

Spin Density Distribution after Electron Transfer from Triethylamine to an $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ Photosensitizer during Photocatalytic Water Reduction

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The photoreduction of the bis(2-phenylpyridinato-)(2,2'-bipyridine)iridium(III) ion ($[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$), used as photosensitizer in photocatalytic water splitting, by triethylamine was studied by means of UV/VIS, XANES, and EPR spectroscopies, supported by theoretical calculations on density functional theory (DFT) and complete active space self-consistent field (CASSCF/CASPT2) levels. The combination of these methods suggests a predominant *bpy* localization of the spin-density of the unpaired electron with notable delocalization to the Ir center. This is particularly evident from EPR and theoretical results and leads to broad EPR lines and a large anisotropy of the *g*-factor.

Supplementary Material

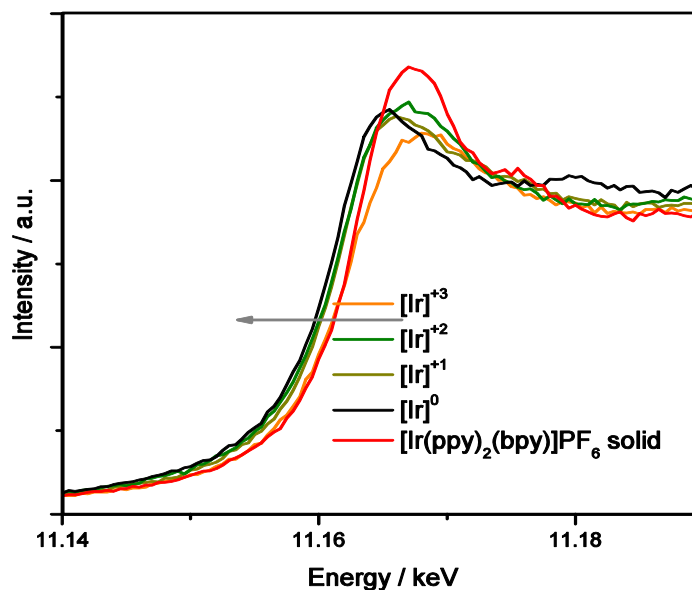


Figure S1. XANES measurements of $[\text{Ir}]^{+3}$ ($[\text{Ir}(\text{H}_2)(\text{TFP})(\text{P}i\text{Pr}_3)_2]$), $[\text{Ir}]^{+2}$ ($[\text{Ir}(\text{Cl})\{\mu_{\text{es}}\text{-Diimin}\}(\text{CN}t\text{Bu})]$), $[\text{Ir}]^{+1}$ ($[\text{Ir}(\mu\text{-Cl})(\text{COOEt})_2]_2$) and $[\text{Ir}]^0$ (iridium foil) and the sample ($[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$).

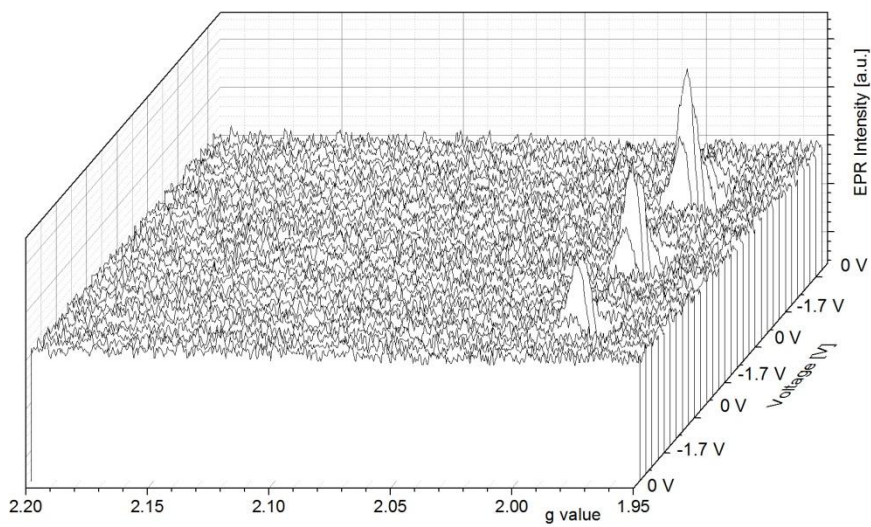


Figure S2. In situ EPR spectroelectrochemistry performed by Cyclovoltametrie (0 to -1.7V) combined with EPR spectroscopy for IrPS.

