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脯氨酸与 Cu、Cu^{+}和 Cu^{2+}配位体系的计算研究

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Computational Study on the Coordinate Systems of Proline with Cu, Cu^{+} and Cu^{2+}

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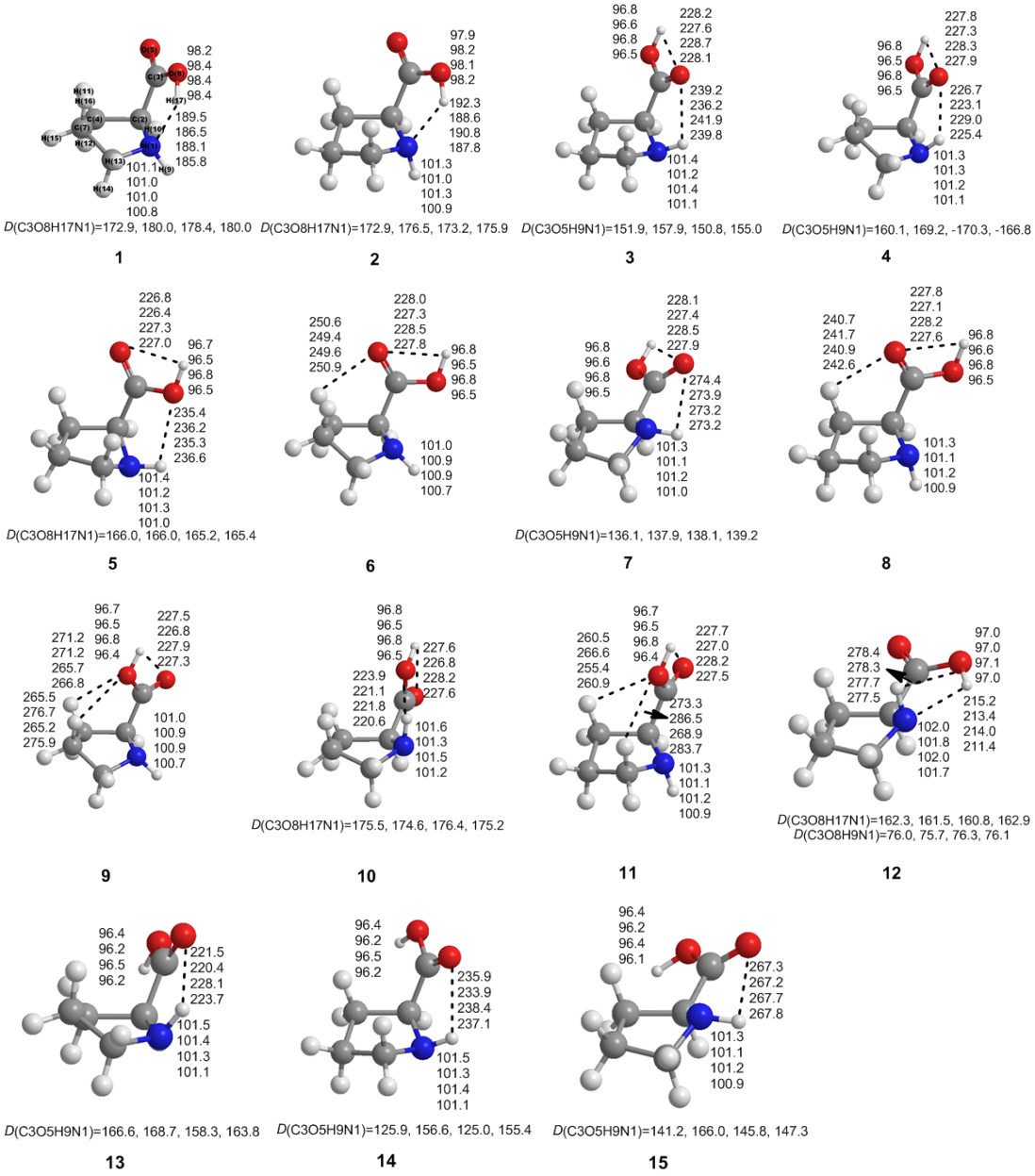
表S1　四种水平计算得到Cu的第一电离势(IP_1)和第二电离势值(IP_2)

Table S1　The first ionization potential (IP_1) and the second ionization potential (IP_2) of Cu were calculated at four levels

Method	IP_1/eV	IP_2/eV
M06-2X/6-311++G(2*d*, *p*)	7.53995	20.20380
M06-2X/TZVP	7.50096	20.02840
ωB97XD/6-311++G(2*d*, *p*)	7.59909	20.53557
ωB97XD/TZVP	7.50952	20.37624
exp[a]	7.72638	20.29240

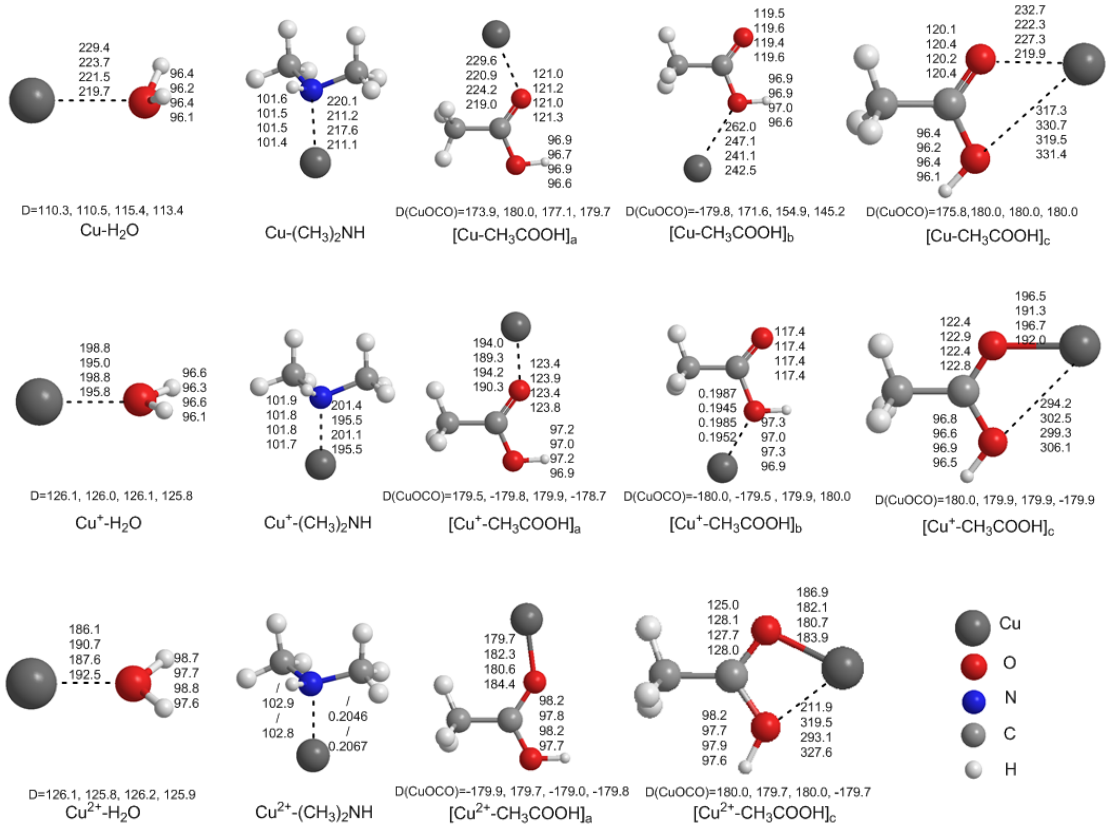
(a)　David, R, L. *CRC Handbook of Chemistry and Physics*; 84th ed; CRC Press Inc.: New York, 2003; 10, p 178



图S1　脯氨酸的稳定几何结构

Fig.S1　Geometrical structures of Proline conformers

The four values from top to bottom corresponding to the results optimized at the M06-2X/6-311++G(2*d*, *p*), ωB97XD/6-311++G(2*d*, *p*), M06-2X/TZVP and ωB97XD/TZVP levels, respectively, bond length in pm and dihedral angles (*D*) in °



