Supporting Information

Anion-controlled photochromism of two bipyridinium-based coordination polymers and nondestructive luminescence readout

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Section 1. Synthesis of ligand H₂DBCbpyBr



Scheme S1 Schematic representation of the synthesis procedure of ligand H2DBCbpyBr.



Fig. S1 ¹H NMR spectrum of H₂BDCbpyBr in DMSO-D6 (400 MHz).

Section 2. Kinetic rate calculations

The photochemical reactions of compounds 1 and 2 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, R_0 , R_t , R_∞ refer to the UV–vis diffuse reflectance intensity values (405 nm for compound 1, 400 nm for compound 2) 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.





Fig. S2 FT-IR spectra of compounds 1 (a) and 2 (b) confirm the existence of NO_3^- anion or SO_4^{2-} anion in the structure, respectively.



Fig. S3 Energy-dispersive X-ray spectroscopy analysis of compounds 1 (a), 2 (b) confirms the existence of elements Br or S in the structure, respectively.



Fig. S4 ORTEP plot showing the crystallographically asymmetric unit in the compounds 1 (a), 2 (b); thermal ellipsoids are given at the 50% probability level. The guest solvent molecules and dissociative anions in compound 1 are highly disordered which cannot be located based on the difference-Fourier maps



Fig. S5 (a) The 2-fold interpenetrated 3D cationic framework in compound **1**. (b) The 3D architecture in compound **2**. The void space between the 2 D cationic layers (green) are occupied by lattice water molecules and sulphate anions. All hydrogen atoms are omitted for clarity.



Fig. S6 PXRD patterns of compounds 1 (a) and 2 (b).



Fig. S7 TGA curves of compounds 1 (a) and 2 (b).



Fig. S8 ESR spectra of compounds **1** (a) and **2** (b) before (black line) and after irradiation (red line). The small ESR signal can be observed for the virgin samples due to ambient light-induced generation of radicals.



Fig. S9 XPS core-level spectra of Zn 2p (a), C 1s (b) of compound 1 before and after irradiation.





Fig. S10 XPS core-level spectra of Zn 2p (a), C 1s (b), S 2p (c), O 1s (d) and N 1s (e&f) of compound **2** before and after irradiation. After irradiation for one hour, the core-level spectra of Zn 2p, C 1s and S 2p do not change almost, while, the core-level spectrum of O1s shifts toward a higher binding energy position. As for the core-level spectrum of N 1s, before irradiation, the N 1s core-level spectrum can be fitted to two peaks at 399.6 eV and 401.3 eV, corresponding to pyridine nitrogen atom, positively charged nitrogen atom, respectively. After irradiation, the peak of positively charged nitrogen atom at 401.4eV becomes weak and a new signal at 398.6 eV appears which corresponds to the nitrogen atom of pyridyl radical. These spectral changes indicate that the O atom is electron donor while the N atom is electron acceptor.



Fig. S11 The distance and orientation between the donor and acceptor in compound 1 (a) and compound 2 (b).



Fig. S12 The dihedral angles between the adjacent pyridine rings of DBCbpy⁻ ligands in compounds 1 (a) and 2 (b).



Fig. S13 The UV-vis diffuse reflectance spectra of compounds 1, 2 in the initial state after being normalized.



Fig. S14 (a) The luminescence emission spectra of compound **2** ($\lambda_{ex} = 450 \text{ nm}$) (black) and DBCbpy⁻ ligand in solution ($\lambda_{ex} = 402 \text{ nm}$) (red). (b) The excitation spectrum of DBCbpy⁻ ligand in solution monitored at 543 nm.



Fig. S15 The close-packing arrangement of the pyridine ring and the benzene ring of adjacent DBCbpyligands in compounds 1(a) and 2 (b).



Fig. S16 The UV-vis diffuse reflectance spectra of compound 2 after irradiation with excitation light ($\lambda = 450$ nm) at 0, 5, 10, 15, 20, 25 and 30 min.



Fig. S17 The optical band gap energy of compound 2.