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Formation of metal-lustrous organic crystals from 2-aryl-1-(4-methoxyphenyl)-5-(5-tricyanoethenyl-2-thienyl)pyrroles

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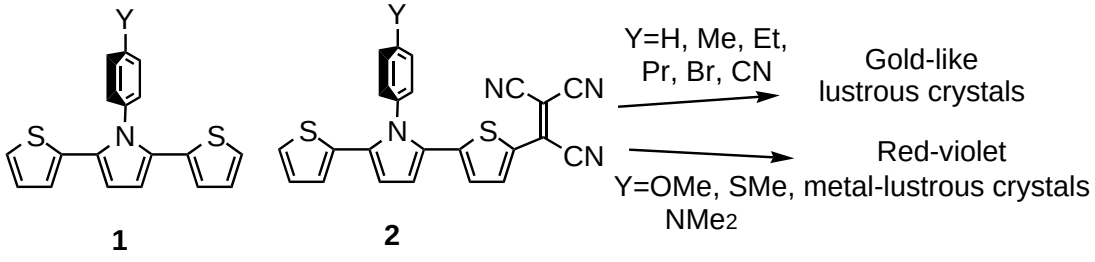
Abstract—Various 2-aryl-1-(4-methoxyphenyl)-5-(5-tricyanoethenyl-2-thienyl)pyrroles (**3**) were synthesized. When the 2-aryl group of **3** is phenyl, 4-tolyl, and 4-methoxyphenyl, organic crystals with greenish yellow metallic luster are formed. In contrast, a 2-(4-fluorophenyl) derivative of **3** gives gold-like lustrous crystals. The relation of their crystal structures with the appearance of metallic color is mentioned.

1. Introduction

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.[1] Introduction of a stronger π-electron withdrawing tricyanoethenyl group into the skeleton of **1** can be achieved by the reaction with tetracyanoethylene to afford various 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-thienyl)pyrroles (**2**) in good yield.[2] Interestingly, the products (**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, in which the intermolecular C–H···N hydrogen bonds between the cyano nitrogen and the olefinic hydrogen (CN···H–C=C) were observed. This makes the adjacent π-systems intermolecularly close to each other to bring about their sufficient intermolecular contact (CN···C=C), which was suggested to play an important role in the appearance of gold-like metallic luster[2a] (Scheme 1).

The essential relationship between their vivid metallic colored appearance and their unique crystal structure motivated us to explore this work more systematically. Recently, we also reported that crystals with orange or red-violet metallic luster were obtained upon the introduction of methoxy group, methylthio group, or dimethylamino group into the 4-position of central *N*-phenyl group.[2b] In these crystals, the molecules are arranged into a heaving ribbon that is shown in Figure 1.

This is obviously different from the planar arrangement of the gold-like analogues that bear halogen, cyano, or short alkyl group at the *para*-position of the *N*-phenyl group. In the



Scheme 1.

Keywords: π-Conjugated molecule; 4-Methoxyphenyl group; Metallic luster; Ribbon-like molecular arrangement; Sheet-like molecular arrangement.
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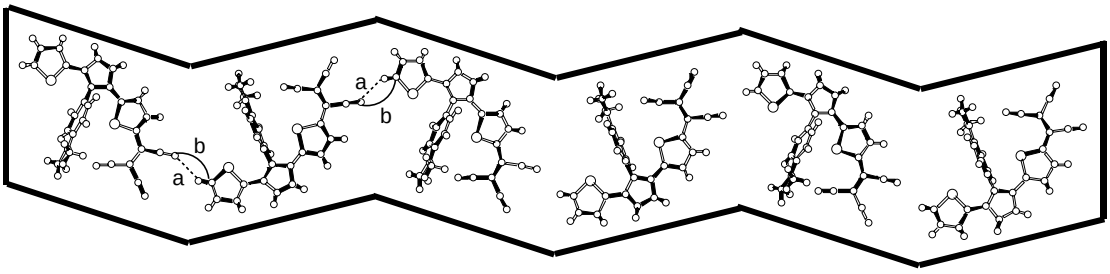
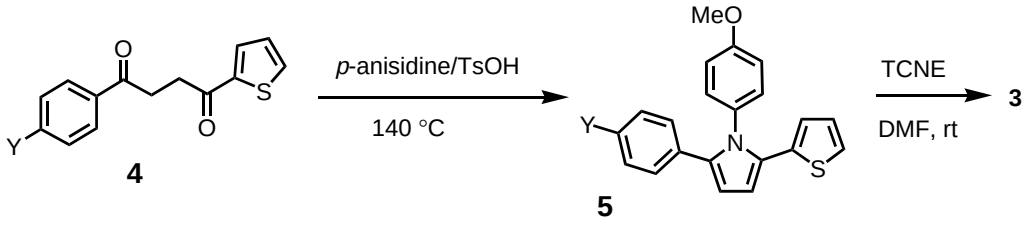


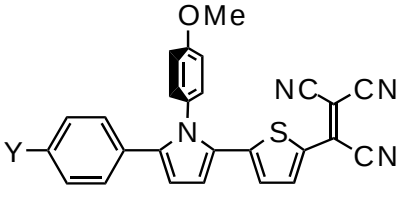
Figure 1. Heaving ribbon structure in crystal of **2** (Y=OMe). (a) 2.69 Å; (b) 3.48 Å.



