Contents lists available at ScienceDirect







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

Synthesis of neutral stable polyradicals and their application on photovoltaic devices

Xiangjian Wan^{a,*}, Xin Lv^a, Guangrui He^a, Ao Yu^b, Yongsheng Chen^{a,*}

^a Key Laboratory for Functional Polymer Materials and Center for Nanoscale Science & Technology, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

^b Central Laboratory, College of Chemistry, Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history: Received 13 October 2010 Received in revised form 6 January 2011 Accepted 24 February 2011 Available online 2 March 2011

Keywords: Conjugated polymers Copolymerization Radical Phenalenyl Photovoltaics

1. Introduction

ABSTRACT

Three stable polyradicals with large π -conjugated planar phenalenyl (PLY) radical units as side chain were synthesized. Due to the different conjugated backbones and the interactions between main chains and side chains, these polyradicals and their corresponding precursor polymers presented diverse optical and electrical properties, which were confirmed by UV–vis, fluorescence and CV detections. Besides, they showed excellent solubility in common organic solvents and good stability in the air. Considering their special characteristics, we have fabricated photovoltaic (PV) devices using these polyradicals or polymers as donor material and PCBM as acceptor material. The significant PV performance improvement was observed using a radical-based active layer in the PV devices.

© 2011 Elsevier Ltd. All rights reserved.

The organic π -conjugated polymers have attracted much attention as a kind of material with various electronic properties since last century. Especially, there is a series of π -conjugated polymers substituted with radicals, the research of magnetic and electronic properties of which are one of the most attractive research fields, and numerous π -conjugated polyradicals have been synthesized and characterized [1-10]. One of the most effective ways to synthesize organic polyradical molecules is to design a π -conjugated backbone with pendant radicals as side chains, because the ferromagnetic spin alignment between unpaired electrons through the π -conjugation can be made strong [7–10]. Currently, the interest in the synthesis of high-spin organic polyradicals is mostly driven by the possibility of attaining purely organic magnetic molecules based upon intramolecular ferromagnetic interaction. At the same time, the multifunctional molecules possessing not only high-spin but also an optical and/or electrical property have been attractive [11,12]. In the past several years, organic photovoltaic devices have been the subject of intense research for their low-cost, light-weight, compatibility with flexible substrates, etc. So far, great progress with PCE up to 6% has been achieved by using low band gap polymers in the BHI solar cells [13–16]. The presence of unpaired electrons in polyradicals prompts us to expect that these materials would offer more charge carriers and efficient charge transportation channel toward optimized overall solar cell performance for possible enhanced short-circuit current [17,18]. Taking the advantages of the intrinsic properties of stable polyradicals, we report the synthesis and characterization of a series of polymer radicals with pendant conjugated phenalenyl radical units, and their initial photovoltaic application results.

2. Results and discussion

The structures of the polymers in this paper are presented in Scheme 1. The synthesis of three kinds of

^{*} Corresponding authors. Tel.: +86 22 23500693; fax: +86 22 2499992. *E-mail addresses*: xjwan@nankai.edu.cn (X. Wan), yschen99@nankai. edu.cn (Y. Chen).

^{0014-3057/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.eurpolymj.2011.02.017



Scheme 1. Structures of the polymers and monomer M1 used in this study.

polymers and corresponding polyradicals were all through a palladium-catalyzed oxidative homocoupling reaction [19] as described in Section 3. The obtained polymers were de-protected by CF_3COOH to give the polyradical precursors. With the oxidation of the precursors using PbO_2 in toluene, the targeted polyradicals were obtained by deposition in methanol. As shown in Table 1, the molecular weight, polymerization degree and polydispersity index (PDI) of the polymers and polyradicals have been summarized. The PDI of all the products is between 1.35 and 1.70, which indicates that the post treatment is effective to remove the polymers with low molecular weight. Besides,

Table 1GPC data of P1, P2 and P3.

Polymer	P1-Boc	P2-Boc	P3-Boc	P1-NH	P2-NH	P3-NH	P1-radical	P2-radical	P3-radical
<i>M_n</i>	7600	16,700	8100	7800	12,100	8700	8500	13,200	8300
PDI	1.48	1.36	1.52	1.53	1.65	1.35	1.70	1.45	1.35
Xn	15	17	12	19	14	16	21	15	15

the oxidation process from polymers to radicals does not decrease the polymerization degree of the polyradicals, which illustrates that the oxidation with fresh PbO_2 does not cut off the chains of the polymers.

As shown in Fig. 1a, the UV-vis spectra of polymers and monomer in CHCl₃ with the concentration of 0.01 mg/mL can be observed. The absorption maximum of P1-Boc, P2-Boc and P3-Boc shifted to longer wavelength compared with that of the monomer M1. But the different backbones made them have different red shift. This suggests different conjugation arising along the main-chain in these polymers. At the same time, we compared the P1-Boc with the polymer PDB-BHO, which had the same main-chain with P1-Boc, but with different sidechains of long alkoxy. We can observe a red-shift of 91 nm for the absorption maximum from P1-Boc compared to PDB-BHO. Considering the difference of the side-chains of the two polymers, we conclude that for P1-Boc there is a better π -conjugation delocalization between the planar π -conjugated side-chain with the main-chain. The absorption spectra of polymer films are shown in Fig. 1b. Comparing the peaks of film with those of their solutions, we find that there is not obvious difference between them. This indicates that there is no additional π - π stacking interaction appearing when going from solution to film, which may be due to the steric hindrance effect of bulky side chain of the polymers, so that the backbones cannot pack to each other well.

From Fig. 1c, we can see that the absorption spectra of polymer films, especially that of P1-Boc, have a compara-

tively good match with solar spectrum. This makes them favorable to be used for photovoltaic devices.

