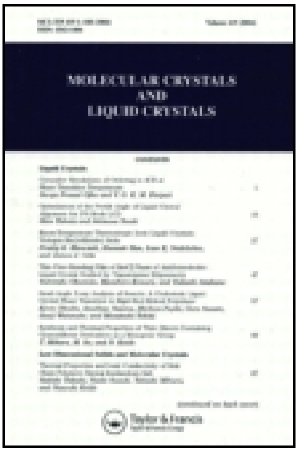


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Novel Oligoimidazoles for Hydrogen-bonded Charge-Transfer Complexes

Yasushi Morita [a] , Tsuyoshi Murata [a] , Satoru Yamada [a] , Makoto Tadokoro [b] & Kazuhiro Nakasuji [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[b] Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

To cite this article: Yasushi Morita, Tsuyoshi Murata, Satoru Yamada, Makoto Tadokoro & Kazuhiro Nakasuji (2003): Novel Oligoimidazoles for Hydrogen-bonded Charge-Transfer Complexes, Molecular Crystals and Liquid Crystals, 379:1, 83-88

To link to this article: http://dx.doi.org/10.1080/713738680

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 83-88
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090309

Novel Oligoimidazoles for Hydrogen-bonded Charge-Transfer Complexes

YASUSHI MORITA[a], TSUYOSHI MURATA[a],
SATORU YAMADA[a], MAKOTO TADOKORO[b],
and KAZUHIRO NAKASUJI[a]

[a]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan and*
[b]*Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*

4,4’-Biimidazole and two kinds of quaterimidazoles were designed and firstly synthesized, aiming at constructing the charge-transfer complexes with the intermolecular hydrogen-bonding interaction. The one-dimensional hydrogen-bonded structure of 4,4’-biimidazole containing protonated 4,4’-biimidazole was confirmed by the crystal structural analysis. TCNQ complexes of the oligoimidazoles exhibited a semiconductive behavior with high conductivity.

Keywords: oligoimidazole; hydrogen-bonding; charge-transfer complexes; hydrogen-bonded ligands; assembled metal complexes

INTRODUCTION

Hydrogen-bonding (H-bonding) interaction plays an important role in the construction of molecular assemblies and supramolecular systems. The creation of H-bonded charge-transfer (CT) complexes and metal complexes can contribute to the development of the advanced molecular-based materials[1]. 2,2'-Biimidazole (**1**), exhibiting intermolecular H-bonding interaction in the solid state, behaves as an electron-active molecule having the redox states coupled with four-step proton- and electron-transfer processes (Figure 1). Actually, it was demonstrated that **1** can form a variety of CT complexes with electron-donating or electron-deficient molecules depending on its redox states[2]. In addition, **1** was found to serve as an interesting building block for the assembled metal complexes through the complementary H-bondings[3].

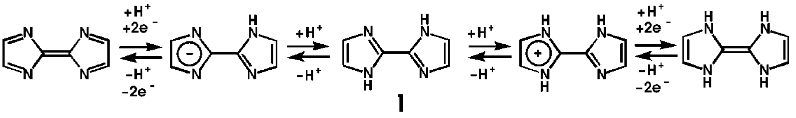
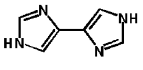
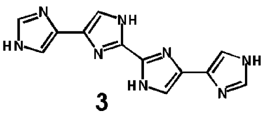
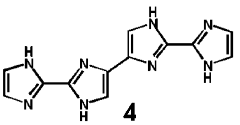


FIGURE 1 Four-step proton- and electron-transfer processes of **1**.

In order to explore a variety of H-bonded CT complexes and the assembled metal complexes, we have designed new oligoimidazoles **2**, **3** and **4**. We report on the synthesis and properties of **2**, **3**, **4** and the CT complexes of **2**–TCNQ and **3**–TCNQ.

