Supporting Information for:

Helical Pitch of *m*-Phenylene Ethynylene Foldamers by Double Spin Labeling

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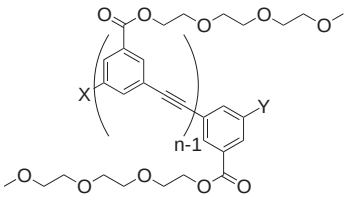
Experimental Procedures

General. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Fischer, Strem Chemicals) and were used without further purification. Dry triethylamine, acetonitrile, THF were obtained using a solvent purification system from Anhydrous Engineering. All air and moisture sensitive reactions were performed under an atmosphere of dry nitrogen. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 pre-coated TLC plates. Visualization was performed with 254 nm ultraviolet lamp. Silica gel coulumn chromatography was carried out with Silica Gel (230-400 mesh) from EM science.

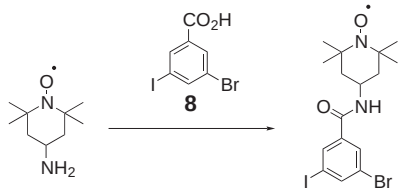
The ^{1}H NMR spectra were recorded at 400 MHz by Varian UNITY 400 spectrometer or at 500 MHz by Varian UNITY 500 spectrometer. The ^{13}C NMR spectra were recorded at 125 MHz by Varian UNITY 500 spectrometer. Chemical shifts are expressed in part per million (δ) using residual solvent protons as internal standards. Electron impact (EI), fast atom bombardment (FAB), and matrix assisted laser desorption ionization (MALDI) mass spectra were obtained by Micromass 70-VSE, Micromass ZAB-SE, and Voyager-DE STR spectrometer, respectively. High-performance liquid chromatography (HPLC) was performed with a Rainin binary gradient system equipped with two SD-200 pumps, a Si 90-125-CS analytical column (4.6 × 250 mm), and a UV detector operating at 290 nm.

The crystallographic data collection was performed on a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo Kα radiation. The data crystal was mounted using oil (paratone-N, Exxon) to a thin glass fiber. The data were collected at 193 K as a series of ω-scan frames, each with a width of 0.25°/frame. The crystal-to-detector distance was 5.007 cm. Crystal decay was monitored by repeating the 335 initial frames at the end of data collection and analyzing the duplicate reflections. Data reduction was performed using SAINTPLUS[1] software, which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by the global refinement. The structure solved by direct methods and refined by full least-squares on F^2 using SHELXTL.[2] The positions of all non-hydrogen-bonded hydrogen atoms were calculated geometrically and refined by the riding model.

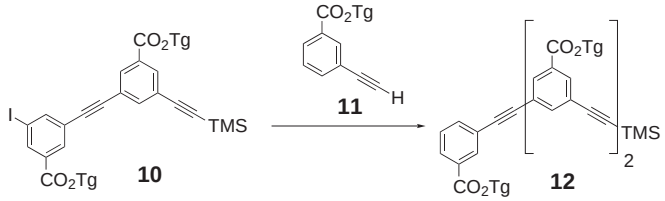


X-A$_n$-Y **S**

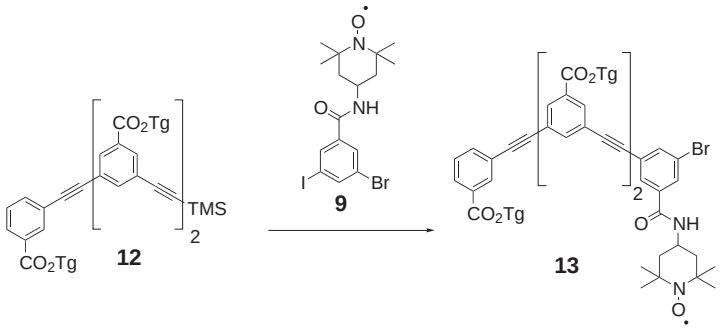
Oligomers are identified using an abbreviated nomenclature. The structure of **X-A$_n$-Y** is shown above. **X** and **Y** represent either a hydrogen (H), an iodine (I), a triazene (N_3Et_2), a trimethylsilyl-protected acetylene (TMS), or a deprotected acetylene (CCH). The spin labeled moiety is denoted as **S**. Tg denotes the 2-[2-(2-methoxyethoxy)ethoxy]ethyl group. 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-ethynylbenzoate (**11**),[3] 2-[2-(2-methoxyethoxy)ethoxy]ethyl 3,5-diethynylbenzoate (**16**),[4] 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-bromo-5-iodobenzoate (**18**),[3] **I-A$_2$-TMS** (**10**),[3] **I-A$_4$-TMS** (**14**),[3] **H-A$_2$-Br** (**21**),[3] **HCC-A$_4$-N$_3$Et$_2$** (**22**),[3] and Ethyl 3,5-dibromobenzoate (**25**)[5] were synthesized according to the previously reported procedure.



3-Bromo-5-iodo-*N*-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)benzamide (9): To a solution of 3-bromo-5-iodobenzoic acid (**8**) (660 mg, 2 mmol) and 4-aminoTEMPO (**7**) (340 mg, 2 mmol) in CH_2Cl_2 (10 mL) was added dicyclohexylcarbodiimide (825 mg, 4 mmol) and 4-dimethylaminopyridine (75 mg, 0.6 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was purified by column chromatography (CH_2Cl_2:EtOAc = 4:10) to give **9** (710 mg, 73%) as an orange microcrystalline product: mp 194.5-195.2 °C; ESR ($CHCl_3$) 1:1:1, 3 lines, g = 2.0053, a_N = 15.8 G; MS(FAB) $[M+2H]^+$ 481.0 calcd for $C_{16}H_{23}BrIN_2O_2$ 481.0; Anal. calcd for $C_{16}H_{21}BrIN_2O_2$: C, 40.02; H, 4.41; N, 5.83; found: C, 39.92; H, 4.21; N, 5.74.

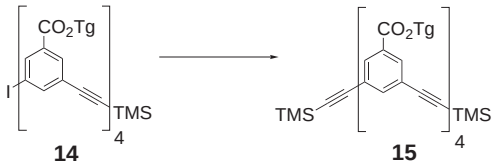


TMS-A_3-H (12): To a sealed tube fitted with a magnetic stirrer was added **I-A_2-TMS** (**10**) (900 mg, 1.15 mmol), 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-ethynylbenzoate (**11**) (330 mg, 1.13 mmol), $Pd_2(dba)_3$ (22 mg, 23 μmol), CuI (4.4 mg, 23 μmol), PPh_3 (30 mg, 115 μmol), and dry triethylamine (5 mL). The degassed mixture was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (hexane:EtOAc = 1:1 ~ 0:1) to give **TMS-A_3-H (12)** (960 mg, 90%) as a yellow oil: ^{1}H NMR δ 8.23 (t, J = 1.7 Hz, 1 H), 8.19 (t, J = 1.6 Hz, 1 H), 8.16 (t, J = 1.6 Hz, 1 H), 8.14 (t, J = 1.6 Hz, 1 H), 8.11 (t, J = 1.6 Hz, 1 H), 8.07 (t, J = 1.5 Hz, 1 H), 8.05 (t, J = 1.5 Hz, 1 H), 7.87 (t, J = 1.6 Hz, 1 H), 7.82 (t, J = 1.6 Hz, 1 H), 7.74 (t, J = 1.5 Hz, 1 H), 7.72 (t, J = 1.4 Hz, 1 H), 7.46 (t, J = 7.8 Hz, 1H), 4.53-4.49 (m, 6 H), 3.88-3.84 (m, 6 H), 3.75-3.64 (m, 18 H), 3.55-3.52 (m, 6 H), 3.36 (s, 3 H), 3.36 (s, 3 H), 3.35 (s, 3 H) 0.27 (s, 9 H); MS(FAB) m/z $[M+H]^+$ calcd for $C_{51}H_{65}O_{15}Si$ 945.4; found, 945.3.



