A novel multichromic Zn (Ⅱ) cationic coordination polymer based on a new flexible viologen ligand exhibiting aniline detection in solid state

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Computational methods and models

All of the DFT calculations were performed by using Vienna ab initio simulation pachage (VASP).[1, 2] The exchange–correlation energy is treated based on the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE).[3] The core–electron interactions are describe by Projector–augmented–wave (PAW) pseudopotentials.[4] The Grimme's dispersion correction (DFT–D3) method is applied to describe the van der Waals (vdW) interaction.[5] A 5 × 3 × 2 Monkhorst–Pack k–point grid was adopted for calculations on Complex **1**. The energy cutoff is set to be 420 eV. All atoms were fully relaxed until the total energy converges to less than 10^{-4} eV and the ionic relaxation were performed until the force on each atom converge to within 0.02 eV $Å^{-1}$.

References

1 G. Kresse and J. Furthmuller, Phys. Rev. B: Condens. Matter Mater. Phys., 1996, 54, 11169.

2 G. Kresse and J. Furthmuller, Comput. Mater. Sci., 1996, 6, 15–50.

3 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.

4 P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953–17979.

5 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104–154123

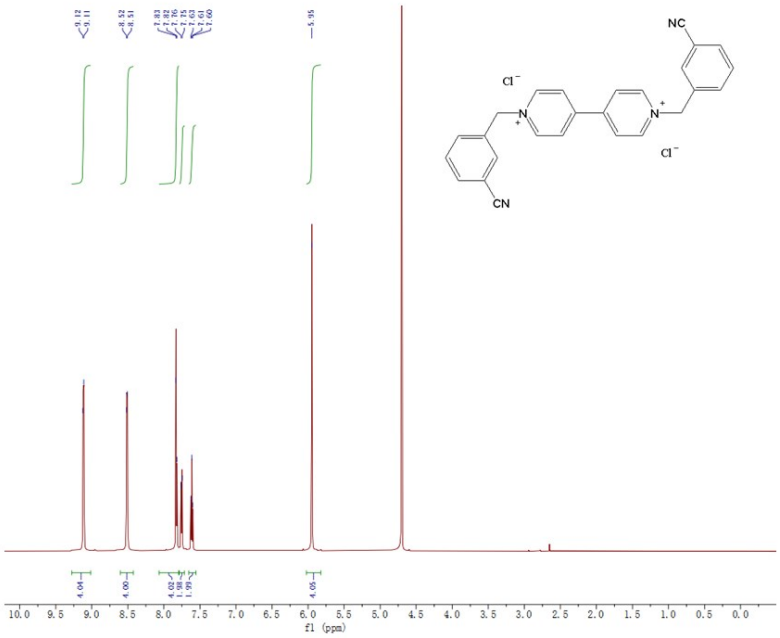

Fig. S1 The ^{1}H NMR spectrum of viologen ligand in D_2O (600 MHz).

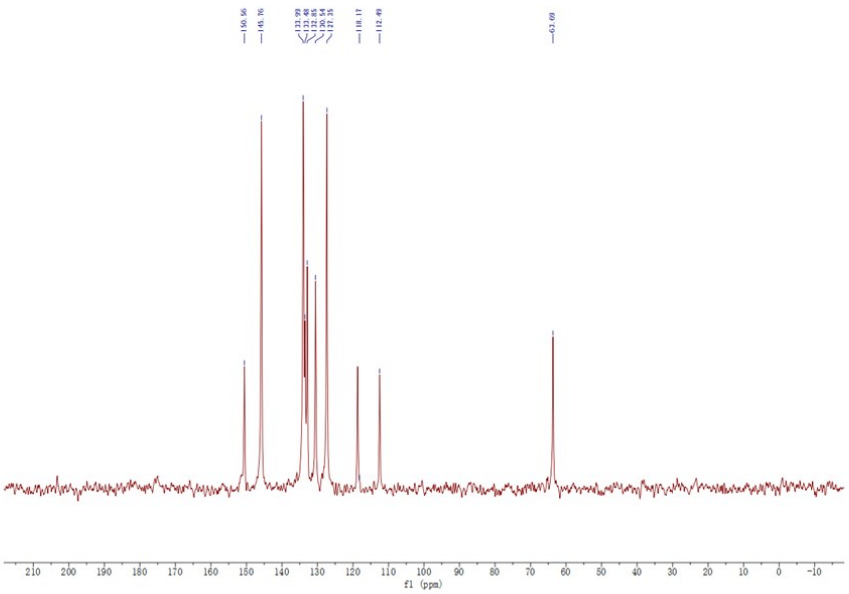

Fig. S2 The ^{13}C-NMR spectrum of viologen ligand in D_2O (600 MHz).

