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Bis(1,3-dithiol-2-ylidene)-[3.3]paracyclophanes: orthogonal intramolecular charge transfer interaction

Katsuya Sako,[a,*] Yukiharu Mase,[a] Yousuke Kato,[a] Tetsuo Iwanaga,[b,c] Teruo Shinmyozu,[c] Hiroyuki Takemura,[d] Mitsuhiro Ito,[a] Kousuke Sasaki[a] and Hitoshi Tatemitsu[a,*]

[a]*Department of Systems, Management and Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan*
[b]*Department of Molecular Chemistry, Graduate School of Sciences, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[c]*Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[d]*Department of Chemical and Biological Science, Faculty of Science, Japan Women's University, Mejirodai 2-8-1, Bunkyo-ku, Tokyo 112-8681, Japan*

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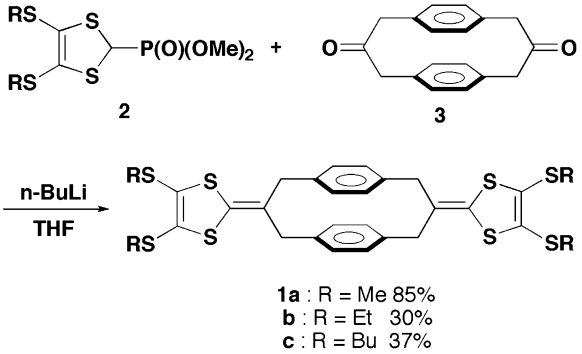
Abstract—A novel donor-cyclophane, orthogonally incorporated 1,3-dithiol-2-ylidene units (DT) to the cyclophane benzene rings, was synthesized in order to observe the intramolecular charge transfer (ICT) between the donor units and the cyclophane benzene rings.

Cyclophanes represent an important class of compounds in many aspects of macrocyclic and supramolecular chemistry.[1] In [2.2]paracyclophane systems, an unpaired electron of the radical anions[2] and radical cation[3] is delocalized over both π-moieties. Similarly, a highly stabilized radical cation is also observed in [3_n]cyclophane systems ($n = 3, 5, 6$).[4] On the other hand, tetrathiafulvalene (TTF) containing macrocyclic compounds, named TTF cyclophanes, have been intensively studied for molecular devices such as sensors, switches for strong noncovalent inter and intramolecular interactions.[5]

Cyclophanes that are linked with orthogonal donor units such as TTF are of particular interest because they enable new types of intramolecular electron transfer interactions, charge separation, and electronic interaction between donor units through a cyclophane framework. We here present the synthesis, electrochemistry, X-ray structure, and intramolecular charge transfer (ICT) properties of novel rigid molecules (**1**) containing 1,3-dithiol-2-ylidene (DT) donor moieties, which are linked by the double bond orthogonally to [3.3]paracyclophane ([3.3]PCP).

The synthesis of **1** was carried out using Wittig–Horner type reaction of phosphonate esters **2**[6] and [3.3]paracyclophane-2,11-dione **3**[7] (Scheme 1). After the generation of phosphonate ester anions of **2** (2 equiv) with *n*-BuLi, **3** was added into the anion solution under Ar atmosphere. After workup, column chromatography and recrystallization, the target 'orthogonal bis(DT)-[3.3]-PCP (DT–PCP) **1**' was obtained as a pale pink powder in 30–85% yields (Scheme 1).[8]



Scheme 1. Synthesis of the compounds **1a**–**c**.

Keywords: Cyclophane; 1,3-Dithiol-2-ylidene; Intramolecular charge transfer; Orthogonal π-system; π-donor.

[*] Corresponding authors. Tel./fax: +81 52 735 5167; e-mail: sako@nitech.ac.jp

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The molecular structure of **1a** was determined by single crystal X-ray diffraction analysis. A general view of the molecular structure of **1a**, together with the crystallographic atom-numbering scheme, is shown in Figure 1.[9] The bridges of the cyclophane take a chair form and the 1,3-dithiole moiety bends outwards with planes A(C12–C11–S1–S2) and B(C10–S1–S2) folding along the S1···S2 lines by 29.65(12)°. The dihedral angle of the DT (planes A and B) moiety with the benzene ring of [3.3]PCP is 83.16(5) and 85.72(8)°, respectively. **1a** has the unique cross tape structure, in which the planes of the DT donor moieties lie orthogonal to the benzene rings of [3.3]PCP. This molecule affords the first example of an orthogonal donor-[3.3]PCP system with built-in through-space interaction between the orthogonal π-systems, including donor components. The intermolecular CH–π interaction between the benzene ring and the methyl group is observed by the distance (2.960(37) Å) between benzene and H13 of the molecule (Fig. 2).[10]

