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Electronic Supplementary Information (ESI)

Fluorescent perylenylpyridine complexes: an experimental and theoretical study†

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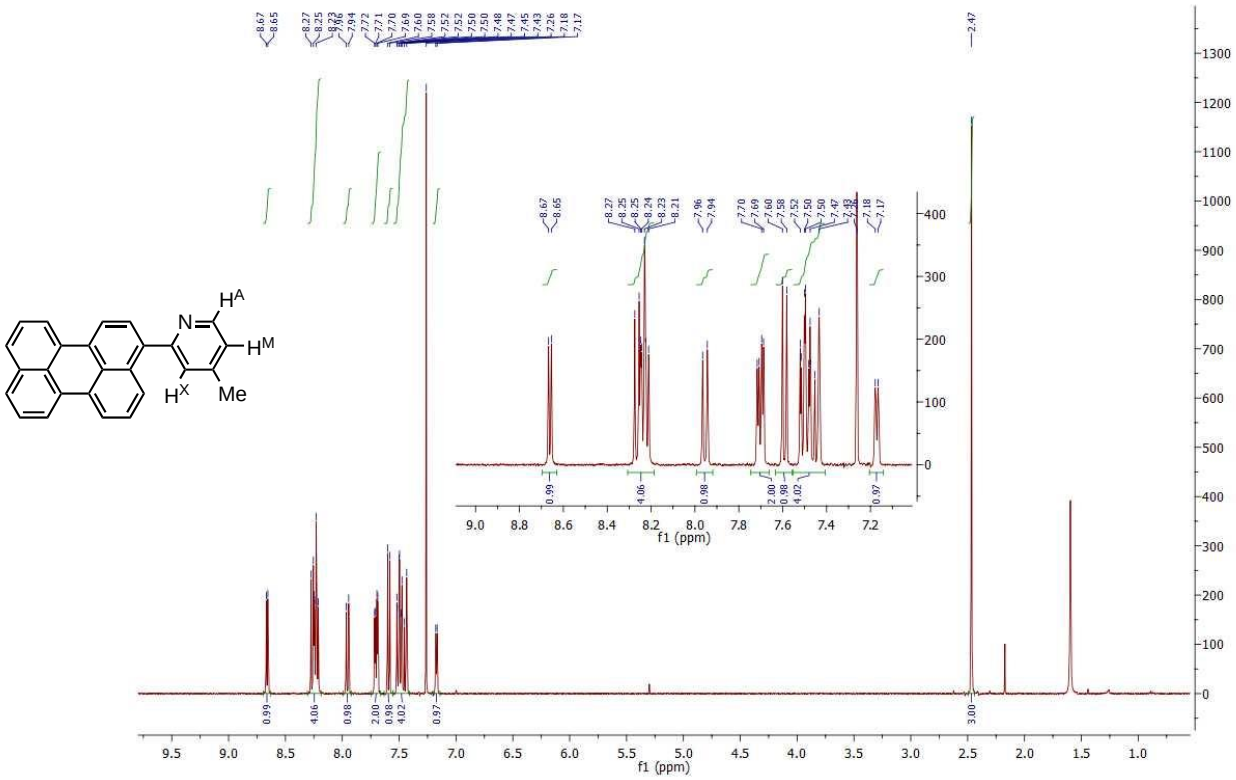


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**.

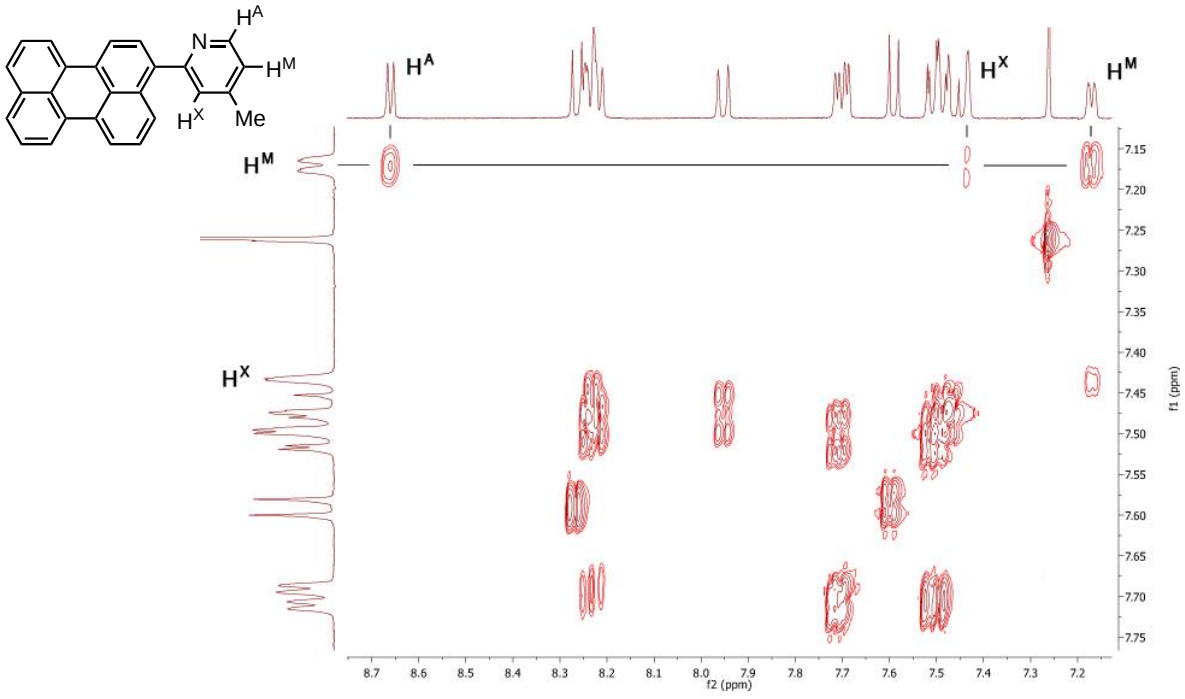


Fig. S2 COSY NMR spectrum of HPerPy **1**.

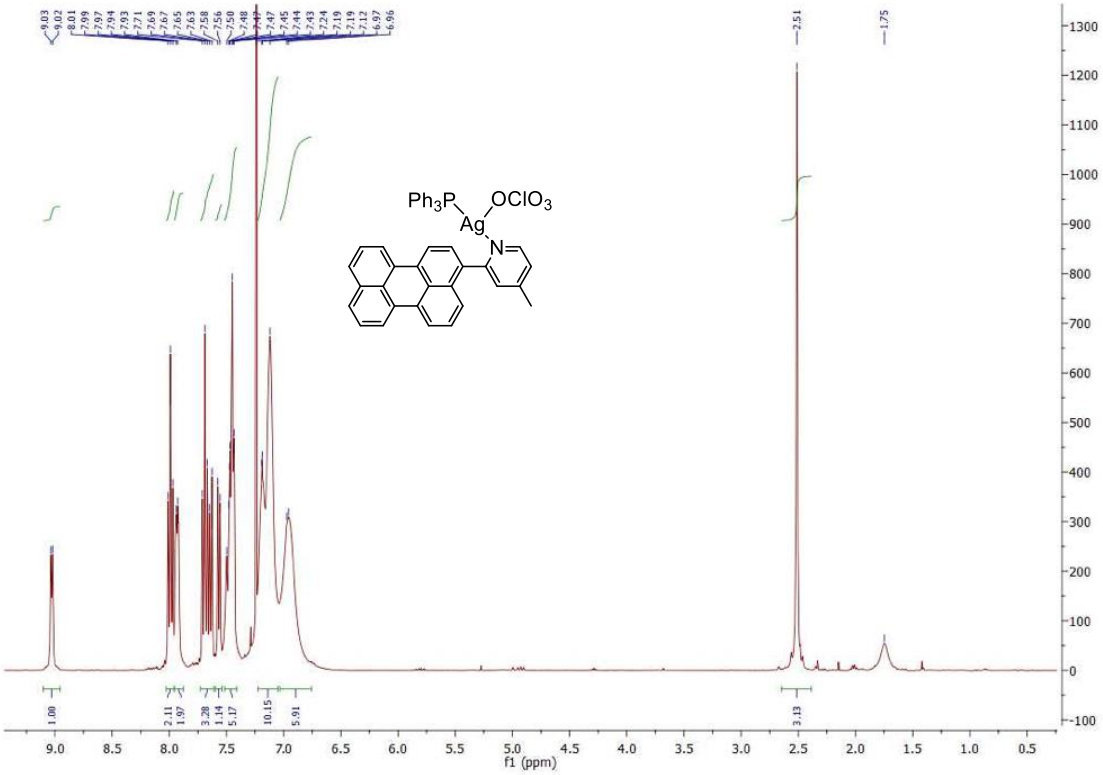


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2**.

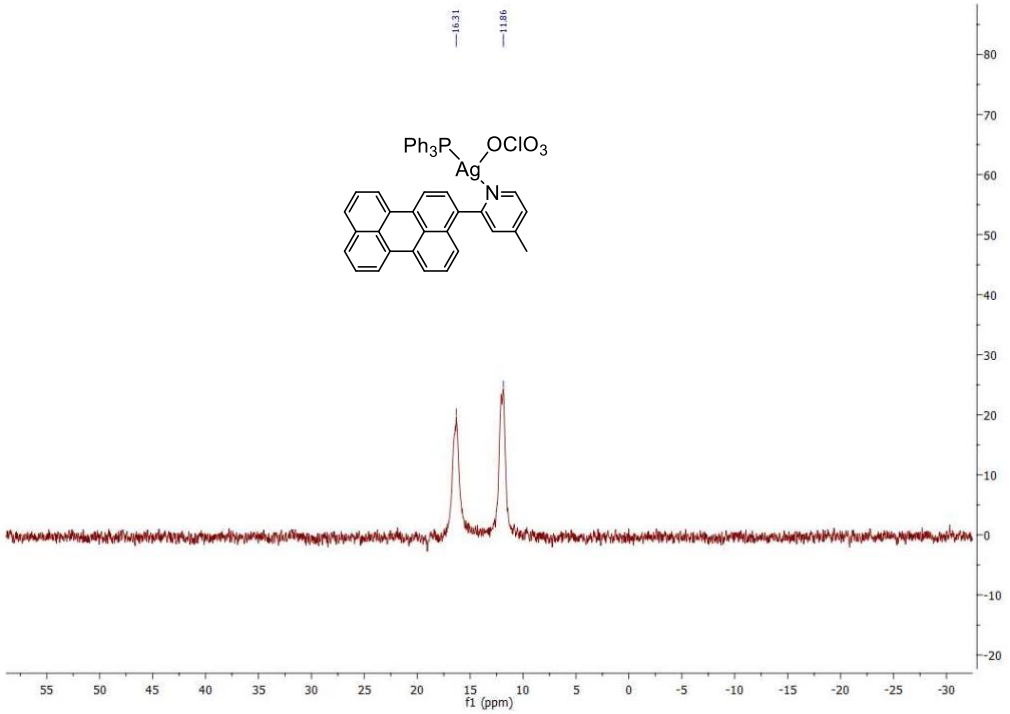


Fig. S4 $^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$) of spectrum of compound **2**.

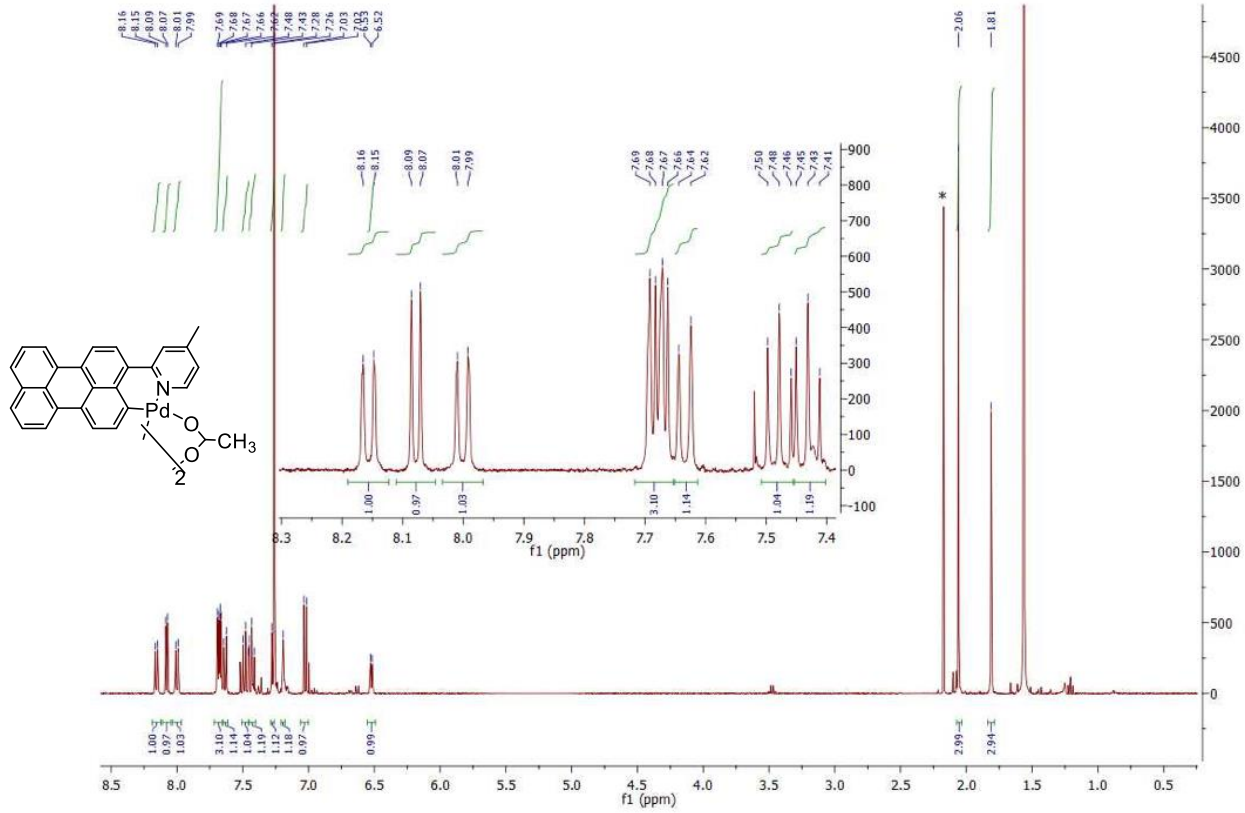


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

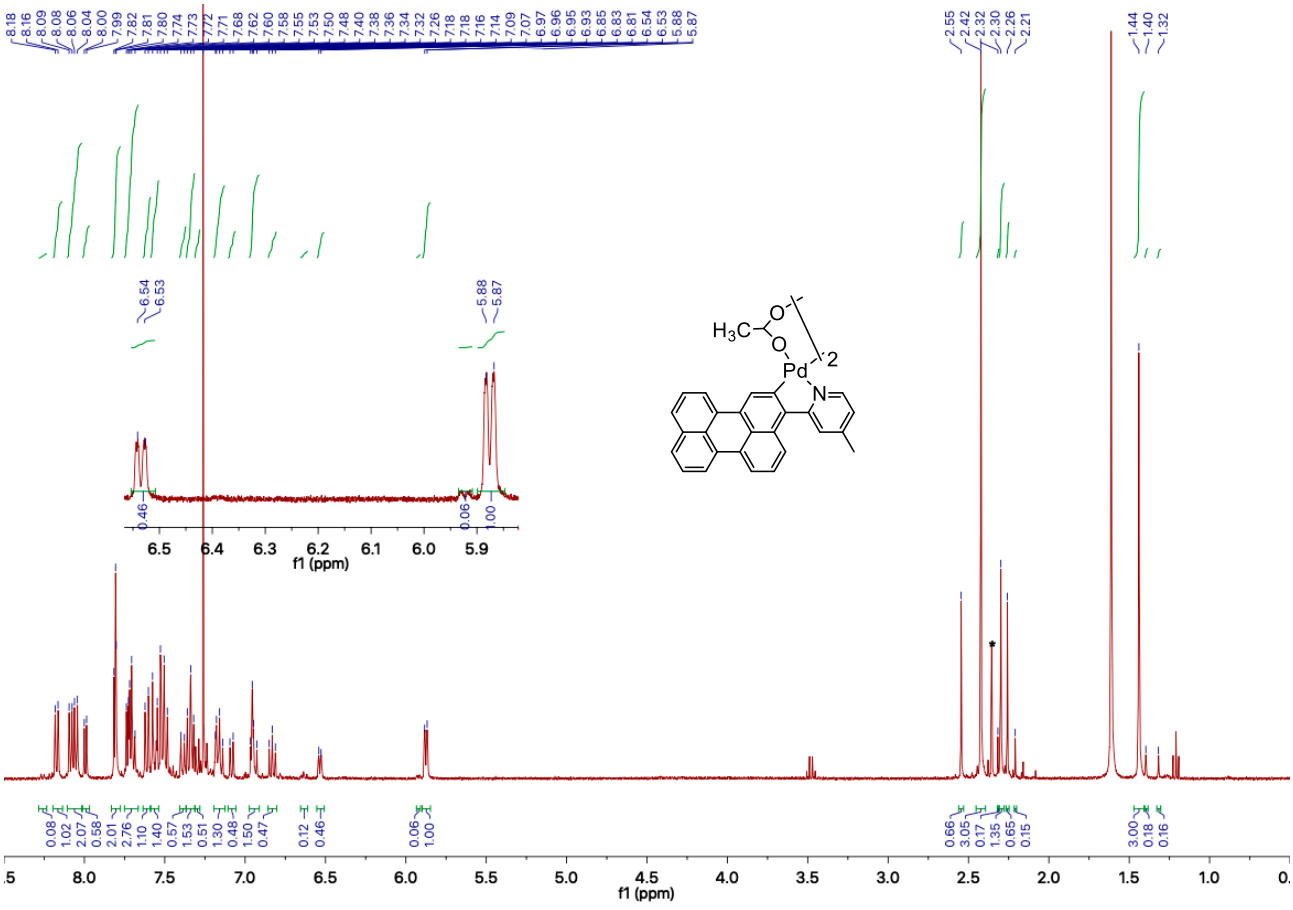


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**: mixture of 5+5 (66%) and 5+6 (34%) isomers.

