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Structure and physical properties of isopropyl TTF semisquarates†

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The synthesis, characterization and physical properties of two isopropyl TTF semisquarates, TTFsq^{i}Pr and EDT-TTFsq^{i}Pr, are reported. These molecules show a solvatochromism effect in solution and electrical conductivity in the solid state in their neutral form. These behaviors can be explained in terms of a small electrical charge redistribution from the TTF-centered HOMO to the semisquarate-centered LUMO of the molecules.

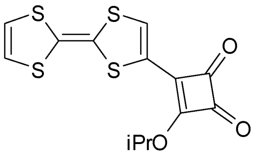
Introduction

The development of molecular solids with two or more different physical properties, such as electron transport and magnetism, is one of the important targets in the field of molecular material science.[1–3] For example, the combination of π-electron-based molecular conductors and transition metal complexes with magnetic moments of d-electrons is expected to give molecular conducting magnets based on the π–d interaction. From this viewpoint, a number of molecular conducting magnets using TTF (tetrathiafulvalene) derivatives have been developed.[4–13] This strategy unfortunately has a drawback: the interaction between two functional parts relies on weak intermolecular van der Waals contacts, hence the magnitude of the interaction is generally weak (~1 K).[14]

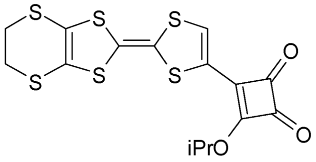
To establish larger interaction between two functionalities (not limited between conductivity and magnetism), a through-bond approach would be favorable. In this strategy, two functional units are covalently linked though a conjugated bridge that enables the interaction *via* conjugated π-electrons. When focused on conductivity and magnetism, direct coordination of paramagnetic metal ions to TTF derivatives with functional groups such as pyridine,[15–20] phosphine[21–26] and acetyl acetonate[27,28] have been investigated.

In this work we adopted a semisquarate (hydroxycyclobutenedione) unit as a substituent of TTF derivatives, expecting large versatility for producing functional molecular materials based on the following peculiarities of the semisquarate group. Since squarate dianion $C_4O_4^{2-}$ is regarded as an aromatic oxocarbon,[29] strong acidity is observed for squaric acid $H_2C_4O_4$ ($pK_{a1} = 0.54$, $pK_{a2} = 3.48$)[30] and its derivatives (phenyl semisquarate: $pK_a = -0.22$, bisquaric acid: $pK_{a2} = -4.49$).[31,32] Due to this acidity, semisquarate derivatives are expected to form intermolecular hydrogen-bonding networks showing dielectric properties.[33,34] Second, carbonyl and hydroxy groups of the semisquarate are suitable to bridge two or more transition metal ions to mediate exchange interaction between magnetic centers.[35,36] Aryl derivatives of squarates, *i.e.* squaraine dyes, also show remarkable optical properties such as non-linear optics[37,38] and photoelectricity.[39]

Here we report the synthesis, characterization and physical properties of isopropyl TTF semisquarates. Although the hydroxyl groups of these molecules are still protected by an isopropyl group, these molecules show remarkable physical properties such as solvatochromism and electrical conductivity in their neutral solid form.



TTFsq^{i}Pr



EDT-TTFsq^{i}Pr

Experimental

Syntheses

All reactions were carried out under argon atmosphere. Dried solvents (diethyl ether and THF) were purchased from Kanto Chemicals Co. Inc. and used without purification. ^{1}H NMR spectra were recorded at 400 MHz. IR spectra were recorded with JASCO FT/IR-4100 spectrometer.

