SUPPLEMENTARY MATERIAL (ESI)

COMPUTATIONAL AND EXPERIMENTAL STUDY ON THE ELECTRONIC STRUCTURE OF A HOMOLOGOUS SERIES OF CYCLOPALLADATED AND CYCLOPLATINATED COMPLEXES

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Synthesis and characterisation

All commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification.

IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped for reflectance measurements.

^{1}H-NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ solutions, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer CHNS/O.

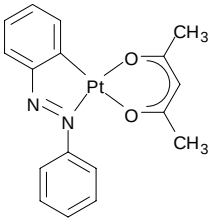
UV-Vis absorption spectra were obtained with a Perkin-Elmer lambda 900 UV/vis spectrometer. Luminescence spectra and lifetimes of the complexes at 77 K were obtained with a Perkin-Elmer LS 50B luminescence spectrometer, equipped with a Hamamatsu R-928 photomultiplier tube. The samples were placed within capillary tubes immersed in liquid nitrogen and the experiments were performed by applying both a temporal delay and gating in order to exclude fast scattering from the apparatus; the excitation source was set at 337 nm in all cases.

Cyclic voltammetric data were measured with IR compensation using an Epsilon electrochemical analyser. The experiments were carried out with 3mL of a *ca*. 10^{-3} M solution of compound at a scan rate of 100 mVs^{-1}. Potentials were measured using a glassy carbon working electrode, a platinum wire as counter electrode and a Ag wire as pseudoreference electrode. Potentials were finally corrected versus ferrocene/ferrocenium$^+$ by adding ferrocene as an internal standard to the studied solution after the experiment. Oxidations and reductions of the complexes were observed in

dry N,N'-dimethylformamide using tetra(*n*-butyl)ammonium hexafluorophosphate (0.1M) as supporting electrolyte, and under nitrogen atmosphere.

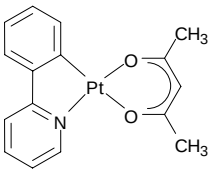
Synthesis

Preparation of (Azo)Pt(acac), ***2a****.*



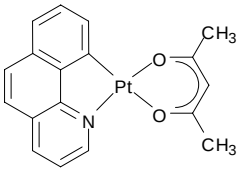
A suspension of thallium-acetylacetonate (0.27 mmol, 0.08 g) in dichloromethane (5 mL) was added to a suspension of the dinuclear chloro-bridged Pt(II) complex (0.13 mmol, 0.11 g,) dissolved in dichloromethane (15 mL). The resulting mixture was stirred for 180 h at room temperature. The reaction was monitored by TLC and, after completion, the reaction mixture was filtered on celite and the solvent was removed under reduced pressure. Recrystallization of the crude product from chloroform/methanol solution afforded **2a** as brown crystalline solid. Yield 70% (0.09 g). Mp. 270 °C. Anal. Calcd. for $C_{17}H_{16}N_2O_2Pt$ (%): C, 42.91; N, 5.89; H, 3.39. Found (%): C, 42.63; N, 5.26; H, 3.84. IR (KBr, cm^{-1}): 3050, 1620, 1572, 1520, 1403, 1350, 1270, 1200, 1150, 1100. ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 8.02 (d, *J* = 7.74 Hz, 1H), 7.92 (d, *J* = 6.38 Hz, 2H), 7.70 (d, *J* = 7.74 Hz, $J(^{195}Pt\text{-}H)$ = 38 Hz, 1H), 7.59-7.48 (m, 3H), 7.38-7.34 (m, 1H), 7.22-7.17 (m, 1H), 5.50 (s, 1H), 2.08 (s, 3H), 1.96 (s, 3H).

Preparation of (PhPy)Pt(acac), ***2b****.*



Yellow crystalline solid. Yield 60% (0.11 g). Mp. 277 °C. Anal. Calcd. for $C_{16}H_{15}NO_2Pt$ (%): C, 42.86; N, 3.12; H, 3.37. Found (%): C, 42.80; N, 3.33; H, 3.32. IR (KBr, cm^{-1}): 3105, 3037, 1609, 1560, 1485, 1421, 1392, 1270, 1160, 1026, 940, 760, 626. ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 9.00 (d, *J* = 5.86 Hz, $J(^{195}Pt\text{-}H)$ = 26.55 Hz, 1H), 7.87-7.81 (m, 1H), 7.78-7.62 (m, 2H), 7.43 (d, *J* = 7.48 Hz, 1H), 7.08-6.90 (m, 3H), 5.49 (s, 1H), 2.09 (s, 3H), 2.06 (s, 3H).

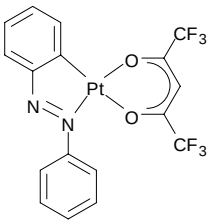
Preparation of (BzQ)Pt(acac), ***2c****.*



Yellow crystalline solid. Yield 52% (0.09 g). Mp. 280 °C. Anal. Calcd. for $C_{18}H_{15}NO_2Pt$ (%): C, 45.60; N, 2.93; H, 3.11. Found (%): C, 46.63; N, 3.03; H, 3.20. IR (KBr, cm^{-1}): 3035, 1514, 1498, 1332, 1272, 1202, 1030, 938, 832, 786,

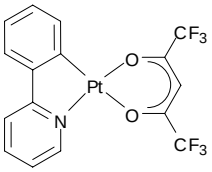
714, 635. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 9.14 (d with broad ^{195}Pt satellites, *J* = 5.29 Hz, 1H), 8.25 (d, *J* = 8.33 Hz, 1H), 7.78-7.70 (m, 2H), 7.63-7.52(m, 3H), 7.44 (d, *J* = 5.44 Hz, 1H), 5.53 (s, 1H), 2.04 (s, 6H).

Preparation of (Azo)Pt(hfacac), ***2d****.*



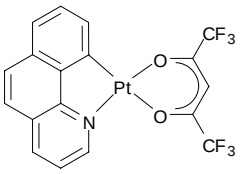
Orange crystalline solid. Yield 62% (0.08 g). Mp. 180 °C. Anal. Calcd. for $C_{17}H_{10}N_2O_4F_6Pt$ (%): C, 35.01; N, 4.80; H, 1.73. Found (%): C, 35.16; N, 4.54; H, 1.76. IR (KBr, cm^{-1}): 3061, 1620, 1556, 1468, 1350, 1210, 1142, 1110, 908, 838, 650. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 7.99 (d, *J* = 7.69 Hz, 1H), 7.81-7.78 (m, 2H), 7.51-7.48 (m, 3H), 7.41 (d, *J* = 7.77 Hz, 1H), 7.35-7.23 (m, 2H), 6.28 (s, 1H).

Preparation of (PhPy)Pt(hfacac), ***2e****.*



Orange solid. Yield 80% (0.20 g). Mp. 220 °C. Anal. Calcd. for $C_{16}H_9F_6NO_2Pt$ (%): C, 34.54; N, 2.56; H, 1.63. Found (%): C, 34.20; N, 2.66; H, 1.53. IR (KBr, cm^{-1}): 3134, 3059, 1645,1587, 1490, 1473, 1348, 1273, 1200, 1142, 1070, 1033, 759, 695. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 8.59 (d with broad ^{195}Pt satellites, *J* = 5.23 Hz, 1H), 7.84 (t, *J* = 3.09, 6.61 Hz, 1H), 7.60 (d, *J* = 7.86 Hz, 1H), 7.34 (d, *J* = 5.73 Hz, 1H), 7.28-7.10 (m, 1H), 7.15-6.89 (m, 3H), 6.02 (s, 1H).

Preparation of (BzQ)Pt(hfacac), ***2d****.*



Yellow solid. Yield 60% (0.20 g). Mp. 280 °C. Anal. Calcd. for $C_{18}H_9F_6NO_2F_6Pt$ (%): C, 37.26; N, 2.41; H, 1.55. Found (%): C, 37.36; N, 2.21; H, 1.85. IR (KBr, cm^{-1}): 3212, 3053, 1626,1547, 1473, 1456, 1410, 1345, 1270, 1090, 947, 825, 710. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, TMS), ppm: 8.51 (d with broad ^{195}Pt satellites, *J* = 5.00 Hz, 1H), 8.20 (d, *J* = 8.01 Hz, 1H), 7.67 (d, *J* = 8.00 Hz, 1H), 7.51-7.37 (m, 3H), 7.32-7.20 (m, 2H), 6.24 (s, 1H).

Table S1. Photophysical data of the cyclometallated ligands in various solvents. For each solvent the polarity parameter E_T is also indicated. Asterisks indicate shoulders or weak bands.

Ligand	Solvent	E_T	λ_{abs}/nm
azobenzene	Cyclohexane	0.006	319, 338*, 346*, 450
	Dichloromethane	0.309	320, 332*, 450
	Dimethylformamide	0.404	320, 345*, 450
	Methanol	0.762	282*, 317, 329*, 346*, 443
2-phenylpyridine	Cyclohexane	0.006	249, 257*, 275, 286*, 297
	Dichloromethane	0.309	247, 276, 298*
	Dimethylformamide	0.404	390*
	Methanol	0.762	244, 276, 296*
benzo[h]quinoline	Cyclohexane	0.006	248*, 259*, 265, 269, 278*, 295, 315, 321, 330, 338, 345
	Dichloromethane	0.309	243*, 259*, 266, 282*, 295*, 314, 330, 346
	Dimethylformamide	0.404	292*, 316, 330, 345
	Methanol	0.762	233*, 264, 282*, 331, 345

Table S2. Photophysical data of the complexes in various solvents. For each solvent the polarity parameter E_T is also indicated. Asterisks indicate shoulders or weak bands.

Complex	Solvent	E_T	λ_{abs}/nm
1a	Cyclohexane	0.006	310, 353, 412, 456, 494*
	Dimethylformamide	0.404	311, 355, 409*, 452*, 490
	Methanol	0.762	245*, 310, 352, 407*, 455*, 485*
1b	Cyclohexane	0.006	263, 267*, 308*, 321, 357, 377
	Dimethylformamide	0.404	310*, 315, 348*, 388*
	Methanol	0.762	258, 263*, 312, 369
1c	Cyclohexane	0.006	245 266*, 301, 325*, 340*, 385, 406
	Dimethylformamide	0.404	296, 317*, 369*, 391, 405*
	Methanol	0.762	240, 245, 296, 321, 386, 400*
1d	Cyclohexane	0.006	292*, 330, 368*, 385*, 449, 478*
	Dimethylformamide	0.404	306, 317, 364*, 387*, 450, 491*
	Methanol	0.762	241, 283*, 304*, 315, 364*, 465
1e	Cyclohexane	0.006	266, 308*, 318*, 348*, 369
	Dimethylformamide	0.404	306, 317*, 348*, 360*
	Methanol	0.762	258, 309, 358*
1f	Cyclohexane	0.006	250*, 274, 293, 316*, 338*, 377, 400
	Dimethylformamide	0.404	292, 304*, 319*, 366, 385
	Methanol	0.762	234, 275*, 292, 308*, 393*
2a	Cyclohexane	0.006	251, 298, 350, 396*, 438*, 458, 540
	Dimethylformamide	0.404	298, 354, 398*, 434*, 452, 527
	Methanol	0.762	251, 261*, 306, 353, 393*, 451, 534
2b	Cyclohexane	0.006	253, 269, 278*, 304*, 316*, 329, 349*, 376, 399*
	Dimethylformamide	0.404	312, 325*, 362, 395*
	Methanol	0.762	245, 274, 310, 324*, 359, 390*
2c	Cyclohexane	0.006	250, 281, 303*, 322, 343*, 384, 417*, 438
	Dimethylformamide	0.404	280*, 295*, 318, 336, 368*, 379*, 416, 432*
	Methanol	0.762	243, 275*, 305*, 320, 371, 411*, 431
2d	Cyclohexane	0.006	246, 283, 335*, 347*, 364, 385, 435, 497*, 526*
	Dimethylformamide	0.404	304, 316*, 359, 387*, 431*, 513
	Methanol	0.762	251*, 262*, 304, 315*, 355, 380*, 467*, 530*
2e	Cyclohexane	0.006	253, 267, 279*, 306*, 319, 329, 374, 405*
	Dimethylformamide	0.404	296*, 305, 320*, 363*, 390*
	Methanol	0.762	238, 248, 264*, 305*, 322*, 364, 387*
2f	Cyclohexane	0.006	245, 272, 296, 310, 331*, 356*, 391, 413*
	Dimethylformamide	0.404	293*, 302, 318*, 379, 411
	Methanol	0.762	239, 248*, 265*, 298, 322*, 377*, 384, 408*

Computational Results

In this section, a detailed presentation of the computational results is reported for all the studied compounds. All the computations have been performed at the MPW1PW91/SDD level of approximation as described in the manuscript text.

(Azo)Pd(acac) (1a)

Table S3. Singlet excited states of (Azo)Pd(acac) (**1a**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.6400 eV 469.64 nm f=0.0012
81 -> 84 93.14 %

Excited State: 2
2.6922 eV 460.53 nm f=0.0906
77 -> 84 2.15 %
80 -> 84 9.42 %
81 -> 86 2.40 %
82 -> 84 3.21 %
83 -> 84 73.46 %

Excited State: 3
3.0066 eV 412.38 nm f=0.0610
77 -> 84 2.01 %
80 -> 84 5.28 %
82 -> 84 74.68 %
83 -> 84 9.79 %

Excited State: 4
3.3279 eV 372.55 nm f=0.0010
75 -> 84 15.60 %
76 -> 84 3.42 %
79 -> 84 71.09 %
81 -> 84 2.46 %

Excited State: 5
3.5180 eV 352.43 nm f=0.2905
80 -> 84 73.78 %
81 -> 86 3.11 %
82 -> 84 5.03 %
83 -> 84 3.54 %

Excited State: 6
3.6585 eV 338.89 nm f=0.0007
75 -> 84 9.31 %
76 -> 84 65.57 %
79 -> 84 13.10 %

Excited State: 7
3.7269 eV 332.67 nm f=0.0788
78 -> 84 5.26 %
81 -> 86 68.58 %
82 -> 84 2.34 %

Excited State: 8
3.7825 eV 327.78 nm f=0.0319
78 -> 84 87.50 %
81 -> 86 3.57 %

Excited State: 9
3.7985 eV 326.40 nm f=0.0000
73 -> 86 6.30 %
75 -> 84 4.84 %
77 -> 86 2.37 %
79 -> 84 5.12 %
80 -> 86 10.11 %
83 -> 86 62.88 %

Excited State: 10
3.9529 eV 313.66 nm f=0.0506
77 -> 84 82.90 %
80 -> 84 2.23 %
82 -> 84 2.12 %
82 -> 85 2.31 %

Excited State: 11
3.9582 eV 313.23 nm f=0.0002
74 -> 86 3.36 %
75 -> 84 8.05 %
77 -> 86 13.49 %
80 -> 86 2.00 %
82 -> 86 54.39 %
83 -> 86 6.01 %

Excited State: 12
4.1082 eV 301.79 nm f=0.0002
75 -> 84 37.06 %
76 -> 84 14.83 %
79 -> 84 3.42 %
81 -> 85 30.06 %
82 -> 86 6.26 %

Excited State: 13
4.1213 eV 300.83 nm f=0.0000
75 -> 84 17.91 %
76 -> 84 6.91 %
81 -> 85 65.07 %

Excited State: 14
4.2011 eV 295.12 nm f=0.0326
80 -> 85 2.91 %
83 -> 85 84.61 %

Excited State: 15
4.2365 eV 292.65 nm f=0.0143
71 -> 86 3.24 %
72 -> 86 3.00 %
75 -> 86 13.62 %
76 -> 86 41.67 %
79 -> 86 29.46 %

Excited State: 16
4.4183 eV 280.61 nm f=0.0004
75 -> 85 4.76 %
79 -> 85 88.66 %

Excited State: 17
4.4339 eV 279.63 nm f=0.0620
73 -> 84 7.04 %
77 -> 85 3.39 %
82 -> 85 76.01 %

Excited State: 18
4.5271 eV 273.87 nm f=0.0048
73 -> 84 71.95 %
74 -> 84 10.27 %
82 -> 85 5.12 %
83 -> 85 2.01 %

81 -> 85 2.06 %

Excited State: 19
4.6893 eV 264.39 nm f=0.0016
73 -> 84 10.16 %
74 -> 84 70.38 %
83 -> 89 3.29 %

Excited State: 20
4.9381 eV 251.08 nm f=0.0001
73 -> 86 4.85 %
77 -> 86 2.24 %
80 -> 86 59.98 %
82 -> 86 11.03 %
83 -> 86 16.84 %

Excited State: 21
4.9515 eV 250.39 nm f=0.0424
80 -> 85 87.66 %

Excited State: 22
5.0284 eV 246.57 nm f=0.0002
75 -> 85 10.03 %
76 -> 85 81.11 %

Excited State: 23
5.0751 eV 244.30 nm f=0.0001
71 -> 84 2.23 %
72 -> 84 86.57 %
77 -> 86 2.13 %
82 -> 86 3.75 %

Excited State: 24
5.1894 eV 238.92 nm f=0.0001
72 -> 84 4.30 %
74 -> 86 7.27 %
77 -> 86 53.73 %
80 -> 86 10.37 %
82 -> 86 15.96 %

Excited State: 25
5.3645 eV 231.12 nm f=0.0621
77 -> 85 24.25 %
78 -> 85 2.89 %
82 -> 87 6.29 %
82 -> 88 3.28 %
83 -> 87 46.61 %
83 -> 89 2.03 %

Figure S1. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

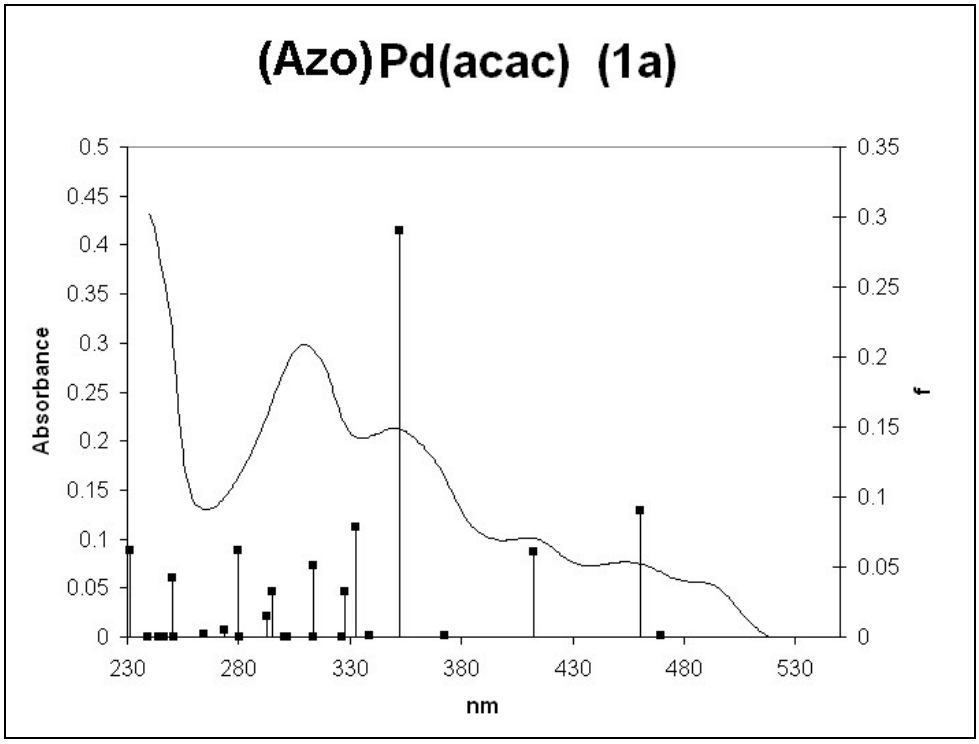


Figure S2. In the following picture, some Kohn-Sham orbitals of (Azo)Pd(acac) (**1a**) are reported that are relevant in describing the low-energy electronic transitions toward S_2, S_3, S_5 and S_7.

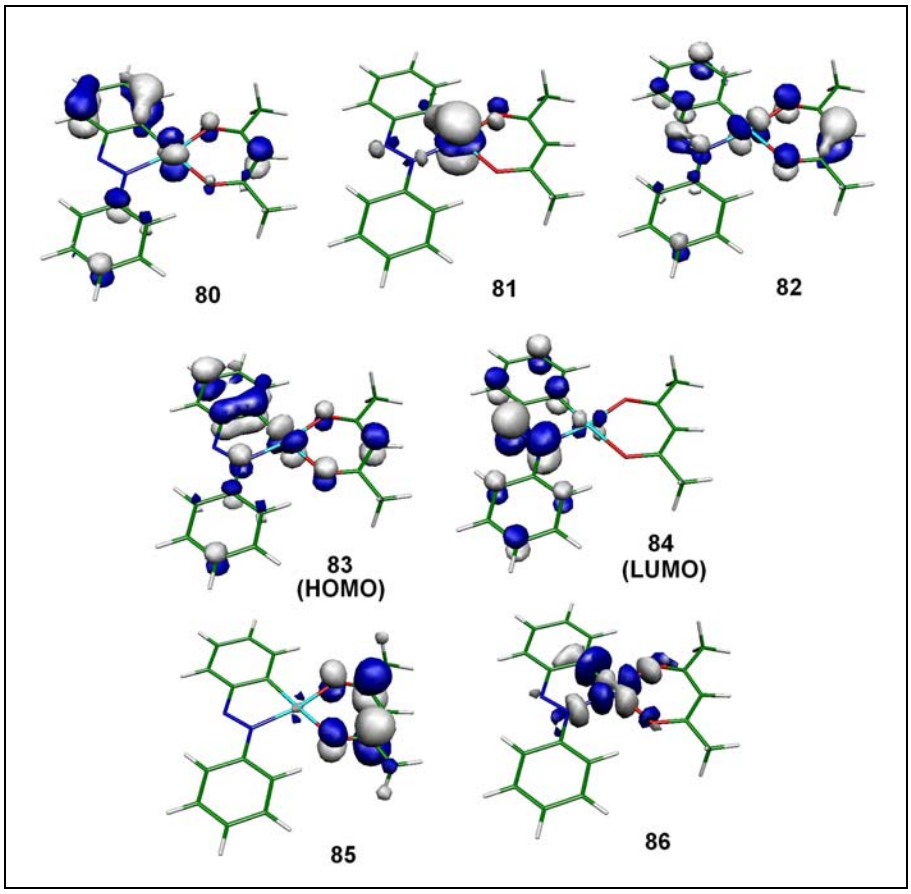


Table S4. Optimized structure of (Azo)Pd(acac) (**1a**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pd	0.54018	-0.08516	-0.00000	H	-1.82096	-1.80408	0.00001
N	-1.32971	0.80595	0.00000	H	-4.05357	-2.89477	0.00001
N	-1.34439	2.10212	0.00001	H	-6.12682	-1.51160	-0.00001
C	-0.08102	2.67833	0.00001	H	-5.94762	0.97639	-0.00002
C	1.04022	1.80684	0.00000	H	-3.70887	2.06243	-0.00002
C	2.31731	2.37715	-0.00000	O	0.08482	-2.14130	0.00000
C	2.45967	3.77651	0.00000	C	0.92619	-3.12914	0.00000
C	1.33584	4.62857	0.00001	C	2.33022	-2.99564	0.00000
C	0.05212	4.08040	0.00001	C	3.03044	-1.77687	-0.00000
C	-2.62879	0.19484	0.00000	O	2.49689	-0.58714	-0.00001
C	-3.79909	0.98472	-0.00001	H	2.91707	-3.90427	0.00000
C	-5.05003	0.36705	-0.00001	C	0.30844	-4.50689	0.00001
C	-5.15179	-1.03579	-0.00001	C	4.53945	-1.77821	-0.00001
C	-3.98570	-1.81200	0.00000	H	1.06000	-5.29768	0.00001
C	-2.72316	-1.20501	0.00001	H	-0.33040	-4.62040	0.88190
H	3.18783	1.73132	-0.00001	H	-0.33041	-4.62041	-0.88187
H	3.45574	4.20947	-0.00000	H	4.94943	-2.78909	-0.00001
H	1.47014	5.70451	0.00001	H	4.90509	-1.24189	-0.88143
H	-0.83693	4.70128	0.00002	H	4.90510	-1.24189	0.88140

(Azo)Pt(acac) (2a)

Table S5. Singlet excited states of (Azo)Pt(acac) (**2a**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.5196 eV 492.08 nm f=0.0464
80 -> 84 4.44 %
83 -> 84 82.55 %

Excited State: 2
2.8076 eV 441.60 nm f=0.0035
81 -> 84 94.16 %

Excited State: 3
3.1366 eV 395.28 nm f=0.1360
80 -> 84 2.85 %
82 -> 84 79.72 %
83 -> 84 3.08 %

Excited State: 4
3.4475 eV 359.63 nm f=0.0037
74 -> 84 3.88 %
77 -> 84 2.86 %
78 -> 84 51.19 %
79 -> 84 37.29 %

Excited State: 5
3.6407 eV 340.55 nm f=0.2570
74 -> 84 3.08 %
76 -> 84 6.35 %
79 -> 84 2.54 %
80 -> 84 71.40 %
82 -> 84 2.45 %

Excited State: 6
3.6579 eV 338.95 nm f=0.0452
74 -> 84 18.73 %
76 -> 84 38.29 %
77 -> 84 2.84 %
78 -> 84 3.85 %
79 -> 84 14.37 %
80 -> 84 10.18 %

Excited State: 7
3.8902 eV 318.71 nm f=0.0045
76 -> 84 19.87 %
78 -> 84 32.05 %
79 -> 84 39.79 %

Excited State: 8
3.8994 eV 317.96 nm f=0.0588
82 -> 85 2.19 %
83 -> 85 89.79 %

Excited State: 9
4.0161 eV 308.71 nm f=0.0256
76 -> 84 3.36 %
77 -> 84 64.51 %
80 -> 84 2.11 %
82 -> 85 17.10 %

Excited State: 10
4.0659 eV 304.93 nm f=0.0002
81 -> 85 96.15 %

Excited State: 11
4.1850 eV 296.25 nm f=0.0744
74 -> 84 3.18 %
77 -> 84 15.14 %
82 -> 85 62.69 %
83 -> 85 3.38 %

Excited State: 12
4.2371 eV 292.62 nm f=0.0123
74 -> 84 56.89 %
76 -> 84 23.48 %
78 -> 84 6.78 %
82 -> 85 2.24 %

Excited State: 13
4.4210 eV 280.44 nm f=0.0005
74 -> 85 3.32 %
77 -> 85 5.68 %
78 -> 85 32.32 %
79 -> 85 48.93 %

Excited State: 14
4.6015 eV 269.44 nm f=0.0095
73 -> 84 20.19 %
74 -> 84 2.36 %
75 -> 84 7.61 %
83 -> 86 2.58 %
83 -> 87 22.24 %
83 -> 88 10.51 %
83 -> 90 16.58 %

Excited State: 15
4.6569 eV 266.24 nm f=0.0029
73 -> 84 53.10 %
81 -> 90 2.38 %
83 -> 87 10.56 %
83 -> 88 3.70 %
83 -> 90 9.75 %

Excited State: 16
4.7159 eV 262.90 nm f=0.0056
73 -> 84 8.59 %
75 -> 84 66.10 %
80 -> 85 3.22 %
83 -> 90 4.78 %

Excited State: 17
4.7812 eV 259.32 nm f=0.0269
74 -> 85 2.10 %
75 -> 84 2.08 %
76 -> 85 30.39 %
78 -> 85 2.89 %
80 -> 85 6.37 %
81 -> 87 14.22 %
81 -> 88 6.49 %
81 -> 90 16.42 %
82 -> 87 2.85 %

Excited State: 18
4.7885 eV 258.92 nm f=0.0180
74 -> 85 2.47 %
75 -> 84 3.86 %
76 -> 85 47.35 %
78 -> 85 2.66 %
80 -> 85 5.09 %
81 -> 87 9.53 %
81 -> 88 4.22 %
81 -> 90 10.81 %

Excited State: 19
4.8890 eV 253.60 nm f=0.0321
80 -> 85 64.29 %
81 -> 87 2.43 %
81 -> 90 2.42 %
82 -> 87 6.25 %
82 -> 90 3.80 %

Excited State: 20
4.9162 eV 252.19 nm f=0.0049
80 -> 85 8.61 %
81 -> 87 2.32 %
81 -> 90 2.70 %
82 -> 86 2.95 %
82 -> 87 26.92 %
82 -> 88 9.01 %
82 -> 90 22.98 %

Excited State: 21
5.1804 eV 239.33 nm f=0.0191
76 -> 87 5.51 %
76 -> 88 3.00 %
76 -> 90 9.12 %
77 -> 85 3.63 %
78 -> 87 12.60 %
78 -> 88 5.83 %
78 -> 90 15.70 %
79 -> 87 9.49 %
79 -> 88 4.53 %
79 -> 90 12.94 %

Excited State: 22
5.2354 eV 236.82 nm f=0.0076
78 -> 85 23.43 %
79 -> 85 17.42 %
82 -> 86 2.72 %
83 -> 86 40.03 %
83 -> 87 7.15 %

Excited State: 23
5.2478 eV 236.26 nm f=0.0381
76 -> 85 2.24 %
77 -> 85 8.46 %
78 -> 85 25.50 %
79 -> 85 11.04 %
79 -> 87 2.11 %
83 -> 86 30.10 %
83 -> 88 6.19 %

Excited State: 24
5.2968 eV 234.07 nm f=0.0496
77 -> 85 21.95 %
78 -> 85 6.84 %
79 -> 85 12.48 %
82 -> 87 4.08 %
83 -> 86 3.67 %
83 -> 87 17.89 %
83 -> 88 17.35 %

Excited State: 25
5.3733 eV 230.74 nm f=0.0054
72 -> 84 87.56 %
77 -> 85 2.66 %
82 -> 87 2.10 %

Figure S3. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

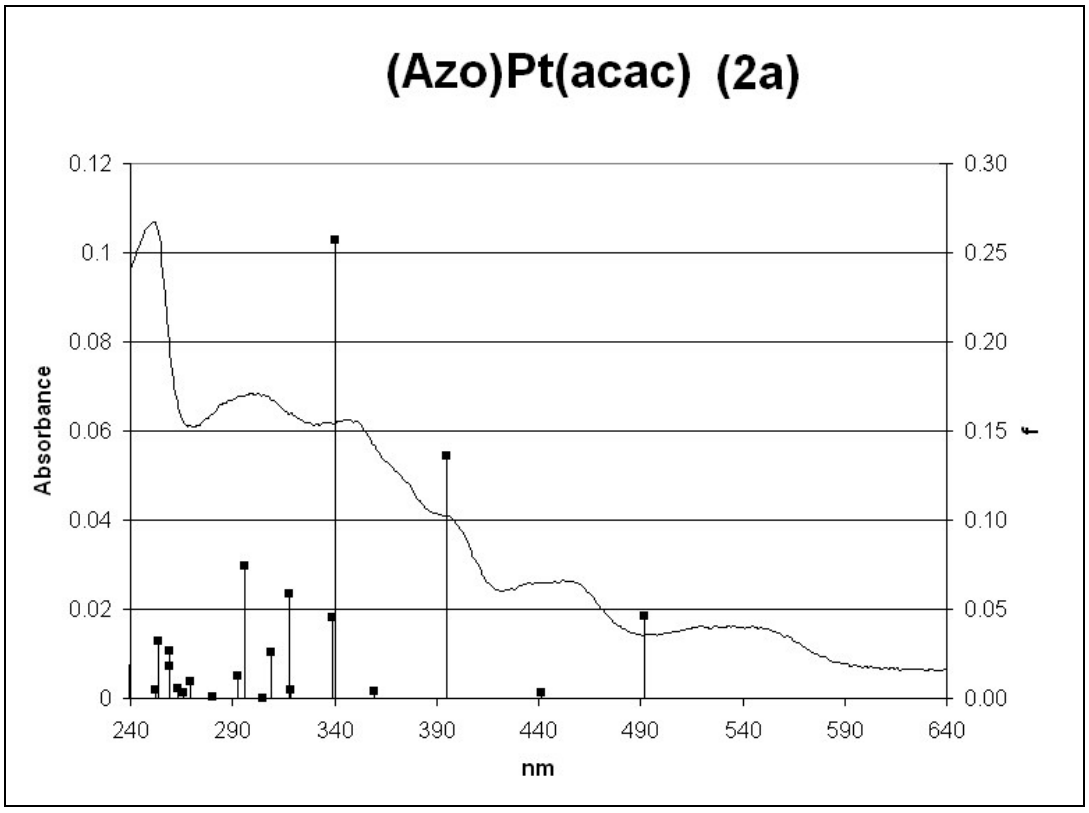


Figure S4. In the following picture, some (Azo)Pt(acac) (**2a**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_2, S_3, and S_5.

