**Supplementary Information**

# Coordination polymers and supramolecular cages based on $[(MS_4)Cu_x]^{x-2}$ cluster units and N-containing ligands

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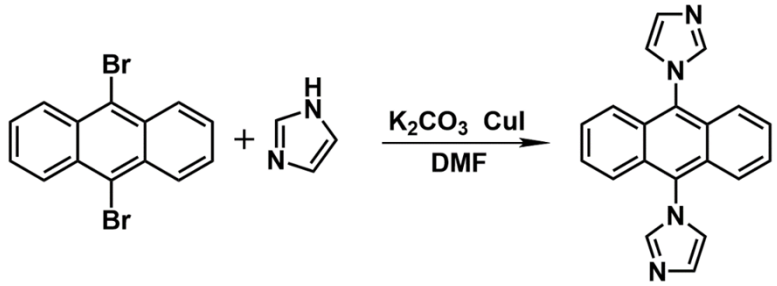
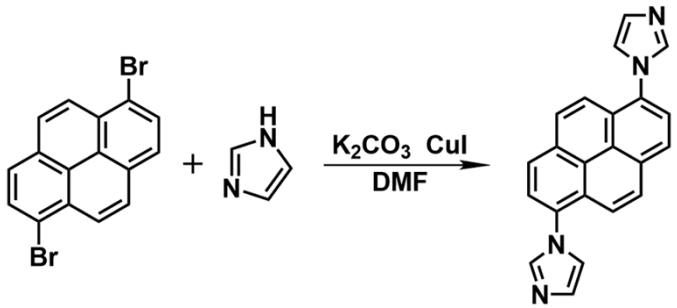
**Synthesis of ligands *dia* (9,10-di(1H-imidazol-1-yl)anthracene),**




Ligand *dia* were synthesized following reported procedures.[1]

$^1$H NMR ($CDCl_3$) $\delta$ 8.33 (t, J = 1.7 Hz, 2H), 8.18 (dd, J = 5.2, 3.2 Hz, 4H), 7.90 (dd, J = 3.8, J =1.6 Hz, 2H), 7.64 (dd, J = 3.8, 1.6 Hz, 2H), 7.46 (dd, J = 5.3, 3.2 Hz, 4H).

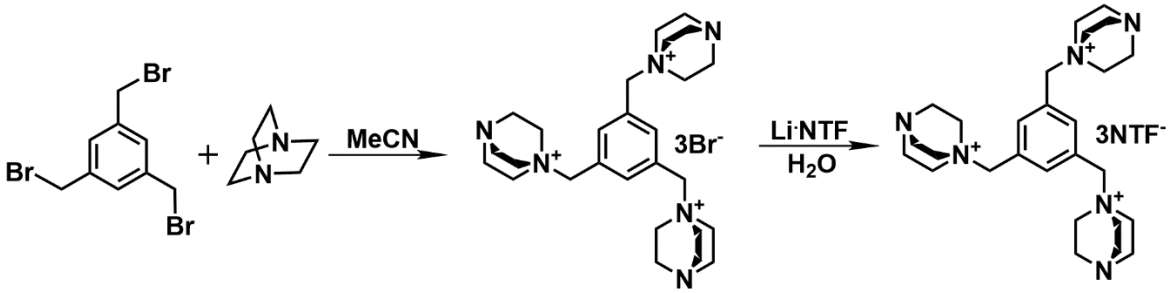
**Synthesis of ligands *dip* (1,6-di(1H-imidazol-1-yl)pyrene),**




Ligand *dip* were synthesized following reported procedures.[1]

$^1$H NMR ($CDCl_3$) $\delta$ 8.37 (t, J = 1.7 Hz, 2H), 8.09 (d, J = 7.7 Hz, 2H), 8.05 (m, br, 1H), 7.93 (dd, J = 3.8, 1.7 Hz,2H), 7.86 (dd, J = 7.7, 0.8 Hz, 2H), 7.79 (d, J = 6.8 Hz, 2H), 7.63 (dd, J = 3.8, 1.6 Hz, 2H).

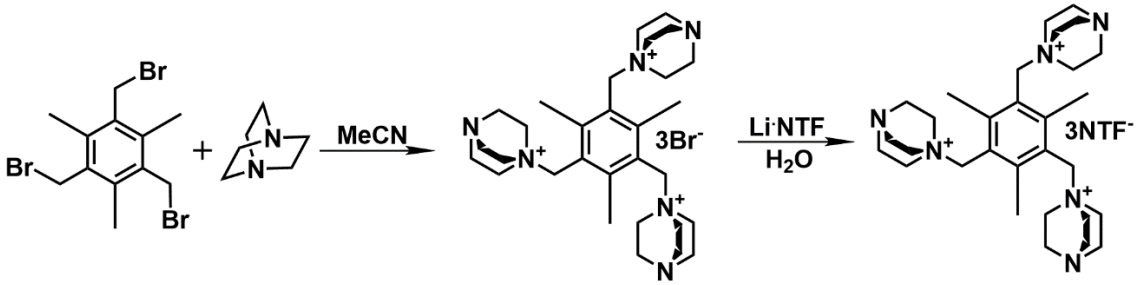
**Synthesis of ligands *bmd* (1,1',1''-(benzene-1,3,5-triyltris(methylene))tris(1,4-diazabicyclo[2.2.2]octan-1-ium) bromide),**




Ligand *bmd·NTF$_3$* were synthesized following reported procedures.[2]

$^1$H NMR ($D_2O$) $\delta$ 7.83 (s, 3H), 4.62 (s, 6H), 3.54 (t, J = 7.5 Hz, 18H), 3.17 (t, J = 7.5 Hz, 18H).

**Synthesis of ligands *mbmd* (1,1',1''-((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(1,4-diazabicyclo[2.2.2]octan-1-ium)),**




Ligand *mbmd·NTF$_3$* were synthesized following reported procedures.[2]

$^1$H NMR ($D_2O$) $\delta$ 4.88 (d, J = 2.6 Hz, 6H), 3.68 (m, br, 18H), 3.22 (m, br, 18H), 2.63 (d, J = 2.6 Hz, 9H).

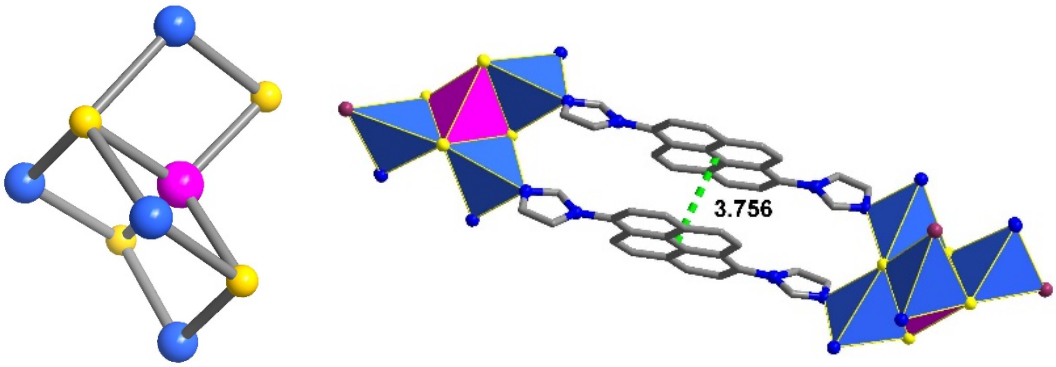



Figure S1. The penta-nuclear $[WS_4Cu_4]^{2+}$ unit and twining arrangement of *dip* ligands in **1**. (C grey, N blue, Cu light blue, W pink, S yellow, I purple)

