

Chemical Communications

Electronic Supplementary Information

for

Duplicating “sunlight” from simple WOLEDs for lighting application

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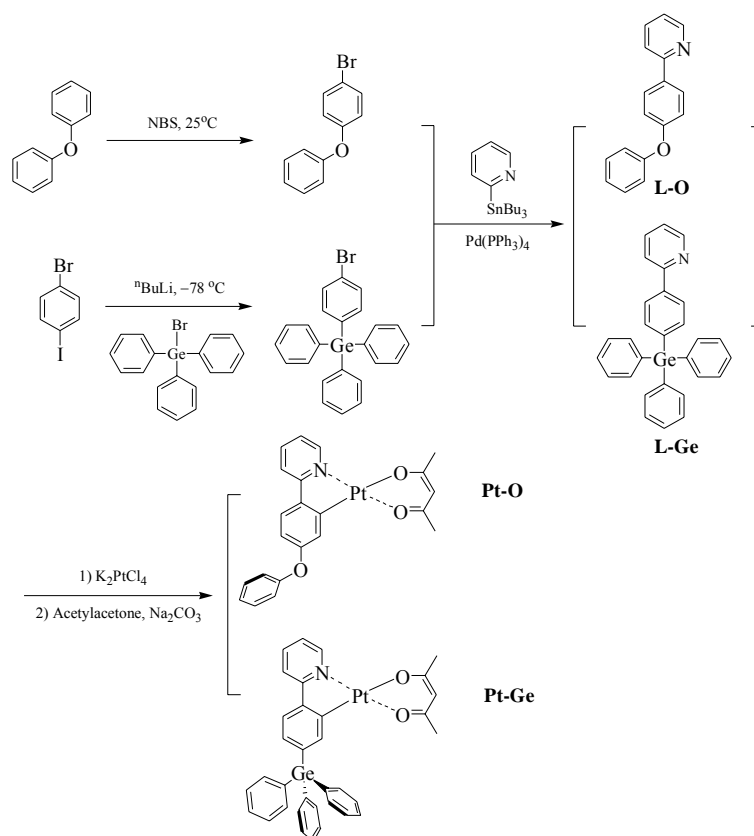
Wang

Experimental

General Information: All reactions were performed under nitrogen atmosphere. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Flash column chromatography and preparative TLC were carried out using silica gel from Merck (230–400 mesh). Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. Proton and ^{13}C - $\{^1\text{H}\}$ NMR spectra were measured in CDCl_3 on a Varian Inova 400 MHz or JEOL GX270 FT-NMR spectrometer; chemical shifts were quoted relative to tetramethylsilane.

Physical Measurements: UV–vis spectra were obtained on a HP-8453 spectrophotometer. The photoluminescent properties and lifetimes of the compounds were probed on the Photon Technology International (PTI) Fluorescence Master Series QM1 system. The phosphorescence quantum yields were determined in CH_2Cl_2 solutions at 293 K against *fac*- $[\text{Ir}(\text{ppy})_3]$ standard ($\Phi_{\text{p}} = 0.40$). Electrochemical measurements were made using a Princeton Applied Research model 273A potentiostat at a scan rate of 100 mV s^{-1} . A conventional three-electrode configuration consisting of a glassy carbon working electrode, a Pt-sheet counter electrode, and a Pt-wire reference electrode was used. The supporting electrolyte was 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc^+) couple. Thermal analyses were performed with the Perkin-Elmer Pyris Diamond DSC and Perkin-Elmer TGA6 thermal analyzers.

Synthesis: The compound 1-bromo-4-phenyloxybenzene^{S1} was prepared following the literature method and the synthesis of other compounds and complexes **Pt-Ge** and **Pt-O** is shown in Scheme S1.



Scheme S1. The synthesis of the main-group element-functionalized platinum(II) complexes.

Synthesis of (4-Bromophenyl)triphenylgermanium. Under a N₂ atmosphere, *n*-butyllithium (1.6 M in hexane) (6.96 mL, 11.13 mmol) was added slowly at -78 °C to a solution of 1-bromo-4-iodobenzene (3.00 g, 10.60 mmol) in dry diethyl ether (50 mL). After the addition, the reaction mixture was kept at -78 °C for 45 min. Then bromotriphenylgermanium (4.07 g, 10.60 mmol) was added to the reaction flask in one portion at the same temperature. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight. Water (40 mL) was added and the mixture was stirred for 45 min. Then the mixture was extracted with CH₂Cl₂

(3 × 60 mL). The combined organic phase was washed with water (3 × 150 mL). The organic phase was separated and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography with hexane/CH₂Cl₂ (12:1, v/v) as the eluent. The product was obtained as white crystals (3.75 g, 77%). ¹H NMR (270 MHz, CDCl₃): δ (ppm) 7.54–7.51 (m, 8H, Ar), 7.43–7.24 (m, 11H, Ar); ¹³C NMR (67.5 MHz, CDCl₃): δ (ppm) 136.82, 135.78, 135.17, 135.04, 131.31, 129.20, 128.28, 123.99 (Ar); FAB-MS (*m/z*): 460 [M]⁺; elemental analysis calcd (%) for C₂₄H₁₉BrGe: C 62.68, H 4.16; found: C 62.55, H 4.20.

