Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Functional heterometallic coordination polymers with metalloligand as tunable luminescent crystalline materials

Dong-Ying Du,[a] Jun-Sheng Qin,[a] Cheng-Xin Sun,[b] Xin-Long Wang,*[a] Shu-Ran Zhang,[a] Ping Shen,[a] Shun-Li Li,[a] Zhong-Min Su*[a] and Ya-Qian Lan*[a]

[a] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China. Fax: (+86) 431-85684009. E-mail: zmsu@nenu.edu.cn; lanyq176@nenu.edu.cn.

[b] School of Life Sciences, Northeast Normal University, Changchun 130024, P. R. China

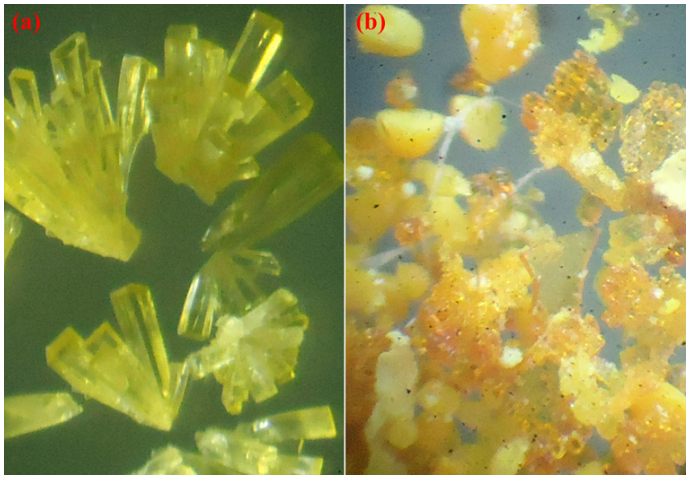


Fig. S1 The images of (a) **IFMC-23** and (b) no addition of BMIB.

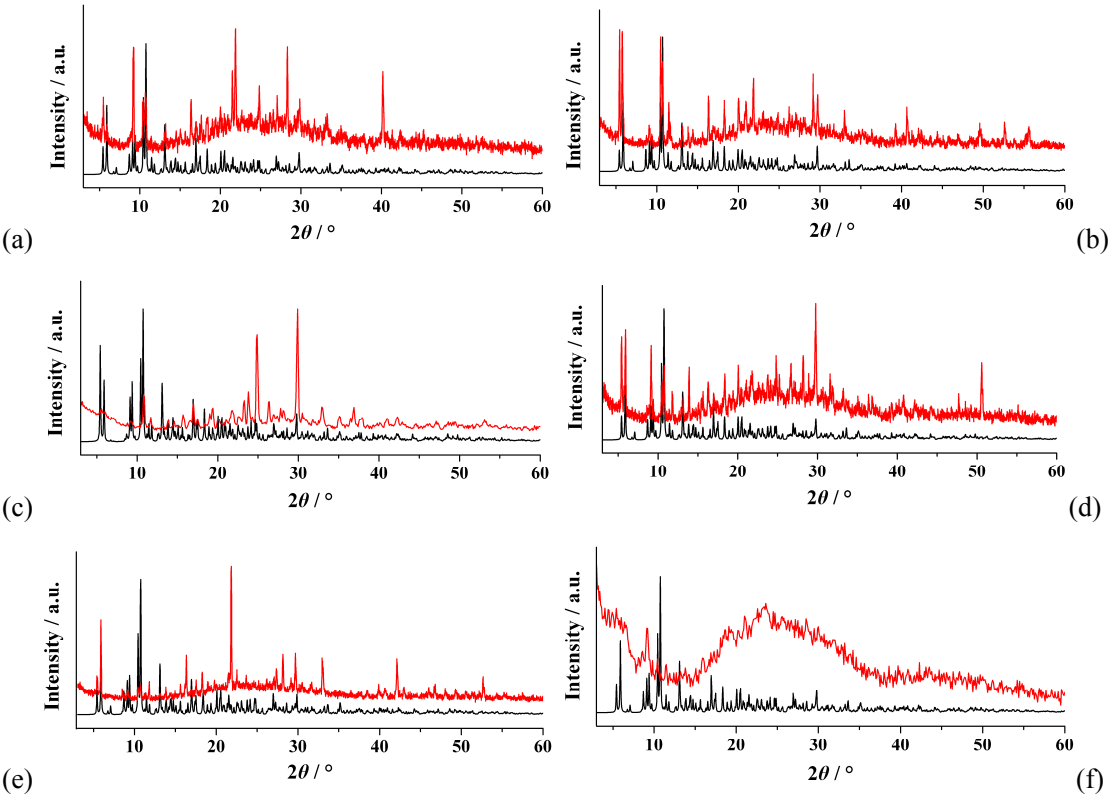


Fig. S2 XRPD patterns (top, red) and simulated patterns (bottom, black) for (a) – (e) **IFMC-21** to **25** and (f) no addition of BMIB, respectively.

