Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Highly fluorescent complexes of gold, palladium and platinum attached to perylene through a tetrafluorophenyl group.

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Table S1. Selected Interatomic Distances (Å) and Angles (°) for the second molecule of complex **1.**

Co(3)-Co(4)	2.463(3)	C(91)-O(11)	1.177(11)
Co(3)-C(93)	1.729(12)	C(92)-O(12)	1.166(10)
Co(3)-C(91)	1.765(12)	C(93)-O(13)	1.151(11)
Co(3)-C(92)	1.766(11)	C(94)-O(14)	1.130(14)
Co(3)-C(71)	1.984(8)	C(95)-O(15)	1.110(12)
Co(3)-C(72)	2.000(9)	C(96)-O(16)	1.123(11)
Co(4)-C(72)	1.924(9)	C(51)-C(71)-Co(3)	130.2(6)
Co(4)-C(71)	1.956(8)	C(51)-C(71)-Co(4)	130.7(6)
Co(4)-C(94)	1.798(14)	C(71)-Co(3)-Co(4)	50.8(2)
Co(4)-C(95)	1.831(14)	C(71)-Co(4)-Co(3)	51.8(2)
Co(4)-C(96)	1.778(12)	C(72)-Co(4)-Co(3)	52.5(3)
		C(72)-Co(3)-Co(4)	49.7(3)
		C(71)-C(72)-Co(3)	70.0(5)
		C(71)-C(72)-Co(4)	71.4(5)

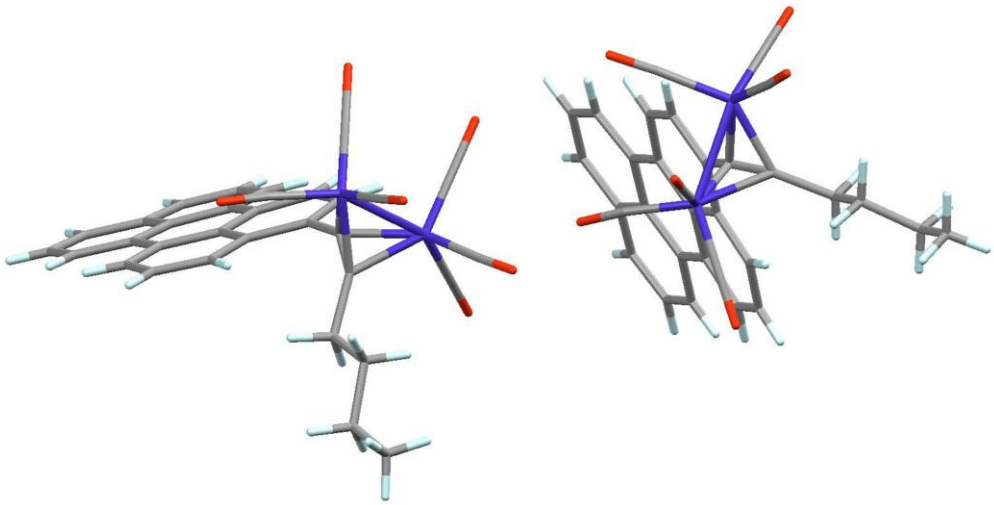


Figure S1. View of the two different molecules of **1** showing the different arrangement of the butyl chain with respect to the perylene.

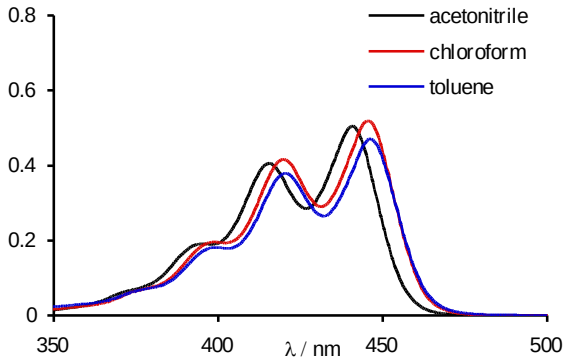


Figure S2. Absorption spectra of **8** in different solvents (ca.10^{-5} M) at room temperature.

