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Synthesis, Characterization and Photovoltaic Properties of Polyplatinaynes with Side Chain Functionalization by Different Electron-Accepting Group

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Abstract

Four new solution-processable platinum-containing polyynes functionalized with triphenylamine backbone and different acceptor fragment in the side chain were synthesized and characterized by spectroscopic, thermal and optical methods. The main- and side-chains show different absorption features in the solar spectrum, resulting in broad absorption coverage of the whole visible region. By changing the acceptor group in the side chain, the photophysical properties including energy levels, absorption wavelength and bandgap of the polymers were finely tuned. As the strength of electron acceptor is increased, the power conversion efficiency (PCE) of organic polymer solar cells fabricated with these polymers as electron donor and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron acceptor was increased. PCE of 1.35% can be obtained from solar cell based on the polyplatinayne with the dicyanovinyl side group under illumination of an AM 1.5 solar cell simulator in a 1:4 (polymer:PCBM) blend ratio.

Graphical Abstract



Keywords Platinum · Metallopolymer · Synthesis · Intramolecular charge transfer · Photovoltaics

Extended author information available on the last page of the article

1 Introduction

Organic polymer solar cells (PSCs) have attracted considerable attention because of their unique advantages, such as low fabrication cost, light-weight, flexibility as well as large area of device and have great potential to be used as flexible devices [1–9]. Bulk heterojunction (BHJ) configuration of PSCs has received extensive studies, because such configuration creates large interfacial areas between the polymers and electron acceptors (e.g. fullerene derivatives, (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM)), thus leading to efficient photoinduced charge separation in the device [1, 2, 10–13]. In this context, low-bandgap conjugated polymers have shown great promises for photoinduced charge generation in BHJ cells to capture a large portion of solar energy. Previously, the power conversion efficiency (PCE) of PSCs based on poly(3-hexylthiophene-2,5-diyl) (P3HT) thin film blended with PCBM has reached up to 4-5% [2, 14, 15]. However, to further improve the efficiency of P3HT-based PSCs its absorption must be broadened in order to match well with the solar spectrum. Since approximately 54% of the sunlight coverage is distributed from 380 to 800 nm, an ideal active layer for a PSC should have a broad and strong absorption spectrum in this range. The mismatch between the absorption spectrum of the photoactive layer and the sunlight spectrum leads to low short-circuit current density $(J_{\rm sc})$, which is responsible for the low PCE of the PSCs in the past. Later on, PSCs fabricated with low bandgap polymers with high J_{sc} reached a PCE over 5% [16–20]. A key characteristic of conjugated polymers is the easy modification of their molecular structure and properties by side chain substitution or copolymerization. The substituents added in the side chain of the polymer could result in the lowering of their bandgaps. Moreover, the structure of these polymers results in the improvement of the isotropic charge transport, which is important for highly efficient PSCs [21-27]. Besides, triarylamine derivatives have propeller shape and strong electron-donating ability, which have been widely used as an electron donor in photoactive materials to afford promising PCEs with improved hole mobility of their PSCs [28 - 34].

As an alternative class of conjugated polymers, it would be interesting to integrate metallated chromophore into the conjugated polymer structures [35-38]. The introduction of metal ions into conjugated polymers offers various possible merits [35-38]: (a) the metal ions may act as architectural templates in the assembly of the organic subunits; (b) they may provide redox-active and paramagnetic centers to generate active species for charge transport and may alter the electronic and optical properties of organic π -systems; (3) they allow fine-tuning of the HOMO–LUMO gap through the interaction of the metal d-orbitals with the ligand orbitals; (4) there is a diversity of molecular frameworks based on different coordination number, geometry and valence shells of different metal atoms. Among these, platinum-containing polymers are good candidates for PSCs since they have high charge-carrier mobility and good absorption properties [39-41]. In this work, we designed a series of new polyplatinayne polymers, which contain both main-chain and sidechain chromophores. The absorption of these polymers was expected to match a majority of the visible part of the sunlight spectrum. Figure 1 shows the design and general structure of the polymers. The main chain and side chain were connected by the Z unit, such as nitrogen atom. The main chain and the side chain would exhibit different absorption range in the solar spectrum. Herein, we report the synthesis and characterization of four new polymetallayne polymers of Pt with triphenylamine backbone and different electron acceptors in the side chain. Photovoltaic properties of these polymers were investigated by fabricating BHJ photovoltaic devices using these polymers as the electron donor and PCBM as the electron acceptor. The results indicated that the J_{sc} and PCE of their PSCs can be significantly enhanced by increasing the strength of the acceptor in the side chain. BHJ solar cells fabricated from these polymers gave the best PCE of 1.35% with a J_{sc} of 4.47 mA cm⁻² under illumination of an AM 1.5 solar cell simulator.

