

Supporting Information

Confinement of unprecedented tetrahedral water tetramers inside 1D hydrophobic channels of metal-organic framework hosts

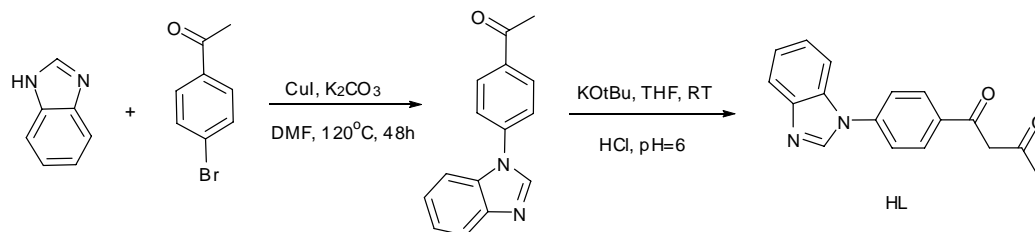
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Synthesis of Ligand 1-(4-(1H-benzimidazol-1-yl)phenyl)butane-1,3-dione (HL)^{S1,S2}



Synthesis of 4-(1H-benzimidazol-1-yl)acetophenone. To a solution of benzimidazole (14 mmol) in 10 mL anhydrous dimethyl formamide (DMF), CuI (0.382 g, 2 mmol), 4-bromoacetophenone (1.99 g, 10 mmol) and K₂CO₃ (2.76 g, 20 mmol) were added under N₂. The reaction mixture was stirred for 30 min at room temperature, and then refluxed for 48 h at 120 °C. The reaction mixture was cooled to room temperature, diluted with 20 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 200 mL of ethyl acetate. The combined organic extracts were concentrated in vacuo. The resulting residue was purified on a silica gel column chromatography using ethyl acetate/petroleum ether (1:1) as eluent. Yield 53%. MS *m/z* = 237 (*M* + 1). ¹H NMR (CDCl₃, 300 MHz): δ 2.698 (s, 3H, -CH₃); δ 7.399 (m, 2H, benzene); δ 7.605 (m, 1H, benzene); δ 7.671 (d, 2H, benzene, *J* = 8.7 Hz); δ 7.915 (m, 1H, benzene); δ 8.200 (d, 3H, benzene and imidazole, *J* = 8.7 Hz). IR (KBr cm⁻¹): 3053 w, 1683 s, 1600 s, 1515 m, 1492 m, 1452 w, 1379 w, 1355 w, 1271 s, 1226 m, 1201 w, 1180 w, 958 w, 887 w, 837 m, 756 m, 597 w, 518 w, 433 w.

Synthesis of HL. To a stirred solution of potassium tert-butoxide (2.24 g, 20 mmol) and 4-benzimidazole- acetophenone (10 mmol) in 10 mL anhydrous tetrahydrofuran (THF), 2 mL ethyl acetate was slowly dropped under N₂ at 0 °C. After that, the reaction mixture was stirred at

room temperature for 2 h. During this course, the appearance of white solid was changed to yellow in a few minutes, indicating that the reaction went smoothly. The yellow precipitates were collected by filtration and washed with ethyl ether. The yellow precipitates were dissolved in water and slowly neutralized by 1 M HCl (pH = 6~7). The resulting solid was collected by filtration, and purified on a silica gel column chromatography using ethyl acetate/petroleum ether (1:1) as eluent. Yield 88%. MS $m/z = 279$ ($M + 1$). ^1H NMR (CDCl_3 , 300 MHz): δ 2.262 (s, 3H, $-\text{CH}_3$); δ 6.237 (s, 1H, $=\text{CH}-$); δ 7.396 (m, 2H, benzene); δ 7.580 (m, 1H, benzene); δ 7.647 (d, 2H, benzene, $J = 8.7$ Hz); δ 7.908 (m, 1H, benzene); δ 8.111 (d, 2H, benzene, $J = 8.7$ Hz); δ 8.207 (s, 1H, imidazole). IR (KBr cm^{-1}): 3091 w, 1606 s, 1515 m, 1488 m, 1452 m, 1361 w, 1284 m, 1236 m, 1207 m, 1082 w, 975 w, 933 w, 854 m, 777 m, 592 w, 524 w, 433 w.

Table 1. Selected bond lengths [\AA] for **1** and **2**.

