Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

A Supramolecular Hyperbranched Polymer with Multi-Responsiveness Constructed by Pillar[5]arene-Based Host–Guest Recognition and Its Application in the Breath Figure Method

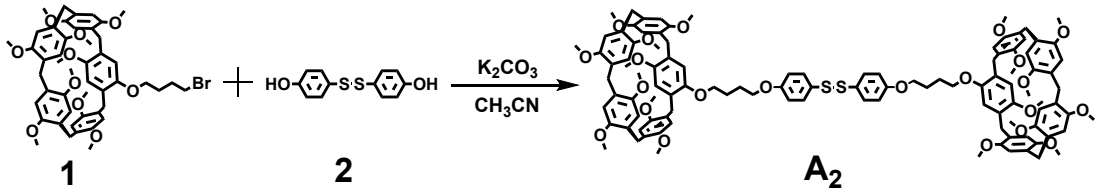
Yuezhou Liu,† Yingyi Zhang,‡ Huangtianzhi Zhu,† Hu Wang,† Wei Tian*,‡ and Bingbing Shi*,†

† Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

‡ Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, P. R. China.

*Corresponding Authors: (B. Shi) Email: bingbingshi@zju.edu.cn; Fax and Tel: +86-571-8795-3189; (W. Tian) E-mail: happytw_3000@163.com.

1. Synthesis and characterizations of compounds



Scheme S1. The synthetic route of compound $\mathbf{A_2}$.

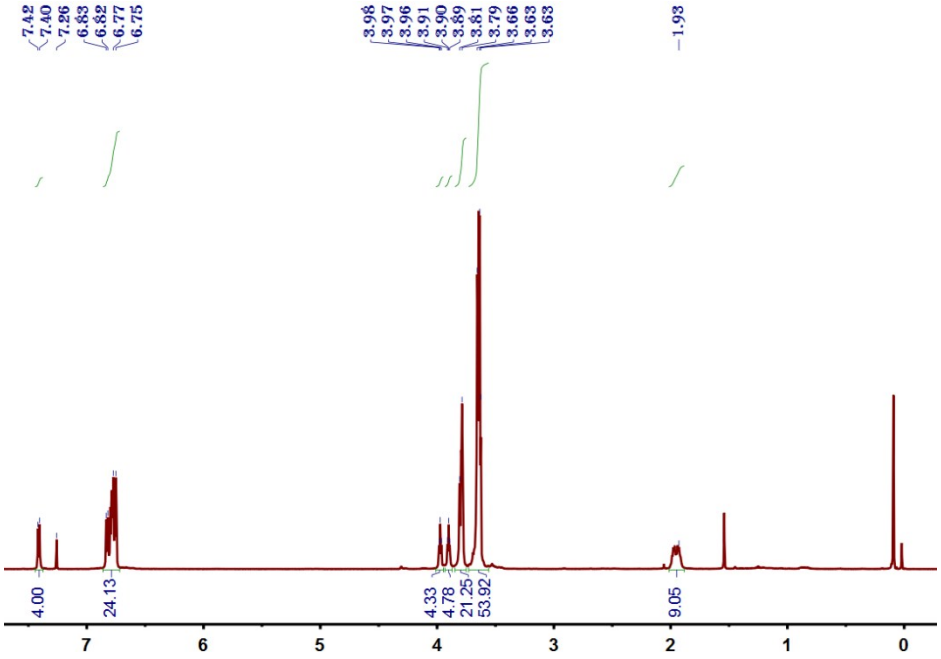


Figure S1. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, room temperature) of $\mathbf{A_2}$.

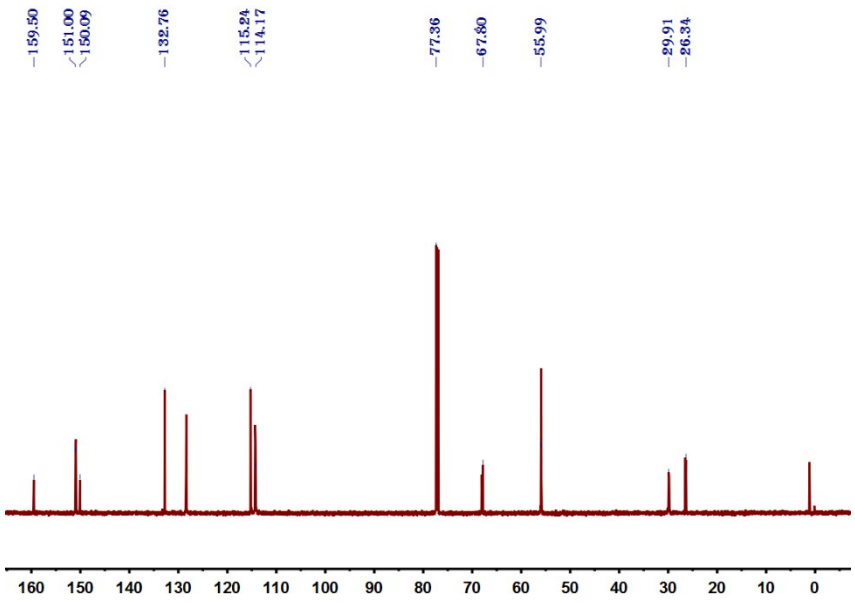
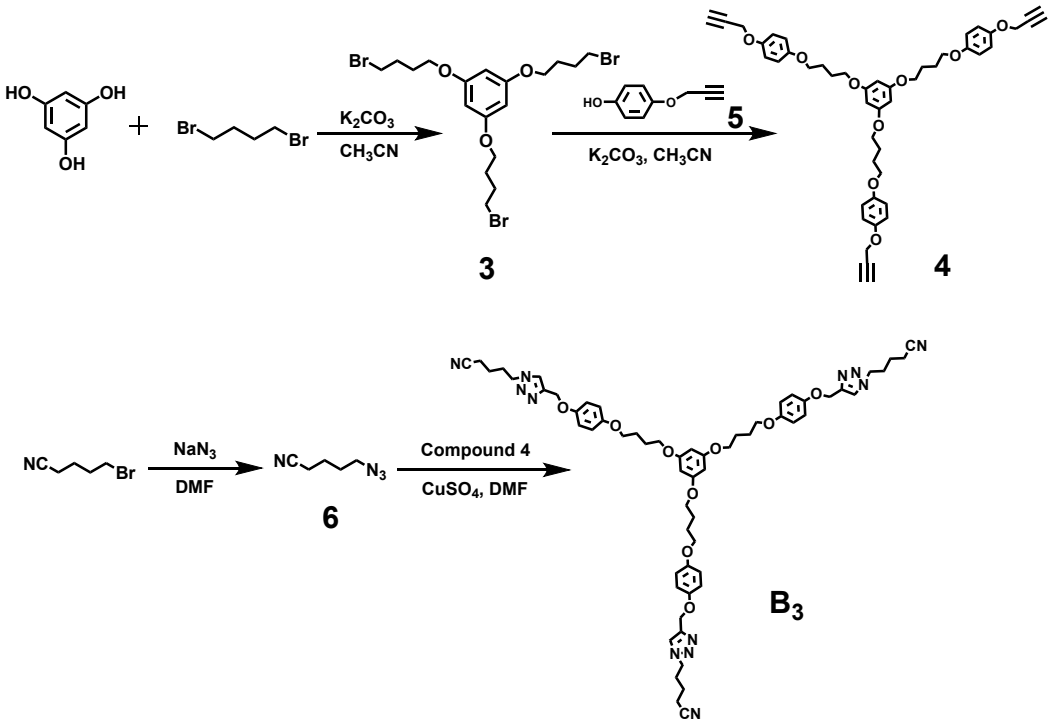


