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Easy formation of gold-like lustrous crystals with a high melting point from 1-aryl-2,5-bis[5-(tricyanoethenyl)-2-thienyl]pyrroles

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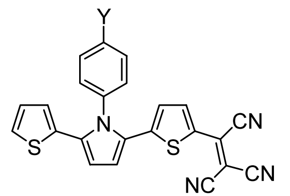
Abstract—A new class of π-conjugated organic compounds, 1-aryl-2,5-bis[5-(tricyanoethenyl)-2-thienyl]pyrroles that form gold-like lustrous crystals with a high melting point were obtained. The molecules in these crystals are arranged in a planar sheet to get close to each other via the intermolecular C–H···N hydrogen bond between the cyano nitrogen and the hydrogen of the nearest thiophene or pyrrole ring, which makes the crystals sparingly soluble in common organic solvents. © 2003 Elsevier Science Ltd. All rights reserved.

Novel π-conjugated organic molecules have attracted strong interest because they are utilized for advanced technologies such as molecule-based sensory, nonlinear optical, photo- and electroluminescent devices, and photovoltaic devices, etc.[1] A further function of such molecules is the formation of metal-like lustrous crystals.[2] Recently, we have reported a new class of donor–acceptor combined π-conjugated compounds, 1-aryl-2-(2-thienyl)-5-[5-(tricyanoethenyl)-2-thienyl]pyrroles **1** that easily form metal-like lustrous crystals.[3] Their metallic color relies on the substitutent on the central *N*-phenyl ring of **1**: when a small substituent is located at the *para*-position of the *N*-phenyl group, gold-like lustrous crystals were formed.[3a] The derivatives of **1** having a longer alkyl chain at the *para* position of the aryl ring gave bronze-like crystals.[3a] Crystals with red–violet metallic luster were obtained in the case that heteroatom combined methyl substituents (OMe, SMe, and NMe_2) are introduced into the *para*-position of the central aryl group.[3b] Interestingly, X-ray structural analysis revealed that, in these crystals, the molecules are arranged into a planar sheet-like, flat lane-like, or heaving ribbon-like structure via the interatomic C–H···N hydrogen bond between the *cyano* group and the olefinic hydrogen (CN···H–C=C) to make their π-system get close to each other. One characteristic feature of these metal-lustrous crystals is that they dissolve easily in common organic solvents and are quickly deposited from the resultant solution upon evaporation. However, this property is disadvantageous when they are utilized as a metal-lustrous pigment.



1

In order to develop gold-like lustrous crystals that are sparingly soluble in common organic solvents, we designed a 1-aryl-2,5-bis[5-(tricyanoethenyl)-2-thienyl]pyrrole π-system having two tricyanoethenyl groups that would play an important role in the intermolecular interaction, and it was found that 1-(*p*-substituted phenyl)-2,5-bis[5-(tricyanoethenyl)-2-thienyl]pyrroles **2** form insoluble gold-like lustrous crystals when the *p*-substituent is relatively small, like cyano and methyl groups. Notably, these crystals show a higher melting

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Keywords: π-conjugated organic compound; gold-like lustrous crystal; high melting point; coplanar sheet-like structure; intermolecular C–H···N hydrogen bond; intermolecular CN···C=C contact.

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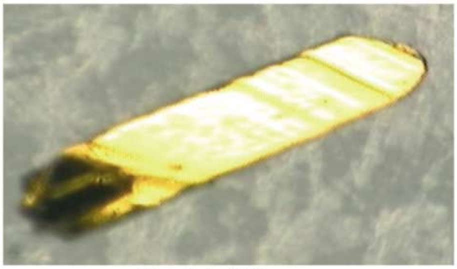
point of more than 300°C, and, especially, the melting point of the crystals of **2c** (Y = CN) is 394°C.

As reported, **1** was formed on treatment of 1-aryl-2,5-di(2-thienyl)pyrrole **3** with tetracyanoethylene in DMF at room temperature.[3a] At an elevated temperature, the reaction proceeds further to give **2**: after **3** was stirred with an excess amount of tetracyanoethene (more than 2.5 mol equiv.) in DMF at 80°C for 1 day, the reaction mixture was cooled to room temperature to deposit gold-like crystals that were separated by filtration. From the filtrate, further crystals were isolated by addition of brine, repeated extraction with toluene, and purification by column chromatography. The compounds synthesized herein[4,5] are summarized in Table 1. Gold-like lustrous crystals with good quality were obtained for the derivatives having *p*-methyl- and *p*-cyanophenyl groups at the central pyrrole ring of **2**. Compounds **2** in solution exhibited their absorption band at a region near 640 nm (see Table 1). It is evident that introduction of two tricyanoethenyl groups at both ends of **3** reflects a higher order of contribution to the bathochromic shift of their light absorption in comparison with that of **1**.

