Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A theoretical study on second-order nonlinear optical properties of Pt(II) bis-acetylide complexes: substituent and redox effects

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General Comments

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Table S4 The dynamic β_{HRS}, DR, β_J, ρ, and $\Phi(\beta_J)$ values of complexes 1-5 obtained at wavelength of 1064 nm and 1340 nm employing CAM-B3LYP/6-311+G(d)/SDD level of theory in DCM solvent.

Fig. S1 Spin density diagrams for one-electron reduced and oxidized species of complexes 1-5.

Fig. S2 Simulated absorption spectra of complex 1 in DCM solvent by four functionals and the experimental result (inset)[44] (The units of Abs: L/mol/cm).

Fig. S3 Molecular orbitals involved in crucial charge transitions of complexes 1-5 and $1^{+/-}$-$5^{+/-}$.

Fig. S4 Relationship between the β_{tot} values and the corresponding $\Delta\mu_{eg}f_{os}/\Delta E^3$ values for complexes 1-5.

Fig. S5 Plots of $-z\rho^{(2)}_{yy}$ for all studied complexes at the CAM-B3LYP/6-311G+(d)/SDD level of theory. Purple color represents a positive

value and blue color represents a negative value.

Table S1 Calculated squared spin operator $<S^2>$ of complexes $1^{+/-}$-$5^{+/-}$.

Complex	$<S^2>$	eigenvalue	Complex	$<S^2>$	eigenvalue
$\mathbf{1}^+$	0.757	0.75	3^-	0.751	0.75
$\mathbf{1}^-$	0.752	0.75	4^+	0.757	0.75
$\mathbf{2}^+$	0.757	0.75	4^-	0.752	0.75
$\mathbf{2}^-$	0.756	0.75	5^+	0.756	0.75
$\mathbf{3}^+$	0.756	0.75	5^-	0.751	0.75

Table S2 Weights of Pt, L_1, L_2, L_3 and L_4 ligands contributed to frontier molecular orbital.

Complex	Frontier MOs	Pt	L_1	L_2	L_3	L_4
1	L	13.94%	40.44%	3.12%	27.97%	14.53%
	H	10.34%	81.68%	2.68%	2.57%	2.73%
2	L	1.29%	83.42%	13.57%	0.90%	0.82%
	H	13.72%	3.76%	80.88%	0.23%	1.41%
3	L	15.10%	33.89%	5.49%	31.19%	14.33%
	H	5.62%	89.51%	1.33%	1.63%	1.91%
4	L	0.020%	0.020%	99.70%	0.25%	0.01%
	H	15.70%	12.61%	69.98%	0.31%	1.40%
5	L	15.43%	28.51%	5.67%	36.60%	13.80%
	H	0.022%	99.91%	0.006%	0.004%	0.058%

Table S3 Obtained λ (nm), ΔE_{ge} (eV), f_{os}, $\Delta\mu_{ge}$ and major molecular orbital contributions of all studied complexes at the B3LYP-D3/6-311+G(d)/SDD level of theory.

