# Supporting Information

## Structure variations of series lanthanide complexes constructed from quinoline carboxylate ligand: photoluminescent properties and PMMA matrices doping

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## Experimental section

### Materials and methods

All reagents were commercially available and used without further purification. Infrared spectra were obtained from KBr pellets, using a Nicolet Avatar–360 Infrared spectrometer in the 4000–400 $cm^{-1}$ region. Elemental analyses were performed on a Perkin–Elmer 240c element analyzer. $^{13}C$ NMR spectra were recorded on a Bruker ACF 400 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5°–50° using Cu Kα radiation with a Shimadzu XRD-6000 X-ray diffractometer. UV–vis spectra were obtained on a Perkin–Elmer Lambda 20 spectrometer. Luminescence analysis and luminescence decay curves were recorded on Edinburgh FLS 920 luminescence spectrometer at 298 K and 77 K.

**Synthesis of $\{[KEu(Hqlc)(qlc)(H_2O)_6(OH)]^{2+}\cdot 2Cl^-\}_n$ (1·Eu)**

A mixture of $EuCl_3\cdot 6H_2O$ (36.6 mg, 0.1 mmol) and $H_2$qldc (32.6 mg, 0.15 mmol) in $CH_3CN$ (6 mL) and KOH (0.3 mL) was stirred at room temperature for 15 min after which the mixture was transferred to a Teflon–lined stainless steel vessel (15 mL). The vessel was heated at 120 $^oC$ for 5 days. Colorless block–shaped crystals were collected and washed with water and then dried in air (43% yield based on Eu(III)). Anal. Calcd. For $C_{20}H_{26}Cl_2N_2O_{11}KEu$: C, 32.80, H, 3.58, N, 3.82%; Found: C, 32.76, H, 3.57, N, 3.82%. IR(KBr/$cm^{-1}$): 3340 (br), 1621 (s), 1564 (s), 1457 (s), 1400 (s), 1298 (w), 1209 (w), 1140 (w), 1064 (w), 874 (w), 785 (m), 590 (m), 469 (w), 425 (w).

**Synthesis of $\{[Eu(qlc)_2(phen)(H_2O)_2]^+\cdot Cl^-\}\cdot CH_3CN$ (2·Eu)**

A mixture of $EuCl_3\cdot 6H_2O$ (36.6 mg, 0.1 mmol), $H_2$qldc (32.6 mg, 0.15 mmol), and phen ligand (29.7 mg, 0.15 mmol) in $CH_3CN$ (6 mL) was stirred at room temperature for 15 min after which the mixture was transferred to a Teflon–lined stainless steel vessel (15 mL). The vessel was heated at 120 $^oC$ for 4 days. Colorless block–shaped crystals were collected and washed with water and then dried in air (43% yield based on Eu(III)). Anal. Calcd. For $C_{34}H_{27}Cl_2N_5O_6Eu$: C, 49.53, H, 3.30, N, 8.49%; Found: C, 49.50, H, 3.29, N, 8.48%. IR(KBr/$cm^{-1}$): 3429 (br), 1800 (w), 1712 (s), 1631 (s), 1579 (m), 1496 (m), 1418 (s), 1296 (s), 1180 (s), 1135 (s), 986 (m), 926 (w), 890 (w), 767 (s), 625 (w), 587 (m), 529 (m), 464 (m).

**Synthesis of $[Eu(qlc)_2(phen)(NO_3)]\cdot H_2O$ (3·Eu)**

A mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (44.6 mg, 0.1 mmol), $H_2$qldc (65.1 mg, 0.3 mmol), and phen ligand (19.8 mg, 0.1 mmol) in $CH_3CN$ (6 mL) was stirred at room temperature for 15 min after which the mixture was transferred to a Teflon–lined stainless steel vessel (15 mL). The vessel was heated at 160 $^oC$ for 4 days. Light yellow block–shaped crystals were collected and washed with water and then dried in air (41% yield based on Eu(III)). Anal. Calcd. For $C_{32}H_{22}EuN_5O_8$: C, 50.80, H, 2.93, N, 9.26%; Found: C, 50.55 H, 2.90, N, 9.19%. IR(KBr/$cm^{-1}$): 3049 (br), 1600 (s), 1421 (s), 1321 (m), 1261 (w), 1205 (w), 1106 (w), 848 (w), 800 (s), 730 (m), 667 (m), 590 (m), 474 (w).

**Synthesis of $[Ln(qlc)_2(H_2O)_4]\cdot(qlc)\cdot(H_2O)$ (Ln = Eu(4·Eu), Sm(5·Sm), Gd(6·Gd), Tb(7·Tb), Dy(8·Dy), Ho(9·Ho))**

Complexes **4-9** were prepared with similar procedure as described below. A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.1 mmol), $H_2$qldc (0.2 mmol), and $NaHSO_3$ ligand (0.1 mmol) in $H_2O$ (3 mL) and $CH_3CN$ (3 mL) was stirred at room temperature for 15 min after which the mixture was transferred to a Teflon–lined stainless steel vessel (15 mL). The vessel was heated at 120 $^oC$ for 4–6 days. After cooling to room temperature, the precipitations were removed through filtrating from the product. Then the product was volatilized for two days at room temperature until block–shaped colorless crystals appeared. The yield of **4·Eu** was 65% based on Eu. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Eu$: C, 47.50, H, 3.72, N, 5.54%; Found: C, 47.43, H, 3.70, N, 5.51%. IR(KBr/$cm^{-1}$): 3200 (br), 1615 (s), 1533 (s), 1411 (s), 1318 (s), 1259 (w), 1197 (w), 1130 (w), 952 (w), 794 (s), 744 (m), 593 (m), 561 (m), 478(w). The yield of **5·Sm** was 63% based on Sm. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Sm$: C,47.60, H, 3.73, N, 5.55%; Found: C, 47.53, H, 3.69, N, 5.52%. IR(KBr/$cm^{-1}$): 3240 (br), 1619 (s), 1540 (s), 1411 (s), 1318 (m), 1260 (w), 1195 (w), 1130 (w), 949 (w), 791 (s), 736 (m), 582 (m), 467 (w). The yield of **6·Gd** was 56% based on Gd. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Gd$: C,47.17, H, 3.69, N, 5.50%，Found: C, 47.53, H, 3.67, N, 5.48%. IR(KBr/$cm^{-1}$): 3250 (br), 1618 (s), 1541 (s), 1408 (s), 1320 (s), 1195(w), 1137(m), 983(w), 792(s), 749(m), 593(m), 467 (w). The yield of **7·Tb** was 58% based on Tb. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Tb$: C,47.07, H, 3.69, N, 5.49%，Found: Tb, 20.67, C, 46.98, H, 3.68, N, 5.48%. IR(KBr/$cm^{-1}$): 3300 (br), 1618 (s), 1541 (s), 1411 (s), 1325 (s), 1269 (w), 1199 (w), 1139 (w), 969 (w), 795 (s), 739 (m), 593 (m), 467 (w). The yield of **8·Dy** was 59% based on Dy. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Dy$: C,46.85, H, 3.67, N,

5.46%，Found: C, 46.78, H, 3.67, N, 5.44%. IR(KBr/$cm^{-1}$)：3300 (br), 1619 (s), 1534 (s), 1411 (s), 1318 (s), 1260 (w), 1195 (w), 1130 (w), 949 (w), 791 (s), 736 (m), 582 (m), 467 (w). The yield of **9·Ho** was 52% based on Ho. Anal. Calcd. For $C_{30}H_{28}N_3O_{11}Ho$: C,46.70, H, 3.66, N, 5.45%, Found: C, 47.58, H, 3.64, N, 5.46%. IR(KBr/$cm^{-1}$): 3100 (br), 1612 (s), 1546 (s), 1417 (s), 1311 (s), 1261 (w), 1192 (w), 1128 (w), 977 (w), 792 (s), 748 (w), 591 (m), 473 (w).

