Electronic supplementary information (ESI)

Selective removal of $Cr_2O_7^{2-}$ in aqueous solution by one nonporous pure crystals of cucurbit[6]uril

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Experimental section

Materials and General Methods. All reagents and solvents were commercially purchased and used as received without further purification. The host molecule cucurbit[6]uril (Q[6]) was synthesized according to the previously reported methods.[1] Powder X-ray diffraction (PXRD) data were collected at room temperature with Cu Kα radiation (1.54059 Å) using a Bruker D8 Advance X-ray diffractometer. Inductively coupled plasma optical emission spectrometer (ICP-OES) measurements were carried out using Optima 5300 DV. UV-vis measurements were conducted at room temperature on a Metash 6100 UV-vis spectrophotometer. The morphology was evaluated using scanning electron microscopy (SEM, Hitachi S-8100) at an accelerating voltage of 5 kV and energy-dispersive X-ray spectroscopy (EDS) was also obtained using the SEM instrument. The molecular particle sizes were measured by a DelsaNanoC DLS analyzer (Beckman. Coulter, Inc., U.S.A.). X-ray photoelectron spectroscopy (XPS) experiments were conducted on a Kratos AXIS Ultra DLD spectrometer.

X-ray crystallography. Intensity data were collected on a Bruker D8 Venture Photon II diffractometer with graphite-monochromated Ga Kα radiation (λ = 1.34139 Å) using the ω-scan technique. The SAINT program was used for the integration of the diffraction data and the intensity correction for the Lorentz and polarization effects.[2] Semi-empirical absorption corrections were applied using a SADABS program.[3] The structures were solved by direct methods and refined with the full-matrix least-squares technique based on F^2 using the SHELXL-2018 program.[4] Some highly disordered water molecules in the unit cell have been taken into account with the SQUEEZE option of the PLATON program.[5] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located from the difference Fourier maps and refined with restraint of the O–H and H···H distance (0.96 Å and 1.52 Å, respectively). Other hydrogen atoms were introduced at the calculated positions. The $Cr_2O_7^{2-}$ is disordered into two positions each with a site occupancy of 0.5. The details of the crystal parameters, data collection, and refinements are listed in Table S1 and selected bond lengths and angles are given in Table S2.

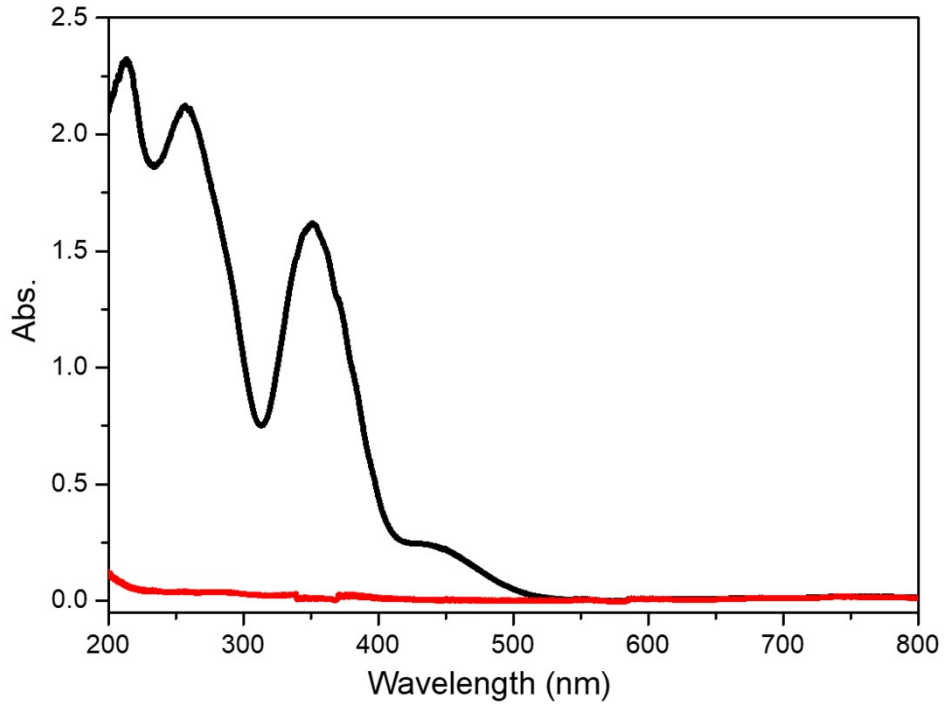
Table S1. Crystal data and structure refinements for **1 (**Q[6]⊂$Cr_2O_7^{2-}$**)**.

