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Headline Articles

Facile Formation of Stable Crystals with Gold-like Metallic Luster from Organic Molecules: 1-Aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles

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The derivatives of 1-phenyl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (**1a**) formed crystals with gold-like or bronze-like metallic luster. When a small substituent is located at the para position of the 1-phenyl group, gold-like lustrous crystals were formed. In contrast, the derivatives of **1** having a longer alkyl chain at the para position of the 1-phenyl group gave bronze-like crystals. The gold-like lustrous crystals have a sheet structure. In the sheet, the molecules of **1** are close to each other via the intermolecular interaction of cyano nitrogen with the hydrogen of the nearest thiophene or pyrrole ring, which enables the side-by-side interaction of the cyano group with the nearest thiophene and pyrrole rings. The bronze-like crystals have a lamella structure of the long alkyl chains that is sandwiched by two π-electron walls. In the wall, the 2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole moieties are arranged in a ribbon structure to interact to each other. The relationship of the arrangement of the 2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole moieties with the metallic color of the crystals is discussed.

Hitherto, chemists have succeeded in producing metal-like organic and organometallic materials. These include electron-conducting polymers[1] such as 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 weights were known to exhibit metallic luster. Recently, Cava et al. reported furan- and pyrrole-containing analogs of 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene that formed golden yellow crystals.[9] Holmes et al. synthesized a fused thiophene, 2,2′-bi(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT) which gave a microcrystalline powder with gold-like luster.[10] The molecules of BDT were shown by X-ray crystallographic analysis to adopt a completely coplanar conformation with a unique π–π stacking. It was indicated that the metallic luster results mainly from vertical interaction among the π-molecular orbitals of BDT and intermolecular interaction between the sulfur atoms. Here, we report novel organic compounds, 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles (**1**), which easily form gold-like and bronze-like lustrous crystals (Fig. 1).

Graduate School of Science and Technology

Results and Discussion

Various derivatives of 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles (**1**) can be easily synthesized. Reaction of 1-aryl-2,5-di(2-thienyl)pyrroles (**2**)[11,12] with tetracyanoethylene occurred at ambient temperature in *N*,*N*-dimethylformamide (DMF) to produce many kinds of **1** that are summarized in Scheme 1.[13] They are soluble in common organic solvents such as chloroform, acetone, and THF to give a deep blue solution because they absorb visible light around the wavelength of 600–620 nm (Fig. 2). To our surprise, slow evaporation of the solvent gave crystals with gold-like metallic luster (Figs. 1a and 1b). All of the compounds except for **1c** exhibited good crystallinity. Interestingly, gold-like lustrous crystals were formed in the case that the *N*-substituent of **1** is the phenyl group having a small substituent (shorter than C3-chain length) at the para position (**1a**–**1j**). Typical photographs of the crystals are shown in Fig. 1. The crystals have shiny flat surfaces as if they are metal. The crystals of **1** were entirely stable in air and no change was observed after being allowed to stand at ambient temperature for more than three years. The gold-like lustrous crystals could be easily formed. When one

drop of a $CHCl_3$ solution of **1** was placed on a glass plate, small crystals were formed as soon as the solvent evaporated.

The typical solid-state UV-vis-NIR diffuse reflection-absorption spectra of these crystals (**1a**, **1b**, **1d**, **1g**, and **1j**) are shown in Fig. 3. Instead of the absorption band around 600–620 nm in solution, strong absorption appeared at longer wavelengths, corresponding to the band gap (or exciton) that is below 1.4 eV, in range of infra-red (longer than 900 nm). This indicates that strong intermolecular interaction among the π-orbitals of **1** is possible in the crystalline state.[14] Generally speaking, the appearance of a solid depends on the degree of absorption and reflectance in the visible region of the spectrum, where photon energies are in the range of 1.5–3 eV (800–400 nm wavelength). With a band gap below 1.5 eV, in the infrared, the solid may appear dark in color or shiny metallic, depending on the reflectivity.[14] The present crystals (**1a**–**1j**) are the latter case. Further, strong absorption appeared below 550–540 nm with a maximum at 490–480 nm in the solid

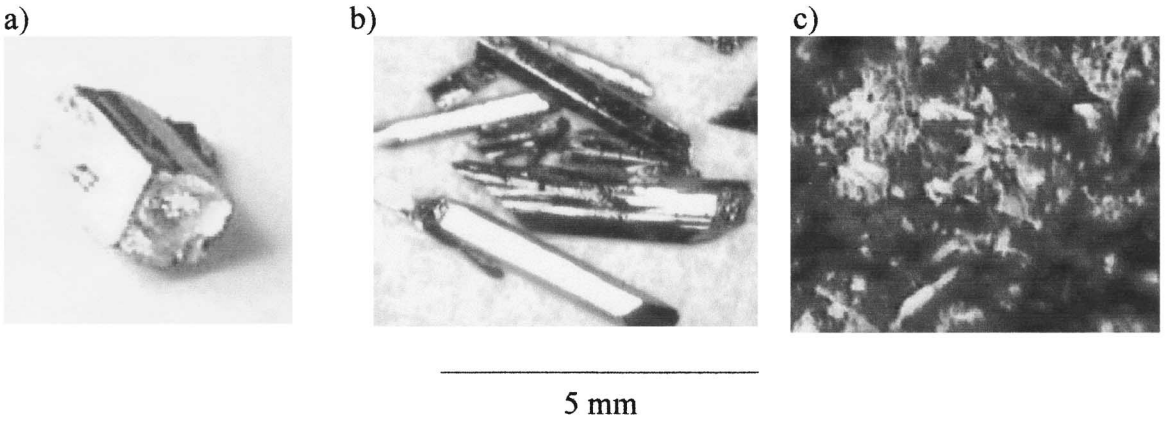
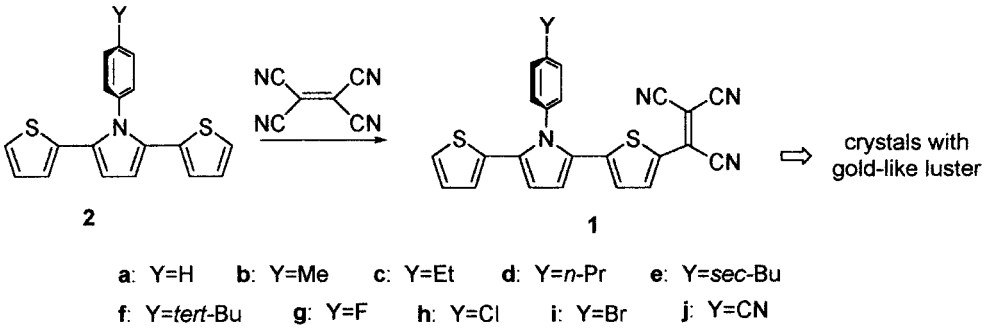


Fig. 1. Typical photographs of gold-like and bronze-like lustrous crystals (see front cover) : a) **1d**. b) **1g**. c) **1k**.



Scheme 1.

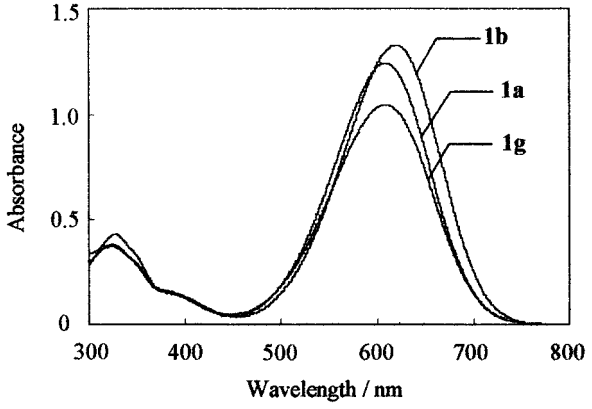


Fig. 2. Typical UV-vis absorption spectra of **1**: **1a** (λ_{max} = 609 nm), **1b** (λ_{max} = 621 nm) and **1g** (λ_{max} = 610 nm) in THF (3×10^{-5} M) (1M = 1 mol dm^{-3}).

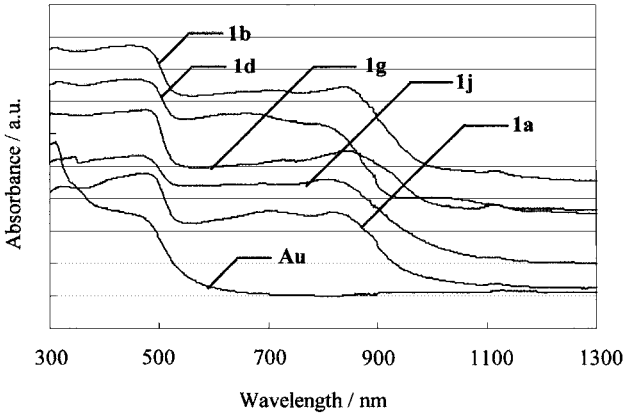


Fig. 3. UV-vis-NIR diffuse reflection-absorption spectra of the gold-like lustrous crystals **1a**, **1b**, **1d**, **1g**, **1j**, and Au plate (bottom line).