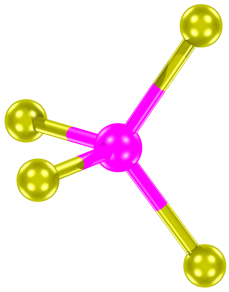


Fig. S3 $[ZnBr_4]^{2-}$ unit in **IFMC-21**.

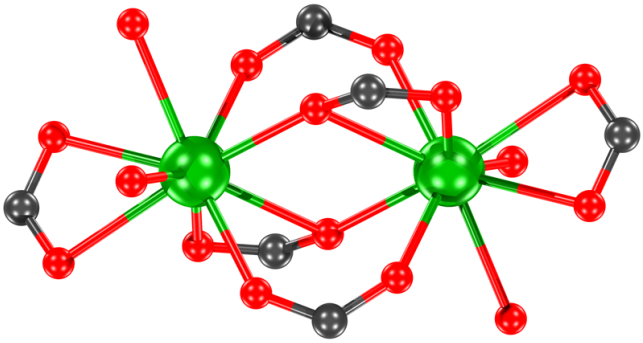


Fig. S4 The coordination mode of the bimetallic unit $[Eu_2(COO)_2(COO)_4(H_2O)_4]$ in **IFMC-21**.

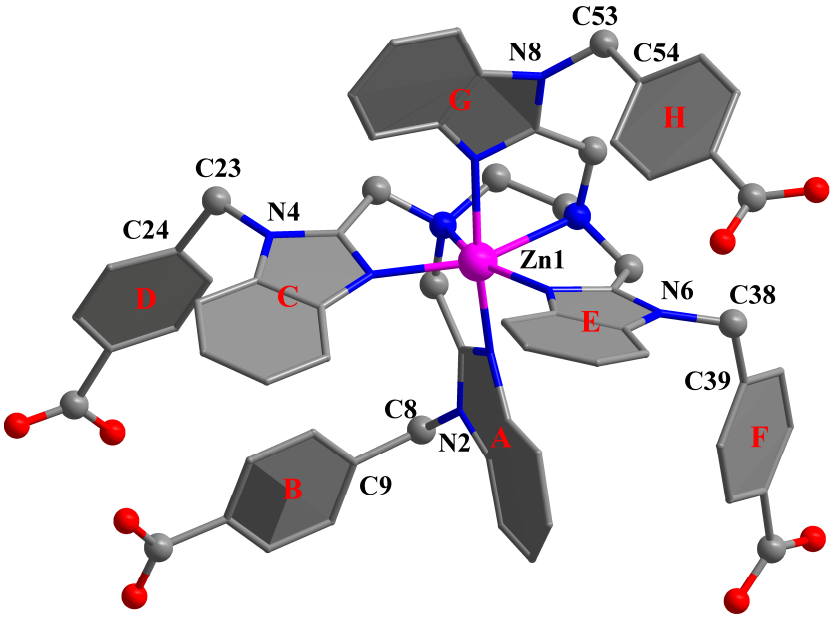
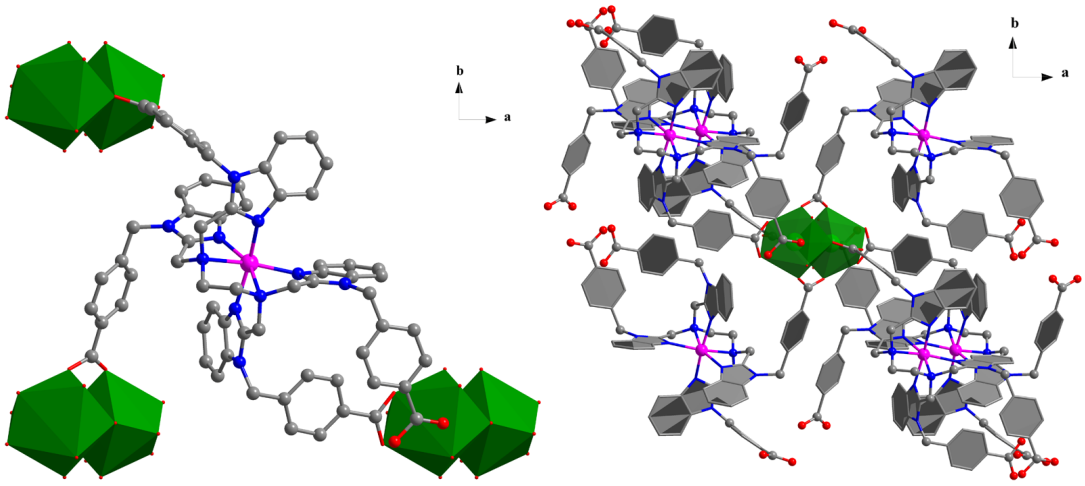


Fig. S5 The binding mode of the carboxylate ligand to Zn(II) ion in **IFMC-21**.



