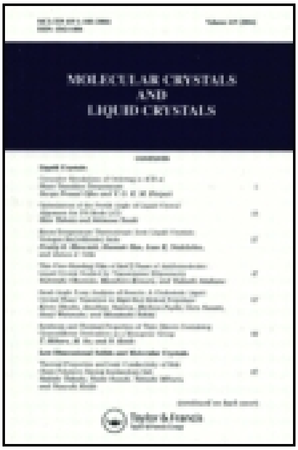
This article was downloaded by: [University of Haifa Library]
On: 16 August 2012, At: 08:57
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Biferrocenium-Based Charge Transfer Salts: An Approach to Molecular Ferroelectric Magnets

Tomoyuki Mochida [a] [b]

[a] Department of Chemistry, Toho University, Miyama, Funabashi, Chiba, 274-8510, Japan

[b] PRESTO, Japan Science and Technology Corporation, Japan

Version of record first published: 24 Sep 2006

To cite this article: Tomoyuki Mochida (2000): Biferrocenium-Based Charge Transfer Salts: An Approach to Molecular Ferroelectric Magnets, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 205-210

To link to this article: http://dx.doi.org/10.1080/10587250008023527

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 205-210
Reprints available directly from the publisher
Photocopying permitted by license only

© 2000 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

Biferrocenium-Based Charge Transfer Salts: an Approach to Molecular Ferroelectric Magnets

TOMOYUKI MOCHIDA[ab*]

[a]*Department of Chemistry, Toho University, Miyama, Funabashi, Chiba 274–8510, Japan, and* [b]*PRESTO, Japan Science and Technology Corporation, Japan*

The electronic features of bimetallocenes are discussed as possible candidates for ferroelectric magnets, based on the coexistence of a dipole moment and a magnetic spin in its mixed-valence state. The dielectric functions were demonstrated for biferrocenium salts. Some charge transfer complexes of biferrocenes with TCNQ derivatives were prepared and characterized.

Keywords: biferrocene; mixed-valence; charge transfer; dielectric response; magnetism

INTRODUCTION

One of our research targets is to realize molecular magnets accompanying ferroelectric functions. For example, a mobile electron in a molecule should lead to the coexistence of an electronic polarity and a magnetic moment, which can be coupled through electron-lattice interactions. As one of the candidates involving such a system, we focus on biferrocenium charge transfer salts (Figure 1); they are representative mixed-valence compounds showing rapid intramolecular

---

* (*mochida@toho-u.ac.jp*)

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

electron transfer (>10^8 Hz), the electronic state of which have been investigated extensively by means of Mössbauer spectroscopy [1]. Focusing on the electronic properties of these compounds, we discuss here one of our approach toward molecular dielectric magnets, taking advantage of the mixed-valent nature of biferrocenium salts.

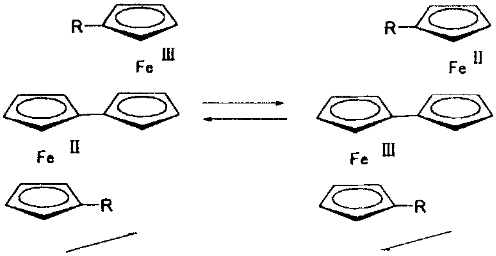


FIGURE 1 Valence tautomerization coupled with electron transfer in biferrocenium salts. The arrows below the molecule denote the electric polarity.

DESIGNING DIELECTRIC AND MAGNETIC FUNCTIONS OF MOLECULAR COMPLEXES

The charge transfer salts have attracted special attention from the viewpoint of fundamental studies of physical properties such as electronic conduction [2] and magnetism [3]. On the other hand, some molecular charge transfer complexes are also used for industrial applications as the electrolyte of solid electrolytic capacitors [4]. If one is to realize molecular-based capacitor with large capacity, one may introduce the mechanism of large polarity inversion in the molecule. Mechanisms of polarity inversion in molecular materials are shown in Figure 2, being the rotational displacement of a molecule [5] and the tautomerization based on intramolecular proton transfer [6, 7], though these processes accompany only low dielectric constants. A new idea we propose here is to focus on intramolecular electron transfer process; the valence tautomerization (Figure 2(c)) should accompany the inversion of a large molecular polarity. Among such compounds showing intramolecular electron transfer, we focus on biferrocenium

