

Supplementary Information

Higher fluorescence in platinum(IV) orthometallated complexes of perylene imine compared with their platinum(II) or palladium(II) analogues

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Fig. S1 Absorption spectra of **4** in different solvents (ca. 10^{-5} M) at room temperature.

Fig. S2 Emission and excitation spectra of **4** in MeTHF (ca. 10^{-5} M) at room temperature (RT) and low temperature (LT, 77 K).

Fig. S3 Emission and excitation spectra of **8** in MeTHF (ca. 10^{-5} M) at room temperature (RT) and low temperature (LT, 77K).

Fig. S4 ^1H , $^1\text{H}/^{195}\text{Pt}$ 2D HMBC and ^{31}P NMR spectra

Fig. S5 Fluorescence decays in dichloromethane, at room temperature

Table S1 Calculated absorption parameters (wavelengths in nm, and their intensities) for Perylene imine ($\text{HC}^{\wedge}\text{N}$), $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})]$, and $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})\text{MeI}]$ in gas phase and chloroform solution. For each entry, main contributions of the orbitals for the transition and their coefficients are shown.

Table S2 Molecular orbitals for Perylene imine ($\text{HC}^{\wedge}\text{N}$), $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})]$, and $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})\text{MeI}]$. Percentage compositions for each one entry are obtained from Natural Populations Analysis.

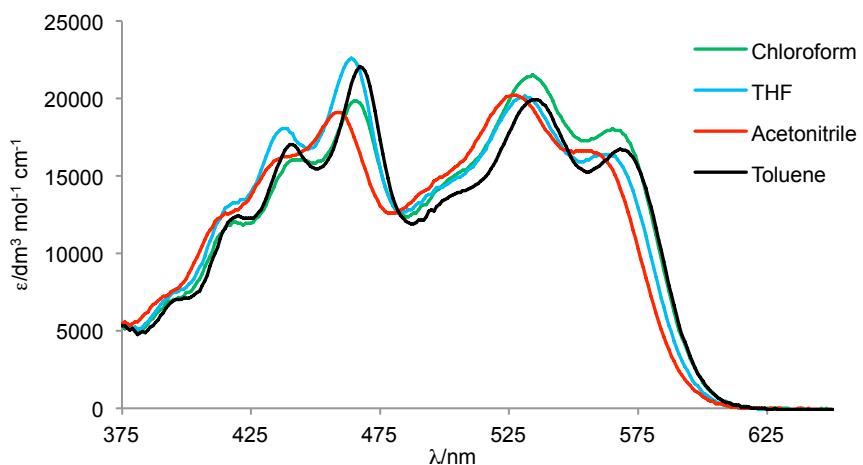


Figure S1. Absorption spectra of of **4** in different solvents (ca. 10^{-5} M) at room temperature.

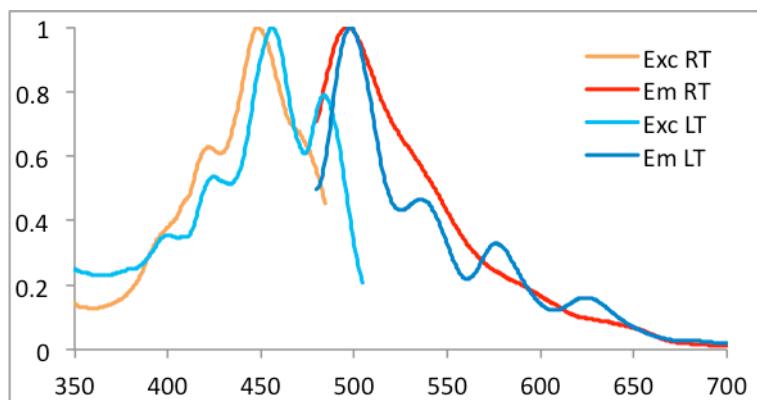


Fig. S2 Emission and excitation spectra of **4** in MeTHF (ca. 10^{-5} M) at room temperature (RT) and low temperature (LT, 77 K).

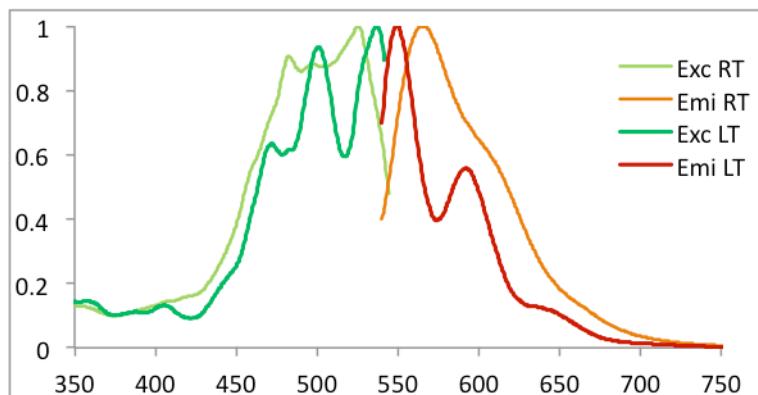
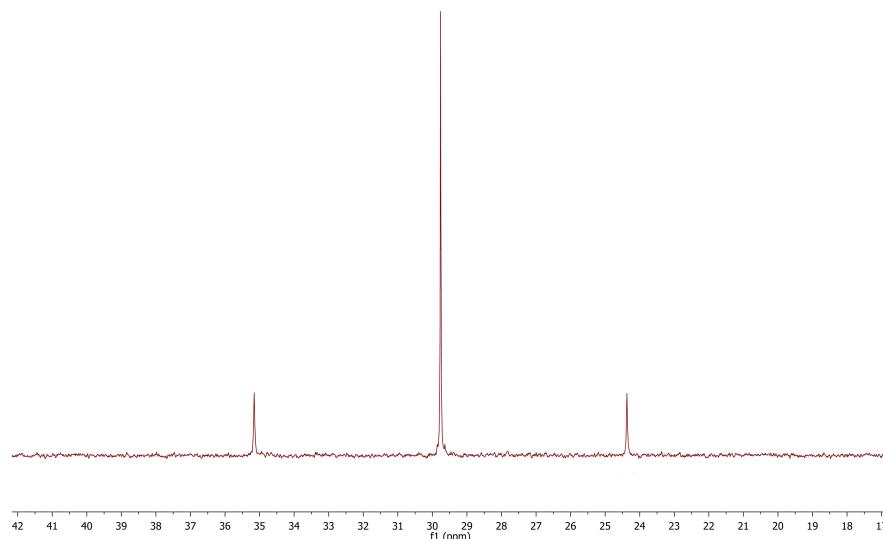


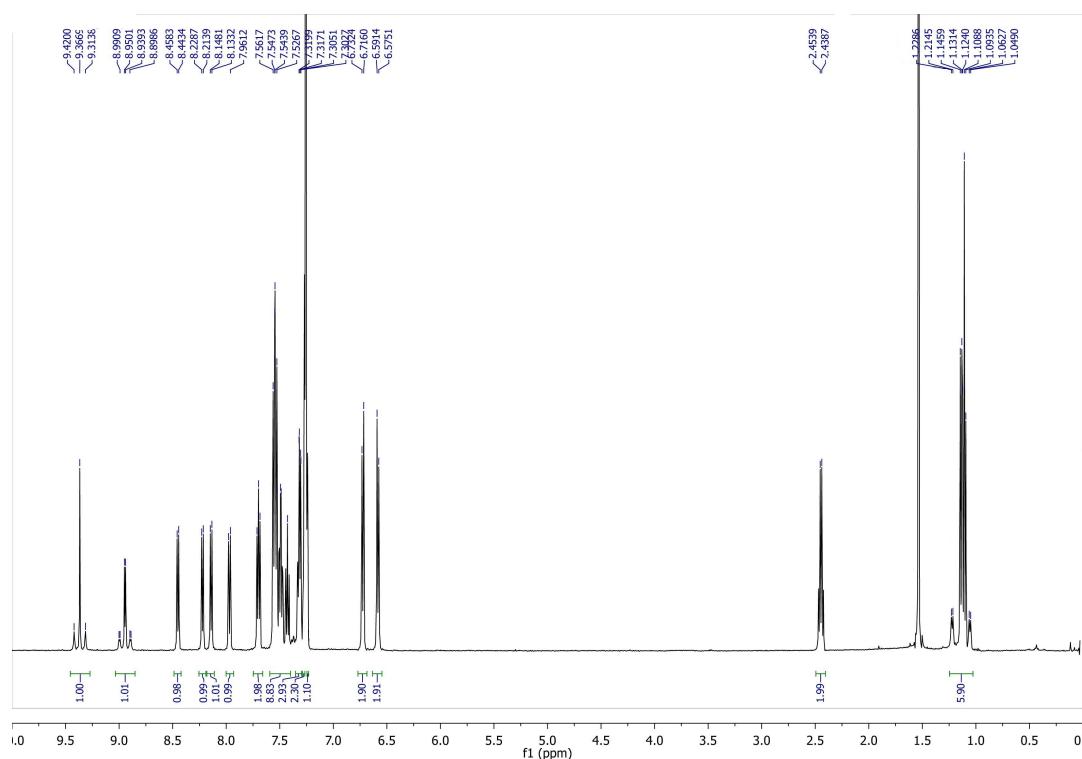
Fig. S3 Emission and excitation spectra of **8** in MeTHF (ca. 10^{-5} M) at room temperature (RT) and low temperature (LT, 77K).

