

Water-stable photochromic MOFs with regulable iodine sorption and efficient removal of dichromate

Jian-Jun Liu,^{*a} Jia-Jia Fu,^a Gui-Jun Li,^a Teng Liu,^a Shu-Biao Xia,^{*a} Fei-Xiang Cheng^{*a}

^aCollege of Chemistry and Environmental Science, Qujing Normal University, Qujing 655011, China. E-mail: jjliu302@163.com (J.-J. Liu); xiashubiao401@163.com (S.-B. Xia); chengfx2019@163.com (F.-X Cheng)

Procedure for anion-exchange

As-synthesized **1-NO₃** (335 mg) was dried 60 °C in 2 hours, divided into 5 equal portions, then immersed in an aqueous solution (10 mL) of K₂Cr₂O₇ at the concentration (2 mM), and the mixture keep static at room temperature for 200 min. The anion exchange process was monitored by liquid UV-vis spectroscopy based on typical absorption of Cr₂O₇²⁻ at 258 nm. 3 mL aqueous K₂Cr₂O₇ solution was pipetted at

different time interval from different vials, and was measured the UV-vis adsorption intensity. After exchange, the solid samples were centrifuged, rinsed with water and dried in the air, namely **1-Cr₂O₇**. The same processes for **1-NO₃** were carried out at 4 mM, 6 mM aqueous solution (10 mL) of K₂Cr₂O₇. After anion exchange, the crystals were filtered, rinsed with deionized water and dried in the air. These samples were used for PXRD, IR, EDX, and ICP measurements.

Release experiment

The release experiment was carried out right after the completion of an ion-exchange process of Cr₂O₇²⁻ on **1-NO₃** at the 6 mM. The **1-Cr₂O₇** washed with water and MeOH before release operation. The sample of **1-Cr₂O₇** (67 mg) was immersed in 10 mL aqueous solution containing 287 mg KNO₃ (100 fold molar ratio of that of Cr₂O₇²⁻) at room temperature. The resulting mixture was monitored by UV-Vis spectroscopy.

Anion Selectivity Studies

As-synthesized sample of **1-NO₃** (67 mg) was immersed in an aqueous solution (10 mL) of K₂Cr₂O₇ (2 mM), and then KNO₃, KCl, KBr or KClO₄ (2 mM or 10 mM) was added. After 24 h, the solutions were monitored by UV-Vis absorption spectroscopy at room temperature.

Capture and release of iodine experiments

At room temperature, 67 mg of **1-NO₃** or photoirradiated **1-NO₃** were respectively added to cyclohexane solution dissolved with iodine (10 mL, 0.5 mM). UV-Vis absorption spectroscopy was applied to monitor the kinetics of iodine adsorption by the materials. The release experiment was carried out right after the completion of iodine adsorption process on **1-NO₃** at the 2 mM of iodine solution. At room temperature, 67 mg of **1-NO₃** or photoirradiated **1-NO₃** was put into an iodine-dissolved cyclohexane solution (10 mL, 2 mM) for 24 h to prepare the iodine-loaded sample (**1-NO₃-I₂**). Then 20 mg of **1-NO₃-I₂** was soaked in ethanol (10 mL). The residual concentration of iodine solution was measured by an UV-Vis spectrometer. These samples **1-NO₃-I₂** and photoirradiated **1-NO₃-I₂** were also used for elemental analyses and XPS measurements.