(a) (b)

Fig. S6 (a) The carboxylate ligand acts as three-connected node and (b) bimetallic unit works as six-connected node in **IFMC-21**, respectively.

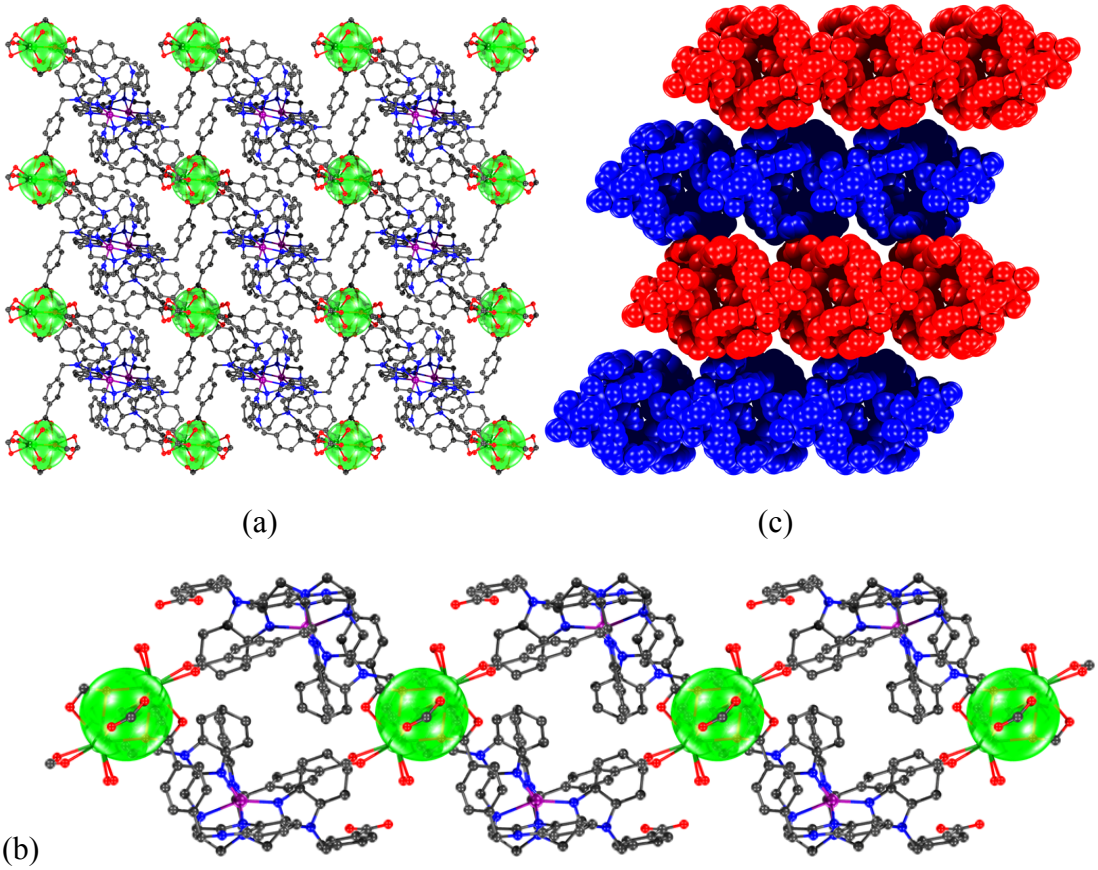


Fig. S7 (a) and (b) Ball-and-stick representations of the 2D sheet-like structure of **IFMC-21**. (c) Spacefill representation of 3D supramolecular structure of **IFMC-21**.

