Multistimuli-responsive materials of two pyridinium ion-based complexes and their applications in tetracycline degradation and information anticounterfeiting

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Content

1. Materials and methods

1.1 Materials and instrumentation

All the reagents used in this work were commercially purchased and used without further purification. Crystal data were collected on a single crystal X-ray diffractometer (D8 FOCUS). Powder X-ray diffraction (PXRD) measurements were performed on a D8 DISCOVER powder X-ray diffractometer with Cu-Kα radiation and $5° \leq 2\theta \leq 50°$. Thermogravimetric analysis was carried out on a NETZSCH TG209 F3 thermal analyzer, Germany, at a temperature of 30 ~ 500 °C under N_2 atmosphere with a ramp rate of 10 °C/min. Fluorescence spectra of the solid samples were performed on a fluorescence spectrophotometer (Cary Eclipse). Infrared data of solid samples were collected on a Fourier Transform Infrared (FTIR-650). Solid UV data were collected on a UV-visible spectrometer (SPECORD 210 plus) with $BaSO_4$ plates as standards. The cyclic voltammetric curves of the samples were measured using a double constant potentiostat (Chenhua CHI760E). Absorption values of tetracycline (TC) were recorded at a maximum wavelength of 357 nm using a UV-visible spectrophotometer (UV758CRT).

1.2 The preparation of complexes 1 and 2 working electrode

A certain amount of poly(methyl methacrylate) and 35 mg (0.05 mmol) of acrylamide were added to 2 mL of propylene carbonate and stirred at 70 °C until complete dissolution to produce a blank gel, which was colorless and transparent. Electrochromic gels were synthesized by incorporating 10 mg complexes 1 and 2 into the blank gel, respectively. Subsequently, the electrochromic gel was encapsulated with ITO conductive glass, which functioned as a transparent conductive electrode.

1.3 The degradation process of tetracycline by complex 1

The solution was then transferred to a tinfoil-wrapped 100 mL beaker covered with a filter sheet and placed under a 500 W xenon lamp (the filter sheet filters light sources with wavelengths less than 420 nm), after which the light source was turned on to carry out the photocatalytic reaction, and the photocatalytic reaction was carried out at 10min intervals by taking 5 mL of dispersion. The photocatalytic reaction was

carried out at 10 min intervals by taking 5 mL of the dispersion, and the reaction was stopped after 120 min, after which the upper solution was removed by centrifugation and the absorbance of the solution at 357 nm was detected by a UV spectrophotometer, and the degradation of tetracycline hydrochloride was investigated by repeating the experiment for several times.

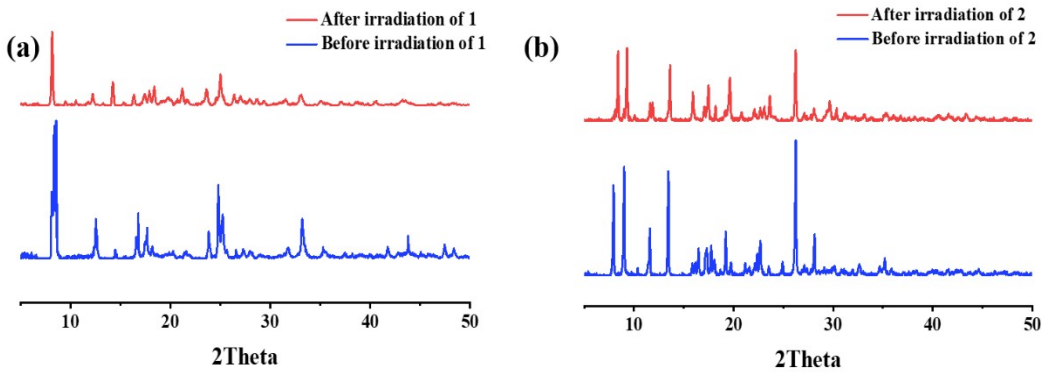

Fig. S1 The PXRD of **1** (a) and **2** (b).