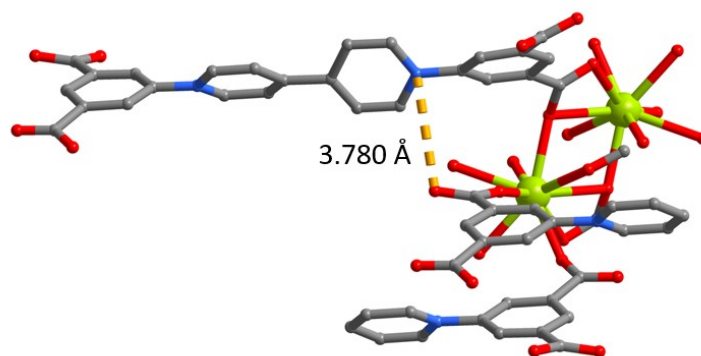


Fig. S1. Distance between the carboxylate O atom of the bdpbpy²⁻ ligand and adjacent bipyridinium in 1-NO₃

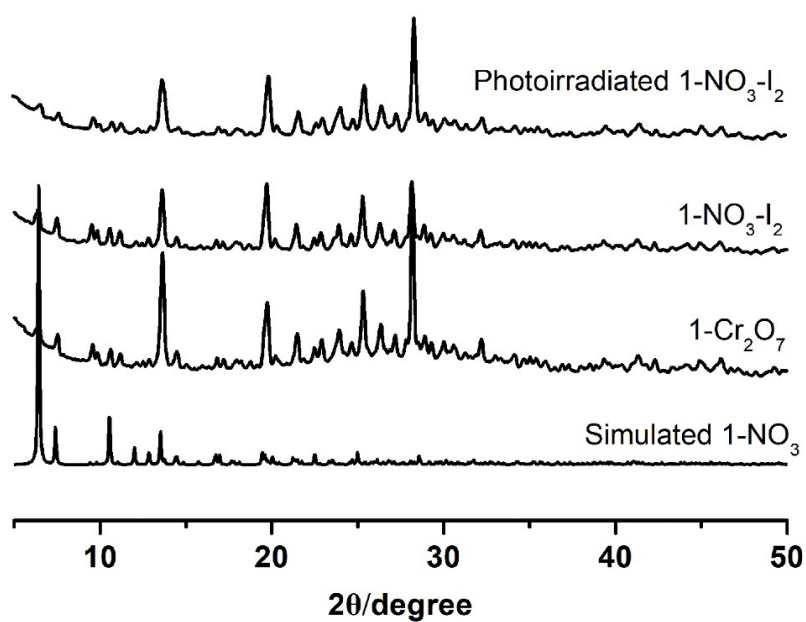


Fig. S2. The PXRD patterns of 1-NO₃ after being treated in different conditions.

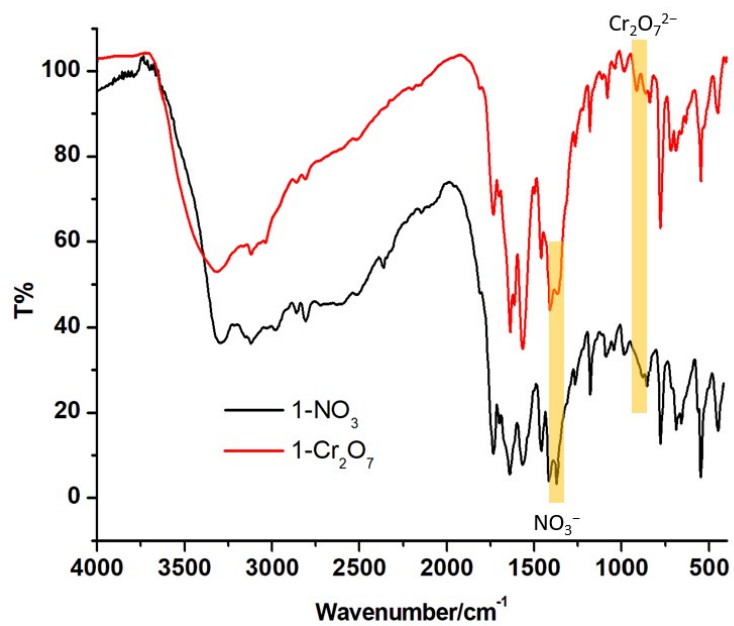


Fig. S3. IR spectra of 1-NO₃ and 1-Cr₂O₇.

