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Multifunctional Spin-carrying Anthraquinone Derivatives

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Several nitroxide radicals derived from 2,3,6,7-tetraalkoxy-9,10-anthraquinone core have been prepared and their magnetic, redox as well as battery properties are studied. Notably, one of the derivatives with a mono-PROXYL-radical substituent exhibits a fairly stable multistep charge–discharge process and a heat-responsive magnetic behavior.

Considerable attention has been paid in recent years to the development of organic functional radicals such as organic photoresponsive radicals,[1] organic liquid crystal (LC) radicals,[2] or organic radical batteries.[3] During the course of our studies toward the development of organic multifunctional spin systems based on nitroxide radicals,[4] we have designed and prepared various organic radicals with liquid crystal and/or heat-responsive properties.[4,5] For example, we have recently reported the first discotic radicals exhibiting magnetoresponsive columnar (Col) mesomorphism.[5] In continuation of this work, we have now turned our attention toward the development of anthraquinone-based nitroxide radicals having alkoxy tails. Such a molecular design stemmed from the fact that anthraquinones with long alkoxy chians display Col LC behavior.[6] Moreover, the redox nature of both nitroxide group and anthraquinone ring is expected to confer relevant battery properties on the resulting systems. Here we report the synthesis and characterization of a number of organic radicals derived from 2,3,6,7-tetraalkoxy-9,10-anthraquinone where the number and nature of the nitroxide radicals have been varied.

The target radical compounds **2a**, **2b**, **3a**, and **3b** (Chart 1) were obtained in good yields by condensing 1,5-dihydroxy-2,3,6,7-tetraoctyloxy-9,10-anthraquinone (**1**)[6] with the required equivalence of 4-carboxy-PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxyl) or 4-carboxy-TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) in the presence of DCC and DMAP. The unsymmetrically substituted radical **4** was prepared by condensing mono-PROXYL-substituted compound **2a** with 4-carboxy-TEMPO in a moderate yield.[7]

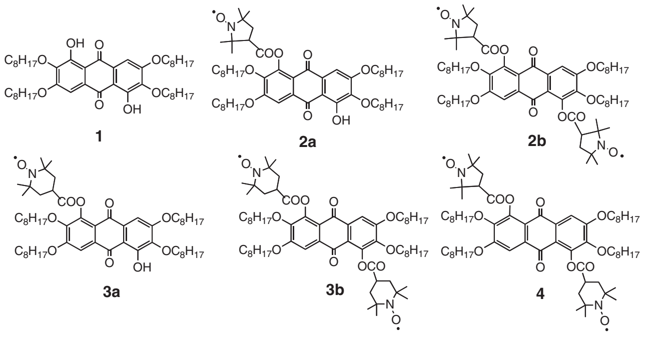

Chart 1.

Table 1. Electrochemical properties of radicals **2**–**4**[a]

Compound	E_1^{RED}	E_2^{RED}	E_1^{OX}
2a	−0.93	−1.31	0.84
2b	−1.04	−1.47	0.88
3a	−0.98	−1.43	0.81
3b	−1.10	−1.58	0.78
4	−1.06	−1.42	0.85
TEMPO			0.70

[a]V vs. SCE, 0.1 M n-Bu_4NClO_4 in PhCN.

The redox data of each derivative were estimated by cyclic voltammetry and are summarized in Table 1.

It is apparent from the data that they are amphoteric compounds displaying both reduction and oxidation potentials. Their reduction potentials indicate that they are weaker acceptors than the previous benzoquinone derivatives with TEMPO-substituent(s),[8] even though the monosubstituted derivatives **2a** and **3a** are somewhat stronger acceptors than disubstituted derivatives **2b**, **3b**, and **4**. Similar oxidation potentials due to the TEMPO group are observed within the five compounds but their electron-donating abilities are weakened because of the attachment of a carbonyl group. Taking such redox data into consideration, we examined the compounds as possible substrates for organic radical batteries.