Synthesis of L-O. Under an inert atmosphere, 1-bromo-4-phenoxybenzene (0.60 g, 2.41 mmol) and 2-(tributylstannyl)pyridine (0.98 g, 2.65 mmol) were mixed in dry toluene (40 mL). Pd(PPh₃)₄ (139 mg, 0.12 mmol) was added and the reaction was allowed to proceed at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH₂Cl₂ (150 mL) was added. The mixture was washed with water (3 × 100 mL). The organic phase was dried over MgSO₄. The solvent was then removed and the residue was purified by column chromatography eluting with CH₂Cl₂/hexane (4:1, v/v). The title product was obtained as a white solid (0.45 g, 76%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.68–8.67 (m, 1H, Ar), 7.93 (m, 2H, Ar), 7.76–7.68 (m, 2H, Ar), 7.37 (t, *J* = 8.0 Hz, 2H, Ar), 7.22–7.06 (m, 6H, Ar); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.19, 156.78, 149.58, 136.71, 134.36, 129.78, 128.37, 126.86, 123.51, 121.74, 120.07, 119.13, 118.77 (Ar); FAB-MS (*m/z*): 247 [M]⁺; elemental analysis calcd (%) for C₁₇H₁₃NO: C 82.57, H 5.30, N 5.66; found: C 82.44, H 5.19, N 5.70.

Synthesis of L-Ge. Under a N₂ atmosphere, (4-bromophenyl)triphenylgermanium (0.50 g, 1.09 mmol) and 2-(tributylstannyl)pyridine (0.44 g, 1.20 mmol) were added in dry toluene (35 mL) in the presence of Pd(PPh₃)₄ (64 mg, 0.055 mmol). The reaction was allowed to proceed at

110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH₂Cl₂ (150 mL) was added. The mixture was washed with water (3 × 100 mL). The organic phase was dried over MgSO₄. The solvent was then removed and the residue was purified by column chromatography eluting with CH₂Cl₂/hexane (3:1, v/v). The title product was obtained as a white solid (0.40 g, 81%). ¹H NMR (270 MHz, CDCl₃): δ (ppm) 8.70 (d, *J* = 4.6 Hz, 1H, Ar), 8.00 (d, *J* = 7.8 Hz, 2H, Ar), 7.75–7.54 (m, 10H, Ar), 7.45–7.36 (m, 9H, Ar), 7.25–7.20 (m, 1H, Ar); ¹³C NMR (67.5 MHz, CDCl₃): δ (ppm) 157.23, 149.61, 140.02, 136.99, 136.62, 135.84, 135.73, 135.27, 129.05, 128.19, 126.54, 122.14, 120.55 (Ar); FAB-MS (*m/z*): 459 [M]⁺; elemental analysis calcd (%) for C₂₉H₂₃NGe: C 76.04, H 5.06, N 3.06; found: C 75.88, H 5.12, N 2.95.

General Procedure for the Synthesis of Platinum Complexes:^{S2} Under a N₂ atmosphere, each appropriate cyclometalating ligand and 0.8–1.0 equiv of K₂PtCl₄ was heated to 100 °C in a mixture of 2-ethoxyethanol and water (3:1, v/v) for 16 h. Then the reaction mixture was cooled to room temperature and water was added. The cyclometalated Pt(II) μ-chloro-bridged dimer was formed as a precipitate which was collected and dried under vacuum. The dimeric Pt complex, 2.5 equiv of acetylacetonate and 10 equiv of Na₂CO₃ were added to 2-ethoxyethanol and the mixture was heated to 100 °C for 12–15 h. After cooling to room temperature and the addition of water, the colored precipitate was collected by filtration and washed with water and dried. The crude product was chromatographed on a silica column using an appropriate eluent to produce a pure sample of each of the title platinum complexes in ~ 20–30% overall yields after solvent evaporation and drying.

Pt-O: (Yield 33%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.95–8.93 (m, 1H, Ar), 7.77–7.74 (m, 1H, Ar), 7.51 (d, *J* = 8.0 Hz, 1H, Ar), 7.41 (d, *J* = 8.4 Hz, 1H, Ar), 7.37–7.33 (m, 2H,

Ar), 7.24 (d, $J = 2.4$ Hz, 1H, Ar), 7.13–7.05 (m, 4H, Ar), 6.71 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz, 1H, Ar), 5.45 (s, 1H, acac), 2.00 (s, 3H, Me), 1.90 (s, 3H, Me); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 185.75, 184.23 (acac), 167.66, 157.75, 156.98, 147.20, 141.54, 139.73, 138.12, 129.58, 124.53, 123.19, 120.53, 119.91, 119.46, 118.01, 113.66 (Ar), 102.50, 28.21, 26.99 (acac); FAB-MS (m/z): 540 $[\text{M}]^+$; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{Pt}$: C 48.89, H 3.54, N 2.59; found: C 48.95, H 3.77, N 2.36.

Pt-Ge: (Yield 23%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.99–8.97 (m, 1H, Ar), 7.86 (s, 1H, Ar), 7.82–7.78 (m, 1H, Ar), 7.64–7.58 (m, 7H, Ar), 7.44–7.34 (m, 10H, Ar), 7.28 (d, $J = 8.0$ Hz, 1H, Ar), 7.13–7.10 (m, 1H, Ar), 5.40 (s, 1H, acac), 1.97 (s, 3H, Me), 1.75 (s, 3H, Me); FAB-MS (m/z): 752 $[\text{M}]^+$; elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{29}\text{NO}_2\text{GePt}$: C 54.28, H 3.89, N 1.86; found: C 54.19, H 3.99, N 1.97.

X-Ray crystallography: X-Ray diffraction data were collected at 293 K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker Axs SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT^{S3} and an absorption correction (SADABS)^{S4} was applied to the collected reflections. The structure was solved by the Direct methods (SHELXTL)^{S5} in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined anisotropically. The crystallographic data for all the complexes (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre with the deposition numbers CCDC-716163 and -716164. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

OLED Fabrication and Measurements: The pre-cleaned ITO glass substrates were treated with ozone for 20 min. Then, a 40 nm thick NPB film was deposited on the ITO glass substrates. The Pt phosphor and CBP host were co-evaporated to form a 20 nm emitting layer. Successively, BCP, Alq₃, LiF and Al were evaporated at a base pressure of less than 10⁻⁶ Torr. The EL spectra and CIE coordinates were measured with a PR650 Spectra colorimeter. The *L-V-J* curves of the devices were recorded using a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All of the experiments and measurements were carried out at room temperature under ambient conditions.

