Preparation and properties of 4-amino-TEMPO-substituted benzoquinone derivatives and related charge-transfer complexes

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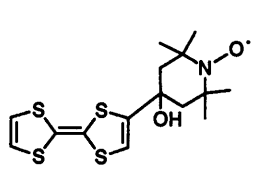
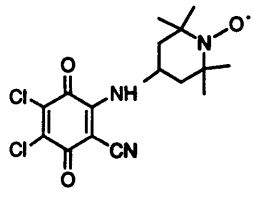
The reaction of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) with 4-amino-TEMPO (4-amino-2,2,6,6-tetramethylpiperidin-1-yloxyl) led to the 5-(4-amino-TEMPO)-substituted benzoquinone derivative 2 as the main product with the replacement of one cyano group, whereas bis(4-amino-TEMPO)-substituted benzoquinone derivatives 4 or 5 were obtained as the main products in the reaction of chloranil† or bromanil † with 4-amino-TEMPO under the same reaction conditions. The benzoquinone acceptor 2 formed charge-transfer complexes with the donors such as TTF (tetrathiafulvalene) or the 4-hydroxy-TEMPO-substituted TTF derivative, showing weak anti-ferromagnetic interactions in the complexes.

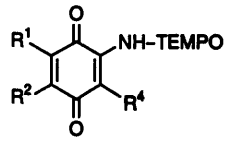
Recently, the search for new organomagnetic materials has been of great interest and several organoferromagnetic materials have been developed quite recently although their T_c values are still very low.[1] We have been interested in preparing new organomagnetic materials by building up charge-transfer (CT) complexes which carry stable radical unit(s) in either the donor or the acceptor part, or both parts, to arrange the unpaired electrons in column structure of the single crystals prepared by a suitable method.[2] As a model of such CT complexes carrying stable radical unit(s) in the donor part, we have recently prepared a hydroxy-TEMPO-substituted TTF **1** which forms CT complexes with several acceptors, *e.g.* I_2, DDQ or $TCNQF_4$ (7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane) and reported on their magnetic properties.[3] In this paper, we wish to report on the preparation of several benzoquinone derivatives (**2**–**5**) carrying stable radical unit(s), *i.e.* amino-TEMPO unit(s), the magnetic properties of **2**, as well as the CT complexes formed between **2** and TTF or hydroxy-TEMPO-substituted TTF **1**.[4]



1



2



3: R^2=NH-TEMPO
R^1=Cl, R^4=CN
4: R^2=NH-TEMPO
R^1=R^4=Cl
5: R^2=NH-TEMPO
R^1=R^4=Br

Results and discussion

Preparation of amino-TEMPO-substituted benzoquinone derivatives 2–5

It was found that by the reaction of DDQ with an equimolecular amount of 4-amino-TEMPO[5] in dichloromethane at ambient temperature 5-(4-amino-TEMPO)-substituted benzoquinone derivative **2** was obtained as the main product in 34% yield. In this reaction, only a small amount (*ca.* 1%) of the bis(4-amino-TEMPO)-substituted derivative **3** was obtained (Scheme 1). It was interesting that dichloromethane was found to be the most suitable solvent studied to obtain **2** rather than **3** in the reaction because the yields of **3** were considerably increased while that of **2** was diminished when other solvents were employed and no tendency was observed between the solvent polarity and the yield of **2** and/or **3** (Table 1).‡

In order to investigate the mechanism of the reaction more closely, we examined the time dependence of the electronic absorption spectra of the reaction. Immediately after mixing each component in dichloromethane, new absorptions at 485 nm as well as at 845 nm were observed (Fig. 1), in which the former is clearly assigned to **2** and the latter broad one to the charge-transfer band. It was observed that each absorption

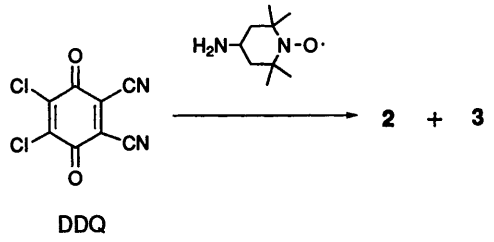
† IUPAC names: chloranil = 2,3,5,6-tetrachloro-1,4-benzoquinone; bromanil = 2,3,5,6-tetrabromo-1,4-benzoquinone.

