Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A Novel Functionalized Pillar[5]arene-based Selective Amino Acid Sensor for L-Tryptophan

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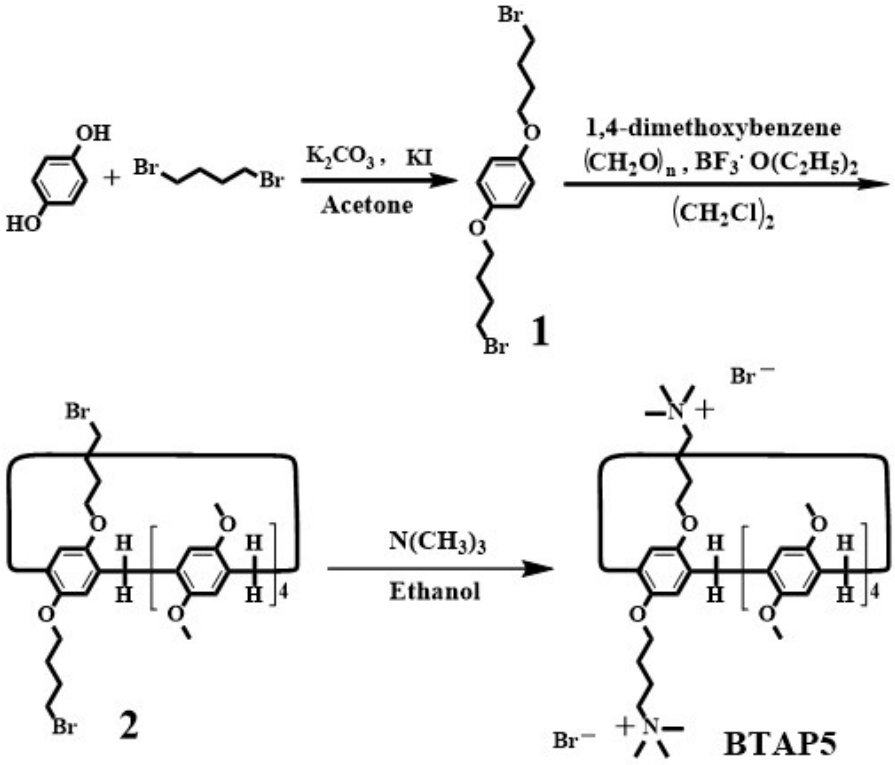
1. Materials and methods

1, 4−Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4−dibromobutane, and was reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^1H NMR spectra were recorded on a Mercury−600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury−600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X−4 digital melting−point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker−FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer.

The binding constants (K_a) were also determined based on the nonlinear fluorescence titration curve using the equation as follows: where $\boldsymbol{I}$ and $\boldsymbol{I}_{max}$ represent the fluorescence intensity of host in the presence and absence of guest, respectively, $\boldsymbol{I}_{min}$ is the saturated fluorescence intensity of host in the presence of excess amount of guest; [$\boldsymbol{G}$] is the concentration of guest added.

$$\log\frac{I-I_{min}}{I_{max}-I}=\log K_a+\log[G]$$

2. Synthesis of functionalized pillar[5]arene BTAP5



Scheme S1 Synthesis of functionalized pillar[5]arene **BTAP5**.

Synthesis of 1,4−bis(4−bromobutoxy)benzene 1: Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,4−dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round–bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2=10 : 1) afforded a white solid(6.0 g, 80%). Mp 83−85°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, J = 0.8 Hz, 4H), 3.96 (t, J =6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H).

