# Harvesting of Organic Triplet Emissions in Metal Diynes and Polyynes of Group 10–12 Transition Elements Containing the Conjugation-Interrupting Diphenylfluorene Unit

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ABSTRACT: Soluble and thermally stable group 10 platinum(II) and group 12 mercury(II) polyyne polymers containing the diphenylfluorene moiety  $trans-[-Pt(PBu_3)_2C \equiv CRC \equiv C-]_n$  and  $[-HgC \equiv CRC \equiv CRC$  $C-J_n$  (R = 9,9-diphenylfluorene) were prepared in good yields by polycondensation polymerization of *trans*- $[PtCl_2(PBu_3)_2]$  or  $HgCl_2$  with 9,9-bis(4-ethynylphenyl)fluorene. We report the optical absorption and photoluminescence spectra of these carbon-rich metal-based polymers and compare the results with their monomeric model complexes trans-[Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>C=CRC=CPt(Ph)(PEt<sub>3</sub>)<sub>2</sub>] and [MeHgC=CRC=CHgMe] as well as the group 11 gold(I) congener [(PPh<sub>3</sub>)AuC=CRC=CAu(PPh<sub>3</sub>)]. The regiochemical structures of the polymers were studied by NMR spectroscopy and by single-crystal X-ray analysis for the model platinum(II) compound. Our investigations indicate that harvesting of the organic triplet emissions can be achieved by the heavy-atom effect of group 10-12 transition metals (i.e., Pt, Au, Hg) which enables a very high efficiency of intersystem crossing from the  $S_1$  singlet excited state to the  $T_1$  triplet excited state. The influence of the metal and the fluorene ring on the intersystem crossing rate and the spatial extent of singlet and triplet excitons is characterized. These phosphorescent metal-organic materials show  $T_1-S_0$  gaps of 2.5 eV or above, which correspond to  $S_1-S_0$  gaps of 3.1 eV or higher. The present work indicates that high-energy triplet states (and concurrently high optical gaps) intrinsically lead to more efficient phosphorescence in metal-containing aryleneethynylenes and can facilitate the radiative decay pathway.

# Introduction

The search for new organic and metal-organic molecular functional materials with optoelectronic applications continues to attract much current attention. 1-4 In particular, conjugated ethynylated materials, such as arylacetylenes, 1-4 poly(aryleneethynylenes)s, 5,6 and metal-containing acetylide complexes and polymers,<sup>7,8</sup> have been extensively studied in this context. Intensive studies of conjugated polymers over the past decade have made it possible to clarify some fundamental issues about the nature of the singlet excited states,<sup>9-11</sup> yet still relatively little is known about the nature of triplet excited states in conjugated polymers. Much of the recent work has shown that triplet states play an important role in optical and electrical processes within conjugated polymers with direct implications for their technological exploitation. $^{12-19}$  It has been demonstrated that the ultimate efficiency of light-emitting diodes (LEDs) is controlled by the fraction of triplet states generated or harvested.<sup>20-24</sup> Therefore, a thorough understanding of triplet photophysics is essential if one intends to develop a full picture of basic excitations in conjugated polymers.

Recently, there has been increasing experimental and theoretical attention focusing on the energy levels of singlet and triplet states in conjugated polymers. The

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A number of literature reports have shown that the nonradiative decay of the triplet states in a series of Pt-containing conjugated polymers and monomers may be quantitatively described by the energy gap law.<sup>25</sup> In other words, work should focus on polymers with highenergy triplets (and concurrently high optical gaps) to avoid competition with nonradiative decay. One promising approach of designing molecular systems with high HOMO-LUMO gap is based on an interruption of the conjugation by incorporating nonconjugated segments into the polymer main chain. It is known that the diphenylfluorene unit containing two aromatic rings in

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the cardo group can be introduced in some organic copolymers as a tetrahedral conjugation-breaking unit to improve the thermal stability and solubility of the materials.<sup>38–40</sup> In this connection, we report here the first examples of group 10-12 metal-acetylide complexes and polymers containing the conjugation-interrupting diphenylfluorene unit so that we can evaluate how the sp<sup>3</sup>-carbon atom of fluorene would limit the effective conjugation length of such conjugated system, and hence, the resulting optoelectronic properties can be controlled and optimized.

### **Experimental Section**

General. 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 GF<sub>254</sub>) prepared in our laboratory. The compounds trans-[PtCl(Ph)(PEt<sub>3</sub>)<sub>2</sub>],<sup>41</sup> trans-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>],<sup>42</sup> trans-[Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>C $\equiv$ C(p-C<sub>6</sub>H<sub>4</sub>)<sub>m</sub>C $\equiv$  $CPt(Ph)(PEt_3)_2$ , and *trans*- $[-Pt(PBu_3)_2C \equiv C(p - C_6H_4)_mC \equiv C - C_6H_4)_mC \equiv C - C_6H_4$ ]<sub>n</sub>  $(m = 1, 2)^{43-45}$  were prepared by literature methods. Infrared spectra were recorded as CH<sub>2</sub>Cl<sub>2</sub> solutions using a Perkin-Elmer Paragon 1000 PC or a Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in appropriate solvents on a JEOL EX270 or a Varian Inova 400 MHz FT-NMR spectrometer, with <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts quoted relative to TMS and <sup>31</sup>P chemical shifts relative to an 85% H<sub>3</sub>PO<sub>4</sub> 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 lockin-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 toluene solutions at 290 K against the anthracene standard ( $\Phi = 0.27$ ). Phosphorescence quantum yields were measured in solid thin films at 20 K relative to the prototypical polymer  $trans{-}[-Pt(PBu_3)_2C \equiv$  $C(p-C_6H_4)C \equiv C - \int_n (\Phi_P = 0.30 \text{ at } 20 \text{ K})$ . 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.

