Electronic Supplementary Information

Two-Dimensional Supramolecular Spring: Coordination Driven Reversible Extension and Contraction of Bridged Half Rings

Dapeng Luo,[a,+] Xuemei Zhang,[b,+] Yongtao Shen,[b] Jing Xu,[b] Lijin Shu,*[a] Qingdao Zeng,*[b] and Chen Wang*[b]

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a Key laboratory of Organosilicol Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China

b CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Centre for Nanoscience and Technology, No.11 ZhongguancunBeiyitiao Beijing 100190, China

[+] These authors contributed equally to this work.

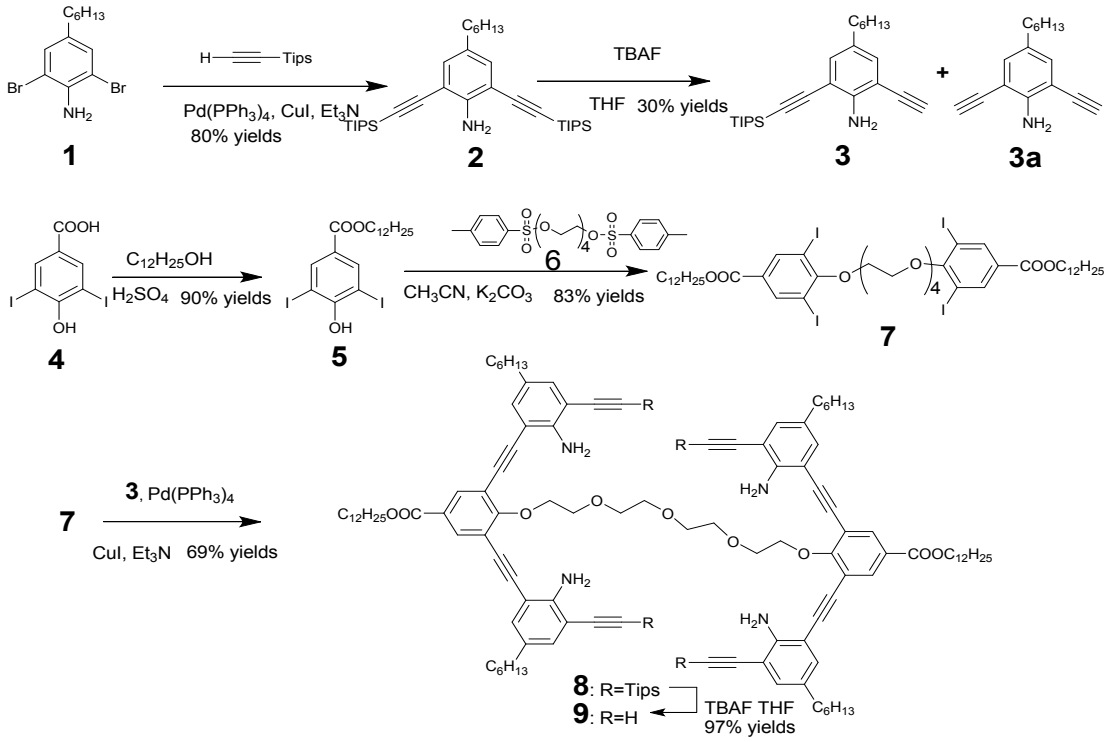
*Corresponding authors.

E-mail: zengqd@nanoctr.cn, wangch@nanoctr.cn, shulj@hznu.edu.cn

Content

1. Synthesis and characterization of target compound **(9)** and **(9+K^+)**

General remarks: All reagents and starting compounds were purchased from commercial sources and used without further purification. Compound **1**[s1] and **6**[s2] were prepared according to literature methods. The solvents were dried using standard methods. All reactions were carried out under nitrogen atmosphere unless otherwise noted. ^{1}H and ^{13}C NMR were recorded on Bruker AV-400 spectrometer with residual solvent peaks ($CDCl_3$: ^{1}H: δ= 7.26, ^{13}C: δ = 77.23). Maldi-Tof MS were recorded on a PerSeptive Biosystem Voyager-DE STR, X-ray powder diffraction data were collected on a Rigaku D/max-2550 PC X powder diffractometer. TEM images and diffrations were obtained by using JEM-2010（HR）.



Scheme S1: Synthesis of target compound **9**.

The synthesis of compound **9** was outlined in **scheme S1**, according to the previous reported literature.[S1, S2] Starting with **1**, Sonogashira coupling reaction of **1** with Tips-protected acetylene yielded double-acetylated **2** in 80% yield after purification by column chromatography (CC) with hexane as eluent. Controlled deprotection of **2** with wet TBAF solution in THF provided mono-protected diyne **3** in 30% yield and **3a** in 10% yield after work-up and CC purification. Esterification of **4** with lauryl alcohol in the presence of concentrated sulfuric acid provided **5** in 90% yield after CC purification. Reaction of **5** and **6** in the presence of potassium carbonate yielded bridged compound **7** after purification by CC. By applying the same Pd-Cu mediated sonogashara-coupling protocol, the assembly of **3** and **7** was done to furnish 8 in 69% yield. Gentle deprotection of **8** with a solution of TBAF in THF furnished targeted product **9** in 97% yield as an orange solid after CC seperation.

All the compounds were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF and HR MALDI-TOF mass spectrometers.

1.1 Synthesis of ***4-hexyl-2,6-bis((triisopropylsilyl)ethynyl)aniline*** (**2**):

To a degassed solution of 1 (3.0 g, 8.95mmol) in triethylamine (30 ml)， $Pd(PPh_3)_4$ (0.1034 g, 0.0895 mmol)，CuI (0.0513 g, 0.2686 mmol)，ethynyltriisopropylsilane (4.409 g, 24.17 mmol) was added. The reaction mixture was stirred under nitrogen at 80 °C for 12 h. The resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (hexane as eluent) to yield 2 (3.85 g, 7.156 mmol) as a yellow oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.11 (s, 2H), 4.60 (br, 2H), 2.46 (t, *J* = 7.7 Hz, 2H), 1.55 (m, 2H), 1.31 (s, 6H), 1.16 (s, 24H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.84, 132.53, 131.29, 107.59, 103.43, 95.73, 34.65, 31.63, 31.48, 28.84, 22.53, 18.65, 13.99, 11.22. MALDI-ToF MS: m/z; $[M]^+$, calcd for $C_{34}H_{59}NSi_2$:537.42; found:537.33.

1.2 Synthesis of ***2-ethynyl-4-hexyl-6-((triisopropylsilyl)ethynyl)aniline*** (**3**) and ***2,6-diethynyl-4-hexylaniline*** **(3a)**

To a stirred solution of **2** (1.43 g, 2.66 mmol) in THF (20 ml) was added drop-wise a solution of TBAF (0.022 g/0.071 mmol) in THF (1.1 ml). The mixture was stirred for 20 minutes under air. After removal of the solvent, the residue was chromatographed (silica gel, hexane/ethyl acetate (100:1/v:v)) to furnish **3** (0.3 g, 0.786 mmol) as a yellow oil in 30% yield and 3a as a brown solid in 10% yield.

compound (3): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.13 (d, *J* = 3.2 Hz, 2H), 4.74 (s, 2H), 3.37 (s, 1H), 2.43 ((t, J=8Hz, 2H), 1.54 (m, 3H), 1.29 (s, 8H), 1.15 (br, 18H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 148.10, 132.87, 132.69, 131.33, 107.75, 105.91, 103.21, 96.06, 82.19, 80.35, 34.55, 31.60, 31.35, 28.73, 22.49, 18.61, 13.98, 11.17. MALDI-ToF MS: m/z; $[M]^+$, calcd for $C_{25}H_{39}NSi$: 381.67; found: 381.80. compound (3a) 1H NMR (400 MHz, CDCl3) δ (ppm) 7.15 (s, 2H), 4.71 (s, 2H), 3.38 (s, 2H), 2.48 – 2.37 (m, 2H), 1.60 – 1.46 (m, 2H), 1.28 (s, 6H), 0.88 (t, J = 6.7 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ (ppm) 148.35, 133.30, 131.50, 106.23, 82.46, 80.33, 77.32, 77.00, 76.68, 34.57, 31.68, 31.32, 28.71, 22.56, 14.05. EI-MS: m/z: [M+H]+, calcd for $C_{16}H_{20}N$: 226.1; found: 226.1

1.3 Synthesis of **compound** (**5**)

To a stirred mixture of **4** (1 g, 2.56 mmol) and lauryl alcohol (2.84 g, 15.2 mmol) in 50 ml flask was added dropwise conc. Sulfuric acid (0.33 ml). The reaction mixture was stirred at 110 °C for 3 h, and then poured into cold ethanol(50 ml) and washed with ethanol for 3 times to provide **5** (1.3 g, 2.33 mmol) in 90 % yield as a white solid .

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.34 (s, 2H), 6.13 (s, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.68 (m, 2H), 1.38 (br , 2H), 1.26 (s, 18H), 0.86 (t, *J* = 8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.43, 156.95,

140.64, 126.21, 81.51, 65.57, 31.79, 29.51, 29.45, 29.37, 29.23, 29.13, 28.50, 25.82, 22.57, 14.03. EI-MS: m/z: $[M-H]^-$, calcd for $C_{19}H_{28}I_2O_3$:557.23; found: 557.46

1.4 Synthesis of **compound (7)**

A mixture of **6** (1.17 g, 2.09 mmol), **5** (0.5 g, 0.995 mmol), potassium carbonate (0.28 g, 1.99 mmol) and acetonitrile (20 ml) was refluxed for 15 h. Subsequently, the solid was filtered and the resulted solution was absorbed on silica gel. CC separation (silica gel, hexane/ethyl acetate (5:1/v:v)) gave **7** (1.05 g, 0.824 mmol) in 83% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (s, 4H), 4.29 (t, *J* = 6.7 Hz, 4H), 4.20 (t, *J* = 5.0 Hz, 4H), 4.00 (t, *J* = 5.0 Hz, 4H), 3.81 (dd, *J* = 5.5, 3.1 Hz, 4H), 3.75 (dd, *J* = 5.4, 3.3 Hz, 4H), 1.79 – 1.68 (m, 4H), 1.39 (d, *J* = 8.8 Hz, 4H), 1.26 (s, 32H), 0.87 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.34, 161.31, 141.14, 129.58, 90.30, 72.36, 70.90, 70.75, 69.97, 65.76, 31.81, 29.53, 29.52, 29.47, 29.39, 29.24, 29.15, 28.54, 25.84, 22.58, 14.01. MALDI-ToF HRMS: m/z; $[M+Na]^+$, calcd for $C_{46}H_{70}O_9I_4Na$: 1297.1069 ; found: 1297.1068.

