Supporting Information

Syntheses of series of lanthanide metal−organic frameworks for efficient UV-light-driven dye degradation: experiment and simulation

Materials and Method

5-(1H-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid was obtained from Jinan Henghua Sci. & Tec. Co. Ltd. and used without further purification. Other reagents for synthesis were obtained from commercial sources and have been used without further purification. Powder X-ray diffraction (PXRD) data were collected using Bruker ADVANCE X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. Fourier transform infrared (FT-IR) spectra for the complexes as KBr pellet were recorded using Nicolet Impact 750 FTIR in the range of 400-4000 cm^{-1}. Thermogravimetric analysis was performed under N_2 atmosphere from room temperature to 900 °C at a heating rate of 10 °C min^{-1}. The photocatalytic activity studies were carried out using Shimadzu UV-Vis 2501PC recording spectrophotometer. Hitachi U-3310 UV-vis spectrometer was selected to perform diffusion reflectance measurement.

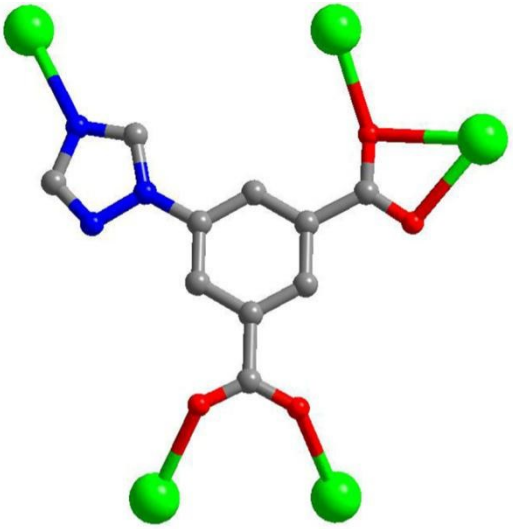
X-ray Crystallography

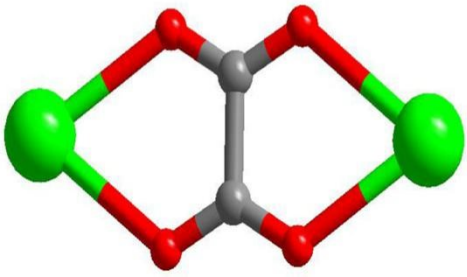
The single crystal X-ray diffraction data were collected on Bruker SMART APEX diffractometer which was equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) by using an ω-scan technique. The structures were solved using direct method (SHLEXS-2014) and refined by full-matrix least-squares procedure based on F^2 (Shelxl-2014). All the hydrogen atoms were generated geometrically and refined isotropically using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details for **1-3** are listed in Tables S1. The selected bond and angles parameters are listed in Tables

S2. CCDC numbers: 2014164 (**1**), 2014166 (**2**) and 2014165 (**3**).

Photocatalytic Method

The photocatalytic reactions were performed as follows: the finely divided sample of **1** (50 mg) was dispersed in 50 mL aqueous solution of methyl violet (10 mg/L) with stirring in dark for 30 min to ensure the establishment of adsorption-desorption equilibrium. The photocatalytic degradation of MV was conducted on XPA-7 type photochemical reactor equipped with 100 W mercury lamp (mean wavelength 365 nm) with light intensity of 12.7 mW/cm^2 at quartz tube positions. Aliquots of 5.0 mL were taken out at specific time intervals and separated through centrifugation and then subsequently analyzed using UV–visible spectrophotometer. In addition, a control experiment was also performed under the identical reaction conditions, but without the addition of catalysts **1**.





Scheme S1. schematic presentation of the coordination modes of the ligands in this work.

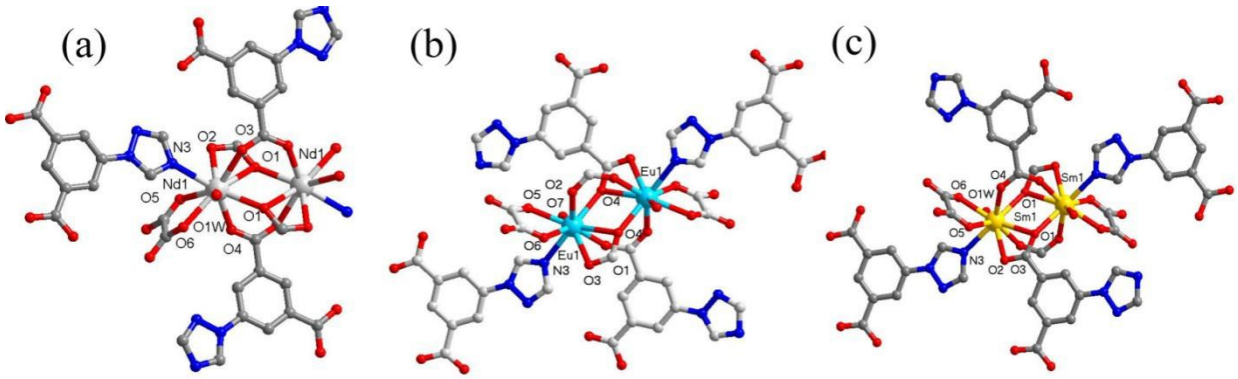


Fig. S1. view of the coordination geometries of Ln ions in this work.

