Supporting Information

Controllable synthesis of microporous, nanotubular and mesocage-like metal–organic frameworks by adjusting the reactant ratio and modulated luminescence properties of Alq3@MOF composites

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Physical measurements: The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7 analyzer under nitrogen atmosphere with a heating rate of 5 °C min^{-1}, room temperature to 800 °C. X-ray powder patterns were measured with a Siemens D5005 diffractometer with Cu KR (λ = 1.5418 Å) radiation in the range of 3–50°. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. The emission spectra were recorded on the F-7000 FL spectrophotometer equipped with a xenon lamp at room temperature. The excited-state lifetime were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photo counting technique. The N_2 sorption measurements were performed on an automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the sample was immersed in dichloromethane for 24 h, and the extract was decanted. Fresh dichloromethane was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates. Before the measurement, the sample was activated by drying under a dynamic vacuum at room temperature overnight and was dried again by using the 'outgas' function of the surface area analyzer for 12 h at room temperature.

Single-crystal X-ray structure determination: Crystal data for **IFMC-6, IFMC-7 and IFMC-8** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied using multi-scan technique. Their structures were solved by direct method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program.[1] Because guest solvent molecules (DMA and CH_3OH) in the frameworks of **IFMC-6, IFMC-7** and **IFMC-8** were highly disordered, the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON[2] and the results were attached to the CIF file. Details for structural analysis were summarized in Table S1. CCDC 867609–867611 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Details for structural analysis of **IFMC-6**, **IFMC-7**, and **IFMC-8**

Compound	**IFMC-6**	**IFMC-7**	**IFMC-8**
Formula	$C_{17}H_{22}N_{14}O_2Zn$	$C_{131}H_{204}N_{90}O_{23}Zn_7$	$C_{22}H_{35}Cl_2N_{15}O_4Zn_2$
Formula weight	519.86	3865.43	775.29
Crystal system	Tetragonal	Trigonal	Hexagonal
Space group	$P4_2/mnm$	R-3	R-3c
a /Å	15.605(3)	29.667(4)	28.993(3)
b /Å	15.605(3)	29.667(4)	28.993(3)
c /Å	13.601(4)	22.161(6)	21.958(5)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	120.00	120.00
V/Å^3	3312.1(13)	16891(6)	15985(3)
Z	4	3	39
$D_{calcd.}$[g cm^{-3}]	1.043	1.140	1.450
μ/mm^{-1}	0.774	0.802	1.551
F(000)	1072	6042	7164
Observed reflection/unique	15841/1628	28890/6684	26637/3207
R_{int}	0.0839	0.1278	0.1107
Goodness-of-fit on F^2	0.957	1.168	0.889
R_1, wR_2 [I > 2σ(I)]	0.0483, 0.1278	0.1142, 0.3152	0.0398, 0.0950
R_1, wR_2 (all data)	0.0789, 0.1355	0.2007, 0.3782	0.0780, 0.0880

Table S2 A summary of the products isolated at different conditions

DMA/CH_3OH	Zn/L, 2:1	Zn/L, 3:1	Zn/L, 4:1	Zn/L, 5:1	Zn/L > 6:1
4:1, 5 mL	None	**IFMC-6**	**IFMC-7**	**IFMC-8**	Unknown
4:1, 10 mL	None	**IFMC-6**	**IFMC-7, IFMC-8**	Unknown	Unknown
1:1, 5 mL	None	Unknown	**IFMC-8**	**IFMC-8**	Unknown

Table S3 ICP for **Alq3@IFMC-8** obtained from saturated **Alq3** ethanol solution

Mass ratio of Al and Zn (experimental)	12.2 / 231.3
Mol ratio of Al and Zn (calculation)	1 / 7.9
Mass percentage of **Alq3** in **Alq3@IFMC-8** (*wt*%)	13.0 %