Figure S2. ^{13}C NMR spectrum (150 MHz, chloroform-*d*, room temperature) of $\mathbf{A_2}$.



Scheme S2. The synthetic route of $\mathbf{B_3}$.

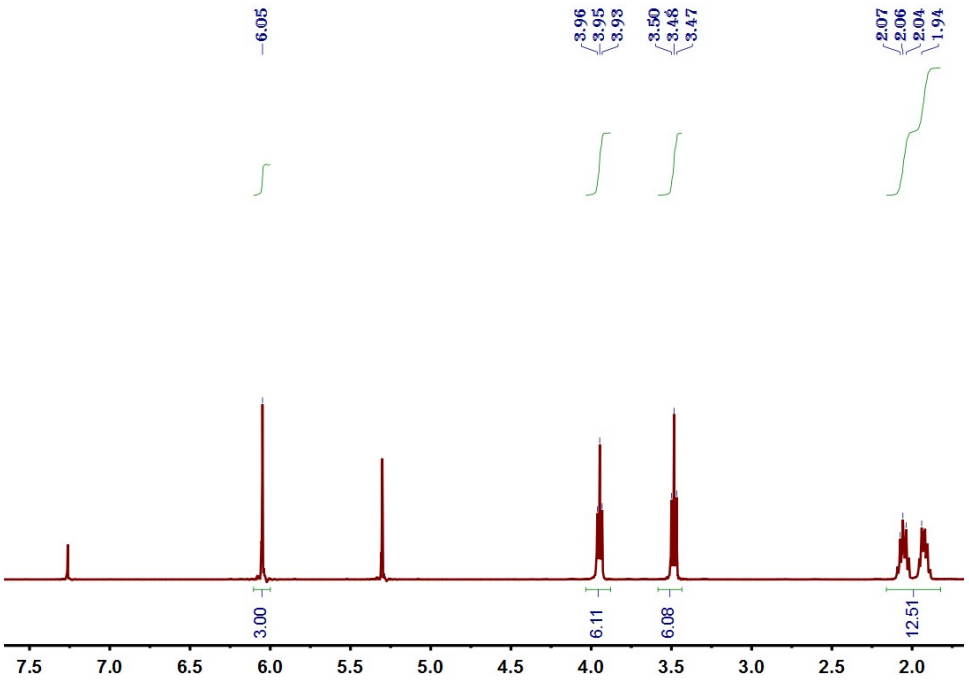


Figure S3. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, room temperature) of **3**.

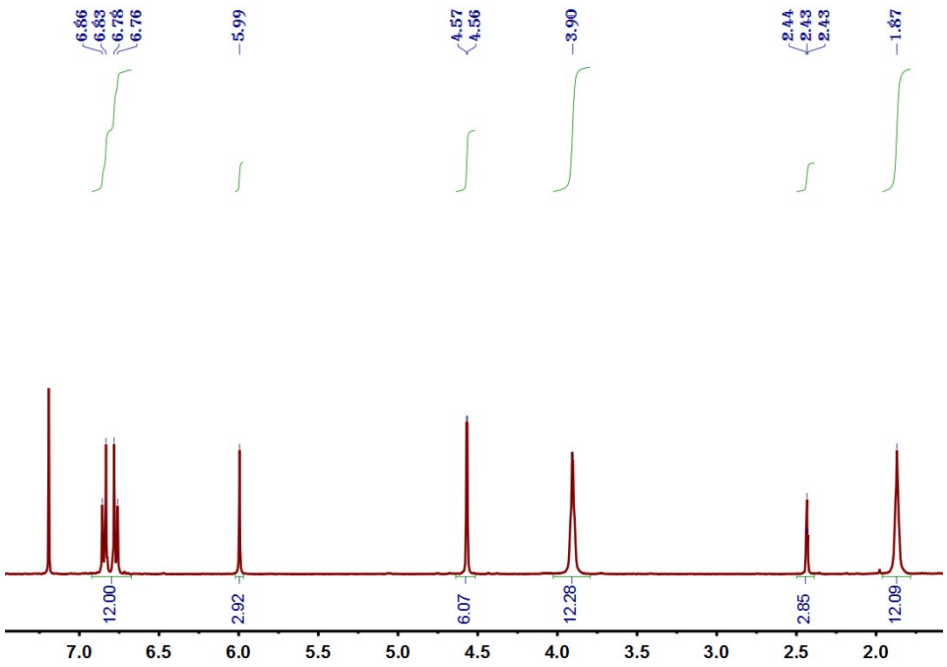


Figure S4. [1]H NMR spectrum (600 MHz, chloroform-*d*, room temperature) of **4**.