Fig. S4 ^1H , $^1\text{H}/^{195}\text{Pt}$ 2D HMBC and ^{31}P NMR spectra

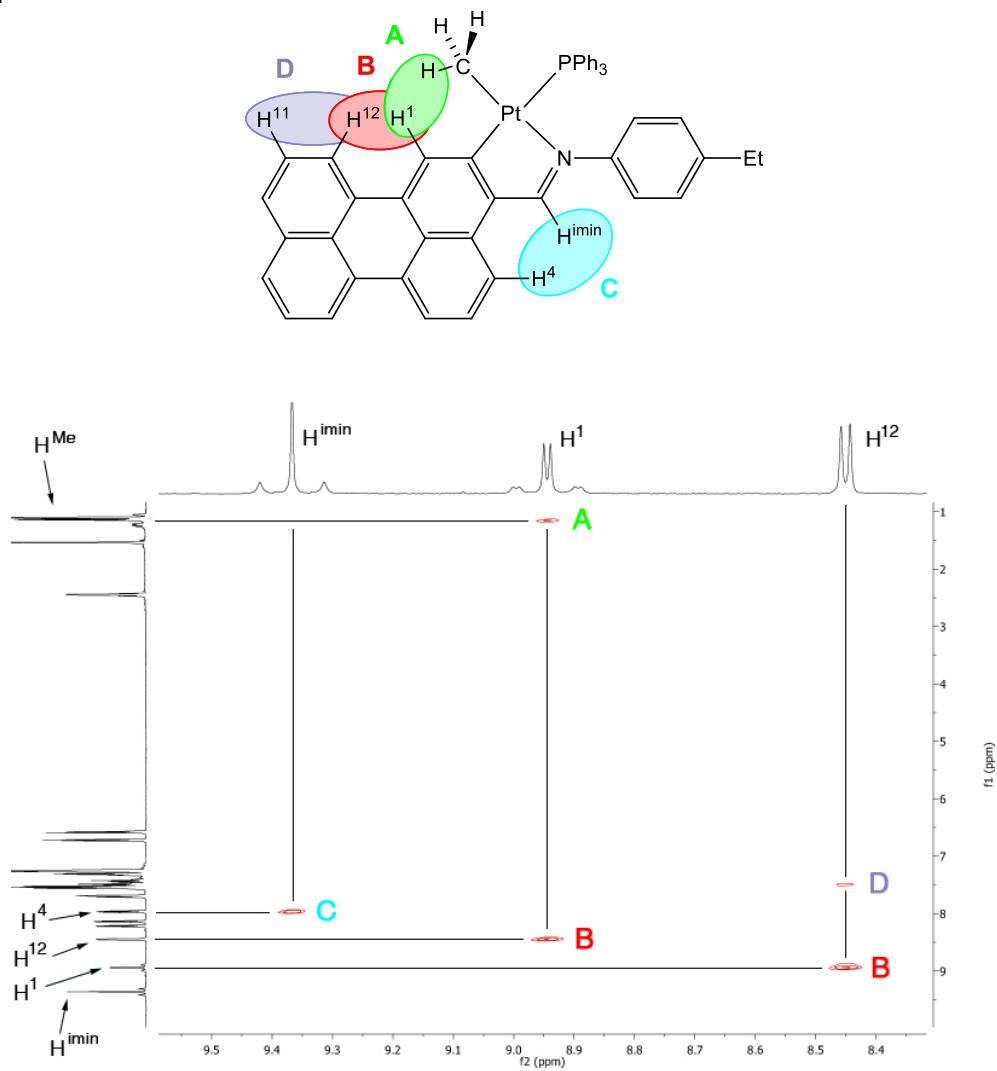
^{31}P NMR **2**



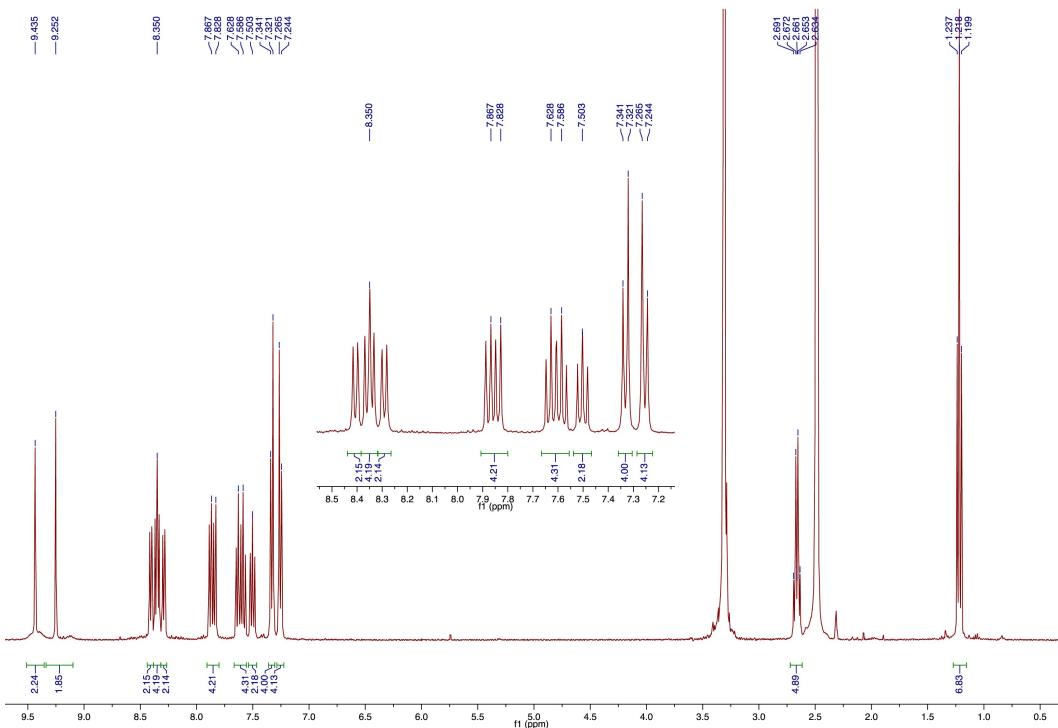
^1H NMR **2**



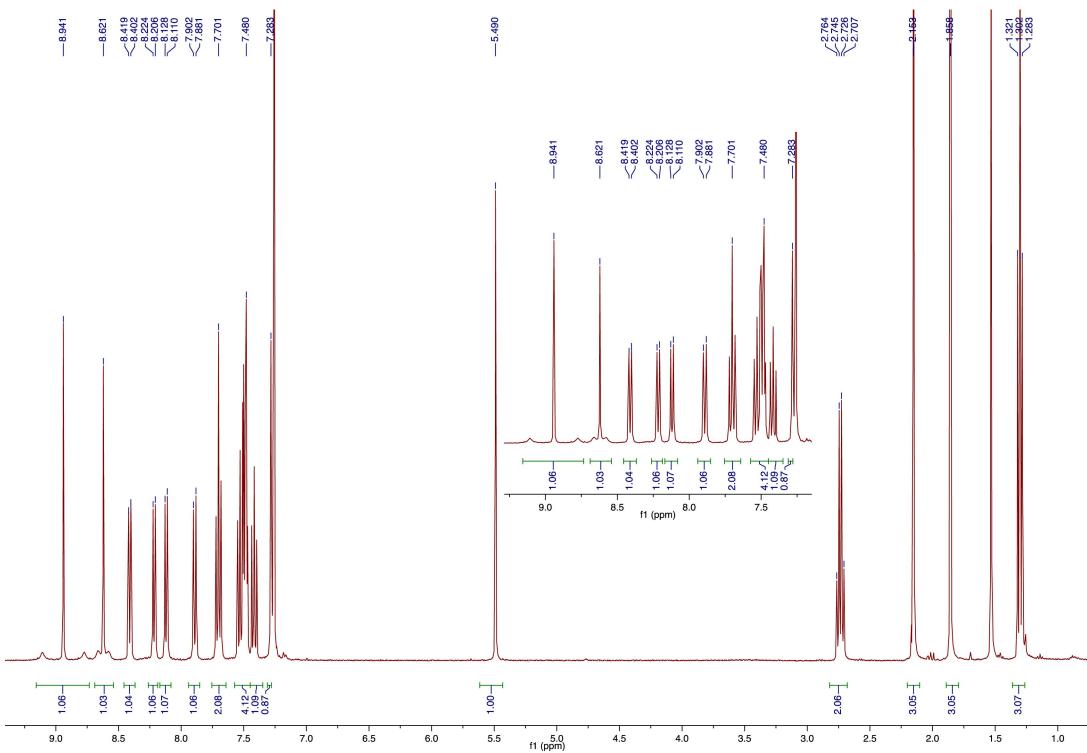
NOESY 2



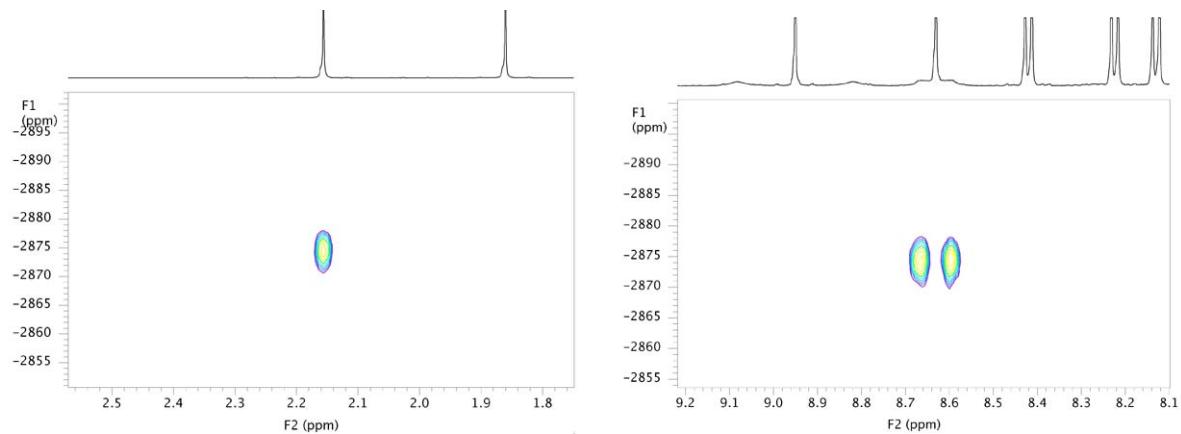
¹H NMR 3



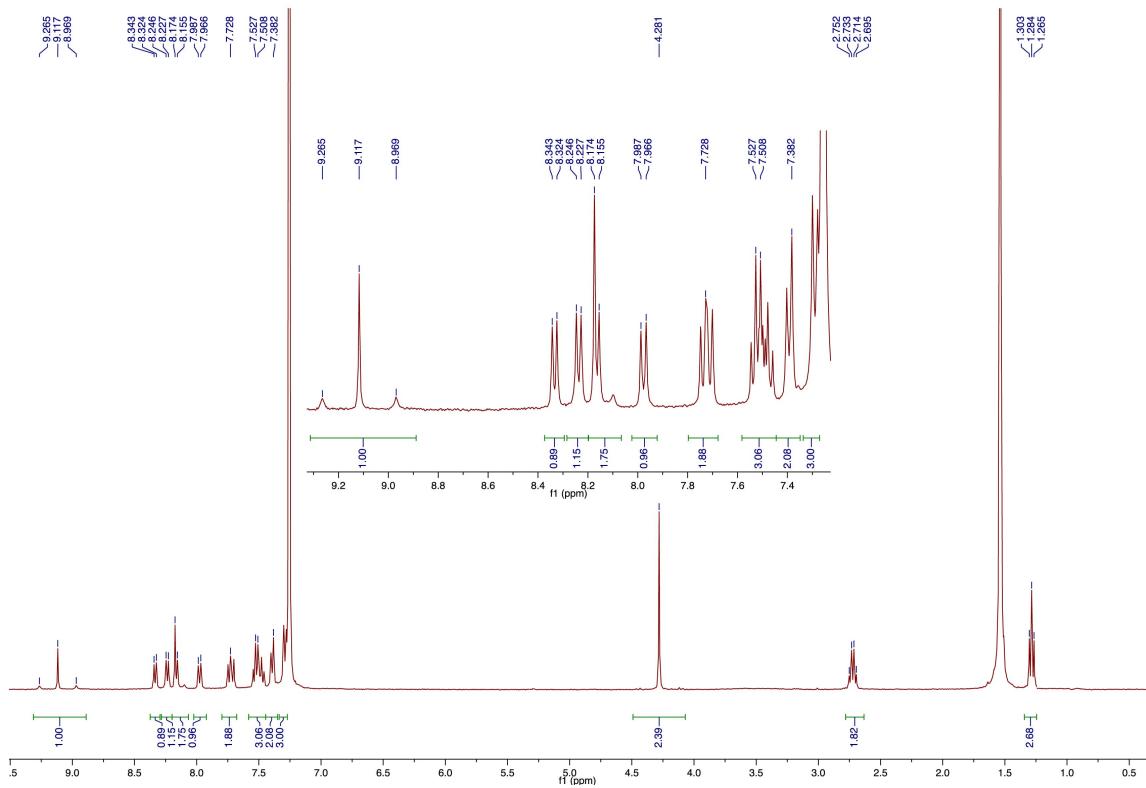
¹H NMR 4



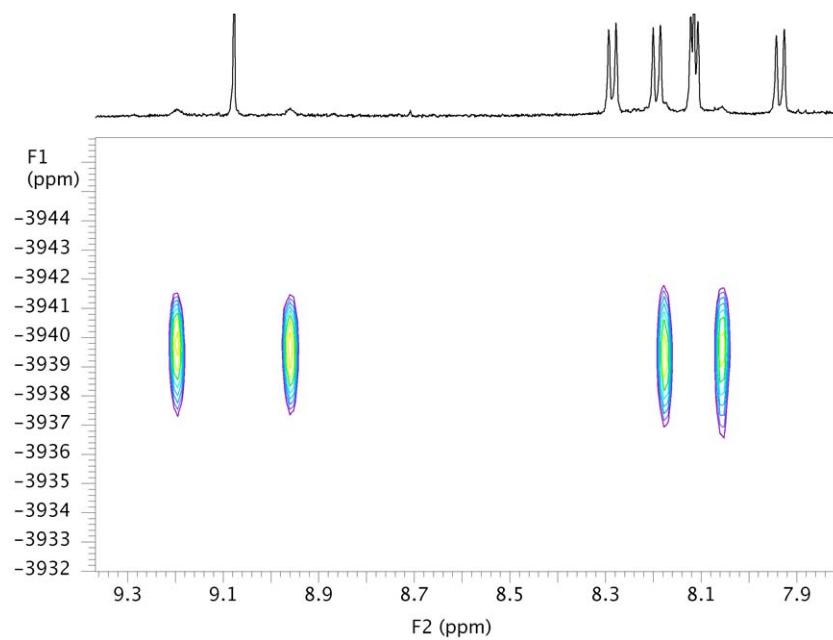
$^1\text{H}/^{195}\text{Pt}$ 2D HMBC spectrum of **4**



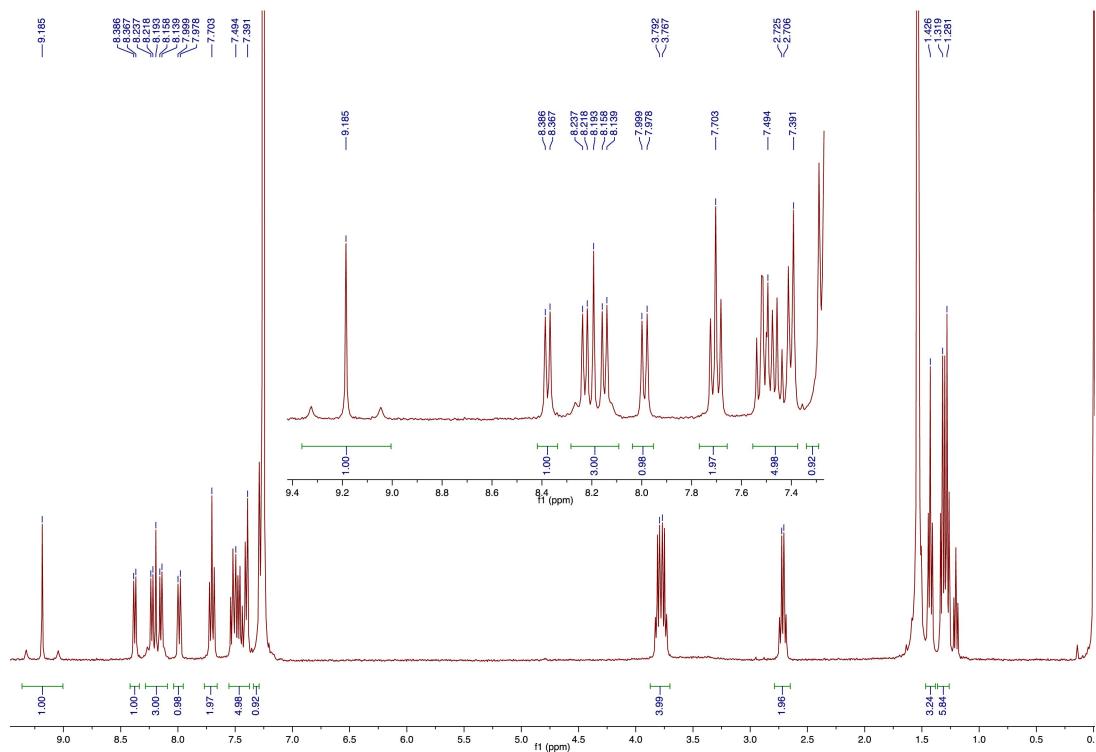
^1H NMR **5**



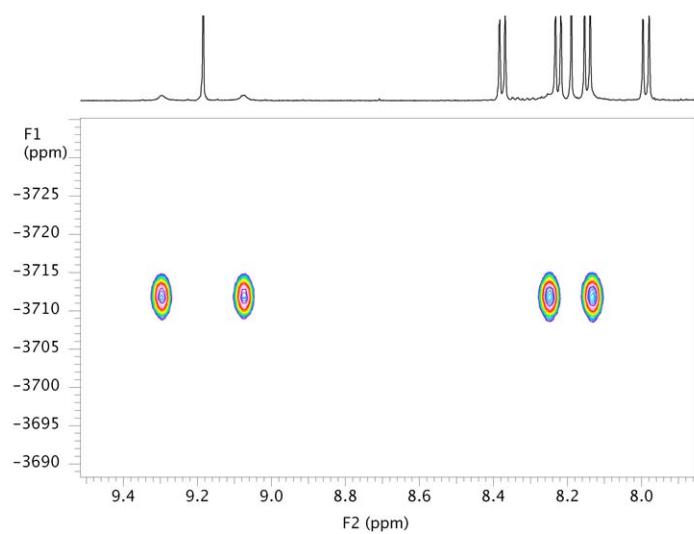
$^1\text{H}/^{195}\text{Pt}$ 2D HMBC spectrum of **5**