References:

- S1 (a) K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi, T. Horaguchi, *Chem. Lett.* 2003, **32**, 932; (b) G.-J. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D.-G. Ma, L.-X. Wang, Z.-Y. Lin, T. B. Marder, A. Beeby, *Adv. Funct. Mater.* 2008, **18**, 499.
- S2 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* 2002, **41**, 3055.
- S3 SAINT+, ver. 6.02a, Bruker, Analytical X-ray System, Inc., Madison, WI, 1998.
- S4 G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, 1997.
- S5 G. M. Sheldrick, SHELXTLTM, Reference Manual, ver. 5.1, Madison, WI, 1997.

Table S1 X-ray crystal data for the platinum(II) complexes.

Compound	Pt-O	Pt-Ge
CCDC no.	716163	716164
formula	C ₂₂ H ₁₉ NO ₃ Pt	C ₃₄ H ₂₉ GeNO ₂ Pt
formula weight	540.47	751.26
crystal system	Orthorhombic	Monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> (Å)	12.255(3)	18.798(2)
<i>b</i> (Å)	12.558(3)	13.3210(17)
<i>c</i> (Å)	24.929(6)	11.9372(15)
α (deg)	90	90
β (deg)	90	107.209(2)
γ (deg)	90	90
<i>V</i> (Å ³)	3836.4(15)	2855.4(6)
<i>Z</i>	8	4
<i>D</i> _{calcd} (g cm ⁻³)	1.871	1.748
μ (mm ⁻¹)	7.336	5.978
<i>F</i> (000)	2080	1464
θ range (deg)	2.33–28.27	1.90–28.25
reflections collected	19650	16214
unique reflections	4489	6485
<i>R</i> _{int}	0.0468	0.0492
observed reflections	3547	4409
no. of parameters	244	352
R1, wR2 [<i>I</i> > 2.0 σ (<i>I</i>)] ^[a]	0.0407, 0.1039	0.0360, 0.0711
R1, wR2 (all data)	0.0538, 0.1147	0.0724, 0.0842
GoF on <i>F</i> ² ^[b]	1.052	0.986

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

[b] $GoF = [(\sum w|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

Table S2 Photophysical and thermal data for **Pt-O** and **Pt-Ge**.

Compound	Absorption (298 K) λ_{abs} [nm] ^a	Emission λ_{em} [nm] ^b 293 K/77 K	Φ_{p} ^c	τ_{p} [μs] ^d	$\Delta T_{5\%}/T_{\text{g}}$ [$^{\circ}\text{C}$] ^e	HOMO/LUMO [eV]
Pt-O	237 (4.51), 252 (4.56), 272 (4.51), 279 (4.50), 288 (4.48), 308 (4.33), 357 (3.93), 373 (3.76)	487, 521, 555sh/483, 518, 548	0.42	0.42	305/135	-5.32/-2.29
Pt-Ge	228 (4.39), 259 (4.52), 282 (4.41), 314 (4.06), 327 (4.00), 368 (3.69) 397 (3.52)	493, 528, 563sh/488, 527, 560, 601sh	0.63	0.40	335/183	-5.28/-2.43

^a Measured in CH_2Cl_2 at a concentration of 10^{-5} M and $\log \epsilon$ values are shown in parentheses. ^b sh = shoulder. ^c In degassed CH_2Cl_2 relative to *fac*-[Ir(ppy)₃] ($\Phi_{\text{p}} = 0.40$), $\lambda_{\text{ex}} = 400$ nm. ^d Measured in degassed toluene at a concentration of 10^{-5} M for the sample solution, the excitation wavelength was set at 370 nm for all the samples at 298 K, and the lifetime has been calibrated. ^e $\Delta T_{5\%}$ is the 5% weight-reduction temperature and T_{g} is the glass transition temperature.

Table S3 Key performance parameters of WOLEDs doped with green-emitting Pt^{II} complexes.

Device	Phosphor dopant	$V_{\text{turn-on}}$ [V]	Luminance L [cd m ⁻²]	η_{ext} [%]	η_{L} [cd A ⁻¹]	η_{p} [lm W ⁻¹]	CRI ^d	CIE	CCT [K]
A1	Pt-Ge (4 wt.-%)	4.3	12540 (13.5) ^a	2.64 (5.9)	5.98 (5.9)	3.71 (4.9)	86	(0.347, 0.409)	5104
			1024 ^b	2.27	5.13	1.72			
			3968 ^c	1.75	3.97	1.12			
A2	Pt-Ge (6 wt.-%)	4.5	12350 (13.7) ^a	2.60 (5.7)	6.18 (5.7)	3.64 (5.1)	86	(0.359, 0.424)	4820
			1050 ^b	2.21	5.26	1.77			
			4071 ^c	1.72	4.08	1.16			
A3	Pt-Ge (8 wt.-%)	4.5	17153 (14.3) ^a	4.02 (5.1)	8.49 (5.1)	5.23 (5.1)	90	(0.337, 0.369)	5340
			1258 ^b	2.97	6.29	2.01			
			4921 ^c	2.33	4.92	1.33			
A4	Pt-Ge (10 wt.-%)	4.1	15264 (12.7) ^a	4.13 (4.9)	8.27 (4.9)	5.48 (4.7)	97	(0.354, 0.360)	4719
			1178 ^b	2.95	5.91	2.14			
			4562 ^c	2.28	4.57	1.38			
B1	Pt-O (4 wt.-%)	7.7	3510 (16.7) ^a	1.31 (10.9)	2.58 (10.9)	0.82 (8.3)	71	(0.262, 0.334)	9562
			480 ^b	1.21	2.40	0.63			
			1733 ^c	0.88	1.74	0.38			
B2	Pt-O (6 wt.-%)	4.9	5450 (15.7) ^a	4.14 (4.9)	8.78 (4.9)	5.63 (4.9)	94	(0.320, 0.340)	6066
			836 ^b	1.98	4.19	1.13			
			2937 ^c	1.39	2.94	0.66			
B3	Pt-O (8 wt.-%)	5.7	4512 (15.9) ^a	2.52 (5.9) [a]	5.35 (5.9)	2.93 (5.7)	91	(0.301, 0.336)	7069
			670 ^b	1.58	3.36	0.90			
			2399 ^c	1.13	2.40	0.55			
B4	Pt-O (10 wt.-%)	4.9	7499 (15.9) ^a	5.09 (4.9)	11.42 (4.9)	7.32 (4.9)	90	(0.313, 0.339)	6428
			989 ^b	2.21	4.94	1.37			
			3445 ^c	1.54	3.44	0.80			

