

A Zwitterionic Ligand-Based Water Stable Metal-Organic Framework Showing Photochromic and Cr(VI) Removal Properties

Chenghui Zhang,^{a,b} Huaizhong Shi,^a Yan Yan,^a Libo Sun,^c Yu Ye,^a Yizhong Lu,^b Zhiqiang Liang^{a*} and Jiyang Li^{a*}

^a State Key Lab of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: lijyang@jlu.edu.cn, liangzq@jlu.edu.cn.

^b School of Materials Science and Engineering, University of Jinan, Jinan 250022, P. R. China.

^c School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, 637459, Singapore.

Table S1. Crystal Data and Structure Refinement for **1**.

Empirical formula	$C_{36}H_{23}In_3N_4O_{12}$
Formula weight	1048.04
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R-3m
Unit cell dimensions	$a = 15.2848(7)$ Å $\alpha = 90^\circ$ $b = 15.2848(7)$ Å $\beta = 90^\circ$ $c = 56.084(3)$ Å $\gamma = 120^\circ$
Volume	11347.2(12) Å ³
Z	9
Density (calculated)	1.380 mg/m ³
Absorption coefficient	1.411 mm ⁻¹
F(000)	4590
Crystal size	0.120 × 0.110 × 0.080 mm ³
Theta range for data collection	2.179 to 28.298°.
Index ranges	-20 ≤ h ≤ 20, -20 ≤ k ≤ 14, -74 ≤ l ≤ 74
Reflections collected	37905
Independent reflections	3459 [$R_{(int)} = 0.0347$]
Completeness to theta = 25.242°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.0962 and 0.0682
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3459 / 198 / 186
Goodness-of-fit on F ²	1.136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0275$, $wR_2 = 0.0793$
R indices (all data)	$R_1 = 0.0285$, $wR_2 = 0.0801$
Extinction coefficient	n/a
Largest diff. peak and hole	0.533 and -0.717 e.Å ⁻³

Note for the final formula of compound **1**: Because bromine atoms couldn't be located by single crystal X-ray data and the framework is neutral, while EDX mapping image and XPS analysis show that there exist bromine atoms in this material, we speculate that bromine is not in the structure of **1**, but might be simply adsorbed on crystal surface of the material containing positively charged pyridinium nitrogen from linkers by electrostatic interaction. Besides, the solvents are insignificant for our research works. So the final formula of compound **1** is identified as $[\text{In}_3(\text{ipbp})_2(\mu_2\text{-OH})(\mu_2\text{-O})_3]$ based on crystallographic data like previously reports (*Chem. Sci.*, 2019, **10**, 1186; *J. Am. Chem. Soc.*, 2019, **141**, 2900).

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

In(1)-O(3)	2.092(2)	In(2)-O(3)	2.084(3)
In(1)-O(4)#2	2.1007(9)	In(2)-O(1)#3	2.156(2)
In(1)-O(4)	2.1007(9)	In(2)-O(1)#5	2.156(2)
In(1)-O(2)#3	2.180(2)	In(2)-O(1)	2.156(2)
In(1)-O(2)	2.180(2)	In(2)-O(1)#4	2.156(2)
In(1)-N(1)	2.266(2)	O(3)-H(3M)	0.9356
In(2)-O(3)#4	2.084(3)		
O(2)-C(1)-O(1)	126.9(2)	O(4)-In(1)-O(2)	88.43(10)
O(2)-C(1)-C(2)	116.5(2)	O(2)#3-In(1)-O(2)	84.69(14)
O(1)-C(1)-C(2)	116.5(2)	O(3)-In(1)-N(1)	168.18(11)
C(3)-C(2)-C(4)	120.0(3)	O(4)#2-In(1)-N(1)	90.56(19)
C(3)-C(2)-C(1)	120.2(2)	O(4)-In(1)-N(1)	90.95(18)
C(4)-C(2)-C(1)	119.7(2)	O(2)#3-In(1)-N(1)	81.23(16)
C(2)#6-C(3)-C(2)	120.1(3)	O(2)-In(1)-N(1)	81.58(18)
C(2)#6-C(3)-H(3A)	119.9	O(3)#4-In(2)-O(3)	180.00(5)
C(2)-C(3)-H(3A)	120.0	O(3)#4-In(2)-O(1)#3	88.51(7)
C(5)-C(4)-C(2)	119.2(3)	O(3)-In(2)-O(1)#3	91.48(7)
C(5)-C(4)-H(4A)	120.5	O(3)#4-In(2)-O(1)#5	91.49(7)
C(2)-C(4)-H(4A)	120.4	O(3)-In(2)-O(1)#5	88.52(7)
C(4)#6-C(5)-C(4)	121.5(4)	O(1)#3-In(2)-O(1)#5	180.00(12)
C(4)#6-C(5)-N(2)#1	119.1(5)	O(3)#4-In(2)-O(1)	88.52(7)
C(4)-C(5)-N(2)#1	119.3(6)	O(3)-In(2)-O(1)	91.48(7)
O(3)-In(1)-O(4)#2	97.01(9)	O(1)#3-In(2)-O(1)	89.96(14)
O(3)-In(1)-O(4)	97.01(9)	O(1)#5-In(2)-O(1)	90.04(14)
O(4)#2-In(1)-O(4)	97.52(14)	O(3)#4-In(2)-O(1)#4	91.49(7)
O(3)-In(1)-O(2)#3	89.89(7)	O(3)-In(2)-O(1)#4	88.52(7)
O(4)#2-In(1)-O(2)#3	88.43(10)	O(1)#3-In(2)-O(1)#4	90.04(14)
O(4)-In(1)-O(2)#3	170.24(10)	O(1)#5-In(2)-O(1)#4	89.96(14)
O(3)-In(1)-O(2)	89.89(7)	O(1)-In(2)-O(1)#4	180.0
O(4)#2-In(1)-O(2)	170.24(9)		