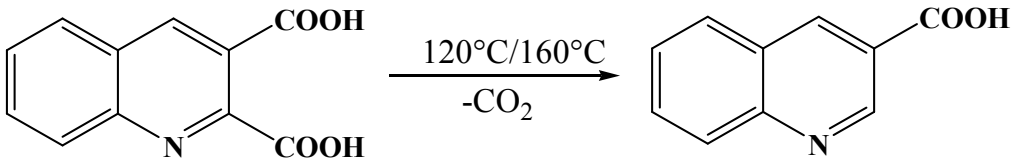
**Fabrication of 3–PMMA and 4–PMMA films**

The PMMA powder was dissolved in *N,N′*–dimethylformamide (DMF), followed by addition of the required of complexes **3** or **4** in DMF solution and resulting mixture was heated at 50~55 $^oC$ for 45 min. The polymer film was obtained after the total evaporation of excess solvent at 60 $^oC$ according to the literatures.

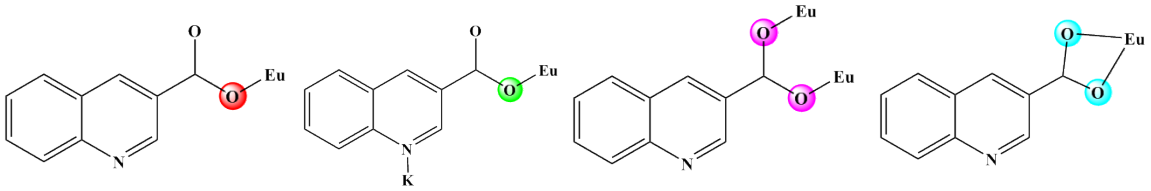
**X–ray crystallography**

The X–ray diffraction data taken at room temperature for complexes **1–9** were collected on a Rigaku R–AXIS RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite–monochromated Mo K$\alpha$ radiation ($\lambda$ = 0. 71073 Å). Complex **1** is a twin crystal. The structures of **1–9** were solved by direct methods and refined on $F^2$ by the full–matrix least squares using the SHELXTL–97 crystallographic software.[1] Anisotropic thermal parameters are refined to all of the non–hydrogen atoms. The hydrogen atoms were held in calculated positions on carbon atoms and nitrogen atoms and that were directly included in the molecular formula on water molecules. The CCDC 1041890–1041898 contain the crystallographic data **1–9** of this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit. Crystal structure data and details of the data collection and the structure refinement are listed as Table 1, selected bond lengths and bond angles of complexes **1–9** are listed as Table S1 and Table S2 (Supporting Information).

[1] Shelxtl N.T.1999. Crystal structure analysis package, version 5.10, Bruker AXS, Analytical X-ray System, Madison, WI.

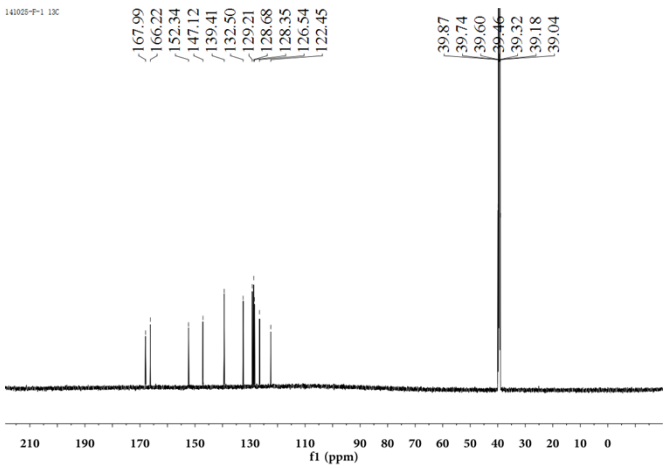



**Scheme S1**. Hydrothermal decarboxylation from $H_2$qldc to Hqlc.

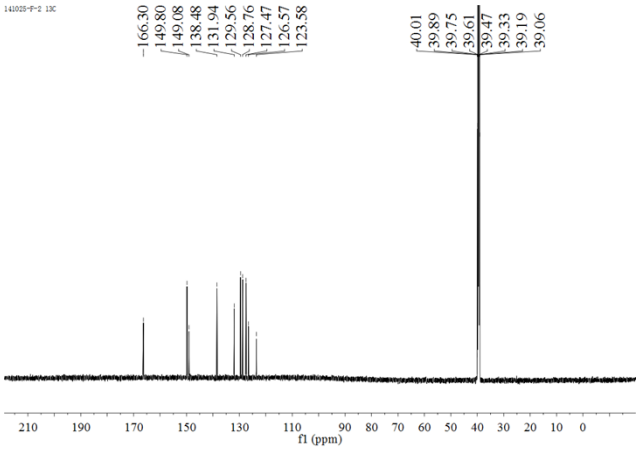



$\mu_1$-$\eta_O{}^1$ (I) $\mu_2$-$\eta_O{}^1$ : $\eta_N{}^1$ (II) $\mu_2$-$\eta_O{}^1$:$\eta_O{}^1$ (III) $\mu_1$-$\eta_O{}^1$:$\eta_O{}^1$ (IV)

**Scheme S2**. Different coordination modes observed for the $qlc^-$ ligand.




(a)




(b)

**Fig. S1** The $^{13}C$ NMR spectra of $H_2$qldc (a) and Hqlc (b) ligand.

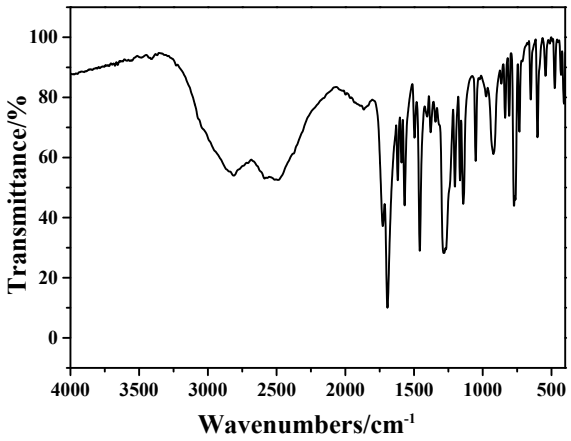



**Fig. S2** The IR spectra of free ligand.

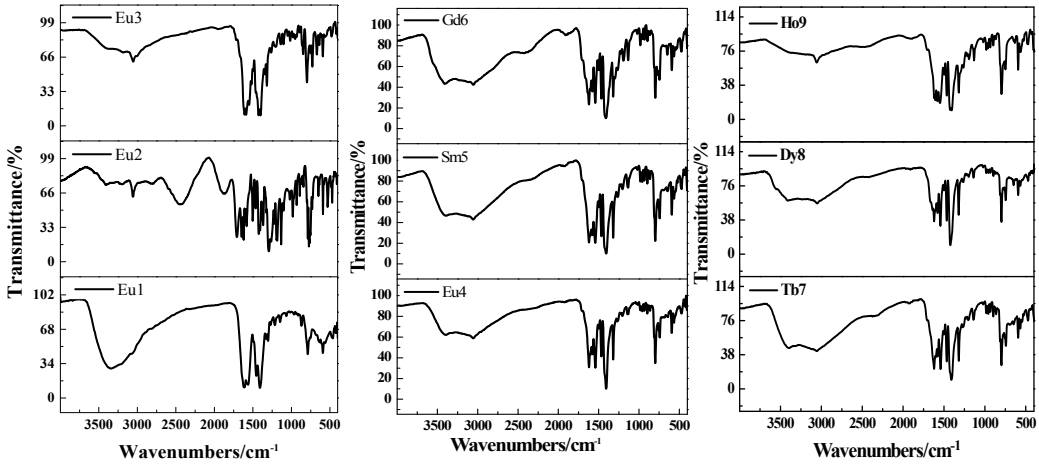



**Fig. S3** The IR spectra of complexes **1-9**.

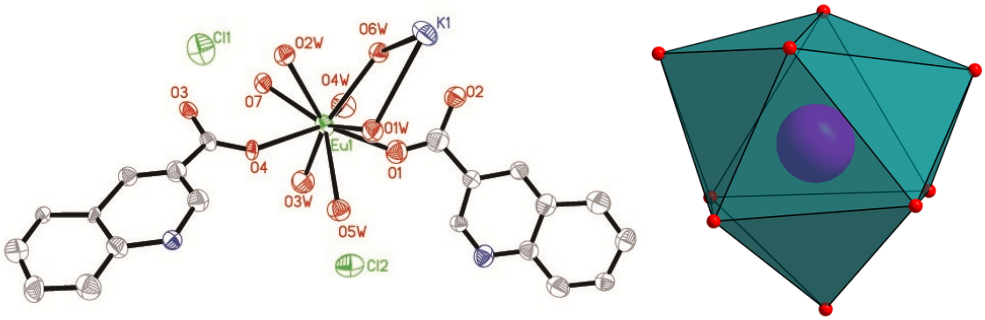



**Fig. S4** The metal coordination environment in **1** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity) and polyhedral representation of the coordination sphere of the $Eu^{3+}$ centre in **1**.

