Electronic Supplementary Information

A selective picomolar level fluorometric sensing of Cr(VI)-oxoanion in water medium by a novel metal-organic complex

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Crystallographic Details:

Table S1 Crystallographic data of MOC

*CCDC No.	874430
Formula	$C_{24}H_{38}CuO_{10}N_4$
Formula Weight	606.13
Crystal System	Triclinic
Space group	$P\bar{1}$ (No. 2)
a[Å]	9.802(3)
b[Å]	11.002(4)
c[Å]	14.295(5)
α[º]	85.036(6)
β[º]	87.910(6)
γ[º]	65.323(5)
V [$Å^3$]	1395.6(8)
Z	2
D(calc) [g/cm^3]	1.442
μ(MoKα) [mm^{-1}]	0.843
F(000)	638
Crystal Size [mm^3]	0.00 × 0.00 × 0.00
Temperature [K]	293
Radiation [Angstrom]	MoKα 0.71073
Theta Min-Max [°]	1.4, 23.9
Number of Reflections	8466
Unique Data	4183
R(int)	0.038
Observed data [I > 2.0 sigma(I)]	3470
N_{ref}	4183
N_{par}	352
R	0.1143
wR2	0.3309
S	1.13
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-1.27, 2.49

*****CCDC 874430 contains the Supplementary crystallographic data for MOC. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S2 Some selected bond lengths (Å) of MOC

Cu1-O1	1.944(8)	Cu1-O1W	2.308(9)
Cu1-O7	1.941(8)	O1-C1	1.260(15)
Cu1-O3	1.930(8)	Cu1-O5	1.926(7)
O2-C1	1.233(15)	O3-C3	1.239(14)
O4-C3	1.261(12)	O5-C8	1.250(15)
O8-C10	1.233(14)	C1-C2	1.515(15)
O6-C8	1.234(13)	O7-C10	1.291(14)
C2-C3	1.523(15)	C2-C4	1.521(18)
C6-C7	1.51(4)	C8-C9	1.511(15)
C11-C12	1.47(2)	C12-C13	1.43(4)
C4-C5	1.51(3)	C5-C6	1.51(4)
C9-C10	1.522(15)	C9-C11	1.545(19)
C13-C14	1.61(3)		

Table S3 Some selected bond angles (º) of MOC

O1-Cu1-O1W	104.8(3)	O1-Cu1-O	92.6(3)	O1-Cu1-O5	88.0(3)
O1-Cu1-O7	159.3(3)	O1W-Cu1-O3	85.9(3)	O1W-Cu1-O5	90.9(3)
O1W-Cu1-O7	95.9(3)	O3-Cu1-O5	176.9(4)	O3-Cu1-O7	88.2(3)
O5-Cu1-O7	92.3(3)	Cu1-O1-C1	127.2(7)	Cu1-O3-C3	127.4(7)
Cu1-O5-C8	125.5(6)	Cu1-O7-C10	124.0(7)	O1-C1-O2	121.0(10)
O1-C1-C2	120.9(10)	O2-C1-C2	118.1(11)	C1-C2-C3	116.0(9)
C1-C2-C4	109.6(10)	C3-C2-C4	108.5(10)	O3-C3-O4	121.4(10)
O3-C3-C2	121.6(9)	O4-C3-C2	116.9(10)	C2-C4-C5	116.3(15)
C4-C5-C6	114.7(18)	C5-C6-C7	118(3)	O5-C8-O6	122.5(10)
O5-C8-C9	120.3(9)	O6-C8-C9	117.3(11)	C8-C9-C10	114.5(9)
C8-C9-C11	109.1(11)	C10-C9-C11	107.3(10)	O7-C10-O8	121.3(10)
O7-C10-C9	120.0(10)	O8-C10-C9	118.7(10)	C9-C11-C12	118.0(14)
C11-C12-C13	116.2(18)	C12-C13-C14	115(2)		

Table S4 Selective Hydrogen bond donor/acceptor scheme (Å, °)

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)	Symmetry Code
N1-H1···O2	0.86	1.79	2.626(12)	163	-
O1W-H1W1···O4	0.85	2.04	2.810(11)	150	1-x,-y,1-z
O1W-H2W1···O6	0.85	2.04	2.868(11)	164	-x,1-y,1-z
N2-H2A···O1	0.86	2.12	2.967(13)	168	-
N2-H2B···O2W	0.86	2.06	2.914(16)	175	-
N3-H3···O7	0.86	1.95	2.810(11)	174	x,1+y,z
O2W-H1W2···O6	0.85	2.11	2.862(13)	147	-
O2W-H2W2···O4	0.85	2.03	2.776(13)	146	-1+x,1+y,z
N4-H4C···O8	0.86	1.96	2.806(13)	166	x,1+y,z
N4-H4D···O1W	0.86	2.25	3.095(14)	167	-x,1-y,1-z

Table S5 π···π interaction (Å, °)

Cg-Cg	Cg-Cg distance (Å)	Dihedral angle (i,j) (°)	Perpendicular distances between baricentres (i,j) (Å)	Symmetry code
Cg1···Cg2	3.603(7)	8.3(6)	3.296(5)	x,y,z

Table S6 Supramolecular lone-pair···π interaction

Y-X···Cg	X···Cg (Å)	Y···Cg (Å)	Y-X···Cg (°)	Symmetry code
C10-O8···Cg2	3.579(11)	3.774(13)	89.4(7)	-X,1-Y,1-Z

Table S7 Fluorescence lifetimes (τ) of the aqueous solution of the pure MOC probe in absence and in presence of Cr(VI)-oxoanion

System	τ_1 (ns)	α_1 (%)	$\langle\tau\rangle$ (ns)	χ^2
MOC	7.73	100	7.737	1.08
MOC + Cr(VI)-oxoanion	6.32	100	6.33	1.06

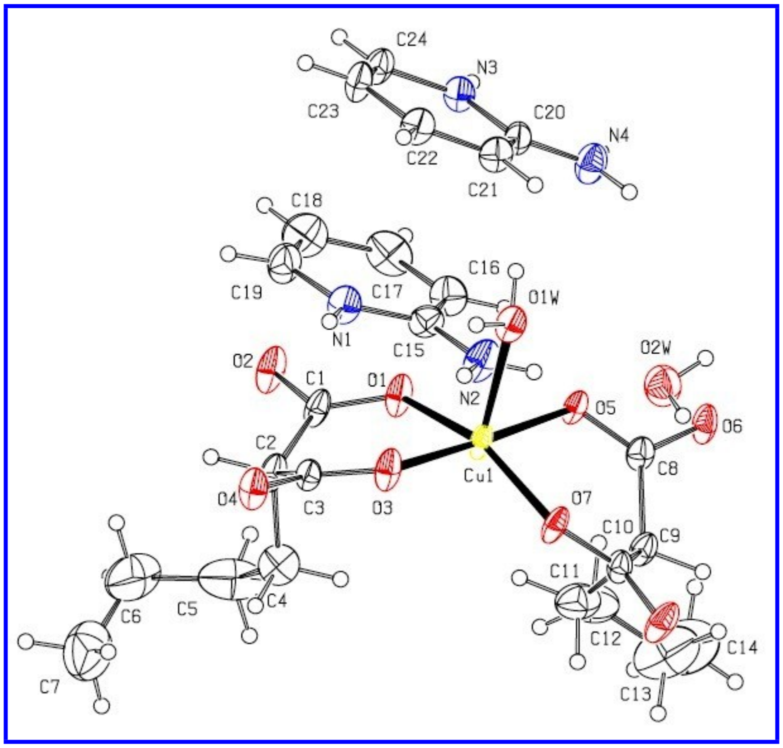


Fig. S1 The ORTEP diagram of MOC with 30% ellipsoidal probability.

Hirshfeld Surface

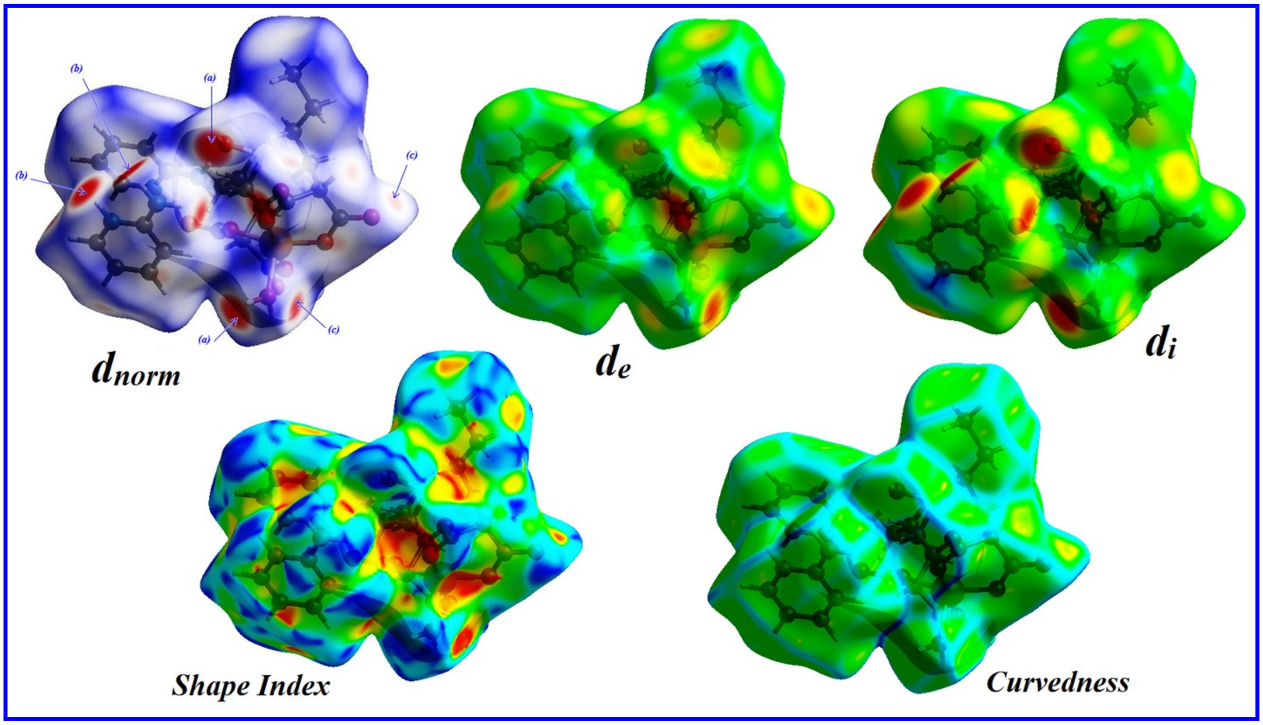


Fig. S2. Hirshfeld surface mapped with d_{norm}, d_i, d_e, shape index and curvedness for MOC.