^a Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. ^b Values collected at 20 mA m⁻². ^c Values collected at 100 mA m⁻².

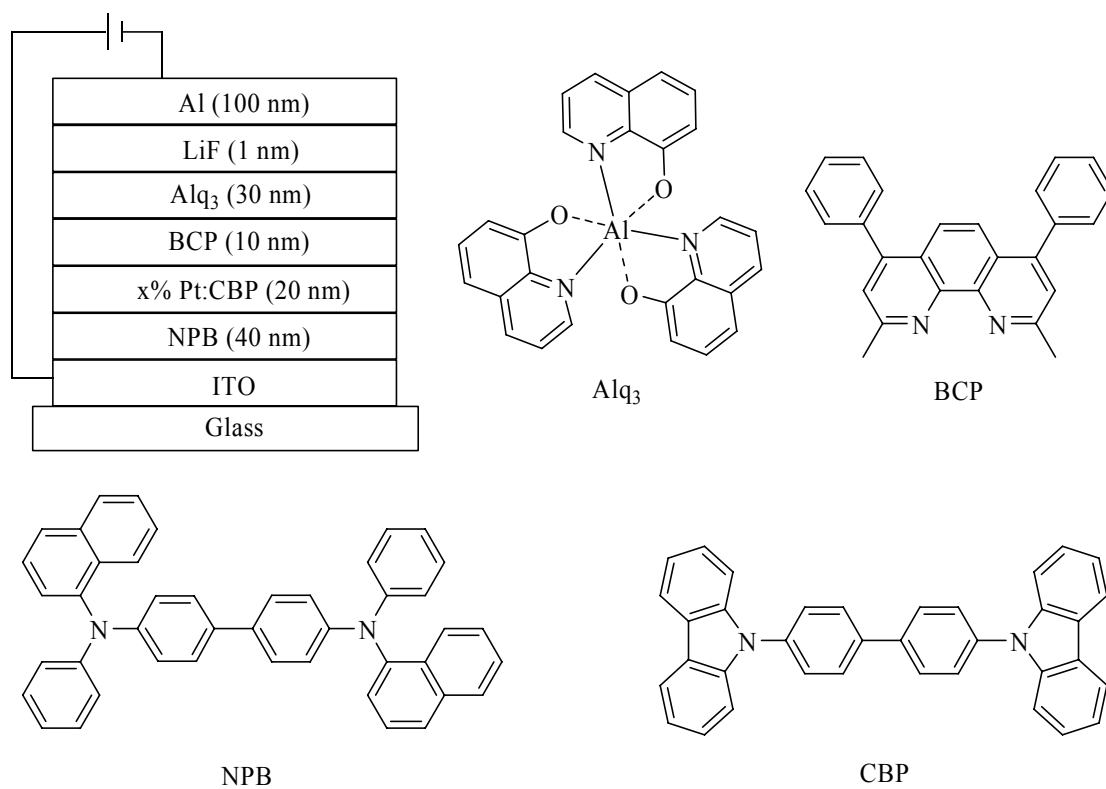
^d CRI describes how well colors will be perceived when illuminated by the light source based on relative quantities of red, green and blue.

Table S4 The dependence of CIE coordinates of the WOLEDs on the driving voltage.

Driving voltage [V]	CIE	
	Device A4	Device B4
9	(0.396, 0.417)	(0.355 0.394)
11	(0.372 0.400)	(0.338 0.374)
13	(0.349 0.374)	(0.325 0.356)
15	(0.354 0.360)	(0.313 0.339)

Table S5 Comparison of the white-light quality from our simple single-dopant WOLEDs with that from typical traditional lighting sources and some state-of-the-art WOLEDs.

Lighting sources and WOLEDs	CIE	CRI	CCT (K)	Ref.
High pressure sodium	(0.591, 0.417)	24	2100	1b
Xenon	(0.324, 0.324)	94	5920	1b
Tungsten halogen (CIE Standard Illuminant A)	(0.448, 0.407)	100	2865	1b
Sunlight (CIE Standard Illuminant D ₆₅)	(0.313, 0.329)	90	6500	1b
Fluorescent, cool white	(0.375, 0.367)	89	4080	1b
Fluorescent, warm white	(0.440, 0.403)	72	2940	1b
Incandescent bulb	(0.448, 0.408)	100	2854	1b
WOLED with triple-doped phosphorescent EML	(0.430, 0.450)	80	-	4b
WOLED with fluorescent/phosphorescent EML	(0.380, 0.400)	85	-	4a
WOLED with multilayer phosphor	(0.350, 0.360)	60	-	4c
WOLED with Pt phosphorescent excimer	(0.340, 0.350)	75	-	7a
WOLED with Pt phosphorescent excimer	(0.360, 0.440)	67	-	7b
WOLED with Pt phosphorescent excimer	(0.400, 0.430)	81	-	7d
Device A3 with Pt-Ge as emitter	(0.337, 0.369)	90	5340	This work
Device A4 with Pt-Ge as emitter	(0.354, 0.360)	97	4719	This work
Device B2 with Pt-O as emitter	(0.320, 0.340)	94	6066	This work
Device B4 with Pt-O as emitter	(0.313, 0.339)	90	6428	This work



Dopant	Devices and doping level
Pt-Ge	A1 (4 wt.-%), A2 (6 wt.-%), A3 (8 wt.-%), A4 (10 wt.-%)
Pt-O	B1 (4 wt.-%), B2 (6 wt.-%), B3 (8 wt.-%), B4 (10 wt.-%)

Fig. S1 The general configuration for WOLEDs and the molecular structures of the relevant compounds used in these devices.

