Supporting information

Zinctungstate Encapsulated into infrequent Zn(II)-Viologen Framework with Photochromic, Electrochromic and Chemochromic Properties

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Crystal Structure Determinations

The intensity data of the same single crystal **1** before and after coloration were collected on a Rigaku Pilatus 200 K diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54056 Å), respectively. The colored sample (**1a**) was illuminated with Cu Kα X-ray for 20 min. Data reduction and absorption corrections were performed using Lorentz and polarization effects. The structures were solved by direct methods refined by full-matrix least-squares methods using a suite of SHELX programs via the Olex2 program[s1]. The non-hydrogen atoms were refined with anisotropic displacement parameters. Technical details of data collection and refinement are summarized in Table S1. The main bond lengths and angles of **1** and **1a** are shown in Table S2.

Table S1 Crystallographic data for **1** and **1a**.

Compound	1	1a
Formula	$C_{78}H_{76}N_6O_{64}W_{12}Zn_4$	$C_{78}H_{76}N_6O_{64}W_{12}Zn_4$
Fw	4589.08	4589.08
Crystal system	trigonal	trigonal
Space group	R $\bar{3}$	R $\bar{3}$
a/(Å)	17.9542(4)	18.0082(3)
b/(Å)	17.9542(4)	18.0082(3)
c/(Å)	27.4233(8)	27.5563(5)
α/(°)	90	90
β/(°)	90	90
γ/(°)	120	120
Volume/(Å^3)	7655.7(12)	7739.1(3)
Z	3	3
Temperature/(K)	100	293
ρ_{calc} (g/cm^3)	2.934	2.944
F(000)	6174.0	6270.0
μ/(mm^{-1})	14.485	25.906
Reflections collected	21341	9168
Independent reflections	4404	3458
R1 [I>=2σ (I)]	0.0598	0.0651
wR_2 [all data]	0.1823	0.1927
GOF on F^2	1.028	1.050

Table S2. Comparison between selective bond distances (Å) of compounds **1** and **1a**.

1		**1a**	
Bond	Length/Å	Bond	Length/Å
W1-O1	2.492(14)	**W1-O1**	2.471(13) ↓
W1-O2	2.504(14)	**W1-O2**	2.475(12) ↓
W1-O3	1.687(10)	**W1-O3**	1.681(10)
W1-O4[1]	1.924(11)	**W1-O4**[4]	1.928(11)
W1-O4	1.882(11)	**W1-O4**	1.864(11) ↓
W1-O5	1.881(11)	**W1-O5**	1.883(10)
W1-O8[2]	1.892(10)	**W1-O8**[5]	1.892(11)
W2-O2[3]	2.423(13)	**W2-O2**[6]	2.462(11) ↑
W2-O2	2.439(13)	**W2-O2**	2.437(12)
W2-O5	1.951(12)	**W2-O5**	1.922(10) ↓
W2-O6	1.712(10)	**W2-O6**	1.700(9)
W2-O7[3]	1.908(10)	**W2-O7**	1.915(10)
W2-O7	1.905(10)	**W2-O7**[6]	1.910(10)
W2-O8	1.919(11)	**W2-O8**	1.934(11) ↑
Zn1-O1	1.53(3)	**Zn1-O1**	1.56(2) ↑
Zn1-O2	1.558(13)	**Zn1-O2**	1.552(13)
Zn2-O10	2.064(15)	**Zn2-O10**	2.066(14)
Zn3-O9	1.991(17)	**Zn3-O9**	2.006(16)
Zn3-O1W	2.13(7)	**Zn3-O1W**	2.12(6)
O9-C13	1.25(2)	**O9-C13**	1.22(2)
O10-C13	1.24(2)	**O10-C13**	1.26(2)
N1-C6	1.53(2)	**N1-C6**	1.57(2) ↑

[1]-Y,+X-Y,+Z; [2]-Y+X,+X,1-Z; [3]+Y,-X+Y,1-Z;[4]1-Y,1+X-Y,+Z; [5]-1/3+Y,1/3-X+Y,1/3-Z; [6]2/3-Y+X,1/3+X,1/3-Z

Table S3. Photoresponsive rate of some viologen-based photochromic hybrids.

