Theoretical investigation of electronic structures, second-order NLO responses of cyclometalated Ir(ɪɪɪ) and Rh(ɪɪɪ) counterpart complexes: effect of metal center

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The solid phase molecule can be gained by using (PCM)-tuned method. The dielectric constant ε of solid-state molecular can be evaluated by the Clausius-Mossotti equation, which expressed as:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi\alpha}{3V} \tag{1}$$

where V is the volume occupied by a single molecule, α is the isotropic component of molecular polarizability. The V and α calculated at B3LYP/6-31G(d)/SDD level and given in Table S1.

Experimentally, HRS is the most effective method to calculate the second-order NLO responses. The frequency-dependent first hyperpolarizability (β_{HRS}) values are calculated at ωB97XD/6-31+G(d)/SDD level in dichloromethane (DCM) solution as shown in Table S3. The $\beta_{\mathrm{HRS}}(-2\omega; \omega, \omega)$ that can be extracted from HRS data is described by Bersohn's expression:[1, 2]

$$\beta_{\mathrm{HRS}}(-2\omega; \omega, \omega) = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZXX}^2 \rangle} \tag{2}$$

Table S1 The volume (V, Bohr^3), polarizabilities (α, Bohr^3) and dielectric constant (ε) simulated in the solid phase environment for all studied complexes

Complex	Ir-1	Rh-1	Ir-2	Rh-2	Ir-3	Rh-3	Ir-4	Rh-4
V	3928.0	3922.1	5156.3	5151.6	5093.0	5090.1	4248.1	4240.7
α	397.6	391.7	482.8	478.2	540.7	532.3	408.5	404.0
ε	3.2	3.2	2.9	2.9	3.4	3.3	3.0	3.0

Table S2 Values of β_{tot} (a.u.) of all studied complexes calculated at various functionals

Gas phase					
Complex	BHandHLYP	M06-2X	CAM-B3LYP	ωB97XD	LC-BLYP
Ir-1	1221.0	1169.2	1414.8	1402.4	996.5
Rh-1	738.9	695.7	855.0	837.6	605.3
Ir-2	654.0	610.4	745.2	725.9	772.6
Rh-2	356.6	274.8	443.0	461.3	525.8
Ir-3	1405.1	1367.3	1556.8	1517.0	1131.2
Rh-3	950.4	904.1	1030.0	981.8	751.6
Ir-4	801.5	779.0	847.3	820.7	653.1
Rh-4	599.4	581.9	613.6	586.0	476.8
Liquid phase					
Complex	BHandHLYP	M06-2X	CAM-B3LYP	ωB97XD	LC-BLYP
Ir-1	1972.2	1884.0	2302.8	2278.5	1557.8
Rh-1	1160.7	1063.5	1309.1	1272.6	907.0
Ir-2	935.2	884.0	1147.3	1113.6	1247.2
Rh-2	454.5	326.7	624.7	668.9	854.6
Ir-3	2449.9	2385.7	2731.8	2668.6	1847.5
Rh-3	1554.3	1456.0	1664.0	1562.1	1112.6
Ir-4	1605.8	1519.5	1705.9	1646.6	1272.1
Rh-4	1129.3	993.0	1127.4	1055.6	879.9
Solid phase					
Complex	BHandHLYP	M06-2X	CAM-B3LYP	ωB97XD	LC-BLYP
Ir-1	1727.4	1653.5	2013.0	1993.8	1380.1
Rh-1	1028.0	953.6	1171.5	1142.5	817.6
Ir-2	832.8	783.2	988.9	960.5	1053.9
Rh-2	422.7	312.4	544.5	584.6	716.9
Ir-3	2139.7	2084.7	2374.8	2316.6	1656.1
Rh-3	1394.3	1316.0	1496.6	1413.5	1041.9
Ir-4	1269.2	1214.5	1348.3	1304.0	1017.0
Rh-4	907.3	831.8	917.8	867.0	714.1

Table S3 The values of β_{HRS} for all studied complexes calculated at ωB97XD/6-31+G(d)/SDD level in liquid phase

Complex	1064 nm	1340 nm	1460 nm	1907 nm
Ir-1	783.4	625.1	590.8	524.4
Rh-1	427.9	347.8	330.3	296.0
Ir-2	128.1	110.7	109.1	108.0
Rh-2	201.8	147.8	137.1	117.9
Ir-3	1357.0	1045.8	984.3	869.8
Rh-3	1061.7	834.6	788.1	700.7
Ir-4	715.7	578.0	548.5	491.7
Rh-4	511.4	425.8	407.4	371.8

Reference

1.   R. Bersohn, Y. H. Pao and H. L. Frisch, *J. Chem. Phys.*, 1966, **45**, 3184-3198.

2.   F. Castet, E. Bogdan, A. Plaquet, L. Ducasse, B. Champagne and V. Rodriguez, *J. Chem. Phys.*, 2012, **136**, 024506.