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Synthesis and Properties of Triphenodioxazine-Based Conjugated Polymers for Polymer Solar Cells

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Abstract: As a fused-ring conjugated unit, triphenodioxazine has been developed as two series of thiophene-free conjugated polymers for polymer solar cells in this article. The polymers were synthesized via a multi-step synthetic route, and it is found that the substituent groups had a great effect on the reactivity of the reactants. The relationships among polymer structures, thermal, optical and electrochemical properties were investigated in detail by experimental data analysis and theoretical simulation. The polymers possess highly planar backbones, broad visible-near-infrared absorption bands, suitable frontier molecular orbital energies and low bandgaps ranging from 1.3 to 1.8 eV. The power conversion efficiencies of their photovoltaic devices are about 1%. Introducing longer alkyl side-chains into a polymer can bring about a better film-forming ability and improve the photovoltaic performance.

century^[5], is an electron-rich fused heterocycle with 22 atoms and 24 π -electrons containing three aromatic benzene rings and two nonaromatic oxazine rings (Scheme 1). Compared with heavy-atom-containing compounds, triphenodioxazine is composed entirely of light atoms, so it is a more stable system due to its tighter structure and stronger bonds; the p orbitals of all the conjugated atoms have similar energies and sizes, leading to larger orbital overlapping and better π -electron conjugation. Derivatives based on triphenodioxazine show the advantages of outstanding fluorescence characteristic, good heat stability and chemical stability, developed synthetic routes and processes^[5d, 5e]. Furthermore, the planar structure of this fused-ring compound is probably beneficial to charge conduction and molecule π - π stacking.

Introduction

Benefiting from structural variety, high solubility and film-forming ability, conjugated polymers are key components to achieve lightweight, low-cost, and flexible polymer solar cells (PSCs)^[1], which are an attractive alternative to the traditional silicon photovoltaics. Although there are less systematic and accurate theories about the mechanism of organic photovoltaic conversion, some qualitative empirical conclusions have been developed to improve the performances of PSCs^[2]. For example, a photovoltaic polymer serving as an electron donor (D) and light absorber should has a low bandgap below 1.8 eV and matching frontier orbitals for electrode materials; appropriate compatibility between the polymer and the electron acceptor (A) is essential to form favorable inter-penetrating D/A network structure.

Thiophene-based conjugated polymers are a major part of organic photovoltaic materials nowadays.^[3] Thiophene ring is more stable in synthetic reactions than other penta-heterocyclic compounds since it is more difficult to be oxidized, added or ring-opened^[4], therefore various substituted monomers can be derived from thiophene core; on the other hand, the bandgap of a polymer based on six-membered aromatic rings, like benzene, is too large for high-efficiency PSC devices, and the significant steric hindrance of ortho substituents in six-membered-ring units will lengthen the chemical bonds between adjacent units, or even twist the polymer, both of these effects will weaken the π -conjugation.

Triphenodioxazine, whose micromolecule derivatives have been developed as pigments and dyes for more than half a

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Scheme 1. Chemical structure of triphenodioxazine and its position numbers.

11 12 13 14

10

1

5

2

In spite of this, there are few reports^[6] on triphenodioxazine derivatives used as potential materials for organic electronics. Here, we investigate two series of triphenodioxazine-based conjugated polymers, poly(2-vinyl-3,10-dialkoxytriphenodioxazine) and poly(2-ethynyl-3,10-dialkoxytriphenodioxazine) (PVnT and PEnT, n is the number of carbon atoms in a alkyl chain). The synthesis, optical and electrochemical properties of the eight polymers as well as the photovoltaic performances are described.

Results and Discussion

Synthesis

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The synthetic route of the polymers is depicted in Scheme 2. In Route I, the bromination and nitration proceed smoothly since the steric hindrance of a shorter alkyl group (n = 8, 10, 12) was not large enough to hinder the ortho-substitution reactions. The alkyl group at the meta-position to the bromine atom played a role in protecting the hydroxyl group and in directing subsequent electrophilic aromatic substitution. It was attached to hydroquinone at the very beginning of the route together with another same alkyl group using for increasing the polymer solubility, which saved an additional protecting reaction step. Later, aluminium chloride was used to carry out nitro-groupdirected selective dealkylation and restore the hydroxyl group. However, the bromination process was too slow to be monitored by TLC when an n-hexadecyl group was introduced instead of a shorter alkyl group. Obviously, the larger steric hindrance of the hexadecyl group inhibited the reaction. In view of this, 2-bromo-

1,4-dihydroxybenzene was synthesized by bromination of hydroquinone at first, alkylation was followed to give 2,5-dihexadecylbromobenzene, and then the product was nitrated.

But also because the large steric hindrance of the alkyl group, that attempt failed when we found the nitration reaction had not occurred even after 24 hours.