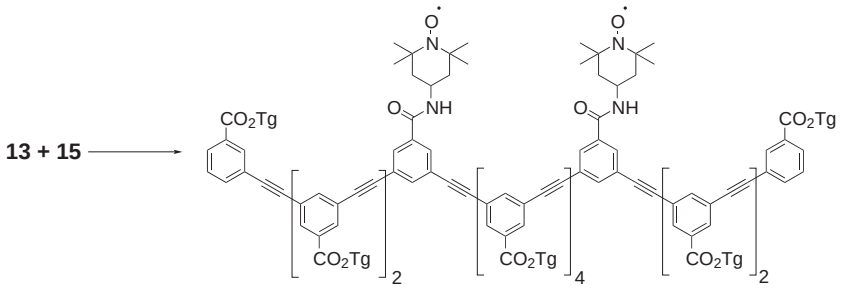
Br-S-A_3-H (13): To a solution of **TMS-A_3-H** (**12**) (200 mg, 0.22 mmol) in THF (20 mL) was added AcOH (12.6 μL) and a solution of tetrabutylammonium fluoride in wet THF (0.28 mL, 1.0 M). After the solution was stirred for 30 s, the solvent was evaporated and the residue was purified by silica gel column chromatography (hexane:acetone = 1:1) to give **HCC-A_3-H** (184 mg, 100%). To a sealed tube fitted with a magnetic stirrer was added **HCC-A_3-H** (70 mg, 80 μmol), 3-Bromo-5-iodo-*N*-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)benzamide (**9**) (38 mg, 80 μmol), $Pd_2(dba)_3$ (1.5 mg, 1.6 μmol), CuI (0.3 mg, 1.6 μmol), PPh_3 (2.1 mg, 8 μmol), dry triethylamine

(0.5 mL), and dry acetonitrile (0.5 mL). The degassed mixture was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (hexane:EtOAc:acetone = 1:1:0 ~ 1:0:1) to give **Br-S-A$_3$-H (13)** (90 mg, 92%) as a yellow oil: MS(FAB) *m*/*z* [M+2H]$^+$ calcd for $C_{64}H_{78}BrN_2O_{17}$ 1225.4; found, 1225.3.



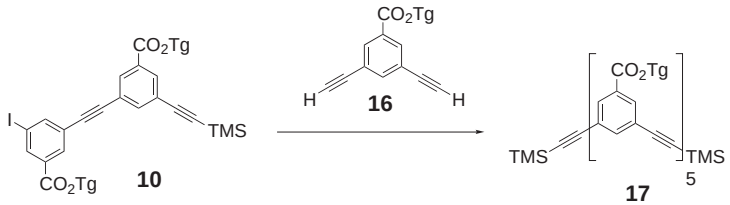
14 **15**

TMS-A$_4$-TMS (15): To a sealed tube fitted with a magnetic stirrer was added **I-A$_4$-TMS** (**14**) (720 mg, 0.53 mmol), $Pd_2(dba)_3$ (18 mg, 20 μmol), CuI (3.8 mg, 20 μmol), PPh_3 (26 mg, 100 μmol), dry triethylamine (3 mL), and dry acetonitrile (3 mL). Trimethylsilylacetylene (0.5 mL, 3.4 mmol) was added to the degassed mixture and the tube was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (hexane:acetone = 2:1) to give **TMS-A$_4$-TMS (15)** (700 mg, 99%) as a yellow oil: ^{1}H NMR δ 8.20 (t, *J* = 1.6 Hz, 2 H), 8.18 (t, *J* = 1.6 Hz, 2 H), 8.15 (t, *J* = 1.6 Hz, 2 H), 8.11 (t, *J* = 1.6 Hz, 2 H), 7.88 (t, *J* = 1.6 Hz, 2 H), 7.82 (t, *J* = 1.6 Hz, 2 H), 4.54-4.49 (m, 8 H), 3.89-3.84 (m, 8 H), 3.74-3.64 (m, 24 H), 3.55-3.53 (m, 8 H), 3.36 (s, 6 H), 3.35 (s, 6 H) 0.27 (s, 18 H); MS(MALDI) *m*/*z* [M+Na]$^+$ calcd for $C_{72}H_{90}O_{20}Si_2Na$ 1353.5; found, 1353.5.

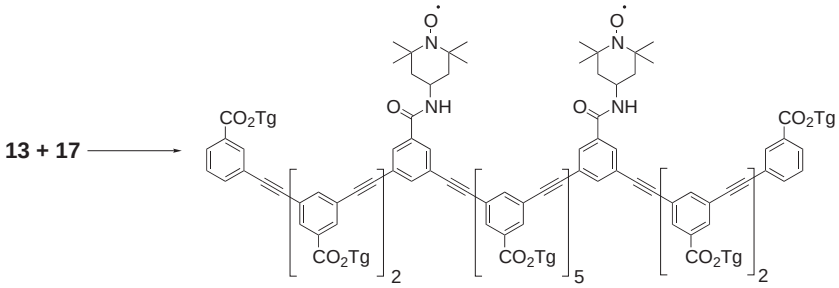


3

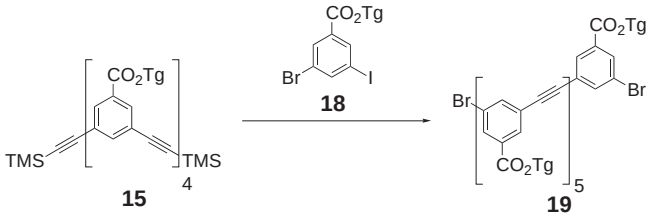
H-A$_3$-S-A$_4$-S-A$_3$-H (3): To a solution of **TMS-A$_4$-TMS** (**15**) (70 mg, 53 μmol) in THF (10 mL) was added AcOH (6.2 μL) and a solution of tetrabutylammonium fluoride in wet THF (0.11 mL, 1.0 M). After the solution was stirred for 30 s, the solvent was evaporated and purified with silica gel column chromatography (hexane:acetone = 2:1) to give **HCC-A$_4$-CCH** (52 mg, 82%). To a sealed tube fitted with a magnetic stirrer was added **HCC-A$_4$-CCH** (20 mg, 17 μmol), **Br-S-A$_3$-H** (**13**) (54 mg, 44 μmol), $Pd(P^tBu_3)_2$ (1.7 mg, 3.2 μmol), CuI (0.6 mg, 3.2 μmol), dry diisopropylamine (1 mL), and dry THF (1 mL). The degassed mixture was sealed and heated at room temperature for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (dichloromethane:acetone = 1:1) to give **H-A$_3$-S-A$_4$-S-A$_3$-H (3)** (42 mg, 73%) as a yellow oil: ESR ($CHCl_3$) 1:1:1, 3 lines, *g* = 2.0057, a_N = 15.9 G; MS(MALDI) *m*/*z* [M+Na]$^+$ calcd for $C_{194}H_{224}N_4O_{54}Na$ 3496.5; found, 3498.5; HPLC ($CHCl_3$:*i*-PrOH = 96:4, retention time 9.1 min) indicated >99% purity.



