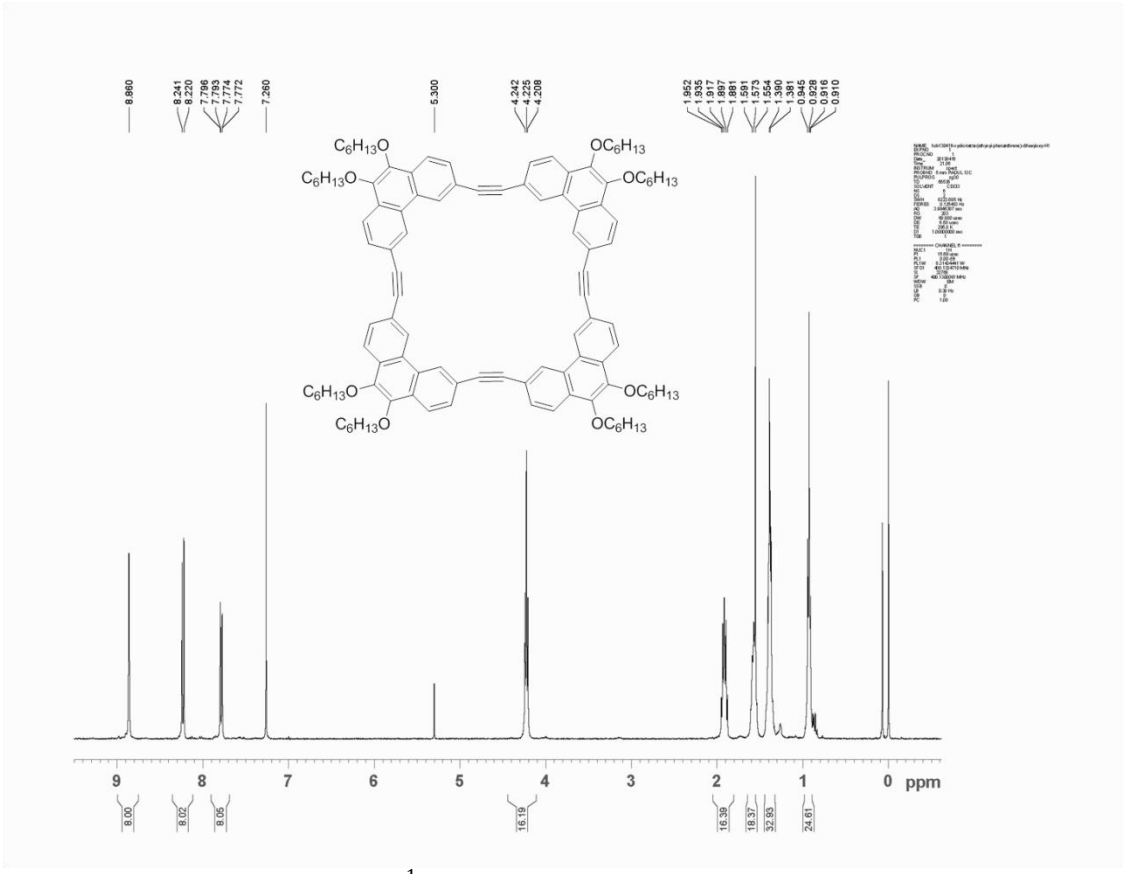
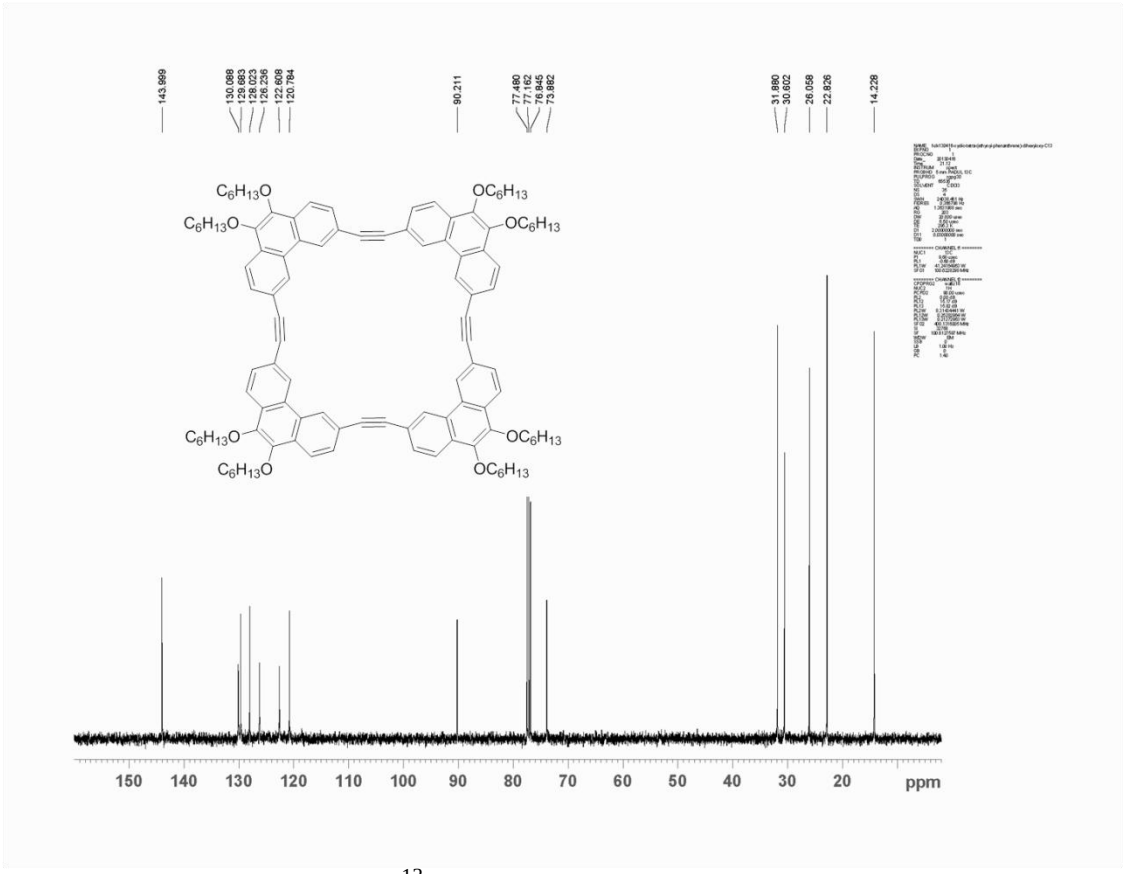
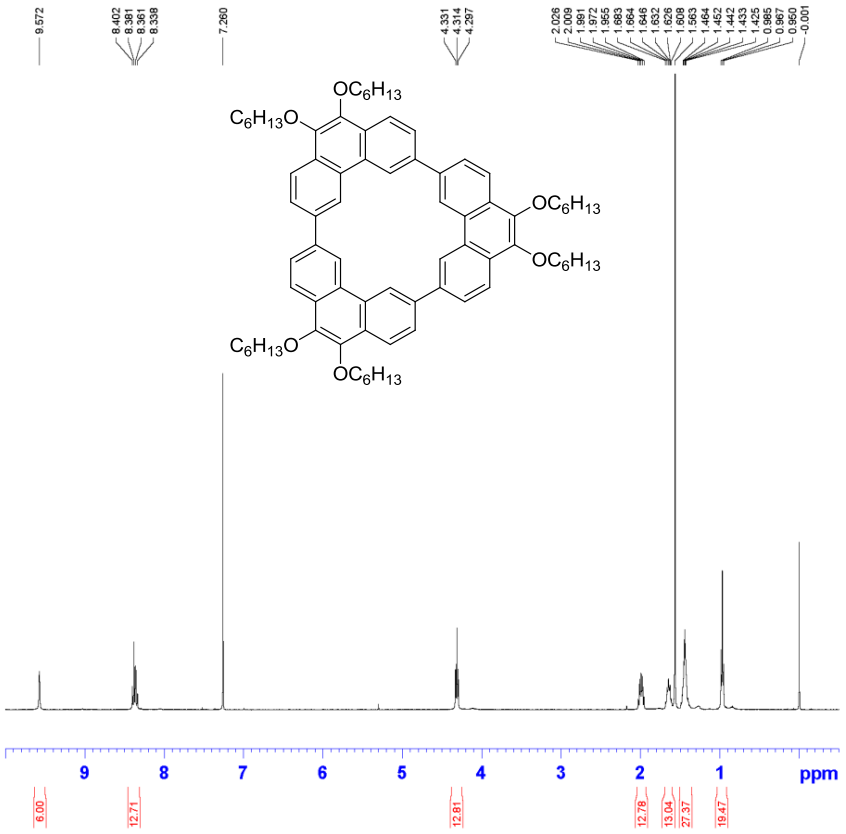


