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# Supramolecular aggregates constructed by pillar[5]arene-based host-guest interaction with aggregation-induced emission

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## Experimental Section

### General Methods

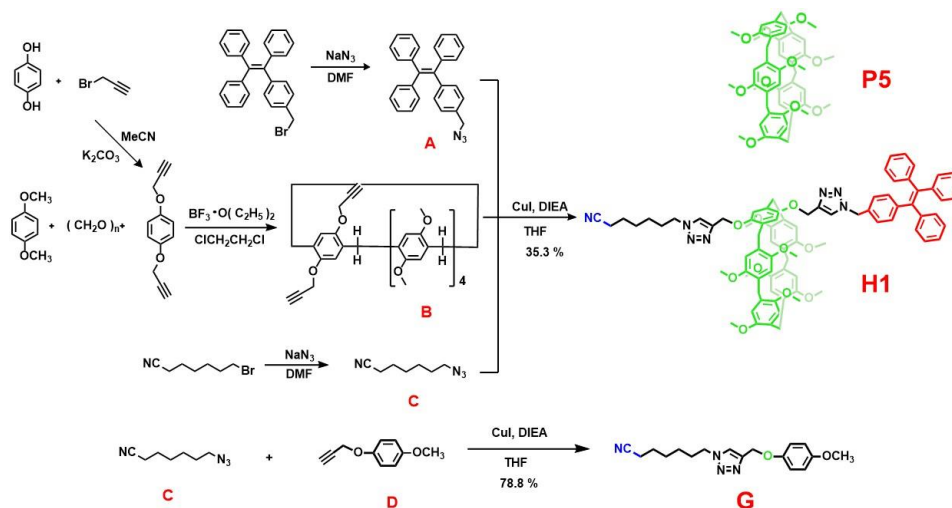
<sup>1</sup>H NMR, <sup>13</sup>C NMR and 2D NOESY spectra were measured on a Brüker 400 spectrometer. The ESI-TOF-MS were acquired on an AB Sciex TripleTOF<sup>®</sup> 6600 mass spectrometer. Fluorescent spectra were recorded on a HITACHI F-7000 spectrophotometer. SEM images were recorded on a ZEISS Sigma 300 apparatus. DLS were recorded on a Malvern Zetasizer Nano ZS90. Fluorescent quantum efficiencies were determined using a Hamamatsu C11347-13 Quantaaurus-QY spectrometer.

### Materials

Chemicals were used as received from Adamas. All solvents were reagent grade and were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopies and ESI-TOF-MS.

## Synthesis

The compound **A**, compound **B**, compound **C**, compound **D** and pillar[5]arene (**P5**) were synthesized according to previous reports [1-5].



**Fig. S1.** The synthesis routes of **H1** and **G**

### Synthesis of **H1**

**H1** was prepared in a closed reaction flask with a [**A**]:[**B**]:[**C**]:[CuI]:[DIEA] ratio of 1:1:1:2.5:20. Compound **A** (14.561 mg, 0.0376 mmol), compound **B** (30.000 mg, 0.0376 mmol), compound **C** (5.719 mg, 0.0376 mmol), CuI (17.892 mg, 0.0939 mmol) and DIEA (97.132 mg, 0.7516 mmol) were dissolved in 10.0 ml dry THF, then the reaction mixture was reaction under 80 °C for 12 hours with argon. The mixture was dissolved in 50.0 ml dichloromethane, washed twice with pure water, and then dried with  $\text{MgSO}_4$ . After filtering, the solvent was removed by evaporation. The residue was purified by column chromatography ( $\text{SiO}_2$ , dichloromethane/Methanol=100:1) to give purified monomer **H1** (yield = 35.3 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298K):  $\delta$  7.66 (s, 1H), 7.62 (s, 1H), 7.10-6.98 (m, 29H), 5.45-5.27 (m, 6H), 3.85-3.73 (m, 34H), 1.71(s, 1H), 1.31-1.13 (m, 3H), -0.70 (d,  $J = 6.4$  Hz, 4H), -1.61 (t,  $J = 6.2$  Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 298K):  $\delta$  151.0, 150.7, 150.6, 150.2, 150.1, 150.0, 149.8, 146.4, 144.9, 144.4, 143.5, 143.4, 143.3, 141.8, 139.5, 132.6, 132.0, 131.3, 131.2, 130.0, 129.1, 129.0, 128.7, 128.5, 128.2, 128.0, 127.8, 127.7, 127.6, 127.3, 126.7, 126.6, 124.9, 122.8, 120.7, 115.8, 114.9, 114.1, 114.0, 113.7, 113.4, 113.3, 113.1, 113.0, 112.8, 61.9, 59.6, 57.7, 56.3, 56.1, 55.6, 55.4, 55.3, 55.2, 53.8, 53.4, 49.5, 30.6, 29.6, 29.3, 28.5, 27.4, 26.2, 23.6, 22.6, 13.6. ESI-TOF-MS( $m/z$ ): [ $\text{M}+\text{H}$ ] $^+$ : calcd for  $\text{C}_{83}\text{H}_{84}\text{N}_7\text{O}_{10}$ , 1338.6274; found, 1338.6275.