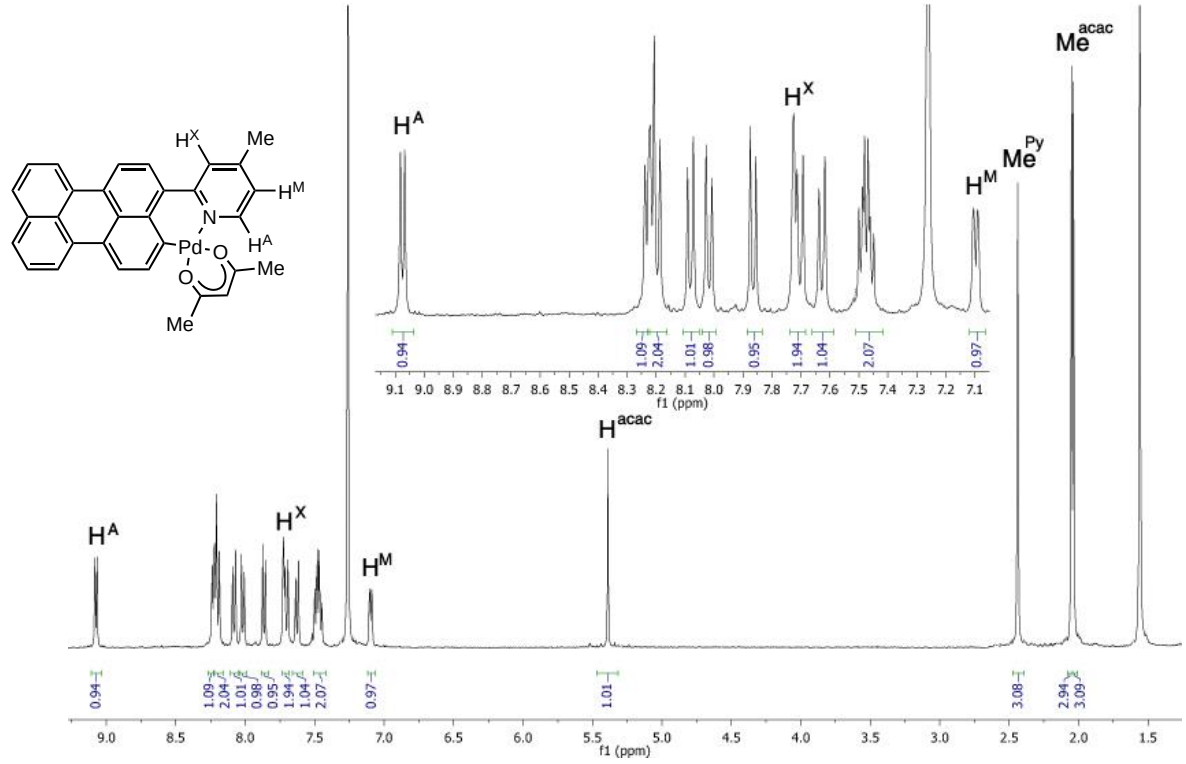


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**.

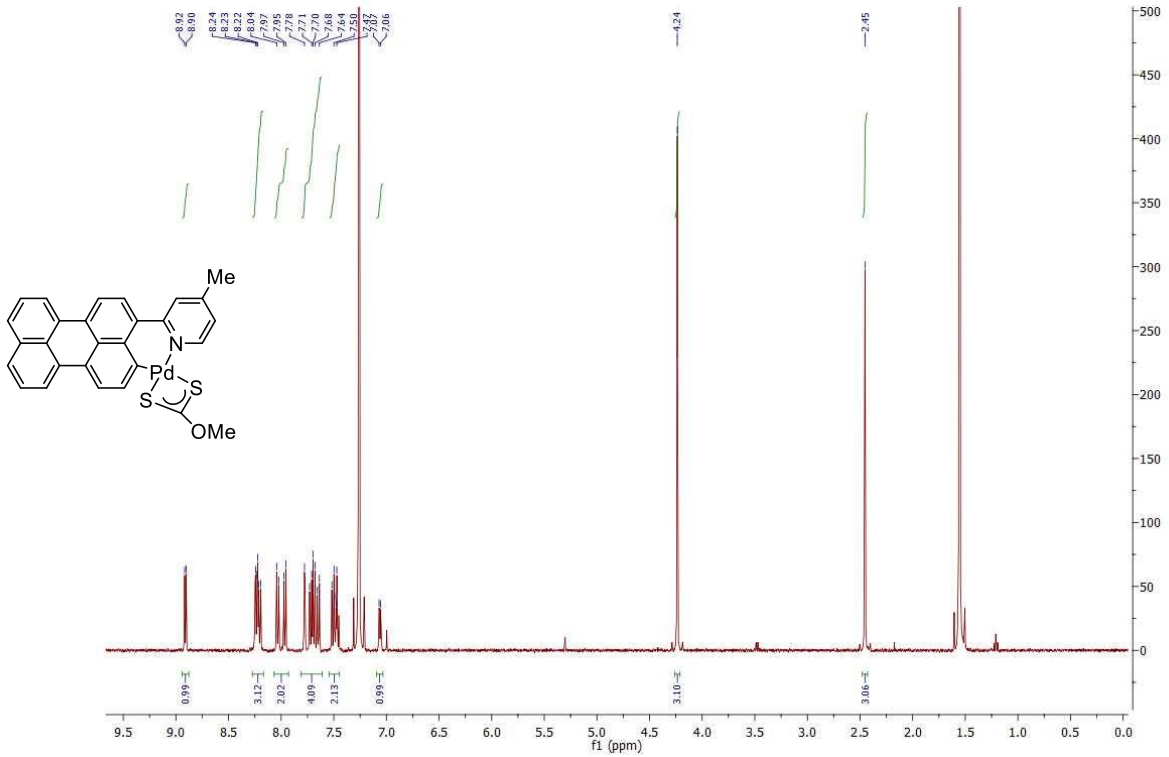


Fig. S8 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**.

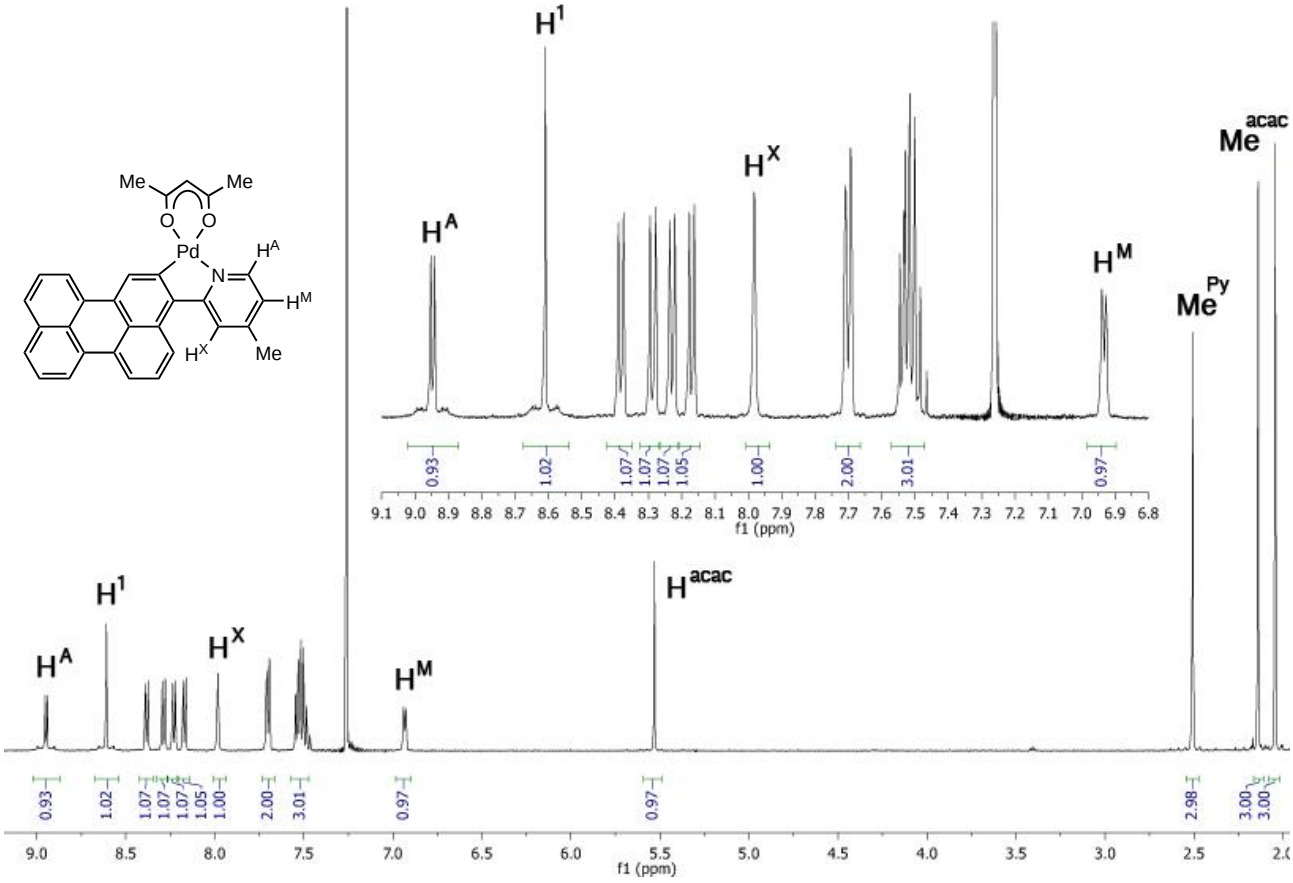


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**.

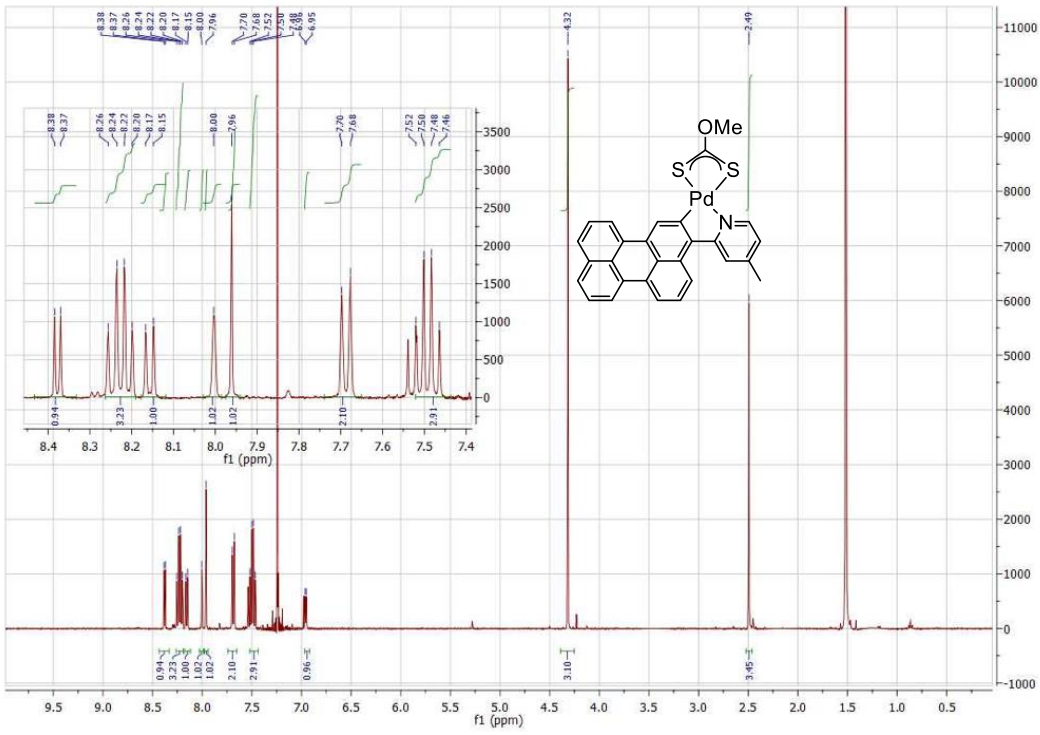


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**.

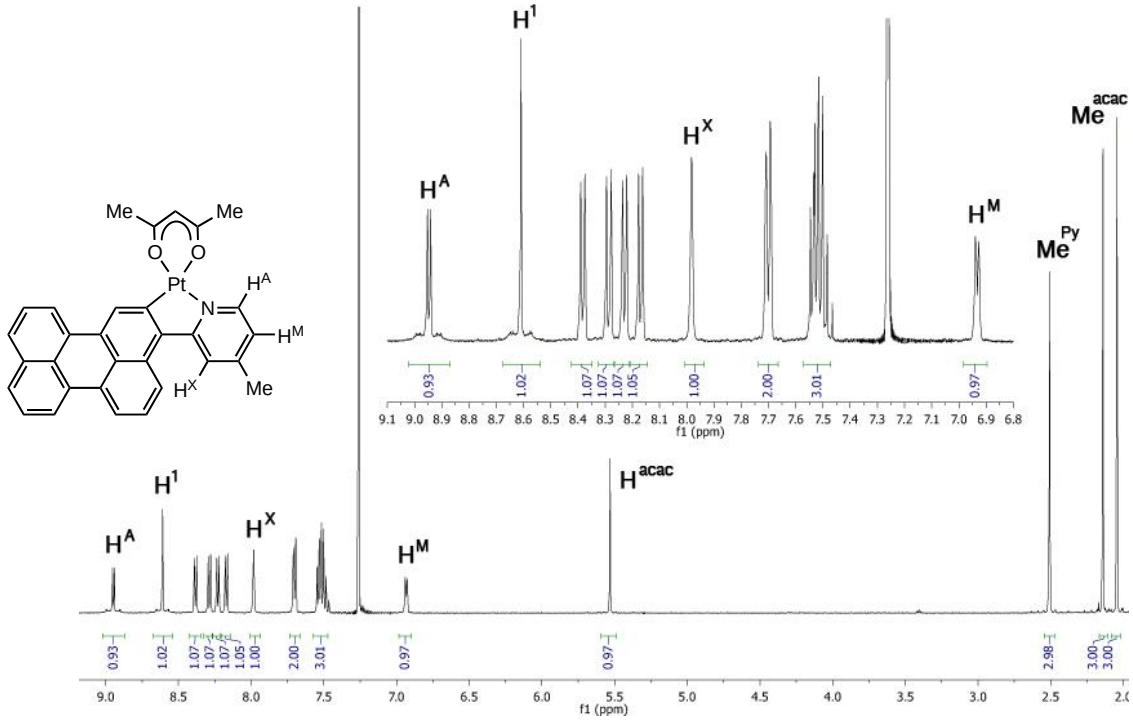


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**.

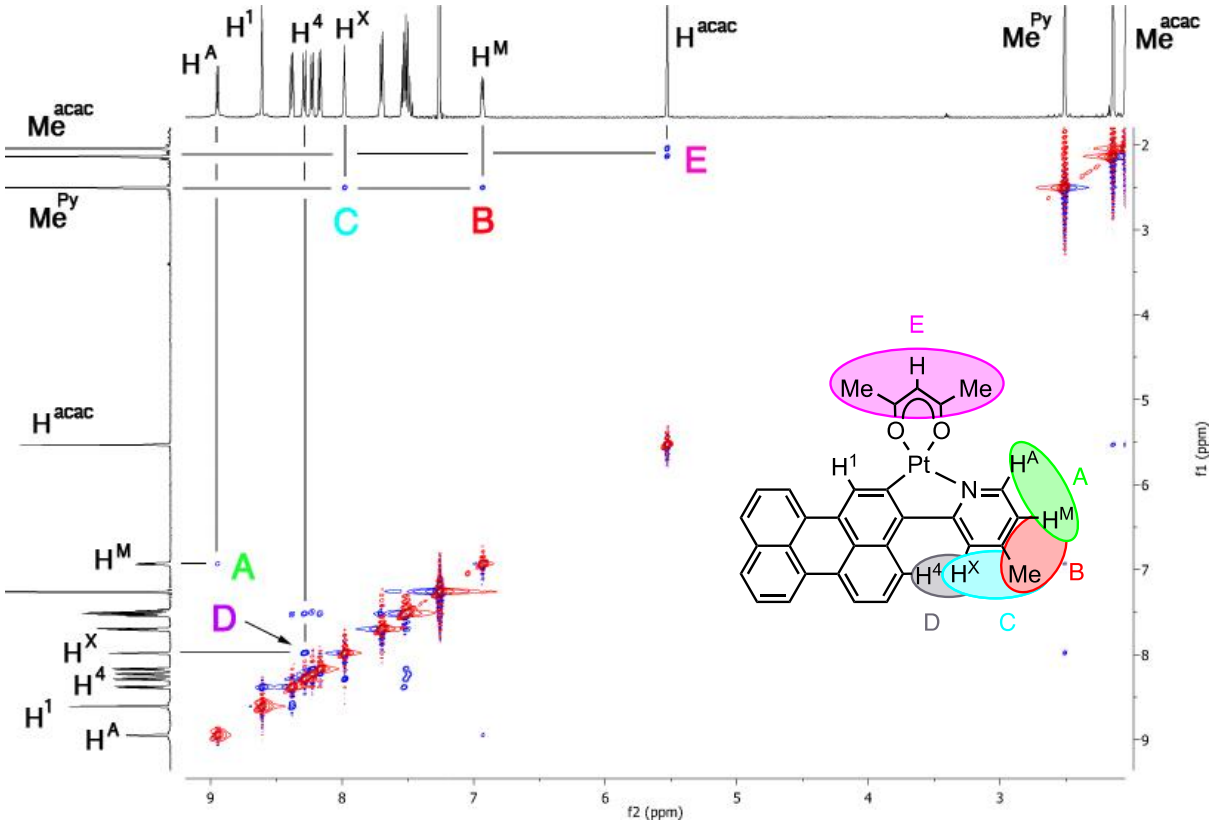


Fig. S12 NOESY NMR spectrum of compound **9**.

