

Invited Paper

**SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENT PROPERTIES
OF NEW PLATINUM-CONTAINING POLY(FLUORENYLENEETHYNYLENE)
ANCHORED WITH CARBAZOLE PENDANTS***

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Abstract A new luminescent and thermally stable platinum(II) polyyne polymer *trans*-[Pt(PBu₃)₂C≡CArC≡C]_n (**P1**) containing the 2,7-fluorene chromophoric spacer substituted by pendant carbazolyl group *via* long alkyl bridges. The regiochemical structures of these compounds were studied by various spectroscopic analyses. We report the photophysical properties of this group 10 polymetallayne and a comparison was made to its binuclear model complex *trans*-[Pt(Ph)(PEt₃)₂C≡CArC≡C] (**M1**) as well as to those with non-carbazole-containing fluorene spacer (**P2** and **M2**). Upon photoexcitation, each of **P1** and **M1** emits an intense purple-blue fluorescence emission in the near-UV to visible region in dilute fluid solutions at room temperature. Harvesting of organic triplet emissions harnessed through the strong heavy-atom effects of platinum metal was examined and at 77 K, each of the metalated compounds displayed dual emission bands, *viz.* both the fluorescence and the lower-lying phosphorescence. Spectroscopic results revealed that the formation of excimers was suppressed by introducing carbazole side groups. The spatial extent of the lowest singlet and triplet excitons in **P1** and **M1** was fully elucidated. Such organometallic poly(fluorenyleneethynylene)s anchored with the carbazole pendants was found to have an improved thermal stability and suppressed aggregation.

Keywords: Alkyne; Carbazole; Fluorene; Photoluminescence; Platinum.

INTRODUCTION

The use of electroluminescent polymers as the emitting layers in polymer light-emitting diodes (PLEDs) has attracted considerable academic and commercial interest because of the potential of these materials as components in flat-panel displays and lighting applications^[1–3]. In particular, polyfluorene (PF) and its derivatives have emerged as suitable materials for PLED or organic light-emitting diodes (OLEDs) due to their high photoluminescence (PL) quantum efficiencies, good thermal stabilities, and amenability to functionalization at the 9-position of fluorene. However, PF suffers from some deficiencies as a potential candidate for PLEDs of blue and other colors. First, PF tends to aggregate and form excimers on heating during device formation or operation under forward biases and this problem has been shown to be partially relieved *via* side-chain substitution at the C-9 position of the fluorene moieties^[4, 5]. Next, there is an unbalance in charge injection and transportation due to large injection barriers and different charge carrier mobilities. The lack of phosphorescence of organic based polymers also limits the efficiency of such kind of materials in PLED applications. Therefore, metal-containing molecules are the subject of intense attention in the scientific research

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areas^[6–11]. The insertion of a metal center into the polymeric chain contributes to the delocalized π -electron system and often gives electronic interaction between the transition metal and the organic molecular framework to generate the more abundant triplet states, thus enhancing the efficiencies of PLEDs. One of the interesting classes of conjugated organometallic polymers in this context goes to platinum(II) polyyne complexes. The desired physical and functional properties of these materials can be easily fine-tuned by the exploitation of different bridging spacers of the organic ligands. The key feature is that the incorporation of a heavy platinum metal in the backbone of the polymers can facilitate intersystem crossing, hence strongly populating the triplet excited states. The enhancement in triplet state population leads on one hand to the potential application of white light emission in OLED and PLED, but also on a fundamental standpoint, to other channels of photo-induced electronic communication such as the triplet-triplet energy transfer along the molecular main chain on (donor-acceptor)-containing organometallic polymers^[12]. In this connection, the resulting optoelectronic properties can be controlled and optimized through structural modifications of the donor-acceptor motifs^[13].

In previous works, we and others have reported a series of metallopolyyne bearing various fluorene-based functionalities^[14, 15]. By virtue of the fact that when bulky groups are incorporated into the C-9 position of the fluorene units, it can not only provide large steric hindrance and reduce interchain interaction but also enhance good thermal and morphological stability without substantially changing the electronic properties of the polymer backbone^[4]. Herein, we synthesize and study the photoluminescence properties of the first platinum(II) polyyne polymer consisting of a central fluorene ring substituted at the C-9 position by side chains attached to the bulky carbazole unit *via* long alkyl bridges.

EXPERIMENTAL

Materials

Solvents were predried and distilled from appropriate drying agents. All chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. The compounds *trans*-[PtCl(Ph)(PEt₃)₂]^[16], *trans*-[PtCl₂(PBu₃)₂]^[17] and **L**₁^[18] were prepared by the literature methods. 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. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory.

