

Electronic Supplementary Information

General Experimental. All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory. Infrared spectra were recorded as CH₂Cl₂ solutions using a Perkin Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl₃ on a Jeol EX270 or a Varian Inova 400 MHz FT-NMR spectrometer, with ¹H and ¹³C NMR chemical shifts quoted relative to TMS and ³¹P chemical shifts relative to an 85% H₃PO₄ external standard. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a HP 8453 UV/Vis spectrometer. For solid-state emission spectral measurements, the 325 nm line of a He-Cd laser was used as an excitation source. The luminescence spectra were analyzed by a 0.25 m focal length double monochromator with a Peltier cooled photomultiplier tube and processed with a lock-in-amplifier. For the low temperature experiments, samples were mounted in a closed-cycle cryostat (Oxford CC1104) in which the temperature can be adjusted from 10 to 330 K. The solution emission spectra were measured on a PTI Fluorescence Master Series QM1 spectrophotometer. The fluorescence quantum yields were determined in CH₂Cl₂ solutions at 290 K against the quinine sulfate standard in 0.1 N H₂SO₄ ($\Phi_f = 0.54$). Phosphorescence quantum yields were measured in solid thin films at 20 K relative to the prototypical polymer *trans*-[-Pt(PBu₃)₂C≡C-*p*-C₆H₄-C≡C-]_n ($\Phi_p = 0.30$ at 20 K). The molecular weights of the polymers were determined by GPC (HP 1050 series HPLC with visible wavelength and

fluorescent detectors) using polystyrene standards and thermal analyses were performed with a Perkin-Elmer Pyris Diamond DSC and Perkin-Elmer DTA-7 thermal analyzers.

Experimental Procedures and Spectroscopic Data for OFEG

1a-1c: To a chilled solution of 2,7-diethynyl-9,9-dihexylfluorene **I** (1.80 g, 4.70 mmol) in dried THF (20 cm³) at -78 °C, ⁿBuLi (1.6 M in hexane, 7.10 mmol) was added dropwise. The mixture was stirred for 0.5 h at this temperature and then 1 h at room temperature (r.t.). The resulting solution was again cooled to -78 °C and a solution of Me₂GeCl₂ (0.3 cm³, 2.40 mmol) in THF (10 cm³) was added over 0.5 h and the reaction mixture was stirred for a further 0.5 h before stirring was continued for another 1 h at r.t.. The volatile components were evaporated and the residue was extracted with CH₂Cl₂. The filtrate was subjected to preparative TLC isolation on silica plates using *n*-hexane as the eluent. From the second (*R_f* = 0.30), third (*R_f* = 0.13) and fourth (*R_f* = 0.06) bands, compounds **1a** (310 mg, 15%), **1b** (350 mg, 22%) and **1c** (150 mg, 10%) were obtained as pale-yellow to yellow-orange solids. Although the yields of these oligomers were not very high, the recovered **I** (20%) could be reused to prepare more **1a-1c**. **1a:** pale yellow solid. (Found: C, 83.10; H, 8.15. C₆₀H₇₂Ge requires C, 83.23; H, 8.38). IR (KBr): 3298 (ν_{CH}), 2153 and 2104 cm⁻¹ (ν_{C≡C}); ¹H NMR (400 MHz): δ 7.62-7.45 (m, 12H, Ar), 3.14 (s, 2H, C≡CH), 1.97 (m, 8H, CH₂), 1.14-1.03 (m, 24H, (CH₂)₃), 0.78-0.73 (m, 18H, CH₃), 0.58 (m, 8H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ 150.76, 150.68, 140.75, 140.55, 130.97, 126.23, 121.54, 120.74, 119.71 (Ar), 105.48, 90.44, 84.32, 77.39 (C≡C), 55.10 (quat C), 40.24, 31.44, 29.59, 23.65, 22.53, 13.94 (C₆H₁₃), 0.99 (CH₃); FAB-MS: *m/z* 866 [*M*]⁺. **1b:** yellow solid. (Found: C, 80.92; H, 8.10. C₉₁H₁₁₀Ge₂ requires C, 81.02; H, 8.22). IR (KBr): 3298 (ν_{CH}), 2153 and 2104 cm⁻¹ (ν_{C≡C}); ¹H NMR (400 MHz): δ 7.64-7.61 (m, 6H, Ar), 7.52-7.46 (m, 12H, Ar), 3.16 (s, 2H, C≡CH), 1.97 (m, 12H, CH₂), 1.16-1.04 (m, 36H, (CH₂)₃), 0.82-0.75 (m, 30H, CH₃), 0.57 (m, 12H, CH₂CH₃); ¹³C{¹H} NMR (100.6

