Electronic Supplementary Information

Photophysical Behaviour of Cyclometalated Iridium (III) Complexes with Phosphino(terthiophene) Ligands

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DFT and TDDFT Calculations

All calculations were performed with the 2012.01 version of the Amsterdam Density Functional (ADF) program.[1] All electrons were included in the variational treatment (i.e., no frozen-core approximation was applied). Experimental X-ray crystallographic geometries were used as a starting point in the NOSYM (C_1 point group) geometry optimizations.

Energies, geometries, and the orbital electronic structure were calculated using the generalized gradient approximation (GGA) of density functional theory (DFT) at the BP86 level. The GGA proceeds from the local density approximation (LDA), where exchange is described by Slater's $X\alpha$ potential[1h] and correlation is treated in the Vosko-Wilk-Nusair (VWN) parameterization,[1i] and is augmented with nonlocal corrections to exchange due to Becke[1j,k] and correlation due to Perdew[1l] added self-consistently.[1m] Relativistic effects were taken into account in all cases using the zeroth-order relativistic approximation (ZORA)[2] and all-electron TZ2P basis sets from the ADF ZORA basis sets library were used for all atoms. [1f] The SAOP XC functional was used for TDDFT[3]

calculations of excitation energies. Spin-orbit coupling and CH_3CN solvation effects (with the COSMO[4] formalism in ADF) were included in some calculations.

Table S1. Selected crystallographic data for $Ir(ppz)_2PT_3Cl$-*P*, $[Ir(ppz)_2PT_3$-*PS*$](BF_4)$, and $Ir(ppz)_2PT_3$-*PC*

	$Ir(ppz)_2PT_3Cl$-*P*	$[Ir(ppz)_2PT_3$-*PS*$](BF_4)$	$Ir(ppz)_2PT_3$-*PC*
Formula	$C_{43}H_{33}N_4PS_3IrCl_3$	$C_{44}H_{35}BN_4F_4PS_3IrCl_4$	$C_{42}H_{30}IrN_4PS_3$
Crystal Colour, Habit	yellow, irregular	yellow, blade	brown, prism
Dimensions / mm	0.10 × 0.10 × 0.15	0.02 × 0.10 × 0.35	0.20 × 0.28 × 0.29
T / K	90 (1)	90(1)	100(1)
Crystal System	triclinic	orthorhombic	monoclinic
Space Group	*P* -1 (#2)	*P* $2_12_12_1$ (#19)	*P* $2_1/n$ (#14)
a / Å	9.8502(11)	9.1409(8)	9.9313(3)
b / Å	13.0136(14)	20.640(2)	17.0695(4)
c / Å	16.0601(17)	24.406(2)	20.9214(5)
α /deg	78.905(6)	90	90
β /deg	76.782(7)	90	91.624(1)
γ /deg	89.430(7)	90	90
V / $Å^3$	1965.4(4)	4604.7(7)	3545.2(2)
Z	2	4	4
ρ_{calc} / g cm^{-1}	1.743	1.684	1.705
μ (Mo kα) /cm^{-1}	38.40	33.56	40.26
*R*1[a] (*I* > 2.00σ(*I*))	0.032	0.031	0.020
*wR*2[a] (I > 2.00σ(*I*))	0.077	0.071	0.042
Goodness of fit	1.06	1.04	1.03

[a]Function minimized. $\Sigma w(F_o^2-F_c^2)^2$, $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2)/ \Sigma w(F_o^2)^2]^{1/2}$

