

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, characterization and photovoltaic behavior of platinum acetylide polymers with electron-deficient 9,10-anthraquinone moiety

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ARTICLE INFO

Article history: Received 5 August 2010 Received in revised form 15 August 2010 Accepted 24 August 2010

Keywords: Anthraquinone Metallopolymers Photovoltaics Platinum Thiophene

ABSTRACT

A new class of soluble, solution-processable platinum(II) acetylide polymers functionalized with electron-deficient 9,10-anthraquinone spacer and their corresponding diplatinum model complexes were synthesized and characterized. The organometallic polymers exhibit good thermal stability and show low-energy broad absorption bands in the visible region. The effect of the presence of thiophene rings along the polymer chain on the optical and photovoltaic properties of these metallated materials was examined. The low-bandgap polymer with thiophene–anthraquinone–thiophene (donor–acceptor–donor) fragment can serve as a good electron donor for fabricating bulk heterojunction polymer solar cells by blending with a methanofullerene electron acceptor. At the same donor:acceptor blend ratio of 1:4, the light-harvesting ability and solar cell efficiency notably increase when the anthraquinone ring is sandwiched by two thiophene units. Photoexcitation of such polymer to [6,6]-phenyl C₆₁-butyric acid methyl ester with power conversion efficiency up to ~ 0.35%. For safety concern, these metallopolymers were also tested for possible cytotoxicity and they do not show significant cytotoxic activity on human liver derived cells and skin keratinocytes at reasonable doses, rendering these functional materials safe to use in practical devices.

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1. Introduction

The rapidly growing global energy demand and the increase of CO_2 emissions associated with the burning of fossil fuels are the key driving forces for the development of inexpensive renewable energy sources. The sun is the primary source of most forms of energy found on the earth and can give out a large amount of solar energy. Solar energy is one of most important renewable sources of energy in this century, which can be used over and over again. Besides, it causes little pollution and does not contribute to the greenhouse effect. In this context, polymeric solar cells (PSCs) have attracted considerable attention for their great advantages over the existing inorganic solar cells, such as ease of processing, light weight, flexibility, low cost, and so forth [1–3]. The bulk heterojunction (BHJ) concept has

improved the power conversion efficiency (PCE) of the PSCs significantly by forming a donor–acceptor (D–A) bicontinuous interpenetrated network, which creates large interfacial areas between the polymers and electron acceptors (e.g. fullerene derivatives), thus leading to efficient photoinduced charge separation in a device [4–8]. In order to capture a larger portion of solar energy, various types of low-bandgap polymers have been designed and investigated as a new donor structure in PSCs [9–12].

Although recent advances in organic photovoltaics are largely based on conjugated organic polymers, a possible alternative approach to harvest sunlight for generating electrical power involves adding metals into organic-based polymers. This interest derives from the fact that incorporation of heavy metals into an organic framework can have a significant influence on their electronic and optical properties [1,13–20]. Among these, metal-containing polymers stand out to be particularly interesting candidates in this area [21–34]. We report here the synthesis, characterization and photovoltaic properties of some donor-acceptor-based metal acetylide polymers containing electron-deficient 9,10-anthraquinone spacer. Quinones and their derivatives constitute an important class of redox mediators and electron-transfer quenchers. They

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are found in the electron transport chain of biological systems and are involved in photosynthesis of plants and bacteria [35,36]. In general, quinones are naturally colored and therefore have been used extensively as colorants in the dyestuff industry but also as sensitizers in the phototendering of cellulose or in the photooxidative degradation of polymeric materials [37]. Quinones play an important role in electron transport in photosynthesis [38], 9.10-Anthraquinone is a tricvclic molecule which possesses two units of electron-withdrawing carbonyl groups and so 9,10-anthraquinone is an electron-deficient organic molecule with both high electron affinity and good thermal and electrochemical stability. Currently, quinones are considered together with other traditional colorants for application in technologies such as optical data transmission and storage, bioanalytical probes and solar energy conversion, which all require absorption and/or emission of long wavelength light, preferably in the near-infrared [39–41]. Thus, as expected, extending the conjugation of parent naphtha- and anthraquinones by electron donors and/or acceptors pushes the electronic absorption spectrum beyond 700 nm [39]. By introduction of thienyl rings to the anthraquinone chromophore in a Pt-acetylide chain, which changes the absorption features and possibly charge transport properties of the resulting polymer, the PSCs can reach PCE of 0.35%.

2. Experimental

2.1. General information

Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reagents for the chemical syntheses were purchased from Aldrich or Acros Organics. [6,6]-Phenyl C₆₁-butyric acid methyl ester (PCBM) was purchased from American Dyes. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron VPAI 4083) was purchased from H. C. Starck. Reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using Schlenk techniques. All reactions were monitored by thin-layer chromatography (TLC) with Merck precoated glass plates. Flash column chromatography and preparative TLC were carried out using silica gel from Merck (230-400 mesh). Infrared spectra were recorded as CH₂Cl₂ solutions using a Perkin-Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer, using CaF₂ cells with a 0.5 mm path length. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. NMR spectra were measured in CDCl₃ on a Varian Inova 400 MHz FT-NMR spectrometer and chemical shifts are quoted relative to tetramethylsilane for ¹H and ¹³C nuclei and H₃PO₄ for ³¹P nucleus. The synthesis of 2,7-dibromo-9,10-anthraquinone LO-2Br was synthesized according to the literature method [42].

