

Preparation, X-ray structures and unique redox reactions of novel 2,2'-(2,2-dimethylpropane-1,3-diylidene)bis(1,3-benzodithiole)-type electron donors fused with a naphthalene ring

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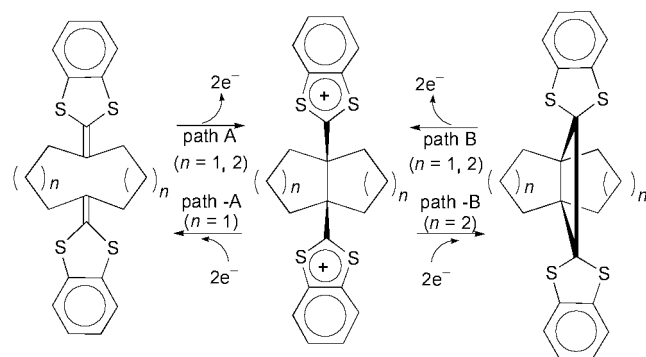
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The title π -extended TTF derivatives **1** and **2** were prepared from the corresponding diketones by Wittig–Horner reactions. Donor **1** with a naphthalene-1,8-diyl skeleton adopts a butterfly-shaped geometry; its oxidation caused transannular C–C bonding to give the dicationic cyclopropane derivative 4^{2+} , from which **1** was regenerated upon $2e^-$ -reduction. The 2,3-diyl isomer **2** possesses, on the other hand, an almost planar π -system and underwent 2-stage $1e^-$ -oxidation, thus allowing the isolation of both 2^{+} and 2^{2+} as stable salts.

Introduction

Recently much attention has been focused on molecules whose structures and properties can be controlled by external stimuli.¹ Among them, redox systems that undergo drastic geometrical changes upon electron transfer (ET) are of special interest^{2,3} because they might be applicable to the construction of molecular switches or memories based on their electrochemical response and bistability.⁴ In this regard, we previously studied a series of tetrathiafulvalene (TTF) analogues inserted by a cycloalkane moiety, and their redox behaviors were compared with those of the corresponding tricyclic isomers (Scheme 1).⁵



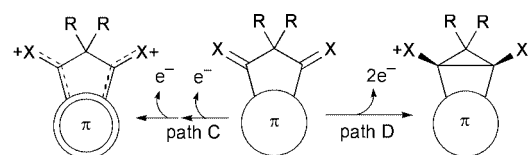
Scheme 1

Upon $2e^-$ -oxidation, both types of donors transformed into the bicyclic dications *via* path A and B, respectively.† Upon $2e^-$ -reduction, the dicationic bicyclo[3.3.0]octane derivative ($n = 1$) exclusively underwent C–C bond fission to the diolefin (path –A), whereas the higher homologue ($n = 2$) gave only the tricyclic compound by C–C bonding (path –B). These results indicate that slight perturbation in the bridging units alters orbital interaction between the chromophores, thus switching the reaction pathway from one to another in these redox cycles.

In our continuing efforts to construct dynamic redox systems that undergo reversible C–C bond breaking/making upon ET,³ we have become interested in the redox behavior of the π -inserted TTF derivatives. Quite a few compounds of this type

† The cyclohexane-1,4-diylidene derivative ($n = 0$) did not give the similar bicyclic dication, probably due to the difficulty in forming the bicyclo[2.2.0]hexane framework.

have been prepared as new candidates for organic conducting materials.⁶ They form stable cationic species upon ET, whose spin and/or charge are delocalized over the inserted π -system (e.g., path C in Scheme 2). However, there would be certain



Scheme 2

conditions that prefer the transannular-bonding pathway (path D) over the competing path C, which might be attained by structural perturbation in the bridging π -unit.