Compound	**Photoresponsive rate (s^{-1})**	**Ref.**
$[(AV^{2+})(p\text{-}AV)(EuW_{10}O_{36})]_n \cdot 2nH_2O$	1.27×10^{-2}	[S2]
ZnW_{12}@MV	1.39×10^{-2}	This work
$\{Cu(1,1\text{-}pmbby)_2(H_2O)[H_2(\beta\text{-}Mo_8O_{26})_2]\}\cdot 5H_2O\cdot C_2H_7N$	2.38×10^{-2}	[S3]
$\{Co(1,4\text{-}bcbpy)_2(H_2O)_2[H_2(\beta\text{-}Mo_8O_{26})]\}\cdot 2H_2O\cdot 2CH_2O$	2.601×10^{-2}	[S3]
$[Zn(CPBPY)_2(H_2O)_3]PF_6 \cdot NO_3 \cdot 4H_2O$	4.60×10^{-2}	[S4]
$[Zn_7(bpybc)_3(o\text{-}BDC)_6]\cdot 2NO_3\cdot 6H_2O$	6×10^{-3}	[S5]
$\{[Zn(Mebpy)(Hbtc)Cl]\cdot 2H_2O\}_n$	5.33×10^{-3}	[S6]
$\{[Zn_3(Cebpy)_2(Hbtc)(H_2btc)_2(OH)_2]\cdot 4H_2O\}_n$	4.29×10^{-3}	[S6]
$[Zn(CPBPY)(HBTC)]\cdot H_2O$	5.4×10^{-4}	[S7]

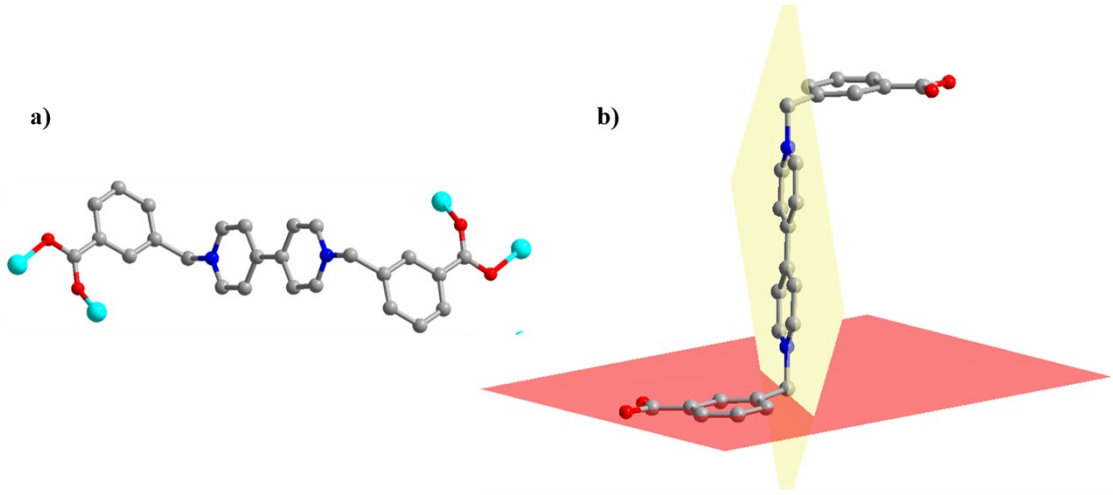

Figure S1 (a) Coordination mode of the Bcbpy in **1**. (b) The dihedral angle between the pyridine ring and the benzene ring.

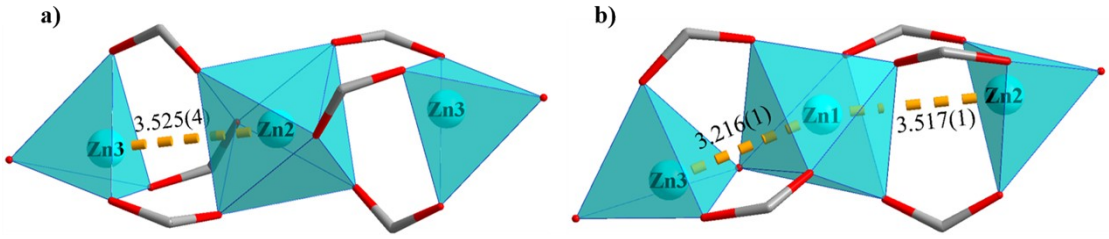

Figure S2 (a) The trinuclear $Zn_3O_{14}C_6$ cluster (Zn_3SBU) of **1**. (b) The trinuclear $Zn_3O_{13}C_6$ cluster of PNMOF-1.