To confirm the absorption peaks of radicals, we first studied the change of the spectra (Fig. 1d) of the small molecule radical M1-radical in $CHCl_3$ solution with the time at ambient conditions, as we know this radical would degrade with time in solution when exposed to air [18] as shown below. As shown in Fig. 1d, there is a new peak at 600 nm from the solution of M1-radical compared with that of its precursor M1 shown in Fig. 1a. Furthermore, the intensity of this new peak from M1-radical decreases with time. So we believe the peak at ~600 nm is due to the absorption of radical.

In Table 2, we summarize the absorption maximum of the polymers and polyradicals in CHCl₃ solution or as film separately, and calculate the band gap of them. According to these data, we can observe that the band gaps of the

Table 2UV-vis data of P1, P2, P3 in $CHCl_3$ and film, and their band gap data.

Polymer	Solution	Film		
	λ_{\max} (nm)	λ_{\max} (nm)	E_g^{opt} (eV)	
P1-Boc	533	534	1.90	
P2-Boc	431	433	2.61	
P3-Boc	423	424	2.22	
P1-radical	541	542	1.59	
P2-radical	421	429	1.99	
P3-radical	423	421	2.02	



Fig. 1. UV-vis data of (a) P1-Boc, P2-Boc, P3-Boc, PDB-BHO and M1 in CHCl₃ solution with the concentration of 0.01 mg/ml; (b) P1-Boc, P2-Boc and P3-Boc film; (c) P1-radical, P2-radical and P3-radical film with the comparison of solar simulator spectrum (AM 1.5 G); (d) M1-radical in CHCl₃ solution with different time.



Fig. 2. Cyclic voltammograms of (A1) P1-Boc (A2) P1-radical, (B1) P2-Boc (B2) P2-radical, (C1) P3-Boc (C2) P3-radical films on a Pt/C electrode in 0.01 M tetrabutylammonium perchlorate (TBACIO₄), acetonitrile solution.

polyradicals are smaller than their corresponding precursor polymers. As mentioned above, the absorption peak of small molecule radical is at 600 nm. After the polymerization, comparing the peaks of polymers and polyradicals, we expect that the absorption peaks caused by the radical blocks in polyradicals are at longer wavelength than the peaks from the corresponding neutral polymers. That's why the polyradicals have smaller band gap than that of polymers.

Electrochemistry study is an effective tool to measure the oxidation and reduction potentials of polymers to understand their abilities to gain or lose electrons, and

 Table 3

 Electrochemical onset potentials and electronic energy levels of the polymer films.

Polymer	$E_{\rm on}^{\rm ox}/{\rm HOMO}~({\rm eV})$	$E_{\rm on}^{\rm red}/{ m LUMO}~({ m eV})$	$E_{\rm g}^{\rm cv}~({\rm eV})$
P1-Boc	0.24/-5.04	-1.55/-3.25	1.79
P2-Boc	0.91/-5.71	-3.10 ^a	-
P3-Boc	0.55/-5.35	-3.31ª	-
P1-radical	0.21/-5.01	-1.42/-3.38	1.63
P2-radical	0.48/-5.28	-3.29 ^a	-
P3-radical	0.54/-5.34	-1.24/-3.56	1.78

^a *Note:* Is the LUMO calculated according the HOMO and band gap from absorption spectra.

then calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. We use cyclic voltammetry (CV) to study the oxidation and reduction characters of these polymers (Fig. 2), with the sweep rate of 100 mV s⁻¹ in the acetonitrile solution with tetrabutylammonium perchlorate (TBACIO₄) as the electrolyte.

The onsets of oxidation and reduction peaks of polymers and polyradicals were listed in the Table 3. All the polymers and polyradicals (except P2-Boc) have oxidation potentials. On the basis of the onsets, the values for HOMO and LUMO were also calculated. It can be observed that the oxidation potentials are in the range of 0.24–0.91 V, which are so small that it indicates their weak oxidation resistance and easiness to lose electrons. With the smaller oxidation potentials, the absolute value of HOMO is bigger, indicating that it is easier for the hole carriers to inject. We calculate the value of LUMO using the reduction potentials or the HOMO above and band gap from the absorption spectra. Some of the polymers and polyradicals have no reduction potentials, but the existing data calculated by the two methods have a good match with each other.

The M1-radical and polyradicals are characterized by ESR spectra in toluene solution as shown in Fig. 3. We can observe the hyperfine structure of M1-radical (Fig. 3A). which proves the spin density distribution on the planar 1,3-diazaphenalenyl. To further explain it, we simulate the ESR spectrum of M1-radical (Fig. 3B) with density functional theory based on the DFT calculation by using Gaussian 03 at the UB3LYP/EPR-II level of theory. The π -spin density distribution of M1-radical is shown in Fig. 3C. The black dots denote carbon atoms. From the result, we can affirm that the main spin density distribution is on 1, 3, 4, 6, 7 and 9 positions. It is observed that the spin density disperses among the whole system and the appearance of weak conjunction to the top benzene rings. M1-radical gives a g value of 2.0033 and the hyperfine coupling constants (mT) are estimated by spectral simulation which referring to the calculation data: $a_{\text{Ha}} = -0.720$, $a_{\text{Hb}} =$ -0.631, $a_{\text{Ht-Bu}} = 0.011$, $a_{\text{N}} = 0.283$, $a_{\text{Hc}} = 0.020$, $a_{\text{Hd}} = -0.007$, and a_{He} = 0.018. The values of the g and hyperfine coupling constants for this model radial are consistent with other similar phenalenyl radicals [20,21]. The fine coupling structure of ESR spectra of the three polyradicals disappears with different extents, and the peaks widen comparing with that of M1-radical.

