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5,10-Dihydrobenzo[*a*]indolo[2,3-*c*]carbazole: A Highly Fluorescent Disk-shaped Electron Donor Exhibiting Dual UV–vis–NIR and Fluorescence Spectral Changes upon Electrolysis

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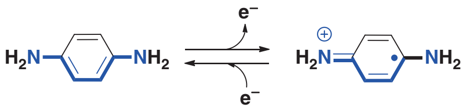
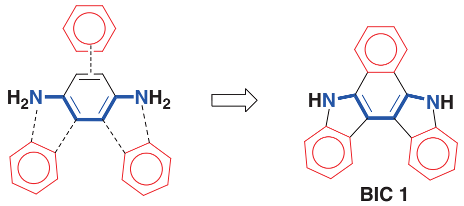
Through gold(I)-catalyzed cascade cyclization as a key step, the title electron donor was prepared, which adopts a planar geometry, as confirmed by an X-ray analysis. Due to 1,4-phenylenediamine moiety incorporated in the framework, it undergoes reversible one-electron oxidation. Upon electrolysis, it exhibited an electrochromic response in the UV–vis–NIR region, which was accompanied by a drastic change in the fluorescence spectrum since only the neutral donor is highly fluorescent.

1,4-Phenylenediamines have been known as representative organic redox systems since their cation radical species are stable enough for spectroscopic detection or even for isolation as exemplified by Wurster's Blue (Scheme 1).[1] Based on the reversible interconversion with the corresponding oxidized states, they can serve as promising electrochromic materials,[2] by which the electrochemical input is transduced into UV–vis spectral output.[3] During the course of our study pursing the advanced chromic materials,[4] we got interested in the two-way-output molecular response systems, by which the electrochemical input causes two kinds of spectral changes, e.g., UV–vis and fluorescence.[5–7] Although emission efficiency of phenylenediamines is not high,[8] some structural modification would make it possible to attain higher fluorescence quantum yield.

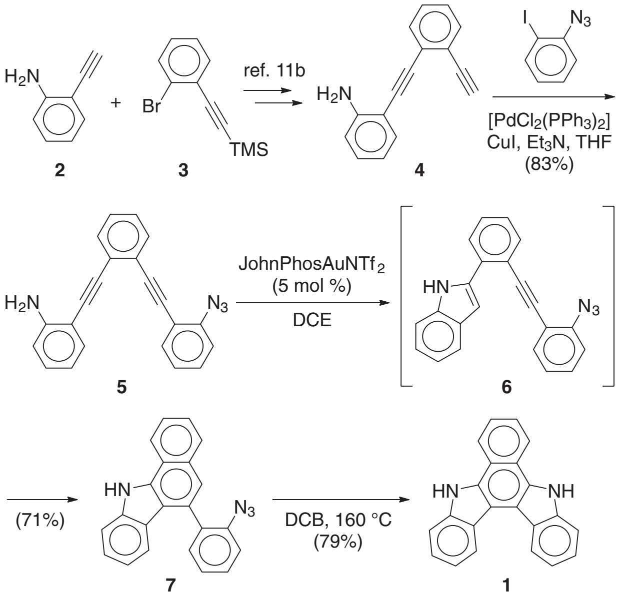
By considering that the benzannulated polycyclic amines are highly fluorescent, as well demonstrated by carbazoles,[9] we designed here 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (BIC **1**), in which three benzene nuclei are attached to 1,4-phenylenediamine moiety, as shown in Scheme 2. The central point of this design is that the newly attached Clar's sextets would remain intact even after one-electron oxidation, and thus, loss of resonance energy could be minimized upon oxidation of **1**. In this paper, preparation, X-ray structure, and spectral and redox properties are reported along with its electrochromic behavior.



Scheme 1. Redox scheme of 1,4-phenylenediamine.



Scheme 2. Molecular design of benzindolocarbazole (BIC).



Scheme 3. Synthesis of BIC **1** via gold-catalyzed cascade cyclization.

We synthesized BIC **1** by a combination of two reliable strategies for carbazole synthesis (Scheme 3): (1) reaction integration[10] of gold-catalyzed hydroamination of diynylanilines and subsequent hydroarylation developed by our group[11] and (2) intramolecular nitrene insertion by thermal decomposition of 2-azido-1,1′-biphenyls developed by Sapi et al.[12] Thus, the known diynylaniline **4** was prepared by the Sonogashira coupling between 2-ethynylaniline (**2**) and 1-alkynyl-2-bromobenzene **3**, according to our reported procedure.[11b] Introduction of the azidobenzene moiety to **4** was carried out by the second Sonogashira coupling to give the cyclization precursor **5**,[13] which was subjected to the gold-catalyzed integrated reaction. As we expected, treatment of **5** with JohnPhosAuNTf$_2$ (5 mol %) in 1,2-dichloroethane (DCE) gave benzocarbazole **7**[13] bearing an azido group in 71% yield. Finally, exposure of **7** to the nitrene insertion conditions at 160 °C in dichlorobenzene (DCB) provided the target compound **1**[13] in 79% yield.

