Calix[4]arenes Bearing Four Redox-Active π-Conjugated Pendant Groups for a Dimensionally Oriented Redox System

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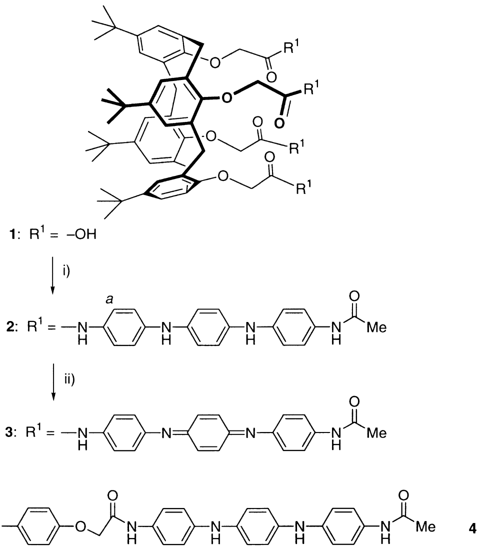
A *p*-*t*-butylcalix[4]arene bearing four redox-active phenylenediamine pendant groups on the lower rim was synthesized and characterized spectroscopically and electrochemically. The interconversion of the oxidation states of the pendant groups was demonstrated both chemically and electrochemically.

π-Conjugated compounds, such as aniline[1] and thiophene[2] telomer or oligomer, have recently attracted much attention as redox-active building blocks to create functionalized electronic materials. The regulated orientation of redox-active π-conjugated chains is envisioned to provide an efficient redox system. The utilization of a molecular scaffold is considered to be a convenient approach to orient the π-conjugated chains. For this purpose, redox-active phenylenediamine pendant groups were demonstrated to be incorporated into a porphyrin[3] or ruthenium bipyridyl complex[4] in a previous study. The preorganized macrocyclic conformation of calixarenes has been focused on for supramolecular systems, such as molecular capsules,[5] rotaxanes, and catenanes.[6] Calix[4]arene is envisaged to be a scaffold for constructing a dimensionally oriented π-conjugated electronic system, which is considered to be promising for potential applications to, for example, redox-switching receptors and efficient catalysts.[7] From these points of view, we herein report on the synthesis of a *p*-*t*-butylcalix[4]arene bearing four redox-active phenylenediamine pendant groups.

The reaction of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(carboxymethoxy)calix[4]arene (**1**) with 1,1′-carbonyldiimidazole, followed by a treatment with excess amounts of *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine, led to the formation of calix[4]arene **2** bearing four phenylenediamine pendant groups on the lower rim via the corresponding acylimidazolide (42%, Scheme 1).[8,9] The four pendant groups were incorporated successfully. The structure of **2** was determined by a comparison of spectral data with those of **4**, a single-strand unit of **2**.[10] The IR spectrum (KBr pellet) of **2** showed amide NH and C=O stretching bands at 3385 and 1663 cm^{-1}, respectively. In the ^{1}H NMR spectrum of **2**, the protons attributable to the four pendant groups were observed equally. Furthermore, the broad signals of H$_a$ in DMSO-d_6 indicate a restricted conformation of the pendant groups (**2**: 7.40 ppm (br), **4**: 7.43 ppm (d, $J = 9.0$ Hz)).



Scheme 1. i) 1,1′-Carbonyldiimidazole, THF, rt, 1.5 h; *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine, THF, reflux, 2 days, 42%. ii) Ag$_2$O, 18-crown-6, DMF, room temperature, 20 h.

The oxidation states of the redox-active phenylenediamine pendant groups of **2** could be interconverted chemically. The treatment of **2** with Ag$_2$O in DMF at room temperature resulted in the oxidation of the phenylenediamine moieties to the quinonediimine ones to afford the calix[4]arene **3** quantitatively, which bears four quinonediimine pendant groups.[11] The formation of **3** was supported by the disappearance of the amine NH stretching band at 3385 cm^{-1} and the appearance of a quinonoid ring breathing band at 1594 cm^{-1} in the IR spectrum (KBr pellet).[12] The conversion from **2** to **3** was also monitored spectroscopically. As the oxidation reaction proceeded, a broad CT band assignable to the quinonediimine moieties appeared at around 500 nm. It should be noted that the treatment of the thus-obtained solution of **3** with 10 molar amounts of $NH_2NH_2 \cdot H_2O$ at room temperature for 12 h under argon led to a disappearance of the CT band along with the formation of the reduced derivative **2**.

