The modulation effect of pi–pi interactions on electronic and photochromic properties of viologen complexes containing *N*,*N′*-bis(carboxyethyl)-4,4′-bipyridinium

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1. Experimental section

1.1. Materials and instruments

All chemicals and reagents were purchased from commercial sources and used in the synthesis without further purification. *N*,*N′*-bis(carboxyethyl)-4,4′-bipyridinium (BCEbpy) was prepared on the basis of literature procedure [1]. FT-IR spectra were recorded from pure KBr pellets with a Nicolet 5DX spectrometer in the range of 4000–500 cm^{-1}. UV-vis diffuse reflectance spectrum was measured at room temperature on a Varian Cary 5000 spectrophotometer. Elemental analyses (C, N and H) were obtained on a Vario EL III CHNOS elemental analyzer. Electron paramagnetic resonance (EPR) spectrum was conducted on a Bruker A300-10/12 spectrometer at room temperature. The powder X-ray diffraction (PXRD) patterns were reported using a Rigaku Ultima IV-185 diffractometer.

1.2. Synthesis

1.2.1. Synthesis of **1**

BCEbpy (27.23 mg, 0.1 mmol) and $(CH_3COO)_2Zn\cdot 2H_2O$ (21.95 mg, 0.1 mmol) were added into 7 mL H_2O after stirring for 6 min, then obtained solution A. 1,4-Benzenedicarboxylic acid (16.61 mg, 0.1 mmol) was dissolved in a mixed solvent of *N*,*N*-dimethylformamide (DMF) (5 mL), methanol (5 mL) and H_2O (10 mL), then stirred at 40℃ and obtained solution B. The solutions A and B were mixed and filtrated after stirring for another 5 min. The filter liquor was left for slow evaporation at room temperature to yield light yellow blocks within 5 days. The yield was 32.9% based on BCEbpy. Elemental analysis (%): Calculated for $C_{22}H_{34}ZnN_2O_{17}$: C, 39.82; H, 5.13; N, 4.22. Found: C, 40.21; H, 5.68; N, 4.73. IR (KBr, cm^{-1}): 3729, 2859, 1868, 1514, 1467, 1159, 1032, 932.

1.2.2. Synthesis of **2**

BCEbpy (27.23 mg, 0.1 mmol) and $(CH_3COO)_2Co\cdot 4H_2O$ (24.91 mg, 0.1 mmol) were added into 7 mL H_2O after stirring for 6 min, then obtained solution A. 1,4-Benzenedicarboxylic acid (16.61 mg, 0.1 mmol) was dissolved in a mixed solvent of *N*,*N*-dimethylformamide (DMF) (5 mL), methanol (5 mL) and H_2O (10 mL), then stirred at 40℃ and obtained solution B. The solutions A and B were mixed and filtrated after stirring for another 5 min. The filter liquor was left for slow evaporation at room temperature to yield light yellow blocks within 4 days. The yield was 37.6% based on BCEbpy. Elemental analysis (%): Calculated for $C_{22}H_{34}CoN_2O_{17}$: C, 40.18; H, 5.18; N, 4.26. Found: C, 40.65; H, 5.87; N, 4.86. IR (KBr, cm^{-1}): 3756, 3086, 1902, 1474, 1313, 1233, 1019, 952, 704.

1.3. X-ray crystallography

The X-ray diffraction data of viologen complexes were collected on an Oxford Gemini diffractometer with graphite monochromated Cu-Kα (λ = 1.54184 Å) for **1** and Mo-Kα (λ = 0.71073 Å) for **2**. An empirical absorption correction with spherical harmonics was carried out by SCALE3 ABSPACK scaling algorithm [2]. The structures of viologen complexes were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELXTL program with anisotropic thermal parameters for all non-hydrogen atoms [3].