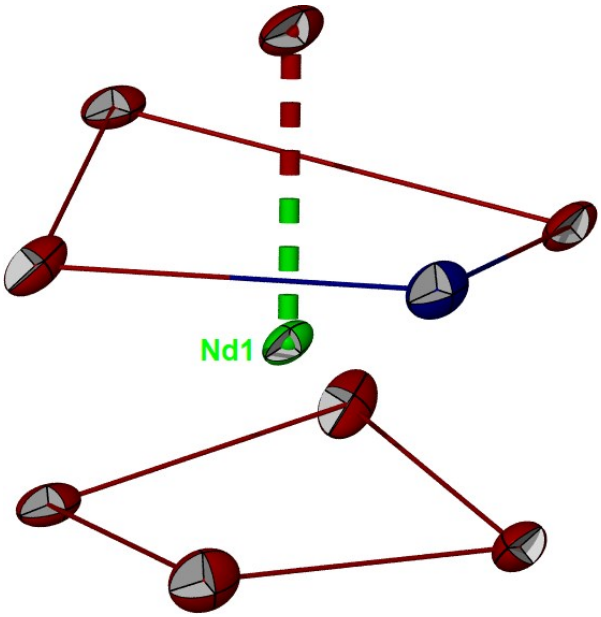


Fig. S2. view of the coordination geometries of the Nd^{3+} ion in **1**-Nd.

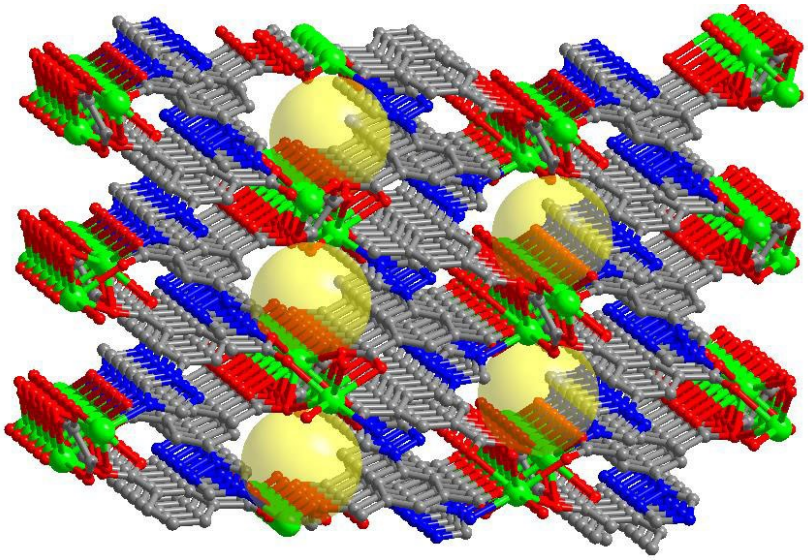


Fig. S3. view of the 3D framework in **1**-Nd.

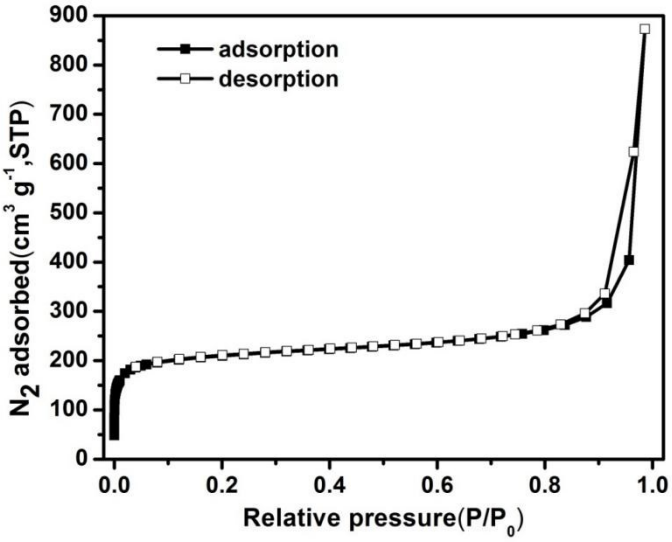
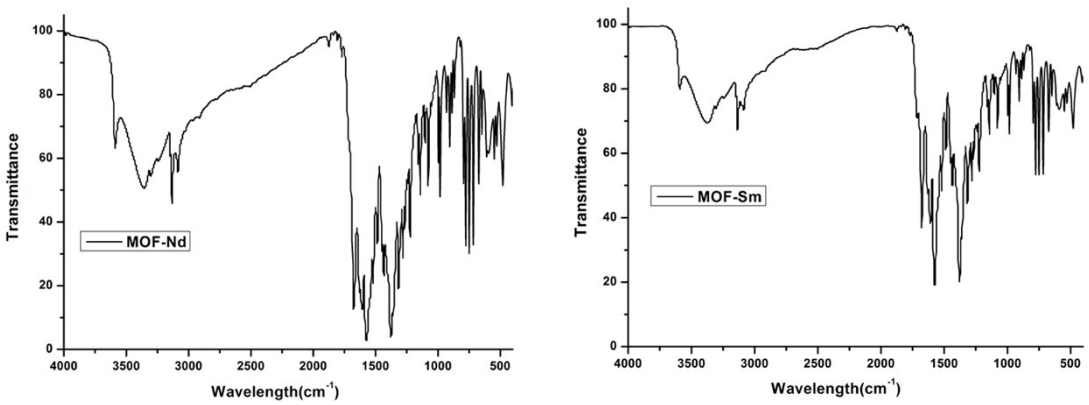


Fig. S4. nitrogen adsorption-desorption isotherms in **1**-Nd.