	1 (Q[6]⊂$Cr_2O_7^{2-}$**)**
Formula	$C_{36}H_{54}N_{24}O_{27}Cr_2$
Formula weight	1359.03
T (K)	293(2)
λ (Å)	1.34139
Crystal system	Orthorhombic
Space group	*Pnnm*
a (Å)	15.901(2)
b (Å)	11.616(2)
c (Å)	15.297(3)
V (Å^3)	2825.5(8)
Z	2
D_{calc} (g cm^{-3})	1.597
μ /mm^{-1}	2.796
F(000)	1404
θ for data collection (°)	4.100 - 54.006
Reflections collected	9527
Independent reflections	2665
Data / restraints / parameters	2665 / 60 / 261
Goodness-of-fit on F^2	1.115
R_1[a] [$I > 2\sigma(I)$]	0.1063
wR_2[b] [I > 2σ(*I*)]	0.2534
R_1 [all data]	0.1740
R_1 [all data]	0.2850

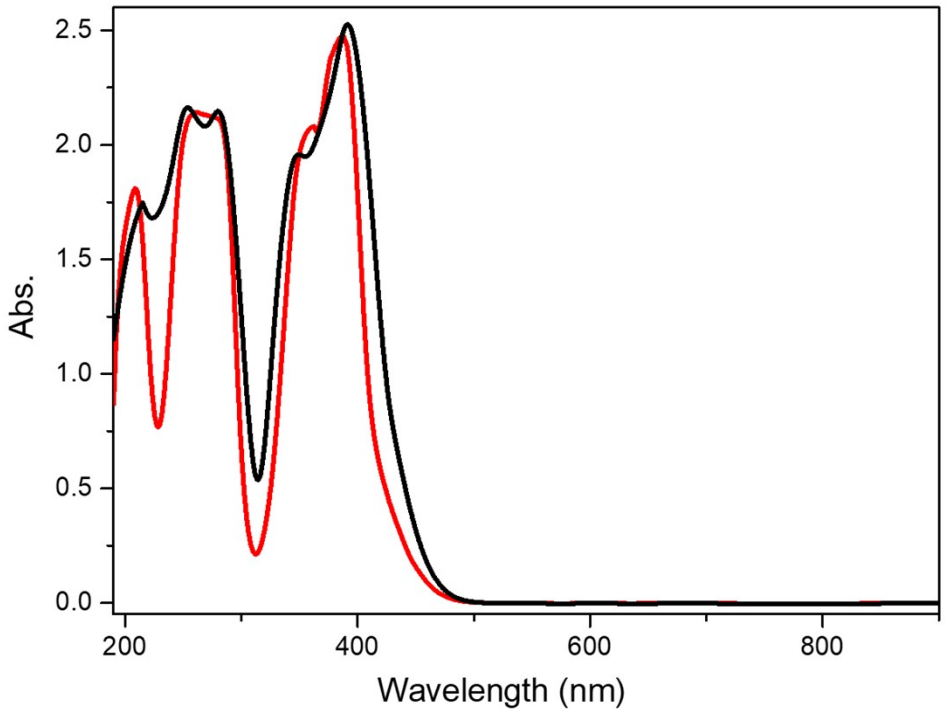
[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where w = m= $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. P = $(F_o^2 + 2F_c^2)/3$