MHz): δ 150.85, 150.78, 140.87, 140.75, 140.64, 131.07, 126.33, 121.54, 121.48, 120.69, 119.78, 119.74 (Ar), 105.60, 105.55, 90.47, 90.44, 84.44, 77.30 (C \equiv C), 55.22 (quat C), 40.40, 31.53, 29.66, 23.70, 22.61, 14.00 (C₆H₁₃), 1.13 (CH₃); FAB-MS: m/z 1349 [M]⁺. **1c**: yellow-orange solid. (Found: C, 79.72; H, 8.05. C₁₂₂H₁₄₈Ge₃ requires C, 79.97; H, 8.14). IR (KBr): 3296 (ν_{CH}), 2153 and 2104 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$); ¹H NMR (400 MHz): δ = 7.64-7.61 (m, 8H, Ar), 7.53-7.48 (m, 16H, Ar), 3.16 (s, 2H, C \equiv CH), 1.98 (m, 16H, CH₂), 1.14-1.05 (m, 48H, (CH₂)₃), 0.81-0.76 (m, 42H, CH₃), 0.58 (m, 16H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ = 150.87, 150.78, 140.90, 140.77, 140.66, 131.13, 126.35, 121.58, 121.50, 120.69, 119.81, 119.75 (Ar), 105.65, 105.59, 90.50, 90.46, 84.49, 77.32 (C \equiv C), 55.24 (quat C), 40.35, 31.58, 29.72, 23.72, 22.66, 14.05 (C₆H₁₃), 1.19 (CH₃); FAB-MS: m/z 1832 [M]⁺.

2a-2c: To a chilled solution of **I** (1.00 g, 4.90 mmol) in dried THF (20 cm³) at -78 °C, ⁿBuLi (1.6 M in hexane, 6.70 mmol) was added dropwise under N₂. The mixture was stirred for 0.5 h at this temperature and then 1 hr at r.t.. The resulting solution was again cooled to -78 °C and a solution of Ph₂GeCl₂ (0.5 cm³, 2.50 mmol) in THF (10 cm³) was added dropwise over 0.5 h and the reaction mixture was stirred for a further 0.5 h before stirring was continued for another 1 h at r.t.. The volatile components were evaporated and the residue was extracted with CH₂Cl₂. The filtrate was concentrated and purified by preparative TLC on silica plates eluting with *n*-hexane/CH₂Cl₂ (4:1, v/v). From the second (R_f = 0.48), third (R_f = 0.30) and fourth (R_f = 0.20) fluorescent bands, pure samples of compounds **2a** (250 mg, 10%), **2b** (220 mg, 11%) and **2c** (173 mg, 10%) were obtained. The starting 2,7-diethynyl-9,9-dihexylfluorene was also recovered in a pure form from the top band (16 %). **2a**: yellow-orange solid. (Found: C, 84.82; H, 7.55. C₇₀H₇₆Ge requires C, 84.93; H, 7.74). IR (KBr): 3298 (ν_{CH}), 2156 and 2107 cm⁻¹ ($\nu_{\text{C}\equiv\text{C}}$); ¹H NMR (400 MHz): δ 7.90-7.86 (m, 4H, Ar), 7.67-7.48 (m, 18H,

Ar), 3.17 (s, 2H, C≡CH), 1.97 (m, 8H, CH₂), 1.16-1.00 (m, 24H, (CH₂)₃), 0.78 (t, *J* = 8.1 Hz, 12H, CH₃), 0.57 (m, 8H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ 151.35, 151.22, 141.35, 141.26, 134.59, 134.19, 131.79, 131.47, 130.25, 128.85, 126.84, 126.75, 121.65, 121.06, 120.24, 120.14 (Ar), 108.28, 87.34, 84.78, 77.59 (C≡C), 55.50 (quat C), 40.52, 31.74, 29.87, 23.88, 22.82, 14.22 (C₆H₁₃); FAB-MS: *m/z* 990 [*M*]⁺. **2b**: yellow-orange solid. (Found: C, 83.40; H, 7.40. C₁₁₁H₁₁₈Ge₂ requires C, 83.47; H, 7.45). IR (KBr): 3299 (ν_{C≡CH}), 2156 and 2107 cm⁻¹ (ν_{C≡C}); ¹H NMR (400 MHz): δ 7.88-7.83 (m, 6H, Ar), 7.65-7.46 (m, 32H, Ar), 3.15 (s, 2H, C≡CH), 1.96 (m, 12H, CH₂), 1.14-1.02 (m, 36H, (CH₂)₃), 0.76 (t, *J* = 8.1 Hz, 18H, CH₃), 0.55 ppm (m, 12H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ 151.14, 151.03, 141.32, 141.27, 133.97, 133.51, 131.38, 130.99, 130.04, 128.64, 126.40, 126.30, 121.35, 121.31, 120.33, 120.20 (Ar), 108.04, 108.01, 86.89, 86.76, 84.00, 78.64 (C≡C), 55.32 (quat C), 39.76, 31.37, 29.37, 23.68, 22.33, 13.41 (C₆H₁₃); FAB-MS: *m/z* 1597 [*M*]⁺. **2c**: yellow-orange solid. (Found: C, 82.68; H, 7.19. C₁₅₂H₁₆₀Ge₃ requires C, 82.81; H, 7.31). IR (KBr): 3298 (ν_{C≡CH}), 2156 and 2107 cm⁻¹ (ν_{C≡C}); ¹H NMR (400 MHz): δ 7.88-7.84 (m, 8H, Ar), 7.66-7.45 (m, 46H, Ar), 3.16 (s, 2H, C≡CH), 1.95 (m, 16H, CH₂), 1.14-1.00 (m, 48H, (CH₂)₃), 0.76 (t, *J* = 8.1 Hz, 24H, CH₃), 0.54 ppm (m, 16H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ 151.27, 151.19, 141.38, 141.25, 134.56, 134.18, 131.78, 131.45, 130.24, 128.83, 126.81, 126.74, 121.62, 121.01, 120.24, 120.13 (Ar), 108.06, 108.02, 87.07, 84.54, 77.21 (C≡C), 55.25 (quat C), 40.32, 31.50, 29.63, 23.63, 22.58, 13.98 (C₆H₁₃); FAB-MS: *m/z* 2205 [*M*]⁺.

