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Synthesis and photophysical properties of five-membered ring π-conjugated materials based on bisthiazol-2-yl-amine and their metal complexation studies

Junghoon Lee, Jonggi Kim, Gyoungsik Kim, Changduk Yang *

Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, South Korea

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ABSTRACT

Poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**) is prepared by nickel(0) mediated Yamamoto-type coupling. The photoluminescence (PL) spectrum of **PBTA** in THF solution displays pure blue emission with a peak centered at 444 nm without any shoulder peaks and the HOMO and LUMO values for **PBTA** are estimated to be 5.11 and 2.90 eV, respectively. In addition, we have synthesized a novel bisthiazol-2-yl-amine (**BTA**)-cored donor–acceptor (D–A) chromophore system, namely 5-(4-(diphenylamino)phenyl)-*N*-(5-(4-(diphenylamino)phenyl)thiazol-2-yl)-*N*-octylthiazol-2-amine (**2-TPA-BTA**) in which the electron-donating (D) moiety is triphenylamine group and the electron-withdrawing (A) unit is thiazole group. Furthermore, in this report, we present the complexation studies of both the **BTA** and **2-TPA-BTA** chromophores with Cu(II) and Pd(II), respectively. The crystal structures are established by single-crystal X-ray diffraction analysis. These studies not only provide the general photophysical principles of the materials based on **BTA** moiety but also encourage progress toward realizing the full potential of its hybrid metal–organic frameworks.

1. Introduction

A study of organic materials with delocalized π-electrons as electronic semiconductors has blossomed into a mature field over the last six decades.[1] Considerable effort has been made for the design and synthesis of functional π-conjugated oligomers and polymers whose electronic properties can be modulated with external stimuli.[2–9] In this regard, five-membered ring π-conjugated materials have especially attracted attention due to their potential use as components for electronic applications.[10–17] Among them, thiazole containing the electron-withdrawing imine nitrogen in place of the carbon atom at the 3-position of thiophene is an interesting building block for π-conjugated materials because of its attractive properties such as stable *n*-doping and metal complex forming ability.[18–24]

There exists another family of π-conjugated polymers in which p_z orbitals of nitrogen can contribute to the conjugation, such as polyaniline (PANI) and polyazomethines. Such polymers show distinctly different chemistry when compared to other well-known π-conjugated systems, such as polyacetylene, poly-*p*-phenylene, and polythiophene.

These points have attracted our attention to chemically combine the thiazole unit and nitrogen atom in a single architecture so that the synergistic effects between the two can enhance and induce their outstanding properties. Although such a structural chromophore of two thiazole units bridged by a nitrogen atom, namely bisthiazol-2-yl-amine (**BTA**) was prepared in 1956,[25] to the best of our knowledge, the structural properties as well as the metalation have not been evaluated yet.

With the hope of clarifying the detailed properties and the potential applications of **BTA**-based materials, herein we report the synthesis and characterization of a semiconducting polymer, i.e., poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**) as well as a π-conjugated donor–acceptor single molecule (5-(4-(diphenylamino)phenyl)-*N*-(5-(4-(diphenylamino)phenyl)thiazol-2-yl)-*N*-octylthiazol-2-amine, **2-TPA-BTA**) containing electron-donating triphenylamine and electron-accepting thiazole units (see Fig. 1). Besides, features unique to **BTA**-cored metal–organic hybrid materials, illustrating the changed coordination sites and geometries as a function of the different metals, such as Cu(II) and Pd(II), are presented for usage in optical or electronic devices in the future.

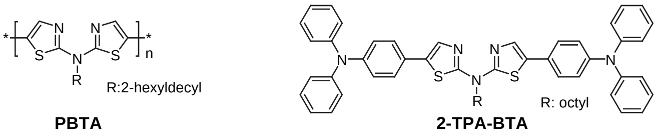

Fig. 1. Molecular structure of **PBTA** and **2-TPA-BTA**.

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* Corresponding author. Tel.: +82 52 217 2920; fax: +82 52 217 2909; e-mail address: yang@unist.ac.kr (C. Yang).