‡ As described in the Experimental section, we continued the reaction for 1 h to establish constant reaction conditions from the preparative point of view, and hence it was not the optimal reaction condition.

Table 1 Reactions of DDQ with 4-amino-TEMPO in various solvents[a]

Entry	Solvent	ε_r[b]	Yield of 2[c] (%)	Yield of 3[c] (%)
1	CH_2Cl_2	8.93	34	1
2	Benzene	2.27	25	3
3	THF	7.58	23	10
4	MeCN	35.94	22	6
5	EtOH	24.55	21	7

[a] Reaction conditions; DDQ 0.44 mmol, amino-TEMPO 0.44 mmol in 10 ml of each solvent, reaction time 1 h at ambient temperature. [b] Relative permittivity at 25 °C. [c] Isolated yield.



Scheme 1

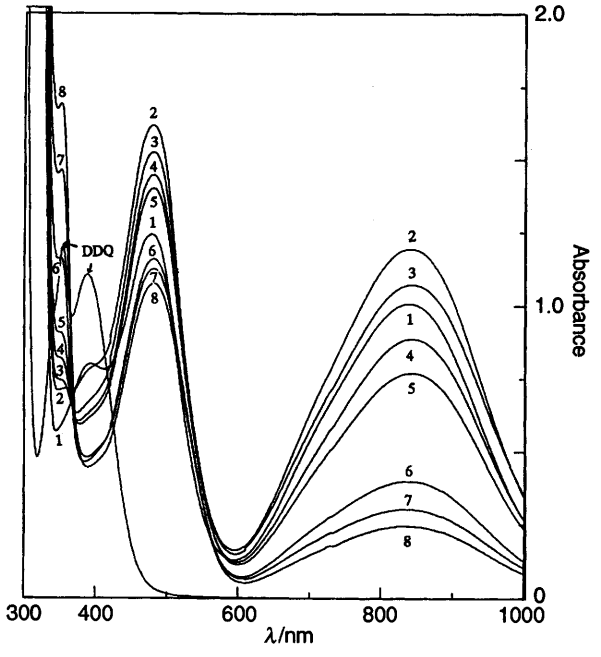
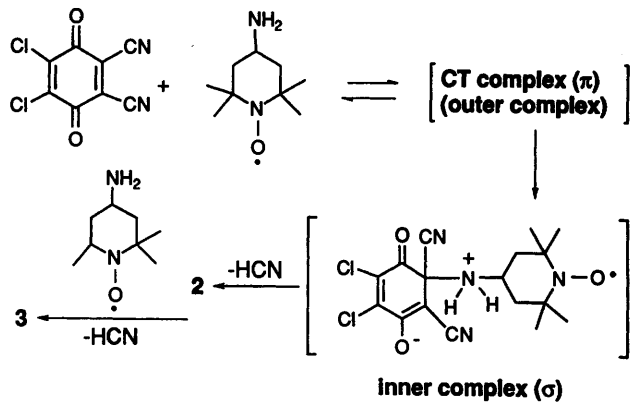


Fig. 1 Temperature dependence of the electronic absorption spectra of DDQ (4.41×10^{-4} M)-4-amino-TEMPO (4.41×10^{-4} M) system in dichloromethane at room temperature: 1, immediately after mixing the DDQ solution with the 4-amino-TEMPO solution; 2, 5 min; 3, 10 min; 4, 15 min; 5, 20 min; 6, 40 min; 7, 60 min; 8, 80 min

reached a maximum after 5 min and then decreased gradually along the time course of the reaction. In turn, a new absorption at *ca.* 355 nm increased with time indicating the gradual formation of **3**.§ In the recent paper by Tanemura *et al.*[6] and an early paper by Bergman *et al.*,[7] it was reported that carbon–carbon adducts were found to be formed by the reaction of DDQ with indole derivatives, which were considered to be formed through a CT complex by nucleophilic attack of indole on DDQ. In our

