Electronic supplementary information (ESI)

The simultaneous modulation effect of *N*-substituents on photochromic and electrochromic properties of naphthalenediimide-based coordination polymers

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1. Experimental Section

Preparation of the 1@FTO film and 2@FTO film working electrode

The FTO glass is cleaned with soap water and rinsed with deionized water. Then, the FTO glass is treated ultrasonically in ethanol and acetone and subsequently dried in the air. Compound **1** is finely ground. **1** (30 mg) and H_2O (200 μL) are added to the bottle and the mixture is treated ultrasonically for 30 min. The suspension is evenly dispersed on FTO glass by a pipette gun and allowed to dry at room temperature. Afterwards, the **1**@FTO film is heated at 60 °C for 5 h. **2**@FTO film is prepared in the same way.

2. Figures

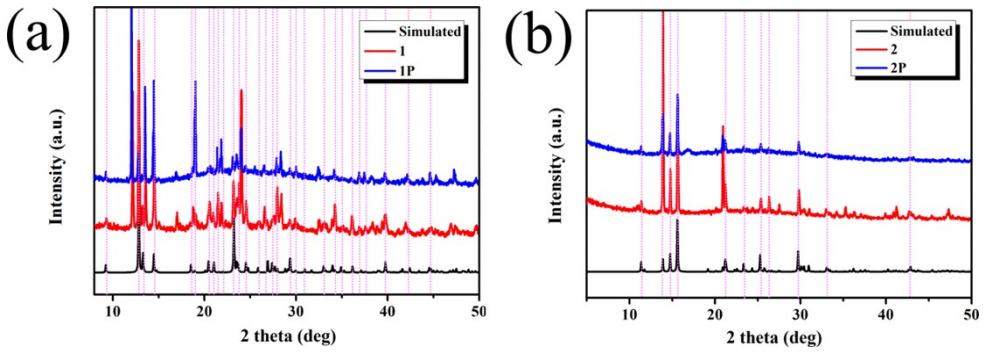


Fig. S1. (a) PXRD patterns of **1** and **1P** at room temperature. (b) PXRD patterns of **2** and **2P** at room temperature.

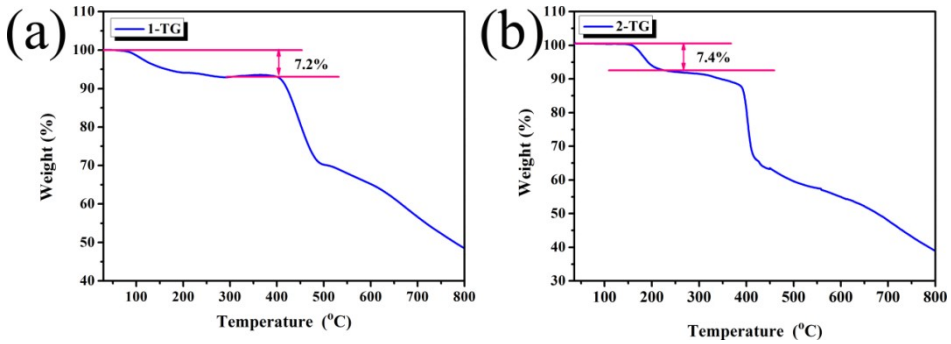


Fig. S2. (a) TGA curve of **1**. (b) TGA curve of **2**.