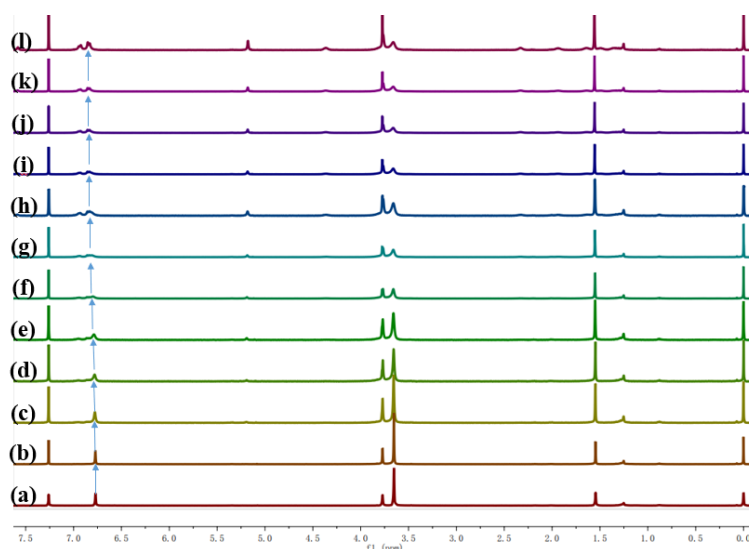
### Synthesis of **G**

**G** was synthesized in a closed reaction flask with a [**C**]:[**D**] ratio of 1:1. Compound **C** (42.600 mg, 0.308 mmol), compound **D** (50.000 mg, 0.308 mmol), CuI (88.07 mg, 0.462 mmol) and DIEA (597.64 mg, 4.62 mmol) were dissolved in 10.0 ml dry THF, then the reaction mixture was

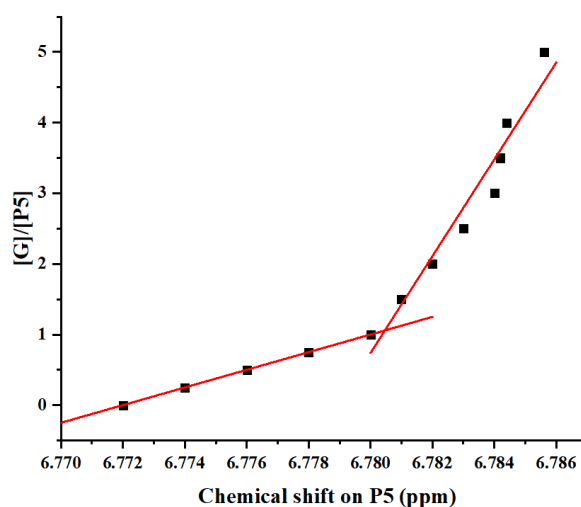
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reaction under 80 °C for 12 hours with argon. The mixture was dissolved in 50.0 ml dichloromethane, washed twice with pure water, and then dried with MgSO<sub>4</sub>. After filtering, the solvent was removed by evaporation. The residue was purified by column chromatography (SiO<sub>2</sub>, dichloromethane/Methanol=50:1) to give purified monomer **G** (yield = 78.8 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298K): δ 7.57 (s, 1H), 6.94-6.90 (m, 2H), 6.85-6.81 (m, 2H), 5.16 (s, 2H), 4.36(t, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.32 (t, *J* = 6.8 Hz, 2H), 1.97-1.89 (m, 2H), 1.67-1.60 (m, 2H), 1.52-1.45 (m, 2H), 1.38-1.31 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298K): δ 154.2, 152.3, 144.6, 122.4, 119.5, 115.9, 114.7, 62.8, 55.7, 50.1, 30.0, 28.0, 25.7, 25.1, 17.0. ESI-TOF-MS (*m/z*): [M+Na]<sup>+</sup>: calcd for C<sub>17</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>Na, 337.1635; found, 337.1629.