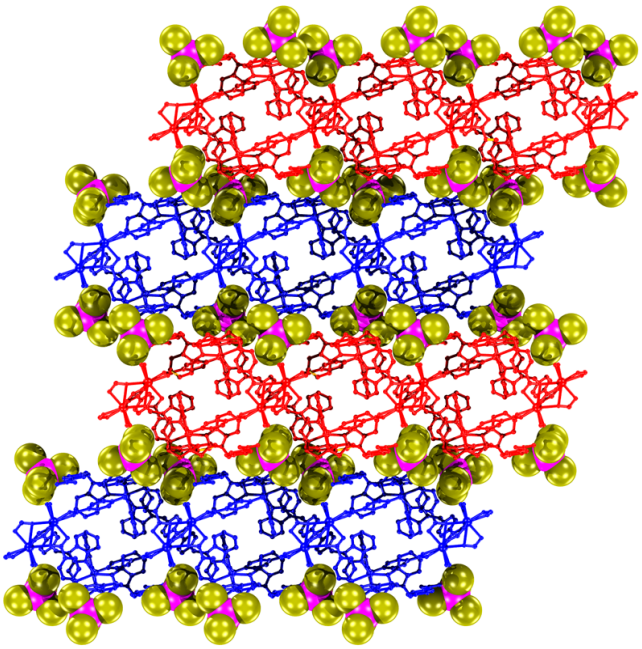


Fig. S8 The packing arrangement of **IFMC-21** in the *ac* plane, with isolated $[ZnBr_4]^{2-}$ located in the interspaces of the 2D sheet-like structure.

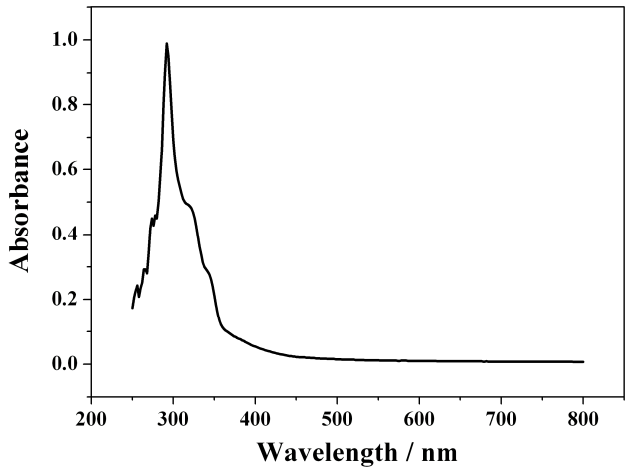


Fig. S9 The UV absorption spectrum of ligand H_4L.

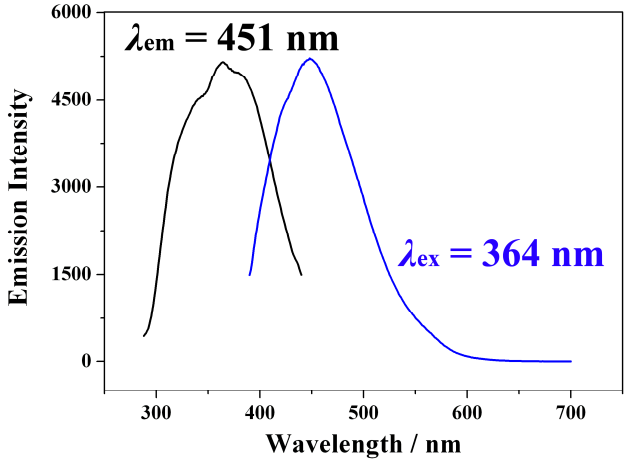


Fig. S10 Excitation and emission spectra of H_4L in the solid state at room temperature.

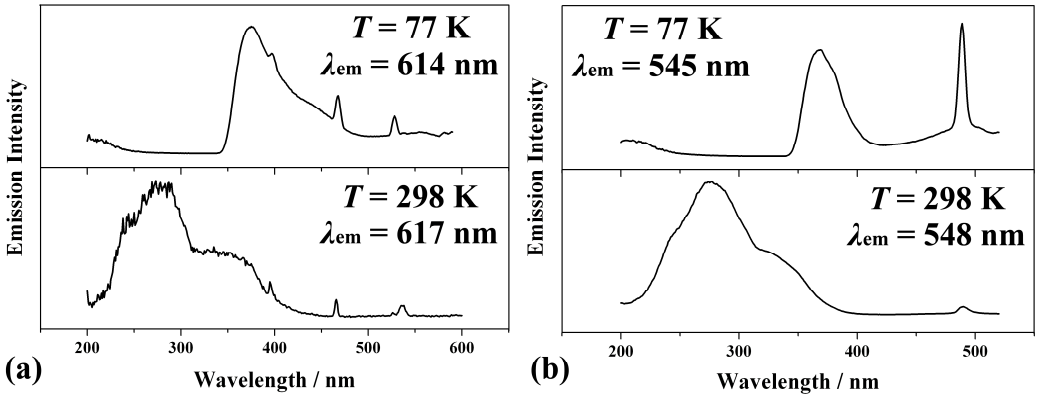


Fig. S11 Excitation spectra of **IFMC-21** (a) and **IFMC-25** (b) in the solid state, respectively.

