Supporting Information for

Luminescent lanthanide–MOFs with millisecond order lifetime based on conjugated 1, 1'–ethynebenzene–3, 3', 5, 5'–tetracarboxylate ligand: syntheses, structures and photoluminescent properties

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Details for the preparation of 2–9

$[Ce_2(EBTC)_{1.5}(CH_3OH)_4]\cdot 6H_2O$ (2). An identical procedure with **1** was followed to prepare **2** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Ce(NO_3)_3\cdot 6H_2O$. Colorless block-shaped crystals were achieved (yield: 72% based on Ce). Anal. Calcd for $C_{31}H_{29}Ce_2O_{18}$: C, 38.39; H, 2.99. Found: C, 38.16; H, 2.97. Selected IR data (KBr pellet, cm^{-1}): 3438 (m), 3067 (w), 3004 (w), 2913 (w), 1626 (s), 1550 (s), 1436 (s), 1378 (s), 1018 (s), 786 (m), 717 (m).

$[Pr_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (3). An identical procedure with **1** was followed to prepare **3** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Pr(NO_3)_3\cdot nH_2O$. Light-green crystals of **3** were obtained (yield: 68% based on Pr). Anal. Calcd for $C_{31}H_{29}Pr_2O_{18}$: C, 38.33; H, 3.01. Found: C, 38.23; H, 3.03. Selected IR data (KBr pellet, cm^{-1}): 3369

(m), 3072 (w), 3005 (w), 2915 (w), 1628 (s), 1559 (s), 1436 (s), 1375 (s), 1004 (s), 786 (m), 717 (m).

$[Nd_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (4). An identical procedure with **1** was followed to prepare **4** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Nd(NO_3)_3\cdot 6H_2O$. Light-purple crystals of **4** were obtained (yield: 62% based on Nd). Anal. Calcd for $C_{31}H_{29}Nd_2O_{18}$: C, 38.07; H, 2.99. Found: C, 38.13; H, 2.94. Selected IR data (KBr pellet, cm^{-1}): 3394 (m), 3073 (w), 3001 (w), 2918 (w), 1628 (s), 1559 (s), 1436 (s), 1375 (s), 1011 (s), 786 (m), 717 (m).

$[Sm_2(EBTC)_{1.5}(CH_3OH)_4]\cdot 6H_2O$ (5). An identical procedure with **1** was followed to prepare **5** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Sm(NO_3)_3\cdot nH_2O$. Light-yellow crystals of **5** were obtained (yield: 60% based on Sm). Anal. Calcd for $C_{31}H_{29}Sm_2O_{18}$: C, 37.60; H, 2.95. Found: C, 37.34; H, 2.84. Selected IR data (KBr pellet, cm^{-1}): 3438 (m), 3067 (w), 3004 (w), 2914 (w), 1626 (s), 1550 (s), 1436 (s), 1378 (s), 1018 (s), 786 (m), 717 (m).

$[Eu_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (6). An identical procedure with **1** was followed to prepare **6** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Eu(NO_3)_3\cdot nH_2O$. Light-yellow crystals of **6** were obtained (yield: 65% based on Eu). Anal. Calcd for $C_{31}H_{29}Eu_2O_{18}$: C, 37.48; H, 2.92. Found: C, 37.18; H, 2.90. Selected IR data (KBr pellet, cm^{-1}): 3470 (m), 3067 (w), 3003 (w), 2915 (w), 1626 (s), 1550 (s), 1436 (s), 1378 (s), 1018 (s), 786 (m), 717 (m).

$[Gd_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (7). An identical procedure with **1** was followed to prepare **7** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Gd(NO_3)_3\cdot nH_2O$. Colorless crystals of **7** were obtained (yield: 60% based on Gd). Anal. Calcd for $C_{31}H_{29}Gd_2O_{18}$: C, 37.08; H, 2.89. Found: C, 36.75; H, 2.86. Selected IR data (KBr pellet, cm^{-1}): 3421 (m), 3069 (w), 3004 (w), 2915 (w), 1626 (s), 1550 (s), 1440 (s), 1380 (s), 1014 (s), 786 (m), 717 (m).

$[Tb_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (8). An identical procedure with **1** was followed to prepare **8** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Tb(NO_3)_3\cdot nH_2O$. Light-yellow crystals of **8** were obtained (yield: 66% based on Tb). Anal. Calcd for $C_{31}H_{29}Tb_2O_{18}$: C, 36.96; H, 2.88. Found: C, 36.63; H, 2.85. Selected IR data (KBr pellet, cm^{-1}): 3457

(m), 3070 (w), 3004 (w), 2912 (w), 1628 (s), 1558 (s), 1436 (s), 1378 (s), 1018 (s), 786 (m), 717 (m).

