

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

Li Wang,^{ab} Tao Tao,^a Shu-Jun Fu,^a Cheng Wang,^a Wei Huang^{*a} and Xiao-Zeng You^a

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Three one-dimensional Ag^I/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 1 exhibits extraordinarily enhanced solid-state fluorescence and conductance because of its more condensely 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.^{1–5} 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.^{6–8} 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}

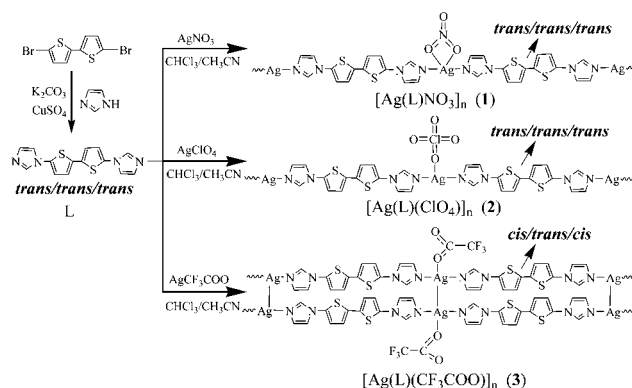
Transition-metal-catalyzed carbon–carbon (C–C) bond cross-coupling reactions have been proven to be effective methods to attain a linear extension of oligothiophenes.¹² In our previous studies, a series of oligothiophenes with specific molecular lengths have been reported and they are used to fabricate photoresponsive semiconducting nanocomposite films and nanodevices.⁸ 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^I⋯Ag, Ag^I⋯ π , and Ag^I⋯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(1*H*-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^I/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^I/imidazole/thiophene coordination polymers 1–3 exhibit different coordinating and packing fashions, in which 1 shows extraordinarily enhanced solid-state fluorescence and conductance.

X-Ray structural analyses of L and Ag^I/imidazole/thiophene complexes 1–3 reveal that the four five-membered heterocycles of 5,5'-di(1*H*-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^I centers is observed. In 1, the Ag^I 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^I 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 Ag(1)⋯O(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 μ_2 -bridge linking adjacent Ag^I centers to form one-dimensional (1D) chains along the



Scheme 1 Schematic illustration for the preparation of L and silver(I) complexes 1–3.

^aState Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P.R. China. E-mail: whuang@nju.edu.cn; Fax: +86 25 8331 4502; Tel: +86 25 8368 6526

^bSchool of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, P.R. China

† 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

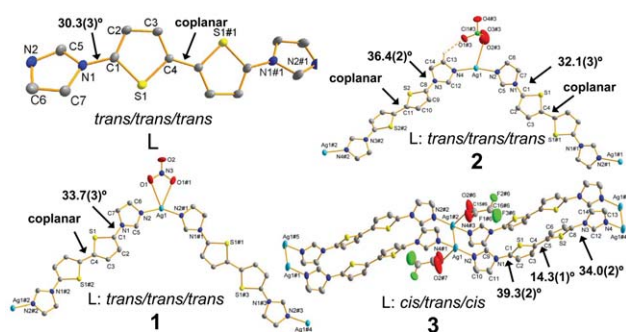


Fig. 1 ORTEP drawing (30% ellipsoid probability) of the molecular structures of L, **1**, **2** and **3**. Hydrogen atoms are omitted for clarity.