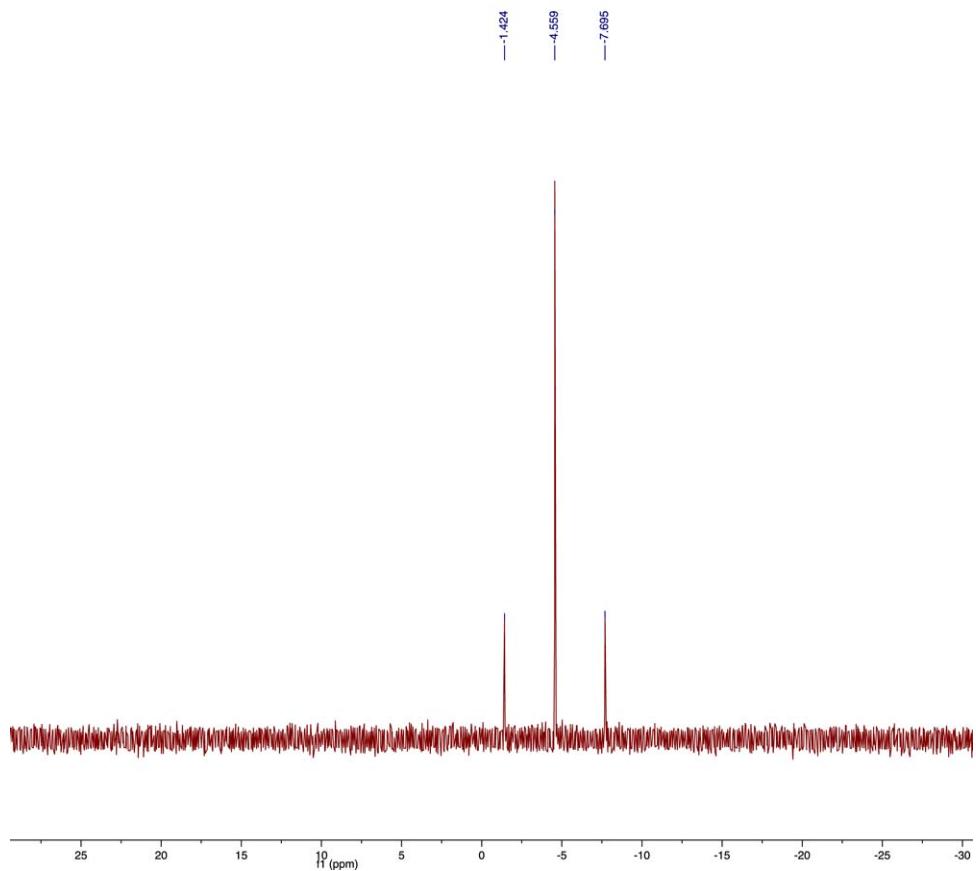
^1H NMR **6**



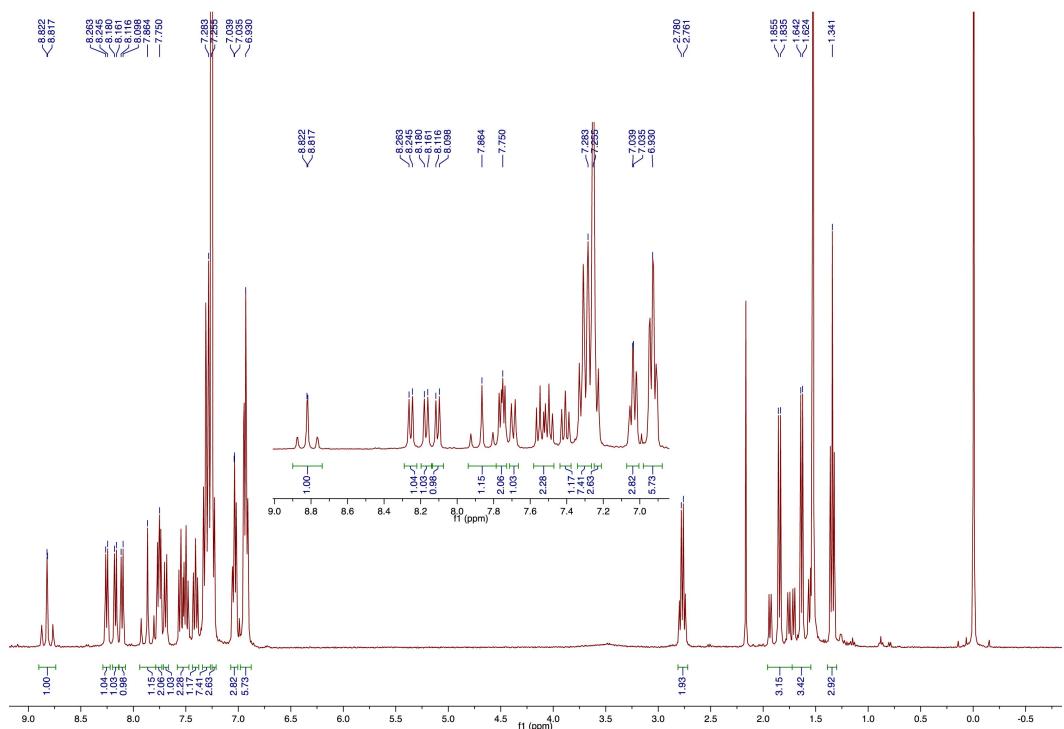
$^1\text{H}/^{195}\text{Pt}$ 2D HMBC spectrum of **6**



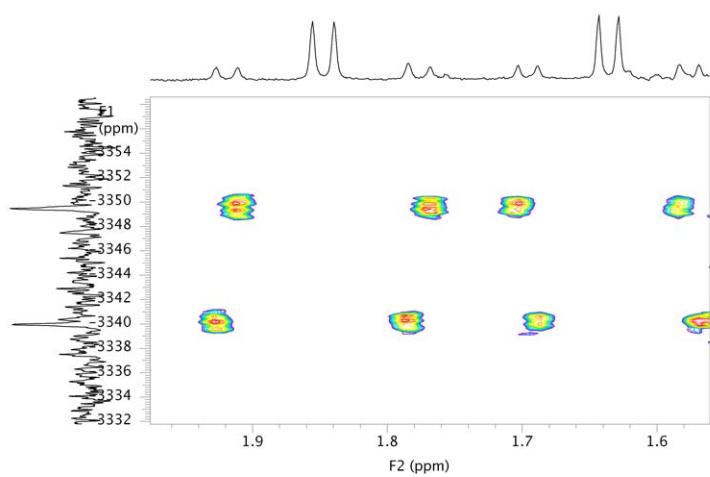
^{31}P NMR **7**



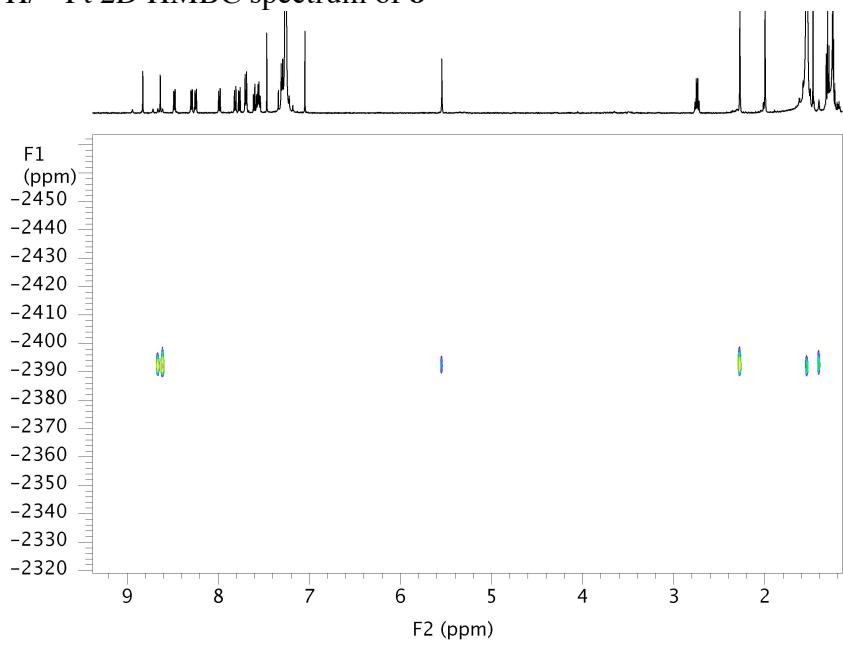
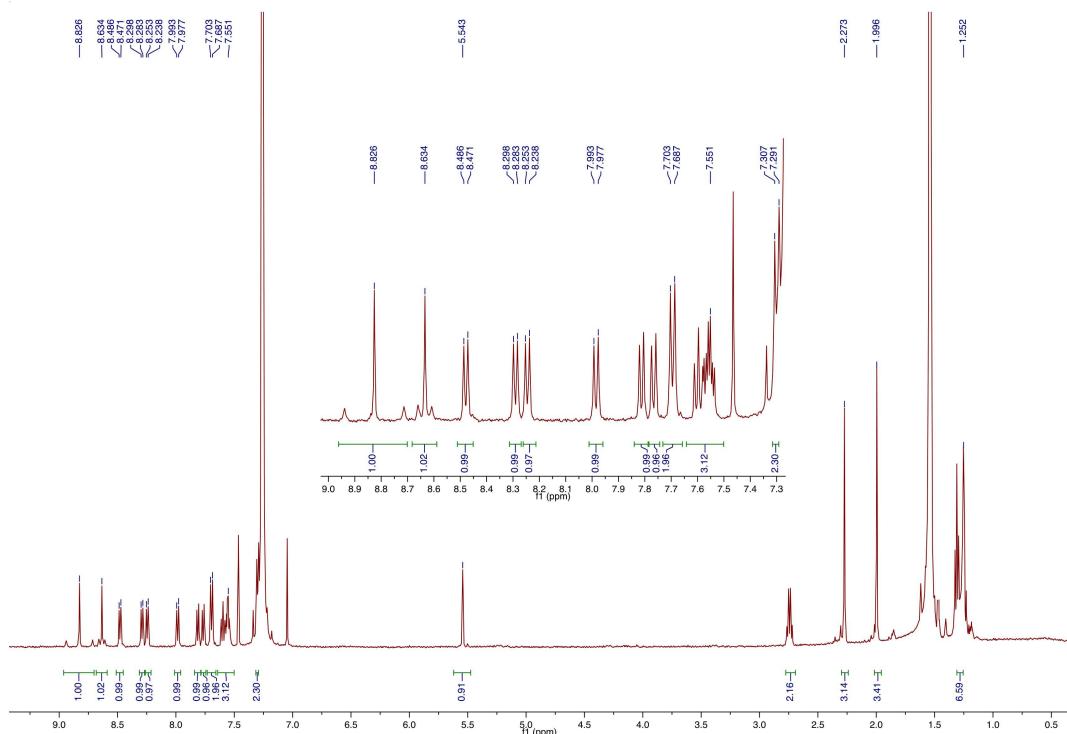
¹H NMR 7