$[Dy_2(EBTC)(CH_3OH)_4]\cdot 6H_2O$ (9). An identical procedure with **1** was followed to prepare **9** except $La(NO_3)_3\cdot 6H_2O$ was replaced by $Dy(NO_3)_3\cdot nH_2O$. Colorless crystals of **9** were obtained (yield: 61% based on Dy). Anal. Calcd for $C_{31}H_{29}Dy_2O_{18}$: C, 36.70; H, 2.88. Found: C, 36.87; H, 2.81. Selected IR data (KBr pellet, cm^{-1}): 3438 (m), 3067 (w), 3003 (w), 2915 (w), 1628 (s), 1560 (s), 1448 (s), 1378 (s), 1016 (s), 786 (m), 718 (m).

Table S1 Cell Parameters of Compounds

$C_{31}H_{29}Ln_2O_{18}$ (Ln = La (**1**), Ce (**2**), Pr (**3**), Nd (**4**), Sm (**5**), Gd (**7**), Dy (**9**)

Space group: *P2(1)/n*

Compound	Ln	a (Å)	b(Å)	c(Å)	β / Å	V(Å^3)
1	La	14.674(4)	16.331(4)	21.113(5)	105.917(4)	4866(2)
2	Ce	14.651(4)	16.444(5)	20.994(6)	106.051(4)	4861(2)
3	Pr	14.578(3)	16.669(4)	19.790(4)	107.057(3)	4597.2(18)
4	Nd	14.5952(12)	16.7329(11)	19.5713(14)	107.344(3)	4562.4(6)
5	Sm	14.4388(18)	16.4128(19)	19.3310(12)	107.606(3)	4366.5(8)
7	Gd	14.41(4)	17.08(4)	19.55(5)	107.72(4)	4579(20)
9	Dy	14.4821(18)	16.7137(19)	19.2130(12)	108.039(3)	4421.9(8)

Table S2 Selected bond angles (°) in **4, 5** and **9**

	4		
O6–Nd1–O14	82.82(15)	O6–Nd1–O10	139.68(15)
O14–Nd1–O10	129.59(15)	O6–Nd1–O13	78.62(17)
O14–Nd1–O13	153.69(16)	O10–Nd1–O13	75.68(16)
O6–Nd1–O1	80.90(15)	O14–Nd1–O1	87.32(16)
O10–Nd1–O1	78.06(15)	O13–Nd1–O1	107.75(16)
O6–Nd1–O4	127.69(16)	O14–Nd1–O4	88.42(15)
O10–Nd1–O4	82.13(15)	O13–Nd1–O4	88.33(16)
O1–Nd1–O4	150.23(13)	O6–Nd1–O3	75.90(16)
O14–Nd1–O3	79.63(16)	O10–Nd1–O3	126.89(16)
O13–Nd1–O3	77.88(16)	O1–Nd1–O3	154.56(14)
O4–Nd1–O3	51.80(14)	O6–Nd1–O9	148.73(16)
O14–Nd1–O9	75.81(15)	O10–Nd1–O9	53.89(14)
O13–Nd1–O9	128.12(16)	O1–Nd1–O9	75.61(13)
O4–Nd1–O9	74.78(14)	O3–Nd1–O9	121.19(14)
O2–Nd2–O15	78.03(15)	O2–Nd2–O5	83.68(17)
O15–Nd2–O5	115.05(15)	O2–Nd2–O8	129.29(16)
O15–Nd2–O8	79.44(16)	O5–Nd2–O8	146.93(17)
O2–Nd2–O16	136.18(16)	O15–Nd2–O16	75.88(16)
O5–Nd2–O16	76.43(18)	O8–Nd2–O16	79.06(18)
O2–Nd2–O11	79.91(16)	O15–Nd2–O11	150.43(16)
O5–Nd2–O11	81.54(16)	O8–Nd2–O11	100.03(17)
O16–Nd2–O11	133.40(17)	O2–Nd2–O12	131.26(16)
O15–Nd2–O12	150.50(16)	O5–Nd2–O12	77.16(16)

