Supplemental Information

New Strategy for Enhancing Second-Order Nonlinear Optical Properties of the Pt(II) Dithienylethene Complexes: Substituent Effect, π-Conjugated Influence, and Photoisomerization Switch

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General Comments

§ Table S1 Calculated bond distances (Å) and bond angles (°) of systems **1ao** and **2ao** obtained at different methods compared with their corresponding experimental data (The atom labeling scheme is shown in Figure **1**)

§ Table S2 Calculated absorption wavelengths (nm) of open-ring systems **1ao**, **2ao**, **1bo**, **2bo** and the corresponding closed-ring systems **1ac**, **2ac**, **1bc**, **2bc**

§ Table S3 The $\beta_{tot}(-\omega;\ \omega,\ 0)$ values of all studied systems at a frequency range from 0.000 to 0.065 a.u.

§ Table S4 The $\beta_{tot}(-2\omega;\ \omega,\ \omega)$ values of all studied systems at a frequency range from 0.000 to 0.065 a.u.

§ The validation of calculation method

Table S1 Calculated bond distances (Å) and bond angles (°) of systems **1ao** and **2ao** obtained at different methods compared with their corresponding experimental data (The atom labeling scheme is shown in Figure **1**)

1ao	Exp[a]	B3LYP	PBE1PBE	CAM-B3LYP
Pt-N1	1.998	2.038	2.015	2.028
Pt-C1	1.979	2.004	1.985	1.996
Pt-O1	2.065	2.128	2.103	2.106
Pt-O2	1.989	2.035	2.013	2.019
N1-Pt-C1	81.6	81.2	81.4	81.1
O1-Pt-O2	92.4	90.6	91.1	90.5
2ao	Exp[a]	B3LYP	PBE1PBE	CAM-B3LYP
Pt-N1	2.006	2.038	2.014	2.028
Pt-C1	1.985	2.003	1.984	1.995
Pt-O1	2.064	2.122	2.098	2.101
Pt-O2	1.999	2.032	2.011	2.016
N1-Pt-C1	81.7	81.2	81.4	81.1
O1-Pt-O2	92.4	90.8	91.2	90.7

[a] Experimental values are from ref. 34.

Table S2 Calculated absorption wavelengths (nm) of open-ring systems **1ao**, **2ao**, **1bo**, **2bo** and the corresponding closed-ring systems **1ac**, **2ac**, **1bc**, **2bc**

Complex	B3LYP	PBE1PB	CAM-B3LY	LC-wPBE
1ao	425.1	410.2	380.8	356.1
2ao	446.4	430.3	397.5	371.8
1bo	446.6	431.3	399.8	373.3
2bo	468.5	452.1	417.4	373.3
1ac	755.5	729.1	628.4	559.7
2ac	819.5	787.6	664.9	586.2
1bc	691.1	665.5	575.1	514.5
2bc	740.6	708.1	594.2	526.4

Table S3 The $\beta_{tot}(-\omega;\ \omega,\ 0)$ values of all studied systems at a frequency range from 0.000 to 0.065 a.u.