§ Because of the complex nature of the reaction process, we could not clarify the exact kinetics of the reaction. Quite different absorption spectra were observed when a larger amount (> *ca.* 9 equiv.) of 4-amino-TEMPO compared with DDQ was used in the dichloromethane solution indicating the existence of another reaction path which does not yield **2** or **3** and thus preventing the determination of the equilibrium constant of the charge-transfer complex by a Benesi–Hildebrand-type procedure.



Scheme 2

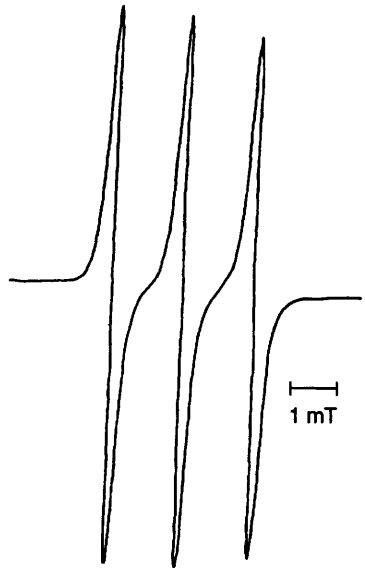


Fig. 2 EPR spectrum of **2** in benzene at room temperature

reaction of DDQ and amino-TEMPO in dichloromethane, it could be considered from the observation of the charge-transfer band¶ as shown in Fig. 1 as well as greenish precipitates formed during the reaction‖ that, although the exact reaction mechanism is not clear yet, the reaction proceeded through a CT complex (outer complex)[8] and inner complex (σ-complex) with a nitrogen–carbon σ-bond which then eliminates one molecule of hydrogen cyanide to give benzoquinone derivative **2** and successive nucleophilic attack of amino-TEMPO on **2** could then afford the bis-adduct **3** (Scheme 2).[9,10] On the contrary, however, bis(4-amino-TEMPO)-substituted derivatives **4** or **5** were the major products in the reaction of chloranil or bromanil with 4-amino-TEMPO suggesting the last step affording the bis-adduct is very fast.

Properties of benzoquinone derivatives 2–5 and the CT complexes formed between 2 and TTF or the TTF derivative 1

Three-line signals due to aminoxyl radicals were observed in the EPR spectra in benzene solutions of **2–5** (each $g = 2.007$ and $a_N = 1.58$ mT, see Experimental section). A similar spectrum was observed for 4-amino-TEMPO itself ($g = 2.007$, $a_N = 1.53$ mT in benzene) suggesting the localized nature of the unpaired electrons at the aminoxyl groups in **2–5** (*cf.* Fig. 2). The redox

¶ It was estimated from the observed charge-transfer band of the complex that the oscillator strength (f) and the transition dipole moment (μ) of the complex was fairly large (calculated to be $f = 0.440$, $\mu = 8.90$).[12]

‖ The greenish precipitates of the CT complex were formed when using CH_2Cl_2 or benzene as solvent, whereas no precipitates were formed in THF, CH_3CN or EtOH.

Table 2 Reduction potentials of benzoquinones[a]

Benzoquinones	CH_2Cl_2			MeCN		
	E_1^{RED}/V	E_2^{RED}/V	ΔE/V	E_1^{RED}/V	E_2^{RED}/V	ΔE/V
BQ	−0.64	−1.25	0.61	−0.57	−1.27	0.70
DDQ	0.52	−0.32	0.84	0.47	−0.31	0.78
2	−0.19	−0.88	0.69	−0.19	−0.83	0.64
3	−0.36	−0.90	0.54	−0.34	−0.86	0.52
4	−0.29	−0.95	0.66	−0.28	−0.87	0.59
5	−0.40	−0.90	0.50	−0.35	−0.88	0.53

[a] V *vs.* SCE; supporting electrolyte: 0.1 M TBAP; scan rate: 20 mV s^{-1}.

