Supporting Information

Contents

Experimental Section

Materials and methods

All chemicals were reagent grade and used as purchased without further purification, including the organic amine 1,3,5-tris(4-pyridyl)benzene (TPB) and hydroxyethylidene diphosphonate (HEDP).

Synthesis of 1: Dy_2O_3 (0.09 g, 0.4 mmol), TPB (0.03 g, 0.01 mmol), 60% HEDP (0.3 mL, 0.7 mmol), and 5 mL H_2O were added in a sealed Teflon-lined autoclave (20 mL), then heated to 120 ℃ for 7 days. After cooling for 4 hours at room temperature, yellow block crystals were obtained. Yield: ca. 37% based on TPB. Elemental analysis for compound **1** (%): Anal. calcd for $C_{50}H_{64}N_6O_{32}P_8Dy_2$ (1833.83): C, 32.75; H, 3.52; N, 4.58; O, 27.92. Found: C, 35.55; H, 4.52; N, 4.82; O, 28.05. IR before irradiation (KBr pellets, cm^{-1}): 3400(s), 3080(s), 2340(w), 2140(w), 1630(s), 1500(m), 1400(w), 1150(s), 1070(s), 926(s), 810(s), 654(m), 565(s), 447(m). IR after irradiation (KBr pellets, cm^{-1}): 3410(s), 3090(s), 2330(w), 2150(w), 1630(s), 1500(m), 1410(w), 1150(s), 1060(s), 932(s), 808(s), 655(m), 555(s), 443(m).

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra of **1** were performed using a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. The photo-luminescence data were analyzed by an F-4700 Fluorescence spectrometer. The solid-state UV-Vis spectra were measured at RT using $BaSO_4$ as a reference on a Puxi Tu-1901 spectrophotometer. The electron paramagnetic resonance (EPR) spectroscopy was recorded on a Bruker E500 spectrometer using powder samples. Thermogravimetric (TG) analyses were measured using a powder sample under N_2 atmosphere on a TG-DTA 8121 analyzer. Magnetic measurements of the powder samples of **1** 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 (320−780 nm, 150 w, at least 60 min) was equipped to prepare the colored samples of UV-vis, PXRD ESR and magnetic studies.

X-ray Crystallography.

The single-crystal X-ray diffraction data of **1** was collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å). SHELX-2016 software was used to solve the structure. Detailed crystallographic data for **1** was summarized in Table S1, and the selected bond lengths and angles were listed in Table S3. Full crystallographic data for **1** has been deposited with the CCDC (2024837).

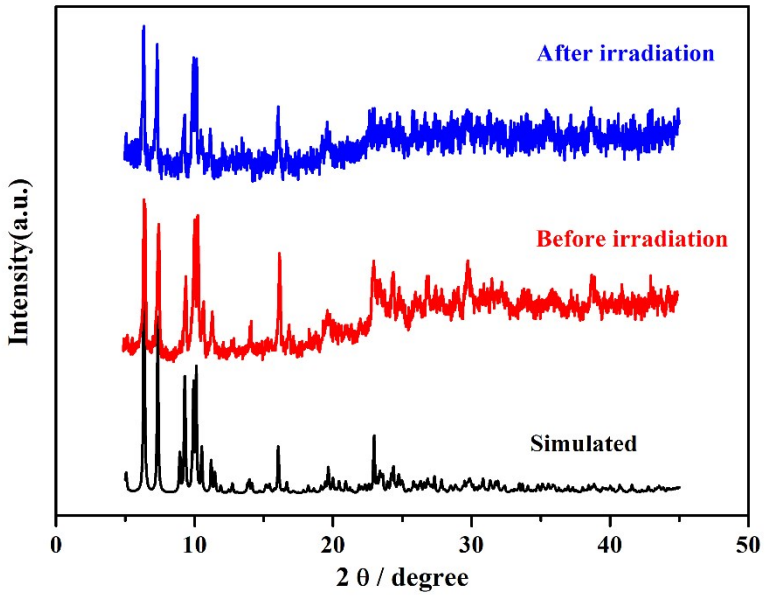

Figure S1 Simulated(black), before(red) and after(blue) irradiated PXRD patterns of **1**.

