Supporting Information for

Unprecedented Near-Infrared (NIR) Emission in Diplatinum(III) (d^7-d^7) Complexes at Room Temperature

Martin A. Bennett, Suresh K. Bhargava, Eddie Chung-Chin Cheng, Wai Han Lam, Terence Kwok-Ming Lee, Steven H. Privér, Jörg Wagler, Anthony C. Willis and Vivian Wing-Wah Yam**

School of Applied Sciences (Applied Chemistry), RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia, Research School of Chemistry, Australian National University, Canberra, A.C.T. 0200, Australia, and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China.

Table S1. Selected bond distances (Å) and angles (deg) for two modifications of $[Pt_2(\kappa^2\text{-}C_6H_3\text{-}5\text{-}CHMe_2\text{-}2\text{-}AsPh_2)_2(\mu\text{-}C_6H_3\text{-}5\text{-}CHMe_2\text{-}2\text{-}AsPh_2)_2]\cdot CH_2Cl_2$ (**1b**).

Pt···Pt	3.4298(2)	4.3843(2)
Pt(1)–C(48)	2.027(3)	2.022(3)
Pt(1)–C(6)	2.039(3)	2.050(3)
Pt(2)–C(27)	2.027(3)	2.021(3)
Pt(2)–C(69)	2.034(3)	2.038(3)
Pt–As	2.4236(3)–2.4578(3)	2.4255(3)–2.4695(3)
C(6)–Pt(1)–As(1)	69.71(9)	69.46(8)
As(1)–Pt(1)–As(2)	104.824(10)	108.079(10)
C(69)–Pt(2)–As(4)	69.92(8)	69.37(8)
As(3)–Pt(2)–As(4)	102.786(10)	107.429(10)

Table S2. Selected bond distances (Å) and angles (deg) for complexes $[Pt_2(\mu\text{-}C_6H_3\text{-}5\text{-}CHMe_2\text{-}2\text{-}AsPh_2)_4X_2]\cdot nCH_2Cl_2$, X = Cl, n = 2 (**3b**), X = Br, n = 0 (**4b**), X = I, n = 0 (**5b**).

	3b	**4b**	**5b**
Pt(1)–Pt(2)	2.6896(2)	2.7526(3)	2.7929(7)
Pt(1)–X(1)	2.4519(10)	2.6368(7)	2.8261(11)
Pt(2)–X(2)	2.4687(10)	2.6146(7)	2.8015(11)
Pt(1)–C(112)	2.085(4)	2.111(6)	2.129(13)
Pt(1)–C(212)	2.099(4)	2.107(6)	2.133(13)
Pt(2)–C(312)	2.105(4)	2.113(6)	2.119(13)
Pt(2)–C(412)	2.103(4)	2.101(6)	2.127(13)
Pt–As	2.4617(4)–2.4726(4)	2.4604(7)–2.4858(6)	2.4694(15)–2.4975(15)
X(1)–Pt(1)–Pt(2)	169.13(3)	166.318(17)	165.74(3)
X(2)–Pt(2)–Pt(1)	168.77(3)	165.869(18)	165.31(3)

Table S3. Selected bond distances (Å) and angles (deg) for $[Pt_2(\mu\text{-}C_6H_3\text{-}5\text{-}CHMe_2\text{-}2\text{-}AsPh_2)_4(CN)_2]\cdot CH_2Cl_2$ (**6b**).

Pt(1)–Pt(1)* [a]	2.7823(2)	Pt(2)–Pt(2)* [b]	2.7924(2)
Pt(1)–C(1)	2.068(3)	Pt(2)–C(2)	2.055(3)
Pt(1)–C(212)* [a]	2.108(3)	Pt(1)–C(112)* [a]	2.108(3)
Pt(2)–C(412)* [b]	2.110(3)	Pt(2)–C(312)* [b]	2.104(3)
Pt–As	2.4487(3)–2.4690(3)		
C(1)–N(1)	1.142(4)	C(2)–N(2)	1.151(4)
Pt(1)*–Pt(1)–C(1)	169.09(9)	Pt(2)*–Pt(2)–C(2)	169.54(9)
Pt(1)–C(1)–N(1)	174.7(3)	Pt(2)–C(2)–N(2)	176.6(3)

[a] Symmetry code -*x*+2, -*y*+1, -*z*. [b] Symmetry code -*x*+1, -*y*, -*z*+1.

Table S4. Contribution of the Pt atomic orbitals to the selected molecular orbitals (H = HOMO and L = LUMO) for complexes **3a**–**6a**.

Complex	MOs	Contribution of Pt atomic orbitals (%)[a]		
		s	p_z	dz^2
3a	L	1	3	51
	H–1	4	6	22
4a	L	2	3	48
	H–1	5	10	26
5a	L	5	0	43
	H	2	5	10
6a	L	0	5	41
	H	5	22	29

[a] The Pt–Pt bond is along the z-axis.