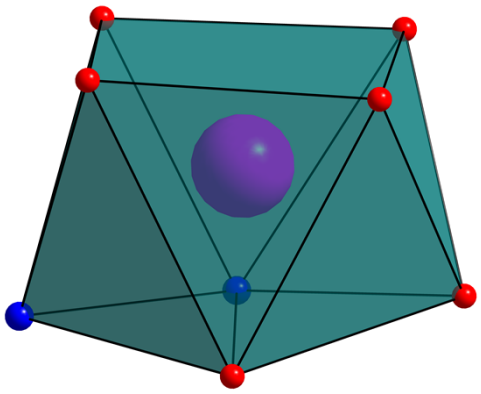


**Fig. S5** Polyhedral representation of the coordination sphere of the $Eu^{3+}$ centre in **2**.

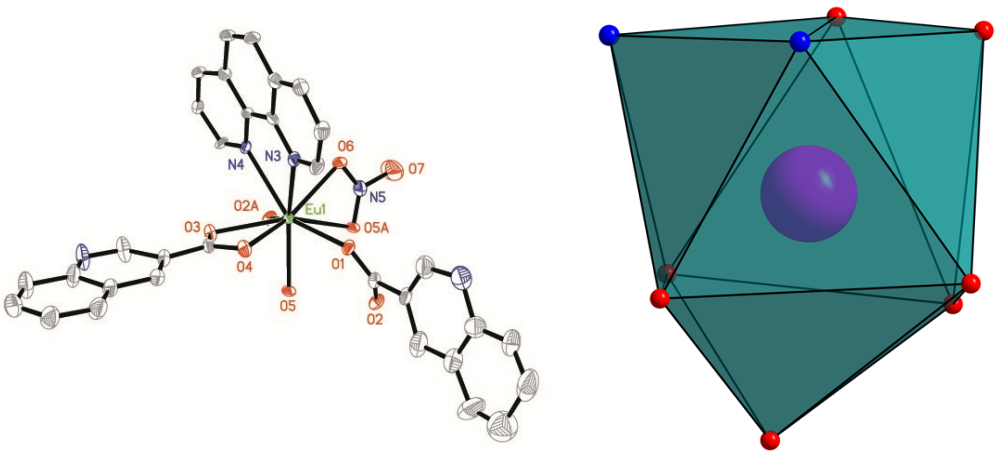



**Fig. S6** The metal coordination environment in **3** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms and free water molecule are omitted for clarity) and polyhedral representation of the coordination sphere of the $Eu^{3+}$ centre in **3**.

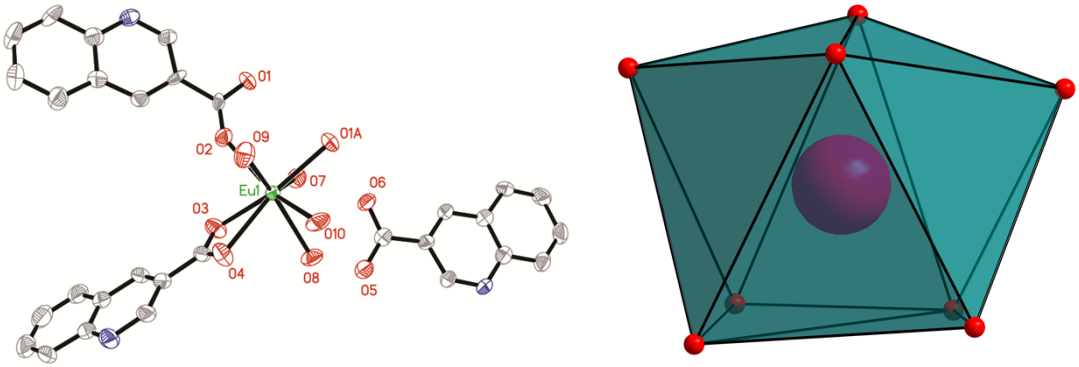



**Fig. S7** The metal coordination environment in **3** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms and free water molecule are omitted for clarity) and Polyhedral representation of the coordination sphere of the $Eu^{3+}$ centre in **4**.

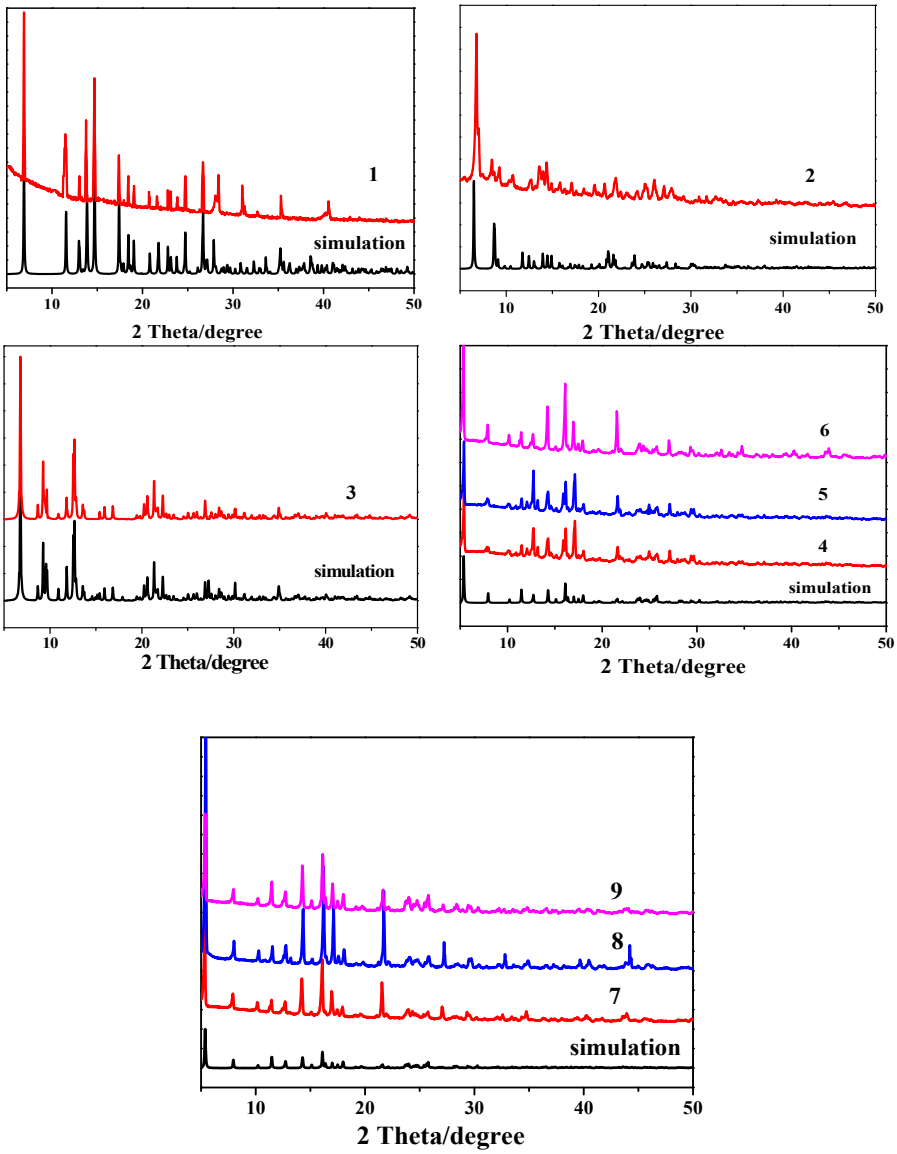



**Fig. S8** The PXRD patterns of complexes **1-9** with the relevant simulated patterns.

**UV-vis properties**

The UV–vis spectra of Hqlc and complexes **1–8** were measured in $CH_3CN$ at room temperature ($c$ = 2 × $10^{-5}$ M). As illustrated in Fig. S9, the maximum absorption bands are at 240 nm for Hqlc ligand and 286–294 nm for complexes **1–8**. The electronic absorption spectra of complexes **1–8** are similar and red shifted in contrast to Hqlc ligand, which is attributed to the metal perturbed intraligand π→π* transition.

