Electronic supplementary information

Photochemical reduction of Cr(VI) compounds by amino acid Schiff base copper complexes with hydroxyl group and titanium oxide composites in aqueous solutions

Yoshito Miyagawa[a], Arshak Tsaturyan[b,c*], Tomoyuki Haraguchi[a], Igor Shcherbakov[d] and Takashiro Akitsu[a]

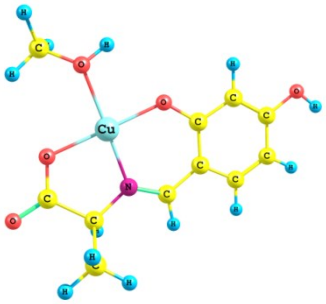
[a.] *Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
[b.] *Institute of Physical and Organic Chemistry, Southern Federal University, Stachki Av. 194/2, 344090 Rostov-on-Don, Russian Federation caturyan@sfedu.ru*
[c.] *Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Torino, Italy*
[d.] *Department of Chemistry, Southern Federal University, 7, Zorge Str., Rostov-on-Don, 344090 Russia*

Table 1 Crystallographic data for **CuGDB**, **CuADB**, **CuPDB** and **CuVDB**.

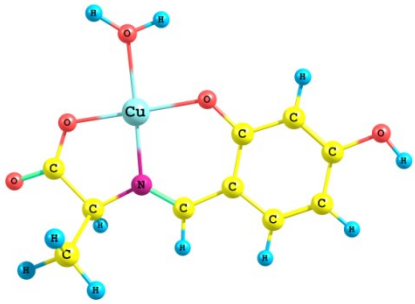
Compound	**CuGDB**	**CuADB**	**CuPDB**	**CuVDB**
Empirical formula	$C_9H_8CuNO_4$	$C_{10}H_{11}CuNO_5$	$C_{35}H_{40}Cu_2N_2O_{12}$	$C_{24}H_{30}Cu_2N_2O_{10}$
Formula weight	257.70	288.74	807.79	633.59
Crystal size, mm	0.600×0.100×0.100	0.35×0.33×0.32	0.275×0.105×0.056	-
Temperature, K	173	173	173	298
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1$	$P2_1$
a, Å	6.3126(13)	5.8152(7)	7.3484 (10)	14.11(2)
b, Å	13.094(3)	19..930(3)	14.6316(19)	14.386(13)
c, Å	11.740(3)	9.4998(12)	16.822(2)	12.833(17)
β, °	91.632(8)	102.749(2)	99.035(2)	114.93(9)
V, Å^3	970.0(4)	1073.9(2)	1786.2(4)	2362(5)
Z	4	4	2	2
$\rho_{(calc)}$, g/cm^3	1.765	1.786	1.502	0.890
μ, mm^{-1}	2.243	2.043	1.256	-
F(000)	520.0	588.0	836.0	652.0
Reflections collected	11551	5919	9909	-
Independent reflections	2260	4192	5618	-
Rint	0.0265	0.0439	0.0481	-
Θ range for data collection/°	2.334 – 27.86	2.198 - 27.50	1.86 - 27.50	-
Data / restraints / parameters	2260/0/152	4192/1/324	5618/0/476	-
Goodness-of-fit	0.968	1.005	0.976	6.085
R1, wR2 [I>2sigma(I)]	R1= 0.0348 wR_2= 0.1294	R1= 0.0211 wR_2= 0.0473	R1= 0.0296 wR_2= 0.0671	-
R1, wR2 (all data)	R1= 0.0459 wR_2= 0.1029	R1= 0.0226 wR_2= 0.0478	R1= 0.0343 wR_2= 0.0653	-
R_{wp}	-	-	-	3.35
R_p	-	-	-	2.20
Flack parameters	-	0.017(6)	0.023(9)	-
CCDC numbers	1984655	1984638	1984653	-

Table S2 Selected bond lengths (Å) and angles (°) for **CuGDB**, **CuPDB** and **CuVDB**.