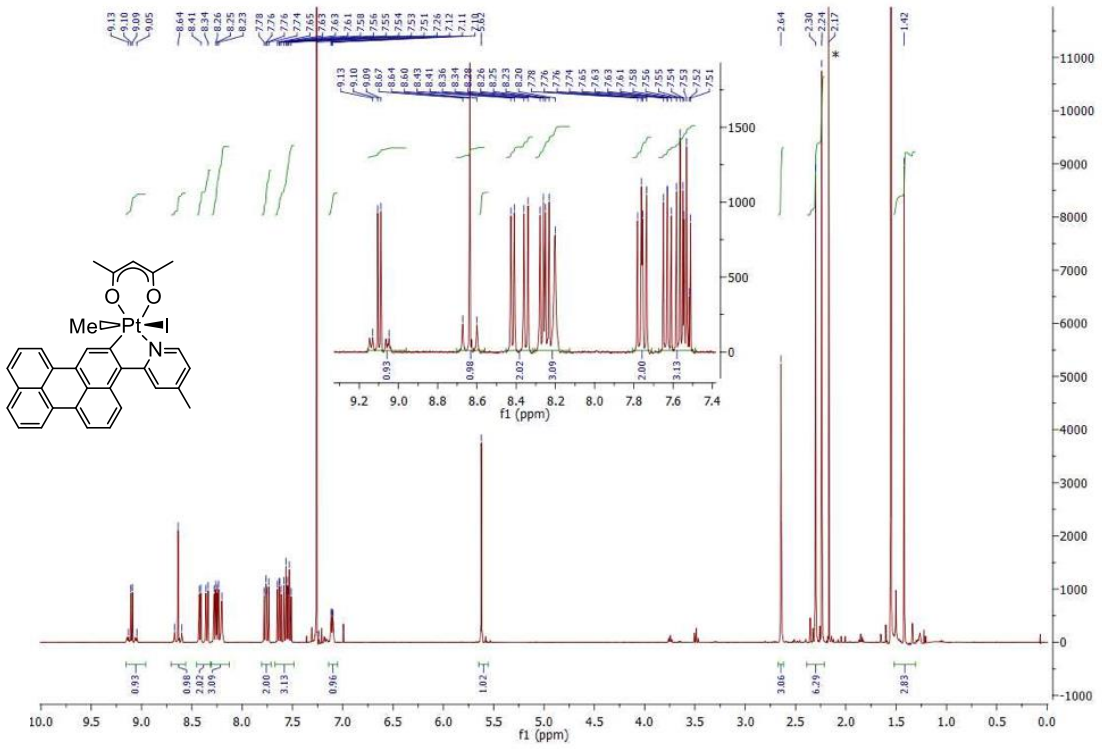


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**.

Table S1. Reaction conditions (solvent, temperature, time) to obtain dinuclear Pd(II) complexes **3** and **4**. Percentage obtained by synthesizing the mononuclear complexes (estimated by ^{1}H NMR spectrum).

Solvent	Temperature/ºC	Time/h	5-membered ring (%)	6-membered ring (%)
CH_3COOH	40	24	38	62
CH_3COOH	70	24	82	18
CH_3COOH	70	6	**88**	12
Toluene	30	16	30	70
Toluene	60	2	40	60
Toluene	80	2	37	63
Toluene	100	4	32	68
THF	40	24	30	70
CH_2Cl_2	25	5	40	60
Methanol	25	5	31	69
Methanol	25	15	21	**79**
Methanol	25	20	24	76

Table S2. Crystal and structure refinement data for **2**, **4**, **5**, **8**, **9**, and **10**.

Compound	**2**	**4**	**5**
Empirical formula	$C_{44}H_{32}AgClNO_4P$	$C_{56}H_{38}N_2O_4Pd_2$	$C_{31}H_{23}NO_2Pd$
Formula weight	812.99	1015.68	547.90
Temperature/K	293	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c	$P2_1/n$
a/Å	18.675(2)	18.6782(8)	7.9917(2)
b/Å	10.7526(12)	17.1192(5)	15.8643(5)
c/Å	19.190(3)	16.1066(7)	18.4722(4)
α/°	90	90	90
β/°	109.521(14)	116.206(6)	100.131(2)
γ/°	90	90	90
Volume/Å^3	3632.0(8)	4620.8(4)	2305.45(11)
Z	4	4	4
ρ_{calc}g/cm^3	1.487	1.460	1.579
μ/mm^{-1}	0.718	0.827	0.835
F(000)	1656.0	2048.0	1112.0
Crystal size/mm^3	0.2692 × 0.1184 × 0.0667	0.4132 × 0.3198 × 0.1502	0.22 × 0.14 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.406 to 57.778	4.758 to 58.922	4.48 to 59.064
Index ranges	-23 ≤ h ≤ 25, -13 ≤ k ≤ 14, -19 ≤ l ≤ 25	-25 ≤ h ≤ 25, -23 ≤ k ≤ 23, -21 ≤ l ≤ 21	-10 ≤ h ≤ 9, -21 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	15923	12093	11815
Independent reflections	7991 [R_{int} = 0.0320, R_{sigma} = 0.0548]	5402 [R_{int} = 0.0254, R_{sigma} = 0.0402]	5490 [R_{int}= 0.0447, R_{sigma}= 0.0841]
Data/restraints/parameters	7991/0/498	5402/0/291	5490/0/319
Goodness-of-fit on F^2	1.018	1.011	0.993
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.0961	R_1 = 0.0329, wR_2 = 0.0741	R_1= 0.0488, wR_2= 0.0710
Final R indexes [all data]	R_1 = 0.0960, wR_2 = 0.1146	R_1 = 0.0506, wR_2 = 0.0841	R_1= 0.1084, wR_2= 0.0888
Largest diff. peak/hole / e Å^{-3}	0.47/-0.33	0.52/-0.44	0.53/-0.52

Compound	**8**	**9**	**10**
Empirical formula	$C_{28}H_{19}NOS_2Pd$	$C_{31}H_{23}NO_2Pt$	$C_{32}H_{26}INO_2Pt$
Formula weight	555.96	636.59	778.53
Temperature/K	293(2)	293	293
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	$Pna2_1$	Pbca	P-1
a/Å	19.8850(4)	7.8450(2)	7.7315(5)
b/Å	15.3326(3)	19.7471(6)	12.3683(5)
c/Å	7.25084(18)	29.7999(10)	13.9478(4)
α/°	90	90	80.964(3)
β/°	90	90	84.500(4)
γ/°	90	90	81.117(4)
Volume/Å^3	2210.70(8)	4616.5(2)	1297.91(10)
Z	4	8	2
ρ_{calc}g/cm^3	1.670	1.832	1.992
μ/mm^{-1}	1.051	6.109	6.626
F(000)	1120.0	2480.0	744.0
Crystal size/mm^3	0.30 × 0.25 × 0.19	0.37 × 0.12 × 0.04	0.30 × 0.25× 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.882 to 58.684	4.126 to 59.096	4.154 to 59.252
Index ranges	-18 ≤ h ≤ 25, -20 ≤ k ≤ 14, -9 ≤ l ≤ 6	-8 ≤ h ≤ 10, -17 ≤ k ≤ 26, -40 ≤ l ≤ 40	-9 ≤ h ≤ 8, -14 ≤ k ≤ 16, -14 ≤ l ≤ 19
Reflections collected	8215	17667	10089
Independent reflections	3776 [R_{int} = 0.0294, R_{sigma} = 0.0379]	5650 [R_{int} = 0.0291, R_{sigma} = 0.0343]	6049 [R_{int}= 0.0289, R_{sigma}= 0.0567]
Data/restraints/parameters	3776/1/301	5650/0/319	6049/0/338
Goodness-of-fit on F^2	1.068	1.069	1.036
Final R indexes [I>=2σ (I)]	R_1= 0.0308, wR_2 = 0.0608	R_1= 0.0325, wR_2= 0.0530	R_1= 0.0356, wR_2= 0.0673
Final R indexes [all data]	R_1= 0.0416, wR_2 = 0.0675	R_1= 0.0574, wR_2= 0.0596	R_1= 0.0482, wR_2= 0.0751
Largest diff. peak/hole / e Å^{-3}	0.27/-0.60	0.47/-0.74	0.58/-1.22

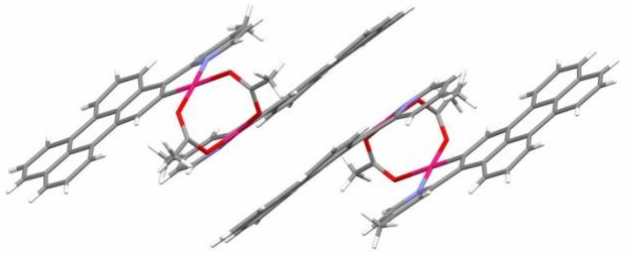


Fig. S14 X-ray packing view of dinuclear Pd(II) compound **4** showing intermolecular π-stacking of the perylene groups. The plane-to-plane stacking of perylene rings is 3.358 Å.

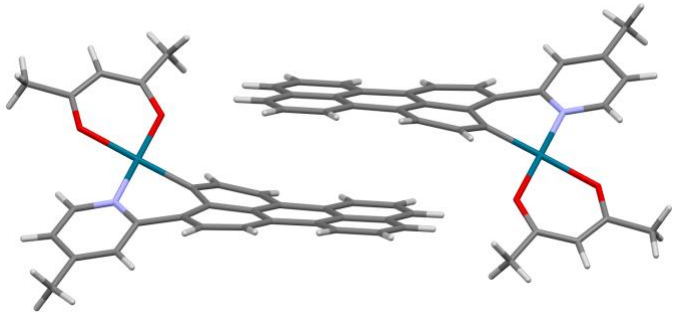


Fig. S15 X-ray packing view of compound **5** showing partial intermolecular π-stacking of the perylene groups. The plane-to-plane stacking of perylene rings is 3.373 Å.

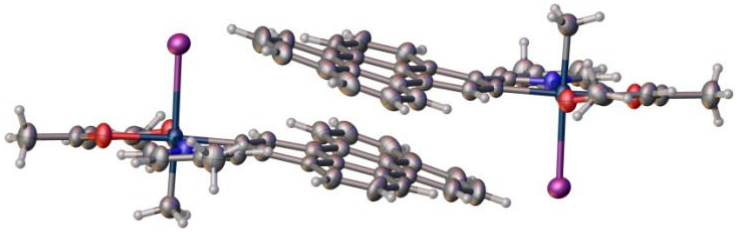


Fig. S16 X-ray packing view of Pt(IV) compound **10** showing intermolecular π-stacking of the perylene groups. The plane-to-plane stacking of perylene rings is 3.523 Å.

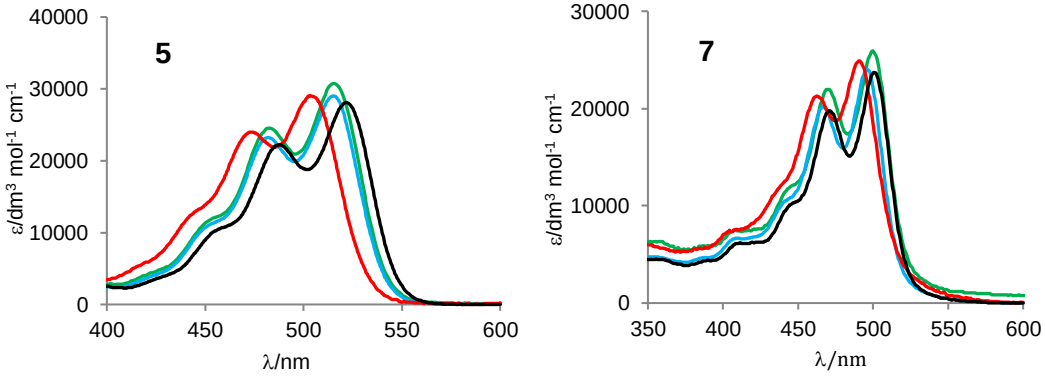


Fig. S17. Absorption spectra of complexes **5** and **7** in different solvents (green: $CHCl_3$, blue: THF, red: CH_3CN, black: toluene) at room temperature.

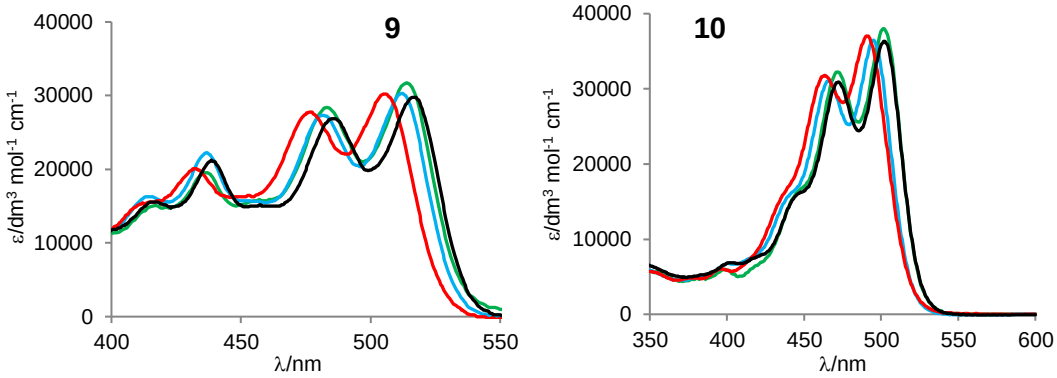


Fig. S18 Absorption spectra of complexes **9** and **10** in different solvents (green: $CHCl_3$, blue: THF, red: CH_3CN, black: toluene) at room temperature.

Table S3. Relative free energies (in kcal/mol) between 5-membered and 6-membered isomers of [M(PerPy)(acac)] complexes (M = Pd, Pt). The 5-membered ones are always the most stable in both Pd and Pt systems.

Solvent	?	Pd	Pt
Gas phase	-	4.35	5.89
C_6H_{14}	1.88	4.16	5.72
PhMe	2.37	4.10	5.66
CS_2	2.61	4.08	5.63
Et_2O	4.24	3.96	5.52
$CHCl_3$	4.71	3.94	5.50
THF	7.43	3.86	5.43
CH_2Cl_2	8.93	3.83	5.40
Me_2CO	20.49	3.74	5.32
MeOH	32.61	3.71	5.29

Table S4. Calculated absorption parameters (wavelengths in nm and their intensities) for HPerPy compounds in gas phase and chloroform solution. For each entry, main contributions of the orbitals for the transition and their coefficients are shown.

(*a*) HPerPy **1**

Gas phase		$CHCl_3$	
λ (*f*)	Assignment	λ (*f*)	Assignment
450 (0.55)	Perylene: HOMO → LUMO [0.70]	465 (0.69)	Perylene: HOMO → LUMO [0.71]
259 (0.22)	Perylene: HOMO → π*(Per) [0.44] π(Py) → LUMO [0.34] π(Per) → LUMO [0.32]	261 (0.37)	Perylene: HOMO → π*(Per) [0.48] π(Per) → LUMO [0.34] π(Py) → LUMO [0.31]
235 (0.16)	ILCT (Per → Py): π(Per) → π*(Py) [0.48] π(Per,Py) → π*(Py) [0.40]	235 (0.17)	ILCT (Per → Py): π(Per) → π*(Py) [0.45] π(Per,Py) → π*(Py) [0.40]
…		…	…

(*b*) [Pd(PerPy)(acac)]-six-membered **5**

Gas phase		CHCl3	
λ (*f*)	Assignment	λ (*f*)	Assignment
533 (0.44)	Perylene: HOMO → LUMO [0.69]	534 (0.64)	Perylene: HOMO → LUMO [0.70]
402 (0.03)	ILCT (Per → Py): HOMO → π*(Py) [0.61] π(acac) → LUMO [0.21]	383 (0.04)	ILCT (Per → Py): HOMO → π*(Py) [0.58] HOMO → π*(acac) [0.21]
397 (0.04)	MLCT (Pd → Per): *z*2 → LUMO [0.56] π(acac) → LUMO [0.40]	388 (0.04)	MLCT (Pd → Per): *z*2 → LUMO [0.58] π(acac) → LUMO [0.37]
357 (0.04)	Perylene: π(Per) → LUMO [0.47] HOMO → π*(acac) [0.33] HOMO → π*(acac),πd [0.26]	351 (0.04)	Perylene: π(Per) → LUMO [0.53] HOMO → π*(Py) [0.25] HOMO → π*(acac) [0.21]
354 (0.04)	LLCT (Per → Py,acac): HOMO → π*(acac),πd [0.40] π(Per) → LUMO [0.40] HOMO → π*(acac) [0.32] HOMO → π*(Py) [0.21]	355 (0.02)	LLCT (Per → Py,acac): HOMO → π*(Py) [0.54] HOMO → π*(acac) [0.24] π(Per) → LUMO [0.23]
339 (0.07)	Perylene + MLCT (Pd → acac): HOMO → π*(Per) [0.33] *z*2 → π*(acac),πd [0.31] *z*2 → π*(acac) [0.26] π(Per) → LUMO [0.24] π(Per) → LUMO [0.23]	337 (0.08)	Perylene + MLCT (Pd → acac): HOMO → π*(Per) [0.35] π*(Per) → LUMO [0.29] *z*2 → π*(acac) [0.24] π(Per) → LUMO [0.24] *z*2 → π*(acac),πd [0.24]
304 (0.05)	LLCT (acac → Py): π(acac) → π*(Py) [0.42] πd → LUMO [0.24] π(Per) → LUMO [0.20]	296 (0.02)	LLCT (acac → Py): π(acac) → → π*(Py) [0.55] HOMO → π*(Per) [0.21]
277 (0.02)	acac: π(acac) → π*(acac) [0.43] π(acac) → π*(acac),πd [0.38]	279 (0.08)	acac: π(acac) → π*(acac) [0.44] π(acac) → π*(acac),πd [0.41]
275 (0.07)	Perylene: HOMO → π*(Per) [0.44] HOMO → π*(Per) [0.31] π(Per) → LUMO [0.24]	274 (0.15)	Perylene: HOMO → π*(Per) [0.47] π(Per) → LUMO [0.28] π(acac) → π*(Py) [0.22]
273 (0.06)	Perylene + ILCT (Per → Py): HOMO → π*(Per) [0.35] π(Per) → π*(Py) [0.33] πd,π(Per) → LUMO [0.26]	275 (0.06)	LLCT (acac → Py): π(acac) → π*(Py) [0.45] π(acac) → π*(acac),πd [0.27] *z*2 → π*(acac),πd [0.22]
		…	…