Thus, the hexadecyl derivative was prepared following Route II. The experiments shown that: due to the very small steric hindrance of the alkyl group, the bromination, hexadecylation, and nitration reactions were fast and complete when commercial 4-methoxyphenol or 4-ethoxyphenol was used as a starting compound instead of experimental synthetic 4-nbutoxyphenol. But as we attempted to dealkylate selectively, the reaction did not occurred with equivalent aluminium chloride. Unexpectedly, the hexadecyl group was preferentially removed after increasing the amount of aluminium chloride. As a result, messy hydrosoluble products were formed while the target compound should be water-insoluble. However, when 4-nbutoxyphenol served as a starting compound, aluminium chloride removed the butyl group successfully and had less





The probable reaction mechanism of selective dealkylation using aluminium chloride^[7] is shown in Scheme 3. The coordination of the aluminium atom in aluminium chloride with the heteroatom of the substituted alkoxy benzene induces the aluminium atom to bond with the oxygen atom in the alkoxy group at the ortho-position, which activates the α-carbon atom in the alkoxy group for the nucleophilic substitution reaction. Since a six-membered-ring intermediate is more stable and easily formed than a five-membered-ring intermediate, a nitrosubstituted compound is more reactive than a bromo-substituted compound containing a same alkyl group. However, the alkyl group also has a great effect on the dealkylation activity. In our synthetic experiments, methoxy- and ethoxy-substituted compounds showed a very weak reactivity even with a highly reactive ortho nitro group, which agreed with the reference^[7]. 2-n-hexadecoxy-4-nitro-5-methoxy-When or ethoxybromobenzene was treated with equivalent amounts of aluminium chloride, aluminium chloride was preferentially coordinated with the two oxygen atoms in the nitro and methoxy or ethoxy groups, but could not dealkylate the compound. After adding more aluminium chloride, the excessive aluminium chloride was coordinated with the bromine atom and the oxygen atom in the hexadecoxy group, resulting in the dealkylation of the highly electrophilic active hexadecoxy group. With a highly reactive butoxy group instead of an inert methoxy or ethoxy group, 2-n-hexadecoxy-4-nitro-5-n-butoxybromobenzene could be successfully dealkylated by equivalent amounts of aluminium chloride without affecting the para hexadecoxy group.

In deed, monomers with octyl, decyl, and dodecyl groups (n = 8, 10, 12) also can be prepared by Route II, but Route I is the better way to synthetize these derivatives because Route II has an additional protecting reaction and a lower yield.

Several features of the monomer synthesis are listed below. a. The raw materials were inexpensive and plentiful, and the reaction conditions were mild with no need for special equipment;

b. Convenient purification operations, including filtration, extraction and recrystallization, were the major aftertreatment strategies , while relatively tedious column chromatography was required just once, which saved a lot of time and effort;

c. Several new asymmetric multi-substituted compounds, intermediate products $(7) \sim (10)$, have been prepared by determining a right protecting group and selective deprotection;

d. The last reaction generating monomers proceed in low yield because the starting compounds (10) were easily oxidizable, even though hydrogen chloride had been used to stabilize the aniline derivatives.

Eight polymers were synthesized by Stille coupling reactions using a Pd(0)-based catalyst. At room temperature, these polymers show acceptable solubility in chloroform and 1,2-dichlorobenzene (see Table 1), poor solubility in toluene and tetrahydrofuran, and cannot be dissolved by highly polar solvents. A polymer with longer alkyl chains is more soluble. The polymer solutions are dark blue, and the films are almost black with conspicuously metallic luster like copper.

Theoretical Calculations

Calculations of density functional theory with periodic boundary conditions (DFT-PBC) were carried out for a better evaluation of structure properties of PVnT and PEnT. All of the alkyl groups were replaced by methyl groups to simplify the calculations. The molecular geometries and surface plots are displayed in Figure 1.



Figure 1. DFT optimized geometries and frontier molecular orbitals of PVnT and PEnT (red middle lines indicate extensional direction of backbones).

These results suggest that the backbone of both PVnT and PEnT are highly planar in their most stable conformations. Because the small vinylene and ethynylene units increase the distance between triphenodioxazine units, the large alkoxy groups hardly create steric hindrance which will break the planarity of the backbone. The bond between triphenodioxazine and the sp hybridized carbon atom in adjacent vinylene units in PVnT is 0.145 nm, longer than the bond between triphenodioxazine and the sp² hybridized carbon in ethynylene units in PEnT (0.141 nm), so the rotational energy barriers of PEnT units are higher than that of PVnT.

In a D-A alternating polymer^[8], the electron density of the HOMO is mainly localized on the donor units, while the electron density of the LUMO is mainly localized on the acceptor units. However, the electron density of the HOMO and LUMO of the triphenodioxazine-based polymers are spread over the whole backbone. The higher degree of orbital overlap between HOMO and LUMO implies a stronger electronic transition between HOMO and LUMO^[8b], leading to a stronger optical absorbance.

The two-dimensional structures of the π - π stacked polymers are shown in Figure 2. The distances between adjacent planes of the backbone of PVnT and PEnT are 0.387 nm and 0.374 nm, respectively. The energy of a π - π stacked repeating unit is lower than that of a gaseous repeating unit (the structures in Figure 1), the energy differences (ΔE (RB+HF-LYP)) of PVnT and PEnT are -7.559 kJ mol⁻¹ and -7.207 kJ mol⁻¹, respectively, so the two polymers tend to form stable π - π stacks along out-of-plane direction.