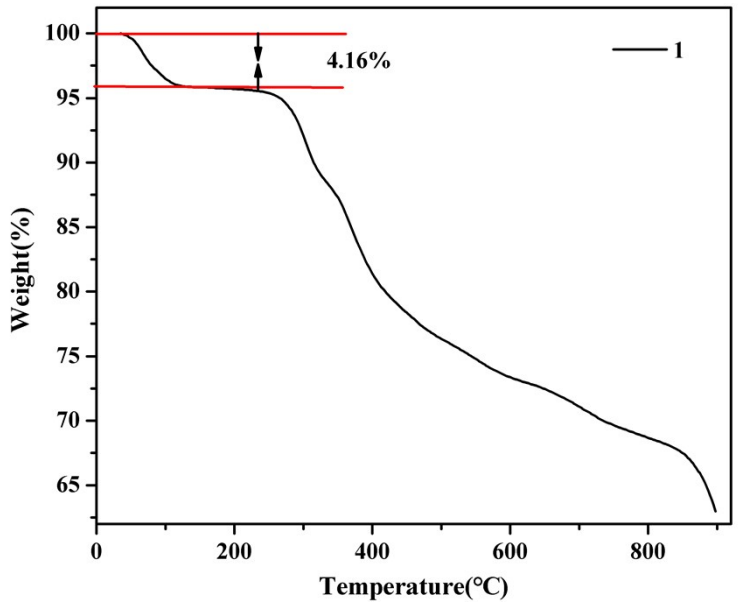

Figure S2 The TG plot of **1**.

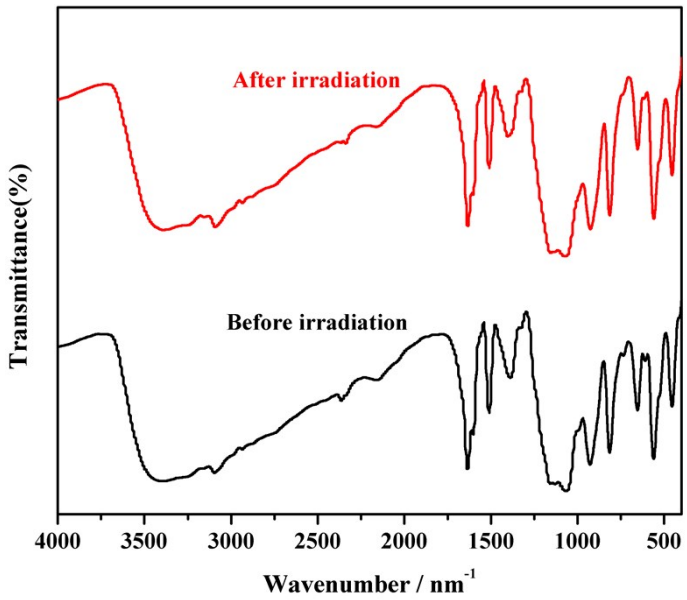

Figure S3 IR spectra of **1** before (black) and after (red) light irradiation.

Figure S4 Color changes of the powder samples for **1** upon light and heating/dark treatment.

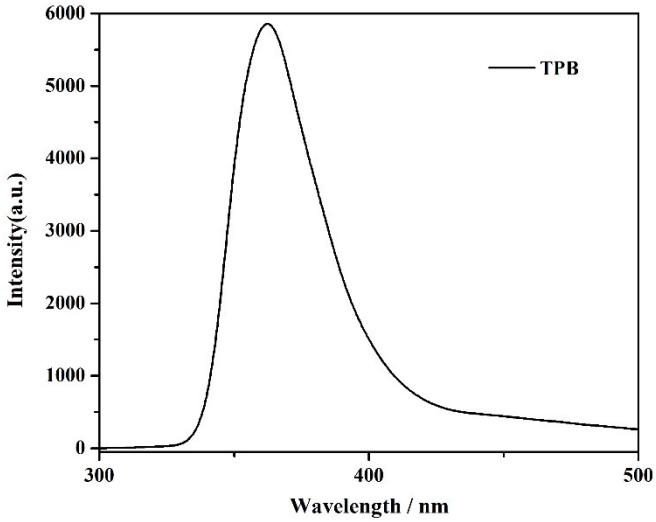

Figure S5 Fluorescence spectrum of TPB ligand at solid state.

