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Spin-Carrying Benzoquinone Derivatives

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Formation of Single-Component CT Complex

Several 1,4-benzoquinone derivatives carrying oxy-TEMPO radical(s) at the 2-position or 2,5-positions were found to give black crystals by recrystallization from pale yellow solutions and it was revealed from their crystal structures that unusual single-component CT complexes were formed, in which a nitroxide moiety plays the roll of a donor part and a 1,4-benzoquinone group of the same molecule works as an acceptor part, respectively. On the contrary, no CT formation was found for the derivatives carrying oxy-TEMPO radicals at 2,6-positions and one of the TEMPO groups contributes to a CT formation in a 1,4-benzoquinone derivative carrying amino-TEMPO radicals at 2,5-positions derived from fluoranil, while the other one has a close oxygen-to-oxygen contact with another neighboring molecule to give a very large exchange coupling of $J/k_B = -154$ K.

Introduction

A charge-transfer (CT) complex generally consists of a donor molecule and an acceptor molecule and is a two-component compound.[1] On the other hand, a large number of molecules are known in which both electron-donating and electron-accepting groups are incorporated in a single molecule such as merocyanine dyes[2] or unimolecular electrical rectifiers[3] but they normally do not form CT complexes by themselves and then examples of single-component CT complexes are still rare.[4] It is probably because of the difficulty of controlling the donating and accepting ability in a molecule and/or steric effects detrimental to forming a CT complex with sufficient CT interaction. Moreover, to our knowledge, there has been so far no intrinsic example of a single-component CT complex based on stable radicals, even though some single-component organic conductors based on

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(1) Cf: (a) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587. (b) *Organic Charge-transfer Complexes*; Foster, R., Ed.; Academic Press: London, UK, 1969. (c) *The Donor-Acceptor Approach to Molecular Interactions*; Gutmann, V., Ed.; Plenum Press: New York, 1978.

(2) Cf.: (a) *Organic Chemistry in Colour*; Gordon, P. F., Gregory, P., Eds.; Springer-Verlag: Berlin, Germany, 1987. (b) *Color Chemistry*; Zollinger, H., Ed.; Verlag Helvetica Chimica Acta: Zürich, Switzerland, 2003. (c) Shirinian, V. Z., Shimkin, A. A. In *Heterocyclic Polymethine Dyes: Synthesis, Properties and Applications*; Topics in Heterocyclic Chemistry, Vol. 14, Springer-Verlag: Berlin, Germany, 2008; Chapter 5.

(3) Cf.: (a) Metzger, R. M. *Acc. Chem. Res.* **1999**, *32*, 950. (b) Metzger, R. M. *Chem. Rev.* **2003**, *103*, 3803.

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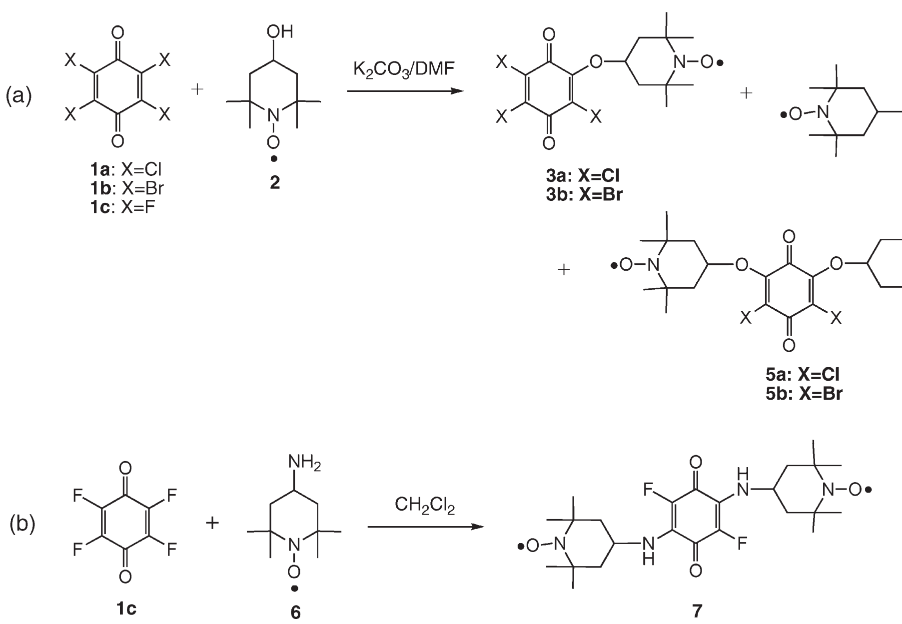
SCHEME 1