(a) (b)



(c)

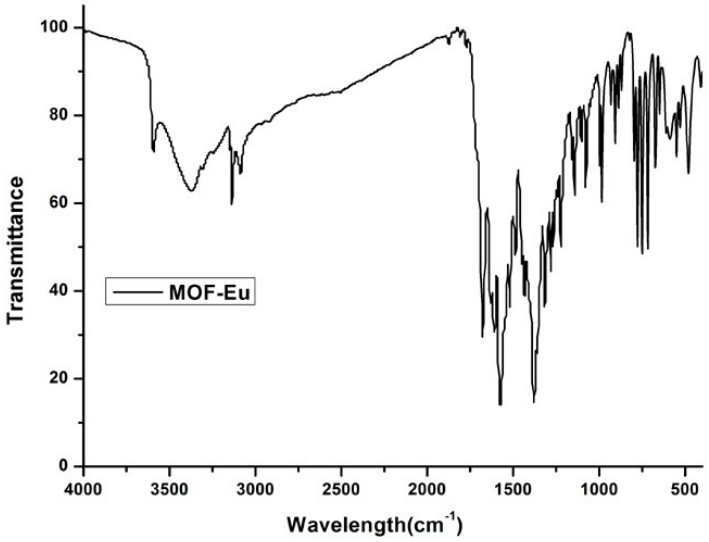


Fig. S5. IR spectra pattern for **1-3** (a-c).

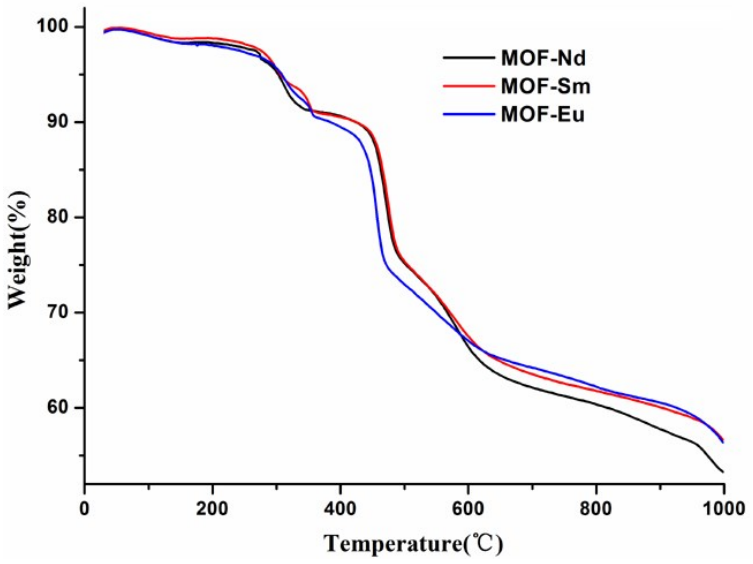


Fig. S6. TG curves for compounds **1-3 (**30−1000 °C)

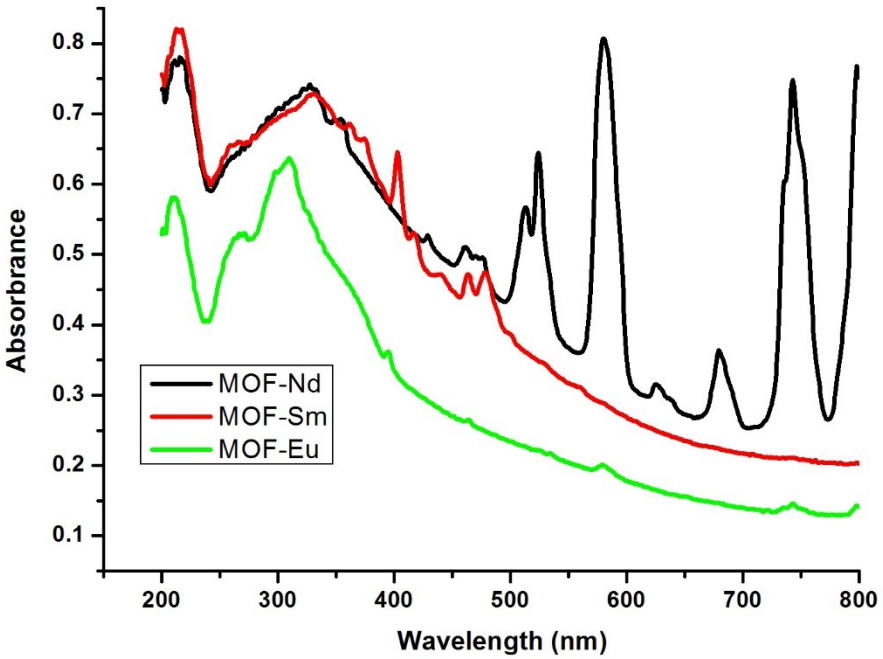
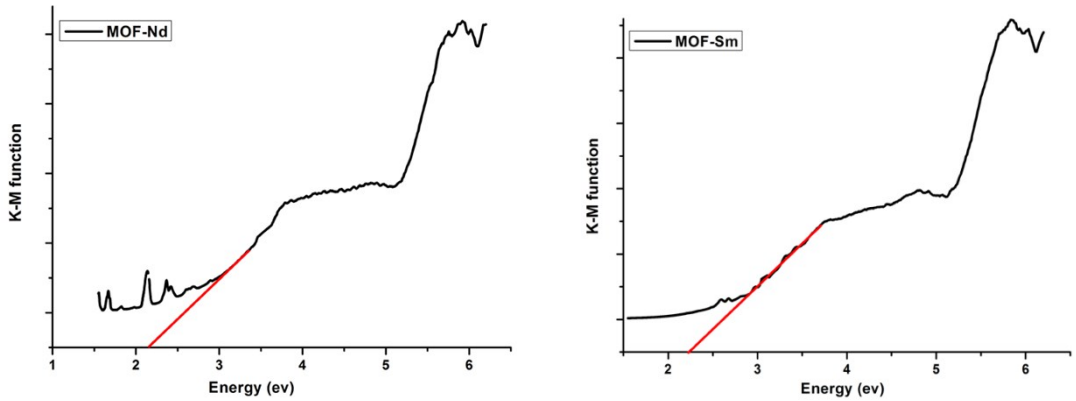