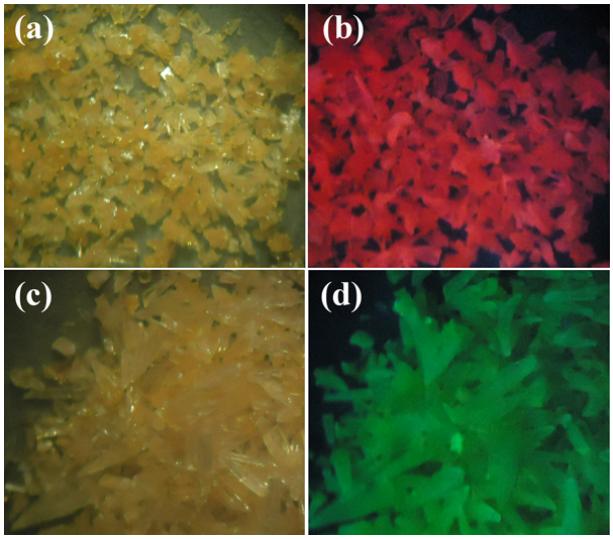


Fig. S12 The photographs of **IFMC-21** ((a) and (b)) and **IFMC-25** ((c) and (d)). (a) and (c): under natural light; (b) and (d): under a UV lamp.

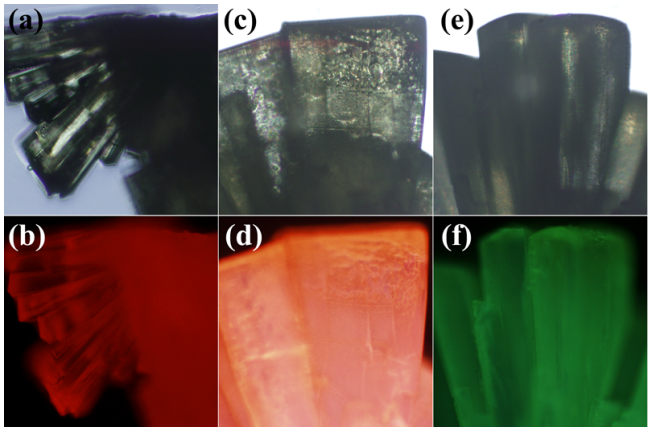


Fig. S13 Fluorescence camera images of **IFMC-21** (a, b), **IFMC-23** (c, d) and **IFMC-25** (e, f) under different light sources (a, c and e: under natural light; b, d and f: under UV light).

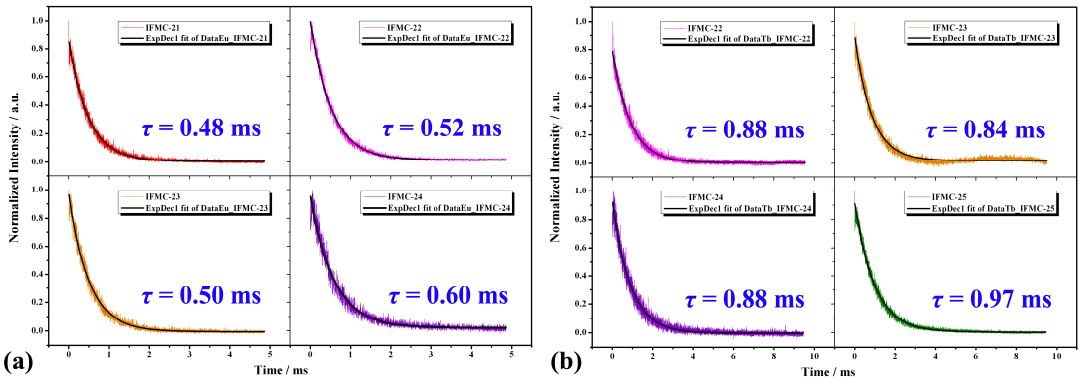


Fig. S14 Solid state fluorescence decay curves of **IFMC-21** – **25** (Monitor wavelengths: a, 617 nm and b, 545 nm).