2.2. Physical measurements

UV/Vis spectra were obtained on an HP-8453 diode array spectrophotometer. The solution emission spectra and lifetimes of the compounds were measured on a Photon Technology International (PTI) Fluorescence QuantaMaster Series QM1 spectrophotometer. The quantum yields were determined in degassed CH₂Cl₂ solutions at 293 K against quinine sulfate in 0.1 N H₂SO₄ ($\Phi_F = 0.54$) [43]. CV measurements were carried out at a scan rate of 50 mV s⁻¹ using a eDAQ EA161 potentiostat electrochemical interface equipped with a thin film coated ITO covered glass working electrode, a platinum counter electrode and a Ag/AgCl (in 3 M KCl) reference electrode. The solvent in all measurements was

deoxygenated MeCN, and the supporting electrolyte was 0.1 M [ⁿBu₄N]BF₄. Thin polymer films were deposited on the working electrode by dip-coating in chlorobenzene solution (6 mg mL⁻¹). Where appropriate, the oxidation and reduction potentials were used to determine the HOMO and LUMO energy levels using the equations $E_{\text{HOMO}} = [-(E_{\text{ox}} (\text{vs. Ag/AgCl}) - E_{(\text{N.H.E. vs. Ag/AgCl})}] - 4.50 \text{ eV}$ and $E_{\text{LUMO}} = [-(E_{\text{red}} (\text{vs. Ag/AgCl}) - E_{(\text{N.H.E. vs. Ag/AgCl})}] - 4.50 \text{ eV}$, where the potentials for N.H.E. versus vacuum and N.H.E. versus Ag/AgCl are 4.50 and -0.22 V, respectively [44,45].

2.3. Preparation of compounds

2.3.1. Synthesis of 2,7-bis(4-hexylthiophen-2-yl)-9,10-

anthraquinone

To a solution of **L0-2Br** (171 mg, 0.47 mmol) in freshly distilled THF (20 mL) was added Pd(PPh₃)₄ (27 mg, 0.023 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (857 mg, 1.87 mmol) and the mixture was stirred at room temperature for 30 min. Then the mixture was stirred at 80 °C for 24 h. The solvent was evaporated and water (20 mL) was added to the residue which was extracted into CH₂Cl₂ (3 × 10 mL). The organic layer was dried over MgSO₄ and then concentrated under reduced pressure and purified by chromatography on a silica column eluting with *n*-hexane/CH₂Cl₂ (1:1, v/v) to afford a yellow solid (216 mg, 86%).

Spectral Data: IR (KBr): v(C=O) 1672, 1594 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.48 (d, *J* = 1.9 Hz, 2H, Ar), 8.29 (d, *J* = 8.2 Hz, 2H, Ar), 7.95 (dd, *J* = 1.9, 8.2 Hz, 2H, Ar), 7.44 (s, 2H, Ar), 7.04 (s, 2H, Ar), 2.65 (t, *J* = 7.6 Hz, 4H, C₅H₁₁CH₂) 1.68–1.62 (m, 4H, C₄H₉CH₂CH₂), 1.34–1.33 (m, 12H, CH₃C₃H₆CH₂CH₂), 0.91 (t, *J* = 6.6 Hz, 6H, CH₃C₃H₆CH₂CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 182.93, 181.68 (C=O), 144.96, 141.57, 139.96, 133.90, 131.76, 130.24, 128.08, 126.90, 123.33, 122.21 (Ar), 31.65, 30.53, 30.37, 28.99, 22.60, 14.09 (C₆H₁₃) ppm. FAB-MS (*m*/*z*): 541.

2.3.2. Synthesis of L1-2Br

2,7-Bis(4-hexylthiophen-2-yl)-9,10-anthraquinone (237 mg, 0.44 mmol) was dissolved in a mixture of chloroform (20 mL) and acetic acid (2 mL). NBS (172 mg, 0.96 mmol) was added to the solution and the mixture was stirred overnight in the dark. The solvents were removed on a rotary evaporator in *vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane/CH₂Cl₂ (1:1, v/v) to provide **L1-2Br** (246 mg, 80%) as a deep yellow solid.

Spectral Data: IR (KBr): v(C=0) 1672, 1595 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.27$ (d, J = 1.9 Hz, 2H, Ar), 8.19 (d, J = 8.2 Hz, 2H, Ar), 7.77 (dd, J = 1.9, 8.2 Hz, 2H, Ar), 7.23 (s, 2H, Ar), 2.57 (t, J = 7.6 Hz, 4H, C₅H₁₁CH₂) 1.64–1.61 (m, 4H, C₄H₉CH₂CH₂), 1.40–1.33 (m, 12H, CH₃C₃H₆CH₂CH₂), 0.92 (t, J = 6.8 Hz, 6H, CH₃C₃H₆CH₂CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 182.57$, 181.37 (C=0), 143.94, 141.10, 139.02, 133.86, 131.88, 129.88, 128.25, 126.39, 122.96, 111.55 (Ar), 31.61, 29.67, 28.97, 22.61, 14.11 (C₆H₁₃) ppm. FAB-MS (*m*/*z*): 697.

2.3.3. Synthesis of LO-2TMS

To an ice-cooled mixture of **L0-2Br** (150 mg, 0.41 mmol) in freshly distilled triethylamine (10 mL) and CH_2Cl_2 (10 mL) solution under nitrogen was added Pd(OAc)₂ (30 mg), PPh₃ (98 mg) and Cul (11 mg). After the solution was stirred for 30 min, trimethylsilylacetylene (155 mg, 1.03 mmol) was then added and the suspension was stirred for another 30 min in the ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 50 °C for 24 h. The solution was then allowed to cool to room temperature and the solvents were removed on a rotary evaporator in *vacuo*. The crude product was purified by column chromatography on silica gel eluting with

n-hexane/CH₂Cl₂ (1:1, v/v) to provide **L0-2TMS** (56 mg, 34%) as a deep yellow solid. IR (KBr): v(C=O) 1678, 1593, v(C=C) 2160 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.36 (d, *J* = 1.4 Hz, 2H, Ar), 8.23 (d, *J* = 8.0 Hz, 2H, Ar), 7.83 (dd, *J* = 1.4, 8.0 Hz, 2H, Ar), 0.29 (s, 18H, Si(CH₃)₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 182.30, 182.18 (C=O), 137.32, 133.54, 132.83, 131.12, 129.82, 127.66 (Ar), 103.43, 100.71 (C=C), 0.08 (Si(CH₃)₃) ppm. FAB-MS (*m*/*z*): 401. Anal. Calc. for C₂₄H₂₄O₂Si₂: C, 71.95; H, 6.04. Found: C, 71.78; H, 6.34%.

