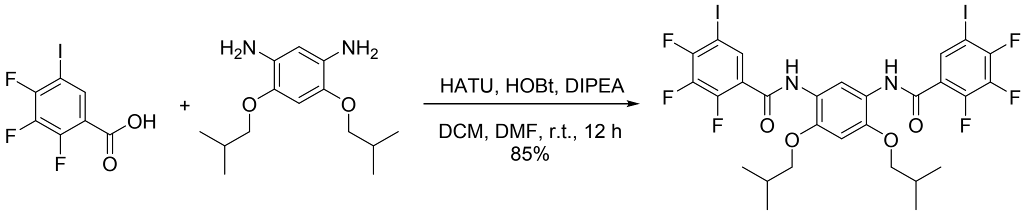
Crystals were measured using Bruker D8 Venture-Metaljet diffractometer equipped with an PHOTON II area detector and HELIOS multilayer optics monochrommated Cu-K and Mo-K alpha radiation (lambda = 1.54184 and 0.71073 Å). Crystal structures were solved by direct method and refined by full-matrix least-squares methods based on F2 using SHELXL-2014 software. CCDC 1887341, 1887343, 1887357, 1887359, and 1887363 contain the related crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The PXRD patterns were measured with a Bruker D8 advance superspeed powder diffractometer, which operated at ambient temperature, using Cu-Kα radiation (λ = 0.15406 Å). FT-IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer by using a KBr pellet. Raman spectra were recorded on an XploRA spectrometer. Compounds **6**[1] and **7**[2] were prepared according to reported methods.



Compound 2. To a stirred solution of 2,3,4-trifluoro-5-iodobenzoic acid **6** (0.53 g, 1.7 mmol) in the mixture of CH_2Cl_2 (10 mL) and DMF (5 mL) at room temperature were added HOBt (0.21 g, 1.6 mmol), HATU (1.5 g, 4.0 mmol), DIPEA (0.35 mL, 2.0 mmol). Then the reaction mixture was stirred for 20 minutes at room temperature. After that, 4,6-diisobutoxybenzene-1,3-diamine **7** (0.20 g, 0.79 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with H_2O (10 mL) and the solvent was evaporated. The resulting residue was extracted with EtOAc (2 × 30 mL) and the organic layer was washed with 1*N* HCl (10 mL), water (10 mL), saturated $NaHCO_3$ solution (10 mL) and brine (20 mL). The organic layer was further dried over anhydrous Na_2SO_4 and then concentrated at high vacuum. Chromatography (CH_2Cl_2/n-hexane 3:7) over silica gel (100–200 mesh) provided pure compound **2** (white powder, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.91 (d, $J = 13.6$ Hz, 1H), 8.39 (s, 1H), 8.02 (s, 1H), 6.47 (s, 1H), 3.75 (s, 4H), 2.14-2.12 (m, 2H), 1.07 (brs, 12H) ppm. HRMS (ESI) calculated for $C_{28}H_{25}F_6I_2N_2O_4$: (M^++H) 820.9808; found 820.9801.

References

[1] C.-Z. Liu, S. Koppireddi, H. Wang, D.-W. Zhang and Z.-T. Li, *Angew. Chem. Int. Ed.*, 2019, **58**, 226–230.
[2] Y.-Y. Zhu, G.-T. Wang and Z.-T. Li, *Org. Biomol. Chem.*, **2009**, *7*, 3243–3250.

Table S1 Hydrogen bonds for **1** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(2)	0.86(5)	1.99(5)	2.687(4)	138(4)
N(1)-H(1A)...O(3)	0.86(5)	2.23(5)	2.620(5)	107(4)

Table S2 Hydrogen bonds for **1•3** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(1)	0.860	2.241	2.638(4)	108.1
N(2)-H(2)...O(3)	0.860	1.961	2.660(6)	137.7
N(3)-H(3)...O(4)	0.860	2.034	2.704(5)	134.1
N(3)-H(3)...O(6)	0.860	2.251	2.640(4)	107.5

Table S3 Hydrogen bonds for **1•4** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(3)	0.881	2.288	2.666(7)	105.8
N(2)-H(2)...O(4)	0.881	2.049	2.711(6)	131.2
N(3)-H(3)...O(5)	0.880	2.014	2.694(6)	133.2
N(3)-H(3)...O(6)	0.880	2.273	2.645(7)	105.3