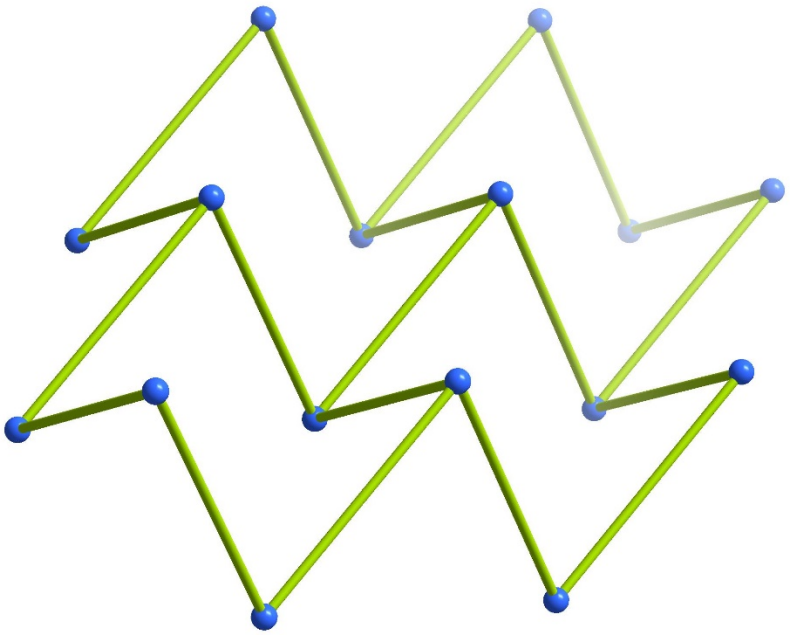


Figure S2. The schematic view of the layer strucutre in **1** with the penta-nuclear $[WS_4Cu_4]^{2+}$ unit showing as blue balls and dip twin ligands as green sticks.

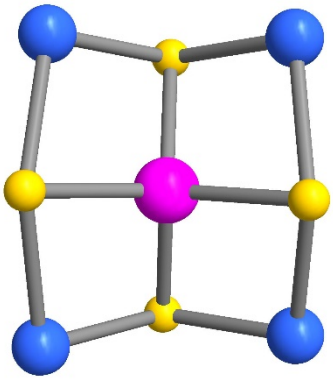


Figure S3. The penta-nuclear $[(WS_4)Cu_4]^{2+}$ unit in **2**.

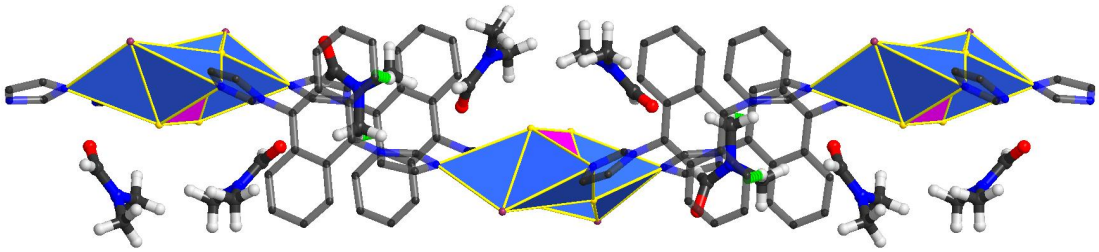


Figure S4. The zigzag $[(WS_4Cu_4)I_2(dia)_2]_n$ chain and chain of DMF in **2**.

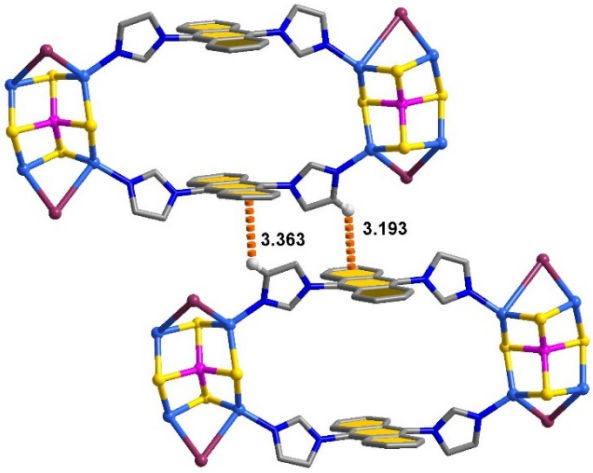



Figure S5. The C–H···π interaction between *dia* ligands of adjacent zigzag chains in **2**.

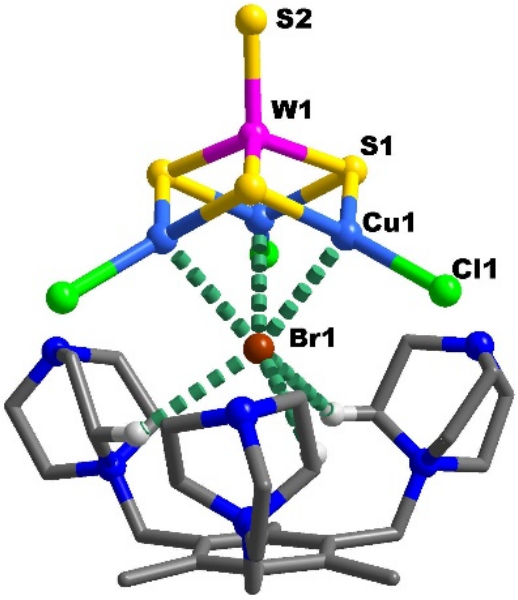
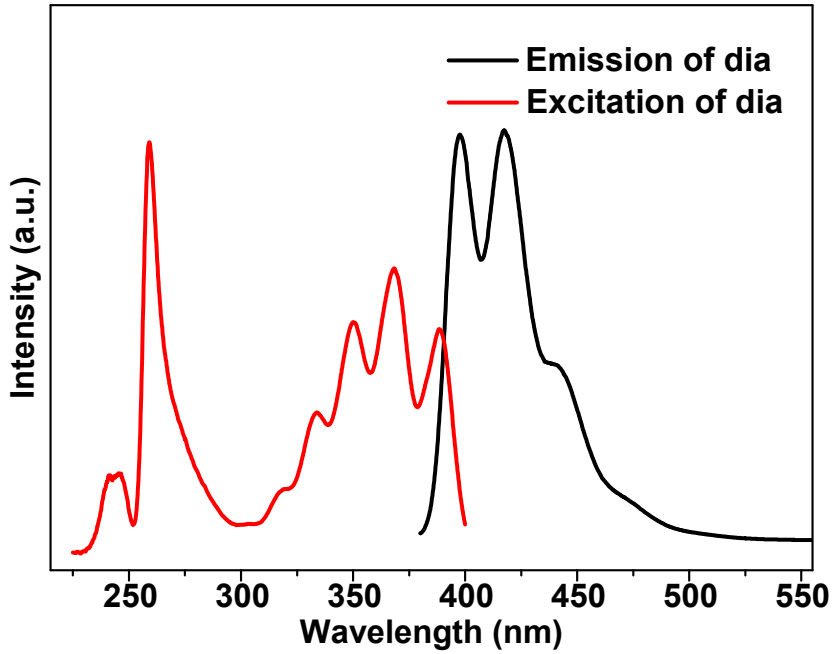



Figure S6. The crystal structure of **7**. (C grey, H light grey, N blue, Cu light blue, W pink, S yellow, Cl green, Br brown).




FigureS7. Fluorescent spectra for *dia* ligand in dilute DMF solution at room temperature.