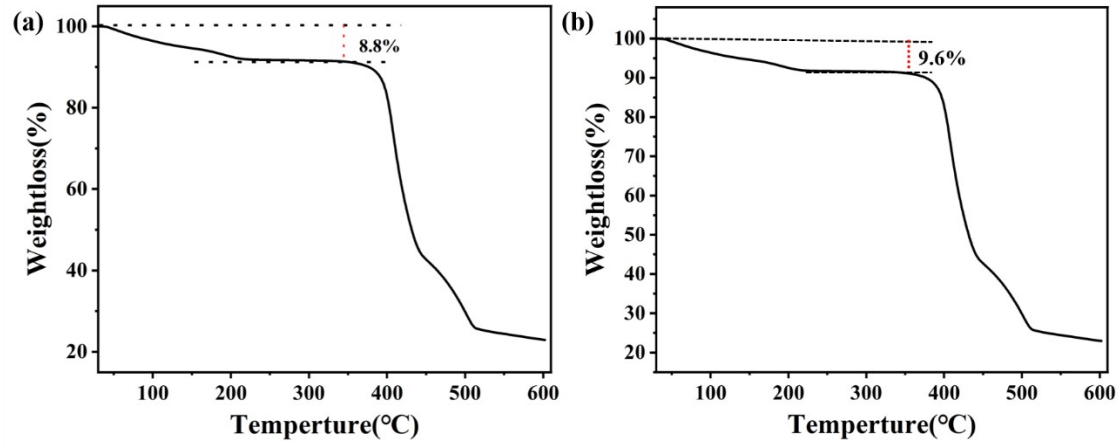

Fig. S2 The TGA of **1** (a) and **2** (b).

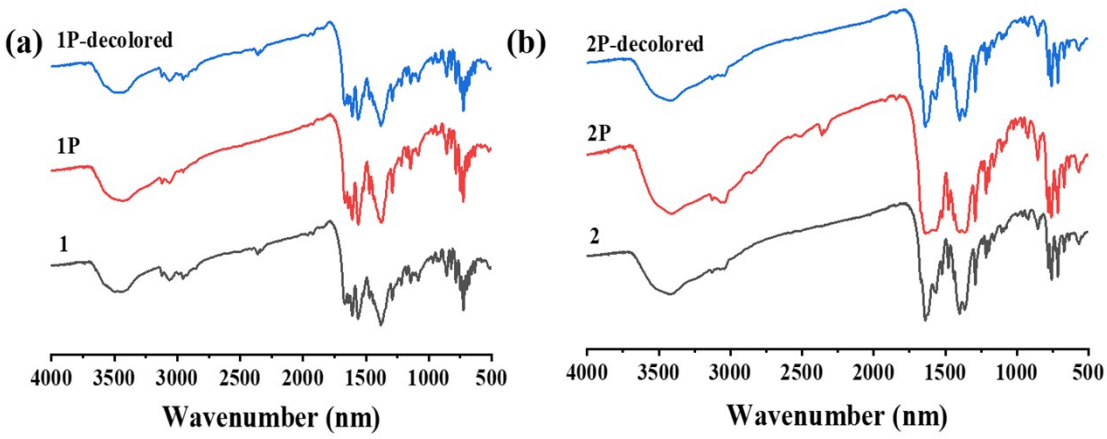

Fig. S3 The IR spectra of complexes **1** and **2** before and after irradiation and after fading.

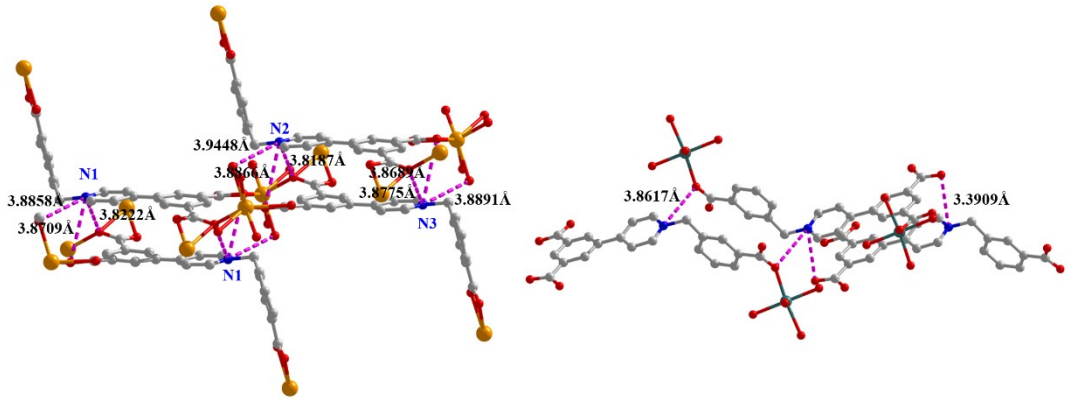

Fig. S4 The possible electron transfer pathways of complexes **1** and **2**.

