Electronic Supplementary Information

Symmetrically Backfolded Molecules Emulating the Self-Similar Features of the Sierpinski Triangle

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EXPERIMENTAL

General Procedures. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich and Acros) and used without further purification. LC60A 40-63 micron DAVISIL silica gel (Grace GmbH & Co.) was used for flash column chromatography. ^{1}H NMR spectra were measured using a Varian YH300 300 MHz superconducting-magnet high-field NMR spectrometer using tetramethylsilane as the internal reference. Chemical shifts (δ) are expressed in ppm relative to the residual ^{1}H (7.26 ppm) and the ^{13}C signal of chloroform (77.0 ppm). Coupling constants are expressed in hertz. Elemental analysis was performed using a Vario EL III CHNOS elemental analyzer. Infrared spectra were recorded in the range 400–4000 cm^{-1} on a Perkin–Elmer Model FTIR-1600 spectrometer, UV-vis spectra on a PerkinElmer 750 UV/vis spectrometer. Electrochemical measurements were performed on a CH Instruments Electrochemical Workstation CHI 660C. Mass spectra were measured using a PE SCIEX API 365 LC/MS/MS system. High resolution mass spectrometric measurements were carried out using a Bruker Autoflex matrix-assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). Luminescent spectra were measured using a Horiba Jobin Yvon FL-1057 spectrofluorometer. The X-ray dataset of the single crystal sample was collected on a Bruker AXS SMARTAPEX CCD system using Mo Kα (λ = 0.71073 Å) radiation at 100(2) K. Data collection was set up using the Apex2 suite of programs[A], the data were integrated using SAINT[B] and corrected for absorption and other systematic errors using SADABS[C]. The structures were solved using SHELXS-97 (Sheldrick, 2008)[D] and refined by full-matrix least-squares on F_o^2 using SHELXL-2017/1 (Sheldrick, 2017)[E] and SHELXLE Rev853 (Hübschle *et al.*, 2011)[F]. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for aromatic C-H, and 0.99 and 0.98 Å for aliphatic CH_2 and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C) with 1.5

for CH_3 and 1.2 for C-H, CH_2 units, respectively. Selected crystallographic results are summarized in Table S1, and full details of the crystallographic study in cif format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1570192 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

A) Apex2 v2.1-4 (Bruker, 2007) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

B) SAINT V7.34A (Bruker, 2014) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

C) Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48 3-10.

D) Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

E) Sheldrick G. M. (2015). Acta Cryst., C71, 3-8.

F) Hübschle, C. B., Sheldrick, G. M. and Dittrich, B. (2011). J. Appl. Cryst., 44, 1281--1284.

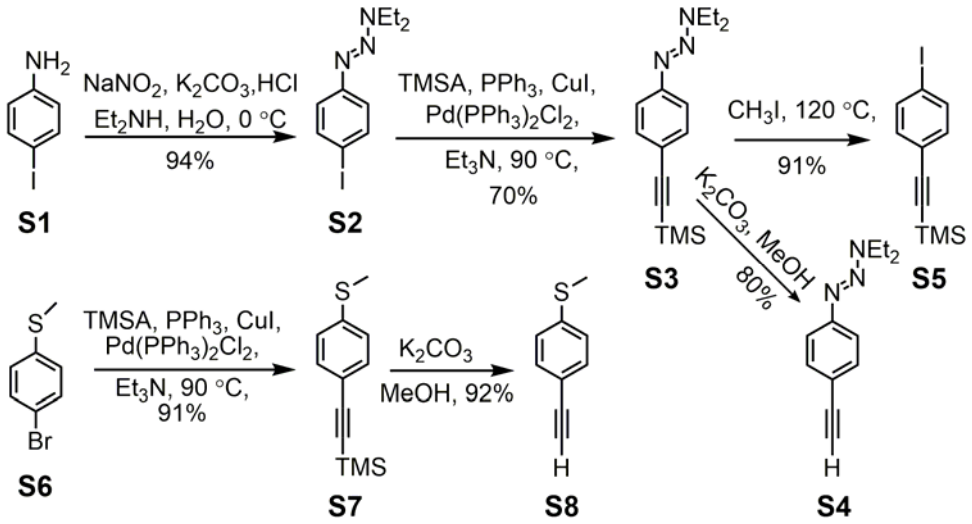


Fig. S1. Synthetic steps for molecules **S8**, **S4**, and **S5**. TMSA: trimethylsilyl acetylene.

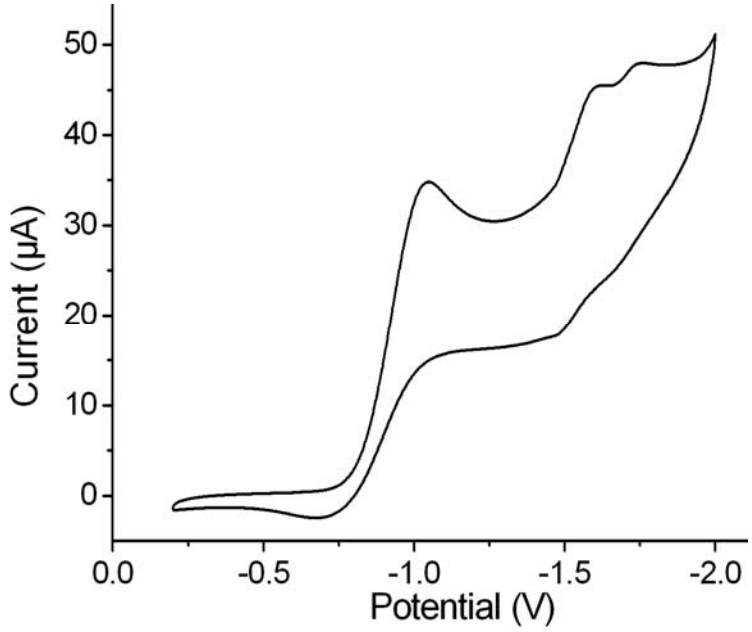


Fig. S2. A cyclic voltammogram of 1×10^{-4} M **G3** in CH_2Cl_2 (0.1M *n*-Bu_4NPF_6) at a scan rate of 100mVs^{-1}. Working electrode: glass carbon, counter electrode: Pt, reference electrode: Ag/Ag^+ (0.01 M $AgNO_3$). The reduction onset potential is -0.82 eV, followed by a steep and large increase of current beyond -1.50 eV (e.g., all the way down to -2.0 eV) corresponding to further reduction with an irreversible character. The lowest unoccupied molecular orbital (LUMO) can be roughly estimated to be -3.76 eV according to the equation $E_{LUMO}=-[eE_{red,onset}-E_{1/2}(Fc/Fc^+)+4.8]$ eV. (Half wave potential of ferrocene/ferrocenium (Fc/Fc+) redox couple was estimated to be 0.22V. The energy level of Fc/Fc^+ was assumed at –4.8 eV to vacuum).

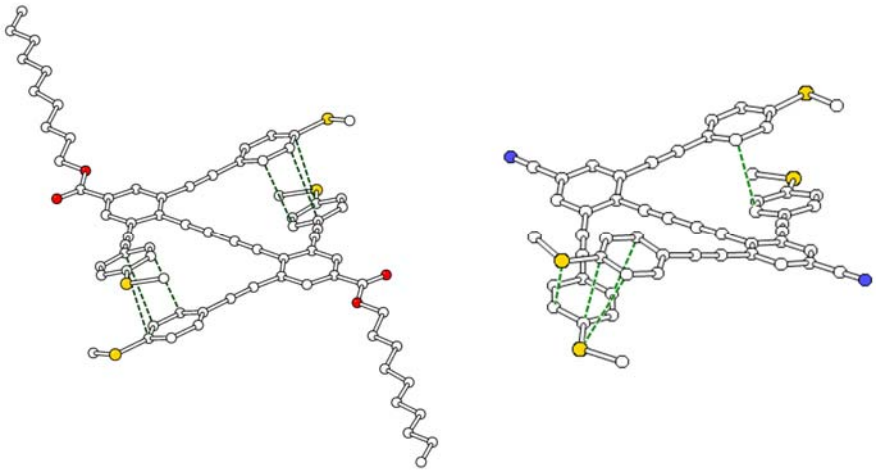


Fig. S3 The butterfly conformation in the crystal structure of **G2** (left) and the dihedral conformation (right) observed of a similar back-folded molecule in an earlier crystal structure (CCDC 646837). The dashed bonds indicate close contacts (e.g., C···C distances below 3.5 Å). Color code: S, orange; O, red; C, grey; N, blue.

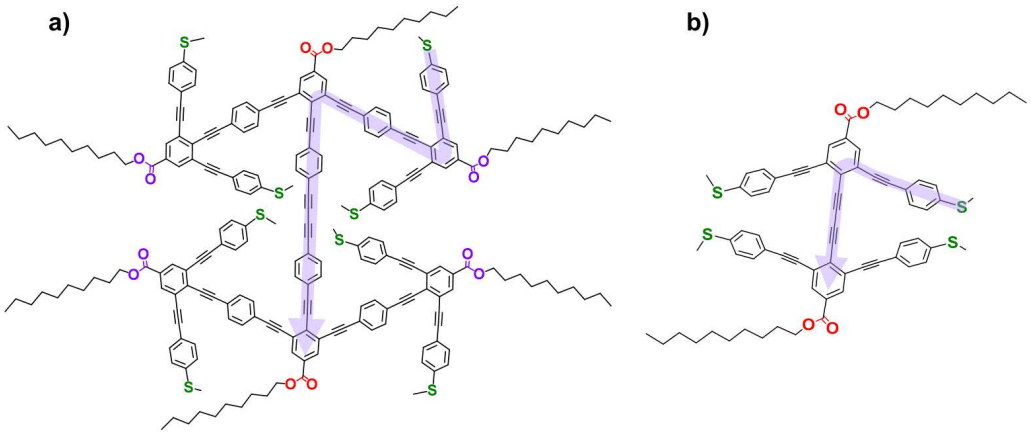
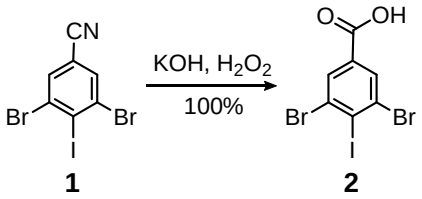


Fig. S4. A scheme of π-electron delocalization facilitated by the push-pull pathway between the sulfur and the carboxyl group of a) **G3;** and b) **G2**.

Synthesis and Characterizations.

Synthesis of 3,5-dibromo-4-iodo-benzenecarboxylic acid (2).



1 **2**

A specific synthesis for 3,5-dibromo-4-iodobenzoic acid (**2**) was not found in the literature. The current procedure is adapted from a published synthesis recipe of 2-amino-4-chloro-5-methylbenzoic acid (*J. Med. Chem.,* **2002**, *45*, 3692). A mixture of 3,5-dibromo-4-iodobenzonitrile, **1** (5.80 g, 15 mmol), an aqueous solution of KOH (30%, w/w; 35 mL), together with a stirring bar were loaded in a round-bottom flask equipped with a condenser. The flask was placed in an oil bath preheated to 130 °C, and the reaction mixture was stirred for 2 hours (a clear solution was obtained after the first hour). The clear solution was then allowed to cool to room temperature, diluted with H_2O (100 mL), acidified with 3 M HCl (about 75 mL) to reach a pH below 5.5, and left to stand at room temperature for several hours. The resultant white precipitate was collected by suction filtration, washed copiously with water and dried under vacuum to give the product as a white solid (5.48 g, 90% based on **1**). The product thus prepared was found to be sufficiently pure (by NMR) and was used for the subsequent reaction without further purification. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ116.4, 131.6, 131.9, 135.7, 165.6. IR (neat): 3072(w), 1693(s, υ_{COOH}), 1531(m), 1437(m), 1363(s), 1271(s), 900(w), 767(m), 740(m) cm^{-1}. ESI-MS *m/z* (%): calcd, 405.75 for (M^+) (100%); found, 405.3 (100%) (M^+). Anal. Calcd. for $C_7H_3Br_2IO_2$: C, 20.72; H, 0.75. Found: C, 21.26; H, 0.90.

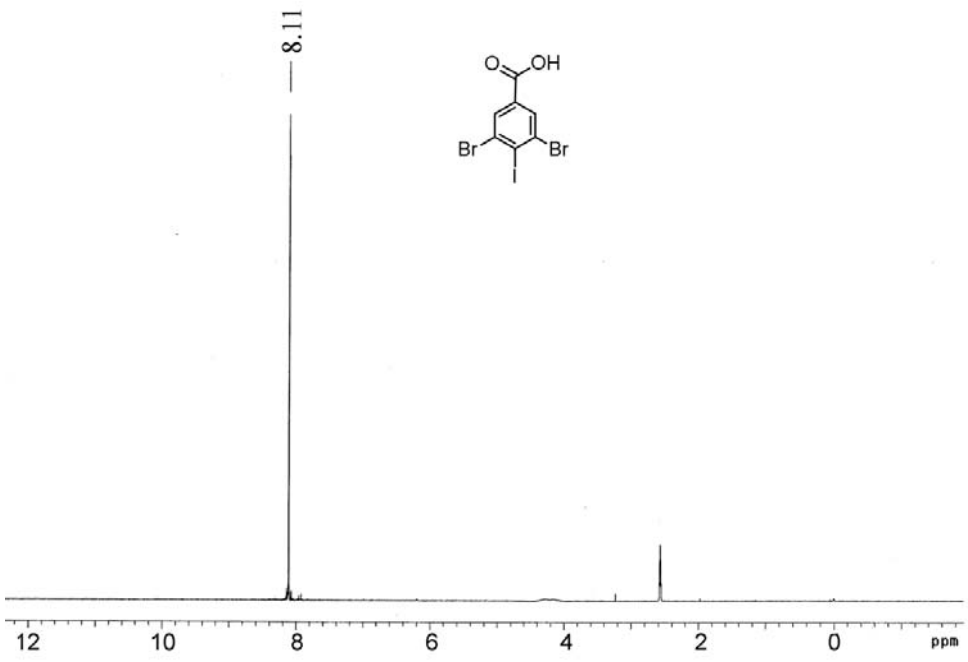


Fig. S5. The ^{1}H NMR spectrum of 3,5-dibromo-4-iodobenzoic acid (**2**) (300 MHz, DMSO-d_6): δ = 8.11 (s, 1H).

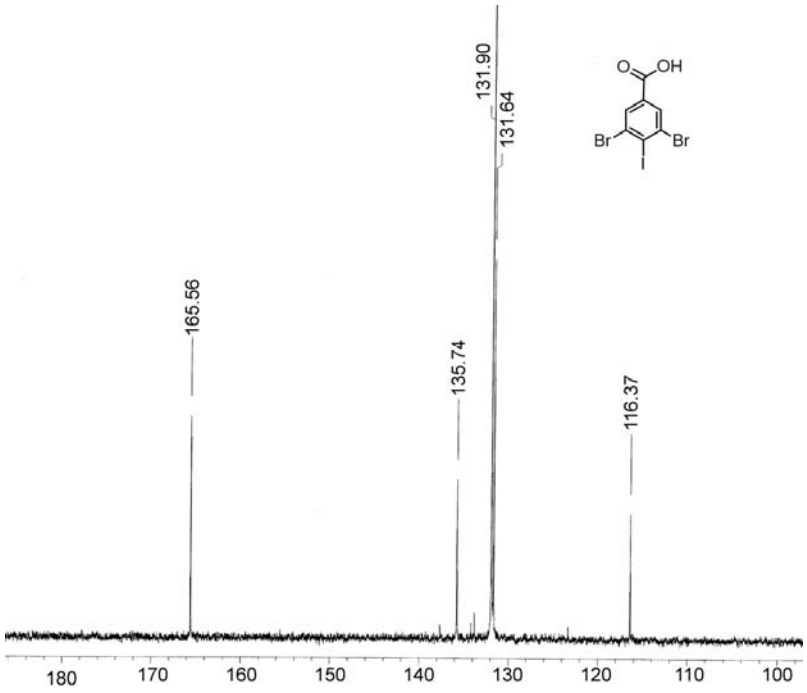


Fig. S6. ^{13}C NMR spectrum of 3,5-dibromo-4-iodobenzoic acid (**2**) (75 MHz, $CDCl_3$): δ = 116.4, 131.6, 131.9, 135.7, 165.6.