Table S2. Selected bond lengths (Å) and angles (°) for **1.**

1			
Cr(1)-O(5)	1.474(19)	Cr(1)-O(6)	1.592(15)
Cr(1)-O(10)#1	1.710(14)	Cr(1)-O(10)	1.710(14)
Cr(1)-O(7)	2.21(3)	Cr(1)-O(7)#1	2.21(3)
Cr(2)-O(7)	1.43(3)	Cr(2)-O(7)#2	1.43(3)
Cr(2)-O(9)#2	1.58(3)	Cr(2)-O(9)	1.58(3)
Cr(2)-O(8)	1.67(2)	Cr(2)-O(8)#2	1.67(2)
Cr(2)-O(10)#1	2.038(15)	Cr(2)-O(10)#3	2.038(15)
O(5)-Cr(1)-O(6)	107.1(9)	O(5)-Cr(1)-O(10)#1	110.1(6)
O(6)-Cr(1)-O(10)#1	110.8(5)	O(5)-Cr(1)-O(10)	110.1(6)
O(6)-Cr(1)-O(10)	110.8(5)	O(10)#1-Cr(1)-O(10)	108.0(10)
O(5)-Cr(1)-O(7)	128.5(8)	O(6)-Cr(1)-O(7)	107.8(8)
O(10)-Cr(1)-O(7)	91.2(9)	O(10)#1-Cr(1)-O(7)#1	91.2(9)
O(7)-Cr(2)-O(9)	115.5(14)	O(7)#2-Cr(2)-O(9)	104.6(14)
O(9)#2-Cr(2)-O(9)	124.6(19)	O(7)-Cr(2)-O(8)	120.1(14)
O(7)#2-Cr(2)-O(8)	120.5(14)	O(9)-Cr(2)-O(8)	108.6(13)
O(7)#2-Cr(2)-O(10)#1	103.8(12)	O(9)#2-Cr(2)-O(10)#1	102.7(10)
O(9)-Cr(2)-O(10)#1	102.9(10)	O(8)-Cr(2)-O(10)#1	114.6(9)
O(8)#2-Cr(2)-O(10)#1	103.7(9)	O(10)#1-Cr(2)-O(10)#3	123.1(8)
Symmetry codes: #1 x, y, -z+1; #2 -x+1, -y, z; #3 -x+1, -y, -z+1.			



(a)



(b)

Fig. S1. UV-vis spectra and photographical images of the solution of $Cr_2O_7^{2-}$ (a) and CrO_4^{2-} after the addition of Q[6] powder.

