Preparation and Characterization of Solution Processable Phthalocyanine-Containing Polymers via a Combination of RAFT Polymerization and Post-Polymerization Modification Techniques

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ABSTRACT: In this work, a benzenedinitrile functionalized monomer, 2-methyl-acrylic acid 6-(3,4-dicyano-phenoxy)-hexyl ester, was successfully polymerized via the reversible addition-fragmentation chain transfer method. The polymerization behavior conveyed the characteristics of "living"/controlled radical polymerization: the first-order kinetics, linear increase of number-average molecular weight with monomer conversion, narrow molecular weight distribution, and successful chain-extension experiment. The soluble Zn(II) phthalocyanine (Pc)-containing (ZnPc) polymers were achieved by post-polymerization modification of the obtained polymers. The Zn(II) phthalocyanine-functionalized polymer was characterized by FTIR, UV–vis, fluorescence, atomic absorption spectroscopy, and thermogravimetric analysis. The potential application of above ZnPc-functionalized polymer as electron donor material in bulk heterojunction organic solar cell was studied. The device with ITO/PEDOT:PSS/ZnPc-Polymer/$PC_{61}BM$/LiF/Al structure provided a power conversion efficiency of 0.014%, fill factor of 0.24, open circuit voltage (V_{oc}) of 0.21 V, and short-circuit current (J_{sc}) of 0.28 mA/cm^2. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 691–698

KEYWORDS: functionalization of polymers; living polymerization; phthalocyanine; addition-fragmentation chain transfer (RAFT); solar cell

INTRODUCTION Phthalocyanines (Pcs) and metallophthalocyanines (MtPcs) have recently received considerable attention due to their unique properties, such as high thermal and chemical stability, excellent photoconductivity, intense optical absorptions in visible–near infrared optical region, and the well-defined coupling of the electronic π-systems.[1–5] Because of these special properties, Pcs and MtPcs have been widely studied as photosensitizer in solar energy conversion,[6–8] photodynamic therapy,[9,10] catalysts,[11–13] information storage,[14,15] optically active self-assembly, and so on.[16,17] However, the poor solubility and slippery π–π stacks limited their applications. To overcome these drawbacks, several approaches were explored.[18–20] Among them, polymeric Pcs/MtPcs have been paid much attention recently, which offers a unique combination of good properties of polymers and Pcs/MtPcs. Two kinds of polymeric Pcs/MtPcs, main-chain and side-chain types, have been reported.[21–23] The main-chain polymeric Pcs/MtPcs were mainly synthesized by the coordination of bidentate ligands with MtPcs and cyclotetramerization reactions of bifunctional monomers. The side-chain polymeric Pcs/MtPcs were mainly prepared via polymerization of Pc/MtPc-containing monomers or "grafting to" reactions. However, the synthesis of Pc/MtPc containing monomers or asymmetric Pcs is relatively difficult due to the relatively low yield.

With the development of "living"/controlled radical polymerization (LRP) techniques, such as atom transfer radical polymerization (ATRP),[24,25] nitroxide-mediated radical polymerization (NMRP),[26] reversible addition-fragmentation chain transfer (RAFT),[27–29] reversible chain transfer catalyzed polymerization (RTCP),[30] and single-electron-transfer mediated living radical polymerization (SET-LRP),[31] a wide variety of polymers with precise control over molecular weights, compositions, and architectures are possible to be synthesized. As one of the most promising LRP techniques, RAFT method has been successfully used to prepare the polymers with various functional groups due to its higher

Jian Zhang and Laibing Wang contributed equally to this work tolerance to many functional groups like allyl, amino, epoxy, hydroxyl, and vinyl groups present in the monomers.[32–35] Post-polymerization modification, also known as polymer-analogous modification, is the other attractive approach for preparation of functional polymers, allowing incorporation of functionality incompatible with the polymerization and greatly facilitates the establishment of structure-property relationships.[36,37] Up to now, several chemical reactions, such as Michael-type addition, radical thiol addition, thiol exchange, Huisgen 1,3-Dipolar cycloaddition reactions, and so on, have been successfully used to prepare functional polymers via post-polymerization modification technique.[38–41]

In this work, we reported the synthesis of the well-defined side-chain benzenedinitrile-containing polymers via RAFT technique. The post-polymerization modification of the above polymer precursors, by reaction between benzenedinitrile groups in the polymer chain and the added excess benzenedinitrile derivatives, produced Zn(II) phthalocyanine-functionalized polymer. The potential application of above ZnPc-functionalized polymer as electron donor material in Bulk Heterojunction (BHJ) organic solar cell (OSC) was also investigated.

EXPERIMENTAL

Materials

6-Bromo-1-hexanol (99%, J&K Chemical), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (99%, J&K Chemical), 1-bromooctane (99%, J&K Chemical), and 3,4-dicyanophenol (99%, J&K Chemical) were used as received. Azobisisobutyronitrile (AIBN, 99%, J&K Chemical) was recrystallized twice from ethanol before use. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the reference.[42] Unless otherwise specified, all other chemicals were purchased from Shanghai Chemical Reagents and used as received without any further purification.

