Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Solvent- and anion-controlled photochromism of viologen-based metal-organic hybrid materials

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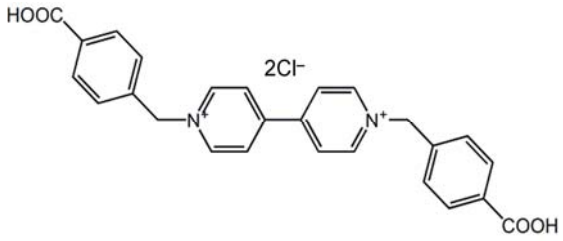
Additional characterization data and figures



Sheme S1. Carboxybenzyl-substituted viologen derivative $H_2BpybcCl_2$.

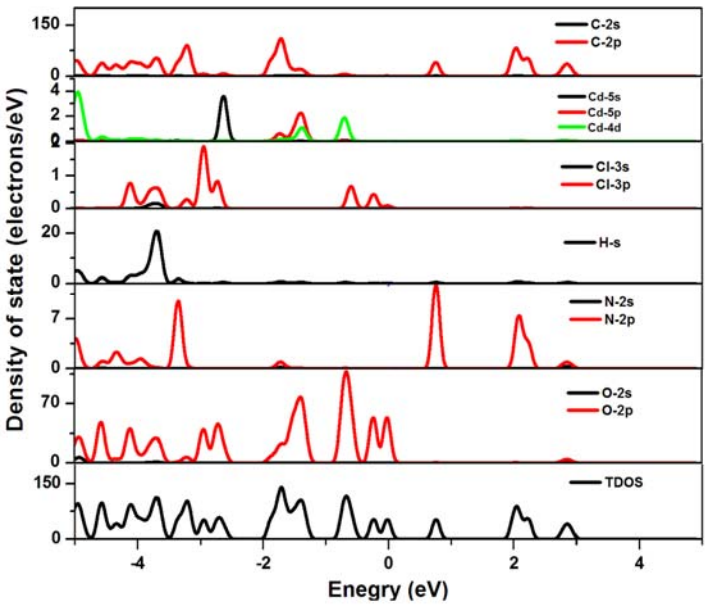


Fig. S1 Total and partial density of states for **1** (The Fermi level is set at 0 eV).

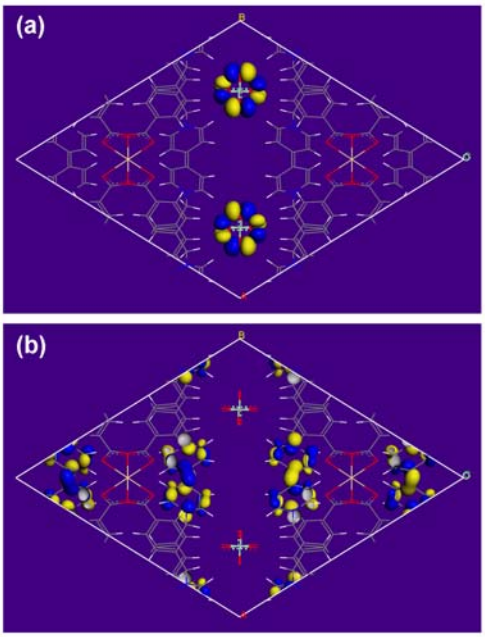


Fig. S2 Electron-density distribution of the (a) highest occupied (HOMO) and (b) lowest unoccupied frontier orbitals (LUMO) for **1**.

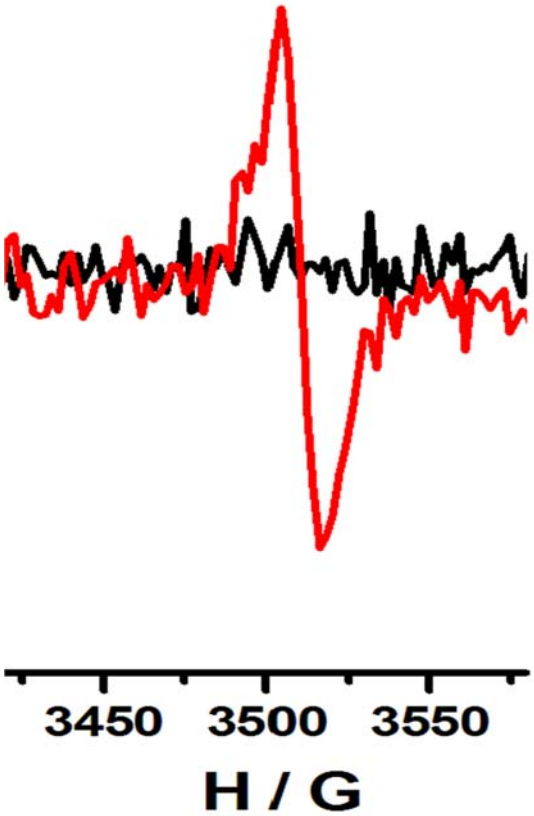


Fig. S3 The ESR spectra of **1** before (dark) and after (red) heat-treatment (g = 2.0027).

