Supporting Information

Optoelectronic Properties of High Triplet $\sigma$–$\pi$-Conjugated Poly[(biphenyl group IV-A-atom (C, Si, Ge, Sn)) Backbones

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S2. Materials and Methods
S1. Measurements and Physical Properties

A. General measurement and characterization

$^1$H NMR spectra were recorded using VARIAN UNITYINOVA 500 NMR. Ultraviolet-visible (UV-Vis) spectra and photoluminescent (PL), photoexcitation (PLE) and electroluminescence (EL) spectra were measured using an UV-Vis spectrometer (Perkin-Elmer, Lambda 35) and a fluorescence spectrometer (Jobin Yvon Horiba, Fluoromax-3), respectively. The thicknesses of solid films were measured by a Tencor P-10 Surface Profiler. Gel permeation chromatography (from Waters) assembled with a UV detector and three columns in series (StyrAgel HR2~4 from Waters) was used to measure molecular weight distributions relative to polystyrene standards at 40 °C.

B. Phosphorescence measurement

The triplet energies of the polymers are determined by taking the onset values of the phosphorescence spectra from their solid films by using delayed phosphorescence measurement.$^1$ The solid film samples were dropped cast from the solutions of P(dBPh-C), P(dBPh-Si), P(dBPh-Ge) and P(dBPh-Sn) in chlorobenzene (10mg/ml), and attached to the plain sample holder in a nitrogen cryostat (JANIS ST-100 Optical Cryostat). The samples were excited at 300nm by 150 fs pulsed Ti:sapphire laser (Spectra-Physics Hurricane) at 10 Hz repetition rate in conjunction with an ultrafast optical parametric amplifier (Quantronix TOPAS). The luminescence from the solution was allowed to pass through a monochromator (Princeton Instruments Acton SpectraPro 2300i) and then to a gated intensified CCD camera (Princeton Instruments PIMAX). The detection window of 20 ms width of the intensified CCD was operated synchronously but delayed by 1 ms with respect to the laser pulse. To increase the signal to noise ratio, each final spectrum was obtained by averaging the accumulated spectra obtained from 100 pulses. The laser intensity was about 7 μJ/pulse. All measurements were carried out in a cryostat at 77 K and under a dynamic vacuum of 10$^{-5}$ Torr.
C. Electrochemical Study

All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of the polymer film on platinum (Pt) plate as working electrode, Pt plate as counter electrode, and a nan-aqueous Ag/AgNO$_3$ (0.01 M in acetonitrile) as reference electrode. In all experiment, the 0.1M $n$-Bu$_4$NPF$_6$ in acetonitrile used as the supporting electrolyte and the ferrocene/ferrocenium (Fc/Fc$^+$) couple served as internal standard, and the cyclic voltammogram (CV) were observed at scan rates of 25, 50 and 100 mV/s, respectively. According to Leeuw et al,$^2$ the ionization potential ($E_{\text{HOMO}}$) of a polymer is approximately equal to the onset oxidation potential relative to that of Fc$^+$/Fc plus 4.8 eV (the Fc$^+$/Fc energy level below the vacuum level), which means that $E_{\text{HOMO}}$ can be calculated using $E_{\text{HOMO}}$ [eV] = $E_{\text{onset}}$ + 4.8 eV. The energy level of LUMO was deduced from the onset of UV-vis spectrum (band gap) and that of HOMO, which means that $E_{\text{LUMO}}$ [eV] = $E_{\text{HOMO}}$ + band gap.

D. Exciton lifetime measurement

All measurements were carried out in a cryostat at room temperature and under a dynamic vacuum of $10^{-6}$ Torr. The solid film samples with or without 12wt% FIrpic doped in polymer were excited at 350 nm using a 150 fs pulsed Ti:sapphire laser (Spectra-Physics Hurricane) as the light source at repetition rate of 1kHz. The lifetime was measured using a 1024-channel time-correlated single photon counting (TCSPC) system with a microchannel plate photomultiplier tube (Hamamatsu Photonics R3809U-50) and a spectrometer (Edinburgh, Lifespec-ps with TCC900 data acquisition card). Time-to-amplitude converter (TAC) range is 5μs for 12wt% FIrpic doped in the polymer films. Monitored wavelengths were at the emission maxima for the polymer films and at 470 nm for 12wt% FIrpic doped in the polymer films. The predetermined number of counts for each collection of emission lifetime was set for 5000 counts and emission lifetimes were obtained by exponential tail fit of the emission decay curves.
E. Device fabrication

