# Electronic Supplementary Information for

9-Silafluorene and 9-Germafluorene: Novel Platforms for Highly

Efficient Red Phosphorescent Organic Light-Emitting Diodes

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**Table S1** Molecule optimized structure, FMO distributions and energy levels, and energy band gaps of carbon-, silicon-, and germanium-bridged molecules.

Fig. S1 Cyclic voltammograms of DPS, DPG, and ferrocene (inset).

Fig. S2 EQE–*J* plot, TTA and SPA mode for the red devices.

Fig. S3 <sup>1</sup>H NMR spectrum of 1 (400 MHz, Chloroform-d).

Fig. S4 <sup>1</sup>H NMR spectrum of 2 (400 MHz, Chloroform-*d*).

Fig. S5  $^{1}$ H NMR spectrum of 3 (400 MHz, Chloroform-*d*).

**Fig. S6** <sup>1</sup>H NMR spectrum of **DPS** (400 MHz, Chloroform-*d*).

Fig. S7 <sup>13</sup>C NMR spectrum of DPS (151 MHz, Chloroform-*d*).

Fig. S8 <sup>1</sup>H NMR spectrum of DPG (600 MHz, Chloroform-*d*).

Fig. S9 <sup>1</sup>H NMR spectrum of DPG (151 MHz, Chloroform-*d*).

#### **General Information**

All chemicals and reagents were used as received from commercial sources without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in chloroform-d (CDCl<sub>3</sub>) on a Bruker 400 and Agilent DD2-600 MHz NMR spectrometer at room temperature. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a BRUKER ultrafleXtreme MALDI-TOF/TOF. UV-vis absorption spectra were recorded on Cary 60 spectrometer (Agilent Technologies). PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. The glass transition temperatures  $(T_g)$  were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature  $(T_d)$ . Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc<sup>+</sup>/Fc) as the internal standard. The oxidative scans were performed using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> (TBAPF<sub>6</sub>) in deaerated DMF as the supporting electrolyte. A conventional three-electrode configuration consisting of a Pt-wire counter electrode, an Ag/AgCl reference electrode, and a platinum working electrode was used. The cyclic voltammograms were measured at a scan rate of 100 mV s<sup>-1</sup>. DFT calculations were performed using B3LYP/6-31 G(d) basis set using Gaussian 09.

### **Device Fabrication and Characterization**

The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, with the ITO conductive layer having a thickness of ca. 100 nm and a sheet resistance of ca. 30  $\Omega$  per-square. The active area of each device is 0.09 cm<sup>2</sup>. The ITO glasses were ultrasonically cleaned by ethanol, acetone and deionized water for 10 min subsequently, and then exposed to UV-ozone for 15 min. All of the organic materials and metal layers under a vacuum of ca. 10<sup>-6</sup> Torr. The deposition rate was

controlled at 2 Å s<sup>-1</sup> for HAT-CN, 0.2-0.4 Å s<sup>-1</sup> for Liq, 1-2 Å s<sup>-1</sup> for other organic layers and 5-8 Å s<sup>-1</sup> for Al anode. The EL spectra, CIE coordinates, *J*-V-*L* curves, CE, and PE of the devices were measured with a programmable spectra scan photometer (PHOTO RESEARCH, PR 655) and a constant current source meter (KEITHLEY 2400) at room temperature.

Molecule	Structure	FMO distribution and energy level			$\mathbf{E}_{(\mathbf{a}\mathbf{V})}$
		НОМО	LUMO	HOMO/LUMO (eV)	$L_{g}(\mathbf{ev})$
С	and a			-4.94/-1.39	3.55
Si	Sale of the second seco			-4.92/-1.57	3.35
Ge	and and a			-4.91/-1.52	3.39

Table S1. Molecule optimized structure, FMO distributions and energy levels, and energy band gaps of carbon-, silicon-, and germanium-bridged molecules.



Fig. S1 Cyclic voltammograms of DPS, DPG, and ferrocene (inset).

Triplet-triplet annihilation (TTA) mode (Equation  $\mathbf{S1}$ )<sup>S1</sup>

$$\eta_{EQE}^{TTA}(J) = \frac{J_0}{4J} \times \left(\sqrt{\left(1 + 8\frac{J}{J_0}\right)} - 1\right) \times \eta_{EQE}^0 \qquad S1$$

 $\eta_{EQE}^{0}$ : the quantum efficiency without TTA, approximated as the maximum EQE;  $J_{0}$ : the current density when EQE is a half of the maximum value.

Singlet-polaron annihilation (SPA) mode (Equation S2)<sup>S2</sup>

$$\eta_{EQE}^{SPA}(J) = \frac{1}{1 + \left(\frac{J}{J_0}\right)^{\frac{1}{1+l}}} \times \eta_{EQE}^0 \qquad S2$$

 $\eta^0_{EQE}$ : the quantum efficiency without SPA, approximated as the maximum EQE;  $J_0$ : the current density when EQE is a half of the maximum value. *l*: the fitting parameter.



Fig. S2 EQE–J plot, TTA and SPA modes for the red devices.

## Reference

- S1 M. A. Baldo, C. Adachi and S. R. Forrest, Phys. Rev. B, 2000, 62, 10967.
- S2 Y.-K. Wang, S.-H. Li, S.-F. Wu, C.-C. Huang, S. Kumar, Z.-Q. Jiang, M.-K. Fung
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8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.

Fig. S3 <sup>1</sup>H NMR spectrum of **1** (400 MHz, Chloroform-*d*).





Fig. S4 <sup>1</sup>H NMR spectrum of **2** (400 MHz, Chloroform-*d*).







Fig. S6 <sup>1</sup>H NMR spectrum of **DPS** (400 MHz, Chloroform-*d*).



Fig. S8 <sup>1</sup>H NMR spectrum of **DPG** (600 MHz, Chloroform-*d*).



Fig. S9 <sup>1</sup>H NMR spectrum of **DPG** (151 MHz, Chloroform-*d*).