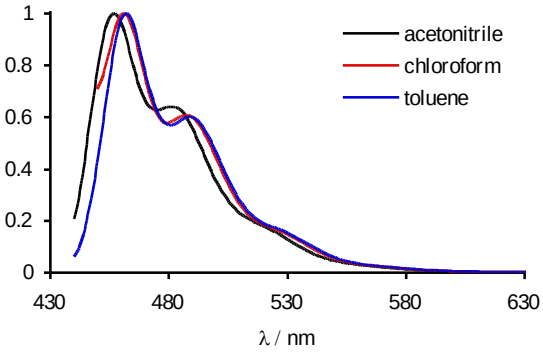


Figure S3. Emission spectra of **8** in different solvents (ca.10^{-5} M) at room temperature

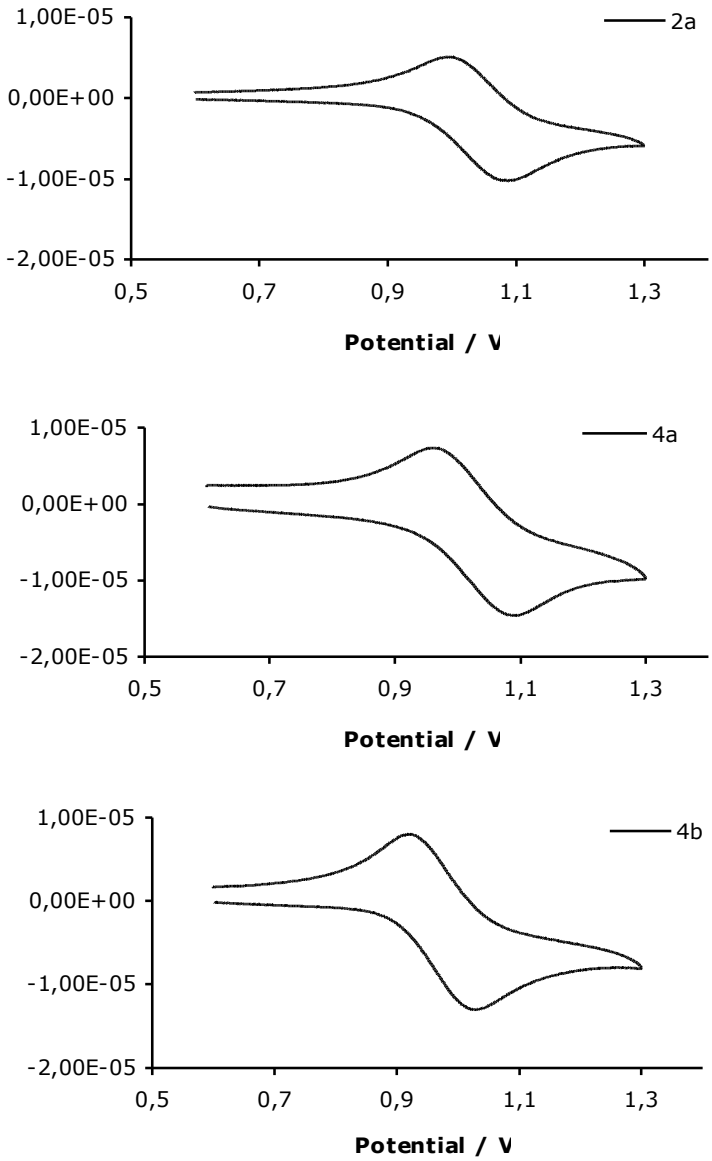
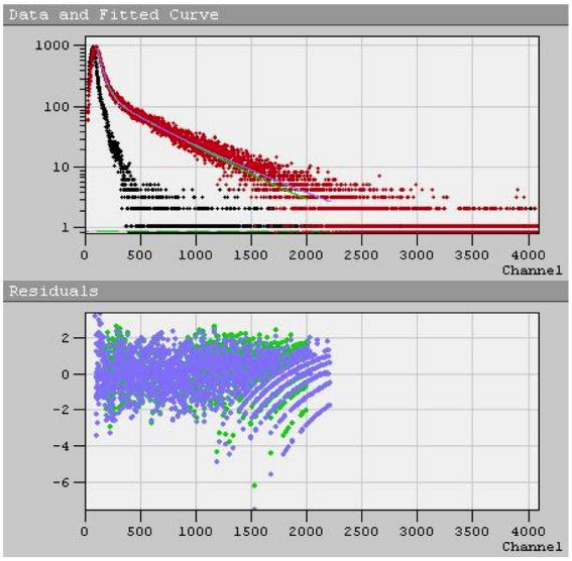


