

Novel organic crystals with red–violet metallic luster: 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole derivatives bearing a heteroatom combined methyl substituent

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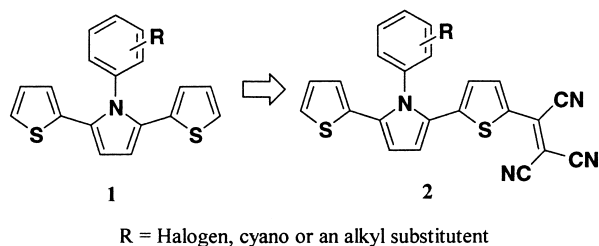
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Abstract—A new class of π -conjugated organic compounds that form crystals with red-violet metallic luster were obtained upon introduction of a heteroatom combined methyl substituent (OMe, SMe, or NMe₂) into the *para*-position of the central *N*-phenyl group of 1-phenyl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole. The molecule in crystals adopts a heaving ribbon-like molecular arrangement. This is obviously different from the planar arrangement of the gold-like analogues that bear halogen, cyano, or short alkyl group at *para*-position of the central *N*-phenyl group. Within the crystal lattice, an intermolecular C–H···N hydrogen bond occurs to make the adjacent π -systems (CN···C=C) close enough, which is suggested to be responsible for the red-violet metallic color. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Novel conjugated organic molecules containing both donor and acceptor moieties have attracted much attention because they are critical components for many great advanced technologies such as non-linear optical, photo- and electro-luminescent devices, and photovoltaic devices etc. Hence, a large number of papers have been published about the compounds with such D–A structures.¹ Employment of conjugated thiophene and pyrrole derivatives² as donor combined with cyano-substituted ethenyl acceptors are promising candidates among such D–A systems due to their numerous potential applications.³ Recently, we have reported a new class of π -electron rich compounds, 1-aryl-2,5-di(2-thienyl)pyrroles **1**, which serve as strong π -electron donor.⁴ Introduction of tricyanoethenyl group as the acceptor unit to the skeleton of **1** leads to the formation of 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles **2** in good yield.⁵ To our surprise, the novel pyrrole derivatives **2** bearing halogen, cyano group, or a comparatively short alkyl substituent (less than propyl) at the *para*-position of the central *N*-phenyl group easily form stable crystals with gold-like metallic luster. X-Ray structural analysis revealed that most of the gold-like lustrous crystals

possess a coplanar sheet-like structure, and the intermolecular C–H···N hydrogen bonds between the cyano nitrogen and the olefinic hydrogen (CN···H–C=C) result in the sufficient intermolecular approach of the adjacent π -systems (CN···C=C), which was suggested to play an important role in the appearance of gold-like metallic luster.⁵ Furthermore, it was also found that compounds **2** bearing a longer alkyl chain (more than butyl) form crystals with bronze-like metallic luster (Scheme 1). This motivated our current interest in this class of materials because optimal control of the metallic luster by alteration of the *para*-substituents with different properties is an appealing work. Thus, we have synthesized various **2** bearing different substituents at the *para*- or *ortho*-position of the *N*-phenyl group. Herein we present one of the interesting discoveries during this investigation: compounds (**3a–c**) giving crystals with red-violet metallic luster were obtained upon introduction of heteroatom combined methyl substituents (OMe, SMe, or NMe₂) into the *para*-position of the central

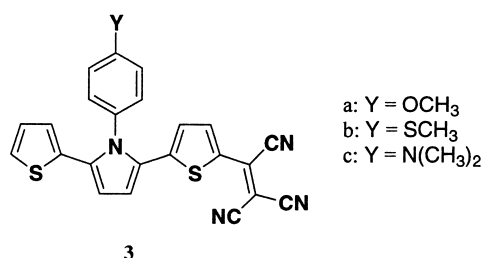


Scheme 1. Structures of the novel π -conjugated system, 1-aryl-2,5-di(2-thienyl)pyrroles **1** and its tricyanoethenyl derivatives **2** showing metallic colored appearance.

Keywords: π -conjugated organic compound; heteroatom combined methyl substituent; red-violet metallic luster; ribbon-like molecular arrangement; intermolecular CN···C=C interaction.

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N-phenyl group. The origin of this novel metallic color is discussed based on the results of X-ray structural analysis.