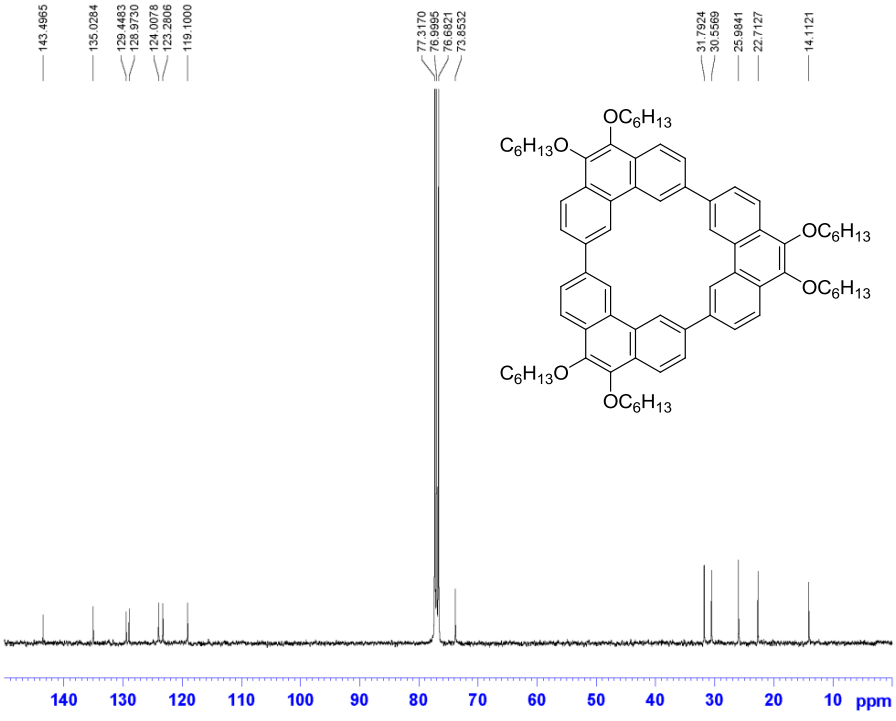
^{1}H-NMR of **8** in $CDCl_3$.



^{13}C-NMR of **8** in $CDCl_3$.



