Supporting information

New insight of effect of N^N ligand isomerization and methyl modification on the phosphorescence properties of Cu(I) complexes with (1-(2-pyridyl) pyrazole/imidazole) ligands

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Calculations of the $\left\langle T_m \left| \hat{H}_{SOC} \right| S_n \right\rangle$ matrix elements

$\left\langle T_m \left| \hat{H}_{SOC} \right| S_n \right\rangle$ presents the SOC matrix elements in $T_m \rightarrow S_n$ transition, and the SOC Hamiltonian is given by Eq.(3)

$$H_{SOC} = \sum_i \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{2m_e^2c^2} \frac{1}{r^3} l_i s_i \tag{3}$$

in which ε_0, Z, m_e, c, r, l_i, s_i are the permittivity of vacuum, charge of the nucleus, electron rest mass, speed of light, mean cubic radial distribution, angular momentum operators for orbital and spin, respectively.

The excited-state wave function ($^{1,3}\Psi$) obtained by TD-DFT is expressed as a linear combination of one-electron excitation configurations ($^{1,3}\psi i$) from an occupied molecular orbital to an unoccupied molecular orbital (e.g. From HOMO to LUMO):

$$^{1,3}\Psi = \sum_i a_i {}^{1,3}\psi_i \tag{3a}$$

where a_i is the coefficient of the configuration ($^{1,3}\psi i$) to the excited-state wave function ($^{1,3}\Psi$) .

The molecular orbitals (ψ_i)can be expanded using natural atomic orbitals (χ_k):

$$\psi_i = \sum_k c_{ki} \chi_k \tag{3b}$$

where C_{ki} is the coefficient of AO χ_k to MO ψ_i.

The one-electron one-center spin-orbit integral is non-vanishing only when the T_m and S_n states involve the same unoccupied π^* orbital but different occupied d orbitals. Then the SOC matrix elements $\left\langle T_m \left| \hat{H}_{SOC} \right| S_n \right\rangle$ can be written as follows:

$$\left\langle {}^3\Psi_m \left| \hat{H}_{SOC} \right|^1 \Psi_n \right\rangle = \left\langle \sum_i {}^3a_i {}^3\psi_i \left| \hat{H}_{SOC} \right| \sum_j {}^1a_j {}^1\psi_j \right\rangle$$
$$= \left\langle \sum_i {}^1a_i \left(\sum_k c_{ki} {}^3\left(d_{ki}\pi^*\right) \right) \left| \hat{H}_{SOC} \right| \sum_j {}^1a_j \left(\sum_l c_{lj} {}^1\left(d_{lj}\pi^*\right) \right) \right\rangle \quad (3c)$$

In which, the spin-orbit integrals $\left\langle {}^3\psi_i \left| \hat{H}_{SOC} \right|^1 \psi_j \right\rangle$ can be proximately expressed as follows:

$$\left\langle {}^3\psi_i \left| \hat{H}_{SOC} \right|^1 \psi_j \right\rangle = \zeta_c \left\langle {}^3d_{ki}\pi^* \left| \hat{l}\hat{s} \right|^1 d_{lj}\pi^* \right\rangle \quad (3d)$$

$\hat{l}$ and $\hat{s}$ are angular momentum operators for orbital and spin, and ζ_c presents the one-electron spin-orbit coupling constant of the d orbital, respectively. The ζ_c value for the 3d electron of Cu is 829 cm^{-1}. And the matrix elements $\langle {}^3d_{ki}\pi^* \left| \hat{l}\hat{s} \right| {}^1d_{lj}\pi^* \rangle$ are listed in Table S1.

Non-radiative decay rates

a) the formula of inverted region

$$k_{nr} = \frac{\left\langle T_1 \left| H_{SOC} \right| S_0 \right\rangle^2}{\hbar} \left(\frac{2\pi}{\hbar\omega_M \left(\left| \Delta E \right| - \lambda_S \right)} \right)^{1/2} \times \exp\left[-\frac{\lambda_M}{\hbar\omega_M} - \frac{\gamma\left(\left| \Delta E \right| - \lambda_S \right)}{\hbar\omega_M} + \left(\frac{\gamma+1}{\hbar\omega_M} \right)^2 \lambda_S k_B T \right] \quad (5)$$

$$\gamma = \ln\left[\left(\left| \Delta E \right| - \lambda_S \right) / \lambda_M \right] - 1$$

Ep. (5) can be applied when low-frequency mode is in the high-temperature limit and high-frequency mode is in the low-temperature limit: $\hbar\omega_{lf} \ll k_B T \ll \hbar\omega_{hf}$. among which *hf* and *lf* designate the high-frequency ligand skeletal modes ($1700 > \omega_{hf} > 1000 cm^{-1}$) and low-frequency modes ($\omega_{lf} < 1000 cm^{-1}$) ,respectively. ΔE is the zero-point energy difference between the excited state (T_1)and the ground state (S_0), and λ_S being the reorganization energy contributed by low-frequency modes of complexes. Assuming harmonic oscillators modes,

$$\lambda_S = \sum_{j \in lf} S_j \hbar\omega_j \quad (5a)$$

$$\lambda_M = \sum_{j \in hf} S_j \hbar\omega_j \quad (5b)$$

Where S_j denotes the Huang-Rhys factor, means the mixing degree between corresponding vibrational modes from the initial state and the final state, and also represents the contribution of the *j*th vibrational mode to structural deformation. S_M is

the Huang-Rhys factor of the effective high-frequency mode of $\hbar\omega_M$:

$$S_M = \sum_{j\in hf} S_j \tag{5c}$$

$$\mathsf{h}\omega_M = \frac{\lambda_{\mathrm{M}}}{S_M} \tag{5d}$$

b) the formula of convolution method

$$\begin{aligned} k_{nr} &= \frac{2\pi}{\mathsf{h}}\left\langle T_1\left|H_{SOC}\right|S_0\right\rangle\left[2\pi\mathsf{h}^2(D^2+P^2)\right]^{-1/2} \\ &\times\exp\left[-\frac{(\Delta E - n_M\mathsf{h}_M - \lambda_1 - \mu)^2}{2\pi\mathsf{h}^2(D^2+P^2)}\right]\exp(-S_M)\frac{S_M^{n_M}}{n_M!} \end{aligned} \tag{4}$$

$$\lambda_1 = \sum_{j\in lf}\frac{S_j\mathsf{h}\omega_j^s}{b_j}$$

$$\mu = \frac{1}{2}\sum_{j\in lf}\mathsf{h}\omega_j^s\frac{1-b_j^2}{b_j}\coth\frac{\mathsf{h}\omega_j^T}{2k_BT}$$

$$\mathsf{h}^2P^2 = \frac{1}{2}\sum_{j\in lf}\left[\mathsf{h}\omega_j^s\frac{1-b_j^2}{b_j}\coth\frac{\mathsf{h}\omega_j^T}{2k_BT}\right]^2$$

$$\mathsf{h}^2D_1^2 = \sum_{j\in lf}S_j\left(\frac{\mathsf{h}\omega_j^s}{b_j}\right)^2\coth\frac{\mathsf{h}\omega_j^T}{2k_BT}$$

$$b_j = \frac{\omega_j^T}{\omega_j^S}$$

$$n_M = \frac{\Delta E - \lambda_1 - \mu}{\mathsf{h}\omega_M}$$

Eq. (4) is applied by considering that the low-frequency modes are treated in the strong coupling limit and the high-frequency modes in the weak coupling. μ is the temperature-dependent term. n_M is the number of vibrational quanta of $\hbar\omega_M$.

Table S1 SOC matrix elements between the $^3(d_k\pi^*)$ and $^1(d_l\pi^*)$ states.

	$^1(d_{xz}\pi^*)$	$^1(d_{yz}\pi^*)$	$^1(d_{z^2}\pi^*)$	$^1(d_{xy}\pi^*)$	$^1(d_{x^2-y^2}\pi^*)$
$^3(d_{xz}\pi^*)$	0	$\frac{c_{xz}c_{yz}}{2}$	$-\frac{\sqrt{3}}{2}c_{xz}c_{z^2}$	$-\frac{c_{xz}c_{xy}}{2}$	$-\frac{c_{xz}c_{x^2-y^2}}{2}$
$^3(d_{yz}\pi^*)$	$-\frac{c_{yz}c_{xz}}{2}$	0	$-\frac{\sqrt{3}}{2}c_{yz}c_{z^2}$	$-\frac{c_{yz}c_{xy}}{2}$	$\frac{c_{yz}c_{x^2-y^2}}{2}$
$^3(d_{z^2}\pi^*)$	$\frac{\sqrt{3}}{2}c_{z^2}c_{xz}$	$\frac{\sqrt{3}}{2}c_{z^2}c_{xz}$	0	0	0

$^3(d_{xy}\pi^*)$	$\frac{c_{xy}c_{xz}}{2}$	$\frac{c_{xy}c_{xz}}{2}$	0	0	$-c_{xy}c_{x^2-y^2}$
$^3(d_{x^2-y^2}\pi^*)$	$\frac{c_{x^2-y^2}c_{yz}}{2}$	$-\frac{c_{x^2-y^2}c_{yz}}{2}$	0	$c_{x^2-y^2}c_{xy}$	0

Table S2 Partial optimized geometric structural parameters of py-ch3 in ground states by B3LYP, PBE0 and M06 functions, together with the experimental values.

	B3LYP	PBE0	M06	Expt.
Cu-P_1	2.3666	2.3256	2.2832	2.2810(10)
Cu-P_2	2.3853	2.3490	2.3532	2.2489(11)
Cu-N_1	2.2126	2.1854	2.1564	2.091(3)
Cu-N_2	2.1545	2.1252	2.1385	2.079(3)
P_1-Cu-P_2	116.12	115.39	116.78	114.33
N_1-Cu-N_2	75.51	75.75	76.67	78.82
P_1-Cu-N_2	117.66	120.75	118.11	106.02
P_2-Cu-N_2	111.93	110.18	100.39	117.95
N_1-Cu-P_2	115.29	115.30	102.62	118.68
N_1-Cu-P_1	114.03	113.64	132.40	115.64

Table S3 Absorption and emissions spectra of py-ch3 calculated by employed different functions with basis sets of LANL2DZfor Cu and 6-31G (d) for nonmetal atoms, together with the experimental values

		B3LYP	PBE0	M06	Expt.
py-ch3	λ_{abs}/nm	350.56	333.78	332.74	346
	λ_{emi}/nm	602.06	596.01	532.90	536

Table S4 Molecular orbital compositions in the ground state for complexes by DFT//M06/ LANL2DZ&6-31G(d)

orbital	Energy/ev	Contribution %			
		Cu	Nn6	Nn5	P^P
py-pop					
H-4	-9.305	13.9	3.3	1.5	81.3
H-3	-9.219	17.4	5.4	13.2	64.0
H-2	-8.915	18.5	2.2	1.0	78.4
H-1	-8.791	17.5	1.7	2.4	78.4

H	-8.209	29.4/20.7	1.9	1.9	66.8
L	-3.861	5.7	67.4	21.1	5.8
L+1	-3.477	5.6	75.4	12.9	6.1
L+2	-3.089	7.1	2.5	1.8	88.7
L+3	-2.894	3.2	0.4	0.5	95.8
py-ch3					
H-4	-9.291	33.1	7.9	4.7	54.3
H-3	-9.227	30.9	5.7	9.8	53.5
H-2	-8.907	18.3	2.4	0.7	78.5
H-1	-8.766	18.2	1.4	3.0	77.4
H	-8.188	29.4/20.7	2.0	2.3	66.3
L	-3.793	4.3	65.2	24.7	5.8
L+1	-3.434	7.5	74.5	10.2	7.8
L+2	-3.083	4.5	2.2	1.2	92.1
L+3	-2.859	3.3	0.3	0.5	95.8
py-meta					
H-4	-9.261	5.6	2.2	1.8	90.5
H-3	-9.196	17.4	3.9	7.6	71.1
H-2	-8.891	18.2	1.8	1.1	78.8
H-1	-8.720	16.9	1.2	2.9	78.9
H	-8.194	29.8/20.9	1.7	2.1	66.4
L	-3.832	5.5	62.4	26.3	5.9
L+1	-3.438	6.0	76.0	10.3	7.7
L+2	-3.060	4.5	1.9	1.1	92.5
L+3	-2.838	3.5	1.1	1.4	94.1
py-para					
H-4	-9.233	32.3	6.3	9.2	52.3
H-3	-9.180	19.0	2.8	6.5	71.8
H-2	-8.889	18.2	1.7	1.3	78.8
H-1	-8.722	16.3	1.2	3.1	79.3
H	-8.162	30.4/21.8	2.2	2.4	65.0
L	-3.848	7.0	63.7	23.4	5.9
L+1	-3.389	3.9	76.4	12.7	6.9
L+2	-3.078	4.7	2.0	1.4	91.9
L+3	-2.844	3.1	0.8	1.4	94.7
cu-pyim					
H-4	-9.158	13.5	24.5	49.6	12.4
H-3	-9.149	53.6	17.0	15.2	14.3
H-2	-8.791	23.9	2.2	2.8	71.0
H-1	-8.774	17.4	4.0	1.3	77.3

H	-8.130	29.0/21.1	1.2	1.9	67.9
L	-3.954	2.7	61.7	31.2	4.4
L+1	-3.266	5.9	80.5	6.1	7.6
L+2	-2.974	4.5	4.1	0.9	90.4
L+3	-2.856	2.3	1.1	0.3	96.3

