Supramolecular Control over Pillararene-based LCST Phase Behaviour
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Electronic Supplementary Information

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1. Materials and methods

**Materials.** All reagents were commercially available and used as supplied without further purification. **P5** was synthesized according to reported methods.\textsuperscript{51}

**Measurements.** All the 2D NOESY, variable temperature \textsuperscript{1}H NMR and \textsuperscript{1}H NMR spectra were collected on a Bruker Ascend TM 400MHz spectrometer. The transmittance experiments were measured at 550 nm using a Lambda 950 UV/Vis/NIR spectrometer with a temperature controllable system. The heating rate was adjusted at 1.0 °C min\textsuperscript{−1}. Unless otherwise stated, samples were dissolved in Milli-Q water. MALDI-TOF mass spectrometry was performed on a Shimadzu Biotech AXIMA Performance instrument.
2. $^1$H NMR spectra of equimolar mixture of P5 and G1 in D$_2$O

*Figure S1.* $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G1 (2.00 mM); (c) G1 (2.00 mM).
Figure S2. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G2 (2.00 mM); (c) G2 (2.00 mM).
Figure S3. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G3 (2.00 mM); (c) G3 (2.00 mM).
Figure S4. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G4 (2.00 mM); (c) G4 (2.00 mM).
Figure S5. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G5 (2.00 mM); (c) G5 (2.00 mM).
Figure S6. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of: (a) P5 (2.00 mM); (b) P5 (2.00 mM) and G6 (2.00 mM); (c) G6 (2.00 mM).
G9 is an organic salt with a long alkyl chain (with more than four CH₂ units). Guests with alkyl chains have the same binding mode with Pillar[5]arene, four consecutive CH₂ units will be located in the cavity of the pillar[5]arene via the multiple CH-π interactions.

From ¹H NMR spectra (Figure S6 and S7) and NOESY (Figure S50 and Figure S51) of P5-G6 and P5-G9, after the complexation, up field NMR shifts are observed, indicating that these four CH₂ units are located in the cavity of P5, and the adjacent CH₂ units are near the rim of the cavity, and the driven forces are four CH-π interactions. However due the difference of groups in guest (imidazolium units in G6 and SO₃⁻ in G9), the alkyl positions of G6 and G9 in P5 are different. Since no crystal structures are available, we cannot get the direct and detailed information about the location sites.
3. Stoichiometry and association constant determination for the complexation between P5 and G

To determine the stoichiometry and association constant between P5 and G, NMR titrations were done with solutions which had a constant concentration of P5 (2 mM) and varying concentrations of G. G was dissolved in 2 mM P5 solution, so during the whole titration process, the concentration of P5 is always 2 mM. With P5⊃G1 as an example, by a non-linear curve-fitting method, the association constant ($K_a$) of P5⊃G1 was estimated. By a mole ratio plot, a 1:1 stoichiometry was obtained.
Figure S8. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G1 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 300.00 μL, (l) 360.00 μL, (m) 400.00 μL.
**Figure S9.** Mole ratio plot for P5 and G1. The plot indicates a 1:1 stoichiometry.

The non-linear curve-fitting was based on the equation:\textsuperscript{S2}

\[ \Delta \delta = (\Delta \delta_{\infty}[H]_0) (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5 (([G]_0)^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}) \]

(Eq. S1)

Where \( \Delta \delta \) is the chemical shift change of \( H_a \) on P5 at \([G]_0\), \( \Delta \delta_{\infty} \) is the chemical shift change of \( H_a \) when the host is completely complexed, \([H]_0\) is the fixed initial concentration of the host, and \([G]_0\) is the initial concentration of G.

**Figure S10.** The chemical shift changes of \( H_a \) on P5 upon addition of G1.
Figure S11. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G2 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 265.00 μL, (l) 365.00 μL, (m) 465.00 μL.
Figure S12. Mole ratio plot for P5 and G2. The plot indicates a 1:1 stoichiometry.

Figure S13. The chemical shift changes of Hₐ on P5 upon addition of G2.

R² = 0.994
Kₐ = 254 ± 41 M⁻¹
Figure S14. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G3 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 300.00 μL, (l) 360.00 μL, (m) 400.00 μL.
Figure S15. Mole ratio plot for P5 and G3. The plot indicates a 1:1 stoichiometry.

Figure S16. The chemical shift changes of Hₐ on P5 upon addition of G3.
Figure S17. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G4 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 300.00 μL, (l) 360.00 μL, (m) 400.00 μL.
**Figure S18.** Mole ratio plot for P5 and G4. The plot indicates a 1:1 stoichiometry.

**Figure S19.** The chemical shift changes of H\textsubscript{a} on P5 upon addition of G4.
Figure S20. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G5 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 265.00 μL, (l) 365.00 μL, (m) 465.00 μL.
Figure S21. Mole ratio plot for P5 and G5. The plot indicates a 1:1 stoichiometry.