An indium tin oxide (ITO) glass substrate was exposed to oxygen plasma at a power of 50 W and a pressure of 200 mTorr for 5 min. A thin layer (30 nm) of poly(styrenesulfonic acid)-doped poly(ethylenedioxythiophene)—the mixture of CLEVIOS™ P VP Al 4083 and CLEVIOS™ P VP CH 8000 (2:1 in volume ratio), was spin-coated on the treated ITO as a hole injection layer. All the polymers with 12wt% FIrpic or 8wt% DMAC-TRZ as the sky-blue emission dopant were dissolved in chlorobenzene (10 mg/ml) to obtain the emitting layer (EML) solutions, and then spin-coated on top of the PEDOT:PSS layer (30nm). The 1,3,5-Tri(diphenylphosphoryl-phen-3-yl) benzene (TP3PO) layer (3 nm) and 1,3,5-Tri(m-pyridin-3-ylphenyl)benzene (TmPyPB) layer (52 nm) were used as a high triplet exciton blocker and a hole blocking/electron transport layer, respectively, which were deposited on top of the EML layer by thermal evaporation in a vacuum of $2 \times 10^{-6}$ Torr. Finally, a thin layer of CsF (about 1 nm) covered with aluminum (100 nm) was deposited in a vacuum thermal evaporator through a shadow mask at a vacuum of $2 \times 10^{-6}$ Torr. The active area of device was about 4 mm$^2$. I–V characteristics of the devices were measured using a KEITHLEY-238 source meter and brightness measured with a TOPCON BM-8 luminance meter.
F. Physical and optoelectronic characteristics for the polymers with different central atoms

1. Density functional theory (DFT) calculation

(a) $X = C, Si, Ge,$ and $Sn$

(b) $d(\text{MeOPh-C})$

- HOMO: 5.40 eV
- LUMO: 0.77 eV

(c) $d(\text{MeOPh-Si})$

- HOMO: 5.54 eV
- LUMO: 0.99 eV

(d) $d(\text{MeOPh-Ge})$

- HOMO: 5.53 eV
- LUMO: 0.91 eV

(e) $d(\text{MeOPh-Sn})$

- HOMO: 5.55 eV
- LUMO: 0.93 eV
**Figure S1.** Calculated spatial distributions of HOMO and LUMO for the analogs of polymer backbones. All these repeat unit structures were optimized by the DFT/B3LYP level with the 6-31G (d,p) basis set, only the Sn-based repeat unit with the LANL08d basis set.

**Figure S2.** DFT calculation for the unit structure dBu-Ge, which was optimized by the DFT/B3LYP level with the 6-31G (d,p) basis set.

2. **Photophysical properties**

**Figure S3.** a) UV-vis absorption spectra of P(dBPh-Sn) in diluted solution (1x10^{-5} M in CHCl3) and in film, and b) PLE spectra of P(dBPh-Sn) film.
3. Transient photoluminescence

The parameters were obtained by exponentially fitting the decay curves in Figure 4b with the following equation:

\[ I_{PL}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad \text{(Equation 1)} \]

Where \( I_{PL} \) is the photoluminescence intensity, \( A_1 \) and \( A_2 \) are the quantities of emission components, \( t \) is decay time, and \( \tau_1 \) and \( \tau_2 \) are the lifetimes of the corresponding emission components.

**Table S1.** Fitting parameters of the exciton lifetimes for 12wt\% FIrpic doped in the polymers and PS.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \tau_1 )</th>
<th>( A_1/(A_1+A_2) )</th>
<th>( \tau_2 )</th>
<th>( A_2/(A_1+A_2) )</th>
<th>( \langle \tau \rangle^a )</th>
<th>( \chi^2 ) ( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dBPh-C) + 12wt% FIrpic</td>
<td>155</td>
<td>26.79</td>
<td>735</td>
<td>73.21</td>
<td>580</td>
<td>1.46</td>
</tr>
<tr>
<td>(dBPh-Si) + 12wt% FIrpic</td>
<td>130</td>
<td>14.03</td>
<td>951</td>
<td>85.97</td>
<td>836</td>
<td>1.35</td>
</tr>
<tr>
<td>(dBPh-Ge) +12wt% FIrpic</td>
<td>217</td>
<td>15.71</td>
<td>1017</td>
<td>84.29</td>
<td>891</td>
<td>1.29</td>
</tr>
<tr>
<td>(dBPh-Sn) +12wt% FIrpic</td>
<td>112</td>
<td>46.90</td>
<td>679</td>
<td>53.10</td>
<td>413</td>
<td>1.49</td>
</tr>
<tr>
<td>Polystyrene (PS) + 12wt% FIrpic</td>
<td>270</td>
<td>17.86</td>
<td>1030</td>
<td>82.14</td>
<td>894</td>
<td>1.19</td>
</tr>
</tbody>
</table>

