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Reversible σ-Dimerizations of Persistent Organic Radical Cations**

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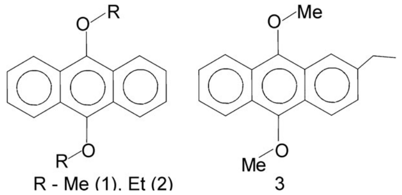
C–C bond formation and cleavage are basic events in organic chemistry. The oxidative σ-dimerization of conjugated aromatic systems involving C–C coupling plays an essential role in organic syntheses,[1] such as oxidative oligo- and polymerization,[2] where a σ-dimeric dication is suggested as a key intermediate.[2–4] Fast-scan cyclic voltammetry and NMR spectroscopic studies have suggested the existence of a doubly charged σ-dimeric species in solution.[3] Effenberger and co-workers succeeded in isolating a dimeric σ-complexed dication of 1,3,5-tripyrrolidinobenzene in 1969 and proved the existence of the σ-dimer in the solid state.[4] More examples of dimeric complexes have been isolated subsequently.[5] In the previously reported oxidative dimerizations, however, the radical cations have not been directly observed and well confirmed owing to their short lifetime.[4,5] In fact, all of the dimerized structures of persistent[6] radical cations of π-conjugated systems observed in the solid state are π-dimers.[3b,7,8]

On the other hand, the polyfluoroalkoxy aluminate superweak anion $[Al(OR_F)_4]^-$ ($OR_F = OC(CF_3)_3$) has been shown to be effective not only in stabilizing intriguing cationic species by delocalization of their positive charges through fluorine–cation contacts, but also in increasing solubility of formed salts owing to its large radius.[9a,b] By using this anion, we recently have successfully isolated radical cations of biphenyl systems.[9c] We now plan to stabilize and characterize radical cations of anthracenes (Scheme 1), the derivatives of which have attracted considerable attention owing to their potential applications to molecular electronics, nanotechnology, and for single-molecule conductivity studies.[10,11] It has been reported that one-electron oxidation of anthracenes afforded either monomeric or π-dimeric radical cations,[12a–c] while oxidative σ-dimerization of anthracenes was suggested during anodic oxidation.[12d]



Scheme 1. Neutral 9,10-dialkoxyanthracenes.

Herein, we present a class of well-defined reversible σ-dimerizations of 9,10-dialkoxyanthracene radical cations with phase and dramatic color changes: σ-dimer in the solid state (yellow) and radical cation in solution (purple). The work unambiguously demonstrates reversible σ-dimerizations of persistent radical cations of aromatic systems.

The 9,10-dialkoxyanthracenes (**1**, **2**, and **3**) were prepared according to the literature.[13] Cyclic voltammetry of them in CH_2Cl_2 at room temperature with nBu$_4$N$[Al(OR_F)_4]$[14] as a supporting electrolyte showed well-defined reversible oxidation waves at different scans (Figure 1; Supporting Information, Figure S1), indicating radical cations $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{3}^{\cdot+}$ are stable under these conditions. However, cyclic

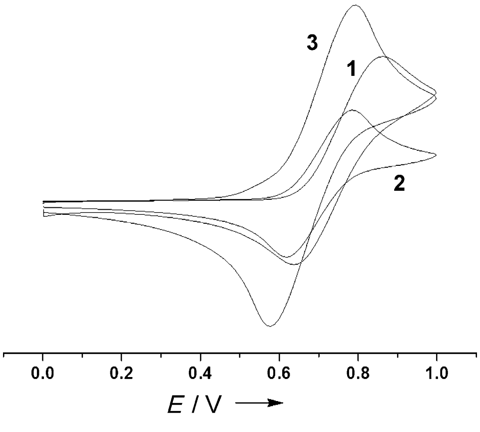


Figure 1. The cyclic voltammograms of **1**–**3** (2.5×10^{-3} M) in CH_2Cl_2, containing 0.04 M nBu$_4$N$[Al(OR_F)_4]$, were measured at 100 mV s^{-1} at 20 °C.