[Pt-T(DPF)T]... A mixture of 9,9-bis(4-ethynylphenyl)fluorene, [H-T(DPF)T]1 (75.0 mg, 0.20 mmol), and trans-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] (134.1 mg, 0.20 mmol) in a 1:1 molar ratio in Pr2NH/CH2Cl2 (50 mL, 1:1, v/v) was allowed to react in the presence of CuI (3 mg). The solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a silica gel column using the same solvent as the eluent to give a yellow solution. Upon removal of solvent, the product was then reprecipitated twice from a CH<sub>2</sub>Cl<sub>2</sub>/MeOH mixture followed by washing with MeOH to afford a light yellow powder in 69% yield (132.8 mg). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\breve{C}\equiv\breve{C})$  2101 cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\breve{C}DCl_3$ ):  $\delta$  (ppm) 7.73 (d, J = 7.6 Hz, 2H, Ar), 7.38 (d, J = 7.2 Hz, 2H, Ar), 7.32 (m, 2H, Ar), 7.23 (m, 2H, Ar), 7.17 (m, 2H, Ar), 7.09 (d, J = 7.6 Hz, 4H, Ar), 7.00 (d, J = 8.4 Hz, 2H, Ar), 2.07 (m, 12H, PCH<sub>2</sub>), 1.53 (m, 12H, PCH<sub>2</sub>CH<sub>2</sub>), 1.39 (m, 12H, P(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.87 (m, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 151.28, 142.25, 140.06, 130.46, 128.99, 128.19, 127.67, 127.50, 127.20, 126.20,

125.26, 119.99 (Ar), 108.45, 77.20 (C=C), 65.14 (quat C), 26.27, 24.34, 23.69, 13.81 (Bu). <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 3.90 (<sup>1</sup>*J*<sub>P-Pt</sub> = 2361 Hz). GPC (THF as eluent): *M*<sub>w</sub> = 45 700, *M*<sub>n</sub> = 43 410, polydispersity = 1.05. Anal. Calcd for (C<sub>53</sub>H<sub>68</sub>P<sub>2</sub>Pt)<sub>n</sub>: C, 66.16; H, 7.12. Found: C, 66.02; H, 7.05.

[Pt-T(DPF)T]<sub>1</sub>. A solution of [H-T(DPF)T]<sub>1</sub> (36.6 mg, 0.10 mmol) and 2 equiv of trans-[PtCl(Ph)(PEt<sub>3</sub>)<sub>2</sub>] (108.8 mg, 0.20 mmol) in <sup>1</sup>Pr<sub>2</sub>NH/CH<sub>2</sub>Cl<sub>2</sub> (16 mL, 1:1, v/v) was charged into a 100 mL Schlenk flask, and a small amount of CuI (3 mg) was then added. The resulting mixture was stirred at room temperature over a period of 15 h, after which all the volatile components were evaporated to dryness. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was purified on preparative TLC plates eluting with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:2, v/v,  $R_f = 0.55$ ) to give the title complex as an off-white crystalline solid in an isolated yield of 69% (95.3 mg). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C= C) 2098 cm<sup>-1</sup>. <sup>1</sup>H ŇMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.75 (m, 2H, Ar), 7.39–7.22 (m, 10H, Ar +  $H_{ortho}$  of Ph–Pt), 7.14–7.02 (m, 8H, Ar), 6.95 (t, J = 7.6 Hz, 4H, H<sub>meta</sub> of Ph-Pt), 6.79 (t, J = 7.6Hz, 2H, H<sub>para</sub> of Ph-Pt), 1.72 (m, 24H, CH<sub>2</sub>CH<sub>3</sub>), 1.06 (m, 36H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 151.46, 150.18, 146.01, 141.93, 140.03, 139.15, 131.86, 130.52, 127.69, 127.20, 126.18, 125.97, 121.55, 121.11, 120.27, 119.97, 112.96, 109.72 (Ar), 104.74, 94.41 (C=C), 65.14 (quat C), 15.00, 7.97 (Et). <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 10.96 ( ${}^{1}J_{P-Pt} = 2628$  Hz). FAB-MS (m/ z): 1381 [M<sup>+</sup>]. Anal. Calcd for  $C_{65}H_{86}P_4Pt_2$ : C, 56.51; H, 6.27. Found: C, 56.34; H, 6.08.

[Hg-T(DPF)T]... A solution of HgCl<sub>2</sub> (135.8 mg, 0.50 mmol) in MeOH (10 mL) was mixed with  $[H-T(DPF)T]_1$  (183.2 mg, 0.50 mmol) in MeOH (10 mL). To this mixture, 12.5 mL of 0.20 M basic MeOH (2.50 mmol, prepared by dissolving 0.40 g of NaOH in 50 mL of MeOH) was added. Within several minutes, an off-white solid precipitated from the homogeneous solution. The reaction was complete after stirring for 12 h, and the solid was collected by filtration, washed with MeOH (2 imes20 mL), and air-dried to furnish the polymer in 80% yield (226.0 mg). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=C) 2146 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.77 (d, J = 7.6 Hz, 2H, Ar), 7.37–7.27 (m, 10H, Ar), 7.14–7.11 (m, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 150.45, 146.66, 146.50, 140.44, 132.70, 132.49, 128.40, 128.29, 126.39, 121.06, 120.89, 120.62 (Ar), 105.80, 94.38 (C=C), 65.56 (quat C). GPC (THF as eluent):  $M_{\rm w}$  = 8900,  $M_{\rm n}$  = 8590, polydispersity = 1.04. Anal. Calcd for  $(C_{29}H_{16}Hg)_n$ : C, 61.65; H, 2.85. Found: C, 61.48; H, 2.75.

**[Hg−T(DPF)T]**<sub>1</sub>. The organic diyne  $[H−T(DPF)T]_1$  (36.6 mg, 0.10 mmol) in MeOH (10 mL) was first combined with MeHgCl (50.2 mg, 0.20 mmol) in MeOH (10 mL). 0.20 M basic MeOH (2.5 mL, 0.50 mmol) was subsequently added to produce a pale yellow suspension. The solvent was then decanted, and the light yellow solid (68.4 mg, 86%) was washed with MeOH (2 × 10 mL) and air-dried. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C≡C) 2137 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.75 (d, J = 8.1 Hz, 2H, Ar), 7.38 – 7.26 (m, 10H, Ar), 7.10 (d, J = 8.1 Hz, 4H, Ar), 0.66 (s, <sup>2</sup> $J_{Hg-H} = 146$  Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 150.23, 145.42, 142.80, 140.01, 131.95, 127.92, 127.75, 127.62, 125.97, 121.54, 120.20 (Ar), 104.92, 92.26 (C≡C), 65.25 (quat C), 7.19 (CH<sub>3</sub>). Anal. Calcd for C<sub>31</sub>H<sub>22</sub>Hg<sub>2</sub>: C, 46.79; H, 2.79. Found: C, 46.55; H, 2.59.