Complex	λ	ΔE_{ge}	f_{os}	$\Delta\mu_{ge}$	Major contributions
$\mathbf{1}^{+}$	589	2.11	0.239		βH-8→βL(68%), βH-7→βL(27%)
	310	4.00	0.322		αH→αL(58%)
1	306	4.06	0.839	1.426	H→L(95%)
	276	4.49	0.395	3.472	H-2→L(64%), H-1→L+1(28%)
$\mathbf{1}^{-}$	663	1.87	0.082		αH→αL+1(97%)
	342	3.63	0.229		βH→βL(48%)
$\mathbf{2}^{+}$	613	2.02	0.146		βH-7→βL(90%)
	363	3.42	0.462		αH-2→αL(32%), βH→βL+1(14%)
2	426	2.91	0.358	8.605	H→L(81%)
	399	3.11	0.632	6.624	H-1→L+1(58%), H-1→L(23%)
$\mathbf{2}^{-}$	422	2.94	0.654		αH-2→αL(17%), βH→βL(55%)
	399	3.11	0.315		αH-4→αL(22%), βH-1→βL(36%)
$\mathbf{3}^{+}$	712	1.74	0.206		βH-2→βL(78%)
	345	3.60	0.690		αH-1→αL(32%), αH→αL(32%)
3	335	3.70	0.945	5.989	H→L(90%)
	287	4.32	0.465	2.694	H-1→L+4(45%), H-1→L+2(23%)
$\mathbf{3}^{-}$	736	1.69	0.083		αH→αL(94%)
	356	3.49	0.220		αH-1→αL(15%), βH→βL(43%)
$\mathbf{4}^{+}$	623	1.99	0.112		βH-6→βL(88%)
	590	2.10	0.156		βH-9→βL(53%), βH-10→βL(18%)
4	309	4.02	0.684	1.487	H→L+4(93%)
	272	4.56	0.297	3.456	H-1→L+5(65%)
$\mathbf{4}^{-}$	330	3.76	0.339		βH→βL+4(32%), αH-1→αL+3(28%), βH→βL+3(20%)

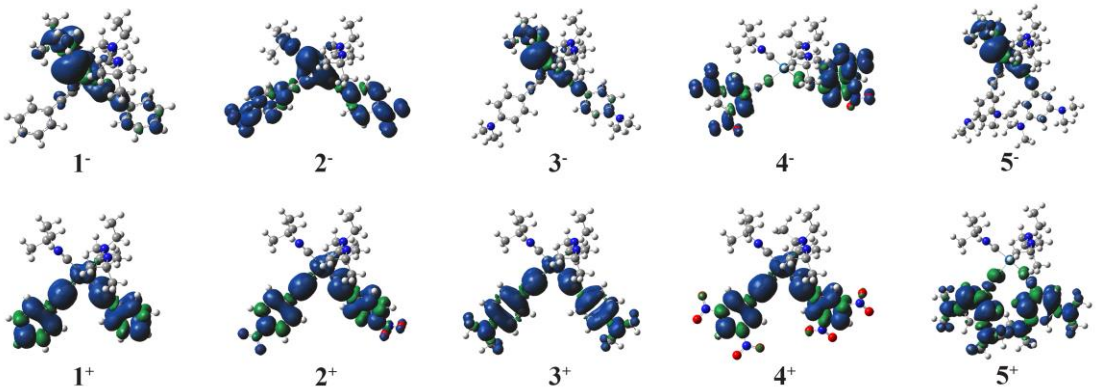
	305	4.07	0.148		βH-7→βL+2(33%), βH-6→βL+2(15%)
$\mathbf{5}^{+}$	319	3.89	0.253		αH-1→αL(43%), βH-1→βL+1(40%)
	271	4.58	0.142		αH-2→αL+1(42%)
5	300	4.13	0.406	3.371	H-3→L(74%)
	274	4.53	0.330	1.770	H-1→L+5(38%), H-6→L(22%)
$\mathbf{5}^{-}$	644	1.93	0.091		αH→αL(83%)
	341	3.64	0.078		βH-2→βL(13%)

Note: H = HOMO, L = LUMO.

Table S4 The dynamic β_{HRS}, DR, β_J, ρ, and $\Phi(\beta_J)$ values of complexes 1-5 obtained at wavelength of 1064 nm and 1340 nm employing CAM-B3LYP/6-311+G(d)/SDD level of theory in DCM solvent.