图S2　[L-Cu]$^{0/1+/2+}$(L= H_2O、$(CH_3)_2NH$和CH_3COOH)体系几何结构

Fig.S2　Geometrical structures of [L-Cu]$^{0/1+/2+}$ (L= H_2O, $(CH_3)_2NH$, and CH_3COOH) complexes

The four values from top to bottom corresponding to the results optimized at the M06-2X/6-311++G(2*d*, *p*), ωB97XD/6-311++G(2*d*, *p*), M06-2X/TZVP and ωB97XD/TZVP levels, respectively, bond length in pm and dihedral angles (*D*) in °

表S2　20种[Pro-Cu]结构的相对能(E_{R1}和E_{R2})、结合能(E_B)、变形能(E_D)、相对吉布斯自由能($\Delta\Delta G$)和前线轨道能差$\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO})

Table S2　Relative energies (E_{R1} and E_{R2}), binding energies (E_B), deformation energies (E_D), relative Gibbs free energies ($\Delta\Delta G$) and $\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO}) of twenty kinds of [Pro-Cu] complexes

	Complex		A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	6.3	9.3	10.0	13.7	17.0	17.5	18.1	18.6	20.3
		TZVP	0.0	5.0	10.6	8.3	17.2	17.6	18.0	21.2	19.1	21.9
	ωB97XD	6-311++G(2*d*, *p*)	0.0	6.5	13.8	12.2	15.2	18.1	18.6	21.0	20.6	19.6
		TZVP	0.0	5.8	13.2	10.7	17.6	17.8	18.7	23.1	20.9	20.3
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-43.8	-37.5	-34.6	-33.9	-30.2	-26.8	-26.4	-25.7	-25.2	-23.5
		TZVP	-50.8	-45.8	-40.2	-42.5	-33.5	-33.1	-32.7	-29.5	-31.7	-28.9
	ωB97XD	6-311++G(2*d*, *p*)	-43.1	-36.6	-29.4	-30.9	-27.9	-25.0	-24.6	-22.1	-22.6	-23.5
		TZVP	-48.5	-42.6	-35.3	-37.7	-30.8	-30.6	-29.8	-25.4	-27.6	-28.2
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-47.7	-47.9	-48.5	-47.8	-30.2	-41.5	-41.5	-25.7	-40.2	-46.7
		TZVP	-56.3	-57.2	-56.2	-58.5	-33.5	-49.1	-49.4	-29.5	-48.0	-54.9
	ωB97XD	6-311++G(2*d*, *p*)	-50.1	-50.3	-46.1	-47.6	-27.9	-42.4	-42.7	-22.1	-40.5	-49.1
		TZVP	-57.4	-57.8	-54.0	-56.5	-30.8	-49.0	-49.7	-25.4	-46.7	-56.0
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	2.0	1.1	1.5	0.5	2.0	1.6	1.4	1.4	3.5	2.0
		TZVP	2.1	1.2	1.3	-0.2	1.7	1.4	1.5	1.6	3.5	2.2
	ωB97XD	6-311++G(2*d*, *p*)	2.5	1.7	2.2	0.9	2.1	2.8	2.4	1.4	5.0	2.3
		TZVP	2.2	1.7	2.2	0.5	1.8	2.8	2.2	2.0	5.5	2.1
ΔΔG /(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	6.1	8.1	10.3	12.5	15.6	16.3	15.7	18.9	21.0
		TZVP	0.0	4.4	10.1	8.3	15.3	17.1	16.9	17.9	19.3	22.2
	ωB97XD	6-311++G(2*d*, *p*)	0.0	6.4	13.9	12.5	15.2	16.3	18.7	18.3	21.6	20.1
		TZVP	0.0	6.2	13.9	11.6	17.8	16.7	19.2	21.1	22.5	20.9
Δε/eV	M06-2X	6-311++G(2*d*, *p*)	4.10	4.10	3.75	3.99	3.93	3.89	3.87	3.91	3.87	4.08
		TZVP	4.86	4.89	4.71	4.85	4.89	4.71	4.94	4.89	4.91	4.97
	ωB97XD	6-311++G(2*d*, *p*)	6.06	6.08	5.88	5.99	5.95	5.86	5.87	5.94	5.85	5.99
		TZVP	6.59	6.60	6.56	6.64	6.72	6.53	6.70	6.74	6.70	6.71

	Complex		A11	A12	A13	A14	A15	A16	A17	A18	A19	A20
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	23.4	24.6	27.9	31.5	32.4	34.5	35.0	35.3	42.7	49.6
		TZVP	23.6	27.6	30.2	37.1	34.9	37.4	39.2	40.9	48.4	57.4
	ωB97XD	6-311++G(2*d*, *p*)	20.7	23.7	30.7	32.9	35.7	41.1	43.0	40.4	48.4	52.9
		TZVP	22.3	28.7	33.3	36.7	35.6	43.5	45.4	43.9	51.2	59.6
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-20.5	-19.2	-15.9	-12.4	-11.4	-9.3	-8.8	-8.5	-1.1	5.8
		TZVP	-27.2	-23.2	-20.6	-13.7	-15.9	-13.4	-11.6	-9.9	-2.4	6.6
	ωB97XD	6-311++G(2*d*, *p*)	-22.4	-19.4	-12.5	-10.2	-7.4	-2.1	-0.1	-2.7	5.3	9.8
		TZVP	-26.2	-19.8	-15.2	-11.7	-12.9	-5.0	-3.0	-4.5	2.8	11.1
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-35.5	-22.2	-19.8	-22.8	-45.9	-13.2	-13.0	-23.6	-24.4	-17.5
		TZVP	-43.5	-26.1	-26.1	-25.1	-53.5	-18.9	-18.0	-26.6	-28.4	-19.4
	ωB97XD	6-311++G(2*d*, *p*)	-40.3	-22.2	-19.5	-24.0	-44.0	-9.1	-7.3	-19.7	-20.3	-15.8
		TZVP	-45.4	-22.4	-24.1	-26.9	-51.9	-13.9	-12.3	-23.3	-25.0	-16.7
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	10.9	1.4	2.0	2.0	1.5	0.4	0.3	1.5	2.4	0.9
		TZVP	12.3	1.4	2.1	1.9	1.5	0.6	0.4	1.8	3.5	0.9
	ωB97XD	6-311++G(2*d*, *p*)	9.6	1.4	2.8	3.1	2.4	0.5	0.3	1.7	3.2	1.1
		TZVP	12.2	1.3	3.4	2.5	3.1	0.7	0.7	1.9	3.7	1.1
ΔΔG /(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	21.3	23.1	24.2	25.0	32.5	30.3	29.9	30.2	40.4	44.0
		TZVP	21.3	23.4	25.3	32.2	35.1	33.2	33.0	36.9	46.0	52.3
	ωB97XD	6-311++G(2*d*, *p*)	19.8	19.8	27.1	28.0	35.6	37.9	35.7	35.6	45.0	47.8
		TZVP	26.8	26.1	30.5	33.4	35.9	37.0	40.5	39.2	47.6	56.0
Δε/eV	M06-2X	6-311++G(2*d*, *p*)	4.06	3.37	4.34	4.65	3.66	5.12	5.21	4.23	4.19	3.71
		TZVP	4.97	4.66	4.94	5.14	4.71	5.72	5.82	4.88	5.02	4.49
	ωB97XD	6-311++G(2*d*, *p*)	5.87	5.51	6.46	6.63	5.88	7.15	7.14	6.29	6.20	5.84
		TZVP	6.66	6.36	6.82	7.02	6.70	7.74	7.64	6.64	6.75	6.33

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S3　16种[Pro−Cu]$^+$结构的相对能(E_{R1}和E_{R2})、结合能(E_B)、变形能(E_D)、相对吉布斯自由能($\Delta\Delta G$)和前线轨道能差$\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO})

Table S3　Relative energies (E_{R1} and E_{R2}), binding energies (E_B), deformation energies(E_D), relative Gibbs free energies ($\Delta\Delta G$) and $\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO}) of sixteen kinds of [Pro−Cu]$^+$ complexes