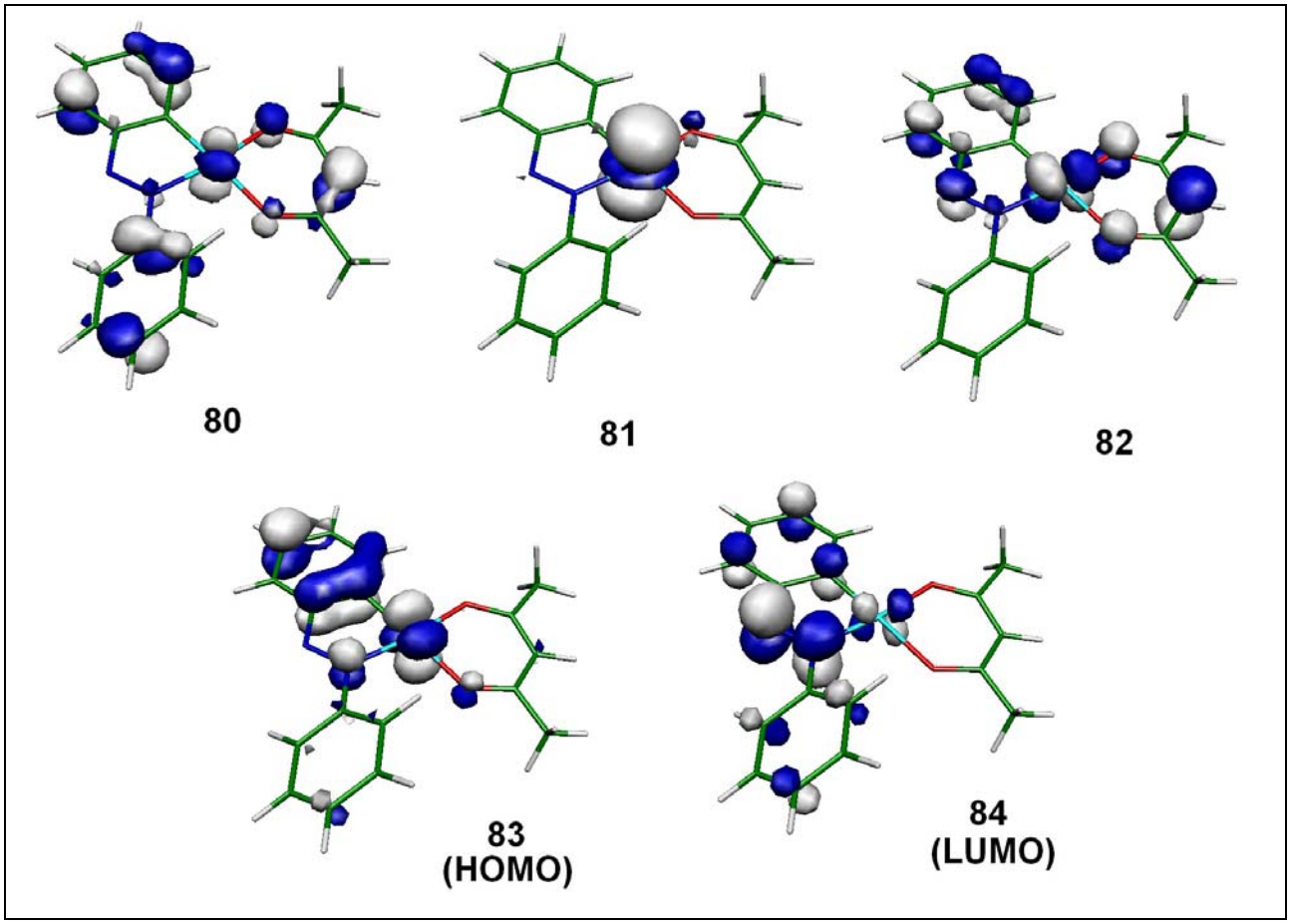


Table S6. Optimized structure of (Azo)Pt(acac) (**2a**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pt	0.46087	-0.13154	0.04352	H	-2.16250	-1.11081	1.20514
N	-1.15934	1.06480	0.04614	H	-4.55475	-1.79449	1.24376
N	-0.97631	2.35283	-0.00129	H	-6.26151	-0.43288	0.04429
C	0.36890	2.70624	0.00692	H	-5.56651	1.62974	-1.17181
C	1.31442	1.64241	0.05449	H	-3.17150	2.32819	-1.16593
C	2.67491	1.98402	0.07554	O	-0.48287	-2.01184	-0.04020
C	3.06098	3.33395	0.05525	C	0.09844	-3.16930	-0.13966
C	2.10610	4.37369	0.00950	C	1.49521	-3.37364	-0.17184
C	0.74676	4.06289	-0.01548	C	2.47099	-2.36776	-0.09900
C	-2.53129	0.65112	0.02413	O	2.24187	-1.08260	-0.00203
C	-3.48893	1.43049	-0.65066	H	1.84471	-4.39381	-0.25718
C	-4.82886	1.03463	-0.64426	C	-0.83473	-4.35179	-0.21201
C	-5.22009	-0.12899	0.03917	C	3.93439	-2.72433	-0.13059
C	-4.25836	-0.89723	0.71123	H	-0.30563	-5.28327	-0.41849
C	-2.91151	-0.51626	0.70146	H	-1.37090	-4.45320	0.73790
H	3.42132	1.19827	0.10721	H	-1.58405	-4.17739	-0.98944
H	4.11747	3.58530	0.07542	H	4.09188	-3.80030	-0.21546
H	2.43114	5.40801	-0.00589	H	4.41510	-2.22225	-0.97607
H	-0.01786	4.83103	-0.05011	H	4.41953	-2.36050	0.78066

(Azo)Pd(hfacac) (1d)

Table S7. Singlet excited states of (Azo)Pd(hfacac) (**1d**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.8148 eV 440.48 nm f=0.0952
103 -> 108 2.02 %
105 -> 108 6.97 %
105 -> 110 4.01 %
106 -> 108 5.10 %
107 -> 108 54.30 %
107 -> 109 12.11 %

Excited State: 2
2.8785 eV 430.72 nm f=0.0054
105 -> 108 62.31 %
105 -> 109 16.60 %
106 -> 108 6.45 %
107 -> 108 3.33 %

Excited State: 3
3.0138 eV 411.38 nm f=0.0231
105 -> 108 3.13 %
105 -> 109 11.26 %
107 -> 108 16.06 %
107 -> 109 64.36 %

Excited State: 4
3.0660 eV 404.38 nm f=0.0058
105 -> 108 16.02 %
105 -> 109 59.52 %
106 -> 108 2.16 %
106 -> 109 7.13 %
107 -> 108 2.31 %
107 -> 109 8.17 %

Excited State: 5
3.3066 eV 374.96 nm f=0.0297
105 -> 108 2.23 %
105 -> 109 3.12 %
106 -> 108 36.14 %
106 -> 109 41.67 %

Excited State: 6
3.3730 eV 367.58 nm f=0.1605
105 -> 108 2.17 %
105 -> 110 5.57 %
106 -> 108 37.89 %
106 -> 109 32.01 %
107 -> 108 2.23 %
107 -> 109 2.05 %

Excited State: 7
3.5588 eV 348.38 nm f=0.0239
100 -> 108 2.26 %
101 -> 108 10.03 %
101 -> 109 3.41 %
102 -> 108 3.82 %
104 -> 108 50.61 %
104 -> 109 10.77 %
107 -> 110 2.54 %

Excited State: 8
3.6448 eV 340.16 nm f=0.0648
101 -> 108 2.17 %
102 -> 108 4.42 %
103 -> 108 30.50 %
103 -> 109 5.87 %
104 -> 108 12.32 %
104 -> 109 2.33 %
105 -> 110 7.82 %
106 -> 110 5.93 %
107 -> 110 13.39 %

Excited State: 9
3.6737 eV 337.49 nm f=0.0855
101 -> 108 8.54 %
101 -> 109 2.48 %
103 -> 108 39.16 %
104 -> 108 7.09 %
106 -> 110 5.55 %
107 -> 108 2.49 %
107 -> 110 15.55 %

Excited State: 10
3.7079 eV 334.38 nm f=0.0496
100 -> 108 2.29 %
101 -> 108 5.29 %
102 -> 108 2.30 %
103 -> 108 5.74 %
105 -> 110 31.82 %
106 -> 109 3.53 %
107 -> 110 20.07 %

Excited State: 11
3.7282 eV 332.56 nm f=0.0426
100 -> 109 4.24 %
101 -> 108 22.28 %
102 -> 108 6.03 %
103 -> 108 4.48 %
104 -> 108 8.40 %
105 -> 110 18.89 %
106 -> 109 2.48 %
106 -> 110 6.31 %
107 -> 110 7.07 %

Excited State: 12
3.7821 eV 327.81 nm f=0.0014
98 -> 108 2.66 %
98 -> 109 2.29 %
100 -> 108 9.82 %
100 -> 109 4.17 %
101 -> 108 3.78 %
101 -> 109 33.87 %
102 -> 108 2.52 %
102 -> 109 13.74 %
104 -> 109 13.03 %

Excited State: 13
3.8647 eV 320.81 nm f=0.0145
102 -> 108 2.89 %
103 -> 109 7.26 %
104 -> 108 11.65 %
104 -> 109 63.80 %
105 -> 110 2.44 %

Excited State: 14
3.9459 eV 314.21 nm f=0.0364
99 -> 108 2.41 %
99 -> 109 3.03 %
101 -> 108 2.35 %
101 -> 109 2.30 %
103 -> 109 58.88 %
104 -> 108 2.72 %
104 -> 109 4.53 %
105 -> 110 2.47 %
106 -> 110 5.65 %

Excited State: 15
4.0114 eV 309.08 nm f=0.0044
97 -> 110 4.42 %
98 -> 108 2.52 %
99 -> 110 5.62 %
101 -> 109 3.31 %
103 -> 109 2.45 %
103 -> 110 23.77 %
105 -> 110 3.27 %
106 -> 110 35.60 %
107 -> 110 3.34 %

Excited State: 16
4.1315 eV 300.09 nm f=0.0009
99 -> 108 2.04 %
100 -> 108 53.43 %
100 -> 109 14.41 %
101 -> 108 3.12 %
101 -> 109 4.14 %
102 -> 108 6.69 %
102 -> 109 4.63 %
107 -> 110 2.05 %

Excited State: 17
4.2285 eV 293.21 nm f=0.0006
98 -> 108 13.00 %
98 -> 109 23.52 %
100 -> 108 8.14 %
100 -> 109 43.22 %

Excited State: 18
4.2988 eV 288.42 nm f=0.0069
98 -> 110 18.17 %
100 -> 110 39.52 %
101 -> 110 15.15 %
102 -> 110 10.40 %

Excited State: 19
4.3422 eV 285.53 nm f=0.0127
97 -> 108 4.45 %
99 -> 108 12.62 %
99 -> 109 5.16 %
101 -> 108 13.93 %
101 -> 109 5.80 %
102 -> 108 32.16 %
102 -> 109 9.72 %
103 -> 108 3.14 %

Excited State: 20
4.4974 eV 275.68 nm f=0.0115
97 -> 109 3.58 %
98 -> 109 2.22 %
100 -> 109 2.44 %
101 -> 108 3.88 %
101 -> 109 9.71 %
102 -> 108 20.44 %
102 -> 109 48.16 %

Excited State: 21
4.5898 eV 270.13 nm f=0.0040
98 -> 108 55.26 %
98 -> 109 5.53 %
99 -> 108 3.04 %
100 -> 109 4.00 %
101 -> 109 4.31 %
103 -> 110 4.27 %
106 -> 110 5.63 %
107 -> 110 8.15 %

Excited State: 22
4.6567 eV 266.25 nm f=0.0037
99 -> 108 30.59 %
99 -> 109 3.64 %
99 -> 110 5.57 %
100 -> 108 2.86 %
100 -> 109 2.84 %
101 -> 108 3.34 %
102 -> 108 4.29 %
102 -> 109 5.13 %
103 -> 110 10.43 %
106 -> 110 6.04 %
107 -> 110 8.44 %
107 -> 113 2.12 %

Excited State: 23
4.6646 eV 265.80 nm f=0.0053
98 -> 109 46.41 %
99 -> 109 3.27 %
100 -> 108 6.19 %
100 -> 109 10.16 %
101 -> 108 7.30 %
101 -> 109 16.60 %

Excited State: 24
4.6867 eV 264.54 nm f=0.0318
97 -> 108 3.47 %
98 -> 108 16.48 %
98 -> 109 8.60 %
99 -> 108 12.99 %
99 -> 109 3.09 %
99 -> 110 4.47 %
103 -> 110 18.14 %
106 -> 110 8.38 %
107 -> 110 9.47 %

Excited State: 25
4.7891 eV 258.89 nm f=0.0408
97 -> 108 5.67 %
97 -> 109 11.08 %
99 -> 108 17.79 %
99 -> 109 49.33 %
100 -> 109 2.27 %
103 -> 109 2.43 %

Figure S5. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

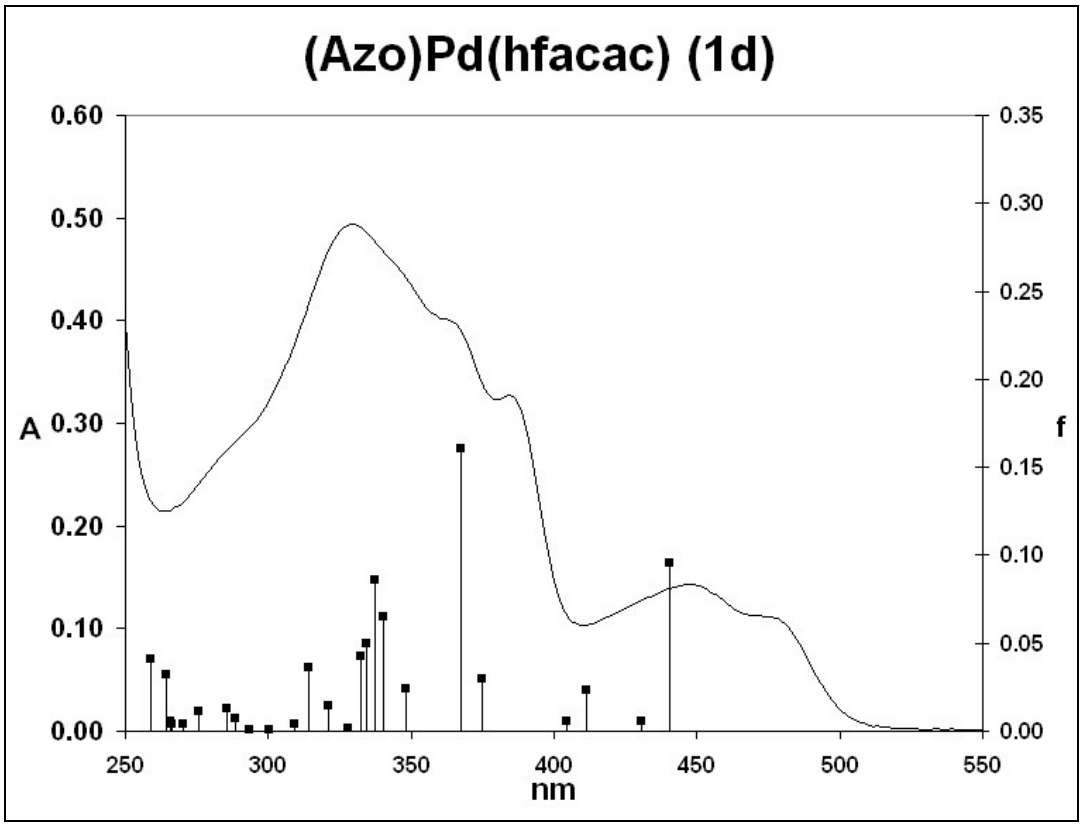


Figure S6. In the following picture, some (Azo)Pd(hfacac) (**1d**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_3, S_5, and S_6.

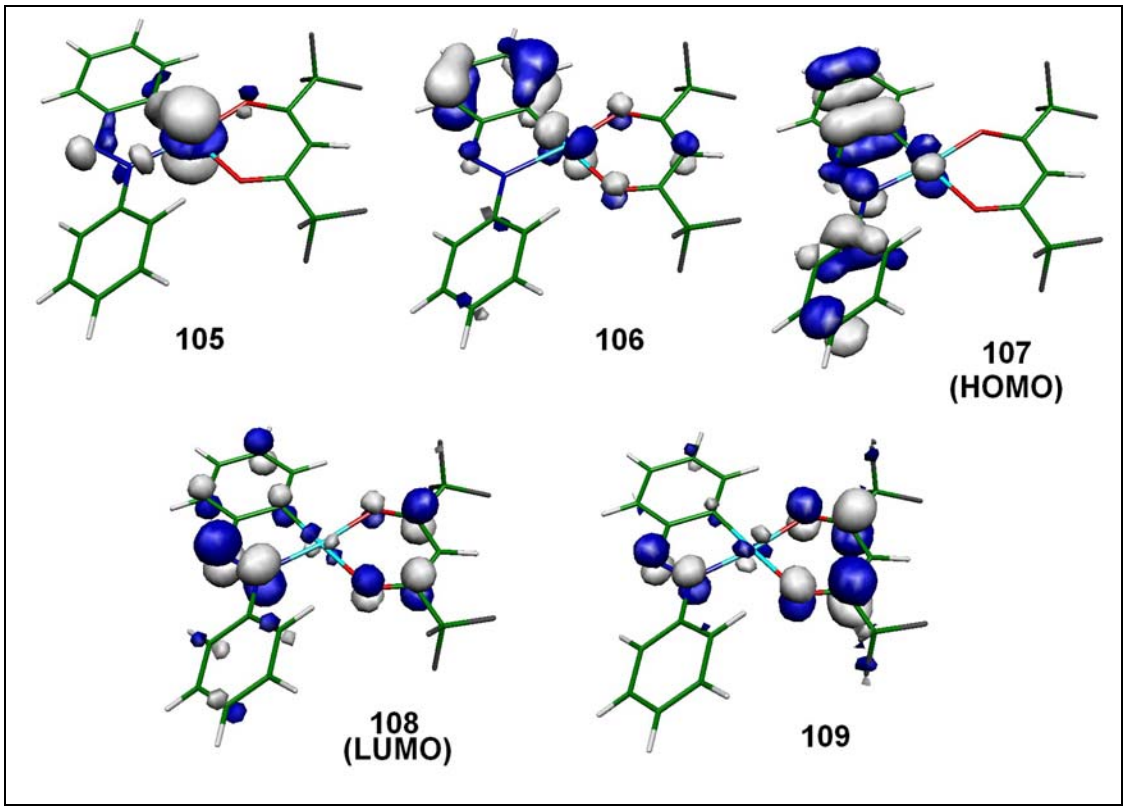


Table S8. Optimized structure of (Azo)Pd(hfacac) (**1d**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pd	0.27980	0.55693	-0.06838	H	1.54417	-1.99107	-1.01773
N	2.31398	0.37929	-0.06669	H	2.86971	-4.08103	-1.01175
N	3.00177	1.47431	-0.01150	H	5.14574	-4.11804	0.00363
C	2.20999	2.61858	-0.01094	H	6.08916	-2.03772	1.00196
C	0.80064	2.44175	-0.05222	H	4.76079	0.07032	0.96916
C	-0.01646	3.57244	-0.05438	O	-0.35151	-1.47143	-0.03345
C	0.57243	4.85206	-0.02411	C	-1.55772	-1.89298	0.02431
C	1.97068	5.01603	0.01398	C	-2.73954	-1.13561	0.05942
C	2.80290	3.89374	0.02214	C	-2.71323	0.26215	0.02914
C	3.07638	-0.83121	-0.03226	O	-1.69721	1.04874	-0.02718
C	4.36362	-0.84133	0.54155	H	-3.69128	-1.64328	0.10615
C	5.10236	-2.02550	0.55237	C	-1.66947	-3.42263	0.07440
C	4.56965	-3.19919	-0.00934	C	-4.04308	1.02321	0.05160
C	3.28883	-3.17985	-0.57886	F	-2.97416	-3.87522	-0.07321
C	2.53550	-2.00061	-0.58832	F	-0.91457	-4.01294	-0.93009
H	-1.09464	3.46577	-0.07911	F	-1.20063	-3.91584	1.28636
H	-0.06788	5.72861	-0.03015	F	-5.14073	0.18595	0.19941
H	2.39884	6.01152	0.03780	F	-4.08121	1.93824	1.09386
H	3.88308	3.98055	0.05306	F	-4.22755	1.73491	-1.12811

(Azo)Pt(hfacac) (2d)

Table S9. Singlet excited states of (Azo)Pt(hfacac) (**2d**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.6677 eV 464.76 nm f=0.0587
103 -> 109 2.80 %
106 -> 109 4.63 %
107 -> 108 30.30 %
107 -> 109 50.45 %

Excited State: 2
2.7642 eV 448.53 nm f=0.0519
106 -> 108 6.11 %
107 -> 108 56.51 %
107 -> 109 29.04 %

Excited State: 3
2.9505 eV 420.21 nm f=0.0010
105 -> 108 86.59 %
106 -> 108 8.47 %

Excited State: 4
3.0400 eV 407.84 nm f=0.0146
105 -> 108 6.80 %
105 -> 109 16.85 %
106 -> 108 58.21 %
106 -> 109 4.47 %
107 -> 108 4.54 %

Excited State: 5
3.0628 eV 404.81 nm f=0.0140
105 -> 108 2.22 %
105 -> 109 74.36 %
106 -> 108 14.88 %

Excited State: 6
3.3709 eV 367.81 nm f=0.2455
105 -> 109 2.30 %
106 -> 108 2.23 %
106 -> 109 74.62 %
107 -> 109 2.16 %
107 -> 111 2.02 %

Excited State: 7
3.5453 eV 349.71 nm f=0.0389
100 -> 109 2.29 %
101 -> 108 2.60 %
103 -> 108 29.90 %
103 -> 109 4.38 %
104 -> 108 25.45 %
104 -> 109 21.00 %

Excited State: 8
3.5690 eV 347.39 nm f=0.0462
100 -> 108 2.72 %
101 -> 108 5.46 %
101 -> 109 2.40 %
102 -> 108 4.90 %
103 -> 108 32.80 %
103 -> 109 5.23 %
104 -> 108 23.49 %
104 -> 109 14.57 %

Excited State: 9
3.6375 eV 340.85 nm f=0.0237
100 -> 108 2.04 %
100 -> 109 3.84 %
101 -> 108 33.65 %
102 -> 108 19.25 %
103 -> 108 6.87 %
103 -> 109 5.30 %
104 -> 108 7.50 %
104 -> 109 12.33 %

Excited State: 10
3.6965 eV 335.40 nm f=0.0206
100 -> 108 5.89 %
100 -> 109 2.46 %
101 -> 108 5.19 %
101 -> 109 9.35 %
102 -> 108 4.97 %
102 -> 109 5.03 %
103 -> 109 10.39 %
104 -> 108 36.07 %
104 -> 109 15.19 %

Excited State: 11
3.7588 eV 329.85 nm f=0.0097
100 -> 109 5.75 %
101 -> 108 4.48 %
101 -> 109 20.44 %
102 -> 108 2.16 %
102 -> 109 9.47 %
103 -> 108 4.61 %
103 -> 109 11.76 %
104 -> 108 4.56 %
104 -> 109 27.62 %

Excited State: 12
3.8234 eV 324.27 nm f=0.1210
100 -> 108 3.96 %
100 -> 109 5.33 %
101 -> 109 8.49 %
102 -> 109 3.22 %
103 -> 108 10.30 %
103 -> 109 48.06 %
104 -> 109 3.10 %

Excited State: 13
3.9686 eV 312.41 nm f=0.0047
100 -> 108 8.63 %
100 -> 109 47.99 %
101 -> 109 13.91 %
102 -> 109 18.78 %

Excited State: 14
4.1099 eV 301.67 nm f=0.0013
96 -> 108 2.99 %
98 -> 108 32.98 %
100 -> 108 41.46 %
100 -> 109 9.94 %
101 -> 108 2.58 %

Excited State: 15
4.3017 eV 288.22 nm f=0.0143
97 -> 108 3.56 %
100 -> 108 2.73 %
101 -> 108 28.00 %
102 -> 108 54.56 %

Excited State: 16
4.3850 eV 282.74 nm f=0.0053
99 -> 108 6.26 %
99 -> 109 16.16 %
101 -> 109 24.84 %
102 -> 108 2.02 %
102 -> 109 38.08 %

Excited State: 17
4.4396 eV 279.27 nm f=0.0094
99 -> 110 2.58 %
103 -> 110 2.42 %
106 -> 110 5.89 %
107 -> 110 69.03 %
107 -> 111 2.90 %
107 -> 113 2.64 %

Excited State: 18
4.5952 eV 269.81 nm f=0.0003
98 -> 108 45.30 %
99 -> 108 4.84 %
100 -> 108 18.33 %
100 -> 109 7.78 %
101 -> 108 8.50 %
105 -> 110 3.62 %

Excited State: 19
4.6244 eV 268.11 nm f=0.0023
98 -> 108 2.78 %
99 -> 109 11.07 %
101 -> 108 2.19 %
105 -> 110 59.73 %
105 -> 111 2.81 %
105 -> 113 3.18 %

Excited State: 20
4.6646 eV 265.80 nm f=0.0683
97 -> 108 4.27 %
97 -> 109 2.44 %
99 -> 108 70.61 %
100 -> 108 3.29 %
101 -> 109 2.22 %
102 -> 109 3.47 %

Excited State: 21
4.7108 eV 263.19 nm f=0.0222
98 -> 109 16.62 %
99 -> 108 3.00 %
99 -> 109 40.60 %
100 -> 109 3.12 %
101 -> 109 3.08 %
102 -> 109 7.12 %
105 -> 110 10.48 %

Excited State: 22
4.7773 eV 259.52 nm f=0.0068
97 -> 109 6.13 %
98 -> 109 55.49 %
99 -> 109 8.94 %
103 -> 110 3.18 %
106 -> 110 11.74 %

Excited State: 23
4.8598 eV 255.12 nm f=0.0004
97 -> 110 2.09 %
98 -> 109 10.59 %
103 -> 110 15.16 %
105 -> 110 3.52 %
106 -> 110 44.50 %
106 -> 111 2.30 %
107 -> 110 3.24 %

Excited State: 24
5.0578 eV 245.13 nm f=0.0909
97 -> 108 69.82 %
98 -> 108 3.51 %

Excited State: 25
5.1383 eV 241.29 nm f=0.0088
97 -> 109 59.15 %
98 -> 109 2.96 %
99 -> 109 4.30 %
100 -> 110 2.67 %
101 -> 110 10.42 %
102 -> 110 6.33 %

Figure S7. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

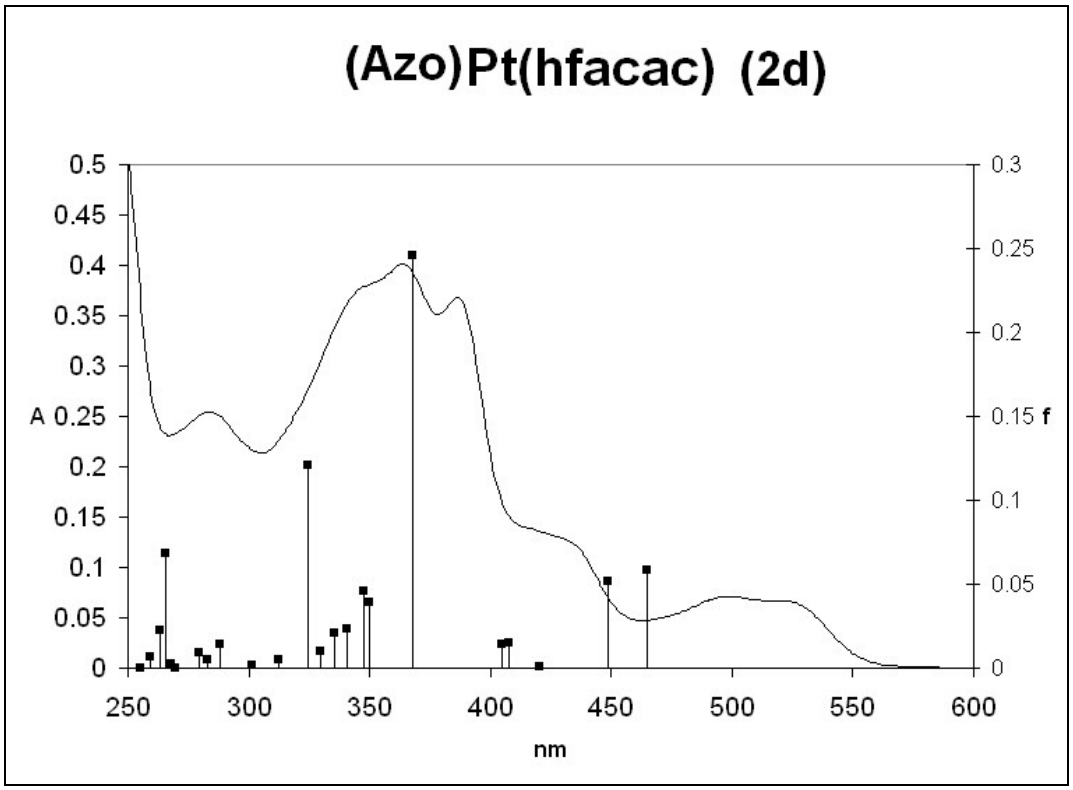


Figure S8. In the following picture, some (Azo)Pt(hfacac) (**2d**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_2, S_4, S_5, and S_6.

