Electronic Supplementary Information

Allosteric Cooperativity in Ternary Complexes with Low Symmetry

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1. Properties of 2a and 2b

Fig. S1  Chemical structures and $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 298 K) of two isomers of bis-ester naphthotubes 2a (the one with high polarity) and 2b (the one with low polarity). Peaks were assigned according to the following 2D NMR spectra. “*” indicates solvent impurities.
**Fig. S2** $^1$H,$^1$H-COSY NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of 2a.
Fig. S3  $^1$H, $^1$H-ROESY NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of 2a. No NOE effect was detected between the alkyl protons (9-12) and aromatic protons (1 and 2). But NOE contact between protons 2 and 2’ was observed, which suggests this isomer as the syn compound.
Fig. S4 $^{1}$H, $^{1}$H-COSY NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of 2b.
Fig. S5 $^1$H-$^1$H-ROESY NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of 2b. No NOE effect was detected between the alkyl protons (9-12) and aromatic protons (1 and 2).
2. Characterization Data of Host-Guest Complexes

Fig. S6  Full $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$;CD$_3$CN=1:1, 2.0 mM, 298 K) of 2a in the absence or the presence of one equivalent of individual guest D2D$^2+$ - D8D$^2+$. 2a does not bind D2D$^2+$ - D3D$^2+$, as indicated no obvious shift of both the guest and the host. For the guests D4D$^2+$ - D8D$^2+$, the complexes are slow-exchanging at the NMR timescale. Therefore, the binding constants can be determined by integration method. In general, the binding constants are smaller than 10$^4$ M$^{-1}$. Thus, these bindings are too weak to be determined by our Nano ITC instrument. These experiments together with peak integration indicate 1:1 binding stoichiometry between 2a and the DABCO-based organic cations D4D$^2+$ - D8D$^2+$. 
Fig. S7  Selected region of the $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$ : CD$_3$CN = 1 : 1, 298 K) of 2a and 1:1 and 2:1 mixture of 2a with guest D9D$^{2+}$. In the mixture of 2a and D9D$^{2+}$, free host and complex D9D$^{2+}@2a$ predominate. The 1:2 complex D9D$^{2+}@2a_2$ can be observed only in the presence of excess 2a and exist in very small amount. “*” indicates complex D9D$^{2+}@2a_2$. 
**Fig. S8** Selected region of the $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of 2a and 1:1 and 2:1 mixture of 2a with individual guest D10D$^{2+}$ - D12D$^{2+}$. In the mixture of 2a and different guests, there have some free host but two complexes were detected. They undergo stepwise binding with two 2a. The one increased in the 2:1 mixtures is DnD$^{2+}$@2a$_2$. A, B and C are used to denote free host (A), DnD$^{2+}$@2a$_2$ (B), and DnD$^{2+}$@2a (C) respectively. The complexes are slow-exchanging at the NMR timescale, therefore, the stepwise binding constants can be determined by integration method. Notably, the 1:1 complex D10D$^{2+}$@2a and D11D$^{2+}$@2a only exist in very small amount in the 1:2 mixture of guest and host, while complex D10D$^{2+}$@2a$_2$ and D11D$^{2+}$@2a$_2$ predominates. This suggests the high stability and robustness of D10D$^{2+}$@2a$_2$, D11D$^{2+}$@2a$_2$, which originates from strong allosteric cooperativity.
Fig. S9 Selected region of the $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of 2a and 1:1 and 2:1 mixture of 2a with individual guest D$_{13}$D$^{2+}$-D$_{14}$D$^{2+}$. Similar phenomena as those for guests D$_{10}$D$^{2+}$-D$_{12}$D$^{2+}$ were observed. Therefore, they also undergo stepwise binding with two 2a. However, the 1:2 complex DnD$^{2+}$@2a only exist in very small amount, the free host and complex DnD$^{2+}$@2a predominate. This suggests 2a form weak binding with D$_{13}$D$^{2+}$ or D$_{14}$D$^{2+}$ in 2:1 binding stoichiometry and no allosteric cooperativity.
Fig. S10 $^1$H-$^1$H-COSY NMR spectrum (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM, 298 K) of D6D$^{2+}$@2a.
Fig. S11  $^1$H,$^1$H-ROESY NMR spectrum (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM, 298 K) of D6D$^{2+}@2a$. All the peaks can unambiguously assigned according the COSY and ROESY NMR spectra. The NOE cross peaks of protons $a'$+$b'$ with protons $1$+$1'$ but not with proton 2 suggest that one of the DABCO protrudes the cavity. This is in line with the fact that one of DABCO undergo downfield shift in the complex.
Fig. S12 $^1$H,$^1$H-COSY NMR spectrum (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM, 298 K) of D11D$^{2+}@2a$. 
Fig. S13 $^1$H-$^1$H-ROESY NMR spectrum (500 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM, 298 K) of D11D$^{2+}$@2a. All the peaks can unambiguously assigned according the COSY and ROESY NMR spectra. No NOE contact between proton of DABCO and the host was detected.
**Fig. S14** Mass spectra of \(\text{D}^4\text{D}^2@2\text{a} - \text{D}^8\text{D}^2@2\text{a}\) in the mixture of CH\(_3\)CN and CH\(_2\)Cl\(_2\) (1:10). The peaks assigned to the corresponding 1:1 complexes and free host 2a were detected, suggesting 2a binds with these DABCO guests in 1:1 binding stoichiometry.
The association constants which were calculated by single-point method:

\[ G + H \xrightleftharpoons[K_1]{\kappa_1} G@H \]
\[ G@H + H \xrightleftharpoons[K_2]{\kappa_2} G@H_2 \]

\[ K_1 = \frac{[G@H]}{[G] \cdot [H]} \]
\[ K_2 = \frac{[G@H_2]}{[G@H] \cdot [H]} \]

Cooperativity factor (\(\alpha\)):
\[ \alpha = 4 \frac{K_1}{K_2} \]

\[ 1^H \text{NMR spectrum (500 MHz, 298 K, } \text{CDCl}_3: \text{CD}_3 \text{CN} = 1:1, \text{ 2.0 mM)} \text{ of the equimolar mixture of } \text{D4D}^{2+} \text{ and } 2a. \text{ From complexed and uncomplexed } H_2 \text{ and } H_4 \text{ of } 2a, \] \[ K_a(H_4) = \frac{[0.08 \times 2.0 \times 10^{-3}]}{[0.92 \times 2.0 \times 10^{-3}]} / [2.0 \times 10^{-3} - 0.08 \times 2.0 \times 10^{-3}] \text{ M}^{-1} = 47 \text{ M}^{-1}; \] \[ K_a(H_2) = \frac{[0.09 \times 2.0 \times 10^{-3}]}{[0.91 \times 2.0 \times 10^{-3}]} / [2.0 \times 10^{-3} - 0.09 \times 2.0 \times 10^{-3}] \text{ M}^{-1} = 54 \text{ M}^{-1}. \] Finally, \(K_a = (47 + 54) / 2 = 50 (\pm 5) \text{ M}^{-1}.\]
Fig. S16 ¹H NMR spectrum (500 MHz, 298 K, CDCl₃:CD₃CN = 1:1, 2.0 mM) of the equimolar mixture of D₅D²⁺ and 2a. From complexed and uncomplexed H₂' and H₅+5' of 2a, $K_a(H_2') = \left[ \frac{0.65 \times 2.0 \times 10^{-3}}{0.35 \times 2.0 \times 10^{-3}} \right] / \left[ (2.0 \times 10^{-3} - 0.65 \times 2.0 \times 10^{-3}) \right] M^{-1} = 2653 M^{-1};$ $K_a(H_{5+5'}) = \left[ \frac{(0.68/1.07) \times 2.0 \times 10^{-3}}{(0.39/1.07) \times 2.0 \times 10^{-3}} \right] / \left[ (2.0 \times 10^{-3} - (0.68/1.07) \times 2.0 \times 10^{-3}) \right] M^{-1} = 2492 M^{-1}$. Finally, $K_a = \left( \frac{2653 + 2492}{2} \right) = 2572 (\pm 114) M^{-1}$. 
Fig. S17 $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of the equimolar mixture of D6D$^{2+}$ and 2a. From complexed and uncomplexed H$_2^-$ and H$_{5+5'}$ of 2a, $K_a$(H$_2^-$) = 

\[
\frac{(0.81 \times 2.0 \times 10^{-3})}{(0.19 \times 2.0 \times 10^{-3})} / [2.0 \times 10^{-3} - 0.81 \times 2.0 \times 10^{-3}] \text{ M}^{-1} = 11219 \text{ M}^{-1};
\]

$K_a$(H$_{5+5'}$) = 

\[
\frac{0.81 \times 2.0 \times 10^{-3}}{0.20 \times 2.0 \times 10^{-3}} / [2.0 \times 10^{-3} - 0.81 \times 2.0 \times 10^{-3}] \text{ M}^{-1} = 10658 \text{ M}^{-1}.
\]