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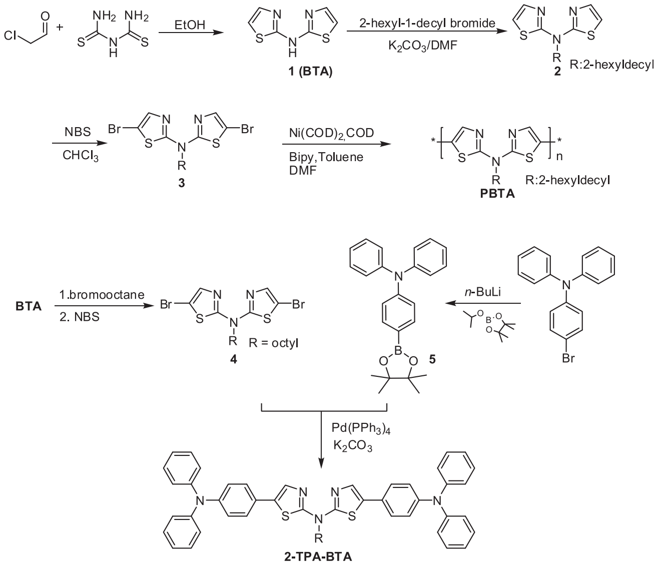
2. Results and discussion

2.1. Poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (PBTA)

The synthesis of material based on bisthiazole (poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine), (**PBTA**)) was carried out as depicted in Scheme 1. Bisthiazol-2-yl-amine (**1**, **BTA**) was synthesized from chloroacetaldehyde and dithiobiuret in 60% isolated yield.[25] N-alkylation of **1** with 2-hexyl-1-decyl bromide generated (2-hexyldecyl)-bisthiazol-2-yl-amine (**2**), which was brominated using NBS to give bis-(5-bromo-thiazol-2-yl)-(2-hexyldecyl)-amine (**3**). Poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**) was prepared by Yamamoto-type polycondensation. **PBTA** has limited solubility in common organic solvents (THF, toluene, chloroform, etc.) due to the rigid nature of bisthiazole units in the main backbone. For the THF-soluble part, GPC analysis of **PBTA** exhibits a M_n value of 5.7×10^3 g/mol with a polydispersity of 2.2 (THF, PS standards).



Scheme 1. Synthetic route to poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**) and 5-(4-(diphenylamino)phenyl)-*N*-(5-(4-(diphenylamino)phenyl)thiazol-2-yl)-*N*-octylthiazol-2-amine (**2-TPA-BTA**).

2.2. BTA-cored push–pull architecture

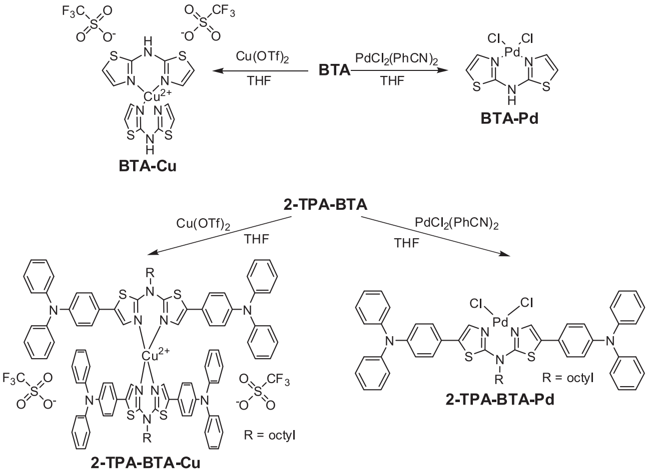
Alternating donor–acceptor chain structures have allowed the optical, redox, and electroluminescent properties to be tuned over a wide range.[26–33] To establish a new conjugated donor–acceptor semiconductor based on **BTA** as the electron acceptor chromophore, a straightforward synthesis toward **BTA**-cored push–pull single skeleton is performed through the selection of triphenylamine units as π-excessive building blocks.

Firstly, **BTA** was alkylated at nitrogen using 1-bromooctane (yield=95%) and subsequently brominated using NBS to give bis-(5-bromo-thiazol-2-yl)-octyl-amine (**4**) as previously mentioned (yield=97%). 4-Bromo-triphenylamine was converted into 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (**5**) by lithiation and subsequent reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The synthesis of 5-(4-(diphenylamino)phenyl)-*N*-(5-(4-(diphenylamino)phenyl)thiazol-2-yl)-*N*-octylthiazol-2-amine (**2-TPA-BTA**) as the target donor–acceptor molecule by using **4** and **5** was successful via Suzuki coupling[34] under Pd$(PPh_3)_4/K_2CO_3$ in isolated overall yield 30% (Scheme 1).