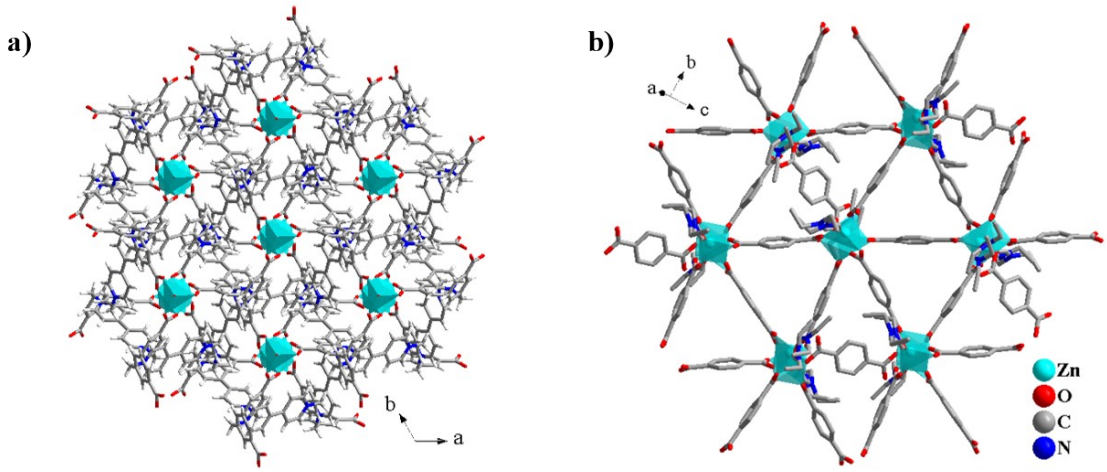

Figure S3 (a) The 3D zinc-viologen cationic $Zn_3(Bcbpy)_6(H_2O)_{2n}^{6n+}$ network. (b) The 2D network of $Zn_3(BDC)_3(DEF)_2$.

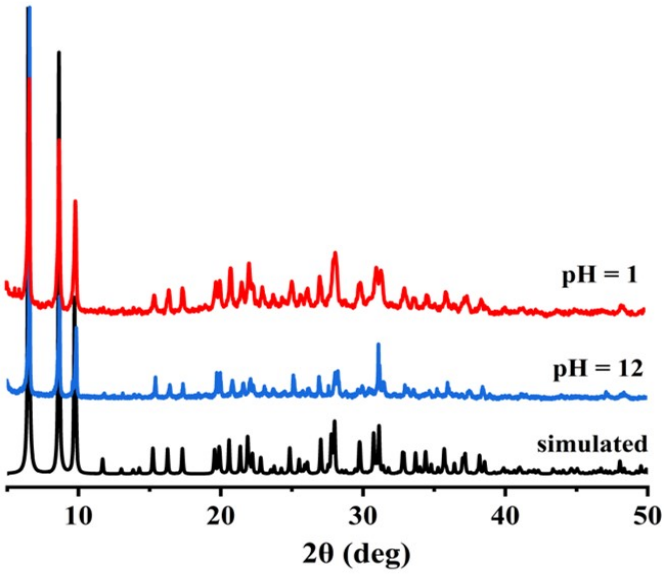

Figure S4 PXRD patterns of **1** immersed in H_2SO_4 solutions (pH =1) and NaOH solutions (pH =12).

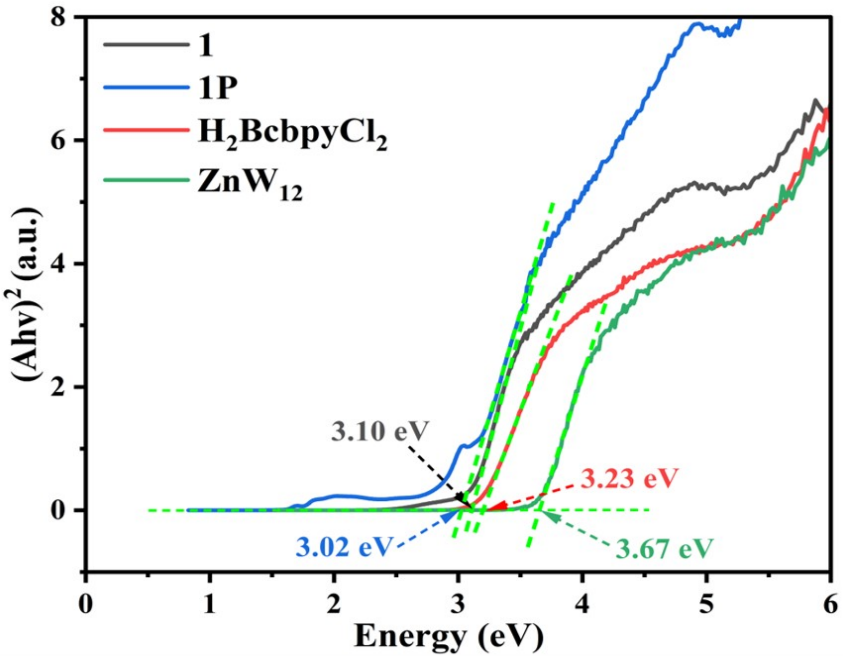

Figure S5 The UV−vis spectra of **1**, **1P**, $H_2BcbpyCl_2$ and ZnW_{12} at room temperature.