1.5 Synthesis of **compound (8)**

To a degassed solution of **7 (**0.2 g, 0.157 mmol) in triethylamine (10 ml)，was added $Pd(PPh_3)_4$ (0.0218 g, 0.0188 mmol)，CuI (0.006 g,

0.031 mmol)，**3** (0.24 g, 0.63 mmol). The reaction mixture was stirred under nitrogen at rt. for 12h. The resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (hexane/ethyl acetate (100:1/v:v)) as eluent) to yield **8** (0.25 g, 0.11 mol) as a yellow oil in 69 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (s, 4H), 7.14 (d, *J* = 2.1 Hz, 8H), 4.93 (s, 8H), 4.56 (t, J=4Hz, 4H), 4.34(t, J=6.4Hz, 4H), 3.82(t, J=4Hz, 4H), 3.55(t, J=4Hz, 4H), 3.43(t, J=4Hz, 4H), 2.45(t, J=4Hz, 8H), 1.85 – 1.74 (m, 4H), 1.57 (d, *J* = 5.4 Hz, 8H), 1.44 (m, 4H), 1.31(s, 56H), 1.28(s, 12H), 1.16 (s, 72H), 0.94 – 0.87 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 164.82, 163.00, 147.86, 134.01, 132.89, 132.00, 131.20, 125.83, 117.53, 107.64, 106.60, 103.35, 95.94, 91.50, 89.70, 73.17, 70.32, 65.38, 34.58, 31.78, 31.60, 31.38, 29.53, 29.50, 29.49, 29.40, 29.22, 29.19, 28.76, 28.62, 25.87, 22.55, 22.48, 18.59, 13.96, 11.16. MALDI-ToF HRMS: m/z; $[M+H]^+$, calcd for $C_{146}H_{223}N_4O_9Si_4$: 2288.6209 ; found: 2288.6200.

1.6 Synthesis of **compound (9**)

To a stirred solution of **8** (0.20 g, 0.087 mmol) in THF (20 ml) was added dropwise a solution of TBAF (0.05 g,0.019 mmol) in THF (2.5 ml) in 30 minutes. Subsequent CC (silica gel, hexane/THF (10:1/v:v)) furnish **9** (0.14 g, 0.084 mmol) in 97 % yield as a orange solid. ^{1}H NMR (400

MHz, CDCl3) δ (ppm) 8.07 (s, 4H), 7.16 (d, J = 1.7 Hz, 4H), 7.13 (d, J = 1.8 Hz, 4H), 4.94 (s, 8H), 4.57 – 4.53 (m, 4H), 4.32 (t, J = 6.8 Hz, 4H), 3.86 – 3.82 (m, 4H), 3.61 (dd, J = 5.6, 3.4 Hz, 4H), 3.53 (dd, J = 5.5, 3.4 Hz, 4H), 3.38 (s, 4H), 2.46 – 2.41 (m, 8H), 1.82 – 1.74 (m, 4H), 1.53 (dd, J = 14.3, 6.9 Hz, 8H), 1.43 (dd, J = 15.3, 6.9 Hz, 4H), 1.28 (d, J = 10.2 Hz, 56H), 0.91 – 0.85 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ(ppm) 164.78, 162.75, 148.05, 133.92, 133.16, 132.39, 131.04, 125.75, 117.37, 106.58, 105.86, 91.32, 89.70, 82.47, 80.28, 77.23, 76.91, 76.59, 72.87, 70.36, 70.06, 65.39, 34.42, 31.73, 31.55, 31.24, 29.49, 29.46, 29.38, 29.19, 29.16, 28.66, 28.52, 25.82, 22.52, 22.44, 13.96. MALDI-ToF HRMS: m/z; $[M+H]^+$, calcd for $C_{110}H_{143}N_4O_9$:1664.0872; found:1664.0871.

References

(S1) H. W. Gibson, H. Wang, K. Bonrad, J. W. Jones, C. Slebodnick, L. N. Zackharov, A. L. Rheingold, B. Habenicht, P. Lobue, A. Ratliff, *Org. Biomol. Chem*., **2005**, 3, 2114.

(S2) L. J. Shu, M. Mayor, *Chem. Commun.,* **2006**, 4134.

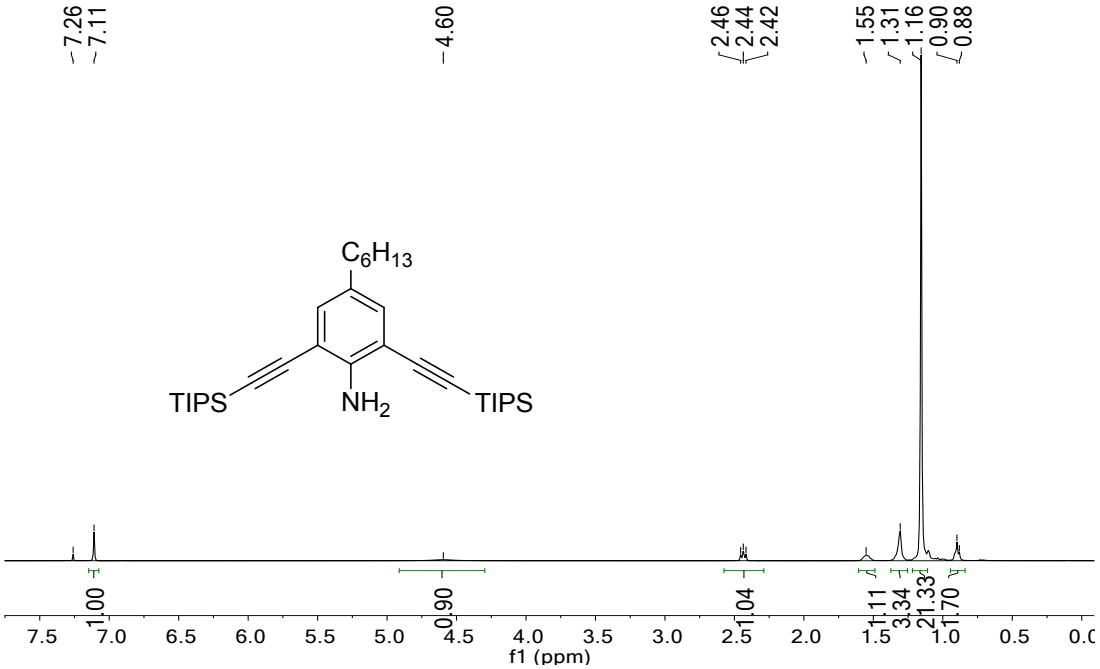


Fig. S1 ^{1}H NMR of ***4-hexyl-2,6-bis((triisopropylsilyl)ethynyl)aniline*** (**2**)

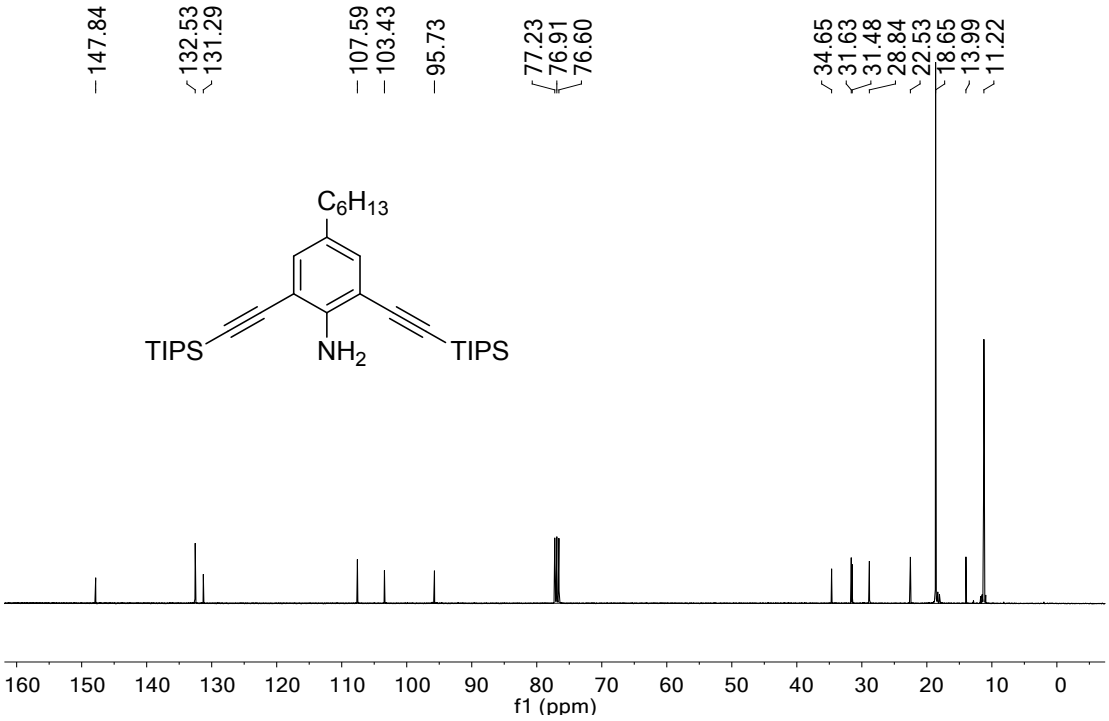


Fig. S2 ^{13}C NMR of ***4-hexyl-2,6-bis((triisopropylsilyl)ethynyl)aniline*** (**2**)

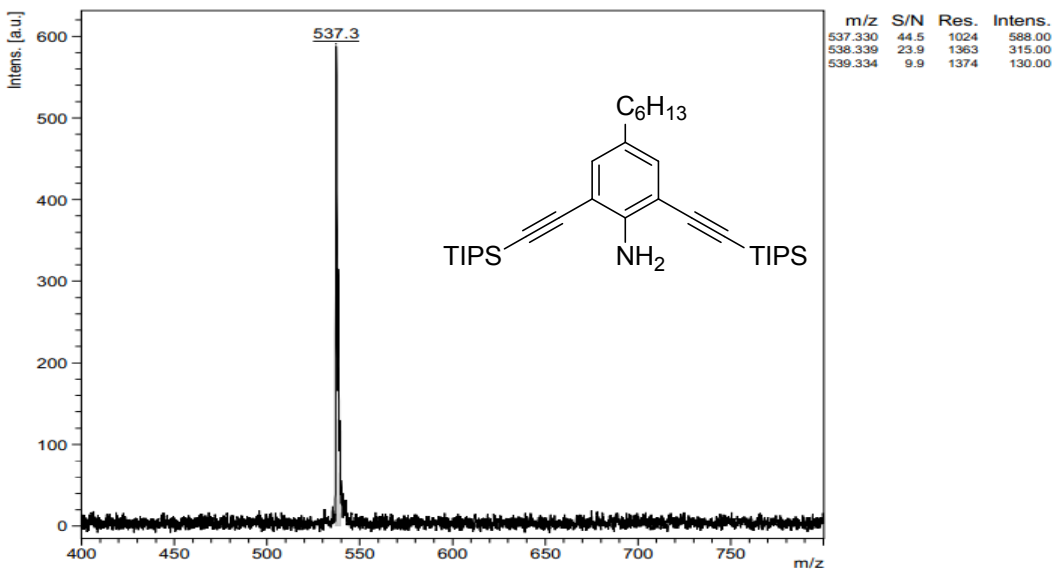


Fig. S3 MALDI-TOF of

4-hexyl-2,6-bis((triisopropylsilyl)ethynyl)aniline (**2**)