Instrumentation

Infrared spectra were recorded as CH₂Cl₂ solutions using the 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 ¹H and ¹³C chemical shifts quoted relative to SiMe₄ 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. The solution emission spectra were measured on a PTI Fluorescence Master Series QM1 spectrophotometer. The fluorescence quantum yields (Φ_F) were determined in CH₂Cl₂ at 293 K against the quinine sulphate standard in 0.5 mol/L H₂SO₄ standard ($\Phi_F = 0.54$)^[19]. 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 done with the Perkin-Elmer DTA-7 thermal analyzer.

Synthesis of **L**₁-2TMS

To a round-bottom flask, **L**₁-2Br (3.60 g, 4.37 mmol) with a catalytic amount of CuI, PPh₃ and Pd(OAc)₂ was added in a THF/NEt₃ solvent mixture. Under stirring, trimethylsilylacetylene (0.83 g, 8.74 mmol) was added. The reaction mixture was allowed to reflux overnight at 60°C. After cooling down the mixture to room temperature, the solvent was removed under reduced pressure. The obtained product was purified by silica column using a mixture of hexane/chloroform (1:1, *V/V*) as the eluent. The product was obtained as pale yellow crystals in 96% yield (3.60 g). Spectral data: MS (FAB): *m/z* 856 (*M*⁺). IR (CH₂Cl₂): $\nu(\text{C}\equiv\text{C})$ 2151 cm⁻¹. ¹H-NMR (CDCl₃): δ = 8.09 (d, 4H, Ar), 7.51 (m, 10H, Ar), 7.38 (m, 8H, Ar), 4.13 (m, 4H, CH₂), 1.81 (m, 4H,

CH₂), 1.61 (m, 4H, CH₂) 1.02 (m, 8H, CH₂) 0.50 (m, 4H, CH₂), 0.19 (s, 18H, SiMe₃). Anal. Calcd for C₅₉H₆₄N₂Si₂: C, 82.66; H, 7.52; N, 3.27. Found: C, 82.55; H, 7.34; N, 3.20.

Synthesis of **L**₁

L₁-2TMS (3.00 g, 3.51 mmol) was deprotected by KOH (0.50 g, 8.90 mmol) in MeOH solution. After stirring at room temperature for 3 h, the solution mixture was concentrated and poured into 1 mol/L HCl solution. The mixture was extracted by chloroform for four times. The organic layer was collected, dried over magnesium sulfate, and concentrated under reduced pressure. The obtained product was purified by silica column eluting with a mixture of hexane/chloroform (1:1, *V/V*). The product was obtained as a yellow solid in 94% yield (2.35 g). Spectral data: MS (FAB): *m/z* 712 (M⁺). IR (CH₂Cl₂): ν(C≡C) 2103 cm⁻¹, ν(C≡CH) 3283 cm⁻¹. ¹H-NMR (CDCl₃): δ = 8.05 (d, 4H, Ar), 7.57 (m, 2H, Ar), 7.43 (m, 8H, Ar), 7.25 (m, 8H, Ar), 4.11 (m, 4H, CH₂), 3.14 (s, 2H, C≡CH), 1.82 (m, 4H, CH₂), 1.62 (m, 4H, CH₂) 1.04 (m, 8H, CH₂) 0.49 (m, 4H, CH₂). Anal. Calcd for C₅₃H₄₈N₂: C, 89.28; H, 6.79; N, 3.93. Found: C, 89.34; H, 6.88; N, 3.80.

Synthesis of **P**1

Polymerization was carried out by mixing **L**₁ (25 mg, 0.035 mmol), *trans*-[PtCl₂(PBU₃)₂] (24 mg, 0.035 mmol) and CuI (3 mg) in ⁱPr₂NH/CH₂Cl₂ (20 mL, 1:1, *V/V*). After stirring at room temperature overnight, the solution mixture was evaporated to dryness. The residue was redissolved in CH₂Cl₂ and the mixture was filtered through a short column using pure CH₂Cl₂ as eluent to give a pale brown solution of the polymeric material. After removal of solvent by a rotary evaporator, a pale yellow-brown powder was obtained. Further purification can be accomplished by precipitating the polymer solution in CH₂Cl₂ from MeOH to give a pale yellow solid of **P**1 (69%, 32 mg). Spectral data: IR (CH₂Cl₂): ν(C≡C) 2099 cm⁻¹. ¹H-NMR (CDCl₃): δ = 8.05–8.03 (d, 4H, *J* = 5.4 Hz, Ar), 7.45–7.39 (m, 6H, Ar), 7.29–7.15 (m, 12H, Ar), 4.15–4.11 (d, 4H, *J* = 10.8 Hz, CH₂), 2.12 (m, 16H, PBU₃ + CH₂), 1.66–1.38 (m, 32H, PBU₃ + CH₂), 1.11 (m, 4H, CH₂), 0.88 (t, 18H, *J* = 8.1 Hz, PBU₃), 0.59 (m, 4H, CH₂). ³¹P (CDCl₃): δ = 3.91 (¹*J*_{Pt-P} = 2349 Hz). Anal. Calcd for (C₇₇H₁₀₀N₂P₂Pt)_{*n*}: C, 70.56; H, 7.69; N, 2.14. Found: C, 70.34; H, 7.89; N, 2.30. TGA (N₂): *T*_{dec} = 351°C. GPC (THF): *M*_w = 33110, *M*_n = 14770.