Fig. S7 The diffuse-reflectance UV-vis spectra for compounds **1-3**



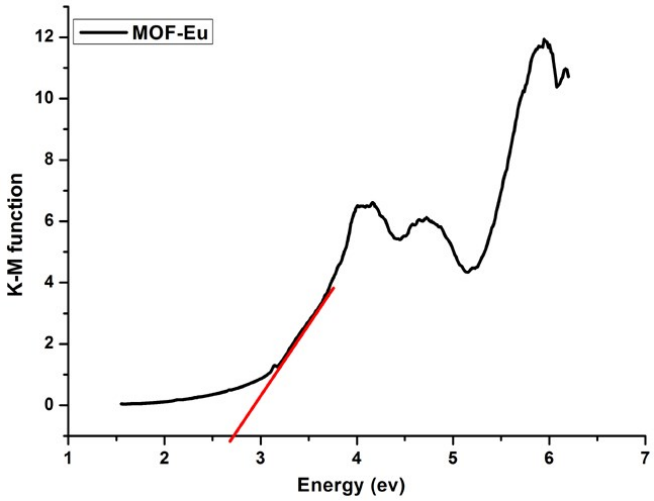


Fig. S8. Kubelka-Munk-transformed diffuse reflectance for MOFs **1-3**

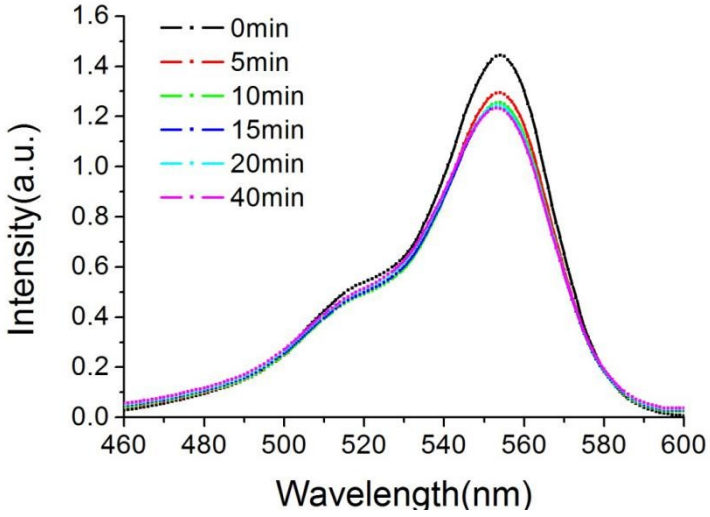
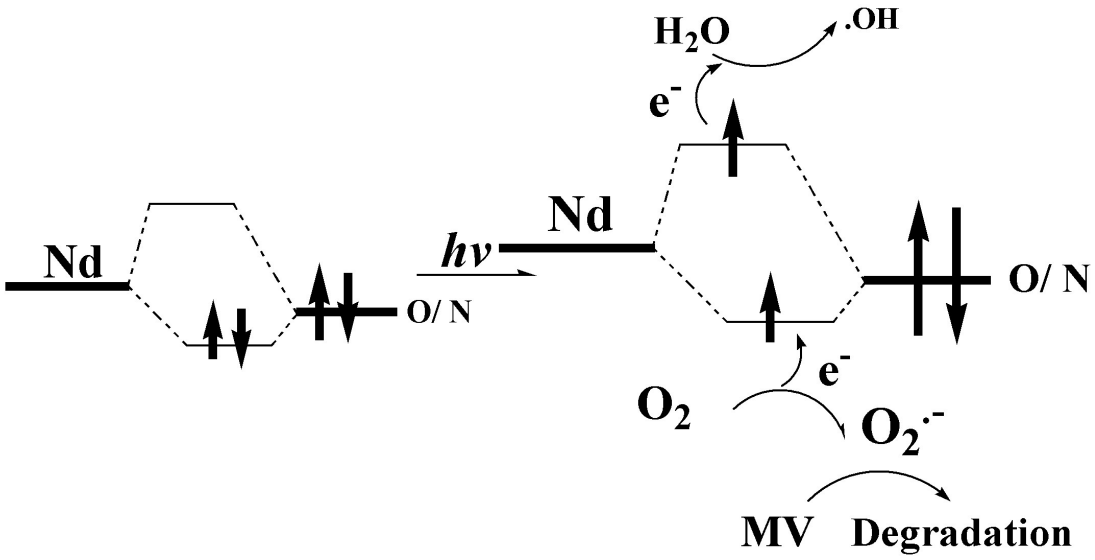