2. Results and discussion

The conversion of **1** to **3** was performed favorably according to the conventional procedures that we have published.⁵ The obtained pyrrole derivatives **3a–c** were easily dissolved in CHCl₃ or THF to give a deep-blue solution due to their absorption bands exhibiting at a region near 620 nm [λ_{\max} (THF, 3×10^{-5} mol dm⁻³): **3a**, 625 nm (log ϵ 4.56), **3b**, 619 nm (4.58), **3c**, 637 nm (4.66)]. It is evident that the electronic property of the heteroatoms reflects a higher order of contribution to the bathochromic shift.

The red-violet crystals of **3a–c** with superior quality were obtained by crystallization from their CHCl₃ solution. The solid-state UV–Vis–NIR reflection–absorption spectra of these crystals were identical with each other but quite different from their UV spectra in solution (Fig. 1). They display a peculiar broadened absorption band in the whole visible region, reflecting the stronger interaction between the π -systems.^{5,6} The strong absorption lies in the region of green to yellowish green (corresponding to the wavelength of 530–580 nm) whose complementary color is red-violet to violet. The appearance of the absorption band at a longer wavelength than the gold-like analogues (λ_{\max} ca. 480 nm) suggests formation of a unique crystal structure related to the red-violet metallic luster of **3a–c**.

X-Ray crystallographic analysis reveals that **3a–c** crystallize in same orthorhombic unit cells, containing eight molecules of each compound. Fig. 2 shows an ORTEP plot of the crystal **3c** at 298 K. Similar to our previous study,⁵ the π -conjugation consisting of thiophene–pyrrole–thiophene and tricyanoethenyl group adopts an approximate planar conformation to which the central *N*-phenyl group is almost

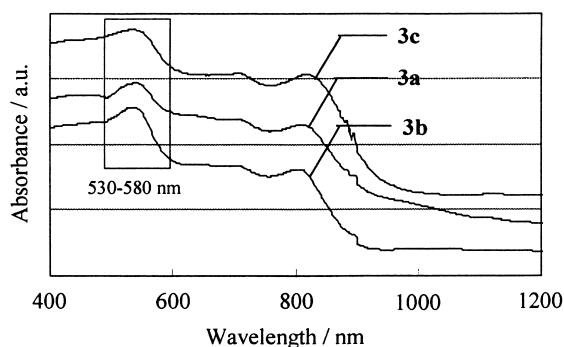


Figure 1. Solid-state UV–Vis–NIR diffuse reflection–absorption spectra of the red-violet crystals of **3a–c**. The absorption band in a range of 530–580 nm determine the red-violet metallic color of **3a–c**.

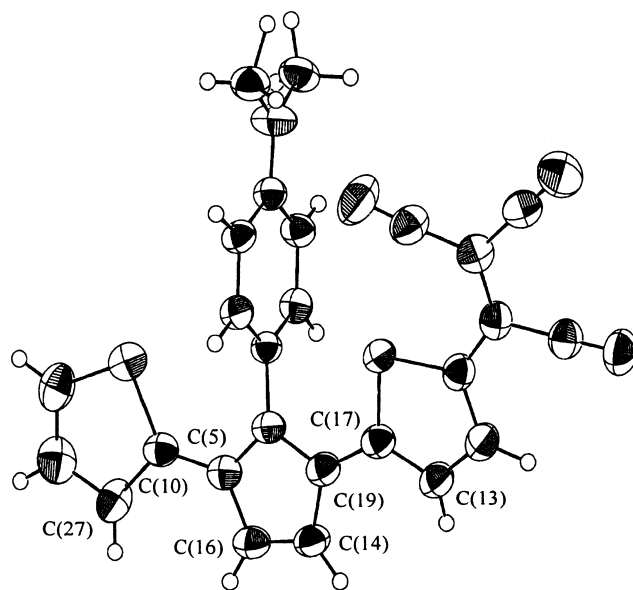


Figure 2. An ORTEP plot of the crystal of **3c** at 298 K. The ellipsoids are drawn at the 50% probability level. Selected intramolecular torsion angles with standard deviation (deg.): C(13)–C(17)–C(19)–C(14) 13.5(2)°, C(16)–C(5)–C(10)–C(27) 1.7(2)°.