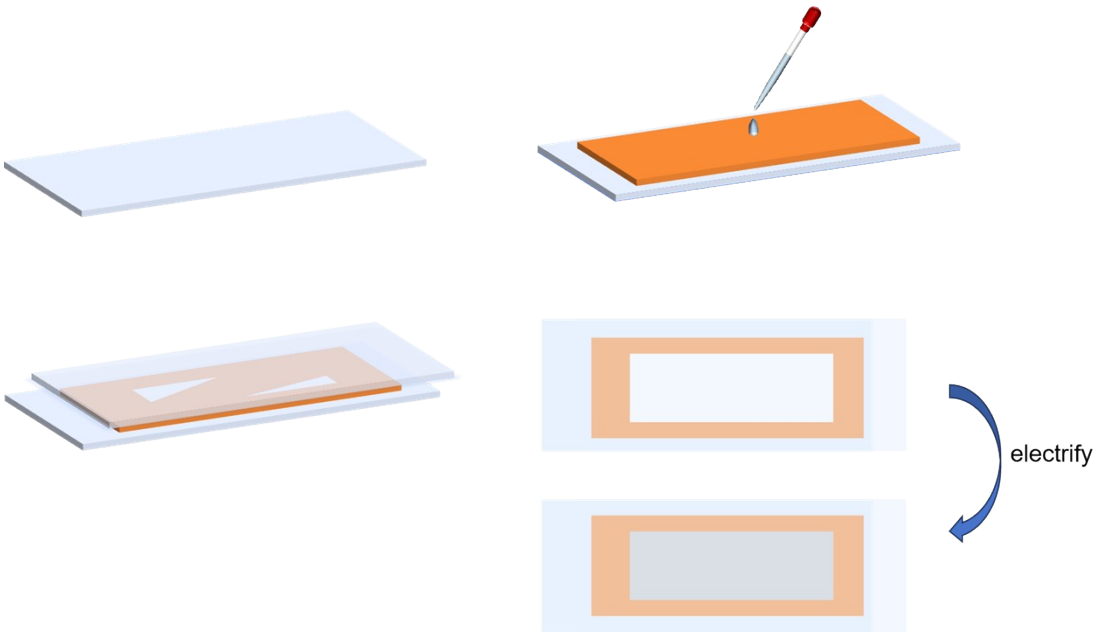

Fig. S5 Preparation flow chart of electrochromic device.

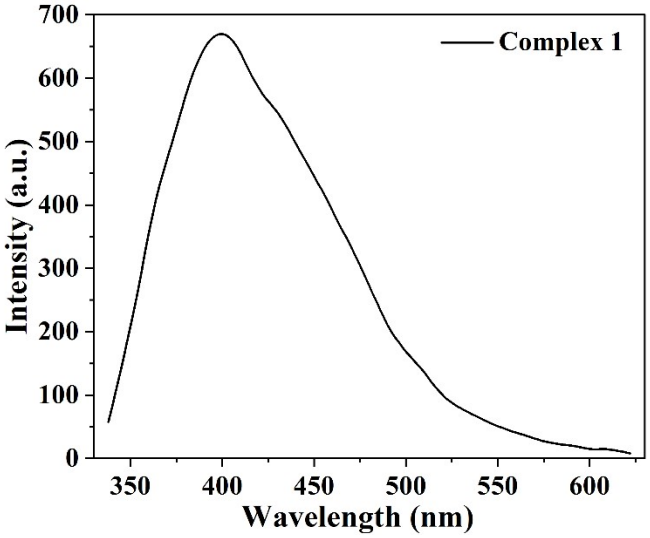

Fig. S6 The suspensions of complex **1** have photoluminescence properties at room temperature.

