Wurster's Blue-type Cation Radicals Framed in a 5,10-Dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (BIC) Skeleton: Dual Electrochromism with Drastic Changes in UV/Vis/NIR and Fluorescence

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Abstract: Electron-donating dihydrobenzindolocarbazoles (BICs) **1a–c**, which adopt planar disk-shaped geometries, were prepared by gold(I)-catalyzed cyclization as a key step. Due to the presence of a 1,4-phenylenediamine (PD) moiety in the framework, they undergo reversible one-electron oxidation to the corresponding Wurster's Blue (WB)-type species that exhibits NIR absorptions up to $\lambda = 1200$ nm. In the case of the N,N'-dimethyl derivative, cation radical $1c^{+}$ is stable enough to be isolated as a salt and Xray analysis indicated paraquinoid-type bond alternation in the WB core unit, whereas the bond lengths in the pe-

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ripheral benzene rings are identical to those in the neutral donor. Upon electrochemical interconversion, the redox pairs of **1a–c** and **1a–c⁺⁻** exhibited an electrochromic response in the UV/Vis/ NIR region, which was accompanied by a drastic change in the fluorescence spectrum because only neutral donors **1a–c** are highly emissive (Φ_F : 0.7–0.8).

Introduction

Wurster's Blue and its derivatives (WBs) are robust cation radicals.^[1] They can be easily generated upon one-electron oxidation of 1,4-phenylenediamines (PDs) and isolated as stable salts (Scheme 1). Based on their reversible redox interconversion, PD/WB pairs can serve as promising electrochromic materials,^[2] by which electrochemical input can be



Scheme 1. Redox scheme for *N*,*N*,*N*'-tetramethyl-1,4-phenylenediamine (TMPD) and Wurster's Blue (WB).

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transduced into UV/Vis spectral output.^[3] During the course of our study^[4] of advanced molecular response systems,^[5,6] we became interested in dual electrochromic systems, in which an electrochemical input causes two kinds of spectral changes, for example, UV/Vis and fluorescence (FL).^[6–8] In general, cation radicals, including WB, show redshifted UV/ Vis absorption and their excited states undergo nonradiative decay more easily than the corresponding neutral electron donors. Thus, highly emissive PDs could be promising candidates for realizing the on/off switching of FL accompanied by a color change. Although PDs do not exhibit high emission efficiency,^[9] proper structural modification, such as benzannulation, should increase the FL quantum yield ($\Phi_{\rm F}$) due to the presence of a carbazole skeleton.^[10]

These are the central points for our design of 5,10dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (BIC)^[11] as a novel polycyclic PD derivative with a disk-shaped geometry, in which three benzene nuclei are attached to the PD core, as shown in Scheme 2. The method for annulation was designed so that the newly attached Clar's sextets would remain intact even when a WB-type unit was generated in the center of the framework.



Scheme 2. Molecular design of benzindolocarbazole (BIC).

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In this way, the loss of resonance energy upon oxidation could be minimized, whereas the charge and spin of BIC⁺ are allowed to delocalize over the peripheral benzene rings. Herein, we report the preparation, X-ray structure, and spectral and redox properties of the parent BIC $(1a)^{[13]}$ and its *N*-methyl (1b) and *N*,*N'*-dimethyl derivatives (1c). We achieved dual electrochromic behavior including FL, and changes in absorption occurred not only in the UV/Vis region but also in the NIR region up to $\lambda = 1200$ nm. Furthermore, X-ray analysis of the isolated $1c^{+}$ salt revealed paraquinoid-type bond alternation characteristic of WB.

Results and Discussion

Synthetic Strategy for the Parent BIC (1a) and its *N*-Methylated Derivatives (1b,c)

BIC **1a** was first prepared by a combination of two reliable strategies for carbazole synthesis (Scheme 3): 1) reaction integration^[15] of the gold-catalyzed hydroamination of diynylanilines and subsequent hydroarylation developed by our group,^[16] and 2) intramolecular nitrene insertion by the thermal decomposition of 2-azido-1,1'-biphenyls developed by Sapi et al.^[17]

Thus, the introduction of an azidobenzene moiety to known diynylaniline $2^{[16b]}$ was carried out by a Sonogashira



Scheme 3. Synthesis of BIC $1 a\mbox{-} c$ through a gold-catalyzed cascade cyclization.

coupling with 2-iodophenylazide to give cyclization precursor **3**, which was subjected to the gold-catalyzed integrated reaction. As expected, treatment of **3** with JohnPhosAuNTf₂ (5 mol%) in 1,2-dichloroethane (DCE) gave benzocarbazole **5** bearing an azido group in 71% yield. Finally, exposure of **5** to the nitrene insertion conditions at 160°C in 1,2-dichlorobenzene (DCB) provided parent BIC **1a** in 79% yield.^[14] Azide **5** is also a useful synthon for *N*-alkylated BICs. Thus, treatment of **5** with NaH/MeI in DMF followed by heating exclusively gave monomethylated derivative **1b** in 88% yield, which was then effectively converted to dimethylated derivative **1c** (66% over three steps from **5**).