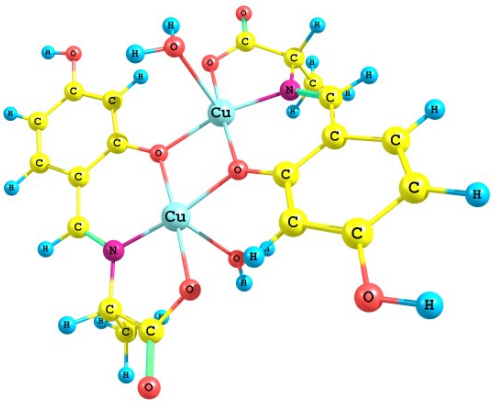
CuGDB			**CuPDB**			**CuVDB**		
Geometry parameters	XRD data	DFT	Geometry parameters	XRD data	DFT	Geometry parameters	PXRD data	
Cu1-O2	1.935(2)	1.928	Cu1-O5	1.940(2)	1.955	Cu1-O1	2.027(3)	1.962
Cu1-N1	1.942(2)	1.936	Cu1-O3	1.936(2)	1.927	Cu1-O6	1.922(3)	1.928
Cu1-O3	2.219(2)	1.960	Cu1-N1	1.932(3)	1.935	Cu1-N2	1.988(2)	1.931
-	-		Cu1-O4	2.316(3)	2.409	Cu1-O8	2.435(17)	2.550
-	-		Cu1-Cu2	3.022(6)	3.038	Cu1-Cu2	3.199(6)	3.027
	--		Cu1-O6	1.996(3)	2.026	Cu1-O2	2.055(3)	1.990
O4-Cu1-O2	176.66(10)	176.51	O5-Cu1-O3	166.70(11)	176.87	O1-Cu1-O6	166.54(2)	173.46
O4-Cu1-N1	93.94(9)	92.76	O5-Cu1-N1	94.98(11)	92.91	O1-Cu1-N2	93.04(12)	93.13
O2-Cu1-N1	84.61(9)	84.08	O3-Cu1-N1	83.24(11)	83.96	O6-Cu1-N2	83.39(12)	84.03
O4-Cu1-O3	92.01(9)	99.98	O5-Cu1-O4	96.91(11)	101.73	O1-Cu1-O8	85.30(7)	111.96
O2-Cu1-O3	91.32(10)	79.50	O3-Cu1-O4	96.38(11)	79.05	O6-Cu1-O8	108.16(7)	74.48
O4'-Cu01-O3	92.35(9)	88.52	O6-Cu01-O4	91.21(11)	88.40	O2-Cu01-O8	77.64(7)	83.86



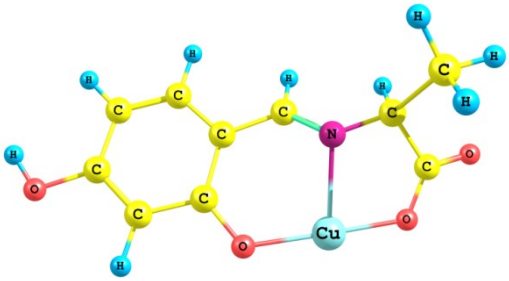
$Cu^{II}ADBMeOH$



$Cu^{II}ADBH_2O$



$Cu_2(ADB)_2H_2O$



$Cu^{I}ADB$

Fig. S1 The modeled structures of the **Cu^{II}ADB** with methanol and water coordinated molecule, **Cu^{I}ADB** and dimmer formed like to the crystal structure