Figure S4. Cvs of compounds **2a, 4a** and **4b**

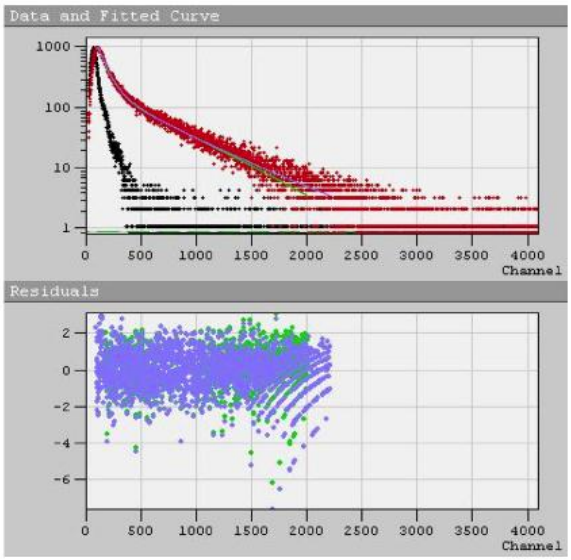


v **Discrete Components Analysis (Reconvolution)**

Fitting range : [150; 2000] channels
c^2 : 1.034

Exp Num	B	f	t (ns)
1	0.029	49.34	0.250
2	0.003	50.66	2.180

Background : 0.739
Shift : -0.034 ns



v **Discrete Components Analysis (Reconvolution)**

Fitting range : [150; 2000] channels
c^2 : 1.044

Exp Num	B	f	t (ns)
1	0.023	48.40	0.412
2	0.004	51.60	2.416

Background : -0.693
Shift : -0.013 ns

Figure S5. Fluorescence decays for **4a** (τ_1 = 0.25 ns, τ_2 = 2.18 ns, χ^2 = 1.034) and **4b** (τ_1 = 0.41 ns, τ_2 = 2.42 ns, χ^2 = 1.044) in dichloromethane, at room temperature.

Table S2. Calculated absorption spectra parameters such as wavelength (nm), and intensity for PerC_6F_4-Y compounds, in gas phase and in chloroform. For each transition, main contributions and their coefficients are shown. In the tables each entry corresponds to one contribution, indicating the topology of involved orbitals. 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.
- C_6F_4 indicates a π/π* occupied/empty orbitals centered in the tetrafluorophenyl ring. Only C_6F_4(Per) is used to identify a C_6F_4 orbital with a minor but significant perylene contribution.
- CNMe designates the π orbitals centered in the isocyanide C≡N triple bond.
- 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.
- In square-planar transition complexes, πd is used to design the occupied *d*-orbitals related to the metal-ligand back-bonding having antibonding contribution.

(*a*) PerC_6F_4H

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
442 (0.49)	Perylene: HOMO → LUMO [0.70]	455 (0.62)	Perylene: HOMO → LUMO [0.70]
257 (0.13)	Perylene: π(Per) → LUMO [0.52] HOMO → π*(Per) [0.25]	259 (0.36)	Perylene: HOMO → π*(Per) [0.39] π(Per) → LUMO [0.33] π(Per) → LUMO [0.31]
255 (0.15)	Perylene: π (Per) → LUMO [0.41] HOMO → π*(Per) [0.39]	257 (0.09)	Perylene: π (Per) → LUMO [0.57] HOMO → π*(Per) [0.28] π(Per) → LUMO [0.20]
241 (0.03)	C_6F_4 ring: π → π* [0.62]	241 (0.04)	C_6F_4 ring: π → π* [0.62]

(*b*) PerC_6F_5

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
442 (0.49)	Perylene: HOMO → LUMO [0.70]	455 (0.62)	Perylene: HOMO → LUMO [0.70]
256 (0.27)	Perylene: HOMO → π*(Per) [0.46] π(Per) → LUMO [0.34]	258 (0.42)	Perylene: HOMO → π*(Per) [0.48] π(Per) → LUMO [0.29]
237 (0.01)	C_6F_4 ring: π → π* [0.45]	237 (0.01)	C_6F_4 ring: π → π* [0.38]

(*c*) PerC$_6$F$_4$Au(CNMe)

