A convenient and scalable strategy for post-functionalization of poly(phenylene-ethynylene)s and phenylene-ethynylene arrays from boronate ester derivatives using the thienyl group as an example. Furthermore, poly(2,2′-(1-(4-(1,2-di(thiophen-2-yl)vinyl)phenyl)-2-(2,5-dioctylphenyl)ethene-1,2-diyl)dithiophene) showed good field-effect transistor performance with an excellent mobility up to 0.723 cm² V⁻¹ s⁻¹ and an on–off ratio of 10⁴.

Conjugated polymeric materials, such as poly(phenylene ethynylene)s (PPEs), have been some of the most widely investigated materials because of their relative ease of synthesis and promising performance for a range of applications. Fine tuning of their properties by proper functionalization of the phenylene rings of the main chain allows one to tailor materials for specific applications in organic optics and electronics. More successful applications in organic light-emitting diodes, molecular wires and sensitive fluorescent chemosensors, especially in biosensing applications, have been reported. The easy access to high-quality PPEs makes them an attractive candidate for analogous polymer reactions. However, despite this interest, there are few studies on the availability of unsaturated bonds in PPEs. In the last decade, reduction to their fully hydrogenated counterparts or coordination of organo-platinum fragments has been described. Nevertheless, appending organic groups to the ethynylene moieties based on PPEs have been rarely reported. In this research, thienyl is taken as an example to describe a novel and convenient synthetic method to prepare a post-functionalized polymer poly(2,2′-(1-(4-(1,2-di(thiophen-2-yl)vinyl)phenyl)-2-(2,5-dioctylphenyl)ethene-1,2-diyl)dithiophene) (PDIPDT), in which the addition of boronate ester to ethynylene moieties for poly(2,2′- (1-(4-(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)-2-(2,5-dioctylphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)) (PDBPDB), a versatile building block, is the key process.

Among the various synthetic approaches to diphenylethylen, the Sonogashira reaction is the most widely used method. In general, the reaction features the cross-coupling between an aryl-ethyne and an aryl bromide in the presence of a palladium(0)/copper iodide (Pd(0)/CuI) cocatalyst and a base at approximately 80 °C. The homo-coupling by-product and branet product formed during the Sonogashira reaction are worrying problems. In this research, aryl iodides were targeted for the synthesis of the phenylene-ethynylene array 2–4 at room temperature because of their high reactivity (ESI† Scheme S1). The corresponding iodides react considerably faster with excellent yields (>98%) and can easily be isolated in a pure form. The large amount of 2–4 is the key to successive reactions. Boronate esters are an attractive class of compounds that have been utilized as synthetic intermediates. The traditional methods for their synthesis are the nucleophilic substitution of trialkoxyborates or haloboranes with Grignard or organolithium reagents, or the addition of hydroboranes to unsaturated hydrocarbons. The uncatalyzed reactions are different from the catalyzed reactions and using a catalyst is an interesting strategy to obtain stereoselectivities.

Ishiyama et al. reported the first example of the syn-selective addition of bis(pinacolato)diboron to alkynes and applied the addition to diphenylethylene. However, no detailed crystalline structure has been offered, and in the case of product 5, virtually few references to display its configuration. Recently, the single-crystal of 5 obtained by us has verified that it has a Z-type structure. According to the reaction, the addition of bis(pinacolato)diboron was extended to compounds 1–4 (Scheme 1). Furthermore, the single crystal of 6 was fortunately recrystallized from dichloromethane (CH₂Cl₂)/n-hexane solution.
Its ORTEP drawing is shown in Fig. 1a, which reconfirms the validity of the Z-selection of the reaction. Interestingly, the diboration of alkynes was catalyzed excellently by platinum(0) complexes, whereas the platinum(II) complexes\(^{21}\) such as cis-bis(triphenylphosphine)platinum(II) dichloride \([\text{PtCl}_2(\text{PPh}_3)_2]\), and the platinum(IV) catalyst tetrachloroplatinum dihydrochloride hydrate \((\text{H}_2\text{Cl}_6\text{OPt})\) were ineffective in our experiments. It is an efficient and convenient approach to synthesize Z-selective and complex analogues. To confirm the potential ability of adducts for use in the boron cross-coupling reaction, compounds 5–8 were allowed to react with 2-bromothiophene. Thiophene derivatives are promising organic semiconductors because of their superior mobility but it is difficult to achieve.\(^{22–25}\) Nevertheless, the elaborate structures 9–12 were readily prepared using a Suzuki reaction. During the whole reaction, the structure of 2, 1-iodo-4-(phenylethynyl)benzene and 9 were also confirmed using accurate, single crystal X-ray diffraction (XRD) data (ESI† Fig. S1 and Table S1).