The solid-state UV–vis–NIR diffused reflection–absorption spectra of these crystals were identical with each other but quite different from their UV spectra in solution. A typical photograph together with the solid-state UV–vis–NIR diffused reflection–absorption spectra is shown in Figure 1. Notably, they also resemble the gold-like lustrous crystals of **1** in the shape of the solid-state spectra. They display a peculiar broadened absorption band in the whole visible region, reflecting the stronger interaction between the π-systems. The strong absorption lies in the region of blue to green (corresponding to the wavelength of 400–550 nm) whose complementary color is yellow.

(a)



Crystal of **2b**

(b)

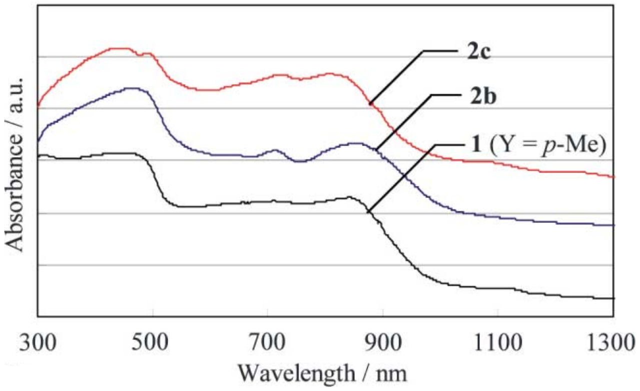
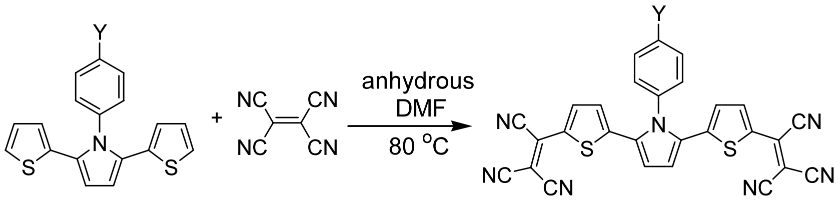


Figure 1. Photograph (a) of a gold-like lustrous crystal of **2b** (Y = p-CH_3) and solid-state UV–vis–NIR diffuse absorption–reflection spectra (b) of **2b**, **2c** (Y = p-CN) and **1** (Y = p-CH_3). The λ_{max} of absorption bands on the visible region is 480–490 nm.

Table 1. Synthesis and physical properties of compounds **2** with gold-like metallic luster



3 **2**

Compd	Y	Absorption λ_{max}/nm (log ε)[a]	T_m (°C)[b]	Crystal appearance
2a	H	644 (4.80)	317	–[d]
2b	Me	654 (4.79)	340	Gold-like prism[e]
2c	CN	627 (4.73)	394[c]	Gold-like thin-rod[f]
2d	Cl	636 (4.78)	335	Gold-like thin-rod[e]
2e	Br	636 (4.65)	334	Gold-like thin-plate[e]
2f	Et	656 (4.78)	329	Gold-like prism

[a] Measured in 3×10^{-5} mol L^{-1} THF solution.

[b] Determined by TG-DSC.

[c] Decomposition or sublimation.

[d] Greenish metallic colored microcrystal.

[e] Acetone was used as solvent for crystallization.

[f] Single crystals were prepared by slow diffusion of $CHCl_3$ vapor into a DMF solution of compound **2c**.

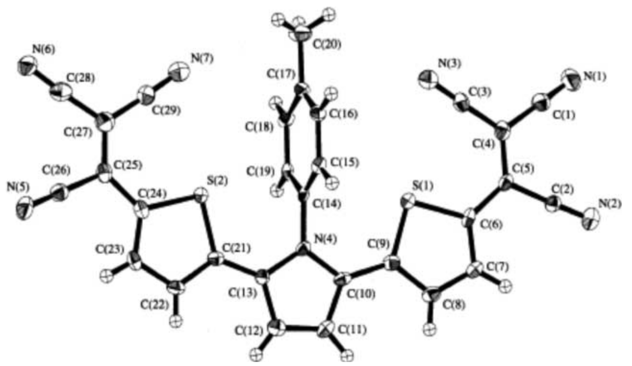


Figure 2. An ORTEP plot of the crystal of **2b** at 103.2 K. The ellipsoids are drawn at the 50% probability level. Selected intramolecular torsion angles with standard deviation: C(2)–C(5)–C(6)–C(7) 1.9(7)°, C(8)–C(9)–C(10)–C(11) 4.7(8)°, C(12)–C(13)–C(21)–C(22) 0.9(8)°, C(23)–C(24)–C(25)–C(26) 11.0(7)°.

