# Synthesis and Magnetic Properties of Conjugated Radical Polymer

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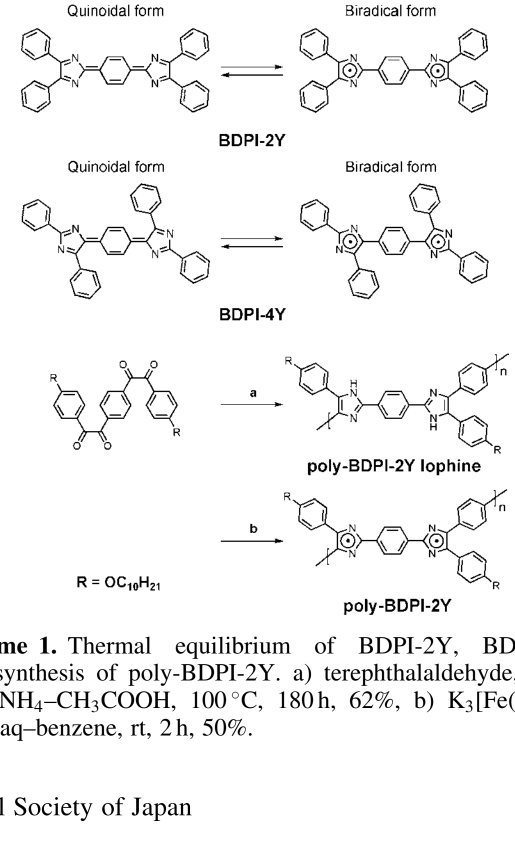
An unprecedented conjugated radical polymer, poly-BDPI-2Y, consisting of imidazolyl radical was prepared and its magnetic properties were investigated. The SQUID measurement proves the presence of the ferromagnetic fraction at 300 K.

Since the discovery of the first genuinely organic ferromagnet, *p*-nitrophenyl nitronyl nitroxide in 1991, much attention has been paid to the chemistry of high-spin molecules and to the search for the possibility of organic ferromagnet.[1] In order to obtain organic ferromagnet, it is necessary to design and then to synthesize high-spin molecules as the first step. Pendant polyradicals, i.e., those having a continuous conjugated backbone to which radical sites are pendantly attached, are found to be attractive, because ferromagnetic through-bond interactions between the pendant spins have been predicted theoretically by using simple polyene models.[2] Since polyradical ferromagnets promise many significant and useful properties, they are the focus of current research and development in many fields, and a variety of organic conjugated polyradicals have been synthesized.[3] Though very few polyradicals showing ferromagnetism at room temperature have so far been reported, there is still great room for the reproducibility of the magnetic data.[4] We report a new type of conjugated radical polymer, which contains the ferromagnetic fraction at 300 K.

1,4-Bis(4,5-diphenylimidazole-2-ylidene)cyclohexa-2,5-diene (BDPI-2Y) was first prepared by Zimmermann et al. in 1996 and was obtained as a deep greenish-blue fine prism with metallic luster.[5a] BDPI-2Y is an EPR active species and the presence of a thermal equilibrium between a diamagnetic closed-shell quinoidal ground state and a paramagnetic thermally excited triplet biradical state was proved by EPR measurements.[5] Controlling the equilibrium between a closed-shell quinoidal state and an open-shell biradical state will provide significant progress in the field of biradical chemistry. Though only 0.1% of BDPI-2Y in solution lies in the paramagnetic state at room temperature, we succeeded in increasing the population of the paramagnetic state of fluorinated BDPI-2Y (0.4%), substituted four hydrogen atoms at the central phenylene ring of BDPI-2Y with fluorine atoms. The fluorinated BDPI-2Y shows a radical–radical recombination reaction to yield a photochromic imidazole dimer distinct from BDPI-2Y.[6a,6b] We also developed 1,4-bis(2,5-diphenylimidazole-4-ylidene)cyclohexa-2,5-diene (BDPI-4Y), which is a structural isomer of BDPI-2Y.[6c] A significant increase in the spin concentration (1.6%) was achieved for BDPI-4Y owing to deviation from the planarity in BDPI-4Y as compared with BDPI-2Y. The deviation from the planarity of conjugated biradicals induces the destabilization of a closed-shell quinoidal state, whereas an open-shell biradical state is stabilized. Consequently, we came up with an idea to increase the spin populations by incorporating BDPI-2Y and BDPI-4Y units into a continuous conjugated backbone. The synthesis and magnetic properties of a conjugated polymer, poly-BDPI-2Y, having BDPI-2Y and BDPI-4Y units in the polymer main chain will be described.

Synthesis of poly-BDPI-2Y is outlined in Scheme 1. A precursor polymer, poly-BDPI-2Y lophine, was prepared by a condensation reaction with terephthalaldehyde and bisbenzil derivative.[7] Number-average molecular weight ($M_n$, g/mol) and polydispersity index ($M_w/M_n$) of poly-BDPI-2Y lophine was determined by gel permeation chromatography (GPC) using polystyrene standard. GPC analysis showed a unimodal distribution, and $M_n$ and $M_w/M_n$ values were determined to be 3190 and 1.29, respectively. Oxidation of poly-BDPI-2Y lophine in benzene with alkaline $K_3Fe(CN)_6$ afforded poly-BDPI-2Y as a deep blue powder in 50% yield.[7] Molecular weight of poly-BDPI-2Y is considered to be nearly equal to that of poly-BDPI-2Y lophine. It should be noted that poly-BDPI-2Y is soluble in common organic solvents, and can be dissolved in benzene in a concentration of 5 mg/mL.

