Time-integrated One-pot Synthesis, X-ray Structure, and Redox Properties of Electrochromic 1,3-Diarylisobenzofurans

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(Received May 23, 2013; CL-130479; E-mail: tak@mail.sci.hokudai.ac.jp)

1,3-Bis[4-(dimethylamino)phenyl]isobenzofuran (1a) and a derivative were efficiently prepared through a sequence of reactions in a single batch reactor (time integration). The *o*-quinodimethane-type π -conjugation in 1a was confirmed by bond alternation determined by a low-temperature X-ray analysis. Brightly colored heterocycle 1a undergoes reversible two-stage one-electron oxidation, and electrolysis of 1a induces a vivid change in UV-vis-NIR absorptions exhibiting several isosbestic points (electrochromism).

o-Quinodimethane (oQD) is an attractive molecule that contains a cross-conjugating π -electron system. This hydrocarbon as well as its derivatives are considered versatile building blocks in synthetic chemistry.¹ At the same time, the oQD skeleton provides a unique scaffold in designing novel organic redox systems since the Clar's sextet is generated upon oneelectron transfer, thus stabilizing the resulting ionic states (Scheme 1). Recently, we found that bis(diarylmethylene)dihydrophenanthrenes (DMPs), novel oQD-type electron donors, exhibit an interesting electrochromic behavior (Scheme 2; Ar: 4-MeOC₆H₄).² For further pursuing utility of the oQD skeleton in material sciences, we now design isobenzofuran (IBF)-type electron donors **1**, whose preparation, X-ray structure, and spectral and redox properties are reported herein along with the electrochromic behavior.³

By considering a smaller number of aryl groups in 1 than in DMP, stronger electron-donating groups (e.g., $4-Me_2NC_6H_4$) would be necessary to stabilize the cationic states of 1. According to our recent one-pot synthetic method⁴ for IBF,⁵ symmetric IBF derivative $1a^6$ appended with two (dimethyla-



Scheme 1. Redox scheme of an oQD-based electron donor.



Scheme 2. Molecular design based on the oQD skeleton.

mino)phenyl groups at 1,3-positions was prepared in 63% yield by treatment of methyl 2-formylbenzoate (2) with 3.3 equiv of [4-(dimethylamino)phenyl]magnesium bromide $(-40 \rightarrow 0 \,^{\circ}\text{C})$ and subsequent acidic work-up (Scheme 3). Similarly, unsymmetrical IBF derivative **1b**, having a phenyl and a (dimethylamino)phenyl group at 1,3-positions, was obtained by sequential nucleophilic addition of two aryl Grignard reagents to the starting material **2**. IBFs **1a** and **1b** were isolated as brilliant orange- and yellow-colored crystals, and their solutions are highly fluorescent (Table 1). The absorption and emission of **1a** are shifted to longer-wavelength than those of **1b**, which can be accounted for by the higher HOMO-level of **1a** than that of **1b** (vide infra) due to the presence of two electron-donating amino groups.

To gain insight into the precise molecular structure, a lowtemperature X-ray structural analysis⁸ was conducted on **1a** (Figure 1). The crystal contains two crystallographically independent molecules ($P2_1/n$, Z = 8), whose structural parameters are nearly identical. The molecule adopts a planar geometry, and thus the aryl groups at 1,3-positions lie on the same plane as the IBF core [dihedral angles: 3.1(4) and 8.1(3)° in molecule-1; 6.2(3) and 16.6(4)° in molecule-2]. From the comparisons of bond lengths of the IBF skeleton, the bond alternation expected for the oQD-type conjugation is evident (Tables 2 and S1⁷). Thus, bonds **a**, **c**, and **e** have a much smaller π -bond order⁹



Scheme 3. One-pot synthesis of IBFs 1a and 1b.

 Table 1. UV-vis and fluorescence spectral data of 1a and 1b

 measured in MeCN

| | 1a | 1b |
|---|---------------|---------------|
| UV–vis: $\lambda_{\text{max}}/\text{nm} (\log \varepsilon)$ | 455 (4.00), | 441 (3.96), |
| | 348sh (4.35), | 338sh (3.79), |
| | 324 (4.39), | 308 (4.04), |
| | 276sh (4.05), | 273sh (4.09), |
| | 245sh (4.28) | 252 (4.34) |
| Fluorescence: λ_{max}/nm | 557 | 543 |



Figure 1. Two views of ORTEP drawings of **1a** (molecule-1) determined by an X-ray analysis measured at 150 K along with bond notation for Table 2. a) Top view; b) side view.

