An Extremely Redox-Active Air-Stable Neutral π Radical: Dicyanomethylene-Substituted Triangulene with a Threefold Symmetry

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Organic molecules possessing multistage redox ability play important roles in a wide range of scientific fields from chemistry and biology to materials science and physics.^[1-4] *p*-Benzoquinone derivatives are typical examples of such multistage redox systems.^[1] They usually exhibit two-stage one-electron reduction behavior and form the radical anion and dianion species (Figure 1 a). This multistage redox fea-



Figure 1. a) Two-stage redox behavior of the *p*-benzoquinone system. b) General transformation scheme from *p*-benzoquinone derivatives to their tetracyano-*p*-quinodimethane analogues.

ture is attributable to the electron-accepting ability of the two carbonyl groups as well as an aromatic stabilization effect in the six-membered ring in the anionic states. Furthermore, transformation to the corresponding tetracyano-p-quinodimethane (TCNQ)-type analogues by the replacement of the oxygen atoms of the p-benzoquinone derivatives with dicyanomethylene groups, which have stronger electron-accepting ability (Figure 1b), has frequently been performed to modulate their redox abilities, electronic structures, and salient physical properties.^[2]

Most of the well-studied multistage redox systems are based on intrinsically closed-shell neutral organic molecules.

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However, some kinds of stable open-shell neutral organic molecules (neutral radicals), such as phenalenyl and verdazyl derivatives, also show the multistage redox behavior.^[5,6] For example, we reported that tri-*tert*-butylated 6-oxophenalenoxyl (**60PO** in Figure 2a), a phenalenyl-based air-stable



Figure 2. a) Two-stage redox behavior of the **60PO** system. Chemical structures of b) **TOT** and **TOT**⁻ and c) **1** and **1**⁻.

neutral radical with two carbonylic oxygen atoms, shows reversible two-stage redox behavior and gives the anion and radical dianion species.^[5,7] Importantly, in this redox process, charge and spin states of the generated chemical species are in sharp contrast to the quinoid-type system that forms the radical anion and dianion species (Figure 1a). This unique redox feature in the oxophenalenoxyl systems enabled us to explore various exotic electronic-spin properties and functionalities.^[5,7,8] Notably, we recently revealed that tri-tert-butylated trioxotriangulene (TOT in Figure 2b), an extremely air-stable neutral π radical with a C₃-symmetric extended π conjugated system and is derived from 60PO, exhibits a four-stage reduction process due to the small SOMO-LUMO gap as well as the doubly degenerate LUMOs.^[7e] Taking advantage of this four-stage redox ability, we succeeded in developing a new secondary battery that shows a higher discharge capacity than Li-ion batteries.^[7e]

In order to further investigate this kind of the fused polycyclic neutral π radical with the multistage redox ability, in

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this study we have designed, synthesized, and isolated a novel C_3 -symmetric triangulene^[9]-type neutral π radical **1**[•] (Figure 2 c), in which three dicyanomethylene groups with stronger electron-accepting ability are introduced instead of the oxygen atoms of **TOT**. High air-stability of both **1**[•] and the anionic species **1**⁻ has allowed us to experimentally disclose electronic effects of the dicyanomethylene groups on the redox properties and solid-state properties of fused polycyclic giant π -electronic molecular systems with the help of theoretical calculations. In particular, we emphasize that this chemical modification enables the **1**[•] system to exhibit eight-stage redox ability exceeding the **TOT**[•] system, due to the extremely small SOMO–LUMO gap and the significantly lowered frontier orbital energies of **1**[•] together with the degenerate LUMOs.

As depicted in Scheme 1, the neutral radical **1** was synthesized in four steps from diketoalcohol $2^{[7e]}$ in a relatively high total yield (71%). The two carbonyl oxygen atoms in **2**



Scheme 1. Synthesis of neutral radical **1**[:] a) $CH_2(CN)_2$, $TiCl_4$, pyridine, CHCl₃, 70 °C, 90%; b) TsCl, pyridine, CHCl₃, room temperature, 86%; c) i) NaH, $CH_2(CN)_2$, [PdCl₂(PPh₃)₂], THF, room temperature; ii) Bu₄NCl, MeOH, room temperature, 94%; d) DDQ, CH_2Cl_2 , room temperature, 97%. Ts=p-toluenesulfonyl, DDQ=2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

were converted to dicyanomethylene groups by a condensation reaction with malononitrile in the presence of TiCl₄ and pyridine, to give **3**. After the hydroxyl group of **3** was tosylated, the coupling reaction of the tosylate **4** with malononitrile and subsequent treatment with Bu₄NCl were performed to yield the anion salt Bu₄N⁺·1⁻ as air-stable green crystals.^[10] Oxidation of Bu₄N⁺·1⁻ by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) quantitatively gave neutral radical **1** as brown crystals. Similar to **TOT**, this neutral π radical **1** is stable in air at room temperature, not only in the crystalline state but also in solution.^[11]