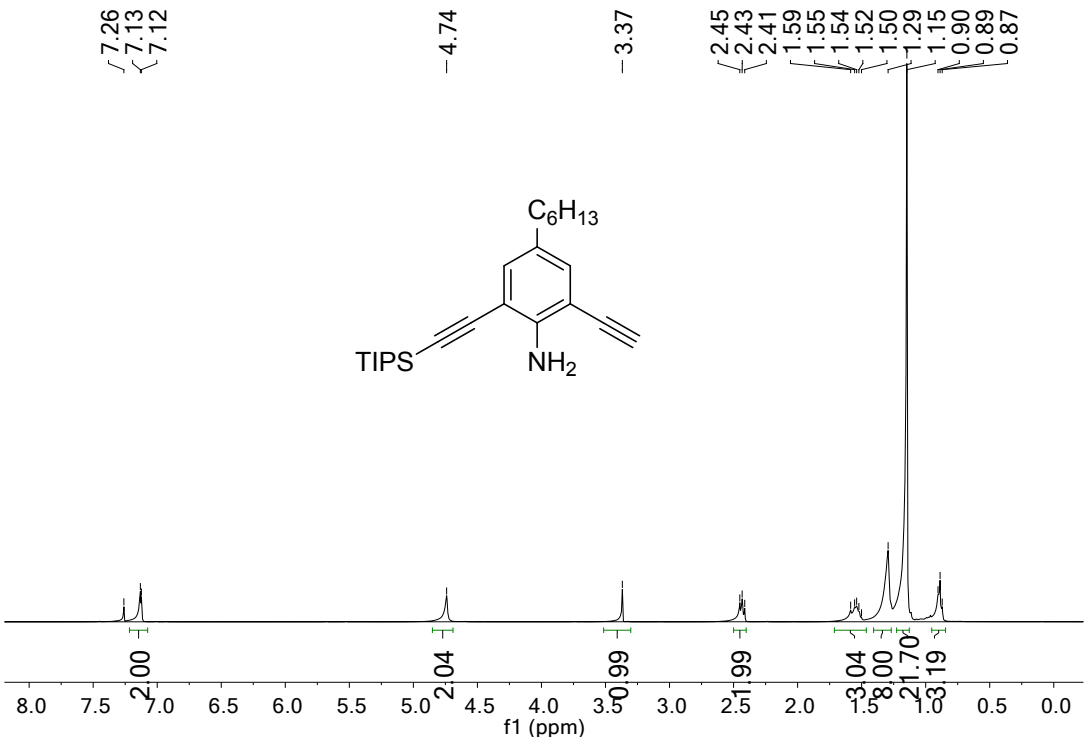


Fig. S4 ^{1}H NMR of

2-ethynyl-4-hexyl-6-((triisopropylsilyl)ethynyl)aniline (**3**)

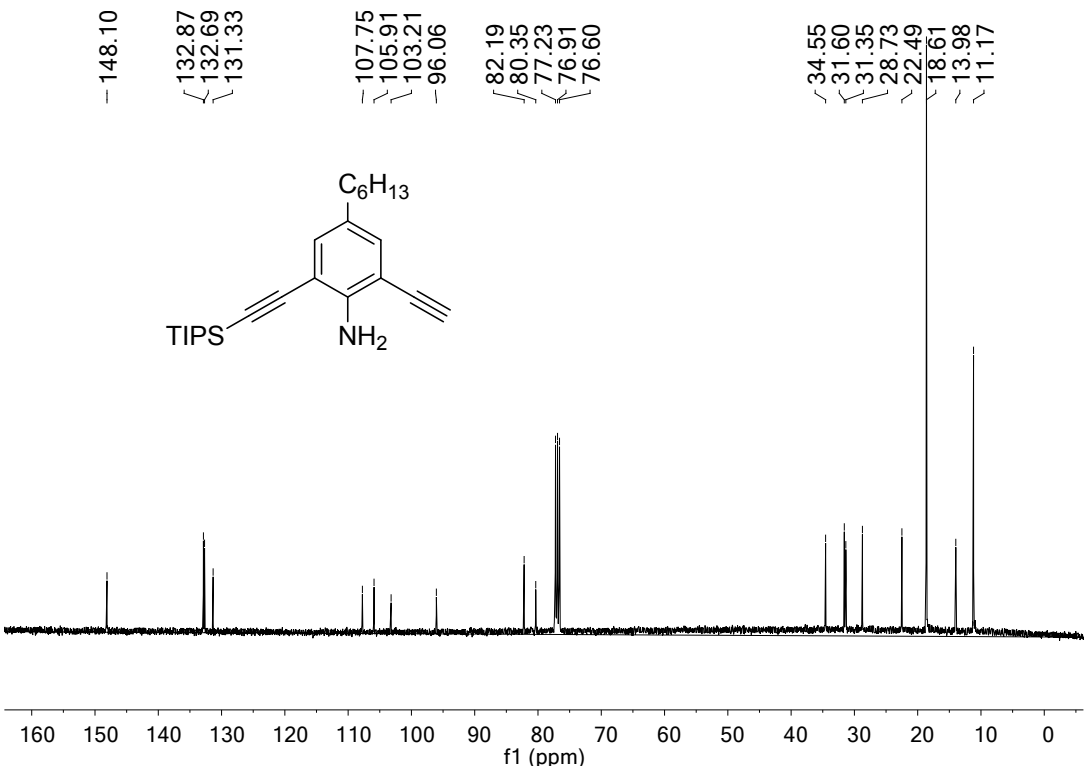


Fig. S5 ^{13}C NMR of

2-ethynyl-4-hexyl-6-((triisopropylsilyl)ethynyl)aniline **(3)**

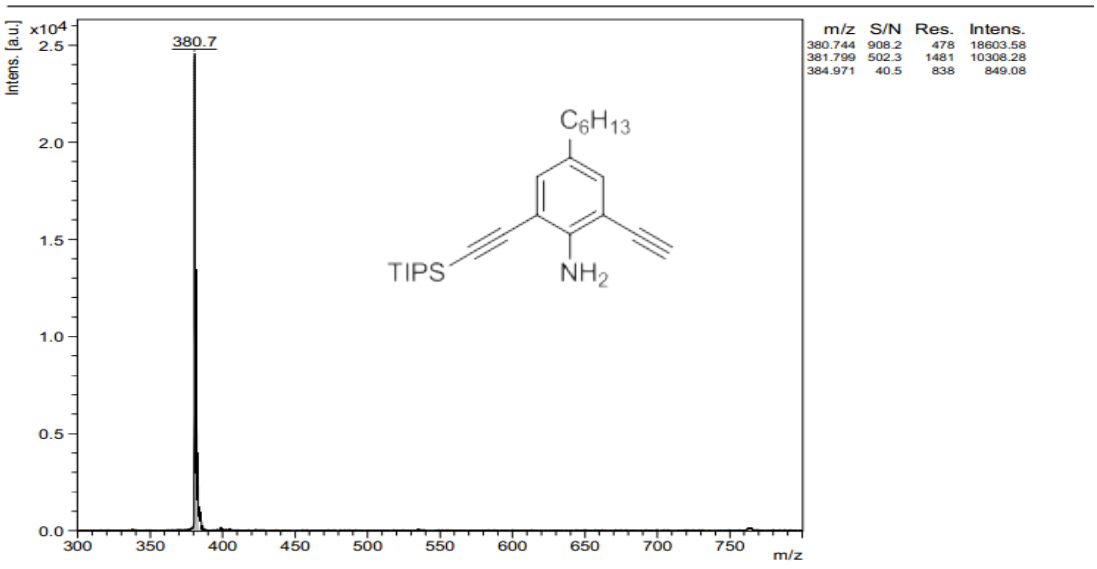


Fig. S6 MALDI-TOF of

2-ethynyl-4-hexyl-6-((triisopropylsilyl)ethynyl)aniline **(3)**

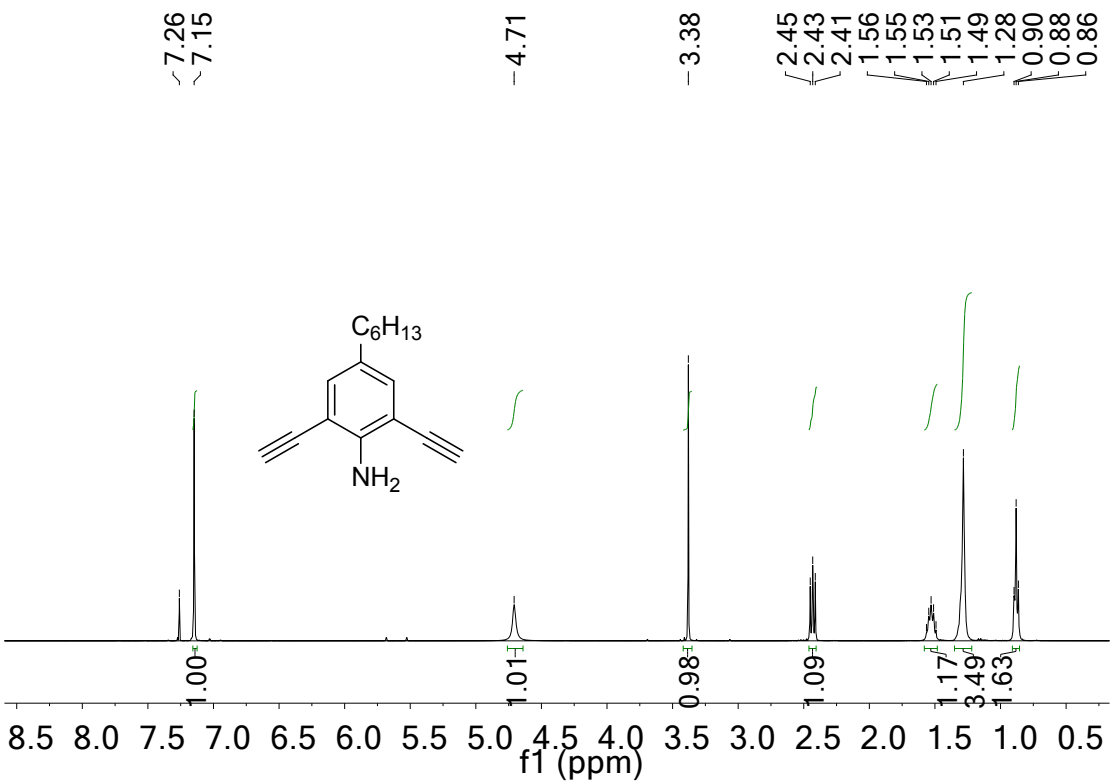


Fig. S7 [1]H NMR of ***2,6-diethynyl-4-hexylaniline*** (**3a**)

