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ARTICLE TYPE

Phosphonated Conjugated Polymers for Polymer Solar Cells with Non-Halogenated Solvent Process

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Normal photovoltaic polymers must be processed with halogenated solvents, which are harmful for environment and cannot be used for mass production of polymer solar cells (PSCs). We report a novel approach to develop photovoltaic polymers suitable for non-halogenated solvent processing by attaching polar and inert phosphonate moiety to side chain of conventional photovoltaic polymers. The pendant phosphonate moiety does not obviously affect the electronic structure of the conjugated polymer backbone but greatly changes the solubility of the polymers. The phosphonated polymers are soluble in several polar non-halogenated solvents, such as methoxybenzene (MOB), methylbenzoate (MBz), *o*-dimethoxybenzene (*o*-DMOB), etc. PSCs of the phosphonated polymers processed with MOB exhibit better photovoltaic performance than those of the devices processed with common halogenated solvents. A power conversion efficiency (PCE) of 2.11% is achieved with the device processed with MOB, in comparison to the PCE of 0.90% with chlorobenzene (CB) as the processing solvent and the PCE of 1.59% with *o*-dichlorobenzene (*o*-DCB) as the processing solvent. These results indicate that pendant phosphonate moiety is an effective approach to develop photovoltaic polymers towards PSCs fabricated with environmental-friendly solvents.

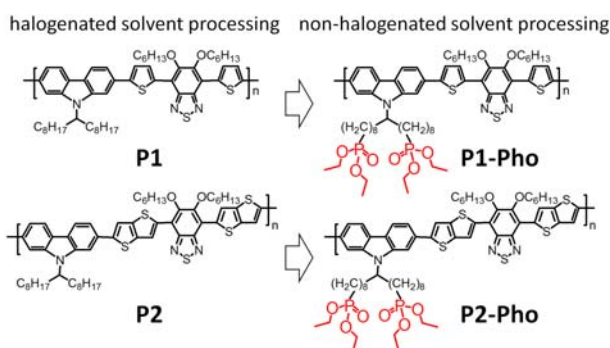
Introduction

Polymer solar cells (PSCs) have recently received great attention due to their great advantages of low-cost, light weight and flexibility.¹⁻⁴ In the past decade, the power conversion efficiency (PCE) of PSCs has increased rapidly to around 10%, which is close to the critical point of industrialization.⁵⁻¹⁵ For the large-scale manufacturing of PSCs, the impact of processing solvents on environment must be seriously considered.¹⁶⁻¹⁹ Till now, the most widely used solvent for PSC device fabrication are some halogenated solvents, such as chlorobenzene (CB) and *o*-dichlorobenzene (*o*-DCB), which are harmful for environment and human health. These halogenated solvents cannot be used in large-scale manufacturing of PSCs. Therefore, it is urgent to develop PSC devices and materials suitable for PSCs processed with non-halogenated solvents.²⁰⁻²⁶

Normal donor polymers are suitable for processing with halogenated solvents because they have non-polar alkyl side chains for solubility in the halogenated solvents with low polarity. To make donor polymers suitable for non-halogenated solvent processing, the general strategy is to increase the polarity of the side chains, including, i) replacing alkyl chains with oligo(ethylene oxide) chains²⁵ and ii) attaching polar moieties (e.g. tertiary amine unit) to the alkyl side chains.²⁶ However, hydrophilic oligo(ethylene oxide) side chains greatly change the ordered solid-state organization of hydrophobic conjugated polymer backbone and result in great difficulty in the control of

active layer morphology in PSC devices.²⁵ Polar moieties are always opto-electronically active and can deteriorate PSC device performance.²⁶ For example, Huang et al reported a donor polymer bearing pendant tertiary amino moieties which could be processed with butanol.²⁶ Owing to the charge trapping of the tertiary amino moieties, the polymer exhibited no photovoltaic response when used in the active layer of PSCs. Indeed, PSCs processed with pure polar non-halogenated solvents all exhibit poor photovoltaic performance with PCE lower than 2%. In this manuscript, we report a novel approach to design donor polymers suitable for polar non-halogenated solvent processing by attaching inert and polar phosphonate moiety to side chain of normal donor polymers.

