

Supporting Information

Direct White-Light and Dual-channel Barcode Module from Pr(III)-MOF Crystals

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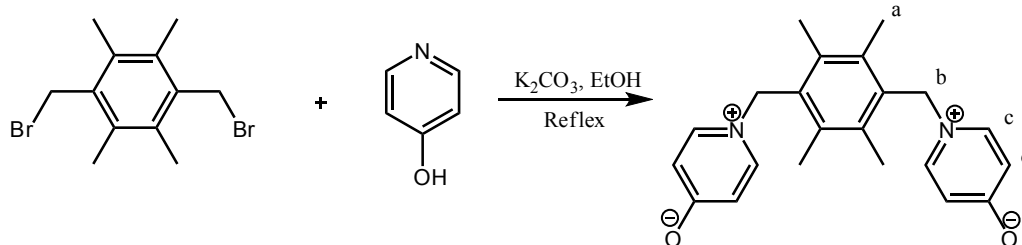
Materials and methods

Experimental reagents were of AR grade and used as purchased without further purification unless otherwise stated. 4-hydroxypyridine was purchased from Beijing J & K Co. Ltd. The C, H, and N elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. ¹H NMR spectrum was recorded on Bruker Avance 400 NMR spectrometer. TG curves were measured on a NETZSCH TG 209 instrument. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K α , $\lambda = 1.5418 \text{ \AA}$). UV-Vis absorption spectra were recorded using a Shimadzu UV-250PC spectrophotometer. IR spectra were performed on a Nicolet/Nexus-670 FT-IR spectrometer with KBr pellets (4000–400 cm^{-1}). Photoluminescence spectra and decay lifetime were measured on EDINBURGH FLS980 fluorescence spectrophotometer.

Crystallography

The single-crystal diffraction data were collected on an Agilent Gemini S Ultra diffractometer with the Enhance X-ray Source of Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) using the ω - ϕ scan technique. Absorption corrections were applied using multiscan technique. The structures were solved by direct method of SHELXS and refined against F^2 using the SHELXL programs.¹ The non-hydrogen atoms were treated with anisotropic parameters, while H atoms were placed in calculated positions and refined using a riding model. The solvent molecules were squeezed in the structure of LIFM-19Gd. Crystallographic data and structural refinement information are listed in Table S1. The selected bond lengths and bond angles for compounds are listed in Table S2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1403408 and 1407912.

Synthesis of ligand



Scheme S1. Synthetic route of the ligand TMPBPO.

1,1'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene) dipyridinium-4-olate (**TMPBPO**): A mixture of 4-hydroxypyridine (0.627 g, 6.5 mmol) and K_2CO_3 (1.6 g, 12 mmol) was refluxed in ethanol (30 ml) for 4 hours, and then 1,4-bis(bromomethyl)-2,3,5,6-tetramethyl benzene (0.95 g, 3 mmol) was added. The reaction mixture was then refluxed at 80 °C for 24 h. Upon completion of the reaction, ethanol was evaporated to get yellow oily product, into which 100 ml ethyl ether was added and a large quantity of white precipitates were obtained. The precipitates were filtrated and dried under vacuum overnight to get the final product. Yield: 80 %. 1H -NMR (400 MHz, D_2O , 25 °C): δ 7.59 (t, $J = 8.6$ Hz, 4H), 6.50 – 6.34 (m, 4H), 5.40 – 5.25 (m, 4H), 2.12 (s, 12H). IR (cm^{-1}): 3419, 2989, 2062, 1640, 1571, 1486, 1396, 1172, 1067, 1002, 850, 786, 482.