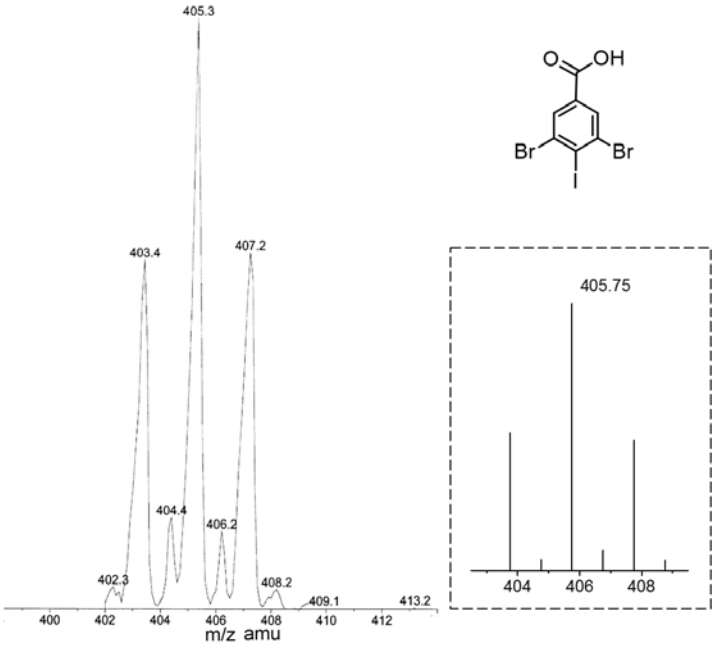
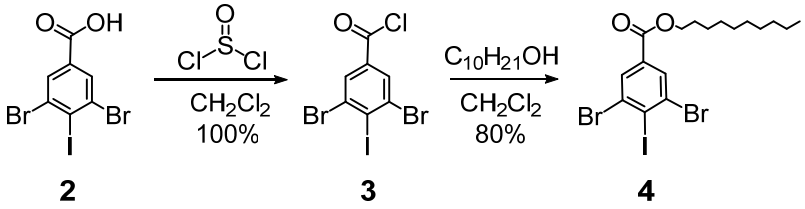


Fig. S7. The observed (left) and simulated peak (right) profiles for the molecular ion (M^+) of 3,5-dibromo-4-iodobenzoic acid (**2**); *m/z* (%): calcd, 405.75 for (M^+) (100%); found, 405.3 (100%). The mass spectrum was measured using electrospray ionization.

Synthesis of decyl 3,5-dibromo-4-iodobenzoate (4).



The ester **4** was synthesized in a two-step procedure, with the first step targeting 3,5-dibromo-4-iodobenzoyl chloride, **3**. Compound **2** (4.06 g, 10 mmol), thionyl chloride (20 mL), one drop of DMF (as catalyst) and a magnetic stirrer were loaded into a two-neck round-bottom flask equipped with a condenser. The reaction mixture was then stirred and heated at 80 °C by an oil bath for 2 h. After the excess thionyl chloride was removed on a rotary evaporator, crude 3,5-dibromo-4-iodobenzoyl chloride (**3**) was obtained (4.26 g, 100% based on **2**), which was used for the ensuing esterification without further purification. Under N_2 protection (e.g., via a Schlenk line), acyl chloride **3** (3.25 g, 8.0 mmol) and anhydrous CH_2Cl_2 (10 mL) were mixed

to give a solution in a two-neck round-bottom flask equipped with a magnetic stirrer. The flask was then cooled with an ice-bath, and a solution of decyl alcohol (1.27 g, 8.0 mmol) and pyridine (0.10 mL) in 5.0 mL of anhydrous CH_2Cl_2 was added dropwise under N_2 protection (over a period of 15 min). After the reaction mixture was stirred at rt overnight, the solvents were then removed on a rotary evaporator and the residue was purified via silica gel column chromatography (hexane/CH_2Cl_2 4:1) to provide a white solid as the product (3.49 g, 80% based on **3**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, *J* = 6.0, 3H), 1.26 (m, 14H), 1.73-1.75 (m, 2H), 4.31 (t, *J* = 6.9, 2H), 8.15 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 9.6, 18.1, 21.4, 24.0, 24.7, 24.8, 25.0, 27.4, 28.3, 61.6, 111.0, 127.0, 128.2, 159.5. IR (neat): 2925(w), 1716(s), 1526(m), 1465(m), 1357(s), 1263(s), 1135(s), 954(s), 744(s) cm^{-1}. ESI-MS *m/z* (%): calcd, 546.92 (100%); found, 547.1 (100%) $(M+H)^+$. Anal. Calcd. for $C_{17}H_{23}Br_2IO_2$: C, 37.39; H, 4.25. Found: C, 37.45; H, 4.34.

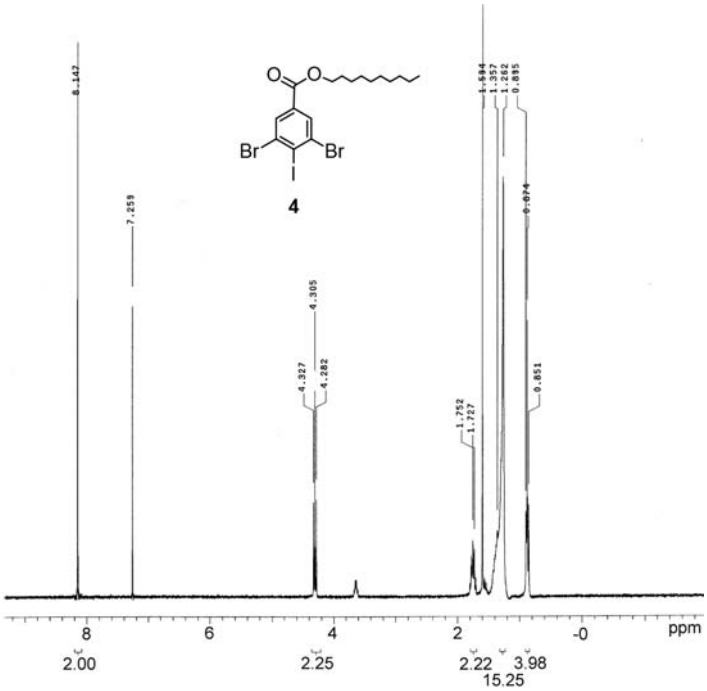


Fig. S8. ^{1}H NMR spectrum of decyl 3,5-dibromo-4-iodobenzoate (**4**) (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.0, 3H), 1.26 (m, 14H), 1.73-1.75 (m, 2H), 4.31 (t, *J* = 6.9, 2H), 8.15 (s, 2H).

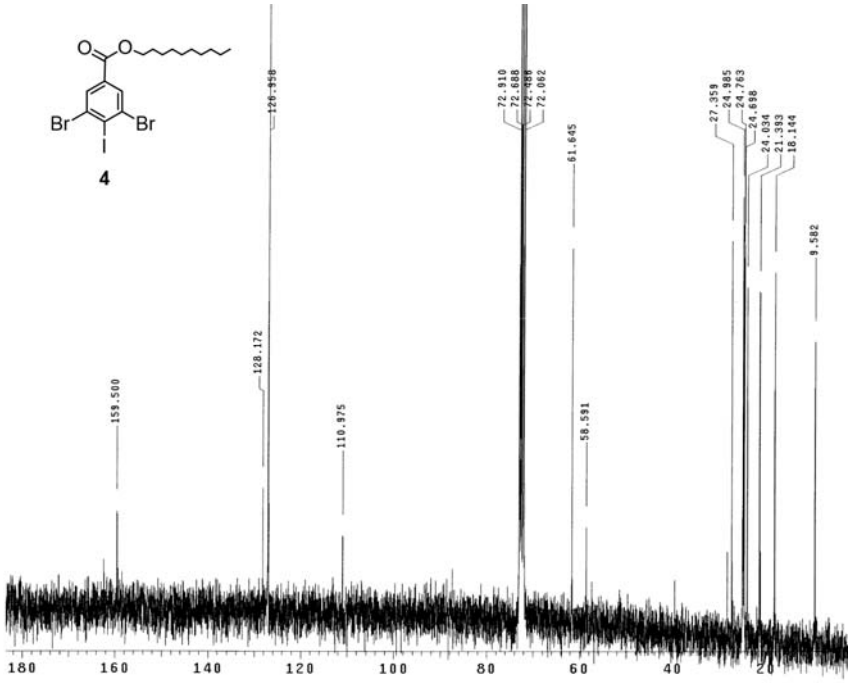


Fig. S9. A ^{13}C NMR spectrum of decyl 3,5-dibromo-4-iodobenzoate (**4**) (75 MHz, $CDCl_3$): δ =9.6, 18.1, 21.4, 24.0, 24.7, 24.8, 25.0, 27.4, 28.3, 61.6, 111.0, 127.0, 128.2, 159.5.

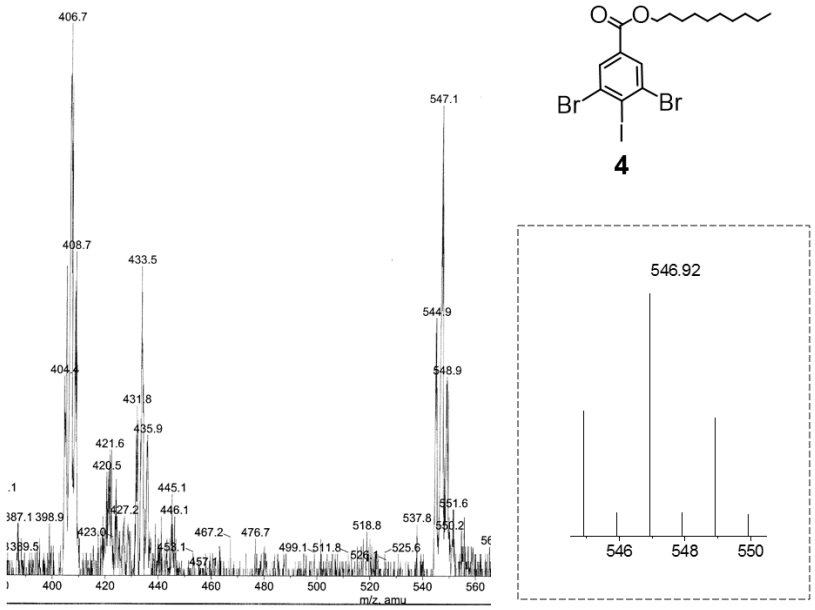
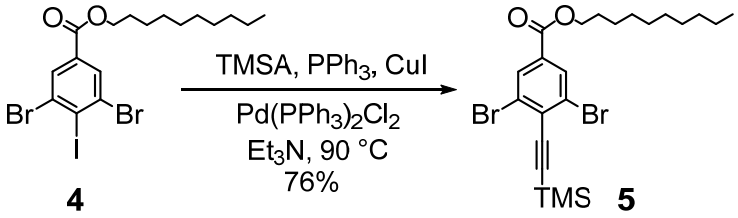


Fig. S10. A mass spectrum (ESI) of 3,5-dibromo-4-iodobenzoate (**4**), *m/z* (%): calcd, 546.92 for the pseudo molecular ion $(M+H)^+$ (100%); found, 547.1 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **4** $(M+H)^+$ ion.

Synthesis of decyl 3,5-dibromo-4-trimethylsilylethynylbenzoate (**5**)**.**



4 **5**

A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (56.1 mg, 0.08 mmol), triphenylphosphine (104.8 mg, 0.40 mmol), copper(I) iodide (22.8 mg, 0.12 mmol), **4** (2.18 g, 4.0 mmol) and triethylamine (30 mL). The Schlenk tube was then connected to a vacuum gas manifold and the suspension inside was bubbled with N_2 gas for 5 min. Trimethylsilylacetylene (TMSA, 98%, 0.30 g, 3.0 mmol) in triethylamine (3.0 mL, bubbled with N_2 gas for 5 min) was injected into the mixture via cannula under a positive N_2 pressure. The Schlenk tube was then sealed with a plug and stirred at 70 °C overnight (15 h). After being cooled to rt, the reaction mixture was poured into 100 mL of a 1:1 hexane/CH_2Cl_2 mixture, filtered through a silica gel plug and rinsed with a 1:1 hexane/CH_2Cl_2 mixture. The solvents were then removed on a rotary evaporator and the light-yellow residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 20:1) to provide a light-yellow liquid product (0.82 g, 76% based on TMSA). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.31 (s, 9H), 0.88 (t, J = 6.9, 3H), 1.26 (m, 14H), 1.78 (m, 2H), 4.26 (t, J = 6.9, 2H), 8.17 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.1, 14.6, 23.2, 26.5, 29.1, 29.8, 29.8, 29.9, 30.1, 32.4, 66.6, 101.9, 109.4, 126.8, 131.4, 131.9, 132.4, 164.2. IR (neat): 2925(s), 2845(w), 2165(w), 1726(s), 1529(m), 1452(w), 1360(m), 1270(s), 1128(m), 860(s), 756(m) cm^{-1}. ESI-MS *m/z* (%): calcd, 517.06 (100%) for $(M+H)^+$; found, 517.4 (100%) $(M+H)^+$. Anal. Calcd. for $C_{22}H_{32}Br_2O_2Si$: C, 51.17; H, 6.25. Found: C, 51.55; H, 6.25.

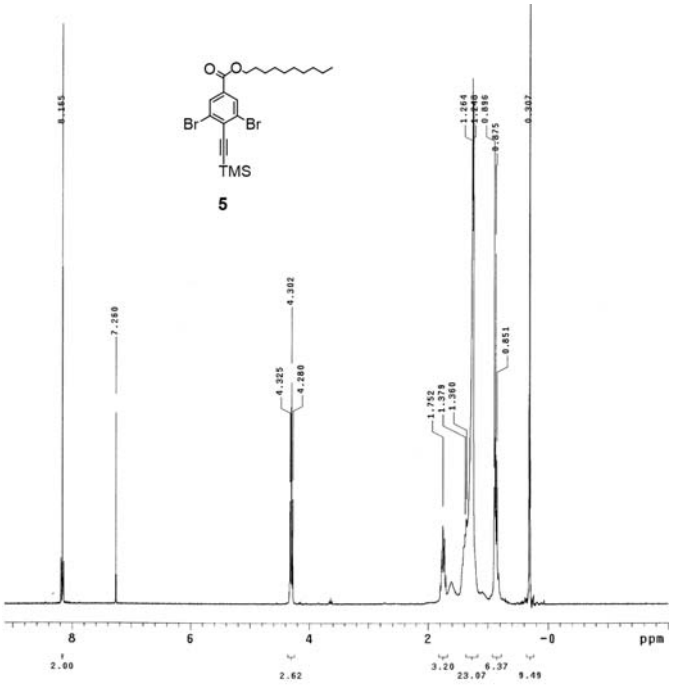


Fig. S11. [1]H NMR spectrum of compound **5** (300 MHz, $CDCl_3$): δ = 0.31 (s, 9H), 0.88 (t, *J* = 6.9, 3H), 1.26 (m, 14H), 1.78 (m, 2H), 4.26 (t, *J* = 6.9, 2H), 8.17 (s, 2H).