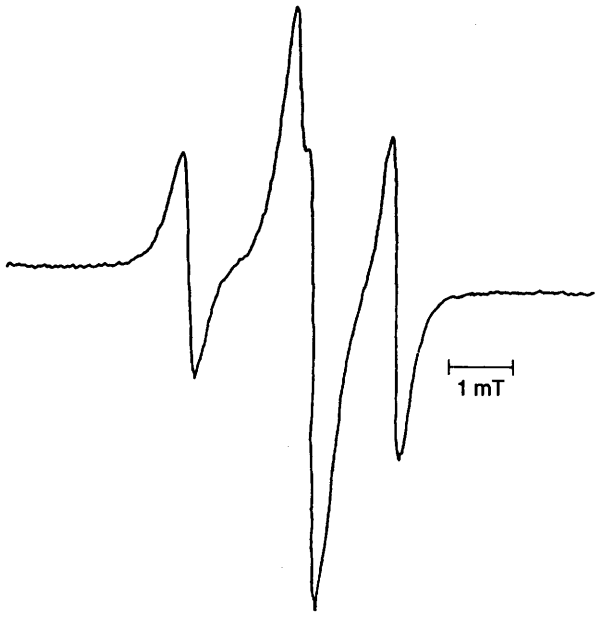


Fig. 3 EPR spectrum of the CT compex **6** in EtOH at room temperature

behaviour of **2–5** was investigated by cyclic voltammetry in CH_2Cl_2 as well as in CH_3CN and was found to have first reduction potentials lower than DDQ, but higher than benzoquinone suggesting that they have intermediate electron-accepting ability between DDQ and benzoquinone (Table 2). It was also noticeable that the first reduction of **2** was the highest among **2–5**, which suggested that **2** was the most suitable acceptor to form a CT complex with an appropriate donor molecule.

As expected from the redox behaviour, it was found that the charge-transfer complex **6** was formed between **2** and TTF while there was no evidence for the formation of CT complexes between **3–5** and TTF. Interestingly, **2** formed the CT complex **7** with 4-hydroxy-TEMPO-substituted TTF **1**, which is the first isolated CT complex with unpaired electrons in both the donor and acceptor molecules.[11] The large red shifts of the absorption maxima in the longest wavelength region observed in the UV–VIS spectra of **6** and **7** in MeOH showing 579 nm ($\varepsilon = 3540$ dm^3 mol^{-1} cm^{-1}) for **6** and 610 nm ($\varepsilon = 730$ dm^3 mol^{-1} cm^{-1}) for **7** compared with **2** [477 nm ($\varepsilon = 1730$ dm^3 mol^{-1} cm^{-1}) in CH_3CN] suggested the formation of CT complexes. The EPR spectra of the complexes show three-line signals of unequal intensity, *e.g.* the spectrum of complex **6** is given in Fig. 3, suggesting the existence of overlapping signal(s) of the TTF radical-cation and/or benzoquinone radical-anion with the triplet of the aminoxyl. Furthermore, the observation of M^+ (or M + 1) peaks corresponding to their donor components (attributed presumably to the peak of each radical-cation) in the FAB–MS spectra of **6** (*m/z* 204, corresponding to M^+ of TTF) and **7** (*m/z* 375, corresponding to M + 1 of **1**) indicated charge-transfer complex formation with no formation of covalent bonds between each donor and acceptor. We have