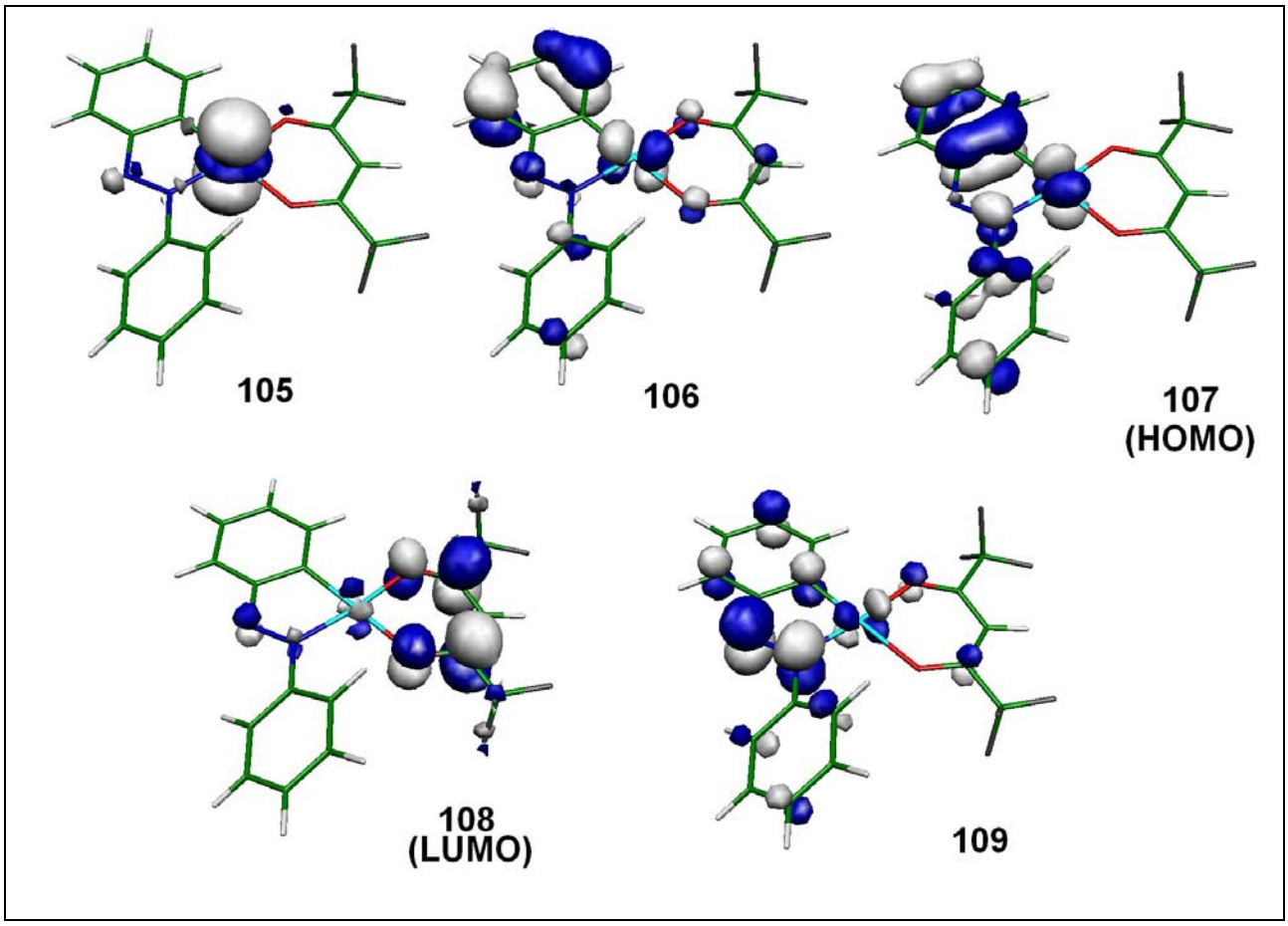


Table S10. Optimized structure of (Azo)Pt(hfacac) (**2d**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pt	-0.26812	-0.50496	-0.06351
N	-2.25545	-0.20322	-0.05702
N	-3.03452	-1.24031	0.00775
C	-2.33551	-2.44251	0.01001
C	-0.91575	-2.36273	-0.04644
C	-0.18841	-3.55782	-0.05476
C	-0.87005	-4.78718	-0.01449
C	-2.27833	-4.84856	0.03921
C	-3.02418	-3.66913	0.05259
C	-2.91563	1.06803	-0.03466
C	-4.12650	1.21312	0.66732
C	-4.77406	2.45062	0.67050
C	-4.22446	3.53935	-0.02760
C	-3.02038	3.38241	-0.72899
C	-2.35873	2.14969	-0.73236
H	0.89460	-3.53503	-0.09161
H	-0.29805	-5.70977	-0.02479
H	-2.77746	-5.81020	0.07037
H	-4.10744	-3.67423	0.09382
H	-1.43071	2.02889	-1.27315
H	-2.59138	4.21751	-1.27094
H	-4.72805	4.49986	-0.02006
H	-5.70156	2.56895	1.21977
H	-4.53723	0.36397	1.19883
O	0.43134	1.50162	-0.01313
C	1.65538	1.87815	0.04767
C	2.80563	1.07359	0.07679
C	2.73003	-0.31995	0.03709
O	1.68143	-1.07106	-0.02510
H	3.77628	1.54382	0.12854
C	1.81825	3.40034	0.10234
C	4.02326	-1.13574	0.05582
F	3.14488	3.80142	0.01139
F	1.13210	4.01388	-0.93727
F	1.31542	3.91486	1.29001
F	5.15235	-0.34105	0.20195
F	4.02692	-2.05147	1.09762
F	4.17704	-1.85279	-1.12439

(PhPy)Pd(acac) (1b)

Table S11. Singlet excited states of (PhPy)Pd(acac) (**1b**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
3.4019 eV 364.45 nm f=0.0402
74 -> 77 13.38 %
75 -> 80 3.80 %
76 -> 77 74.86 %

Excited State: 2
3.4481 eV 359.57 nm f=0.0033
75 -> 77 97.18 %

Excited State: 3
3.7256 eV 332.78 nm f=0.0343
74 -> 77 49.85 %
75 -> 80 23.83 %
76 -> 77 17.26 %

Excited State: 4
3.8694 eV 320.42 nm f=0.0307
71 -> 80 3.35 %
74 -> 77 16.14 %
75 -> 80 32.91 %
76 -> 78 25.64 %
76 -> 79 6.01 %

Excited State: 5
3.8828 eV 319.31 nm f=0.0001
75 -> 78 61.70 %
75 -> 79 27.44 %
76 -> 80 7.12 %

Excited State: 6
3.9620 eV 312.93 nm f=0.0000
69 -> 80 8.11 %
75 -> 78 6.66 %
75 -> 79 2.01 %
76 -> 80 69.51 %

Excited State: 7
4.0302 eV 307.64 nm f=0.0658
74 -> 77 9.92 %
74 -> 78 2.32 %
75 -> 80 10.86 %
76 -> 78 64.20 %
76 -> 79 2.70 %

Excited State: 8
4.1069 eV 301.89 nm f=0.0013
73 -> 77 8.03 %
74 -> 79 3.44 %
75 -> 80 6.14 %
76 -> 79 72.11 %

Excited State: 9
4.1605 eV 298.00 nm f=0.0000
70 -> 77 2.14 %
72 -> 80 22.49 %
73 -> 80 2.58 %
74 -> 80 57.11 %

Excited State: 10
4.1992 eV 295.26 nm f=0.0000
75 -> 78 29.15 %
75 -> 79 66.72 %

Excited State: 11
4.2559 eV 291.32 nm f=0.0467
72 -> 78 2.15 %
73 -> 77 34.66 %
74 -> 78 36.55 %
74 -> 79 8.16 %
76 -> 78 2.13 %
76 -> 79 10.87 %

Excited State: 12
4.4079 eV 281.28 nm f=0.0424
70 -> 80 2.49 %
72 -> 77 4.29 %
72 -> 78 3.10 %
73 -> 77 11.40 %
74 -> 78 39.55 %
74 -> 79 21.25 %
75 -> 80 2.61 %

Excited State: 13
4.4433 eV 279.03 nm f=0.0021
68 -> 80 4.89 %
70 -> 80 71.20 %
71 -> 80 9.65 %

Excited State: 14
4.5229 eV 274.12 nm f=0.0002
70 -> 77 21.20 %
71 -> 77 49.29 %
71 -> 78 15.65 %
71 -> 79 7.57 %

Excited State: 15
4.5356 eV 273.36 nm f=0.0987
72 -> 77 27.17 %
73 -> 77 29.52 %
74 -> 78 5.91 %
74 -> 79 28.28 %

Excited State: 16
4.5733 eV 271.10 nm f=0.0005
70 -> 77 32.84 %
71 -> 77 2.72 %
71 -> 78 34.11 %
71 -> 79 22.44 %

Excited State: 17
4.6906 eV 264.32 nm f=0.0000
70 -> 77 39.46 %
71 -> 77 44.49 %
71 -> 78 7.39 %
71 -> 79 3.58 %

Excited State: 18
4.7343 eV 261.88 nm f=0.1588
69 -> 77 2.17 %
72 -> 77 48.10 %
73 -> 78 10.50 %
74 -> 79 23.25 %

Excited State: 19
4.8328 eV 256.54 nm f=0.0001
70 -> 78 58.03 %
70 -> 79 32.73 %
71 -> 78 2.16 %

Excited State: 20
4.9351 eV 251.23 nm f=0.1130
72 -> 77 6.02 %
73 -> 78 73.96 %
73 -> 79 6.26 %

Figure S9. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

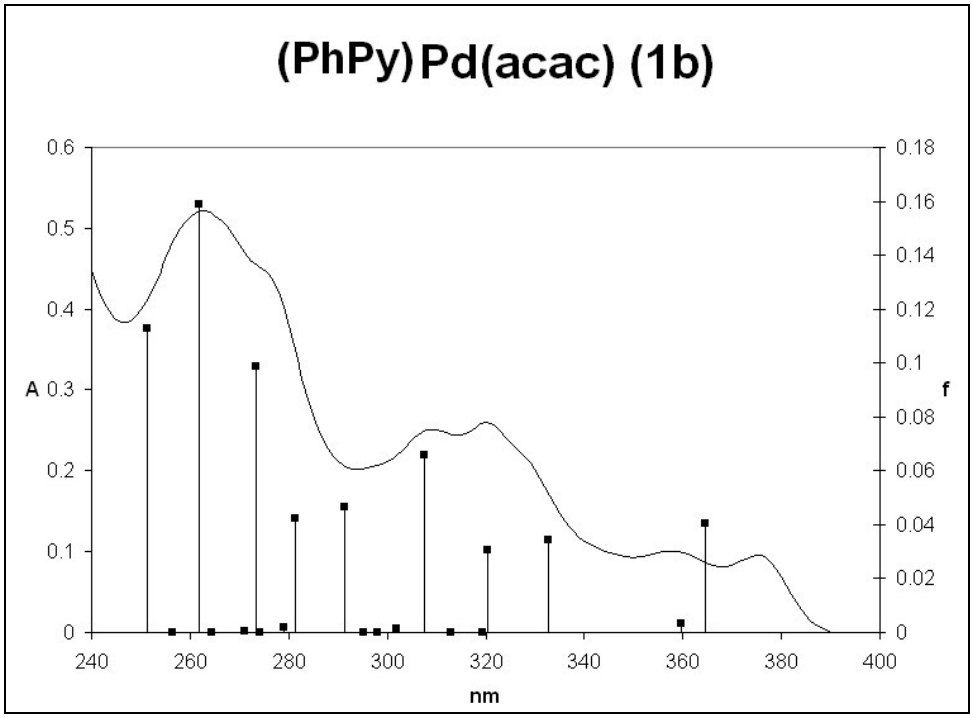


Figure S10. In the following picture, some (PhPy)Pd(acac) (**1b**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_2, S_3, S_4, and S_7.

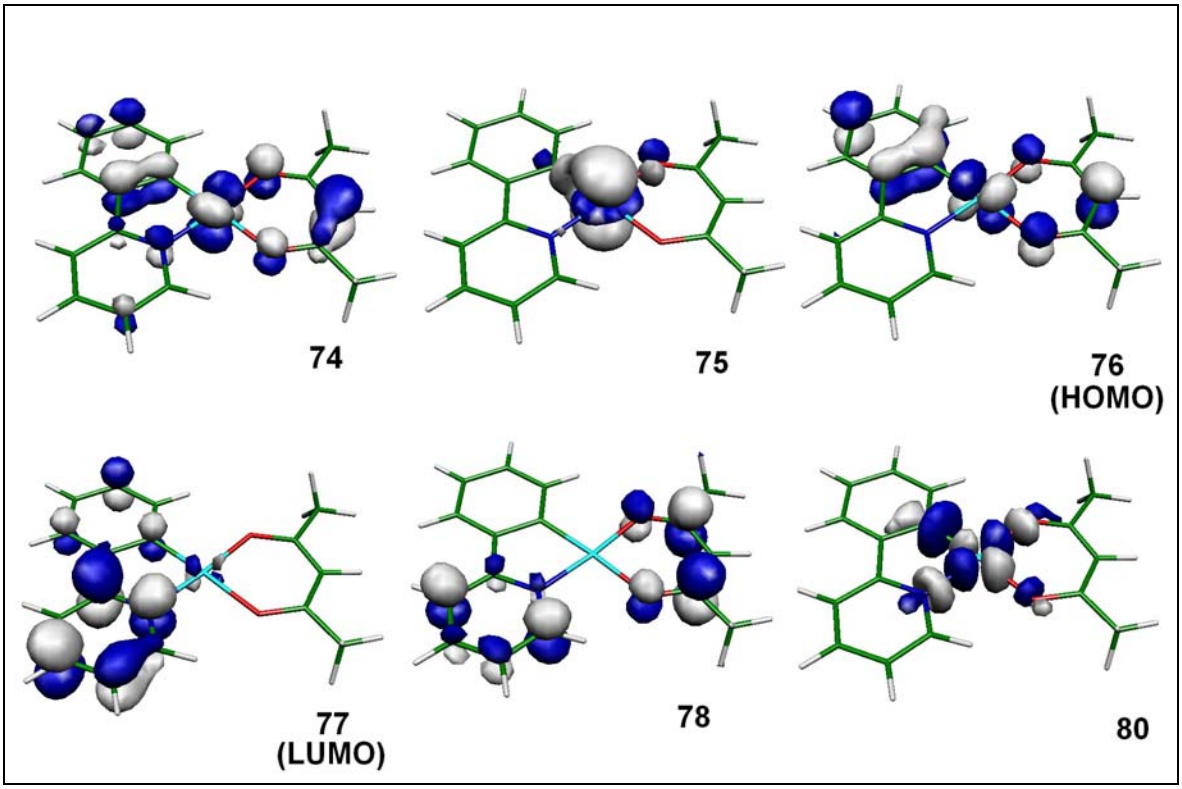


Table S12. Optimized structure of (PhPy)Pd(acac) (**1b**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

C	3.33052	-2.98315	-0.00028	H	4.19103	-3.64295	-0.00038
C	3.51061	-1.59772	-0.00017	H	4.32644	3.52281	0.00058
C	2.39172	-0.74821	-0.00005	H	2.07292	4.57865	0.00048
N	1.13102	-1.29366	-0.00006	H	0.01945	3.16341	0.00015
C	0.94902	-2.63179	-0.00014	O	-1.80054	1.46920	-0.00035
C	2.03008	-3.51396	-0.00025	C	-3.14419	-1.24083	0.00021
C	2.39337	0.71253	0.00009	C	-3.75087	0.03429	-0.00003
C	3.55399	1.50862	0.00029	C	-3.08928	1.27922	-0.00031
H	4.54101	1.05489	0.00036	C	-3.90269	2.55136	-0.00051
H	4.50595	-1.17233	-0.00018	C	-4.01454	-2.47544	0.00086
C	3.43667	2.90194	0.00041	H	-4.83269	0.06005	0.00009
C	2.16102	3.49602	0.00037	H	-4.97598	2.35577	-0.00075
C	1.00186	2.70376	0.00018	H	-3.64556	3.14792	0.88060
C	1.10003	1.30482	0.00003	H	-3.64513	3.14793	-0.88148
Pd	-0.39175	0.01992	-0.00011	H	-5.07834	-2.23323	-0.00134
O	-1.86447	-1.46216	0.00019	H	-3.78393	-3.08446	-0.87935
H	-0.08264	-2.96096	-0.00010	H	-3.78705	-3.08129	0.88410
H	1.85410	-4.58201	-0.00032				

(PhPy)Pt(acac) (2b)

Table S13. Singlet excited states of (PhPy)Pt(acac) (**2b**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
3.1491 eV 393.71 nm f=0.0265
75 -> 77 8.92 %
76 -> 77 83.19 %

Excited State: 2
3.4557 eV 358.78 nm f=0.0034
74 -> 77 97.38 %

Excited State: 3
3.5791 eV 346.41 nm f=0.0090
75 -> 77 30.51 %
76 -> 77 5.73 %
76 -> 78 55.07 %

Excited State: 4
3.7067 eV 334.49 nm f=0.1574
75 -> 77 48.34 %
76 -> 77 3.04 %
76 -> 78 34.24 %
76 -> 79 4.69 %

Excited State: 5
3.7882 eV 327.29 nm f=0.0003
74 -> 78 92.56 %
74 -> 79 6.05 %

Excited State: 6
3.8776 eV 319.74 nm f=0.0289
73 -> 77 2.35 %
75 -> 77 2.08 %
75 -> 78 3.33 %
76 -> 78 2.48 %
76 -> 79 83.55 %

Excited State: 7
4.0373 eV 307.09 nm f=0.0565
71 -> 78 2.66 %
73 -> 77 3.20 %
75 -> 78 78.24 %
75 -> 79 2.14 %
76 -> 79 6.06 %

Excited State: 8
4.1847 eV 296.28 nm f=0.0144
71 -> 77 2.59 %
73 -> 77 38.88 %
75 -> 78 3.76 %
75 -> 79 44.55 %

Excited State: 9
4.2262 eV 293.37 nm f=0.0000
72 -> 77 95.29 %

Excited State: 10
4.2491 eV 291.79 nm f=0.0001
74 -> 78 6.32 %
74 -> 79 92.54 %

Excited State: 11
4.4494 eV 278.65 nm f=0.0000
72 -> 78 85.43 %
72 -> 79 7.62 %
76 -> 82 2.34 %

Excited State: 12
4.4852 eV 276.43 nm f=0.1717
71 -> 77 10.59 %
73 -> 77 40.60 %
75 -> 79 35.14 %
76 -> 81 2.28 %

Excited State: 13
4.6543 eV 266.39 nm f=0.0007
70 -> 77 12.71 %
70 -> 78 66.96 %
70 -> 79 6.84 %
76 -> 82 5.74 %

Excited State: 14
4.6925 eV 264.21 nm f=0.0473
71 -> 77 53.32 %
73 -> 78 28.83 %
74 -> 82 2.19 %
75 -> 79 4.52 %

Excited State: 15
4.6998 eV 263.81 nm f=0.0002
69 -> 82 4.09 %
70 -> 77 4.56 %
70 -> 78 2.72 %
72 -> 78 3.21 %
76 -> 80 5.81 %
76 -> 82 69.32 %

Excited State: 16
4.7872 eV 258.99 nm f=0.0406
73 -> 78 16.71 %
74 -> 80 4.18 %
74 -> 82 65.69 %

Excited State: 17
4.8466 eV 255.82 nm f=0.1126
69 -> 77 4.96 %
71 -> 77 18.66 %
71 -> 78 4.78 %
73 -> 78 46.43 %
74 -> 82 12.42 %
75 -> 79 3.49 %

Excited State: 18
4.8809 eV 254.02 nm f=0.0001
70 -> 77 73.17 %
70 -> 78 13.64 %
75 -> 82 4.75 %

Excited State: 19
4.9638 eV 249.78 nm f=0.0000
70 -> 77 6.05 %
71 -> 82 6.59 %
73 -> 82 2.55 %
75 -> 80 7.93 %
75 -> 82 65.37 %

Excited State: 20
4.9760 eV 249.16 nm f=0.0296
73 -> 79 86.51 %
76 -> 81 2.76 %

Excited State: 21
5.0582 eV 245.11 nm f=0.0000
72 -> 78 7.53 %
72 -> 79 89.98 %

Excited State: 22
5.1288 eV 241.74 nm f=0.0798
69 -> 77 19.04 %
71 -> 77 5.27 %
71 -> 78 43.15 %
72 -> 82 3.85 %
74 -> 82 3.01 %
76 -> 81 7.57 %

Excited State: 23
5.2266 eV 237.22 nm f=0.0010
76 -> 80 90.66 %
76 -> 82 6.33 %

Excited State: 24
5.2382 eV 236.69 nm f=0.0072
69 -> 77 60.79 %
71 -> 78 17.83 %
72 -> 82 5.64 %

Excited State: 25
5.2694 eV 235.29 nm f=0.0051
71 -> 78 8.29 %
71 -> 79 3.03 %
72 -> 80 3.14 %
72 -> 82 73.32 %

Excited State: 26
5.3755 eV 230.65 nm f=0.0448
71 -> 79 70.88 %
72 -> 82 3.79 %
76 -> 81 13.81 %

Excited State: 27
5.4361 eV 228.07 nm f=0.3676
69 -> 77 2.20 %
71 -> 78 5.49 %
71 -> 79 12.42 %
73 -> 81 3.00 %
76 -> 81 51.11 %
76 -> 83 2.71 %
76 -> 84 2.55 %

Excited State: 28
5.5454 eV 223.58 nm f=0.0066
69 -> 78 5.08 %
71 -> 79 3.33 %
75 -> 81 72.00 %
76 -> 83 8.33 %

Excited State: 29
5.5558 eV 223.16 nm f=0.0137
70 -> 79 23.00 %
74 -> 81 70.34 %

Excited State: 30
5.5794 eV 222.22 nm f=0.0000
75 -> 80 87.46 %
75 -> 82 7.75 %

Figure S11. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

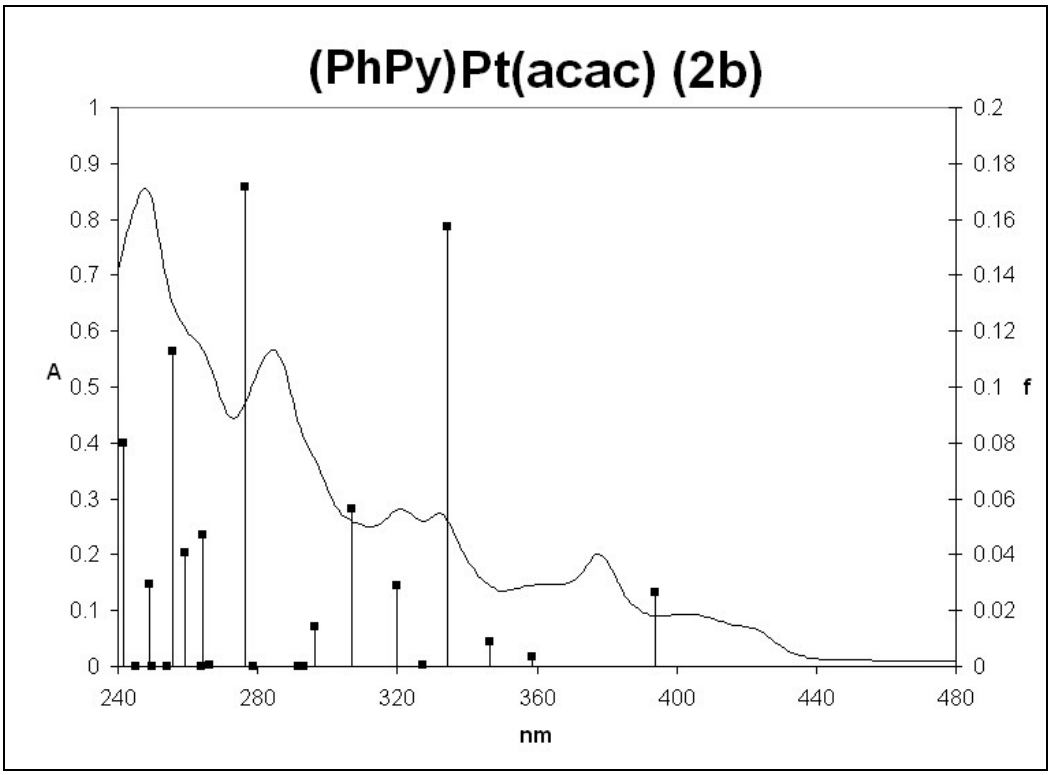


Figure S12. In the following picture, some (PhPy)Pt(acac) (**2b**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_4, S_6, S_7, and S_{12}.

