Supporting Information for

Two photochromic complexes assembled by nonphotochromic ligand: photogenerated radicals enhanced room temperature phosphorescence

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Contents

Experimental Section

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra of **1** and **2** were performed using a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. The luminescence, phosphorescence and phosphorescent decay data were analyzed by an F-4700 Fluorescence spectrometer, while the fluorescence decay curves data of TPB ligand were analyzed by a JY HORIBA FluoroLog-3, **1** and **2** were used by FLS-980 fluorescence spectrometer, respectively. The solid-state UV-Vis spectra were measured at RT using $BaSO_4$ as a reference on a Puxi Tu-1901 spectrophotometer. The crystal samples were crushed as polycrystalline powders and dispersed on barium sulfate plate. The electron spin resonance (ESR) spectroscopy was recorded on a Bruker E500 spectrometer using powder samples at a frequency of 9.84 GHz. X-ray photoelectron spectra were measured on Thermo Scientific ESCALAB Xi+ at room temperature. Thermogravimetric (TG) analyses were measured using a powder sample under air atmosphere on a TG-DTA 8121 analyzer. Magnetic measurements of the powder samples of **1** and **2** before irradiation were carried out on a Quantum Design SQUID MPMS3 magnetometer. Data were corrected for the diamagnetic contribution calculated from Pascal constants. Through a Rigaku standard MiniFlex600 diffractometer, powder X-ray diffraction (PXRD) spectra were performed. Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program with free method supported on the Internet at http://www.iucr.org. For the light irradiation experiments, a Perfect Light PLS-SXE 300 Xe lamp (320−800 nm, 100 w, at least 10 min) was equipped to prepare the colored samples of UV-vis, PXRD and ESR studies.

X-ray Crystallography

The single-crystal X-ray diffraction data of **1** and **2** was collected on a

Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å). Then using the SHELX-2016 software to solve the structures. For both compounds, several solvent molecules were detected, but most of them were largely disordered, and could not be located in the crystal structural refinement. The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON to remove diffuse electron density, so all the solvent contributions were subtracted from the data during the refinement. Detailed crystallographic data for **1** and **2** were summarized in Table 1, and the selected bond lengths and angles were listed in Table S2 and S3. Full crystallographic data for **1** and **2** have been deposited with the CCDC-2018534 for **1** and 2018535 for **2**.

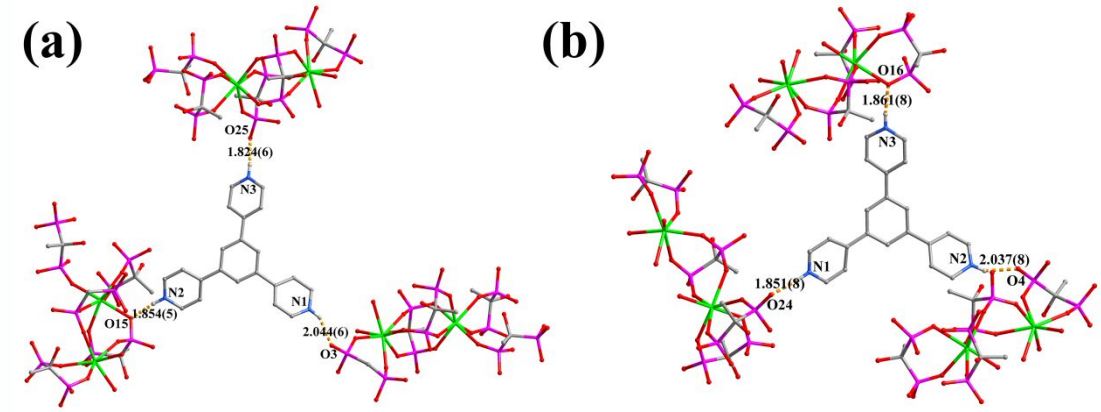

Figure S1 (a) Hydrogen bonding interactions between TPB and HEDP units of **1** (a) and **2** (b).

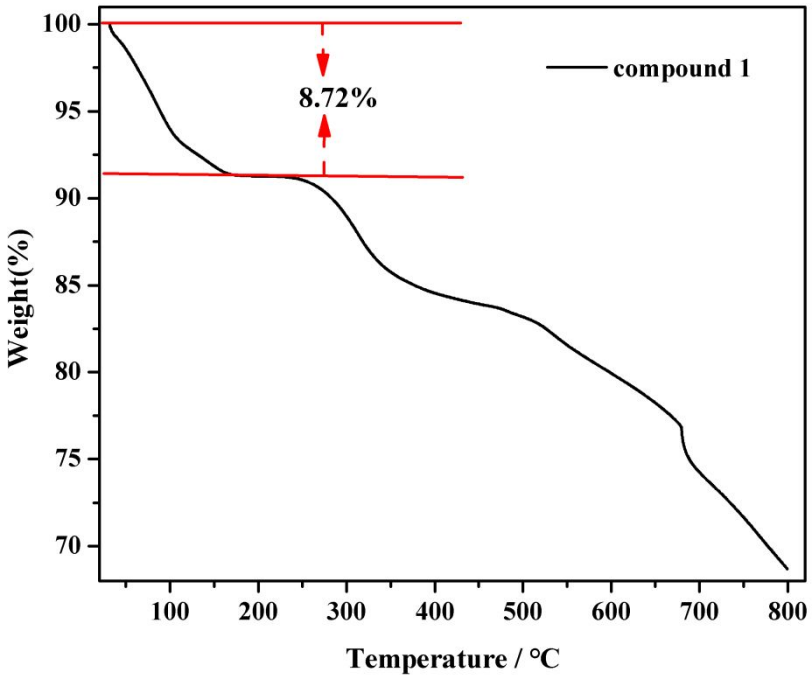

Figure S2 The TG plot of **1**.

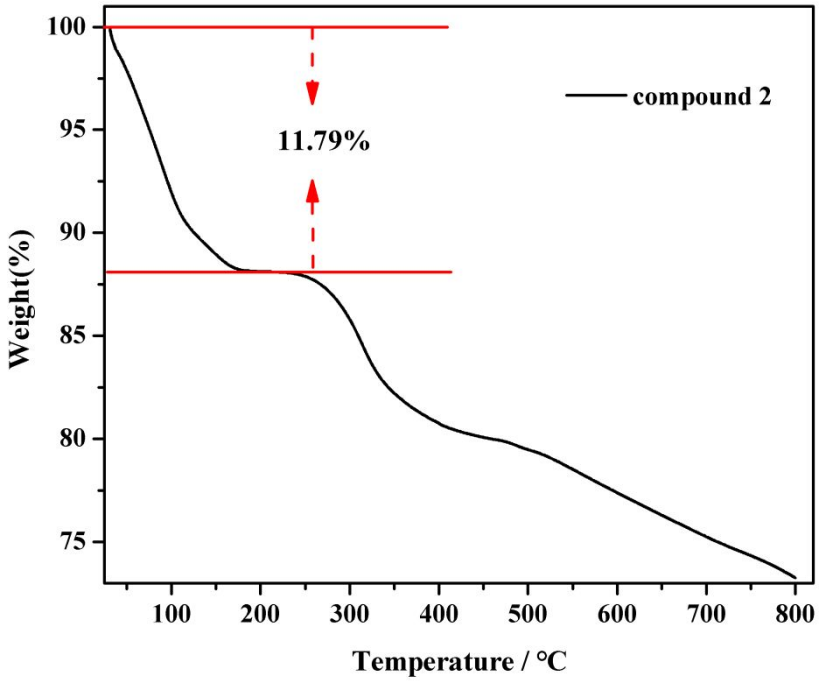

Figure S3 The TG plot of **2**.