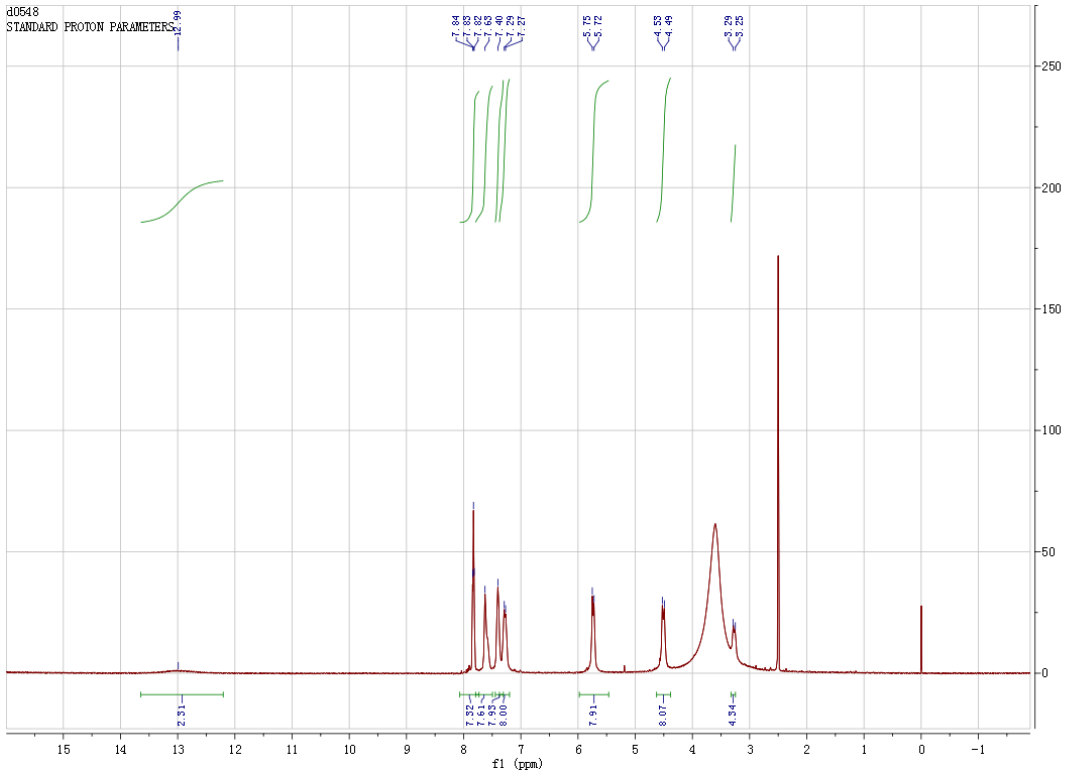
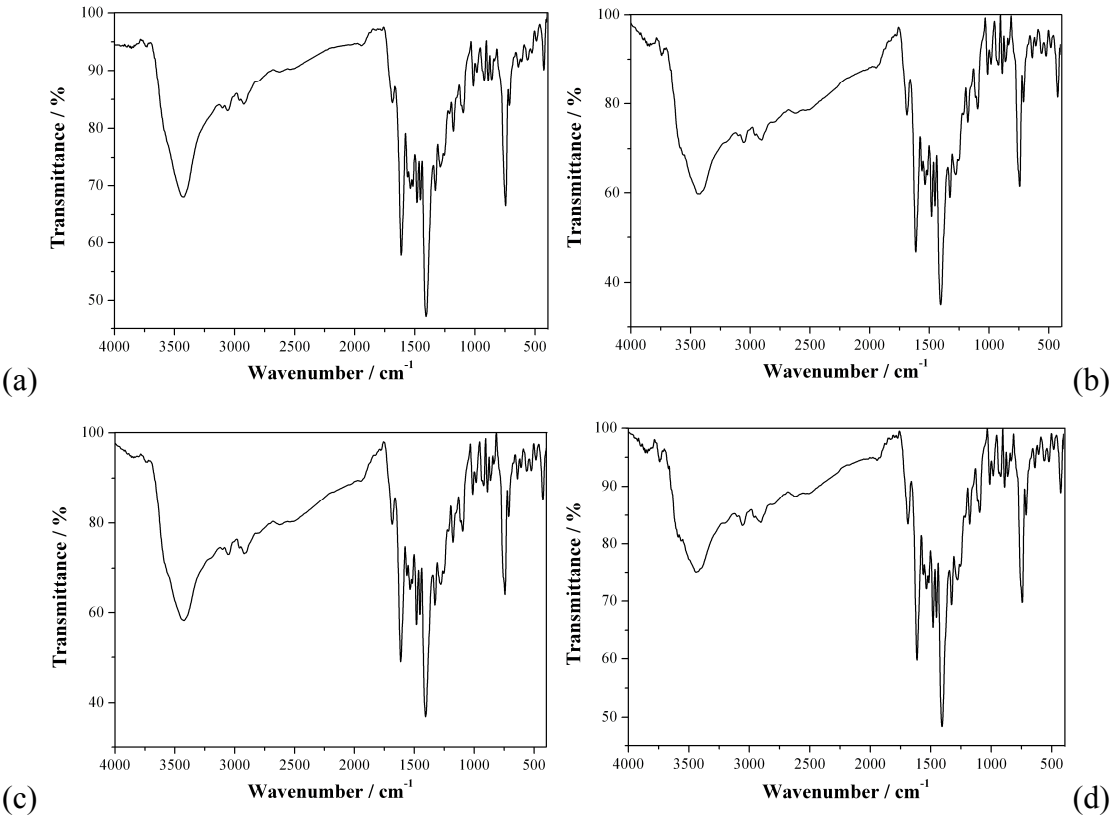
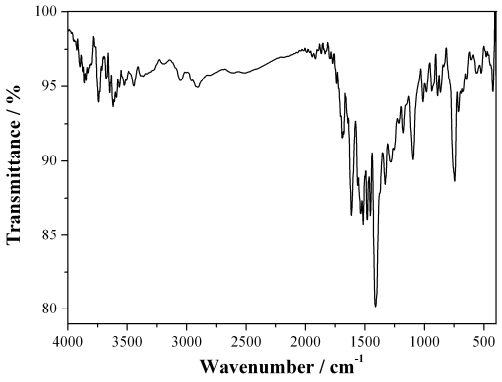