Figure 2. DFT optimized geometries of π - π stacked PVnT and PEnT (red and green lines indicate extensional direction of backbones and π - π stacking, respectively).

Thermal Properties

The tight structures of triphenodioxazine derivatives have a stabilizing effect against thermal. Figure 3 shows the thermogravimetric analysis (TGA) spectra of the triphenodioxazine-based conjugated polymers. The 5 wt% weight loss temperatures of all polymers are above 300 °C under nitrogen atmosphere, respectively. PEnT is a little more thermostable than PVnT.

The thermal transition temperatures of the polymers were investigated by differential scanning calorimetry (DSC). The glass transition temperatures (T_g) of PVnT decrease with the growth of the alkyl group, the opposite tendency is apparent upon comparison of the T_g of PEnT (Figure 4). The alkyl chains have two opposite effects on the T_g : their steric hindrance tries to twist the polymer backbones, which will weaken the polymer stacking and decrease T_g ; while their Van der Waals forces try to strengthen the polymer interaction, which will increase T_g .

Although the steric hindrance of the side-chains tries to break the backbone planarity, the effect is not powerful enough to counter the large rotational energy barriers of comparatively rigid PEnT. Therefore, longer alkyl groups increase the T_g of PEnT by their larger Van der Waals forces. With a lower rotational energy barriers of units (see Section "Theoretical Calculations"), PVnT is more likely to be twisted by the steric hindrance of the sidechains, so longer alkyl groups decrease the T_g of PEnT due to the loose polymer stacking.



Figure 3. TGA curves of the polymers under nitrogen.



Figure 4. DSC curves of the polymers under nitrogen (dotted arrows indicate direction of change in T_g).

Optical and Electrochemical Properties

The polymers are not photoluminescent in solution or as films at room temperature in air, so only the absorption spectra of the polymers in chloroform solutions and as spin-coated films were measured (Figure 5). The optical properties of the polymers are summarized in Table 1.

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Figure. 5. Normalized UV-Vis-NIR absorption spectra of the polymers in chloroform solution and as thin films (annealed at 150 °C for 10 min).

The absorption bands of the polymer films are significantly broader than the solutions, probably due to the better planarization of the backbone and increased packing ability in the solid state^[9]. Although both the solution and the film of a same polymer have similar wavelengths of maximum absorbance, a conspicuous red-shift of the absorbance onset is apparent in going from a solution to a corresponding thin film, and a weak shoulder peak appears at about 700 nm in the spectrum of the film, which can be interpreted as the effect of interchain interaction between planar π-systems. In addition, the polymerization degree grows with the increase of the polymer solubility arising from longer alkyl groups, and the extension of electron delocalization reduces the bandgap and shifts the peak to longer wavelength. The optical bandgaps (E_q^{opt}) of PVnT and PEnT estimated by the absorption onset are about 1.35 and 1.5 eV, respectively, which values meet the requirement of being low-bandgap polymers for efficient PSC devices.

The electrochemical properties of the polymers were investigated by using cyclic voltammetry to determine the HOMO and LUMO energy levels. The cyclic voltammetry (CV) curves are shown in Figure 6, and the data are also summarized in Table 1. The results show that the electrochemical bandgap (E_g^{CV}) of PVnT is about 1.45 eV, smaller than that of PEnT (about 1.8 eV), in line with the trend of the optical bandgaps. The frontier molecular orbital energies of the polymers match well with those of the electron acceptor (PCBM) in PSC devices^[10].



Figure 6. CV curves of the polymer films.

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rable 1. Oblubility, optical and electrochemical properties of the polymers.										
Polymer	PV8T	PV10T	PV12T	PV16T	PE8T	PE10T	PE12T	PE16T		
Solubility in CHCl ₃ (mg mL ⁻¹) ^[1]	5	7	9	13	4	6	9	14		
λ_{\max} (solution, nm)	639	665	675	683	602	648	649	645		
E_{g}^{opt} (solution, eV)	1.63	1.63	1.53	1.42	1.79	1.79	1.74	1.51		
λ_{\max} (film, nm)	629	644	659	678	583	620	621	632		
E_{g}^{opt} (film, eV)	1.41	1.39	1.36	1.30	1.56	1.55	1.53	1.46		
LUMO ^{CV} (film, eV)	-3.82	-3.83	-3.84	-3.69	-3.80	-3.76	-3.68	-3.65		
HOMO ^{CV} (film, eV)	-5.19	-5.24	-5.29	-5.28	-5.47	-5.54	-5.48	-5.49		
E_{g}^{CV} (film, eV)	1.37	1.41	1.45	1.59	1.67	1.78	1.80	1.84		
LUMO ^{DFT} (methyl derivative, eV)	-3.07				-3.11					
HOMO ^{DFT} (methyl derivative, eV)	-4.36				-4.52					
E_{g}^{DFT} (methyl derivative, eV)	1.29				1.41					

Table 1. Solubility, optical and electrochemical properties of the polymers.