Firstly, we investigated the electronic-spin structure of the obtained neutral radical **1**[•] by liquid-phase ESR and ¹H-ENDOR/TRIPLE spectroscopy (Figure 3). An ESR spectrum of **1**[•] in a degassed toluene $(2 \times 10^{-4} \text{ m};$ Figure 3a) showed a well-resolved hyperfine structure. The observed *g*-value of **1**[•] was 2.0028, which is similar to that of tri-*tert*-butylated phenalenyl (g=2.0028),^[12] but significantly smaller than that of **TOT**[•] (g=2.0042).^[13] This result indicates that heteroatomic contribution to the *g*-value of **1**[•] is less, that is, the unpaired electron of **1**[•] has a substantial hydrocarbon-radical character (no significant influence by CN), in con-

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Figure 3. a) Observed ESR spectrum of **1**[•] in a degassed toluene (2×10^{-4} M) at 293 K. The microwave frequency used is 9.40005 GHz and the observed *g*-value is 2.0028. The field modulation frequency of 12.5 kHz with low modulation depth was used to observe a sideband-free and highly resolved spectrum. b) Simulated ESR spectrum. c) ¹H-ENDOR and d) ¹H-TRIPLE (pump frequency, 15.691 MHz) spectra of **1**[•] in degassed toluene (2×10^{-4} M) at 273 K.

trast to **TOT** with an aroxyl-radical character. This is due to the replacement of the oxygen atoms of **TOT** with the dicyanomethylene groups. Furthermore, ¹H-ENDOR/TRIPLE spectroscopy allowed us to unequivocally determine the hyperfine coupling constants (hfccs) and relative signs of the protons in the triangulene skeleton (H(Ar)) and *tert*-butyl groups (H(*t*Bu); Figure 3 c, d).^[14] These hfccs were successfully assigned with the help of the DFT calculations (Table 1).^[15] Also, the hfcc of the nitrogen nucleus in the dicyanomethylene groups was determined by ESR spectral simulation (Figure 3 b, Table 1, and see the Supporting Infor-

Table 1. Observed and calculated hfccs [in mT] of 1. H(Ar), H(*t*Bu), and N represent hfccs of the protons in the triangulene skeleton, *tert*-butyl protons, and nitrogen nucleus in the dicyanomethylene groups, respectively. The *g*-value for 2.0028 is used for the unit conversion of the hfccs from MHz to mT.

	H(Ar)	H(tBu)	Ν
obsd ^[a]	+0.090	+0.0082	$\pm 0.0535^{[b]}$
calcd ^[c]	+0.146	+0.008	+0.073
-			

[a] Values and relative signs were determined by the ¹H-ENDOR/ TRIPLE spectroscopy. [b] Value was determined by the ESR spectral simulation. [c] Hfccs of the optimized structure calculated at the UB3LYP/6-31G(d,p) level of theory. Considering the molecular symmetry, hfccs for the equivalent nuclei were averaged. mation for the detailed analysis).^[16] The experimental and calculated hfccs are in good agreement. Thus, as shown in Figure 4a, the unpaired electron of **1** in solution extensively delocalizes over the whole 37π -conjugated molecular skele-



Figure 4. Spin density distribution of a) **1** (left: top view, right: side view) and b) **TOT** calculated at the UB3LYP/6-31G(d,p) level of theory. The red and blue colors denote positive and negative spin densities, respectively. Hydrogen atoms are omitted for clarity.

ton with C_3 symmetry. In addition, the spin density on the triangulene π skeleton of **1** (68% of the total spin densities, Figure 4a) is much less than that of **TOT** (88% of the total spin densities, Figure 4b), indicating that significant portion of spin density delocalizes onto the dicyanomethylene groups from the triangulene skeleton. This change in the spin density distribution can also be interpreted in terms of the electronic resonance effect of the dicyanomethylene group (see the Supporting Information).