2.3.4. Synthesis of L1-2TMS

It was prepared following the same procedures as for **L0-2TMS** but **L1-2Br** was used instead.

Orange solid (86%). Spectral Data: IR (KBr): v(C=O) 1675, 1593, v (C=C) 2142 cm^{-1.} ¹H NMR (400 MHz, CDCl₃): δ = 8.44 (d, *J* = 1.9 Hz, 2H, Ar), 8.27 (d, *J* = 8.2 Hz, 2H, Ar), 7.77 (dd, *J* = 1.9, 8.2 Hz, 2H, Ar), 7.34 (s, 2H, Ar), 2.71 (t, *J* = 7.5 Hz, 4H, C₅H₁₁CH₂) 1.72–1.65 (m, 4H, C₄H₉CH₂CH₂), 1.40–1.34 (m, 12H, CH₃C₃H₆CH₂CH₂), 0.91 (t, *J* = 6.9 Hz, 6H, CH₃C₃H₆CH₂CH₂), 0.28 (s, 18H, Si(CH₃)₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 183.17, 181.94 (C=O), 150.66, 141.61, 139.65, 134.31, 132.45, 130.78, 128.63, 126.94, 123.95, 120.77 (Ar), 103.79, 97.28 (C=C), 31.91, 30.37, 30.02, 29.26, 22.95, 14.46 (C₆H₁₃), 0.25 (Si(CH₃)₃) ppm. FAB-MS (*m*/*z*): 733. Anal. Calc. for C₄₄H₅₂O₂S₂Si₂: C, 72.08; H, 7.15. Found: C, 72.12; H, 7.01%.

2.3.5. Synthesis of LO-L1

The diethynyl ligands were prepared by the desilylation of each of the TMS derivatives. A typical procedure was given for **L0** starting from **L0-2TMS**.

A mixture of **L0-2TMS** (84 mg, 0.21 mmol) and K_2CO_3 (61 mg, 0.44 mmol) in a solution mixture of methanol (6 mL) and CH₂Cl₂ (15 mL), under a nitrogen atmosphere, was stirred at room temperature overnight. The solvents were removed on a rotary evaporator in *vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-hexane/CH₂Cl₂ (1:1, v/ v) to provide **L0** (48 mg, 91%) as a deep yellow solid.

Spectral Data: IR (KBr): v(C=0) 1673, 1593, v(C=C) 2109, v(C=CH) 3272 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 8.40 (d, J = 1.6 Hz, 2H, Ar), 8.27 (d, J = 8.0 Hz, 2H, Ar), 7.88 (dd, J = 1.6, 8.0 Hz, 2H, Ar), 3.38 (s, 2H, C=CH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 181.75, 181.70 (C=O), 137.31, 133.24, 132.80, 130.97, 128.52, 127.43 (Ar), 82.13, 81.93 (C=C) ppm. FAB-MS (m/z): 256. Anal. Calc. for C₁₈H₈O₂: C, 84.37; H, 3.15. Found: C, 84.20; H, 3.34%.

L1: Orange solid (97%). *Spectral Data*: IR (KBr): v(C=O) 1673, 1596, $v(C\equivC)$ 2096, $v(C\equivCH)$ 3296 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.43$ (d, J = 1.9 Hz, 2H, Ar), 8.27 (d, J = 8.2 Hz, 2H, Ar), 7.90 (dd, J = 1.9, 8.2 Hz, 2H, Ar), 7.35 (s, 2H, Ar), 3.58 (s, 2H, C \equiv CH), 2.73 (t, J = 7.6 Hz, 4H, C₅H₁₁CH₂), 1.71–1.64 (m, 4H, C₄H₉CH₂CH₂), 1.41–1.33 (m, 12H, CH₃C₃H₆CH₂CH₂), 0.91 (t, J = 6.9 Hz, 6H, CH₃C₃H₆CH₂CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 182.74$, 181.57 (C=O), 150.63, 141.68, 139.16, 133.95, 132.19, 130.51, 128.30, 126.49, 123.66, 119.08 (Ar), 85.29, 76.29 (C=C), 31.60, 30.13, 29.65, 28.96, 22.60, 14.11 (C₆H₁₃) ppm. FAB-MS (*m/z*): 589. Anal. Calc. for C₃₈H₃₆O₂S₂: C, 77.51; H, 6.16. Found: C, 77.34; H, 6.32%.

2.3.6. Synthesis of platinum acetylide polymers PO-P1

The polymers were prepared by the dehydrohalogenative polycondensation between *trans*-[PtCl₂(PBu₃)₂] [46] and each of **L0–L1**. A typical procedure was given for **P0** starting from **L0**.

To a stirred mixture of **L0** (47 mg, 0.18 mmol) and *trans*-[PtCl₂(PBu₃)₂] (123 mg 0.18 mmol) in freshly distilled triethylamine (8 mL) and CH₂Cl₂ (15 mL) solution was added CuI (3 mg). The solution was stirred at room temperature for 24 h under a nitrogen atmosphere. The solvents were removed on a rotary evaporator in *vacuo*. The residue was redissolved in CH₂Cl₂ and filtered through a short aluminium 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 (3×15 mL) followed by methanol (3×15 mL) and drying in *vacuo* to obtain **P0** (60 mg, 38%) as an orange solid.

Spectral Data: IR (KBr): v(C=O) 1673, 1586, v(C=C) 2085 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.16-8.12$ (m, 4H, Ar), 7.59 (d, J = 6.9 Hz, 2H, Ar), 2.17–2.13 (m, 12H, PCH₂C₃H₇), 1.65–1.62 (m, 12H, PCH₂CH₂C₂H₅), 1.52–1.43 (m, 12H, PCH₂CH₂CH₂CH₃), 0.99 (t, J = 7.2 Hz, 18H, PCH₂CH₂CH₂CH₂CH₃) ppm. ³¹P NMR (161 MHz, CDCl₃): $\delta = 3.52$ (¹ $J_{P-Pt} = 2307$ Hz) ppm. Anal. Calc. for (C₄₂H₆₀O₂P₂Pt)_n: C, 59.07; H, 7.08. Found: C, 59.35; H, 7.29%. GPC (THF): $M_W = 12980$, $M_n = 7270$, DP = 9, PDI = 1.78.