	Complex		CI1	CI2	CI3	CI4	CI5	CI6	CI7	CI8
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	3.1	21.5	24.2	25.2	26.8	43.0	48.1
		TZVP	0.0	2.2	23.8	26.7	25.8	28.3	39.3	50.5
	ωB97XD	6-311++G(2*d*, *p*)	0.0	2.7	19.8	22.9	26.8	26.2	44.4	49.0
		TZVP	0.0	2.2	23.6	26.6	26.8	27.3	41.7	50.2
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311+G(2*d*, *p*)	-310.4	-307.3	-288.9	-286.2	-285.2	-283.6	-267.3	-262.3
		TZVP	-319.7	-317.5	-295.9	-293.0	-294.0	-291.4	-280.4	-269.2
	ωB97XD	6-311++G(2*d*, *p*)	-317.1	-314.4	-297.3	-294.2	-290.3	-290.9	-272.7	-268.1
		TZVP	-320.0	-317.8	-296.4	-293.4	-293.2	-292.7	-278.3	-269.8
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-325.5	-311.5	-288.9	-289.1	-299.1	-306.8	-282.1	-296.8
		TZVP	-336.5	-323.9	-295.9	-295.9	-310.0	-318.2	-296.4	-306.9
	ωB97XD	6-311++G(2*d*, *p*)	-335.2	-321.5	-297.3	-296.9	-307.0	-316.8	-290.1	-304.6
		TZVP	-340.0	-327.1	-296.4	-296.0	-312.0	-321.3	-296.7	-308.8
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	13.8	24.8	83.6	88.9	25.4	28.9	13.8	26.7
		TZVP	14.9	25.1	83.5	89.7	26.5	29.7	16.2	28.1
	ωB97XD	6-311++G(2*d*, *p*)	14.8	25.8	73.7	78.8	27.9	30.4	14.8	29.9
		TZVP	15.3	25.5	77.2	82.5	28.2	30.5	16.9	30.3
$\Delta\Delta G$/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	3.2	20.3	22.2	24.9	26.9	41.0	47.7
		TZVP	0.0	2.9	23.0	25.0	26.2	29.6	35.9	50.8
	ωB97XD	6-311++G(2*d*, *p*)	0.0	2.9	16.3	18.9	26.2	25.8	39.7	48.2
		TZVP	0.0	1.7	21.1	24.0	26.7	27.1	38.8	49.8
$\Delta\varepsilon$/eV	M06-2X	6-311++G(2*d*, *p*)	8.03	7.96	7.99	7.99	8.01	8.02	7.88	8.05
		TZVP	7.75	7.68	7.71	7.71	7.73	7.75	7.60	7.78
	ωB97XD	6-311++G(2*d*, *p*)	8.86	8.82	8.84	8.83	8.88	8.84	8.89	8.88
		TZVP	8.74	8.70	8.63	8.62	8.76	8.72	8.75	8.77
	Complex		CI9	CI10	CI11	CI12	CI13	CI14	CI15	CI16
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	55.8	78.8	94.5	103.9	107.1	108.1	112.7	152.3
		TZVP	52.8	80.6	100.2	110.5	113.1	114.0	110.2	152.8
	ωB97XD	6-311++G(2*d*, *p*)	58.2	73.6	95.3	104.3	108.6	109.6	112.0	163.5
		TZVP	55.0	75.3	100.2	109.8	113.8	114.0	115.8	162.7
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-254.5	-231.6	-215.8	-206.5	-203.3	-202.3	-197.6	-158.0
		TZVP	-267.0	-239.1	-219.6	-209.2	-206.7	-205.7	-209.5	-166.9
	ωB97XD	6-311++G(2*d*, *p*)	-258.9	-243.5	-221.8	-212.8	-208.5	-207.5	-205.1	-153.6
		TZVP	-265.0	-244.7	-219.8	-210.2	-206.2	-206.0	-204.2	-157.3
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-269.6	-231.6	-237.0	-229.7	-226.5	-225.5	-208.0	-172.0
		TZVP	-283.7	-239.1	-242.7	-235.9	-232.7	-232.4	-220.9	-182.9
	ωB97XD	6-311++G(2*d*, *p*)	-275.9	-243.5	-244.5	-238.7	-234.1	-233.3	-218.9	-170.3
		TZVP	-283.7	-244.7	-244.1	-238.7	-234.0	-234.6	-219.3	-176.0
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	18.8	13.4	10.0	25.6	10.4	11.8	13.4	13.2
		TZVP	21.6	13.0	10.2	25.5	10.5	11.1	15.1	13.8
	ωB97XD	6-311++G(2*d*, *p*)	19.4	14.5	11.1	26.5	11.6	14.3	14.0	15.2
		TZVP	21.0	14.2	11.1	25.7	11.9	13.1	14.3	15.1
$\Delta\Delta G$/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	54.3	75.6	90.2	97.9	100.8	101.8	107.1	149.6
		TZVP	52.1	75.9	96.7	104.2	112.1	109.4	107.8	151.5
	ωB97XD	6-311++G(2*d*, *p*)	56.2	71.2	91.9	98.6	103.4	103.4	106.9	160.5
		TZVP	53.6	72.5	97.2	104.2	109.2	108.0	110.5	160.2
$\Delta\varepsilon$/eV	M06-2X	6-311++G(2*d*, *p*)	8.02	6.45	6.39	5.39	5.28	5.16	5.13	5.70
		TZVP	7.73	6.22	6.18	5.11	5.03	4.89	5.41	5.44
	ωB97XD	6-311++G(2*d*, *p*)	9.00	8.08	7.99	6.95	6.81	6.70	6.65	7.27
		TZVP	8.86	8.00	7.91	6.79	6.66	6.55	6.49	7.10

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S4　16种[Pro−Cu]$^{2+}$结构的相对能(E_{R1}和E_{R2})、结合能(E_B)、变形能(E_D)、相对吉布斯自由能($\Delta\Delta G$)和前线轨道能差$\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO})

Table S4　Relative energies (E_{R1} and E_{R2}), binding energies (E_B), deformation energies (E_D), relative Gibbs free energies ($\Delta\Delta G$) and $\Delta\varepsilon$(ε_{LUMO}-ε_{HOMO}) of sixteen kinds of [Pro-Cu]$^{2+}$ complexes

	Complex		CII1	CII2	CII3	CII4	CII5	CII6	CII7	CII8
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	4.9	8.3	10.2	15.5	27.4	44.6	46.3
		TZVP	0.0	5.1	11.3	11.6	18.3	30.9	50.7	52.1
	ωB97XD	6-311++G(2*d*, *p*)	0.0	5.2	6.8	8.4	14.2	24.9	30.0	32.2
		TZVP	0.0	5.1	8.7	9.7	16.3	27.0	36.6	38.4
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-1034.1	-1029.2	-1025.9	-1023.9	-1018.7	-1006.7	-989.5	-987.8
		TZVP	-1024.4	-1019.3	-1013.1	-1012.8	-1006.1	-993.5	-973.7	-972.3
	ωB97XD	6-311++G(2*d*, *p*)	-1083.7	-1078.5	-1076.9	-1075.3	-1069.5	-1058.8	-1053.7	-1051.5
		TZVP	-1073.6	-1068.5	-1064.9	-1063.9	-1057.3	-1046.5	-1037.0	-1035.2
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-1048.8	-1041.2	-1049.1	-1027.8	-1041.9	-1029.9	-992.5	-987.8
		TZVP	-1040.4	-1032.2	-1039.2	-1018.3	-1032.8	-1019.5	-976.6	-972.3
	ωB97XD	6-311++G(2*d*, *p*)	-1101.1	-1093.7	-1102.5	-1082.3	-1095.4	-1084.4	-1056.4	-1051.5
		TZVP	-1092.0	-1084.4	-1092.7	-1072.8	-1085.8	-1074.3	-1039.6	-1035.2
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	39.8	38.5	47.9	48.7	49.8	41.2	152.3	148.6
		TZVP	38.8	38.4	47.2	47.4	48.0	39.3	152.9	148.2
	ωB97XD	6-311++G(2*d*, *p*)	38.8	37.7	46.8	47.8	49.3	40.7	156.0	152.0
		TZVP	37.2	36.2	45.4	45.6	46.8	39.2	160.7	155.6
$\Delta\Delta G$/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	0.0	4.5	10.3	10.8	17.0	28.4	50.0	51.6
		TZVP	0.0	-0.6	12.2	11.3	18.0	30.8	55.1	56.3
	ωB97XD	6-311++G(2*d*, *p*)	0.0	4.6	9.3	10.4	16.0	26.5	34.6	37.4
		TZVP	0.0	4.2	9.6	10.5	17.1	26.9	39.8	40.7
$\Delta\varepsilon$/eV	M06-2X	6-311++G(2*d*, *p*)	9.00	8.98	9.27	8.92	9.23	9.29	7.72	7.67
		TZVP	8.86	8.83	9.03	8.76	9.00	9.05	7.71	7.67
	ωB97XD	6-311++G(2*d*, *p*)	9.90	9.89	9.82	9.84	9.81	9.84	10.06	10.01
		TZVP	9.77	9.78	9.68	9.70	9.67	9.70	10.04	10.00