2. Computational methods

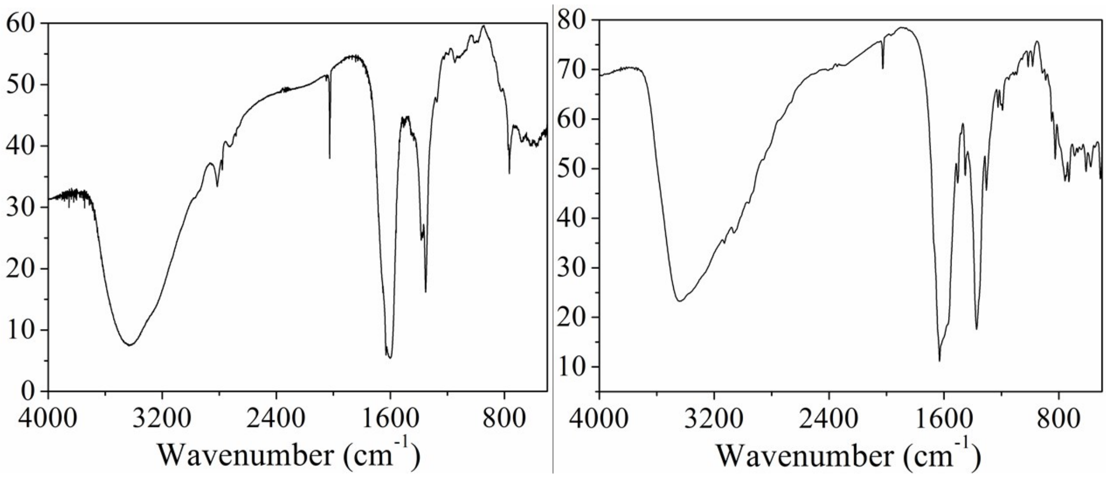
Single point energies calculations were conducted at the B3LYP/6-311 (d,p) level of DFT with Gaussian 09 suite [4]. Hirshfeld surfaces and two dimensional (2D) fingerprint plots were exhibited by Crystal Explorer 17 [5]. The normalized contact distance (d_{norm}) mapped on Hirshfeld surface was analyzed by Equation (1):

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}} \qquad (1)$$

where d_{i} and d_{e} mean the distances from the surface to the nearest atom inside and outside the surface, respectively; r_i^{vdw} and r_e^{vdw} mean the van der Waals (vdW) radius of two atoms inside and outside the surface, respectively.

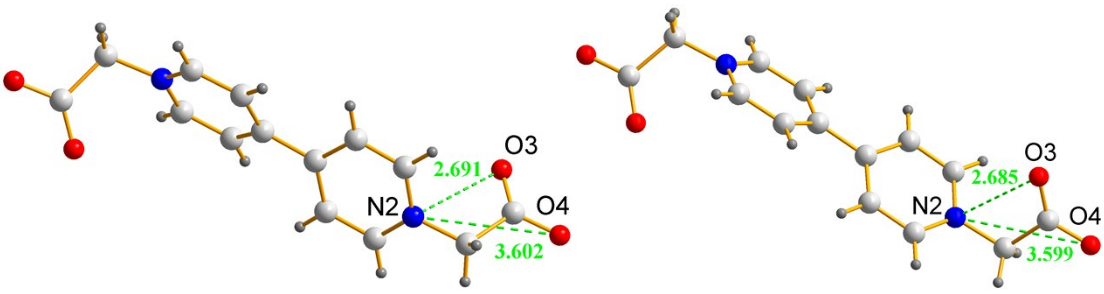
Table S1. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