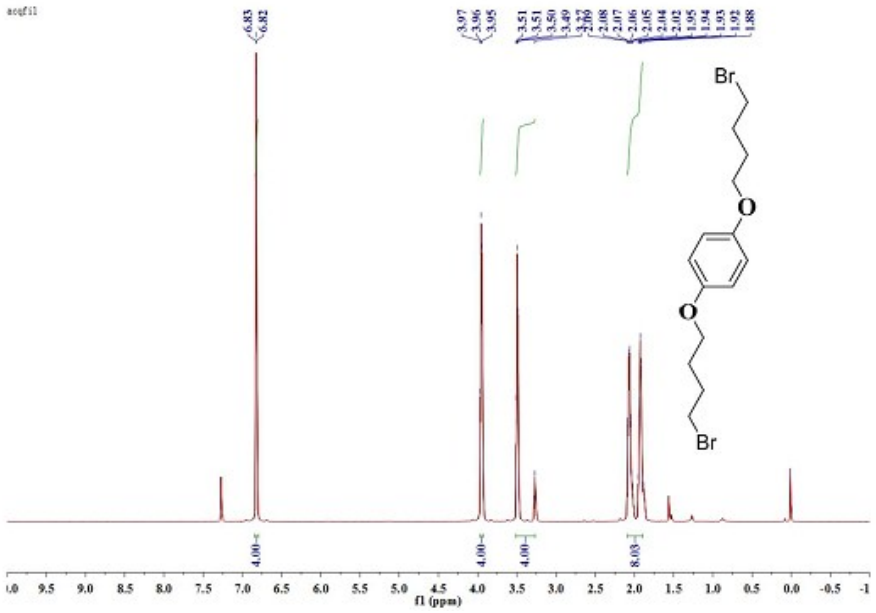


Fig. S1 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

Synthesis of a copillar[5]arene 2: To a solution of 1,4−bis(4−bromobutoxy) benzene (1.9 g, 5.0 mmol) and 1,4−dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2−dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1,*v*/*v*) to give **2**(1.69 g, 34%) as a white solid. Mp 187−189 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84–6.74 (m, 10H), 3.87 (t, *J*= 5.9 Hz, 4H), 3.83–3.78 (m, 10H), 3.72 (t, *J*= 19.9 Hz, 24H), 3.33 (s, 4H), 1.94 (s, 4H), 1.84 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.21–150.05 (m), 128.28 (s), 114.43–113.26 (m), 67.27–66.80 (m), 55.66 (s), 33.49 (s), 29.55 (s), 28.32 (s). ESI−MS m/z: $(M+NH_4)^+$ Calcd for $C_{51}H_{64}O_{10}Br_2N$ 1010.2871; Found 1010.2878.

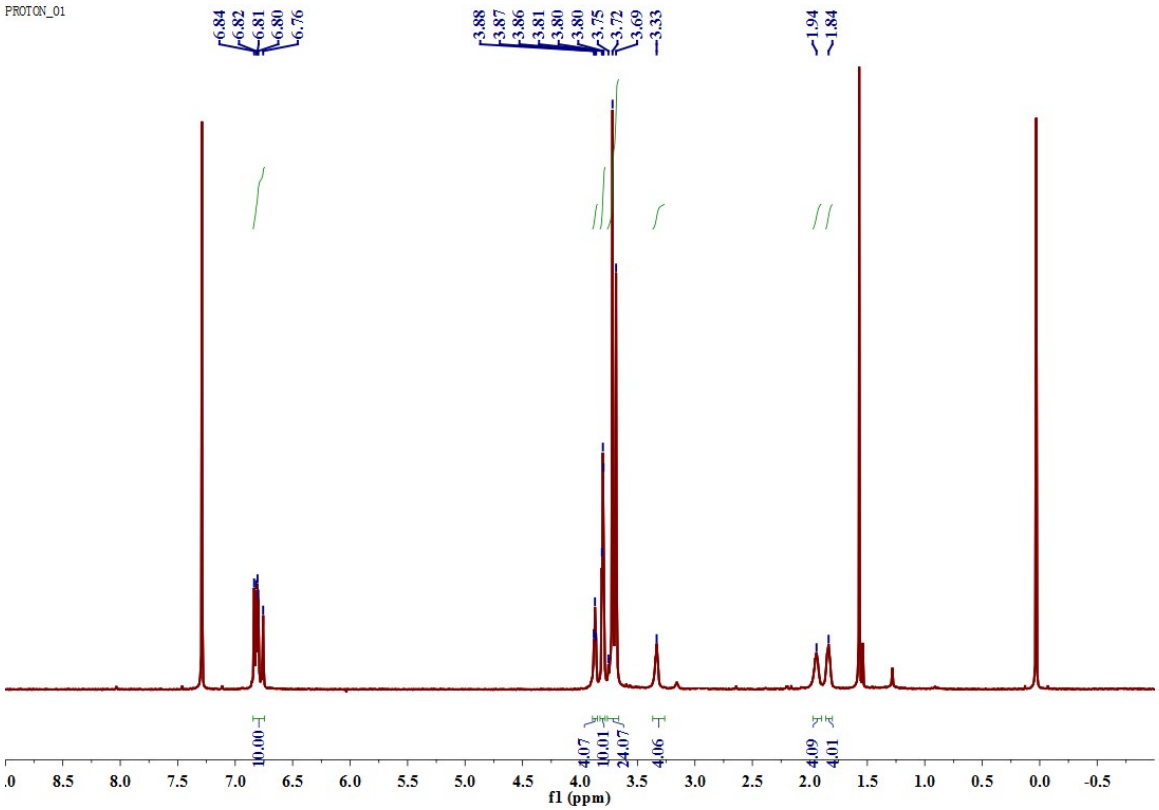


Fig. S2 ^{1}H NMR spectra(600 MHz, $CDCl_3$) of a copillar[5]arene **2**.