It is worth noting that the procedure based on the phenylene-ethynylene array is highly versatile not only for the syntheses of oligomers 9–12 but for the preparation of analogous polymers as well. In order to obtain Polymer 1 with a moderate number average molecular weight \((M_n = 7300 \text{ g mol}^{-1})\), the reaction was conducted with 1,4-diiodo-2,5-diocytlybenzene at 45 °C for 24 h. Under mild conditions, the formation of defects was minimized. After the long octyl groups attached, the solubility of the Polymer 1 was satisfactory, and the toluene was a much better choice for the addition reaction than DMF. A subsequent Suzuki reaction of the PDTPDB yielded the corresponding PDTPDT \((85\%\) yield) (Scheme 1). The product is reasonably soluble in common organic solvents, such as dichloromethane, toluene, and tetrahydrofuran (THF).

All monomer structures were confirmed using mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy before proceeding with the reaction. The polymers were characterized at each step using gel permeation chromatography (GPC), proton-NMR (\(^1\)H-NMR) and carbon-13-NMR (\(^{13}\)C-NMR) analysis (see ESI† for further details), confirming the transformations from PPEs. In Fig. 1b, the GPC traces for polymers in THF obtained with different elution times are shown. After several precipitations in methanol, PDTPDB has a molecular weight of \(1.63 \times 10^4 \text{ g mol}^{-1}\) with a narrow molecular weight distribution based on Polymer 1 (Table 1). The polydispersity index (PDI) of PDTPDT has slightly increased to 1.20 but is still quite low because of the use of the Suzuki process. Meanwhile, the GPC data agree with the calculated \(M_n\) for Polymer 1 (Table 1). These features strongly suggest that the new strategy discussed in this paper is straightforward but effective even throughout the entire polymerization.

The detailed structures, including the local position of the wheel component, were verified using NMR spectral analyses.

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**Scheme 1** Synthetic routes to Compounds 5–12. i. Pt(\(\text{PPh}_3\))\(_4\), dimethylformamide (DMF), 90 °C, 24 h; ii. Pd(\(\text{PPh}_3\))\(_4\), toluene, potassium carbonate/water (\(\text{K}_2\text{CO}_3/\text{H}_2\text{O}\)), 87 °C, 48 h. R: \(\text{C}_4\text{H}_9\); Pd(\(\text{PPh}_3\))\(_4\): tetrakis(triphenylphosphine)palladium(0); DIPA: diisopropylamine; Pt(\(\text{PPh}_3\))\(_4\): tetrakis(triphenylphosphine)-platinum(0).
Fig. 2 shows the $^1$H-NMR spectra of Polymer 1, PDBPDB and PDTPDT (400 MHz, deuterated chloroform). The aliphatic region in the $^1$H-NMR spectrum showed the main chain methyl (0.8 ppm) and methylene (1.27–1.36, 1.62–1.71, 2.65 ppm) of the octyl group, the intensity of which relies on the length of the polymeric chains.26 The signal of the aromatic protons shift to the range of $\delta = 7.30–7.68$ ppm, which has the proper proportion of aliphatic and aromatic regions in Fig. 2a. After addition of the boronate ester, the ratio of aliphatic and aromatic regions, which can be clearly observed in Fig. 2b, increases to an appropriate value. However, the ratio corresponding to the PDTPDT decreases because of the use of the Suzuki reaction (Fig. 2c).

The thermogravimetric analysis curve of the as-synthesized PDTPDT showed a decomposition temperature $>230$ °C under a nitrogen atmosphere which is shown in Fig. S2 (ESI†). Interestingly, the exothermic peak at 107 °C in PDTPDT is thought to be a cold crystallization temperature, and the solid phase finally melts at about 139 °C (ESI,† Fig. S3). Such crystalline characteristics could be vital for achieving the high field-effect transistor (FET) device, which is discussed later.

Table 1 Characterization results of the polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>$M_n,\text{calc}$ (g mol⁻¹)</th>
<th>$M_n,\text{GPC}$ (g mol⁻¹)</th>
<th>$M_w,\text{GPC}$ (g mol⁻¹)</th>
<th>PDI</th>
</tr>
</thead>
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<tr>
<td>Polymer 1</td>
<td>81.5</td>
<td>7300⁦</td>
<td>7300</td>
<td>10 800</td>
<td>1.47</td>
</tr>
<tr>
<td>PDBPDB</td>
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<td>16 500</td>
<td>16 300</td>
<td>17 900</td>
<td>1.10</td>
</tr>
<tr>
<td>PDTPDT</td>
<td>85.0</td>
<td>13 300</td>
<td>13 100</td>
<td>15 700</td>
<td>1.20</td>
</tr>
</tbody>
</table>

⁦The data is based on the results of the analysis of Polymer 1 by GPC.