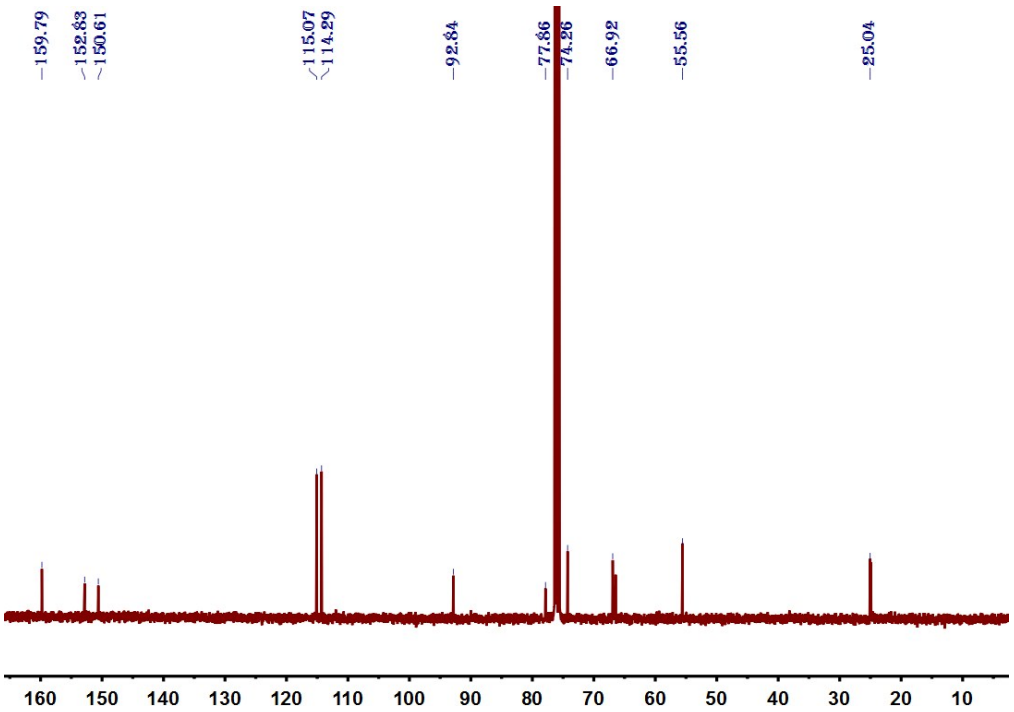


Figure S5. [13]C NMR spectrum (150 MHz, chloroform-*d*, room temperature) of **4**.

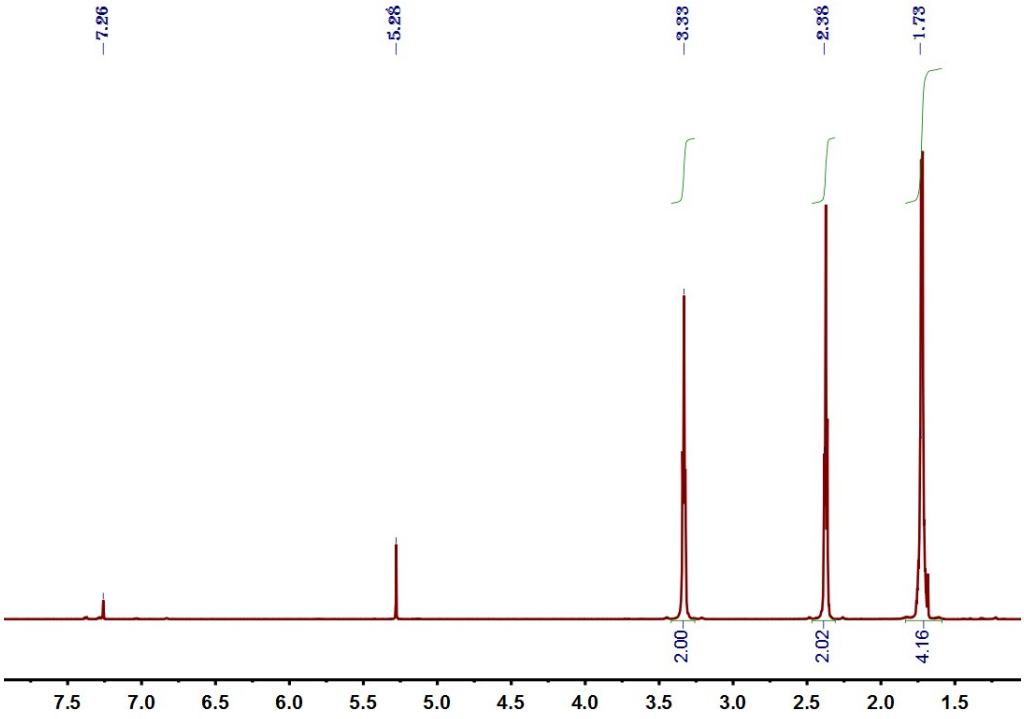


Figure S6. [1]H NMR spectrum (600 MHz, chloroform-*d*, room temperature) of **6**.