2 Experimental Section

2.1 Materials and Instruments

All the chemicals were purchased from Acros or Aldrich and used as received unless otherwise specified. 5'-Bromo-2,2'bithiophene-5-carbaldehyde [42-44], *trans*-[Pt(PEt₃)₂PhCl] [45] and *trans*-[Pt(PBu₃)₂Cl₂] [46] were prepared using the methods reported in the literature. THF was dried by distillation from sodium with benzophenone as an indicator under a nitrogen atmosphere. Separation and purification of products were achieved by column chromatography on silica gel. TLC was carried out in air using laboratory grade solvents as eluents.



Fig. 1 The general skeleton of the polyplatinaynes containing both main chain and side chain chromophores

The positive-ion fast atom bombardment (FAB) mass spectra were recorded in *m*-nitrobenzyl alcohol matrices on a Finngin-MAT SSQ710 mass spectrometer. Infrared spectra were recorded on the Nicolet Magna 550 Series II FTIR spectrometer, using KBr pellets for solid state spectroscopy. NMR spectra were measured in deuterated solvents as the lock and reference on Varian INOVA 400 instrument or Bruker AV 400 MHz FT-NMR spectrometer, with ¹H and ¹³C NMR chemical shifts quoted relative to Me₄Si standard and ³¹P chemical shifts relative to an 85% H₃PO₄ external reference. Electronic absorption spectra were obtained with a Hewlett Packard 8453 spectrometer. Solution state photoluminescence measurements were obtained by the LS50B fluorescent spectrometer. For lifetime measurements, the third harmonics, 355 nm line of a Q-switched Nd: YAG laser was used as the excitation light source. The emission was recorded by using a PMT and a HP54522A 500 MHz oscilloscope. The PL spectra were measured in CH₂Cl₂ with a PTI Fluorescence Master Series QM1 spectrophotometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) (HP 1050 series HPLC with visible wavelength and fluorescent detectors) using polystyrene standards. Thermal analysis was performed with a Perkin-Elmer TGA6 thermal analyzer.

2.2 Fabrication and Characterization of Polymer Solar Cells

PCBM was purchased from American Dyes while PEDOT/ PSS (Baytron P VPAI 4083) was purchased from H. C. Starck. Device configuration of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/ polymer:PCBM/Al was applied in this study. Indium tin oxide (ITO) coated glass substrates (10 Ω per square) were cleaned by sonication in toluene, acetone, ethanol, and deionized water, dried in an oven, and then cleaned with UV ozone for 300 s. As-received PEDOT:PSS solution was passed through the 0.45 µm filter and spin-coated on patterned ITO substrates at 5000 rpm for 3 min, followed by baking in N2 at 150 °C for 15 min. P1-P4:PCBM (1:4 by weight) active layer was prepared by spin-coating the toluene solution (4 mg mL⁻¹ of metallopolyyne and 16 mg mL⁻¹ of PCBM) at 800 rpm for 2 min. The substrates were dried at room temperature under vacuum for 1 h and then stored under high vacuum $(10^{-5}-10^{-6} \text{ Torr})$ overnight. An Al electrode (100 nm) was evaporated through a shadow mask to define the active area of the devices $(2 \text{ mm}^2 \text{ circle})$. All the fabrication procedures (except drying, PEDOT:PSS annealing, and Al deposition) and cell characterization were performed in air. Power conversion efficiency (PCE) was determined from J-V curve measurement (using a Keithley 2400 sourcemeter) under white light illumination (at 100 $mW cm^{-1}$). For white light efficiency measurements, an Oriel 66002 solar light simulator with an AM1.5 filter was used. The light intensity was measured by a Molectron Power Max 500D laser power meter. For the measurement of the external quantum efficiency (EQE), different wavelengths were selected with an Oriel Cornerstone 74000 monochromator, while the photocurrent was measured with a Keithley 2400 sourcemeter. The light intensity was measured with a Newport 1830-C optical power meter equipped with a 818-UV detector probe.