Table S4 Excited-state lifetime of **Alq3** and **Alq3@IFMC-8** in ethanol

Alq3	**IFMC-8**	τ_1 (nm)	α1 (%)	τ_2 (nm)	α2 (%)	Average life (nm)
2000 μmol/L	none	11.95	100.00	0	0	11.95
4 mL	30 mg	10.45	36.00	22.20	64.00	17.94
1000 μmol/L	none	9.52	72.96	15.72	27.04	11.86
4 mL	30 mg	8.48	27.02	22.40	72.98	20.68
500 μmol/L	none	9.66	76.38	18.30	23.62	12.85
4 mL	30 mg	5.29	28.85	22.75	71.15	21.25
200 μmol/L	none	10.01	82.54	23.00	17.46	14.26
4 mL	30 mg	2.74	33.57	17.79	66.43	19.68
100 μmol/L	none	10.18	79.22	23.95	20.78	15.54
4 mL	30 mg	2.48	22.65	21.36	77.35	20.73
50 μmol/L	none	8.57	53.00	24.38	47.00	19.82
4 mL	30 mg	2.15	23.02	26.55	76.98	25.97
	10 mg	2.35	12.34	17.74	87.66	17.46
500 μmol/L	30 mg	5.29	28.85	22.74	71.15	21.24
4 mL	60 mg	6.56	42.17	24.74	87.83	22.69
	90 mg	7.69	36.88	27.51	63.49	24.74
	10 mg	4.97	22.30	26.31	77.70	25.21
50 μmol/L	30 mg	2.15	23.00	26.55	77.00	25.97
4 mL	60 mg	8.39	16.00	31.85	84.00	30.73
	90 mg	11.00	18.00	33.3	82.00	31.79

IFMC-6:

$H_3BTT + ZnCl_2 \longrightarrow Zn(HBTT) + 2HCl$ 46%

IFMC-7:

$Zn^{2+} + 6DMA \longrightarrow [Zn(DMA)_6]^{2+} + 2Cl^-$

$6H_3BTT + 6ZnCl_2 + [Zn(DMA)_6]^{2+} \longrightarrow [Zn(DMA)_6][Zn_6H_4(BTT)_6] + 12HCl + 2H^+$ 25%

IFMC-8:

$H_3BTT + 2ZnCl_2 \longrightarrow [Zn_2(HBTT)Cl_2] + 2HCl$ 72%

Scheme S1 The rational reaction equations for three MOFs.

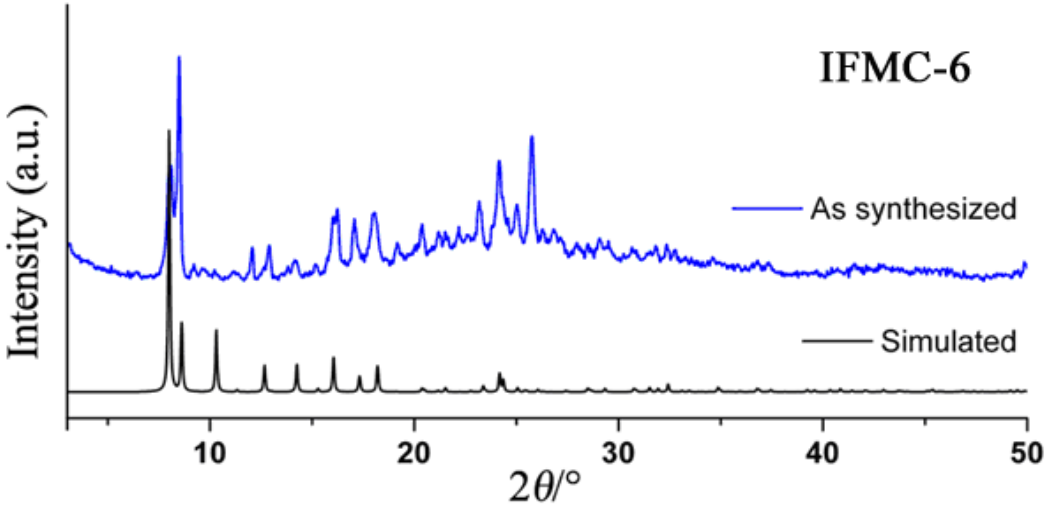

Fig. S1 PXRD patterns of **IFMC-6**.

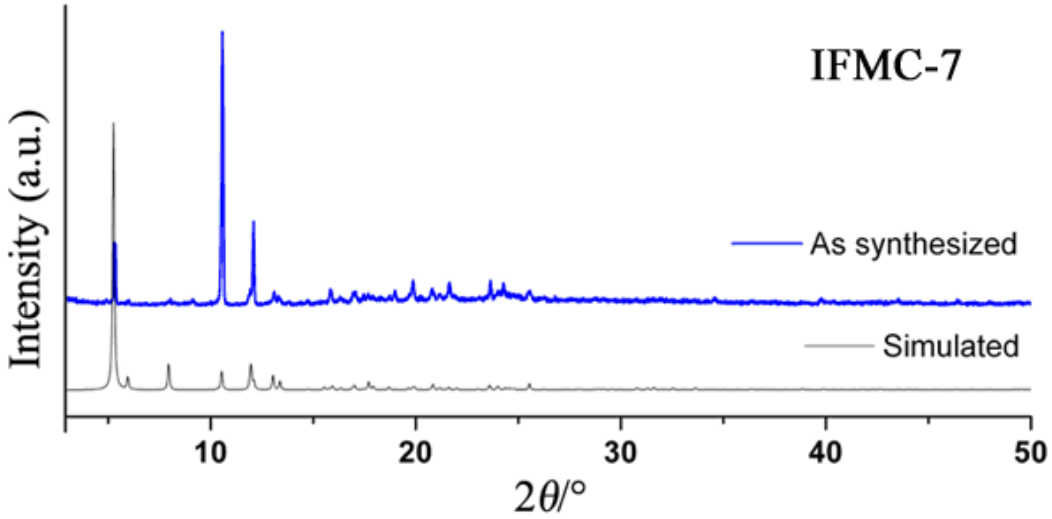

Fig. S2 PXRD patterns of **IFMC-7**.