Although a solution of poly-BDPI-2Y shows deep-blue color, the color gradually faded in almost all solvents except for benzene. This discoloration would be attributable to hydrogen abstraction from solvent molecules, which is characteristic



**Scheme 1.** Thermal equilibrium of BDPI-2Y, BDPI-4Y, and synthesis of poly-BDPI-2Y. a) terephthalaldehyde, $CH_3COONH_4$–$CH_3COOH$, 100 °C, 180 h, 62%, b) $K_3[Fe(CN)_6]$, KOHaq–benzene, rt, 2 h, 50%.

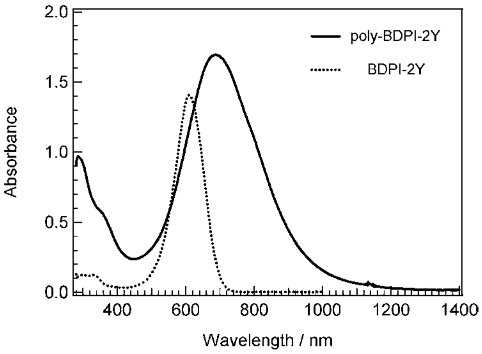


**Figure 1.** UV–vis absorption spectra of poly-BDPI-2Y (solid line, 0.75 mg/mL) and BDPI-2Y (dashed line, $1.25 \times 10^{-5}$ mol/L) in benzene. The measurements were carried out by using a 10 mm cell.

of a reactive radical species. The UV–vis absorption spectra of poly-BDPI-2Y together with BDPI-2Y in benzene are shown in Figure 1. Compared with the absorption spectrum of BDPI-2Y, poly-BDPI-2Y shows a red-shifted, broad absorption band, indicating the presence of delocalized $\pi$-electrons in the polymer main chain.

The magnetic susceptibility was measured on a Quantum Design SQUID magnetometer. Field-cooled (FC) and zero field-cooled (ZFC) magnetizations in the 150 Oe dc field as a function of temperature were measured in the temperature range of 2 to 300 K.[7] The difference between the ZFC and FC curves was undetectable. The magnetization increased below 30 K owing to the Curie fractions originating from the incomplete oxidation of poly-BDPI-2Y lophine, whereas the magnetization values were temperature independent above 30 K. Magnetization measured as a function of magnetic field at 300 K is shown in Figure 2. The "S"-shaped hysteresis, characteristic of ferromagnetism, is clearly observed. The saturation magnetization ($M_s$), residual magnetization ($M_r$), and coercive force ($H_c$) are determined to be $3.02 \times 10^{-4}$ emu Oe g$^{-1}$, $4.32 \times 10^{-5}$ emu Oe g$^{-1}$ and 10 Oe, respectively. Though the resulting $M_s$ is small among reported organic ferromagnets, the reproducibility of this ferromagenetism is satisfactory. The magnetization of poly-BDPI-2Y stored in a refrigerator under an inert atmosphere decreases with time. Moreover, the ferromagnetic fraction almost completely disappeared without any significant color changes four months after preparation.[7] This result precludes any significant interference from magnetic metals on the reported magnetic behavior for poly-BDPI-2Y. The strongest evidence for the presence of ferromagnetic fraction in the fleshly prepared sample is provided by the essentially diamagnetic behavior of the thermally decomposed sample of poly-BDPI-2Y.[7] While the detailed mechanism is not clear at the present stage, these results indicate the presence of a room-temperature ferromagnetic fraction in poly-BDPI-2Y.

In summary, we have synthesized and characterized genuinely organic polymer having conjugated biradical unit in the polymer main chain, which contains the ferromagnetic fraction. To the best of our knowledge, this is the first report of conjugated radical polymer based on a delocalized biradical unit. Molecular weight dependence on the magnetization and magneto–optical properties of a thin film of poly-BDPI-2Y are currently under way.

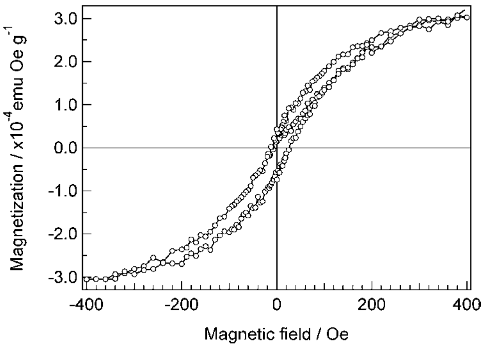


**Figure 2.** Magnetic hysteresis loop of poly-BDPI-2Y at 300 K.

This work was partially supported by a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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7 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) May 31, 2008; doi:10.1246/cl.2008.694