2.3 General Procedures for the Synthesis of Polyplatinayne Polymers P1–P2

The synthesis of P1 was taken as a typical example.

To a stirred mixture of L1 and *trans*- $[Pt(PBu_3)_2Cl_2]$ in a 1:1 molar ratio in freshly distilled triethylamine and CH₂Cl₂ solution (1:1, v/v), CuI (3.0 mg) was added. The solution was stirred at room temperature for 24 h under a nitrogen atmosphere. The solvent was removed on a rotary evaporator in vacuo. The residue was dissolved in CH₂Cl₂ and filtered through a short aluminum oxide column using the same eluent to remove ionic impurities and catalyst residue. After removal of the solvent, the crude product was washed with hexane followed by methanol and then repeated precipitation from CH₂Cl₂/hexane and dried in vacuo to afford polymer **P1** (62%) as a red solid. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 9.85$ (s, 1H, CHO), 7.68 (m, 1H, Ar), 7.45–7.42 (m, 2H, Ar), 7.32 (m, 1H, Ar), 7.24 (m, 1H, Ar), 7.18-7.16 (m, 5H, Ar), 7.0–7.03 (m, 2H, Ar), 6.97–6.94 (m, 4H, Ar), 2.17–2.13 (m, 12H, PC_4H_0), 1.62–1.56 (m, 12H, PC_4H_0), 1.48–1.43 (m, 12H, PC₄H₉), 0.93 (t, J = 7.2 Hz, 18H, PC₄H₉) ppm. ³¹P NMR (161 MHz, CDCl₃): $\delta = 2.76 ({}^{1}J_{P,Pt} = 2345 \text{ Hz}) \text{ ppm}.$ IR (KBr) (cm⁻¹): 2098 ($\nu_{C=C}$); 1667 (ν_{CHO}).

P2: Red solid. Yield: 65%. ¹H NMR (400 MHz, CDCl₃): δ = 9.86 (s, 1H, CHO), 7.68 (m, 1H, Ar), 7.50–7.44 (m, 6H, Ar), 7.33 (m, 1H, Ar), 7.26 (m, 1H, Ar), 7.20 (m, 1H, Ar), 7.13–7.09 (m, 6H, Ar), 7.04 (m, 2H, Ar), 6.80 (m, 2H, Ar), 2.15–2.11 (m, 12H, PC₄H₉), 1.62–1.58 (m, 12H, PC₄H₉), 1.51–1.46 (m, 12H, PC₄H₉), 0.95 (t, *J*=7.2 Hz, 18H, PC₄H₉) ppm. ³¹P NMR (161 MHz, CDCl₃): δ =3.29 (¹*J*_{P-Pt}=2315 Hz) ppm. IR (KBr) (cm⁻¹): 2085 (ν _{C≡C}); 1666 (ν _{CHO}).

2.4 General Procedures for the Synthesis of Polyplatinayne Polyynes P3–P4

The synthesis of **P3** was taken as a typical example.

To a mixture of **P1** (40 mg) and malononitrile (3 mg) in dry chloroform (10 mL), triethylamine (1 drop) was added under a nitrogen atmosphere. The resulting mixture was heated to reflux for 2 h. After cooling down to room temperature, the solvents were removed and methanol (20 mL) was added. The precipitate was collected and



Scheme 1 Synthetic routes to dinuclear model compounds M1-M2

washed with methanol and dried to provide **P3** (38 mg, 95%) as a dark red solid. ¹H NMR (400 MHz, CDCl₃): δ =7.74 (s, 1H, HC=C(CN)₂), 7.63 (m, 2H, Ar), 7.45–7.40 (m, 3H, Ar), 7.26 (m, shielded by CHCl₃ proton, 1H, Ar) 7.21–7.17 (m, 5H, Ar), 7.05–7.03 (m 2H, Ar), 6.97–6.95 (m, 4H, Ar), 2.15–2.13 (m, 12H, PC₄H₉), 1.60–1.59 (m, 12H, PC₄H₉), 1.48–1.43 (m, 12H, PC₄H₉), 0.95–0.88 (m, 18H, PC₄H₉) ppm. ³¹P NMR (161 MHz, CDCl₃): δ =2.78 (¹*J*_{P-Pt}=2348 Hz) ppm. IR (KBr) (cm⁻¹): 2220 (ν _{CN}); 2095 (ν _{C=C}).