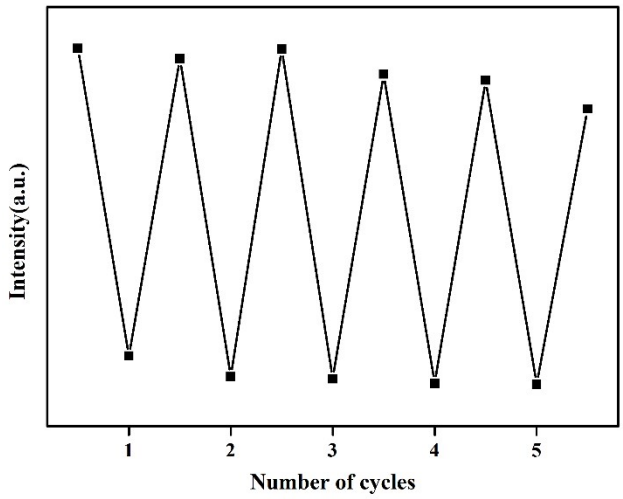

Figure S6 The switching of photoinduced coloration and decoloration process in five cycles.

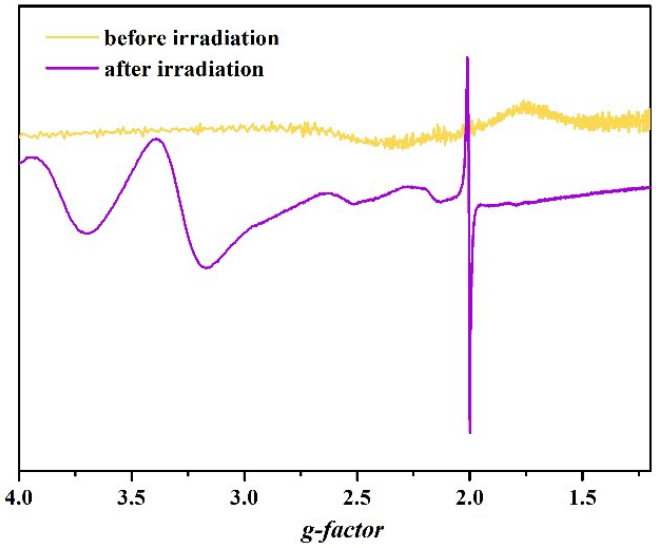

Figure S7 EPR spectra of **1** at 110 K at a frequency of 9.41 GHz.

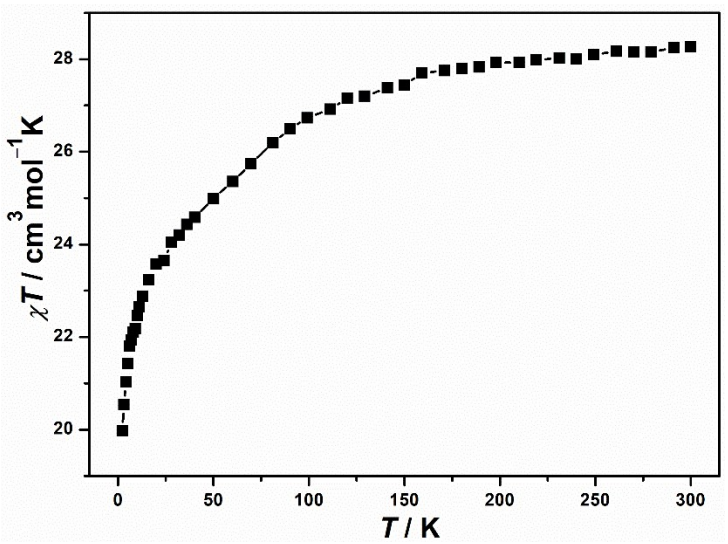

Figure S8 Plots of χT vs T of **1** after decoloration under a dc field of 1000 Oe. After the dark gray sample returned to the initial dark yellow one, the χT value at room temperature also increased to the initial one of 28.23 cm^3 mol^{-1} K.