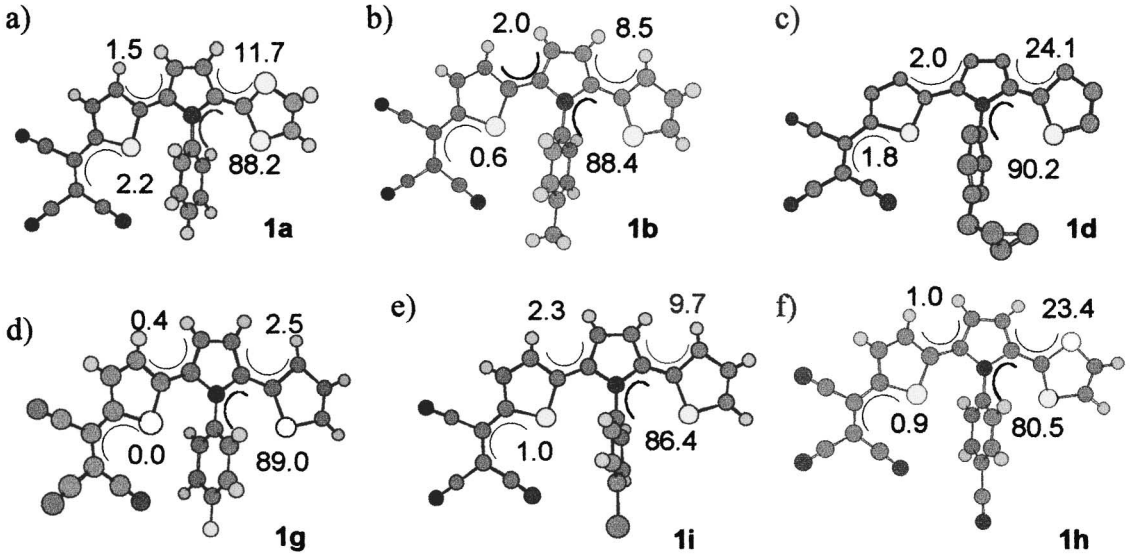


Fig. 4. Conformation of the molecule in crystals. a) **1a**. b) **1b**. c) **1d**. d) **1g**. e) **1i**. f) **1j**. The values mean the dihedral angle of the day in which it is located. The value of 80–90° is the torsion angle between the pyrrole and aryl rings. For the molecules **1a** and **1j**, the disorder of the terminal thiophene ring was observed. In **1d**, all H atoms are omitted for clarity because some H atoms cannot be assigned precisely due to the disordered propyl group.

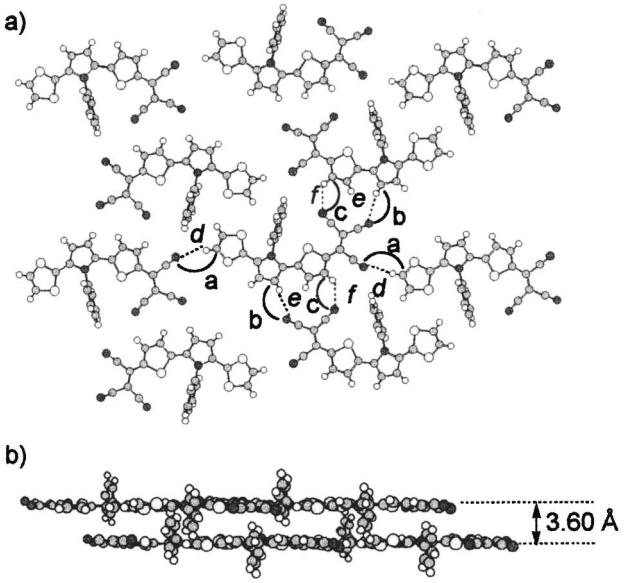


Fig. 5. The crystal structure of **1a**. a) The coplanar sheet-like structure. The distance between C and N atoms: a, 3.63 Å; b, 3.58 Å; c, 3.33 Å. The distance between H and N atoms: d, 2.67 Å; e, 2.68 Å; f, 2.56 Å. b) A side view of the stacking layers. The layer distance is 3.60 Å (by PXRD).

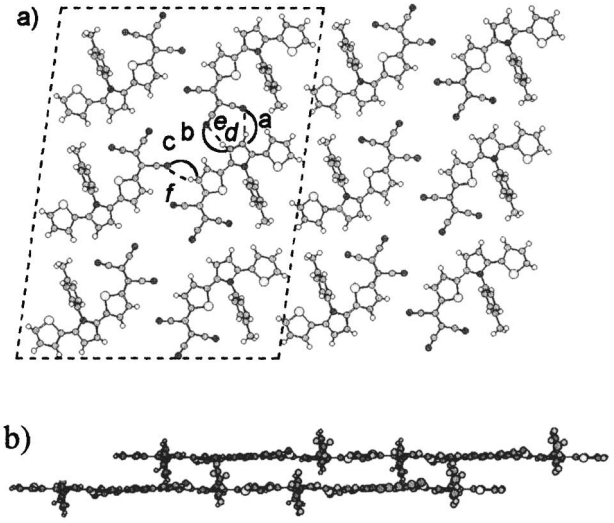
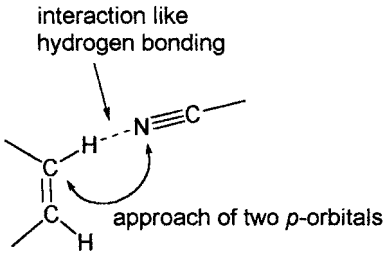


Fig. 6. The crystal structure of **1b**. a) The coplanar sheet-like structure. The distance between N and C atoms: a, 3.57 Å; b, 3.45 Å; c, 3.39 Å. The distance between N and H: d, 2.68 Å; e, 2.61 Å; f, 2.63 Å. b) A side view of the stacking layers. The layer distance is 3.60 Å (by PXRD).

state spectra of **1a**–**1j**. Consequently, the spectra of the present crystals in the region of visible light (400–800 nm) resemble that of gold plate, as shown in Fig. 3.

Fortunately, crystals of sufficient quality for structural studies were obtained for the compounds **1a**, **1b**, **1d**, **1g**, **1i**, and **1j**. It is noteworthy that all of these crystals contain two-dimensional layers. As described in the literature,[15] this seems to indicate that the molecules in one layer are held together by strong intermolecular interactions and the adjacent layers are held by weak interactions. The molecules in these crystals adopt a flat conformation as summarized in Fig. 4. The tricyanoethenyl group, 2,5-thienylene ring, and the central pyrrole ring are arranged with perfect coplanarity (torsion angle $< 3°$), but the terminal thiophene ring was somewhat deviated from the pyrrole plane. The crystal structures of **1a** (Y = H) and **1b** (Y = CH_3) are given in Figs. 5 and 6, respectively.

In both of the crystals, the flat molecules form completely planar sheets which stack to produce the crystal lattice. In the sheet of **1a** (Fig. 5), the molecules are held together with inter-



Scheme 2.

molecular interactions between the cyano nitrogen and the hydrogen of pyrrole or thiophene (marked with the letters d, e, and f). Hitherto, a cyano group has been reported to assist the formation of a sheet structure in a crystal with the aid of intermolecular contact with aromatic hydrogen[16] or chalcogen atoms.[17] In the present cases, the cyano nitrogen approaches the olefinic hydrogen of pyrrole or thiophene ring so that the cyano nitrogens are close to the sp^2 carbons of pyrrole and thiophene (Scheme 2) at many points (marked with a, b, and c: 3.3–3.6 Å).

The sheet structure of **1b** (Fig. 6) is different from that of **1a**. The molecules of **1b** in the sheet are arranged by means of the interaction of the cyano nitrogen with the hydrogen of thiophene (surrounded by a dotted line). Another interaction was observed between cyano nitrogen and the pyrrole hydrogen (d and e). As a result of these interactions, the cyano nitrogens are close to the sp^2 carbons of pyrrole and thiophene (marked with a, b, and c: 3.3–3.6 Å). As summarized in Fig. 7, the crystal structures of **1d**, **1g**, **1i**, and **1j** are similar to that of **1b**.