Complex	0.000	0.050	0.010	0.015	0.020	0.025	0.030
1ao	13.5	13.6	13.7	13.8	14.1	14.1	14.9
2ao	18.5	18.5	18.7	19.0	19.4	19.9	20.6
3ao	50.0	50.1	50.6	51.6	52.9	54.8	57.2
1ac	32.3	32.4	33.1	34.2	35.8	38.2	41.6
2ac	50.6	50.9	52.0	54.1	57.2	61.8	68.4
3ac	146.6	147.7	151.7	158.9	169.9	186.3	210.6
1bo	23.2	23.3	23.5	23.9	24.4	25.1	26.0
2bo	33.3	33.3	33.6	34.2	35.0	36.1	37.6
3bo	80.4	80.6	81.6	83.3	85.7	89.1	93.4
1bc	38.3	38.4	39.0	40.1	41.8	44.1	47.3
2bc	62.8	63.0	64.2	66.2	69.2	73.4	79.2
3bc	155.7	156.6	160.0	165.8	174.5	187.0	204.4
1co	33.3	33.4	33.7	34.3	35.1	36.2	37.6
2co	49.7	49.8	50.3	51.2	52.6	54.4	56.7
3co	112.3	112.7	114.2	116.7	120.3	125.3	131.8
1cc	48.6	48.7	49.5	50.8	52.8	55.4	59.0
2cc	82.6	82.9	84.3	86.8	90.4	95.4	102.2
3cc	196.2	197.3	201.2	208.0	218.2	232.6	252.4
1do	43.4	43.5	44.0	44.8	46.0	47.5	49.6
2do	68.1	68.1	68.9	70.3	72.2	74.9	78.4
3do	148.7	148.7	150.8	154.3	159.4	166.5	175.7
1dc	53.0	53.2	54.1	55.6	57.8	60.9	65.0
2dc	96.9	97.2	98.9	101.8	106.1	112.0	120.0
3dc	223.8	225.0	229.4	237.0	248.3	264.1	285.7
Complex	0.035	0.040	0.045	0.050	0.055	0.060	0.065
1ao	15.4	16.1	17.0	18.0	19.2	20.8	22.7
2ao	21.5	22.6	24.0	25.6	27.7	30.3	33.6
3ao	60.2	64.0	68.9	75.0	82.9	93.1	106.8
1ac	46.3	53.2	63.6	80.6	111.7	179.2	382.7
2ac	77.9	92.4	115.6	156.8	242.2	476.1	1682.2
3ac	247.6	307.4	413.8	637.5	1277.3	5243.5	100635.6
1bo	27.1	28.5	30.3	32.4	35.1	38.5	42.9
2bo	39.4	41.7	44.5	48.1	52.6	58.4	65.9
3bo	99.0	106.1	115.2	126.9	142.3	162.9	191.2
1bc	51.5	57.2	65.0	76.3	93.3	121.4	174.1
2bc	87.1	97.9	113.2	136.0	171.9	235.1	368.0
3bc	228.7	263.7	315.8	398.9	545.6	854.0	1756.5
1co	39.4	41.7	44.5	48.0	52.4	58.0	65.4
2co	59.7	63.5	68.2	74.2	81.8	91.7	104.7

3co	140.2	151.0	164.8	182.9	206.8	239.1	284.4
1cc	63.8	70.1	78.6	90.3	107.2	132.9	176.0
2cc	111.3	123.5	140.3	164.1	199.3	255.4	355.8
3cc	279.6	317.5	371.6	452.6	582.3	813.2	1303.7
1do	52.1	55.4	59.5	64.7	71.3	79.8	91.1
2do	82.9	88.5	95.7	104.9	116.7	132.3	153.2
3do	187.7	203.3	223.5	250.1	285.7	334.7	404.7
1dc	70.4	77.6	87.2	100.5	119.5	148.0	194.9
2dc	130.6	144.8	164.1	191.1	230.3	291.0	394.4
3dc	315.1	355.3	411.8	494.0	620.2	830.9	1232.5

Table S4 The $\beta_{tot}(-2\omega;\ \omega,\ \omega)$ values of all studied systems at a frequency range from 0.000 to 0.065 a.u.