perpendicular. However, compared with those showing gold-like metallic luster, the thiophene ring bearing tricyanoethenyl group is slightly but definitely distorted from the plane of pyrrole–thiophene conjugation with an angle of 13.5°, which is a common motif exclusively present in all of the three crystals (14.1° for **3a**, and 13.3° for **3b**). This particular torsion can be largely ascribed to favorable formation of a C–H/n type^{7–9} intramolecular C–H···N hydrogen bond⁸ between the top of the cyano nitrogen and the hydrogen on the heteroatom combined methyl group. The distances of the X–C–H···N (X=O, S, or N) hydrogen bond derived from the X-ray study are 2.83, 2.69, and 2.82 Å with the corresponding C–H···N angles of 155.3°, 170.3°, and 151.3°, corresponding to **3a–3c**, respectively (also see Table 1 given below). These intramolecular C–H···N interactions are far weaker than O–H···O and N–H···O hydrogen bonds, but they are assumed to associate with the slight distortion of the π -conjugation, which leads to the formation of a coplanar sheet-like structure become difficult, and, as a result, the crystal packing adopts a heaving ribbon-like style, as schematically shown in Fig. 3.

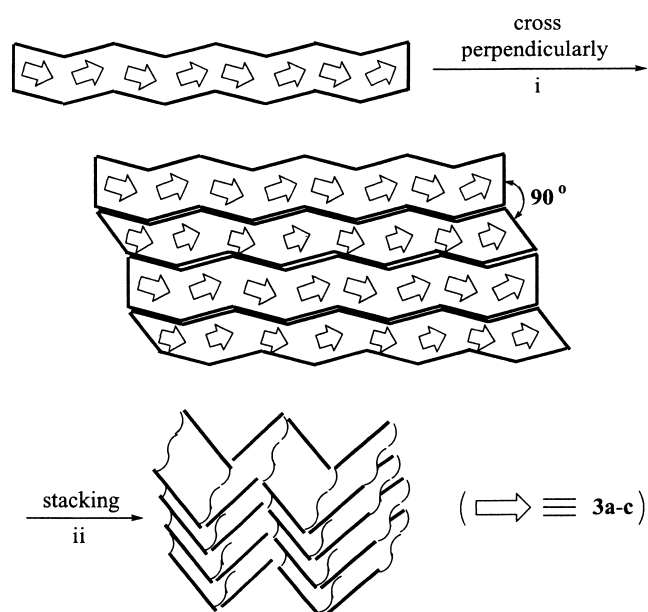
The molecules of **3c** aggregate in a slow ribbon in which each molecule overlaps with head (tricyanoethenyl group) of itself to tail (free terminal thiophene ring) of the neighbouring molecule by the intermolecular C–H···N hydrogen bond between the cyano nitrogen and the adjacent olefinic hydrogen (CN···H–C=C, Fig. 4). This C–H···N intermolecular hydrogen bond^{8b,9} (bond length: 2.69 Å, C–H···N angle: 151.9°) results in an edge-to-edge type CN···C=C contact (3.48 Å) between the π -electrons of thiophene ring and cyano group, which substantially contribute to the crystal architecture of **3c** (Fig. 4(a)). Because of the slightly distorted plane of π -conjugation of **3c**, one molecule and its neighboring one are not in the same plane, but somewhat lean to the opposite direction with a dihedral angle of ca. 10° as depicted in Fig. 4(b). This

Table 1. Information of the intramolecular C–H···N interaction and intermolecular C–H··· π interaction in crystals **3a–3c**

Crystal	Intermolecular C–H···N distance a (Å)	C–H···N angle (deg.)	Intermolecular C–H···Ar distance b (Å) ^a	C–H···Ar angle (deg.)
3a	2.83	155.3	3.05	122.3
3b	2.69	170.3	2.95	118.1
3c	2.82	151.3	2.86	111.6

^a Based on the shortest interatomic distance as shown above. O and N atoms are slightly shaded.

hampers the intermolecular interaction of the p-orbitals in an upright manner that the gold-like lustrous crystals of **2** adopt.⁵ This interaction extends repeatedly to provide successive rows of the heaving ribbon. The slightly wavy ribbons orientate perpendicularly to form a larger infinite zigzag ribbon (Fig. 4(c)), which stacks to give the red-violet crystals of **3c** as the final result (Fig. 4(d)). It is notable that weak intermolecular CH– π interaction¹⁰ (X–C–H···Ar, X=O, S, or N; Ar=2-thienyl group) occurs between the hydrogen of the heteroatom combined methyl group of one molecule and the terminal thiophene ring of its perpendicularly adjacent analogue. The N–C–H···Ar distance is 2.86 Å with a C–H···Ar angle of 111.6°, as mapped basing