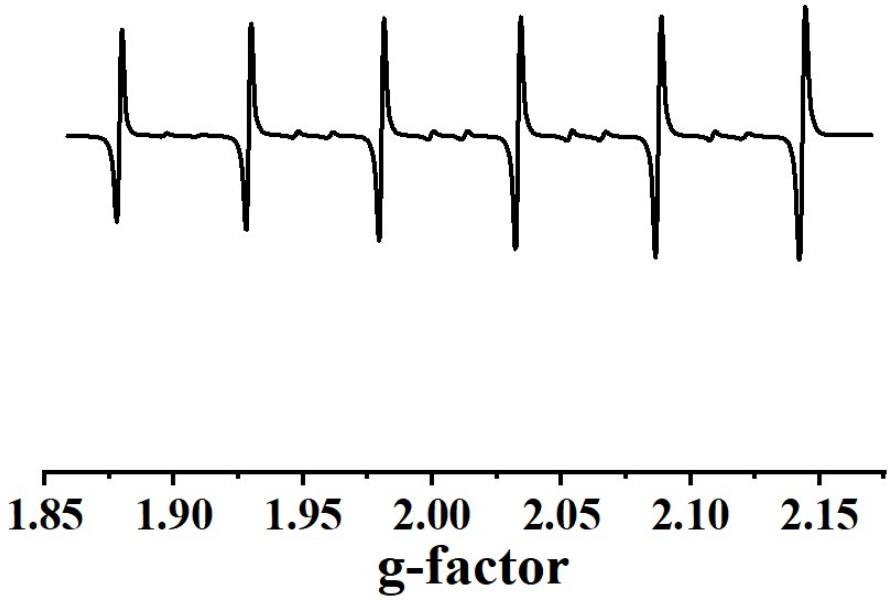

Figure S6 The EPR spectra of **1**.