Experimental Procedures and Spectroscopic Data for Platinum(II) Polyynes

3a-3c: CuI (3.0 mg) was added to a mixture of **1a** (80.0 mg, 0.09 mmol) and *trans*-[PtCl₂(PBu₃)₂] (62.0 mg, 0.09 mmol) in ⁱPr₂NH/CH₂Cl₂ (20 cm³, 1:1, v/v). The yellow solution was stirred at r.t. over 15 h,

after which all solvents were evaporated off. The residue was redissolved in CH_2Cl_2 , and filtered through a silica column using the same eluent. The polymer film obtained was purified by precipitation in toluene from MeOH to afford a yellow solid of **3a** (94.0 mg, 71 %). Polymers **3b** and **3c** can be synthesized from **1b** and **1c** using the same procedures with isolated yields of 52 and 47%, respectively.

3a: yellow powder. (Found: C, 68.78; H, 8.44. $(\text{C}_{84}\text{H}_{124}\text{GeP}_2\text{Pt})_n$ requires C, 68.94; H, 8.54). IR (CH_2Cl_2): 2153 and 2095 cm^{-1} ($\nu_{\text{C}=\text{C}}$); ^1H NMR (400 MHz): δ 7.53–7.45 (m, 4H, Ar), 7.24–7.17 (m, 8H, Ar), 2.20 (m, 12H, PCH_2 of Bu), 1.91 (m, 8H, CH_2 of Hex), 1.67 (m, 12H, PCH_2CH_2 of Bu), 1.50–1.46 (m, 12H, CH_2CH_3 of Bu), 1.10–0.92 (m, 42H, CH_3 of Bu + $(\text{CH}_2)_3$ of Hex), 0.80–0.77 (m, 18H, CH_3 of Hex + GeMe), 0.59 ppm (m, 8H, CH_2CH_3 of Hex); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz): δ 150.68, 150.52, 141.88, 137.36, 131.12, 129.69, 128.98, 128.17, 126.26, 125.25, 119.51, 119.06 (Ar), 110.25, 108.81, 106.05, 89.86 ($\text{C}\equiv\text{C}$), 54.83 (quat C), 40.57, 31.56, 29.75, 23.79, 22.62, 13.97 (Hex), 26.36, 24.13, 22.62, 13.81 (Bu), 1.11 (Me); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz): δ 3.99 ($J_{\text{P-Pt}} = 2352$ Hz); **3b**: yellow powder. (Found: C, 70.69; H, 8.24. $(\text{C}_{115}\text{H}_{162}\text{Ge}_2\text{P}_2\text{Pt})_n$ requires C, 70.95; H, 8.39). IR (CH_2Cl_2): 2153 and 2096 cm^{-1} ($\nu_{\text{C}=\text{C}}$); ^1H NMR (400 MHz): δ 7.62–7.46 (m, 12H, Ar), 7.26–7.17 (m, 6H, Ar), 2.19 (m, 12H, PCH_2 of Bu), 1.92 (m, 12H, CH_2 of Hex), 1.66 (m, 12H, PCH_2CH_2 of Bu), 1.50–1.44 (m, 12H, CH_2CH_3 of Bu), 1.12–0.90 (m, 54H, CH_3 of Bu + $(\text{CH}_2)_3$ of Hex), 0.78–0.74 (m, 30H, CH_3 of Hex + GeMe), 0.54 (m, 12H, CH_2CH_3 of Hex); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz): δ 151.16, 150.93, 150.79, 142.18, 141.15, 137.59, 131.48, 131.39, 129.95, 128.35, 126.65, 126.50, 125.38, 121.80, 120.43, 120.07, 119.78, 119.33 (Ar), 110.50, 106.40, 105.88, 90.84, 89.95 ($\text{C}\equiv\text{C}$), 55.46, 55.09 (quat C), 40.83, 40.67, 31.82, 30.02, 29.93, 24.03, 22.86, 14.24 (Hex), 26.61, 24.69, 23.88, 14.08 (Bu), 1.37, 1.23 (Me); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz): δ 3.95 ($J_{\text{P-Pt}} = 2365$ Hz). **3c**: yellow powder. (Found: C, 72.02; H, 8.20. $(\text{C}_{146}\text{H}_{200}\text{Ge}_3\text{P}_2\text{Pt})_n$ requires C, 72.17; H, 8.30). IR (CH_2Cl_2): 2153 and 2096 cm^{-1} ($\nu_{\text{C}=\text{C}}$); ^1H NMR (400