### Complexation between P5 and G.



**Fig. S2.** <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 298K) of **P5** at a concentration of 2.0 mM upon addition of **G** (15.0 mM): (a) 0.0 μl, (b) 10.0 μl, (c) 20.0 μl, (d) 30.0 μl, (e) 40.0 μl, (f) 60.0 μl, (g) 80.0 μl, (h) 100.0 μl, (i) 120.0 μl, (j) 140.0 μl, (k) 160.0 μl, (l) 200.0 μl.



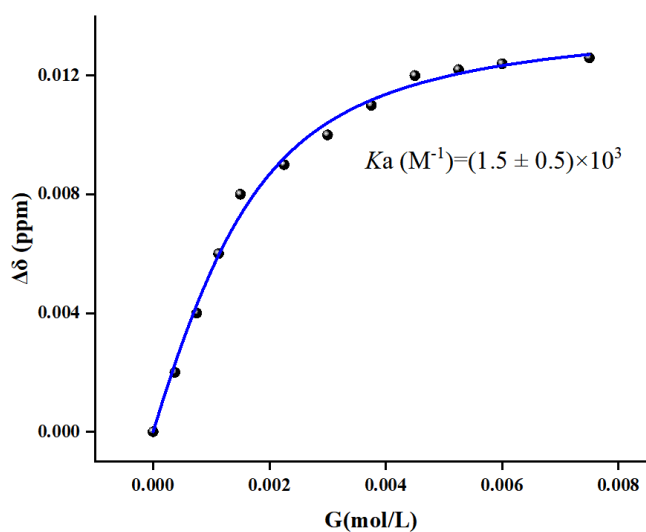
**Fig. S3.** Mole ratio plot for **P5** and **G**. The plot indicates a 1:1 stoichiometry.

**Determination of the association constant.**

For **G**, chemical exchange is fast on the NMR time scale (Figure S2). To determine the association constant, NMR titrations were done with solutions which had a constant concentration of **P5** and varying concentrations of **G**. Using the nonlinear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation:

$$A = (A_{\infty}/[P5]_0) (0.5[G]_0 + 0.5([P5]_0 + 1/Ka) - (0.5([G]_0^2 + 2[G]_0(1/Ka - c)) + (1/Ka + [P5]_0)^2)^{0.5})$$

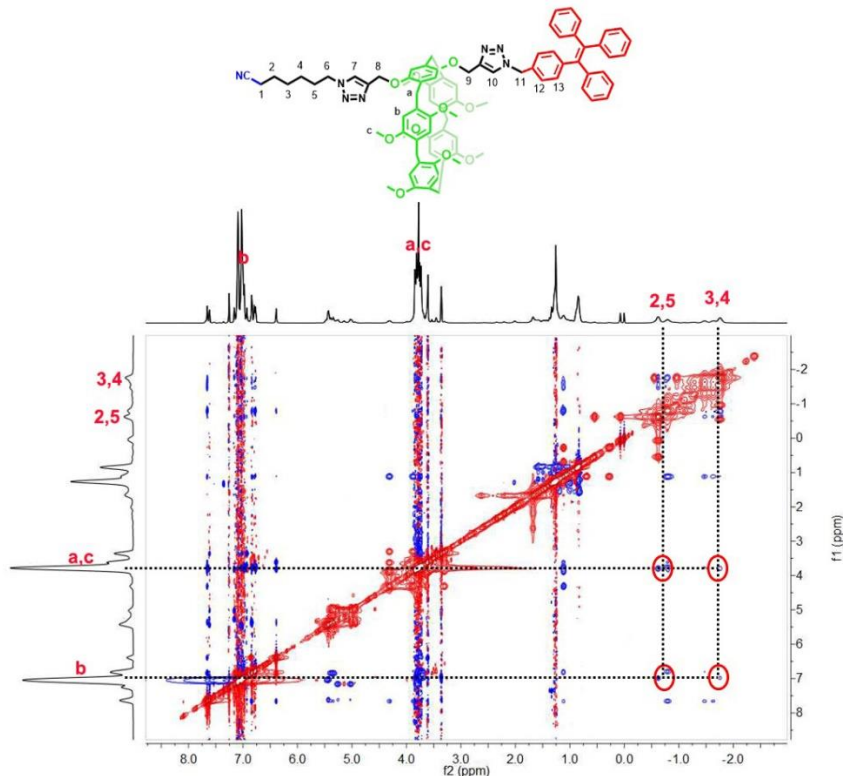
Where A is the chemical shift change of aromatic proton on P5 host at  $[G]_0$ ,  $A_{\infty}$  is the chemical shift change of P5 when the host is completely complexed,  $[P5]_0$  is the fixed initial concentration of the P5 host, and  $[G]_0$  is the initial concentration of guest.