\(^a\) Averaged lifetime that was calculated as \( \langle \tau \rangle = \sum a_i \tau_i \), where \( \tau_i \) and \( a_i \) are the exciton lifetime and their fractions of \( A_1 \) and \( A_2 \), respectively. \(^b\) Chi-spaure value for exponentially fitting of the decay curve.
4. Single carrier devices

The hole-only (ITO/PEDOT:PSS/polymer (80nm)/MoO$_3$ (10nm)/Al) and electron-only (glass/Al (60nm)/Ca (20nm)/polymer (80nm)/CsF (1nm)/Al) devices were measured for their current density versus applied voltage as shown in Figure S4. By applying the space-charge limited current (SCLC) equation, \( J = \frac{9}{8} \epsilon \epsilon_0 \mu V^2 d^{-3} \) (where \( J \) is the current density, \( V \) the applied voltage, \( \mu \) the carrier, \( \epsilon \) the relative vacuum permittivity (about 3 for organic materials), and \( \epsilon_0 \) the vacuum permittivity), the hole and electron mobilities were determined.\(^4\)

![Figure S4. Single carrier devices for (a) hole-only device: ITO/PEDOT:PSS/polymer/MoO$_3$/Al and (b) electron-only device: glass/Al/Ca/polymer/CsF/Al.](image-url)
- The reported data of high performance blue Ph-OLEDs with the difference in $E_T$ of host to guest

**Table S2** Relationship between device performance and difference in $E_T$ of host and guest for the high performance blue Ph-OLEDs

<table>
<thead>
<tr>
<th>Host (Triplet energy)</th>
<th>Emitter (Triplet energy)</th>
<th>$E_{T, \text{host}}-E_{T, \text{guest}}$</th>
<th>Device performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mCP:B3PYMPM exciplex ($E_T=2.68$ eV)</td>
<td>FIrpic ($E_T=2.62$ eV)</td>
<td>0.06 eV</td>
<td>CE$<em>{\text{max}}=62.2$ cd/A EQE$</em>{\text{max}}=29.5%$</td>
<td>[5]</td>
</tr>
<tr>
<td>mCP:PO-T2T Exciplex ($E_T=2.64$ eV)</td>
<td>FIrpic ($E_T=2.63$ eV)</td>
<td>0.01 eV</td>
<td>PE$<em>{\text{max}}=66.0$ lm/W EQE$</em>{\text{max}}=30.3%$</td>
<td>[6]</td>
</tr>
<tr>
<td>mCBP:PO-T2T exciplex ($E_T=2.63$ eV)</td>
<td>FIrpic ($E_T=2.62$ eV)</td>
<td>0.01 eV</td>
<td>PE$<em>{\text{max}}=79.6$ lm/W EQE$</em>{\text{max}}=34.1%$</td>
<td>[7]</td>
</tr>
<tr>
<td>2,6-DCzPPy ($E_T=2.71$ eV)</td>
<td>Fac-Ir(mpim)$_3$ ($E_T=2.62$ eV)</td>
<td>0.09 eV</td>
<td>CE$<em>{100}=80.1$ cd/A PE$</em>{100}=86.0$ lm/W EQE$_{100}=32.5%$</td>
<td>[8]</td>
</tr>
<tr>
<td>CzBPCb ($E_T=2.75$ eV)</td>
<td>FIrpic ($E_T=2.65$ eV)</td>
<td>0.10 eV</td>
<td>CE$<em>{100}=53.6$ cd/A PE$</em>{100}=50.6$ lm/W EQE$_{100}=30.1%$</td>
<td>[9]</td>
</tr>
</tbody>
</table>
S2. Materials and Methods

**Scheme S1.** Synthetic route for compound 2, 3, 4, 5

**Tetraphenylmethane (1).**

A mixture of triphenylmethyl chloride (19.5 g, 70 mmol) and aniline (19.6 g, 210 mmol) was heated at 220°C for 5 min and then cooled to 90°C. Treated with 2N HCl (110 ml) and methanol (100 ml), and the resulting mixture refluxed for 1h. The reaction mixture was cooled to room temperature and filtered to get a gray solid, which was then dissolved in a mixture of ethanol (140 ml) and concentrated H_2SO_4 (22 ml). The resulting mixture was cooled to -10°C, stirred, and isopentynitrile (14 ml, 105 mmol) was added dropwise into the reaction. The mixture was then stirred for 1h, treated with 50% hypophosphorous acid (50 ml), and heated to reflux for 1h. The reaction mixture was cooled to room temperature and then filtered to provide an olive solid, which was washed with ethanol and dried in vacuum to afford compound 2 (16.0 g, 71%) as a pale colored solid. ^1^HNMR (500 MHz, CDCl_3). δ (ppm): 7.09-7.03 (m, 20H).