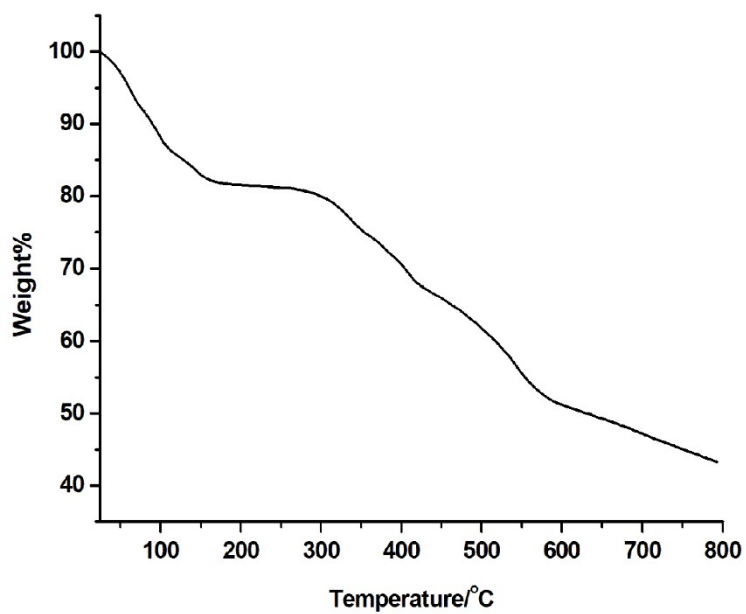


Fig. S4. TGA curve of 1-NO₃.

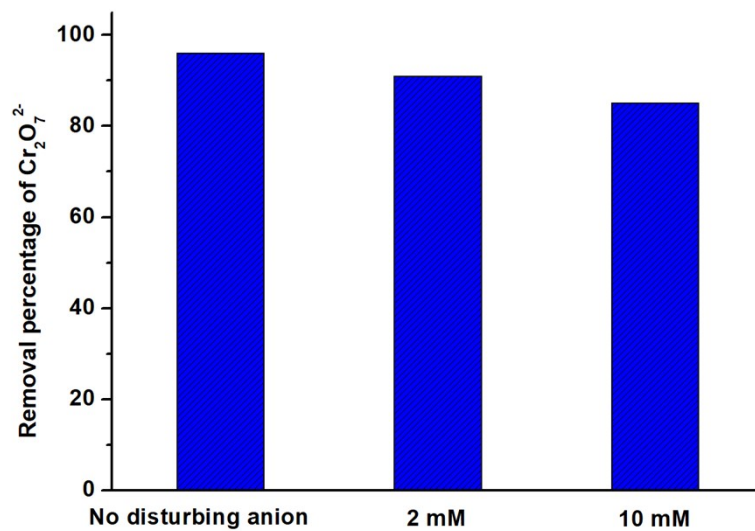


Fig. S5. Effects of the competing anions on the removal of $\text{Cr}_2\text{O}_7^{2-}$ by $\mathbf{1-NO}_3$. The initial concentration of $\text{Cr}_2\text{O}_7^{2-}$ is 2 mM. The mixed solution containing of NO_3^- , Cl^- , Br^- and ClO_4^- . The concentration of each anion is 0 mM, 2 mM, and 10 mM.