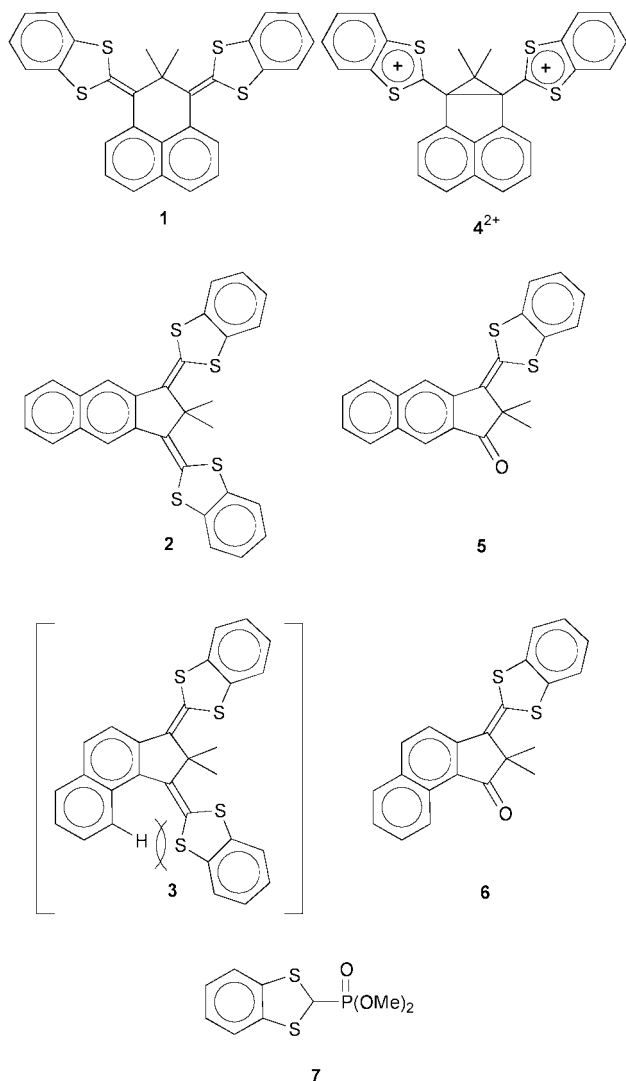
From such a viewpoint, we have designed the title electron donors. The 1,3-benzodithiol-2-ylidene moiety was selected as end groups (X) in anticipation of high stability and crystallinity of the cationic species for isolation. Two methyl groups are attached on C² of the propane unit (R = Me) to avoid deprotonation from the dications after ET.⁷ The naphthalene nucleus is a π -system of choice. Geometrical features and electronic structures may depend on its bridging position, so different redox behaviors are expected in the isomeric extended dibenzo-TTF derivatives **1–3** with naphthalene-1,8-, -2,3- and -1,2-diyl unit, respectively.

It is worth noting that the 1,8-isomer **1** gave the dication with a cyclopropane ring (path D), whereas the 2,3-isomer **2** underwent two-stage $1e^-$ -oxidation (path C), thus successfully realizing the divergent pathways in the closely related isomeric compounds.

Results and discussion

Preparation and molecular geometry

The Wittig–Horner reaction of 2,3-dihydro-2,2-dimethyl-1*H*-phenalene-1,3-dione⁸ with 3 equivalents of 2-dimethoxyphosphinoyl-1,3-benzodithiole⁹ **7** proceeded smoothly to give the 1,8-isomer **1** as yellow crystals in 90% yield. Under similar conditions, two other diketonic precursors⁸ with an indane-1,3-dione skeleton were converted to the monofunctionalized derivatives **5** and **6** in 97 and 87% yield, respectively. Although the isolated monoketone **5** could be transformed into the 2,3-isomer **2** by repeating the same procedure (86% yield based on



consumed **5**), another monoketone **6** remained unchanged. The low electrophilicity of the C=O group in **6** ($\nu_{\text{C=O}}$ 1684 cm^{-1})[‡] by conjugation with a 1,3-dithiol-2-ylidene group may account for the difficulty in forming the 1,2-isomer **3**. At the same time, severe steric repulsion between the S atom and the *peri*-hydrogen at C⁸ in **3** might prevent **6** from undergoing further Wittig–Horner reaction.

