Electronic Supplementary Material (ESI) for Dalton Transactions.

Metal-dependent photosensitivity of three isostructural 1D CPs based on 1,1′-bis(3-carboxylatobenzyl)-4,4′-bipyridinium moiety

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S1. Experimental section

S1.1 Materials and methods

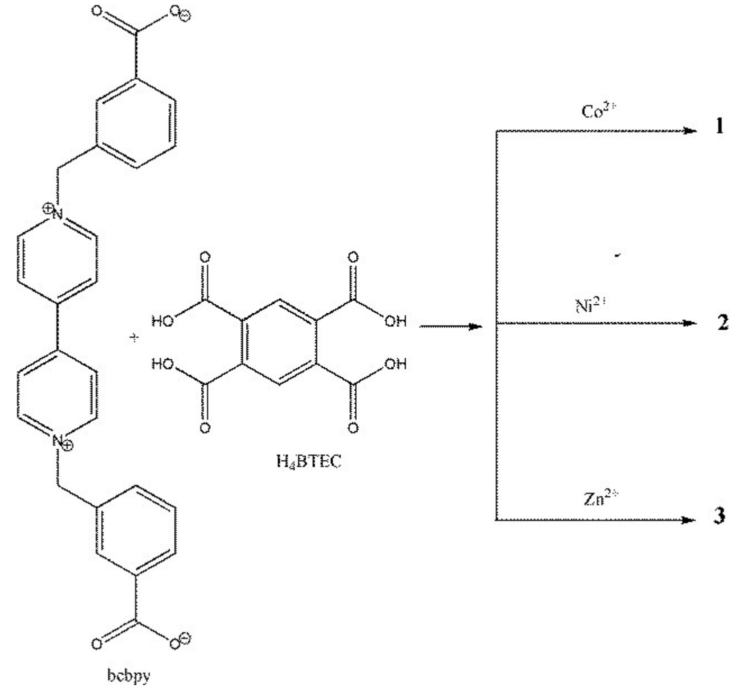
$Zn(CH_3COO)_2\cdot 2H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, 4,4′-bipyridine, 3-(chloromethyl)benzoic acid, N,N-dimethylformamide, CH_3OH, NaOH, 1,2,4,5-benzenetetracarboxylic acid and 1,4-benzenedicarboxylic acid and acetonitrile were purchased commercially and used without further purification. The viologen unit 1,1′-bis((3-carboxylatobenzyl)-4,4′-bipyridinium)-dichloride ($H_2bcbpyCl_2$) was synthesized according to the same procedures reported in the literature [1]; X-ray powder diffraction (PXRD) pattern was collected using a Rigaku Ultima IV-185 diffractometer; using Vario EL III CHNOS elemental analyzer for elemental analysis of C, H and N; preparation of a Nicolet 5DX spectrometer using KBr pellets to obtain FT-IR spectra (4000–500 cm $^{-1}$); Solid-state UV–Vis diffuse reflectance spectra were recorded on a Varian Cary 500 UV–Vis spectrophotometer equipped with an integrating sphere at room temperature in the range of 200−750 nm; Electron paramagnetic resonance (EPR) spectroscopy at room temperature was recorded using a Bruker A300-10 / 12 spectrometer; HTG-3 equipment at 30–700 °C, 10 °C·min^{-1} was used to perform thermogravimetric (TG) experiments in air; A ThermoFisher ESCALAB 250 X-ray photoelectron spectrometer (powered at 150 W) by Al Kα radiation (λ = 8.357 Å; spot size, 500 m) was used to perform X-ray photoelectron spectroscopy (XPS).

Preparation of $\{[M(H_2O)_6][M(BTEC)(H_2O)_4]\cdot(bcbpy)\cdot 4H_2O\}_n$ *M= Co (**1**), Ni (**2**), Zn (**3**)*

The general procedures for preparations of compounds **1**–**3** were as follows: A mixture of TM^{2+} (0.2 mmol) and $H_2bcbpyCl_2$ (50 mg, 0.1 mmol) was added into 10 mL water. Another mixture of NaOH (16.0 mg, 0.4 mmol) and H_4BTEC (25.4 mg, 0.1 mmol) was heated to dissolve in 20 mL water, and filtrated. After the mixture was stirred for 10 min, the residue was filtered. The filtrate was allowed to stand for several days to give block crystals. Yield for orange **1**: 31%, for light blue **2**: 33%, for colorless **3**: 35%, based on $H_2bcbpyCl_2$. IR (KBr pellet, cm^{-1}): 3392, 2026, 1608, 1494, 1382, 1315, 1216, 1149, 960, 755, 709, 670, 539. Elemental analysis: Anal. Calcd for $C_{36}H_{50}Co_2N_2O_{26}$ (compound **1**, 1044.64):