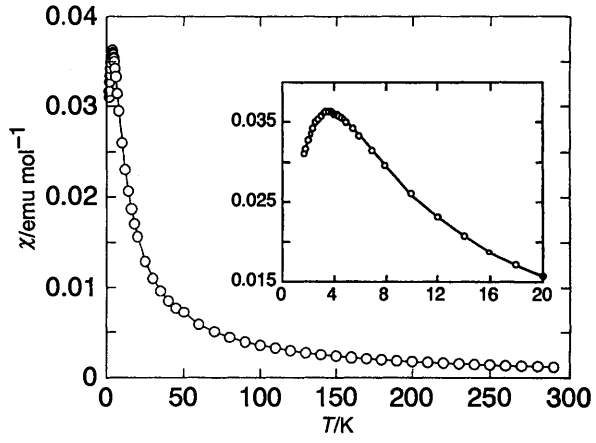


Fig. 4 Temperature dependence of χ for **2**. Inset is an enlargement of the lower temperature region.

further tried to prepare single crystals of the CT complexes, but no adequate single crystal for crystallographic or further physicochemical studies has been available so far.

Magnetic susceptibility of 2 as well as CT complexes 6 and 7

The magnetic susceptibility of **2** as well as the CT complexes (**6**, **7**) obtained were measured on their polycrystalline samples by a SQUID susceptometer at temperatures between 2 and 300 K. It was found from the susceptibility data that **2** has its susceptibility maxima at *ca.* 3.8 K (Fig. 4) and the experimental data were well reproduced by theoretical data estimated by the one-dimensional Heisenberg anti-ferromagnetic model with $J = 3$ K and $\chi_{max} = 0.037$ emu mol^{-1} (Weiss temperature $\theta = -0.55$ K). In the CT complexes of **2**, the susceptibility data showed a Curie–Weiss curve with a Weiss temperature of as large as −1 K (*e.g.* the data for **6** in Fig. 5) and apparent decrease in magnetic susceptibility compared with **2** was observed for each complex by CT formation resulting probably from the intra- and/or inter-molecular singlet formation between unpaired electrons.

Conclusions

5-(4-Amino-TEMPO)-substituted benzoquinone derivatives **2–5** have been prepared by the reaction of DDQ, chloranil and bromanil with 4-amino-TEMPO. In the reaction of DDQ and 4-amino-TEMPO, the benzoquinone derivative **2** was obtained as the main product with the replacement of one cyano group, whereas in the reaction of chloranil or bromanil with 4-amino-TEMPO under the same reaction condition, bis-4-amino-TEMPO-substituted benzoquinone derivatives **4** or **5** were obtained as the main products. The benzoquinone acceptor **2** showed anti-ferromagnetic one-dimensional ordering in its magnetic susceptibility while the CT complexes (**6**, **7**) formed from **2** with TTF or the 4-hydroxy-TEMPO-substituted TTF derivative **1** showed weak anti-ferromagnetic interactions in the complexes with a decrease in susceptibility compared with **2**.

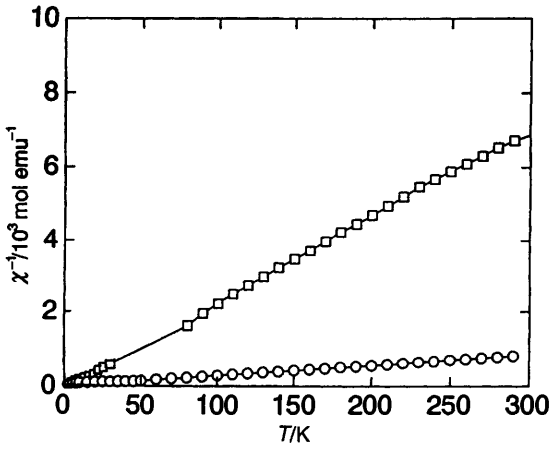


Fig. 5 Temperature dependence of $1/\chi$ for **2** (○) and **6** (□)

Experimental

Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. IR spectra were recorded on a JASCO Report-100 spectrometer. UV–VIS spectra were obtained on a JASCO Ubest-35 spectrometer. Cyclic voltammograms were obtained on a YANACO P-1100 instrument. MS spectra were recorded on a JEOL JMS-AX 303 mass spectrometer. EPR spectra were obtained on a JEOL JES-FE3XG spectrometer and each g value was determined using Mn^{2+}–MnO as an internal standard. Susceptibility measurements were carried out on a QUANTUM DESIGN MPMS-5 SQUID susceptometer using *ca.* 10 mg for each powdered sample at 0.5–1 T from 4.5 to 300 K and at 0.1 T below 4.5 K. The diamagnetic contribution was corrected from Pascal's constants. The reaction was carried out under a nitrogen atmosphere.