Table S5. Selected singlet-singlet transitions in $[Pt_2(\mu\text{-}C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4Cl_2]$ (**3a**) computed by TDDFT, the orbitals involved in the excitations (H = HOMO and L = LUMO) with transition coefficients in parentheses, vertical excitation wavelengths λ (nm), oscillator strengths (*f*), and character of the transitions.

Transition[a]	Excitation[b]	λ (nm)	*f*	Character
$S_0 \rightarrow S_2$	H−1→L (0.56)	445	0.035	MC/XMMCT/LMMCT
$S_0 \rightarrow S_3$	H−2→L (0.65)	435	0.025	LMMCT
$S_0 \rightarrow S_5$	H−18→L (−0.41)	407	0.003	LMMCT/MC/XMMCT
$S_0 \rightarrow S_8$	H−4→L (−0.60)	394	0.016	LMMCT
$S_0 \rightarrow S_{10}$	H−9→L (0.53)	380	0.035	LMMCT/XMMCT
$S_0 \rightarrow S_{13}$	H−14→L (0.52)	358	0.011	LMMCT/XMMCT
$S_0 \rightarrow S_{14}$	H−13→L (0.57)	356	0.024	LMMCT

[a] Only the transitions with $f > 0.001$ are listed. [b] Excitation with the largest absolute value of transition coefficient.

Table S6. Selected singlet-singlet transitions in $[Pt_2(\mu\text{-}C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4Br_2]$ (**4a**) computed by TDDFT, the orbitals involved in the excitations (H = HOMO and L = LUMO) with transition coefficients in parentheses, vertical excitation wavelengths λ (nm), oscillator strengths (*f*), and character of the transitions.

Transition[a]	Excitation[b]	λ (nm)	*f*	Character
$S_0 \rightarrow S_2$	H−1→L (0.46)	463	0.032	XMMCT/MC
$S_0 \rightarrow S_4$	H−2→L (0.65)	447	0.017	LMMCT
$S_0 \rightarrow S_7$	H−6→L (0.46)	415	0.018	XMMCT/LMMCT
$S_0 \rightarrow S_9$	H−4→L (0.47)	405	0.023	LMMCT/XMMCT
$S_0 \rightarrow S_{11}$	H−10→L (0.43)	392	0.037	LMMCT/MC
$S_0 \rightarrow S_{13}$	H−12→L (0.55)	369	0.007	LMMCT
$S_0 \rightarrow S_{15}$	H−15→L (−0.43)	363	0.027	LMMCT

[a] Only the transitions with $f > 0.001$ are listed. [b] Excitation with the largest absolute value of transition coefficient.

Table S7. Selected singlet-singlet transitions in $[Pt_2(\mu\text{-}C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4I_2]$ (**5a**) computed by TDDFT, the orbitals involved in the excitations (H = HOMO and L = LUMO) with transition coefficients in parentheses, vertical excitation wavelengths λ (nm), oscillator strengths (*f*), and character of the transitions.

Transition[a]	Excitation[b]	λ (nm)	*f*	Character
$S_0 \rightarrow S_1$	H→L (0.56)	560	0.002	XMMCT/MC
$S_0 \rightarrow S_2$	H−2→L (0.65)	534	0.003	XMMCT
$S_0 \rightarrow S_3$	H−3→L (0.59)	522	0.004	XMMCT
$S_0 \rightarrow S_4$	H−4→L (0.57)	518	0.003	XMMCT
$S_0 \rightarrow S_5$	H−5→L (0.49)	456	0.086	LMMCT
$S_0 \rightarrow S_6$	H−5→L (0.47)	450	0.083	LMMCT
$S_0 \rightarrow S_7$	H−7→L (0.60)	424	0.018	LMMCT
$S_0 \rightarrow S_8$	H−6→L (0.50)	423	0.087	LMMCT
$S_0 \rightarrow S_9$	H−8→L (0.65)	412	0.016	LMMCT
$S_0 \rightarrow S_{10}$	H−9→L (0.68)	395	0.001	LMMCT
$S_0 \rightarrow S_{11}$	H−12→L (0.52)	392	0.001	LMMCT
$S_0 \rightarrow S_{12}$	H−10→L (0.51)	387	0.056	LMMCT
$S_0 \rightarrow S_{13}$	H−11→L (0.67)	381	0.008	LMMCT
$S_0 \rightarrow S_{14}$	H−13→L (0.53)	370	0.008	LMMCT
$S_0 \rightarrow S_{15}$	H−14→L (0.47)	365	0.023	LMMCT

[a] Only the transitions with $f > 0.001$ are listed. [b] Excitation with the largest absolute value of transition coefficient.

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