Symmetry transformations used to generate equivalent atoms:

#1 $y+1/3, -x+y+2/3, -z+2/3$ #2 $-x+y, -x+1, z$ #3 $-y+1, -x+1, z$

#4 $-x+1, -y+1, -z+1$ #5 $y, x, -z+1$ #6 $-x+y+1, y, z$

Table S3. Comparison of Cr(VI) adsorption ability of compound **1** with selected MOFs.

Absorbent	Maximum Capacity (mg g ⁻¹)	References
UTSA-74	790	<i>Angew. Chem. Int. Ed.</i> 2017, 56 , 16376.
Zn-MOF-74	750	
MOR-2	193.7	<i>J. Mater. Chem. A</i> 2017, 5 , 14707.
MOR-2-HA	162.8	
TMU-30	145	<i>Inorg. Chem.</i> 2016, 55 , 5507.
MOR-1-HA	108.2-124.6	<i>Chem. Sci.</i> 2016, 7 , 2427.
MOR-1 (protonated)	123.6-114	
MOR-1 (nonprotonated)	117.4-139.5	
Cu-MOF	107	<i>Chem. Eur. J.</i> 2018, 24 , 2718.
ABT-2ClO ₄	102.9	<i>Angew. Chem. Int. Ed.</i> 2013, 52 , 13769.
Ag-MOF	99.6	<i>Chem. Commun.</i> 2017, 53 , 9206-9209.
1-SO ₄	79.9	<i>Angew. Chem. Int. Ed.</i> 2016, 55 , 7811.
1-NO ₃ -OH	74.5	<i>Dalton Trans.</i> , 2018, 47 , 9103.
1	74.4	This work
FIR-54	49.6	<i>Chem. Mater.</i> , 2015, 27 , 205.
JLU-MOF50	44.3	<i>J. Mater. Chem. A</i> , 2018, 6 , 6363.
NU-1000	36.1	<i>Inorg. Chem.</i> , 2017, 56 , 14178.
FIR-53	35.7	<i>Chem. Mater.</i> , 2015, 27 , 205.
SLUG-35	30.7	<i>Chem. Mater.</i> , 2013, 25 , 647.
1-ClO ₄	28.2	<i>Chem. Commun.</i> , 2012, 48 , 8231.
SLUG-21	26.9	<i>J. Am. Chem. Soc.</i> , 2011, 133 , 11110.