[1] The rough solubility was determined by weighing the residue after evaporation of chloroform from 1mL polymer solution (20 mg/mL) which had been filtered at 0.45 µm.

Structural defects in a polymer molecule, like irregularity and twisting, weaken the π -conjugation and intermolecular π - π interaction, which enlarge the bandgap. But the weak π - π interaction also enlarges the distance between adjacent polymer molecules, leading to a high contact probability between the molecule and the electrolyte, and making the molecule more reactive in an electrochemical reaction and outputting stronger electrochemical signals than well structured polymer molecules. As a result, the large steric hindrance of long alkyl chains creates more defects than that of short alkyl chains, so the electrochemical bandgap are bigger than the corresponding optical bandgaps, and a longer alkyl group leads to a larger electrochemical bandgap, which is contrary to the results obtained from the optical absorption spectra.

The experimental bandgaps are generally in consistent with the results from the theoretical calculations. The E_g^{DFT} is smaller than the experimental E_g , because the theoretical models are absolutely regular polymers with infinite degrees of polymerization, whereas the actual polymers are not so perfect, structure defects and limited degrees of polymerization weaken their conjugation and enlarge the bandgaps. Both the experimental and theoretical data show that the LUMOs of PVnT and PEnT are similar, and the HOMOs of PVnT are higher. Since the vacuum levels (zero reference energy levels) of electrochemical and DFT potentials are different, there is no comparability between an electrochemical level and a DFT level.

Photovoltaic Performance

Unoptimized PSC devices were fabricated as an attempt to investigate the photovoltaic properties of the triphenodioxazinebased conjugated polymers, in which PVnT and PVnT served as electron donors, while [6,6]-Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) served as a electron acceptor. The current densityvoltage (J-V) curves of PSCs are shown in Figure 7, and the device performances are summarized in Table 2.

The PSCs with different polymers have similar open circuit voltage (V_{OC}) and short circuit current density (J_{SC}), which values are about 0.7 V and about 4 mA cm⁻², respectively. The fill factor (FF) and power conversion efficiency (PCE) are low.



Figure 7. J-V characteristics of PVnT and PEnT-based PSC devices under illumination of AM 1.5G, 100 mW cm $^{-2}$.

During the spin-coating process, it is found that the polymer/PC₇₁BM blend films were more or less discontinuous and uneven, even tended to detach from the substrates. A probable reason for the low film-forming ability of the polymers is the high planarity and rigidity of the polymer molecules. Unlike most reported conjugated polymers^[1, 11], the conjugated units of

PVnT and PEnT are completely confined to the center axes of the backbones, while there are only flexible alkyl chains outside the backbones, which make it relatively difficult to twist the molecules around their center axes, just like moving a lever with its short arm. Consequently, the perfect planarity of the polymers causes excessively strong π - π interaction among the polymer molecules, leading to strong self-aggregation tendency and low appetency with other materials.

The surface morphology of the blend films on glass substrates were measured by atomic force microscope (AFM) and the images are depicted in Figure 8. The height images show that with the growth of the alkyl chains, the films become smoother, and irregular large particles gradually disappear and are replaced with regular small particles or wrinkles, which are uniform in size and shape. Moreover, the phases in the phase images become more compatible and organized as the alkyl chains grow, which suggests that longer alkyl chains are beneficial to the compatibility of polymer with PC₇₁BM. Strangely, there are many doughnut-like cavities distributing on the film surface, which may caused by a certain kind of molecular clusters.

Table 2. Photovoltaic perfor	mances of the							
Polymer	PV8T	PV10T	PV12T	PV16T	PE8T	PE10T	PE12T	PE16T
V _{oc} (V)	0.18	0.56	0.74	0.69	0.18	0.73	0.76	0.69
J _{SC} (mA cm ⁻²)	3.97	3.77	4.03	4.40	3.24	3.43	4.03	6.07
FF	0.27	0.33	0.32	0.36	0.27	0.28	0.39	0.33
PCE (%)	0.20	0.77	0.90	1.04	0.21	0.82	1.19	1.33



Figure 8. AFM height and phase images of the polymer/PC₇₁BM blend films (1:2, w/w, annealed at 150 °C for 10 min) on glass substrates. The units of the height and phase scales are nm and degree, respectively.

The low film-forming properties and strong exclusiveness of the polymers greatly limited the performances of corresponding PSC devices, especially the FF. Since the shorter the alkyl group a polymer has, the more compactly the molecules stack together, the film quality and the device performance improves with the alkyl chain lengthening. The difference between vinyl and ethynyl units has little effect on the performance. By comparison, PVnT slightly outperforms PEnT with short alkyl groups, whereas long alkyl-substituted polymers exhibit an opposite trend. That is because PVnT is more flexible than PEnT, relaxing the structural rigidity is more beneficial to the performance of a rigid polymer containing short alkyl groups, while maintaining the structural planarity and π -conjugation is beneficial to the performance of a flexible polymer containing long alkyl groups.