The charge–discharge profiles of the anthraquinone derivatives were measured with a coin cell which was fabricated by stacking cathode and Li-metal anode with porous polyolefin separator film. A cathode was formed by pressing the composites of an anthraquinone derivatives (10 wt %), carbon fiber (80 wt %), and fluorinated polyolefin binder (10 wt %). A composite solution of ethylene carbonate (30 vol %)/diethyl carbonate (70 vol %) containing 1 M of $LiPF_6$ was used as an electrolyte. The charge–discharge profile of **2a** is shown in Figure 1. After the initial charging, discharge of one-electron oxidation occurred at 3.6 V followed by one-electron reduction at 2.9 V, which is supposed to have originated from the redox properties of the PROXYL group. Further discharging below ca. 2 V may be attributed to the redox of the anthraquinone moiety with a capacity of over 120 A h kg^{-1}, indicating the applicability of this compound as a cathode-active material for a rechargeable battery. Thus, multistep discharging is found in **2a** and the charge–discharge process is fairly stable, although the response is gradually diminished through repetition. On the contrary, such a process in the corresponding disubstituted compound **2b** was unstable (SI-1), since the discharging capacity was found to be largely lost from the second cycle.

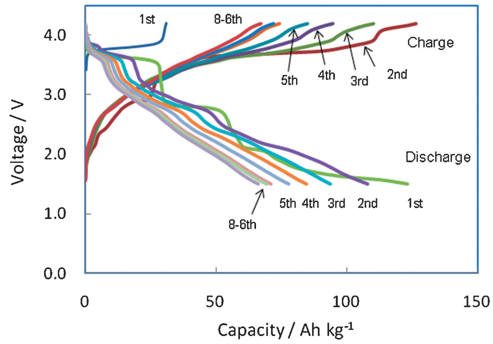

Figure 1. Charge–discharge profile of **2a** at a constant current density of ca. 0.05 A g^{-1} in a cell voltage range of 1.5–4.2 V in 7 cycles.

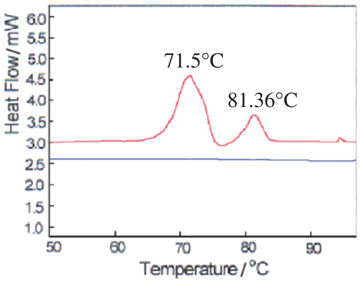

Figure 2. The DSC traces obtained for the radical **2a** during the first heating (red-trace) and cooling (blue-trace) cycles.

The thermal behavior of the synthesized radicals was examined with the aid of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). In the DSC thermograms, two endothermic peaks were observed during the heating cycle for **2a** (at 72 and 81 °C as illustrated in Figure 2), **2b** (at 133 and 137 °C), and **3a** (at 95 and 102 °C), while only one exothermic peak or no peak was apparent during cooling for the compounds (no peak for **2a**, at 100 °C for **2b**, and at 81 °C for **3a**) (SI-2–SI-5).[9] Further examinations by using POM revealed that the peaks observed in the DSC traces are not due to the liquid crystal behavior of the compounds but can be ascribed to originating from the solid-to-solid phase transitions during the heating of each compound. The detrimental effect of the bulky TEMPO or PROXYL may result in the absence of liquid crystal phases in these radical compounds as suggested from the crystal structures of **2b** and **4**.

The magnetic data for the radical compounds **2a**, **2b**, **3a**, **3b**, and **4** obtained by SQUID measurements in the temperature range of 2–300 K are summarized in Table 2. The Curie constants of the radical compounds are close to the theoretical values (0.375 for $S = 1/2$ spin or 0.75 for non-interacting $S = 1$ spin) indicating that the spins are alive and weak ferromagnetic (F) intermolecular interactions predominantly occur for all the compounds with the exception of **2b** for which a negative Weiss temperature (antiferromagnetic, AF, interaction) is evidenced.

