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Greenish metal-lustrous organic crystals formed from 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrroles

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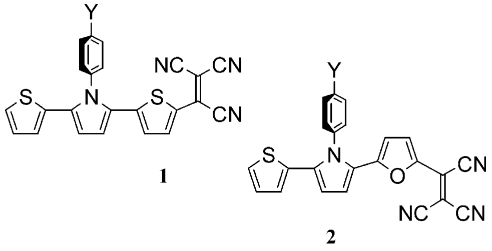
Abstract—On the treatment of 1-aryl-2-(2-furyl)-5-(2-thienyl)pyrroles with tetracyanoethylene, 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrroles were produced. These compounds formed crystals with greenish metallic luster. In their solid-state UV–vis–NIR diffuse reflection–absorption spectra, absorption band corresponding to metallic reflection spreads in the range of 550–900 nm. Furthermore, strong absorption appeared below 520–540 nm. This absorption results in the appearance of green color. Single-crystal X-ray crystallographic analysis revealed the crystal structure of 1-(4-methoxyphenyl)-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole (**2c**). The distinct features of the crystal structure are as follows: (1) the thiophene–pyrrole–furan–tricyanoethenyl π-system is approximately flat; (2) the conformational relation between the pyrrole ring and the furan ring is anti, that is, these rings are pointing in opposite directions and the dihedral angle of N–C–C–O = 180°; (3) as a result, the tricyanoethenyl group is far from the 4-methoxyphenyl group; (4) the molecules of **2c** are arranged in a ribbon structure; (5) the ribbons are assembled side-by-side to form a terraced layer; (6) the layers stack so that the π-orbitals of **2c** become close to each other.

1. Introduction

Chemical scientists have been developing metal-like organic materials such as electron-conducting polymers[1] that are represented by polythiophenes[2] and polyacetylenes,[3] molecular metals that require charge transfer between two different chemical species,[4–6] and highly conducting crystals consisting of single-component neutral nickel complexes.[7,8] Some organic π-conjugated molecules with relatively lower molecular weight are known to exhibit metallic luster such as furan- and pyrrole-containing analogues of α-quinquethiophene[9] and α,α′-bis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT).[10] Recently, we also found novel organic compounds, 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-thienyl)pyrroles (**1**), which easily form crystals with gold-like, bronze-like, or red-violet metallic luster through the intermolecular side-by-side interaction between their π-molecular orbitals.[11–15] With these intriguing findings, we were interested in the role of the thiophene rings: how do they contribute to the appearance of the metallic luster? (Scheme 1).



Scheme 1.

Hence, our investigation was started on the synthesis of 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrroles (**2**), which have a furan ring[16] instead of the inner thiophene ring of **1**. Here, we would like to report that these compounds (**2**) form crystals with greenish metallic luster.

2. Results and discussion

First of all, 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrroles (**2**) were easily synthesized from 1-(2-furyl)-4-(2-thienyl)-1,4-butanedione (**3**).[17] The reaction of 1-aryl-2-(2-furyl)-5-(2-thienyl)pyrroles (**4**), which were prepared by the Paal–Knorr reaction of **3** with anilines, with tetracyanoethylene occurred at ambient temperature

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Keywords: Metallic luster; Reflection; Organic Crystal; Furan; Pyrrole; Thiophene; Tricyanoethenyl.

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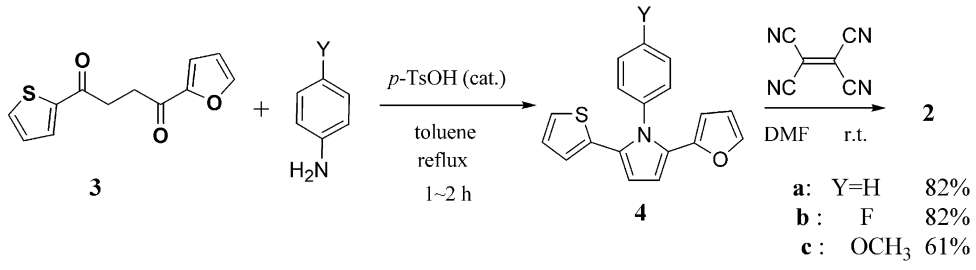

Scheme 2.