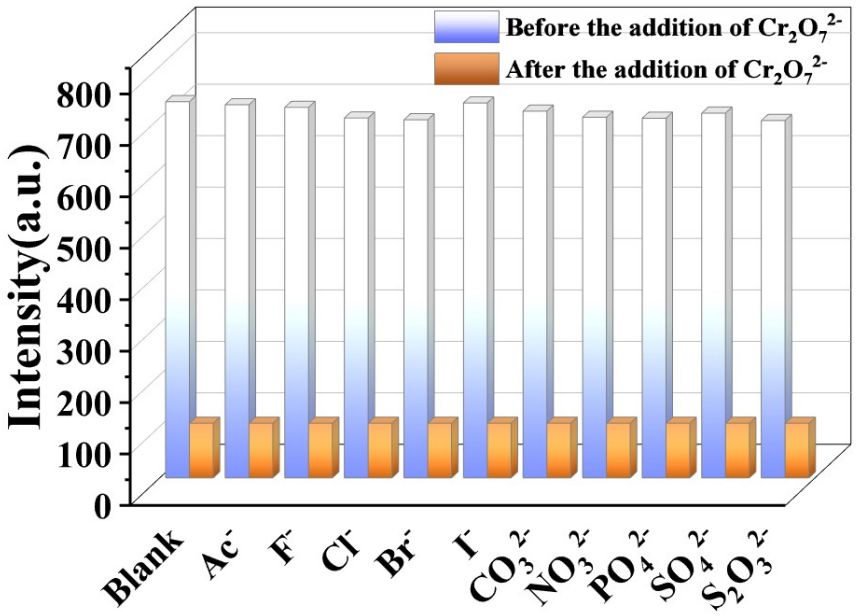

Fig. S7 Interference of different anions in solution with $Cr_2O_7^{2-}$ ions.

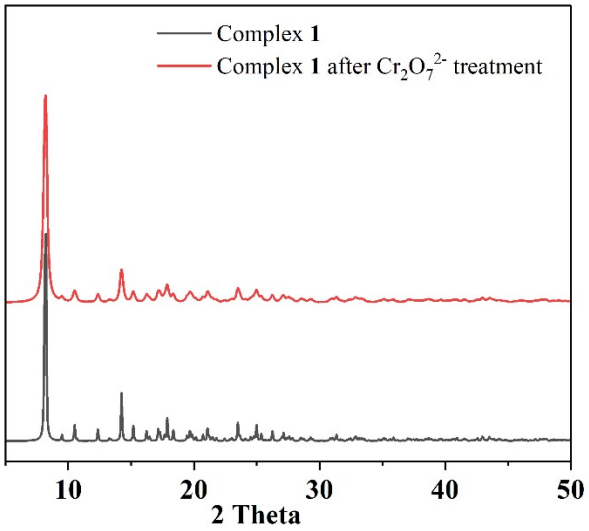

Fig. S8 The PXRD of **1** and after $Cr_2O_7^{2-}$ treatment.

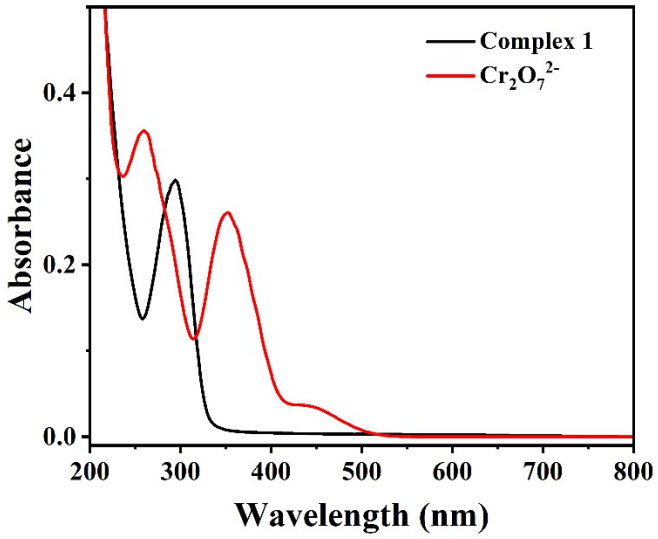

Fig. S9 UV spectra of complex **1** and $Cr_2O_7^{2-}$.