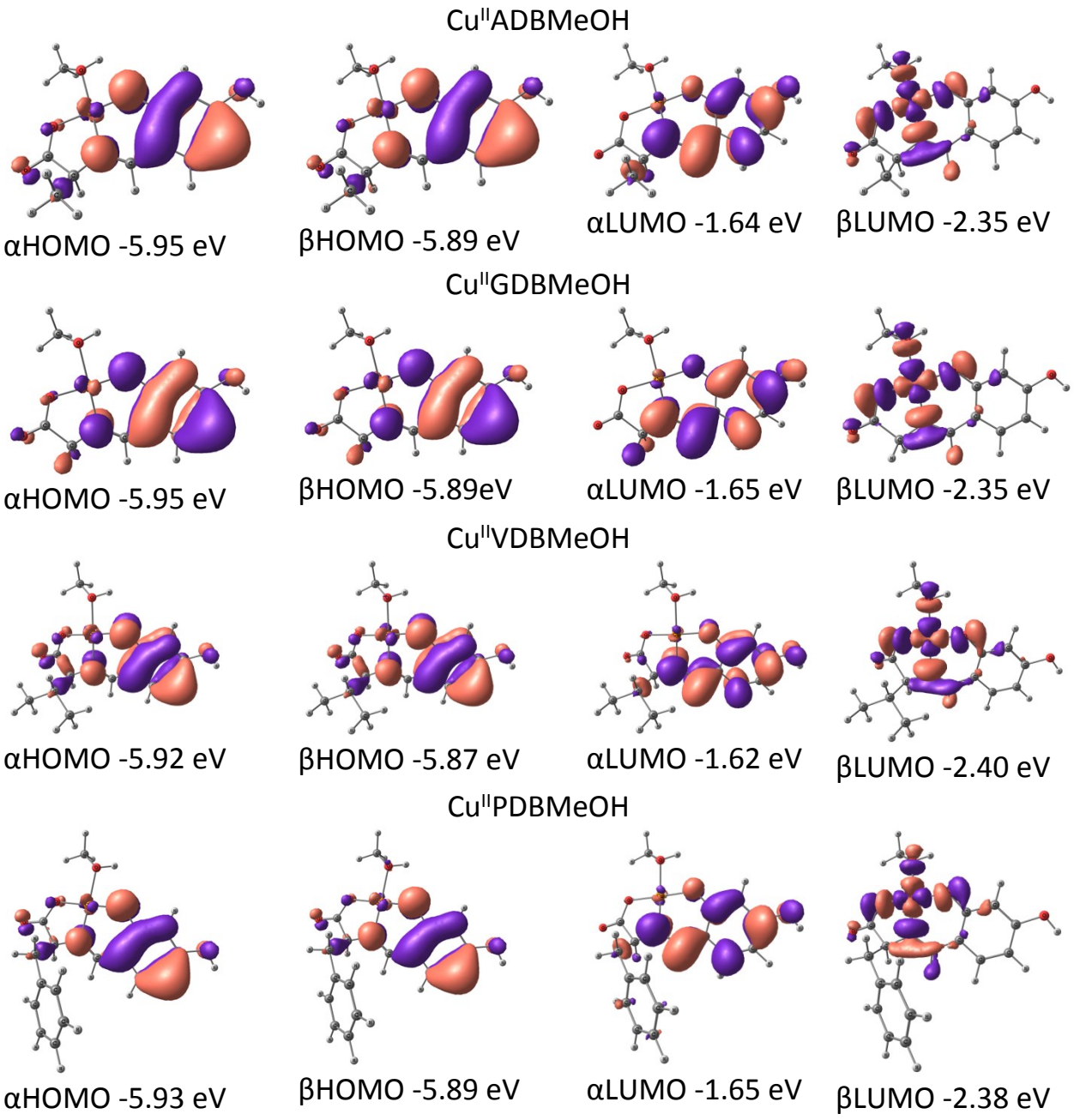


Fig. S2 Graphical view of the HOMO and LUMO (Isodensity contour 0.03) of the Cu(II) complexes with energy levels (eV) of molecular orbitals