**Tetra(p-bromophenyl)methane (2).**

It was prepared according to the procedure reported in the literature. For compound 2: A pale brown solid (7.94 g, 42%). ^1^HNMR (500 MHz, CDCl_3). δ (ppm): 7.38 (d, J= 8.5 Hz, 8H), 6.98 (d, J= 8.5 Hz, 8H).

**Tetra(p-bromophenyl)silane (3).**

It was prepared according to the procedure reported in the literature. For compound 3: A white solid (18.3 g, 65.0%). ^1^HNMR (500 MHz, CDCl_3). δ (ppm): 7.52 (d, J= 7.5 Hz, 8H), 7.32 (d, J= 7.5 Hz, 8H).

**Tetra(p-bromophenyl)germane (4).**
It was prepared according to the same procedure for compound 3. For compound 4: A white solid (10.5 g, 42 %). $^1$HNMR (500 MHz, CDCl$_3$). $\delta$ (ppm): 7.51 (d, J= 8.5 Hz, 8H), 7.28 (d, J= 8.5 Hz, 8H).

**Tetra(p-bromophenyl)stannane (5).**

It was prepared according to the same procedure of compound 3. For compound 5: A white solid (8.4 g, 38 %). $^1$HNMR (500 MHz, CDCl$_3$). $\delta$ (ppm): 7.53 (d, J= 8.0 Hz, 8H), 7.35 (d, J= 8.0 Hz, 8H).

**Scheme S2.** Synthetic route for P(dBPh-C), P(dBPh-Si), P(dBPh-Ge) and P(dBPh-Sn).

**Bis(4-bromophenyl)-di(p-(2-ethylhexyloxy)diphenyl)methane 6.**

The mixture of tetra(p-bromophenyl)methane 2 (3.2 g, 5 mmol), 2-(4-(2-ethylhexyloxy)phenyl)-4,4,5,5- tetramethyl-1,3,2- dioxaborolane$^{13}$ (4.2 g, 12.5 mmol), Pd(PPh$_3$)$_4$ (289 mg, 0.25 mmol) was dissolved in 60ml THF, following the addition of 2M $\text{K}_2\text{CO}_3$ aqueous solution (20ml). The solution was degassed with nitrogen for 0.5 h and then stirring for 12 h at reflux temperature. The reaction mixture was extracted with ethyl acetate and washed with water, and the organic layer was dried over anhydrous MgSO$_4$$_4$, filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography using n-hexane/ CH$_2$Cl$_2$= 10: 1 as eluent to obtain the clear sticky compound 6 (1.94 g, 26 %). $^1$HNMR (500 MHz, CDCl$_3$). $\delta$ (ppm): 7.48 (d, J= 8.5 Hz, 4H), 7.44 (d, J= 8.5 Hz, 4H), 7.38 (d, J= 8.5 Hz, 4H), 7.20 (d, J= 8.5 Hz, 4H), 7.12 (d, J= 8.5 Hz, 4H), 6.93 (d, J= 8.5 Hz, 4H), 3.85 (d, J= 4.5 Hz, 4H), 1.75 (m, 2H), 1.47 (m, 8H), 1.31 (m, 8H), 0.92 (m, 12H).

**Bis(4-bromophenyl)-di(p-(2-ethylhexyloxy)diphenyl)silane 7.**

The mixture of tetra(p-bromophenyl)silane (6.52 g, 10 mmol), 2-(4-(2-ethylhexyloxy)phenyl)-4,4,5,5- tetramethyl-1,3,2- dioxaborolane (8.4 g, 25 mmol), Pd(PPh$_3$)$_4$ (578 mg, 0.5 mmol) was dissolved in 50ml toluene, following the addition of 2M $\text{K}_2\text{CO}_3$ aqueous solution (50ml). The solution was degassed with nitrogen for 0.5 h and then stirring for 12 h at reflux
temperature. The reaction mixture was extracted with ethyl acetate and washed with water, and the organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography using n-hexane/CH$_2$Cl$_2$ = 10:1 as eluent to obtain the clear sticky compound 7 (1.58 g, 18%). $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.57 (m, 8H), 7.52 (d, J= 8.0 Hz, 8H), 7.43 (d, J= 8.0 Hz, 4H), 6.96 (d, J= 8.5 Hz, 4H), 3.87 (d, J= 4.0 Hz, 4H), 1.75 (m, 2H), 1.46 (m, 8H), 1.32 (m, 8H), 0.92 (m, 12H).