C, 41.39; H, 4.83; N, 2.68%. Found: C, 41.67; H, 4.80; N, 2.77%. Anal. Calcd for $C_{36}H_{50}Ni_2N_2O_{26}$ (compound **2**, 1044.20): C, 41.41; H, 4.83; N, 2.68%. Found: C, 41.77; H, 4.82; N, 2.61%. Anal.Calcd for $C_{36}H_{50}Zn_2N_2O_{26}$ (compound **3**, 1057.52): C, 40.88; H, 4.78; N, 2.65%. Found: C, 41.12; H, 4.79; N, 2.57%.

In the meantime, their purities were investigated by the powder X-ray diffraction technique, which revealed that all crystalline materials are in a pure phase (Fig. S1).



Scheme 1: Preparation of three CPs.

S1.2 X-ray crystallorgraphy

X-ray diffraction data of Compounds **1**–**3** was collected on an Oxford Gemini diffractometer at 293 K using graphite monochrome Mo-Kα ($\lambda = 0.71073$). The SCALE3 ABSPACK scaling algorithm was used to perform empirical absorption correction of spherical harmonics [2]. The SHELXTL-97 program was used to solve and refine the structure on F^2 by direct method and full matrix least squares technique [3]. All non-hydrogen atoms were anisotropically refined. The selected bond length and bond angle are listed in Table S1.

1. L. Li, Z. M. Tu, Y. Hua, X. N. Li, H. Y. Wang and H. Zhang, *Inorg. Chem. Front.*, 2019, **6**, 3077−3082.
2. CrysAlisPro, version 1.171.33.56. Oxfordshire. UK: oxford diffraction Ltd 2010.
3. (a) G. M. Sheldrick, *Crystallogr.*, 2008, **A64**, 112−122; (b) G. M. Sheldrick, Göttingen University: Germany, 1997.

Table S1. Selected bond lengths (Å) and bond angles (°) for **1**–**3**

Compound **1**			
Co(1)–O(8)	2.1720(12)	Co(1)–O(7)	2.0588(14)
Co(1)–O(5)	2.0764 (11)	Co(2)–O(9)	2.0943 (12)
Co(2)–O(10)	2.1213 (13)	Co(2)–O(11)	2.0912(12)
O(8)–Co(1) –O(8)	180.0	O(7)–Co(1) –O(8)	87.26(5)
O(7)–Co(1) –O(8)	92.74(5)	O(7)–Co(1) –O(7)	180.0
O(7)–Co(1) –O(5)	91.94(5)	O(7)–Co(1) –O(5)	88.06(5)
O(5)–Co(1) –O(8)	93.80(8)	O(5)–Co(1) –O(8)	86.20(5)
O(5)–Co(1) –O(5)	180.0	O(9)–Co(2) –O(9)	180.0
O(9)–Co(2) –O(10)	89.69(5)	O(9)–Co(2) –O(10)	90.31(5)
O(10)–Co(2) –O(10)	180.0	O(11)–Co(2) –O(9)	89.58(5)
O(11)–Co(2) –O(9)	90.42(5)	O(11)–Co(2) –O(10)	90.48(5)
O(11)–Co(2) –O(10)	89.52(5)	O(11)–Co(2) –O(11)	180.0
Compound **2**			
Ni(1)–O(7)	2.1122(15)	Ni(1)–O(8)	2.0390(16)
Ni(1)–O(4)	2.0474(14)	Ni(2)–O(9)	2.0726(15)
Ni(2)–O(10)	2.0691(16)	Ni(2)–O(11)	2.0652(14)
O(7)–Ni(1) –O(7)	180.00(8)	O(7)–Ni(1) –O(8)	93.40(6)
O(7)–Ni(1) –O(8)	86.60(6)	O(8)–Ni(1) –O(8)	180.00(5)
O(8)–Ni(1) –O(4)	91.78(7)	O(8)–Ni(1) –O(4)	88.22(7)
O(4)–Ni(1) –O(7)	93.72(6)	O(4)–Ni(1) –O(7)	86.28(6)
O(4)–Ni(1) –O(4)	180.00(9)	O(9)–Ni(2) –O(9)	180.00
O(9)–Ni(2) –O(11)	89.63(6)	O(9)–Ni(2) –O(11)	90.37(6)
O(10)–Ni(2) –O(10)	180.0	O(10)–Ni(2) –O(9)	90.00(6)
O(10)–Ni(2) –O(9)	90.00(6)	O(11)–Ni(2) –O(10)	90.80(6)
O(11)–Ni(2) –O(10)	89.20(6)	O(11)–Ni(2) –O(11)	180.00(8)
Compound **3**			
Zn(1)–O(7)	2.1932(14)	Zn(1)–O(8)	2.0661(15)
Zn(1)–O(6)	2.0670 (12)	Zn(2)–O(9)	2.1049(13)
Zn(2)–O(10)	2.0983 (13)	Zn(2)–O(11)	2.1116(14)
O(7)–Zn(1) –O(7)	180.00(4)	O(7)–Zn(1) –O(8)	86.91(6)
O(7)–Zn(1) –O(8)	92.74(5)	O(8)–Zn(1) –O(8)	180.0
O(8)–Zn(1) –O(6)	91.89(6)	O(8)–Zn(1) –O(6)	88.11(6)
O(6)–Zn(1) –O(7)	93.50(5)	O(6)–Zn(1) –O(7)	86.50(5)