Table S1. Crystallographic data for **1** at 293 K

	1
Chemical formula	$C_{50}H_{64}N_6O_{32}P_8Dy_2$
M_r	1833.83
space group	$P\bar{1}$
Crystal system	Triclinic
a (Å)	10.3969 (6)
b (Å)	18.2975 (9)
c (Å)	19.3503 (8)
V (Å^3)	3490.6 (3)
Z	2
F(000)	1828
Dc (gcm^{-3})	1.745
μ (mm^{-1})	2.398
R_{int}	0.0339
limiting indices	-12<=h<=10 -21<=k<=21 -23<=l<=23
Collected reflections	19376
Unique reflections	12281
GOF on F_2	0.999
R_1, wR_2 [$I>2\sigma(I)$]	0.0381, 0.0876
R_1, wR_2 [all data]	0.0576, 0.0952

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

Table S2. Continuous Shape Measure (CShM) analyses of geometries for compound **1** by SHAPE 2.0 Software.

Geometry	**1**-Dy1	**1**-Dy2
Heptagon(D_{7h})	31.911	33.154
Hexagonal pyramid(C_{6v})	21.087	20.148
Pentagonal bipyramid(D_{5h})	6.663	5.720
Capped octahedron(C_{3v})	1.160	1.330
Capped trigonal prism(C_{2v})	0.341	0.436
Johnson pentagonal bipyramid J13(D_{5h})	9.629	8.838
Johnson elongated triangular pyramid J7(C_{3v})	19.328	19.996

Table S3. Selected bond lengths (Å) and angles (°) for **1** at 293 K

1			
C(43)−P(2)	1.841(5)	O(2)−P(2)	1.566(4)
C(43)−P(1)	1.836(5)	O(4)−P(1)	1.579(4)
C(45)−P(7)	1.842(5)	O(5)−P(1)	1.503(4)
C(45)−P(8)	1.847(5)	O(6)−P(2)	1.503(4)
C(47)−P(3)	1.829(6)	O(7)−P(1)	1.502(4)
C(47)−P(4)	1.859(6)	O(8)−P(3)	1.567(4)
C(49)−P(5)	1.831(6)	O(9)−P(3)	1.522(4)
C(49)−P(6)	1.850(5)	O(11)−P(4)	1.559(4)
Dy(1)−O(5)#1	2.265(4)	O(12)−P(4)	1.485(4)
Dy(1)−O(22)	2.262(3)	O(13)−P(3)	1.496(4)
Dy(1)−O(14)	2.295(3)	O(14)−P(4)	1.500(4)
Dy(1)−O(15)	2.314(4)	O(15)−P(5)	1.510(4)
Dy(1)−O(1)#1	2.347(3)	O(16)−P(5)	1.502(4)
Dy(1)−O(21)	2.370(4)	O(17)−P(5)	1.549(4)
Dy(1)−O(13)	2.438(4)	O(19)−P(6)	1.503(4)
Dy(2)−O(16)#2	2.236(4)	O(20)−P(6)	1.534(4)
Dy(2)−O(28)	2.284(3)	O(21)−P(6)	1.518(4)
Dy(2)−O(12)	2.279(4)	O(22)−P(8)	1.506(4)
Dy(2)−O(19)#2	2.296(4)	O(23)−P(8)	1.526(4)
Dy(2)−O(27)	2.350(4)	O(24)−P(7)	1.580(4)

Dy(2)−O(6)	2.361(3)	O(26)−P(7)	1.486(4)
Dy(2)−O(7)	2.403(4)	O(27)−P(7)	1.499(4)
O(1)−P(2)	1.505(3)	O(28)−P(8)	1.522(4)