2.3. Complexation studies

Conjugated metallooligomers consisting of metals or metal clusters coordinated to multifunctional organic ligands not only offer unprecedented levels of permanent porosity in the context of crystalline materials but also lie at the forefront of contemporary materials research because their modular nature combines nanoscale porosity with enormous diversity of structure/property.[35] Up to now, tremendous progress has been made toward the development of the conjugated metallooligomers, however novel hybrid metal–organic materials still need to realize their potential as well as intrinsic properties.

BTA-based materials have the potential to bind transition-metal ions, which can be used to tune their electronic, electrochemical, and physical properties. Therefore, the coordination of metal centers directly to the **BTA** unit is undertaken. The reaction of **BTA** with Cu(II) triflate gave a copper complex **BTA–Cu** in THF solution at room temperature (Scheme 2). It was difficult for **BTA–Cu** to be spectroscopically characterized by ^{1}H NMR, ^{13}C NMR or Field Desorption Mass Spectrometry (FD-MS). The NMR spectra of inorganic compounds are often more complicated than simple organics due to additional splitting from NMR active nuclei. It was found that **BTA–Cu** is paramagnetic, which was confirmed by electron paramagnetic resonance (EPR) spectroscopy (see SI). X-ray diffraction can provide the most unambiguous characterization of such complexes. X-ray structural analysis of **BTA–Cu** reveals two **BTA** units complexed to a copper and a distorted tetrahedral geometry around the copper (Fig. 2 top). In further studies on complexation behavior, Pd(II)$Cl_2(PhCN)_2$ was reacted with **BTA** and a orange single crystal was obtained by slow diffusion of ether into a *N*,*N*-dimethylformamide solution of the Pd(II) complex **BTA–Pd** and analyzed by X-ray crystallography. In contrast, the resulting data displays one **BTA** unit coordinated to one palladium and a square-planar geometry around the palladium (the bottom of Fig. 2). On the basis of our metal complex studies, a detailed investigation of various metals complexation on the polymer **PBTA** as well as their conductivity in progress and will reported in a future paper.



Scheme 2. Cu(II) and Pd(II) complexes with **BTA** and **2-TPA-BTA**, respectively.

2.4. Photophysical properties

The UV–vis absorption and photoluminescence (PL) spectra of **PBTA** in dilute THF solution are shown in Fig. 3.The absorption of **PBTA** has a distinct absorption band with a maximum at 390 nm

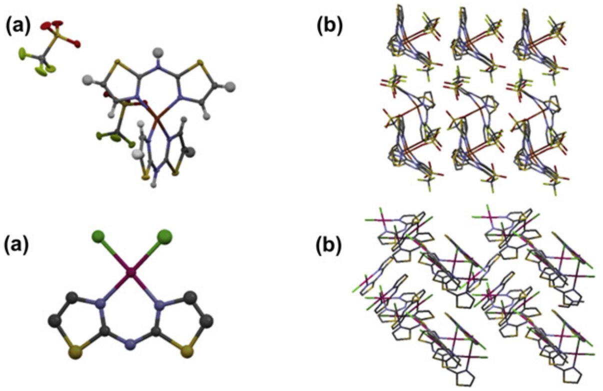


Fig. 2. X-ray crystal structure of (top) **BTA–Cu** and (bottom) **BTA–Pd**. (a) top view (it is colorized by elements) (b) side view and (c) packing projection. It is colorized by elements, respectively. The solvents are omitted for clarity.

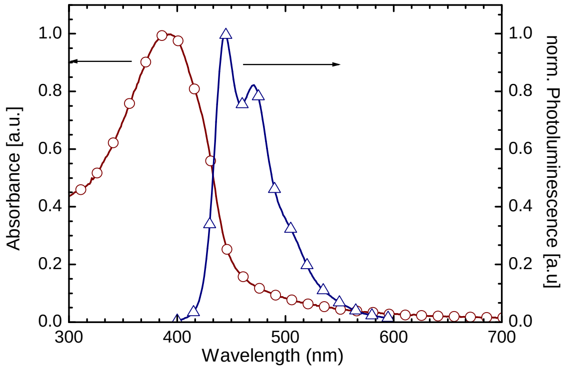


Fig. 3. UV–vis absorption and photoluminescence (λ_{exc}=370 nm) of **PBTA** in THF solution.

without any vibronic features. The PL spectrum of **PBTA** in solution shows a blue emission region with a maximum at 444 nm and a shoulder peak at 471 nm. The position of the emission maximum is very close to that of a semiladder-type poly(pentaphenylene) (445 nm),[36,37] which is one of the best candidates as blue emitters in PLEDs.