Syntheses of Ln(III)-MOFs (Ln=Pr, Gd)

[Pr(TMPBPO) $_2$ (NO $_3$) $_3$]·C $_3$ H $_6$ O·H $_2$ O–LIFM-17(Pr): A solution of TMPBPO (10.5 mg, 0.03 mmol) in water (1 ml) was added to a solution of Pr(NO $_3$) $_3$ ·3H $_2$ O (8.7 mg, 0.02 mmol) in acetone (3 ml) at room temperature. The mixture was stirred for 30 min. After filtration, slow diffusion of acetone into the filtrate over 5 days afforded light green crystals of LIFM-17(Pr). Yield: 68%. Anal. Calc. (%) for C $_{47}$ H $_{56}$ PrN $_7$ O $_{15}$: C, 51.32; H, 5.13; N, 8.91. Found: C, 51.15; H, 4.97; N, 9.33. IR (cm^{-1}): 3463, 2989, 1794, 1636, 1549, 1383, 1345, 1194, 1166, 872, 712, 499.

[Gd(TMPBPO) $_2$ (NO $_3$) $_2$]·(NO $_3$)·C $_3$ H $_6$ O·8H $_2$ O–LIFM-19(Gd): Following a similar procedure as above except for using Gd(NO $_3$) $_3$ ·3H $_2$ O instead of Pr(NO $_3$) $_3$ ·3H $_2$ O. Yield: 63 %. Anal. Calc. (%) for C $_{47}$ H $_{70}$ GdN $_7$ O $_{22}$: C, 45.44; H, 5.64; N, 7.90. Found: C, 45.50; H, 5.79; N, 8.08. IR (cm^{-1}): 3428, 1636, 1531, 1434, 1383, 1314, 1198, 1164, 1021, 863, 830, 569, 502.

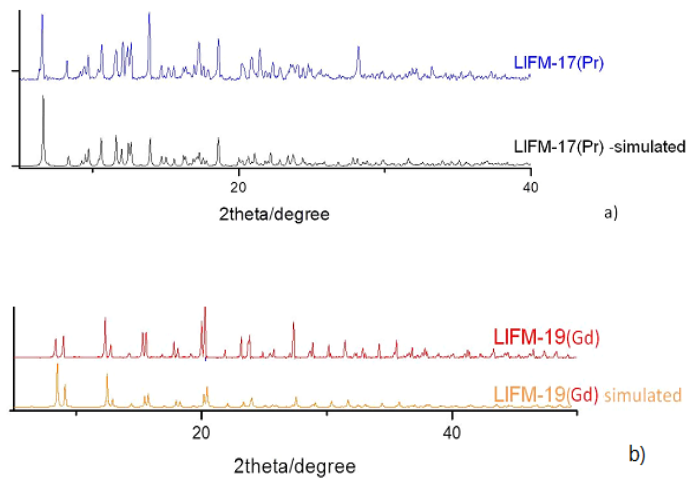


Fig. S1 The measured powder XRD pattern of complexes LIFM-17(Pr) (a) and LIFM-19(Gd) (b) in comparison with the simulated pattern from single-crystal data .

