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Journal Name

COMMUNICATION

Boronate ester Post-Functionalization of PPEs: Versatile Building Blocks for Poly(2,2'-(1-(4-(1,2-di(thiophen-2-yl)vinyl)phenyl)-2-(2,5-dioctylphenyl)ethene-1,2-diyl)dithiophene) and Application in Field Effect Transistor

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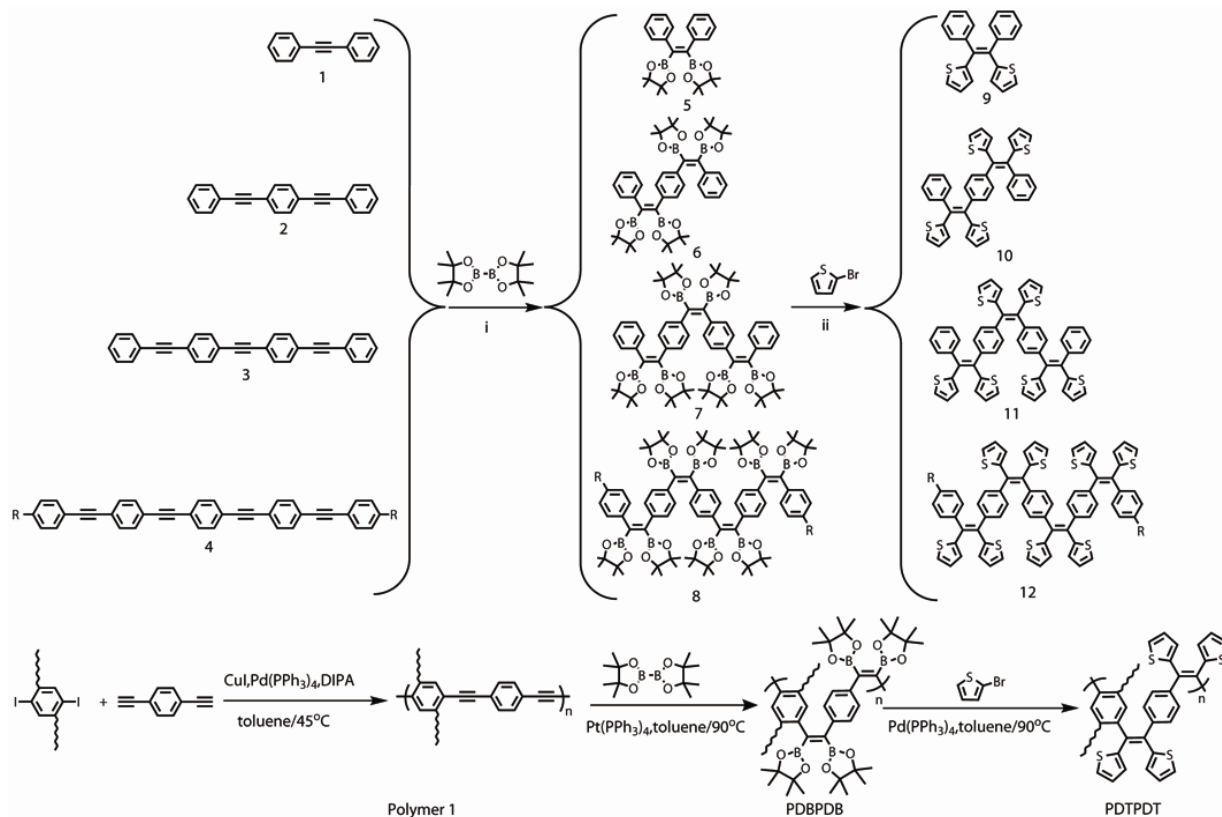
A convenient and scalable strategy to post-functionalization of poly(phenyleneethynylene)s and phenylene-ethynylene array from boronate ester derivatives and triumphantly take the thienyl group as an example. Furthermore, Poly(2,2'-(1-(4-(1,2-di(thiophen-2-yl)vinyl)phenyl)-2-(2,5-dioctylphenyl)ethene-1,2-diyl)dithiophene) (PDTPDT) shows great FET performance with excellent mobility up to $0.723 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on-off ratio of 10^4 .

