Photochromic and photocontrolled luminescent rare-earth D-A

hybrid crystals based on rigid viologen acceptors

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Fig. S1. The intermolecular interactions in 3D framework diagrams in 2. For clarity, a part of C H O N atoms are omitted.



Fig. S2. (a) View of the asymmetric unit of 3. (b) the 1D chain of 3 viewed along the a-axis direction.



Fig. S3. PXRD patterns of 1 (a), 2 (b) and 3 (c) before and after light irradiation room-temperature.



Fig. S4. Infrared spectra of 1 (a), 2 (b) and 3 (c) before and after light irradiation room-temperature.



Fig. S5. ESR spectra of 1 (a), 2 (b) and 3 (c) before and after light irradiation room-temperature.



Fig. S6. Luminescence decays of 1 (a) and 2 (b) under ambient conditions.



Fig. S7. The luminescence emission of 1 (a), 2 (b) and 3 (c) the original sample and the restored sample.



Fig. S8. The TG curve of 1 (a), 2 (b) and 3 (c) under N_2 atmosphere with a heating rate of 10 °C/min.

Photoluminescence spectra of 2 dispersed in various pure solvents.

The luminescence spectra of **2** have been studied after dispersing it in different organic solvents. Before luminescence study, 2.0 mg of **2** was finely ground and suspended in 3 mL of various solvents Acetonitrile (MeCN),

Tetrahydrofuran (THF), Ethanol (EtOH), Acetone, Dichloromethane (DCM) and sonicated for 30 min. Surprisingly, the luminescent intensity of **2** in MeCN solvent was obviously higher than the other solvents. The PXRD patterns and IR spectra of samples after immersion in above mentioned solvents are agreed with the original sample (Fig. S9), suggesting that the structure of hybrid compound 2 is stable in these organic solvents.



Fig. S9. Photoluminescence spectra of 2 dispersed in various pure solvents.



Fig. S10. PXRD patterns (a) and IR (b) of 2 soaking in in various pure solvents for 12 h.





Fig. S11. PXRD patterns (a) and IR (b) of 2 soaking in MeCN solution (1mM) added benzene series molecules for

12 h.



Fig. S12. The Stern-Volmer plot of quenched by 4-nitroaniline in MeCN. The red line corresponds to a linear

fitting result.



Fig. S13. The UV-vis absorption spectra of benzene series molecules and the excitation spectrum of 2.



Fig. S14. XPS core level spectra of Co atom in complex 3 and K₃Co(CN)₆.



Fig. S15. The luminescence emission of ligand (cbp.Cl) and $K_3Co(CN)_6$.



the weaker broad emission component centered at ca. 550 nm, which can be assigned to intraligand charge transition of conjugated ligand cbp; weak red emission originating from the d-d transition of $[Co^{III}(CN)_6]^{3-}$ ions, resulting in a broad band centered at around 625 nm.

Fig. S16. Room temperature solid-state vis-NIR emission spectra of hybrid compound 3 under various excitation wavelengths.