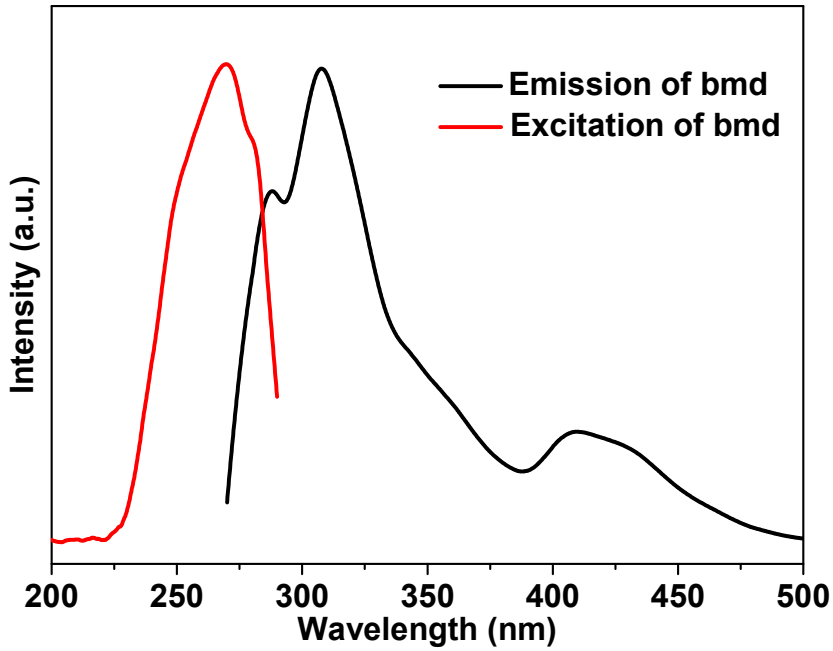



Figure S8. Fluorescent spectra for *bmd* ligand in dilute EtOH solution at room temperature.

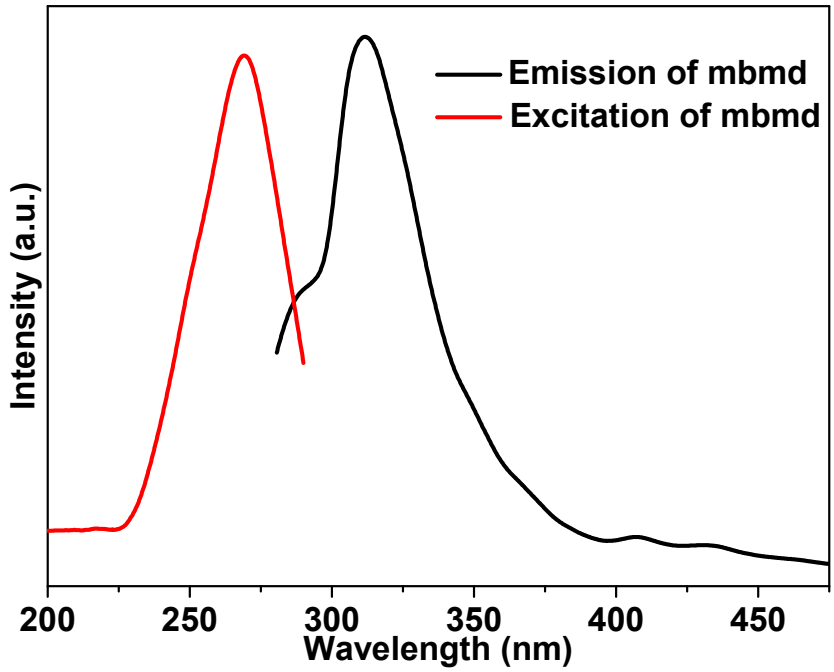



Figure S9. Fluorescent spectra for *mbmd* ligand in dilute EtOH solution at room temperature.

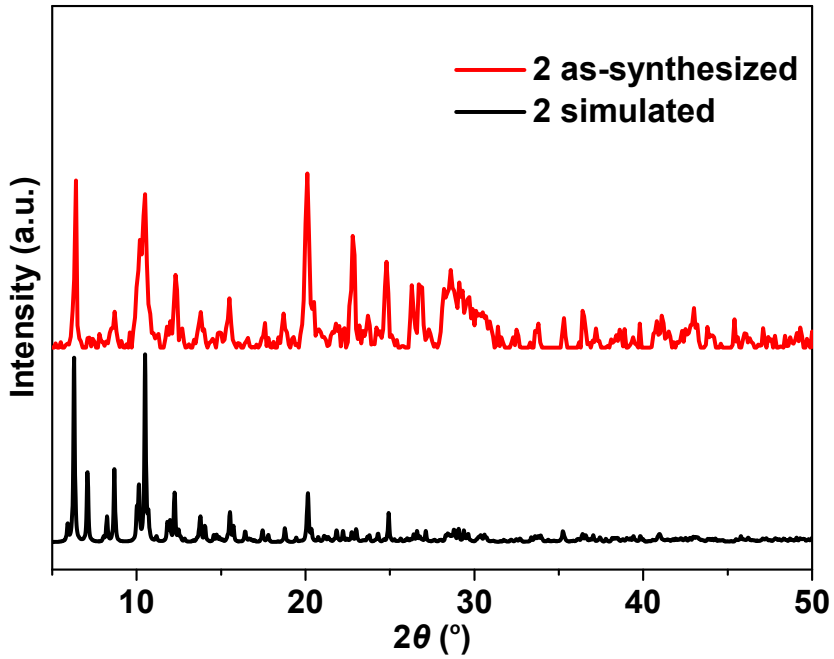



Figure S10. Powder XRD patterns for **2**.

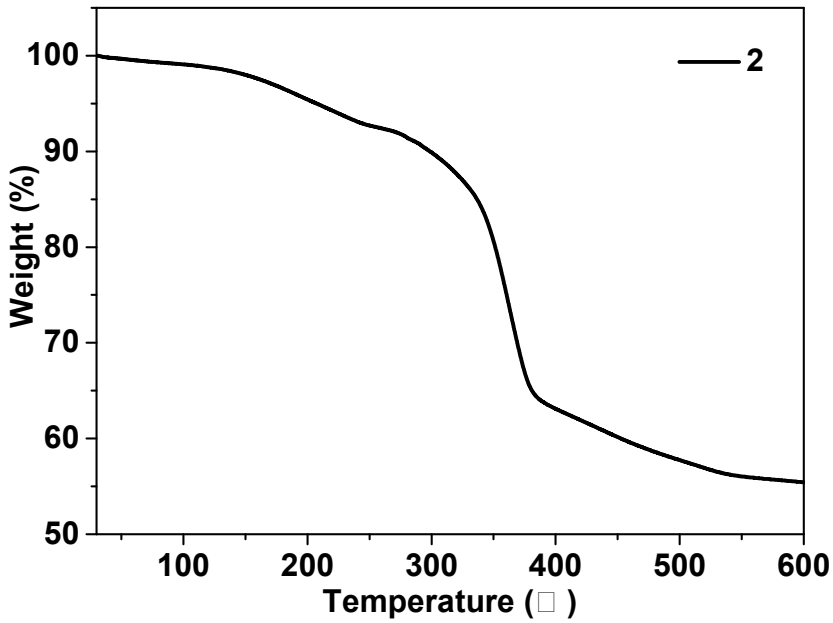



Figure S11. TG profile for **2**.

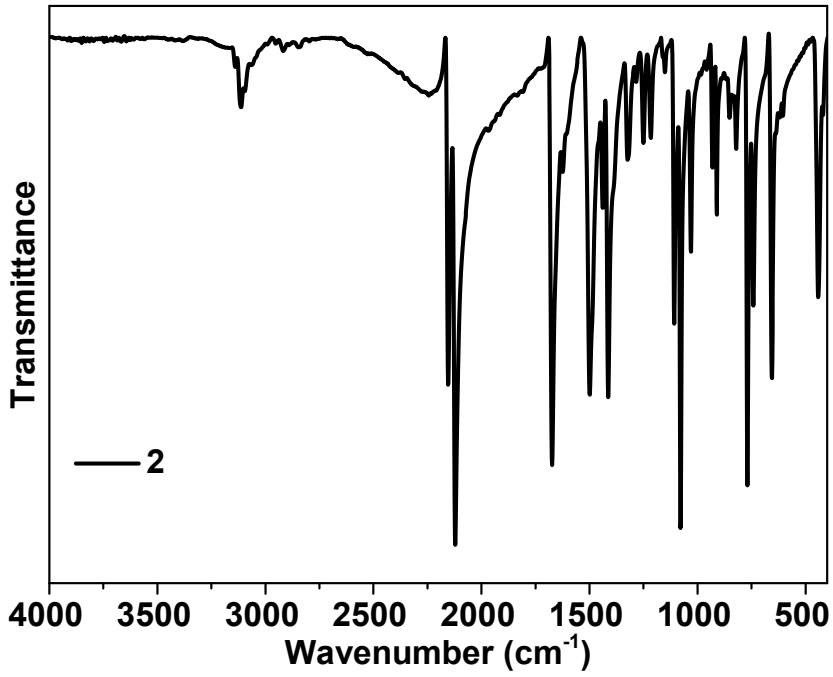



Figure S12. IR profile for **2**.