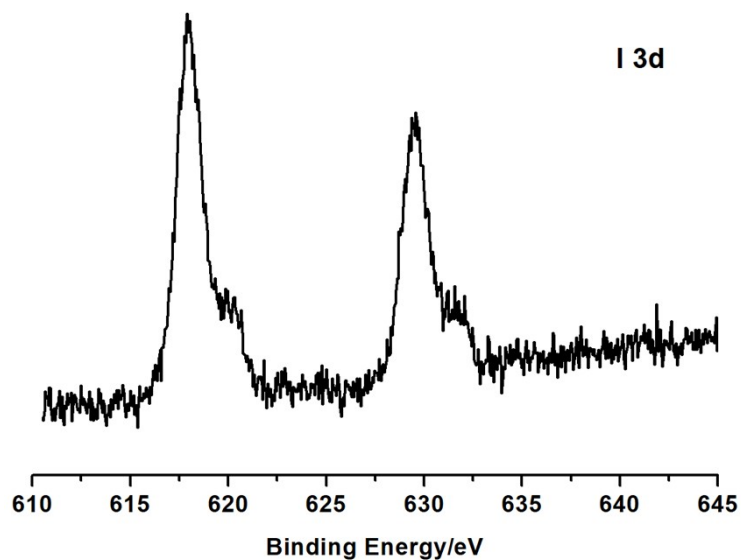


Fig. S6. XPS core-level spectra of I 3d of $\mathbf{1-NO}_3\text{-I}_2$.

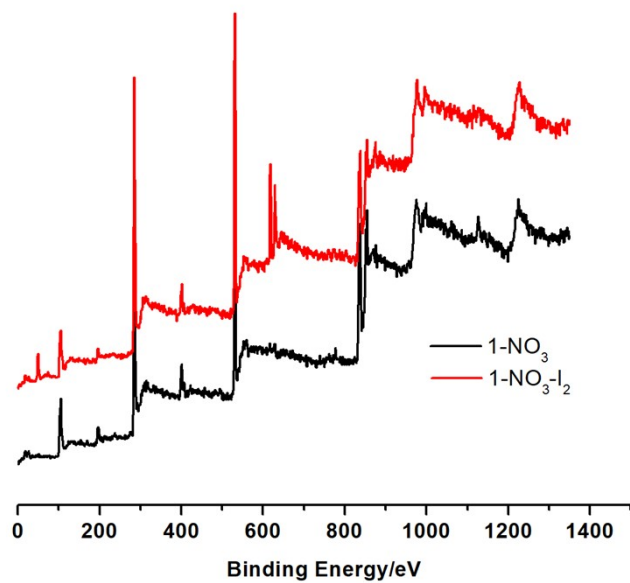


Fig. S7. XPS for 1-NO_3 and $1\text{-NO}_3\text{-I}_2$.

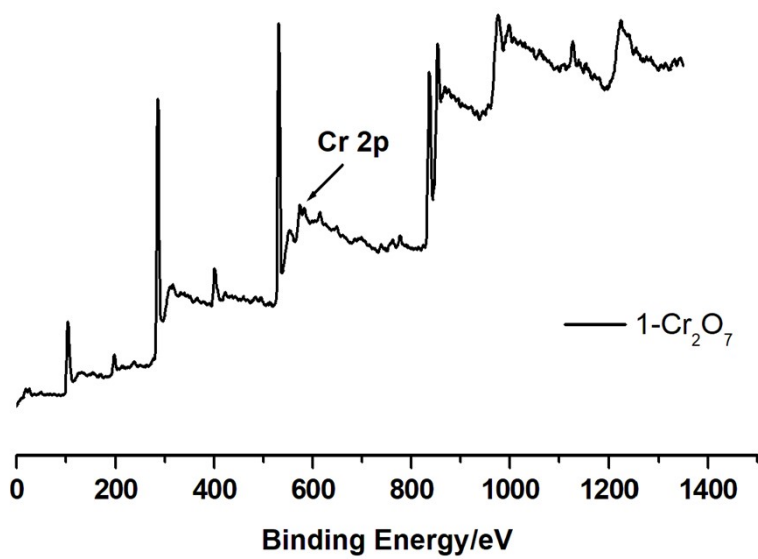


Fig. S8. XPS for $1\text{-Cr}_2\text{O}_7$.