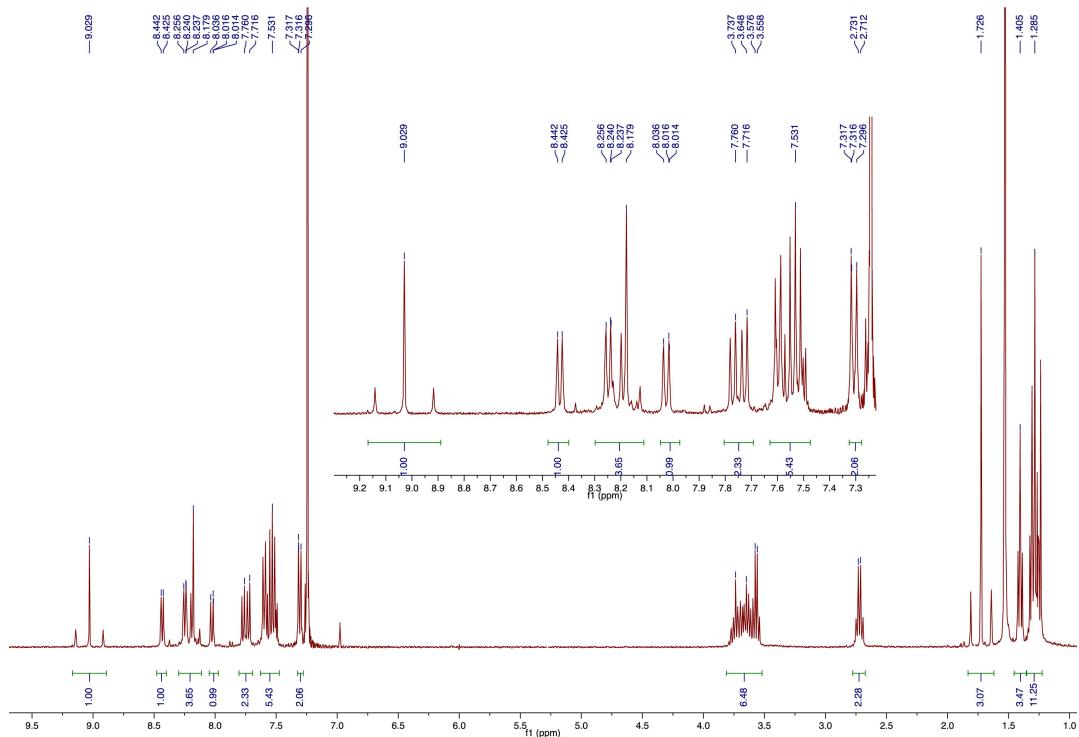
¹H/¹⁹⁵Pt 2D HMBC spectrum of 7



¹H NMR **8**



¹H NMR **9**



¹H/¹⁹⁵Pt 2D HMBC spectrum of **9**

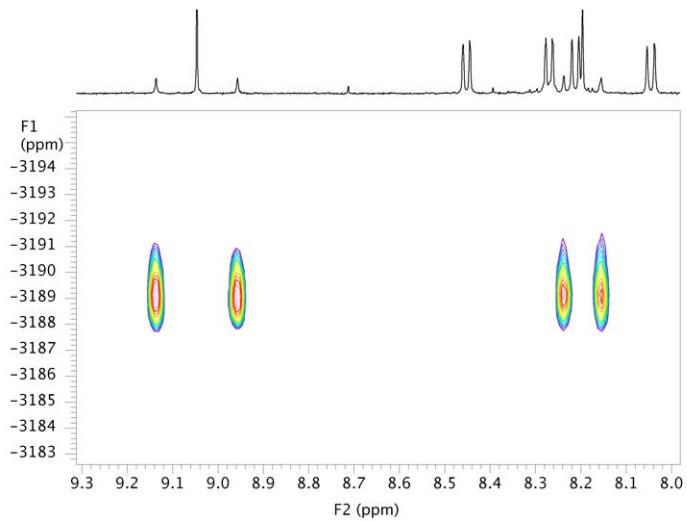


Table S1. Calculated absorption parameters (wavelengths in nm, and their intensities) for Perylene imine ($\text{HC}^{\wedge}\text{N}$), $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})]$, and $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})\text{MeI}]$ in gas phase and chloroform solution. For each entry, main contributions of the orbitals for the transition and their coefficients are shown.

(a) Perylene imine $\text{HC}^{\wedge}\text{N}$

Gas phase		CHCl_3	
$\lambda (\text{f})$	Assignation	$\lambda (\text{f})$	Assignation
486 (0.79)	Perylene: HOMO \rightarrow LUMO [0.70]	506 (0.95)	Perylene: HOMO \rightarrow LUMO [0.70]
397 (0.02)	ILCT ($\text{Ar} \rightarrow \text{Per}$): $\pi(\text{Ar}) \rightarrow \text{LUMO}$ [0.67]	394 (0.04)	ILCT ($\text{Ar} \rightarrow \text{Per}$): $\pi(\text{Ar}) \rightarrow \text{LUMO}$ [0.67]
362 (0.03)	Perylene: HOMO $\rightarrow \pi^*(\text{Per,C=N})$ [0.64]	366 (0.03)	Perylene: HOMO $\rightarrow \pi^*(\text{Per,C=N})$ [0.66]
301 (0.06)	Perylene: HOMO $\rightarrow \pi^*(\text{Per})$ [0.39] $\pi(\text{Per,C=N}) \rightarrow \text{LUMO}$ [0.28] HOMO $\rightarrow \pi^*(\text{Per})$ [0.26] $\pi(\text{Per,Ar}) \rightarrow \text{LUMO}$ [0.20] $\pi(\text{C=N}) \rightarrow \text{LUMO}$ [0.20]	302 (0.12)	Perylene: HOMO $\rightarrow \pi^*(\text{Per})$ [0.37] $\pi(\text{Per}) \rightarrow \text{LUMO}$ [0.28] HOMO $\rightarrow \pi^*(\text{Per})$ [0.26] $\pi(\text{Per,Ar}) \rightarrow \text{LUMO}$ [0.26] $\pi(\text{Per,C=N}) \rightarrow \text{LUMO}$ [0.23]
295 (0.23)	ILCT ($\text{Ar} \rightarrow \text{Per}$): $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.56] $\pi(\text{Per,C=N}) \rightarrow \text{LUMO}$ [0.29]	294 (0.21)	ILCT ($\text{Ar} \rightarrow \text{Per}$): $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.58] $\pi(\text{C=N}) \rightarrow \text{LUMO}$ [0.23]
264 (0.22)	Perylene: HOMO $\rightarrow \pi^*(\text{Per})$ [0.46] HOMO $\rightarrow \pi^*(\text{Per,Ar})$ [0.31] $\pi(\text{Per}) \rightarrow \text{LUMO}$ [0.24]	267 (0.27)	Perylene: HOMO $\rightarrow \pi^*(\text{Per})$ [0.44] HOMO $\rightarrow \pi^*(\text{Ar})$ [0.35] HOMO $\rightarrow \pi^*(\text{Per,Ar})$ [0.19]
259 (0.07)	Perylene: HOMO $\rightarrow \pi^*(\text{Per,Ar})$ [0.53] HOMO $\rightarrow \pi^*(\text{Per})$ [0.26]	261 (0.09)	Perylene: HOMO $\rightarrow \pi^*(\text{Per,Ar})$ [0.58] HOMO $\rightarrow \pi^*(\text{Per})$ [0.20]

Annotation for the involved orbitals:

- $\pi(\text{Per})$ and $\pi^*(\text{Per})$ indicate generic occupied and empty orbitals of perylene. Since all perylene orbitals are of type π , only HOMO and LUMO are emphasized.
- $\pi(\text{Ar})$, $\pi(\text{C=N})$, $\pi(\text{acac})$ and $\sigma(\text{acac})$ indicate occupied bonding orbitals of ethylphenyl substituent, imine group and acetylacetone ligand. Analogously, $\pi^*(\text{Ar})$, $\pi^*(\text{C=N})$, $\pi^*(\text{acac})$ and $\sigma^*(\text{acac})$ are empty antibonding ones. I specify a lone pair of iodide ligand
- x^2-y^2 , z^2 and πd (xy , xz or yz) indicate a d -orbital centered in the metal, assuming the most symmetric environment for the metal.

(b) [Pd(C[^]N)(acac)]

Gas phase		CHCl ₃	
$\lambda (\text{f})$	Assignation	$\lambda (\text{f})$	Assignation
524 (0.60)	Perylene: HOMO → LUMO [0.70]	545 (0.76)	Perylene: HOMO → LUMO [0.70]
429 (0.01)	Perylene+LLCT (acac → Per): $\pi(\text{acac}) \rightarrow \text{LUMO}$ [0.69]	423 (0.07)	Perylene+LLCT (acac → Per): $\pi(\text{acac}) \rightarrow \text{LUMO}$ [0.68]
353 (0.06)	Perylene: $\pi(\text{Per,Ar}) \rightarrow \text{LUMO}$ [0.62]	356 (0.10)	Perylene: $\pi(\text{Per,Ar}) \rightarrow \text{LUMO}$ [0.64]
344 (0.04)	<i>d-d</i> band: $z^2 \rightarrow x^2-y^2$ [0.41] $\pi(\text{acac}) \rightarrow x^2-y^2$ [0.32]	344 (0.07)	<i>d-d</i> band: $z^2 \rightarrow x^2-y^2$ [0.50] $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow x^2-y^2$ [0.22]
286 (0.08)	Perylene: HOMO → $\pi^*(\text{Per})$ [0.50] $\pi\text{d} \rightarrow \text{LUMO}$ [0.21]	286 (0.09)	Perylene: HOMO → $\pi^*(\text{Per})$ [0.47] $z^2 \rightarrow \pi^*(\text{Per,C=N})$ [0.34]
279 (0.02)	MLCT (Pd → Per): $\pi\text{d} \rightarrow \text{LUMO}$ [0.42] HOMO → $\pi^*(\text{Ar})$ [0.31] HOMO → $\pi^*(\text{Per})$ [0.23] HOMO → $\pi^*(\text{Per})$ [0.22]	278 (0.11)	MLCT (Pd → Per): $\pi\text{d} \rightarrow \text{LUMO}$ [0.44] HOMO → $\pi^*(\text{Per})$ [0.37]
270 (0.10)	Perylene: HOMO → $\pi^*(\text{Per})$ [0.36] $\pi(\text{Per,Ar}) \rightarrow x^2-y^2$ [0.24] $\pi(\text{acac}) \rightarrow \pi^*(\text{acac})$ [0.23] $\pi\text{d} \rightarrow \text{LUMO}$ [0.22]	271 (0.19)	Perylene: $\pi\text{d} \rightarrow \text{LUMO}$ [0.38] HOMO → $\pi^*(\text{Per})$ [0.36]
267 (0.03)	LLCT (Per → acac): $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.49] $z^2 \rightarrow \pi^*(\text{acac})$ [0.30] $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow x^2-y^2$ [0.20]	268 (0.06)	LLCT (Per → acac): $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.44] $z^2 \rightarrow \pi^*(\text{acac})$ [0.23] $\pi\text{d} \rightarrow x^2-y^2$ [0.20]
262 (0.08)	Perylene: HOMO → $\pi^*(\text{Per,Ar})$ [0.47] $\pi(\text{Per,Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.30] $\sigma(\text{acac}) \rightarrow \text{LUMO}$ [0.20]	263 (0.09)	Perylene: HOMO → $\pi^*(\text{Per,Ar})$ [0.52] $\pi(\text{Per,Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.31]
259 (0.06)	LMCT (Per → Pd): $\pi(\text{Per,Ar}) \rightarrow x^2-y^2$ [0.34] $\sigma(\text{acac}) \rightarrow \text{LUMO}$ [0.27] $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow x^2-y^2$ [0.27] $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.22]	262 (0.11)	LMCT (Per → Pd): $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow x^2-y^2$ [0.30] $\pi(\text{Per,Ar}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.28] $\pi(\text{Per,Ar}) \rightarrow x^2-y^2$ [0.28] $\pi\text{d} \rightarrow x^2-y^2$ [0.24]

(c) [Pt(C^N)(acac)]

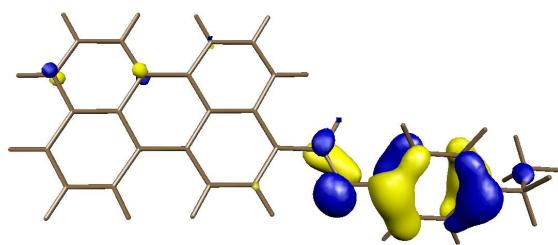
Gas phase		CHCl ₃	
$\lambda (f)$	Assignation	$\lambda (f)$	Assignation
535 (0.51)	Perylene: HOMO → LUMO [0.66]	553 (0.67)	Perylene: HOMO → LUMO [0.69]
440 (0.13)	Perylene+LLCT (acac → Per):: $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \text{LUMO}$ [0.63]	441 (0.14)	Perylene+LLCT (acac → Per):: $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \text{LUMO}$ [0.63]
348 (0.08)	ILCT (Ar → Per): $\pi(\text{Ar},\text{Per}) \rightarrow \text{LUMO}$ [0.62]	353 (0.13)	ILCT (Ar → Per): $\pi(\text{Ar},\text{Per}) \rightarrow \text{LUMO}$ [0.56] HOMO → $\pi^*(\text{Per,C=N})$ [0.36]
289 (0.12)	<i>No be classified:</i> $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.50] HOMO → $\pi^*(\text{Per})$ [0.23] $\pi(\text{Per}),\pi\text{d} \rightarrow \text{LUMO}$ [0.20]	289 (0.14)	<i>No be classified:</i> HOMO → $\pi^*(\text{Per})$ [0.38] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.36] $z^2 \rightarrow \pi^*(\text{Per,C=N})$ [0.23]
271 (0.08)	Perylene: $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Ar}),x^2-y^2$ [0.29] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.28] HOMO → $\pi^*(\text{Per})$ [0.23]	272 (0.18)	Perylene: $\pi\text{d},\pi(\text{Per}) \rightarrow \text{LUMO}$ [0.34] HOMO → $\pi^*(\text{Per})$ [0.31] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Ar}),x^2-y^2$ [0.26] $\pi(\text{Ar},\text{Per}) \rightarrow \pi^*(\text{Per,C=N})$ [0.20]
270 (0.07)	LLCT (Per → acac): $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.40] $\pi(\text{Ar},\text{Per,acac}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.27] HOMO → $\pi^*(\text{Per})$ [0.22]	269 (0.03)	LLCT (Per → acac): $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{acac})$ [0.40] $\pi(\text{Ar}) \rightarrow \pi^*(\text{acac})$ [0.33] $\pi(\text{Ar},\text{Per}) \rightarrow \pi^*(\text{Per,C=N})$ [0.21] $\sigma(\text{acac}) \rightarrow \pi^*(\text{acac})$ [0.20]
263 (0.05)	Perylene: $\pi(\text{Ar},\text{Per}) \rightarrow \pi^*(\text{Per,C=N})$ [0.44] HOMO → $\pi^*(\text{Per})$ [0.26] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Ar}),x^2-y^2$ [0.23]	265 (0.07)	Perylene: $\pi(\text{Ar},\text{Per}) \rightarrow \pi^*(\text{Per,C=N})$ [0.49] HOMO → $\pi^*(\text{Per})$ [0.25] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Ar}),x^2-y^2$ [0.22]
259 (0.08)	Perylene: $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Per})$ [0.60]	259 (0.12)	Perylene: HOMO → $\pi^*(\text{Per}),x^2-y^2$ [0.46] $\pi(\text{acac},\text{Per}),\pi\text{d} \rightarrow \pi^*(\text{Per})$ [0.37]