Because we assumed that the cascade cyclization of **3** to **5** proceeded via indole intermediate **4**, another route was examined as shown in Scheme 4. Thus, 2-(2'-ethynylphenyl)in-



Scheme 4. Alternative route to azide intermediate 5.

dole **7** was prepared in 69% yield by a Sonogashira coupling of 2-(2'-bromophenyl)indole **6** and ethynyltrimethylsilane, followed by desilylation. The second Sonogashira coupling of **7** with 2-iodophenylazide gave **4** in 53% yield. Hydroarylation of **4** proceeded smoothly upon treatment with John-PhosAuNTf₂ (2.5 mol%) in DCB to give **5** in 94% yield. This route is advantageous in terms of easier access to starting material **6**, which was obtained by the reaction of phenylhydrazine and 2-bromoacetophenone.^[18]

Redox Properties of BICs and Isolation of Cation Radical of *N*,*N*'-Dimethyl Derivative 1c

According to the results of voltammetric analyses in MeCN, parent BIC **1a** undergoes a two-stage one-electron oxidation $(E_1^{\text{ox}} + 0.63 \text{ V}, E_2^{\text{ox}} + 0.98 \text{ V} \text{ vs. SCE}),^{[19]}$ as in the case of PDs. The slightly higher donating properties of *N*-methylated derivatives **1b** and **1c** are indicated by the less positive E_1^{ox} values (+0.60 V for **1b** and +0.59 V for **1c**, respectively).^[19] The electron-donating abilities of **1a–c** are weaker than those of *N*,*N*,*N'*,*N'*-tetramethyl-PD (TMPD) (E_1^{ox} +0.10 V)^[19] and *N*,*N*,*N'*,*N'*-tetramethylbenzidine (+ 0.41 V),^[19] but much stronger than that of *N*-methylcarbazole (+1.12 V, irreversible).^[19]

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Figure 1. Cyclic voltammograms of a) **1a** and b) **1c** measured in MeCN ($0.1 \text{ M} \text{ Et}_4 \text{NCIO}_4$, Pt electrode, scan rate 0.1 Vs^{-1} ; see also Figure S4 in the Supporting Information). The dotted line in a) shows the voltammogram returned at +0.8 V



Scheme 5. Redox scheme of BICs 1a-c.

Comparisons of the peak heights suggested that the second oxidation of 1a involving the dication is quasi-reversible, whereas the first oxidation is completely reversible (Figure 1a). Quite similar behavior was observed for monomethylated 1b. Such behavior can be best accounted for by partial deprotonation from dications $1a_{,b}^{2+}$ (Scheme 5). In contrast, N,N-dimethylated 1c exhibited a perfectly reversible voltammogram (Figure 1b), which shows that the oxidized states could be made infinitely stable by double N-alkylation of the BIC framework. In fact, upon treatment of 1c with one equivalent of $(4-BrC_6H_4)_3N^+X^-$ (X=BF₄ or SbCl₆), cation radical salts $1c^{+}X^{-}$ were isolated as stable blue-green solids. The ESR spectrum of $1c^+BF_4^-$ in degassed MeCN showed multiple well-resolved lines (g =2.0030) (Figure 2). The hyperfine coupling constants were deduced by using the Winsim program,^[20] as follows: $a_N =$ 3.91 G (2N); $a_{\rm H}$ = 3.27 (6H), 1.27 (2H), 1.27 (2H), 1.07 (2H), 0.62 (2H), 0.29 (2H), 0.28 G (2H). Comparisons of these values with those of WB (g=2.0031, $a_N=6.99$ G (2N); $a_{\rm H} = 6.76 \ (12 \, {\rm H}), \ 1.97 \, {\rm G} \ (4 \, {\rm H}))^{[1d]}$ clearly show that $1 \, {\rm c}^{+ \cdot}$ is basically a WB-type species. The smaller a_N value in $1c^{+}$ indicates that the unpaired electron is partially delocalized over the fused benzene rings in BIC+. The calculated spin density distribution (UB3LYP/6-31G*) also supports the above explanation (Figure 3).



Figure 2. a) The X-band ESR spectrum of $1c^{+}BF_4^{-}$ in degassed MeCN at 298 K and b) its simulated spectrum.



Figure 3. a) Spin density and b) SOMO of 1c⁺⁻ calculated by using a DFT method (UB3LYP/6-31G*).