TMS-A$_5$-TMS (17): To a sealed tube fitted with a magnetic stirrer was added **I-A$_2$-TMS** (**10**) (910 mg, 1.17 mmol), 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3,5-diethynylbenzoate (**16**) (180 mg, 0.59 mmol), $Pd_2(dba)_3$ (22 mg, 23 μmol), CuI (4.4 mg, 23 μmol), PPh_3 (30 mg, 115 μmol), and dry triethylamine (5 mL). The degassed mixture was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (hexane:EtOAc:acetone = 1:1:0 ~ 1:0:1) to give **TMS-A$_5$-TMS (17)** (830 mg, 87%) as a yellow oil: ^{1}H NMR δ 8.21-8.20 (m, 4 H), 8.18 (t, *J* = 1.6 Hz, 2 H), 8.15 (t, *J* = 1.6 Hz, 2 H), 8.11 (t, *J* = 1.6 Hz, 2 H), 7.90 (t, *J* = 1.6 Hz, 1 H), 7.88 (t, *J* = 1.5 Hz, 2 H), 7.82 (t, *J* = 1.6 Hz, 2 H), 4.54-4.49 (m, 10 H), 3.89-3.85 (m, 10 H), 3.74-3.65 (m, 30 H), 3.55-3.53 (m, 10 H), 3.36 (s, 6 H), 3.35 (s, 9 H) 0.27 (s, 18 H); MS(MALDI) *m/z* $[M+Na]^+$ calcd for $C_{88}H_{108}O_{25}Si_2Na$ 1643.7; found, 1644.0.



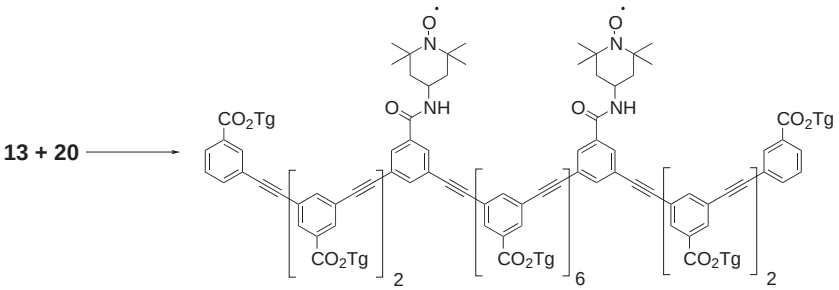
H-A$_3$-S-A$_5$-S-A$_3$-H (4): To a solution of **TMS-A$_5$-TMS** (**17**) (100 mg, 62 μmol) in THF (10 mL) was added AcOH (7.6 μL) and a solution of tetrabutylammonium fluoride in wet THF (0.16 mL, 1.0 M). After the solution was stirred for 30 s, the solvent was evaporated and purified with silica gel column chromatography (hexane:acetone = 1:1) to give **HCC-A$_5$-CCH** (90 mg, 99%). To a sealed tube fitted with a magnetic stirrer was added **HCC-A$_5$-CCH** (20 mg, 14 μmol), **Br-S-A$_3$-H** (**13**) (50 mg, 41 μmol), $Pd(P^tBu_3)_2$ (1.6 mg, 3.1 μmol), CuI (0.6 mg, 3.1 μmol), dry diisopropylamine (1 mL), and dry THF (1 mL). The degassed mixture was sealed and heated at room temperature for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (dichloromethane:acetone = 1:1) to give **H-A$_3$-S-A$_5$-S-A$_3$-H (4)** (36 mg, 71%) as a yellow oil: ESR ($CHCl_3$) 1:1:1, 3 lines, g = 2.0055, a_N = 15.7 G; MS(MALDI) *m/z* $[M+Na]^+$ calcd for $C_{210}H_{242}N_4O_{59}Na$ 3786.6; found, 3787.2; HPLC ($CHCl_3$:*i*-PrOH = 96:4, retention time 10.5 min) indicated >99% purity.



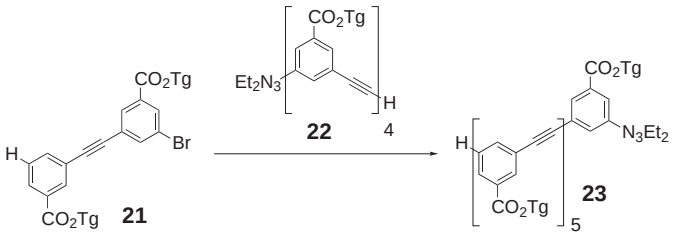
Br-A$_6$-Br (19): To a solution of **TMS-A$_4$-TMS** (**15**) (100 mg, 75 μmol) in THF (15 mL) was added AcOH (9.3 μL) and a solution of tetrabutylammonium fluoride in wet THF (0.17 mL, 1.0 M). After the solution was stirred for 30 s, the solvent was evaporated and purified with silica gel column chromatography (hexane:acetone = 2:1) to give **HCC-A$_4$-CCH** (80 mg, 89%). To a sealed tube fitted with a magnetic stirrer was added **HCC-A$_4$-CCH** (105 mg, 87 μmol), 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 3-bromo-5-iodobenzoate (**17**) (190 mg, 400 μmol),

$Pd_2(dba)_3$ (3.6 mg, 4 μmol), CuI (0.8 mg, 4 μmol), PPh_3 (5.2 mg, 20 μmol), dry triethylamine (3 mL), and dry acetonitrile (3 mL). The degassed mixture was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (hexane:dichloromethane:acetone = 2:0:1 ~ 0:2:1) to give **Br-A_6-Br (19)** (160 mg, 98%) as a yellow oil: ^{1}H NMR δ 8.22-8.21 (m, 6 H), 8.19 (t, *J* = 1.6 Hz, 2 H), 8.17 (t, *J* = 1.7 Hz, 2 H), 8.15 (t, *J* = 1.5 Hz, 2 H), 7.91 (t, *J* = 1.6 Hz, 2 H), 7.89 (t, *J* = 1.6 Hz, 2 H), 7.88 (t, *J* = 1.7 Hz, 2 H), 4.55-4.49 (m, 12 H), 3.89-3.84 (m, 12 H), 3.74-3.65 (m, 36 H), 3.55-3.53 (m, 12 H), 3.36 (s, 6 H), 3.35 (s, 12 H); MS(MALDI) *m*/*z* $[M+Na]^+$ calcd for $C_{94}H_{108}O_{30}Br_2Na$ 1897.5; found, 1897.3.