<i>Complex 1</i>					
C(2)–O(1)	1.254(10)	C(37)–C(38)	1.394(12)	Co(1)–O(3)	2.055(6)
C(2)–C(3)	1.425(10)	C(38)–O(6)	1.280(11)	Co(1)–N(2)a	2.114(8)
C(3)–C(4)	1.374(12)	C(53)–O(7)	1.256(11)	Co(1)–N(6)	2.146(8)
C(4)–O(2)	1.284(10)	C(53)–C(54)	1.428(10)	Co(2)–O(6)	2.049(5)
C(19)–O(3)	1.266(10)	C(54)–C(55)	1.372(13)	Co(2)–O(2)	2.041(5)
C(19)–C(20)	1.417(10)	C(55)–O(8)	1.310(11)	Co(2)–O(1)	2.043(6)
C(20)–C(21)	1.410(13)	Co(1)–O(4)	2.043(6)	Co(2)–O(5)	2.049(6)
C(21)–O(4)	1.304(12)	Co(1)–O(7)	2.052(6)	Co(2)–N(8)	2.132(7)
C(36)–O(5)	1.263(10)	Co(1)–O(8)	2.049(5)	Co(2)–N(4)	2.161(7)
C(36)–C(37)	1.404(9)				
<i>Complex 2</i>					
C(2)–O(1)	1.269(8)	C(37)–C(38)	1.399(10)	O(6)–Zn(1)	2.078(4)
C(2)–C(3)	1.409(8)	C(38)–O(6)	1.259(9)	Zn(1)–O(8)b	2.071(4)
C(3)–C(4)	1.398(9)	C(53)–O(7)	1.247(8)	Zn(1)–O(7)b	2.079(5)
C(4)–O(2)	1.289(7)	C(53)–C(54)	1.423(8)	N(5)–Zn(2)	2.173(6)
C(19)–O(3)	1.252(8)	C(54)–C(55)	1.381(9)	N(7)–Zn(2)	2.186(5)
C(19)–C(20)	1.416(8)	C(55)–O(8)	1.271(8)	Zn(2)–O(2)c	2.061(4)
C(20)–C(21)	1.395(9)	N(1)–Zn(1)	2.157(5)	Zn(2)–O(4)d	2.065(4)
C(21)–O(4)	1.259(8)	N(3)–Zn(1)	2.172(5)	Zn(2)–O(1)c	2.075(5)
C(36)–O(5)	1.246(8)	O(5)–Zn(1)	2.095(5)	Zn(2)–O(3)d	2.094(5)
C(36)–C(37)	1.418(8)				

Symmetry transformations used to generate equivalent atoms:

a $-y + 4/3, x - y + 5/3, z - 1/3$ b $x - 2/3, y - 1/3, z - 1/3$ c $-x + y + 5/3, -x + 4/3, z + 1/3$ d $-x + y + 2,$

$-x + 1, z$

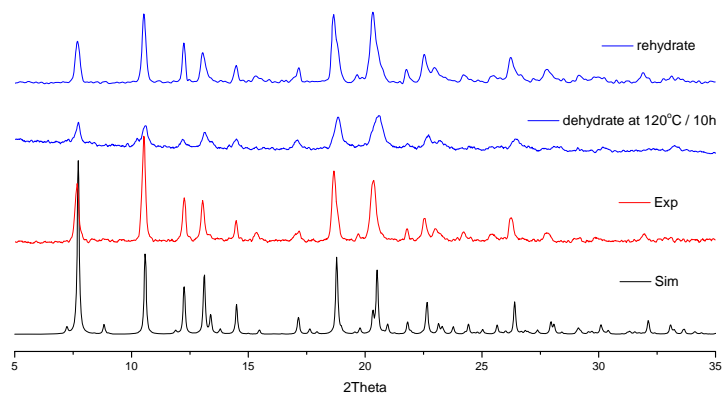


Figure S1. XRD patterns of 1 and the simulated pattern based on the single crystal 1.