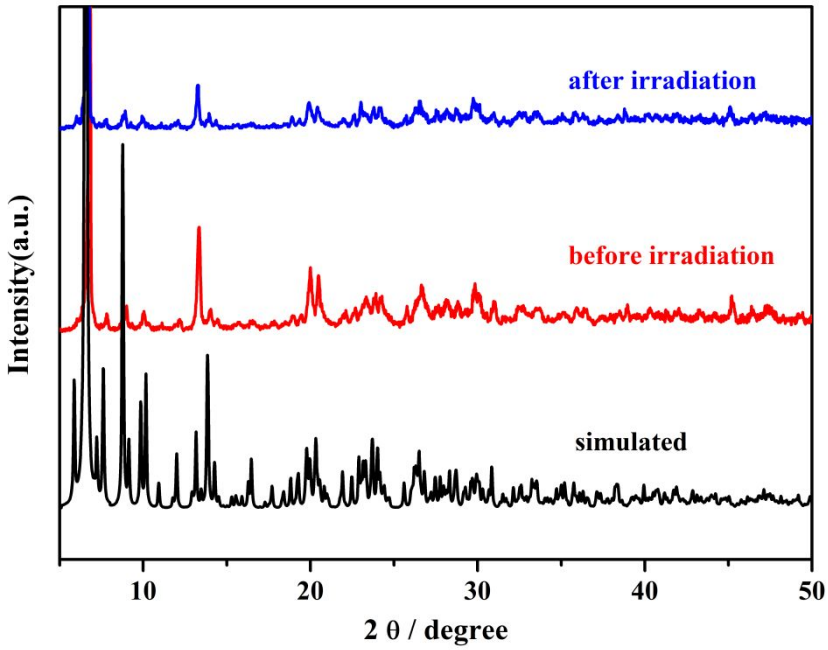

Figure S4 Simulated (black), before (red) and after (blue) irradiated PXRD patterns of **1**.

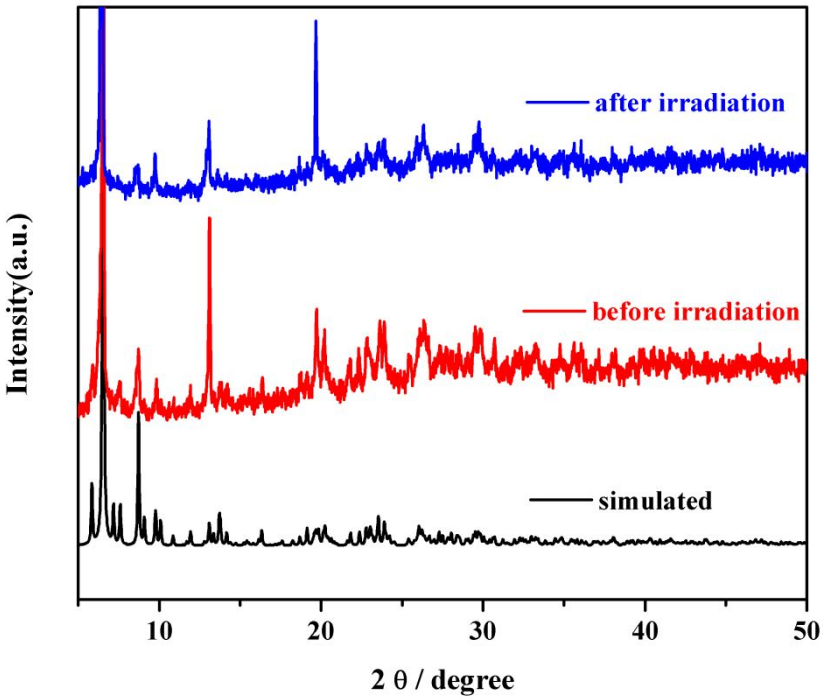

Figure S5 Simulated (black), before (red) and after (blue) irradiated PXRD patterns of **2**.

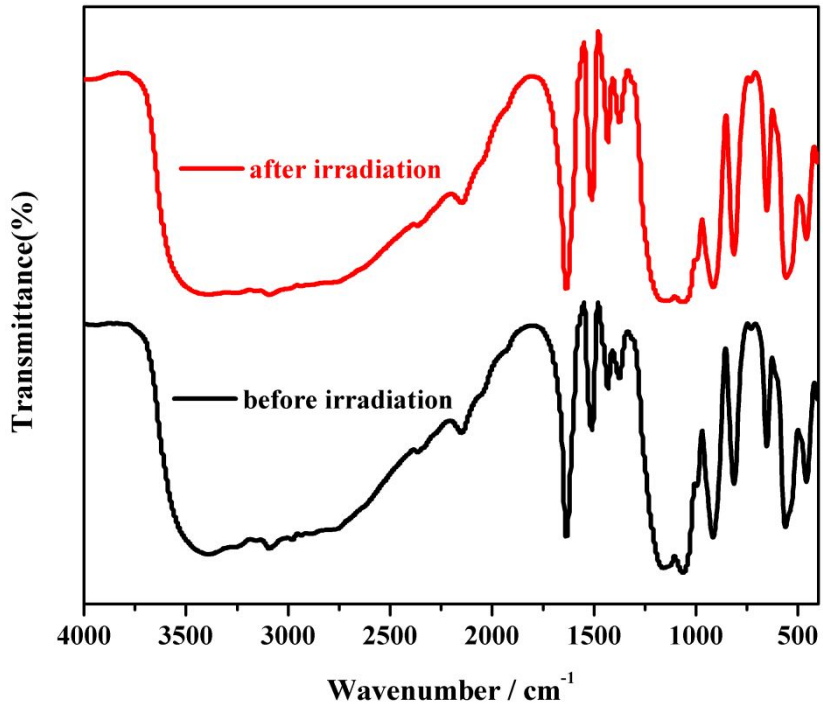

Figure S6 IR spectra of **1** before (black) and after (red) light irradiation.