	Complex		CII9	CII10	CII11	CII12	CII13	CII14	CII15	CII16
E_{R1}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	53.9	74.9	77.5	77.8	90.4	112.2	145.8	179.2
		TZVP	55.2	73.8	81.1	77.4	91.5	115.4	138.8	180.0
	ωB97XD	6-311++G(2*d*, *p*)	46.3	76.9	69.2	81.3	81.8	102.9	135.7	178.3
		TZVP	49.5	74.9	74.6	79.1	85.0	107.7	131.1	176.4
E_{R2}/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-980.2	-959.3	-956.7	-956.4	-943.7	-922.0	-888.3	-854.9
		TZVP	-969.2	-950.6	-943.3	-947.0	-932.9	-909.0	-885.6	-844.4
	ωB97XD	6-311++G(2*d*, *p*)	-1037.4	-1006.8	-1014.5	-1002.4	-1001.9	-980.8	-948.0	-905.4
		TZVP	-1024.1	-998.6	-999.0	-994.5	-988.6	-965.9	-942.5	-897.1
E_B/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	-995.4	-963.2	-979.9	-971.4	-957.6	-956.4	-903.1	-866.9
		TZVP	-985.9	-956.1	-969.3	-963.3	-948.9	-946.7	-901.6	-857.3
	ωB97XD	6-311++G(2*d*, *p*)	-1055.6	-1013.8	-1040.1	-1020.3	-1018.7	-1017.3	-965.4	-920.5
		TZVP	-1044.0	-1007.6	-1026.8	-1013.7	-1007.4	-1004.9	-960.9	-913.1
E_D/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	46.9	47.1	66.7	35.4	67.9	73.1	47.2	77.0
		TZVP	48.9	43.8	69.5	33.2	69.5	75.7	50.0	76.8
	ωB97XD	6-311++G(2*d*, *p*)	48.2	45.9	69.5	34.0	71.1	77.4	38.2	50.5
		TZVP	49.1	42.8	71.4	31.9	71.8	79.0	39.8	50.1
$\Delta\Delta G$/(kJ·mol^{-1})	M06-2X	6-311++G(2*d*, *p*)	61.7	74.8	85.5	77.6	98.5	119.5	155.9	180.2
		TZVP	62.0	71.0	87.9	77.1	98.4	121.5	147.9	179.9
	ωB97XD	6-311++G(2*d*, *p*)	55.4	76.1	79.0	80.8	90.5	111.5	142.3	181.6
		TZVP	57.0	73.0	83.1	78.9	92.7	115.3	137.0	178.6
$\Delta\varepsilon$/eV	M06-2X	6-311++G(2*d*, *p*)	7.68	8.44	7.90	8.37	7.31	7.58	7.28	7.84
		TZVP	7.63	8.36	7.85	8.29	7.26	7.55	7.27	7.73
	ωB97XD	6-311++G(2*d*, *p*)	9.96	9.72	10.14	9.67	9.65	9.90	9.36	9.54
		TZVP	9.90	9.61	10.10	9.58	9.60	9.86	9.30	9.46

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S5　22种[Pro-Cu]结构的转动系数(*A*、*B*和*C*)、偶极矩(*μ*)和O−H与N−H的伸缩振动频率

Table S5　Rotational constants (*A*, *B* and *C*), dipole moment (*μ*) and stretching vibrational frequencies (ν_{O-H} and ν_{N-H}) of twenty kinds of [Pro-Cu] complexes

	Complex		A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
A/GHz	M06-2X	6-311++G(2*d*, *p*)	2.094	2.166	1.439	1.356	2.209	1.600	1.514	2.184	1.645	2.046
		TZVP	2.129	2.183	1.434	1.369	2.200	1.581	1.513	2.134	1.618	2.067
	ωB97XD	6-311++G(2*d*, *p*)	1.922	2.081	1.433	1.373	2.288	1.504	1.482	2.288	1.600	1.904
		TZVP	1.922	2.096	1.425	1.376	2.248	1.501	1.480	2.169	1.578	1.893
B/GHz	M06-2X	6-311++G(2*d*, *p*)	0.682	0.694	1.100	1.135	0.643	0.985	0.999	0.667	0.946	0.687
		TZVP	0.685	0.700	1.095	1.139	0.655	0.997	1.012	0.693	0.973	0.689
	ωB97XD	6-311++G(2*d*, *p*)	0.720	0.717	1.066	1.113	0.633	1.006	1.005	0.631	0.947	0.722
		TZVP	0.722	0.718	1.080	1.123	0.647	1.014	1.017	0.685	0.969	0.726
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.637	0.630	0.738	0.777	0.552	0.701	0.690	0.597	0.716	0.639
		TZVP	0.643	0.636	0.760	0.788	0.559	0.705	0.701	0.610	0.730	0.643
	ωB97XD	6-311++G(2*d*, *p*)	0.639	0.638	0.745	0.767	0.548	0.699	0.693	0.549	0.712	0.641
		TZVP	0.640	0.642	0.763	0.779	0.553	0.702	0.701	0.595	0.721	0.641
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	4.40	3.89	5.61	4.86	6.70	5.05	5.56	6.88	5.40	3.28
		TZVP	4.86	4.89	4.71	4.85	4.89	4.71	4.94	4.89	4.91	4.97
	ωB97XD	6-311++G(2*d*, *p*)	5.11	4.11	5.54	5.08	7.30	5.22	5.75	7.68	5.62	4.52
		TZVP	4.69	3.71	4.95	4.72	7.15	4.81	5.40	7.22	5.35	4.39
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3499	3529	3539	3530	3588	3523	3524	3594	3523	3491
		TZVP	3510	3532	3550	3533	3596	3520	3524	3612	3528	3498
	ωB97XD	6-311++G(2*d*, *p*)	3527	3554	3556	3553	3614	3520	3531	3615	3537	3524
		TZVP	3536	3561	3561	3560	3619	3526	3537	3628	3544	3532
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3813	3828	3814	3825	3404	3798	3816	3410	3813	3863
		TZVP	3801	3817	3811	3814	3386	3789	3810	3371	3795	3852
	ωB97XD	6-311++G(2*d*, *p*)	3829	3833	3825	3831	3389	3821	3833	3374	3826	3869
		TZVP	3825	3830	3824	3829	3366	3818	3831	3364	3824	3861
	Complex		A11	A12	A13	A14	A15	A16	A17	A18	A19	A20
A/GHz	M06-2X	6-311++G(2*d*, *p*)	1.751	1.995	1.602	3.093	1.416	1.925	1.779	1.900	1.421	2.654
		TZVP	2.075	2.155	1.655	3.075	1.427	1.983	1.951	1.957	1.415	2.652
	ωB97XD	6-311++G(2*d*, *p*)	1.640	3.511	1.451	3.244	1.418	1.828	1.964	1.937	1.448	2.886
		TZVP	1.917	3.466	1.406	3.106	1.408	1.932	2.032	1.957	1.411	2.602
B/GHz	M06-2X	6-311++G(2*d*, *p*)	0.826	0.686	0.810	0.496	1.095	0.611	0.600	0.649	0.908	0.514
		TZVP	0.683	0.624	0.825	0.503	1.084	0.646	0.622	0.653	0.948	0.520
	ωB97XD	6-311++G(2*d*, *p*)	0.787	0.464	0.914	0.503	1.060	0.613	0.590	0.640	0.920	0.498
		TZVP	0.716	0.463	0.970	0.512	1.073	0.633	0.614	0.642	0.964	0.520
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.695	0.627	0.587	0.467	0.746	0.503	0.494	0.534	0.647	0.477
		TZVP	0.635	0.559	0.600	0.474	0.762	0.529	0.524	0.540	0.664	0.481
	ωB97XD	6-311++G(2*d*, *p*)	0.628	0.433	0.642	0.473	0.754	0.494	0.500	0.532	0.644	0.451
		TZVP	0.638	0.431	0.669	0.482	0.774	0.517	0.525	0.535	0.668	0.477
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	5.67	3.28	4.10	2.80	7.09	1.22	1.61	4.49	4.86	6.38
		TZVP	4.97	4.66	4.94	5.14	4.71	5.72	5.82	4.88	5.02	4.49
	ωB97XD	6-311++G(2*d*, *p*)	5.64	9.69	3.69	3.24	6.98	1.58	1.61	4.98	5.66	7.05
		TZVP	4.18	9.17	3.02	2.51	6.65	1.58	1.81	4.56	5.11	6.44
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3528	3586	3534	3579	3545	3562	3556	3531	3557	3567
		TZVP	3537	3572	3529	3584	3560	3571	3576	3545	3559	3573
	ωB97XD	6-311++G(2*d*, *p*)	3497	3607	3580	3600	3556	3592	3581	3557	3578	3594
		TZVP	3547	3614	3596	3606	3564	3601	3603	3564	3593	3603
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3872	3480	3819	3638	3872	3813	3820	3810	3868	3839
		TZVP	3862	3447	3811	3613	3870	3777	3803	3805	3851	3825
	ωB97XD	6-311++G(2*d*, *p*)	3872	3430	3822	3573	3881	3820	3823	3823	3865	3863
		TZVP	3864	3422	3818	3520	3874	3809	3813	3820	3859	3855