Compound		4 → 5		5 → 3	
	Y	Time (h)	Yield (%)	Time (h)	Yield (%)
a	H	6.0	99	4.0	54
b	Me	2.5	99	2.0	99
c	OMe	3.0	61	24	61
d	F	2.0	99	4.0	98

Scheme 2.

heaving ribbon, an intermolecular C–H···N hydrogen bond between the terminal thiophene and cyano groups occurs to make the adjacent π-systems (CN···C=C) close enough. Thus, the terminal thiophene seems to be essential to the ribbon-like arrangement of the π-molecules in crystals. This consideration prompted us to examine what kind of crystal structure is constructed by crystallization of the π-molecule bearing an aryl group instead of the terminal thiophene of **2** (Y=OMe). Here, we report the synthesis of various 2-aryl-1-(4-methoxyphenyl)-5-(5-tricyanoethenyl-2-thienyl)pyrroles (**3**) and the metallic luster of their crystals.



2. Results and discussion

The compounds (**3**) were prepared according to the conventional procedures that we have published.[2] Reaction of 2-aryl-1-(4-methoxyphenyl)-5-(2-thienyl)pyrroles (**5**), which were easily derived from 1-aryl-4-(2-thienyl)-1,4-butanediones (**4**), with tetracyanoethylene occurred smoothly at an ambient temperature in *N*,*N*-dimethylformamide (DMF) to produce **3**, as summarized in Scheme 2.

The present compounds (**3**) are soluble in regular organic solvents such as chloroform, acetone, and THF to give a deep blue solution because they absorb visible light around the wavelength of 600–612 nm (Fig. 2). It is reasonably

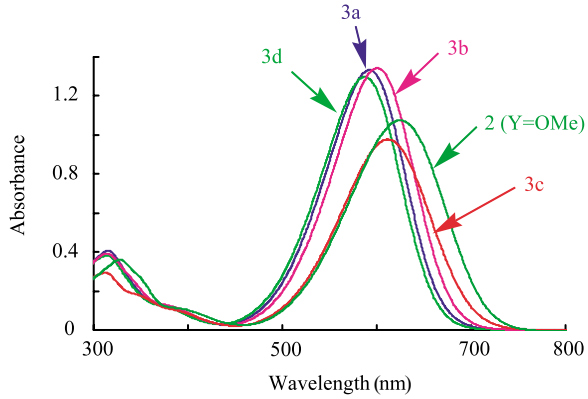


Figure 2. Solution UV–vis absorption spectra of **3** in THF (3.0×10^{-5} M). **3a**: λ_{max} 592 nm (ε 44,400); **3b**: 601 nm (ε 44,800); **3c**: 612 nm (ε 32,600); **3d**: 588 nm (ε 43,200); **2** (Y=OMe): 625 nm (ε 35,800).

thought by analogy with 1-aryl-1,2,2-tricyanothenes[3] that these absorption bands are due to intramolecular charge-transfer transition from the thiophene–pyrrole–thiophene part into the tricyanoethene part. It is noteworthy that **3c** (Y=OMe) shows its λ_{max} at a longer wavelength (612 nm) with a relatively lower extinction coefficient (32,600) in comparison with those of other compound (**3**). This behavior is attributable to the electron-donating property of the 4-methoxy group because the absorption of **2** (Y=OMe) appears at 625 nm with a comparable extinction coefficient (35,800).

By slow evaporation of the solvent, metal-lustrous crystals were formed. The color of the metallic luster is changeable according to the 4-substituent of 2-aryl group. Typical photographs are shown in Figure 3. Interestingly, crystals of **3d** (Y=F) look like gold metal, but **3a**, **3b**, and **3c** form greenish yellow or light greenish yellow metal-lustrous crystals.

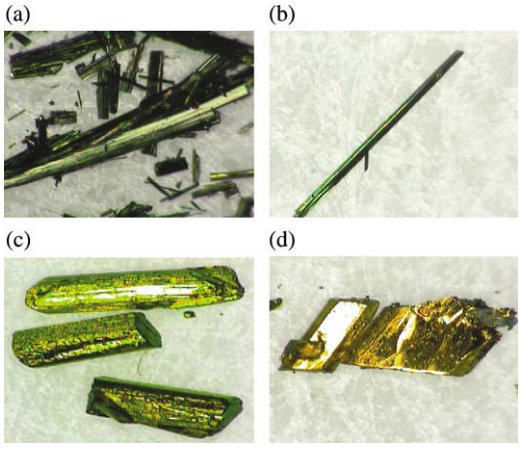


Figure 3. Photographs of metal-lustrous crystals of **3**. (a) **3a** (from acetone). (b) **3b** (from ethyl acetate). (c) **3c** (from chloroform). (d) **3d** (from ethyl acetate).

The solid-state UV–vis–NIR diffuse reflection–absorption spectra of these crystals were summarized in Figure 4. Apparently, the spectrum of gold-like lustrous crystals (**3d**) resemble to that of gold (Au) plate in the visible light region.

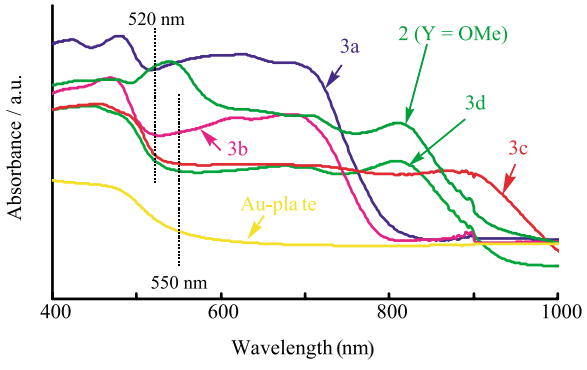


Figure 4. Solid UV–vis–NIR diffuse reflection–absorption spectra of **2** (Y = OMe), **3**, and Au-plate.