To judge the stability of polyradicals, we take P1-radical as an example to explain it (Fig. 4). We place P1-radical solution and powder in the tubes separately, and put them in the air at room temperature for one month. Comparing the ESR spectra before and after the placement, we can observe that there are almost no radicals left for the P1-radical solution, but the intensity and shape of the peaks of solid ESR signals did not change at all. These results



Fig. 3. The hyperfine ESR spectra of (A) the observed M1-radical (1 mM), (B) simulated for M1-radical, (C) π -spin density distribution of M1-radical calculated by DFT method using Gaussian 03 (UB3LYP/EPR-II), and the observed ESR spectra for the polymers (5 mM of the repeating unit concentration) (D) P1-radical, (E) P2-radical, (F) P3-radical in toluene at room temperature.



Fig. 4. The ESR spectra of (A) fresh P1-radical (1 mM of the repeating unit concentration) in toluene, (B) P1-radical (1 mM of the repeating unit concentration) in toluene placed in air for one month (the intensity is enlarged for 600 times), (C) P1-radical power, (D) P1-radical power in air for one month.



Fig. 5. UV-vis data of (A) P1-Boc, P2-Boc, P3-Boc and (B) P1-Boc:PCBM = 1:0.6, P2-Boc:PCBM = 1:0.6, P3-Boc:PCBM = 1:0.6 in CHCl₃ solution with the polymer concentration of 0.01 mg/ml.

indicate that these polyradicals are rather stable at room temperature, even in air at solid state.

We mixed the polymers and PCBM with mol ratio of 1:0.6 to do UV-vis spectra. As shown in Fig. 5, there is no obvious change of the peaks of polymers before and after addition of PCBM. However, there is one more peak appearing in Fig. 5B, at 325 nm. According to the literature [22], they belong to the absorption of PCBM. So the absorption spectra of the mixtures are just the simple addition of the two components, which means that there is no significant interaction between polymers and PCBM at ground state.

As shown in Fig. 6, after addition of PCBM, the fluorescence intensity of polymers is quenched largely, indicating the occurrence of electron transfer process in the interface of two materials at excited states.

We fabricate the photovoltaic devices with polymer/ PCBM or polyradical/PCBM with the molar ratio of 1:0.6 as active layer. The structure of the device is ITO/PEDOT– PSS/Polymer–PCBM (or polyradical–PCBM)/LiF/Al as shown in Fig. 7. The devices were studied under illumination (AM 1.5, 50 mW cm⁻²) in the air for their photovoltaic performance.

The OPV results are summarized in Table 4, which gave a best efficiency of 0.17%. Though the efficiencies of the devices are not high, the devices with polyradical/PCBM as the active layer have higher short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) than those with corresponding



Fig. 6. Photoluminescence of (A) P1-Boc and P1-Boc/PCBM (1/0.6 w/w), (B) P2-Boc and P2-Boc/PCBM (1/0.6 w/w), (A) P3-Boc and P3-Boc/PCBM (1/0.6 w/w) in CHCl₃ solution with the concentration of 0.01 mg/mL according to the polymer units, excited at 380 nm.



Fig. 7. A schematic device structure based on polymer/PCBM hybrid materials, the device structure is ITO/PEDOT-PSS/Polymer-PCBM (active layer)/LiF/Al.

 Table 4

 Properties of ITO/PEDOT-PSS/active layer/LiF/Al photovoltaic cells.

Polymer	$V_{\rm oc}\left({\sf V}\right)$	$I_{\rm sc} ({\rm mA/cm^2})$	FF	PCE (%)
P1-Boc	0.44	0.25	0.24	0.053
P1-radical	0.86	0.39	0.24	0.17
P2-Boc	0.47	0.26	0.27	0.064
P2-radical	0.66	0.32	0.25	0.11
P3-Boc	0.09	0.14	0.24	0.006
P3-radical	0.29	0.22	0.26	0.033

polymer/PCBM, so that the power conversion efficiency of polyradical/PCBM devices are improved significantly. There may be several reasons behind this. First, we argue that the presence of the unpaired electrons may increase the carrier concentration [23], which is crucial to determine the short-circuit current [24]. In addition, the improvement of the hole extraction of the device may lead to the shift of its quasi Fermi level, resulting in an increase in the $V_{\rm oc}$ [25].

3. Experimental

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques, and solvents were purified by standard procedures. ¹H NMR spectra were recorded on a Bruker AC-400 spectrometer. Chemical shifts. δ , are reported in ppm relative to the internal standard TMS. UV-vis-NIR spectra were obtained using IASCO-V570 spectrometers. Gel permeation chromatography (GPC) analvsis was performed on a Waters 510 system using polystyrene as the standard and THF as eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C. Cyclic voltammetric measurement was performed on a LK98BII Microcomputer-based Electrochemical Analyzer, using a Pt wire electrode with n-Bu₄ NClO₄ as the supporting electrolyte, with a Ag/Ag⁺ reference electrode. After measurement, the reference electrode was calibrated with ferrocene (Fc) and the potential axis was corrected to Fc/Fc⁺. The synthesis procedures of P1-P3 were shown in the Schemes 2-4, respectively.