neutral radicals[5] and a variety of two-component CT complexes involving stable radicals have been reported.[6]

In the course of our studies toward the development of organic multifunctional spin systems based on nitroxide radicals,[7] we prepared several 1,4-benzoquinone derivatives carrying 4-amino-TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical to form CT complexes with TTF and its derivative.[8] Furthermore it was clarified that 4-amino-TEMPO derivatives act themselves as donors to afford intermolecular CT complexes with some acceptors.[9] However, all of them are usual CT complexes composed of two components of a donor and an acceptor. In this paper, we wish to report the preparation of several 1,4-benzoquinone derivatives carrying TEMPO radical at one or two positions and serendipitous formations of single-component (unimolecular) CT complexes in some of them together with their structures and magnetic properties.[10]

Results and Discussion

Preparation of 1,4-Benzoquinone Derivatives and Their Redox and UV−Vis Absorption Properties. The reactions of chloranil **1a** or bromanil **1b** with 4-hydroxy-TEMPO **2** in the presence of potassium carbonate in DMF gave after separation by column chromatography on SiO$_2$ and recrystallization 2-(4-oxy-TEMPO)-3.5.6-trihalo-1,4-bezoquinone **3a** (48%) or **3b** (65%) as the major products (reaction a in Scheme 1). Further examination of other eluants revealed the formation of bis-TEMPO-substituted benzoquinones **4** and **5** as the minor products (each < 10%), which could be purified by recrystallization and elucidated by X-ray analyses. While the formation of 2,5-disubstituted product is common in this kind of nucleophilic substitution reaction onto 1,4-benzoquinone derivatives,[11] that of the 2,6-disubstituted one is very unusual but the reason for the formation is still unclear.

Noteworthy was the black color of the recrystallized crystals of **3a** and **3b** from the pale yellow pentane−*n*-hexane (1:1) solution, indicating occurrence of charge transfer between the molecules in the crystals. Also black crystals were obtained in the cases of **4a** and **4b**, while orange crystals were grown in the cases of **5a** and **5b**, suggesting the occurrence of CT in the former crystals but not in the latter.

A somewhat different reaction profile was revealed for fluoranil **1c** from that of chloranil **1a** or bromanil **1b**, i.e., the main reaction product in the similar reaction was 2,5-disubstituted derivative **4c**, which again was isolated as black crystals in 21% yield, but the corresponding monosubstituted or 2,6-disubstituted one could not be isolated. Also, 2,5-disubstituted derivative **7** was the main product (41%) for the reaction of fluoranil with

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TABLE 1. CV Data of Benzoquinone Derivatives[a]

compd	E_1^{RED}	E_2^{RED}	E_1^{OX}
3a	−0.26	−0.92	0.72
3b	−0.27	−0.92	0.72
4a	−0.40	−0.91	0.75
4b	−0.39	−0.96	0.74
4c	−0.41	−1.01	0.73
5a	−0.37	−0.96	0.73
5b	−0.39	−0.92	0.75
7	−0.78	−0.99	0.74
chloranil	−0.13	−0.84	
bromanil	−0.12	−0.79	
TEMPO			0.70

[a] V vs. SCE, 0.1 M n-BuNClO$_4$ in CH$_3$CN; scan rate = 50 mV/s.

4-amino-TEMPO and the color of the isolated product was violet in this case.[12]

To verify the reduction and oxidation potentials of each benzoquinone derivative, cyclic voltammetry measurements were carried out and the data are summarized in Table 1.