Though less pronounced than in **3**, similar steric hindrance seems to be the reason for the butterfly-shaped deformation of **1**. X-Ray structural analysis revealed that the central 6-membered ring adopts an envelope form (dihedral angle 56.1°), and the two benzodithioles at the 1,3-positions of the propane unit are sticking out in roughly the same direction from the naphthalene plane (Fig. 1). As a consequence, the dihedral angle between the two planes of exocyclic double bonds is only 104.0° and the non-bonded interatomic distance between C¹ and C³ decreases to 2.39 Å. Such structural features are advantageous to transannular C–C bonding to form a bicyclo[3.1.0] skeleton upon ET. In contrast, the 2,3-isomer **2** possesses an almost planar geometry (Fig. 2). The dihedral angle between the *exo* methylene bond and the naphthalene plane is only 2.4°, thus making the structure suitable for delocalization of π electrons. Due to the geometrical variation in **1** and **2**, their redox behaviors are quite different from each other.

[‡] This frequency is much lower than that in the precursor diketone (1746 cm^{-1}). In the case of another monoketone **5** (1712 cm^{-1}), contribution of a polarized form is much less than in **6**, probably due to the 2,3-naphthoquinodimethane skeleton in the zwitterionic structure for **5**. Low reactivities of polarized ketone functions were also found in preparing other extended TTF derivatives (*e.g.*, ref. 10).

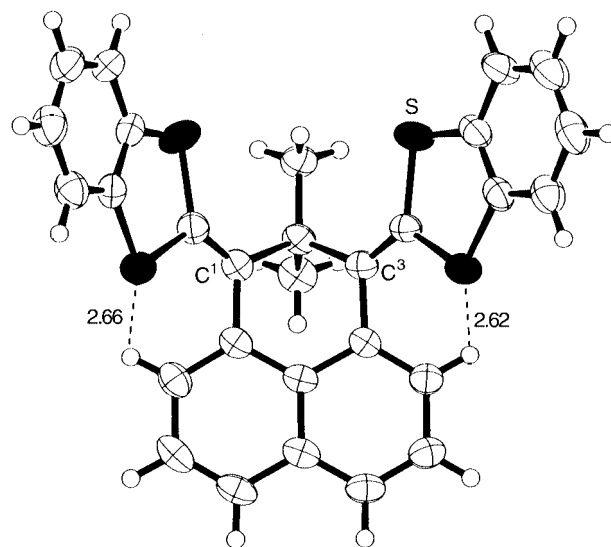


Fig. 1 Molecular geometry of **1** determined by X-ray analysis at 193 K. Non-bonded C¹...C³ distance is 2.39 Å. Short S...H contacts of 2.62 and 2.66 Å are shown by dotted line.

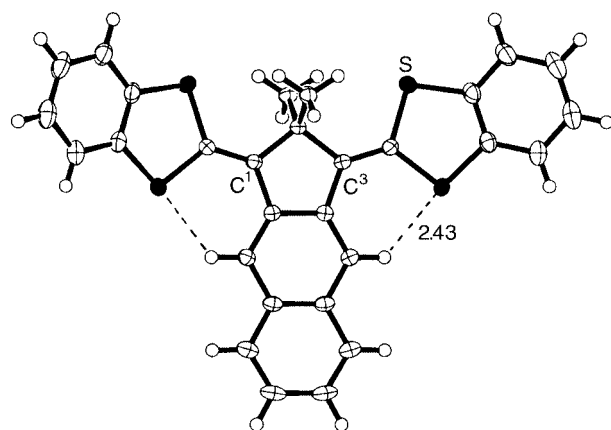


Fig. 2 Molecular geometry of **2** determined by X-ray analysis at 203 K. Non-bonded C¹...C³ distance is 2.42 Å. Short S...H contacts of 2.43 Å are shown by dotted line.