An X-ray analysis of **1** was conducted to reveal the structural feature of benzo[*a*]indolo[2,3-*c*]carbazole skeleton, which is a less explored heterocyclic system. BIC **1** crystallizes in the orthorhombic space group of *Fdd*2 ($Z = 16$).[15,16] As

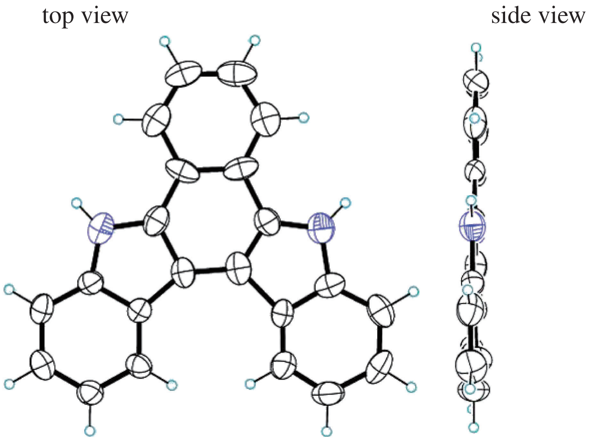


Figure 1. Two views of ORTEP drawings of **1** determined by an X-ray analysis measured at 173 K.

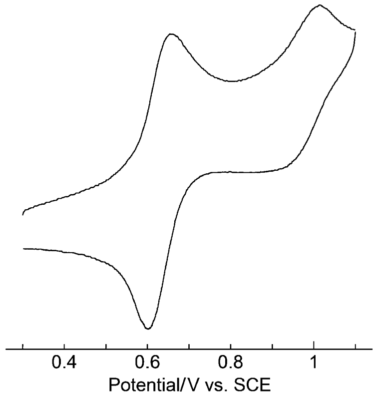
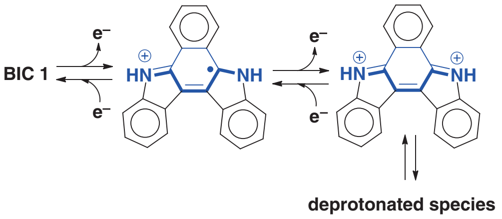


Figure 2. Cyclic voltammogram of **1** measured in MeCN (0.1 M Et_4NClO_4, E/V vs. SCE, Pt electrode, 100 mV s^{-1}).



Scheme 4. Redox scheme of BIC **1**.

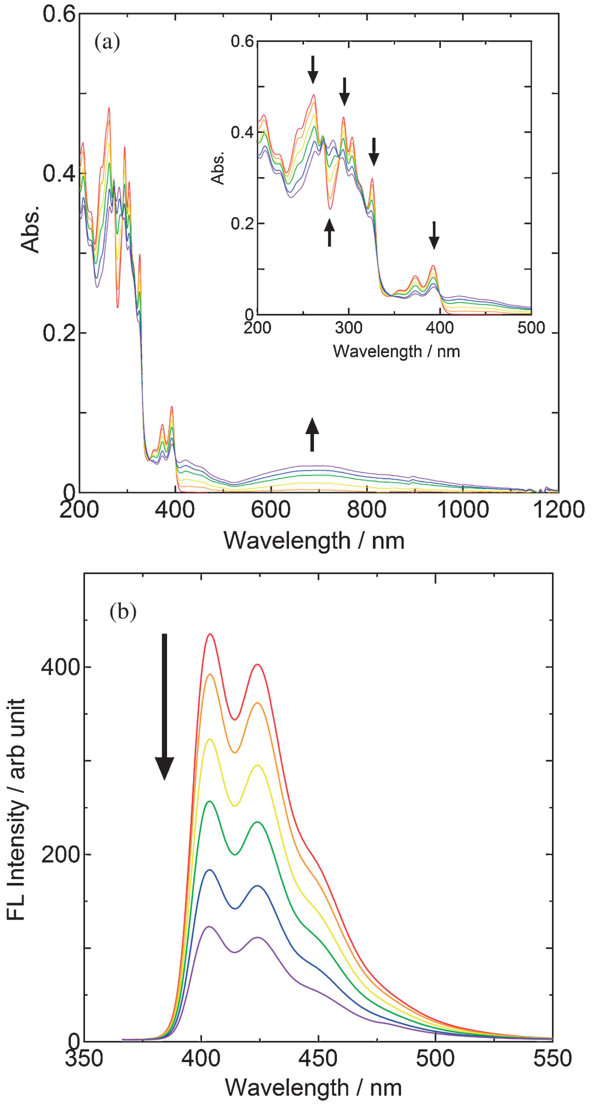


Figure 3. Continuous changes in (a) UV–vis–NIR and (b) fluorescence spectra upon constant current electrochemical oxidation of **1** (1.1×10^{-5} M) in MeCN containing 0.05 M Et_4NClO_4 (20 µA, every 60 s).