O8–Nd2–O12	77.64(16)	O16–Nd2–O12	81.72(16)
O11–Nd2–O12	53.36(16)	O2–Nd2–O7	81.72(15)
O15–Nd2–O7	80.56(15)	O5–Nd2–O7	155.81(15)
O8–Nd2–O7	50.01(15)	O16–Nd2–O7	126.93(17)
O11–Nd2–O7	76.99(15)	O12–Nd2–O7	98.37(16)
	5		
O6–Sm1–O10	140.0(2)	O6–Sm1–O14	82.9(2)
O10–Sm1–O14	129.1(2)	O6–Sm1–O13	78.9(2)
O10–Sm1–O13	75.8(2)	O14–Sm1–O13	154.0(2)
O6–Sm1–O1	80.9(2)	O10–Sm1–O1	78.0(2)
O14–Sm1–O1	87.6(2)	O13-Sm1-O1	107.6(2)
O6–Sm1–O4	128.0(2)	O10-Sm1-O4	81.7(2)
O14–Sm1–O4	88.4(2)	O14–Sm1–O4	88.2(2)
O1–Sm1–O4	150.00(18)	O6–Sm1–O3	75.8(2)
O10–Sm1–O3	126.8(2)	O14–Sm1–O3	79.9(2)
O13–Sm1–O3	77.7(2)	O1–Sm1–O3	154.7(2)
O4–Sm1–O3	52.17(19)	O6–Sm1–O9	148.3(2)
O10–Sm1–O9	54.0(2)	O14–Sm1–O9	75.3(2)
O13–Sm1–O9	128.4(2)	O1–Sm1–O9	75.52(18)
O4–Sm1–O9	74.71(19)	O3–Sm1–O9	121.36(19)
O2–Sm2–O15	78.4(2)	O2–Sm2–O8	129.9(2)
O15– Sm2–O8	79.7(2)	O2– Sm2–O5	83.2(2)
O15– Sm2–O5	114.5(2)	O8– Sm2–O5	146.8(2)
O2– Sm2–O11	79.4(2)	O15– Sm2–O11	150.5(2)
O8– Sm2–O11	100.4(2)	O5– Sm2–O11	81.7(2)
O2– Sm2–O16	136.5(2)	O15– Sm2–O16	75.7(2)
O8– Sm2–O16	78.5(2)	O5– Sm2–O16	76.6(2)
O11– Sm2–O15	133.6(2)	O2– Sm2–O12	131.3(2)
O15– Sm2–O12	150.2(2)	O8– Sm2–O12	77.4(2)
O5– Sm2–O12	77.3(2)	O11– Sm2–O12	54.1(2)
O16– Sm2–O12	81.1(2)	O2– Sm2–O7	81.5(2)
O15– Sm2–O7	81.0(2)	O8– Sm2–O7	50.8(2)
O5– Sm2–O7	155.5(2)	O11– Sm2–O7	76.8(2)
O16– Sm2–O7	127.2(2)	O12– Sm2–O7	98.8(2)
	9		
O6–Dy1–O1	80.86(12)	O6–Dy1–O13	78.80(14)
O1–Dy1–O13	106.76(12)	O6–Dy1–O14	82.39(13)
O1–Dy1–O14	88.33(13)	O13–Dy1–O14	153.49(14)
O6–Dy1–O10	139.68(13)	O1–Dy1–O10	77.82(12)
O13–Dy1–O10	75.23(14)	O14–Dy1–O10	130.24(13)
O6–Dy1–O14	127.91(13)	O1–Dy1–O4	150.00(11)
O13–Dy1–O4	89.28(12)	O14–Dy1–O4	87.69(12)
O10–Dy1–O4	82.22(13)	O6–Dy1–O3	75.49(13)
O1–Dy1–O3	154.21(12)	O13–Dy1–O3	78.75(13)

O14–Dy1–O3	78.58(13)	O10–Dy1–O3	127.42(13)
O4–Dy1–O3	52.43(12)	O6–Dy1–O9	148.62(13)
O1–Dy1–O9	76.02(11)	O13–Dy1–O9	128.09(14)
O14–Dy1–O9	76.08(13)	O10–Dy1–O9	54.26(13)
O4–Dy1–O9	74.17(12)	O3–Dy1–O9	121.08(11)
O2–Dy2–O5	82.95(14)	O2–Dy2–O8	130.47(13)
O5–Dy2–O8	146.54(14)	O2–Dy2–O15	78.05(13)
O5–Dy2–O15	114.22(13)	O8–Dy2–O15	79.76(13)
O2–Dy2–O16	135.30(13)	O5–Dy2–O16	76.92(14)
O8–Dy2–O16	78.13(14)	O15–Dy2–O16	74.72(13)
O2–Dy2–O11	80.48(14)	O5–Dy2–O11	81.64(13)
O8–Dy2–O11	100.32(13)	O15–Dy2–O11	151.20(13)
O16–Dy2–O11	133.82(14)	O2–Dy2–O12	131.64(14)
O5–Dy2–O12	77.84(14)	O8–Dy2–O12	77.04(13)
O15–Dy2–O12	150.16(13)	O16–Dy2–O12	82.32(14)
O11–Dy2–O12	53.19(13)	O2–Dy2–O7	82.59(12)
O5–Dy2–O7	155.87(13)	O8–Dy2–O7	50.53(13)
O15–Dy2–O7	81.38(13)	O16–Dy2–O7	126.43(13)
O11–Dy2–O7	77.00(13)	O12–Dy2–O7	97.78(13)

Table S3 Crystallographic data and structural refinements for **1** and **3**

Compound	**1**	**3**
Formula	$C_{31}H_{29}La_2O_{18}$	$C_{31}H_{29}Pr_2O_{18}$
Formula weight	966.35	971.33
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal size /mm	0.20×0.20×0.15	0.19×0.17×0.14
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)/n*
a / *Å*	14.674(4)	14.578(3)
b / *Å*	16.331(4)	16.669(4)
c / *Å*	21.113(5)	19.790(4)
β / *Å*	105.917(4)	107.057(3)
V / *Å*^{3}	4866(2)	4597.2(18)
Z	4	4
F(000)	1892	1892
$\theta_{min,max}$/°	1.51–25.00	1.90–26.00
GOF	1.166	1.042
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.2050, 0.4868	0.1287, 0.3054