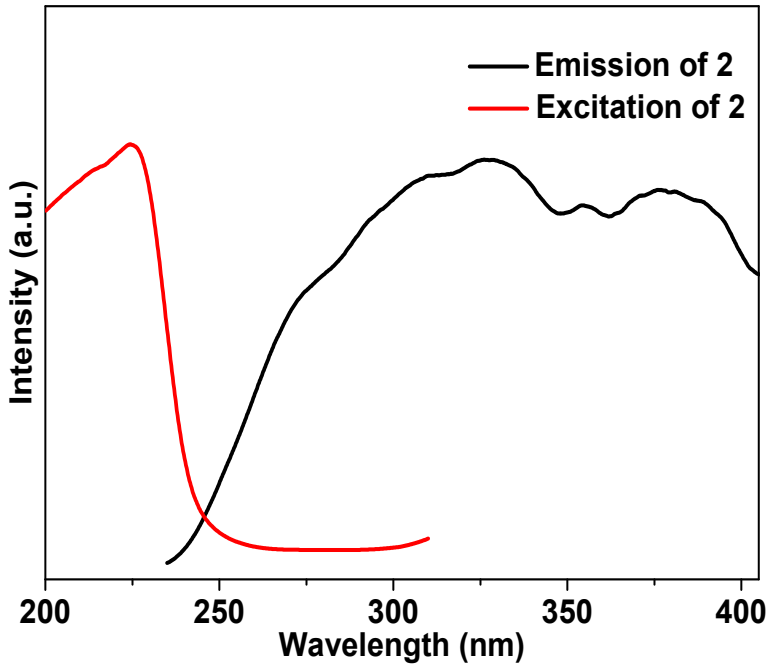



Figure S13. Fluorescent spectra for **2** in solid state at room temperature.

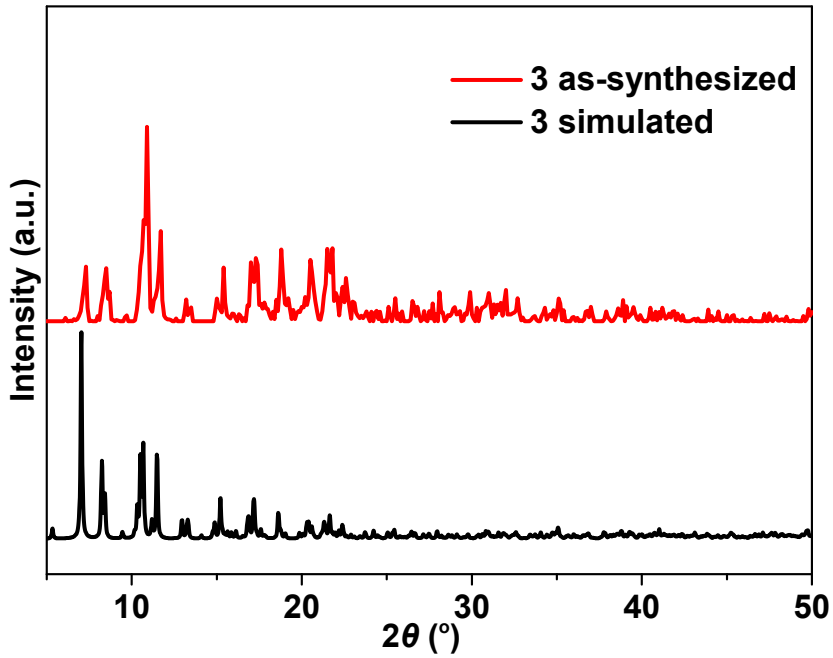



Figure S14. Powder XRD patterns for **3**.

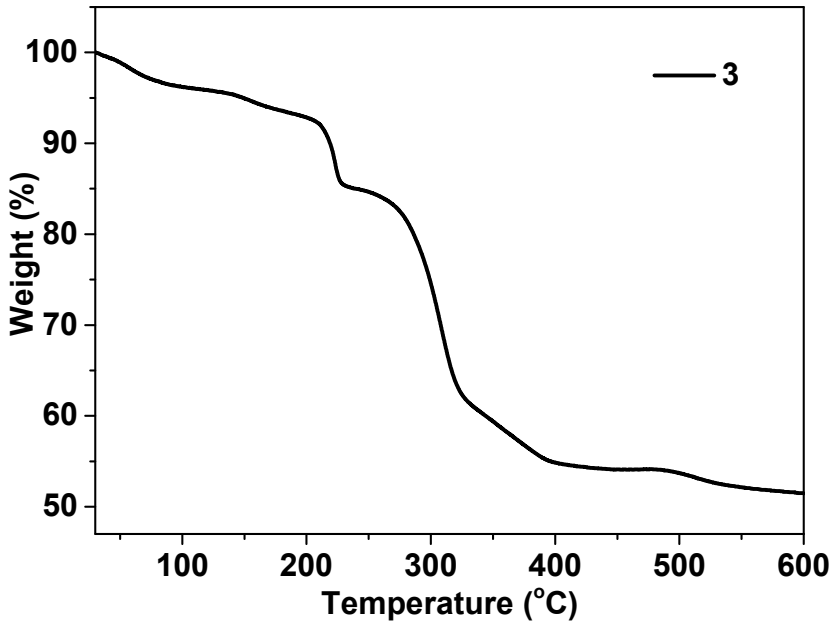



Figure S15. TG profile for **3**.

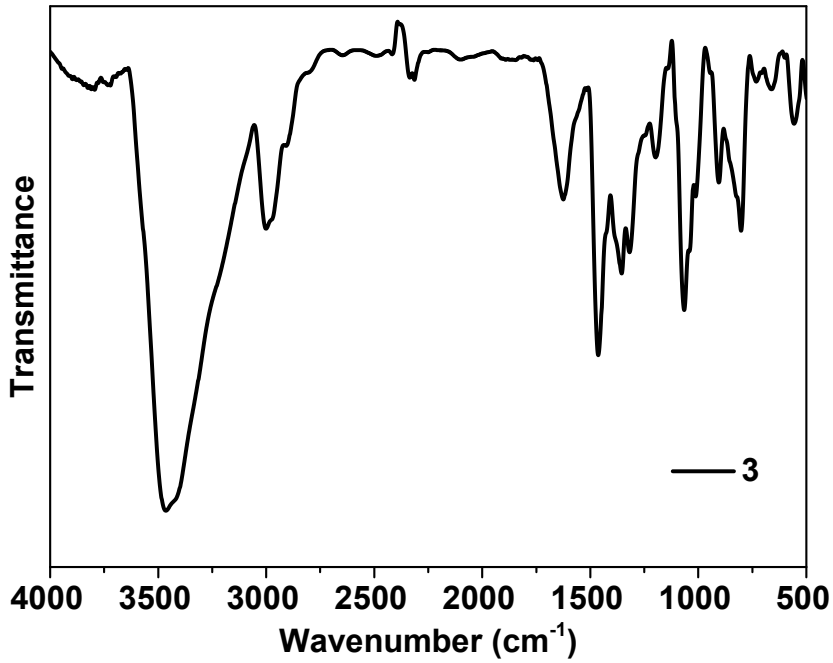



Figure S16. IR profile for **3**.