Preparation of 2 and 3

To a stirred solution of DDQ (0.10 g, 0.44 mmol) in CH_2Cl_2 (20 cm^3) was added 4-amino-TEMPO (75 mg, 0.44 mmol) in CH_2Cl_2 (10 cm^3) at ambient temperature. The resulting deep-red solution with deposition of a greenish solid was stirred for 1 h. The reaction mixture was poured onto water, washed with brine and dried over anhydrous $MgSO_4$. After reducing the volume of the reaction mixture under reduced pressure, the dark red solid thus obtained was separated by column chromatography on silica gel (Merck Kieselgel 60, 15 g) with CH_2Cl_2–diethyl ether as the eluent. From the fraction of 10% diethyl ether–CH_2Cl_2 elute **2** was obtained (56 mg, 34%) as dark red crystals (recrystallized from CH_2Cl_2). Mp >222 °C (decomp.) (Found: C, 51.62; H, 4.89; N, 11.30; Cl, 19.56. $C_{16}H_{18}N_3O_3Cl_2$ requires C, 51.77; H, 4.88; N, 11.32; Cl, 19.10%); ν_{max}(Nujol)/cm^{-1} 3200 (NH), 2200 (CN) and 1700 (CO); λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 257 (9910), 302 (9510) and 477 nm (1730); *m/z* (FAB–MS) 372 (M + 2); EPR (benzene) $g = 2.007$, $a_N = 1.58$ mT. From the fraction of 10–20% diethyl ether–CH_2Cl_2 elute **3** was obtained (2 mg, 1%) as dark red crystals. Mp >255 °C (decomp.) (Found: C, 59.23; H, 7.00; N, 13.73; Cl, 6.96. $C_{25}H_{36}N_5O_4Cl$ requires C, 59.34; H, 7.17; N, 13.84, Cl, 7.00%); ν_{max}(Nujol)/cm^{-1} 3250 (NH), 2200 (CN) and 1670 (CO); λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 348 (10 700) and 508 nm (3210); FAB–MS (*m/z*) 506 (M^+); EPR (benzene) $g = 2.007$, $a_N = 1.58$ mT. In another experiment using a larger amount of DDQ (0.4 g, 1.7 mmol) with an equimolar amount of 4-amino-TEMPO, **3** was obtained in somewhat diminished yield (30%) while **4** was obtained in the same yield as above.