Table 2. Bond length $(d)^{a}$ of **1a** determined by X-ray analysis and Pauling π -bond order $(p)^{b}$ calculated based on d

| Bond | $d/{ m \AA}$ | р |
|------|--------------|------|
| а | 1.424(3) | 0.31 |
| b | 1.354(3) | 0.88 |
| c | 1.424(3) | 0.31 |
| d | 1.383(3) | 0.65 |
| e | 1.440(3) | 0.19 |
| f | 1.445(3) | 0.15 |
| g | 1.375(3) | — |

^aAveraged over assumed C_2 -symmetry for the two crystallographically independent molecules. ^bFrom the following linear correlation reported in ref 9: d (C–C) = 1.463 – 0.124p.

(p: 0.31, 0.31, 0.19) than bonds **b** and **d** (0.88, 0.65). The slightly smaller value for bond **d** than for **b** can be accounted for by conjugation of bond **d** with the aryl group and oxygen through bonds **f** and **g**.

The pronounced bond alternation should be diminished upon electron transfer as shown in Scheme 1, and the resulting cationic species would be stabilized by delocalization of positive charges over the electron-donating aryl groups at 1,3-positions (Scheme 4). In fact, bis(dimethylamino)-derivative **1a** undergoes reversible two-stage one-electron oxidation at +0.09 (E_1^{ox}) and +0.29 (E_2^{ox}) V (Figure 2a).¹⁰ The donating ability of **1a** is similar to that of N,N,N',N'-tetramethyl-1,4-phenylenediamine ($E_1^{\text{ox}} + 0.10 \text{ V}, E_2^{\text{ox}} + 0.62 \text{ V})$).¹⁰ and the smaller $\Delta E (\equiv E_2^{\text{ox}} - E_1^{\text{ox}})$ in **1a** can be accounted for by a reduced on-site Coulombic repulsion in dication **1a**²⁺. In fact, the ΔE value of **1a** is close to that of N,N,N',N'-tetramethyl-1,4-benzidine ($E_1^{\text{ox}} + 0.41 \text{ V}, E_2^{\text{ox}}$



follow-up reaction (e.g. dimerization)

Scheme 4. Redox scheme of IBFs 1a (Y = NMe₂) and 1b (Y = H).



Figure 2. Cyclic voltammograms of (a) **1a** and (b) **1b** measured in MeCN (0.1 M Et₄NClO₄, E/V vs. SCE, Pt electrode, 500 mV s⁻¹).

+0.59 V),¹⁰ in which the positive charges of the dication can be delocalized over the extended π -electron system. On the other hand, reference compound **1b** with only one dimethylamino group shows irreversible oxidation at +0.26 V (Figure 2b), showing that **1b** is a weaker electron donor than **1a** and that **1b**⁺⁺ is less stable than **1a**⁺⁺.¹¹

Upon electrochemical oxidation in MeCN, clean conversion of **1a** was observed exhibiting several isosbestic points (Figure 3). Thus, the intensity of the bands at 320 and 450 nm decreases with concomitant appearance of new absorptions in the NIR region (λ_{max} : 725, 810, and 970 nm). Based on the twostage one-electron oxidation process of **1a** in the voltammogram as well as development of the low-energy absorption bands, it is most probable that the observed chromism results from the conversion between **1a** and **1a'**, although the cation radical is too labile to be isolated as salts. Since the electrochromic systems exhibiting the NIR-spectral changes are rare,¹³ the electron-donating IBF can serve as a novel scaffold in developing interesting materials in the less-developed category of electrochromism.



Figure 3. A continuous change in UV–vis–NIR spectrum upon constant current electrochemical oxidation of **1a** $(1.4 \times 10^{-5} \text{ M})$ in MeCN containing 0.05 M Et₄NClO₄ (30 µA, every 30 s).

This work was supported by Grant-in-Aid for Scientific Research on Innovative Areas: "Organic Synthesis Based on Reaction Integration" (No. 2105) from MEXT, Japan.