Conjugated polymeric materials, such as Poly(phenyleneethynylene)s (PPEs) have been one of the most widely investigated materials because of its relative ease of synthesis and promising performance in a range of applications.^{1, 2} 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.^{3, 4} More successful applications in organic light-emitting diodes (OLEDs),⁵ molecular wires⁶ and sensitive fluorescent chemosensors,⁷⁻⁹ especially in biosensing applications,¹⁰ are reported. The facile 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. Until the last decade, reduction to their fully hydrogenated counterparts¹¹ or coordination of organo-platinum fragments¹² has been described. Nevertheless, appending organic groups to the ethynylene moieties based on PPEs have been rarely reported. In this paper, we take thienyl as an example to describe a novel and convenient synthetic method to prepare a post-functionalized polymer (PDTPDT), 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 diphenylethyne, the Sonogashira reaction is the most widely used method. In general, the reaction features the cross-coupling between an arylethyne and an aryl bromide in the presence of a Pd(0)/CuI cocatalyst and a base at approximately 80 °C.¹³ The homo-coupling byproduct and brunet product formed during the Sonogashira reaction are thorny problems. We target aryl iodides for synthesis of phenylene-ethynylene array **2-4** at room temperature because of the high reactivity (Scheme S1). The corresponding iodides do react considerably faster in excellent yields (>98%) and be easily isolated in a pure form. The large amount of **2-4** is the key to react successively. Boronate esters are an attractive class of compounds that have been utilized as synthetic intermediates.^{14, 15} The traditional methods for their synthesis are the nucleophilic substitution of trialkoxyborates or haloboranes with Grignard or organolithium reagents^{16, 17} or the addition of hydroboranes to unsaturated hydrocarbons.¹⁸ Different from the uncatalyzed reactions, catalyzed reactions are an interesting strategy to obtain stereoselectivities. Miyaura and co-workers¹⁹ have reported the first example of the syn-selective addition of bis(pinacolato)diboron to alkynes and applied the addition to diphenylethyne. However, no detailed crystal structure has been offered, and in the case of product **5** virtually few intuitive to display its configuration. Recently, the single-crystal of **5** obtained by us verifies the Z-type structure.²⁰ According to the reaction, we extended the addition of bis(pinacolato)diborane to compounds **1-4** (Scheme 1). Furthermore, the single-crystal of **6** was fortunately recrystallized from its CH₂Cl₂/n-hexane solution. Its ORTEP drawing is shown in Fig. 1a, which reconfirms the validity Z-selection of the reaction. Interestingly, the diboration of alkynes was excellently catalyzed by platinum(0) complexes, while the platinum(II) complexes²¹ such as PtCl₂(PPh₃)₂, and the platinum(IV) catalyst H₄Cl₆O₄Pt were ineffective in our experiments. It is an efficient and convenient approach to

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† Electronic supplementary information (ESI) available: experimental section including materials, measurements and characterizations; mass spectra, NMR data for new compounds and polymers, DSC, TGA spectra and XRD profile for the polymer, AIE figures, cyclic voltammetry data and CCDC reference numbers 1415294-1415297. For ESI or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1 Synthetic routes to Compounds **5-12**. i. $\text{Pt}(\text{PPh}_3)_4$, DMF, 90°C , 24h; ii. $\text{Pd}(\text{PPh}_3)_4$, toluene, $\text{K}_2\text{CO}_3/\text{H}_2\text{O}$, 87°C , 48h. R: C_4H_9

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 due to the superior mobility but difficult to achieve.²²⁻²⁵ Nevertheless, the elaborate structures **9-12** were readily prepared by Suzuki reaction. During the whole reaction, the structure of **2**, 1-iodo-4-(phenylethynyl)benzene and **9** were also confirmed by accurate single-crystal X-ray data (Fig. S1 and Table S1).