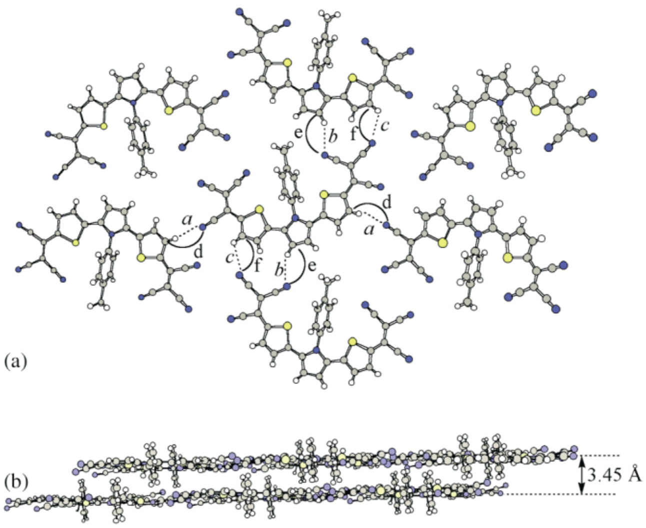


Figure 3. Packing diagram of crystal **2b**. (a) Sheet-like molecular arrangement. The intermolecular C–H···N hydrogen bonds [*a*: 2.57 Å (175.5°); *b*: 2.70 Å (152.2°); *c*: 2.77 Å (118.7°)] are drawn as dotted lines, and the sidewise CN···C=C interactions (d: 3.46 Å; e: 3.55 Å; f: 3.33 Å) are drawn as dashed lines. (b) A side view of two stacking layers. The layer distance is ca. 3.45 Å (determined by PXRD analysis).

Single crystals of **2b** and **2c** were obtained for structural analysis. X-Ray crystallographic analysis[†] reveals that **2b**[4] and **2c**[5] crystallize in the same monoclinic unit cells, containing four molecules of each compound. Figure 2 shows an ORTEP plot of the crystal **2b** at 103.2 K. Similarly to our previous study,[3] the π-conjugation of thiophene–pyrrole–thiophene scaffold and tricyanoethenyl group adopts an approximate planar conformation to which the central *N*-phenyl group is almost perpendicular.

The molecules of **2b** aggregate in a planar sheet in which each molecule overlaps with the neighboring molecule by the interatomic C–H···N hydrogen bond[3,6] between the π-electrons of the thiophene or pyrrole ring and the *cyano* group, which substantially contributes to the crystal architecture of **2b** (Fig. 3). It is noteworthy that the *cyano* groups are intermolecularly located face-to-face to be close to each other. The distance between these cyano nitrogens was 3.39 Å.

The crystal packing of **2c** is analogous to that of **2b** so that the interatomic interactions described above are very similar, as shown in Figure 4. For **2c**, the intermolecular C–H···N hydrogen bond lengths are in a