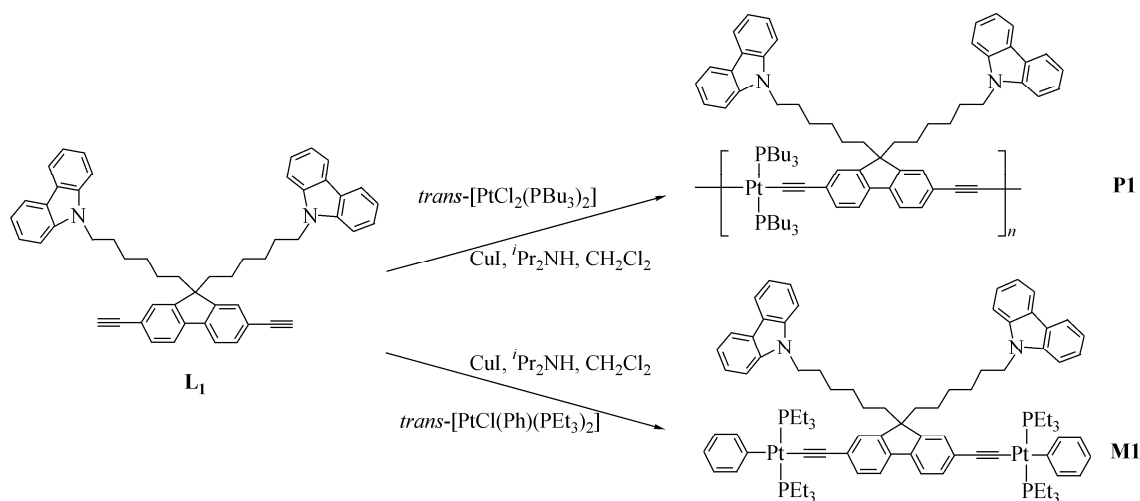
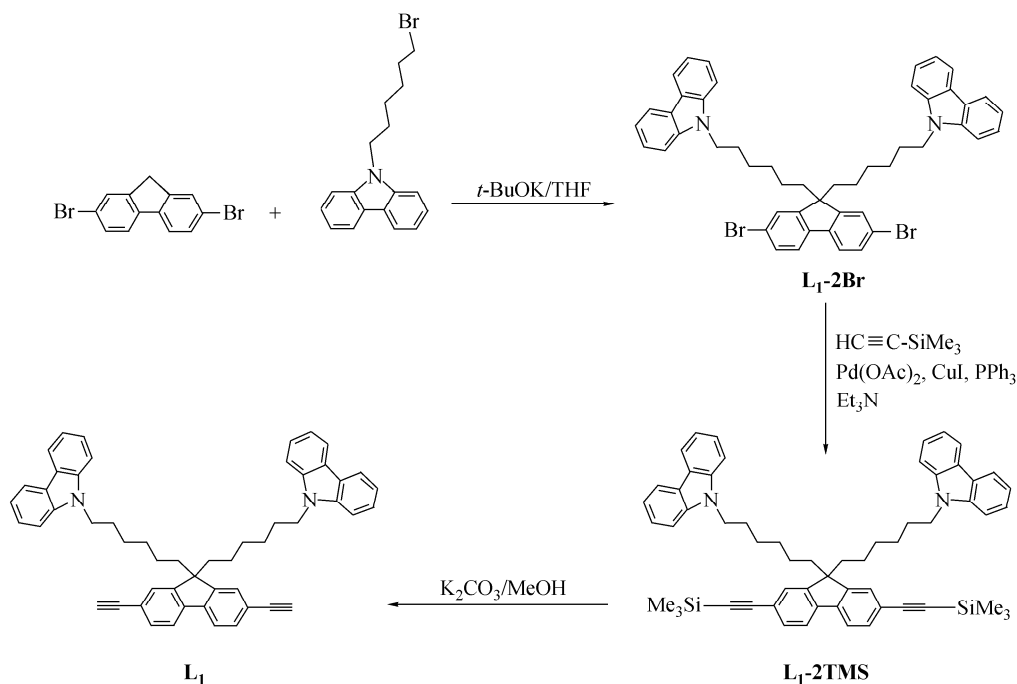
Synthesis of **M**1