They display a peculiar broadened absorption band in the whole visible region (below 1000 nm for **3c** and below 930 nm for **3d**). This is reflected in the metallic luster that results from the intermolecular interaction between the π-systems.[2,4] In these spectra, the stronger absorption appears in the region of shorter wavelength than 550 nm. In contrast, the crystals of **3a**, **3b**, and **3c** show the corresponding strong absorption that covers the region of a relatively shorter wavelength than 510–520 nm, whose complementary color is greenish yellow. This is the reason why the crystals of **3a**, **3b**, and **3c** exhibit greenish yellow metallic luster.

The powder X-ray diffraction (PXRD) patterns of these crystals are summarized in Figure 5 that includes the PXRD pattern of **3d** for reference. From these patterns, it was not suggested that the crystals of **3a**, **3b**, and **3c** adopt the same structure.

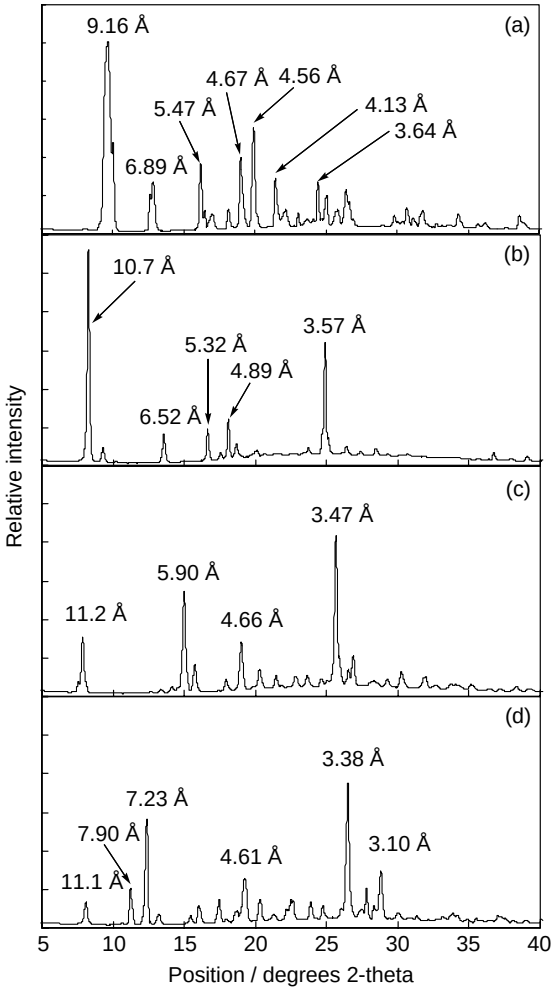


Figure 5. The PXRD patterns of **3**. (a) **3a**. (b) **3b**. (c) **3c**. (d) **3d**.

Among them, single crystals of **3a** with a good quality were fortunately obtained by crystallization from acetone. X-ray crystallographic analysis reveals that **3a** crystallize in a triclinic unit cell, containing two molecules. These two molecules are somewhat different from one another in conformation (note Conformer A and Conformer B).

Figure 6 shows an ORTEP plot of the crystal **3a** (Fig. 6a) together with **2** (Y=OMe) (Fig. 6c) that was reported in our previous study.[2b] Similar to the molecule of **2** (Y=OMe), the thiophene ring bearing tricyanoethenyl group is slightly but definitely distorted from the plane of pyrrole–thiophene conjugation (torsion angle: 28.0° (Conformer A) or 28.1° (Conformer B)), which is larger by 9.5° than that of **2** (Y=OMe). This particular torsion can be mainly ascribed to favorable formation of a CH/N type intramolecular C–H···N hydrogen bond[5–7] between the top of the cyano nitrogen and the hydrogen on methoxy group. The distance of the O–C–H···N hydrogen bond was 2.70 and 2.78 Å for Conformer A and Conformer B, respectively. Furthermore, the terminal phenyl group was also distorted by 33.7° (Conformer A) and 30.4° (Conformer B) from the central pyrrole ring, resulting in the edge-to-face interaction (CH/π interaction)[8] between the *N*-phenyl and the terminal phenyl groups (the distance between the *ipso* carbon of the central phenyl and the *ortho* hydrogen of the terminal phenyl: 2.64 Å).

To our surprise, the crystal structure of **3a** resembles to that of **2** (Y=OMe). The molecules of **3a** aggregate in a ribbon and the formed ribbons cross perpendicularly to each other to form a zig-zag layer as depicted illustratively in Figure 7. It is noteworthy that two kinds of ribbons exist: one ribbon consists of the molecules that adopt the conformation A. Another one consists of the molecules with the conformation B. These ribbons that are very similar to one another are arranged alternatively to form the zig-zag layer. The zig-zag layers stack to form a crystal. It is noteworthy that the present ribbon is flat. This is different from the heaving

