## **Supplementary Information**

# Three viologen-derived Zn-organic materials: photochromism, photomodulated fluorescence, inkless and erasable prints

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#### Section 1. Kinetic rate calculations

The photochemical reactions of compounds 2 and 3 all exhibit first order kinetics which can be analyzed with eq[1]:

$$\ln\!\left(\frac{R_0-R_\infty}{R_t-R_\infty}\right)=kt$$

where k is the first-order rate constant, R0, Rt,  $R\infty$  refer to the UV–vis diffuse reflectance intensity values (609 nm for compound **2**, 605 nm for compound **3**) at the beginning, versus time, and at the end of the reaction, respectively.

Reference

[1] J. Sworakowski, K. Janus and S. Nešpůrek, Adv. Colloid Interface Sci., 2005, 116, 97.

### Section 2. Additional Data and Figure



Fig. S1 The PXRD (L) patterns and IR (R) spectra of the compound 1 before and after irradiation.

The IR spectra of compound **1** exhibit wide and medium absorption peaks at 3551 and 3343 cm<sup>-1</sup> which are associated with the v(O-H) and v(Ar-H), respectively. The sharp peaks at 3047 cm<sup>-1</sup> correspond to the stretching bands of C-H of methyl groups of Mebpy ligand.



**Fig. S2** The PXRD (L) patterns and IR (R) spectra of the compound **2** before and after irradiation. IR spectra of **2** exhibit strong bands at 1705, 1639, 1611, 1439 cm<sup>-1</sup> associated with v(C=O). There are peaks observed at 1705 cm<sup>-1</sup> indicating that the carboxyl group are not completely deprotonated, which are good agreement with the crystallographic data.



**Fig. S3** The PXRD (L) patterns and IR (R) spectra of the compound **3** before and after irradiation. IR spectra of **3** exhibit strong bands at 1652, 1576, 1487cm<sup>-1</sup> associated with v(C=O). There are not peaks observed over 1700 cm<sup>-1</sup> indicating that the carboxyl group are completely deprotonated, which are good agreement with the crystallographic data.



Fig. S4 IR spectrum of the HCebpyCl ligand.

**IR of Hcebpy ligand (ATR, cm<sup>-1</sup>)**: 3035(w),2554(w), 2282(m), 1721(s), 1631(m), 1611(m), 1562(w), 1497(w), 1466(m), 1226(s), 1194(s), 813(s),680(m), 515(m).



Fig. S5 (a) IR spectrum of the H<sub>3</sub>btc ligand. (b) IR spectrum of the H<sub>2</sub>IPA ligand.

**IR of H<sub>3</sub>btc (ATR, cm<sup>-1</sup>)**: 2282(w),2538(w), 1692(s), 1606(w), 1450(m), 1400(s), 1266(s),1108(w), 886(m), 739(m), 683(s),613(w),533(m).

**IR of H<sub>2</sub>IPA (ATR, cm<sup>-1</sup>)**: 2818(w),2542(w), 1679(s), 1608(m), 1577(w), 1414(m), 1268(s), 1159(w), 918(m), 827(w), 722(s), 684(s),531(m).



Scheme. S1. In situ decarboxylation reactions of HCebpyCl ligand.

The decarboxylation of HCebpyCl was observed during the syntheses of compound 1 by hydrothermal method. In our experiments, the solvent is a key factor. When the mixed solvent of DMF and H<sub>2</sub>O is used, compound 1 was obtained by the decarboxylation of HCebpyCl. However, the decarboxylation of HCebpyCl did not occur in compound 2 and 3 when the mixed solvent of water and ethanol, or water and acetone was used.



Fig. S7 The dihedral angle of the pyridine ring in compound 2.



**Fig S8.** (a) View of the linear centrosymmetric trinuclear  $Zn_3O_2$  cluster units. (b) view of the tetranuclear zinc cluster with chair conformation in the compound **3**. Color code: Zn, cyan; O, red; N, blue; and C, grey.



**28.463°** Fig. S9 The dihedral angle of the pyridine ring in compound 3.



**Figure S10.** The photographs show the color change of 1 before and after being exposed to the light with different wavelengths.



Figure S11. The photographs show the color change of 2 before and after being exposed to the light with different wavelengths.







Fig. S13 The photographs of compounds 1, 2 and 3 after thermo-treatment.

After continuous heating from room temperature to 140, 150, 160  $^{\circ}$ C in darkness for compounds 1, 2 and 3 respectively, the crystals of 1, 2 and 3 still keep their color. It is concluded that the crystals 1, 2 and 3 do not have thermochromism. The heat of the Xenon lamp does not make the compound discolor.



Fig. S14 Possible pathways for the transfer of electrons between the donors and the pyridinium N atoms in the compound 1 and 1-P.



Fig. S15 Possible pathways for the transfer of electrons between the donors and the pyridinium N atoms in the compound 2 and 2-P.



Fig. S16 Possible pathways for the transfer of electrons between the donors and the pyridinium N atoms in the compound 3 and 3-P.



Fig. S17 (a) and (b) are reusable patterns of 2-paper and 3-paper, respectively.