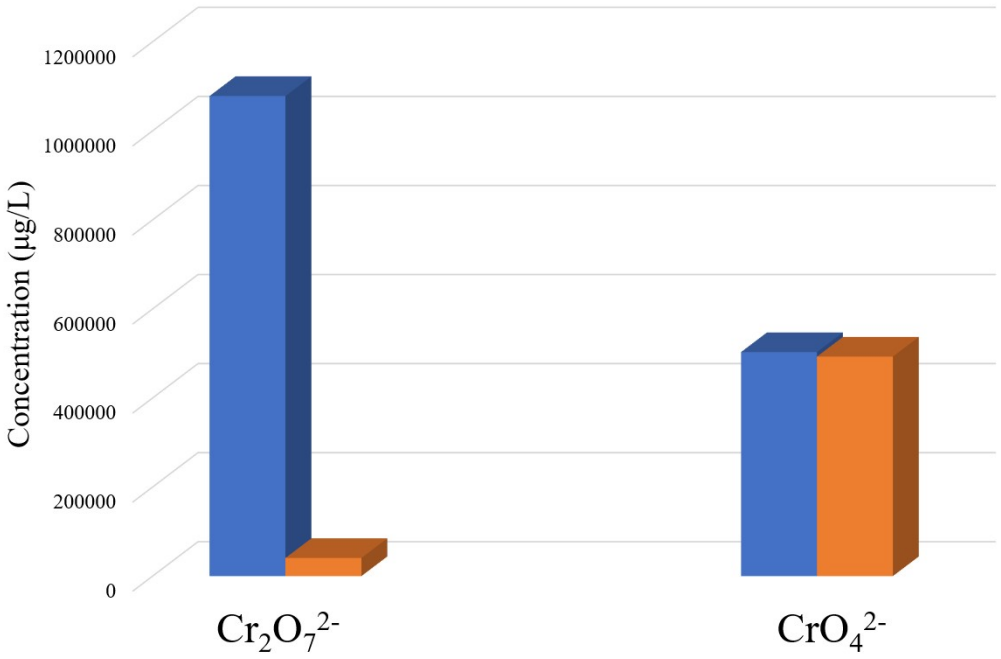


Fig. S2. ICP results of the supernatant solution of $Cr_2O_7^{2-}$ and CrO_4^{2-} before and after addition of Q[6].