注：Nn5 five-membered heterocyclic rings , Nn6 represents pyridine moiety

Table S5 Molecular orbital compositions in the T_1 State for complexes by DFT /U/M06/LANL2DZ&6-31G(d).

orbital	Energy/eV	Contribution %			
		Cu/ d-orbital	Nn6	Nn5	P^P
py-pop					
H-5	-7.471	4.8	10.5	9.5	75.2
H-4	-7.322	18.7	14.6	15.1	51.6
H-3	-7.209	55.0	9.9	14.2	20.9
H-2	-7.038	12.7	1.8	4.5	81.0
H-1	-6.836	29.1	3.8	3.2	64.0
H	-5.944	26.6/19.3	1.5	1.7	70.2
L	-1.826	12.2	38.9	18.0	30.9
L+1	-1.488	6.3	23.3	4.5	65.9
py-ch3					
H-5	-7.419	14.8	6.7	5.4	73.1
H-4	-7.327	28.1	31.1	32.6	8.2
H-3	-7.240	43.1	15.1	22.4	19.4
H-2	-7.026	9.9	1.9	2.9	85.4
H-1	-6.823	27.7	3.3	4.0	65.0
H	-6.068	27.7/19.8	1.2	2.5	68.6
L	-1.678	6.1	58.3	25.7	9.9
L+1	-1.491	10.9	3.1	2.3	83.7
py- meta					
H-5	-7.403	1.0	0.7	1.2	97.1
H-4	-7.310	5.8	32.1	44.2	17.9
H-3	-7.110	49.8	10.2	11.8	28.2
H-2	-7.033	10.1	2.2	0.4	87.3
H-1	-6.954	22.6	3.2	3.5	70.7
H	-5.556	33.7/29.6	6.4	7.4	52.5
L	-2.111	6.7	57.0	28.9	7.5
L+1	-1.263	6.9	65.8	14.8	12.5
py- para					
H-5	-7.414	10.1	13.2	18.7	58.0
H-4	-7.383	2.2	2.0	3.8	91.9
H-3	-7.067	41.7	12.1	6.2	40.0

H-2	-7.027	8.4	1.0	2.6	88.1
H-1	-6.911	34.3	1.3	10.7	53.7
H	-5.517	34.1/30.0	6.9	6.6	52.4
L	-2.116	8.3	60.3	23.5	7.8
L+1	-1.213	6.3	55.3	13.3	25.1
cu-pyim					
H-5	-7.416	1.8	0.6	0.3	97.4
H-4	-7.148	58.1	14.6	12.5	14.8
H-3	-6.992	11.4	1.5	2.7	84.4
H-2	-6.927	38.5	8.8	2.2	50.4
H-1	-6.647	2.6	35.7	56.7	5.0
H	-6.224	29.2/22.2	2.3	3.6	64.9
L	-2.310	2.7	53.1	40.2	4.0
L+1	-1.175	4.9	5.6	1.3	88.2

note：Nn5 notes five-membered heterocyclic rings , Nn6 represents pyridine moiety

Table S6 Electronic transitions of py-pop calculated at the T_1 optimized geometry by TD-DFT in CH_2Cl_2 solution

S_m/T_m	Energy(eV)	Wavelength(nm)	f_n	Major contribution
T_1	2.1501	591.0	0	H→L+1 29%
				H→L 26%
				H-1→L+1 11%
T_2	3.0987	400.11	0	H→L 56%
				H→L+1 18%
S_1	3.2003	387.42	0.0238	H→L 97%
S_2	3.5998	344.42	0.1952	H→L+1 94%
S_3	3.8283	323.86	0.0107	H→L+2 80%
				H→L+3 15%
S_4	3.8725	320.16	0.0218	H→L+3 76%
				H→L+2 16%
S_5	3.9983	310.09	0.0676	H→L+5 45%
				H→L+4 42%
S_6	4.0512	306.04	0.0379	H→L+4 47%
				H→L+5 43%
S_7	4.0835	303.62	0.0064	H-3→L 45%

				H-1→L 30%
S_8	4.1449	299.12	0.0197	H-1→L 57%
				H-3→L 24%
S_9	4.3223	286.84	0.0647	H→L+6 88%
S_{10}	4.4439	279.00	0.0227	H→L+7 38%
				H→L+8 36%

Table S7 Electronic transitions of py-ch3 calculated at the T_1 optimized geometry by TD-DFT in CH_2Cl_2 solution

S_m/T_m	Energy(eV)	Wavelength(nm)	f_n	Major contribution
T_1	2.3265	532.93	0	H→L+1 39%
				H-1→L+1 25%
T_2	3.2560	380.79	0	H→L 60%
T_3	3.3240	372.99	0	H→L+5 10%
S_1	3.5173	352.50	0.0624	H→L 94%
S_2	3.6569	339.04	0.1356	H→L+1 94%
S_3	3.9307	315.42	0.0046	H→L+2 94%
S_4	3.9509	313.82	0.0452	H→L+3 93%
S_5	4.0937	302.86	0.0735	H→L+4 92%
S_6	4.1952	295.54	0.0426	H→L+5 84%
S_7	4.2442	292.13	0.0250	H-1→L 37%
				H-3→L 19%
				H-4→L 14%
				H-2→L 10%
S_8	4.2708	290.31	0.0116	H-1→L 49%
				H-3→L 29%
S_9	4.4383	279.35	0.0761	H-1→L+1 65%
				H→L+6 23%
S_{10}	4.4657	277.63	0.0357	H-1→L+1 71%
				H→L+6 21%

Table S8 Electronic transitions of py-meta calculated at the T_1 optimized geometry by TD-DFT in CH_2Cl_2 solution

S_m/T_m	Energy(eV)	Wavelength(nm)	f_n	Major contribution
T_1	2.1624	573.37	0.000	H→L 94%
S_1	2.4125	513.92	0.0436	H→L 97%
S_2	3.3131	374.22	0.0012	H→L+1 96%
S_3	3.4273	361.75	0.0134	H→L+2 95%
S_4	3.4891	355.34	0.0686	H→L+3 89%
S_5	3.5912	345.25	0.0392	H→L+4 88%
S_6	3.8045	325.89	0.0519	H→L+5 69%
				H-3→L 21%
S_7	3.8227	324.33	0.0660	H-3→L 55%
				H→L+5 27%
S_8	3.8977	318.10	0.0305	H-2→L 18%
				H-1→L 58%
S_9	3.9304	315.45	0.0604	H→L+6 92%
S_{10}	4.0631	305.15	0.0369	H→L+7 90%

Table S9 Electronic transitions of py-para calculated at the T_1 optimized geometry by TD-DFT in CH_2Cl_2 solution

S_m/T_m	Energy(eV)	Wavelength(nm)	f_n	Major contribution
T_1	2.1456	577.86	0	H→L 95%
S_1	2.3368	530.58	0.0282	H→L 97%
S_2	3.3138	374.14	0.0017	H→L+1 88%
S_3	3.3878	365.97	0.0126	H→L+2 86%
S_4	3.4578	358.56	0.0637	H→L+3 90%
S_5	3.5759	346.73	0.0383	H→L+4 90%
S_6	3.7139	333.84	0.0437	H-1→L 59%
				H-3→L 22%

S_7	3.7516	330.49	0.0719	H→L+5 93%
S_8	3.8944	318.37	0.0669	H→L+6 95%
S_9	3.9434	314.41	0.0344	H-3→L 59%
				H-1→L 24%
S_{10}	4.0462	306.42	0.0583	H→L+7 94%

Table S10 Electronic transitions of cu-pyim calculated at the T_1 optimized geometry by TD-DFT in CH_2Cl_2 solution

S_m/T_m	Energy(eV)	Wavelength(nm)	f_n	Major contribution
T_1	2.0834	595.12	0	H-1→L 86%
T_2	2.9100	426.07	0	H→L 86%
S_1	3.0473	406.86	0.0656	H→L 98%
S_2	3.4539	358.97	0.0061	H-4→L 57%
				H-2→L 30%
S_3	3.6522	339.47	0.3775	H→L 95%
S_4	3.6630	338.48	0.0059	H-2→L 60%
				H-4→L 22%
S_5	4.1032	302.16	0.0075	H-3→L 57%
				H→L+1 27%
S_6	4.1153	301.28	0.0083	H→L+1 66%
				H-3→L 22%
S_7	4.1869	296.13	0.1233	H→L+2 84%
S_8	4.2728	290.17	0.0396	H→L+3 81%
S_9	4.3304	286.31	0.0150	H-6→L 41%
				H-5→L 26%
				H→L+4 17%
S_{10}	4.3528	284.84	0.0057	H→L+4 75%

Table S11 SOC matrix elements$<T_m|Hsoc|S_n>$(cm^{-1}), the oscillator strengths f_n of py-pop calculated at T_1 optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant kr is also given.

$E(T_1)$= 17341cm^{-1}			
	SOC	$E(S_n)$	$f(S_n)$
S_1	-9.980	25812	0.0238
S_2	-10.660	29034	0.1952
S_5	1.364	32248	0.0676
S_6	0.628	32675	0.0379
S_7	1.897	32936	0.0064
S_8	-7.070	33431	0.0197
S_{10}	-1.503	35842	0.0227
kr			133.86

$E(T_2)$= 24992cm^{-1}			
	SOC	$E(S_n)$	$f(S_n)$
S_1	-4.863	25812	0.0238
S_2	0.718	29034	0.1952
S_5	3.280	32248	0.0676
S_6	6.202	32675	0.0379
S_7	23.867	32936	0.0064
S_8	-39.835	33431	0.0197
S_{10}	1.101	35842	0.0227
kr			1048.72

Table S12 SOC matrix elements<T_m|Hsoc|S_n>(cm^{-1}), the oscillator strengths f_n of py-ch3 calculated at T_1 optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant kr is also given.

$E(T_1)$=18764cm^{-1}			
	SOC	$E(S_n)$	$f(S_n)$
S1	-2.044	28369	0.0624
S_2	-11.037	29495	0.1356
S_5	0.958	33018	0.0735
S_6	-0.157	33837	0.0426
S_7	-2.340	34232	0.025
S_8	10.506	34446	0.0116
S_9	35.542	35797	0.0761
S_{10}	-20.271	36018	0.0357
kr			1.14

$E(T_2)$=26261cm^{-1}

	SOC	$E(S_n)$	$f(S_n)$
S1	8.329	28369	0.0624
S_2	-1.505	29495	0.1356
S_5	7.032	31703	0.0046
S_6	-1.040	31866	0.0452
S_7	5.149	33018	0.0735
S_8	2.187	33837	0.0426
S_9	4.004	34232	0.025
S_{10}	39.692	34446	0.0116
kr			3346.82

$E(T_3)=26810\ cm^{-1}$			
	SOC	$E(S_n)$	$f(S_n)$
S1	5.609	31866	0.0426
S_2	-2.604	33018	0.0250
kr			13.06

Table S13 SOC matrix elements$<T_m|Hsoc|S_n>(cm^{-1})$, the oscillator strengths f_n of py-meta calculated at T_1 optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant kr is also given.

$E(T_1)=17452cm^{-1}$			
	SOC	$E(S_n)$	$f(S_n)$
S_1	9.928	19473	0.0438
S_6	-35.127	24884	0.0502
S_7	51.202	30830	0.0671
S_8	7.021	31439	0.0313
kr			469.21

Table S14 SOC matrix elements$<T_m|Hsoc|S_n>(cm^{-1})$, the oscillator strengths f_n of py-para calculated at T_1 optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant kr is also given.

$E(T_1)=17305cm^{-1}$			
	SOC	$E(S_n)$	$f(S_n)$
S_1	4.870	18848	0.0282
S_6	9.788	29955	0.0437
S_9	28.616	32635	0.0344
kr			445.93

Table S15 SOC matrix elements<T_m|Hsoc|S_n>(cm^{-1}), the oscillator strengths f_n of cu-pyim calculated at T_1 optimized geometry with solvent CH_2Cl_2 included. The radiative decay rate constant kr is also given.

$E(T_1)=16803cm^{-1}$			
	SOC	$E(S_n)$	$f(S_n)$
S_1	-11.543	24578	0.0656
S_2	-4.726	27858	0.0061
S_3	-3.713	29457	0.3775
S_4	1.613	29544	0.0059
S_5	-3.202	33095	0.0075
S_6	-1.908	33192	0.0083
S_9	-4.924	34927	0.015
S_{10}	-2.418	35108	0.0057
kr			72.58

$E(T_2)=23470cm^{-1}$			
	SOC	$E(S_n)$	$f(S_n)$
S_1	-3.506	24578	0.0656
S_2	15.002	27858	0.0061
S_3	11.334	29457	0.3775
S_4	-83.882	29544	0.0059
S_5	-7.128	33095	0.0075
S_6	-6.165	33192	0.0083
S_9	-3.869	34927	0.015
S_{10}	-3.705	35108	0.0057
kr			392.00

Table S16 The vibration source of the largest reorganization energies for complexes.