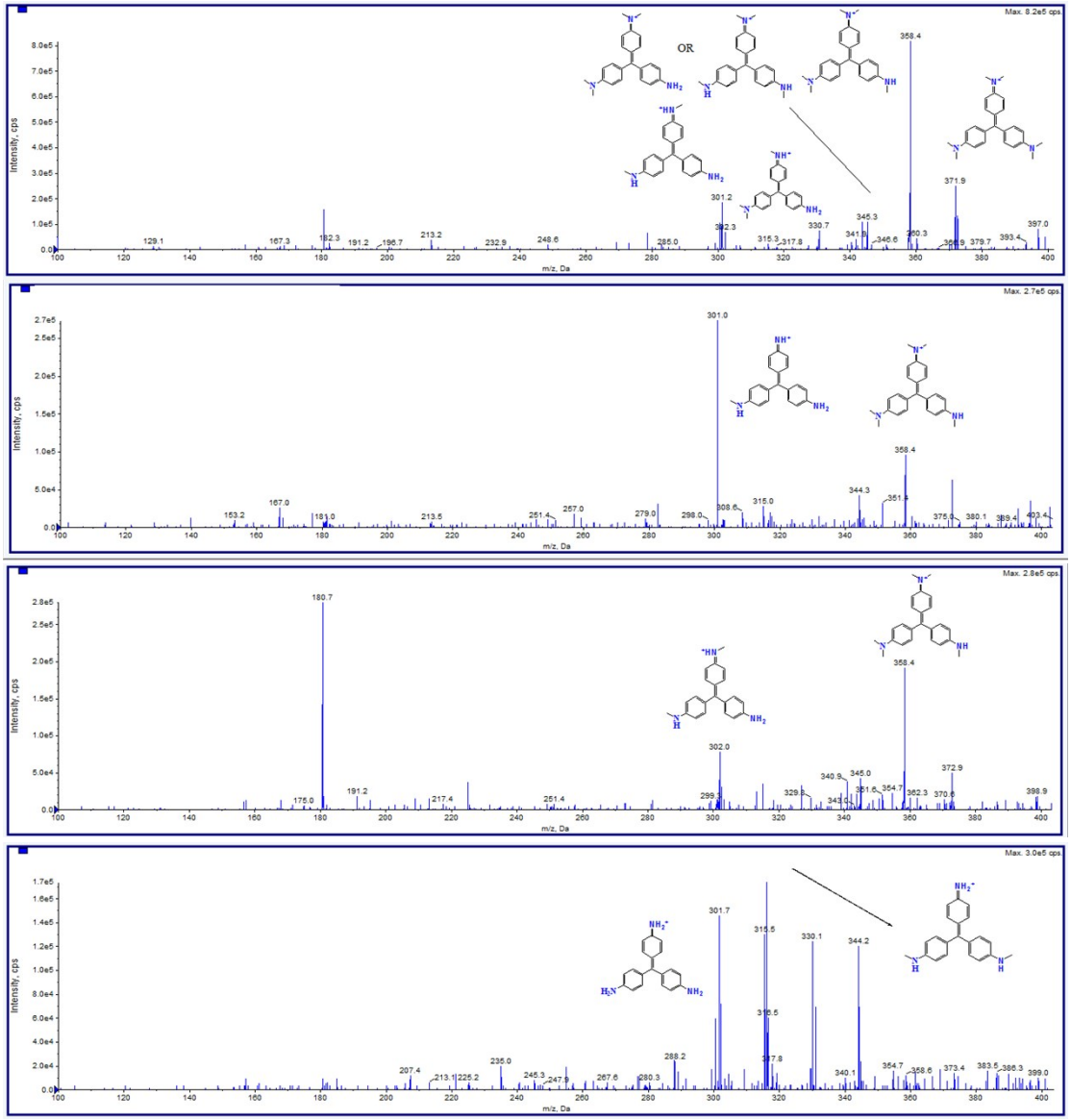


Fig. S9. the UV–Vis absorption spectra of the MV solution during the decomposition reaction in the presence of **1**-Nd in dark.



Scheme S2. the possible mechanism of the photodegradation process of MV.