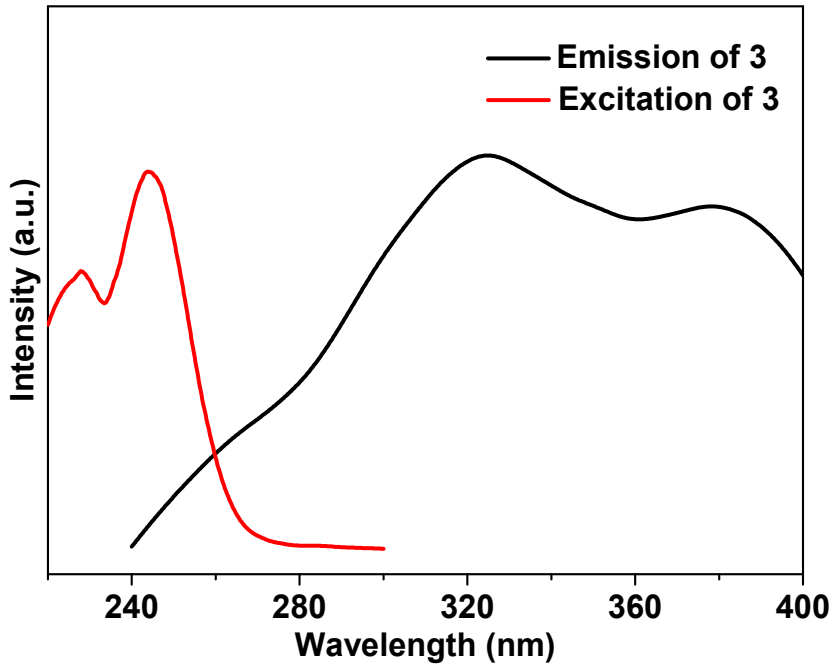



Figure S17. Fluorescent spectra for **3** in solid state at room temperature.

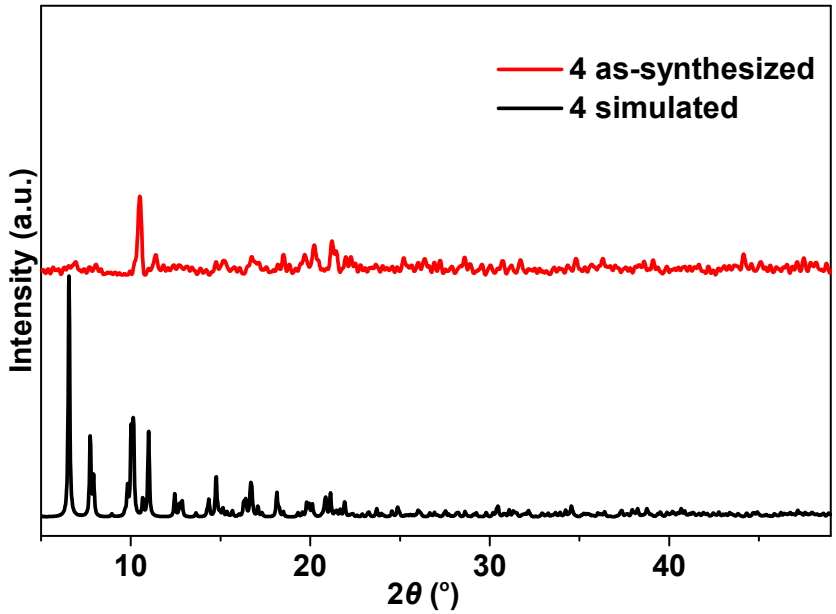



Figure S18. Powder XRD patterns for **4**. (The PXRD patterns for as-synthesized **4** did not match the simulated ones, probably because **4** were not stable in air.)

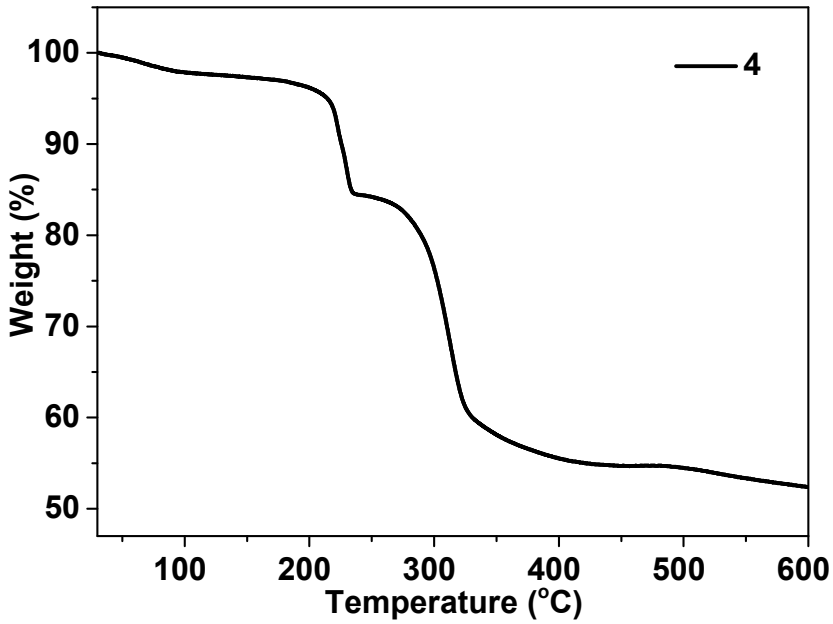



Figure S19. TG profile for **4**.

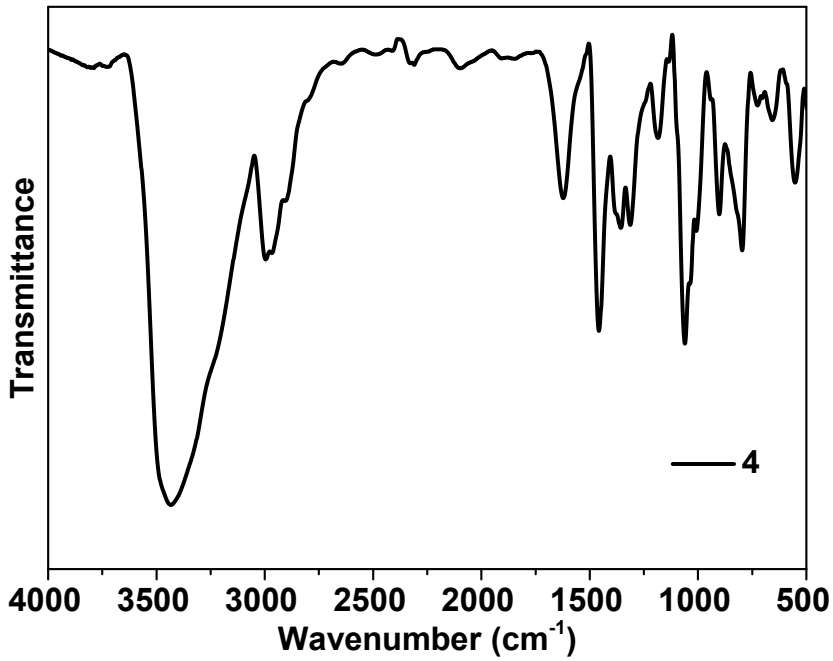



Figure S20. IR profile for **4**.