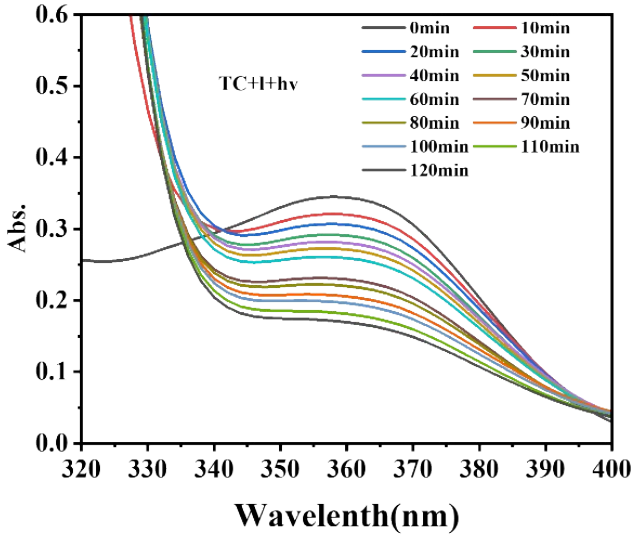

Fig. S10 UV-Vis absorption spectra of the catalytic degradation of TC by complex **1** driven by xenon lamp.

Table S1 Crystallographic data and structure refinement optimization parameters for complexes **1** and **2**.

Complex	1	2
Formula	$C_{63}H_{39}Cd_3N_3O_{18}$	$C_{21}H_{25}MnNO_{12}$
Mr	1463.17	538.36
Crystal system	Triclinic	Triclinic
T (K)	296	296
a (Å)	9.7951(6)	7.4959(7)
b (Å)	14.9487(10)	12.2572(11)
c (Å)	25.7483(17)	15.6005(15)
α (°)	104.032(2)°	77.314(3)°
β (°)	92.466(2)°	86.620(3)°
γ (°)	106.853(2)°	73.170(2)°
V (Å3)	3474.4(4)	1338.5(2)
Z	2	2
Dx /Mg m^{-3}	1.399	1.336
F(000)	1452	558
μ(mm^{-1})	0.98	0.55
GOF	1.058	1.049
R_1 [I > 2σ(I)]	0.062	0.061
wR_2 [I > 2σ(I)]	0.203	0.150

Complex	1	2
*R*int	0.051	0.077
CCDC	2420346	2420347

Table S2 Selected bond distances (Å) and angles (degree) of complexes **1** and **2**.

Cd1—O1	2.255 (8)	Cd3—O6	2.256 (8)
Cd1—O2	2.545 (8)	Cd3—O8^{iii}	2.216 (8)
Cd1—O5^{i}	2.222 (8)	Cd3—O9	2.266 (7)
Cd1—O7	2.263 (7)	Cd3—O10	2.494 (7)
Cd1—O11^{ii}	2.415 (11)	Cd3—O13^{iv}	2.440 (11)
Cd1—O12^{ii}	2.291 (11)	Cd3—O14^{iv}	2.305 (11)
Cd2—O3	2.261 (8)	Cd2—O16^{iv}	2.418 (10)
Cd2—O4	2.487 (8)	Cd2—O17^{v}	2.250 (9)
Cd2—O15^{iv}	2.260 (10)	Cd2—O18^{iii}	2.284 (9)
O1—Cd1—O2	53.6 (3)	O7—Cd1—O11^{ii}	94.0 (3)
O1—Cd1—O7	86.2 (3)	O7—Cd1—O12^{ii}	122.5 (3)
O1—Cd1—O11^{ii}	89.5 (3)	O11^{ii}—Cd1—O2	103.4 (3)
O1—Cd1—O12^{ii}	132.4 (4)	O12^{ii}—Cd1—O2	100.8 (3)
O5^{i}—Cd1—O1	113.8 (3)	O12^{ii}—Cd1—O11^{ii}	54.7 (3)
O5^{i}—Cd1—O2	81.4 (3)	O6—Cd3—O9	84.7 (3)
O5^{i}—Cd1—O7	101.3 (3)	O6—Cd3—O10	133.8 (3)
O5^{i}—Cd1—O11^{ii}	152.6 (3)	O6—Cd3—O13^{iv}	94.2 (3)
O5^{i}—Cd1—O12^{ii}	97.9 (3)	O6—Cd3—O14^{iv}	122.7 (3)
O7—Cd1—O2	135.2 (3)	O6—Cd3—C50^{iv}	109.3 (4)
O8^{iii}—Cd3—O6	100.8 (3)	O9—Cd3—O13^{iv}	87.2 (3)
O8^{iii}—Cd3—O9	115.5 (3)	O9—Cd3—O14^{iv}	133.1 (4)