^{1}H-NMR of cyclo-3,6-tris(9, 10-di(hexyloxy)phenanthrene (**4**) in $CDCl_3$.



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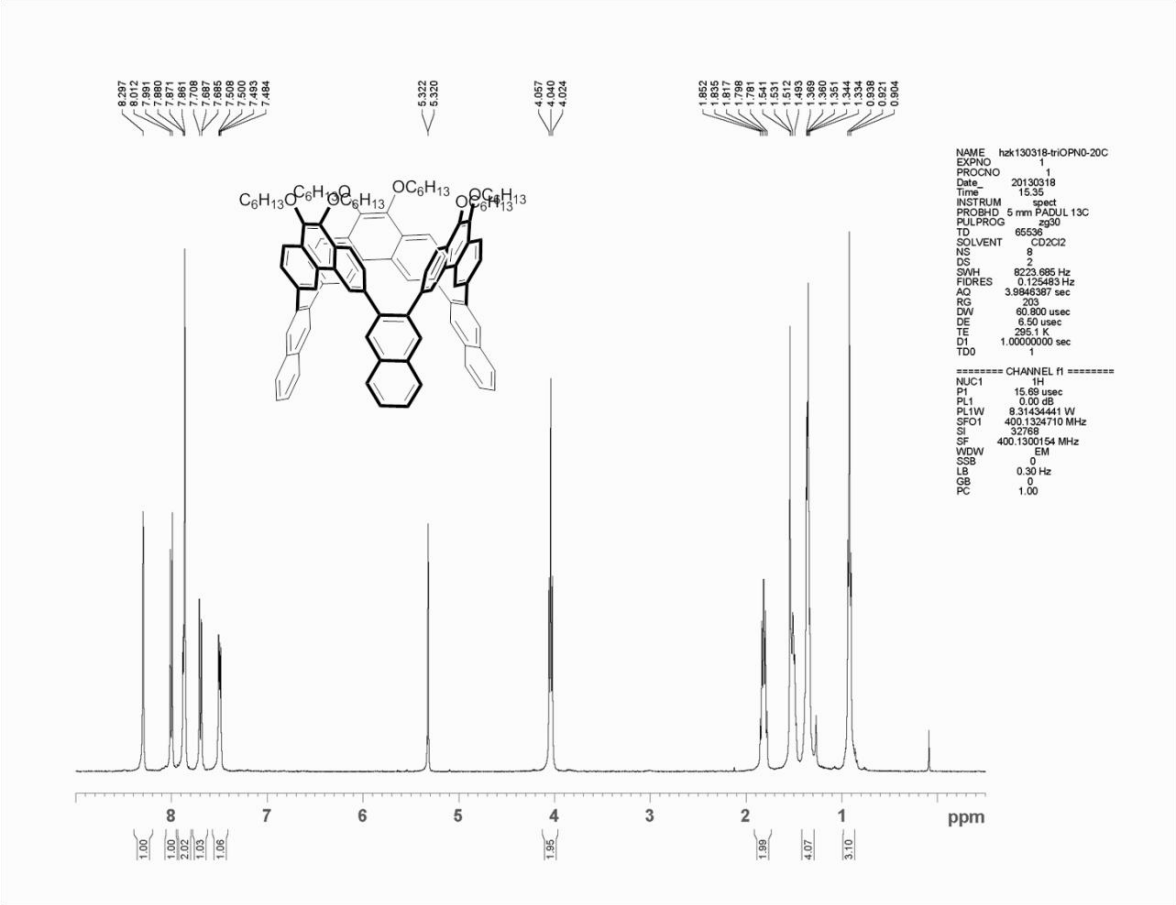
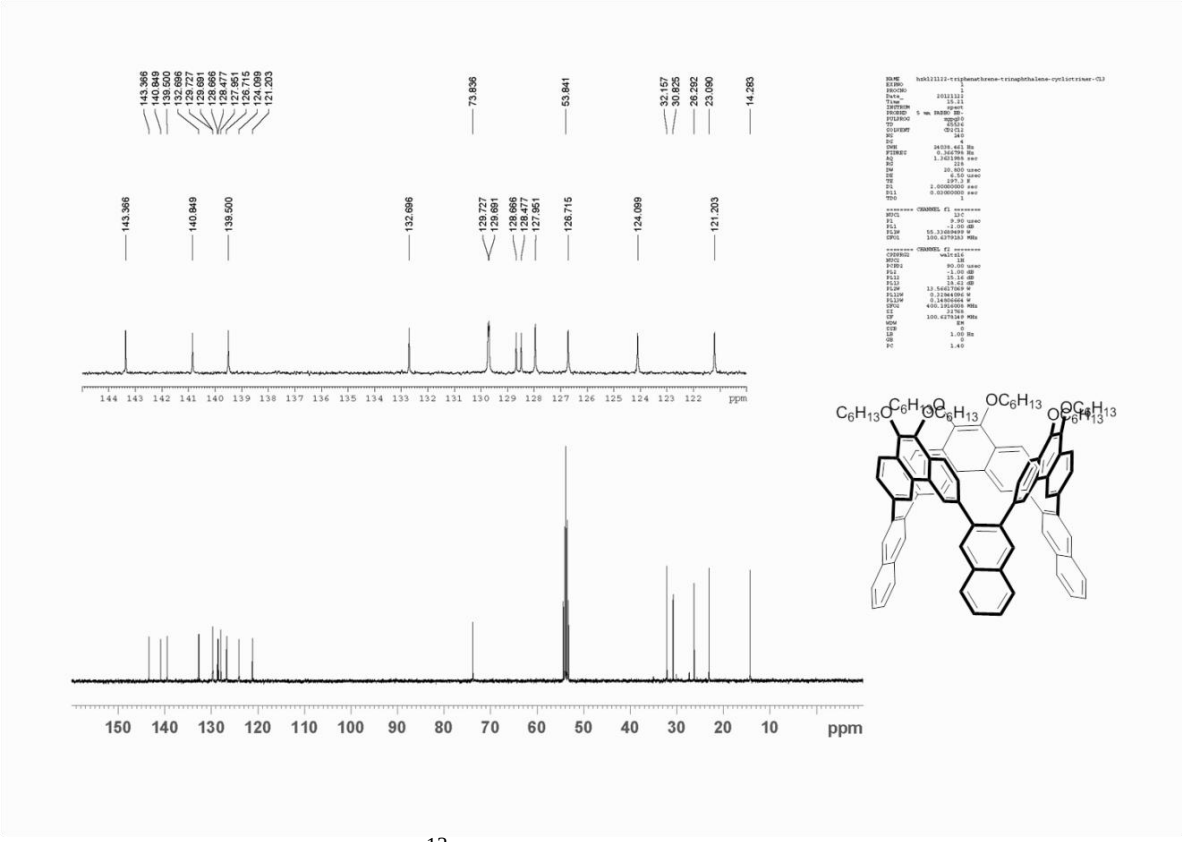


^{1}H-NMR of **1** in CD_2Cl_2.