Complex	$\boldsymbol{\beta_{HRS}}$	**DR**	$\lvert\boldsymbol{\beta_{J=1}}\rvert$	$\lvert\boldsymbol{\beta_{J=3}}\rvert$	$\boldsymbol{\rho}$	$\boldsymbol{\Phi(\beta_{J=1})}$	$\boldsymbol{\Phi(\beta_{J=3})}$
			λ=1064nm				
1	7.90×10^{2}	2.09	8.41×10^{2}	2.20×10^{3}	2.62	0.28	0.72
2	1.22×10^{4}	4.28	2.17×10^{4}	2.16×10^{4}	1.01	0.50	0.50
3	2.35×10^{3}	3.67	3.93×10^{3}	4.70×10^{3}	1.20	0.45	0.55
4	2.26×10^{3}	7.29	4.63×10^{3}	1.92×10^{3}	0.42	0.71	0.29
5	5.61×10^{2}	6.28	1.11×10^{3}	6.42×10^{2}	0.58	0.63	0.37
			λ=1340nm				
1	6.96×10^{2}	2.09	7.43×10^{2}	1.95×10^{3}	2.62	0.28	0.72
2	7.84×10^{3}	4.16	1.38×10^{4}	1.42×10^{4}	1.03	0.49	0.51
3	1.77×10^{3}	3.58	2.82×10^{3}	3.49×10^{3}	1.24	0.45	0.55

4	1.80×10^{3}	6.93	3.65×10^{3}	1.72×10^{3}	0.47	0.68	0.32
5	4.79×10^{2}	6.24	9.48×10^{2}	5.53×10^{2}	0.58	0.63	0.37



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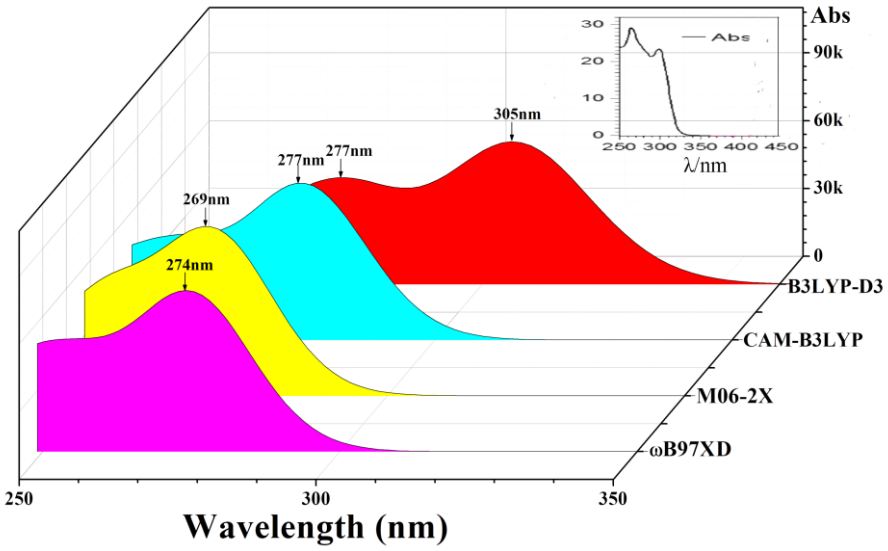