shown in Figure 1, it adopts a planar geometry, despite a closer contact between the two hydrogen atoms at C1 and C14 (1.96 Å) than the sum of vdW radii for H···H (2.4 Å).[17] This planar disk-shaped molecule has an approximate atom-to-atom diameter of 10.5 Å, which is arranged in a one-dimensional columnar stack along the *c* axis (dihedral angle 0°; interplanar distance: 3.36 Å) (sum of vdW radii for C···C: 3.40 Å).[17] The columns are further packed in a herring-bone manner exhibiting several (N–H···π)-type (2.51 and 2.88 Å) and (C–H···π)-type (2.78 and 2.89 Å) contacts (Figures S1 and S2).[14]

Adoption of the planar molecular geometry in solution was suggested by the UV spectrum of **1** that shows vibrational structures (Figures S3 and S4).[14] The fluorescence spectrum (λ_{em} = 403, 424, and 447sh nm) resembles the mirror image of the absorption of the first band [λ_{max} ($\log \varepsilon$) = 393 (3.99), 373 (3.89), and 357 (3.69) nm], indicating that the vibrational energy level spacing is similar for the ground and excited states in **1**. Noteworthy is a very high fluorescence quantum yield of **1** ($\Phi_F = 0.91$),[18] so that the desired emission efficiency was successfully attained by our molecular design.

According to the voltammetric analysis in MeCN,[19] **1** undergoes two-stage one-electron oxidation. Comparisons of the peak heights suggested that the second process (E_2^{ox} +0.98 V) involving the dication is quasi-reversible whereas the first process is completely reversible (E_1^{ox} +0.63 V vs. SCE) (Figure 2). Such a behavior can be best accounted for by partial deprotonation from dication $\mathbf{1}^{2+}$ (Scheme 4). It is interesting to find that $\mathbf{1}^{\bullet+}$ was stable under the conditions employed, which prompted us to examine the electrochromic behavior of **1**.

Upon electrochemical oxidation in MeCN, clean conversion of **1** was observed with several isosbestic points (Figure 3a). Thus, the intensity of the UV bands decreased with a concomitant appearance of a new broad absorption in the longer-wavelength region ($\lambda_{max} = $ ca. 700 nm) with an absorption tail extended to 1200 nm. Based on the two-stage one-electron oxidation process of **1** in the voltammogram as well as development of the low-energy absorption band in the NIR region, the observed chromism must be due to the conversion between **1** and **1**$^{\bullet+}$, although the cation radical was too labile to be isolated as salts.[20] When the same electrolysis was followed by fluorescence spectrum, a continuous decrease in emission intensity was observed (Figure 3b), showing that the present heterocycle can serve as a novel two-way-output response system. Further studies are now in progress on the highly fluorescent BIC **1** and its derivatives.[21,22]

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13 Experimental detail and ^{1}H and ^{13}C spectral data are given in Supporting Information (ref 14).

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

15 Crystal data of **1**: MF $C_{22}H_{14}N_2$, FW 306.37, orthorhombic *Fdd*2 (No. 43), $a = 20.059(7)$, $b = 57.22(2)$, $c = 5.037(2)$ Å, $V = 6091(4)$ Å^3, $\rho(Z = 16) = 1.336\,g\,cm^{-3}$, $T = 173$ K, $R = 10.11\%$. CCDC: 932782.

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19 Cyclic voltammetry was conducted in MeCN containing 0.1 M Et_4NClO_4 as a supporting electrolyte (E/V vs. SCE, Pt electrode, scan rate $100\,mV\,s^{-1}$). Ferrocene undergoes one-electron oxidation at +0.38 V under the similar conditions.

20 A preliminary study on 5,10-dialkylated derivative of **1** allowed us to isolate its cation radical salt, whose spectrum resembles that of the oxidized state of **1** in Figure 3a.

21 Indolo[2,3-*c*]carbazole, a structurally related heterocycle to BIC **1**, was first synthesized in 1997 (ref 22), yet its spectral and redox properties have not been reported so far.

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