X-ray Analyses of BICs and the Cation Radical of *N*,*N*'-Dimethyl Derivative 1 c

X-ray analyses of BICs **1a–c** were conducted to reveal the structural features of the benzo[*a*]indolo[2,3-*c*]carbazole skeleton, which is a less-explored heterocyclic system.^[11] As shown in Figure S1 in the Supporting Information, **1a**^[21] adopts a planar geometry despite closer contact (1.96 Å) between the two hydrogen atoms at C1 and C14 than the sum of the van der Waals (vdW) radii for H–H (2.4 Å)^[22] in the bay region of the BIC framework. This planar disk-shaped molecule has an approximate atom-to-atom diameter of 10.5 Å.

Similar planar disk-shaped geometries were observed in *N*-methylated derivatives **1b**,**c** (Figure 4a and Figure S1 in the Supporting Information).^[21] Although there are short interatomic contacts between the methyl group on N and the sp2 carbon (C6 or C9) on the fused benzene ring (3.08-3.11 Å; sum of vdW radii for C_{Me}-C_{Ar}: 3.70 Å),^[22] these molecules partly relieve the steric repulsion by in-plane deformation of the N-methylpyrrole unit. Thus, the methyl groups are relocated in the direction opposite C6 (or C9). As a result, one of the two external bond angles around the nitrogen ($< C_{Me}$ -N-C_a) is much larger (129.4(1)-128.8(1)°) than the other (122.4(1)-121.9(1)°; see Figure S2 in the Supporting Information). A similar in-plane deformation was previously observed in structurally related N-methylbenzo[a]carbazoles that also adopt planar geometries despite the short C_{Me} - C_{Ar} contacts (3.14, 3.17 Å).^[23]

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Figure 4. ORTEP drawings of a) 1c and b) $1c^{+}$ in $1c^{+}BF_{4}^{-}$ salt as determined from X-ray structural analyses at 123 K. The thermal ellipsoids are shown at the 50% probability level.

After many attempts, we succeeded in growing a singlecrystal sample of $1c^{+}BF_4^{-}$ from DMSO/benzene, which contains an equivalent of benzene molecules in the crystal lattice.^[21] The disk-shaped open-shell species also adopts a planar geometry^[24] with pseudo-C2 symmetry within the experimental error (Figure 4b). Comparisons of the bond lengths in 1c and $1c^{+}$ clearly show that a considerable bond alternation is induced upon one-electron oxidation of 1c to form a paraquinoid-type conjugation in the central hexagon in $1c^{+}$ (Table 1). Thus, bonds *a* and *c* (*c'*) are shortened whereas bonds *b* (*b'*) and *d* (*d'*) are elongated. In contrast, the bond lengths in the perpheral benzene rings remain un-

altered (Figure S2 in the Supporting Information). This observation is consistent with our molecular design for novel WB-type species with an extended π system.

Spectral Properties of BICs and the Cation Radical of *N*,*N*'-Dimethyl Derivative 1 c

BICs 1a-c show strong absorption bands only in the UV region (Figure 5a). The vibrational structures are consistent with the expected planarity and rigidity of the disk-shaped BIC skeleton in solution. The slight redshift for N-methylated derivatives 1b,c can be rationalized by their higher HOMOs compared with that in **1a** (Table 2). The fluorescence spectra of 1ac resemble mirror images of the absorption of the first bands (Figure 5b), which indicates that the vibrational energy level spacing is similar for the ground and excited states in 1a-c. They show very high fluoTable 1. Comparisons of bond lengths in 1c and $1c^{+}$ in $1c^{+}BF_{4}^{-}$ salt determined by X-ray structural analyses at 123 K.

bond	1c [Å]	1c+· [Å]	$\Delta d [\text{\AA}]$
а	1.429(2)	1.358(7)	-0.071
b, b'	1.404(2), 1.398(2)	1.450(4), 1.441(4)	+0.045
c, c'	1.391(2), 1.395(2)	1.356(6), 1.354(6)	-0.038
d, d'	1.370(2), 1.379(2)	1.412(5), 1.396(4)	+0.030

Table 2. UV/Vis and FL spectral data of 1a-c along with UV/Vis/NIR spectral data of $1c^+BF_4^-$ measured in MeCN at 298 K.

