Electronic Supplementary Information

A reversible cross-linked polymer network based on conjugated polypseudorotaxanes

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1. General Considerations.

2-(4-Bromophenyl)-1,3-dioxolane[S1], **3**[S2], **6**[S3] and 1,4-bis((2-ethylhexyl)oxy)-1,3-diiodobenzene[S4] were prepared using previously reported procedures, respectively. All reaction operations were performed under an anhydrous Ar atmosphere. Anhydrous tetrahydrofuran (THF) were distilled over Na and benzophenone. Anhydrous diisopropylamine (*i*-Pr_2NH) was dried over CaH_2. All chemicals were used as received without any further treatment. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz or JNM-ECS400 spectrometers with tetramethylsilane (TMS) as an internal standard. Melting points were determined on a Kofler apparatus. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker microTOF-Q II. Matrix-assisted laser desorption/ionization time-of-flight mass spectra were recorded on an autoflexIII smartbeam mass spectrometer (Bruker Daltonics). DLS measurements were performed on a Brookhaven BI-200SM spectrometer. TEM images were acquired with an JEM 2100 microscope operating at 200 kV. Luminescence measurements were made on a Hitachi F-7000 spectrofluorimeter with a xenon lamp as the excitation source. Fluorescence lifetimes in solution were measured by using a commercially available time-correlated single-photon counting instrument (Edinburgh Instruments, model FL920 CDT)

excited with a nanosecond flash lamp. The lifetime data were deconvoluted from the instrumental response and fitted to double-exponential equations.

2. Synthetic Procedures

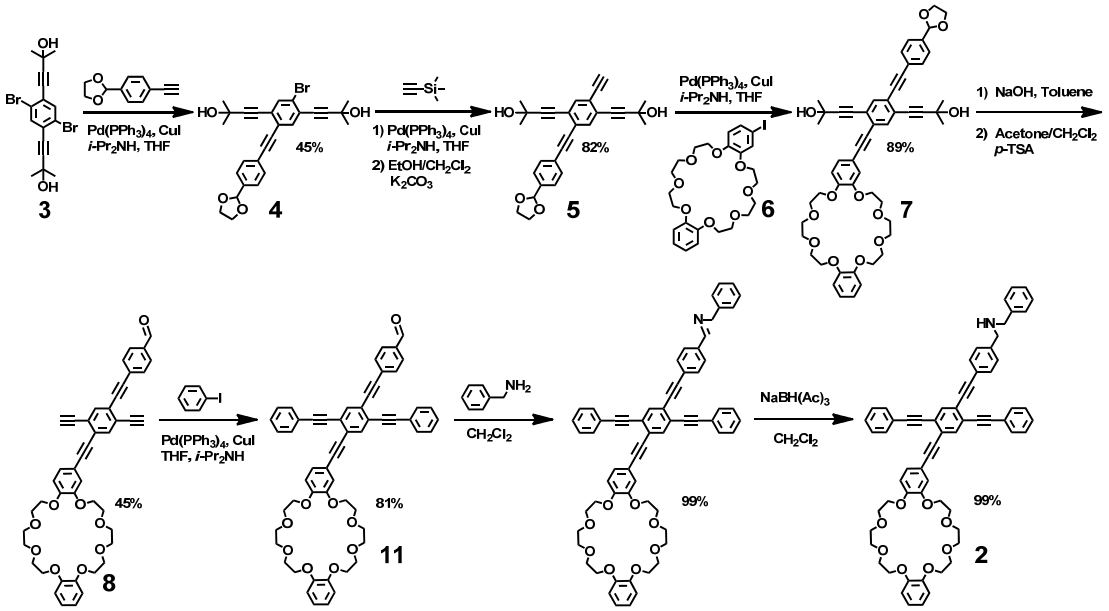

Fig. S1 synthetic routes of monomer **8** and model compound **2**.

2-(4-Ethynylphenyl)-1,3-Dioxolane: 2-(4-bromophenyl)-1,3-dioxolane[S1] (0.458 g, 2 mmol), trimethylsilyl acetylene (0.22g, 2.2 mmol), $Pd(PPh_3)_4$ (120 mg, 0.1 mmol), and CuI (40.0 mg, 0.20 mmol) were dissolved in anhydrous *i*-Pr_2NH (40mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 75 °C overnight. Removal of the solvent and further purification by column chromatograph on silica gel (Ethyl acetate/Petroleum ether = 1/10) to give a yellow solid. The resulting yellow solid was dissolved in EtOH (20 mL) and CH_2Cl_2 (20 mL). K_2CO_3 (0.56 g) was added and the mixture was stirred at r.t. for 3 h. The mixture was filtered, evaporated, and dried under vacuum to give 2-(4-ethynylphenyl)-1,3-dioxolane as a yellow solid (0.279 g, 80% yield, m.p. 46-47 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 3.01 (s, 1H, H_e), 4.03-4.11 (m, 4H, H_d), 5.81 (s, 1H, H_c), 7.45 (d, 2H, *J* = 8.0 Hz, H_a), 7.52 (d, 2H, *J* = 8.0 Hz, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 138.5, 132.1, 126.4, 122.9, 103.1, 83.3, 77.7, 65.3; ESI-MS calcd for $[C_{11}H_{10}O2+Na]^+$ 197.0578, found 197.0812.

4: Solid **3**[S2] (0.96 g, 2.4 mmol), 2-(4-ethynylphenyl)-1,3-dioxolane (0.348 g, 2mmol), $Pd(PPh_3)_4$ (0.12 g, 0.1mmol), and CuI (40.0 mg, 0.20 mmol) were dissolved

in anhydrous THF (40mL) and *i*-Pr_2NH (0.5 g, 5 mmol) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 45 °C overnight. Removal of the solvent and further purification by column chromatograph on silica gel (Ethyl acetate/Petroleum ether = 2/3) to give **4** as a yellow solid (0.445 g, 45% yield, m.p. 64-65 °C). ^{1}H NMR **(**400 MHz, $CDCl_3$, 25 °C) δ = 1.63 (s, 12H, H_h), 2.05 (2H, H_g), 4.06-4.14 (m,4H, H_f), 5.82 (s,1H, H_e), 7.47-7.49 (d, 2H, *J* = 8.0 Hz, H_d), 7.55-7.57 (d, 2H, *J* = 8.0 Hz, H_c), 7.60 (s, 1H, H_b), 7.67 (s, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 138.5, 135.8, 135.7, 135.3, 135.2, 131.6, 127.8, 126.6, 125.9, 124.8, 124.7 123.48, 103.2, 103.1, 100.5, 100.4, 94.2, 86.96, 80.0 79.9, 65.7, 65.6, 65.4, 65.3, 65.2, 31.4, 31.3, 31.2, 31.1; ESI-MS calcd for $[C_{27}H_{25}O_4Br+Na]^+$ 515.0834, found 515.0674.

5: **4** (0.493 g, 1 mmol), trimethylsilyl acetylene (0.13 g, 1.3 mmol), $Pd(PPh_3)_4$ (60 mg, 0.05mmol), and CuI (20.0 mg, 0.10 mmol) were dissolved in anhydrous THF (20mL) and *i*-Pr_2NH (0.3 g, 3mmol) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at at 30 °C for two days. Removal of the solvent and further purification by column chromatograph on silica gel (Ethyl acetate/Petroleum ether = 2/3) to give a yellow solid. The resulting yellow solid was dissolved in EtOH (10 mL) and CH_2Cl_2 (5 mL). K_2CO_3 (0.28 g) was added and the mixture was stirred at r.t. for 3 h. The mixture was filtered and the solvent was evaporated under reduced pressure. Then, the crude sample was further purified by column chromatograph on silica gel (Ethyl acetate/Petroleum ether = 1/1) to give **5** as a yellow solid (0.36 g, 82% yield, m.p. 67.2-68.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 1.63 (s, 12H, H_i), 2.05 (2H, H_h), 3.38 (s, 1H, H_g), 4.06-4.14 (m, 4H, H_f), 5.82 (s, 1H, H_e), 7.48-7.50 (d, 2H, *J* = 8.0 Hz, H_d), 7.55-7.57 (d, 2H, *J* =8.0 Hz, H_c), 7.58 (s, 1H, H_a), 7.60 (s, 1H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 138.4, 135.6, 134.9, 131.7, 126.6, 125.8, 125.3, 124.7, 124.2, 123.5, 103.2, 103.1, 100.0, 99.9, 95.0, 87.4, 82.8, 81.0, 79.7, 79.6, 65.6, 65.3, 31.4, 31.3, 31.2; ESI-MS calcd for $[C_{29}H_{26}O_4+Na]^+$ 461.1729, found 461.2267.

7: **5** (0.439 g, 1 mmol), **6**[S3] (0.69 g, 1.2mmol), $Pd(PPh_3)_4$ (60 mg, 0.05mmol), and CuI (20.0 mg, 0.10 mmol) were dissolved in anhydrous THF (20mL) and *i*-Pr_2NH

(0.3 g, 3mm0l) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 25 °C for 24 hours. After removal of the solvent, the crude sample was further purification by column chromatograph on silica gel (Chloroform/Acetone = 2/3) to give **7** as a yellow solid (0.717 g, 81 % yield, m.p. 70.0-71.2 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 1.64 (s, 12H, H_g), 2.05 (2H, H_f), 3.85 (s, 8H, H_γ), 3.93-3.40 (m, 8H, H_β), 4.06-4.14 (m, 4H, H_f), 4.14-4.16 (m, 8H, H_α) 5.83 (s, 1H, H_e), 6.81-6.83(d, 1H, *J* = 8.0 Hz, H_i), 6.86-6.91 (m, 4H, H_k), 7.07 (s, 1H, H_j), 7.11-7.13 (d, 1H, *J* = 8.0 Hz, H_h), 7.48-7.50 (d, 2H, *J* = 8.0 Hz, H_d), 7.56-7.58 (d, 2H, *J* = 8.0 Hz, H_c), 7.59 (s,1H, H_b), 7.61 (s, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 149.6, 148.7, 148.3, 138.3, 134.8, 134.6, 131.6, 126.5, 125.6, 124.7, 121.5, 116.7, 115.3, 114.1, 113.3, 103.1, 99.8, 95.5, 94.6, 87.7, 86.0, 79.8, 69..6, 69.2, 65.5, 65.3, 31.4; ESI-MS calcd for $[C_{53}H_{56}O_{16}+Na]^+$ 907.3669, found 907.3665.