As mentioned above, 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles (**1k**–**1p**) that have long alkyl groups at the para position of the central phenyl group formed crystals with bronze-like metallic luster (Fig. 1c). Their solid-state UV-vis-NIR diffuse reflection-absorption spectra that are shown in Fig. 8 are quite different from those of the crystals of **1a**–**1j** that exhibit gold-like metallic luster. Interestingly, the powder X-ray diffraction patterns of these crystals (Scheme 3) exhibited intense peaks in the lower-angle region [**1k** (n = 4), 18.7 Å; **1l** (n = 6), 20.4 Å; **1m** (n = 10), 24.3 Å; **1n** (n = 12), 25.9 Å; **1o** (n = 14), 27.9 Å; **1p** (n = 16), 29.5 Å]. It is likely that these intense signals correspond to the layer distance of

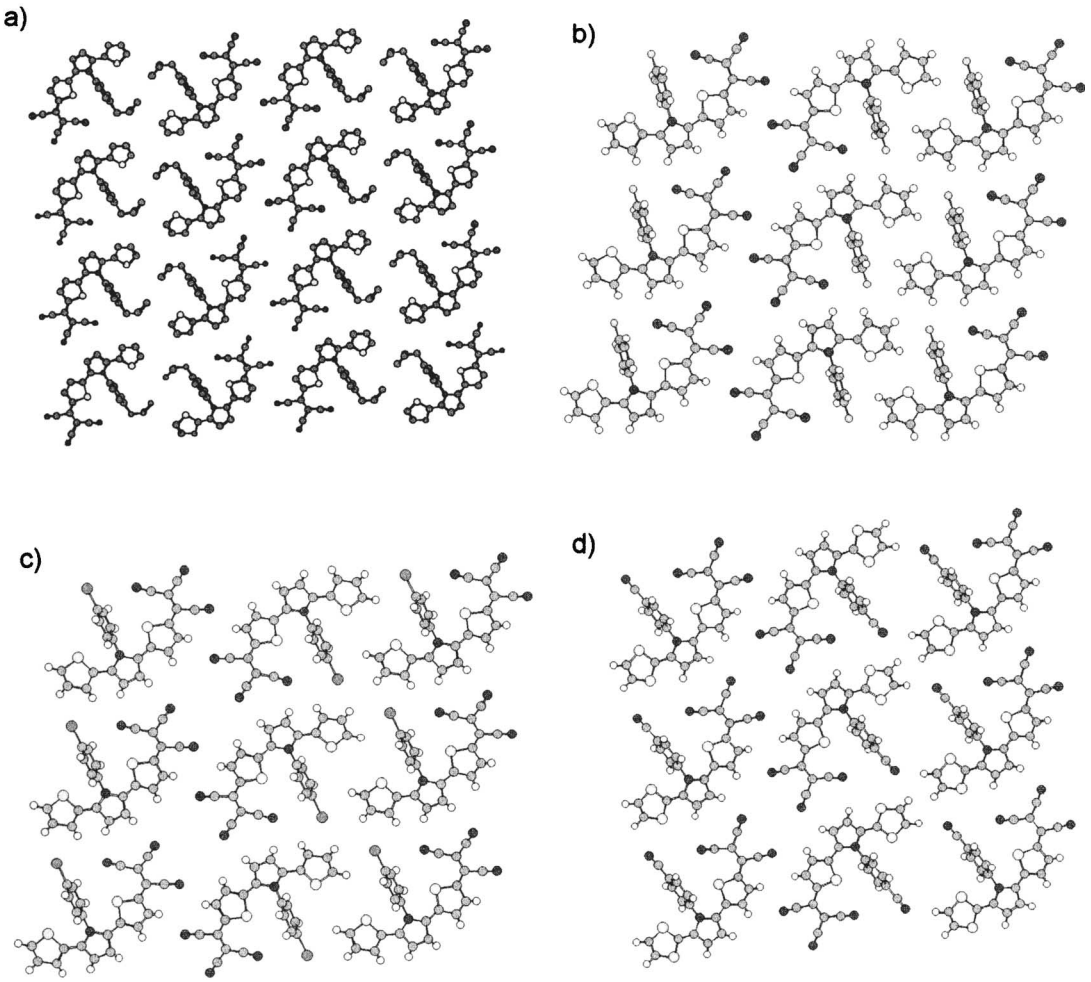


Fig. 7. The sheet structures (top view) in crystal. a) **1d**. Some H atoms could not be assigned so that all H atoms are omitted for clarity. The disorder of the central carbon of propyl group was observed. b) **1g**. c) **1i**. d) **1j**. The disorder of the terminal thiophene ring was observed.

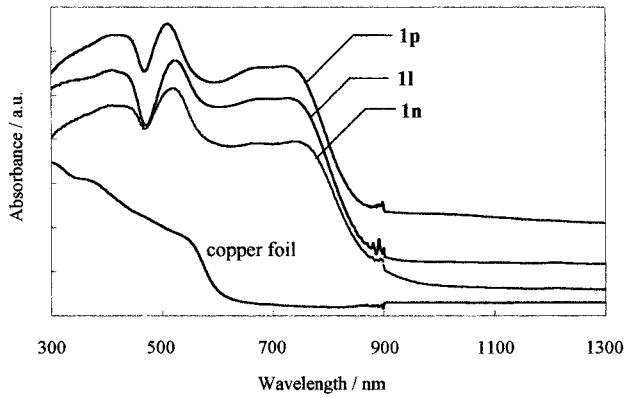
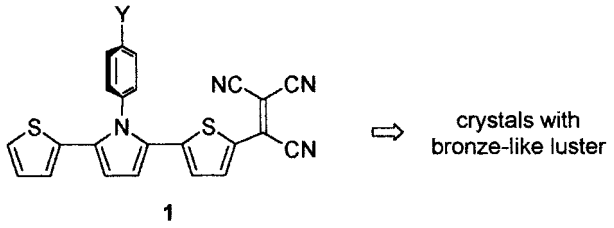


Fig. 8. Typical UV-vis-NIR diffuse reflection-absorption spectra of the bronze-like lustrous crystals (**1l**, **1n**, and **1p**) and copper foil.



Scheme 3.

the crystal. We could obtain a linear relationship of the length of alkyl (Y) group with the layer distance (Fig. 9). It is noteworthy that the layer distances of the gold-like crystals of **1a–d** are almost same (about 3.60 Å) and deviated from the linear relationship. This line can be represented with an equation:

$$d = 0.91 \times n + 15.0$$

wherein d and n are the layer distance (Å) and the carbon number of the alkyl chain, respectively. Thus, we can envisage the crystal structures of **1k–1p** that have a lamella structure of the alkyl chain sandwiched between the walls (width: about 15.0/2 Å) that are constructed by stacking of the π-systems of **1**, as depicted illustratively in Fig. 10. The value of 0.91, the coefficient of *n*, means that the alkyl chain is not perpendicular to the wall, which is common to the crystals of **1k–1p** bearing a long alkyl chain. The inclination angle of the alkyl chain is calculated to be 44°, based on the length of tetradecyl chain (17.8 Å in the crystal structure of **1o**·acetone) and the value of 0.91 × 14 Å. In order to confirm the illustration (Fig. 10), we concentrated on the formation of single crystals of **1k–1p** that are suitable for X-ray crystallographic analysis. By recrystallization of **1o** (Y = n-$C_{14}H_{29}$) from acetone, we fortunately obtained single crystals with sufficient quality for structural study. These crystals include an equimolar amount of acetone. The PXRD pattern of the single crystals showed a sharp signal at a lower angle (d = 29.63 Å) together with two sharp signals (d = 14.87 Å and 9.92 Å). In the crystalline state, the expected lamella structure of the alkyl chains was observed (Fig. 11). The lamellas stack to construct the layer of the tetradecyl chains. The lamella layer was sandwiched between the walls that consist of 1-phenyl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole systems. Acetone molecules are located between the walls. The solid-state UV-vis-NIR diffuse reflection-absorption spectra are different from those of the gold-like lustrous crystals of **1a–1d**. The metallic luster of the crystal indicates the presence of strong interactions among the π-systems in the wall. The wall is constructed by stacking of the ribbon-like structures of 2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole π-systems. In the ribbon, the π-systems are arranged via the so-called hydrogen bond of the cyano nitrogen and terminal thiophene hydrogen so that the p-orbital of cyano group are close enough to the p-orbital of the thiophene carbon to interact with each other in a side-by-side manner.

Finally, we wish to comment here on the interaction of the molecular π-orbitals between the neighboring sheets. The interaction seems to be possible because these planar sheets are close enough (average layer distance: 3.6–3.7 Å by PXRD) to interact with each other. It was found that the compound (**3**)(Chart 1) bearing a long alkyl chain (decyl group) at the *ortho* position of the 1-phenyl group also formed crystals with gold-like metallic luster. In these crystals, two conformers of **3** are paired as depicted in Fig. 12. These pairs were arranged in a side-by-side manner to form two sheets that were separated

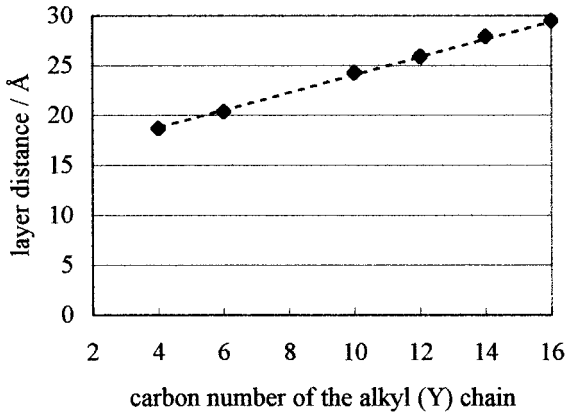


Fig. 9. Relationship between the carbon number of the alkyl (Y) chain and the layer distance in crystals of **1**.