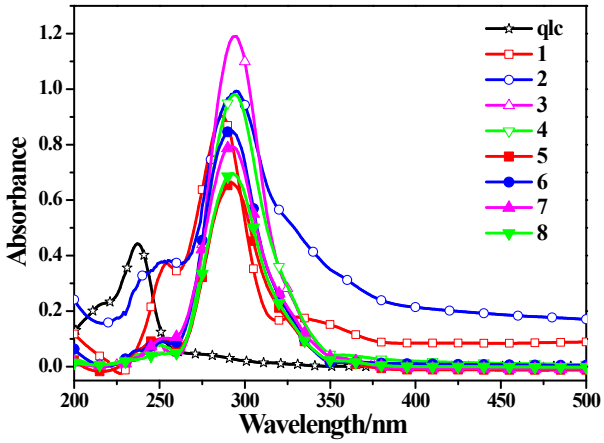



**Fig. S9** UV–vis absorption spectra of Hqlc ligand and complexes **1–8** in $CH_3CN$ solution.

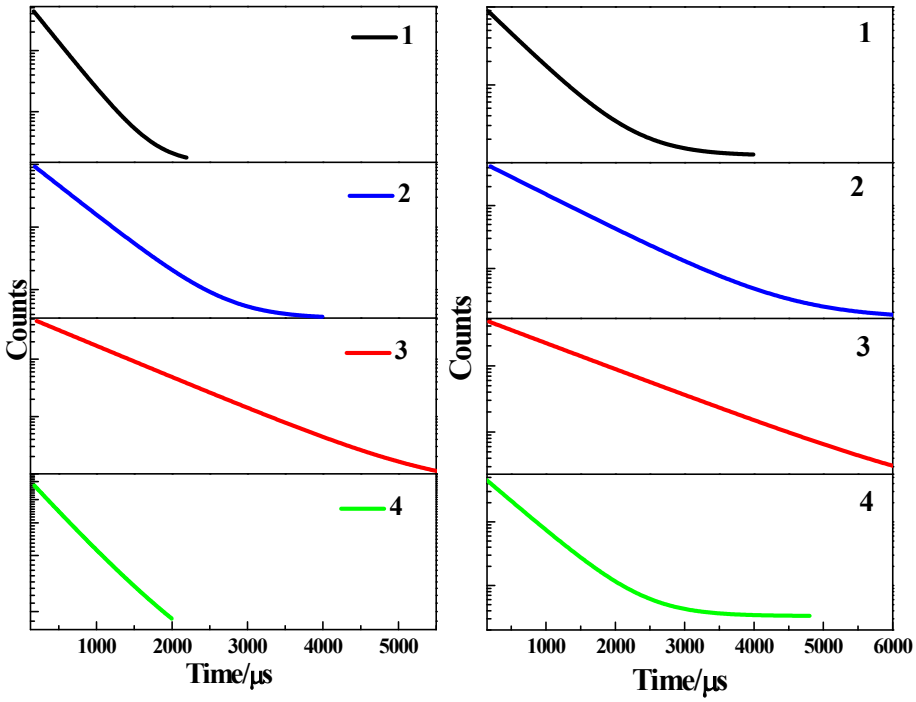



**Fig. S10** Luminescence decay curves of complexes **1-4** recorded at 298 K (left) and 77 K (right) monitored at 614 nm.

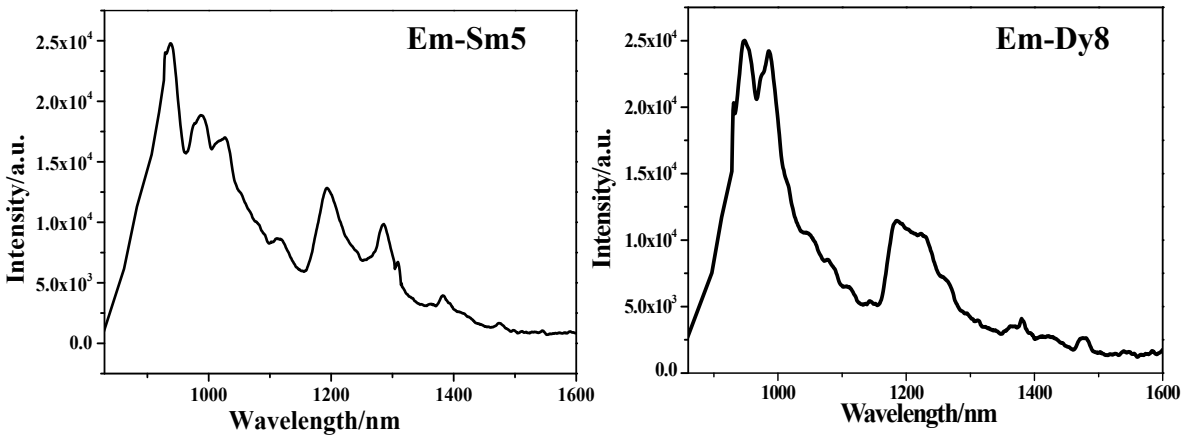



**Fig. S11** NIR emission spectra of complexes **5** (left) and **8** (right) in the solid state at 298 K.

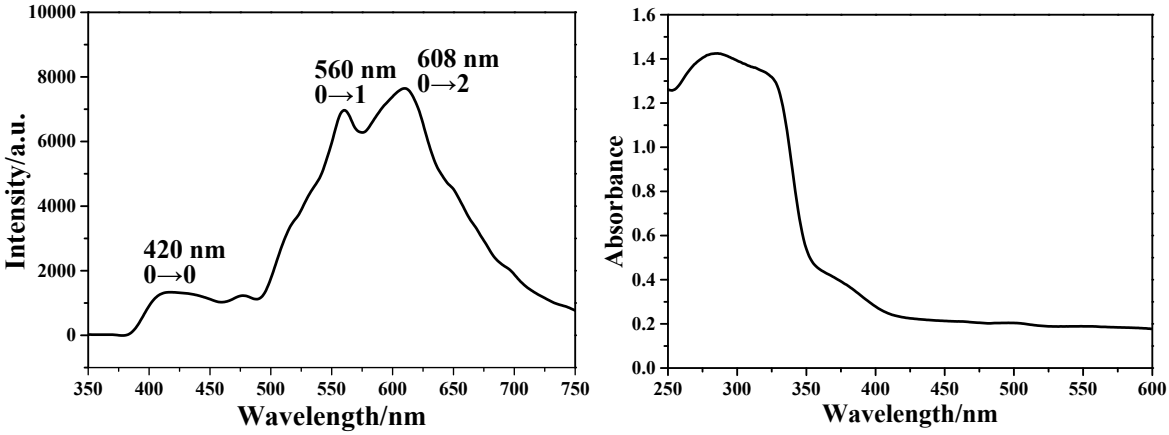



**Fig. S12** Phosphorescence spectra of complex **6** in the solid-state at 77 K (left) and UV-vis absorption spectrum of Hqlc ligand in the solid state (right).