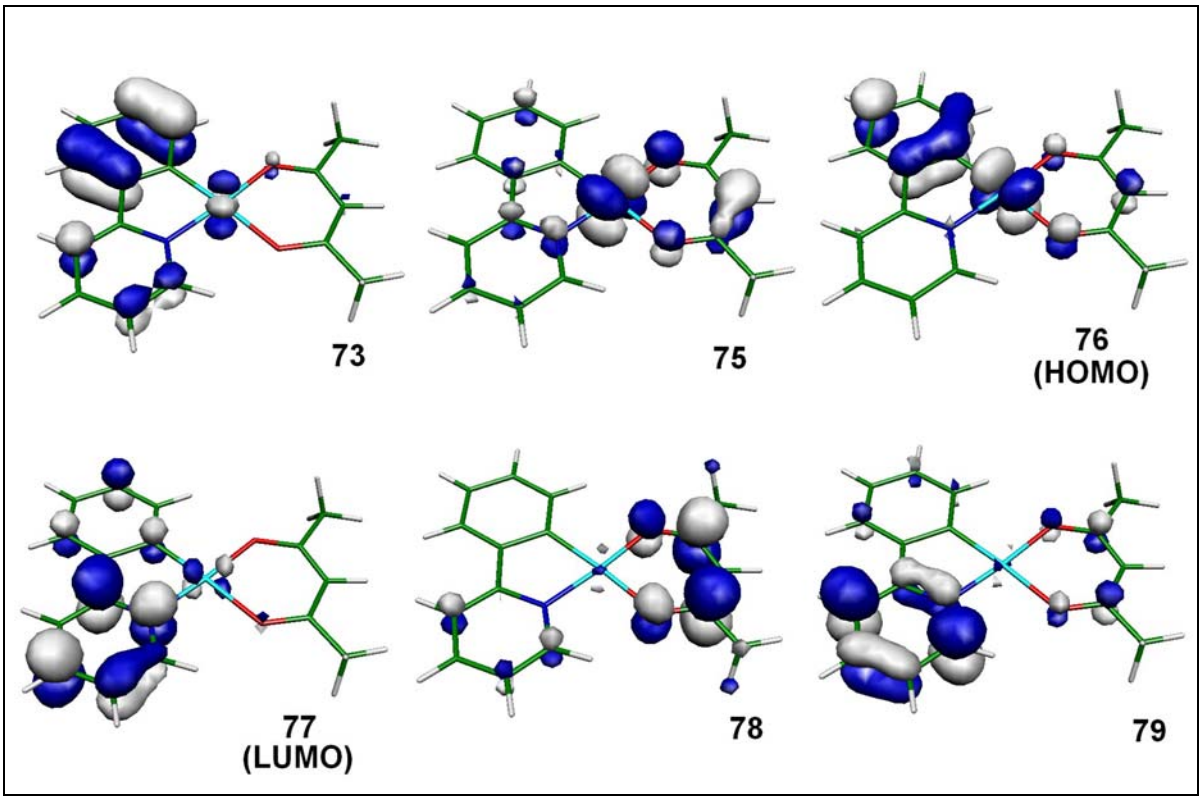


Table S14. Optimized structure of (PhPy)Pt(acac) (**2b**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

C	-3.34994	3.02067	-0.00043	H	-4.20090	3.69248	-0.00062
C	-3.54739	1.63869	-0.00022	H	-4.45319	-3.46357	0.00100
C	-2.44358	0.77006	0.00001	H	-2.21679	-4.55634	0.00056
N	-1.17134	1.29820	-0.00006	H	-0.14235	-3.18180	0.00003
C	-0.97298	2.63739	-0.00022	O	1.74223	-1.47497	-0.00046
C	-2.04098	3.53170	-0.00040	C	3.11213	1.22349	0.00054
C	-2.47047	-0.68828	0.00017	C	3.70580	-0.05717	0.00012
C	-3.64528	-1.46338	0.00050	C	3.03600	-1.29513	-0.00027
H	-4.62388	-0.99189	0.00070	C	3.82885	-2.57769	-0.00075
H	-4.54803	1.22623	-0.00029	C	3.98774	2.45242	0.00110
C	-3.55328	-2.85766	0.00067	H	4.78726	-0.09277	-0.00016
C	-2.28629	-3.47234	0.00044	H	4.90448	-2.39638	-0.00028
C	-1.11484	-2.70175	0.00014	H	3.56339	-3.17132	0.87977
C	-1.18261	-1.29768	-0.00004	H	3.56402	-3.17026	-0.88218
Pt	0.33076	-0.02409	-0.00012	H	5.04984	2.20323	-0.00115
O	1.83270	1.45509	0.00045	H	3.76142	3.06281	-0.87917
H	0.06222	2.95345	-0.00021	H	3.76457	3.05970	0.88434
H	-1.84859	4.59686	-0.00052				

(PhPy)Pd(hfacac) (1e)

Table S15. Singlet excited states of (PhPy)Pd(hfacac) (**1e**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.8149 eV 440.45 nm f=0.0000
98 -> 101 98.19 %

Excited State: 2
2.8493 eV 435.13 nm f=0.0159
99 -> 101 4.19 %
100 -> 101 89.59 %

Excited State: 3
3.3241 eV 372.98 nm f=0.0375
97 -> 101 8.97 %
99 -> 101 74.97 %
100 -> 101 6.15 %

Excited State: 4
3.5521 eV 349.04 nm f=0.0419
97 -> 101 7.06 %
98 -> 104 20.55 %
99 -> 101 2.66 %
100 -> 102 61.26 %

Excited State: 5
3.6527 eV 339.43 nm f=0.0286
96 -> 101 2.89 %
97 -> 101 63.03 %
99 -> 101 14.21 %
100 -> 102 12.66 %

Excited State: 6
3.7917 eV 326.99 nm f=0.0000
93 -> 104 6.63 %
95 -> 101 7.56 %
98 -> 102 2.23 %
99 -> 104 5.35 %
100 -> 104 68.63 %

Excited State: 7
3.8074 eV 325.64 nm f=0.0042
98 -> 102 94.86 %

Excited State: 8
3.8317 eV 323.57 nm f=0.0276
97 -> 101 4.53 %
98 -> 104 55.00 %
99 -> 102 6.48 %
100 -> 102 16.35 %

Excited State: 9
3.9021 eV 317.74 nm f=0.0000
94 -> 101 6.47 %
95 -> 101 78.45 %
97 -> 104 2.10 %
100 -> 104 5.93 %

Excited State: 10
4.0240 eV 308.11 nm f=0.0007
91 -> 101 4.98 %
94 -> 101 82.48 %
95 -> 101 6.11 %

Excited State: 11
4.1526 eV 298.57 nm f=0.0000
95 -> 101 3.26 %
96 -> 104 9.17 %
97 -> 104 48.98 %
99 -> 104 24.61 %

Excited State: 12
4.1966 eV 295.44 nm f=0.0872
98 -> 104 2.17 %
99 -> 102 66.03 %
100 -> 103 18.17 %
100 -> 105 2.43 %

Excited State: 13
4.2943 eV 288.71 nm f=0.0225
97 -> 102 32.75 %
99 -> 102 11.12 %
100 -> 103 46.45 %

Excited State: 14
4.4347 eV 279.57 nm f=0.0016
88 -> 104 2.06 %
94 -> 104 5.65 %
95 -> 104 80.61 %

Excited State: 15
4.5175 eV 274.45 nm f=0.0165
93 -> 101 14.38 %
95 -> 104 2.27 %
96 -> 101 58.02 %
97 -> 102 5.97 %
99 -> 103 2.83 %
100 -> 103 4.22 %

Excited State: 16
4.5519 eV 272.38 nm f=0.1676
93 -> 101 7.06 %
96 -> 101 8.28 %
97 -> 102 36.93 %
99 -> 102 2.17 %
99 -> 103 14.66 %
100 -> 103 21.00 %

Excited State: 17
4.5922 eV 269.99 nm f=0.0000
98 -> 103 98.61 %

Excited State: 18
4.8662 eV 254.78 nm f=0.0577
93 -> 101 16.01 %
96 -> 101 3.13 %
97 -> 102 6.13 %
97 -> 103 2.38 %
99 -> 103 54.79 %

Excited State: 19
4.9384 eV 251.06 nm f=0.0001
95 -> 102 6.21 %
96 -> 104 3.81 %
97 -> 104 20.62 %
99 -> 104 57.56 %
100 -> 104 8.82 %

Excited State: 20
4.9409 eV 250.93 nm f=0.2079
93 -> 101 47.57 %
96 -> 101 7.46 %
96 -> 102 4.33 %
97 -> 102 6.72 %
99 -> 103 12.12 %
100 -> 105 2.31 %

Figure S13. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

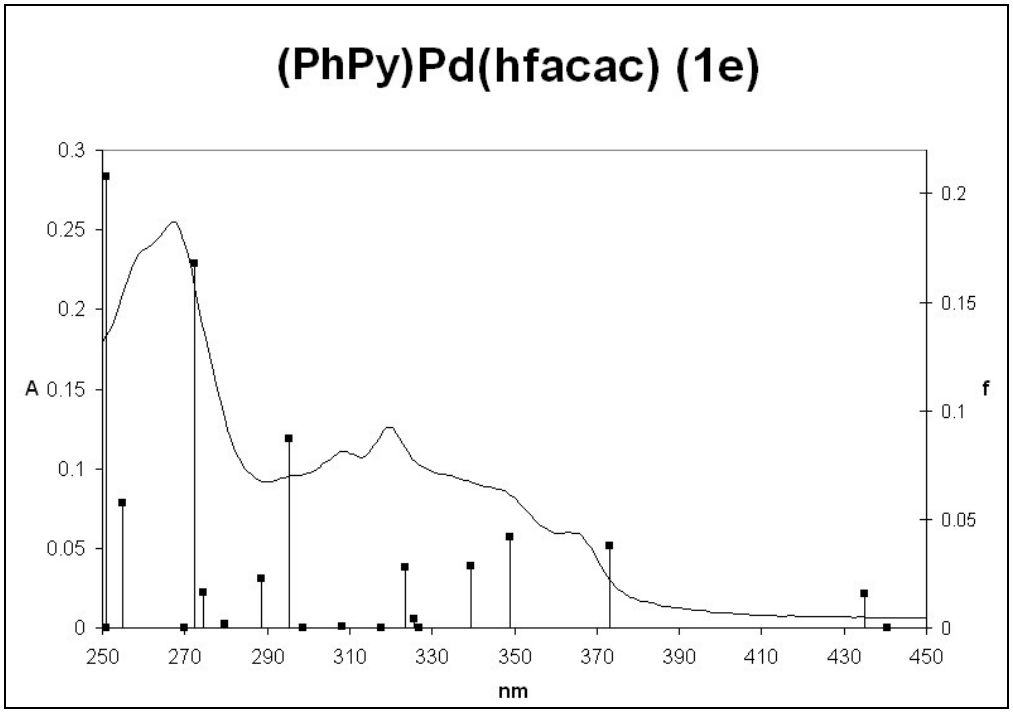


Figure S14. In the following picture, some (PhPy)Pd(hfacac) (**1e**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_2, S_3, S_4, S_5, S_8, and S_{12}.

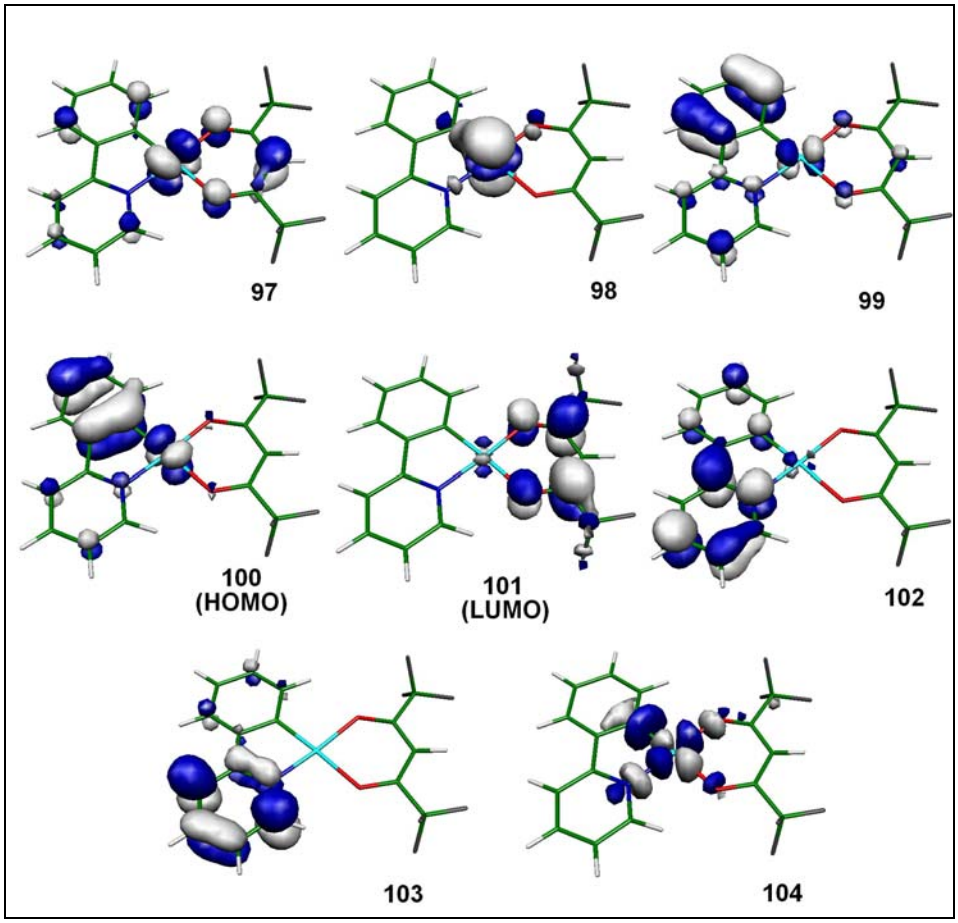


Table S16. Optimized structure of (PhPy)Pd(hfacac) (**1e**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

C	4.23151	-2.99497	-0.00011	H	5.09203	-3.65429	-0.00015
C	4.41140	-1.60937	-0.00007	H	5.20077	3.52217	0.00010
C	3.29270	-0.76170	-0.00003	H	2.94134	4.56301	0.00013
N	2.03246	-1.30815	-0.00002	H	0.90004	3.14236	0.00009
C	1.84988	-2.64704	-0.00006	O	-0.92565	1.44477	0.00002
C	2.93203	-3.52704	-0.00010	C	-2.26254	-1.21569	-0.00002
C	3.29070	0.69808	0.00002	C	-2.90102	0.03423	-0.00009
C	4.44426	1.50257	0.00004	C	-2.19503	1.24495	-0.00005
H	5.43408	1.05608	0.00002	C	-2.99594	2.55204	-0.00008
H	5.40631	-1.18345	-0.00008	C	-3.13442	-2.47705	0.00004
C	4.31567	2.89533	0.00008	H	-3.98023	0.06572	-0.00018
C	3.03795	3.48179	0.00010	F	-4.36941	2.34433	-0.00029
C	1.88197	2.68300	0.00008	F	-2.69994	3.32070	1.11843
C	1.99905	1.28855	0.00004	F	-2.69960	3.32087	-1.11836
Pd	0.51340	0.00341	0.00002	F	-4.49496	-2.20083	-0.00089
O	-1.00576	-1.46520	0.00001	F	-2.87592	-3.26266	-1.11748
H	0.82237	-2.98679	-0.00005	F	-2.87727	-3.26156	1.11868
H	2.75600	-4.59473	-0.00013				

(PhPy)Pt(hfacac) (2e)

Table S17. Singlet excited states of (PhPy)Pt(hfacac) (**2e**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
2.5257 eV 490.90 nm f=0.0237
99 -> 101 5.28 %
100 -> 101 86.48 %

Excited State: 2
2.7161 eV 456.47 nm f=0.0000
98 -> 101 98.22 %

Excited State: 3
3.0822 eV 402.26 nm f=0.0660
97 -> 101 6.81 %
99 -> 101 75.53 %
100 -> 101 6.89 %

Excited State: 4
3.3798 eV 366.84 nm f=0.0610
100 -> 102 88.63 %

Excited State: 5
3.4533 eV 359.02 nm f=0.0306
97 -> 101 80.83 %
99 -> 101 13.09 %

Excited State: 6
3.5544 eV 348.82 nm f=0.0000
96 -> 101 96.27 %

Excited State: 7
3.8246 eV 324.18 nm f=0.0046
98 -> 102 97.31 %

Excited State: 8
4.0391 eV 306.96 nm f=0.0992
97 -> 102 5.97 %
98 -> 104 3.10 %
99 -> 102 77.17 %
100 -> 105 2.18 %

Excited State: 9
4.0946 eV 302.80 nm f=0.0111
97 -> 102 14.64 %
99 -> 102 4.50 %
100 -> 103 75.65 %

Excited State: 10
4.1010 eV 302.32 nm f=0.0008
91 -> 101 5.03 %
94 -> 101 88.72 %

Excited State: 11
4.3662 eV 283.96 nm f=0.0633
95 -> 101 8.42 %
97 -> 102 48.20 %
99 -> 103 20.52 %
100 -> 103 14.43 %

Excited State: 12
4.4041 eV 281.52 nm f=0.0968
93 -> 101 13.37 %
95 -> 101 68.32 %
97 -> 102 4.17 %
99 -> 102 2.02 %

Excited State: 13
4.5054 eV 275.19 nm f=0.0001
93 -> 104 2.62 %
95 -> 104 3.00 %
96 -> 102 6.02 %
100 -> 104 78.40 %

Excited State: 14
4.6483 eV 266.73 nm f=0.0001
98 -> 103 98.88 %

Excited State: 15
4.6902 eV 264.34 nm f=0.0277
98 -> 104 82.99 %
98 -> 106 2.20 %

Excited State: 16
4.7281 eV 262.23 nm f=0.0000
96 -> 102 87.96 %
99 -> 104 2.43 %
100 -> 104 4.65 %

Excited State: 17
4.7844 eV 259.14 nm f=0.1309
93 -> 101 9.31 %
97 -> 102 11.60 %
97 -> 103 4.14 %
99 -> 103 56.56 %

Excited State: 18
4.9416 eV 250.90 nm f=0.1689
93 -> 101 52.40 %
95 -> 101 5.45 %
95 -> 102 5.58 %
97 -> 102 4.02 %
97 -> 103 2.14 %
99 -> 103 5.64 %
100 -> 105 4.71 %

Excited State: 19
4.9427 eV 250.84 nm f=0.0000
96 -> 102 3.90 %
97 -> 104 38.32 %
99 -> 104 42.47 %

Excited State: 20
5.0583 eV 245.11 nm f=0.0005
92 -> 101 12.99 %
95 -> 102 3.77 %
97 -> 103 70.56 %
99 -> 103 4.29 %

Figure S15. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

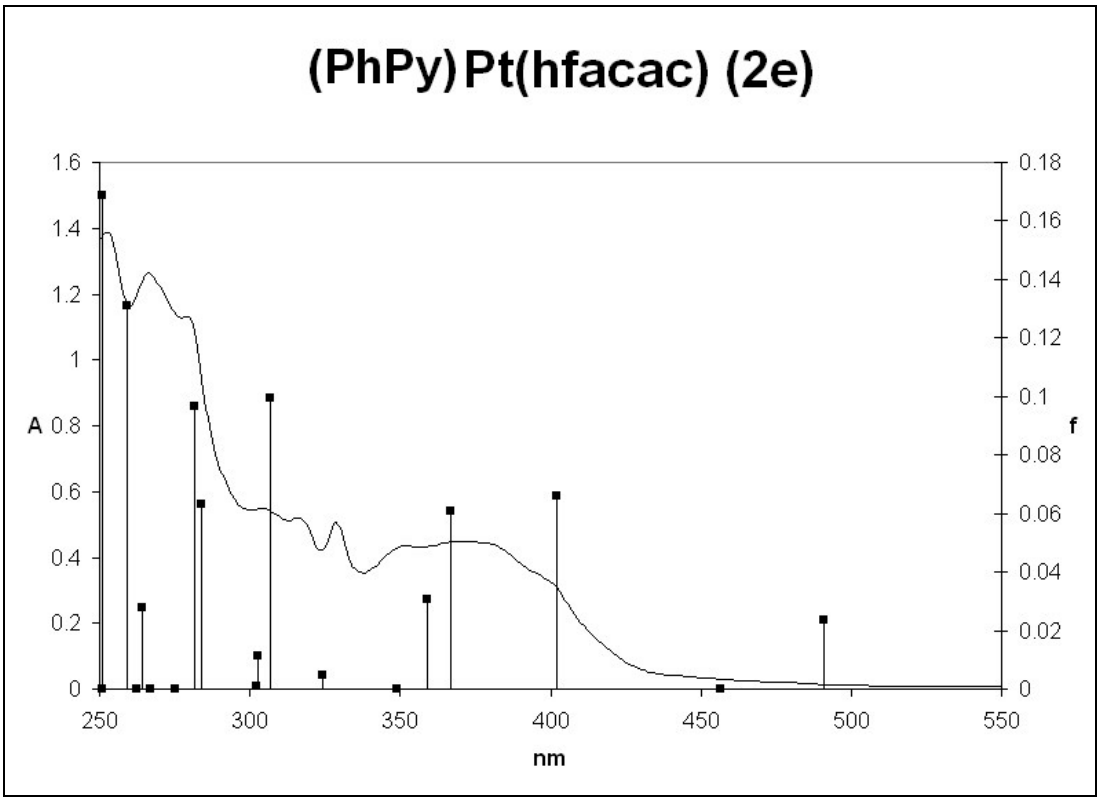


Figure S16. In the following picture, some (PhPy)Pt(hfacac) (**2e**) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1, S_3, S_4, S_5 and S_8.

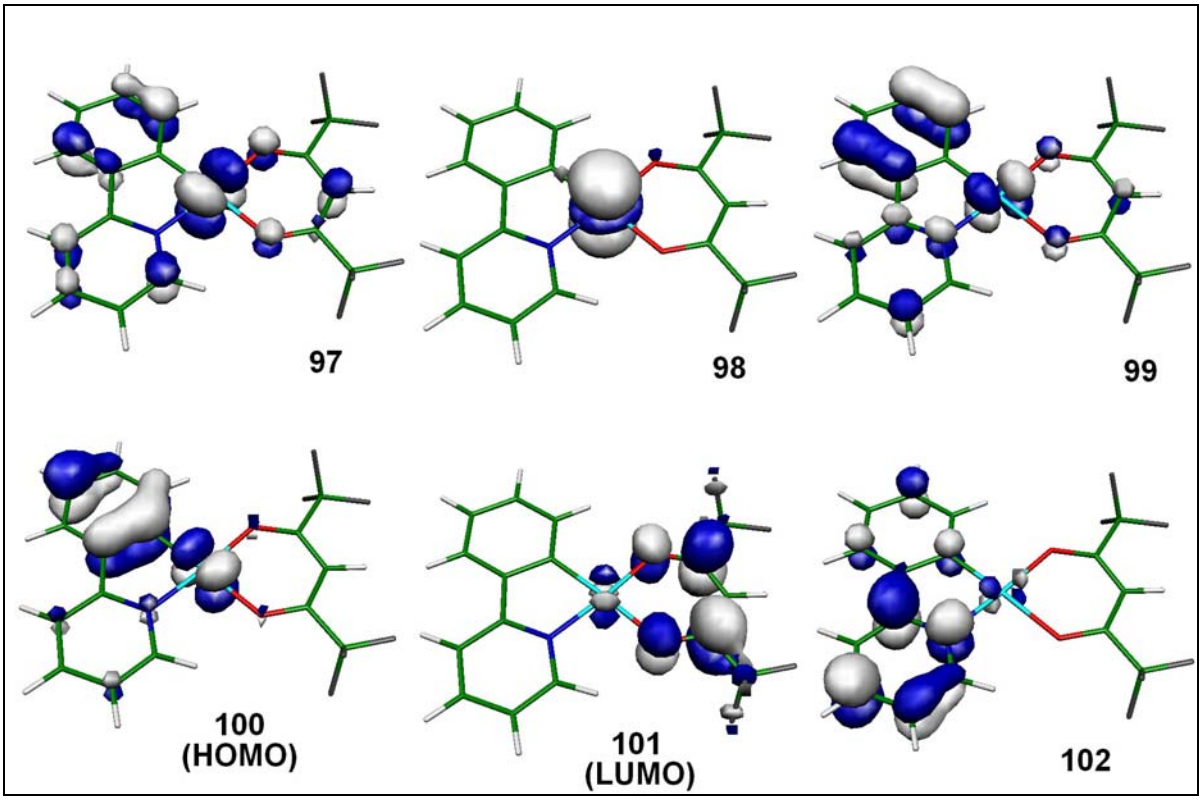


Table S18. Optimized structure of (PhPy)Pt(hfacac) (**2e**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

C	4.12271	-3.03430	-0.00006	H	4.97380	-3.70551	-0.00007
C	4.32021	-1.65237	-0.00003	H	5.20826	3.45669	0.00005
C	3.21634	-0.78529	-0.00002	H	2.96856	4.53990	0.00008
N	1.94544	-1.31551	-0.00002	H	0.90227	3.16307	0.00006
C	1.74585	-2.65521	-0.00005	O	-0.97944	1.44960	0.00001
C	2.81488	-3.54727	-0.00006	C	-2.34254	-1.20310	-0.00005
C	3.24119	0.67258	0.00001	C	-2.96732	0.05305	-0.00009
C	4.41157	1.45276	0.00002	C	-2.25532	1.25781	-0.00004
H	5.39212	0.98644	0.00001	C	-3.03599	2.57288	-0.00004
H	5.32047	-1.23961	-0.00003	C	-3.21826	-2.45811	0.00002
C	4.31145	2.84685	0.00005	H	-4.04636	0.09396	-0.00016
C	3.04367	3.45695	0.00006	F	-4.41112	2.37855	-0.00022
C	1.87382	2.68209	0.00005	F	-2.73163	3.33820	1.11822
C	1.95602	1.28195	0.00002	F	-2.73137	3.33837	-1.11811
Pt	0.44669	0.00536	0.00000	F	-4.57638	-2.17143	-0.00081
O	-1.08443	-1.46230	-0.00002	F	-2.96501	-3.24553	-1.11729
H	0.71433	-2.98096	-0.00005	F	-2.96620	-3.24452	1.11835
H	2.62288	-4.61211	-0.00008				

(BzQ)Pd(acac) (1c)

Table S19. Singlet and triplet excited states of (BzQ)Pd(acac) (**1c**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state. This computation has been performed on the relaxed (optimized) geometry.

Singlet Excited States

Excited State: 1
3.2265 eV 384.26 nm f=0.0471
80 -> 83 5.78 %
82 -> 83 83.09 %

Excited State: 2
3.3806 eV 366.75 nm f=0.0018
81 -> 83 96.67 %

Excited State: 3
3.6148 eV 342.98 nm f=0.0183
80 -> 83 61.37 %
81 -> 86 14.68 %
82 -> 83 8.16 %
82 -> 84 6.57 %

Excited State: 4
3.7652 eV 329.29 nm f=0.0097
77 -> 86 3.16 %
80 -> 83 7.92 %
81 -> 86 49.94 %
82 -> 84 17.71 %
82 -> 85 6.55 %

Excited State: 5
3.8496 eV 322.07 nm f=0.0000
75 -> 86 8.29 %
78 -> 86 2.33 %
79 -> 86 2.26 %
81 -> 84 3.12 %
81 -> 85 6.92 %
82 -> 86 66.53 %

Excited State: 6
3.8913 eV 318.62 nm f=0.0743
79 -> 83 21.73 %
80 -> 83 17.78 %
81 -> 86 3.19 %
82 -> 84 47.32 %

Excited State: 7
3.9165 eV 316.57 nm f=0.0004
81 -> 84 40.48 %
81 -> 85 47.25 %
82 -> 86 6.94 %

Excited State: 8
4.0123 eV 309.01 nm f=0.0242
79 -> 83 8.23 %
81 -> 86 8.50 %
82 -> 84 2.46 %
82 -> 85 69.27 %

Excited State: 9
4.0832 eV 303.64 nm f=0.0000
75 -> 86 4.08 %
78 -> 86 19.22 %
79 -> 86 4.37 %
80 -> 86 57.66 %

Excited State: 10
4.1025 eV 302.22 nm f=0.0857
75 -> 83 2.61 %
78 -> 83 4.36 %
79 -> 83 49.35 %
80 -> 84 2.32 %
80 -> 85 4.25 %
82 -> 84 15.19 %
82 -> 85 9.70 %

Excited State: 11
4.1479 eV 298.91 nm f=0.0022
81 -> 84 52.90 %
81 -> 85 42.90 %

Excited State: 12
4.2948 eV 288.68 nm f=0.0345
78 -> 83 31.04 %
78 -> 84 2.93 %
79 -> 83 6.35 %
79 -> 84 18.09 %
79 -> 85 2.10 %
80 -> 84 20.73 %
80 -> 85 5.06 %
82 -> 85 2.98 %

Excited State: 13
4.3463 eV 285.26 nm f=0.0009
73 -> 86 4.60 %
76 -> 86 64.68 %
77 -> 86 14.15 %
80 -> 84 6.45 %

Excited State: 14
4.4043 eV 281.50 nm f=0.0086
76 -> 86 3.93 %
78 -> 83 13.60 %
79 -> 85 3.84 %
80 -> 84 49.58 %
80 -> 85 11.04 %

Excited State: 15
4.4177 eV 280.65 nm f=0.0001
76 -> 83 13.48 %
77 -> 83 76.74 %
77 -> 85 5.52 %

Excited State: 16
4.5359 eV 273.34 nm f=0.0332
75 -> 83 3.78 %
78 -> 83 6.32 %
78 -> 85 3.37 %
79 -> 84 11.37 %
80 -> 84 5.69 %
80 -> 85 56.59 %
82 -> 87 3.03 %

Excited State: 17
4.5507 eV 272.45 nm f=0.0005
76 -> 83 51.56 %
76 -> 85 3.13 %
77 -> 84 11.95 %
77 -> 85 26.50 %

Excited State: 18
4.6354 eV 267.47 nm f=0.0001
76 -> 83 28.65 %
77 -> 83 17.92 %
77 -> 84 16.66 %
77 -> 85 30.40 %

Excited State: 19
4.7300 eV 262.12 nm f=0.0792
75 -> 83 40.36 %
78 -> 83 20.31 %
79 -> 83 2.08 %
79 -> 84 9.36 %
80 -> 85 4.36 %
80 -> 87 2.14 %
82 -> 87 10.84 %

Excited State: 20
4.8012 eV 258.23 nm f=0.0617
75 -> 83 44.07 %
78 -> 83 7.41 %
78 -> 84 2.46 %
79 -> 84 12.34 %
79 -> 87 2.08 %
80 -> 87 4.38 %
82 -> 87 16.30 %

Excited State: 21
4.8448 eV 255.91 nm f=0.0001
76 -> 84 31.92 %
76 -> 85 58.60 %

Excited State: 22
4.9711 eV 249.41 nm f=0.0424
78 -> 84 11.25 %
79 -> 84 19.35 %
79 -> 85 49.94 %
82 -> 87 7.78 %

Excited State: 23
5.0336 eV 246.31 nm f=0.0550
74 -> 83 2.02 %
78 -> 83 3.55 %
78 -> 84 24.24 %
78 -> 85 6.28 %
79 -> 84 4.25 %
79 -> 85 30.80 %
82 -> 87 17.14 %

Excited State: 24
5.1357 eV 241.41 nm f=0.0009
77 -> 84 15.51 %
77 -> 85 6.10 %
78 -> 86 4.71 %
79 -> 86 9.19 %
80 -> 86 5.63 %
81 -> 87 52.37 %

Excited State: 25
5.1746 eV 239.60 nm f=0.0016
76 -> 84 4.50 %
76 -> 85 2.77 %
77 -> 84 32.15 %
77 -> 85 15.37 %
79 -> 86 2.22 %
81 -> 87 36.02 %

Triplet Excited States

Excited State: 1
2.4708 eV 501.80 nm f=0.0000
74 -> 83 4.06 %
75 -> 84 2.66 %
78 -> 84 3.32 %
78 -> 87 2.11 %
79 -> 83 38.25 %
79 -> 87 4.70 %
80 -> 83 2.39 %
80 -> 84 6.61 %
80 -> 85 2.19 %
82 -> 83 32.22 %
82 -> 84 23.18 %
82 -> 85 6.28 %
82 -> 87 3.82 %

Excited State: 2
2.8460 eV 435.65 nm f=0.0000
79 -> 83 3.82 %
80 -> 83 7.52 %
80 -> 84 6.88 %
81 -> 86 22.32 %
82 -> 83 50.97 %
82 -> 84 6.74 %
82 -> 85 6.74 %