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

Table S4 Selected bond lengths (Å) and angles (°) in **1** and **3**

1

bond lengths

La1–O10	2.62(3)	La1–O5	2.56(3)	La1–O1	2.58(3)
La1–O6	2.69(3)	La1–O8	2.63(2)	La1–O13	2.58(4)
La1–O4	2.43(2)	La1–O14	2.51(3)	La2–O7	2.43(2)
La2–O3	2.47(3)	La2–O12	2.50(4)	La2–O11	2.48(3)
La2–O16	2.69(2)	La2–O15	2.59(3)	La2–O2	2.62(2)
La2–O9	2.60(3)				

bond angles

O4–La1–O14	84.5(9)	O4–La1–O5	123.5(8)	O14–La1–O5	146.4(9)
O4–La1–O1	82.4(10)	O14–La1–O1	137.8(10)	O5–La1–O1	70.3(10)
O4–La1–O13	153.6(8)	O14–La1–O13	77.6(9)	O5–La1–O13	69.4(9)
O1–La1–O13	123.7(10)	O4–La1–O10	74.2(8)	O14–La1–O10	142.9(9)
O5–La1–O10	50.3(8)	O1–La1–O10	69.5(10)	O13–La1–O10	109.5(8)
O4–La1–O8	77.9(8)	O14–La1–O8	73.1(8)	O5–La1–O8	126.7(8)
O1–La1–O8	65.0(10)	O13–La1–O8	114.4(8)	O10–La1–O8	128.9(8)
O6–La1–O4	127.0(8)	O14–La1–O6	80.0(8)	O5–La1–O6	94.0(8)
O1–La1–O6	76.5(10)	O13–La1–O6	69.0(8)	O10–La1–O6	137.0(8)
O8–La1–O6	49.0(8)	O7–La2–O3	80.1(9)	O7–La2–O11	152.6(9)
O3–La2–O11	90.8(9)	O7–La2–O12	94.4(10)	O3–La2–O12	144.2(11)
O11–La2–O12	78.1(10)	O7–La2–O15	85.4(8)	O3–La2–O15	77.8(9)
O11–La2–O15	118.0(9)	O12–La2–O15	137.4(10)	O7–La2–O9	70.8(8)
O3–La2–O9	138.6(9)	O11–La2–O9	127.8(9)	O12–La2–O9	68.6(10)
O15–La2–O9	71.3(8)	O7–La2–O2	120.2(8)	O3–La2–O2	141.5(8)
O11–La2–O2	82.6(8)	O12–La2–O2	71.2(10)	O15–La2–O2	72.4(8)
O9–La2–O2	49.6(7)	O7–La2–O16	128.3(7)	O3–La2–O16	70.7(8)
O11–La2–O16	70.7(8)	O12–La2–O16	133.5(9)	O15–La2–O16	47.9(8)
O9–La2–O16	105.3(7)	O2–La2–O16	71.4(7)		

3

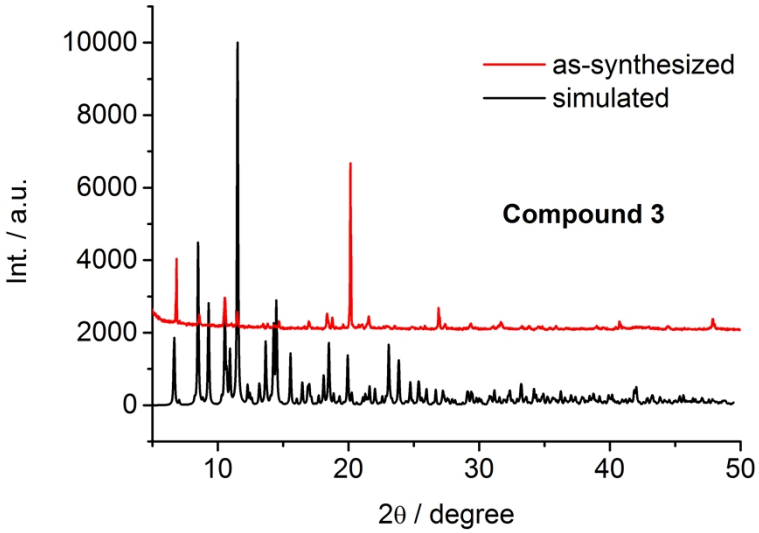
bond lengths

Pr1–O1	2.390(11)	Pr1–O3	2.581(13)	Pr1–O4	2.481(14)
Pr1–O6	2.489(17)	Pr2–O9	2.465(14)	Pr2–O10	2.592(11)
Pr2–O13	2.343(13)	Pr2–O14	2.550(14)	Pr1–O2	2.47(3)
Pr1–O7	2.575(15)	Pr1–O8	2.432(13)	Pr2–O16	2.39(2)
Pr1–O5	2.483(18)	Pr2–O11	2.397(12)	Pr2–O15	2.499(13)
Pr2–O12	2.35(2)				

bond angles

O1–Pr1–O8	84.1(4)	O1–Pr1–O2	81.4(8)	O8–Pr1–O2	131.8(12)
O1–Pr1–O4	128.8(4)	O8–Pr1–O4	143.6(5)	O2–Pr1–O4	75.3(11)
O1–Pr1–O5	151.2(6)	O8–Pr1–O5	83.5(7)	O2–Pr1–O5	87.7(9)