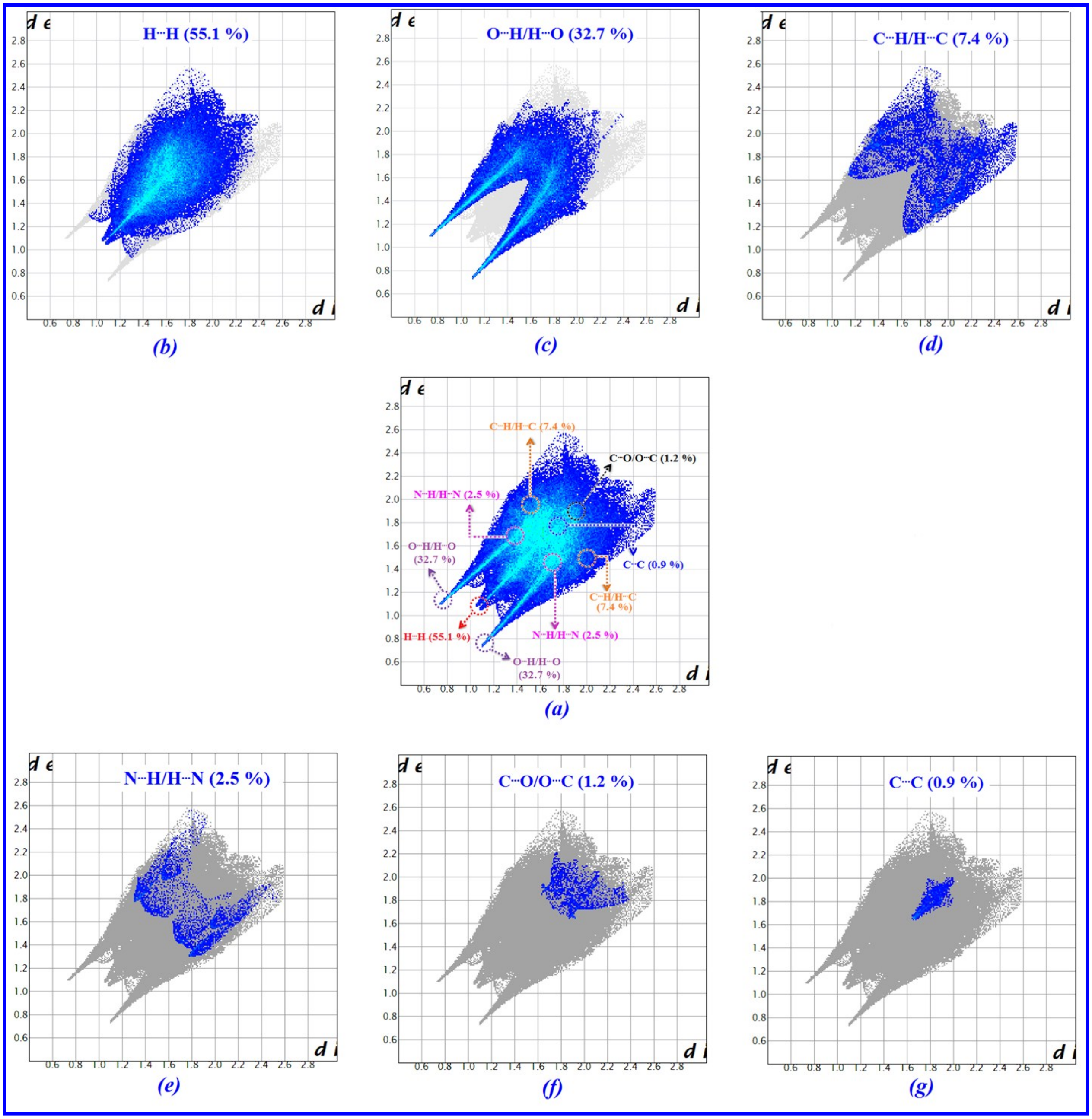


Fig. S3. Fingerprint plots of MOC: Full (a) and resolved into H···H (b), O···H/H···O (c), C···H/H···C (d), N···H/H···N (e), O···C/C···O (f) and C···C (g) contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of MOC.

Infrared Spectroscopic analysis:

IR spectral result for MOC in solid-state:

The broad and intense IR bands in the frequency range 3329-3475 cm^{-1} are due to the *v*(OH) vibrations of the hydrogen bonded hydroxyl groups. The strong bands at the frequency of 3163 cm^{-1} are due to the *v*(NH) vibrations for protonated 2-aminopyridine moieties. The IR absorption bands centered at 2939 cm^{-1} are assigned to the *v*(C-H) vibrations.

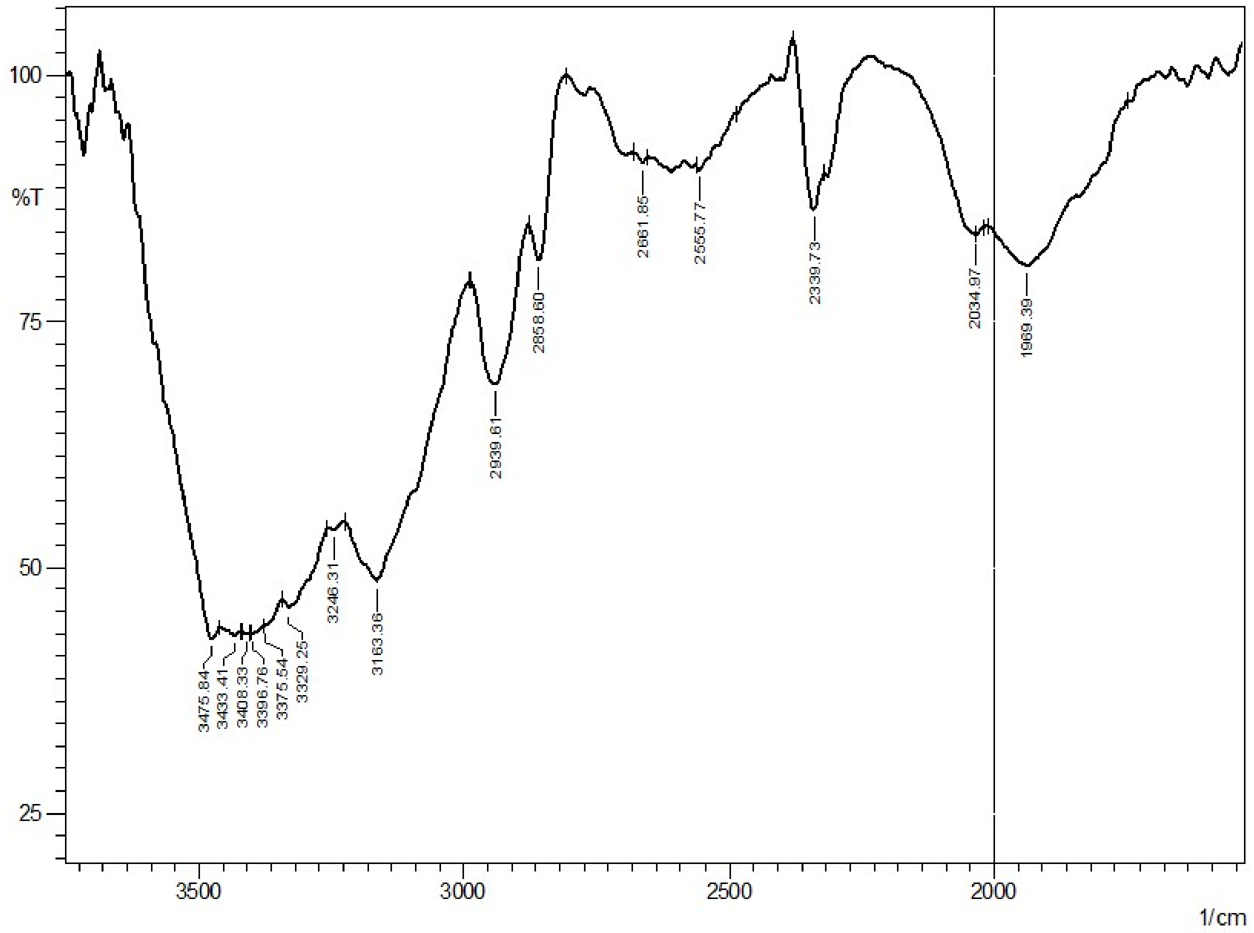


Fig. S4. IR spectra of the probe (MOC) in solid-state (Fig. 9).

IR spectral result for MOC and Cr(VI)-oxoanion:

The broad and intense IR bands in the frequency range 3376-3547 cm^{-1} are due to the ν(OH) vibrations of the hydrogen bonded hydroxyl groups. The bands at the frequency of 3221 cm^{-1} are due to the ν(NH) vibrations for protonated 2-aminopyridine moieties. The IR absorption bands centered at 2956 cm^{-1} are assigned to the ν(C-H) vibrations.

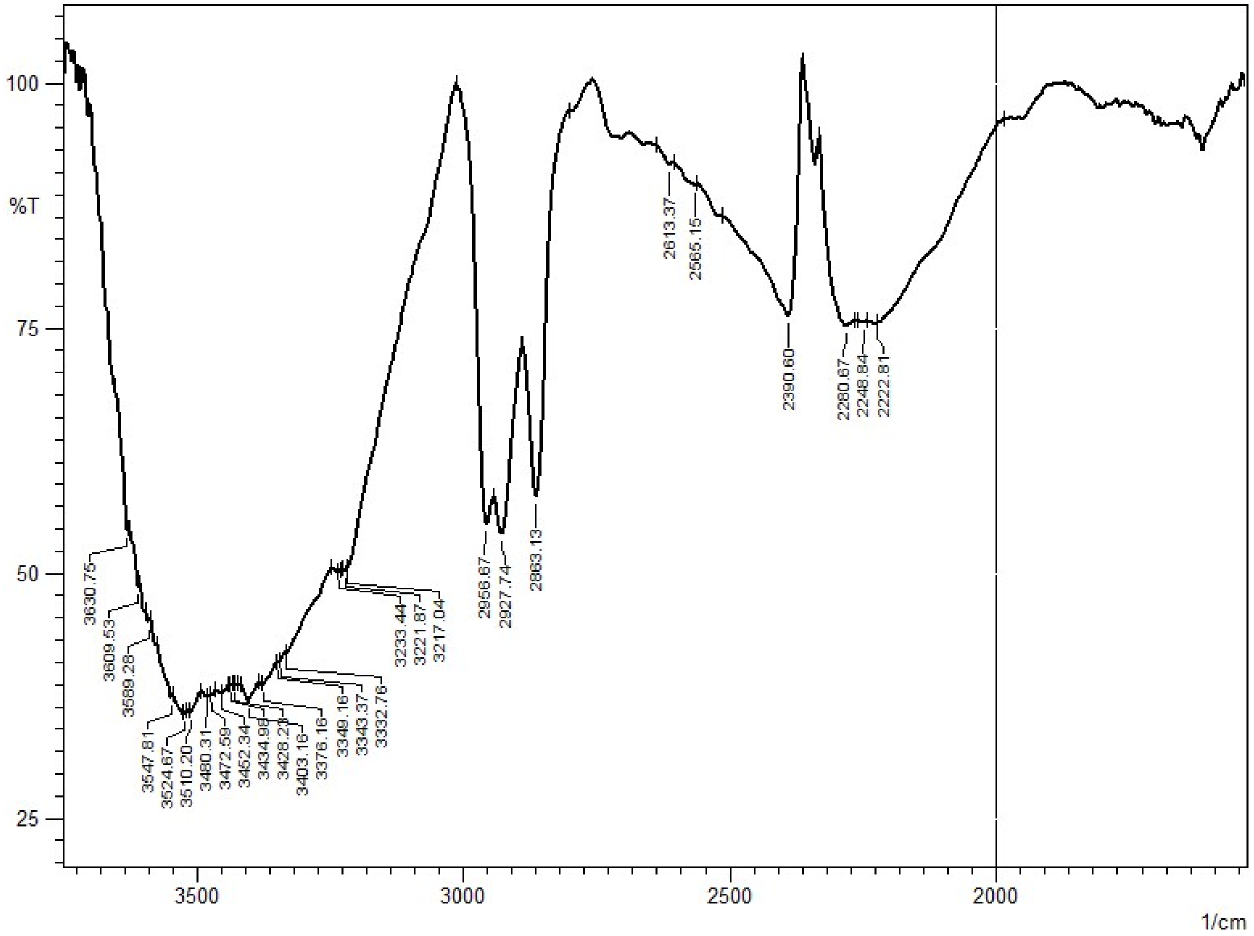


Fig. S5. IR spectra of the dried (using $CaCl_2$ based closed desiccator) sample of the water solution of the probe (MOC) and Cr(VI)-oxoanion (Fig. 9).