Cyclic voltammetry (CV) against Ag/Ag$^+$ was employed to investigate the redox behavior of **PBTA**.[38] This film deposited on a platinum plate electrode was scanned both positively and negatively in 0.1 M anhydrous acetonitrile solution of tetrabutylammonium perchlorate (Bu_4NClO_4), using a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode (see Supplementary data). The oxidation onset was determined to be 0.71 V and estimating the band gap from the absorption onset, the HOMO and LUMO energy levels of **PBTA** are found to be −5.11 and −2.90 eV, respectively.

The optical properties of the metal free compound **BTA** and metal complexes (**BTA–Cu** and **BTA–Pd**) were investigated in dimethylsulfoxide (DMSO) solution by UV–vis spectroscopy. As depicted in Fig. 4, the absorption bands of **BTA** are broad with a maximum centered at 339 nm, which can be clearly attributed to a $\pi-\pi^*$ transition. In contrast, both the complexes of **BTA–Cu** and **BTA–Pd** reveal an absorption peak centered at 352 nm and shoulder peaks at 362 and 372 nm, respectively. The downhill shift in UV–vis spectra of metalated derivatives (**BTA–Cu** and **BTA–Pd**) is attributed to more extended conjugation systems in the metal complex due to their increased planarity.

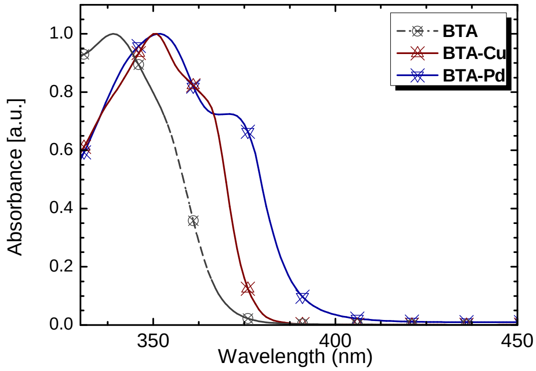


Fig. 4. UV–vis absorption spectra of **BTA**, **BTA–Cu**, **BTA–Pd**, **2-TPA-BTA**, **2-TPA-BTA–Cu**, and **2-TPA-BTA–Pd** in DMSO solution.

3. Conclusion

In efforts to develop five-member heterocyclic polymer based on bisthiazole building block, poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**) has been prepared by nickel(0) mediated Yamamoto-type coupling. **PBTA** shows a pure blue emission maximum at 444 nm and its HOMO and LUMO levels are estimated to be 5.11 and 2.90 eV, respectively. The bisthiazol-2-yl-amine (**BTA**) unit has coordination sites to bind metals, which allows us to study the properties of the metal–organic hybrid materials and compare them with the parent materials. Metal complexes with (Cu(II) and Pd(II)) are synthesized, which exhibits paramagnetic behavior. The crystal structure of the Cu(II) complex **BTA–Cu** with **BTA** comprises **BTA** and copper in a 2:1 ratio with tetrahedral geometry around the copper while the Pd(II) complex **BTA–Pd** displays a 1:1 ratio with square-planar geometry. Besides, from the interesting donor–acceptor concept, 5-(4-(diphenylamino)phenyl)-*N*-(5-(4-(diphenylamino) phenyl)thiazol-2-yl)-*N*-octylthiazol-2-amine (**2-TPA-BTA**) comprising thiazole representing *n*-type unit and triphenylamine representing *p*-type unit is prepared. This work marks the first attempt has been made to use the conjugated metal hybrid strategy to build conjugated material containing **BTA** units. These studies provide a basis for understanding the photophysical properties of metal-organic based **BTA**, which in turn will guide the design of new materials based on **BTA** that find application as the active materials in electronic and photonic devices in the future.