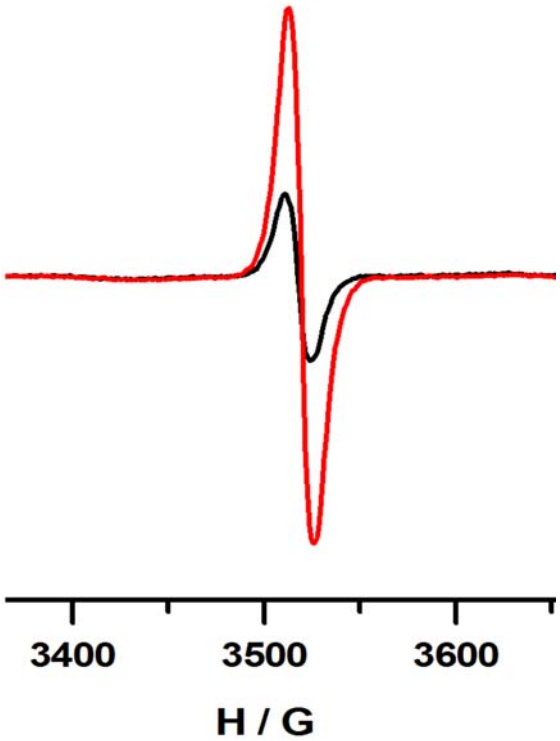


Fig. S4 The ESR spectra of **4** before (dark) and after (red) photoirradiation.