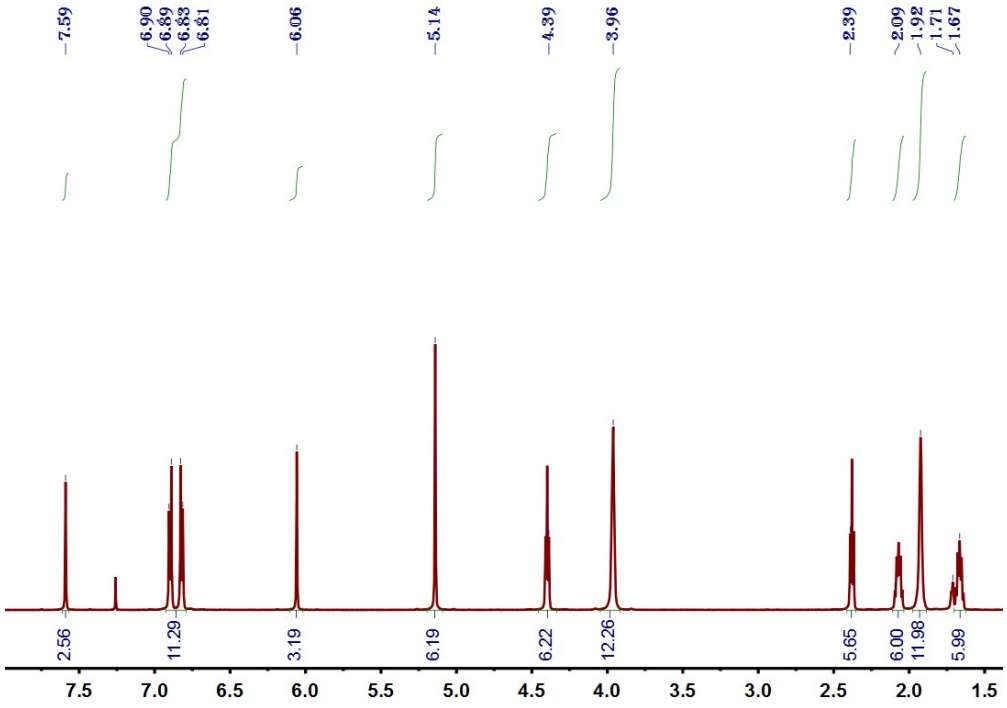


Figure S7. [1]H NMR spectrum (600 MHz, chloroform-*d*, room temperature) of $\mathbf{B_3}$.

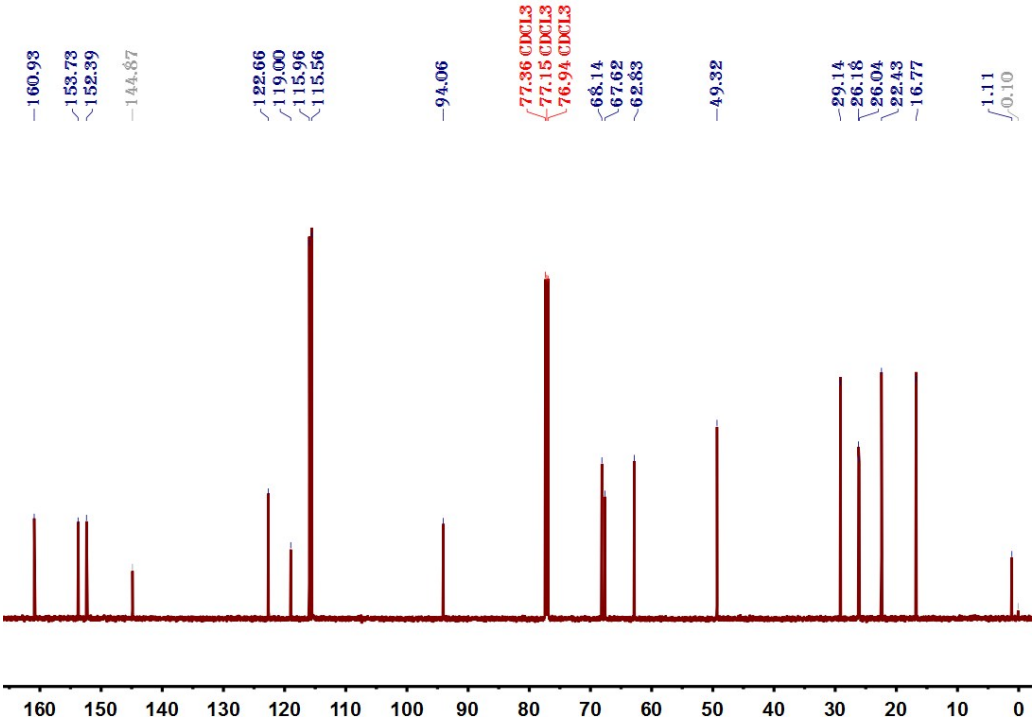


Figure S8. ^{13}C NMR spectrum (150 MHz, chloroform-*d*, room temperature) of $\mathbf{B_3}$.