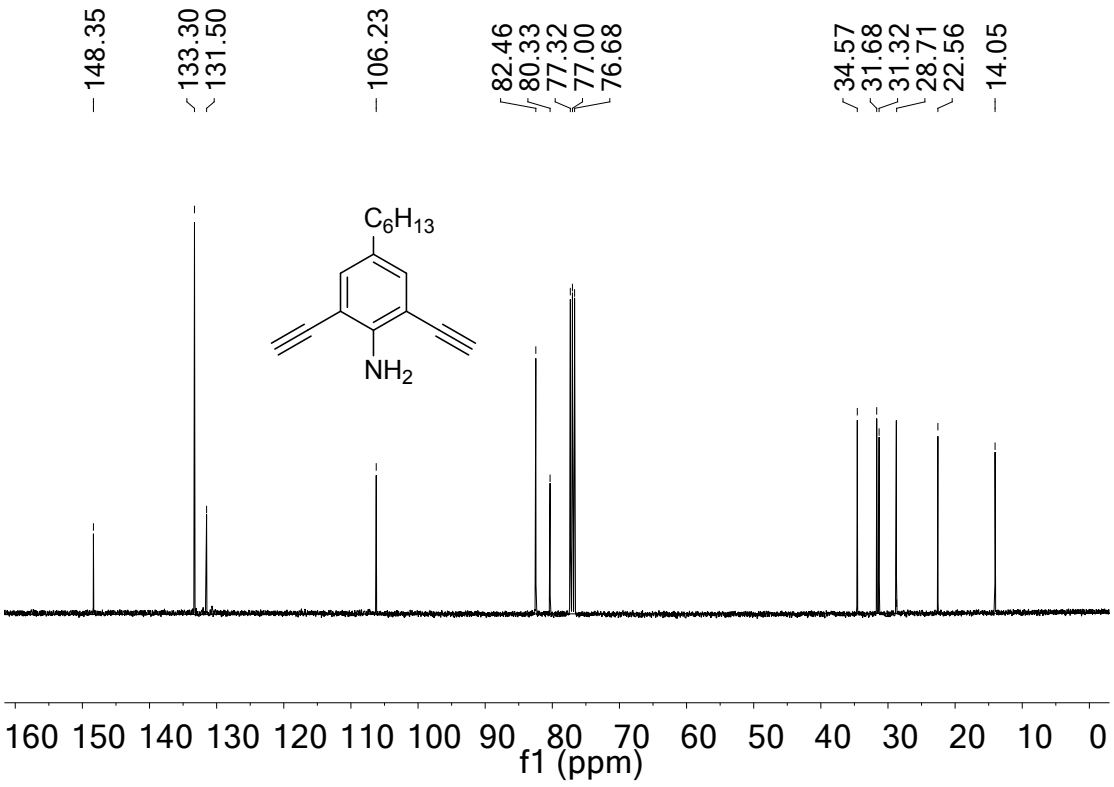


Fig. S8 [13]C NMR of ***2,6-diethynyl-4-hexylaniline*** (**3a**)

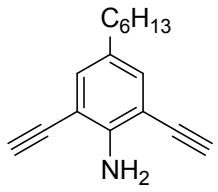


Fig. S9 ESI of ***2,6-diethynyl-4-hexylaniline*** (**3a**)

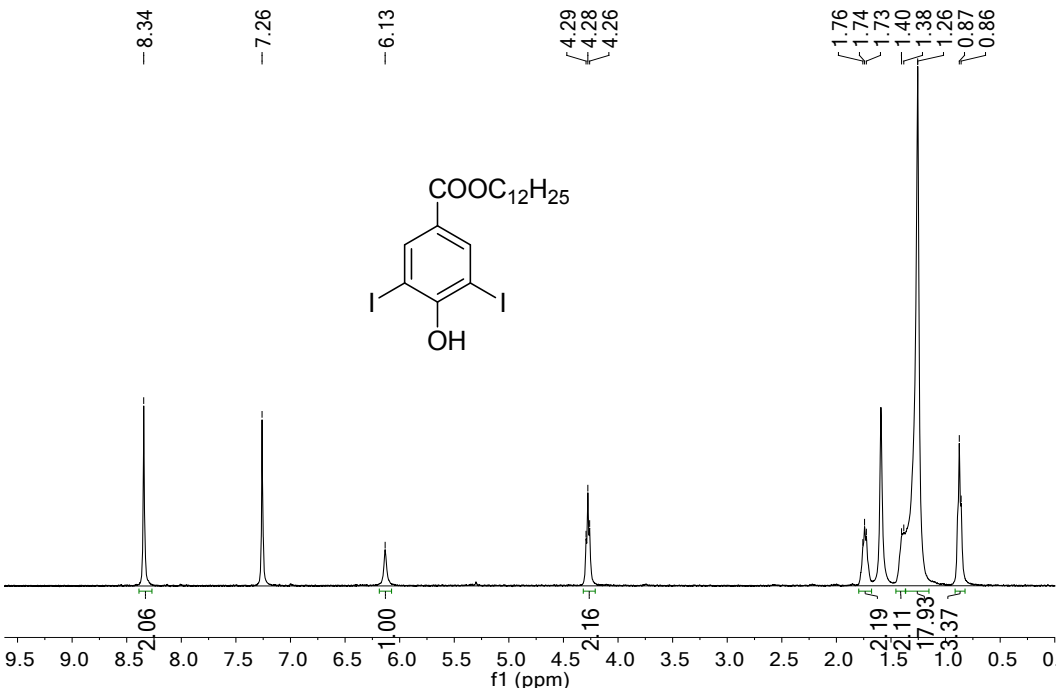


Fig. S10 ^{1}H NMR of **compound** (**5**)

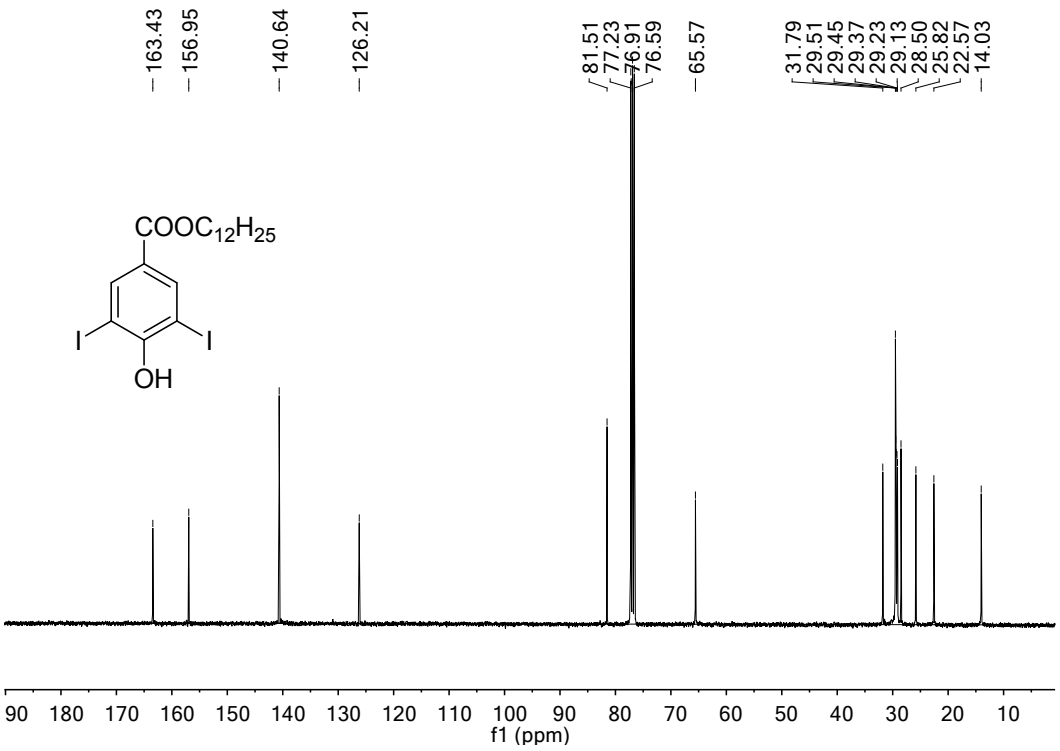


Fig. S11 ^{13}C NMR of **compound** (**5**)