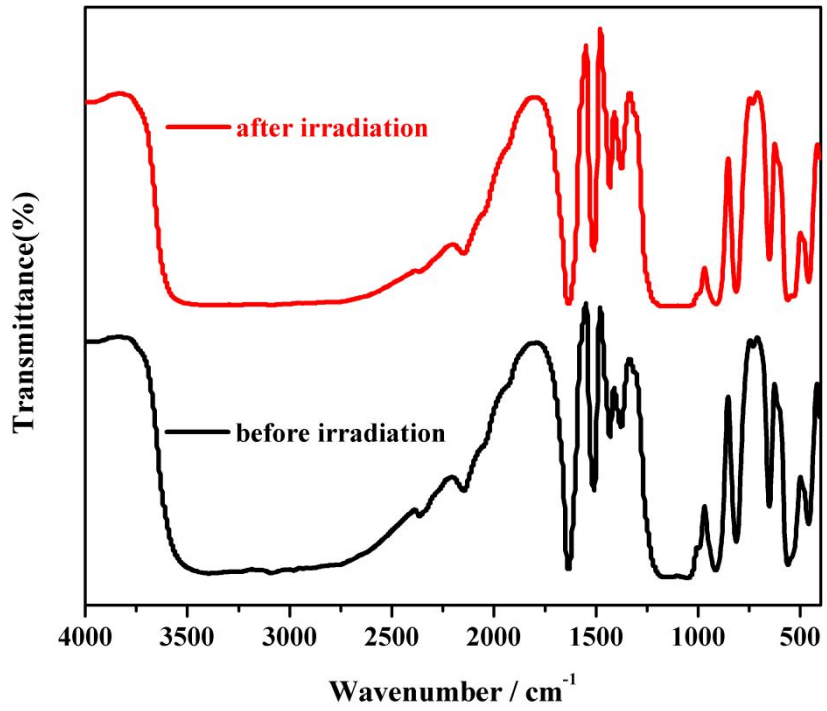

Figure S7 IR spectra of **2** before (black) and after (red) light irradiation.

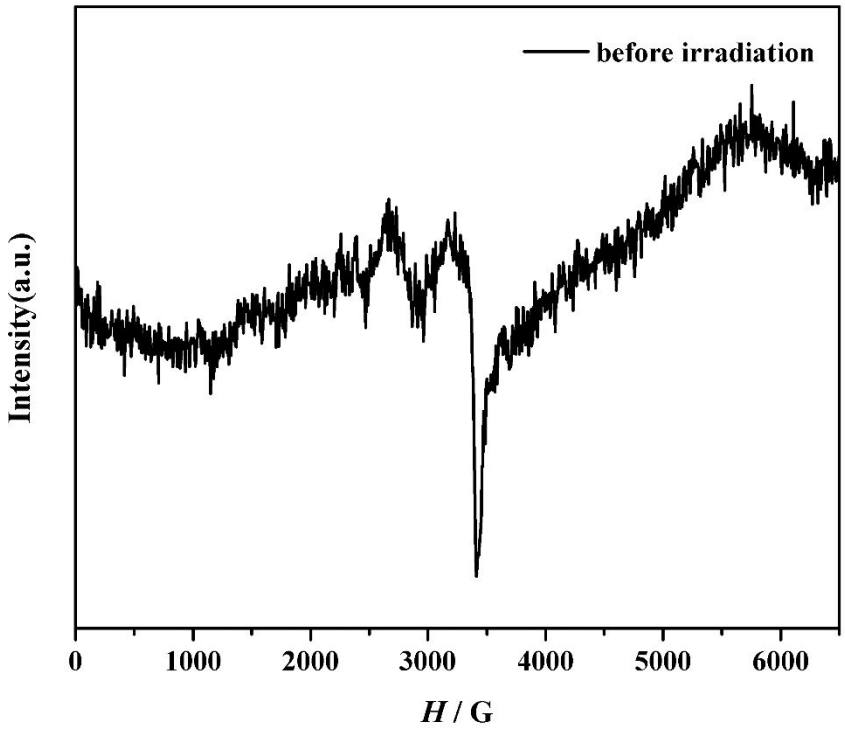

Figure S8 ESR spectra of **1** at 296 K before Xe-lamp light illumination.

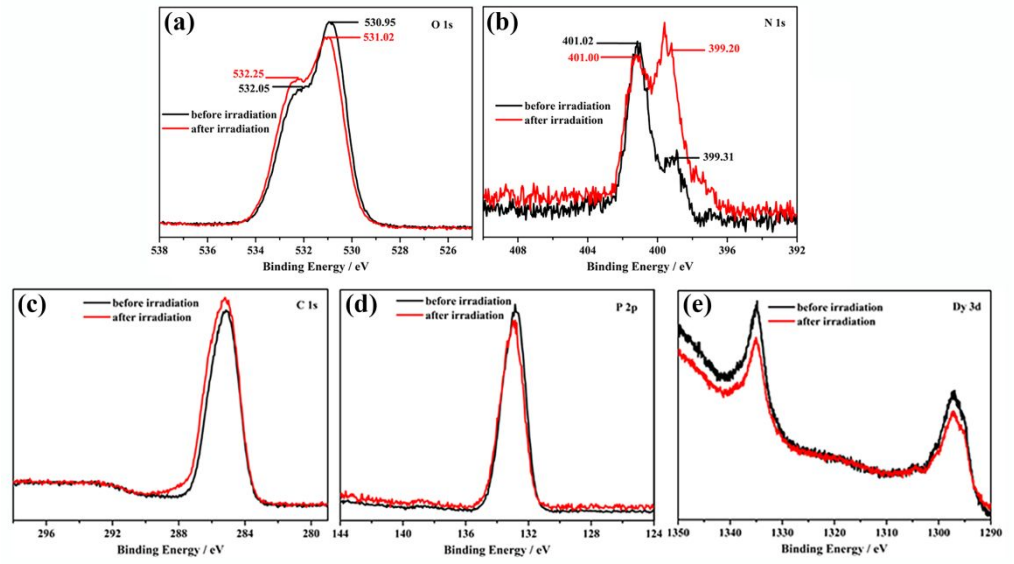

Figure S9 The O 1s (a), N 1s (b), C 1s (c), P 2p (d) and Dy 3d (e) of XPS core-level spectra for **1** before and after light irradiation.

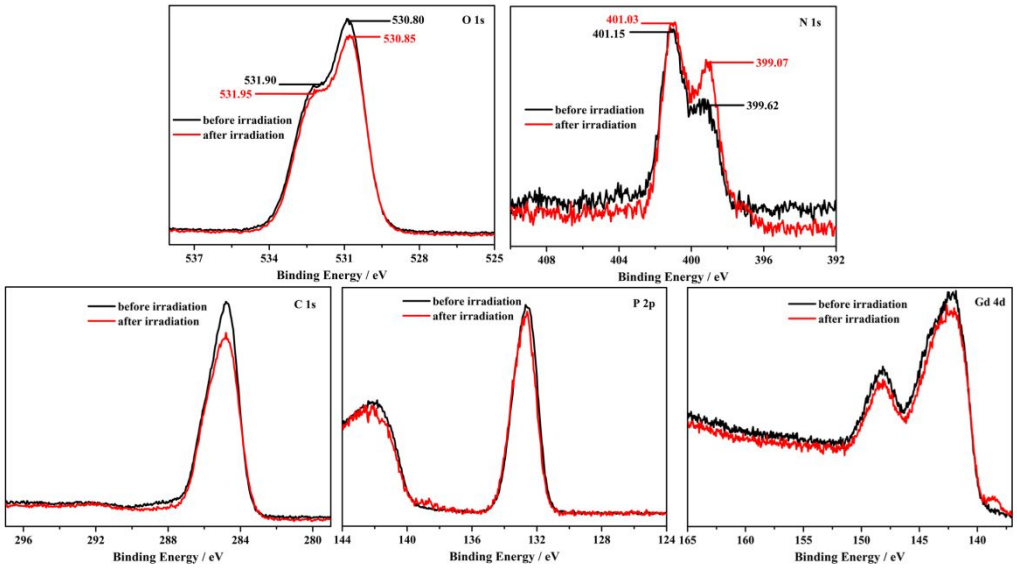

Figure S10 The O 1s (a), N 1s (b), C 1s (c), P 2p (d) and Gd 4d (e) of XPS core-level spectra for **2** before and after light irradiation.