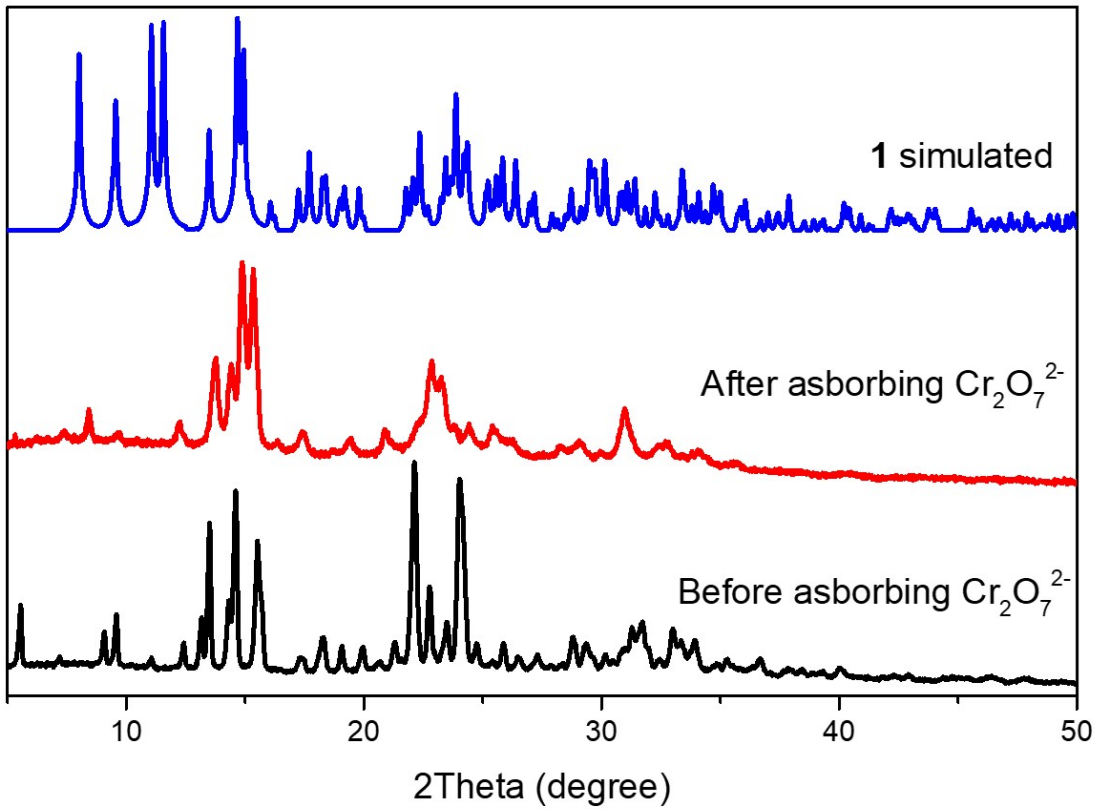
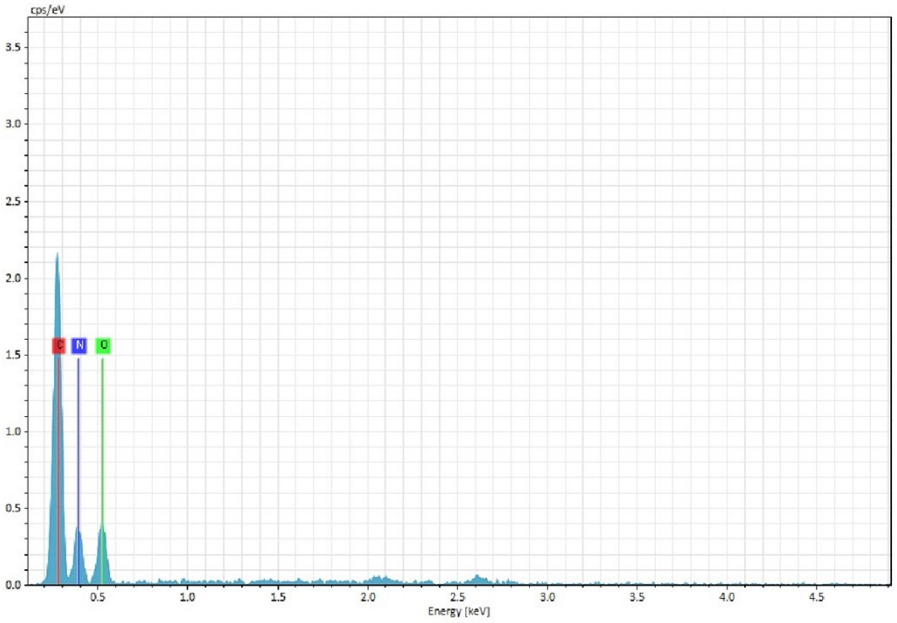
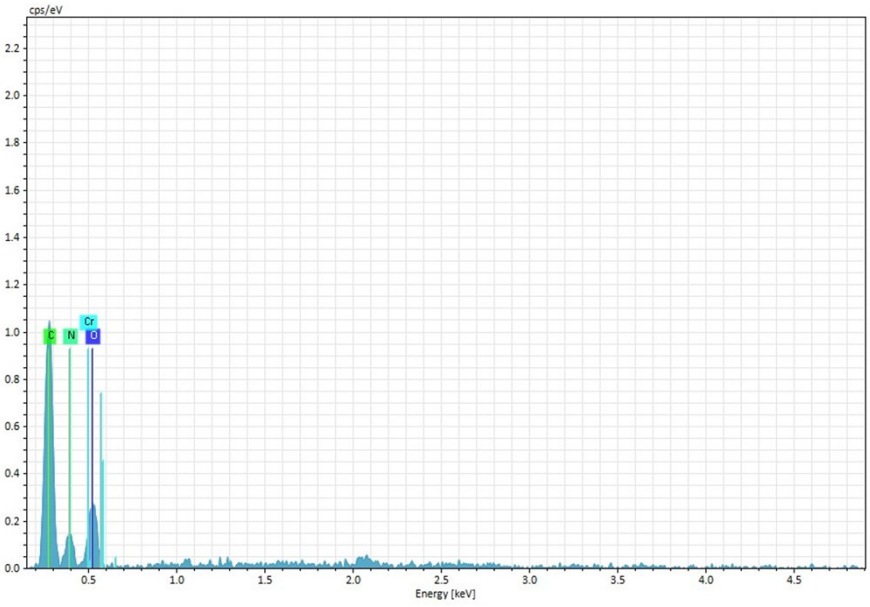


Fig. S3. PXRD patterns of Q[6] before and after absorbing $Cr_2O_7^{2-}$.