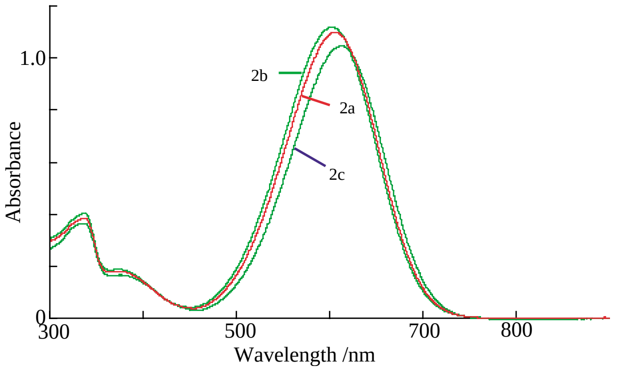

Figure 1. Solution UV–vis absorption spectra of **2** in THF (3.0×10^{-5} M). **2a**: λ_{max} 607 nm (ε 36,600), λ_{min} 455 nm (ε 1270); **2b**: 603 nm (ε 37,300), 453 nm (ε 1410); **2c**: 613 nm (ε 34,900), 457 nm (ε 1020).

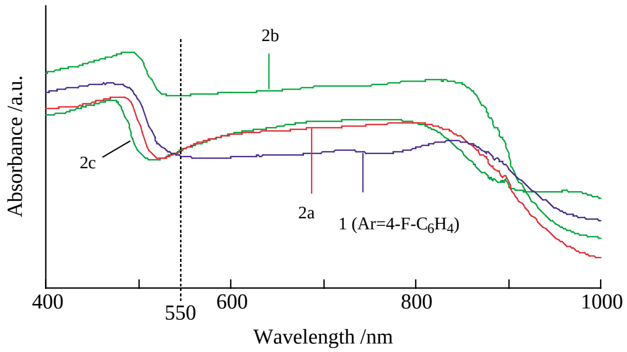

Figure 3. Solid state UV–vis NIR diffuse reflection–absorption spectra of **1** and **2**.

in *N*,*N*-dimethylformamide (DMF) to produce the corresponding **2** in good to high yields. Interestingly, an alternative product, 1-aryl-2-(2-furyl)-5-(5-tricyanoethenyl-2-thienyl)-pyrrole that is produced by the attack of tetracyanoethylene on the thiophene part of **4**, was not detected in the reaction mixture (Scheme 2).

They 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 nm (Fig. 1). It is noteworthy that their absorption maxima are shifted to the shorter wavelength compared with those of **1** (λ_{max} in THF: Y = H, 613 nm; *F*, 609 nm; CH_3O, 625 nm).

To our surprise, slow evaporation of the solvent gave crystals with greenish metallic luster, as shown in Figure 2. Their solid-state UV–vis–NIR diffuse reflection–absorption spectra are shown in Figure 3. Instead of the absorption band around 600 nm in a solution, a peculiar broadened absorption band was observed in a visible region of 500–1000 nm wavelength. This broad band contributes to the appearance of metallic luster: the appearance of a solid depends on the degree of absorption and reflectance in the visible region of the spectrum. With a band below 1.5 eV (800 nm), in the infrared, the solid may appear dark in color or shiny metallic, depending on the reflectivity.[18] The latter is the present case. Further, stronger absorption appeared below 520–540 nm with a maximum at 500–520 nm in the solid state spectra of **2**. This is the reason why the crystals of **2** exhibit greenish metallic luster.

Fortunately, crystals of sufficient quality for structural studies were obtained for the compound **2c**. The crystal structure of **2c** was shown in Figure 4. The molecule adopts a flat conformation, in which the pyrrole and furan rings are placed in an anti fashion. The anti fashion means the torsion angle of N–C–C–O is approximately 180°. The distance between the phenyl *ipso* carbon and the 3-hydrogen of

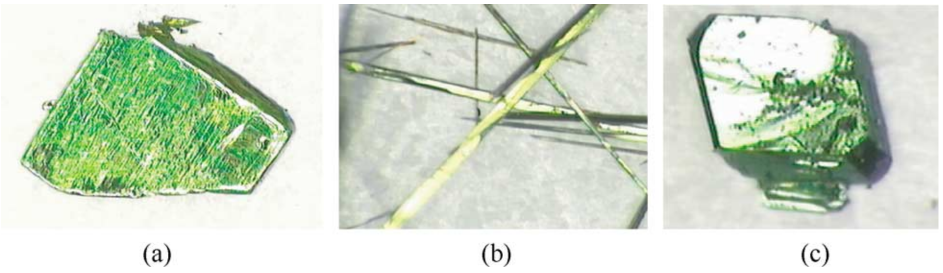
(a) (b) (c)

Figure 2. Crystal photographs. (a) A crystal of **2a** from acetone. (b) Crystals of **2b** from acetone. (c) A crystal of **2c** from chloroform.