A mixture of **L**₁ (15 mg, 0.021 mmol) and *trans*-[PtCl(Ph)(PEt₃)₂] (23 mg, 0.042 mmol) with CuI (3 mg) in ⁱPr₂NH (10 mL) and CH₂Cl₂ (10 mL) was stirred at room temperature overnight. The title complex was purified by preparative TLC on silica using CH₂Cl₂/hexane (2:1, *V/V*) as eluent to afford a pale yellow solid (10 mg, 28%). Spectral data: MS (positive FAB): *m/z* 1727 (M⁺). IR (CH₂Cl₂): ν(C≡C) 2099 cm⁻¹. ¹H-NMR (CDCl₃): δ = 8.05–8.03 (d, 4H, *J* = 5.4 Hz, Ar), 7.45–7.31 (m, 6H, Ar), 7.30–7.26 (m, 8H, Ar), 7.22–7.15 (m, 6H, Ar), 6.96–6.79 (m, 8H, Ar), 4.16–4.12 (t, 4H, *J* = 10.8 Hz, CH₂), 1.78 (m, 28H, PEt₃ + CH₂), 1.14 (m, 46H, PEt₃ + CH₂), 0.65 (m, 6H, CH₂). ³¹P (CDCl₃): δ = 10.71 (¹*J*_{Pt-P} = 2639 Hz). Anal. Calcd for C₈₉H₁₁₆N₂P₄Pt₂: C, 61.86; H, 6.77; N, 1.62. Found: C, 61.98; H, 6.67; N, 1.87.

RESULTS AND DISCUSSION

Synthesis and Characterization of Platinum(II) Polyyne and Diyne

The synthetic routes of the free alkyne precursor **L**₁ and the platinum(II) polyyne **P**1 and diyne **M**1 are illustrated in Schemes 1 and 2. The dibromo derivative of **L**₁^[20] was prepared according to the literature method, which was then reacted with Me₃SiC≡CH *via* the Sonogashira coupling reaction sequence followed by the proto-desilylation with K₂CO₃ in MeOH to afford the diethynyl organic precursor **L**₁^[21]. The metallocopolymer **P**1 was synthesized by reacting **L**₁ and *trans*-[PtCl₂(PBU₃)₂] at the stoichiometric ratio of 1:1 in the CuI/ⁱPr₂NH catalytic medium. Purification of the polymer was effected by silica column chromatography using CH₂Cl₂ as eluent followed by precipitation in a CH₂Cl₂/MeOH solvent mixture and it was obtained as a pale yellow solid in good yield. The metal diyne **M**1 was obtained by the dehydrohalogenating route from the reaction between **L**₁ and *trans*-[PtCl(Ph)(PEt₃)₂]^[6, 11–15]. The dimeric complex is considered as a model and good building block for the corresponding polymer in which useful information can be obtained.



The good solubilities of our complexes with long alkyl chains allow complete spectroscopic studies to be performed. All of the new compounds were unequivocally characterized by common spectroscopic techniques including FTIR and multinuclear NMR (^1H and ^{31}P) spectroscopies and FAB mass spectrometry. Each of the IR spectra of **P1** and **M1** shows a characteristic $\nu(\text{C}\equiv\text{C})$ IR vibration in which the stretching band appears at *ca.* 2099 cm^{-1} . It is also worthy of note that the absence of $\nu(\text{C}\equiv\text{CH})$ vibration at around 3300 cm^{-1} indicates completeness of the reactions with a concomitant formation of the metal-C(sp) σ -bonds. The $\nu(\text{C}\equiv\text{C})$ values of the platinum complex and polymer are also lower than that of the corresponding terminal acetylide ligand. This may be attributed to either (i) the metal-to-alkyne π back bonding or (ii) the $\text{M}^{\delta+}\text{-C}^{\delta-}$ polarity^[22]. The NMR