(*c*) [Pd(PerPy)(acac)]-five-membered **7**

Gas phase		$CHCl_3$	
λ (*f*)	Assignment	λ (*f*)	Assignment
500 (0.50)	Perylene: HOMO → LUMO [0.70]	514 (0.66)	Perylene: HOMO → LUMO [0.70]
408 (0.06)	LLCT (acac → Per): π(acac) → LUMO [0.68]	403 (0.07)	LLCT (acac → Per): π(acac) → LUMO [0.68]
322 (0.06)	Perylene: π(Per) → LUMO [0.46] π(Per) → LUMO [0.30] π(Per) → LUMO [0.20]	321 (0.08)	Perylene: π(Per) → LUMO [0.47] π(Per) → LUMO [0.30] HOMO → π*(Py) [0.20]
301 (0.03)	MLCT + ILCT (Pd,Per,acac → Py): πd → LUMO [0.46] πd,π(Per) → π*(Py,Per) [0.25] z^2 ✶ x^2-y^2 [0.22]	303 (0.04)	MLCT + ILCT (Pd,Per,acac → Py): π(acac) → π*(Py,Per) [0.41] π(acac) → LUMO [0.33] πd → LUMO [0.31] π(acac) → x^2-y^2 [0.20]
287 (0.04)	acac: π(acac) → π*(acac) [0.51] πd,π(Per) → π*(Py,Per) [0.27]	286 (0.08)	acac: HOMO → π*(Per) [0.44] π(acac) → π*(acac) [0.36] π(Per) → LUMO [0.20]
273 (0.11)	Perylene: πd → LUMO [0.38] HOMO → π*(Per) [0.37] π(Per) → LUMO [0.20]	273 (0.29)	Perylene: HOMO → π*(Per) [0.47] πd → LUMO [0.27] π(Per) → LUMO [0.23]
265 (0.07)	MLCT (Pd → Per): πd,π(Per) → LUMO [0.38] π(Per) → π*(Py,Per) [0.28] HOMO → π*(Per) [0.27] π(acac) → π*(acac) [0.25] π(Per) → π*(Py,Per) [0.21]	263 (0.10)	MLCT (Pd → Per): πd,π(Per) → LUMO [0.49] HOMO → π*(Per) [0.24] πd,π(Per) → π*(acac) [0.22]
261 (0.04)	MLCT + ILCT (Pd,Per → Py): πd,π(Per) → π*(Py) [0.48] z^2 → π*(Py) [0.25] HOMO → π*(Per) [0.22]	255 (0.05)	MLCT + ILCT (Pd,Per → Py): π(Per) → π*(Py,Per) [0.41] πd,π(Per) → π*(Py) [0.40] z^2 → π*(Py) [0.21]
…	□□□	…	…

(*c*) [Pt(PerPy)(acac)]-six-membered

Gas phase		$CHCl_3$	
λ (*f*)	Assignment	λ (*f*)	Assignment
563 (0.39)	Perylene: HOMO → LUMO [0.69]	559 (0.58)	Perylene: HOMO → LUMO [0.70]
425 (0.04)	ILCT (Per → Py): HOMO → π*(Py) [0.69]	408 (0.04)	ILCT (Per → Py): HOMO → π*(Py) [0.69]
397 (0.06)	LLCT (acac → Per): π(acac),πd → LUMO [0.66]	394 (0.07)	LLCT (acac → Per): π(acac),πd → LUMO [0.68]
373 (0.17)	ILCT (Per → Py): πd,π(Per) → LUMO [0.52] HOMO → π*(Py,Per) [0.41]	366 (0.09)	ILCT (Per → Py): HOMO → π*(Py,Per) [0.63] πd,π(Per) → LUMO [0.22]
298 (0.07)	Acac + MLCT (Pt ✶ acac): π(acac),πd → π*(acac) [0.55] πd,π(Per) → π*(Py) [0.24]	295 (0.09)	Acac + MLCT (Pt → acac): π(acac),πd → π*(acac) [0.59]
291 (0.08)	MLCT + ILCT (Pt,Per → Py): πd,π(Per) → π*(Py) [0.45] π(acac) → LUMO [0.29]	287 (0.13)	MLCT + ILCT (Pt,Per → Py): πd,π(Per) → π*(Py) [0.59]
279 (0.10)	Perylene: HOMO → π*(Per) [0.35] HOMO → π*(Per) [0.27] π(Per) → LUMO [0.21] π(Per) → π*(Py) [0.21]	278 (0.15)	Perylene: HOMO → π*(Per) [0.36] HOMO → π*(Per) [0.33] HOMO → π*(Per) [0.27] π(Per) → LUMO [0.21]
277 (0.03)	Perylene: HOMO → π*(Per) [0.32] π(Per),πd → LUMO [0.32] πd,π(Per) → π*(acac) [0.24] πd,π(Per) → π*(Py,Per) [0.21] z^2 → π*(Py,Per) [0.18]	278 (0.08)	Perylene: HOMO → π*(Per) [0.43] πd,π(Per) → π*(acac) [0.29] π(Per),πd → LUMO [0.21]
271 (0.05)	MLCT (Pt → Py,Per): πd,π(Per) → π*(Py,Per) [0.46] π(Per) → π*(Py) [0.23] π(Per),πd → LUMO [0.20]	264 (0.07)	MLCT (Pt → Py,Per): πd,π(Per) → π*(Py,Per) [0.54] πd,π(Per) → π*(acac) [0.21]
…	...	…	…

(*d*) [Pt(PerPy)(acac)]-five-membered **9**

Gas phase		$CHCl_3$	
λ (*f*)	Assignment	λ (*f*)	Assignment
507 (0.45)	Perylene: HOMO → LUMO [0.69]	519 (0.61)	Perylene: HOMO → LUMO [0.70]
422 (0.12)	MLCT + ILCT (Pt,acac,Per → Per): π(Per,acac),πd → LUMO [0.67]	420 (0.14)	MLCT + ILCT (Pt,acac,Per → Per): π(Per,acac),πd → LUMO [0.68]
391 (0.06)	LLCT (acac → Per): πd,π(acac) → LUMO [0.62] HOMO → π(Py,Per) [0.24]	390 (0.06)	LLCT (acac → Per): HOMO → π(Py,Per) [0.56] πd,π(acac) → LUMO [0.37]
322 (0.06)	Perylene: π(Per) → LUMO [0.48] π(Per) → LUMO [0.33] HOMO → π*(Per) [0.20]	321 (0.07)	Perylene: π(Per,acac),πd → π(Py,Per) [0.37] π(Per) → LUMO [0.37] π(Per) → LUMO [0.27] HOMO → π*(Py) [0.24]
302 (0.05)	MLCT + ILCT (Pt,acac → Py): πd,π(acac) → π(Py,Per) [0.43] z^2 → π*(Per) [0.29] π(Per) → LUMO [0.27]	300 (0.09)	MLCT + ILCT (Pt,acac → Py): πd,π(acac) → π(Py,Per) [0.59]
290 (0.07)	MLCT (Pt,acac → acac) + Perylene: π(acac) → LUMO [0.50] πd,π(acac) → π*(acac) [0.39]	292 (0.13)	MLCT (Pt,acac → acac) + Perylene: πd,π(acac) → π*(acac) [0.42] HOMO → π*(Per) [0.36] HOMO → π*(Per) [0.21]
275 (0.05)	Perylene: πd,π(Per) → LUMO [0.42] HOMO → x^2-y^2,π*(Per) [0.36]	276 (0.14)	Perylene: HOMO → π*(Per) [0.44] πd,π(Per) → LUMO [0.35] π(Per) → LUMO [0.20]
275 (0.03)	MLCT (Pt → Py): πd,π(acac) → π(Py) [0.60]	271 (0.08)	MLCT (Pt → Py): πd,π(acac) → π*(Py) [0.53]
267 (0.14)	Perylene: πd,π(Per) → LUMO [0.41] π(Per) → π(Py,Per) [0.22] HOMO → π*(Per) [0.32] π(Per) → π(Py,Per) [0.21]	267 (0.16)	Perylene: πd,π(Per) → LUMO [0.46] HOMO → π*(Per) [0.28] z^2 → x^2-y^2,π*(Per) [0.23]
…		…	…

(*e*) [Pt(PerPy)(acac)MeI)]-five-membered **10**.

Gas phase		CHCl3	
λ (*f*)	Assignment	λ (*f*)	Assignment
502 (0.49)	Perylene: HOMO → LUMO [0.65] *p*(I) → LUMO [0.25]	519 (0.65)	Perylene: HOMO → LUMO [0.70]
411 (0.02)	ILCT (Per → Py): *p*(I) → π*(Py) [0.46] HOMO → π*(Py) [0.37] *p*(I) → π*(Py) [0.25]	410 (0.07)	ILCT (Per → Py): HOMO → π*(Py) [0.69]
324 (0.03)	Perylene: π(Per) → LUMO [0.48] *p*(I) → πd,π*(Per) [0.30] HOMO → πd,π*(Per) [0.25] π(Per) → LUMO [0.21]	336 (0.06)	Perylene: π(Per) → LUMO [0.52] HOMO → πd,π*(Per) [0.24] HOMO → π*(Per) [0.21] π(Per,Py) → LUMO [0.20]
315 (0.03)	Perylene: π(Per) → LUMO [0.40] π(Per) → LUMO [0.39] π(Per) → LUMO [0.28] HOMO → πd,π*(Per) [0.20]	327 (0.02)	Perylene: π(Per,Py) → LUMO [0.43] HOMO → π*(Per) [0.31] π(Per) → LUMO [0.23] *p*(I),π(acac) → π*(Py) [0.21]
337 (0.01)	LLCT (I,acac → Py,acac): *p*(I),π(acac) → π*(Py) [0.46] *p*(I),π(acac) → π*(acac)[0.45]	323 (0.06)	LLCT (I,acac → Py,acac): *p*(I),π(acac) → π*(Py) [0.41] *p*(I),π(acac) → π*(acac) [0.27] π(Per,Py) → LUMO [0.25]
315 (0.05)	Perylene: π(Per) → LUMO [0.43] HOMO → π*(Per),πd [0.35] HOMO → πd,π*(Per) [0.29]	318 (0.05)	Perylene: π(Per) → LUMO [0.58] HOMO → π*(Per) [0.19]
306 (0.03)	Perylene: HOMO → LUMO [0.44] π(Per) → LUMO [0.35] HOMO → π*(Per) [0.30]	308 (0.02)	Perylene: HOMO → π*(Per) [0.41] π(Per) → LUMO [0.28] HOMO → π*(Per) [0.24]
315 (0.01)	LLCT (I,acac → Py): *p*(I),π(acac) → π*(Py,Per),πd [0.38] π(acac) → π*(Py) [0.33] *p*(I),π(acac) → π*(Py) [0.27] π(acac) → π*(acac) [0.23]	306 (0.06)	LLCT (I,acac → Py): π(acac,Per) → π*(Py) [0.33] *p*(I),π(acac) → π*(Py) [0.31] *p*(I),π(acac) → π*(acac) [0.30] *p*(I) → π*(Py,acac),πd [0.20]
275 (0.05)	LLCT (acac → Py): π(acac,Per) → π(Py,Per),πd [0.48] π(Per,acac) → π*(Py) [0.22] π(acac,Per) → π*(Py) [0.21]	275 (0.07)	LLCT (acac → Py): π(acac,Per) → π*(Py,acac),πd [0.54] *p*(I),π(acac) → π*(Py) [0.23]
272 (0.08)	LLCT (acac → Py): π(Per,acac) → π*(Py) [0.36]	271 (0.04)	LLCT (I,acac → Py): *p*(I),π(acac) → π*(Py) [0.52]

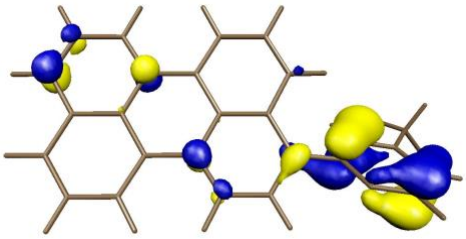
	π(Per,acac) → π*(acac) [0.31] π(Py),πd → LUMO [0.30]		*p*(I),π(acac) → π*(Py,acac),πd [0.22]
270 (0.06)	Perylene: HOMO → π*(Per) [0.39] π(Per) → π*(Py) [0.31] π(Per,acac) → π*(acac) [0.29]	273 (0.18)	Perylene: HOMO → π*(Per) [0.41] π(Per,Py) → π*(Py) [0.27] *p*(I),π(acac) → π*(Py) [0.25] π(Per) → π*(Py) [0.25]
269 (0.08)	LLCT (I,acac → Per): *p*(I),π(acac) → πd,π*(Per) [0.34] *p*(I) → π*(Per) [0.34] π(Py),πd → LUMO [0.21]	268 (0.04)	LLCT (I,acac → Per): *p*(I),π(acac) → πd,π*(Per) [0.33] π(acac,Per) → πd,π*(Per) [0.29] π(Per,Py) → π*(Py) [0.21]
263 (0.06)	LLCT (acac → Py,Per): π(acac,Per) → πd,π*(Per) [0.32] π(acac,Per) → π*(Py) [0.31] *p*(I),π(acac) → πd,π*(Per) [0.22]	261 (0.09)	LLCT (acac → Py,Per): π(Py),πd → LUMO [0.28] π(acac,Per) → π*(Py) [0.25] *p*(I),π(acac) → πd,π*(Per) [0.24] π(Per) → π*(Py) [0.24]
250 (0.11)	ILCT (Per → Py): π(Per) → π*(Py) [0.35] π(Per,acac) → π*(Py,Per),πd [0.26]	255 (0.11)	ILCT (Per → Py): π(Per) → π*(Py) [0.41] π(Per,Py) → π*(acac) [0.37]

Annotation for the involved orbitals:

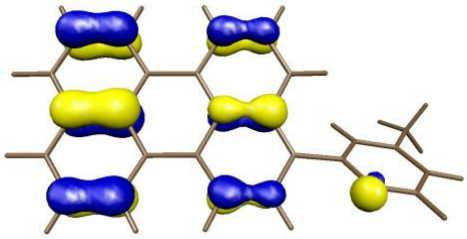
- π(Per) and π*(Per) indicates generic occupied and empty orbitals of perylene. Since all perylene orbitals are of type π, only HOMO and LUMO are emphasized. Analogously, for π(Py) and π*(Py), or π(acac) and π*(acac).
- z^2 indicates a *d*-orbital centered in the metal considering the most symmetric environment for the metals, as bonding-axes for lineal Au complexes or perpendicular to square-planar environment ones.
- x^2-y^2 indicate an empty *d*-orbital centered in the metal having σ-antibonding character.
- πd is used to design occupied *d*-orbitals related to the metal-ligand back-bonding having antibonding contribution.

Table S5. Molecular orbitals for the ligand HPerPy and its complexes. Percentage compositions for each one entry from Natural Populations Analysis are shown.

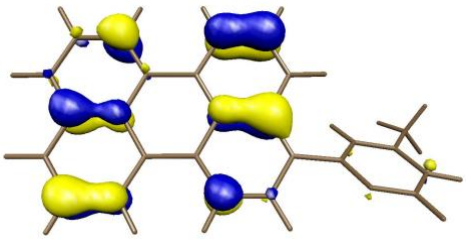
(*a*) HPerpy **1**



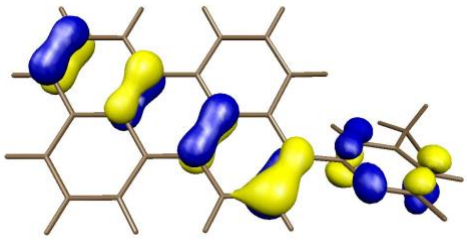
MO 84: -0.266 Ha
Py (61), **Per (33)**



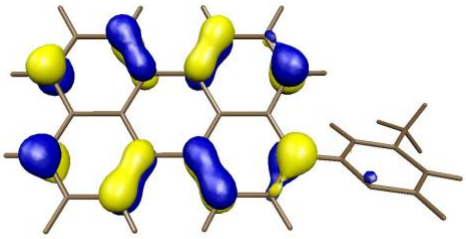
MO 87: -0.245 Ha
Per (92), Py (4)



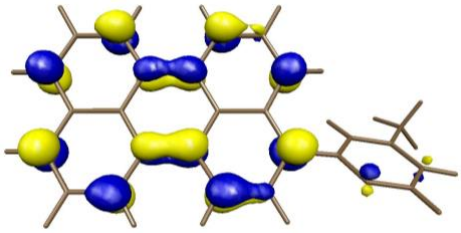
MO 88: -0.240 Ha
Per (90), Py (5)



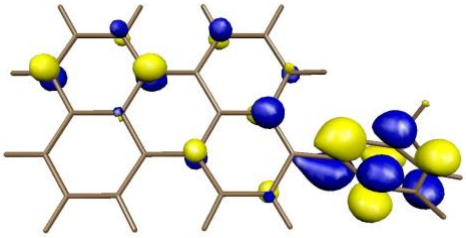
MO 89: -0.237 Ha
Per (69), Py (26)



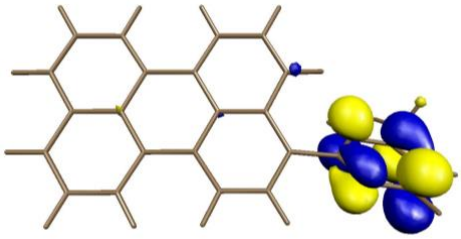
MO 90 (*HOMO*): -0.179 Ha
Per (94), Py (2)



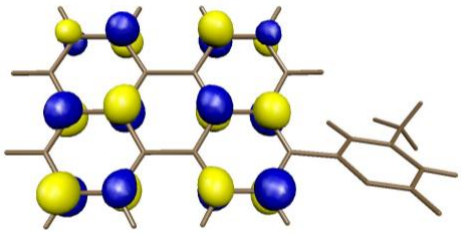
MO 91 (*LUMO*): -0.072 Ha
Per (91), Py (5)