O8^{iii}—Cd3—O10	82.2 (3)	O9—Cd3—C50^{iv}	111.4 (4)
O8^{iii}—Cd3—O13^{iv}	153.6 (3)	O10—Cd3—C50^{iv}	105.3 (4)
O8^{iii}—Cd3—O14^{iv}	97.2 (3)	O13^{iv}—Cd3—O10	102.9 (3)
O8^{iii}—Cd3—C50^{iv}	125.8 (4)	O13^{iv}—Cd3—C50^{iv}	27.8 (3)
O9—Cd3—O10	54.2 (2)	O14^{iv}—Cd3—O10	102.2 (3)
O14^{iv}—Cd3—O13^{iv}	56.4 (3)	O3—Cd2—O4	53.3 (3)
O14^{iv}—Cd3—C50^{iv}	28.6 (3)	O3—Cd2—O16^{iv}	89.4 (3)
O15^{iv}—Cd2—O3	132.5 (4)	O3—Cd2—O18^{iii}	114.7 (4)
O15^{iv}—Cd2—O4	101.7 (3)	O3—Cd2—C44^{iv}	112.5 (4)
O15^{iv}—Cd2—O16^{iv}	54.2 (3)	O4—Cd2—C44^{iv}	104.7 (4)
O15^{iv}—Cd2—O18^{iii}	96.3 (3)	O17^{v}—Cd2—O3	86.7 (3)
O15^{iv}—Cd2—C44^{iv}	27.0 (3)	O17^{v}—Cd2—O4	135.1 (3)
O16^{iv}—Cd2—O4	103.0 (3)	O17^{v}—Cd2—O15^{iv}	121.9 (3)
O16^{iv}—Cd2—C44^{iv}	27.2 (3)	O17^{v}—Cd2—O16^{iv}	95.1 (3)
O17^{v}—Cd2—O18^{iii}	102.7 (3)	O18^{iii}—Cd2—O16^{iv}	150.4 (3)
O17^{v}—Cd2—C44^{iv}	109.6 (4)	O18^{iii}—Cd2—O4	80.8 (3)

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*, *y*-1, *z*; (iii) *x*-1, *y*, *z*; (iv) *x*, *y*+1, *z*; (v) -*x*+2, -*y*+2, -*z*+1.

Mn1—O1	2.163 (3)	Mn1—O8	2.273 (3)
Mn1—O6^{i}	2.156 (3)	Mn1—O9	2.155 (3)
Mn1—O7	2.157 (3)	Mn1—O10	2.166 (3)
O1—Mn1—O8	81.15 (10)	O7—Mn1—O10	88.72 (11)
O1—Mn1—O10	173.80 (10)	O9—Mn1—O1	94.40 (10)
O6^{i}—Mn1—O1	95.12 (10)	O9—Mn1—O6^{i}	86.05 (11)
O6^{i}—Mn1—O7	93.76 (11)	O9—Mn1—O7	178.42 (11)
O6^{i}—Mn1—O8	172.95 (11)	O9—Mn1—O8	88.27 (11)
O6^{i}—Mn1—O10	89.79 (11)	O9—Mn1—O10	89.71 (11)
O7—Mn1—O1	87.18 (10)	O10—Mn1—O8	94.36 (12)
O7—Mn1—O8	92.04 (12)		

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, *y*, *z*-1.