Observation of Ground State Triplet Spins which are Stable at Ambient Temperature in an Organic Solid State of Doped Bis(2,3,6,7,10,11-hexamethoxytriphenylene)–2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane, $(HMT)_2$–$TCNQF_4$

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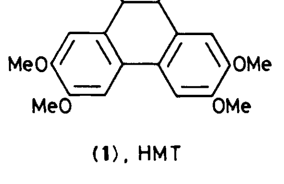
Triplet e.s.r. signals from the dicationic 2,3,6,7,10,11-hexamethoxytriphenylene (HMT) were observed to be stable from 5 K to room temperature in the solid state of an HMT based organic charge-transfer complex.

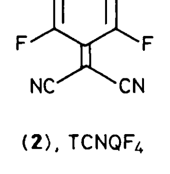
The systematic study of low-dimensional organic donor (D)–acceptor (A) charge transfer complexes with a segregated-stack crystal structure has led to great advances in the discovery of highly conducting organic metals.[1] However, studies on the magnetic properties of charge-transfer complexes have been limited since, unlike many of the inorganic transition metals, most of the organic materials are diamagnetic or weakly paramagnetic. Current research[2,3] on the syntheses of magnetic organic materials is aimed towards development of organic ferromagnets. Among several theories[4,5] for the design of organic ferromagnets, McConnell's model[5] proposes a mix-stacked charge-transfer complex capable of forming a ground-state triplet neutral donor or acceptor diradical as the spin-carrying source for ferromagnetic interactions. This model was modified by Breslow to introduce dicationic triplet molecules as donors.[2] However, the dicationic triplet organic materials are not thermally stable. For example the ground state triplet dication of 2,3,6,7,10,11-hexamethoxytriphenylene[6] (**1**) (HMT) is not stable above −80 °C. The triplet signals of HMT can be observed by e.s.r. spectroscopy only in dilute solution at low temperatures. Other ground-state triplet molecules in solution, such as Breslow's Et_6-HAT (hexaethylhexa-azatritetralin) and HOC (hexa-azaoctadecahydrocoronene), were found to be stable at room temperature only for a short time.[2] The question thus arises as to whether the preferred triplet character exists in the solid and is thermally stable at high temperature. Here we provide e.s.r. evidence for the existence of an ambient temperature-stable ground-state triplet dication in the solid state of one HMT-based charge-transfer complex.

Recently we have studied an approach to the synthesis of organic ferromagnets extended from both McConnell's and Breslow's models. Our approach[7] has been to manipulate an array of ground-state high-spin radicals into an ordered matrix such that they are molecularly separated by a second set of radicals with a different spin state. This is accomplished by a chemical doping technique in the solid state of organic charge-transfer complexes in order to oxidise donor molecules to diradicals with triplet states while the preformed structure of the complex is preserved. The sample used in the study was synthesized by a charge-transfer reaction between HMT as a donor and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**2**) ($TCNQF_4$) as an acceptor. The resulting complex of $(HMT)_2$–$TCNQF_4$ (**3**), with a mix-stacked structure (· · · DADDAD · · ·), was subsequently doped with AsF_5 in the solid state for 9 h to give a complex with a chemical composition of $(HMT)_2$–$TCNQF_4$–$(As_2F_{11})_{4.2}$ (**4**).

The $(HMT)_2$–$TCNQF_4$ complex had a weak e.s.r. spectrum which is centred at g = 2.0031. The low-spin concentration is consistent with a low degree of charge transfer between HMT



(**1**), HMT



(**2**), $TCNQF_4$

$(HMT)_2 - TCNQF_4$ (**3**)

$(HMT)_2 - TCNQF_4 - (As_2F_{11})_{4.2}$ (**4**)

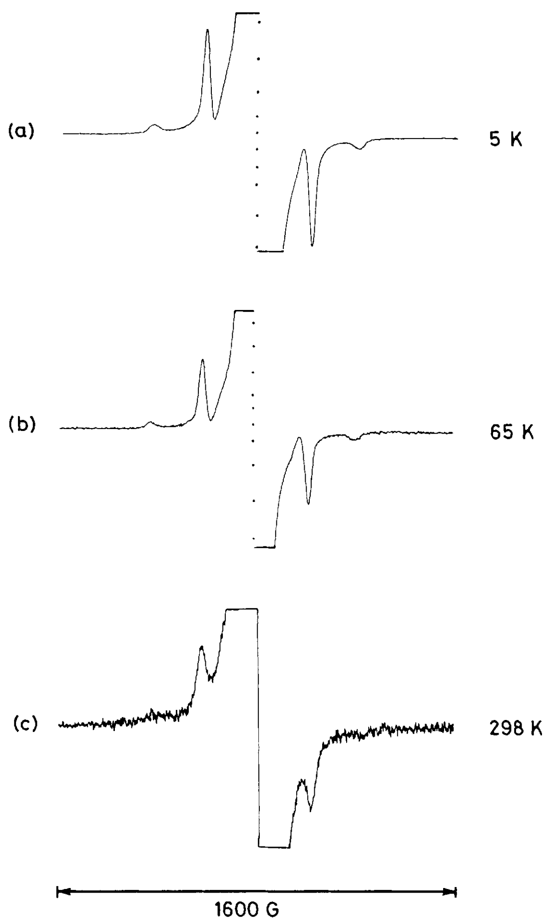


Figure 1. Triplet resonances in the solid state of $(HMT)_2$–$TCNQF_4$–$(As_2F_{11})_{4.2}$ at (a) 5 K, (b) 65 K, and (c) 298 K (1 G = 10^{-4} T).

and $TCNQF_4$ (0.2 per $TCNQF_4$ molecule) in complex (**3**) as measured by the shift of cyano frequency in the i.r. spectrum due to the degree of charge presence on $TCNQF_4$ molecules.[8] This is in good agreement with a spin density of 14% on each HMT molecule calculated from the shift of this g value from that of monocationic HMT ($g = 2.0036$) and monoanionic $TCNQF_4$ ($g = 2.0029$). The doped sample of complex (**4**) exhibited a doublet signal with a Lorentzian line-shape profile and a g value of 2.0036. The spin density of 0.3 (spin $\frac{1}{2}$) per formula unit obtained from the double integration of the e.s.r. spectrum is lower than the 1.3 (spin $\frac{1}{2}$) per formula unit obtained from static susceptibility measurements.[7] This difference is perhaps due to a spin-exchange interaction, consistent with the Lorentzian lineshape.