3-[2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl]-4-(propan-2-yloxy)-cyclobut-3-ene-1,2-dione (TTFsq^{i}Pr). To a stirred solution of TTF (1.02 g, 5.0 mmol)[40] in diethyl ether (60 cm^3) at −80 °C under Ar atmosphere, a 2.0 M heptane solution of lithium diisopropylamide (LDA, Aldrich, 3.0 cm^3, 6.0 mmol) was syringed over 5 min. The slurry of monolithio-TTF was stirred for 2 h, and 3,4-bis(propan-2-yloxy)cyclobut-3-ene-1,2-dione (diisopropyl squarate, 1.13 g, 5.7 mmol) dissolved in diethyl ether (30 cm^3) was slowly added. After the reaction mixture was stirred at −80 °C for a further 3 h, the reaction was quenched with 15 cm^3 of saturated aqueous ammonium chloride, then the solution was warmed up to room temperature. The reaction mixture was poured into 100 cm^3 of water and extracted with $CHCl_3$ (3 × 50 cm^3). The combined extracts were dried and evaporated under reduced pressure to leave a red–brown oil, which was dissolved in $CHCl_3$ (150 cm^3) with

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0.5 cm^3 of concentrated hydrochloric acid and stirred overnight. After the removal of the solvent, the residual solid was chromatographed on silica gel using $CHCl_3$ as eluent. The main purple fraction was collected and the solvent was evaporated, then the residue was recrystallized from $CHCl_3$–EtOH (3 : 1) to give TTFsq^{i}Pr (1.26 g, 74%) as purple shiny elongated plates (Found: C, 45.65; H, 2.87; S; 37.31. Calc. for $C_{13}H_{10}O_3S_4$: C, 45.59; H, 2.94; S, 37.45%). ν_{max}(KBr)/cm^{-1} 3076, 2986, 1777, 1725, 1586, 1397, 1227, 1099, 824, 766; δ_H (400 MHz; $CDCl_3$, Me_4Si) 1.52 (d, 6H, J = 6.4 Hz, $(CH_3)_2$CH), 5.5 (hept, 1H, J = 6.4 Hz, $(CH_3)_2CH$), 6.36 (s, 2H, CH=CH), 7.61 (s, 1H, CH=C).

3-[2-(5,6-Dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-1,3-dithiol-4-yl]-4-(propan-2-yloxy)cyclobut-3-ene-1,2-dione (EDT-TTFsq^{i}Pr). To a stirred solution of EDT-TTF (1.47 g, 5.0 mmol)[41] in THF (65 mL) at −80 °C under Ar atmosphere, 2.0 M heptane solution of LDA (2.7 cm^3, 5.4 mmol) was syringed over 5 min, and the stirring of the red solution was continued for 3 h. A solution of diisopropyl squarate (1.13 g, 5.7 mmol) in THF (20 cm^3) was added to this solution. After the reaction mixture was stirred at −80 °C for a further 4 h, the reaction was quenched with 10 cm^3 of water, then the solution was warmed up to room temperature. The reaction mixture was poured into 100 cm^3 of saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (2 × 200 cm^3). The combined extracts were dried and evaporated under reduced pressure to leave a red–brown oil, which was dissolved in CH_2Cl_2 (100 cm^3) with 0.5 cm^3 of concentrated hydrochloric acid and stirred overnight. After the removal of the solvent, the residual solid was chromatographed on silica gel using CH_2Cl_2 as an eluent. The main blue–purple fraction was collected and the solvent was evaporated, then the residue was recrystallized from $CHCl_3$–EtOH (3 : 1) to give EDT-TTFsq^{i}Pr (0.84 g, 40%) as blue–purple powder (Found: C, 41.94; H, 2.88; S; 44.17. Calc. for $C_{15}H_{12}O_3S_6$: C, 41.64; H, 2.80; S, 44.47%). ν_{max}(KBr)/cm^{-1} 3058, 2979, 1775, 1737, 1581, 1487, 1392, 1225, 1095, 820, 771; δ_H (400 MHz; $CDCl_3$, Me_4Si) 1.52 (d, 6H, J = 6.0 Hz, $(CH_3)_2$CH), 3.31 (s, 4H, SCH_2CH_2S), 5.51 (hept, 1H, J = 6.0 Hz, $(CH_3)_2CH$), 7.61 (s, 1H, CH=C).