Previously, we have found that pendant phosphonate moiety can make conjugated polymers soluble in polar organic solvents (e.g. ethanol) and that pendant phosphonate moieties do not affect the electronic structure of conjugated polymer backbone.²⁷⁻³¹ Tu et al have also used phosphonate moieties to develop amphiphilic conjugated polymers.³² The polar and inert property of phosphonate moieties enable us to design donor polymers suitable for non-halogenated solvent processing by changing solubilizing behavior of normal donor polymers without affecting opto-electronic properties of conjugated polymer backbone.^{27,28} Among the reported donor polymers, PCDTBT series polymers with alternating carbazole unit and 4,7-dithienyl-2,1,3-benzothiadiazole unit (see Scheme 1) are particularly attractive and can give PCE higher than 7%.³³⁻³⁶ Herein, we introduce phosphonate moieties to the side chain of PCDTBT analogous



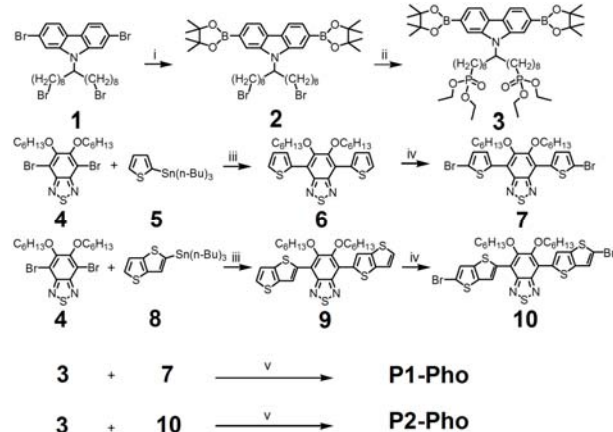
Scheme 1 Chemical structures of **P1-Pho**, **P2-Pho**, **P1** and **P2**.

polymer backbone to develop two new polymers, **P1-Pho** and **P2-Pho**. Scheme 1 shows their chemical structures. Both the two polymers exhibits good solubility in some polar non-halogenated solvents, such as methoxybenzene (MOB), methylbenzoate (MBz), *o*-dimethoxybenzene (*o*-DMOB), etc. PSC devices of the two phosphonated polymers processed with MOB show better photovoltaic performance than those of the devices processed with halogenated solvents, CB or *o*-DCB. A PCE of 2.11% is demonstrated with **P2-Pho** processed with MOB, which is among the highest reported for PSCs fabricated with pure non-halogenated solvent without additives.^{25, 26}

Results and Discussion

Synthesis and Characterization

Scheme 1 shows the chemical structures of **P1-Pho** and **P2-Pho**, as well as the corresponding polymers without pendant phosphonate moieties, **P1** and **P2**. The synthetic routes for **P1-Pho** and **P2-Pho** were depicted in Scheme 2. The phosphonate-functionalized monomer **3** was synthesized following the procedures in our previous publication.³¹ The monomers **7** and **10** were prepared through sequential Stille coupling and bromination reaction starting from **4**. We synthesized **P1-Pho** and **P2-Pho** using Pd(0)-catalyzed Suzuki polycondensation with the di-boronic ester monomer and the di-bromo monomer. The chemical



Scheme 2 Synthetic routes for **P1-Pho** and **P2-Pho**. (Reagents and conditions: i) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, 1,4-dioxane, 80 °C; ii) triethyl phosphite, reflux; iii) Pd(PPh₃)₄, CuI, toluene, reflux; iv) NBS, dichloromethane; v) Pd(PPh₃)₄, K₂CO₃ (aq. 2M), toluene, Aliquat 336, 100 °C.).

structures of the polymers are confirmed by ¹H NMR and elemental analysis. Their molecular weights were estimated by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent and monodisperse polystyrene as the standards. The number-average molecular weight (M_n) and polydispersity index (PDI) of **P1-Pho** and **P2-Pho** are 41300, 2.4 and 55100, 3.3, respectively (see Table 1). According to thermogravimetric analysis (TGA), both **P1-Pho** and **P2-Pho** have good thermal stability with thermal degradation temperature (T_d) higher than 300 °C (Table 1).

Table 1 Molecular weights and thermal properties of the polymers.

polymer	M _n (g/mol) ^a	PDI	T _d (°C) ^b
P1-Pho	41,300	2.4	325
P1	58,000	2.1	312
P2-Pho	55,100	3.3	307
P2	67,100	3.1	316

^a Number-average molecular weight. ^b Temperature at weight loss of 5 wt%.

Photophysical Properties

UV-Vis absorption spectra in *o*-DCB solution at 90 °C and in film of **P1-Pho**, **P2-Pho**, **P1** and **P2** are shown in Figure 1. **P1-Pho** in solution presents two absorption bands peaked at 391 and 523 nm, which are attributed to the π-π* transition and the charge transfer of the conjugated polymer backbone, respectively.³⁷ In solid film, the two absorption peaks red-shift to 394 and 540 nm, respectively, due to the strong interaction of polymer chains in solid state. The absorption spectra in solution and in film of **P1-Pho** resemble those of **P1** (Figure 1a), similar phenomenon is observed in the absorption spectra of **P2-Pho** and **P2** (Figure 1b).