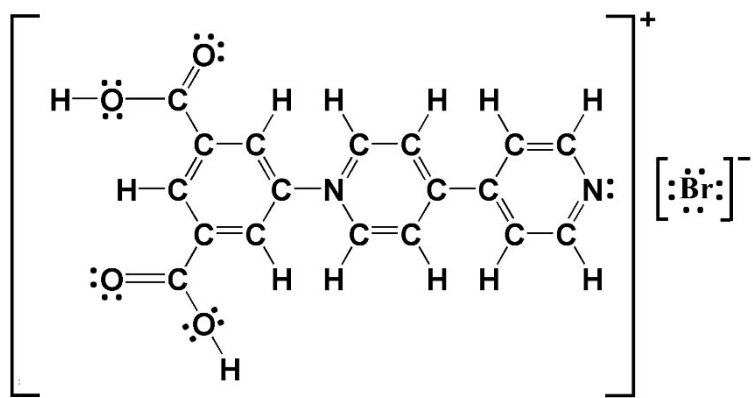


Fig. S1 Illustration of Lewis structure of $\text{H}_2(\text{ipbp})\text{Br}$ linker.

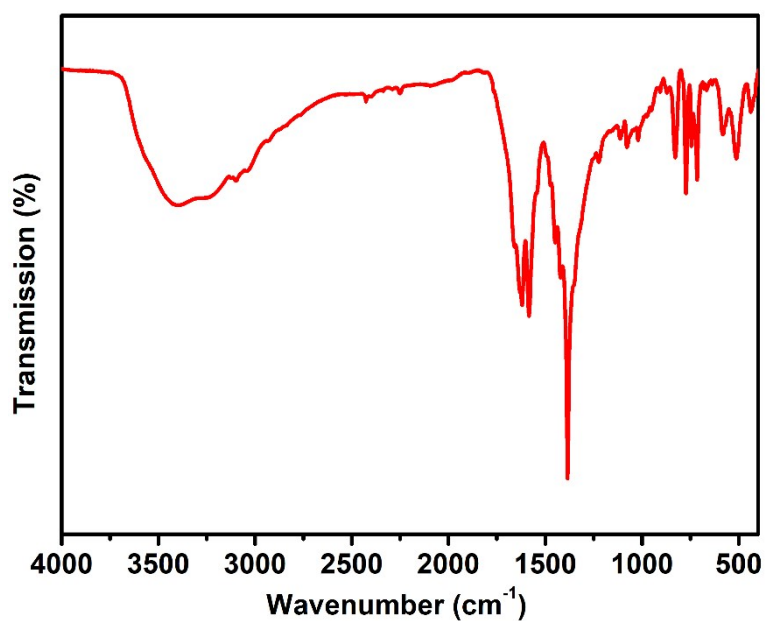


Fig. S2 IR spectrum of compound **1**. The absence of absorption around 1700 cm^{-1} confirms that the carboxylic groups ($-\text{COOH}$) in $\text{H}_2(\text{ipbp})\text{Br}$ ligands are completely deprotonated and exist as $-\text{COO}^-$, thus giving the stretch vibrations around 1619 cm^{-1} and 1385 cm^{-1} .^{1, 2} Moreover, the characteristic absorption around 1630 cm^{-1} confirms the existence of $\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching vibrations of the pyridinium group in compound **1**.²

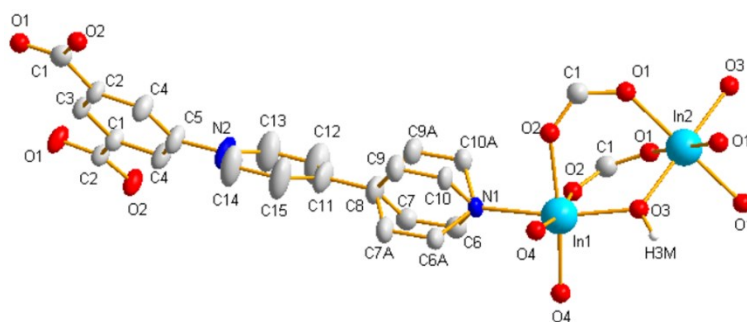


Fig. S3 The coordination environment of **1**. The hydrogen atoms from linkers are omitted for clarity.