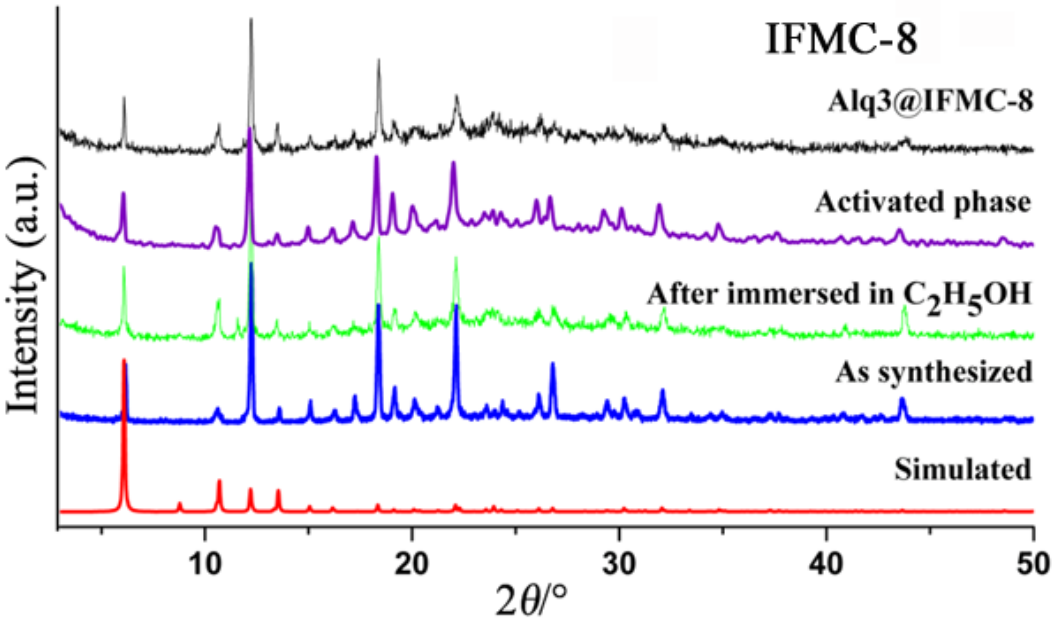

Fig. S3 PXRD patterns of **IFMC-8**.