The cyclic voltammogram of **2** in a THF solution showed two one-electron redox processes attributable to the phenylenediamine moiety at −86 and 328 mV (E_{pa}) vs Fc/Fc$^+$ (Scheme 2, Fig. 1). These redox potentials were shifted cathodically in comparison with those of **4** (E_{pa}: −2 and +400 mV). This difference might be due to the presence of the four pendant groups on the lower rim.[13]

In conclusion, phenylenediamine pendant groups were introduced into the lower rim of the calix[4]arene scaffold, providing a dimensionally oriented redox system. The interconversion of the oxidation states of the pendant groups can be performed by chemical or electrochemical redox reaction.

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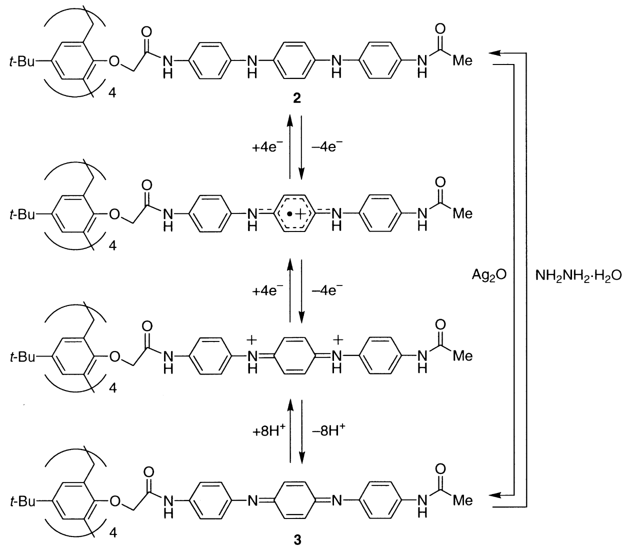

Scheme 2. Redox processes of **2**.

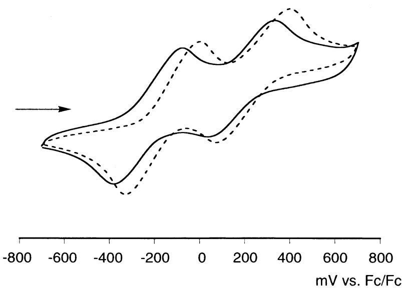

Fig. 1. Cyclic voltammograms of **2** (0.25 mM, solid line) and **4** (1.0 mM, dotted line). Solv. THF containing 0.1 M Bu_4NClO_4, scan rate: 100 mV s^{-1}.

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7 Calixarenes bearing TTF or terphenoquinone moieties have been reported, for example: a) J.-B. Regnouf-de-Vains, M. Sallé, and R. Lamartine, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 2461. b) K. Takahashi, A. Gunji, D. Guillaumont, F. Pichierri, and S. Nakamura, *Angew. Chem., Int. Ed.*, **39**, 2925 (2000).

8 The calix[4]arene **1** was prepared according to the reported method: P. Lhotak and S. Shinkai, *Tetrahedron Lett.*, **36**, 4829 (1995).

9 A mixture of **1** (88 mg, 0.10 mmol) and 1,1′-carbonyldiimidazole (81 mg, 0.50 mmol) in THF (20 mL) was stirred at room temperature for 1.5 h. Then, a THF (20 mL) solution of *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine (166 mg, 0.50 mmol) was added to the reaction mixture, which was stirred at refluxing temperature for 2 days. The reaction mixture was dropwise added to methanol to reprecipitate the solid. The thus-obtained solid was purified by chromatography on silica-gel column eluting with methanol and further reprecipitation from ether to give **2** in 42% yield. **2**: a pale purple solid; Mp 263–265 °C (decomp); IR (KBr) 3385, 3309, 1663, 1508 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6 1.0 mM, 25 °C) δ 9.92 (bs, 4H), 9.65 (bs, 4H), 7.69 (bs, 4H), 7.64 (bs, 4H), 7.40 (br, 8H), 7.35 (d, 8H, J = 8.4 Hz), 6.89 (bs, 16H), 6.87–6.83 (m, 24H), 4.77–4.67 (m, 12H), 3.25 (d, 4H, J = 14.7 Hz), 1.98 (s, 12H), 1.06 (s, 36H); MS (MALDI-TOF) *m*/*z* 2140.0 ($M^+ + 2H$).