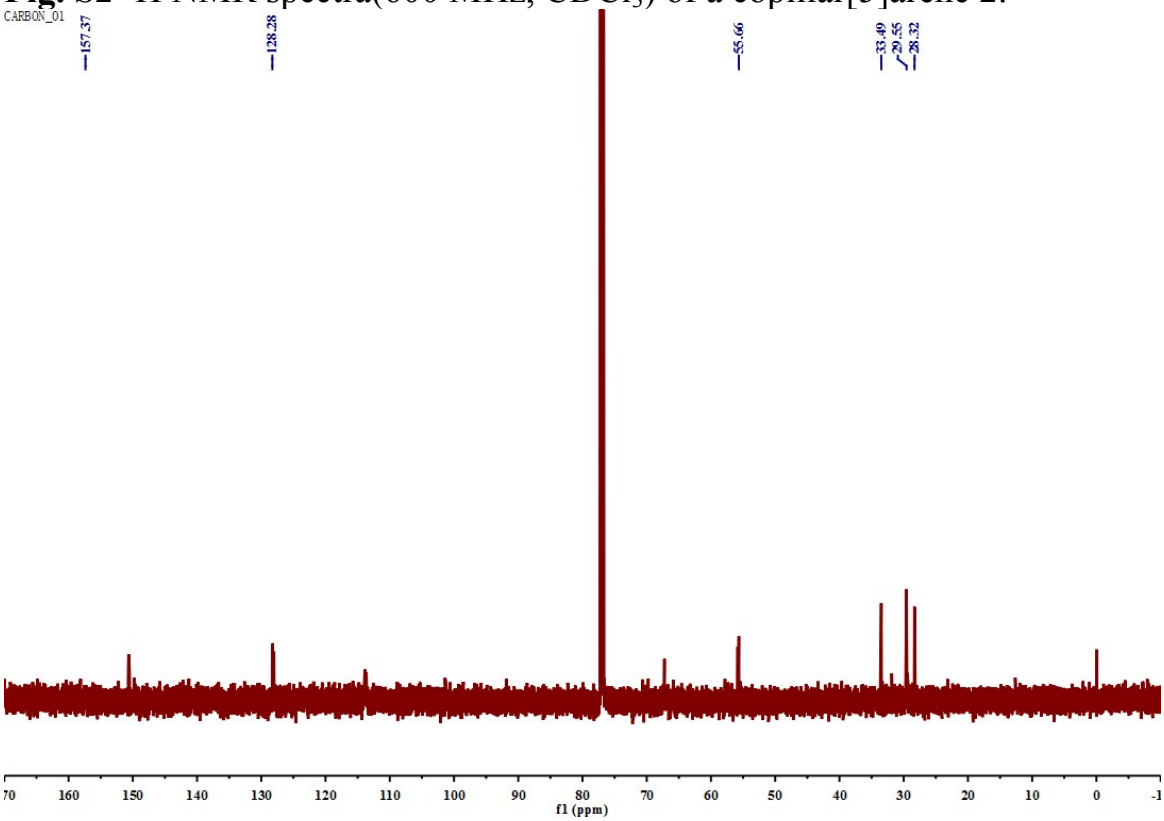


Fig. S3 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of a copillar[5]arene **2**.