Compound **1**			
Zn(1)–O(7)	2.1002 (16)	Zn(1)–O(5)	2.0830 (3)
Zn(1)–O(8)	2.043 (2)	Zn(1)–O(10)	2.0834 (17)
Zn(1)–O(9)	2.086 (2)	Zn(1)–O(6)	2.0861 (17)
O(5)–Zn(1)–O(7)	93.72(7)	O(5)–Zn(1)–O(10)	88.41 (8)
O(5)–Zn(1)–O(9)	170.96 (10)	O(5)–Zn(1)–O(6)	83.20 (9)
O(8)–Zn(1)–O(7)	89.84 (8)	O(8)–Zn(1)–O(5)	93.57 (11)
O(8)–Zn(1)–O(10)	87.45 (8)	O(8)–Zn(1)–O(9)	94.69 (12)
O(8)–Zn(1)–O(6)	176.10 (10)	O(10)–Zn(1)–O(7)	176.65 (7)
O(10)–Zn(1)–O(9)	88.30 (8)	O(10)–Zn(1)–O(6)	94.63 (7)
O(9)–Zn(1)–O(7)	89.96 (8)	O(9)–Zn(1)–O(6)	88.68 (9)
O(6)–Zn(1)–O(7)	88.19 (7)		
Compound **2**			
Co(1)–O(14)	2.1114 (12)	Co(1)–O(9)	2.0793 (13)
Co(1)–O(10)	2.0969 (13)	Co(1)–O(13)	2.0415 (15)
Co(1)–O(12)	2.0687 (13)	Co(1)–O(11)	2.0755 (15)
O(9)–Co(1)–O(14)	88.16 (5)	O(9)–Co(1)–O(10)	94.22 (6)
O(10)–Co(1)–O(14)	177.22 (5)	O(13)–Co(1)–O(14)	90.73 (6)
O(13)–Co(1)–O(9)	177.20 (8)	O(13)–Co(1)–O(10)	86.95 (6)
O(13)–Co(1)–O(12)	93.01 (8)	O(13)–Co(1)–O(11)	93.42 (8)
O(12)–Co(1)–O(14)	89.79 (6)	O(12)–Co(1)–O(9)	89.56 (7)
O(12)–Co(1)–O(10)	88.80 (6)	O(12)–Co(1)–O(11)	172.86 (8)
O(11)–Co(1)–O(14)	93.22 (6)	O(11)–Co(1)–O(9)	84.07 (7)
O(11)–Co(1)–O(10)	88.46 (6)		



(a) (b)

Fig. S1. FT-IR spectra of compounds **1** (a) and **2** (b).



(a) (b)

Fig. S2. The N2–O3 and N2–O4 distances in compounds **1** (a) and **2** (b).

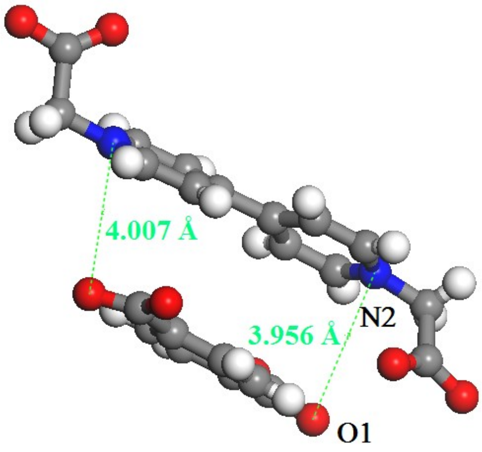
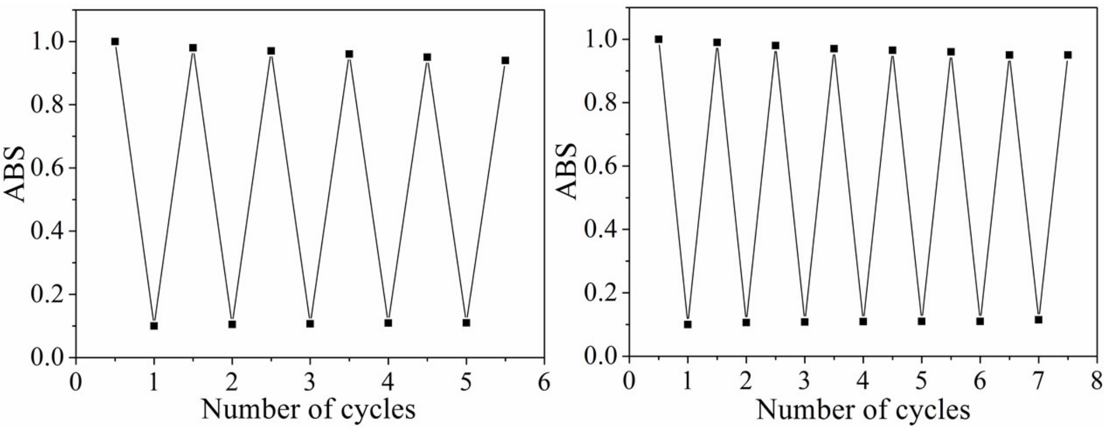


Fig. S3. The orientation diagrams of compound **2**.