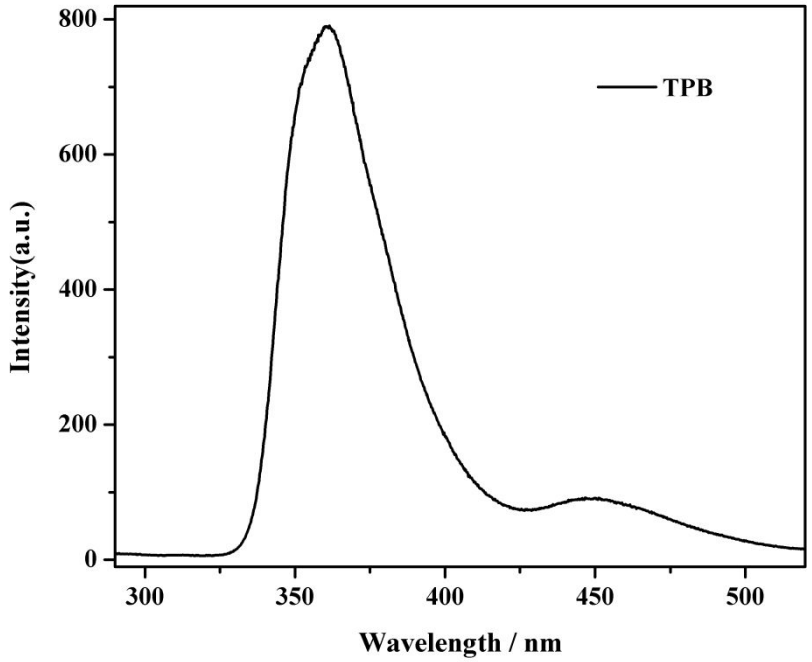

Figure S11 Fluorescence spectrum of TPB ligand at solid state.

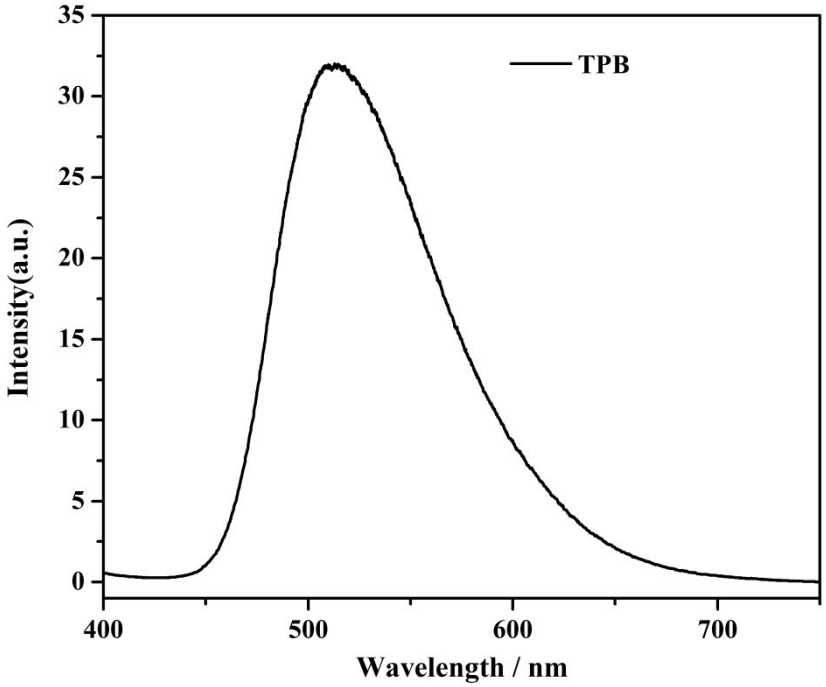

Figure S12 Room temperature phosphorescent spectrum of TPB ligand excited at 270 nm.

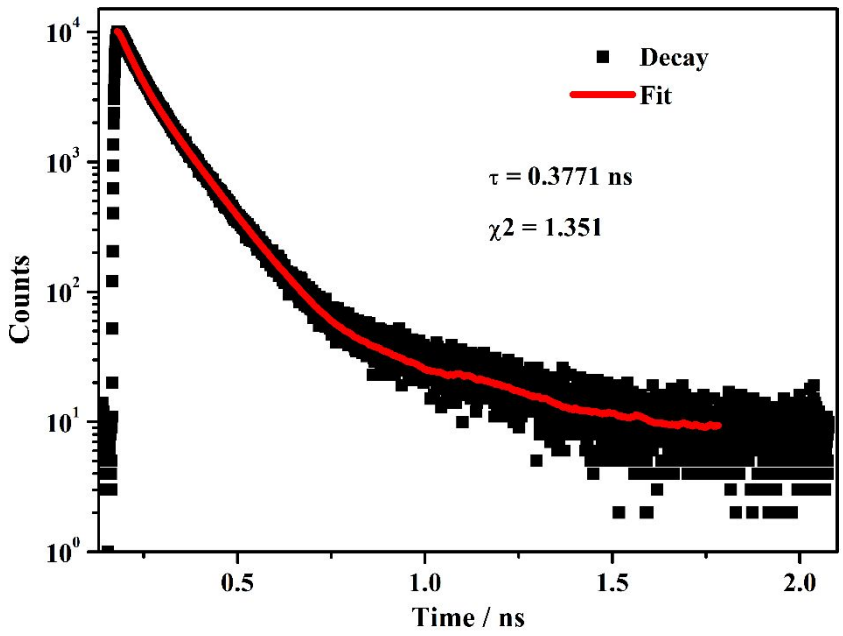

Figure S13 PL decay spectra of TPB ligand at 361 nm excited by a picosecond pulsed diode laser.