[Au−T(DPF)T]<sub>1</sub>. To the solution of [H−T(DPF)T]<sub>1</sub> (33.0 mg, 0.09 mmol) in MeOH (10 mL) was added 2 mol equiv of Au-(PPh<sub>3</sub>)Cl (89.0 mg, 0.18 mmol), followed by NaOMe/MeOH (0.20 M, 0.45 mmol). The mixture was stirred at room temperature overnight, and the pale yellow powdery solid was then collected by decantation which was washed with MeOH (2 × 10 mL) and air-dried to give 109.7 mg (95%) of the pure product. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C≡C) 2113 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.73 (d, J = 7.3 Hz, 2H, Ar), 7.57−7.30 (m, 40H, Ar), 7.05 (d, J = 8.4 Hz, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 150.73, 144.15, 139.95, 134.24, 134.03, 132.03, 131.39, 131.31, 130.04, 129.22, 129.05, 128.88, 127.65, 127.55, 127.29, 126.14, 123.06, 119.95 (Ar), 103.69, 77.21 (C≡C), 65.22 (quat C). <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 43.69. Anal. Calcd for C<sub>65</sub>H<sub>46</sub>P<sub>2</sub>Au<sub>2</sub>: C, 60.85; H, 3.61. Found: C, 60.62; H, 3.45.

**X-ray Crystallography.** Colorless crystals of [Pt–T(D-PF)T], suitable for X-ray diffraction studies were grown by slow





<sup>*a*</sup> Reagents and conditions: (i) NaNO<sub>2</sub>/HBr, CuBr; (ii) trimethylsilylacetylene, Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, CuI, <sup>*i*</sup>Pr<sub>2</sub>NH, 75 °C; (iii) K<sub>2</sub>CO<sub>3</sub>, MeOH, rt.

# Scheme 2. Synthesis of Diphenylfluorene-Based Metal Alkynyls<sup>a</sup>



#### [Pt−T(DPF)T]<sub>∞</sub>

<sup>*a*</sup> Reagents and conditions: (i) *trans*-[PtPh(Cl)(PEt<sub>3</sub>)<sub>2</sub>] (2 equiv), CuI, <sup>*i*</sup>Pr<sub>2</sub>NH, rt; (ii) *trans*-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] (1 equiv), CuI, <sup>*i*</sup>Pr<sub>2</sub>NH, rt; (iii) Au(PPh<sub>3</sub>)Cl (2 equiv), NaOH/MeOH, rt; (iv) MeHgCl (2 equiv), NaOH/MeOH, rt; (v) HgCl<sub>2</sub> (2 equiv), NaOH/MeOH, rt.

evaporation of its solution in a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å) on a Bruker Axs SMART 1000 CCD area detector. The collected frames were processed with the software SAINT,<sup>46</sup> and an absorption correction was applied (SADABS)<sup>47</sup> to the collected reflections. The structure was solved by direct methods (SHELXTL)<sup>48</sup> in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on  $F^2$ . All non-hydrogen atoms were assigned with anisotropic displacement parameters. Crystal data:  $C_{65}H_{86}P_4Pt_2$ , M = 1381.40, monoclinic, space group  $P2_1/$ *n*, a = 8.9602(3), b = 17.6088(6), c = 42.253(2) Å,  $\beta = 91.999$ -(1)°, U = 6662.6(4) Å<sup>3</sup>, Z = 4, T = 293 K,  $\mu$ (Mo K $\alpha$ ) = 4.325 mm<sup>-1</sup>, 33 055 reflections measured, 11 722 unique,  $R_{\rm int} =$ 0.0405, final  $R_1 = 0.0464$ ,  $wR_2 = 0.1169$  for 8235  $[I > 2\sigma(I)]$ observed reflections (CCDC deposition number 235990).

### **Results and Discussion**

**Synthesis.** The synthesis of 9,9-bis(4-ethynylphenyl)fluorene,  $[H-T(DPF)T]_1$ , is outlined in Scheme 1. The compound 9,9-bis(4-bromophenyl)fluorene was prepared from the corresponding commercially available diamine by a classical Sandmayer procedure,<sup>39</sup> which then reacted with Me<sub>3</sub>SiC=CH via the Sonogashira coupling

reaction sequence followed by the proto-desilylation with K<sub>2</sub>CO<sub>3</sub> in MeOH to afford the diethynyl organic precursor [H-T(DPF)T]<sub>1</sub> in overall good yield.<sup>26-33</sup> Scheme 2 shows the chemical structure and the synthetic strategies to the polymers and their model complexes in the present study. The triple bonds are abbreviated by T and the diphenylfluorene ring by DPF. Model monomer complexes and polymers are differentiated by use of the subscripts 1 and  $\infty$ , respectively. The organic ligand  $[H-T(DPF)T]_1$  can serve as a versatile synthon to form a series of group 10-12 metal-acetylide complexes and polymers by adaptation of the dehydrohalogenation procedures reported in the literature.<sup>26–33</sup> The feed mole ratios of the platinum chloride precursors and the diethynyl ligand were 2:1 and 1:1 for the monomer and polymer syntheses, respectively, and each product was carefully purified to remove ionic impurities and catalyst residues. The monomer [Pt-T(DPF)T]1 was isolated by preparative TLC on silica. Purification of the polymer [Pt−T(DPF)T]<sub>∞</sub> was accomplished by silica column chromatography using  $CH_2Cl_2$  as the eluent, and it was obtained in high purity. Mercuration of  $[H-T(DPF)T]_1$ with a stoichiometric quantity of HgCl<sub>2</sub> using methan-



