

Supporting Information for the manuscript:

Photochromic and photomodulated luminescent properties of two metal-viologen complexes constructed by a tetracarboxylate anchored bipyridinium-based ligand

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Table S1. Crystallographic data for complexes **1** and **2**

Complex	1	2
formula	C ₃₀ H ₂₆ Cd ₃ Cl ₆ N ₂ O ₁₀	C ₁₆ H ₁₃ EuN ₃ O ₁₂
fw	1124.43	591.25
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	8.0685(4)	8.0365(4)
<i>b</i> (Å)	11.3449(4)	9.9090(7)
<i>c</i> (Å)	11.3700(5)	12.1201(8)
α (°)	66.307(4)	94.619(6)
β (°)	75.977(4)	95.775(5)
γ (°)	72.054(4)	94.636(5)
<i>V</i> (Å ³)	898.25(7)	953.29(10)
<i>Z</i>	1	2
<i>D_c</i> (g·cm ⁻³)	2.079	2.060
<i>F</i> (000)	546.0	578.0
reflns collected	6098	11611
Independent reflns	3171	3884
<i>R</i> (int)	0.0213	0.1168
GOF on <i>F</i> ²	1.065	1.094
<i>R</i> ₁ ^{<i>a</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0321	0.0689
<i>wR</i> ₂ ^{<i>b</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0801	0.1663

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

Table S2. Selected Bond Distances and Angles for Complexes **1** and **2**

Complex 1 ^a					
Cd1–Cl3	2.6320(12)	O24–Cd1#2	2.300(3)	Cd1–O24#2	2.300(3)
Cd1–Cl3#1	2.7271(11)	Cl3–Cd1#1	2.7271(11)	Cd2–Cl5#3	2.6385(12)
Cd1–Cl4	2.5071(12)	Cd2–O23#4	2.264(3)	Cd2–Cl5	2.6385(12)
Cd1–Cl5	2.5892(11)	Cd2–O25	2.385(3)	Cd2–O23#2	2.264(3)
Cd1–O20	2.442(3)	Cd2–O25#3	2.385(3)	O23–Cd2#5	2.264(3)
Cl3–Cd1–Cl3#1	82.51(4)	C19–O20–Cd1	139.4(3)	O25–Cd2–Cl5#3	90.64(9)
Cl4–Cd1–Cl3	96.92(4)	C22–O24–Cd1#2	129.6(3)	O25–Cd2–Cl5	89.36(9)
Cl4–Cd1–Cl3#1	94.55(4)	O23#2–Cd2–O25	90.46(12)	O25#3–Cd2–Cl5#3	89.36(9)
Cl4–Cd1–Cl5	95.54(4)	O23#4–Cd2–O25	89.54(12)	O20–Cd1–Cl3	91.20(8)
Cl5–Cd1–Cl3#1	169.89(4)	O23#4–Cd2–O25#3	90.46(12)	O20–Cd1–Cl3#1	83.58(7)
Cl5–Cd1–Cl3	96.92(4)	O23#2–Cd2–O25#3	89.54(12)	O20–Cd1–Cl4	171.37(8)
O20–Cd1–Cl5	86.35(7)	O25#3–Cd2–Cl5	90.64(9)	Cl5#3–Cd2–Cl5	180
O24#2–Cd1–Cl3#1	88.55(8)	O25–Cd2–O25#3	180.00(15)	O23#4–Cd2–Cl5	88.16(9)
O24#2–Cd1–Cl3	169.05(8)	Cd1–Cl3–Cd1#1	97.49(4)	O23#4–Cd2–Cl5#3	91.84(9)
O24#2–Cd1–Cl4	90.05(8)	Cd1–Cl5–Cd2	107.11(4)	O23#2–Cd2–Cl5#3	88.16(9)
O24#2–Cd1–Cl5	90.76(8)	C22–O23–Cd2#5	126.1(3)	O23#2–Cd2–O23#4	180
O24#2–Cd1–O20	81.49(11)	O23#2–Cd2–Cl5	91.84(9)		
Complex 2 ^b					
Eu1–O2	2.562(7)	C12–C12#2	1.51(2)	Eu1–O7	2.710(8)
Eu1–O1	2.436(7)	Eu1–O6	2.423(8)	Eu1–O8	2.542(8)
Eu1–O3#1	2.518(7)	Eu1–O11	2.584(8)	O3–Eu1#3	2.518(7)
Eu1–O4#1	2.431(7)	Eu1–O10	2.533(8)	Eu1–O5	2.449(7)
O4–Eu1#3	2.431(7)				
O1–Eu1–O2	52.1(2)	O5–Eu1–O2	81.9(3)	O3#1–Eu1–O11	139.6(3)
O1–Eu1–O3#1	119.0(2)	O5–Eu1–O3#1	87.8(3)	O3#1–Eu1–O10	132.0(3)
O1–Eu1–O7	160.2(3)	O5–Eu1–O7	70.2(3)	O3#1–Eu1–O2	152.0(3)
O1–Eu1–O8	114.2(3)	O5–Eu1–O8	118.6(3)	O3#1–Eu1–O7	68.0(2)
O1–Eu1–O5	126.4(3)	O5–Eu1–O11	119.5(3)	O3#1–Eu1–O8	70.1(3)
O1–Eu1–O11	70.3(3)	O5–Eu1–O10	71.4(3)	O6–Eu1–O2	78.6(3)
O1–Eu1–O10	107.9(3)	C11–C12–C12#2	122.3(12)	O6–Eu1–O1	78.6(3)
O2–Eu1–O7	130.6(2)	C11–C12–C13	117.9(11)	O6–Eu1–O3#1	73.5(3)
O2–Eu1–O11	66.8(3)	C8–O3–Eu1#3	91.3(6)	O6–Eu1–O4#1	79.3(3)
O4#1–Eu1–O2	121.0(2)	C6–C8–Eu1#3	177.2(7)	O6–Eu1–O7	120.8(3)
O4#1–Eu1–O1	70.2(2)	O3–C8–Eu1#3	62.8(5)	O6–Eu1–O8	143.1(3)
O4#1–Eu1–O3#1	52.1(2)	O4–C8–Eu1#3	58.8(5)	O6–Eu1–O5	65.1(2)
O4#1–Eu1–O7	107.6(3)	C8–O4–Eu1#3	95.0(6)	O6–Eu1–O11	143.1(3)
O4#1–Eu1–O8	73.8(3)	N3–O7–Eu1	93.2(6)	O7–N3–Eu1	62.4(5)
O4#1–Eu1–O5	133.1(2)	N3–O8–Eu1	101.1(6)	O8–N3–Eu1	54.8(5)
O4#1–Eu1–O11	107.3(3)	C16–O5–Eu1	121.5(6)	O6–Eu1–O10	128.3(3)
O4#1–Eu1–O10	152.2(3)	C15–O6–Eu1	118.2(7)	O11–Eu1–O7	92.4(3)