4. Experimental section

4.1. General

All solvents were purified and freshly distilled prior to use according to literature procedures. Commercially available materials were used as received unless noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VNRS 600 MHz (Varian USA) spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. UV–vis-NIR spectra were taken on Cary 5000 (Varian USA) spectrophotometer. Photoluminescence spectra were recorded on a Cary Eclipse (Varian USA), using a xenon arc lamp as excitation source and a photomultiplier tube as detector system. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with Agilent 1200 HPLC Chemstation using a series of mono disperse polystyrene as standards in THF (HPLC grade) at 308 K. Mass spectrometry and elemental analysis were performed by HCT Basic System (Bruker, Germany) and Flash 200 (Thermo Scientific, Netherlands), respectively. Cyclic voltammetry (CV) measurements were performed on Solartron SI 1287 with a three-electrode cell in a 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) solution in acetonitrile at a scan rate of 50 mV/s at room temperature under argon. A silver wire, a platinum wire, and a platinum plate were used as the reference electrode, counter electrode, and working electrode, respectively.

*4.1.1. (2-Hexyldecyl)-bisthiazol-2-yl-amine (**2**).* To a solution of **1** (1.0 g, 5.46 mmol) in 20 mL of *N*,*N*-dimethylformamide was added K_2CO_3 (1.13 g, 8.17 mmol, 1.5 equiv) and 2-hexyl-1-decyl bromide (2.0 g, 6.54 mmol, 1.2 equiv) and refluxed at 120 °C overnight. The cooled mixture was extracted with diethyl ether, washed with brine, and then dried over $MgSO_4$. The crude product was chromatographed on silica using 0–10% ethylacetate in hexane as eluent. Isolated yield=0.75 g (34%) as a yellow liquid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44 (d, J=3.60 Hz, 2H), 6.85 (d, J=3.60 Hz, 2H), 4.27 (d, J=7.59 Hz, 2H), 2.22–2.10 (m, 1H), 1.31–1.20 (m, 24H), 0.87 (t, J=6.82 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 163.61, 137.76, 110.96, 56.55, 35.63, 31.63, 31.23, 29.69, 29.36, 29.04, 26.14, 22.42, 13.87. MS (ESI mode)=407.70 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{22}H_{37}N_3S_2$: C, 64.81; H, 9.15; N, 10.31; S, 15.73; found: C, 65.03; H, 9.29; N, 10.14; S, 15.58.

*4.1.2. Bis-(5-bromo-thiazol-2-yl)-(2-hexyldecyl)-amine (**3**).* A mixture of **2** (0.637 g, 1.56 mmol) *N*-bromosuccinimide (0.596, 3.354 mmol, 2.15 equiv) and chloroform (15 mL) was stirred at room temperature for 24 h under argon. The mixture was then extracted into ether, washed with brine, and dried. The crude product was chromatographed on silica using 0–10% ethylacetate in hexane as eluent. Isolated yield=0.58 g (65%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.32 (s, 2H), 4.11 (d, J=7.65 Hz, 2H), 2.20–2.11 (m, 1H), 1.32–1.21 (m, 24H), 0.90 (t, J=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 162.25, 138.20, 100.16, 55.49, 35.40, 31.43, 30.97, 29.44, 29.02, 28.83, 25.89, 22.23, 13.68. MS (ESI mode)=565.10 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{22}H_{35}Br_2N_3S_2$: C, 46.73; H, 6.24; Br, 28.26; N, 7.43; S, 11.34; found: C, 46.87; H, 6.31; N, 7.41; S, 11.14.

*4.1.3. Poly(5,5′-(2-hexyldecyl)-bisthiazol-2-yl-amine) (**PBTA**).* Bis(cyclooctadiene)nickel (589.0 mg, 2.17 mmol, 2.4 equiv), cyclooctadiene (266.0 mL, 2.17 mmol, 2.4 equiv), and 2,2′-bipyridine (335 mg, 2.17 mmol, 2.4 equiv) were dissolved in anhydrous toluene (7 mL) and anhydrous *N*,*N*-dimethylformamide (7 mL) in a Schlenk flask in a glovebox. The mixture was heated at 60 °C with stirring under argon for 20 min to generate the catalyst, and then a solution of the dibromide **3** (512 mg, 0.905 mmol) in anhydrous toluene (10 mL) was added. The reaction was heated 75 °C for 3 days. Then a mixture of toluene (4 mL) and bromobenzene (0.10 mL) was added and the mixture was heated at 75 °C for an additional 12 h. This was then poured into a mixture of methanol and concentrated NH_4OH (1:1, 300 mL) and stirred for 4 h and filtered. The precipitated solid was washed with methanol (200 mL) and subjected Soxhlet extraction for 2 days in acetone. Isolated yield of **PBTA**=230 mg (63%). GPC analysis M_n=5.71×10^3 g/mol, M_w=6.02×10^3 g/mol, and D=2.22 (against PS standard). Only soluble portion was measured by GPC. Elemental analysis: calculated for $C_{22}H_{35}N_3S_2$: C, 65.14; H, 8.70; N, 10.36; S, 15.81; found: 65.05; H, 8.99; N, 10.14; S, 15.58.