Complex	0.000	0.050	0.010	0.015	0.020	0.025	0.030
1ao	13.5	13.6	13.9	14.5	15.3	16.5	18.2
2ao	18.5	18.6	19.1	20.0	21.3	23.2	26.0
3ao	50.0	50.4	52.1	55.0	59.7	66.7	77.3
1ac	32.3	32.7	34.3	37.4	42.7	52.4	75.2
2ac	50.6	51.4	54.5	60.5	71.5	93.9	160.2
3ac	146.6	150.0	161.7	185.5	233.4	351.2	1032.4
1bo	23.2	23.4	24.1	25.2	26.9	29.4	33.1
2bo	33.3	33.5	34.5	36.3	39.0	43.1	49.2
3bo	80.4	81.3	84.2	89.6	98.1	111.1	131.5
1bc	38.3	38.7	40.4	43.6	48.8	57.5	73.3
2bc	62.8	63.6	66.8	72.9	83.1	100.7	135.9
3bc	155.7	158.6	168.4	187.3	221.0	285.0	439.0
1co	33.3	33.6	34.6	36.4	39.1	43.2	49.3
2co	49.7	50.1	51.7	54.7	59.2	66.0	76.4
3co	112.3	113.7	118.1	126.1	139.0	159.0	190.8
1cc	48.6	49.2	51.4	55.5	62.1	73.0	91.6
2cc	82.6	83.7	87.9	95.7	108.6	130.3	170.1
3cc	196.2	199.7	211.7	234.5	274.2	345.7	494.4
1do	43.4	43.8	45.3	47.8	51.8	57.8	66.9
2do	67.9	68.6	71.0	75.9	82.2	92.7	108.8
3do	148.1	150.0	156.3	167.8	186.3	215.3	262.5
1dc	53.0	53.8	56.3	60.9	68.5	80.8	102.0
2dc	96.9	98.2	103.2	112.4	127.7	153.1	198.5
3dc	223.8	227.8	241.1	266.3	309.5	385.3	533.8
Complex	0.035	0.040	0.045	0.050	0.055	0.060	0.065
1ao	20.7	24.4	30.5	42.2	74.5	2281.4	40.4
2ao	30.1	36.6	48.0	72.6	176.4	166.6	46.1
3ao	94.2	124.0	187.9	428.2	761.7	120.1	384.8
1ac	211.0	135.4	111.0	262.4	315.6	33.9	1009.4
2ac	32316.9	153.1	176.1	695.0	209.8	297.3	371.3
3ac	620.5	305.9	653.2	3195.2	359.9	1107.4	125764.6
1bo	38.6	47.4	63.0	98.2	264.1	224.7	51.1
2bo	58.5	74.0	103.8	185.9	2826.8	125.0	89.3
3bo	165.7	230.9	400.4	2115.6	447.4	129.6	2757.2
1bc	112.4	841.0	144.6	235.2	964.5	610.2	370.0
2bc	244.4	1060.4	222.8	465.7	30082.2	625.0	479.3
3bc	1398.2	653.1	624.5	5227.1	840.7	857.9	6761.4
1co	58.7	74.0	102.9	175.1	708.3	264.1	78.8
2co	92.6	120.5	177.6	357.5	2407.7	172.5	378.0

3co	245.3	353.5	660.0	9511.3	568.6	398.8	736.9
1cc	131.0	331.5	186.4	355.1	7317.6	570.2	930.6
2cc	265.2	1175.2	304.3	842.7	1844.4	814.2	612.7
3cc	973.9	3462.8	792.2	11054.7	2351.9	751.8	884.4
1do	81.1	105.3	153.5	289.5	3187.1	313.1	100.9
2do	180.7	180.7	281.6	667.6	1348.9	218.8	971.8
3do	520.0	520.0	1084.4	8088.9	674.6	550.4	1108.3
1dc	145.5	334.4	220.2	480.3	12798.4	577.8	2507.6
2dc	299.7	911.1	393.1	1302.8	2075.2	1635.9	3160.0
3dc	934.0	19377.7	1164.7	9008.1	4114.8	1681.7	2861.0

The validation of calculation method

The CAM-B3LYP functional is taken as an example to evaluate the qualitative second-order NLO responses of the studied systems. To validate the calculation method, we calculate the frequency-dependent first hyperpolarizabilities of open-ring (L)Re(CO)3Br and closed-ring (L)Re(CO)3Br by using coupled perturbed density functional theory (CPDFT) at CAM-B3LYP/LanL2DZ/6-31+G(d) level. The frequency-dependent first hyperpolarizabilities value of open-ring form at 1.91 μm is 60.1×10^{-30} esu, while the value of closed-ring form is 684.2×10^{-30} esu. The enhancement of hyperpolarizabilities is consistent with experimental measurements[1], and the further supporting a full cyclization of the DTE. Of course, the values do not exactly match the experimental reference, an expected fact for this kind of molecules that can be partially explainable by the selected functionals (that is qualitatively but not necessarily quantitatively optimal), relatively compact basis set and solvent models.

References

(1) Ordronneau, L.; Nitadori, H.; Ledoux, I.; Singh, A.; Williams, J. A. G.; Akita, M.; Guerchais, V.; Le Bozec, H., Photochromic Metal Complexes: Photoregulation of both the Nonlinear Optical and Luminescent Properties. *Inorg Chem* **2012**, 51, 5627-5636.