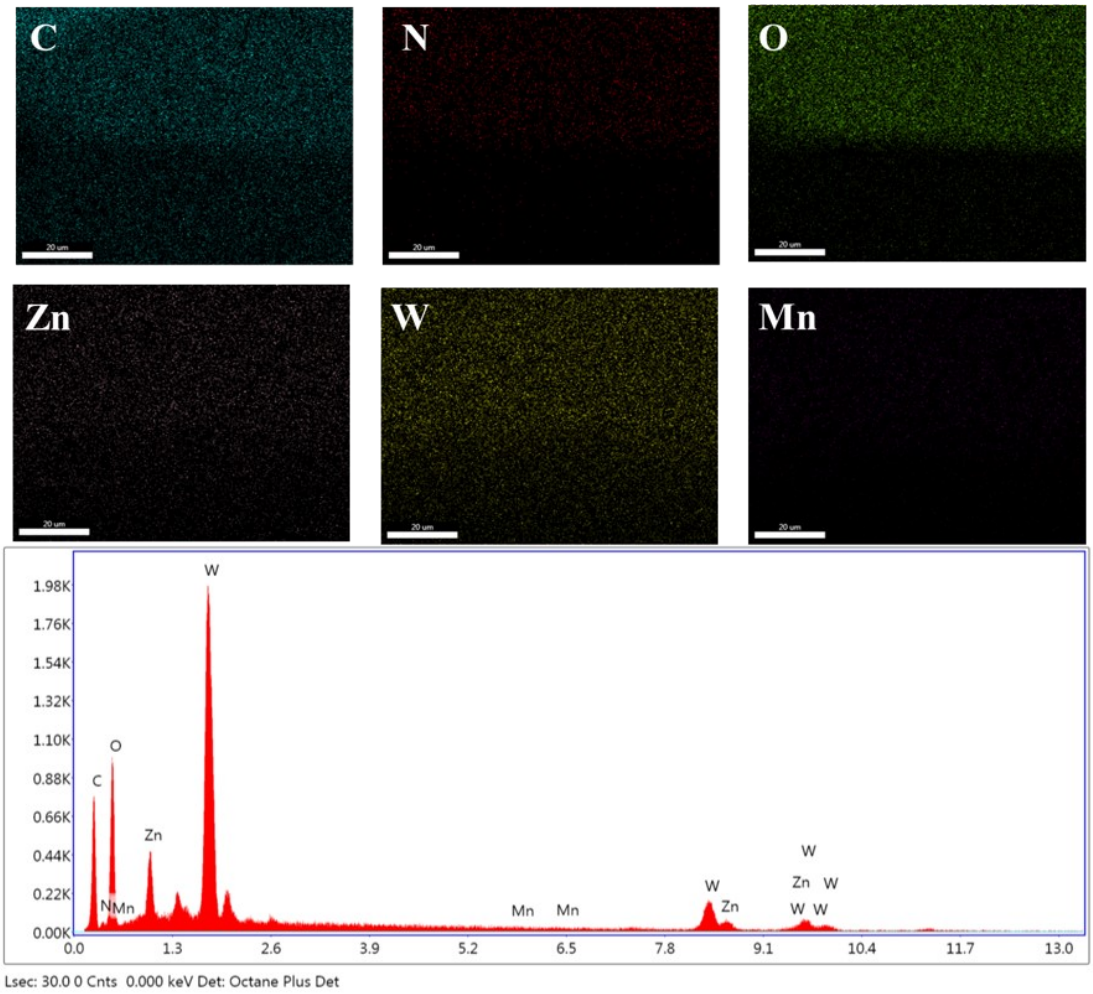

Figure S7 The EDS elemental mapping images and spectrum of **1**.

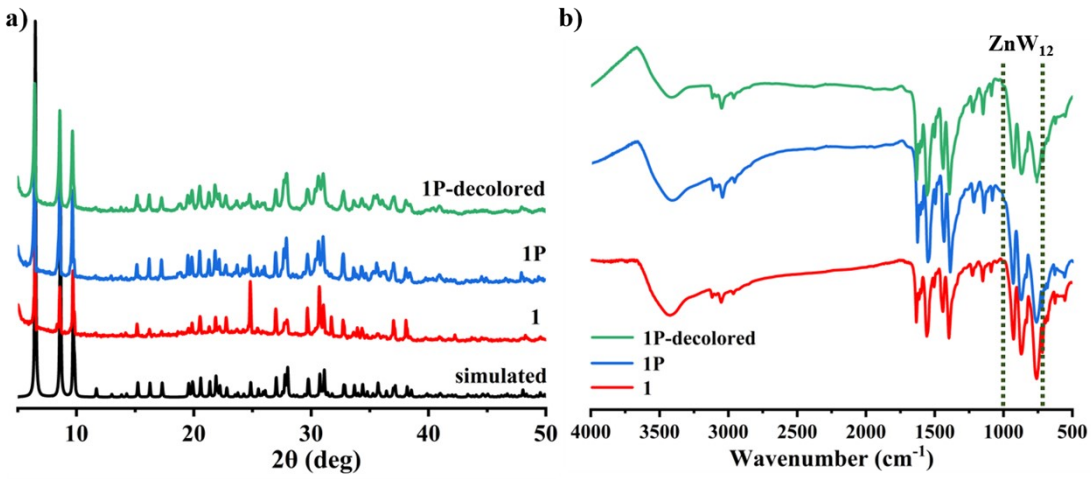

Figure S8 (a) Simulated, experimental, photochromic, and decolored PXRD patterns of **1**. (b) IR spectra of **1** before and after coloration.

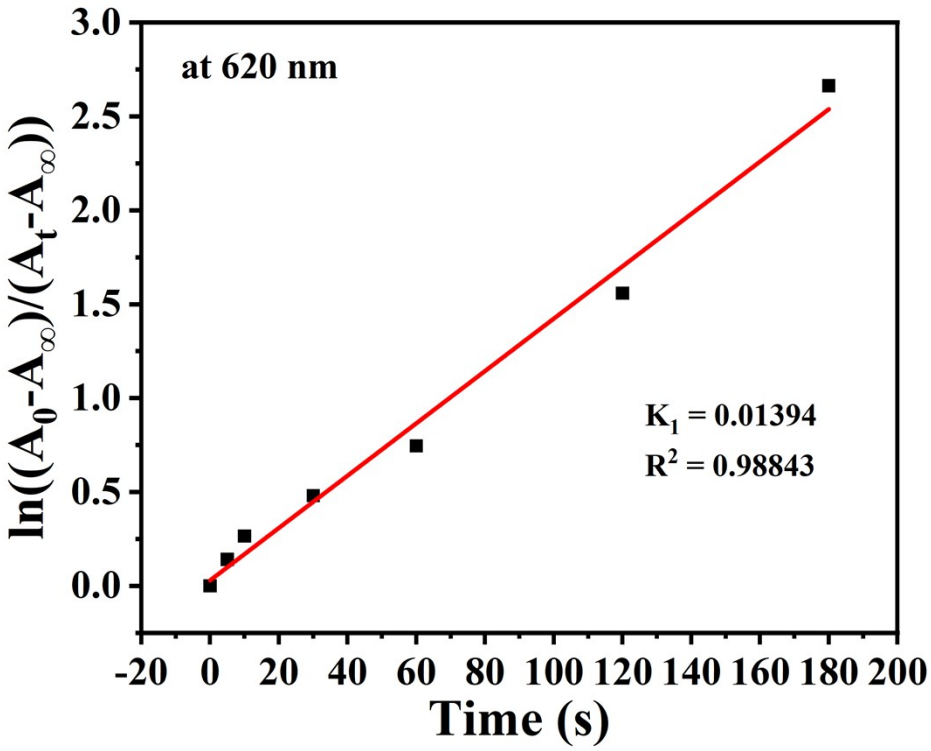

Figure S9 Solid state photoresponsive rate plots of **1** upon photo-irradiation based on UV absorption at 620 nm.