MHz): δ 7.63-7.46 (m, 18H, Ar), 7.25-7.23 (m, 6H, Ar), 2.18 (m, 12H, PCH₂ of Bu), 1.89 (m, 16H, CH₂ of Hex), 1.62 (m, 12H, PCH₂CH₂ of Bu), 1.50-1.42 (m, 12H, CH₂CH₃ of Bu), 1.12-0.90 (m, 66H, CH₃ of Bu + (CH₂)₃ of Hex), 0.78-0.73 (m, 42H, CH₃ of Hex + GeMe), 0.53 (m, 16H, CH₂CH₃ of Hex); ¹³C{¹H} NMR (100.6 MHz): δ 150.92, 150.69, 150.55, 141.94, 140.95, 140.91, 137.35, 131.25, 131.15, 129.73, 128.12, 126.41, 126.26, 125.15, 121.58, 121.50, 120.19, 119.84, 119.54, 119.09 (Ar), 110.25, 106.16, 105.72, 105.63, 90.62, 90.44, 89.71 (C≡C), 55.23, 54.85 (quat C), 40.59, 40.43, 31.56, 29.77, 29.68, 23.79, 22.61, 13.99 (Hex), 26.37, 24.45, 23.64, 13.84 (Bu), 1.23, 1.13 (Me); ³¹P{¹H} NMR (161.9 MHz): δ 3.97 ($J_{\text{P-Pt}} = 2354$ Hz).

4a-4c: Polymerization was carried out by mixing **2a** (40.0 mg, 0.04 mmol), *trans*-[PtCl₂(PBU₃)₂] (27.1 mg, 0.04 mmol) and CuI (3.0 mg) in ⁱPr₂NH/CH₂Cl₂ (20 cm³, 1:2, v/v). After stirring at r.t. for 15 h, the solution mixture was evaporated to dryness. The residue was redissolved in CH₂Cl₂, and filtered through a silica column using the same eluent to remove ionic impurities and catalyst residues. After removal of the solvent, the crude product was purified by precipitation in toluene from MeOH. Subsequent washing with *n*-hexane and drying *in vacuo* gave a pure sample of **4a** (28.0 mg, 44 %). Similar synthetic methodologies can be employed to give polymers **4b** (41%) and **4c** (65%) based on **2b** and **2c**, respectively. **4a:** yellow-orange powder. (Found: C, 71.04; H, 8.04. (C₉₄H₁₂₈GeP₂Pt)_n requires C, 71.11; H, 8.13). IR (CH₂Cl₂): 2154 and 2095 cm⁻¹ ($\nu_{\text{C=C}}$); ¹H NMR (400 MHz): δ 7.87 (m, 4H, Ar), 7.57-7.48 (m, 12H, Ar), 7.25-7.18 (m, 6H, Ar), 2.20 (m, 12H, PCH₂ of Bu), 1.91 (m, 8H, CH₂ of Hex), 1.65 (m, 12H, PCH₂CH₂ of Bu), 1.52-1.45 (m, 12H, CH₂CH₃ of Bu), 1.14-0.93 (m, 42H, CH₃ of Bu + (CH₂)₃ of Hex), 0.77 (t, $J = 7.2$ Hz, 12H, CH₃ of Hex), 0.58 (m, 8H, CH₂CH₃ of Hex); ¹³C{¹H} NMR (100.6 MHz): δ 150.80, 150.61, 142.17, 137.31, 134.60, 133.96, 131.44, 129.91, 129.73, 129.01,