By increasing the R.F. power to saturate the doublet e.s.r. signals and increasing the sensitivity, we were able to observe triplet resonances from 5 K up to room temperature as shown in Figure 1. This is apparently the first instance that a polymolecular dicationic triplet has been found to be stable to room temperature in an organic solid. The triplet e.s.r. spectrum was analysed using the zero-field splitting parameters D and E from the spin Hamiltonian **H** with an applied field H_0 [equation (1)]. From Figure 1, we obtain $D = 0.038 \text{ cm}^{-1}$ and $E \simeq 0$, consistent with the trigonal symmetry of the parent molecule and with previous measurements of the triplet state of HMT in solution.[6]

$$\mathbf{H} = g\beta H_0 S + DS_z^2 + \mathrm{E}(S_x^2 - S_y^2) \qquad (1)$$

Interestingly, the oxidation of HMT in the solid state with a preformed alternating D–A molecular matrix stabilizes the resulting triplet dicationic product that reverses the previous observation on the thermal instability of HMT^{2+} in solution. We see no significant changes in the e.s.r. or i.r. spectrum or the magnetic susceptibility data after storage for a few days of complex (**4**) at room temperature under Ar. This stabilization may be attributed to the trapping of HMT radicals between nearly neutral $TCNQF_4$ spacers along the stacking axes in the crystal which prevents the spin pairing between adjacent HMT radicals. The triplet splittings indicate that $TCNQF_4$ molecules without C_3 or higher symmetry apparently do not disturb the M.O. degeneracy of HMT previously observed in the solution phase.

In conclusion, we have observed triplet e.s.r. signals from dicationic HMT molecules in the solid state of a doped $(HMT)_2$–$TCNQF_4$ charge-transfer complex. This triplet state is stable from 5 K to room temperature. Since stable ground-state triplet organics are thought to be essential components in the design of organic ferromagnetic solids, the results suggest that $(HMT)_2$–$TCNQF_4$ may be a good model complex for the study of organic ferromagnets.

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References

1 D. O. Cowan and F. M. Wiygul, *Chem. Eng. News*, July 21, 1986, pp. 28—45; F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227; K. Bechgaard and D. Jerome, *Sci. Am.*, 1982, **247**, 52.

2 R. Breslow, *Pure Appl. Chem.*, 1982, **54**, 927; R. Breslow, B. Juan, R. Kluttz, and C. Xia, *Tetrahedron*, 1982, **38**, 863; T. J. LePage and R. Breslow, *J. Am. Chem. Soc.*, 1987, **109**, 6412; J. Thomaides, P. Maslak, and R. Breslow, *ibid.*, 1988, **110**, 3970.

3 T. Sugawara, S. Bandow, K. Kimura, and H. Iwamura, *J. Am. Chem. Soc.*, 1984, **106**, 6450; T. Sugawara, S. Murata, K. Kimura, and H. Iwamura, *ibid.*, 1985, **107**, 5293; H. Iwamura, T. Sugawara, K. Itoh, and T. Takui, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 251; E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus, and F. Wudl, *J. Am. Chem. Soc.*, 1987, **109**, 2594; J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.

4 A. A. Ovchinnikov, *Dokl. Akad. Nauk. SSSR*, 1977, **236**, 928; A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297; A. L. Buchachenko, *Dokl. Akad. Nauk. SSSR*, 1979, **244**, 1146; N. Mataga, *Theor. Chim. Acta*, 1968, **10**, 372.

5 H. McConnell, Proc. R. A. Welch Found. Conf., 1967, **11**, 144; H. McConnell, *J. Chem. Phys.*, 1963, **39**, 1910.

6 K. Bechgaard and V. D. Parker, *J. Am. Chem. Soc.*, 1972, **94**, 4749; O. C. Musgrave and C. J. Webster, *J. Chem. Soc.*, 1971, 1397; L. Y. Chiang, D. C. Johnston, J. P. Stokes, and A. N. Bloch, *Synthetic Metals*, 1987, **19**, 697.

7 L. Y. Chiang, D. C. Johnston, D. P. Goshorn, and A. N. Bloch, *Synthetic Metals*, 1988, **27**, B639; the inverse magnetic susceptibilities of complex (**4**) *vs.* temperature, corrected for ferromagnetic impurities and the temperature-independent diamagnetic susceptibilities, followed a good linear relationship to the Curie–Weiss law from room temperature to near 2 K with a room-temperature paramagnetic susceptibility of 1.8×10^{-3} cm^3/mol. The Curie constant C_M ($\text{cm}^3 \text{ K mol}^{-1}$) of 0.534 corresponds to a spin density of 1.3 (spin $\frac{1}{2}$) per formula unit. These static susceptibilities data reflect a ground-state nature of the observed triplet state of dicationic HMT.

8 J. S. Chappell, W. A. Bryden, M. Maxfield, D. O. Cowan, and A. N. Bloch, *J. Am. Chem. Soc.*, 1981, **103**, 2442.