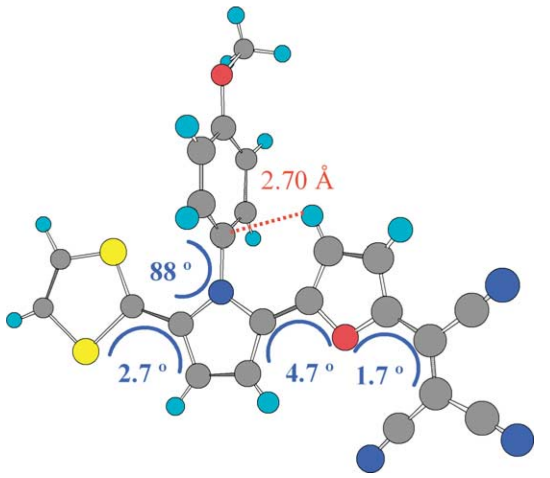

Figure 4. Crystal structure of **2c**. The thiopene ring is disordered: the sulfur that is located at the bottom of the above formula has a larger population (66%). Dihedral angles are shown with blue letters. The distance between the phenyl *ipso* carbon and the 3-hydrogen of the furan ring is shown with red letters.

the furan ring is 2.70 Å, meaning that a CH/π interaction[19] works in this system.

In a solution, this interaction seems to be valid, because, in the ^{1}H NMR spectrum ($CDCl_3$), the chemical shift of the 3-proton of the furan ring was observed at a higher field (δ 5.28) than those of the usual furan derivatives (furan δ 6.37; furfuryl acetate, δ 6.35; 2-furaldehyde, δ 6.63 and 7.28). This tendency was also observed in the ^{1}H NMR of **4** (Y = H, δ 5.17; CH_3O, 5.20; F, 5.28). Therefore, it seems to be general that, in 1-aryl-2-(2-furyl)-5-(2-thienyl)pyrroles, the CH/π interaction is effective in a solution and in crystalline state for settling the furan ring to be anti to the pyrrole ring. Thus, the tricyanoethenyl group is far from the 4-methoxyphenyl group. This anti conformation is in a sharp contrast with that of **1**, because the tricyanoethenyl group and the 1-aryl group are always pointed toward the same direction in the crystalline state of **1** investigated hitherto. Figure 5 summarizes the arrangement of the π-molecules in the crystal of **2c**.

The π-molecules are arranged in a ribbon. The ribbons are assembled in a side-by-side manner to form a terraced plane. The terraced planes stack vertically to form crystals. In the ribbon, the π-molecules are aligned side-by-side so that the cyano group is placed 3.97 Å from the pyrrole carbon of the neighboring π-molecule. This distance is longer than those observed in the crystal layer of **1**. It is likely that the 4-methoxyphenyl group interacts with the terminal thiophene ring through the CH/π interaction to maintain the ribbon structure. Interestingly, the close approach of π-molecules was observed between the terraced planes.

As shown in Figure 6, there are two types of stacking (Stacking A and Stacking B). These two stacking modes are alternatively arranged. In Stacking A, the furan ring and the pyrrole ring are very close to the tricyanoethenyl group of