Crystal structure determination

A single crystal of TTFsq^{i}Pr (0.4 × 0.2 × 0.05 mm) was mounted on a Rigaku AFC-7R four-circle diffractometer, and intensity data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) in the range of $2\theta \leq 55°$. The structure was solved with direct methods using the *SIR2004* program,[42] and refined on F^2 with full-matrix least-squares method using the *SHELXL 97* program.[43]

Crystal data: $C_{13}H_{10}O_3S_4$, M = 342.48, triclinic, space group $P\bar{1}$ (no. 2), a = 10.224(2), b = 11.407(3), c = 7.0403(18) Å, α = 107.95(2), β = 104.63(2), γ = 93.175(18)°, V = 747.8(3) Å^3, T = 290 K, Z = 2, 3428 reflections measured. The final R_1 and $wR(F_2)$ were 0.066 and 0.215 ($I > 2\sigma(I)$). Full bond lengths and bond angles, atomic coordinates and complete crystal structure results are given as ESI.†

Physical property measurements

UV-vis spectra were recorded with a JASCO V-650 spectrometer. Cyclic voltammograms were recorded in acetonitrile with HAB-151 potentiostat (Hokuto-Denko Corp.), using 0.1 M Bu_4NClO_4 as a supporting electrolyte. The electrical resistivity were measured with Keithley 2400 source meter using a dc two-probe technique between room temperature and *ca.* 220 K where the resistances exceed the measurement limit (~3 GΩ). The electrical contacts were made with gold wire (25 μm diameter) and carbon paste (Dotite XC-12, Fujikura-Kasei Co., Ltd.). High-pressure resistivities of TTFsq^{i}Pr were measured using a Be–Cu clamp cell up to 10 kbar with a pressure medium of Daphne #7373 oil (Idemitsu Kosan Co.). The magnetic susceptibility was measured for non-oriented single crystals in the temperature range 1.8–300 K using Quantum Design MPMS-5 SQUID magnetometer.

Theoretical calculations

The molecular orbitals were calculated using a semi-empirical PM5 Hamiltonian with MOPAC package.[44] The overlap integrals S between HOMOs of adjacent molecules were calculated using the extended Hückel Hamiltonian.[45]

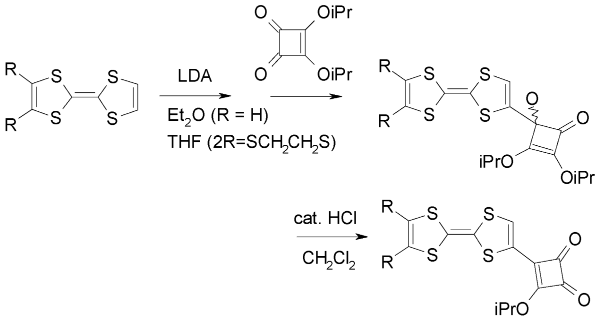
Results

Synthesis

The target molecules were prepared using the procedure for substituted semisquaric acids by Liebeskind *et al.*[46] as shown in Scheme 1. Organolithium TTF derivatives react with diisopropyl squarate to give stable 1,2-adducts, which are treated with a catalytic amount of acid to give semisquaric acid derivatives. For TTFsq^{i}Pr diethyl ether was used instead of THF as a solvent to avoid formation of bis-lithiated TTF.[47] Compared to TTFsq^{i}Pr (75%), EDT-TTFsq^{i}Pr (40%) was obtained in lower yield, presumably because of a ring-opening side-reaction of the ethylenedithio group.[48]

Crystal structure of TTFsq^{i}Pr

Both TTF and semisquarate moieties of TTFsq^{i}Pr are planar (maximum deviation from the least-squares planes: S(4) 0.0742(10), C(7): 0.035(3) Å), and these two planes are nearly coplanar to each other (angle: 7.41(11)°). The bond lengths and angles of the TTF part have typical values of neutral TTF molecules within experimental error.[49,50] The semisquarate



Scheme 1 Syntheses of TTFsq^{i}Pr and EDT-TTFsq^{i}Pr.