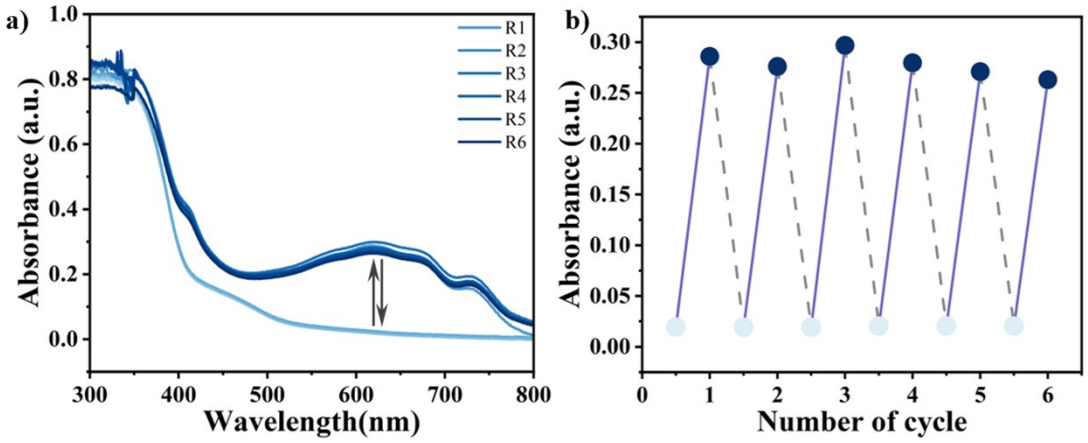

Figure S10 (a) The photochromic of the color change in 6 cycles. (b) The absorbance at λ=620 nm in the photochromism-decoloration cycles of **1**.

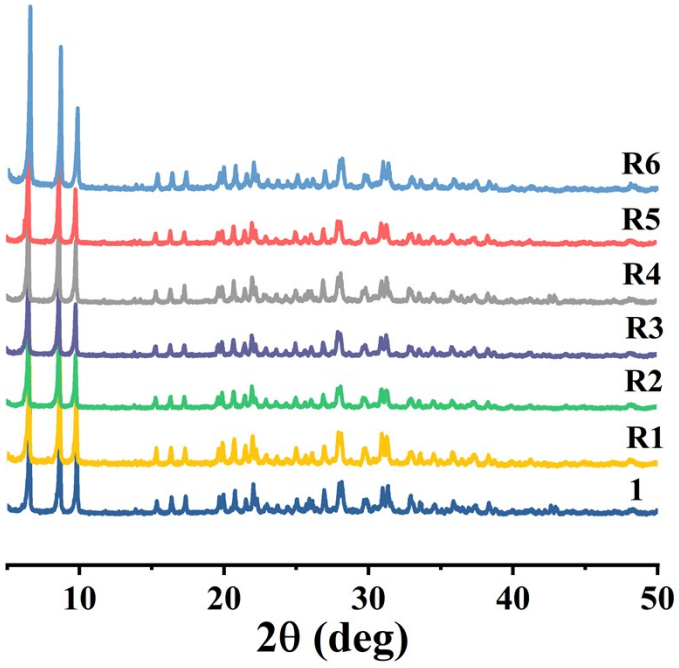

Figure S11 The PXRD patterns of colored sample **1** in the 6 cycles.