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	$\lambda_{abs} [nm]$	$\varepsilon [\mathrm{M}^{-1} \mathrm{cm}^{-1}]$	$\lambda_{em}^{[b]}$ [nm]	$arPsi_{ ext{F}}^{[ext{c}]}$
1a	393 ^[a]	9900	403	0.73
1b	401 ^[a]	9900	412	0.78
1c	408 ^[a]	9600	420	0.71
1c+·BF ₄ -	435, 702	6800, 6300		

[a] The wavelengths for the longest absorption peaks are given. [b] Excitation wavelength was $\lambda = 360$ nm. [c] Fluorescence quantum yields were determined by using 9,10-diphenylanthracene as an external standard.

rescence quantum yields ($\Phi_{\rm F}$: 0.7–0.8)^[26] and our molecular design achieved the desired emission efficiency.

In contrast, cation radical salt $1c^{+}$ is not fluorescent at all.^[27] Instead, it exhibits a broad absorption band in the NIR region ($\lambda_{max} = 702 \text{ nm}$; log $\varepsilon = 3.80$) with an absorption tail that extends to $\lambda = 1200 \text{ nm}$ (Figure 5c), which is assigna-



Figure 5. a) UV/Vis and b) FL spectra of 1a-c measured in MeCN at 298 K. c) UV/Vis/NIR spectrum of $1c^+BF_4^-$ in MeCN.

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ble to the HOMO–SOMO transition. This band is redshifted by $\lambda \approx 150$ nm compared with that in WB ($\lambda = 566$ nm; $\log \epsilon = 4.11$),^[28] which can be rationalized by the narrower HOMO–HOMO–1 gap due to tribenzannulation in BIC **1c** than in TMPD. The lack of decay of absorptions of **1c⁺⁻** indicates that this WB-type cation radical is infinitely stable even in an aerated solution.

Dual Electrochromism of BICs and their Cation Radicals that Exhibit a UV/Vis/NIR and FL Response

The sharp contrast in the spectral properties of redox pair $1c/1c^{+}$ prompted us to examine its electrochromic behavior by following the redox reactions in situ. Upon electrochemical oxidation in MeCN, the clean conversion of 1c was reflected by the UV/Vis/NIR spectrum, which showed several isosbestic points (Figure 6a). Thus, the intensity of the UV bands decreased with a concomitant appearance of new broad signals in the Vis/NIR region up to $\lambda = 1200$ nm. The final spectrum was identical to that of the isolated salt of $1c^{+}$. When the same electrolysis was followed by monitoring the fluorescence spectrum, a continuous decrease in emission intensity was observed (Figure 6b), which demonstrated dual electrochromic behavior.

The reversibility of chromism was confirmed by electrochemical reduction of as-prepared $1c^+$ by switching the po-



Figure 6. Continuous changes in a) UV/Vis/NIR and b) FL spectra upon constant-current electrochemical oxidation (20 μ A, every 2 min) in MeCN that contained 0.05 M Et₄NClO₄ as the electrolyte. Continuous changes in c) UV/Vis/NIR and d) FL spectra upon constant-current electrochemical reduction of as-prepared **1c⁺⁺** to **1c** (10 μ A, every 2 min).

larity of the electrodes (Figure 6c, d). A similar two-wayoutput response was observed with electrolysis of parent BIC **1a** (Figure S3 in the Supporting Information).^[14] However, due to the insufficient stability of oxidized states with acidic N–H groups, prolonged electrolysis of **1a** caused incomplete reversibility of the spectral changes.

Conclusion

The present work demonstrates that the newly designed molecular framework of BIC 1 is the π -extended analogue of PD, but exhibits high FL efficiencies ($\Phi_{\rm F}$: 0.7–0.8) regardless of the presence/absence of an alkyl group on the nitrogen atoms. Thus, this could be used as a unique platform for constructing new molecular response systems that exhibit changes in both absorption and FL spectra. The electrochromic behavior in the NIR region is particularly worthy of note and should attract much attention for potential use in optical electrocommunication networks.[29] Hitherto, heterocycle-based polymers^[30] or metal complexes^[31] have been considered to be promising candidates for NIR chromism and only a limited number of purely organic monomeric materials have been reported.^[32] Studies of BIC and related systems^[11] are now in progress to better understand their potential for use as novel chromic materials.

> CCDC-982170 (1c), -982171 (1c⁺·BF₄⁻·benzene), and -982172 (1b·AcOEt) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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were done at the Center for Instrumental Analysis of Hokkaido University. Mass spectra were measured by Dr. Eri Fukushi at the GC-MS & NMR Laboratory (Faculty of Agriculture, Hokkaido University).

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FULL PAPER

Potential for change: Both UV/Vis/ NIR and fluorescence can be reversibly modified by application of electric potential to the highly fluorescent π extended *p*-phenylenediamines with disk-shaped geometries to form stable cation radical species (see figure).



Electrochromism

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Wurster's Blue-type Cation Radicals Framed in a 5,10-Dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (BIC) Skeleton: Dual Electrochromism with Drastic Changes in UV/Vis/NIR and Fluorescence

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