O8–Eu1–O2	137.3(2)	O8–Eu1–O7	48.5(2)	N2–O11–Eu1	94.8(6)
O8–Eu1–O11	70.6(2)				

Symmetry codes: ^a#1: $-x+2, -y, -z+1$, #2: $-x+1, -y, -z+2$, #3: $x+1, y-1, z$, #4: $-x+1, -y+1, -z+1$, #5: $x-1, y+1, z$, #6: $-x+2, -y+1, -z$; ^b#1: $+x, 1+y, +z$, #2: $-x, 1-y, 3-z$, #3: $+x, -1+y, +z$.

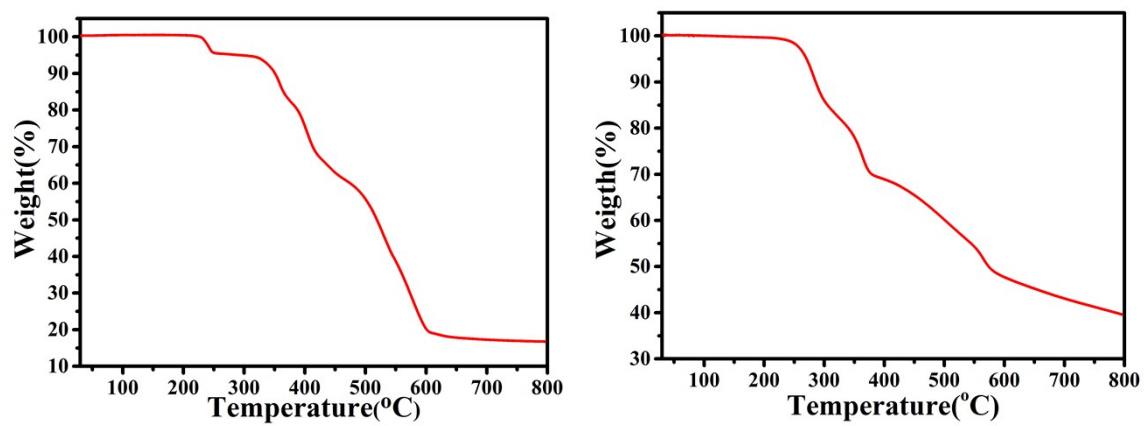


Figure S1. Thermogravimetric curves of the complexes **1** (left) and **2** (right).