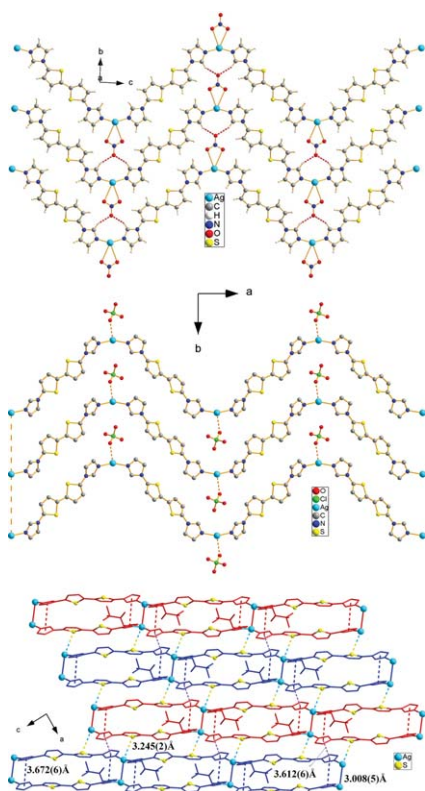


Fig. 2 Perspective view of different 1D Ag⁺/thiophene/imidazole coordination polymers of **1** (top), **2** (middle) and **3** (bottom), together with the hydrogen bonds, Ag⁺⋯Ag, Ag⁺⋯π, Ag⁺⋯S and π–π stacking interactions.

crystallographic *c* or *a* axis in **1** or **2**. However, in the case of **3**, another type of 1D dimeric ladder-like chain is constituted with the help of intrachain π–π stacking and Ag⁺⋯Ag interactions. The separation between the centroids of adjacent electron-attracting imidazole rings is 3.672(6) Å and that between the Ag⁺ centers is 3.008(5) Å.

Three 1D coordination polymers of **1–3** are further extended into different supramolecular networks by means of interchain C–H⋯O hydrogen-bonding, Ag⁺⋯Ag, Ag⁺⋯π, Ag⁺⋯S, and π–π stacking interactions (Fig. S1–S4, ESI[†]). In **1**, the wave-like 1D chains are linked by C–H⋯O hydrogen bonds between the oxygen atom of coordinated nitrate anions and the two contiguous hydrogen atoms

of imidazole carbon atoms down the *b* axis forming eight-membered hydrogen-bonding rings. Furthermore, they are connected by interpolymeric Ag⁺⋯Ag and face-to-face π–π stacking interactions between all neighboring aromatic rings. It is noted that the interchain Ag⁺⋯Ag and π–π centroid–centroid separations are all the same as 3.817(6) Å, forming a condensely packed 3D framework. In contrast, novel alternating and offset π–π 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 Ag⁺⋯π stacking interactions between the silver(i) ions and the thiophene rings of ligand L with the Ag⁺–centroid contacts of 3.324(5) and 3.747(5) Å.

In the crystal packing of 1D ladder-like chain **3**, multiple π–π stacking, Ag⁺⋯Ag and Ag⁺⋯S interactions are found. As shown in Fig. 2, intraladder Ag⁺⋯Ag interactions of 3.008(5) Å as well as face-to-face π–π stacking interactions of 3.672(6) Å between imidazole rings of adjacent L ligands are observed, while interladder Ag⁺⋯S interactions of 3.245(2) Å as well as offset π–π 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. S19, ESI[†]) which could be contributed to the most rigid polymeric structure fixed by N–Ag coordinative bonds, condensed face-to-face π–π layer packing and Ag⁺⋯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 stainless mask with 1 × 3 mm² 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 × 10⁹ Ω m for **1**, while a control experiment gave the average resistivity of 9.3 × 10¹² Ω m for L showing 2.7 × 10² 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⁺/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⁺ 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⁺⋯Ag and face-to-face π–π layer packing of contiguous 1D polymeric chains down the *a* axis.