The electronic spectrum of **1b** in cyclohexane shows a broad absorption in the 400–600 nm region, centered at ca. 450 nm ($\varepsilon \sim 150$), probably due to a weak charge transfer interaction. This absorption was not observed in [3.3]PCP-dione **3** itself. The intensity of this broad absorption varied according to the Beer–Lambert law, as expected for the ICT band (Fig. 3). Although the ICT band intensity decreased by increasing the mixed ratio of CH_2Cl_2 to cyclohexane, the absorption intensities of **1b** at 335 and 365 nm enhanced. The UV–vis spectra of **1b** in much polar solvents (THF, mixed solvent of THF and cyclohexane (1:1)) observed no broad band in the 400–600 nm region, although other absorptions (300, 335, 365 nm in cyclohexane) due to π–π^* transition of DT and the cyclophane units appeared at almost the same wavelengths and increases the intensities of these bands. The intensity of the ICT band decreased and shifted to a shorter region by increasing the ratio of the polar solvent. The absorption due to the ICT interaction was overlapped with other strong ones.[11]

The oxidation potentials of **1a**–**c** and TTF measured by cyclic voltammetry are summarized in Table 1. The cyclic voltammograms of **1a**–**c** in CH_2Cl_2 consist of one-pair of reversible waves (the first processes), one-pair

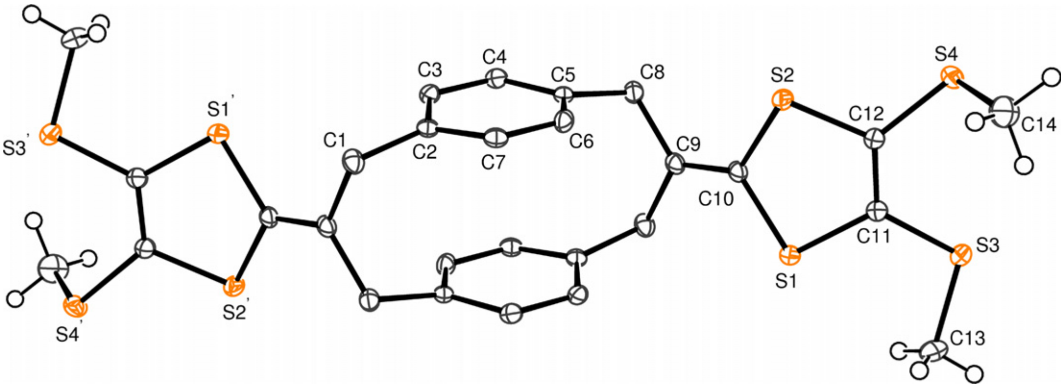


Figure 1. The molecular structure of **1a** with atom labeling scheme.