**Figure 3.** Schematic representation of the molecular arrangement style and crystal formation of **3a–c**.

on the shortest interatomic distance. On the other hand, the π -conjugation in **3c** partially overlap in layers 3.57 Å apart (Fig. 4(d), determined by powder X-ray diffraction analysis) with an *offset stacked* arrangement which is a favorable face-to-face style of π – π stacking.¹¹ This value relates well with our previous study⁵ for those showing gold-like metallic luster. Therefore, the offset stacked arrangement of π – π interaction is proposed to be not so essential for the red-violet metallic luster.

The crystal packing of **3c** is analogous to those of **3a** and **3b** so that the interatomic interactions described above are very similar. For **3a**, the intermolecular C–H···N hydrogen bond length is 2.73 Å with a C–H···N angle of 140.1°, and the intermolecular CN···C=C contact distance is 3.43 Å; for **3b**, the corresponding values are 2.73 Å (151.2°) and 3.51 Å. The π -conjugation in **3a** and **3b** partially overlap in layers with a same value of 3.55 Å apart, as revealed by PXRD analysis. Interestingly, the heteroatom combined methyl groups in **3a** and **3b** also turn their head toward the face of the adjacent thiophene ring, which is a perfect pattern favorable to formation of the intermolecular CH– π interaction.¹² The detailed information about the X–C–H···N (X=O, S, or N) intramolecular hydrogen bond and the weak intermolecular CH– π interaction are summarized in Table 1.

Allowing for that molecules containing both donor and acceptor units are expected to exhibit unusual electrical properties owing to intramolecular charge transfer,^{8b,13} we tested the electrical conductivity of **3a–c** and found that the new D–A compounds themselves show only low electrical conductivity ($<10^{-8}$ S cm⁻¹), but this can be obviously raised by chemical doping with iodine (p-doping). After a 12 hours' iodine (vapor)-doping process, compounds **3a** and **3b** exhibit the electrical conductivity of 1.8×10^{-6} and 1.4×10^{-6} S cm⁻¹, respectively, whereas compound **3c** gives a slightly higher value of 5.4×10^{-6} S cm⁻¹. The