P4: Dark red solid. Yield: 89%. ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (s, 1H, C = CH), 7.63 (m, 1H, Ar), 7.50–7.47 (m, 6H, Ar), 7.41 (m, 1H, Ar), 7.27 (m, 1H, Ar), 7.13–7.09 (m, 6H, Ar), 7.05 (m, 2H, Ar), 7.80 (m, 2H, Ar), 2.15–2.11 (m, 12H, PC₄H₉), 1.62–1.56 (m, 12H, PC₄H₉), 1.51–1.46 (m, 12H, PC₄H₉), 0.97–0.94 (m, 18H, PC₄H₉) ppm. ³¹P NMR (161 MHz, CDCl₃): δ = 3.30 (¹*J*_{P-Pt}=2318 Hz) ppm. IR (KBr) (cm⁻¹): 2221 (*ν*_{CN}); 2084 (*ν*_{C=C}).

2.5 General Procedures for the Synthesis of Dinuclear Pt(II) Model Complexes M1–M2

The synthesis of M1 was taken as a typical example.

To a stirred mixture of L1 (24 mg, 0.03 mmol) and trans-[Pt(PEt₃)₂PhCl] (35 mg, 0.064 mmol) in freshly distilled triethylamine (10 mL) and CH₂Cl₂ (10 mL) was added CuI (3.0 mg). The solution was stirred at room temperature under nitrogen over a period of 24 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel eluting with hexane/ CH_2Cl_2 (1:1, v/v) to give M1 (57%) as a red solid. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 9.85$ (s, 1H, CHO), 7.67 (d, J = 4.0 Hz, 1H, Ar), 7.43 (d, J = 8.8 Hz, 2H, Ar), 7.34-7.31 (m, 5H, Ar), 7.24 (d,J = 4.0 Hz, 1H, Ar), 7.20 (d, J = 8.4 Hz, 4H, Ar), 7.16 (d, J=3.6 Hz, 1H, Ar), 7.05 (d, J=8.8 Hz, 2H, Ar), 6.98–6.94 (m, 8H, Ar), 6.82-6.78 (m, 2H, Ar), 1.80-1.74 (m, 24H, PC₂H₅), 1.14–1.06 (m, 36H, PC₂H₅) ppm. ¹³C NMR $(100 \text{ MHz}, \text{CDCl}_3)$: $\delta = 182.41$ (CHO), 156.42, 148.04, 147.60, 146.59, 143.67, 141.12, 139.20, 137.51, 135.21, 133.73, 131.80, 127.28, 126.45, 126.28, 125.02, 124.60, 124.54, 123.64, 122.89, 122.37, 121.19 (Ar), 112.75,

109.68 (C=C), 15.24, 15.08, 14.90, 8.05 (PC₂H₅) ppm. ³¹P NMR (161 MHz, CDCl₃): δ =9.87 (¹*J*_{Pt-P}=2625 Hz) ppm. FAB-MS (*m*/*z*): 1500.7 [M+1]⁺. IR (KBr) (cm⁻¹): 2093 ($\nu_{C=C}$); 1664 (ν_{CHO}).

M2: Red solid. Yield: 44%. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.86$ (s, 1H, CHO), 7.67 (d, J = 4.0 Hz, 1H, Ar), 7.49–7.45 (m, 6H, Ar), 7.33–7.31 (m, 5H, Ar), 7.25 (d, J = 4.0 Hz, 2H, Ar), 7.20 (d, J = 4.0 Hz, 1H, Ar), 7.14–7.08 (m, 6H, Ar), 7.04 (d, J = 3.6 Hz, 2H, Ar), 6.99–6.95 (m, 4H, Ar), 6.83–6.81 (m, 4H, Ar), 1.78–1.72 (m, 24H, PC₂H₅), 1.14–1.06 (m, 36H, PC₂H₅) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 182.43$ (CHO), 155.92, 147.45, 147.43, 146.17, 145.60, 141.27, 139.86, 139.07, 138.98, 137.48, 134.15, 130.16, 129.48, 128.02, 127.43, 127.35, 127.27, 126.67, 126.33, 124.78, 123.78, 123.47, 123.29, 122.16 (Ar), 121.35, 102.41 (C=C), 15.30. 15.13, 14.96, 8.05 (PC₂H₅) ppm. ³¹P NMR (161 MHz, CDCl₃): $\delta = 9.96$ (¹ $J_{Pt-P} = 2613$ Hz) ppm. FAB-MS (m/z): 1663.6 [M + 1]⁺. IR (KBr) (cm⁻¹): 2080 ($\nu_{C=C}$); 1663 (ν_{CHO}).