Characterizations

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2412), using HR1 (pore size: 100 Å, 100–5000 Da), HR2 (pore size: 500 Å, 500–20,000 Da), and HR4 (pore size 10,000 Å, 50–100,000 Da) columns (7.8 × 300 mm^2, 5 μm beads size) with molecular weights ranging from 10^2 to 5×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. GPC samples were injected using a Waters 717 plus auto sampler and calibrated with poly(methyl methacrylate) standards. ^{1}H NMR and ^{13}C NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Elemental analysis of C, H, and N was measured with an EA1110 CHNO-S instrument. The UV–vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer. FTIR spectra were recorded on a Nicolette-6700 FTIR spectrometer. The fluorescence spectra of polymers in THF solution were recorded by HITACHI F-2500 fluorescence spectrophotometer. Atomic absorption spectrometry was detected by Varian Spectra 220FS atomic absorption spectrometer. Thermogravimetric analysis (TGA) was performed with the PerkinElmer instruments (TGA 7) analyzer well equipped with a PC at a heating rate of 10 °C/min under nitrogen atmosphere (20 cm^3/min) and in the temperature range of 30–900 °C. Current–voltage characteristics of the solar cells in the dark and under illumination of 100 mW/cm^2 white light from a Hg–Xe lamp filtered by a Newport 81094 Air Mass Filter, using a GWinstek SFG-1023 source meter. Monochromatic light from Hg–Xe lamp (Newport 67005) in combination with monochromator (Oriel, Cornerstone 260) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Newport 70104 Merlin). A calibrated Si cell was used as reference. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis of 4-(6-Hydroxyhexyloxy) Phthalonitrile

The typical synthetic procedures of 4-(6-hydroxyhexyloxy) phthalonitrile (HHPN) are as following: potassium carbonate (0.36 g, 2.6 mmol) and 3,4-dicyanophenol (0.29 g, 2.0 mmol) were dissolved in dry DMF (15 mL). The mixture was stirred at 80 °C for 3 h. Then 6-bromo-1-hexanol (0.29 g, 1.6 mmol) and a small amount of potassium iodide were added into above mixture. The resulting mixture was refluxed for 12 h, and then was allowed to cool slowly to room temperature. Then ethyl acetate (100 mL) was added. The mixture was washed with deionized water (3 × 100 mL). After being dried over anhydrous $MgSO_4$ overnight, ethyl acetate was evaporated under reduced pressure and crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/8, v/v) to yield a white solid (0.33 g, 60%). Anal. calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83%; H, 6.60%; N, 11.47%. Found: C, 68.55%; H, 6.82%; N, 11.52%.

^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.99–8.05 (d, 1H, phenyl), 7.70–7.78 (s, 1H, phenyl), 7.40–7.46 (d, 1H, phenyl), 4.32–4.38 (s, 1H, OH), 4.08–4.16 (t, 2H, OCH_2), 3.35–3.42 (t, 2H, CH_2OH), 1.65–1.78 (t, 2H, CH_2), 1.28–1.48 (m, 4H, CH_2CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.48, 135.49, 119.93, 119.61, 117.30, 116.08, 115.60, 69.43, 62.65, 32.66, 28.87, 25.81, 25.61.

Synthesis of 2-Methyl-acrylic Acid 6-(3,4-Dicyano-phenoxy)-hexyl Ester

Into THF (10 mL) solution of HHPN (0.24 g, 1.00 mmol) and triethylamine (1.0 mL) under ice-bath condition, methacryloyl chloride (1.05 g, 1.00 mmol) in 10 mL THF was added. The solution was stirred overnight at room temperature and ethyl acetate (100 mL) was added to above solution. After washing with water three times, the mixture was dried with anhydrous $MgSO_4$ overnight. Then ethyl acetate was evaporated under reduced pressure and crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/10, v/v) to yield a white solid (1.10 g, 85%). Anal. calcd. for $C_{18}H_{20}N_2O_3$: C, 69.21%; H, 6.45%; N, 8.97%. Found: C, 69.07%; H, 6.20%; N, 8.79%.

^1H NMR (400 MHz, $CDCl_3$, δ): 7.65–7.76 (d, 1H, phenyl), 7.22–7.30 (s, 1H, phenyl), 7.12–7.21 (d, 1H, phenyl), 6.05–6.15 (s, 1H, $C{=}CH_2$), 5.52–5.60 (s, 1H, $C{=}CH_2$), 4.11–4.22 (t, 2H, OCH_2), 3.99–4.10 (t, 2H, OCH_2), 1.91–1.98 (s, 3H, CH_3), 1.79–1.90 (m, 2H, CH_2), 1.65–1.78 (m, 2H, CH_2), 1.40–1.58 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.69, 162.43, 136.65, 135.47, 125.54, 119.84, 119.59, 117.54, 116.04, 115.59, 107.15, 69.38, 64.70, 28.87, 28.70, 25.89, 25.74, 18.56.

