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

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1. Synthesis and characterizations of compounds

Scheme S1. The synthetic route of compound A₂.

Figure S1. ¹H NMR spectrum (600 MHz, chloroform-d, room temperature) of A₂.

Figure S2. ¹³C NMR spectrum (150 MHz, chloroform-d, room temperature) of A₂.
Scheme S2. The synthetic route of B₃.

Figure S3. ¹H 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 B$_3$. 
Figure S8. $^{13}$C NMR spectrum (150 MHz, chloroform-$d$, room temperature) of 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 A$_2$ and 5.0 mM 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, CDCl₃, 298 K) of mixtures of 3:2 molar ratio of A₂, B₃ (5.00 mM A₂).

Figure S13. 2D DOSY NMR spectrum (600 MHz, CDCl₃, 298 K) of mixtures of 3:2 molar ratio of A₂, B₃ (10.0 mM A₂).
Figure S14. 2D DOSY NMR spectrum (600 MHz, CDCl₃, 298 K) of mixtures of 3:2 molar ratio of A₂, B₃ (20.0 mM A₂).

Figure S15. 2D DOSY NMR spectrum (600 MHz, CDCl₃, 298 K) of mixtures of 3:2 molar ratio of A₂, B₃ (30.0 mM A₂).
4. The temperature-variant NMR experiments of $A_2 \cdot B_3$ complex in CDCl$_3$

![NMR spectra](image)

**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 $A_2$ 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).