Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2021

Supporting Information for

Multimetal lanthanide phosphonocarboxylate frameworks: structures, colour tuning and near-infrared emission

Huiru Jing,[a] Wenyan Dan,[b] Jiaxing Zhu,[a] Yun Ling,[a] Yu Jia,[a] Yongtai Yang,[a] Xiaofeng Liu[a], Zhenxia Chen[a,] and Yaming Zhou[a,]**

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200438, China

E-mail:zhxchen@fudan.edu.cn; ymzhou@fudan.edu.cn

Table of Contents

Section 1. Details of synthesis.

Synthesis of TbPCF.

$Tb(NO_3)_3 \cdot 6H_2O$ (0.023 g, 0.05 mmol), H_4pbpdc (0.016 g, 0.05 mmol), DMF (4 mL), deionized water (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol , centrifuged, and dried to obtain colorless needle crystals. Yield: 55%. Elemental Analysis: Found (%) C 33.19, N 1.57, H 2.69; Calc. (%) C 33.00, N 1.60, H 2.58. FT-IR: (KBr 4000 - 400 cm^{-1}): 3256(b), 1655(s), 1610(s), 1547(vs), 1508(m), 1470(m), 1443(s), 1406(s), 1383(s), 1162(s), 1139(s), 1054(m), 1025(m), 988(s), 796(w), 779(m), 737(m), 706(s), 600(m), 552(w).

Synthesis of EuPCF.

$Eu(NO_3)_3 \cdot 6H_2O$ (0.023 g, 0.05mmol), H_4pbpdc (0.016 g, 0.05 mmol), DMF (4 mL), deionized water (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol , centrifuged, and dried to obtain colorless needle crystals. Yield: 52%. Elemental Analysis: Found (%) C 33.75, N 1.60, H 2.78; Calc. (%) C 33.47, N 1.63, H 2.61. FT-IR: (KBr 4000 - 400 cm^{-1}): 3256(b), 1655(s), 1610(s), 1545(vs), 1470(m), 1444(s), 1406(s), 1381(s), 1161(s), 1139(s), 1054(m), 1025(m), 988(s), 795(w), 779(m), 737(m), 706(s), 600(m), 552(w).

Synthesis of GdPCF.

$Gd(NO_3)_3 \cdot 6H_2O$ (0.023 g, 0.05mmol), H_4pbpdc (0.016 g, 0.05 mmol), DMF (4 mL), deionized water (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals. Yield: 60%. Elemental Analysis: Found (%) C 33.21, N 1.57, H 2.68; Calc. (%) C 33.11, N 1.61, H 2.59. FT-IR: (KBr 4000 - 400 cm^{-1}): 3255(b), 1655(s), 1610(s), 1546(vs), 1508(m), 1471(m), 1443(s), 1406(s), 1383(s), 1161(s), 1139(s), 1056(m), 1024(m), 987(s), 796(w), 779(m), 737(m), 706(s), 600(m), 552(w).

Synthesis of NdPCF.

$Nd(NO_3)_3 \cdot 6H_2O$ (0.022 g, 0.05 mmol), H_4pbpdc (0.016 g, 0.05 mmol), DMF (4 mL), deionized water (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals. Yield:46%. FT-IR: (KBr 4000 - 400 cm^{-1}): 3256(b), 1655(s), 1610(s), 1547(vs), 1508(m), 1470(m), 1443(s), 1406(s), 1383(s), 1162(s), 1139(s), 1054(m), 1025(m), 988(s), 796(w), 779(m), 737(m), 706(s), 600(m), 552(w).

Synthesis of Tb_xGd_{1-x}PCF.

$Tb(NO_3)_3·6H_2O$ (0.05 x mmol, x = 0.05, 0.5), $Gd(NO_3)_3·6H_2O$ (0.05 (1-x) mmol), H_4pbpdc (0.05 mmol), DMF (4 mL), H_2O (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals.

Synthesis of Tb_xEu_{1-x}PCF.

$Tb(NO_3)_3·6H_2O$ (0.05x mmol, x = 0.99, 0.98, 0.95, 0.9, 0.5), $Eu(NO_3)_3·6H_2O$ (0.05(1 - x) mmol), H_4pbpdc (0.05 mmol), DMF (4 mL), H_2O (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals.

Synthesis of $Tb_{0.5}Nd_{0.5}$PCF.

$Tb(NO_3)_3·6H_2O$ (0.012 g, 0.025 mmol), $Nd(NO_3)_3·6H_2O$ (0.012 g, 0.025 mmol), H_4pbpdc (0.016 g, 0.05 mmol), DMF (4 mL), H_2O (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals.

Synthesis of $Tb_xGd_{0.5}Nd_{0.5-x}$PCF.

$Tb(NO_3)_3·6H_2O$ (0.025x mmol, x = 0.3, 0.4), $Gd(NO_3)_3·6H_2O$ (0.025 mmol), $Nd(NO_3)_3·6H_2O$ (0.025 - 0.025x mmol), H_4pbpdc (0.05 mmol), DMF (4 mL), H_2O (2 mL) were added to the Teflon reactor, heated at 140 °C for 48 hours, then slowly cooled to room temperature. The product was washed with DMF, ethanol, centrifuged, and dried to obtain colorless needle crystals.

Section 2. The crystal data and structural refinement parameters for LnPCF

Table S1. Crystal data and structure refinements for TbPCF, GdPCF and EuPCF.