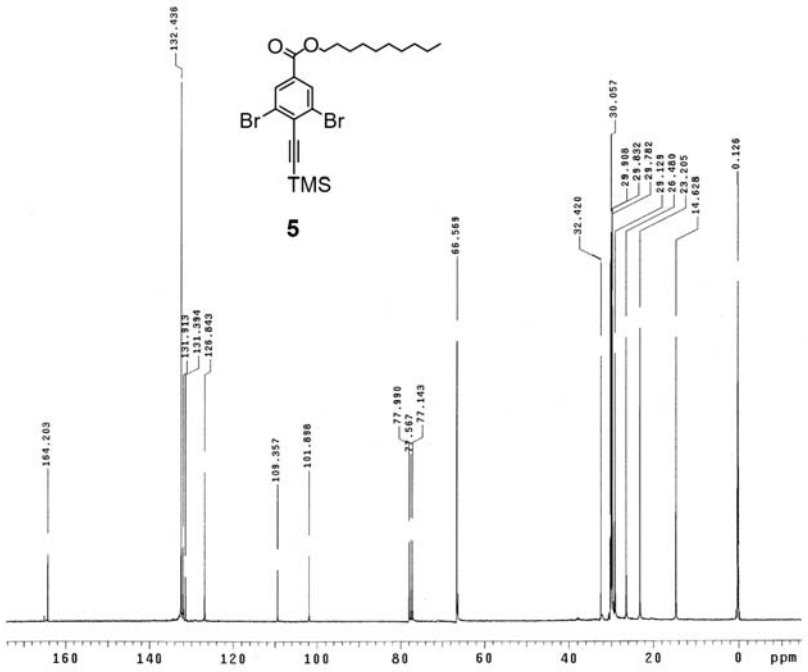


Fig. S12. [13]C NMR spectrum of compound **5** (75 MHz, $CDCl_3$): δ = 0.1, 14.6, 23.2, 26.5, 29.1, 29.8, 29.8, 29.9, 30.1, 32.4, 66.6, 101.9, 109.4, 126.8, 131.4, 131.9, 132.4, 164.2.

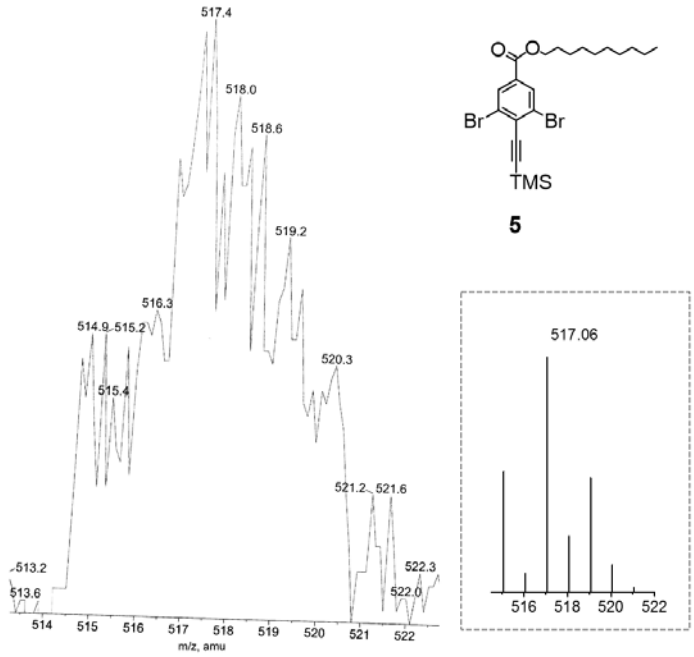
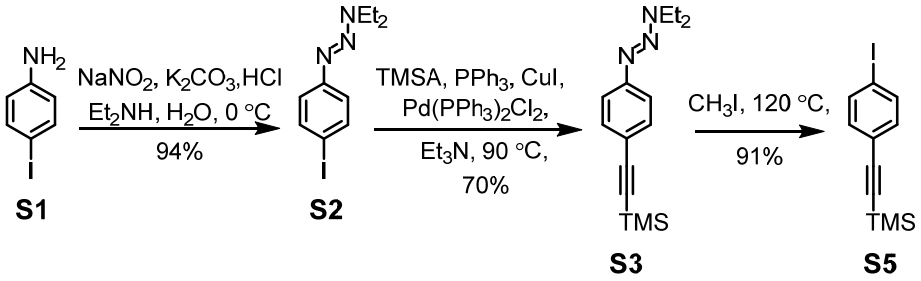


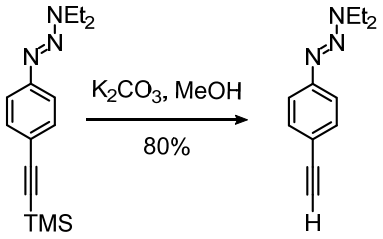
Fig. S13. A mass spectrum (ESI) of compound **5**, *m/z* (%): calcd, 517.06 for the pseudo molecular ion $(M+H)^+$ (100%); found, 517.4 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **5** $(M+H)^+$ ion.

Synthesis of 1-(4-iodophenyl)-3,3-diethyltriazene (S2), 1-[4-[2-(trimethylsilyl) ethynyl]phenyl]-3,3-diethyltriazene (S3), and 1-[2-(trimethylsilyl)ethynyl]-4-iodo benzene (S5).



The procedures were the same as those reported by Holmes, B. T.; Pennington, W. T.; Hanks, T. W. *Synth. Comm.*, **2003**, *33*, 2447-2461. The ^{1}H- and ^{13}C-NMR spectra were in agreement with the literature.

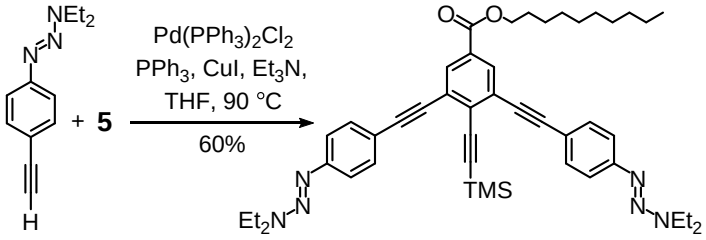
Synthesis of 4-Ethynyl-1-diethyltriazenylbenzene (S4).



S3 **S4**

This procedure was the same as that reported by Li, G.; Wang, X.; Li, J.; Zhao, X.; Wang, F. *Tetrahedron*, **2006**, *62*, 2576-2582. The ^{1}H- and ^{13}C-NMR spectra were in agreement with the literature.

Synthesis of decyl 3,5-bis((4-(3,3-diethyltriaz-1-en-1-yl)phenyl)ethynyl)-4-((tri methylsilyl)ethynyl)benzoate (6).



S4 **6**

A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphospine)-palladium(II) chloride (9.0 mg, 0.012 mmol), triphenylphosphine (18.0 mg, 0.068 mmol), copper(I) iodide (3.6 mg, 0.018 mmol), **5** (0.17 g, 0.33 mmol), **S4** (0.16 g, 0.8 mmol), triethylamine 8 mL) and THF (2 mL), The Schlenk tube was then connected to a Schlenk line and the reaction mixture inside was bubbled with N_2 gas for 5 min. The tube was then sealed under N_2 and stirred at 90 °C overnight (15 h). After it was cooled to rt, the solvents were then removed on a rotary evaporator and the brown residue was purified by flash chromatography (silica gel, 1:2 hexane/CH_2Cl_2) to provide a brown solid product (0.15 g, 60% based on **5**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32 (s, 9H), 0.88 (t, J = 6.9, 3H), 1.25-1.30 (m, 26H), 1.76 (m, 2H), 3.78 (q, J = 7.5, 8H), 4.33 (t, J = 6.7, 2H),

7.44 (d, J = 8.4, 4H), 7.53 (d, J = 8.1, 4H), 8.08 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.0, 14.0, 22.6, 22.7 26.0, 28.7, 29.3, 29.5, 29.5, 31.6, 31.9, 65.7, 87.2, 95.2, 101.8, 106.3, 119.0, 120.4, 127.2, 129.7, 130.9, 131.4, 132.6, 151.4, 165.2. IR (neat): 2927(s), 2852(w), 2204(s), 1722(s), 1596(m), 1548(m), 1465(m), 1392(s), 1326(m), 1236(s), 1157(w), 1095(m), 841(s), 763(m), 711(w) cm^{-1}. ESI-MS *m/z* (%): calcd, 757.46 (100%) for $(M+H)^+$; found, 757.8 (100%) $(M+H)^+$. Anal. Calcd. for $C_{46}H_{60}N_6O_2Si$: C, 72.98; H, 7.99. Found: C, 72.88; H, 7.92.

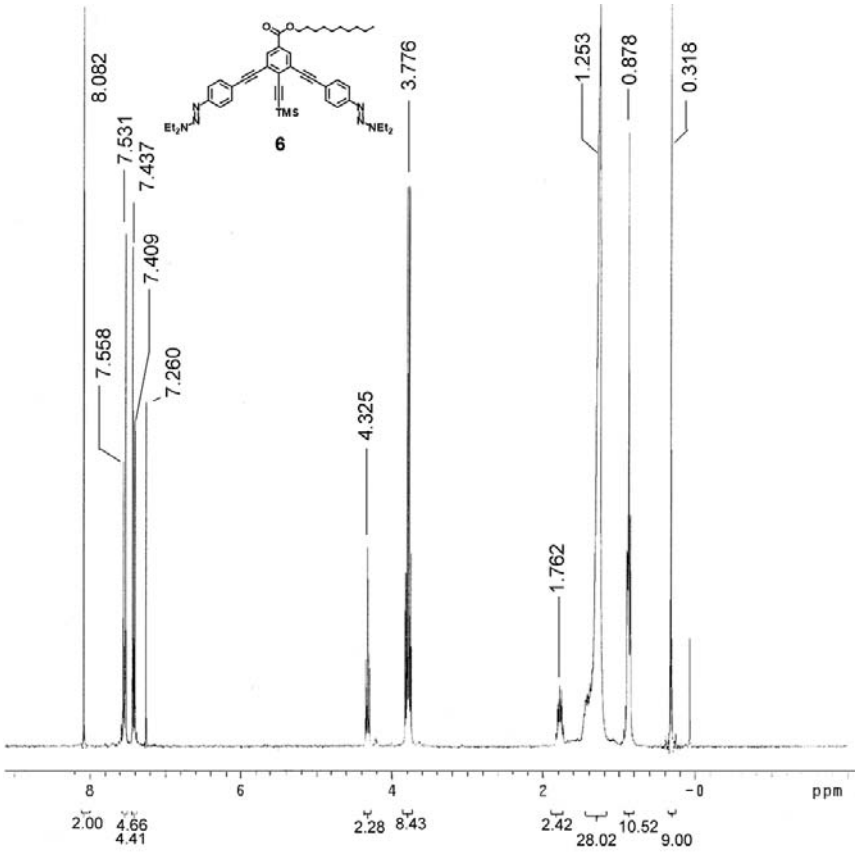


Fig. S14. A ^{1}H NMR spectrum of compound **6** (300 MHz, $CDCl_3$): δ = 0.32 (s, 9H), 0.88 (t, J = 6.9, 3H), 1.25-1.30 (m, 26H), 1.76 (m, 2H), 3.78 (q, J = 7.5, 8H), 4.33 (t, J = 6.7, 2H), 7.44 (d, J = 8.4, 4H), 7.53 (d, J = 8.1, 4H), 8.08 (s, 2H).

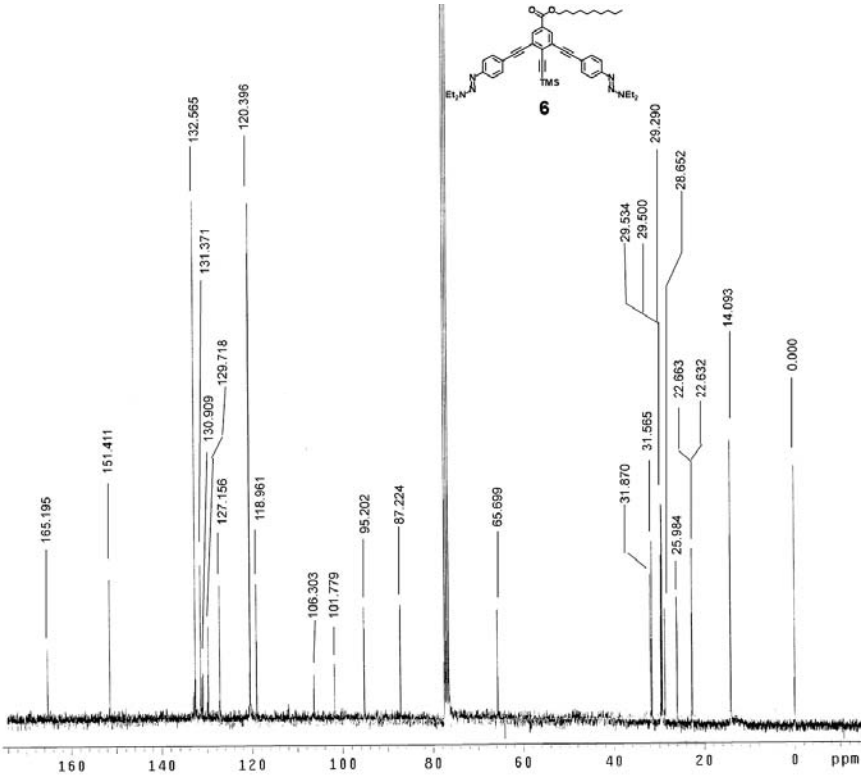


Fig. S15. ^{13}C NMR spectrum of compound **6** (75 MHz, $CDCl_3$): δ = 0.0, 14.0, 22.6, 22.7 26.0, 28.7, 29.3, 29.5, 29.5, 31.6, 31.9, 65.7, 87.2, 95.2, 101.8, 106.3, 119.0, 120.4, 127.2, 129.7, 130.9, 131.4, 132.6, 151.4, 165.2.

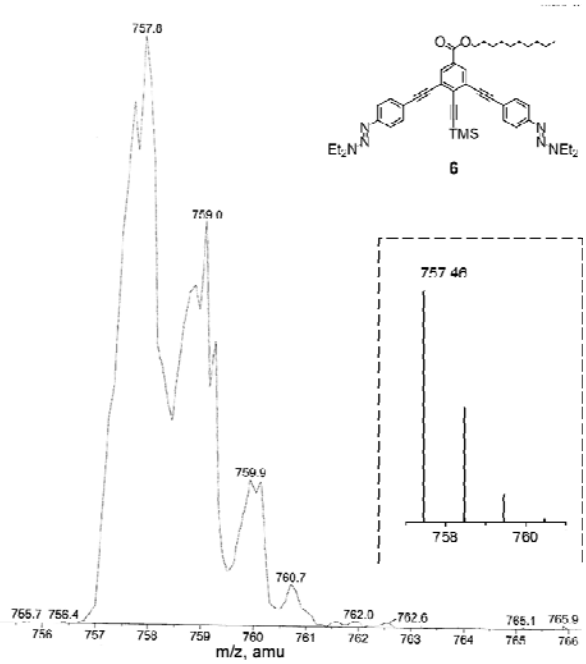
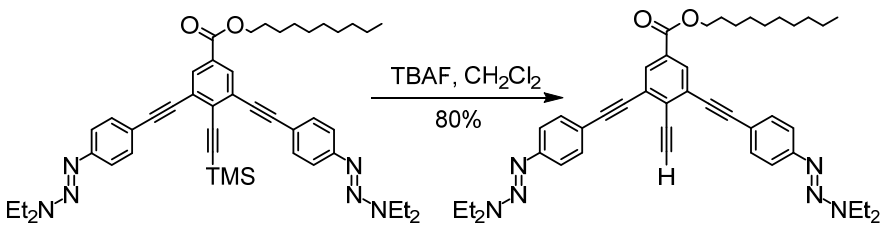


Fig. S16. A mass spectrum (ESI) of compound **6**, *m/z* (%): calcd, 757.46 for the pseudo molecular ion $(M+H)^+$ (100%); found, 757.8 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **6** $(M+H)^+$ ion.

Synthesis of decyl 3,5-bis((4-((E)-3,3-diethyltriaz-1-en-1-yl)phenyl)ethynyl)-4-et hynylbenzoate (7).