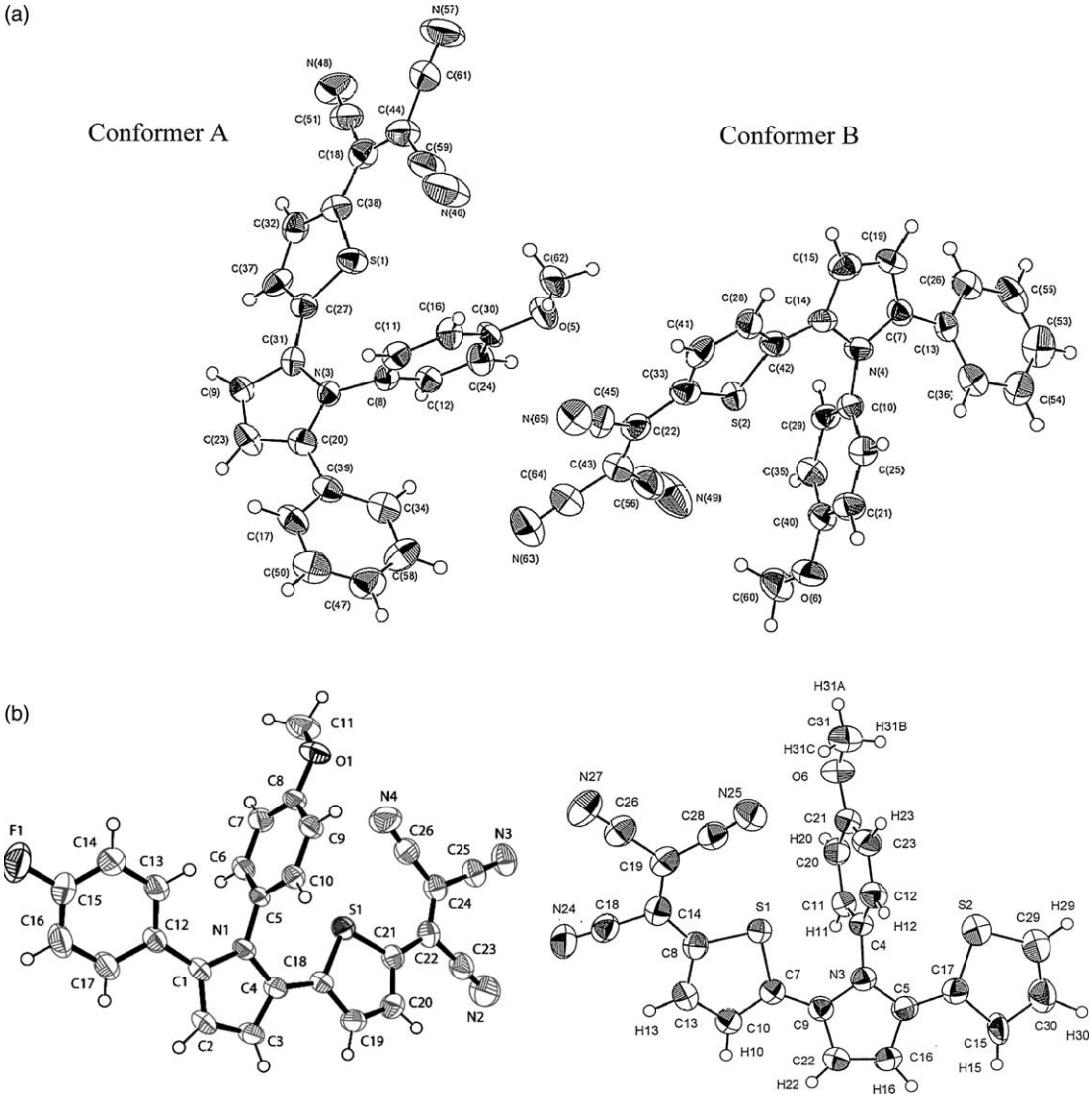


Figure 6. ORTEP polts of the crystals. (a) The crystal of **3a**, in which two conformers (A and B) exist. Selected torsion angles: [Conformer A] C(44)–C(18)–C(38)–S(1) 0.0°, N(3)–C(31)–C(27)–S(1) 28.0°, C(31)–N(3)–C(8)–C(12) 73.0°, N(3)–C(20)–C(39)–C(34) 33.7°. [Conformer B] C(43)–C(22)–C(33)–S(2) 3.20°, N(4)–C(14)–C(42)–S(2) 28.1°, C(14)–N(4)–C(10)–C(25) 76.8°, N(4)–C(7)–C(13)–C(36) 30.4°. Selected bond length: [Conformer A] N(46)–HC(62) 2.70 Å, C(8)–HC(34) 2.64 Å. [Conformer B] N(49)–HC(60) 2.78 Å, C(10)–HC(36) 2.64 Å. (b) The crystal of **3d**. Selected torsion angles: C(24)–C(22)–C(21)–S(1) 8.0°, N(1)–C(4)–C(18)–S(1) 10.1°, C(18)–N(1)–C(5)–C(10) 76.5°, N(1)–C(1)–C(12)–C(13) 21.4°. Selected bond length: N(4)–HC(11) 2.89 Å, C(5)–HC(13) 2.44 Å. (c) The crystal of **2** (Y=OMe).[2b]

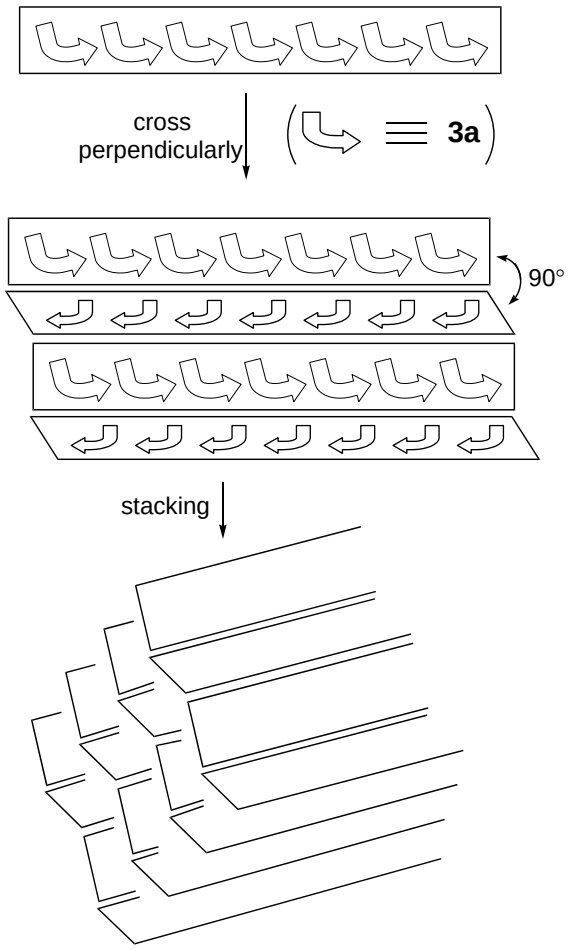


Figure 7. Schematic representation for the molecular arrangement style and the crystal formation of **3a**.