P1: Red solid (77%). *Spectral Data*: IR (KBr): ν(C=O) 1672, 1595, ν (C=C) 2081 cm⁻¹.¹H NMR (400 MHz, CDCl₃): δ = 8.43 (s, 2H, Ar), 8.26 (d, *J* = 8.1 Hz, 2H, Ar), 7.88 (d, *J* = 8.1 Hz, 2H, Ar), 7.36 (s, 2H, Ar), 2.71 (br, 4H, alkyl), 2.18 (br, 12H, alkyl), 1.63 (br, 16H, alkyl), 1.54–1.49 (m, 12H, alkyl), 1.36 (br, 12H, alkyl), 0.98 (t, *J* = 7.1 Hz, 18H, alkyl), 0.92 (t, *J* = 6.8 Hz, 6H, alkyl) ppm. ³¹P NMR (161 MHz, CDCl₃): δ = 3.69 (¹*J*_{P-Pt} = 2333 Hz) ppm. Anal. Calc. for (C₆₂H₈₈O₂P₂S₂Pt)_n: C, 62.76; H, 7.48. Found: C, 62.98; H, 7.54%. GPC (THF): *M*_w = 61,040, *M*_n = 16,250, DP = 14, PDI = 3.76.

2.3.7. Synthesis of platinum model complexes MO-M1

All of them were synthesized following the dehydrohalogenating coupling between *trans*-[PtCl(Ph)(PEt₃)₂] [47] and the corresponding diterminal alkynes. A typical procedure was given for **M0** starting from **L0**.

To a stirred mixture of ligand **L0** (7 mg, 0.03 mmol) and two molar equivalents of *trans*-[PtCl(Ph)(PEt₃)₂] (31 mg, 0.06 mmol) in NEt₃ (10 mL) and CH₂Cl₂ (10 mL), CuI (3 mg) was added as the catalyst. The solution was stirred at room temperature for 15 h under nitrogen, after which all volatile components were removed under vacuum. The crude product was taken up in CH₂Cl₂ and purified on preparative silica TLC plates with a mixture of *n*-hexane/ethyl acetate (5:1, v/v) as eluent. A deep yellow band consisting of **M0** was obtained as a yellow solid (24 mg, 70%).

Spectral Data: IR (KBr): v(C=O) 1672, 1587, v(C=C) 2092 cm⁻¹. ¹H NMR (CDCl₃): $\delta = 8.14-8.10$ (m, 4H, Ar), 7.61 (dd, J = 1.9, 8.2 Hz, 2H, Ar), 7.38–7.29 (m, 4H, Ar), 7.00–6.97 (m, 4H, Ar), 6.84–6.80 (m, 2H, Ar), 1.79–1.74 (m, 24H, PCH₂CH₃), 1.16–1.08 (m, 36H, PCH₂CH₃) ppm. ¹³C NMR (CDCl₃): $\delta = 184.55$, 182.75 (C=O), 139.29, 136.35, 135.78, 133.78, 130.17, 129.24, 127.77, 127.40, 125.36, 121.80 (Ar), 111.24 (C=C), 15.43, 8.38 (PEt₃). ³¹P NMR (CDCl₃): $\delta = 10.07$ ppm (¹ $J_{Pt-P} = 2622$ Hz). FAB-MS: m/z = 1271 (M⁺). Anal. Calc. for C₅₄H₇₆O₂P₄Pt₂: C, 51.02; H, 6.03. Found: C, 51.21; H, 6.23%.

M1: Red solid (65%). *Spectral Data*: IR (KBr): v(C=O) 1672, 1592, v(C=C) 2080 cm⁻¹. ¹H NMR (CDCl₃): $\delta = 8.41$ (d, J = 1.9 Hz, 2H, Ar), 8.24 (d, J = 8.1 Hz, 2H, Ar), 7.88 (dd, J = 1.9, 8.1 Hz, 2H, Ar), 7.35–7.32 (m, 6H, Ar), 7.00–6.96 (m, 4H, Ar), 6.84–6.80 (m, 2H, Ar), 2.70 (t, J = 7.7 Hz, 4H, C₅H₁₁CH₂), 1.80–1.66 (m, 28H, PCH₂-CH₃ + C₄H₉CH₂CH₂), 1.43–1.32 (m, 12H, CH₃C₃H₆CH₂CH₂), 1.16–1.08 (m, 36H, PCH₂CH₃), 0.91 (t, J = 6.9 Hz, 6H, CH_3 C₃H₆CH₂CH₂) ppm. ¹³C NMR (CDCl₃): $\delta = 183.95$, 182.15 (C=O), 143.96, 140.57, 139.40, 136.29, 134.40, 131.55, 129.97, 128.58, 128.41, 127.74, 127.34, 123.15, 121.73 (Ar), 102.31 (C=C), 32.23, 30.95, 30.22, 29.77, 23.04, 15.50, 14.50, 8.39 (C₆H₁₃ + PEt₃). ³¹P NMR (CDCl₃): $\delta = 10.28$ (¹ $J_{Pt-P} = 2630$ Hz). FAB-MS: m/z = 1604 (M⁺). Anal. Calc. for C₇₄H₁₀₄O₂P₄Pt₂S₂: C, 55.42; H, 6.54. Found: C, 55.34; H, 6.72%.