3.1. 2,5-Bis((trimethylsilyl)ethynyl)benzaldehyde (1)

A 250 mL two-necked round-bottomed flask equipped with a stir bar was charged with 2,5-dibromo-benzaldehyde (2.64 g, 10 mmol, 1 equiv), dichlorobis(triphenyl phosphine)-palladium (II) (420.8 mg, 0.60 mmol, 0.06 equiv) and copper (I) iodide (228.8 mg, 1.20 mmol, 0.12 equiv) under nitrogen atmosphere, and then toluene (100 mL), diisopropylamine (4 mL, 28 mmol, 2.8 equiv) and (trimethylsilyl)acetylene (TMSA) (3.0 mL, 21.8 mmol, 2.2 equiv) were successively added. After evacuated and back filled with nitrogen three times, the black solution was stirred at 80 °C for 3 h. After cooled to room temperature, saturated ammonium chloride solution was added. and the mixture was stirred for 30 min. Organic laver was then separated, and washed three times with saturated ammonium chloride solution. After dried with sodium sulfate and filtered, the solution was concentrated to give a dark black oil which was chromatographed on silica gel (1/10 = ethyl acetate/hexane) to afford the product **1** as a yellow oil (2.98 g, \sim 100%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 0.26 (d, 18H, J = 10.4 Hz, $-SiCH_3$), 7.50 (d, 1H, J = 8 Hz, ArH), 7.59 (d, 1H, J = 8 Hz, ArH), 7.97 (s, 1H, ArH), 1.49 (s, 1H, -COH).

3.2. 2-(2,5-Bis((trimethylsilyl)ethynyl)phenyl)-5,8-di-tertbutyl-1H-perimidine-1-carboxylate (**2**)

Compound **1** (2.34 g, 7.5 mmol) and 1,8-diamino-3,6di-tert-butylnaphthalene (2.03 g, 7.5 mmol) were placed in a 250 mL round-bottomed flask equipped with a reflux condenser and mixed with ethanol (90 mL), then NaHSO₃ (0.79 g, 7.5 mmol) was added. The mixture was refluxed at 85 °C oil bath overnight. Once the reaction was cooled to room temperature, the mixture was filtered and the solid was dissolved in CH_2Cl_2 . After washed with water for



Scheme 2. Synthesis of polymer P1.

three times, the combined organic layer was dried with sodium sulfate, then filtered and concentrated. The generated product as a red oil was used directly for next step.

A solution of the red oil from last step in THF (100 mL) was placed in a 250 mL two-necked round-bottomed flask eq ped with a stir bar. After 4-(dimethylamino) pyridine (DMAP) (610 mg, 5 mmol) and Et₃N (1.4 mL, 10 mmol) were added, the flask was capped and nitrogen was bubbled through the solution for 20 min. Di-tert-butyldicarbonate ((BocO)₂O) was then added to the flask under nitrogen. After the mixture was stirred at room temperature for 4 h, it was concentrated, the remained oil was chromatographed on silica gel (0.3% ethyl acetate and 99.7% hexane) to give a yellow powder product 2 (1.71 g, 35%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 0.13 (s, 9H, -SiCH₃), 0.25 (s, 9H, -SiCH₃), 1.21 (s, 9H, -O-tert-butyl), 1.38 (d, 18H, *J* = 6.4 Hz, naphthalene-tert-butyl), 7.39 (d, 2H, 4.4 Hz, ArH), 7.48 (s, 2H, naphthalene-H), 7.52 (br, 1H, naphthalene-H), 7.68 (br, 1H, naphthalene-H), 7.79 (s, 1H, ArH); ESI MS, *m/z* 649 (M⁻, 100%).

3.3. tert-Butyl 5,8-di-tert-butyl-2-(2,5-diethynylphenyl)-1H-perimidine-1-carboxylate (**3**)

Compound **2** (648 mg, 1 mmol) was dissolved in degassed THF (15 mL) and methanol (7 mL), then aqueous potassium hydroxide (168 mg, 3 mmol; dissolved in 1 mL of DDI water) was added. After the solution was stirred for 4 h, it was washed with aqueous saturated ammonium chloride and extracted with CH_2Cl_2 three times. The combined organic layer was washed with water and then dried with sodium sulfate and concentrated to provide an orange solid which was recrystallized from hexane to provide product **3** (452 mg, 90%). ¹H NMR (d-DMSO, 400 MHz), δ (ppm): 1.13 (s, 9H, –O-tert-butyl), 1.34 (d, 18H, *J* = 5.6 Hz, naphthalene-tert-butyl), 4.44 (s, 1H, alkyne-H), 4.62 (s, 1H, alkyne-H), 7.24 (s, 1H, naphthalene-H), 7.50 (d, 2H, *J* = 11.2 Hz, ArH), 7.58 (s, 2H, naphthalene-H), 7.65 (s, 1H, naphthalene-H), 7.78 (s, 1H, ArH); ESI MS, *m*/*z* 505 (M⁺, 55%), 405 (M-Boc, 100%).

3.4. 2-(2,5-Dibromophenyl)-1H-perimidine (4)

2,5-Dibromo-benzaldehyde (1.66 g, 6.3 mmol, 1 equiv) and 1,8-diaminonaphthalene were placed in a 100 mL round-bottomed flask equipped with a reflux condenser and dissolved in ethanol (10 mL), then NaHSO₃ aqueous solution (0.6 g NaHSO₃ dissolved in 10 mL DDI water) was added. The mixture was refluxed at 90 °C with oil bath overnight. The cooled mixture was filtered and dissolved in CHCl₃, then washed with water for several times. The organic layers were collected together and dried with



Scheme 3. Synthesis of polymer P2.

Na₂SO₄, then filtered and concentrated to provide orange powder for chromatograph on silica gel (25% ethyl acetate and 75% hexane) to give a yellow powder product **4** (0.53 g, 21%). ¹H NMR (DMSO, 400 MHz), δ (ppm): 6.30 (d, 1H, *J* = 7.2 Hz, naphthalene-H), 6.60 (d, 1H, *J* = 7.2 Hz, naphthalene-H), 7.03 (d, 1H, *J* = 8.2 Hz, naphthalene-H), 7.10 (t, 2H, *J* = 7.5 Hz, naphthalene-H), 7.18 (t, 1H, *J* = 7.9 Hz, naphthalene-H), 7.65 (d, 1H, *J* = 8.6 Hz, -ArH), 7.71 (d, 1H, *J* = 8.6 Hz, -ArH), 7.84 (s, 1H, -ArH); ESI MS, *m/z* 403 (M⁺, 100%). Elem. Anal. Calcd. for C₁₇H₁₀Br₂N₂: C, 50.8%; H, 2.5%; N, 7.0%. Found: C, 51.0%; H, 2.8%; N, 6.4%.