Excited State: 3
2.8719 eV 431.72 nm f=0.0000
79 -> 83 2.02 %
80 -> 83 2.69 %
81 -> 86 87.12 %
82 -> 83 11.55 %
82 -> 84 2.72 %

Excited State: 4
2.9104 eV 426.00 nm f=0.0000
75 -> 85 3.32 %
79 -> 84 2.62 %
79 -> 85 6.59 %
80 -> 83 3.72 %
80 -> 84 11.79 %
80 -> 85 43.36 %
82 -> 84 16.00 %
82 -> 85 30.72 %

Excited State: 5
3.1809 eV 389.77 nm f=0.0000
69 -> 83 2.84 %
72 -> 83 2.81 %
79 -> 83 17.09 %
80 -> 83 36.43 %
82 -> 84 25.05 %
82 -> 85 5.03 %
82 -> 86 2.38 %
82 -> 87 7.26 %

Excited State: 6
3.1810 eV 389.76 nm f=0.0000
74 -> 86 6.75 %
75 -> 86 17.61 %
78 -> 86 9.21 %
79 -> 86 5.25 %
82 -> 86 62.30 %

Excited State: 7
3.2414 eV 382.50 nm f=0.0000
75 -> 86 14.12 %
78 -> 86 30.55 %
79 -> 86 5.36 %
80 -> 86 55.02 %
82 -> 86 2.87 %

Excited State: 8
3.2812 eV 377.86 nm f=0.0000
81 -> 83 92.49 %
81 -> 84 3.23 %

Excited State: 9
3.5784 eV 346.48 nm f=0.0000
75 -> 83 7.84 %
78 -> 83 2.91 %
79 -> 83 39.29 %
79 -> 87 2.41 %
80 -> 83 27.17 %
80 -> 84 7.40 %
82 -> 83 5.48 %
82 -> 84 4.50 %
82 -> 85 2.21 %

Excited State: 10
3.7290 eV 332.48 nm f=0.0000
70 -> 86 3.04 %
73 -> 86 6.05 %
76 -> 86 78.69 %
77 -> 86 16.66 %

Excited State: 11
3.7591 eV 329.83 nm f=0.0000
74 -> 83 7.76 %
74 -> 84 2.69 %
75 -> 83 5.59 %
78 -> 83 46.53 %
79 -> 84 3.04 %
79 -> 87 4.89 %
80 -> 83 2.66 %
82 -> 83 3.11 %
82 -> 84 2.89 %
82 -> 87 15.54 %

Excited State: 12
3.8253 eV 324.11 nm f=0.0000
76 -> 85 2.32 %
81 -> 84 42.23 %
81 -> 85 52.15 %

Excited State: 13
3.9232 eV 316.03 nm f=0.0000
78 -> 85 8.80 %
79 -> 84 20.68 %
80 -> 83 7.00 %
80 -> 84 23.64 %
80 -> 85 8.29 %
82 -> 85 24.77 %
82 -> 87 2.69 %

Excited State: 14
3.9569 eV 313.33 nm f=0.0000
78 -> 84 8.68 %
79 -> 84 29.61 %
79 -> 85 13.46 %
80 -> 83 3.25 %
80 -> 85 28.18 %
82 -> 84 5.96 %
82 -> 85 9.19 %

Excited State: 15
4.0529 eV 305.91 nm f=0.0000
81 -> 83 3.48 %
81 -> 84 50.53 %
81 -> 85 42.53 %

Excited State: 16
4.1378 eV 299.63 nm f=0.0000
74 -> 84 3.81 %
75 -> 84 8.60 %
78 -> 83 31.32 %
78 -> 84 6.10 %
79 -> 84 4.72 %
80 -> 87 4.28 %
82 -> 87 27.85 %
82 -> 89 3.06 %

Excited State: 17
4.2261 eV 293.38 nm f=0.0000
75 -> 84 8.84 %
78 -> 83 3.76 %
79 -> 84 6.11 %
79 -> 85 4.18 %
79 -> 87 2.20 %
80 -> 84 30.53 %
80 -> 85 13.77 %
82 -> 84 14.83 %
82 -> 85 2.06 %
82 -> 87 7.88 %

Excited State: 18
4.2434 eV 292.18 nm f=0.0000
71 -> 85 2.62 %
76 -> 85 2.31 %
77 -> 83 20.59 %
77 -> 84 15.69 %
77 -> 85 56.74 %

Excited State: 19
4.3887 eV 282.51 nm f=0.0000
72 -> 83 4.92 %
75 -> 83 37.79 %
75 -> 85 6.20 %
78 -> 85 13.30 %
79 -> 84 7.04 %
79 -> 85 8.05 %
79 -> 87 2.55 %
80 -> 83 4.12 %
82 -> 85 4.84 %

Excited State: 20
4.4140 eV 280.89 nm f=0.0000
76 -> 83 33.97 %
76 -> 85 2.05 %
77 -> 83 47.03 %
77 -> 84 7.28 %
77 -> 85 7.07 %

Figure S17. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

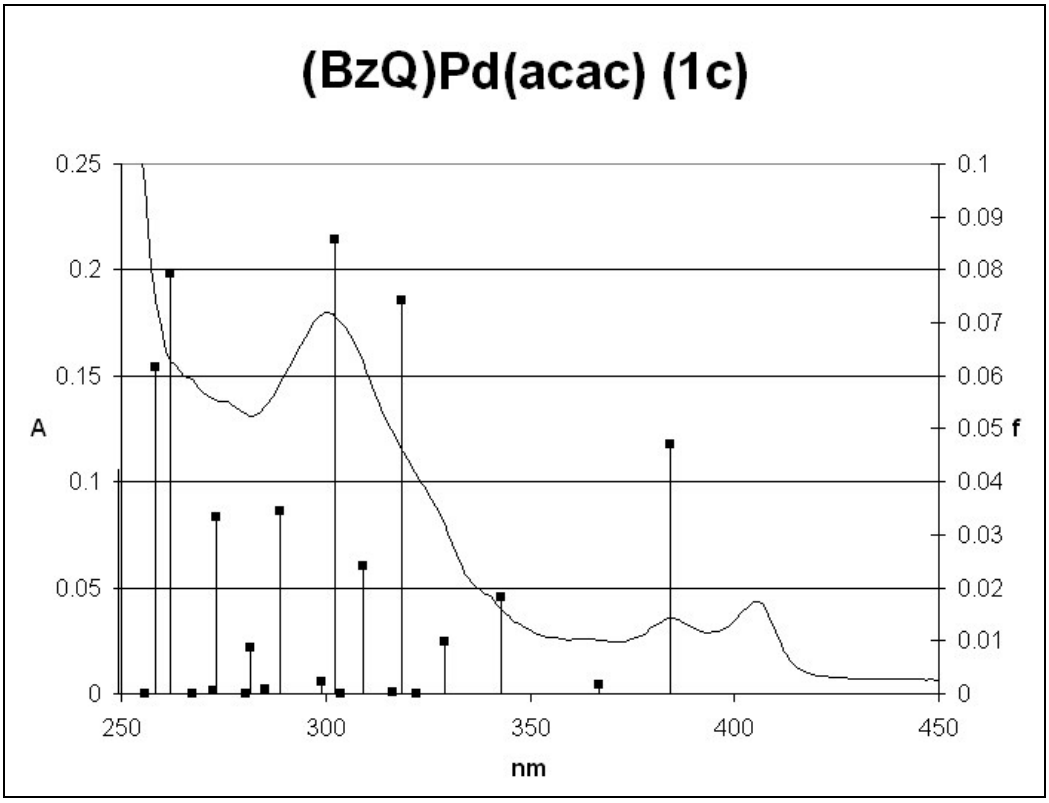


Figure S18. In the following picture, some (BzQ)Pd(acac) (**1c**) Kohn-Sham orbitals are reported that are relevant in describing the low-in-energy electronic transitions).

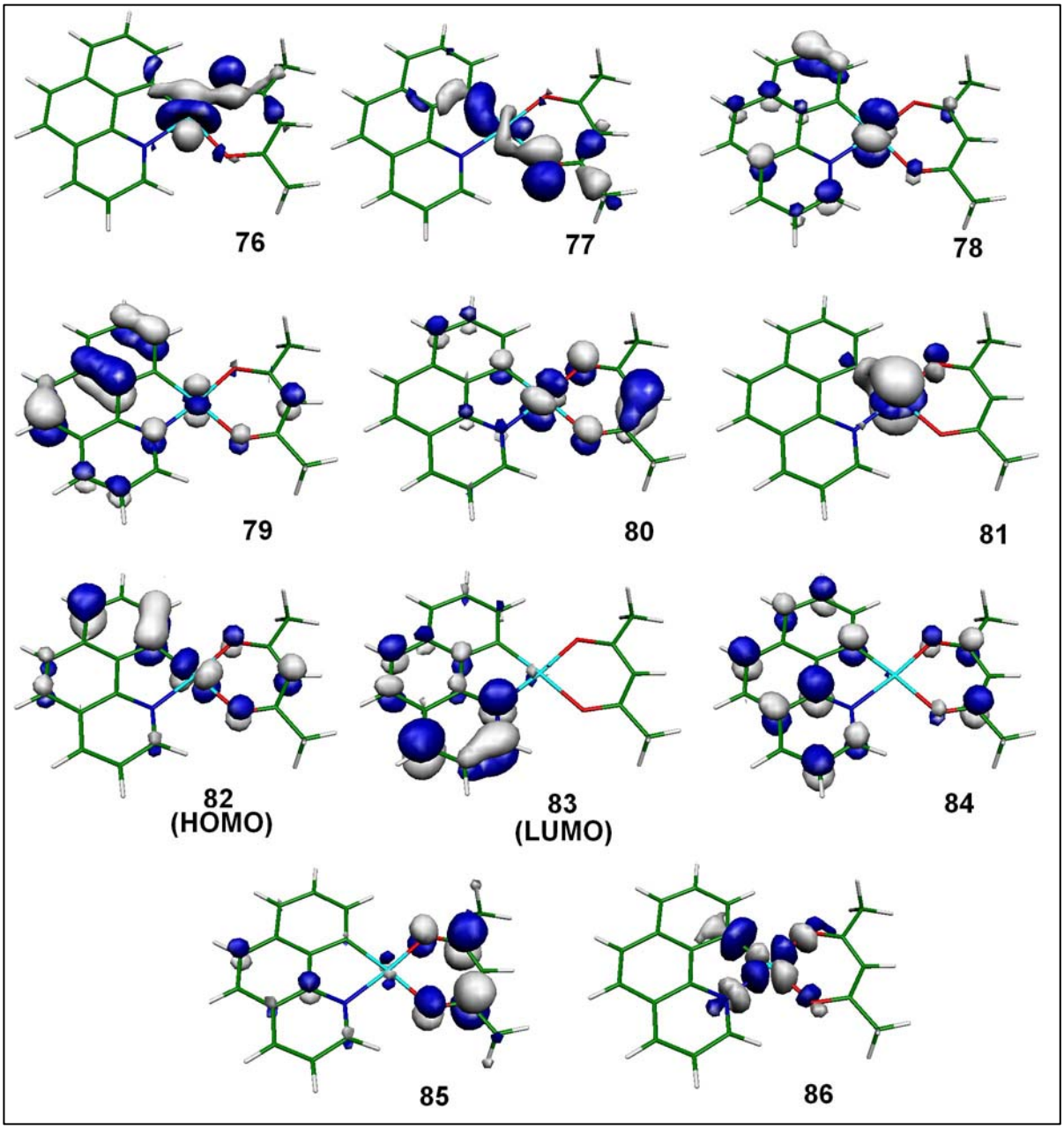


Table S20. Optimized structure of (BzQ)Pd(acac) (**1c**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pd	-0.73600	0.02392	-0.00019	N	0.79240	-1.30617	-0.00005
C	0.74577	1.33603	-0.00014	C	0.69476	-2.64276	0.00000
C	2.02303	0.70844	-0.00001	C	1.84657	-3.45724	0.00010
C	3.24946	1.41801	0.00007	C	3.11200	-2.87192	0.00017
C	3.18453	2.83305	-0.00001	H	-0.30941	-3.04747	-0.00005
C	1.93968	3.46364	-0.00012	H	1.72846	-4.53356	0.00013
C	0.72355	2.72924	-0.00013	H	4.00372	-3.49058	0.00026
C	4.47382	0.65167	0.00017	H	5.41902	1.18687	0.00022
C	4.46895	-0.72343	0.00022	H	5.40360	-1.27564	0.00031
C	3.23034	-1.46133	0.00014	H	4.09837	3.41921	0.00004
C	2.03113	-0.71278	0.00002	H	1.89502	4.54904	-0.00012

H	-0.22623	3.25339	-0.00017
O	-2.14362	1.46748	0.00002
C	-3.43084	1.26336	0.00019
C	-4.08048	0.01228	0.00016
C	-3.46472	-1.25899	-0.00003
O	-2.18372	-1.47268	-0.00018
H	-5.16248	0.02904	0.00032
C	-4.25591	2.52782	0.00045
C	-4.32650	-2.49949	0.00004
H	-5.32729	2.32217	0.00014
H	-4.00420	3.12638	0.88175
H	-4.00377	3.12705	-0.88025
H	-5.39193	-2.26460	0.00018
H	-4.09312	-3.10526	-0.88165
H	-4.09292	-3.10532	0.88165

Table S21. 1c singlet and triplet excited states computed at the deformed geometry obtained by a 0.10 Å shift of the central metal out of the ligands average plane. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 82 -> 83 for the HOMO -> LUMO transition when the HOMO is the 82th orbital and the LUMO is the 83th one). The second way assign the "0" label to the HOMO, the "–1" label to the HOMO-1 orbital and so on, the "0" label to the LUMO, "1" to LUMO+1 and so on (thus, 0 -> 0 is the HOMO -> LUMO transition, -2 -> 1 is the HOMO-2 -> LUMO+1 transition).

Singlet Excited States

eV	nm	cm^{-1}	f
3.182	389.64	25664.7	0.0353
3.3848	366.3	27300.0	0.0107
3.5929	345.08	28978.8	0.0204
3.6748	337.39	29639.3	0.0079
3.7549	330.19	30285.6	0.0076
3.803	326.01	30673.9	0.0666
3.8135	325.12	30757.9	0.0034
3.8761	319.86	31263.7	0.0115
3.9464	314.17	31829.9	0.0024
4.0058	309.51	32309.1	0.0530

HOMO is orbital 82 and LUMO is orbital 83

Excited State: 1
3.182eV 389.64 nm 25665 cm^{-1} f=0.0353

80 ->	83	9.35%	-2 ->	0
82 ->	83	80.01%	0 ->	0

Excited State: 2
3.3848eV 366.3 nm 27300 cm^{-1} f=0.0107

80 ->	83	6.89%	-2 ->	0
81 ->	83	83.88%	-1 ->	0
82 ->	83	2.48%	0 ->	0

Excited State: 3
3.5929eV 345.08 nm 28979 cm^{-1} f=0.0204

80 ->	83	41.79%	-2 ->	0
80 ->	86	7.15%	-2 ->	3
81 ->	83	4.67%	-1 ->	0
81 ->	84	3.55%	-1 ->	1
81 ->	86	15.9%	-1 ->	3
82 ->	83	8.6%	0 ->	0
82 ->	85	3.69%	0 ->	2

Excited State: 4
3.6748eV 337.39 nm 29639 cm^{-1} f=0.0079

80 ->	83	17.93%	-2 ->	0
80 ->	86	2.22%	-2 ->	3
81 ->	84	4.2%	-1 ->	1
81 ->	85	4.54%	-1 ->	2
81 ->	86	13.45%	-1 ->	3
82 ->	84	25.78%	0 ->	1
82 ->	85	6.34%	0 ->	2
82 ->	86	9.86%	0 ->	3

Excited State: 5
3.7549eV 330.19 nm 30286 cm^{-1} f=0.0076

75 ->	86	3.71%	-7 ->	3
78 ->	86	4.37%	-4 ->	3
79 ->	86	3.24%	-3 ->	3
80 ->	83	3.5%	-2 ->	0
81 ->	84	5.95%	-1 ->	1
81 ->	85	9.47%	-1 ->	2
81 ->	86	6.8%	-1 ->	3
82 ->	86	43.59%	0 ->	3

Excited State: 6
3.803eV 326.01 nm 30674 cm^{-1} f=0.0666

79 ->	83	14.58%	-3 ->	0
80 ->	83	11.59%	-2 ->	0
80 ->	84	3.99%	-2 ->	1
81 ->	83	2.11%	-1 ->	0
81 ->	86	6.29%	-1 ->	3
82 ->	84	41.57%	0 ->	1
82 ->	86	5.12%	0 ->	3

Excited State: 7
3.8135eV 325.12 nm 30758 cm^{-1} f=0.0034

79 ->	83	7.24%	-3 ->	0
80 ->	84	8.02%	-2 ->	1
80 ->	85	11.94%	-2 ->	2
81 ->	84	6.94%	-1 ->	1
81 ->	85	10.96%	-1 ->	2
81 ->	86	18.27%	-1 ->	3
82 ->	84	2.21%	0 ->	1
82 ->	85	19.46%	0 ->	2

Excited State: 8
3.8761eV 319.86 nm 31264 cm^{-1} f=0.0115

80 ->	84	4.36%	-2 ->	1
80 ->	85	2.52%	-2 ->	2
81 ->	84	13.91%	-1 ->	1
81 ->	85	3.77%	-1 ->	2
82 ->	84	2.78%	0 ->	1
82 ->	85	47.08%	0 ->	2
82 ->	86	9.78%	0 ->	3

Excited State: 9
3.9464eV 314.17 nm 31830 cm^{-1} f=0.0024

77 ->	86	10.74%	-5 ->	3
78 ->	86	6.07%	-4 ->	3
80 ->	83	2.09%	-2 ->	0
80 ->	86	51.48%	-2 ->	3
81 ->	84	3.57%	-1 ->	1

Excited State: 10
4.0058eV 309.51 nm 32309 cm^{-1} f=0.0530

78 ->	83	2.79%	-4 ->	0
79 ->	83	47.54%	-3 ->	0
81 ->	84	8.29%	-1 ->	1
81 ->	85	12.21%	-1 ->	2
82 ->	84	10.75%	0 ->	1

82 -> 85 2.93% 0 -> 2

Triplet Excited States

	eV	nm	cm-1
1	2.4663	502.71	19892.2
2	2.7985	443.04	22571.3
3	2.8375	436.95	22885.9
4	2.8922	428.69	23326.9
5	3.1111	398.53	25092.2
6	3.163	391.99	25510.9
7	3.2098	386.27	25888.6
8	3.2639	379.86	26325.5
9	3.5832	346.02	28900.1
10	3.6867	336.3	29735.4

HOMO is orbital 82 and LUMO is orbital 83

Excited State: 1
2.4663eV 502.71 nm 19892 cm^{-1} f=0.0000
74 -> 83 3.93% -8 -> 0
75 -> 84 2.28% -7 -> 1
78 -> 84 3.63% -4 -> 1
79 -> 83 35.33% -3 -> 0
79 -> 87 4.49% -3 -> 4
80 -> 83 6.28% -2 -> 0
80 -> 84 2.71% -2 -> 1
81 -> 84 3.74% -1 -> 1
81 -> 85 2.09% -1 -> 2
82 -> 83 30.32% 0 -> 0
82 -> 84 22.29% 0 -> 1
82 -> 85 6.36% 0 -> 2
82 -> 87 3.79% 0 -> 4

Excited State: 2
2.7985eV 443.04 nm 22571 cm^{-1} f=0.0000
80 -> 86 24.14% -2 -> 3
81 -> 85 3.3% -1 -> 2
81 -> 86 62.06% -1 -> 3
82 -> 85 3.14% 0 -> 2
82 -> 86 9.23% 0 -> 3

Excited State: 3
2.8375eV 436.95 nm 22886 cm^{-1} f=0.0000
79 -> 83 5% -3 -> 0
80 -> 83 6.19% -2 -> 0
80 -> 84 5.62% -2 -> 1
81 -> 83 2.76% -1 -> 0
81 -> 84 3.55% -1 -> 1
82 -> 83 60.87% 0 -> 0
82 -> 84 6.44% 0 -> 1
82 -> 85 10.93% 0 -> 2

Excited State: 4
2.8922eV 428.69 nm 23327 cm^{-1} f=0.0000
79 -> 84 2.91% -3 -> 1
79 -> 85 5.86% -3 -> 2
80 -> 83 3.38% -2 -> 0
80 -> 84 7.1% -2 -> 1
80 -> 85 24.05% -2 -> 2
81 -> 84 3.3% -1 -> 1
81 -> 85 12.73% -1 -> 2
81 -> 86 3.69% -1 -> 3
OK
82 -> 83 4.16% 0 -> 0
82 -> 84 18.76% 0 -> 1
82 -> 85 25.19% 0 -> 2

Excited State: 5
3.1111eV 398.53 nm 25092 cm^{-1} f=0.0000
74 -> 86 4.05% -8 -> 3
75 -> 86 2.89% -7 -> 3
78 -> 86 18.51% -4 -> 3
79 -> 83 4.31% -3 -> 0
79 -> 86 7.85% -3 -> 3
80 -> 83 7.82% -2 -> 0
80 -> 86 6.51% -2 -> 3
81 -> 86 11.15% -1 -> 3
82 -> 84 8.11% 0 -> 1
82 -> 86 63% 0 -> 3
82 -> 87 3.28% 0 -> 4

Excited State: 6
3.163eV 391.99 nm 25511 cm^{-1} f=0.0000
75 -> 86 12.82% -7 -> 3
77 -> 86 7.75% -5 -> 3
79 -> 83 3.72% -3 -> 0
80 -> 83 9.47% -2 -> 0
80 -> 86 13.76% -2 -> 3
81 -> 83 5.2% -1 -> 0
82 -> 84 8.06% 0 -> 1
82 -> 86 33.73% 0 -> 3

Excited State: 7
3.2098eV 386.27 nm 25889 cm^{-1} f=0.0000
75 -> 86 2.65% -7 -> 3
77 -> 86 9.69% -5 -> 3
78 -> 86 9.09% -4 -> 3
79 -> 83 7.54% -3 -> 0
80 -> 83 12.38% -2 -> 0
80 -> 86 26.32% -2 -> 3
81 -> 83 4.12% -1 -> 0
81 -> 86 5.48% -1 -> 3
82 -> 84 8.87% 0 -> 1
82 -> 85 5.12% 0 -> 2
82 -> 87 3.46% 0 -> 4

Excited State: 8
3.2639eV 379.86 nm 26325 cm^{-1} f=0.0000
80 -> 83 16.55% -2 -> 0
81 -> 83 72.07% -1 -> 0
81 -> 84 4.51% -1 -> 1

Excited State: 9
3.5832eV 346.02 nm 28900 cm^{-1} f=0.0000
75 -> 83 4.14% -7 -> 0
77 -> 83 4.53% -5 -> 0
78 -> 83 2.04% -4 -> 0
79 -> 83 42.34% -3 -> 0
79 -> 87 2.32% -3 -> 4
80 -> 83 20.74% -2 -> 0
80 -> 84 6.78% -2 -> 1
81 -> 83 2.55% -1 -> 0
82 -> 83 4.36% 0 -> 0
82 -> 84 4.86% 0 -> 1
82 -> 85 2.41% 0 -> 2

Excited State: 10
3.6867eV 336.3 nm 29735 cm^{-1} f=0.0000
70 -> 86 2.82% -12 -> 3
73 -> 86 4.96% -9 -> 3
75 -> 86 7.42% -7 -> 3
76 -> 86 66.53% -6 -> 3
77 -> 86 16.99% -5 -> 3

(BzQ)Pt(acac) (2c)

Table S22. Singlet and triplet excited states of (BzQ)Pt(acac) (**2c**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Excited State: 1
3.0044 eV 412.68 nm f=0.0344
81 -> 83 7.53 %
82 -> 83 83.71 %

Excited State: 2
3.3577 eV 369.25 nm f=0.0018
80 -> 83 97.02 %

Excited State: 3
3.4579 eV 358.55 nm f=0.0149
81 -> 83 52.83 %
82 -> 83 6.77 %
82 -> 84 29.60 %
82 -> 85 2.98 %

Excited State: 4
3.6357 eV 341.01 nm f=0.1190
81 -> 83 21.01 %
82 -> 84 58.12 %
82 -> 85 12.10 %

Excited State: 5
3.7989 eV 326.37 nm f=0.1100
78 -> 83 2.80 %
79 -> 83 8.81 %
81 -> 83 8.67 %
81 -> 84 2.23 %
82 -> 84 3.14 %
82 -> 85 66.48 %

Excited State: 6
3.8009 eV 326.20 nm f=0.0004
80 -> 84 89.59 %
80 -> 85 8.78 %

Excited State: 7
4.0027 eV 309.75 nm f=0.0285
76 -> 83 3.28 %
78 -> 83 3.22 %
79 -> 83 63.89 %
81 -> 85 15.20 %
82 -> 85 4.63 %

Excited State: 8
4.0660 eV 304.92 nm f=0.0441
78 -> 83 4.80 %
78 -> 84 2.19 %
79 -> 83 8.28 %
81 -> 84 69.17 %
81 -> 85 4.68 %

Excited State: 9
4.1437 eV 299.21 nm f=0.0000
77 -> 83 93.82 %

Excited State: 10
4.1871 eV 296.11 nm f=0.0048
78 -> 83 22.49 %
79 -> 83 7.15 %
79 -> 84 2.06 %
79 -> 85 4.37 %
81 -> 83 2.35 %
81 -> 84 13.29 %
81 -> 85 33.30 %
82 -> 85 4.39 %

Excited State: 11
4.1948 eV 295.57 nm f=0.0029
80 -> 84 8.39 %
80 -> 85 87.78 %

Excited State: 12
4.4379 eV 279.37 nm f=0.0709
78 -> 83 30.88 %
78 -> 85 2.73 %
79 -> 84 7.58 %
79 -> 85 11.58 %
81 -> 85 35.79 %
82 -> 86 3.54 %

Excited State: 13
4.4528 eV 278.44 nm f=0.0000
77 -> 84 79.37 %
77 -> 85 9.47 %
82 -> 88 5.34 %

Excited State: 14
4.6209 eV 268.31 nm f=0.0001
75 -> 83 6.81 %
75 -> 84 15.00 %
75 -> 85 2.56 %
76 -> 88 2.18 %
77 -> 84 2.59 %
82 -> 87 5.19 %
82 -> 88 52.68 %

Excited State: 15
4.6428 eV 267.05 nm f=0.0006
75 -> 83 40.47 %
75 -> 84 23.25 %
75 -> 85 7.41 %
77 -> 84 3.86 %
82 -> 88 14.78 %

Excited State: 16
4.6680 eV 265.60 nm f=0.0459
76 -> 83 15.42 %
78 -> 83 12.53 %
79 -> 84 13.97 %
80 -> 87 2.32 %
80 -> 88 20.72 %
82 -> 86 21.46 %

Excited State: 17
4.6775 eV 265.06 nm f=0.0209
76 -> 83 10.53 %
78 -> 83 7.94 %
79 -> 84 2.22 %
79 -> 85 7.66 %
80 -> 88 35.52 %
81 -> 86 5.25 %
82 -> 86 17.20 %

Excited State: 18
4.8024 eV 258.17 nm f=0.0095
76 -> 83 62.15 %
79 -> 84 3.59 %
79 -> 85 2.38 %
80 -> 88 18.71 %

Excited State: 19
4.8184 eV 257.31 nm f=0.0002
75 -> 83 41.81 %
75 -> 84 37.20 %
75 -> 85 3.12 %
81 -> 88 6.75 %

Excited State: 20
4.8599 eV 255.12 nm f=0.0264
78 -> 84 3.11 %
79 -> 84 55.10 %
79 -> 85 14.27 %
80 -> 88 4.86 %
82 -> 86 10.60 %

Excited State: 21
4.8768 eV 254.23 nm f=0.0000
75 -> 83 7.14 %
75 -> 84 3.97 %
76 -> 88 2.00 %
77 -> 84 2.03 %
77 -> 85 11.04 %
78 -> 88 4.77 %
81 -> 87 6.34 %
81 -> 88 52.81 %

Excited State: 22
4.9803 eV 248.95 nm f=0.0686
78 -> 83 3.40 %
78 -> 84 12.59 %
78 -> 85 10.36 %
79 -> 85 39.99 %
80 -> 88 2.23 %
81 -> 86 3.56 %
82 -> 86 13.80 %
82 -> 89 2.27 %

Excited State: 23
5.0020 eV 247.87 nm f=0.0000
77 -> 84 8.15 %
77 -> 85 73.25 %
81 -> 88 11.02 %

Excited State: 24
5.1043 eV 242.90 nm f=0.0411
77 -> 88 7.14 %
78 -> 84 64.45 %
78 -> 85 5.27 %
79 -> 84 2.45 %
81 -> 86 4.37 %
82 -> 86 4.97 %

Excited State: 25
5.1840 eV 239.17 nm f=0.0016
82 -> 87 88.50 %
82 -> 88 6.96 %

Excited State: 26
5.1846 eV 239.14 nm f=0.0035
76 -> 84 3.42 %
77 -> 87 3.52 %
77 -> 88 64.47 %
78 -> 84 3.19 %
81 -> 86 13.81 %

Excited State: 27
5.2187 eV 237.57 nm f=0.0005
74 -> 83 7.59 %
77 -> 88 7.30 %
78 -> 84 2.90 %
78 -> 85 22.43 %
81 -> 86 43.16 %
82 -> 86 4.06 %

Excited State: 28
5.2274 eV 237.18 nm f=0.0050
80 -> 86 95.34 %

Excited State: 29
5.2796 eV 234.84 nm f=0.0893
74 -> 83 7.63 %
76 -> 84 23.11 %
77 -> 88 6.19 %
78 -> 85 26.71 %
78 -> 86 2.21 %
79 -> 85 2.08 %
79 -> 86 7.23 %
81 -> 86 5.65 %
82 -> 86 5.70 %