O4–Pr1–O5	72.7(6)	O1–Pr1–O6	79.3(6)	O8–Pr1–O6	79.5(7)
O2–Pr1–O6	140.8(10)	O4–Pr1–O6	90.9(7)	O5–Pr1–O6	123.5(7)
O1–Pr1–O7	127.5(4)	O8–Pr1–O7	72.8(5)	O2–Pr1–O7	147.3(9)
O4–Pr1–O7	74.0(6)	O5–Pr1–O7	72.6(6)	O6–Pr1–O7	50.9(5)
O1–Pr1–O3	77.7(4)	O8–Pr1–O3	148.2(6)	O2–Pr1–O3	71.0(11)
O4–Pr1–O3	51.8(4)	O5–Pr1–O3	123.7(6)	O6–Pr1–O3	71.7(7)
O7–Pr1–O3	98.1(6)	O13–Pr2–O12	85.1(8)	O13–Pr2–O16	76.9(10)
O12–Pr2–O16	154.5(9)	O13–Pr2–O11	80.0(5)	O12–Pr2–O11	88.0(7)
O16–Pr2–O11	106.2(10)	O13–Pr2–O9	139.1(7)	O12–Pr2–O9	129.8(6)
O16–Pr2–O9	74.3(8)	O11–Pr2–O9	80.8(5)	O13–Pr2–O15	128.9(5)
O12–Pr2–O15	88.6(9)	O16–Pr2–O15	88.8(11)	O11–Pr2–O15	150.4(4)
O9–Pr2–O15	79.0(6)	O13–Pr2–O14	78.0(5)	O12–Pr2–O14	81.5(9)
O16–Pr2–O14	77.3(10)	O11–Pr2–O14	156.3(5)	O 9–Pr2–O14	122.1(6)
O15–Pr2–O14	51.0(4)	O13–Pr2–O10	151.6(5)	O12–Pr2–O10	78.8(6)
O16–Pr2–O10	124.6(8)	O11–Pr2–O10	76.2(4)	O 9–Pr2–O10	51.0(4)
O15–Pr2–O10	74.3(4)	O14–Pr2–O10	121.8(4)		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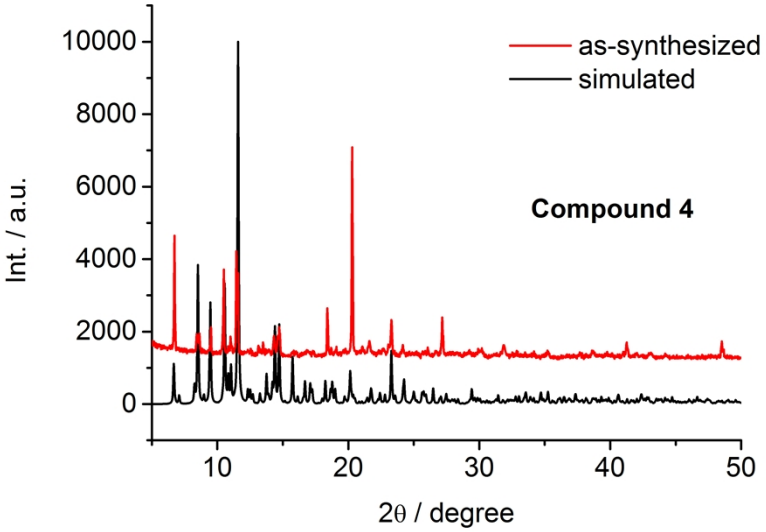
40
50


as-synthesized
simulated
Compound 4
Int. / a.u.
2θ / degree
10000
8000
6000
4000
2000
0
10
20
30
40
50