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voltammograms at higher concentrations show irreversible redox properties (Supporting Information, Figure S2), indicating the possibility of σ-dimer formation.[3a,d]

One-electron oxidation of **1**, **2**, or **3** with $NOSbF_6$ and $Li[Al(OR_F)_4]$[15] in CH_2Cl_2 gave deep purple solutions with a colorless precipitate ($LiSbF_6$) and gaseous nitric oxide. UV/Vis and EPR spectroscopic analyses indicated the formation of $DA^{\bullet+}[Al(OR_F)_4]^-$ (DA = **1**, **2** or **3**, that is, dialkoxyanthracene) [Eq. (1)]. Their absorption spectra as CH_2Cl_2 solutions

$$DA + NOSbF_6 + Li[Al(OR_F)_4] \xrightarrow{CH_2Cl_2} DA^{\bullet+}[Al(OR_F)_4]^- + LiSbF_6\downarrow + NO\uparrow \quad (1)$$

(Figure 2) are similar to that of previously reported 2,3,6,7-tetramethoxy-9,10-dimethylanthracene monomeric radical cation.[12b] No π-dimeric radical cation was observed by UV/Vis spectroscopic studies at various concentrations and temperatures (Supporting Information, Figures S3, S4). The nonexistence of π-dimeric radical cations is also indicated by absence of absorption band in the near-infrared region (Supporting Information, Figures S3, S4).[12b] The simulated EPR spectra are in good agreement with the experimental EPR spectra (Figure 3 for $\mathbf{2}^{\bullet+}$; for $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, see the Supporting Information, Figures S5, S6), revealing patterns resulting from interactions with H_{ring} and H_{OEt} atoms.[16]

The well-resolved solution EPR spectra are consistent with radical species that exhibit spin delocalization over the whole molecule. This is supported by the calculated spin-density map (Figure 4 for $\mathbf{2}^{\bullet+}$) and the shortened C–O bond length in the radical species in comparison to that of neutral anthracene (1.339 Å versus 1.382 Å; see the Supporting Information, Figure S8 for calculated geometries of $\mathbf{2}^{\bullet+}$ and **2**).[17] These features of radical cations can be rationalized as the single charge is stabilized by quinoidal valence bond resonance structures (Scheme 2).

Concentrating and cooling the purple solution of $\mathbf{2}^{\bullet+}[Al(OR_F)_4]^-$ resulted in yellow crystals, which were identified as a dimeric σ-complex $[\mathbf{2}\text{-}\mathbf{2}]^{2+}\{[Al(OR_F)_4]^-\}_2$ by single-crystal X-ray crystallographic analysis and FTIR spectroscopy. The observed σ-dimer structure is distinct from the previously reported π-dimer structures of oxidized anthracenes.[12b,c]

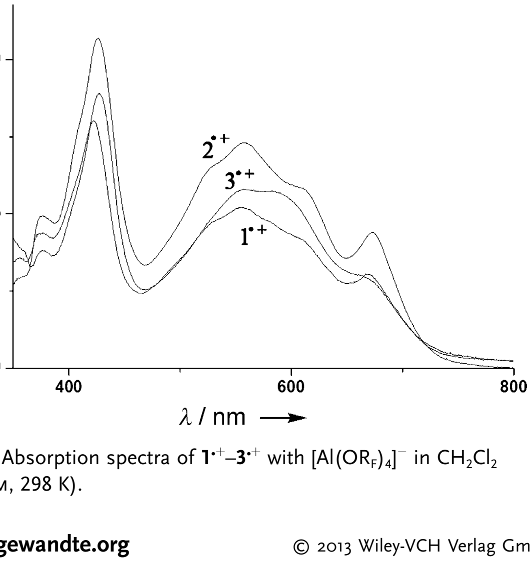


Figure 2. Absorption spectra of $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ with $[Al(OR_F)_4]^-$ in CH_2Cl_2 (1×10^{-4} M, 298 K).