128.55, 128.20, 126.44, 125.16, 119.63, 119.12 (Ar), 110.29, 108.49, 86.41 (C≡C), 54.90 (quat C), 40.52, 31.56, 29.74, 24.01, 22.64, 14.00 (Hex), 26.40, 24.44, 23.65, 13.83 (Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz): δ 4.02 ($J_{\text{P,Pt}} = 2348$ Hz). **4b**: yellow-orange powder. (Found: C, 73.58; H, 7.60. ($\text{C}_{135}\text{H}_{170}\text{Ge}_2\text{P}_2\text{Pt}$)_n requires C, 73.87; H, 7.81). IR (CH_2Cl_2): 2155 and 2095 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$); ^1H NMR (400 MHz): δ 7.87–7.85 (m, 6H, Ar), 7.63–7.47 (m, 24H, Ar), 7.26–7.19 (m, 8H, Ar), 2.18 (m, 12H, PCH_2 of Bu), 1.92 (m, 12H, CH_2 of Hex), 1.65 (m, 12H, PCH_2CH_2 of Bu), 1.51–1.43 (m, 12H, CH_2CH_3 of Bu), 1.10–0.90 (m, 54H, CH_3 of Bu + $(\text{CH}_2)_3$ of Hex), 0.76 (t, $J = 7.2$ Hz, 18H, CH_3 of Hex), 0.56 (m, 12H, CH_2CH_3 of Hex); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz): δ 150.88, 150.62, 150.46, 142.11, 141.00, 137.18, 134.36, 133.85, 131.43, 131.34, 129.87, 129.63, 128.92, 128.48, 128.12, 126.50, 126.32, 125.19, 125.08, 121.34, 119.89, 119.83, 119.53, 119.02 (Ar), 108.54, 107.91, 87.19, 86.20 (C≡C), 55.34, 54.93 (quat C), 40.60, 40.41, 31.64, 31.61, 29.84, 29.72, 24.30, 24.06, 22.74, 22.70, 14.12 (Hex), 26.47, 24.55, 23.74, 13.96 (Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz): δ 3.98 ($J_{\text{P,Pt}} = 2349$ Hz). **4c**: yellow-orange solid. (Found: C, 75.08; H, 7.45. ($\text{C}_{176}\text{H}_{212}\text{Ge}_3\text{P}_2\text{Pt}$)_n requires C, 75.43; H, 7.62). IR (CH_2Cl_2): 2155 and 2093 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$); ^1H NMR (400 MHz): δ 7.78 (m, 18H, Ar), 7.57–7.39 (m, 34H, Ar), 7.18–7.07 (m, 12H, Ar), 2.08 (m, 12H, PCH_2 of Bu), 1.85 (m, 16H, CH_2 of Hex), 1.57 (m, 12H, PCH_2CH_2 of Bu), 1.38 (m, 12H, CH_2CH_3 of Bu), 1.02–0.85 (m, 66H, CH_3 of Bu + $(\text{CH}_2)_3$ of Hex), 0.68 (m, 24H, CH_3 of Hex), 0.47 (m, 16H, CH_2CH_3 of Hex); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz): δ 151.30, 151.03, 150.87, 142.50, 141.44, 141.37, 138.11, 137.55, 134.73, 134.59, 134.22, 131.81, 130.27, 130.00, 129.28, 128.84, 128.47, 126.85, 125.54, 121.72, 121.64, 120.19, 119.88, 119.37 (Ar), 110.54, 108.87, 108.33, 108.26, 87.51, 87.34, 86.51 (C≡C), 55.58, 55.16 (quat C), 40.81, 40.60, 31.83, 31.78, 30.02, 29.90, 26.35, 24.23, 24.06, 22.91, 22.86, 14.26 (Hex), 26.64, 24.72, 23.91, 14.11 (Bu); $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz): δ 4.02 ($J_{\text{P,Pt}} = 2348$ Hz).

Preparation and Spectroscopic Data of $[-C\equiv C(9,9\text{-dihexylfluorene-2,7-diyl})C\equiv CGePh_2-]_n$

A dried two-necked flask, equipped with a condenser and magnetic stirrer bar was charged with $Ph_2Ge(C\equiv CH)_2$ (54.5 mg, 0.20 mmol), 9,9-dihexyl-2,7-diiodofluorene (115.5 mg, 0.20 mmol), CuI (5.0 mg) and $Pd(PPh_3)_4$ (20.0 mg). The flask was evacuated and filled with nitrogen. iPr_2NH (15 cm³) and THF (15 cm³) were then added *via* syringe. The reaction mixture was stirred at 75 °C for 20 h. After the reaction mixture was cooled to r.t., the precipitate was removed by filtration and solvents of the filtrate were pumped off. The residue was dissolved in CH_2Cl_2 and the solution was passed through a silica gel chromatography column eluting with CH_2Cl_2 . The solution was concentrated and added dropwise into methanol with vigorous stirring. The yellow precipitate was collected and dried under vacuum. Yield: 83.1 mg (69%). (Found: C, 80.78; H, 6.77. $(C_{41}H_{42}Ge)_n$ requires C, 81.08; H, 6.97). IR (KBr): 2155 cm⁻¹ ($\nu_{C\equiv C}$); ¹H NMR (400 MHz): δ 7.87-7.30 (m, 16H, Ar), 1.96 (m, 4H, CH₂), 1.11-1.03 (m, 12H, (CH₂)₃), 0.76 (t, J = 6.8 Hz, 6H, CH₃), 0.55 (m, 4H, CH₂CH₃); ¹³C{¹H} NMR (100.6 MHz): δ 151.03, 141.14, 140.25, 133.94, 131.54, 129.97, 128.58, 126.56, 122.85, 119.93 (Ar), 108.06, 87.07 (C≡C), 55.30 (quat C), 40.34, 31.51, 29.68, 23.64, 22.59, 13.99 (C₆H₁₃). GPC (THF): M_w = 8850, M_n = 6700, DP = 15; λ_{abs} (CH_2Cl_2): 298, 309, 329, 346 nm; TGA (N₂): T_{dec} = 419 °C.

Calculations for k_{nr} and k_r

Since the intersystem crossing (ISC) efficiency (Φ_{ISC}) can be roughly taken to be unity for third row metal chromophores, the radiative (k_r) and nonradiative (k_{nr}) decay rates are related to the measured lifetime of triplet emission (τ_P) and the phosphorescence quantum yield (Φ) by Eqs. (1) and (2):

$$k_{nr} = (1 - \Phi) / \tau_P \quad [\text{Eq. (1)}]$$

$$k_r = \Phi / \tau_P \quad [\text{Eq. (2)}]$$

X-ray Crystallographic Details

Light yellow crystals of **1a** and **2a** suitable for X-ray diffraction studies were grown by slow evaporation of their solutions in CH₂Cl₂/hexane at room temperature. Geometric and intensity data were collected at 293 K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Axs SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT and an absorption correction (SADABS) was applied to the collected reflections. The structure was solved by the Direct methods (SIR92) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F using the software “CRYSTALS”. Except for some of the carbon atoms in the hexyl chains of **1a**, all non-hydrogen atoms were assigned with anisotropic displacement parameters. Hydrogen atoms were generated in their idealized positions and allowed to ride on the parent carbon atoms.