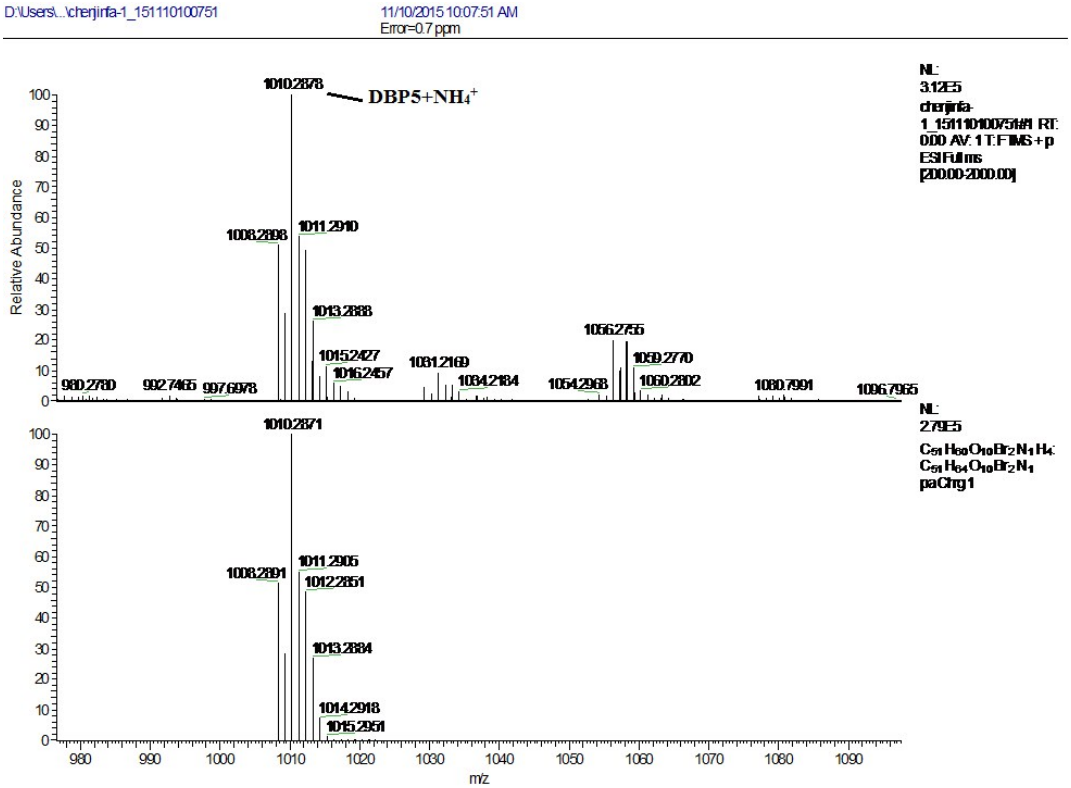


Fig. S4 High resolution mass data of a copillar[5]arene **2**.

Synthesis of functionalized pillar[5]arene BTAP5: Copillar[5]arene **2** (0.5 g, 0.5 mmol) and trimethylamine (33 % in ethanol, 1.0 mL, 3.7 mmol) were added to ethanol (80 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, you can afford a white solid. After white solid was washed by diethyl ether to obtain **BTAP5** as a white solid (0.52 g, 93 %). Mp 176−178 °C. ^{1}H NMR (600 MHz, D_2O/DMSO-d_6 (4 : 1 , v/v)) δ 6.84 – 6.54 (m, 10H), 3.65 (s, 4H), 3.51 (dd, J= 23.6, 16.5 Hz, 18H), 3.23 (t, J= 24.3 Hz, 10H), 3.07 – 2.94 (m, 24H), 1.76 (d, J= 84.5 Hz, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 150.42, 150.36, 149.64, 128.24, 128.07, 128.02, 127.92, 113.85, 67.59, 65.49, 56.10, 56.03, 56.00, 55.97, 52.62, 29.41, 26.72, 19.72. ESI−MS m/z: $(M-2Br)^{2+}$ Calcd for $C_{57}H_{78}O_{10}N_2$ 475.2823; Found 475.2828.