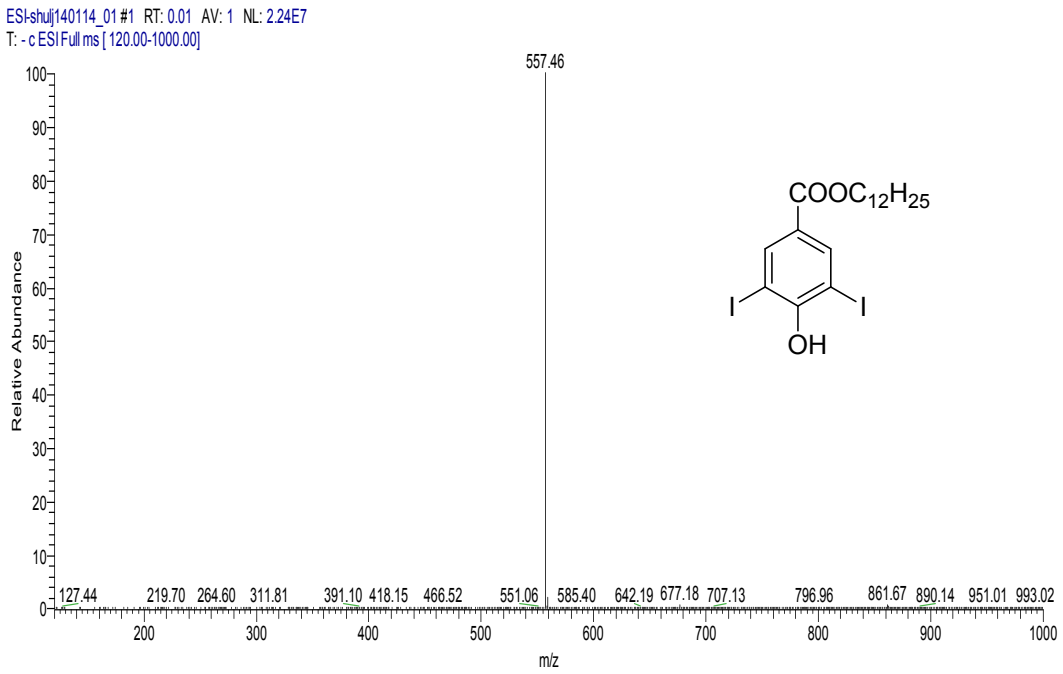


Fig. S12 MALDI-TOF of **compound** (**5**)

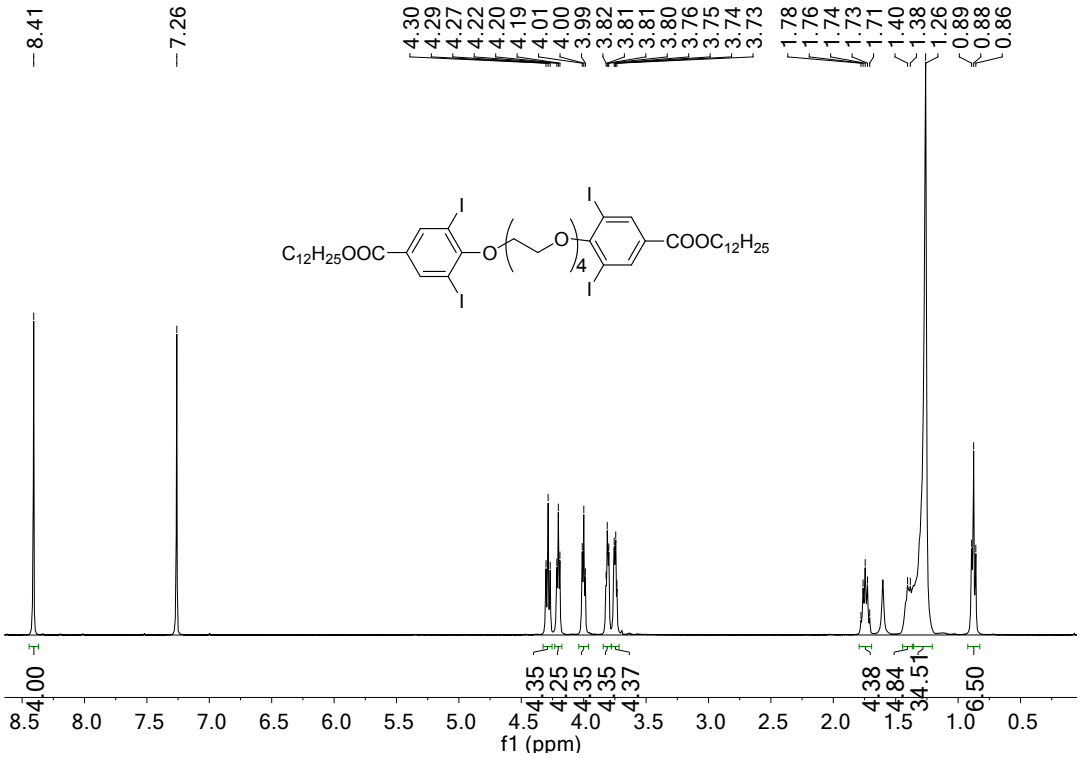


Fig. S13 ^{1}H NMR of **compound** (**7**)

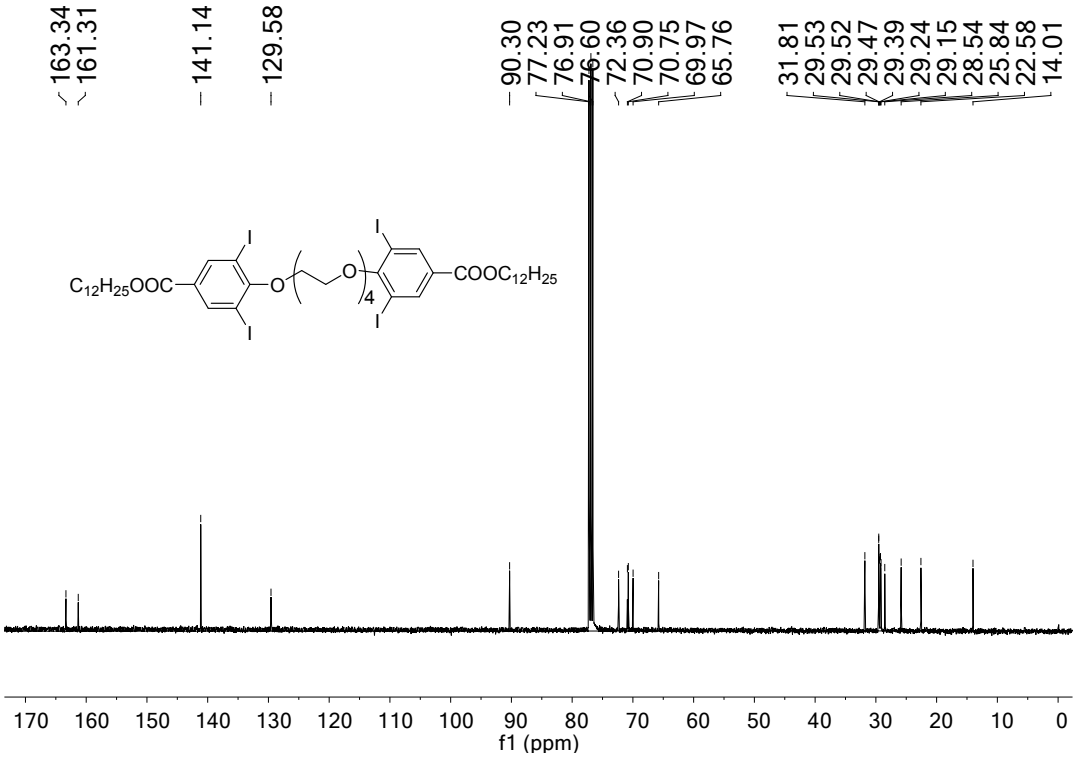


Fig. S14 ^{13}C NMR of **compound** (**7**)

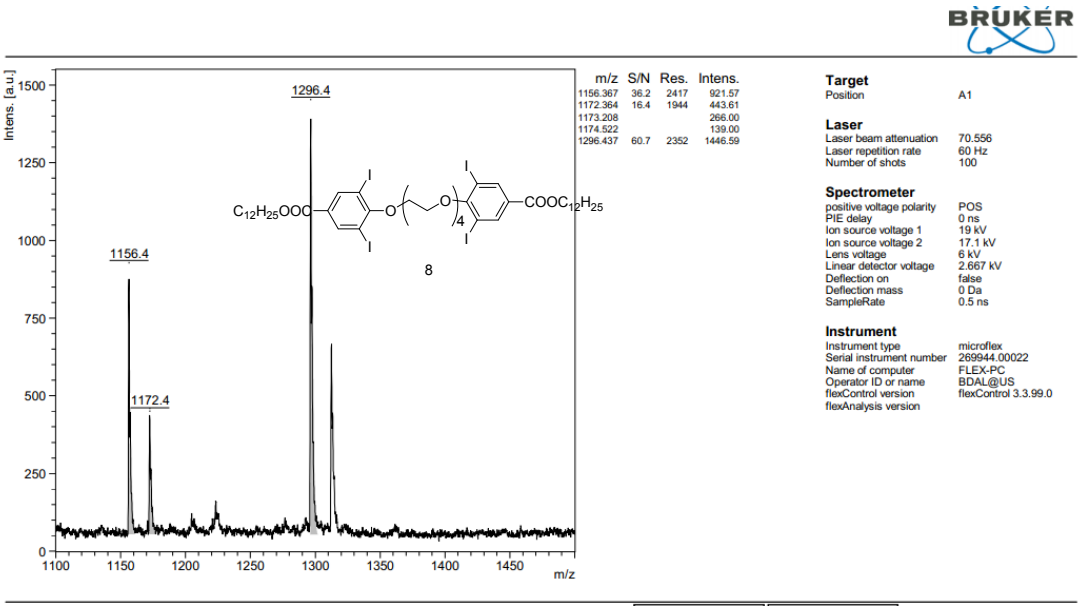


Fig. S15 MALDI-TOF of **compound** (**7**)

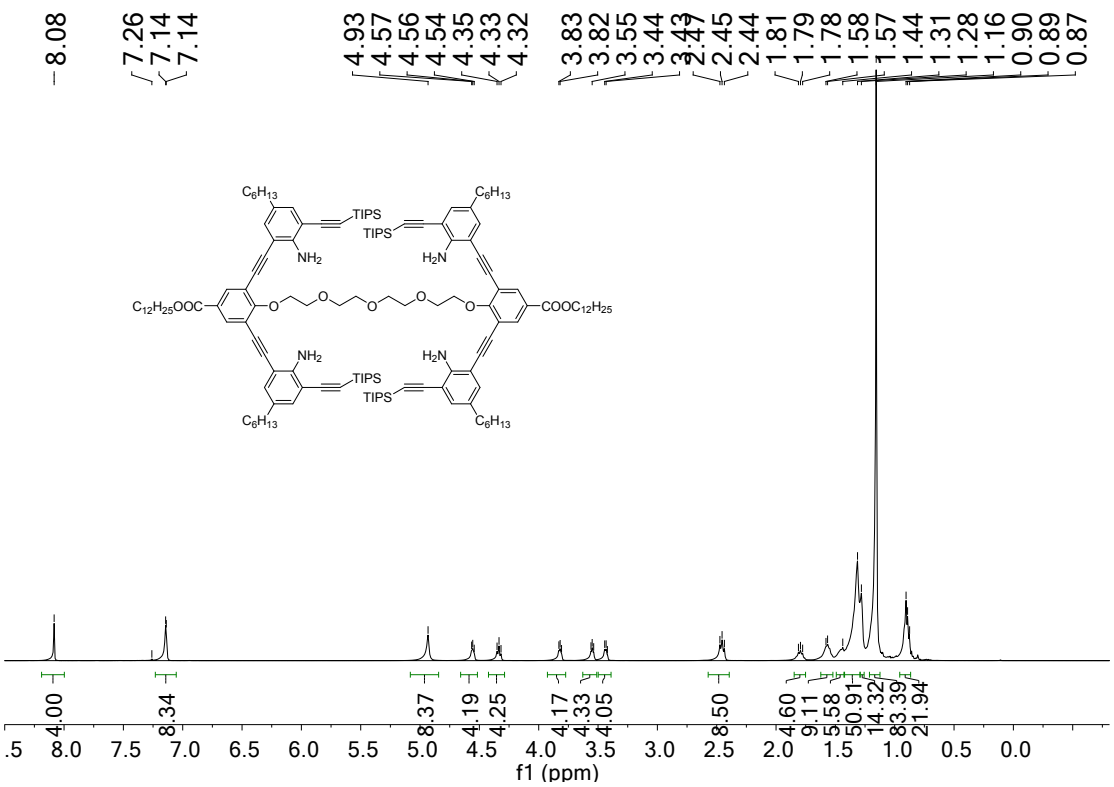


Fig. S16 ^{1}H NMR of **compound** (**8**)