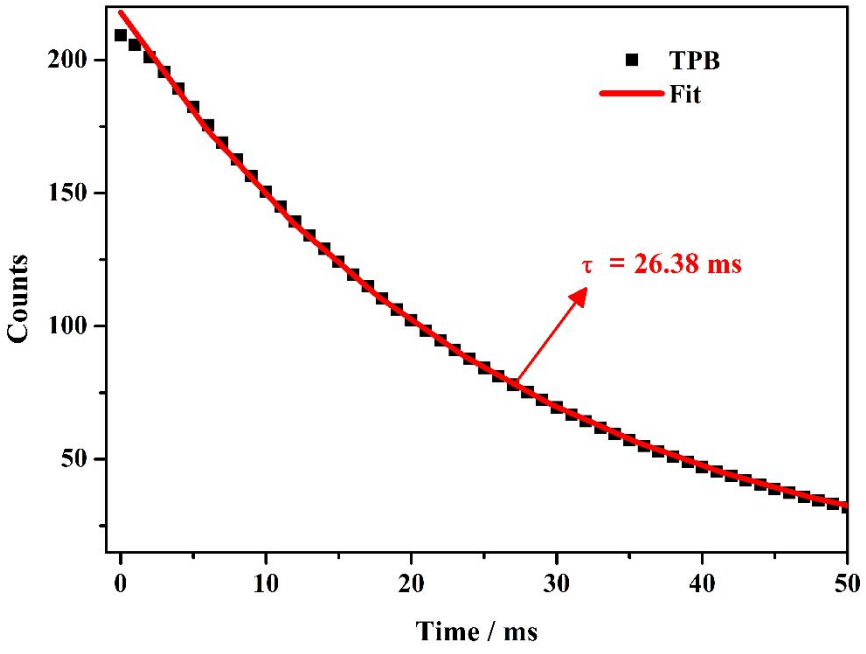

Figure S14 Phosphorescence decay curves of TPB ligand detected at 525 nm.

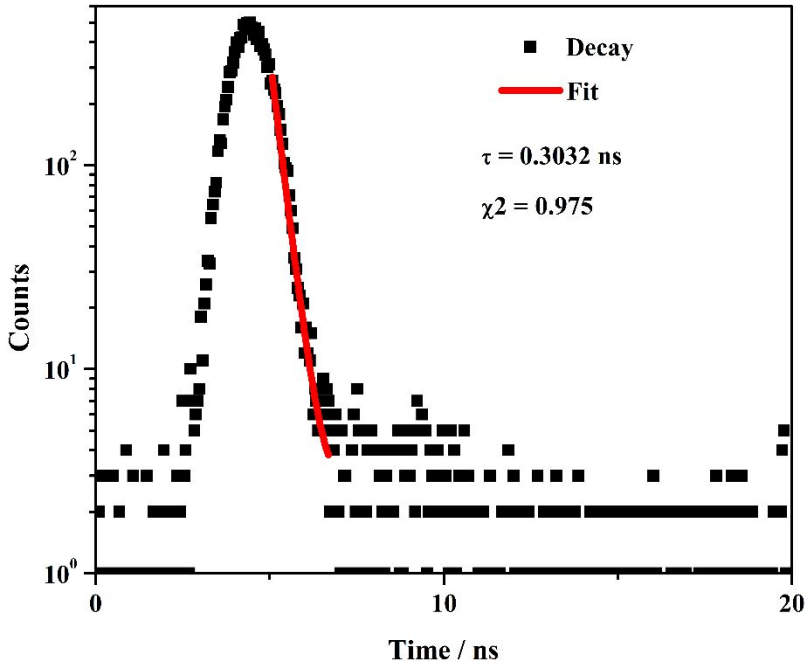

Figure S15 PL decay spectra of compound **1** at 364 nm excited by a picosecond pulsed diode laser.

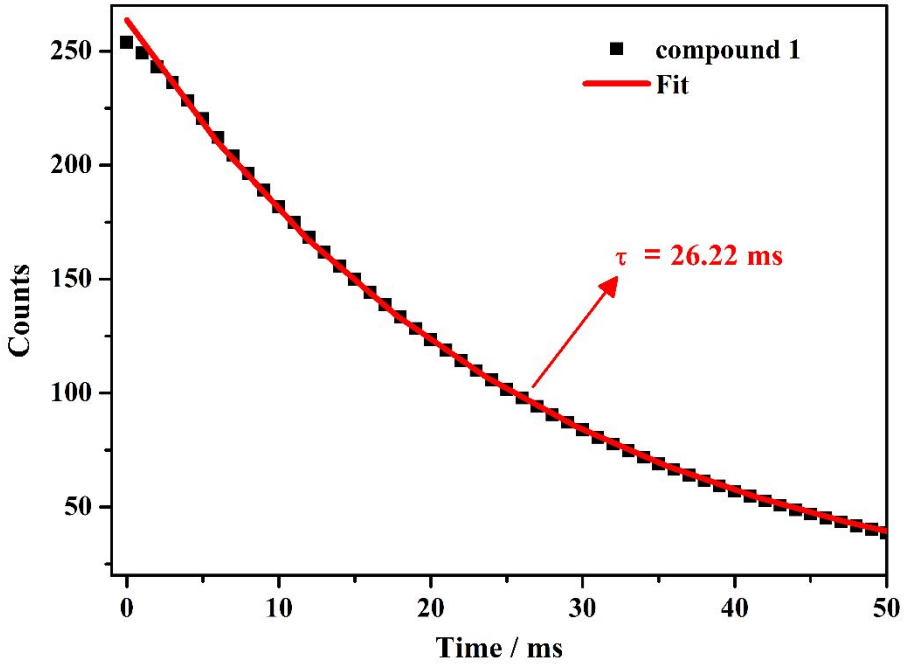

Figure S16 Phosphorescence decay curves of **1** detected at 525 nm.

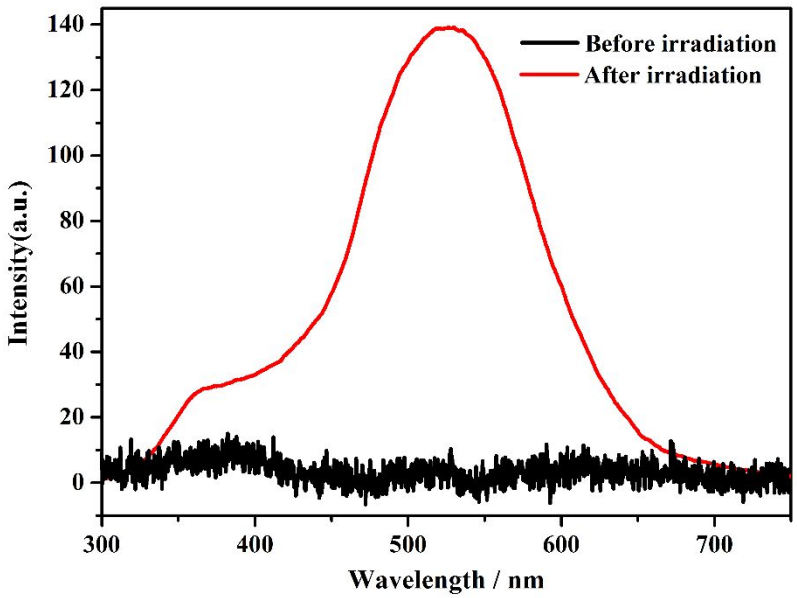

Figure S17 Phosphorescent spectra excited at 270 nm of **1** before (black) and after (red) irradiation.