8: 7 (0.885 g, 1mmol), sodium hydroxide (0.5 g, 12.5 mmol), and toluene (25 ml) were added to a Schlenk tube under argon. And the mixture was stirred at 110 °C overnight. The mixture was filtered and the solvent was evaporated under reduced pressure. Then, the crude sample was further purified by column chromatograph on silica gel (Chloroform/Acetone = 2/3) to give a yellow solid. The resulting yellow solid was dissolved in acetone (10 mL) and CH_2Cl_2 (5 mL). *p*-Toluenesulfonic acid (0.28 g) was added and the mixture was stirred at r.t. for overnight. The resulting yellow solution was washed with water (10 mL), extracted with CH_2Cl_2 (3 × 10 mL), and dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum to give **8** as a yellow solid (0.327 g, 45% yield, m.p. 114.0-115.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 3.47-3.48 (m,2H, H_e), 3.85 (s, 8H, H_γ), 3.94 (m, 8H, H_β), 4.16 (m, 8H, H_α), 6.82-6.84(d, 1H, *J* = 8.0 Hz, H_g), 6.86-6.91 (m, 4H, H_i), 7.07 (s, 1H, H_h), 7.14-7.16 (d, 1H, *J* = 8.0 Hz, H_f), 7.70 (2H, H_c), 7.71 (2H, H_d) 7.88 (d, 2H, H_b), 10.04 (s, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 191.3, 150.0, 148.8, 148.4, 135.8, 135.7, 135.5, 132.3, 129.6, 128.0, 126.7, 125.9, 125.0, 124.6, 124.4, 121.4, 116.8, 115.0, 114.0, 113.2, 96.5, 94.2, 90.6, 85.6, 83.4, 83.2, 80.9, 80.8,

71.2, 69.9, 69.5, 69.4, 69.3； ESI-MS calcd for $[C_{45}H_{40}O_9+Na]^+$ 747.2570, found 747.2554.

9: 1,4-bis((2-ethylhexyl)oxy)-1,3-diiodobenzene[S4] (0.137 g, 0.233 mmol), **8** (0.169 g, 0.233 mmol), $Pd(PPh_3)_4$ (13 mg, 11.65 μmol), and CuI (4.4 mg, 23.30 umol) were dissolved in anhydrous THF (20 mL) and *i*-Pr_2NH (5 ml) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 45 °C for three days. Upon cooling to room temperature, the solution was concentrated to a small volume and precipitated into methanol (200 mL), leading to the formation of a yellow solid. This dissolution-precipitation process was repeated for three times to give **10** as a yellow solid (181 mg, 74% yield, M_n = 18.5 kDa, PDI = 1.86). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 0.87 (br, 12H, $H_{p,q}$), 1.27 (br, 16H, H_{l-o}), 1.69 (br, 2H, H_k), 3.81 (m, 8H, H_γ), 3.84 (s, 4H, H_k), 3.90 (m, 8H, H_β), 4.01 (m, 2H, $H_{\alpha 1}$), 4.14 (m, 6H, $H_{\alpha \alpha'}$), 6.79 (d, 1H, J = 8.4 Hz, H_h), 6.86-6.91 (m, 4H, H_i), 7.01 (s, 1H, H_g), 7.01-7.08 (m, 2H, H_e), 7.16 (d, 1H, J = 8.4 Hz, H_f), 7.71-7.73 (2H, H_c) 7.73-7.75 (2H, H_d) , 7.85-7.87 (2H, H_b), 10.02 (s, 1H).

10: 9 (120 mg) and benzylamine were dissolved in anhydrous THF (15 mL) and in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 40 °C for two days. The *in-situ* ^{1}H NMR spectra revealed that the reaction conversion was larger than 99%. Upon cooling to room temperature, the solution was concentrated to a small volume and precipitated into methanol (200 mL), leading to the formation of a yellow solid. The solid was dissolved in CH_2Cl_2 (20 mL) and washed with a 5% K_2CO_3 aqueous solution. After drying over MgSO4, the solvent was removed under a reduced pressure. The residue was redissolved in a small volume of CH_2C1_2 and precipitated into a large volume of acetone. This polymer was further purified by the two dissolution-precipitation cycles. The precipitate was separated, washed with acetone and dried *in vacuo.* The polymer **10** was obtained as a yellow solid (119 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 0.82 (br, 12H, $H_{t,u}$), 1.25 (br, 16H, H_{p-s}), 1.69 (br, 2H, H_o), 3.80 (m, 8H, H_γ), 3.84 (m, 4H, H_c),

3.90 (m, 8H, H_{β}), 3.99 (m, 2H, $H_{\alpha 1}$), 4.13 (m, 6H, $H_{\alpha \alpha'}$), 4.83 (s, 2H, H_a), 6.77 (d, 1H, J = 8.4Hz, H_e), 6.86 (m, 4H, H_g)7.00 (s, 1H, H_f), 7.07 (m, 2H, H_o), 7.15 (d, 1H, J = 8.4Hz, H_d), 7.31-7.34 (m, 5H, $H_{l\text{-}n}$), 7.62 (2H, H_j), 7.71-7.73 (2H, H_h) 7.75-7.77 (2H, H_k), 8.36 (s, 1H, H_b).

1: 9 (115mg) and sodium triacetoxyborohydride were dissolved in anhydrous CH_2Cl_2 (20 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 35 °C for two days. The *in-situ* ^{1}H NMR spectra revealed that the reaction conversion was larger than 99%. Upon cooling to room temperature, the solution was filtered, concentrated to a small volume, and precipitated into methanol (200 mL), leading to the formation of a yellow solid. The polymer was further purified by the two dissolution-precipitation cycles. The polymer **1** was obtained as a yellow solid (107 mg, 93% yield). ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ = 0.76 (br, 12H, $H_{t,u}$), 1.19 (br, 16H, $H_{p\text{-}s}$), 1.60 (br, 2H, H_o) 3.66 (m, 8H, H_{γ}), 3.68 (m, 4H, $H_{a,b}$), 3.71 (m, 12H, $H_{\beta,o}$), 3.88 (m, 2H, $H_{\alpha 1}$), 4.02 (m, 6H, $H_{\alpha \alpha'}$), 6.73 (1H, H_e) 6.79 (m, 4H, H_g), 6.95 (s, 1H, H_f), 7.03 (s, 2H, H_i), 7.09 (s, 1H, H_d), 7.16 (s, 1H, H_n), 7.24-7.30 (m, 6H, $H_{k\text{-}m}$), 7.48 (m, 2H, H_j), 7.64 (m, 2H, H_h).

11: Iodobenzene (0.137 g, 0.233 mmol), **8** (0.169 g, 0.233 mmol), $Pd(PPh_3)_4$ (13 mg, 11.65 μmol), and CuI (4.4 mg, 23.30 μmol) were dissolved in anhydrous THF (20 mL) and *i*-Pr_2NH (0.2 g, 2 mmol) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 45 °C for one day. After removal of the solvent, the crude product was further purified by column chromatograph on silica gel (Chloroform/Acetone = 2/3) to give **11** as a yellow solid (166 mg, 81 % yield, m.p. 125-126 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 3.85 (m, 8H, H_{α}), 3.94 (m, 8H, H_{β}), 4.01 (s, 2H, $H_{\alpha 1}$), 4.16 (m, 6H, $H_{\alpha \alpha'}$), 6.82 (d, 1H, J = 8.0 Hz, H_i), 6.89 (m, 4H, H_k), 7.01 (s, 1H, H_j), 7.15 (d, 1H, J = 8.0 Hz, H_h), 7.46-7.36 (m, 6H, $H_{g,h}$), 7.58 (m, 4H, H_e), 7.72 (d, 2H, H_c), 7.77 (d, 2H, H_d), 7.88 (d, 2H, H_b),10.04 (s, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 191.5, 149.9, 149.0, 148.8, 135.0, 134.7, 133.1, 132.3, 132.2, 132.1, 132.0, 131.9, 131.8, 131.7,

129.8, 129.3, 129.0, 128.9, 128.6, 128.5, 128.2, 126.5, 124.1, 123.1, 123.0, 122.9, 121.5, 116.5, 114.0, 113.2, 95.8, 95.6, 91.6, 87.6, 87.4, 71.5, 71.4, 70.0, 69.5, 69.4. ESI-MS calcd for $[C_{45}H_{40}O_9+Na]^+$ 899.3196, found 899.3211.

12: 11 (160 mg, 0.205 mmol) and benzylamine (44 mg, 0.41 mmol) were dissolved in anhydrous THF (10 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 40 °C for a day. The *in-situ* ^{1}H NMR spectra revealed that the reaction conversion was larger than 99%. The solvent was removed under a reduced pressure. The crude product was recrystallised from dichloromethane and methanol. Compound **12** was isolated as a yellow solid (162 mg, 92% yield, m.p. 130-131 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 3.84 (m, 8H, H_γ), 3.92 (m, 8H, H_β), 4.01 (m, 2H, $H_{\alpha 1}$), 4.16 (m, 4H, $H_{\alpha\alpha'}$), 4.85 (s, 2H, H_b), 6.80-6.82 (d, 1H, *J* = 8.0 Hz, H_n) 6.86-6.91 (m, 4H, H_p) 7.01 (s, 1H, H_o) 7.13-7.15 (d, 1H, *J* = 8.0 Hz, H_m), 7.29 (m, 1H, H_l), 7.33-7.37 (m, 10H, H_{h-k}), 7.57-7.60 (m, 4H, H_g) 7.60-7.62 (m, 2H, H_f), 7.74-7.75 (m, 2H, $H_{c,d}$), 7.77-7.79 (d, 2H, H_e), 8.40 (s, 1H, H_a); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) *δ* = 160.1, 148.8, 148.0, 147.5, 133.8, 133.5, 130.7, 127.7, 127.4, 127.2, 126.1, 124.6, 124.4, 124.3, 124.2, 122.1, 120.4, 115.6, 113.1, 112.3, 94.9, 94.4, 94.2, 86.7, 86.6, 86.4, 85.4, 70.4, 70.3, 69.0, 68.8, 68.4, 68.3, 64.1; ESI-MS calcd for $[C_{64}H_{56}NO_8+Na]^+$ 989.3904, found 989.3877.