	TbPCF	**GdPCF**	**EuPCF**
Empirical formula	$C_{96}H_{90}N_4O_{49}P_6Tb_7$	$C_{96}H_{76}N_4O_{49}P_6Gd_7$	$C_{96}H_{70}N_4O_{49}P_6Eu_7$
Formula weight	3381.97	3356.17	3313.10
Crystal system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnnm*	*Pnnm*	*Pnnm*
Unit cell dimensions (Å)	14.4585(4) 20.3696(6) 22.7805(7)	14.4962(6) 20.3758(8) 22.8688(11)	14.5138(5) 20.4301(8) 22.9139(9)
α, β, γ (°)	90	90	90
Volume (Å^3)	6709.2(3)	6754.8(5)	6794.4(4)
Z	2	2	2
D (g·cm^{-3})	1.674	1.650	1.619
Theta range for data collection (°)	3.261-61.985	3.140-61.957	3.136-64.363
Index ranges	-18<h<19; -26<k<26; -29<l<24	-13<h<18; -25<k<26; -30<l<18	-19<h<15; -26<k<21; -26<l<29
F (000)	3262	3220	3194
Collected / unique	45729/8164	48154/ 8210	43814/8611
GOF on F^2	1.031	1.048	1.109
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0562, 0.1531	0.0567, 0.1571	0.0550, 0.1519
R_1, wR_2 (all data)	0.0837, 0.1703	0.0789, 0.1742	0.0617, 0.1585

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

Section 3. Description of single crystal structure.

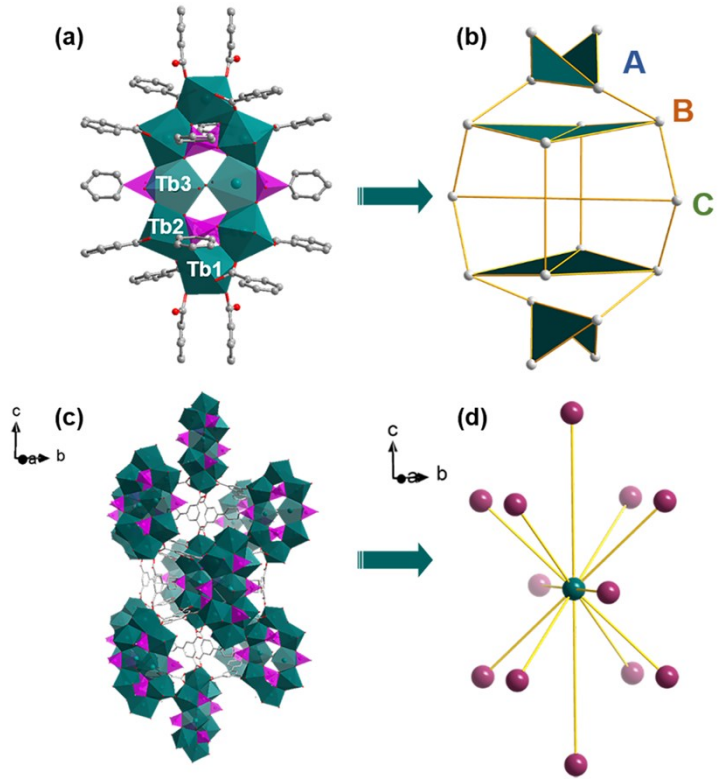


Fig. S1: (a) The 18-connected Tb_7-cluster. **(b)** The 18 nodes of Tb_7-cluster is divided into three parts (A, B and C). **(c) (d)** The 18-connected Tb_7-cluster is linked to another twelve Tb_7-clusters by triangular $pbpdc^{4-}$ ligands.

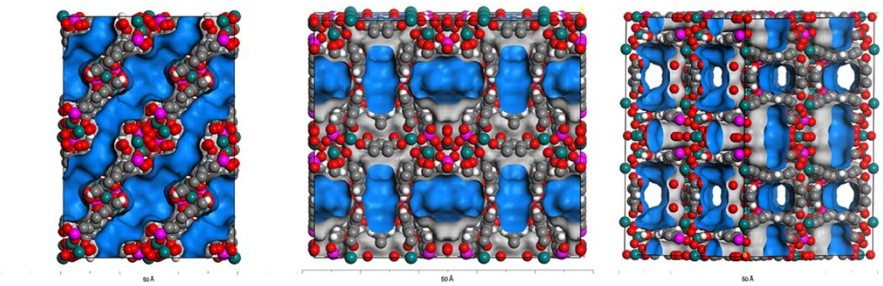


Fig. S2: 2 × 2 × 2 unit cell of TbPCF (the blue surface is the Connolly surface calculated by the probe radii of 1.4 Å) shows the 1D ultra-micro channel (4.1 × 3.8 $Å^2$).