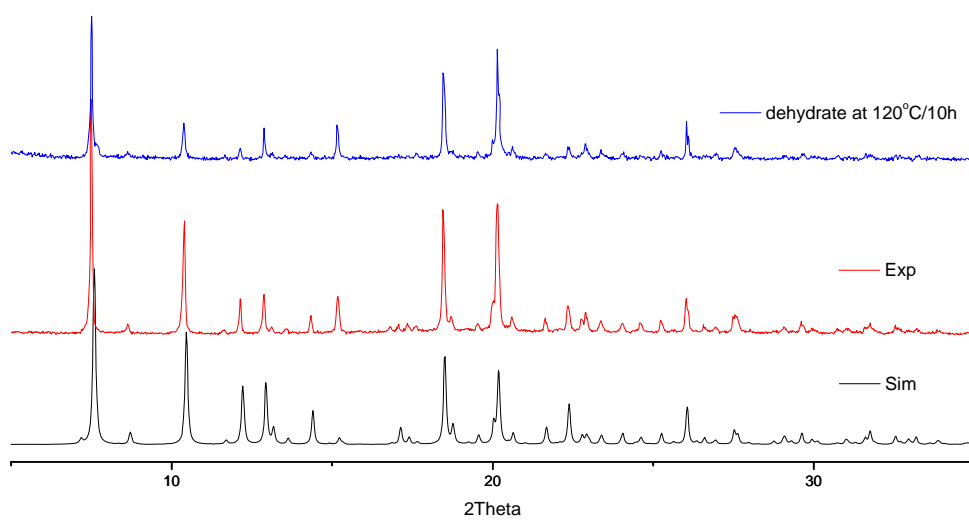


Figure S2. XRD patterns of 2 and the simulated pattern based on the single crystal 2.

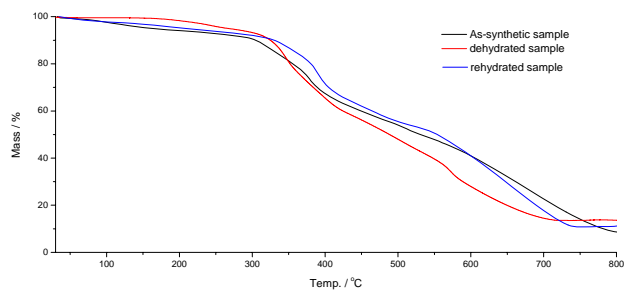


Figure S3. TGA of complex **1**.

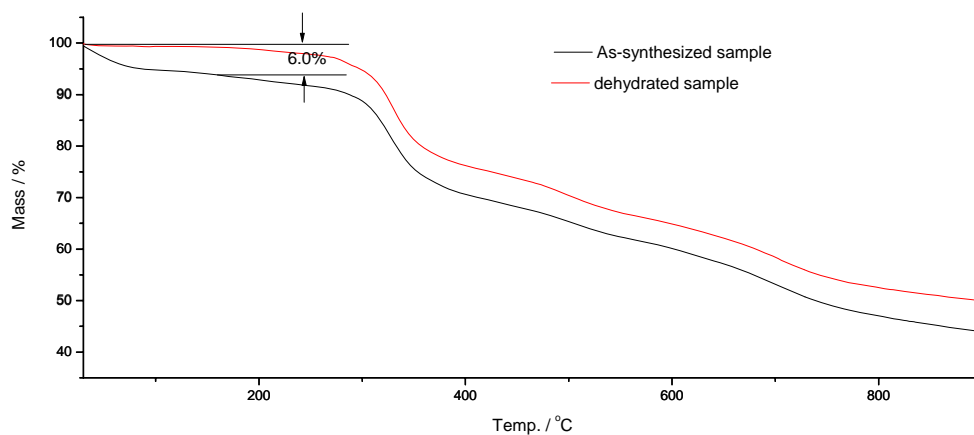


Figure S4. TGA of complex **2**.

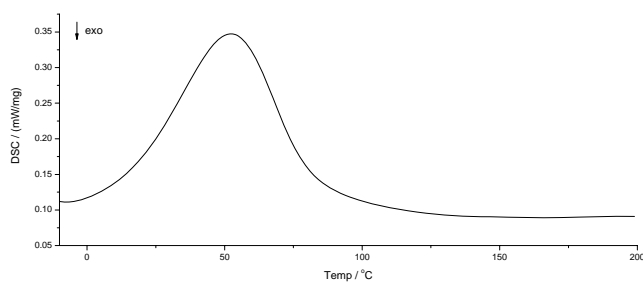


Figure S5. DSC plot displaying an endotherm for the loss of water molecules in **1**.

References

- S1. L. Zhu, P. Guo, G. Li, J. Lan, R. Xie and J. You, *J. Org. Chem.*, 2007, **72**, 8535.
- S2. N. S. Nandurkar, M. J. Bhanushali, D. S. Patil and B. M. Bhanage, *Synth. Commun.*, 2007, **37**, 4111.