Finally, $K_a = (11219 + 10658) / 2 = 10938 (\pm 397) \text{ M}^{-1}$.
Fig. S18  $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of the equimolar mixture of D7D$^{2+}$ and 2a. From complexed and uncomplexed H$_2$ and H$_{5+5'}$ of 2a, $K_a$(H$_2$) = $\left[\frac{(0.60/0.99) \times 2.0 \times 10^{-3}}{(0.39/0.99) \times 2.0 \times 10^{-3}}\right]/\left[(2.0 \times 10^{-3} - (0.60/0.99) \times 2.0 \times 10^{-3})\right]$ M$^{-1}$ = 1923 M$^{-1}$; $K_a$(H$_{5+5'}$) = $\left[\frac{0.60 \times 2.0 \times 10^{-3}}{0.40 \times 2.0 \times 10^{-3}}\right]/\left[(2.0 \times 10^{-3} - 0.60 \times 2.0 \times 10^{-3})\right]$ M$^{-1}$ = 1875 M$^{-1}$. Finally, $K_a = (1923 + 1875)/2 = 1899 \pm 34$ M$^{-1}$.
Fig. S19 ¹H NMR spectrum (500 MHz, 298 K, CDCl₃:CD₃CN = 1:1, 2.0 mM) of the equimolar mixture of D8D²⁺ and 2a. From complexed and uncomplexed H₂⁺ and H₅⁺⁺⁺⁺ of 2a, $K_a(H₂⁺) = \frac{[0.56 \times 2.0 \times 10^{-3}] / [0.46 \times 2.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.56 \times 2.0 \times 10^{-3}]$ M⁻¹ = 1383 M⁻¹; $K_a(H₅⁺⁺⁺⁺) = \frac{[0.55 \times 2.0 \times 10^{-3}] / [0.45 \times 2.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.55 \times 2.0 \times 10^{-3}]$ M⁻¹ = 1358 M⁻¹. Finally, $K_a = \frac{(1383 + 1358)}{2} = 1371 \pm 19$ M⁻¹.
**Fig. S20** Mass spectra of D9D\(^{2+}\)@2a – D14D\(^{2+}\)@2a in the mixture of CH\(_3\)CN and CH\(_2\)Cl\(_2\) (1:10). The peaks assigned to the corresponding 1:1, 2:1 complexes and free host 2a were detected, suggesting 2a binds with these DABCO guests both in 1:1 and 2:1 binding stoichiometry.
**Fig. S21** ¹H NMR spectrum (500 MHz, 298 K, CDCl₃:CD₃CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D⁹D²⁺ and 2a and (b) the 1:2 mixture of D⁹D²⁺ and 2a. It is quite difficult to accurately determine the stepwise binding constants in 1:1 mixture of D⁹D²⁺ and 2a since the complex D⁹D²⁺@2a₂ only exist in very small amount. In figure (b), from complexed and uncomplexed H₄₊⁺ and H₂⁺ of 2a, $K_1(H₄₊⁺) = [(0.65 / 2.00) \times 4.0 \times 10^{-3}] / [(1.26 / 2.00) \times 4.0 \times 10^{-3}] / [4.0 \times 10^{-3} - (0.65 / 2.00) \times 4.0 \times 10^{-3} - (0.09 / 2.00) \times 4.0 \times 10^{-3} / 2] M^{-1} = 846 M^{-1}$; $K_2(H₄₊⁺) = [(0.09 / 2.00) \times 4.0 \times 10^{-3} / 2] / [(0.65 / 2.00) \times 4.0 \times 10^{-3}] / [(0.65 / 2.00) \times 4.0 \times 10^{-3}] M^{-1} = 27 M^{-1}$; $K_1(H₂⁺) = [(0.31 / 0.98) \times 4.0 \times 10^{-3}] / [(0.61 / 0.98) \times 4.0 \times 10^{-3}] / [4.0 \times 10^{-3} - (0.31 / 0.98) \times 4.0 \times 10^{-3} - (0.06 / 0.98) \times 4.0 \times 10^{-3} / 2] M^{-1} = 830 M^{-1}$; $K_2(H₂⁺) = [(0.06 / 0.98) \times 4.0 \times 10^{-3} / 2] / [(0.31 / 0.98) \times 4.0 \times 10^{-3}] / [(0.61 / 0.98) \times 4.0 \times 10^{-3}] M^{-1} = 39 M^{-1}$; Finally, $K_1 = (846 + 830) / 2 = 838 (±11) M^{-1}$, $K_2 = (27 + 39) / 2 = 33 (±8) M^{-1}$, $α = 4K_2 / K_1 = 4 \times 33 / 838 = 0.16$. 