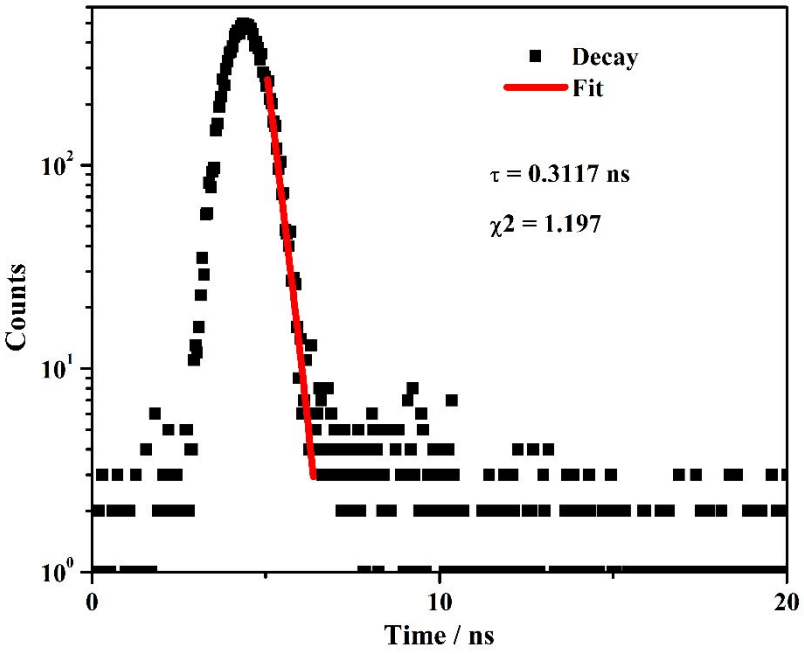

Figure S18 PL decay spectra of compound **2** at 364 nm excited by a picosecond pulsed diode laser.

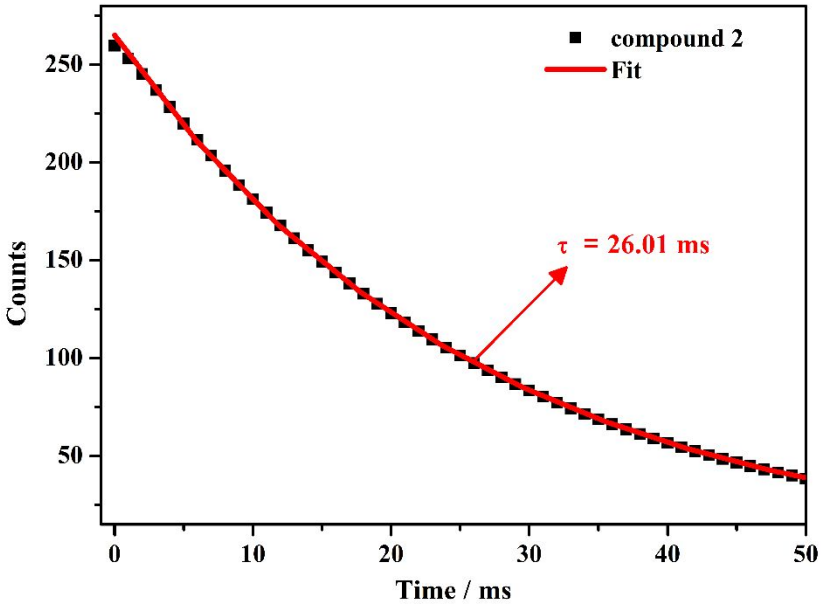

Figure S19 Phosphorescence decay curves of **2** detected at 550 nm.

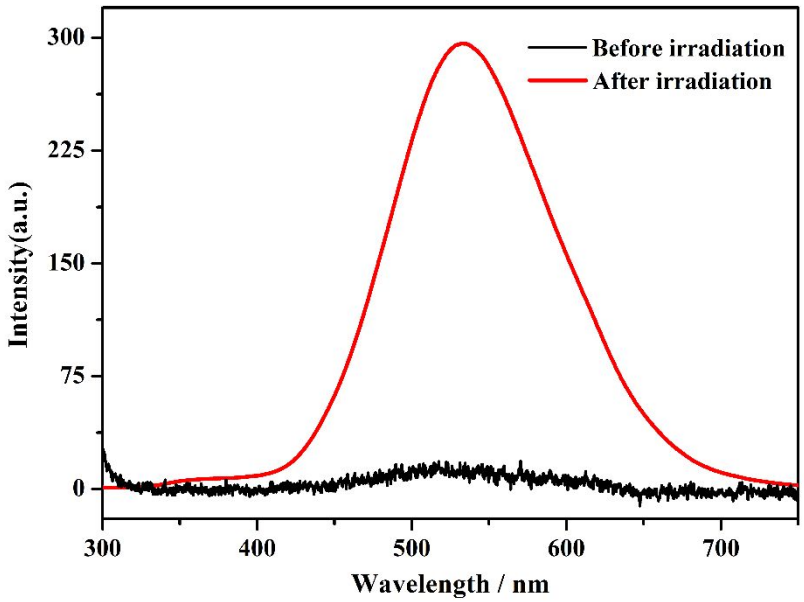

Figure S20 Phosphorescent spectra excited at 270 nm of **2** before (black) and after (red) irradiation.

Table S1. Continuous Shape Measure (CShM) analyses of geometries for compound **1** and **2** by SHAPE 2.0 Software.

Geometry	**1**-Dy1	**1**-Dy2	**2**-Gd1	**2**-Gd2
Heptagon(D_{7h})	31.947	31.492	32.042	31.302
Hexagonal pyramid(C_{6v})	22.553	22.134	22.264	22.228
Pentagonal bipyramid(D_{5h})	3.09	2.435	3.417	2.581
Capped octahedron(C_{3v})	2.623	2.902	2.374	2.728
Capped trigonal prism(C_{2v})	0.96	1.761	0.789	1.713
Johnson pentagonal bipyramid J13(D_{5h})	6.214	5.651	6.659	5.661
Johnson elongated triangular pyramid J7(C_{3v})	20.457	19.356	20.268	19.047

Table S2. Selected bond lengths (Å) and angles (°) for **1** at 293 K.