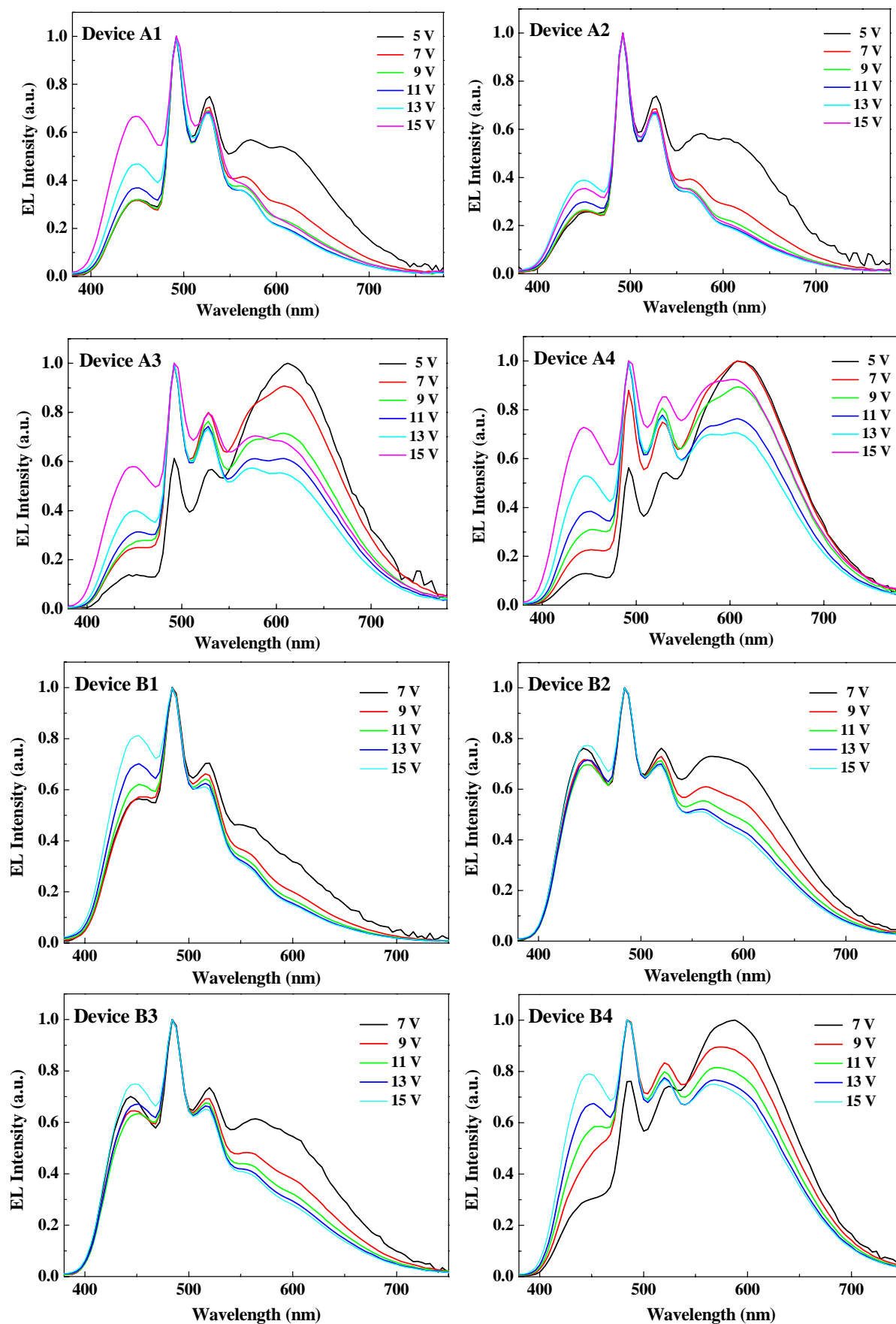


Fig. S2 EL spectra for all the devices at different driving voltages.