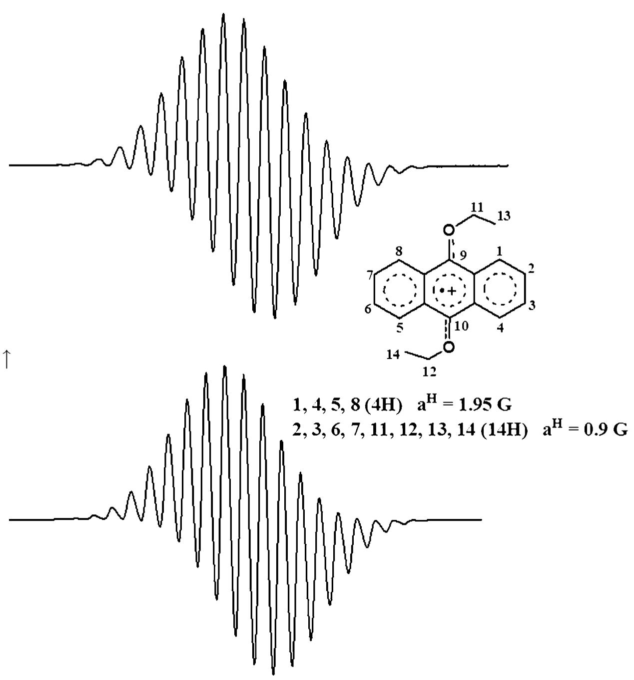


Figure 3. Experimental (top; CH_2Cl_2, 1×10^{-4} M, 293 K) and simulated (bottom) EPR spectra of $\mathbf{2}^{\bullet+}[Al(OR_F)_4]^-$.

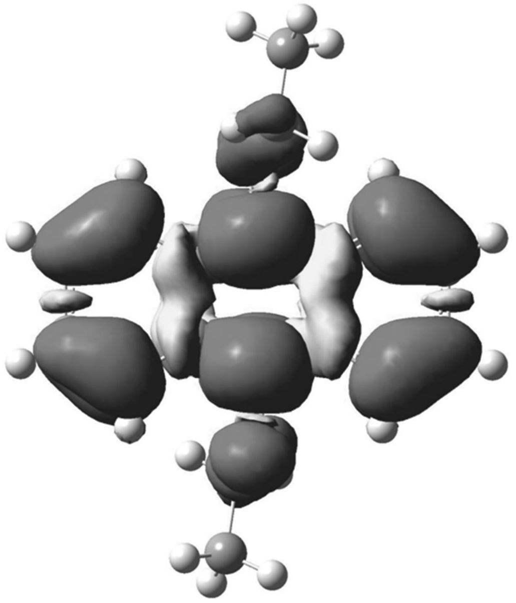
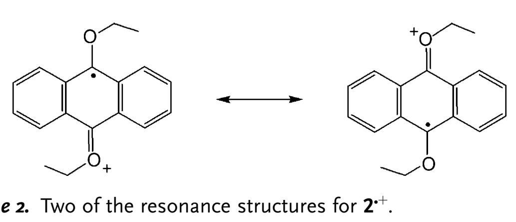
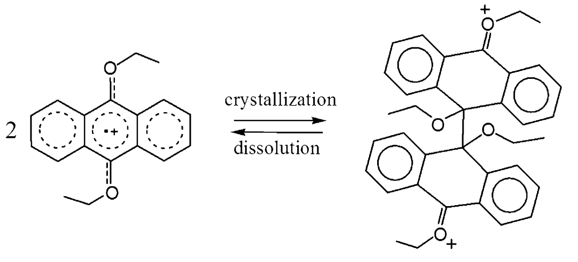


Figure 4. Spin-density map for $\mathbf{2}^{\bullet+}$ calculated with the UB3LYP/6-31G-(d, p) method. The spin density was drawn at the isovalue of 4×10^{-4} e/bohr^3.



Scheme 2. Two of the resonance structures for $\mathbf{2}^{\bullet+}$.

Redissolving $[\mathbf{2}\text{-}\mathbf{2}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$ in CH_2Cl_2 immediately gave a purple solution with an identical absorption spectrum to $\mathbf{2}^{\cdot+}[\mathrm{Al(OR_F)_4}]^-$. The crystallization and dissolution accompanying with intense color changes clearly demonstrate a reversible process between radical cation and σ-dimer, as shown in Scheme 3. In contrast to short-lived radical species during previously reported oxidative σ-dimerizations,[3–5] the purple solution of $\mathbf{2}^{\cdot+}$ remains unchanged for more than three weeks under anhydrous conditions at room temperature as periodically checked by UV/Vis spectroscopy. Similar reversible processes with dramatic color change were observed during oxidation of **1** and **3**. To investigate whether the σ-complex $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$ also exists in solution, we attempted to carry out UV/Vis and ^{1}H NMR measurements at lower temperatures. No signal due to the dimeric species was observed. Instead, a pale yellow solid gradually precipitated as the temperature was lowered, and the purple solution became colorless below −50 °C. It seems that the σ-dimerization is phase-dependent.