General Procedures for RAFT Polymerization of 2-Methyl-acrylic Acid 6-(3,4-Dicyano-phenoxy)-hexyl Ester

2-Methyl-acrylic acid 6-(3,4-dicyano-phenoxy)-hexyl ester (MADCE) (0.5 g, 1.6 mmol), AIBN (0.60 mg, 0.032 mmol), and CPDN (1.74 mg, 0.064 mmol) were dissolved in 1 mL DMF in a 5 mL dried ampoule. The ampoule was bubbled with argon for 20 min to remove the dissolved oxygen from the solution. Then the ampoule was flame-sealed and placed in an oil bath held by a thermostat at the desired temperature (70 °C). At the desired reaction time, the ampoule was cooled by immersing it into cold water. Then the ampoule was opened and the contents were dissolved in 10 mL of THF, and precipitated into 400 mL of methanol. The polymer (PMADCE) was obtained by filtration and dried under vacuum at 30 °C until a constant weight. The monomer conversion was determined gravimetrically.

Chain Extension of PMADCE Using PMADCE as a Macro-CTA

The PMADCE sample prepared by RAFT polymerization ($M_{n(GPC)} = 9500$ g/mol, $M_w/M_n = 1.10$) was used as a macro-CTA for the chain extension reaction with MADCE. PMADCE (0.23 g, 0.026 mmol), AIBN (2.05 mg, 0.013 mmol), and MADCE (0.2 g, 0.64 mmol) were dissolved in 1 mL of DMF in a 5 mL dried ampoule. The following procedures were similar to those described above, except that the CPDN was replaced by PMADCE. The monomer conversion was determined gravimetrically. The M_n and M_w/M_n values ($M_{n(GPC)} = 15{,}100$ g/mol, $M_w/M_n = 1.15$) were determined by GPC with PMMA standards.

The Pretreatment of PMADCE

To eliminate the possible effect of the thiocarbonylthio groups on the next post-polymerization modification reaction, thiocarbonylthio groups at the ends of PMADCE chains were removed using the procedure previously reported by Perrier et al.[43] The obtained PMADCE was treated with a large amount of AIBN. PMADCE (0.1 mmol) and AIBN (1.5 mmol) (10 times more than the amounts of PMADCE) were dissolved in dry THF (20 mL). The mixture was stirred at 70 °C for 12 h under nitrogen atmosphere. Then the reaction solution was precipitated into large amounts of methanol. A white powder was isolated by filtration along with a pink filtrate. Then the processed PMDCHE was purified by precipitating twice from THF to methanol and dried under vacuum at 30 °C until a constant weight.

Synthesis of 4-(Octyloxy) Phthalonitrile

4-(Octyloxy) phthalonitrile (OPN) was prepared with the similar procedure to that of HHPN. The product was recrystallized from methanol to yield a white solid (0.42 g, 78%). Anal. calcd. for $C_{16}H_{20}N_2O$: C, 74.97%; H, 7.86%; N, 10.93%. Found: C, 74.82%; H, 7.92%; N, 11.02%.

^1H NMR (400 MHz, DMSO-d_6, δ): 8.02–8.07 (d, 1H, phenyl), 7.74–7.77 (s, 1H, phenyl), 7.41–7.46 (d, 1H, phenyl), 4.08–4.17 (t, 2H, OCH_2), 4.11–4.22 (t, 2H,), 3.99–4.10 (t, 2H, OCH_2), 1.68–1.77 (m, 2H, CH_2), 1.34–1.43 (m, 2H, CH_2), 1.20–1.32 (m, 6H, $CH_2CH_2CH_2CH_2$), 0.83–0.88 (t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.49, 135.43, 119.84, 119.55, 117.47, 116.05, 115.59, 106.99, 69.57, 31.95, 29.39, 28.93, 26.00, 22.83.

Synthesis of Polymeric Zn(II) Phthalocyanine (PMADCE–ZnPc)

PMADCE (0.09 g, $M_{n(GPC)} = 9500$ g/mol, $M_w/M_n = 1.10$), OPN (0.75 g, 2.93 mmol), and zinc acetate dihydrate (0.1 g, 0.45 mmol) were mixed in 15 mL of dry *N*,*N*-dimethylacetamide (DMAC) and heated at 80 °C. After adding a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the temperature was raised to 130 °C. The mixture was kept at 130 °C overnight. The contents were dissolved in 10 mL of THF, and then precipitated into 500 mL of methanol. The polymeric phthalocyanine (PMADCE–ZnPc) was obtained by filtration. The crude product was extracted in a Soxhlet Extractor with ether. The final product was dried under vacuum at 30 °C until a constant weight to afford a dark green solid.