2: 12 (154 mg，0.159 mmol) and sodium triacetoxyborohydride (67 mg, 0.32 mmol) were dissolved in anhydrous CH_2Cl_2 (20 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting solution was allowed to stir at 35 °C for two days. The *in-situ* ^{1}H NMR spectra revealed that the reaction conversion was larger than 99%. The solvent was removed under a reduced pressure. The crude product was recrystallised from dichloromethane and methanol. Compound **2** was isolated as a yellow solid (0.145 mg, 94% yield, m.p. 134-135 °C). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ = 7.68 (s, 1H, H_c), 7.66 (s, 1H, H_d), 7.53 (m, 4H, H_e), 7.47-7.49 (2H, H_f), 7.32 (m, 8H, H_{g-i}), 7.27 (m, 4H, $H_{j,k}$), 7.18 (m, 1H, H_l), 7.09 (m,1H, H_o), 6.96 (dd, 1H, H_m), 6.80 (m, 4H, H_p) 6.77 (d, 1H, H_n), 4.07- 4.03 (m, 6H, $H_{\alpha\alpha'}$), 3.93 (m, 2H, $H_{\alpha 1}$),

3.80 (3.80, 8H, H_{β}), 3.76 (br, 4H, $H_{a,b}$), 3.69 (m, 8H, H_{γ}); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) δ = 149.8，149.0, 148.5, 134.8, 134.5, 131.8, 131.7, 128.7, 128.4, 128.2, 127.1, 125.4, 123.1, 123.0, 121.6, 121.4, 116.6, 115.5, 114.1, 113.3, 95.9, 95.4, 95.2, 87.7, 87.6, 87.4, 86.4, 71.4, 71.3, 70.0, 69.8, 69.7, 69.4, 69.3; ESI-MS calcd for $[C_{64}H_{57}NO_8+Na]^+$ 990.3982, found 990.4005.

3. Details of the experiments for cross-linking / de-crosslinking.

Details of the experiments for cross-linking/de-crosslinking in fluorescence titration experiment: **A.** 20.7 mg 60% HFA aqueous solution were dissolved in 20 ml CH_3CN, resulting in a CH_3CN solution of HFA with a concentration of 4.25×10^{-3}mol/L. The solution of **1** (1.7×10^{-5} mol/L, 2 mL) was treated stepwise with the above HFA solution. **B.** 21.5 mg P_1-*t*-Bu were dissolved in 13 ml CH_2Cl_2, resulting in a CH_2Cl_2 solution of P_1-*t*-Bu with a concentration of 4.25×10^{-3} mol/L. The solution was used to titrate the solution of HFA-**1**.

Dissolution of 60% HFA aqueous solution in CD_3CN and P_1-*t*-Bu in CD_2Cl_2 were used to carry out ^1H NMR experiments for cross-linking/de-crosslinking.

The system was not biphase and 60% HFA aqueous solution were dissolved in acetonitrile. The 60% HFA aqueous solution were purchased from Alfa Aesar.

4. Additional Experimental Data and Figures.

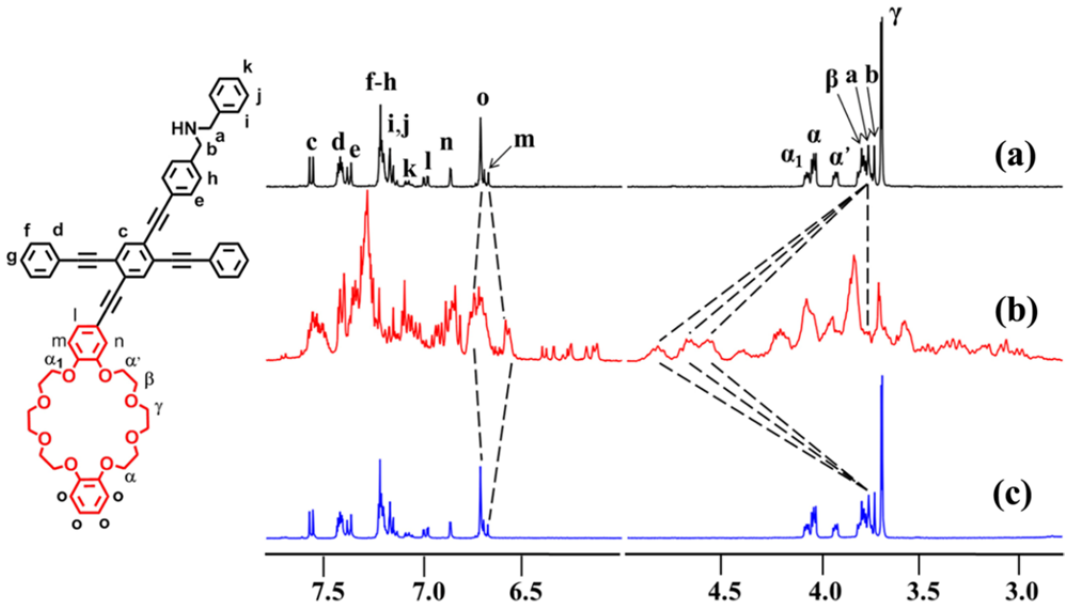

Fig. S2 Left: Chemical struture of **2**. Right: ^{1}H NMR spectra (400 MHz, in CD_2Cl_2, 2.0×10^{-3} mol L^{-1}) recorded on **2** (a), HFA-**2** produced by adding 1.1 eq of HFA into the solution of **2** (b), and **2** obtained by treating 1.2 eq of P_1-*t*-Bu to HFA-**2** (c).

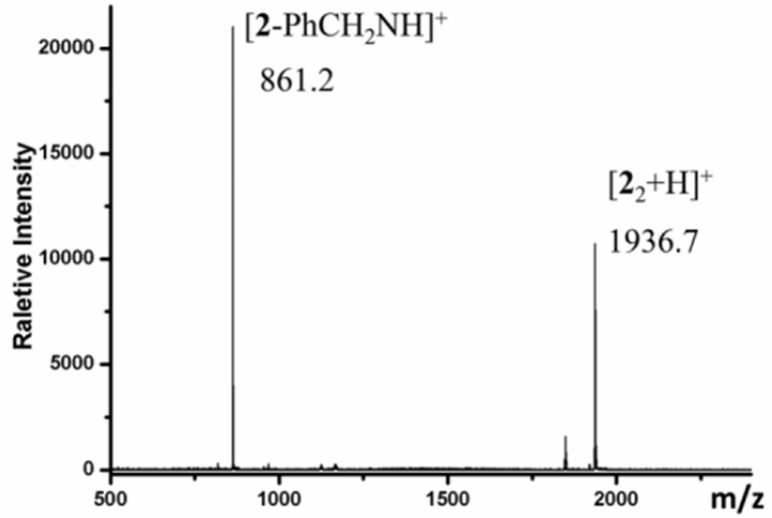

Fig. S3 MALDI-TOF mass spectrum of HFA-**2** measured in the positive-ion mode using CH_2Cl_2 as the solvent.

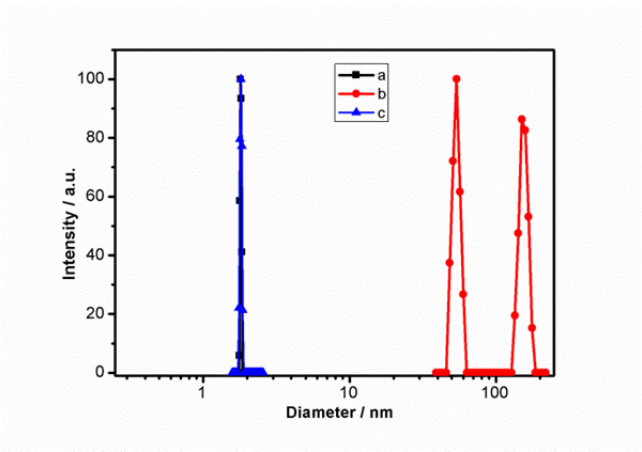

Fig. S4 DLS plots of a) **2** (in CH_2Cl_2, 2.0×10^{-3} mol L^{-1} for the DB24C8 group), b) HFA-**1** produced by adding 1 eq of HFA into the solution of **2**, c) **2** obtained by treating HFA-**2** with 1.1 eq of P_1-*t*-Bu.

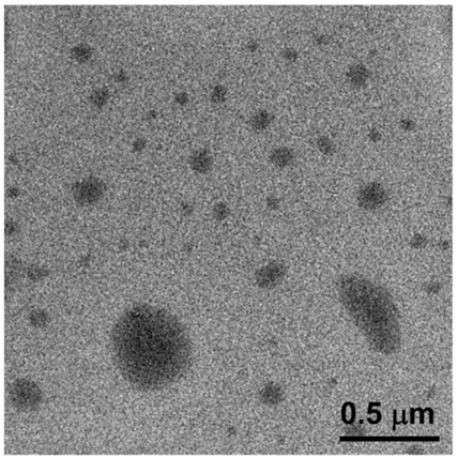

Fig. S5 A TEM image of HFA-**2** as drop cast onto a carbon-coated copper grid at the DB24C8 concentration of 2×10^{-3} mol L^{-1}.

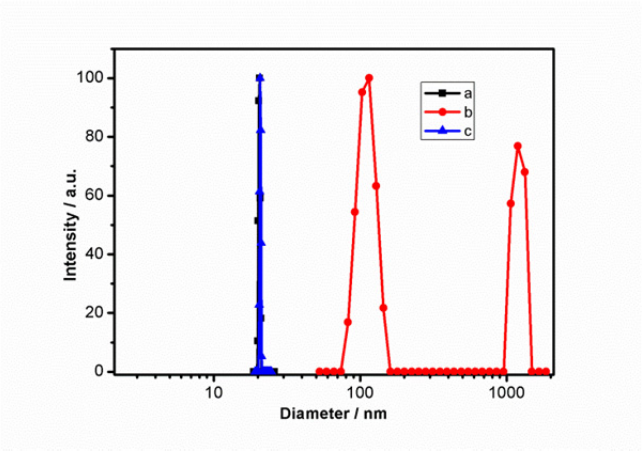

Fig. S6 DLS plots of a) **1** (in CH_2Cl_2, 2.0×10^{-3} mol L^{-1} for the DB24C8 group), b) HFA-**1** produced by adding 1 1.1 eq of HFA into the solution of **1**, c) **1** obtained by treating HFA-**1** with 1.1 eq of P_1-*t*-Bu.