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S6　16种[Pro−Cu]$^+$结构的转动系数(*A*、*B*和*C*)、偶极矩(μ)和O−H与N−H的伸缩振动频率

Table S6　Rotational constants (*A*, *B* and *C*), dipole moment (μ) and stretching vibrational frequencies (ν_{O-H} and ν_{N-H}) of sixteen kinds of [Pro-Cu]$^+$ complexes

	Complex		CI1	CI2	CI3	CI4	CI5	CI6	CI7	CI8
A/GHz	M06-2X	6-311++G(2*d*, *p*)	1.575	1.512	3.209	3.647	1.594	1.500	1.721	1.599
		TZVP	1.576	1.511	3.186	3.654	1.591	1.504	1.700	1.597
	ωB97XD	6-311++G(2*d*, *p*)	1.574	1.477	3.376	3.788	1.579	1.485	1.647	1.590
		TZVP	1.565	1.479	3.294	3.742	1.571	1.470	1.624	1.581
B/GHz	M06-2X	6-311++G(2*d*, *p*)	1.176	1.282	0.607	0.564	1.100	1.285	1.079	1.091
		TZVP	1.176	1.287	0.609	0.563	1.102	1.287	1.090	1.094
	ωB97XD	6-311++G(2*d*, *p*)	1.208	1.341	0.573	0.540	1.136	1.329	1.136	1.128
		TZVP	1.211	1.340	0.593	0.555	1.138	1.339	1.148	1.130
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.718	0.785	0.576	0.524	0.670	0.785	0.723	0.668
		TZVP	0.719	0.788	0.579	0.523	0.671	0.788	0.719	0.669
	ωB97XD	6-311++G(2*d*, *p*)	0.728	0.796	0.544	0.503	0.681	0.793	0.721	0.680
		TZVP	0.728	0.797	0.564	0.516	0.680	0.794	0.717	0.679
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	1.46	1.51	4.63	4.72	0.98	3.89	4.28	3.20
		TZVP	1.60	1.63	4.67	4.76	1.11	4.07	4.37	3.37
	ωB97XD	6-311++G(2*d*, *p*)	1.26	1.34	4.03	4.20	0.72	3.95	4.08	3.28
		TZVP	1.39	1.44	4.50	4.64	0.91	4.03	4.23	3.38
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3536	3544	3263	3296	3427	3539	3480	3428
		TZVP	3542	3549	3248	3281	3429	3544	3483	3429
	ωB97XD	6-311++G(2*d*, *p*)	3556	3554	3197	3255	3464	3556	3529	3465
		TZVP	3563	3563	3204	3256	3470	3561	3538	3471
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3792	3779			3776	3832	3765	3830
		TZVP	3776	3760			3765	3816	3770	3819
	ωB97XD	6-311++G(2*d*, *p*)	3792	3792			3784	3847	3781	3850
		TZVP	3790	3794			3781	3842	3784	3845

	Complex		CI9	CI10	CI11	CI12	CI13	CI14	CI15	CI16
A/GHz	M06-2X	6-311++G(2*d*, *p*)	1.568	2.510	3.941	2.562	2.913	2.542	2.363	1.717
		TZVP	1.578	2.723	3.983	2.578	2.851	2.539	1.828	1.713
	ωB97XD	6-311++G(2*d*, *p*)	1.531	2.523	3.855	2.478	2.763	2.423	2.405	1.693
		TZVP	1.534	2.540	3.862	2.456	2.753	2.439	2.369	1.695
B/GHz	M06-2X	6-311++G(2*d*, *p*)	1.108	0.621	0.485	0.581	0.559	0.616	0.642	0.947
		TZVP	1.109	0.564	0.484	0.580	0.562	0.617	0.914	0.951
	ωB97XD	6-311++G(2*d*, *p*)	1.143	0.628	0.487	0.592	0.567	0.623	0.636	0.988
		TZVP	1.144	0.623	0.485	0.593	0.564	0.619	0.644	0.980
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.671	0.542	0.441	0.537	0.514	0.567	0.553	0.630
		TZVP	0.673	0.505	0.440	0.538	0.516	0.569	0.646	0.632
	ωB97XD	6-311++G(2*d*, *p*)	0.676	0.548	0.441	0.543	0.515	0.565	0.549	0.643
		TZVP	0.677	0.545	0.440	0.543	0.513	0.562	0.551	0.639
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	4.11	4.60	4.17	4.14	5.52	5.40	5.06	5.68
		TZVP	4.13	4.70	4.20	4.26	5.62	5.47	3.52	5.80
	ωB97XD	6-311++G(2*d*, *p*)	4.08	4.36	3.92	3.88	5.20	5.05	5.01	5.26
		TZVP	4.20	4.62	4.08	3.99	5.37	5.20	5.21	5.51
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3433	3587	3449	3623	3597	3616	3600	3572
		TZVP	3436	3592	3449	3633	3597	3628	3617	3576
	ωB97XD	6-311++G(2*d*, *p*)	3471	3605	3480	3638	3625	3640	3630	3602
		TZVP	3478	3613	3481	3651	3640	3657	3644	3610
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3770	3104	3573	3807	3793	3812	3766	3765
		TZVP	3757	3015	3535	3798	3785	3801	3756	3758
	ωB97XD	6-311++G(2*d*, *p*)	3785	3090	3517	3824	3819	3818	3784	3775
		TZVP	3786	3045	3495	3820	3815	3814	3780	3780

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S7　16种[Pro-Cu]$^{2+}$结构的转动系数(*A*、*B*和*C*)、偶极矩(μ)和O−H与N−H的伸缩振动频率

Table S7　Rotational constants (*A*, *B* and *C*), dipole moment (μ) and stretching vibrational frequencies (ν_{O-H} and ν_{N-H}) of sixteen kinds of [Pro-Cu]$^{2+}$ complexes