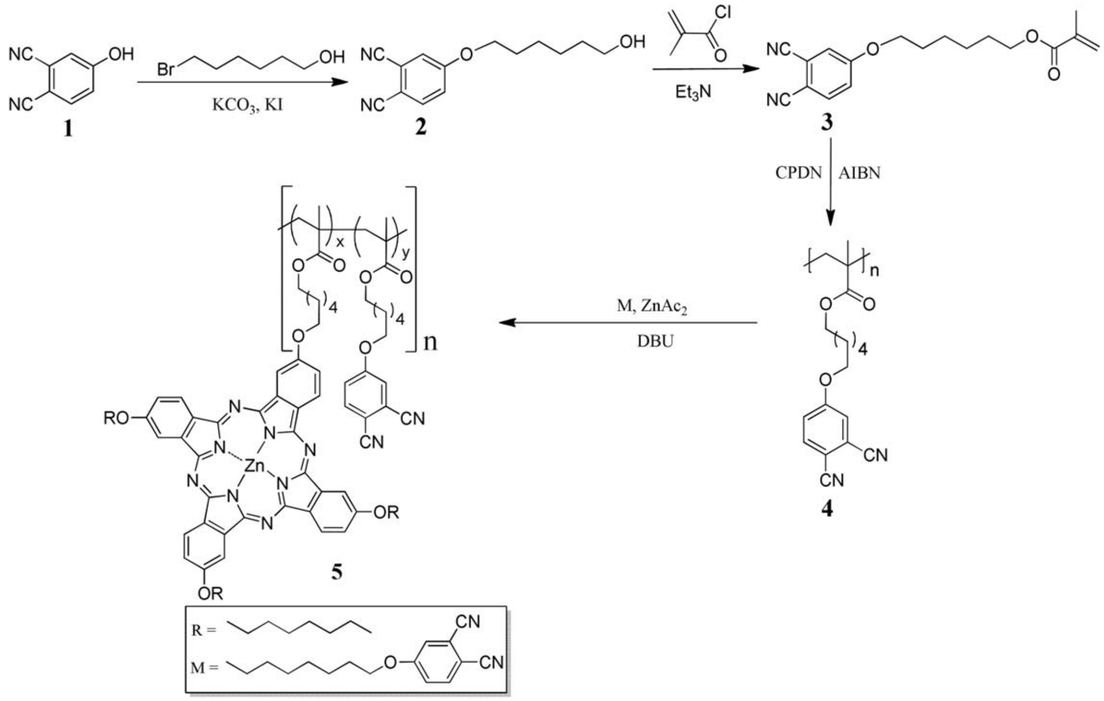
Device Fabrication

The active layer contained a blend of PMADCE–ZnPc as electron donor and $PC_{61}BM$ as electron acceptor was prepared from weight ratios (1:1, w/w) by solution (15 mg/mL of PMADCE–ZnPc) in chlorobenzene. After spin coating the blend from solution at 1000–1400 rpm, the device was completed by evaporating a 0.8 nm LiF layer protected by 100 nm of Al at a base pressure of 4×10^{-4} Pa. The effective photovoltaic area defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 12 mm^2.

RESULTS AND DISCUSSION

RAFT Polymerization of MADCE

The synthetic pathways of monomer (MADCE) and corresponding polymer (PMADCE) are presented in Scheme 1. RAFT polymerization of MADCE was performed with a feed ratio of $[MADCE]_0:[AIBN]_0:[CPDN]_0 = 50:1:2$, using CPDN as the RAFT agent and AIBN as the initiator at 70 °C in DMF (MADCE/DMF = 0.5 g/1.0 mL). The results are shown in Figures 1 and 2. The first-order kinetics was observed in Figure 1, demonstrating the propagating radical concentrations kept constant during the polymerization process. The linear increase of number-average molecular weight ($M_{n(GPC)}$) with



SCHEME 1 The synthetic routes of the MADCE and polymeric Zn(II) phthalocyanine.

monomer conversion with the narrow molecular weight distribution ($M_w/M_n < 1.15$) was found in Figure 2. Furthermore, the $M_{n(GPC)}$ values of the obtained polymers are very close to their corresponding theoretical ones as presented in Figure 2. The theoretical molecular weight of the polymer was calculated from the following equation:

$$M_{n(th)} = \frac{[MADCE]_0}{[CPDN]_0} \times M_{MADCE} \times Conversion + M_{CPDN},$$

where $[MADCE]_0$ and $[CPDN]_0$ are the initial concentrations of the MADCE and the RAFT agent, M_{MADCE} and M_{CPDN} are the molar mass of the monomer and CPDN. All the above results indicated that the polymerization of MADCE can be well-controlled via a RAFT process.

