Supporting Information for:

Predicting phosphorescent lifetimes and zero-field splitting of organometallic complexes with time-dependent density functional theory including spin-orbit coupling

K. Mori,^a T. P. M. Goumans,^b E. van Lenthe^b and F. Wang^c

^{*a*} Ryoka Systems Inc., Science and Technology Systems Division, Tokyo Skytree East Tower 1-1-2, Oshiage, Sumida-ku, Tokyo 131-0045, Japan, mori@rsi.co.jp

^b Scientific Computing & Modelling NV, Vrije Universiteit, Theoretical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

^c College of Chemistry, Sichuan University, 24, South Section 1, Yihuan Road, Chengdu, 610064 Sichuan, P. R. China

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No.	Compound ^a	Symmetry	$\Delta E(ZFS)$				τ ^r (300K)			
			Gas		COSMO		Gas		COSMO	
			pSOC- TDDFT	SOC- TDDFT	pSOC- TDDFT	SOC- TDDFT	pSOC- TDDFT	SOC- TDDFT	pSOC- TDDFT	SOC- TDDFT
1	[Rh(bpy) ₃] ³⁺	C_2	0.2	0.2	0.2	0.1	2.9E+03	1.5E+04	3.7E+03	5.6E+03
2	$[Ir(bpy)_3]^{3+}$	C_2	5.5	1.9	5.6	1.6	181.0	167.0	171.8	87.1
3	Pd(thpy) ₂	C_1	3.4	2.3	1.9	0.9	302.5	574.7	221.7	287.8
4	Pt(s1-thpy)(acac)	C_1	8.0	9.3	4.2	4.5	95.5	104.8	103.7	47.5
5	Re(pbt)(CO) ₄	C_1	2.4	3.2	1.4	1.3	125.2	124.4	180.4	78.0
6	Pt(thpy)(acac)	C_1	16.3	12.1	11.0	5.8	90.2	87.7	100.2	38.7
7	Pt(4,6-dFpthiq)(dpm)	C_1	32.6	24.6	15.7	9.7	34.1	28.5	39.4	14.3
8	Pt(4,6-dFppy)(acac)	C_1	48.4	36.3	24.7	14.9	37.6	30.9	38.4	11.3
9	Pt(pbt)(acac)	C_1	38.7	28.6	21.5	13.1	36.0	47.1	32.0	15.9
10	Pt(thpy) ₂	C_1	36.8	35.6	17.7	13.6	7.8	57.8	18.8	20.0
11	Ir(s1-thpy) ₂ (acac)	C_2	25.9	35.7	29.8	34.5	9.2	25.0	9.4	10.1
12	Ir(btp) ₂ (acac)	C_1	26.2	20.7	18.4	17.7	51.1	61.7	44.0	25.4
13	Ir(thpy) ₂ (acac)	C_2	52.7	40.9	51.1	38.0	12.8	22.1	12.2	8.0
14	Ir(4,6-dFppy) ₂ (pic)	C_1	71.5	98.6	42.1	53.6	14.9	7.4	14.4	3.2
15	Ir(piq) ₃	C_1	74.4	114.4	55.8	71.8	9.6	7.1	14.1	3.4
16	$[Ru(bpy)_{3}]^{2+}$	C_2	88.6	125.3	90.3	122.0	29.7	14.6	20.0	4.9
17	Ir(biqa) ₃	C_1	101.1	150.6	87.7	118.2	3.4	3.2	3.7	1.5
18	Ir(piq) ₂ (acac)	C_1	111.1	148.9	81.1	95.7	12.8	7.7	15.9	3.4
19	Ir(pbt) ₂ (acac)	C_1	170.7	220.8	148.2	181.0	6.6	8.2	5.8	2.8
20	Ir(4,6-dFppy) ₂ (acac)	C_1	107.3	143.8	101.0	124.0	6.8	5.4	4.7	1.9
21	Ir(dm-2-piq) ₂ (acac)	C_2	98.3	157.5	112.1	134.7	7.6	3.7	6.2	1.1
		C_1	n/a	n/a	146.5	168.3	n/a	n/a	9.1	2.1
22	Ir(ppy) ₃	C_1	101.8	143.6	83.6	105.3	7.5	5.6	5.5	2.1
23	$[Os(bpy)_3]^{2+}$	D_3	148.9	217.9	153.2	180.7	2.1	2.0	2.1	0.6
		C_2	n/a	n/a	559.9	690.5	n/a	n/a	11.0	5.9
¹ abbreviation for ligands same as in main paper.										

Table S1. Calculated ZFS (cm⁻¹) and radiative lifetime τ^r (µs) at the 4 levels of theory, perturbative or full SOC, gas phase or COSMO solvation.

	Gas				COSMO				
	pSOC-	pSOC-	SOC-	-	pSOC-	pSOC-	SOC-		
	TDDFT	TDDFT	TDDFT	_	TDDFT	TDDFT	TDDFT		
No. of excitations ^b	20 (10/10)	40 (20/20)	4		20 (10/10)	40 (20/20)	4		
No. of TDDFT iterations ^c	15 (6/9)	16 (7/9)	11		15 (6/9)	20 (11/9)	11		
Total CPU time	22870	47362	57637		23262	60431	78147		
CPU time/TDDFT iteration	1525	2960	5240		1551	3022	7104		

Table S2. CPU timings (s) for Ir(ppy)₃ calculations at the 4 levels of theory, perturbative or full SOC, gas phase or COSMO solvation.^a

^a Calculations were run on a dual hexa core Intel(R) Xeon(R) CPU E5-2620 @ 2.00GHz.