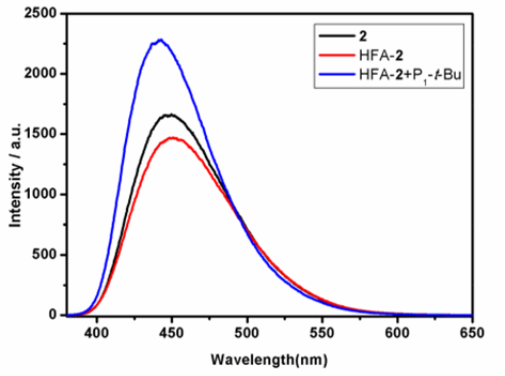

Fig. S7 Fluorescence spectra of **2** (2.5×10^{-5} mol L^{-1}) upon titration with 1.1 eq of HFA and 1.2 eq of P_1-*t*-Bu.

Table S1. Luminescence Lifetimes [a] (τ_1 and τ_2) for **1** and TFA-**1**.

Sample	τ_1 (ns)	RW_1 (%) [b]	τ_2 (ns)	RW_2 (%) [b]
1	0.55±0.06	38.65±1.93	1.12±0.11	61.35±3.07
HFA-**1** [c]	0.66±0.07	55.16±2.76	1.32±0.13	44.84±2.24
1 [d]	0.49±0.05	32.90±1.63	1.07±0.11	67.10±3.36

[a] 1.7×10^{-5} mol L^{-1} CH_2Cl_2 solutions (for the DB24C8 group) monitored at 483 nm upon excitation at 360 nm. [b] Relative weighting (RW) of components in double exponential fits. [c] Produced by adding 1.0 eq of HFA into the solution of **1**. [d] Produced by adding 1.1 eq of P_1-*t*-Bu into the solution of HFA-**1**.

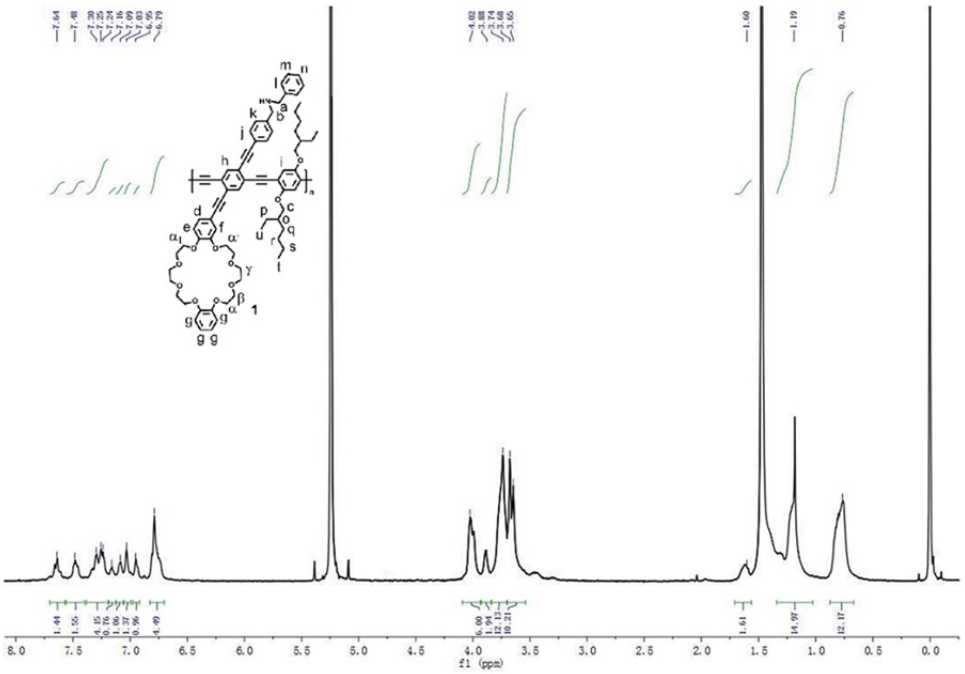

Fig. S8 ^{1}H NMR spectrum (600 MHz, in CD_2Cl_2, 25 °C) of **1**.

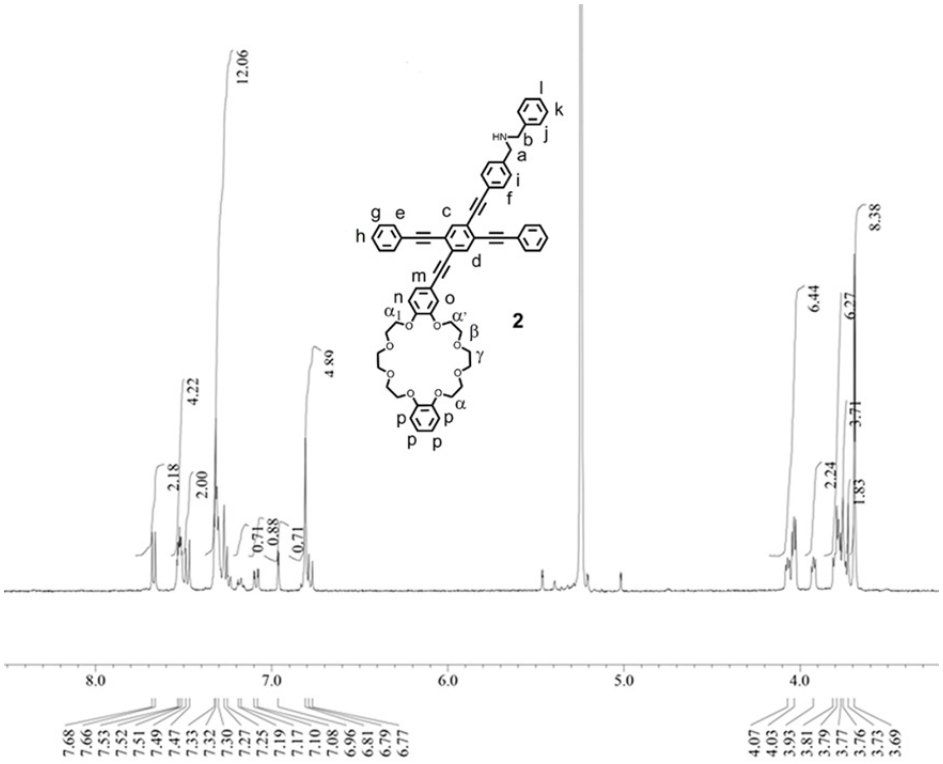

Fig. S9 ^{1}H NMR spectrum (400 MHz, in CD_2Cl_2, 25 °C) of **2**.

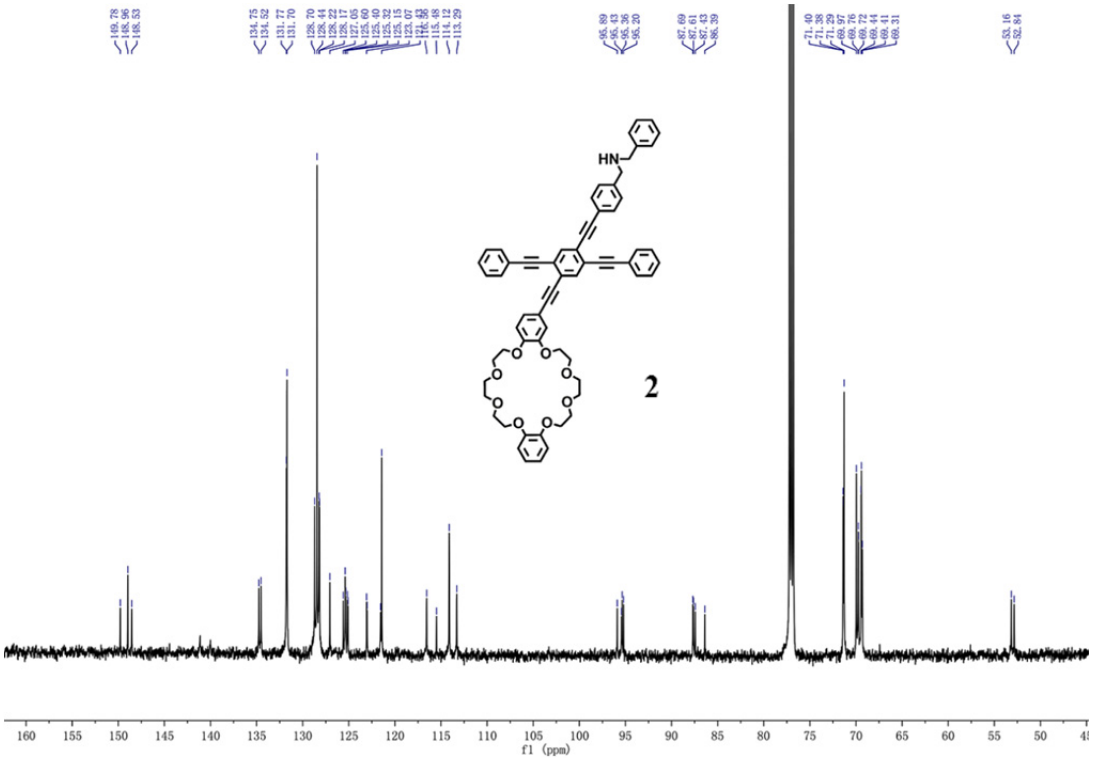

Fig. S10 ^{13}C NMR spectrum (150 MHz, in $CDCl_3$, 25 °C) of **2**.