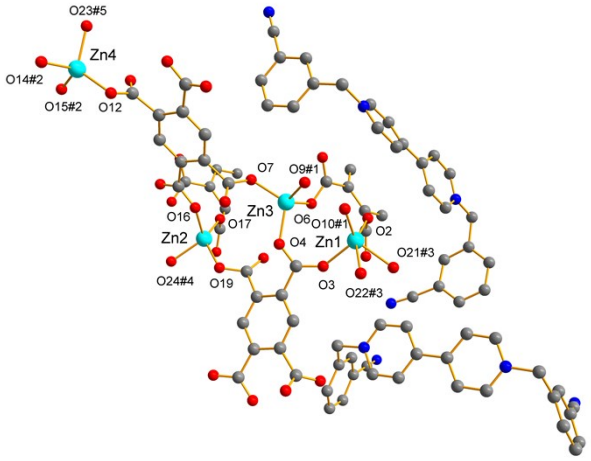

Fig. S3 The asymmetric unit of complex 1 (all H atoms were omitted for clarity) **Symmetry codes**: for complex: #1: 1-x, -y, 1-z; #2: 2-x, -y, 1-z; #3: 1-x, 1-y, 2-z; #4: 2-x, 1-y, 2-z; #5: x, -1+y, -1+z .

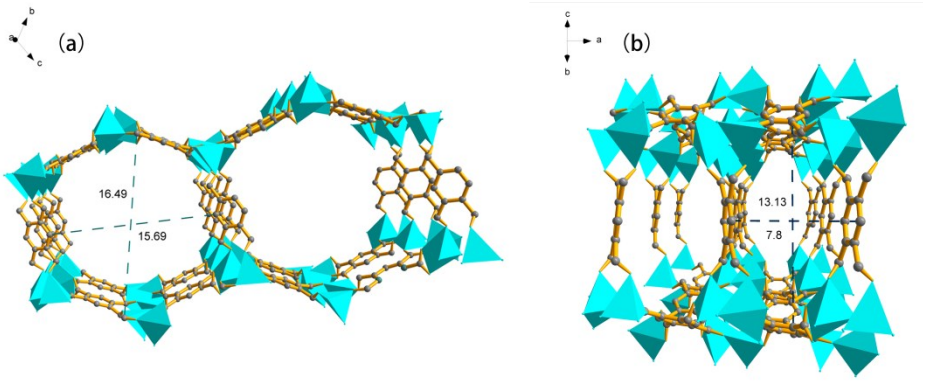

Fig. S4 Three-dimensional channels in the crystal.

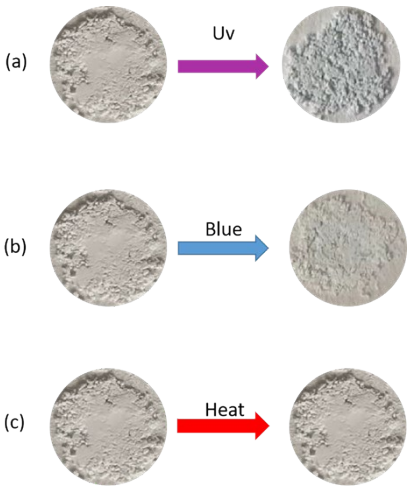

Fig. S5 Discoloration of viologen ligand (a)Uv irradiation (b)Blue ray irradiation (c)heat at 120℃

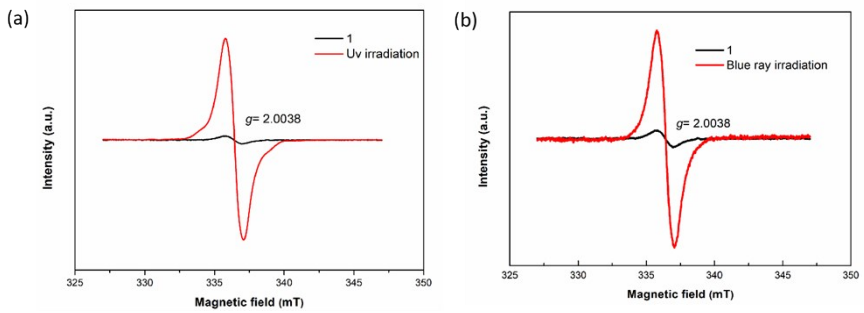

Fig. S6 EPR data of complex **1** before and after (a)Uv irradiation (b)Blue rays irradiation.