Section 4. Supporting Characterizations of LnPCF

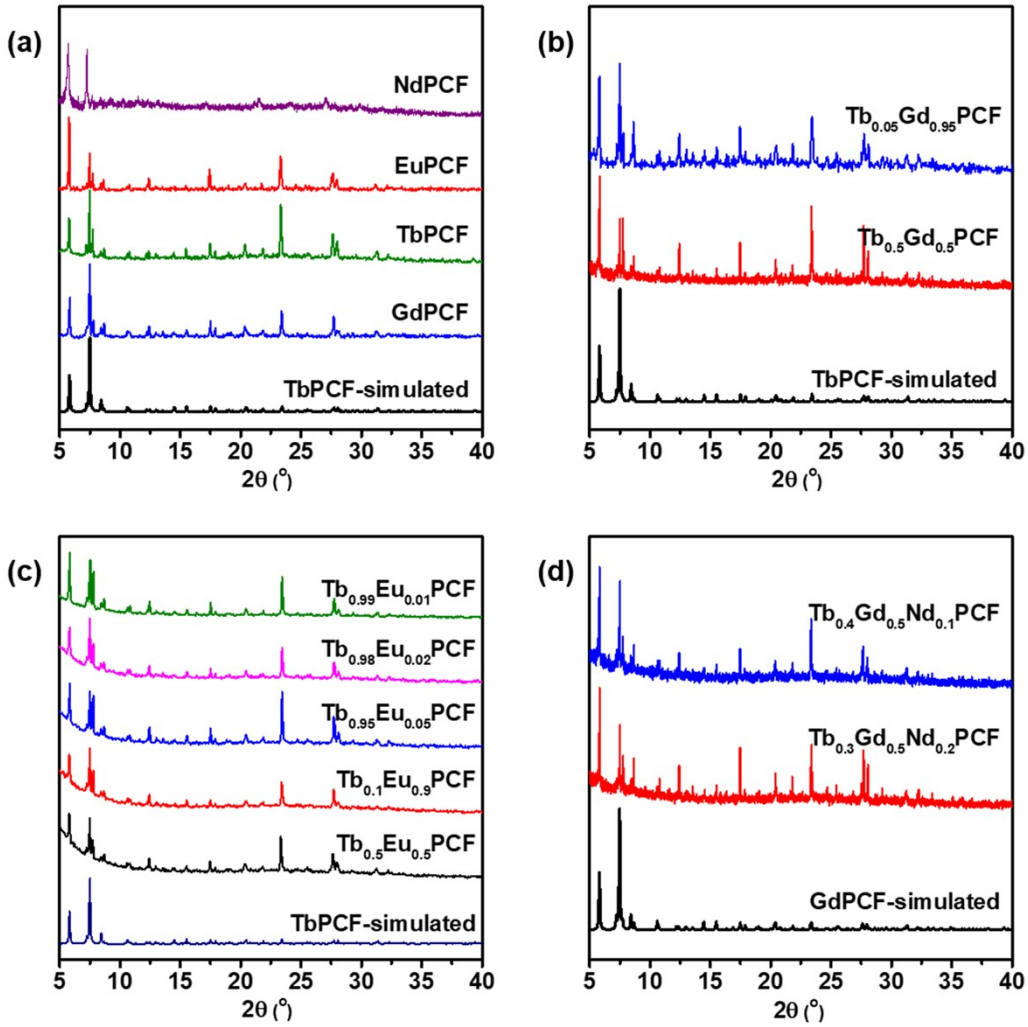


Fig. S3 PXRD patterns of **(a)** LnPCF (Ln= Tb, Gd, Eu, Nd). **(b)** $Tb_{0.05}Gd_{0.95}$PCF and $Tb_{0.5}Gd_{0.5}$PCF. **(c)** $Tb_{0.99}Eu_{0.01}$PCF, $Tb_{0.98}Eu_{0.02}$PCF, $Tb_{0.95}Eu_{0.05}$PCF, $Tb_{0.9}Eu_{0.1}$PCF, and $Tb_{0.5}Eu_{0.5}$PCF. **(d)** $Tb_{0.4}Gd_{0.5}Nd_{0.1}$PCF and $Tb_{0.3}Gd_{0.5}Nd_{0.2}$PCF.