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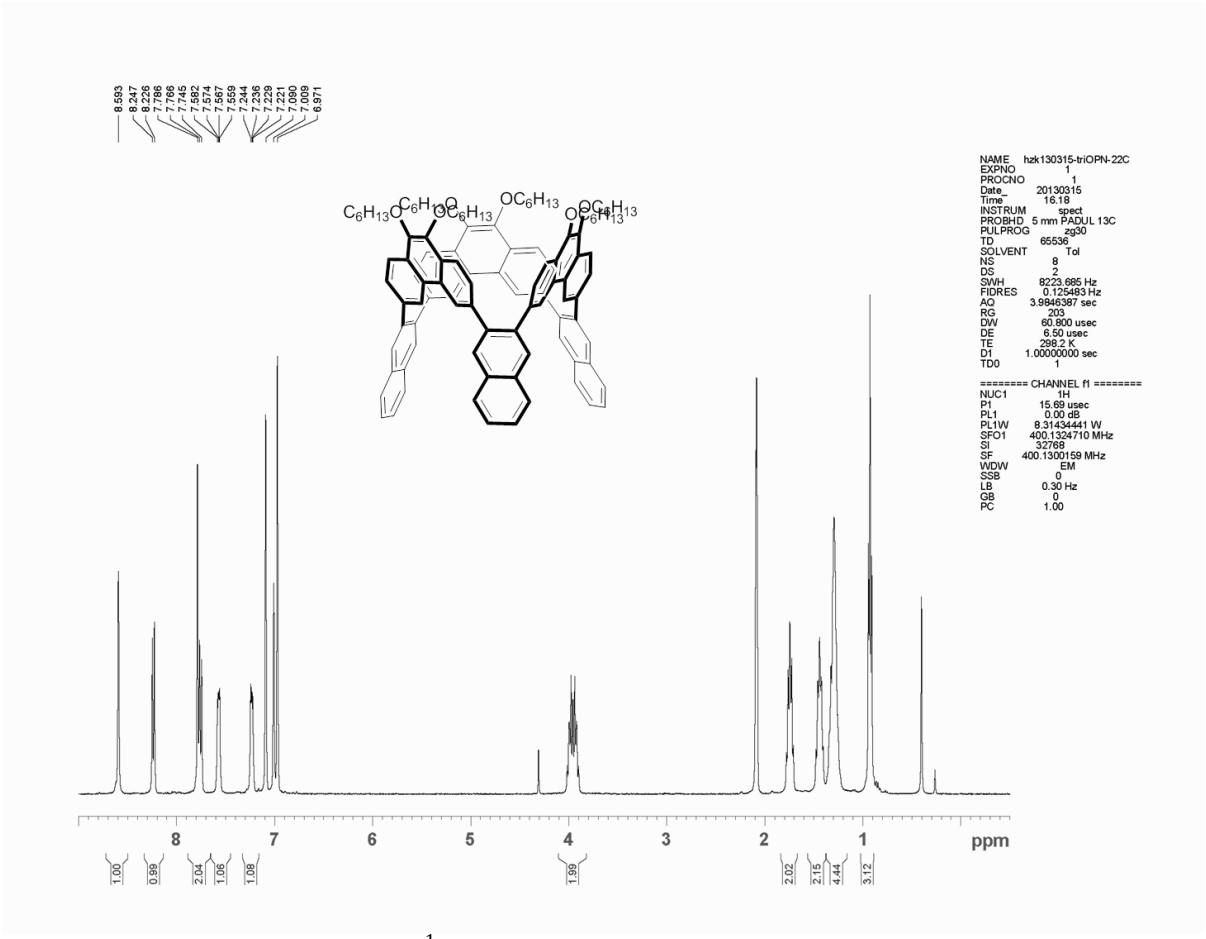

^{1}H-NMR of **1** in toluene-d_8