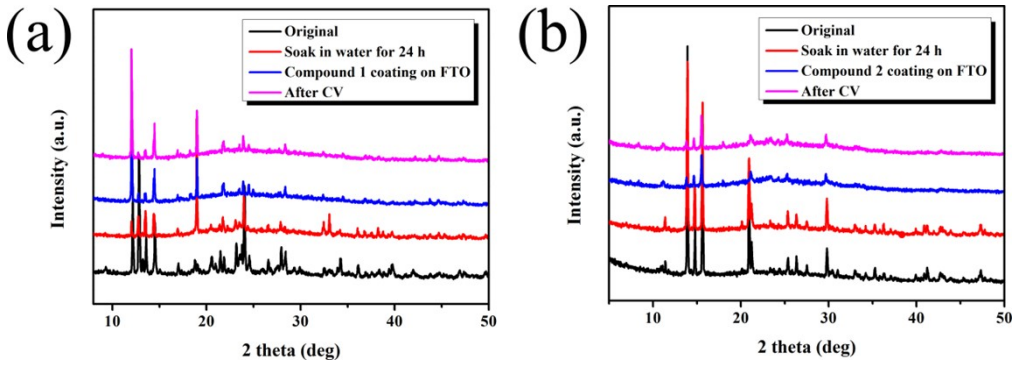
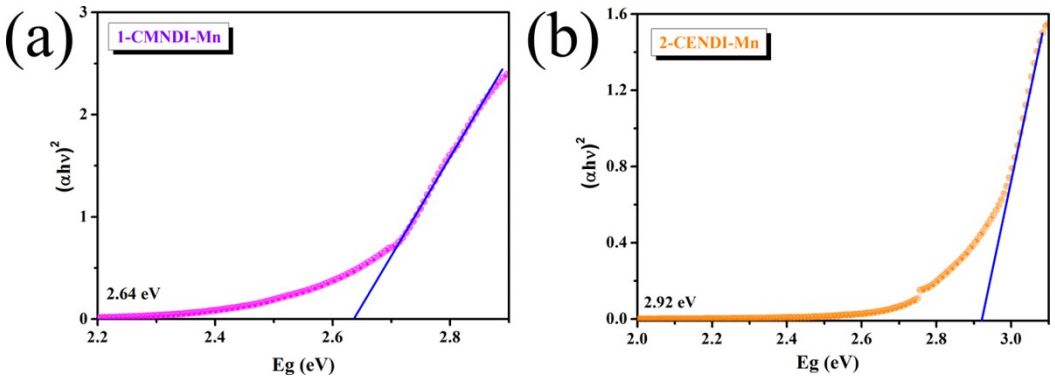


Fig. S3. (a) The stability of **1** and **1**@FTO film. (b) The stability of **2** and **2**@FTO film.



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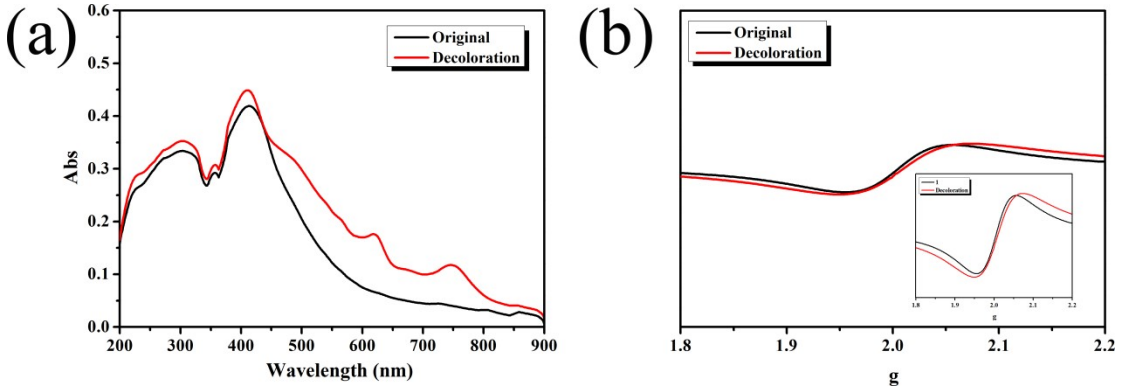