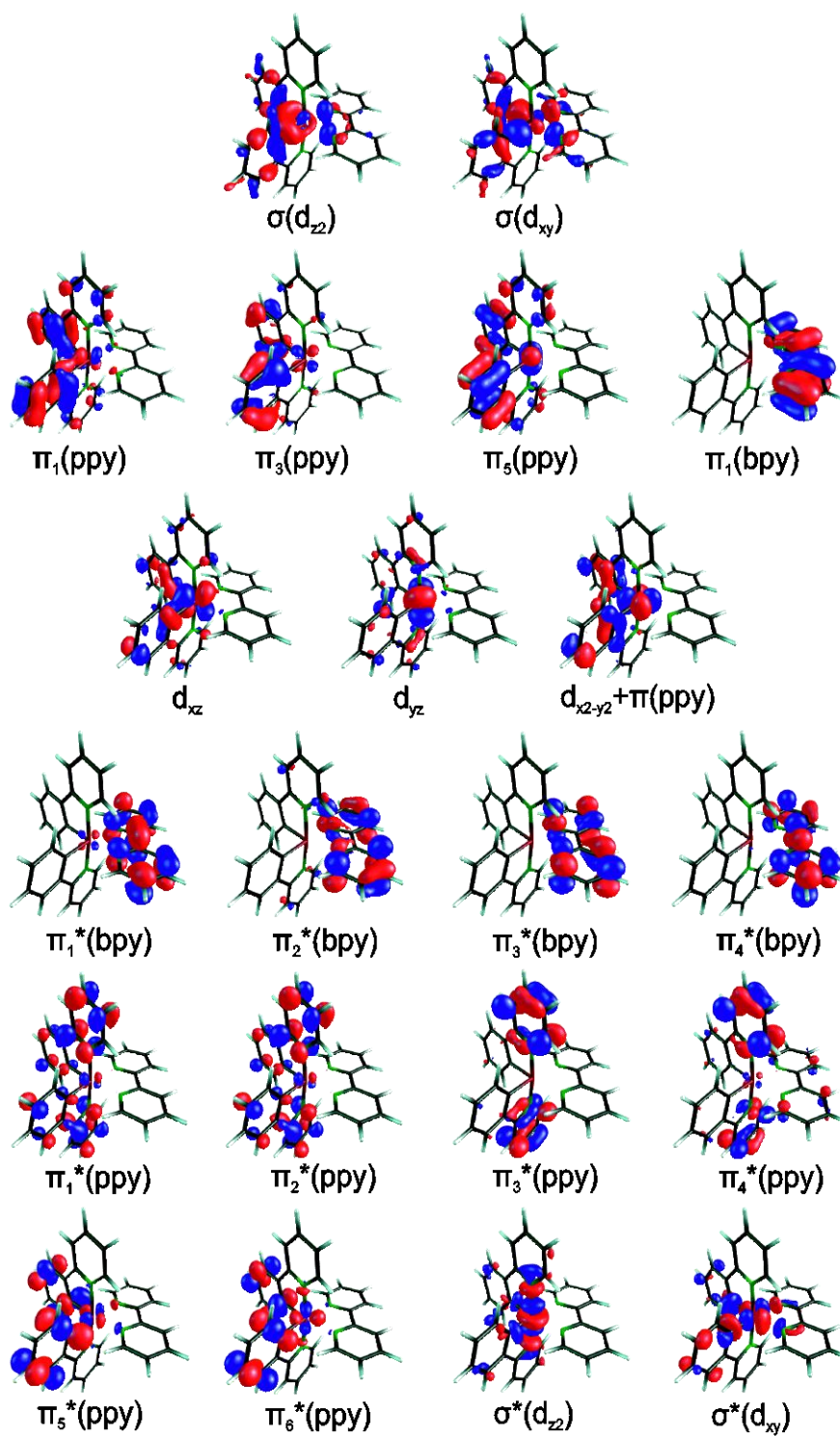


Figure S3. MOs most important for electronic spectrum.

Table S1. Vertical electronic transitions of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^0$ as predicted by TDDFT (LC-BLYP, $\omega=0.18 \text{ bohr}^{-1}$) in THF (PCM).