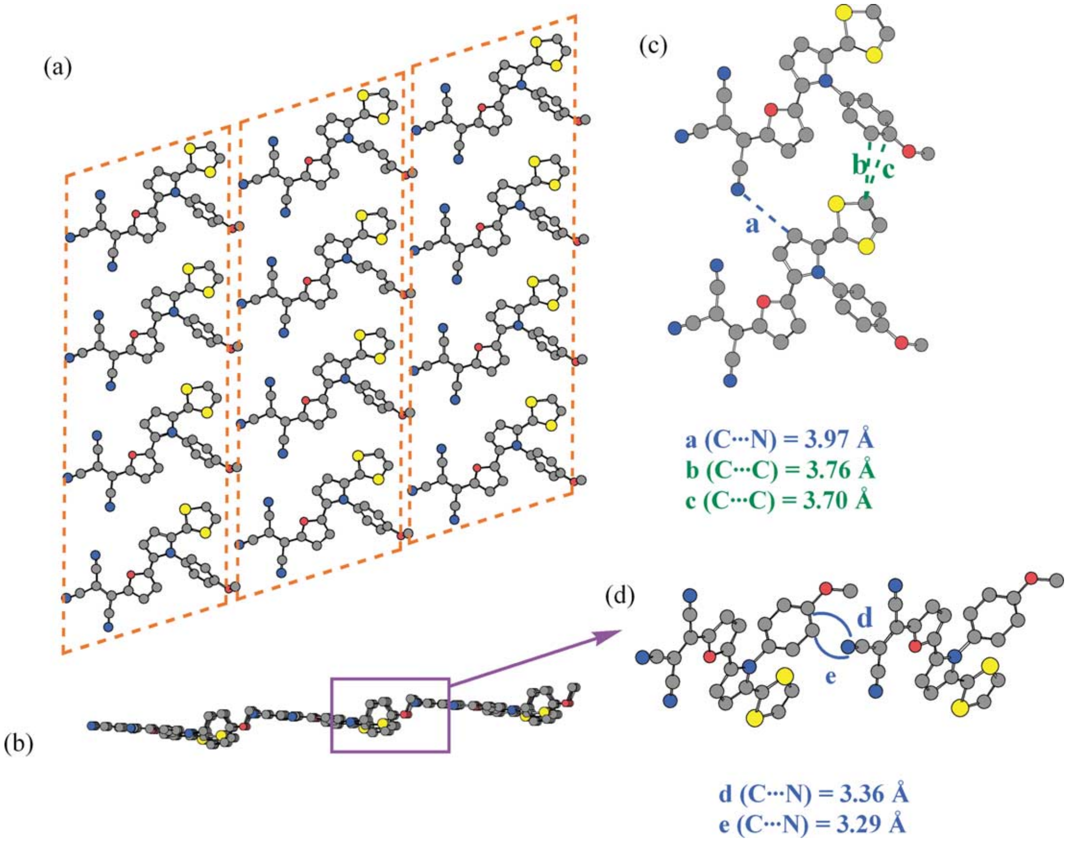

Figure 5. The terraced plane of the **2c** crystal. (a) Top view of the plane. The dashed lines depict the ribbon structures. (b) Side view of the plane. (c) The approach of two molecules in the ribbon. (d) The nearest molecules between the adjacent ribbons.

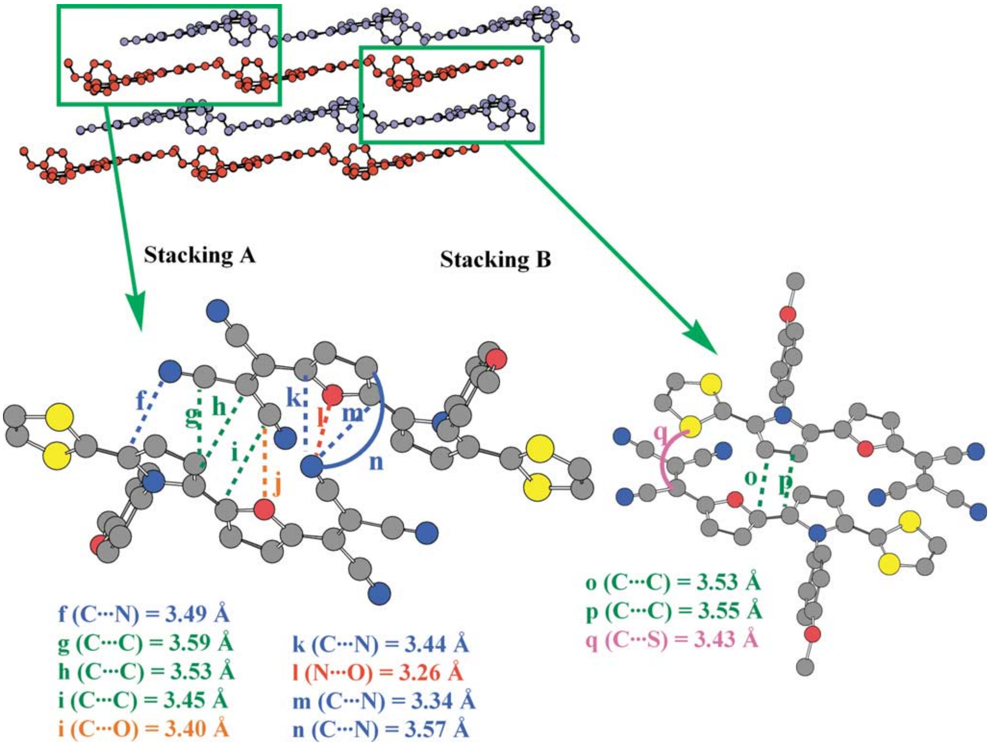

Figure 6. Interlayer interactions between the molecules in the crystal of **2c**.