2. NOESY NMR spectrum of A_2–B_3 complex in $CDCl_3$

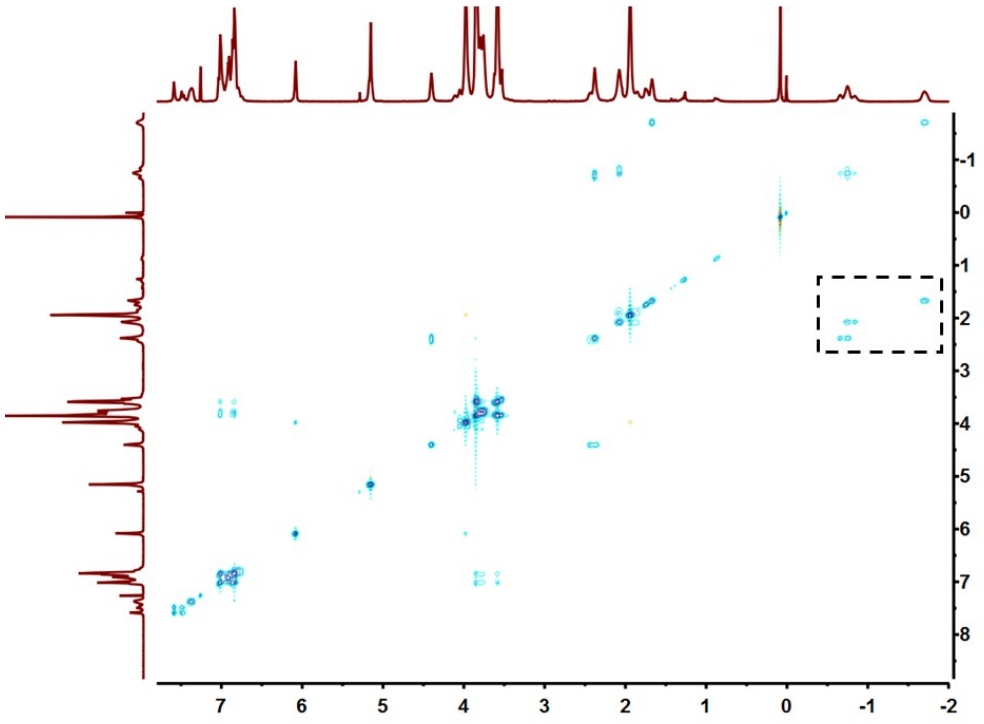


Figure S9. 2D NOESY NMR spectrum (600 MHz, room temperature) in $CDCl_3$ of 7.5 mM $\mathbf{A_2}$ and 5.0 mM $\mathbf{B_3}$.

3. Representative 2D DOSY NMR spectra of A_2–B_3 complex

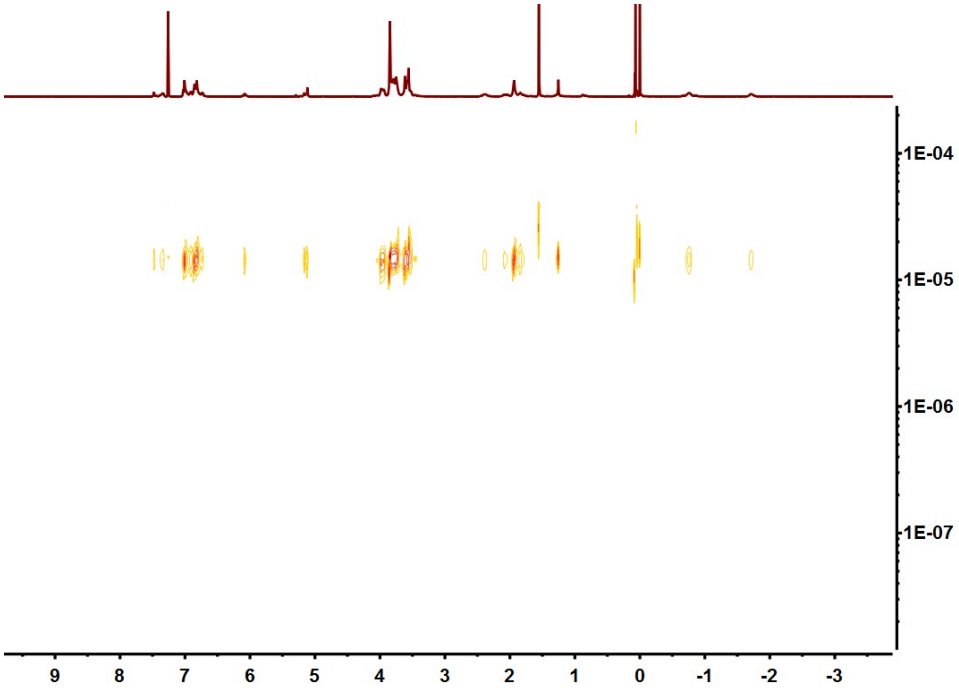


Figure S10. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (1.00 mM **A_2**).

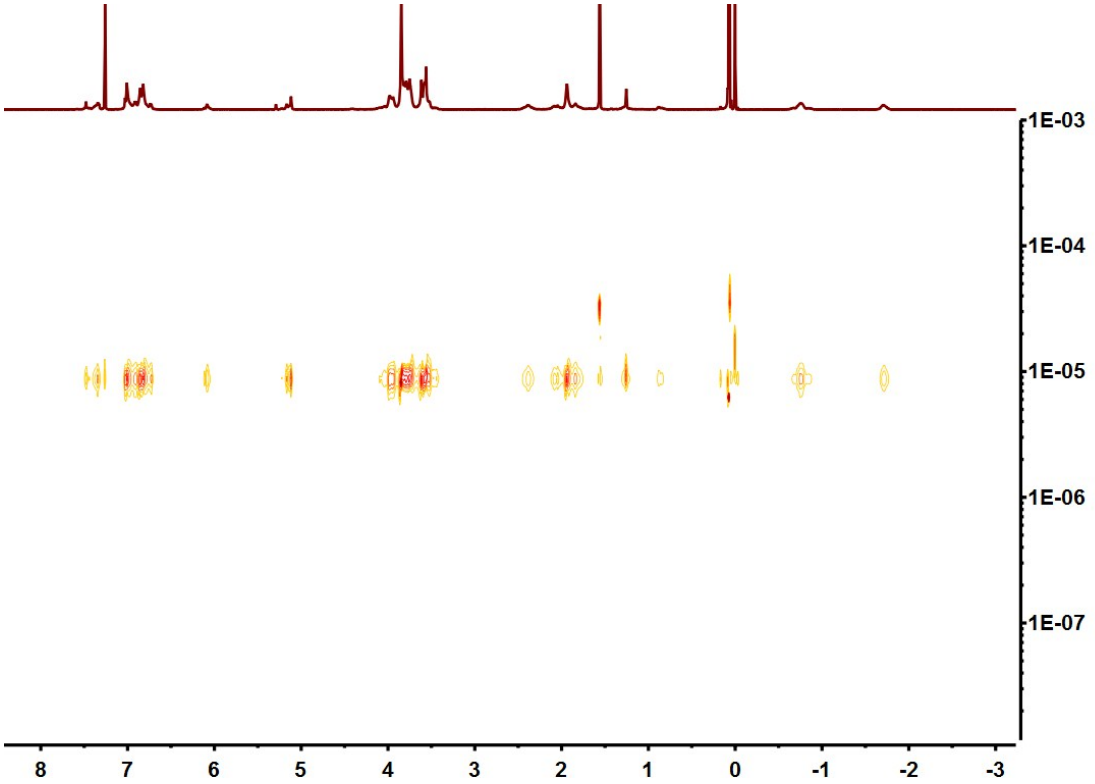


Figure S11. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (2.00 mM **A_2**).