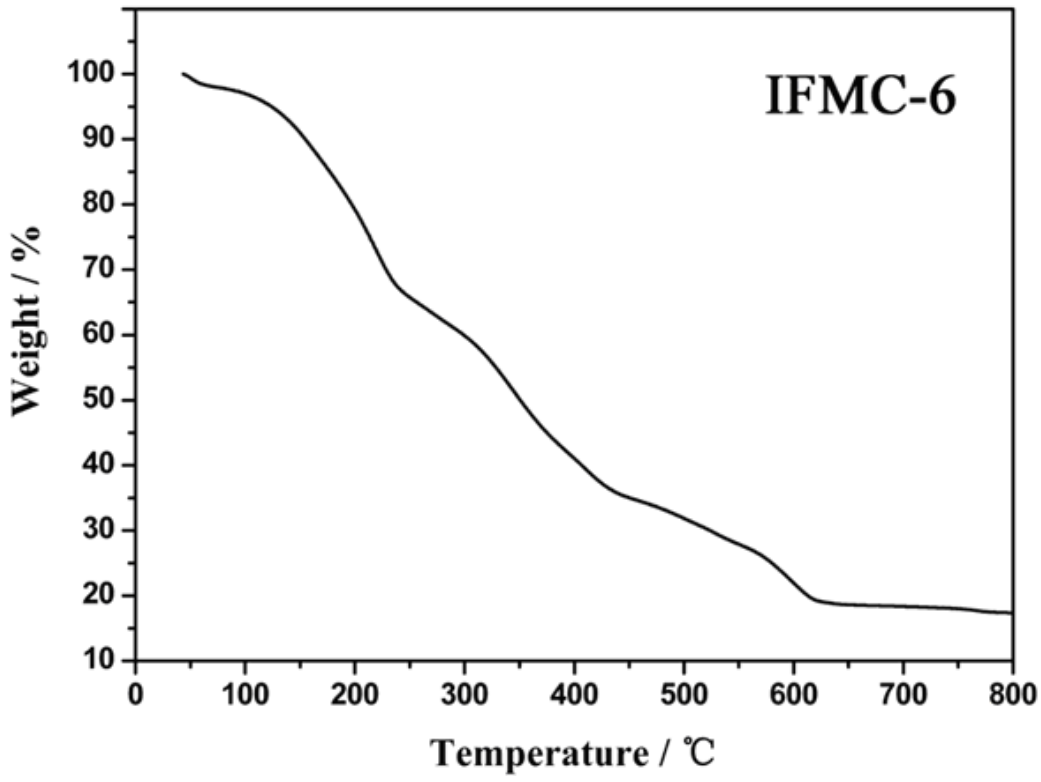

Fig. S4 TGA curve of **IFMC-6**.

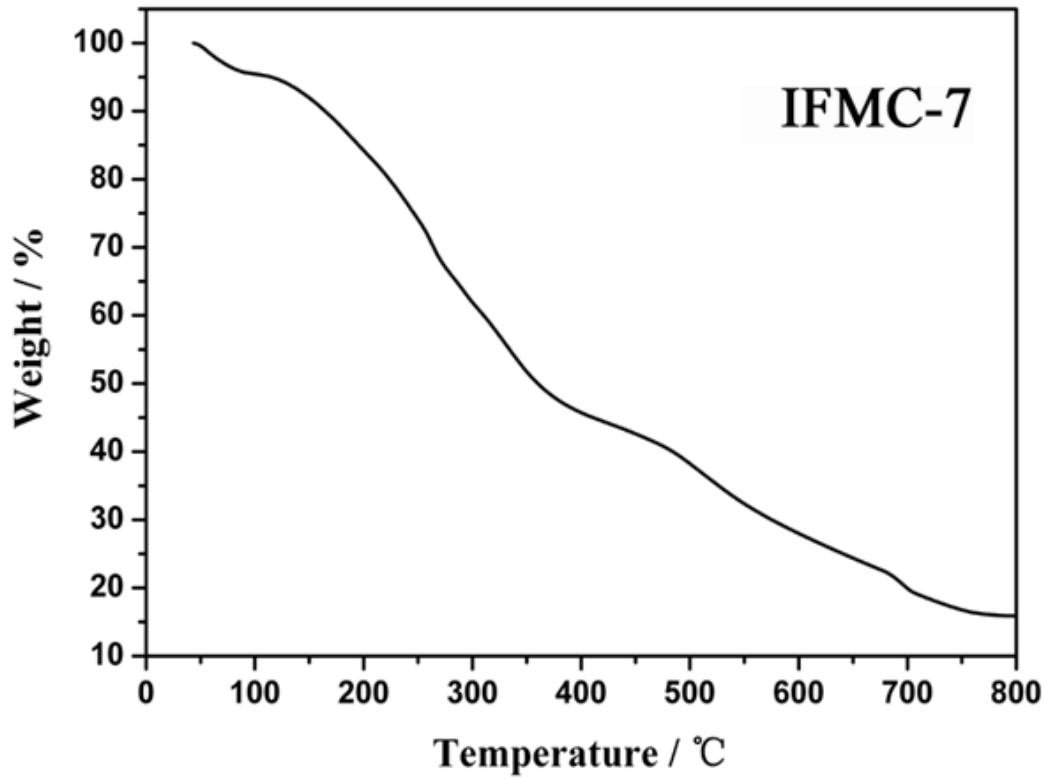

Fig. S5 TGA curve of **IFMC-7**.