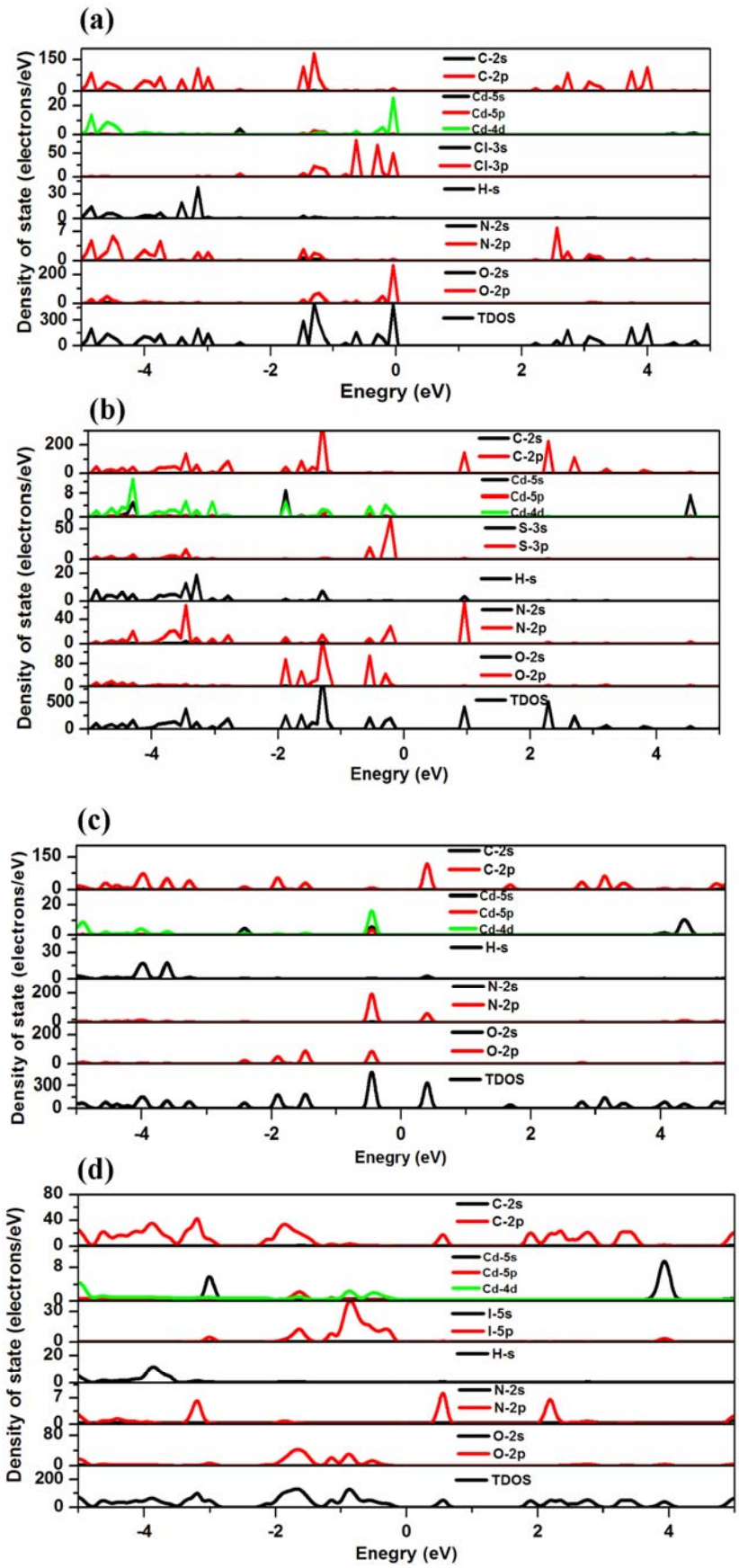


Fig. S5 Total and partial density of states for **2** (a), **3** (b), **4** (c), **5** (d). (The Fermi level is set at 0 eV).

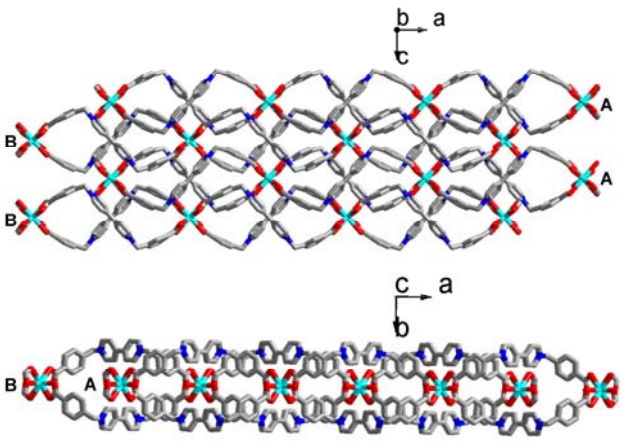


Fig. S6 The view from two sides of the 2D supramolecular layer formed by alternative double helical chains in **1**.

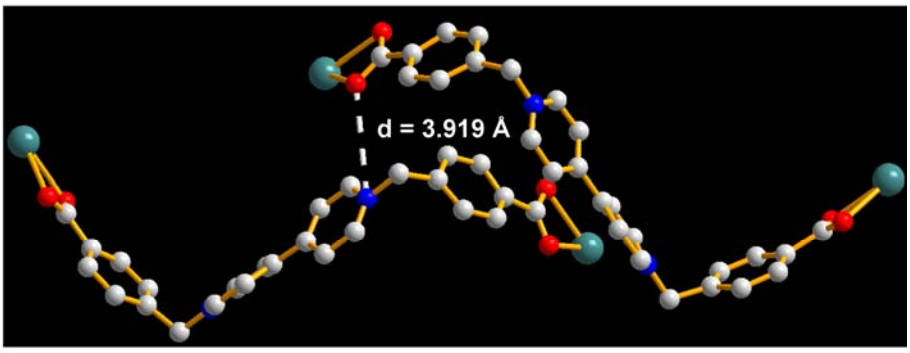


Fig. S7 The distance and orientation between the $O^{-}\cdots N^{+}$ ions in **1**. All hydrogen atoms are omitted for clarity (C grey; N blue; O red; Cd green).

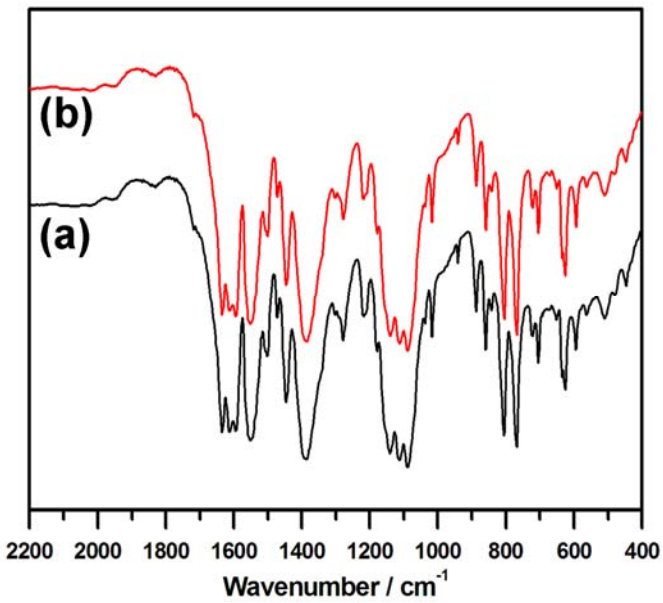


Fig. S8 IR spectra of **1** before (black) and after (red) heat-treatment. The spectra show no detectable change in band positions after heat-treatment.