ribbon observed in the crystal of **2** (Y=OMe). In the ribbon, the molecules interact with head (tricyanoethenyl group) of itself to tail (central pyrrole ring) of the neighboring molecule by the intermolecular C–H···N interaction between the cyano nitrogen and the adjacent pyrrole hydrogen (CN···H–C=C, Fig. 8). The C–H···N interaction[6b,7] (distance: 2.54 and 2.80 Å) results in an edge-to-edge type CN···C=C contact (3.34 and 3.63 Å) between the π-electrons of pyrrole ring and cyano group, which substantially contribute to the crystal architecture of **3a** (Fig. 8c). This interaction extends repeatedly to provide successive rows of the flat ribbon. As shown in Figure 8d, weak intermolecular CH···N interaction works between the hydrogen of the terminal phenyl group of one ribbon and the cyano group of its perpendicularly adjacent analogue (CN···HC distance: 2.62 Å). Furthermore, the interlayer approach of the cyano groups was also observed (Fig. 8e): the cyano group of one molecule is close to that of the neighboring molecule of the adjacent ribbon layer in an inverse direction.

Next, we wish to describe the crystal structure of **3d**, which exhibits gold-like metallic luster. As mentioned in the introduction, **2** (Y=a small substituent such as H, halogen, or short alkyls) forms gold-like lustrous crystals. These crystals have a sheet structure and, in the sheet, the molecules are close to each other. In a similar manner to these crystals, a sheet structure was constructed in the crystals of **3d**. The sheets, which are slightly waving, stack to form a crystalline architecture, as shown in Figure 9b. Interestingly, the fluorine atom at the 4-position of the terminal phenyl plays a significant role in the formation of the sheet structure. The molecules of **3d** are arranged in a ribbon that is indicated by a pink quadrangle. The molecules interact with each other with head (tricyanoethenyl group) of itself to tail (central pyrrole ring) of the neighboring molecule by means of two intermolecular C–H···N interactions (b and c in Fig. 9a). These intermolecular interactions[6b,7] results in an edge-to-edge type CN···C=C contact (3.57 Å) between the π-electrons of pyrrole ring and cyano group. The interaction between the cyano nitrogen and the 3-hydrogen of the terminal 4-fluorophenyl should be noted. This is probably due to the strong inductive effect of the fluorine that makes the neighboring proton more acidic. Furthermore, the flat ribbons interact with each other by a side-by-side manner via the so-called hydrogen bonding[9] between the fluorine atom and the pyrrole hydrogen that is marked by the letter 'd' (C=CH···F 2.59 Å) in Figure 9a. This distance is smaller than the sum of the van der Waals radii[10] of fluorine and hydrogen atoms (1.47 and 1.20 Å).

3. Conclusion

In summary, we have successfully developed a new class of π-electron conjugated system, 2-aryl-1-(4-methoxyphenyl)-5-(5-tricyanoethenyl-2-thienyl)pyrrole (**3**), that forms crystals with metallic luster. The color of the metallic luster is changeable from greenish yellow to gold-like, depending on the substituent of the terminal aryl group. The greenish yellow metal-lustrous crystals were given by recrystallization of **3a** (aryl=phenyl) from acetone. The essential motif present in these crystals is an infinite, intermolecular, linear network of CN···H–C=C interaction, which organizes the molecules to arrange regularly in a row of the flat ribbon. The CN···H–C=C interaction originates from the unique effect of the tricyanoethenyl group, making the adjacent π-orbitals (CN···C=C) close enough to partially overlap with each other. Furthermore, the flat ribbons are arranged into a zig-zag layer. On the other hand, **3d** (aryl=4-fluorophenyl) formed gold-like lustrous crystals. X-ray crystallographic analysis revealed that the crystals adopt a slightly waving sheet structure. The sheet consists of the flat ribbons, in which the molecules interact with each other by two intermolecular C=C–H···NC hydrogen bonds to result in an edge-to-edge type CN···C=C contact. In these crystals, the fluorine atom of the terminal phenyl takes an important role in the connection of the flat ribbons to form a sheet. From these results, it is concluded that a 2-(5-tricyanoethenyl-2-thienyl)pyrrole moiety is essential to the appearance of metallic luster in the present π-system: the central pyrrole of one molecule is close to the cyano group of the adjacent molecule to make the π-systems contact to each other successively in a ribbon, while the terminal aryl group contributes to the formation of the crystal structure.