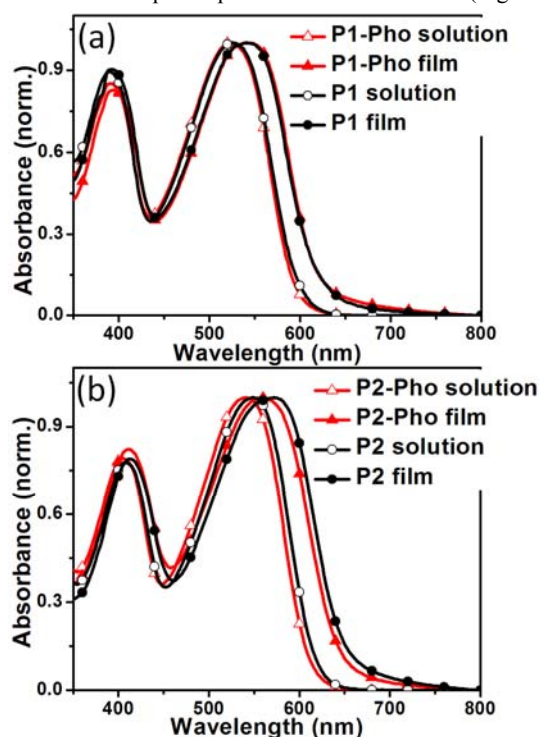


Figure 1 (a) UV-vis absorption spectra of **P1-Pho** and **P1** in *o*-DCB solution (90 °C) and in film. (b) UV-vis absorption spectra of **P2-Pho** and **P2** in *o*-DCB solution (90 °C) and in film.

These results indicate that the phosphonate moieties on the side chain of **P1-Pho** and **P2-Pho** do not obviously affect the electronic properties of the conjugated polymer backbone.²⁷⁻³¹ Compared with that of **P1-Pho**, the absorption spectrum of **P2-Pho** in solution is redshifted by 18 nm because the more effective conjugation with the thieno[3,2,b]thiophene unit in **P2-Pho**.^{37, 38} The onset of the absorption of **P1-Pho** and **P2-Pho** in film is 618 nm and 644 nm, corresponding to optical bandgap of 2.01 eV and 1.93 eV, respectively.

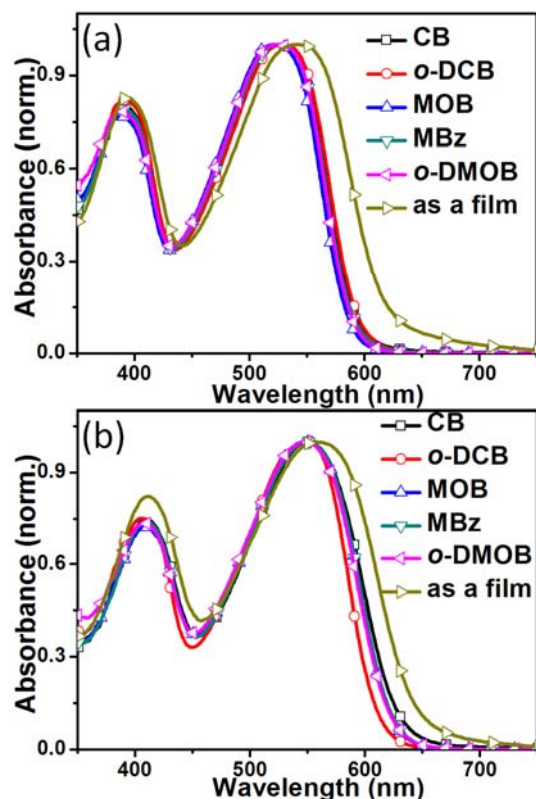


Figure 2 UV-vis absorption spectra of (a) **P1-Pho** and (b) **P2-Pho** in different solvents at room temperature and in thin film.

