Linear extension of bithiophene compounds by the combination of C–N covalent bond cross-coupling and N–Ag coordinative bond formation†

Li Wang,a,b Tao Tao,a Shu-Jun Fu,a Cheng Wang,a Wei Huang*a and Xiao-Zeng Youa

Received 4th October 2010, Accepted 16th November 2010
DOI: 10.1039/c0ce00689k

Three one-dimensional Ag/imidazole/thiophene coordination polymers 1–3 bearing the same linear imidazole-terminated bithiophene linker but different counterions have been prepared by the first combination of carbon–nitrogen covalent bond cross-coupling and nitrogen–silver coordinative bond formation, in which I exhibits extraordinarily enhanced solid-state fluorescence and conductance because of its more condensed packed structure.

Investigation on polythiophenes has attracted a lot of interests in the past decades because of their fascinating potential applications on organic and polymeric semiconducting materials and optoelectronic devices in nanometre scale.1–4 One of the central issues on these compounds is the study of oligothiophenes and their derivatives because the molecular structures of oligothiophenes can be finely tuned such as size, symmetry, conformation, dihedral angle between adjacent aromatic heterocycles, solubility and reaction activity by introducing different alkyl substituted groups in the thiophene backbone.5–8 In particular, syntheses and properties of novel π-conjugated copolymers composed of different electron-donating thiophene units and electron-attracting N-containing heterocycles have been the subject of many recent papers.9–11 Transition-metal-catalyzed carbon–carbon (C–C) bond cross-coupling reactions have been proven to be effective methods to attain a linear extension of oligothiophenes.12 In our previous studies, a series of oligothiophenes with specific molecular lengths have been reported and they are used to fabricate photoresponsive semiconducting nano-composite films and nanodevices.13 However, transition-metal-catalyzed carbon–nitrogen (C–N) cross-coupling reactions are less explored in the case of extending the delocalized π-systems of oligothiophenes by contrast.

On the other hand, coordinative bond formation is another powerful tool to extend the oligothiophene molecules having metal-binding sites at both ends. In view of the fascinating properties of polymeric silver(i) complexes originated from the unique coordination geometry and d10 electronic configuration of silver(i) ion as well as versatile Ag…Ag, Ag…π, and Ag…S interactions facilitating the charge delocalization between molecules,13 we focus herein on the combination of C–N covalent bond cross-coupling reaction to prepare a new ligand 5,5′-di(1H-imidazol-1-yl)-2,2′-bithiophene (L) by using Ullmann condensation methods14 and nitrogen–silver (N–Ag) coordinative bond formation to produce three novel Ag/thiophene/imidazole coordination polymers, i.e. [Ag(L)NO3]n (1), [Ag(L)ClO4]n (2) and [Ag(L)(CF3COO)]n (3).† L is a molecule bearing a mixture of electron donors and acceptors, which not only retains the advantages of oligothiophenes but also possesses nitrogen donors (imidazole units) in terms of coordination chemistry. Due to the use of dissimilar counterions (NO3–, ClO4– or CF3COO–) (Scheme 1), three Ag/imidazole/thiophene coordination polymers 1–3 exhibit different coordinating and packing fashions, in which I shows extraordinarily enhanced solid-state fluorescence and conductance.

X-Ray structural analyses of L and Ag/imidazole/thiophene complexes 1–3 reveal that the four five-membered heterocycles of 5,5′-di(1H-imidazol-1-yl)-2,2′-bithiophene molecule adopt the trans/trans/trans conformation in L, 1 and 2, whereas the cis/trans/cis conformation is observed in 3 with different dihedral angles between neighboring aromatic rings (Fig. 1).‡ In addition, dissimilar coordination geometry of Ag centers is observed. In 1, the Ag center exhibits a four-coordinate distorted tetrahedron comprised of a pair of N atoms from two L as well as two chelating O atoms from one bidentate nitrate anion with longer Ag–O bond lengths of 2.745(8) Å. In 2 and 3, the Ag centers show three-coordinated T-shaped coordination geometry with two L ligands and one O atom of the perchlorate anion with weak coordination bond of 2.843(6) Å in 2, and one O atom of the trifluoroacetate anion with the Ag1···OC2(2)2 – x, 1 – y, – z] bond length of 2.738(9) Å in 3. The N–Ag–N bond angles are 152.1(2), 159.1(2)° and 170.0(1)° in 1–3, respectively.