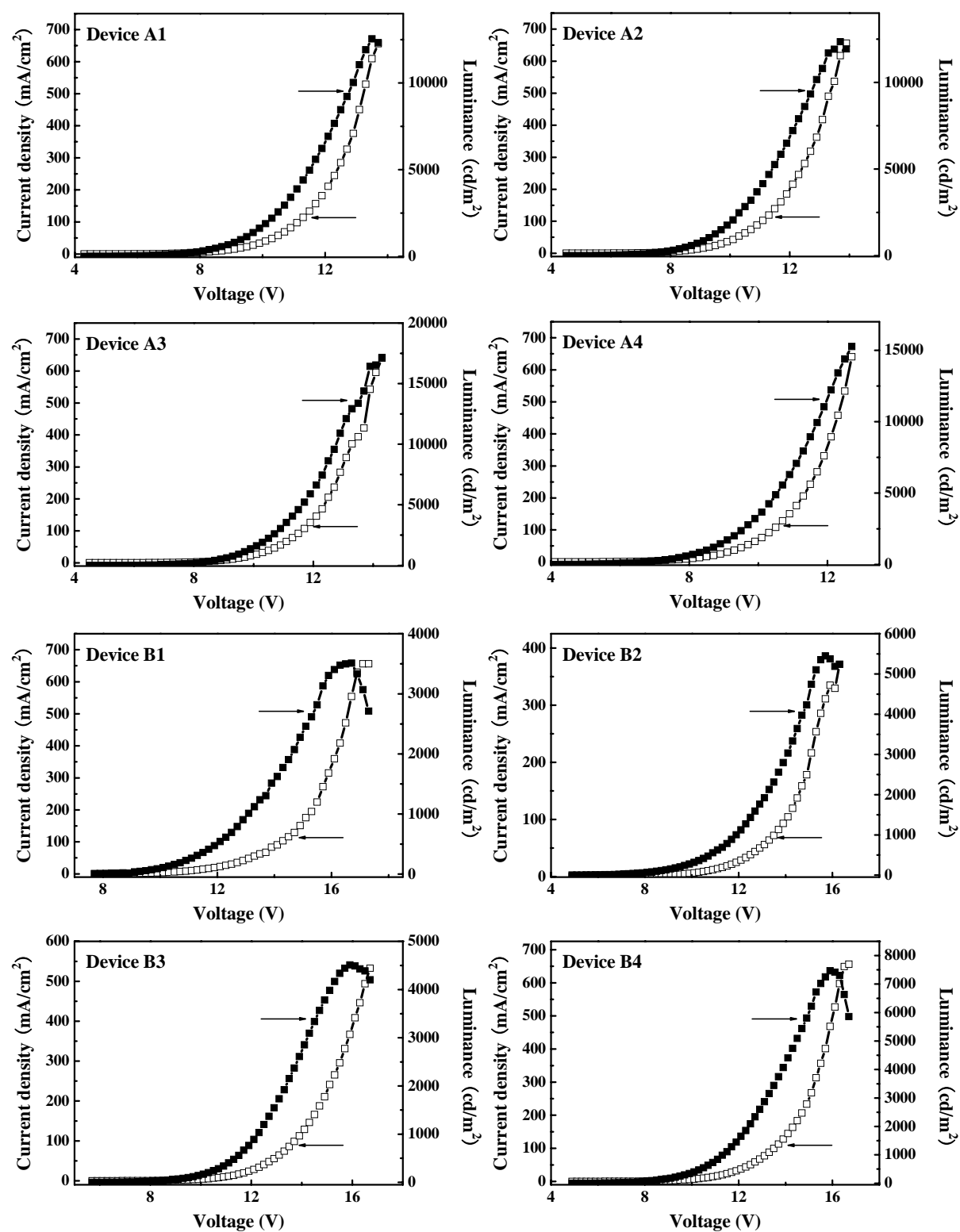


Fig. S3 The current density–voltage–luminance (J – V – L) characteristics for all the devices.

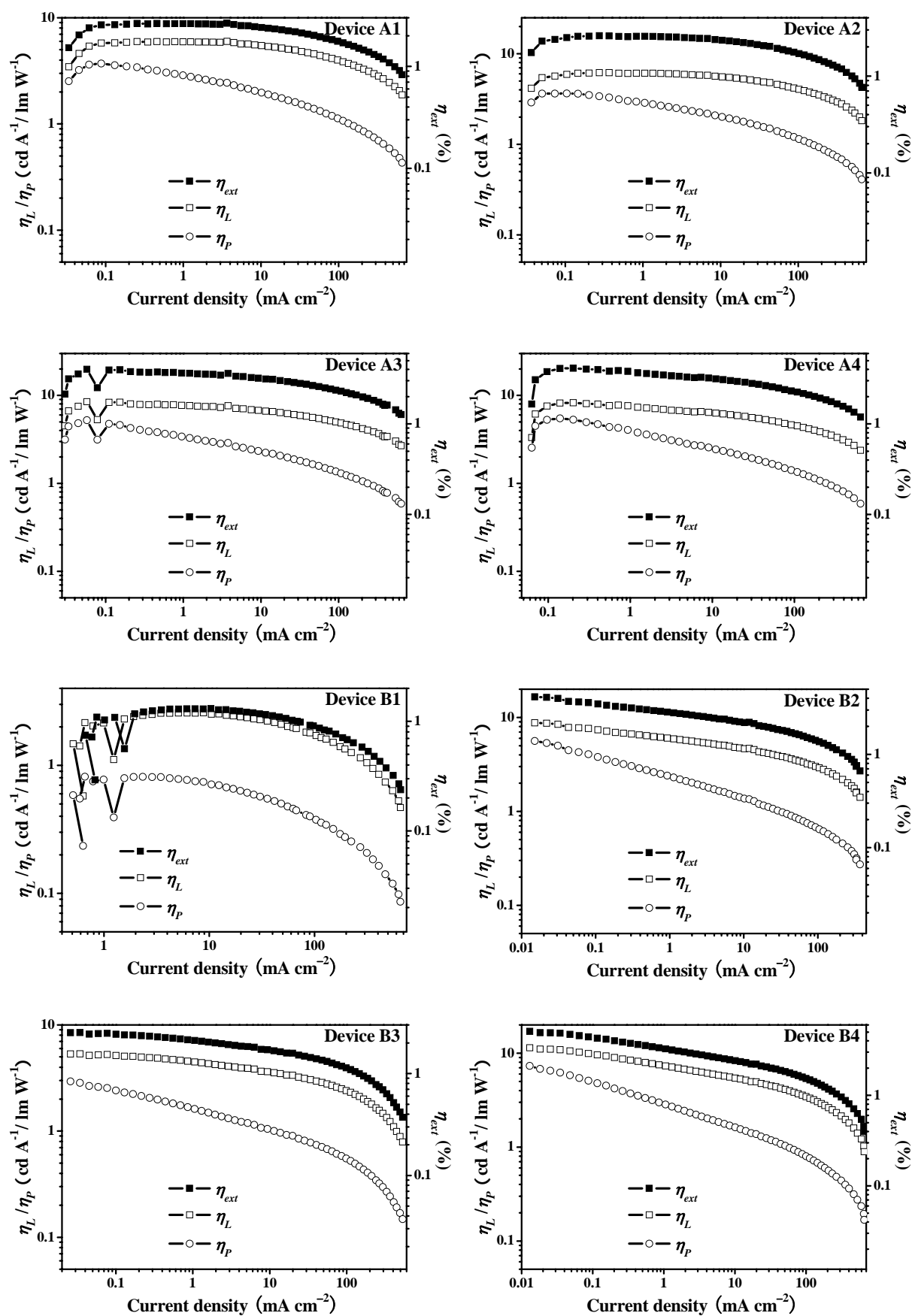


Fig. S4 External quantum efficiency, luminance efficiency and power efficiency as a function of current density for all the devices.