It is worth noting that the procedure based on phenylethynylene 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 molecule weight ($M_n=7300$ g/mol), the reaction was conducted with 1,4-diiodo-2,5-dioctylbenzene at 45°C for 24h. Under the mild conditions, the formation of defects was minimized. After the long octyl groups attached, the solubility of the **polymer 1** was good enough, and the toluene was a much better choice for the addition reaction than DMF. Subsequent Suzuki reaction of the **PDBPDB** yielded the corresponding **PDT PDT** (85% yield) (Scheme 1). The product is reasonably soluble in common organic solvents, such as dichloromethane, toluene, and THF.

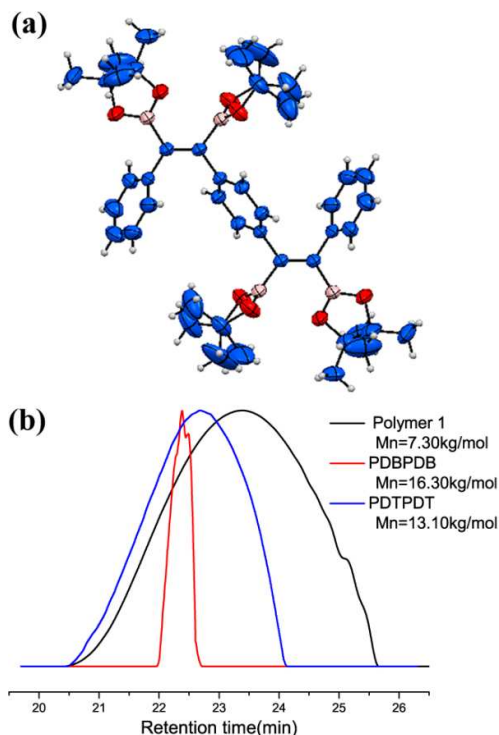


Fig. 1 (a) The ORTEP drawing of **6**. (b) GPC profiles of **Polymer 1**, **PDBPDB** and **PDT PDT** (eluent: THF).

All monomers are confirmed by mass spectrometry and NMR before proceeding to react. The polymers were characterized at each step using GPC, ^1H NMR and ^{13}C NMR analysis (Electronic Supporting Information), confirming the transformations from poly(phenyleneethynylene)s. As shown in Fig. 1b, the gel permeation chromatography (GPC) traces for polymers in THF obtained with different elution times. After several times precipitation in methanol, **PDBPDB** has a molecular weight of 1.63×10^4 g/mol with a narrow molecular weight distribution based on **Polymer 1** (Table 1). The polydispersity index of **PDTPDT** has slightly increased to 1.20 but still quite low through the Suzuki process. Meanwhile, the GPC data agree with the calculated M_n on the basis of the **polymer 1** (Table 1). These features strongly suggest that new strategy we communicate is straightforward but effective even throughout the entire polymerization.

Table 1 Characterization results of the polymers.

Sample	Yield (%)	$M_{n,\text{calc}}$ (g/mol)	$M_{n,\text{GPC}}$ (g/mol)	$M_{w,\text{GPC}}$ (g/mol)	PDI
Polymer 1	81.5	7,300 ^a	7,300	10,800	1.47
PDBPDB	72.2	16,500	16,300	17,900	1.10
PDTPDT	85.0	13,300	13,100	15,700	1.20

^aThe data was based on the results of **polymer 1** by GPC.