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**Fig. S22** $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D10D$^{2+}$ and 2a and (b) the 1:2 mixture of D10D$^{2+}$ and 2a. In figure (a), $K_1 = [0.16 \times 2.0 \times 10^{-3}]/[0.3 \times 2.0 \times 10^{-3}]/[2.0 \times 10^{-3} - 0.16 \times 2.0 \times 10^{-3} - 0.54 \times 2.0 \times 10^{-3}]/2$ M$^{-1} = 468$ M$^{-1}$; $K_2 = [0.54 \times 2.0 \times 10^{-3}/2]/[0.16 \times 2.0 \times 10^{-3}]/[0.3 \times 2.0 \times 10^{-3}]$ M$^{-1} = 2813$ M$^{-1}$; In figure (b), $K_1 = [0.08 \times 4.0 \times 10^{-3}]/[0.33 \times 4.0 \times 10^{-3}]/[2.0 \times 10^{-3} - 0.08 \times 4.0 \times 10^{-3} - 0.59 \times 4.0 \times 10^{-3}]/2$ M$^{-1} = 485$ M$^{-1}$; $K_2 = [0.59 \times 4.0 \times 10^{-3}/2]/[0.08 \times 4.0 \times 10^{-3}]/[0.33 \times 4.0 \times 10^{-3}]$ M$^{-1} = 2794$ M$^{-1}$; Finally, $K_1 = (468 + 485)/2 = 476$ (±12) M$^{-1}$, $K_2 = (2813 + 2794)/2 = 2803$ (±13) M$^{-1}$, $\alpha = 4K_2/K_1 = 4 \times 2803 / 476 = 24$. 
**Fig. S23** $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D11D$^{2+}$ and 2a and (b) the 1:2 mixture of D11D$^{2+}$ and 2a. In figure (a), $K_1 = \frac{[0.15 \times 2.0 \times 10^{-3}] / [0.27 \times 2.0 \times 10^{-3}] / [(2.0 \times 10^{-3} - 0.15 \times 2.0 \times 10^{-3} - 0.58 \times 2.0 \times 10^{-3} / 2] \text{ M}^{-1}}{496 \text{ M}^{-1}}$; $K_2 = \frac{[0.58 \times 2.0 \times 10^{-3} / 2] / [0.15 \times 2.0 \times 10^{-3}] / [(0.27 \times 2.0 \times 10^{-3}] \text{ M}^{-1}}{3580 \text{ M}^{-1}}$; In figure (b), $K_1 = \frac{[(0.08/1.01) \times 4.0 \times 10^{-3}] / [(0.30 / 1.01) \times 4.0 \times 10^{-3}] / [(2.0 \times 10^{-3} - (0.08/1.01) \times 4.0 \times 10^{-3} - (0.63 / 1.01) \times 4.0 \times 10^{-3} / 2] \text{ M}^{-1}}{612 \text{ M}^{-1}}$; $K_2 = \frac{[(0.63 / 1.01) \times 4.0 \times 10^{-3} / 2] / [(0.08 / 1.01) \times 4.0 \times 10^{-3}] / [(0.30 / 1.01) \times 4.0 \times 10^{-3}] \text{ M}^{-1}}{3750 \text{ M}^{-1}}$; Finally, $K_1 = (496 + 507) / 2 = 502 (\pm 8) \text{ M}^{-1}$, $K_2 = (3580 + 3750) / 2 = 3665 (\pm 120) \text{ M}^{-1}$, $\alpha = 4K_2 / K_1 = 4 \times 3665 / 502 = 29$. 