spectral data can give precise information about the regiochemical structure of the compounds in the solution phase. The ^1H -NMR resonances arising from the protons of the organic and phosphine groups were clearly observed. The single $^{31}\text{P}\{^1\text{H}\}$ NMR signal flanked by platinum satellites for **P1** and **M1** are consistent with a *trans* geometry of the square-planar $-\text{Pt}(\text{PR}_3)_2-$ ($\text{R} = \text{Et}$ or Bu) unit. The $^1J_{\text{P-Pt}}$ value of **P1** and **M1** is 2349 and 2639 Hz, respectively, which is analogous to those for related *trans*- PtP_2 systems^[23–37]. The model complex **M2** was successfully confirmed by positive FAB mass spectrometry with the detection of the respective molecular ion peak at $m/z = 1727$. The average molecular weights of **P1** were obtained by gel permeation chromatography (GPC) in THF against a monodisperse polystyrene (PS) calibration. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) are 33110 and 14770, respectively, from which a polydispersity index (PDI) of 2.24 can be obtained. This narrow PDI value indicates the polymer is a polycondensate with the proposed linear polymeric structure and has eleven repeating units per polymer chain on average. Since GPC does not give absolute values of molecular weights but provides a measure of hydrodynamic volume only, calibration of the method with the flexible PS polymer is likely to inflate the values of the molecular weights of our rodlike polyyne polymer to some extent^[38]. However, the lack of discernible end-group resonances in the NMR spectrum of the polymer solution supports a high molecular weight in **P1**. The thermal stability of the polymer evaluated by thermogravimetric analysis (TGA) indicates that the onset degradation temperature (T_d) of 5% weight loss in nitrogen is 351°C for **P1**, which is notably higher than those for *trans*- $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{Ar}-\text{C}\equiv\text{C}-]_n$ ($\text{Ar} = \text{C}_6\text{H}_4$, 300°C, bithienyl, 278°C, terthienyl, 290°C, oligopyridyl, 169–320°C, fluorenyl, 295°C and anthrylene, 315°C)^[39–41]. On the basis of the experimentally observed % weight loss, the decomposition step can be ascribed to the elimination of tributylphosphine group. In other words, the addition of two carbazole groups at the peripheral ends can enhance the thermal stability of the metallopolyne. Platinum polymer **1** also revealed no discernible glass transition in the DSC curve.

Optical Absorption Spectroscopy and Photoluminescence Properties

The electronic absorption spectra of all new platinum(II) complexes together with the diethynyl free ligand and the non-carbazole-containing species (**L2**, **P2** and **M2**, Chart 1) were investigated at room temperature in CH_2Cl_2 solutions. Metal-free **L1** exhibited strong absorption peaks that are related to the spin-allowed $\pi-\pi^*$ intraligand transitions in the near UV region. As compared to **L2** without the carbazole pendants, the shape and peak maximum of the absorption curves are quite similar, except for the additional well-resolved absorption peaks at 265 and 295 nm in **L1** attributable to the carbazole moieties (c.f. λ_{abs} of 9H-carbazole = 246, 257, 292, 321, 333 nm). Figure 1 shows the absorption spectra of **L1** and **L2**. With reference to the absorption maxima for their free ligands, we note a bathochromic shift of the position of the lowest energy absorption band when metal fragments are introduced. This reveals that π -conjugation of the ligands is preserved through the metal site by mixing of the frontier orbitals of the metal and the ligand. The transition energies of **P1** are lowered with respect to those of **M1**, indicating that the first optical absorption transition in the polymer arises from an electronic excitation that is delocalized over more than one repeat unit^[14, 35]. We associate the lowest energy peak with the $S_0 \rightarrow S_1$ transition from the HOMO to the LUMO and are easier to be recognized in energy terms and the HOMO–LUMO energy gaps (E_g) as measured from the onset wavelength in the solution phase are determined (Table 1). Figure 2 illustrates the energy level diagram for all of the compounds. The E_g follows the order diethynyl ligands > Pt(II) diynes > Pt(II) polyyne. The optical band gaps of the polymers estimated from the edge absorption of the polymer solutions **P1** and **P2** are almost identical, regardless of various carbazole pendants. This illustrates that the pendant groups do not appreciably change the excited state of the polymers, which implies similar distribution of effective conjugation lengths in the solution state of these polymers.