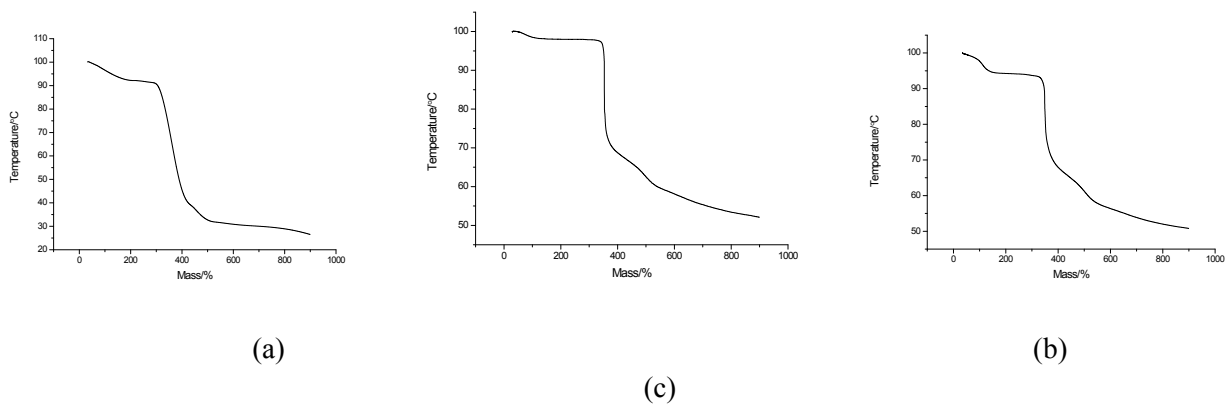
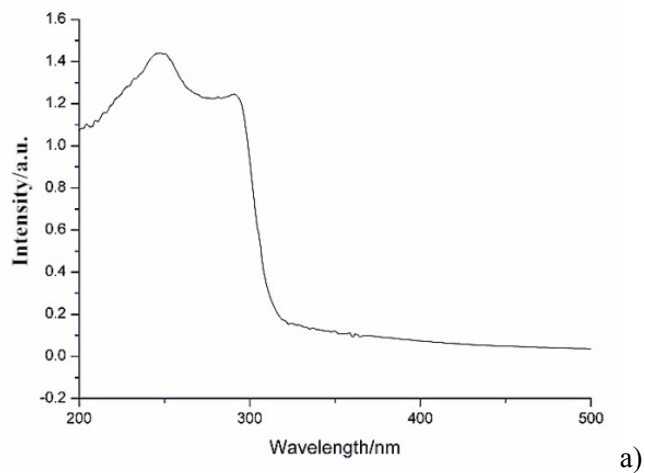
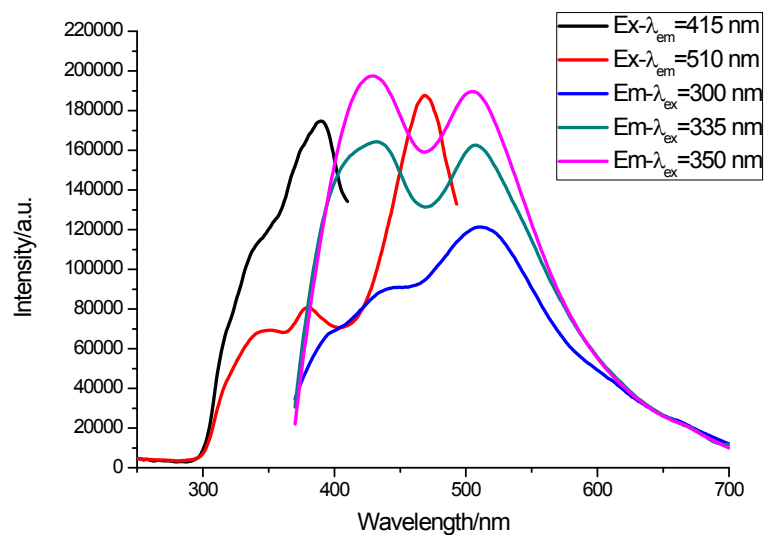


Fig. S2 TG curves for the ligand TMPBPO, complexes LIFM-17(Pr) and LIFM-19(Gd) (a-c).





b)

Fig. S3 Solid-state UV-vis absorption (a) and luminescence spectra (b) of TMPBPO ligand (room temperature).