Analysis of Chain End of Polymer and Chain-Extension Experiment

The chain end of the PMADCE prepared via RAFT polymerization was characterized by ^1H NMR spectrum as given in Figure 3. The characteristic signals corresponding to the phenyl protons of the benzenedinitrile group were observed from 7.20 to 8.10 ppm (a, b, c). The signals at 4.0 ppm (d, e) are assigned to the methylene group of $-CH_2-O-$ in the side chain. The peak at around $\delta = 8.10–8.20$ (f) ($I_{8.10–8.20} = 1.00$) is ascribed to the 8-position proton of the

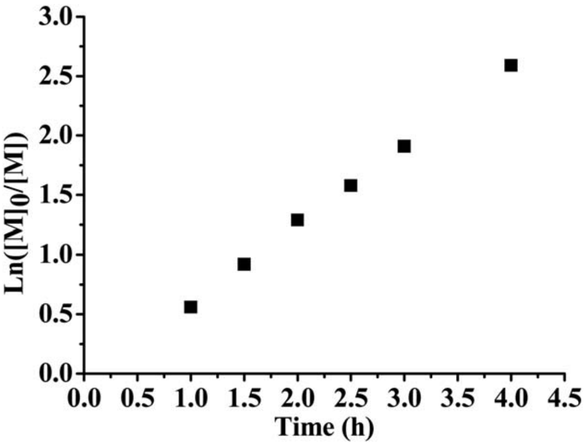


FIGURE 1 Ln($[M]_0$/[M]) versus polymerization time for RAFT polymerization of MADCE. Polymerization conditions: $[MADCE]_0$/$[CPDN]_0$/$[AIBN]_0$ = 50/2/1, T = 70 °C, MADCE/DMF = 0.5 g/mL.

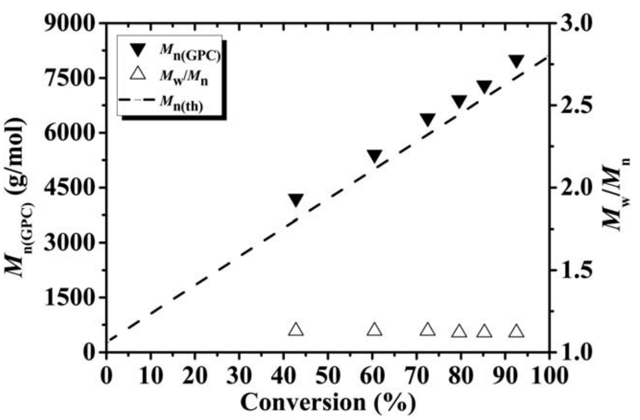


FIGURE 2 Dependence of the molecular weights and the molecular weight distributions on the monomer conversions for the RAFT polymerization of MADCE. The polymerization conditions are the same as in Figure 1.

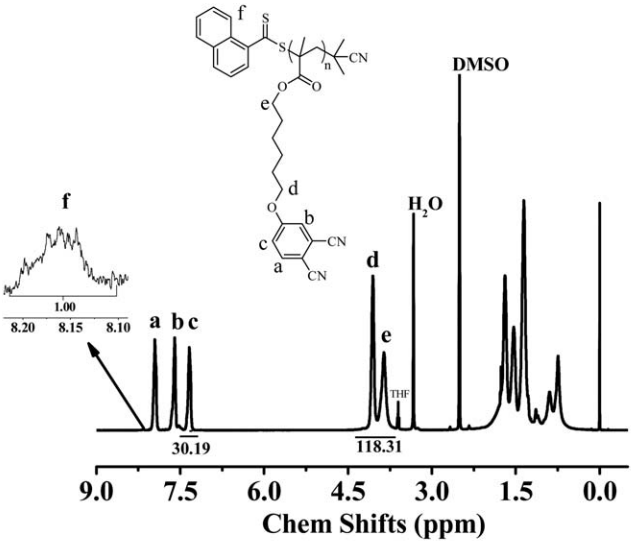


FIGURE 3 ^{1}H NMR spectrum of the PMADCE ($M_{n(GPC)} = 9500$ g/mol, $M_w/M_n = 1.10$) with DMSO-d_6 as the solvent and TMS as the internal standard.

naphthalene unit in CPDN units, revealing that the dithioester units were successfully attached to the polymer chain ends (ω-chain end). The peak at around $\delta = 7.25$–7.41 (c) ($I_{7.25–7.41} = 30.19$) corresponds to the aromatic proton of the benzene unit in MADCE repeat units. Assuming that each polymer chain was captured by a naphthyl moiety from CPDN, the molecular weight ($M_{n(NMR)}$) of PMAECD can be calculated from the corresponding integrals in ^{1}H NMR spectrum, according to the following equation:

$$M_{n(NMR)}\ (\text{g/mol}) = (I_{7.25-7.41})\frac{312.36}{(I_{8.10-8.20})} + 271.5,$$

where 312.36 and 271.5 are the molecular weights of MADCE and CPDN, respectively. The molecular weight of PMADCE calculated from ^{1}H NMR spectrum was 9700 g/mol, which is consistent with that from normal GPC measurement ($M_{n(GPC} = 9500$ g/mol), indicating that PMADCE was end-capped by CPDN species with high fidelity.