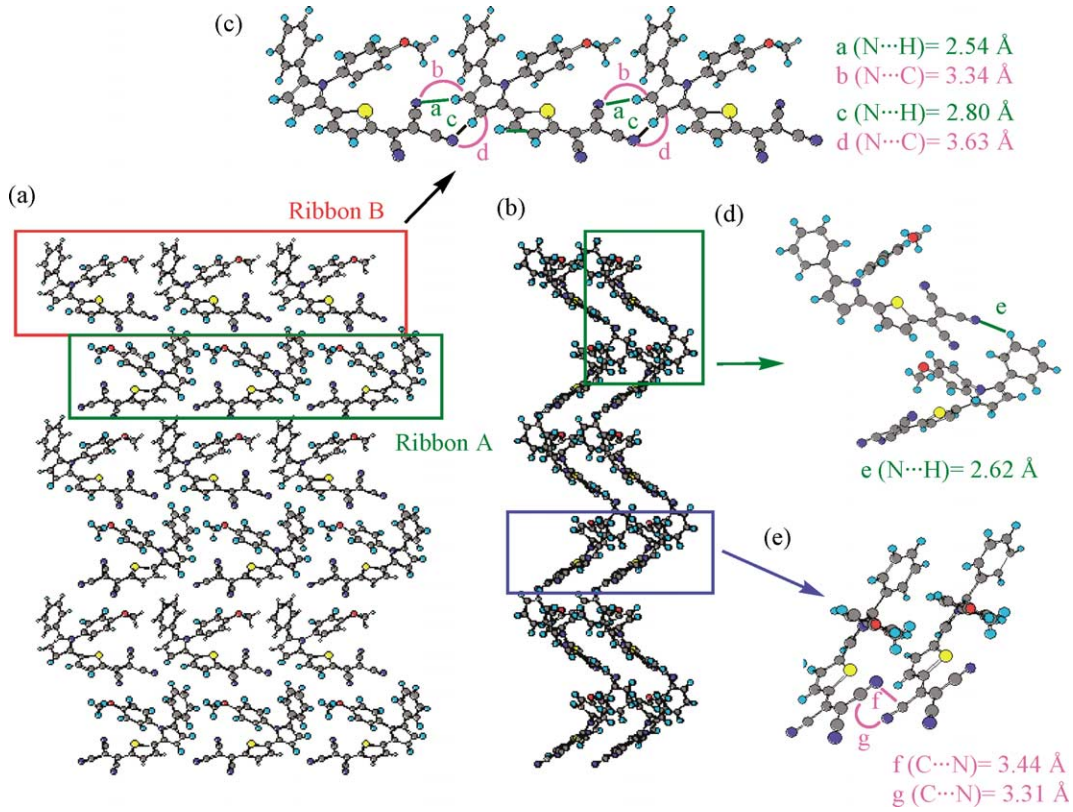


Figure 8. Crystal structure and CN···C═C overlapping mode of **3a**. (a) Molecular arrangement in a zig-zag layer. Ribbon A, which consists of conformer A molecules, and Ribbon B, which consists of conformer B molecules, are alternatively arranged. (b) The side view of two stacking zig-zag layers. (c) The molecular arrangement and intermolecular interactions in the ribbon. (d) Intermolecular interaction in the connection between the ribbons. (e) The approach of cyano groups between the neighboring layers.

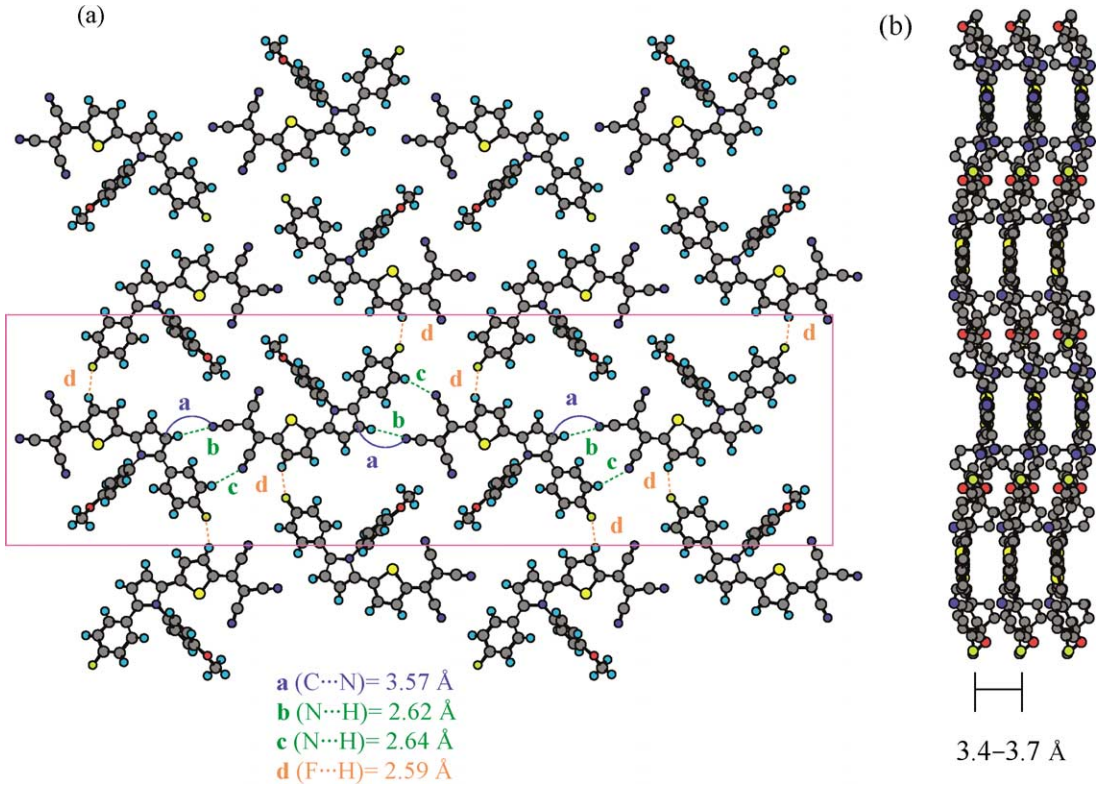


Figure 9. Crystal structure of **3d**. (a) Molecular arrangement in a waving layer. The area surrounded with four pink lines exhibits the ribbon, in which the molecules are arranged by head-to-tail interaction. (b) The side view of two stacking layers. The distance between the stacking layers was estimated to be 3.4–3.7 Å.