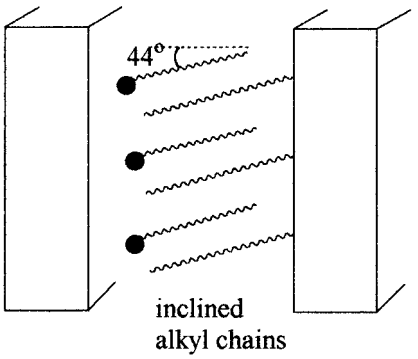


Fig. 10. The schematic desctiption of the crystal structure of the compounds (**1k–p**) having a long alkyl chain as Y.

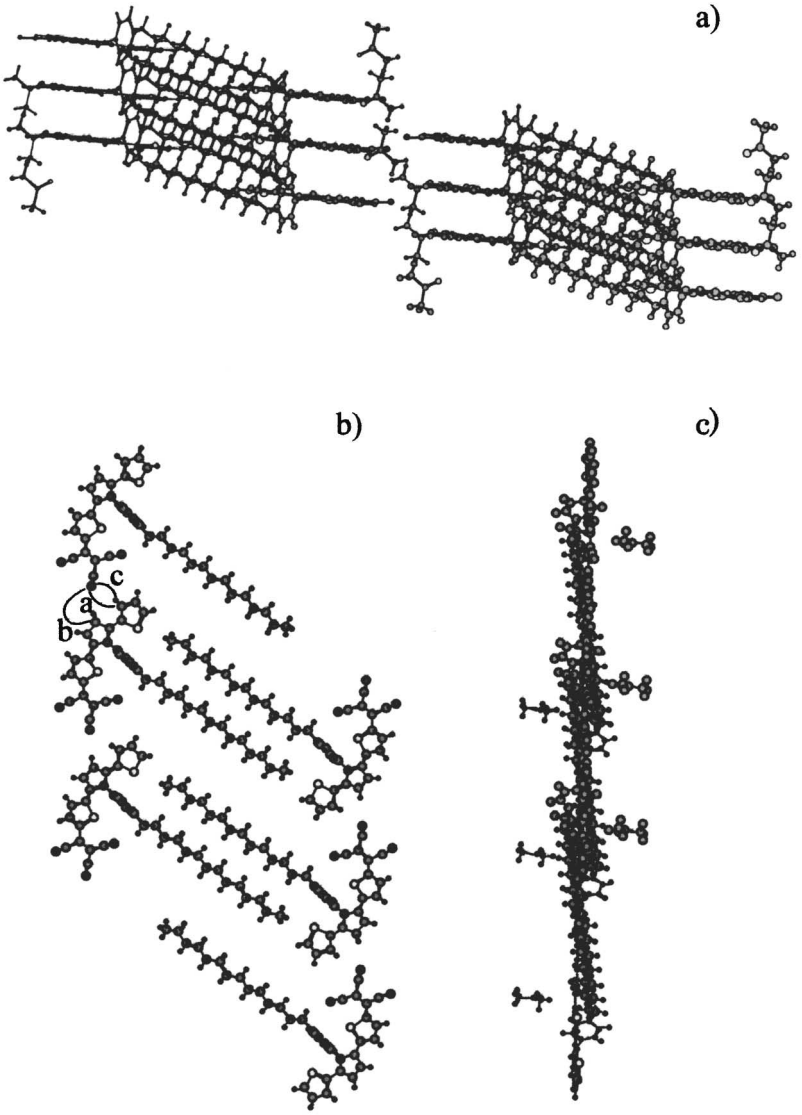
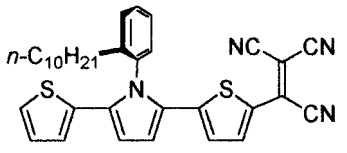


Fig. 11. Crystal structure of **1o**·acetone. a) A side view of the crystal. b) The top view of one layer. For simplicity, the acetone molecules are omitted. The distance between C and N atoms: a, 3.58 Å; b, 3.67 Å. The distance between H and N atoms: c, 2.64 Å. c) The side view of the plane b).



3

Chart 1.

by the decyl chain layer. Consequently, a bilayer structure was constructed (Fig. 13). The molecules of **3** in Chart 1 are enough close to each other via the hydrogen bonding between the cyano nitrogen and the olefinic hydrogen (Fig. 13a). Since their solid diffuse reflection-absorption spectra in the visible light region resembled that of gold plate (Fig. 14), we concluded *that the arrangement of the molecules in a planar sheet plays an important role in the origin of the gold-like metallic luster*.

Experimental

General Methods. 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 absorption spectra were recorded in THF (concentration: 3×10^{-5} M) (1 M = 1 mol dm^{-3}) on a JASCO V-570 spectrophotometer. Solid-state UV-vis-NIR diffuse reflection-absorption spectra were also recorded on a JASCO V-570 spectrophotometer: single crystals were uniformly broken into powder and then put into a quartz glass cell, and the response was adjusted to the absorption mode for measurement. Infrared spectra were measured on a JASCO FT/IR-350 spectrophotometer. Melting points are determined on a hot-stage microscope ap-

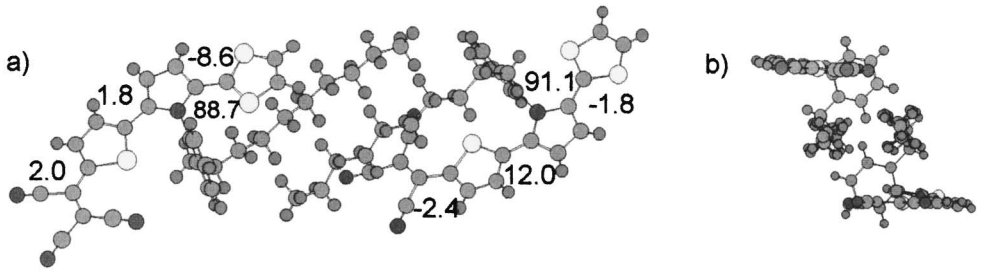


Fig. 12. Conformation of **3** in crystals. a) Two conformations of **3** were paired. The values mean the dihedral angle of the bay in which it is located. The values 88.7 and 91.1 are the torsion angles between the pyrrole and *o*-decylphenyl rings. b) The view from the left bottom of the paired conformations.

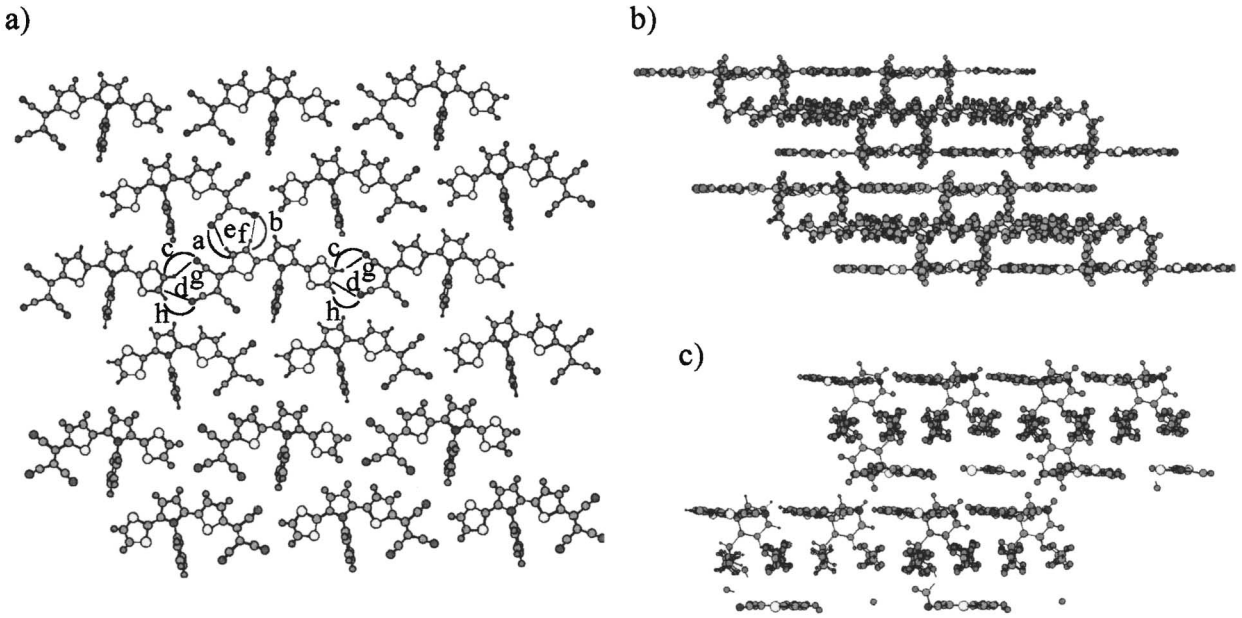


Fig. 13. Crystal structure of **3**. a) The top view of a layer. The alkyl chains are omitted for simplicity. The distance between C and N atoms: a, 3.52 Å; b, 3.53 Å; c, 3.55 Å; d, 3.41 Å. The distance between N and H atoms; e, 2.66 Å; f, 2.63 Å; g, 2.63 Å; h, 2.61 Å. b) A side view. c) A side view perpendicular to b).