**Figure 1.** A perspective drawing of  $[Pt-T(DPF)T]_1$  with the ellipsoids shown at the 25% probability level. All hydrogen atoms have been omitted for clarity.

| Table 1. Structural | and | Therma | Properties of the |  |  |
|---------------------|-----|--------|-------------------|--|--|
| Polymers            |     |        |                   |  |  |

|   |               | v             |                       |   |
|---|---------------|---------------|-----------------------|---|
| polymer   | $M_{ m w}$    | Mn            | $M_{\rm w}/M_{\rm n}$ | T <sub>decomp</sub> (onset) (°C)                |
| $\begin{array}{l} [Pt-T(DPF)T]_{\infty} \\ [Hg-T(DPF)T]_{\infty} \end{array}$ | 45700<br>8900 | 43410<br>8590 | 1.05<br>1.04          | $\begin{array}{c} 347\pm5\\ 292\pm5\end{array}$ |

olic NaOH at room temperature gave an off-white solid identified as  $[Hg-T(DPF)T]_{\infty}{}^{37}$  Complex  $[Hg-T(D-T)]_{\infty}{}^{37}$ PF)T]<sub>1</sub>, as a model complex of [Hg−T(DPF)T]<sub>∞</sub>, was also synthesized by treatment of  $[H-T(DPF)T]_1$  with 2 equiv of MeHgCl, in which one coordination site is protected by a Me group, under similar basic conditions.<sup>49,50</sup> Likewise, we have also prepared the  $d^{10}$  digold(I) diacetylide counterpart [Au-T(DPF)T]<sub>1</sub>, an isoelectronic and isolobal analogue of  $[Hg-T(DPF)T]_1$ , by reaction of Au(PPh<sub>3</sub>)Cl with  $[H-T(DPF)T]_1$  in a mole ratio of 2:1 in the presence of a base.<sup>51</sup> The yields of these transformations are high in each case. All the new complexes and polymers are air-stable and can be stored without any special precautions. They generally exhibit good solubility in chlorocarbons such as CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> but are insoluble in hydrocarbons. However, we note that only the lower molecular weight fraction of [Hg- $T(DPF)\tilde{T}]_{\infty}$  can readily dissolve in chlorinated solvents, and there is always some insoluble portion left in the solution (presumably consisting of polymer chains of very high molecular weights) which requires filtration prior to characterization. Estimates of the molecular weights using gel permeation chromatography (GPC) in THF indicate that the degree of polymerization calculated from  $M_n$  are 46 and 16 for  $[Pt-T(DPF)T]_{\infty}$  and  $[Hg-T(DPF)T]_{\infty}$  (soluble portion), respectively (Table 1). The GPC values should be used with great care, and the GPC method does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. Rodlike polymers in solution possess different hydrodynamic properties than flexible polymers. So, calibration of the GPC with polystyrene standards might overestimate the values of the molecular weights of the polyynes to some extent. Similar molecular weight distributions have been observed for other reported platinum(II) polyynes based on the same

reference standard. However, the absence of end-group NMR resonances is suggestive of their high molecular weight. We found that both polymers can cast tough, free-standing thin films of good quality from appropriate solvents for optical characterization.

**Chemical Characterization.** The good solubilities of our new compounds render them amenable to spectroscopic studies. The IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P), MS, and elemental analysis data shown in the Experimental Section are in line with their chemical structures. The solution IR spectra are each characterized by a single sharp  $\nu(C \equiv C)$  absorption band at ca. 2098–2146 cm<sup>-1</sup>. The insoluble component of [Hg−T(DPF)T]<sub>∞</sub> also exhibits a characteristic solid-state IR  $\nu$ (C=C) band, similar to that for the soluble portion. The single <sup>31</sup>P {<sup>1</sup>H} NMR signals flanked by platinum satellites for [Pt-T(D- $PF)T]_{\infty}$  and  $[Pt-T(DPF)T]_1$  are consistent with a trans geometry of the square-planar Pt unit. The  ${}^{1}J_{P-Pt}$  values in  $[Pt-T(DPF)T]_{\infty}$  and  $[Pt-T(DPF)T]_1$  are typical of those for related *trans*-PtP<sub>2</sub> systems.<sup>52–54</sup> The formulas of the model complexes [Pt-T(DPF)T]<sub>1</sub>, [Hg-T(DPF)T]<sub>1</sub>, and  $[Au-T(DPF)T]_1$  were successfully established by the presence of intense molecular ion peaks in their respective positive FAB mass spectra. NMR analyses clearly indicate that a well-defined and symmetrical structure has been obtained for each compound. In all cases, <sup>1</sup>H NMR resonances arising from the protons of the organic moieties were observed. Notably, two distinct <sup>13</sup>C NMR signals for the  $\alpha$ - and  $\beta$ -acetylenic carbon atoms were observed, and the  $\alpha$ -acetylide chemical shifts are shifted downfield with respect to the free dialkyne, in agreement with the formation of metal-C(sp)  $\sigma$ -bond. The aromatic region of their <sup>13</sup>C NMR spectra also gives more precise information about the regiochemical structure of the main-chain skeleton and reveals a high degree of structural regularity in the polymers. For instance, only 18 well-defined peaks appear in the aromatic region, related to the 36 aromatic carbon atoms of the symmetric diplatinum structure for  $[Pt-T(DPF)T]_1$ . In each case, the carbon resonances due to the butyl or ethyl groups are clearly identified, and