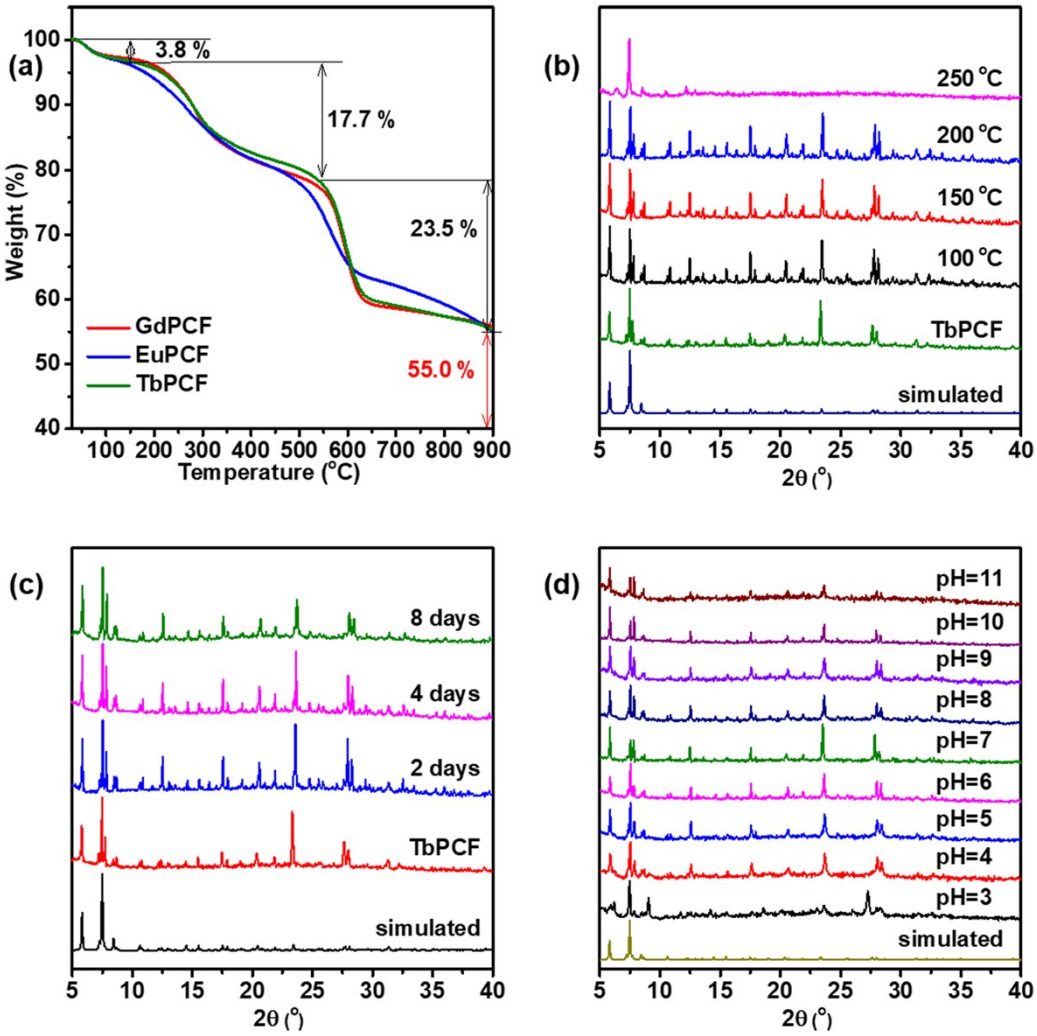


Fig. S4 (a) The TGA curves of TbPCF, GdPCF and EuPCF. **(b)** Temperature dependent PXRD patterns of TbPCF. **(c)** PXRD patterns of TbPCF after being immersed in water for different time. **(d)** PXRD patterns of TbPCF after being immersed in different pH (3-11) solutions.

Section 5. Supporting Characterizations of mixed metal LnPCFs

Table S2. The lanthanide molar ratios of the mixed metal LnPCFs in precursors and calculated from ICP-AES.

	Molar ratios in precursors			Molar ratios calculated from ICP		
	Tb (*x*)	**Gd (1-*x*)**		**Tb (*x*)**	**Gd (1-*x*)**	
Tb_xGd_{1-x}PCF	0.05	0.95		0.059	0.941	
	0.50	0.50		0.525	0.475	
	Tb (*x*)	**Eu (1-*x*)**		**Tb (*x*)**	**Eu (1-*x*)**	
Tb_xEu_{1-x}PCF	0.99	0.01		0.990	0.010	
	0.98	0.02		0.980	0.020	
	0.95	0.05		0.949	0.051	
	0.90	0.10		0.897	0.103	
	0.50	0.50		0.515	0.485	
	Tb (*x*)	**Gd (0.5)**	**Nd (0.5-*x*)**	**Tb (*x*)**	**Gd (0.5)**	**Nd (0.5-*x*)**
$Tb_xGd_{0.5}Nd_{0.5-x}$PCF	0.40	0.50	0.10	0.412	0.470	0.118
	0.30	0.50	0.20	0.337	0.443	0.220
	Tb (*x*)	**Nd (1-*x*)**		**Tb (*x*)**	**Nd (1-*x*)**	
Tb_xNd_{1-x}PCF	0.50	0.50		0.446	0.554	