10 Solubility

P1 and **P2** are soluble in halogenated CB and *o*-DCB. However, in some aromatic non-halogenated solvents, such as MOB, *o*-DMOB and MBz, **P1** is poorly soluble and **P2** is insoluble at all. In contrast, **P1-Pho** and **P2-Pho** both are readily soluble in either halogenated CB and *o*-DCB or non-halogenated MOB, *o*-DMOB and MBz. The good solubility of **P1-Pho** and **P2-Pho** in the non-halogenated aromatic organic solvents is ascribed to the pendant polar phosphonate moieties. To confirm the dissolving of the polymers, we measured the absorption spectra of **P1-Pho** and **P2-Pho** in different solvents and in film. As shown in Figure 2, for both **P1-Pho** and **P2-Pho**, the absorption spectra in all the

Table 2 Photophysical and electrochemical properties of the polymers.

polymer	$\lambda_{\max}^{\text{sol}}$ (nm) ^a	$\lambda_{\max}^{\text{film}}$ (nm)	E_g^{opt} (eV)	$E_{\text{onset}}^{\text{ox}}$ (V) ^b	$E_{\text{onset}}^{\text{red}}$ (V) ^b	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
P1-Pho	523	540	2.01	0.57	-1.65	-5.37	-3.15	2.22
P1	525	541	2.01	0.62	-1.77	-5.42	-3.03	2.39
P2-Pho	541	557	1.93	0.36	-1.63	-5.16	-3.17	1.99
P2	548	572	1.92	0.45	-1.73	-5.25	-3.07	2.18

^a Measured in 10^{-5} M *o*-DCB solution at 90 °C. ^b Onset potential vs. Fc/Fc⁺.

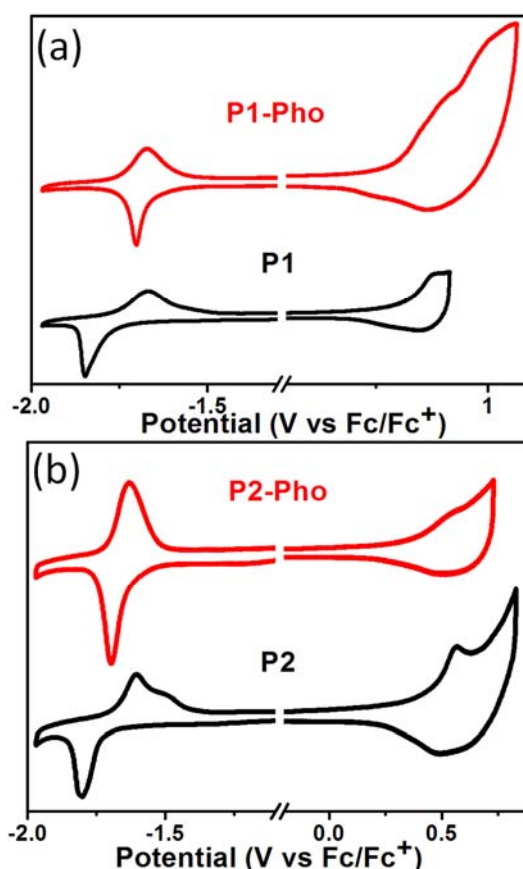


Figure 3 Cyclic voltammograms of (a) **P1-Pho** and **P1**, (b) **P2-Pho** and **P2**.

solvents are blue-shifted by 20-30 nm compared to in film, suggesting that the two polymers are well dissolved in all the solvents rather than dispersed in the solvents.

25 Electrochemical Properties

To determine the HOMO/LUMO energy levels of the polymers, cyclic voltammetry (CV) was carried out with the polymer films spin-coated on glassy carbon working electrode. As shown in Figure 3, all the four polymers show both oxidation waves and reduction waves assigned to the polymer backbone. The onset oxidation/reduction potentials of **P1-Pho** and **P2-Pho** are 0.57 V/-1.65 V and 0.36 V/-1.63 V, respectively (see Table 2). Compared to the corresponding polymers without pendant phosphonate moieties, **P1-Pho** and **P2-Pho** exhibit slightly lower onset oxidation potential and slightly higher onset reduction potential by 0.10-0.12 V.^{27, 28, 31} Based on the onset oxidation/reduction potential, we estimate the HOMO/LUMO energy levels of the polymers and summarize the results in Table 2. **P1-Pho** and **P2-Pho** have the HOMO/LUMO energy levels of -5.37 eV/-3.15 eV and -5.16 eV/-3.17 eV, respectively.

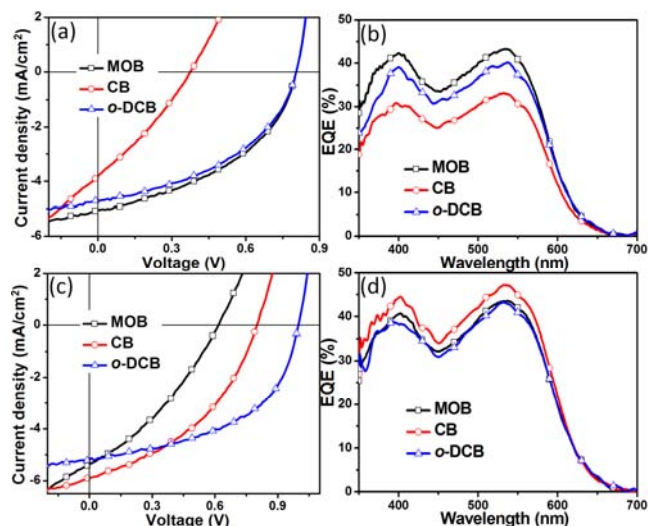


Figure 4 J-V curves (a) and EQE curves (b) of the PSC devices based on **P1-Pho** fabricated with different solvents. J-V curves (c) and EQE curves (d) of the PSC devices based on **P1** fabricated with different solvents.