3 Results and Discussion

3.1 Synthesis and Characterization of Pt(II) Complexes

The synthetic routes of dinuclear model compounds M1-M2 and polymers P1-P4 are shown in Schemes 1 and 2, respectively. The experimental details of the diethynyl precursors are described in the supporting information [47]. The polymers P1-P2 were prepared by the Sonogashira-type dehydrohalogenation reaction between platinum dichloride precursors and the corresponding diethynyl ligands [48–52]. The feed mole ratio of the platinum precursors and the ethynyl ligands were 1:1 and 2:1 for the synthesis of polymers P1-P2 and dimers M1-M2, respectively, and each product was purified carefully to remove ionic impurities and catalyst residues. The dinuclear Pt complexes serve as good discrete molecular model complexes for the corresponding polymers as far as their spectroscopic and photophysical properties are concerned. However, to our surprise, for the polymers **P3** and **P4**, they cannot be prepared from their diethynyl



Scheme 2 Synthetic routes to polymers P1-P4

precursors, which may be due to the poor stabilities of their respective precursors under the reaction condition. Instead, they were successfully synthesized from their respective polymers **P1** and **P2** in high yields via the Knoevenagel condensation reaction using the facile procedure of treating **P1** or **P2** with malononitrile in chloroform in the presence of a catalytic amount of triethylamine [44, 53]. The polymers **P3** and **P4** can be purified by column chromatography over aluminium oxide followed by the repeated precipitation and isolated in good yields and high purity. All of these Pt(II) compounds are thermally and air-stable solids and they are soluble in common chlorinated hydrocarbons and toluene.

The chemical structures of the Pt(II) complexes and polymers were verified by NMR (¹H and ³¹P) and IR spectroscopies. The single ${}^{31}P$ -{ ${}^{1}H$ } NMR signal flanked by platinum satellites for each of the platinum(II) complexes is consistent with a *trans* geometry of the $Pt(PBu_3)_2$ or $Pt(PEt_3)_2$ in such square-planar geometry. The ${}^{1}J_{P-Pt}$ values of around 2320 Hz for the PBu₃ moieties and 2620 Hz for the PEt₃ are typical of those for related *trans*-PtP₂ systems [48–52]. All the terminal alkynyl ligands and Pt(II) compounds were subjected to IR measurements in which the vibrational frequencies of the acetylenic functional groups were detected. In the IR spectra of the diethynyl ligands, L1–L2 display IR $\nu_{C=C}$ absorption at around 2095–2102 cm⁻¹. The corresponding terminal acetylenic C≡C-H stretching vibrations occur at around 3271-3277 cm⁻¹. The C=C stretching frequencies for **P1–P4** are located in the range of 2084–2098 cm⁻¹, which are lower than those for the corresponding free alkynyl precursors, in line with a higher degree of conjugation in the former [50]. The ν_{CHO} vibrations appear at the region of

Table 1 GPC and TGA data of P1-P4

Polymer	M _n ^a	$M_{ m w}^{ m b}$	PDI ^c	DP ^d	$T_{\rm dec} [^{\circ}{\rm C}]$
P1	12,130	21,990	1.89	11	331
P2	17,600	33,440	1.90	14	393
P3	12,700	22,860	1.80	11	353
P4	18,330	35,390	1.93	14	363

 ${}^{a}M_{n} =$ Number-average molecular weight

 ${}^{b}M_{w}$ = Weight-average molecular weight

^cPDI = Polydispersity index

^dDP = Degree of polymerization (calculated from M_n values)

1663–1667 cm⁻¹ for M1–M2 and P1–P2 whereas the $\nu_{C\equiv N}$ stretching bands vibrate at 2220 cm⁻¹ for P3–P4.