Redox properties

The donating properties of **1** and **2** are comparable to that of dibenzo-TTF [$E_1^{\text{ox}} = +0.74$ V; $E_2^{\text{ox}} = +1.13$ V vs. standard calomel electrode (SCE)] as shown by the first oxidation potentials (E_1^{ox}) measured by cyclic voltammetry in CH_2Cl_2 . The 2,3-isomer **2** [$E_1^{\text{ox}} = +0.76$ V; $E_2^{\text{ox}} = +1.02$ V (quasi-reversible)] underwent two-stage 1e-oxidation as in many TTF derivatives. However, the 1,8-isomer **1** showed a 2e-oxidation wave in its voltammogram ($E_1^{\text{ox}} = +0.77$ V) similar to the cases of cycloalkane-inserted TTFs that exhibit dynamic redox properties.

Upon treatment of **1** with 2 eq. of (*p*-BrC₆H₄)₃N⁺SbCl₆[−] in CH_2Cl_2 , the dication salt **4**²⁺(SbCl₆[−])₂ was obtained in 74% yield as a stable pale tan precipitate with low solubility (Scheme 3). Although formation of a transannular C–C bond should be easily confirmed by the NMR spectra, only featureless broad signals were obtained due to rapid decomposition of **4**²⁺ upon dissolution. Its suspension in EtOH, however, reacted smoothly with NaBH₄ to give the colorless hydride adduct quantitatively, whose structure was unambiguously determined to be the cyclopropane derivative H₂**4** by X-ray crystallography (Fig. 3). The newly formed transannular bond in H₂**4** [1.556(5) Å] is longer than the typical cyclopropane bond (1.51 Å).¹¹ Further expansion of the corresponding bond is expected in the dication **4**²⁺ by repulsive electrostatic interaction between two benzodithiolium moieties. This elongation is responsible for its ready fission upon 2e-reduction; **1** was regenerated from

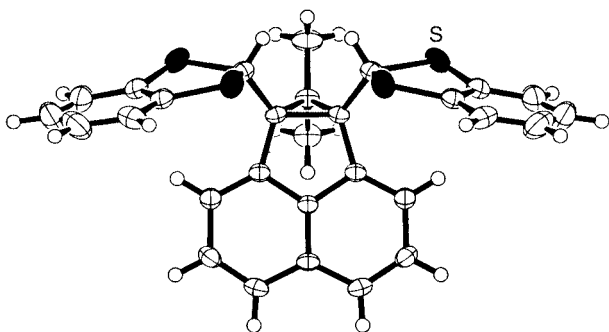
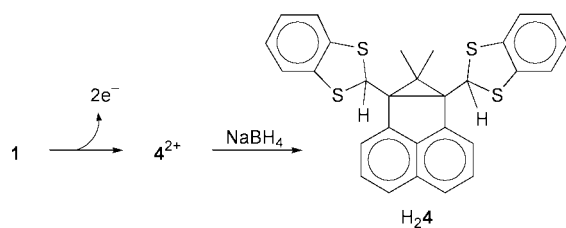


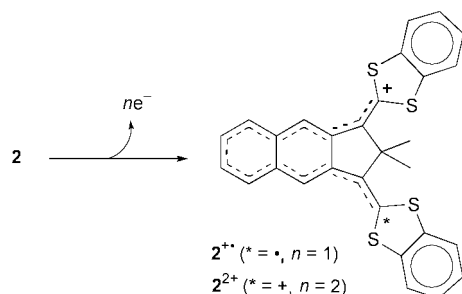
Fig. 3 Molecular geometry of $H_2.4$ determined by X-ray analysis at 213 K.



Scheme 3

$4^{2+}(\text{SbCl}_6^-)_2$ in 76% yield upon treatment with Zn dust in EtOH. These results show that the extended TTF derivative **1** and the cyclopropane-type dication 4^{2+} can constitute a 'reversible' redox cycle, and that the dynamic redox system can be constructed by the molecules with π -conjugated end groups, such as **1**.