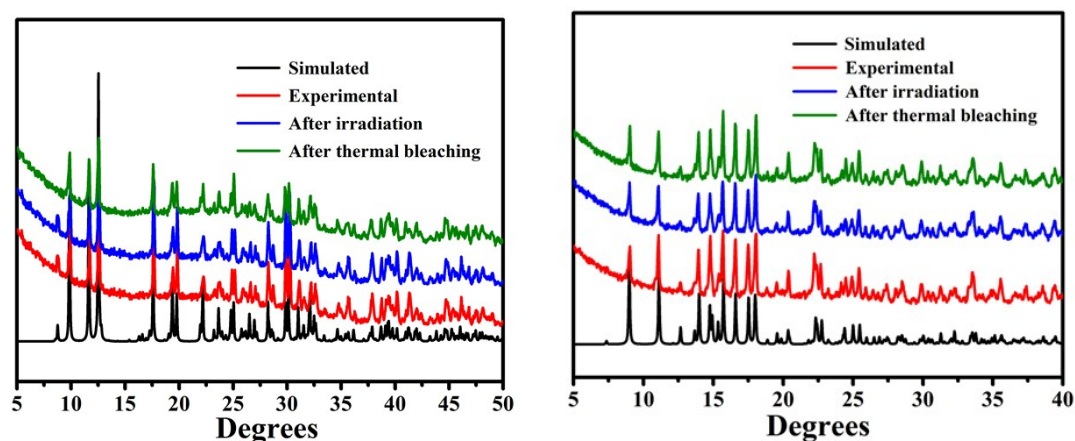


Figure S2. The simulated and experimental as well as before and after the irradiation PXRD patterns for complexes **1** (left) and **2** (right) (black-simulated, red-as synthesized, blue-after irradiation and dark green-after thermal bleaching).

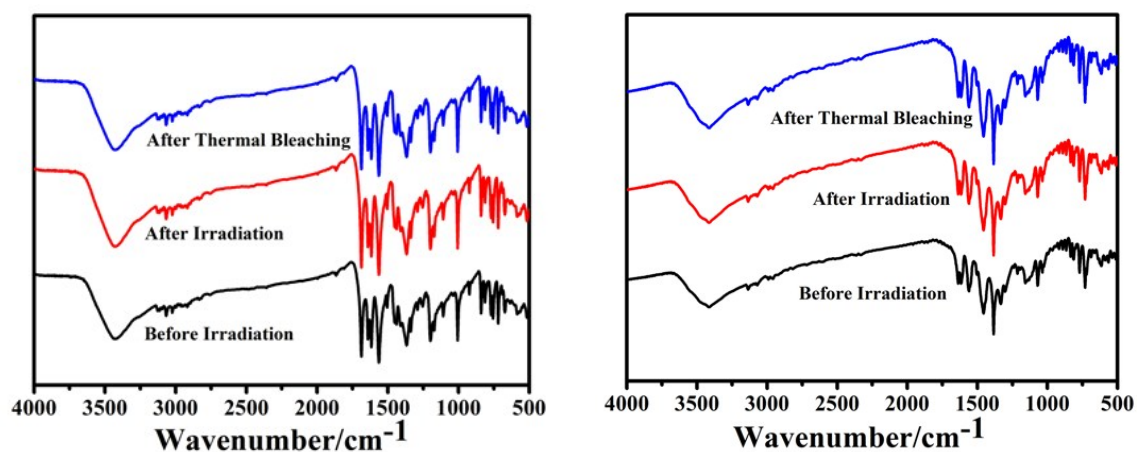


Figure S3. The IR spectra of complexes **1** (left) and **2** (right) before irradiation, after irradiation and after thermal bleaching.

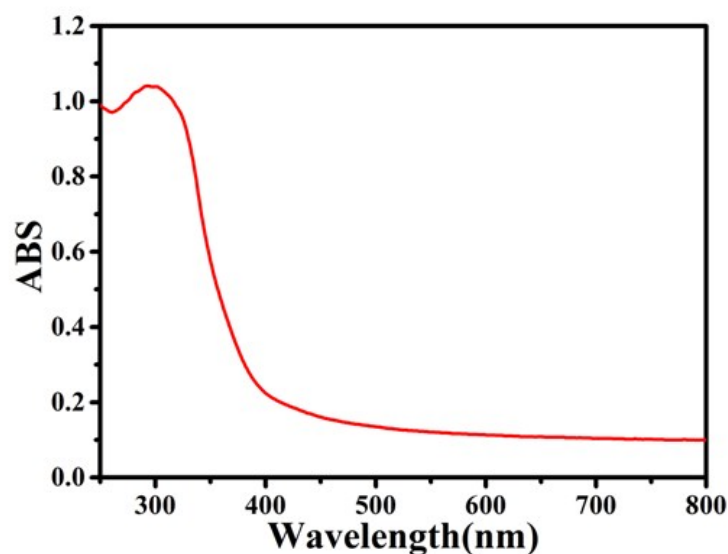


Figure S4. The solid-state UV-vis spectrum of the ligand $\text{H}_4\text{L}\cdot\text{Cl}_2$.