It is apparent from their first reduction potentials that monoradicals **3a** and **3b** are weaker acceptors compared to choranil or bromanil and more weaker acceptors are biradicals **4** and **5**. There is no significant difference between the redox data of the chloro-, bromo-, or fluoro-series and between 2,5-disubustituted compounds **4** and 2,6-disubstituted ones **5**. In spite of the similarity of their redox properties, the colors of the crystals of **4** and **5** are different and that implies the difference of their crystal structures. Evidently, the amino substituent weakens the electron-accepting property more than the oxy-substituent as seen for the first reduction potential of **7** compared to that of **4c**. On the contrary, the first oxidation potentials due to the TEMPO group of the radical compounds are rather similar, indicating the existence of similar donating ability of the radical compounds. Thus, the coexistence of accepting and donating ability in each molecule is apparently found from the CV data, enabling the occurrence of some CT interaction between them.

The UV−vis spectra of the radical compounds were then measured in solution as well as in the solid state. The $\lambda_{\max}$-values of **3a** in acetonitrile are observed at 290 and 415 nm, respectively, and they reflect the yellow color of the solution of **3a**. Meanwhile a weak and very broad absorption at around 650 nm with its tail over 800 nm appears in the diffuse reflectance UV−vis spectrum of **3a** in the solid state as shown in Figure 1, thus indicating the actual presence of charge transfer in **3a** in the solid state to give the black color of the crystal. Similarly, CT bands are observed in the diffuse reflectance UV−vis spectra of the compounds **3b**, **4a**, **4b**, and **7** but there is no CT band in the spectra of **5a** and **5b** to give the orange colors of the crystals.

Crystal Structures of 1,4-Benzoquinones. The X-ray analyses of the 1,4-benzoquinone derivatives were performed by using each single crystal grown from an appropriate solvent and their crystal data are summarized in the Supporting Information, SI-1 and SI-2.

The X-ray analyses of **3a** (Figure 2) and **3b** (SI-3, Supporting Information) indicate that they have similar molecular/crystal structures of monoclinic system with space group $P2_1/n$. The N−O distance of nitroxide moiety amounts to 1.28 Å, indicating the existence of a $S = {}^1/_2$ spin in the molecule. The TEMPO groups of **3a** and **3b** are largely distorted from the corresponding benzoquinone π-planes and a couple of benzoquinone rings face each other with the plane-to-plane distance of 3.61 Å in **3a** and 3.64 Å in **3b**, respectively. The most remarkable features of their crystal structures are the very close proximities of oxygen atoms of the radical moieties to the neighboring benzoquinone rings in **3a** and **3b** (2.79 Å in **3a** and 2.83 Å in **3b**), which are shorter than the sum of VDW radii (3.1 Å) and suggest the occurrence of charge transfer between them. Thus, the black colors of their crystals (vide supra) can be well understood from the crystal structures as well.

Similar molecular/crystal structures are apparent between 2,5-disubstituted derivatives **4a** (Figure 3) and **4b** (SI-4, Supporting Information) too. In this case, the benzoquinone ring of a molecule is being put between two TEMPO groups of two neighboring molecules with a short oxygen-to-benzoquinone distance of 2.90 Å for **4a** and 2.89 Å for **4b**, respectively, resulting in the occurrence of charge transfer between the donor and acceptor groups also in these compounds, though their donor−acceptor−donor arrangements are different from those of **3a** and **3b** with donor−acceptor−acceptor−donor arrangements.[13]

Contrary to the previous crystals, no close contact is seen between TEMPO and benzoquinone groups in the crystals of **5a** and **5b**, while somewhat short distances are observed between the oxygen atoms of a TEMPO group in a molecule and that of a neighboring molecule (4.28 Å for **5a** and 4.37 Å for **5b**) and between the oxygen atom of another TEMPO group of the molecule and the carbon atom of a methyl group of another neighboring molecule (3.32 Å for **5a** and 3.35 Å for **5b**) as shown in Figure 4 for **5a** (and SI-5 in the Supporting Information for **5b**). The orange color of the crystals indicates no occurrence of charge transfer interactions in the crystals as was suggested from their crystal structures as well as diffuse reflectance UV−vis spectra.