3.5. tert-Butyl 2-(2,5-dibromophenyl)-1H-perimidine-1-carboxylate (**5**)

A 100 mL two-necked round-bottomed flask equipped with a stir bar was charged with **4** (0.34 g, 0.85 mmol) resolved in THF, then DMAP (103.7 mg, 0.85 mmol) and Et₃N 0.85 mL were added, the flask was capped and nitrogen was bubbled through the solution for 20 min. (BocO)₂O was then added to the flask under nitrogen. After the mixture was stirred at room temperature for 1 h, it was concentrated, the remained oil was chromatographed on silica gel (1% ethyl acetate and 99% hexane) to give a yellow powder product **5** (0.39 g, 92%). ¹H NMR (d-DMSO, 400 MHz), δ (ppm): 7.12 (d, 1H, *J* = 8.2 Hz, naphthalene-H), 7.40–7.57 (br, 5H, naphthalene-H), 7.18 (t, 1H, *J* = 7.9 Hz, naphthalene-H), 7.66 (d, 1H, *J* = 8.6 Hz, –ArH), 7.71 (d, 1H, *J* = 8.5 Hz, –ArH), 7.89 (s, 1H, –ArH); ESI MS, *m/z* 403 (M⁺-Boc, 100%). Elem. Anal. Calcd. for C₂₂H₁₈Br₂N₂O₂: C, 52.6%; H, 3.6%; N, 5.6%. Found: C, 53.6%; H, 3.6%; N, 5.2%.

3.6. 4-(Thiophen-3-yl) benzaldehyde (6)

3-Thiopheneboronic acid (1.85 g, 10 mmol) and 4-bromo-benzaldehyde (1.41 g, 11 mmol) were dissolved in xylene (20 mL), Pd(PPh₃)₄ (0) (0.60 g, 0.52) and Na₂CO₃ aqueous solution (2.12 g Na₂CO₃ dissolved in 20 mL DDI water) were added. The mixture was reacted at 95 °C with



Scheme 4. Synthesis of polymer P3.

oil bath for 3 h. After cooling to room temperature, extraction with CH_2Cl_2 , then the organic layer was washed by water. The solution was dried by Na_2SO_4 , concentrated, the remained solid was chromatographed on silica gel (2% ethyl acetate and 98% hexane) to give a yellow powder product **6** (1.80 g, 96%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.45 (br, 2H, thiophene-H), δ 7.62 (t, 1H, *J* = 2.1 Hz, thiophene-H), 7.77 (d, 2H, *J* = 8.2 Hz, -ArH), 7.92 (t, 2H, *J* = 8.2 Hz, -ArH), 10.03 (s, 1H, -CHO). Elem. Anal. Calcd. for C₁₁H₈OS: C, 70.2%; H, 4.3%. Found: C, 68.7%; H, 4.1%.

3.7. 4-(2,5-Dibromothiophen-3-yl)-4-(thiophen-3-yl) benzaldehyde (**7**)

(0.80 g, 4.3 mmol) resolved in the mixed acetic acid (20 mL) and CHCl₃ (20 mL), then the flask was capped and nitrogen was bubbled through the solution for 20 min, after that NBS (1.53 g, 8.6 mmol) was added. The mixture reacted under stirring overnight. After the dilution with water, the solution was extracted with CH₂Cl₂. The organic layer was collected and dried with Na₂SO₄, filtration, concentration. The remained solid was recrystallized by ethyl acetate to get **7** (0.81 g, 54%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.07 (s, 1H, thiophene-H), 7.69 (d, 2H, *J* = 8.0 Hz, -ArH), 7.95 (d, 1H, *J* = 8.0 Hz, -ArH), 10.06 (s, 1H, -CHO). Elem. Anal. Calcd. for C₁₁H₆Br₂OS: C, 38.2%; H, 1.8%. Found: C, 38.3%; H, 1.9%.

3.8. tert-Butyl 5,8-di-tert-2-(4-(2,5-dibromophenyl-3-yl) phenyl)-1H-perimidine-1-carboxylate (**8**)

Compound **7** (0.35 g, 1 mmol) and 1,8-diamino-3,6-ditert-butylnaphthalene (0.27 g, 1 mmol) were placed in a 100 mL round-bottomed flask equipped with a reflux condenser and mixed with DMF (10 mL), then NaHSO₃ aqueous solution (0.01 g NaHSO₃ resolved in 5 mL DDI water) was added. The mixture was refluxed at 90 °C oil bath for 6 h. Once the reaction was cooled to room temperature, the mixture was diluted with water, then filtered to get orange solid, which was used directly for the next step.

The orange solid from last step resolved in THF (20 mL) was placed in a 100 mL two-necked round-bottomed flask equipped with a stir bar. After 4-(dimethylamino) pyridine (DMAP) (120 mg, 1 mmol) and Et₃N (0.14 mL, 1 mmol) were added, the flask was capped and nitrogen was bubbled through the solution for 20 min. Di-tert-butyldicarbonate ((BocO)₂O) (0.46 mL) was then added to the flask under nitrogen. After the mixture was stirred at room temperature for 1 h, it was concentrated, then recrystallized with hexane to give a yellow powder product **8** (0.37 g, 53%). Elem. Anal. Calcd. for C₃₄H₃₂Br₂N₂O₂S: C, 58.6%; H, 5.2%; N, 4.0%. Found: C, 57.6%; H, 5.6%; N, 4.2%.