O(6)–Zn(1) –O(6)	180.00(8)	O(9)–Zn(2) –O(9)	180.00(8)
O(9)–Zn(2) –O(11)	89.89(6)	O(9)–Zn(2) –O(11)	90.11(6)
O(10)–Zn(2) –O(10)	180.0	O(10)–Zn(2) –O(9)	89.71(6)
O(10)–Zn(2) –O(9)	90.29(6)	O(11)–Zn(2) –O(10)	90.14(6)
O(11)–Zn(2) –O(10)	89.86(6)	O(11)–Zn(2) –O(11)	180.00(6)

Table S2. The hydrogen bond lengths (Å) in **1**–**3**

Compound **1**

O(9)–H···O(1)	1.967	O(8)–H···O(1)	1.900
O(7)–H···O(2)	1.691	O(13)–H···O(3)	2.180
O(12)–H···O(3)	1.909	O(9)–H···O(4)	1.785
C(8)–H···O(4)	2.543	O(11)–H···O(6)	2.786
O(7)–H···O(13)	1.855	O(8)–H···O(6)	1.872
O(7)–H···O(2)	1.691	O(13)–H···O(8)	2.214
C(8)–H···O(8)	2.691	O(10)–H···O(12)	2.652
O(10)–H···O(3)	2.002	O(11)–H···O(12)	1.768
C(10)–H···O(11)	2.604	C(9)–H···O(13)	2.665
Compound **2**			
O(7)–H···O(1)	1.897	O(9)–H···O(1)	1.988
O(8)–H···O(2)	1.737	C(16)–H···O(2)	2.697
O(7)–H···O(3)	1.861	O(11)–H···O(3)	1.942
O(13)–H···O(5)	2.298	O(10)–H···O(5)	2.208
O(12)–H···O(5)	1.929	C(8)–H···O(6)	2.549
O(7)–H···O(1)	1.897	C(8)–H···O(7)	2.668
O(13)–H···O(7)	2.321	O(8)–H···O(13)	1.950
O(9)–H···O(12)	2.231	O(10)–H···O(12)	2.621
C(9)–H···O(11)	2.599	O(11)–H···O(12)	1.708
C(10)–H···O(13)	2.658		
Compound **3**			
O(7)–H···O(1)	1.895	O(10)–H···O(1)	1.976
O(8)–H···O(2)	1.706	C(18)–H···O(2)	2.712
O(10)–H···O(3)	1.791	C(8)–H···O(3)	2.547
O(11)–H···O(4)	2.507	O(13)–H···O(4)	2.156
O(12)–H···O(4)	1.916	O(9)–H···O(5)	1.928
O(7)–H···O(5)	1.875	O(8)–H···O(13)	2.969
C(8)–H···O(7)	2.670	C(9)–H···O(9)	2.585
O(9)–H···O(12)	1.767	O(11)–H···O(12)	2.587
C(10)–H···O(13)	2.663		

