Supplementary information

Luminescent cyclometallated Ir(III) and Pt(II) complexes with β-diketonate ligands as highly active second-order NLO chromophores.

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Synthesis and characterization of [Ir(ppy)$_2$(3-(2,4-Dinitro-phenyl)-pentane-2,4-dione)]. A solution of 3-(2, 4-dinitro-phenyl)-pentane-2, 4-dione[1] (34.6 mg, 0.13 mmol) in CH_3CN (100 mL) was added with $AgBF_4$ (25.4 mg, 0.13 mmol) and stirred for 10 min under nitrogen atmosphere in the dark (the flask was covered with aluminium foil). Then a stoichiometric quantity of $[Ir(ppy)_2Cl]_2$[2] (70 mg, 0.065 mmmol) was added and the mixture was heated under reflux for 6 h. The solution was evaporated to dryness under reduced pressure affording a solid which was dissolved in CH_2Cl_2 and filtered to remove the residual traces of inorganic salts. The filtrate was evaporated to dryness and dissolved in the minimum amount of distilled dichloromethane. Pentane was layered onto the green solution, and the mixture was cooled to ~0 °C. Green plates of the desired product formed overnight (37% yield). ^1H NMR (400 MHz, CD_2Cl_2) δ ppm: 9.07 (td, J = 1.22 Hz, 2H), 8.024 (m, 5H), 7.65 (dd, J = 7.85 Hz, 4H), 7.47 (dt, J = 5.79 Hz 2H), 6.96 (dt, J = 7.57 Hz, 2H), 6.82 (dt, J = 7.46 Hz, 2H), 6.13 (dd, J = 7.76 Hz, 2H), 2.38 (s, 6H). Anal. Calcd for $C_{33}H_{25}N_4O_6Ir$: C 51.76%, H 3.29%, N 7.32%. Trovato: C 51.34%, H 3.16%, N 7.11%. Absorption maxima in $CHCl_3$ in nm [ε (10^{-3} $M^{-1}cm^{-1}$]: 251 [58], 294 [29], 337 [6], 366 [3.3], 386 [1.9]. The emission quantum yield in de-aerated $CHCl_3$ is 0.1%, as determined by using the method of Demas and Crosby[3a] by comparison with the emission of Coumarine 540, employed as a standard.[3b]

For comparison: the absorption maxima of [Ir(ppy)$_2$(MeCOCHCOMe)] in $CHCl_3$ in nm [ε (10^{-3} $M^{-1}cm^{-1}$]: 260 (45), 345 (38), 412 (34), 460 (33), 497 (30); the absorption maxima of

[Ir(ppy)$_2$(PhCOCHCOPh)] in CHCl$_3$ in nm [ε (10^{-3} $M^{-1}cm^{-1}$]: 269 (71), 343 (19), 362 (13), 402 (9.9), 468 (4); the absorption maxima of [Pt(ppy)(MeCOCHCOMe)] in CHCl$_3$ in nm [ε (10^{-3} $M^{-1}cm^{-1}$]: 269 (32), 292 (28), 310 (22), 360 (11), 389 (6.0), 410 sh (3.7); the absorption maxima of [Pt(ppy)(PhCOCHCOPh)] in CHCl$_3$ in nm [ε (10^{-3} $M^{-1}cm^{-1}$]: 259 (65), 274 (56), 307 (26), 358 (20).

TABLE S1. Comparison between calculated and X-ray main geometrical parameters for the Ir and Pt complexes.

M = Ir or Pt	[Ir(ppy)$_2$acac]		[Pt(ppy)acac]	
Parameter	Exp.[a]	Theor.	Exp.[b]	Theor.
M-N	2.010(9)	2.038	1.978(5)	1.997
M-C	2.003(9)	1.993	1.954(5)	1.961
M-O	2.146(6)	2.171	2.082(4) 2.006(4)	2.114 2.025
C-C	---	1.449	---	1.448
<N-M-N	176.3(4)	174.0		---
<O-M-O	90.0(3)	89.1	90.55(15)	92.7
<N-M-C	81.7(4)	80.7	80.9(2)	81.5
<N-M-O	94.5(3)	92.6	93.70(18)	93.3

[a]Reference 4. [b]Reference 5; for the related [Pt(ppy)(PhCOCHCOPh)] complex.