In contrast, not only the dication but also the cation radical of **2** could be isolated by treating **2** with 2 eq. or 1 eq. of $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ in CH_2Cl_2 , respectively (Scheme 4).



Scheme 4

Such results are in accord with stepwise ET suggested by the voltammetric analysis of **2** with an almost planar geometry. The electrical conductivity of $2^{+•}\text{SbCl}_6^-$ ($\sigma = 3.7 \times 10^{-6} \text{ S cm}^{-1}$) is not spectacular but is high enough to suggest delocalization of the unpaired electron over the π -system through the 2,3-naphthoquinodimethane skeleton.

Conclusions

This study has revealed that the π -extended TTF derivative can exhibit dynamic redox behavior under certain conditions as shown by the redox pair of **1** and 4^{2+} . Preference for C–C transannular bonding (path D) over charge delocalization into the annelated π -system (path C) may be related to the difficulty in attaining a planar geometry in the hypothetical dication 1^{2+} . At the same time, the non-Kekulé structure of 1,8-naphthoquinodimethane seems to favor transannular bonding of 1^{2+} to 4^{2+} with an acenaphthene skeleton. Similar C–C bonding in 2^{2+} would induce too large a strain energy, due to formation of a bicyclo[2.1.0]pent-2-ene skeleton, which could not be compensated for even if the 2,3-naphthoquinodimethane is aromatized to naphthalene.

Experimental

Preparation of new donors

To a solution of 2-dimethoxyphosphinoyl-1,3-benzodithiole⁹ **7** (597 mg, 2.28 mmol) in dry tetrahydrofuran (THF) (20 mL) was added dropwise BuLi (1.55 mol dm^{-3} in *n*-hexane; 1.47 mL, 2.28 mmol) at -78°C under Ar. After being stirred for 1.5 h at this temperature, the resultant yellow solution was added portionwise to a precooled solution of 2,3-dihydro-2,2-dimethyl-1*H*-phenalene-1,3-dione⁸ (170 mg, 0.76 mmol) in dry THF (6 mL) at -78°C . The whole mixture was allowed to warm to rt over a period of 3 h. After quenching by addition of water and extraction with CHCl_3 , the organic layer was washed with brine and dried over Na_2SO_4 . Evaporation of solvent followed by recrystallization from acetone– CHCl_3 gave 2,2'-(2,3-dihydro-2,2-dimethyl-1*H*-phenalene-1,3-diylidene)bis(1,3-benzodithiole) **1** as yellow cubes (335 mg, 90%).

Similar procedures on 2,3-dihydro-2,2-dimethyl-1*H*-benz[*f*]indene-1,3-dione^{8§} and 2,3-dihydro-2,2-dimethyl-1*H*-benz[*e*]indene-1,3-dione^{8§} gave the corresponding *mono* methylenedione derivatives (**5** and **6**) as orange crystals in 97 and 87% yield, respectively. The further Wittig–Horner reaction of **5** by using 3 eq. of **7**/BuLi gave 2,2'-(2,3-dihydro-2,2-dimethyl-1*H*-benz[*f*]indene-1,3-diylidene)bis(1,3-benzodithiole) **2** as yellow crystals (24% yield; 72% recovery of **5**).

Data for **1**: mp $238.5\text{--}247.0^\circ\text{C}$ (decomp.) (Found: C, 69.8; H, 4.2; S, 25.7. Calc. for $\text{C}_{29}\text{H}_{20}\text{S}_4$: C, 70.1; H, 4.05; S, 25.8%). λ_{max} (CH_2Cl_2)/nm 397 sh (log ϵ 3.98), 364 (4.20), 316 (4.17), 305 (4.17), 292 sh (4.09); δ_{H} (400 MHz; CDCl_3 ; TMS) 7.95 (2H, dd, J 7.3, 1.0 Hz), 7.72 (2H, dd, J 8.3, 1.0 Hz), 7.45 (2H, dd, J 8.3, 7.3 Hz), 7.18–7.20 (2H, m), 7.06–7.08 (2H, m), 6.97–7.03 (4H, m), 1.78 (6H, s); ν_{max} (KBr)/ cm^{-1} 3052, 2960, 1530, 1516, 1484, 1452, 1126, 830, 738; m/z (EI) 496 (M^+ , 100%), 344 (46), 240 (44).