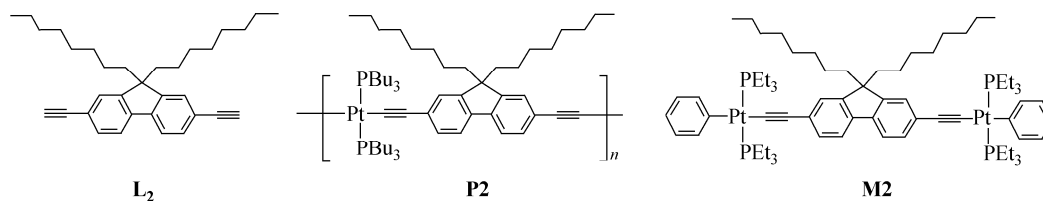


Chart 1 Model compounds containing 9,9-dioctyl-2,7-diethynylfluorene

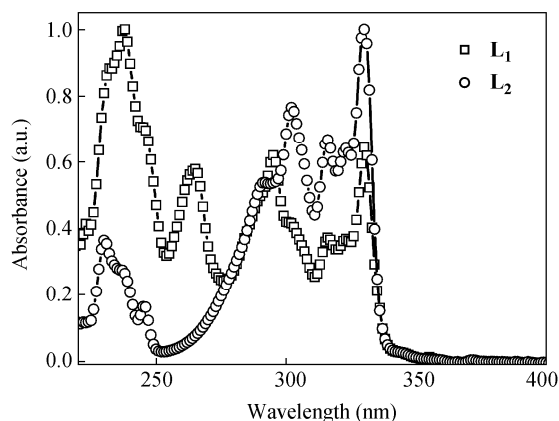


Fig. 1 UV spectra of **L₁** and **L₂** in CH₂Cl₂ at 293 K

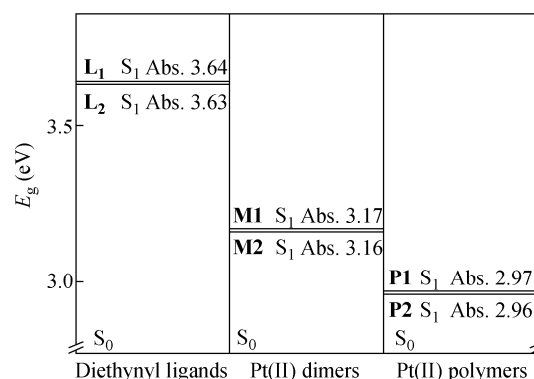


Fig. 2 The energy level diagram of diethynyl free ligands, Pt(II) polyynes and Pt(II) diynes
All the energy terms are in eV.

In the solution state, **P1** and **M1** are strongly luminescent in the blue region at room temperature. The measured photoluminescence (PL) lifetimes for the main emission peaks for these compounds are all very short in the nanosecond regime^[42]. These results together with the small Stokes shift from their absorption spectra suggest the emitting state to be characteristic of the spin-allowed singlet emission at room temperature. The influence of heavy platinum(II) center, which is mainly responsible for the efficient intersystem crossing, also renders **P1** weakly triplet-emitting at room temperature, so that a weak phosphorescence band appeared at 553 nm. This spectrum bears a similarity to that of **P2** which is phosphorescent at 552 nm (Fig. 3). To provide a deeper insight into the PL properties, the fluorescence quantum yields were recorded which are listed in Table 1.

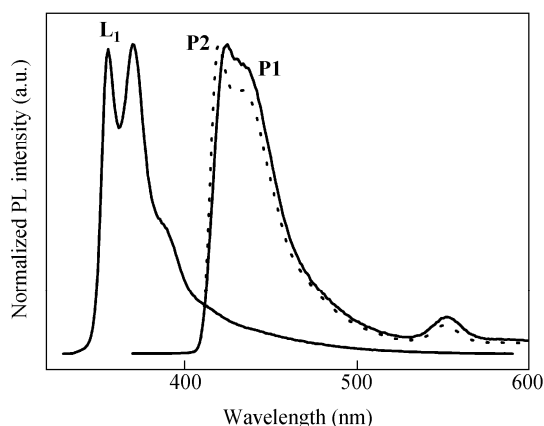


Fig. 3 PL spectra of **L₁**, **P1** (solid line) and **P2** (dotted line) at 293 K

The fluorescence quantum yields (Φ_F) of **M1** and **P1** are 4.60% and 0.91%, respectively. Both values are lower than those for **M2** (12.1%) and **P2** (2.01%). Hence, the existence of carbazole pendants together with the aliphatic long-chain attached is somehow detrimental to the singlet emission quantum yields of platinum(II) diyne and polyyne. Presumably, the carbazolyl group as an electron donor can transfer electrons to the main part of the compound by photo-induced process, and the long alkyl chains will improve the molecular vibration relaxation, leading to the emission quenching.

Table 1. Photophysical data of ligands and their corresponding platinum(II) complexes and polymers

