# Supporting information

## Synthesis, Structures and Luminescent Properties of 3d-4f Heterometallic-organic Frameworks (HMOFs) Constructed by Different Copper Halide Clusters

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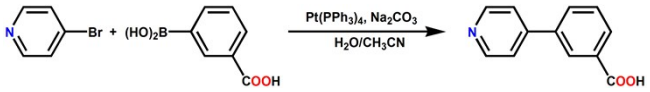
Synthesis of 3-(pyridine-4-yl) benzoic acid (Hpba)




Hpba was synthesized according the previous report.1 To a degassed solution of 3-Carboxyphenylboronic acid (1.70 g, 10.2 mmol), 4-bromopridine hydrochloride (2.01 g, 10.3 mmol), and sodium carbonate (2.10 g, 19.8 mmol) in 100mL of a mixed solution (1:1 $CH_3CN$:$H_2O$) at room temperature, $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) was added under $N_2$ pressure. The reaction mixture was refluxed for 22 h. the hot suspension was filtered. The filtrate was concentrated to about half of the original volume and then washed with $CH_2Cl2$. The aqueous layer was acidified with concentrated HCl; the resulting white precipitate was collected, washed with $CH_3CN$.

1. Sekiya, R.; Nishikiori, S.; Ogura, K. *Inorganic Chemistry*, **2006**, 45, 9233.

Table S1. Selected bond lengths (Å) in compound **1**

| | | | |
|---|---|---|---|
| **Gd(1)-O(6)#1** | 2.312(6) | **Gd(1)-O(3)** | 2.343(5) |
| **Gd(1)-O(2)#2** | 2.349(6) | **Gd(1)-O(1)** | 2.372(6) |
| **Gd(1)-O(5)** | 2.394(6) | **Gd(1)-O(7)** | 2.416(7) |
| **Gd(1)-O(4)#2** | 2.437(6) | **Gd(1)-O(3)#2** | 2.753(6) |
| **Cu(1)-I(2)** | 2.6956(15) | **Cu(1)-I(1)** | 2.7219(15) |
| **I(1)-Cu(1)#4** | 2.7220(15) | **I(2)-Cu(1)#4** | 2.6956(15) |
| **Cu(1)-Cu(1)#4** | 2.791(2) | **Cu(1)-N(1)** | 2.042(7) |
| **Cu(1)-N(2)#3** | 2.058(7) | | |

**Symmetry codes: #1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1 #3 x,y,z-1 #4 x,-y+1/2,z #5 x,y,z+1**

Table S2. Selected bond lengths (Å) in compound **2**

| | | | |
|---|---|---|---|
| **Gd(1)-O(1')** | 2.262(18) | **Gd(1)-O(1')#1** | 2.262(18) |
| **Gd(1)-O(3)#1** | 2.293(9) | **Gd(1)-O(3)** | 2.293(9) |
| **Gd(1)-O(2)#2** | 2.315(7) | **Gd(1)-O(2)#3** | 2.315(7) |
| **Gd(1)-O(4')#1** | 2.44(6) | **Gd(1)-O(4')** | 2.44(6) |
| **Gd(1)-O(1)** | 2.466(15) | **Gd(1)-O(1)#1** | 2.466(15) |
| **Gd(1)-O(4)** | 2.50(6) | **Gd(1)-O(4)#1** | 2.50(6) |
| **Cu(1)-N(1)** | 2.048(8) | **Cu(1)-I(1)#4** | 2.6469(15) |
| **Cu(1)-Cu(1)#5** | 2.660(2) | **Cu(1)-Cu(1)#6** | 2.661(2) |
| **Cu(1)-I(1)#6** | 2.6765(15) | **Cu(1)-I(1)** | 2.7347(15) |
| **Cu(1)-Cu(1)#4** | 2.759(2) | **I(1)-Cu(1)#4** | 2.6470(15) |
| **I(1)-Cu(1)#5** | 2.6765(15) | | |

**Symmetry codes: #1 -x+1/2,y,-z+3/4 ; #2 -x+1/2,-y+1/2,z-1/2 ; #3 x+0,-y+1/2,-z+5/4 ; #4 -x+1,-y+1,z ; #5 y,-x+1,-z+1 ; #6 -y+1,x,-z+1 ;**