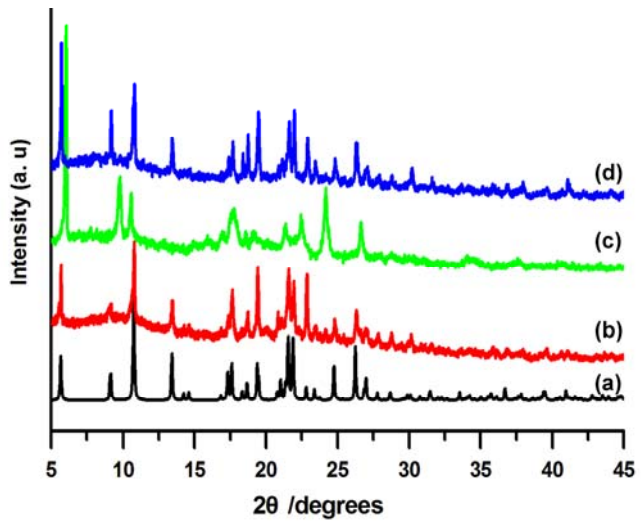


Fig. S9 The PXRD patterns of **1:** (a) stimulated, (b) as synthesized, (c) after heat-treated, (d) after standing in humid air overnight.

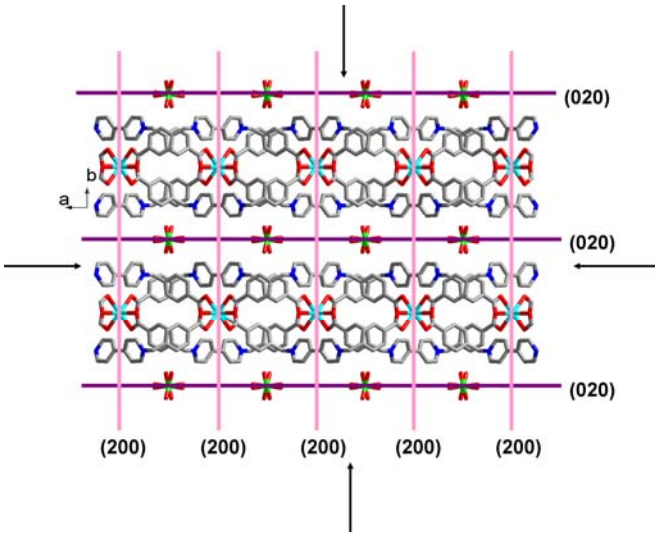


Fig. S10 The shrink corresponding to (020) and (200) crystal faces of compound **1** after heat-treatment.

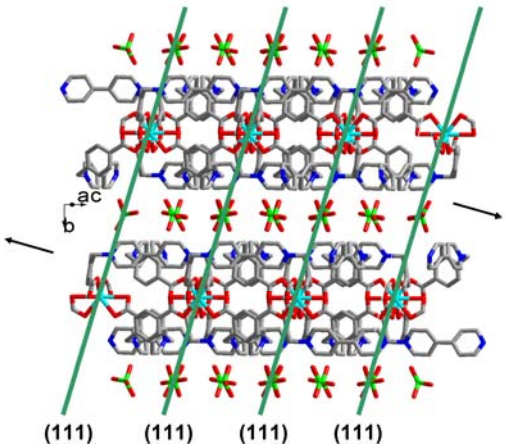


Fig. S11 The small expansion corresponding to (111) crystal faces of compound **1** after heat-treatment.

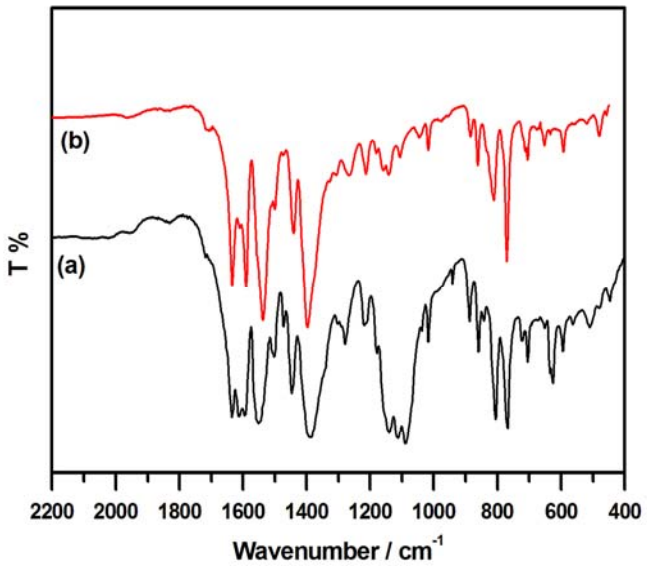


Fig. S12 The IR spectra recorded for the transformation from **1** to **2**, (a) as synthesized sample **1**, (b) after immersing **1** in 0.2 M NaCl solution for several hours. The disappearance of strong vibration bands of the ClO_4^- ion between 1080-1150 cm^{-1} demonstrates the occurrence of anion exchange process.