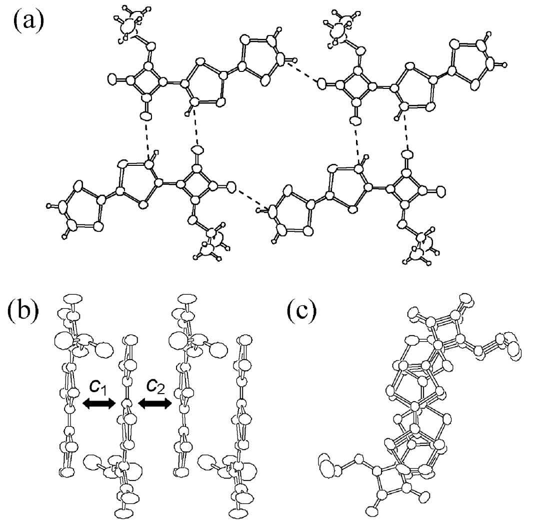


Fig. 1 The crystal structure of TTFsq^{i}Pr: (a) projected along the normal of the (11$\bar{2}$) plane; intermolecular CH···O type hydrogen bonds are depicted with dashed lines; (b) viewed along the side-by-side direction of the TTF moiety; hydrogen atoms are omitted for clarity; arrows c_1 and c_2 indicate two crystallographically independent intermolecular overlapping modes; (c) viewed along the stacking direction, parallel to the c-axis.

moiety has a trapezoidal shape, whose C=C double bond (1.387(5) Å) is shorter than the corresponding value in the ordered phase of squaric acid (1.414(1) Å).[51]

The TTFsq^{i}Pr molecules are stacked so that their molecular plane is nearly parallel to the (11$\bar{2}$) plane. Between the adjacent molecules intermolecular CH···O type hydrogen bonds are observed as shown in Fig. 1(a), whose C···O distances (3.192(5), 3.204(6) Å) are slightly shorter than the corresponding van der Waals distance (3.22 Å).[52] The TTF moieties are stacked along the c-direction to form columns (Fig. 1(b)). The interplanar distances are 3.483(5) and 3.623(5) Å, hence these columns are slightly dimerized. Inside the column the TTF units are stacked in a ring-over-bond motif as shown in Fig. 1(c), and the semisquarate group comes above the periphery of the neighboring TTF unit. There are moderate S···S contacts (distance: 3.889(3) Å) existing inside the column, whereas no side-by-side S···S contacts are observed due to the presence of the bulky isopropyloxy group.

Spectrometric studies

Fig. 2 shows the UV-vis spectra of TTFsq^{i}Pr (top panel) and EDT-TTFsq^{i}Pr (bottom panel) in chloroform, plotted together with the spectra of unsubstituted TTF and EDT-TTF as references. The TTF-semisquarates have a broad and intense (ε ~4000 L mol^{-1} cm^{-1}) absorption band in the range of 500–550 nm. The absorption maximum wavelength $\lambda_{\max}$ of EDT-TTFsq^{i}Pr is lower than that of TTFsq^{i}Pr, and for both compounds $\lambda_{\max}$ depend on the solvents as summarized in Table 1. The $\lambda_{\max}$ value of TTFsq^{i}Pr varies from 523 nm (acetone) to 549 nm (chloroform), whereas the corresponding values of EDT-TTFsq^{i}Pr are 490 nm (acetone) and 529 nm (chloroform). This strong absorption and its solvatochromic properties are commonly observed for TTF–π-acceptor molecules[53,54], especially in TTF–CH=CH–C_6H_4–NO_2.[55] In the latter compound, the acceptor unit gives rise to a low energy intramolecular charge transfer (ICT) band around 500 nm. The difference in the ICT band between TTFsq^{i}Pr and EDT-TTFsq^{i}Pr can be explained by the decreasing donor strength of the EDT-TTF moiety by ethylenedithio substitution, which shifts the ICT band to higher energy.