Conclusions

Two series of triphenodioxazine-based conjugated polymers without any thiophene units have been synthesized via an optimized route.

The theoretical simulation shows that the introduction of vinyl and ethynyl eliminates the steric hindrance between units and endows these triphenodioxazine-based polymers highly planar structures, which ensures continuity of the backbone conjugation. The polymers are thermostable, and PVnT is more flexible than PEnT. Their optical absorption bands range from the visible to the near-infrared. The optical and electrochemical bandgaps of a polymer are similar, to which the length of the alkyl groups make little difference. The values of PEnT and PEnT are about 1.4 eV and 1.6 eV, respectively.

Although the planar fused-ring structures, broad optical absorption bands, ideal bandgaps and distribution of the frontier molecular orbitals of the triphenodioxazine-based polymers should be beneficial to the photovoltaic performances of the PSC devices, the low quality of the blend films was adverse to achieving high FF and PCE, which could be partially solved by introducing long alkyl side-chains.

Experimental Section

Materials

2,5-Dihydroxy-1,4-benzoquinone, trans-1,2-bis(tri-n-butylstannyl)ethylene, 1,2-bis(trimethylstannyl)acetylene, and

tetrakis(triphenylphosphine)palladium were purchased from Acros. PEDOT:PSS water solution (Baytron P VP AI 4083) and PC₇₁BM was purchased from H. C. Starck and American Dye Source, respectively. All chemical reagents, unless otherwise specified, were used as received. Chloroform and toluene were freshly distilled over appropriate drying agents prior to use and stored under nitrogen.

Measurements and characterizations

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AV-500 spectrometer. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded at a Nicolet 5700 spectrometer from KBr pellets. ESI-MS were run on an Agilent 1100 Series LC/MSD instrument. MALDI-TOF-MS spectra were acquired on a Bruker Reflex-TOF-MS instrument. Elementary analyses were performed on a vario EL cube elementar. TGA and DSC data were collected on a thermal analysis instrument (SDT-Q600 and STA 409, TA Instruments) with a heating rate of 10 °C min⁻¹ and a nitrogen flow of 100 mL min⁻¹. AFM images were obtained on an Asylum Research MFP-3D microscope under the tapping mode. Gel permeation chromatography (GPC) measurements were performed on a GPC-220 chromatograph using a differential refractometer at room temperature with tetrahydrofuran as an eluent at a flow rate of 1 mL min⁻¹. And because the polymers dissolved slightly in tetrahydrofuran, an indirect measurement was carried out, which is described in Supplementary data. DFT-PBC calculations were performed at the B3LYP/6-31G(d) level using Gaussian 09 program package^[12].

The UV-Vis-NIR spectra were obtained using an Agilent Cary 5000 spectrophotometer. The following equation^[13] is used to calculate a optical bandgap energy (E_g^{opt}):

$$E_{\rm g}^{\rm opt}({\rm eV}) = \frac{1240}{\lambda_{\rm onset}({\rm nm})}$$

where λ_{onset} is the onset of the long wavelength band in an absorption spectrum.

CV measurements were carried out on an electrochemical workstation (CHI660E, Shanghai Chenhua Co. Ltd, China) with a three-electrode cell in tetrabutylammonium tetrafluoroborate (TBABF₄)/acetonitrile electrolyte (0.1 mol L⁻¹) using a scan rate of 100

$$E_{\text{HOMO}} / E_{\text{LUMO}}(\text{eV}) = -E_{\text{onset}}^{\text{polymer}}(\text{eV}) + E_{\text{onset}}^{\text{Fc/Fc}}(\text{eV}) - 4.8\text{eV}$$

mV s⁻¹. A Pt electrode coated with a polymer film, a Pt wire, and an Ag/AgCl (with 0.1 mol L⁻¹ KCl aqueous solution) electrode served as a working electrode, a counter electrode and a reference electrode, respectively. The potentials were internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc⁺), which is estimated to have an oxidation potential of -4.8 eV vs vacuum. The redox potential of Fc/Fc⁺, measured under the same condition as polymer samples, was located at 0.33 V related to the Ag/AgCl electrode. The energies of HOMO and LUMO (E_{HOMO} and E_{LUMO}) were calculated according to the following equation^[14]:

where $E_{\text{onset}}^{\text{polymer}}$ and $E_{\text{onset}}^{\text{Fc/Fc}}$ are the onset potentials of a polymer film and Fc/Fc⁺, respectively.

Synthesis

1,4-Dialkoxybenzene (n = 8, 10, 12) (1) was prepared according to the literature^[15]. The products were further purified by recrystallization from ethanol to afford compound 1 as white sheets (~80% yield). n = 8: ¹H NMR (CDCl₃, δ) 6.81 (s, 4 H), 3.89 (t, 4 H), 1.74 (m, 4 H), 1.28 (m, 20 H), 0.88 (t, 6 H); n = 10: ¹H NMR (CDCl₃, δ) 6.81 (s, 4 H), 3.89 (t, 4 H), 1.75 (m, 4 H), 1.27 (m, 28 H), 0.88 (t, 6 H); n = 12: ¹H NMR (CDCl₃, δ) 6.81 (s, 4 H), 1.74 (m, 4 H), 0.88 (t, 6 H); n = 12: ¹H NMR (CDCl₃, δ) 6.81 (s, 4 H), 1.74 (m, 4 H), 1.26 (m, 36 H), 0.88 (t, 6 H).