2.4. Solar cell fabrication and characterization

The device structure was ITO/PEDOT:PSS/polymer:PCBM blend/ Al. The ITO 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



Reagents and conditions: (i) (a) fuming HNO₃, $5 \sim 25$ C, (b) CH₃COOH, 25 C, 1 week; (ii) Na₂S, NaOH, EtOH/H₂O, reflux, 6 h; (iii) (a) CuBr, *t*-BuNO₂, 65° C, (b) aq. HCl; (iv) tributyl(4-hexylthiophen-2-yl)stannane, Pd(PPh₃)₄; (v) NBS, AcOH; (vi) trimethylsilylacetylene, CuI, Pd(OAc)₂, PPh₃, NEt₃; (vii) K₂CO₃, MeOH; (viii) *trans*-[PtCl₂(PBu₃)₂], CuI, NEt₃; (ix) *trans*-[PtCl(Ph)(PEt₃)₂], CuI, NEt₃

Scheme 1. Synthesis of anthraquinone-based diethynyl ligands and their Pt(II) complexes.

PEDOT:PSS solution was passed through the 0.45 um filter and spincoated on patterned ITO substrates at 5000 r.p.m. for 3 min. followed by baking in N₂ at 150 °C for 15 min. The metallopolymer:PCBM (1:4 by weight) active layer was prepared by spin-coating the chlorobenzene solution (20 mg per mL, for example 6 mg of metallopolymer and 24 mg of PCBM in 1.8 mL of solvent for 1:4 blend) at 1000 r.p.m. for 2 min. The substrates were dried at room temperature in low vacuum (vacuum oven) for 1 h, and then stored in high vacuum (10 $^{-5}$ -10 $^{-6}$ Torr) overnight. Al electrode (100 nm) was evaporated through a shadow mask to define the active area of the devices (2 mm diameter circle). All the fabrication procedures (except drying, PEDOT:PSS annealing and Al deposition) and cell characterization were performed in air. Power conversion efficiency was determined from J-V curve measurement (using a Keithley 2400 sourcemeter) under white light illumination (at 100 mW cm⁻²). For white light efficiency measurements, Oriel 66002 solar light simulator with AM1.5 filter was used. The light intensity was measured by a Molectron Power Max 500D laser power meter.

2.5. In vitro toxicology test

Human cells including HaCaT skin keratinocytes and liver derived Hep3B cells were removed from 75 mL sterile cell culture flasks with trypsin and neutralized with fetal bovine serum. After washing with phosphate buffered saline and centrifugation, cancer cells were re-suspended in complete cell culture medium at a concentration of approximately 1×10^5 cells per mL and counted manually using a haematocytometer under an inverted microscope. Human cells seeded in the 96 wells microtitre plates for 24 h were prepared for the screening of the synthesized polymers. The two polymers were dissolved in tetrahydrofuran (THF) at a stock concentration of 50 mg mL⁻¹. *Cis*-platin (CDDP) was used as the positive reference compound and it was added at

a starting concentration of $50 \ \mu g \ m L^{-1}$. Polymers were also added at a starting concentration of $50 \ \mu g \ m L^{-1}$ followed by a serial of two-fold dilutions and incubated with cells for a further period of 48 h. Afterwards, the evaluation of possible anti-proliferative potential of our synthesized polymers was performed by the sulforhodamine B protein staining methods [48–51]. Briefly, cancer cells were fixed with trichloroacetic acid, washed with distilled water and stained with sulforhodamine B. Afterwards, cells were washed again with acetic acid and stained cells were dissolved in 100 μ L unbuffered Tris-base. Finally, optical absorptions were measured at 575 nm using a microplate reader (Victor V form Perkin Elmer, Life Sciences).

3. Results and discussion

3.1. Synthetic methodologies and chemical characterization

The chemical structures and synthesis of new platinum(II) acetylide polymers PO and P1 are shown in Scheme 1. Anthrone was stirred in fuming nitric acid and acetic acid to afford yellow crystals of 2,7-dinitro-9,10-anthraquinone [42]. Then, the two nitro groups were converted into the amino groups by reacting 2,7dinitro-9,10-anthraquinone with sodium sulfide and sodium hydroxide in a solution mixture of ethanol and water. The resulting precipitate was recrystallized from ethanol/water mixture and isolated as 2.7-diamino-9.10-anthraguinone. Conversion of the nitro groups into bromo groups was accomplished by reacting the diamino derivative with anhydrous copper(I) bromide and tertbutyl nitrite in anhydrous acetonitrile. The crude product was subjected to column chromatography and obtained as 2,7-dibromo-9,10-anthraquinone (L0-2Br). 2,7-Bis(trimethylsilylethynyl)-9,10-anthraquinone can be obtained by reacting L0-2Br and trimethylsilylacetylene in a THF/NEt₃ mixture using Cul, Pd (OAc)₂ and PPh₃ as the catalysts. The Me₃Si groups were converted to the terminal C=CH by desilylation with potassium carbonate in methanol. The final diethynyl ligand LO was obtained as a pale yellow solid. The dibromo precursor L1-2Br can be obtained by the Stille coupling of Bu₃Sn-substituted hexylthiophene with LO-2Br to yield 2,7-bis(4-hexylthiophen-2-yl)-9,10-anthraquinone followed by bromination with N-bromosuccinimide (NBS). Conversion of the dibromide derivatives to their corresponding diethynyl congeners can be similarly achieved following the typical organic synthetic protocols for alkynylation of aromatic halides [52]. The Pt(II) alkynyl compounds were prepared by the Sonogashira-type dehydrohalogenation between each of the diethynyl precursors and suitable platinum(II) chloride precursors [30-34,53-63]. Dinuclear complexes (MO and M1) consisting of well-defined structures were also made to serve as good molecular model system to investigate the spectroscopic and photophysical properties of the corresponding polymers. The feed mole ratio of the platinum precursors and the diethynyl ligands were 1:1 and 2:1 for the polymer and dimer synthesis, respectively, and each product was carefully purified to remove ionic impurities and catalyst residues. The polymers can be purified by silica column chromatography and repeated precipitation. All of the Pt compounds are thermally- and air-stable solids and they are soluble in common chlorinated hydrocarbons and toluene. From the gel permeation chromatography (GPC) analysis on PO and P1, the number-average molecular weights (M_n) of **PO** and **P1** calibrated against polystyrene standards were 7270 and 16250, respectively, corresponding to the degree of polymerization (DP) of about 9 and 14, respectively. There are ~ 42 heterocyclic rings in total for P1, confirming its polymeric nature. The low molecular weight of PO was presumably due to its poor solubility, since a certain portion of P0 formed was found to be

Table 1

Electronic absorption and emission data of L0 and L1 and the corresponding metallated compounds.