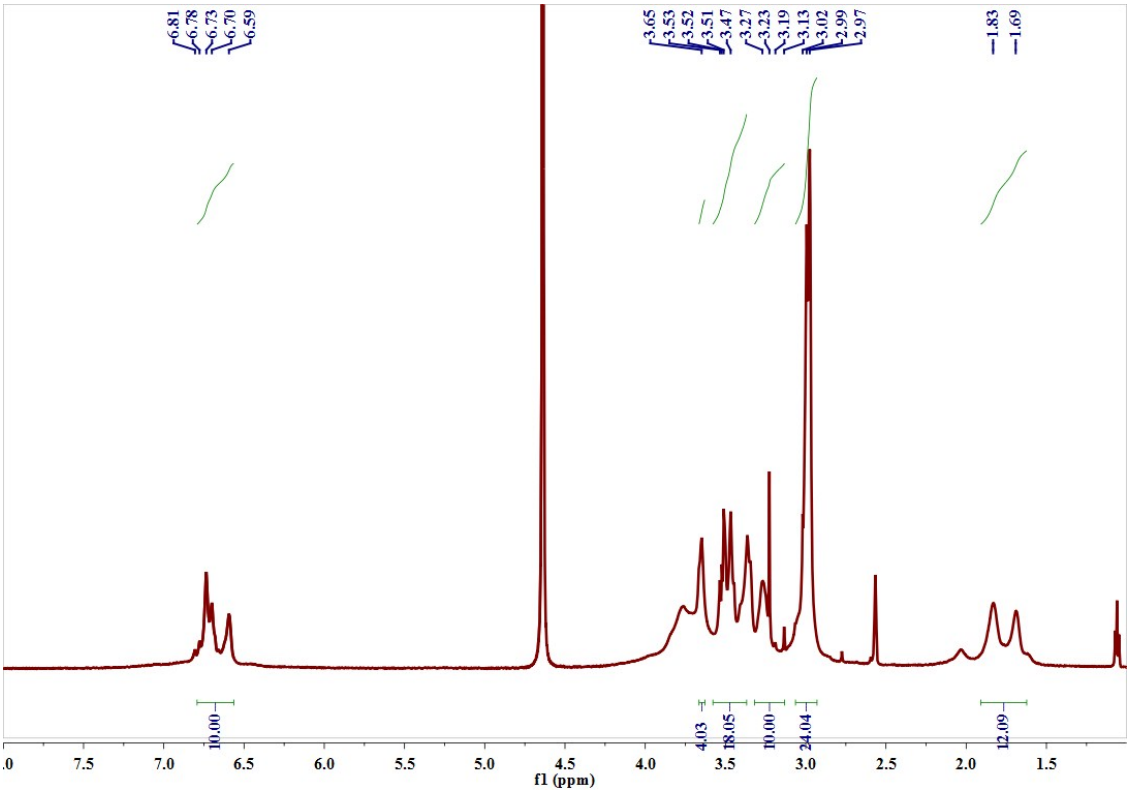


Fig. S5 ^{1}H NMR spectra(600 MHz, D_2O/DMSO-d_6 (4 : 1 , v/v)) of functionalized pillar[5]arene **BTAP5**.

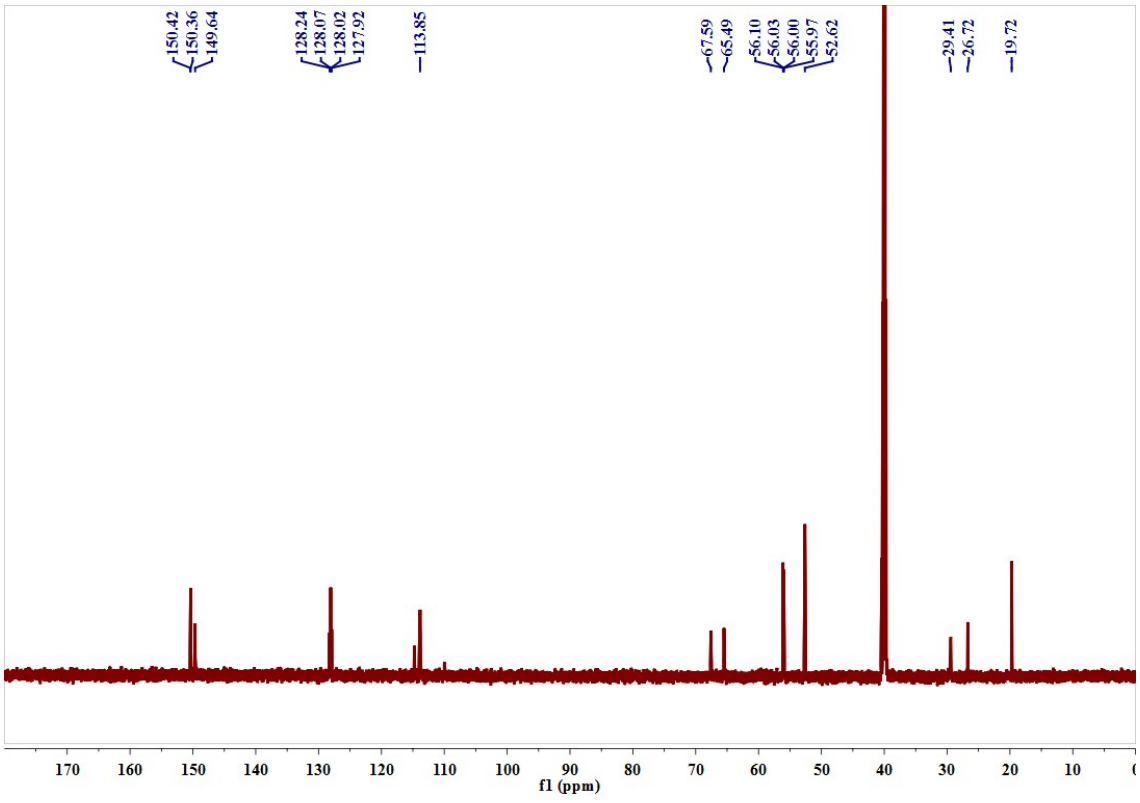


Fig. S6 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of functionalized pillar[5]arene **BTAP5**.