4. Experimental

Melting points are determined on a hot-stage microscope apparatus (Yamato MP-500D) and uncorrected. All chemicals were obtained from commercial suppliers and used without further purification. ^{1}H 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–NIR absorption spectra were recorded on a JASCO V-570 spectrophotometer. Infrared spectra were measured on a JASCO FT/IR-350 spectrophotometer. Elemental analyses were performed by Chemical Analysis Center of Chiba University.

4.1. Preparation of 1-(4-methoxyphenyl)-2-phenyl-5-(5-tricyanoethenyl-2-thienyl)pyrrole (3a). A typical procedure

A mixture of 1-phenyl-4-(2-thienyl)-1,4-butanedione (505 mg, 2.07 mmol), 4-methoxyaniline (714 mg, 5.94 mmol), and 4-toluenesulfonic acid monohydrate (117 mg, 0.616 mmol) was magnetically stirred at 140 °C for 6 h. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel (eluent: toluene) to give **5a** as colorless crystals (678 mg; 99% yield).

4.1.1. Compound 5a. Colorless needles; mp 201.6–202.3 °C (from acetone); ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 3H), 6.45 (d, J=3.6 Hz, 1H), 6.53 (dd, J=1.2, 3.6 Hz, 1H), 6.55 (d, J=3.8 Hz, 1H), 6.84 (d, J=8.8 Hz, 2H), 6.85 (dd, J=3.7, 4.8 Hz, 1H), 7.07 (dd, J=1.2, 5.1 Hz, 1H), 7.10 (d, J=9.0 Hz, 2H), 7.10–7.19 (m, 5H); IR (KBr) 1602, 1514, 1469, 1295, 1249, 1025, 833, 754, 698 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23. Found: C, 76.17; H, 5.29; N, 4.09.

A solution of **5a** (446 mg, 1.34 mmol) and tetracyanoethylene (351 mg, 2.69 mmol) in 10 mL of anhydrous DMF was stirred for 2 h at room temperature. The reaction mixture was poured into brine (100 mL) and was extracted with toluene (100 mL×3). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The dark blue residue was purified by column chromatography on silica gel (eluent: a 4:1 mixture of chloroform and hexane) to give **3a** as greenish gold-like lustrous crystals (175 mg; 54% yield).

4.1.2. Compound 3a. Greenish gold-like lustrous crystals; mp 209.7–210.5 °C (from chloroform); ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H), 6.63 (d, J=4.2 Hz, 1H), 6.99 (d, J=9.0 Hz, 2H), 7.07 (d, J=4.5 Hz, 1H), 7.10 (d, J=4.2 Hz, 1H), 7.18–7.25 (m, 5H), 7.22 (d, J=9.0 Hz, 2H), 7.76 (d, J=4.7 Hz, 1H); IR (KBr) 2217, 1513, 1497, 1449, 1421, 1346, 1249, 1198, 1102, 1057 cm^{-1}; UV (3.0×10^{-5} M in THF): λ_{max} 592 nm (ε 44,400); HRMS (FAB): calcd for $C_{26}H_{16}N_4OS$ 432.1045, found 432.1049. Anal. Calcd for $C_{26}H_{16}N_4OS\cdot0.1CHCl_3$: C, 70.70; H, 3.66; N, 12.64. Found: C, 70.77; H, 3.68; N, 12.74.

In a similar manner, compounds **3b**, **3c**, and **3d** were prepared.

4.1.3. Compound 5b. Colorless crystals; mp 168.2–168.3 °C (from acetone); ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H), 3.82 (s, 3H), 6.41 (d, J=3.8 Hz, 1H), 6.52 (dd, J=1.2, 3.6 Hz, 1H), 6.54 (d, J=3.7 Hz, 1H), 6.83 (dd, J=3.6, 5.2 Hz, 1H), 6.84 (d, J=8.7 Hz, 2H), 6.96–7.03 (m, 4H), 7.06 (dd, J=1.2, 5.2 Hz, 1H), 7.10 (d, J=9.0 Hz, 2H); IR (KBr) 1515, 1500, 1459, 1295, 1249, 1027, 833, 769, 702 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.49; H, 5.54; N, 4.05. Found: C, 76.20; H, 5.61; N, 3.94.

4.1.4. Compound 5c. Colorless crystals; mp 174.5–174.9 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3H), 3.82 (s, 3H), 6.37 (d, J=3.7 Hz, 1H), 6.51 (dd, J=1.2, 3.6 Hz, 1H), 6.53 (d, J=3.7 Hz, 1H), 6.72 (d, J=9.0 Hz, 2H), 6.83 (dd, J=3.5, 5.2 Hz, 1H), 6.84 (d, J=8.7 Hz, 2H), 7.04 (d, J=8.7 Hz, 2H), 7.06 (dd, J=1.2, 4.8 Hz, 1H), 7.09 (d, J=9.0 Hz, 2H); IR (KBr) 1516, 1498, 1284, 1248, 1178, 1030, 831, 766, 696 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.30; N, 3.88. Found: C, 72.97; H, 5.22; N, 3.73.

4.1.5. Compound 5d. Colorless crystals; mp 193.0–193.7 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.40 (d, J=3.6 Hz, 1H), 6.53 (dd, J=1.4, 3.6 Hz, 1H), 6.54 (d, J=3.6 Hz, 1H), 6.82–6.87 (m, 2H), 6.84 (dd, J=3.6, 5.2 Hz, 1H), 6.88 (d, J=8.7 Hz, 2H), 7.05–7.10 (m, 2H), 7.08 (dd, J=1.2, 5.2 Hz, 1H), 7.08 (d, J=9.0 Hz, 2H); IR (KBr) 3006, 1547, 1514, 1495, 1294, 1248, 1221, 833, 768, 704 cm^{-1}. Anal. Calcd for $C_{21}H_{16}FNOS$: C, 72.18; H, 4.62; N, 4.01. Found: C, 72.38; H, 4.72; N, 3.95.