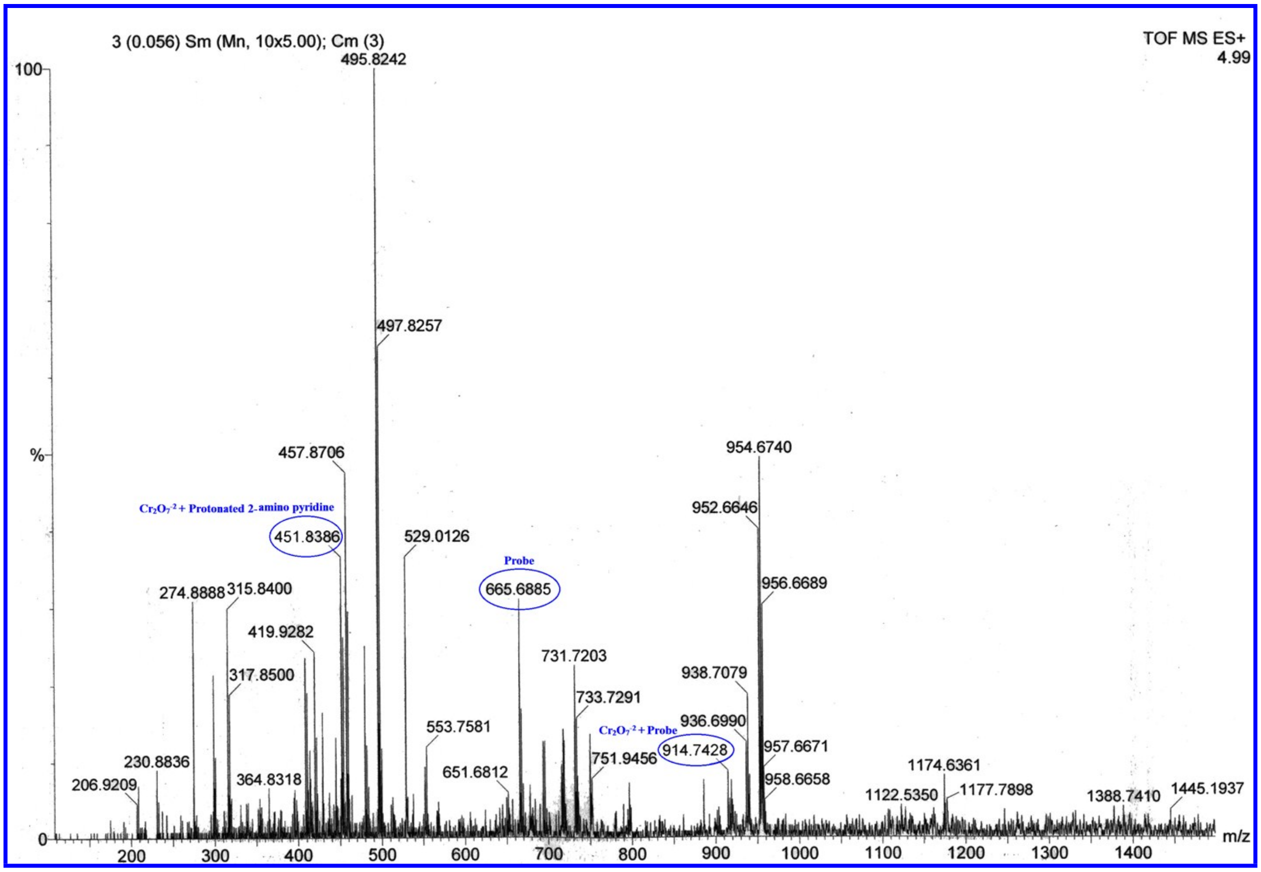


Fig. S6. ESI-MS spectra of the water solution of MOC and Cr(VI)-oxoanion.

Theoretical Analysis: Gas-phase optimized structure of MOC

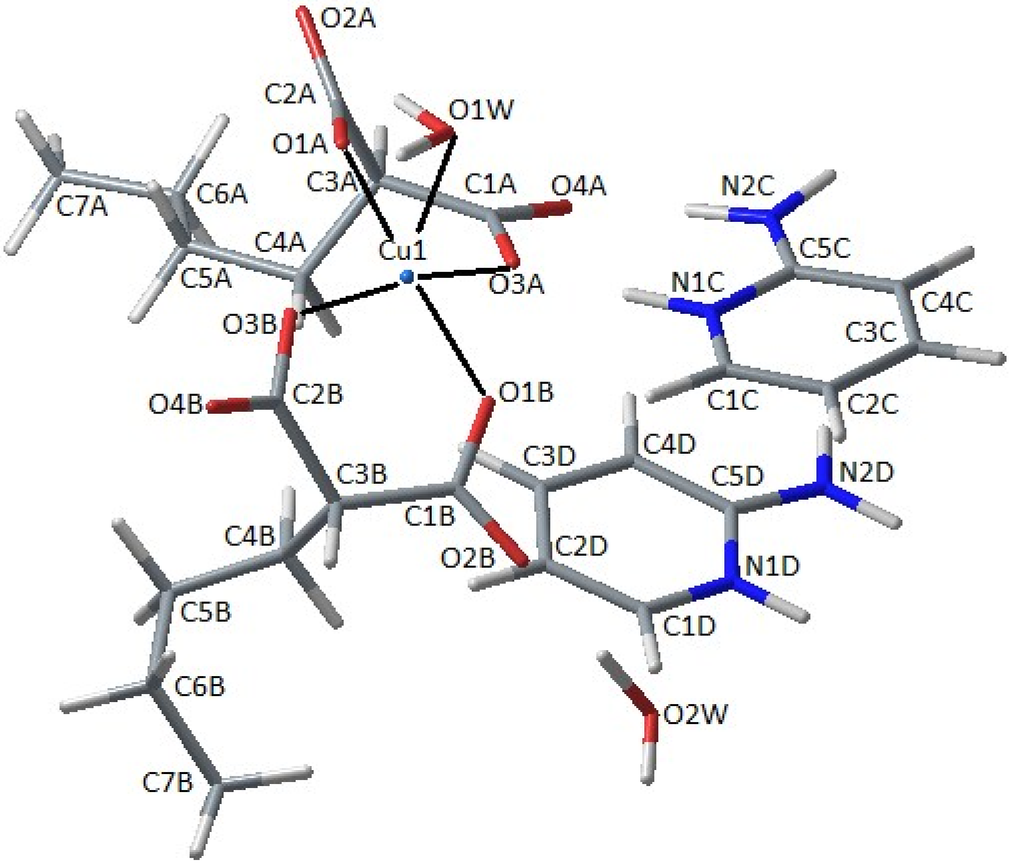
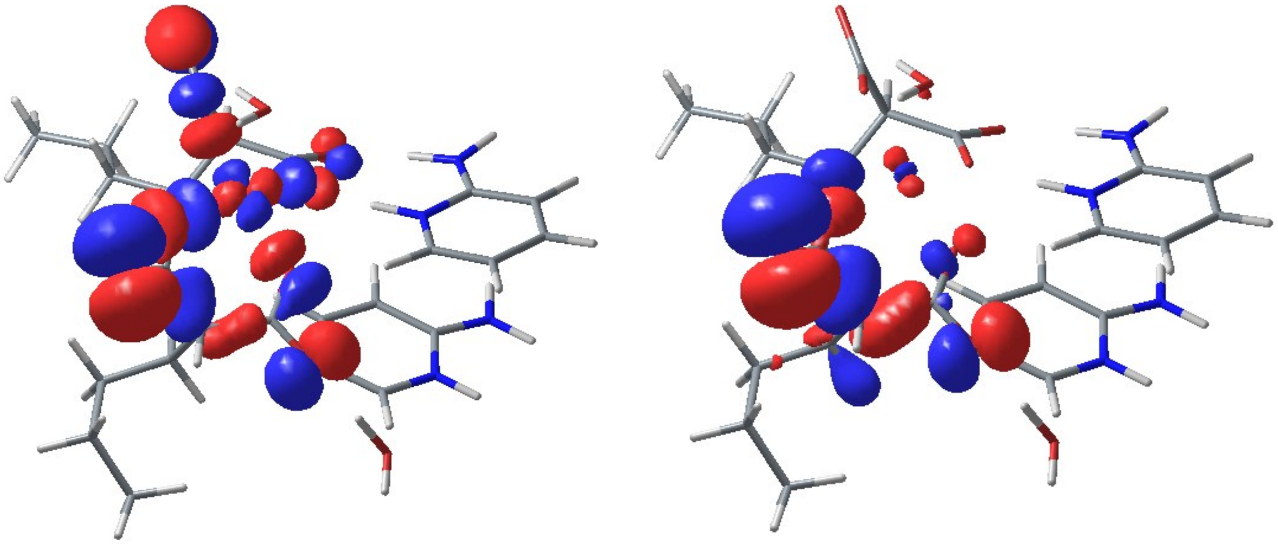
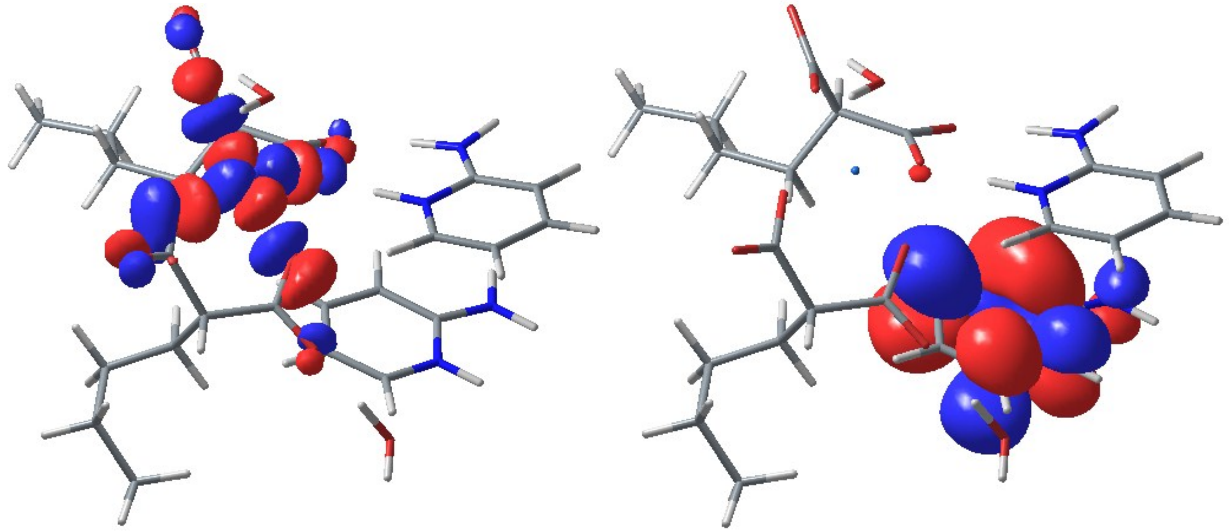


Fig. S7. Gas-phase DFT optimized structure of Cu(II) unit of MOC. The atoms are numbered.

The MOs are also shown below.



SOMO SOMO-1



LUMO LUMO+1

Fig. S8. The frontier orbitals of the MOC, showing M-L type orbitals.