TMS-A_6-TMS (20): To a sealed tube fitted with a magnetic stirrer was added **Br-A_6-Br** (**19**) (160 mg, 85 μmol), $Pd_2(dba)_3$ (6 mg, 6.6 μmol), CuI (1.3 mg, 6.6 μmol), PPh_3 (9 mg, 33 μmol), dry triethylamine (3 mL), and dry acetonitrile (3 mL). Trimethylsilylacetylene (0.2 mL, 1.1 mmol) was added to the degassed mixture and the tube was sealed and heated at 65 °C for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (dichloromethane:acetone = 2:1) to give **TMS-A_6-TMS (20)** (160 mg, 98%) as a yellow oil: ^{1}H NMR δ 8.21-8.21 (m, 4 H), 8.20 (t, *J* = 1.6 Hz, 2 H), 8.19 (t, *J* = 1.6 Hz, 2 H), 8.15 (t, *J* = 1.6 Hz, 2 H), 8.11 (t, *J* = 1.7 Hz, 2 H), 7.91 (t, *J* = 1.6 Hz, 2 H), 7.88 (t, *J* = 1.6 Hz, 2 H), 7.82 (t, *J* = 1.6 Hz, 2 H), 4.54-4.50 (m, 12 H), 3.89-3.85 (m, 12 H), 3.74-3.64 (m, 36 H), 3.55-3.53 (m, 12 H), 3.36 (s, 6 H), 3.35 (s, 12 H) 0.27 (s, 18 H); MS(MALDI) *m*/*z* $[M+Na]^+$ calcd for $C_{104}H_{126}O_{30}Si_2Na$ 1933.8; found, 1934.5.



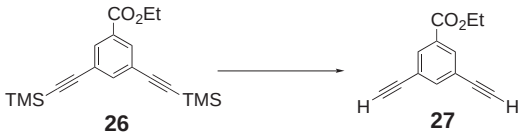
H-A_3-S-A_6-S-A_3-H (5): To a solution of **TMS-A_6-TMS** (**20**) (80 mg, 42 μmol) in THF (10 mL) was added AcOH (5.6 μL) and a solution of tetrabutylammonium fluoride in wet THF (0.10 mL, 1.0 M). After the solution was stirred for 30 s, the solvent was evaporated and purified with silica gel column chromatography (dichloromethane:acetone = 2:1) to give **HCC-A_6-CCH** (68 mg, 92%). To a sealed tube fitted with a magnetic stirrer was added **HCC-A_6-CCH** (20 mg, 11 μmol), **Br-S-A_3-H** (**13**) (37 mg, 30 μmol), $Pd(P^tBu_3)_2$ (1.2 mg, 2.2 μmol), CuI (0.4 mg, 2.2 μmol), dry diisopropylamine (1 mL), and dry THF (1 mL). The degassed mixture was sealed and heated at room temperature for 12 h. The solvent was removed in vacuo to leave a brown residue. The residue was purified by silica gel column chromatography (dichloromethane:acetone = 2:1) to give **H-A_3-S-A_6-S-A_3-H (5)** (20 mg, 44%) as a yellow oil: ESR ($CHCl_3$) 1:1:1, 3 lines, g = 2.0053, a_N = 15.9 G; MS(MALDI) *m*/*z* $[M+Na]^+$ calcd for $C_{226}H_{260}N_4O_{64}Na$ 4076.7; found, 4079.8; HPLC ($CHCl_3$:*i*-PrOH = 96:4, retention time 13.2 min) indicated >97% purity.



H-A$_6$-N$_3$Et$_2$ (23): To a sealed tube fitted with a magnetic stirrer was added $Pd_2(dba)_3$ (13.8 mg, 0.015 mmol), CuI (3.4 mg, 0.017 mmol), Ph_3P (10.3 mg, 0.039 mmol), **H-A$_2$-Br (21)** (233 mg, 0.337 mmol), and **HCC-A$_4$-N$_3$Et$_2$ (22)** (352 mg, 0.279 mmol). The tube was evacuated and back-filled with nitrogen three times and then dry acetonitrile (4.5 mL) and dry triethylamine (0.5 mL) were added. The solution was then degassed again and allowed to react at 70 ˚C for 18 h. The mixture was concentrated and purified by silica gel column chromatography (CH_2Cl_2:acetone = 2:1) to give 0.355 g (0.195 mmol, 70%) of **H-A$_6$-N$_3$Et$_2$ (23)** as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (t, *J* = 1.3 Hz, 1 H), 8.21-8.17 (m, 7 H), 8.16 (t, *J* = 1.6 Hz, 1 H), 8.05 (t, *J* = 1.8 Hz, 1 H), 8.03 (dt, *J* = 8.0, 1.5 Hz, 1 H), 7.95 (t, *J* = 1.7 Hz, 1 H), 7.89-7.88 (m, 4H), 7.76 (t, *J* = 1.7 Hz, 1 H), 7.71 (dt, *J* = 8.3, 1.4 Hz, 1 H), 7.45 (t, *J* = 8.1 Hz, 1 H), 4.52-4.48 (m, 12 H), 3.87-3.82 (m, 12 H), 3.78 (q, *J* = 3.4 Hz, 4 H), 3.73-3.70 (m, 12 H), 3.68-3.66 (m, 12 H), 3.66-3.62 (m, 12 H), 3.52-3.50 (m, 12 H), 3.34-3.33 (m, 18 H), 1.34-1.20 (bs, 6 H); MS (MALDI) *m/z* [M + Na]$^+$ calcd for $C_{98}H_{119}N_3O_{30}Na$ 1842.0; found, 1843.5; TLC R_f = 0.30 (CH_2Cl_2:acetone = 2:1).

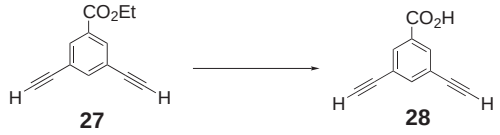
H-A$_6$-I (24): To a sealed tube fitted with a magnetic stirrer was added **H-A$_6$-N$_3$Et$_2$ (23)** (329.2 mg, 0.181 mmol) and iodomethane (6 mL). The mixture was evacuated and back-filled three times, sealed under nitrogen, and stirred at 110 ˚C for 18 h. The resulting solution was concentrated to a dark oil in vacuo. The crude product was concentrated and purified by silica gel column chromatography (CH_2Cl_2:acetone = 4:1, 3:1, 5:2) to give 241.8 mg (0.131 mmol, 72%) of **H-A$_6$-I (24)** as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (t, *J* = 1.6 Hz, 1 H), 8.21 (t, *J* = 1.8 Hz, 1 H), 8.19-8.16 (m, 9 H), 8.05 (t, *J* = 1.6 Hz, 1 H), 8.03 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.89-7.88 (m, 3 H), 7.87 (t, *J* = 1.6 Hz, 1 H), 7.72 (dt, *J* = 7.9, 1.4 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 1 H), 4.52-4.48 (m, 12 H), 3.87-3.83 (m, 12 H), 3.72-3.63 (m, 36 H), 3.53-3.51 (m, 12 H), 3.34-3.33 (m, 18 H); MS (MALDI) *m/z* [M + Na]$^+$ calcd for $C_{94}H_{109}O_{30}INa$ 1868.8; found, 1868.6; TLC R_f = 0.17 (CH_2Cl_2:acetone = 3:1).