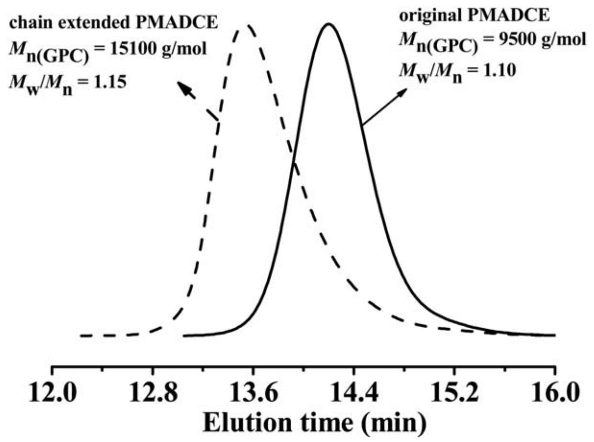


FIGURE 4 GPC curves of PMADCE before and after chain extension. Polymerization conditions: $[\text{MADCE}]_0/[\text{PMADCE}]_0/[\text{AIBN}]_0 = 50/2/1$, $T = 70$ °C, $t = 6$ h, MADCE/DMF = 0.5 g/mL.

The living feature of the obtained polymer was further verified by a chain-extension experiment. As presented in Figure 4, an apparent peak shift from the macro-CTA with $M_{n(GPC)} = 9500$ g/mol and $M_w/M_n = 1.10$ to the chain extended PMADCE with $M_{n(GPC)} = 15{,}100$ g/mol and $M_w/M_n = 1.15$ was found, respectively. The presence of species of RAFT agent in the polymer chain and the successful chain extension experiment both proved the functionality of the obtained polymer and feature of the "living"/controlled polymerization of MADCE.

Preparation of Polymeric Zn(II) Phthalocyanine PMADCE–ZnPc Via Post-polymerization Modification Technique

Post-polymerization modification technique is a powerful tool for the preparation of functional polymers, which can avoid the limited functional-group to tolerance of polymerization methods and difficulty existed in synthesizing corresponding monomers.[21–23] The polymeric Pcs/MtPcs can improve the solubility and processability of Pc materials.[36,37] However, the synthesis of asymmetric Pc derivatives is relatively difficult with relatively low yields, which limited the preparation of side chain Pc-containing polymers. Here, we described the preparation of side chain Pc-containing polymers via post-polymerization modification technique. PMADCE–ZnPc was synthesized via chemical reaction between benzenedinitrile groups in PMADCE and those in added reagent (M in Scheme 1). The obtained PMADCE–ZnPc was analyzed by UV–vis, fluorescence, FTIR, and TGA as shown in Figures 5–8.

Photophysical Properties

UV–Vis Absorption and Fluorescence Spectra

Phthalocyanines consisting of four isoindole units presenting an 18π-electron heterocyclic aromatic system, their intrinsic absorption spectra indicate intense Q-bands in the visible–near infrared optical region, approximately from 600 to 700 nm.[44,45] Figure 5 shows the typical UV–vis spectra of the polymer precursor (PMADCE) and the Zn(II) phthalocyanine-

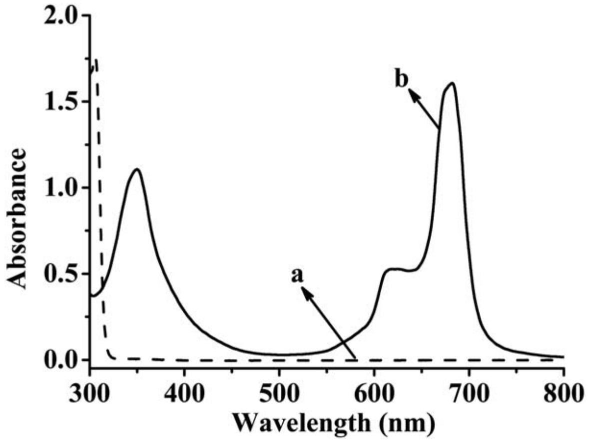


FIGURE 5 UV–vis spectra of (a) PMADCE and (b) PMADCE–ZnPc in THF solution ($C_n = 1.1 \times 10^{-5}$ mol/L ZnPc mesogens).