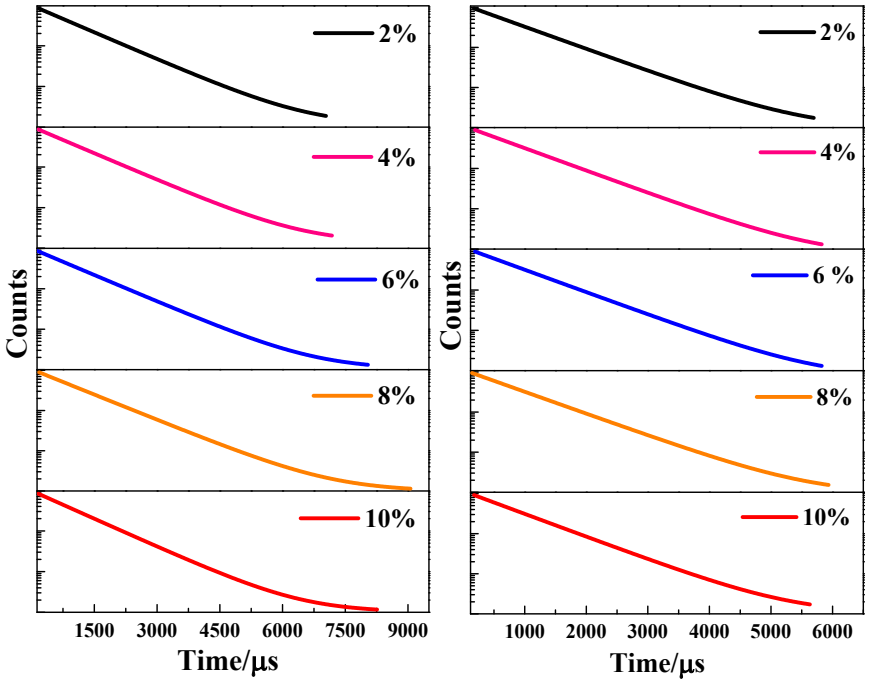



**Fig. S13** The luminescence decay curves of **3**–PMMA and **4**–PMMA at different concentrations.

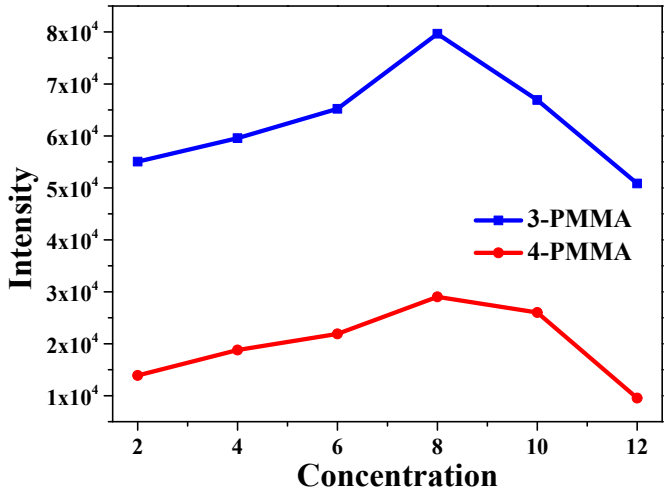



**Fig. S14** Photoluminescence intensity of **3**-PMMA and **4**-PMMA with different doping concentrations.

**Table S1**. Selected bond length in complexes **1-9**.

| **1** | | **2** | | **3** | |
|---|---|---|---|---|---|
| Eu(1)-O(1) | 2.282(17) | Eu(1)-O(1) | 2.319(3) | Eu(1)-O(5) | 2.354(6) |
| Eu(1)-O(4) | 2.383(14) | Eu(1)-O(4) | 2.329(3) | Eu(1)-O(1) | 2.376(6) |
| Eu(1)-O(3W) | 2.392(17) | Eu(1)-O(2)#3 | 2.357(3) | Eu(1)-O(2)#4 | 2.384(7) |
| Eu(1)-O(4W) | 2.409(19) | Eu(1)-O(3) | 2.361(3) | Eu(1)-O(3) | 2.454(6) |
| Eu(1)-O(1W) | 2.439(15) | Eu(1)-O(5) | 2.423(3) | Eu(1)-O(6) | 2.491(7) |
| Eu(1)-O(7) | 2.510(16) | Eu(1)-O(6) | 2.480(3) | Eu(1)-O(4) | 2.497(6) |
| Eu(1)-O(2W) | 2.515(15) | Eu(1)-N(1) | 2.594(3) | Eu(1)-N(4) | 2.584(8) |
| Eu(1)-O(6W) | 2.564(15) | Eu(1)-N(2) | 2.647(3) | Eu(1)-O(5)#4 | 2.593(6) |
| Eu(1)-O(5W) | 2.603(11) | Eu(1)-Eu(1)#3 | 4.3638(4) | Eu(1)-N(3) | 2.620(8) |
| K(1)-N(1)#1 | 3.03(2) | | | Eu(1)-Eu(1)#4 | 3.9432(9) |
| K(1)-O(1W) | 3.049(16) | | | | |
| K(1)-O(6W) | 3.060(15) | | | | |
| K(1)-O(4W)#2 | 3.202(19) | | | | |
| **4** | | **5** | | **6** | |
| Eu(1)-O(1)#5 | 2.303(7) | Sm(1)-O(3) | 2.325(3) | Gd(1)-O(3) | 2.303(3) |
| Eu(1)-O(2) | 2.363(7) | Sm(1)-O(4) | 2.364(3) | Gd(1)-O(4) | 2.345(3) |
| Eu(1)-O(9) | 2.417(8) | Sm(1)-O(10) | 2.429(3) | Gd(1)-O(9) | 2.405(3) |
| Eu(1)-O(7) | 2.428(7) | Sm(1)-O(9) | 2.436(3) | Gd(1)-O(10) | 2.407(3) |
| Eu(1)-O(4) | 2.440(8) | Sm(1)-O(7) | 2.440(3) | Gd(1)-O(8) | 2.413(3) |
| Eu(1)-O(8) | 2.433(7) | Sm(1)-O(8) | 2.462(3) | Gd(1)-O(2) | 2.442(3) |
| Eu(1)-O(10) | 2.441(7) | Sm(1)-O(2) | 2.467(3) | Gd(1)-O(7) | 2.444(3) |
| Eu(1)-O(3) | 2.453(8) | Sm(1)-O(1) | 2.469(3) | Gd(1)-O(1) | 2.456(3) |
| Eu(1)-O(1)#5 | 2.303(7) | Sm(1)-O(3) | 2.325(3) | Gd(1)-O(3) | 2.303(3) |
| Eu(1)-O(2) | 2.363(7) | Sm(1)-O(4) | 2.364(3) | Gd(1)-O(4) | 2.345(3) |
| **7** | | **8** | | **9** | |
| Tb(1)-O(3) | 2.282(12) | Dy(1)-O(3) | 2.301(3) | Ho(1)-O(4) | 2.259(5) |
| Tb(1)-O(4) | 2.353(14) | Dy(1)-O(4) | 2.349(3) | Ho(1)-O(3) | 2.315(5) |
| Tb(1)-O(10) | 2.358(14) | Dy(1)-O(10) | 2.403(3) | Ho(1)-O(5) | 2.367(5) |
| Tb(1)-O(7) | 2.396(14) | Dy(1)-O(9) | 2.406(3) | Ho(1)-O(7) | 2.372(5) |
| Tb(1)-O(8) | 2.399(15) | Dy(1)-O(8) | 2.408(3) | Ho(1)-O(8) | 2.383(5) |
| Tb(1)-O(9) | 2.411(12) | Dy(1)-O(7) | 2.445(3) | Ho(1)-O(1) | 2.405(5) |
| Tb(1)-O(2) | 2.419(15) | Dy(1)-O(2) | 2.446(3) | Ho(1)-O(6) | 2.397(5) |
| Tb(1)-O(1) | 2.433(15) | Dy(1)-O(1) | 2.453(3) | Ho(1)-O(2) | 2.409(5) |
| Tb(1)-O(3) | 2.282(12) | Dy(1)-O(3) | 2.301(3) | Ho(1)-O(4) | 2.259(5) |
| Tb(1)-O(4) | 2.353(14) | Dy(1)-O(4) | 2.349(3) | Ho(1)-O(3) | 2.315(5) |

Symmetry transformations used to generate equivalent atoms: #1 x+1, y-1, z; #2 x+1, y, z; #3 -x+2, -y+2, -z+1; #4 -x+1, -y+2, -z; #5 -x, -y, -z.