the neighboring layer. The distances are in the range of 3.26–3.60 Å. In Stacking B, the pyrrole ring and the sulfur atom in the thiophene approach to the furan ring and the tricyanoethenyl group, respectively, of the adjacent layer. The thiopene ring is disordered, but the sulfur that can contact to the tricyanoethenyl group has a larger population (66%). These facts imply that the π-molecules interact to each other between the terraced planes. In the present crystals, the vertical continuous stacking of the π-molecules seems to play an important role in the appearance of metallic luster. Hence, we examined what oscillating direction of a plane-polarized light effectively contributes to the metallic luster, using the faces of the single crystal. The single crystal of **2c** (Fig. 2c) was used for this analysis. We selected three large faces [Miller indices: (001), (01−1), and (11−1)] and their reflection spectra were measured with microscopic UV–vis-NIR spectrophotometer (JASCO MSV-370) (Fig. 7). All of the faces reflect the incident light with the wavelength longer than 480 nm.

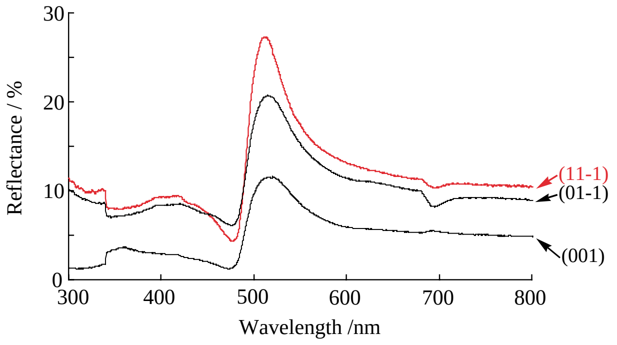

Figure 7. UV–vis-NIR reflection spectrum for each face of a single crystal of **2c**. The Miller indices of the face are shown at the right side.

Furthermore, we investigated the relationship between the arrangement of the π-systems of **2c** and the metallic luster. The (11−1) face of the single crystal was selected because this face made us view the arrangement of the molecules clearly. The plane-polarized light was incident vertically on the (11−1) surface to give a reflection spectrum. In Figure 8, the molecular arrangement is shown together with the (11−1) face. To our expectations, the reflective intensity is changeable according to the angle of the oscillation plane of the plane-polarized light, as summarized in Figure 9: the spectra were taken every 10 degrees of the oscillation plane. When the oscillation plane is approximately parallel to the layer (the angle of the oscillation plane = 0° in Figure 9), the reflection is the weakest. In contrast, we obtained the strongest reflection in case the oscillation plane is at nearly right angles to the layer (the angle of the oscillation plane = 90°). These results suggest that the interlayer movement of electrons contributes to the light reflection. This is consistent with the afore-mentioned fact that the π-orbitals of **2c** in the crystalline state are close between the layers.

3. Conclusion

Interestingly, 1-aryl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrroles formed crystals with green metallic luster. In their solid-state UV–vis–NIR diffuse reflection–absorption spectra, broad absorption bands appeared in the range of 550–900 nm, corresponding to the appearance of the metallic luster. Further, strong absorption was observed below 520–540 nm, resulting in the appearance of greenish color. From single-crystal X-ray crystallographic analysis of 1-(4-methoxyphenyl)-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole (**2c**), it was shown that, in a crystalline state,