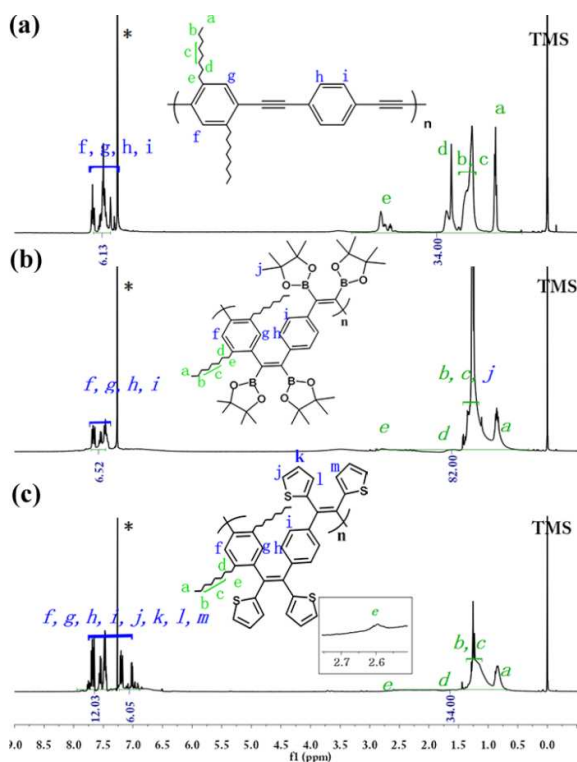


Fig. 2 ^1H NMR spectra of (a) **polymer 1**, (b) **PDBPDB**, (c) **PDTPDT** (400 MHz, CDCl_3).

The detailed structures, including the local position of the wheel component, were verified by NMR spectral analyses. Fig. 2 shows the ^1H NMR spectra of **polymer 1** (Fig. 2a), **PDBPDB** (Fig. 2b) and **PDTPDT** (Fig. 2c). The aliphatic region in the ^1H 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 is rely on the length of the polymeric

chains.²⁶ The signal of aromatic protons shift to the range of $\delta = 7.30$ – 7.68 ppm, which has a proper proportion of aliphatic and aromatic region in Fig. 2a. After addition of the boronate ester, the ratio of aliphatic and aromatic region clearly observed in Fig. 2b, increases to an appropriate value. On the contrary, the ratio corresponding to the **PDTPDT** suitably decreases through the Suzuki reaction (Fig. 2c).

The TGA curve of the as-synthesized **PDTPDT** showed decomposition temperature $> 230^\circ\text{C}$ under nitrogen atmosphere in Fig. S2. 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 (Fig. S3). Such crystalline characteristics could be vital for achieving the high FET device, as discussed later.

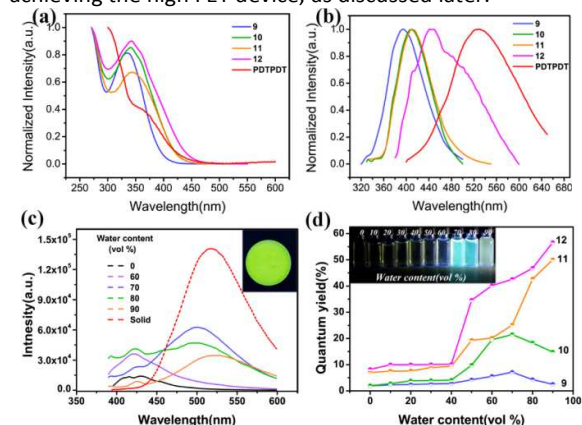


Fig. 3 (a) Normalized UV-vis spectra of **9**, **10**, **11**, **12**, and **PDTPDT** in CH_2Cl_2 . (b) Normalized PL spectra of **9**, **10**, **11**, **12** and **PDTPDT** in CH_2Cl_2 . (c) PL spectra of **10** solutions in THF–water mixtures. Inset: an optical photograph of **10** in solid state. (d) Fluorescence quantum yield of oligomers versus solvent composition of the THF–water mixtures. The inset shows **10** solutions in THF–water mixtures containing different volume fractions of water.

UV-vis absorptions and photoluminescence data of **9–12** and **PDTPDT** in DCM are shown in Fig. 3 and Table S2. Absorption peaks of **9–12** were located at 333, 341, 343, and 344 nm, respectively, with an inconspicuous red shift. It is quite different from **PDTPDT**, which displays a broaden absorption peak at 370 nm. With respect to PL, the emission peak positions of **9–12** and **PDTPDT** present a significant bathochromic shift, which have 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 restriction of intramolecular rotation (Fig. S4). All of these bathochromic-shifted tendencies indicated that the broader planarization of the molecular chain and the conjugated degree change from oligomers to polymers. Intriguingly, the solid state of **10** can emit bright chartreuse light under the UV lamp comparing to the aphotic solution. This unusual phenomenon, aggregation-induced emission (AIE), was first reported by Tang's group,²⁷ but studies on thienyl compounds were less mentioned. To provide further evidence for the phenomenon, the quantum yields (Φ_f) and PL intensities of **10** in THF/ H_2O were conducted. Addition of water content into