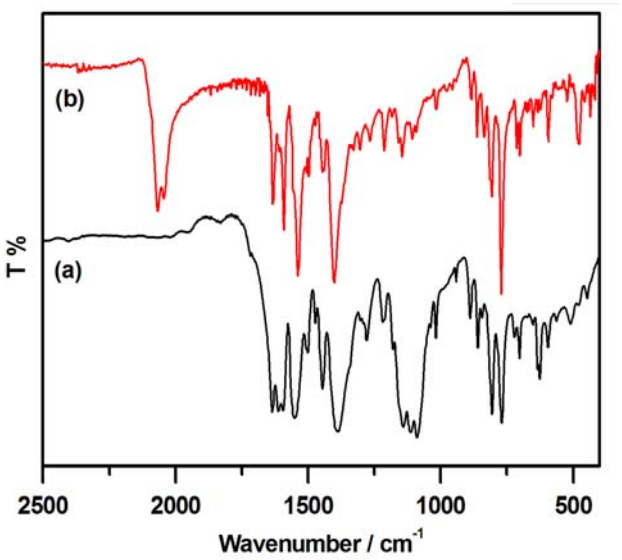


Fig. S13 The IR spectra recorded for the transformation from **1** to **3**, (a) as synthesized sample **1**, (b) after immersing **1** in 0.2 M KSCN solution for several hours. The appearance of new bands at 2069 and 2044 cm^{-1} attributed to the asymmetric stretching vibrations of the SCN^- ions is consistent with the single crystal structure analysis.

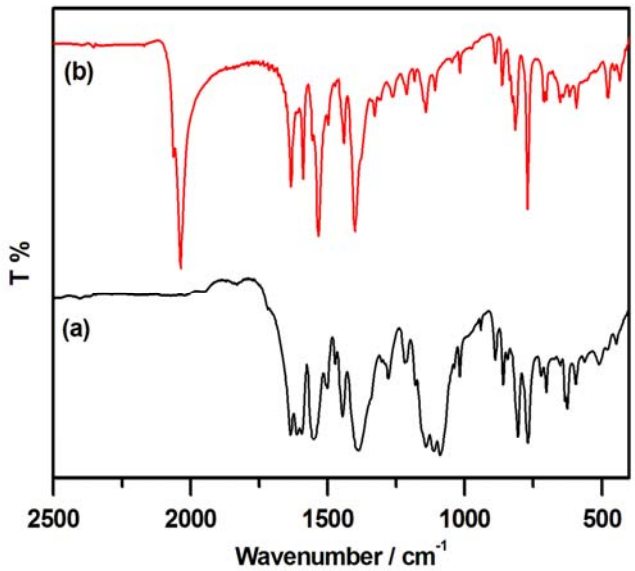


Fig. S14 The IR spectra recorded for the transformation from **1** to **4**, (a) as synthesized sample **1**, (b) after immersing **1** in 0.2 M NaN_3 solution for several hours. The appearance of new bands at 2063 and 2037 cm^{-1} attributed to the asymmetric stretching vibrations of the N_3^- ions is consistent with the single crystal structure analysis.

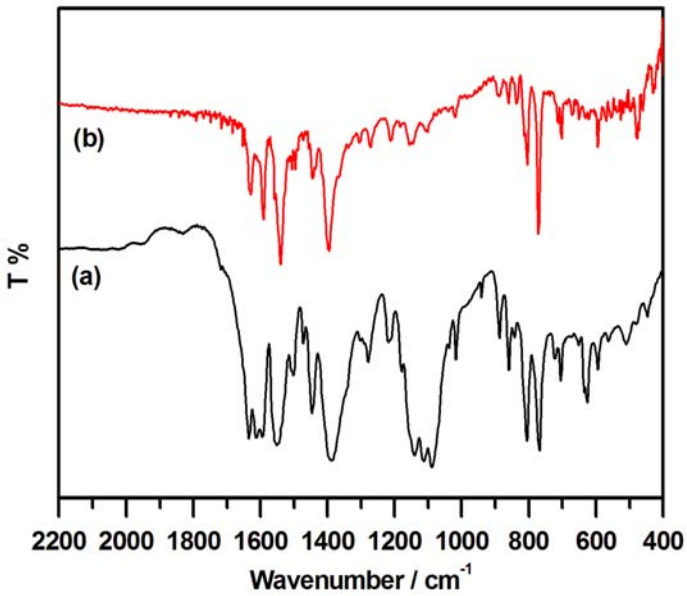


Fig. S15 The IR spectra recorded for the transformation from **1** to **5**, (a) as synthesized sample **1**, (b) after immersing **1** in 0.2 M KI solution for several hours. The disappearance of strong vibration bands of the ClO_4^- ion between 1080-1150 cm^{-1} demonstrates the occurrence of anion exchange process

