

Supporting Information for:

**Thermodynamic Origins of Selective Binding Affinity Between
p-Sulfonatocalix[4,5]arenes with Biguanidiniums**

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TABLE S1: The chemical shift change $\Delta\delta$ values (ppm) of MFM in the presence of SC4A or SC5A in aqueous solution (pD 2.0 and 7.2).

| pD | Hosts | H(-CH ₃) |
|-----|-------|----------------------|
| 7.2 | SC4A | -2.19 |
| | SC5A | -1.67 |
| 2.0 | SC4A | -1.91, -2.14 |
| | SC5A | -1.71, -1.88 |

TABLE S2: The chemical shift change $\Delta\delta$ values (ppm) of PFM in the presence of SC4A or SC5A in aqueous solution (pD 2.0 and 7.2).

| pD | Hosts | H _a | H _b | H _c | H _d | H _e |
|-----|-------|----------------|----------------|----------------|----------------|----------------|
| 7.2 | SC4A | -1.54 | -1.24 | -0.94 | -0.94 | -0.79 |
| | SC5A | -1.20 | -1.17 | -1.50 | -1.41 | -1.25 |
| 2.0 | SC4A | -2.10 | -1.64 | -1.09 | -0.86 | -0.62 |
| | SC5A | -1.12 | -1.09 | -1.25 | -1.13 | -0.69 |