A unique feature is disclosed in the structure of compound **7**. A close contact of ca. 3 Å is observed between the oxygen atom of a TEMPO group in a molecule and a carbon atom on the benzoquinone ring of another molecule, i.e., a CT interaction is revealed in one side of a molecule (Figure 5). On the other hand, a very short oxygen-to-oxygen contact of 3.17 Å is found between the nitroxide groups of the molecule and the other neighboring molecule. Thus, CT interaction occurred only on one side of a molecule in this crystal.

Magnetic Properties of 1,4-Benzoquinones. The magnetic measurements of the solid samples were carried out by using a SQUID susceptometer in the temperature range of 2 to 300 K and the data are summarized in Table 2.

Antiferromagenetic interactions obeying the Curie−Weiss law are observed in the spins of **3a** and **3b** with a Weiss temperature of −0.41 K for **3a** and −1.87 K for **3b**, respectively. As no close contact is observed in their crystal structures other than those described above (vide supra), the antiferromagnetic interactions observed for both radical

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[12] The preparations and some properties of the corresponding chloro- and bromo-derivative of **7** are reported in ref 8, although neither crystal structure determinations nor susceptibility measurements were carried out on the compounds.

[13] Neither single-crystal X-ray analysis of **4c** nor its powder X-ray diffraction measurement to see if its crystal structure is isomorphic with that of **4a** or **4b** was successful probably due to its glassy nature.

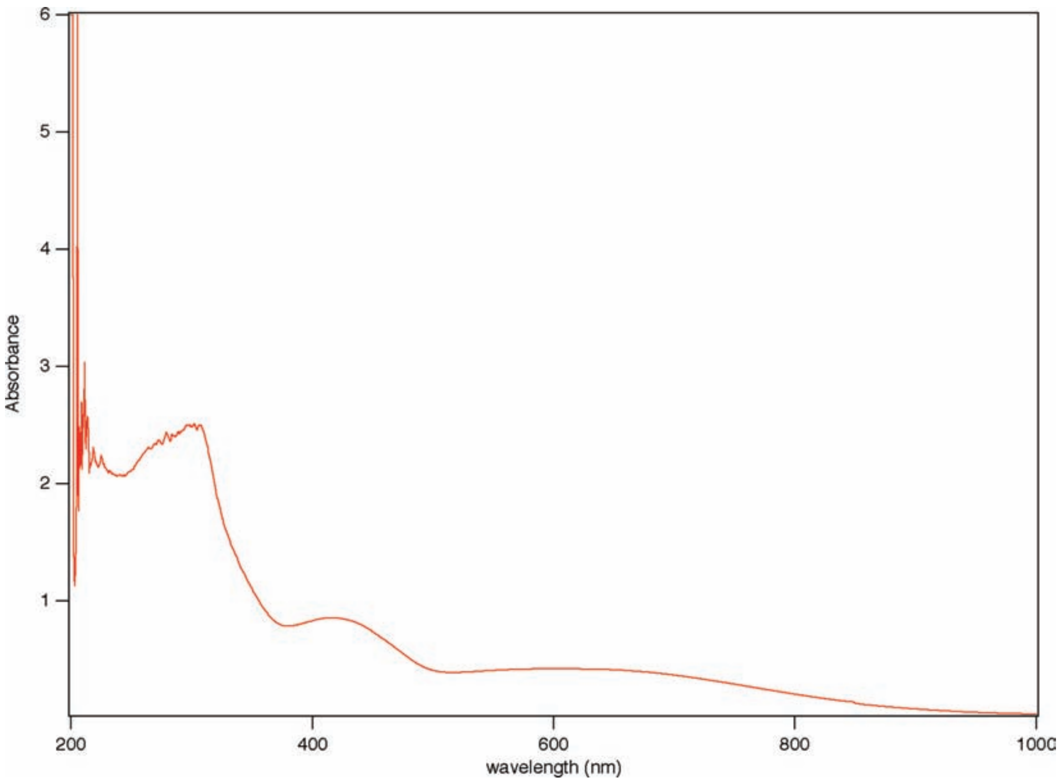

FIGURE 1. Diffuse reflectance UV−vis spectrum of **3a** in the solid state.