State nr.	Energy / cm^{-1}	Osc. str.	Configuration	Weight
1	10893	0.005	$\pi 1^*(\text{bpy}) \rightarrow \pi 2^*(\text{bpy})$	0.45
2	11492	0.000	$\pi 1^*(\text{bpy}) \rightarrow \pi 1^*(\text{ppy})$	0.75
3	11921	0.002	$\pi 1^*(\text{bpy}) \rightarrow \pi 2^*(\text{ppy})$	0.94
4	12907	0.026	$\pi 1^*(\text{bpy}) \rightarrow \pi 3^*(\text{bpy})$	0.94
5	16421	0.002	$\pi 1^*(\text{bpy}) \rightarrow \pi 3^*(\text{ppy})$	0.63
6	16744	0.000	$\pi 1^*(\text{bpy}) \rightarrow \pi 4^*(\text{ppy})$	0.94
7	22294	0.000	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 1^*(\text{ppy})$	0.38
8	22604	0.108	$\pi 1^*(\text{bpy}) \rightarrow \pi 4^*(\text{bpy})$	0.67
9	22790	0.000	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 1^*(\text{ppy})$	0.35
10	24742	0.052	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 1^*(\text{ppy})$	0.47
11	25705	0.002	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 2^*(\text{ppy})$	0.49
12	25904	0.000	$\text{d}yz \rightarrow \pi 2^*(\text{ppy})$ $\text{dx}z \rightarrow \pi 1^*(\text{bpy})$ $\text{dx}z \rightarrow \pi 1^*(\text{ppy})$	0.16 0.16 0.14
13	25940	0.001	$\text{d}yz \rightarrow \pi 1^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 1^*(\text{bpy})$	0.2 0.15
14	26116	0.001	$\pi 1^*(\text{bpy}) \rightarrow \sigma^*(\text{dz}2)$	0.56
15	26779	0.000	$\pi 1^*(\text{bpy}) \rightarrow \pi 5^*(\text{ppy})$	0.76
16	27033	0.061	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 2^*(\text{ppy})$	0.44
17	27920	0.003	$\text{d}yz \rightarrow \pi 1^*(\text{bpy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 3^*(\text{ppy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 3^*(\text{ppy})$	0.15 0.15 0.14
18	28129	0.000	$\text{d}yz \rightarrow \pi 1^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 2^*(\text{ppy})$ $\pi 1(\text{bpy}) \rightarrow \pi 1^*(\text{ppy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 4^*(\text{ppy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 4^*(\text{ppy})$	0.16 0.15 0.08 0.06 0.06
19	28462	0.056	$\text{dx}2\text{-}\gamma 2 \rightarrow \pi 2^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 1^*(\text{bpy})$	0.2 0.18
20	28466	0.038	$\text{d}yz \rightarrow \pi 2^*(\text{ppy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 2^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 1^*(\text{ppy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 3^*(\text{ppy})$	0.13 0.12 0.11 0.1
21	29118	0.008	$\text{dx}z \rightarrow \pi 1^*(\text{bpy})$ $\text{dx}2\text{-}\gamma 2 \rightarrow \pi 4^*(\text{ppy})$	0.34 0.16
22	29166	0.057	$\text{d}yz \rightarrow \pi 1^*(\text{ppy})$	0.31
23	29272	0.011	$\pi 1^*(\text{bpy}) \rightarrow \text{diff}$	0.46
24	29317	0.006	$\pi 1^*(\text{bpy}) \rightarrow \text{diff}$ $\text{dx}z \rightarrow \pi 1^*(\text{bpy})$	0.22 0.17

			$dx^2-y^2 \rightarrow \pi^4^*(ppy)$	0.09
25	29498	0.004	$\pi^1^*(bpy) \rightarrow \pi^6^*(ppy)$	0.52
26	29609	0.047	$dxz \rightarrow \pi^2^*(ppy)$	0.45
27	29713	0.014	$dxz \rightarrow \pi^1^*(ppy)$ $\pi^1^*(bpy) \rightarrow \pi^6^*(ppy)$	0.33 0.17
28	30017	0.000	$dyz \rightarrow \pi^2^*(ppy)$	0.44
29	30232	0.019	$dx^2-y^2 \rightarrow \pi^3^*(ppy)$	0.43
30	30837	0.097	$dxz \rightarrow \pi^2^*(ppy)$	0.53
31	30852	0.001	$dxz \rightarrow \pi^2^*(ppy)$ $dxz \rightarrow \pi^1^*(ppy)$	0.25 0.16
32	31084	0.000	$\pi^1^*(bpy) \rightarrow \text{diff}$	0.6
33	31202	0.001	$\pi^1^*(bpy) \rightarrow \text{diff}$	0.67
34	31689	0.000	$dx^2-y^2 \rightarrow \pi^4^*(ppy)$	0.34
35	31951	0.038	$dyz \rightarrow \pi^3^*(ppy)$ $\pi^1(ppy) \rightarrow \pi^2^*(ppy)$ $dyz \rightarrow \pi^3^*(ppy)$ $\pi^1(bpy) \rightarrow \pi^3^*(ppy)$	0.17 0.14 0.09 0.05
36	32051	0.126	$\pi^1(ppy) \rightarrow \pi^2^*(ppy)$	0.5
37	32269	0.002	$dyz \rightarrow \pi^3^*(ppy)$ $dyz \rightarrow \pi^3^*(ppy)$ $\pi^1(bpy)+\pi^5(ppy) \rightarrow \pi^1^*(ppy)$ $\pi^1(ppy) \rightarrow \pi^2^*(ppy)$	0.12 0.11 0.11 0.11
38	32339	0.000	$\pi^1(ppy) \rightarrow \pi^1^*(ppy)$ $\pi^1(bpy)+\pi^5(ppy) \rightarrow \pi^1^*(bpy)$ $dxz \rightarrow \pi^3^*(ppy)$ $dxz \rightarrow \pi^3^*(ppy)$	0.13 0.12 0.12 0.07
39	32494	0.000	$dyz \rightarrow \pi^4^*(ppy)$ $dyz \rightarrow \pi^4^*(ppy)$ $dxz \rightarrow \pi^3^*(ppy)$ $\pi^1(bpy) \rightarrow \pi^4^*(ppy)$ $dxz \rightarrow \pi^3^*(ppy)$ $dx^2-y^2 \rightarrow \pi^6^*(ppy)$ $\pi^3(ppy) \rightarrow \pi^3^*(ppy)$ $\pi^3(ppy) \rightarrow \pi^3^*(ppy)$	0.1 0.09 0.09 0.05 0.04 0.03 0.03 0.03
40	33176	0.009	$\pi^1^*(bpy) \rightarrow \pi^7^*(ppy)$	0.55
41	33294	0.001	$\pi^1^*(bpy) \rightarrow \pi^8^*(ppy)$	0.65
42	33560	0.002	$dyz \rightarrow \pi^3^*(ppy)$ $dyz \rightarrow \pi^3^*(ppy)$	0.28 0.21
43	33665	0.000	$dx^2-y^2 \rightarrow \pi^6^*(ppy)$ $dx^2-y^2 \rightarrow \pi^6^*(ppy)$ $\pi^3(ppy) \rightarrow \pi^1^*(ppy)$ $\pi^1(bpy)+\pi^5(ppy) \rightarrow \pi^5^*(ppy)$	0.18 0.16 0.06 0.06
44	33762	0.011	$dyz \rightarrow \pi^2^*(bpy)$ $\pi^1(ppy) \rightarrow \pi^2^*(bpy)$	0.14 0.12