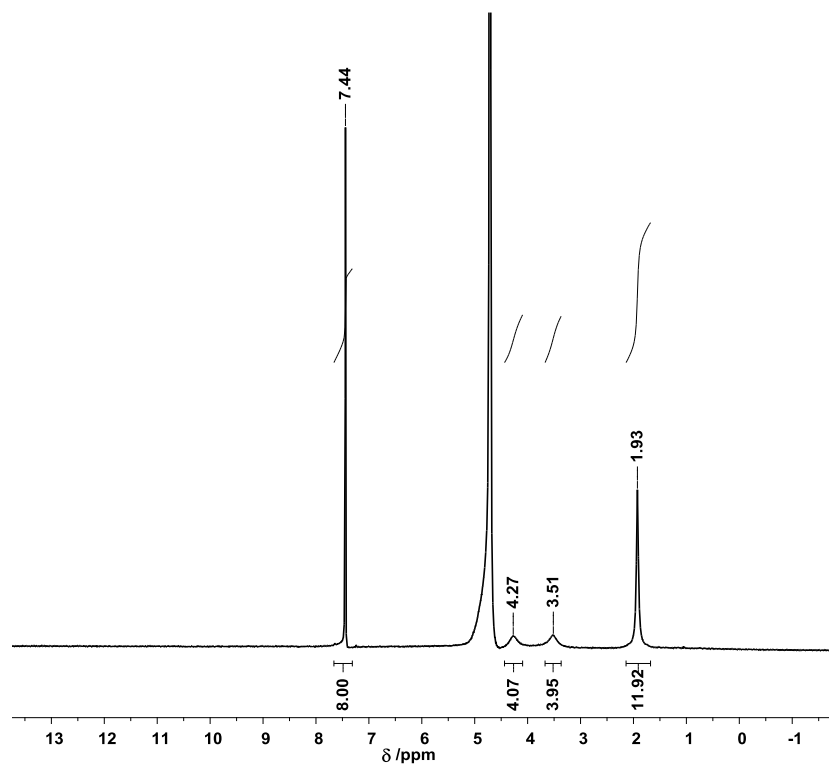


FIGURE S1. The ¹H NMR spectrum of single-crystal complex MFM-SC4A in D₂O

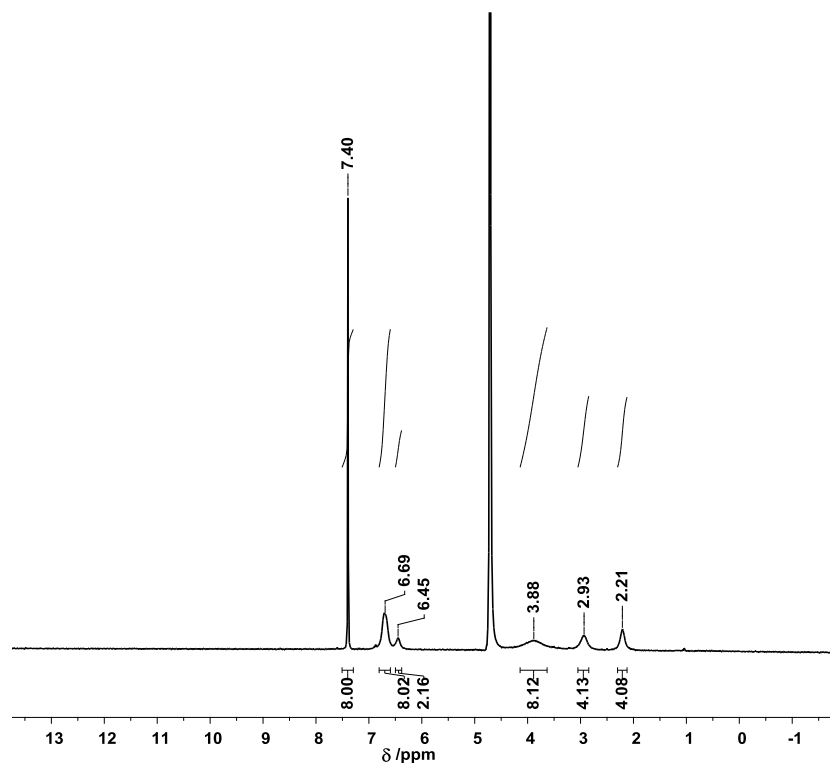


FIGURE S2. The ¹H NMR spectrum of single-crystal complex PFM-SC4A in D₂O

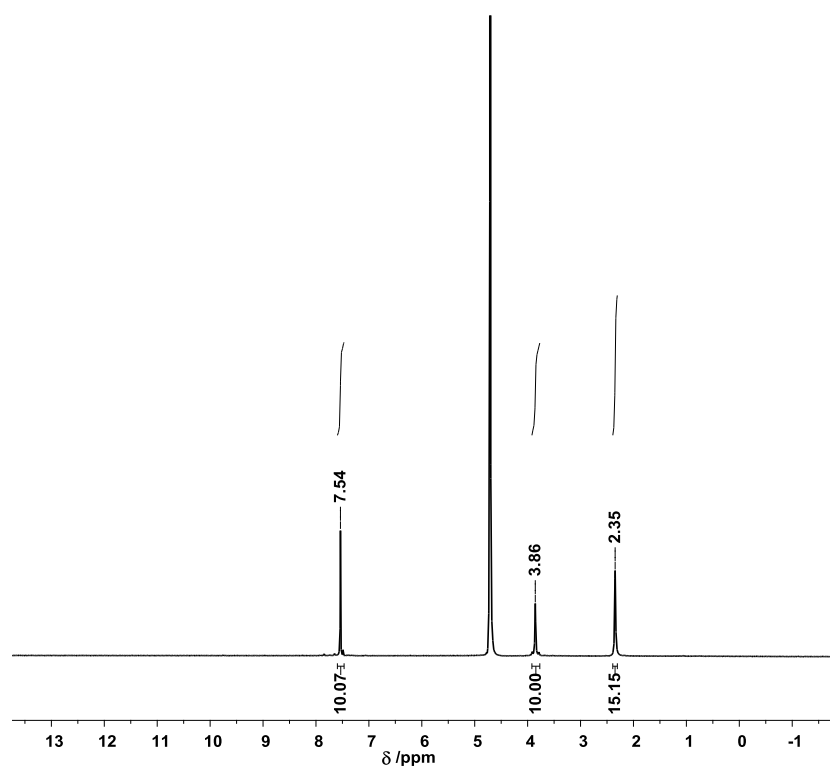


FIGURE S3. The ¹H NMR spectrum of single-crystal complex MFM-SC5A in D₂O

In complex MFM \subset SC4A, there is another kind of complex we have not discussed. It shows that MFM is immerse into the cavity of SC4A in a more perpendicular orientation *via* one N–H $\cdots\pi$ interaction (N4–H4 \cdots ring of C15–20, 3.215(1) Å, 176.6(3) $^\circ$) and two C–H $\cdots\pi$ interactions (C59–H59 \cdots ring of C8–13, 2.539(1) Å, 141.5(4) $^\circ$; C60–H60 \cdots ring of C1–6, 3.340(1) Å, 116.1(5) $^\circ$), while the positive guanidinium group is fixed at the upper-rim of SC4A, captured by one sulfonate group through one unconventional hydrogen bond (N1 \cdots O8, 2.786(7)Å, 163.3(4) $^\circ$) (Figure S4). It also shows the SC4A cone structure is pinched to give a C_{2v} symmetry with sulfur distances of 11.447(3)Å and 8.366(3)Å for oppositely oriented sulfonate groups. Moreover, the actual φ and χ torsion angle values are 103.0(7), $-82.6(8)$; 75.6(7), $-91.8(7)$; 96.2(7), $-78.2(7)$; 74.7(8), $-98.7(1)$.

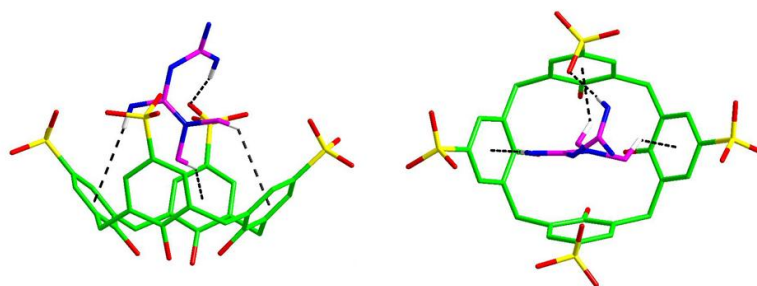


FIGURE S4. Solid-state inclusion structure of MFM \subset SC4A. The broken lines represent the intermolecular hydrogen bonds, the C–H $\cdots\pi$ interactions, or the N–H $\cdots\pi$ interactions between host and guest.