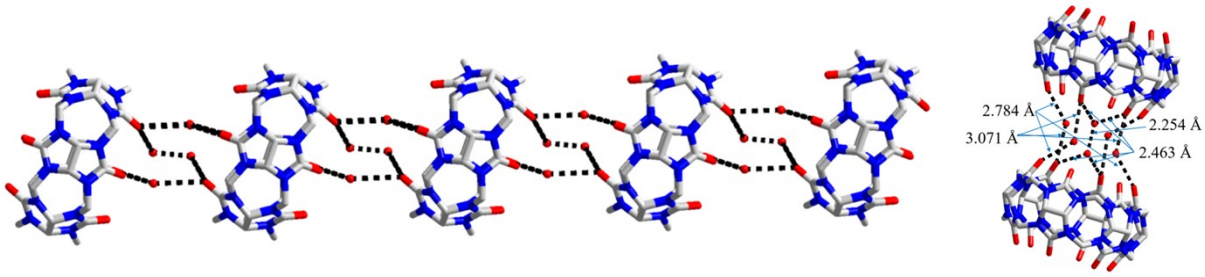


(a)

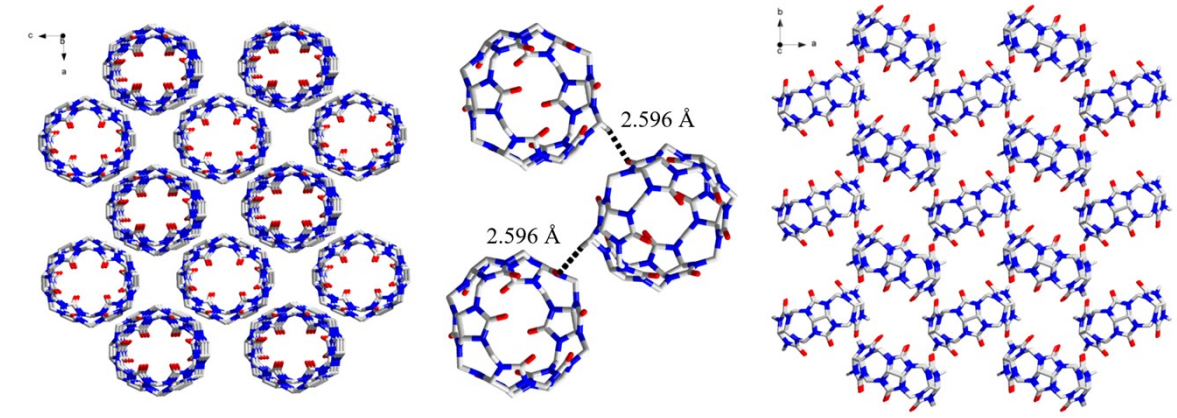


(b)

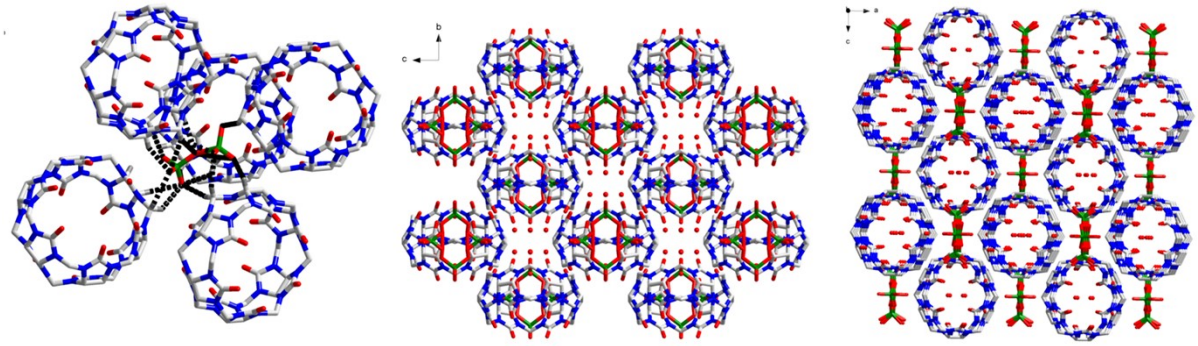
Fig. S4. EDS spectra of Q[6] before (a) and after (b) absorbing $Cr_2O_7^{2-}$.