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
448 (0.59)	Perylene: HOMO → LUMO [0.70]	457 (0.72)	Perylene: HOMO → LUMO [0.70]
293 (0.11)	Perylene: HOMO → π*(*Per*) [0.43] π(*Per*) → LUMO [0.23] π(*Per*) → LUMO [0.23] LLCT: C_6F_4 → LUMO [0.24] HOMO□→ C_6F_4(Per) [0.23]	291 (0.03)	Perylene: HOMO → π*(*Per*) [0.43] π(*Per*) → LUMO [0.23] π(*Per*) → LUMO [0.22] LLCT: HOMO□→ C_6F_4(Per) [0.28] C_6F_4(Per) → LUMO [0.27]
288 (0.18)	LLCT: C_6F_4 → CNR [0.63]	266 (0.46)	LLCT: C_6F_4 → CNR [0.66]
261 (0.05)	LLCT: HOMO → C_6F_4 & CNMe [0.50] HOMO → π*(*Per*) [0.23]	260 (0.33)	Perylene: HOMO → π*(*Per*) [0.48] π(*Per*) → LUMO [0.34]
259 (0.07)	LLCT: π(*Per*) → CNMe [0.35] HOMO → C_6F_4 & CNMe [0.32]	257 (0.02)	LLCT: HOMO → C_6F_4 & CNMe [0.57] HOMO → C_6F_4 [0.32]
254 (0.08)	LLCT: π(*Per*) → CNMe [0.36] π(*Per*) → CNMe [0.36]	239 (0.06)	LLCT: π(*Per*) → CNMe [0.49] z^2 → CNR [0.38]
252 (0.08)	LLCT: HOMO → C_6F_4 [0.55]	255 (0.06)	LLCT: HOMO → C_6F_4 [0.59] HOMO → C_6F_4 & CNMe [0.24]
248 (0.02)	LLCT: C_6F_4(Per) → CNMe [0.69]	231 (0.02)	LLCT: C_6F_4(Per) → CNMe [0.68]
246 (0.02)	MLCT: z^2 → CNMe [0.57] LLCT: π(*Per*) → CNMe [0.38]	232 (0.05)	MLCT: z^2 → CNMe [53] LLCT: π(*Per*) → CNMe [0.39]
240 (0.01)	LLCT: C_6F_4 → C_6F_4(Per) [0.61]	234 (0.01)	LLCT: C_6F_4 → C_6F_4(Per) [0.62]

231 (0.22)	LLCT: $C_6F_4 \rightarrow C_6F_4$(Per) [0.63]	227 (0.18)	LLCT: $C_6F_4 \rightarrow C_6F_4$(Per) [0.57] π(*Per*) $\rightarrow \pi^*$(*Per*) [0.22]

(*d*) PerC$_6$F$_4$PdBr(PMe$_3$)$_2$

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
443 (0.61)	Perylene: HOMO $\rightarrow$ LUMO [0.70]	456 (0.74)	Perylene: HOMO $\rightarrow$ LUMO [0.70]
298 (0.05)	LMCT: $C_6F_4 \rightarrow x^2$-y^2 [0.63] *d-d* band: πd $\rightarrow x^2$-y^2 [0.22]	293 (0.11)	LMCT: $C_6F_4 \rightarrow x^2$-y^2 [0.54] *d-d* band: πd $\rightarrow x^2$-y^2 [0.40]
264 (0.01)	Perylene: HOMO $\rightarrow \pi^*$(Per) [0.52]	257 (0.09)	Perylene: HOMO $\rightarrow \pi^*$(Per) [0.51]
259 (0.01)	*d-d* band: πd $\rightarrow x^2$-y^2 [0.60]	252 (0.03)	*d-d* band: πd $\rightarrow x^2$-y^2 [0.55]
256 (0.26)	Perylene: HOMO $\rightarrow \pi^*$(*Per*) [0.46] π(*Per*) $\rightarrow$ LUMO [0.37]	259 (0.31)	Perylene: HOMO $\rightarrow \pi^*$(*Per*) [0.34] HOMO $\rightarrow \pi^*$(*Per*) [0.34] p(*Per*) $\rightarrow$ LUMO [0.31]
251 (0.05)	MLCT: πd $\rightarrow C_6F_4$(Per) [0.41] LMCT: Br $\rightarrow x^2$-y^2 [0.40]	243 (0.03)	MLCT: πd $\rightarrow C_6F_4$(Per) [0.34] LMCT: π□(*Per*) $\rightarrow x^2$-y^2 [0.34] Br $\rightarrow x^2$-y^2 [0.28]
245 (0.02)	LMCT: π(*Per*) $\rightarrow x^2$-y^2 [0.57]	243 (0.06)	LMCT: p(*Per*) $\rightarrow x^2$-y^2 [0.43]
244 (0.07)	MLCT: pd $\rightarrow C_6F_4$(Per) [0.51]	238 (0.06)	MLCT: πd $\rightarrow C_6F_4$(Per) [0.51]
243 (0.08)	MLCT: πd $\rightarrow \pi$□(*Per*) [0.62]	246 (0.02)	MLCT: πd $\rightarrow \pi^*$(*Per*) [0.68]
243 (0.00)	LMCT: p(*Per*) $\rightarrow x^2$-y^2 [0.57]	242 (0.10)	LMCT: π(*Per*) $\rightarrow x^2$-y^2 [0.65]
242 (0.45)	MLCT: πd $\rightarrow C_6F_4$(Per) [0.41] πd $\rightarrow$ LUMO [0.30] LMCT: Br $\rightarrow x^2$-y^2 [0.31]	242 (0.84)	MLCT: πd $\rightarrow C_6F_4$(Per) [0.47] LMCT: Br $\rightarrow x^2$-y^2 [0.34]