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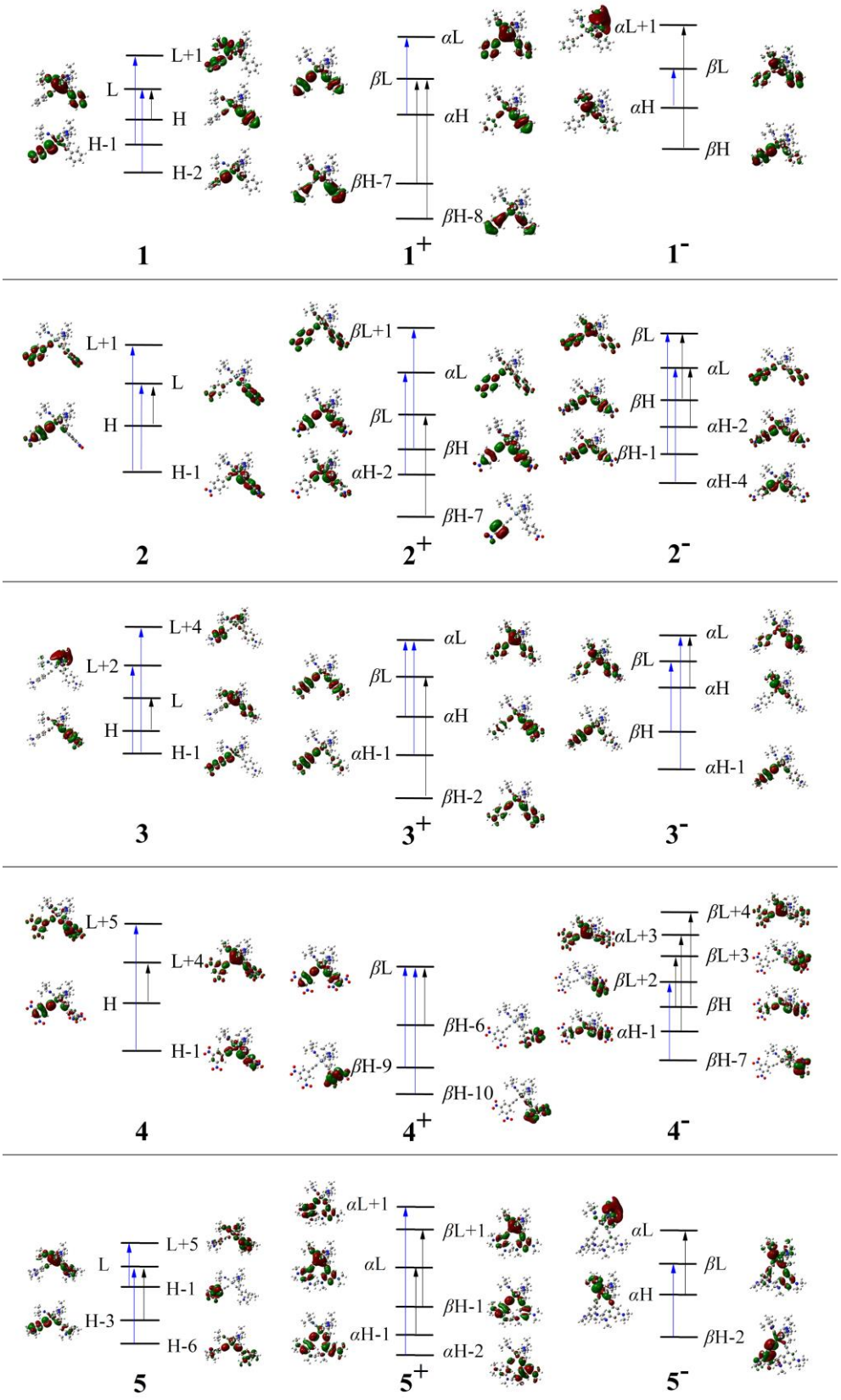

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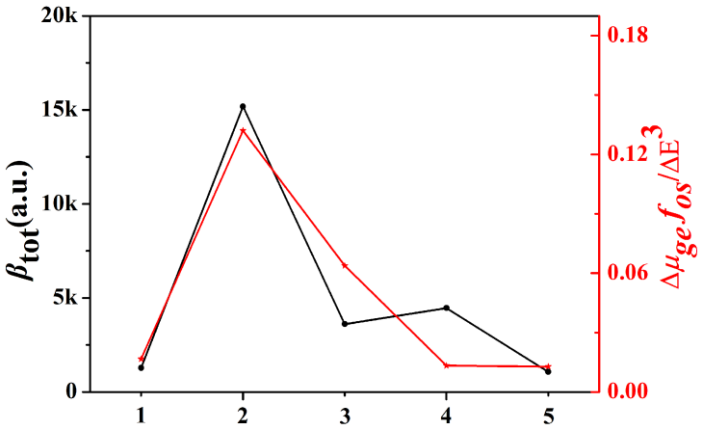