6 **7**

6 (0.50 g, 0.66 mmol) was loaded in a round-bottom flask and dissolved with CH_2Cl_2 (20 mL). The flask was cooled to 0 °C, and tetrabutylammonium fluoride (0.76 mL of a 1 M solution in THF, 0.76 mmol) was added via a syringe. The reaction mixture was stirred for 2 h at 0 °C and then filtered through a silica gel plug. The solvents were removed on a rotary evaporator to provide a yellow crystalline solid product (0.36 g, 80% based on **6**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, *J* = 6.7, 3H), 1.28-1.42 (m, 26H), 1.77 (m, 2H), 3.76 (s, 1H), 3.78 (q, *J* = 7.3, 8H), 4.32 (t, *J* = 6.7, 2H), 7.43 (d, *J* = 8.5, 4H), 7.53 (d, *J* = 8.7, 4H), 8.13 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ14.3, 22.9, 26.2, 28.9, 29.5, 29.8, 32.1, 66.0, 80.8, 87.2, 87.9, 95.7, 119.0, 120.7, 120.8, 127.8, 130.4, 131.7, 132.9, 151.8, 165.4. IR (neat): 3428(w), 3280(m), 2925(s), 2852(w), 2204(s), 1720(s), 1596(m), 1552(m), 1466(m), 1396(s), 1328(m), 1238(s), 1159(w), 1095(m), 841(s), 767(m), 543(w) cm^{-1}. ESI-MS *m/z* (%): calcd, 685.42 (100%) for $(M+H)^+$; found, 685.9 (100%) $(M+H)^+$. Anal. Calcd. for $C_{43}H_{52}N_6O_2$: C, 75.41; H, 7.65. Found: C, 75.25; H, 7.62.

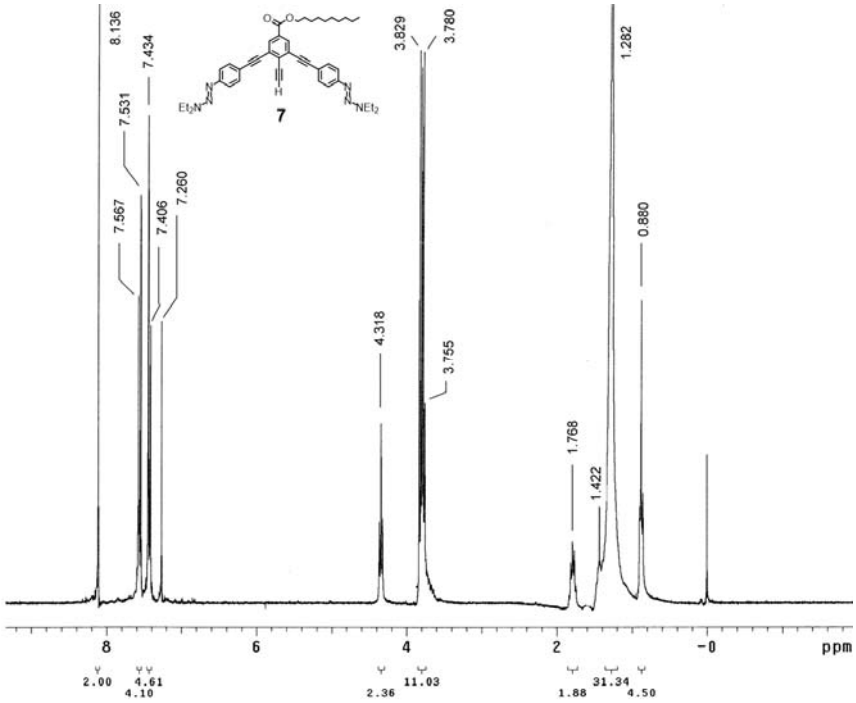


Fig. S17. ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7, 3H), 1.28-1.42 (m, 26H), 1.77 (m, 2H), 3.76 (s, 1H), 3.78 (q, *J* = 7.3, 8H), 4.32 (t, *J* = 6.7, 2H), 7.43 (d, *J* = 8.5, 4H), 7.53 (d, *J* = 8.7, 4H), 8.13 (s, 2H).

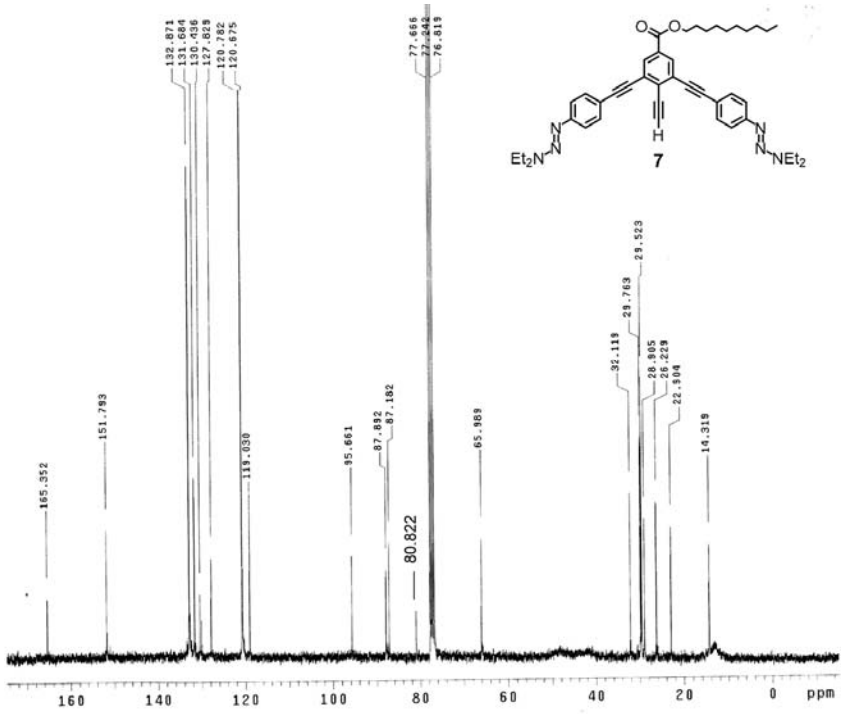


Fig. S18. ^{13}C NMR spectrum of compound **7** (75 MHz, $CDCl_3$): δ = 14.3, 22.9, 26.2, 28.9, 29.5, 29.8, 32.1, 66.0, 80.8, 87.2, 87.9, 95.7, 119.0, 120.7, 120.8, 127.8, 130.4, 131.7, 132.9, 151.8, 165.4.

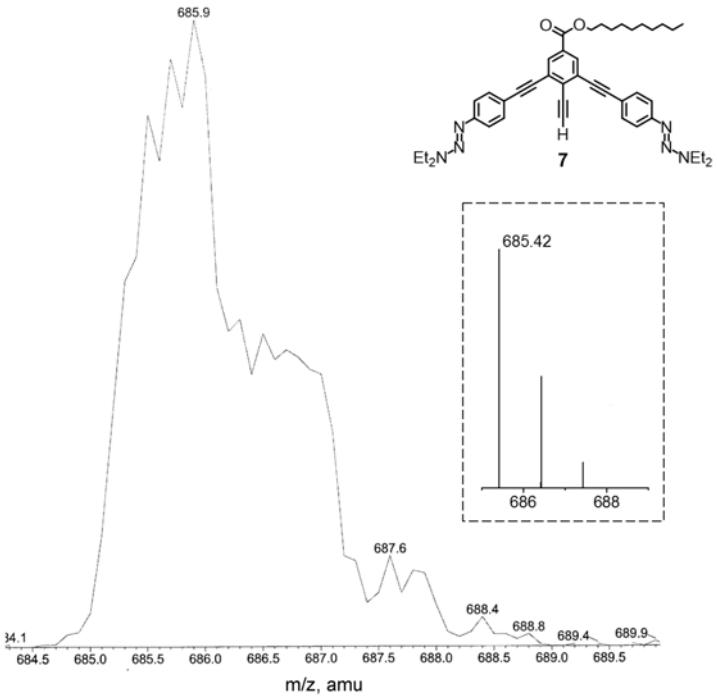
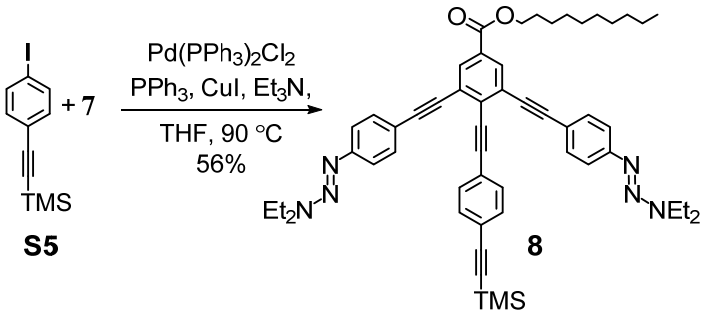


Fig. S19. A mass spectrum (ESI) of compound **7,** *m/z* (%): calcd, 685.42 for the pseudo molecular ion $(M+H)^+$ (100%); found, 685.9 (100%) ($M + H^+$). Inset: a simulated isotopic pattern for the **7** $(M+H)^+$ ion.

Synthesis of decyl 3,5-bis((4-((E)-3,3-diethyltriaz-1-en-1-yl)phenyl)ethynyl)-4-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzoate (8).



A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphospine)-palladium(II) chloride (10.2 mg, 0.014 mmol), triphenylphosphine (18.0 mg, 0.068 mmol), copper(I) iodide (3.6 mg, 0.018 mmol), **7** (0.50 g, 0.73 mmol), **S5** (0.23 g, 0.77 mmol), triethylamine (8 mL) and THF (2 mL). The Schlenk tube was then connected to a Schlenk line and the reaction mixture

inside was bubbled with N_2 gas for 5 min. The tube was then sealed with a plug under nitrogen and stirred at 90 °C overnight (15 h). After it was cooled to rt, the solvents were then removed on a rotary evaporator and the brown residue was purified by flash chromatography (silica gel, 1:1 hexane/CH_2Cl_2) to provide a brown solid product **8** (0.35 g, 56% based on **7**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.27 (s, 9H), 0.88 (t, J = 6.9, 3H), 1.22-1.31 (m, 26H), 1.80 (m, 2H), 3.78 (q, J = 7.2, 8H), 4.34 (t, J = 6.6, 2H), 7.41-7.47 (m, 6H), 7.54-7.58 (m, 6H), 8.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.0, 14.2, 22.8, 26.1, 28.8, 29.4, 29.6, 32.0, 65.8, 87.4, 89.7, 95.6, 96.5, 100.1, 101.8, 119.0, 120.6, 123.3, 123.7, 126.9, 129.9, 131.1, 131.6, 131.7, 132.1, 132.6, 151.7, 165.3. IR (neat): 3450, 2923(s), 2852(w), 2202(s), 2154(m), 1720(s), 1596(w), 1546(m), 1463(m), 1394(s), 1330(m), 1249(s), 1157(w), 1093(m), 978(w), 835(s), 763(m), 541(m) cm^{-1}. ESI-MS *m/z* (%): calcd, 857.49 (100%) for $(M+H)^+$; found, 858.4 (100%) $(M+H)^+$. Anal. Calcd. for $C_{54}H_{64}N_6O_2Si$: C, 75.66; H, 7.53. Found: C, 75.27; H, 7.47.

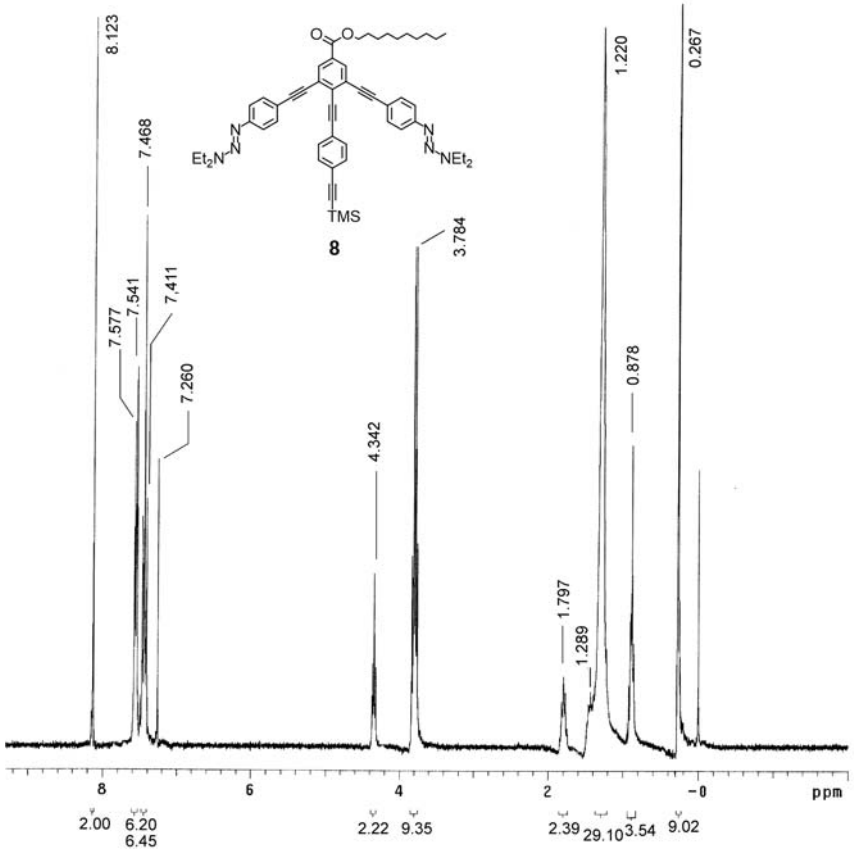


Fig. S20. ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.88 (t, J =

6.9, 3H), 1.22-1.31 (m, 26H), 1.80 (m, 2H), 3.78 (q, *J* = 7.2, 8H), 4.34 (t, *J* = 6.6, 2H), 7.41-7.47 (m, 6H), 7.54-7.58 (m, 6H), 8.12 (s, 2H).

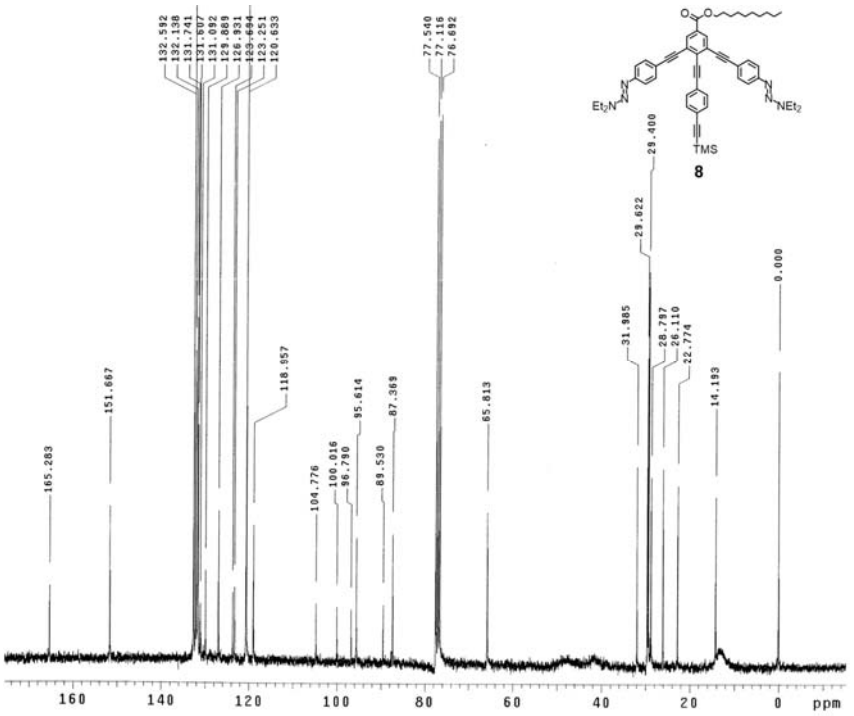


Fig. S21. ^{13}C NMR spectrum of compound **8** (75 MHz, $CDCl_3$): δ = 0.0, 14.2, 22.8, 26.1, 28.8, 29.4, 29.6, 32.0, 65.8, 87.4, 89.7, 95.6, 96.5, 100.1, 101.8, 119.0, 120.6, 123.3, 123.7, 126.9, 129.9, 131.1, 131.6, 131.7, 132.1, 132.6, 151.7, 165.3.