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Pt-T(DPF)T]<sub>1</sub>

| Pt(1)-P(1)Pt(2)-P(3)Pt(1)-C(19)C(19)-C(20)C(24)-C(27)   | $\begin{array}{c} 2.2811(16)\\ 2.266(2)\\ 2.013(5)\\ 1.199(7)\\ 1.546(6) \end{array}$ | Pt(1)-P(2)Pt(2)-P(4)Pt(2)-C(47)C(46)-C(47)C(27)-C(40)  | 2.2886(16)<br>2.3065(18)<br>2.009(5)<br>1.211(7)<br>1.528(6) |
|---|---|--|--|
| $\begin{array}{l} P(1) - Pt(1) - P(2) \\ P(2) - Pt(1) - C(19) \\ P(3) - Pt(2) - C(47) \\ Pt(1) - C(19) - C(20) \\ Pt(2) - C(47) - C(46) \\ Pt(2) - C(47) - C(47) \\ Pt($ | 177.68(6)<br>90.91(15)<br>87.4(2)<br>177.8(5)<br>178.0(7)                             | $\begin{array}{l} P(1) - Pt(1) - C(19) \\ P(3) - Pt(2) - P(4) \\ P(4) - Pt(2) - C(47) \\ C(19) - C(20) - C(21) \\ C(43) - C(46) - C(47) \end{array}$ | 87.45(15)<br>175.11(9)<br>91.7(2)<br>174.9(6)<br>176.7(7)    |
| C(24) - C(27) - C(40)   | 112.7(3)  |  |  |
|   |   |  |  |

the characteristic peak at about 65.0 ppm corresponds to the sp<sup>3</sup>-carbon atom of the fluorene ring. Similarly, the <sup>13</sup>C NMR spectral features of [Pt-T(DPF)T]<sub>∞</sub> and [Hg-T(DPF)T]<sub>∞</sub> agree with the polymer structures shown. The three-dimensional molecular structure of  $[Pt-T(DPF)T]_1$ , as confirmed by X-ray crystallography, also helped to establish polymer structure in the solid state (Figure 1). Pertinent bond distances and angles are given in Table 2. The coordination geometry at each Pt center is square-planar with the two PEt<sub>3</sub> groups trans to each other, and the metal capping groups are connected by the 9,9-bis(4-phenylethynyl)fluorene ligand. To our knowledge, this is the first structurally characterized example of a diphenylfluorene-linked metal  $\sigma$ -alkynyl complex. The C=C bond length [average 1.205(7) Å] is characteristic of metal-alkynyl  $\sigma$ -bonding. The central fluorene ring is essentially planar which makes dihedral angles of 107° and 81° with the C(21)and C(40)-phenyl planes. The sp<sup>3</sup>-hybridized carbon atom C(27) was shown to adopt a tetrahedral geometry. The bond angles of  $177.8(5)^{\circ}$  and  $178.0(7)^{\circ}$  for the two Pt−C≡C units conform to the rigid-rod nature of this monomer.

**Thermal Analysis.** The thermal properties of the polymers were examined by thermal gravimetry (TG) and differential scanning calorimetry (DSC) under nitrogen (Table 1). Analysis of the TG trace (heating rate 20 °C/min) for  $[Pt-T(DPF)T]_{\infty}$  and  $[Hg-T(DPF)T]_{\infty}$ 

shows that they exhibit good thermal stability. Decomposition commences at 347 and 292 °C for [Pt-T(D- $PF)T]_{\infty}$  and  $[Hg-T(DPF)T]_{\infty}$ , respectively, and decomposition onset was defined as a mass loss of 2%. The onset temperature for the former is comparable to those for the dialkylfluorene-substituted platinum polyynes but is higher than those in related polymers trans- $[-Pt(PBu_3)_2C \equiv CRC \equiv C-]_n$  (R = phenylene, thienylene, pyridyl)<sup>27,33</sup> and *trans*- $[-Pt(PBu_3)_2C \equiv C(p-C_6H_4)_2C \equiv C \tilde{J}_n$  (296 °C). The onset of decomposition for [Hg-T(DPF)T]<sub>∞</sub> takes place at a higher temperature than those for  $[-HgC = CRC = C-]_n$  (R = dialkylfluorene) (200-280 °C).37 Introduction of the diphenylfluorene group with its unique cardo structure has the added effect of enhancing the thermal stability of this class of metal polyynes. We observe a sharp weight loss of 35% between 347 and 430 °C for [Pt-T(DPF)T]<sub>∞</sub> whereas 32% of the weight was lost for  $[Hg-T(DPF)T]_{\infty}$  as the temperature rose from 292 to 400 °C. The decomposition step is ascribed to the removal of six butyl groups from  $[Pt-T(DPF)T]_{\infty}$  and the loss of two phenyl plus one C= C groups from [Hg–T(DPF)T]<sub>∞</sub>. Both polymers did not display discernible glass transition in the DSC curves. The polymer [Pt-T(DPF)T]<sub>∞</sub> exhibits a minor endotherm coincident with mass loss due to decomposition. On the contrary, an exothermic peak was present at ca. 350 °C for  $[Hg-T(DPF)T]_{\infty}$ , and such a transition releases ca. 88.4 J/g of energy. Both polymer samples decompose without melting.

**Optical Absorption and Photoluminescence Spectroscopy.** The photophysical data of the new compounds are shown in Table 3. All the metal alkynyls in the present study display similar structured absorption bands in the near-UV region. The lowest energy transitions are predominantly intraligand in nature and exhibit both acetylenic and aromatic  $1(\pi\pi^*)$  character, possibly mixed with some admixture of metal orbitals. The 0–0 absorption peak is assigned as the S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital

|                           | $\lambda_{\max}$ (n              | m)    |                          | $\lambda_{ m em} \ ( m nm)^e$                        |              |             |                                       |
|---------------------------|----------------------------------|-------|--------------------------|--|--------------|-------------|---------------------------------------|
|                           | $\mathrm{CH}_2\mathrm{Cl}_2{}^a$ | film  | $E_{\rm g}~({\rm eV})^b$ | CH <sub>2</sub> Cl <sub>2</sub> (290 K) <sup>c</sup> | film (290 K) | film (11 K) | frozen $CH_2Cl_2$ (77 K) <sup>d</sup> |
| [Pt-T(DPF)T] <sub>1</sub> | 263 (11.2)                       | 270   | 3.60                     | 367  | 450          | 451         | $451~(29.4\pm 0.4)$                   |
|                           | 291 (8.7)                        | 291   |                          | 384*   | 514*         | 473*        | 472*                                  |
|                           | 321 (7.8)                        | 326   |                          | (0.022)  | 555*         | 483*        | 501*                                  |
|                           |                                  |       |                          |  |              | 496*        |                                       |
| [Pt−T(DPF)T] <sub>∞</sub> | 267                              | 270   | 3.38                     | 369  | 459          | 458         | $455~(24.6\pm 0.6)$                   |
|                           | 291                              | 290   |                          | 419*   | 512*         | 478*        | 486*                                  |
|                           | 331                              | 332br |                          | 456*   | 547*         | 490*        | 501*                                  |
|                           | 342                              |       |                          | 509*   |              | 505*        | 542*                                  |
|                           |                                  |       |                          | (0.003)  |              |             |                                       |
| [Hg–T(DPF)T] <sub>1</sub> | 267 (4.2)                        | 274   | 3.82                     | 386  | 490 br       | 494 br      | $462~(11.9\pm 1.9)$                   |
|                           | 280 (3.7)                        | 288   |                          | (0.013)  |              |             |                                       |
|                           | 309 (0.5)                        | 312   |                          |  |              |             |                                       |
| [Hg−T(DPF)T]∞             | 260                              | 263   | 3.80                     | 374*   | 470 br       | 473         | $465~(35.7\pm 2.8)$                   |
|                           | 275                              | 278   |                          | 390  |              | 498         |                                       |
|                           | 289                              | 298   |                          | (0.005)  |              | 523*        |                                       |
|                           | 309                              | 312   |                          |  |              |             |                                       |
| $[Au-T(DPF)T]_1$          | 262 (4.0)                        | 279   | 3.76                     | 369*   | 479          | 454*        | 452                                   |
|                           | 275 (4.9)                        | 293   |                          | 390  | 499*         | 482         | 470*                                  |
|                           | 287 (4.8)                        | 307   |                          | 413*   | 533*         | 499         | $485~(48.1\pm2.4)$                    |
|                           | 300 (4.8)                        |       |                          | (0.007)  |              | 532*        | 500*<br>525*                          |
| $[H-T(DPF)T]_1$           | 257 (3.3)                        | 253   | 3.92                     | 379  |              |             |                                       |
|                           | 297 (0.07)                       | 298   |                          | (0.22)   |              |             |                                       |
|                           | 309 (0.16)                       | 311   |                          |  |              |             |                                       |

**Table 3. Photophysical Data for the Monomers and Polymers** 

<sup>*a*</sup> Extinction coefficients are shown in parentheses. <sup>*b*</sup> Estimated from the onset wavelength of the solid-state optical absorption. <sup>*c*</sup> Fluorescence quantum yields shown in parentheses are measured in toluene relative to anthracene. <sup>*d*</sup> Phosphorescence lifetimes ( $\mu$ s) at 77 K for the peak maxima are shown in parentheses. <sup>*e*</sup> Asterisks indicate emission peaks appear as shoulders or weak bands. br = broad.

(LUMO), which are mainly delocalized  $\pi$  and  $\pi^*$  orbitals. Coordination of each of the metal entities to the organic system results in enhanced  $\pi \rightarrow \pi^*$  transitions for the aryleneethynylene moiety. As compared to the band at 309 nm in  $CH_2Cl_2$  for  $[H-T(DPF)T]_1$ , we find that the position of the lowest energy absorption band is redshifted after the inclusion of platinum fragment in [Pt- $T(DPF)T]_1$  and  $[Pt-T(DPF)T]_{\infty}$ . This reveals that  $\pi$ conjugation is preserved through the Pt site by mixing of the frontier orbitals of Pt and the ligand.<sup>55</sup> However, the absence of marked bathochromic shift in the lowest energy absorption peak for the corresponding Au(I) and Hg(II) compounds is indicative of little metal throughbond conjugation in these cases. The transition energies of the polymer  $[Pt-T(DPF)T]_{\infty}$  are lowered with respect to those of the monomer  $[Pt-T(DPF)T]_1$ , suggesting a well-extended singlet excited state in the Pt(II) polymer. The apparent lack of an energy shift in the  $S_0-S_1$ transition between [Hg-T(DPF)T]<sub>1</sub> and [Hg-T(DPF)T]<sub>∞</sub> shows that the lowest singlet excited state is confined to a single repeat unit, which is in contrast to their platinum(II) congeners. In energy terms, the experimentally determined HOMO–LUMO energy gaps ( $E_g$ ) as measured from the onset wavelength in solid film state are also tabulated in Table 3. According to the nature of the metal groups, the optical energy gaps of the polyynes follow the experimental order [Hg-T(D- $PF(T)_{\infty} > [Pt-T(DPF)T]_{\infty}$  and those of the monomers  $[Hg-T(DPF)T]_1 > [Au-T(DPF)T]_1 > [Pt-T(DPF)T]_1.$ With reference to other similar bi(p-phenylene)-linked compounds [(Cy<sub>3</sub>P)AuC=C(p-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CAu(PCy<sub>3</sub>)] (323 nm),<sup>34</sup> trans- $[Pt(Ph)(PEt_3)_2C \equiv C(p-C_6H_4)_2C \equiv CPt(Ph) (PEt_3)_2$ ] (349 nm), and *trans*-[-Pt(PBu\_3)\_2C=C(p-C\_6H\_4)\_2C=  $C-]_n$  (372 nm), we note that the presence of the non- $\pi$ -conjugated diphenylfluorene unit hinders conjugation in this molecular system (cf. 300, 321, and 342 nm for  $[Au-T(DPF)T]_1$ ,  $[Pt-T(DPF)T]_1$ , and  $[Pt-T(DPF)T]_{\infty}$ , respectively). In other words, the energy of the  $S_1$  singlet state (and hence the  $E_g$  value) can be varied depending on the electronic properties of the central spacer group, which is found to be vital for governing the efficiency of triplet-state emission (vide infra).