5 Photovoltaic Properties

In view of the solubility of **P1-Pho** and **P2-Pho**, MOB, MBz and *o*-DMOB seem to be suitable for PSC device fabrication. Among the three solvents, MBz and *o*-DMOB have high boiling points exceeding 200 °C, which leads to difficulty in film formation with solution processing. Fortunately, MOB with the medium boiling point of 153 °C is very suitable for PSC device fabrication. Therefore, we select MOB as the non-halogenated solvent to fabricate PSCs.

PSC devices of all the four polymers were prepared with the device structure of indium tin oxide (ITO) / poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) / polymer:PC₆₁BM / LiF / Al. The ratio of polymer:PC₆₁BM in the active layer was fixed to be 1:4. To test the effect of processing solvent on device performance, non-halogenated solvent MOB and classical halogenated solvents, CB and *o*-DCB, were used for all the four polymers. We failed to fabricate the device of **P2** with MOB as the solvent because **P2** was insoluble in MOB. The current density-voltage (*J*-*V*) characteristics and external quantum efficiency (EQE) curves of the devices under simulated AM1.5G solar illumination at 100 mW/cm² are shown in Figure 4 and Figure 6. The corresponding device performance data are summarized in Table 3.

Figure 4a shows the *J*-*V* curves of the **P1-Pho** devices processed with different solvents. The device with CB as the processing solvent exhibits low PCE of 0.43% probably due to the poor solubility of **P1-Pho** in CB. In comparison, using MOB as the processing solvent, the device shows good photovoltaic performance with an open-circuit voltage (*V*_{OC}) of 0.81 V, a short-circuit current density (*J*_{SC}) of 5.05 mA/cm², and a fill factor (FF) of 0.44, corresponding to a PCE of 1.79%. This performance is much better than that in the case of CB (PCE=0.43%) and is fairly comparable to that in the case of *o*-DCB (PCE=1.70%), indicating that MOB is a suitable processing solvent for the phosphonate-functionalized polymer **P1-Pho**. For **P1** without pendant phosphonate moieties, as usual, the halogenated solvent *o*-DCB affords better device performance

than that with the non-halogenated solvent MOB (Figure 4c and 4d). The PCE of the device of **P1**:PC₆₁BM processed with CB is lower than that of our previous report for **P1**:PC₇₁BM because of the different electron acceptor materials in PSC devices. The trend of the PSC device performance of **P1-Pho** and **P1** processed with the three solvents is confirmed by the EQE curves (Figure 4b,d). Comparison of the effect of processing solvents on PSC device performance of **P1** and **P1-Pho** suggests that the pendant phosphate moieties make the resulting polymer more suitable for processing with non-halogenated solvent MOB without sacrifice of overall device performance. We notice that *V*_{OC} of device of **P1-Pho** seems to be lower than that of **P1**. The reason for the *V*_{OC} difference is not clear yet and need further investigation.

Processing solvent plays an important role in the phase separation morphology of donor:acceptor blend in active layers of PSCs. It is widely accepted that bi-continuous interpenetrating network morphology is desirable for efficient charge separation and transportation to give excellent photovoltaic performance.³⁹ We have used transmission electron microscopy (TEM) to investigate the morphologies of the films of **P1-Pho**:PC₆₁BM blend and **P1**:PC₆₁BM blend processed with MOB or CB. The results are shown in Figure 5. The bicontinuous interpenetrating network morphology can be observed for **P1-Pho**:PC₆₁BM processed with MOB (Figure 5a) and for **P1**:PC₆₁BM processed with CB (Figure 5d), despite the larger domain sizes (>50 nm) than ideal. These morphologies are consistent with the reasonable photovoltaic performance of the two devices. In comparison, severe phase separation is observed for **P1-Pho** processed with CB (Figure 5b), which would likely confine charge carriers in the segregated domains and decrease device photovoltaic efficiency.