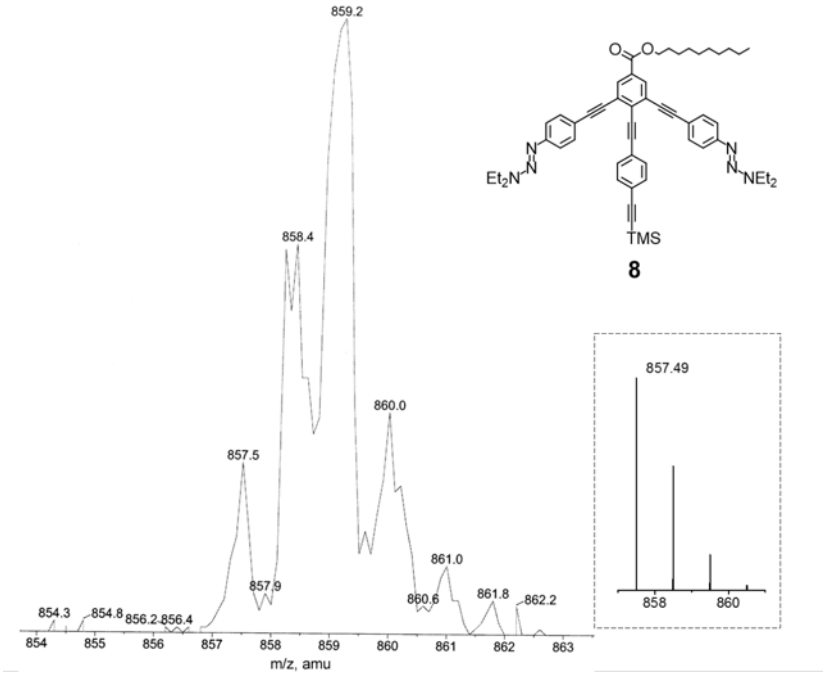
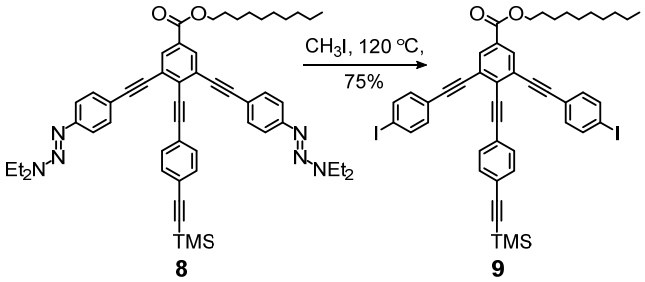


Fig. S22. A mass spectrum (ESI) of compound **8**, *m/z* (%): calcd, 857.49 for the pseudo

molecular ion $(M+H)^+$ (100%); found, 858.4 (100%) ($M + H^+$). Inset: a simulated isotopic pattern for the **8** $(M+H)^+$ ion.

Synthesis of decyl 3,5-bis((4-iodophenyl)ethynyl)-4-((4-((trimethylsilyl)ethynyl) phenyl)ethynyl)benzoate (9).



8 **9**

A Schlenk tube was charged with a magnetic stirring bar, CH_3I (10 mL) and **8** (0.35 g, 0. 4 mmol). The mixture was then bubbled with N_2 gas for 5 min and then the tube was sealed and stirred at 120 °C overnight (24 h). After it was cooled to rt, the extra CH_3I was then removed in vacuo and the brown residue was purified by flash chromatography (silica gel, 1:1 hexane/CH_2Cl_2) to provide a brown solid product **9** (0.28 g, 75% based on **8**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.27 (s, 9H), 0.88 (t, J = 6.9, 3H), 1.26-1.31 (m, 14H), 1.78 (m, 2H), 4.34 (t, J = 6.9, 2H), 7.26 (d, J = 8.4, 4H), 7.46-7.47 (m, 4H), 7.70 (d, J = 8.4, 4H), 8.13 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.0, 14.2, 22.8, 26.1, 28.8, 29.4, 29.6, 29.7, 32.0, 66.0, 88.6, 88.9, 93.8, 95.1, 97.3, 100.3, 104.4, 122.3, 122.8, 124.1, 126.3, 130.0, 131.4, 131.6, 132.2, 132.2, 133.2, 137.8, 164.9. IR (neat): 3450, 2921(s), 2850(w), 2206(s), 2154(m), 1718(s), 1594(w), 1546(m), 1481(m), 1388(s), 1249(m), 1155(w), 1056(w), 1004(m), 883(s), 840(s), 761(m), 518(m) cm^{-1}. ESI-MS *m/z* (%): calcd, 911.13 (100%) for $(M+H)^+$; found, 911.6 (100%) $(M+H)^+$. Anal. Calcd. for $C_{46}H_{44}I_2O_2Si$: C, 60.66; H, 4.87. Found: C, 60.79; H, 4.64.

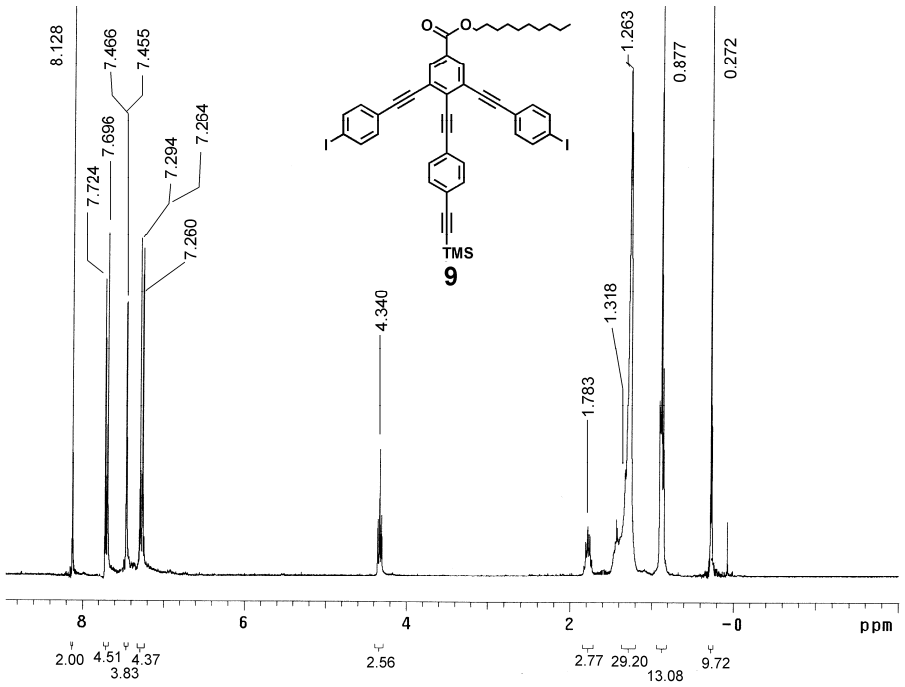


Fig. S23. [1]H NMR spectrum of compound **9** (300 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.88 (t, *J* = 6.9, 3H), 1.26-1.31 (m, 14H), 1.78 (m, 2H), 4.34 (t, *J* = 6.9, 2H), 7.26 (d, *J* = 8.4, 4H), 7.46-7.47 (m, 4H), 7.70 (d, *J* = 8.4, 4H), 8.13 (s, 2H)..

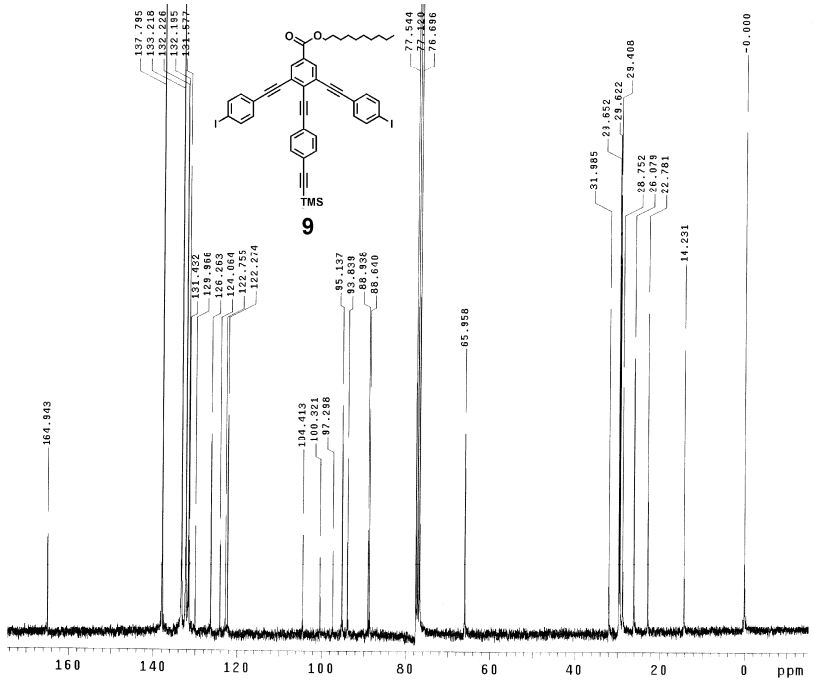


Fig. S24. [13]C NMR spectrum of compound **9** (75 MHz, $CDCl_3$): δ = 0.0, 14.2, 22.8, 26.1, 28.8, 29.4, 29.6, 29.7, 32.0, 66.0, 88.6, 88.9, 93.8, 95.1, 97.3, 100.3, 104.4, 122.3, 122.8, 124.1, 126.3, 130.0, 131.4, 131.6, 132.2, 132.2, 133.2, 137.8, 164.9.

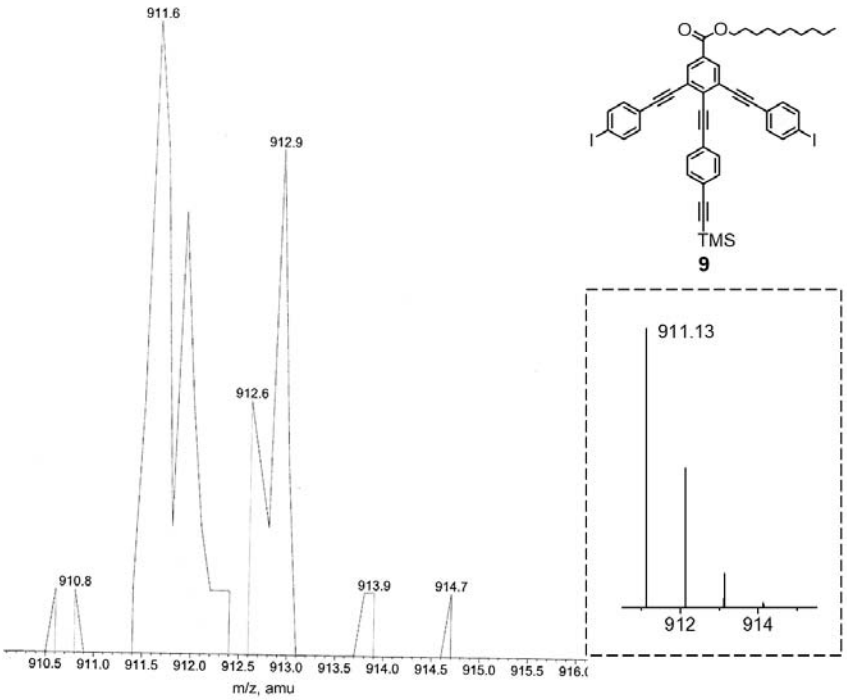
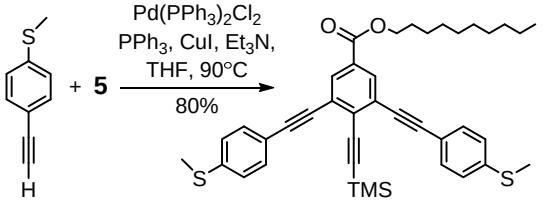


Fig. S25. A mass spectrum (ESI) of the compound **9** molecule, *m/z* (%): calcd, 911.13 (100%) for the pseudo molecular ion $(M+H)^+$; found, 911.6 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **9** $(M+H)^+$ ion.

Synthesis of decyl 3,5-bis((4-(methylthio)phenyl)ethynyl)-4-((trimethylsilyl)ethynyl)benzoate (10).



A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (45.1 mg, 0.06 mmol), triphenylphosphine (90 mg, 0.34 mmol), copper(I) iodide (18.0 mg, 0.09 mmol), **S8** (0.35 g, 2.2 mmol), **5** (0.52 g, 1 mmol), triethylamine (15 mL) and THF (15 mL). The mixture was then bubbled with N_2 gas for 5 min. The Schlenk tube was then sealed with a plug under N_2 flow and stirred while it was heated to 90 °C overnight (15 h).

After it was cooled to rt, the reaction mixture was poured into 100 mL of a 1:1 hexane/CH_2Cl_2 mixture and then filtered through a silica gel plug (hexane/CH_2Cl_2 = 1:1). The solvents were then removed on a rotary evaporator and the brown residue was purified by flash chromatography (silica gel, 4:1 hexane/CH_2Cl_2) to provide a yellow crystalline solid product (0.46 g, 80% based on **S8)**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.31 (s, 9H), 0.87 (t, *J* = 6.9, 3H), 1.27 (m, 14H), 1.79 (m, 2H), 2.51 (s, 6H), 4.32 (t, *J* = 6.9, 2H), 7.3 (d, *J* = 6.9, 4H), 7.47 (d, *J* = 6.9, 4H), 8.09 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.0, 14.1, 15.2, 22.7, 26.0, 28.6, 29.3, 29.3, 29.5, 29.5, 31.9, 65.8, 87.4, 94.3, 101.6, 106.4, 119.0, 125.7, 126.9, 129.8, 131.0, 131.6, 132.0, 140.2, 165.0. IR (neat): 3449(w), 2921(s), 2850(w), 2206(s), 1720(s), 1592(w), 1548(m), 1490(m), 1415(w), 1251(m), 1159(w), 1056(w), 973(m), 842(s), 761(m), 522(m) cm^{-1}. ESI-MS *m/z* (%): calcd, 651.28 (100%) for $(M+H)^+$; found, 651.4 (100%) $(M+H)^+$. Anal. Calcd. for $C_{40}H_{46}O_2S_2Si$: C, 73.80; H, 7.12. Found: C, 73.55; H, 6.91.

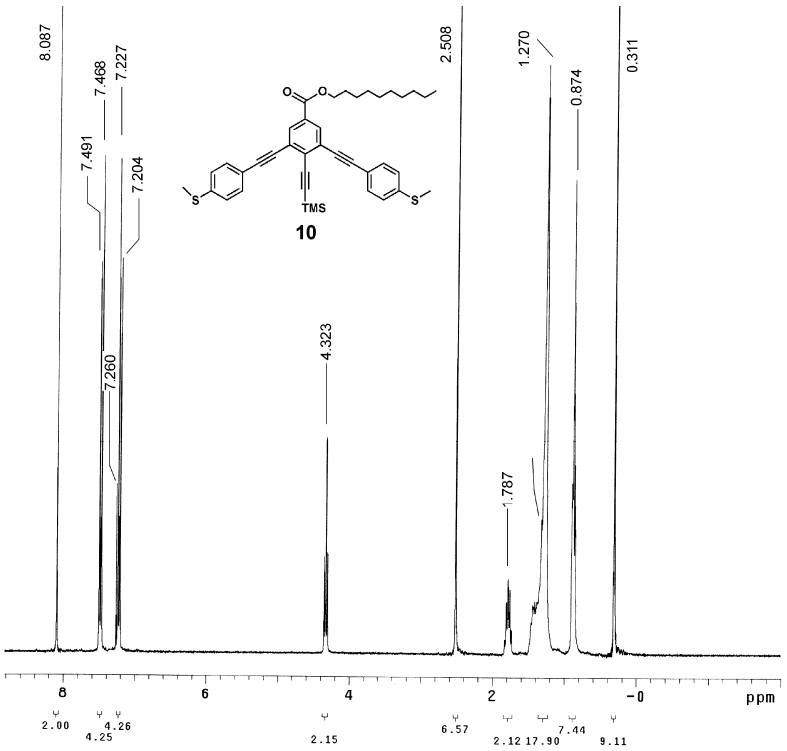


Fig. S26. ^{1}H NMR spectrum of compound **10** (300 MHz, $CDCl_3$): δ = 0.31 (s, 9H), 0.87 (t, *J* = 6.9, 3H), 1.27 (m, 14H), 1.79 (m, 2H), 2.51 (s, 6H), 4.32 (t, *J* = 6.9, 2H), 7.3 (d, *J* = 6.9, 4H), 7.47 (d, *J* = 6.9, 4H), 8.09 (s, 2H).