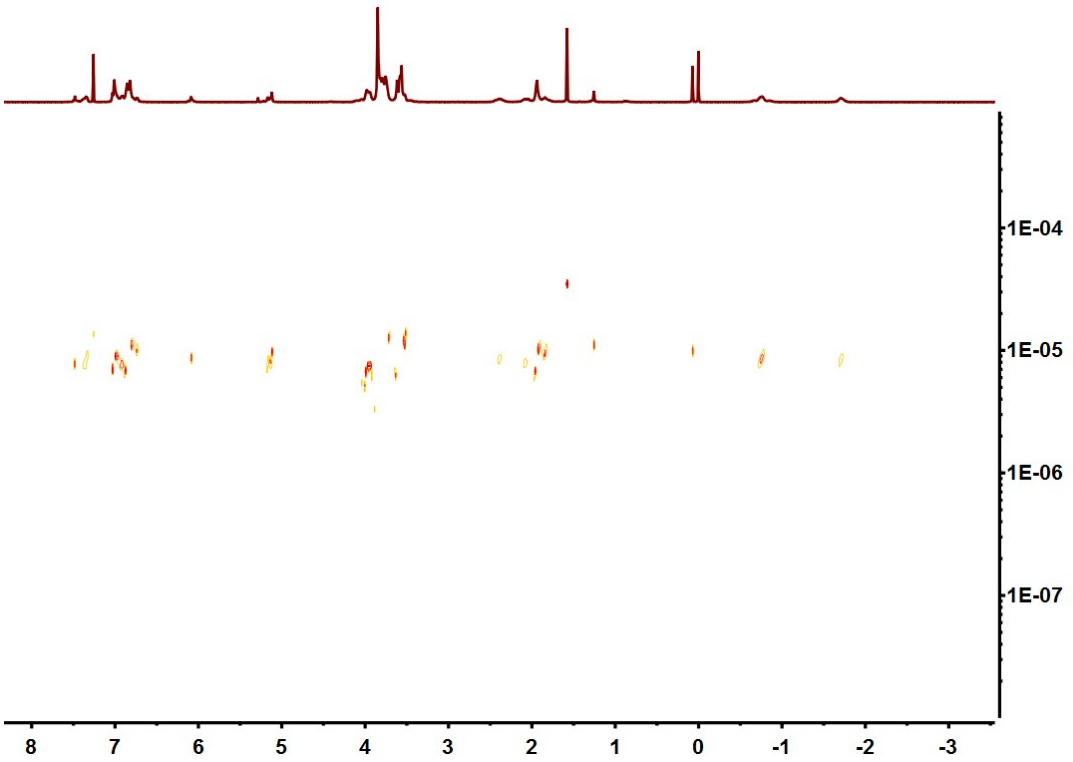


Figure S12. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (5.00 mM **A_2**).

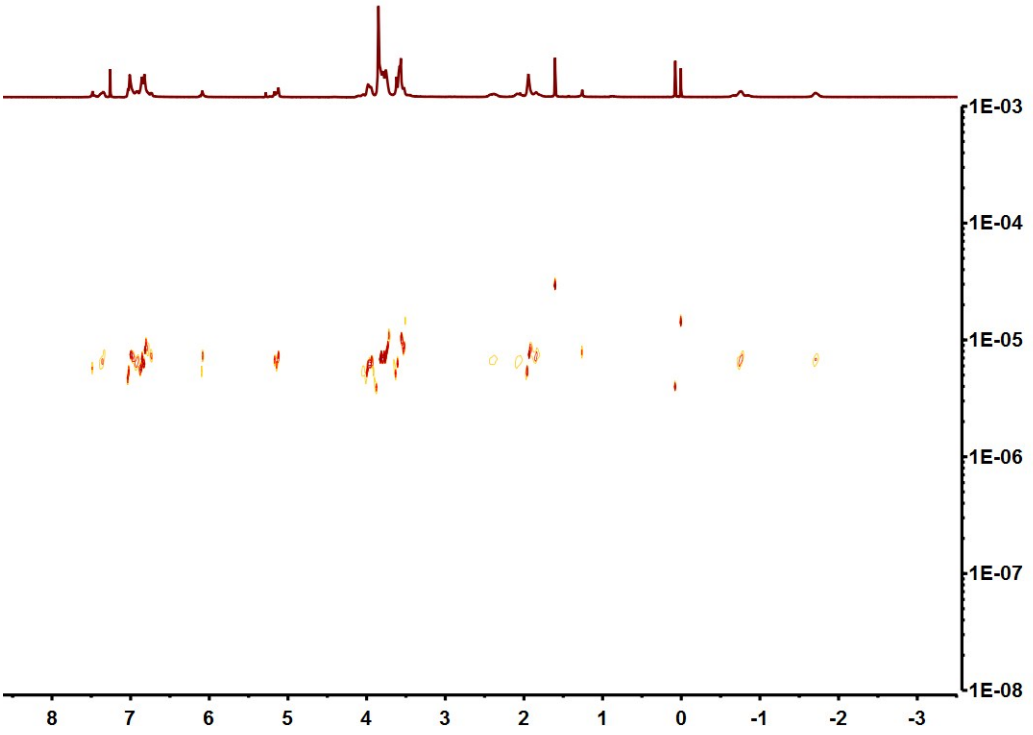


Figure S13. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (10.0 mM **A_2**).