	Absorption (293 K)	Emission (293 K)			
	λ_{abs} (nm) CH ₂ Cl ₂ ^a	Bandgap E _g (eV) ^b	$\lambda_{em} (nm)$ CH ₂ Cl ₂	Φ (%)	$\tau_{\rm P}\left({\rm ns}\right)$
LO	229 (4.4), 276 (10.3) 293 (2.7), 348 (0.76)	3.19	548	0.60	2.65
L1	241(3.0), 274 (2.1) 322 (4.8), 357 (2.7) 431(1.9)	2.46	569	8.50	4.10
M0	235 (4.8), 318 (4.8) 342 (2.3), 357 (3.0) 465 (1.5)	2.32	593	0.30	0.89
M1	230 (8.6), 265 (5.3) 348 (5.0), 405 (5.8) 526 (3.4)	1.91	672 ^c	d	d
P0 P1	237, 320, 357, 468 230, 267, 354, 408, 529	2.30 1.88	600 697 ^c	0.20 d	1.11 d

^a Molar extinction coefficients ε (10⁴ dm³ mol⁻¹ cm⁻¹) are shown in parentheses.

^b Optical bandgaps determined from the onset of absorption in solution phases.

^c Weakly emissive in solid state.

^d Too weak to be determined accurately.

organic insoluble, and the molecular weight of the soluble fraction was relatively low. Hence, it was found that **P1** can cast tough, freestanding thin film from its solution more readily. The structures of these Pt compounds were unequivocally characterized using mass spectrometry, IR and NMR spectroscopies (see Experimental section). The NMR data are consistent with the proposed structure of the polymers and model compounds. The peaks arising from terminal $-C \equiv CH$ groups are absent in the NMR and IR spectra, confirming metal–alkynyl bond formation.

The thermal properties of the polymers were also examined by thermal gravimetric analysis (TGA) under nitrogen. Both of them exhibit good thermal stability with the decomposition onsets at ~ 336 (for **P0**) and 318 °C (for **P1**), which are higher than those for *trans*-[-Pt(PBu₃)₂C=CArC=C-]_n (Ar = C₆H₄, 300 °C [56], anthrylene, 315 °C [63], oligothienylene, 278–290 °C [32]). Decomposition onset was defined by a 5 wt.-% loss in each case.

3.2. Photophysical and electrochemical characterization

The UV-vis spectroscopy of 9,10-anthraquinone and its derivatives has been the subject of many papers and reviews [64–66]. The



Fig. 1. Absorption spectra of L0, L1, P0 and P1 in CH₂Cl₂ solution at 293 K.



Fig. 2. Absorption spectra of MO and M1 in CH₂Cl₂ solution at 293 K.

UV-vis spectrum of anthraquinone typically displays four electronic transitions above 240 nm and the lowest energy transition band near 400 nm, with a very small extinction coefficient, possesses a $n-\pi^*$ nature [42]. The three more intense bands near 250, 270 and 320 nm are intra-ligand π - π * transitions and exhibit quinonoid and benzenoid characters. The absorption and emission spectra of the ligands, polymers and complexes were measured in CH₂Cl₂ solutions at 293 K (Table 1 and Figs. 1–3). Similar to the UV pattern of anthraquinone, the UV spectrum of LO without any thienyl rings exhibits three intense absorption bands in the near-UV region, which are ascribed to the $\pi - \pi^*$ transitions. Besides, there is a low-energy broad transition band around 350 nm which tails off to 390 nm and it is assigned as a $n-\pi^*$ transition. For ligand L1, the introduction of thienyl rings to the molecue shifts the absorption bands towards the longer wavelength. Presumably, a higher degree of conjugation with the additional thienyl units reduces the energy gap (E_g). The E_g of L1 is about 0.73 eV lower than that of L0. The absorption of polymers PO and P1 each shows intense and broad absorption bands in the UV and visible region. Similar to the diethynyl ligand precursors which absorb strongly in the near-UV and visible region, the absorption of PO and P1 is each characterized by strong near-UV intraligand $\pi - \pi^*$ bands below 400 nm and another low-lying band peaking near 468 and 529 nm, respectively.



Fig. 3. Photoluminescence (PL) spectra of L0, L1, M0 and P0 in CH_2Cl_2 solution.

Table 2

Absorption maxima (n	m) of P0 in	different	solvents.
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	CCl ₄	Toluene	CH ₃ CO ₂ Et	THF	CHCl₃	CH ₂ Cl ₂
λ _{max}	-	463	461	460	468	468
λ_{em}	506	507	525	528	567	593

We attribute the low-energy bands in the Pt-containing polymers as predominantly intramolecular charge transfer (ICT) in nature from the donor to the acceptor. Anthraquinone possesses two electron-withdawing carbonyl groups forming its core structure, making anthraquinone an electron deficient organic moiety. By incorporating the electron-poor anthraquinone organic moiety into the electron-rich Pt metal center through the acetylenic groups, strong ICT can take place within the molecule from the metal group to the 9,10-anthraguinone moiety. Due to the presence of an extended π -electron delocalized system through anthraquinone segment and the electron-rich Pt ion, the bandgap of polymer PO is about 0.89 eV lower than that of ligand LO. As far as the emission properties are concerned, ligands L0, L1, dimer M0 and polymer P0 can emit intense fluorescence from the singlet excited states at 548, 569, 593 and 600 nm, respectively, under ambient conditions in CH₂Cl₂ solutions. However, M1 and P1 were shown to be nonemissive in CH₂Cl₂ but weakly luminescent in the solid state. The observation of solid-state emission for M1 and P1 suggests that rapid and efficient internal conversion deactivates the lowest excited state in fluid solution whereas the more ordered solid state allows luminescence at room temperature [64]. The measured photoluminescence (PL) lifetimes for PO at 293 K and 77 K for the main peaks are very short at 1.11 ns and 0.51 ns, respectively, characteristic of the spin-allowed singlet emission [56]. These results together with the small Stokes shift observed preclude the emitting state as a triplet excited state. We observed no such longlived emission over the measured spectral window between 1.2 and 3.1 eV for the Pt compounds. The observation of efficient triplet emission is intrinsically more difficult for low-bandgap Pt-acetylides, which manifests the fate of energy gap law for Pt-acetylide conjugated polymers and their model divnes [67]. Theoretically, the law predicts that the rate of radiationless deactivation increases as the emission gap decreases due to the matching of wavefunctions between the emitting state and highly vibrational levels of the ground electronic state, resulting in a fast $T_1 \rightarrow S_0$ internal conversion, followed by the solvent (or lattice in the solid state) deactivation. This quenching mechanism is intrinsic and probably