The thin film photoluminescence (PL) spectra of the new compounds were measured at various temperatures. In dilute fluid solutions at 290 K, we observe an intense purple-blue  $(\pi\pi^*)$  emission peak near 400 nm for each of them which is due to fluorescence  $(S_1 \rightarrow S_0)$ . As the temperature is cooled to 11 K, we observe virtually no fluorescence band but only the phosphorescence band associated with the organic chromophore. At 11 K, the principal emissive peak occurs at ca. 458 and 498 nm for [Pt-T(DPF)T], and [Hg-T(DPF)T], respectively, and at ca. 451, 499, and 494 nm for [Pt- $T(DPF)T_{1}$ ,  $[Au-T(DPF)T_{1}]$ , and  $[Hg-T(DPF)T_{1}]$ , respectively. The large Stokes shifts of these lower-lying emission peaks from the dipole-allowed absorptions (1.46-1.56 eV, see Figures 2 and 3) plus the long emission lifetimes are indicative of their triplet parentage, and they are thus assigned to the  ${}^{3}(\pi\pi^{*})$  excited states of the bis(ethynylphenyl)fluorene core.<sup>25,34,37</sup> The assignment can also be interpreted in terms of the observed temperature dependence of the PL data, in accordance with earlier work on platinum(II) polyynes. Representative examples of the temperature dependencies of the PL spectra for the monomers and the polymers are displayed in Figures 4-7. In each case, when the temperature is lowered, the triplet emission



**Figure 2.** Room temperature optical absorption spectrum and the photoluminescence (PL) spectrum (11 K) of  $[Pt-T(DPF)T]_{\infty}$  in solid.



**Figure 3.** Room temperature optical absorption spectrum and the PL spectrum (11 K) of  $[Hg-T(DPF)T]_{\infty}$  in solid.



**Figure 4.** Temperature dependence of the PL of  $[Pt-T(DPF)T]_1$ .

band increases in intensity, which is accompanied by a well-resolved vibronic structure, and such an increase in intensity indicates a long-lived triplet excited state that is more sensitive to thermally activated nonradiative decay mechanisms. The lifetime ( $\tau$ ) values at the peak maxima were found to be in the microsecond regime (11.9 ± 1.9 to 48.1 ± 2.4  $\mu$ s) at 77 K, in line with those for the phosphorescence observed in similar polymetallaynes previously reported.<sup>25–33</sup> In contrast, the solid-state emission appears broad and unstructured at room temperature for our mercurial compounds, which is characteristic of an aggregate or excimer site that is only weakly emissive.<sup>56</sup>



Figure 5. Temperature dependence of the PL of  $[Pt-T(DPF)T]_{\infty}$ .



Figure 6. Temperature dependence of the PL of  $[Hg-T(DPF)T]_{\infty}$ .



Figure 7. Temperature dependence of the PL of  $[Au-T(DPF)T]_1$ .

To examine the spatial extent of the singlet and triplet excitons in our systems, values of  $\Delta E(S_0-T_1)$  (energy gap between  $S_0$  and  $T_1$ ) were compiled to be 2.48–2.75 eV for all the metal diynes and polyynes. The measured  $\Delta E(S_1-T_1)$  values are 0.63, 0.65, 0.70, 0.69, and 0.70 eV for [Pt-T(DPF)T]\_1, [Pt-T(DPF)T]\_{\infty}, [Hg-T(DPF)T]\_1, [Hg-T(DPF)T]\_{\infty}, and [Au-T(DPF)T]\_1, respectively, and they correspond well with the  $S_1-T_1$  energy gap of 0.7  $\pm$  0.1 eV for similar  $\pi$ -conjugated Pt(II), Au(I), and Hg-(II) polyynes<sup>25,34,37</sup> and are close to the gaps estimated for a series of related organic conjugated polymers.<sup>17,57,58</sup> We attribute such a constant  $\Delta E(S_1-T_1)$  value to the exchange energy and possibly some additional constant contribution due to the admixture of the metal orbit-



**Figure 8.** Electronic energy level diagram of diphenylfluorene-based metal alkynyls determined from absorption and PL data. Dashed lines represent the levels for  $[Pt-T(BP)T]_1$  and  $[Pt-T(BP)T]_{\infty}$ . The S<sub>0</sub> levels are arbitrarily shown to be of equal energy.

als.<sup>28</sup> This finite exchange energy implies an excited state which is self-localized. According to the energy gap law, efficient phosphorescence is more readily accessible for higher  $S_0-T_1$  energy gaps, and we have shown that the organic triplet emissions of diphenylfluorene-based aryleneethynylenes of large optical gaps have been "illuminated" by the heavy-atom effect of group 10-12 transition metal elements.

On the basis of the absorption and PL data, we can construct an energy scheme for the lower-lying excitations shown in Figure 8 for the new polymers and the monomers. The energy values are absolute values with respect to the S<sub>0</sub> ground state. For the d<sup>8</sup> Pt(II) and d<sup>10</sup> Hg(II) systems, the lowest  $T_1$  state remains strongly localized, as can be inferred from the small energy difference between triplet emissions in the monomers and in the polymers. Previous calculations performed for *trans*- $[-Pt(PBu_3)_2C \equiv C(p-C_6H_4)C \equiv C-]_n$  (abbreviated) as  $[Pt-T(P)T]_{\infty}$ ) have also shown the triplet to be confined onto the phenylene ring.<sup>55</sup> Substitution of the metal groups does not seem to alter this strong confinement. For all these efficient phosphorescent metalorganic systems containing the conjugation-interrupting diphenylfluorene segment, they show  $T_1-S_0$  gaps of 2.5 eV or above, which correspond to  $S_1(PL) - S_0$  gaps of over 3.1 eV (3.18–3.38 eV). Apparently, the  $T_1$  levels for the Pt(II) compounds are higher than those for the corresponding Au(I) and Hg(II) congeners in the present system. The hindered conjugation by the use of diphenylfluorene unit in [Pt-T(DPF)T]<sub>1</sub> and [Pt-T(DPF)T]<sub>∞</sub> shifts the phosphorescence to the blue by 0.46 and 0.45 eV, respectively, compared to the bi(p-phenylene)containing Pt(II) counterparts [Pt-T(BP)T]1 and [Pt- $T(BP)T]_{\infty}$  (Chart 1). These data reveal that the intensity of phosphorescence reduces with the energy of the T<sub>1</sub>-S<sub>0</sub> emission and the rate of intersystem crossing (ISC) is higher for metal polyyne system with a larger optical gap. This was also supported by the peak height ratio from triplet emission to singlet emission at 77 K,  $\Delta E(T_1 \rightarrow S_0, S_1 \rightarrow S_0)$  (Table 4), which can serve as a good indicator to evaluate the relative ISC efficiency. Clearly, the order of  $S_1 - T_1$  crossover efficiency is  $[Pt - T(DPF)T]_{\infty}$  $(68) > [Pt-T(BP)T]_{\infty} \approx [Pt-T(P)T]_{\infty}$  (19) and  $[Pt-T(P)T]_{\infty}$  $T(DPF)T]_1$  (30) >  $[Pt-T(BP)T]_1 \approx [Pt-T(P)T]_1$  (6). Based on the work by others that the ISC efficiency





 $[Pt-T(DPF)T]_1$ 

<sup>*a*</sup> BP represents the bi(*p*-phenylene) moiety.