^b The numbers of singlet and triplet excitation used in pSOC-TDDFT are reported within parentheses as (singlet/triplet).

^c The numbers of TDDFT iterations which were needed for singlet and triplet excitations in pSOC-TDDFT are reported within parentheses as (singlet/triplet).

While the computational effort of pSOC-TDDFT is about ten times smaller than that of SOC-TDDFT for a given number of excitations,¹ the pSOC approach uses a truncated space for the perturbation expansion, and consequently more excitations are needed for a better description of the spin-mixed excitations obtained in pSOC-TDDFT. For the choice of 40 (20 singlet + 20 triplet) excitations in pSOC-TDDFT, which were used in main paper, the gain in computational efficiency over SOC-TDDFT with 4 spin-mixed excitations is reduced.

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Method	$\Delta E_{1,2}$	$\Delta E_{1,3}$	k_1^{r}	k_2^{r}	k_3^r	k _{av} ^r (300K)	$\tau_{av}{}^{r}(300K)$
pSOC-TDDFT/Gas at T ₁	14	102	6.2E+02	1.0E+05	4.0E+05	1.3E+05	7.5
SOC-TDDFT/Gas at T ₁	14	144	1.2E+02	8.3E+03	8.5E+05	1.8E+05	5.6
pSOC-TDDFT/COSMO at T ₁	11	84	9.8E+02	1.0E+05	5.6E+05	1.8E+05	5.5
SOC-TDDFT/COSMO at T ₁	13	105	1.9E+02	1.8E+04	2.0E+06	4.7E+05	2.1
pSOC-TDDFT/Gas at S ₀	95	95	1.2E+03	1.5E+06	1.5E+06	8.3E+05	1.2
SOC-TDDFT/Gas at S ₀	133	133	6.8E+02	1.1E+06	1.1E+06	5.8E+05	1.7
Other pSOC approach at T ₁ ^{a,b}	17	107	6.7E+02	2.0E+04	3.1E+05	8.2E+04	12.2
Other pSOC approach at T ₁ ^{b,c}	54	69	1.2E+05	1.3E+05	3.2E+05	1.8E+05	5.5
Other pSOC approach at S ₀ ^{b,c}	33	104	2.3E+04	1.5E+06	1.5E+06	9.0E+05	1.1
Exp. ^{d,e}	12-12.4	114-135	5.7E+03	5.8E+04	2.9E+06	6.9E+05	1.5
Exp. ^{f.g}	13-14	85-150				6.1E+05 ^h	1.6 ^h
Exp. ^{g,i}	19	170				5.6E+05	1.8

Table S3. Calculated ZFS (cm⁻¹) and radiative rates (s⁻¹) and lifetimes (µs) for Ir(ppy)₃ with (p)SOC-TDDFT compared with previous theoretical studies^{2, 3} and experimental data.⁴

^a B3PW91/LanL2DZ(Ir):D95(rest) in condensed phase with an Onsager model; ref 2.

^b Reported values are corrected for the refractive index of CH₂Cl₂ (n=1.42) according to the Strickler-Berg relationship.
^c B3LYP/SDD(Ir):6-311G*(rest) in gas phase; ref 3.

^d In PMMA; ref 4.

e The averaged radiative rate is calculated by use of the three individual radiative decay times and of the zero-field splitting values according to Eq. (1) for a temperature of 300K. ^f In THF; ref 4.

^g The individual radiative rates of the triplet substates are not available. The averaged radiative rate is calculated from the emission quantum yield and the decay time measured at ambient temperature according to Eq. (2).

^h In 2-MeTHF; ref 4.

ⁱ In CH₂Cl₂; ref 4.

$$\tau_{av}^{r} = \frac{1}{k_{av}^{r}} = \left(\frac{1 + e^{-(\Delta E_{1,2}/k_{B}T)} + e^{-(\Delta E_{1,3}/k_{B}T)}}{k_{1}^{r} + k_{2}^{r}e^{-(\Delta E_{1,2}/k_{B}T)} + k_{3}^{r}e^{-(\Delta E_{1,3}/k_{B}T)}}\right)$$
(1)
$$\Phi_{PL} = \frac{k^{r}}{k^{r} + k^{nr}} = \tau k^{r}$$
(2)



Figure S1. Calculated ZFS (top, in cm⁻¹) and τ^r (bottom, in μ s) at the COSMO + SOC-TDDFT level for several Ir(N^C)₂(acac) and Pt(N^C)(acac) compounds, compared to experimental data.⁴



Figure S2. Calculated ZFS (top, in cm⁻¹) and τ^r (bottom, in μ s) at the 4 levels of theory (perturbative or full SOC, gas phase or COSMO solvation), compared to experimental data.⁴⁻⁹

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