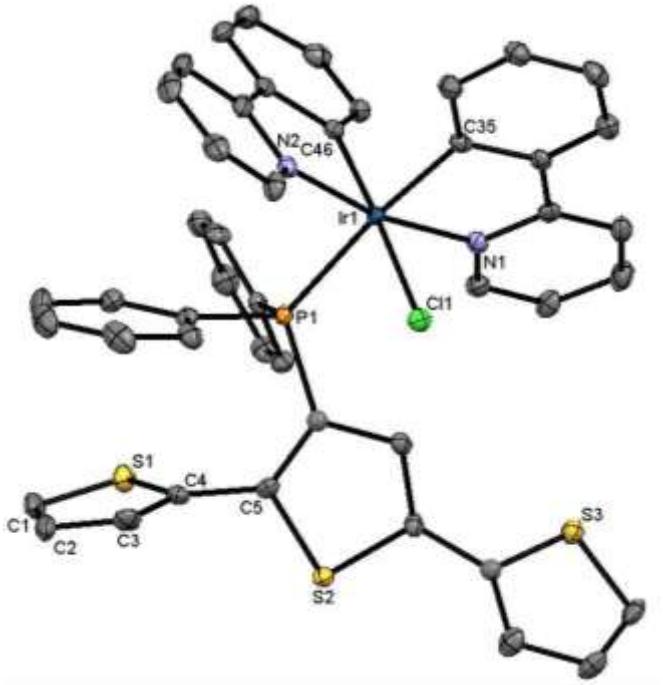

Figure S1. Solid-state structure of Ir(ppy)$_2$PT$_3$Cl-*P*, (**4**). Hydrogen atoms and solvent in lattice are removed for clarity. Thermal ellipsoids drawn at 50% probability.

Table S2. Selected crystallographic data for $Ir(ppy)_2PT_3Cl$-*P* (**4**)

	$Ir(ppy)_2PT_3Cl$-*P*
Formula	$C_{47}H_{35}N_2PS_3IrCl_3$
Crystal Colour, Habit	yellow, irregular
Dimensions / mm	0.04 × 0.06 × 0.16
T / K	90 (1)
Crystal System	monoclinic
Space Group	*P n* (#7)
a / Å	11.420(1)
b / Å	11.204(1)
c / Å	16.843(1)
α /deg	90°
β /deg	106.532(2)
γ /deg	90°
V / $Å^3$	2065.8(3)
Z	2
ρ_{calc} / g cm^{-1}	1.694
μ (Mo kα) /cm^{-1}	36.54
*R*1[a] (*I* > 2.00σ(*I*))	0.036
*wR*2[a] (*I* > 2.00σ(*I*))	0.052
Goodness of fit	0.874

[a]Function minimized. $\Sigma w(F_o^2-F_c^2)^2$, $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2)/ \Sigma w(F_o^2)^2]^{1/2}$