Some of the structural parameters are

Table S8 Theoretically calculated bond distances (in Å)

Cu1—O1B	1.95826	Cu1—O1A	1.96051	Cu1—O3A	2.02918
Cu1—O3B	1.92699	Cu1—O1W	2.50669	O1A—C2A	1.32863
C2A—O2A	1.25862	C2A—C3A	1.56659	C3A—C1A	1.53134
C1A—O3A	1.32870	C1A—O4A	1.28284	C3A—C4A	1.56786
C4A—C5A	1.55348	C5A—C6A	1.55299	C6A—C7A	1.54985
C1B—O1B	1.31822	C1B—O2B	1.27875	C1B—C3B	1.53991
C3B—C2B	1.55984	C2B—O3B	1.33052	C2B—O4B	1.26150
C3B—C4B	1.57162	C4B—C5B	1.55458	C5B—C6B	1.55551
C6B—C7B	1.55265	C1C—C2C	1.39980	C2C—C3C	1.43102
C3C—C4C	1.40512	C4C—C5C	1.43908	C5C—N2C	1.36411
C5C—N1C	1.37954	C1C—N1C	1.37629	C1D—C2D	1.39420
C2D—C3D	1.42652	C3D—C4D	1.40574	C4D—C5D	1.42331
C5D—N2D	1.37613	C5D—N1D	1.37850	C1D—N1D	1.38796

Table S9 Theoretically calculated hydrogen bonds (in Å)

O3A—H	1.55661	H—N1C	1.09066	O4A—H	1.64075
H—N2C	1.06334	O1A—H	1.82583	H—O1W	1.00115
O2B—H	1.59722	H—O2W	1.01676	O1B—H	2.06730
H—C1C	1.10235	O2W—H	1.86096	H—C1D	1.11312

Table S10 Theoretically calculated Bond angles (°)

O1A—Cu1—O1W	71.293	O1A—Cu1—O3A	87.810
O1A—Cu1—O1B	173.323	O1A—Cu1—O3B	94.417
O1W—Cu1—O3A	107.541	O1W—Cu1—O1B	107.584
O1W—Cu1—O3B	86.388	O3A—Cu1—O1B	86.291
O3A—Cu1—O3B	165.824	O1A—C2A—O2A	125.061
O3A—C1A—O4A	120.339	O1B—C1B—O2B	121.232
O3B—C2B—O4B	124.044	C2A—C3A—C1A	110.676
C2A—C3A—C4A	110.669	C3A—C4A—C5A	113.986
C4A—C5A—C6A	114.398	C5A—C6A—C7A	112.400
C2B—C3B—C1B	114.681	C2B—C3B—C4B	110.895
C3B—C4B—C5B	114.943	C4B—C5B—C6B	115.390
C5B—C6B—C7B	114.359	C1C—C2C—C3C	117.847
C2C—C3C—C4C	120.906	C3C—C4C—C5C	119.373
C4C—C5C—N2C	123.534	N2C—C5C—N1C	118.480
C5C—N1C—C1C	123.001	N1C—C1C—C2C	120.864
C1D—C2D—C3D	118.662	C2D—C3D—C4D	121.138
C3D—C4D—C5D	119.123	C4D—C5D—N2D	122.966
N2D—C5D—N1D	118.980	C5D—N1D—C1D	123.821
N1D—C1D—C2D	119.193		

Table S11 Theoretically calculated dihedral angles (°)

Cu1—O3A—C1A—O4A	177.173	Cu1—O1A—C2A—O2A	-172.742
Cu1—O3B—C2B—O4B	159.748	Cu1—O1B—C1B—O2B	-174.899
O1A—C2A—C3A—C1A	-55.288	O1A—C2A—C3A—C4A	110.669
O2A—C2A—C3A—C1A	125.189	O2A—C2A—C3A—C4A	-111.021
O3A—C1A—C3A—C2A	53.571	O4A—C1A—C3A—C2A	-128.441
C1A—C3A—C4A—C5A	-175.279	C3A—C4A—C5A—C6A	67.845
C4A—C5A—C6A—C7A	175.529	O3B—C2B—C3B—C1B	49.041
O4B—C2B—C3B—C1B	-134.123	C2B—C3B—C1B—O1B	-42.060
C2B—C3B—C1B—O2B	142.334	C1B—C3B—C4B—C5B	170.703
C3B—C4B—C5B—C6B	-63.696	C4B—C5B—C6B—C7B	-56.529
C1C—C2C—C3C—C4C	-1.152	C2C—C3C—C4C—C5C	-0.281
C3C—C4C—C5C—N2C	-177.732	C3C—C4C—C5C—N1C	1.444
C4C—C5C—N1C—C1C	-1.203	C5C—N1C—C1C—C2C	-0.263
N1C—C1C—C2C—C3C	1.440	C1D—C2D—C3D—C4D	1.102
C2D—C3D—C4D—C5D	-0.567	C3D—C4D—C5D—N2D	179.753
C3D—C4D—C5D—N1D	-0.001	C4D—C5D—N1D—C1D	0.026
C5D—N1D—C1D—C2D	0.520	N1D—C1D—C2D—C3D	-1.056

The only electronic transition of significance was at $\Delta E = 3.207455$ eV ($\lambda = 386.55$ nm). This is composed of H-1 → L+3 (72.22%) and H-1 → L+2 (11.31%). This was in gas phase.

From the structure, we can see that the complex contains a Cu atom with two units of n-butyl-malonic acid (BMA), two units of 2-aminopyridine (AP), and two units of water. One of the water molecules is directly bound to Cu, the other is not. We shall refer to these as BMAu (upper, termed A in ORTEP), BMAl (lower, termed B in ORTEP), APu (upper, termed C in ORTEP) and Apl (lower, termed D in ORTEP). The water molecules are W1 (bound) and W2 (not bound).

From the energy level diagram, shown in Fig. S6 below, it is clear that the highest set of orbitals, all virtual or unoccupied MOs, are of π character: the one at -0.4395 eV is mostly on BMAu, the one at -0.8572 eV is on APu, the ones at -1.2286 and -1.9103 eV are on APl and APu respectively. The MO at -2.3756 eV is a π MO on APl. This is the LUMO.

The SOMO is at -2.5824 eV and is of M-L type. The one immediately below it i.e. at -6.3947 eV is the HOMO, again of M-L character. H-1 is another M-L MO at -6.6287 eV. However, H-2 and H-3, at -6.6764 and -6.6886 eV, are π MOs, on the two AP units. H-4 at -6.7417 eV is distributed equally on the two AP units. H-5, H-6, H-7, H-8 are all of mixed metal-ligand type, at -6.7947, -7.0097, -7.1131 and -7.1893 eV respectively. H-5 is less on Cu, more on the two BMA units. H-6 has more density on Cu, less on the two BMA units, and little on the nearest neighbours of Cu. H-7 has some dπ of Cu mixed with some pπ of the BMA units, and much more of APl. H-8 is similar, except for dσ of Cu instead of dπ. H-9 is mostly π density on BMAu, with some Cu d and less π density on nearest neighbours of Cu on BMAl. H-10 is a σ MO onb the two BMA units. H-11 is similar to H-9. After these, we have some more π MOs, less σ MOs and some M-L mixed MOs.

Hence, our TDDFT calculations give the significant transition to be a M-L to Ligand π→π* transition.

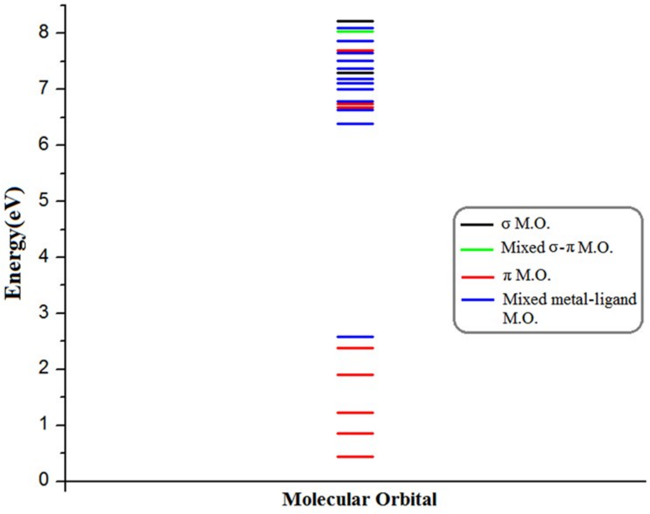


Fig. S9. Energy level diagrams of orbitals near the frontier MOs. Note the SOMO and LUMO are both mixed metal-ligand type orbitals.

We next present the gas-phase optimized structure of the MOC complexed with a dichromate anion. Structure of the complex is shown below.

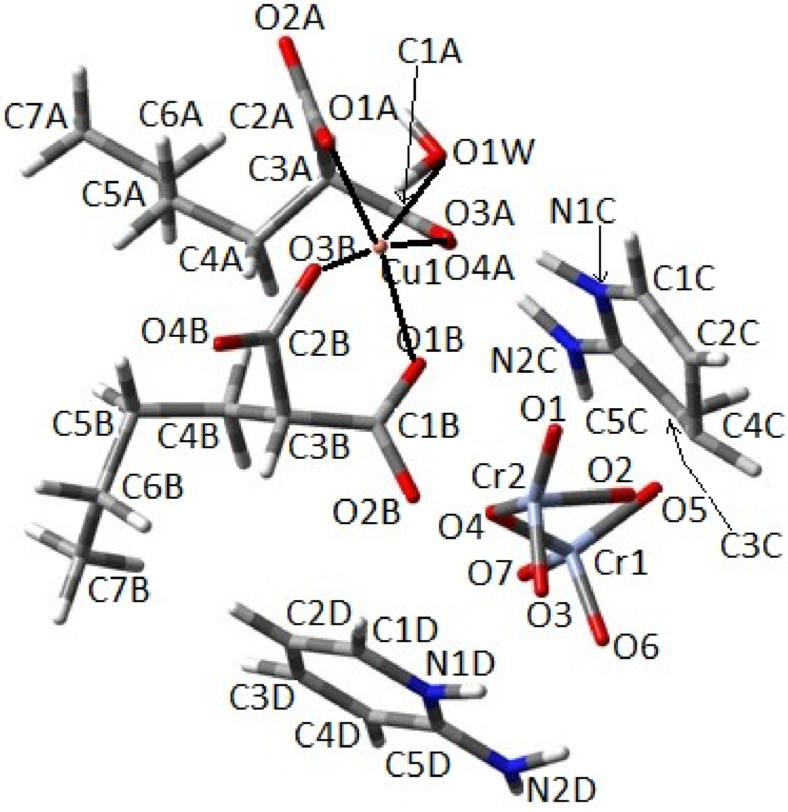


Fig. S10. Gas-phase optimized structure of the MOC-dichromate complex.

Some of the structural parameters are given below.

Table S12 Theoretically calculated bond distances (in Å)

Cu1—O1B	2.00525	Cu1—O1A	1.93423	Cu1—O3A	1.98511
Cu1—O3B	1.96813	Cu1—O1W	2.38389	O1A—C2A	1.34544
C2A—O2A	1.26501	C2A—C3A	1.56781	C3A—C1A	1.53526
C1A—O3A	1.33745	C1A—O4A	1.28841	C3A—C4A	1.57769
C4A—C5A	1.55729	C5A—C6A	1.55473	C6A—C7A	1.55306
C1B—O1B	1.28673	C1B—O2B	1.33220	C1B—C3B	1.52984
C3B—C2B	1.58647	C2B—O3B	1.33432	C2B—O4B	1.26469
C3B—C4B	1.57942	C4B—C5B	1.56135	C5B—C6B	1.56040
C6B—C7B	1.55668	C1C—C2C	1.37308	C2C—C3C	1.51191
C3C—C4C	1.56368	C4C—C5C	1.55046	C5C—N2C	1.33528
C5C—N1C	1.35627	C1C—N1C	1.42347	C1D—C2D	1.39742
C2D—C3D	1.43393	C3D—C4D	1.40452	C4D—C5D	1.43554
C5D—N2D	1.37071	C5D—N1D	1.38321	C1D—N1D	1.38623
Cr1 — O5	1.84373	Cr1 — O6	1.62216	Cr1 — O7	1.60195
Cr1 — O4	1.72591	O4 — Cr2	2.01122	Cr2 — O1	1.59173
Cr2 — O2	1.84432	Cr2 — O3	1.58894		

Table S13 Theoretically calculated hydrogen bonds (in Å)

O3A—H	1.57396	H—N1C	1.08188	O4A—H	1.52961
H—N2C	1.09767	O1A—H	2.05429	H—O1W	1.00139
O2B—H	2.29851	H—C1D	1.10014	O3B — H	2.05878
H — O1W	0.99625	O4B — H	2.57871	H — C5B	1.11149
O6 — H	2.00912	H — N2D	1.03665	O6 — H	2.45960
H — N1D	1.03393	O3 — H	2.56487	H — N1D	1.03393
O2 — H	2.07237	H — C4C	1.10998		