4.1.4. Octyl-bisthiazol-2-yl-amine. To a mixture solution of **1** (4.0 g, 21.85 mmol) and NaH (60% in oil, 1.2 equiv) in 25 mL of *N*,*N*-dimethylformamide at room temperature was added 1-octylbromide (1.2 equiv) dropwise under argon. This solution was stirred at room temperature for 12 h. The mixture was then extracted into ether, washed with brine, and dried. The crude product was chromatographed on silica gel eluting with 0–10% ethylacetate in hexane. Isolated yield=3.12 g (48.4%, first fraction) as yellow solid and 3.01 (46.5% second fraction) as a yellow liquid. The first fraction was used for the next step. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (d, J=3.62 Hz, 2H), 6.86 (d, J=3.63 Hz, 2H), 4.26 (t, J=7.82 Hz, 2H), 1.87 (td, J=15.56, 7.65, 7.65 Hz, 2H), 1.51–1.16 (m, 10H), 0.87 (t, J=6.70, 6.70 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 162.80, 137.92, 110.91, 52.70, 31.52, 28.99, 28.93, 26.55, 22.37, 13.83. MS (ESI mode)=295.30 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{14}H_{21}N_3S_2$: C, 56.91; H, 7.16; N, 14.22; S, 21.70; found: C, 56.78; H, 7.29; N, 14.34; S, 21.98.

*4.1.5. Bis-(5-bromo-thiazol-2-yl)-octyl-amine (**4**).* A mixture of octyl-bisthiazol-2-yl-amine (2.5 g, 8.46 mmol), *N*-bromosuccinimide (3.3, 18.37 mmol, 2.2 equiv), and chloroform (25 mL) was stirred at room temperature for 24 h under argon. The mixture was then extracted into ether, washed with brine, and dried. The crude product was chromatographed on silica using 0–10% ethylacetate in hexane as eluent. Isolated yield=3.7 g (97%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.34 (s, 2H), 4.21–4.07 (m, 2H), 1.81 (td, J=15.43, 7.69, 7.69 Hz, 2H), 1.51–1.17 (m, 10H), 0.88 (t, J=6.72, 6.72 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 161.69, 138.37, 100.45, 51.90, 31.51, 28.94, 28.90, 26.48, 22.37, 13.85. MS (ESI mode): 452.90 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{13}H_{18}Br_2N_3S_2$: C, 37.10; H, 4.23; Br, 35.26; N, 9.27; S, 14.15; found: C, 36.87; H, 4.51; N, 9.41; S, 14.27.

*4.1.6. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (**5**).* To (4-bromo-phenyl)-diphenyl-amine (2.0 g, 6.17 mmol) in a 250 mL Schlenk flask, 30 mL of anhydrous THF is added and cooled to −78 °C in an acetone/dry ice bath. To this, 5.78 mL of 1.6 M *n*-butyllithium (1.5 equiv) is added slowly and stirred for 30 min. Then 2.14 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.7 equiv) is added and slowly allowed to warm to room temperature. The reaction is stirred overnight and then quenched with saturated salt, the product is then extracted into ether, washed with brine, and dried. The crude product was chromatographed on silica gel eluted with 0–10% ethylacetate in hexane. Isolated yield=91.6% as a yellow oily liquid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.75 (d, J=7.93 Hz, 2H), 7.37–7.26 (m, 5H), 7.18 (d, J=7.20 Hz, 4H), 7.11 (d, J=7.31 Hz, 3H), 1.40 (s, 12H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 150.38, 147.18, 135.67, 129.09, 128.98, 124.76, 123.95, 123.15, 122.45, 121.59, 83.31, 24.66. MS (ESI mode): 371.20 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{24}H_{26}BNO_2$: C, 77.64; H, 7.06; B, 2.91; N, 3.77; O, 8.62; found: C, 77.89; H, 7.25; N, 3.75.