Analysis of the hyperpolarizability tensor:

The static β_{EFISH} is the projection of the hyperpolarizability tensor β along the dipole moment components, defined as: $\beta_{EFISH}=\Sigma\mu\beta_i/(\Sigma\mu_i^2)^{1/2}$, where i=x,y,z, μ_i are the dipole moment components and $\beta_i=\beta_{iii}+1/3\Sigma_{i\neq j}(\beta_{ijj}+\beta_{jij}+\beta_{jji})$. In Table S2 and S3 we report β_I values for the Ir and Pt compounds.
As it can be noticed, the only non-zero dipole component of the Ir-compound is that oriented along the acac-metal axis (y axis in Figure S1), so that this is eventually the only non-zero component of the EFISH hyperpolarizability response, even though other non-zero β components are calculated along the x and z axes. For the Pt-compound, the major dipole component is oriented along phenyl – pyridine axis (x in Figure S1) and only a minor component is calculated along the acac-metal axis. Therefore the largest contribution to the EFISH response is that originated from transitions oriented along the x axis, since the strong and positive β contributions calculated along the y axis are screened by the low dipole moment.

Table S2. Dipole moment (Debye) and hyperpolarizability (atomic units) components for the [Ir(ppy)$_2$acac] complex, as a function of the lowest 40 excited states, see Figure S1 for the molecular framework and orientation.

μ_x= 0.1100 μ_y=3.0027 μ_z=0.0182

1	-69.74241	-6.768599	12.53844
2	-68.88422	-10.89592	12.44564
3	-89.45986	210.1328	7.229845
4	-85.64581	276.4617	6.874839
5	-84.75710	246.8762	6.394830
6	-80.05123	225.0561	4.442577
7	-80.00310	213.8457	4.429057
8	-207.0121	426.9469	-17.55318
9	-196.9351	502.9069	-16.16429
10	-197.7544	493.5537	-14.54918
11	-197.0453	508.3042	-13.97455
12	-194.3673	515.8244	-13.94290
13	-258.1270	458.7075	23.42364
14	-239.2071	399.1251	19.00520
15	-289.4344	418.1299	32.21389
16	-291.7153	200.9353	35.11880
17	-308.7694	248.4702	30.74684
18	-209.7050	327.5351	67.71622
19	-209.4761	323.1456	67.83064
20	-459.1895	163.5135	171.5395
21	-377.4860	-42.53786	162.8248
22	-384.8094	-67.35318	163.7485
23	-375.3758	-93.34657	158.1453
24	-375.2393	-132.4492	159.0537
25	-424.2084	-293.2229	166.9362
26	-366.5634	-359.6772	150.2168
27	-410.8538	-498.0425	157.6677
28	-397.8657	-619.7323	155.5210
29	-359.4581	-686.9756	167.2681
30	-369.7346	-725.2111	166.2635
31	-361.1026	-730.6414	157.7115
32	-365.1689	-767.4606	163.9314
33	-355.1482	-1136.365	131.2402
34	-346.0302	-864.6406	135.0363
35	-346.4267	-866.1071	135.6301
36	-346.9951	-878.3587	136.9284
37	-346.7604	-872.4850	136.3209
38	-339.6358	-850.5463	136.4556
39	-340.3014	-887.1959	143.3250
40	-339.7290	-864.4430	143.5752

Table S3. Dipole moment (Debye) and hyperpolarizability (atomic units) components for the [Pt(ppy)acac] complex, as a function of the lowest 40 excited states see Figure S1 for the molecular framework and orientation.