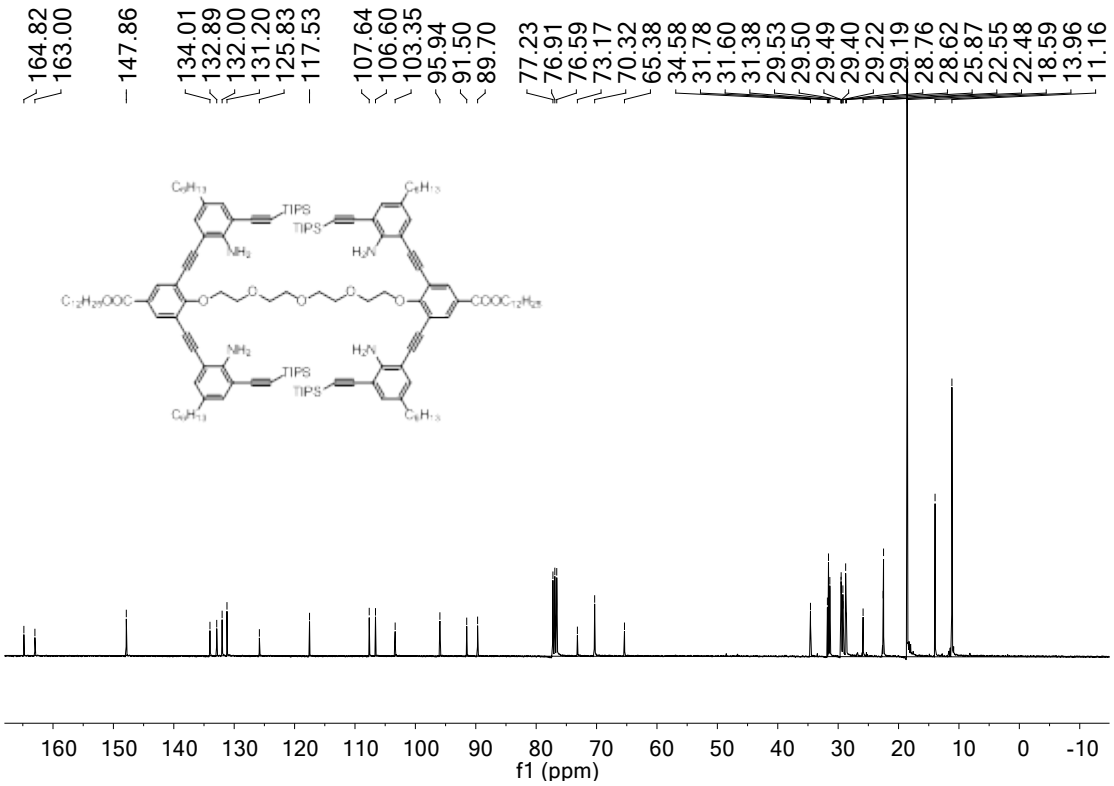


Fig. S17 ^{13}C NMR of **compound** (**8**).

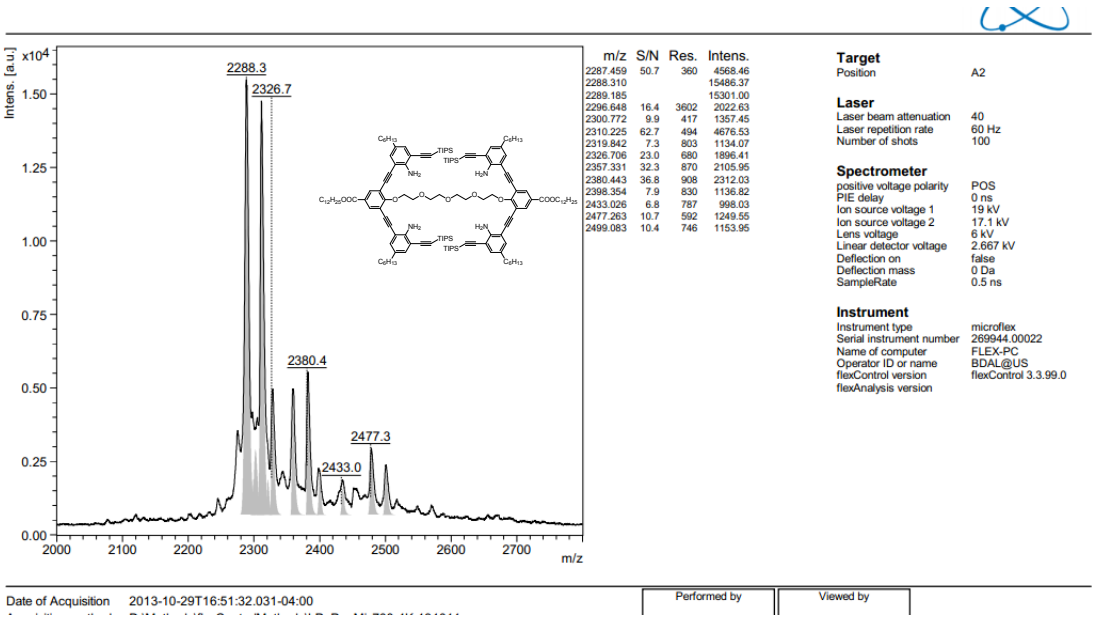


Fig. S18 MALDI-TOF of **compound** (**8**).

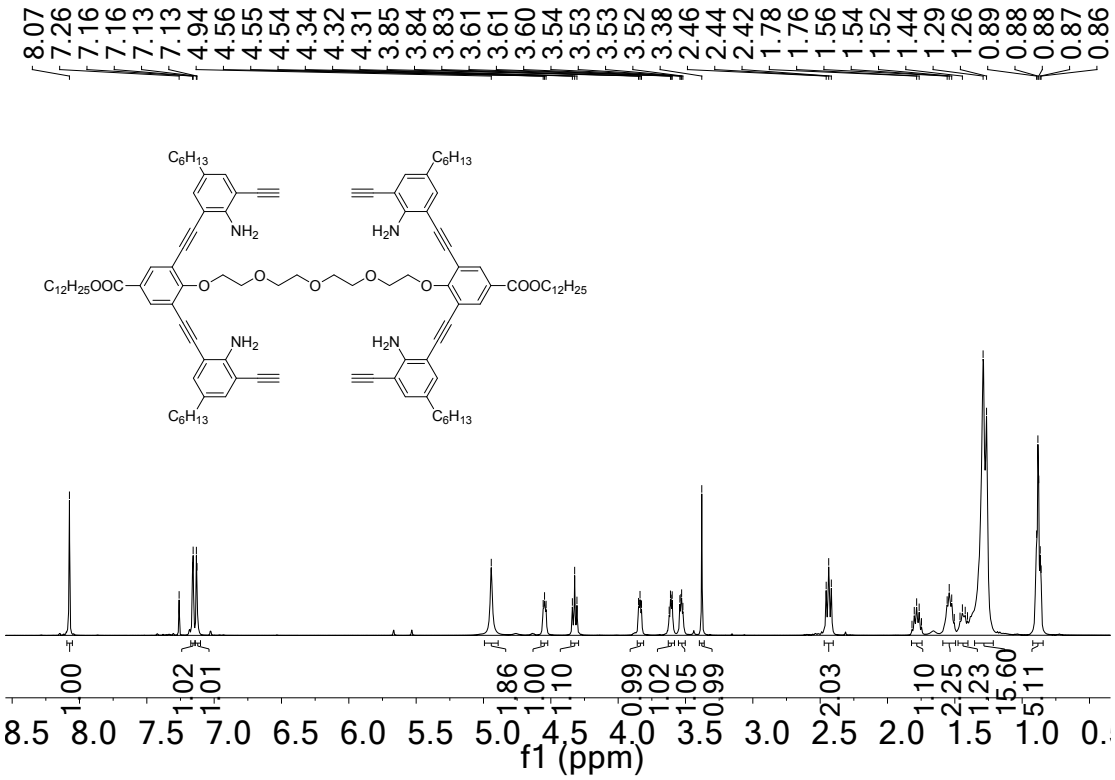


Fig. S19 ^{1}H NMR of **compound** (**9**)