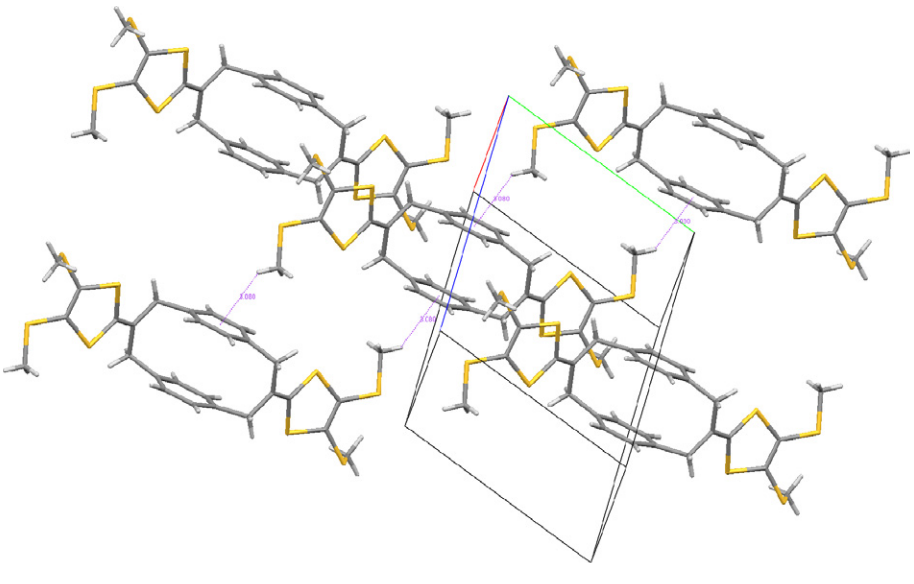


Figure 2. The crystal packing in **1a** viewed side [010].

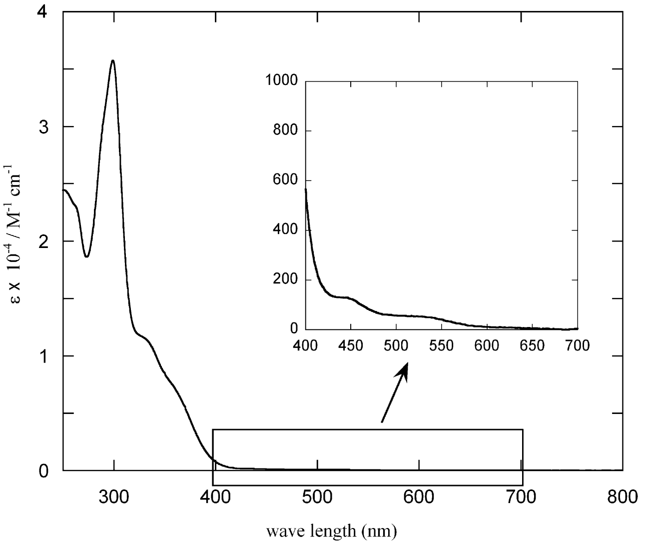
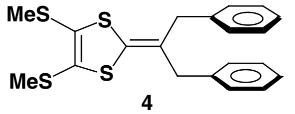


Figure 3. UV–vis spectrum of **1b** in cyclohexane at 25 °C.

Table 1. Redox potentials of DT–PCPs (**1**) and TTF

Compound	E_1	E_2	E_3	$\Delta E(=E_2 - E_1)$
1a	+0.31	+0.64	+1.19	0.33
1b	+0.32	+0.65	+1.20	0.33
1c	+0.32	+0.66	+1.21	0.34
4	+0.29	+0.64		0.35
TTF	−0.08	+0.37		0.45

Conditions: 0.1 mol dm^{-3} n-Bu$_4$NClO$_4$, dichloromethane, 25 °C, Pt working, and counter electrodes. The potentials were measured against an Ag/Ag$^+$ electrode. E in V versus Fc/Fc$^+$.



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of quasi-reversible waves (the second processes) (Fig. 4). By CV measurement up to 1.8 V, the third process appears as one-pair of irreversible waves. The first redox potentials (E_1 0.31–0.32 V) of **1a**–**c** were almost the same. The first and second redox steps were characteristic for 1,3-dithiol-2-ylidene moieties and the third irreversible step was ascribed to the redox of the benzene rings of [3.3]PCP unit. The E_1 values of **1a**–**c** were higher by 0.40 V compared with that of TTF, and similar to that of bis(benzyl)DT derivative **4**. The cyclic voltammogram patterns of **1a**–**c** are quite similar and similar redox potentials are observed. The ΔE ($=E_2 - E_1$) values (0.33–0.34 V for **1a**–**c**) were ca. 0.12–0.11 V smaller than that of TTF. These data suggest that the on-site Coulombic repulsion in their dication states is decreased by delocalization of the two positive charges in the two 1,3-dithiol-2-ylidene (DT) units and the ICT interaction does not affect the redox potentials. If there is an interaction between DT units through cyclophane skeleton in CV measurement, then the redox patterns would become more complex ones. Furthermore, from CV data, **1**, it is proposed that the exomethylene bond of DT became the single bond and is the cause for the structural change in the form, which was parallel to cyclophane benzene ring in the diradical state. However, the proposed structure change should be further confirmed.