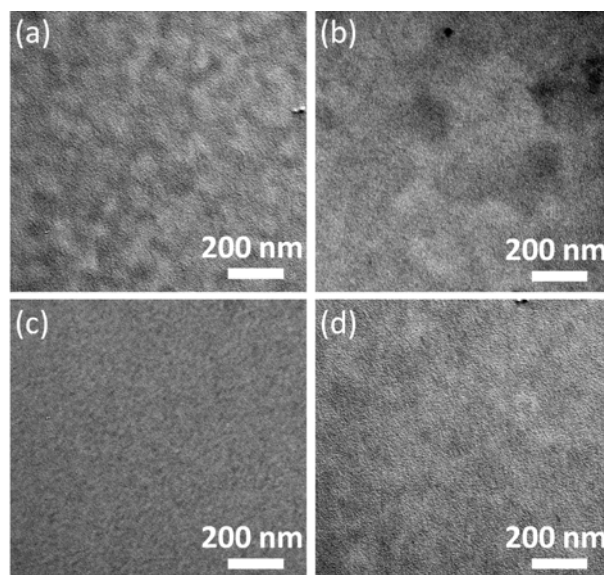


Figure 5 TEM images of the films of **P1-Pho**:PC₆₁BM processed by MOB (a), **P1-Pho**:PC₆₁BM processed by CB (b), **P1**:PC₆₁BM processed by MOB (c) and **P1**:PC₆₁BM processed by CB (d).

As shown in Figure 6c and 6d, **P2** exhibits good photovoltaic performance when processed with CB or *o*-DCB. However, **P2** cannot be solution-processed with MOB because of insolubility. For **P2-Pho** functionalized with pendant phosphonate moieties,

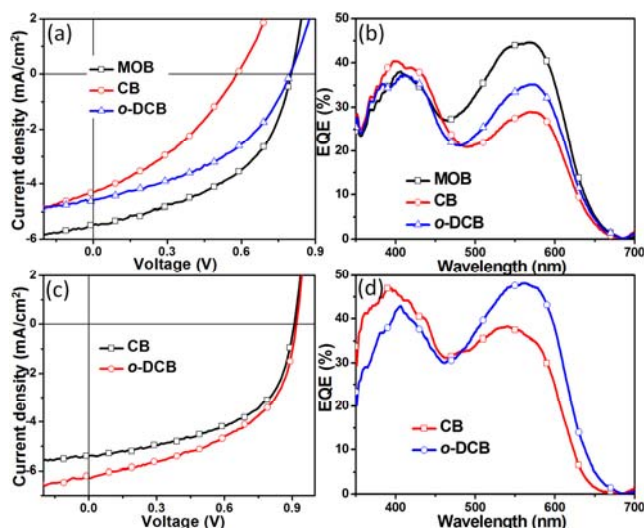


Figure 6 J-V curves (a) and EQE curves (b) of the PSC devices based on **P2-Pho** fabricated with different solvents. J-V curves (c) and EQE curves (d) of the PSC devices based on **P2** fabricated with different solvents.

the device processed with MOB exhibits the V_{OC} of 0.80 V, J_{SC} of 5.48 mA/cm^2 , FF of 0.48, corresponding to the PCE of 2.11% (Figure 6a). This performance is much better than that of the device processed with CB (PCE=0.90%) or *o*-DCB (PCE=1.59%).

To our best knowledge, the PCE of **P2-Pho** device processed with MOB is among the highest reported for PSCs processed with a single non-halogenated solvents without additives.^{21, 22} Comparison of the J-V curves of the **P2-Pho** device processed with the three solvents (Figure 6a) indicates that **P2-Pho** is suitable for processing with MOB rather than with CB or *o*-DCB. The TEM image of **P2-Pho**:PC₆₁BM active layer shown in Figure 7a also supports the good device performance when processed with MOB (Figure 7a). The large phase separation of **P2-Pho**:PC₆₁BM when processed with CB (Figure 7b) is avoided when processed with MOB (Figure 7a).

Table 3 Photovoltaic properties of the PSC devices based on the polymers processed by different solvents under the illumination of AM 1.5G, 100 mW/cm^2 .