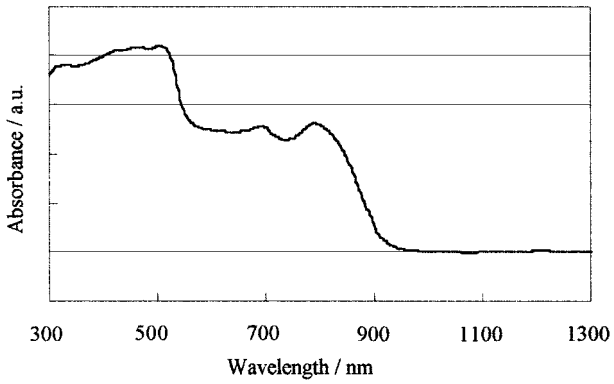


Fig. 14. UV-vis-NIR diffuse reflection spectra of gold-like lustrous crystals of **3**.

paratus (Yanaco MP-500D) and are uncorrected. Elemental analysis was performed by the Chemical Analysis Center of Chiba University. All powder X-ray diffraction (PDXR) analyses were taken on a MAC Science MXP powder diffractometer using graphite-monochromated Cu $K\alpha$ 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.

Typical Procedure for the Preparation of 1-Aryl-2,5-di(2-thienyl)pyrrole (2). Method A. A 50 mL three-necked round-bottomed flask equipped with a Dean-stark trap, a reflux condenser (used as one set with the Dean-stark trap), and a nitrogen-filled balloon was charged with 1,4-di(2-thienyl)-1,4-butanedione (500 mg, 2.00 mmol) and the corresponding aniline derivative (8.00 mmol) in 30 mL of 3:1 (v/v) toluene–acetic acid solution. The reaction mixture was refluxed at 140–150 °C (oil bath temperature) for suitable times (monitored the reaction progress with TLC) and then cooled to room temperature. After the dark brown solution was transferred to a 300 mL beaker, a saturated Na_2CO_3 aqueous solution was added to make the reaction mixture basic. The organic layer was separated and then the aqueous layer was extracted with toluene (10 mL × 2). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by column chromatography (silica gel, toluene) and then recrystallized from acetone to afford **2** as a pure product.

Method B. A mixture of 1,4-di(2-thienyl)-1,4-butanedione (500 mg, 2.00 mmol), the corresponding aniline derivative (8.00 mmol), and *p*-toluenesulfonic acid monohydrate (76.2 mg, 0.400 mmol) was heated at 110 °C for 5–24 h under stirring (monitored the reaction progress with TLC) and then cooled to room temperature. After toluene (20–30 mL) was added to dissolve the crude product, the insoluble solid was filtered off. The obtained toluene solution was concentrated in vacuo and then purified by a procedure similar to that described in method **A**.

1-Phenyl-2,5-di(2-thienyl)pyrrole (2a). Method **B**, 83% yield: pale yellow crystals; mp 180.8–181.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.51 (dd, J = 1.1 and 3.7 Hz, 2H), 6.54 (s, 2H), 6.81 (dd, J = 3.7 and 5.2 Hz, 2H), 7.05 (dd, J = 1.1 and 5.1 Hz, 2H), 7.30–7.48 (m, 5H); IR (KBr) 1497, 1413, 1349, 1200, 1041, 843, 773, 695 cm^{-1}. Anal. Calcd for $C_{18}H_{13}NS_2$: C, 70.32; H, 4.26; N, 4.56%. Found: C, 70.02; H, 4.20; N, 4.50%.

1-*p*-Tolyl-2,5-di(2-thienyl)pyrrole (2b). Method **A**, 73% yield: pale brown solid; mp 159.0–160.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 6.53 (dd, J = 1.1 and 3.7 Hz, 2H), 6.54 (s, 2H), 6.82 (dd, J = 3.6 and 5.1 Hz, 2H), 7.04 (dd, J = 1.1 and 5.1 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H); IR (KBr) 1509, 1420, 1261, 1041, 801, 689 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NS_2$: C, 70.99; H, 4.70; N, 4.36%. Found: C, 70.85; H, 4.86; N, 4.53%.

1-(*p*-Ethylphenyl)-2,5-di(2-thienyl)pyrrole (2c). Method **A**, 90% yield: pale brown crystals; mp 138.5–139.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J = 7.6 Hz, 3H), 2.76 (q, J = 7.6 Hz, 2H), 6.51 (dd, J = 1.1 and 5.1 Hz, 2H), 6.52 (s, 2H), 6.79 (dd, J = 3.6 and 5.1 Hz, 2H), 7.04 (dd, J = 1.1 and 3.6 Hz, 2H), 7.23 (br-s, 4H); IR (KBr) 1514, 1459, 1415, 1200, 1041, 846, 760, 701 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NS_2$: C, 71.61; H, 5.11; N, 4.18%. Found: C, 71.53; H, 5.09; N, 4.14%.

1-(*p*-Propylphenyl)-2,5-di(2-thienyl)pyrrole (2d). Method **A**, 85% yield: pale yellow crystals; mp 147.5–148.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.70 (tq-like, 2H), 2.67 (t, J = 7.6 Hz, 2H), 6.52 (dd, J = 1.1 and 3.7 Hz, 2H), 6.53 (s, 2H), 6.80 (dd, J = 3.7 and 5.1 Hz, 2H), 7.04 (dd, J = 1.1 and 5.1 Hz, 2H), 7.22 (br-s, 4H); IR (KBr) 1509, 1413, 1330, 1220, 1032, 831, 760, 693 cm^{-1}. Anal. Calcd for $C_{21}H_{19}NS_2$: C, 72.16; H, 5.48; N, 4.01%. Found: C, 71.97; H, 5.45; N, 3.95%.

1-(*p*-*sec*-Butylphenyl)-2,5-di(2-thienyl)pyrrole (2e). Method **A**, 86% yield: pale yellow crystals; mp 133.0–134.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.3 Hz, 3H), 1.30 (d, 3H), 1.64 (tq-like, 2H), 2.69 (dq-like, 1H), 6.52 (dd, J = 1.2 and 3.6 Hz, 2H), 6.54 (s, 2H), 6.80 (dd, J = 3.6 and 5.1 Hz, 2H), 7.30 (dd, J = 1.2 and 5.2 Hz, 2H), 7.23 (br-s, 4H); IR (KBr) 1512, 1458, 1416, 1200, 1041, 845, 762, 691 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NS_2$: C, 72.68; H, 5.82; N, 3.85%. Found: C, 72.46; H, 5.82; N, 3.89%.

1-(*p*-*tert*-Butylphenyl)-2,5-di(2-thienyl)pyrrole (2f). Method **A**, 52% yield: pale yellow crystals; mp 157.0–157.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9H), 6.51 (dd, J = 1.2 and 3.6 Hz, 2H), 6.54 (s, 2H), 6.80 (dd, J = 3.6 and 5.2 Hz, 2H), 7.30 (dd, J = 1.1 and 5.1 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H); IR (KBr) 1512, 1413, 1219, 1111, 1035, 837, 767, 695 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NS_2$: C, 72.68; H, 5.82; N, 3.85%. Found: C, 72.51; H, 5.82; N, 3.86%.

1-(*p*-Fluorophenyl)-2,5-di(2-thienyl)pyrrole (2g). Method **A** or **B**, 62% or 85% yield, respectively: pale yellow crystals; mp 198.0–198.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.53 (s, 2H), 6.56 (dd, J = 1.1 and 3.6 Hz, 2H), 6.84 (dd, J = 3.6 and 5.1 Hz, 2H), 7.08 (dd, J = 1.1 and 5.1 Hz, 2H), 7.11 (dd, J = 8.4 and 8.8 Hz, 2H), 7.28 (dd, J = 4.9 and 8.9 Hz, 2H); IR (KBr) 1510, 1415, 1222, 1163, 1051, 843, 764, 696 cm^{-1}. Anal. Calcd for $C_{18}H_{12}FNS_2$: C, 66.44; H, 3.72; N, 4.30%. Found: C, 66.31; H, 3.62; N, 4.16%.

1-(*p*-Chlorophenyl)-2,5-di(2-thienyl)pyrrole (2h). Method **A** or **B**, 58% or 74% yield, respectively: pale yellow crystals; mp 189.0–190.0 °C; ^{1}H NMR ($CDCl_3$) δ 6.53 (s, 2H), 6.55 (dd, J = 1.2 and 3.7 Hz, 2H), 6.84 (dd, J = 3.7 and 5.2 Hz, 2H), 7.09 (dd, J = 1.2 and 5.2 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.38 (dd, J = 8.9 Hz, 2H); IR (KBr) 1509, 1490, 1415, 1265, 1091, 1023, 832, 763, 699 cm^{-1}. Anal. Calcd for $C_{18}H_{12}ClNS_2$: C, 63.24; H, 3.54; N, 4.10%. Found: C, 63.21; H, 3.56; N, 3.94%.