Data for **2**: mp $>300^\circ\text{C}$ (Found: C, 69.5; H, 4.2; S, 26.0. Calc. for $\text{C}_{29}\text{H}_{20}\text{S}_4$: C, 70.1; H, 4.05; S, 25.8%). λ_{max} (CH_2Cl_2)/nm 448 (log ϵ 4.05), 422 (4.12), 387 (4.62), 370 (4.58), 343 (4.61); δ_{H} (400 MHz; CD_2Cl_2 ; TMS) 8.13 (2H, br), 7.90 (2H, AA'BB'), 7.52 (2H, AA'BB'), 7.45 (4H, AA'BB'), 7.22 (4H, br), 1.89 (6H, s); ν_{max} (KBr)/ cm^{-1} 3056, 2924, 1568, 1518, 1448, 1436, 1388, 856, 848, 738; m/z (EI) 496.0443 (M^+ . $\text{C}_{29}\text{H}_{20}\text{S}_4$ requires M , 496.0448), 481 (100), 329 (14), 241 (17).

Data for **5**: mp $181.7\text{--}182.6^\circ\text{C}$ (Found: C, 73.45; H, 4.6; S, 17.9. Calc. for $\text{C}_{22}\text{H}_{16}\text{OS}_2$: C, 73.3; H, 4.5; S, 17.8%). δ_{H} (400 MHz; CDCl_3 ; TMS) 8.40 (1H, s), 8.29 (1H, s), 8.02 (1H, d, J 8.3 Hz), 7.98 (1H, d, J 8.3 Hz), 7.62 (1H, ddd, J 8.3, 6.8, 1.0 Hz), 7.49–7.53 (2H, m), 7.43 (1H, AA'BB'), 7.23 (2H, AA'BB'), 1.53 (6H, s); ν_{max} (KBr)/ cm^{-1} 3060, 2928, 1712, 1624, 1572, 1546, 1504, 1452, 1160, 736; m/z (FD) 360 (M^+).

Data for **6**: mp $161.4\text{--}162.8^\circ\text{C}$ (Found: C, 73.35; H, 4.65; S, 17.6. Calc. for $\text{C}_{22}\text{H}_{16}\text{S}_2$: C, 73.3; H, 4.5; S, 17.8%). δ_{H} (400 MHz; CDCl_3 ; TMS) 9.26 (1H, br d, J 8.3 Hz), 8.16 (2H, m), 7.89 (1H, br d, J 7.8 Hz), 7.70 (1H, ddd, J 8.3, 6.8, 1.0 Hz), 7.57 (1H, ddd, J 8.3, 6.8, 1.0 Hz), 7.41–7.46 (2H, m), 7.22 (2H, AA'BB'), 1.51 (6H, s); ν_{max} (KBr)/ cm^{-1} 3052, 2924, 1684, 1572, 1546, 1514, 1436, 1156, 810, 732; m/z (FD) 360 (M^+).

Redox reactions

Oxidation of donor 1 to dication 4^{2+} . To a solution of **1** (80 mg, 0.16 mmol) in dry CH_2Cl_2 (8 mL) was added $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ (263 mg, 0.32 mmol) under Ar, and the mixture was stirred at rt for 2 h. Filtration of the pale tan precipitate gave the dication salt $4^{2+}(\text{SbCl}_6^-)_2$ (143 mg) in 74% yield: mp $128.0\text{--}129.5^\circ\text{C}$ (decomp.) (Found: C, 30.2; H, 1.8; S, 11.1. Calc. for $\text{C}_{29}\text{H}_{20}\text{Cl}_{12}\text{S}_4\text{Sb}_2$: C, 29.9; H, 1.7; S, 11.0%); ν_{max} (KBr)/ cm^{-1} 3092, 1616, 1552, 1438, 1418, 1104, 780, 748.