Complex			CII1	CII2	CII3	CII4	CII5	CII6	CII7	CII8
A/GHz	M06-2X	6-311++G(2*d*, *p*)	3.011	3.273	3.282	2.838	2.579	4.065	3.925	3.448
		TZVP	2.962	3.100	3.244	2.824	2.538	4.040	3.911	3.402
	ωB97XD	6-311++G(2*d*, *p*)	3.179	3.156	3.220	2.846	2.542	4.043	3.967	3.495
		TZVP	3.012	3.025	3.222	2.812	2.522	4.028	3.976	3.431
B/GHz	M06-2X	6-311++G(2*d*, *p*)	0.469	0.470	0.492	0.492	0.559	0.431	0.576	0.614
		TZVP	0.471	0.483	0.493	0.492	0.567	0.429	0.573	0.615
	ωB97XD	6-311++G(2*d*, *p*)	0.470	0.487	0.499	0.503	0.566	0.438	0.568	0.603
		TZVP	0.474	0.490	0.496	0.502	0.567	0.433	0.562	0.604
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.416	0.444	0.443	0.433	0.510	0.419	0.533	0.581
		TZVP	0.417	0.449	0.443	0.432	0.518	0.418	0.531	0.584
	ωB97XD	6-311++G(2*d*, *p*)	0.421	0.450	0.447	0.443	0.512	0.425	0.526	0.570
		TZVP	0.420	0.450	0.445	0.442	0.514	0.423	0.521	0.573
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	2.48	2.65	3.40	2.12	3.93	5.18	2.70	2.71
		TZVP	2.40	2.59	3.40	2.21	3.95	5.13	2.75	2.74
	ωB97XD	6-311++G(2*d*, *p*)	2.83	2.93	3.58	2.04	4.09	5.39	2.83	2.90
		TZVP	2.57	2.71	3.49	2.12	4.03	5.21	2.87	2.94
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3492	3490	3487	3511	3494	3487	3422	3411
		TZVP	3486	3483	3481	3494	3491	3484	3416	3404
	ωB97XD	6-311++G(2*d*, *p*)	3533	3531	3534	3542	3537	3517	3455	3444
		TZVP	3537	3537	3537	3544	3541	3522	3459	3446
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3734	3741	3785	3758	3761	3800		
		TZVP	3728	3724	3768	3744	3751	3783		
	ωB97XD	6-311++G(2*d*, *p*)	3765	3759	3795	3780	3792	3820		
		TZVP	3760	3750	3792	3777	3790	3816		

Complex			CII9	CII10	CII11	CII12	CII13	CII14	CII15	CII16
A/GHz	M06-2X	6-311++G(2*d*, *p*)	1.600	2.248	1.603	2.722	1.643	1.641	1.521	2.046
		TZVP	1.589	2.112	1.598	2.645	1.635	1.634	1.500	2.059
	ωB97XD	6-311++G(2*d*, *p*)	1.585	2.200	1.589	2.575	1.634	1.632	1.484	1.985
		TZVP	1.569	2.115	1.580	2.550	1.625	1.624	1.466	1.995
B/GHz	M06-2X	6-311++G(2*d*, *p*)	1.274	0.557	1.263	0.523	1.178	1.172	1.308	0.708
		TZVP	1.276	0.610	1.261	0.541	1.175	1.170	1.326	0.710
	ωB97XD	6-311++G(2*d*, *p*)	1.293	0.586	1.283	0.552	1.191	1.186	1.354	0.752
		TZVP	1.299	0.615	1.283	0.558	1.188	1.183	1.373	0.749
C/GHz	M06-2X	6-311++G(2*d*, *p*)	0.759	0.466	0.755	0.485	0.708	0.705	0.759	0.621
		TZVP	0.758	0.490	0.754	0.496	0.706	0.703	0.763	0.626
	ωB97XD	6-311++G(2*d*, *p*)	0.762	0.482	0.758	0.499	0.711	0.709	0.771	0.651
		TZVP	0.762	0.494	0.757	0.503	0.708	0.706	0.776	0.651
$10^{30}\mu$/(C·m)	M06-2X	6-311++G(2*d*, *p*)	2.93	2.58	3.44	3.48	2.76	2.59	5.90	3.10
		TZVP	3.05	2.66	3.65	3.51	2.86	2.78	5.93	3.12
	ωB97XD	6-311++G(2*d*, *p*)	2.24	2.64	3.31	3.38	1.90	2.42	5.26	2.94
		TZVP	2.35	2.67	3.48	3.42	1.98	2.59	5.31	3.07
ν_{N-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3444	3474	3447	3491	3378	3381	3451	3437
		TZVP	3447	3478	3449	3474	3378	3380	3446	3428
	ωB97XD	6-311++G(2*d*, *p*)	3478	3513	3481	3524	3418	3420	3462	3466
		TZVP	3483	3510	3489	3526	3425	3428	3473	3468
ν_{O-H}/cm^{-1}	M06-2X	6-311++G(2*d*, *p*)	3660	3660	3753	3683	3643	3750	3650	3630
		TZVP	3650	3650	3740	3673	3635	3735	3655	3622
	ωB97XD	6-311++G(2*d*, *p*)	3702	3684	3772	3686	3692	3763	3674	3685
		TZVP	3703	3691	3770	3691	3694	3761	3684	3691

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S8　20种[Pro−Cu]结构的部分原子电荷数

Table S8　Some atoms natural charge population(q) of twenty kinds of [Pro-Cu] complexes

Complex			A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.751	-0.750	-0.743	-0.751	-0.743	-0.740	-0.744	-0.744	-0.748	-0.750
		TZVP	-0.675	-0.674	-0.667	-0.671	-0.659	-0.665	-0.671	-0.661	-0.675	-0.675
	ωB97XD	6-311++G(2*d*, *p*)	-0.740	-0.737	-0.733	-0.736	-0.732	-0.734	-0.732	-0.733	-0.735	-0.739
		TZVP	-0.671	-0.666	-0.655	-0.659	-0.649	-0.657	-0.661	-0.650	-0.664	-0.670
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.625	-0.606	-0.603	-0.596	-0.684	-0.607	-0.598	-0.678	-0.602	-0.593
		TZVP	-0.588	-0.568	-0.570	-0.560	-0.638	-0.574	-0.559	-0.644	-0.562	-0.553
	ωB97XD	6-311++G(2*d*, *p*)	-0.624	-0.605	-0.603	-0.594	-0.679	-0.614	-0.599	-0.689	-0.603	-0.592
		TZVP	-0.584	-0.564	-0.568	-0.555	-0.629	-0.576	-0.557	-0.645	-0.560	-0.551
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.708	-0.728	-0.709	-0.717	-0.689	-0.705	-0.723	-0.691	-0.720	-0.692
		TZVP	-0.672	-0.692	-0.671	-0.684	-0.647	-0.670	-0.694	-0.651	-0.693	-0.655
	ωB97XD	6-311++G(2*d*, *p*)	-0.692	-0.714	-0.691	-0.702	-0.671	-0.683	-0.703	-0.671	-0.699	-0.677
		TZVP	-0.653	-0.675	-0.651	-0.666	-0.627	-0.647	-0.671	-0.629	-0.670	-0.638
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.401	0.399	0.388	0.390	0.384	0.378	0.381	0.382	0.383	0.405
		TZVP	0.406	0.404	0.399	0.398	0.384	0.382	0.384	0.383	0.387	0.409
	ωB97XD	6-311++G(2*d*, *p*)	0.409	0.404	0.399	0.397	0.384	0.383	0.384	0.383	0.386	0.412
		TZVP	0.413	0.408	0.404	0.401	0.384	0.386	0.387	0.382	0.389	0.416
$q_{H(-O)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.496	0.499	0.497	0.500	0.518	0.500	0.502	0.519	0.502	0.483
		TZVP	0.495	0.499	0.496	0.499	0.512	0.498	0.502	0.513	0.502	0.479
	ωB97XD	6-311++G(2*d*, *p*)	0.495	0.499	0.495	0.498	0.509	0.495	0.498	0.509	0.498	0.482
		TZVP	0.492	0.496	0.492	0.495	0.500	0.492	0.495	0.501	0.496	0.476
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	-0.046	-0.044	-0.051	-0.050	-0.023	-0.049	-0.047	-0.016	-0.045	-0.045
		TZVP	-0.039	-0.036	-0.037	-0.038	-0.018	-0.037	-0.036	-0.004	-0.035	-0.037
	ωB97XD	6-311++G(2*d*, *p*)	-0.072	-0.070	-0.074	-0.074	-0.038	-0.064	-0.065	-0.016	-0.065	-0.070
		TZVP	-0.061	-0.059	-0.059	-0.059	-0.031	-0.053	-0.052	-0.006	-0.053	-0.059