(d) [Pt(C^N)(acac)MeI]

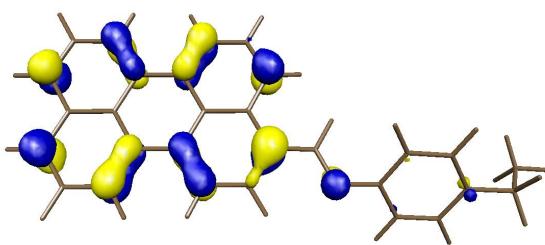
Gas phase		CHCl ₃	
$\lambda (f)$	Assignation	$\lambda (f)$	Assignation
518 (0.60)	Perylene: HOMO → LUMO [0.66] I → LUMO [0.23]	547 (0.72)	Perylene: HOMO → LUMO [0.70]
390 (0.04)	Perylene+LLCT (acac → Per): $\pi(\text{acac}) \rightarrow \text{LUMO}$ [0.67]	388 (0.04)	Perylene+LLCT (acac → Per): $\pi(\text{Ar}) \rightarrow \text{LUMO}$ [0.67]
381 (0.03)	Perylene: HOMO → $\pi^*(\text{Per,C=N})$ [0.50] $\pi(\text{Ar}) \rightarrow \text{LUMO}$ [0.38]	380 (0.05)	Perylene+LLCT (acac → Per): HOMO → $\pi^*(\text{Per,C=N})$ [0.59] $\pi(\text{acac}) \rightarrow \text{LUMO}$ [0.34]
363 (0.04)	ILCT+Perylene: $\pi(\text{Ar}) \rightarrow \text{LUMO}$ [0.48] HOMO → $\pi^*(\text{Per,C=N})$ [0.28] HOMO → x^2-y^2 [0.23]	365 (0.13)	LLCT+Perylene: $\pi(\text{acac}) \rightarrow \text{LUMO}$ [0.59] HOMO → $\pi^*(\text{Per,C=N})$ [0.34]
332 (0.05)	Perylene: $\pi(\text{Per}) \rightarrow \text{LUMO}$ [0.63]	324 (0.06)	Perylene: $\pi(\text{Per}) \rightarrow \text{LUMO}$ [0.61]
291 (0.07)	LLCT+LMCT (acac → Per,Pt): $\pi(\text{acac}) \rightarrow \pi^*(\text{Per-CN})$ [0.50] $\pi(\text{acac}) \rightarrow x^2-y^2$ [0.31] $\pi(\text{Ar}) \rightarrow x^2-y^2$ [0.22]	286 (0.10)	ILCT+LLCT (Ar,I → Per,Pt): $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.48] I → $\pi^*(\text{Per}),z^2$ [0.31]
278 (0.11)	ILCT+LMCT (Ar → Per,Pt): $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.53] $\pi(\text{Ar}) \rightarrow x^2-y^2$ [0.32]	276 (0.05)	CT (Ar,acac → Per,Pt): $\pi(\text{Ar}) \rightarrow x^2-y^2$ [0.38] $\pi(\text{acac}) \rightarrow \pi^*(\text{Per,C=N})$ [0.26] $\pi(\text{acac}) \rightarrow x^2-y^2$ [0.25] I, $\pi(\text{acac}) \rightarrow \pi^*(\text{Per}),z^2$ [0.23]
274 (0.05)	LLCT (acac,Per → Per,Ar): I, $\pi(\text{acac}) \rightarrow \pi^*(\text{Per}),z^2$ [0.31] HOMO → $\pi^*(\text{Ar})$ [0.28] I → $\pi^*(\text{Ar})$ [0.27] $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.23]	276 (0.14)	LLCT (acac,Ar → Per): $\pi(\text{acac}) \rightarrow \pi^*(\text{Per,C=N})$ [0.40] I, $\pi(\text{acac}) \rightarrow \pi^*(\text{Per}),z^2$ [0.39] $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per,C=N})$ [0.21]
268 (0.05)	Perylene+CT (I → Pt): I → $\pi^*(\text{Per})$ [0.40] HOMO → $\pi^*(\text{Per})$ [0.28] $\pi d \rightarrow \text{LUMO}$ [0.23]	269 (0.09)	Perylene+CT (Ar → acac,Pt): HOMO → $\pi^*(\text{Per})$ [0.35] $\pi(\text{Ar}) \rightarrow \pi^*(\text{acac})$ [0.34] $\pi(\text{Ar}) \rightarrow x^2-y^2$ [0.20]
266 (0.08)	No be classified: $\pi(\text{acac}) \rightarrow \pi^*(\text{acac})$ [0.31] $\pi d \rightarrow \text{LUMO}$ [0.25] $\pi(\text{Per}) \rightarrow x^2-y^2$ [0.22] I, $\pi(\text{acac}) \rightarrow \pi^*(\text{Per}),z^2$ [0.20] HOMO → $\pi^*(\text{Per})$ [0.20]	261 (0.10)	No be classified: $\pi(\text{Per}) \rightarrow x^2-y^2$ [0.26] $\pi(\text{Ar}) \rightarrow \pi^*(\text{Per}),z^2$ [0.25] I, $\pi(\text{acac}) \rightarrow \pi^*(\text{Per}),z^2$ [0.22] $\pi(\text{Per}) \rightarrow x^2-y^2$ [0.21]

Table S2. Molecular orbitals for Perylene imine ($\text{HC}^{\wedge}\text{N}$), $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})]$, and $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})\text{MeI}]$. Percentage compositions for each one entry are obtained from Natural Populations Analysis.

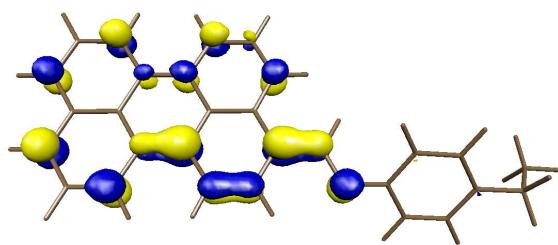
(a) Perylene imine $\text{HC}^{\wedge}\text{N}$



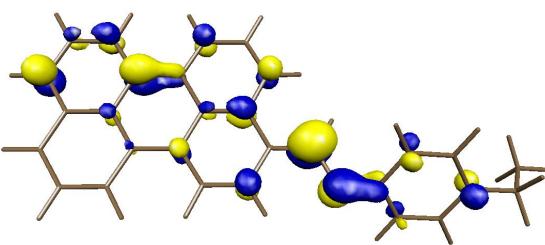
MO 100: -0.215 Ha
Ar (55), imine (22), Per (13)



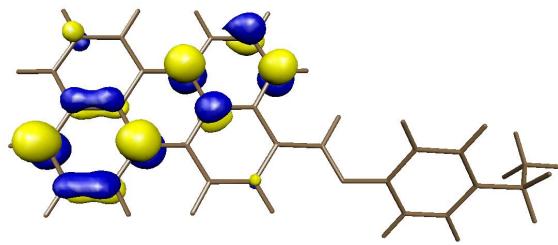
MO 101 (*HOMO*): -0.183 Ha
Per (86), imine (5), Ar (6)



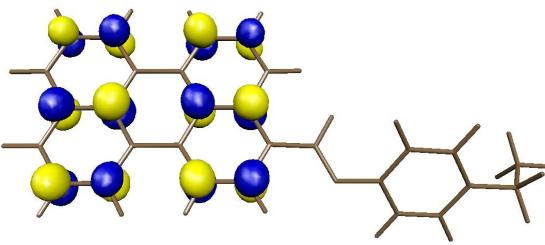
MO 102 (*LUMO*): -0.083 Ha
Per (79), imine (12), Ar (3)



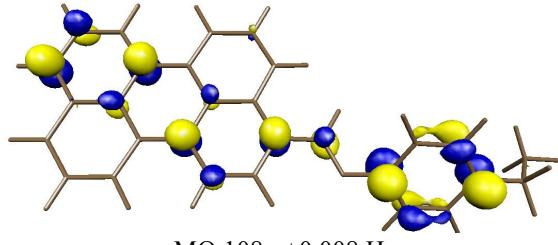
MO 103: -0.041 Ha
Per (51), imine (27), Ar (13)



MO 105: -0.006 Ha
Per (95)

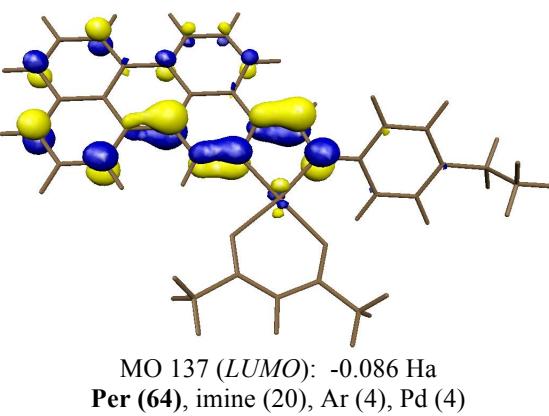
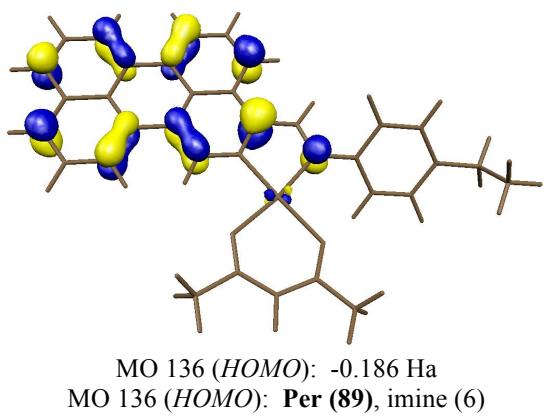
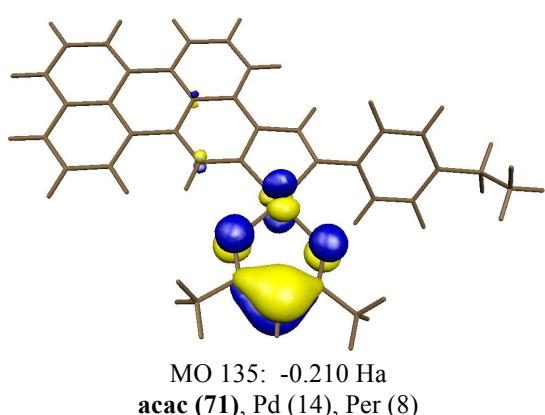
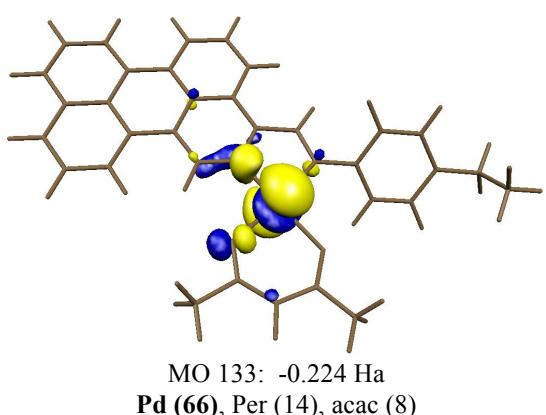
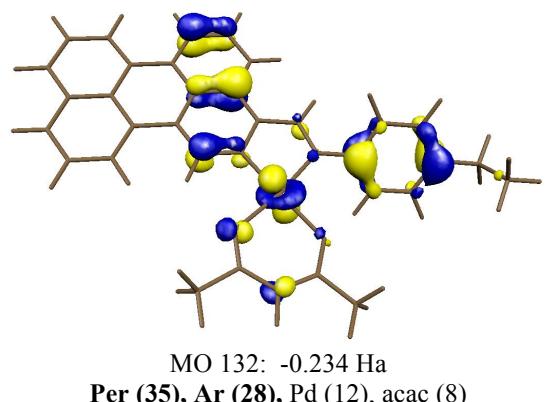
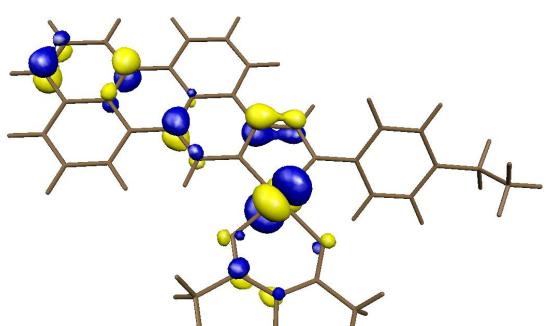
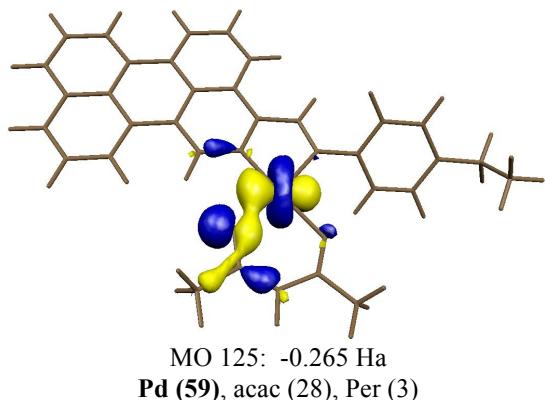
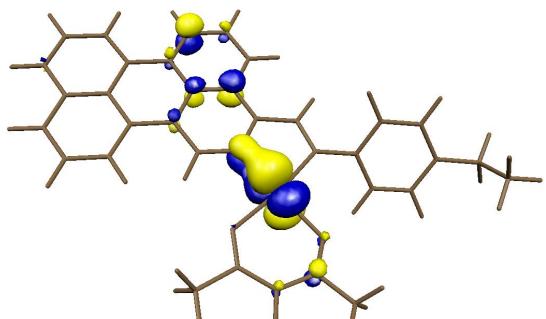