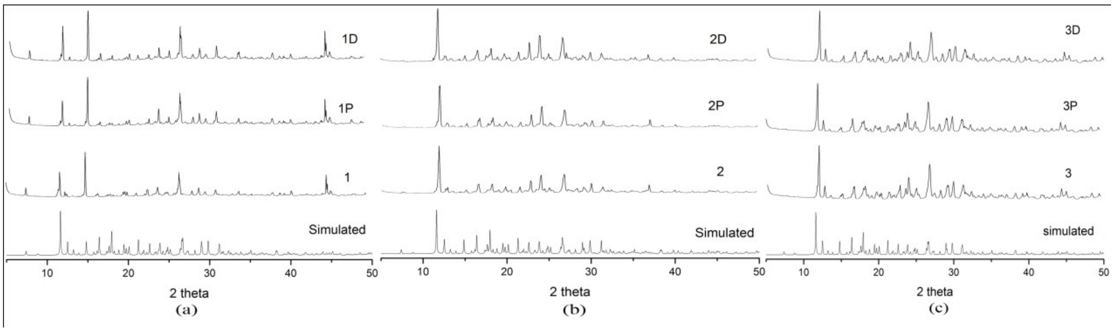


Fig. S1. The PXRD spectra before and after UV irradiation for **1** (a), **2** (b) and **3** (c).

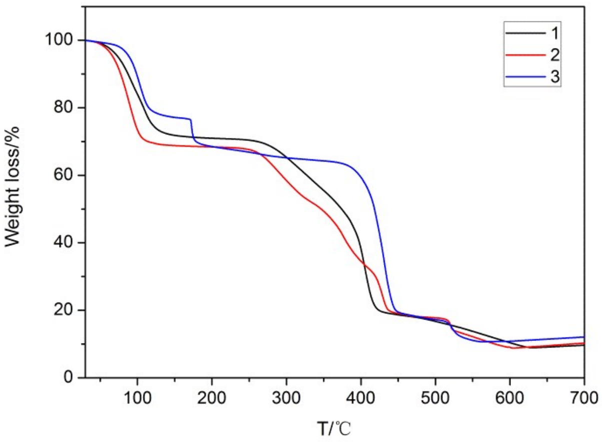


Fig. S2. TG tests of three compounds.

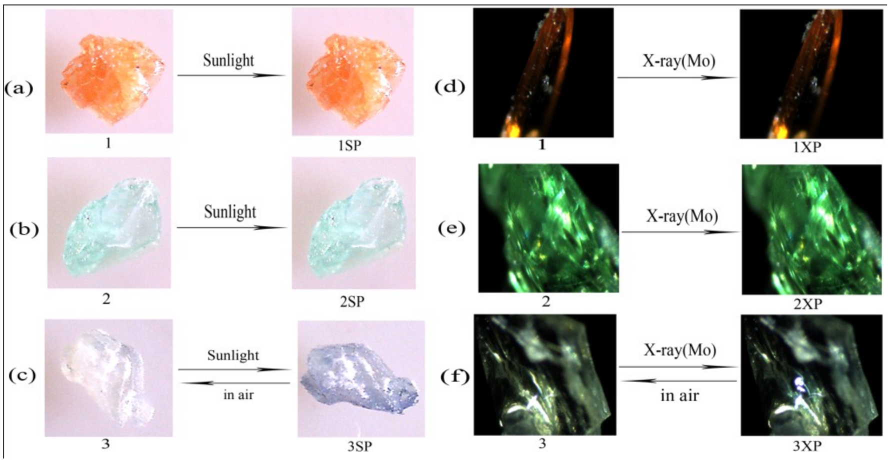


Fig. S3. Photographs of **1** (a), **2** (b) and **3** (c) subjected to irradiation by sunlight and showing photochromism; Photographs of **1** (d), **2** (e) and **3** (f) subjected to irradiation by X-ray (Mo) and showing photochromism.