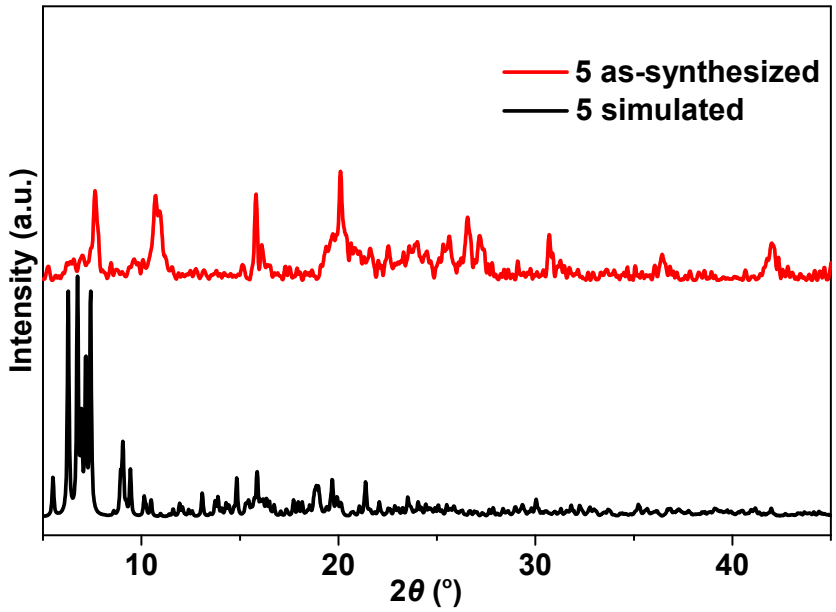



Figure S21. Powder XRD patterns for **5**. (The PXRD patterns for as-synthesized **5** did not match the simulated ones, probably because **5** were not stable in air.)

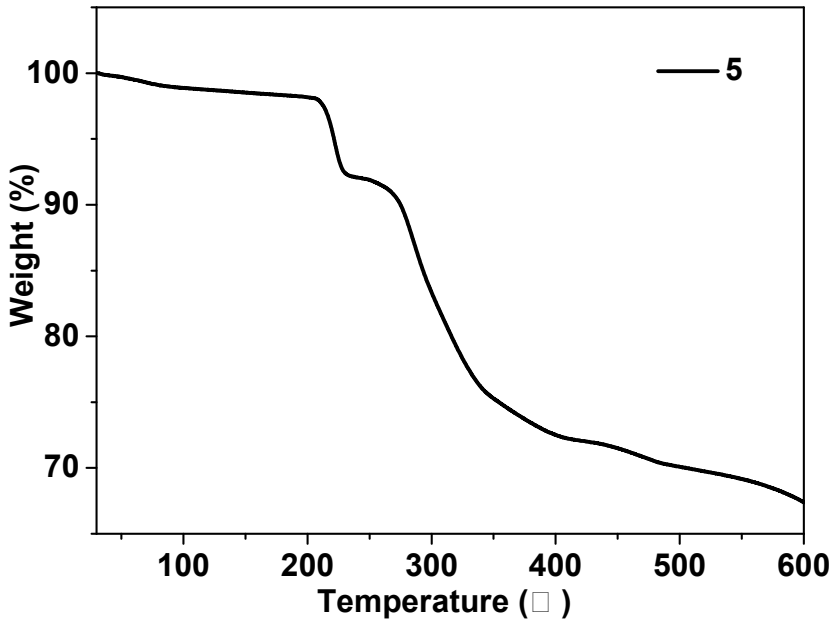



Figure S22. TG profile for **5**.

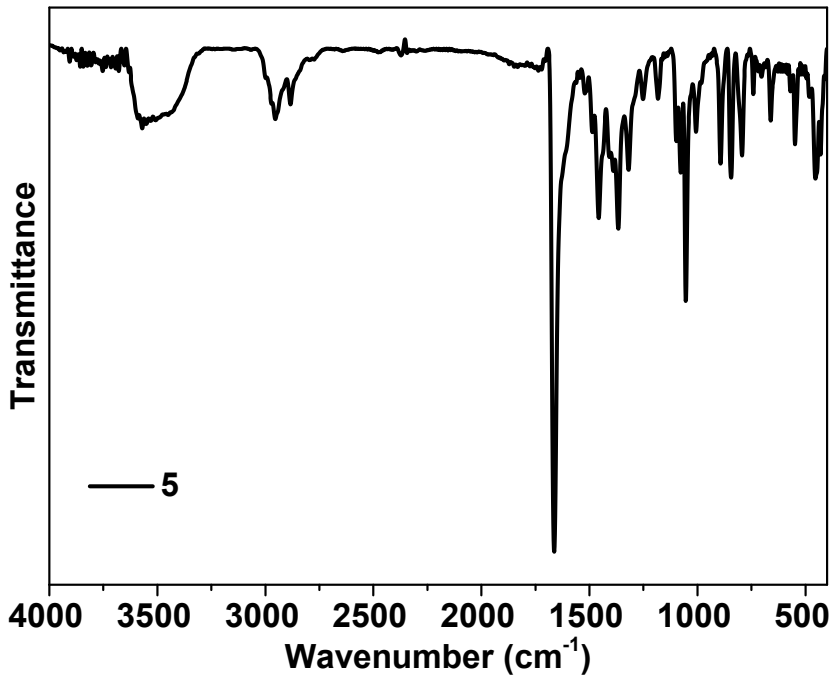



Figure S23. IR profile for **5**.

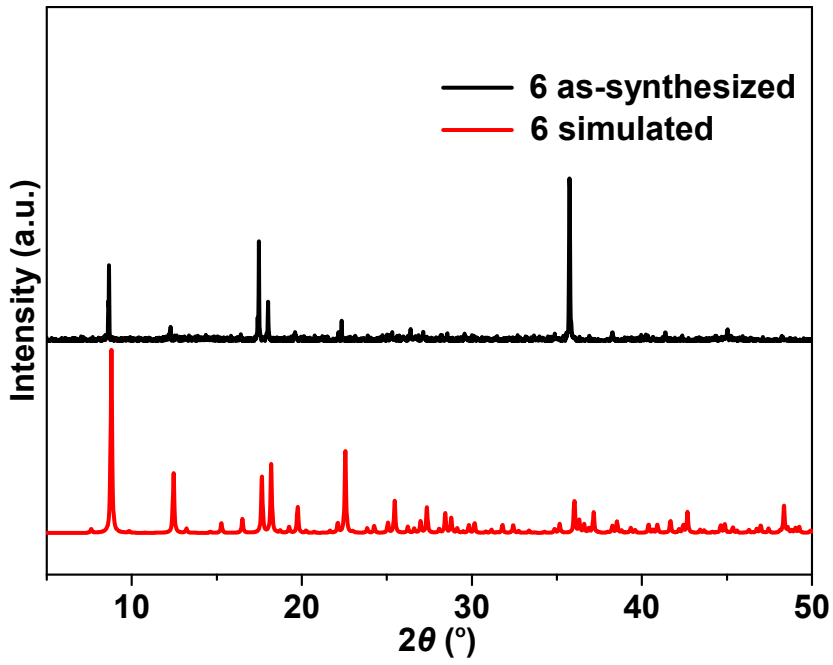



Figure S24. Powder XRD patterns for **6**.

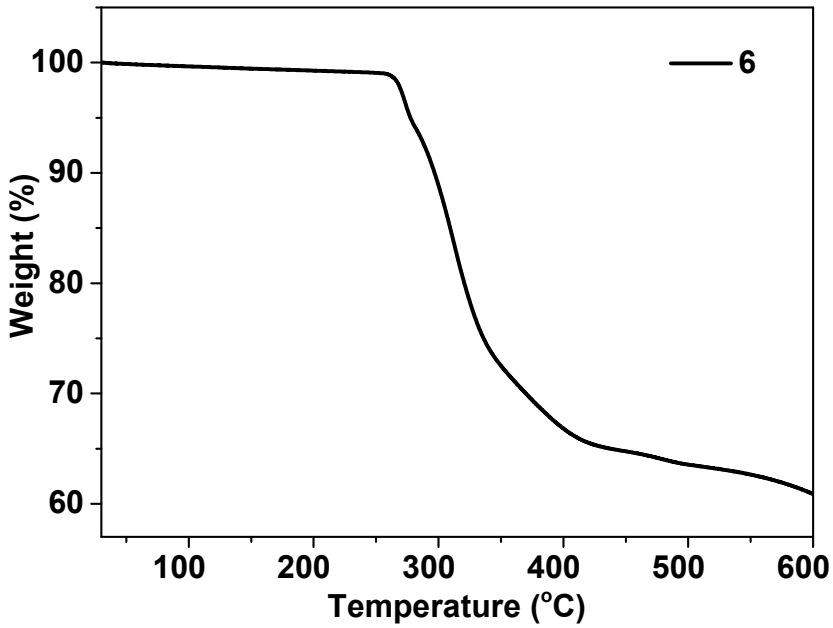


Figure S25. TG profile for **6**.