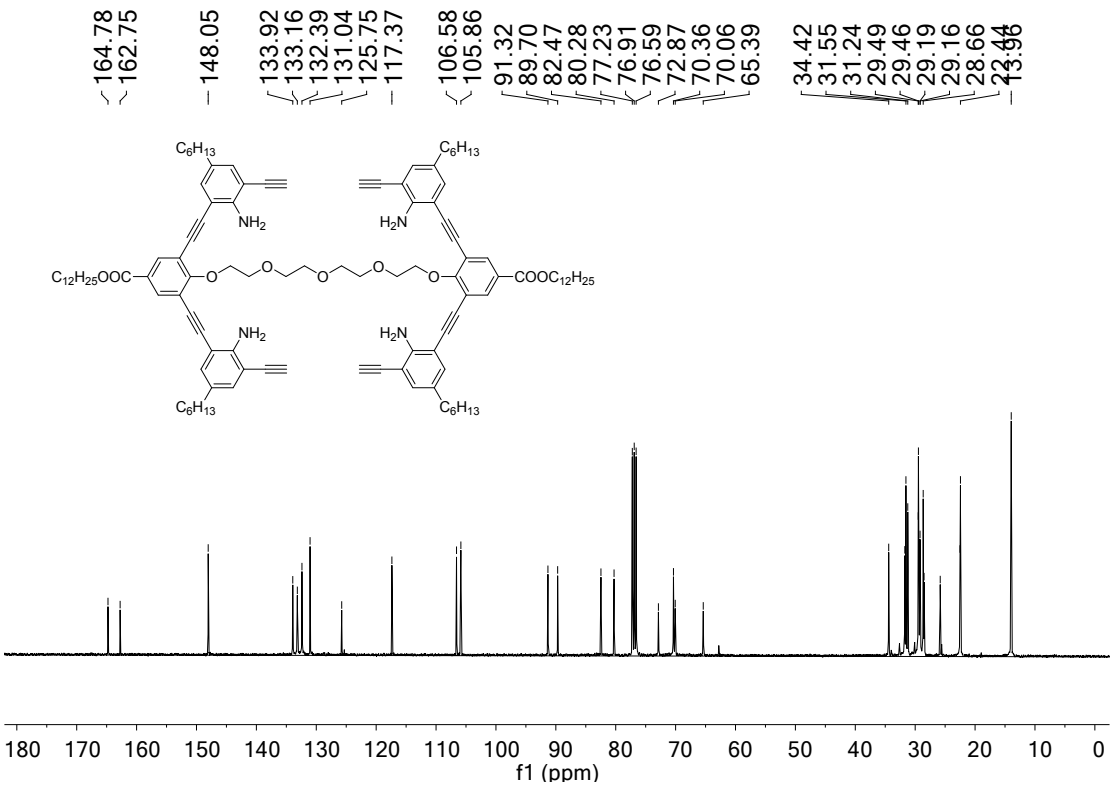


Fig. S20 ^{13}C NMR of **compound** (**9**).

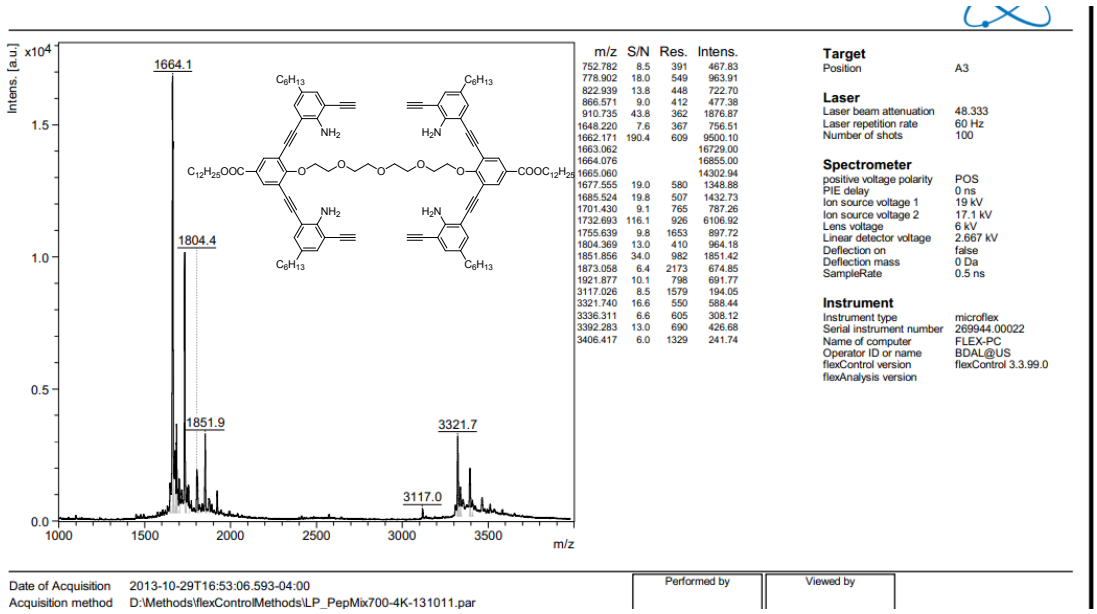


Fig. S21 MALDI-TOF of **compound** (**9**)

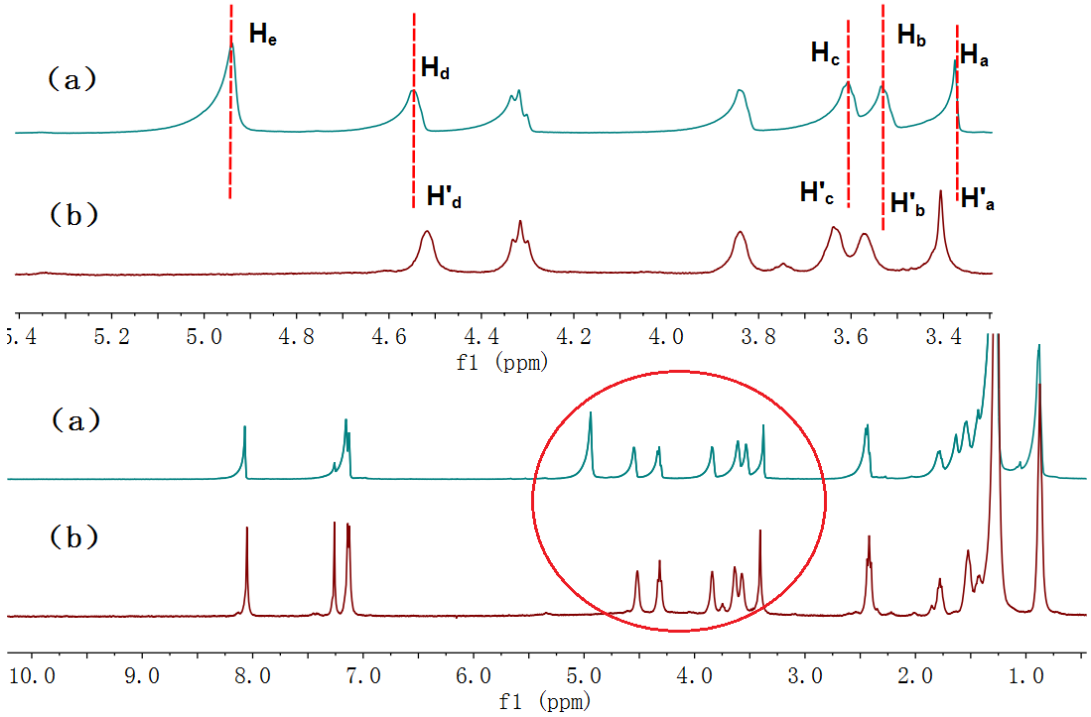


Fig. S22 Comparison of ^{1}H NMR spectra for **9** and (**9**+K^+) in $CDCl_3$.[a]

[a]sample of (**9**+K^+) was obtained by mixing the equal molar amount of **9** and CF_3SO_3K (Here, potassium trifluoromethanesolfonate was used due to the solubility reasons) in DMF. Parts of ^{1}H NMR for **9**: H_a：3.375 ppm , H_b: 3.535 ppm, H_c: 3.607 ppm, H_d: 4550 ppm, H_e: 4.940 ppm; for **9**+K^+ H'_a: 3.406 ppm, H'_b: 3.574 ppm, H'_c:3.638 ppm , H'_d: 4.516 ppm. No significant changes were observed for the aromatic and side chains in the proton spectra except the dissapearance of the amine groups in **9**.

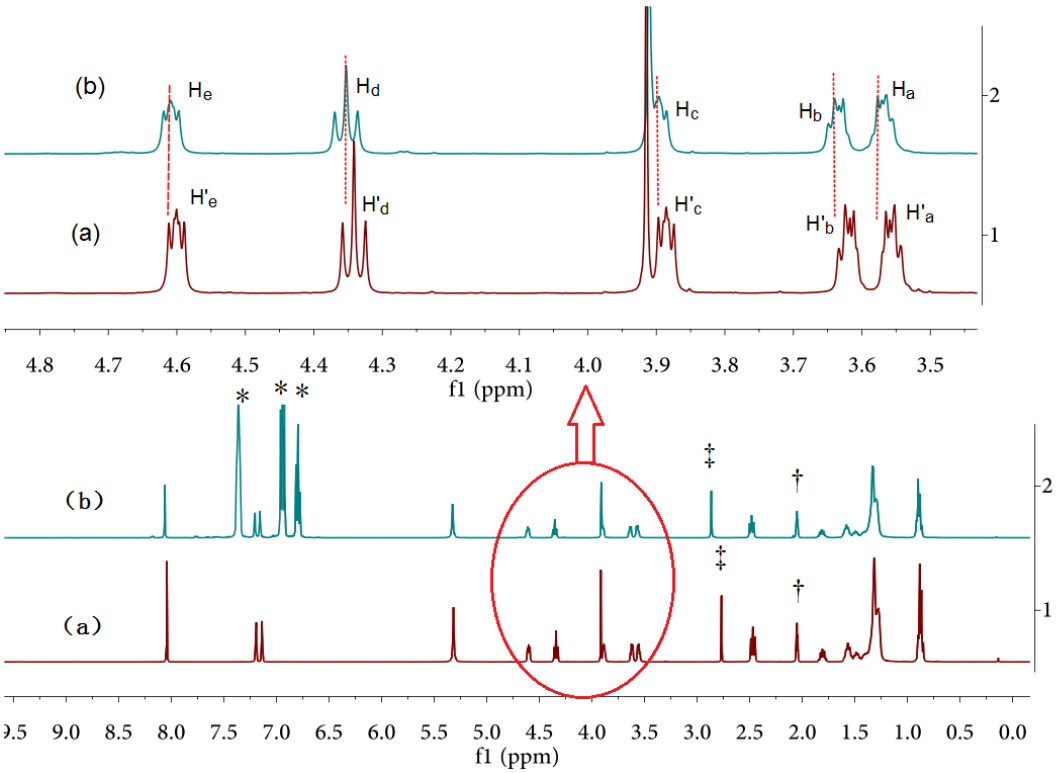


Fig. S23 1H NMR spectra for (a) **9** in acetone-d6 at RT（b）**9** + 10 equv. $K(Ph)_4B$ at RT.

The corresponding data for the tetraethylene glycol parts are as follows:

(a) H_a, 3.565 ppm; H_b, 3.624 ppm; H_c, 3.886 ppm; H_d, 4.341 ppm; H_e, 4.601 ppm

(b) H'_a, 3.577 ppm; H'_b, 3.640 ppm; H'_c, 3.896 ppm; H'_d, 4.353 ppm; H'_e, 4.609 ppm.

(c) *resonance of the phenyl parts for $K(Ph)_4B$; †residue of acetone-d6; ‡H_2O.