Table S14 Theoretically calculated other bonds (in Å)

O5 — C4C	2.47883	O5 — C3C	1.45771	O2 — C4C	1.48719
O2 — C3C	2.39586	O2B — Cr2	1.97729		

Table S15 Theoretically calculated bond angles (°)

O1A—Cu1—O1W	79.060	O1A—Cu1—O3A	88.534
O1A—Cu1—O1B	166.058	O1A—Cu1—O3B	97.199
O1W—Cu1—O3A	107.640	O1W—Cu1—O1B	114.882
O1W—Cu1—O3B	77.274	O3A—Cu1—O1B	86.961
O3A—Cu1—O3B	173.145	O1A—C2A—O2A	123.360
O3A—C1A—O4A	119.828	O1B—C1B—O2B	119.287
O3B—C2B—O4B	125.816	C2A—C3A—C1A	113.910
C2A—C3A—C4A	109.391	C3A—C4A—C5A	112.381
C4A—C5A—C6A	112.934	C5A—C6A—C7A	112.525
C2B—C3B—C1B	110.735	C2B—C3B—C4B	109.600
C3B—C4B—C5B	112.643	C4B—C5B—C6B	114.288
C5B—C6B—C7B	113.195	C1C—C2C—C4C	119.275
C2C—C4C—C3C	113.108	C4C—C3C—C5C	112.026
C3C—C5C—N2C	118.704	N2C—C5C—N1C	121.603
C5C—N1C—C1C	122.440	N1C—C1C—C2C	122.296
C1D—C2D—C3D	118.452	C2D—C3D—C4D	120.746
C3D—C4D—C5D	119.404	C4D—C5D—N2D	122.906
N2D—C5D—N1D	118.889	C5D—N1D—C1D	123.105
N1D—C1D—C2D	120.086	O5 — Cr1 — O6	113.001
O5 — Cr1 — O7	98.076	O6 — Cr1 — O7	106.569
O1 — Cr2 — O2	99.171	O1 — Cr2 — O3	110.926
O2 — Cr2 — O3	102.529	Cr1 — O4 — Cr2	108.533

Table S16 Theoretically calculated dihedral angles (°)

Cu1—O3A—C1A—O4A	-155.590	Cu1—O1A—C2A—O2A	-172.527
Cu1—O3B—C2B—O4B	-168.554	Cu1—O1B—C1B—O2B	-167.061
O1A—C2A—C3A—C1A	-48.957	O1A—C2A—C3A—C4A	75.791
O2A—C2A—C3A—C1A	133.003	O2A—C2A—C3A—C4A	-102.249
O3A—C1A—C3A—C2A	31.157	O4A—C1A—C3A—C2A	-150.417
C1A—C3A—C4A—C5A	-167.222	C3A—C4A—C5A—C6A	76.503
C4A—C5A—C6A—C7A	-176.205	O3B—C2B—C3B—C1B	37.775
O4B—C2B—C3B—C1B	-141.219	C2B—C3B—C1B—O1B	-50.480
C2B—C3B—C1B—O2B	126.002	C1B—C3B—C4B—C5B	174.631
C3B—C4B—C5B—C6B	-72.811	C4B—C5B—C6B—C7B	-80.371
C1C—C2C—C4C—C3C	30.552	C2C—C4C—C3C—C5C	-38.102
C4C—C3C—C5C—N2C	-152.862	C4C—C3C—C5C—N1C	25.396
C3C—C5C—N1C—C1C	-1.846	C5C—N1C—C1C—C2C	-8.924
N1C—C1C—C2C—C4C	-6.840	C1D—C2D—C3D—C4D	3.458
C2D—C3D—C4D—C5D	-2.621	C3D—C4D—C5D—N2D	177.851
C3D—C4D—C5D—N1D	1.440	C4D—C5D—N1D—C1D	-1.186
C5D—N1D—C1D—C2D	2.095	N1D—C1D—C2D—C3D	-3.134
O5—Cr1—O4—Cr2	-80.743	O6—Cr1—O4—Cr2	56.538
O7—Cr1—O4—Cr2	169.797	Cr1—O4—Cr2—O1	113.489
Cr1—O4—Cr2—O2	25.569	Cr1—O4—Cr2—O3	-73.173

Structure of the MOC-dichromate complex shows some structural disruption of the molecule especially on BMAu and BMAl, with more on BMAu, as the dichromate binds in the space in between these two moieties, forming bonds and deforming the original C-H, C-C bonds etc.

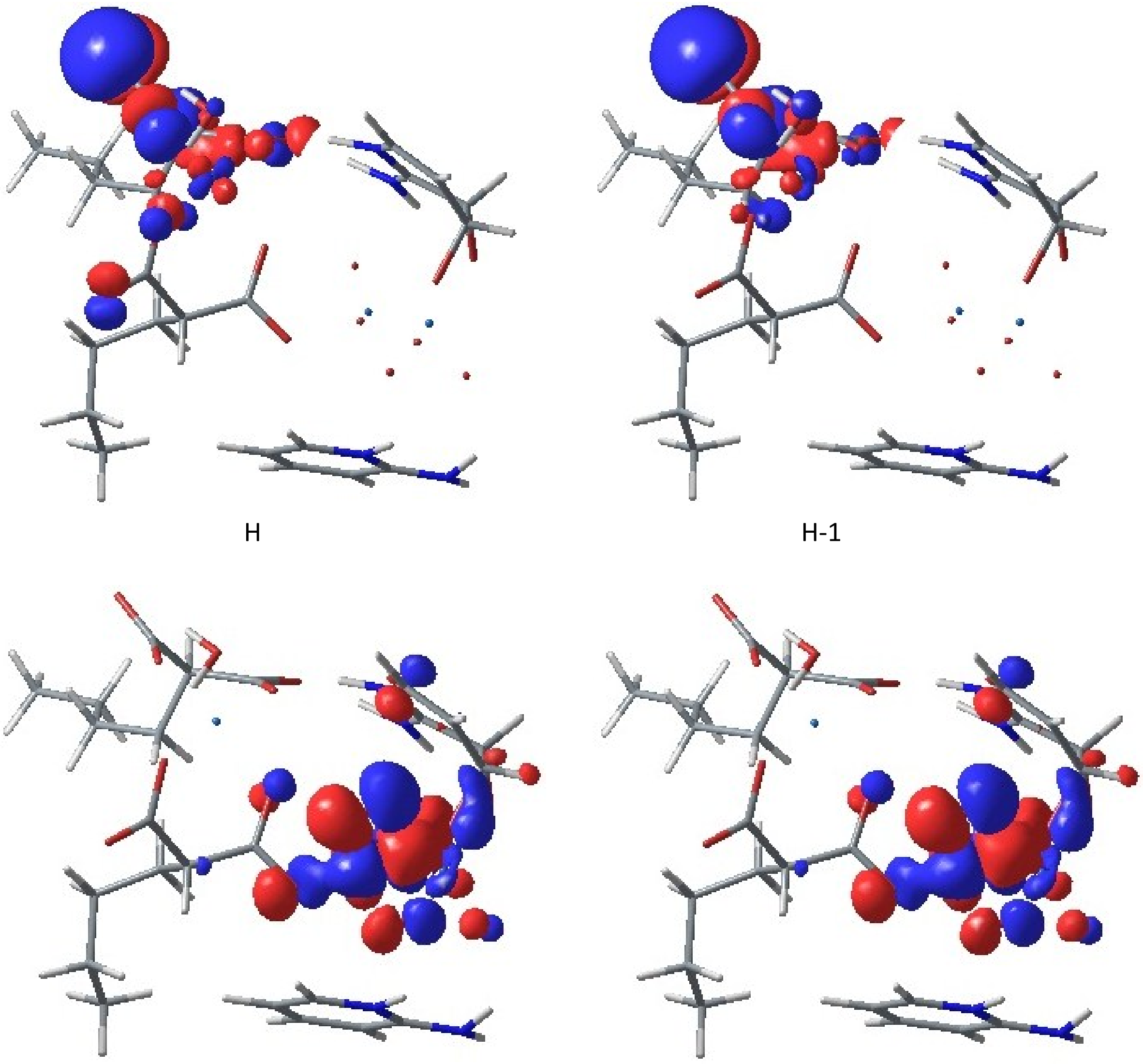


Fig. S11. Gas-phase frontier orbitals of the MOC-dichromate complex.

Now, a description of the energy level diagram, given in Fig. S9 below, is in order.

L+5, at -3.3250 eV is mostly in chromate and a little π density on APu. L+4 at -3.5914 eV is very similar to L+5, with a little density on near neighbor atoms of the metal on BMAl. L+3 at -4.1285 eV is very similar to L+5 in appearance. L+2 at -4.3928 eV consists of electron density on the chromate and its near neighbours atoms on APu and BMAl. L+1 at -4.4692 eV again resembles L+5. L at -4.7169 eV resembles L+2.

The SOMO at -6.1468 eV is made up of π density on BMAu and some metal d electrons, with little density on BMAl, close to metal. No density on the butyl chains is seen. The next MO i.e. HOMO at -6.5098 eV has less electrons on copper, more on its near neighbor atoms in BMAu, with no density on butyl chain. H-1 at -6.7517 is made up of mostly near neighbor atoms of copper on BMAu and BMAl, mostly π electrons, with less density on copper. H-2 at -6.8954 consists of some copper electrons, π electrons in BMAu, less π on BMAl (mostly near neighbours of metal), and little on butyl chains. H-3 at -7.0571 eV is similar, with more π density on BMAu than BMAl, and no density on the butyl chains. H-4 at -7.3754 eV is mostly on APu, and little of its neighbouring atoms on BMAu, with little densities on chromate and less on copper. H-5 at -7.4497 eV has some density on metal and its nearby atoms on BMAu and BMAl, with more on the former.

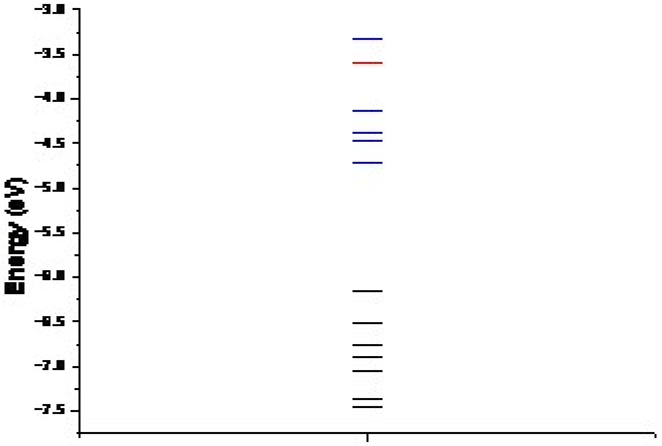


Fig. S12. Energy level diagram of molecular orbitals of the MOC-dichromate complex. Mostly chromate orbital is shown in red, dichromate – metal orbitals are shown in blue and ligand (of the complex) and metal orbitals are shown in black. All of the dichromate and ligand orbitals appearing in the above diagram are of π type.

Theoretical UV-visible spectra of the molecule and its complex with dichromate are shown below.