	Frequency with large reorganization energies/cm^{-1}	Vibration displacement/Å	Vibration source
py-pop			
	1655	-1.261	in-plane vibration of the benzene ring which is linked to C_{23}（in-plane stretching vibration and bending vibration）
	229	-2.46	out-plane bending vibration of the benzene ring which is linked to C_{23}, and swing of total P^P ligand
	232	-2.374	out-plane bending vibration of the benzene ring which is linked to C_{23}, and swing of total P^P ligand

py-ch3			
	1655	1.238	in-plane stretching vibration of the benzene ring which is linked to C_{67}
	1131	-1.036	in-plane vibration of the benzene ring which is linked to C_{67}（in-plane stretching vibration and bending vibration）
	73	3.898	out-plane bending vibration of the benzene ring which is linked to C_{23}, and swing of total P^P ligand
py-meta			
	141	9.93	out-plane bending vibration of the benzene ring which is linked to C_{20}, torsion of N^N ligand, rocking of the methyl, swing of total molecule
	17	-4.573	in-plane vibration in the same direction of the benzene in P^P ligand, rocking of the methyl, swing of total molecule
	71	-9.438	torsion of the benzene ring which is linked to C_{20}, rocking of the methyl
py-para			
	101	6.133	torsion of the benzene ring which is linked to C_{19}, torsion of N^N ligand, rocking of the methyl, swing of total molecule
	40	-8.695	torsion of the benzene ring which is linked to C_{19}, torsion of N^N ligand, rocking of the methyl, swing of total molecule
	65	4.242	torsion of the benzene ring which is linked to C_{19}, swing of total molecule
cu-pyim			
	1669	-1.057	in-plane vibration of N^N ligand (in-plane stretching vibration and bending vibration)
	1609	-0.716	in-plane vibration of N^N ligand (in-plane stretching vibration and bending vibration)
	1531	-0.723	in-plane vibration of N^N ligand (in-plane stretching vibration and bending vibration)

Table S17 Vibrational frequencies(cm^{-1}) at the optimized S_0 state, Huang-Rhys factor S_i, and reorganization energy λ_i of py-pop.

	ω_i/cm^{-1}	ΔQ	λ_i/cm^{-1}	S_i
1	0	0	0	0.00
2	0	0	0	0.00
3	0	0	0	0.00
4	0	0	0	0.00
5	0	0	0	0.00
6	0	0	0	0.00
7	23	3.686	157.6	6.79
8	26	0.319	1.3	0.05
9	29	-2.141	66.7	2.29
10	34	0.105	0.2	0.01
11	39	-5.249	537.3	13.78
12	40	-1.305	34.5	0.85
13	49	-2.664	174.4	3.55

14	52	-3.163	258.3	5.00
15	53	-1.234	40.7	0.76
16	62	-1.226	46.4	0.75
17	66	-1.096	39.9	0.60
18	69	1.521	80.2	1.16
19	72	-1.209	52.4	0.73
20	79	-2.152	183.4	2.32
21	83	-1.864	143.6	1.74
22	87	-0.513	11.4	0.13
23	92	1.801	149.5	1.62
24	113	-0.355	7.1	0.06
25	122	1.046	66.9	0.55
26	130	-0.221	3.2	0.02
27	137	0.125	1.1	0.01
28	140	-0.514	18.5	0.13
29	141	-0.587	24.3	0.17
30	148	-0.426	13.5	0.09
31	159	-0.227	4.1	0.03
32	164	0.48	19	0.12
33	166	0.244	4.9	0.03
34	181	-0.551	27.6	0.15
35	194	1.223	144.9	0.75
36	205	-0.344	12.1	0.06
37	214	1.344	193.6	0.90
38	220	0.053	0.3	0.00
39	221	0.061	0.4	0.00
40	229	-2.46	694.6	3.03
41	232	-2.374	652.9	2.82
42	236	-0.932	102.5	0.43
43	251	0.974	118.8	0.47
44	264	0.216	6.2	0.02
45	267	0.763	77.8	0.29
46	284	-0.329	15.4	0.05
47	289	-0.397	22.8	0.08
48	305	-0.024	0.1	0.00
49	369	-0.373	25.7	0.07
50	396	-0.014	0	0.00
51	407	-0.007	0	0.00
52	413	-0.844	146.8	0.36
53	416	0.151	4.8	0.01
54	420	0.029	0.2	0.00
55	422	0.006	0	0.00
56	424	0.049	0.5	0.00
57	429	0.042	0.4	0.00

58	433	0.083	1.5	0.00
59	437	0.347	26.4	0.06
60	445	-0.45	45	0.10
61	455	-0.004	0	0.00
62	476	-0.183	8	0.02
63	476	-0.263	16.5	0.03
64	482	-0.194	9.1	0.02
65	498	-0.408	41.5	0.08
66	500	-0.011	0	0.00
67	508	-0.115	3.4	0.01
68	519	0.026	0.2	0.00
69	532	-0.036	0.3	0.00
70	534	0.015	0.1	0.00
71	539	-0.009	0	0.00
72	556	0.283	22.3	0.04
73	592	-0.001	0	0.00
74	615	0.11	3.7	0.01
75	621	0.003	0	0.00
76	622	0.007	0	0.00
77	622	0.064	1.3	0.00
78	623	0.198	12.2	0.02
79	628	0.066	1.4	0.00
80	634	0.06	1.2	0.00
81	659	0.245	19.8	0.03
82	680	-0.141	6.8	0.01
83	687	-0.125	5.4	0.01
84	704	0.139	6.8	0.01
85	705	0.241	20.5	0.03
86	707	0.882	274.7	0.39
87	709	0.018	0.1	0.00
88	714	-0.275	26.9	0.04
89	716	-0.419	62.9	0.09
90	720	0.139	7	0.01
91	725	0.056	1.1	0.00
92	725	0.016	0.1	0.00
93	731	0.056	1.2	0.00
94	747	-0.203	15.5	0.02
95	749	0.38	54.1	0.07
96	750	-0.505	95.4	0.13
97	756	0.298	33.5	0.04
98	760	0.043	0.7	0.00
99	764	-0.002	0	0.00
100	766	0.154	9.1	0.01
101	774	-0.046	0.8	0.00

102	780	0.071	2	0.00
103	784	0.022	0.2	0.00
104	818	-0.016	0.1	0.00
105	855	-0.011	0	0.00
106	863	0.023	0.2	0.00
107	866	0.001	0	0.00
108	868	0.205	18.3	0.02
109	872	0.092	3.7	0.00
110	884	-0.021	0.2	0.00
111	885	0.03	0.4	0.00
112	888	-0.04	0.7	0.00
113	893	-0.01	0	0.00
114	919	0.006	0	0.00
115	931	-0.049	1.1	0.00
116	936	-0.255	30.5	0.03
117	939	0.021	0.2	0.00
118	943	0.52	127.3	0.14
119	949	-0.026	0.3	0.00
120	954	0.03	0.4	0.00
121	957	0.013	0.1	0.00
122	966	-0.088	3.7	0.00
123	970	-0.037	0.7	0.00
124	978	0.023	0.3	0.00
125	982	-0.292	41.9	0.04
126	988	-0.019	0.2	0.00
127	995	-0.015	0.1	0.00
128	995	-0.008	0	0.00
129	1001	0.596	177.8	0.18
130	1001	-0.001	0	0.00
131	1002	-0.024	0.3	0.00
132	1004	-0.111	6.2	0.01
133	1005	-0.1	5.1	0.01
134	1005	-0.513	132.5	0.13
135	1006	0.004	0	0.00
136	1008	0	0	0.00
137	1011	0.008	0	0.00
138	1019	0.003	0	0.00
139	1042	-0.052	1.4	0.00
140	1051	-0.007	0	0.00
141	1053	0.001	0	0.00
142	1054	0.513	138.8	0.13
143	1054	-0.488	125.4	0.12
144	1058	-0.012	0.1	0.00
145	1061	0.007	0	0.00

146	1067	-0.049	1.3	0.00
147	1072	0.053	1.5	0.00
148	1078	-0.002	0	0.00
149	1082	-0.073	2.9	0.00
150	1089	-0.01	0.1	0.00
151	1103	0.001	0	0.00
152	1104	0.02	0.2	0.00
153	1106	-0.101	5.7	0.01
154	1107	0.002	0	0.00
155	1126	0.005	0	0.00
156	1129	-1.066	640.8	0.57
157	1129	-0.013	0.1	0.00
158	1130	-0.092	4.8	0.00
159	1132	-0.047	1.3	0.00
160	1141	0.045	1.2	0.00
161	1144	-0.04	0.9	0.00
162	1160	0.039	0.9	0.00
163	1168	-0.001	0	0.00
164	1169	-0.007	0	0.00
165	1169	0.001	0	0.00
166	1170	0.201	23.6	0.02
167	1171	0.147	12.7	0.01
168	1173	-0.013	0.1	0.00
169	1174	0.061	2.2	0.00
170	1192	-0.01	0.1	0.00
171	1195	0.185	20.5	0.02
172	1197	0.838	420.2	0.35
173	1200	-0.017	0.2	0.00
174	1229	0.055	1.8	0.00
175	1240	0.048	1.4	0.00
176	1262	0.012	0.1	0.00
177	1279	-0.004	0	0.00
178	1286	-0.003	0	0.00
179	1303	0.064	2.6	0.00
180	1314	0.007	0	0.00
181	1319	0.063	2.6	0.00
182	1322	-0.003	0	0.00
183	1322	-0.075	3.7	0.00
184	1336	-0.018	0.2	0.00
185	1349	-0.02	0.3	0.00
186	1352	0.001	0	0.00
187	1357	0.069	3.2	0.00
188	1361	0.005	0	0.00
189	1362	0.277	52.1	0.04

190	1362	0.03	0.6	0.00
191	1365	0.067	3.1	0.00
192	1390	-0.011	0.1	0.00
193	1458	-0.01	0.1	0.00
194	1467	0.007	0	0.00
195	1469	-0.094	6.5	0.00
196	1470	-0.225	37.2	0.03
197	1472	0.094	6.6	0.00
198	1472	0.048	1.7	0.00
199	1474	-0.057	2.4	0.00
200	1478	-0.046	1.5	0.00
201	1483	0.01	0.1	0.00
202	1499	0.006	0	0.00
203	1505	0.011	0.1	0.00
204	1514	-0.001	0	0.00
205	1515	-0.001	0	0.00
206	1516	0.013	0.1	0.00
207	1517	0.254	49.1	0.03
208	1526	0.017	0.2	0.00
209	1589	0.052	2.2	0.00
210	1632	-0.009	0.1	0.00
211	1638	0	0	0.00
212	1640	0.149	18.3	0.01
213	1640	0.345	97.6	0.06
214	1641	0.128	13.5	0.01
215	1643	-0.205	34.4	0.02
216	1647	0.04	1.3	0.00
217	1655	-0.39	125.9	0.08
218	1655	-0.035	1	0.00
219	1655	-1.261	1315.7	0.80
220	1657	-0.091	6.9	0.00
221	1657	0.289	69.2	0.04
222	1660	0.014	0.2	0.00
223	1669	-0.009	0.1	0.00
224	3141	0.008	0.1	0.00
225	3148	-0.055	4.8	0.00
226	3156	-0.006	0.1	0.00
227	3158	0.009	0.1	0.00
228	3170	-0.002	0	0.00
229	3174	-0.002	0	0.00
230	3176	0	0	0.00
231	3176	0.001	0	0.00
232	3179	-0.009	0.1	0.00
233	3181	0.003	0	0.00

234	3184	0.001	0	0.00
235	3184	0.002	0	0.00
236	3185	0.002	0	0.00
237	3187	0.003	0	0.00
238	3187	-0.007	0.1	0.00
239	3191	0.001	0	0.00
240	3192	0.001	0	0.00
241	3195	0	0	0.00
242	3195	0.004	0	0.00
243	3196	0	0	0.00
244	3197	-0.001	0	0.00
245	3199	0.002	0	0.00
246	3200	-0.001	0	0.00
247	3201	0	0	0.00
248	3204	0	0	0.00
249	3204	-0.001	0	0.00
250	3206	-0.002	0	0.00
251	3207	0.013	0.3	0.00
252	3207	-0.044	3.1	0.00
253	3210	0	0	0.00
254	3216	-0.001	0	0.00
255	3222	0.001	0	0.00
256	3250	-0.025	1	0.00
257	3267	0.005	0	0.00
258	3288	-0.002	0	0.00

Table S18 Vibrational frequencies(ω_i/cm^{-1}) at the optimized S_0 state, Huang-Rhys factor S_i, and reorganization energy λ_i of py-ch3.