Complex			A11	A12	A13	A14	A15	A16	A17	A18	A19	A20
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.754	-0.737	-0.696	-0.689	-0.742	-0.690	-0.697	-0.678	-0.702	-0.690
		TZVP	-0.681	-0.648	-0.613	-0.603	-0.665	-0.606	-0.613	-0.596	-0.618	-0.605
	ωB97XD	6-311++G(2*d*, *p*)	-0.747	-0.727	-0.693	-0.684	-0.732	-0.694	-0.692	-0.673	-0.693	-0.688
		TZVP	-0.676	-0.646	-0.612	-0.598	-0.654	-0.607	-0.608	-0.589	-0.611	-0.602
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.593	-0.668	-0.692	-0.685	-0.573	-0.616	-0.621	-0.677	-0.660	-0.646
		TZVP	-0.553	-0.642	-0.655	-0.648	-0.538	-0.573	-0.578	-0.640	-0.622	-0.614
	ωB97XD	6-311++G(2*d*, *p*)	-0.591	-0.668	-0.698	-0.683	-0.576	-0.614	-0.615	-0.678	-0.665	-0.652
		TZVP	-0.551	-0.631	-0.652	-0.640	-0.540	-0.570	-0.571	-0.634	-0.618	-0.613
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.691	-0.687	-0.698	-0.705	-0.690	-0.740	-0.726	-0.703	-0.680	-0.685
		TZVP	-0.654	-0.650	-0.662	-0.672	-0.653	-0.725	-0.711	-0.669	-0.642	-0.649
	ωB97XD	6-311++G(2*d*, *p*)	-0.674	-0.667	-0.675	-0.684	-0.674	-0.729	-0.727	-0.684	-0.663	-0.665
		TZVP	-0.637	-0.625	-0.636	-0.650	-0.633	-0.704	-0.701	-0.649	-0.624	-0.628
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.405	0.379	0.375	0.375	0.394	0.375	0.381	0.363	0.384	0.382
		TZVP	0.407	0.374	0.375	0.376	0.404	0.378	0.381	0.366	0.385	0.383
	ωB97XD	6-311++G(2*d*, *p*)	0.413	0.379	0.379	0.375	0.405	0.383	0.381	0.363	0.383	0.385
		TZVP	0.415	0.379	0.378	0.375	0.409	0.380	0.380	0.363	0.383	0.384
$q_{H(-O)}$/(e)	M06-2X	6-311++G(2*d*, *p*)	0.482	0.522	0.497	0.494	0.483	0.497	0.497	0.502	0.485	0.488
		TZVP	0.479	0.515	0.496	0.494	0.480	0.506	0.504	0.502	0.482	0.485
	ωB97XD	6-311++G(2*d*, *p*)	0.482	0.512	0.497	0.489	0.484	0.501	0.501	0.500	0.485	0.487
		TZVP	0.476	0.503	0.493	0.484	0.479	0.503	0.503	0.498	0.479	0.481
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	-0.042	-0.043	-0.015	-0.021	-0.048	-0.007	-0.005	-0.018	-0.007	-0.035
		TZVP	-0.034	-0.007	-0.008	-0.017	-0.032	-0.002	-0.001	-0.014	-0.001	-0.027
	ωB97XD	6-311++G(2*d*, *p*)	-0.067	-0.052	-0.021	-0.034	-0.071	-0.012	-0.013	-0.029	-0.021	-0.041
		TZVP	-0.055	-0.034	-0.012	-0.022	-0.056	-0.006	-0.006	-0.023	-0.010	-0.030

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

表S9　16种[Pro-Cu]$^{+}$结构的部分原子电荷数

Table S9　Some atoms natural charge population(q) of sixteen kinds of [Pro-Cu]$^{+}$ complexes

	Complex		CI1	CI2	CI3	CI4	CI5	CI6	CI7	CI8
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.794	-0.796	-0.592	-0.586	-0.782	-0.791	-0.800	-0.776
		TZVP	-0.723	-0.723	-0.521	-0.516	-0.713	-0.718	-0.730	-0.705
	ωB97XD	6-311++G(2*d*, *p*)	-0.779	-0.778	-0.579	-0.574	-0.772	-0.775	-0.788	-0.766
		TZVP	-0.713	-0.710	-0.509	-0.505	-0.707	-0.705	-0.723	-0.700
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.703	-0.707	-0.768	-0.767	-0.698	-0.679	-0.527	-0.672
		TZVP	-0.664	-0.666	-0.725	-0.724	-0.658	-0.633	-0.487	-0.628
	ωB97XD	6-311++G(2*d*, *p*)	-0.693	-0.696	-0.809	-0.804	-0.685	-0.667	-0.527	-0.660
		TZVP	-0.649	-0.651	-0.731	-0.725	-0.641	-0.619	-0.485	-0.613
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.658	-0.660	-0.815	-0.815	-0.648	-0.642	-0.806	-0.632
		TZVP	-0.621	-0.622	-0.786	-0.785	-0.611	-0.603	-0.776	-0.593
	ωB97XD	6-311++G(2*d*, *p*)	-0.640	-0.641	-0.736	-0.741	-0.632	-0.625	-0.784	-0.616
		TZVP	-0.602	-0.603	-0.738	-0.743	-0.594	-0.585	-0.753	-0.577
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.402	0.407	0.435	0.431	0.382	0.407	0.398	0.382
		TZVP	0.403	0.408	0.436	0.432	0.384	0.409	0.400	0.384
	ωB97XD	6-311++G(2*d*, *p*)	0.405	0.409	0.433	0.430	0.388	0.409	0.403	0.388
		TZVP	0.406	0.411	0.435	0.432	0.390	0.411	0.405	0.390
$q_{H(-O)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.518	0.518			0.519	0.503	0.534	0.508
		TZVP	0.519	0.518			0.520	0.500	0.536	0.504
	ωB97XD	6-311++G(2*d*, *p*)	0.516	0.516			0.517	0.502	0.532	0.506
		TZVP	0.515	0.515			0.515	0.497	0.532	0.500
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	0.878	0.878	0.886	0.885	0.888	0.878	0.893	0.889
		TZVP	0.882	0.877	0.888	0.888	0.891	0.878	0.896	0.892
	ωB97XD	6-311++G(2*d*, *p*)	0.846	0.843	0.865	0.863	0.858	0.844	0.861	0.858
		TZVP	0.853	0.846	0.867	0.866	0.865	0.847	0.869	0.866