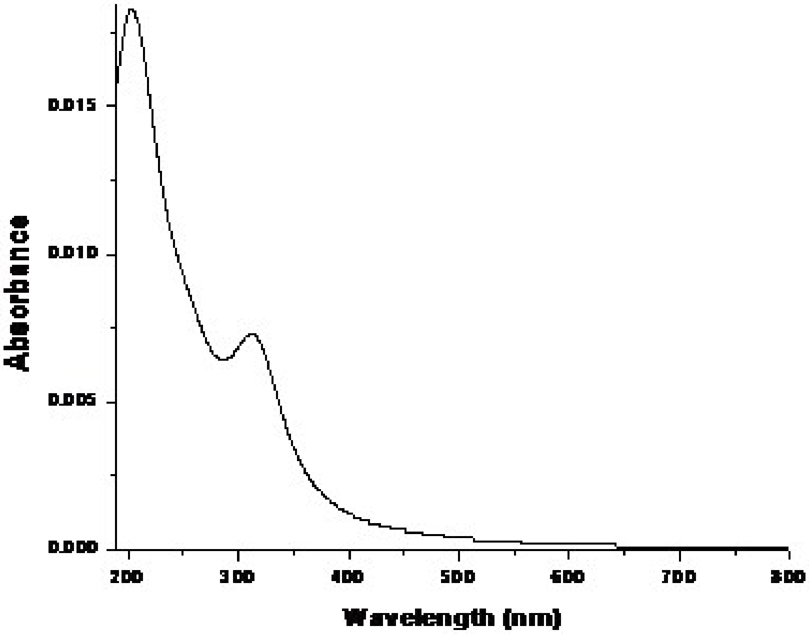


Fig. S13. Theoretical UV-Visible spectrum of the MOC showing λ_{max} at 204.07 and 313.28 nm.

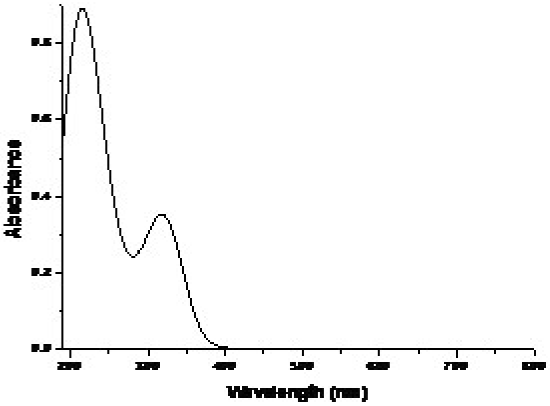


Fig. S14. Theoretical UV-visible spectrum of the MOC-dichromate complex showing λ_{max} at 217 and 320 nm.

Next, we show the results of calculations in water medium. The basis set and density functional remain the same.

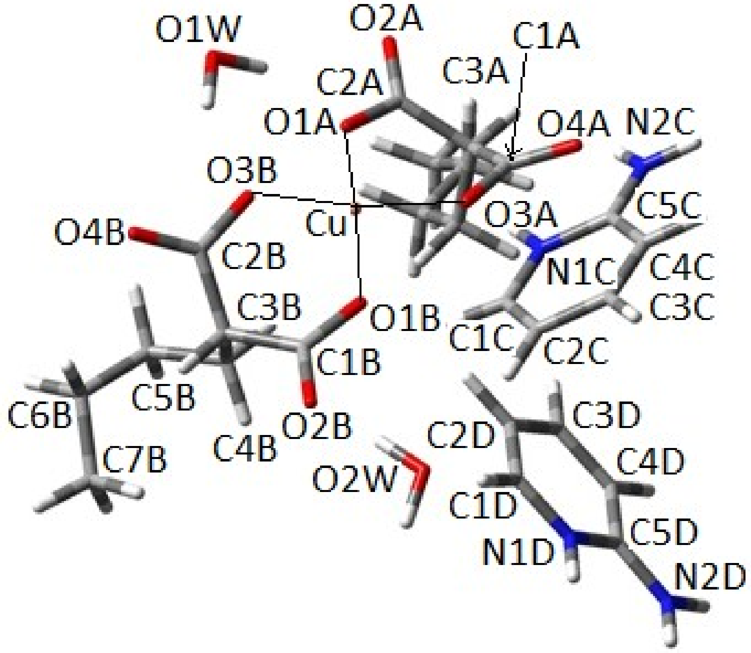


Fig. S15. DFT optimized structure of Cu(II) unit of MOC in water medium.

Table S17. Theoretically calculated distances (in Å)

Cu—O1B	1.95429	Cu—O1A	1.95033	Cu—O3A	1.97263
Cu—O3B	1.94351	Cu—O1W	3.70233	O1A—C2A	1.32584
C2A—O2A	1.25527	C2A—C3A	1.53296	C3A—C1A	1.52293
C1A—O3A	1.32570	C1A—O4A	1.26299	C3A—C4A	1.56395
C4A—C5A	1.54285	C5A—C6A	1.54274	C6A—C7A	1.53889
C1B—O1B	1.31574	C1B—O2B	1.26714	C1B—C3B	1.52774
C3B—C2B	1.52904	C2B—O3B	1.32674	C2B—O4B	1.25570
C3B—C4B	1.56495	C4B—C5B	1.54430	C5B—C6B	1.54604
C6B—C7B	1.54064	C1C—C2C	1.38051	C2C—C3C	1.42287
C3C—C4C	1.38807	C4C—C5C	1.42710	C5C—N2C	1.34649
C5C—N1C	1.37488	C1C—N1C	1.37275	C1D—C2D	1.38132
C2D—C3D	1.42279	C3D—C4D	1.38739	C4D—C5D	1.42312
C5D—N2D	1.34728	C5D—N1D	1.37258	C1D—N1D	1.37588

Table S18 Theoretically calculated hydrogen bonds

O3A—H	1.71786	H—N1C	1.05428	O4A—H	1.74578
H—N2C	1.04034	O1A—H	1.84107	H—O1W	0.99678
O2B—H	1.62753	H—O2W	1.01429	O1B—H	2.28915
H—C1C	1.09188	O2W—H	2.00179	H—C1D	1.10267
O3B—H	1.84855	H—O1W	0.99582		

Table S19 Theoretically calculated bond angles (°)

O1A—Cu—O1W	46.418	O1A—Cu—O3A	90.951
O1A—Cu—O1B	169.787	O1A—Cu—O3B	90.187
O1W—Cu—O3A	128.780	O1W—Cu—O1B	136.847
O1W—Cu—O3B	46.069	O3A—Cu—O1B	90.561
O3A—Cu—O3B	164.139	O1A—C2A—O2A	122.178
O3A—C1A—O4A	121.635	O1B—C1B—O2B	122.301
O3B—C2B—O4B	121.977	C2A—C3A—C1A	111.986
C2A—C3A—C4A	111.046	C3A—C4A—C5A	114.951
C4A—C5A—C6A	114.997	C5A—C6A—C7A	112.780
C2B—C3B—C1B	112.906	C2B—C3B—C4B	110.910
C3B—C4B—C5B	114.689	C4B—C5B—C6B	115.916
C5B—C6B—C7B	114.591	C1C—C2C—C3C	118.213
C2C—C3C—C4C	120.634	C3C—C4C—C5C	119.952
C4C—C5C—N2C	123.679	C4C—C5C—N1C	117.514
N2C—C5C—N1C	118.806	C5C—N1C—C1C	122.928
N1C—C1C—C2C	120.724	C1D—C2D—C3D	118.598
C2D—C3D—C4D	120.904	C3D—C4D—C5D	119.692
C4D—C5D—N2D	123.390	C4D—C5D—N1D	117.368
N2D—C5D—N1D	119.242	C5D—N1D—C1D	123.889
N1D—C1D—C2D	119.548		

Table S20 Theoretically calculated dihedral angles (°)

Cu—O3A—C1A—O4A	160.762	Cu—O1A—C2A—O2A	-173.434
Cu—O3B—C2B—O4B	170.463	Cu—O1B—C1B—O2B	-171.250
O1A—C2A—C3A—C1A	-51.115	O1A—C2A—C3A—C4A	72.806
O2A—C2A—C3A—C1A	131.120	O2A—C2A—C3A—C4A	-104.959
O3A—C1A—C3A—C2A	57.897	O4A—C1A—C3A—C2A	-123.681
C1A—C3A—C4A—C5A	-179.733	C3A—C4A—C5A—C6A	58.411
C4A—C5A—C6A—C7A	172.466	O3B—C2B—C3B—C1B	51.446
O4B—C2B—C3B—C1B	-131.054	C2B—C3B—C1B—O1B	-51.484
C2B—C3B—C1B—O2B	130.849	C1B—C3B—C4B—C5B	177.430
C3B—C4B—C5B—C6B	-56.678	C4B—C5B—C6B—C7B	-57.888
C1C—C2C—C3C—C4C	-1.110	C2C—C3C—C4C—C5C	-0.189
C3C—C4C—C5C—N2C	-177.886	C3C—C4C—C5C—N1C	1.725
C4C—C5C—N1C—C1C	-2.046	C5C—N1C—C1C—C2C	0.766
N1C—C1C—C2C—C3C	0.853	C1D—C2D—C3D—C4D	-0.110
C2D—C3D—C4D—C5D	0.104	C3D—C4D—C5D—N2D	-179.841
C3D—C4D—C5D—N1D	0.047	C4D—C5D—N1D—C1D	-0.202
C5D—N1D—C1D—C2D	0.199	N1D—C1D—C2D—C3D	-0.036

Next we consider the aqueous-phase optimized structure of the MOC-dichromate complex.

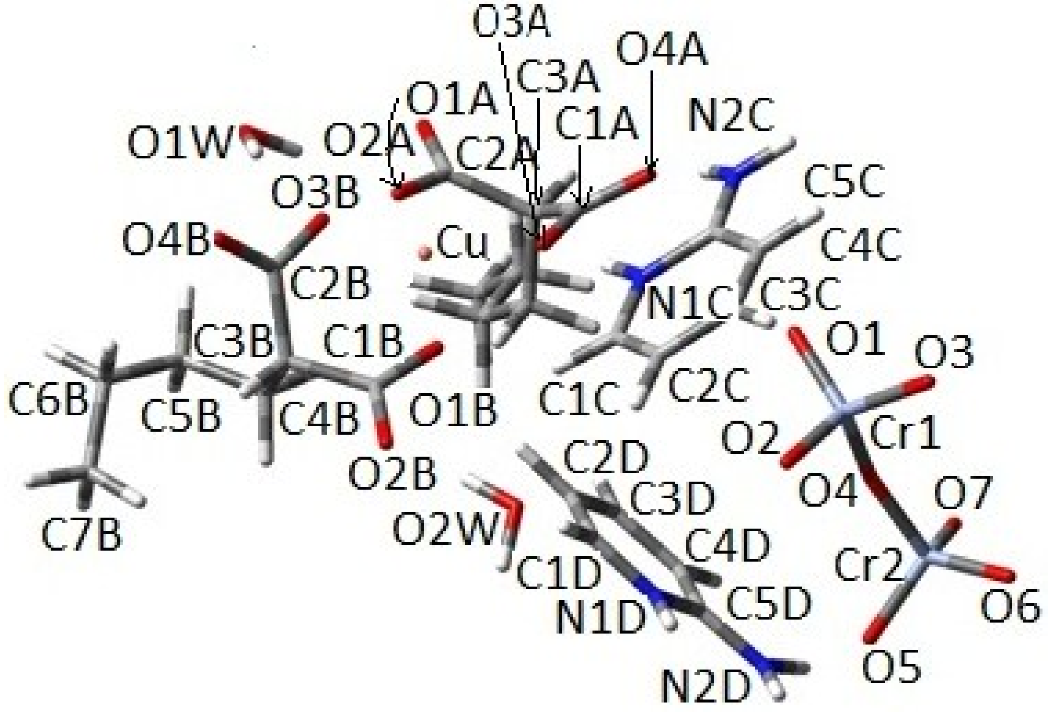


Fig. S16. Aqueous-phase optimized structure of the MOC-dichromate complex.