§ The IUPAC names for benz[*e*]indene and benz[*f*]indene are cyclopenta[*a*]naphthalene and cyclopenta[*b*]naphthalene respectively.

Reduction of dication 4^{2+} with Zn. To a suspension of $4^{2+}(\text{SbCl}_6^-)_2$ (50 mg, 0.043 mmol) in dry EtOH (5 mL) was added Zn dust (40 mg, 0.61 mmol). After stirring of the mixture for 20 min, most of EtOH was evaporated, and the mixture was extracted with CHCl_3 . The combined extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvent gave pure **1** (16 mg) in 76% yield.

Reduction of dication 4^{2+} with NaBH_4 . To a suspension of $4^{2+}(\text{SbCl}_6^-)_2$ (70 mg, 0.060 mmol) in dry EtOH (10 mL) was added NaBH_4 (68 mg, 1.79 mmol). After being stirred for 15 min, the resultant yellow solution was diluted with water. The whole mixture was extracted with benzene, and the combined extracts were washed with brine and dried over Na_2SO_4 . Evaporation of solvent gave essentially pure **2,2'-[2,3-dihydro-2,2-dimethyl-1H-1,3-cyclophenalene-1,3-diyl]bis(1,3-benzodithiole)** **H₂4** quantitatively, and recrystallization from acetone- CH_2Cl_2 gave colorless crystals (26 mg, 87%), mp 259.2–267 °C (decomp.) (Found: C, 69.7; H, 4.6; S, 25.55. Calc. for $\text{C}_{29}\text{H}_{22}\text{S}_4$: C, 69.85; H, 4.45; S, 25.70%); λ_{max} (CH_2Cl_2)/nm 315 (log ϵ 3.81), 302 (3.93), 291 (3.84), 278 (3.79); δ_{H} (400 MHz; CDCl_3 ; TMS) 7.71 (2H, br d, J 7.3 Hz), 7.58 (2H, br d, J 7.8 Hz), 7.25–7.30 (4H, m), 6.97–7.08 (6H, m), 5.95 (2H, s), 1.59 (3H, s), 0.44 (3H, s); δ_{C} (100 MHz; CDCl_3 ; TMS) 140.11, 139.30, 138.48, 137.91, 130.42, 126.81, 125.56, 125.45, 124.07, 123.16, 122.21, 121.84, 53.96, 51.28, 42.21, 19.89, 18.79; ν_{max} (KBr)/ cm^{-1} 3056, 2928, 1620, 1564, 1448, 1432, 1120, 836, 740; m/z (FD) 498 (M^+).

Oxidation of donor **2 to cation radical $2^{\cdot+}$.** To a suspension of **2** (20 mg, 0.040 mmol) in dry CH_2Cl_2 (10 mL) was added (*p*- BrC_6H_4)₃ $\text{N}^+\text{SbCl}_6^-$ (33 mg, 0.040 mmol) under Ar, and the black mixture was stirred overnight. Filtration of the black precipitate gave the cation radical salt $2^{\cdot+}\text{SbCl}_6^-$ (33 mg, 82%), mp 208.2–214.7 °C (decomp.) (Found: C, 41.8; H, 2.5; Cl, 25.7; S, 15.5. Calc. for $\text{C}_{29}\text{H}_{20}\text{Cl}_6\text{S}_4\text{Sb}$: C, 41.9; H, 2.4; Cl, 25.6; S, 15.4%); ν_{max} (KBr)/ cm^{-1} 1634, 1474, 1402, 1386, 1364, 1218, 1146, 1096, 742. Its electrical conductivity was measured on a compressed pellet by a two-probe method at rt. The value for TTF-TCNQ, the representative molecular metal, is 2.7 S cm^{-1} under the same conditions.