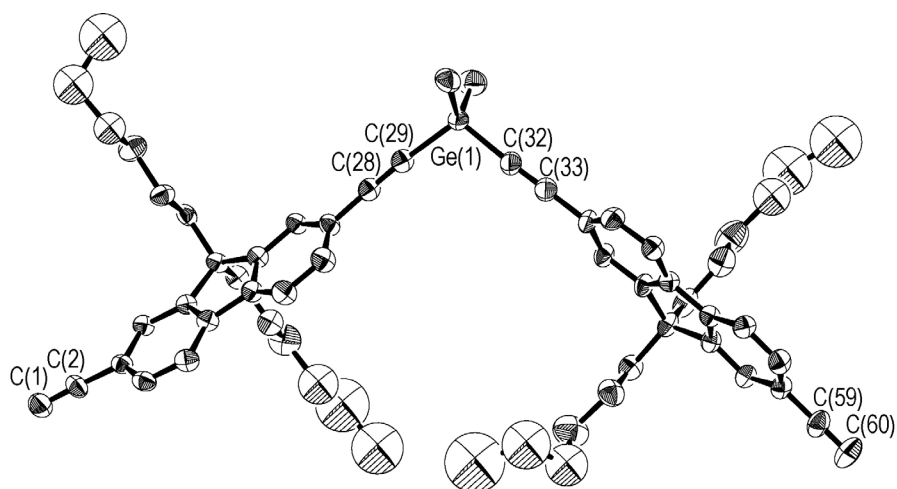


Fig. S1 ORTEP plot (at the 25% probability level) of **1a**. Selected bond lengths [Å] and angles [°]:
Ge(1)-C(29) 1.90(1), Ge(1)-C(32) 1.87(1), C(1)-C(2) 1.16(2), C(28)-C(29) 1.20(2), C(32)-C(33) 1.21
(2), C(59)-C(60) 1.13(2); Ge(1)-C(29)-C(28) 175.6(8), Ge(1)-C(32)-C(33) 176(1).

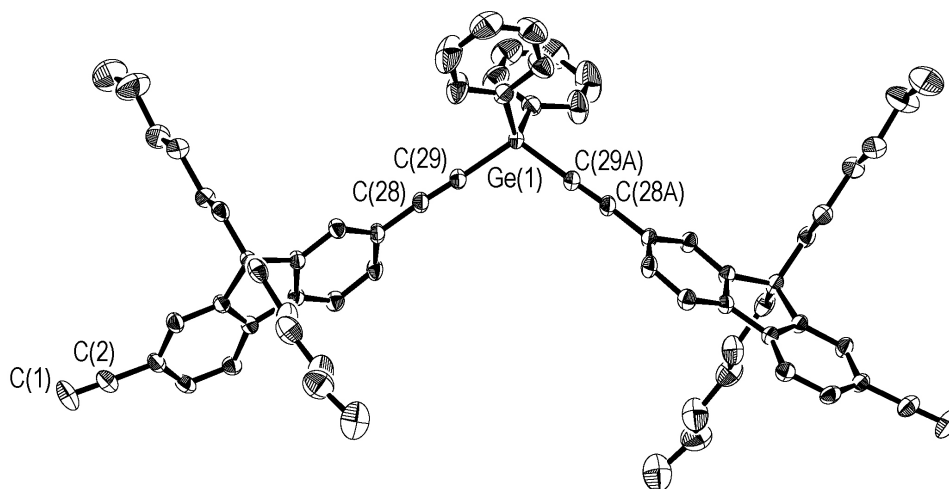


Fig. S2 ORTEP plot (at the 25% probability level) of **2a**. Selected bond lengths [\AA] and angles [$^\circ$]:
Ge(1)-C(29) 1.904(3), C(1)-C(2) 1.144(6), C(28)-C(29) 1.191(5),; Ge(1)-C(29)-C(28) 176.5(3).

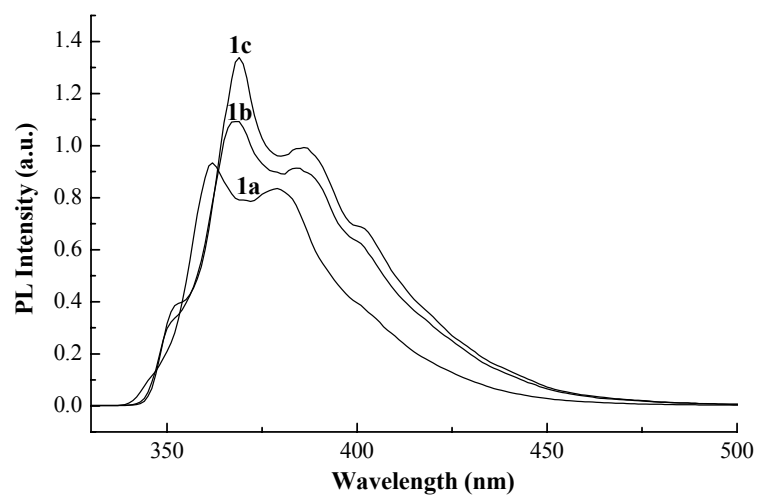


Fig. S3 Photoluminescence spectra of **1a-1c** in CH_2Cl_2 at room temperature.