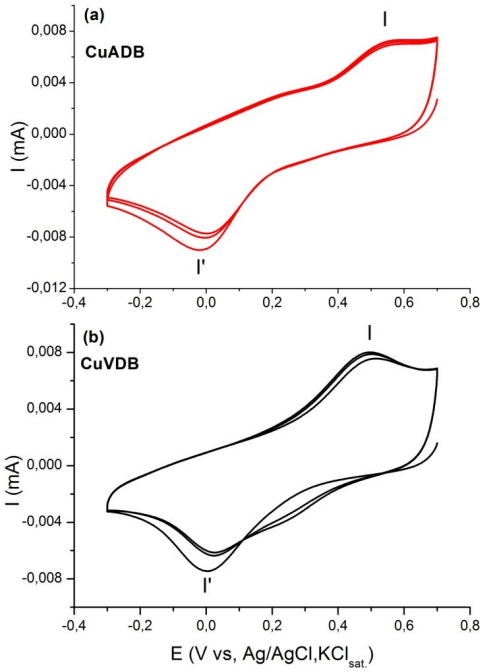


Fig. S3 Cyclic voltammetry for **CuADB** (a) and **CuVDB** (b) in aqueous solution.

Born–Haber thermodynamic cycle (Fig. S4) relates the electron attachment in the condensed phase to the corresponding process in the gas phase through the free energies of solvation for reactants and products.

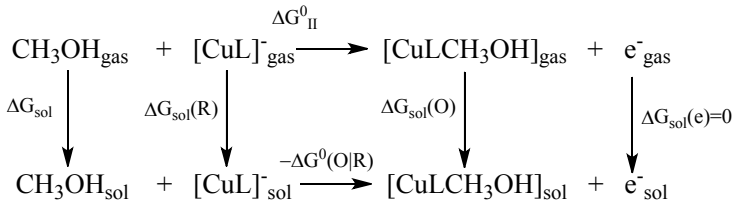


Fig. S4 Born–Haber cycle for the calculation of redox potential of copper complexes.

In order to evaluate the standard Gibbs free energy change $\Delta G^0_{O|R}$ from gas phase calculations and solvation theory calculations, a Born–Haber cycle is designed (Fig. 9), and the Gibbs free energy change is

$$-\Delta G^0_{O/R} = \Delta G^0_{II} + \Delta\Delta G^0_s \qquad (2)$$

where the Gibbs free energy change of solvation is

$$\Delta\Delta G^0_s = \Delta G^0_s(O) - \Delta G^0_s(R) - \Delta G^0_{sol} \quad (3)$$

and the Gibbs free energy change for the gas phase oxidation reaction is

$$\Delta G^0_{II} = \Delta G^0_g(O) - \Delta G^0_g(R) - \Delta G^0_g(CH_3OH) \qquad (4)$$

The absolute redox potential was calculated by following equation:

$$E^0_{O|R} = -\frac{\Delta G^0_{O|R}}{F} \qquad (5)$$

where F is the Faraday constant.

Table S3. Calculated Redox potentials (V, Ag/AgCl) for **CuGDB**, **CuADB**, **CuPDB** and **CuVDB** complexes.

Complex	E (V vs Ag/AgCl)		E (V absolute value)	
	MeOH	H_2O	MeOH	H_2O
CuADB	-0.352	-0.376	3.842	3.843
CuGDB	-0.352	-0.379	3.866	3.838
CuVDB	-0.319	-0.356	3.898	3.861
CuPDB	-0.332	-0.335	3.886	3.883

Table S4 Reaction conditions

Cu(II) complex	TiO_2	Wavelength [nm]	Solvent
CuGDB, **CuADB**, **CuPDB**, **CuVDB**, **CuESA**	×	Vis: 350 – 800	MeOH
CuGDB, **CuADB**, **CuPDB**, **CuVDB**, **CuESA**	×	UV: 300 – 400	MeOH
CuADB	×	Vis: 400 – 440, 460 – 495, 515 – 560, 575 – 625, 600 - 690	MeOH
CuGDB, **CuADB**, **CuPDB**, **CuVDB**, **CuESA**	○	UV: 300 – 400	MeOH
CuADB, **CuVDB**, **CuESA**	○	UV: 300 – 400	H_2O: pH 7
CuADB	○	UV: 300 – 400	H_2O: pH 3 - 10

Table S5 Cr(VI) reduction reaction kinetics with reaction time Cu(II) complex-methanol system under visible light (a) and UV light (b) irradiations.