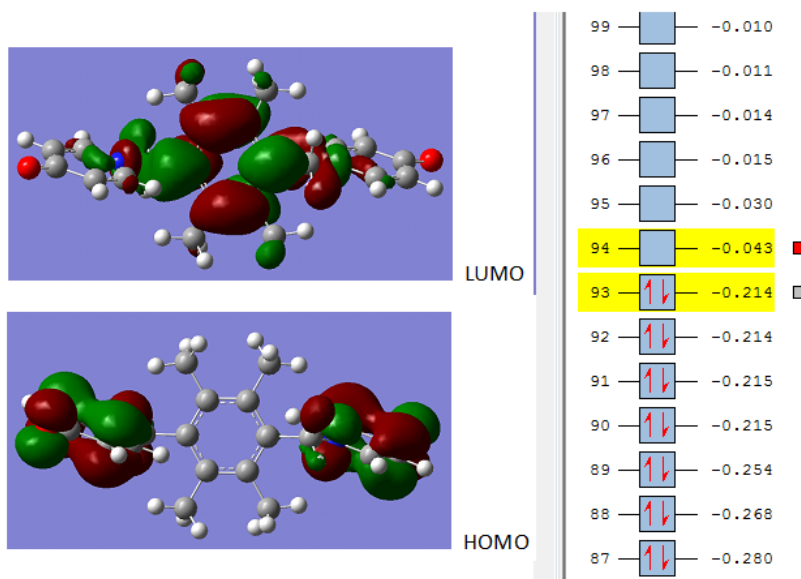


Fig. S4 Optimized geometry of TMPBPO ligand with HOMO and LUMO orbitals highlighted.

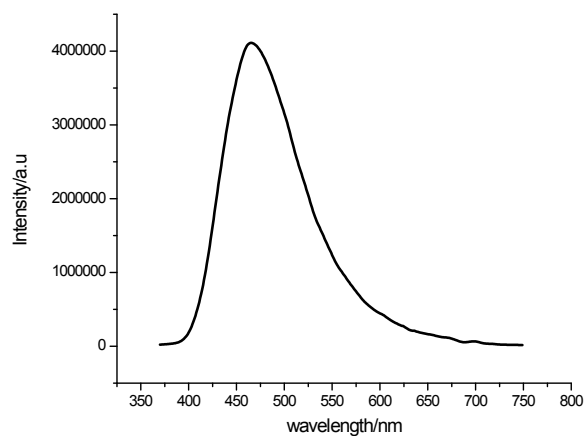
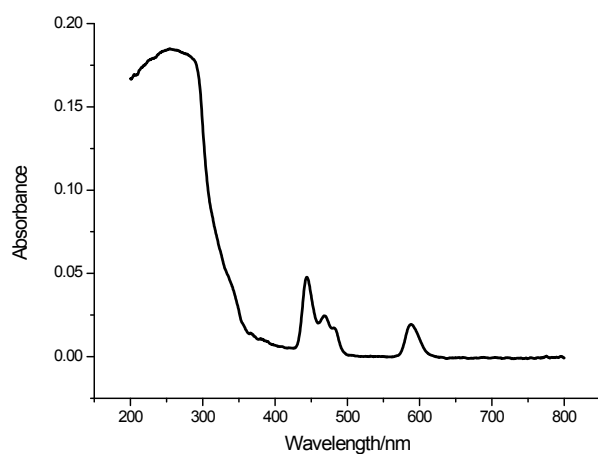
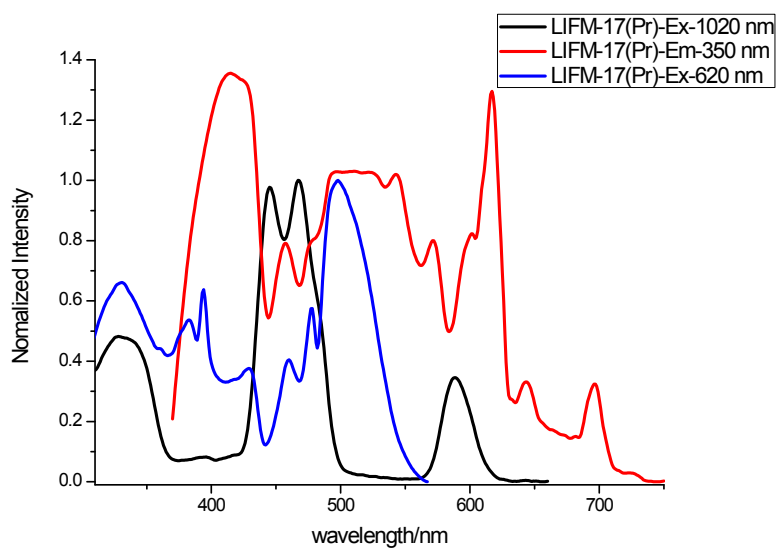


Fig. S5 Solid-state phosphorescence spectra of complex LIFM-19(Gd) measured at 77 K.



a)



b)

Fig. S6 Solid state UV-vis absorption (a) and excitation and emission (b) spectra of LIFM-17(Pr) measured at room temperature.