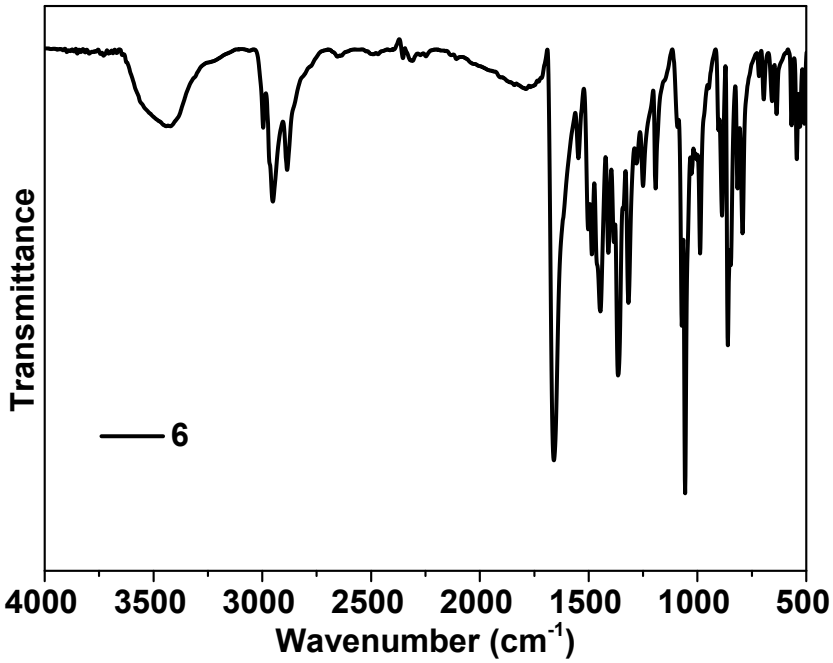


Figure S26. IR profile for **6**.

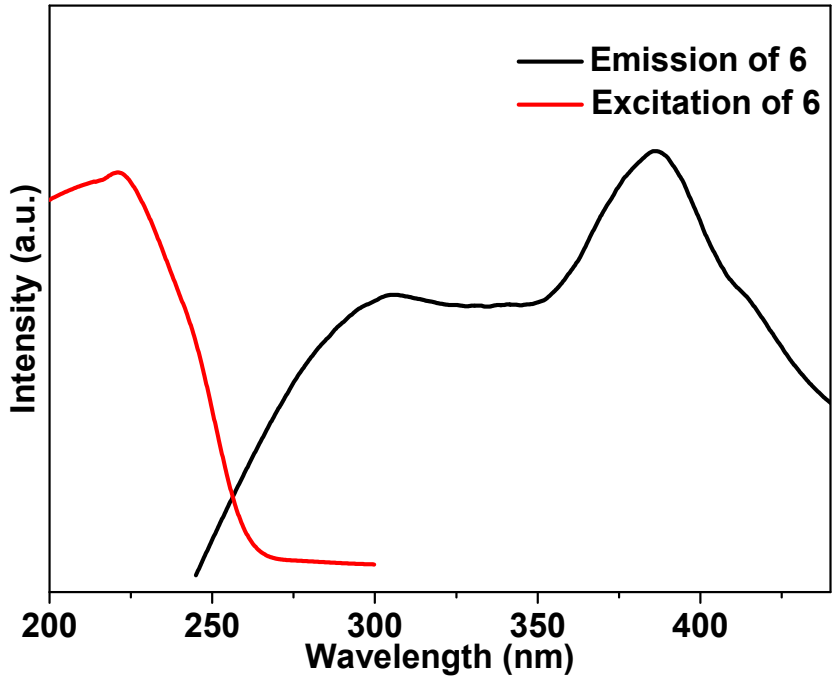



Figure S27. Fluorescent spectra for **6** in solid state at room temperature.

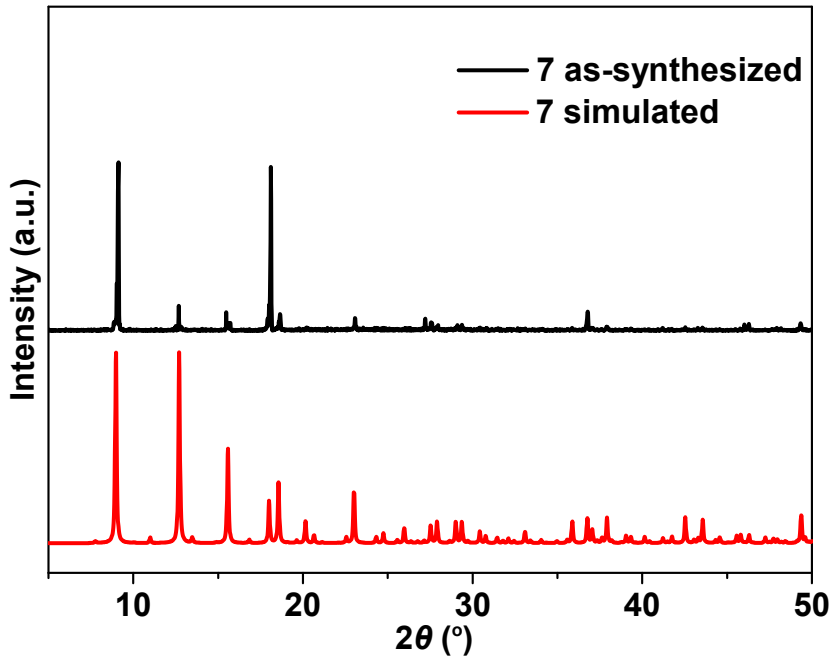



Figure S28. Powder XRD patterns for **7**.

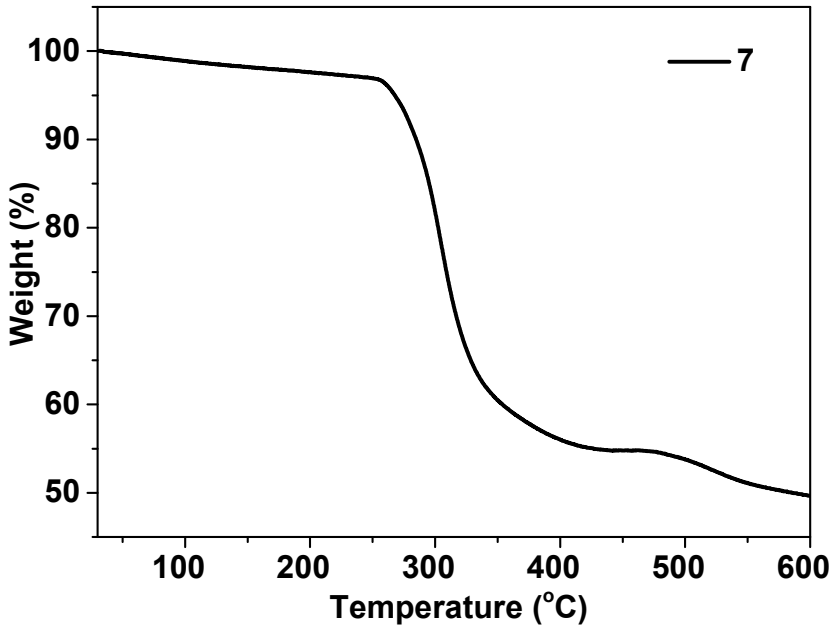


Figure S29. TG profile for **7**.