**Fig. S4.** The non-linear curve-fitting (NMR titrations) for the complexation of P5 host (2.0 mM) with **G** in  $CDCl_3$  at 298 K. The concentration of **G** was 0.375 mM, 0.75 mM, 1.12 mM, 1.15 mM, 2.25 mM, 3.00 mM, 3.75 mM, 4.50 mM, 5.25 mM, 6.00 mM, 7.50 mM.

**2D NOESY spectra of H1 in CDCl<sub>3</sub> solution**

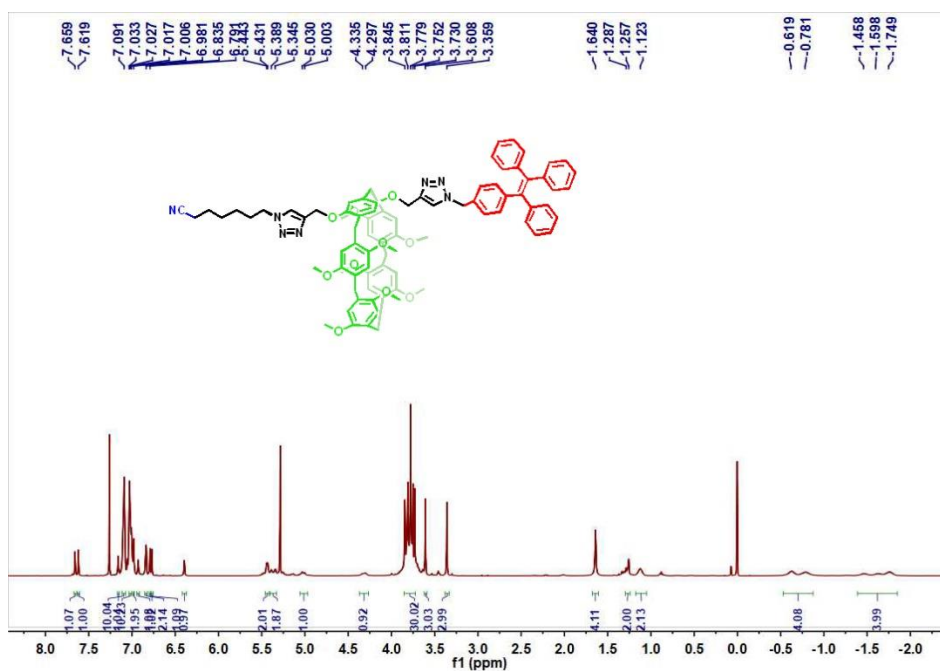
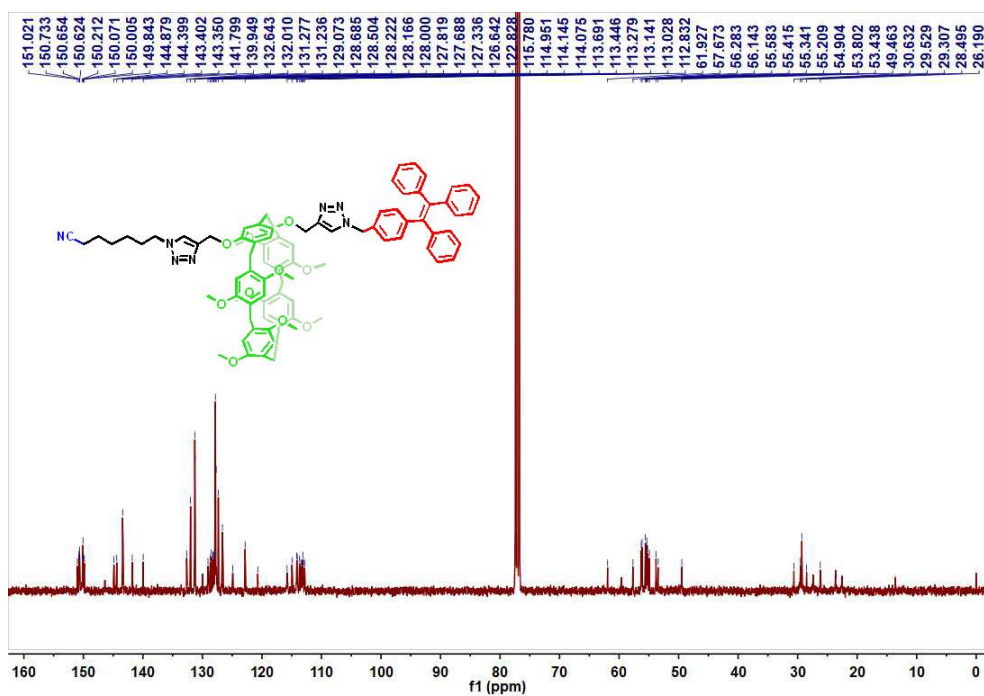
The 2D-NOESY NMR spectrum of the solution of **H1** showed the NOE peaks between protons Hb and H2, H5, H3, H4, as well as Ha/Hc and H2, H5, H3, H4, which clearly confirmed the complexation between pillar[5]arene and neutral nitrile group.