$\mathbf{2}^{\cdot+}$ (solution, purple)

$[\mathbf{2}\text{-}\mathbf{2}]^{2+}$ (crystal, yellow)

Scheme 3. The reversible process between radical cation $\mathbf{2}^{\cdot+}$ and σ-dimer $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$.

Single-crystal X-ray diffraction[18] showed that $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$ is composed of two symmetric subunits coupled through the σ-bond C1−C1′ (Figure 5). The two complex units of the dimer are bent, in contrast to the planar structure of the monomeric radical cation (Supporting Information, Figure S8). The C1−C1′ bond (1.637(5) Å) connecting the two units is long, and longer than the 1.600(5) Å in the dimeric σ-complex of 1,3,5-tripyrrolidinobenzene radical cations.[4] However, it is shorter than the C−C bond distances (more than 1.7 Å) in crowded hydrocarbons, which are stabilized by dispersion forces.[19,20] The C1−O2 single bond (1.428(3) Å) is consistent with carbon sp^3 hybridization, while the shorter C4−O1 bond (1.265(4) Å) has double-bond character, which was confirmed by IR spectroscopy ($\nu_{C=O} = 1595\ \mathrm{cm^{-1}}$).[21] Similar vibrational frequencies assigned to C=O partial double bonds were observed for $[\mathbf{1}\text{-}\mathbf{1}]^{2+}$ (1596 cm^{-1}) and $[\mathbf{3}\text{-}\mathbf{3}]^{2+}$ (1599 cm^{-1}).

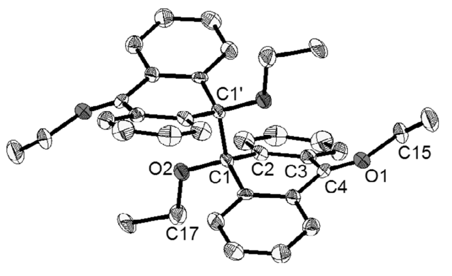


Figure 5. ORTEP of $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$. Ellipsoids are set at 50% probability, and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C1′ 1.637(5), C1–O2 1.428(3), C1–C2 1.503(4), O2–C17 1.453(4), C2–C3 1.410(4), C3–C4 1.451(4), C4–O1 1.265(4), O1–C15 1.477(4); C1′-C1-O2 102.7(2), C1-O2-C17 115.7(2), C1′-C1-C2 109.4(3), C1-C2-C3 120.6(2), C2-C3-C4 117.6(2), C3-C4-O1 126.9(3), C4-O1-C15 129.2(3).

The dimeric structure of $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$ (chair isomer) was well-reproduced by DFT calculation at the level of B3LYP/6-31G(d, p) (Supporting Information, Figure S9). A boat isomer was also found as a minimum but it is more unstable than the chair isomer by about 5.9 kcal mol^{-1}. This is presumably due to the steric crowding. The calculated C−C′ bond lengths in $[\mathbf{1}\text{-}\mathbf{1}]^{2+}$ (1.680 Å) and $[\mathbf{3}\text{-}\mathbf{3}]^{2+}$ (1.679 Å) are similar to that in $[\mathbf{2}\text{-}\mathbf{2}]^{2+}$ (1.684 Å) (Supporting Information, Figures S9, S10).[22] Similarity of C1−C1′ bond lengths as well as UV/Vis absorbance indicates no considerable substituent effect for these dimeric species.

In summary, we have shown that 9,10-dialkoxyanthracenes have been successfully oxidized to radical cations in solution, which dimerize upon crystallization and return to being radical cations upon dissolution. The identity and stability of radical cations have been unequivocally confirmed by EPR and UV/Vis spectroscopy. The work has provided conclusive evidence for reversible σ-dimerizations of persistent organic radical cations. Study of such reversible process may have an impact on exploring mechanism of oxidative oligo- and polymerization of aromatic systems. Investigation of the origin of these reversible processes, as well as reactivity of the radical species, is underway.