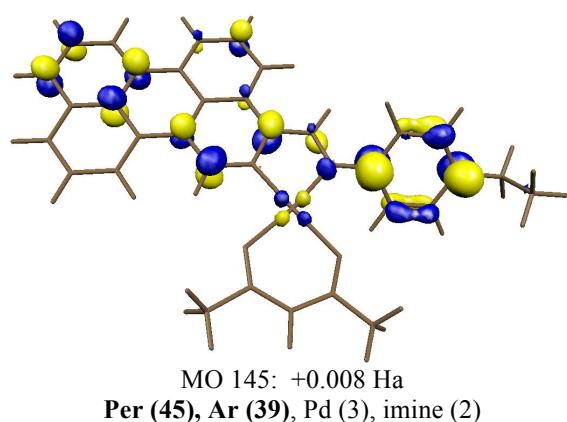
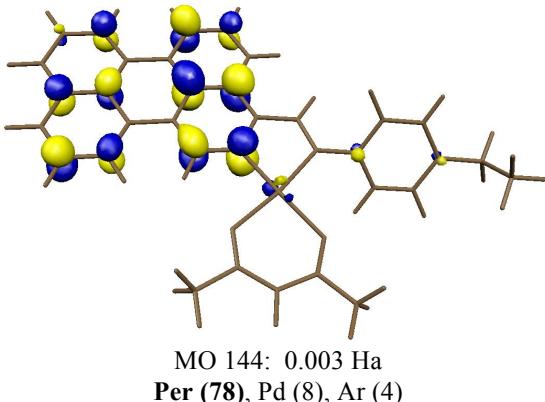
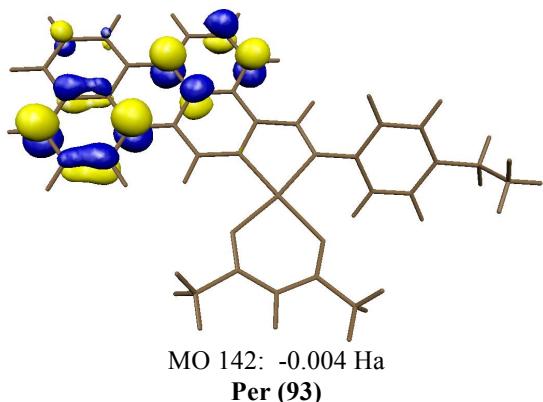
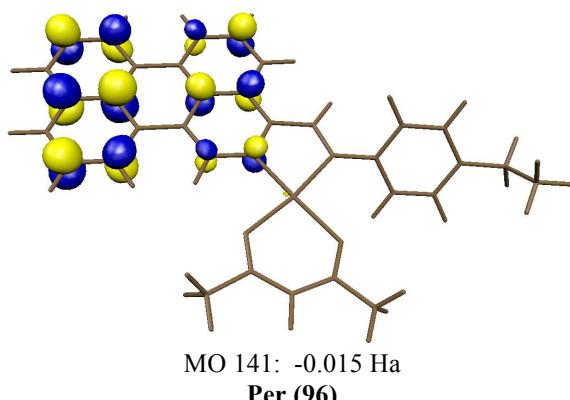
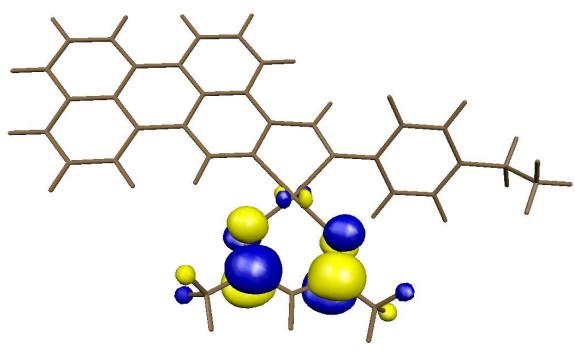
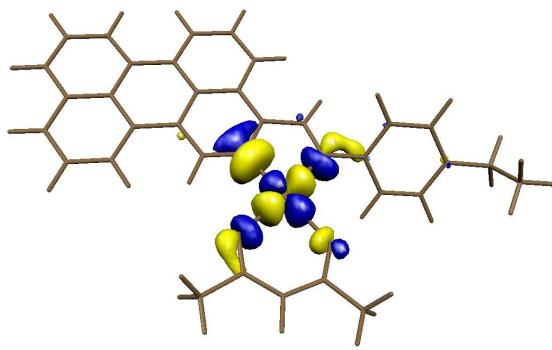
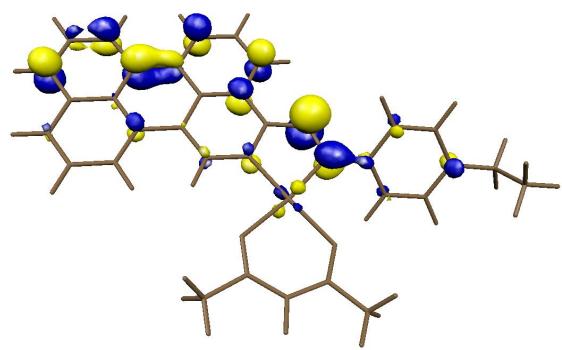
MO 106: -0.001 Ha
Per (98)



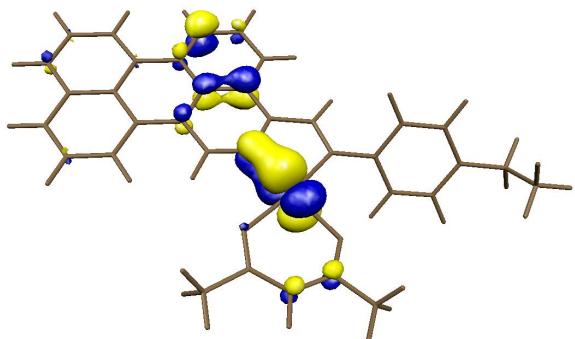
MO 108: +0.008 Ha
Per (50), Ar (35), imine (5)

(b) $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{acac})]$

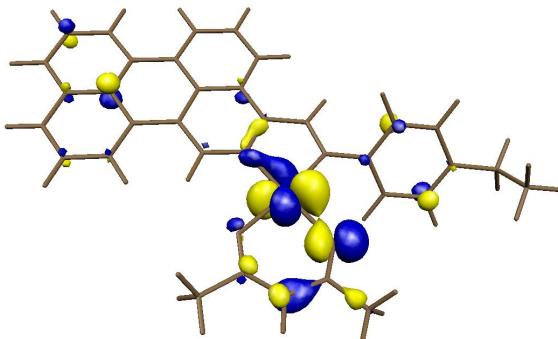




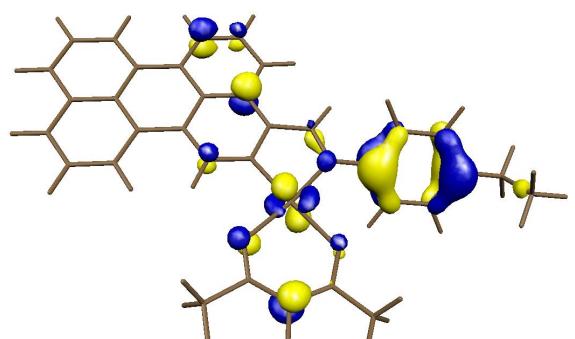
(c) $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})]$



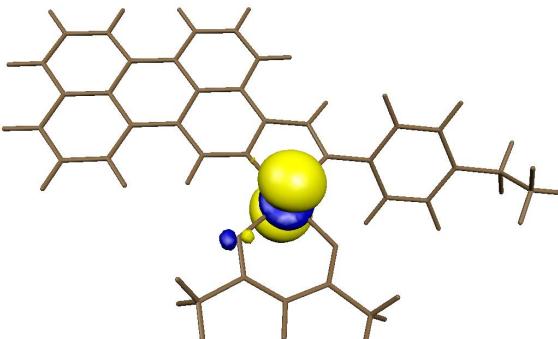
Per (45), Pt (42), acac (6)



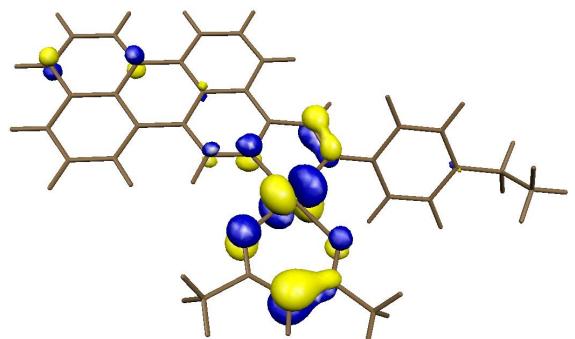
Pt (30), acac (25), Per (25), Ar (11)



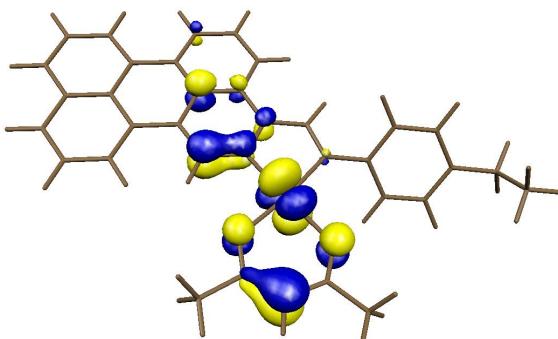
Ar (41), Per (24), acac (12), Pt (8), imine (4)



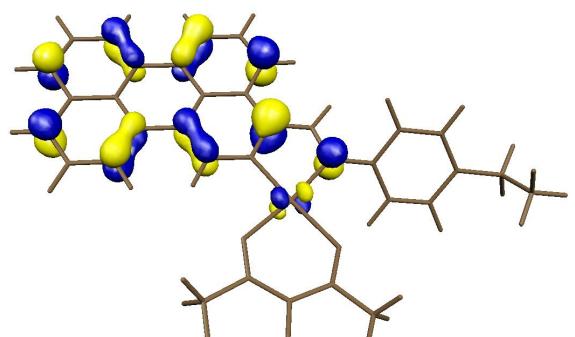
Pt (89), Per (3), acac (2)



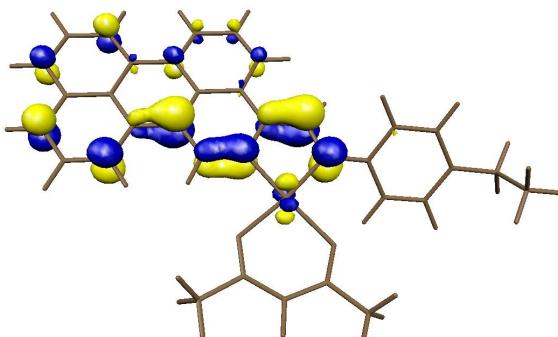
Pt (31), acac (26), Per (20), imine (8), Ar (4)



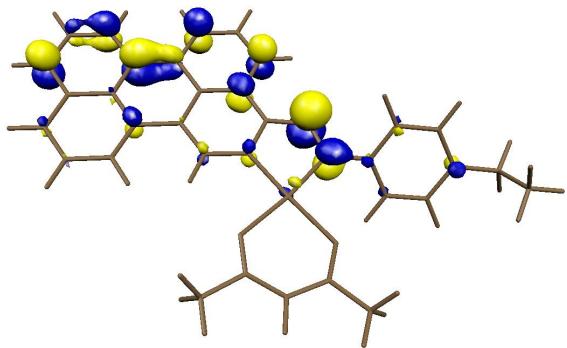
Pt (30), acac (30), Per (30)