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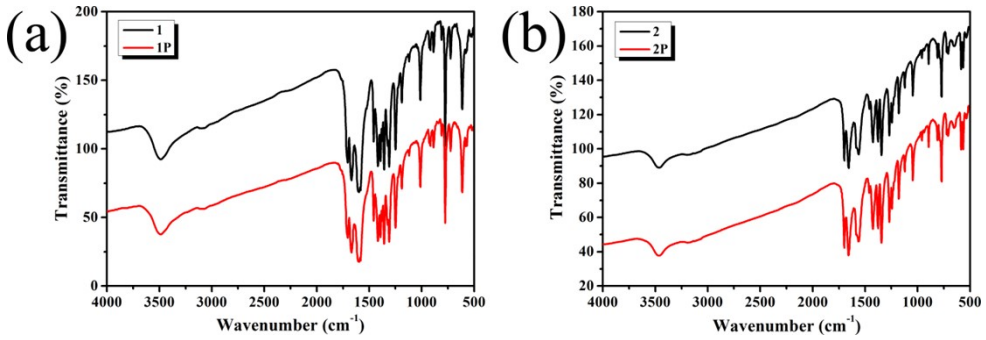
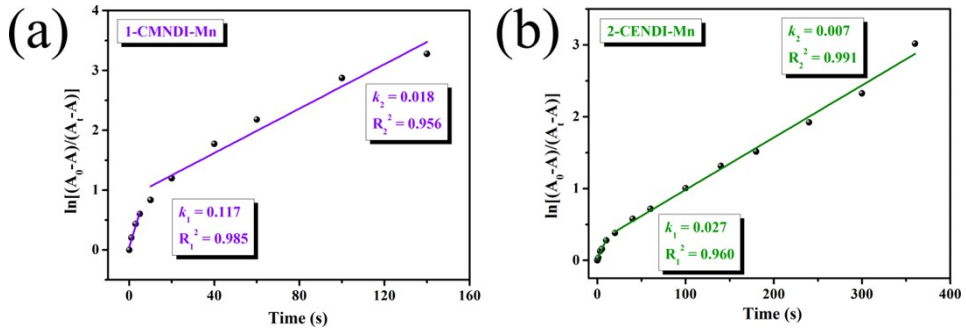


Fig. S6. (a) FT-IR spectra of **1** and **1P**. (b) FT-IR spectra of **2** and **2P**.



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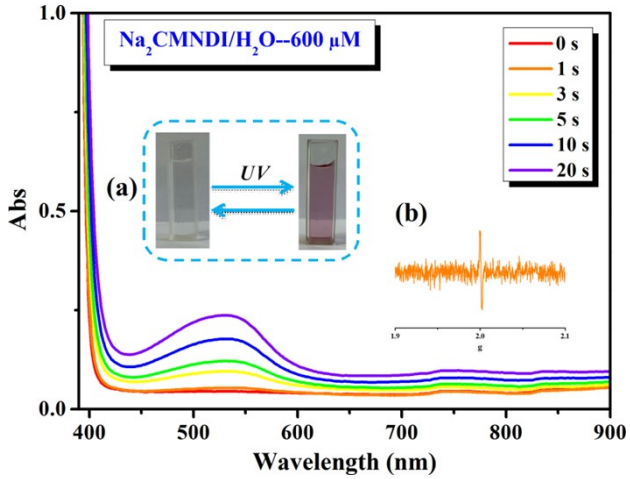

Fig. S8. Time-dependent UV-vis absorption spectra of Na_2CMNDI/H_2O solution (600 μM) (insert: (a) Photochromic behavior of Na_2CMNDI/H_2O solution and (b) EPR spectra of Na_2CMNDI/H_2O solution after UV light irradiation).

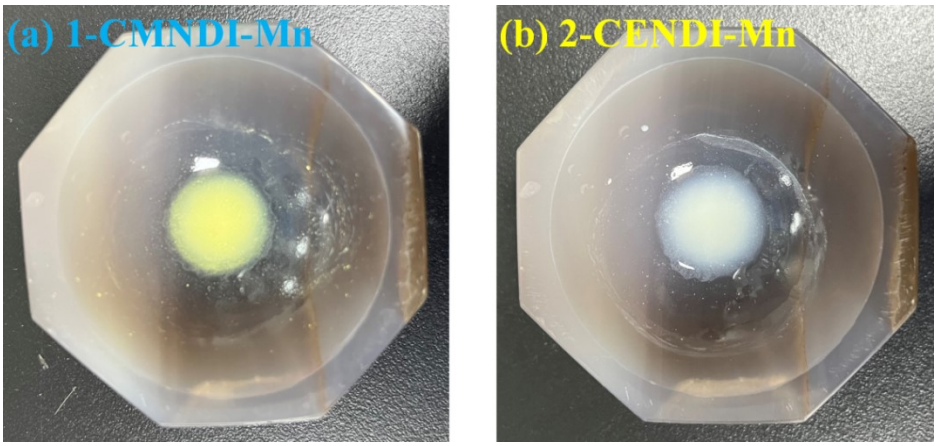

Fig. S9. (a) Electronic photo of suspension of **1**. (b) Electronic photo of suspension of **2**.