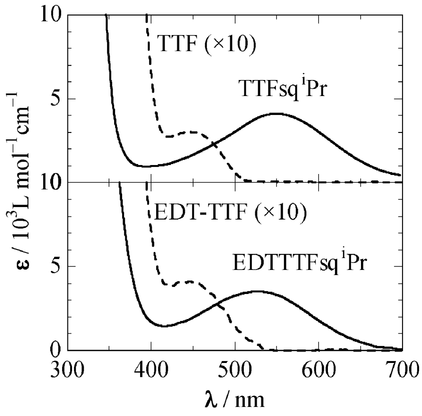


Fig. 2 UV-vis absorption spectra of TTFsq^{i}Pr (top panel, 2 × 10^{-5} M) and EDT-TTFsq^{i}Pr (bottom panel, 2 × 10^{-5} M) in $CHCl_3$, together with the spectra of unsubstituted TTF and EDT-TTF (×10, 1 × 10^{-3} M), respectively.

Table 1 The absorption maximum wavelength $\lambda_{\max}$ of TTFsq^{i}Pr and EDT-TTFsq^{i}Pr in various solvents

	$\lambda_{\max}$/nm	
Solvent	TTFsq^{i}Pr	EDTTTFsq^{i}Pr
Acetone	523	490
Ethyl acetate	523	496
CH_3CN	524	495
Hexane	525	[a]
THF	525	495
Diethyl ether	528	501
Toluene	536	514
Ethanol	537	507
CH_2Cl_2	544	519
PhCl	545	524
2-Propanol	547	[a]
$CHCl_3$	549	529

[a] No reliable data were obtained due to the low solubility.

Table 2 shows the formal oxidation potentials of TTFsq^{i}Pr and EDT-TTFsq^{i}Pr, with the corresponding values of the parent compounds TTF and EDT-TTF. Both the first (E_1) and second (E_2) redox peaks are electrochemically reversible, indicating the stability and high solubility of the neutral, mono- and di-cation species in acetonitrile. Due to the electron

Table 2 Format oxidation potentials of TTFsq^{i}Pr, EDT-TTFsq^{i}Pr and their parent compounds TTF, EDT-TTF (*vs.* Fc/Fc^{+} in CH_3CN, 0.1 V s^{-1})

	E_1/V	E_2/V	ΔE/V
TTFsq^{i}Pr	0.08	0.40	0.33
TTF	−0.07	0.30	0.37
EDT-TTFsq^{i}Pr	0.15	0.42	0.27
EDT-TTF	0.02	0.32	0.30

negativity of the semisquarate substituents, the oxidation potentials of TTFsq^{i}Pr, EDT-TTFsq^{i}Pr are 0.10–0.15 V higher than TTF and EDT-TTF, respectively. The separation between the two oxidation peaks of TTFsq^{i}Pr and EDT-TTFsq^{i}Pr are 0.03–0.04 V larger than that of TTF and EDT-TTF, showing the partial delocalization of the π-electron system in the TTF moieties.

Physical properties

The resistivity of the neutral molecules were measured for a single-crystal sample of TTFsq^{i}Pr and for a compaction pellet sample of EDT-TTFsq^{i}Pr, as single crystals could not be obtained for the latter. The resistivity at room temperature is estimated at 2×10^6 and 5×10^5 Ω cm at 290 K for TTFsq^{i}Pr and EDT-TTFsq^{i}Pr, respectively, which is comparable to TTF species with long alkyl chains (10^5–10^8 Ω cm)[56] or thiophene-fused TTF (10^5 Ω cm).[57] The activation energies for TTFsq^{i}Pr and EDT-TTFsq^{i}Pr are estimated to be 0.25 and 0.30 eV, respectively.