Compound	1	1-P	2	2-P	3	3-P	
Formula	C <sub>20</sub> H <sub>19</sub> ClN <sub>2</sub> O <sub>8</sub>	$C_{20}H_{19}ClN_2O_8  C_{51}H_{45}N_4O_{28}Zn_3$		C51H45N4O	$C_{48}H_{38}N_4O_{20}Z$	C48H38N4O2	
	Zn	Zn		28Zn3	n <sub>4</sub>	0Zn4	
Mr (g mol <sup>-1</sup> )	516.19	516.19	1358.02	1358.02	1252.29	1252.29	
Crystal	triclinic	triclinic	triclinic	triclinic	orthorhombi	orthorhombic	
system					c		
Space group	P-1	P-1	P-1	P-1	Pna2 <sub>1</sub>	Pna21	
a (Å)	8.7183(16)	8.6484(4)	11.8799(5)	11.7907(16)	26.415(6)	26.3267(17)	
<b>b</b> (Å)	9.4583(18)	9.4482(5)	12.1277(5)	12.0397(17)	13.808(3)	13.8160(9)	
c (Å)	14.634(3)	14.5074(7)	20.5165(9)	20.483(3)	13.183(3)	13.1739(9)	
α (°)	72.424(3)	72.5780(10)	99.407(10)	99.429(2)	90.00	90.00	
β (°)	86.889(4)	87.6630(10)	96.491(10)	96.685(2)	90.00	90.00	
γ (°)	65.525(3)	65.5600(10)	92.289(10)	93.266(2)	90.00	90.00	
V (Å3)	1043.5(3)	1024.98(9)	2892.3(2)	2840.3(7)	4808.4(18)	4791.7(5)	
Ζ	2	2	2	2	4	4	
Dc (g cm <sup>-3</sup> )	1.643	2.316	1.559	1.686	1.727	1.708	
μ/(mm <sup>-1</sup> )	1.357	6.441	1.326	1.362	2.058	2.063	
Reflns	6371	5401	22041	16904	17657	17458	
collected/							
unique							
R <sub>int</sub>	0.0172	0.0087	0.0175	0.0207	0.0337	0.0199	
2θ range/°	4.94-50.06	2.96-50.05	3.42-49.94	3.48- 50.26	3.32-50.06	4.28- 49.84	
<i>F</i> (000)	528.0	681.0	1386.0	1476.0	2528.0	2488.0	
GOOF on $F^2$	1.038	1.076	1.068	1.042	1.036	1.065	
$\mathbf{R_1}^a$	0.0307	0.0478	0.0331	0.0630	0.0345	0.0375	
wR2 <sup>b</sup> (I	0.0701	0.1159	0.0868	0.1543	0.0824	0.1001	
>2 <i>\sigma(I)</i> )							



Fig. S18 The excitation spectrum of the compound 1 monitored at 557 nm.



Fig. S19 The excitation spectrum of the compound 2 monitored at 560 nm.



Fig. S20 The excitation spectrum of the compound 3 monitored at 526 nm.



Fig. S21 (a) The emission spectrum of the HCebpyCl ligand monitored at 418nm.

(b) The excitation spectrum of the HCebpyCl ligand monitored at 519nm.







Fig. S23 (a) The emission spectrum of the H<sub>2</sub>IPA ligand monitored at 345nm.(b) The excitation spectrum of the H<sub>2</sub>IPA ligand monitored at 390nm.



Fig. S24 The photographs of compounds 1, 2 and 3 after thermo-treatment.

After continuous heating from room temperature to 140, 150, 160  $^{\circ}$ C in darkness for compounds 1, 2 and 3 respectively, the crystals of 1, 2 and 3 still keep their color. It is concluded that the crystals 1, 2 and 3 do not have thermochromism. The heat of the xenon lamp does not make the compound discolor.



Fig. S25 The TGA diagrams of compound 1.

Thermal gravimetric analyses (TGA) of were performed under nitrogen atmosphere in the range 25–800 °C to determine the thermal stabilities of complexes 1-3. As shown in Fig.S12, There is a two-step weight loss for 1. The first weight loss of 6.90% in 1 from 40 to 230 °C corresponding to the release of the free water molecules (calcd 6.97%). Above 230 °C, the network begins to decompose.



Fig. S26 The TGA diagrams of compound 2.

The TGA curve of compound **2** shows a weight loss of 5.18 % at 30 to  $105^{\circ}$  C corresponding to the release of four free water molecules (calcd 5.30%), and then the frameworks collapse upon further heating.



The TGA curve of compound **3** shows a weight loss of 2.73% at 30 to 200 ° C corresponding to the release of two free water molecules (calcd 2.87%), and then the frameworks collapse upon further heating.

TD 1	1	C	0	1	1
Lono	$\int \sigma V$	tor	( om	nound	- 1
ropo	US y	101	Com	pound	•

Atom Zn1 links by bridge ligands and has

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Common vertex with					R(A-A)	
Zn 1	0.3513	0.6786	0.7564	(000)	10.943A	1
Zn 1	0.3513	0.6786	-0.2436	(00-1)	10.943A	1
Zn 1	0.3513	-0.3214	0.7564	(0-10)	10.943A	1
Zn 1	0.3513	-0.3214	-0.2436	(0-1-1)	10.943A	1
Zn 1	0.6487	0.3214	0.2564	(000)	13.354A	1
Zn 1	-0.3513	0.3214	0.2564	(-1 0 0)	13.354A	1
Zn 1	0.1487	1.1786	0.2564	(010)	13.808A	1
Zn 1	0.1487	-0.8214	0.2564	(0-10)	13.808A	1

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Structural group analysis

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#### Structural group No 1

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Structure consists of 3D framework with Zn

Coordination sequences

\_\_\_\_\_

 Zn1:
 1
 2
 3
 4
 5
 6
 7
 8
 9
 10

 Num
 8
 26
 56
 98
 152
 218
 296
 386
 488
 602

 Cum
 9
 35
 91
 189
 341
 559
 855
 1241
 1729
 2331

TD10=2331

Vertex symbols for selected sublattice

\_\_\_\_\_

\_\_\_\_\_

Point symbol for net: {3^6.4^18.5^3.6} 8-c net; uninodal net