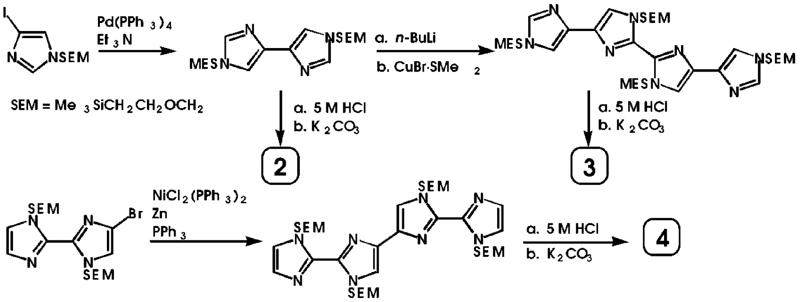

2


3


4

RESULTS AND DISCUSSION

New oligoimidazoles **2**, **3** and **4** were synthesized by the method outlined in Scheme 1. These compounds showed broad stretching absorption band around 2500~3500 cm^{-1} in IR spectra in KBr, which indicate the strong N-H···N intermolecular H-bonding interactions.



SCHEME 1 Synthetic method for oligoimidazoles **2**, **3** and **4**.

Recrystallization of (**2**)(HCl)$_2$ from MeOH–aqueous NH$_3$ gave a single crystal composed of (**2**)$_2$[(**2**)(HCl)$_2$](H$_2$O)$_2$. Its crystal data and molecular structure were summarized in Table 1 and Figure 2, respectively.

TABLE 1 Crystal data of (**2**)$_2$[(**2**)(HCl)$_2$](H$_2$O)$_2$

crystal system	monoclinic
space group	*C*2/c
lattice constants	a = 23.445(3) Å, b = 6.949(3) Å
	c = 15.974(2) Å, β = 111.514(7) Å
unit cell volume	2421.2(9) Å^3
Z	4
density (calc)	1.403 g/cm^3
R-value	0.053

The neutral 4,4’-biimidazole formed dimer structure through the complementary double N-H···N H-bondings (Figure 2A), and each component of a dimer was twisted by 20.2° (Figure 2B). Furthermore, neutral dimers interacted with dication of **2** on the both molecules by single N-H···N H-bonding, resulting in the formation of one-dimensional H-bonded structure elongated along *c*-axis. The imidazole ring of the dication molecule found to be twisted by 20.2° against central C–C bond, and stacked with the neutral 4,4’-biimidazole.

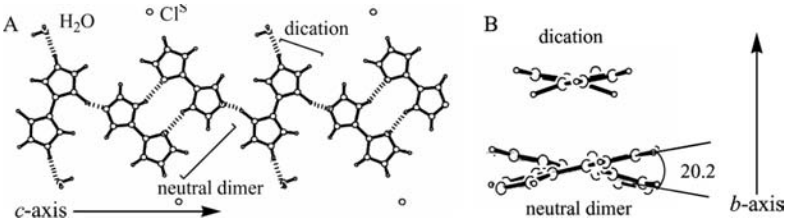
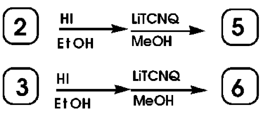


FIGURE 2 A) One-dimensional H-bonded structure elongated along *c*-axis, B) stacking of the neutral dimer with the dication molecule elongated along *b*-axis.

The CT complexes, $(\mathbf{2})(TCNQ)_3(H_2O)_2$ **5** and $(\mathbf{3})(TCNQ)_4(H_2O)_2$ **6**, were obtained by the metathesis method of HI salts of **2** and **3** with LiTCNQ, respectively (Scheme 2). The black colored CT complexes, **5** and **6**, showed the nitrile stretching frequencies of TCNQ moieties at 2194 and 2200 cm^{-1}, respectively, indicating the degree of CT for **5** and **6** to be 0.75 and 0.61 by the Chappell’s equation[4]. Electronic spectra for **5** and **6** showed A-band near 3500 cm^{-1}, which might be inferred an intrastack CT transition of TCNQ moieties in the segregated stack[5] (Figure 3).