Excited State: 30
5.4004 eV 229.58 nm f=0.2230
74 -> 83 7.82 %
76 -> 84 52.65 %
78 -> 85 9.58 %
79 -> 86 7.14 %
82 -> 89 3.32 %

Triplet Excited States

Excited State: 1
1.9520 eV 635.17 nm f=0.0000
100 -> 107 12.16 %
102 -> 107 4.84 %
103 -> 107 32.22 %
105 -> 107 8.84 %
106 -> 107 64.77 %

Excited State: 2
2.3566 eV 526.11 nm f=0.0000
98 -> 107 4.44 %
100 -> 107 2.39 %
102 -> 107 3.68 %
103 -> 107 30.70 %
105 -> 107 39.40 %
105 -> 108 4.27 %
106 -> 107 25.97 %
106 -> 108 2.73 %
106 -> 109 2.76 %

Excited State: 3
2.4749 eV 500.97 nm f=0.0000
98 -> 108 2.45 %
102 -> 107 3.85 %
102 -> 108 3.50 %
102 -> 109 6.56 %
103 -> 108 2.71 %
103 -> 110 3.24 %
105 -> 107 8.56 %
105 -> 108 33.74 %
106 -> 108 24.41 %
106 -> 109 34.13 %
106 -> 110 3.77 %

Excited State: 4
2.6456 eV 468.64 nm f=0.0000
104 -> 107 100.00 %

Excited State: 5
2.7893 eV 444.49 nm f=0.0000
105 -> 108 10.59 %
106 -> 108 72.97 %
106 -> 109 19.37 %
106 -> 114 2.17 %

Excited State: 5
2.7893 eV 444.49 nm f=0.0000
105 -> 108 10.59 %

106 -> 108 72.97 %
106 -> 109 19.37 %
106 -> 114 2.17 %

Excited State: 6
 3.1344 eV 395.56 nm f=0.0000
100 -> 107 27.60 %
102 -> 107 18.12 %
103 -> 107 15.45 %
105 -> 107 24.20 %
105 -> 108 7.30 %
106 -> 107 10.37 %

Excited State: 7
 3.1761 eV 390.37 nm f=0.0000
 94 -> 108 2.61 %
 97 -> 108 2.29 %
105 -> 107 3.85 %
105 -> 108 45.89 %
106 -> 109 38.30 %
106 -> 110 7.24 %

Excited State: 8
 3.3808 eV 366.73 nm f=0.0000
101 -> 107 97.91 %

Excited State: 9
 3.5393 eV 350.31 nm f=0.0000
100 -> 107 6.95 %
102 -> 107 39.91 %
102 -> 108 3.29 %
103 -> 107 20.36 %
103 -> 108 4.41 %
105 -> 107 17.64 %
106 -> 110 3.42 %

Excited State: 10
 3.6321 eV 341.35 nm f=0.0000
104 -> 108 95.25 %
104 -> 109 3.18 %

Excited State: 11
 3.7052 eV 334.62 nm f=0.0000
 98 -> 108 2.11 %
100 -> 107 3.73 %
102 -> 107 2.41 %
102 -> 108 12.91 %
103 -> 107 3.81 %
103 -> 108 45.08 %
105 -> 107 4.09 %
105 -> 108 2.72 %
105 -> 110 4.69 %
106 -> 109 7.46 %
106 -> 110 10.70 %

Excited State: 12
 3.7848 eV 327.59 nm f=0.0000
 98 -> 107 8.06 %
100 -> 107 29.36 %
102 -> 107 15.70 %
102 -> 108 14.51 %
103 -> 107 6.55 %
103 -> 108 10.13 %
104 -> 111 2.13 %
105 -> 109 9.63 %
106 -> 108 2.47 %

Excited State: 13
 3.8045 eV 325.89 nm f=0.0000
 95 -> 107 6.34 %
 96 -> 107 6.54 %
 99 -> 107 86.58 %

Excited State: 14
 3.8513 eV 321.92 nm f=0.0000
 98 -> 107 10.69 %
100 -> 107 14.50 %
100 -> 108 2.49 %
102 -> 107 7.90 %
102 -> 108 20.86 %
103 -> 107 2.96 %
103 -> 108 4.56 %
103 -> 109 4.02 %
105 -> 109 23.99 %

Excited State: 15
 3.9061 eV 317.41 nm f=0.0000
 98 -> 111 7.03 %
102 -> 111 15.09 %
103 -> 111 6.72 %
106 -> 111 73.20 %

Excited State: 16
 3.9310 eV 315.40 nm f=0.0000
104 -> 111 99.94 %

Excited State: 17
 4.0119 eV 309.04 nm f=0.0000
100 -> 108 2.72 %
102 -> 108 9.53 %
102 -> 109 3.02 %
103 -> 108 19.87 %
103 -> 109 12.10 %
105 -> 108 2.84 %
105 -> 109 43.86 %
106 -> 110 5.41 %

Excited State: 18
 4.0853 eV 303.49 nm f=0.0000
100 -> 111 7.28 %
102 -> 111 8.76 %
103 -> 111 36.12 %
105 -> 111 51.72 %

Excited State: 19
 4.1651 eV 297.67 nm f=0.0000
 98 -> 109 2.28 %
100 -> 109 4.37 %
102 -> 108 29.06 %
102 -> 109 19.20 %
103 -> 109 2.91 %
106 -> 110 35.69 %
106 -> 114 3.34 %
106 -> 118 2.16 %

Excited State: 20
 4.4283 eV 279.98 nm f=0.0000
100 -> 109 6.23 %
102 -> 109 17.78 %
103 -> 108 2.01 %
103 -> 109 18.59 %
103 -> 110 2.68 %
105 -> 109 10.95 %
105 -> 110 2.30 %
106 -> 109 6.71 %
106 -> 110 21.33 %
106 -> 113 2.64 %
106 -> 114 2.18 %

Figure S19. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

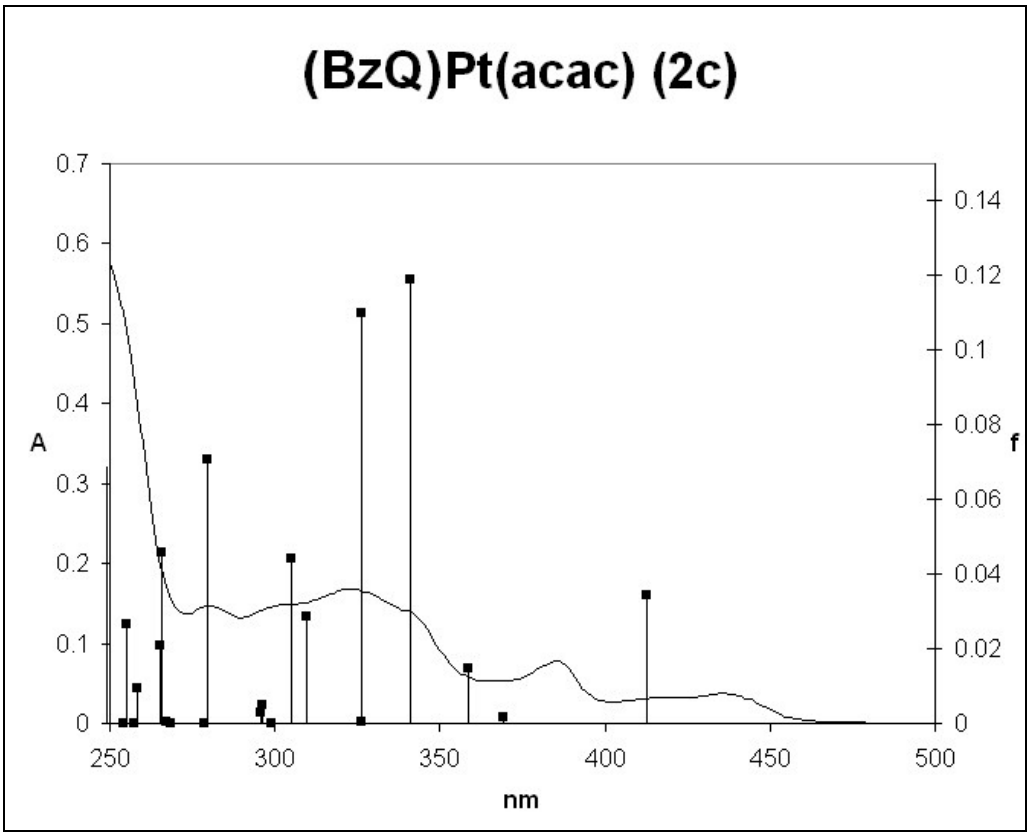


Figure S20. In the following picture, some (BzQ)Pt(acac) (**2c**) Kohn-Sham orbitals are reported that are relevant in describing the low-in-energy electronic transitions.

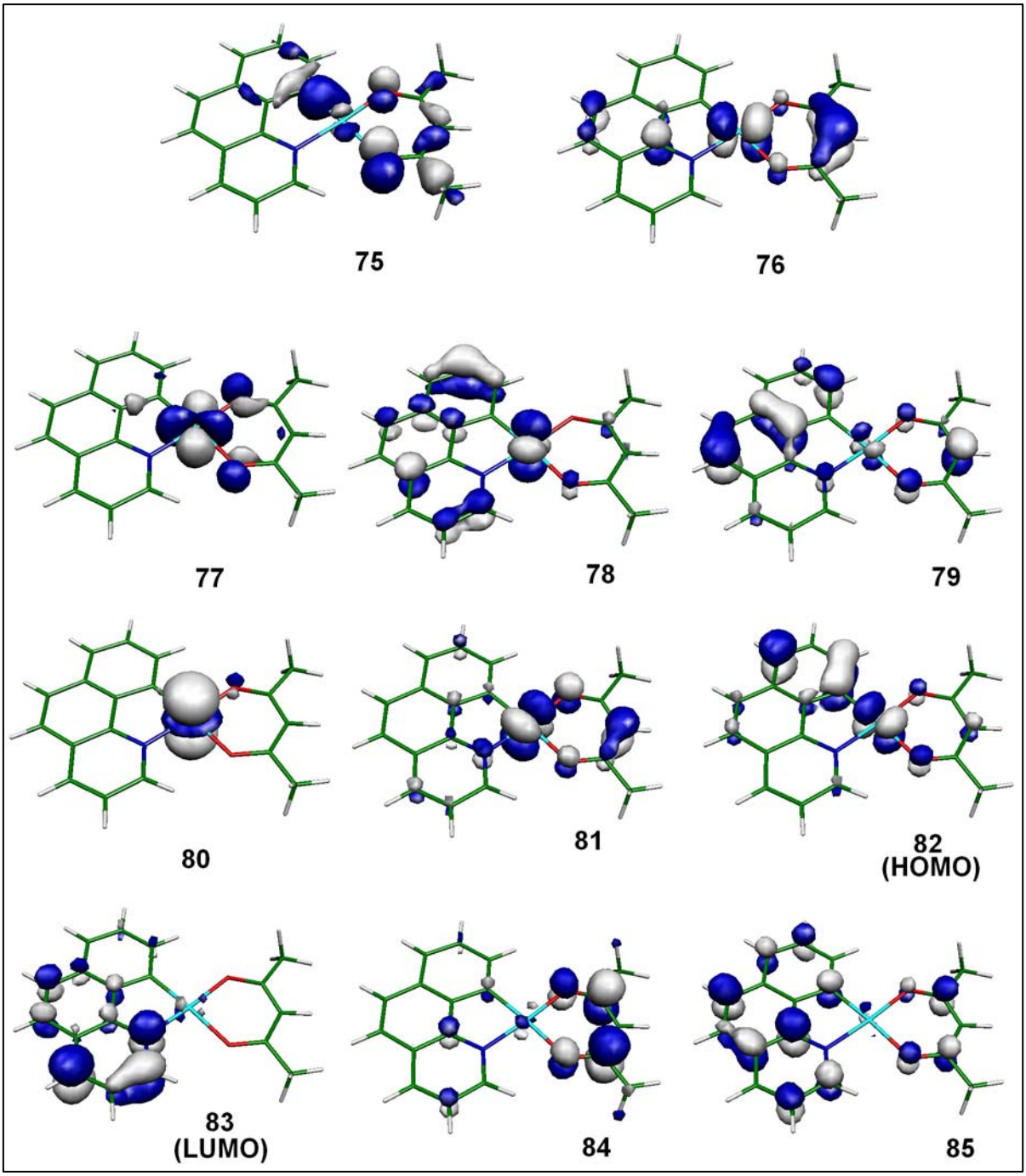


Table S23. Optimized structure of (BzQ)Pt(acac) (**2c**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pt	-0.62834	0.02875	-0.00008
C	0.86928	1.33527	-0.00009
C	2.14518	0.69994	0.00001
C	3.37944	1.39423	0.00006
C	3.33105	2.80918	0.00000
C	2.09112	3.45129	-0.00008
C	0.86804	2.73185	-0.00011
C	4.59344	0.61178	0.00014
C	4.57032	-0.76317	0.00016
C	3.32236	-1.48554	0.00010
C	2.13505	-0.71944	0.00003
N	0.88516	-1.29694	-0.00003
C	0.77180	-2.63539	-0.00003
C	1.91280	-3.46115	0.00003
C	3.18692	-2.89376	0.00010
H	-0.23664	-3.02788	-0.00007

H	1.77977	-4.53566	0.00003
H	4.07012	-3.52423	0.00014
H	5.54576	1.13421	0.00017
H	5.49746	-1.32784	0.00022
H	4.25060	3.38612	0.00003
H	2.05799	4.53712	-0.00011
H	-0.07389	3.26976	-0.00014
O	-2.04761	1.46698	0.00003
C	-3.33865	1.26475	0.00012
C	-3.98853	0.01613	0.00009
C	-3.37858	-1.25730	-0.00001
O	-2.09649	-1.47440	-0.00007
H	-5.07040	0.03618	0.00020
C	-4.15200	2.53421	0.00029
C	-4.23886	-2.49690	0.00005
H	-5.22453	2.33543	-0.00015
H	-3.89676	3.13118	0.88155
H	-3.89612	3.13185	-0.88033
H	-5.30396	-2.26095	0.00023
H	-4.00651	-3.10286	-0.88171
H	-4.00624	-3.10298	0.88165

Table S24. 2c singlet and triplet excited states computed at the deformed geometry obtained by a 0.10 Å shift of the central metal out of the ligands average plane. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 82 -> 83 for the HOMO -> LUMO transition when the HOMO is the 82th orbital and the LUMO is the 83th one). The second way assign the "0" label to the HOMO, the "–1" label to the HOMO-1 orbital and so on, the "0" label to the LUMO, "1" to LUMO+1 and so on (thus, 0 -> 0 is the HOMO -> LUMO transition, -2 -> 1 is the HOMO-2 -> LUMO+1 transition).

Singlet Excited State

HOMO is orbital 82 and LUMO orbital 83

eV	nm	cm^{-1}	f
2.9734	416.98	23982.0	0.0310
3.3183	373.64	26763.7	0.0056
3.4534	359.02	27853.6	0.0083
3.5893	345.43	28949.4	0.1092
3.7778	328.19	30470.2	0.1192
3.7853	327.54	30530.6	0.0029
3.9818	311.37	32116.1	0.0189
4.0069	309.42	32318.5	0.0346
4.0267	307.91	32477.0	0.0036
4.1377	299.65	33372.3	0.0016

Excited State: 1
2.9734 eV 416.98 nm 23982 cm^{-1} f=0.0310

80 -> 83	3.24%	-2	0
81 -> 83	4.4%	-1	0
82 -> 83	84.32%	0	0

Excited State: 2
3.3183 eV 373.64 nm 26764 cm^{-1} f=0.0056

80 -> 83	46.49%	-2	0
81 -> 83	47.02%	-1	0

Excited State: 3
3.4534 eV 359.02 nm 27854 cm^{-1} f=0.0083

80 -> 83	31.8%	-2	0
81 -> 83	17.09%	-1	0
82 -> 83	5.7%	0	0
82 -> 84	34.73%	0	1
82 -> 85	2.34%	0	2

Excited State: 4
3.5893 eV 345.43 nm 28949 cm^{-1} f=0.1092

80 -> 83	8.88%	-2	0
80 -> 84	2.57%	-2	1
81 -> 83	16.2%	-1	0
82 -> 84	48.41%	0	1
82 -> 85	12.48%	0	2

Excited State: 5
3.7778 eV 328.19 nm 30470 cm^{-1} f=0.1192

78 -> 83	2.61%	-4	0
79 -> 83	7.41%	-3	0
80 -> 83	2.85%	-2	0
81 -> 83	6.47%	-1	0
81 -> 84	4.58%	-1	1

Excited State: 6
3.7853eV 327.54nm 30531 cm^{-1} f=0.0029

80 -> 84	68.56%	-2	1
80 -> 85	5.5%	-2	2
81 -> 84	13.98%	-1	1
82 -> 85	4.46%	0	2

Excited State: 7
3.9818eV 311.37nm 32116 cm^{-1} f=0.0189

76 -> 83	2.09%	-6	0
77 -> 83	3.26%	-5	0
78 -> 83	3.81%	-4	0
79 -> 83	58.99%	-3	0
81 -> 84	2.86%	-1	1
81 -> 85	15.9%	-1	2
82 -> 85	3.94%	0	2

Excited State: 8
4.0069eV 309.42nm 32319 cm^{-1} f=0.0346

78 -> 84	2.05%	-4	1
79 -> 83	10.09%	-3	0
80 -> 84	14.4%	-2	1
81 -> 84	57.62%	-1	1
81 -> 85	2%	-1	2

Excited State: 9
4.0267eV 307.91nm 32477 cm^{-1} f=0.0036

77 -> 83	39.49%	-5	0
78 -> 83	12.01%	-4	0
80 -> 85	16.39%	-2	2
81 -> 84	2.42%	-1	1
81 -> 85	12.36%	-1	2

Excited State: 10
4.1377eV 299.65nm 33372 cm^{-1} f=0.0016

77 -> 83	38.93%	-5	0
78 -> 83	10.13%	-4	0
79 -> 83	2.94%	-3	0
80 -> 85	35.82%	-2	2

Triplet Excited States

HOMO is orbital 82 and LUMO orbital 83

eV	nm	cm^{-1}	f
2.3778	521.43	19178.0	0
2.663	465.57	21479.0	0
2.8207	439.55	22750.5	0
2.9708	417.34	23961.3	0
3.2090	386.37	25881.9	0
3.4108	363.5	27510.3	0
3.4905	355.21	28152.4	0
3.6700	337.83	29600.7	0
3.7024	334.88	29861.4	0
3.8872	318.95	31352.9	0

Excited State: 1
2.3778eV 521.43nm 19178 cm^{-1} f=0.0000

74	->	83	3.58%	-8	0
78	->	85	5.34%	-4	2
79	->	83	21.9%	-3	0
79	->	85	2.81%	-3	2
79	->	86	3.87%	-3	3
80	->	83	9.19%	-2	0
81	->	83	12.65%	-1	0
81	->	85	2.46%	-1	2
82	->	83	40.77%	0	0
82	->	84	5.24%	0	1
82	->	85	16.82%	0	2
82	->	86	2.75%	0	3

Excited State: 2
2.663eV 465.57nm 21479 cm^{-1} f=0.0000

79	->	83	5.07%	-3	0
80	->	83	3.32%	-2	0
81	->	83	12.53%	-1	0
81	->	84	2.7%	-1	1
82	->	83	61.23%	0	0
82	->	84	3.87%	0	1
82	->	85	14.22%	0	2

Excited State: 3
2.8207eV 439.55nm 22751 cm^{-1} f=0.0000

76	->	84	5.24%	-6	1
79	->	83	2.09%	-3	0
79	->	84	12.7%	-3	1
79	->	85	2.35%	-3	2
81	->	83	2.79%	-1	0
81	->	84	33.94%	-1	1
81	->	85	7.19%	-1	2
82	->	84	39.02%	0	1
82	->	85	8.1%	0	2

Excited State: 4
2.9708eV 417.34nm 23961 cm^{-1} f=0.0000

76	->	83	2.19%	-6	0
80	->	83	5.88%	-2	0
81	->	83	44.8%	-1	0
82	->	84	12.6%	0	1
82	->	85	26.23%	0	2
82	->	86	8.07%	0	3

Excited State: 5
3.209eV 386.37nm 25882 cm^{-1} f=0.0000

80	->	83	74.38%	-2	0
81	->	83	16.94%	-1	0
81	->	84	2.66%	-1	1

Excited State: 6
3.4108eV 363.5nm 27510 cm^{-1} f=0.0000

78	->	84	4.57%	-4	1
79	->	83	7.95%	-3	0
80	->	84	8.15%	-2	1
81	->	84	42.72%	-1	1
81	->	85	3.19%	-1	2
82	->	84	24.46%	0	1
82	->	85	4.73%	0	2

Excited State: 7
3.4905eV 355.21nm 28152 cm^{-1} f=0.0000

76	->	83	4.69%	-6	0
78	->	83	4.33%	-4	0
79	->	83	52.16%	-3	0
79	->	86	2.01%	-3	3
80	->	83	2.02%	-2	0
80	->	85	2.21%	-2	2
81	->	83	4.15%	-1	0
81	->	85	3.92%	-1	2
82	->	85	19.56%	0	2

Excited State: 8
3.67eV 337.83nm 29601 cm^{-1} f=0.0000

74	->	83	5.53%	-8	0
74	->	85	2.38%	-8	2
75	->	83	3.14%	-7	0
76	->	83	2.49%	-6	0
78	->	83	59.43%	-4	0
79	->	85	2.35%	-3	2
79	->	86	2.96%	-3	3
80	->	85	3.14%	-2	2
81	->	85	3.97%	-1	2
82	->	84	3.18%	0	1
82	->	86	8.53%	0	3

Excited State: 9
3.7024eV 334.88nm 29861 cm^{-1} f=0.0000

79	->	84	2.48%	-3	1
80	->	84	74.21%	-2	1
80	->	85	4.59%	-2	2
80	->	88	4.73%	-2	5
81	->	84	7.13%	-1	1

Excited State: 10
3.8872eV 318.95nm 31353 cm^{-1} f=0.0000

78	->	84	2.12%	-4	1
78	->	85	8.63%	-4	2
79	->	84	8.07%	-3	1
79	->	85	11.34%	-3	2
80	->	85	5.07%	-2	2
81	->	83	5.12%	-1	0
81	->	84	5.18%	-1	1
81	->	85	37.98%	-1	2
82	->	86	6.93%	0	3

(BzQ)Pd(hfacac) (1f)

Table S25. Singlet and triplet excited states of (BzQ)Pd(hfacac) (**1f**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Singlet Excited States

Excited State: 1
2.7038 eV 458.56 nm f=0.0090
106 -> 107 93.93 %

Excited State: 2
2.8368 eV 437.06 nm f=0.0000
104 -> 107 97.99 %

Excited State: 3
3.3689 eV 368.03 nm f=0.0492
100 -> 107 2.35 %
103 -> 107 7.59 %
105 -> 107 67.44 %
106 -> 108 13.70 %

Excited State: 4
3.3767 eV 367.18 nm f=0.0636
103 -> 107 3.21 %
104 -> 110 7.94 %
105 -> 107 9.13 %
105 -> 109 2.26 %
106 -> 108 68.75 %

Excited State: 5
3.6160 eV 342.88 nm f=0.0244
100 -> 107 2.00 %
103 -> 107 35.37 %
104 -> 110 29.35 %
105 -> 107 16.50 %
106 -> 108 3.88 %

Excited State: 6
3.6726 eV 337.59 nm f=0.0000
98 -> 110 3.97 %
102 -> 110 8.44 %
103 -> 110 4.69 %
106 -> 110 71.72 %

Excited State: 7
3.7526 eV 330.39 nm f=0.0051
100 -> 107 3.41 %
103 -> 107 33.27 %
104 -> 110 36.64 %
105 -> 107 3.01 %
105 -> 108 5.23 %
106 -> 108 2.58 %

Excited State: 8
3.7757 eV 328.37 nm f=0.0027
104 -> 108 96.62 %

Excited State: 9
3.8836 eV 319.24 nm f=0.0001
101 -> 107 85.31 %
105 -> 110 2.28 %

Excited State: 10
3.9492 eV 313.95 nm f=0.0017
104 -> 110 5.25 %
105 -> 108 50.93 %
106 -> 109 33.67 %

Excited State: 11
4.0377 eV 307.06 nm f=0.0648
98 -> 107 2.24 %
102 -> 107 86.76 %
105 -> 108 2.78 %

Excited State: 12
4.0456 eV 306.46 nm f=0.0007
96 -> 107 3.78 %
99 -> 107 80.89 %
103 -> 110 2.93 %
105 -> 110 2.98 %

Excited State: 13
4.0736 eV 304.36 nm f=0.0000
99 -> 107 6.83 %
100 -> 110 6.52 %
101 -> 107 7.22 %
102 -> 110 9.29 %
103 -> 110 30.52 %
105 -> 110 27.54 %

Excited State: 14
4.2858 eV 289.29 nm f=0.1017
102 -> 107 2.86 %
102 -> 108 3.23 %
105 -> 108 25.30 %
105 -> 111 2.20 %
106 -> 109 49.24 %

Excited State: 15
4.3338 eV 286.08 nm f=0.0039
93 -> 110 2.12 %
99 -> 110 8.65 %
101 -> 110 58.27 %
103 -> 108 23.42 %

Excited State: 16
4.3726 eV 283.55 nm f=0.0169
99 -> 110 9.01 %
101 -> 110 15.82 %
103 -> 108 65.84 %

Excited State: 17
4.4784 eV 276.85 nm f=0.0365
102 -> 108 33.59 %
102 -> 109 2.14 %
105 -> 109 48.95 %
106 -> 111 7.39 %

Excited State: 18
4.5380 eV 273.21 nm f=0.0028
104 -> 109 96.09 %

Excited State: 19
4.8390 eV 256.21 nm f=0.0242
100 -> 107 66.26 %
102 -> 108 3.84 %
103 -> 107 3.02 %
105 -> 109 4.81 %

Excited State: 20
4.8477 eV 255.76 nm f=0.0005
98 -> 110 4.65 %
101 -> 108 2.84 %
102 -> 110 9.90 %
103 -> 110 37.12 %
105 -> 110 22.98 %
106 -> 110 16.51 %

Excited State: 21
4.8994 eV 253.06 nm f=0.1490
100 -> 107 8.40 %
102 -> 108 33.62 %
102 -> 109 3.93 %
103 -> 109 4.32 %
105 -> 109 7.24 %
105 -> 111 5.51 %
106 -> 111 24.49 %

Excited State: 22
4.9854 eV 248.69 nm f=0.0000
101 -> 108 84.68 %
105 -> 110 7.14 %

Excited State: 23
5.0213 eV 246.91 nm f=0.0359
98 -> 107 4.43 %
102 -> 108 7.20 %
102 -> 109 4.42 %
103 -> 109 61.34 %
105 -> 109 9.63 %
106 -> 111 4.76 %

Excited State: 24
5.0879 eV 243.68 nm f=0.0000
96 -> 107 17.91 %
98 -> 110 4.02 %
101 -> 108 5.15 %
102 -> 110 32.75 %
105 -> 110 27.37 %
106 -> 110 3.62 %

Excited State: 25
5.1125 eV 242.51 nm f=0.0636
98 -> 107 83.01 %
102 -> 107 2.23 %
103 -> 109 2.25 %

Triplet Excited States

Excited State: 1
2.1283 eV 582.53 nm f=0.0000
100 -> 107 15.45 %
103 -> 107 70.18 %
105 -> 107 7.25 %
106 -> 107 36.63 %

Excited State: 2
2.5029 eV 495.36 nm f=0.0000
102 -> 108 4.71 %
102 -> 109 5.23 %
103 -> 107 4.00 %
105 -> 108 35.71 %
105 -> 111 3.56 %
106 -> 107 3.31 %
106 -> 108 21.80 %
106 -> 109 42.99 %
106 -> 111 5.05 %

Excited State: 3
2.7355 eV 453.23 nm f=0.0000
98 -> 107 2.85 %
102 -> 107 5.73 %
103 -> 107 16.68 %
104 -> 110 16.30 %
105 -> 107 15.01 %
105 -> 108 2.93 %
106 -> 107 43.72 %
106 -> 109 2.86 %

Excited State: 4
2.7536 eV 450.25 nm f=0.0000
103 -> 107 3.38 %
104 -> 110 95.49 %
105 -> 107 2.34 %
106 -> 107 8.52 %

Excited State: 5
2.7723 eV 447.22 nm f=0.0000
104 -> 107 98.94 %

Excited State: 6
2.9258 eV 423.75 nm f=0.0000
102 -> 108 2.15 %
105 -> 108 7.51 %
106 -> 108 75.87 %
106 -> 109 16.44 %

Excited State: 7
3.0676 eV 404.17 nm f=0.0000
98 -> 110 14.09 %
102 -> 110 20.49 %
103 -> 110 8.90 %
106 -> 110 62.96 %

Excited State: 8
3.2142 eV 385.74 nm f=0.0000
97 -> 110 2.60 %
100 -> 110 17.73 %
102 -> 110 19.01 %
103 -> 110 43.17 %
105 -> 110 28.31 %

Excited State: 9
3.2909 eV 376.74 nm f=0.0000
94 -> 108 3.01 %
97 -> 108 3.56 %
105 -> 107 4.97 %
105 -> 108 47.68 %
106 -> 109 35.69 %
106 -> 111 6.58 %

Excited State: 10
3.3252 eV 372.86 nm f=0.0000
100 -> 107 19.21 %
102 -> 107 17.73 %
103 -> 107 5.55 %
105 -> 107 44.45 %
105 -> 108 5.92 %
106 -> 107 7.72 %

Excited State: 11
3.6323 eV 341.33 nm f=0.0000
95 -> 107 5.15 %
96 -> 107 2.12 %
99 -> 107 23.81 %
101 -> 107 67.49 %

Excited State: 12
3.6492 eV 339.76 nm f=0.0000
104 -> 108 94.24 %
104 -> 109 3.38 %