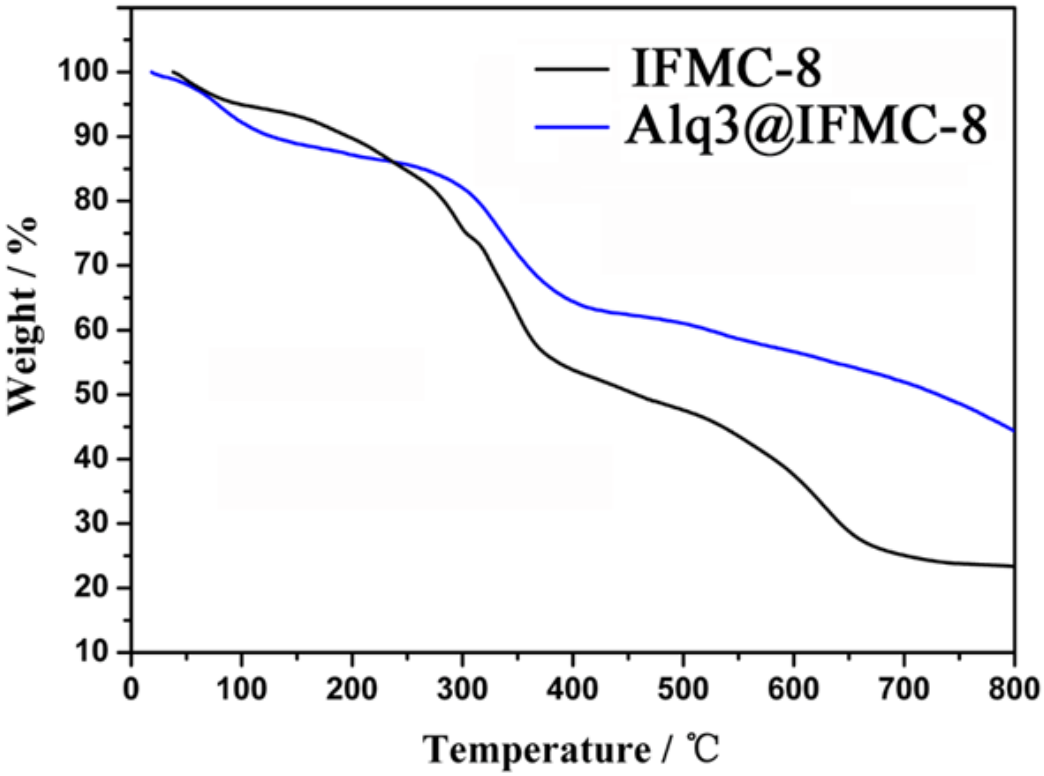

Fig. S6 TGA curves of **IFMC-8** and **Alq3@IFMC-8**.