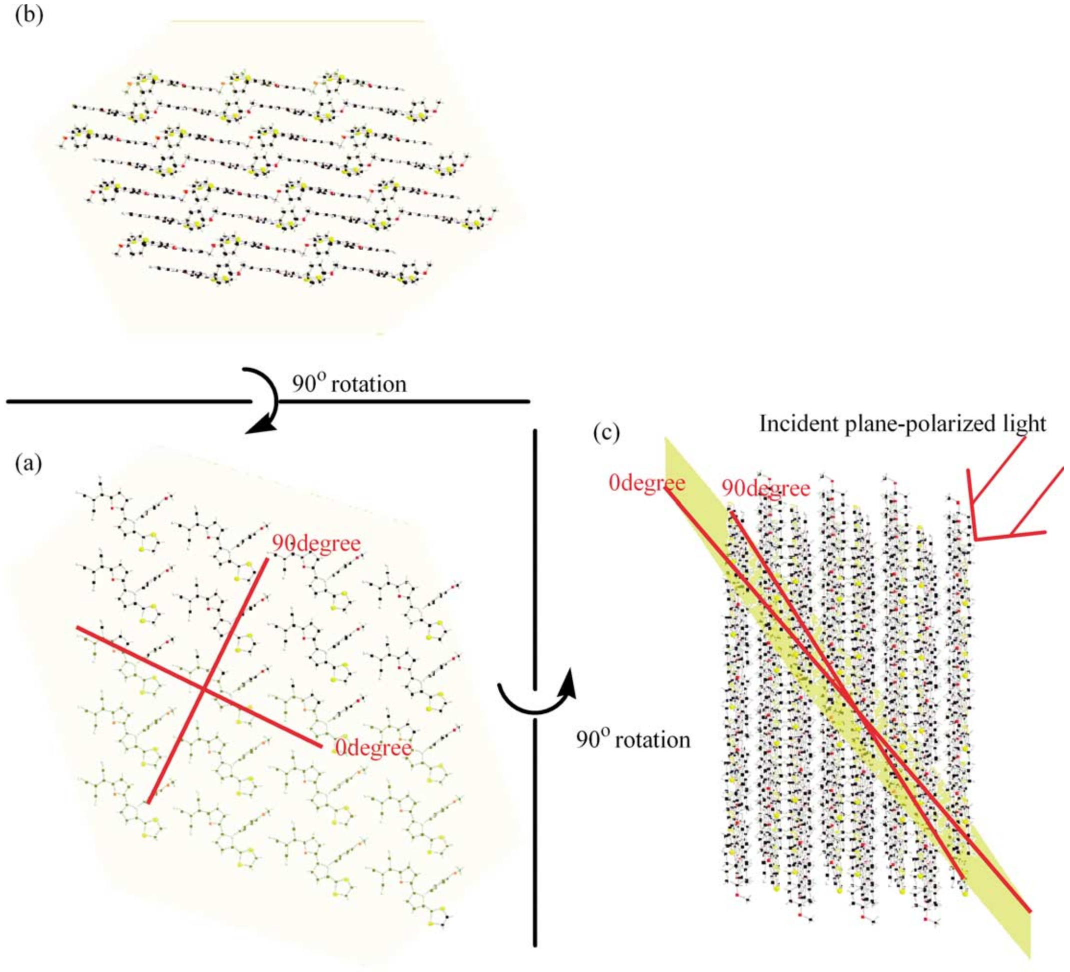

Figure 8. The terraced layers, the (11 − 1) face (yellow plane), and the plane-polarized light that is incident vertically to the (11 − 1) face. (a) The front view of one terraced layer and the (11 − 1) face. The red lines show the plane angle of the indient light. (b) The top view. Eight layers are shown. (c) The side view of eight layers.

the thiophene–pyrrole–furan–tricyanoethenyl π-system of **2c** is approximately flat and the flat molecules of **2c** are arranged in a ribbon structure. The ribbons are assembled side-by-side to form a terraced layer. The layers stack to form the crystal structure. The stacking of the layers makes that the π-orbitals of **2c** much close to each other. This seems to be related with the appearance of metallic luster.

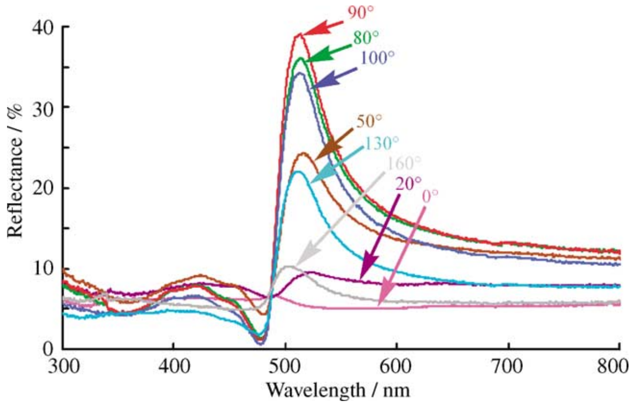

Figure 9. UV–vis–NIR Reflection spectra of the (11 − 1) face with plane-polarized light. Refer the angle of the oscillation plane of the incident light to Figure 8.

4. Experimental

Melting points are determined on a hot-stage microscope apparatus (Yanaco 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-phenyl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole. A typical procedure

A solution of 1-(2-furyl)-4-(2-thienyl)-1,4-butanedione (0.500 g, 1.72 mmol), aniline (1.03 g, 11.0 mmol), and *p*-toluenesulfonic acid monohydrate (0.123 g, 0.647 mmol) in toluene (10 mL) was refluxed under occasionally removing the distillated toluene. The reaction progress was monitored with TLC, showing that the reaction completed after 2 h. The solution was subjected to column chromatography on silica gel (eluent: toluene) to give

2-(2-furyl)-1-phenyl-5-(2-thienyl)pyrrole (**4a**) as colorless solid (0.304 g: 60% yield). This product was too sensitive to air to be isolated in a completely pure form. From the following physical data, we confirmed its structure and subjected it to the next reaction.