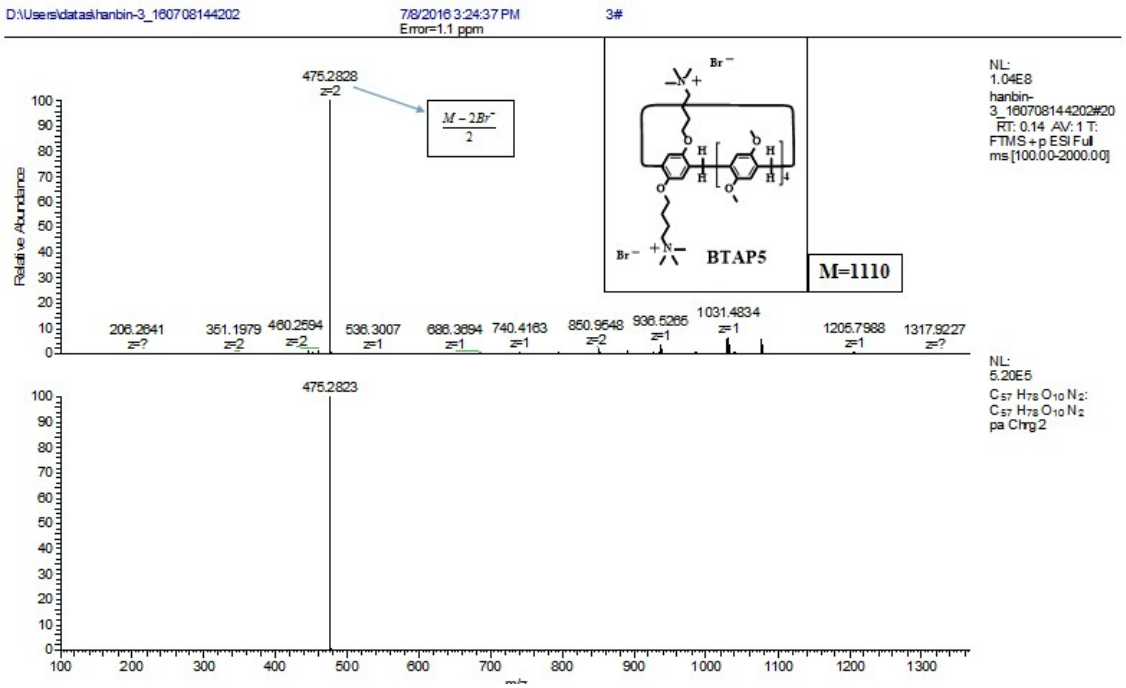


Fig. S7 High resolution mass data of functionalized pillar[5]arene **BTAP5**.