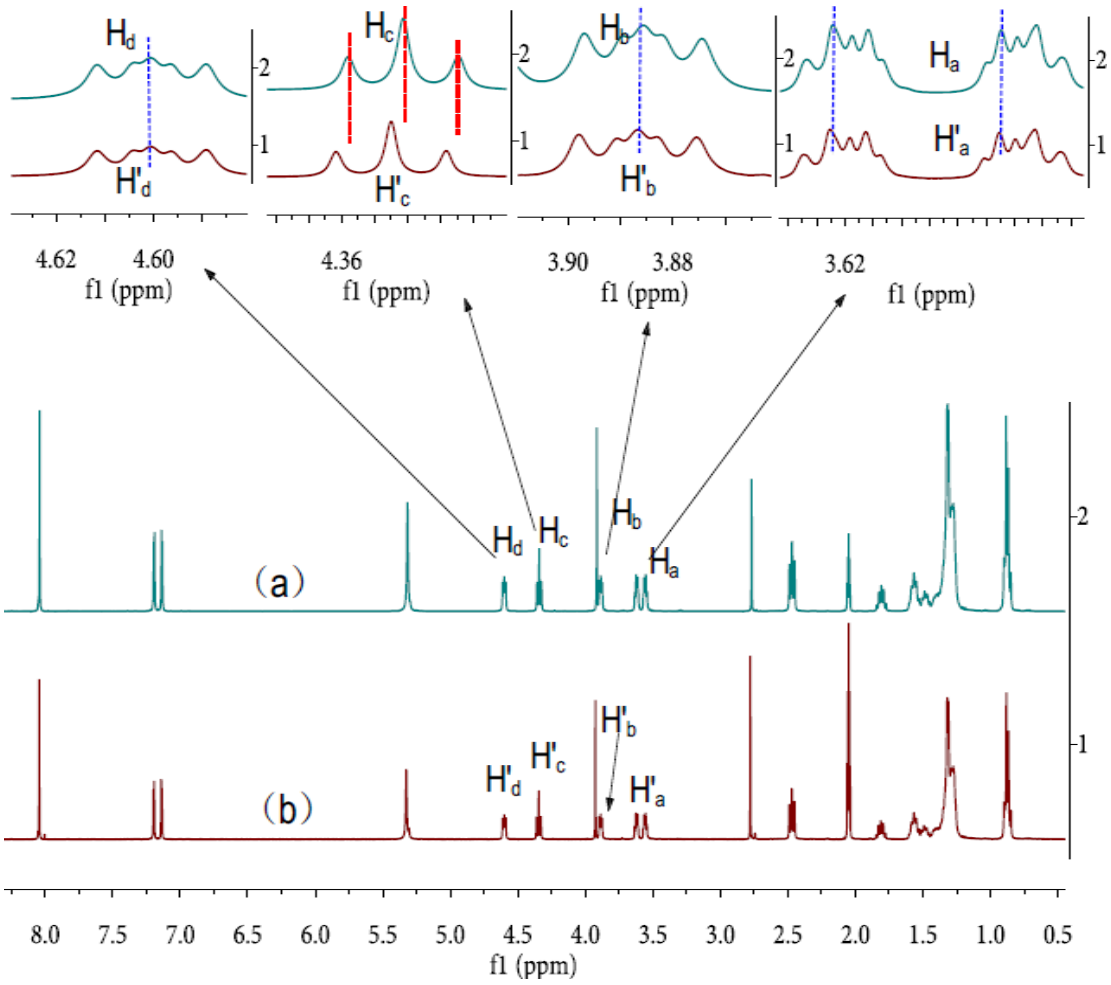


Fig. S24 Comparison of ^{1}H NMR for compound **9** (a) and **9+K_2CO_3** in acetone-d6 with molar ratio of 1:1 (b).

As can be observed, the chemical shift for H_a and H'_a, H_b and H'_b, H_d and H'_d remained unchanged. After addition of K_2CO_3, chemical shift for one of the tetraethylene glycol methyl moved from 4.341 ppm to 4.345 ppm (H'_c).

2. STM investigation

STM measurements were performed with a Nanoscope IIIa (Bruker, USA) under atmosphere conditions. The STM images presented were acquired in constant current mode using a mechanically formed Pt/Ir (80/20) tip. All STM images provided were raw data without any treatment except for the flattening procession and the drift was calibrated using the underlying graphite lattice as a reference. The specific tunneling conditions including tunneling current (I_{set}) and sample bias (V_t) are given in the corresponding figure captions. The molecular models were built with a HyperChem software package.

All the materials were dissolved by the mixed EtOH/H2O solution with a volume ration of 5:3 (EtOH:H_2O), and the concentration was less than 10^{-4} M.

A droplet (0.5 μL) of solution containing the target compound **9** was drop-cast onto the basal plane of highly oriented pyrolytic graphite (HOPG) (grade ZYB, NTMDT, Russia) surface. The sample was then characterized by STM at the solid-gas interface. After imaging the assembled structure of compound **9** by STM, a drop of mixed solution (0.5 μL) containing K_2CO_3 (about 10^{-3} g/L) was added into this HOPG surface. And then, the sample was placed at room temperature about 15 min, and following it was multi-washed with the mixed solution. After that, the surface treated by K_2CO_3 was again investigated by STM at the

gas/solid interface. Next, a drop of solution containing 18-crown-6 was added into the reacted surface. Kept about 15 min, the sample was multi-washed by the mixed solution. In the end, the STM investigation was also performed at solid/gas interface.

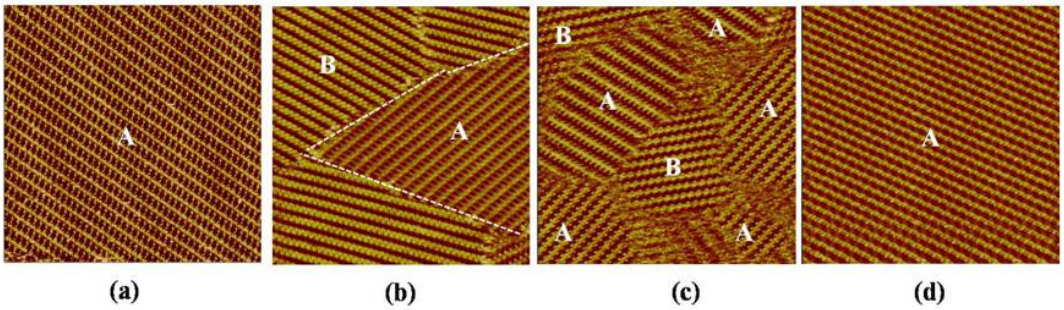


Fig. S25 Large-scale STM images of a monolayer of **9** with different treatment.

(a) STM image of **9**, scan size: 67 × 67 nm^2, I_{set} = 320.2 PA, V_{bias} = 710.5 mV. (b) STM image of **9** after the K_2CO_3 solution was added (**9**+**K**$^+$). Scan aize: 67 × 67 nm^2, I_{set} = 290.1 PA, V_{bias} = 740.7 mV. (c) STM image of **9** after the K_2CO_3 and the 18-crown-6 solution was subsequently added, (**9**+**K**$^+$+**18-crown-6**), about 15mins later. Scan aize: 57 × 57 nm^2, I_{set} = 299.1 PA, V_{bias} = 700.9 mV. (d) STM image of **9** after the K_2CO_3 and the 18-crown-6 solution was subsequently added (**9**+**K**$^+$+**18-crown-6**), about 40mins later. Scan aize: 61 × 61 nm^2, I_{set} = 299.1 PA, V_{bias} = 700.9 mV. (a), (d) show lamellar structure (domain A), whereas (b) and (c) exhibit the mixed lamellar (domain A) and zigzag structure (domain B).

3. TEM pattern of compound **9** and **9**+$\mathbf{K}^+$

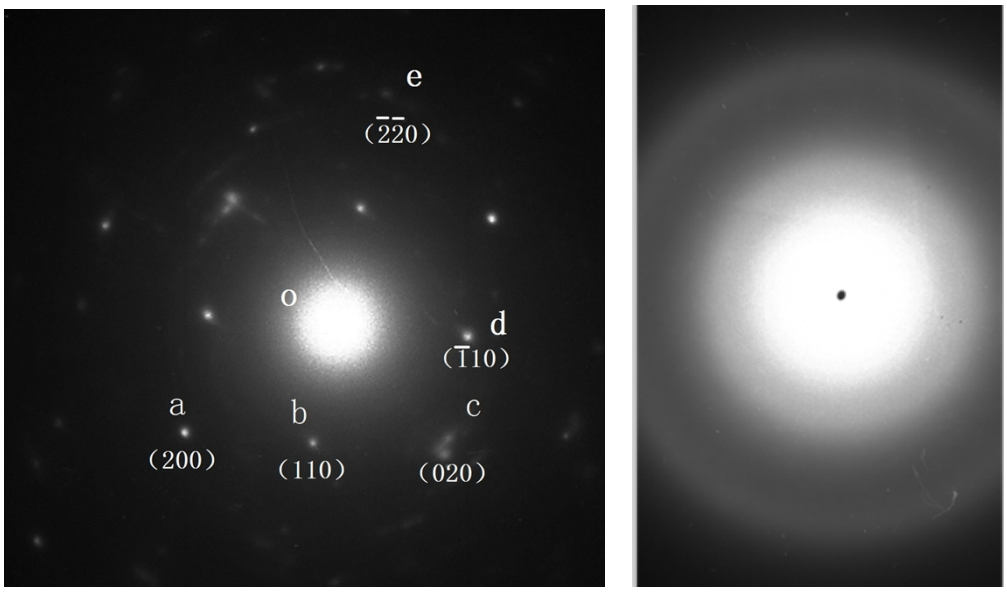


Fig. S26 Diffraction pattern of TEM of specimen **9** (Left) and **9**+$\mathbf{K}^+$ (Right), respectively.

In the pattern above, roa = 0.95 cm，rob = 0.6 cm ，roc = 0.8 cm，rod = 0.65 cm，roe = 1.2cm, rob ≈ rod. The ratios of rod/ rob≈1, roc/rob = 1.33, corresponding to around that of √2:1. The ratios of rob：roc：roa ：roe ≈ 1：√2：√3：2. Therefore, a rectangular lattice morphology with spacings of 0.209 (doe), 0.264 (doa), 0.313 (doc) and 0.418 nm (dob) can be obtained, representing the reflections of the outer alkyl chains. The electron diffraction in sample **9**+K^+ only shows diffraction halo rings, indicating an amorphous structure.