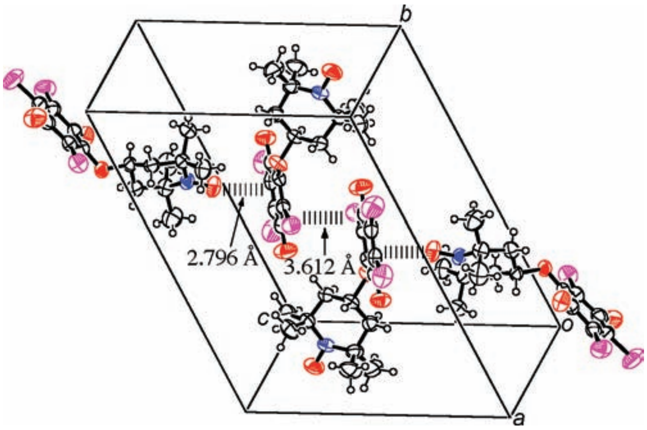

FIGURE 2. Crystal structures of **3a**. Four molecules are depicted and the broken lines indicate short intermolecular contacts. The edges of the molecules in the figure also have similar contacts, making higher order contacts on the whole.

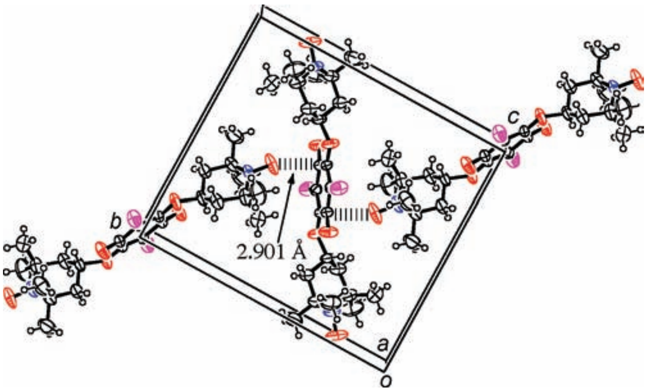

FIGURE 3. Crystal structures of **4a**. Three molecules are depicted and the broken lines indicate short intermolecular contacts. The edges of the molecules in the figure also have similar contacts, making higher order contacts on the whole.

compounds are probably due to those between the spin centers mediated by a couple of benzoquinone rings.

On the other hand, the magnetic data of 2,5-disubstituted derivatives **4a** and **4b** obey a singlet−triplet model and almost the same weak antiferromagnetic interactions with $J = -2.9$ K for **4a** and $J = -3.0$ K for **4b** are estimated from the data originating apparently from the intermolecular spin−spin interactions.[14] Although the magnetic data cannot be well understood yet, singlet formation is possibly operating through a benzoquinone ring at the cryogenic temperature for each crystal.

Although the crystal structures of 2,6-disubstituted derivatives **5a** and **5b** are similar on the whole, their intermolecular magnetic interactions are different, i.e., while the intermolecular magnetic interactions of **5a** are antiferromagnetic, weak ferromagnetic interactions are observed in the spins of **5b**. The difference of the magnetic interactions is supposed to reflect the difference of the distances between the spins as seen in their crystal structures. The shorter O−O distance found in **5a** compared to that of **5b** may result in the predominance of antiferromagnetic interactions in **5a**, while ferromagnetic interactions due to the spin polarization through the hydrogen bonds may comparatively contribute

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[14] The *J*-values were estimated by using the Bleany−Bowers equation: Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