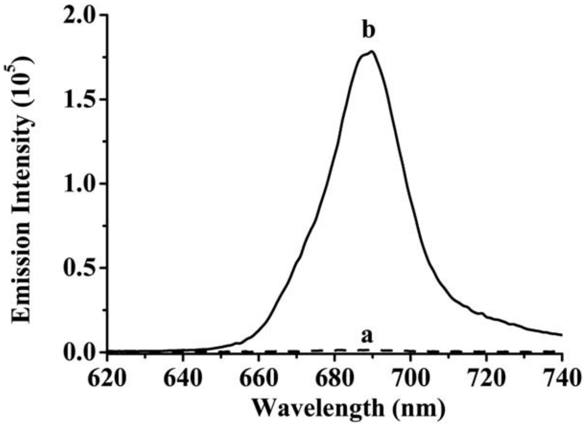


FIGURE 6 Fluorescence spectra of (a) PMADCE and (b) PMADCE–ZnPc in THF solution ($C_n = 1.1 \times 10^{-6}$ mol/L ZnPc mesogens), $\lambda_{ex} = 380$ nm.

functionalized polymer (PMADCE–ZnPc) in THF. As presented in Figure 5, the intense π–π bands in the visible (from 660 to 690 nm, $\lambda_{max} = 682$ nm) and UV (from 330 to 360 nm, $\lambda_{max} = 350$ nm) spectral regions ascribed to the typical Q-band and B-band of Pc ring were observed after post-polymerization modification. The fluorescence spectra of PMADCE and PMADCE–ZnPc in THF are shown in Figure 6. As compared with the fluorescence spectrum of PMADCE, PMADCE–ZnPc showed the strong emission with a major peak between 670 and 700 nm with an excitation wavelength of 380 nm. As discussed above, we have prepared the polymeric phthalocyanine (PMADCE–ZnPc) successfully.

Infrared Spectra

Further confirmation of the phthalocyanine-forming reaction can be taken from IR spectra. Figure 7 shows the IR spectra of the PMADCE (a) and PMADCE–ZnPc (b). The strong signal at 2230 cm^{-1} assigned to the cyano groups existed in PMADCE almost disappeared after post-polymerization modification reaction, which proved the reaction leading to the covalently bound polymeric phthalocyanine while the absorptions at 2940 and 1725 cm^{-1} remain. Moreover, the typical absorptions of Pc ring in PAMDCE-ZnPc at 1330, 1090, 750, and 460 cm^{-1} were observed, respectively.[46]

Thermal Properties

Thermal stabilities of the polymers (PMADCE and PMADCE–ZnPc) were investigated with thermogravimetric analysis (TGA) under N_2 at a heating rate of 10 °C/min and the results are shown in Figure 8. The TGA analysis showed that the onset decomposition temperatures with 5% weight loss of PMADCE and PMADCE–ZnPc are 295 °C and 349 °C in N_2, respectively. This indicates that the PMADCE–ZnPc had better thermostability compared to that of PMADCE.

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy was also used to study the zinc content of the functionalized polymer PMACDE–ZnPc. The sample PMACDE–ZnPc (2.9 mg) was placed on the combustion boat in a horizontal quartz tube furnace, and then heated to 850 °C for 12 h with a constant oxygen gas flow. After being cooling naturally, the white powder was found on the combustion boat. The ashed sample was dissolved in dilute hydrochloric acid (0.05 mol/L, 100 mL). Zinc content was analyzed by atomic absorption spectroscopy to be 1.05 mg/L, and the zinc content in the PMADCE–ZnPc was calculated to be 3.6%. Based on the above result, about 64% molar ratio of cyano groups in PMADCE took part in the chemical reaction with 4-(octyloxy) phthalonitrile in the presence of zinc acetate dihydrate, which resulted in covalently bound Zn(II) phthalocyanine-functionalized polymer (PMADCE–ZnPc) with a loading about 32% of Pc ring.

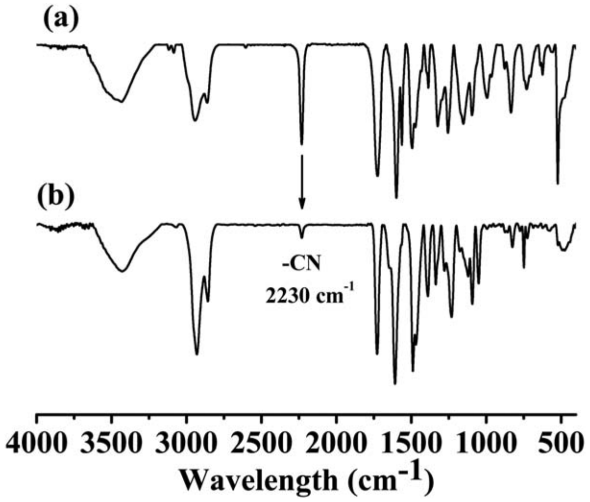


FIGURE 7 FTIR spectra of (a) PMADCE and (b) PMADCE–ZnPc.