1-(*p*-Bromophenyl)-2,5-di(2-thienyl)pyrrole (2i). Method **A**, 78% yield: pale yellow crystals; mp 189.0–190.0 °C; ^{1}H NMR ($CDCl_3$) δ 6.52 (s, 2H), 6.54 (dd, J = 1.1 and 3.6 Hz, 2H), 6.85 (dd, J = 3.6 and 5.1 Hz, 2H), 7.10 (dd, J = 1.1 and 5.2 Hz, 2H), 7.17 (d, J = 8.7Hz, 2H), 7.54 (dd, J = 8.7 Hz, 2H); IR (KBr) 1508, 1490, 1416, 1265, 1091, 843, 764, 696 cm^{-1}. Anal. Calcd for $C_{18}H_{12}BrNS_2$: C, 55.96; H, 3.13; N, 3.63%. Found: C, 55.61; H, 3.03; N, 3.52%.

1-(*p*-Cyanophenyl)-2,5-di(2-thienyl)pyrrole (2j). Method **A** or **B**, 18% or 64% yield, respectively: pale yellow needles; mp 211.0–211.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.52 (dd, J = 1.2 and 3.7 Hz, 2H), 6.54 (s, 2H), 6.86 (dd, J = 3.6 and 5.1 Hz, 2H), 7.03 (dd, J = 1.1 and 5.1 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.67 (dd, J = 8.7 Hz, 2H); IR (KBr) 2228, 1508, 1412, 1200, 1033, 846, 764, 702 cm^{-1}. Anal. Calcd for $C_{19}H_{12}N_2S_2 \cdot 0.50CH_3COCH_3$: C, 68.12; H, 4.18; N, 7.75%. Found: C, 67.97; H, 3.86; N, 7.76%.

1-(*p*-Butylphenyl)-2,5-di(2-thienyl)pyrrole (2k). Method **A**, 86% yield: pale yellow crystals; mp 122.0–123.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.37 (tq-like, 2H), 1.65 (tq-like, 2H), 2.69 (t, J = 7.7 Hz, 2H), 6.52 (dd, J = 1.1 and 3.6 Hz, 2H), 6.53 (s, 2H), 6.80 (dd, J = 3.6 and 5.2 Hz, 2H), 7.04 (dd, J = 1.1 and 5.1 Hz, 2H), 7.22 (br-s, 4H); IR (KBr) 1510, 1458, 1415, 1349, 1200, 1041, 846, 763, 693 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NS_2$: C, 72.68; H, 5.82; N, 3.85%. Found: C, 72.48; H, 5.90; N, 3.99%.

1-(*p*-Hexylphenyl)-2,5-di(2-thienyl)pyrrole (2l). Method **A**, 69% yield: pale yellow crystals; mp 123.5–124.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.29–1.50 (m, 6H), 1.70–1.80 (m, 2H), 2.69 (t, J = 7.6 Hz, 2H), 6.52 (dd, J = 1.1 and 3.6 Hz, 2H), 6.53 (s, 2H), 6.80 (dd, J = 3.7 and 5.1 Hz, 2H), 7.03 (dd, J = 1.1 and 5.1 Hz, 2H), 7.21 (br-s, 4H); IR (KBr) 1510, 1467, 1415, 1349, 1198, 1040, 836, 759, 690 cm^{-1}. Anal. Calcd for $C_{24}H_{25}NS_2$: C, 73.61; H, 6.43; N, 3.58%. Found: C, 73.65; H, 6.43; N, 3.52%.

1-(*p*-Decylphenyl)-2,5-di(2-thienyl)pyrrole (2m). Method **B**, 53% yield: pale yellow crystals; mp 107.0–108.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.27 (m, 14H), 1.66 (m, 2H), 2.69 (t, J = 7.7 Hz, 2H), 6.53 (dd, J = 1.4 and 4.1 Hz, 2H), 6.54 (s, 2H), 6.80 (dd, J = 3.7 and 5.1 Hz, 2H), 7.03 (dd, J = 1.1 and 5.1 Hz, 2H), 7.22 (br-s, 4H); IR (KBr) 1509, 1469, 1411, 1350, 1197, 1040, 847, 763, 688 cm^{-1}. Anal. Calcd for $C_{28}H_{33}NS_2$: C, 75.12; H, 7.43; N, 3.13%. Found: C, 75.25; H, 7.49; N, 3.11%.

1-(*p*-Dodecylphenyl)-2,5-di(2-thienyl)pyrrole (2n). Method **A**, 69% yield: pale yellow crystals; mp 108.5–109.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.20–1.38 (m, 18H), 1.61–1.76 (m, 2H), 2.69 (t, J = 7.6 Hz, 2H), 6.52 (dd, J = 1.2 and 3.8 Hz, 2H), 6.54 (s, 2H), 6.80 (dd, J = 3.7 and 5.1 Hz, 2H), 7.03 (dd, J = 1.2 and 5.2 Hz, 2H), 7.22 (br-s, 4H); IR (KBr) 1509, 1470, 1410, 1351, 1199, 1041, 846, 761, 687 cm^{-1}. Anal. Calcd for $C_{30}H_{37}NS_2$: C, 75.74; H, 7.84; N, 2.94%. Found: C, 75.90; H, 7.86; N, 2.89%.

1-(*p*-Tetradecylphenyl)-2,5-di(2-thienyl)pyrrole (2o). Method **B**, 66% yield: pale yellow crystals; mp 110.0–111.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.29 (m, 22H), 1.66 (m, 2H), 2.69 (t, J = 7.6 Hz, 2H), 6.52 (dd, J = 1.2 and 3.6 Hz, 2H), 6.53 (s, 2H), 6.80 (dd, J = 3.6 and 5.2 Hz, 2H), 7.03 (dd, J = 1.1 and 5.1 Hz, 2H), 7.22 (br-s, 4H); IR (KBr) 1513, 1468, 1415, 1197, 1040, 846, 764, 688 cm^{-1}. Anal. Calcd for $C_{32}H_{41}NS_2$: C, 76.29; H, 8.20; N, 2.78%. Found: C, 76.09; H, 8.38; N, 2.71%.

1-(*p*-Hexadecylphenyl)-2,5-di(2-thienyl)pyrrole (2p). Method **A**, 70% yield: pale yellow crystals; mp 113.0–114.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.28 (m, 26H), 1.66 (m, 2H), 2.69 (t, J = 7.7 Hz, 2H), 6.52 (dd, J = 1.4 and 3.9 Hz, 2H), 6.53 (s, 2H), 6.80 (dd, J = 3.7 and 5.1 Hz, 2H), 7.03 (dd, J = 1.1 and 5.1 Hz, 2H), 7.21 (br-s, 4H); IR (KBr) 1509, 1465, 1410, 1351, 1198, 1041, 845, 764, 688 cm^{-1}. Anal. Calcd for $C_{34}H_{45}NS_2$: C, 76.78; H, 8.53; N, 2.63%. Found: C, 76.71; H, 8.59; N, 2.56%.

1-(*o*-Decylphenyl)-2,5-di(2-thienyl)pyrrole. Method **A**, 79% yield: pale yellow crystals; mp 102.0–103.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3H), 1.21 (m, 16H), 2.17 (t, J = 8.0 Hz, 2H), 6.49 (dd, J = 1.1 and 3.7 Hz, 2H), 6.59 (s, 2H), 6.78 (dd, J = 3.7 and 5.1 Hz, 2H), 7.00 (dd, J = 1.1 and 5.1 Hz, 2H), 7.34 (m, 3H), 7.46 (dt-like, 1H); IR (KBr) 1491, 1456, 1427, 1408, 1350, 1158, 1045, 843, 764, 690 cm^{-1}. Anal. Calcd for $C_{28}H_{33}NS_2$: C, 75.12; H, 7.43; N, 3.13%. Found: C, 75.11; H, 7.47; N, 3.16%.

A Typical Procedure for the preparation of 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles (1 and 3). A mixture of 1-aryl-2,5-di(2-thienyl)pyrrole (0.400 mmol) and TCNE (0.800 mmol) in 10 mL of anhydrous DMF was stirred for 24 h at room temperature. The reaction mixture was poured into a saturated NaCl aqueous solution, and the aqueous layer was extracted with toluene (20 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The dark blue residue was purified by column chromatography (silica gel, $CHCl_3$) and then recrystallized from $CHCl_3$ to give the pure product.

1-Phenyl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1a). Yellowish gold-like lustrous crystals; 69% yield: mp 248.0–249.0 °C; ^{1}H NMR ($CDCl_3$) δ 6.74 (d, J = 4.3 Hz, 1H), 6.75 (dd, J = 1.2 and 3.6 Hz, 1H), 6.88 (dd, J = 3.8 and 5.1 Hz, 1H), 6.94 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.17 (dd, J = 1.0 and 5.1 Hz, 1H), 7.42 (d, J = 7.0 Hz, 2H), 7.61 (dd, J = 7.3 and 7.4 Hz, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.75 (d, J = 4.5 Hz, 1H); IR (KBr) 2210, 1498, 1451, 1420, 1400, 1363, 1323, 1242, 1178, 1108, 1068 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 613 (54000). Anal. Calcd for $C_{23}H_{12}N_4S_2$: C, 67.63; H, 2.96; N, 13.72%. Found: C, 67.58; H, 2.85; N, 13.68%.