			$\pi 1(\text{ppy}) \rightarrow \pi 3^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 3^*(\text{ppy})$	0.12 0.1
45	33883	0.031	$\pi 1(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 4^*(\text{ppy})$	0.21 0.14 0.13
46	34110	0.000	$\text{d}x^2-\text{y}^2 \rightarrow \pi 5^*(\text{ppy})$ $\text{d}x^2-\text{y}^2 \rightarrow \pi 5^*(\text{ppy})$ $\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$ $\pi 3(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$	0.16 0.16 0.07 0.07
47	34312	0.003	$\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 4^*(\text{ppy})$	0.2 0.12 0.1
48	34782	0.001	$\pi 1^*(\text{bpy}) \rightarrow \sigma^*(\text{dxy})$	0.51
49	34796	0.003	$\text{d}xz \rightarrow \pi 4^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 4^*(\text{ppy})$ $\text{d}x^2-\text{y}^2 \rightarrow \pi 3^*(\text{ppy})$ $\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.29 0.07 0.06 0.05
50	35146	0.103	$\text{d}yz \rightarrow \pi 3^*(\text{ppy})$ $\pi 1(\text{bpy})+\pi 5(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 4^*(\text{ppy})$	0.18 0.17 0.14
51	35174	0.006	$\text{d}yz \rightarrow \pi 4^*(\text{ppy})$ $\pi 1(\text{ppy}) \rightarrow \pi 3^*(\text{bpy})$ $\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}x^2-\text{y}^2 \rightarrow \pi 4^*(\text{ppy})$ $\pi 1(\text{bpy}) \rightarrow \pi 3^*(\text{bpy})$ $\text{d}x^2-\text{y}^2 \rightarrow \pi 4^*(\text{ppy})$ $\pi 1(\text{ppy}) \rightarrow \pi 4^*(\text{ppy})$	0.17 0.07 0.06 0.04 0.04 0.04 0.03
52	35191	0.001	$\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 3^*(\text{bpy})$	0.18 0.15 0.1
53	35500	0.008	$\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}yz \rightarrow \pi 3^*(\text{bpy})$ $\text{d}yz \rightarrow \pi 3^*(\text{bpy})$ $\pi 1(\text{bpy})+\pi 5(\text{ppy}) \rightarrow \pi 1^*(\text{bpy})$	0.15 0.13 0.1 0.08
54	35517	0.060	$\text{d}yz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 4^*(\text{ppy})$ $\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.17 0.13 0.12
55	35676	0.010	$\text{d}yz \rightarrow \pi 4^*(\text{ppy})$	0.43
56	36080	0.059	$\text{d}x^2-\text{y}^2 \rightarrow \pi 2^*(\text{bpy})$ $\text{d}xz \rightarrow \pi 4^*(\text{ppy})$	0.33 0.12
57	36144	0.001	$\text{d}yz \rightarrow \pi 4^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 3^*(\text{ppy})$ $\text{d}xz \rightarrow \pi 2^*(\text{bpy})$ $\text{d}x^2-\text{y}^2 \rightarrow \pi 3^*(\text{bpy})$	0.11 0.09 0.09 0.08