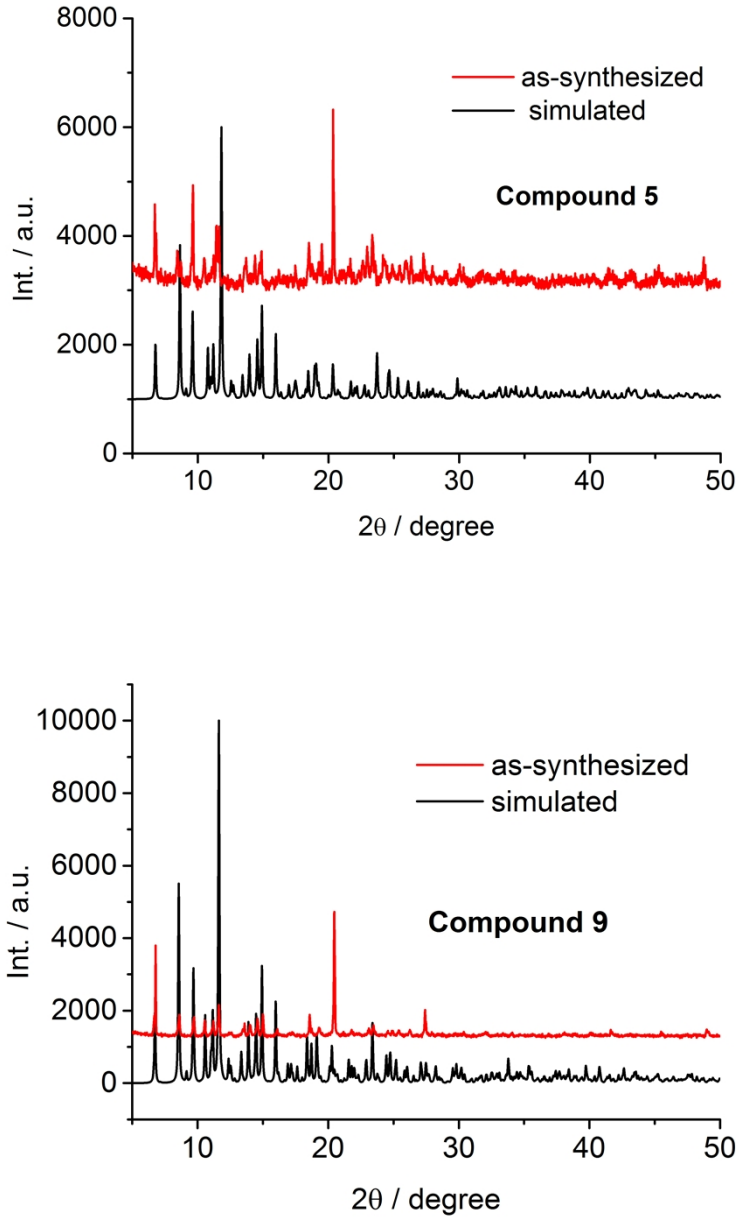


Fig. S1 PXRD patterns of simulated from the X–ray single–crystal structures and as-synthesized samples of **3**, **4**, **5** and **9**.

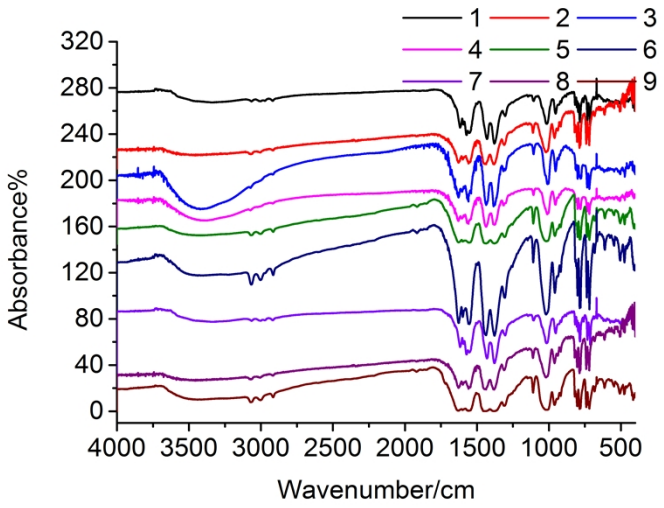


Fig. S2 The IR spectra of **1–9** recorded from a KBr pellet.