Ethyl 3,5-bis-(trimethylsilylethynyl)benzoate (26): To a sealed tube fitted with a magnetic stirrer was added $Pd_2(dba)_3$ (181 mg, 0.198 mmol), CuI (38 mg, 0.20 mmol), Ph_3P (258 mg, 0.986 mmol), ethyl 3,5-dibromobenzoate (**25**) (3.04 g, 9.88 mmol), and dry triethylamine (50 mL). This solution was degassed and charged with trimethylsilylethynylene (14 mL, 0.21 mol) sealed and allowed to react at 65 ˚C for 12 hours. The mixture was concentrated and purified by silica gel column chromatography (hexanes:ether = 1:0, 99:1) to give 2.73 g (7.96 mmol, 81%) of **26** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.4 Hz, 2 H), 7.70 (t, *J* = 1.6 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 1.37 (t, *J* = 7.1 Hz, 3 H), 0.23 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 139.0, 132.6, 130.8, 123.8, 103.0, 96.0, 61.4, 14.2. -0.26; TLC R_f = 0.57 (hexanes:ether = 19:1); HRMS (FAB) *m/z* [M+H]$^+$ calcd for $C_{19}H_{27}O_2Si_2$ 343.1550; found, 343.1551.



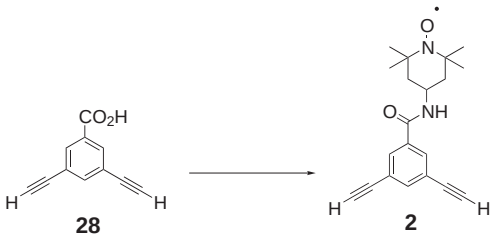
26 **27**

Ethyl 3,5-diethynylbenzoate (27): To a solution of **26** (2.00g, 5.85 mmol) in THF (200 mL) was added acetic acid (0.67 ml, 0.64 g, 11 mmol) and a solution of tetrabutylammonium flouride in THF (12 mL, 1.0 M). Solution was allowed to react for a minute then was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexanes:ether = 49:1, 97:3) to give 0.872 g (4.40 mmol, 76%) of **27** as a light yellow solid: m.p. 92-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.4 Hz, 2 H), 7.74 (t, *J* = 1.5 Hz, 1 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 3.12 (s, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 139.2, 133.2, 131.1, 122.9, 78.5, 78.8, 61.5, 14.2; MS (EI, 70 eV) *m*/*z* M^+ 198.1; TLC R_f = 0.18 (hexanes:ether = 97:3); Anal. calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09; N, 0.00; found: C, 78.79; H, 5.26; N, 0.27.



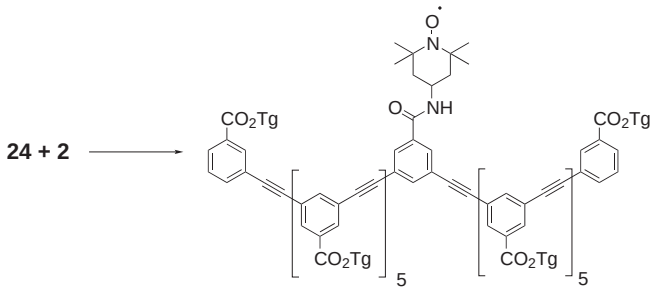
27 **28**

3,5-diethynylbenzoic acid (28): A 250 mL round bottom flash was charged with **27** (0.42 g, 2.2 mmol), methanol (80 mL), and 1N sodium hydroxide aqueous solution (4 mL) and allowed to stir at room temperature for 12 h. The resulting solution was acidified with citric acid (0.5 M), extracted with ether, washed with water, dried with sodium sulfate and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexanes:ethyl acetate = 1:1) to give 0.178 g (1.05 mmol, 50%) of **28** as a light pale yellow solid: m.p. 173 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.3 Hz, 2H), 7.79 (t, *J* = 1.5 Hz, 1 H), 3.15 (s, 2 H); ^{13}C NMR (125 MHz, CD_3OD) δ 167.8, 139.8, 134.0, 133.1, 124.7, 82.4, 80.6; TLC R_f = 0.35 (hexanes:ethyl acetate = 1:9); HRMS (EI) *m*/*z* M^+ calcd for $C_{11}H_6O_2$ 170.0368; found, 170.0360.



28 **2**

3,5-diethynyl-*N*-(1-oxy-2,2,6,6-tetramethyl-piperidin-4-yl)-benzamide (2): A 25 mL round bottom flask was charged with carboxylic acid **28** (0.103 g, 0.605 mmol), 4-amino-TEMPO (0.110 g, 0.643 mmol), and CH_2Cl_2 (5 mL). The solution was then cooled to 0 °C in an ice bath, then 1,4-dicylohexylcarbodiimide (0.291 g, 1.41 mmol) and 4-(dimethylamino)pyridine (26 mg, 0.21 mmol) were added. The solution was allowed to warm to room temperature under nitrogen and the reaction was allowed to proceed for 18 h. The resulting solution was concentrated in vacuo and purified by two successive silica gel column chromatography (1st: hexanes:ethyl acetate = 3:1; 2nd:hexanes:ethyl acetate = 2:1) to give 64.1 mg (0.198 mmol, 33%) of **2** as a orange solid: m.p. 196-199 °C; ESR ($CHCl_3$): 1:1:1, 3 lines, *g* = 2.0062, a_N = 15.9 G.; MS (FAB) *m*/*z* $[M+2H]^+$ calcd for $C_{20}H_{25}N_2O_2$ 325.2; found, 325.2; TLC R_f = 0.19 (hexanes:ethyl acetate = 3:1); Anal. calcd for $C_{20}H_{23}N_2O_2$: C, 74.28; H, 7.17; N, 8.66; found: C, 74.39; H, 7.36; N, 8.43.



6

H-A$_6$-S-A$_6$-H (6). To a sealed tube fitted with a magnetic stirrer was added **H-A$_6$-I (24)** (48.7 mg, 0.0264 mmol), and **2** (4.28 mg, 0.0132 mmol), and CuI (0.85 mg, 0.0047 mmol). The tube transferred to a dry box where bis (tri-t-butylphosphine) palladium (2.4 mg, 0.0047 mmol), dry THF (1.5 mL), and dry diisopropyl amine (0.5 mL) were added under an argon atmosphere. The solution was allowed to react at room temperature for 18 h. The crude product was precipitated from solution and washed with excessive amounts of hexane to remove catalyst and purified by preparatory HPLC silica gel column chromatography (chloroform:isopropyl alcohol = 4:1) to give 4.2 mg (1.1 μmol, 8%) of **H-A$_6$-S-A$_6$-H (6)** as a light yellow-orange waxy oil: ESR ($CHCl_3$): 1:1:1, 3 lines, g = 2.0055, a_N = 15.9 G.; MS (MALDI) m/z $[M+Na]^+$ calcd for $C_{208}H_{239}N_2O_{62}Na$ 3782.1; found, 3780.3; TLC R_f = 0.06 (CH_2Cl_2:acetone = 2:1); HPLC ($CHCl_3$:*i*-PrOH = 96:4, retention time 8.6 min) indicated >99% purity.

References

(1) *SAINTPLUS Software Package*; Bruker AXS; Madison, WI, 2001, Version 6.

(2) *SHELXTL Software Package*; Bruker AXS; Madison, WI, 2000, Version 6.

(3) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114-3121.

(4) Zhao, D.; Moore, J. S. *J. Org. Chrem.* **2002**, *67*, 3548-3554.

(5) Smith, J. C. Probing the high polymer limit of phenylene ethynylene foldamers M.S. Thesis, University of Illinois at Urbana-Champaign, 2001.