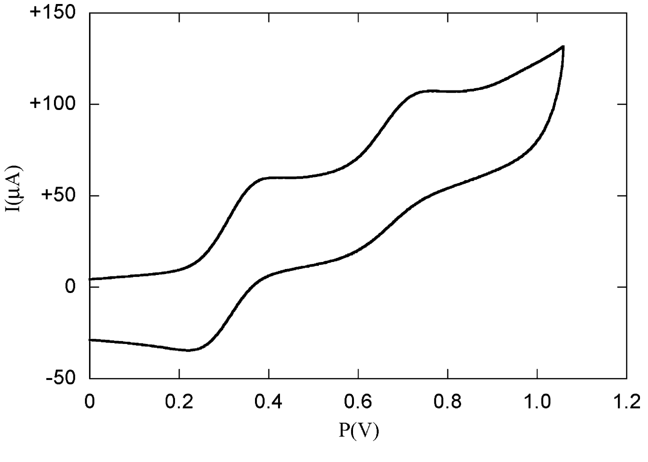

Figure 4. Cyclic voltammogram of **1a** in dichloromethane.

Compounds **1a**–**c** are the first examples of the introduction of 1,3-dithiol-2-ylidenyl moieties in orthogonal arrangement into [3.3]PCP. Electrochemical and electronic spectral properties of orthogonal bis(DT)-[3.3]PCPs indicated the presence of intramolecular charge transfer interaction between the DT moieties as donor units and the benzene rings of [3.3]PCP as acceptor units.

Acknowledgements

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8. Compound **1a**: pale pink crystals; mp >230 °C (decomp.); ^{1}H NMR ($CDCl_3$, 90 MHz): δ 2.46 (6H, s, SCH_3), 3.37 (8H, s, benzylic H), 6.68 (8H, s, benzene H); HRMS (FAB): Calcd for $C_{28}H_{28}S_8 = 619.9957$. Found: 619.9954. Compound **1b**: pale pink crystals; mp 200–202 °C; ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.95 (12H, t, $J = 7.3$ Hz, CH_3), 2.88 (8H, dd, $J = 7.1$, 14.7 Hz, SCH_2), 3.37 (8H, s, benzylic H), 6.67 (8H, s, benzene H); HRMS (FAB): Calcd for $C_{32}H_{36}S_8 = 676.0583$. Found: 676.0590. Compound **1c**: pale pink crystals; mp 138–140 °C; ^{1}H NMR ($CDCl_3$ 90 MHz): δ 0.95 (12H, t, $J = 6.7$ Hz, CH_3), 1.24–1.75 (16H, m, CH_2CH_2), 2.86 (8H, t, $J = 6.7$ Hz, SCH_2), 3.37 (8H, s, benzylic H), 6.68 (8H, s, benzene H); HRMS (FAB): Calcd for $C_{40}H_{52}S_8 = 788.1835$. Found: 788.1832.
9. *Crystal data of* **1a**: $C_{28}H_{28}S_8$, colorless block, triclinic, space group P-1(#2), $a = 7.4362(1)$ Å, $b = 9.9139(4)$ Å, $c = 10.8778(1)$ Å, $\alpha = 68.955(1)°$, $\beta = 70.242(1)°$, $\gamma = 85.515(2)°$, $V = 703.53(3)$ Å^3, $Z = 1$, $T = -160$ °C, $D_c = 1.466$ g/cm^3, $F(000) = 324.00$, $\mu(\text{MoK}\alpha) = 6.53$ cm^{-1}, graphite monochromated MoKα ($\lambda = 0.71069$ Å), $2\theta_{max} = 55°$, total data 6163, unique data 3100 ($R_{int} = 0.030$), $R = 0.033$ and $R_w = 0.112$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 296370. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 0331 e-mail:deposit@ccdc.cam.ac.uk).
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11. UV–vis (cyclohexane) λ_{max} (ε) 525 (50), 451 (120), 365 (6300), 335 (11000), 299 (35700), 263 (22900), 252 (24400) nm; UV–vis (CH_2Cl_2) 367 (7500), 337 (14400), 299 (34600), 258 (30800) nm; UV–vis (THF) 365 (6700), 334 (13500), 298 (33900), 262 (26200), 254 (27900) nm.