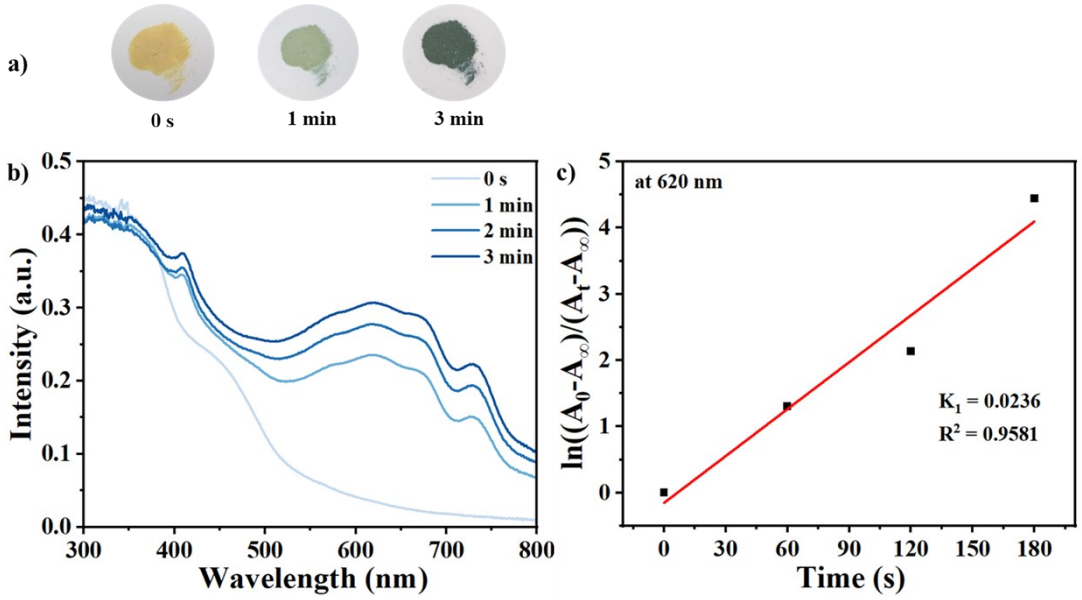

Figure S12 (a) The color transitions process of **1T**. (b) The in-situ solid-state UV-vis spectra of **1T**. (c) Solid state photoresponsive rate plots of **1T** upon photo-irradiation based on UV absorption at 620 nm.

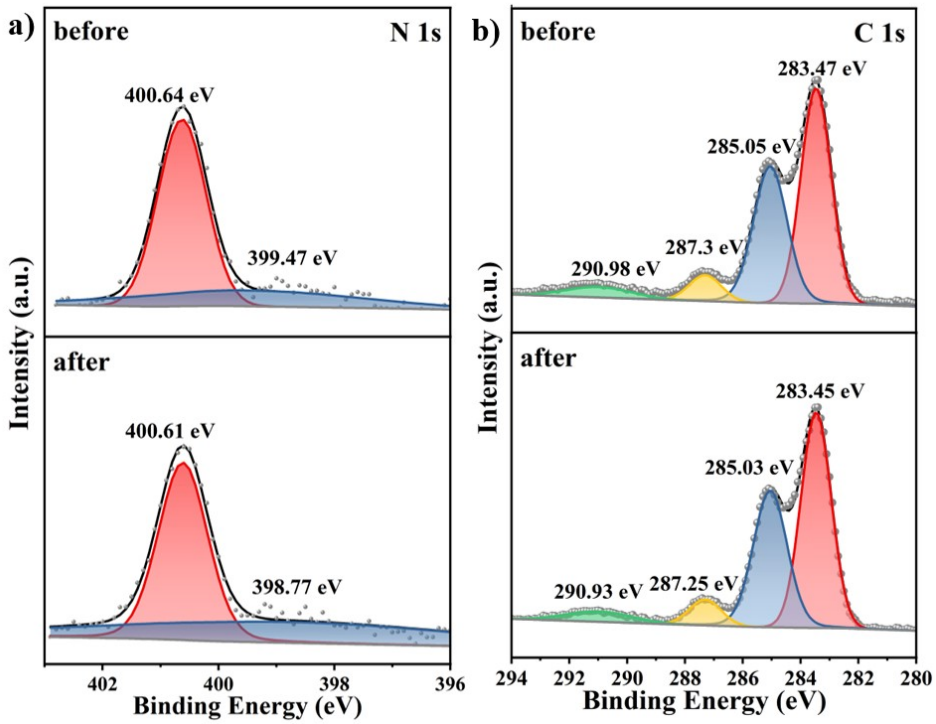

Figure S13 The XPS spectrum of **1** before and after UV photoirradiation: (a) N 1s, (b) C 1s.