	ω_i/cm^{-1}	ΔQ	λ_i/cm^{-1}	S_i
1	0	0	0	0.00
2	0	0	0	0.00
3	0	0	0	0.00
4	0	0	0	0.00
5	0	0	0	0.00
6	0	0	0	0.00
7	22	-1.815	35.6	1.65
8	28	-0.62	5.4	0.19
9	32	0.042	0	0.00
10	33	-2.415	96.1	2.92
11	41	-1.25	32.2	0.78
12	45	-1.398	44.2	0.98
13	45	0.132	0.4	0.01
14	52	1.039	28	0.54

15	58	0.501	7.2	0.13
16	59	-3.195	299.6	5.10
17	65	0.125	0.5	0.01
18	73	3.898	556	7.60
19	78	1.017	40.4	0.52
20	83	-0.148	0.9	0.01
21	89	-2.108	197.2	2.22
22	90	-0.576	14.9	0.17
23	95	-1.424	96.7	1.01
24	103	-2.687	370.8	3.61
25	113	-0.665	25	0.22
26	120	-1.778	189.2	1.58
27	121	-0.856	44.4	0.37
28	125	-0.197	2.4	0.02
29	134	-0.021	0	0.00
30	142	-0.408	11.8	0.08
31	150	0.282	5.9	0.04
32	155	0.924	66.3	0.43
33	161	0.247	4.9	0.03
34	167	-1.251	131	0.78
35	184	0.557	28.5	0.16
36	199	-0.4	16	0.08
37	210	-1.188	147.9	0.71
38	215	0.965	100.2	0.47
39	218	0.128	1.8	0.01
40	226	-1.579	282	1.25
41	230	-0.958	105.5	0.46
42	238	-0.272	8.8	0.04
43	247	-0.505	31.5	0.13
44	252	0.362	16.5	0.07
45	265	-0.439	25.5	0.10
46	271	-0.337	15.4	0.06
47	283	-0.184	4.8	0.02
48	286	-0.234	7.8	0.03
49	306	0.036	0.2	0.00
50	333	0.017	0	0.00
51	370	0.094	1.6	0.00
52	374	0.221	9.1	0.02
53	405	0.142	4.1	0.01
54	408	0.004	0	0.00
55	412	-0.789	128.3	0.31
56	417	0.059	0.7	0.00
57	419	-0.024	0.1	0.00
58	422	0.146	4.5	0.01

59	425	0.136	3.9	0.01
60	428	0.373	29.8	0.07
61	432	0.006	0	0.00
62	438	-0.14	4.3	0.01
63	447	-0.366	29.9	0.07
64	456	0.001	0	0.00
65	477	-0.193	8.9	0.02
66	482	-0.268	17.3	0.04
67	494	0.288	20.5	0.04
68	501	0.163	6.6	0.01
69	503	-0.003	0	0.00
70	510	0.068	1.2	0.00
71	518	0.067	1.2	0.00
72	523	-0.105	2.9	0.01
73	532	-0.115	3.5	0.01
74	533	-0.007	0	0.00
75	554	-0.271	20.3	0.04
76	592	0	0	0.00
77	615	-0.009	0	0.00
78	622	0.189	11.1	0.02
79	623	0.336	35.1	0.06
80	627	-0.016	0.1	0.00
81	628	0.009	0	0.00
82	629	0.004	0	0.00
83	633	-0.03	0.3	0.00
84	666	-0.027	0.2	0.00
85	678	-0.014	0.1	0.00
86	681	0.092	2.9	0.00
87	689	0.168	9.7	0.01
88	705	0.179	11.3	0.02
89	707	0.186	12.2	0.02
90	709	0.823	239.8	0.34
91	709	0.185	12.2	0.02
92	715	0.115	4.7	0.01
93	718	-0.032	0.4	0.00
94	721	-0.281	28.5	0.04
95	726	0.022	0.2	0.00
96	734	0.037	0.5	0.00
97	735	0.052	1	0.00
98	745	0.005	0	0.00
99	745	-0.011	0	0.00
100	753	0.521	102.3	0.14
101	757	0.05	1	0.00
102	758	0.021	0.2	0.00

103	760	-0.19	13.8	0.02
104	764	0.048	0.9	0.00
105	773	0.053	1.1	0.00
106	778	-0.033	0.4	0.00
107	779	-0.033	0.4	0.00
108	817	-0.014	0.1	0.00
109	857	0.027	0.3	0.00
110	860	-0.019	0.2	0.00
111	861	0.066	1.9	0.00
112	874	-0.349	53.1	0.06
113	875	0.004	0	0.00
114	877	-0.117	6	0.01
115	880	0.006	0	0.00
116	881	-0.064	1.8	0.00
117	897	0.006	0	0.00
118	931	0.001	0	0.00
119	937	-0.078	2.9	0.00
120	938	0.429	86.3	0.09
121	943	0.06	1.7	0.00
122	956	0.015	0.1	0.00
123	957	-0.017	0.1	0.00
124	965	-0.046	1	0.00
125	969	0.003	0	0.00
126	975	-0.006	0	0.00
127	980	0.088	3.8	0.00
128	986	0.005	0	0.00
129	987	-0.455	102	0.10
130	990	0.066	2.1	0.00
131	993	0	0	0.00
132	995	0.009	0	0.00
133	1002	0.195	19.1	0.02
134	1002	0.756	286	0.29
135	1004	0.059	1.8	0.00
136	1005	0.012	0.1	0.00
137	1006	-0.063	2	0.00
138	1006	-0.309	48.1	0.05
139	1007	-0.006	0	0.00
140	1008	-0.019	0.2	0.00
141	1011	-0.048	1.1	0.00
142	1016	0.041	0.9	0.00
143	1040	-0.034	0.6	0.00
144	1054	0.761	305.4	0.29
145	1054	-0.076	3	0.00
146	1056	0.082	3.5	0.00

147	1056	0.161	13.7	0.01
148	1057	-0.152	12.3	0.01
149	1063	0.001	0	0.00
150	1064	-0.033	0.6	0.00
151	1067	0.003	0	0.00
152	1077	0.016	0.1	0.00
153	1086	-0.008	0	0.00
154	1097	0.02	0.2	0.00
155	1104	0	0	0.00
156	1108	0.016	0.1	0.00
157	1108	-0.141	11	0.01
158	1110	-0.014	0.1	0.00
159	1119	0.007	0	0.00
160	1131	-1.036	606.6	0.54
161	1131	0.289	47.1	0.04
162	1134	0.016	0.1	0.00
163	1137	0.085	4.1	0.00
164	1143	0.03	0.5	0.00
165	1144	0.012	0.1	0.00
166	1151	-0.06	2.1	0.00
167	1172	-0.007	0	0.00
168	1173	-0.05	1.5	0.00
169	1173	0.34	67.7	0.06
170	1174	0.008	0	0.00
171	1176	0.003	0	0.00
172	1177	-0.01	0.1	0.00
173	1177	0.027	0.4	0.00
174	1196	0.002	0	0.00
175	1203	-0.714	306.2	0.25
176	1203	-0.505	153.2	0.13
177	1209	0.005	0	0.00
178	1237	0.022	0.3	0.00
179	1248	0.001	0	0.00
180	1282	0.011	0.1	0.00
181	1293	0.003	0	0.00
182	1298	-0.021	0.3	0.00
183	1299	-0.01	0.1	0.00
184	1318	-0.002	0	0.00
185	1326	0.094	5.8	0.00
186	1329	0.017	0.2	0.00
187	1330	-0.083	4.5	0.00
188	1339	-0.017	0.2	0.00
189	1349	0.005	0	0.00
190	1352	-0.001	0	0.00

191	1360	0.048	1.6	0.00
192	1363	-0.265	47.9	0.04
193	1363	0.01	0.1	0.00
194	1366	-0.019	0.2	0.00
195	1367	-0.055	2.1	0.00
196	1406	0.031	0.7	0.00
197	1438	-0.008	0	0.00
198	1448	0.019	0.3	0.00
199	1469	0.007	0	0.00
200	1470	-0.304	67.8	0.05
201	1472	-0.012	0.1	0.00
202	1473	-0.086	5.4	0.00
203	1475	-0.025	0.5	0.00
204	1480	0.044	1.4	0.00
205	1484	0.002	0	0.00
206	1489	-0.02	0.3	0.00
207	1502	-0.095	6.8	0.00
208	1507	-0.01	0.1	0.00
209	1507	0.006	0	0.00
210	1514	-0.015	0.2	0.00
211	1516	-0.002	0	0.00
212	1519	-0.248	46.5	0.03
213	1520	-0.005	0	0.00
214	1521	0.024	0.5	0.00
215	1530	0.015	0.2	0.00
216	1607	0.008	0	0.00
217	1633	-0.016	0.2	0.00
218	1641	-0.193	30.5	0.02
219	1641	0.762	476.9	0.29
220	1642	-0.104	8.8	0.01
221	1643	-0.056	2.5	0.00
222	1644	0.254	53.2	0.03
223	1649	0.017	0.2	0.00
224	1655	1.238	1267.7	0.77
225	1656	-0.291	69.9	0.04
226	1657	0.165	22.5	0.01
227	1659	-0.019	0.3	0.00
228	1659	0.153	19.5	0.01
229	1659	-0.026	0.6	0.00
230	1669	0.003	0	0.00
231	3041	0.006	0.1	0.00
232	3117	-0.004	0	0.00
233	3145	0.032	1.6	0.00
234	3148	-0.009	0.1	0.00

235	3157	0.008	0.1	0.00
236	3157	0.006	0	0.00
237	3159	-0.088	12.2	0.00
238	3170	-0.003	0	0.00
239	3171	0	0	0.00
240	3174	0	0	0.00
241	3177	-0.003	0	0.00
242	3178	0	0	0.00
243	3182	-0.001	0	0.00
244	3183	0.003	0	0.00
245	3184	0	0	0.00
246	3185	-0.003	0	0.00
247	3186	0	0	0.00
248	3186	0.004	0	0.00
249	3189	0.001	0	0.00
250	3191	0	0	0.00
251	3193	-0.001	0	0.00
252	3193	-0.003	0	0.00
253	3194	-0.001	0	0.00
254	3195	-0.002	0	0.00
255	3201	0	0	0.00
256	3202	0.001	0	0.00
257	3202	0	0	0.00
258	3204	-0.001	0	0.00
259	3204	-0.002	0	0.00
260	3206	-0.059	5.6	0.00
261	3208	-0.001	0	0.00
262	3209	-0.003	0	0.00
263	3210	0.001	0	0.00
264	3221	0	0	0.00
265	3227	-0.002	0	0.00
266	3266	0	0	0.00
267	3284	0	0	0.00

Table S19 Vibrational frequencies (ω_i/cm^{-1}) at the optimized S0 state, Huang-Rhys factor S_i, and reorganization energy λ_i of py-meta.

	ω_i/cm^{-1}	ΔQ	λ_i/cm^{-1}	S_i
1	0	0	0	0.00
2	0	0	0	0.00
3	0	0	0	0.00
4	0	0	0	0.00
5	0	0	0	0.00
6	0	0	0	0.00

7	12	-4.786	135.7	11.45
8	17	-9.438	774.8	44.54
9	26	3.833	189.4	7.35
10	31	2.551	100.1	3.25
11	36	-1.776	56.5	1.58
12	40	-2.75	151.4	3.78
13	45	1.054	25.1	0.56
14	50	1.722	74.2	1.48
15	55	-2.917	236	4.25
16	60	2.169	140.2	2.35
17	67	-0.958	30.6	0.46
18	71	-4.573	747.4	10.46
19	74	0.501	9.3	0.13
20	79	-0.728	20.9	0.26
21	84	-1.36	77.5	0.92
22	87	-0.004	0	0.00
23	88	-2.97	389.7	4.41
24	106	-1.228	80.2	0.75
25	108	0.445	10.7	0.10
26	115	1.601	146.7	1.28
27	122	-0.073	0.3	0.00
28	127	-3.736	886.7	6.98
29	131	-0.746	36.4	0.28
30	137	0.06	0.2	0.00
31	141	-4.456	1404.1	9.93
32	145	-1.632	192.8	1.33
33	148	1.98	290.4	1.96
34	163	0.924	69.6	0.43
35	166	1.292	138.4	0.83
36	181	-0.107	1	0.01
37	194	-1.294	162.7	0.84
38	207	0.512	27.2	0.13
39	213	1.208	155.7	0.73
40	215	-0.425	19.4	0.09
41	226	0.003	0	0.00
42	227	0.005	0	0.00
43	231	0.203	4.8	0.02
44	238	-0.297	10.5	0.04
45	252	0.904	102.9	0.41
46	259	-0.017	0	0.00
47	269	-0.009	0	0.00
48	282	0.444	27.8	0.10
49	306	-0.141	3	0.01
50	312	0.934	136	0.44

51	327	-0.015	0	0.00
52	371	-0.068	0.9	0.00
53	378	-0.201	7.6	0.02
54	410	0.108	2.4	0.01
55	415	-0.186	7.2	0.02
56	415	0.178	6.6	0.02
57	417	-0.406	34.3	0.08
58	422	0.687	99.6	0.24
59	423	-0.017	0.1	0.00
60	427	-0.089	1.7	0.00
61	431	-0.105	2.4	0.01
62	438	-0.598	78.2	0.18
63	445	0.133	4	0.01
64	457	-0.09	1.9	0.00
65	478	0.324	25.1	0.05
66	486	0.487	57.6	0.12
67	493	-0.176	7.6	0.02
68	499	0.08	1.6	0.00
69	502	0.249	15.6	0.03
70	511	-0.124	3.9	0.01
71	518	0.163	6.9	0.01
72	521	0.359	33.6	0.06
73	531	-0.268	19.1	0.04
74	533	-0.37	36.4	0.07
75	553	-0.593	97.3	0.18
76	594	-0.042	0.5	0.00
77	613	0.169	8.8	0.01
78	622	0.063	1.2	0.00
79	623	0.046	0.7	0.00
80	624	0.051	0.8	0.00
81	625	0.164	8.4	0.01
82	628	0.014	0.1	0.00
83	636	-0.308	30.2	0.05
84	656	-0.013	0.1	0.00
85	667	0.125	5.2	0.01
86	681	0.137	6.4	0.01
87	689	-0.015	0.1	0.00
88	705	0.02	0.1	0.00
89	707	-0.028	0.3	0.00
90	709	0.065	1.5	0.00
91	711	-0.028	0.3	0.00
92	716	-0.091	3	0.00
93	718	0.222	17.7	0.02
94	720	-0.037	0.5	0.00