(a)



(b)

Fig. S5 The image of the objects with different perceived colors (blue-green-yellow-red) when illuminated under (a) our **Pt-O** doped WOLEDs and (b) the sunlight, showing an excellent true color reproduction.



Fig. S6 A photograph of a single-dopant WOLED fabricated from **Pt-Ge**.

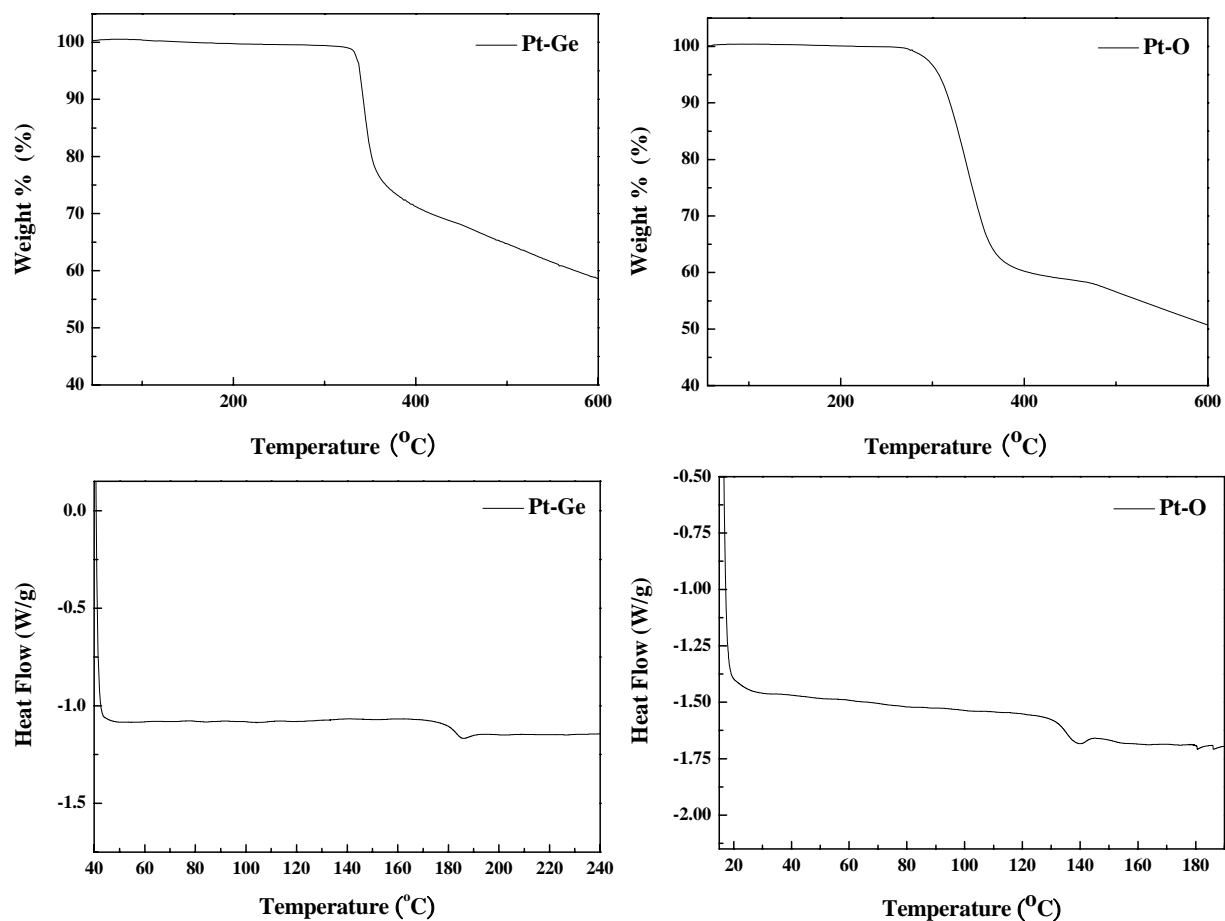


Fig. S7. The TGA and DSC curves for **Pt-Ge** and **Pt-O**.



Fig. S8. The solid-state emission colours of (a) **Pt-Ge** and (b) **Pt-O** upon UV irradiation. In each case, intense green emission was observed on the wall with a low density of the emitter. Near-white light can be observed at the centre of the sample vials where a very high density of the emitter results in an extremely intense light emission.