Table S4 Hydrogen bonds for **1•5** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(7)	1.17(4)	1.37(4)	2.543(3)	177(4)
N(2)-H(2)...O(4)	0.87(3)	1.94(3)	2.659(2)	138(2)
N(2)-H(2)...O(5)	0.87(3)	2.20(3)	2.606(2)	108(2)
N(3)-H(3)...O(3)	0.87(3)	1.91(3)	2.632(2)	139(2)
N(3)-H(3)...O(6)	0.87(3)	2.22(3)	2.614(3)	107(2)
O(9)-H(9)...N(4)	0.95(4)	1.61(4)	2.564(3)	176(4)

Table S5 Hydrogen bonds for **2** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	0.91(9)	2.07(7)	2.573(5)	114(6)
N(1)-H(1)...F(3)	0.91(9)	2.06(7)	2.737(5)	130(6)
N(2)-H(2)...O(3)	0.81(5)	2.26(6)	2.599(5)	106(4)
N(2)-H(2)...F(6)	0.81(5)	2.06(5)	2.752(5)	142(5)

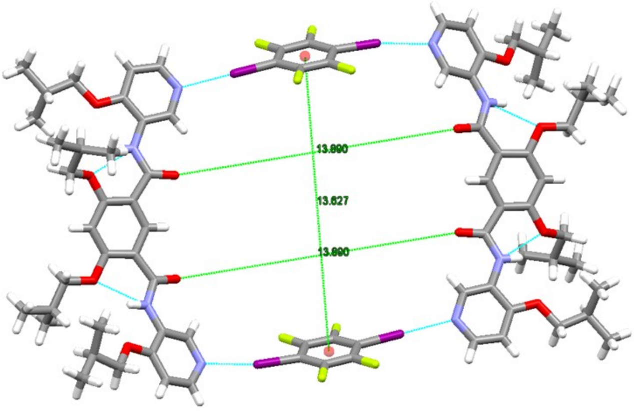


Fig. S1 The cavity size of the rectangular 2+2 co-crystal **1•3** is measured to be of about 1.39 nm × 1.36 nm. The distance between the two corresponding carbonyl oxygens is 1.389 nm, and that between the two centroids of the two compound **3** is 1.363 nm.

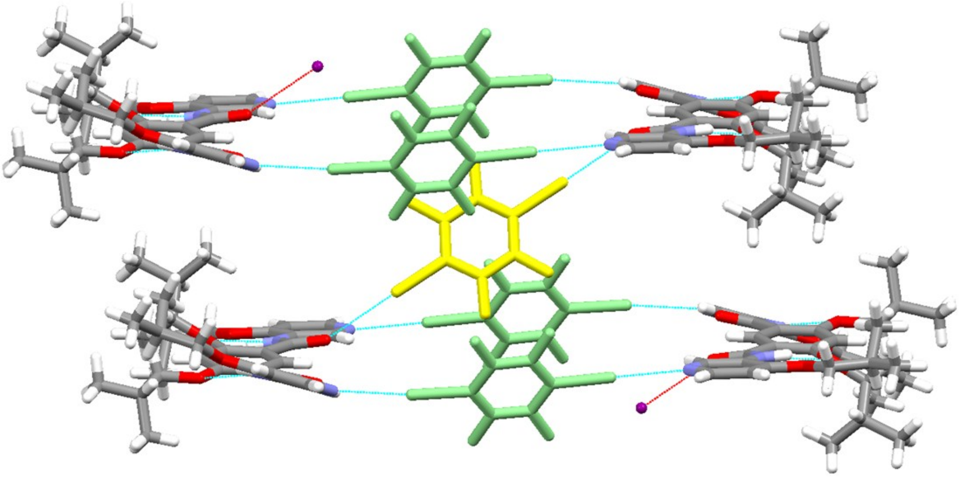


Fig. S2 The capsulation of compound **3** (in yellow) by halogen bonding with two carbonyl oxygens of two compounds **1** at neighbouring layers.