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Fig. S24  $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D$_{12}$D$^{2+}$ and 2a and (b) the 1:2 mixture of D$_{12}$D$^{2+}$ and 2a. In figure (a), $K_1 = [0.29 \times 2.0 \times 10^{-3}] / [0.54 \times 2.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.29 \times 2.0 \times 10^{-3} - 0.17 \times 2.0 \times 10^{-3} / 2]$ M$^{-1} = 430$ M$^{-1}$; $K_2 = [0.17 \times 2.0 \times 10^{-3} / 2] / [0.29 \times 2.0 \times 10^{-3}] / [(0.54 \times 2.0 \times 10^{-3})$ M$^{-1} = 271$ M$^{-1}$; In figure (b), $K_1 = [0.20 \times 4.0 \times 10^{-3}] / [0.56 \times 4.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.20 \times 4.0 \times 10^{-3} - 0.24 \times 4.0 \times 10^{-3} / 2]$ M$^{-1} = 496$ M$^{-1}$; $K_2 = [0.24 \times 4.0 \times 10^{-3} / 2] / [0.20 \times 4.0 \times 10^{-3}] / [0.56 \times 4.0 \times 10^{-3}]$ M$^{-1} = 268$ M$^{-1}$; Finally, $K_1 = (430 + 496) / 2 = 463$ (±46) M$^{-1}$, $K_2 = (271 + 268) / 2 = 270$ (±2) M$^{-1}$, $\alpha = 4K_2 / K_1 = 4 \times 270 / 463 = 2$. 
Fig. S25 $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D13D$^{2+}$ and 2a and (b) the 1:2 mixture of D13D$^{2+}$ and 2a. In figure (a), $K_1 = [0.33 \times 2.0 \times 10^{-3}] / [0.58 \times 2.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.33 \times 2.0 \times 10^{-3} - 0.08 \times 2.0 \times 10^{-3} / 2] \ M^{-1} = 452 \ M^{-1}$; $K_2 = [0.08 \times 2.0 \times 10^{-3} / 2] / [0.33 \times 2.0 \times 10^{-3}] / [(0.58 \times 2.0 \times 10^{-3}] \ M^{-1} = 104 \ M^{-1}$; In figure (b), $K_1 = [0.24 \times 4.0 \times 10^{-3}] / [0.63 \times 4.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.24 \times 4.0 \times 10^{-3} - 0.13 \times 4.0 \times 10^{-3} / 2] \ M^{-1} = 421 \ M^{-1}$; $K_2 = [0.13 \times 4.0 \times 10^{-3} / 2] / [0.24 \times 4.0 \times 10^{-3}] / [0.63 \times 4.0 \times 10^{-3}] \ M^{-1} = 100 \ M^{-1}$; Finally, $K_1 = (452 + 421) / 2 = 436 (\pm 22) \ M^{-1}, \ K_2 = (104 + 100) / 2 = 102 (\pm 3) \ M^{-1}, \ \alpha = 4K_2 / K_1 = 4 \times 102 / 436 \approx 0.9.$
**Fig. S26** $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1, 2.0 mM) of (a) the 1:1 mixture of D14D$^{2+}$ and 2a and (b) the 1:2 mixture of D14D$^{2+}$ and 2a. In figure (a), $K_1 = [0.33 \times 2.0 \times 10^{-3}] / [0.60 \times 2.0 \times 10^{-3}] / [2.0 \times 10^{-3} - 0.33 \times 2.0 \times 10^{-3} - 0.06 \times 2.0 \times 10^{-3} / 2] \ M^{-1} = 430 \ M^{-1}$; $K_2 = [0.06 \times 2.0 \times 10^{-3} / 2] / [0.33 \times 2.0 \times 10^{-3}] / [0.60 \times 2.0 \times 10^{-3}] \ M^{-1} = 76 \ M^{-1}$; In figure (b), $K_1 = [0.24 \times 4.0 \times 10^{-3}] / [0.65 \times 4.0 \times 10^{-3}] / [(2.0 \times 10^{-3} - 0.24 \times 4.0 \times 10^{-3} - 0.12 \times 4.0 \times 10^{-3} / 2] \ M^{-1} = 462 \ M^{-1}$; $K_2 = [0.12 \times 4.0 \times 10^{-3} / 2] / [0.24 \times 4.0 \times 10^{-3}] / [0.65 \times 4.0 \times 10^{-3}] \ M^{-1} = 96 \ M^{-1}$; Finally, $K_1 = (430 + 462) / 2 = 446 (\pm 23) \ M^{-1}$, $K_2 = (76 + 96) / 2 = 86 (\pm 14) \ M^{-1}$, $\alpha = 4K_2 / K_1 = 4 \times 86 / 446 = 0.8$. 
**Fig. S27** $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$:CD$_3$CN = 1:1) of 2:1 mixture of 2a with guest D9D-2BArF (2.0 mM). It is quite difficult to accurately determine the stepwise binding constants in 1:1 mixture of D9D$^{2+}$ and 2a since the complex D9D$^{2+}$@2a only exist in very small amount. In figure (b), from complexed and uncomplexed H$_4$+ and H$_2'$ of 2a, $K_1$(H$_4$+) = \[(0.64 / 2) \times 4.0 \times 10^{-3} \] / \[(1.25 / 2) \times 4.0 \times 10^{-3} \] / \[4.0 \times 10^{-3} - (0.64 / 2) \times 4.0 \times 10^{-3} - (0.11 / 2) \times 4.0 \times 10^{-3} / 2\] M$^{-1}$ = 839 M$^{-1}$; $K_2$(H$_4$+) = \[(0.11 / 2) \times 4.0 \times 10^{-3} / 2\] / \[(0.64 / 2) \times 4.0 \times 10^{-3} / 2\] / \[4.0 \times 10^{-3} - (0.31 / 0.99) \times 4.0 \times 10^{-3} - (0.07 / 0.99) \times 4.0 \times 10^{-3} / 2\] M$^{-1}$ = 820 M$^{-1}$; $K_2$(H$_2'$) = \[(0.07 / 0.99) \times 4.0 \times 10^{-3} / 2\] / \[(0.31 / 0.99) \times 4.0 \times 10^{-3} / 2\] / \[(0.61 / 0.99) \times 4.0 \times 10^{-3} / 2\] M$^{-1}$ = 46 M$^{-1}$; Finally, $K_1 = (839 + 820) / 2 = 830 \pm 13$ M$^{-1}$, $K_2 = (34 + 46) / 2 = 40 \pm 8$ M$^{-1}$, $\alpha = 4K_2 / K_1 = 4 \times 40 / 830 = 0.2$. 

**Fig. S28** Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 298 K) of 2a and 1:1 and 2:1 mixture of 2a with guest D9D-2BArF (2.0 mM). The counterion is BArF$^-$, D9D$^{2+}$ can undergo stepwise binding with two 2a.
Fig. S29  Selected region of $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 2.0 mM, 298 K) of (a) 2:1 mixture of 1a with D10D-2BArF; (b) the equimolar mixture of 1a, D10D-2BArF, and 2a; (c) 2:1 mixture of 2a with D10D-2BArF. In the equimolar mixture of 1a, 2a and D9D-2BArF, a set of new peaks was detected besides the peaks of $1a_{D10D^{2+}}$ and $2a_{D10D^{2+}}$, indicated the formation of another complex. “*” indicated the new complex.
Diffusion ordered NMR spectroscopy (DOSY). A LED29 pulse sequence (ledbpgp2s) was used for the diffusion experiments with a sine-shape pulsed gradient duration $\delta$ (P30) of 800 ms incremented from 0.68 to 32.4 G cm$^{-1}$ in 16 steps. The pulsed gradient separation $\Delta$ (D20) was 200 ms, the spoil gradient (P19) was set to 600 µs, and the eddy current delay (D21) was 5 ms. The reported diffusion coefficients were obtained using the T1/T2 relaxation module in TopSpin 3.2 software.