**Table S2**. Selected bond angles (°) for complexes **1-9**.

| **1** | | **2** | | **3** | |
|---|---|---|---|---|---|
| O(1)-Eu(1)-O(4) | 140.9(5) | O(1)-Eu(1)-O(4) | 77.25(11) | O(5)-Eu(1)-O(1) | 77.5(2) |
| O(1)-Eu(1)-O(3W) | 81.4(6) | (1)-Eu(1)-O(2)#3 | 125.54(11) | O(5)-Eu(1)-O(2)#4 | 75.4(2) |
| O(4)-Eu(1)-O(3W) | 81.8(5) | O(4)-Eu(1)-O(2)#3 | 74.08(10) | O(1)-Eu(1)-O(2)#4 | 136.4(2) |
| O(1)-Eu(1)-O(4W) | 69.1(6) | O(1)-Eu(1)-O(3) | 76.81(11) | O(5)-Eu(1)-O(3) | 80.8(2) |
| O(4)-Eu(1)-O(4W) | 133.5(6) | O(4)-Eu(1)-O(3) | 124.94(10) | O(1)-Eu(1)-O(3) | 130.5(2) |
| O(3W)-Eu(1)-O(4W) | 67.2(6) | O(2)#3-Eu(1)-O(3) | 83.18(10) | O(2)#4-Eu(1)-O(3) | 77.4(2) |
| O(1)-Eu(1)-O(1W) | 72.4(6) | O(1)-Eu(1)-O(5) | 141.34(11) | O(5)-Eu(1)-O(6) | 125.6(2) |
| O(4)-Eu(1)-O(1W) | 93.3(5) | O(4)-Eu(1)-O(5) | 83.59(10) | O(1)-Eu(1)-O(6) | 86.8(2) |
| O(3W)-Eu(1)-O(1W) | 131.1(5) | O(2)#3-Eu(1)-O(5) | 79.25(10) | O(2)#4-Eu(1)-O(6) | 82.0(2) |
| O(4W)-Eu(1)-O(1W) | 133.3(6) | O(3)-Eu(1)-O(5) | 140.39(11) | O(3)-Eu(1)-O(6) | 140.7(2) |
| O(1)-Eu(1)-O(7) | 134.7(5) | O(1)-Eu(1)-O(6) | 138.49(11) | O(5)-Eu(1)-O(4) | 82.1(2) |
| O(4)-Eu(1)-O(7) | 75.6(5) | O(4)-Eu(1)-O(6) | 143.03(11) | O(1)-Eu(1)-O(4) | 80.6(2) |
| O(3W)-Eu(1)-O(7) | 79.7(6) | O(2)#3-Eu(1)-O(6) | 75.00(10) | O(2)#4-Eu(1)-O(4) | 127.7(2) |
| O(4W)-Eu(1)-O(7) | 65.6(6) | O(3)-Eu(1)-O(6) | 70.11(10) | O(3)-Eu(1)-O(4) | 52.5(2) |
| O(1W)-Eu(1)-O(7) | 146.1(5) | O(5)-Eu(1)-O(6) | 71.14(10) | O(6)-Eu(1)-O(4) | 146.3(2) |
| O(1)-Eu(1)-O(2W) | 140.6(5) | O(1)-Eu(1)-N(1) | 77.95(12) | O(5)-Eu(1)-N(4) | 143.1(2) |
| O(4)-Eu(1)-O(2W) | 69.1(5) | O(4)-Eu(1)-N(1) | 139.01(11) | O(1)-Eu(1)-N(4) | 138.8(2) |
| O(3W)-Eu(1)-O(2W) | 136.7(5) | O(2)#3-Eu(1)-N(1) | 146.39(11) | O(2)#4-Eu(1)-N(4) | 77.0(2) |
| O(4W)-Eu(1)-O(2W) | 111.2(5) | O(3)-Eu(1)-N(1) | 79.52(10) | O(3)-Eu(1)-N(4) | 69.7(2) |
| O(1W)-Eu(1)-O(2W) | 83.4(5) | O(5)-Eu(1)-N(1) | 96.23(11) | O(6)-Eu(1)-N(4) | 73.2(2) |
| O(2W)-Eu(1)-O(5W) | 125.4(7) | O(6)-Eu(1)-N(1) | 72.08(11) | O(4)-Eu(1)-N(4) | 96.2(3) |
| O(6W)-Eu(1)-O(5W) | 127.5(7) | O(1)-Eu(1)-N(2) | 75.09(11) | O(5)-Eu(1)-O(5)#4 | 74.4(2) |
| N(1)#1-K(1)-O(1W) | 168.0(5) | O(4)-Eu(1)-N(2) | 79.85(10) | O(1)-Eu(1)-O(5)#4 | 71.9(2) |
| N(1)#1-K(1)-O(6W) | 113.7(5) | O(2)#3-Eu(1)-N(2) | 140.46(10) | O(2)#1-Eu(1)-O(5)#4 | 68.2(2) |
| O(1W)-K(1)-O(6W) | 56.6(4) | O(3)-Eu(1)-N(2) | 136.36(10) | O(3)-Eu(1)-O(5)#4 | 141.5(2) |
| N(1)#4-K(1)-O(4W)#2 | 80.0(5) | O(5)-Eu(1)-N(2) | 68.62(10) | O(6)-Eu(1)-O(5)#4 | 51.3(2) |
| O(1W)-K(1)-O(4W)#2 | 95.6(5) | O(6)-Eu(1)-N(2) | 113.42(10) | O(4)-Eu(1)-O(5)#4 | 146.9(2) |
| O(6W)-K(1)-O(4W)#2 | 107.2(5) | N(1)-Eu(1)-N(2) | 62.46(10) | N(4)-Eu(1)-O(5)#4 | 116.6(2) |
| **4** | | **5** | | **6** | |
| O(1)#5-Eu(1)-O(2) | 91.9(3) | O(3)-Sm(1)-O(4) | 91.84(10) | O(3)-Gd(1)-O(4) | 91.62(10) |
| O(1)#5-Eu(1)-O(9) | 81.6(3) | O(3)-Sm(1)-O(10) | 100.76(11) | O(3)-Gd(1)-O(9) | 101.07(11) |
| O(2)-Eu(1)-O(9) | 72.7(3) | O(4)-Sm(1)-O(10) | 143.18(12) | O(4)-Gd(1)-O(9) | 143.64(11) |
| O(1)#5-Eu(1)-O(7) | 75.4(3) | O(3)-Sm(1)-O(9) | 81.37(11) | O(3)-Gd(1)-O(10) | 81.96(11) |
| O(2)-Eu(1)-O(7) | 78.1(3) | O(4)-Sm(1)-O(9) | 72.83(11) | O(4)-Gd(1)-O(10) | 72.97(11) |
| O(9)-Eu(1)-O(7) | 141.9(3) | O(10)-Sm(1)-O(9) | 142.95(12) | O(9)-Gd(1)-O(10) | 142.15(11) |
| O(1)#5-Eu(1)-O(4) | 154.0(3) | O(3)-Sm(1)-O(7) | 75.27(11) | O(3)-Gd(1)-O(8) | 75.76(11) |
| O(2)-Eu(1)-O(4) | 103.5(3) | O(4)-Sm(1)-O(7) | 78.58(10) | O(4)-Gd(1)-O(8) | 78.73(10) |
| O(9)-Eu(1)-O(4) | 83.3(3) | O(10)-Sm(1)-O(7) | 71.61(11) | O(9)-Gd(1)-O(8) | 71.81(10) |
| O(7)-Eu(1)-O(4) | 127.8(3) | O(9)-Sm(1)-O(7) | 142.19(11) | O(10)-Gd(1)-O(8) | 143.20(11) |
| O(1)#5-Eu(1)-O(8) | 101.5(3) | O(3)-Sm(1)-O(8) | 74.50(11) | O(3)-Gd(1)-O(2) | 153.99(11) |
| O(2)-Eu(1)-O(8) | 143.3(3) | O(4)-Sm(1)-O(8) | 142.57(11) | O(4)-Gd(1)-O(2) | 103.24(10) |
| O(9)-Eu(1)-O(8) | 142.7(3) | O(10)-Sm(1)-O(8) | 74.22(11) | O(9)-Gd(1)-O(2) | 79.53(11) |