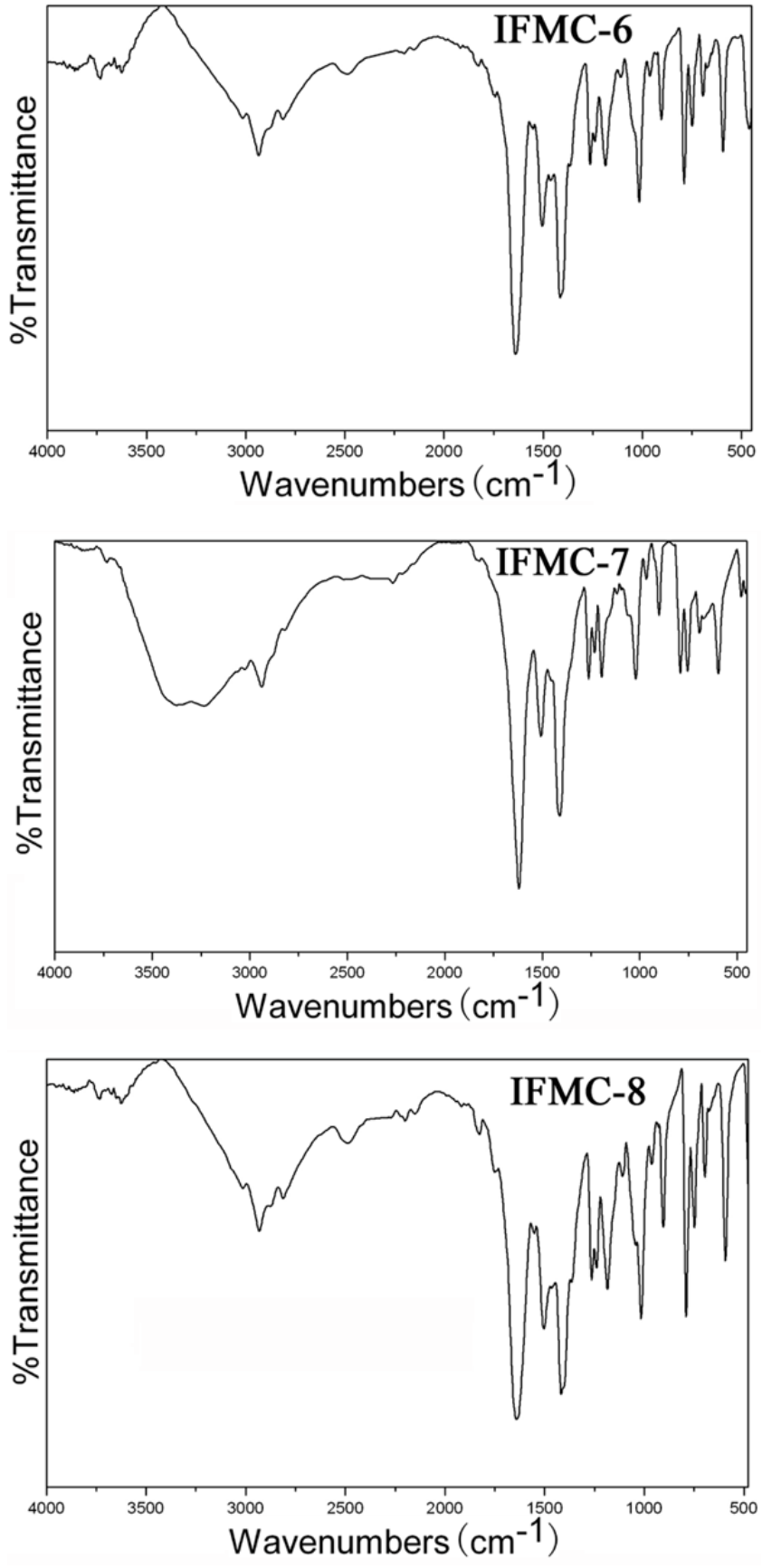

Fig. S7 IR data of **IFMC-6**, **IFMC-7** and **IFMC-8**.

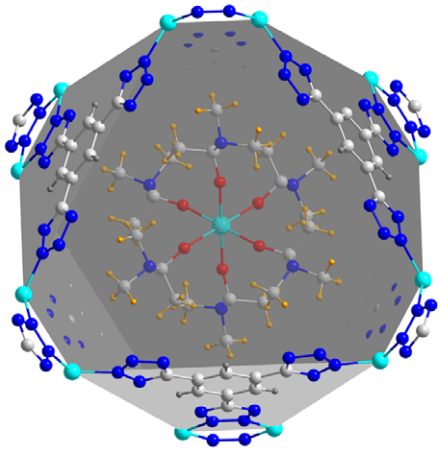

Fig. S8 Structural representation of the smaller octahedral cage encapsulating one $Zn(DMA)_6^{2+}$ macroation.