(a)



(b)



(c)

Fig. S5. (a) The supramolecular chains constructed from Q[6] via the O-H…O hydrogen bonds between the carbonyl groups and the solvent water molecules or hydronium cations. (b) The 3D supramolecular structure constructed from the 1D chains via the C-H…O hydrogen bonds between Q[6] molecules (solvent water molecule and hydronium cations are omitted for clarity). (c) The hydrogen bonds among the $Cr_2O_7^{2-}$ anions, solvent water molecules and carbonyl groups of Q[6] and the final structure of **1** with water molecules and hydronium cations. Hydrogen atoms were omitted for clarity.

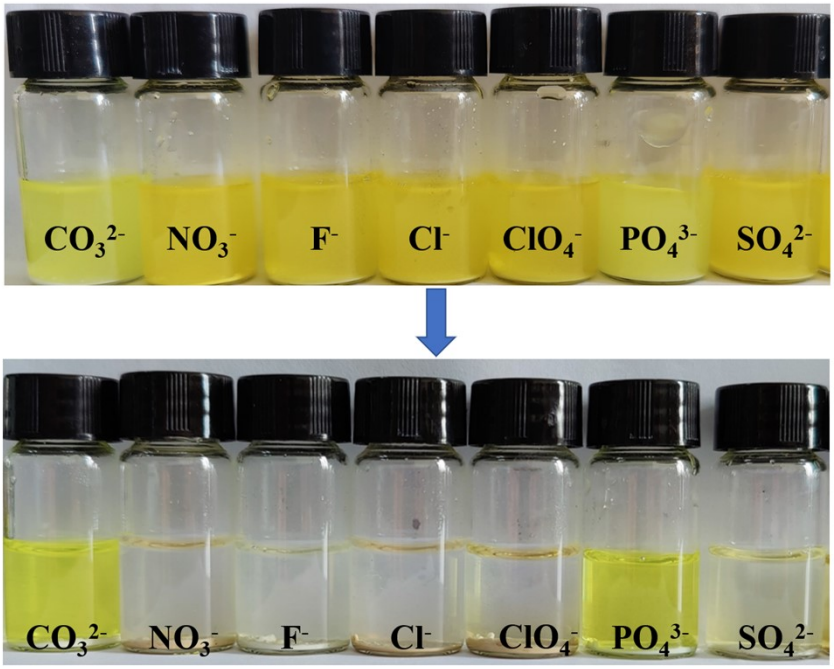


Fig. S6. The pictures of the solution of $Cr_2O_7^{2-}$ after the addition of Q[6] in the presence of different anions.