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Notes and references

† *Synthesis of L*: 5,5'-dibromo-bithiophene (2.000 g, 6.2 mmol), K_2CO_3 (3.500 g, 26.4 mmol), imidazole (1.682 g, 24.7 mmol), and anhydrous $CuSO_4$ (0.025 g, 0.156 mmol) were mixed and heated at 180 °C under N_2 atmosphere for 4 h. After being cooled to room temperature, the resultant mixture was washed with water and the residue was extracted with $CHCl_3$ (5×30 cm³). The organic layer was separated, dried over anhydrous sodium sulfate, evaporated to dryness, and recrystallized from water and ethanol. Yield: 80%. Mp 198–199 °C. Anal. Calcd for $C_{14}H_{10}N_4S_2$: C, 56.35; H, 3.38; N, 18.78%. Found: C, 56.28; H, 3.51; N, 18.74%. FT-IR (KBr, ν , cm⁻¹): 3448 (m), 3107 (m), 3050 (m), 1556 (s), 1491 (s), 1462 (m), 1367 (w), 1340 (w), 1305 (s), 1266 (s), 1107 (m), 1049 (s), 923 (m), 905 (w), 834 (m), 807 (s), 717 (s), and 651 (s). ¹H NMR (500 MHz, CD_3Cl , 298 K, TMS, ppm): δ = 7.81 (2H), 7.22–7.24 (4H), 7.06–7.07 (2H), and 6.97 (2H). ¹³C NMR (125 MHz, $CDCl_3$): δ = 137.9, 136.8, 132.5, 130.6, 123.0, 119.9, 119.4. UV-Vis (CH_3OH) λ_{max} = 329 and 242 nm. The light yellow needle-like single crystals of L suitable for X-ray diffraction determination were grown from a solution of $CHCl_3$ by slow evaporation in air at room temperature. *Synthesis of I*: a buffer layer of a solution (13 cm³) of acetonitrile/chloroform in a ratio of 3 : 1 was carefully layered over a solution of L (4.500 mg, 0.015 mmol) in chloroform (1.5 cm³). Then a solution of $AgNO_3$ (2.500 mg, 0.015 mmol) in acetonitrile (1.5 cm³) was layered over the buffer layer. Yellow crystals were isolated after one week. Yield: 66%. Anal. Calcd for $C_{14}H_{10}AgN_5O_3S_2$: C, 35.91; H, 2.15; N, 14.96%. Found: C, 35.83; H, 2.17; N, 14.89%. FT-IR (KBr, ν , cm⁻¹): 3016 (m), 1637 (w), 1618 (w), 1556 (s), 1518 (w), 1490 (m), 1460 (m), 1384 (s), 1302 (s), 1242 (m), 1115 (m), 1067 (m), 1046 (s), 930 (m), 863 (m), 802 (m), 719 (m), and 649 (m). UV-Vis (CH_3OH) λ_{max} = 330 and 246 nm. *Synthesis of 2*: **2** was prepared by the same procedure as **1** except that $AgClO_4$ was used instead of $AgNO_3$. Yield: 77%. Anal. Calcd for $C_{14}H_{10}AgClN_4O_4S_2$: C, 33.25; H, 1.99; N, 11.08%. Found: C, 33.29; H, 1.82; N, 11.14%. FT-IR (KBr, ν , cm⁻¹): 3015 (s), 1551 (s), 1519 (m), 1499 (s), 1456 (m), 1385 (w), 1349 (m), 1310 (s), 1257 (m), 1243 (m), 1208 (m), 1085 (s), 1042 (s), 939 (m), 921 (m), 864 (m), 800 (m), 735 (m), 648 (m), and 620 (s). UV-Vis (CH_3OH) λ_{max} = 334 and 244 nm. *Synthesis of 3*: a buffer layer of a solution (10 cm³) of acetonitrile/chloroform in a ratio of 1 : 1 was carefully layered over a solution of L (9.000 mg, 0.03 mmol) in chloroform (3 cm³). Then a solution of $AgCF_3COO$ (6.600 mg, 