Table S21 Theoretically calculated distances (in Å)

Cu—O1B	1.96429	Cu—O1A	1.94825	Cu—O3A	1.95861
Cu—O3B	1.94836	Cu—O1W	3.70284	O1A—C2A	1.32769
C2A—O2A	1.25590	C2A—C3A	1.53365	C3A—C1A	1.52452
C1A—O3A	1.32715	C1A—O4A	1.26172	C3A—C4A	1.56543
C4A—C5A	1.54324	C5A—C6A	1.54247	C6A—C7A	1.54053
C1B—O1B	1.31660	C1B—O2B	1.26717	C1B—C3B	1.53411
C3B—C2B	1.53167	C2B—O3B	1.33032	C2B—O4B	1.25627
C3B—C4B	1.56734	C4B—C5B	1.54382	C5B—C6B	1.54769
C6B—C7B	1.53682	C1C—C2C	1.38150	C2C—C3C	1.42285
C3C—C4C	1.38939	C4C—C5C	1.42693	C5C—N2C	1.34740
C5C—N1C	1.37295	C1C—N1C	1.37136	C1D—C2D	1.37655
C2D—C3D	1.43421	C3D—C4D	1.37961	C4D—C5D	1.42303
C5D—N2D	1.33758	C5D—N1D	1.37960	C1D—N1D	1.37057
O1—Cr1	1.61230	O2—Cr1	1.61519	O3—Cr1	1.61993
Cr1—O4	1.79875	O4—Cr2	1.75373	O5—Cr2	1.63712
O6—Cr2	1.61302	O7—Cr2	1.61567		

Table S22 Theoretically calculated hydrogen bonds

O3A—H	1.70184	H—N1C	1.05215	O4A—H	1.78201
H—N2C	1.03900	O1A—H	1.81557	H—O1W	0.99995
O2B—H	1.63763	H—O2W	1.01493	O1B—H	2.33957
H—C1C	1.09154	O2W—H	2.08171	H—C1D	1.10379
O3B—H	1.86999	H—O1W	0.99387	O5—H	1.75477
H—N2D	1.03617	O1—H	3.08931	H—N2C	1.03900

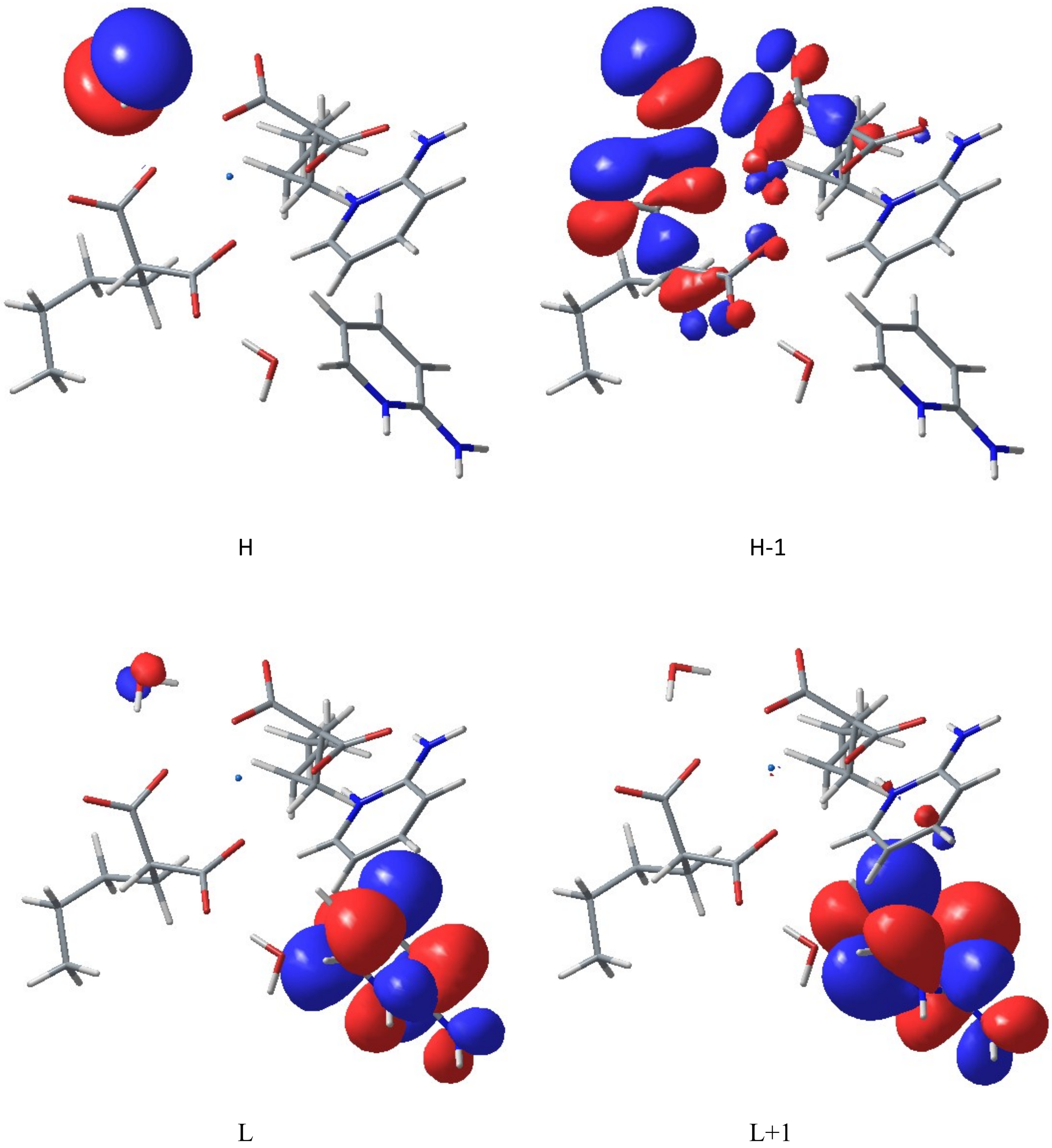
Table S23 Theoretically calculated bond angles (°)

O1A—Cu—O1W	45.898	O1A—Cu—O3A	92.259
O1A—Cu—O1B	158.250	O1A—Cu—O3B	92.340
O1W—Cu—O3A	133.115	O1W—Cu—O1B	132.969
O1W—Cu—O3B	46.517	O3A—Cu—O1B	93.857
O3A—Cu—O3B	152.765	O1A—C2A—O2A	121.886
O3A—C1A—O4A	121.743	O1B—C1B—O2B	122.683
O3B—C2B—O4B	122.132	C2A—C3A—C1A	113.125
C2A—C3A—C4A	110.814	C3A—C4A—C5A	115.357
C4A—C5A—C6A	115.191	C5A—C6A—C7A	112.762
C2B—C3B—C1B	111.245	C2B—C3B—C4B	111.315
C3B—C4B—C5B	114.814	C4B—C5B—C6B	115.844
C5B—C6B—C7B	114.336	C1C—C2C—C3C	118.082
C2C—C3C—C4C	120.712	C3C—C4C—C5C	119.916
C4C—C5C—N2C	123.854	C4C—C5C—N1C	117.429
N2C—C5C—N1C	118.709	C5C—N1C—C1C	123.153
N1C—C1C—C2C	120.696	C1D—C2D—C3D	118.773
C2D—C3D—C4D	121.094	C3D—C4D—C5D	119.140
C4D—C5D—N2D	122.098	C4D—C5D—N1D	117.788
N2D—C5D—N1D	120.113	C5D—N1D—C1D	123.817
N1D—C1D—C2D	119.296	O1—Cr1—O2	110.649
O1—Cr1—O3	110.290	O2—Cr1—O3	109.973
O1—Cr1—O4	107.813	O2—Cr1—O4	109.354
O3—Cr1—O4	108.707	Cr1—O4—Cr2	154.360
O4—Cr2—O5	109.095	O4—Cr2—O6	109.596
O4—Cr2—O7	108.995	O5—Cr2—O6	109.854
O5—Cr2—O7	109.700	O6—Cr2—O7	109.583

Table S24 Theoretically calculated dihedral angles (°)

Cu—O3A—C1A—O4A	150.579	Cu—O1A—C2A—O2A	-171.823
Cu—O3B—C2B—O4B	164.664	Cu—O1B—C1B—O2B	-175.051
O1A—C2A—C3A—C1A	-47.135	O1A—C2A—C3A—C4A	76.624
O2A—C2A—C3A—C1A	135.583	O2A—C2A—C3A—C4A	-100.658
O3A—C1A—C3A—C2A	58.459	O4A—C1A—C3A—C2A	-123.413
C1A—C3A—C4A—C5A	179.536	C3A—C4A—C5A—C6A	59.495
C4A—C5A—C6A—C7A	173.804	O3B—C2B—C3B—C1B	59.432
O4B—C2B—C3B—C1B	-123.190	C2B—C3B—C1B—O1B	-53.291
C2B—C3B—C1B—O2B	127.820	C1B—C3B—C4B—C5B	-171.743
C3B—C4B—C5B—C6B	-56.356	C4B—C5B—C6B—C7B	-60.267
C1C—C2C—C3C—C4C	-0.374	C2C—C3C—C4C—C5C	-0.105
C3C—C4C—C5C—N2C	179.870	C3C—C4C—C5C—N1C	0.934
C4C—C5C—N1C—C1C	-1.346	C5C—N1C—C1C—C2C	0.893
N1C—C1C—C2C—C3C	0.006	C1D—C2D—C3D—C4D	-0.624
C2D—C3D—C4D—C5D	0.195	C3D—C4D—C5D—N2D	-178.565
C3D—C4D—C5D—N1D	1.845	C4D—C5D—N1D—C1D	-3.686
C5D—N1D—C1D—C2D	3.303	N1D—C1D—C2D—C3D	-1.038
O1—Cr1—O4—Cr2	159.571	O2—Cr1—O4—Cr2	-80.068
O3—Cr1—O4—Cr2	40.010	Cr1—O4—Cr2—O5	107.019
Cr1—O4—Cr2—O6	-13.294	Cr1—O4—Cr2—O7	-133.216

We next present the frontier orbitals of the MOC alone in water medium.



H

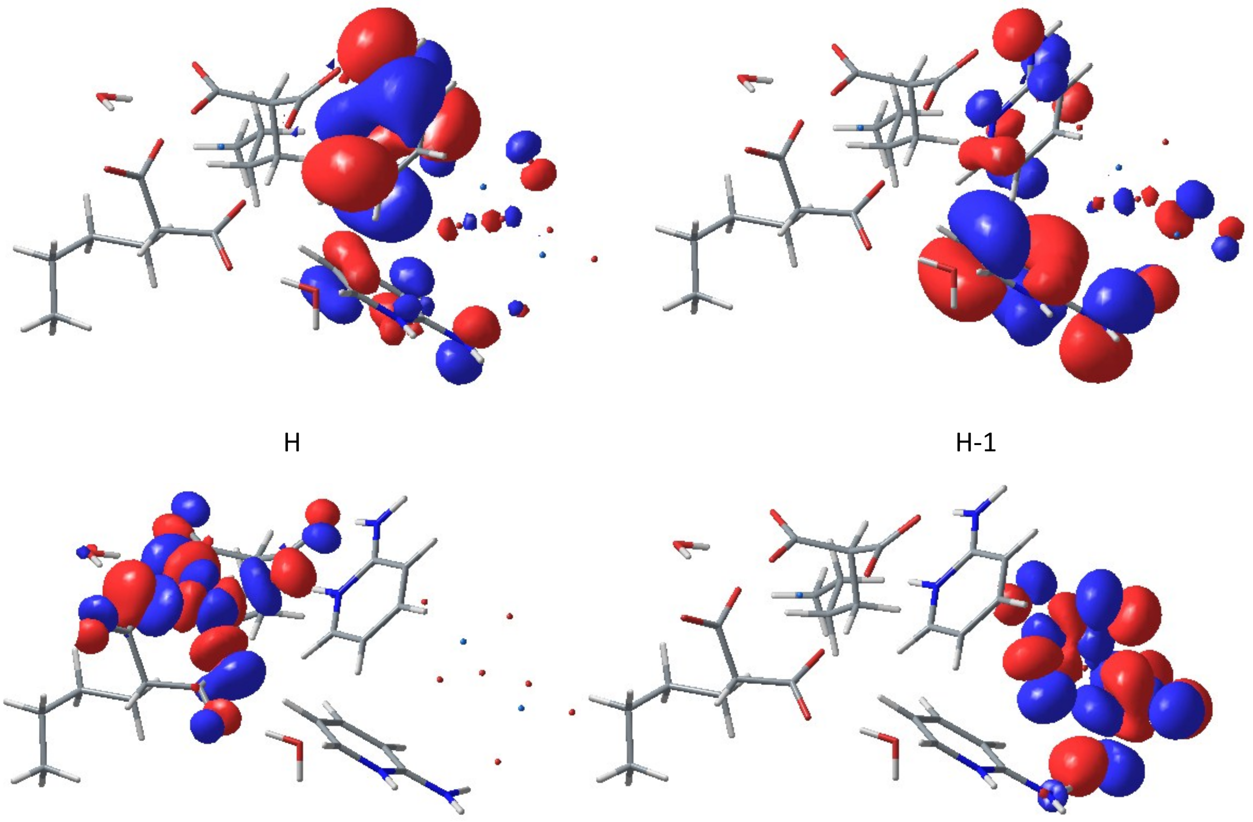
H-1

L

L+1

Fig. S17. The frontier orbitals of the Cu(II) unit of MOC in water medium.