Compound **4a**. Colorless solid; mp 130.4–131.4 °C; ^{1}H NMR (CDCl$_3$) δ 5.17 (dd, $J=0.7$, 3.4 Hz, 1H), 6.17 (dd, $J=$ 1.8, 3.4 Hz, 1H), 6.53 (dd, $J=1.2$, 3.6 Hz, 1H), 6.56 (d, $J=$ 3.8 Hz, 1H), 6.66 (d, $J=3.8$ Hz, 1H), 6.80 (dd, $J=3.6$, 5.2 Hz, 1H), 7.04 (dd, $J=1.2$, 5.2 Hz, 1H), 7.28 (dd, $J=0.7$, 1.7 Hz, 1H), 7.34–7.37 (m, 2H), 7.50–7.51 (m, 3H); IR (KBr) 1496, 1412, 1203, 1011, 773, 762, 742, 694, 679, 594 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{13}NOS$ 291.0718, found 291.0693.

A mixture of **4a** (0.253 g, 0.870 mmol, 1.00 equiv) and tetracyanoethylene (0.135 g, 1.05 mmol, 1.21 equiv) in anhydrous DMF (10 mL) was stirred for 1.5 h at room temperature. The reaction mixture was poured into brine (100 mL), and the resulting mixture was extracted with ethyl acetate (100 mL × 3). The combined organic layers were dried (MgSO$_4$) and evaporated in vacuo. The dark blue residue was purified by column chromatography on silica gel using toluene as an eluent to give **2a** as greenish metal-lustrous crystals (0.279 g: 82% yield).

4.1.1. 1-Phenyl-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole (2a).

Greenish metal-lustrous crystals; mp 197.7–198.2 °C (from CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.21 (broad d, $J=3.2$ Hz, 1H) [this signal became a doublet ($J=$ 4.3 Hz) at -30 °C], 6.79 (d, $J=4.3$ Hz, 1H), 6.79 (dd, $J=$ 1.1, 3.8 Hz, 1H), 6.89 (dd, $J=3.7$, 5.1 Hz, 1H), 7.18 (dd, $J=1.1$, 5.1 Hz, 1H), 7.19 (broad s, 1H), 7.34 (d, $J=4.3$ Hz, 1H), 7.42 (d, $J=7.4$ Hz, 2H), 7.59–7.71 (m, 3H); IR (KBr) 2214, 1593, 1518, 1471, 1442, 1352, 1248, 1211, 1036, 978 cm^{-1}. UV–vis (THF, 3×10^{-5} M) λ_{max} (nm) (ε, M^{-1} cm^{-1}) 607 (36,600). Anal. Calcd for $C_{23}H_{12}N_4OS$: C, 70.39; H, 3.08; N, 14.28. Found: C, 70.47; H, 3.09; N, 14.32.

4.1.2. 1-(4-Flurophenyl)-2-(2-furyl)-5-(2-thienyl)pyrrole (4b).

Pale yellow crystals (77% yield); mp 153.3–154.0 °C (from acetone); ^{1}H NMR (CDCl$_3$) δ 5.28 (d, $J=3.5$ Hz, 1H), 6.20 (dd, $J=1.9$, 3.2 Hz, 1H), 6.55 (d, $J=3.8$ Hz, 1H), 6.57 (d, $J=3.8$ Hz, 1H), 6.64 (dd, $J=0.9$, 3.5 Hz, 1H), 6.84 (dd, $J=3.7$, 5.2 Hz, 1H), 7.07 (dd, $J=1.1$, 5.1 Hz, 1H), 7.15–7.21 (m, 2H), 7.28–7.35 (m, 3H); IR (KBr) 3116, 3072, 1508, 1414, 1215, 841, 762, 735, 700, 681 cm^{-1}. Anal. Calcd for $C_{18}H_{12}FNOS$: C, 69.88; H, 3.91; N, 4.53. Found: C, 69.86; H, 3.96; N, 4.39.

4.1.3. 1-(4-Fluorophenyl)-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole (2b).