1-(*p*-Tolyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]-pyrrole (1b). Gold-like lustrous crystals; 77% yield: mp 222.0–222.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H), 6.74 (d, J = 4.3 Hz, 1H), 6.80 (dd, J = 1.1 and 3.7 Hz, 1H), 6.89 (dd, J = 3.7 and 5.2 Hz, 1H), 7.04 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.17 (dd, J = 1.2 and 5.1 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 4.5 Hz, 1H); IR (KBr) 2207, 1491, 1450, 1420, 1398, 1362, 1326, 1178, 1162, 1108 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (21300). Anal. Calcd for $C_{24}H_{14}N_4S_2$: C, 68.22; H, 3.34; N, 13.26%. Found: C, 68.12; H, 3.27; N, 13.11%.

1-(*p*-Ethylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1c). Gold lustrous crystals; 70% yield: mp 211.5–212.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.6 Hz), 2.82 (q, J = 7.6 Hz, 2H), 6.74 (d, J = 4.4 Hz, 1H), 6.79 (dd, J = 1.1 and 3.7 Hz, 1H), 6.89 (dd, J = 3.7 and 5.1 Hz, 1H), 7.03 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.17 (dd, J = 1.1 and 5.1 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 4.5 Hz, 1H); IR (KBr) 2214, 1508, 1458, 1421, 1395, 1247, 1181, 1107, 1051 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (44400). Anal. Calcd for $C_{25}H_{16}N_4S_2$: C, 68.78; H, 3.69; N, 12.83%. Found: C, 68.60; H, 3.54; N, 12.55%.

1-(*p*-Propylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1d). Gold-like lustrous crystals; 83% yield: mp 199.0–200.0 °C (acetone); ^{1}H NMR ($CDCl_3$) δ 1.02 (t, J = 7.3 Hz, 3H), 1.76 (tq-like, 2H), 2.73 (t, J = 7.7 Hz, 2H), 6.74 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.8 and 5.0 Hz, 1H), 6.99 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.4 Hz, 1H), 7.16 (dd, J = 1.1 and 5.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 4.7 Hz, 1H); IR (KBr) 2213, 1508, 1492, 1451, 1421, 1399, 1362, 1244, 1164, 1107, 1067 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (40300). Anal. Calcd for $C_{26}H_{18}N_4S_2$: C, 69.31; H, 4.03; N, 12.43%. Found: C, 69.23; H, 3.86; N, 12.12%.

1-(*p*-*sec*-Butylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1e). Gold-like lustrous crystals; 89% yield: mp 188.0–189.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.5 (d, 3H), 1.69 (dq-like, 2H), 2.77 (dq-like, 1H), 6.74 (d, J = 4.3 Hz, 1H), 6.76 (dd, J = 1.0 and 3.7 Hz, 1H), 6.87 (dd, J = 3.7 and 5.1 Hz, 1H), 6.97 (d, J = 4.7 Hz, 1H), 7.06 (d, J = 4.3 Hz, 1H), 7.16 (dd, J = 1.0 and 5.1 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 4.7 Hz, 1H); IR (KBr) 2215, 1508, 1499, 1458, 1425, 1402, 1362, 1250, 1170, 1103, 1060 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 619 (40200). Anal. Calcd for $C_{27}H_{20}N_4S_2$: C, 69.80; H, 4.34; N, 12.06%. Found: C, 69.47; H, 4.25; N, 11.86%.

1-(*p*-*tert*-Butylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1f). Gold-like lustrous crystals; 89% yield: mp 235.5–236.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9H), 6.74 (d, J = 4.3 Hz, 1H), 6.76 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 7.03 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.4 Hz, 1H), 7.16 (dd, J = 1.1 and 5.1 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 4.7 Hz, 1H); IR (KBr) 2212, 1498, 1451, 1423, 1400, 1362, 1321, 1249, 1166, 1108 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (42100). Anal. Calcd for $C_{27}H_{20}N_4S_2$: C, 69.80; H, 4.34; N, 12.06%. Found: C, 69.80; H, 4.18; N, 11.69%.

1-(*p*-Fluorophenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1g). Gold-like lustrous crystals; 80% yield: mp 246.2–247.0 °C; ^{1}H NMR ($CDCl_3$) δ 6.73 (d, J = 4.3 Hz, 1H), 6.81 (dd, J = 1.1 and 3.7 Hz, 1H), 6.91 (dd, J = 3.7 and 5.1 Hz, 1H), 7.03 (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), 7.29 (dd, J = 8.4 and 8.8 Hz, 2H), 7.42 (dd, J = 4.9 and 8.9 Hz, 2H), 7.76 (d, J = 4.7 Hz, 1H); IR (KBr) 2206, 1508, 1490, 1397, 1361, 1247, 1163, 1110, 1061 cm^{-1}; UV-vis (THF, 3 × 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 610 (35000). Anal. Calcd for $C_{23}H_{11}FN_4S_2$: C, 64.77; H, 2.60; N, 13.14%. Found: C, 64.63; H, 2.40; N, 12.95%.

1-(*p*-Chlorophenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1h). Gold-like lustrous crystals; 98% yield: mp 245.0–245.8 °C; ^{1}H NMR ($CDCl_3$) δ 6.73 (d, J = 4.3 Hz, 1H), 6.79 (dd, J = 1.1 and 3.8 Hz, 1H), 6.91 (dd, J = 3.8 and 5.2 Hz, 1H), 6.98 (d, J = 4.5 Hz, 1H), 7.06 (d, J = 4.3 Hz, 1H), 7.20 (dd, J = 1.2 and 5.1 Hz, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.58 (d, J =

8.8 Hz, 2H), 7.76 (d, J = 4.5 Hz, 1H); IR (KBr) 2206, 1514, 1491, 1398, 1362, 1321, 1255, 1163, 1116, 1075 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 606 (30000). Anal. Calcd for $C_{23}H_{11}ClN_4S_2$: C, 62.37; H, 2.50; N, 12.65%. Found: C, 62.09; H, 2.29; N, 12.46%.

1-(*p*-Bromophenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1i). Gold-like lustrous crystals; 98% yield: mp 251.0–251.8 °C; ^{1}H NMR ($CDCl_3$) δ 6.72 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.8 Hz, 1H), 6.91 (dd, J = 3.8 and 5.2 Hz, 1H), 6.96 (d, J = 4.5 Hz, 1H), 7.06 (d, J = 4.3 Hz, 1H), 7.20 (dd, J = 1.1 and 5.1 Hz, 1H), 7.30 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 4.5 Hz, 1H); IR (KBr) 2207, 1492, 1450, 1419, 1399, 1362, 1243, 1163, 1107, 1073 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 605 (34000). Anal. Calcd for $C_{23}H_{11}BrN_4S_2$: C, 56.68; H, 2.27; N, 11.50%. Found: C, 56.45; H, 2.05; N, 11.37%.

1-(*p*-Cyanophenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1j). Gold-like lustrous crystals; 99% yield: mp 268.0–269.0 °C; ^{1}H NMR ($CDCl_3$) δ 6.73 (d, J = 4.1 Hz, 1H), 6.74 (dd, J = 3.6 and 1.2 Hz, 1H), 6.92 (dd, J = 3.7 and 5.1 Hz, 1H), 6.97 (d, J = 4.5 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.22 (dd, J = 1.1 and 5.1 Hz, 1H), 7.56 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 4.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 2H); IR (KBr) 2207, 1508, 1491, 1449, 1419, 1397, 1236, 1173, 1107, 1065, 848 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 597 (33000). Anal. Calcd for $C_{24}H_{11}N_5S_2 \cdot 0.15CHCl_3$: C, 64.26; H, 2.49; N, 15.51%. Found: C, 64.24; H, 2.34; N, 15.66%.

1-(*p*-Butylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1k). Bronze-like lustrous crystals; 89% yield: mp 171.5–172.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3H), 1.43 (tq-like, 2H), 1.72 (tq-like, 2H), 2.77 (t, J = 7.9 Hz, 2H), 6.73 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 6.98 (d, J = 4.8 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.16 (dd, J = 1.1 and 5.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 4.5 Hz, 1H); IR (KBr) 2217, 1502, 1457, 1428, 1400, 1348, 1322, 1246, 1208, 1061 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (33700). Anal. Calcd for $C_{27}H_{20}N_4S_2$: C, 69.80; H, 4.34; N, 12.06%. Found: C, 69.61; H, 4.18; N, 11.92%.

1-(*p*-Hexylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1l). Bronze-like lustrous crystals; 80% yield: mp 156.0–157.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 3H), 0.89–1.43 (m, 8H), 2.76 (t, J = 7.9 Hz, 2H), 6.73 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 6.98 (d, J = 4.7 Hz, 1H), 7.06 (d, J = 4.3 Hz, 1H), 7.16 (dd, J = 1.1 and 5.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 4.7 Hz, 1H); IR (KBr) 2216, 1503, 1456, 1428, 1401, 1348, 1322, 1247, 1209, 1060 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 618 (22800). Anal. Calcd for $C_{29}H_{24}N_4S_2$: C, 70.70; H, 4.91; N, 11.37%. Found: C, 70.41; H, 4.75; N, 11.31%.