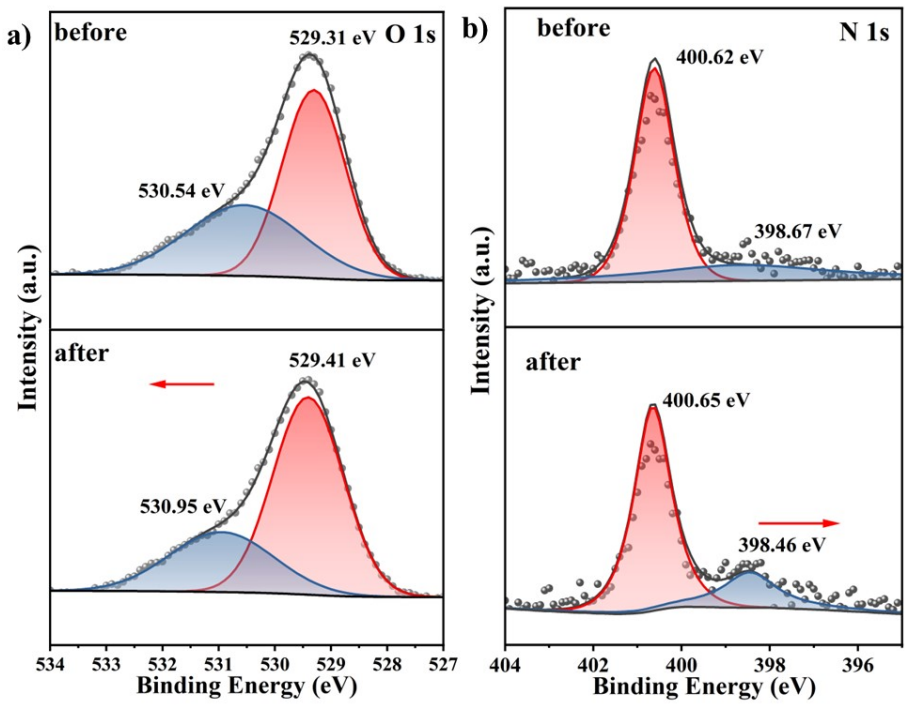

Figure S14 The XPS spectrum of **1** before and after X-ray photoirradiation: (a) O 1s, (b) N 1s.

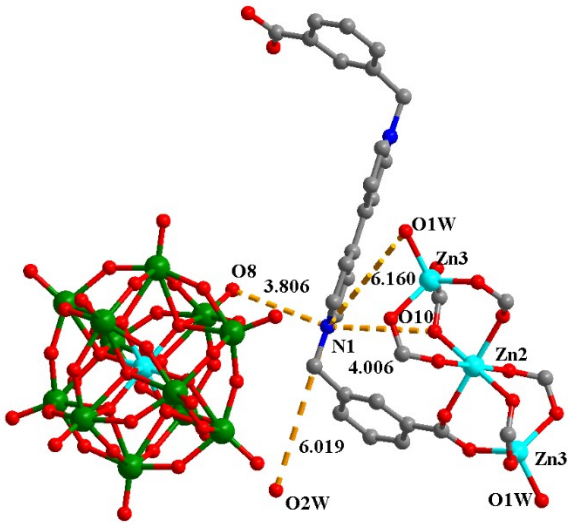

Figure S15 The selected distances between the O atoms (from ZnW_{12}, Bcbpy and H_2O molecules) to the N atoms from bipyridinium.

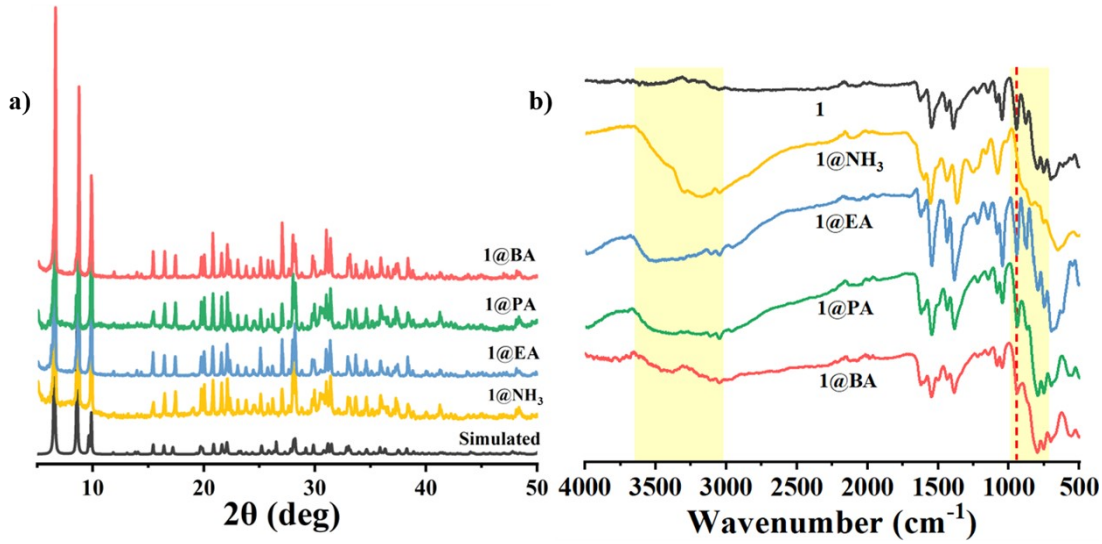

Figure S16 The PXRD patterns (a) and IR spectra (b) of **1** after exposure to different amines.

References

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