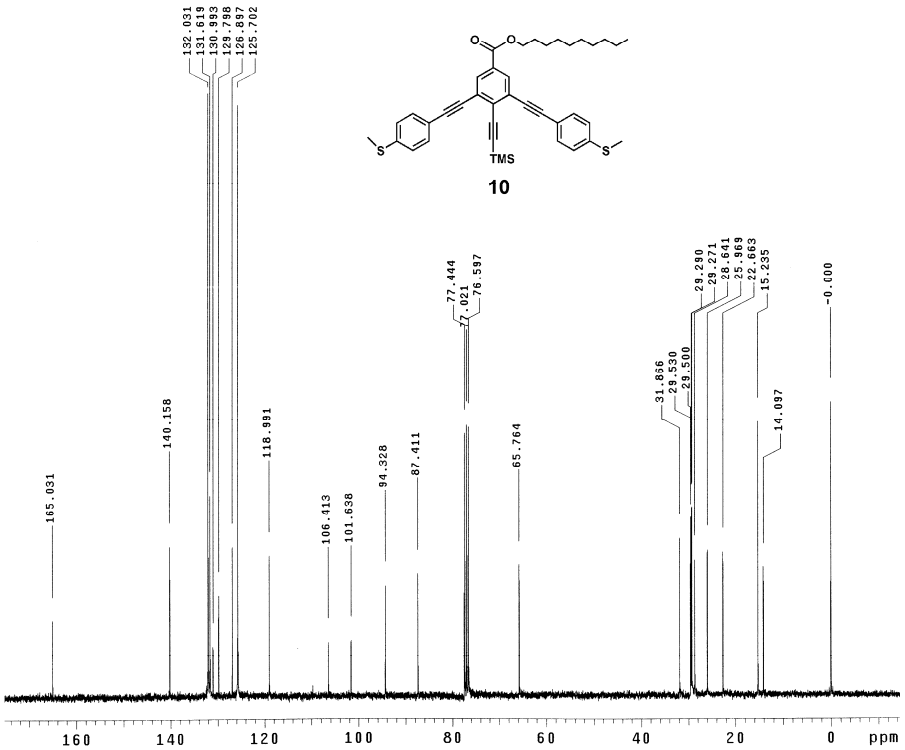


Fig. S27. ^{13}C NMR spectrum of compound **10** (75 MHz, $CDCl_3$): δ = 0.0, 14.1, 15.2, 22.7, 26.0, 28.6, 29.3, 29.3, 29.5, 29.5, 31.9, 65.8, 87.4, 94.3, 101.6, 106.4, 119.0, 125.7, 126.9, 129.8, 131.0, 131.6, 132.0, 140.2, 165.0.

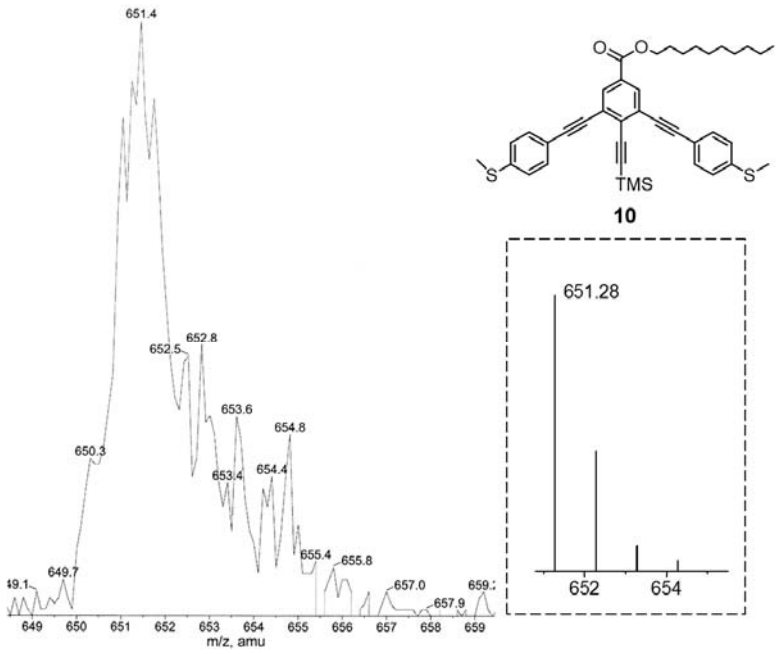
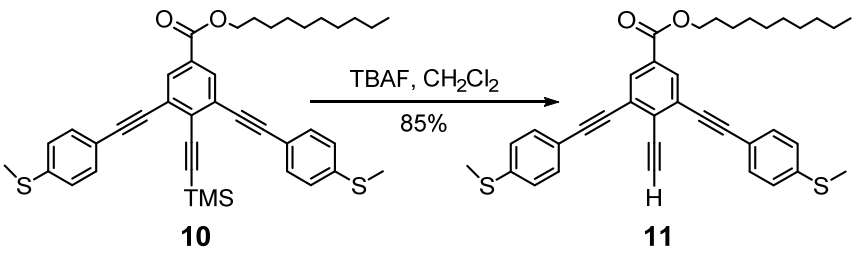


Fig. S28. A mass spectrum (ESI) of compound **10**, *m/z* (%): calcd, 651.28 (100%) for the pseudo molecular ion $(M+H)^+$; found, 651.4 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **10** $(M+H)^+$ ion.

Synthesis of decyl 4-ethynyl-3,5-bis((4-(methylthio)phenyl)ethynyl)benzoate (11).



Compound **10** (0.14 g, 0.28 mmol) was placed in a round-bottom flask and dissolved in CH_2Cl_2 (10 mL). The flask was cooled to 0 °C, and tetrabutylammonium fluoride (0.30 mL of a 1 M solution in THF, 0.30 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C and then filtered through a silica gel plug (hexane/ CH_2Cl_2 = 1:1). The solvents were then removed in vacuo to provide a yellow crystalline solid product (0.11 g, 85% based on **10**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, 3H), 1.27 (m, 14H), 1.83 (m, 2H), 2.51 (s, 6H), 3.79 (s, 1H), 4.31 (t, J = 6.9, 2H), 7.24 (d, J = 9.0, 4H), 7.48 (d, J = 8.4, 4H), 8.10 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.1, 14.1, 21.7, 24.2, 27.7, 28.3, 28.5, 30.9, 64.3, 81.5, 82.9, 86.0, 94.8, 117.2, 124.6, 127.0, 128.8, 129.6, 130.2, 131.10, 139.3, 163.9. IR (neat): 3425(w), 3300(m), 2919(s), 2210(s), 1718(s), 1552(m), 1490(m), 1434(w), 1259(s), 1160(w), 1091(m), 975(m), 813(s), 765(m), 647(m), 522(w) cm^{-1}. ESI-MS *m/z* (%): calcd, 579.24 (100%) for $(M+H)^+$; found, 579.4 (100%) $(M+H)^+$. Anal. Calcd. for $C_{37}H_{38}O_2S_2$: C, 76.78; H, 6.62. Found: C, 76.87; H, 6.60. Compound **11** thus prepared was used for the next step without further purification.

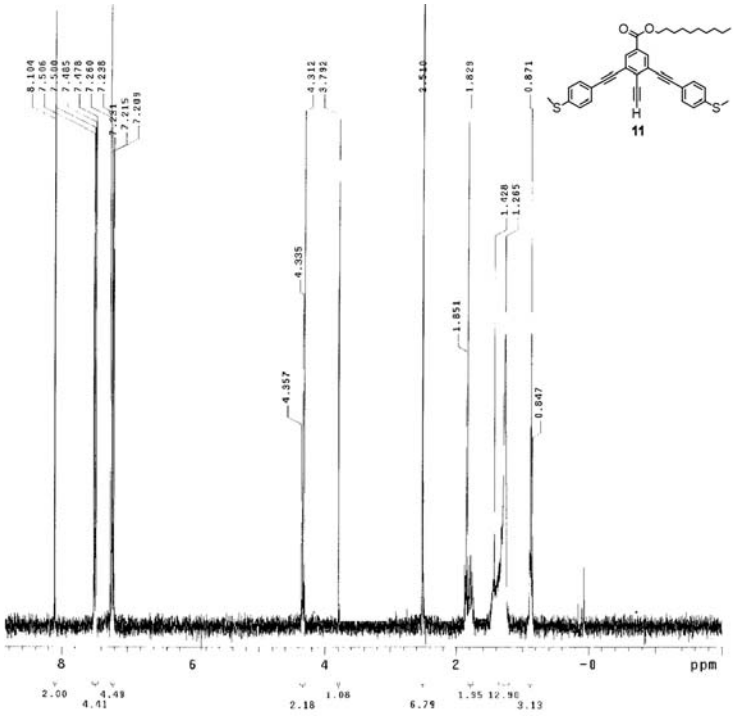


Fig. S29. ^{1}H NMR spectrum of compound **11** (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H), 1.27 (m, 14H), 1.83 (m, 2H), 2.51 (s, 6H), 3.79 (s, 1H), 4.31 (t, *J* = 6.9, 2H), 7.24 (d, *J* = 9.0, 4H), 7.48 (d, *J* = 8.4, 4H), 8.10 (s, 2H).

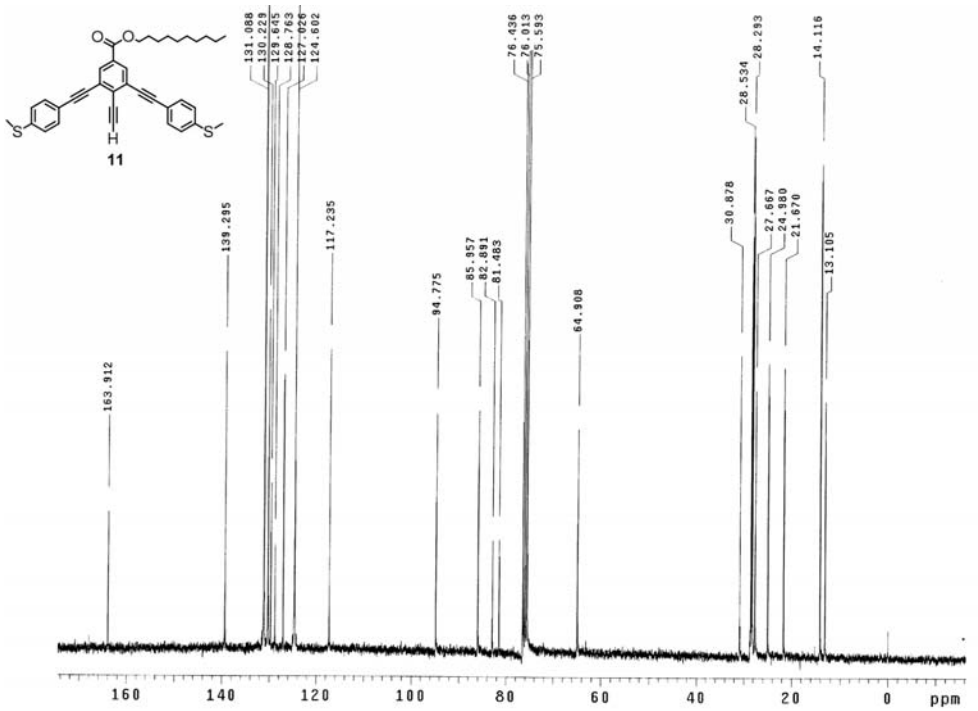


Fig. S30. ^{13}C NMR spectrum of compound **11**(75 MHz, $CDCl_3$): δ = 13.1, 14.1, 21.7, 24.2, 27.7, 28.3, 28.5, 30.9, 64.3, 81.5, 82.9, 86.0, 94.8, 117.2, 124.6, 127.0, 128.8, 129.6, 130.2, 131.1, 139.3, 163.9.

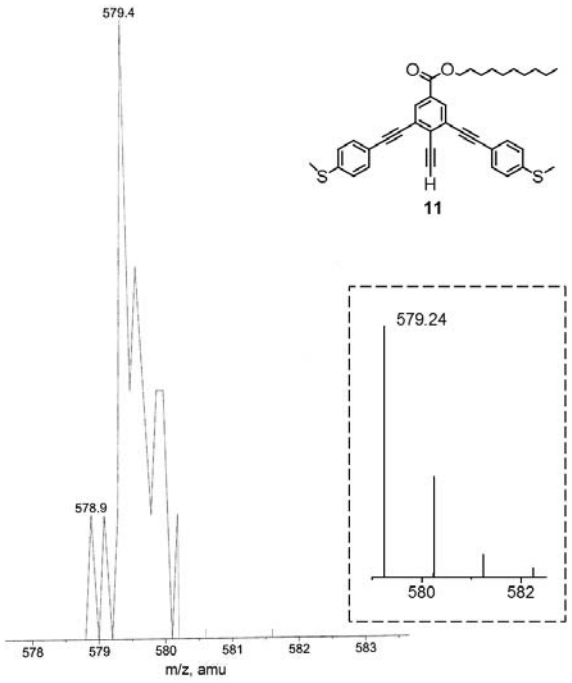
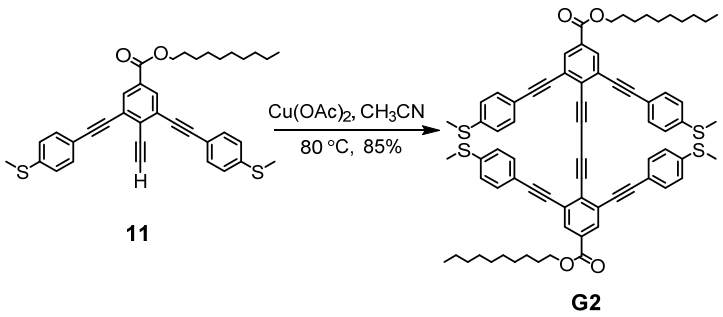


Fig. S31. A mass spectrum (ESI) of compound **11**, *m/z* (%): calcd, 579.24 (100%) for the pseudo molecular ion $(M+H)^+$; found, 579.4 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **10** $(M+H)^+$ ion.

Synthesis of compound G2.



A mixture of **11** (0.19 g, 0.33 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (0.26 g, 1.2 mmol) in acetonitrile (5 mL) was stirred for 2 h at 80 °C. After cooling, the solvent was removed on a rotary evaporator. The residue was dispersed in CH_2Cl_2 (50 mL), and the insoluble matter was removed by filtration. The filtrate was washed with water (×2) and dried over anhydrous $MgSO_4$. The solvent was then removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (hexane:

CH_2Cl_2 = 1:4). 0.16 g of **G2** was obtained (85% yield based on **11**). Recrystallization from acetonitrile/benzene afforded single-crystals of **G2** (CCDC 1570192 contains the supplementary crystallographic data for **G2**, see also Figure S3, Table S1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, 3H), 1.28 (m, 14H), 1.81 (m, 2H), 2.38 (s, 6H), 4.36 (t, *J* = 6.9, 2H), 6.97-7.00 (d, *J* = 8.4, 4H), 7.39-7.42 (d, *J* = 8.4, 4H), 8.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.1, 14.1, 21.7, 25.0, 27.7, 28.3, 28.5, 30.9, 64.9, 81.5, 82.9, 86.0, 94.8, 117.2, 124.6, 127.0, 128.8, 129.6, 130.2, 131.1, 139.3, 163.9. IR (neat): 2921(s), 2853(m), 2204(s), 1724(s), 1587(m), 1541(m), 1492(s), 1415(w), 1228(s), 1158(m), 1093(m), 977(m), 814(s), 766(m), 741(m), 590(m), 522(m) cm^{-1}. Anal. Calcd. for $C_{74}H_{74}O_4S_4$: C, 76.91; H, 6.45. Found: C, 77.41; H, 6.18.