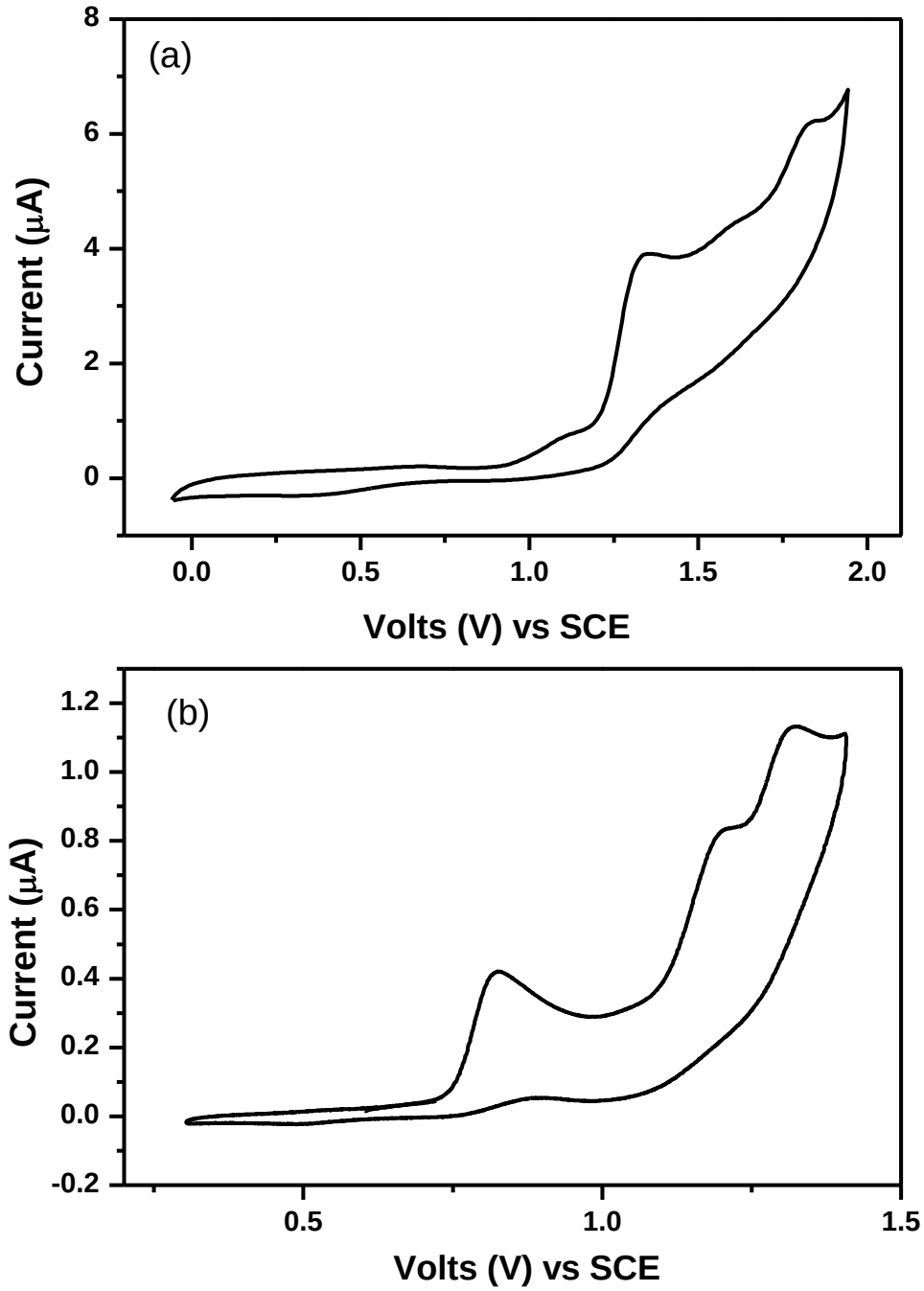

Figure S2. Cyclic voltammetry of (a) [Ir(ppz)$_2$PT$_3$-*P*,*S*](PF$_6$), (**2**), and (b) Ir(ppz)$_2$PT$_3$-*P*,*C*, (**3**), on a Pt disk electrode (scan rate 100 mv/s), electrolyte = 0.1 M [*n*-Bu$_4$N](PF$_6$), solvent = CH$_3$CN.