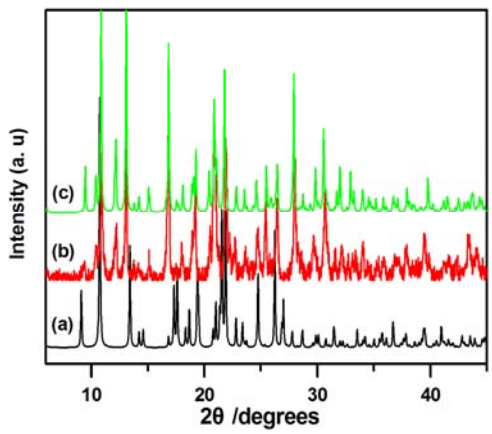


Fig. S16 PXRD recorded for the transformation from bulk sample **1** to **2**, (a) calculated pattern from single crystal **1,** (b) after immersing **1** in 0.2 M NaCl solution for several hours, (c) calculated pattern from single crystal **2**.

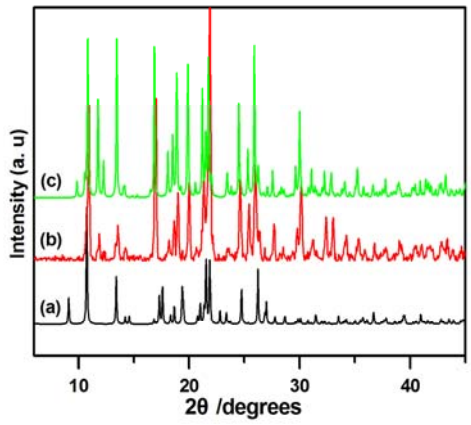


Fig. S17 PXRD recorded for the transformation from bulk sample **1** to **3**, (a) calculated pattern from single crystal **1,** (b) after immersing **1** in 0.2 M KSCN solution for several hours, (c) calculated pattern from single crystal **3**.

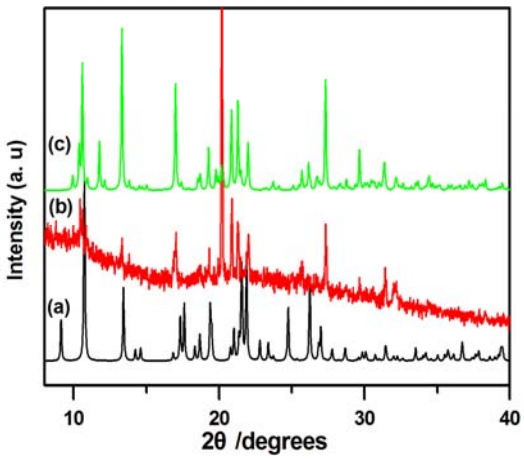


Fig. S18 PXRD recorded for the transformation from bulk sample **1** to **4**, (a) calculated pattern from single crystal **1,** (b) after immersing **1** in 0.2 M NaN_3 solution for several hours, (c) calculated pattern from single crystal **4**.

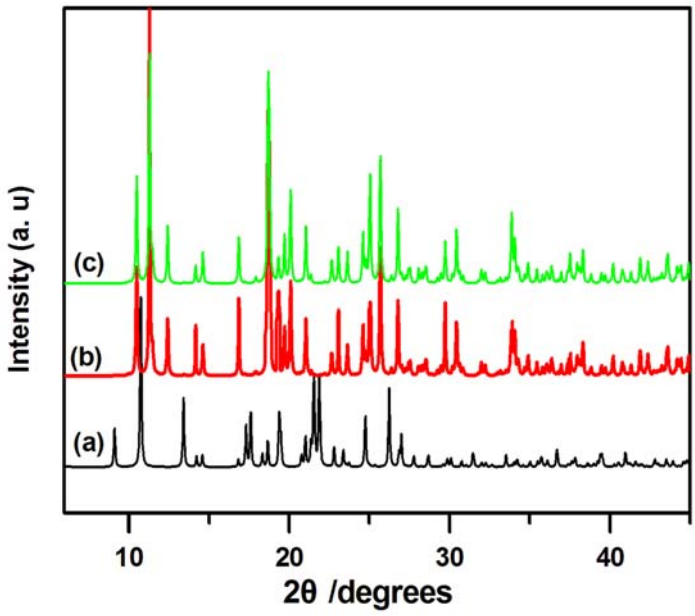


Fig. S19 PXRD recorded for the transformation from bulk sample **1** to **5**, (a) calculated pattern from single crystal **1,** (b) after immersing **1** in 0.2 M KI solution for several hours, (c) calculated pattern from single crystal **5**.