The electronic effect on the multistage redox ability by the introduced dicyanomethylene groups was evaluated by means of cyclic voltammetry (CV) of the salts $Bu_4N^+\cdot \mathbf{1}^-$ and $Bu_4N^+\cdot \mathbf{TOT}^-$ in DMF (Figure 5) with the help of theoretical



Figure 5. Cyclic voltammograms (vs. Fc/Fc⁺) of a) Bu₄N⁺·**TOT**⁻ (3 mm) and b) Bu₄N⁺·**1**⁻ (1 mm) measured in DMF with 0.1 m Bu₄NClO₄ as a supporting electrolyte at room temperature.

calculations (Figure 6). As illustrated in Figure 5b, the dicyanomethylene derivative $Bu_4N^+ \cdot 1^-$ exhibited six reduction processes and two oxidation ones. A series of the redox waves were observed reversibly and reproducibly. These results mean that the number of redox stages increased to eight from four of the **TOT** system by the replacement of the three oxygen atoms of **TOT** with the dicyanomethylene groups. Focusing on the first, second, and third reduction processes and the first oxidation one of both the systems, we



Figure 6. Frontier molecular orbital energy levels and distributions of the neutral radicals **TOT** (left)^[7e] and **1** (right) calculated at the ROB3LYP/ 6-31G(d,p)//UB3LYP/6-31G(d,p) level of theory. Each SOMO–LUMO energy gap is denoted by the number in blue.

found that all of the peak potentials in 1^- ($E_p^{\text{redl}} = -1.17$, $E_p^{\text{red2}} = -1.28$, $E_p^{\text{red3}} = -2.09$, and $E_p^{\text{ord}} = +0.09$ V, Figure 5b) are significantly positively shifted from those of **TOT**⁻ ($E_p^{\text{red1}} = -2.14$, $E_p^{\text{red2}} = -2.53$, $E_p^{\text{red3}} = -3.18$, and $E_p^{\text{ord}} = -0.26$ V, Figure 5a). According to the molecular orbital calculations of 1' and TOT' (Figure 6),^[17] these four redox events should be related to the SOMO and doubly degenerate LUMOs: the three reduction processes provide the radical dianion, diradical trianion, and radical tetraanion, and the one oxidation process generates the neutral radical.^[18] Thus, the experiments suggest that the SOMO and LUMO energy levels of 1' remarkably decrease in comparison with those of TOT. Furthermore the potential difference between E_p^{red1} and E_p^{ox1} , corresponding to the SOMO–LUMO energy gap, significantly decreases from 1.88 V of **TOT**⁻ to 1.26 V of $1^{-.[19]}$ The calculated results (Figure 6) show the similar trends with the experimental observation: the theoretical energy levels of the SOMO and LUMOs of 1° (-3.53) and -3.46 eV) are much lower than those of **TOT** (-3.11and -2.29 eV) and thus the estimated SOMO-LUMO energy gap of 1 is much smaller (0.07 eV) than that of TOT (0.82 eV). Also, the potential difference between $E_{\rm p}^{\rm red2}$ and $E_{\rm p}^{\rm red1}$ of 1^- is also found to be much smaller (0.09 V) than that of TOT⁻ (0.39 V; Figure 5). This means that the trianionic state of 1 is more easily generated than that of TOT. Namely, the intramolecular Coulomb repulsion in 1^{3-} is smaller than that in **TOT**^{3–} due to the extended π -electronic system. At more negative potentials, we observed three other reduction processes (-2.49, -2.80, -2.98 V) in the system 1. One can imagine that the further three electrons are sequentially added to the LUMO and LUMO+1 of 1;^[18b] because the LUMO+1 is located at still a lower energy level (-2.16 eV) similar to the LUMO of TOT

(-2.29 eV) as shown in Figure 6. Furthermore, the system **1** showed the second oxidation wave at +0.56 V, suggesting that a cationic species might be formed.^[18b] Taking account of the lower SOMO energy level of **1** than **TOT**, this observation is probably not due to the electronic effect of the dicyanomethylene groups, but rather to the higher solubility and/or stability of the **1**⁺ ion compared to **TOT**^{+,[20]} All these intriguing multistage redox and MO features of **1** are attributable to both the enhanced electron-accepting ability and the extended π -electronic system due to the replacement of the oxygen atoms of **TOT**⁻ with the dicyanomethylene groups.