Oxidation of donor **2 to dication 2^{2+} .** To a suspension of **2** (25 mg, 0.050 mmol) in dry CH_2Cl_2 (15 mL) was added (*p*- BrC_6H_4)₃ $\text{N}^+\text{SbCl}_6^-$ (82 mg, 0.10 mmol) under Ar, and the blue mixture was stirred overnight. Filtration of the black precipitate gave the dication salt $2^{2+}(\text{SbCl}_6^-)_2$ (44 mg, 75%); mp 141.8–148.0 °C (decomp.) (Found: C, 29.3; H, 1.95; Cl, 35.68; Calc. for $\text{C}_{29}\text{H}_{20}\text{Cl}_{12}\text{S}_4\text{Sb}_2\cdot\text{H}_2\text{O}$: C, 29.4; H, 1.9; Cl, 35.95%); ν_{max} (KBr)/ cm^{-1} 1634, 1550, 1378, 1362, 1212, 1152, 1114, 1064, 752.

Upon treatment of this salt with NaBH_4 , **2** was re-produced as the sole product. This result indicates that no skeletal transformation occurs during the oxidation of **2** to the dication.

Measurement of redox potentials. Oxidation potentials (E^{ox}) were measured by cyclic voltammetry in dry CH_2Cl_2 containing 0.1 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte. Ferrocene undergoes 1e-oxidation at +0.53 V under the same conditions. All the values shown in the text are in E/V vs. SCE, and Pt was used as the working electrode.

Crystallographic study

Data collection was conducted by a Rigaku Mercury charge-coupled device (CCD) apparatus or a RAPID IP apparatus with Mo- $K\alpha$ radiation at low temperatures (a liquid N_2 flow method). Crystallographic data are as follows.†

1: $\text{C}_{29}\text{H}_{20}\text{S}_4$, M 496.72, tetragonal $P\bar{4}2_1c$ (No. 114), $a = 27.004(8)$, $c = 6.429(2)$ Å, $V = 4687(2)$ Å³, $\rho(Z = 8) = 1.408$ g cm^{-3} , $T = 203$ K, $\mu = 4.22$ cm^{-1} . The final R - and R_w -values were 0.033 and 0.048 for 2365 reflections with $I > 3\sigma I$ (independent 2982) and 299 parameters.

2: $\text{C}_{29}\text{H}_{20}\text{S}_4$, M 496.72, orthorhombic $Pnma$ (No. 62), $a = 11.9083(3)$, $b = 20.3741(5)$, $c = 9.3598(5)$ Å, $V = 2270.9(1)$ Å³, $\rho(Z = 4) = 1.453$ g cm^{-3} , $T = 203$ K, $\mu = 4.36$ cm^{-1} . The final R - and R_w -values were 0.030 and 0.045 for 2065 reflections with $I > 3\sigma I$ (independent 2693) and 154 parameters. Molecule adopts S_1 symmetry in crystal, and the carbon atoms of the dimethylmethano bridge are located on the crystallographic mirror plane.

H₂4: $\text{C}_{29}\text{H}_{22}\text{S}_4$, M 498.73, orthorhombic $Cmc2_1$ (No. 36), $a = 21.9307(8)$, $b = 15.1049(6)$, $c = 7.2110(3)$ Å, $V = 2388.7(1)$ Å³, $\rho(Z = 4) = 1.387$ g cm^{-3} , $T = 213$ K, $\mu = 4.14$ cm^{-1} . The final R - and R_w -values were 0.024 and 0.028 for 1391 reflections with $I > 3\sigma I$ (independent 1520) and 156 parameters. Molecule adopts S_1 symmetry in crystal, and the carbon atoms of the dimethylmethano bridge as well as C^{4a} and C^{8a} of the naphthalene ring are located on the crystallographic mirror plane.

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