A Density Functional Theory Protocol for the Calculation of Redox Potentials of Copper Complexes

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Supplementary Information:

The choice of the calculation method, including the density functional, basis set, and solvation model, is based on the following calculations.

First, we optimized the Cu(I)/Cu(II) complexes with ligand **L1**, bis(1*H*-imidazol-2-yl)-methylamine, in gas phase using four functionals, CAM-B3LYP, B3PW91, CAM-B3LYP-D3, and ωB97X-D, in combination with five basis sets, 6-31G(d), 6-31G(d,p), 6-31G(2d,p), 6-31+G(d,p), and 6-31+G(2d,p) using the GAUSSIAN 09 suite of programs. The optimized structures of the two complexes are depicted in **figure SI-1**, and their optimized energies are summarized in **table SI-1**. From **figure SI-2** and **table SI-2**, it can be seen that evaluated Gibbs free energy change of the redox reaction in gas phase converges at basis set 6-31+G(d,p) for all the four functionals; therefore, the 6-31+G(d,p) will be applied for all the following calculations.

And then, the Cu(I)/Cu(II) complexes with ligand **L1** in aqueous solution are optimized using these four functionals in combination with three solvation models, SMD, IEFPCM, and CPCM, and the Gibbs free energy of solvation is summarized in **table SI-3**.

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Finally, the Gibbs free energy change of redox reaction in aqueous solution is evaluated using four functionals in combination with three solvation models. From **table SI-4**, it could be seen that the variation of Gibbs free energy change of the redox reaction is the smallest if the SMD model is used in combination with all the four functionals; therefore, it could be concluded that the SMD is the most stable solvation model among the three solvation models. In addition, it could be also concluded that the CAM-B3LYP functional is the most stable functional among the four functionals as the variation of Gibbs free energy change of the redox reaction is the smallest if the CAM-B3LYP functional is used in combination with all the three solvation models. Based on these calculations, we decide to use the CAM-B3LYP functional in combination with the SMD solvation model in all the other calculations.

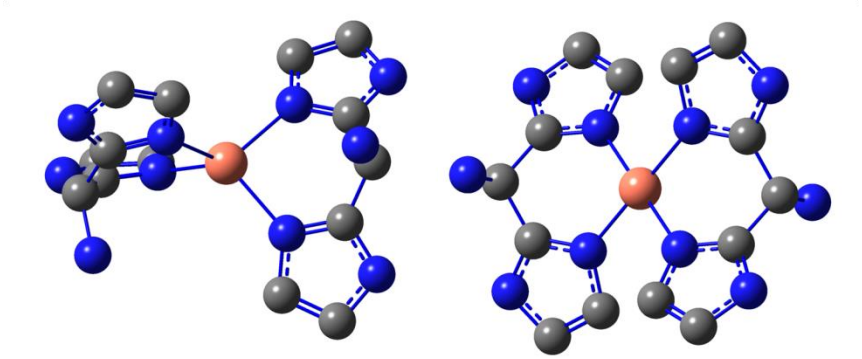

Figure SI-1. Optimized structures of the Cu(I)/Cu(II) complexes with ligand **L1**

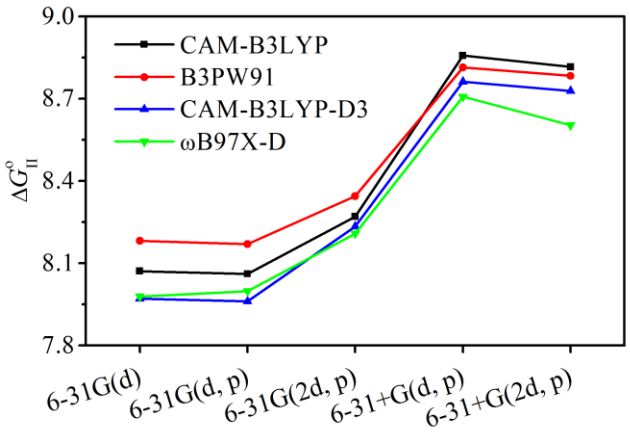

Figure SI-2. Gibbs free energy change of the redox reaction in gas phase evaluated using four functionals in combination with five basis sets

Table SI-1 Total energies of the Cu(I)/Cu(II) complexes in gas phase evaluated using four functionals in combination with five basis sets (unit: hartree)

Basis set	CAM-B3LYP	B3PW91	CAM-B3LYPD3	ωB97X-D
	Cu(I) complex			
6-31G(d)	-2731.18685	-2731.22247	-2731.23954	-2731.33363
6-31G(d,p)	-2731.22980	-2731.26479	-2731.28249	-2731.37510
6-31G(2d,p)	-2731.26793	-2731.30578	-2731.31984	-2731.41706
6-31+G(d,p)	-2731.31801	-2731.34255	-2731.36878	-2731.45518
6-31+G(2d,p)	-2731.33810	-2731.36505	-2731.38893	-2731.47836
	Cu(II) complex			
6-31G(d)	-2730.89361	-2730.92481	-2730.94671	-2731.04317
6-31G(d,p)	-2730.93696	-2730.96748	-2730.99005	-2731.08458
6-31G(2d,p)	-2730.96713	-2731.00178	-2731.02037	-2731.11847
6-31+G(d,p)	-2730.99888	-2731.02387	-2731.05156	-2731.13952
6-31+G(2d,p)	-2731.02051	-2731.04786	-2731.07325	-2731.16426

Table SI-2 Gibbs free energy change of the redox reaction in gas phase evaluated using four functionals in combination with five basis sets (unit: eV)

Basis set	CAM-B3LYP	B3PW91	CAM-B3LYP-D3	ωB97X-D
6-31G(d)	8.071	8.181	7.971	7.978
6-31G(d,p)	8.061	8.170	7.961	7.998
6-31G(2d,p)	8.270	8.345	8.234	8.208
6-31+G(d,p)	8.857	8.814	8.762	8.707
6-31+G(2d,p)	8.816	8.783	8.728	8.603

Table SI-3 Gibbs free energy of solvation in aqueous solution for the Cu(I) and Cu(II) complexes evaluated using three solvation models in combination with four functionals and 6-31+G(d,p) basis set (unit: eV)

Solvation model	CAM-B3LY	B3PW91	CAM-B3LYP-D3	ωB97X-D
		Cu(I)		
SMD	-1.704	-1.666	-1.733	-1.744
IEFPCM	-2.005	-1.987	-2.025	-2.040
CPCM	-2.010	-2.052	-2.028	-2.045
		Cu(II)		
SMD	-5.919	-5.893	-5.879	-5.835
IEFPCM	-6.185	-6.962	-6.222	-6.190
CPCM	-6.204	-6.183	-6.222	-6.194

Table SI-4 Gibbs free energy change of the redox reaction in aqueous solution evaluated using three solvation models in combination with four functionals and 6-31+G(d,p) basis set (unit: eV)

	SMD	IEFPCM	CPCM	Range*
CAM-B3LYP	4.678	4.642	4.663	0.035
B3PW91	4.639	4.586	4.683	0.096
CAM-B3LYP-D3	4.565	4.615	4.568	0.050
ωB97X-D	4.557	4.616	4.558	0.060
Range*	0.121	0.056	0.125	

*The range is evaluated as the difference between the maximum value and the minimum value of the same row or the same column.