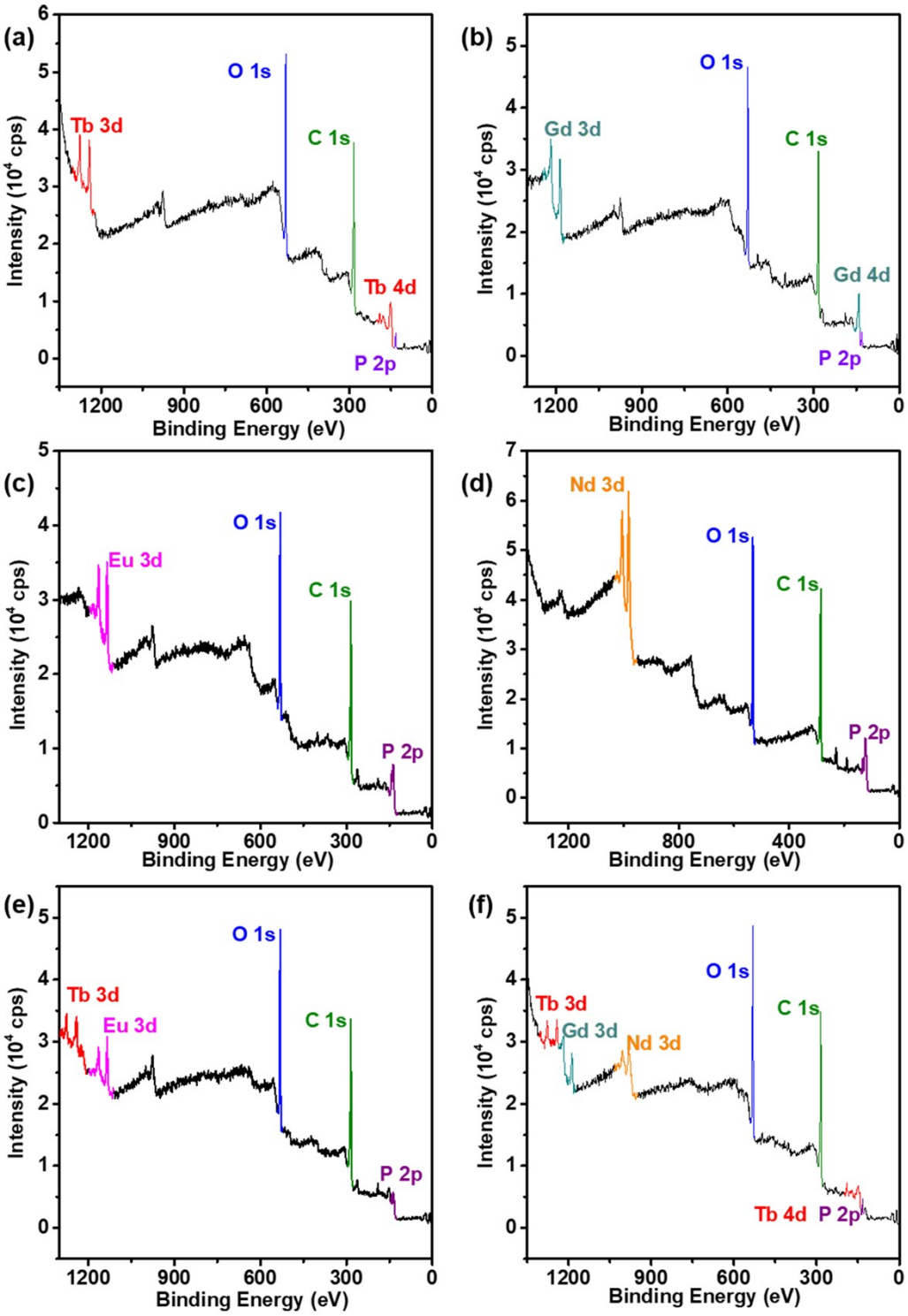
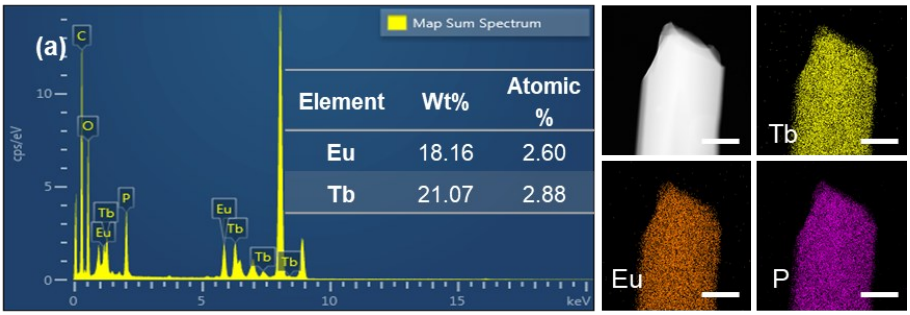
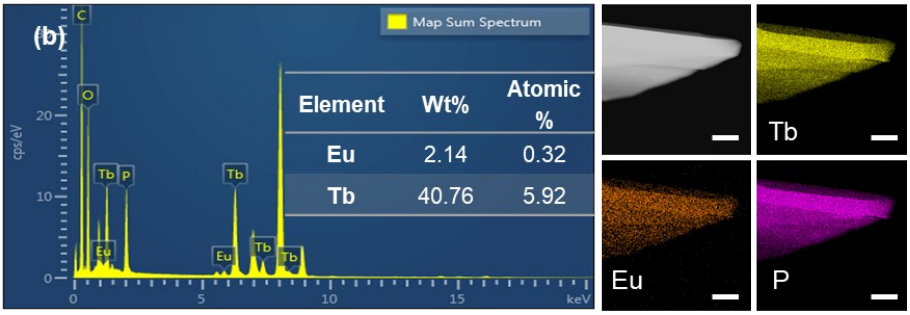
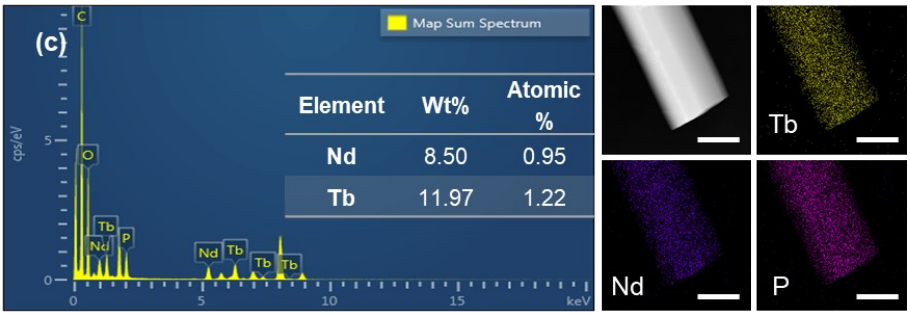
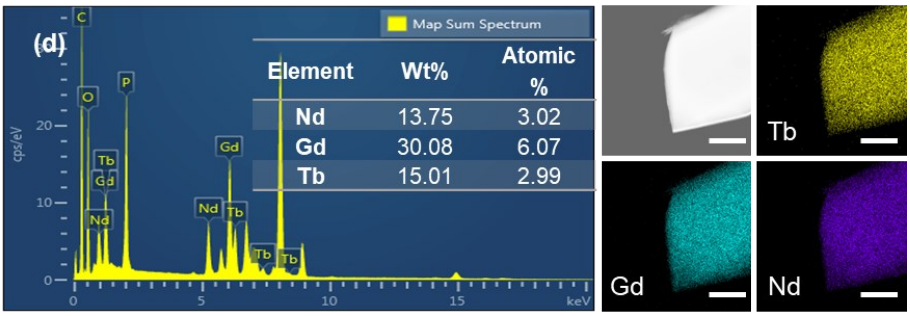