(a) (b)

Fig. S4. UV−vis diffuse-reflectance spectra of **1** (a) and **2** (b) upon irradiation and decoloration.

3. Kinetic rate calculations

The photochemical reactions of compounds **1** and **2** both exhibit first order kinetics which can be analyzed with Equation (2) [6]:

$$\ln(\frac{R_0 - R_\infty}{R_t - R_\infty}) = kt \qquad (2)$$

where k is the first-order rate constant, R_0, R_t, R_∞ refer to the UV−Vis diffuse reflectance intensity values (404 nm for compound **1**, 402 nm for compound **2**) at the beginning, versus time, and at the end of the reaction, respectively.

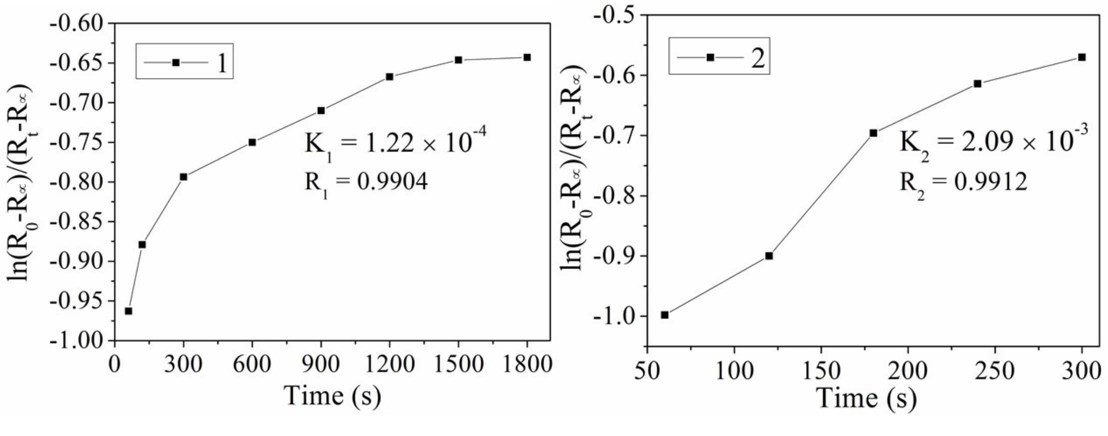


Fig. S5. Solid-state first-order photoresponsive rate plot for compounds **1** and **2**.

References

[1] Andrew DP, Zhao FF, Wee HA, Rosario S, Paul JD. A crystallographic story of snakes and ladders: Encapsulated water polymers and rigid metal complexes based on mono-*N*-substituted carboxylate 4,4′-bipyridine, Crystal Growth & Design, 2009, 9(4): 1966-1978.

[2] CrysAlisPro, version 1.171.33.56, Oxford diffraction Ltd, Oxfordshire UK, 2010.

[3] Sheldrick GM. SHELXS-97, a program for X-ray crystal structure solution, and SHELXL-97, a program for X-ray structure refinement, Göttingen University, Germany, 1997.

[4] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, Revision A.02, Gaussian Inc, Wallingford CT, 2009.

[5] Turner MJ, McKinnon JJ, Wolff SK, Grimwood DJ, Spackman PR, Jayatilaka D, Spackman MA. Crystal Explorer 17, University of Western Australia, 2017.

[6] Sworakowski J, Janus K, Nešpůrek S. Kinetics of photochromic reactions in condensed phases, Advances in Colloid and Interface Science, 2005, 116(1-3): 97-110.