MO 92: -0.026 Ha
Py (57), **Per (36)**

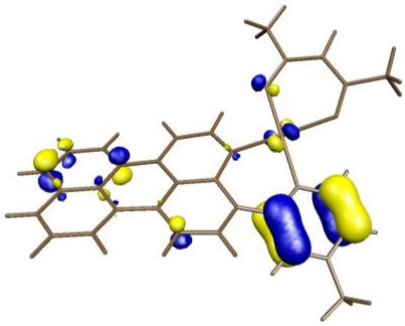


MO 94: -0.004 Ha
Py (83), Per (4)

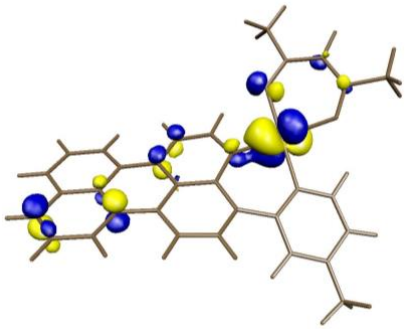


MO 96: +0.004 Ha
Per (94)

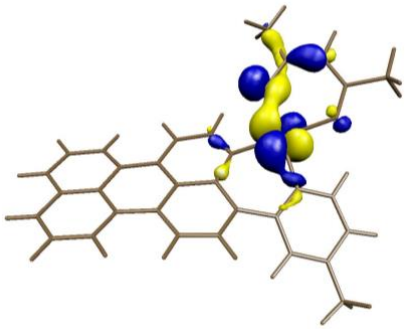
(*b*) [Pd(PerPy)(acac)]-six-membered **5**



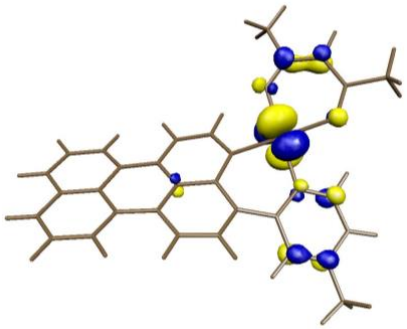
MO 114: -0.279 Ha
Py (54), **Per (33)**, Pd (4**)**



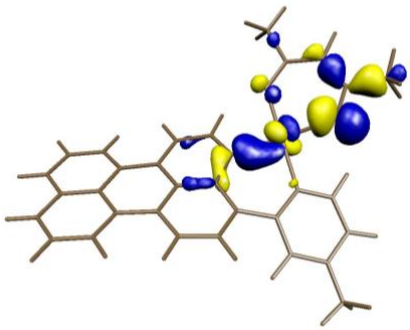
MO 115: -0.265 Ha
Pd (48), **Per (33)**, acac (9)



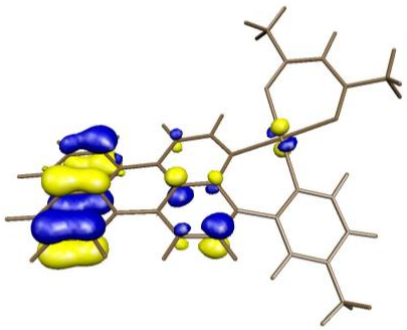
MO 116: -0.255 Ha
Pd (56), **acac (31)**



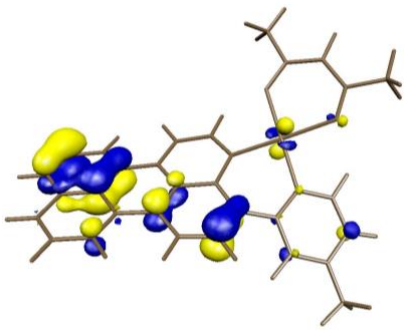
MO 117: -0.247 Ha
Pd (56), Py (14), acac (13), Per (6)



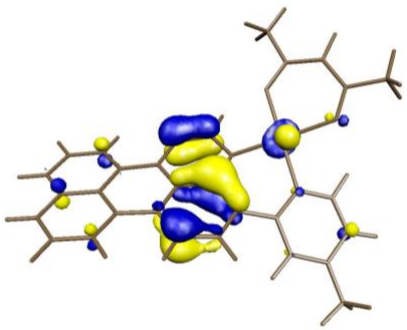
MO 118: -0.244 Ha
acac (59), Per (13), Pd (12)



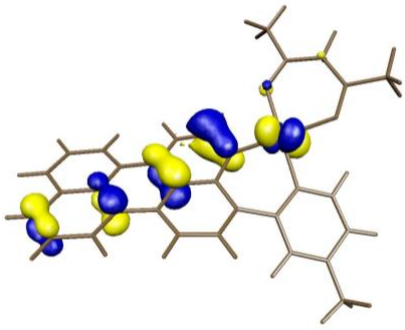
MO 119: -0.242 Ha
Per (91), Pd (4)



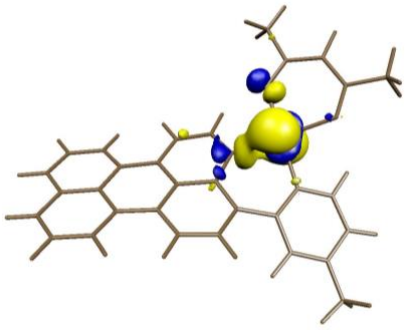
MO 120: -0.238 Ha
Per (79), Py (8), Pd (4)



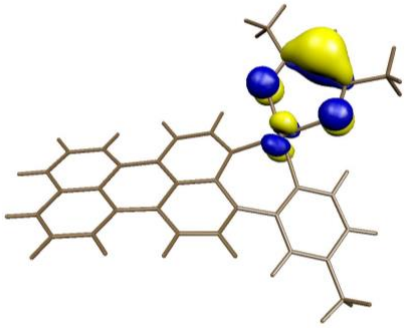
MO 121: -0.234 Ha
Per (78), Pd (9), Py (7)



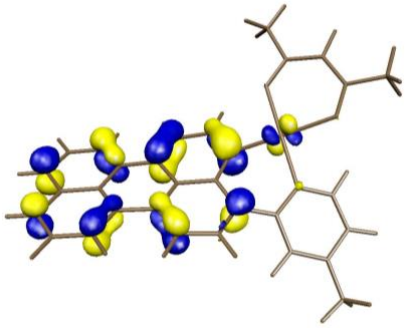
MO 122: -0.228 Ha
Per (66), Pd (23), acac (4)



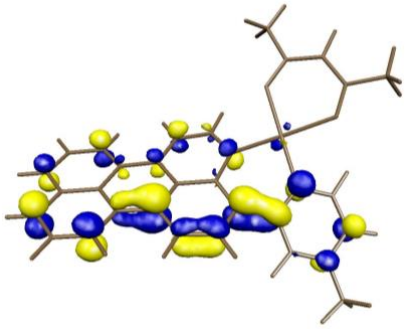
MO 123: -0.216 Ha
Pd (70), Per (13), acac (7)



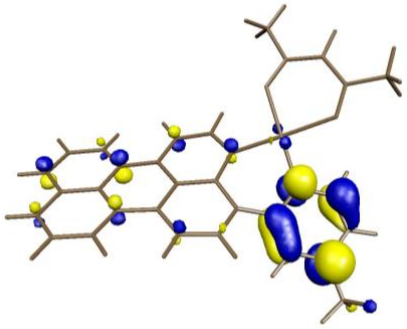
MO 124: -0.208 Ha
acac (75), Pd (13)



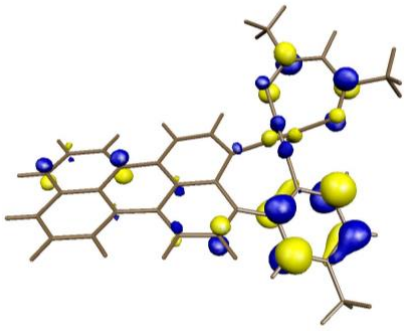
MO 125 (*HOMO*): -0.172 Ha
Per (85), Pd (5)



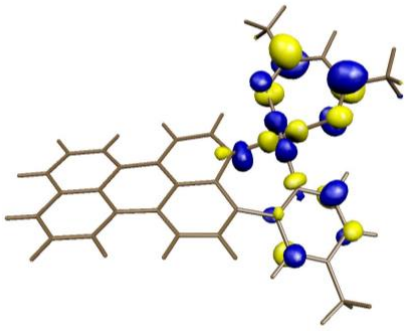
MO 126 (*LUMO*): -0.076 Ha
Per (71), Py (23)



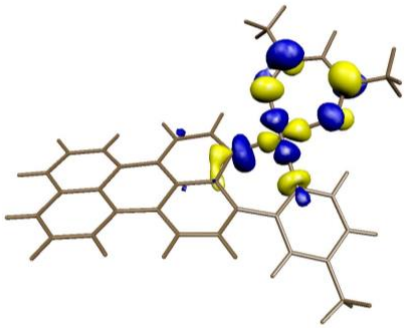
MO 127: -0.040 Ha
Py (66), Per (25)



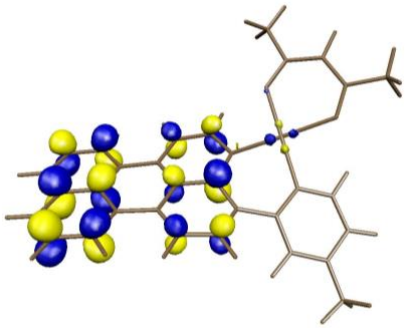
MO 128: -0.029 Ha
Py (45), Per (22), acac (17), Pd (4)



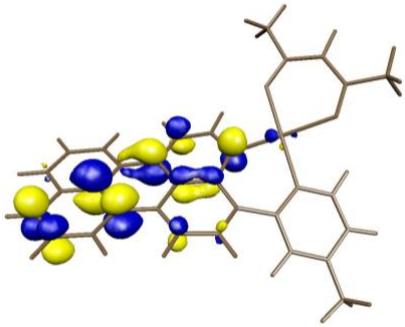
MO 129: -0.027 Ha
acac (44), Py (19), Pd (14), Per (6)



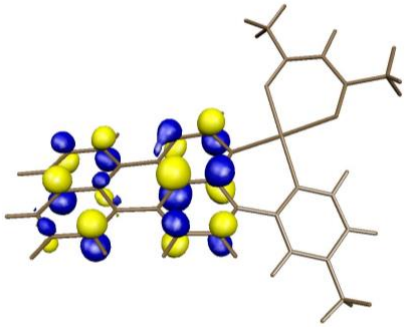
MO 130: -0.023 Ha
acac (34), **Pd (31)**, Per (14), Py (5)



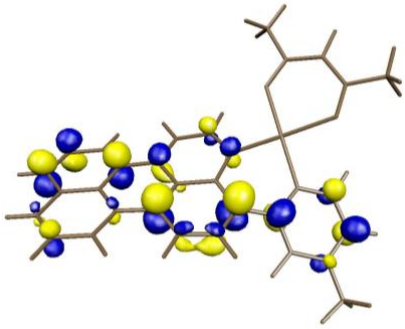
MO 131: -0.010 Ha
Per (92)



MO 132: +0.005 Ha
Per (92), Pd (7)

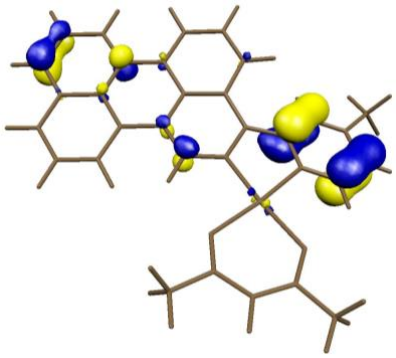


MO 133: +0.009 Ha
Per (95)

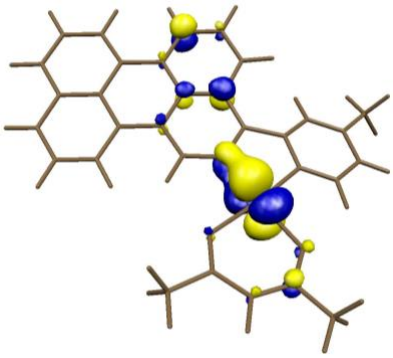


MO 134: +0.013 Ha
Per (72), Py (21)

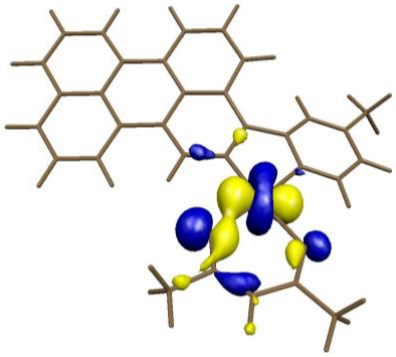
(c) [Pd(PerPy)(acac)]-five-membered **7**



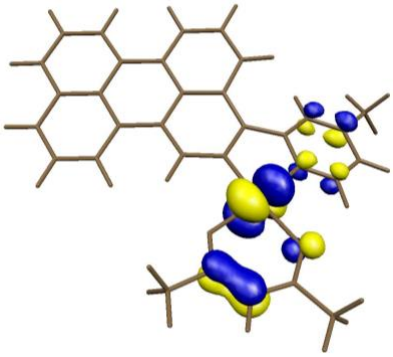
MO 114: -0.279 Ha
Py (56), Per (38)



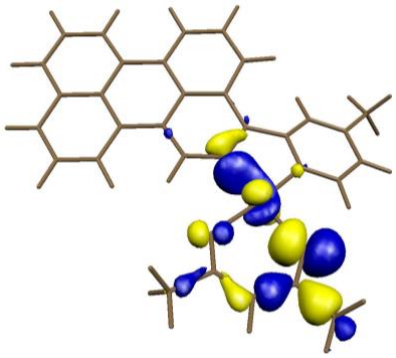
MO 115: -0.270 Ha
Pd (53), **Per (30)**, acac (5)



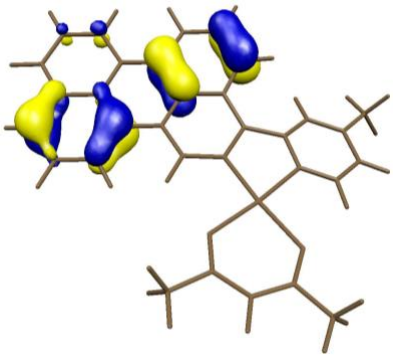
MO 116: -0.261 Ha
Pd (62), acac (28)



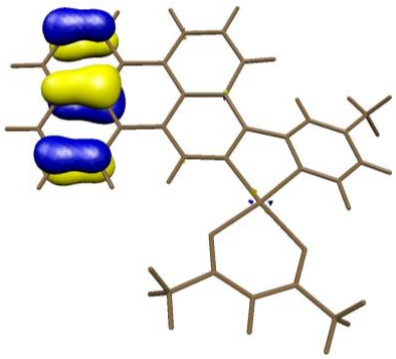
MO 117: -0.249 Ha
Pd (57), acac (18), Py (12)



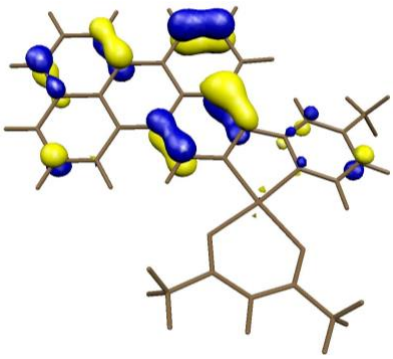
MO 118: -0.248 Ha
acac (62), Pd (13), Per (10)



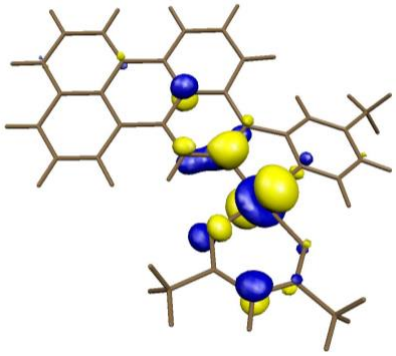
MO 119: -0.246 Ha
Per (96)



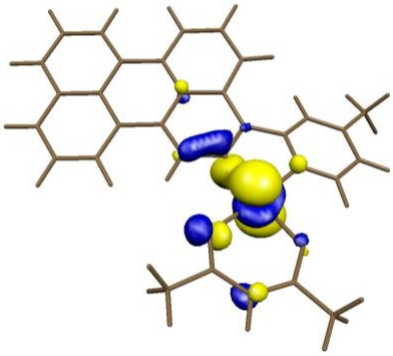
MO 120: -0.242 Ha
Per (92)



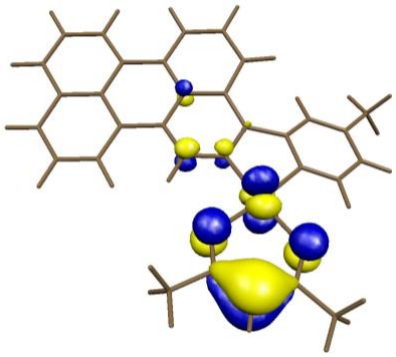
MO 121: -0.237 Ha
Per (83), Py (11)



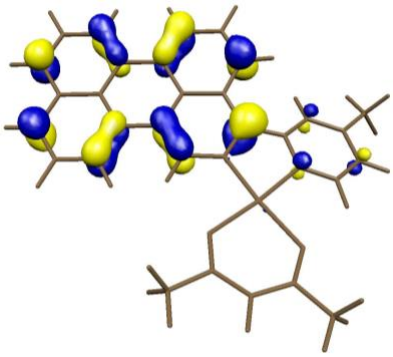
MO 122: -0.222 Ha
Pd (42), **Per (31)**, acac (14), Py (4)



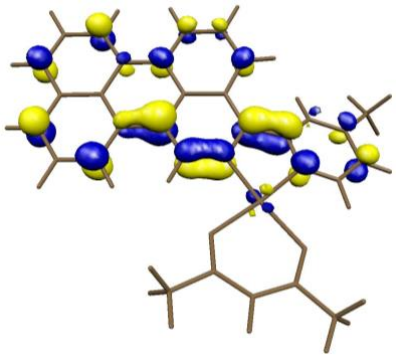
MO 123: -0.219 Ha
Pd (57), Per (19), acac (11)