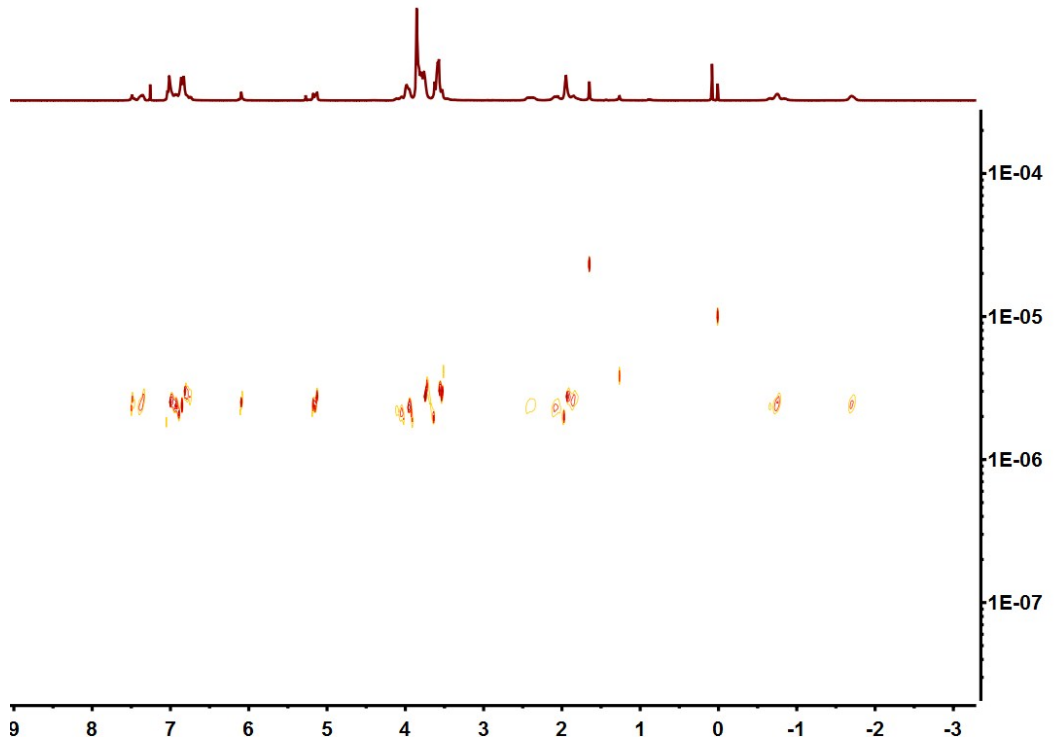


Figure S14. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (20.0 mM **A_2**).

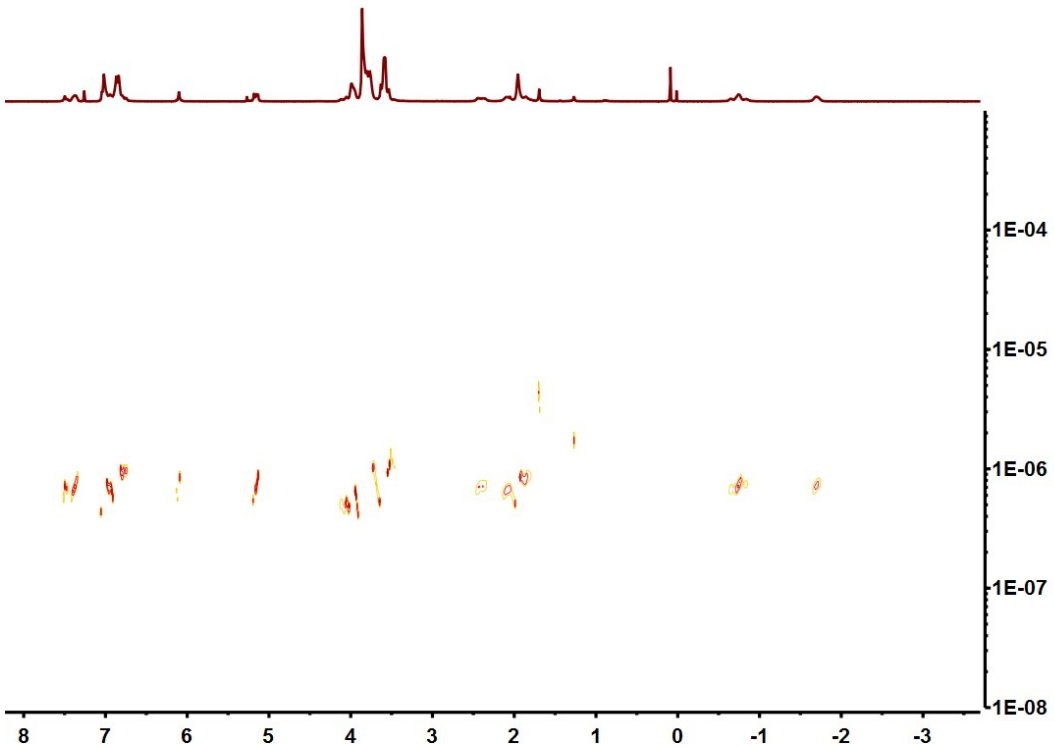


Figure S15. 2D DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of mixtures of 3:2 molar ratio of **A_2, B_3** (30.0 mM **A_2**).