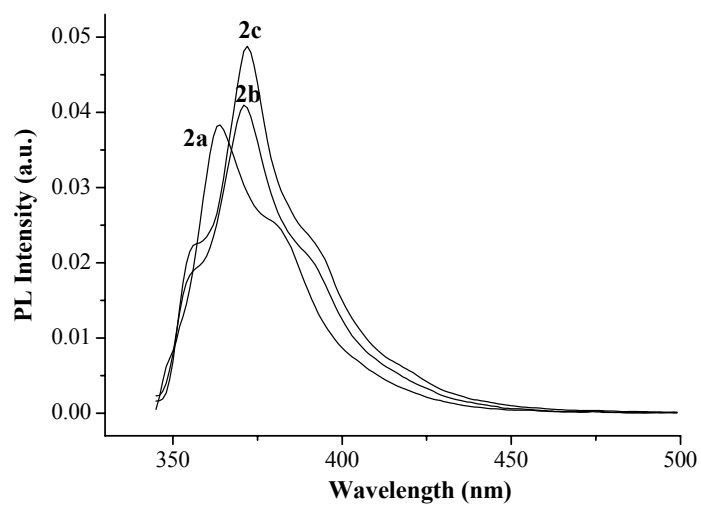


Fig. S4 Photoluminescence spectra of **2a-2c** in CH₂Cl₂ at room temperature.

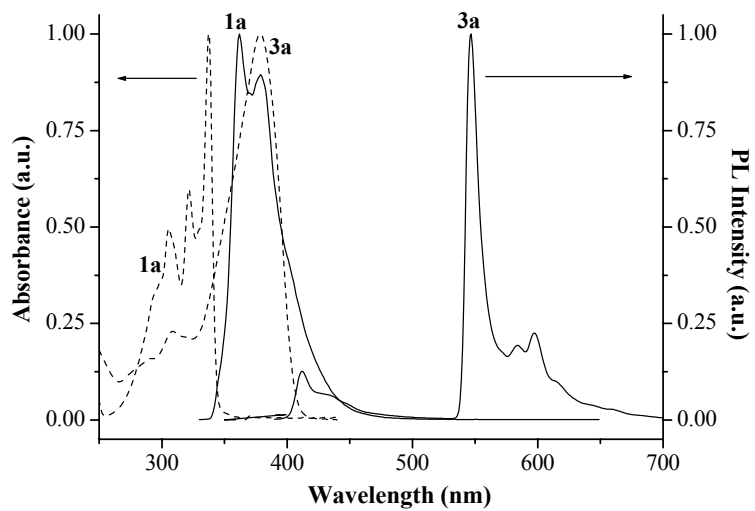


Fig. S5 Absorption (· · ·) and emission (—) spectra of **1a** and **3a**. The emission spectrum of **3a** was taken at 77 K.

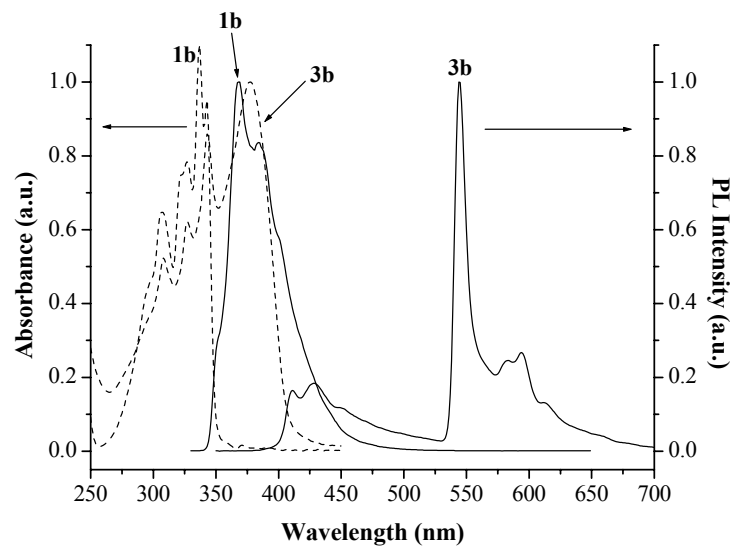


Fig. S6 Absorption (· · ·) and emission (—) spectra of **1b** and **3b**. The emission spectrum of **3b** was taken at 77 K.