Fig. S5 XPS spectra of **(a)** TbPCF. **(b)** GdPCF. **(c)** EuPCF. **(d)** NdPCF. **(e)** $Tb_{0.5}Eu_{0.5}$PCF and **(f)** $Tb_{0.4}Gd_{0.5}Nd_{0.1}$PCF.


(a)
Map Sum Spectrum
Element Wt% Atomic %
Eu 18.16 2.60
Tb 21.07 2.88
Tb
Eu
P


(b)
Map Sum Spectrum
Element Wt% Atomic %
Eu 2.14 0.32
Tb 40.76 5.92
Tb
Eu
P


(c)
Map Sum Spectrum
Element Wt% Atomic %
Nd 8.50 0.95
Tb 11.97 1.22
Tb
Nd
P


(d)
Map Sum Spectrum
Element Wt% Atomic %
Nd 13.75 3.02
Gd 30.08 6.07
Tb 15.01 2.99
Tb
Gd
Nd

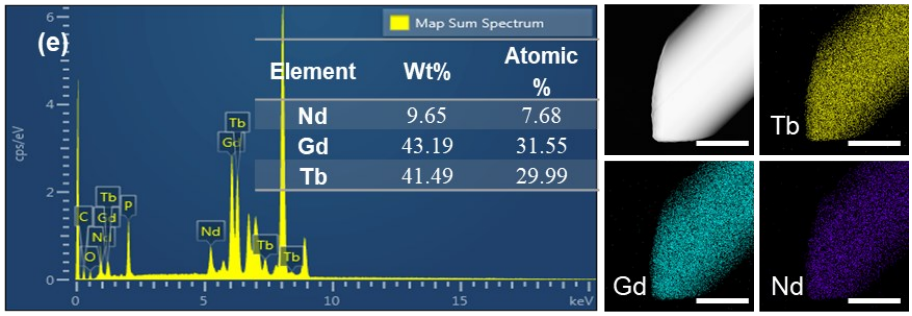


Fig. S6: Elemental analysis results of EDS mapping for bi- and trimetallic LnPCFs. **(a)** $Tb_{0.5}Eu_{0.5}$PCF (Scale bar: 1 μm). **(b)** $Tb_{0.95}Eu_{0.05}$PCF (Scale bar: 1 μm). **(c)** $Tb_{0.5}Nd_{0.5}$PCF (Scale bar: 200 nm). **(d)** $Tb_{0.3}Gd_{0.5}Nd_{0.2}$PCF (Scale bar: 1 μm). **(e)** $Tb_{0.4}Gd_{0.5}Nd_{0.1}$PCF (Scale bar: 1 μm).

Section 6. Luminescence properties

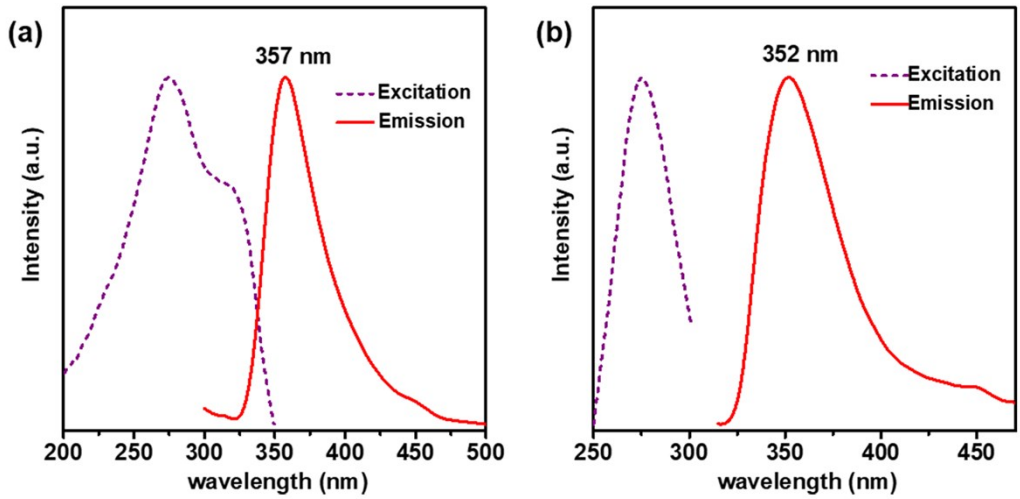


Fig. S7 (a) Exicitation and emission spectra of H_4pbpdc in solid state, in which the broad emission at 357 nm was caused by $\pi^* \rightarrow \pi$ transition. **(b)** Exicitation and emission spectra of GdPCF in solid state, in which the emission band of GdPCF was similar to H_4pbpdc, except the peak was blue-shifted by 5 nm.