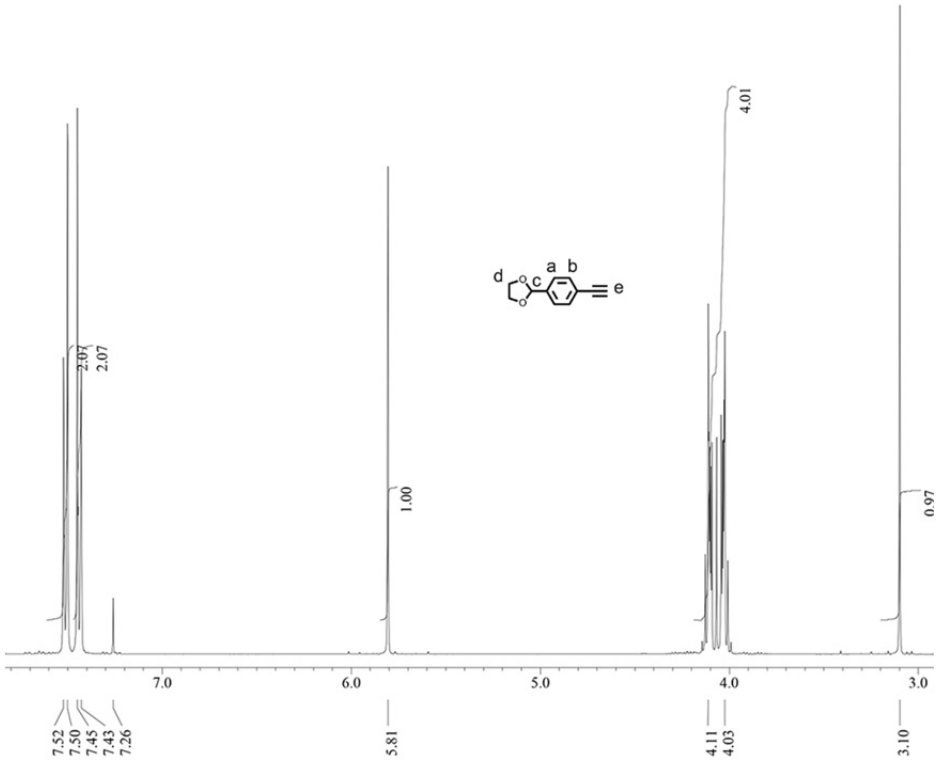

Fig. S11 ^{1}H NMR spectrum (400 MHz, in CDCl3, 25 °C) of 2-(4-Ethynylphenyl)-1,3-Dioxolane.

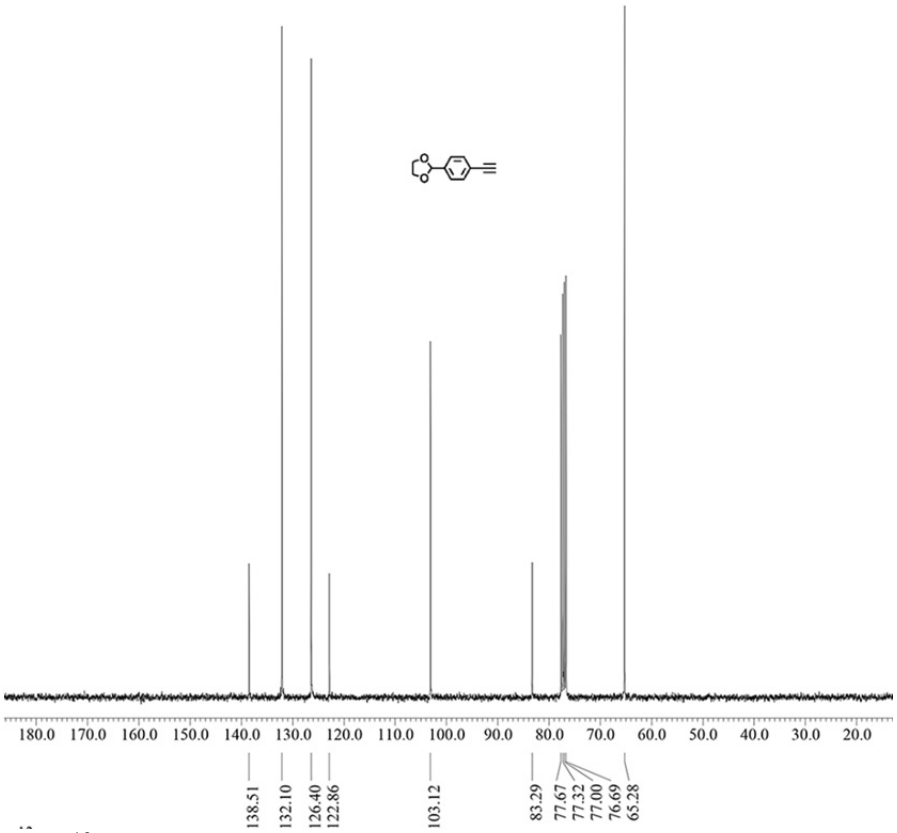

Fig. S12 ^{13}C NMR spectrum (100 MHz, in CDCl3, 25 °C) of 2-(4-Ethynylphenyl)-1,3-Dioxolane.

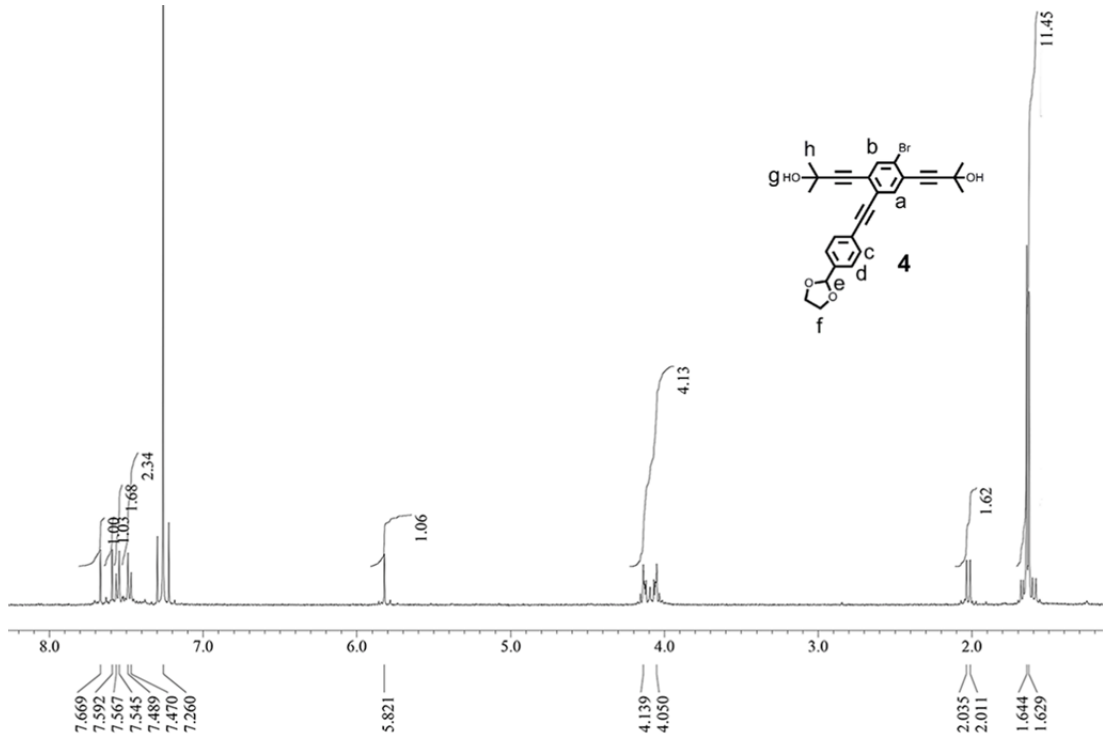

Fig. S13 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **4**.

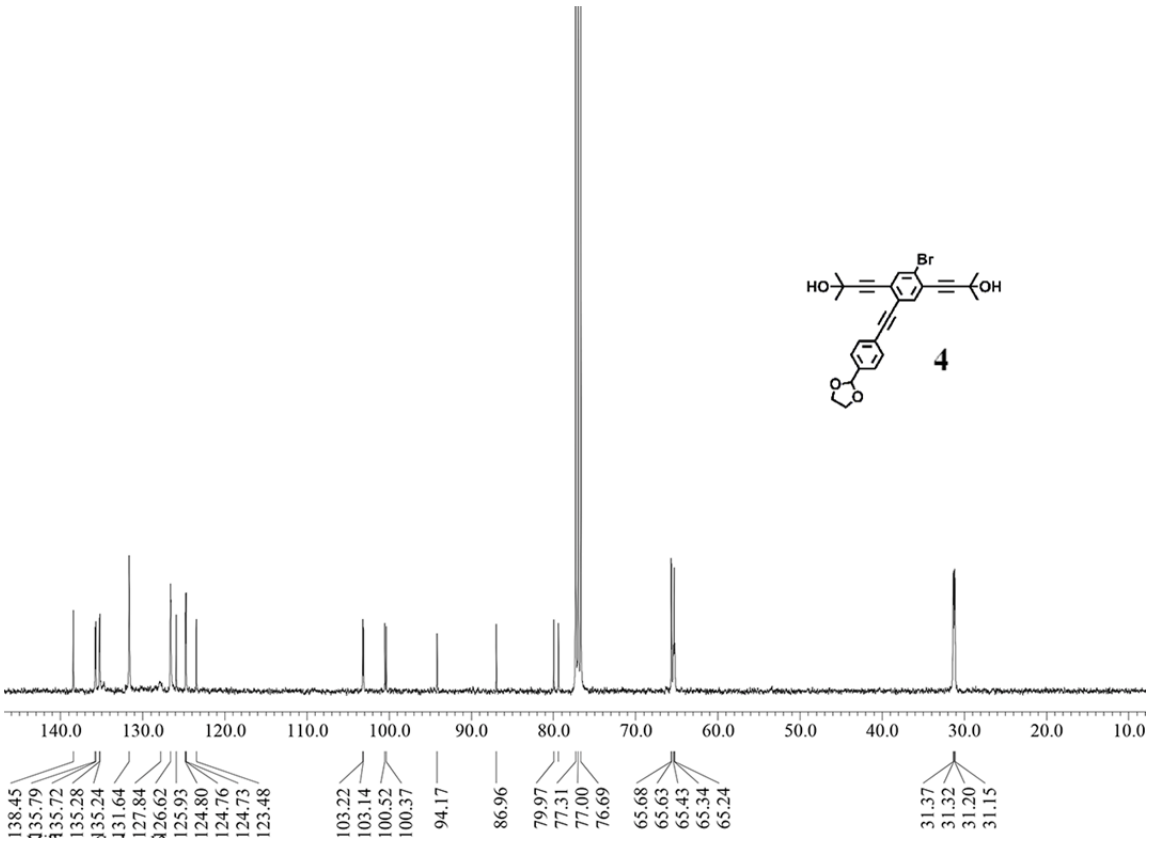

Fig. S14 ^{13}C NMR spectrum (100 MHz, in $CDCl_3$, 25 °C) of **4**.