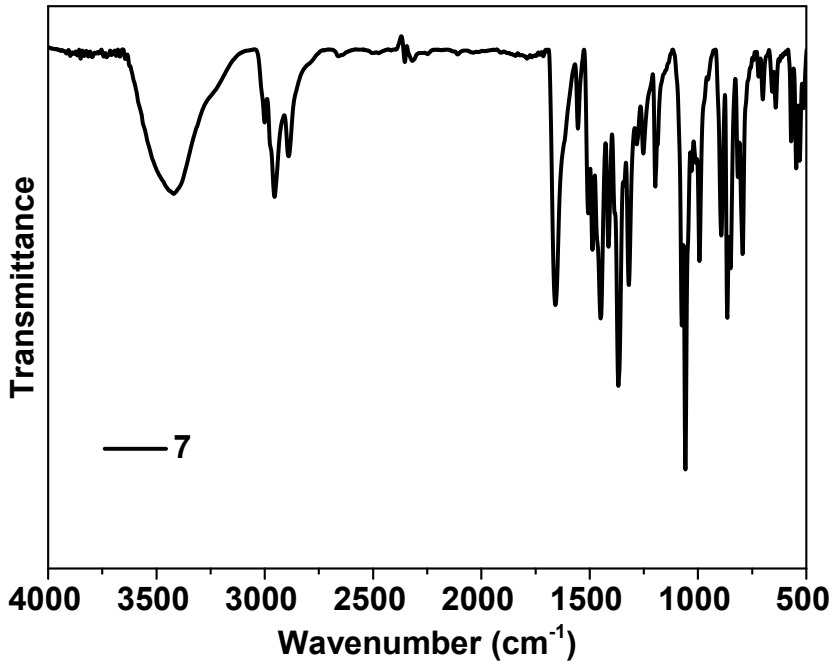


Figure S30. IR profile for **7**.

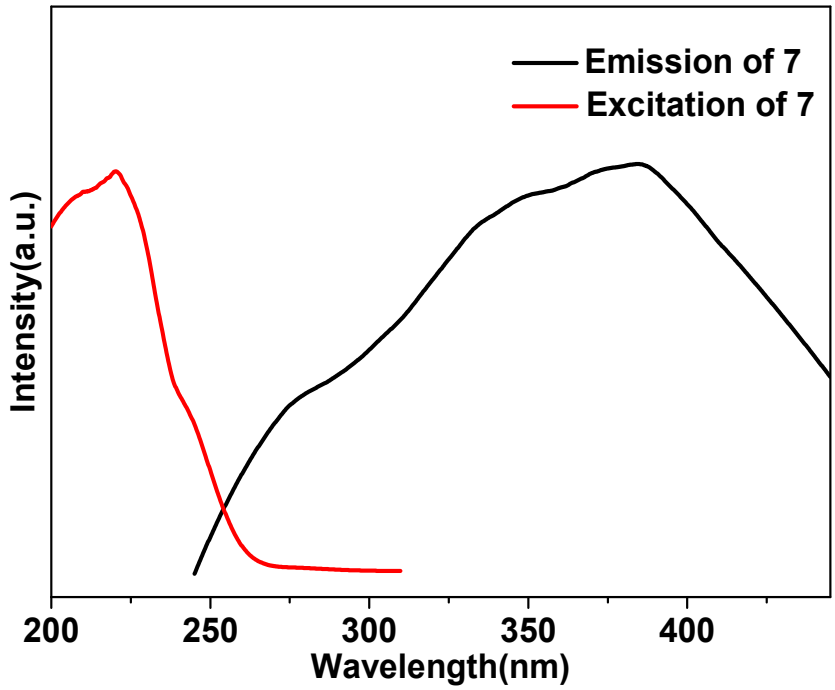



Figure S31. Fluorescent spectra for **7** in solid state at room temperature.

Table S1. Crystal data and structure refinement details for compounds **1** - **7**.

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{66}H_{42.82}Cu_4I_2N_{12}S_4W$ | $C_{49}H_{49}Cu_4I_2N_{11}O_3S_4W$ | $C_{66}H_{125}Br_2Cl_8Cu_8N_{12}O_6S_{14}W_2$ |
| Molecular weight | 1823.99 | 1660.04 | 2951.05 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | *C*2/*c* | $P2_1/n$ | $P2_1$ |
| a (Å) | 45.2038(8) | 13.5150(4) | 11.3261(7) |
| b(Å) | 19.0461(3) | 17.6465(7) | 13.5698(8) |
| c(Å) | 28.9481(5) | 28.1103(9) | 33.110(2) |
| α (°) | 90 | 90 | 90 |
| β (°) | 114.7000(10) | 93.475(2) | 90.112(3) |
| γ (°) | 90 | 90 | 90 |
| V ($Å^3$) | 22642.8(7) | 6691.8(4) | 5088.7(5) |
| Z | 8 | 4 | 2 |
| F(000) | 7063 | 3216 | 2926 |
| $\mu$ ($mm^{-1}$) | 7.861 | 13.253 | 11.766 |
| $D_c$ ($g/cm^3$) | 1.070 | 1.648 | 1.926 |
| R(int) | 0.0706 | 0.0665 | 0.0450 |
| GOF on $F^2$ | 1.060 | 1.049 | 1.052 |
| $R_1$ | 0.0479 | 0.0497 | 0.0467 |
| $wR_2$ | 0.1389 | 0.1370 | 0.1346 |

| | **4** | **5** | **6** | **7** |
|---|---|---|---|---|
| Formula | $C_{31}H_{57}C_{l5}Cu_4N_6O_2S_6W$ | $C_{54}H_{90}Cu_{10}I_{12}Mo_2N_{12}S_8$ | $C_{30}H_{51}Cu_3I_4N_6S_4W$ | $C_{30}H_{51}BrCl_3Cu_3N_6S_4W$ |
| Molecular weight | 1353.44 | 3513.93 | 1506.07 | 1184.73 |
| Crystal system | Orthorhombic | Triclinic | Cubic | Cubic |
| Space group | $P2_12_12_1$ | $P1$ | $Pa3$ | $Pa3$ |
| a (Å) | 11.3271(5) | 11.8390(7) | 20.0824(3) | 19.6933(3) |
| b(Å) | 13.5211(6) | 13.8931(8) | 20.0824(3) | 19.6933(3) |
| c(Å) | 33.2108(16) | 21.9722(14) | 20.0824(3) | 19.6933(3) |
| α (°) | 90 | 82.885(4) | 90 | 90 |
| β (°) | 90 | 77.181(4) | 90 | 90 |
| γ (°) | 90 | 89.955(3) | 90 | 90 |
| V (Å$^3$) | 5086.4(4) | 3495.5(4) | 8099.3(4) | 7637.6(3) |
| Z | 4 | 1 | 8 | 8 |
| F(000) | 2688 | 1636 | 5680 | 4672 |
| $\mu$ (mm$^{-1}$) | 10.905 | 25.148 | 7.673 | 6.159 |
| $D_c$ (g/cm$^3$) | 1.767 | 1.669 | 2.470 | 2.061 |
| R(int) | 0.0607 | | 0.0654 | 0.0898 |
| GOF | 1.059 | 0.976 | 1.063 | 0.912 |
| $R_1$[a] | 0.0636 | 0.0902 | 0.0311 | 0.0612 |
| $wR_2$[b] | 0.1468 | 0.2442 | 0.0958 | 0.1989 |

## Reference


1 C.-Q. Qiu, L.-Q. Li, S.-L. Yao, S.-J. Liu, H. Xu and T.-F Zheng, *Polyhedron*, 2021, **199**, 115100.

2 A. Peuronen, A. I. Taponen, E. Kalenius, A. Lehtonen and M. Lahtinen, *Angew. Chem.-Int. Ed.*, 2023, **135**, e202215689.