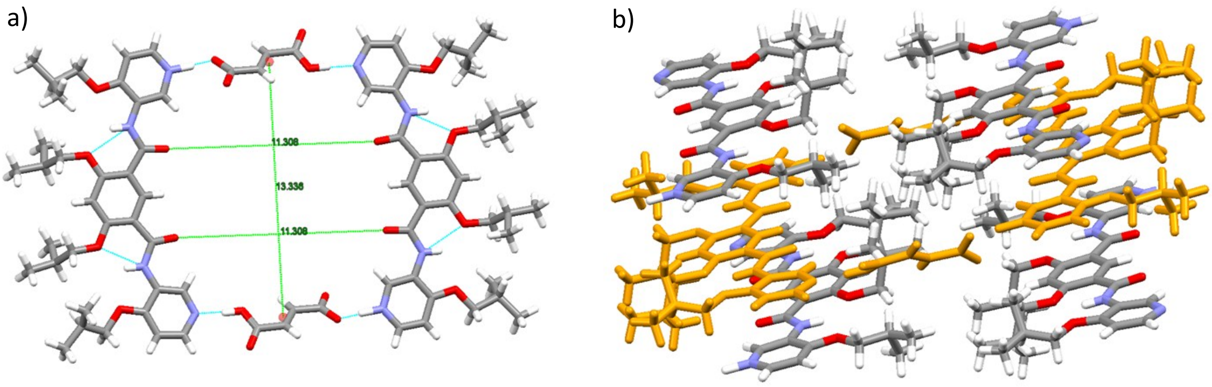


Fig. S3 a) The cavity size of the rectangular 2+2 co-crystal **1•5** is measured to be of about 1.13 nm × 1.33 nm. The distance between the two corresponding carbonyl oxygens is 1.131 nm, and that between the two centroids of the two compound **5** is 1.334 nm. b) The cavity of the orange macrocycle is seized by the iso-butyl groups of the molecules of **1** from other hydrogen-bonded macrocycles.

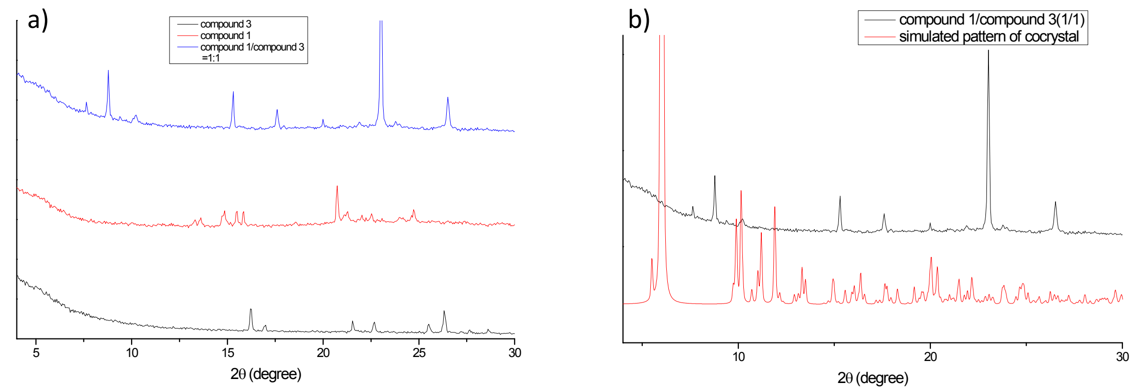


Fig. S4. PXRD patterns of **1•3**. (a) Comparison of pure compound **1** (red line), compound **3** (black line), and the mixture of compound **1** / compound **3** (1:1, blue line); (b) Comparison of the mixture of compound **1** / compound **3** (1:1, black line) and simulated PXRD pattern of the cocrystal (red line).

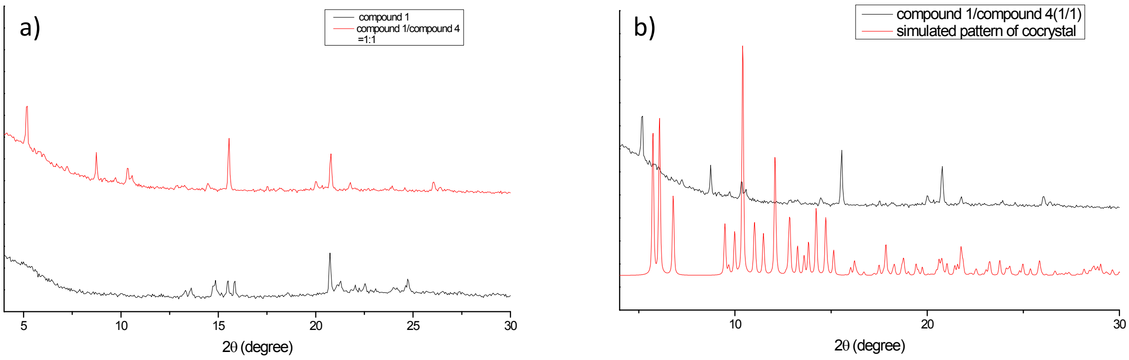


Fig. S5. PXRD patterns of **1•4**. (a) Comparison of pure compound **1** (black line), and the mixture of compound **1** / compound **4** (1:1, red line); (b) Comparison of the mixture of compound **1** / compound **4** (1:1, black line) and simulated PXRD pattern of the cocrystal (red line).