*4.1.7. 5-(4-(Diphenylamino)phenyl)-N-(5-(4-(diphenylamino)phenyl)thiazol-2-yl)-N-octylthiazol-2-amine (2-**TPA**-**BTA**).* The boronic ester **5** (0.81 g, 2.18 mmol), **4** (0.4 g, 0.88 mmol) were dissolved in THF (20 mL) in a 100 mL Schlenk flask. To this solution were added aqueous 2 M K_2CO_3 solution (10 mL). The solution was purged with argon for 20 min, and the tetrakis(triphenylphosphine)palladium (61 mg, 0.06 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and after 2 days was worked up. The cooled mixture was extracted with diethyl ether, and the extract was washed with brine and then dried over $MgSO_4$. The crude product so obtained was purified by chromatography on silica with 0–30% dichloromethane in hexane as eluent and more purified by recrystallization from THF in EtOH to afford 0.23 g (33.4%) of the title compound as yellow powders. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.49 (s, 2H), 7.31 (d, J=8.60 Hz, 4H), 7.18 (dd, J=10.36, 5.24 Hz, 8H), 7.10–6.84 (m, 16H), 4.49–4.04 (m, 2H), 2.04–1.65 (m, 2H), 1.51–1.20 (m, J=54.59 Hz, 10H), 0.80 (t, J=6.47, 6.47 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 160.69, 147.39, 147.27, 131.19, 129.31, 126.79, 125.60, 124.50, 123.71, 123.15, 31.77, 29.27, 29.18, 26.93, 26.80, 22.61, 14.08. MS (ESI mode): 781.30 ($M^{+\bullet}$). Elemental analysis: calculated for $C_{50}H_{47}N_5S_2$: C, 76.79; H, 6.06; N, 8.95; S, 8.20; found: C, 76.99; H, 6.25; N, 8.15; S, 8.37.

*4.1.8. Cu(II) complex of **BTA** (**BTA**–**Cu**).* To a solution of **BTA** (0.5 g, 2.7 mmol) in THF (30 mL) was added copper(II) triflate (1.0 equiv) solution in THF (30 mL) and stirred for 15 h at room temperature.

Precipitated product was filtered, washed with THF, and dried. Isolated yield=20.1% as a purple solid. The product was dissolved in *N*,*N*-dimethylformamide, and diethyl ether was diffused into the solution, forming a mixture of purple crystals precipitate.

*4.1.9. Pd(II) complex of **BTA** (**BTA**–**Pd**).* To a solution of **BTA** (0.5 g, 2.7 mmol) in THF (30 mL) was added dichlorobis (benzonitrile) palladium(II) (1.0 equiv) solution in THF (30 mL), and stirred for 15 h at room temperature. Precipitated product was filtered, washed with THF, and dried. Isolated yield=0.84 g (85.1%) as an orange solid. The product was dissolved in *N*,*N*-dimethylformamide, and diethyl ether was diffused into the solution, forming a mixture of orange crystals precipitate.

*4.1.10. Cu(II) complex of 2-**TPA**-**BTA** (2-**TPA**-**BTA**–**Cu**).* To a solution of **2**-**TPA**-**BTA** (50 mg, 0.063 mmol) in THF (5 mL) was added copper (II) triflate (1.2 equiv) solution in THF (10 mL), and stirred for 15 h at room temperature. The solvent was evaporated and then washed with methanol. The crude product was filtered, washed with methanol again, and then purified by recrystallization from *N*,*N*-dimethylformamide in ether to afford 15 mg (12.6%) of title compound as greenish powders.

*4.1.11. Pd(II) complex of 2-**TPA**-**BTA** (2-**TPA**-**BTA**–**Pd**).* To a solution of **2**-**TPA**-**BTA** (50 mg, 0.063 mmol) in THF (5 mL) was added dichlorobis (benzonitrile) palladium(II) (1.5 equiv) solution in THF (10 mL), and stirred for 15 h at room temperature. The solvent was evaporated and then washed with acetone. The crude product was filtered, washed with acetone again, and then purified by recrystallization from *N*,*N*-dimethylformamide in ether to afford 30 mg (49.5%) of title compound as orange powders.