Among the anthraquinone derivatives thus prepared, single crystals suitable for X-ray analysis could be obtained for the compounds **2b** and **4** and their structures were solved by using X-ray diffractomety.[10]

Table 2. Magnetic data of radicals **2a**, **2b**, **3a**, **3b**, and **4**

Compd.	Magnetic interaction[a]	C^{b}	θ^{c}
2a	F	0.37	0.17
2b	AF	0.75	−3.04
3a	F	0.37	0.50
3b	F	0.75	0.63
4	F	0.74	0.20

[a] Curie–Weiss model. F: Ferromagnetic interaction. AF: Antiferromagnetic interaction. [b] Curie constant (emu K mol^{-1}). [c] Weiss temperature (K).

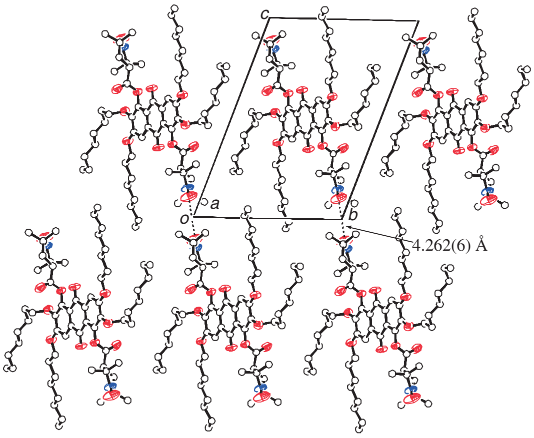

Figure 3. Crystal structure of the radical compound **2b**. Hydrogen atoms are omitted for clarity.

The bulky oxycarbonyl-PROXYL moiety together with long octyl groups in a molecule of **2b** extend above and below the anthraquinone mean plane as shown in Figure 3. The structural feature appears to be detrimental to the formation of a liquid crystal phase in this compound. The molecules are stacking in stepwise and slanted manner along the *b* axis.

A chiral structure with space group *P*1 is found in **4**, based possibly on the presence of different substituents (TEMPO and PROXYL) in the crystal. Similar to the molecular structure of **2b**, the bulky oxycarbonyl-TEMPO and -PROXYL together with long octyl groups in **4** extend above and below the anthraquinone mean plane to disturb the formation of LC phase in the compound (Figure 4a). The molecules also display rather similar stacking profile to that of **2b**, that is, the anthraquinone planes of the compound **4** are also stacking regularly and in a slanted manner along the *a* axis.

Although it is not easy to see the origins of the magnetic interactions observed in **2b** and **4** from their crystal structures, a relatively short oxygen-to-oxygen distance between the spin centers (4.26 Å) may contribute at least in part to the antiferromagnetic interaction observed in **2b**. In turn, a couple of short contacts between the oxygen atom of a TEMPO group and each methyl group of a neighboring molecule (3.66 and 3.88 Å in Figure 4b) may result in the ferromagnetic behavior observed in **4**.

In order to see the heat-responsive properties of this class of radical compounds, the magnetic properties of compound **2a** were investigated as a representative example from 2 to 370 K