From the results of gel-permeation chromatography (GPC), the number-average molecular weights (M_n) of **P1–P4** were calibrated against polystyrene standards, which ranged from 12,130 to 18,330 g/mol (Table 1). Their polydispersity indexes (PDI ~ 1.80–1.93) are consistent with the proposed linear structure from the condensation polymerization [48–52]. The thermal properties of the polymers were also examined by thermal gravimetric analysis (TGA) under a nitrogen atmosphere (Table 1). All the polymers exhibit good thermal stability with the decomposition onsets over 330 °C.

3.2 Optical Properties

The photophysical properties of all new Pt(II) complexes were investigated by UV-Vis and photoluminescence (PL) spectroscopies in CH_2Cl_2 solution and the related data are Table 2Photophysical data ofM1–M2 and P1–P4

	Absorption (293 K)	Emission (293 K)		Emission (77	Emission (77 K)	
	λ_{abs} [nm]	$\overline{E_{g} [eV]^{b}}$	$\lambda_{\rm em}$ [nm]	$\lambda_{\rm em}$ [nm]	τ [ns]	
M1	377 (6.2), 449 (3.2)	2.31	571	594	3.46	
M2	418 (9.0), 449sh	2.37	578	591	3.26	
P1	357, 453	2.33	587	641	3.49	
P2	403, 453sh	2.30	601	612	2.88	
P3	377, 536	1.92	675	_ ^c	_c	
P4	412, 528	1.91	634	_ ^c	_c	

^aMolar extinction coefficients ($\times 10^4$ dm³ mol⁻¹ cm⁻¹) are shown in parentheses

^bOptical bandgaps are determined from the onset of absorption in solution phases

^cIntensity is too weak to be detected accurately

sh shoulder



Fig. 2 Normalized absorption spectra of M1–M2 and P1–P4 in CH_2Cl_2 at 293 K

summarized in Table 2. All the compounds were characterized by two bands in their absorption spectra (Fig. 2). The first intense absorption band in the range of 270–450 nm is mainly attributed to the π - π * transition in the metal–organic π -conjugation system. The second one appeared from 450 nm and up to 650 nm is assigned to the intramolecular charge transfer (ICT) band between the π -conjugated main chain and the acceptor unit in the side chain [54]. Because

of such ICT interaction, there is a notable narrowing of the bandgap (E_{a}) from the value of 2.72 eV for the Pt-polymer with a methyl substituent on the triphenylamine moiety [55] to the value of 2.30 eV for P2 and 1.91 eV for P4. Relative to the free alkynes (λ_{max} = 346, 421 nm for L1; 398 nm for L2, see Figs. S3 and S4), there is a slight red shift in the absorption wavelength for their corresponding platinum(II) compounds. The spectroscopic properties of these complexes offer a quick guide to their effective conjugation length and bandgaps. Interestingly, the addition of an extra thiophene ring in the main chain in P2 does not affect much the value of E_{σ} as compared to **P1**. Instead, the π - π * absorption of P2 is red-shifted relative to P1, indicating that P2 has a slightly longer effective π -conjugation. Moreover, due to the bathochromic shift of the π - π * bands in **P2**, overlapping of its π - π ^{*} and ICT absorption bands was detected. Similar phenomena were observed in their corresponding dinuclear complexes M1–M2. The molar extinction coefficients (ε) can also be enhanced by the addition of peripheral thienyl group in P1-P2. The triphenylamine at the core of polymers P1-P2 connects the conjugated moieties via three-way branched network, which serves as a spacer and a conjugated

interrupter, thus effectively controlling the conjugated length of the polymers (Fig. 3). Therefore, the λ_{max} between polymers and their corresponding diynes do not show a significant red shift. Taking advantage of the strongly electronaccepting dicyanovinyl functional group at the side chain, λ_{max} with 536 and 528 nm were measured in P3 and P4, respectively, which display a broader absorption coverage in comparison to P1 and P2. Compared to P1 and P2, the second band of P3 and P4 is red-shifted by about 80 nm due to the stronger ICT interaction in the presence of the strong electron-accepting CN groups in the side chain [56]. Hence, the E_{σ} value is lowered from **P1** and **P2** to **P3** and **P4** by replacing the aldehyde group with the dicyanovinyl moiety. It is worth noting that, apart from the conjugated main chain backbones as the efficient light-harvesting chromophores, functionalized side chain would also serve as the effective absorption antennae.