1			
C(1)−P(1)	1.816(7)	O(2)−P(1)	1.513(4)
C(1)−P(2)	1.842(7)	O(3)−P(1)	1.498(5)
C(3)−P(3)	1.825(7)	O(4)−P(1)	1.550(5)
C(3)−P(4)	1.834(6)	O(6)−P(2)	1.561(5)
C(5)−P(6)	1.826(7)	O(7)−P(2)	1.512(5)
C(5)−P(5)	1.832(7)	O(8)−P(4)	1.502(5)
C(7)−P(7)	1.824(7)	O(9)−P(3)	1.498(5)
C(7)−P(8)	1.840(7)	O(10)−P(3)	1.558(4)
Dy(1)−O(28)#1	2.270(4)	O(12)−P(4)	1.568(5)

Dy(1)−O(17)#1	2.286(4)	O(13)−P(3)	1.500(4)
Dy(1)−O(9)	2.292(5)	O(14)−P(4)	1.494(4)
Dy(1)−O(1)	2.312(4)	O(15)−P(5)	1.526(4)
Dy(1)−O(21)#1	2.322(4)	O(16)−P(6)	1.498(5)
Dy(1)−O(2)	2.338(4)	O(17)−P(5)	1.514(4)
Dy(1)−O(8)	2.399(5)	O(18)−P(5)	1.496(5)
Dy(2)−O(18)#1	2.232(5)	O(20)−P(6)	1.568(5)
Dy(2)−O(16)	2.314(4)	O(21)−P(6)	1.500(4)
Dy(2)−O(23)	2.335(5)	O(22)−P(7)	1.486(5)
Dy(2)−O(15)	2.339(4)	O(23)−P(8)	1.492(5)
Dy(2)−O(22)	2.338(4)	O(24)−P(8)	1.572(5)
Dy(2)−O(13)	2.348(4)	O(25)−P(8)	1.491(5)
Dy(2)−O(14)	2.386(4)	O(27)−P(7)	1.561(5)
O(1)−P(2)	1.500(4)	O(28)−P(7)	1.519(4)

O(28)#1−Dy(1)−O(17)#1	86.00(15)	O(3)−P(1)−C(1)	109.7(3)
O(28)#1−Dy(1)−O(9)	159.32(17)	O(2)−P(1)−C(1)	106.7(3)
O(17)#1−Dy(1)−O(9)	91.74(16)	O(4)−P(1)−C(1)	104.3(3)
O(28)#1−Dy(1)−O(1)	78.45(16)	O(1)−P(2)−O(7)	115.7(3)
O(17)#1−Dy(1)−O(1)	135.61(16)	O(1)−P(2)−O(6)	108.0(3)
O(9)−Dy(1)−O(1)	116.25(16)	O(7)−P(2)−O(6)	109.8(3)
O(28)#1−Dy(1)−O(21)#1	113.51(16)	O(1)−P(2)−C(1)	108.6(3)
O(17)#1−Dy(1)−O(21)#1	75.91(15)	O(7)−P(2)−C(1)	107.6(3)
O(9)−Dy(1)−O(21)#1	85.70(16)	O(6)−P(2)−C(1)	106.7(3)

O(1)−Dy(1)−O(21)#1	72.93(15)	O(13)−P(3)−O(9)	115.1(3)
O(28)#1−Dy(1)−O(2)	89.24(17)	O(13)−P(3)−O(10)	107.6(3)
O(17)#1−Dy(1)−O(2)	145.25(16)	O(9)−P(3)−O(10)	109.9(3)
O(9)−Dy(1)−O(2)	80.94(17)	O(13)−P(3)−C(3)	109.1(3)
O(1)−Dy(1)−O(2)	76.38(16)	O(9)−P(3)−C(3)	108.8(3)
O(21)#1−Dy(1)−O(2)	136.46(16)	O(10)−P(3)−C(3)	106.0(3)
O(28)#1−Dy(1)−O(8)	79.82(16)	O(14)−P(4)−O(8)	118.4(3)
O(17)#1−Dy(1)−O(8)	72.29(15)	O(14)−P(4)−O(12)	110.1(3)
O(9)−Dy(1)−O(8)	79.92(16)	O(8)−P(4)−O(12)	109.3(3)
O(1)−Dy(1)−O(8)	142.37(15)	O(14)−P(4)−C(3)	107.7(3)
O(21)#1−Dy(1)−O(8)	144.49(15)	O(8)−P(4)−C(3)	106.5(3)
O(2)−Dy(1)−O(8)	72.98(16)	O(12)−P(4)−C(3)	103.8(3)
O(18)#1−Dy(2)−O(16)	94.12(16)	O(18)−P(5)−O(17)	113.8(3)
O(18)#1−Dy(2)−O(23)	110.18(18)	O(18)−P(5)−O(15)	111.9(2)
O(16)−Dy(2)−O(23)	134.76(16)	O(17)−P(5)−O(15)	109.4(3)
O(18)#1−Dy(2)−O(15)	168.14(15)	O(18)−P(5)−C(5)	107.5(3)
O(16)−Dy(2)−O(15)	80.42(15)	O(17)−P(5)−C(5)	107.4(3)
O(23)−Dy(2)−O(15)	80.77(17)	O(15)−P(5)−C(5)	106.4(3)
O(18)#1−Dy(2)−O(22)	78.06(16)	O(16)−P(6)−O(21)	118.5(3)
O(16)−Dy(2)−O(22)	74.65(16)	O(16)−P(6)−O(20)	107.2(3)
O(23)−Dy(2)−O(22)	73.99(15)	O(21)−P(6)−O(20)	108.7(3)
O(15)−Dy(2)−O(22)	110.22(15)	O(16)−P(6)−C(5)	106.2(3)
O(18)#1−Dy(2)−O(13)	95.50(16)	O(21)−P(6)−C(5)	107.6(3)
O(16)−Dy(2)−O(13)	146.44(15)	O(20)−P(6)−C(5)	108.2(3)

O(23)−Dy(2)−O(13)	70.34(15)	O(22)−P(7)−O(28)	114.8(3)
O(15)−Dy(2)−O(13)	83.74(15)	O(22)−P(7)−O(27)	111.8(3)
O(22)−Dy(2)−O(13)	138.85(16)	O(28)−P(7)−O(27)	109.2(2)
O(18)#1−Dy(2)−O(14)	82.04(16)	O(22)−P(7)−C(7)	108.1(3)
O(16)−Dy(2)−O(14)	74.38(15)	O(28)−P(7)−C(7)	107.5(3)
O(23)−Dy(2)−O(14)	144.28(15)	O(27)−P(7)−C(7)	105.0(3)
O(15)−Dy(2)−O(14)	86.34(15)	O(25)−P(8)−O(23)	115.4(3)
O(22)−Dy(2)−O(14)	141.57(15)	O(25)−P(8)−O(24)	105.9(3)
O(13)−Dy(2)−O(14)	75.25(15)	O(23)−P(8)−O(24)	111.0(3)
O(3)−P(1)−O(2)	114.8(3)	O(25)−P(8)−C(7)	108.7(3)
O(3)−P(1)−O(4)	110.7(3)	O(23)−P(8)−C(7)	108.4(3)
O(2)−P(1)−O(4)	110.1(3)	O(24)−P(8)−C(7)	107.1(3)

Symmetry codes: #1 -x+1/2,y-1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2.

Table S3. Selected bond lengths (Å) and angles (°) for **2** at 293 K.