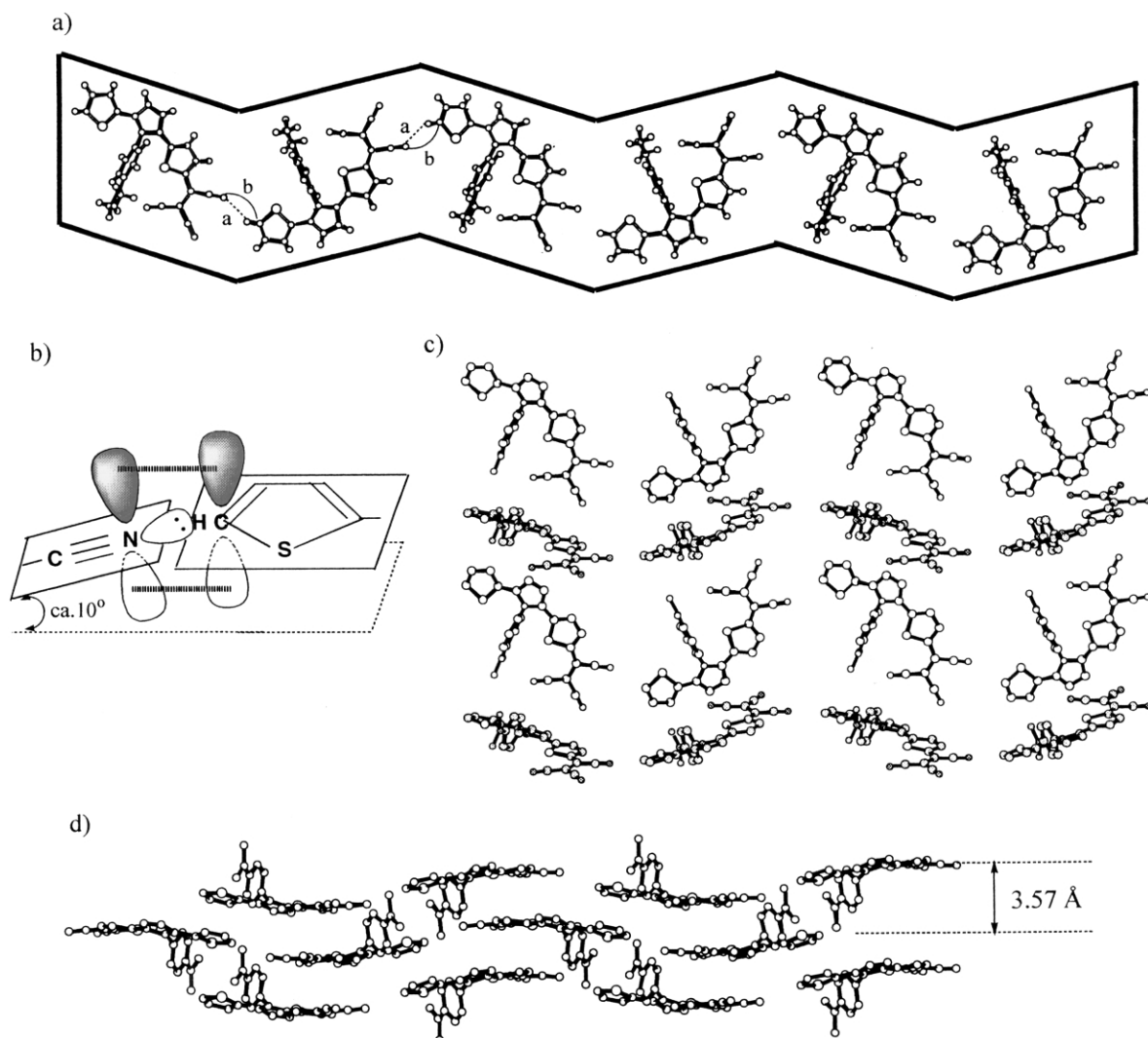


Figure 4. Crystal structure and $\text{CN}\cdots\text{C}=\text{C}$ overlapping mode of **3c**. (a) Molecular arrangement and interatomic interactions on the heaving ribbon. (i): $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond: 2.69 Å (151.9°); (ii): $\text{CN}\cdots\text{C}=\text{C}$ contact: 3.48 Å; (b) the adjacent p-orbitals ($\text{CN}\cdots\text{C}=\text{C}$) interact with each other in a somewhat inclined manner (dihedral angle between the plane of tricyanoethenyl group and the adjacent thiophene ring: ca. 10°); (c) the slightly wavy ribbons cross perpendicularly to form an infinite zigzag ribbon. Hydrogen atoms are omitted for clarity; (d) the ribbons stack to construct a crystal. Hydrogen atoms are omitted for clarity. The layer distance of π - π stacking determined by PXRD is 3.57 Å.

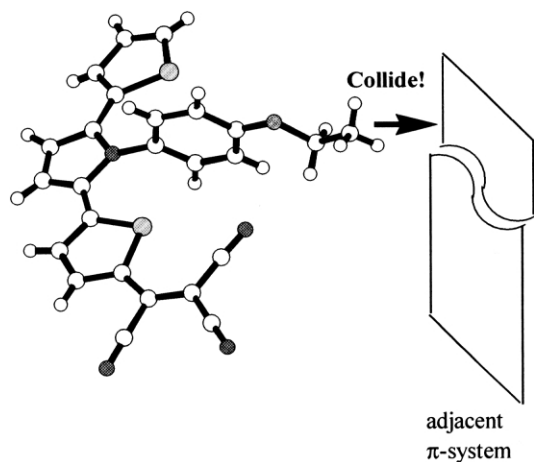
electrical conductivity of **3a–c** are in the same order with that of a series of π -conjugated copolymers consisting of both electron-donating thiophene unit and electron-withdrawing pyrido[3,4-*b*]pyrazine unit under the iodine-doping conditions.^{1c}