Bis(4-bromophenyl)-di(p-(2-ethylhexyloxy)diphenyl)germane 8.

It was prepared with the same procedure for compound 7 but tetra(p-bromophenyl)germane 4 was used as the starting material. For compound 8: A clear sticky product (1.94 g, 26%). $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.58 (d, J= 8.0 Hz, 4H), 7.53 (m, 12H), 7.41 (d, J= 8.0 Hz, 4H), 6.98 (d, J= 9Hz, 4H), 3.88 (d, J= 4.5 Hz, 4H), 1.76 (m, 2H), 1.48 (m, 8H), 1.33 (m, 8H), 0.93 (m, 12H).

Bis(4-bromophenyl)-di(p-(2-ethylhexyloxy)diphenyl)stannane 9.

It was prepared with the same procedure for compound 7 but tetra(p-bromophenyl)stannane 5 was used as the starting material. For compound 9: A clear sticky product (0.93 g, 12%). $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.60 (m, 8H), 7.53 (m, 8H), 7.47 (d, J= 8Hz, 4H), 6.97 (d, J= 9.0 Hz, 4H), 1.76 (m, 2H), 1.47 (m, 8H), 1.33 (m, 8H), 0.93 (m, 12H).

General polymerization procedure for these polymers: P(dBPh-C), P(dBPh-Si), P(dBPh-Ge) and P(dBPh-Sn).

The monomer (0.6 mmol), bis(1,5-cyclooctadiene) nickel (0) (Ni(COD)$_2$) (363 mg, 1.32 mmol), 2,2-bipyridyl (BPY) (206 mg, 1.32 mmol), 1,5-cyclooctadiene (COD) (143 mg, 1.32 mmol), anhydrous DMF (3 mL) and anhydrous toluene (3mL) were added into a reactor under nitrogen atmosphere. The polymerization proceeded at 80°C for 4 days, and then 1-bromo-4-tert-butylbenzene as end-capping agent (0.020 mL, 0.12 mmol) was added to the reaction mixture and continually reacted for additional 24 h. The resulting polymer was poured into methanol, and stirred for 30 min. The precipitate was collected by filtration and dried and then dissolved in CHCl$_3$. The organic layer was washed with water, dried over anhydrous MgSO$_4$, and evaporated under reduced pressure. The material was re-dissolved in CHCl$_3$, and precipitated in methanol. The precipitate was collected by filtration and dried under high vacuum. The solid was further purified by sequential Soxhlet extraction with methanol, acetone and hexane. After that, the solid was re-dissolved in CHCl$_3$ and then precipitated in methanol. Finally, the solid product was collected and dried under vacuum.

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**P(dBPh-C):** white solid. GPC analysis showed its weight-average molecular weight ($M_w$) and polydispersity of 19,000 Da and 2.06, respectively, relative to polystyrene standards. $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.50 (12H), 7.35 (8H), 6.94 (4H), 3.85 (4H), 1.72 (2H), 1.40 (8H), 1.30 (8H), 0.90 (12H).

**P(dBPh-Si):** white solid. GPC analysis showed its $M_w$ and polydispersity of 63,000 Da and 2.55, respectively, relative to polystyrene standards. $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.67 (12H), 7.55 (8H), 6.94 (4H), 3.84 (4H), 1.71 (2H), 1.40 (8H), 1.30 (8H), 0.90 (12H).

**P(dBPh-Ge):** white solid. GPC analysis showed its $M_w$ and polydispersity of 110,000 Da and 2.59, respectively, relative to polystyrene standards. $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.70-7.51 (20H), 6.94 (4H), 3.84 (4H), 1.72 (2H), 1.42 (8H), 1.30 (8H), 0.90 (12H).

**P(dBPh-Sn):** white solid. GPC analysis showed its $M_w$ and polydispersity of 430,000 Da and 7.81, respectively, relative to polystyrene standards. $^1$HNMR (500 MHz, CDCl$_3$). δ (ppm): 7.74-7.45 (20H), 6.96 (4H), 3.86 (4H), 1.72 (2H), 1.41 (8H), 1.31 (8H), 0.91 (12H).

**References**