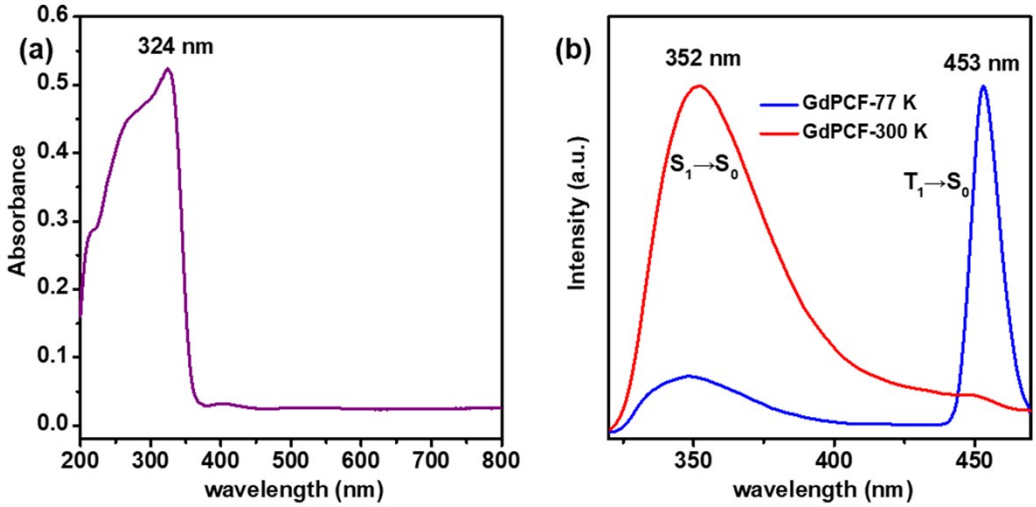
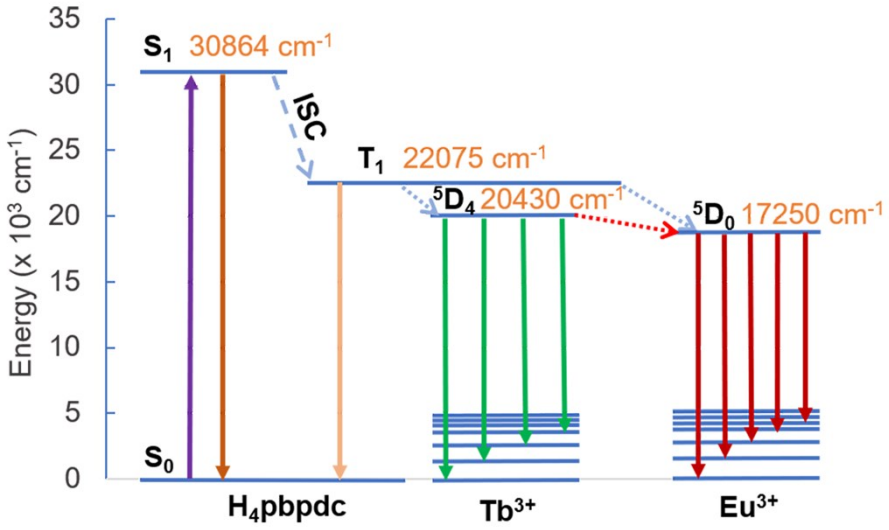


Fig. S8 (a) UV-vis absorption spectrum of H_4pbpdc. **(b)** Normalized emission spectra of GdPCF at 300 K and 77 K.



Scheme S1. The schematic emission and "antenna effect" processed in LnPCF.

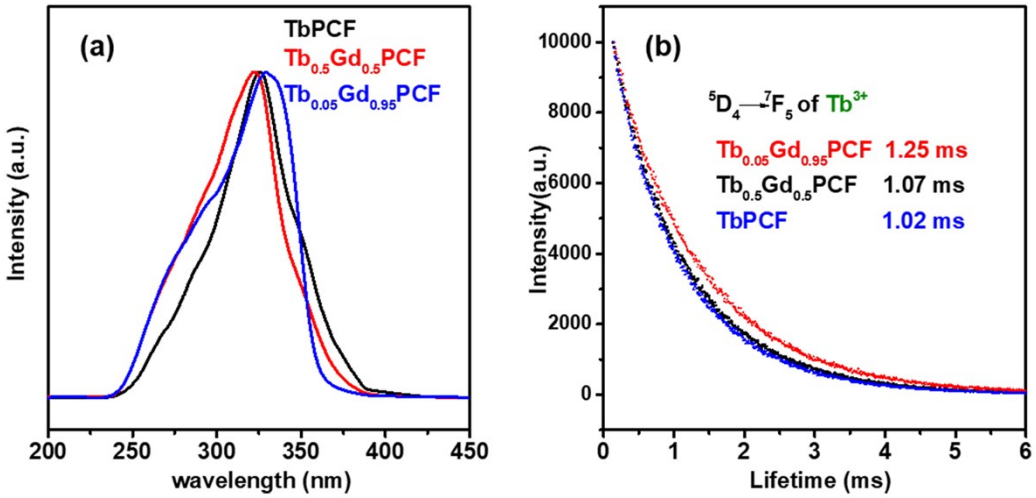


Fig. S9 (a) Excitation spectra and **(b)** temporal decay curves of the TbPCF, $Tb_{0.5}Gd_{0.5}$PCF, $Tb_{0.05}Gd_{0.95}$PCF excited at 330 nm.