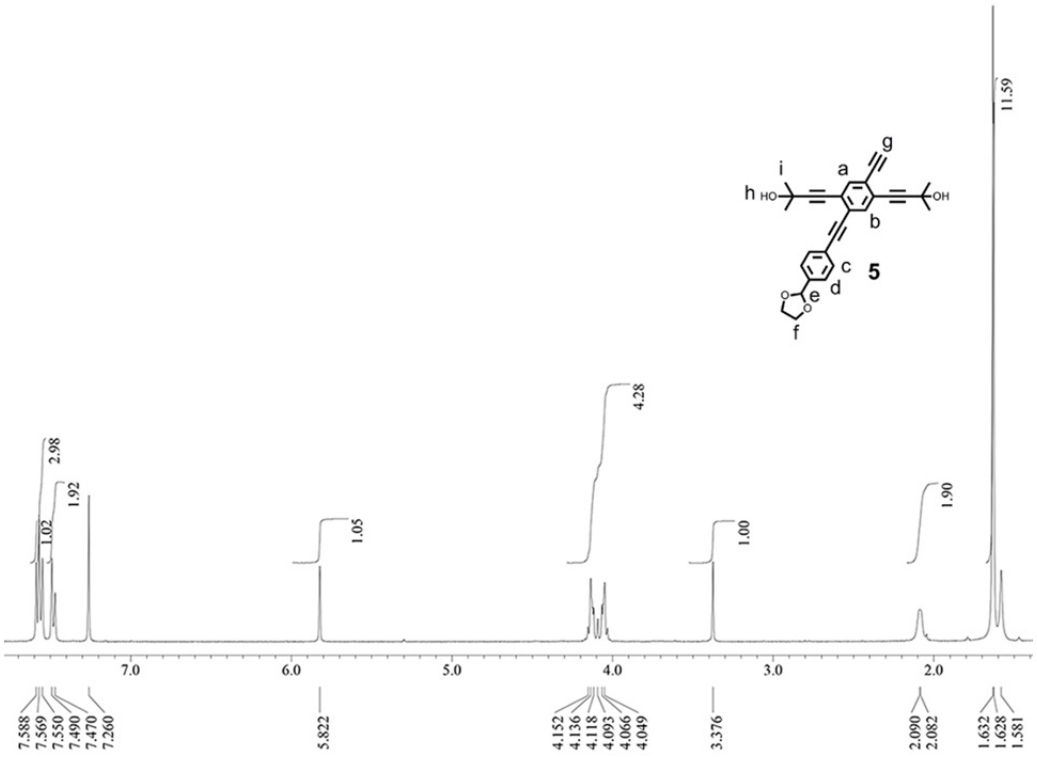

Fig. S15 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **5**.

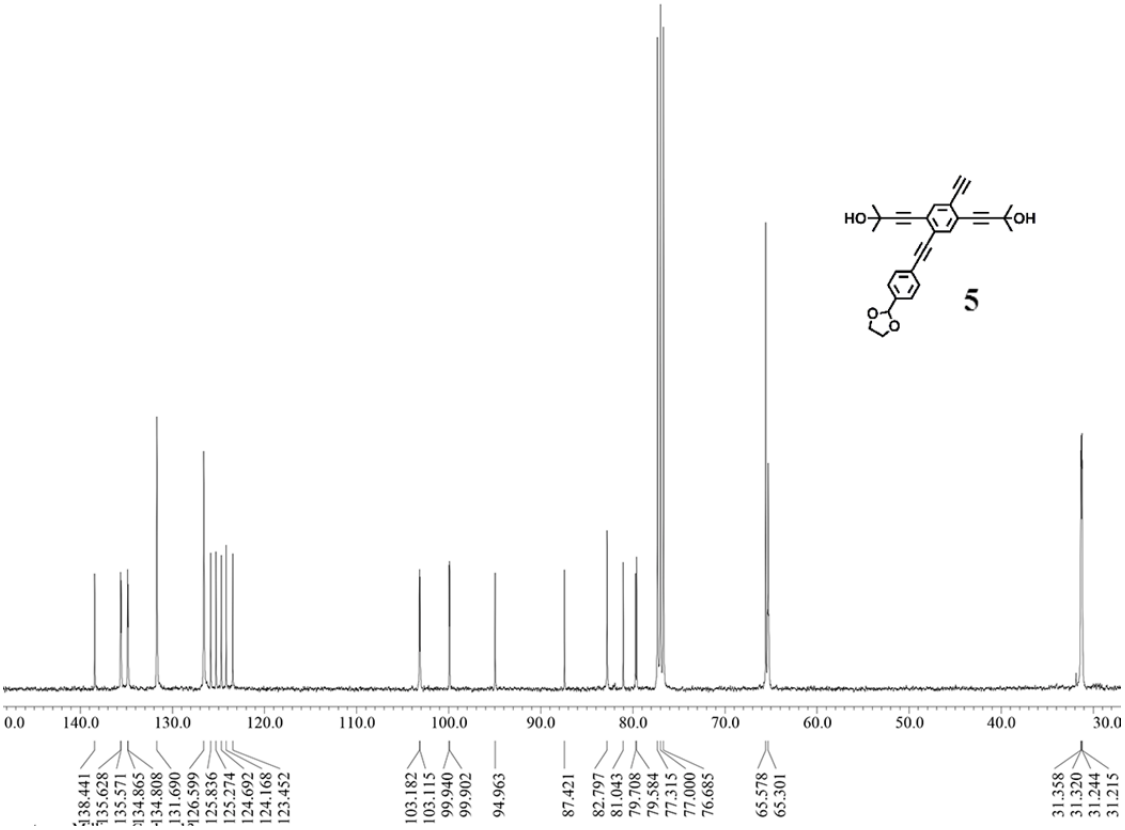

Fig. S16 ^{13}C NMR spectrum (100 MHz, in $CDCl_3$, 25 °C) of **5**.

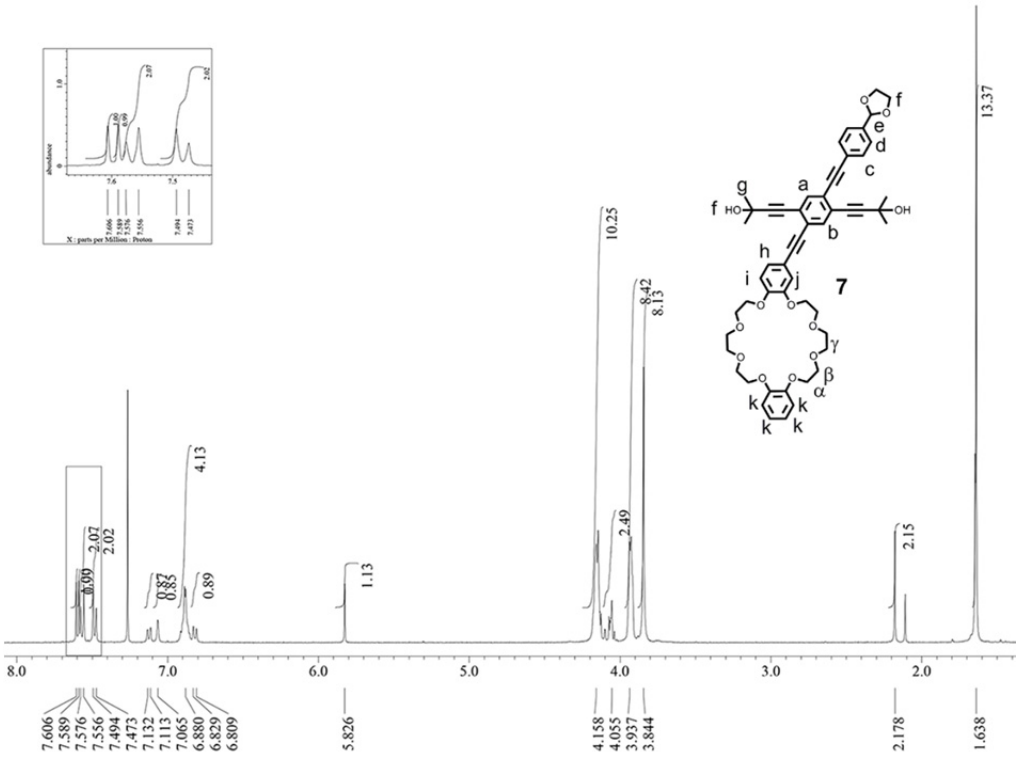

Fig. S17 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **7**.

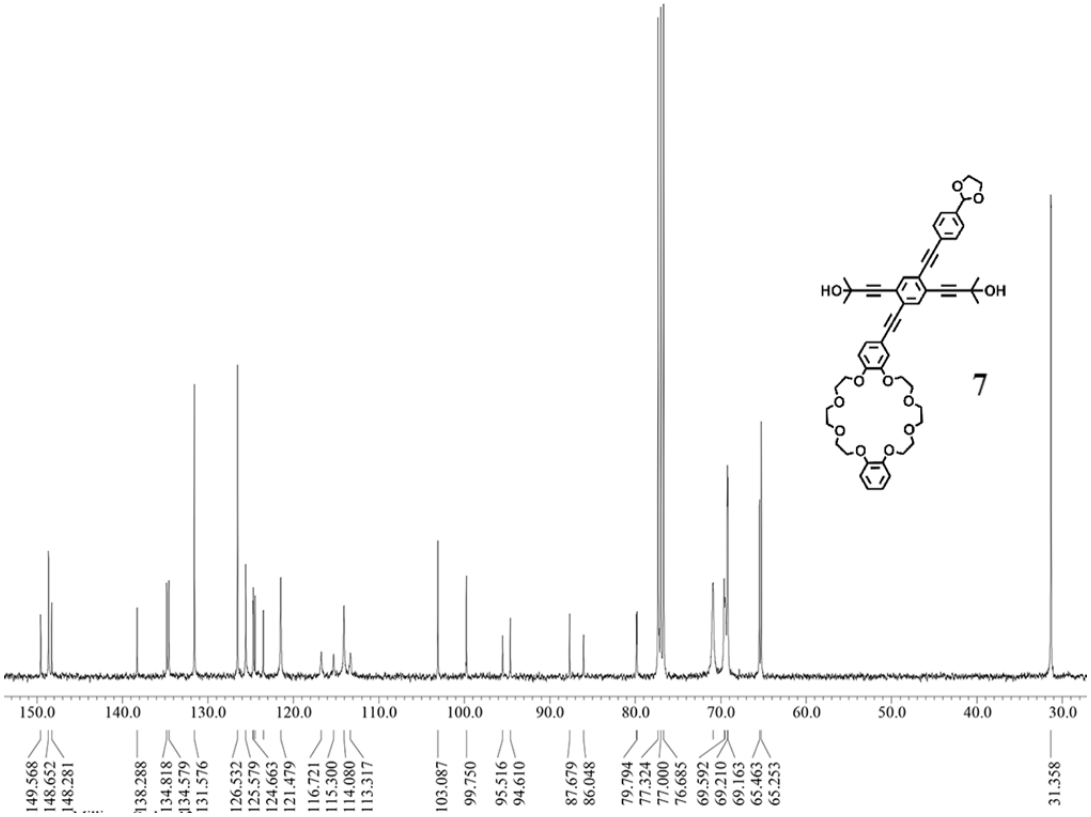

Fig. S18 ^{13}C NMR spectrum (100 MHz, in $CDCl_3$, 25 °C) of **7**.