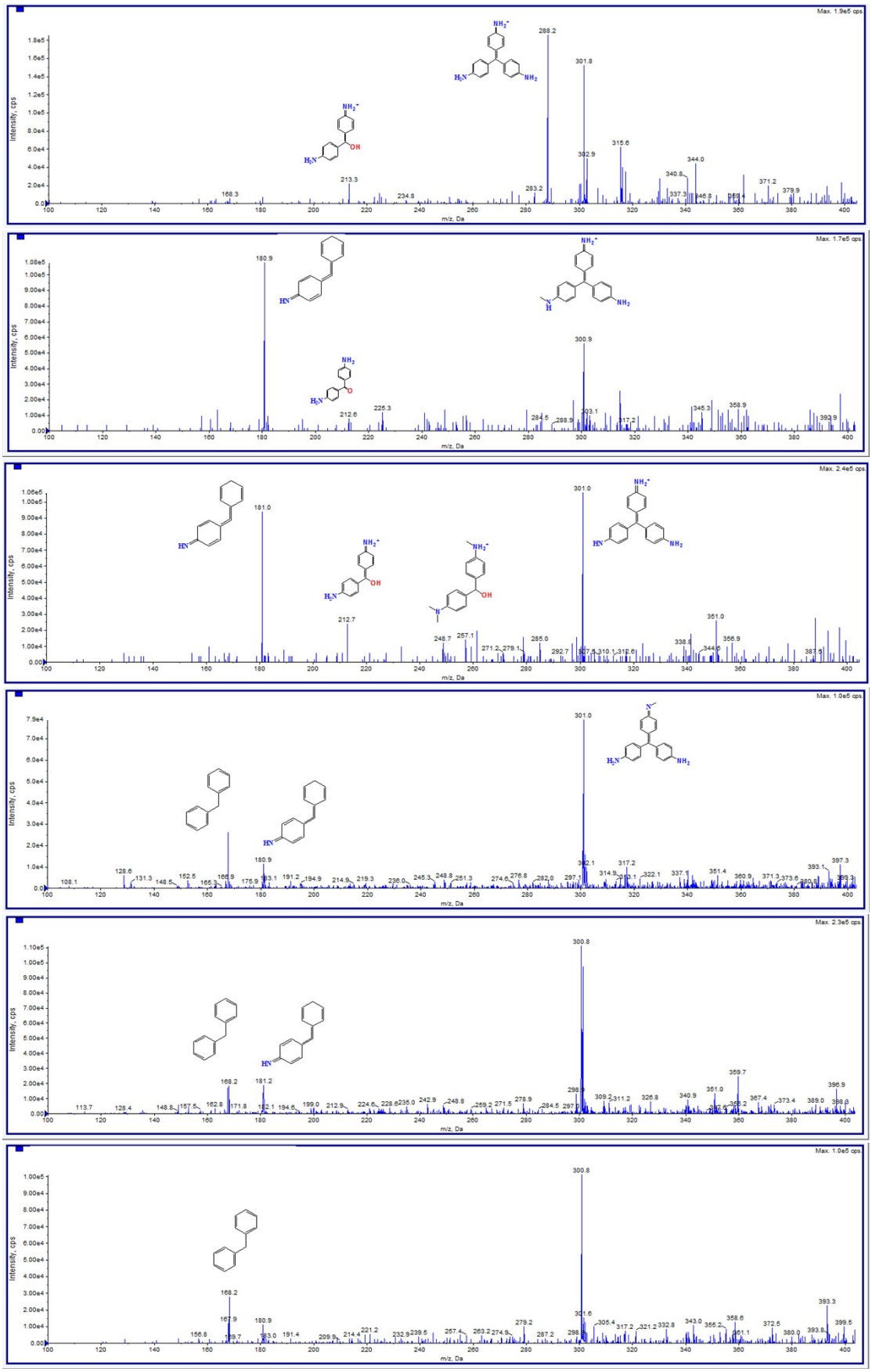


Fig. S10. LC-MS spectra from the MV degradation

Table S1. Crystallographic data and structural refinement parameters for complexes[a]

Compounds	**1**	**2**	**3**
Empirical formula	$C_{22}H_{14}N_6Nd_2O_{14}$	$C_{22}H_{14}N_6O_{14}Sm_2$	$C_{22}H_{14}Eu_2N_6O_{14}$
Formula weight	874.87	887.09	890.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c	P 21/c
a /Å	9.6704(8)	9.6045(10)	9.5741(8)
b /Å	18.4228(16)	18.370(2)	18.3271(15)
c /Å	6.7919(6)	6.7842(7)	6.7762(6)
α/°	90	90	90
β/°	100.184(2)	100.0762(18)	100.0570(10)
γ/°	90	90	90
V/Å^3	1190.95(18)	1178.5(2)	1170.72(17)
Z	2	2	2
ρ_{calc} (g ·cm^{-3})	2.440	2.500	2.526
μ (mm^{-1})	4.406	5.029	5.404
F (000)	840	848	852
Reflections collected	6342	6196	6338
Reflections unique	2365	2378	2374
S on F^2	1.021	0.975	1.085
R_{int}	0.0236	0.0247	0.0184

parameters	199	199	220
R_1, wR_2[a] [I>2σ(I)]	0.0242, 0.0560	0.0266, 0.0613	0.0203, 0.0454
R_1, wR_2[a] (all data)	0.0308, 0.0585	0.0363, 0.0655	0.0220, 0.0461

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

Table S2. Selected bond distances /Å and bond angles /° for **1-3**

Compound **1**			
Nd(1)-O(6)#1	2.447(3)	Nd(1)-O(3)#2	2.458(3)
Nd(1)-O(4)#3	2.459(3)	Nd(1)-O(2)#4	2.484(3)
Nd(1)-O(1)	2.494(3)	Nd(1)-O(5)	2.514(3)
Nd(1)-O(1W)	2.554(3)	Nd(1)-N(3)#5	2.601(3)
Nd(1)-O(1)#4	2.699(3)	O(1)-C(1)	1.285(4)
O(1)-Nd(1)#4	2.699(3)	O(2)-C(1)	1.249(5)
O(2)-Nd(1)#4	2.484(3)	O(3)-C(8)	1.259(4)
O(3)-Nd(1)#6	2.458(3)	O(4)-C(8)	1.250(4)
O(4)-Nd(1)#7	2.459(3)	O(5)-C(11)	1.243(5)
O(6)-C(11)	1.247(5)	O(6)-Nd(1)#1	2.447(3)