(*e*) $PerC_6F_4PtBr(PMe_3)_2$

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
443 (0.61)	Perylene: HOMO → LUMO [0.70]	457 (0.74)	Perylene: HOMO → LUMO [0.71]
298 (0.01)	*d-d* band: πd → x^2-y^2 [0.63]	304 (0.02)	*d-d* band: πd → x^2-y^2 [0.63]
258 (0.15)	MLCT: πd → C_6F_4(Per) [0.51]	254 (0.16)	MLCT: πd → C_6F_4(Per) [0.53]
255 (0.05)	*d-d* band: πd → x^2-y^2 [0.67]	252 (0.08)	*d-d* band: πd → x^2-y^2 [0.65]
255 (0.19)	Perylene: HOMO → π*(*Per*) [0.43] π(*Per*) → LUMO [0.34]	259 (0.34)	Perylene: HOMO → π*(*Per*) [0.39] HOMO → π*(*Per*) [0.36] π(*Per*) → LUMO [0.32]
248 (0.04)	MLCT: πd → C_6F_4(Per) [0.56]	247 (0.02)	MLCT: πd → C_6F_4(Per) [0.60]
243 (0.02)	MLCT: πd → π*(*Per*) [0.55] C_6F_4□ ring C_6F_4 → C_6F_4(Per) [0.28]	242 (0.05)	MLCT: πd → π*(*Per*) [0.38] C_6F_4□ ring C_6F_4 → C_6F_4(Per) [0.35]
242 (0.08)	MLCT: πd → π*(*Per*) [0.39] πd → C_6F_4(Per) [0.31] πd → π*(*Per*) [0.27]	239 (0.09)	MLCT: πd → π*(*Per*) [0.44] πd → π*(*Per*) [0.31] πd → C_6F_4(Per) [0.28]
240 (0.16)	MLCT: πd → C_6F_4(Per) [0.40] πd → LUMO [0.29]	233 (0.17)	MLCT: πd → C_6F_4(Per) [0.58]

(*f*) $C_6F_5Au(CNMe)$

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
287 (0.22)	LLCT: $C_6F_4 \rightarrow CNR$ [0.70]	262 (0.31)	LLCT: $C_6F_4 \rightarrow CNR$ [0.70]
248 (0.04)	MLCT: $z^2 \rightarrow CNR$ [0.70]	238 (0.08)	MLCT: $z^2 \rightarrow CNR$ [0.70]
244 (0.03)	MLCT: $z^2 \rightarrow CNR$ [0.70]	232 (0.06)	MLCT: $z^2 \rightarrow CNR$ [0.69]

(*g*) $C_6F_5PdBr(PMe_3)_2$

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
304 (0.06)	LMCT: $C_6F_4 \rightarrow x^2\text{-}y^2$ [0.65] *d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.25]	299 (0.11)	LMCT: $C_6F_4 \rightarrow x^2\text{-}y^2$ [0.54] *d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.42]
250 (0.08)	*d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.48] MLCT: $\pi d \rightarrow C_6F_4$ [0.45]	242 (0.16)	*d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.53] MLCT: $\pi d \rightarrow C_6F_4$ [0.35]

(*h*) $C_6F_5PtBr(PMe_3)_2$

Gas phase		$CHCl_3$	
λ (*f*)	Assignation	λ (*f*)	Assignation
300 (0.01)	*d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.67]	306 (0.01)	*d-d* band: $\pi d \rightarrow x^2\text{-}y^2$ [0.69]
260 (0.04)	LMCT: $C_6F_4 \rightarrow x^2\text{-}y^2$ [0.69]	257 (0.07)	LMCT: $C_6F_4 \rightarrow x^2\text{-}y^2$ [0.69]
256 (0.02)	MLCT: $\pi d \rightarrow C_6F_4$ [0.66]	251 (0.04)	MLCT: $\pi d \rightarrow C_6F_4$ [0.56]