			$dyz \rightarrow \pi 3^*(bpy)$	0.07
58	36449	0.098	$dxz \rightarrow \pi 4^*(ppy)$ $\pi 1(ppp) \rightarrow \pi 2^*(ppy)$	0.36 0.12
59	36840	0.055	$dx^2-y^2 \rightarrow \pi 2^*(bpy)$	0.42
60	36860	0.080	$\pi 3(ppp) \rightarrow \pi 1^*(bpy)$ $\pi 3(ppp) \rightarrow \pi 1^*(ppy)$ $\pi 1(ppp) \rightarrow \pi 1^*(ppy)$	0.19 0.19 0.09
61	36916	0.074	$\pi 1(ppp) \rightarrow \pi 1^*(bpy)$ $dyz \rightarrow \pi 1^*(bpy)$ $\pi 1(ppp) \rightarrow \pi 2^*(ppy)$	0.34 0.08 0.07
62	37125	0.000	$dx^2-y^2 \rightarrow \sigma^*(dz^2)$ $dx^2-y^2 \rightarrow \sigma^*(dz^2)$	0.2 0.2
63	37206	0.004	$dx^2-y^2 \rightarrow \pi 3^*(bpy)$	0.48
64	37427	0.026	$\pi 6(ppp) \rightarrow \pi 1^*(ppy)$ $\pi 6(ppp) \rightarrow \pi 1^*(bpy)$ $\pi(lig) \rightarrow \pi 1^*(ppy)$ $dx^2-y^2 \rightarrow \pi 5^*(ppy)$ $\pi 3(ppp) \rightarrow \pi 2^*(ppy)$ $\pi(lig) \rightarrow \pi 2^*(ppy)$ $\pi 1(bpy)+\pi 5(ppp) \rightarrow diff$ $\pi(bpy) \rightarrow \pi 1^*(bpy)$ $\pi 1(ppp) \rightarrow \pi 7^*(ppy)$	0.07 0.06 0.06 0.06 0.04 0.04 0.03 0.03 0.03
65	37460	0.103	$\pi 1(ppp) \rightarrow \pi 1^*(bpy)$ $\pi 1(bpy) \rightarrow \pi 1^*(bpy)$ $dxz \rightarrow \pi 4^*(ppy)$ $\pi 3(ppp) \rightarrow \pi 1^*(ppy)$	0.19 0.08 0.06 0.05
66	37468	0.024	$dx^2-y^2 \rightarrow \pi 3^*(bpy)$ $\pi 1(ppp) \rightarrow \pi 1^*(bpy)$ $\pi(lig) \rightarrow \pi 1^*(bpy)$ $dx^2-y^2 \rightarrow \pi 3^*(bpy)$ $\pi 6(ppp) \rightarrow \pi 2^*(ppy)$ $\pi(lig) \rightarrow \pi 1^*(ppy)$ $dx^2-y^2 \rightarrow \sigma^*(dz^2)$ $\pi 1(ppp) \rightarrow \pi 1^*(ppy)$ $\pi 6(ppp) \rightarrow \pi 1^*(ppy)$ $\sigma(dxy) \rightarrow \pi 1^*(bpy)$	0.13 0.04 0.03 0.03 0.03 0.02 0.02 0.02 0.02 0.02
67	37600	0.004	$\sigma(dxy) \rightarrow \pi 2^*(ppy)$ $\pi 1(bpy)+\pi 5(ppp) \rightarrow \pi 2^*(ppy)$	0.25 0.22
68	37635	0.015	$dx^2-y^2 \rightarrow \pi 2^*(bpy)$	0.59
69	37757	0.002	$\pi 1(ppp) \rightarrow \pi 1^*(ppy)$	0.45
70	38191	0.000	$\sigma(dxy) \rightarrow \pi 1^*(bpy)$ $\sigma(dxy) \rightarrow \pi 1^*(ppy)$ $\sigma(dxy) \rightarrow \pi 2^*(ppy)$	0.16 0.16 0.07
71	38227	0.001	$\pi 1(ppp) \rightarrow \pi 1^*(ppy)$	0.11