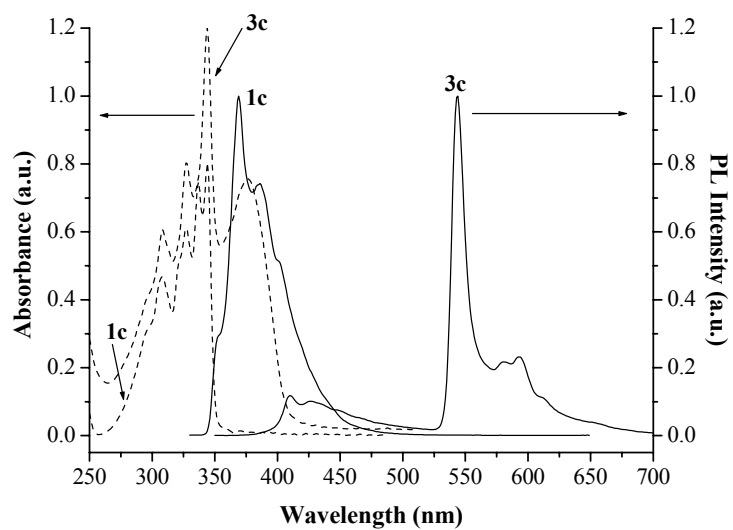


Fig. S7 Absorption (· · ·) and emission (—) spectra of **1c** and **3c**. The emission spectrum of **3c** was taken at 77 K.

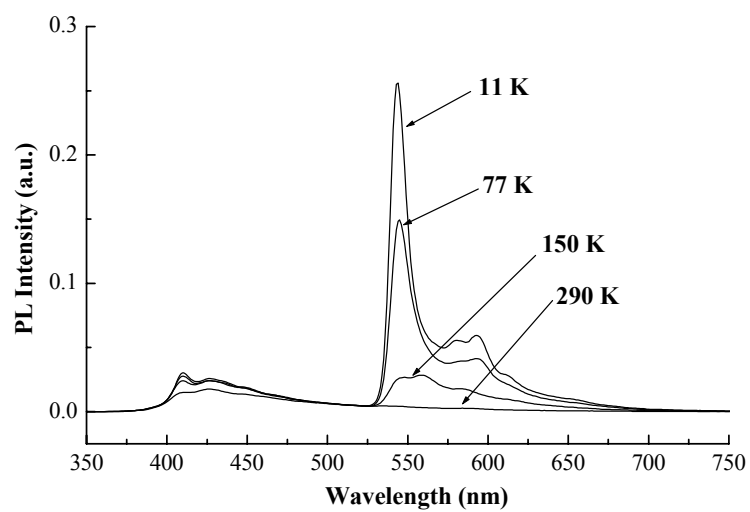


Fig. S8 Temperature dependence of the photoluminescence of **3c**.

Table S1: Structural and thermal properties of **3a-3c** and **4a-4c**

Polymer	M_w^a	M_n^a	DP	$T_{dec}/^\circ\text{C}$	$\lambda_{abs}/\text{nm}^b$	E_{gap}/eV	λ_{em}/nm^c	τ_F/ns^d
3a	42970	13580	29	410	379	3.05	412, 547	1.23 (1.44)
3b	22950	11150	12	414	378	3.04	411, 544	1.23 (1.31)
3c	22790	16150	10	407	376	3.04	410, 544	1.47 (1.26)
4a	23970	10400	15	404	382	3.00	414, 548	1.58 (1.26)
4b	28350	12830	13	407	380	3.00	411, 545	1.34 (1.18)
4c	22600	17550	9	418	380	3.00	411, 545	1.33 (1.13)

^a Calibration against polystyrene. ^b In CH_2Cl_2 . ^c In solid film at 77 K. ^d Φ_F (%) in parentheses.

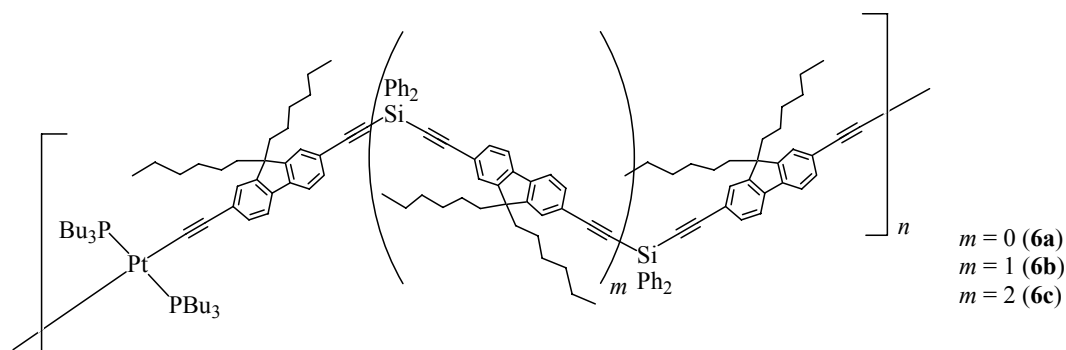


Table S2: Structural and thermal properties of **6a-6c**

Polymer	M_w^a	M_n^a	DP	λ_{em}/nm (film) ^b	$\tau_p/\mu\text{s}$	Φ_F	$(k_{nr})_p/\text{s}^{-1}$	$(k_r)_p/\text{s}^{-1}$
6a	8550	14620	10	420, 550	2.12	0.10	4.2×10^5	4.8×10^4
6b	10010	16300	8	420, 550	3.02	0.12	2.9×10^5	4.1×10^4
6c	11270	16000	6	414, 545	5.67	0.13	1.5×10^5	2.4×10^4

^a Calibration against polystyrene. ^b At 77 K.