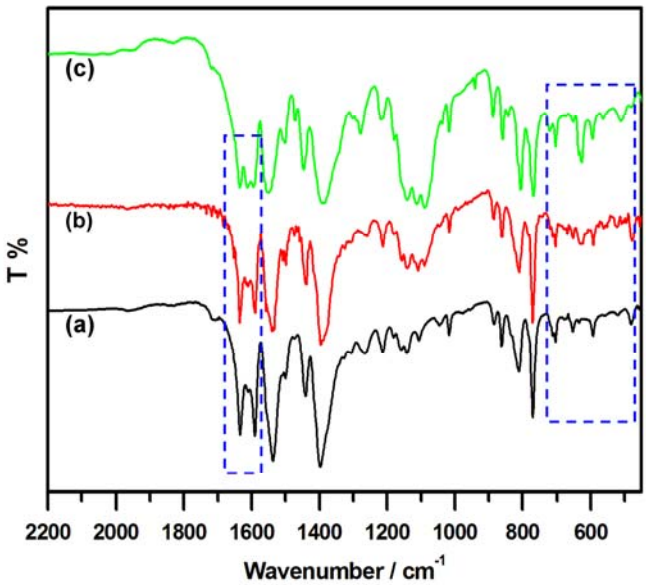


Fig. S20 The IR spectra recorded for the irreversible transformation from **2** to **1**, (a) as synthesized sample **2**, (b) sample **2′:** after immersing **2** in 0.2 M $NaClO_4$ solution for a week, (c) as synthesized sample **1**. The relative vibration intensity of the ClO_4^- ions in **2′** is weaker than that of **1**, and most of vibrations bands between 1580-1640 cm^{-1} and in fingerprint region are still quite consistent with that **2**. Moreover, **2′** show a photochromic property, therefore we speculate that **2′** is compositionally more similar to **2**, the weak band corresponding to the vibration of ClO_4^- ions observed in **2′** may origin from the adsorption of the ClO_4^- ions on the surface of materials.

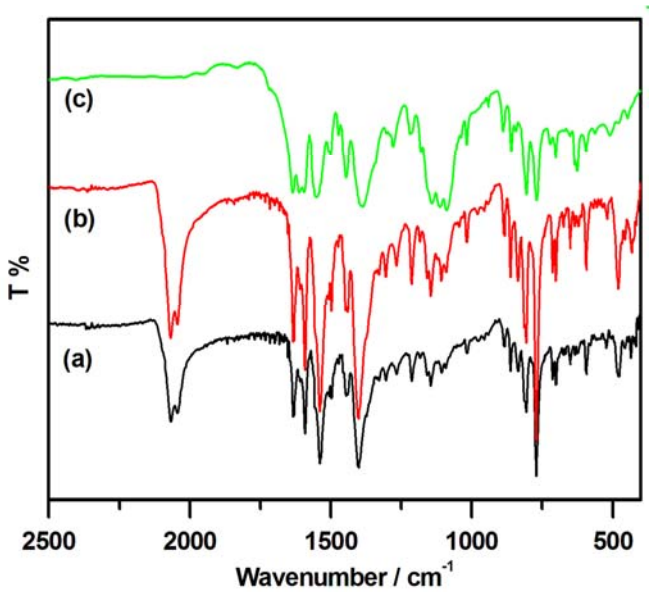


Fig. S21 The IR spectra recorded for the irreversible transformation from **3** to **1**, (a) as synthesized sample **3**, (b) after immersing **3** in 0.2 M $NaClO_4$ solution for a week. The almost unchanged spectra demonstrate the strong coordination propensity of terminated SCN^- anion, (c) as synthesized sample **1**.