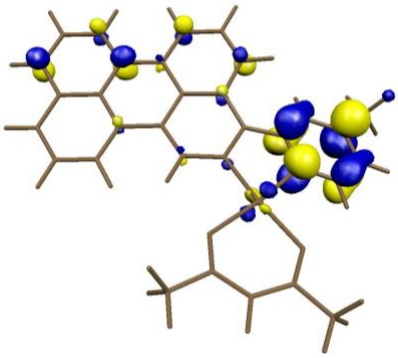
MO 124: -0.207 Ha
acac (60), Pd (17), Per (14)



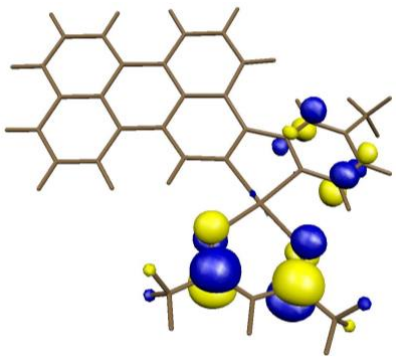
MO 125 (*HOMO*): -0.177 Ha
Per (88), Py (8)



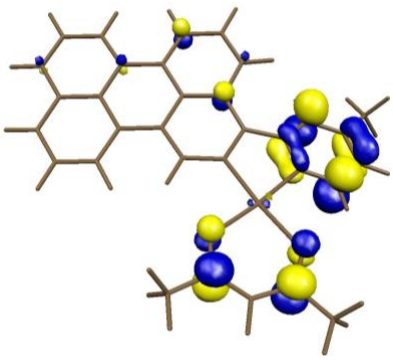
MO 126 (*LUMO*): -0.077 Ha
Per (71), Py (20), Pd (3)



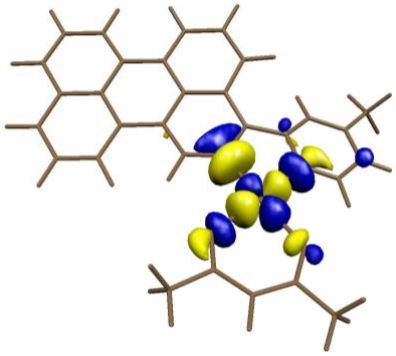
MO 127: -0.043 Ha
Py (55), **Per (33)**, Pd (3)



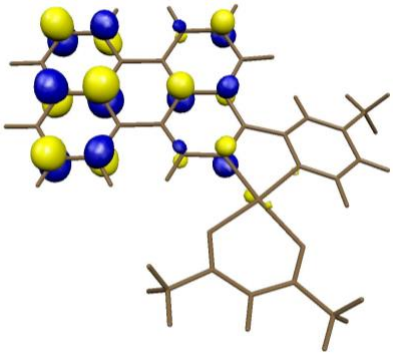
MO 128: -0.029 Ha
acac (63), Py (20), Per (4)



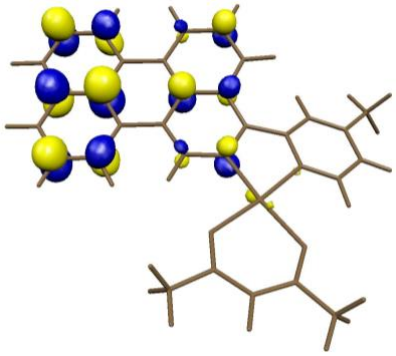
MO 129: -0.026 Ha
Py (45), acac (26), Per (17)



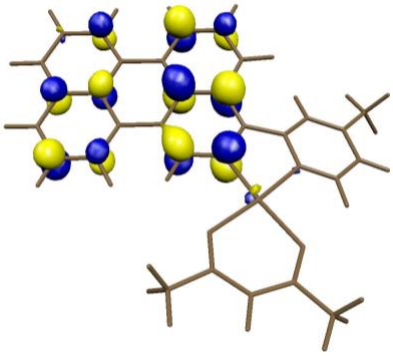
MO 130: -0.022 Ha
Pd (49), Per (18), Py (12), acac (8)



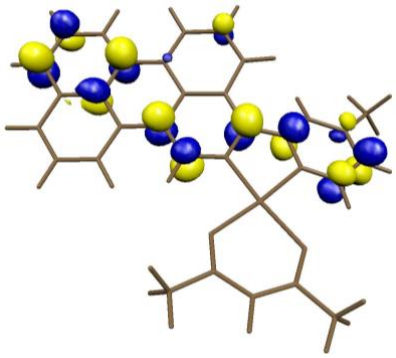
MO 131: -0.010 Ha
Per (89)



MO 132: +0.000 Ha
Per (90)

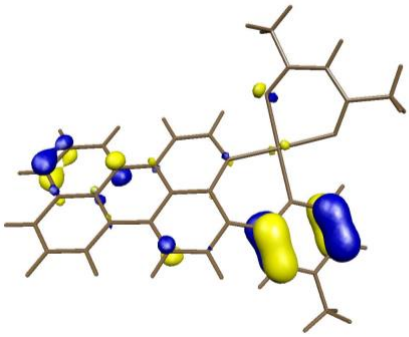


MO 133: +0.008 Ha
Per (84), Pd (7)

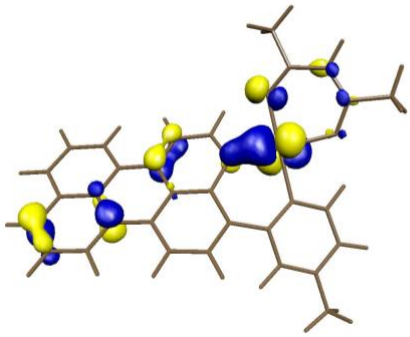


MO 134: +0.017 Ha
Per (66), Py (24)

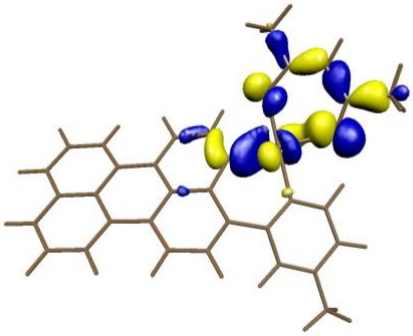
(*d*) [Pt(PerPy)(acac)]-six-membered



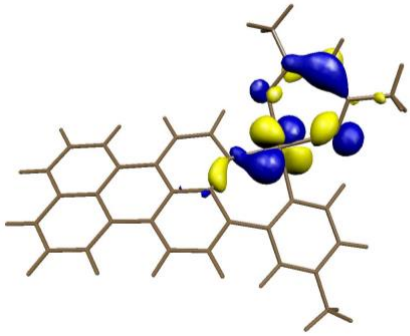
MO 114: -0.279 Ha
Py (56), **Per (36)**



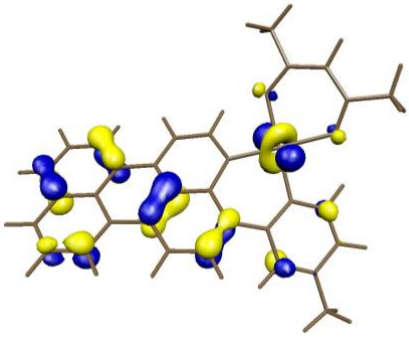
MO 115: -0.261 Ha
Per (42), **Pt (35)**, acac (11)



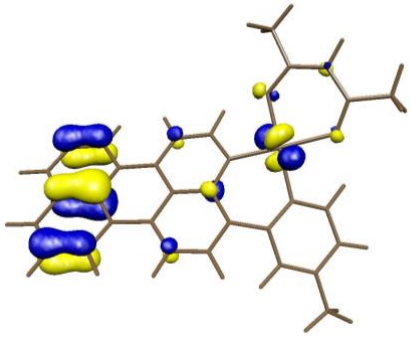
MO 116: -0.253 Ha
acac (57), Pt (17), Per (16)



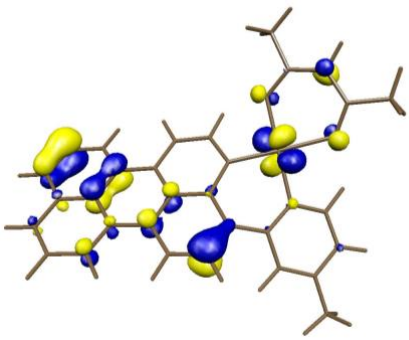
MO 117: -0.247 Ha
Pt (47), **acac (35)**, Per (7)



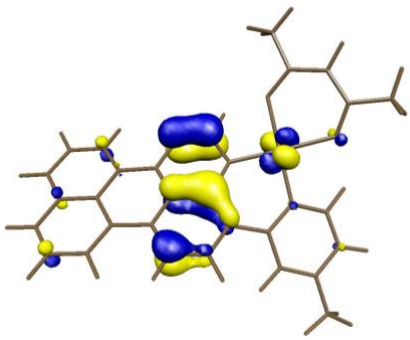
MO 118: -0.241 Ha
Per (60), Pt (18), Py (12), acac (4)



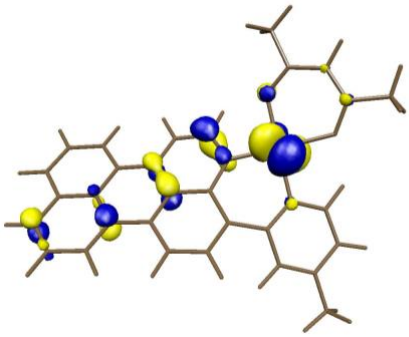
MO 119: -0.239 Ha
Per (70), Pt (13), acac (5)



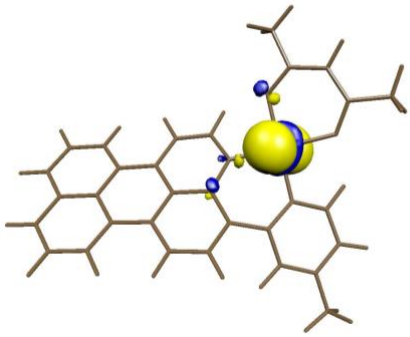
MO 120: -0.236 Ha
Per (62), Pt (15), acac (11), Py (4)



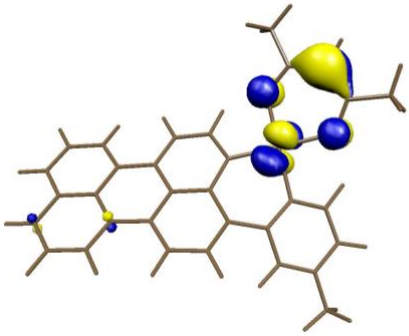
MO 121: -0.231 Ha
Per (79), Pt (9)



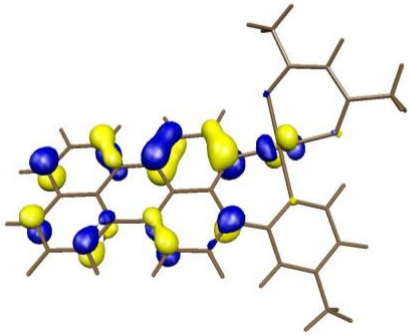
MO 122: -0.220 Ha
Pt (44), **Per (38)**, acac (6)



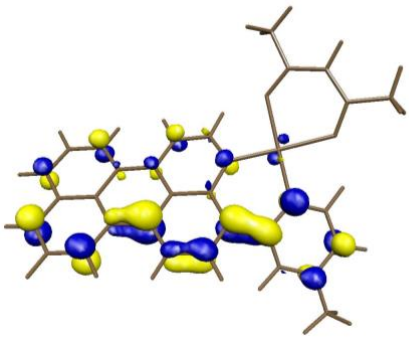
MO 123: -0.215 Ha
Pt (83), Per (7)



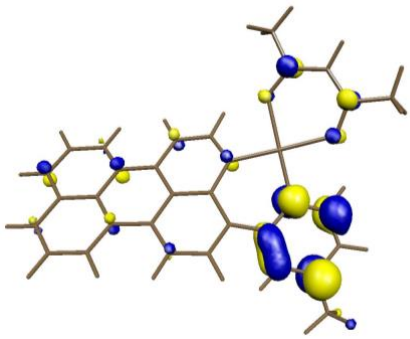
MO 124: -0.208 Ha
acac (49), Pt (27), Per (10)



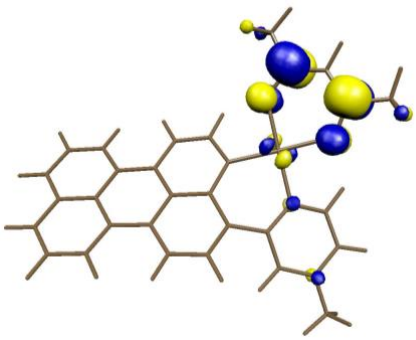
MO 125 (*HOMO*): -0.167 Ha
Per (80), Pt (9)



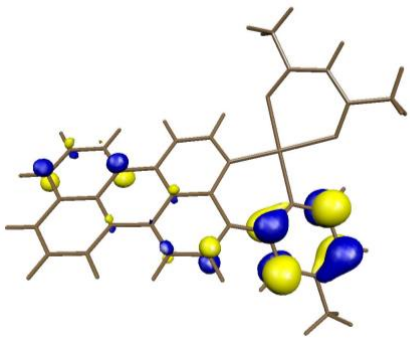
MO 126 (*LUMO*): -0.075 Ha
Per (66), Py (25)



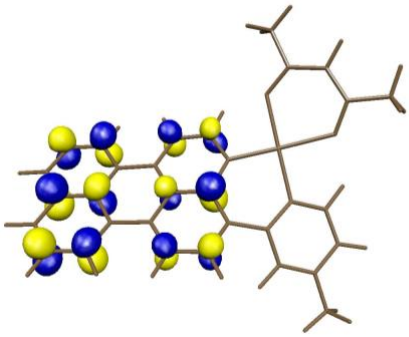
MO 127: -0.042 Ha
Py (59), Per (17), acac (11)



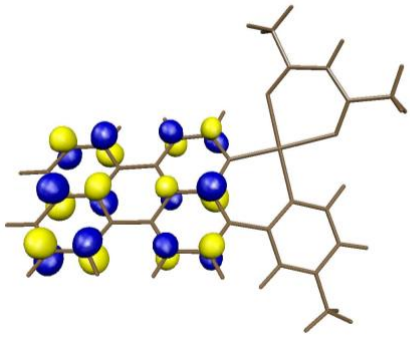
MO 128: -0.032 Ha
acac (82), Py (5), Pt (3)



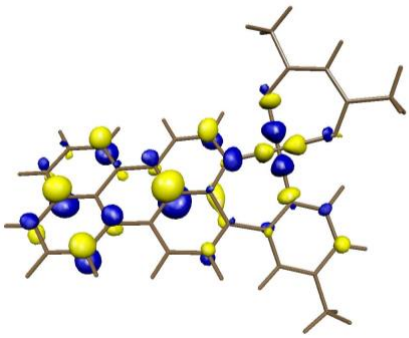
MO 129: -0.028 Ha
Py (62), Per (28)



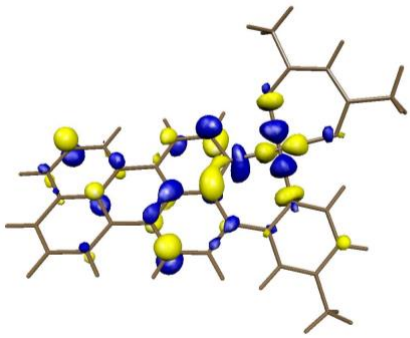
MO 130: -0.008 Ha
Per (94)



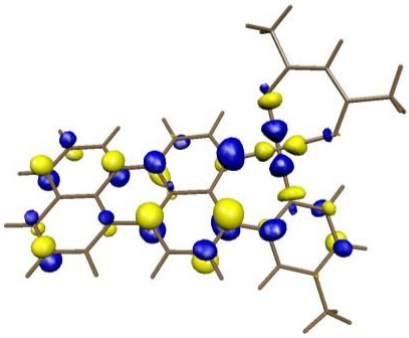
MO 131: +0.005 Ha
Per (73), Pt (15)



MO 132: +0.009 Ha
Per (64), Pt (15), Py (7)

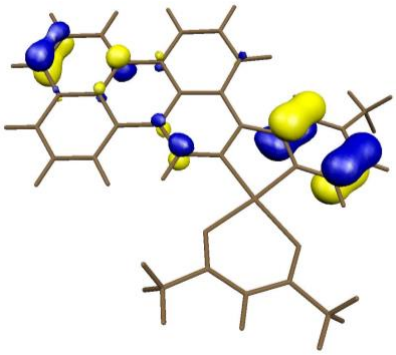


MO 133: +0.013 Ha
Per (57), Pt (20), Py (7)

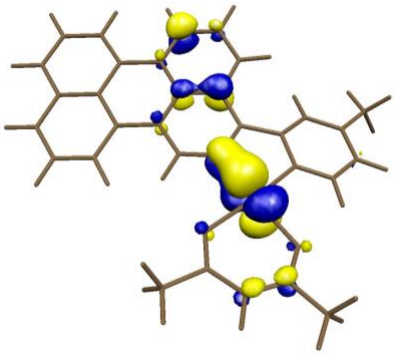


MO 134: +0.016 Ha
Per (61), Py (15), Pt (13)

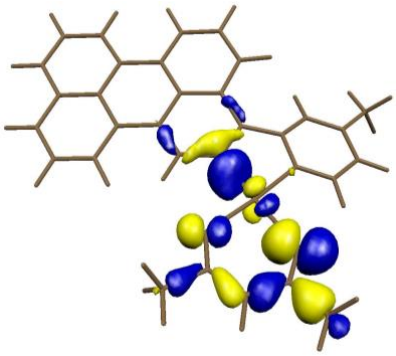
(e) [Pt(PerPy)(acac)]-five-membered **9**



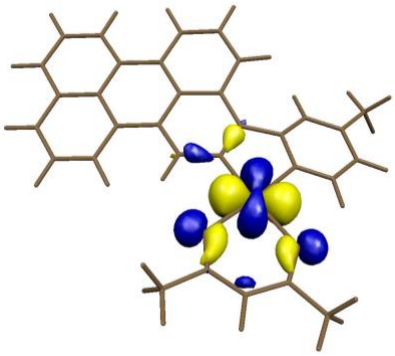
MO 114: -0.278 Ha
Py (55), Per (40)