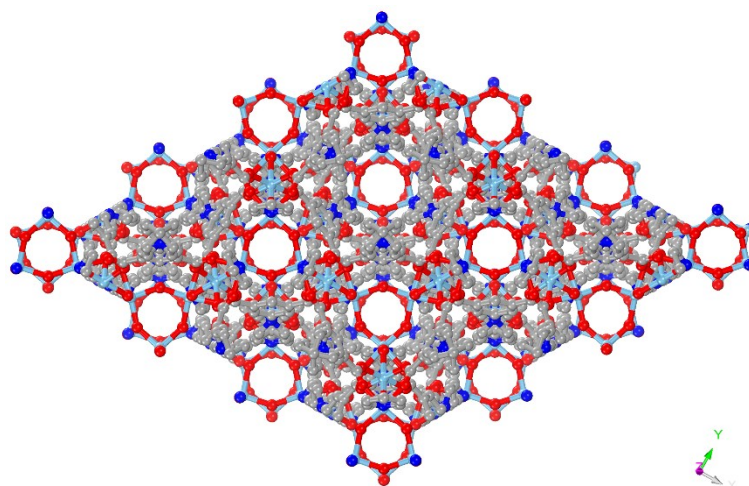


Fig. S4 The 3D framework of compound **1**.

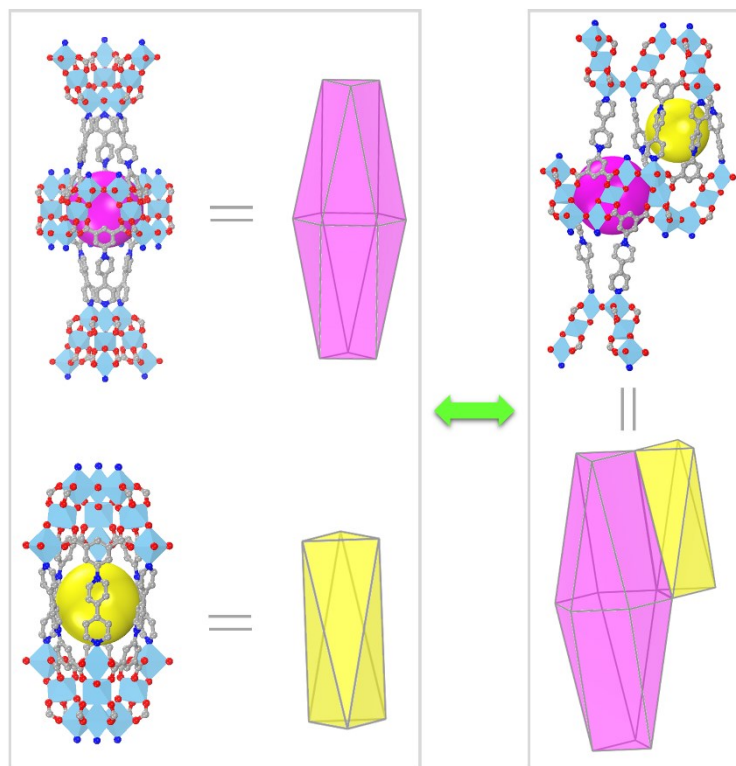


Fig. S5 View of two different cages in compound **1**.

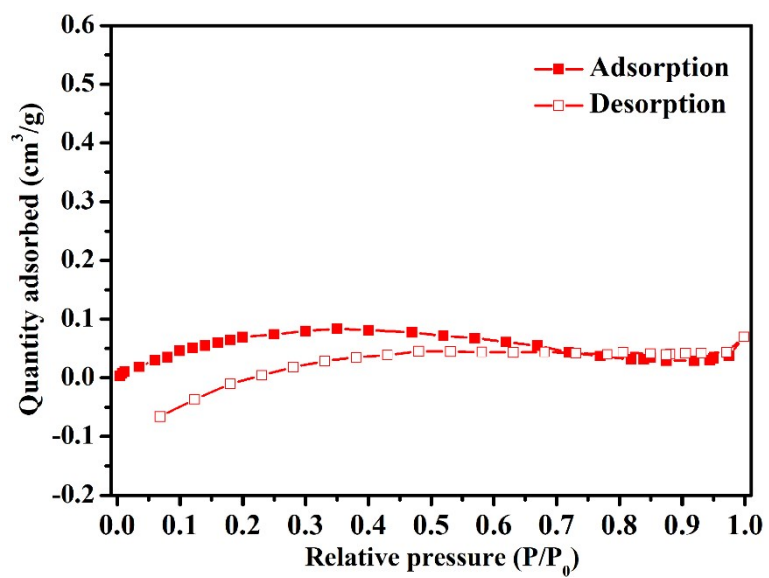


Fig. S6 N₂ adsorption-desorption isotherms of compound **1** at 77 K.