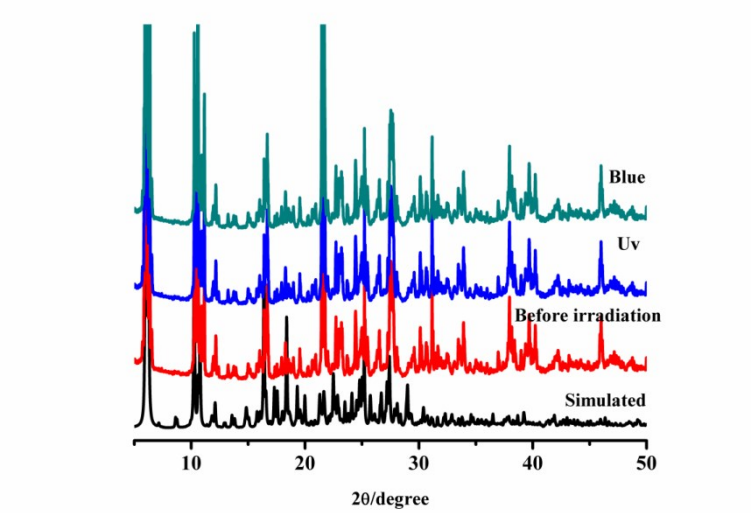

Fig. S7 PXRD patterns of 1 before irradiation, after irradiated by UV and blue rays, respectively. The black line is the simulated curve.

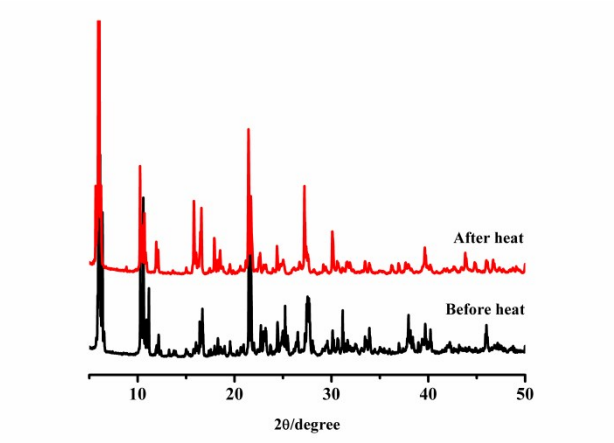

Fig. S8 PXRD patterns of **1** before and after heated at 120 ℃.

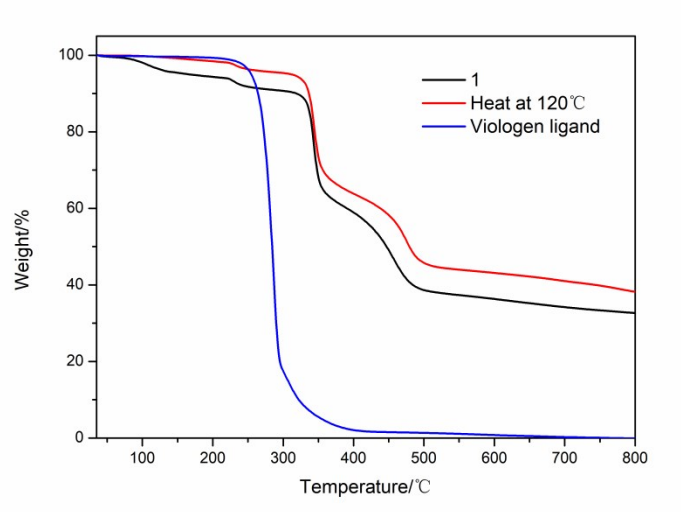

Fig. S9 The TGA date of **1**, heat at 120 ℃ and the viologen ligand.

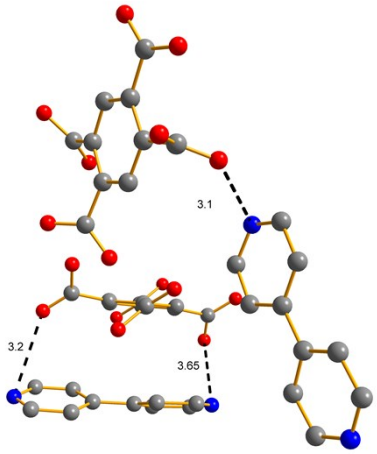

Fig. S10 The electron transfer pathways of **1** studied by VASP.

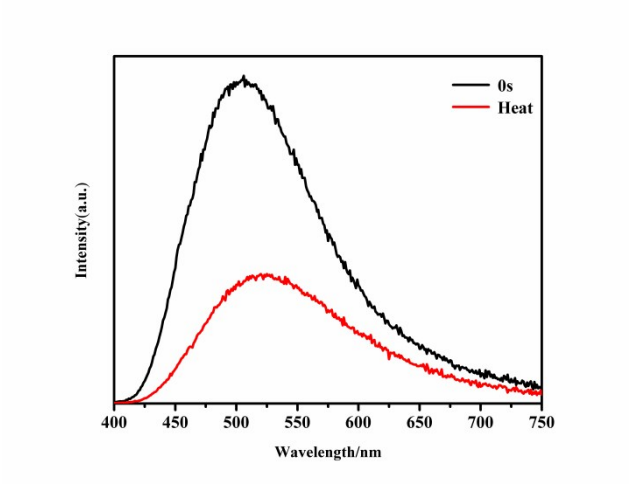

Fig. S11 The luminescence spectra of **1** before and after heated at 120 ℃.