95	726	-0.308	34.5	0.05
96	734	0.117	5	0.01
97	740	-0.14	7.2	0.01
98	749	0.318	37.9	0.05
99	751	0.089	2.9	0.00
100	759	-0.058	1.3	0.00
101	760	0.068	1.8	0.00
102	763	0.024	0.2	0.00
103	764	0.038	0.6	0.00
104	770	0.032	0.4	0.00
105	777	0.034	0.4	0.00
106	780	0.076	2.3	0.00
107	797	0.102	4.1	0.01
108	820	-0.082	2.8	0.00
109	864	-0.024	0.3	0.00
110	869	0.022	0.2	0.00
111	871	-0.124	6.7	0.01
112	872	0.096	4	0.00
113	874	0.059	1.5	0.00
114	878	-0.092	3.7	0.00
115	891	-0.046	0.9	0.00
116	894	-0.117	6.2	0.01
117	928	0.382	67.7	0.07
118	937	0	0	0.00
119	942	-0.004	0	0.00
120	945	0.065	2	0.00
121	949	0.012	0.1	0.00
122	950	0.008	0	0.00
123	964	-0.005	0	0.00
124	971	0.137	9.2	0.01
125	978	0.031	0.5	0.00
126	984	0.055	1.5	0.00
127	985	0.026	0.3	0.00
128	987	0.01	0	0.00
129	993	0.099	4.9	0.00
130	995	0.118	6.9	0.01
131	999	0.022	0.2	0.00
132	1002	0.009	0	0.00
133	1003	-0.235	27.6	0.03
134	1004	0.021	0.2	0.00
135	1004	0.034	0.6	0.00
136	1005	0.006	0	0.00
137	1006	0.086	3.7	0.00
138	1010	0.045	1	0.00

139	1011	0.027	0.4	0.00
140	1015	0.159	12.9	0.01
141	1017	0.401	81.7	0.08
142	1036	0.042	0.9	0.00
143	1047	0.354	65.7	0.06
144	1051	-0.02	0.2	0.00
145	1054	-0.041	0.9	0.00
146	1054	0.054	1.5	0.00
147	1055	-0.05	1.3	0.00
148	1059	-0.008	0	0.00
149	1061	0.085	3.8	0.00
150	1069	-0.035	0.7	0.00
151	1071	-0.125	8.4	0.01
152	1079	0.003	0	0.00
153	1089	-0.07	2.7	0.00
154	1092	-0.072	2.9	0.00
155	1101	-0.088	4.2	0.00
156	1107	-0.029	0.5	0.00
157	1110	-0.038	0.8	0.00
158	1112	0.191	20.2	0.02
159	1123	0.066	2.4	0.00
160	1129	-0.025	0.4	0.00
161	1132	-0.069	2.7	0.00
162	1133	0.045	1.2	0.00
163	1135	-0.039	0.9	0.00
164	1143	0.001	0	0.00
165	1155	-0.012	0.1	0.00
166	1169	-0.085	4.2	0.00
167	1170	0.051	1.5	0.00
168	1171	0.028	0.4	0.00
169	1172	-0.247	35.6	0.03
170	1173	-0.008	0	0.00
171	1174	-0.014	0.1	0.00
172	1178	-0.02	0.2	0.00
173	1191	0.047	1.3	0.00
174	1202	0.002	0	0.00
175	1204	0.112	7.5	0.01
176	1206	-0.168	16.9	0.01
177	1232	0.539	178.7	0.15
178	1232	-0.006	0	0.00
179	1252	-0.411	105.8	0.08
180	1265	0.058	2.1	0.00
181	1288	0.039	1	0.00
182	1295	0.001	0	0.00

183	1303	0.29	54.8	0.04
184	1314	-0.001	0	0.00
185	1322	0.002	0	0.00
186	1327	-0.004	0	0.00
187	1327	0.089	5.3	0.00
188	1341	-0.084	4.8	0.00
189	1347	-0.073	3.6	0.00
190	1353	0.203	27.8	0.02
191	1357	0.017	0.2	0.00
192	1361	-0.098	6.6	0.00
193	1362	0.048	1.6	0.00
194	1363	0.024	0.4	0.00
195	1366	-0.009	0.1	0.00
196	1407	-0.201	28.3	0.02
197	1432	-0.206	30.3	0.02
198	1449	-0.252	45.9	0.03
199	1466	-0.018	0.2	0.00
200	1469	0.334	82.2	0.06
201	1472	0.008	0	0.00
202	1472	0.008	0	0.00
203	1472	0.049	1.8	0.00
204	1473	0.017	0.2	0.00
205	1478	-0.042	1.3	0.00
206	1480	0.001	0	0.00
207	1484	0.235	41	0.03
208	1498	-0.004	0	0.00
209	1501	-0.015	0.2	0.00
210	1509	-0.05	1.9	0.00
211	1514	-0.011	0.1	0.00
212	1518	-0.011	0.1	0.00
213	1519	0.049	1.8	0.00
214	1519	-0.033	0.8	0.00
215	1527	-0.654	326.4	0.21
216	1631	-0.08	5.2	0.00
217	1638	-0.059	2.9	0.00
218	1640	-0.044	1.6	0.00
219	1641	0.132	14.4	0.01
220	1641	0.503	207.6	0.13
221	1643	0.019	0.3	0.00
222	1643	0.053	2.3	0.00
223	1655	-0.024	0.5	0.00
224	1655	-0.018	0.3	0.00
225	1656	-0.045	1.7	0.00
226	1656	-0.044	1.6	0.00

227	1657	-0.008	0.1	0.00
228	1658	-0.032	0.8	0.00
229	1659	0.018	0.3	0.00
230	1670	0.203	34.4	0.02
231	3048	-0.006	0.1	0.00
232	3122	0.012	0.2	0.00
233	3142	0.012	0.2	0.00
234	3146	0.011	0.2	0.00
235	3153	-0.013	0.3	0.00
236	3162	0.099	15.5	0.00
237	3164	-0.025	1	0.00
238	3169	0.017	0.5	0.00
239	3172	0.003	0	0.00
240	3173	-0.001	0	0.00
241	3175	-0.009	0.1	0.00
242	3180	0.008	0.1	0.00
243	3181	0	0	0.00
244	3182	-0.004	0	0.00
245	3183	0.004	0	0.00
246	3183	0.035	2	0.00
247	3187	0	0	0.00
248	3189	0.001	0	0.00
249	3189	-0.008	0.1	0.00
250	3191	0.006	0.1	0.00
251	3193	-0.002	0	0.00
252	3195	-0.012	0.2	0.00
253	3196	-0.001	0	0.00
254	3199	0.013	0.3	0.00
255	3201	0.003	0	0.00
256	3202	0.002	0	0.00
257	3203	0.009	0.1	0.00
258	3203	0.009	0.1	0.00
259	3206	-0.002	0	0.00
260	3207	0.018	0.5	0.00
261	3208	0.007	0.1	0.00
262	3209	0.003	0	0.00
263	3210	-0.004	0	0.00
264	3225	0.008	0.1	0.00
265	3229	0.001	0	0.00
266	3239	0.058	5.4	0.00
267	3267	-0.022	0.8	0.00

Table S20 Vibrational frequencies(ω_i/cm^{-1}) at the optimized S_0 state, Huang-Rhys factor S_i, and reorganization energy λ_i of py-para.

	ω_i/cm^{-1}	ΔQ	λ_i/cm^{-1}	S_i
1	0	0	0	0.00
2	0	0	0	0.00
3	0	0	0	0.00
4	0	0	0	0.00
5	0	0	0	0.00
6	0	0	0	0.00
7	16	-4.313	146.8	9.30
8	17	8.178	561.6	33.44
9	30	1.372	28	0.94
10	32	1.929	58.7	1.86
11	36	1.303	30.3	0.85
12	40	-8.695	1516.1	37.80
13	43	4.434	426.8	9.83
14	48	-2.82	189.6	3.98
15	54	3.257	285.1	5.30
16	60	1.852	103	1.71
17	61	-1.078	35.2	0.58
18	65	4.242	589.1	9.00
19	77	1.966	148.2	1.93
20	78	-3.602	508.5	6.49
21	86	-1.606	111	1.29
22	87	2.896	365.5	4.19
23	89	-1.109	54.8	0.61
24	101	6.133	1905.4	18.81
25	104	-0.224	2.6	0.03
26	111	-1.445	116.2	1.04
27	114	-1.318	99.2	0.87
28	122	0.597	21.7	0.18
29	129	1.922	239.2	1.85
30	136	-0.212	3.1	0.02
31	143	0.574	23.6	0.16
32	154	-1.726	228.8	1.49
33	162	1.253	127.4	0.79
34	166	-0.48	19.2	0.12
35	190	-2.246	478.1	2.52
36	198	-0.037	0.1	0.00
37	209	0.022	0	0.00
38	211	-0.611	39.3	0.19
39	215	0.918	90.4	0.42
40	226	-0.406	18.6	0.08
41	232	-0.099	1.1	0.00

42	237	0.163	3.1	0.01
43	251	0.104	1.3	0.01
44	258	1.155	172.1	0.67
45	264	-0.173	4	0.01
46	266	0.249	8.3	0.03
47	287	0.181	4.7	0.02
48	293	-0.201	5.9	0.02
49	307	-0.243	9.1	0.03
50	335	-0.502	42.1	0.13
51	353	1.126	223.5	0.63
52	371	-0.007	0	0.00
53	393	0.26	13.3	0.03
54	407	0.093	1.8	0.00
55	408	-0.111	2.5	0.01
56	410	-0.283	16.4	0.04
57	418	-0.001	0	0.00
58	420	-0.349	25.6	0.06
59	427	0.222	10.5	0.02
60	427	-0.203	8.8	0.02
61	432	0.289	18	0.04
62	440	-0.678	101.2	0.23
63	447	-0.106	2.5	0.01
64	456	-0.032	0.2	0.00
65	477	-0.201	9.6	0.02
66	485	-0.47	53.7	0.11
67	495	-0.292	21.1	0.04
68	499	0.265	17.6	0.04
69	501	-0.378	35.8	0.07
70	511	0.143	5.2	0.01
71	520	-0.311	25.1	0.05
72	534	0.604	97.3	0.18
73	535	0.159	6.7	0.01
74	540	0.03	0.2	0.00
75	557	-0.497	68.9	0.12
76	591	-0.007	0	0.00
77	621	-0.089	2.5	0.00
78	621	-0.064	1.3	0.00
79	623	-0.006	0	0.00
80	627	-0.011	0	0.00
81	627	-0.027	0.2	0.00
82	633	0.22	15.3	0.02
83	640	-0.322	33.1	0.05
84	654	-0.068	1.5	0.00
85	673	0.117	4.6	0.01

86	681	0.169	9.7	0.01
87	689	0.018	0.1	0.00
88	704	0.005	0	0.00
89	704	0.055	1	0.00
90	707	-0.016	0.1	0.00
91	711	-0.005	0	0.00
92	713	-0.098	3.4	0.00
93	715	0.181	11.7	0.02
94	721	-0.093	3.1	0.00
95	723	0.094	3.2	0.00
96	736	0.061	1.4	0.00
97	739	0.317	37.2	0.05
98	749	-0.052	1	0.00
99	752	0.077	2.3	0.00
100	754	0.056	1.2	0.00
101	759	-0.025	0.2	0.00
102	761	0.044	0.7	0.00
103	767	-0.055	1.2	0.00
104	770	0.057	1.3	0.00
105	777	-0.042	0.7	0.00
106	786	-0.023	0.2	0.00
107	816	0.037	0.5	0.00
108	824	-0.188	14.5	0.02
109	858	-0.071	2.2	0.00
110	864	0.023	0.2	0.00
111	866	-0.006	0	0.00
112	869	-0.01	0	0.00
113	875	0.175	13.3	0.02
114	885	0.054	1.3	0.00
115	887	-0.011	0.1	0.00
116	892	0.126	7.1	0.01
117	930	0.002	0	0.00
118	934	-0.051	1.2	0.00
119	936	0.005	0	0.00
120	936	-0.041	0.8	0.00
121	941	-0.068	2.1	0.00
122	948	-0.004	0	0.00
123	951	0.239	27.1	0.03
124	961	-0.013	0.1	0.00
125	972	0.027	0.3	0.00
126	977	0.027	0.4	0.00
127	981	-0.113	6.3	0.01
128	984	-0.04	0.8	0.00
129	988	0.059	1.7	0.00

130	993	-0.003	0	0.00
131	996	0.028	0.4	0.00
132	1001	0.048	1.1	0.00
133	1002	-0.075	2.8	0.00
134	1004	-0.017	0.1	0.00
135	1005	-0.071	2.5	0.00
136	1005	0.122	7.5	0.01
137	1006	0.017	0.1	0.00
138	1010	-0.017	0.1	0.00
139	1010	-0.024	0.3	0.00
140	1012	-0.054	1.5	0.00
141	1013	-0.033	0.6	0.00
142	1018	-0.422	90.4	0.09
143	1052	-0.025	0.3	0.00
144	1055	-0.01	0.1	0.00
145	1055	-0.007	0	0.00
146	1056	-0.134	9.4	0.01
147	1056	-0.053	1.5	0.00
148	1057	0.034	0.6	0.00
149	1058	0.33	57.7	0.05
150	1069	-0.023	0.3	0.00
151	1079	0.021	0.2	0.00
152	1080	0.061	2	0.00
153	1091	-0.002	0	0.00
154	1091	-0.057	1.8	0.00
155	1105	-0.088	4.3	0.00
156	1107	0.025	0.3	0.00
157	1108	0.04	0.9	0.00
158	1109	0.061	2.1	0.00
159	1130	-0.025	0.3	0.00
160	1131	-0.028	0.4	0.00
161	1132	-0.024	0.3	0.00
162	1134	0.061	2.1	0.00
163	1135	-0.042	1	0.00
164	1144	0.001	0	0.00
165	1156	-0.001	0	0.00
166	1166	-0.184	19.8	0.02
167	1168	-0.002	0	0.00
168	1169	0.206	24.9	0.02
169	1171	0.016	0.1	0.00
170	1172	-0.044	1.1	0.00
171	1176	0.013	0.1	0.00
172	1176	-0.001	0	0.00
173	1177	-0.006	0	0.00