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μ_x=3.8017 μ_y=-0.6247 μ_z=0.0001

1	-657.1094	527.5921	0.000000
2	-669.4301	558.4367	-9.4542034E-02
3	-709.7158	787.4123	-7.2882585E-02
4	-1211.551	2625.367	-8.1494279E-02
5	-1211.648	2625.567	-8.2484715E-02
6	-1352.773	2830.630	-8.2484715E-02
7	-1296.542	3205.346	-8.4981807E-02
8	-1558.787	3258.228	-8.3610676E-02
9	-1558.795	3258.247	-8.3407968E-02
10	-1558.845	3258.262	-8.0660306E-02
11	-3024.052	3848.284	-8.6791091E-02
12	-3024.050	3848.384	-8.6791091E-02
13	-3375.750	4032.572	-8.4509693E-02
14	-3375.842	4033.056	-8.4509693E-02
15	-3876.673	4158.918	-5.6043409E-02
16	-3876.698	4158.929	-6.2479928E-02
17	-3876.798	4159.328	-6.4227864E-02
18	-3876.910	4159.684	-6.3911706E-02
19	-4106.330	4280.255	-6.3911706E-02
20	-4106.330	4280.255	-6.3904718E-02
21	-4134.268	4360.035	-5.7715088E-02
22	-4134.285	4360.042	-5.7715088E-02
23	-4151.263	4382.238	-5.7715088E-02
24	-3881.807	5117.720	-5.1410578E-02
25	-4079.934	5128.587	-4.9339194E-02
26	-3978.434	5213.456	1.3410214E-02
27	-3950.024	5254.417	-0.1357365
28	-3949.031	5257.636	-0.1358934
29	-3949.253	5257.846	-0.1358934
30	-3957.593	5263.999	-0.1358934
31	-4002.122	5282.779	-0.1358934
32	-4002.485	5283.149	-0.1358934
33	-4014.419	5280.240	-0.1358934
34	-4014.606	5280.292	-0.1358934
35	-4010.894	5287.774	-0.1382168
36	-4252.586	5394.487	-0.1369456
37	-4252.821	5394.985	-0.1333515
38	-4253.111	5397.034	-0.1343881
39	-4241.011	5466.904	-0.4464176
40	-4240.873	5467.101	-0.4392595

Figure S1. Molecular orientation and reference system used for the dipole and hyperpolarizability calculations.