Fig. S15 The ^{1}H NMR spectrum of H_4L: ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm) 12.99 (s, 4H), 7.83 (t, J = 6.8, 8H), 7.63 (s, 8H), 7.40 (s, 8H), 7.28 (d, J = 11.4, 8H), 5.73 (d, J = 15.6, 8H), 4.51 (d, J = 17.7, 8H), 3.27 (d, J = 20.1, 4H).





(e)

Fig. S16 IR curves for **IFMC-21** to **25**.

Table S1. Crystal data and structure refinements for **IFMC-21** to **25**

	IFMC-21	**IFMC-22**	**IFMC-23**
Empirical formula	$C_{66}H_{59}N_{10}O_{11}Br_4Zn_2Eu$	$C_{66}H_{59}N_{10}O_{11}Br_4Zn_2Eu_{0.75}Tb_{0.25}$	$C_{66}H_{59}N_{10}O_{11}Br_4Zn_2Eu_{0.5}Tb_{0.5}$
*M*w	1770.57	1772.31	1774.05
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	15.6650(10)	15.7550(12)	15.6800(9)
b (Å)	13.5120(8)	13.5370(10)	13.5150(8)
c (Å)	33.082(2)	33.101(3)	33.051(2)
β (deg)	99.9330(10)	99.7820(10)	99.786(8)
V (Å^3)	6897.4(7)	6957.0(9)	6902.1(7)
Z	4	4	4
D_c (Mg·m^{-3})	1.705	1.692	1.707
Abs.coeff. (mm^{-1})	3.971	3.965	4.026
F(000)	3504	3506	3508
reflns collected	34093	41097	39658
Independent reflns	12212	15842	15047
θ range (deg)	1.25 – 25.08	1.25 – 27.73	1.55 – 27.06
GOF on F^2	1.044	0.989	1.044
R_{int}	0.0556	0.0478	0.0477
R_1[a]	0.0545	0.0601	0.0517
wR_2 (all data)[b]	0.1744	0.2174	0.1638
	IFMC-24	**IFMC-25**	
Empirical formula	$C_{66}H_{59}N_{10}O_{11}Br_4Zn_2Eu_{0.25}Tb_{0.75}$	$C_{66}H_{59}N_{10}O_{11}Br_4Zn_2Tb$	
*M*w	1775.79	1777.53	
Crystal system	Monoclinic	Monoclinic	
Space group	$P2_1/n$	$P2_1/n$	
a (Å)	15.676(2)	15.6340(8)	
b (Å)	13.5140(17)	13.4910(7)	
c (Å)	33.055(4)	33.0790(18)	
β (deg)	99.803(2)	99.7480(10)	
V (Å^3)	6900.3(15)	6876.2(6)	
Z	4	4	
D_c (Mg·m^{-3})	1.709	1.717	
Abs.coeff. (mm^{-1})	4.056	4.099	
F(000)	3510	3512	
reflns collected	33958	36569	
Independent reflns	12051	13485	
θ range (deg)	1.25 – 24.96	1.25 – 26.00	
GOF on F^2	1.029	1.034	
R_{int}	0.0661	0.0431	
R_1[a]	0.0557	0.0491	
wR_2 (all data)[b]	0.1786	0.1543	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