Excited State: 13
3.7080 eV 334.37 nm f=0.0000
100 -> 107 9.25 %
101 -> 110 3.05 %
102 -> 107 35.22 %
102 -> 108 6.09 %
103 -> 107 8.27 %
103 -> 108 3.14 %
105 -> 107 19.20 %
105 -> 109 3.20 %
106 -> 111 6.40 %

Excited State: 14
3.7307 eV 332.33 nm f=0.0000

93 -> 110 3.94 %
99 -> 110 18.85 %
101 -> 110 80.81 %
102 -> 107 2.06 %

Excited State: 15
3.8000 eV 326.27 nm f=0.0000
96 -> 107 8.02 %
99 -> 107 63.36 %
101 -> 107 27.26 %

Excited State: 16
3.8094 eV 325.47 nm f=0.0000
98 -> 108 2.93 %
100 -> 107 6.07 %
102 -> 107 5.83 %
102 -> 108 21.66 %
102 -> 109 2.79 %
103 -> 107 3.30 %
103 -> 108 16.13 %
105 -> 107 8.00 %
105 -> 108 5.66 %
105 -> 111 4.05 %
106 -> 109 5.27 %
106 -> 111 16.95 %

Excited State: 17
3.9266 eV 315.75 nm f=0.0000
102 -> 108 9.41 %
103 -> 108 8.31 %
103 -> 109 4.28 %
105 -> 109 65.23 %
106 -> 108 3.74 %
106 -> 118 2.77 %

Excited State: 18
4.0179 eV 308.58 nm f=0.0000
98 -> 107 15.26 %
100 -> 107 47.59 %
102 -> 107 20.30 %
103 -> 107 9.37 %
103 -> 108 2.03 %
105 -> 109 3.43 %

Excited State: 19
4.1196 eV 300.96 nm f=0.0000
100 -> 108 8.45 %
102 -> 108 8.84 %
102 -> 109 3.27 %
103 -> 108 49.02 %
103 -> 109 2.87 %
105 -> 109 15.89 %
106 -> 111 3.98 %

Excited State: 20
4.2802 eV 289.67 nm f=0.0000
98 -> 109 2.78 %
100 -> 109 4.97 %
102 -> 108 39.41 %
102 -> 109 17.63 %
103 -> 109 2.38 %
105 -> 111 2.40 %
106 -> 111 23.70 %
106 -> 113 2.83 %
106 -> 114 3.97 %

Figure S21. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

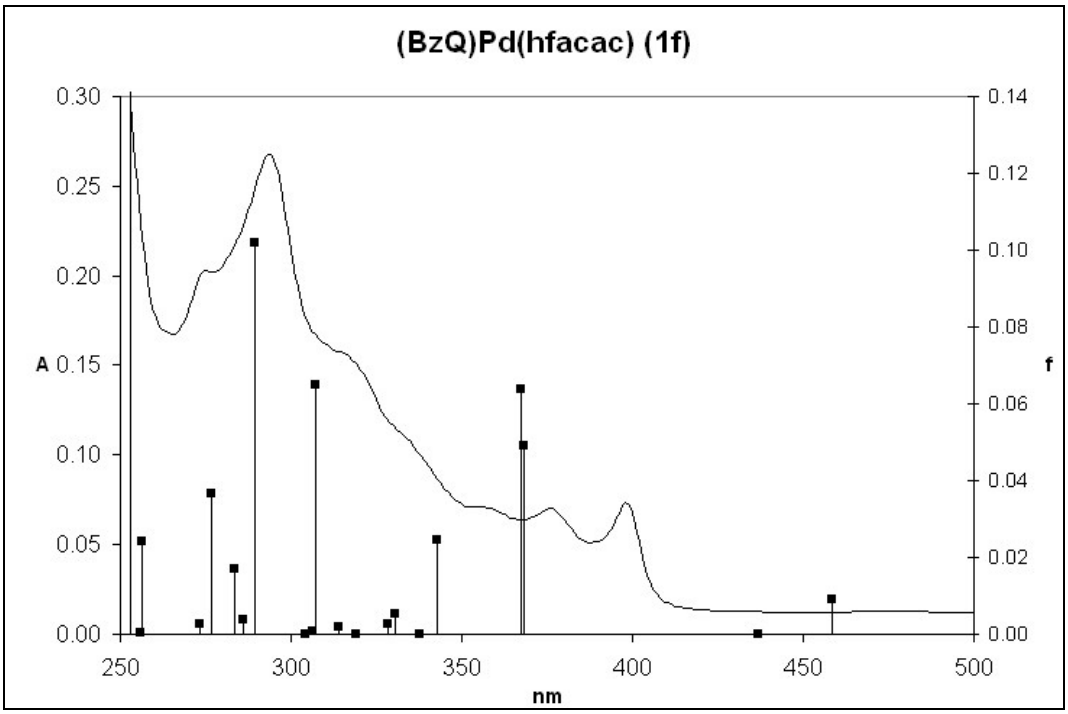


Figure S22. In the following picture, some (BzQ)Pd(hfacac) (**1f**) Kohn-Sham orbitals are reported that are relevant in describing the low-in-energy electronic transitions.

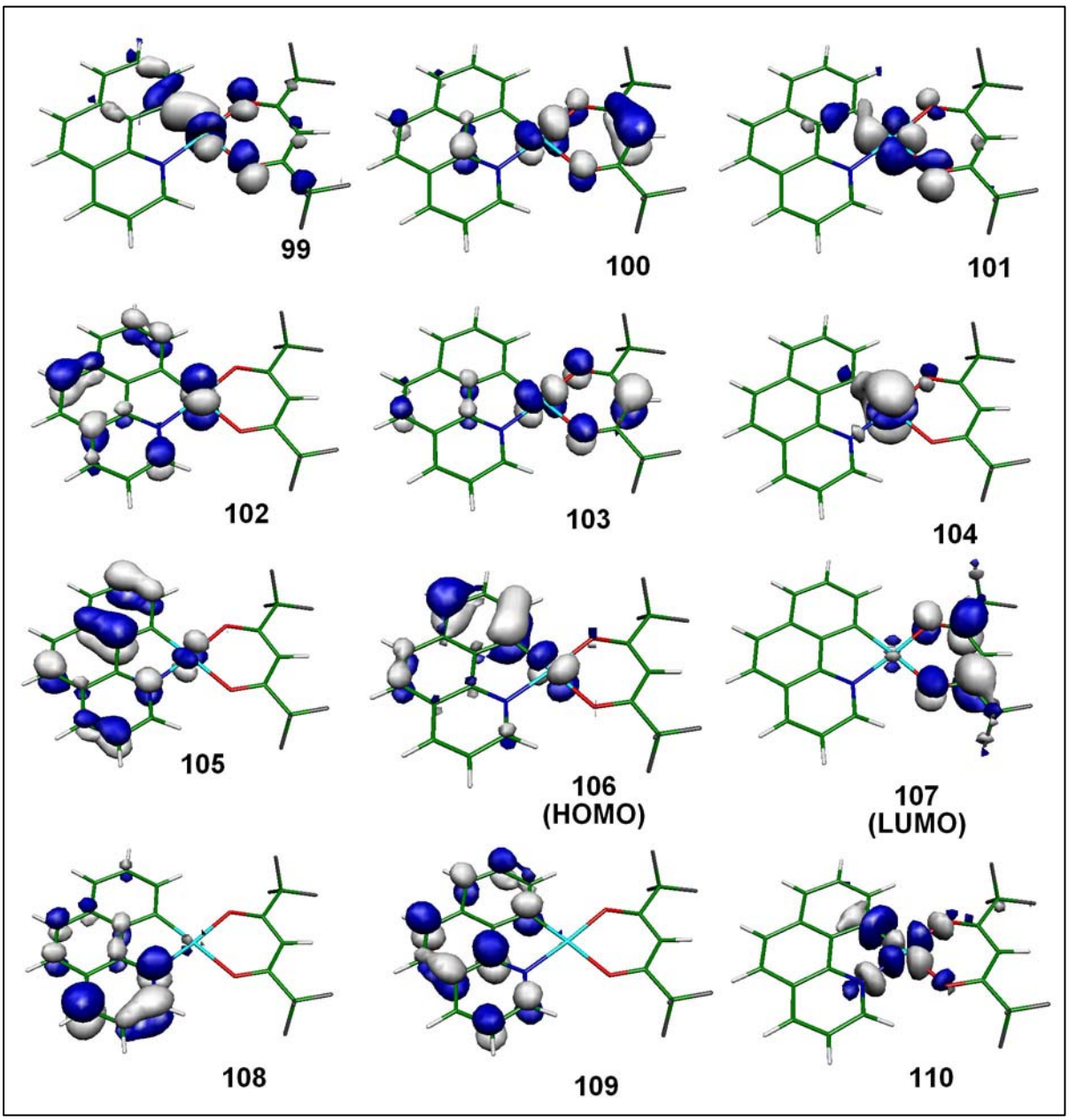


Table S26. Optimized structure of (BzQ)Pd(hfacac) (**1f**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pd	0.19027	0.01170	0.00001	C	4.15196	-1.46776	0.00028
C	1.66597	1.32341	-0.00022	C	2.95158	-0.72322	0.00013
C	2.94029	0.69613	-0.00013	N	1.71389	-1.31845	0.00024
C	4.16171	1.41171	-0.00030	C	1.61739	-2.65593	0.00051
C	4.08753	2.82683	-0.00059	C	2.77148	-3.46653	0.00068
C	2.84117	3.45209	-0.00070	C	4.03550	-2.87864	0.00056
C	1.62631	2.71309	-0.00052	H	0.61811	-3.07152	0.00059
C	5.38872	0.64964	-0.00016	H	2.65471	-4.54264	0.00091
C	5.38797	-0.72549	0.00012	H	4.92755	-3.49637	0.00069

H	6.33195	1.18760	-0.00029
H	6.32429	-1.27424	0.00022
H	4.99758	3.41825	-0.00074
H	2.79000	4.53654	-0.00093
H	0.67693	3.23694	-0.00062
O	-1.24318	1.45037	0.00001
C	-2.51113	1.23721	-0.00007
C	-3.20635	0.02036	-0.00017
C	-2.56133	-1.22672	-0.00010
O	-1.30347	-1.47146	0.00005
H	-4.28579	0.04434	-0.00030
C	-3.32365	2.53709	0.00037
C	-3.42722	-2.49229	-0.00040
F	-4.69579	2.31636	-0.00286
F	-3.03769	3.30639	1.12054
F	-3.03300	3.31032	-1.11576
F	-4.78942	-2.22185	0.00105
F	-3.16745	-3.27488	-1.11933
F	-3.16544	-3.27691	1.11658

Table S27. 1f singlet and triplet excited states computed at the deformed geometry obtained by a 0.10 Å shift of the central metal out of the ligands average plane. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 82 -> 83 for the HOMO -> LUMO transition when the HOMO is the 82th orbital and the LUMO is the 83th one). The second way assign the "0" label to the HOMO, the "–1" label to the HOMO-1 orbital and so on, the "0" label to the LUMO, "1" to LUMO+1 and so on (thus, 0 -> 0 is the HOMO -> LUMO transition, -2 -> 1 is the HOMO-2 -> LUMO+1 transition).

Singlet Excited States

HOMO is orbital 106 and LUMO is orbital 107

eV	nm	cm-1	f
2.6725;	463.92;	21555.4;	0.0075
2.8258;	438.76;	22791.5;	0.0014
3.3380;	371.43;	26923.0;	0.0556
3.3557;	369.47;	27065.8;	0.0506
3.5849;	345.84;	28915.1;	0.0232
3.6537;	339.34;	29469.0;	0.0005
3.7081;	334.36;	29907.9;	0.0042
3.7658;	329.24;	30373.0;	0.0025
3.8568;	321.46;	31108.1;	0.0098
3.9405;	314.64;	31782.4;	0.0011
3.9527;	313.67;	31880.6;	0.0070
4.0384;	307.01;	32572.2;	0.0005
4.1461;	299.03;	33441.5;	0.0639
4.2754;	290.00;	34482.8;	0.0915
4.3244;	286.70;	34879.7;	0.0003
4.3599;	284.37;	35165.5;	0.0145
4.4569;	278.18;	35947.9;	0.0320
4.5314;	273.61;	36548.4;	0.0131
4.7897;	258.85;	38632.4;	0.0353
4.8251;	256.96;	38916.6;	0.0122
4.8736;	254.40;	39308.2;	0.1312
4.9886;	248.53;	40236.6;	0.0009
5.0031;	247.81;	40353.5;	0.0231
5.0661;	244.73;	40861.4;	0.0283
5.0834;	243.90;	41000.4;	0.0207

Excited State: 1
2.6725 eV 463.92 nm 21555.cm-1 f=0.0075
104 -> 107 3.29 % -2 -> 0
105 -> 107 2.99 % -1 -> 0
106 -> 107 87.91 % 0 -> 0

Excited State: 2
2.8258 eV 438.76 nm 22792.cm-1 f=0.0014
103 -> 107 2.76 % -3 -> 0
104 -> 107 39.21 % -2 -> 0
105 -> 107 49.66 % -1 -> 0
106 -> 107 5.59 % 0 -> 0

Excited State: 3
3.3380 eV 371.43 nm 26923.cm-1 f=0.0556
103 -> 107 11.90 % -3 -> 0
104 -> 107 42.79 % -2 -> 0
105 -> 107 29.77 % -1 -> 0

Excited State: 4
3.3557 eV 369.47 nm 27066.cm-1 f=0.0506
104 -> 110 3.26 % -2 -> 3
105 -> 108 2.42 % -1 -> 1
105 -> 110 3.72 % -1 -> 3
106 -> 108 78.84 % 0 -> 1

Excited State: 5
3.5849 eV 345.84 nm 28915.cm-1 f=0.0232
101 -> 107 4.17 % -5 -> 0
103 -> 107 29.75 % -3 -> 0
104 -> 107 6.16 % -2 -> 0
104 -> 110 9.39 % -2 -> 3
105 -> 107 9.97 % -1 -> 0
105 -> 110 11.81 % -1 -> 3
106 -> 108 5.49 % 0 -> 1
106 -> 110 8.77 % 0 -> 3

Excited State: 6
3.6537 eV 339.34 nm 29469.cm-1 f=0.0005
98 -> 110 3.08 % -8 -> 3
102 -> 110 9.32 % -4 -> 3
103 -> 107 6.79 % -3 -> 0
103 -> 110 3.63 % -3 -> 3
104 -> 107 2.29 % -2 -> 0
104 -> 110 2.51 % -2 -> 3
106 -> 110 60.08 % 0 -> 3

Excited State: 7
3.7081 eV 334.36 nm 29908.cm-1 f=0.0042
101 -> 107 9.01 % -5 -> 0
103 -> 107 22.60 % -3 -> 0
103 -> 110 2.30 % -3 -> 3
104 -> 110 13.51 % -2 -> 3
105 -> 107 3.18 % -1 -> 0
105 -> 108 10.54 % -1 -> 1
105 -> 110 19.87 % -1 -> 3
106 -> 108 3.50 % 0 -> 1

Excited State: 8
3.7658 eV 329.24 nm 30373.cm-1 f=0.0025
104 -> 108 48.75 % -2 -> 1
104 -> 110 2.71 % -2 -> 3
105 -> 108 38.29 % -1 -> 1
105 -> 110 3.08 % -1 -> 3

Excited State: 9
3.8568 eV 321.46 nm 31108.cm-1 f=0.0098
99 -> 107 12.10 % -7 -> 0
100 -> 107 2.04 % -6 -> 0
101 -> 107 36.37 % -5 -> 0
102 -> 107 30.66 % -4 -> 0
103 -> 107 4.09 % -3 -> 0

Excited State: 10
3.9405 eV 314.64 nm 31782.cm-1 f=0.0011
99 -> 107 2.22 % -7 -> 0
101 -> 107 3.60 % -5 -> 0
102 -> 107 6.86 % -4 -> 0
104 -> 108 21.47 % -2 -> 1
105 -> 108 21.19 % -1 -> 1
105 -> 110 2.18 % -1 -> 3
106 -> 109 30.94 % 0 -> 2

Excited State: 11
3.9527 eV 313.67 nm 31881.cm-1 f=0.0070
99 -> 107 6.31 % -7 -> 0
100 -> 107 16.35 % -6 -> 0
101 -> 107 13.49 % -5 -> 0
101 -> 110 2.09 % -5 -> 3
102 -> 107 19.63 % -4 -> 0
102 -> 110 2.60 % -4 -> 3
103 -> 107 2.89 % -3 -> 0
103 -> 110 6.34 % -3 -> 3
104 -> 108 5.33 % -2 -> 1
104 -> 110 8.73 % -2 -> 3
105 -> 108 4.05 % -1 -> 1
106 -> 109 2.56 % 0 -> 2

Excited State: 12
4.0384 eV 307.01 nm 32572.cm-1 f=0.0005
99 -> 107 8.96 % -7 -> 0
100 -> 107 10.35 % -6 -> 0
100 -> 110 5.54 % -6 -> 3
101 -> 107 7.00 % -5 -> 0
102 -> 110 5.82 % -4 -> 3
103 -> 110 25.31 % -3 -> 3
104 -> 110 13.93 % -2 -> 3
105 -> 110 9.03 % -1 -> 3

Excited State: 13
4.1461 eV 299.03 nm 33441.cm-1 f=0.0639
98 -> 107 4.19 % -8 -> 0
99 -> 107 35.79 % -7 -> 0
100 -> 107 5.62 % -6 -> 0
101 -> 107 4.83 % -5 -> 0
102 -> 107 28.36 % -4 -> 0
103 -> 110 2.64 % -3 -> 3
106 -> 109 2.11 % 0 -> 2

Excited State: 14
4.2754 eV 290.00 nm 34483.cm-1 f=0.0915
102 -> 107 3.70 % -4 -> 0
102 -> 108 3.46 % -4 -> 1
104 -> 108 11.67 % -2 -> 1
105 -> 108 12.90 % -1 -> 1
106 -> 109 47.53 % 0 -> 2

Excited State: 15
4.3244 eV 286.70 nm 34880.cm-1 f=0.0003
93 -> 110 2.08 % -13 -> 3
99 -> 110 3.71 % -7 -> 3
100 -> 107 2.69 % -6 -> 0
100 -> 110 21.76 % -6 -> 3
101 -> 110 50.03 % -5 -> 3
103 -> 108 10.04 % -3 -> 1

Excited State: 16
4.3599 eV 284.37 nm 35165.cm-1 f=0.0145
99 -> 110 2.50 % -7 -> 3
100 -> 110 5.10 % -6 -> 3
101 -> 110 3.42 % -5 -> 3
103 -> 108 76.35 % -3 -> 1
105 -> 109 2.37 % -1 -> 2

Excited State: 17
4.4569 eV 278.18 nm 35948.cm-1 f=0.0320
102 -> 108 33.29 % -4 -> 1
103 -> 108 2.25 % -3 -> 1
104 -> 109 5.33 % -2 -> 2
105 -> 109 45.90 % -1 -> 2
106 -> 111 6.53 % 0 -> 4

Excited State: 18
4.5314 eV 273.61 nm 36548.cm-1 f=0.0131
102 -> 108 3.26 % -4 -> 1
104 -> 109 62.42 % -2 -> 2
105 -> 109 24.76 % -1 -> 2

Excited State: 19
4.7897 eV 258.85 nm 38632.cm-1 f=0.0353
96 -> 107 2.83 % -10 -> 0
99 -> 107 11.07 % -7 -> 0
100 -> 107 42.94 % -6 -> 0
101 -> 107 8.66 % -5 -> 0
103 -> 107 3.43 % -3 -> 0
104 -> 109 2.92 % -2 -> 2
105 -> 110 2.09 % -1 -> 3

Excited State: 20
4.8251 eV 256.96 nm 38917.cm-1 f=0.0122
98 -> 110 3.95 % -8 -> 3
100 -> 107 2.85 % -6 -> 0
102 -> 110 11.58 % -4 -> 3
103 -> 110 30.33 % -3 -> 3
104 -> 110 4.72 % -2 -> 3
105 -> 110 14.28 % -1 -> 3
106 -> 110 15.22 % 0 -> 3

Excited State: 21
4.8736 eV 254.40 nm 39308.cm-1 f=0.1312
101 -> 108 2.39 % -5 -> 1
102 -> 108 34.31 % -4 -> 1
102 -> 109 2.83 % -4 -> 2
103 -> 109 2.55 % -3 -> 2
104 -> 109 5.37 % -2 -> 2
104 -> 111 2.21 % -2 -> 4
105 -> 109 5.52 % -1 -> 2
105 -> 111 2.58 % -1 -> 4
106 -> 111 22.68 % 0 -> 4

Excited State: 22
4.9886 eV 248.53 nm 40237.cm-1 f=0.0009
100 -> 108 11.45 % -6 -> 1
101 -> 108 61.88 % -5 -> 1
102 -> 110 2.26 % -4 -> 3
103 -> 109 5.08 % -3 -> 2
103 -> 110 2.83 % -3 -> 3
104 -> 110 4.35 % -2 -> 3
105 -> 110 4.55 % -1 -> 3

Excited State: 23
5.0031 eV 247.81 nm 40353.cm-1 f=0.0231
98 -> 107 5.26 % -8 -> 0
101 -> 108 2.44 % -5 -> 1
102 -> 108 4.68 % -4 -> 1
102 -> 109 4.96 % -4 -> 2
103 -> 109 53.60 % -3 -> 2
104 -> 109 5.72 % -2 -> 2
104 -> 110 2.15 % -2 -> 3
105 -> 109 2.23 % -1 -> 2
106 -> 111 5.84 % 0 -> 4

Excited State: 24
5.0661 eV 244.73 nm 40861.cm-1 f=0.0283
98 -> 107 19.44 % -8 -> 0
98 -> 110 2.61 % -8 -> 3
100 -> 108 3.60 % -6 -> 1
101 -> 108 9.51 % -5 -> 1
102 -> 110 24.08 % -4 -> 3
103 -> 109 4.52 % -3 -> 2
104 -> 110 10.86 % -2 -> 3
105 -> 110 6.73 % -1 -> 3
106 -> 110 2.42 % 0 -> 3

Excited State: 25

5.0834 eV 243.90 nm 41000.cm-1 f=0.0207
96 -> 107 18.88 % -10 -> 0
98 -> 107 38.14 % -8 -> 0
99 -> 107 7.09 % -7 -> 0
101 -> 108 2.14 % -5 -> 1
102 -> 110 12.40 % -4 -> 3
104 -> 110 5.43 % -2 -> 3
105 -> 110 3.53 % -1 -> 3

Triplet Excited States

Excited State: 1
2.1053eV 588.9 nm f=0.0000
99 -> 107 2.25 % -7 -> 0
100 -> 107 9.81 % -6 -> 0
101 -> 107 4.23 % -5 -> 0
102 -> 107 2.14 % -4 -> 0
103 -> 107 56.86 % -3 -> 0
104 -> 107 18.34 % -2 -> 0
106 -> 107 36.61 % 0 -> 0

Excited State: 2
2.4971eV 496.51 nm f=0.0000
102 -> 108 4.12 % -4 -> 1
102 -> 109 5.27 % -4 -> 2
103 -> 107 4.41 % -3 -> 0
103 -> 111 2.06 % -3 -> 4
104 -> 108 14.78 % -2 -> 1
105 -> 108 20.28 % -1 -> 1
105 -> 111 2.13 % -1 -> 4
106 -> 107 4.12 % 0 -> 0
106 -> 108 20.64 % 0 -> 1
106 -> 109 42.14 % 0 -> 2
106 -> 111 4.93 % 0 -> 4

Excited State: 3
2.6446eV 468.81 nm f=0.0000
103 -> 107 7.33 % -3 -> 0
104 -> 107 5.98 % -2 -> 0
104 -> 110 28.68 % -2 -> 3
105 -> 107 23.95 % -1 -> 0
105 -> 110 36.72 % -1 -> 3
106 -> 110 2.06 % 0 -> 3

Excited State: 4
2.7014eV 458.97 nm f=0.0000
98 -> 107 2.41 % -8 -> 0
102 -> 107 7.02 % -4 -> 0
103 -> 107 12.77 % -3 -> 0
104 -> 107 21.88 % -2 -> 0
104 -> 110 2.24 % -2 -> 3
106 -> 107 48.01 % 0 -> 0
106 -> 109 3.08 % 0 -> 2

Excited State: 5
2.8317eV 437.84 nm f=0.0000
103 -> 107 7.51 % -3 -> 0
104 -> 107 16.79 % -2 -> 0
104 -> 110 18.62 % -2 -> 3
105 -> 107 37.65 % -1 -> 0
105 -> 110 17.84 % -1 -> 3
106 -> 110 2.5 % 0 -> 3

Excited State: 6
2.9199eV 424.62 nm f=0.0000
102 -> 108 2.22 % -4 -> 1
104 -> 108 4.19 % -2 -> 1
105 -> 108 3.06 % -1 -> 1
106 -> 108 76.45 % 0 -> 1
106 -> 109 16.51 % 0 -> 2

Excited State: 7
3.0389eV 407.99 nm f=0.0000
98 -> 110 11.44 % -8 -> 3
102 -> 110 22.98 % -4 -> 3
103 -> 110 7.91 % -3 -> 3
104 -> 110 3.37 % -2 -> 3
106 -> 107 2.45 % 0 -> 0
106 -> 110 56.32 % 0 -> 3

Excited State: 8
3.1471eV 393.96 nm f=0.0000
100 -> 107 2.96 % -6 -> 0
100 -> 110 9.29 % -6 -> 3
101 -> 110 3.84 % -5 -> 3
102 -> 110 11.89 % -4 -> 3
103 -> 110 41.3 % -3 -> 3
104 -> 110 14.49 % -2 -> 3
105 -> 110 10.6 % -1 -> 3

Excited State: 9
3.2909eV 376.74 nm f=0.0000
94 -> 108 2.95 % -12 -> 1
97 -> 108 3.82 % -9 -> 1
104 -> 108 24.9 % -2 -> 1
105 -> 108 26.79 % -1 -> 1
106 -> 109 34.52 % 0 -> 2
106 -> 111 6.58 % 0 -> 4

Excited State: 10
3.3266eV 372.7 nm f=0.0000
99 -> 107 4.99 % -7 -> 0
100 -> 107 10.9 % -6 -> 0
102 -> 107 17.42 % -4 -> 0
103 -> 107 6.1 % -3 -> 0
103 -> 110 3.72 % -3 -> 3
104 -> 107 23.16 % -2 -> 0
104 -> 110 2.07 % -2 -> 3
105 -> 107 20.16 % -1 -> 0
106 -> 107 7.35 % 0 -> 0

Excited State: 11
3.5837eV 345.97 nm f=0.0000
95 -> 107 3.22 % -11 -> 0
99 -> 107 7.19 % -7 -> 0
100 -> 110 6.67 % -6 3
101 -> 107 65.05 % -5 0
101 -> 110 8.43 % -5 3
102 -> 107 4.66 % -4 0

Excited State: 12
3.6292eV 341.63 nm f=0.0000
104 -> 108 48.61 % -2 1
105 -> 108 42.87 % -1 1

Excited State: 13
3.6546eV 339.25 nm f=0.0000
96 -> 107 2.01 % -10 0
99 -> 107 21.98 % -7 0
100 -> 110 9.06 % -6 3
101 -> 110 12.73 % -5 3
102 -> 107 22.02 % -4 0
103 -> 107 4.77 % -3 0
104 -> 107 5.9 % -2 0
105 -> 107 9.1 % -1 0

Excited State: 14
3.7157eV 333.67 nm f=0.0000
99 -> 107 2.29 % -7 0
99 -> 110 3.18 % -7 3
100 -> 107 9.5 % -6 0
100 -> 110 11.81 % -6 -> 3
101 -> 107 11.47 % -5 -> 0
101 -> 110 28.64 % -5 -> 3
102 -> 107 8.44 % -4 -> 0
102 -> 108 2.02 % -4 -> 1
103 -> 107 7.52 % -3 -> 0

104 -> 107 2.75 % -2 -> 0
105 -> 107 4.52 % -1 -> 0
106 -> 111 2.74 % 0 -> 4

Excited State: 15
3.7913eV 327.02 nm f=0.0000
94 -> 108 2.17 % -12 -> 1
98 -> 108 2.86 % -8 -> 1
99 -> 107 6.85 % -7 -> 0
101 -> 107 3.73 % -5 -> 0
101 -> 110 3.03 % -5 -> 3
102 -> 108 20.19 % -4 -> 1
102 -> 109 2.61 % -4 -> 2
103 -> 108 18.15 % -3 -> 1
105 -> 107 2.4 % -1 -> 0
105 -> 108 3.48 % -1 -> 1
105 -> 111 2.98 % -1 -> 4
106 -> 109 5.08 % 0 -> 2
106 -> 111 17.07 % 0 -> 4

(BzQ)Pt(hfacac) (2f)

Table S28. Singlet and triplet excited states of (BzQ)Pt(hfacac) (**2f**) computed at the MPW1PW92/SDD level of approximation. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important monoelectronic excitations for each excited state.