Fig. 4. PL spectra of PO in different solvents at 293 K.

Table 3 Electrochemical data and frontier orbital energy levels for P0 and P1.

Polymer	$E_{\rm ox}({\rm V})^{\rm a}$	$E_{\rm red}({\sf V})^{\sf a}$	$E_{\rm HOMO}~({\rm eV})^{\rm b}$	$E_{\rm LUMO}~({\rm eV})^{\rm b}$	$E_{g}^{ec} (eV)^{c}$	$E_{g}^{opt} (eV)^{d}$
PO	е	-0.96	-6.06^{f}	-3.76	е	2.30
P1	1.24	-0.94	-5.96	-3.78	2.18	1.88

^a E_{ox} and E_{red} are the oxidation and reduction potentials, respectively. ^b $E_{\text{red}} = (E_{\text{red}} + 4.72) \text{ eV}$ and $E_{\text{red}} = (E_{\text{red}} + 4.72) \text{ eV}$

^b $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.72) \text{ eV} \text{ and } E_{\text{LUMO}} = -(E_{\text{red}} + 4.72) \text{ eV}.$

^c $E_{g}^{ec} = \text{Electrochemical bandgap.}$ ^d $E_{g}^{opt} = \text{Optical bandgap.}$

 $E_{g'} \equiv Optical b$ e Not observed.

^f Determined from $-(E_g^{opt} - E_{LUMO})$.

poses the main obstacle for phosphorescence for these Pt materials. In addition, the fully extended heteroaryl rings in the ligand chromophore greatly reduce the influence of heavy metal ion in **P1** and **M1** which is mainly responsible for the intersystem crossing and hence the phosphorescence emission. Therefore, we consider a ligand-dominating singlet excited state instead of the triplet state to contribute to the efficient photoinduced charge separation in the energy conversion for **P1** and **P2** (vide infra).

Due to their similar emission pattern, we consider that the emission features in the metal-free ligand precursors and the Pt compounds should have the same origin. The absorption maxima of PO exhibit negligible bathochromic solvatochromic shifts in solvents of increasing polarity, consistent with very small groundstate dipole moments. In contrast to their absorption behavior, PO exhibits pronounced positive solvatochromism in their fluorescence spectra (Table 2), which can be attributed to the more polarized excited states [68,69]. In other words, their emission spectra shift towards longer wavelengths with increasing polarity of the solvents. Solvent-dependent emission in solution has been frequently observed for the related electron-deficient acridone derivatives [70]. As shown in Fig. 4, the shift of the emission maximum with solvents is dramatic because the present system consists of alternating donor- π -acceptor structural units along the polymer chain and this agrees with our expectation for donoracceptor compounds exhibiting significant ICT interaction. For example, in the less polar solvent, toluene, the emission maximum of **P0** is located at 507 nm, while in CH₂Cl₂, the emission maximum appears at 593 nm.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of stable P0-P1 were determined from electrochemical measurements using cyclic voltammetry. The experiments were performed by casting the polymer films on the glassy-carbon working electrode with a Ag/AgCl wire as the reference electrode, at a scan rate of 50 mV s⁻¹. The solvent in all measurements was deoxygenated MeCN, and the supporting electrolyte was 0.1 M [ⁿBu₄N]BF₄. The relevant data are collected in Table 3. From the values of oxidation potential (E_{ox}) and reduction potential (E_{red}), the HOMO and LUMO levels of P1 were calculated according to the following equations $E_{HOMO} = -(E_{ox} + 4.72)$ eV and $E_{LUMO} = -(E_{red} + 4.72) \text{ eV}$ (where the unit of potential is V versus Ag/ AgCl) [44,45]. When the thiophene ring is added on both sides of anthraquinone ring, polymer P1 shows an irreversible oxidation wave at 1.24 V, which is absent in PO and can be attributed to the oxidation of thiophene unit. The electrooxidation of oligothiophene

Table 4	
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Solar cell performance of devices with PO and P1.ª

Polymer	$V_{\rm oc}\left({\sf V}\right)$	$J_{\rm sc}~({\rm mA~cm^{-2}})$	FF	PCE (%)
P0	0.70	0.14	0.20	0.03
P1	0.78	1.40	0.32	0.35

^a Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE).

1.0 Current Density (mA cm⁻²) 0.5 0.0 -0.5 -1.0 PO -1.5 **P1** -2.0 -2.5 -3.00.0 0.2 0.4 0.6 0.8 1.0 Voltage (V)

Fig. 5. *J*–*V* curves of solar cells with **P0** and **P1**:PCBM (1:4, w/w) active layers under simulated AM1.5 solar irradiation.

is often irreversible because the electrogenerated cations readily undergo rapid coupling reactions leading to higher oligomers or polymers [71–75]. The quasi-reversible cathodic wave is attributed to the reduction of the anthraquinone moiety [66]. While the LUMO levels are similar between **P0** and **P1**, the HOMO levels tend to be elevated upon incorporating thiophene rings from **P0** (–6.06 eV) to **P1** (–5.96 eV). It provides a clue that the incorporation of electrondonating thiophene rings into the electron-accepting organic spacer can cause a significant narrowing of E_{g} .