| | | | | | |
|---|---|---|---|---|---|
| O(7)-Eu(1)-O(8) | 72.6(3) | O(9)-Sm(1)-O(8) | 70.77(11) | O(10)-Gd(1)-O(2) | 82.18(12) |
| O(4)-Eu(1)-O(8) | 78.5(3) | O(7)-Sm(1)-O(8) | 128.39(10) | O(8)-Gd(1)-O(2) | 127.68(11) |
| O(1)#5-Eu(1)-O(10) | 74.5(3) | O(3)-Sm(1)-O(2) | 152.88(11) | O(3)-Gd(1)-O(7) | 74.42(11) |
| O(2)-Eu(1)-O(10) | 143.2(3) | O(4)-Sm(1)-O(2) | 73.41(11) | O(4)-Gd(1)-O(7) | 142.76(10) |
| O(9)-Eu(1)-O(10) | 71.6(3) | O(10)-Sm(1)-O(2) | 80.23(11) | O(9)-Gd(1)-O(7) | 73.57(11) |
| O(7)-Eu(1)-O(10) | 128.3(3) | O(9)-Sm(1)-O(2) | 114.27(10) | O(10)-Gd(1)-O(7) | 71.01(11) |
| O(4)-Eu(1)-O(10) | 80.8(3) | O(7)-Sm(1)-O(2) | 79.48(10) | O(8)-Gd(1)-O(7) | 128.15(10) |
| O(8)-Eu(1)-O(10) | 73.6(3) | O(8)-Sm(1)-O(2) | 130.53(10) | O(2)-Gd(1)-O(7) | 80.98(10) |
| O(1)#5-Eu(1)-O(3) | 152.8(3) | O(3)-Sm(1)-O(1) | 154.57(11) | O(3)-Gd(1)-O(1) | 152.85(10) |
| O(2)-Eu(1)-O(3) | 73.2(3) | O(4)-Sm(1)-O(1) | 103.63(10) | O(4)-Gd(1)-O(1) | 73.39(11) |
| O(9)-Eu(1)-O(3) | 113.9(3) | O(10)-Sm(1)-O(1) | 78.88(11) | O(9)-Gd(1)-O(1) | 80.43(11) |
| O(7)-Eu(1)-O(3) | 79.3(3) | O(9)-Sm(1)-O(1) | 84.06(12) | O(10)-Gd(1)-O(1) | 113.63(10) |
| O(4)-Eu(1)-O(3) | 53.2(3) | O(7)-Sm(1)-O(1) | 127.14(11) | O(8)-Gd(1)-O(1) | 79.11(10) |
| O(8)-Eu(1)-O(3) | 79.9(3) | O(8)-Sm(1)-O(1) | 81.07(11) | O(2)-Gd(1)-O(1) | 53.16(10) |
| **7** | | **8** | | **9** | |
| O(3)-Tb(1)-O(4) | 91.1(5) | O(3)-Dy(1)-O(4) | 91.76(12) | O(4)-Ho(1)-O(3) | 91.00(18) |
| O(3)-Tb(1)-O(10) | 75.9(5) | O(3)-Dy(1)-O(10) | 101.18(13) | O(4)-Ho(1)-O(5) | 81.3(2) |
| O(4)-Tb(1)-O(10) | 144.4(6) | O(4)-Dy(1)-O(10) | 143.32(12) | O(3)-Ho(1)-O(5) | 73.12(19) |
| O(3)-Tb(1)-O(7) | 75.8(5) | O(3)-Dy(1)-O(9) | 82.09(13) | O(4)-Ho(1)-O(7) | 102.24(19) |
| O(4)-Tb(1)-O(7) | 78.4(5) | O(4)-Dy(1)-O(9) | 72.63(12) | O(3)-Ho(1)-O(7) | 143.0(2) |
| O(10)-Tb(1)-O(7) | 127.8(5) | O(10)-Dy(1)-O(9) | 142.72(12) | O(5)-Ho(1)-O(7) | 142.5(2) |
| O(3)-Tb(1)-O(8) | 81.5(5) | O(3)-Dy(1)-O(8) | 75.55(12) | O(4)-Ho(1)-O(8) | 76.08(19) |
| O(4)-Tb(1)-O(8) | 72.9(5) | O(4)-Dy(1)-O(8) | 78.27(12) | O(3)-Ho(1)-O(8) | 78.55(18) |
| O(10)-Tb(1)-O(8) | 72.5(5) | O(10)-Dy(1)-O(8) | 72.17(12) | O(5)-Ho(1)-O(8) | 143.14(19) |
| O(7)-Tb(1)-O(8) | 142.8(5) | O(9)-Dy(1)-O(8) | 142.46(13) | O(7)-Ho(1)-O(8) | 71.62(18) |
| O(3)-Tb(1)-O(9) | 101.7(5) | O(3)-Dy(1)-O(7) | 74.26(12) | O(4)-Ho(1)-O(1) | 153.5(2) |
| O(4)-Tb(1)-O(9) | 143.6(5) | O(4)-Dy(1)-O(7) | 142.82(12) | O(3)-Ho(1)-O(1) | 103.33(18) |
| O(10)-Tb(1)-O(9) | 72.0(5) | O(10)-Dy(1)-O(7) | 73.84(12) | O(5)-Ho(1)-O(1) | 81.77(19) |
| O(7)-Tb(1)-O(9) | 72.1(5) | O(9)-Dy(1)-O(7) | 71.42(12) | O(7)-Ho(1)-O(1) | 79.63(19) |
| O(8)-Tb(1)-O(9) | 142.3(5) | O(8)-Dy(1)-O(7) | 128.33(12) | O(8)-Ho(1)-O(1) | 128.21(18) |
| O(3)-Tb(1)-O(2) | 153.9(5) | O(3)-Dy(1)-O(2) | 154.21(11) | O(4)-Ho(1)-O(6) | 74.91(18) |
| O(4)-Tb(1)-O(2) | 104.0(5) | O(4)-Dy(1)-O(2) | 103.03(12) | O(3)-Ho(1)-O(6) | 142.61(19) |
| O(10)-Tb(1)-O(2) | 79.6(5) | O(10)-Dy(1)-O(2) | 79.48(13) | O(5)-Ho(1)-O(6) | 70.62(18) |
| O(7)-Tb(1)-O(2) | 127.6(5) | O(9)-Dy(1)-O(2) | 82.35(13) | O(7)-Ho(1)-O(6) | 74.35(19) |
| O(8)-Tb(1)-O(2) | 82.8(5) | O(8)-Dy(1)-O(2) | 127.78(12) | O(8)-Ho(1)-O(6) | 128.63(18) |
| O(9)-Tb(1)-O(2) | 78.7(5) | O(7)-Dy(1)-O(2) | 81.34(12) | O(1)-Ho(1)-O(6) | 80.32(18) |
| O(3)-Tb(1)-O(1) | 152.8(5) | O(3)-Dy(1)-O(1) | 152.87(11) | O(4)-Ho(1)-O(2) | 152.81(19) |
| O(4)-Tb(1)-O(1) | 73.1(5) | O(4)-Dy(1)-O(1) | 73.18(13) | O(3)-Ho(1)-O(2) | 73.42(18) |
| O(10)-Tb(1)-O(1) | 129.4(5) | O(10)-Dy(1)-O(1) | 80.33(13) | O(5)-Ho(1)-O(2) | 113.83(19) |
| O(7)-Tb(1)-O(1) | 79.3(5) | O(9)-Dy(1)-O(1) | 113.26(12) | O(7)-Ho(1)-O(2) | 79.78(19) |
| O(8)-Tb(1)-O(1) | 113.3(5) | O(8)-Dy(1)-O(1) | 79.29(11) | O(8)-Ho(1)-O(2) | 79.01(18) |
| O(9)-Tb(1)-O(1) | 80.8(5) | O(7)-Dy(1)-O(1) | 130.85(12) | O(1)-Ho(1)-O(2) | 53.67(18) |
| O(2)-Tb(1)-O(1) | 53.3(5) | O(2)-Dy(1)-O(1) | 52.92(11) | O(6)-Ho(1)-O(2) | 130.49(17) |

Symmetry transformations used to generate equivalent atoms: #1 x+1, y-1, z; #2 x+1, y, z; #3 -x+2, -y+2, -z+1; #4 -x+1, -y+2, -z; #5 -x, -y, -z.