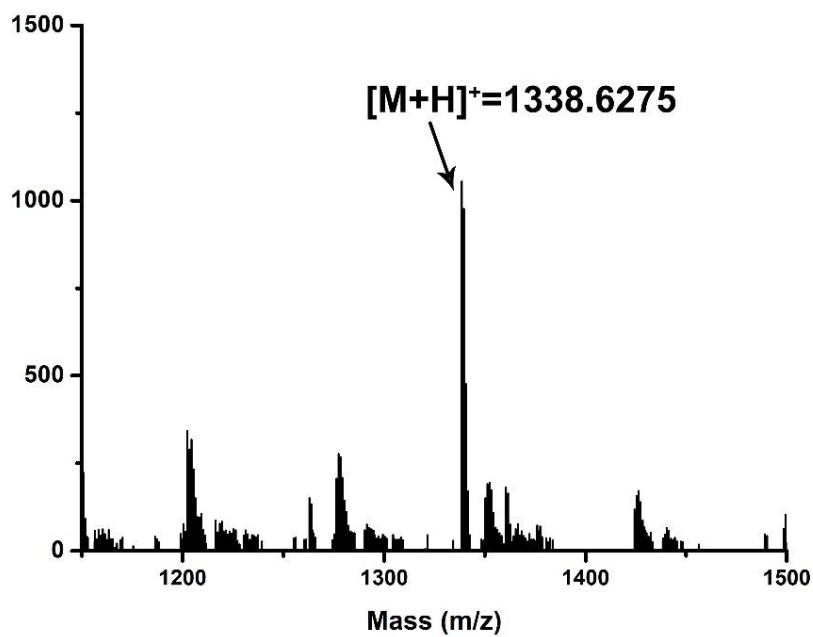


**Fig. S5.** 2D-NOESY analysis of **H1** in CDCl<sub>3</sub> (400 MHz, 298 K, 32.7 mM)

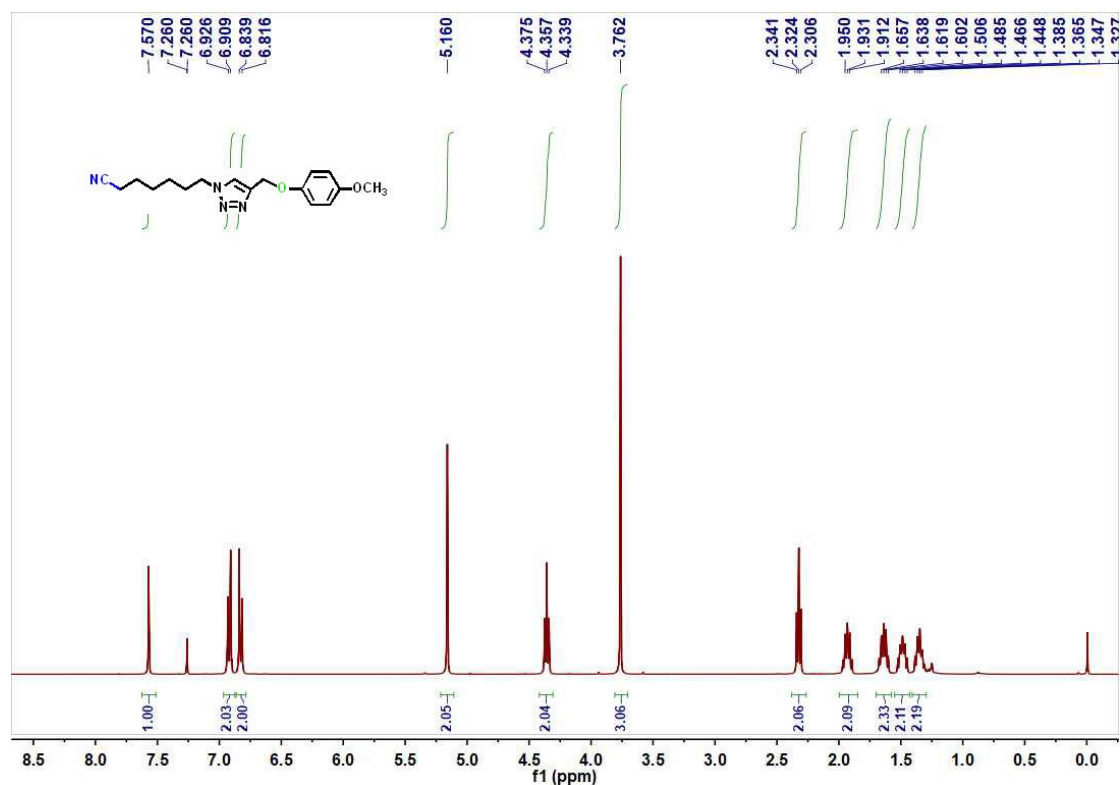
**Reference:**

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S2. J.-C. Ji, W.-H. Wu, X.-Q. Wei, M. Rao, D.-Y. Zhou, G. Cheng, Q.-Y. Gong, K. Luo and C. Yang, *Chem. Commun.*, 2020, **56**, 6197-6200.  
S3. F. Sebest, J. J. Dunsford, M. Adams, J. Pivot, P. D. Newman and S. Díez-González, *ChemCatChem.*, 2018, **10**, 2041-2045.  
S4. P.-S. Hellwing, A.-M. Barcellos, R. Cargnelutti, T. Barcellos and G. Perin, *J. Org. Chem.*, 2022, **87**, 15050-15060.  
S5. D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721-9723.

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectra**Fig. S6.**  $^1\text{H}$  NMR spectra (CDCl<sub>3</sub>, 298 K, 400 MHz) of **H1**.**Fig. S7.**  $^{13}\text{C}$  NMR spectra (CDCl<sub>3</sub>, 298 K, 400 MHz) of **H1**.