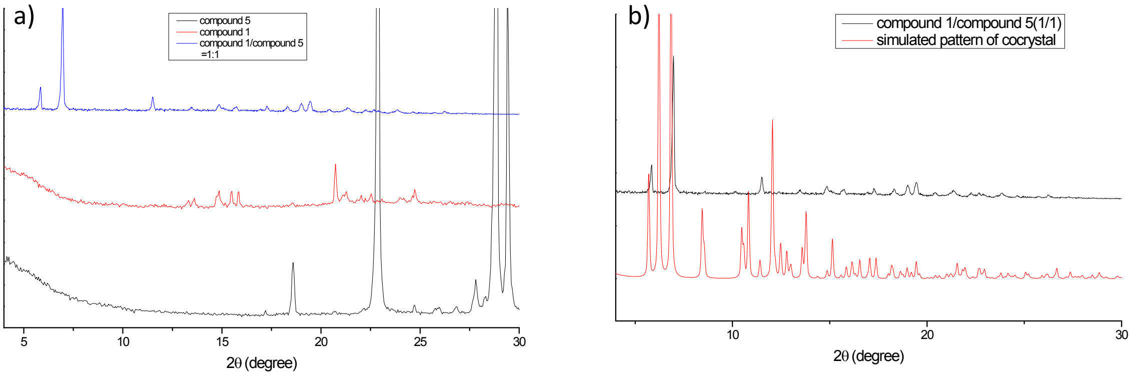


Fig. S6. PXRD patterns of **1•5**. (a) Comparison of pure compound **1** (red line), compound **5** (black line), and the mixture of compound **1** / compound **5** (1:1, blue line); (b) Comparison of the mixture of compound **1** / compound **5** (1:1, black line) and simulated PXRD pattern of the cocrystal (red line).

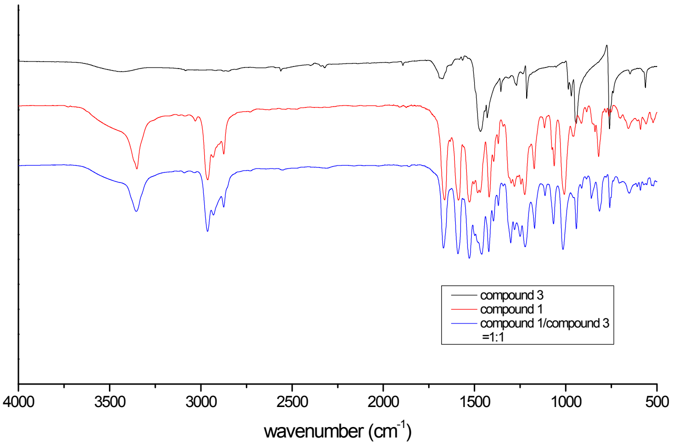


Fig. S7. FT-IR spectra of pure compound **1** (red line), compound **3** (black line), and the mixture of compound **1** / compound **3** (1:1, blue line).

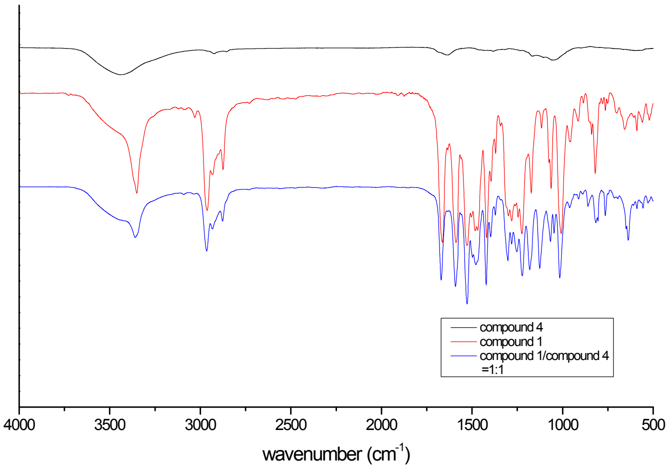


Fig. S8. FT-IR spectra of pure compound **1** (red line), compound **4** (black line), and the mixture of compound **1** / compound **4** (1:1, blue line).