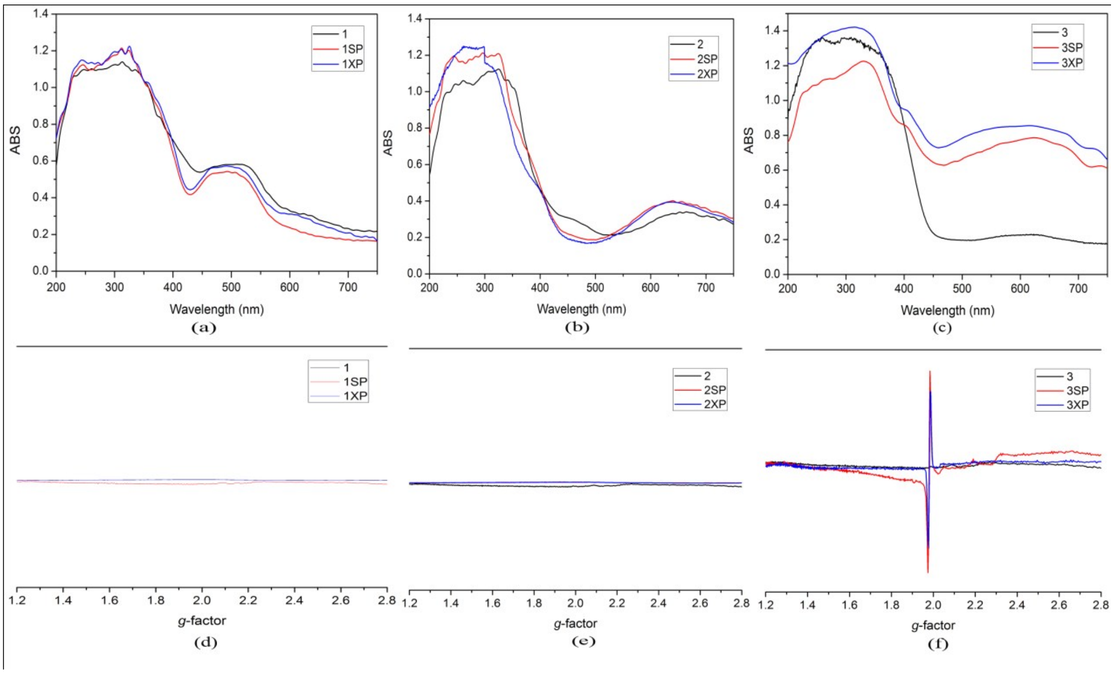


Fig. S4. UV-Vis spectra before and after sunlight and X-ray irradiation for **1** (a), **2** (b) and **3** (c); The EPR spectra before and after sunlight and X-ray irradiation for **1** (d), **2** (e) and **3** (f).

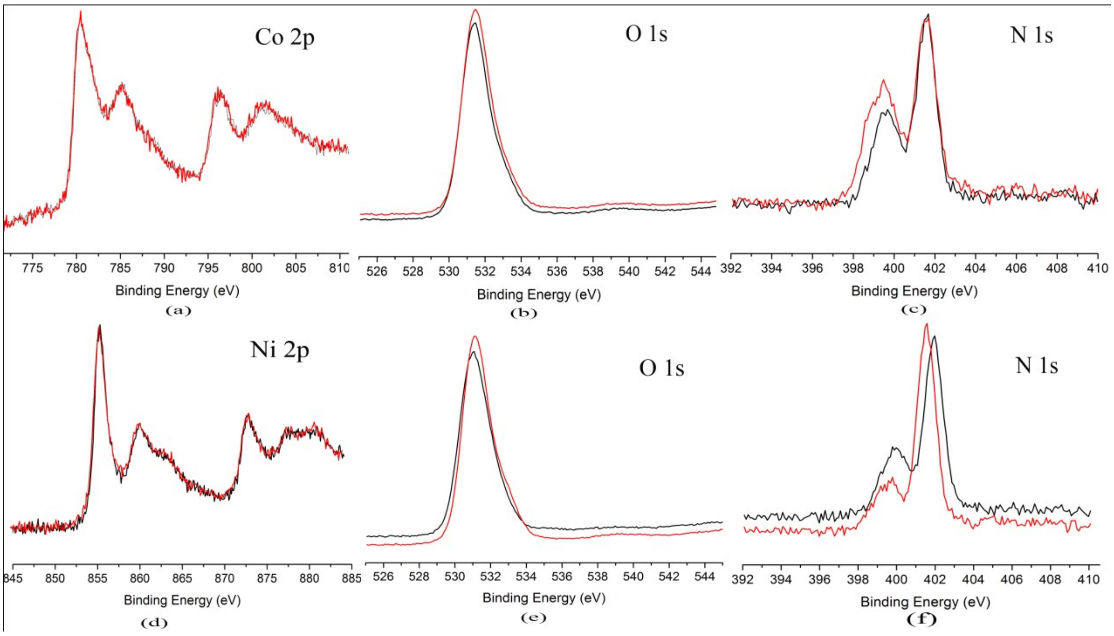


Fig.S5. XPS core-level spectra of **1** before (**1**: a, b, c, black line) and after UV irradiation (**1P**: a, b, c, red line); XPS core-level spectra of **2** before (**2**: d, e, f, black line) and after UV irradiation (**2P**: d, e, f, red line).