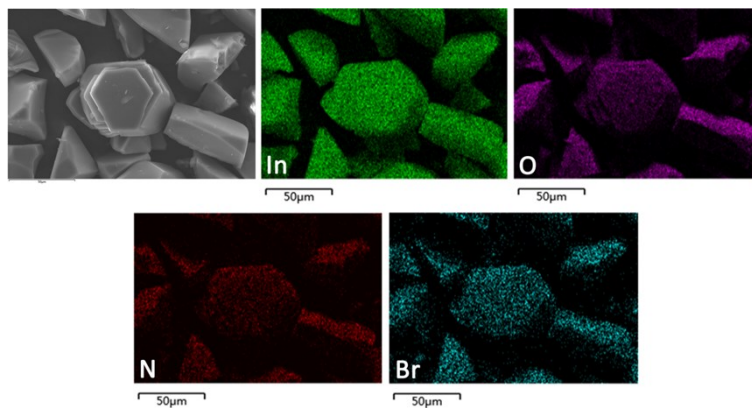


Fig. S7 SEM image and elemental mapping images of compound **1**.

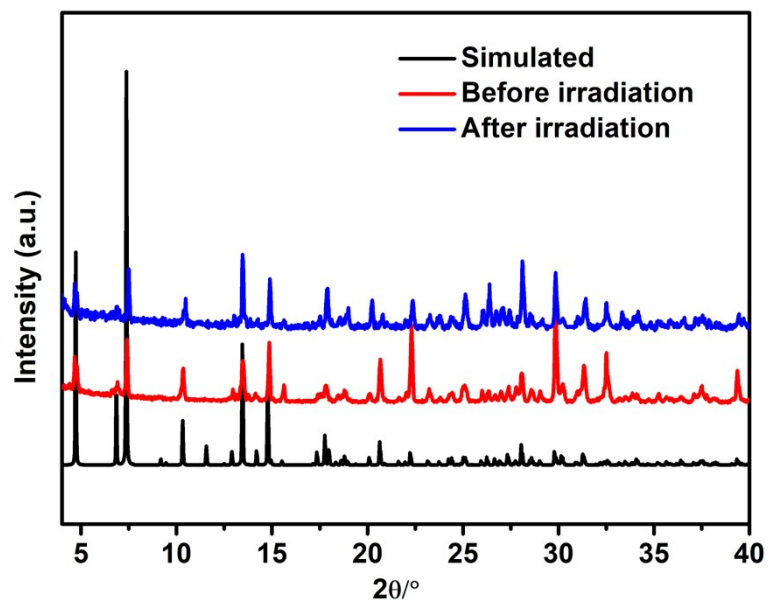


Fig. S8 PXRD patterns of simulated, before and after irradiation of compound **1**.

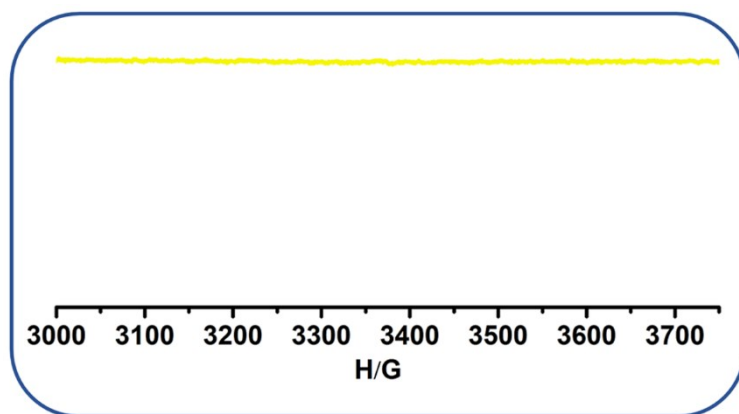


Fig. S9 EPR signal of compound **1** after decolored.