3. Conclusion

In summary, we have successfully developed a new class of π -electron conjugated system **3** that gives crystals with red-violet metallic luster. The essential motif present in these crystals is an infinite, intermolecular, linear network of $\text{C}-\text{H}\cdots\text{N}$ ($\text{CN}\cdots\text{H}-\text{C}=\text{C}$) interaction which organizes the molecules to arrange regularly in a row of the wavy ribbon. The $\text{CN}\cdots\text{H}-\text{C}=\text{C}$ interaction originates from the unique effect of the tricyanoethenyl group, making the adjacent p-orbitals ($\text{CN}\cdots\text{C}=\text{C}$) close enough to partially overlap with each other. We prefer to propose that this short $\text{CN}\cdots\text{C}=\text{C}$ contact which works with a somewhat slanting

manner within the crystal lattice of **3a–c** is closely related to the red-violet metallic color. On the other hand, the heteroatom combined methyl groups are also noteworthy because the heteroatom with high electronegativity provides more acidity to the methyl hydrogen, which significantly assists in formation of the intramolecular $\text{X}-\text{C}-\text{H}\cdots\text{N}$ ($\text{X}=\text{O}$, S, or N) hydrogen bond and the intermolecular $\text{CH}-\pi$ interaction;^{10a} moreover, their suitable size appropriate for the zigzag ribbon-like crystal arrangement. One can assume that if a longer alkyl substituent exists on the heteroatom, the zigzag ribbon-like structure adoption will become more difficult because the perpendicular rows on the adjacent ribbon cannot avoid colliding against each other. The electrical conductivity of the new D–A compounds reaches $10^{-6} \text{ S cm}^{-1}$ order upon doping with iodine (vapor), which exhibits possibility applied to organic semiconductors. At present, the other analogues of **3** bearing heteroatom combined bulkier alkyl group are being undertaken investigation, and some completed results and studies will be disclosed in the next paper. Further studies

such as the possibility of creating new metallic colors of this kind of compounds, as well as their potential properties applied to the new functional materials, are still in progress now.



4. Experimental

4.1. General methods

^1H NMR spectra were recorded at 300 MHz using a Varian Gemini-2000 NMR spectrometer and chemical shifts were referenced to TMS as internal standard. UV–Vis absorption spectra in THF solution were recorded on a JASCO V-570 spectrophotometer. Solid-state UV–Vis–NIR diffuse reflection–absorption spectra were recorded on a JASCO V-570 spectrophotometer equipped with an integral detector. Single crystals of the corresponding compounds were uniformly broken into powder and were put into a quartz glass cell for measurement under the absorption response mode. Infrared spectra were measured on a JASCO FT/IR-350 spectrophotometer. Melting points are uncorrected. Elemental analyses were performed by Chemical Analysis Center of Chiba University. All powder X-ray diffraction (PXRD) analyses were taken on a MAC Science MXP powder diffractometer using graphite-monochromated Cu–K α radiation (40 kV, 300 mA). The spectra were measured between 2° and 50° in the $2\theta/\theta$ -scan mode with steps of 0.01° in 2θ and 4°min^{-1} . For the electrical conductivity measurements under iodine-doping conditions, Ag-paste (DOTITE, Fujikura Kasei, Japan), Au-wires (ϕ 0.1 mm, Tanaka Noble Metals, Japan), and a digital model 2000 multimeter (Keithley Instruments, Inc., USA) were used. The actual samples for test were prepared by compressing the corresponding powders of **3a–c** into hard pellets with radius of 0.15 cm and thickness of 0.05 cm. All measurements were conducted under iodine atmosphere by the two-probe method at room temperature.

4.2. Materials

All chemicals were obtained from commercial suppliers and used without further purification. Compounds **3a–c**, together with the corresponding precursors **1** were prepared according to the literature procedures we have published.^{4,5}

4.2.1. 1-(4-Methoxyphenyl)-2,5-di(2-thienyl)pyrrole (1a). Colorless crystals; mp (toluene/hexane) $184.7\text{--}185.0^\circ\text{C}$; ^1H NMR (CDCl_3) δ 3.86 (s, 3H), 6.53 (s, 2H), 6.57 (dd, $J=1.0$ and 3.6 Hz, 2H), 6.82 (dd, $J=3.6$ and 5.0 Hz, 2H), 6.93 (d, $J=8.9$ Hz, 2H), 7.04 (dd, $J=1.0$ and 5.0 Hz, 2H), 7.23 (d, $J=8.9$ Hz, 2H); IR (KBr) 1510, 1468, 1418, 1300, 1244, 1022, 842, 760, 700 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NOS}_2$: C, 67.62; H, 4.48; N, 4.15. Found: C, 67.77; H, 4.46; N, 4.01.