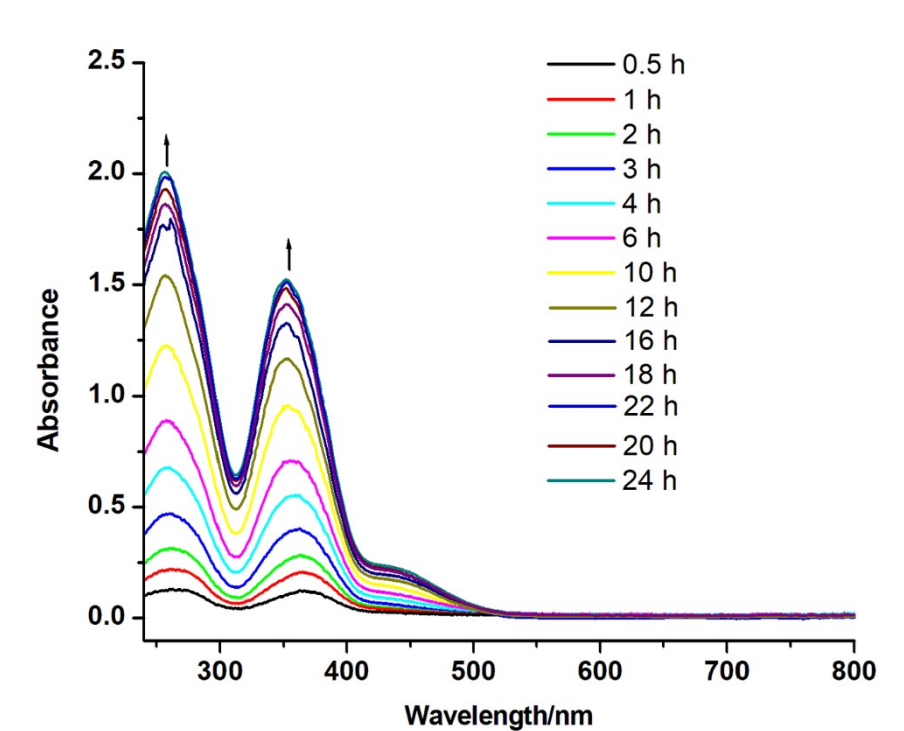


Fig. S9. The UV-vis absorbance spectra of $\text{Cr}_2\text{O}_7^{2-}$ releasing process (100 fold molar ratio of that of $\text{Cr}_2\text{O}_7^{2-}$).

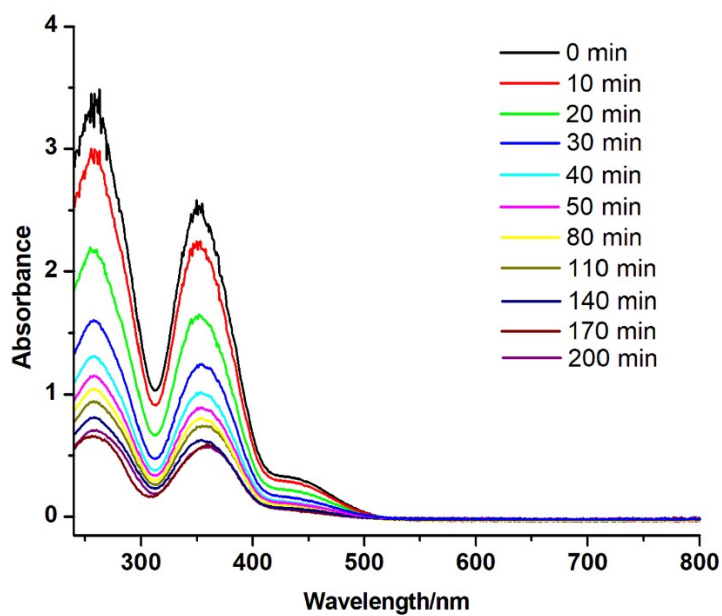


Fig. S10. Time-dependent UV-Vis absorption spectra of the $\text{Cr}_2\text{O}_7^{2-}$ aqueous (4 mM) in the presence of 1- NO_3 .