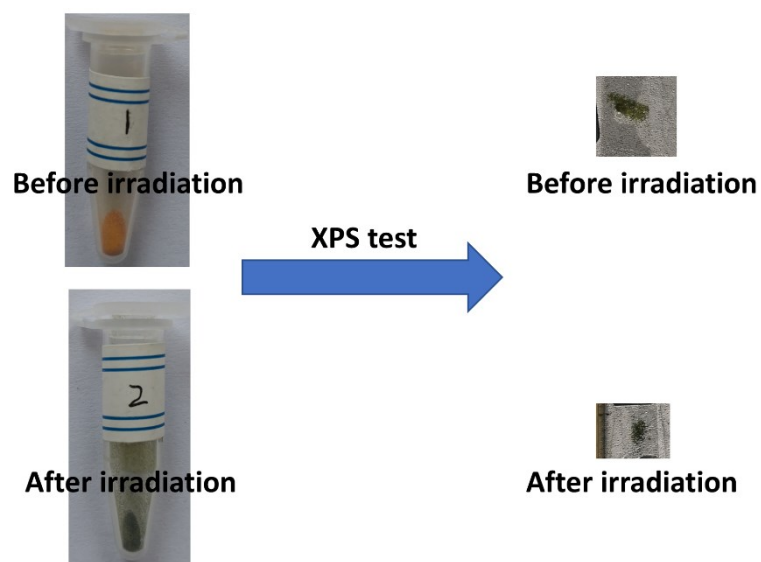


Fig. S10 Photographs showing crystal colors of compound **1** after irradiation and XPS test.

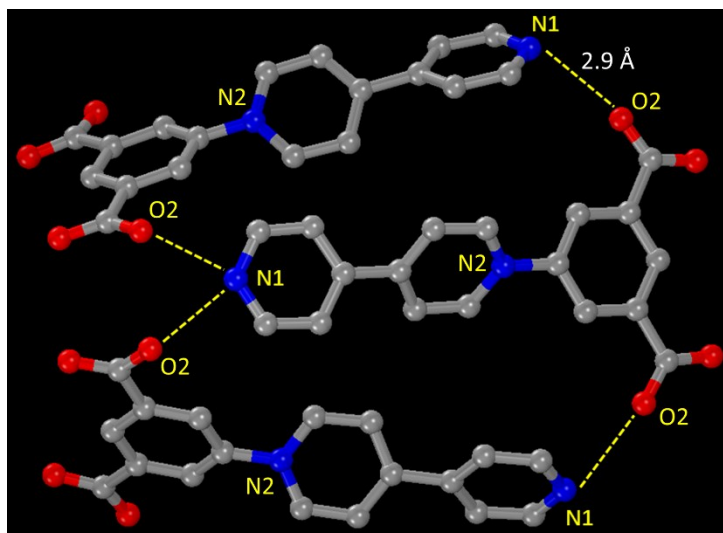


Fig. S11 The electron transfer pathways between the oxygen atom of carboxylate and nitrogen atom of bipyridinium units from adjacent ligands in the structure of compound **1**.

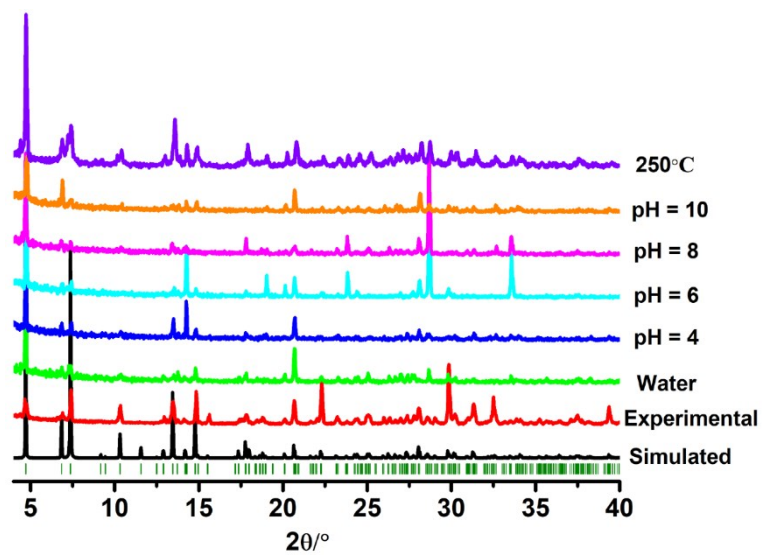


Fig. S12 PXR D patterns of compound **1** after immersed in water for one week, in aqueous solution with various pH for 48 h or heated at 250 °C for 10 min.

