## Redox-induced Conformational Changes in 1,3-Propylene- and *m*-Xylylenebis[5-(10-butyl-5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazole)]: Twin-BIC Donors that Form Sandwich-like Dimeric Cations Exhibiting NIR Absorption

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The title electron-donors with two units of a disk-shaped heterocyclic diamine undergo two-stage stepwise one-electron oxidation to the corresponding cation radicals and dication diradicals. They adopt a stacked geometry as in pimers and  $\pi$ -dimers, respectively. In contrast, the third and fourth oxidation processes occur nearly at the same potential, indicating that tricationic/tetracationic species prefer the extended geometry. The similar redox-induced conformational changes were not observed in 1,5-pentylene or *o*-xylylene derivatives, which prefer the extended geometry irrespective of the oxidation states.

## Keywords: Redox system | Electrochromism | Twin donor

Redox-controlled formation of sandwich-like dimeric entities is interesting as an advanced feature for the development of molecular response systems based on organic  $\pi$ -electron systems.<sup>1</sup> The twintype electron donors having two redox-active chromophores (electrophores) connected by a proper spacer have been investigated in terms of the pimer (stacked cation radical) and  $\pi$ -dimer (stacked dication diradical) formation.<sup>2-4</sup> During the course of our continuing studies on novel redox-based response systems,<sup>5,6</sup> we became interested in the title electron-donors with two units of 5,10dihydrobenzo[a]indolo[2,3-c]carbazole (BIC, 1a)<sup>7</sup> by considering that the disk-shaped large  $\pi$ -systems<sup>8</sup> are favorable to gain bonding term in the stacked geometry (Schemes 1 and 2). Based on the onedimensional columnar stack formation in the cation radical salt of 5,10-dimethyl-BIC (1 $c^{+}BF_4^{-}$ ),<sup>7b</sup> we envisioned that the  $\pi$ -system of BIC is large enough to reduce the Coulombic repulsion between two cation radical units overlapped in a face-to-face manner, and so that, the  $\pi$ -dimer as well as the pimer with a stacked geometry would be formed in the twin-BIC donors even when the two electrophores are connected by a flexible spacer.

Here we report preparation and redox properties of electron donors consisting of two units of monoalkylated-BIC tethered with an alkylene chain of the chain length (n) of 3, 4, or 5. The twin donors with an *o*- or *m*-xylylene spacer were also studied. It was found that the longest chain (n = 5) and *o*-xylylene spacer are not suitable for adopting the stacked geometry, whereas drastic



[1a: R = R' = H; 1b: R = Me, R' = H; 1c: R = R' = Me; 1d: R = Bu, R' = H]





Scheme 2. A geometrical change in twin-BIC donors.



Scheme 3. Preparation of twin-BIC donors 3-6.

structural changes between the extended and stacked geometries occur upon redox reactions of the donor with the shortest chain (n = 3) or *m*-xylylene spacer, and thus, the redox-induced conformational changes were demonstrated in the title twin-BIC donors.

As shown in Scheme 3, benzocarbazole 2a bearing an azido group was selected as a key synthon, which was prepared by the gold-catalyzed cyclization<sup>9</sup> using JohnPhosAuNTf<sub>2</sub> (2.5 mol %) in dichloromethane (y. 96%), as we reported previously.7b N-Butyl derivative 2d<sup>10</sup> was obtained upon treatment of 2a with NaH/BuBr in DMF (y. 93%). Exposure of 2d to the nitrene insertion conditions at 160 °C in 1,2-dichlorobenzene provided 5-butyl-BIC 1d<sup>10</sup> in 71% yield. By the reactions of 1d with NaH followed by Br-(CH<sub>2</sub>)<sub>n</sub>-Br (n = 3, 4, or 5) in DMF, the desired twin-BIC donors  $3^{10}$  (n = 3, y). 17%),  $4^{10}$  (n = 4, y. 72%), and  $5^{10}$  (n = 5, y. 84%) were prepared as pale yellow crystals. The N-butyl groups on nitrogen atoms play an important role in attaining enough solubility for a series of measurements in Cl<sub>2</sub>CHCH<sub>2</sub>Cl, Cl<sub>2</sub>CHCHCl<sub>2</sub>, and DMSO. When the similar reaction was conducted by using 5-methyl-BIC  $1b^{7b}$  with 1,3-dibromopropane, twin-type donor 3' (n = 3) with N-methyl groups was obtained (y. 37%), which is less soluble in common



Figure 1. ORTEP drawing of 3' determined by an X-ray analysis measured at 150 K.