			$\pi_3(\text{bpy}) \rightarrow \pi_2^*(\text{ppy})$	0.11
			$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{bpy})$	0.07
			$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$	0.07
			$\pi_1^*(\text{bpy}) \rightarrow \text{diff}$	0.05
			$\pi_1^*(\text{bpy}) \rightarrow \pi^*(\text{bpy})$	0.04
			$\sigma(\text{dxy}) \rightarrow \pi_2^*(\text{ppy})$	0.04
72	38497	0.001	$\pi_1^*(\text{bpy}) \rightarrow \text{diff}$	0.64
73	38565	0.001	$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$	0.26
			$\sigma(\text{dxy}) \rightarrow \pi_2^*(\text{ppy})$	0.18
74	38746	0.003	$\text{dx}^2\text{-y}^2 \rightarrow \pi_3^*(\text{bpy})$	0.67
75	39082	0.069	$\text{d}_{yz} \rightarrow \pi_2^*(\text{bpy})$	0.36
76	39159	0.040	$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$	0.35
77	39430	0.034	$\sigma(\text{dz}^2) \rightarrow \pi_1^*(\text{ppy})$	0.18
			$\sigma(\text{dxy}) \rightarrow \pi_2^*(\text{ppy})$	0.17
			$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$	0.12
78	39578	0.057	$\text{d}_{yz} \rightarrow \pi_3^*(\text{bpy})$	0.18
			$\text{dxz} \rightarrow \pi_2^*(\text{bpy})$	0.12
			$\pi_3(\text{bpy}) \rightarrow \pi_2^*(\text{ppy})$	0.06
			$\text{d}_{yz} \rightarrow \sigma^*(\text{dz}^2)$	0.06
79	39683	0.038	$\text{d}_{yz} \rightarrow \sigma^*(\text{dz}^2)$	0.12
			$\text{d}_{yz} \rightarrow \pi_3^*(\text{bpy})$	0.11
			$\text{d}_{yz} \rightarrow \sigma^*(\text{dz}^2)$	0.11
			$\text{d}_{yz} \rightarrow \text{diff}$	0.07
			$\text{d}_{yz} \rightarrow \pi_8^*(\text{ppy})$	0.06
80	39958	0.005	$\pi_1(\text{bpy}) + \pi_5(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$	0.25
			$\pi_1(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$	0.23

Table S2. Vertical electronic transitions of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ as predicted by TDDFT (LC-BLYP, $\omega=0.18 \text{ bohr}^{-1}$) in THF (PCM).

State nr.	Energy / cm^{-1}	Osc. str.	Configuration	Weight
1	22230	0.001	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 1^*(\text{bpy})$	0.90
2	25844	0.001	$\text{d}yz \rightarrow \pi 1^*(\text{bpy})$	0.86
3	26032	0.071	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$	0.92
4	26967	0.035	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.58
5	27249	0.092	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.32
6	30107	0.010	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 2^*(\text{bpy})$	0.88
7	31419	0.077	$\text{d}yz \rightarrow \pi 1^*(\text{ppy})$	0.86
8	31644	0.006	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 3^*(\text{bpy})$	0.62
9	32073	0.006	$\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$	0.46
10	32558	0.003	$\text{d}yz \rightarrow \pi 2^*(\text{ppy})$	0.48
11	32699	0.074	$\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.58
12	32827	0.008	$\text{d}xz \rightarrow \pi 1^*(\text{bpy})$	0.30
13	33017	0.031	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 4^*(\text{ppy})$	0.78
14	33318	0.013	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 3^*(\text{ppy})$	0.38
15	33895	0.012	$\text{d}yz \rightarrow \pi 2^*(\text{bpy})$	0.68
16	34446	0.050	$\text{d}xz \rightarrow \pi 1^*(\text{ppy})$ $\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{bpy})$	0.36 0.16
17	34795	0.063	$\pi 5(\text{ppy}) \rightarrow \pi 1^*(\text{bpy})$	0.54
18	34954	0.002	$\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 2^*(\text{bpy})$ $\text{d}xz \rightarrow \pi 2^*(\text{bpy})$	0.28 0.28
19	35278	0.069	$\pi 5(\text{ppy}) \rightarrow \pi 1^*(\text{bpy})$ $\text{d}xz \rightarrow \pi 2^*(\text{ppy})$	0.30 0.20
20	35634	0.005	$\pi 3(\text{ppy}) \rightarrow \pi 1^*(\text{bpy})$	0.48
21	35653	0.130	$\pi 1(\text{bpy}) \rightarrow \pi 1^*(\text{bpy})$ $\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 3^*(\text{bpy})$	0.26 0.22
22	36274	0.038	$\text{d}yz \rightarrow \pi 3^*(\text{bpy})$	0.68
23	36520	0.033	$\pi 3(\text{ppy}) \rightarrow \pi 1^*(\text{ppy})$	0.40
24	36903	0.016	$\pi 3(\text{ppy}) \rightarrow \pi 2^*(\text{ppy})$	0.34
25	37318	0.436	$\pi 1(\text{bpy}) \rightarrow \pi 1^*(\text{bpy})$	0.34
26	38090	0.255	$\text{d}yz \rightarrow \pi 4^*(\text{ppy})$	0.68
27	38150	0.000	$\sigma(\text{d}xy) \rightarrow \pi 1^*(\text{bpy})$	0.58
28	38354	0.014	$\text{d}yz \rightarrow \pi 3^*(\text{ppy})$	0.76
29	38573	0.187	$\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 3^*(\text{ppy})$	0.50
30	38903	0.195	$\text{d}xz+\pi 1(\text{ppy}) \rightarrow \pi 4^*(\text{ppy})$	0.40
31	39055	0.001	$\sigma(\text{d}z^2) \rightarrow \pi 1^*(\text{bpy})$	0.88
32	39574	0.003	$\text{d}xz \rightarrow \pi 2^*(\text{bpy})$	0.34
33	40364	0.001	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \sigma^*(\text{d}z^2)$ $\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi 6^*(\text{ppy})$	0.38 0.14
34	40416	0.062	$\text{d}xz \rightarrow \pi 3^*(\text{ppy})$	0.22