Table 4. Triplet Energies and Intersystem CrossingEfficiencies of Platinum(II) Monomers and PolymersContaining Diphenylfluorene, Bi(p-phenylene), andp-Phenylene Groups

|                           | $E(T_1-S_0)/eV$ | $\Delta E(\mathbf{T}_1 \rightarrow \mathbf{S}_0, \mathbf{S}_1 \rightarrow \mathbf{S}_0)^a$ |
|---------------------------|-----------------|--|
| $[Pt-T(DPF)T]_1$          | 2.75            | 29.6   |
| [Pt−T(DPF)T] <sub>∞</sub> | 2.71            | 68.0   |
| $[Pt-T(BP)T]_1$           | 2.29            | 6.0  |
| $[Pt-T(BP)T]_{\infty}$    | 2.26            | 18.9   |
| $[Pt-T(P)T]_1^b$          | 2.39            | 5.9  |
| $[Pt-T(P)T]_{\infty}^{b}$ | 2.38            | 18.5   |

<sup>*a*</sup> Ratio of the intensities of triplet emission to singlet emission at 77 K. <sup>*b*</sup> [Pt-T(P)T]<sub>1</sub> and [Pt-T(P)T]<sub> $\infty$ </sub> refer to the Pt diyne and polyyne containing *p*-phenylene spacer, and the data were taken from ref 29.

 $(\Phi_{\rm ISC})$  is close to unity for third-row transition metal chromophores,<sup>59–61</sup> the radiative  $(k_{\rm r})$  and nonradiative  $(k_{\rm nr})$  decay rates are related to the measured lifetime of triplet emission  $(\tau_{\rm T})$  and the phosphorescence quantum yield  $(\Phi_{\rm P})$  by the following expressions:

$$k_{
m nr} = (1-\Phi_{
m P})/ au_{
m T}$$
 $k_{
m r} = \Phi_{
m P}/ au_{
m T}$ 

The measured  $\Phi_P$  and  $\tau_T$  values for  $[Pt-T(DPF)T]_{\infty}$  are 0.25 ± 0.05 and 10.0 ± 0.5  $\mu$ s at 20 K, respectively. For  $[Pt-T(DPF)T]_{\infty}$ , the values calculated for  $k_{nr}$  and  $k_r$  are  $(9.5 \pm 0.5) \times 10^4 \text{ s}^{-1}$  and  $(2.5 \pm 0.5) \times 10^4 \text{ s}^{-1}$  at 20 K, respectively. For phosphorescence in aromatic hydrocarbon molecules,  $k_r$  is typically found to be between 0.1 and 1 s<sup>-1</sup>.<sup>62</sup> So, the heavy-atom effect of Pt increases the radiative decay rate for the triplet emission by 4 orders of magnitude, and incorporation of the 9,9-diphenylfluorene group in the present system displaying larger  $T_1$ -S<sub>0</sub> gaps can speed up the radiative decay rate as compared to the *p*-phenylene-spaced Pt polymer ( $k_r = (6 \pm 4) \times 10^3 \text{ s}^{-1}$  at 20 K).<sup>25</sup> The findings corroborate with the previous work that high-energy triplet states (and concurrently high optical gaps)





intrinsically lead to the more efficient phosphorescence in metal-containing aryleneethynylenes. The successful use of the conjugation-interrupting  $sp^3$ -carbon atom in the cardo diphenylfluorene structure in such metal polyynes can limit the effective conjugation length and gives rise to efficient crossover between  $S_1$  and  $T_1$  states.

## **Concluding Remarks**

The work reported here describes the synthesis of a new series of metal divnes and polyvnes of group 10-12 transition metals incorporating the diphenylfluorene moiety. All the compounds were analytically and spectroscopically characterized to possess a well-defined size and structure. The materials are organic-soluble, solution-processable, and thermally stable. While the sp<sup>3</sup>carbon atom in the cardo group hinders conjugation, these diphenylfluorene-based materials display strong organic triplet emissions. All the three transition metals (viz. Pt, Au, and Hg) can exert heavy-atom effects in the enhancement of ISC rate, and the effect is most significant for Pt having the highest T<sub>1</sub> energy state. Reduced conjugation in the presence of the non- $\pi$ conjugated segment shifts the optical gap and the phosphorescence band to the blue as compared to other platinum polyynes with carbocyclic and heterocyclic spacers. We consider that the sp<sup>3</sup>-carbon site in diphenylfluorene is an effective conjugation-interrupter to limit the conjugation length in metal polyynes, leading to materials of high optical gaps and high-energy triplet states. Our results further demonstrate that higher S<sub>0</sub>-T<sub>1</sub> energy gaps can facilitate efficient phosphorescence. It is anticipated that a structure-function (i.e., photoluminescence) relationship can be established, and valuable insight into the photophysical nature of  $(-C \equiv$  $C-Ar-C \equiv C-$ )<sub>n</sub> conjugated materials can be eventually derived. Future work should focus on polymers with high-energy triplets (and concurrently high optical gaps), and such an investigation is desirable for optoelectronic applications that utilize the T<sub>1</sub> state for light emission through light-harvesting techniques.

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**Supporting Information Available:** Preparations of ligand precursors, tables of X-ray crystal data for  $[Pt-T(DPF)T]_1$ , and phosphoresecence spectra of  $[Pt-T(DPF)T]_{\infty}$  and  $[Pt-T(BP)T]_{\infty}$  at 77 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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