Table S1. Crystallographic data for complexes LIFM-17(Pr) and LIFM-19(Gd).

	<i>LIFM-17(Pr)</i>	<i>LIFM-19(Gd)</i>
<i>Formula</i>	$C_{44}H_{48}N_7O_{15}Pr$	$C_{44}H_{48}N_6O_{10}Gd$
<i>F.w.</i>	1055.80	978.13
<i>T (K)</i>	150(2)	173(2)
<i>Crystal system</i>	monoclinic	tetragonal
<i>Space group</i>	$P2_1/c$	$I-4$
<i>a (Å)</i>	12.6863(5)	19.4684(2)
<i>b (Å)</i>	19.0520(7)	19.4684(2)
<i>c (Å)</i>	18.5676(8)	12.3837(3)
α (°)	90	90
β (°)	91.855(1)	90
γ (°)	90	90
<i>V (Å³)</i>	4485.4(3)	4693.65(15)
<i>Z</i>	4	4
<i>D_c (g cm⁻³)</i>	1.563	1.384
μ (mm ⁻¹)	1.165	9.636
<i>F(000)</i>	2160	1992
<i>GOF</i>	1.084	1.122
<i>R₁ (>2σ)</i>	0.0504	0.0642
<i>wR₂(all data)</i>	0.1404	0.1791

Table S2 Selected bond lengths (Å) and angles (°) for complexes LIFM-17(Pr) and LIFM-19(Gd).

Complex LIFM-17(Pr)		O(1)-Pr(1)	2.383(3)
O(3)-Pr(1)	2.427(3)	O(2)#-Pr(1)	2.458(3)
O(4)#-Pr(1)	2.422(3)	O(8)-Pr(1)	2.653(3)
O(5)-Pr(1)	2.608(3)	O(9)-Pr(1)	2.680(3)
O(6)-Pr(1)	2.731(3)	O(11)-Pr(1)	2.646(3)
O(1)-Pr(1)-O(2)#	157.42(10)	O(4)#-Pr(1)-O(2)#	75.15(10)
O(1)-Pr(1)-O(3)	73.62(10)	O(4)#-Pr(1)-O(3)	77.75(12)
O(1)-Pr(1)-O(4)#	85.07(10)	O(4)#-Pr(1)-O(5)	148.12(11)
O(1)-Pr(1)-O(5)	75.72(9)	O(4)#-Pr(1)-O(6)	127.74(12)
O(1)-Pr(1)-O(6)	117.46(10)	O(4)#-Pr(1)-O(8)	133.11(12)
O(1)-Pr(1)-O(8)	78.21(9)	O(4)#-Pr(1)-O(9)	142.33(10)
O(1)-Pr(1)-O(9)	123.18(9)	O(4)#-Pr(1)-O(11)	79.39(11)
O(1)-Pr(1)-O(11)	113.08(10)	O(4)#-Pr(1)-O(12)	69.01(12)
O(1)-Pr(1)-O(12)	66.23(9)	O(5)-Pr(1)-O(6)	47.78(10)
O(2)#-Pr(1)-O(5)	116.41(10)	O(5)-Pr(1)-O(8)	67.71(10)
O(2)#-Pr(1)-O(6)	69.10(11)	O(5)-Pr(1)-O(9)	68.92(9)