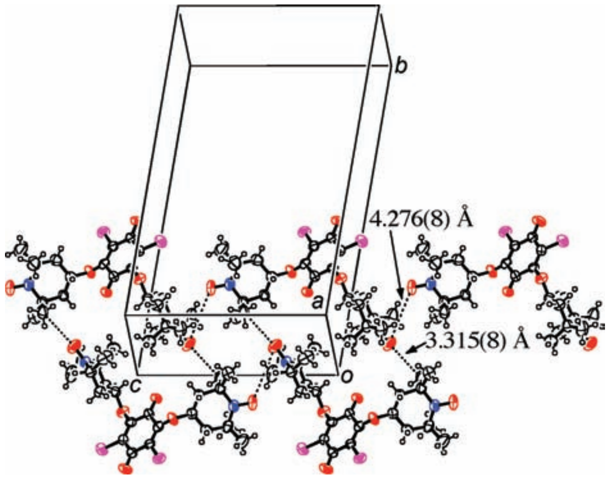

FIGURE 4. Crystal structures of **5a**. Five molecules are depicted and the broken lines indicate short intermolecular contacts. The edges of the molecules in the figure also have similar contacts, making higher order contacts on the whole.

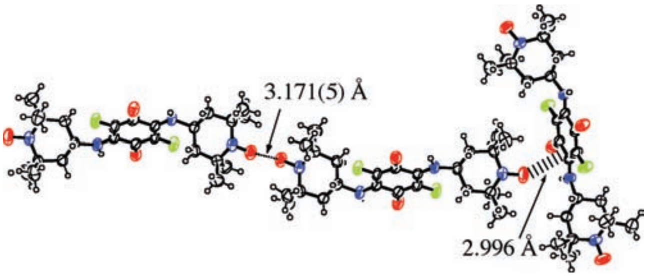

FIGURE 5. Crystal structure of **7**. Three molecules are depicted and a couple of short contacts are indicated. The edges of the molecules in the figure also have similar contacts, making higher order contacts on the whole.

TABLE 2. Magnetic Data of Benzoquinone Derivatives

compd	magnetic interaction[a]	C^b/emu K mol^{-1}	θ^c/K	$J/k_B{}^d$/K
3a	antiferromagnetic	0.38 (100)	−0.41	
3b	antiferromagnetic	0.38 (100)	−1.87	
4a	antiferromagnetic	0.75 (100)		−2.9
4b	antiferromagnetic	0.75 (100)		−3.0
4c	antiferromagnetic	0.75 (100)	−5.94	
5a	antiferromagnetic	0.75 (100)	−0.31	
5b	ferromagnetic	0.73 (97)	0.39	
7	antiferromagnetic[e]	0.73 (97)	−0.21	−154

[a] Fitting for the Curie−Weiss law. [b] Curie constant. Numbers in parentheses denote the estimated spin concentrations, by using a theoretical value of 0.375 emu K mol^{-1} for monoradicals and 0.75 for emu K mol^{-1} for diradicals, respectively. [c] Weiss temperature. [d] Exchange interactions obtained by fitting for a singlet−triplet model. [e] See text for the magnetic behavior.

to the ferromagnetic interactions observed between the spins of **5b**.

The magnetic behavior of compound **7** can be well analyzed by the combination of a Curie−Weiss behavior of antiferromagnetic interaction with a small Weiss temperature (θ = −0.21 K) and a singlet−triplet one of antiferromagnetic interaction with a very large J/k_B-value (J/k_B = −154 K) as shown in Figure 6. Such a large J/k_B-value is still rare in nitroxide-based organic radical compounds[15] and is apparently based on the close proximity of a couple of oxygen atoms of nitroxide groups in neighboring molecules and another oxygen atom may contribute to the Curie−Weiss term through the CT interaction.

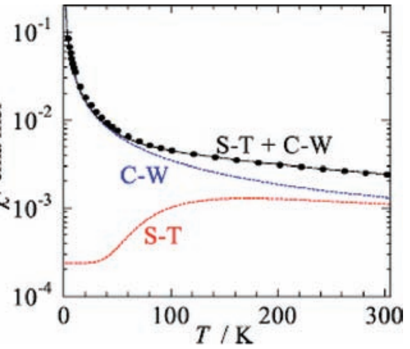

FIGURE 6. The magnetic data of **7**, analyzed by the combination of a Curie−Weiss (CW) and a singlet−triplet (ST) model. The black open circles indicate the experimental data and the dotted lines are the theoretical ones (red: ST; blue: CW; green: combination of ST and CW), respectively.