**Fig. S30** DOSY NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) showing the very similar diffusion behavior of the complex D10D-2BarF@1a, D10D-2BarF@1b, and D10D-2BarF@2a. The diffusion coefficient for the three complexes D10D-2BarF@1a, D10D-2BarF@1b, and D10D-2BarF@2a was calculated to be $3.94 \times 10^{-10}$ m$^2$s$^{-1}$, $3.91 \times 10^{-10}$ m$^2$s$^{-1}$, and $3.96 \times 10^{-10}$ m$^2$s$^{-1}$ respectively.
**Fig. S31**  ESI mass spectrum of the equimolar mixture of 1a, D10D-2BArF, and 2a.
3. Single Crystal X-Ray Crystallography

Suitable single crystals of 2a and 2b for structural determination were obtained by slow evaporation of the CH$_2$Cl$_2$ solution of 2a and 2b.

Single crystal X-ray data for 2a and 2b were collected with Agilent Super-Nova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Cu-Kα ($\lambda = 1.54178$ Å) radiation. Program CrysAlisPro was used for the data collection and reduction. The intensities were corrected for absorption using muti-scan absorption correction method for all the data. The structures were solved with direct methods ($SHELXT$) and refined by full-matrix least squares on $F^2$ using SHELXL-2017 program. Anisotropic displacement parameters were assigned to non-H atoms. All hydrogen atoms were refined using riding models.

Crystal data and the structure refinements are summarized in Table S1. These crystal structures have been deposited in the Cambridge Crystallographic Data Centre (CCCD NO. are found in Table S1). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystal data and structure refinement for 2a and 2b.

<table>
<thead>
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<th>entry</th>
<th>2a</th>
<th>2b</th>
</tr>
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<tr>
<td>Moiety formula</td>
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<td>$C_{66}H_{64}O_{12}$</td>
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<td>$P-1$</td>
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<tr>
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<td>$c$/Å</td>
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<td>110.921(2)</td>
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<td>73.714(2)</td>
<td>90.774(2)</td>
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<td>$\gamma$/°</td>
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<tr>
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<td>$\mu$/mm$^{-1}$</td>
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<td>12607</td>
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<td>Independent reflections</td>
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<td>3701 [$R_{int} = 0.0346, R_{sigma} = 0.0355$]</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>Final R indexes [I&gt;=2σ (I)]</td>
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<td>$R_1 = 0.0408$, $wR_2 = 0.0934$</td>
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<td>Final R indexes [all data]</td>
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2a

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575

Calculated sin(theta_max)/wavelength = 0.5555

Response: The crystal has too weak diffraction to obtain high resolution data.

PLAT420_ALERT_2_B D-H Without Acceptor O5A --H18A . Please Check

PLAT420_ALERT_2_B D-H Without Acceptor O5B --H19A . Please Check

PLAT420_ALERT_2_B D-H Without Acceptor O7B --H35B . Please Check

Response: Carbonyl O5A, O7A (the second site of O5B, O7B) is on the ester group which is disordered although low temperature was used for the data collection.

2b

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575

Calculated sin(theta_max)/wavelength = 0.5565

Response: The crystal has too weak diffraction to obtain high resolution data.

PLAT420_ALERT_2_B D-H Without Acceptor O5A --H18B . Please Check

PLAT420_ALERT_2_B D-H Without Acceptor O5B --H19B . Please Check

Response: Carbonyl O5A (the second site of O5B) is on the ester group which is disordered although low temperature was used for the data collection.
4. Experimental Section

4.1 General Method. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. Thin-layer chromatography (TLC) was carried out on 0.25 mm Yantai silica gel plates (60F-254). Column chromatography was performed on silica gel 60 (Tsingdao40 – 63 nm, 230 – 400 mesh). \(^1\)H, \(^13\)C, \(^1\)H-\(^1\)H COSY, \(^1\)H-\(^1\)H ROESY, and DOSY NMR spectra were recorded on Bruker Avance-400 or 500 spectrometers. All chemical shifts are reported in ppm with residual solvents or TMS (tetramethylsilane) as the internal standards. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t triplet; m, multiplet. Electrospray-ionization time-of-high-resolution mass spectra (ESI-HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer. All the computations were performed at the AM1 level of theory by using Spartan’14 (Wavefunction, Inc.). The synthesis of guests D2D\(^{2+}\) - D8D\(^{2+}\), \(^5\)D10D\(^{2+}\) and D12D\(^{2+}\), \(^6\)D9D\(^{2+}\) and D11D\(^{2+}\) - D14D\(^{2+}\), \(^7\)and compounds S1\(^8\) and S2\(^7\) has been reported.