3.9. tert-Butyl 5,8-tert-butyl-2-phenyl-1H-perimidine-1-carboxylate (M1)

Benzalbehyde (275.6 mg, 2.6 mmol) and 1,8-diamino-3,6-di-tert-butylnaphthalene (540 mg, 2.0 mmol) were placed in a 50 mL round-bottomed flask equipped with a reflux condenser and dissolved in xylene (20 mL), then Pd/C (10%, 6.4 mg) was added. The mixture was refluxed at 150 $^{\circ}$ C with oil bath for 4 h. The cooled mixture was filtered, then concentrated and recrystallized from hexane to provide orange powder (0.48 g) for next step.

A solution of the orange powder (71.2 mg) above in THF (10 mL) was placed in a 50 mL two-necked round-bottomed flask equipped with a stir bar. After 4-(dimethylamino)pyridine (DMAP) (24.4 mg, 0.2 mmol) and Et₃N (0.1 mL, 0.7 mmol) were added, the flask was capped and nitrogen bubbled through the solution for 20 min. Di-tertbutyldicarbonate (0.1 mL, 0.4 mmol) was then added to the flask under nitrogen, and the mixture was stirred at room temperature for 1 h. After concentrated, the oil was recrystallized from hexane to give yellow powder (50 mg, 55%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.11 (s, 9H, –Otert-butyl), 1.38 (s, 9H, naphthalene-tert-butyl), 1.41(s, 9H, naphthalene-tert-butyl), 7.32 (s, 1H, naphthalene-H), 7.39 (dd, 2H, naphthalene-H), 7.44 (m, 3H, naphthalene-H and ArH), 7.79 (m, 3H, ArH); ESI MS, *m/z* 456 (M⁻, 100%).

3.10. Poly(2-(tert-butyl-5,8-di-tert-butyl-1H-perimidine-1-carboxylate)-1,4-diethynylbenzene) (P1-Boc)

A 50 mL two-necked round-bottomed flask equipped with a stir bar was charged with 3 (252 mg, 0.5 mmol, 1 equiv), dichlorobis(triphenylphosphine)-palladium (II) (7.0 mg, 0.01 mmol, 0.02 equiv), copper (I) iodide (3.8 mg, 0.02 mmol, 0.04 equiv) and iodine (127 mg, 0.5 mmol, 1 equiv) under nitrogen. Then THF (12 mL) and diisopropylamine (12 mL) were successively added using syringe. The mixture was stirred at room temperature for 48 h. The reaction solution was washed with aqueous Na₂S₂O₃ for several times to get rid of iodine. After dried with sodium sulfate, the solution was filtered and concentrated and then it was added to methanol (~200 mL) to precipitate the product polymer out. The product was collected by filtration and rinsed with small amount of warm methanol and dried under vacuum to yield poly(tert-butyl 5, 8-di-tert-butyl-2-diethynylbenzene-1H-perimidine-1-carboxylate) (PDB-PLY) as a brown solid (212 mg, 85%). The $M_n = 7600 \text{ g mol}^{-1}$ with a polydispersity index (M_w/M_n) of 1.48; degree of polymerization is 15. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.26 (br, 9H, –O-tert-butyl) 1.43 (br, 18H, naphthalene-tert-butyl), 6.6-8.0 (br, 7H, naphthalene and ArH). Elem. Anal. Calcd. for (C₃₄H₃₄N₂O₂)_n: C, 81.08%; H, 7.00%; N, 5.56%. Found: C, 80.11%; H, 6.70%; N, 4.98%.

3.11. Poly(1,4-diethynyl-2,5-bis(hexadecyloxy) benzene)-copoly(tert-butyl-2-(2,5-dibromophenyl)-1H-perimidine-1carboxylate) (P2-Boc)

A 50 mL two-necked round-bottomed flask equipped with a stir bar was charged with 5 (314.9 mg, 0.63 mmol, 1 equiv), 1,4-diethynyl-2,5-bis(hexadecyloxy) benzene (391.5 mg, 0.65 mmol, 1.03 equiv), Pd(PPh_3)₄ (21.7 mg, 0.019 mmol, 0.03 equiv) and CuI (7.2 mg, 0.038 mmol, 0.06 equiv) under nitrogen. Then toluene (30 mL) and diisopropylamine (2 mL) were successively added using syringe. The mixture was stirred at 80 °C for 48 h. After the cooling to room temperature, the solution was concentrated to just little toluene left, then adding methanol

200 mL. Filtrate and wash with hexane for many times to get yellow product P2-Boc (146 mg, 24%). The $M_n = 16,700 \text{ g mol}^{-1}$ with a polydispersity index (M_w/M_n) of 1.36; degree of polymerization is 17. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 0.88 (t, 6H, -CH₃), 1.21–1.54 (br, 65H, -O-tert-butyl and alkyl chain), 3.45–4.06 (br, 4H, O-CH₂), 6.82–7.98 (br, 11H, naphthalene and ArH). Elem. Anal. Calcd. (C₆₄H₈₆N₂O₄)_n: C, 81.14%; H, 9.15%; N, 2.96%. Found: C, 79.94%; H, 7.97%; N, 2.86%.