Conclusions

By the reaction of chloranil or bromanil with 4-hydroxy-TEMPO under basic condition, monosubstituted compounds **3a** and **3b** were obtained as the major products together with 2,5- (**4a**, **4b**) and 2,6-disubstituted compounds (**5a**, **5b**) as the minor compounds, respectively. On the other hand, 2,5-disubstituted compound **4c** or **7** was predominantly available by the reaction of fluoranil with 4-hydroxy- or 4 amino-TEMPO. While there appears to be no large difference of the crystal structures and the magnetic properties between the chloro- and bromo-series, the packing features of the monosubstituted derivatives and the disubstituted ones are significantly different, leading to the difference of their magnetic properties. Remarkably, single-component CT crystals were found to form in monosubstituted (**3a**, **3b**) and 2,5-disubtituted ones (**4a**, **4b**) by the interactions between a benzoquinone ring of a molecule and a nitroxide group of neighboring molecules with donor−acceptor−acceptor−donor arrangement in the former two derivatives and donor−acceptor−donor arrangement in the latter two ones, respectively, giving unique and rare examples of single-component CT complexes involving nitroxide radical. An intriguing structural feature was disclosed in compound **7**, in which one of the amino-TEMPO groups contributes to a CT formation while the other has a close oxygen-to-oxygen contact with another neighboring molecule to give a very large exchange coupling.

Experimental Section

Materials. Commercial grade chloranil, bromanil, fluoranil, 4-hydroxy-TEMPO, and 4-amino-TEMPO was used for the reactions described in the text.

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(15) (a) Minguet, M.; Amabilino, D. B.; Vidal-Gancedo, J.; Wurst, K.; Veciana, J. *J. Mater. Chem.* **2002**, *12*, 570. (b) Nakatsuji, S.; Amano, T.; Akutsu, H.; Yamada, J. *J. Phys. Org. Chem.* **2006**, *19*, 333. To our knowledge, this J/k_B-value of −154 K is the largest one reported so far among the nitroxide-based radical compounds.

Instrumentation. Melting points of the solid samples are uncorrected. The UV−visible spectra were measured in acetonitrile solution or in the solid state at ambient temperature. The data of FAB-MS spectra were obtained by using *m*-nitrobenzyl alcohol as the matrix and appropriate polyethylene glycol samples as the internal standard. EPR spectra were taken for solid samples and *g*-values were determined by using the Mn^{2+}/MgO maker as the internal standard. Magnetic susceptibility measurements were carried out on a SQUID susceptometer using ca. 10 mg for each powdered sample. Crystal structures of all compounds were determined at room temperature. X-ray diffraction data were recorded with a CCD area detector on a diffractometer and crystal structures were solved by the direct method. The refinements were made by the full-matrix least-squares methods. Anisotropic temperature factors were used for the non-hydrogen atoms and the hydrogen atoms were included in the final calculation. All the calculations were performed with the Texan crystallographic software package. Crystal data of **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, and **7** have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

The Reaction of Chloranil with 4-Hydroxy-TEMPO. To a stirred mixture of chloranil **1a** (1.43 g, 5.80 mmol) and 4-hydroxy-TEMPO **2** (1.00 g, 5.8 mmol) in DMF (50 mL) was added potassium carbonate (1.60 g, 11.6 mmol) at ambient temperature. After the solution was stirred for 2 h and the solid substance filtered off, the reaction mixture was concentrated in vacuo and then purified by column chromatography on silica gel with the solvent system of hexane and dichloromethane (1:1) to give monosubstituted compound **3a** (1.13 g, 48%) and disubstituted compounds (mixtures of **4a** and **5a**, 0.238 g, 10%), respectively. Recrystallization of **3a** was performed in a mixed solvent of hexane and pentane (1:1) to give black blocks. Mp 125−127 °C; FAB-MS (*m*/*z*) 382 (M + H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 290 (4.31), 415 (2.85). Anal. Calcd for $C_{15}H_{17}NO_4Cl_3$: C, 47.20; H, 4.49; N, 3.76. Found: C, 47.10; H, 4.34; N, 3.56. Recrystallization of mixtures of **4a** and **5a** in acetonitrile afforded brownish black blocks of **4a** and orange plates of **5a**, which could be easily separated by hand and their data are as follows. **4a**: mp 209−211 °C; FAB-MS (*m*/*z*) 519 (M + 2H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 204 (4.30), 300 (4.19), 408 (2.67). Anal. Calcd for $C_{24}H_{34}N_2O_6Cl_2$: C, 55.71; H, 6.62; N, 5.41. Found: C, 55.59; H, 6.65; N, 5.39. **5a**: mp 153−156 °C; FAB-MS (*m*/*z*) 519 (M + 2H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 203 (4.31), 300 (4.16), 410 (2.67). Anal. Calcd for $C_{24}H_{34}N_2O_6Cl_2$: C, 55.71; H, 6.62; N, 5.41. Found: C, 55.77; H, 6.63; N, 5.28.