Experimental Section

All of the experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques and a glove box. $NOSbF_6$ (Alfa Aesar) was purchased and used upon arrival. The 9,10-dialkoxyanthracenes (**1**, **2**, and **3**)[13] and $\mathrm{Li[Al(OR_F)_4]}$[15] ($\mathrm{OR_F = OC(CF_3)_3}$) were prepared according to literature procedures. Solvents were dried prior to use. Cyclic voltammetry was performed on an IM6ex electrochemical workstation, with platinum as the working and counter electrodes, Ag/AgNO$_3$ as the reference electrode and 0.04 M $n\mathrm{Bu_4N[Al(OR_F)_4]}$[14] as the supporting electrolyte. EPR spectra were obtained using Bruker EMX-10/12 at room temperature. UV/Vis spectra were recorded on UV-3600 and Lambda 35 spectrometers. FTIR spectra were recorded on VECTOR22 FT-IR spectrometer. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences. X-ray crystal structures were obtained by Bruker APEX DUO CCD detector. Single crystals were coated with Paratone-N oil and mounted using a glass fiber. $[\mathbf{1}\text{-}\mathbf{1}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$ and $[\mathbf{3}\text{-}\mathbf{3}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$ were prepared in a similar method to $[\mathbf{2}\text{-}\mathbf{2}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$.

$[\mathbf{2}\text{-}\mathbf{2}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$: Under anaerobic and anhydrous conditions, a mixture of **2** (0.301 g, 1.13 mmol), $NOSbF_6$ (0.304 g, 1.14 mmol), and $\mathrm{Li[Al(OR_F)_4]}$ (1.14 g, 1.17 mmol) in CH_2Cl_2 (ca. 60 mL) were stirred at room temperature for one day. The resultant purple solution ($\mathbf{2}^{\cdot+}[\mathrm{Al(OR_F)_4}]^-$ over a colorless precipitate of $LiSbF_6$) was filtered. The filtrate was then concentrated and stored at about +5 °C for one day to afford X-ray-quality crystals of dicationic salt $[\mathbf{2}\text{-}\mathbf{2}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$. Yield: 1.20 g, 86%. M.p.: 104–106 °C (decomp.). FTIR (nujol, KBr plates): 1595 cm^{-1} ($\nu_{C=O}$). Elemental analysis calcd (%) for $C_{34}H_{18}AlF_{36}O_6$: C 33.11, H 1.47; found C 33.03, H 1.45.

$[\mathbf{1}\text{-}\mathbf{1}]^{2+}[\mathrm{Al(OR_F)_4}]^-_2$:1 (0.105 g, 0.441 mmol), $NOSbF_6$ (0.112 g, 0.421 mmol) and $\mathrm{Li[Al(OR_F)_4]}$ (0.410 g, 0.421 mmol); Yield: 0.196 g, 77%; Mp: 100–102 °C (decomp.); FTIR (nujol, KBr plates):

1596 cm^{-1} ($\nu_{C=O}$); Elemental analysis calcd (%) for $C_{32}H_{14}AlF_{36}O_6$: C 31.87, H 1.17; found C 31.57, H 1.32.

[3-3]$^{2+}$[Al(OR$_F$)$_4$]$^-{}_2$:3 (0.201 g, 0.755 mmol), NOSbF$_6$ (0.202 g, 0.759 mmol), Li[Al(OR$_F$)$_4$] (0.732 g, 0.752 mmol); Yield: 0.372 g, 80%; Mp: 112–114 °C (decomp.); FT-IR (nujol, KBr plates): 1599 cm^{-1} ($\nu_{C=O}$); Elemental analysis calcd (%) for $C_{34}H_{18}AlF_{36}O_6$: C 33.11, H 1.47; found C 32.72, H 1.55.

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[22] Complexes **[1-1]**$^{2+}$[Al(OR$_F$)$_4$]$^-{}_2$ and **[3-3]**$^{2+}$[Al(OR$_F$)$_4$]$^-{}_2$ did not afford crystals suitable for X-ray crystallography, and thus no detailed structures were obtained.