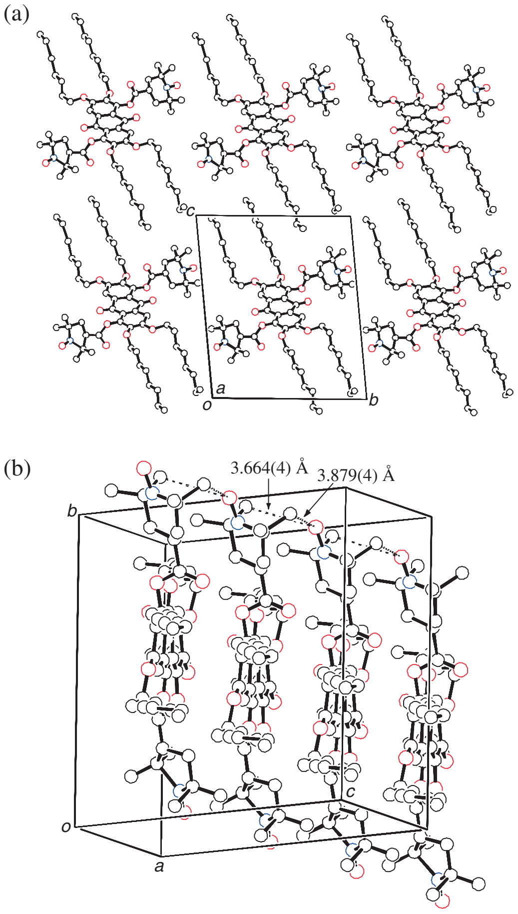

Figure 4. (a) Crystal structure of radical compound **4** viewed along the *a* axis. Hydrogen atoms are omitted for clarity. (b) Crystal structure of **4** depicting four molecules, in which hydrogen atoms are omitted for clarity.

(over the melting point). Apparent increase of χT-values over the melting point (345 K) was revealed from the measurement during heating up to 370 K and at the same time the original weak ferromagnetic interaction observed in heating with $\theta = 0.17$ was found to turn antiferromagnetic ($\theta = -0.81$) on cooling (SI-6). Thus, a heat-responsive magnetic property was elucidated in this radical compound through the phase transitions.

In summary, novel tetraalkoxy-substituted anthraquinones differing in the number and nature of nitroxide radicals have been prepared and characterized. They exhibit electrochemical (redox) activity and paramagnetic behavior. Of the two radicals investigated for their stable multistep discharge, the monosubstituted PROXYL compound appears to be relatively promising when compared to its disubstituted analog suggesting that the increase in the number of radical moieties has no added advantage in discharge. Furthermore, the monosubstituted PROXYL radical shows heat-responsive magnetic properties. Thus, our study reveals that the spin-carrying anthraquinones are intriguing molecular systems exhibiting multiproperties and further investigations on these and related systems are still in progress.[11]

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References and Notes

1 a) K. Matsuda, M. Irie, *J. Photochem. Photobiol., C* **2004**, *5*, 169. b) S. Nakatsuji, *Chem. Soc. Rev.* **2004**, *33*, 348. c) K. Matsuda, M. Irie, *Chem. Lett.* **2006**, *35*, 1204. d) G. I. Likhtenstein, K. Ishii, S. Nakatsuji, *Photochem. Photobiol.* **2007**, *83*, 871.

2 a) R. Tamura, Y. Uchida, N. Ikuma, *J. Mater. Chem.* **2008**, *18*, 2872. b) R. Tamura, in *Nitroxide: Application in Chemistry, Biomedicine, and Materials Chemistry*, ed. by G. I. Likhtenstein, J. Yamauchi, S. Nakatsuji, A. I. Smirnov, R. Tamura, Wiley-VCH, Weinheim, **2008**, Chap. 9, p. 303.

3 a) K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351. b) H. Nishide, T. Suga, *Electrochem. Soc. Interface* **2005**, *14*, 32. c) H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737.

4 a) S. Nakatsuji, *Adv. Mater.* **2001**, *13*, 1719. b) S. Nakatsuji, *J. Synth. Org. Chem., Jpn.* **2003**, *61*, 670.

5 C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, M. Nobusawa, H. Akutsu, J. Yamada, S. Nakatsuji, *J. Mater. Chem.* **2008**, *18*, 3433.

6 V. P. K. Krishnan, V. S. K. Balagurusarmy, *Liq. Cryst.* **2000**, *27*, 1075.

7 All the radical compounds gave satisfactory elemental analysis data.

8 S. Nakatsuji, M. Nobusawa, H. Suzuki, H. Akutsu, J. Yamada, *J. Org. Chem.* **2009**, *74*, 9345.

9 Only one exothemic/endothermic peak couple was observed during heating/cooling process for **3b** and **4** (SI-4 and SI-5).

10 Crystal data of **2b** and **4** reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html.

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.