Compound	$\lambda_{\max}$ (nm) ^a		λ_{em} (nm) ^a		
	CH ₂ Cl ₂	E_g (eV) ^b	CH ₂ Cl ₂ ^c (293 K)	Fluorescence quantum yields ^d (293 K) (%)	Frozen CH ₂ Cl ₂ (77 K) ^e
L₁	265 (13.5)	3.64	356 (12.9), 370*	16.1	--
	295 (14.4)				
	316 (9.0)				
	323 (8.8)				
	330 (14.0)				
P1	265	2.97	425 (2.0), 437*, 553*	0.91	431*, 554 (127.3), 593*, 604*
	295				
	334				
	348				
	399				
M1	264 (5.4)	3.17	413 (11.9), 439*	4.60	414*, 545 (126.5), 582*
	295 (4.2)				
	333 (3.4)				
	358 (3.5)				
	376 (3.0)				
L₂	291 (1.5)	3.63	333*, 346 (1.71)	43.1	--
	302 (2.2)				
	316 (1.9)				
	323 (1.8)				
	330 (3.7)				
P2	306	2.96	420 (1.2), 434*, 552*	2.01	424*, 554 (101.3), 589*, 606*
	399				
M2	308 (0.7)	3.16	410 (1.6), 547*	12.1	393*, 412*, 546 (117.1), 584*, 597*
	332 (1.1)				
	358 (3.9)				
	376 (5.5)				

^a Extinction coefficients ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are shown in parentheses;

^b Estimated from the onset wavelength of the solution-state optical absorption;

^c Fluorescence lifetimes τ_F (ns) at 293 K are shown in parentheses;

^d Fluorescence quantum yields Φ_F are measured in CH₂Cl₂ relative to quinine sulphate;

^e Phosphorescence lifetimes τ_P (μs) at 77 K for the peak maxima are shown in parentheses;

* Weak or shoulder peak

In each case of **P1** and **M1**, when the temperature is lowered to 77 K, the triplet emission band increases in intensity, which is characterized by a well-resolved vibronic structure with most weight in the 0-0 vibrational peak (Fig. 4a). We consider that the strong dependence of the triplet exciton arises from the fact that it is a long-lived triplet excited state and as such is more sensitive to thermally activated nonradiative decay mechanisms. The weak emission at around 431 nm in **P1** is due to singlet emission. The intense feature at the low-energy regime of the emission spectrum of **P1** with the maximum at around 554 nm is due to the emission from a triplet-excited state ($T_1 \rightarrow S_0$). The large energy shift observed between absorption and emission features together with the measured lifetime in the microsecond scale ascertains this emitting state as a T_1 excited state. The presence of carbazole in the side chain does not show a significant influence on the PL pattern of the

resulting complex relative to that for **P2** (Fig. 4b), which confirms that the emission of **P1** is to arise from the fluorene chromophore only (Fig. 4). The carbazole units do not play much role in affecting the emission maxima. Emission from the carbazole pendants is not observed, even when the samples are excited at the absorption peaks of the pendants. This signifies that an efficient energy transfer from the pendants to the polymer backbones has occurred. Thin film and dilute solution of **P1** show nearly identical absorption values and shapes (Fig. 4a), indicating an absence of ground-state aggregation in the solid state. However, thin film of **P1** (λ_{em} ca. 445 nm) reveals a red-shift of ca. 20 nm in PL peaks in contrast to dilute solution, suggesting that light emission from a more planar structure has occurred in the solid state. Φ_{F} is slightly higher for **M1** (or **M2**) than for the corresponding polymer **P1** (or **P2**) in each ligand system (Fig. 5), typical of other luminescent metal polyynes^[43]. In general, the PL efficiency reduces as the size of a molecule is increased as a result of a greater number of quenching sites and the possibility of bimolecular decay.

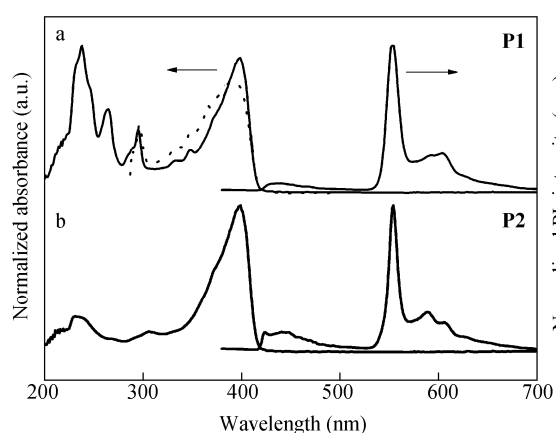


Fig. 4 Absorption (293 K) and PL (77 K) spectra of (a) **P1** and (b) **P2**

The thin film absorption spectrum of **P1** is shown as the dashed line in (a).