Photoelectric Property

Pcs/MtPcs have been widely investigated in BHJ OSC due to their excellent stability, low bandgap, high hole mobility, and so on.[47–49] Recently, many studies on the phthalocyanine/fullerene solar cells have been reported.[50,51] To investigate the photovoltaic property of the PMADCE–ZnPc, the bulk heterojunction photovoltaic cell, with a structure of ITO/PEDOT–PSS/PMADCE–ZnPc:$PC_{61}BM$/LiF/Al was fabricated, where the PMADCE–ZnPc was used as donor and $PC_{61}BM$ as

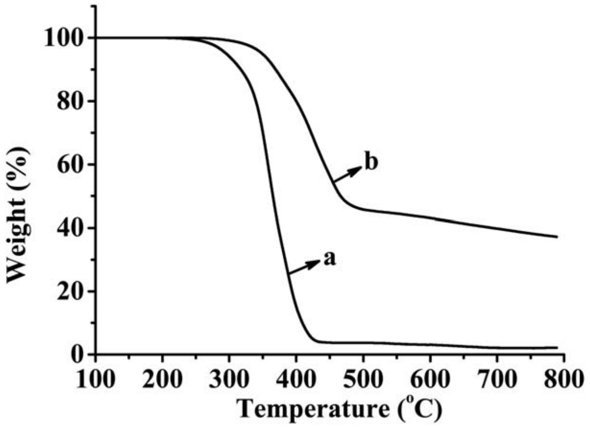


FIGURE 8 TGA curves of (a) PMADCE and (b) PMADCE–ZnPc.

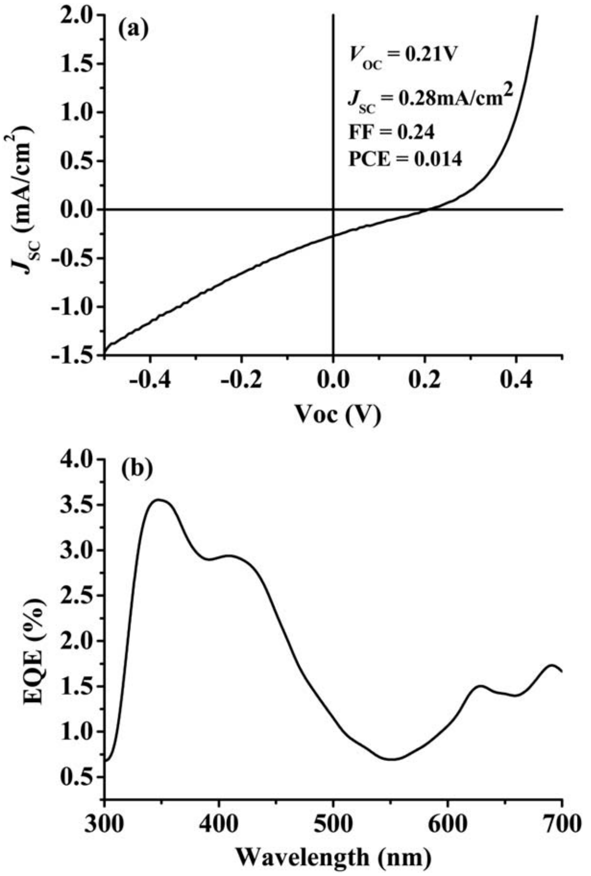


FIGURE 9 (a) Current–voltage characteristics of the solar cells under AM 1.5 (100 mW/cm^2) white light illumination and (b) the corresponding EQE.

acceptor. The active layers of the photovoltaic cells were fabricated from chlorobenzene solutions of PMADCE–ZnPc and PC$_{61}$BM by spin coating with the weight ratio of PMADCE–ZnPc:PC$_{61}$BM at 1:1 (w/w). All devices were characterized under AM 1.5 (100 mW/cm^2) white light with simultaneous recording of their current–voltage characteristics.

Figure 9(a) shows the current–voltage characteristic of solar cells under white light illumination. The active layer based on the PMADCE–ZnPc/PC$_{61}$BM blend film exhibit obvious photovoltaic property with a fill factor of 0.24, open circuit voltage (V_{oc}) of 0.21 V, short circuit current density (J_{sc}) of 0.28 mA/cm^2 and power conversion efficiency of 0.014%. Figure 9(b) shows external quantum efficiency (EQE) spectrum of PMADCE–ZnPc/PC$_{61}$BM-based device. Compared to the pristine components absorption spectra (PMADCE–ZnPc and PC$_{61}$BM),[52] the EQE spectra of the BHJ devices show a similar shape, which has been assigned to the Soret band of PMADCE–ZnPc (UV region), Q-band of PMADCE–ZnPc (600–700 nm), and contribution of PC$_{61}$BM (~400 nm), respectively.

CONCLUSIONS

In summary, we have presented a novel strategy for the synthesis of the polymeric phthalocyanine, by a combination of reversible addition-fragmentation chain transfer (RAFT) polymerization and post-polymerization modification technique. The polymerization of MADCE was a "living"/controlled procedure and the phthalocyanine-forming reaction was performed under mild reaction conditions. Reaction of dinitrile groups in PMADCE with 4-(octyloxy) phthalonitrile in the presence of zinc acetate dihydrate results in the formation of covalently bound Zn(II) phthalocyanine-functionalized polymer. The Zn(II) phthalocyanine-functionalized polymer has good solubility in THF or chlorobenzene and shows good thermal stability. The Zn(II) phthalocyanine-functionalized polymer has potential application as electron donor material in solar cell.

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