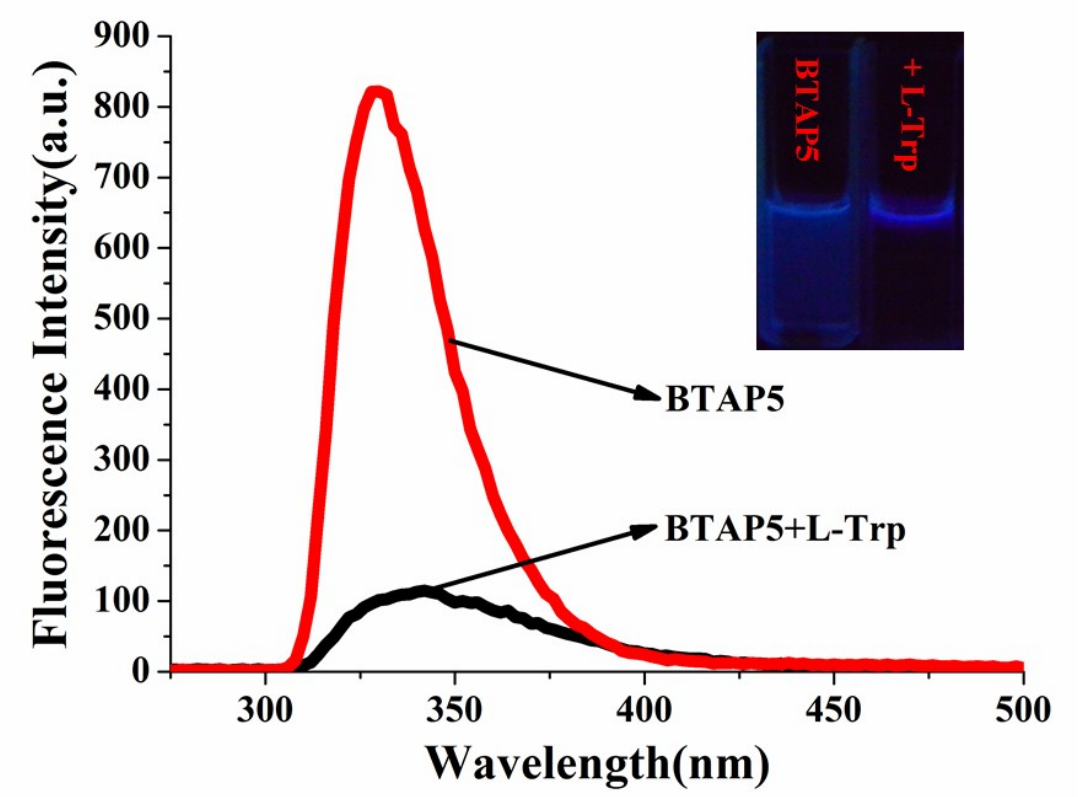


Fig. S8 Fluorescence spectral response of **BTAP5** (2×10^{-4} M) in H_2O/DMSO (7 : 3 , v/v) solution upon addition of 5.0 equiv. of L-Trp (λ_{ex} = 255 nm). Inset: photograph of **BTAP5** (2×10^{-4} M) upon addition of 5.0 equiv. of L-Trp, which was taken under a UV−lamp (253.7 nm).

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.