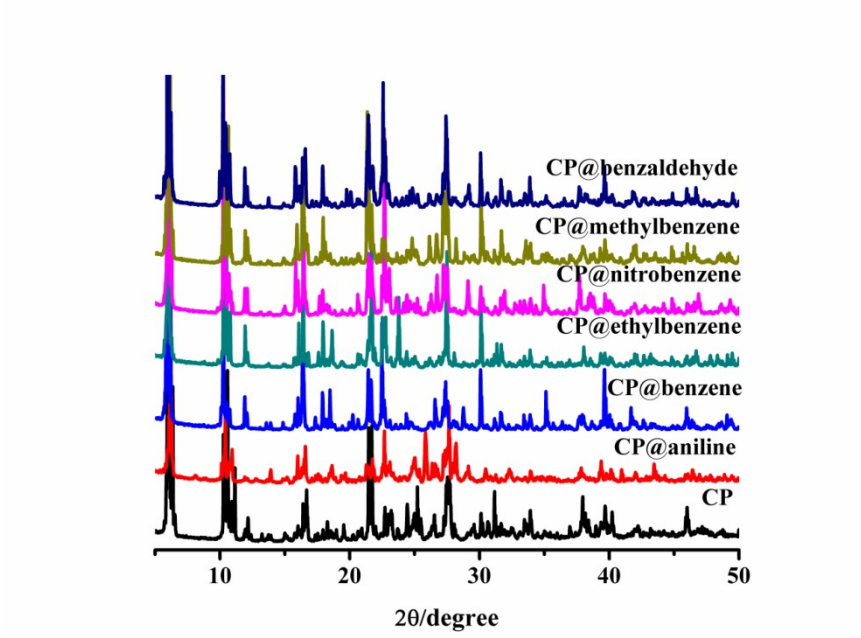

Fig. S12 PXRD patterns of **1** and after detecting different benezes.

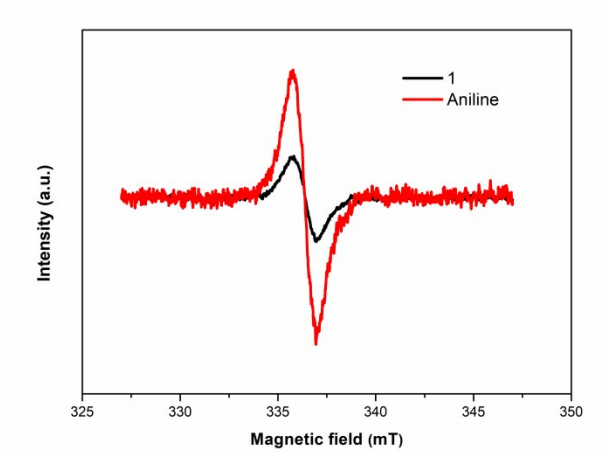

Fig. S13 EPR of complex **1** and after detecting aniline.

Fig. S14 Varied colour changing to detect NO^{2-} from $NaNO_2$ solution with different concentration.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{82}H_{56}N_8O_{29}Zn_4$
Formula weight	1878.82

Crystal system	triclinic
Space group	P-1
a/Å	15.5845(8)
b/Å	16.7477(9)
c/Å	16.9751(9)
α/°	114.048(2)
β/°	100.299(2)
γ/°	101.237(2)
Volume/Å^3	3800.0(4)
Z	2
Temperature/K	297
ρ_{calc}g/cm^3	1.642
μ/mm^{-1}	2.251
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.954 to 101.202
Reflections collected	57367
Independent reflections	8001 [R_{int} = 0.1264, R_{sigma} = 0.0796]
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1553
Final R indexes [all data]	R_1 = 0.0962, wR_2 = 0.1775

Table S2 The main crystal data of **1**, **1**-UV and**1**-blue.

	1	**1**-UV	**1**-blue
a	15.5845(8)	15.5797(7)	15.5861(8)
b	16.7477(9)	16.7473(8)	16.7515(8)
c	16.9751(9)	16.9714(8)	16.9797(8)
α	114.048(2)	114.109(2)	114.137(1)
β	100.299(2)	100.262(2)	100.258(2)
γ	101.237(2)	101.279(2)	101.247(2)
Volume	3800.0(4)	3795.6(3)	3799.7(3)
Space group	P -1	P-1	P-1