2,5-Dialkoxybromobenzene (n = 8, 10, 12) (**2**) was prepared according to the literature^[16] without further purification. The product was obtained as white solid and contained a small amount of 1,4-dialkoxybenzene and 2,5-dialkoxy-1,4-dibromobenzene (~95% yield).

4-Nitro-2,5-dialkoxybromobenzene (n = 8, 10, 12) (3): Compound 2 (24.0 mmol) was dissolved in propionic acid (80 mL) and the solution was heated to 45 °C. Concentrated nitric acid (66 % w/w, 6 mL) was added dropwise in 2 h and stirring was continued for 8 h at the same temperature. The mixture was poured into ice water (100 mL), and then filtered. The filter cake was washed with water several times. The product was dried under vacuum and obtained as a light yellow solid (~0.022 mol,

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~90% yield), which was used directly for the next step without further purification.

4-n-Butoxyphenol (4): Hydroquinone (26.4 g, 0.24 mol), 1bromobutane (27.4 g, 0.2 mol), and sodium hydroxide (8.8 g, 0.22 mol) were suspended in N,N-dimethylformamide (125 mL) and the mixture was stirred at 60 °C for 12 h under nitrogen atmosphere. The reaction mixture was poured into water (500 mL) and extracted with ethyl acetate (150 mL), washed with water several times. The residue of the organic phase after evaporation was purified by recrystallization from petroleum ether to afford Compound 4 as white sheets (29 g, 0.174 mol, 87% yield). ¹H NMR (DMSO-*d*₆, δ) 6.76 (d, 4 H), 3.90 (t, 2 H), 1.74 (m, 2 H), 1.47 (m, 2 H), 0.97 (t, 6 H). Elemental analysis calcd. (%) for C₁₀H₁₄O₂: C, 72.26; H, 8.49; found: C, 72.62; H, 8.57. ESI-MS: calcd. for C₁₀H₁₃O₂ [M-H]⁻ 165.1, found 165.1.

2-Bromo-4-n-butoxyphenol (5): Compound 4 (29.9 g, 0.18 mol) was dissolved in dichloromethane (125 mL) and bromine (30.4 g, 0.19 mol) was added dropwise with stirring in 1 h at 0 °C. The solvent and redundant bromine were removed under reduced pressure to afford a colorless solid, which contained a small amount of unreacted raw materials and dibromide (44 g, 0.18 mol, ~99% yield). The product was used directly for the next step without further purification.

2-n-Hexadecoxy-5-n-butoxybromobenzene (6): Compound 5 (24.5 g, 0.1 mol) and n-Hexadecyl bromide (32.0 g, 0.105 mol) were dissolved in acetone (150 mL). After adding potassium carbonate (14.5 g, 0.105 mol), the mixture was refluxed for 36 h under nitrogen atmosphere. Then it was poured into water (500 mL) and extracted with petroleum ether (300 mL). The organic phase was washed with dilute aqueous sodium hydroxide solutions and water several times. The solvent was removed under reduced pressure to afford a colorless solid (40 g, 0.085 mol, 85% yield). The product was used directly for the next step without further purification.

2-n-Hexadecoxy-4-nitro-5-n-butoxybromobenzene (7): Compound **6** (47.0 g, 0.1 mol) was dissolved in propionic acid (150 mL) and the solution was heated to 45 °C. Concentrated nitric acid (66 % w/w, 20 mL) was added dropwise in 1 h and stirring was continued for an additional 4 h at the same temperature. The mixture was poured into water (500 mL) and extracted with petroleum ether (500 mL), washed with water several times. The solvent was removed to obtain a light yellow solid (46 g, 0.09 mol, 90% yield). The product was used directly for the next step without further purification.