Table S2 The selected bond lengths for compounds **IFMC-21** to **25**

IFMC-21			
N(1)-Zn(1)	2.122(6)	N(7)-Zn(1)	2.151(6)
N(3)-Zn(1)	2.097(6)	N(9)-Zn(1)	2.287(6)
N(5)-Zn(1)	2.076(6)	N(10)-Zn(1)	2.285(6)
Eu(1)-O(6)	2.358(6)	Eu(1)-O(1w)	2.465(5)
Eu(1)-O(5)	2.353(6)	Eu(1)-O(2)	2.521(6)
Eu(1)-O(8)	2.377(5)	Eu(1)-O(2w)	2.638(8)
Eu(1)-O(1)	2.418(6)	Eu(1)-O(8)#3	2.694(5)
Eu(1)-O(7)	2.422(5)		
IFMC-22			
N(1)-Zn(1)	2.069(6)	N(7)-Zn(1)	2.093(6)
N(3)-Zn(1)	2.157(6)	N(9)-Zn(1)	2.286(6)
N(5)-Zn(1)	2.099(6)	N(10)-Zn(1)	2.289(6)
O(1)-Ln(1)	2.363(5)	O(4)-Ln(1)	2.352(5)
O(2)-Ln(1)	2.349(6)	O(4)-Ln(1)#1	2.730(5)
O(1W)-Ln(1)	2.483(6)	O(5)-Ln(1)	2.537(6)
O(3)-Ln(1)	2.416(5)	O(6)-Ln(1)	2.430(6)
O(2W)-Ln(1)	2.582(6)		
IFMC-23			
N(1)-Zn(1)	2.082(5)	N(7)-Zn(1)	2.113(5)
N(3)-Zn(1)	2.156(5)	N(9)-Zn(1)	2.286(5)
N(5)-Zn(1)	2.089(5)	N(10)-Zn(1)	2.287(4)
O(1)-Ln(1)	2.338(5)	O(2W)-Ln(1)	2.637(6)
O(2)-Ln(1)#3	2.350(4)	O(4)-Ln(1)	2.410(4)
O(1W)-Ln(1)	2.455(4)	O(7)-Ln(1)	2.399(5)
O(3)-Ln(1)#3	2.350(4)	O(8)-Ln(1)	2.514(4)
O(3)-Ln(1)	2.698(4)		
IFMC-24			
N(1)-Zn(1)	2.084(6)	N(7)-Zn(1)	2.107(7)
N(3)-Zn(1)	2.155(7)	N(9)-Zn(1)	2.282(6)
N(5)-Zn(1)	2.114(7)	N(10)-Zn(1)	2.285(6)
O(1)-Ln(1)	2.314(7)	O(4)-Ln(1)#1	2.711(6)
O(2)-Ln(1)	2.344(6)	O(2W)-Ln(1)	2.455(6)
O(1W)-Ln(1)	2.604(9)	O(5)-Ln(1)	2.402(7)
O(3)-Ln(1)#3	2.392(6)	O(6)-Ln(1)	2.507(6)
O(4)-Ln(1)	2.334(6)		

IFMC-25			
N(1)-Zn(1)	2.078(5)	N(7)-Zn(1)	2.090(5)
N(3)-Zn(1)	2.154(5)	N(9)-Zn(1)	2.286(5)
N(5)-Zn(1)	2.122(5)	N(10)-Zn(1)	2.282(4)
O(1)-Tb(1)	2.319(5)	O(4)-Tb(1)	2.342(4)
O(2)-Tb(1)#4	2.325(5)	O(4)-Tb(1)#4	2.671(4)
O(1W)-Tb(1)	2.429(5)	O(5)-Tb(1)#3	2.495(4)
O(3)-Tb(1)#2	2.383(4)	O(6)-Tb(1)#3	2.377(4)
O(2W)-Tb(1)	2.676(9)		

Symmetry transformations used to generate equivalent atoms: for **IFMC-21**: #3 -x+3,-y,-z+1; for **IFMC-22**: #1 -x+1,-y-1,-z; for **IFMC-23**: #3 -x,-y,-z+2; for **IFMC-24**: #1 -x+1,-y+1,-z+1; #3 -x+1,-y,-z+1; for **IFMC-25**: #2 x,y-1,z; #3 -x,-y+1,-z; #4 -x+1,-y+1,-z.

Table S3 The angles between the benzimidazole rings and the benzene rings

Compounds	Three atoms	Angle/º	Two planes	Dihedral angle/º
IFMC-21	N2-C8-C9	110.123	AB	88.727
	N4-C23-C24	111.306	CD	85.800
	N6-C38-C39	110.533	EF	87.331
	N8-C53-C54	112.769	GH	88.164
IFMC-22	N2-C8-C9	110.300	AB	88.863
	N4-C23-C24	111.582	CD	87.763
	N6-C38-C39	111.176	EF	87.229
	N8-C53-C54	112.238	GH	85.272
IFMC-23	N2-C8-C9	110.629	AB	87.874
	N4-C23-C24	111.617	CD	88.566
	N6-C38-C39	111.329	EF	84.614
	N8-C53-C54	109.697	GH	88.554
IFMC-24	N2-C8-C9	109.456	AB	87.683
	N4-C23-C24	112.798	CD	88.189
	N6-C38-C39	109.795	EF	88.782
	N8-C53-C54	111.867	GH	84.785
IFMC-25	N2-C8-C9	110.658	AB	87.544
	N4-C23-C24	113.009	CD	88.916
	N6-C38-C39	110.822	EF	88.942
	N8-C53-C54	112.091	GH	84.833