Ultraviolet/visible (UV/vis) absorption and photoluminescence (PL) data of 9–12 and PDTPDT in CH$_2$Cl$_2$ are shown in Fig. 3 and Table S2 (ESI†). Absorption peaks of 9–12 were located at 333, 341, 343, and 344 nm, respectively, with an inconspicuous red shift. This is quite different from PDTPDT, which displays a broadened absorption peak at 370 nm. With respect to PL, the emission peak positions of 9–12 and PDTPDT present a significant bathochromic shift, and show the same trend with the absorptions. Furthermore, the lifetimes of 9–12 and PDTPDT are gradually increasing, indicating that the excited species of the oligomers can relax much more slowly by deepening the restriction of the intramolecular rotation (ESI,† Fig. S4). All of these bathochromic shifted tendencies indicate that the broader planarization of the molecular chain and the degree of conjugation change from oligomers to polymers. Intriguingly, the solid state of 10 can emit a bright chartreuse coloured light under the UV lamp when compared to the aphotic solution. This unusual phenomenon, aggregation-induced emission (AIE), was first reported by Luo et al.,27 but studies on thienyl compounds are less common. To provide further evidence for the AIE phenomenon, the quantum yields ($\Phi_\text{F}$) and PL intensities of 10 in THF/H$_2$O were investigated. Addition of H$_2$O into the THF/H$_2$O mixtures intensifies the emission and causes changes to longer wavelengths (Fig. 3c). Increasing the H$_2$O content to 70% induced a decrease in $\Phi_\text{F}$ because of a morphological change, as suggested by Tong et al.²⁸ The intensities increased with the increasing of the water content were also observed in 9, 11 and 12, different $\Phi_\text{F}$ of
9–12 in pure THF identified the restriction of intramolecular rotation as a main cause for the AIE effect [Fig. 3d and Fig. S5–S7, ESI†]. Obviously, 11 and 12 can emit faint light in solution [so-called aggregation-induced enhanced emission (AIEE)] because of the enough crowded structures (ESI,† Fig. S8).

To better understand the pronounced fluorescence red shift, cyclic voltammetry measurements of the oligomers and polymers were carried out. The corresponding data are summarized in Table S3 (ESI†) as well as in Fig. S9 (ESI†). The highest occupied molecular orbit and lowest unoccupied molecular orbit energy levels of 9 to PDTDPT are −5.39, −5.36, −5.35, −5.32, −5.42 eV and −2.24, −2.43, −2.47, −2.55, −2.71 eV, respectively. The optical band gaps ($\Delta E_g$) of 9 to PDTDPT were found to be 3.15, 2.93, 2.88, 2.77 and 2.71 eV, calculated from the onset wavelength of their UV absorptions. These experimental data also prove that the conjugation length does indeed extend from 9 to PDTDPT.

Thiophene containing polymers have been extensively studied as active layers in FETs.29–32 To investigate the charge transporting characteristics of oligomers and polymers, FETs were fabricated. Fascinatingly, FETs with 10 to PDTDPT semiconductors were obtained using ion gels13 to enable low voltage operation and to effectively diminish the heat generated by the working devices.34,35 Fig. 4a shows the optical images of the devices for the as-synthesized compounds (see the ESI† for device fabrication details). The surface morphology of films was characterized using polarizing optical microscopy (POM) as shown in Fig. 4b–d. When a dilute solution of PDTDPT was cast onto microslides, fiber-like crystals formed (Fig. 4b). However, different morphologies appeared if the concentration of the solution was increased. Either micron sized dendritic crystals, or sizable networks (Fig. 4c and d) were observed, and are most likely to be the results of the aggregation of several PDTDPT chains into cable like bundles. However, the distinct diffraction peak at $2\theta = 14.14^\circ$ corresponds to the d-spacing value of 6.26 Å, which is assigned to the interchain spacing between the polymer main chains, after placing the drop-cast films for seven days. The other diffraction peaks are also shown in Fig. S10 (ESI†), and these imply that there is highly organized packing. The representative transfer and output curves of the PDTDPT devices are shown in Fig. 4e and f and those of 10–12 are shown in Fig. S11 (ESI†). From the saturation regime of the transfer characteristics, the mobility was calculated according to the linear fitting of drain source current $(I_{DS})^{1/2}$ versus gate voltage $(V_G)$ curve. The mobility for the best oligomer FET, the device based on 11, was up to 0.99 cm$^2$ V$^{-1}$ s$^{-1}$ because of the denser intermolecular packing without bulky insulating layers created by long alkyl chains.36 The octyl chains attached improved the solubility to obtain PDTDPT successfully and enable processing from solution. Although with more octyl chains, the mobility of the PDTDPT-based device was measured as high as 0.723 cm$^2$ V$^{-1}$ s$^{-1}$ with an on/off current ratio of 10$^4$. The mobility showed no significant disparity with the reported ion gel used thin film FET devices, which give the best performance.37

In conclusion, a series of thienyl oligomers have been successfully designed and synthesized in high yields. Most important of
all, a novel and effective synthetic strategy of PDTPDT from the important building block, PDBPDB, based on Polymer I has been demonstrated. GPC, NMR spectroscopy, UV/vis absorption, PL, XRD, thermal properties and microscopic studies indicated the formation of PDTPDT. Furthermore, these data changing from oligomers 9–12 to PDTPDT verified the effects of the extended conjugated length. Subsequently, the FET devices fabricated with the PDTPDT possess high performance. Intriguingly, the usefulness of boronate derivatives 5–6 and even PDBPDB, as versatile building blocks, suggests their tremendous potential in well designed syntheses.

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Notes and references