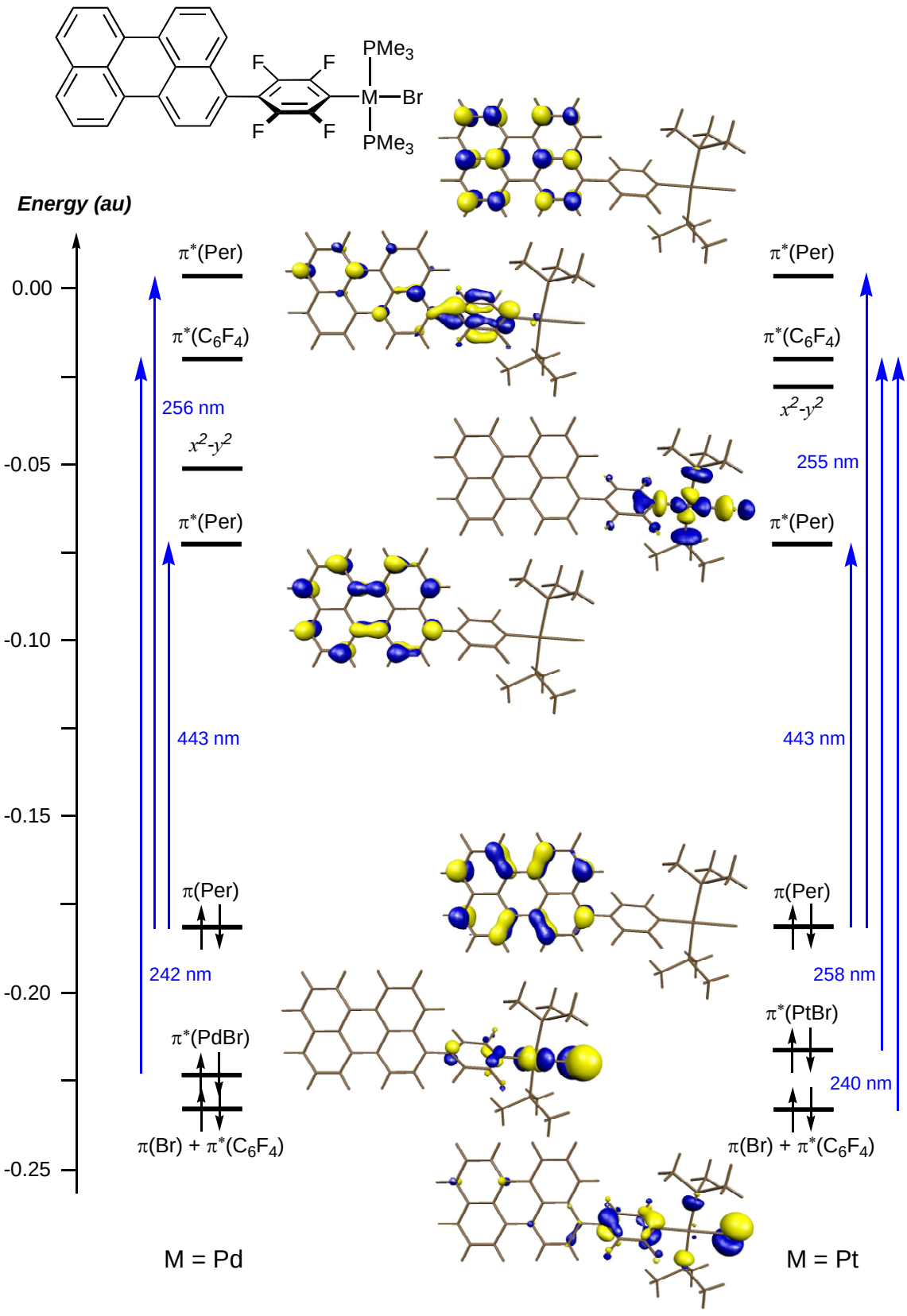


Figure S4. Schematic representation of the main electronic transitions expected in the absorption spectra for the compounds $PerC_6F_4MBr(PMe_3)_2$ (M = Pd or Pt).