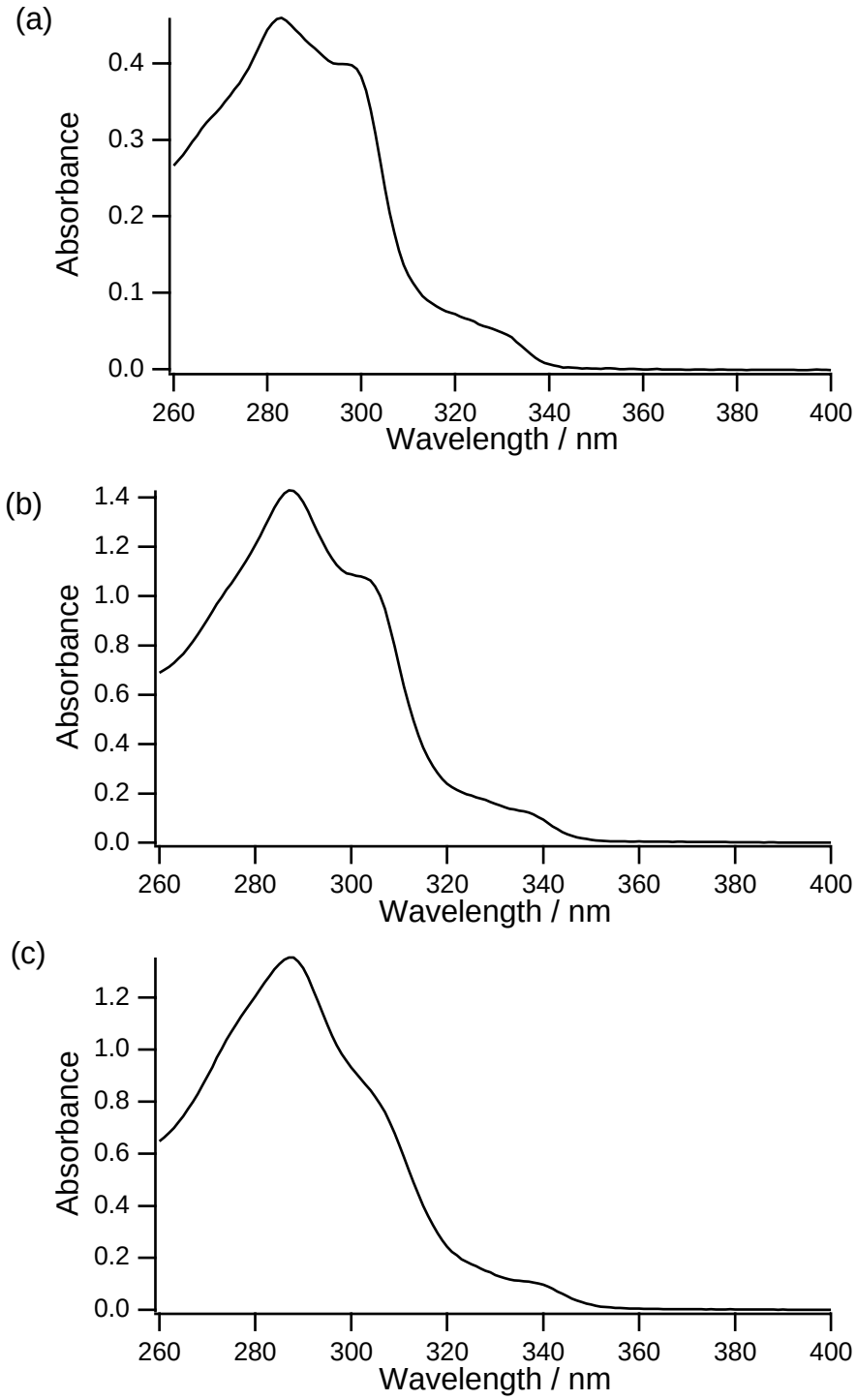


Figure S1. UV-vis spectra of **3** measured in (a) $CHCl_3$, (b) ethyl acetate, (c) acetonitrile.

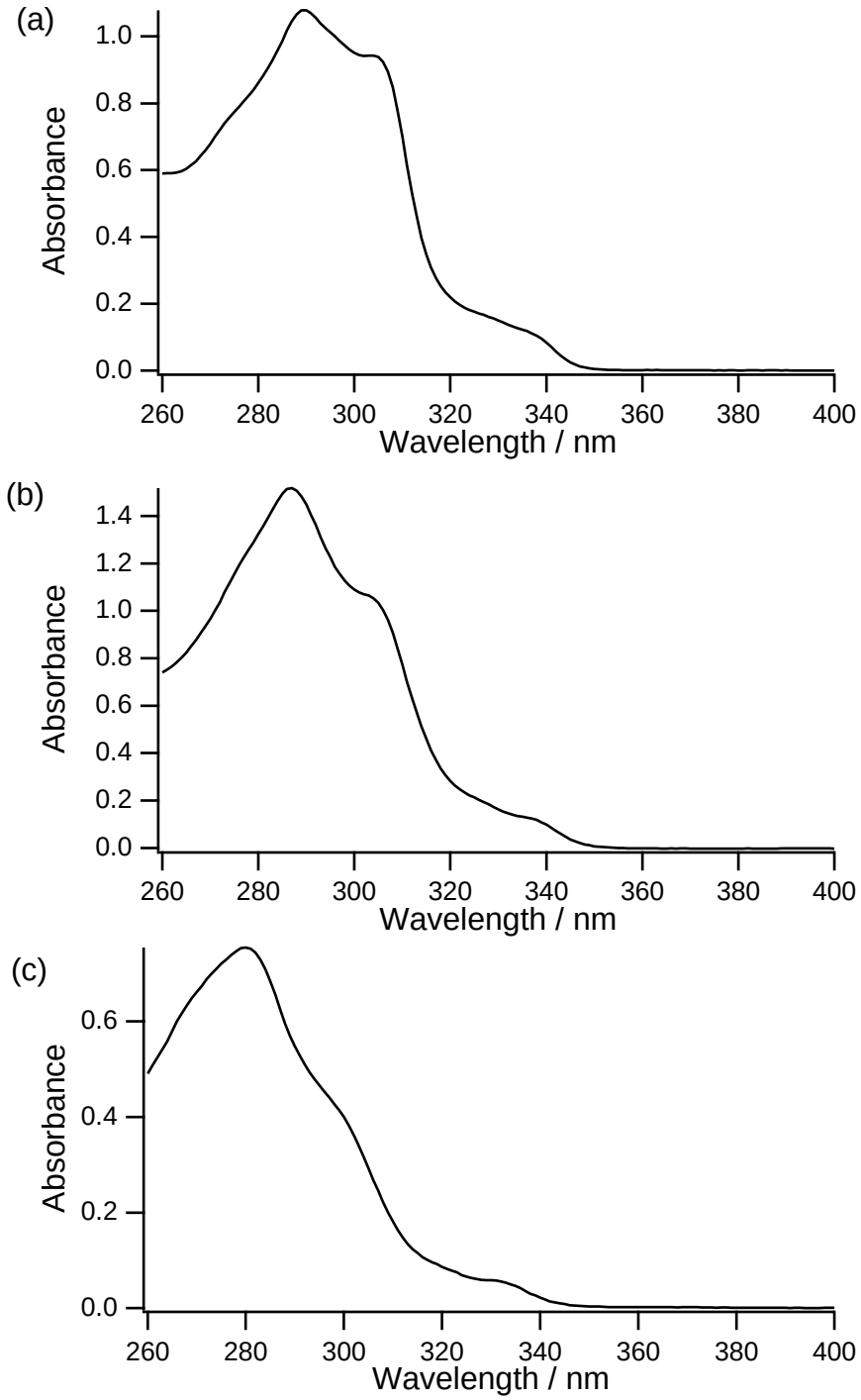


Figure S2. UV-vis spectra of **4** measured in (a) $CHCl_3$, (b) ethyl acetate, (c) acetonitrile.