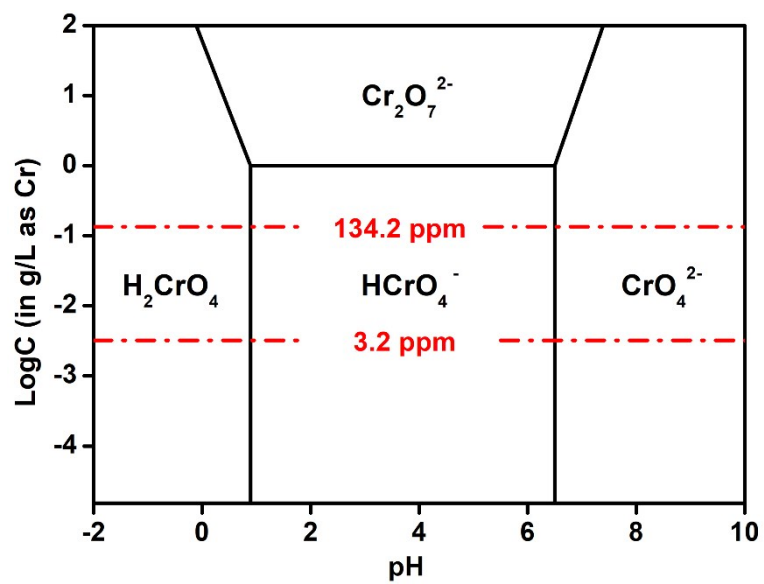


Fig. S13 The predominance diagram showing the relative distribution of different Cr(VI) species in water as a function of pH and total Cr(VI) concentration.

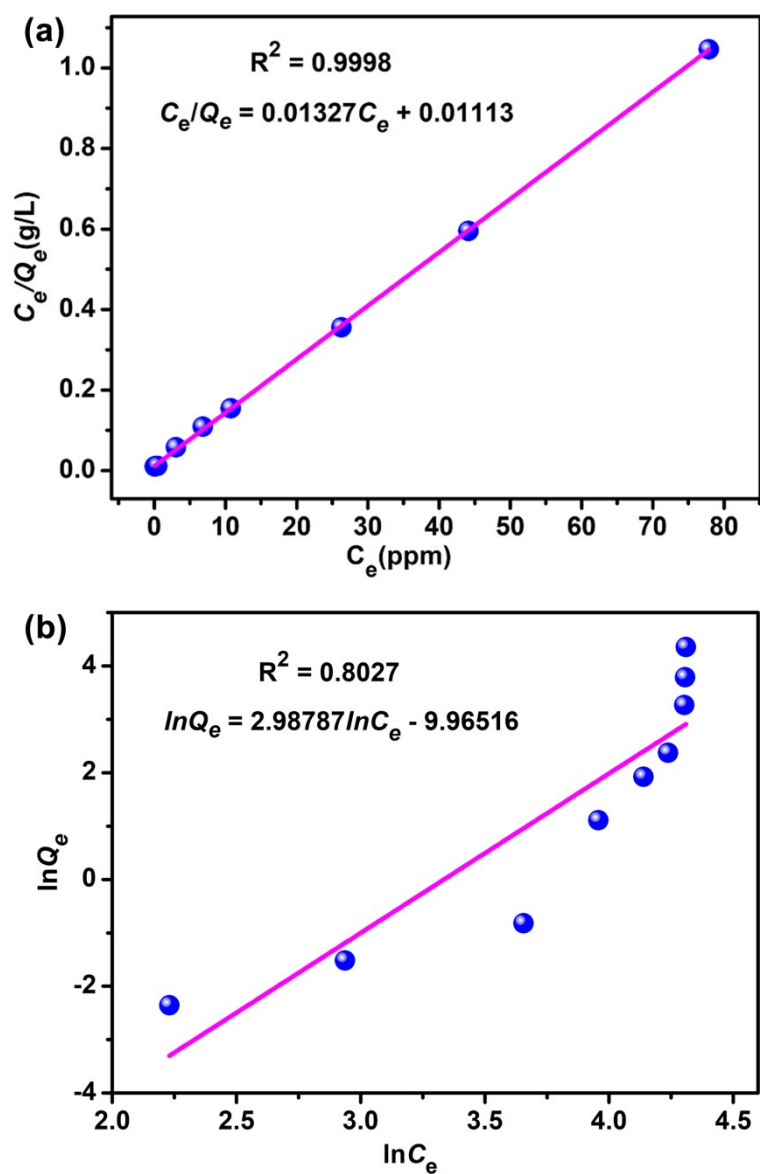


Fig. S14 (a) Langmuir isotherm and (b) Freundlich isotherm fitting model for Cr(VI) removal by compound **1** according to Eq. (1) and (2)³, respectively:

$$C_e/Q_e = C_e/Q_m + 1/(K_L \cdot Q_m) \quad (1)$$

$$\ln Q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

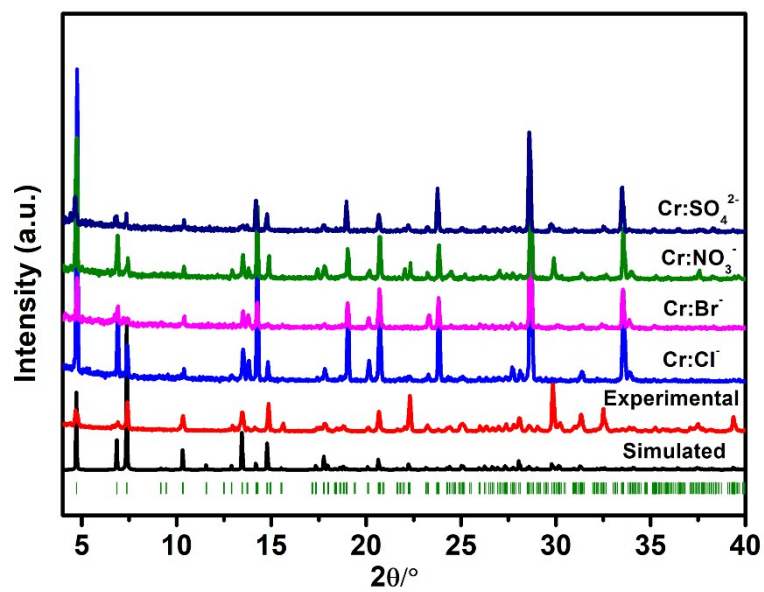


Fig. S15 PXR D patterns of compound **1** before and after Cr(VI) adsorption in the presence of differently competitive ions.

The release of Cr(VI) from Cr(VI)@**1** was done in the following experiments. 10 mg of compound **1** was immersed in 30 mL of Cr(VI) aqueous solutions (134.2 ppm) under stirring condition for 48 h to obtain sample of Cr(VI)@**1**, which was separated by centrifugation and washed by water for three times. Then the obtained dried sample was immersed in 30 mL water containing 200-fold molar amounts of Br⁻ (relative to the absorbed Cr(VI)). After 12 h and 24 h, 2 mL of the mixture was taken out, respectively. Then the supernatant was separated by centrifugation and analyzed by ICP, and the solid sample was washed by water for three times and then analyzed by PXRD (Fig. S16).

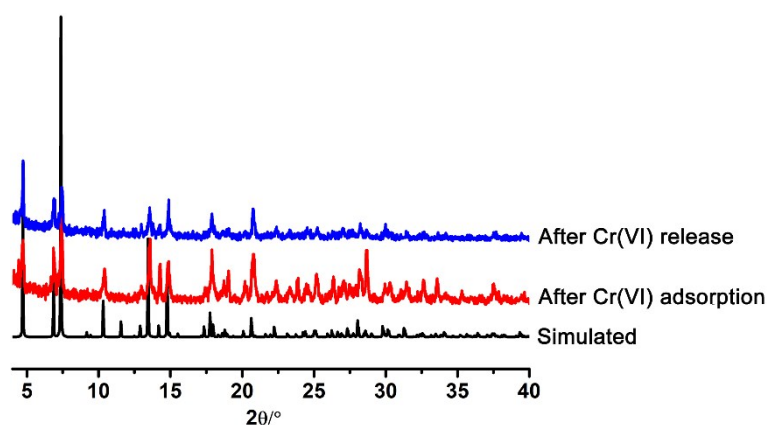


Fig. S16 PXRD patterns of compound **1** after Cr(VI) adsorption and release.

References

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2. J.-K. Sun, P. Wang, C. Chen, X.-J. Zhou, L.-M. Wu, Y.-F. Zhang and J. Zhang, *Dalton Trans.*, 2012, **41**, 13441.
3. M. T. Ge; H. Z Liu. *J. Mater. Chem. A*, 2016, **4**, 16714.