	Complex		CI9	CI10	CI11	CI12	CI13	CI14	CI15	CI16
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.797	-0.737	-0.705	-0.696	-0.681	-0.684	-0.685	-0.684
		TZVP	-0.726	-0.651	-0.622	-0.610	-0.598	-0.602	-0.604	-0.595
	ωB97XD	6-311++G(2*d*, *p*)	-0.786	-0.725	-0.701	-0.688	-0.675	-0.677	-0.678	-0.679
		TZVP	-0.721	-0.639	-0.617	-0.604	-0.594	-0.597	-0.597	-0.590
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.513	-0.821	-0.761	-0.757	-0.764	-0.764	-0.818	-0.503
		TZVP	-0.472	-0.801	-0.719	-0.712	-0.725	-0.722	-0.727	-0.463
	ωB97XD	6-311++G(2*d*, *p*)	-0.515	-0.806	-0.762	-0.756	-0.771	-0.771	-0.813	-0.502
		TZVP	-0.473	-0.763	-0.720	-0.713	-0.727	-0.726	-0.769	-0.460
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.803	-0.634	-0.680	-0.683	-0.690	-0.688	-0.643	-0.848
		TZVP	-0.776	-0.590	-0.644	-0.652	-0.654	-0.655	-0.611	-0.817
	ωB97XD	6-311++G(2*d*, *p*)	-0.777	-0.614	-0.651	-0.658	-0.658	-0.656	-0.624	-0.826
		TZVP	-0.745	-0.566	-0.610	-0.621	-0.622	-0.620	-0.586	-0.795
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.388	0.401	0.355	0.385	0.382	0.383	0.384	0.394
		TZVP	0.389	0.401	0.355	0.387	0.385	0.387	0.397	0.396
	ωB97XD	6-311++G(2*d*, *p*)	0.393	0.400	0.357	0.385	0.381	0.383	0.384	0.397
		TZVP	0.396	0.401	0.357	0.386	0.385	0.386	0.388	0.396
$q_{H(-O)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.532	0.533	0.543	0.515	0.521	0.520	0.518	0.539
		TZVP	0.534	0.524	0.541	0.513	0.518	0.518	0.521	0.540
	ωB97XD	6-311++G(2*d*, *p*)	0.528	0.523	0.536	0.513	0.517	0.517	0.515	0.538
		TZVP	0.528	0.513	0.531	0.508	0.513	0.512	0.514	0.537
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	0.896	0.937	0.920	0.923	0.921	0.920	0.935	0.927
		TZVP	0.901	0.949	0.924	0.923	0.922	0.920	0.923	0.923
	ωB97XD	6-311++G(2*d*, *p*)	0.869	0.916	0.904	0.906	0.906	0.906	0.918	0.910
		TZVP	0.878	0.915	0.910	0.909	0.909	0.908	0.916	0.908

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels

附表10　16种[Pro−Cu]$^{2+}$结构的部分原子电荷数

Table S10　Some atoms natural charge population(q) of sixteen kinds of [Pro-Cu]$^{2+}$ complexes

Complex			CII1	CII2	CII3	CII4	CII5	CII6	CII7	CII8
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.168	-0.160	-0.164	-0.169	-0.151	-0.190	-0.576	-0.576
		TZVP	-0.099	-0.091	-0.096	-0.103	-0.082	-0.124	-0.505	-0.506
	ωB97XD	6-311++G(2*d*, *p*)	-0.166	-0.160	-0.161	-0.165	-0.151	-0.185	-0.559	-0.558
		TZVP	-0.101	-0.095	-0.098	-0.102	-0.086	-0.122	-0.491	-0.491
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.761	-0.762	-0.735	-0.782	-0.729	-0.704	-0.671	-0.673
		TZVP	-0.725	-0.727	-0.700	-0.750	-0.693	-0.668	-0.619	-0.621
	ωB97XD	6-311++G(2*d*, *p*)	-0.756	-0.759	-0.737	-0.777	-0.734	-0.705	-0.584	-0.585
		TZVP	-0.719	-0.721	-0.697	-0.740	-0.693	-0.665	-0.527	-0.528
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.651	-0.648	-0.633	-0.617	-0.638	-0.636	-0.724	-0.727
		TZVP	-0.617	-0.613	-0.595	-0.579	-0.602	-0.598	-0.680	-0.684
	ωB97XD	6-311++G(2*d*, *p*)	-0.632	-0.628	-0.610	-0.599	-0.614	-0.616	-0.646	-0.651
		TZVP	-0.597	-0.593	-0.572	-0.560	-0.577	-0.577	-0.596	-0.602
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.449	0.445	0.451	0.442	0.447	0.446	0.455	0.460
		TZVP	0.452	0.448	0.453	0.443	0.449	0.447	0.455	0.460
	ωB97XD	6-311++G(2*d*, *p*)	0.446	0.444	0.448	0.440	0.444	0.443	0.454	0.458
		TZVP	0.450	0.447	0.451	0.443	0.447	0.445	0.455	0.460
$q_{H(-O)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.539	0.538	0.537	0.531	0.537	0.523		
		TZVP	0.541	0.541	0.535	0.533	0.535	0.520		
	ωB97XD	6-311++G(2*d*, *p*)	0.534	0.533	0.534	0.527	0.534	0.521		
		TZVP	0.535	0.535	0.529	0.527	0.530	0.517		
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	0.978	0.980	0.956	0.967	0.954	0.959	1.510	1.510
		TZVP	0.983	0.984	0.961	0.972	0.959	0.966	1.492	1.492
	ωB97XD	6-311++G(2*d*, *p*)	0.968	0.970	0.947	0.955	0.946	0.950	1.353	1.354
		TZVP	0.978	0.980	0.954	0.961	0.952	0.959	1.329	1.330

Complex			CII9	CII10	CII11	CII12	CII13	CII14	CII15	CII16
q_N/e	M06-2X	6-311++G(2*d*, *p*)	-0.772	-0.155	-0.776	-0.147	-0.758	-0.761	-0.734	-0.674
		TZVP	-0.702	-0.087	-0.706	-0.079	-0.687	-0.690	-0.661	-0.625
	ωB97XD	6-311++G(2*d*, *p*)	-0.685	-0.153	-0.697	-0.145	-0.676	-0.687	-0.618	-0.692
		TZVP	-0.614	-0.090	-0.628	-0.082	-0.607	-0.617	-0.549	-0.639
$q_{O(=C)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.731	-0.485	-0.703	-0.483	-0.723	-0.696	-0.398	-0.286
		TZVP	-0.685	-0.441	-0.653	-0.441	-0.676	-0.645	-0.355	-0.242
	ωB97XD	6-311++G(2*d*, *p*)	-0.677	-0.478	-0.642	-0.475	-0.664	-0.630	-0.387	-0.249
		TZVP	-0.629	-0.435	-0.589	-0.433	-0.613	-0.575	-0.343	-0.209
$q_{O(-H)}/e$	M06-2X	6-311++G(2*d*, *p*)	-0.579	-0.847	-0.565	-0.850	-0.567	-0.554	-0.882	-0.651
		TZVP	-0.540	-0.819	-0.525	-0.823	-0.530	-0.515	-0.848	-0.619
	ωB97XD	6-311++G(2*d*, *p*)	-0.559	-0.837	-0.547	-0.842	-0.550	-0.537	-0.836	-0.631
		TZVP	-0.520	-0.804	-0.506	-0.809	-0.512	-0.497	-0.798	-0.597
$q_{H(-N)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.444	0.456	0.443	0.447	0.423	0.423	0.448	0.452
		TZVP	0.445	0.460	0.444	0.449	0.425	0.424	0.451	0.458
	ωB97XD	6-311++G(2*d*, *p*)	0.444	0.454	0.443	0.446	0.426	0.426	0.450	0.450
		TZVP	0.446	0.458	0.445	0.449	0.429	0.429	0.455	0.457
$q_{H(-O)}/e$	M06-2X	6-311++G(2*d*, *p*)	0.553	0.550	0.544	0.550	0.555	0.547	0.579	0.565
		TZVP	0.554	0.557	0.541	0.554	0.555	0.544	0.580	0.565
	ωB97XD	6-311++G(2*d*, *p*)	0.550	0.551	0.542	0.551	0.551	0.544	0.573	0.560
		TZVP	0.550	0.553	0.538	0.552	0.551	0.540	0.573	0.558
q_{Cu}/e	M06-2X	6-311++G(2*d*, *p*)	1.516	0.976	1.522	0.976	1.509	1.514	1.491	0.975
		TZVP	1.498	0.976	1.506	0.977	1.493	1.499	1.469	0.981
	ωB97XD	6-311++G(2*d*, *p*)	1.364	0.966	1.371	0.967	1.354	1.360	1.307	0.991
		TZVP	1.343	0.969	1.352	0.970	1.337	1.342	1.286	1.001

Note: the results obtained at the M06-2X/6-311++G(2*d*, *p*), M06-2X/TZVP, ωB97XD/6-311++G(2*d*, *p*) and ωB97XD/TZVP levels