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Supplementary data

^{1}H and ^{13}C NMR spectra for all new compounds and cyclic voltammogram of **PBTA** and ESR of **BTA**–**Cu**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.09.087.

References and notes

1. Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2575–2580.
2. Yang, C.; Scheiber, H.; List, E. J. W.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5213–5221.
3. Yang, C.; Jacob, J.; Müllen, K. *Macromol. Chem. Phys.* **2006**, *207*, 1107–1115.
4. Yang, C.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5696–5704.
5. Sudeep, P. K.; James, P. V.; Thomas, K. G.; Kamat, P. V. *J. Phys. Chem. A* **2006**, *110*, 5642–5649.
6. James, P. V.; Sudeep, P. K.; Suresh, C. H.; Thomas, K. G. *J. Phys. Chem. A* **2006**, *110*, 4329–4337.
7. Lu, L. D.; Jenekhe, S. A. *Macromolecules* **2001**, *34*, 6249–6254.
8. Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030–1034.
9. Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.
10. Yang, C.; Lee, J. K.; Heeger, A. J.; Wudl, F. *J. Mater. Chem.* **2009**, *19*, 5416–5423.
11. Yang, C.; Cho, S.; Chiechi, R. C.; Walker, W.; Coates, N. E.; Moses, D.; Heeger, A. J.; Wudl, F. *J. Am. Chem. Soc.* **2008**, *130*, 16524–16526.
12. Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986–7993.
13. Nurulla, I.; Tanimoto, A.; Shiraishi, K.; Sasaki, S.; Yamamoto, T. *Polymer* **2002**, *43*, 1287–1293.
14. Monkman, A. P.; Palsson, L. O.; Higgins, R. W. T.; Wang, C. S.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Am. Chem. Soc.* **2002**, *124*, 6049–6055.
15. Wang, C. S.; Kilitziraki, M.; MacBride, J. A. H.; Bryce, M. R.; Horsburgh, L. E.; Sheridan, A. K.; Monkman, A. P.; Samuel, I. D. W. *Adv. Mater.* **2000**, *12*, 217–222.
16. Politis, J. K.; Curtis, M. D.; Gonzalez, L.; Martin, D. C.; He, Y.; Kanicki, J. *Chem. Mater.* **1998**, *10*, 1713–1719.
17. Epstein, A. J.; Blatchford, J. W.; Wang, Y. Z.; Jessen, S. W.; Gebler, D. D.; Lin, L. B.; Gustafson, T. L.; Wang, H. L.; Park, Y. W.; Swager, T. M.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 253–261.
18. Toba, M.; Nakashima, T.; Kawai, T. *Macromolecules* **2009**, *42*, 8068–8075.
19. Radhakrishnan, S.; Somanathan, N. *J. Mater. Chem.* **2006**, *16*, 2990–3000.
20. Lee, J.; Jung, B. J.; Lee, S. K.; Lee, J. I.; Cho, H. J.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1845–1857.
21. Yamamoto, T.; Uemura, T.; Tanimoto, A.; Sasaki, S. *Macromolecules* **2003**, *36*, 1047–1053.
22. Wolf, M. O.; Wrighton, M. S. *Chem. Mater.* **1994**, *6*, 1526–1533.
23. Jenkins, I. H.; Pickup, P. G. *Macromolecules* **1993**, *26*, 4450–4456.
24. Catellani, M.; Destri, S.; Porzio, W.; Themans, B.; Bredas, J. L. *Synth. Met.* **1988**, *26*, 259–265.
25. Beyer, H.; Berg, G. *Chem. Ber.* **1956**, *89*, 1602–1608.
26. Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806–6808.
27. Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633–640.
28. Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895–905.
29. Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579–589.
30. Jenekhe, S. A.; Zhang, X. J.; Chen, X. L.; Choong, V. E.; Gao, Y. L.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409–412.
31. Tarkka, R. M.; Zhang, X. J.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 9438–9439.
32. Zhang, X. J.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069–2082.
33. Zhang, X. J.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422–7429.
34. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
35. Holliday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, 23–36.
36. Jacob, J.; Sax, S.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *Macromolecules* **2005**, *38*, 9933–9938.
37. Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987–6995.
38. Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453–2455.