O(2)#-Pr(1)-O(8)	123.44(9)	O(5)-Pr(1)-O(11)	131.49(10)
O(2)#-Pr(1)-O(9)	79.39(9)	O(5)-Pr(1)-O(12)	122.91(10)
O(2)#-Pr(1)-O(11)	74.27(11)	O(6)-Pr(1)-O(12)	161.99(10)
O(2)#-Pr(1)-O(12)	114.86(11)	O(8)-Pr(1)-O(6)	98.64(10)
O(3)#-Pr(1)-O(2)	91.36(10)	O(8)-Pr(1)-O(9)	47.90(9)
O(3)-Pr(1)-O(5)	72.57(10)	O(8)-r(1)-O(12)	64.13(10)
O(3)-Pr(1)-O(6)	66.57(10)	O(9)-Pr(1)-O(6)	64.72(10)
O(3)-Pr(1)-O(8)	135.67(10)	O(9)-Pr(1)-O(12)	98.10(10)
O(3)-Pr(1)-O(9)	130.53(10)	O(11)-Pr(1)-O(6)	123.30(10)
O(3)-Pr(1)-O(11)	155.50(10)	O(11)-Pr(1)-O(8)	68.01(10)
O(3)-Pr(1)-O(12)	129.04(10)	O(11)-Pr(1)-O(9)	67.17(10)
O(11)-Pr(1)-O(12)	47.35(10)		
Complex LIFM-19(Gd)		Gd1-O3AA	2.288(9)
Gd1-O2AA	2.539(11)	Gd1-N1AA	2.94(2)
Gd2-O4AA	2.299(9)	Gd2-O7	2.507(11)
Gd2-N0AA	2.96(2)	O3AA-Gd1-O3AA	158.2(5)
O3AA-Gd1-O3AA [#]	92.05(10)	O3AA-Gd1-O3AA ^{#3}	92.06(10)
O3AA-Gd1-O2AA	78.9(3)	O3AA-Gd1-O2AA ^{#3}	81.3(4)
O3AA-Gd1-O2AA ^{#4}	126.1(3)	O3AA-Gd1-O2AA	75.8(3)
O2AA-Gd1-O2AA ^{#2}	145.0(3)	O4AA-Gd2-O4AA ^{#6}	163.1(6)
O4AA-Gd2-O4AA ^{#6}	91.23(8)	O4AA-Gd2-O4AA ^{#8}	91.23(8)
O4AA-Gd2-O7 ^{#3}	123.2(4)	O4AA-Gd2-O7	73.6(4)
O4AA [#] -Gd2-O7	85.3(4)	O4AA-Gd2-O7 ^{#3}	79.4(4)
O7 ^{#6} -Gd2-O7 ^{#3}	145.2(3)	O7 ^{#6} -Gd2-O7 ^{#8}	50.0(5)
O7 ^{#3} -Gd2-O7	50.0(5)	O4AA ^{#6} -Gd2-N0AA ^{#6}	98.4(3)
O4AA ^{#3} -Gd2-N0AA ^{#6}	81.6(3)	O7 ^{#6} -Gd2-N0AA ^{#6}	25.0(2)
O7 ^{#3} -Gd2-N0AA ^{#6}	155.0(2)	O4AA ^{#6} -Gd2-N0AA	81.6(3)
O4AA-Gd2-N0AA	98.4(3)	N0AA ^{#6} -Gd2-N0AA	180.0

Symmetry code: LIFM-17(Pr): 'x, y, z'; '-x, y+1/2, -z+1/2'; '-x, -y, -z'; 'x, -y-1/2, z-1/2'; LIFM-19(Gd): 'x, y, z'; 'y, -x, -z'

'-x, -y, z'; '-y, x, -z'; 'x+1/2, y+1/2, z+1/2'; 'y+1/2, -x+1/2, -z+1/2'; '-x+1/2, -y+1/2, z+1/2'; '-y+1/2, x+1/2, -z+1/2'

References

1. G. Sheldrick, "*SHELXL-2013*", 2013, Universität Göttingen, Göttingen, Germany.