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

salts (Figure 1). It is to be noted that the mobile electron not only induces the molecular polarity but should also leads to magnetic phenomena. Thus charge transfer complexes of bimetallocenes should be interesting, also in view of a ferromagnetic metallocenium-TCNQ salts [3]; they possibly afford the coexistence and coupling of magnetic and dielectric order-disorder phenomena. Another interesting aspects we can expect to mixed-stack complexes is the "neutral-ionic" phase transition [8]. Here we first examine the dielectric response of biferrocenium salts and further discuss the properties of charge transfer salts in combination with various organic acceptors.

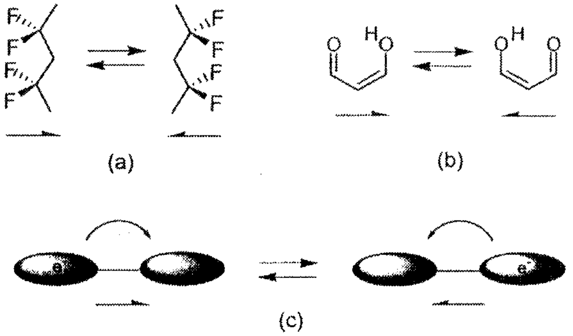


FIGURE 2 Polarity inversion in molecular dielectrics based on molecular reorientation (a), proton tautomerisation (b), and electron transfer (c). The arrows below each units indicate the dipole moments.

DIELECTRIC FUNCTIONS OF BIFERROCENIUM SALTS BASED ON INTRAMOLECULAR ELECTRON TRANSFER

We demonstrate the dielectric functions of biferrocenium salts, by focusing on simple salts with inorganic anions. Among biferrocenium salts, the electronic states of various dialkylbiferrocenium triiodides are well documented [9]. Most of them exhibit charge-ordering phenomena at low temperatures, some of which exhibit ferroelectric-like charge ordering scheme [10] probably due to steric and electronic

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

intermolecular interactions. We show in Figure 3 the dielectric constant of 1',1'''-didodecylbiferrocenium triiodide [11], which shows the averaged-valence state above 230 K [12]. The dielectric constant exhibits a Curie-Weiss-like behavior in the charge-disordered phase, and a maximum is observed at around the valence trapping-detrapping temperature, being reminiscent of an antiferroelectric phase transition. Thus we have demonstrated that polarity inversion coupled with intramolecular electron transfer leads to the dielectric response.

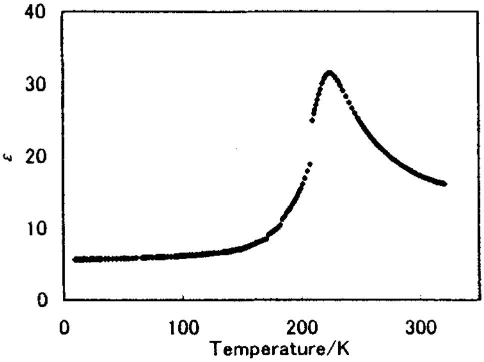


FIGURE 3 Temperature dependence of the real part of dielectric constants of didodecylbiferrocenium triiodide at 10 kHz.

STRUCTURE AND ELECTRONIC PROPERTIES OF BIFERROCENIUM CHARGE TRANSFER SALTS WITH ORGANIC ACCEPTORS

We report the attempts to construct biferrocenium charge transfer complexes with organic acceptors. Despite the good electron donating ability of biferrocenes [13], being comparable to TTF, no structural reports on charge transfer complexes have appeared so far [14]. Actually, though we found that biferrocene-based charge complexes almost always afford non-crystalline powders, we could crystallize some complexes and determined their crystal structures.

Our first examples are TCNQ salts of dialkylbiferrocenes, which

Downloaded by [University of Haifa Library] at 08:57 16 August 2012

are characterized by the stable mixed-valence state down to low temperature [15] as investigated by Mössbauer spectroscopy. The crystal structures of 1',1'''-dibutyl- and 1',1'''-dipropyl-biferrocenium salts were revealed to have segregated-stack structure [11], showing semiconductive electrical conductivities along the TCNQ columns. Their composition is represented as $D^{+}(A_3)^{-}$, in which both D and A molecules have a mixed-valent state.