2			
C(1)−P(1)	1.843(11)	O(2)−P(2)	1.509(7)
C(1)−P(2)	1.828(8)	O(3)−P(2)	1.579(8)
C(3)−P(3)	1.840(9)	O(4)−P(2)	1.517(7)
C(3)−P(4)	1.840(10)	O(5)−P(1)	1.529(7)
C(5)−P(5)	1.812(10)	O(6)−P(1)	1.587(8)
C(5)−P(6)	1.866(12)	O(8)−P(4)	1.501(7)
C(7)−P(8)	1.851(11)	O(9)−P(3)	1.523(6)

C(7)−P(7)	1.864(10)	O(10)−P(3)	1.569(8)
Gd(1)−O(28)#1	2.324(7)	O(12)−P(4)	1.591(7)
Gd(1)−O(17)#1	2.323(7)	O(13)−P(4)	1.492(7)
Gd(1)−O(8)	2.333(7)	O(14)−P(3)	1.499(8)
Gd(1)−O(1)	2.328(6)	O(15)−P(5)	1.498(7)
Gd(1)−O(21)#1	2.355(7)	O(16)−P(6)	1.544(6)
Gd(1)−O(2)	2.375(7)	O(17)−P(6)	1.520(7)
Gd(1)−O(9)	2.421(7)	O(18)−P(6)	1.531(6)
Gd(2)−O(18)#1	2.239(6)	O(20)−P(5)	1.594(7)
Gd(2)−O(23)	2.384(7)	O(21)−P(5)	1.526(7)
Gd(2)−O(15)	2.361(7)	O(22)−P(7)	1.508(8)
Gd(2)−O(22)	2.364(8)	O(23)−P(8)	1.481(8)
Gd(2)−O(16)	2.383(6)	O(24)−P(8)	1.490(7)
Gd(2)−O(13)	2.404(7)	O(25)−P(8)	1.571(8)
Gd(2)−O(14)	2.422(8)	O(27)−P(7)	1.565(7)
O(1)−P(1)	1.523(7)	O(28)−P(7)	1.518(7)

O(28)#1−Gd(1)−O(17)#1	86.0(3)	O(1)−P(1)−C(1)	107.3(4)
O(28)#1−Gd(1)−O(8)	158.3(2)	O(5)−P(1)−C(1)	107.6(4)
O(17)#1−Gd(1)−O(8)	92.3(2)	O(6)−P(1)−C(1)	107.0(4)
O(28)#1−Gd(1)−O(1)	77.9(2)	O(2)−P(2)−O(4)	113.9(4)
O(17)#1−Gd(1)−O(1)	135.1(2)	O(2)−P(2)−O(3)	110.6(5)
O(8)−Gd(1)−O(1)	117.1(2)	O(4)−P(2)−O(3)	110.7(4)
O(28)#1−Gd(1)−O(21)#1	115.4(2)	O(2)−P(2)−C(1)	107.0(4)

O(17)#1−Gd(1)−O(21)#1	76.6(2)	O(4)−P(2)−C(1)	110.7(5)
O(8)−Gd(1)−O(21)#1	85.1(2)	O(3)−P(2)−C(1)	103.3(4)
O(1)−Gd(1)−O(21)#1	73.3(2)	O(14)−P(3)−O(9)	117.3(4)
O(28)#1−Gd(1)−O(2)	88.6(3)	O(14)−P(3)−O(10)	110.7(4)
O(17)#1−Gd(1)−O(2)	145.7(2)	O(9)−P(3)−O(10)	109.3(4)
O(8)−Gd(1)−O(2)	80.6(2)	O(14)−P(3)−C(3)	108.2(4)
O(1)−Gd(1)−O(2)	76.1(2)	O(9)−P(3)−C(3)	106.4(4)
O(21)#1−Gd(1)−O(2)	135.3(2)	O(10)−P(3)−C(3)	104.0(5)
O(28)#1−Gd(1)−O(9)	79.4(2)	O(13)−P(4)−O(8)	115.6(4)
O(17)#1−Gd(1)−O(9)	72.4(2)	O(13)−P(4)−O(12)	107.2(4)
O(8)−Gd(1)−O(9)	79.4(2)	O(8)−P(4)−O(12)	109.9(4)
O(1)−Gd(1)−O(9)	142.0(2)	O(13)−P(4)−C(3)	109.5(4)
O(21)#1−Gd(1)−O(9)	144.5(2)	O(8)−P(4)−C(3)	108.5(4)
O(2)−Gd(1)−O(9)	73.3(3)	O(12)−P(4)−C(3)	105.7(4)
O(18)#1−Gd(2)−O(23)	110.2(3)	O(15)−P(5)−O(21)	118.5(4)
O(18)#1−Gd(2)−O(15)	94.7(2)	O(15)−P(5)−O(20)	108.1(4)
O(23)−Gd(2)−O(15)	134.5(3)	O(21)−P(5)−O(20)	108.0(4)
O(18)#1−Gd(2)−O(22)	78.2(3)	O(15)−P(5)−C(5)	106.9(4)
O(23)−Gd(2)−O(22)	74.4(3)	O(21)−P(5)−C(5)	106.6(4)
O(15)−Gd(2)−O(22)	74.5(3)	O(20)−P(5)−C(5)	108.5(5)
O(18)#1−Gd(2)−O(16)	166.8(3)	O(17)−P(6)−O(18)	113.6(4)
O(23)−Gd(2)−O(16)	81.6(3)	O(17)−P(6)−O(16)	109.9(4)
O(15)−Gd(2)−O(16)	80.1(2)	O(18)−P(6)−O(16)	112.1(4)
O(22)−Gd(2)−O(16)	111.6(2)	O(17)−P(6)−C(5)	105.9(5)

O(18)#1−Gd(2)−O(13)	95.4(2)	O(18)−P(6)−C(5)	108.0(4)
O(23)−Gd(2)−O(13)	70.1(3)	O(16)−P(6)−C(5)	107.0(4)
O(15)−Gd(2)−O(13)	146.4(2)	O(22)−P(7)−O(28)	114.4(4)
O(22)−Gd(2)−O(13)	139.0(2)	O(22)−P(7)−O(27)	111.7(4)
O(16)−Gd(2)−O(13)	82.9(2)	O(28)−P(7)−O(27)	109.5(4)
O(18)#1−Gd(2)−O(14)	81.5(3)	O(22)−P(7)−C(7)	108.4(5)
O(23)−Gd(2)−O(14)	144.5(3)	O(28)−P(7)−C(7)	107.7(5)
O(15)−Gd(2)−O(14)	74.4(2)	O(27)−P(7)−C(7)	104.6(4)
O(22)−Gd(2)−O(14)	141.0(2)	O(24)−P(8)−O(23)	116.0(5)
O(16)−Gd(2)−O(14)	85.4(2)	O(24)−P(8)−O(25)	105.6(5)
O(13)−Gd(2)−O(14)	75.6(2)	O(23)−P(8)−O(25)	111.4(5)
O(1)−P(1)−O(5)	115.2(4)	O(24)−P(8)−C(7)	107.9(5)
O(1)−P(1)−O(6)	108.4(4)	O(23)−P(8)−C(7)	108.2(5)
O(5)−P(1)−O(6)	110.9(4)	O(25)−P(8)−C(7)	107.5(5)

Symmetry codes: #1 -x+1/2,y-1/2,-z+3/2 #2 -x+1/2,y+1/2,-z+3/2