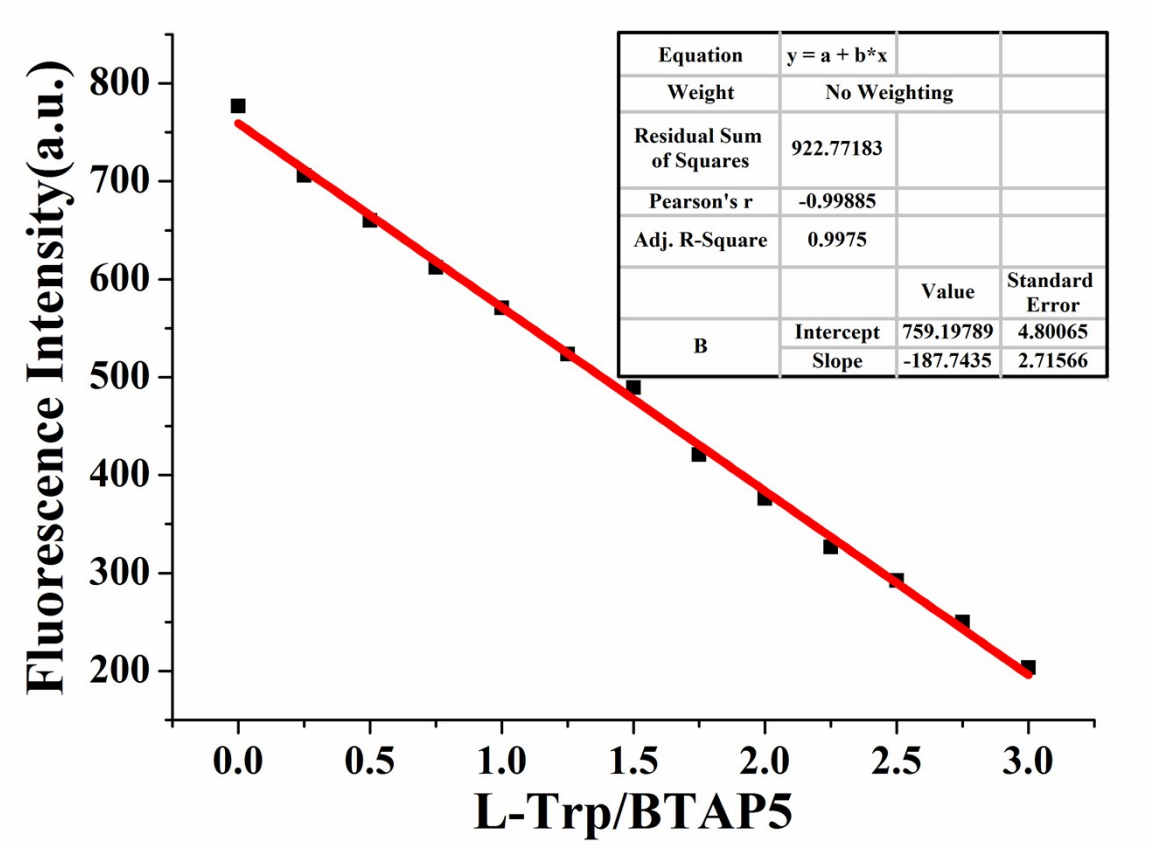


Figure S9 The photograph of the linear range.

Linear Equation: Y=-187.7435X+759.19789 R^2=0.9975

S=187.7435×10^6

$$\delta = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}} = 17.73(n = 20)$$

K=3

LOD =K×δ/S= 2.83 $\times10^{-7}$M

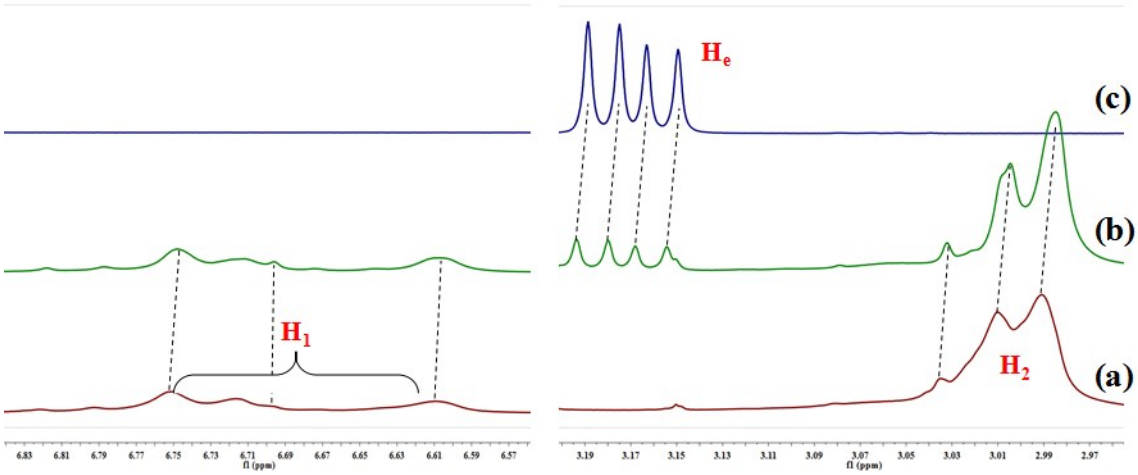


Figure S10 Partial ^{1}H NMR spectra (600 MHz, 298 K) of (a) 20 mM **BTAP5**; (b) 20mM **BTAP5** and L-Trp; (c) 20mM L-Trp. Italics represent complexed host and guest.

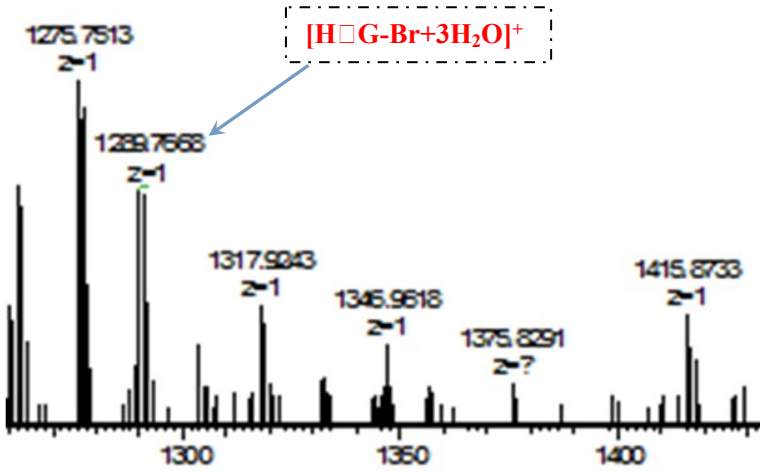


Figure S11 High resolution mass data of the complex of **BTAP5** and L-Trp.

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