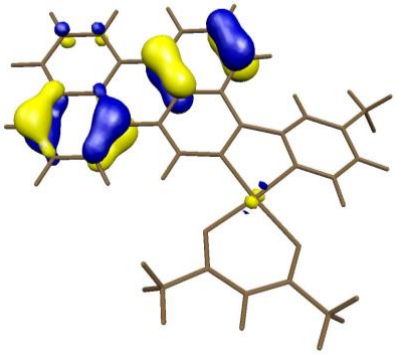
MO 115: -0.266 Ha
Pt (43), **Per (38)**, acac (7), Py (4)



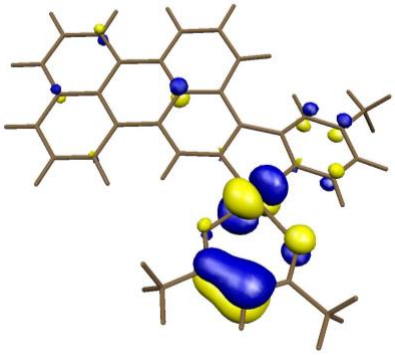
MO 116: -0.256 Ha
acac (64), Per (18), Pt (6)



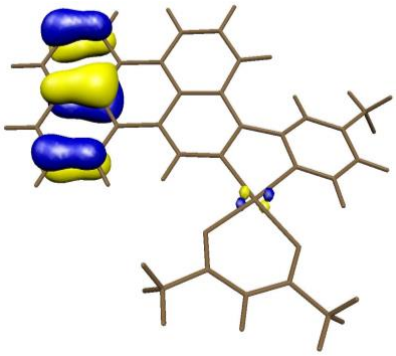
MO 117: -0.249 Ha
Pt (70), acac (16), Per (4)



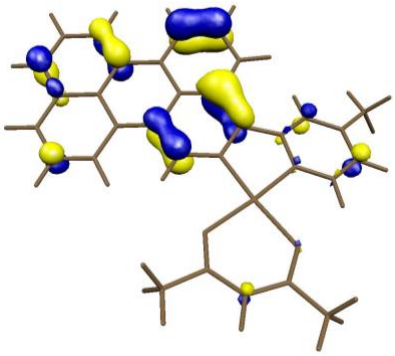
MO 118: -0.245 Ha
Per (90)



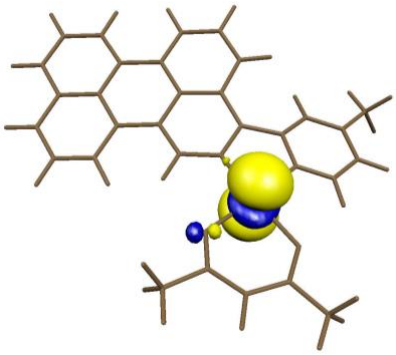
MO 119: -0.244 Ha
acac (33), **Pt (32)**, Per (18), Py (8)



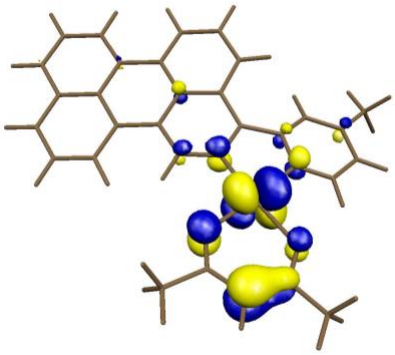
MO 120: -0.240 Ha
Per (89)



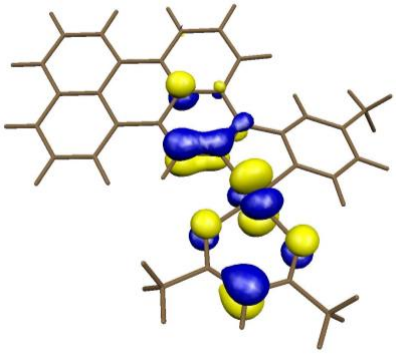
MO 121: -0.236 Ha
Per (78), Py (12)



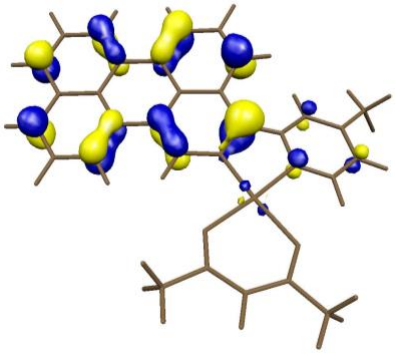
MO 122: -0.221 Ha
Pt (91), Per (3)



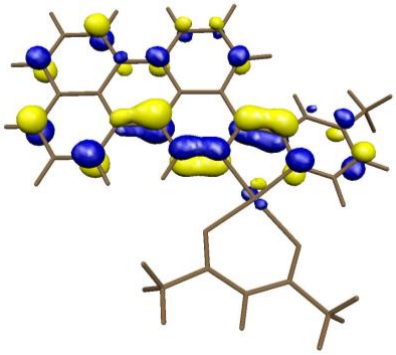
MO 123: -0.214 Ha
Pt (39), **acac (31)**, Per (15), Py (7)



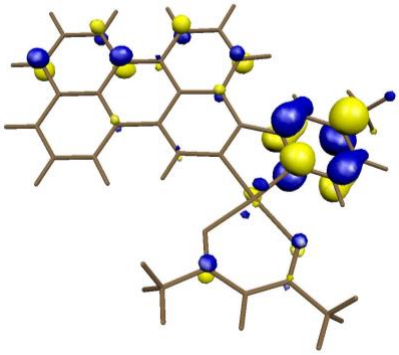
MO 124: -0.203 Ha
Per (35), **Pt (31)**, acac (27)



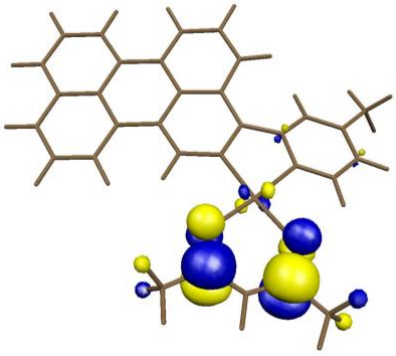
MO 125 (*HOMO*): -0.175 Ha
Per (86), Py (8)



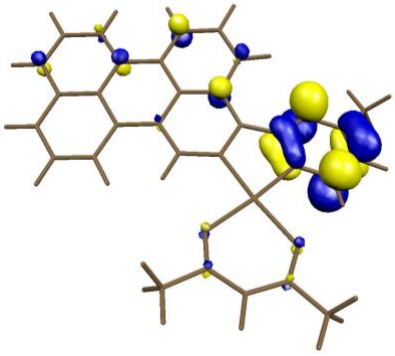
MO 126 (*LUMO*): -0.076 Ha
Per (69), Py (21), Pt (4)



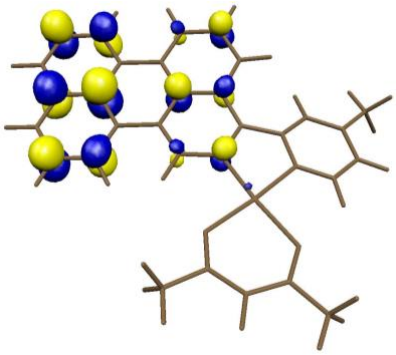
MO 127: -0.043 Ha
Py (53), **Per (30)**, acac (5), Pt (3)



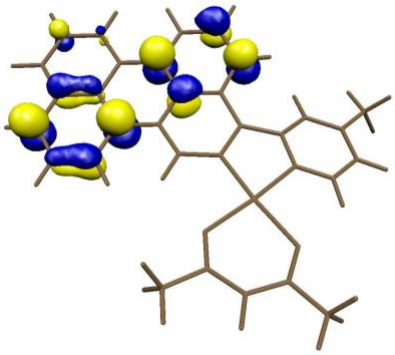
MO 128: -0.035 Ha
acac (83), Py (4)



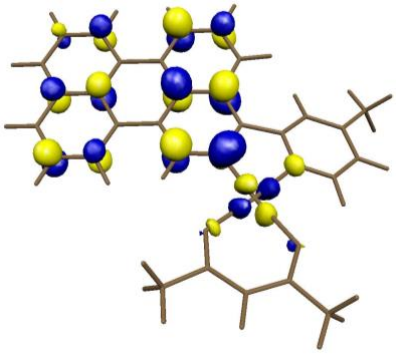
MO 129: -0.025 Ha
Py (64), Per (23), acac (4)



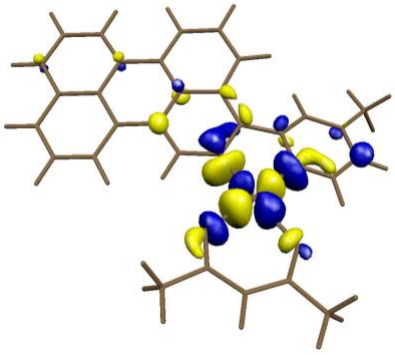
MO 130: -0.009 Ha
Per (90)



MO 131: +0.001 Ha
Per (92)

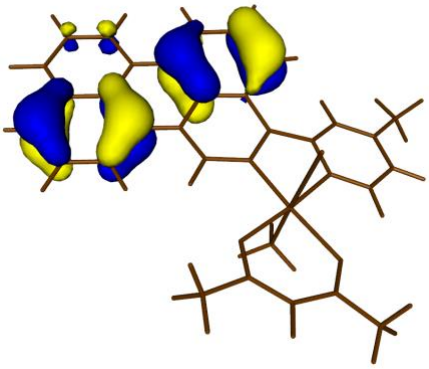


MO 132: +0.009 Ha
Per (77), Pt (14)

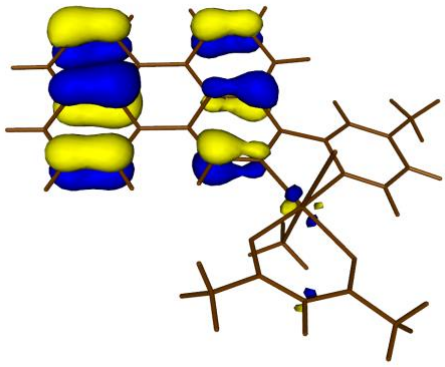


MO 133: +0.012 Ha
Pt (42), Per (24), Py (13), acac (6)

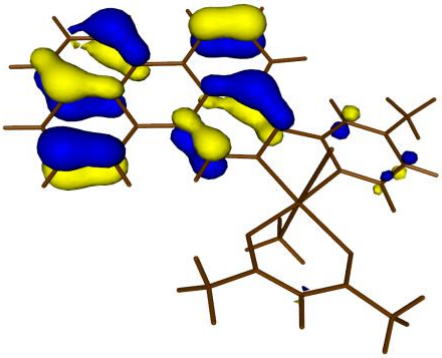
(*f*) [Pt(PerPy)(acac)MeI)]-five-membered **10**



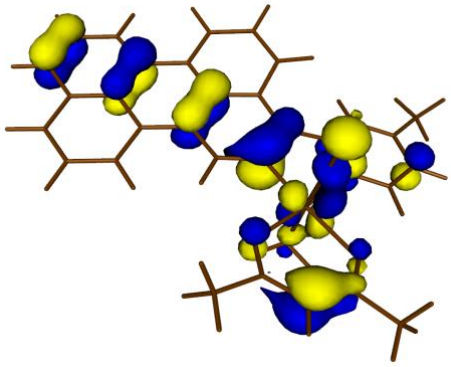
MO 125: -0.253 Ha
Per (95)



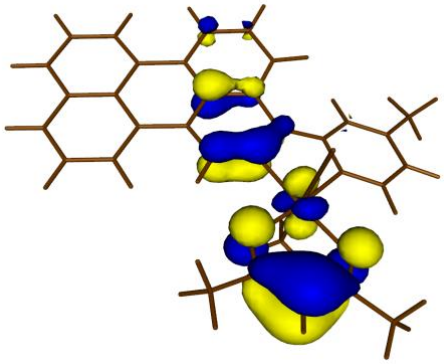
MO 126: -0.249 Ha
Per (87)



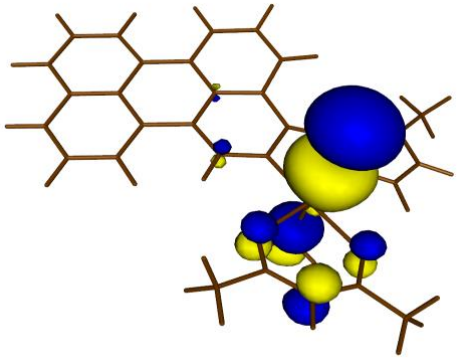
MO 127: -0.245 Ha
Per (85), Py (5)



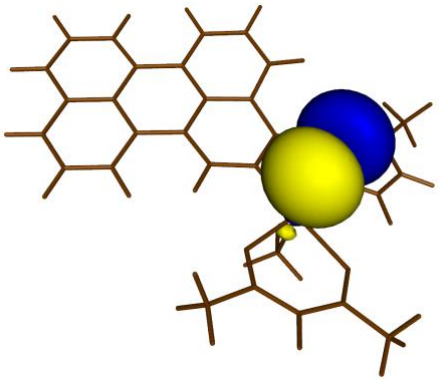
MO 128: -0.241 Ha
Per (48), acac (14), Py (11), Pt(9), I(8)



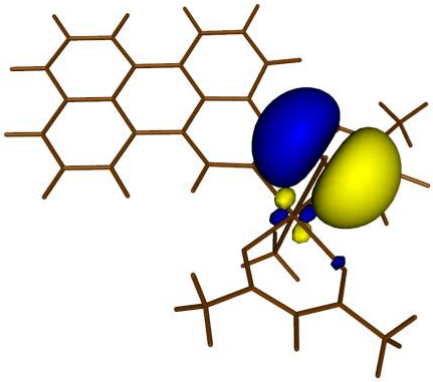
MO 129: -0.227 Ha
acac (56), Per (28), Pt (8)



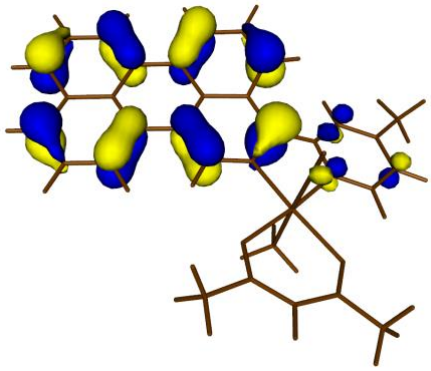
MO 130: -0.209 Ha
I (52), acac (16), Me (14), Pt (7)



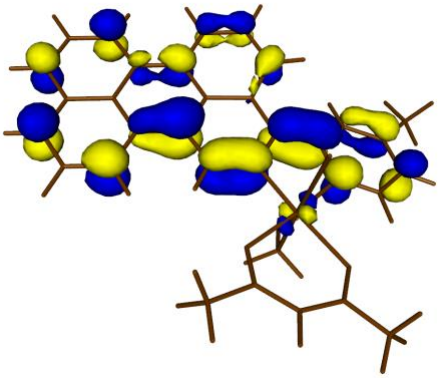
MO 131: -0.191 Ha
I (91), Pt (4)



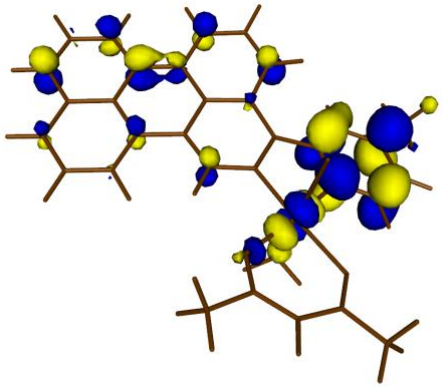
MO 132: -0.190 Ha
I (95), Pt (4)



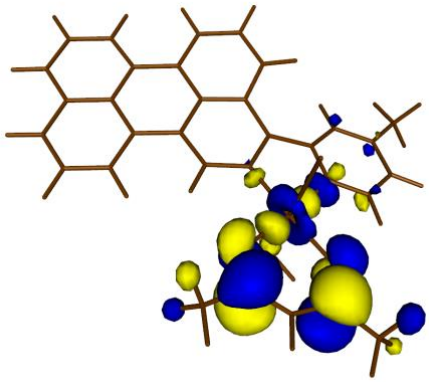
MO 133 (*HOMO*): -0.185 Ha
Per (84), Py (7), I (4)



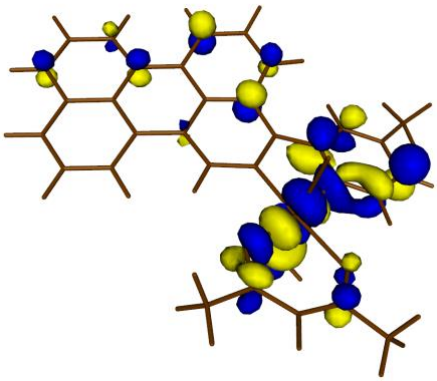
MO 134 (*LUMO*): -0.086 Ha
Per (67), **Py (23)**



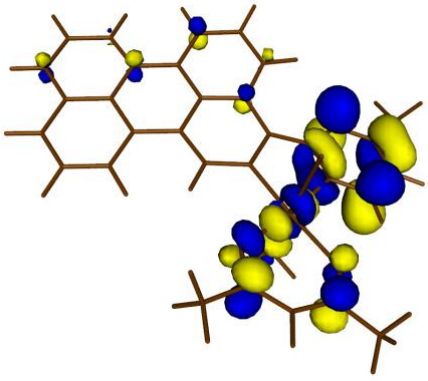
MO 135: -0.055 Ha
Py (49), **Per (26)**, Pt (8), I (4)



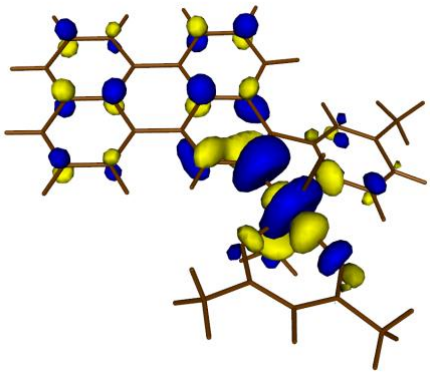
MO 136: -0.047 Ha
acac (68), Py (7)