			$\pi_3(\text{ppy}) \rightarrow \pi_2^*(\text{ppy})$	0.20
35	40462	0.012	$\pi_5(\text{ppy}) \rightarrow \pi_2^*(\text{ppy})$ $\pi_3(\text{ppy}) \rightarrow \pi_1^*(\text{ppy})$	0.34 0.16
36	40551	0.065	$\pi_5(\text{ppy}) \rightarrow \pi_1^*(\text{ppy})$ $\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_5^*(\text{ppy})$	0.26 0.22
37	40751	0.145	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_5^*(\text{ppy})$ $\pi_5(\text{ppy}) \rightarrow \pi_2^*(\text{bpy})$	0.32 0.20
38	41685	0.007	$\pi_3(\text{ppy}) \rightarrow \pi_2^*(\text{bpy})$ $\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$ $\pi_5(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$	0.18 0.18 0.14
39	41821	0.002	$\text{dxz} \rightarrow \pi_4^*(\text{ppy})$ $\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$	0.26 0.20
40	41946	0.047	$\text{dxz} \rightarrow \pi_3^*(\text{bpy})$	0.30
41	41982	0.002	$\sigma(\text{dxy}) \rightarrow \pi_1^*(\text{ppy})$ $\pi_3(\text{ppy}) \rightarrow \pi_2^*(\text{bpy})$	0.26 0.22
42	42118	0.001	$\sigma(\text{dz}^2) \rightarrow \pi_1^*(\text{ppy})$	0.42
43	42617	0.053	$\pi_5(\text{ppy}) \rightarrow \pi_2^*(\text{bpy})$ $\pi_1(\text{bpy}) \rightarrow \pi_2^*(\text{bpy})$ $\text{dxz} \rightarrow \pi_3^*(\text{ppy})$	0.20 0.18 0.08
44	42726	0.007	$\pi_1(\text{bpy}) \rightarrow \pi_3^*(\text{bpy})$ $\pi_2(\text{bpy})+\pi(\text{ppy}) \rightarrow \pi_1^*(\text{bpy})$ $\pi_3(\text{ppy}) \rightarrow \pi_4^*(\text{ppy})$	0.32 0.08 0.08
45	43063	0.037	$\pi_1(\text{bpy}) \rightarrow \pi_2^*(\text{bpy})$ $\pi_5(\text{ppy}) \rightarrow \pi_2^*(\text{bpy})$	0.42 0.08
46	43294	0.000	$\text{dyz} \rightarrow \sigma^*(\text{dz}^2)$	0.44
47	43490	0.112	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_4^*(\text{bpy})$ $\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_6^*(\text{ppy})$	0.30 0.10
48	43510	0.006	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_4^*(\text{bpy})$ $\pi_3(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$ $\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_1^*(\text{bpy})$	0.14 0.12 0.08
49	43529	0.005	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_4^*(\text{bpy})$ $\pi_3(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$ $\pi_1(\text{bpy}) \rightarrow \pi_3^*(\text{bpy})$ $\pi_3(\text{ppy}) \rightarrow \pi_4^*(\text{ppy})$	0.20 0.08 0.06 0.06
50	43593	0.004	$\text{dxz}+\pi_1(\text{ppy}) \rightarrow \sigma^*(\text{dz}^2)$ $\text{dxz} \rightarrow \sigma^*(\text{dz}^2)$ $\text{dxz}+\pi_1(\text{ppy}) \rightarrow \pi_6^*(\text{ppy})$	0.20 0.18 0.14
51	44068	0.007	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \pi_1^*(\text{bpy})$	0.50
52	44550	0.041	$\text{dx}^2\text{-y}^2+\pi(\text{ppy}) \rightarrow \sigma^*(\text{dxy})$ $\sigma(\text{dz}^2) \rightarrow \pi_1^*(\text{ppy})$ $\pi_3(\text{ppy}) \rightarrow \pi_3^*(\text{ppy})$	0.16 0.14 0.14
53	44750	0.085	$\sigma(\text{dz}^2) \rightarrow \pi_2^*(\text{ppy})$ $\sigma(\text{dxy}) \rightarrow \pi_2^*(\text{ppy})$ $\sigma(\text{dz}^2) \rightarrow \pi_1^*(\text{ppy})$	0.22 0.16 0.12