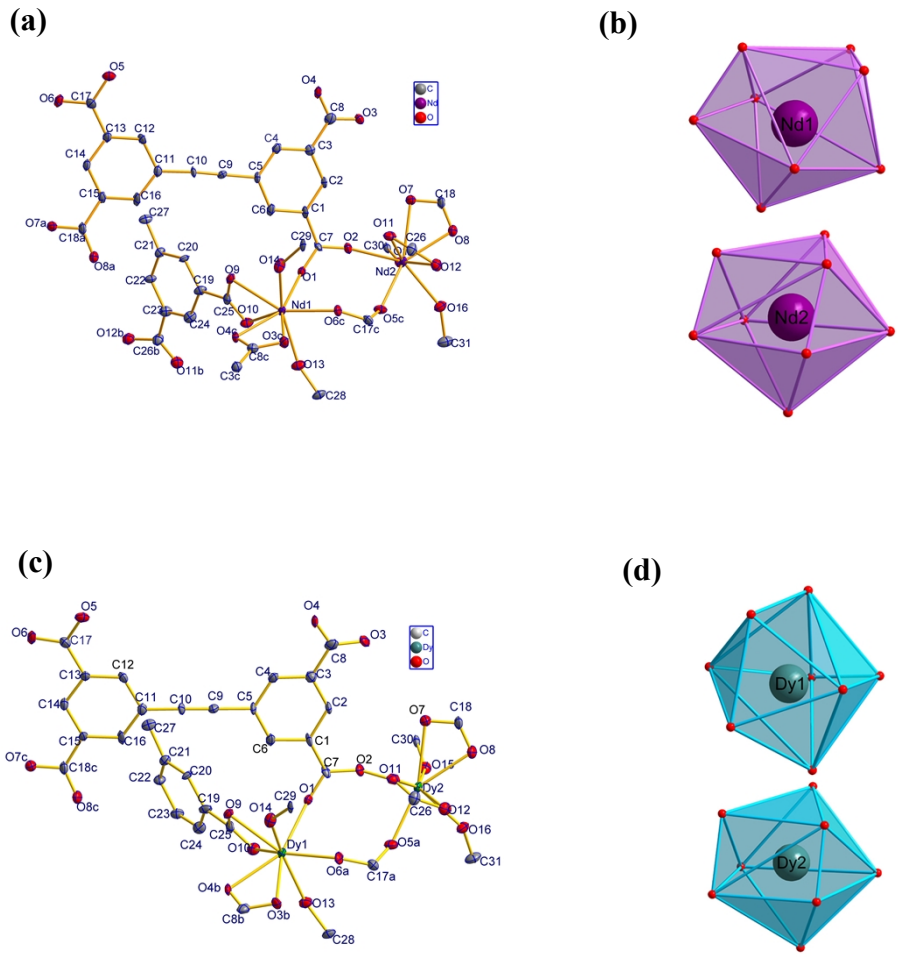


Fig. S3 (a) Coordination environments of Nd^{3+} ions with the H atoms omitted for clarity; symmetry codes: a = -1+x, y, z; b = 1.5-x, 0.5+y, 0.5-z; c = 0.5+x, 0.5-y,-0.5+z; (b) coordination polyhedron of Nd^{3+} ions; (c) coordination environments of Dy^{3+} ions with the H atoms omitted for clarity; symmetry codes: a = 0.5+x, 0.5-y, -0.5+z; b = -0.5+x, 0.5-y, -0.5+z; c = -1+x, y, z; (d) coordination polyhedron of Dy^{3+} ions.

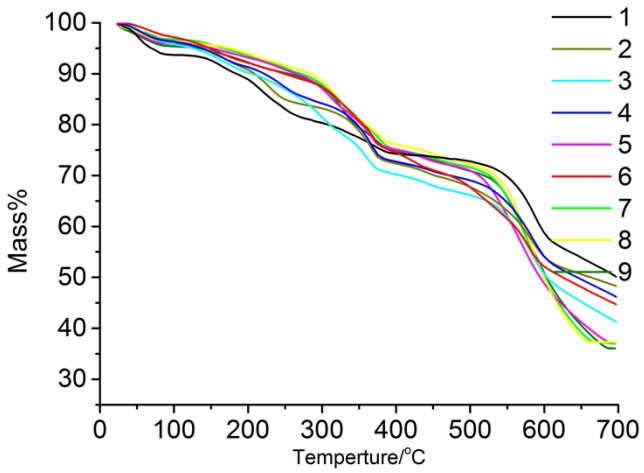


Fig. S4 The TG curves of **1–9**.