**Table S3** Important hydrogen bond interactions in complexes **1–8**.

| | D–H···A | d (D–H) (Å) | d (H···A) (Å) | d (D···A) (Å) | ∠DHA (°) |
|---|---|---|---|---|---|
| **1** | O1W–H1Wb···Cl2 | 0.970 | 2.225 | 3.108 | 150.67 |
| | O7–H7···Cl1 | 0.960 | 2.383 | 3.317 | 163.93 |
| | O3W–H3WA···Cl1 | 0.960 | 2.296 | 3.141 | 146.34 |
| | O2W–H2WB···Cl2 | 0.957 | 2.464 | 3.177 | 131.22 |
| **2** | O5–H5A···Cl1 | 0.850 | 2.359 | 3.100 | 145.85 |
| | O6–H5D···Cl1 | 0.850 | 2.383 | 3.162 | 152.73 |
| | C25–H25A···Cl1 | 0.950 | 2.822 | 3.744 | 163.82 |
| **3** | C25–H25A···O6 | 0.950 | 2.608 | 3.456 | 148.75 |
| | C22–H22A···N2 | 0.950 | 2.661 | 3.495 | 146.86 |
| **4** | O7–H7C···O6 | 0.850 | 2.222 | 2.723 | 117.73 |
| | O8–H8A···O5 | 0.850 | 2.364 | 2.790 | 111.43 |
| | O9–H9A···O5 | 0.850 | 2.210 | 2.819 | 128.54[x–1, y, z] |
| | O10–H10C···N1 | 0.850 | 2.132 | 2.755 | 129.84[x, y+1, z] |
| | OW1–HW1A···O6 | 0.850 | 2.178 | 2.845 | 135.25[–x, –y, –z] |
| | OW1–HW1A···O7 | 0.850 | 2.590 | 3.354 | 150.14[x–1, y, z] |
| | OW1–HW1C···O3 | 0.850 | 2.206 | 2.796 | 126.44[x–1, y, z] |
| **5** | O7-H7D···O6 | 0.850 | 2.113 | 2.870 | 148.01 |
| | O8-H8A···O5 | 0.850 | 2.505 | 2.952 | 113.82[-x+1, -y+1, -z] |
| | O9-H9B···OW1 | 0.850 | 1.912 | 2.661 | 146.18 |
| | O10-H10A···O5 | 0.850 | 2.356 | 2.776 | 110.99[-x+2, -y+1, -z] |
| | O10-H10B···N3 | 0.850 | 2.107 | 2.782 | 135.99[x, y+1, z] |
| | OW1-HW1C···O2 | 0.850 | 2.190 | 2.784 | 126.89[x-1, y, z] |
| **6** | O7-H7A···O5 | 0.850 | 2.516 | 2.954 | 113.00[x+1, y, z] |
| | O8-H8C···O6 | 0.850 | 2.121 | 2.874 | 147.33[-x+1, -y+1, z+1] |
| | O9-H9A···O5 | 0.850 | 2.367 | 2.786 | 110.87 |
| | O10-H10A···O5 | 0.850 | 2.212 | 2.832 | 129.77[x+1, y, z] |
| | O10-H10C···OW1 | 0.850 | 1.927 | 2.670 | 145.25 |
| | OW1-HW1A···O6 | 0.850 | 2.176 | 2.838 | 134.69[-x+2, -y+1, -z+1] |
| | OW1-HW1A···O8 | 0.850 | 2.573 | 3.337 | 150.06[x+1, y, z] |
| **7** | O7-H7C···O5 | 0.850 | 2.131 | 2.886 | 147.86 |
| | O7-H7D···O5 | 0.850 | 2.207 | 2.711 | 117.85[-x, -y+1, -z+1] |
| | O8-H8D···OW1 | 0.850 | 1.922 | 2.661 | 144.50 |
| | O9-H9C···N3 | 0.850 | 2.112 | 2.774 | 134.36[x, y-1, z] |
| | O10-H10B···N2 | 0.850 | 2.115 | 2.711 | 126.81[x, y-1, z] |
| | OW1-HW1A···O5 | 0.850 | 2.164 | 2.832 | 135.30[x+1, y, z] |
| | OW1-HW1A···O7 | 0.850 | 2.569 | 3.327 | 149.16[x+1, y, z] |
| | OW1-HW1B···O1 | 0.850 | 2.207 | 2.798 | 126.62[x+1, y, z] |
| **8** | O7-H7A···O5 | 0.850 | 2.509 | 2.944 | 112.74[x-1, y, z] |
| | O8-H8C···O6 | 0.850 | 2.236 | 2.736 | 117.57 |
| | O9-H9A···O5 | 0.850 | 2.215 | 2.834 | 129.65[x-1, y, z] |
| | O10-H10A···O5 | 0.850 | 2.373 | 2.793 | 110.99 |
| | O10-H10C···N3 | 0.850 | 2.117 | 2.787 | 135.46[-x+1, -y+1, -z+1] |
| | OW1-HW1A···O6 | 0.850 | 2.169 | 2.834 | 134.95[-x, -y, -z+1] |
| | OW1-HW1A···O8 | 0.850 | 2.579 | 3.344 | 150.31[x-1, y, z] |
| | OW1-HW1C···O1 | 0.850 | 2.209 | 2.797 | 126.24[x-1, y, z] |

**Table S4** Luminescence data for complexes **1–8**[a].

| complexes | Emission transitions | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | τ(μs) | conditions |
|---|---|---|---|---|---|
| **1·Eu** | $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–4) | 365 | 578, 593, 613, 650, 699 nm | 456.93 | solid state 298K |
| | | 345 | | 499.33 | solid state 77K |
| **2·Eu** | $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–4) | 350 | 579, 592, 613, 650, 699 nm | 779.62 | solid state 298K |
| | | 340 | | 792.65 | solid state 77K |
| **3·Eu** | $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–4) | 320 | 580, 592, 613, 650, 699 nm | 947.21 | solid state 298K |
| | | 330 | | 1098.59 | solid state 77K |
| **4·Eu** | $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–4) | 340 | 579, 592, 613, 650, 700 nm | 283.70 | solid state 298K |
| | | 345 | | 464.69 | solid state 77K |
| **5·Sm** | $^4G_{5/2} \rightarrow {}^6H_J$ ($J$ = 5/2–11/2) | 325 | 430, 562, 596, 644, 700 nm | 21.43 | solid state 298K |
| | | 325 | 410, 562, 596, 644, 700 nm | 21.77 | solid state 77K |
| **6·Gd** | 0→0,1,2 | 335 | 420, 560, 608 nm | 14.04 | solid state 77K |
| **7·Tb** | $^5D_4 \rightarrow {}^7F_J$ ($J$ = 6–3) | 320 | 412, 490, 545, 589, 621 nm | 5.55 | solid state 298K |
| | | 325 | 423, 490, 545, 589, 621 nm | 8.77 | solid state 77K |
| **8·Dy** | $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ | 325 | 420, 481, 574, 661 nm | 7.09 | solid state 298K |
| | $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2} + {}^6F_{11/2}$ | 325 | 405, 481, 574, 661, 750 nm | 7.97 | solid state 77K |

[a] The luminescence properties of complex **9** was not measured.

**Table S5** Luminescence lifetimes for **3**–PMMA and **4**–PMMA

| | **3** | **4** |
|---|---|---|
| solid sate-298 K | 947.21 | 283.70 |
| 2% PMMA | 982.10 | 539.58 |
| 4% PMMA | 991.74 | 561.67 |
| 6% PMMA | 991.90 | 778.96 |
| 8% PMMA | 1034.12 | 792.33 |
| 10% PMMA | 950.23 | 760.92 |