4.2 Synthetic Route of 2a and 2b

![Chemical Structure of S1, S2, 1a, 1b](image)

Compound 2a and 2b

Potassium carbonate (500 mg, 35.9 mmol) and 500 mL dry DMF were added into a 1000-mL three-neck flask charged with a magnetic stirring bar. The flask was then evacuated and refilled with Ar (using a gas balloon). The solution of S1 (250 mg, 4.5 mmol, in 60 mL dry DMF) and S2 (294 mg, 4.5 mmol, in 60 mL dry DMF) were added dropwise using two separate syringes to the flask via a double-channel syringe pump during 10 h. Then the reaction mixture was stirred for another 24 h at 80 °C. After removing most of the solvent in vacuum, the residue was poured into 1.0 M HCl (200 mL). The precipitate was then filtered and washed with water extensively to give an off-white solid, which was purified by column chromatography (SiO\(_2\), CH\(_2\)Cl\(_2\): Hexane = 1:1
~ 2:1) to afford pure products 2a (510 mg, yield 11%) and 2b (750 mg, yield 16%) as white solids.

2a. m.p. > 300 °C; $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298K) $\delta$ [ppm] = 8.45 (d, $J$ = 9.4 Hz, 2H), 8.38 (d, $J$ = 9.4 Hz, 2H), 7.58 (d, $J$ = 9.2 Hz, 2H), 7.44 (d, $J$ = 9.1 Hz, 2H), 7.25 (d, $J$ = 9.3 Hz, 2H), 7.15 (d, $J$ = 9.3 Hz, 2H), 7.11 (t, $J$ = 8.5 Hz, 4H), 6.28 (d, $J$ = 12.2 Hz, 2H), 5.88 (d, $J$ = 11.7 Hz, 2H), 5.73 (d, $J$ = 11.7 Hz, 2H), 5.33 (d, $J$ = 15.0 Hz, 2H), 4.12 - 4.02 (m, 6H), 3.99 - 3.93 (m, 2H), 2.66 (d, $J$ = 27.2 Hz, 4H), 1.86 - 1.71 (m, 8H), 1.59 - 1.47 (m, 8H), 1.06 - 0.95 (m, $J$ = 20.4, 7.3 Hz, 12H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, 298K) $\delta$ [ppm] = 167.8, 153.7, 151.8, 149.2, 148.9, 129.1, 126.7, 126.0, 125.6, 125.5, 125.3, 123.3, 122.4, 119.7, 119.5, 119.5, 119.1, 119.0, 117.2, 114.4, 114.3, 91.3, 91.1, 69.9, 69.7, 57.4, 31.6, 31.5, 25.8, 25.6, 22.7, 22.5, 22.4, 19.2, 19.0, 13.9, 13.7, 13.6; HRMS (ESI): $m/z$ calcd for [M+NH$_4$]$^+$ C$_{66}$H$_{68}$O$_{12}$N$^+$, 1066.4736; found 1066.4761 (error = -0.4 ppm); calcd for [M+H]$^+$ C$_{66}$H$_{65}$O$_{12}^+$, 1049.4471; found 1049.4473 (error = -0.2 ppm).

$^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of compound 2a
13C NMR spectrum (125 MHz, CD$_2$Cl$_2$, 298 K) of compound 2a

ESI mass spectrum of compound 2a
2b. m.p. > 300 °C; \[^1\text{H} \text{ NMR (500 MHz, CD}_2\text{Cl}_2, 298 \text{ K)} \delta [\text{ppm}] = 8.44 (d, J = 9.4 \text{ Hz, 2H}), \] 8.36 (d, J = 9.4 \text{ Hz, 2H}), 7.62 (d, J = 9.2 \text{ Hz, 2H}), 7.28 (d, J = 9.1 \text{ Hz, 2H}), 7.24 (d, J = 9.4 \text{ Hz, 2H}), 7.20 (d, J = 9.4 \text{ Hz, 2H}), 7.10 (d, J = 9.2 \text{ Hz, 2H}), 7.03 (d, J = 9.1 \text{ Hz, 2H}), 6.26 (d, J = 9.3 \text{ Hz, 2H}), 6.05 (d, J = 11.7 \text{ Hz, 2H}), 5.48 (d, J = 11.7 \text{ Hz, 2H}), 5.37 (s, 1H), 5.32 (s, 1H), 4.15 - 4.09 (m, 4H), 4.06 - 4.00 (m, 4H), 2.67 (dt, J = 10.8, 2.6 \text{ Hz, 4H}), 1.93 - 1.85 (m, 8H), 1.70 - 1.58 (m, 8H), 1.12 (q, J = 7.5 \text{ Hz, 12H}); \[^{13}\text{C} \text{ NMR (125 MHz, CD}_2\text{Cl}_2) \delta [\text{ppm}] = 168.3, 154.0, 151.9, 149.6, 149.3, 129.8, 127.2, 126.3, 125.8, 125.8, 125.6, 123.8, 123.0, 120.1, 119.9, 119.7, 119.6, 119.3, 117.0, 114.5, 114.2, 91.9, 91.8, 69.6, 69.5, 58.2, 32.3, 32.3, 26.5, 26.1, 23.0, 20.0, 19.9, 14.5, 14.4; HRMS (ESI): m/z calcd for [M+H]\(^+\) \text{C}_{66}\text{H}_{65}\text{O}_{12}^+, 1049.4471; found 1049.4501 (error = 3.3 ppm); calcd for [M+Na]\(^+\) \text{C}_{66}\text{H}_{64}\text{O}_{12}\text{Na}^+, 1071.4290; found 1071.4309 (error = 1.8 ppm).
$^{13}$C NMR spectrum (125 MHz, CD$_2$Cl$_2$, 298 K) of compound $2b$