Complex	Pseudo-first order model		Pseudo-second order model	
	k_1 min^{-1}	R^2	k_2 $g^{-1}\cdot min^{-1}$	R^2
		visible light		
CuADB	0.1126	0.9689	18.752	0.7885
CuVDB	0.0963	0.9563	11.859	0.8734
CuPDB	0.0951	0.8422	11.202	0.8765
CuGDB	0.1157	0.8847	17.991	0.8885
MeOH	0.0656	0.8507	5.0302	0.954
CuESA	0.0907	0.997	12.144	0.7298
		UV light		
CuADB	0.0299	0.9406	5.2413	0.827
CuVDB	0.0292	0.9581	4.9507	0.8351
CuPDB	0.0182	0.9562	2.609	0.9157
CuGDB	0.0308	0.9018	6.1797	0.7805
MeOH	0.0428	0.5427	7.2215	0.9108
CuESA	0.0565	0.9447	30.594	0.6952

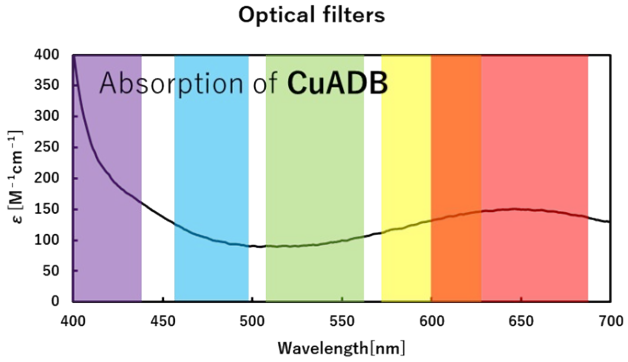


Fig. S5 Absorption vs wavelength plot of **CuADB** and the visible light filter region.

Table S6. Cr(VI) reduction reaction kinetics for **CuADB**-methanol system when irradiated with visible light of different wavelength range.

Wavelength	Pseudo-first order model		Pseudo-second order model	
	k_1 min^{-1}	R^2	k_2 $g^{-1}\cdot min^{-1}$	R^2
400-440 nm	0.0154	0.9918	2.2388	0.9221
460-495 nm	0.0811	0.9614	7.9967	0.8764
515-560 nm	0.0173	0.9249	2.6989	0.8665
575-625 nm	0.0525	0.9826	18.92	0.7384
600-690 nm	0.0467	0.9669	3.3231	0.9366