10 The phenylenediamine **4** was prepared in 91% yield from 1-*t*-butyl-4-carboxymethoxybenzene by the similar procedure to that of **2**. **4**: Mp 206–207 °C; IR (KBr) 3413, 3371, 3306, 1660, 1606, 1514 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6, 4.0 mM) δ 9.81 (bs, 1H), 9.67 (bs, 1H), 7.76 (bs, 1H), 7.72 (bs, 1H), 7.43 (d, 2H, J = 9.0 Hz), 7.37 (d, 2H, J = 9.0 Hz), 7.32 (d, 2H, J = 9.0 Hz), 6.96 (bs, 4H), 6.92–6.89 (m, 6H), 4.60 (s, 2H), 1.99 (s, 3H), 1.25 (s, 9H); MS (MALDI-TOF) *m*/*z* 522.1 (M^+).

11 To a DMF solution (10 mL) of **2** (20 mg, 9.0 µmol) were added 18-crown-6 (24 mg, 90 µmol) and then Ag_2O (61 mg, 72 µmol). The mixture was stirred at room temperature for 20 h and filtered over Cerite and Al_2O_3 column to give the red solid **3**. **3**: a red solid; Mp 216–218 °C (decomp); IR (KBr) 3304, 1670, 1594, 1500 cm^{-1}; A complicated ^1H NMR spectrum was obtained at room temperature, due to the presence of *syn*- and *anti*-quinonediimine pendant groups. A part of the signals for the methylene protons ($ArCH_2Ar$, 2H) were overlapped by the protons of residual H_2O. ^1H NMR (600 MHz, DMSO-d_6, 1.0 mM, 25 °C) δ 10.38–10.27 (m, 2H), 10.19–10.08 (m, 2H), 10.06–9.84 (m, 4H), 7.75–7.43 (m, 16H), 7.41–7.33 (bs, 4H), 7.04–6.41 (m, 34H), 6.29–6.13 (m, 2H), 4.93–4.75 (m, 8H), 4.65–4.42 (m, 4H), 3.59–3.53 (br, 2H), 2.16–1.98 (m, 12H), 1.37–0.96 (m, 36H), (600 MHz, DMSO-d_6, 1.0 mM, 150 °C) δ 9.62 (bs, 4H), 9.38 (bs, 4H), 7.65–7.50 (m, 16H), 7.05–6.60 (m, 40H), 4.90–4.80 (m, 12H), 3.32 (d, J = 13.2 Hz, 4H), 2.06 (bs, 12H), 1.13 (s, 36H); MS (MALDI-TOF) *m*/*z* 2136.0 ($M^+ + 6H$).

12 Y. Cao, S. Li, Z. Xue, and D. Guo, *Synth. Met.*, **16**, 305 (1986).

13 [**2**] = 0.25 mM; containing 0.1 M Bu_4NClO_4 electrolyte; scan rate = 100 mV s^{-1}.

14 In DMF solution, two one-electron redox processes appeared as one redox couple despite the observation of two one-electron oxidation waves in the case of **4**: [E_{pa} (mV vs Fc/Fc^+): **2** (0.25 mM) −58; **4** (1.0 mM) −48 and +37]. The redox behavior of **2** is likely to be accounted for by the more facile intramolecular interchain disproportion of the radical cation species of the phenylenediamine pendant groups to the corresponding phenylenediamine and protonated quinonediimine (two-electron oxidized form) derivatives than the intermolecular interaction of **4** (J. F. Wolf, C. E. Forbes, S. Gould, and L. W. Shacklette, *J. Electrochem. Soc.*, **136**, 2887 (1989)).