3.3. Polymer solar cell behavior

In order to examine if the broad absorption band of these polymers do make a contribution to the photoelectronic energy conversion in PSCs, polymer solar cells were fabricated by using each of **P0** and **P1** as an electron donor and PCBM as an electron acceptor



Fig. 6. Survival percentage of HaCaT skin keratinocytes and liver derived Hep3B human cells after treating cells for 48 h with **P0** and **P1** and compared with cells cultured in untreated complete medium control. Possible cytotoxic activity was determined by the sulforhodamine B protein staining assay. **P0** and **P1** were added at 50 μ g mL⁻¹ containing 0.1% of THF. CDDP was used as a positive reference compound. THF vehicle control was added at 0.1%. Each determination was in triplicate. Three independent experiments were performed and similar results were obtained. Results represent the mean \pm SD from one representative experiment.



Fig. 7. Two human cell lines (Left hand column: HaCaT normal human skin keratinocytes; Right hand column: Hep3B human liver derived cells) were incubated a) 0.1% THF; b) 50 µg mL⁻¹ of **P0**; c) 50 µg mL⁻¹ of **P1** and d) 12.5 µg mL⁻¹ of CDDP for HaCaT and 25 µg mL⁻¹ of CDDP for Hep3B for 48 h and their effects on cell growth were determined by sulforhodamine B assay. Cells were then fixed with trichloroacetic acid, washed and stained with sulforhodamine B. Both of HaCaT and Hep3B cells did not show any growth inhibitory phenomenon. CDDP could significantly induce cellular detachment from the substratum and cell death as shown in d).

(Table 4). The hole collection electrode consisted of indium tin oxide (ITO) with a spin-coated PEDOT:PSS, while Al served as the electron collecting electrode. Fig. 5 portrays the current density-voltage (I-V) characteristics of the PSCs recorded under AM1.5 simulated solar illumination. It can be clearly observed that enhancing the absorption coefficient of the band by increasing the conjugation length of the chain with thienyl rings is a good strategy. A considerable increase in the short circuit current density (I_{sc}) and PCE can be observed in P1 as compared with the corresponding polymer without thienyl rings P0 [76,77]. Although the PCE of solar cells fabricated with PO and PCBM is only 0.03%, it is increased to 0.35% with the cells fabricated from polymer P1 and PCBM. At the same blend ratio of 1:4, the PCE increases in the order **P0** < **P1** and the light-harvesting ability of **P1** can be increased by ~ 12 times relative to P0 simply by adding one thienyl ring on both sides of anthraquinone along the polymeric backbone. Generally, the amount of absorbed light depends not only on the cut-off absorption wavelength, but also on how intense the absorption is. Comparing model complexes **MO** and **M1** with different *m* value, there is an increase in ε_{max} from **M0** to **M1** (from 1.5×10^4 to 3.4×10^4 dm³ mol⁻¹ cm⁻¹ for the lowest-energy peak), which correlates well the higher PCE observed for P1 than P0. Therefore, the design of the low-bandgap

polymers for photovoltaic applications should consider not only lowering the E_g but also increasing the absorption coefficient of the polymer, as well as optimizing the morphology of the blend films. In all diodes, FFs are not very impressive. The relatively low values are at least partly due to the fact that all processing (except PEDOT:PSS annealing and electrode deposition) and measurements have been done in ambient atmosphere which likely results in the presence of traps. We expect FF to improve for fabrication and characterization to be performed in an inert gas environment. Comprehensive study of charge transport and the influence of traps is necessary to further improve FF and overall device performance. Nevertheless, these devices are still not fully optimized. Further studies are needed to optimize devices based on these materials for photovoltaics and tunability of the energy levels of the polymers is expected to be an asset in applicability of this class of materials to organic solar cells with different acceptors.

3.4. Cytotoxicity test of polymers on human cells

Here, we treated the human cells with **P0** and **P1** at 50 μ g mL⁻¹ to test for their possible cytotoxicity. As shown in Fig. 6, we concluded that these two polymers did not exert any observable cytotoxicity towards the HaCaT and Hep3B cells of up to a maximum concentration of 50 μ g mL⁻¹ for 48 h of incubation. Similarly, 0.1% of THF did not exert significant adverse effect on both cell lines. *Cis*-platin (CDDP) at 50 μ g mL⁻¹, on the other hand, was found to be extensively cytotoxic and executed a significant cellular detachment from the substratum and cell death induction on both human cell lines. Morphological changes including cell shrinkage and cell rounding were readily detected (Fig. 7). Hence, it is safe to exploit the polymers in solar cell applications.

4. Conclusion

In summary, two solution-processable Pt(II) acetylide polymers functionalized with electron-deficient anthraquinone spacer were prepared and characterized. Optical spectroscopy and electrochemical data reveal a narrow bandgap system for P1. Intramolecular charge-transfer occurs along the polymer backbone through the involvement of donor-acceptor structural motif. Inclusion of thiophene fragments into the anthraquinone unit further expands the spectral width of absorption appropriate for sunlight harvesting in **P1**, this in turn can raise the performance of the resulting PSCs from 0.02% to 0.35%. Biological studies show that the metallopolymer is non-cytotoxic in vitro of up to 50 μ g mL⁻¹ against HaCaT human skin keratinocytes and liver derived Hep3B cells. All these results reveal that such Pt(II) acetylide polymers can be a promising and safe material for the development of stable PLEDs. Based on their attractive physical, chemical and biological features, we could further make use of them for various purposes in photovoltaic and textile technologies.

Acknowledgements

This work has been supported by the University Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and a Faculty Research Grant from the Hong Kong Baptist University (FRG2/09-10/II-091). We also thank Drs. A. B. Djurišić and Kai-Yin Cheung for their assistance in photovoltaic measurements and Dr. Ka-Leung Wong in solid-state photoluminescence measurements.

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