174	1200	0.023	0.3	0.00
175	1200	-0.047	1.3	0.00
176	1202	0.068	2.8	0.00
177	1204	-0.124	9.3	0.01
178	1229	0.071	3.1	0.00
179	1261	0.144	13.1	0.01
180	1262	0.071	3.2	0.00
181	1288	0.003	0	0.00
182	1296	0.042	1.2	0.00
183	1307	-0.633	261.5	0.20
184	1323	-0.005	0	0.00
185	1324	0.13	11.2	0.01
186	1325	0.128	10.9	0.01
187	1327	-0.047	1.5	0.00
188	1327	0.004	0	0.00
189	1346	0.118	9.3	0.01
190	1349	0.326	71.5	0.05
191	1357	0.017	0.2	0.00
192	1361	0.012	0.1	0.00
193	1363	0.044	1.3	0.00
194	1364	0.07	3.4	0.00
195	1366	-0.002	0	0.00
196	1390	0.293	59.9	0.04
197	1416	0.082	4.8	0.00
198	1428	-0.042	1.2	0.00
199	1469	0.04	1.2	0.00
200	1472	-0.021	0.3	0.00
201	1472	0.059	2.6	0.00
202	1473	-0.035	0.9	0.00
203	1475	-0.004	0	0.00
204	1479	0.009	0.1	0.00
205	1480	-0.037	1	0.00
206	1490	-0.233	40.5	0.03
207	1496	-0.066	3.3	0.00
208	1498	0.011	0.1	0.00
209	1504	0.328	80.7	0.05
210	1509	-0.034	0.9	0.00
211	1517	-0.019	0.3	0.00
212	1518	0.003	0	0.00
213	1519	0.011	0.1	0.00
214	1519	-0.034	0.9	0.00
215	1537	0.586	264.2	0.17
216	1614	0.226	41.1	0.03
217	1631	-0.091	6.7	0.00

218	1639	-0.018	0.3	0.00
219	1640	0.013	0.1	0.00
220	1641	0.035	1	0.00
221	1643	0.009	0.1	0.00
222	1643	-0.054	2.4	0.00
223	1649	0.353	102.8	0.06
224	1655	-0.007	0	0.00
225	1656	0.017	0.2	0.00
226	1657	0.003	0	0.00
227	1658	0.027	0.6	0.00
228	1659	0.004	0	0.00
229	1660	0.02	0.3	0.00
230	1666	-0.384	123.1	0.07
231	3043	0.016	0.4	0.00
232	3116	-0.032	1.6	0.00
233	3142	0.075	8.9	0.00
234	3148	-0.029	1.4	0.00
235	3156	0.005	0	0.00
236	3158	0.001	0	0.00
237	3159	0.012	0.2	0.00
238	3171	0.018	0.5	0.00
239	3171	-0.013	0.3	0.00
240	3173	-0.006	0.1	0.00
241	3174	0.01	0.2	0.00
242	3174	0.006	0.1	0.00
243	3176	0.005	0	0.00
244	3183	0.009	0.1	0.00
245	3183	0.002	0	0.00
246	3185	0	0	0.00
247	3186	0.004	0	0.00
248	3186	-0.003	0	0.00
249	3188	-0.004	0	0.00
250	3190	-0.001	0	0.00
251	3191	-0.003	0	0.00
252	3194	-0.002	0	0.00
253	3194	-0.003	0	0.00
254	3196	-0.001	0	0.00
255	3202	-0.002	0	0.00
256	3203	0.003	0	0.00
257	3204	-0.009	0.1	0.00
258	3205	0.006	0.1	0.00
259	3206	-0.004	0	0.00
260	3206	0	0	0.00
261	3208	0.021	0.7	0.00

262	3209	-0.004	0	0.00
263	3212	-0.004	0	0.00
264	3223	0.011	0.2	0.00
265	3230	0.027	1.2	0.00
266	3256	0.013	0.3	0.00
267	3266	-0.002	0	0.00

Table S21 Vibrational frequencies(ω_i/cm^{-1})at the optimized S_0 state, Huang-Rhys factor S_i, and reorganization energy λ_i of cu-pyim.

	ω_i/cm^{-1}	ΔQ	λ_i/cm^{-1}	S_i
1	0	0	0	0.00
2	0	0	0	0.00
3	0	0	0	0.00
4	0	0	0	0.00
5	0	0	0	0.00
6	0	0	0	0.00
7	21	-1.039	11.1	0.54
8	26	0.49	3.2	0.12
9	32	0.588	5.5	0.17
10	36	0.605	6.5	0.18
11	39	1.14	25.6	0.65
12	43	0.456	4.5	0.10
13	46	-1.864	79.7	1.74
14	49	-0.222	1.2	0.02
15	53	0.118	0.4	0.01
16	62	0.265	2.2	0.04
17	65	-0.455	6.7	0.10
18	69	-1.133	44.5	0.64
19	74	-0.211	1.6	0.02
20	76	-0.329	4.1	0.05
21	86	0.314	4.3	0.05
22	89	0.46	9.4	0.11
23	98	0.018	0	0.00
24	114	-0.304	5.3	0.05
25	118	-0.394	9.2	0.08
26	123	-0.589	21.4	0.17
27	130	-1.046	71	0.55
28	135	0.159	1.7	0.01
29	140	-0.187	2.5	0.02
30	150	-0.97	70.7	0.47
31	153	0.162	2	0.01
32	155	-0.263	5.4	0.03
33	159	0.136	1.5	0.01

34	181	-0.145	1.9	0.01
35	185	-0.116	1.3	0.01
36	199	-0.041	0.2	0.00
37	210	-0.035	0.1	0.00
38	216	-0.078	0.7	0.00
39	219	0.062	0.4	0.00
40	227	0.079	0.7	0.00
41	233	-0.083	0.8	0.00
42	242	-0.043	0.2	0.00
43	252	-0.116	1.7	0.01
44	261	0.04	0.2	0.00
45	267	0.082	0.9	0.00
46	284	-0.025	0.1	0.00
47	291	-0.043	0.3	0.00
48	307	-0.014	0	0.00
49	366	-0.03	0.2	0.00
50	381	0.496	46.8	0.12
51	406	-0.018	0.1	0.00
52	408	0.021	0.1	0.00
53	412	-0.081	1.3	0.00
54	416	0.002	0	0.00
55	419	-0.001	0	0.00
56	424	0.051	0.5	0.00
57	427	-0.159	5.4	0.01
58	433	0.011	0	0.00
59	439	0.083	1.5	0.00
60	444	0.004	0	0.00
61	455	-0.003	0	0.00
62	468	-0.072	1.2	0.00
63	475	-0.019	0.1	0.00
64	481	0.055	0.7	0.00
65	495	0.016	0.1	0.00
66	503	0.026	0.2	0.00
67	509	-0.022	0.1	0.00
68	518	0.004	0	0.00
69	519	0.266	18.4	0.04
70	525	0.068	1.2	0.00
71	535	-0.064	1.1	0.00
72	553	-0.098	2.6	0.00
73	571	-0.543	84.3	0.15
74	590	0.01	0	0.00
75	621	-0.005	0	0.00
76	624	0.006	0	0.00
77	625	0.006	0	0.00

78	627	0.006	0	0.00
79	629	-0.043	0.6	0.00
80	635	-0.088	2.5	0.00
81	637	0.317	32.1	0.05
82	680	0.015	0.1	0.00
83	688	-0.002	0	0.00
84	703	0	0	0.00
85	705	0.002	0	0.00
86	707	-0.007	0	0.00
87	708	0.013	0.1	0.00
88	711	0.006	0	0.00
89	713	0.013	0.1	0.00
90	719	-0.071	1.8	0.00
91	720	-0.036	0.5	0.00
92	720	0.019	0.1	0.00
93	725	0.248	22.4	0.03
94	734	-0.035	0.4	0.00
95	747	0.006	0	0.00
96	757	-0.02	0.2	0.00
97	759	-0.012	0.1	0.00
98	760	0.003	0	0.00
99	762	0.002	0	0.00
100	764	0.094	3.4	0.00
101	768	-0.002	0	0.00
102	769	0.002	0	0.00
103	776	0.008	0	0.00
104	808	0.079	2.5	0.00
105	817	-0.003	0	0.00
106	862	0.001	0	0.00
107	864	-0.004	0	0.00
108	870	0	0	0.00
109	872	0.006	0	0.00
110	874	-0.005	0	0.00
111	880	0.011	0	0.00
112	884	0	0	0.00
113	895	-0.001	0	0.00
114	904	0.024	0.3	0.00
115	929	0.074	2.5	0.00
116	929	-0.083	3.2	0.00
117	934	0.004	0	0.00
118	938	-0.001	0	0.00
119	942	-0.006	0	0.00
120	954	-0.004	0	0.00
121	957	0.001	0	0.00

122	968	-0.836	338.7	0.35
123	976	-0.002	0	0.00
124	978	-0.011	0.1	0.00
125	984	0.03	0.4	0.00
126	987	-0.011	0.1	0.00
127	987	-0.007	0	0.00
128	992	-0.164	13.4	0.01
129	998	-0.002	0	0.00
130	1003	-0.003	0	0.00
131	1004	0.001	0	0.00
132	1005	0.001	0	0.00
133	1005	0.005	0	0.00
134	1006	-0.005	0	0.00
135	1008	0.011	0.1	0.00
136	1008	0.001	0	0.00
137	1012	0.024	0.3	0.00
138	1016	-0.635	205.1	0.20
139	1020	-0.322	53	0.05
140	1053	0.003	0	0.00
141	1054	-0.003	0	0.00
142	1054	-0.003	0	0.00
143	1055	0.003	0	0.00
144	1062	0.001	0	0.00
145	1065	0.008	0	0.00
146	1081	0.025	0.3	0.00
147	1084	-0.139	10.4	0.01
148	1092	0	0	0.00
149	1101	0.021	0.3	0.00
150	1103	-0.245	33.1	0.03
151	1106	-0.001	0	0.00
152	1107	-0.013	0.1	0.00
153	1109	0.005	0	0.00
154	1121	-0.176	17.3	0.02
155	1126	0.008	0	0.00
156	1128	0.003	0	0.00
157	1130	-0.002	0	0.00
158	1130	0.081	3.7	0.00
159	1133	0.007	0	0.00
160	1142	0.006	0	0.00
161	1148	-0.003	0	0.00
162	1171	-0.003	0	0.00
163	1173	0.011	0.1	0.00
164	1173	0.234	32.1	0.03
165	1173	0.142	11.9	0.01

166	1173	0.031	0.6	0.00
167	1174	0.01	0.1	0.00
168	1176	0	0	0.00
169	1183	-0.235	32.6	0.03
170	1195	-0.002	0	0.00
171	1198	0.013	0.1	0.00
172	1200	0.002	0	0.00
173	1202	0.004	0	0.00
174	1218	0.402	98.4	0.08
175	1233	-0.008	0	0.00
176	1272	-0.004	0	0.00
177	1289	-0.01	0.1	0.00
178	1291	0.005	0	0.00
179	1315	-0.166	18.2	0.01
180	1317	-0.001	0	0.00
181	1323	-0.005	0	0.00
182	1324	-0.007	0	0.00
183	1325	0.005	0	0.00
184	1331	0.136	12.3	0.01
185	1349	0.386	100.5	0.07
186	1350	-0.024	0.4	0.00
187	1355	-0.005	0	0.00
188	1360	-0.022	0.3	0.00
189	1364	0.027	0.5	0.00
190	1364	0.005	0	0.00
191	1365	-0.003	0	0.00
192	1421	-0.653	302.8	0.21
193	1457	0.185	25	0.02
194	1468	0.015	0.2	0.00
195	1471	0.003	0	0.00
196	1471	-0.002	0	0.00
197	1473	0.008	0	0.00
198	1474	0.004	0	0.00
199	1477	-0.014	0.2	0.00
200	1483	-0.09	5.9	0.00
201	1502	-0.006	0	0.00
202	1509	0.121	11.1	0.01
203	1514	0.709	380.6	0.25
204	1516	-0.074	4.2	0.00
205	1516	0.025	0.5	0.00
206	1518	0.017	0.2	0.00
207	1518	0.033	0.8	0.00
208	1531	-0.723	399.6	0.26
209	1609	-0.716	412.7	0.26

210	1633	0.002	0	0.00
211	1640	-0.09	6.7	0.00
212	1641	0.031	0.8	0.00
213	1642	-0.002	0	0.00
214	1643	0.108	9.5	0.01
215	1644	-0.375	115.7	0.07
216	1644	0.261	56.1	0.03
217	1654	-0.007	0	0.00
218	1655	0.002	0	0.00
219	1656	-0.023	0.5	0.00
220	1657	-0.001	0	0.00
221	1658	-0.005	0	0.00
222	1658	-0.002	0	0.00
223	1669	-1.057	931.6	0.56
224	3141	0.004	0	0.00
225	3145	-0.003	0	0.00
226	3148	0	0	0.00
227	3156	0.004	0	0.00
228	3170	-0.001	0	0.00
229	3171	-0.002	0	0.00
230	3177	0	0	0.00
231	3177	-0.001	0	0.00
232	3179	0.017	0.5	0.00
233	3181	0	0	0.00
234	3183	-0.002	0	0.00
235	3183	0	0	0.00
236	3186	0	0	0.00
237	3187	0	0	0.00
238	3189	0	0	0.00
239	3189	0	0	0.00
240	3191	-0.001	0	0.00
241	3192	0	0	0.00
242	3193	0	0	0.00
243	3194	-0.001	0	0.00
244	3196	0	0	0.00
245	3196	0	0	0.00
246	3199	0.005	0	0.00
247	3201	0	0	0.00
248	3203	-0.002	0	0.00
249	3203	0	0	0.00
250	3204	0	0	0.00
251	3206	0.001	0	0.00
252	3208	-0.002	0	0.00
253	3209	-0.006	0.1	0.00

254	3210	0	0	0.00
255	3223	0.03	1.4	0.00
256	3262	-0.007	0.1	0.00
257	3286	-0.014	0.3	0.00
258	3646	0.048	4.3	0.00

Fig.S1 Frontier molecular orbital of the optimized S_0 state of py-pop.