0.03 mmol) in acetonitrile (3 cm³) was layered over the buffer layer. Yellow crystals were isolated after one week. Yield: 70%. Anal. Calcd for $C_{16}H_{10}AgF_3N_4O_2S_2$: C, 37.00; H, 1.94; N, 10.79%. Found: C, 37.04; H, 1.89; N, 10.74%. FT-IR (KBr, ν , cm⁻¹): 3420 (b), 1677 (s), 1556 (s), 1517 (m), 1494 (m), 1384 (m), 1341 (m), 1300 (s), 1266 (m), 1240 (m), 1210 (s), 1130 (m), 1103 (m), 1072 (m), 1043 (s), 922 (m), 801 (s), 781 (s), and 724 (s). UV-Vis (CH_3OH) λ_{max} = 334 and 242 nm. § *X-Ray data for L*: $C_{14}H_{10}N_4S_2$, $M = 298.40$, monoclinic, space group, $P2_1/c$, $T = 291(2)$ K, $a = 3.914(4)$ Å, $b = 7.475(3)$ Å, $c = 22.656(8)$ Å, $\beta = 95.447(7)^\circ$, $U = 659.8(4)$ Å³, $Z = 2$, $\mu = 0.397$ mm⁻¹, $D_c = 1.502$ g cm⁻³, $R_{int} = 0.074$, $F(000) = 308$, reflections collected/independent 3090/1150, refinement method, full-matrix least-squares on F^2 , no. of parameters refined 91, $S = 1.21$, $R1 [I > 2\sigma(I)] = 0.0798$, $wR2$ (all data) = 0.1913, residual electron density, 0.51/–0.35 e Å⁻³. *X-Ray data for I*: $C_{14}H_{10}AgN_5O_3S_2$, $M = 468.28$, monoclinic, space group, $P2_1/c$, $T = 291(2)$ K, $a = 3.817(2)$ Å, $b = 7.901(3)$ Å, $c = 26.283(9)$ Å, $\beta = 96.527(6)^\circ$, $U = 787.5(5)$ Å³, $Z = 2$, $\mu = 1.571$ mm⁻¹, $D_c = 1.975$ g cm⁻³, $R_{int} = 0.083$, $F(000) = 464$, reflections collected/independent 3757/1398, refinement method, full-matrix least-squares on F^2 , no. of parameters refined 115, $S = 1.02$, $R1 [I > 2\sigma(I)] = 0.0408$, $wR2$ (all data) = 0.1384, residual electron density, 0.55/–0.75 e Å⁻³. *X-Ray data for 2*: $C_{14}H_{10}AgClN_4O_4S_2$, $M = 505.70$, monoclinic, space group, $P2_1/n$, $T = 291(2)$ K, $a = 13.731(4)$ Å, $b = 8.046(3)$ Å, $c = 15.458(5)$ Å, $\beta = 101.940(4)^\circ$, $U = 1670.9(10)$ Å³, $Z = 4$, $\mu = 1.646$ mm⁻¹, $D_c = 2.010$ g cm⁻³, $R_{int} = 0.059$, $F(000) = 1000$, reflections collected/independent 7929/2907, refinement method, full-matrix least-squares on F^2 , no. of parameters refined 235, $S = 1.01$, $R1 [I > 2\sigma(I)] = 0.0568$, $wR2$ (all data) = 0.1698, residual electron density, 0.89/–0.56 e Å⁻³. *X-Ray data for 3*: $C_{16}H_{10}AgF_3N_4O_2S_2$, $M = 519.29$, triclinic, space group, $P\bar{1}$, $T = 291(2)$ K, $a = 8.259(2)$ Å, $b = 9.689(2)$ Å, $c = 13.045(2)$ Å, $\alpha = 71.193(2)^\circ$, $\beta =$

81.694(2)°, $\gamma = 72.739(2)^\circ$, $U = 942.2(2)$ Å³, $Z = 2$, $\mu = 1.340$ mm⁻¹, $D_c = 1.830$ g cm⁻³, $R_{int} = 0.034$, $F(000) = 512$, reflections collected/independent 4374/3231, refinement method, full-matrix least-squares on F^2 , no. of parameters refined 253, $S = 1.09$, $R1 [I > 2\sigma(I)] = 0.0479$, $wR2$ (all data) = 0.1489, residual electron density, 1.07/–0.64 e Å⁻³.

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