Sodium 2-nitro-4-alkoxy-5-bromophenolate (n = 8, 10, 12, 16) (9): Compound 3 or Compound 7 (0.08 mol), and anhydrous aluminium chloride (11.7 g, 0.088 mol) were suspended in dry, ethanol-free chloroform (500 mL) and the mixture was refluxed for 6 h. The resulting red solution was poured into hydrochloric acid (15% w/w, 500 mL) and extracted with chloroform. After evaporation of solvent, the residue of the organic phase, mainly containing Compound 8, was dissolved in petroleum ether (500 mL), and a solution of sodium ethoxide in ethanol (~2.5 mol L⁻¹, 50 mL) was added dropwise. The mixture was stirred for 15 min, then water (100 mL) was added. The stirring was continued for an additional 30 min. The precipitate formed was collected by filtration, washed with water and petroleum ether. The product was dried under vacuum and obtained as a red solid (~0.06 mol, ~75% yield). n = 8: 1H NMR (DMSO-d₆, δ) 7.26 (s, 1 H), 6.69 (s, 1 H), 3.80 (t, 2 H), 1.66 (m, 2 H), 1.27 (m, 10 H), 0.86 (t, 6 H). ESI-MS: calcd. for C14H19BrNO4 [M-Na] 344.1, found: 344.1. n = 10: ¹H NMR (DMSO-d₆, δ) 7.26 (s, 1 H), 6.69 (s, 1 H), 3.81 (t, 2 H), 1.67 (m, 2 H), 1.25 (m, 14 H), 0.85 (t, 6 H). ESI-MS: calcd. for C₁₆H₂₃BrNO₄ [M-Na]⁻ 372.1, found: 372.1. n = 12: ¹H NMR (DMSO-d₆, δ) 7.25 (s, 1 H), 6.68 (s, 1 H), 3.80 (t, 2 H), 1.66 (m, 2 H), 1.24 (m, 18 H), 0.85 (t, 6 H). ESI-MS: calcd. for C18H27BrNO4 [M-Na] 400.1, found: 400.1. n = 16: ¹H NMR (DMSO-*d*₆, δ) 7.25 (s, 1 H), 6.64 (s, 1 H), 3.79 (t, 2 H), 1.66 (m, 2 H), 1.24 (m, 26 H), 0.85 (t, 6 H). ESI-MS: calcd. for $C_{22}H_{35}BrNO4$ [M-Na] $^{\cdot}456.2,$ found: 456.2. n = 8, 10, 12, 16: FT-IR (vmax, cm $^{-1}$) 3500 (s), 2920 (s), 2850 (m), 1530 (m), 1230 (s), 1180 (m), 860 (m).

2-Amino-4-alkoxy-5-bromophenol hydrochloride (n = 8, 10, 12, 16) (10): Compound 9 (5 mmol) and nickel dichloride (0.8 g, 3.4 mmol) were suspended in a mixed solvent of diethyl ether and ethanol (1:1 v/v, 75 mL). The mixture was cooled to 0 °C, then a suspension of sodium borohydride (1.5 g, 40 mmol) in ethanol (20 mL) was added dropwise with vigorous stirring in 10 min under nitrogen atmosphere. The stirring was continued for 3 h at room temperature. The mixture was slowly poured into concentrated hydrochloric acid (100 mL) and ice (50 g), then filtered. The filter cake was washed with diluted hydrochloric acid and dried under vacuum. The product was obtained as a white solid (~4 mmol ~80% yield). n = 8: ¹H NMR (DMSO- d_6 , δ) 10.46 (br s, 1 H), 9.22 (br s, 3 H), 7.21 (s, 1 H), 7.06 (s, 1 H), 3.90 (t, 2 H), 1.70 (m, 2 H), 1.26 (m, 10 H) 0.86 (t, 6 H). n = 10: ¹H NMR (DMSO- d_6 , δ) 10.42 (br s, 1 H), 9.20 (br s, 3 H), 7.18 (s, 1 H), 7.04 (s, 1 H), 3.90 (t, 2 H), 1.69 (m, 2 H), 1.25 (m, 10 H), 0.85 (t, 6 H). n = 12: ¹H NMR (DMSO-d₆, δ) 10.40 (br s, 1 H), 9.44 (br s, 3 H), 7.18 (s, 1 H), 7.03 (s, 1 H), 3.91 (t, 2 H), 1.70 (m, 2 H), 1.25 (m, 10 H), 0.86 (t, 6 H). n = 16: ¹H NMR (DMSO- d_6 , δ) 10.23 (br s, 1 H), 8.83 (br s, 3 H), 7.13 (s, 1 H), 6.95 (s, 1 H), 3.89 (t, 2 H), 1.69 (m, 2 H), 1.24 (m, 10 H), 0.85 (t, 6 H).