Figure S22. The chemical shift changes of Hₐ on P5 upon addition of G5.
Figure S23. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G6 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 265.00 μL, (l) 365.00 μL, (m) 465.00 μL.
Figure S24. Job plot for P5 and G6. Job plot was conducted by varying the mole fractions of the guest and host. Concentration: [P5] + [G6] = 6 mM. The plot indicates a 1:1 binding between the host and guest.

Figure S25. The chemical shift changes of Hₐ on P5 upon addition of G6.
Figure S26. $^1$H NMR spectra (400 MHz, D$_2$O, room temperature) of P5 at a concentration of 2.0 mM upon addition of G9 (15 mM): (a) 0.00 μL, (b) 10.00 μL, (c) 20.00 μL, (d) 30.00 μL, (e) 40.00 μL, (f) 65 μL, (g) 90.00 μL, (h) 115.00 μL, (i) 165.00 μL, (j) 215.00 μL, (k) 265.00 μL, (l) 365.00 μL, (m) 415.00 μL.
Figure S27. Mole ratio plot for P5 and G9. The plot indicates a 1:1 binding between the host and guest.

Figure S28. The chemical shift changes of H_a on P5 upon addition of G9.
<table>
<thead>
<tr>
<th>Guests</th>
<th>$K_a^* (M^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>160 ± 19</td>
</tr>
<tr>
<td>G2</td>
<td>254 ± 3.56</td>
</tr>
<tr>
<td>G3</td>
<td>$2.70 (± 0.58) \times 10^3$</td>
</tr>
<tr>
<td>G4</td>
<td>$3.57 (± 1.02) \times 10^3$</td>
</tr>
<tr>
<td>G5</td>
<td>$6.67 (± 3.56) \times 10^3$</td>
</tr>
<tr>
<td>G6</td>
<td>$5.0 (± 0.44) \times 10^4$</td>
</tr>
<tr>
<td>G9</td>
<td>$1.0 (± 0.14) \times 10^4$</td>
</tr>
</tbody>
</table>

*Table S1.* Association constant of host-guest complexes between P5 and G1-G6, G9.
4. Mass spectra of host–guest complexes

Figure S29. Mass spectrum of the host–guest complex prepared from P5 and G1.
Figure S30. Mass spectrum of the host–guest complex prepared from P5 and G2.
Figure S31. Mass spectrum of the host–guest complex prepared from P5 and G3.
Figure S32. Mass spectrum of the host–guest complex prepared from P5 and G4.
Figure S33. Mass spectrum of the host–guest complex prepared from \textbf{P5} and \textbf{G5}.
Figure S34. Mass spectrum of the host–guest complex prepared from P5 and G6.
Figure S35. Mass spectrum of the host–guest complex prepared from P5 and G9.
5. Temperature dependence NMR spectra of P5 upon addition of guests

Figure S36. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 (2.00 mM) in D$_2$O.
Figure S37. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G1 (2.00 mM) in D$_2$O.
Figure S38. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G2 (2.00 mM) in D$_2$O.
Figure S39. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G3 (2.00 mM) in D$_2$O.
Figure S40. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G4 (2.00 mM) in D$_2$O.
Figure S41. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G5 (2.00 mM) in D$_2$O.
Figure S42. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G6 (2.00 mM) in D$_2$O.
Figure S43. Variable-temperature $^1$H NMR spectra (400 MHz) of P5 and G9 (2.00 mM) in D$_2$O.
Figure S44. Temperature dependence of normalized intensity for P5 upon addition of guests.
6. 2D NOESY spectra of equimolar mixture of P5 and G in D$_2$O

**Figure S45.** 2D $^1$H-$^1$H NOESY spectrum of P5$\supset$G1 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G1] = 30.0 mM.
Figure S46. 2D $^1$H-$^1$H NOESY spectrum of P5$\supset$G2 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G2] = 30.0 mM.
**Figure S47.** 2D $^1$H-$^1$H NOESY spectrum of P5∙G3 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G3] = 30.0 mM.
Figure S48. 2D $^1$H-$^1$H NOESY spectrum of P5\textsuperscript{5}G4 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G4] = 30.0 mM.
**Figure S49.** 2D $^1$H-$^1$H NOESY spectrum of P5$\supset$G5 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G5] = 30.0 mM.
Figure S50. 2D $^1$H-$^1$H NOESY spectrum of P5$\supset$G6 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G6] = 30.0 mM.
Figure S51. 2D $^1$H-$^1$H NOESY spectrum of P5$\supset$G9 (400 MHz, room temperature, D$_2$O). [P5] = 30.0 mM. [G9] = 30.0 mM.
7. $T_{\text{cloud}}$ of supramolecular pairs by UV/Vis measurements

![Graph showing $T_{\text{cloud}}$ vs concentration of $G$ (mM) with various symbols representing different samples.](image)

*Figure S52. $T_{\text{cloud}}$ of host-guest complexes.*

**References:**