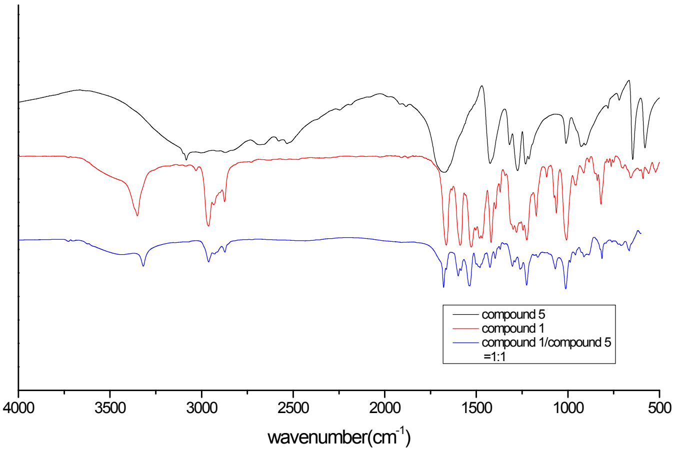


Fig. S9. FT-IR spectra of pure compound **1** (red line), compound **5** (black line), and the mixture of compound **1** / compound **5** (1:1, blue line).

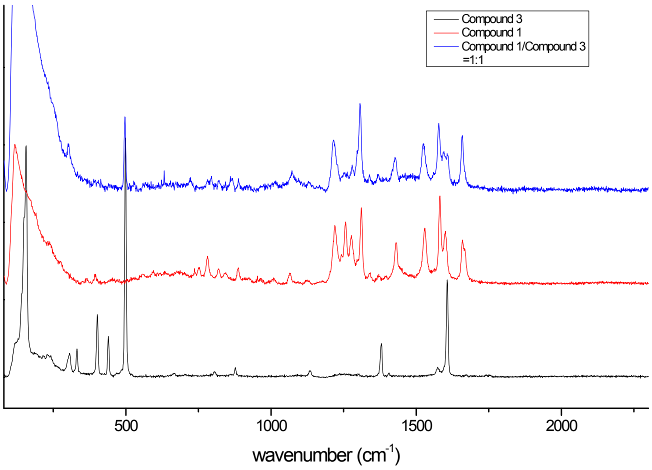


Fig. S10. Raman spectra of pure compound **1** (red line), compound **3** (black line), and the mixture of compound **1** / compound **3** (1:1, blue line).

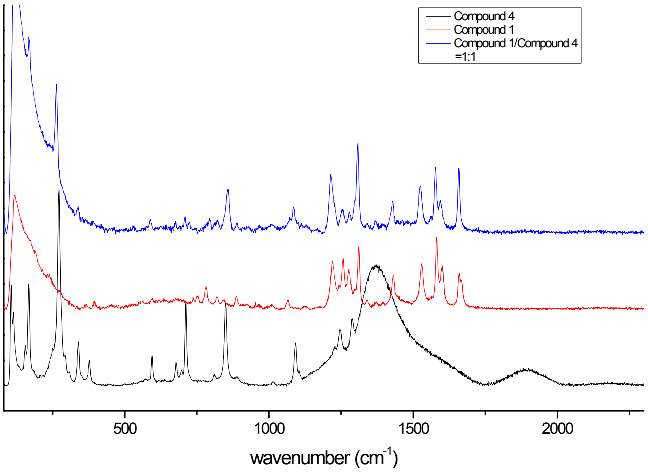


Fig. S11. Raman spectra of pure compound **1** (red line), compound **4** (black line), and the mixture of compound **1** / compound **4** (1:1, blue line).

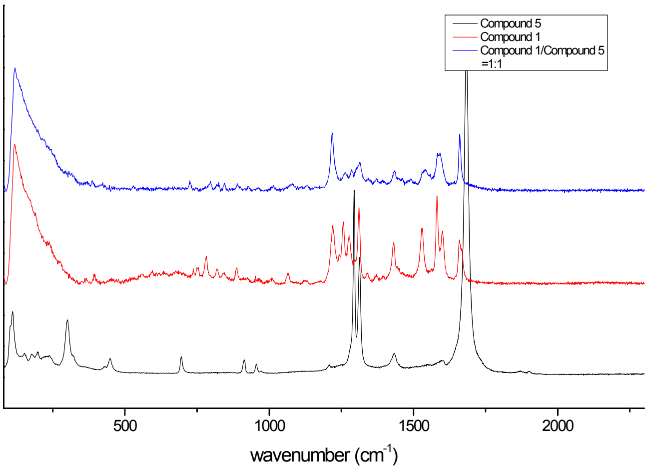


Fig. S12. Raman spectra of pure compound **1** (red line), compound **5** (black line), and the mixture of compound **1** / compound **5** (1:1, blue line).