the THF/H₂O mixtures intensifies the emission and moves to longer wavelengths (Fig. 3c). Increasing the water content to 70% induced a decrease in Φ_F due to a morphological change, as suggested by Tang.²⁸ Such phenomenon also observed in **9**, **11** and **12**, different Φ_F of **9-12** in dilute DCM identified the restriction of intramolecular rotation as a main cause for the AIE effect (Fig. 3d and Fig. S5-S7). Obviously, **11** and **12** can emit faint light in solution (so-called AIEE) because of the enough crowded structures let alone **PDTPDT** (Fig. S8).

To better illuminate the pronounced fluorescence red shift, cyclic voltammetry (CV) measurements of the oligomers and polymers were carried out. The corresponding data are summarized in Table S3 as well as in Fig. S9. The HOMO and LUMO energy levels of **9** to **PDTPDT** 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 (ΔE_g) of **9** to **PDTPDT** 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 indeed extends from **9** to **PDTPDT**.

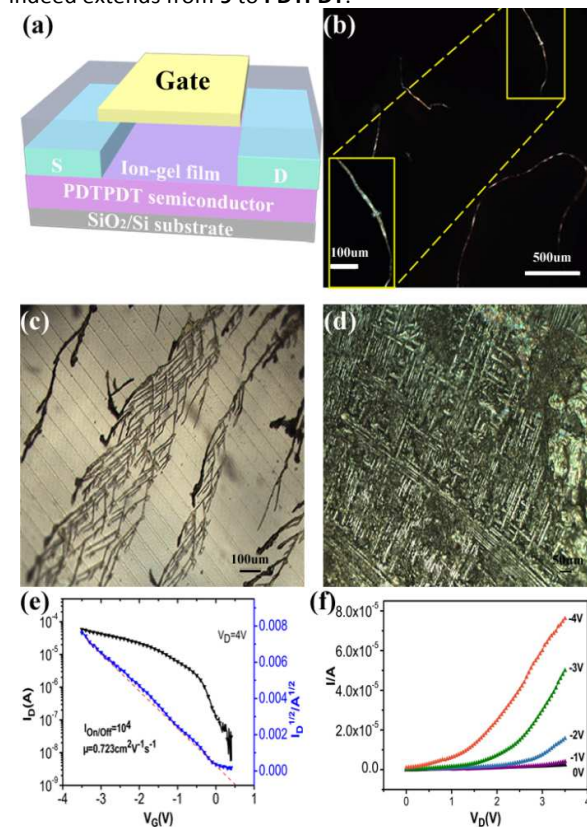


Fig. 4 (a) The geometry of top-gated **PDTPDT** thin-film FETs fabricated using ion gel gate dielectrics. (b) POM image of **PDTPDT** film drop-casted from toluene solutions (1 mg/mL), (c) 2 mg/mL and (d) 4 mg/mL. (e) Transfer and (f) output characteristics of the ion gel gated **PDTPDT** devices ($W = 1000 \mu\text{m}$, $L = 600 \mu\text{m}$) at $V_{DS} = 4\text{V}$.

Thiophene-containing polymers have been extensively studied as active layers in FETs.²⁹⁻³² To investigate the charge transporting characteristics of oligomers and polymers, field effect transistors (FETs) were fabricated. Fascinatingly, FETs