O(5)#1−Dy(1)−O(22)	155.88(13)	O(7)−P(1)−C(43)	107.9(2)
O(5)#1−Dy(1)−O(14)	97.14(14)	O(5)−P(1)−C(43)	105.7(2)
O(22)−Dy(1)−O(14)	85.32(13)	O(4)−P(1)−C(43)	108.0(2)
O(5)#1−Dy(1)−O(15)	78.71(13)	O(6)−P(2)−O(1)	116.5(2)
O(22)−Dy(1)−O(15)	124.84(13)	O(6)−P(2)−O(2)	109.8(2)
O(14)−Dy(1)−O(15)	75.82(13)	O(1)−P(2)−O(2)	108.1(2)
O(5)#1−Dy(1)−O(1)#1	80.21(12)	O(6)−P(2)−C(43)	109.3(2)
O(22)−Dy(1)−O(1)#1	87.12(12)	O(1)−P(2)−C(43)	106.5(2)
O(14)−Dy(1)−O(1)#1	153.97(13)	O(2)−P(2)−C(43)	106.2(2)
O(15)−Dy(1)−O(1)#1	128.06(13)	O(13)−P(3)−O(9)	113.9(2)
O(5)#1−Dy(1)−O(21)	123.98(13)	O(13)−P(3)−O(8)	111.5(2)
O(22)−Dy(1)−O(21)	72.62(13)	O(9)−P(3)−O(8)	106.3(2)
O(14)−Dy(1)−O(21)	122.12(13)	O(13)−P(3)−C(47)	109.2(2)
O(15)−Dy(1)−O(21)	74.94(12)	O(9)−P(3)−C(47)	108.1(3)
O(1)#1−Dy(1)−O(21)	78.79(12)	O(8)−P(3)−C(47)	107.6(2)
O(5)#1−Dy(1)−O(13)	77.59(13)	O(12)−P(4)−O(14)	114.9(2)
O(22)−Dy(1)−O(13)	79.66(12)	O(12)−P(4)−O(11)	109.0(2)
O(14)−Dy(1)−O(13)	76.76(12)	O(14)−P(4)−O(11)	110.2(2)
O(15)−Dy(1)−O(13)	140.87(12)	O(12)−P(4)−C(47)	106.2(2)
O(1)#1−Dy(1)−O(13)	77.39(12)	O(14)−P(4)−C(47)	109.4(2)
O(21)−Dy(1)−O(13)	144.06(12)	O(11)−P(4)−C(47)	106.8(3)
O(16)#2−Dy(2)−O(28)	159.04(14)	O(16)−P(5)−O(15)	114.1(2)
O(16)#2−Dy(2)−O(12)	91.17(14)	O(16)−P(5)−O(17)	108.0(3)
O(28)−Dy(2)−O(12)	83.26(13)	O(15)−P(5)−O(17)	110.6(2)
O(16)#2−Dy(2)−O(19)#2	79.62(13)	O(16)−P(5)−C(49)	106.0(2)
O(28)−Dy(2)−O(19)#2	97.88(13)	O(15)−P(5)−C(49)	107.7(2)
O(12)−Dy(2)−O(19)#2	157.17(14)	O(17)−P(5)−C(49)	110.4(2)
O(16)#2−Dy(2)−O(27)	81.36(14)	O(19)−P(6)−O(21)	113.3(2)
O(28)−Dy(2)−O(27)	77.77(12)	O(19)−P(6)−O(20)	111.4(2)
O(12)−Dy(2)−O(27)	79.72(13)	O(21)−P(6)−O(20)	110.4(2)
O(19)#2−Dy(2)−O(27)	78.27(14)	O(19)−P(6)−C(49)	106.5(2)
O(16)#2−Dy(2)−O(6)	121.84(14)	O(21)−P(6)−C(49)	107.9(2)
O(28)−Dy(2)−O(6)	77.14(12)	O(20)−P(6)−C(49)	107.0(2)
O(12)−Dy(2)−O(6)	124.84(13)	O(26)−P(7)−O(27)	115.8(2)
O(19)#2−Dy(2)−O(6)	77.22(13)	O(26)−P(7)−O(24)	107.4(2)
O(27)−Dy(2)−O(6)	141.84(12)	O(27)−P(7)−O(24)	110.8(2)
O(16)#2−Dy(2)−O(7)	78.78(13)	O(26)−P(7)−C(45)	109.2(2)
O(28)−Dy(2)−O(7)	117.89(12)	O(27)−P(7)−C(45)	108.0(2)
O(12)−Dy(2)−O(7)	71.21(13)	O(24)−P(7)−C(45)	105.1(2)
O(19)#2−Dy(2)−O(7)	126.22(13)	O(22)−P(8)−O(28)	111.5(2)

O(27)−Dy(2)−O(7)	144.14(13)	O(22)−P(8)−O(23)	110.7(2)
O(6)−Dy(2)−O(7)	73.76(12)	O(28)−P(8)−O(23)	110.5(2)
O(7)−P(1)−O(5)	117.2(2)	O(22)−P(8)−C(45)	107.4(2)
O(7)−P(1)−O(4)	110.4(2)	O(28)−P(8)−C(45)	109.2(2)
O(5)−P(1)−O(4)	107.2(2)	O(23)−P(8)−C(45)	107.4(2)

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