4.2.2. 1-[4-(Methylthio)phenyl]-2,5-di(2-thienyl)pyrrole (1b). Pale yellow crystals; mp (acetone) $193.5\text{--}194.5^\circ\text{C}$; ^1H NMR (CDCl_3) δ 2.52 (s, 3H), 6.53 (s, 2H), 6.56 (dd, $J=1.1$ and 3.7 Hz, 2H), 6.83 (dd, $J=3.7$ and 5.2 Hz, 2H), 7.06 (dd, $J=1.1$ and 5.2 Hz, 2H), 7.20 (d, $J=8.9$ Hz, 2H), 7.25 (d, $J=8.9$ Hz, 2H); IR (KBr) 1496, 1413, 1198, 1094, 1039, 846, 821, 756, 697 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NS}_3$: C, 64.55; H, 4.28; N, 3.96. Found: C, 64.36; H, 4.33; N, 3.79.

4.2.3. 1-[4-(*N,N*-Dimethylamino)phenyl]-2,5-di(2-thienyl)pyrrole (1c). Pale yellow crystals; mp (acetone) $196.5\text{--}197.5^\circ\text{C}$; ^1H NMR (CDCl_3) δ 3.03 (s, 6H), 6.53 (s, 2H), 6.63 (dd, $J=1.1$ and 3.6 Hz, 2H), 6.71 (d, $J=8.9$ Hz, 2H), 6.82 (dd, $J=3.6$ and 5.1 Hz, 2H), 7.02 (dd, $J=1.1$ and 5.1 Hz, 2H), 7.15 (d, $J=9.1$ Hz, 2H); IR (KBr) 1610, 1523, 1414, 1362, 1188, 828, 813, 760, 703 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}_2$: C, 68.54; H, 5.18; N, 7.99. Found: C, 68.45; H, 5.23; N, 7.89.

4.2.4. 1-(4-Methoxyphenyl)-2-(2-thienyl)-5-[5-(tricyanoethyl)-2-thienyl]pyrrole (3a). Red-violet crystals; mp (CHCl_3) $219.6\text{--}220.4^\circ\text{C}$; ^1H NMR (CDCl_3) δ 3.93 (s, 3H), 6.75 (d, $J=4.4$ Hz, 1H), 6.87 (dd, $J=1.1$ and 3.7 Hz, 1H), 6.91 (dd, $J=3.7$ and 5.1 Hz, 1H), 7.08 (d, $J=4.4$ Hz, 1H), 7.10 (d, $J=9.0$ Hz, 2H), 7.12 (d, $J=4.5$ Hz, 1H), 7.18 (dd, $J=1.1$ and 5.1 Hz, 1H), 7.32 (d, $J=9.0$ Hz, 2H), 7.74 (d, $J=4.7$ Hz, 1H); IR (KBr) 2208, 1497, 1452, 1424, 1249, 1163, 1108, 844, 670 cm^{-1} . UV–Vis (THF, 3×10^{-5} M) λ_{max} (nm) (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) 625 (36000). Anal. Calcd for $\text{C}_{24}\text{H}_{14}\text{N}_4\text{OS}_2$: C, 65.73; H, 3.22; N, 12.78. Found: C, 65.59; H, 3.08; N, 12.65.

4.2.5. 1-[4-(Methylthio)phenyl]-2-(2-thienyl)-5-[5-(tricyanoethyl)-2-thienyl]pyrrole (3b). Red-violet crystals; mp (CHCl_3) $228.0\text{--}229.0^\circ\text{C}$; ^1H NMR (CDCl_3) δ 2.58 (s, 3H), 6.73 (d, $J=4.3$ Hz, 1H), 6.83 (dd, $J=1.2$ and 3.7 Hz, 1H), 6.91 (dd, $J=3.7$ and 5.1 Hz, 1H), 7.06 (d, $J=4.5$ Hz, 1H), 7.07 (d, $J=4.3$ Hz, 1H), 7.19 (dd, $J=1.1$ and 5.1 Hz, 1H), 7.30 (d, $J=8.9$ Hz, 2H), 7.41 (d, $J=8.7$ Hz, 2H), 7.75 (d, $J=4.5$ Hz, 1H); IR (KBr) 2208, 1498, 1452, 1422, 1398, 1362, 1320, 1248, 1169, 771 cm^{-1} . UV–Vis (THF, 3×10^{-5} M) λ_{max} (nm) (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) 619 (38000). Anal. Calcd for $\text{C}_{24}\text{H}_{14}\text{N}_4\text{S}_3$: C, 63.41; H, 3.10; N, 12.32. Found: C, 63.18; H, 3.09; N, 12.20.