3. Tables

Table S1. Crystallographic data and refinement parameters of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{18}H_{12}N_2O_{10}Mn$	$C_{20}H_{16}N_2O_{10}Mn$
Formula weight	471.24	499.29
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a (Å)	4.694(3)	4.6642(5)
b (Å)	13.298(9)	8.0332(8)
c (Å)	13.810(9)	13.2151(14)
α (°)	90	103.832(3)
β (°)	94.671(16)	96.102(3)
γ (°)	90	94.089(3)
V (Å^3)	859.2(9)	475.66(9)
Z	2	1
D_c (g cm^{-3})	1.821	1.743
μ (mm^{-1})	0.838	0.762
F (000)	478.00	255.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
ϑ range (°)	4.258 to 56.778	6.402 to 56.836
Reflections collected	12356	6042
Unique reflections	2144	2387
R_{int}	0.0763	0.0469
Data/restraints/parameters	2144/0/142	2387/0/152
Goodness-of-fit on F^2	1.052	1.055
R_1/wR_2, $[I \geq 2\sigma(I)]^{a,b}$	0.0487/0.1084	0.0407/0.0889
R_1/wR_2, (all data)	0.0962/0.1230	0.0566/0.0941
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.43/-0.40	0.35/-0.43

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

Table S2. Selected bond lengths (Å) and angles (°) of **1**.

Compound **1**			
Mn1-O3[1]	2.221 (2)	Mn1-O4	2.155 (2)
Mn1-O3[2]	2.221 (2)	Mn1-O5	2.174 (2)
Mn1-O4[3]	2.155 (2)	Mn1-O5[3]	2.174 (2)
O3[1]-Mn1-O3[2]	180.0	O4-Mn1-O5	92.52 (9)
O4-Mn1-O3[1]	88.56 (8)	O4[3]-Mn1-O5[3]	92.53 (9)
O4-Mn1-O3[2]	91.44 (8)	O5[3]-Mn1-O3[2]	88.21 (8)
O4[3]-Mn1-O3[2]	88.56 (8)	O5-Mn1-O3[2]	91.79 (8)
O4[3]-Mn1-O3[1]	91.44 (8)	O5[3]-Mn1-O3[1]	91.79 (8)
O4-Mn1-O4[3]	180.0	O5-Mn1-O3[1]	88.21 (8)
O4-Mn1-O5[3]	87.48 (9)	O5[3]-Mn1-O5	180.0
O4[3]-Mn1-O5	87.48 (9)		
symmetry codes: [1]-x, 2-y, 1-z; [2]1+x, y, z; [3]1-x, 2-y, 1-z.			

Table S3. Selected bond lengths (Å) and angles (°) of **2.**

Compound **2**			
Mn1-O3[1]	2.2178 (14)	Mn1-O4	2.1310 (13)
Mn1-O3[2]	2.2178 (14)	Mn1-O5	2.2286 (16)
Mn1-O4[3]	2.1310 (13)	Mn1-O5[3]	2.2286 (16)
O3[1]-Mn1-O3[2]	180.00 (7)	O4[3]-Mn1-O3[2]	89.92 (5)
O3[2]-Mn1-O5[3]	92.77 (6)	O4[3]-Mn1-O4	180.00 (6)
O3[1]-Mn1-O5[3]	87.23 (6)	O4-Mn1-O5	91.89 (6)
O3[2]-Mn1-O5	87.23 (6)	O4[3]-Mn1-O5	88.11 (6)
O3[1]-Mn1-O5	92.77 (6)	O4-Mn1-O5[3]	88.11 (6)

O4-Mn1-O3[1]	89.92 (5)	O4[3]-Mn1-O5[3]	91.89 (6)
O4[3]-Mn1-O3[1]	90.08 (5)	O5[3]-Mn1-O5	180.0
O4-Mn1-O3[2]	90.08 (5)		

symmetry codes: [1]1-x,-y, -z; [2]1+x, y, z; [3]2-x, -y, -z.

Table S4. Hydrogen bonds of **1** (Å and °).

Compound **1**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O5-H5A···O1[1]	0.85	2.02	2.800(3)	150.9
O5-H5B···O3[2]	0.85	2.14	2.837 (3)	138.3

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

Table S5. Hydrogen bonds of **2** (Å and °).

Compound **2**				
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O5-H5A···O3[1]	0.85	2.05	2.786 (2)	145.1
O5-H5B···O2[2]	0.85	1.98	2.826 (2)	170.4

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