Next, we present the frontier orbitals of the MOC-dichromate complex.



H

H-1

L

L+1

Fig. S18. The frontier orbitals of the MOC-dichromate complex in water medium.

As regards a description of energy levels of the receptor, let us start from the unoccupied (virtual) set. The levels are shown in Fig. S16 below. The SUMO at -3.4042 eV is a ML type orbital, with copper dσ mixing with p type orbitals on near neighbor BMA units, resembling a d_{xy} or d_{x2-y2} orbital. S+1 (-2.1007 eV) is a π MO mostly on AP (D) with little on AP (C) unit. S+2 (-1.7102 eV) is again a π MO mostly on AP (C) unit, with little on the AP (D) unit below. S+3 (-0.9143) is a π orbital of AP (D) unit only. S+4 (-0.5728 eV) is a π orbital of AP (C) unit alone. S+5 (-0.3918 eV) is another π MO, mostly on BMA (A) unit and its near neighbor atoms on AP (C) moiety, with less density on BMA (B) part and very little on copper. S+6 (-0.2313 eV) is a π orbital, mostly in BMA (B) unit, less on BMA (A) part, with a little copper dπ density.

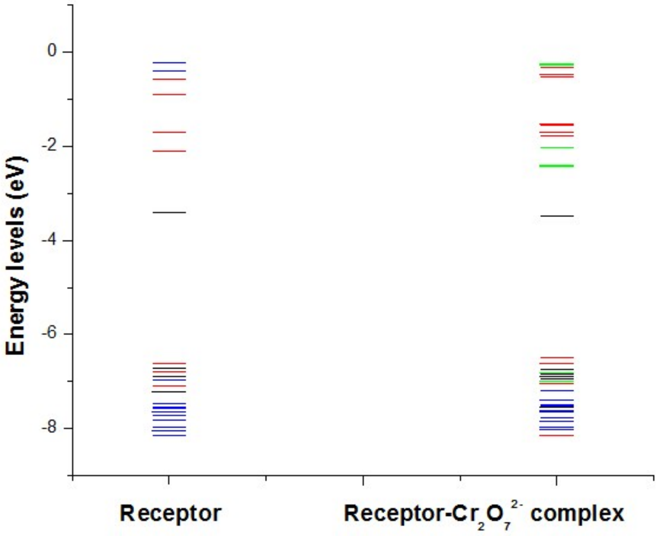


Fig. S19. Energy level diagram of molecular orbitals of MOC and MOC-$Cr_2O_7^{2-}$ complex in water medium.

Note that among this (unoccupied / virtual) set of orbitals, only the SUMO is singly occupied, the rest are all doubly occupied MOs.

The HOMO (-6.6206 eV) is a π MO on AP (C) unit. The H-1 at -6.7131 eV resembles the SUMO, but with less density on copper. This is a singly occupied orbital. H-2 at -6.7920 eV is a π MO on water at upper end. H-3 at -6.8845 eV again resembles H-1, but with much less density on copper and small amount on the two water molecules, more on the upper one. H-4 at -6.9607 eV has almost equal density on the two BMA units, and very little on Cu. This is another singly occupied MO. H-5 (-7.0859 eV) is a π MO on AP (D) unit. H-6 at -7.2138 resembles the SUMO, with much more density on Cu, and some on the upper water. H-7 (-7.4573 eV) is like a dπ-pπ ML type MO with copper and near neighbor atoms on the BMA units, including the water molecules. H-8 (-7.5308 eV) has less density on Cu, more on the two BMAs, with more on the (B) unit, and on the two water molecules. H-9 (-7.5784 eV) is similar to the above, with more density on copper. This is another singly occupied orbital. H-10 (-7.6410 eV) has much less density on Cu, and much more on near neighbor atoms of the BMAs, with more on the A unit, and little on the AP(C). H-11 (-7.7063 eV) has almost equal density on the two BMA units and the two water molecules, besides some on Cu. H-12 and H-13 (-7.8125 and -7.9608 eV) have density on copper, the two BMA units (with a little more on B) and much more on the lower water than the upper one. H-14 (-8.0424 eV) has a lot of Cu d density mixed with near neighbor atoms on the BMA units, with much less density on the water molecules. H-15 (-8.1472 eV) is a singly occupied orbital, with density on copper, the two BMA units and less on the water molecules.

For the complex, the SUMO at -3.4776 eV resembles the SUMO of receptor as described above. S+1, S+2 and S+3, at -2.4109, -2.4302 and -2.0218 eV respectively, are all dichromate MOs. S+4 and S+5 (-1.7905 and -1.7116 eV) are mixed AP (C and D) π and dichromate orbitals. S+6 and S+7 (-1.5674 and -1.5347 eV) are similar, with less density on dichromate. S+8 and S+9 (-0.5361, -0.4789 eV) are mostly π density on the AP units, with little on the BMA units and on dichromate. S+10 at -0.3374 eV consists of π density on the two BMA units, and less on AP (C) unit. S+11 (-0.2803 eV) is a dichromate orbital. S+12 (-0.2694 eV) is mostly π electrons on the BMA units and less on dichromate. S+13 and S+14 (-0.2653, -0.2531 eV) are dichromate orbitals.

The HOMO and H-1 (-6.4791 and -6.6179 eV) consist of π electrons of the AP units, and less of dichromate. While the H has more on AP (C) and less on AP (D), it is the other way round for H-1. H-2 at -6.7294 eV resembles the SUMO, and is a singly occupied orbital. H-3 (-6.8192 eV) is a dichromate orbital. H-4 (-6.8492 eV) again resembles the SUMO, with added density on the two water molecules. This is also a singly occupied orbital. H-5, H-7, H-9 (-6.8845, -6.9335 and -6.9852 eV respectively) are all dichromate orbitals. H-6 at -6.8900 eV is similar to H-4 and is also singly occupied. H-8 (-6.9471 eV) is similar to H-6, but with much more density on the BMAs, and much less on copper and the water molecules. This is also a singly occupied MO. H-10 (-7.0410 eV) is mainly on the upper water and its near neighbours on the two BMA units. H-11 (-7.1947 eV) is mainly on the two BMA units, copper and the upper water molecule. H-12 (-7.3920 eV) has density on the two BMA units, the two water molecules and copper. H-13 (-7.4982 eV) has less density on copper, more on BMA (A) unit, and a little on the dichromate. H-14 and H-16 (-7.5240, -7.5512 eV) are mostly on the dichromate, much less on the BMAs and on copper. H-15 (-7.5403 eV) is another singly occupied MO, with more density on the BMAs, less on Cu and water molecules and little on dichromate. H-17, H-18 and H-19 (at -7.6111, -7.6247 and -7.6383 eV) are three singly occupied orbitals, mostly on the two BMA units, less on Cu and the water molecules. H-20 and H-22 (-7.7757, -7.9662 eV) are mainly Cu, its near neighbor BMA atoms and the two water molecules. H-21 (-7.8410 eV) is similar, with less density on Cu and more on the lower water molecule. H-23 at -8.0111 eV is a singly occupied MO, similar to H-20 and H-22. H-24 (-8.0465 eV) is also singly occupied, with some dichromate density mixed in. H-24 (-8.1363 eV) is mainly on dichromate and less on its neighbouring BMA (A) and AP (D) units.

Binding energy of the the complex = Etotal (complex) – Etotal (receptor) – Etotal (dichromate)

= -6161.50431753 – (-3546.33650958) – (-2615.16349904) a.u.

= -0.00430891 a.u. = -0.11725234 eV = -2.7062 kcal/mol

Table S25 Charges on the various centres are given below

Centre	Water phase			
	MOC		complex	
	Mulliken	Lowdin	Mulliken	Lowdin
Cu	-0.6704	0.2203	0.6740	0.2129
O1A	-0.4966	-0.3051	-0.5056	-0.3070
O2A	-0.3886	-0.3882	-0.3898	-0.3870
O3A	-0.5062	-0.3078	-0.5218	-0.3087
O4A	-0.3896	-0.3765	-0.3812	-0.3678
C1A	0.3424	0.2692	0.3528	0.2718
C2A	0.3051	0.2451	0.3046	0.2478
C3A	-0.1322	-0.1754	-0.1185	-0.1729
C4A	-0.1733	-0.1457	-0.1697	-0.1463
C5A	-0.1222	-0.1696	-0.1324	-0.1712
C6A	-0.1783	-0.1784	-0.1768	-0.1788
C7A	-0.2282	-0.2647	-0.2322	-0.2661
O1B	-0.4638	-0.2869	-0.4631	-0.2889
O2B	-0.4108	-0.3852	-0.4084	-0.3850
O3B	-0.4961	-0.3012	-0.5064	-0.3147
O4B	-0.1555	-0.3913	-0.3839	-0.3884
C1B	0.3576	0.2701	0.3604	0.2689
C2B	0.3105	0.2452	0.3021	0.2422
C3B	-0.1555	-0.1799	-0.1689	-0.1807
C4B	-0.1600	-0.1456	-0.1527	-0.1486
C5B	-0.1069	-0.1696	-0.1258	-0.1771
C6B	-0.1678	-0.1793	-0.1538	-0.1780
C7B	-0.2505	-0.2706	-0.2615	-0.2719
O1W	-0.7246	-0.6495	-0.6959	-0.6293
O2W	-0.5987	-0.5715	-0.6033	-0.5792
C1C	0.0656	0.0416	0.0799	0.0481
C2C	-0.0801	-0.1412	-0.0912	-0.1433
C3C	-0.0034	-0.0320	-0.0061	-0.0341
C4C	-0.0707	-0.1407	-0.0739	-0.1411
C5C	0.2265	0.1818	0.2526	0.1889
N1C	-0.3576	-0.1443	-0.3537	-0.1347
N2C	-0.3513	-0.3134	-0.3564	-0.3095
C1D	0.0947	0.0387	0.0880	0.0345
C2D	-0.1231	-0.1419	-0.1163	-0.1420
C3D	-0.0080	-0.0230	-0.0129	-0.0281
C4D	-0.0615	-0.1270	-0.0525	-0.1241

C5D	0.2352	0.1909	0.2391	0.1940
N1D	-0.2983	-0.1097	-0.2985	-0.1120
N2D	-0.3201	-0.2791	-0.3449	-0.2973
Cr1			0.8038	-0.4885
Cr2			0.8279	-0.4758
O1			-0.4404	-0.1068
O2			-0.4415	-0.1096
O3			-0.4826	-0.1509
O4			-0.6667	-0.0873
O5			-0.5218	-0.1922
O6			-0.4625	-0.1323
O7			-0.4773	-0.1435

The UV-VIS spectra show some red shift from the molecule to its complex with chromate, but the amount is small (between 7 and 13 nm).