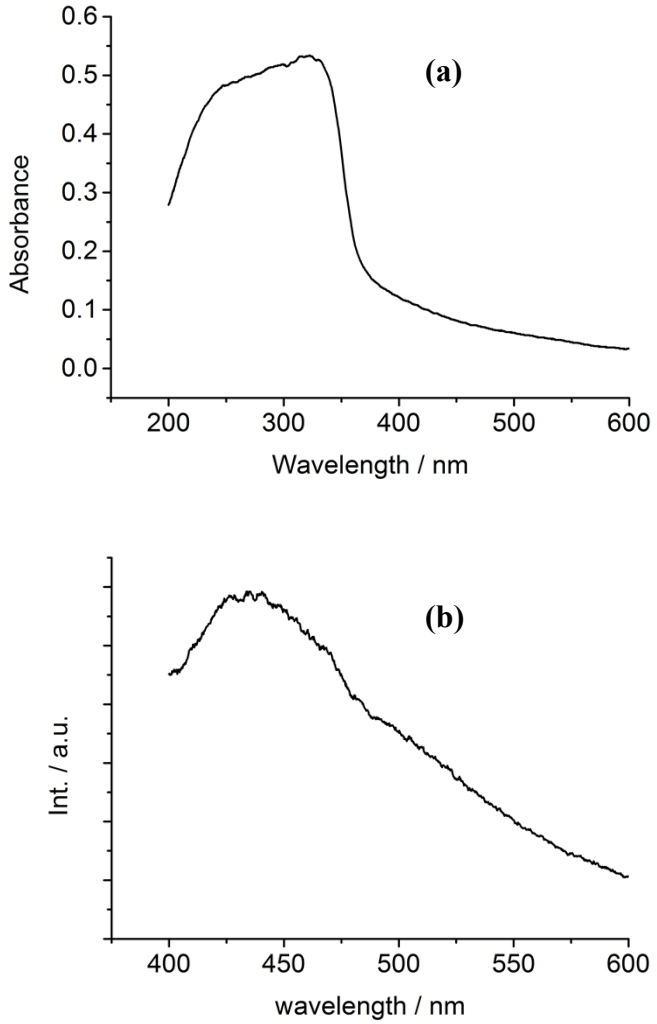


Fig. S5 (a) UV-vis absorption and (b) emission spectra of H_4EBTC in solid state at room temperature.

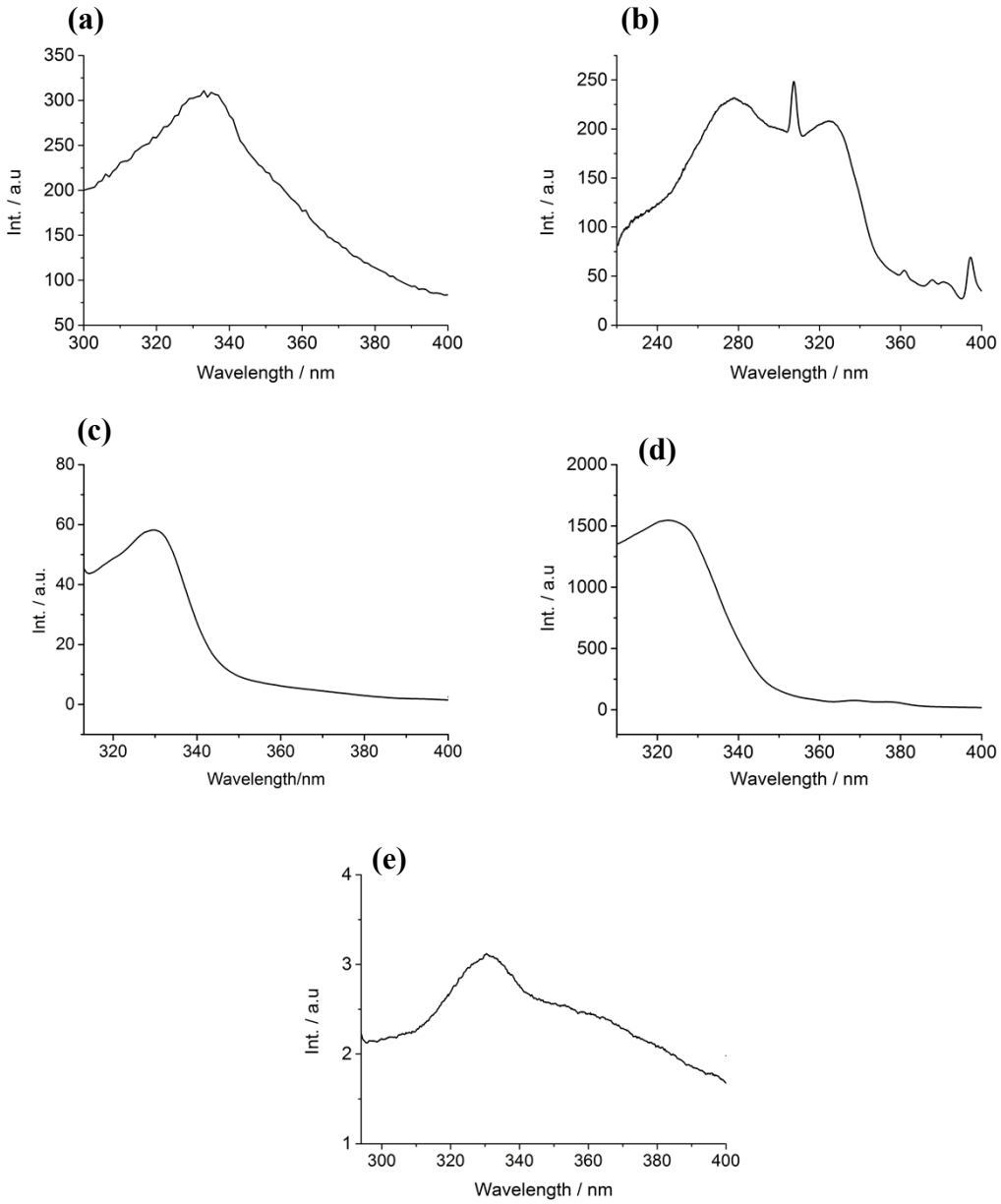


Fig. S6 The excitation spectra of **1** (a), **6** (b), **7** (c), **8** (d), **9** (e) in solid state at room temperature, monitored at 556 nm, 618 nm, 556 nm, 546 nm and 575 nm respectively.