Table S3. Selected bond lengths (Å) in compound **3**

| | | | |
|---|---|---|---|
| **Gd(1)-O(4)#1** | 2.280(5) | **Gd(1)-O(5)** | 2.304(5) |
| **Gd(1)-O(6)#2** | 2.334(5) | **Gd(1)-O(6)#2** | 2.334(5) |
| **Gd(1)-O(1)** | 2.488(5) | **Gd(1)-O(2)** | 2.496(5) |
| **Gd(1)-O(7)** | 2.497(6) | **Gd(1)-O(8)** | 2.518(6) |
| **Cu(1)-N(3)#3** | 2.024(6) | **Cu(1)-Cu(3)** | 2.5686(14) |
| **Cu(1)-I(1)** | 2.6652(13) | **Cu(1)-I(3)** | 2.6670(12) |
| **Cu(1)-I(2)** | 2.6858(11) | **Cu(1)-Cu(2)** | 2.7943(15) |
| **Cu(2)-N(1)** | 2.029(6) | **Cu(2)-I(1)** | 2.6254(11) |
| **Cu(2)-I(1)#4** | 2.6530(12) | **Cu(2)-I(2)** | 2.7026(13) |
| **Cu(2)-Cu(2)#4** | 2.781(2) | **Cu(3)-N(2)** | 1.979(6) |
| **Cu(3)-I(3)** | 2.5220(11) | **Cu(3)-I(2)** | 2.5652(12) |
| **I(1)-Cu(2)#4** | 2.6531(12) | | |

**Symmetry codes: #1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z+1 #3 x-1/2,-y+1/2,z-1/2 #4 -x+1/2,-y+1/2,-z+1 #5 x+1/2,-y+1/2,z+1/2**

Table S4. Selected bond lengths (Å) in compound **4**

| | | | |
|---|---|---|---|
| **Gd(1)-O(2)#1** | 2.304(4) | Gd(1)-O(6)#2 | 2.325(4) |
| **Gd(1)-O(4)#1** | 2.350(4) | Gd(1)-O(5) | 2.357(3) |
| **Gd(1)-O(3)** | 2.371(4) | Gd(1)-O(1) | 2.382(3) |
| **Gd(1)-O(8)** | 2.471(5) | Gd(1)-O(7) | 2.663(6) |
| **Cu(1)-N(1)** | 2.008(5) | Cu(1)-I(3) | 2.6305(10) |
| **Cu(1)-Cu(4)** | 2.6449(14) | Cu(1)-Cu(3) | 2.6621(14) |
| **Cu(1)-I(2)** | 2.7045(11) | Cu(1)-Cu(2) | 2.7142(13) |
| **Cu(1)-I(1)** | 2.7585(15) | Cu(2)-I(4)#3 | 2.6845(11) |
| **Cu(2)-I(1)** | 2.6940(12) | Cu(2)-I(4) | 2.6972(11) |
| **Cu(2)-I(2)** | 2.7161(13) | Cu(2)-Cu(3) | 2.7668(13) |
| **Cu(2)-Cu(4)** | 2.8142(15) | Cu(2)-Cu(2)#3 | 2.8709(18) |
| **Cu(3)-N(2)#4** | 2.011(5) | Cu(3)-I(1) | 2.5643(12) |
| **Cu(3)-I(3)** | 2.6709(13) | Cu(3)-Cu(4) | 2.7268(16) |
| **Cu(3)-I(4)** | 2.8449(13) | Cu(4)-N(3)#5 | 2.030(5) |
| **Cu(4)-I(2)** | 2.6238(11) | Cu(4)-I(3) | 2.7157(11) |
| **Cu(4)-I(4)** | 2.7189(11) | I(4)-Cu(2)#3 | 2.6844(11) |

Symmetry codes: #1 -x+2,-y,-z+1 #2 -x+1,-y,-z+1 #3 -x+1,-y+1,-z #4 -x+1,-y+1,-z+1 #5 x-1,y,z-1 #6 x+1,y,z+1