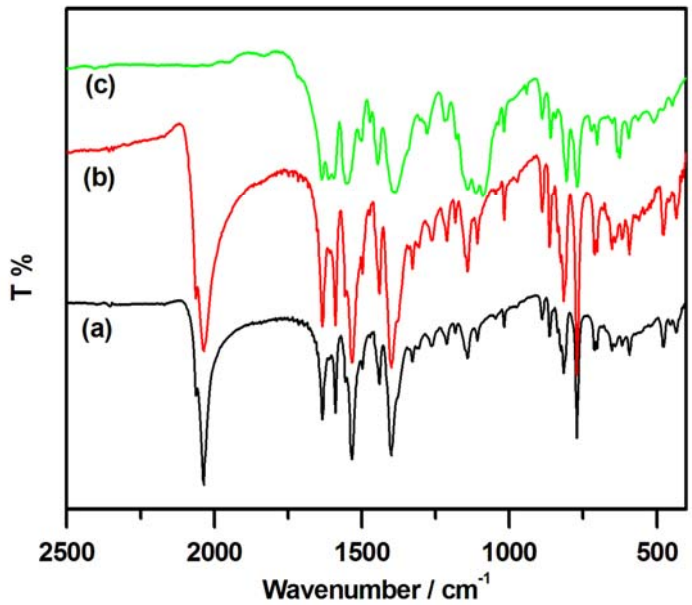


Fig. S22. The IR spectra recorded for the irreversible transformation from **4** to **1**, (a) as synthesized sample **4**, (b) after immersing **4** in 0.2 M $NaClO_4$ solution for a week, the almost unchanged spectra demonstrate the strong coordination propensity of terminated N_3^- anion, (c) as synthesized sample **1**.

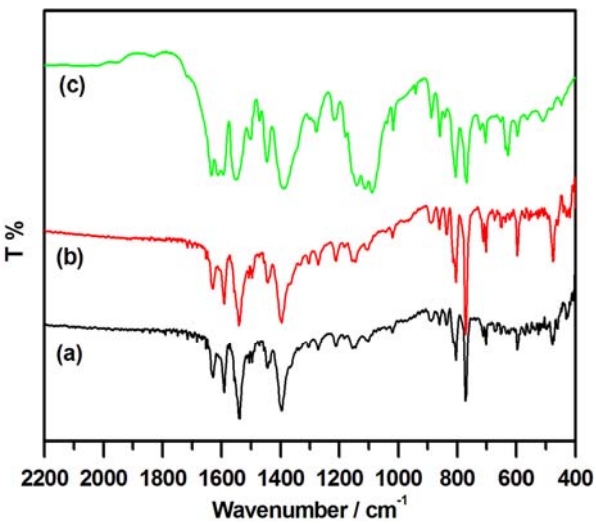


Fig. S23. The IR spectra recorded for the irreversible transformation from **5** to **1**, (a) as synthesized sample **5**, (b) after immersing **5** in 0.2 M $NaClO_4$ solution for a week, the almost unchanged spectra suggest that no structural transformation occurs. (c) as synthesized sample **1**.

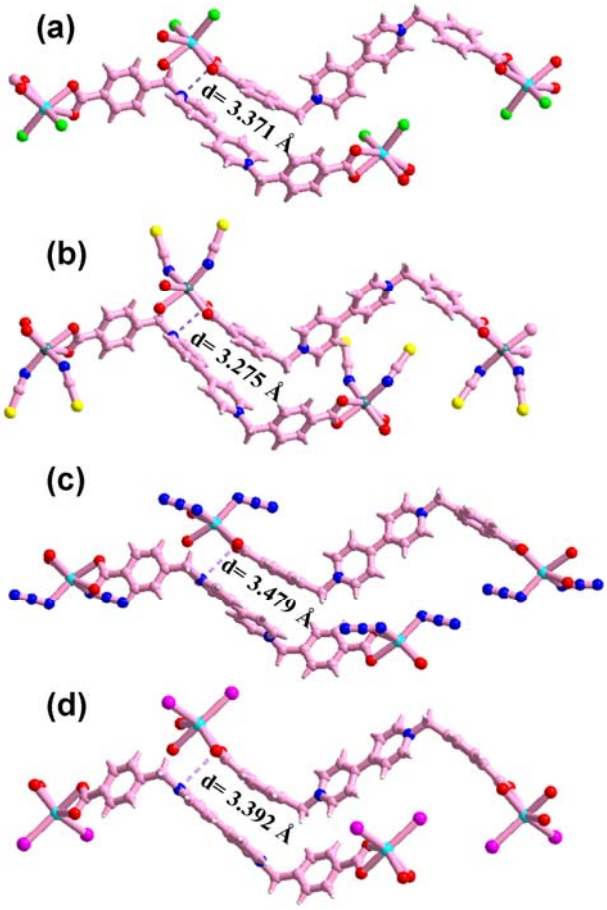


Fig. S24. The nearest distance between the $O^{-}\cdots N^{+}$ ions in **2** (a), **3** (b), **4** (c) and **5** (d). (C rose; N blue; O red; Cd turquoise; Cl bright green; S yellow; I pink; H gray).