3.12. Poly(tert-butyl 2(4-(2,2'-bithiophen-3-yl)phenyl)5,8-ditert-butyl-1H-permidine-1-carboxylate) (P3-Boc)

A 25 mL two-necked round-bottomed flask equipped with a stir bar was charged with 8 (69.6 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)thiophene (41 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), then inject toluene 5 mL under nitrogen. The mixture stirred at room temperature for 48 h. After the reaction, it was added to methanol $(\sim 100 \text{ mL})$ to precipitate the product polymer out. The product was collected by filtration and rinsed with small amount of warm methanol and dried under vacuum to yield P3-Boc as a red solid (48 mg, 74%). The $M_n = 8100 \text{ g mol}^{-1}$ with a polydispersity index (M_w/M_n) of 1.52; degree of polymerization is 12. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.27–1.64 (br, 27H, –O-tert-butyl and naphthalene-tert-butyl), 6.59-8.49 (br, 11H, naphthalene, Ar and thiophene-H). Elem. Anal. Calcd. $(C_{38}H_{38}N_2O_2S_2)_n$ C, 73.75%; H, 6.19%; N, 4.53%. Found: C, 72.13%; H, 5.91%; N, 3.96%.

3.13. Poly(5,8-di-tert-butyl-2-diethynylbenzene-1H-perimidine) (P1-NH)

P1-Boc (100 mg) was dissolved in THF (20 mL), and CF₃COOH (1.5 mL) was added to the solution. The mixture was stirred for 30 min at room temperature, and neutralized with NH₃·H₂O (7 mL, 4%). Then the mixture was extracted with CH₂Cl₂ and washed with water for several times. After dried with anhydrous sodium sulfate, the organic layer was filtrated and evaporated to yield the crude product. It was then dissolved in CHCl₃ and re-precipitated by adding into methanol to yield the P1 as deep purple powder (63 mg, 79%). The M_n = 7800 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.53; degree of polymerization is 19. Elem. Anal. Calcd. ($C_{29}H_{26}N_2$)_n: C, 86.53%; H, 6.51%; N, 6.96%. Found: C, 83.87%; H, 5.65%; N, 5.89%.

The method to synthesize P2-NH and P3-NH is the same with that of P1-NH. The M_n of P2-NH is 12,100 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.65, degree of polymerization is 14. Elem. Anal. Calcd. $(C_{59}H_{78}N_2O_2)_n$: C, 83.64%; H, 9.28%; N, 3.31%. Found: C, 81.78%; H, 8.51%; N, 2.83%. The M_n of P3-NH is 8700 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.35; degree of polymerization is 16. Elem. Anal. Calcd. $(C_{33}H_{30}N_2S_2)_n$: C, 76.41%; H, 5.83%; N, 5.40%. Found: C, 74.89%; H, 4.94%; N, 4.76%.

3.14. Preparation of the polyradical P1-radical

A degassed toluene solution of P1 (60 mg) was treated with 10 equiv of freshly prepared PbO₂ and vigorously stir-

red overnight. After filtration to removed inorganic solid, the solution was poured into methanol and the precipitate was collected by filtration. The crude product was re-dissolved in CHCl₃ and re-precipitated with methanol to yield the polyradical (48 mg, 80%). The M_n = 8500 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.70; degree of polymerization is 21. Elem. Anal. Calcd. ($C_{29}H_{25}N_2$) $_n$: C, 86.75%; H, 6.28%; N, 6.98%. Found: C, 84.21%; H, 4.91%; N, 5.77%.

The method to synthesize P2-radical and P3-radical is the same with that of P1-radical. The M_n of P2-radical is 13,200 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.45; degree of polymerization is 21. Elem. Anal. Calcd. ($C_{59}H_{77}N_2O_2$)_n: C, 83.74%; H, 9.17%; N, 3.31%. Found: C, 81.40%; H, 7.87%; N, 2.68%. The M_n of P3 is 8300 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.35; degree of polymerization is 15. Elem. Anal. Calcd. ($C_{33}H_{29}N_2S_2$)_n: C, 76.56%; H, 5.65%; N, 5.41%. Found: C, 73.90%; H, 4.48%; N, 4.61%.

3.15. Fabrication of PV devices

The ITO glass (ca. 17 Ω sq⁻¹, CSG Inc.) was cleaned in an ultrasonic bath with detergent, acetone and isopropyl alcohol. PEDOT:PSS (Baytron P AI 4083) was then spin-coated (4000 rpm, ca. 30 nm thick) on top of ITO-coated glass. The active layer was prepared by spin-coating (1000 rpm, 60 s) on the above modified ITO glass using a dichlorobenzene solution of polymer/PCBM (1:0.6, w/w). Then lithium fluoride (LiF, ca. 1 nm) and an Al electrode (100 nm) were deposited onto the blend film by thermal evaporation at ca. 4×10^{-4} Pa. A xenon lamp was used as the light source with a power of 100 mW cm⁻² to simulate AM 1.5 global sunlight. The solar cell power conversion efficiency was not certified. The fabrication and measurements were all carried out in air at room temperature.

4. Conclusion

In summary, we synthesized three kinds of polymers and their corresponding neutral stable polyradical with the π -conjugated phenalenyl radical unit. These polyradicals exhibit a good solubility in common organic solvents and stability in air. The conjugation between the side chain of 1,3-diazaphenalenyl unit and backbones cause a substantial red shift of absorption spectrum and the lowering of the band gap. The results of photovoltaic devices show that the active layers using polyradicals as the electron donating material have improved the overall energy conversion efficiency comparing with those with the precursor polymers. We expect that this approach using stable neutral planar polyradicals as the active material for optoelectrical devices should bring more and better results.

Acknowledgements

The authors gratefully acknowledge the financial support from the NSFC (#50933003, 50903044, 50902073) and MOST (#2009AA032304).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj. 2011.02.017.