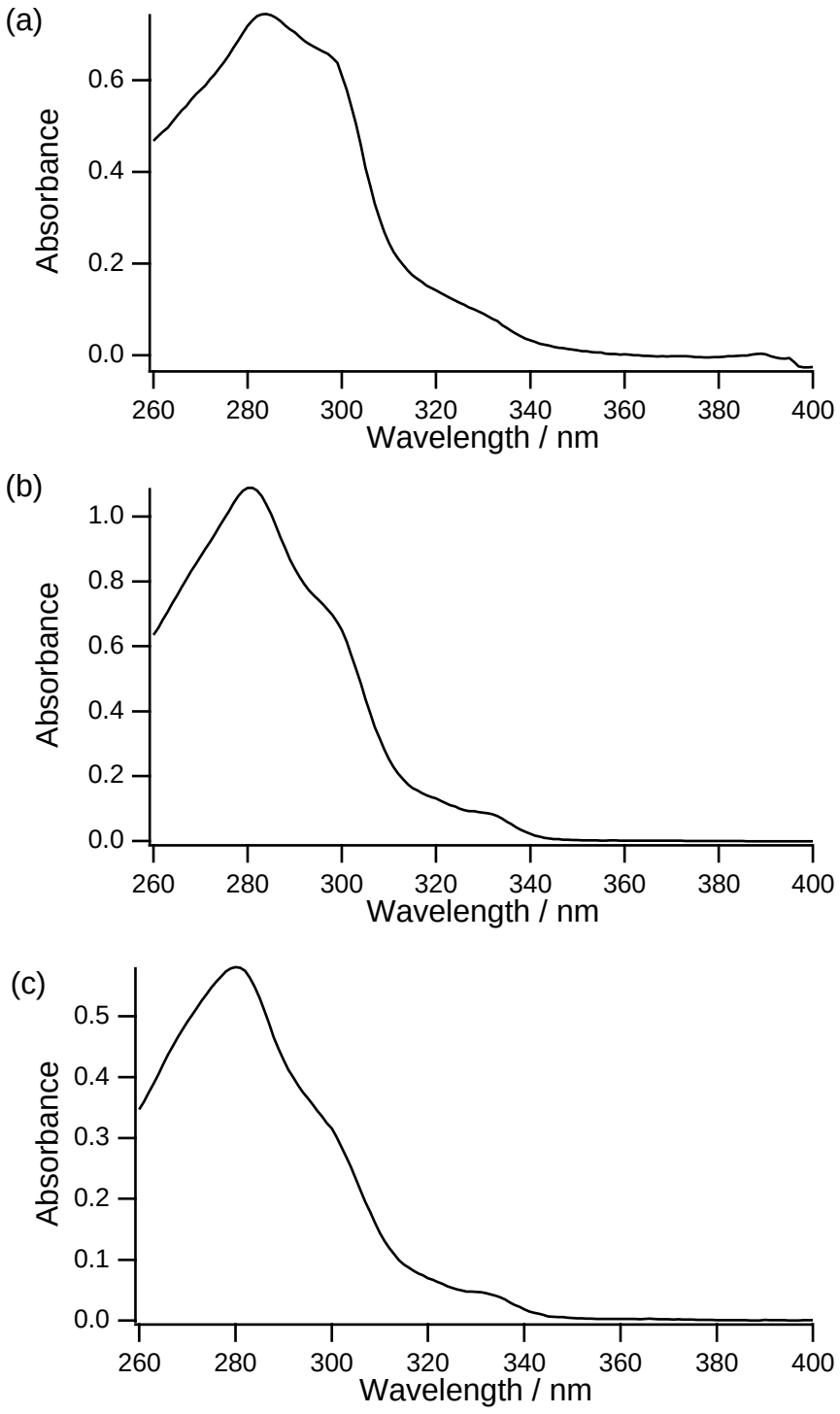


Figure S3. UV-vis spectra of **5** measured in (a) $CHCl_3$, (b) ethyl acetate, (c) acetonitrile.