with **10** to **PDTPDT** semiconductors were obtained with ion gel³³ 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 (Electronic Supporting Information for device fabrication details). The surface morphology of films was characterized with polarizing optical microscopy (POM) as shown in Fig. 4b, 4c, 4d. When a dilute solution of **PDTPDT** was cast onto microslides, fiber-like crystals formed (Fig. 4b). However, different morphologies appeared with the increasing concentration of the solution. Either micron-sized dendritic crystals, or sizable networks (Fig. 4c, 4d) are observed, likely the results of the aggregation of several **PDTPDT** chains into cable-like bundles. On the other hand, the distinct diffraction peak at $2\theta = 14.14^\circ$ corresponds to the d spacing value of 6.26 \AA , which is assigned to the interchain spacing between polymer main chains, after placing the drop-cast films 7 days. The other diffraction peaks are also observed in Fig. S10, implying a highly organized packing. The representative transfer and output curves of the **PDTPDT** devices are shown in Fig. 4e and 4f and those of **10-12** are demonstrated in Fig. S11. From the saturation regime of the transfer characteristics, the mobility was calculated according to the linear fitting of $(I_{DS})^{1/2}$ versus V_G curve. The mobility for the best oligomer FET, the device based on **11**, was up to $0.99 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ due to the denser intermolecular packing without bulky insulating layers created by long alkyl chains.³⁶ Octyl chains attached improved the solubility to obtain **PDTPDT** successfully and enable processing from solution. Although with more octyl chains, the mobility of the **PDTPDT** based device was measured as high as $0.723 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an on/off current ratio of 10^4 . The mobility is no significant disparity with the reported ion gel used thin film FET devices, which have the great performance.³⁷

In conclusion, a series of thienyl-oligomers have been successfully designed and synthesized in high yields. Most important of all, we have demonstrated a novel and effective synthetic strategy of **PDTPDT** from the important building block, **PDBPDB**, based on **Polymer 1**. GPC, NMR spectroscopy, UV/vis absorption, photoluminescence, XRD, thermal property and microscopic studies indicated the formation of **PDTPDT**. Meantime, these data changing from oligomers **9-12** to **PDTPDT** verified the effects of extended conjugated length. Subsequently, the FET devices fabricated with the **PDTPDT** possess high performance. Intriguingly, the usefulness of boronate derivatives **5-6** even **PDBPDB** as versatile building blocks, suggesting their tremendous potential in well-designed synthesis.

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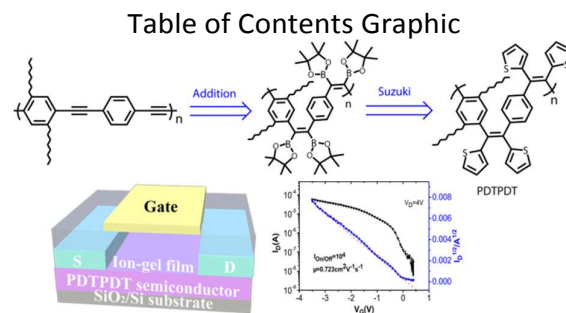
Notes and references