The electronic and steric effects of the introduced dicyanomethylene groups were further studied in terms of the crystal structure and solid-state magnetic properties. Singlecrystal X-ray structure analysis revealed that the triangulene skeleton of **1** is significantly distorted, to form a nonplanar π -conjugated network (Figure 7a, b), which is ascribable to



Figure 7. X-ray crystal structures of 1: a) top and b) side views of 1 molecule (hydrogen atoms on *tert*-butyl groups are omitted), c) top and d) side views of a dimeric pair (hydrogen atoms are omitted), and e) one-dimensional chain structure based on the dimeric pair (hydrogen atoms and *tert*-butyl groups are omitted).

the steric repulsion between the dicyanomethylene groups and the hydrogen atoms at the *peri*-positions. All the dicyanomethylene groups locate at the same (upper) side to the triangulene π surface (Figure 7b), giving a quasi- C_3 molecular symmetry, which agrees with the calculated optimized structure (Figure 4a). In the packing structure, **1**' formed a dimeric pair in a head-to-tail manner (Figure 7c, d) with the shortest intermolecular contacts (3.0–3.2 Å) between the nitrogen atoms at the dicyanomethylene groups of one molecule of **1**' and the carbon atoms at the dicyanomethylene groups or the triangulene skeleton of another molecule of **1**'.^[21] The dimeric pairs further come close each other through interdimer short contacts between the dicyanomethylene groups (ca. 3.2 Å), constructing a one-dimension-

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al chain structure along the *a* axis (Figure 7 e).^[21] This is in sharp contrast to the π -dimer-based columnar structure of the **TOT** crystal.^[7e] This structural feature is also probably due to the modulation of the spin density distribution of **1**: the dicyanomethylene groups have a certain proportion of the spin density (Figure 4a and Table 1). In fact, the magnetic susceptibility measurements and DFT calculations of **1**[•] illustrate that there are significant intermolecular magnetic exchange interactions attributable to the intra- and interdimer short contacts through the dicyanomethylene groups.^[22]

In conclusion, we have designed, synthesized and characterized an extremely redox-active, air-stable, neutral π radical **1** with three dicyanomethylene groups introduced with threefold symmetry into a triangulene π skeleton. Most importantly, besides the degenerate LUMOs due to the inherent *C*₃-symmetric π -electronic molecular skeleton, the enhanced electron-accepting ability and the extended π -electronic system by this simple chemical modification gave an extremely small SOMO–LUMO gap and significantly lowered the frontier orbital energies, leading to the remarkable increase in the redox stages. The spectroscopic identification of the redox species^[18] as well as the investigation of the properties of **1** and **1**⁻ as an electrode-active material for our secondary "molecular spin battery"^[7e] are underway.

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- [16] The simulated ESR spectrum well reproduces the splitting pattern of the experimental spectrum, indicating that the experimental hfccs were correctly determined. The side-band free hyperfine spectrum with the ENDOR data allowed us not only to accurately determine the hfccs, but also to identify a line broadened component with the same g-value (g=2.0028), which is probably attributable to a dimeric species of **1**. The detailed ESR analysis is given in the Supporting Information.
- [17] Molecular orbital calculations for the anion species 1⁻ and TOT⁻ show the similar trend with those for the neutral radicals 1' and TOT⁻ (Figure 6). For details, see the Supporting Information.
- [18] a) As a preliminary result, we have spectroscopically identified the radical dianion and diradical trianion species of the **TOT** system; b) Spectroscopic identification and detailed characterization of all the redox species of the system **1** except for the neutral radical and anion species seen in the CV studies are underway.
- [19] Solution-phase UV/Vis spectra of the neutral radicals 1', TOT and the salts Bu₄N⁺·1⁻, Bu₄N⁺·TOT⁻ also suggest the remarkable decrease of the SOMO-LUMO and HOMO-LUMO energy gaps in 1' and 1⁻, respectively. For details, see the Supporting Information.
- [20] In fact, **1**' and Bu_4N^+ ·**1**⁻ are more soluble in organic solvents than **TOT**' and Bu_4N^+ ·**TOT**⁻, respectively, whereas all of them are stable in air.
- [21] The more detailed crystal structure of **1** is illustrated in the Supporting Information.
- [22] The experimental and theoretical magnetic exchange interactions $2J/k_{\rm B}$ are obtained as -81 and -60 K for the intradimer contacts and -12 and -13 K for the interdimer ones, respectively. For details, see the Supporting Information.

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