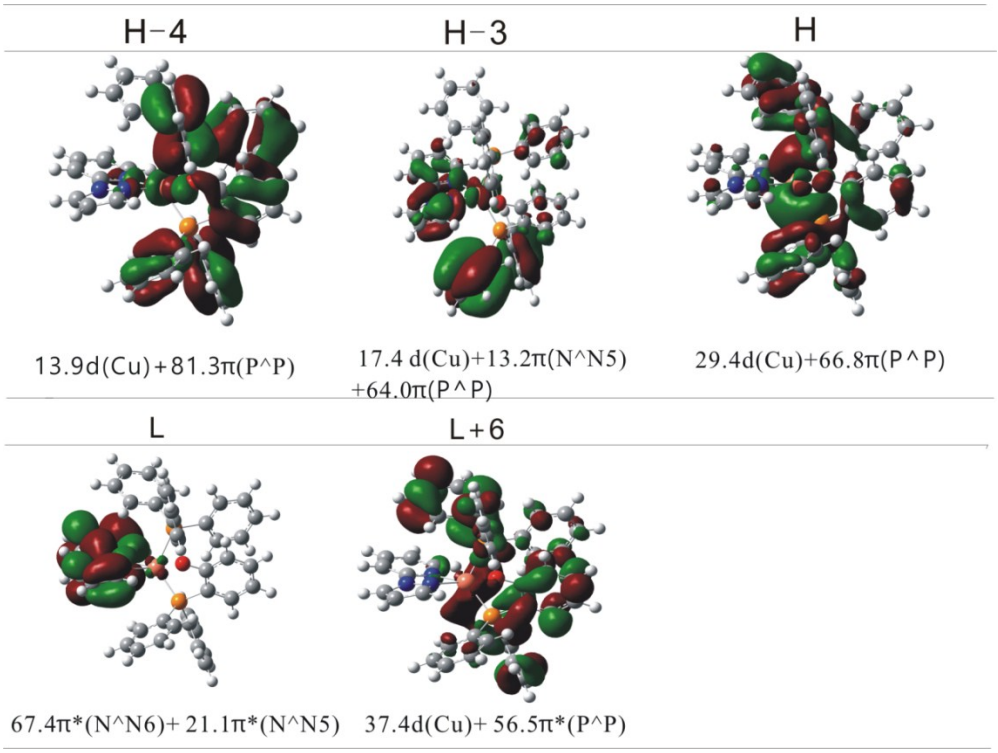


Fig.S2 Frontier molecular orbital of the optimized S_0 state of py-ch3.

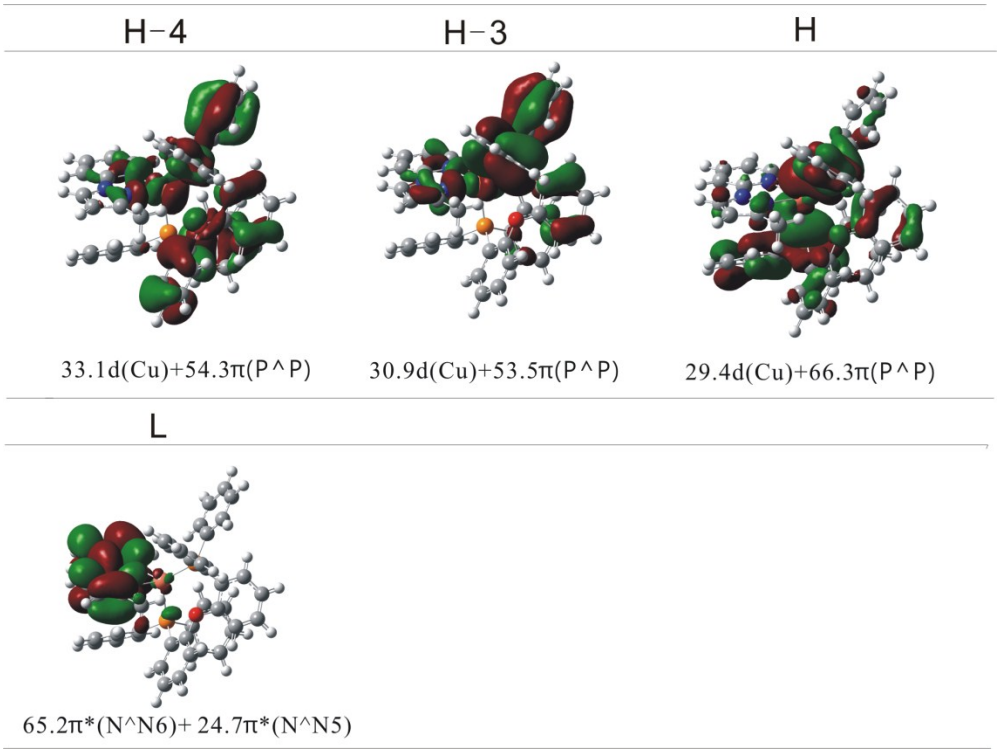


Fig.S3 Frontier molecular orbital of the optimized S_0 state of py-meta.

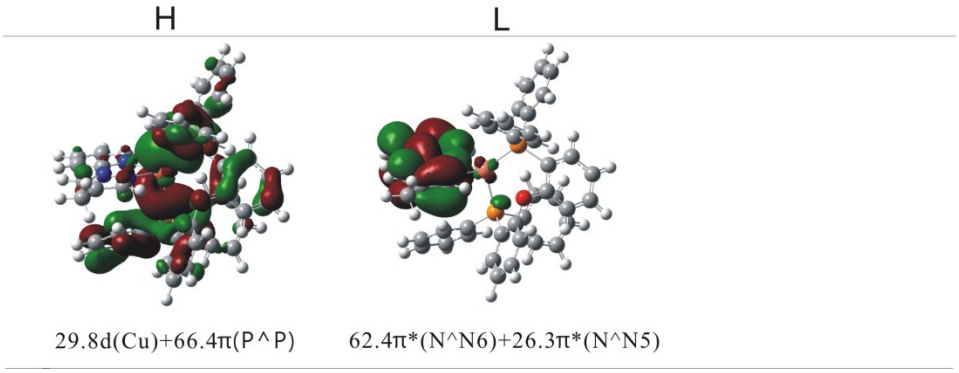


Fig.S4 Frontier molecular orbital of the optimized S_0 state of py-meta.

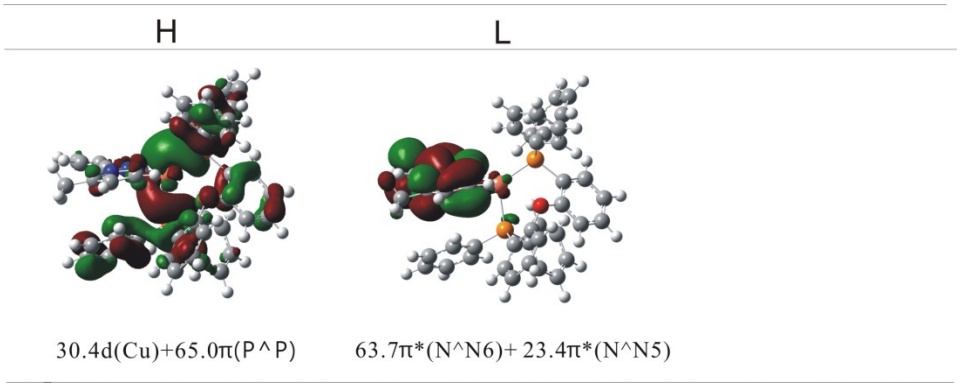


Fig.S5 Frontier molecular orbital of the optimized S_0 state of cu-pyim.

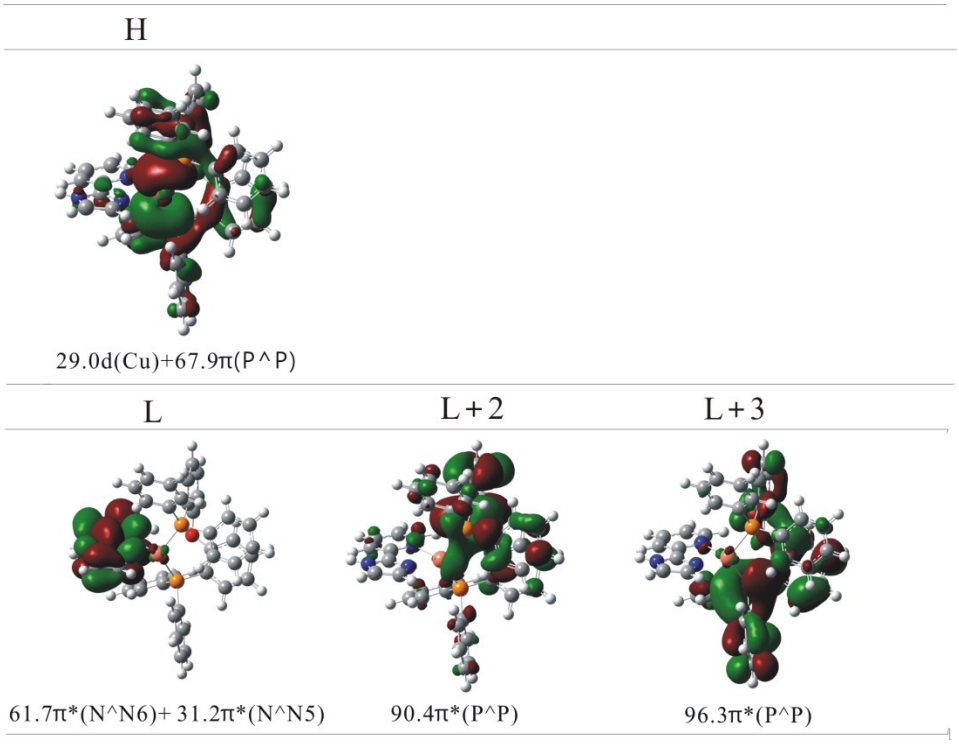


Fig. S6 Electronic density contours of the frontier molecular orbital in the T_1 state for complexes.