As shown in Fig. 2, ligand L in 1–3 serves as a μ2-bridge linking adjacent Ag centers to form one-dimensional (1D) chains along the

† Electronic supplementary information (ESI) available: Tables for selected bond lengths and angles, hydrogen bonding interactions, additional packing diagrams, and simulative and experimental PXRD graphs of L and 1–3. CCDC reference numbers 792210–792213. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00689k

---

**Scheme 1** Schematic illustration for the preparation of L and silver(i) complexes 1–3.
of imidazole carbon atoms down the $b$ axis forming eight-membered hydrogen-bonding rings. Furthermore, they are connected by interpolymeric $\text{Ag} \cdots \text{Ag}$ and face-to-face $\pi-\pi$ stacking interactions between all neighboring aromatic rings. It is noted that the interchain $\text{Ag} \cdots \text{Ag}$ and $\pi-\pi$ centroid–centroid separations are all the same as $3.817(6)$ Å, forming a condensed packed 3D framework. In contrast, novel alternating and offset $\pi-\pi$ donor-acceptor (D–A) stacking interactions between electron-attracting imidazole and electron-donating thiophene rings of adjacent 1D undulating chains are found in 2, being the centroid–centroid separations of $3.596(5)$ and $3.812(5)$ Å, respectively. There are strong $\text{Ag} \cdots \pi$ stacking interactions between the silver(i) ions and the thiophene rings of ligand L with the Ag$i$–centroid contacts of $3.324(5)$ and $3.747(5)$ Å.

In the crystal packing of 1D ladder-like chain 3, multiple $\pi-\pi$ stacking, $\text{Ag} \cdots \text{Ag}$ and $\text{Ag} \cdots \text{S}$ interactions are found. As shown in Fig. 2, intraladder $\text{Ag} \cdots \text{Ag}$ interactions of $3.008(5)$ Å as well as face-to-face $\pi-\pi$ stacking interactions of $3.672(6)$ Å between imidazole rings of adjacent L ligands are observed, while interladder $\text{Ag} \cdots \text{S}$ interactions of $3.245(2)$ Å as well as offset $\pi-\pi$ stacking interactions between imidazole rings of neighboring L ligands with the centroid–centroid separation of $3.612(6)$ Å can be seen. Moreover, weak C–H–O contacts are observed to further stabilize the polymeric structures of 2 and 3.

The pure phase of compounds L and 1–3 is confirmed by powder X-ray diffraction (PXRD) patterns (Fig. S5–S8, ESI†). In comparison with L, 2 and 3, 1 exhibits extraordinarily enhanced solid-state fluorescence at 470 nm (Fig. SI9, ESI†) which could be contributed to the most rigid polymeric structure fixed by N–Ag coordinative bonds, condensed face-to-face $\pi-\pi$ layer packing and $\text{Ag} \cdots \text{Ag}$ interactions, and strong hydrogen bonds down the $c, a$ and $b$ axes, respectively. On considering that the solid-state conductance of semiconducting compounds strongly relies on the packing modes of semiconducting molecules, the solid-state resistivity of condensed plates of L and 1 with the thickness of 0.08–0.1 cm has been determined for comparison. A thin layer of gold was coated on condensed plates via a steelless mask with $1 \times 3$ mm$^2$ gap area, and the $I$−$V$ curves were recorded between the gold pair of electrodes by means of a Lake Shore CRX-4K four-probe system. Linear fitting of the $I$−$V$ curves gave an average resistivity of $2.5 \times 10^6$ Ω m for L, while a control experiment gave the average resistivity of $9.3 \times 10^{12}$ Ω m for L showing $2.7 \times 10^7$ times enhancement of solid-state conductance.

In summary, the electron-attracting imidazole ring has been firstly introduced to the electron-donating thiophene ring to form a new linear imidazole-terminated bithiophene A–D–D–A ligand (L) via a transition-metal-catalyzed C–N covalent bond cross-coupling reaction. Ligand L is further linearly extended to three 1D Ag$i$/imidazole/thiophene semiconducting coordination polymers (1–3) with different silver(i) salts by N–Ag coordinative bond formation, where dissimilar molecular conformation of the L ligand, coordination modes for the central Ag$i$ ions and packing fashions for the 1D chains are observed. Compared with ligand L, compound 1 exhibits extraordinarily enhanced solid-state fluorescence and conductance because of the presence of strong hydrogen-bonding connection along the $b$ axis and condensed Ag$i$–Ag and face-to-face $\pi-\pi$ layer packing of contiguous 1D polymeric chains down the $a$ axis.

We acknowledge the Major State Basic Research Development Program (no. 2011CB933300, 2007CB925101 and 2011CB808704), NSFC (no. 20871065 and 20721002), and the Jiangsu Province project (no. BK2009226).

---

**Fig. 1** ORTEP drawing (30% ellipsoid probability) of the molecular structures of L, 1, 2 and 3. Hydrogen atoms are omitted for clarity.

**Fig. 2** Perspective view of different 1D Ag$i$/thiophene/imidazole coordination polymers of 1 (top), 2 (middle) and 3 (bottom), together with the hydrogen bonds, Ag$i$–Ag, Ag$i$–C, Ag$i$–S and $\pi-\pi$ stacking interactions.
Diffraction determination were grown from a solution of CHCl₃ by slow evaporation in air at room temperature. Yield: 77%. Anal. Calcd for C₁₄H₁₀AgClN₄O₄S₂: C, 33.25; H, 1.99; N, 14.89%. FT-IR (KBr, ν/cm⁻¹): 3420 (b), 1183 (s), 1177 (m), 1067 (s), 1010 (s), 932 (s), 801 (s), 781 (s), and 724 (s). UV-Vis (CH₃OH) λmax (nm): 334 and 246 nm.

The residual electron density, 1.07/e Å⁻³, was calculated to be 0.64 e Å⁻³.