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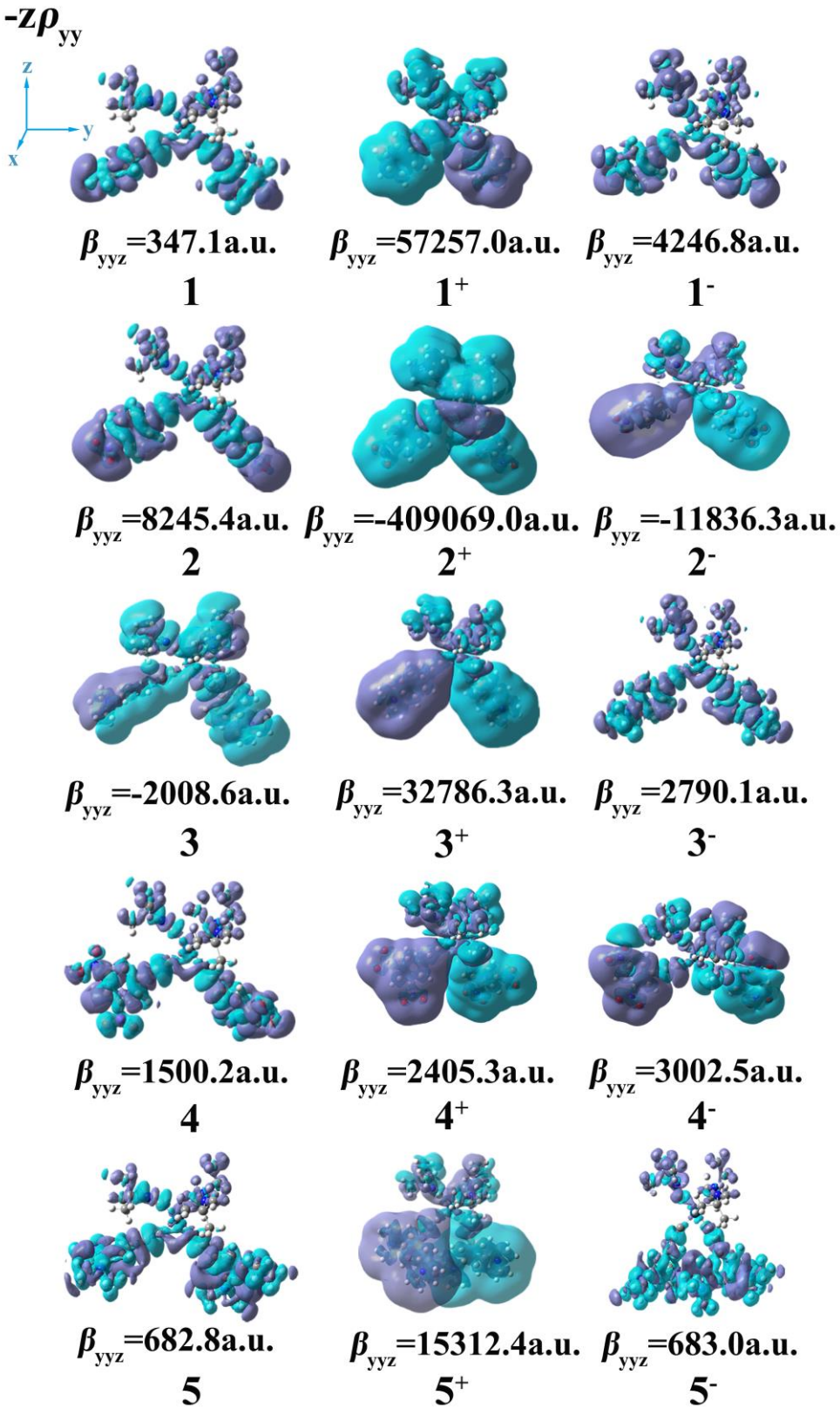

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