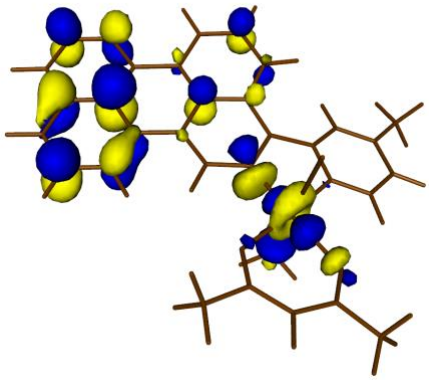
MO 137: -0.038 Ha
Py (24), Pt (19), Per (18), acac (11), Me (11)



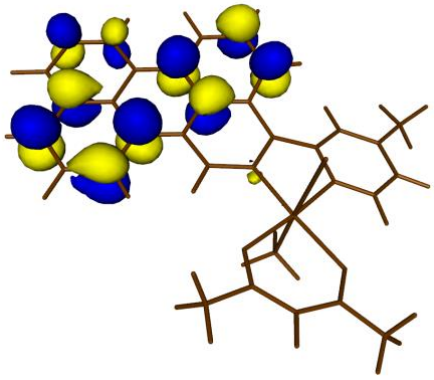
MO 138: -0.036 Ha
Py (51), acac (17), Per (10), Pt (7)



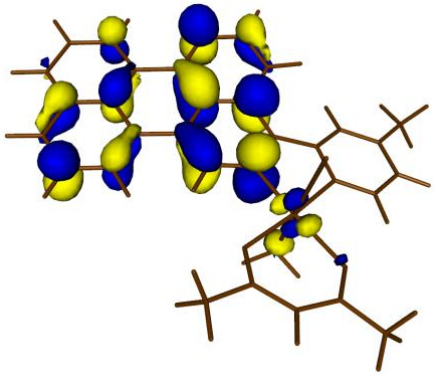
MO 139: -0.022 Ha
Per (46), Pt (25), Py (5), Me (5), I (5)



MO 140: -0.015 Ha
Per (73), Pt (9), Me (4)



MO 141: -0.006 Ha
Per (91)



MO 142: 0.004 Ha
Per (90)

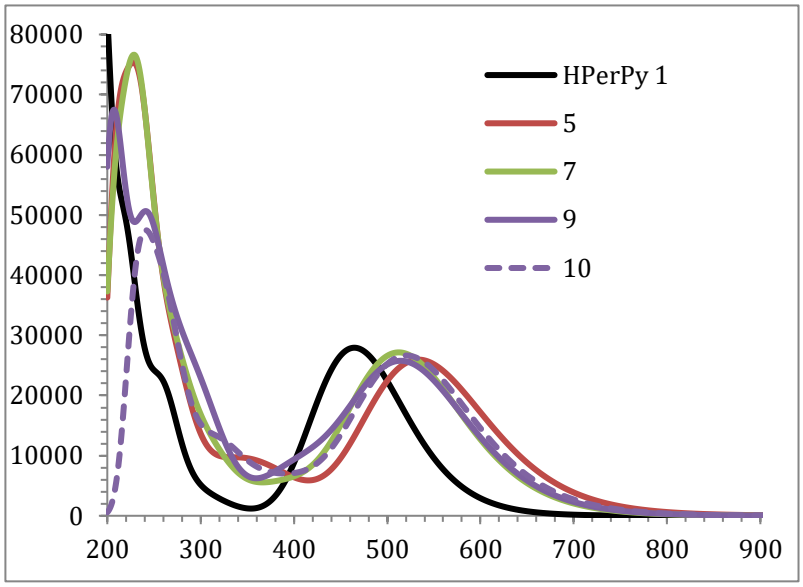


Fig. S19 Calculated electronic spectra in chloroform for HPerPy and its derivatives.

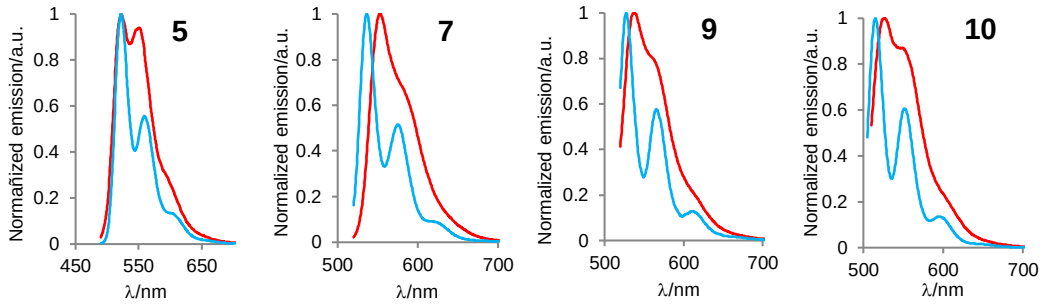


Fig. S20 Normalized emission spectra of complexes **5**, **7**, **9**–**10**, in 2-methyltetrahydrofuran at 298 K (red line) and 77 K (blue line).

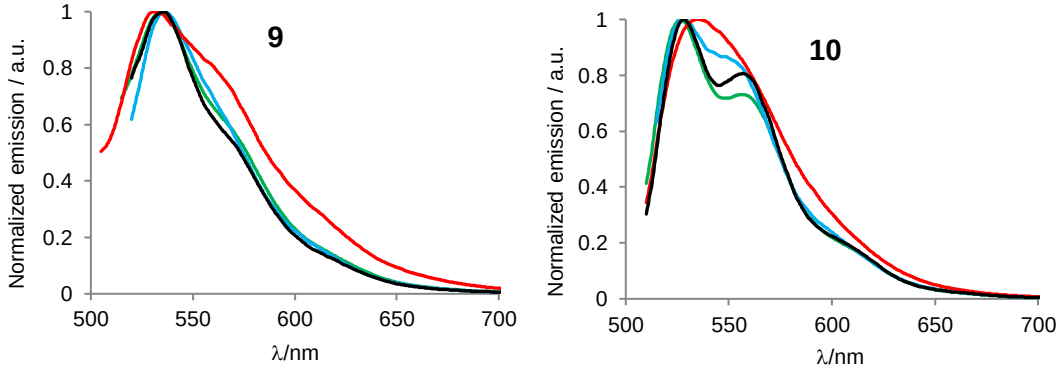


Fig. S21 Normalized emission spectra of platinum complexes **9** and **10** in different solvents (green: $CHCl_3$, blue: THF, red: CH_3CN, black: toluene) at room temperature.

Table S6. Emission and excitation in the solid state (KBr dispersion) at 298 K.

Compound	λ_{ex}/nm	λ_{em}/nm
1	423	605
2	470	561
3	483	666
5	483	665
6	482	661
7	485	662
8	485	665
9	482	661
10	471	644

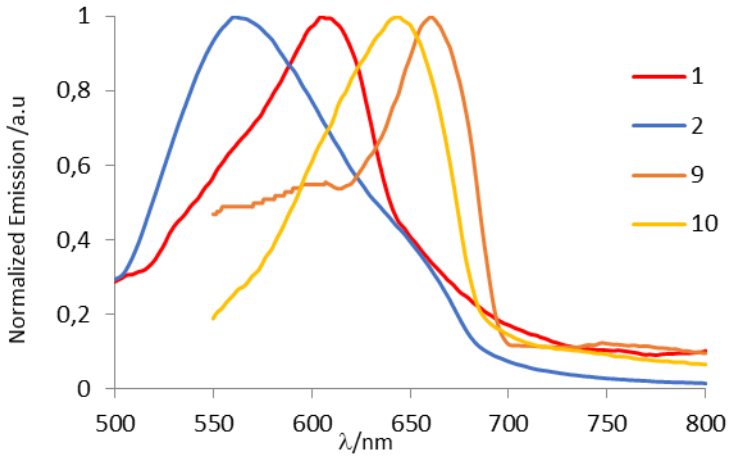


Fig. S22 Normalized emission spectra recorded in KBr dispersions at room temperature of HPerPy (**1**) and its Ag and Pt complexes.

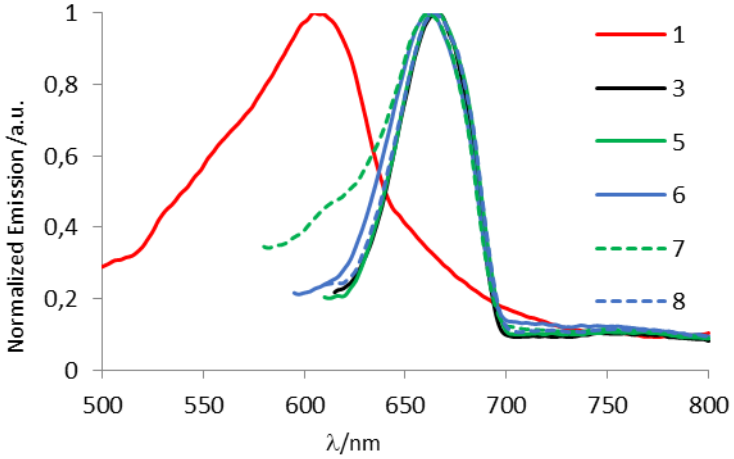


Fig. S23 Normalized emission spectra recorded in KBr dispersions at room temperature of HPerPy (**1**) and its Pd complexes.

Fig. S24 Fluorescence decays in dichloromethane, at room temperature.

Mono-exponential and bi-exponential fluorescence decay models were fitted to each decay. Eqn (1) describes the mono-exponential decay model:

$I(t) = I_0 \cdot \exp(-t/\tau)$ (1)

where I_0 is the relative intensity, t is the time and τ is the fluorescence lifetime, both expressed in ns. The bi-exponential decay model is expressed by Equation (2) as:

$I(t) = A + B_1 \cdot \exp(-t/\tau_1) + B_2 \cdot \exp(-t/\tau_2)$ (2)

where B_1 and B_2 are the relative intensities associated with two lifetimes, τ_1 and τ_2, respectively.

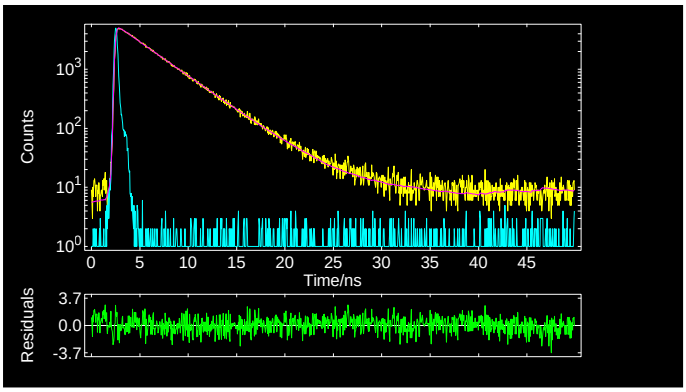
Mono-exponential models are normally used to fit fluorescence decay. Bi-exponential fits may be more appropriate for samples containing non-linear decays. Fitting was done using FAST software from Edinburgh Instruments by a least-squares algorithm using a reconvolution approach. In this method, convolution of Equation (1) or (2) with the instrumental response function (IRF) is done prior to evaluating the goodness of fit with a weighted χ^2 parameter.

Compound **1**

Param.	Value/ns	Std. Dev./ns	Param.	Value	Std. Dev.	Rel.%
τ1	0.51	0.15	B1	0.01	0.00	0.92
τ2	3.74	0.01	B2	0.15	0.00	99.08

A 5.633

χ^2 1.063

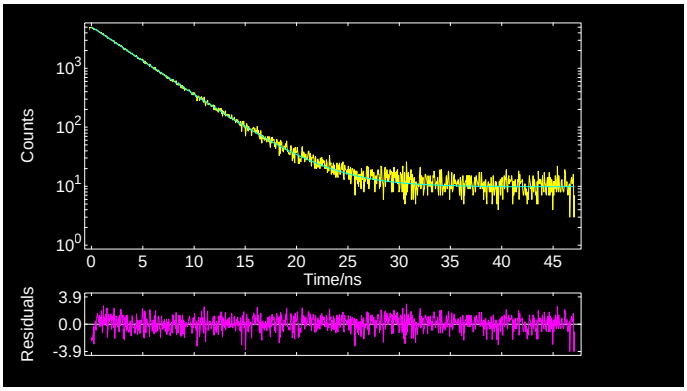


Compound **2**

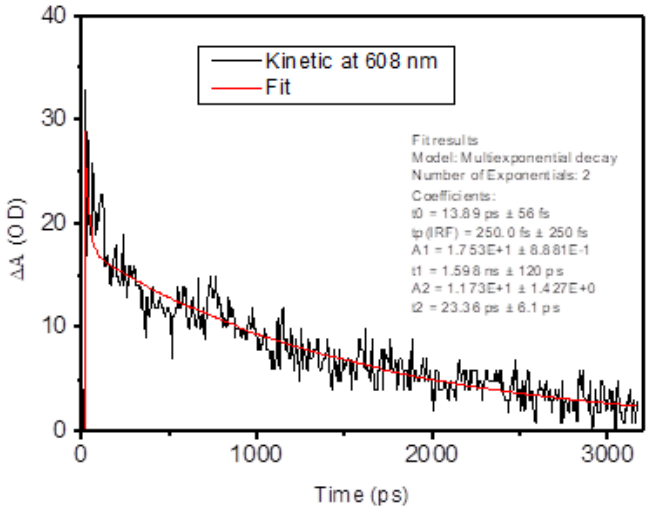
Param	Value/ns	Std. Dev./ns	Param	Value	Std. Dev.	Rel.%
τ1	3.76	0.01	B1	5120.39	0.59	100.00

A 9.772

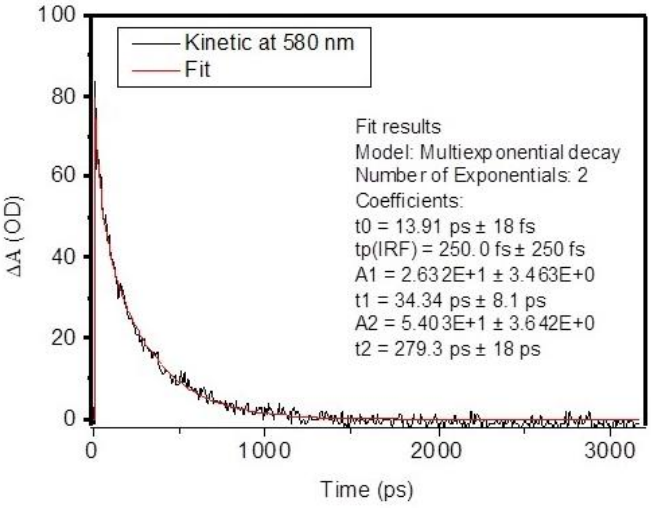
χ^2 1.125



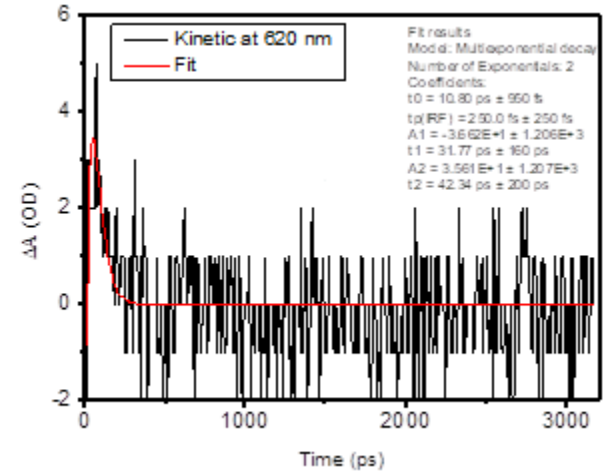
Compound **5**



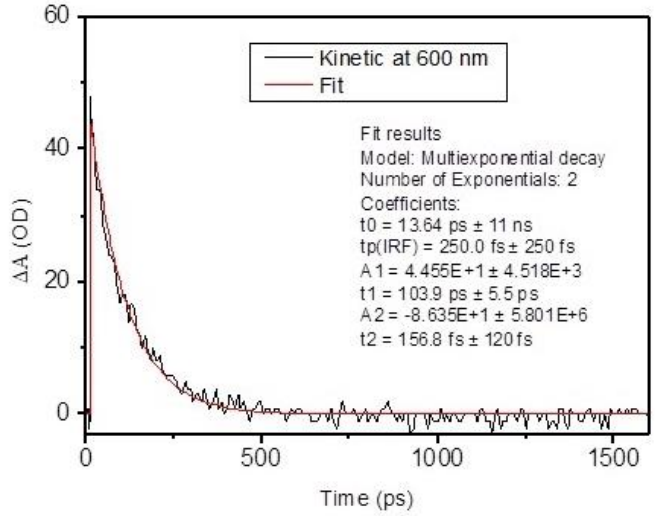
Compound **6**



Compound **7**



Compound **8**

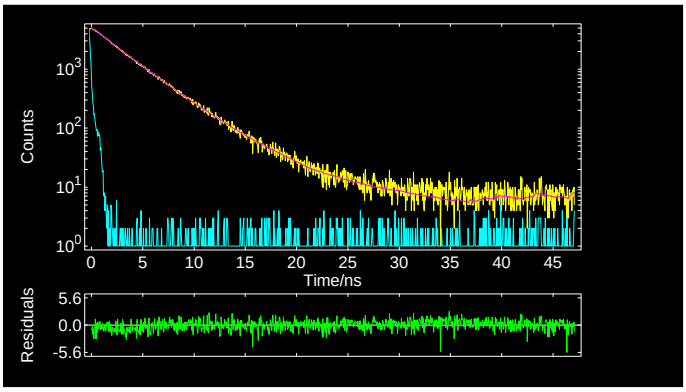


Compound **9**

Param.	Value/ns	Std. Dev./ns	Param.	Value	Std. Dev.	Rel.%
τ1	0.31	0.00	B1	0.36	0.00	88.45
τ2	2.81	0.04	B2	0.01	0.00	11.55

A 0.488

χ^2 1.074



Compound **10**

Param	Value/ns	Std. Dev./ns	Param	Value	Std. Dev.	Rel.%
τ1	0.16	0.00	B1	0.40	0.00	87.55
τ2	3.30	0.05	B2	0.00	0.00	12.45

A 0.794

χ^2 1.112