Preparation of 4 and 5

To a stirred solution of chloranil (0.25 g, 1.0 mmol) in CH_2Cl_2 (30 cm^3) was added 4-amino-TEMPO (0.18 g, 1.0 mmol) in CH_2Cl_2 (20 cm^3) at ambient temperature. The resulting dark red solution with deposition of a greenish solid was stirred for 1 h. The reaction mixture was poured onto water, washed with brine and dried over anhydrous $MgSO_4$. After reduction of the volume of the reaction mixture under reduced pressure, the dark-reddish-yellow solid thus obtained was separated by column chromatography on silica gel (Merck Kieselgel 60, 20 g) with hexane–benzene–diethyl ether as the eluent. From the fraction of 20% diethyl ether–benzene elute **4** was obtained (0.11 g, 16%) as the main product and as reddish-violet crystals. An analytically pure sample was obtained by recrystallization from CH_2Cl_2. Mp >243 °C (decomp.) (Found: C, 55.68; H, 6.86; N, 10.83; Cl, 13.68. $C_{24}H_{36}N_4O_4Cl_2$ requires C, 55.92; H, 7.04; N, 10.87; Cl, 13.75%); ν_{max}(Nujol)/cm^{-1} 3250 (NH) and 1665 (CO); λ_{max}(CH_3CN)/nm (ε/dm^{-3} mol^{-1} cm^{-1}) 355 (23 300) and 527 (220); FAB–MS (*m/z*) 516 (M + 2); EPR (Benzene) $g = 2.007$, $a_N = 1.58$ mT. In a similar manner, **5** was obtained as reddish-violet prisms. Mp 233–235 °C (decomp.) (Found: C, 47.93; H, 5.90; N, 9.23; Br, 26.04. $C_{24}H_{36}N_4O_4Br_2$ requires C, 47.69; H, 6.00; N, 9.27; Br, 26.44%); ν_{max}(Nujol)/cm^{-1} 3250 (NH) and 1660 (CO); λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 355 (25 500) and 523 nm (330); FAB–MS (*m/z*) 606 (M + 2), 608 (M + 4); EPR (benzene) $g = 2.007$, $a_N = 1.58$ mT.

Preparation of the CT complex 6 from 2 and TTF

An acetonitrile solution (30 cm^3) of the mixture of **2** (30 mg, 0.081 mmol) and TTF (33 mg, 0.16 mmol) was heated at reflux for 2 h.†† The dark brown solid deposited after cooling the reaction mixture was filtered, washed with dichloromethane yielding 44 mg (60%) of CT complex **6** as hygroscopic dark-reddish-brown crystals. Mp >*ca.* 180 °C (decomp.) [Found: C, 40.84; H, 3.43; N, 5.17. **2**: TTF = 1:2 ($C_{28}H_{26}N_3O_3S_8Cl_2 \cdot 2H_2O$) requires: C, 41.22; H, 3.71; N, 5.15%]; ν_{max}(Nujol)/cm^{-1} 3400br (NH) and 2205 (CN); λ_{max}(MeOH)/nm (ε/dm^3 mol^{-1} cm^{-1}) 312 (18 300), 436 (13 200) and 579 (3540); FAB–MS (*m/z*) 204 (M^+ of TTF).

Preparation of CT complex 7 of 2 and TTF derivative 1

An acetonitrile solution (30 cm^3) of the mixture of **1** (23 mg, 0.061 mmol) and **2** (23 mg, 0.064 mmol) was heated at reflux for 1.5 h. The dark brown solid deposited after cooling the reaction mixture was filtered, washed with dichloromethane yielding 27 mg (60%) of CT complex **7** as hygroscopic dark brown crystals. Mp > *ca.* 280 °C (decomp.) [Found: C, 46.08; H, 5.57; N, 7.30 **2**:**1** = 1:1 ($C_{31}H_{38}N_4O_5S_4Cl_2 \cdot 3H_2O$) requires C, 46.55; H, 5.54; N, 7.01%]; ν_{max}(Nujol)/cm^{-1} 3380br (OH, NH) and 2200 (CN); λ_{max}(MeOH)/nm (ε/dm^3 mol^{-1} cm^{-1}) 313 (14 900), 375 (8960), 450 (3700), 480 (3070) and 610 (730); FAB–MS (*m/z*) 375 (M + 1 of **1**).

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†† From the preliminary experiments, we have set up the reaction condition as described. Without heating the mixture, CT formation occurred very slowly; 1–2 h was adequate for the reaction time, because the reaction progressed rapidly within the first 1–2 h (monitored by EPR), but prolonged heating diminished the yield of the complex.