References

- [1] Rajca A, Rajca S, Wongsriratanakul J. Very high-spin organic polymer: pi-conjugated hydrocarbon network with average spin of S ≥ 40. J Am Chem Soc 1999;121(26):6308–9.
- [2] Michinobu T, Inui J, Nishide H. *m*-Phenylene-linked aromatic poly(aminium cationic radical)s: persistent high-spin organic polyradicals. Org Lett 2003;5(12):2165–8.
- [3] Miyasaka M, Saito Y, Nishide H. Magnetic force microscopy images of a nanometer-sized purely organic high-spin polyradical. Adv Funct Mater 2003;13(2):113–7.
- [4] Rajca S, Rajca A, Wongsriratanakul J, Butler P, Choi S. Organic spin clusters. A dendritic-macrocyclic poly(arylmethyl) polyradical with very high spin of S = 10 and its derivatives: synthesis, magnetic studies, and small-angle neutron scattering. J Am Chem Soc 2004;126(22):6972–86.
- [5] Fukuzaki E, Nishide H. Room-temperature high-spin organic single molecule: nanometer-sized and hyperbranched poly[1,2,(4)phenylenevinyleneanisylaminium]. J Am Chem Soc 2006;128(3): 996–1001.
- [6] Kulszewicz-Bajer I, Zagorska M, Wielgus I, Pawłowski M, Gosk J, Twardowski A. High-spin radical cations of alternating poly(*m-p*anilines). J Phys Chem B 2007;111(1):34–40.
- [7] Miyasaka M, Yamazaki T, Tsuchida E, Nishide H. Regioregular polythiophene with pendant phenoxyl radicals: a new high-spin organic polymer. Macromolecule 2000;33(22):8211–7.
- [8] Kaneko T, Matsubara T, Aoki T. Synthesis of a pendant polyradical with a new pi-conjugated polymer backbone containing an anthracene skeleton and its ferromagnetic spin coupling. Chem Mater 2002;14(9):3898–906.
- [9] Nishid H, Nambo M, Miyasaka M. Hyperbranched poly(phenylenevinylene) bearing pendant phenoxys for a high-spin alignment. J Mater Chem 2002;12(12):3578–84.
- [10] Kaneko T, Makino T, Miyaji H, Teraguchi M, Aoki T, Miyasaka M, et al. Ladderlike ferromagnetic spin coupling network on a pi-conjugated pendant polyradical. J Am Chem Soc 2003;125(12):3554–7.
- [11] Takeda R, Yamanaka S, Yamaguchi K. Resonating broken-symmetry approach to biradicals and polyradicals. Int J Quantum Chem 2006;106(15):3303–11.

- [12] Hua CW, Leeb KM, Huangc JH, Hsuc CY, Kuoc TH, Yangc DJ, et al. Incorporation of a stable radical 2,2,6,6-tetramethyl-1piperidinyloxy (TEMPO) in an electrochromic device. Solar Energy Mater Solar Cells 2009;93(12):2102–7.
- [13] Chen HY, Hou JH, Zhang SQ, Liang YY, Yang GW, Yang Y, et al. Polymer solar cells with enhanced open-circuit voltage and efficiency. Nat Photonics 2009;3(11):649–53.
- [14] Park SH, Roy A, Beaupre S, Cho S, Coates N, Moon JS, et al. Bulk heterojunction solar cells with internal quantum efficiency approaching 100%. Nat Photonics 2009;3(5):297–303.
- [15] Liang YY, Feng DQ, Wu Y, Tsai ST, Li G, Ray C, et al. Highly efficient solar cell polymers developed via fine-tuning of structural and electronic properties. J Am Chem Soc 2009;131(22):7792–9.
- [16] Hou JH, Chen HY, Zhang SQ, Chen RI, Yang Y, Wu Y, et al. Synthesis of a low band gap polymer and its application in highly efficient polymer solar cells. J Am Chem Soc 2009;131(43):15586-7.
- [17] Shirota Y, Kageyama H. Charge carrier transporting molecular materials and their applications in devices. Chem Rev 2007;107(4): 953–1010.
- [18] Lv X, Mao J, Liu Y-H, Huang Y, Ma Y-F, Yu A, et al. A neutral stable and soluble polymer radical with low band gap and its photovoltaic application. Macromolecules 2008;41(3):501–3.
- [19] Tour MJ. Conjugated macromolecules of precise length and constitution. Organic synthesis for the construction of nanoarchitectures. Chem Rev 1996;96(1):537–54.
- [20] Morita Y, Aoki T, Fukui K, Nakazawa S, Tamaki K, Suzuki S, et al. A new trend in phenalenyl chemistry: a persistent neutral radical, 2,5,8-tri-tert-butyl-1,3-diazaphenalenyl, and the excited triplet state of the gable syn-dimer in the crystal of column motif. Angew Chem Int Ed 2002;41(10):1793–6.
- [21] Goto K, Kubo T, Yamamoto K, Nakasuji K, Sato K, Shiomi D, et al. A stable neutral hydrocarbon radical: synthesis, crystal structure, and physical properties of 2,5,8-tri-tert-butyl-phenalenyl. J Am Chem Soc 1999;121(7):1619–20.
- [22] Li G, Shrotriya V, Huang JS, Yao Y, Moriarty T, Emery K, et al. Highefficiency solution processable polymer photovoltaic cells by selforganization of polymer blends. Nat Mater 2005;4(11):864–8.
- [23] Yamamori A, Adachi C, Koyama T, Taniguchi Y. Doped organic light emitting diodes having a 650-nm-thick hole transport layer. Appl Phys Lett 1998;72(17):2147–9.
- [24] Gunes S, Neugebauer H, Sariciftci NS. Conjugated polymer-based organic solar cells. Chem Rev 2007;107(4):1324–38.
- [25] Vaddiraju S. Radical salt-doped hole transporters in organic photovoltaic devices. Chem Mater 2007;19:4049–55.