References and Notes

- Reviews and highlight: a) J. L. Charlton, M. M. Alauddin, *Tetrahedron* 1987, 43, 2873. b) J. L. Segura, N. Martín, *Chem. Rev.* 1999, 99, 3199. c) H. Yoshida, J. Ohshita, A. Kunai, *Bull. Chem. Soc. Jpn.* 2010, 83, 199. d) S. Shinozaki, T. Hamura, Y. Ibusuki, K. Fujii, H. Uekusa, K. Suzuki, *Synfacts* 2010, 649.
- 2 a) T. Suzuki, Y. Sakano, T. Iwai, S. Iwashita, Y. Miura, R. Katoono, H. Kawai, K. Fujiwara, Y. Tsuji, T. Fukushima, *Chem.—Eur. J.* 2013, 19, 117. b) S. Iwashita, E. Ohta, H. Higuchi, H. Kawai, K. Fujiwara, K. Ono, M. Takenaka, T. Suzuki, *Chem. Commun.* 2004, 2076.
- 3 a) P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, **1995**. doi:10.1002/9783527615377. b) P. M. S.

Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism* and *Electrochromic Devices*, Cambridge Univ. Press, Cambridge, **2007**. doi:10.1017/CBO9780511550959.

- 4 a) S. Suga, D. Yamada, J.-i. Yoshida, *Chem. Lett.* 2010, *39*, 404. b) J.-i. Yoshida, K. Saito, T. Nokami, A. Nagaki, *Synlett* 2011, 1189.
- 5 T. Hamura, R. Nakayama, Chem. Lett. 2013, 42, 1013.
- 6 Experimental detail and selected spectral data are given in Supporting Information (ref 7).
- 7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/ index.html.
- 8 Crystal data of **1a**: MF C₂₄H₂₄N₂O, FW 356.47, monoclinic $P2_1/n$, a = 11.184(4), b = 29.905(8), c = 11.946(4) Å, $\beta = 108.779(4)^\circ$, V = 3782.7(19) Å³, $\rho(Z = 8) = 1.252$ g cm⁻³, T = 150 K, R = 7.13%, wR2 = 20.19%, GOF = 0.995. CCDC 933252.
- 9 W. C. Herndon, C. Párkányi, J. Chem. Educ. 1976, 53, 689.
- 10 Cyclic voltammetry was conducted in MeCN containing 0.1 M Et₄NClO₄ as a supporting electrolyte (E/V vs. SCE, Pt electrode, scan rate 500 mV s⁻¹). For the irreversible oxidation wave of **1b**, the oxidation potential was estimated as $E^{\text{peak}} 0.03$ V. Ferrocene undergoes one-electron oxidation at +0.38 V under the similar conditions.
- 11 In the voltammogram of 1-[4-(dimethylamino)phenyl]-3-phenyl-IBF 1b, the reduction peak in the return cycle appeared in the far cathodic region (Figure 2b), suggesting formation of a closed-shell dication through dimerization of 1b⁺⁺ at 3-position. Similar voltammograms were observed in "dynamic redox systems" exhibiting reversible C–C bond formation/cleavage upon electron transfer (ref 12).
- 12 T. Suzuki, E. Ohta, H. Kawai, K. Fujiwara, T. Fukushima, Synlett 2007, 851.
- 13 a) M. C. Aragoni, M. Arca, F. A. Devillanova, F. Isaia, V. Lippolis, A. Pintus, *Chem.—Asian J.* 2011, *6*, 198. b) Y. Miura, H. Kawai, K. Fujiwara, T. Suzuki, *Chem. Lett.* 2011, *40*, 975. c) S. Wang, X. Li, S. Xun, X. Wan, Z. Y. Wang, *Macromolecules* 2006, *39*, 7502. d) T. Suzuki, Y. Tokimizu, Y. Sakano, R. Katoono, K. Fujiwara, S. Naoe, N. Fujii, H. Ohno, *Chem. Lett.* 2013, *42*, 1001. e) T. Suzuki, Y. Hoshiyama, K. Wada, Y. Ishigaki, Y. Miura, H. Kawai, R. Katoono, K. Fujiwara, T. Fukushima, *Chem. Lett.* 2013, *42*, 1004.