polymer	Processing solvent	Thickness of active layer (nm)	V_{oc}^a (V)	J_{sc}^a (mA/cm^2)	FF ^a	PCE ^a (%)
P1-Pho	MOB	81	0.80 ± 0.01	4.95 ± 0.10	0.43 ± 0.01	1.76 ± 0.03
	CB	87	0.36 ± 0.02	3.71 ± 0.12	0.27 ± 0.02	0.40 ± 0.03
	<i>o</i> -DCB	77	0.79 ± 0.01	4.57 ± 0.15	0.43 ± 0.02	1.64 ± 0.06
P1	MOB	83	0.61 ± 0.01	5.23 ± 0.13	0.32 ± 0.01	1.08 ± 0.03
	CB	85	0.79 ± 0.01	5.74 ± 0.16	0.39 ± 0.02	1.89 ± 0.06
	<i>o</i> -DCB	78	0.98 ± 0.02	5.08 ± 0.11	0.48 ± 0.02	2.55 ± 0.06
P2-Pho	MOB	90	0.79 ± 0.01	5.37 ± 0.11	0.47 ± 0.01	2.07 ± 0.04
	CB	95	0.56 ± 0.02	4.20 ± 0.12	0.35 ± 0.01	0.85 ± 0.05
	<i>o</i> -DCB	87	0.79 ± 0.01	4.52 ± 0.09	0.42 ± 0.01	1.56 ± 0.03
P2	MOB	---	---	---	---	---
	CB	97	0.90 ± 0.01	5.28 ± 0.12	0.52 ± 0.02	2.55 ± 0.08
	<i>o</i> -DCB	89	0.90 ± 0.02	6.10 ± 0.18	0.49 ± 0.01	2.80 ± 0.10

^a The data shown are the average values obtained from 6 devices with standard deviation.

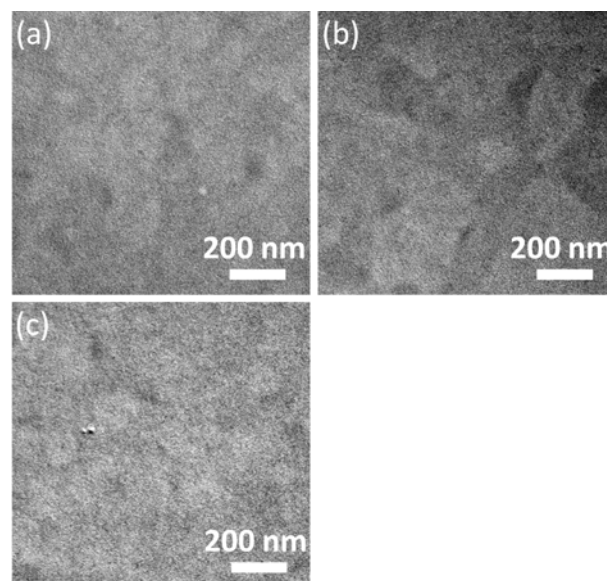


Figure 7 TEM images of the films of **P2-Pho**:PC₆₁BM processed by MOB (a), **P2-Pho**:PC₆₁BM processed by CB (b) and **P2**:PC₆₁BM processed by CB (c).

Conclusions

In conclusion, we have successfully developed two polymers by introducing polar and inert phosphonate moiety to the side chain of PCDTBT analogous polymer. The pendant phosphonate moiety has little effect on the electronic structure of the conjugated polymer backbone but makes the resulting polymers soluble in polar non-halogenated solvents, such as MOB, MBz, *o*-DMOB, etc. Moreover, the phosphonate moiety makes the polymers suitable for PSC device fabrication with non-halogenated solvent, MOB rather than with normal halogenated solvents, CB and *o*-DCB. PSC devices based on **P2-Pho** processed with MOB under AM1.5G illumination exhibit a PCE of 2.11%, which is higher than that of the devices processed with

CB or *o*-DCB. This work suggests that pendant phosphonate moiety is an effective approach to develop photovoltaic polymers towards PSCs fabricated with environmental-friendly solvents.

Experimental Section

Materials

PC₆₁BM was purchased from American Dye Source. **P1** and **P2** were synthesized in our laboratory as reported previously.³⁴ The three monomers, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-9-[1,17-bis(diethyl-phosphonate)heptadecanyl]-carbazole (**3**), 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(hexyloxy)benzo[c][1,2,5]thiadiazole (**7**) and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(hexyloxy)benzo[c][1,2,5]thiadiazole (**10**) were prepared following the literature procedures.⁴¹ All the reagents for synthesis were purchased and used without further purification.

Synthesis of P1-Pho and P2-Pho

A mixture of diboronic acid monomer **3** (0.396 g, 0.426 mmol), 1.00 equiv. of dibromo monomer **7** or **10**, Pd(PPh₃)₄ (0.005 g), Aliquat 336 (0.020 g), degassed toluene (12.0 mL) and aqueous K₂CO₃ (2.0 M, 1.3 mL) was vigorously stirred at 100 °C under argon atmosphere. After 24 hours, phenyl boric acid (0.30 mL 0.5 M solution in anhydrous toluene) was added to the reaction mixture and stirred for 4 hours, then bromobenzene (0.10 mL) was added and stirred for another 4 hours. After cooled down, the resulting mixture was poured to methanol (100 mL) and the precipitate was collected by filtration. The crude polymer was washed in a Soxhlet apparatus with acetone, *n*-hexane and THF in sequential. The THF fraction was concentrated and poured to methanol. The polymer fiber was recovered by filtration and dried in vacuum overnight.