4.1.6. Compound 3b. Greenish metal-lustrous crystals; mp 229.9–230.4 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H), 3.88 (s, 3H), 6.60 (d, J=4.2 Hz, 1H), 7.00 (d, J=9.0 Hz, 2H), 7.02–7.12 (m, 4H), 7.07 (d, J=4.5 Hz, 1H), 7.09 (d, J=4.5 Hz, 1H), 7.22 (d, J=9.0 Hz, 2H), 7.75 (d, J=4.5 Hz, 1H); IR (KBr) 2215, 1542, 1508, 1450, 1419, 1346, 1250, 1197, 1105, 1056 cm^{-1}; UV–vis (3.0×10^{-5} M in THF): λ_{max} 601 nm (ε 44,800); HRMS (FAB): calcd for $C_{27}H_{18}N_4OS$ 446.1201, found 446.1207. Anal. Calcd for $C_{27}H_{18}N_4OS\cdot0.2CH_3COOC_2H_5$: C, 71.94; H, 4.26; N, 12.07. Found: C, 71.85; H, 4.22; N, 12.18.

4.1.7. Compound 3c. Yellowish green metal-lustrous crystal; mp 216.0–216.5 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 3H), 3.88 (s, 3H), 6.57 (d, J=4.2 Hz, 1H), 6.70 (d, J=9.0 Hz, 2H), 7.00 (d, J=9.0 Hz, 2H), 7.06 (d, J=4.5 Hz, 1H), 7.09 (d, J=4.2 Hz, 1H), 7.13 (d, J=9.0 Hz, 2H), 7.22 (d, J=9.0 Hz, 2H), 7.74 (d, J=4.5 Hz, 1H); IR (KBr) 2214, 1514, 1452, 1417, 1390, 1342, 1248, 1186, 1117 cm^{-1}; UV–vis (3.0×10^{-5} M THF): λ_{max} (ε) 612 (32,600); HRMS (FAB) calcd for $C_{27}H_{18}N_4O_2S$ 462.1150, found 462.1162. Anal. Calcd for $C_{27}H_{18}N_4O_2S$: C, 70.11; H, 3.92; N, 12.11. Found: C, 69.94; H, 3.99; N, 12.01.

4.1.8. Compound 3d. Gold-like lustrous crystals; mp 230.3–230.5 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$): δ 3.88 (s, 3H), 6.57 (d, J=4.1 Hz, 1H), 6.89–6.95 (m, 2H), 6.99 (d, J=8.7 Hz, 2H), 7.05 (d, J=4.5 Hz, 1H), 7.07 (d, J=4.5 Hz, 1H), 7.14–7.19 (m, 2H), 7.19 (d, J=9.0 Hz, 2H), 7.76 (d, J=4.8 Hz, 1H); IR (KBr) 2213, 1515, 1496, 1414, 1301, 1250, 1191, 1165, 1102, 839 cm^{-1}. UV–vis (3.0×10^{-5} M THF) λ_{max} 588 nm (ε 43,200); HRMS (FAB): calcd for $C_{26}H_{15}FN_4OS$ 450.0951, found 450.0930. Anal. Calcd for $C_{26}H_{15}FN_4OS$: C, 69.32; H, 3.36; N, 12.44. Found: C, 69.47; H, 3.44; N, 12.39.

4.2. X-ray crystallography

4.2.1. Compound 3a. Data collection was performed on a Mac Science MXC18 four-circle diffractometer with graphite-monochromated Cu Kα ($\lambda=1.54178$) radiation using the 2θ-ω scan technique, and the X-ray intensities were measured up to $2\theta=140°$ at 298 K. The structures were solved by a direct method SIR92[11] and refined against F by a computer program package; maXus[12] from MAC Science. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position.

Crystal data for **3a** $C_{26}H_{16}N_4OS$, $M_r=432.51$, greenish gold-like plates, triclinic, space group $P1$ (no. 1), $a=17.863(5)$ Å, $b=10.911(3)$ Å, $c=5.573(3)$ Å, $\alpha=86.60(3)°$, $\beta=89.89(3)°$, $\gamma=89.97(2)°$, $V=1084.3(6)$ Å^3, $Z=2$, $D_{calcd}=1.325$ g/cm^3, $F(000)=448$, $\mu=1.53$ cm^{-1}; 4589 observed reflections [$I>3\sigma(I)$], 563 parameters, $R=0.061$, $Rw=0.068$.

4.2.2. Compound 3d. Data collection was performed on a Bruker SMART-1000 CCD diffractmeter with graphite monochromated Mo Kα radiation ($\lambda=0.71013$ Å). Empirical absorption correction was applied using SADABS.[13] The structure was solved by a direct method (SHLEXS-97)[14] and refined by full-matrix least-squares method (SHLEXL-97)[15] against F^2. The non-hydrogen atoms were refined anisotropically. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position. All calculations were performed using SHELEXTL[16] computer program package from Bruker AXS.

Crystal data for **3d** $C_{26}H_{15}FN_4OS$, $M_r=450.49$, gold prizsm, monoclinic, space group $P2_1/n$ (no. 14), $a=10.240(3)$ Å, $b=22.171(8)$ Å, $c=10.289(4)$ Å, $\beta=111.478(4)°$, $V=2173.8(13)$ Å^3, $Z=4$, $D_{calcd}=1.376$ g/cm^3, $F(000)=928$, $\mu=0.185$ cm^{-1}; 12702 observed reflections [$I>2\sigma(I)$], 299 parameters, $R=0.0417$, $Rw=0.0852$.

Crystallographic data (excluding structure factors) for two crystal structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 289278 (for **3d**) and 289279 (for **3a**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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