Table S5. Elemental analyses of the four compounds and ground sample of compound **3**

| Name | Calculated | | | Found | | |
|---|---|---|---|---|---|---|
| | C (%) | H (%) | N (%) | C (%) | H (%) | N (%) |
| Compound **1** | 31.65 | 2.51 | 7.03 | 31.39 | 2.46 | 7.17 |
| Compound **2** | 25.78 | 1.94 | 5.73 | 25.59 | 1.78 | 5.87 |
| Compound **3** | 32.87 | 2.31 | 3.05 | 32.69 | 2.19 | 2.94 |
| Ground sample of Compound **3** | — | — | — | 32.71 | 2.17 | 2.95 |
| Compound **4** | 31.19 | 2.71 | 2.37 | 31.30 | 2.56 | 2.47 |

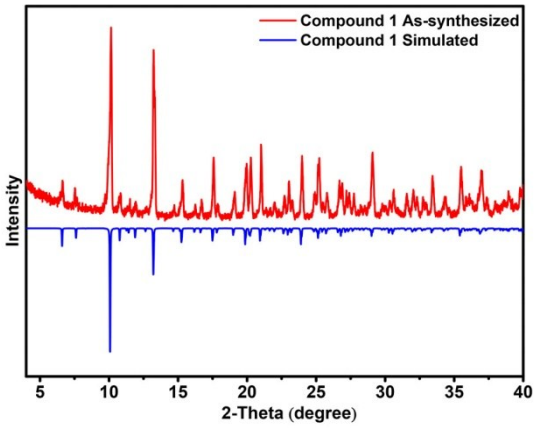



**Figure S1.** The XRD patterns of compound **1**.

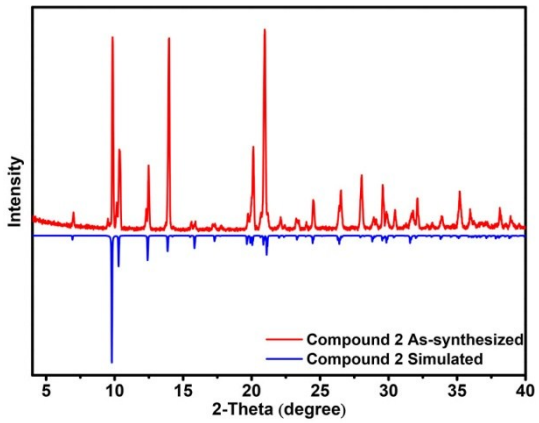



**Figure S2.** The XRD patterns of compound **2**.

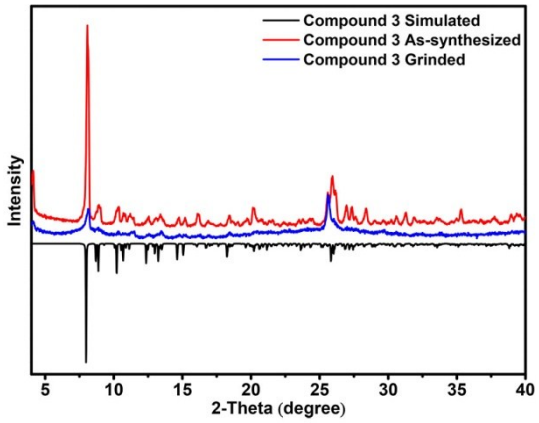



**Figure S3.** The XRD patterns of compound **3** ground sample of **3**.

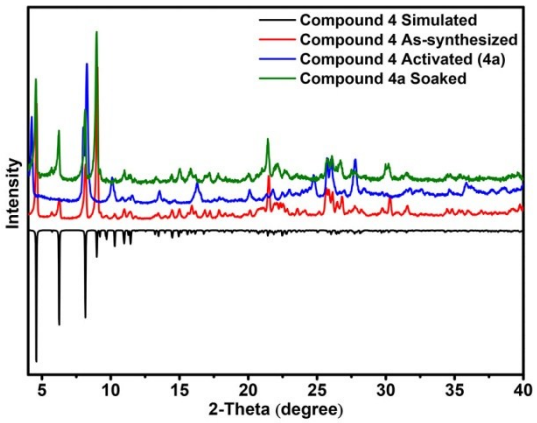



**Figure S4.** The XRD patterns of compound **4**, **4a** and the crystal powder of 4a after soaking in 1, 4-dioxane solvent.