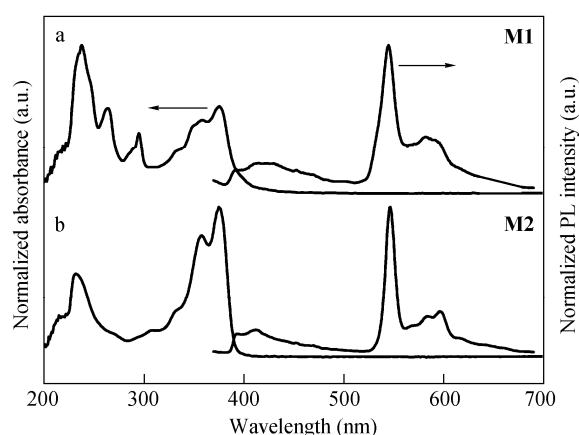


Fig. 5 Absorption (293 K) and PL (77 K) spectra of (a) **M1** and (b) **M2**

The experimentally calculated energy levels for the S_0 , S_1 and T_1 states are listed in Table 2 that allow a spatial extent of the singlet and triplet electronic excitons to be examined in the present metallated system. We observe in all instances that there is virtually little effect on the S_0 , S_1 and T_1 energy levels of a given metal complex with the presence of the carbazolyl pendant groups. There is a negligible shift of the phosphorescence maximum in the frozen glassy state at 77 K with respect to its corresponding spectra in solution, an indication that there is no noticeable molecular conformation change from the solution to solid film state. From Table 2, all of the compounds exhibit T_1 – S_0 gaps of 2.24–2.28 eV, which correspond to S_1 – S_0 gaps of ca. 2.88–3.02 eV. The measured $\Delta E(S_1$ – $T_1)$ values for our present systems lie within (0.7 ± 0.1) eV, corresponding closely to the S_1 – T_1 energy gaps estimated for some organic conjugated polymers^[44, 45]. We ascribe 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 orbitals. Moreover, the lowest T_1 state in the platinum(II) polyyne system is shown to be not delocalized as can be revealed from the insignificant energy difference observed between triplet emissions in **M1** and **P1**. This is also in line with the previous calculations done for *trans*-[–Pt(PBu₃)₂C≡C(*p*-C₆H₄)C≡C–]_n where the triplet states are confined on the phenylene ring^[46]. To enable a satisfactory evaluation of the relative efficiency of intersystem crossing, the peak height ratio from triplet emission to singlet emission at 77 K, $\Delta E(S_1 \rightarrow S_0, T_1 \rightarrow S_0)$, was taken as a good optical probe (Table 2)^[35]. We note a very high efficiency of triplet emission for the platinum polymers in each system and the intersystem crossing is much stronger in polymer than in the corresponding diyne. The order of S_1 – T_1 crossover efficiency is roughly: **P1** > **P2** (Table 2), which attests to the reduced aggregation effect of **P1** in the presence of the carbazole pendants.

Table 2. Experimental values of transition energies among the S_0 , S_1 and T_1 levels and intersystem crossing efficiencies (at 77 K) of platinum(II) diynes and polyynes (All energy units are in eV.)

Compound	$S_0 \rightarrow S_1$	$S_1 \rightarrow S_0^a$	$T_1 \rightarrow S_0^a$	$T_1 \rightarrow S_1^a$	$\Delta E(S_1 \rightarrow S_0, T_1 \rightarrow S_0)^b$
P1	3.11	2.88 (2.92)	2.24 (2.24)	0.68 (0.64)	42.7
P1	3.11	2.92 (2.92)	2.25 (2.24)	0.71 (0.69)	17.8
M1	3.30	3.00 (3.00)	c (2.28)	c (0.72)	5.8
M2	3.30	3.02 (3.01)	2.27 (2.27)	0.75 (0.74)	4.7

^a The data estimated from the PL spectra in CH_2Cl_2 glass at 77 K are shown in parentheses;^b Ratio of the intensities of triplet emission to singlet emission at 77 K;^c Not observed at 293 K

CONCLUSIONS

As a continuation of our earlier studies on the nature of photo-excited states in organometallic conjugated polymers as a function of π -conjugation in the bridging ligand, a new family of metal polyyne and diyne containing a specially functionalized fluorene group were synthesized and fully characterized. Our present work demonstrated that heavy atom effect brought about by the platinum(II) unit facilitates the intersystem crossing and phosphorescence can be readily measured using optical spectroscopy. The incorporation of electron-rich carbazole pendants into the polymer backbone *via* long alkyl spacers can effectively increase the thermal decomposition temperature and depress the tendency of spontaneous aggregation of the polymer chains. Such an approach will have an important impact on the way researchers think in the design of novel metal-containing conjugated polymers for future practical optoelectronic applications. It is anticipated that a structure-function relationship can be established and a valuable insight into the photophysical nature of $(-\text{C}\equiv\text{C}-\text{Ar}-\text{C}\equiv\text{C}-)_n$ conjugated materials can be eventually derived. Work is still in progress to modify the substituents at C-9 or develop other new fluorene-heterocycle hybrid monomers in an attempt to achieve better optical and mechanical performance. Further investigations of PLEDs incorporating these materials are currently underway.

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