SCHEME 2 Preparation of the CT complexes **5** and **6**.

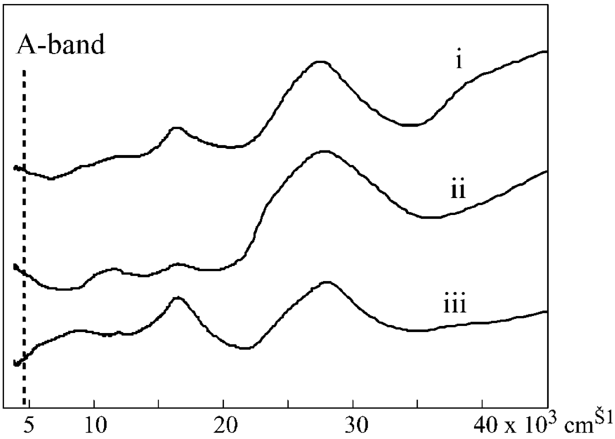


FIGURE 3 The electronic spectra of i) **5**, ii) **6**, iii) LiTCNQ in KBr.

The room-temperature conductivities of the compressed pellets for **5** and **6** were 1.6 x 10^{-1} and 1.0 x 10^{-1} Scm^{-1}, respectively, which were relatively higher conductivities than that of **1**–TCNQ complexes[2b]. The temperature dependence of the conductivities of **5** and **6** showed simple semiconductive behaviors with an activation energy, 113 and 71 meV, respectively (Figure 4).

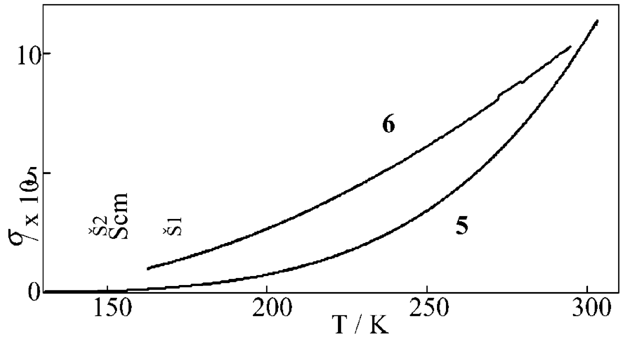


FIGURE 4 The temperature dependence of the conductivities (σ) of **5** and **6**.

In summary we have synthesized novel oligoimidazoles **2**, **3** and **4** for the first time. 4,4'-Biimidazole (**2**) containing protonated **2** found to be formed one-dimensional structure by the intermolecular N-H···N H-bondings between neutral dimers and dication molecules. TCNQ complexes of **2** and **3** showed A-band in electronic spectra, indicating to be segregate structure with partial CT. Furthermore, they exhibited semiconducting behavior with relatively higher conductivities than that of CT complexes composed of **1** and TCNQ. In order to elucidate the molecular packing and the effect of H-bonding interaction on the physical properties, X-ray crystal structure analysis for **5** and **6** is indispensable and in progress.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research on No.297 of Priority Area "Delocalized π-Electronic Systems" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1.] K. Nakasuji, K. Sugiura, T. Kitagawa, J. Toyoda, H. Okamoto, K. Okaniwa, T. Mitani, H. Yamamoto, I. Murata, A. Kawamoto and J. Tanaka, *J. Am. Chem. Soc.*, **113**, 1862 (1991).

[2.] For examples: (a) S. Prasanna and T. P. Radhakrishnan, *Synth. Met.*, **78**, 127 (1996). (b) T. Akutagawa, G. Saito, M. Kusunoki and K. Sakaguchi, *Bull. Chem. Soc. Jpn.*, **69**, 2487 (1996).

[3.] M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro and K. Nakasuji, *Angew. Chem. Int. Ed.*, **38**, 95 (1999).

[4.] J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).

[5.] J. B. Torrance, B. A. Scott and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).