ESI mass spectrum of compound $2b$
4.3 Synthesis of Guests D9D-2BArF & D10D-2BArF

Organic cationic guests D9D$^{2+}$ and D10D$^{2+}$ with BArF$^-$ as counterions were prepared from their bromide salts$^5$ by following the literature procedure.$^9$

**D9D-2BArF:** NaBArF (500 mg, 0.6 mmol) was dissolved in methanol (20 mL). The solution of D9D-2Br (127 mg, 0.25 mmol) in methanol (10 mL) was added dropwise into the saturated solution of NaBArF. The resulting mixture was stirred vigorously overnight. Then the solvent was removed in vacuum. The residue was suspended in H$_2$O (20 mL), extracted with CH$_2$Cl$_2$ (20 mL × 3). The organic layer was collected, washed with H$_2$O (50 mL), dried with Na$_2$SO$_4$. The solvent was then evaporated in vacuum to afford D9D-2BArF as a white solid (490 mg, 95 %). m.p. 152-153 °C; $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) δ [ppm] = 7.72-7.71 (m, 16H), 7.57 (s, 8H), 3.21 (t, $J$ = 7.4 Hz, 10H), 3.10 (t, $J$ = 7.5 Hz, 10H), 3.03-2.98 (m, 4H), 1.67-1.61 (m, 4H), 1.33-1.16 (m, 14H); $^{13}$C NMR (125 MHz, CD$_2$Cl, 298 K) δ [ppm] = 162.3 (q, $^1$J$_{CB}$ = 50 Hz), 135.4, 129.4 (q, $^2$J$_{CF}$ = 50 Hz), 125.2 (q, $^1$J$_{CF}$ = 270 Hz), 118.1, 66.4, 53.9, 45.6, 29.7, 29.4, 26.7, 22.5; HRMS (ESI): m/z calcd for [M-2BArF]$^{2+}$ C$_{21}$H$_{42}$N$_4$$_{2+}$, 175.1699; found 175.1699 (error = -0.1 ppm); calcd for [BArF]$^-$ C$_{32}$H$_{12}$BF$_{24}^-$, 863.0654; found 863.0649 (error = -0.6 ppm).
$^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of compound D9D-2BArF

$^{13}$C NMR spectrum (125 MHz, CD$_2$Cl$_2$, 298 K) of compound D9D-2BArF
ESI mass spectrum (positive mode) of compound D9D-2BArF

ESI mass spectrum (negative mode) of compound D9D-2BArF
D10D-2BArF: It was prepared from its bromide salt by using the same procedure as that for D9D-2BArF; D10D-2BArF was obtained as a white solid (0.50 g, 96 %).

m.p. 149-150 °C; $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ [ppm] = 7.73 - 7.71 (m, 16H), 7.57 (s, 8H), 3.21 (t, $J = 7.4$ Hz, 10H), 3.11 (t, $J = 7.5$ Hz, 10H), 3.04 - 2.99 (m, 4H), 1.66 - 1.62 (m, 6H), 1.33 - 1.15 (m, 14H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ [ppm] = 162.3 (q, $^1$JC = 50 Hz), 135.4, 129.4 (q, $^2$JCF = 50 Hz), 125.2 (q, $^1$JCF = 270 Hz), 118.1, 66.4, 53.9, 45.6, 29.7, 29.6, 26.7, 22.5; HRMS (ESI): $m/z$ calcd for [M-2BArF]$^{2+}$ C$_{22}$H$_{44}$N$_4$^2+, 182.1778; found 182.1777 (error = -0.1 ppm); calcd for [BArF]$^-$ C$_{32}$H$_{12}$BF$_2$^-, 863.0654; found 863.0652 (error = -0.3 ppm).

$^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K) of compound D10D-2BArF
$^{13}$C NMR spectrum (125 MHz, CD$_2$Cl$_2$, 298 K) of compound **D10D-2BArF**

ESI mass spectrum (positive mode) of compound **D10D-2BArF**
5. References.