Fig. 3(a) shows the temperature dependence of resistivity of a TTFsq^{i}Pr single crystal measured along the stacking direction of the molecule ($\parallel c$) under various hydrostatic pressures. The resistivity at room temperature (290 K) and the activation energy are plotted as a function of the pressure in Fig. 3(b). Above *ca.* 240 K the temperature dependence of the resistance shows an activation-type behavior regardless of the external pressure. In the pressure range of $0 < p < 1$ GPa, the room-temperature resistivity monotonically decreases as the pressure increases, whereas the activation energy E_A is almost temperature independent.

The temperature dependence of the magnetic susceptibility of TTFsq^{i}Pr is fitted with the Curie law with Curie constant $C = 3.8 \times 10^{-4}$ emu K mol^{-1}, which corresponds to a spin concentration of 0.1%. Therefore the observed spin is characterized as impurities and/or defects, and cannot be regarded as thermally-excited π-electron spins on the TTF moieties.

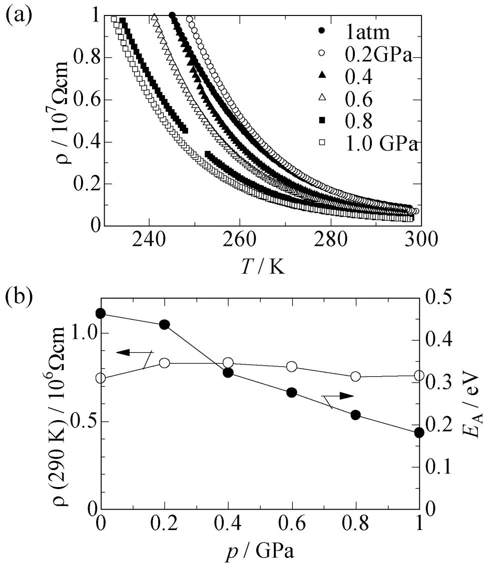


Fig. 3 (a) Temperature dependence of electrical resistivity of TTFsq^{i}Pr under various pressures. (b) Pressure dependence of the resistivity at 290 K (●) and activation energies (○). Solid lines are guides for the eye.

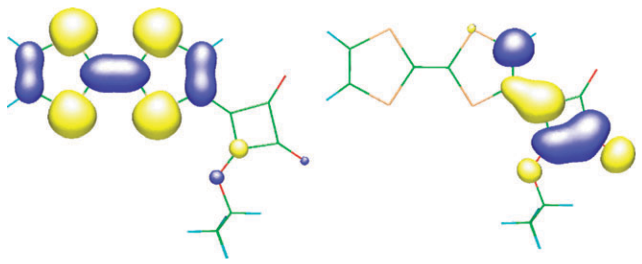


Fig. 4 HOMO (left) and LUMO (right) of TTFsq^{i}Pr calculated using the PM5 Hamiltonian.

Theoretical calculations

Fig. 4 shows the (a) HOMO and (b) LUMO of TTFsq^{i}Pr calculated using the semi-empirical PM5 Hamiltonian after the geometrical optimization. The optimized structure well reproduces the molecular structure experimentally determined by X-ray diffraction. The HOMOs of TTFsq^{i}Pr and EDT-TTFsq^{i}Pr molecules are localized almost on the TTF moiety although a small amount of delocalization to the semisquaric acid moiety is observed. On the other hand the LUMOs of these molecules are mainly distributed on the semisquaric acid part, and the TTF part scarcely participates to the molecular orbital. These HOMO and LUMO distributions are commonly observed in other TTF–π-acceptor molecules.[53,55] The HOMO–LUMO energetic difference is estimated to be 6.16 and 6.27 eV for TTFsq^{i}Pr and EDT-TTFsq^{i}Pr, respectively.