Figure 2. Cyclic voltammograms of 3–5 measured in  $Cl_2CHCHCl_2$  (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, E/V vs. SCE, Pt electrode, 100 mV s<sup>-1</sup>).

organic solvents. Recrystallization of **3'** from hot DMSO gave a single crystalline sample, the X-ray analysis of which revealed its extended conformation in the crystal (Figure 1).<sup>11a</sup> As in the cases of monomeric BIC **1a–1c**,<sup>7</sup> the disk-shaped BIC units of an approximate diameter of 10 Å are planar with the largest deviation of atoms from the least-squares planes of 0.21(1) and 0.30(1) Å. The face-to-face overlap with the van der Waals contacts was observed in the crystal of **3'** (Figure S1, Supporting Information (SI)).

The UV–vis spectra of **3–5** measured in Cl<sub>2</sub>CHCH<sub>2</sub>Cl are quite similar to each other, and their molar extinction coefficients are just doubled to that of monomeric BIC **1c** (Figure S2, SI). The FL spectra of **3–5** also resemble that of **1c**, and the FL quantum yields<sup>12</sup> [ $\Phi$  (Cl<sub>2</sub>CHCH<sub>2</sub>Cl): **3**, 0.37; **4**, 0.39; and **5**, 0.41] are nearly the same to that of **1c** measured in the same solvent (0.36) (Figure S3, SI). Thus, there are no indications that the two BIC units in **3–5** interact significantly, and so that, the major conformers for neutral **3–5** should be the extended form.

According to the voltammetric analysis in Cl<sub>2</sub>CHCHCl<sub>2</sub>,<sup>13</sup> twin donor **5** with the pentamethylene chain (n = 5) undergoes two-stage two-electron oxidation (Figure 2 and Table S1, SI). The oxidation potentials ( $E_1 = E_2 = +0.65$ ,  $E_3 = E_4 = +1.16$  V vs. SCE)<sup>13c</sup> are very close to those of monomeric BIC **1c** measured under the similar conditions ( $E_1 = +0.62$ ,  $E_2 = +1.15$  V).<sup>13c</sup> Thus, the two electrophores in **5** are oxidized independently, showing that its dication diradical and tetracationic species adopt the extended form (Scheme 4c). In contrast, stepwise one-electron oxidation ( $E_1 =$ +0.59,  $E_2 = +0.73$  V)<sup>13c</sup> into the corresponding cation radical and dication diradical was observed for twin donor **3** with the trimethylene chain (n = 3), showing that **3**<sup>++</sup> is the pimer with the stacked geometry where the two electrophores are interacting



Scheme 4. Redox schemes of twin-BIC donors 3-5 showing the predominant/major conformer at each redox state. The species in the bracket have negligible steady-state concentration under the voltammetric conditions.

through the  $\pi$ - $\pi$  overlap. The next oxidation peak of **3** ( $E_3 = E_4 = +1.23 \text{ V})^{13\text{c}}$  is shifted to the anode compared to the corresponding peak in **5** or **1c**, suggesting that  $3^{2+2^*}$  also adopts the stacked form ( $\pi$ -dimer) to encumber further oxidation. The one-wave two-electron oxidation at the third/fourth potential indicates that the tricationic/ tetracationic species of **3** prefer the extended geometry due to the increased Coulombic repulsion (Scheme 4a).

The chain-length dependency shown above is consistent with the redox properties of the precedented twinned electrophores:<sup>2,3</sup> the "n = 3 rule"<sup>14</sup> is often valid as in the present study, and the longer chain is less suitable for the  $\pi$ - $\pi$  stacking.<sup>2a</sup> In this connection, the behavior of twin donor **4** (n = 4) is interesting. It shows stepwise one-electron oxidation processes ( $E_1 = +0.58$ ,  $E_2 = +0.76 \text{ V}$ )<sup>13c</sup> into the corresponding cation radical and dication diradical, whereas the next oxidation potential ( $E_3 = E_4 = +1.17 \text{ V}$ )<sup>13c</sup> is not anodically shifted, suggesting that **4**<sup>+\*</sup> is the pimer with the stacked geometry, whereas **4**<sup>2+2\*</sup> adopts the extended form as in its tricationic/tetracationic species (Scheme 4b).