We also report the structure and properties of mixed stack compounds, in which diamagnetic dimers of Fn-TCNQ stack alternately with 1',1'''-dibromobiferrocenium dications [16]. Figure 4 shows the crystal structure of (dibromobiferrocene) $(F_1\text{-TCNQ})_2$ complex. The F_2-TCNQ complex is also isomorphous.

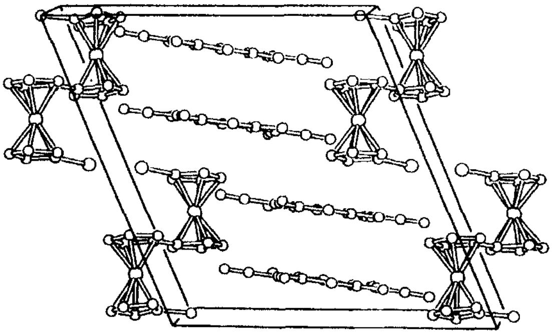


FIGURE 4 X-ray crystal structure of (dibromobiferrocene) $(F_1\text{-TCNQ})_2$ complex.

Their composition is represented as $D^{2+}(A_2)^{2-}$, which belong to non-mixed-valence compounds with a complete charge transfer state, even though the redox potentials of the D-A pair lie on the N-I boundary according to Torrance's plot [8]. They are paramagnets with antiferromagnetic interactions between the iron spins. Mixed stack CT salts with partial charge transfer state should therefore be highly interesting and a search along this line is currently underway in this laboratory.

Acknowledgments

The author is grateful to Mr. S. Suzuki (Toho Univ.) for experimental collaborations, and to Dr. H. Mori (ISTEC) for SQUID measurements.

References

[1] R. J. Webb, P. M. Hagen, R. J. Wittebort, M. Sorai, and D. N. Hendrickson, *Inorg. Chem.*, **31**, 1791 (1992), and references cited therein.

[2] T. Ishiguro, K. Yamaji, and G. Saito, *"Organic Superconductors"*, Springer-Verlag, Berlin (1998).

[3] J. S. Miller, A. J. Epstein, and W. M. Reiff, *Acc. Chem. Res.*, **21,** 114 (1988).

[4] S. Niwa, *Synth. Met.*, **18,** 665 (1987).

[5] T. Mochida, A. Izuoka, T. Sugawara, Y. Moritomo and Y. Tokura, *J. Chem. Phys.*, **100,** 6046 (1994).

[6] T. Sugawara, T. Mochida, A. Miyazaki, A. Izuoka, N. Sato, Y. Sugawara, K. Deguchi, Y. Moritomo, and Y. Tokura, *Solid State Commun.*, **83,** 665 (1992).

[7] T. Mochida, A. Izuoka, T. Sugawara, Y. Moritomo and Y. Tokura, *J. Chem. Phys.*, **101**, 7971 (1994).

[8] J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, **46,** 253 (1981).

[9] S. Iijima, R. Saida, I. Motoyaya, and H. Sano, *Bull. Chem. Soc. Jpn.*, **54,** 1375 (1981).

[10] M. Konno, S. Hyodo, and S. Iijima, *Bull. Chem. Soc. Jpn.*, **55,** 2327 (1982).

[11] T. Mochida, S. Suzuki, S. Ebisawa, and H. Moriyama, to be published elsewhere.

[12] S. Nakashima, Y. Ueki, and H. Sakai, *J. Chem. Soc, Dalton trans.*, 513 (1995).

[13] W. H. Morrison, Jr., S. Krogsrud, and D.N. Hendrickson, *Inorg. Chem.*, **9,** 1998 (1973).

[14] F. Kaufman and D. O. Cowan, *J. Am. Chem. Soc.*, **92,** 6198 (1970).

[15] S. Nakashima, S. Iijima, I. Motoyama, M. Katada, and H. Sano, *Hyperfine Int.*, **40,** 315 (1988).

Downloaded by [University of Haifa Library] at 08:57 16 August 2012