2,9-Dibromo-3,10-dialkoxytriphenodioxazine (n = 8, 10, 12, 16) (11): Compound 10 (7.5 mmol), 2,5-dihyroxy-1,4-benzoquinone (0.50 g, 3.6 mmol), and anhydrous sodium acetate (0.62 g, 7.5 mmol) were suspended in acetic acid (150 mL). The mixture was reacted at 80 °C for 18 h under nitrogen atmosphere, and then was cooled to room temperature. Water (500 mL) was added and the mixture was extracted with dichloromethane. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography eluting with dichloromethane/hexane (3/1) to afford deep purple needles (~1 mmol, ~15%). n = 8: ¹H NMR (CD₂Cl₂, δ) 7.46 (s, 2 H), 7.17 (s, 2 H), 7.00 (s, 2 H), 4.09 (t, 4 H), 2.17~0.89 (m, > 30 H). Elemental analysis calcd. (%) for $C_{34}H_{40}Br_2N_2O_4$: C, 58.30; H, 5.76; N, 4.00; found: C, 58.72; H, 5.85; N, 3.74. MALDI-TOF-MS: calcd. for $C_{34}H_{40}Br_2N_2O_4$ 700.13, found: 700.50. n = 10: ¹H NMR (CDCl₃, δ) 7.40 (s, 2 H), 7.07 (s, 2 H), 6.83 (s, 2 H), 4.05 (t, 4 H), 1.85~0.89 (m, > 38 H). Elemental analysis calcd. (%) for C₃₈H₄₈Br₂N₂O₄: C, 60.32; H, 6.39; N, 3.70; found: C, 60.66; H, 6.46; N, 3.44. MALDI-TOF-MS: calcd. for C₃₈H₄₈Br₂N₂O₄ 756.20, found: 756.54. n = 12: ¹H NMR (CDCl₃, δ) 7.40 (s, 2 H), 7.08 (s, 2 H), 6.81 (s, 2 H), 4.06 (t, 4 H), 1.85~0.88 (m, > 46 H). Elemental analysis calcd. (%) for C₄₂H₅₆Br₂N₂O₄: C, 62.07; H, 6.95; N, 3.45; found: C, 62.44; H, 7.07; N, 3.02. MALDI-TOF-MS: calcd. for C42H56Br2N2O4 812.26, found: 812.60. n = 16: 1 H NMR (CDCl₃, δ) 7.40 (s, 2 H), 7.08 (s, 2 H), 6.82 (s, 2 H), 4.06 (t, 4 H), 1.57~0.88 (m, > 62 H). Elemental analysis calcd. (%) for C₅₀H₇₂Br₂N₂O₄: C, 64.93; H, 7.85; N, 3.03; found: C, 65.44; H, 8.01; N, 2.87. MALDI-TOF-MS: calcd. for $C_{50}H_{72}Br_2N_2O_4$ 924.38, found: 924.69. n = 8, 10, 12, 16: FT-IR (vmax, cm⁻¹) 2920 (s), 2850 (m), 1630 (m), 1560 (s), 1460 (m), 1270 (m), 1180 (s), 860 (m), 580 (m). 13C NMR could not be determined due to low solubility in deuterated solvents

Polymer: Compound 11 (0.375 mmol), trans-1,2-bis(tri-n-0.375 butylstannyl)ethylene (0.24)g, mmol) or 1.2-(0.139 bis(trimethylstannyl)acetylene 0.375 mmol). and g, tetrakis(triphenylphosphine)palladium (0.0347 g, 0.03 mmol) were suspended in toluene (25 mL). The mixture was subjected to five cycles of evacuation and admission of nitrogen, and then heated to 70 °C for several hours (n = 8: 8 h; n = 10: 10 h; n = 12: 12 h; n = 16: 16 h). After cooling to room temperature, the mixture was poured into methanol (100mL) and stirred for 30 min. A black precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 48 h each. It was extracted with hot chloroform in the extractor for 36 h. After removing solvent, a black solid was collected (~45%). PV16T: ¹H NMR (CDCl₃, δ) 7.62~6.51 (br m, 7 H), 4.04 (br s, 4 H), 1.58~0.90 (m, > 62 H). PE16T: ¹H NMR (CDCl₃, δ) 7.62~6.51

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(br m, 6 H), 4.05 (br s, 4 H), 1.58~0.90 (m, > 62 H). PVnT: FT-IR (ν max, cm⁻¹) 2920 (s), 2850 (m), 1560 (s), 1430 (m), 1270 (s), 1180 (s), 850 (m), 580 (s). PEnT: FT-IR (ν max, cm⁻¹) 2920 (s), 2850 (m), 1630 (m), 1560 (s), 1430 (m), 1280 (m), 1170 (s), 850 (m), 580 (s).

PSC device fabrication

FULL PAPER

PSC devices were fabricated on ITO glass substrates with a configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The ITO glass substrates were sequentially cleaned with detergent, deionized water, acetone, and isopropyl alcohol. A PEDOT:PSS layer (45 nm) was spin-coated from its water solution (filtered at 0.45 μ m) onto the ITO glass, and then baked at 150 °C for 10 min. The blend film was spin-coated in a nitrogen filled glove box from a blending solution of the polymer with PC₇₁BM in 1,2-dichlorobenzene (1:2, w/w, filtered at 0.45 μ m), and then annealed at the temperature of 150 °C for 10 min. Subsequently, calcium (30 nm) and aluminum (100 nm) were thermally deposited successively under high vacuum (< 10⁻⁴ Pa) with a shadow mask to define the active area of the devices (10.0 mm²). The *J-V* characteristics were measured using a Keithley 2400 source meter under a simulated AM 1.5G conditions.

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Keywords: triphenodioxazine • conjugated polymers • synthesis • optical and electrochemical properties • polymer solar cells

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER



A series of triphenodioxazine-based conjugated polymers were synthesized via an optimized route. The relationships among polymer structures, thermal, optical, electrochemical and photovoltaic properties were investigated in detail by experimental data analysis and theoretical simulation.

Triphenodioxazine, conjugated polymers

Xiaohui Gong, Pei Han, Hui Wen, Ying Sun, Xueqin Zhang, Hong Yang, and Baoping Lin*

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Synthesis and Properties of Triphenodioxazine-Based Conjugated Polymers for Polymer Solar Cells