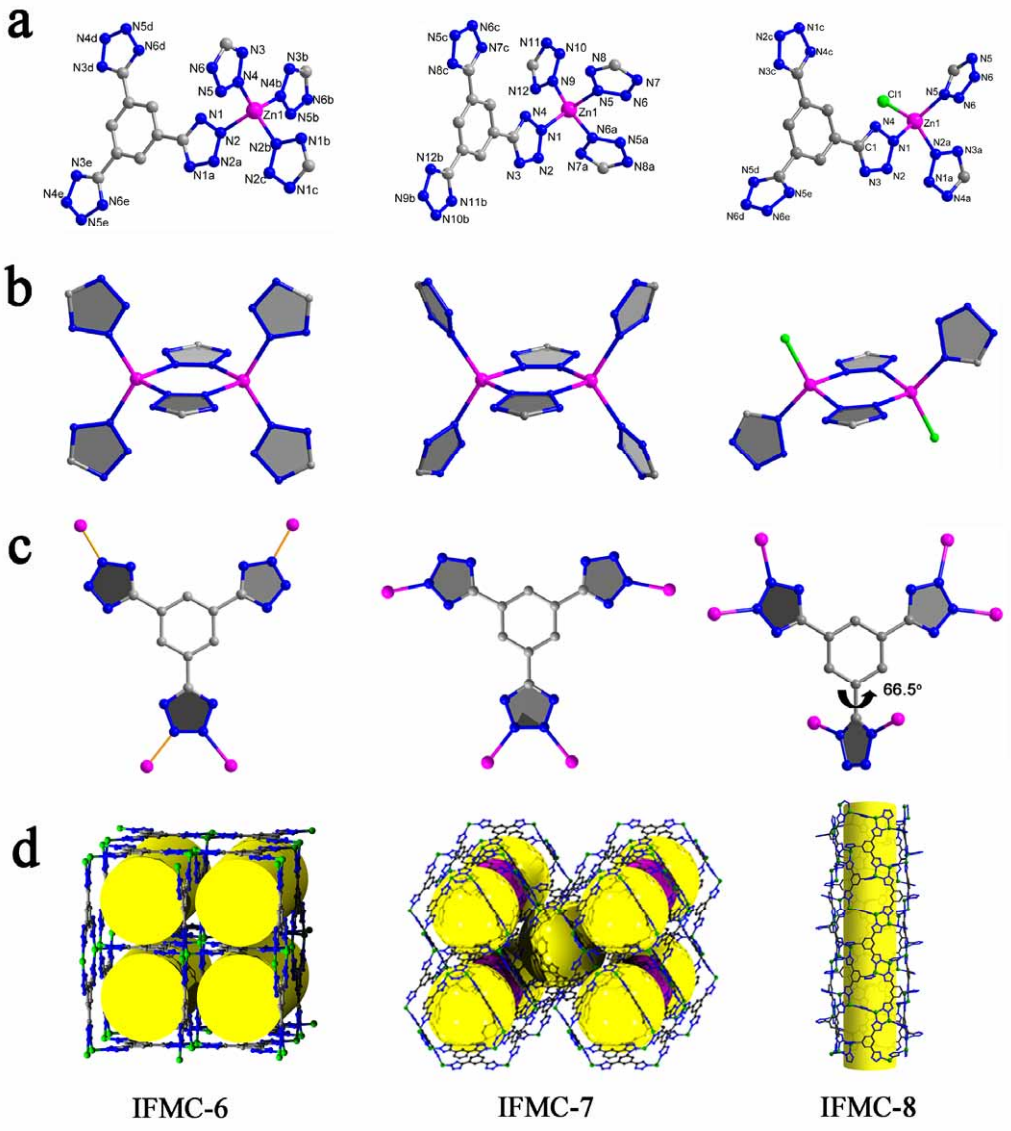

Fig. S9 Structural comparisons of **IFMC-6**, **IFMC-7** and **IFMC-8**: (a) coordination environment of zinc atoms; (b) analogous dinuclear zinc SBUs; (c) coordination mode of H_3BTT; (d) packing diagram.

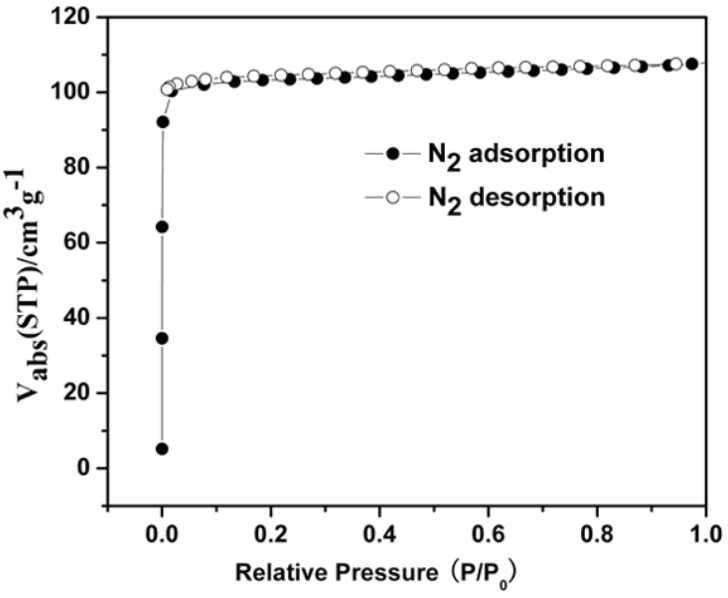

Fig. S10 Gas sorption isotherms of **IFMC-8** for N_2.

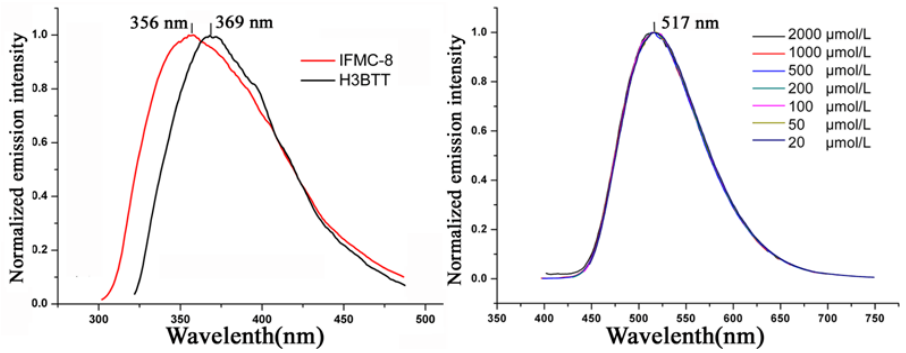

Fig. S11 Photoluminescence spectra of H_3BTT and **IMFC-8** in ethanol solution (Ex = 260 nm) (left); Photoluminescence spectra of **Alq3** in ethanol solution (Ex = 345 nm) (rignt).

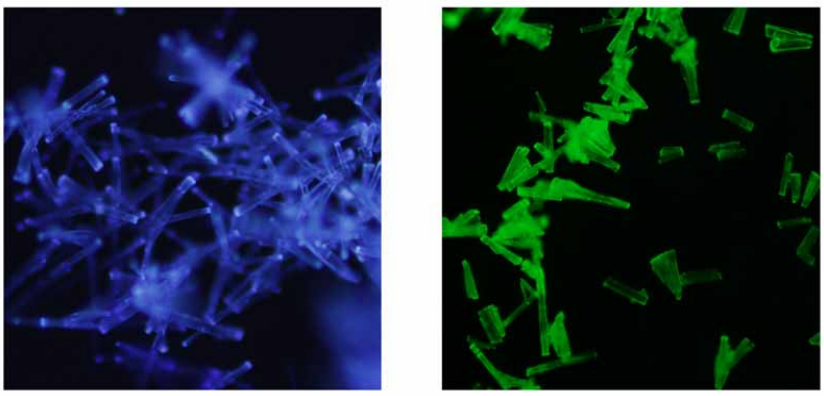

Fig. S12 Fluorescence Images of **IFMC-8** before (Ex = 256 nm) and after (Ex = 365 nm) introduction into **Alq3** solution.