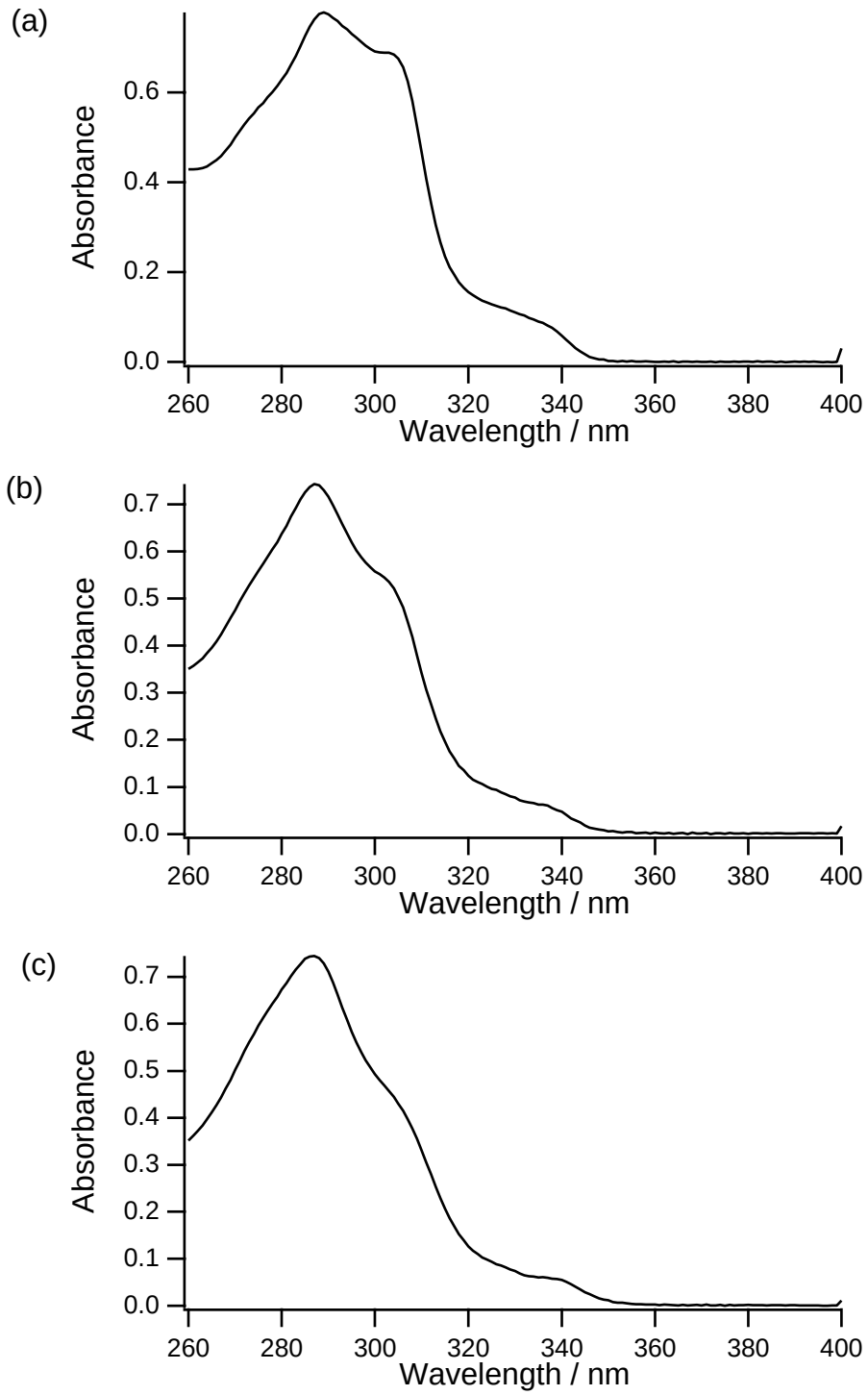


Figure S4. UV-vis spectra of **6** measured in (a) $CHCl_3$, (b) ethyl acetate, (c) acetonitrile.

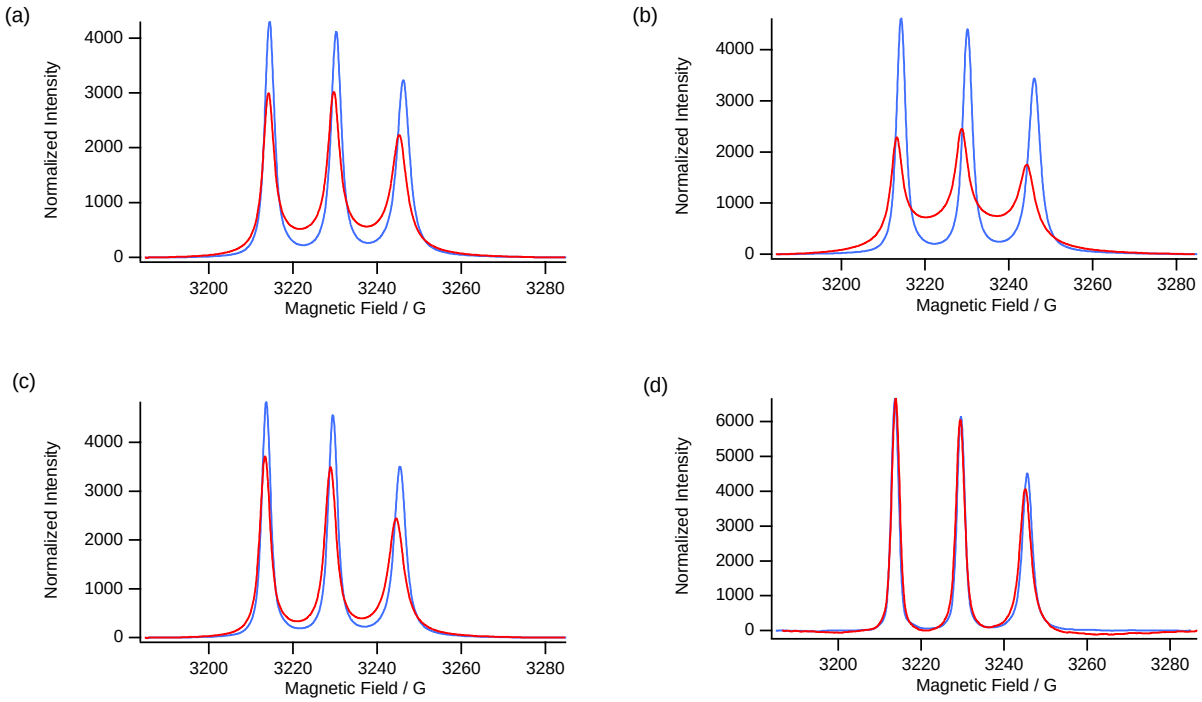
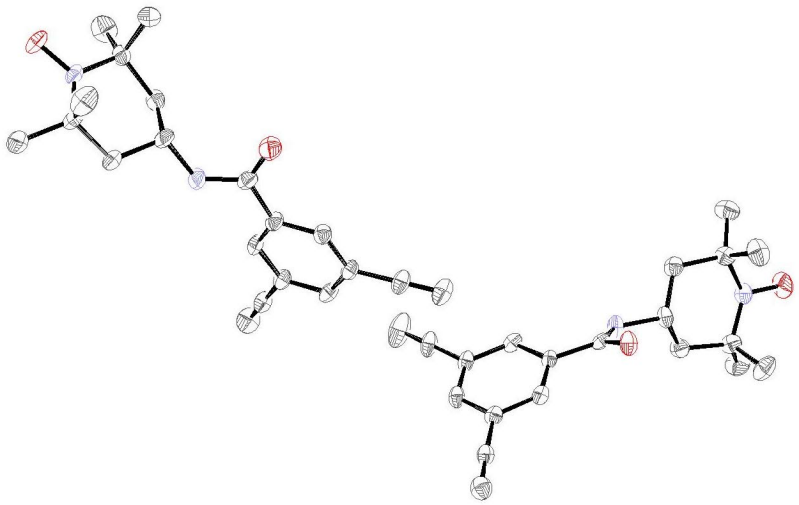


Figure S5. Integrated ESR spectra of (a) **3**, (b) **4**, (c) **5**, and (d) **6** in chloroform (blue) and ethyl acetate (red). The spectra were measured in 0.3 mM solution at 9.07 GHz. Intensity was normalized at double integrated value.

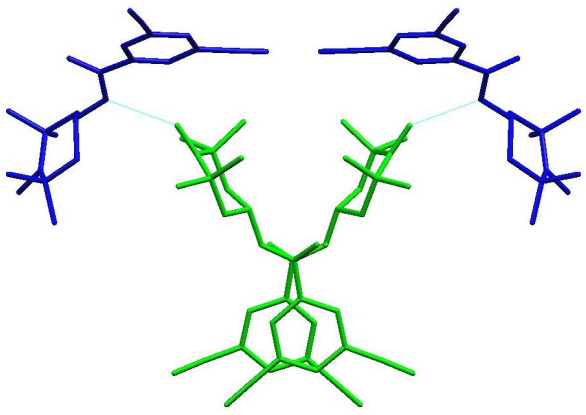
Table S1. Crystallographic Data of **6**.

formula	$C_{20}H_{23}N_2O_2$
formula weight	323.42
crystal color	orange
crystal system	orthorhombic
space group	*Pbcn*
α/Å	30.635(4)
β/Å	7.7786(10)
γ/Å	30.476
V/Å^3	7262.4(16)
Z	16
data/restraints/parameters	6677/0/439
R_1	0.0736
wR_2 (I>2σ)	0.1917

(a)



(b)



(c)

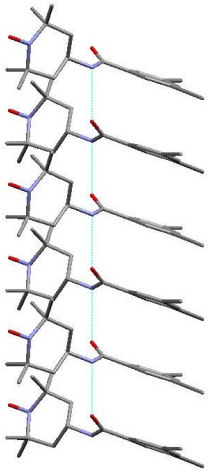


Figure S6. X-ray crystal structure of **6**. (a) ORTEP drawring of the asymmetric unit. Hydrogen atoms are omitted for clarity. (b, c) Projection of π stacking.