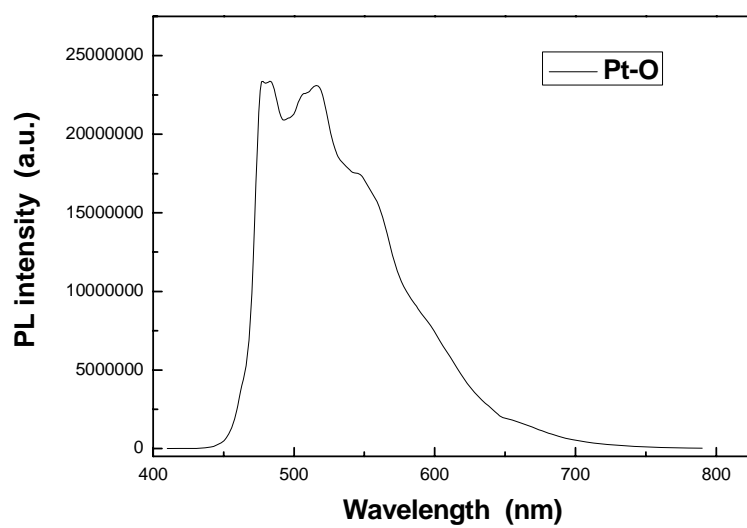
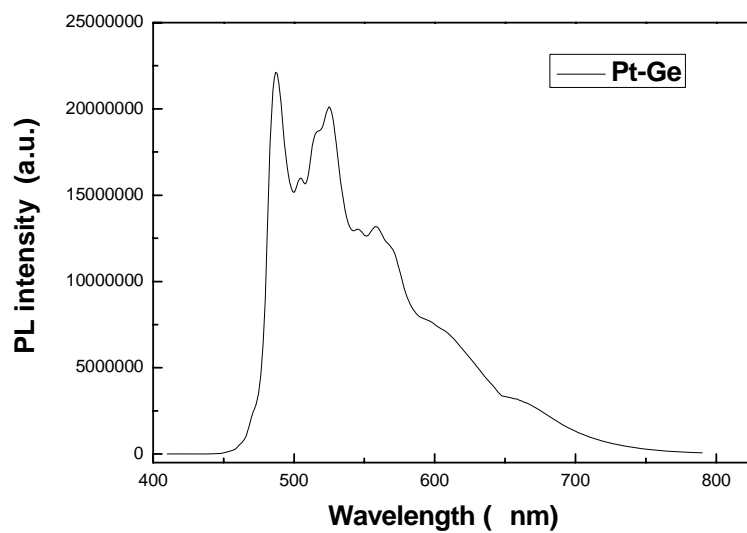


Fig. S9. Solid-state PL spectra of **Pt-Ge** and **Pt-O**.

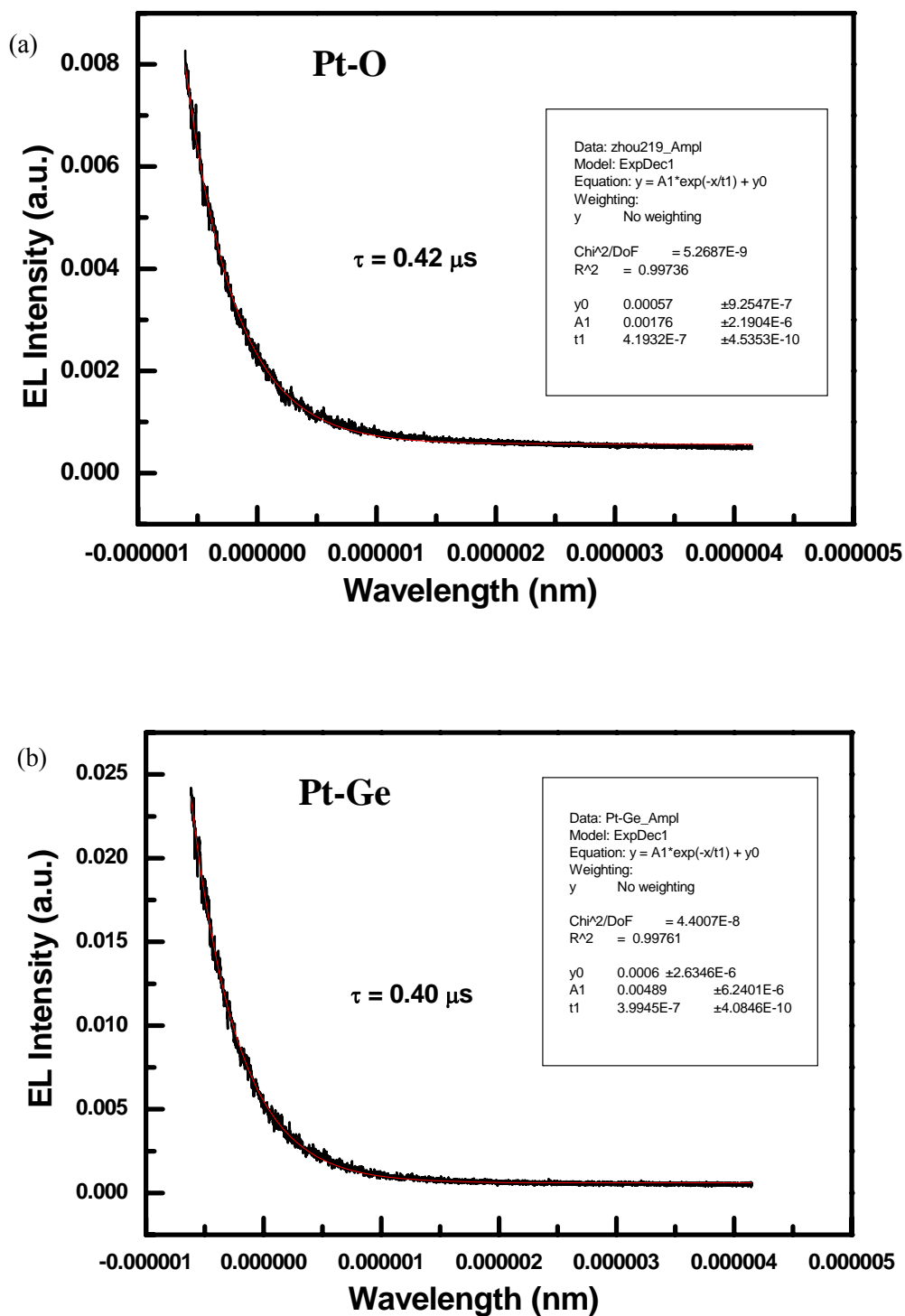


Fig. S10. Phosphorescence decay profiles of (a) Pt-O and (b) Pt-Ge.