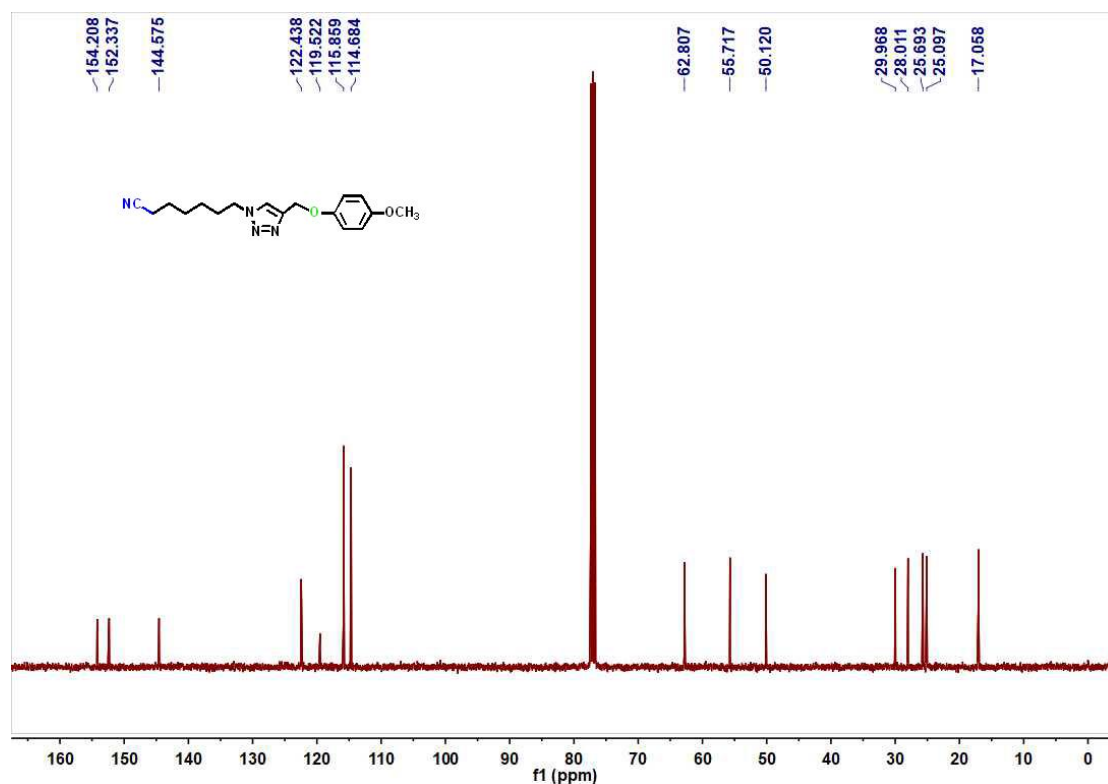


**Fig. S8.** ESI-TOF-MS of H1.

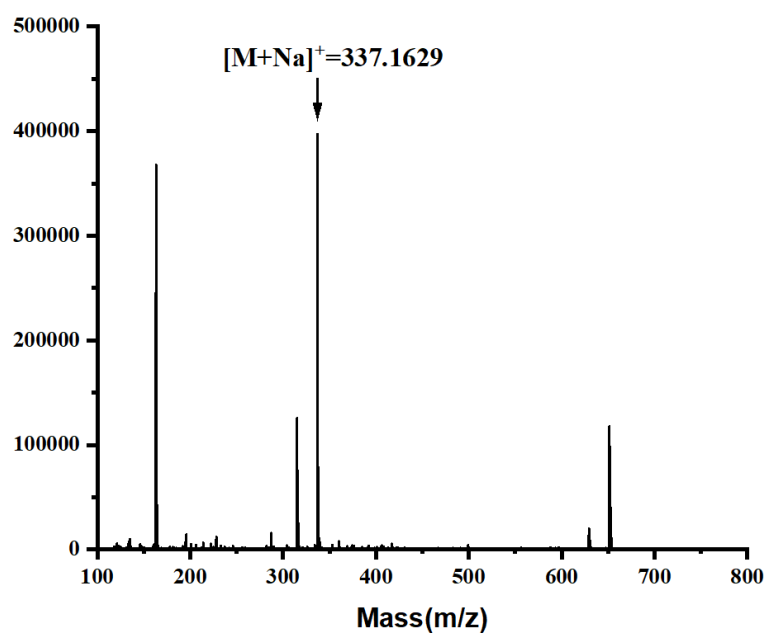


**Fig. S9.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 298 K, 400 MHz) of G.

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**Fig. S10.**  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ , 298 K, 400 MHz) of G.



**Fig. S11.** ESI-TOF-MS of G.