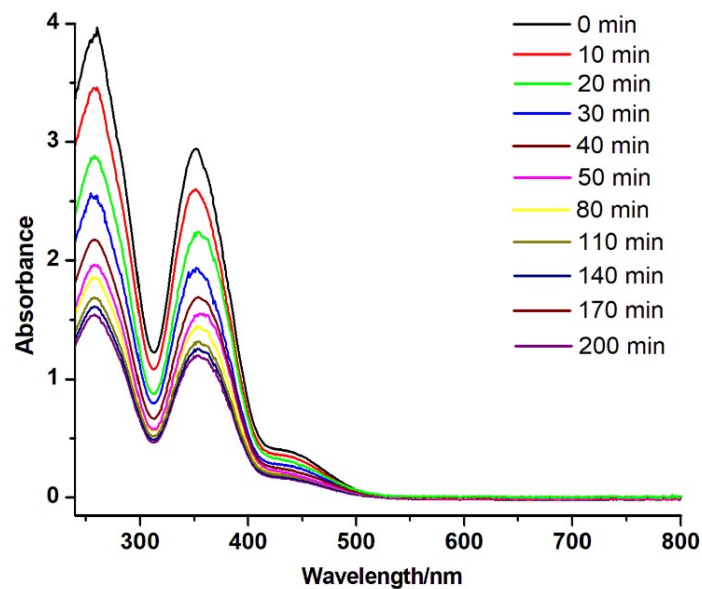


Fig. S11. Time-dependent UV-Vis absorption spectra of the $\text{Cr}_2\text{O}_7^{2-}$ aqueous (6 mM) in the presence of **1-NO₃**.

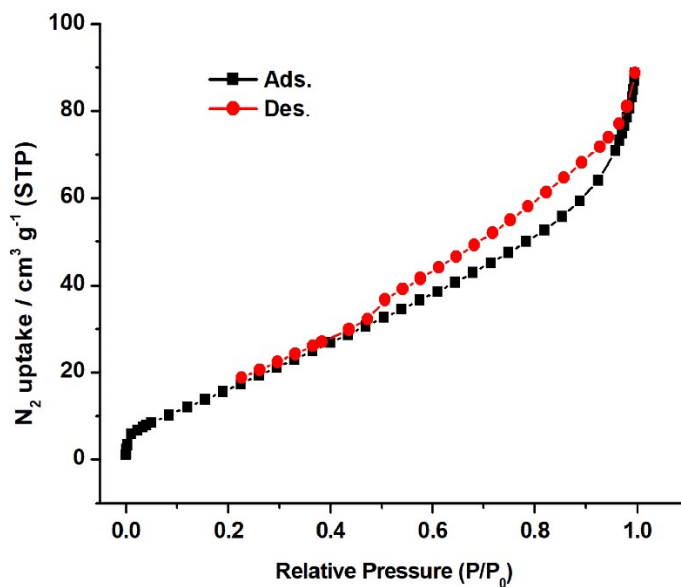


Fig. S12. Nitrogen sorption isotherm for **1-NO₃** at 77 K

Table S1. Elemental analyses (ICP) of **1-Cr₂O₇** (Soak in 6 mM dichromate solution for 200 minutes).

Sample	Wt% Ce	Wt% Cr	Molar ratio of Ce:Cr
1-Cr₂O₇	80.9	19.1	1.92 : 1

Table S2. Elemental analyses of **1-NO₃**, **1-NO₃-I₂**, and Photoirradiated **1-NO₃-I₂**.

Sample	Calculated formula	Experiment (%)		
		C	H	N
1-NO₃	$C_{26}H_{24}LaN_3O_{18}$	38.69	3.06	5.28
1-NO₃-I₂	$C_{26}H_{24}LaN_3O_{18} \cdot 0.078(I_2)$	37.83	2.91	5.09
Photoirradiated 1-NO₃-I₂	$C_{26}H_{24}LaN_3O_{18} \cdot 0.045(I_2)$	38.22	2.93	5.14