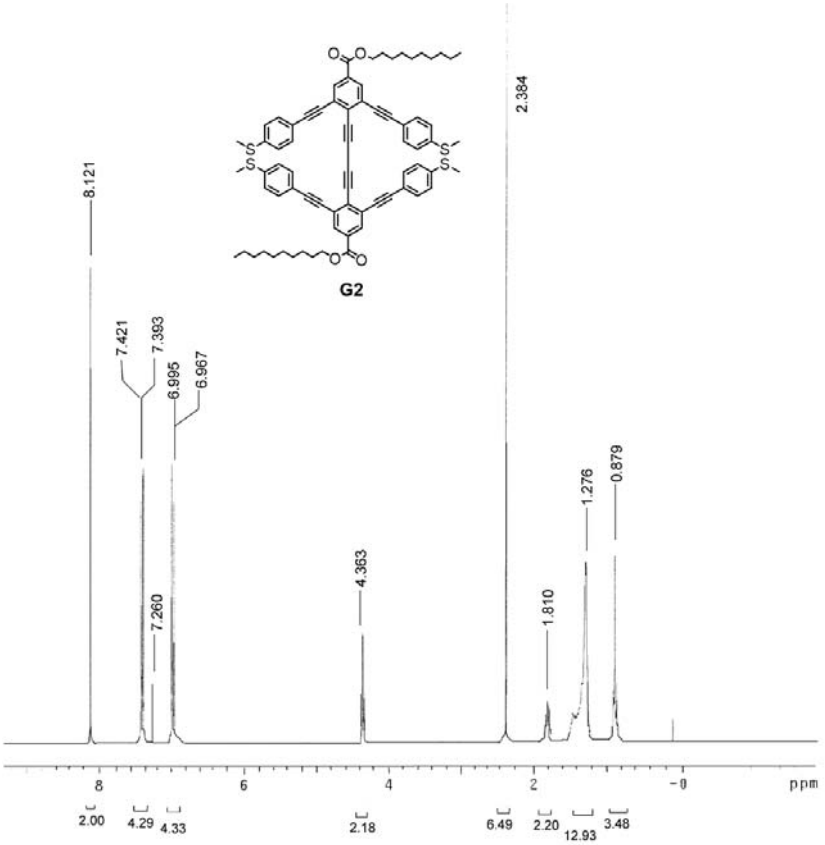


Fig. S32. ^{1}H NMR spectrum of compound **G2** (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H), 1.28 (m, 14H), 1.81 (m, 2H), 2.38 (s, 6H), 4.36 (t, *J* = 6.9, 2H), 6.97-7.00 (d, *J* = 8.4, 4H), 7.39-7.42 (d, *J* = 8.4, 4H), 8.12 (s, 2H).

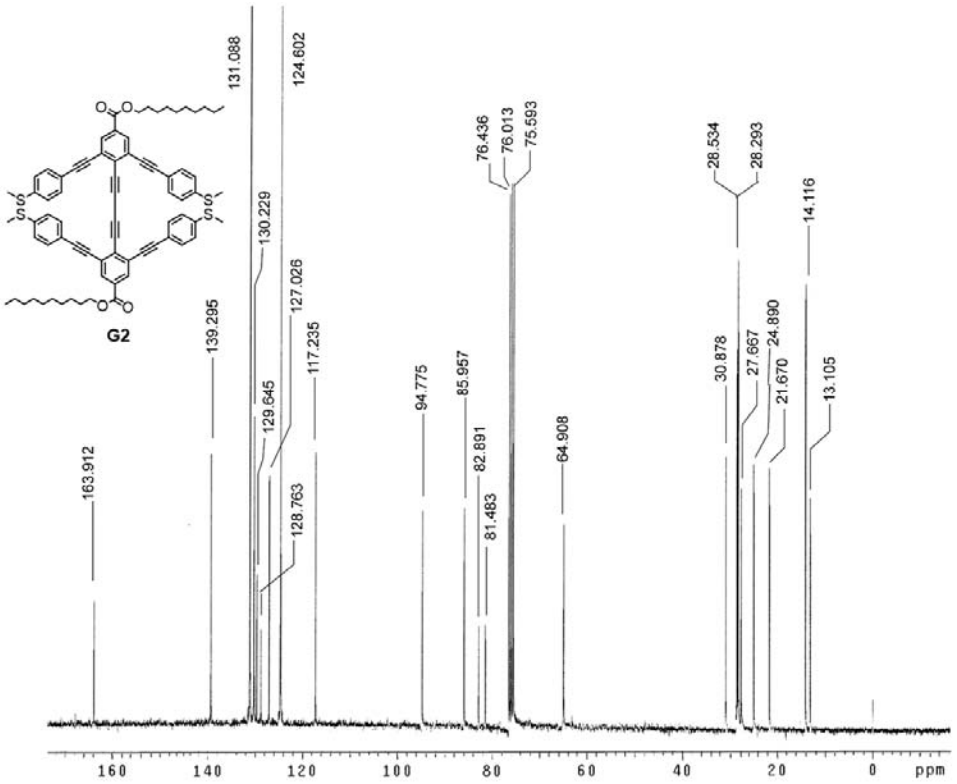
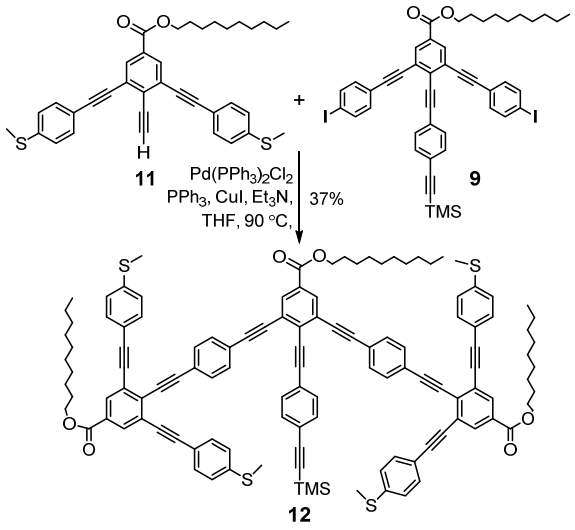


Fig. S33. ^{13}C NMR spectrum of compound **G2** (75 MHz, $CDCl_3$): δ = 13.1, 14.1, 21.7, 25.0, 27.7, 28.3, 28.5, 30.9, 64.9, 81.5, 82.9, 86.0, 94.8, 117.2, 124.6, 127.0, 128.8, 129.6, 130.2, 131.1, 139.3, 163.9.

Synthesis of compound 12.



A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphospine)-palladium(II) chloride (9.0 mg, 0.012 mmol),

triphenylphosphine (18.0 mg, 0.068 mmol), copper(I) iodide (3.6 mg, 0.018 mmol), **11** (0.13 g, 0.22 mmol), **9** (0.091 g, 0.1 mmol), triethylamine 10 mL) and THF (5 mL), The reaction mixture was then bubbled with N_2 gas for 5 min and the tube was sealed with a plug under N_2 flow. The mixture was then stirred at 90 °C overnight (15 h). After it was cooled to rt, the solvents were removed on a rotary evaporator and the brown residue was purified by flash chromatography (silica gel, 1:1 hexane/CH_2Cl_2) to provide a yellow solid product (0.067 g, 37% based on **9**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.21 (s, 9H), 0.85-0.88 (t, 9H), 1.25-1.27 (m, 42H), 1.80 (m, 6H), 2.50 (s, 12H), 4.35 (m, 6H), 7.24 (d, *J* = 8.7, 8H), 7.45 (d, *J* = 7.8, 2H), 7.49 (m, 10H), 7.59 (m, 8H), 8.14 (s, 4H), 8.18 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.0, 11.1, 14.3, 15.4, 22.8, 23.1, 23.9, 26.2, 28.8, 29.1, 29.5, 29.7, 30.5, 32.0, 38.9, 66.0, 66.0, 68.3, 87.6, 89.1, 89.7, 89.8, 94.4, 94.8, 97.6, 100.0, 100.6, 104.5, 119.0, 123.4, 123.7, 126.0, 126.4, 126.8, 128.5, 129.0, 129.8, 130.1, 131.0, 131.1, 131.5, 131.7, 132.0, 132.1, 132.2, 132.5, 134.3, 140.6, 165.0, 165.2. IR (neat): 3448(w), 2923(s), 2854(m), 2208(s), 2152(w), 1722(s), 1548(m), 1492(m), 1463(w), 1251(s), 1158(w), 1014(w), 991(m), 819(s), 763(m), 646(m), 524(w) cm^{-1}. MALDI-TOF-MS, *m/z* (%): calcd, 1812.76 (100%) for $(M+H)^+$; found, 1812.7754 (100%) $(M+H)^+$. Anal. Calcd. for $C_{120}H_{118}O_6S_4Si$: C, 79.52; H, 6.56. Found: C, 79.82; H, 6.30.

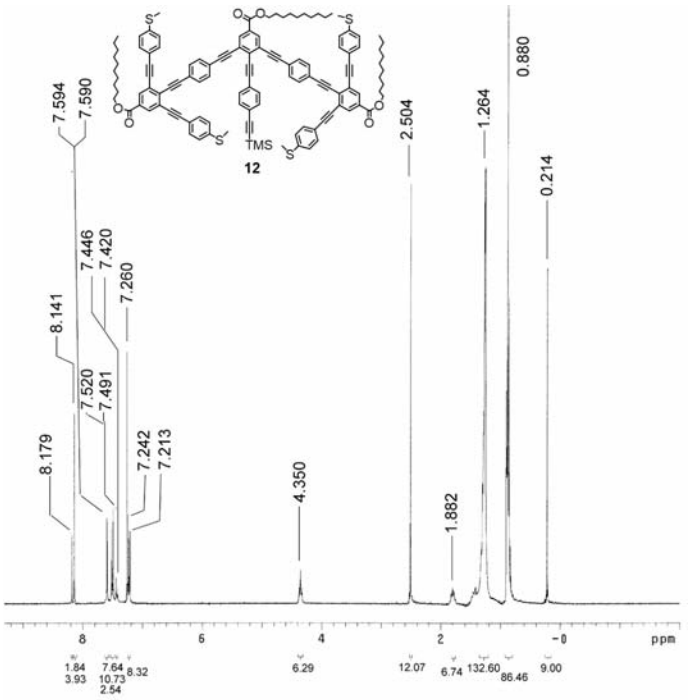


Fig. S34. ^{1}H NMR spectrum of compound **12** (300 MHz, $CDCl_3$): δ = 0.21 (s, 9H), 0.85-0.88 (t, 9H), 1.25-1.27 (m, 42H), 1.80 (m, 6H), 2.50 (s, 12H), 4.35 (m, 6H), 7.24 (d, *J* = 8.7, 8H), 7.45 (d, *J* = 7.8, 2H), 7.49 (m, 10H), 7.59 (m, 8H), 8.14 (s, 4H), 8.18 (s, 2H).

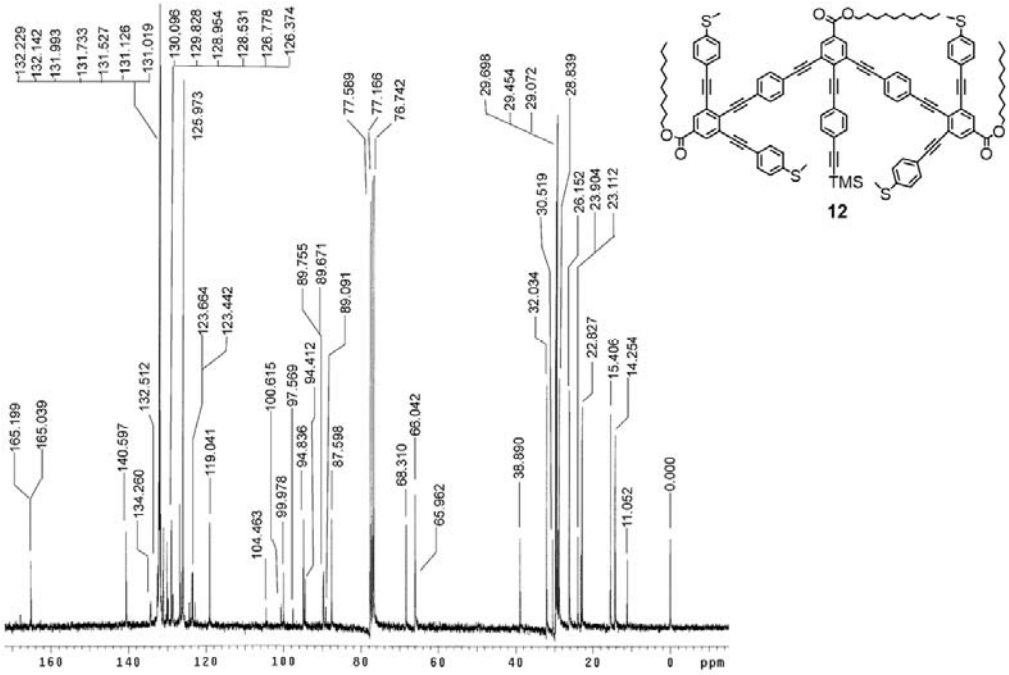


Fig. S35. ^{13}C NMR spectrum of compound **12** (75 MHz, $CDCl_3$): δ = 0.0, 11.1, 14.3, 15.4, 22.8, 23.1, 23.9, 26.2, 28.8, 29.1, 29.5, 29.7, 30.5, 32.0, 38.9, 66.0, 66.0, 68.3, 87.6, 89.1, 89.7, 89.8, 94.4, 94.8, 97.6, 100.0, 100.6, 104.5, 119.0, 123.4, 123.7, 126.0, 126.4, 126.8, 128.5, 129.0, 129.8, 130.1, 131.0, 131.1, 131.5, 131.7, 132.0, 132.1, 132.2, 132.5, 134.3, 140.6, 165.0, 165.2.