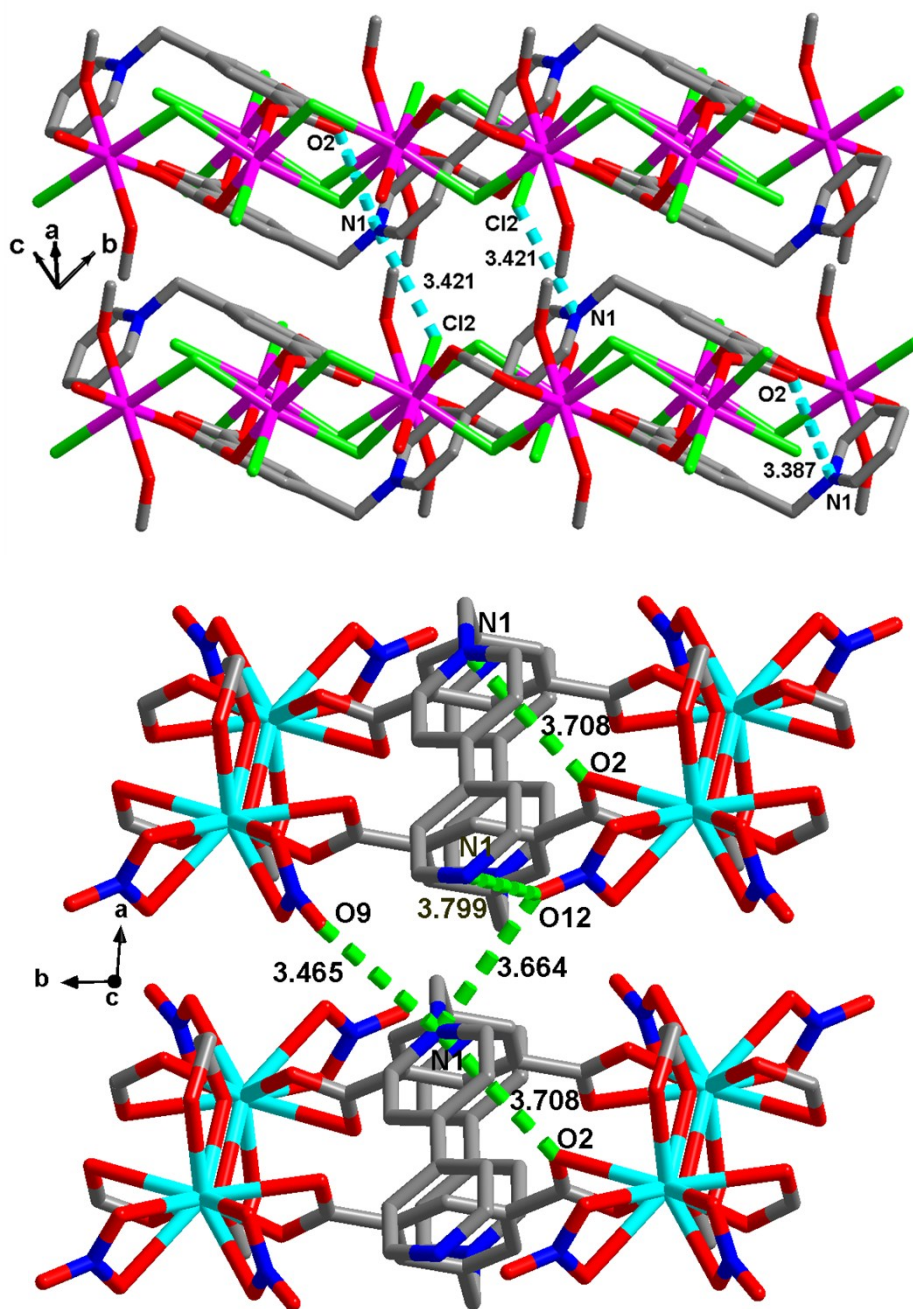


Figure S5. The possible electron transfer pathways in complexes **1** (up) and **2** (down). Distances are in angstrom ($\text{\AA}$).