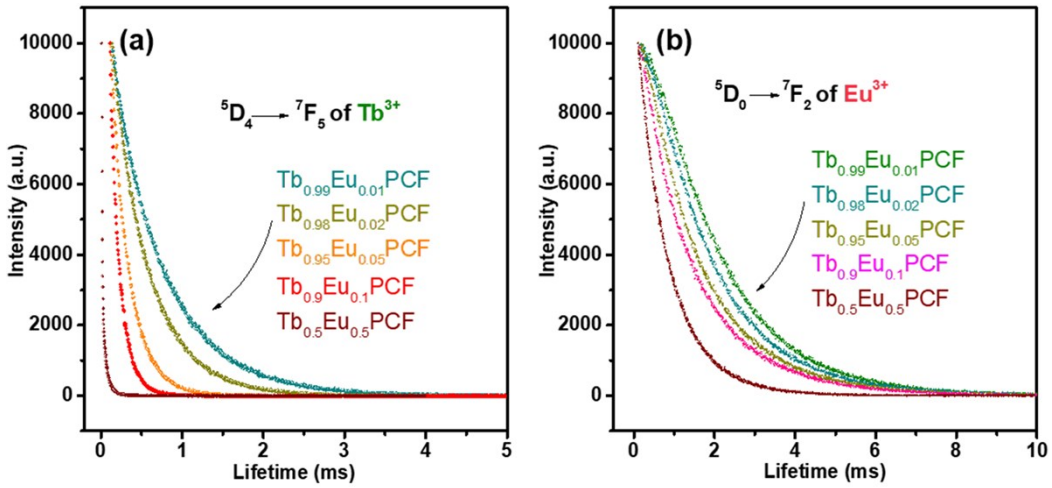


Fig. S10. Temporal decay curves of the $Tb_{0.99}Eu_{0.01}$PCF, $Tb_{0.98}Eu_{0.02}$PCF, $Tb_{0.95}Eu_{0.05}$PCF, $Tb_{0.9}Eu_{0.1}$PCF,and $Tb_{0.5}Eu_{0.5}$PCF: **(a)** monitored at 545 nm ($^5D_4 \rightarrow {}^7F_5$ of Tb^{3+}); **(b)** monitored at 612 nm ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}).

Table S3. The lifetimes of Tb^{3+} and Eu^{3+} in $Tb_xEu_{1-x}PCF$ (x = 0.99, 0.98, 0.95, 0.9, 0.5) and corresponding energy transfer efficiency η between Tb^{3+} and Eu^{3+}; τ_0 = 1.02 ms, which refers to the lifetime of Tb^{3+} in TbPCF.

	τ_1 of Tb^{3+} (ms)	τ_2 of Eu^{3+} (ms)	$\eta = 1-\tau_1/\tau_0$
$Tb_{0.99}Eu_{0.01}PCF$	0.60	1.95	0.412
$Tb_{0.98}Eu_{0.02}PCF$	0.45	1.73	0.559
$Tb_{0.95}Eu_{0.05}PCF$	0.22	1.49	0.784
$Tb_{0.9}Eu_{0.1}PCF$	0.12	1.36	0.882
$Tb_{0.5}Eu_{0.5}PCF$	0.02	0.80	0.980

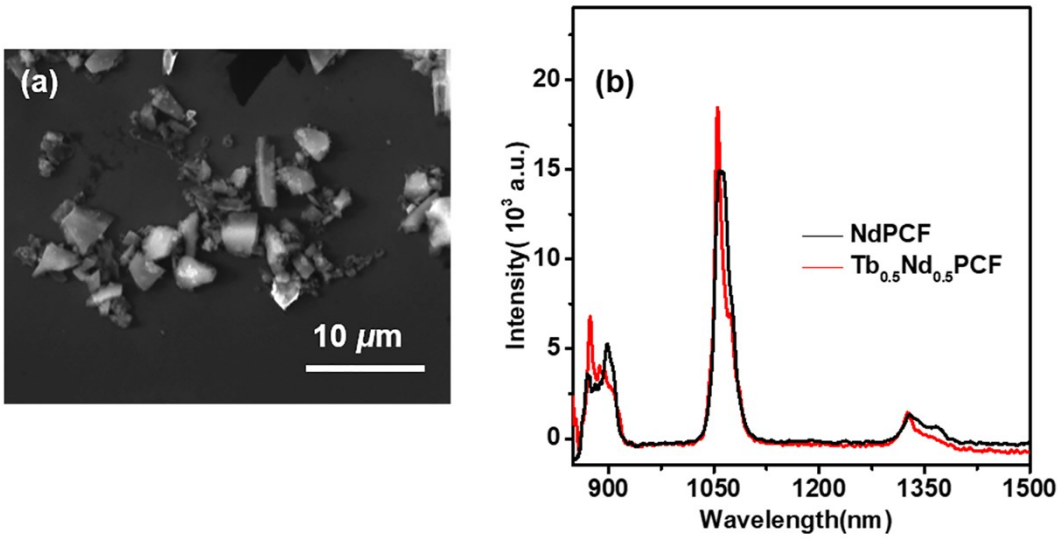


Fig. S11. (a) SEM of TbPCF powder after being ground. **(b)** Emission spectra of the $Tb_{0.5}Nd_{0.5}$PCF and NdPCF excited at 808 nm.