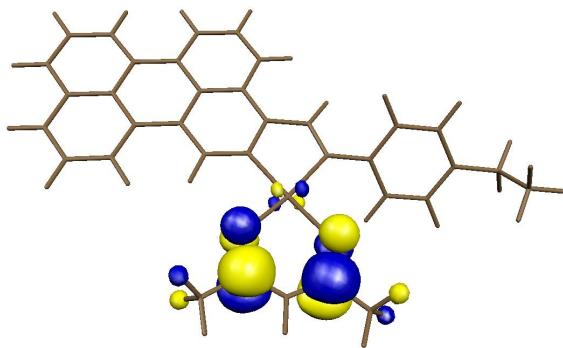
Per (82), imine (7), Pt (4), Ar (3)



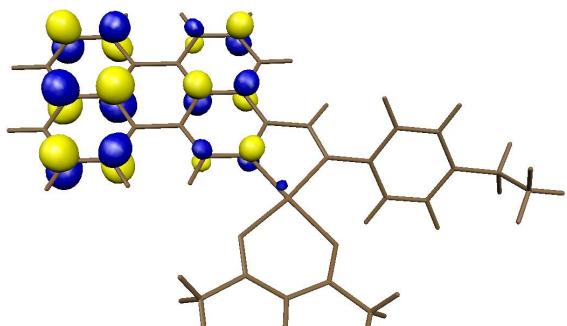
Per (67), imine (19), Pt (5), Ar (3)



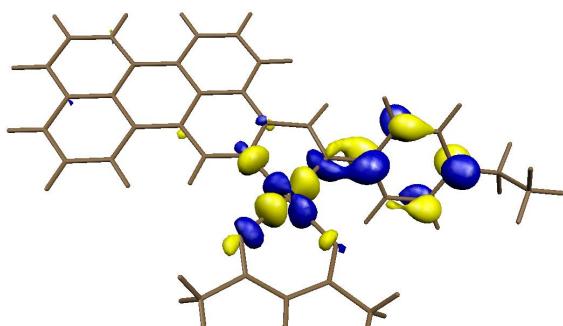
MO 138: -0.044 Ha
Per (60), imine (23), Ar (8), Pt (2)



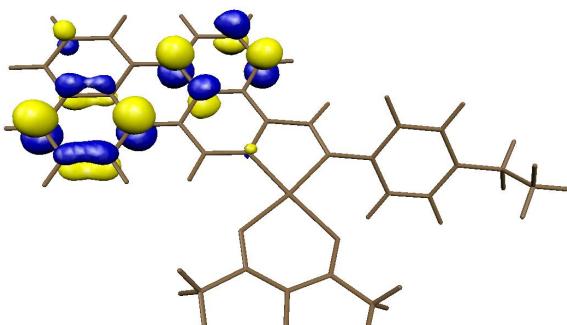
MO 139: -0.035 Ha
acac (93), Pt (2)



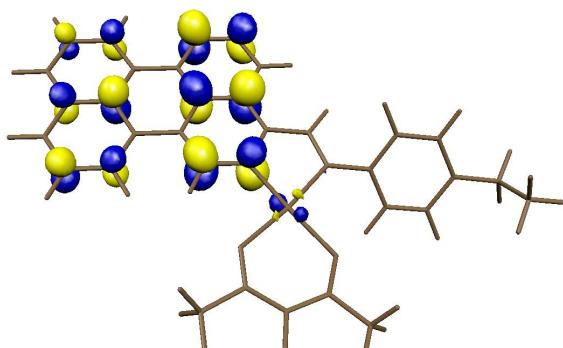
MO 140: -0.014 Ha
Per (92), Pt (1)



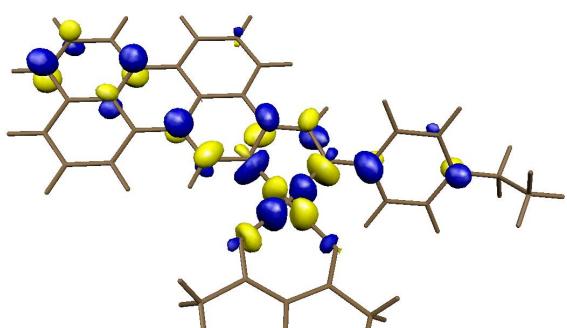
MO 141: -0.007 Ha
Ar (39), Pt (27), Per (13), acac (4), CN (3)



MO 143: +0.002 Ha
Per (92), Pt (2)

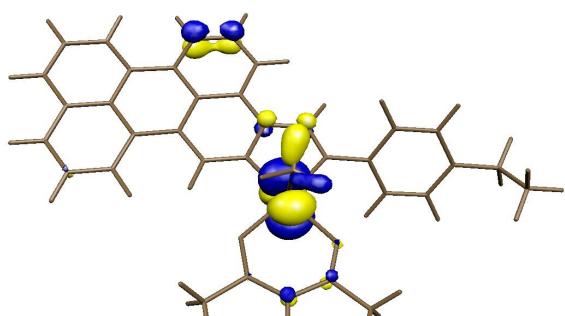


MO 144: +0.006 Ha
Per (86), Pt (8)

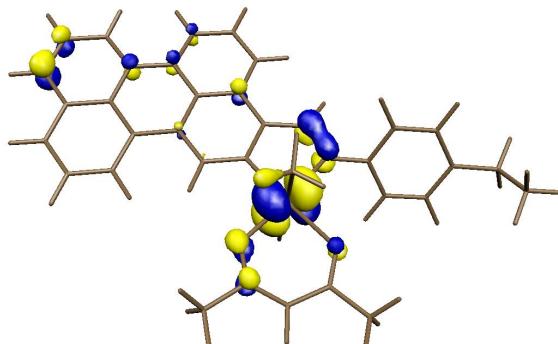


MO 145: +0.016 Ha
Per (44), Pt (21), Ar (12), imine (9), acac (2)

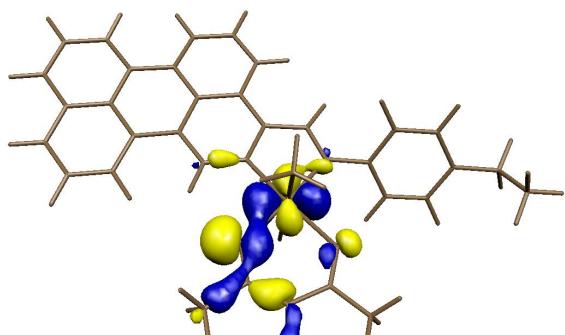
(d) $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{acac})\text{MeI}]$



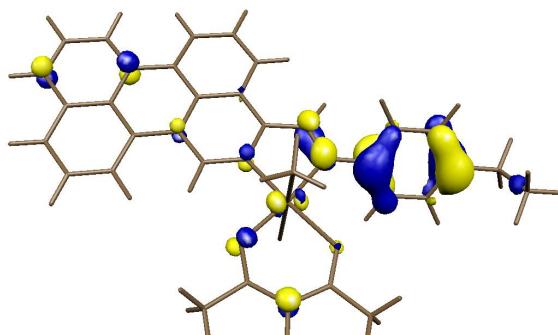
MO 130: -0.309 Ha
Pt (51), Per (25), acac (7), imine (3)



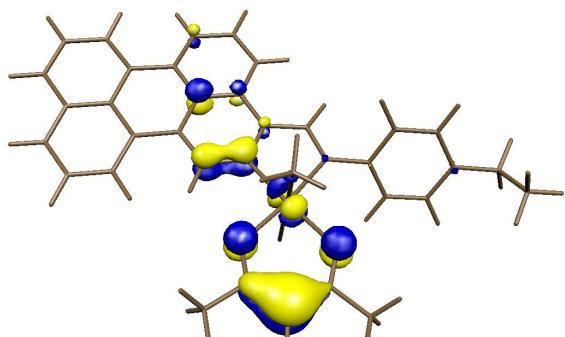
MO 131: -0.093 Ha
Pt (42), Per (29), acac (8), imine (8)



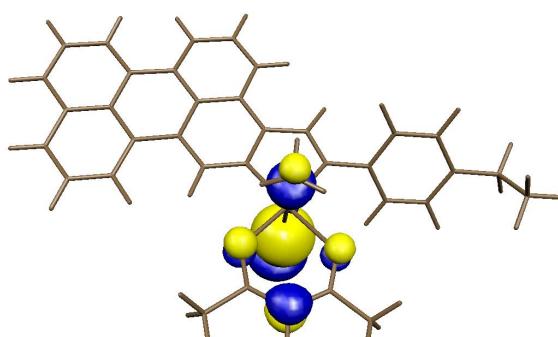
MO 132: -0.289 Ha
acac (48), Pt (38), Per (3)



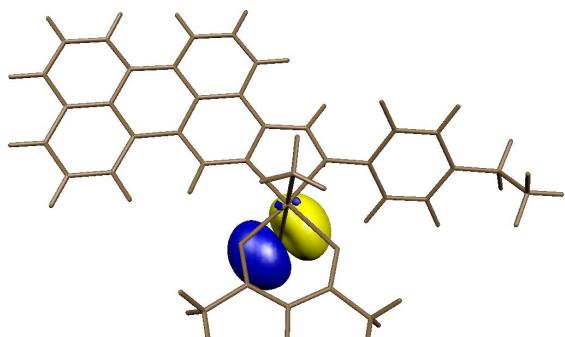
MO 139: -0.235 Ha
Ar (43), Per (22), imine (9), acac (7), Pt (4), I (4)



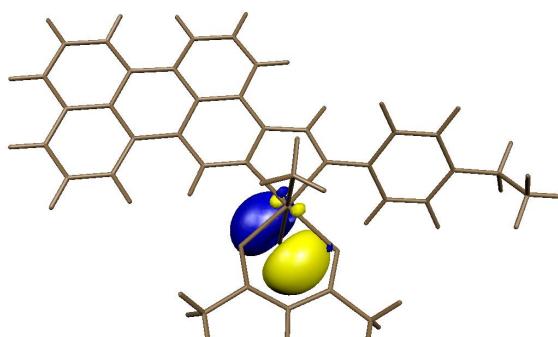
MO 140: -0.230 Ha
acac (47), Per (24), Pt (8), I (6), Ar (3), Me (2)



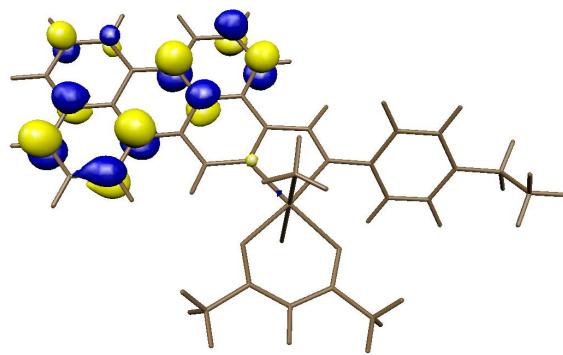
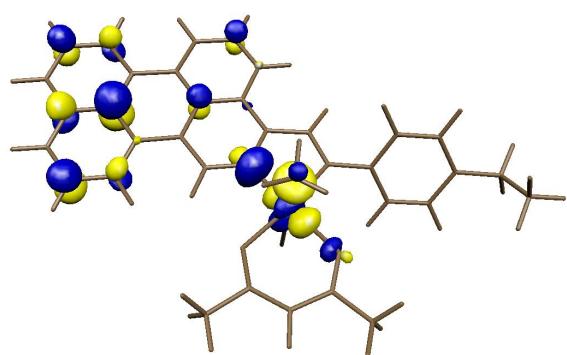
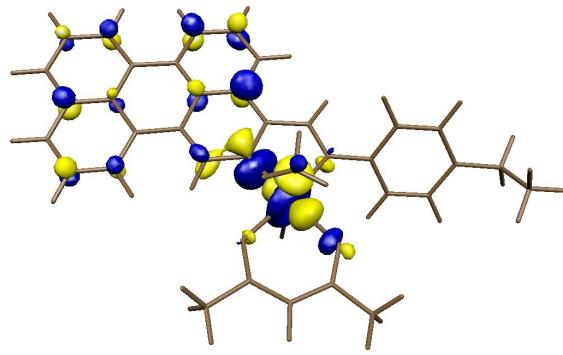
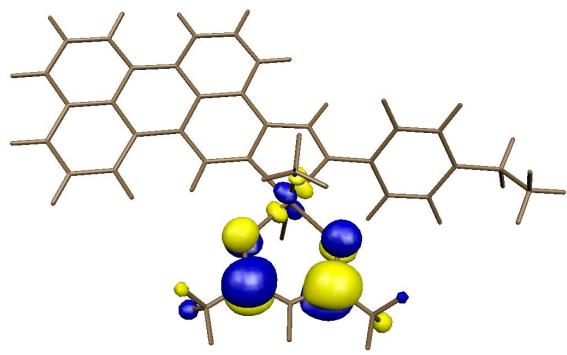
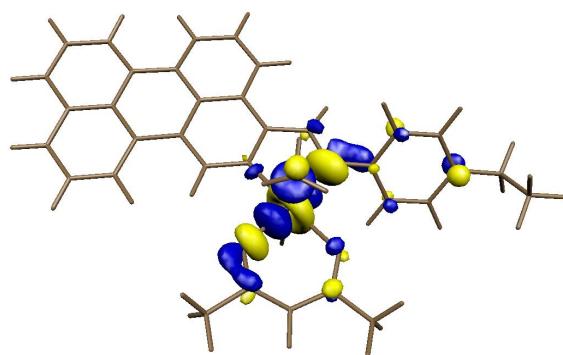
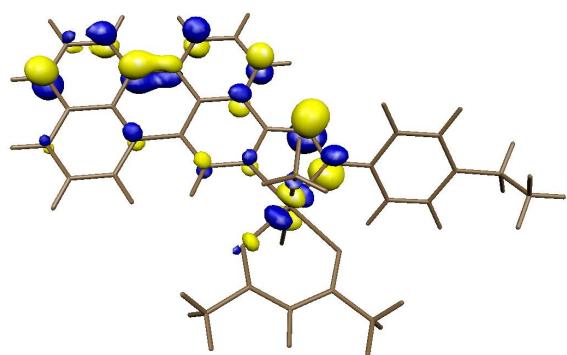
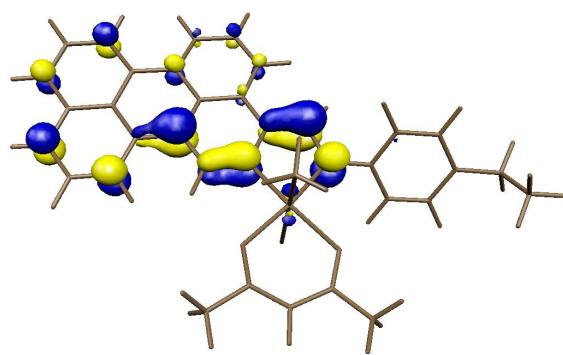
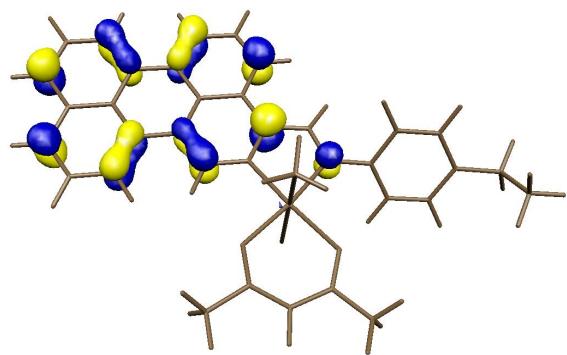
MO 141: -0.212 Ha
I (48), acac (25), Me (13), Pt (6)