P1-Pho: Yield: 69%. ¹H NMR (400 MHz, *d*⁴-*o*-DCB, 125 °C), δ (ppm): 8.67 (br, 2H), 8.15–8.07 (m, 4H), 7.75–7.66 (m, 4H), 4.83 (br, 1H), 4.35 (br, 4H), 4.02 (br, 8H), 2.52 (br, 2H), 2.14 (br, 6H), 1.65–1.17 (m, 52H), 0.96 (br, 6H). Anal. Calcd. for C₆₃H₈₉N₃O₈P₂S₃: C, 64.42; H, 7.64; N, 3.58; S, 8.19. Found: C, 64.99; H, 7.24; N, 3.50; S, 8.23. GPC (THF, polystyrene standard), Mn = 41.3 kDa, PDI = 2.4.

P2-Pho: Yield: 60%. ¹H NMR (400 MHz, *d*⁴-*o*-DCB, 125 °C), δ (ppm): 8.92 (br, 2H), 8.15–8.00 (m, 4H), 7.73–7.64 (m, 4H), 4.83 (br, 1H), 4.35 (br, 4H), 4.04 (br, 8H), 2.52 (br, 2H), 2.12 (br, 6H), 1.65–1.19 (m, 52H), 0.94 (br, 6H). Anal. Calcd. for C₆₇H₈₉N₃O₈P₂S₅: C, 62.54; H, 6.97; N, 3.27; S, 12.46. Found: C, 61.99; H, 6.64; N, 3.07; S, 12.35. GPC (THF, polystyrene standard), Mn = 55.1 kDa, PDI = 3.3.

PSC Devices Fabrication and Measurement

ITO glasses were cleaned successively with detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 10 minutes each. After dried at 120 °C for 30 minutes, the ITO glasses were treated with UV-ozone for 25 minutes. PEDOT:PSS (Baytron P AI 4083) was then spin-coated on the ITO glasses at 5000 rpm for 1 minute and baked at 120 °C for 30 minutes to give a thickness of 40 nm. The polymer:PC₆₁BM active layer was deposited on the PEDOT:PSS layer by spincoating with the solution of polymer (7.0 mg/mL) and PC₆₁BM (28.0 mg/mL) in MOB, CB or *o*-DCB at 1000 rpm for 2 minutes, followed by

heating at 70 °C for 15 minutes. Finally, the device was transferred to a vacuum chamber where LiF (1 nm) and Al (100 nm) was successively deposited at a pressure of ca. 4 × 10⁻⁴ Pa. All the device fabrication were carried out at ambient conditions.

The active area of each device was 8 mm².

The current density-voltage (*J*-*V*) curves were recorded with a Keithley 236 source meter under AM 1.5G irradiation with the light intensity of 100 mW/cm² (Oriel solar simulator, 150 W). The external quantum efficiency (EQE) curves were measured under short-circuit conditions with monochromatic light from a Xenon lamp, and a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz.

Characterization

¹H NMR spectra of the polymers were recorded on a Bruker AV-400 spectrometer with *d*⁴-*o*-DCB as the solvent at 125 °C. Elemental analysis was performed with a Bio-Rad elemental analysis system. GPC was recorded at 35 °C with a Waters 410 instrument using THF as the eluent and monodisperse polystyrene as the standard. Thermal gravimetric analysis (TGA) was performed under nitrogen flow with a Perkin-Elmer-TGA 7 system. UV-visible absorption spectra was carried out with a Perkin-Elmer Lambda 35 UV-Vis spectrometer. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer system using a glassy carbon working electrode, a platinum gauze counter electrode and a Ag/AgCl reference electrode in an argon-saturated solution of 0.1 M Bu₄NClO₄ in acetonitrile. The polymers were spin-coated on the working electrode for measurement. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1011 transmission electron microscope system, the blend films for TEM measurements were prepared using the "floating off" method.

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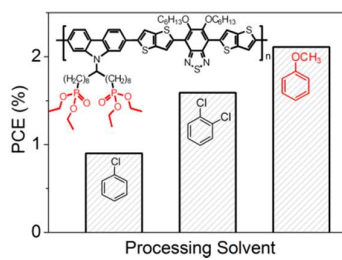
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Phosphonated Conjugated Polymers for Polymer Solar Cells with Non-Halogenated Solvent Process

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Phosphonate moieties on the side chain make donor polymer suitable for polymer solar cells processed with non-halogenated solvent.