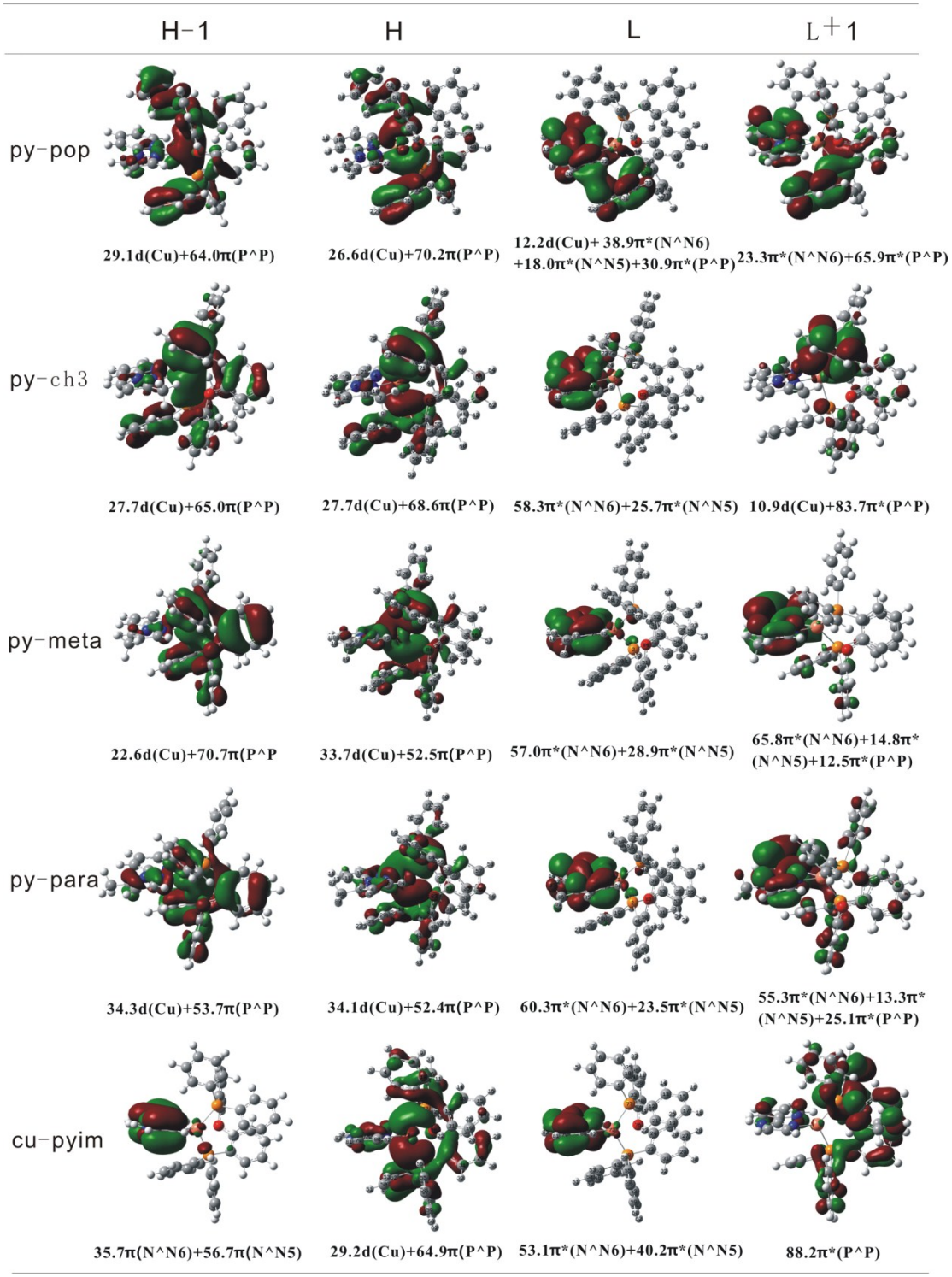


Fig.S7 Diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for py-pop.

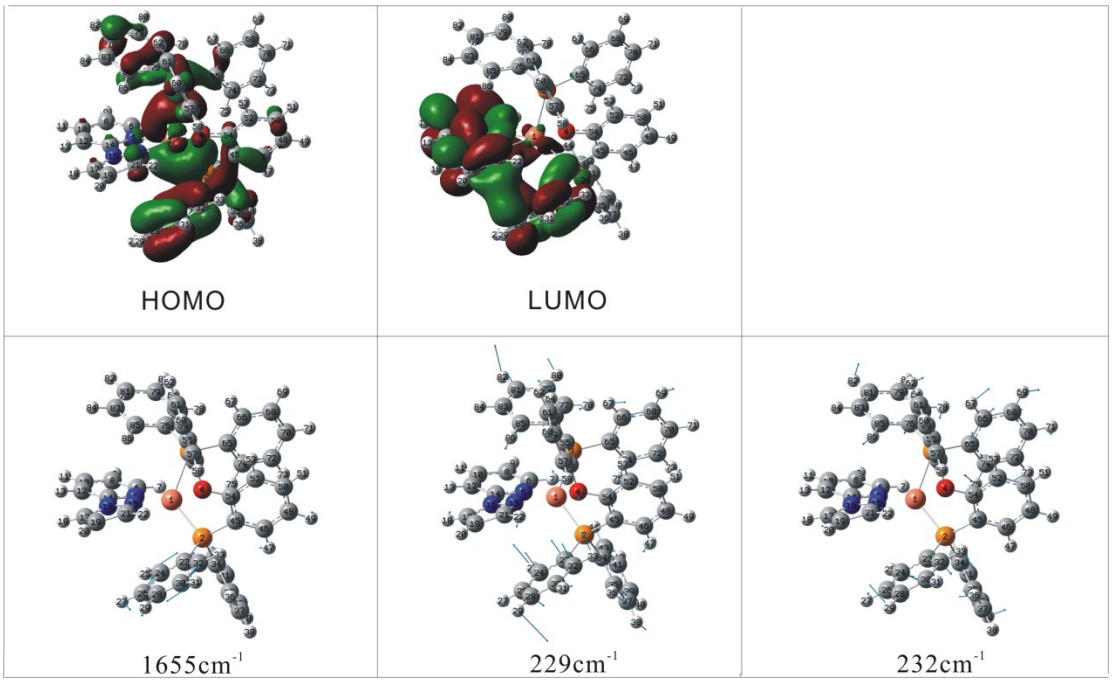


Fig.S8 Diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for py-ch3.

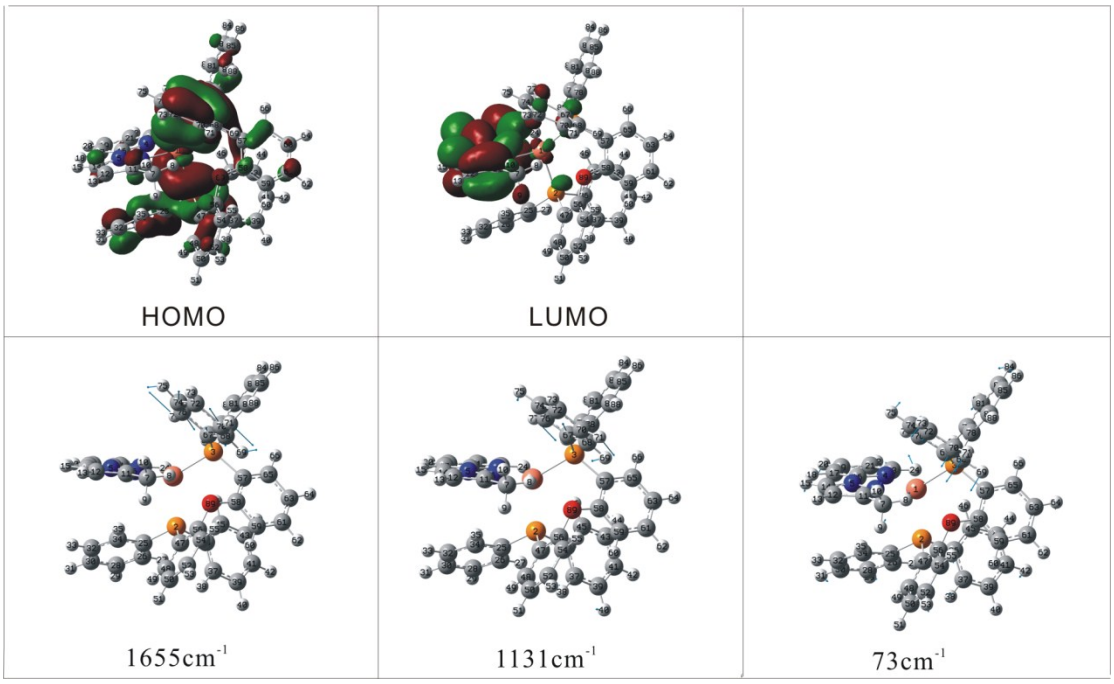


Fig.S9 Diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for py-meta.

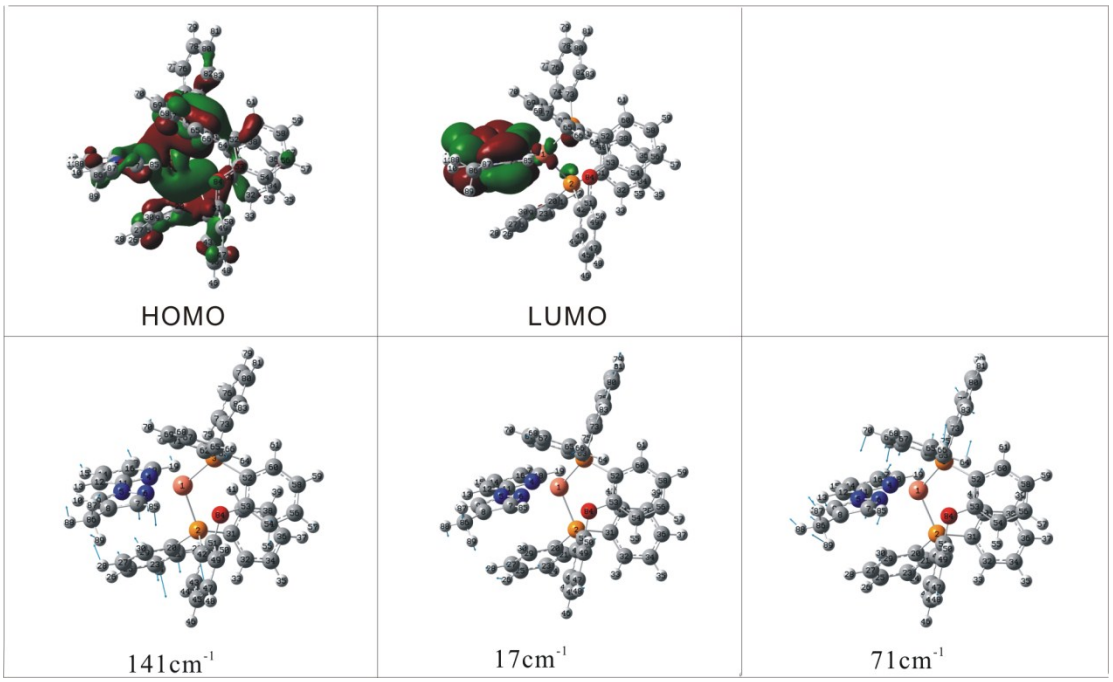


Fig.S10 Diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for py-para

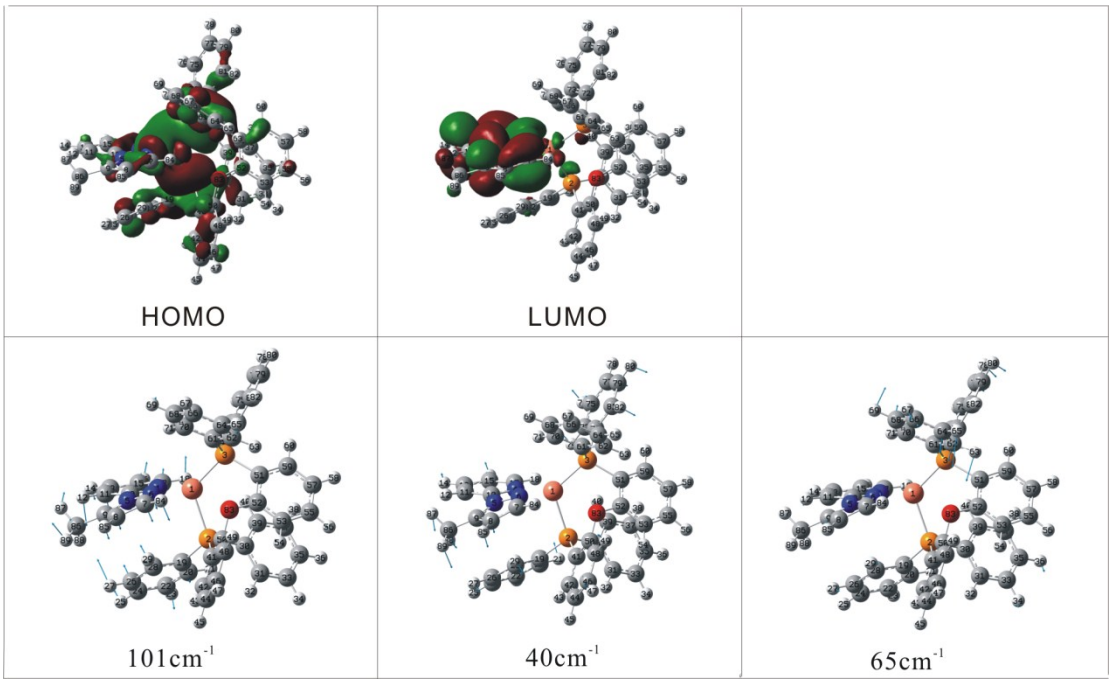
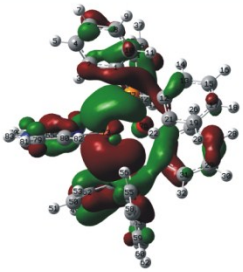
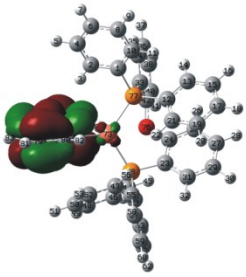
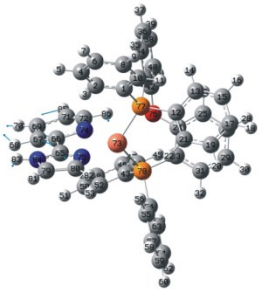
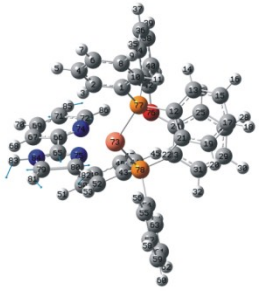
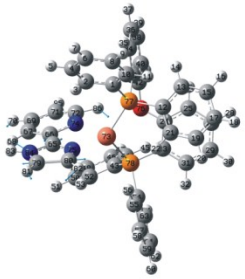


Fig.S11 Diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for cu-pyim

 HOMO	 LUMO	
 1669cm^{-1}	 1609cm^{-1}	 1531cm^{-1}