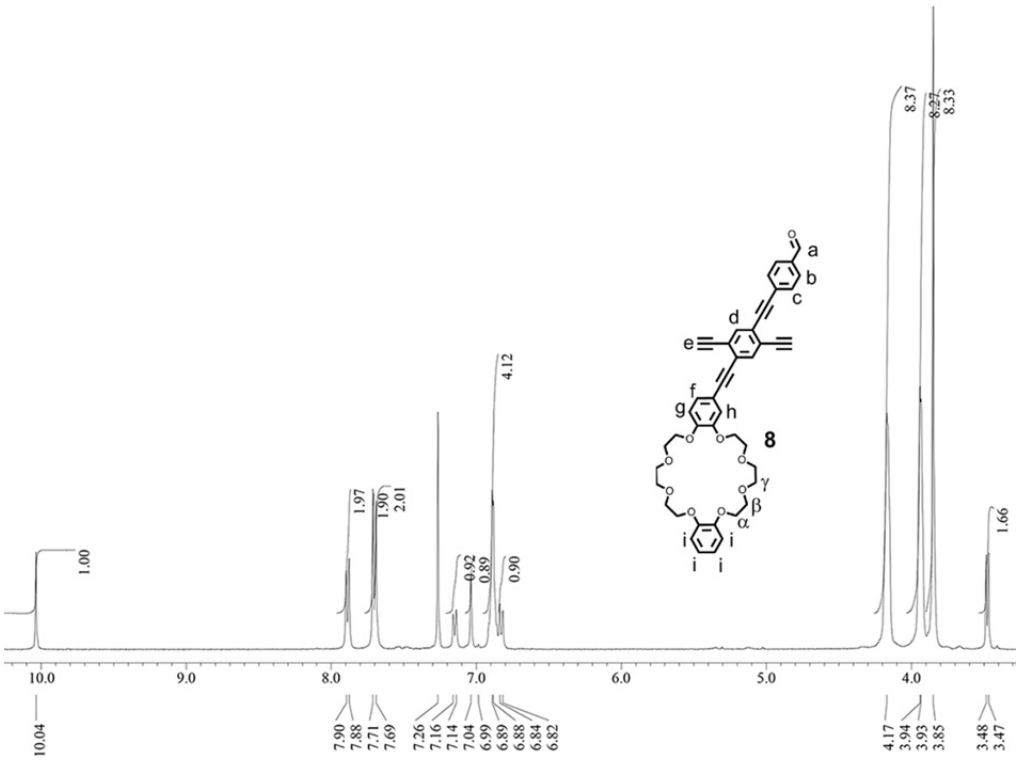

Fig. S19 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **8**.

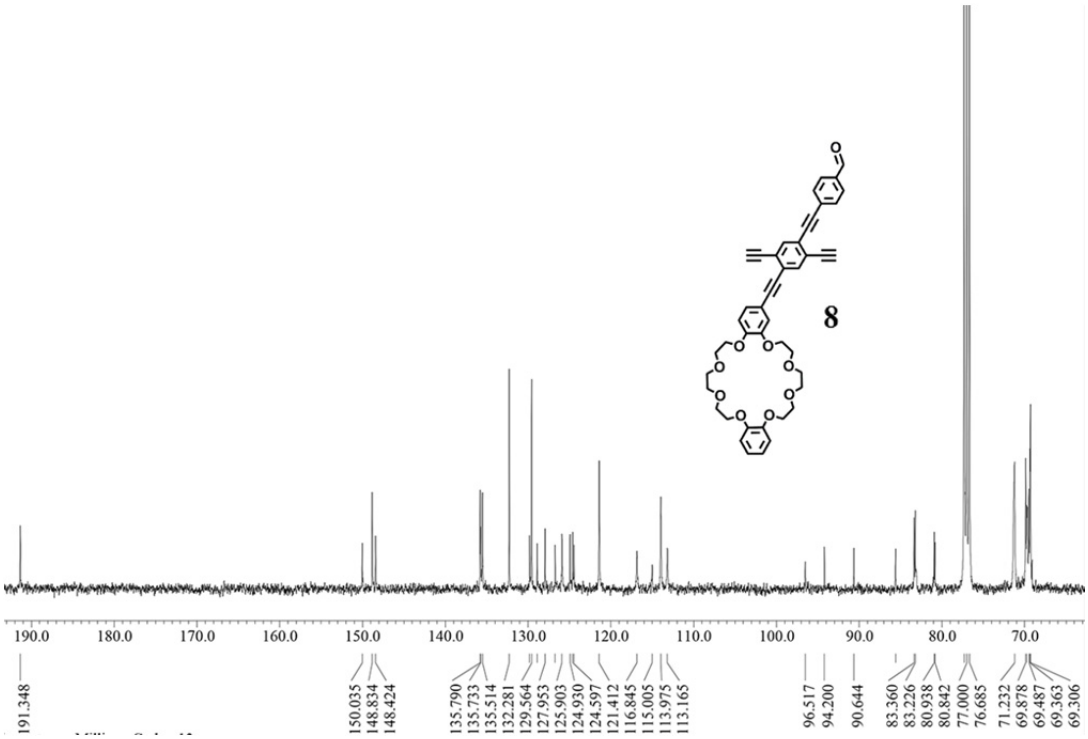

Fig. S20 ^{13}C NMR spectrum (100 MHz, in $CDCl_3$, 25 °C) of **8**.

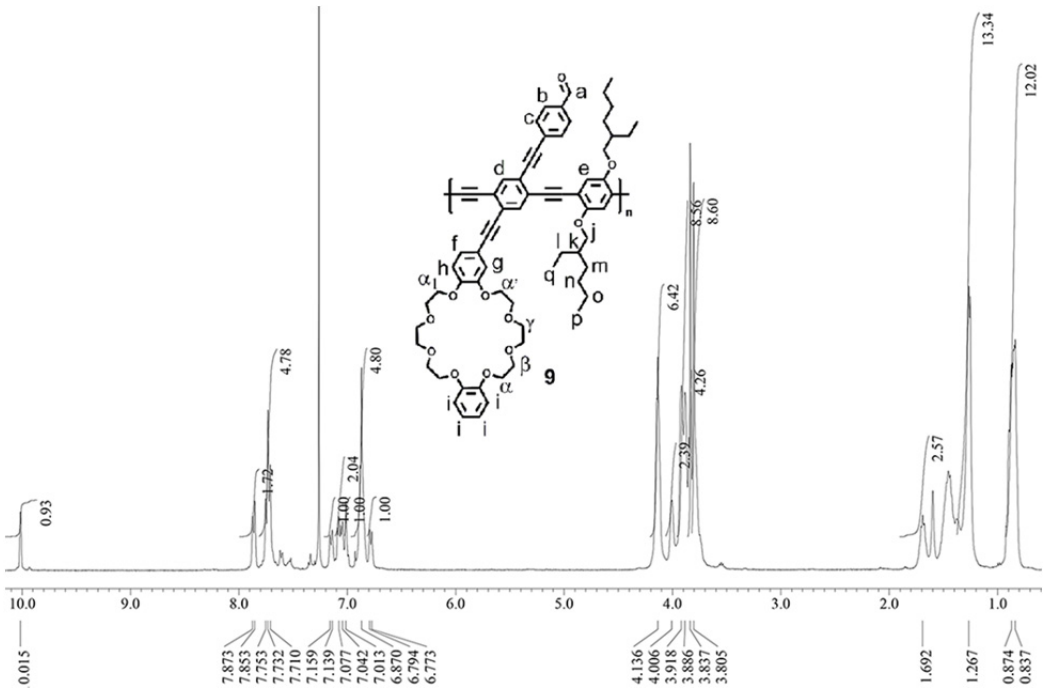

Fig. S21 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **9**.

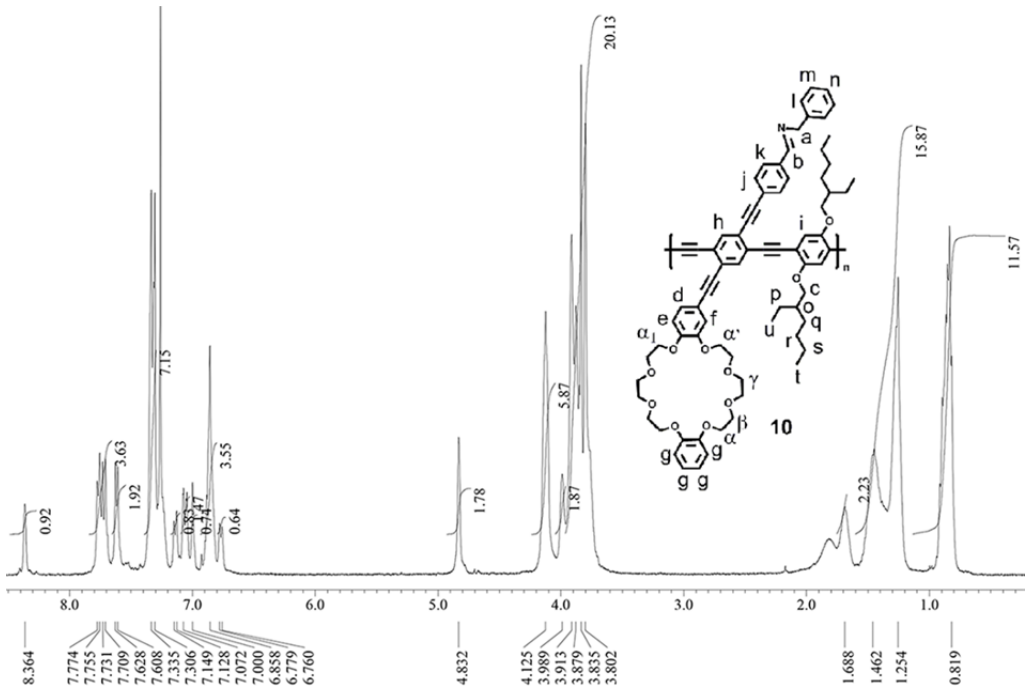

Fig. S22 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **10**.