- 1 U. H. Bunz, *Chem. Rev.*, 2000, **100**, 1605-1644.
- 2 A. Duarte, K.-Y. Pu, B. Liu and G. C. Bazan, *Chem. Mater.*, 2011, **23**, 501-515.
- 3 U. H. Bunz, *Macromol Rapid Commun.*, 2009, **30**, 772-805.
- 4 J.-M. Koenen, X. Zhu, Z. Pan, F. Feng, J. Yang and K. S. Schanze, *ACS Macro Lett.*, 2014, **3**, 405-409.
- 5 C. Schmitz, P. Posh, M. Thelakkat, H. W. Schmidt, A. Montali, K. Feldman, P. Smith and C. Weder, *Adv. Funct. Mater.*, 2001, **11**, 41-46.
- 6 P. Samori, I. Sikharulidze, V. Francke, K. Müllen and J. P. Rabe, *Nanotechnol.*, 1999, **10**, 77-80.
- 7 J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864-11873.
- 8 U. H. F. Bunz, K. Seehafer, M. Bender and M. Porz, *Chem. Soc. Rev.*, 2015, **44**, 4322-4336.
- 9 B. Liu, Y. Bao, F. Du, H. Wang, J. Tian and R. Bai, *Chem. Commun.*, 2011, **47**, 1731-1733.
- 10 M. D. Disney, J. Zheng, T. M. Swager and P. H. Seeberger, *J. Am. Chem. Soc.*, 2004, **126**, 13343-13346.
- 11 A. R. B. Marshall, U. H. F., *Macromolecules*, 2001, **34**, 4688-4690.
- 12 C. Huber, F. Bangerter, W. R. Caseri, C. Weder, *J. Am. Chem. Soc.*, 2001, **123**, 3857-3863.
- 13 H.-F. Chow, C.-W. Wan, K.-H. Low and Y.-Y. Yeung, *J. Org. Chem.*, 2001, **66**, 1910-1913.
- 14 J. A. Carrillo, M. J. Ingleson and M. L. Turner, *Macromolecules*, 2015, **48**, 979-986.
- 15 J. Han, Y. Liu and R. Guo, *J. Am. Chem. Soc.*, 2009, **131**, 2060-2061.
- 16 H. C. Brown, M. Srebnik and T. E. Cole, *Organometallics*, 1986, **5**, 2300-2303.
- 17 H. C. Brown, N. G. Bhat and V. Somayaji, *Organometallics*, 1983, **2**, 1311-1316.
- 18 H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1972, **94**, 4370-4371.
- 19 T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11018-11019.
- 20 W. Huang, H. Zhang, J. Ma, M. Chen, H. Zhu and W. Wang, *J. Mater. Chem. C*, 2015, **3**, 6200-6208.
- 21 T. Ishiyama, N. Matsuda, M. Murata and F. Ozawa, *Organometallics*, 1996, **15**, 713-720.
- 22 Y. Miyata, E. Yoshikawa, T. Minari, K. Tsukagoshi and S. Yamaguchi, *J. Mater. Chem.*, 2012, **22**, 7715.
- 23 P. He, Z. Tu, G. Zhao, Y. Zhen, H. Geng, Y. Yi, Z. Wang, H. Zhang, C. Xu, J. Liu, X. Lu, X. Fu, Q. Zhao, X. Zhang, D. Ji, L. Jiang, H. Dong and W. Hu, *Adv. mater.*, 2015, **27**, 825-830.
- 24 G. li, R. Zhu and Y. Yang, *Nat. Photon.*, 2012, **6**, 153-161.
- 25 R. Zhu, C.-Y. Jiang, B. Liu and S. Ramakrishna, *Adv. mater.*, 2009, **21**, 994-1000.
- 26 T. W. Holcombe, C. H. Woo, D. F. J. Kavulak, B. C. Thompson and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2009, **131**, 14160-14161.
- 27 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, B. Z. Tang, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu and D. Zhu, *Chem. Commun.*, 2001, 1740-1741.
- 28 H. Tong, Y. Dong, M. Häußler, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, J. Sun and B. Z. Tang, *Chem. Commun.*, 2006, 1133-1135.
- 29 J. Ohshita, D.-H. Kim, Y. Kunugi and A. Kunai, *Organometallics*, 2005, **24**, 4494-4496.
- 30 K. Takimiya, S. Shinamura, I. Osaka and E. Miyazaki, *Adv. mater.*, 2011, **23**, 4347-4370.
- 31 J. Mei and Z. Bao, *Chem. Mater.*, 2014, **26**, 604-615.
- 32 M. Tang, T. Okamoto and Z. Bao, *J. Am. Chem. Soc.*, 2006, **128**, 16002-16003.
- 33 T. Fujimoto and K. Awaga, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8983-9006.
- 34 S. N. Bhat, R. D. Pietro and H. Sirringhaus, *Chem. Mater.*, 2012, **24**, 4060-4067.
- 35 B. J. Kim, H. Jang, S. K. Lee, B. H. Hong, J. H. Ahn and J. H. Cho, *Nano Lett.*, 2010, **10**, 3464-3466.
- 36 A. Y. Amin, A. Khassanov, K. Reuter, T. Meyer-Friedrichsen and M. Halik, *J. Am. Chem. Soc.*, 2012, **134**, 16548-16550.
- 37 J. H. Cho, J. Lee, Y. Xia, B. Kim, Y. He, M. J. Renn, T. P. Lodge and C. D. Frisbie, *Nat. mater.*, 2008, **7**, 900-906.

COMMUNICATION

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A series of novel boronate esters synthesized by the post-functionalization of poly(phenyleneethynylene)s and phenylene-ethynylene array can provide an effective and versatile platform for analogous compounds.