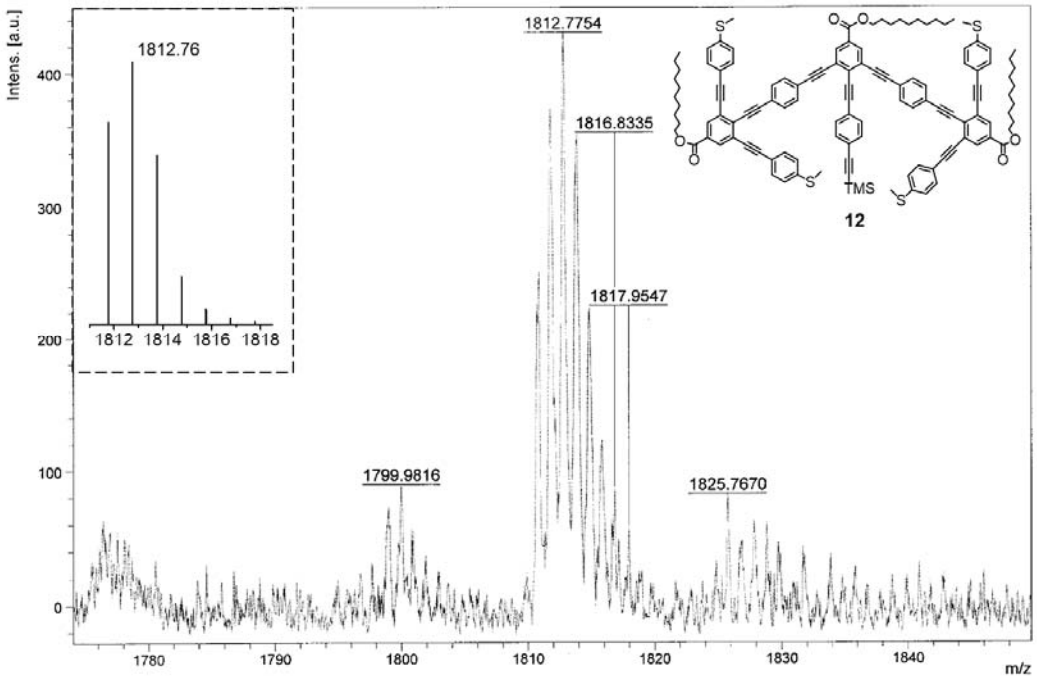
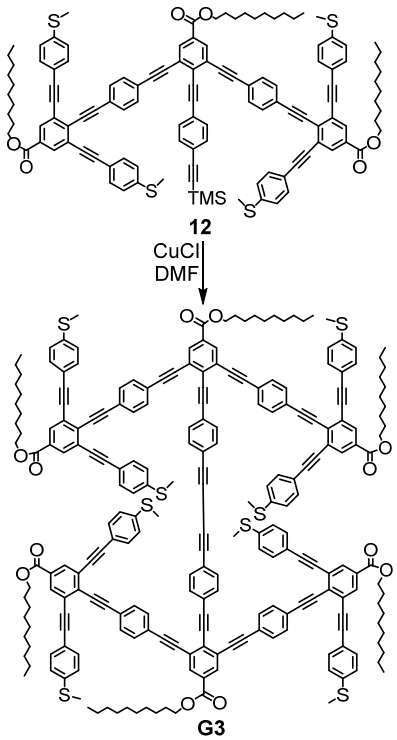


Fig. S36. High resolution mass spectrum (MALDI-TOF) showing the pseudo molecular peak of compound **12**, *m/z* (%): calcd, 1812.76 (100%) for $(M+H)^+$; found, 1812.7754 (100%) $(M+H)^+$. Inset: a simulated isotopic pattern for the **10** $(M+H)^+$ ion.

Synthesis of compound G3.



Silane **12** (50 mg, 27 μmol, 1.00 equiv.) and Cu(I)Cl (11 mg, 110 μmol, 4.00 equiv.) were dissolved in 4 mL of dry dimethylformamide and the solution was stirred vigorously at 60 °C for 5 days. DI Water (30 mL) was added and the mixture was extracted with dichloromethane (3×100 ml). The organic layer was washed with DI water (2×50 ml), dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was further purified by flash chromatography on silica gel (silica gel, 1:2 hexane/CH_2Cl_2) to obtain an orange solid (21 mg, 52 % based on **12**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85-0.89 (t, 9H), 1.26-1.28 (m, 42H), 1.80 (m, 6H), 2.45 (s, 12H), 4.32 (m, 6H), 7.08 (d, *J* = 8.4, 8H), 7.32 (d, *J* = 8.4, 2H), 7.38 (m, 10H), 7.43 (m, 8H), 7.93 (s, 4H), 8.00 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3, 15.4, 22.9, 25.2, 26.3, 28.9, 29.6, 29.6, 29.8, 29.9, 32.1, 65.9, 66.1, 82.5, 87.9, 89.8, 90.2, 94.5, 94.8, 99.9, 100.2, 119.2, 122.7, 123.2, 123.9, 125.7, 126.5, 126.8, 129.8, 129.8, 131.1, 131.8, 131.9, 132.0, 132.2, 132.4, 132.7, 140.5, 164.9, 165.0. IR (neat): 3450(m), 2921(s), 2850(m), 2206(m), 1720(s), 1548(m), 1492(m), 1438(w), 1251(s), 1159(w), 1091(w), 1018(m), 815(s), 768(m), 526(w) cm^{-1}. MALDI-TOF-MS, *m/z* (%): calcd, 3478.435 (100%) $(M+H)^+$; found, 3478.4020 (100%). Anal. Calcd. for $C_{234}H_{218}O_{12}S_8$: C, 80.79; H, 6.32. Found: C, 80.42; H, 6.57.

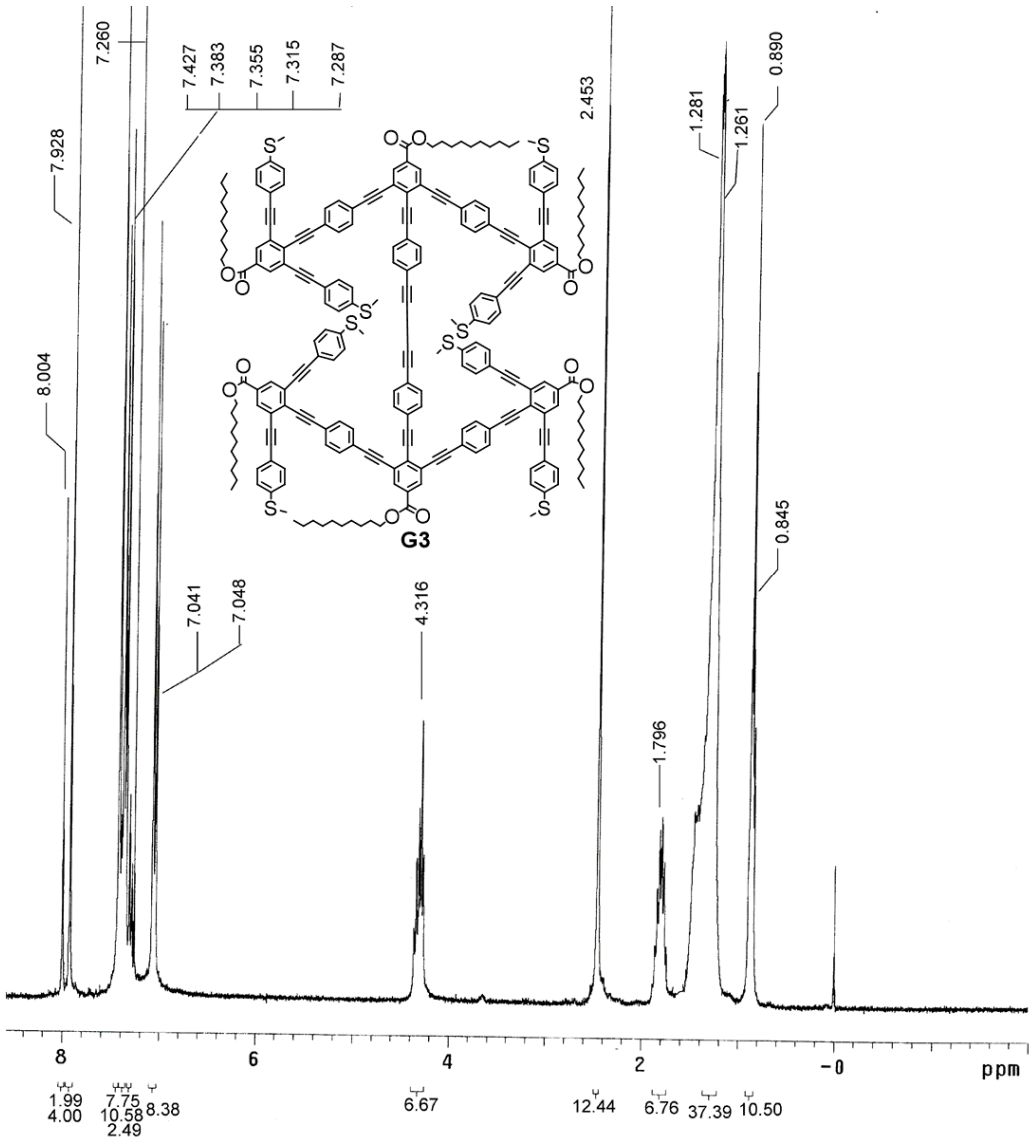


Fig. S37. ^{1}H NMR spectrum of compound **G3** (300 MHz, $CDCl_3$): δ = 0.85-0.89 (t, 9H), 1.26-1.28 (m, 42H), 1.80 (m, 6H), 2.45 (s, 12H), 4.32 (m, 6H), 7.08 (d, *J* = 8.4, 8H), 7.32 (d, *J* = 8.4, 2H), 7.38 (m, 10H), 7.43 (m, 8H), 7.93 (s, 4H), 8.00 (s, 2H).

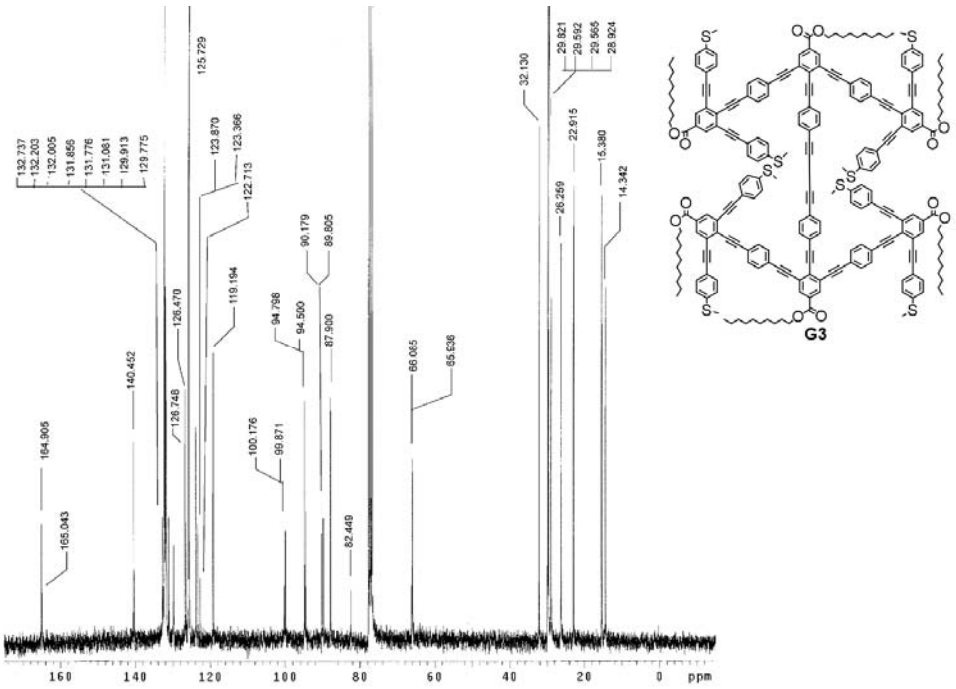


Fig. S38. ^{13}C NMR spectrum of compound **G3** (75 MHz, $CDCl_3$): δ = 14.3, 15.4, 22.9, 25.2, 26.3, 28.9, 29.6, 29.6, 29.8, 29.9, 32.1, 65.9, 66.1, 82.5, 87.9, 89.8, 90.2, 94.5, 94.8, 99.9, 100.2, 119.2, 122.7, 123.2, 123.9, 125.7, 126.5, 126.8, 129.8, 129.8, 131.1, 131.8, 131.9, 132.0, 132.2, 132.4, 132.7, 140.5, 164.9, 165.0.

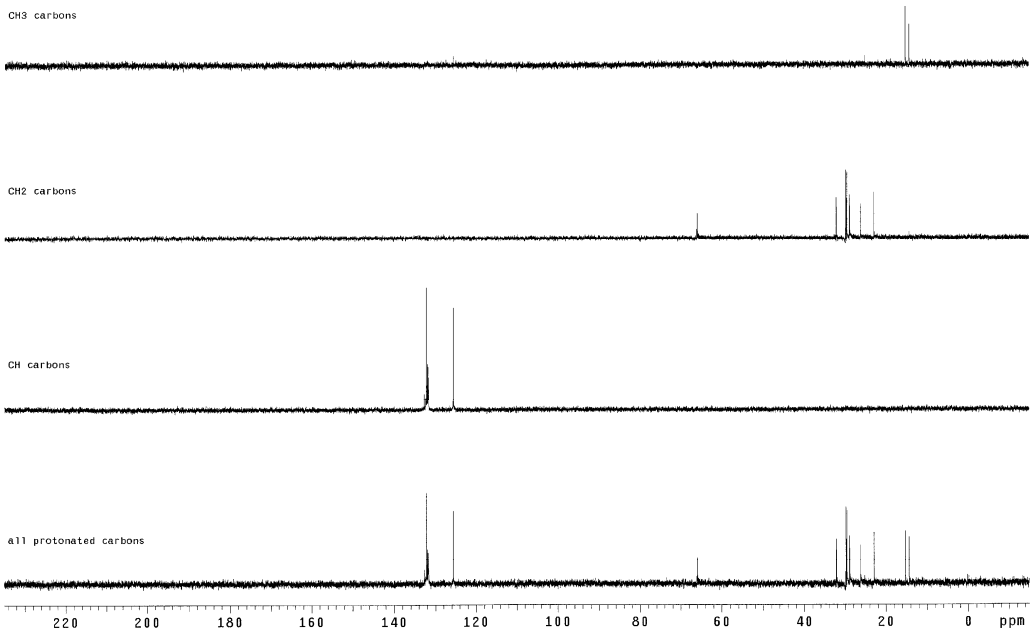


Fig. S39. DEPT ^{13}C NMR spectra of compound **G3** in $CDCl_3$. The carbon signals are assigned to -CH_3. -CH_2, and -CH groups.

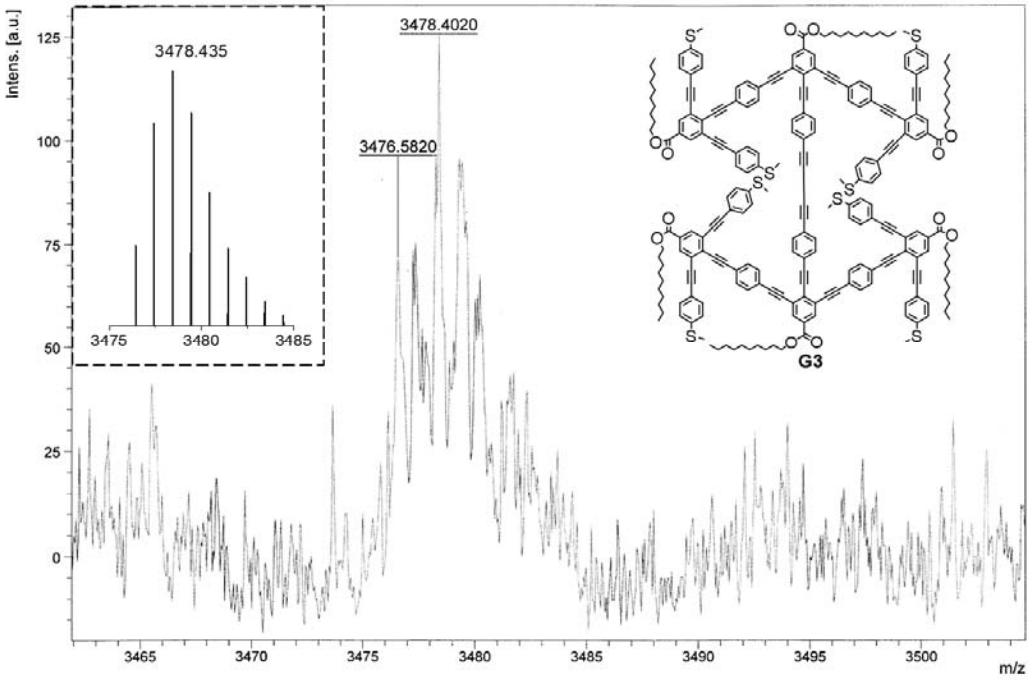


Fig. S40. High-resolution mass spectrum (MALDI-TOF) showing the pseudo molecular peak of **G3**, *m/z* (%): calcd, 3478.435 (100%) $(M+H)^+$; found, 3478.4020 (100%). Inset: simulated isotopic pattern for the **G3** $(M+H)^+$ ion.