For further investigation of the spacer-dependent redox properties of twin-BIC donors, xylylene-bridged derivatives 6 (ortho) and 7 (meta) were prepared from 1d by the reactions with o- and m-xylylene dibromide in respective yields of 100% and 78% (Scheme 3). The X-ray analysis on 7 revealed its extended geometry in the crystal (Figure S1, SI).<sup>11b</sup> Interestingly, 6 with an o-xylylene unit undergoes two-stage oxidation ( $E_1 = E_2 = +0.72$ ,  $E_3 = E_4 =$ +1.26 V vs. SCE in  $Cl_2CHCHCl_2$ )<sup>13</sup> as in 5 or monomeric BIC 1c (Figure S4). This is in sharp contrast to the precedented twin donors with the same spacer, which form pimers (stacked cation radicals)<sup>4a,4b</sup> and  $\pi$ -dimers (stacked dication diradicals).<sup>4c</sup> Thus, the disk-shaped  $\pi$ -system of BIC is too large to adopt the stacked form when connected by an o-xylylene spacer. On the contrary, the voltammogram of 7 ( $E_1 = +0.59$ ,  $E_2 = +0.77$ ,  $E_3 = E_4 = +1.22 \text{ V}$ )<sup>13c</sup> with a *m*-xylylene unit is nearly identical to that of 3, showing that  $7^+$ and  $7^{2+2}$  are the pimer and  $\pi$ -dimer with the stacked geometry, respectively.<sup>15</sup> This finding is quite unique for the BIC electrophore because there have been no reports that show superior  $\pi - \pi$  stacking of the *m*-xylylene-bridged electrophores compared to the corresponding *o*-xylylene-bridged counterparts.<sup>4</sup> The large  $\pi$  system of BIC would enable to realize partial but enough  $\pi$ - $\pi$  overlap even though the two electrophores are arranged at a certain distance. In this way, the present work has revealed that the suitable spacer for



**Figure 3.** A continuous change in UV–vis–NIR spectrum upon constant current electrochemical oxidation of **3**  $(1.65 \times 10^{-5} \text{ M})$  in Cl<sub>2</sub>CHCH<sub>2</sub>Cl containing 0.05 M Bu<sub>4</sub>NPF<sub>6</sub> (20 µA, every 8 min).

the effective  $\pi$ - $\pi$  overlap differs depending on the electrophores according to their bulkiness and the  $\pi$ -area to be overlapped.

The electrochromic systems that exhibit drastic changes in the NIR absorption are rare but attracting increasing recent attention.<sup>5e,7,16</sup> As shown in Figure 3, the twin-BIC donor 3 works as a UV–vis–NIR electrochromic material, as in the cases of monomeric BIC 1.<sup>7</sup> It is well-known that the pimers and  $\pi$ -dimers exhibit the absorption in the further longer-wavelength region,<sup>1–4</sup> in addition to those of unstacked cation radicals. In fact, along with the absorption maximum at 727 nm, an absorption shoulder around 800 nm appeared during the oxidation of 3,<sup>17</sup> which is absent in the cation radical of 1c measured in the same solvent. Further studies are now under way on the pimers and  $\pi$ -dimers in the present systems.

This work was supported by MEXT (No. 15H03790 and Innovative Areas Nos. 2105 and 2707). TS thank Prof. Takanori Fukushima at TITECH and the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

Supporting Information is available on http://dx.doi.org/10.1246/cl.160278.

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- 10 Experimental detail and spectral data for new compounds are given in Supporting Information.
- 11 a) Crystal data of **3'**: MF C<sub>49</sub>H<sub>36</sub>N<sub>4</sub>, FW 680.85, orthorhombic *P*<sub>21</sub>2<sub>121</sub> (No. 19), *a* = 9.367(3), *b* = 17.077(6), *c* = 21.230(7), *V* = 3396(2) Å<sup>3</sup>,  $\rho(Z = 4) = 1.332 \text{ g cm}^{-3}$ , *T* = 123 K, *R* = 6.52%. CCDC 1454678. b) Crystal data of **7**: MF C<sub>60</sub>H<sub>50</sub>N<sub>4</sub>, FW 827.08, monoclinic *P*<sub>21</sub>/*c* (No. 14), *a* = 12.475(4), *b* = 10.108(3), *c* = 34.105(12), *β* = 95.323(7)°, *V* = 4282(3) Å<sup>3</sup>,  $\rho(Z = 4) = 1.283 \text{ g cm}^{-3}$ , *T* = 123 K, *R* = 15.56%. CCDC 1465222.
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- 17 The similar absorption shoulder around 800 nm was also observed upon the electrochemical oxidation of 4 in Cl<sub>2</sub>CHCH<sub>2</sub>Cl, suggesting that the new band could be assigned to the pimers of 3 and 4.