1-(*p*-Decylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1m). Bronze-like lustrous crystals; 65% yield: mp 150.0–151.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.7 Hz, 3H), 1.32 (m, 14H), 1.71 (m, 2H), 2.76 (t, J = 7.9 Hz, 2H), 6.73 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.8 and 5.1 Hz, 1H), 6.98 (d, J = 4.5 Hz, 1H), 7.06 (d, J = 4.4 Hz, 1H), 7.16 (dd, J = 1.2 and 5.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 4.5 Hz, 1H); IR (KBr) 2216, 1503, 1456, 1428, 1402, 1362, 1349, 1248 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 621 (41700). Anal. Calcd for $C_{33}H_{32}N_4S_2$: C, 72.23; H, 5.88; N, 10.21%. Found: C, 72.24; H, 5.92; N, 10.15%.

1-(*p*-Dodecylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1n). Bronze-like lustrous crystals; 70% yield: mp 138.0–139.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.32 (m, 18H), 1.72 (m, 2H), 2.76 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 6.98 (d, J = 4.7 Hz, 1H), 7.06 (d, J = 4.3 Hz, 1H), 7.16 (dd, J = 1.0 and 5.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 4.7 Hz, 1H); IR (KBr) 2215, 1560, 1499, 1458, 1426, 1400, 1248 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 619 (42800). Anal. Calcd for $C_{35}H_{36}N_4S_2$: C, 72.88; H, 6.29; N, 9.71%. Found: C, 72.74; H, 6.25; N, 9.68%.

1-(*p*-Tetradecylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1o). Bronze-like lustrous crystals; 67% yield: mp 138.5–139.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.30 (m, 22H), 1.71 (m, 2H), 2.76 (t, J = 7.8 Hz, 2H), 6.74 (d, J = 4.4 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 6.98 (d, J = 4.7 Hz, 1H), 7.07 (d, J = 4.3 Hz, 1H), 7.16 (dd, J = 1.2 and 5.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 4.5 Hz, 1H); IR (KBr) 2214, 1502, 1455, 1403, 1363, 1323, 1248, 1185, 1110 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (41900). Anal. Calcd for $C_{37}H_{40}N_4S_2$: C, 73.47; H, 6.67; N, 9.26%. Found: C, 73.14; H, 6.65; N, 9.13%.

1-(*p*-Hexadecylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (1p). Bronze-like lustrous crystals; 74% yield: mp 135.0–136.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.28 (m, 26H), 1.70 (m, 2H), 2.76 (t, J = 7.8 Hz, 2H), 6.73 (d, J = 4.3 Hz, 1H), 6.78 (dd, J = 1.1 and 3.7 Hz, 1H), 6.88 (dd, J = 3.7 and 5.1 Hz, 1H), 6.98 (d, J = 4.7 Hz, 1H), 7.06 (d, J = 4.4 Hz, 1H), 7.16 (dd, J = 1.2 and 5.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 4.7 Hz, 1H); IR (KBr) 2215, 1502, 1456, 1427, 1401, 1348, 1322, 1247, 1209 cm^{-1}; UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (41600). Anal. Calcd for $C_{39}H_{44}N_4S_2$: C, 74.01; H, 7.01; N, 8.85%. Found: C, 73.78; H, 6.86; N, 8.71%.

1-(*o*-Decylphenyl)-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrrole (3). Gold-like lustrous plates; 79% yield: mp 102.0–103.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.24 (m, 16H), 2.17 (m, 2H), 6.78 (dd, J = 1.2 and 3.8 Hz, 1H), 6.80 (d, J = 4.4 Hz, 1H), 6.87 (dd, J = 3.7 and 5.1 Hz, 1H), 6.99 (d, J = 4.7 Hz, 1H), 7.12 (d, J = 4.4 Hz, 1H), 7.15 (dd, J = 1.2 and 5.1 Hz, 1H), 7.44 (m, 3H), 7.64 (ddd, J = 1.6 and 7.0 and 8.1 Hz, 1H), 7.75 (d, J = 4.7 Hz, 1H); IR (KBr) 2212, 1498, 1452, 1424, 1364, 1346, 1321, 1172, 847, 772 cm^{-1}. UV-vis (THF, 3 $\times$ 10^{-5} M) λ_{max} (nm) (ε/M^{-1} cm^{-1}) 620 (43100). Anal. Calcd for $C_{33}H_{32}N_4S_2$: C, 72.23; H, 5.88; N, 10.21%. Found: C, 72.25; H, 5.84; N, 10.19%.

X-ray Crystallography. For compounds **1a**, **1b**, **1d**, **1g**, **1i**, and **1j**, data collection was performed on a Mac Science MXC18 four-circle diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ = 1.54178 Å) using the θ–2θ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares methods against F (SIR 92[18] on a computer program package; maXus ver. 1.1 from MAC Science Co. Ltd.). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were refined isotropically. For the complex **1o·acetone**, data collection was performed on a Brukersmart-1000 CCD diffractometer with graphite monochro-

Table 1. Crystallographic Data and Structure Refinement Parameters

compound	**1a**	**1b**	**1d**	**1g**	**1i**	**1j**	**1o**·acetone	**3**
Formula	$C_{23}H_{12}N_4S_2$	$C_{24}H_{14}N_4S_2$	$C_{26}H_{18}N_4S_2$	$C_{23}H_{11}N_4S_2$	$C_{23}H_{11}BrN_4S_2$	$C_{24}H_{10}N_5S_2$	$C_{40}H_{46}N_4S_2O$	$C_{33}H_{64}N_4S_2$
M_w	408.50	422.50	450.60	426.50	487.40	433.50	662.95	548.78
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2	2	2	2	2	2
Cell constants								
a/Å	11.115(3)	10.570(2)	11.057(3)	10.716(2)	10.516(2)	10.678(2)	7.0790(7)	14.197(4)
b/Å	16.826(6)	11.021(2)	11.146(2)	10.830(3)	11.504(3)	11.121(2)	9.4349(9)	16.137(5)
c/Å	10.726(3)	11.293(2)	11.516(2)	10.908(3)	11.238(3)	11.317(2)	30.145(3)	16.205(5)
α/deg	90	110.11(2)	62.10(1)	119.24(2)	109.70(2)	62.94(2)	95.102(2)	69.24(2)
β/deg	101.46(2)	117.64(1)	73.52(2)	105.85(2)	117.03(2)	73.52(2)	93.946(2)	66.57(2)
γ/deg	90	98.08(2)	66.04(2)	101.05(2)	98.07(2)	67.25(1)	107.406(2)	64.34(2)
V/Å^3	1965.9(1)	1020.6(4)	1138.4(4)	979.6(4)	1026.3(5)	1094.1(4)	1903.9(3)	2995.0(2)
μ/mm^{-1}	25.86	25.08	22.80	26.96	47.76	23.71	17.50	18.20
Crystal size/mm	0.6 × 0.3 × 0.1	0.25 × 0.1 × 0.05	0.35 × 0.35 × 0.2	0.6 × 0.4 × 0.25	0.45 × 0.45 × 0.2	0.5 × 0.1 × 0.07	0.45 × 0.45 × 0.04	0.45 × 0.35 × 0.15
D_{calc}/g cm^{-3}	1.38	1.374	1.314	1.445	1.577	1.315	1.156	1.217
T/K	298	298	298	298	298	298	298	298
Reflns measd	4199	4226	4699	4044	4235	4510	11402	11796
Unique reflns	3729	3874	4320	3713	3893	4149	8307	11367
Obsd reflns	3293	2763	3660	3242	3344	3254	2997	4176
R int	0.053	0.037	0.028	0.021	0.028	0.031	0.054	0.052
Criteria of I	1.00	1.50	1.50	3.00	3.00	1.00	3.00	3.00
R	0.074	0.062	0.057	0.069	0.079	0.074	0.064	0.074
wR	0.087	0.064	0.057	0.095	0.097	0.069	0.095	0.123
Final difference								
Peaks/e Å^{-3}	−0.47, 0.49	−0.49, 0.45	−0.24, 0.28	−0.86, 0.74	−1.07, 1.10	−0.29, 0.92	−0.23, 0.27	−0.64, 0.66

mated Mo $K\alpha$ radiation ($\lambda = 0.71013$ Å) to a maximum 2θ value of 57°. The structure was solved by direct methods (SIR 92[18]) and refined by full-matrix least-squares methods against F. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. All calculations for **1o·acetone** were performed using the teXsan crystallographic software package (teXsan[19] for Windows Ver.1.03) of Molecular Structure Corporation (1997). For compound **3**, data collection was performed on a Mac Science MXC18 four-circle diffractometer with graphite monochromated Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) using the θ–2θ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares methods against F (SIR 92[18] on a computer program package; maXus ver. 3.2.1 from MAC Science Co. Ltd.). All non-hydrogen atoms were refined anisotropically. One hydrogen atom (H20) was added at calculated positions and the others on the aromatic rings were located by difference Fourier synthesis and treated as isotropic contributions except that the ones on decyl group were not added. An empirical absorption correction based on ψ-scans was only applied to crystals **1a**, **1b**, and **1i**. The detailed crystallographic data and structure refinement parameters are summarized in Table 1. 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 191825-191832. 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]. The data also were deposited as Document No. 75046 at the Office of the Editorial of Bull. Chem. Soc. Jpn.

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