All the polymers show weak and broad red photoluminescence at room temperature (Fig. 4). In general, red luminescent polymers often suffer from a low emission efficiency since red emissive chromophores are normally prone to aggregation in the solid state and are highly



Fig. 3 Extent of π -conjugation in ligands, dimers and polymers



Fig. 4 Normalized emission spectra of P1-P4 in CH₂Cl₂ at 293 K





Fig. 5 *J-V* curves of solar cells with **P1–P4**:PCBM (1:4, w/w) active layers under simulated AM1.5 solar irradiation

Table 3 PSC performance of the best devices fabricated with P1-P4

PSCs	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
P1:PCBM	0.66	2.36	0.30	0.48
P2:PCBM	0.80	2.72	0.38	0.82
P3:PCBM	0.76	3.77	0.35	1.00
P4:PCBM	0.79	4.47	0.38	1.35

susceptible to concentration quenching [57]. Due to the unstructured nature of their emission bands and the donor-acceptor nature in these systems, their emissions are most probably originated from the charge transfer excited states but not the ligand-centered π - π * excited state. In all cases, no triplet emission was observed which manifests the result of energy gap law for narrow-gap polyplatinaynes [58] and it is also in agreement with the observed emission lifetimes in the nanosecond regime [40]. Hence, we ascribe the ligand-dominating singlet excited state instead of the triplet state to contribute to the photoinduced charge separation in the energy conversion for the polymers.

3.3 Photovoltaic Properties

Since the light-induced intramolecular electron transfer could easily occur from donor to acceptor through the π -conjugation which favors photocurrent generation and the photoelectronic energy conversion in photovoltaic devices, PSCs with BHJ configuration were fabricated by using each of **P1–P4** as electron donor and PCBM as electron acceptor (Fig. 5 and Table 3). The hole collection electrode

consisted of indium tin oxide (ITO) with a spin-coated poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layer, while Al served as the electron collecting electrode. Figure 5 shows the *J-V* curves of PSCs with **P1–P4**:PCBM (1:4, w/w) active layers under simulated AM1.5 solar irradiation. Absorption spectra of the neat films of **P1–P4** blended with PCBM (1:4, w/w) are shown in Fig. S7, and as compared to the absorption spectra of **P1–P4** in solution, they exhibit a wider coverage of the visible spectral range. The higher energy peak in the blend film is less pronounced because of the dramatically enhanced absorption in the UV region by the addition of PCBM [59].

The PSCs based on P3 and P4 show over 60% higher in J_{sc} than that of P1 and P2, while the PCE is notably increased when aldehyde group is replaced by the dicyanovinyl group. A higher PCE of 1.35% can be obtained for P4 with $V_{oc} = 0.79$ V, $J_{sc} = 4.47$ mA cm⁻² and FF = 0.38under illumination of an AM 1.5 solar cell simulator in a 1:4 (P4:PCBM) blend ratio. It indicates that a higher PCE would be obtained if a stronger acceptor is attached to the side chain. This is also consistent with the weaker PL intensity in P3 and P4 with respect to that in P1 and P2 [60]. Addition of one more thiophene ring on both sides along the main chain can also increase PCE progressively from P1 to P2 and P3 to P4.

4 Conclusion

In conclusion, a set of new platinum-containing polymetallayne polymers functionalized with electron-rich triphenylamine backbone and different electron acceptor in the side chain have been successfully synthesized via Sonogashira-type dehydrohalogenation or Knoevenagel condensation reaction. All of them exhibit good solubility in common organic solvents and good thermal stability and show a broad absorption in the visible region. The energy level and bandgap of the polymers could be effectively tuned by changing the strength of the acceptor groups in the side chain. The open-circuit voltage (V_{0c}) , shortcircuit current density (J_{sc}) and the fill factor (FF) values of the device with P4 as electron donor are 0.79 V, 4.47 mA cm⁻² and 0.38, respectively, resulting in a PCE of 1.35%. A marked increase in the J_{sc} and PCE can be observed in P3 and P4 (stronger strength acceptor) relative to P1 and P2 (weaker strength acceptor) at the same blend ratio. We believe that if a stronger cyano acceptor was attached to the side chain, a lower bandgap polymer with an ideal energy level would be obtained, and a higher PCE could be anticipated, which provides valuable information for the production of new light-harvesting polymer materials for electrical power generation. Attempts will be continued to further improve the PCE in the future.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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