N(1)-C(10)	1.326(5)	N(1)-N(2)	1.369(4)
N(1)-C(6)	1.421(4)	N(2)-C(9)	1.303(5)
N(3)-C(10)	1.332(5)	N(3)-C(9)	1.357(5)
N(3)-Nd(1)#5	2.601(3)		
O(6)#1-Nd(1)-O(3)#2	139.17(9)	O(6)#1-Nd(1)-O(4)#3	75.69(9)
O(3)#2-Nd(1)-O(4)#3	135.54(9)	O(6)#1-Nd(1)-O(2)#4	130.36(9)
O(3)#2-Nd(1)-O(2)#4	73.57(10)	O(4)#3-Nd(1)-O(2)#4	106.14(10)
O(6)#1-Nd(1)-O(1)	104.01(9)	O(3)#2-Nd(1)-O(1)	73.43(9)
O(4)#3-Nd(1)-O(1)	70.73(10)	O(2)#4-Nd(1)-O(1)	123.79(9)
O(6)#1-Nd(1)-O(5)	65.42(9)	O(3)#2-Nd(1)-O(5)	140.80(9)
O(4)#3-Nd(1)-O(5)	68.91(9)	O(2)#4-Nd(1)-O(5)	69.35(9)
O(1)-Nd(1)-O(5)	139.63(9)	O(6)#1-Nd(1)-O(1W)	71.87(10)
O(3)#2-Nd(1)-O(1W)	69.00(9)	O(4)#3-Nd(1)-O(1W)	120.27(9)
O(2)#4-Nd(1)-O(1W)	133.09(10)	O(1)-Nd(1)-O(1W)	70.48(9)
O(5)-Nd(1)-O(1W)	132.13(9)	O(6)#1-Nd(1)-N(3)#5	74.87(10)
O(3)#2-Nd(1)-N(3)#5	82.28(10)	O(4)#3-Nd(1)-N(3)#5	141.86(11)
O(2)#4-Nd(1)-N(3)#5	76.17(10)	O(1)-Nd(1)-N(3)#5	140.38(10)
O(5)-Nd(1)-N(3)#5	77.05(10)	O(1W)-Nd(1)-N(3)#5	71.78(10)
O(6)#1-Nd(1)-O(1)#4	149.15(9)	O(3)#2-Nd(1)-O(1)#4	71.24(9)
O(4)#3-Nd(1)-O(1)#4	75.58(9)	O(2)#4-Nd(1)-O(1)#4	50.09(8)
O(1)-Nd(1)-O(1)#4	76.65(9)	O(5)-Nd(1)-O(1)#4	93.72(9)

O(1W)-Nd(1)-O(1)#4	133.89(10)	N(3)#5-Nd(1)-O(1)#4	124.45(9)
Compound **2**			
Sm(1)-O(6)#1	2.420(3)	Sm(1)-O(3)#2	2.428(3)
Sm(1)-O(4)#3	2.435(3)	Sm(1)-O(2)#4	2.459(3)
Sm(1)-O(1)	2.465(3)	Sm(1)-O(5)	2.493(3)
Sm(1)-O(1W)	2.542(3)	Sm(1)-N(3)#5	2.564(4)
Sm(1)-O(1)#4	2.686(3)	O(1)-C(1)	1.281(5)
O(1)-Sm(1)#4	2.686(3)	O(2)-C(1)	1.253(5)
O(2)-Sm(1)#4	2.459(3)	O(3)-C(8)	1.259(5)
O(3)-Sm(1)#6	2.428(3)	O(4)-C(8)	1.251(5)
O(4)-Sm(1)#7	2.435(3)	O(5)-C(11)	1.252(5)
O(6)-C(11)	1.249(5)	O(6)-Sm(1)#1	2.420(3)
N(1)-C(10)	1.333(6)	N(1)-N(2)	1.371(5)
N(1)-C(6)	1.423(5)	N(2)-C(9)	1.311(6)
N(3)-C(10)	1.332(6)	N(3)-C(9)	1.354(6)
N(3)-Sm(1)#5	2.564(4)		
O(6)#1-Sm(1)-O(3)#2	138.88(11)	O(6)#1-Sm(1)-O(4)#3	75.46(11)
O(3)#2-Sm(1)-O(4)#3	135.81(11)	O(6)#1-Sm(1)-O(2)#4	130.78(11)
O(3)#2-Sm(1)-O(2)#4	73.55(11)	O(4)#3-Sm(1)-O(2)#4	106.30(12)
O(6)#1-Sm(1)-O(1)	103.51(11)	O(3)#2-Sm(1)-O(1)	73.51(11)
O(4)#3-Sm(1)-O(1)	70.86(11)	O(2)#4-Sm(1)-O(1)	123.94(10)