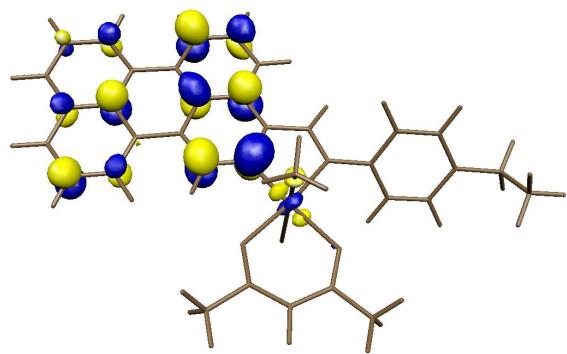


MO 142: -0.195 Ha
I (91), Pt (3)



MO 143: -0.194 Ha
I (94), Pt (4)





MO 153: -0.001 Ha
Per (89), Pt (2)

Fig. S7. 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:

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

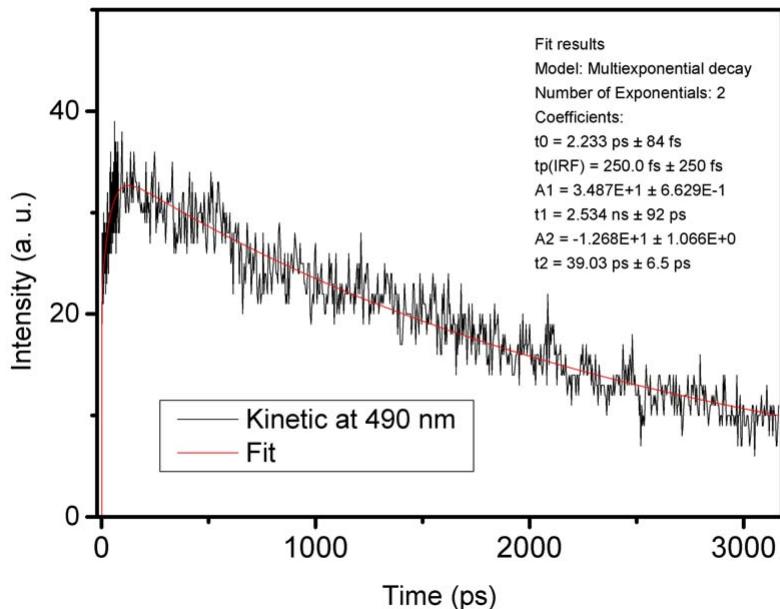
where I_0 is the relative intensity, t is the time and τ is the fluorescence lifetime, both expressed in ns. The bi-exponential decay model is expressed by Equation (2)

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

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 deconvolution 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.

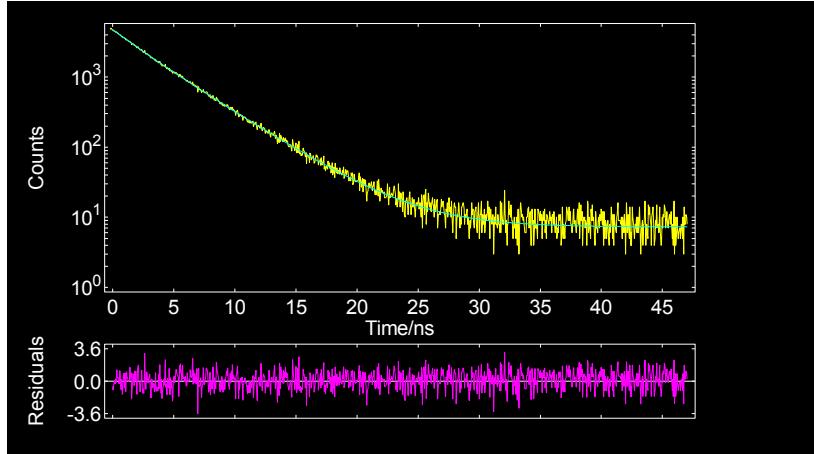
2



3

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	2.14	0.21	12.95
τ_2	4.00	0.05	87.05

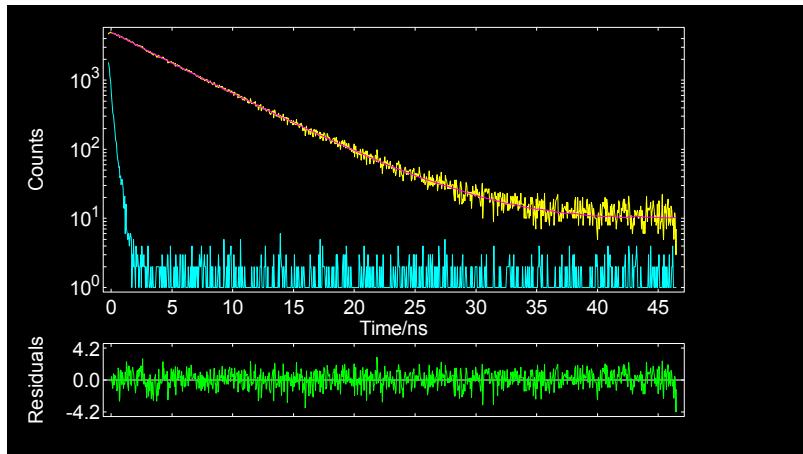
A 7.272
 χ^2 1.051



4

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	2.33	0.50	5.08
τ_2	5.02	0.04	94.92

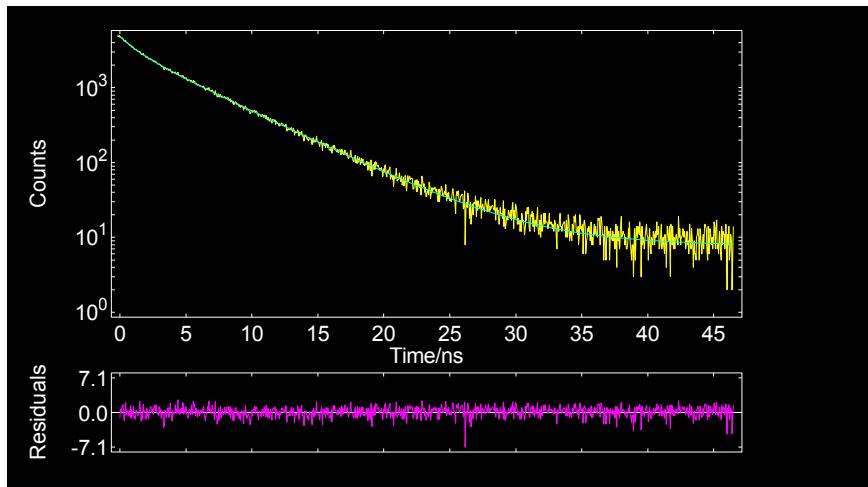
A 7.593
 χ^2 1.182



5

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	1.24	0.05	9.25
τ_2	5.10	0.02	90.75

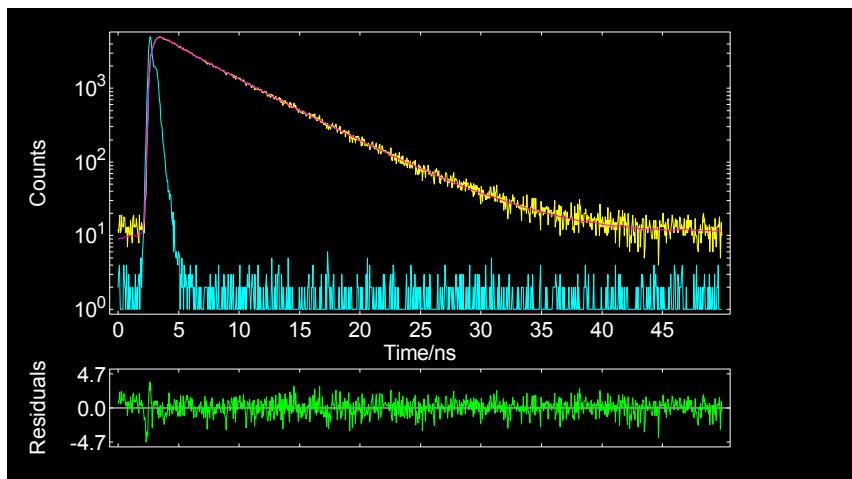
A 7.807
 χ^2 1.131



6

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	1.87	0.18	5.60
τ_2	5.14	0.03	94.40

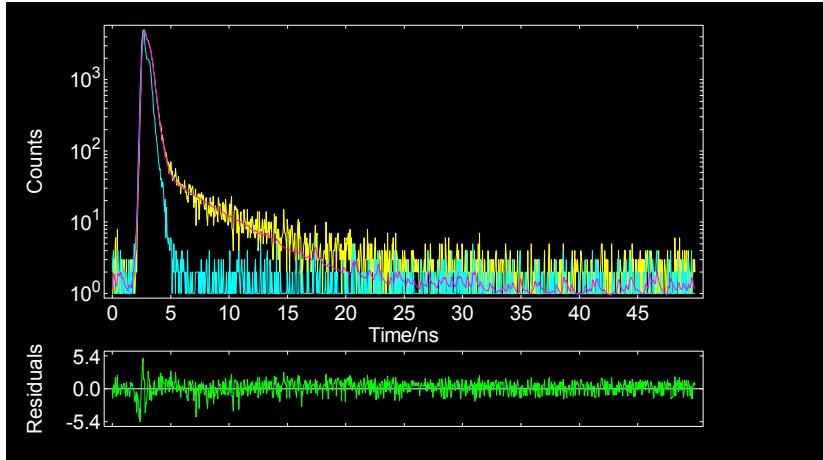
A 8.778
 χ^2 1.246



7

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	0.19	0.00	93.71
τ_2	4.05	0.11	6.29

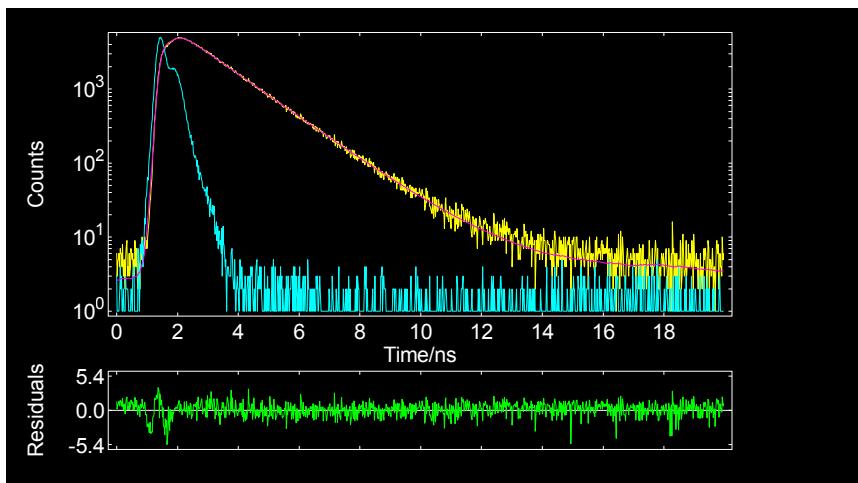
A 0.926
 χ^2 1.201



8

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	1.48	0.01	98.63
τ_2	3.80	0.95	1.37

A 0.926
 χ^2 1.201



9

Param	Value/ns	Std. Dev./ns	Rel.%
τ_1	0.77	0.00	90.68
τ_2	4.77	0.10	9.32

A 1.462
 χ^2 1.262