In a similar manner, the reaction of bromanil **1b** with 4-hydroxy-TEMPO was carried out to give **3b** as the main product in 65% yield together with mixtures of **4b** and **5b** in 9% yield and their data are as follows. **3b**: mp 152−153 °C; FAB-MS (*m*/*z*) 516 (M + H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 203 (4.32), 308 (4.18), 419 (2.72). Anal. Calcd for $C_{15}H_{17}NO_4Br_3$: C, 34.98; H, 3.33; N, 2.72. Found: C, 35.45; H, 3.32; N, 2.66. **4b**: mp 217−219 °C; FAB-MS (*m*/*z*) 608 (M + 2H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 205 (4.32), 310 (4.16), 410 (2.65). Anal. Calcd for $C_{24}H_{34}N_2O_6Br_2$: C, 47.54; H, 5.65; N, 4.62. Found: C, 47.26; H, 5.58; N, 4.73. **5b**: mp 168−170 °C; FAB-MS (*m*/*z*) 608 (M + 2H); EPR (solid), g = 2.007; UV−vis (CH_3CN) 206 (4.41), 310 (4.21), 410 (2.80). Anal. Calcd for $C_{24}H_{34}N_2O_6Br_2$: C, 47.54; H, 5.65; N, 4.62. Found: C, 47.53; H, 5.63; N, 4.53.

The main isolated product of the reaction of fluoranil **1c** with 4-hydroxy-TEMPO was 2,5-disubstituted compound **4c**, regardless of the equivalence of the reagent, and when 2 equiv of 4-hydroxy-TEMPO was used, compound **4c** was obtained in 21% yield. Mp 157 °C; FAB-MS (*m*/*z*) 486 (M + 2H); EPR (solid), g = 2.008; UV−vis (CH_3CN) 282 (4.37), 408 (2.81). Anal. Calcd for $C_{24}H_{34}N_2O_6F_2$: C, 59.49; H, 7.07; N, 5.78. Found: C, 59.13; H, 6.97; N, 5.62.

The Reaction of Fluoranil with 4-Amino-TEMPO. A stirred mixture of fluoranil **1c** (0.10 g, 0.56 mmol) and 4-amino-TEMPO **6** (0.19 g, 1.11 mmol) in CH_3CN (30 mL) was heated to 70 °C for 2 h. The reaction mixture was then cooled to ambient temperature and evaporated in vacuo. The resulting dark solid was then purified by column chromatography on silica gel with dichloromethane to give 2,5-disubstituted derivative **7** (0.11 g, 41%). Recrystallization in a mixed solvent of hexane and dichloromethane gave violet crystals and the data are as follows. Mp >280 °C; FAB-MS (*m*/*z*) 484 (M + 2H); EPR (solid), g = 2.006; UV−vis (CH_3CN) 222 (4.52), 351 (4.46). Anal. Calcd for $C_{24}H_{36}N_4O_4F_2$: C, 59.73; H, 7.52; N, 11.52. Found: C, 59.44; H, 7.63; N, 11.40.

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Supporting Information Available: Tables of crystallographic data of **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, and **7** (Tables 1, SI-1 and Table 2, SI-2), their CIF files, and figures of crystal structures of **3b** (SI-3), **4b** (SI-4), and **5b** (SI-5). This material is available free of charge via the Internet at http://pubs.acs.org.