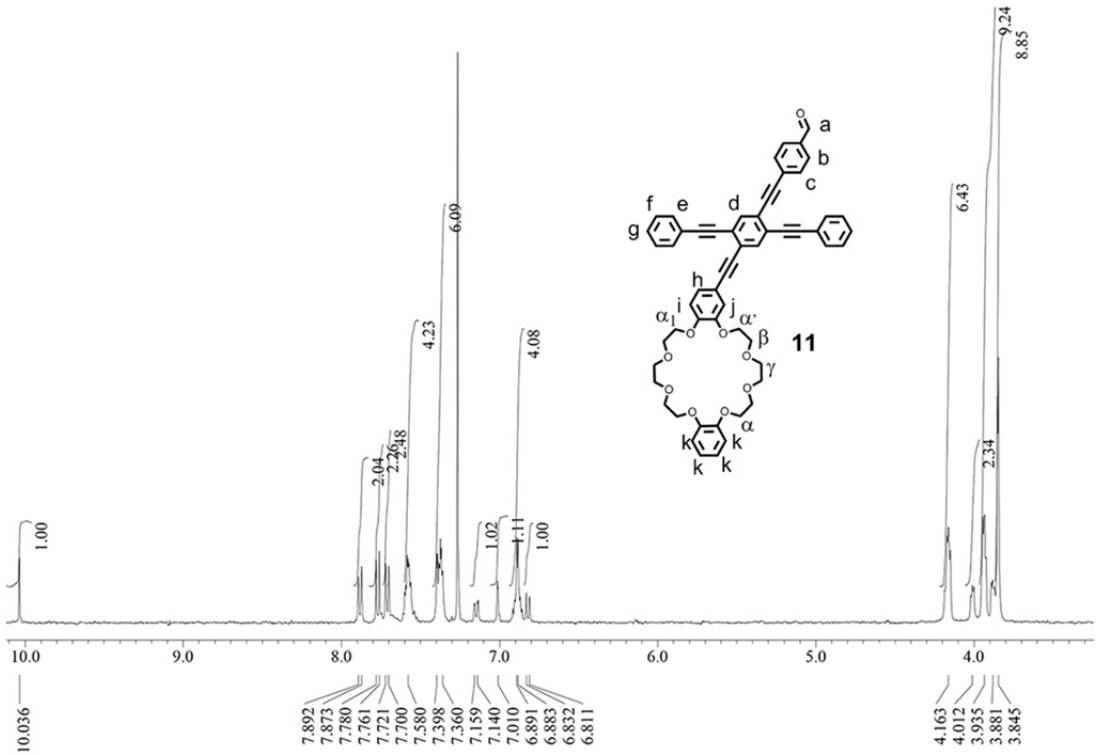

Fig. S23 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **11**.

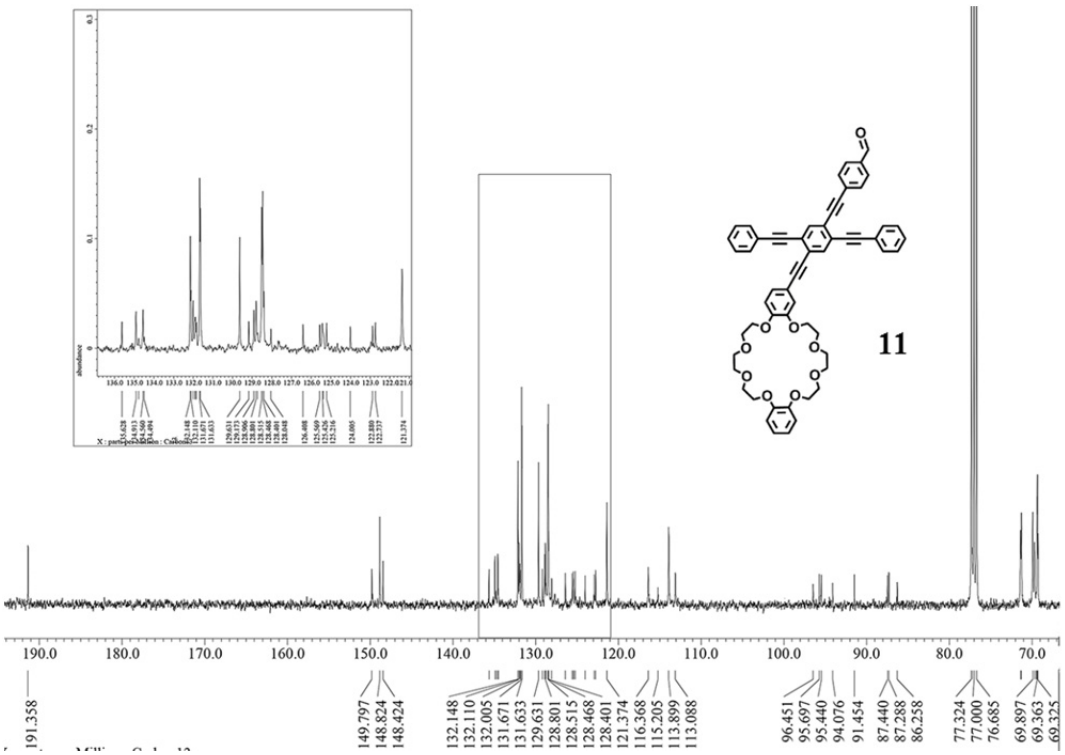

Fig. S24 ^{13}C NMR spectrum (100 MHz, in $CDCl_3$, 25 °C) of **11**.

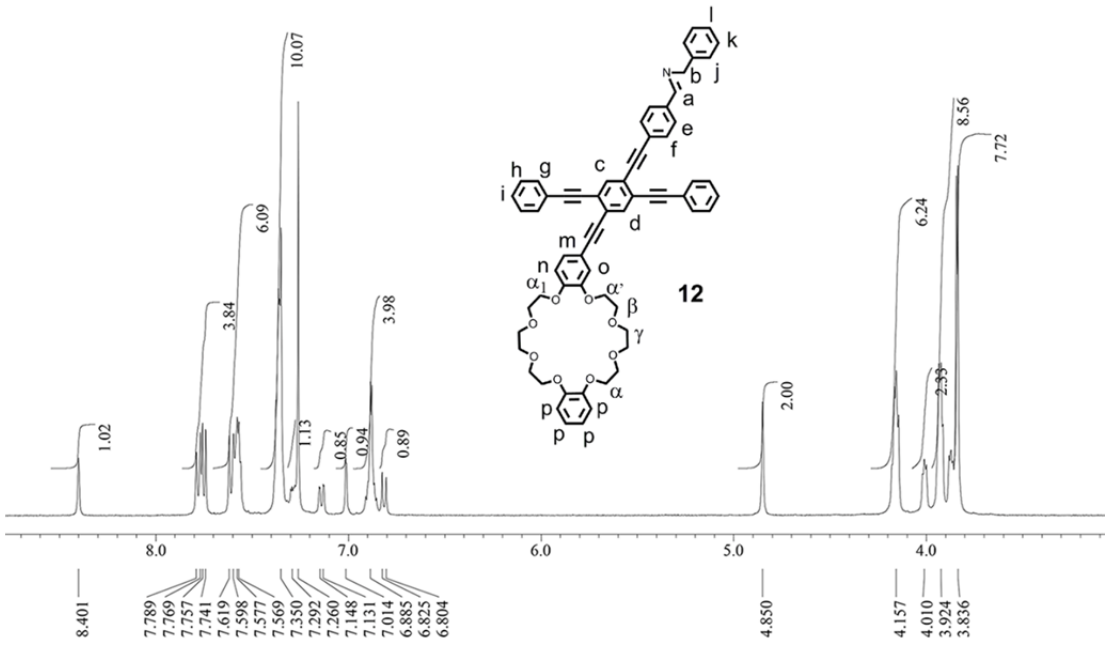

Fig. S25 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$, 25 °C) of **12**.

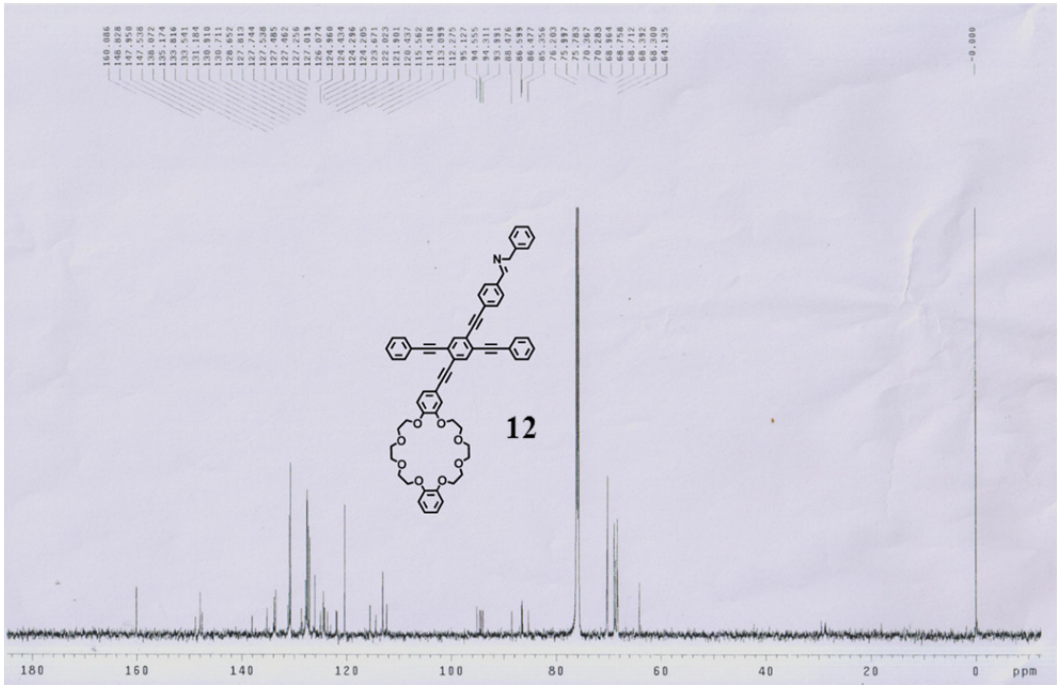

Fig. S26 ^{13}C NMR spectrum (150 MHz, in $CDCl_3$, 25 °C) of **12**.

4. References

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