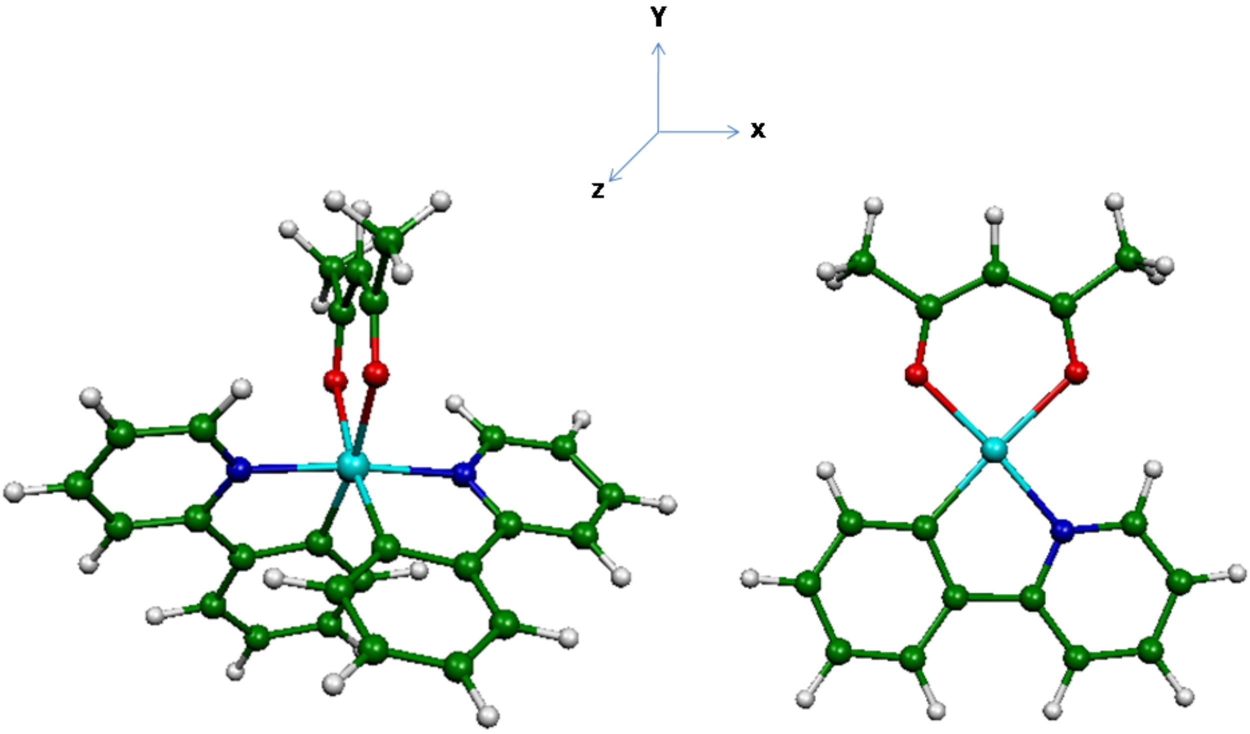
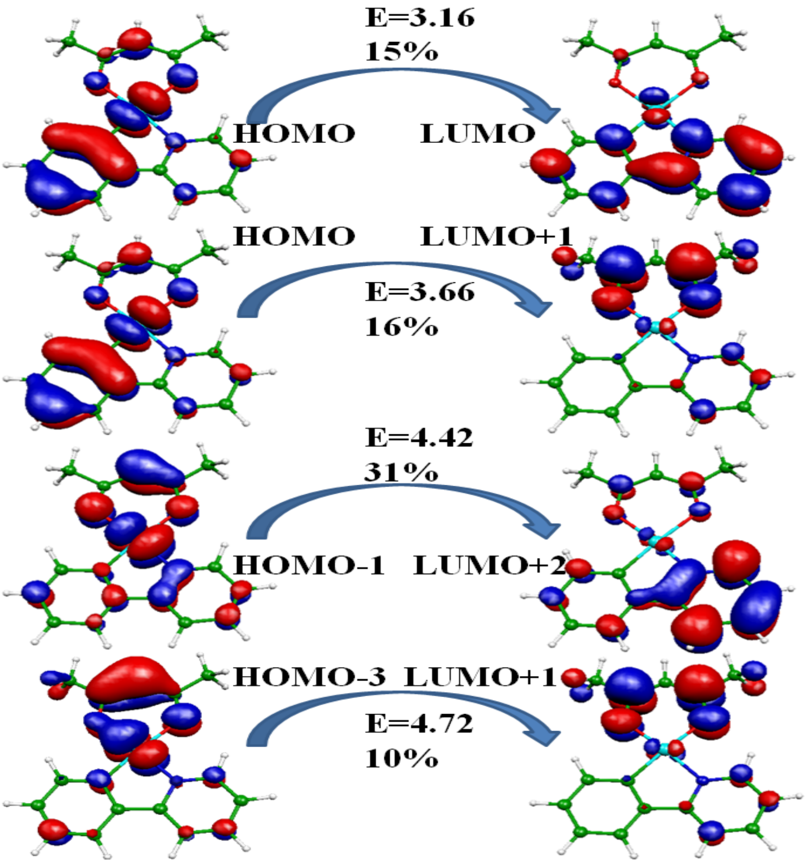


Figure S2. The main electronic transitions and molecular orbitals controlling the quadratic hyperpolarizability of [Pt(ppy)(acac)] together with their transition energies (E in eV) and partial contribution.



References:

1. (a) R. C. B. Copley, C. Lamberth, J. Machell, D. M. P. Mingos, D. M. Murphy and H. Powell, *J. Mater. Chem.*, 1991, **1**, 583. (b) E. M. Armstrong and P. K. Baker, *Inorg. Chim. Acta*, 1988, **143,** 13.

2. S. Sprouse, K.A. King, P.J. Spellane and R.J. Watts, *J. Am. Chem. Soc.,* 1984, **106**, 6647.

3 (a) J.N. Demas, G.A. Crosby, *J. Phys. Chem.,* 1971, **75**, 991. (b) R.F. Kubin, A.N. Fletcher, *Chem. Phys. Lett.* 1983, **99**, 49.

4. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, **40**, 1704.

5. J. Liu, C. J. Yang, Q.Y. Cao, M. Xu, J. Wang, H. N. Peng, W. F. Tan, X. X. Lü, X. C. Gao, *Inorg. Chim. Acta*, 2009, **362**, 575.