Since the TTF column of TTFsq^{i}Pr molecule is slightly dimerized, there are two crystallographically independent intermolecular overlapping modes of TTFsq^{i}Pr molecules, as designated by the arrows c_1 and c_2 in Fig. 1(b). The overlap integrals for these modes are calculated as $S_{c1} = 2.82 \times 10^{-3}$ and $S_{c2} = 2.14 \times 10^{-3}$ using the extended Hückel Hamiltonian. These values correspond to the transfer integrals of 0.02 eV between the adjacent TTF units, assuming that the transfer integral t is approximated as $t = ES$, where E is the energy level of the HOMO of the TTFsq^{i}Pr molecule ($= -10$ eV). The presence of this intermolecular transfer is a consequence of the segregated stacking of the two functional units, which is not observed in the other TTF–π-acceptor molecules.[53,55]

Discussion

The present compounds TTFsq^{i}Pr and EDT-TTFsq^{i}Pr are composed of an electron-donating TTF moiety and an electron-withdrawing semisquarate moiety. The bond lengths of the TTF core and the semisquarate unit of TTFsq^{i}Pr show that both of the moieties can be regarded as neutral. The wavenumbers of the stretching mode of carbonyl groups of four-membered ring in the IR spectra (1775 and 1737 cm^{-1}) are only slightly lower than the corresponding values of isopropylbenzene semisquarate (3-isopropyl-4-phenylcyclobut-3-ene-1,2-dione; 1780, 1747 cm^{-1}),[46] in which the phenyl ring has no donor character. Therefore the intramolecular charge transfer from the TTF unit to the semisquarate unit is negligibly small without UV-light irradiation, and both functional units have closed-shell electron configurations without unpaired electrons.

Despite their closed-shell nature these molecules show conductive behavior in the range of 10^6 Ω cm even in their neutral states, both in single crystal (TTFsq^{i}Pr) and powder (EDT-TTFsq^{i}Pr) forms. As the room-temperature resistivity has little sample and batch dependence, their electronic conduction can be attributed to an intrinsic conduction. The MO calculation shows that the HOMOs of these molecules are mainly delocalized in the TTF skeleton, whereas the LUMOs are mainly populated on the semisquarate unit. Therefore, electronic charge redistribution from TTF to semisquarate units corresponds to a HOMO–LUMO excitation and gives a small electron deficiency in the TTF columns to produce the electrical conductivity, although this effect could not be directly evidenced from crystallographic analysis.

A semiempirical calculation gives the HOMO–LUMO gap of TTFsq^{i}Pr as 6.16 eV, whereas in the UV-vis spectra the ICT band of TTFsq^{i}Pr is observed in the range of 520–550 nm corresponding to a photon energy of 2.3 eV, and the activation energy of the resistivity is estimated to be 0.3 eV. This remarkable suppression in the excitation energy, especially in the solid state, can be explained in terms of a large dielectric constant of the TTFsq^{i}Pr crystal, due to the large electrical dipole moment (5.4 Debye based on the PM5 calculation) of the donor–acceptor structure of the molecules.

Conclusions

Two isopropyl TTF semisquarates, TTFsq^{i}Pr and EDT-TTFsq^{i}Pr, have been prepared. These molecules show a solvatochromism effect due to intramolecular charge transfer from the TTF unit to the semisquarate unit. The crystal structure of TTFsq^{i}Pr is characterized as a one-dimensional slightly dimerized column of TTF units. Due to the charge redistribution and the stacking of the TTF units, these molecules exhibit an electrical conductivity even in their neutral solid form. The semiempirical molecular orbital calculation suggests a relation between the charge redistribution and HOMO–LUMO excitation.

Preliminary experiments suggest that the isopropyl protecting group of these molecules can be removed by base-catalyzed hydrolysis. The characterization of the resulting TTF-semisquaric acids and their ability to form coordination complexes with transition metal ions, are now under investigation, and will be reported elsewhere.

Acknowledgements

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