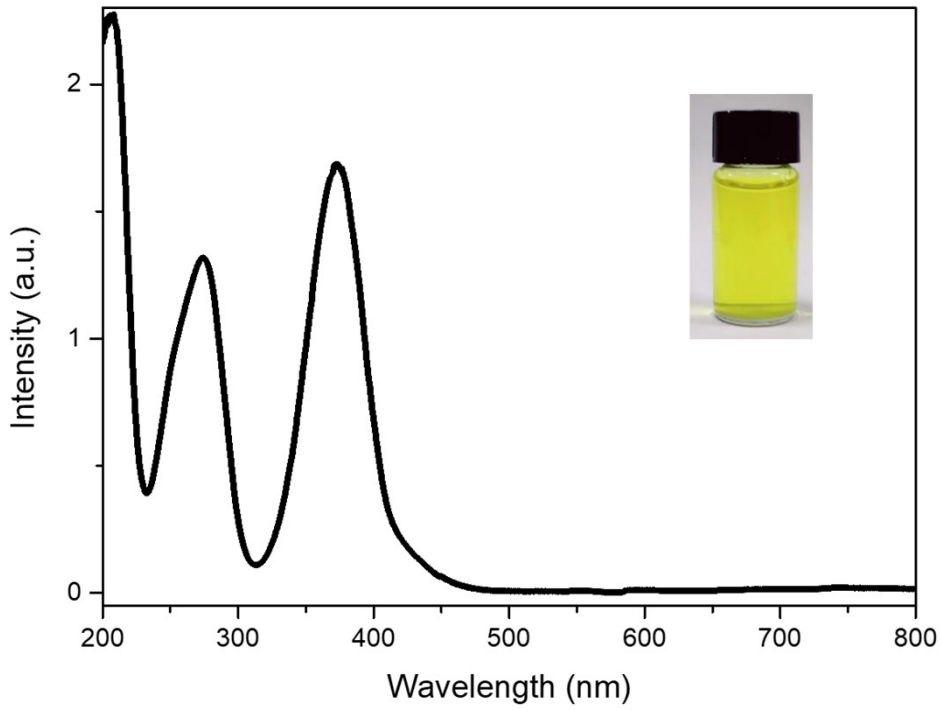


Fig. S7. UV-vis spectra and photographical images after soaking $Cr_2O_7^{2-}$-treated Q[6] in the solution of KOH for 2 h.

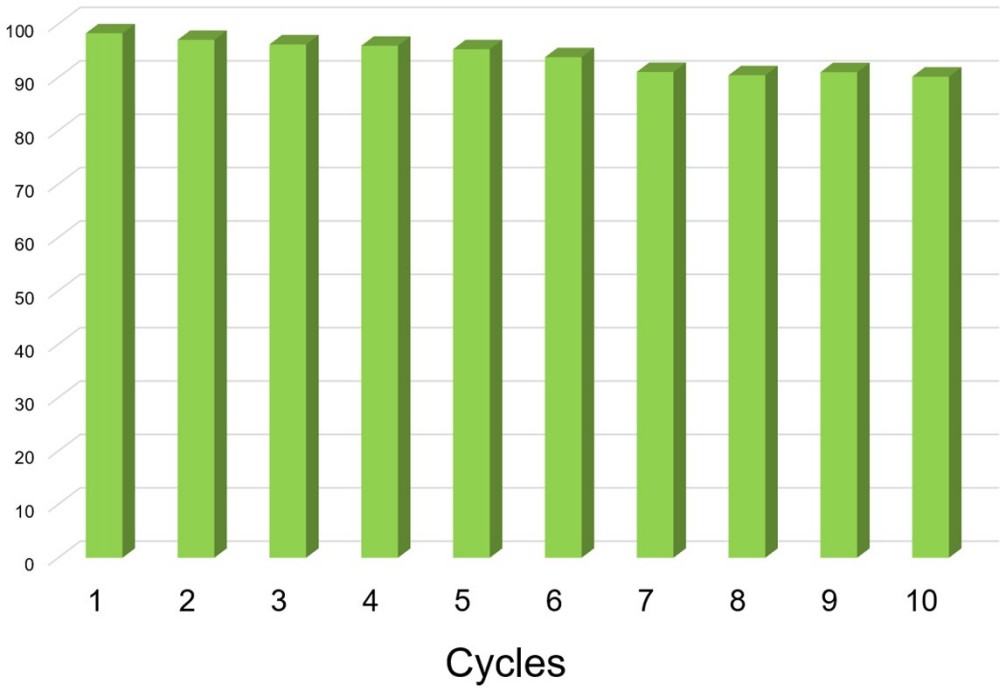


Fig. S8. The removal efficiency of Q[6] for $Cr_2O_7^{2-}$ in ten cycles.

References:

1. A. Day, A. P. Arnold, R. J. Blanch and B. Snushal, *J. Org. Chem.*, 2001, **66**, 8094-8100.

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