4.2.6. 1-[4-(*N,N*-Dimethylamino)phenyl]-2-(2-thienyl)-5-[5-(tricyanoethyl)-2-thienyl]pyrrole (3c). Red-violet crystals; mp (CHCl_3) $252.0\text{--}253.0^\circ\text{C}$; ^1H NMR (CDCl_3) δ 3.08 (s, 6H), 6.75 (d, $J=4.3$ Hz, 1H), 6.81 (d, $J=9.1$ Hz, 2H), 6.91 (dd, $J=3.7$ and 5.1 Hz, 1H), 6.97 (dd, $J=1.2$ and 3.7 Hz, 1H), 7.08 (d, $J=4.4$ Hz, 1H), 7.15 (d, $J=4.5$ Hz, 1H), 7.16 (dd, $J=1.2$ and 5.1 Hz, 1H), 7.18 (d, $J=9.1$ Hz, 2H), 7.74 (d, $J=4.7$ Hz, 1H); IR (KBr) 2207, 1604, 1526,

1497, 1451, 1422, 1399, 1362, 1165, 843, 820, 771 cm^{-1} . UV–Vis (THF, 3×10^{-5} M) λ_{max} (nm) (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) 637 (45900). Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{N}_5\text{S}_2$: C, 66.50; H, 3.79; N, 15.51. Found: C, 66.29; H, 3.73; N, 15.44.

4.3. X-Ray crystallography

Data collection was performed on a Mac Science MXC18 four-circle diffractometer with graphite monochromated $\text{Cu K}\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$) using the $\theta-2\theta$ scan technique at 298 K. The structures were solved by direct methods and refined by full-matrix least-squares methods against F (SIR 92¹⁴) on a computer program package: maXus ver. 3.2.1 from MAC Science Co. Ltd.). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were refined isotropically. No empirical absorption correction was applied to all crystal refinements. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 190269–190271. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Crystal data for 3a: $\text{C}_{24}\text{H}_{14}\text{N}_4\text{OS}_2$, $M_r=438.53$, red-violet plates, orthorhombic, space group $Pbca$ (No. 61), $a=16.532(7) \text{ \AA}$, $b=26.561(9) \text{ \AA}$, $c=9.643(3) \text{ \AA}$, $V=4234.0(3) \text{ \AA}^3$, $Z=8$, $D_{\text{calcd}}=1.376 \text{ g cm}^{-3}$, $F(000)=1807$, $\mu=2.48 \text{ cm}^{-1}$; 2634 observed reflections [$I>3\sigma(I)$], 318 parameters, $R=0.0649$, $R_w=0.0745$.

Crystal data for 3b: $\text{C}_{24}\text{H}_{14}\text{N}_4\text{S}_3$, $M_r=454.60$, red-violet plates, orthorhombic, space group $Pbca$ (No. 61), $a=16.951(6) \text{ \AA}$, $b=26.890(10) \text{ \AA}$, $c=9.353(5) \text{ \AA}$, $V=4264.0(3) \text{ \AA}^3$, $Z=8$, $D_{\text{calcd}}=1.416 \text{ g cm}^{-3}$, $F(000)=1871$, $\mu=3.33 \text{ cm}^{-1}$; 2691 observed reflections [$I>3\sigma(I)$], 322 parameters, $R=0.0613$, $R_w=0.0663$.

Crystal data for 3c: $\text{C}_{25}\text{H}_{17}\text{N}_5\text{S}_2$, $M_r=451.57$, red-violet plates, orthorhombic, space group $Pbca$ (No. 61), $a=17.554(7) \text{ \AA}$, $b=27.140(10) \text{ \AA}$, $c=9.161(5) \text{ \AA}$, $V=4364.0(4) \text{ \AA}^3$, $Z=8$, $D_{\text{calcd}}=1.375 \text{ g cm}^{-3}$, $F(000)=1871$, $\mu=2.39 \text{ cm}^{-1}$; 2999 observed reflections [$I>3\sigma(I)$], 351 parameters, $R=0.0533$, $R_w=0.0584$.

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