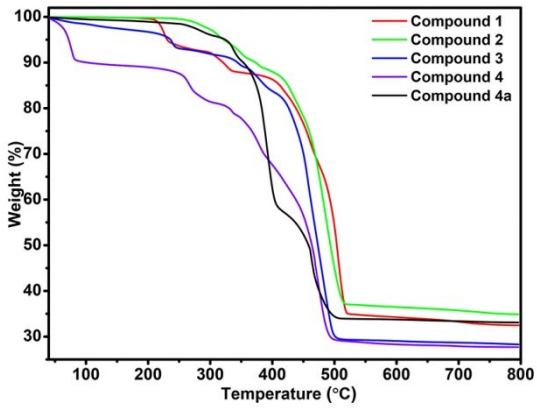



**Figure S5.** Thermogravimetric analysis curves of compound **1**, **2**, **3**, **4** and **4a**. The results suggest the guest solvents have been remved.

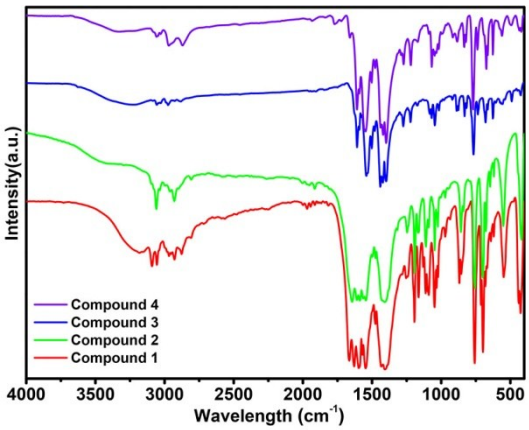



**Figure S6.** The IR spectra of compound **1**, **2**, **3** and **4**.

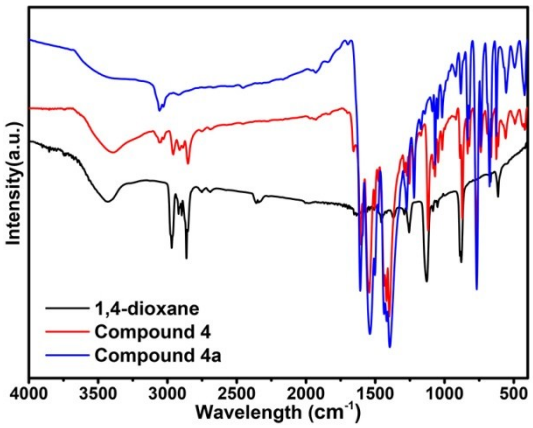



**Figure S7.** The IR spectra of 1, 4-dioxane, compound **4** and **4a**. The characteristic IR absorption peaks of 1, 4-dioxane has disappeared in the IR spectra of 4a. These results are well consistent with the TG analysis curves.

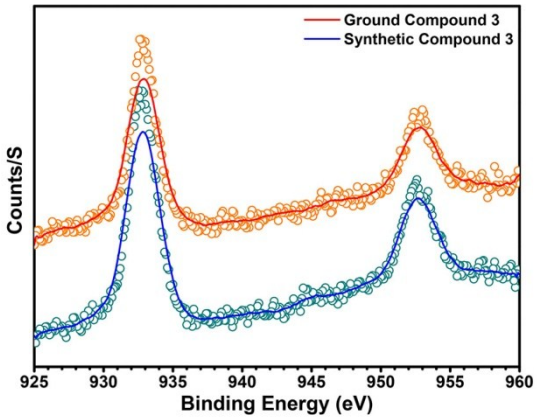



**Figure S8.** The Cu 2p XPS spectra of compound **3** and the ground sample of compound **3**.

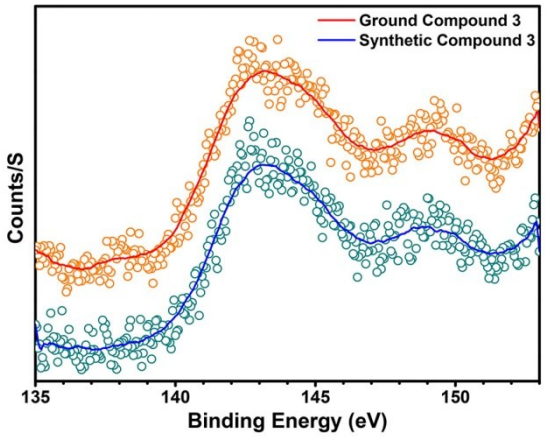



**Figure S9.** The Gd 4d XPS spectra of compound **3** and the ground sample of compound **3**.