Singlet Excited States

Excited State: 1
2.4157 eV 513.23 nm f=0.0176
106 -> 107 90.98 %

Excited State: 2
2.7239 eV 455.18 nm f=0.0000
104 -> 107 98.04 %

Excited State: 3
3.1136 eV 398.20 nm f=0.0757
103 -> 107 6.99 %
105 -> 107 68.59 %
106 -> 107 2.11 %
106 -> 108 11.32 %

Excited State: 4
3.2211 eV 384.91 nm f=0.0876
105 -> 107 10.53 %
105 -> 109 2.11 %
106 -> 108 76.70 %

Excited State: 5
3.4937 eV 354.87 nm f=0.0075
103 -> 107 78.16 %
105 -> 107 13.37 %

Excited State: 6
3.5637 eV 347.91 nm f=0.0000
101 -> 107 95.93 %

Excited State: 7
3.7646 eV 329.34 nm f=0.0028
104 -> 108 96.96 %

Excited State: 8
3.8005 eV 326.23 nm f=0.0127
105 -> 108 55.71 %
106 -> 108 2.25 %
106 -> 109 33.98 %

Excited State: 9
3.8386 eV 322.99 nm f=0.0697
102 -> 107 86.76 %
106 -> 109 5.65 %

Excited State: 10
4.1098 eV 301.68 nm f=0.0008
95 -> 107 3.02 %
96 -> 107 2.78 %
99 -> 107 88.50 %

Excited State: 11
4.1314 eV 300.10 nm f=0.1076
102 -> 107 4.44 %
102 -> 108 3.51 %
105 -> 108 26.58 %
105 -> 109 2.45 %
106 -> 109 46.15 %

Excited State: 12
4.2132 eV 294.27 nm f=0.0067
103 -> 108 88.68 %
104 -> 111 2.42 %

Excited State: 13
4.3429 eV 285.49 nm f=0.0409
102 -> 108 36.58 %
105 -> 108 3.48 %
105 -> 109 47.91 %
106 -> 110 4.61 %

Excited State: 14
4.4106 eV 281.10 nm f=0.0002
98 -> 111 2.08 %
101 -> 108 2.95 %
102 -> 111 7.00 %
103 -> 111 2.43 %
106 -> 111 76.93 %

Excited State: 15
4.6008 eV 269.48 nm f=0.0036
104 -> 109 96.92 %

Excited State: 16
4.6047 eV 269.25 nm f=0.0019
100 -> 107 2.93 %
102 -> 108 3.38 %
103 -> 108 2.24 %
104 -> 111 78.12 %

Excited State: 17
4.6913 eV 264.28 nm f=0.0000
101 -> 108 89.60 %
106 -> 111 2.91 %

Excited State: 18
4.8074 eV 257.90 nm f=0.0597
100 -> 107 2.54 %
102 -> 108 28.34 %
102 -> 109 2.62 %
103 -> 109 6.83 %
104 -> 111 2.56 %
105 -> 109 11.11 %
105 -> 110 4.52 %
106 -> 110 31.03 %

Excited State: 19
4.8397 eV 256.18 nm f=0.0619
98 -> 107 2.94 %
100 -> 107 70.84 %
106 -> 110 5.08 %

Excited State: 20
4.8639 eV 254.90 nm f=0.0704
98 -> 107 2.29 %
100 -> 107 2.16 %
102 -> 108 10.70 %
102 -> 109 2.92 %
103 -> 109 52.93 %
105 -> 109 15.89 %
106 -> 110 5.05 %

Excited State: 21
4.8688 eV 254.65 nm f=0.0000
100 -> 111 2.37 %
101 -> 108 3.23 %
102 -> 111 4.20 %
103 -> 111 26.27 %
105 -> 111 52.87 %

Excited State: 22
5.0448 eV 245.77 nm f=0.0672
98 -> 107 81.97 %

Excited State: 23
5.1945 eV 238.68 nm f=0.0121
101 -> 111 86.21 %

Excited State: 24
5.2416 eV 236.54 nm f=0.1540
101 -> 111 2.22 %
102 -> 108 2.66 %
102 -> 109 36.08 %
103 -> 109 22.74 %
105 -> 110 3.55 %
106 -> 110 16.97 %

Excited State: 25
5.2437 eV 236.44 nm f=0.0006
92 -> 107 2.72 %
93 -> 107 4.65 %
95 -> 107 6.14 %
96 -> 107 74.03 %
99 -> 107 3.95 %
99 -> 108 2.19 %

Excited State: 26
5.3724 eV 230.78 nm f=0.0001
96 -> 107 2.05 %
99 -> 108 90.94 %
104 -> 110 2.36 %

Excited State: 27
5.3963 eV 229.76 nm f=0.0075
97 -> 107 82.69 %
98 -> 108 2.80 %
100 -> 108 6.14 %

Excited State: 28
5.4215 eV 228.69 nm f=0.0025
97 -> 107 12.68 %
98 -> 108 7.22 %
100 -> 108 57.36 %
105 -> 110 15.18 %

Excited State: 29
5.5077 eV 225.11 nm f=0.3997
97 -> 108 3.07 %
98 -> 108 2.58 %
102 -> 109 36.19 %
102 -> 110 3.35 %
103 -> 109 3.97 %
103 -> 110 6.96 %
105 -> 109 5.19 %
105 -> 110 2.06 %
106 -> 110 17.69 %

Excited State: 30
5.5162 eV 224.76 nm f=0.0000
101 -> 109 95.78 %

Triplet Excited States

Excited State: 1
1.9520 eV 635.17 nm f=0.0000
100 -> 107 12.16 %
102 -> 107 4.84 %
103 -> 107 32.22 %
105 -> 107 8.84 %
106 -> 107 64.77 %

Excited State: 2
2.3566 eV 526.11 nm f=0.0000
98 -> 107 4.44 %
100 -> 107 2.39 %
102 -> 107 3.68 %
103 -> 107 30.70 %
105 -> 107 39.40 %
105 -> 108 4.27 %
106 -> 107 25.97 %
106 -> 108 2.73 %
106 -> 109 2.76 %

Excited State: 3
2.4749 eV 500.97 nm f=0.0000
98 -> 108 2.45 %
102 -> 107 3.85 %
102 -> 108 3.50 %
102 -> 109 6.56 %
103 -> 108 2.71 %
103 -> 110 3.24 %
105 -> 107 8.56 %
105 -> 108 33.74 %
106 -> 108 24.41 %
106 -> 109 34.13 %
106 -> 110 3.77 %

Excited State: 4
2.6456 eV 468.64 nm f=0.0000
104 -> 107 100.0 %

Excited State: 5
2.7893 eV 444.49 nm f=0.0000
105 -> 108 10.59 %
106 -> 108 72.97 %
106 -> 109 19.37 %
106 -> 114 2.17 %

Excited State: 6
3.1344 eV 395.56 nm f=0.0000
100 -> 107 27.60 %
102 -> 107 18.12 %
103 -> 107 15.45 %
105 -> 107 24.20 %
105 -> 108 7.30 %
106 -> 107 10.37 %

Excited State: 7
3.1761 eV 390.37 nm f=0.0000
94 -> 108 2.61 %
97 -> 108 2.29 %
105 -> 107 3.85 %
105 -> 108 45.89 %
106 -> 109 38.30 %
106 -> 110 7.24 %

Excited State: 8
3.3808 eV 366.73 nm f=0.0000
101 -> 107 97.91 %

Excited State: 9
3.5393 eV 350.31 nm f=0.0000
100 -> 107 6.95 %
102 -> 107 39.91 %
102 -> 108 3.29 %
103 -> 107 20.36 %
103 -> 108 4.41 %
105 -> 107 17.64 %
106 -> 110 3.42 %

Excited State: 10
3.6321 eV 341.35 nm f=0.0000
104 -> 108 95.25 %
104 -> 109 3.18 %

Excited State: 11
3.7052 eV 334.62 nm f=0.0000
98 -> 108 2.11 %
100 -> 107 3.73 %

102 -> 107 2.41 %
102 -> 108 12.91 %
103 -> 107 3.81 %
103 -> 108 45.08 %
105 -> 107 4.09 %
105 -> 108 2.72 %
105 -> 110 4.69 %
106 -> 109 7.46 %
106 -> 110 10.70 %

Excited State: 12
3.7848 eV 327.59 nm f=0.0000
98 -> 107 8.06 %
100 -> 107 29.36 %
102 -> 107 15.70 %
102 -> 108 14.51 %
103 -> 107 6.55 %
103 -> 108 10.13 %
104 -> 111 2.13 %
105 -> 109 9.63 %
106 -> 108 2.47 %

Excited State: 13
3.8045 eV 325.89 nm f=0.0000
95 -> 107 6.34 %
96 -> 107 6.54 %
99 -> 107 86.58 %

Excited State: 14
3.8513 eV 321.92 nm f=0.0000
98 -> 107 10.69 %
100 -> 107 14.50 %
100 -> 108 2.49 %
102 -> 107 7.90 %
102 -> 108 20.86 %
103 -> 107 2.96 %
103 -> 108 4.56 %
103 -> 109 4.02 %
105 -> 109 23.99 %

Excited State: 15
3.9061 eV 317.41 nm f=0.0000
98 -> 111 7.03 %
102 -> 111 15.09 %
103 -> 111 6.72 %
106 -> 111 73.20 %

Excited State: 16
3.9310 eV 315.40 nm f=0.0000
104 -> 111 99.94 %

Excited State: 17
4.0119 eV 309.04 nm f=0.0000
100 -> 108 2.72 %
102 -> 108 9.53 %
102 -> 109 3.02 %
103 -> 108 19.87 %
103 -> 109 12.10 %
105 -> 108 2.84 %
105 -> 109 43.86 %
106 -> 110 5.41 %

Excited State: 18
4.0853 eV 303.49 nm f=0.0000
100 -> 111 7.28 %
102 -> 111 8.76 %
103 -> 111 36.12 %
105 -> 111 51.72 %

Excited State: 19
4.1651 eV 297.67 nm f=0.0000
98 -> 109 2.28 %
100 -> 109 4.37 %
102 -> 108 29.06 %
102 -> 109 19.20 %
103 -> 109 2.91 %
106 -> 110 35.69 %
106 -> 114 3.34 %
106 -> 118 2.16 %

Excited State: 20
4.4283 eV 279.98 nm f=0.0000
100 -> 109 6.23 %
102 -> 109 17.78 %
103 -> 108 2.01 %
103 -> 109 18.59 %
103 -> 110 2.68 %
105 -> 109 10.95 %
105 -> 110 2.30 %
106 -> 109 6.71 %
106 -> 110 21.33 %
106 -> 113 2.64 %
106 -> 114 2.18 %

Figure S23. The following figure compares the experimental spectrum recorded in cyclohexane and the computed electronic transitions listed above.

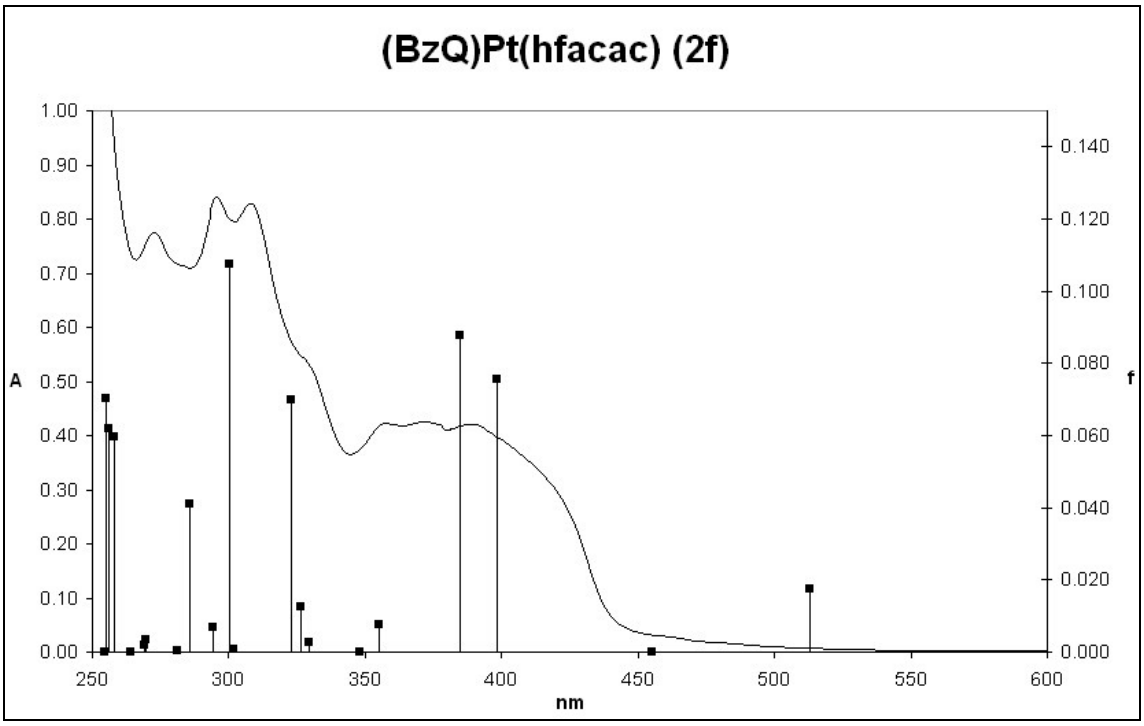


Figure S24. In the following picture, some (BzQ)Pt(hfacac) (**2f**) Kohn-Sham orbitals are reported that are relevant in describing the low-in-energy electronic transitions.

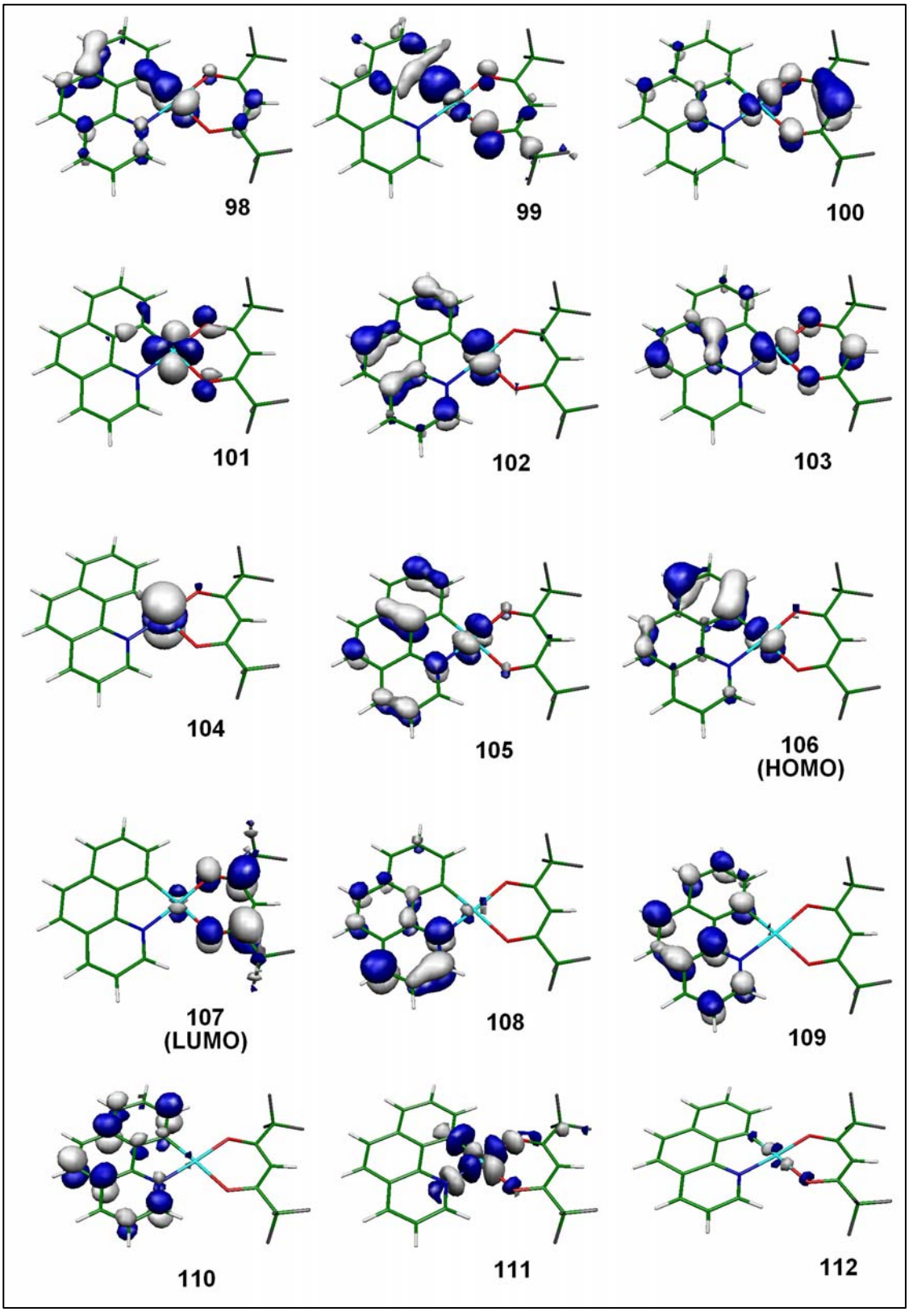


Table S29. Optimized structure of (BzQ)Pt(hfacac) (**2f**) at the MPW1PW91/SDD level of approximation. Cartesian coordinates in Angstrom.

Pt	0.16572	0.01880	-0.00031
C	1.66136	1.32560	-0.00044
C	2.93272	0.68756	-0.00015
C	4.16473	1.38357	-0.00018
C	4.11161	2.79880	-0.00056
C	2.87224	3.43971	-0.00087
C	1.64855	2.71900	-0.00082
C	5.37947	0.60236	0.00019
C	5.35697	-0.77255	0.00058
C	4.10956	-1.49564	0.00062
C	2.92240	-0.73062	0.00022
N	1.67344	-1.30876	0.00019
C	1.55757	-2.64760	0.00059
C	2.69900	-3.47181	0.00103
C	3.97264	-2.90368	0.00101
H	0.55265	-3.04799	0.00056
H	2.56557	-4.54588	0.00136
H	4.85502	-3.53492	0.00134
H	6.33118	1.12514	0.00017
H	6.28424	-1.33637	0.00087
H	5.02941	3.37796	-0.00061
H	2.83644	4.52481	-0.00118
H	0.70815	3.25883	-0.00107
O	-1.26406	1.45397	-0.00003
C	-2.53727	1.24108	0.00015
C	-3.23112	0.02570	0.00003
C	-2.59299	-1.22417	-0.00018
O	-1.33237	-1.47197	-0.00028
H	-4.31062	0.05283	0.00013
C	-3.33808	2.54401	0.00075
C	-3.45587	-2.48811	-0.00039
F	-4.71101	2.32765	-0.00090
F	-3.04783	3.31263	1.11984
F	-3.04552	3.31522	-1.11591
F	-4.81729	-2.21477	0.00079
F	-3.19676	-3.27152	-1.11881
F	-3.19512	-3.27308	1.11655

Table S30. 2f singlet and triplet excited states computed at the deformed geometry obtained by a 0.10 Å shift of the central metal out of the ligands average plane. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 82 -> 83 for the HOMO -> LUMO transition when the HOMO is the 82th orbital and the LUMO is the 83th one). The second way assign the "0" label to the HOMO, the "–1" label to the HOMO-1 orbital and so on, the "0" label to the LUMO, "1" to LUMO+1 and so on (thus, 0 -> 0 is the HOMO -> LUMO transition, -2 -> 1 is the HOMO-2 -> LUMO+1 transition).

Singlet Excited States

HOMO is orbital 106 and LUMO is orbital 107

eV	nm	cm^{-1}	f
2.3866	519.50	19249.3	0.0166
2.7004	459.13	21780.3	0.0009
3.0809	402.43	24849.0	0.077
3.2000	387.45	25809.8	0.0803
3.4401	360.41	27746.2	0.0045
3.5954	344.84	28999.0	0.0037
3.7334	332.09	30112.3	0.003
3.7725	328.65	30427.5	0.0456
3.7930	326.88	30592.3	0.0068
3.8033	325.99	30675.8	0.1046

Excited State: 1
2.3866eV 519.5nm 19249 cm^{-1} f=0.0166
106 -> 107 89.88% 0 -> 0

2 6Excited State:Singlet-A
2.7004eV 459.13nm 21780 cm^{-1} f=0.0009
103 -> 107 3.91% -3 -> 0
104 -> 107 92.63% -2 -> 0

3 8Excited State:Singlet-A
3.0809eV 402.43nm 24849 cm^{-1} f=0.0770
103 -> 107 8.21% -3 -> 0
105 -> 107 69.69% -1 -> 0
106 -> 107 2.08% 0 -> 0
106 -> 108 8.37% 0 -> 1

4 11Excited State:Singlet-A
3.2eV 387.45nm 25810 cm^{-1} f=0.0803
105 -> 107 7.45% -1 -> 0
106 -> 108 79.66% 0 -> 1

5 13Excited State:Singlet-A
3.4401eV 360.41nm 27746 cm^{-1} f=0.0045
101 -> 107 18.61% -5 -> 0
102 -> 107 2.13% -4 -> 0
103 -> 107 57.97% -3 -> 0
104 -> 107 2.31% -2 -> 0
105 -> 107 12.84% -1 -> 0

6 16Excited State:Singlet-A
3.5954eV 344.84nm 28999 cm^{-1} f=0.0037
101 -> 107 74.5% -5 -> 0
103 -> 107 16.4% -3 -> 0
105 -> 107 2.02% -1 -> 0

7 17Excited State:Singlet-A
3.7334eV 332.09nm 30112 cm^{-1} f=0.0030
104 -> 108 92.74% -2 -> 1

8 18Excited State:Singlet-A
3.7725eV 328.65nm 30428 cm^{-1} f=0.0456
99 -> 107 5.03% -7 -> 0
101 -> 107 2.02% -5 -> 0
102 -> 107 74.01% -4 -> 0
105 -> 108 9.43% -1 -> 1

9 19Excited State:Singlet-A
3.793eV 326.88nm 30592 cm^{-1} f=0.0068
102 -> 107 5.38% -4 -> 0
105 -> 108 45.14% -1 -> 1
106 -> 108 2.6% 0 -> 1
106 -> 109 38.23% 0 -> 2

10 20Excited State:Singlet-A

3.8033eV 325.99nm 30676 cm^{-1} f=0.1046
98 -> 107 2.79% -8 -> 0
99 -> 107 12.01% -7 -> 0
102 -> 108 2.8% -4 -> 1
105 -> 108 20.4% -1 -> 1
106 -> 109 36.16% 0 -> 2

Triplet Excited States

	eV	nm	cm-1
1	1.9259	643.78	15533.3
2	2.3241	533.46	18745.5
3	2.4655	502.87	19885.9
4	2.6315	471.15	21224.7
5	2.7787	446.19	22412.0
6	3.1273	396.45	25223.9
7	3.1634	391.93	25514.8
8	3.3561	369.43	27068.7
9	3.5191	352.32	28383.3
10	3.5803	346.3	28876.7

Excited State: 1
1.9259eV 643.78nm 15533 cm^{-1} f=0.0000
100 -> 107 12.14% -6 -> 0
102 -> 107 4.9% -4 -> 0
103 -> 107 23.25% -3 -> 0
104 -> 107 8.87% -2 -> 0
105 -> 107 8.92% -1 -> 0
106 -> 107 64.16% 0 -> 0

Excited State: 2
2.3241eV 533.46nm 18746 cm^{-1} f=0.0000
98 -> 107 3.46% -8 -> 0
100 -> 107 2.96% -6 -> 0
102 -> 107 4.09% -4 -> 0
103 -> 107 24.28% -3 -> 0
104 -> 107 5.77% -2 -> 0
105 -> 107 41.58% -1 -> 0
105 -> 108 2.93% -1 -> 1
106 -> 107 27.16% 0 -> 0

Excited State: 3
2.4655eV 502.87nm 19886 cm^{-1} f=0.0000
102 -> 107 3.14% -4 -> 0
102 -> 108 3.35% -4 -> 1
102 -> 109 7.02% -4 -> 2
103 -> 108 2.26% -3 -> 1
103 -> 110 3.37% -3 -> 3
105 -> 107 7.31% -1 -> 0
105 -> 108 34.71% -1 -> 1
106 -> 108 24.1% 0 -> 1
106 -> 109 34.7% 0 -> 2
106 -> 110 3.71% 0 -> 3

Excited State: 4
2.6315eV 471.15nm 21225 cm^{-1} f=0.0000
103 -> 107 11% -3 -> 0
104 -> 107 84.12% -2 -> 0
105 -> 107 2.17% -1 -> 0

Excited State: 5
2.7787eV 446.19nm 22412 cm^{-1} f=0.0000
105 -> 108 9.9% -1 -> 1
106 -> 108 73.9% 0 -> 1
106 -> 109 18.94% 0 -> 2
106 -> 114 2.14% 0 -> 7

Excited State: 6
3.1273eV 396.45nm 25224 cm^{-1} f=0.0000
100 -> 107 28.64% -6 -> 0
102 -> 107 19.29% -4 -> 0
103 -> 107 14.68% -3 -> 0
105 -> 107 21.25% -1 -> 0
105 -> 108 7.85% -1 -> 1
106 -> 107 9.82% 0 -> 0

Excited State: 7
3.1634eV 391.93nm 25515 cm^{-1} f=0.0000
94 -> 108 2.5% -12 -> 1
97 -> 108 2.32% -9 -> 1
105 -> 107 3.88% -1 -> 0
105 -> 108 45.17% -1 -> 1
106 -> 109 37.86% 0 -> 2
106 -> 110 6.79% 0 -> 3

Excited State: 8
3.3561eV 369.43nm 27069 cm^{-1} f=0.0000
100 -> 107 3.9% -6 -> 0
101 -> 107 91.17% -5 -> 0

Excited State: 9
3.5191eV 352.32nm 28383 cm^{-1} f=0.0000
99 -> 107 2.15% -7 -> 0
100 -> 107 3.29% -6 -> 0
102 -> 107 39.88% -4 -> 0
102 -> 108 2.77% -4 -> 1
103 -> 107 21.09% -3 -> 0
103 -> 108 4.3% -3 -> 1
105 -> 107 18.05% -1 -> 0
106 -> 110 2.72% 0 -> 3

Excited State: 10
3.5803eV 346.3nm 28877 cm^{-1} f=0.0000
104 -> 108 88.2% -2 -> 1
104 -> 109 2.31% -2 -> 2
104 -> 110 2.14% -2 -> 3
104 -> 111 2.7% -2 -> 4

Figure S25. Comparison of the low energy parts of the **1b** and **1e** absorption spectra in cyclohexane. The computed excitation wavelengths and oscillator strengths (f) are reported. Both the spectra are the same ones reported in Figures S9 and S13 respectively. Both of them have been enlarged of a factor 10 with the aim to evidence the presence of the weak absorption band at longer wavelengths in the case of **1e**. Such a band is not present in **1b**.

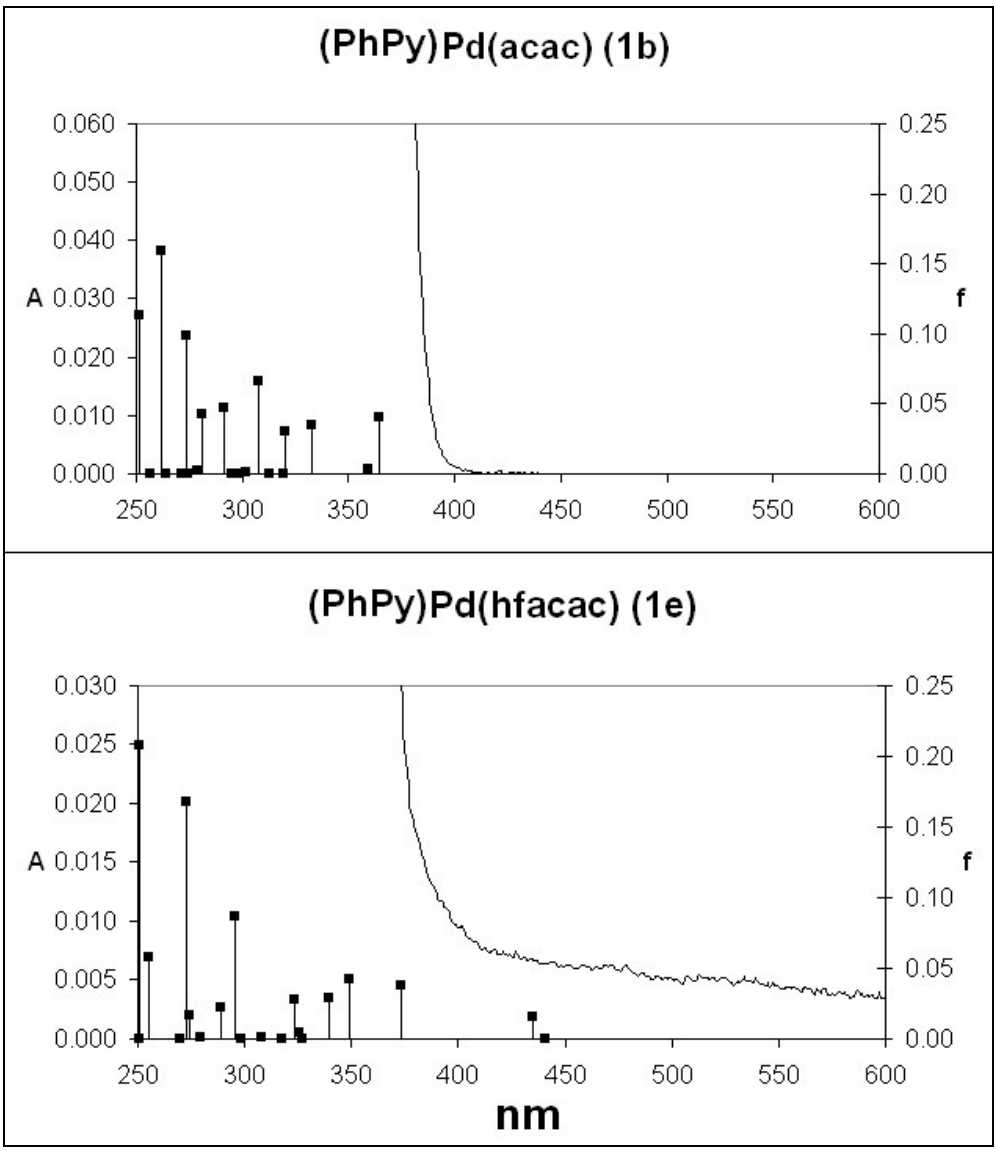


Figure S26. Comparison of the low energy parts of the **2b** and **2e** absorption spectra in cyclohexane. The computed excitation wavelengths and oscillator strengths (f) are reported. Both the spectra are the same ones reported in Figures S11 and S15 respectively. Both of them have been enlarged of a factor 20 with the aim to evidence the presence of the weak absorption band at longer wavelengths in the case of **2e**. Such a band is not present in **2b**.