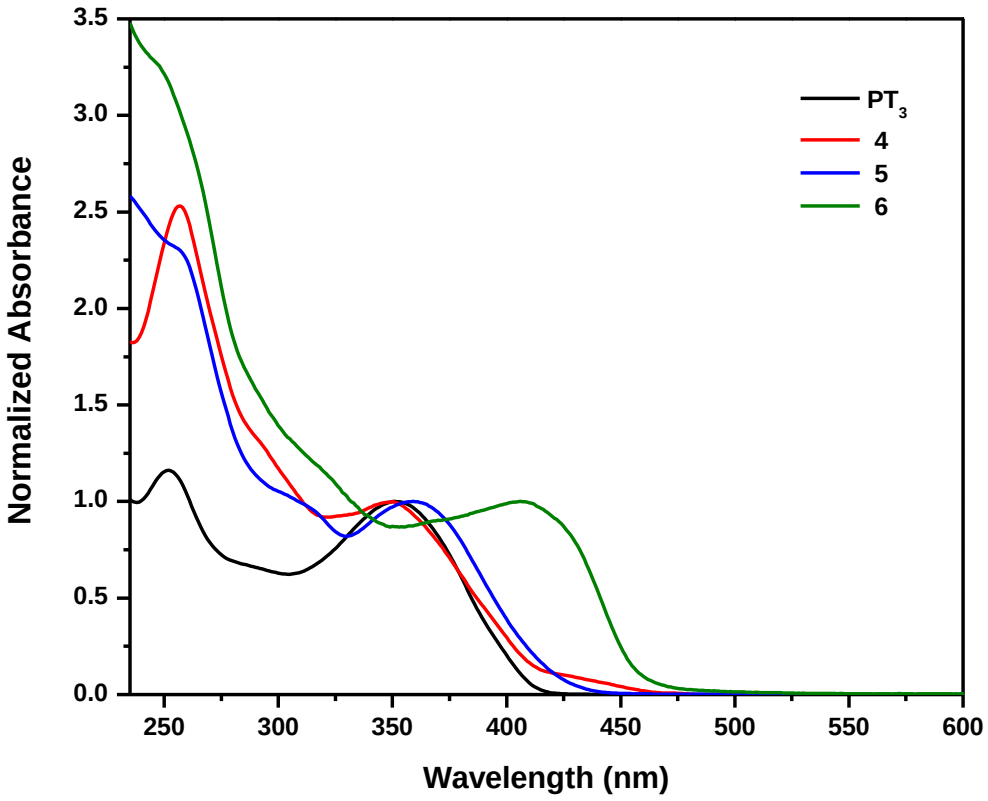

Figure S3. Solution absorption spectra of PT_3, $Ir(ppy)_2PT_3Cl$-*P* (**4**), [$Ir(ppy)_2PT_3$-*P*,*S*](PF_6) (**5**), $Ir(ppy)_2PT_3$-*P*,*C* (**6**) in CH_3CN

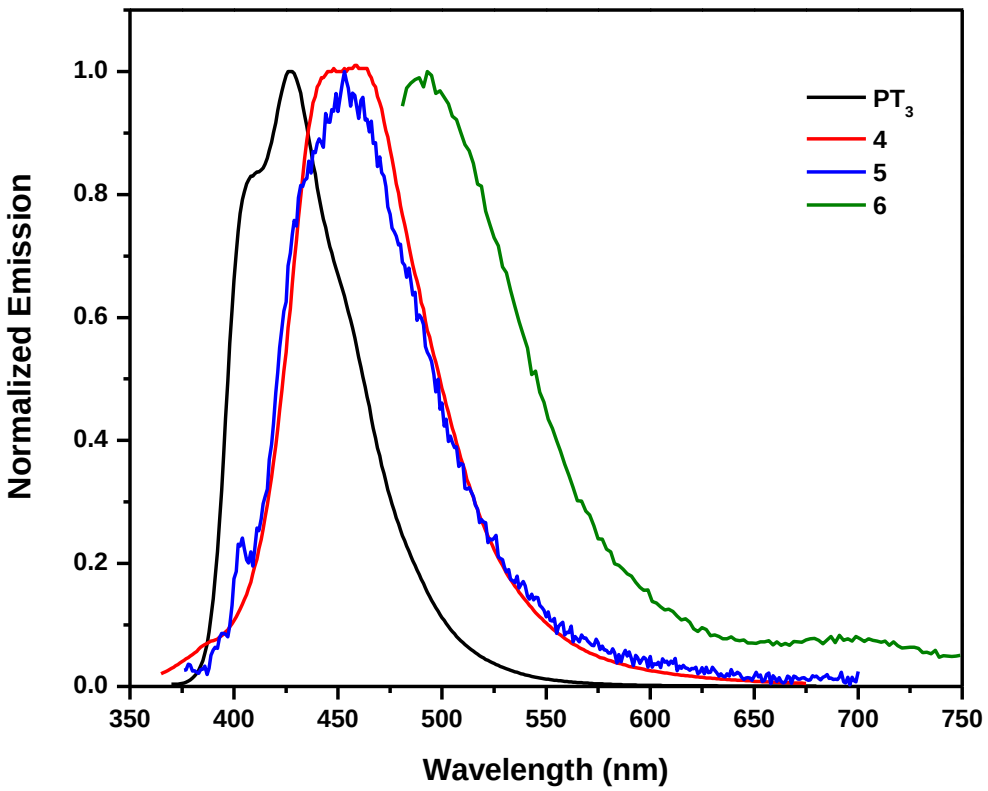

Figure S4. Emission spectra of PT_3 (λ_{ex}= 352 nm), $Ir(ppy)_2PT_3Cl$-*P* (4) (λ_{ex}= 349 nm), $[Ir(ppy)_2PT_3$-*P*,*S*$](PF_6)$ (5) (λ_{ex}= 359 nm), $Ir(ppy)_2PT_3$-*P*,*C* (6) (λ_{ex}= 400 nm) in CH_3CN.