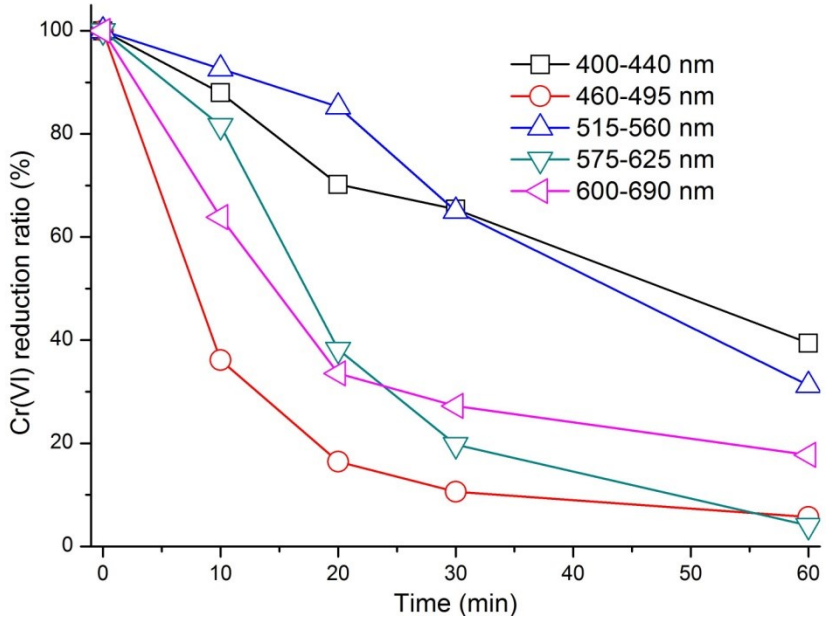


Fig. S6 Cr(VI) reduction in **CuADB**-methanol system when irradiated with visible light of different wavelength range

Table S7 Cr(VI) reduction reaction kinetics with reaction time of Cu(II) complex-TiO_2 hybrid system under UV light irradiation in methanol and aqueous solutions.

Complex	Pseudo-first order model		Pseudo-second order model	
	k_1 min^{-1}	R^2	k_2 $g^{-1}\cdot min^{-1}$	R^2
Methanol solutions				
CuADB+TiO_2	0.1053	0.9843	20.928	0.7171
CuVDB+TiO_2	0.092	0.9983	12.371	0.7551
CuPDB+TiO_2	0.0999	0.9849	17.647	0.7253
CuGDB+TiO_2	0.13	0.9995	36.659	0.7119
CuESA+TiO_2	0.1985	0.7296	107.61	0.8651
TiO_2	0.0703	0.7345	5.4732	0.9687
MeOH	0.0656	0.8507	5.0302	0.954
Aqueous solutions				
CuADB+TiO_2	0.0195	0.9951	1.6723	0.9653
CuVDB+TiO_2	0.037	0.9852	2.7358	0.8839
CuESA+TiO_2	0.0328	0.9978	2.3918	0.9201
TiO_2	0.0136	0.9353	1.4036	0.9928
H_2O	0.0025	0.942	1.0638	0.9996

Table S8 Cr(VI) reduction reaction kinetics in different pH values

pH	Pseudo-first order model		Pseudo-second order model	
	k_1 min^{-1}	R^2	k_2 $g^{-1}\cdot min^{-1}$	R^2
pH 3	0.0289	0.9825	2.1736	0.9153
pH 4	0.0240	0.9971	1.8857	0.9494
pH 5	0.0183	0.9957	1.61	0.971
pH 6	0.0131	0.9663	1.3919	0.991
pH 7	0.0157	0.9517	1.4823	0.9899
pH 8	0.0083	0.9982	1.2406	0.9939
pH 9	0.0094	0.914	1.2642	0.9956
pH 10	0.0092	0.969	1.278	0.9881

The reaction for first-order can be expressed by following:

A→B

The kinetic equation of the reaction expressed by

$$V = k_1 C_A = -\frac{dC}{dt} \quad (1)$$

After integration of eq 1 the eq 2 is obtained

$$\ln(C) = \ln(C_0) - k_1 t \quad (2)$$

The rate constant of pseudo-first order kinetic model is expressed

$$k_1 = \frac{1}{t} ln \frac{C_0}{C} \quad (3)$$

The reaction for second-order can be expressed by following:

A+B→C

The kinetic equation of the reaction expressed by

$$V = k_2 C_A C_B \quad (4)$$

In the case of C_A=C_B, eq 4 changes to

$$V = k_2 C^2 = -\frac{dC}{dt} \quad (5)$$

After integration of eq 4 the eq 5 is obtained

$$\frac{1}{C} = k_2 t + \frac{1}{C_0} \quad (6)$$

The rate constant of pseudo-second order kinetic model is expressed

$$k_2 = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right) \quad (7)$$