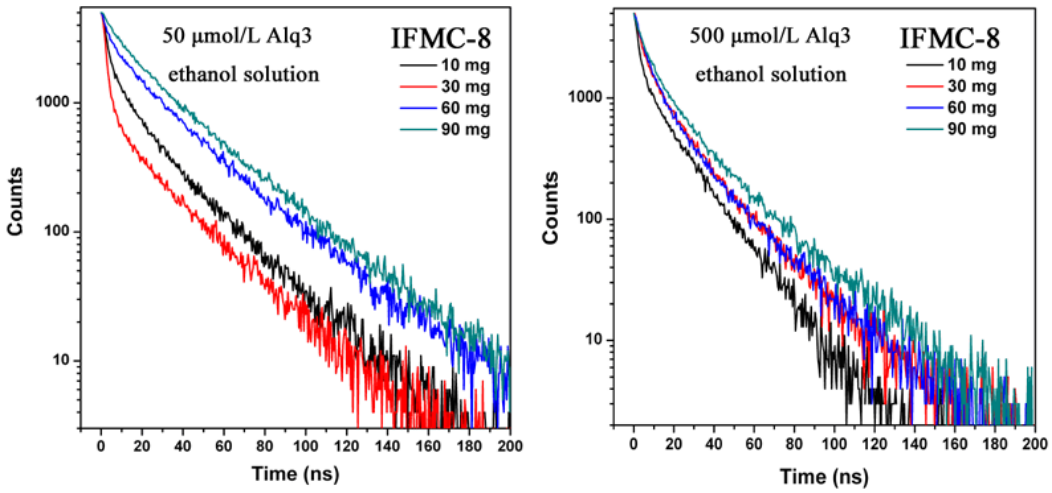

Fig. S13 Excited-state lifetime of different amount of **IFMC-8** dispersed in 50 asnd 500 μmol/L **Alq3** ethanol solution.

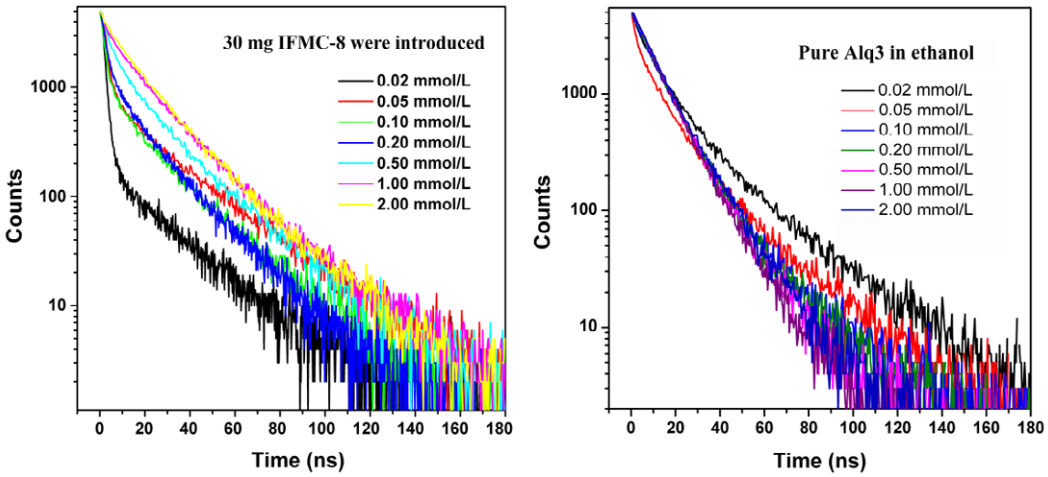

Fig. S14 Excited-state lifetime of fixed amount of **IFMC-8** dispersed in varying concentration of **Alq3** ethanol solution (left); Excited-state lifetime of pure **Alq3** ethanol solution with different concentrations (right).

References

1 G. M. Sheldrick, *SHELXL-97, Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

2 (*a*) P. van der Sluis and A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194; (*b*) A. L. Spek, *PLATON, A multipurpose crystallographic tool*, Utrecht. University, The Netherlands, 2001.