4. The temperature-variant NMR experiments of A_2–B_3 complex in $CDCl_3$

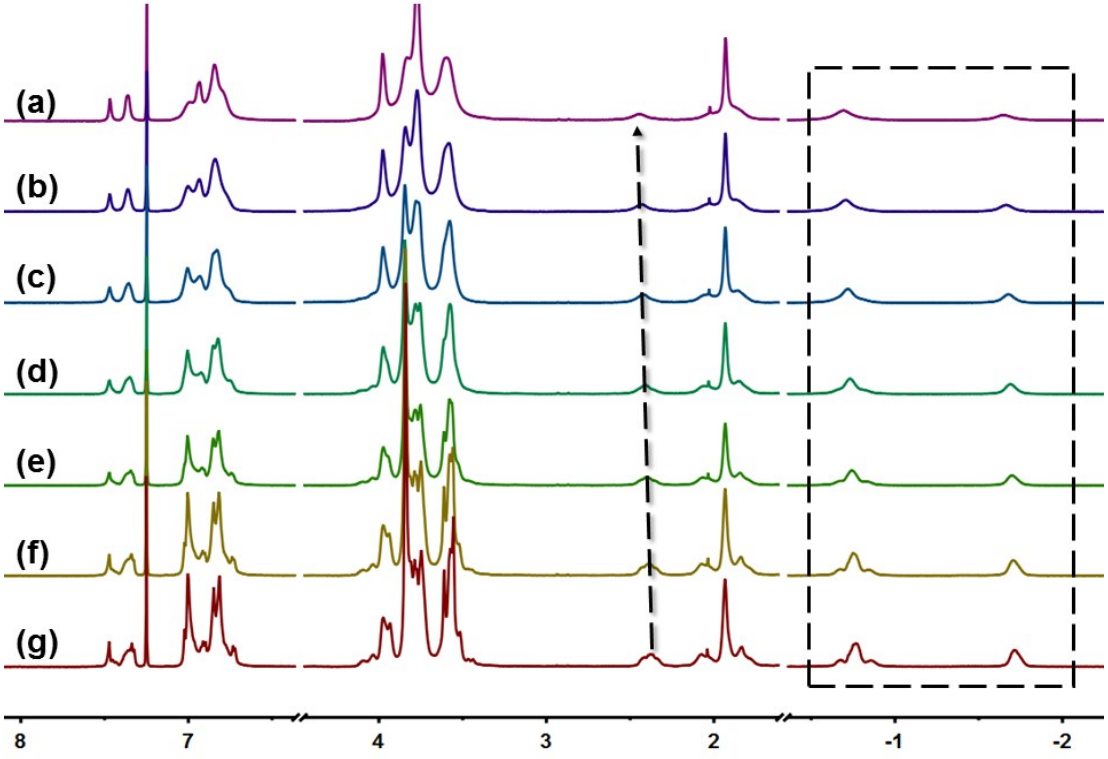


Figure S16. ^{1}H NMR spectra (600 MHz) of mixtures of 3:2 molar ratio of **A_2, B_3** (5.00 mM **A_2**) in $CDCl_3$ at various temperature: (a) 328 K; (b) 323 K; (c) 318 K; (d) 313 K; (e) 308 K; (f) 303 K; (g) 298 K.

5. Cyclic voltammetry curves and partial ^{1}H NMR spectra of DMP5 and DMP5 with excess I_2

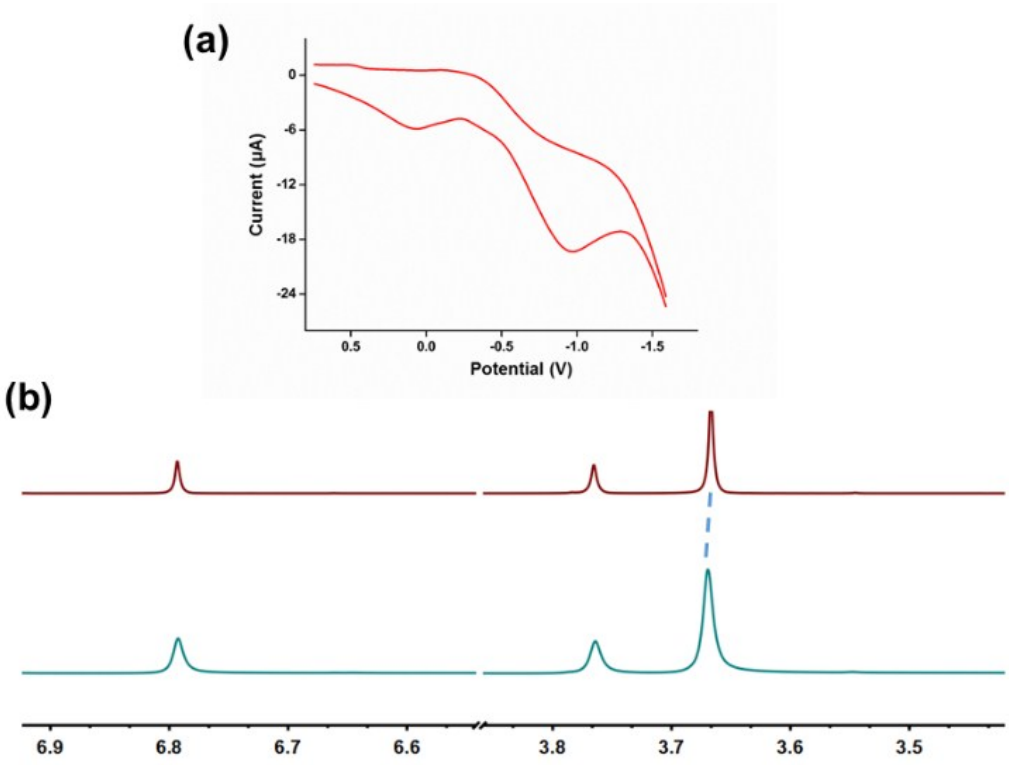


Figure 17. (a) Cyclic voltammetry curves (0.1 V/s) of 1.0 mM $\mathbf{A_2}$ in the solution of Tetrabutylammonium Hexafluorophosphate (0.10 mM in $CHCl_3$); (b) Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of DMP5 (red line) and DMP5 with excess I_2 (blue line).