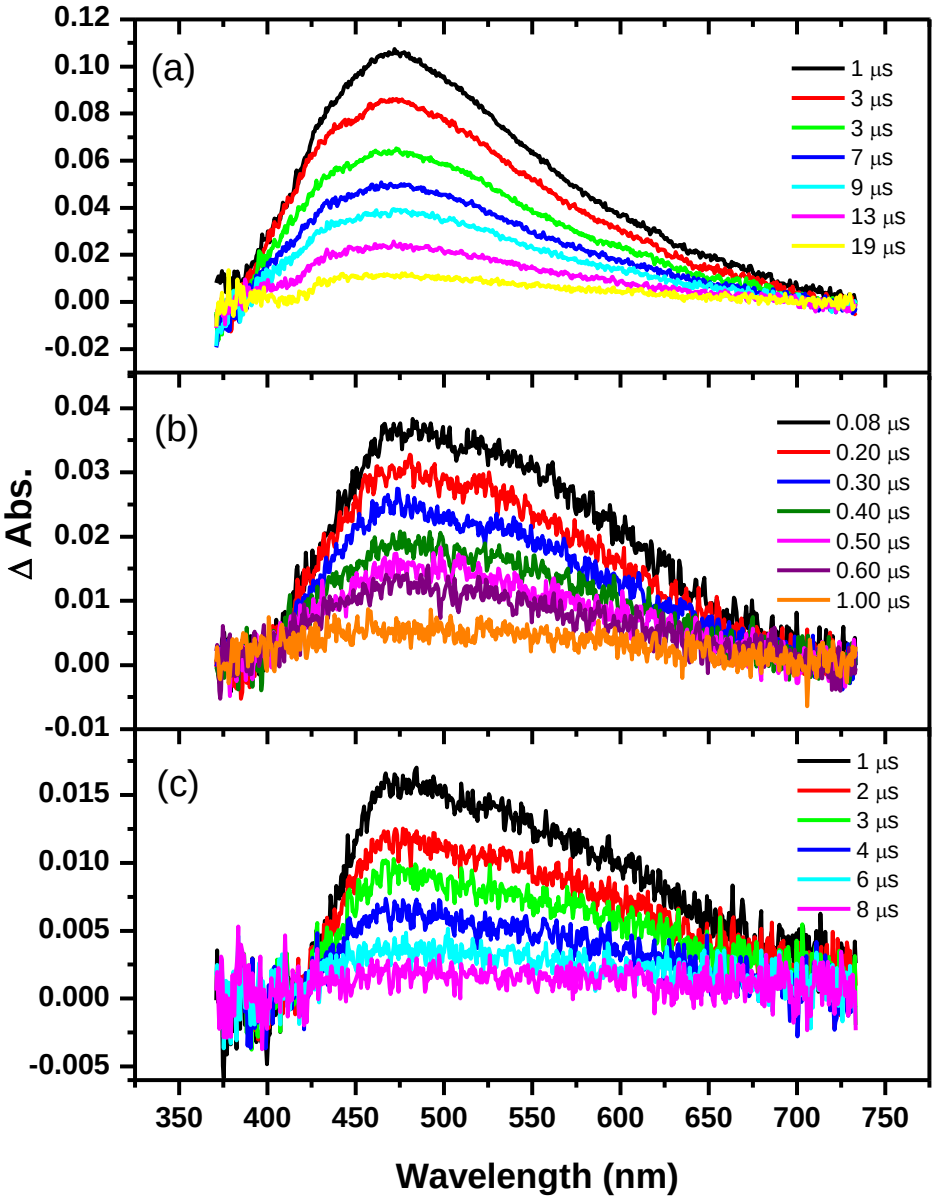

Figure S5. Transient absorption spectra of (a) $Ir(ppy)_2PT_3Cl$-*P*, (**4**), (b) [$Ir(ppy)_2PT_3$-*P*,*S]*(PF_6), (**5**), and (c) $Ir(ppy)_2PT_3$-*P*,*C*, (**6**), in argon-sparged CH_3CN.

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