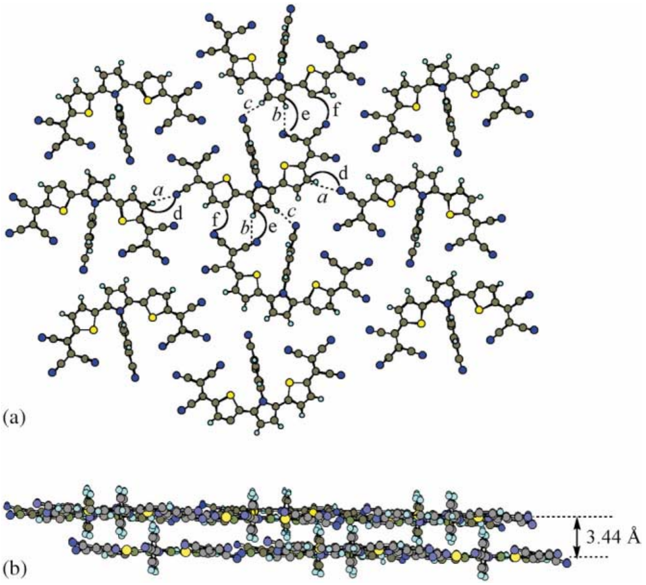


Figure 4. Packing diagram of crystal **2c**. (a) Sheet-like molecular arrangement. The intermolecular C–H···N hydrogen bonds [*a*: 2.58 Å (174.9°); *b*: 2.69 Å (148.1°); *c*: 2.45 Å (177.3°)] are drawn as dotted lines, and the sidewise CN···C=C interactions (d: 3.52 Å; e: 3.53 Å; f: 3.30 Å) are drawn as dashed lines. (b) A side view of two stacking layers. The layer distance is ca. 3.44 Å (determined by PXRD analysis).

[†] **X-Ray Crystallography**. Data collections were performed on a Bruker SMART-1000 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71013$ Å). For **2b**, the structure was solved by direct methods (SIR-92[7]) and refined by full-matrix least-squares methods against *F*. The non-hydrogen atoms were refined anisotropically. The hydrogen atom coordinates were refined but their isotropic B's were held fixed. All calculations were performed using the teXsan[8] crystallographic software package (teXsan for Windows Ver.1.03) of Molecular Structure Corporation (1997). For **2c**, the structure was solved by direct methods (SIR-97[9]) and refined by full-matrix least-squares methods against F^2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan[8] crystallographic software package (teXsan for Windows Ver.1.11) of Molecular Structure Corporation (1999). 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 201342–201343. 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].

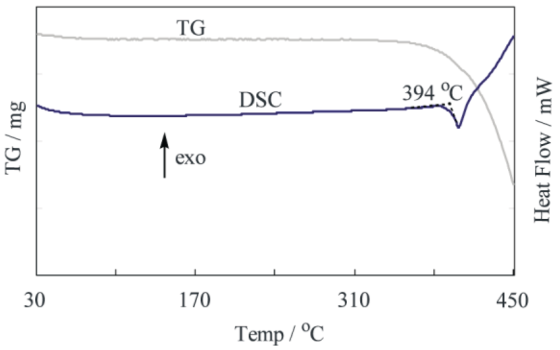


Figure 5. Thermograms (TG-DSC) of compound **2c**.

range of 2.45–2.69 Å. Accordingly, the distance between the *cyano* groups that stand face-to-face in the sheet becomes shorter to 3.12 Å. Within the crystals of **2c**, the nitrogen of the *p*-cyanophenyl group also interacts with the olefinic hydrogen atom on the central pyrrole ring of the neighboring molecule [2.45 Å (177.3°)]. The π-conjugation in **2b** and **2c** partially overlaps in layers with almost the same value of 3.45 Å apart, as revealed by PXRD analysis. As mentioned above, the crystals of **2c** melt at a high temperature of 394°C. This is coincident with the fact that the molecules in the crystalline state strongly interact with each other. The thermal gravimetry (TG) and differential scanning calorimetry (DSC) traces for **2c** are shown in Figure 5. The DSC trace shows a sharp exotherm at a narrow range around 394°C due to the melt of **2c**, and the weight loss curve clearly indicates that the crystals melt in a single step, and decompose or sublimate simultaneously.

In summary, we have successfully developed a new class of π-electron conjugated system **2** that gives crystals with gold-like metallic luster and a high melting point of more than 300°C. The essential motif present in these crystals is an infinite, intermolecular network of CN···H–C=C interactions which organize the molecules to arrange regularly into a planar sheet. The number of CN···H–C=C interactions that originate from the unique effect of two tricyanoethenyl groups make the crystals sparingly soluble in organic solvents including DMF and DMSO. This property promises the crystals to be utilized as an organic pigment with gold-like metallic luster, which is our on-going subject.

Acknowledgements

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5. *Crystal data for **2c***: $C_{29}H_{10}N_8S_2$, $M=534.57$, gold-like thin-rods, 0.55×0.08×0.03 mm, monoclinic, space group $P2_1/n$ (no. 14), $a=10.326$ (2), $b=21.616$ (4), $c=10.678$ (2) Å, $\beta=90.945$ (4)°, $V=2383.1$ (8) Å^3, $Z=4$, $D_{calcd}=1.490$ g/cm^3, $F(000)=1088$, $\mu=2.62$ cm^{-1}, $T=90.2$ K. 14533 reflections (5636 unique, $R_{int}=0.068$), 3399 observed reflections [$I>1.50\sigma(I)$], 353 parameters, $R=0.047$, $Rw=0.044$, GOF = 0.850.
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