Greenish metal-lustrous crystals (82% yield); mp 177.4–177.9 °C (from ethyl acetate); ^{1}H NMR (CDCl$_3$) δ 5.33 (broad s, 1H) [this signal became a doublet ($J=4.3$ Hz) at -30 °C], 6.75 (d, $J=$ 4.3 Hz, 1H), 6.83 (dd, $J=1.2$, 3.8 Hz, 1H), 6.92 (dd, $J=3.8$, 5.2 Hz, 1H), 7.20 (dd, $J=1.1$, 5.1 Hz, 1H), 7.24 (broad s, 1H), 7.31 (d, $J=4.0$ Hz, 1H), 7.31–7.33 (m, 2H), 7.40–7.44 (m, 2H); IR (KBr) 2216, 1520, 1510, 1473, 1442, 1358, 1252, 1211, 1038, 978 cm^{-1}. UV–vis (THF, 3×10^{-5} M) λ_{max} (nm) (ε, M^{-1} cm^{-1}) 603 (37,300). Anal. Calcd for $C_{23}H_{11}FN_4OS$: C, 67.31; H, 2.70; N, 13.65. Found: C, 67.26; H, 2.62; N, 13.57.

4.1.4. 2-(2-Furyl)-1-(4-methoxyphenyl)-5-(2-thienyl)pyrrole (4c).

Pale yellow solid (41% yield; air-sensitive); mp 140.8–141.2 °C; ^{1}H NMR (CDCl$_3$) δ 3.89 (s, 3H), 5.20 (dd, $J=0.6$, 3.4 Hz, 1H), 6.18 (dd, $J=1.8$, 3.4 Hz, 1H), 6.56 (d, $J=4.0$ Hz, 1H), 6.60 (dd, $J=1.1$, 3.7 Hz, 1H), 6.64 (d, $J=4.0$ Hz, 1H), 6.82 (dd, $J=3.6$, 5.1 Hz, 1H), 7.00 (d, $J=$ 8.9 Hz, 2H), 7.04 (dd, $J=1.1$, 5.1 Hz, 1H), 7.24–7.29 (m, 3H); IR (KBr) 1516, 1412, 1296, 1250, 1203, 1026, 833, 762, 741, 702 cm^{-1}. HRMS (FAB) calcd for $C_{19}H_{15}NO_2S$ 321.0824, found 321.0805.

4.1.5. 1-(4-Methoxyphenyl)-2-(2-thienyl)-5-(5-tricyanoethenyl-2-furyl)pyrrole (2c).

Greenish metal-lustrous crystals (61% yield); mp (from CHCl$_3$) 212.8–213.2 °C; ^{1}H NMR (CDCl$_3$) δ 3.95 (s, 3H), 5.28 (broad s, 1H) [this signal became a doublet ($J=4.3$ Hz) at -30 °C], 6.76 (d, $J=4.3$ Hz, 1H), 6.87 (dd, $J=1.2$, 3.7 Hz, 1H), 6.92 (dd, $J=$ 3.7, 5.0 Hz, 1H), 7.09 (d, $J=8.9$ Hz, 2H), 7.18 (dd, $J=1.2$, 5.1 Hz, 1H), 7.20 (broad s, 1H), 7.31 (d, $J=4.3$ Hz, 1H), 7.32 (d, $J=8.9$ Hz, 2H); IR (KBr) 2218, 1523, 1442, 1473, 1362, 1252, 1209, 1171, 1032, 980 cm^{-1}. UV–vis (THF, 3×10^{-5} M) λ_{max} (nm) (ε, M^{-1} cm^{-1}) 613 (34,900). Anal. Calcd for $C_{24}H_{14}N_4O_2S$: C, 68.23; H, 3.34; N, 13.26. Found: C, 68.00; H, 3.40; N, 13.22.

4.2. X-ray crystallographic analysis of a single crystal of 2c

Data collection was performed on a Mac Science MXC18 four-circle diffractometer with graphite monochromated Cu Kα radiation ($\lambda=1.54178$ Å) using the θ–2θ scan technique at 298 K. The structure was solved by direct methods and refined by full-matrix least-squares methods against F (SIR 92[20]) 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. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 286697. 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].

Crystal data of **2c**. $C_{24}H_{14}N_4O_2S$, $M_r=422.46$, greenish metal-lustrous plates, triclinic, space group $P\bar{1}$, $a=$ 8.993(4) Å, $b=10.023(5)$ Å, $c=12.316(5)$ Å, $\alpha=$ 99.25(4)°, $\beta=99.40(3)$°, $\gamma=104.48(4)$°, $V=1036.4(8)$ Å^3, $Z=2$, $D_{calcd}=1.354$ g cm^{-3}, $F(000)=436$, $\mu=1.63$ cm^{-1}, 4176 observed reflections($I>2.00\sigma(I)$), 334 parameters, $R=0.071$, $wR=0.111$.

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