O(6)#1-Sm(1)-O(5)	66.26(10)	O(3)#2-Sm(1)-O(5)	140.25(11)
O(4)#3-Sm(1)-O(5)	69.17(11)	O(2)#4-Sm(1)-O(5)	68.85(11)
O(1)-Sm(1)-O(5)	140.03(11)	O(6)#1-Sm(1)-O(1W)	71.79(11)
O(3)#2-Sm(1)-O(1W)	68.73(11)	O(4)#3-Sm(1)-O(1W)	120.24(11)
O(2)#4-Sm(1)-O(1W)	132.95(11)	O(1)-Sm(1)-O(1W)	70.20(11)
O(5)-Sm(1)-O(1W)	132.62(11)	O(6)#1-Sm(1)-N(3)#5	75.39(12)
O(3)#2-Sm(1)-N(3)#5	81.79(12)	O(4)#3-Sm(1)-N(3)#5	142.09(12)
O(2)#4-Sm(1)-N(3)#5	76.04(12)	O(1)-Sm(1)-N(3)#5	140.02(12)
O(5)-Sm(1)-N(3)#5	77.18(12)	O(1W)-Sm(1)-N(3)#5	71.74(12)
O(6)#1-Sm(1)-O(1)#4	149.20(10)	O(3)#2-Sm(1)-O(1)#4	71.35(10)
O(4)#3-Sm(1)-O(1)#4	75.60(10)	O(2)#4-Sm(1)-O(1)#4	50.44(10)
O(1)-Sm(1)-O(1)#4	76.49(11)	O(5)-Sm(1)-O(1)#4	93.60(10)
O(1W)-Sm(1)-O(1)#4	133.51(11)	N(3)#5-Sm(1)-O(1)#4	124.57(11)
Compound **3**			
Eu(1)-O(1)#1	2.420(2)	Eu(1)-O(2)#2	2.416(2)
Eu(1)-O(3)#3	2.444(2)	Eu(1)-O(4)#3	2.671(2)
Eu(1)-O(4)#4	2.453(2)	Eu(1)-O(5)	2.410(2)
Eu(1)-O(6)	2.475(2)	Eu(1)-O(7)	2.526(2)
Eu(1)-N(3)	2.552(3)	O(1)-Eu(1)#6	2.420(2)
O(1)-C(1)	1.251(4)	O(2)-Eu(1)#7	2.416(2)
O(2)-C(1)	1.261(4)	O(3)-Eu(1)#8	2.444(2)

O(3)-C(8)	1.245(4)	O(4)-Eu(1)#4	2.453(2)
O(4)-Eu(1)#8	2.671(2)	O(4)-C(8)	1.281(4)
O(5)-C(11)#5	1.251(4)	O(6)-C(11)	1.258(4)
N(1)-N(2)	1.365(4)	N(1)-C(4)	1.425(4)
N(1)-C(9)	1.332(4)	N(2)-C(10)	1.308(5)
N(3)-C(9)	1.327(5)	N(3)-C(10)	1.351(5)
C(11)-O(5)#5	1.251(4)		
O(1)#1-Eu(1)-O(3)#3	73.50(8)	O(1)#1-Eu(1)-O(4)#3	71.39(8)
O(1)#1-Eu(1)-O(4)#4	73.56(8)	O(1)#1-Eu(1)-O(6)	140.12(8)
O(1)#1-Eu(1)-O(7)	68.45(8)	O(1)#1-Eu(1)-N(3)	81.70(9)
O(2)#2-Eu(1)-O(1)#1	135.93(8)	O(2)#2-Eu(1)-O(3)#3	106.29(9)
O(2)#2-Eu(1)-O(4)#3	75.53(8)	O(2)#2-Eu(1)-O(4)#4	70.88(8)
O(2)#2-Eu(1)-O(6)	69.09(8)	O(2)#2-Eu(1)-O(7)	120.45(9)
O(2)#2-Eu(1)-N(3)	142.04(9)	O(3)#3-Eu(1)-O(4)#4	123.83(8)
O(3)#3-Eu(1)-O(4)#3	50.61(7)	O(3)#3-Eu(1)-O(6)	68.76(8)
O(3)#3-Eu(1)-O(7)	132.71(9)	O(3)#3-Eu(1)-N(3)	75.84(9)
O(4)#4-Eu(1)-O(4)#3	76.21(8)	O(4)#4-Eu(1)-O(6)	139.97(8)
O(4)#4-Eu(1)-O(7)	70.24(8)	O(4)#4-Eu(1)-N(3)	140.24(9)
O(5)-Eu(1)-O(1)#1	138.53(8)	O(5)-Eu(1)-O(2)#2	75.72(8)
O(5)-Eu(1)-O(3)#3	130.91(8)	O(5)-Eu(1)-O(4)#4	103.56(8)
O(5)-Eu(1)-O(4)#3	149.49(8)	O(5)-Eu(1)-O(6)	66.62(8)

O(5)-Eu(1)-O(7)	71.76(8)	O(5)-Eu(1)-N(3)	75.32(8)
O(6)-Eu(1)-O(4)#3	93.57(7)	O(6)-Eu(1)-O(7)	132.96(8)
O(6)-Eu(1)-N(3)	77.15(9)	O(7)-Eu(1)-O(4)#3	133.18(8)
O(7)-Eu(1)-N(3)	71.91(9)	N(3)-Eu(1)-O(4)#3	124.55(8)

Symmetry codes:

For **1**: #1 (-x+2, -y+1, -z+1), #2 (-x+1, y+1/2, -z+3/2), #3 (x, -y+1/2, z-1/2), #4 (-x+1, -y+1, -z+1), #5 (-x+2, -y+1, -z+2), #6 (-x+1, y-1/2, -z+3/2), #7 (x, -y+1/2, z+1/2);

For **2**: #1 (x-1, -y+1/2, z-1/2), #2 (-x, y-1/2, -z+1/2), #3 (x-1, y, z-1), #4 (-x, -y, -z+1), #5 (-x, -y, -z), #6 (x+1, -y+1/2, z+1/2), #7 (-x, y+1/2, -z+1/2), #8 (x+1, y, z+1);

For **3**: #1 (-x+2, -y+1, -z+1), #2 (-x+1, y+1/2, -z+3/2), #3 (x, -y+1/2, z-1/2), #4 (-x+1, -y+1, -z+1), #5 (-x+2, -y+1, -z+2), #6 (-x+1, y-1/2, -z+3/2), #7 (x, -y+1/2, z+1/2).