54	44762	0.083	$\sigma(dz_2) \rightarrow \pi_2^*(ppy)$ $\sigma(dxy) \rightarrow \pi_2^*(ppy)$ $\sigma(dz_2) \rightarrow \pi_1^*(ppy)$	0.20 0.16 0.12
55	44846	0.020	$dx_2-y_2+\pi(ppy) \rightarrow \pi_6^*(ppy)$ $\sigma(dz_2) \rightarrow \pi_2^*(ppy)$	0.28 0.20
56	45098	0.000	$\pi_5(ppy) \rightarrow \pi_3^*(bpy)$	0.38
57	45321	0.010	$dyz \rightarrow \pi_5^*(ppy)$	0.66
58	45685	0.006	$\pi_3(ppy) \rightarrow \pi_3^*(bpy)$ $\sigma(dxy) \rightarrow \pi_3^*(bpy)$ $\pi_5(ppy) \rightarrow \pi_3^*(ppy)$ $\sigma(dxy) \rightarrow \pi_2^*(bpy)$	0.16 0.12 0.08 0.08
59	45687	0.004	$\pi_5(ppy) \rightarrow \pi_3^*(ppy)$ $\sigma(dxy) \rightarrow \pi_2^*(bpy)$ $\pi_3(ppy) \rightarrow \pi_2^*(bpy)$	0.14 0.12 0.10
60	46088	0.002	$dxz+\pi_1(ppy) \rightarrow \pi_5^*(ppy)$	0.44
61	46219	0.014	$\sigma(dxy) \rightarrow \pi_3^*(bpy)$ $\pi_5(ppy) \rightarrow \pi_4^*(ppy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_1^*(ppy)$	0.18 0.16 0.08
62	46561	0.001	$\sigma(dz_2) \rightarrow \pi_2^*(bpy)$	0.52
63	46758	0.003	$\pi_3(ppy) \rightarrow \pi_4^*(ppy)$ $dxz \rightarrow \pi_5^*(ppy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_7^*(ppy)$	0.24 0.10 0.06
64	46794	0.004	$\pi_3(ppy) \rightarrow \pi_3^*(ppy)$ $\sigma(dz_2) \rightarrow \pi_2^*(bpy)$	0.22 0.22
65	46883	0.006	$\pi_1(bpy) \rightarrow \pi_1^*(ppy)$	0.86
66	46936	0.014	$\pi_3(ppy) \rightarrow \pi_4^*(ppy)$ $\pi_5(ppy) \rightarrow \pi_3^*(ppy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_7^*(ppy)$	0.16 0.14 0.10
67	47264	0.010	$dyz \rightarrow \pi_4^*(bpy)$	0.58
68	47391	0.004	$dxz+\pi_1(ppy) \rightarrow \pi_4^*(bpy)$	0.36
69	47474	0.013	$\pi_6(ppy) \rightarrow \pi_1^*(bpy)$ $\sigma(dxy) \rightarrow \pi_3^*(bpy)$	0.26 0.22
70	47584	0.002	$\pi_1(bpy) \rightarrow \pi_2^*(ppy)$	0.64
71	47674	0.014	$\pi_6(ppy) \rightarrow \pi_1^*(bpy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_1^*(ppy)$ $\pi_7(ppy) \rightarrow \pi_2^*(ppy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_2^*(bpy)$ $\sigma(dxy) \rightarrow \pi_3^*(bpy)$	0.16 0.12 0.06 0.06 0.06
72	47765	0.028	$\pi_7(ppy) \rightarrow \pi_1^*(bpy)$	0.26
73	47841	0.019	$\pi_6(ppy) \rightarrow \pi_1^*(bpy)$ $dx_2-y_2+\pi(ppy) \rightarrow \pi_1^*(ppy)$	0.22 0.14
74	47866	0.027	$dyz \rightarrow \pi_6^*(ppy)$	0.44
75	48104	0.004	$\pi_7(ppy) \rightarrow \pi_1^*(bpy)$ $dyz \rightarrow \pi_6^*(ppy)$	0.28 0.16

76	48422	0.026	$\sigma(dz^2) \rightarrow \pi 3^*(bpy)$	0.58
77	48597	0.160	$\pi 2(bpy) + \pi(\rho\rho y) \rightarrow \pi 1^*(bpy)$ $\pi 2(bpy) \rightarrow \pi 1^*(bpy)$	0.30 0.2
78	48668	0.017	$\pi 6(\rho\rho y) \rightarrow \pi 1^*(\rho\rho y)$ $\pi 7(\rho\rho y) \rightarrow \pi 2^*(\rho\rho y)$	0.26 0.14
79	48889	0.002	$\sigma(dxy) \rightarrow \pi 4^*(\rho\rho y)$ $\sigma(dz^2) \rightarrow \pi 3^*(bpy)$	0.30 0.14
80	48903	0.004	$\pi 3(bpy) \rightarrow \pi 1^*(bpy)$ $\pi 6(\rho\rho y) \rightarrow \pi 1^*(bpy)$	0.32 0.12