References

1 For the reviews on organomagnetic materials, see for example, H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179; J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385 and references cited therein. Several organic ferromagnets have been reported recently, *e.g.*, M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe and Maruyama, *Chem. Lett.*, 1991, 1225; P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner and J. D. Thompson, *Science*, 1991, **253**, 301; R. Chiarelli, M. A. Novak, A. Rassat and J. L. Tholence, *Nature*, 1993, **363**, 147; T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda and M. Ishikawa, *Chem. Lett.*, 1994, 29; T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda and M. Ishikawa, *J. Chem. Soc., Chem. Commun.*, 1994, 1723; T. Mukai, K. Konishi, K. Nedachi and K. Takeda, *J. Magn. Mater.*, 1995, **140–144**, 1449.

2 K. Yamaguchi, H. Nishimoto, T. Fueno, T. Nogami and Y. Shirota, *Chem. Phys. Lett.*, 1990, **166**, 408; K. Yamaguchi, M. Okumura, T. Fueno and K. Nakasuji, *Synth. Met.*, 1991, **41–43**, 3631.

3 S. Nakatsuji, S. Satoki, K. Suzuki, T. Enoki, N. Kinoshita and H. Anzai, *Synth. Met.*, 1995, **71**, 1819; S. Nakatsuji, N. Akashi, K. Suzuki, T. Enoki, N. Kinoshita and H. Anzai, *Mol. Cryst. Liq. Cryst.*, 1995, **268**, 153; a portion of this work was presented at the 12th International Conference on the Chemistry of the Organic Solid State (ICCOSS XII), Matsuyama, Japan, July 9–14, 1995, Abstract p. 177; S. Nakatsuji, N. Akashi, Y. Komori, K. Suzuki, T. Enoki and H. Anzai, *Mol. Cryst. Liq. Cryst.*, 1996, **279**, 73.

4 Quite recently, three organic ferromagnets of charge-transfer complex consisting of pyridinium substituted imidazoline-1-oxyl–$TCNQF_4$ or hexacyanobutadienide have been developed by T. Sugimoto; T. Sugimoto, M. Tsujii, T. Suga, N. Hosoita, M. Ishikawa, T. Takeda and M. Shiro, *Mol. Cryst. Liq. Cryst.*, 1995, **272**, 183.

5 For the reviews on the chemistry of aminoxyl radicals, see for example, E. Rozantsev and V. D. Scolle, *Synthesis*, 1971, 190; J. F. W. Keana, *Chem. Rev.*, 1978, **78**, 37.

6 K. Tanemura, T. Suzuki and T. Horaguchi, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1235.

7 J. Bergman, R. Carlsson and S. Misztal, *Acta Chem. Scand., Ser. B*, 1976, **30**, 853.

8 Among stable radicals, di-*tert*-butyl-*N*-oxide is known to form CT complexes with several acceptors including DDQ; Y. Murata and N. Mataga, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 354.

9 For the related mechanism of the reaction of chloranil with primary amines, see *e.g.*, T. Nogami, K. Yoshihara, H. Hosoya and S. Nagakura, *J. Phys. Chem.*, 1969, **73**, 2670; P. C. Dwivedi and R. Agarwal, *Indian J. Chem., Sect. A*, 1985, **24**, 100.

10 The reaction of *p*-chloranil with nucleophiles such as amines is known to give a di-substituted product substitution taking place predominantly at the 2,5-position; *cf.* R. Neef and O. Bayer, *Chem. Ber.*, 1957, **90**, 1137; T. Nogami, T. Yamaoka, K. Yoshihara and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 380; I. Shaaban and R. Solima, *Pharmazie*, 1978, **33**, 642; S. Iwatsuki, M. Kubo and H. Iwase, *Chem. Lett.*, 1993, 517.

11 Very recently, Sugawara *et al.* reported on the interactions in the diradical-ions derived from their open-shell donor and acceptor; R. Kumai, M. M. Matsushita, A. Izuoka and T. Sugawara, *J. Am. Chem. Soc.*, 1994, **116**, 4523.

12 *Cf.* H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, 1961, **83**, 2085; P. Venuvanalingam, U. S. Singh and N. R. Subbaratnam, *Spectrochim. Acta, Part A*, 1981, **37**, 505.

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