Synthesis, Optical and Electrochemical Properties of Benzofuro[2,3-c]carbazoloquinol Fluorescent Dyes

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ABSTRACT

Benzofuro[2,3-c]carbazoloquinol derivatives, a new type of fluorescent dyes, were derived from the corresponding quinone, and their optical and electrochemical properties were investigated by photoabsorption and fluorescence spectroscopy, cyclic voltammetry (CV) and density functional theory (DFT) calculation. The quinol derivatives in 1,4-dioxane showed the photoabsorption band at around 435 nm (molar extinction coefficient ($\varepsilon_{\text{max}}$) = ca. 6000–8000 M$^{-1}$ cm$^{-1}$) and the fluorescence band at around 520 nm (fluorescence quantum yield ($\Phi_{\text{fl}}$) = 0.24–0.28). The CV demonstrated that the quinol derivatives exhibit an irreversible oxidation wave at around 0.28 V versus Fc/Fc$^+$. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the quinol derivatives which were calculated using DFT at the B3LYP/6-31G(d,p) level are in good agreement with the experimental results.

Key word: Benzofuro[2,3-c]carbazoloquinol; Photoabsorption; Fluorescence; Redox
1. Introduction

Organic fluorescent dyes have gained more and more attention as one of promising functional dyes to be applied to sensors for target species and probes for bioimaging, as well as emitters for optoelectronic devices such as organic light-emitting diodes (OLEDs).\textsuperscript{1–5} In general, conventional fluorophores such as perylene, xanthene, cyanine, coumarin, and BODIPY skeletons have been modified by introducing various substituents or fusing aromatic ring to function as the desired sensors, probes or emitters for precision applications.\textsuperscript{6–10} On the other hand, the development of new type of fluorophores can create new applications, as well as leading to dramatic improvement in fluorescence sensing and imaging and device performances. Thus, for this purpose, we have developed benzofuro[2,3-c]carbazoloquinone BfCzQ-1 as a useful intermediate which allows us to create various kinds of fluorophores (Fig. 1).\textsuperscript{11} Actually, we demonstrated that the quinone BfCzQ-1 was allowed to react with the arylaldehydes to give the donor–π–acceptor (D–π–A) structural isomers of benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type and benzofuro[2,3-c]oxazolo[5,4-a]carbazole-type fluorescent dyes, under the condition using ammonium acetate.\textsuperscript{12–15} In this work, a new type of fluorescent dyes, benzofuro[2,3-c]carbazoloquinol derivatives (YK-1 and YK-2) were designed and developed from the quinone BfCzQ-1. Herein we report synthesis of the quinol-type fluorescent dyes and their optical and electrochemical properties based on photoabsorption and fluorescence spectroscopy, cyclic voltammetry (CV), and density functional theory (DFT) calculation.

2. Experimental
2.1. General

$^{1}$H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. Cyclic voltammograms were recorded in acetonitrile/Et$_4$NClO$_4$ (0.1 M) solution with a three-electrode system consisting of Ag/Ag$^+$ as reference electrode, Pt plate as working electrode, and Pt wire as counter electrode, by using a Hokuto Denko HAB-151 potentiostat equipped with a functional generator. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral). Photoabsorption spectra were observed with a Shimadzu UV-3150 spectrophotometer, and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields ($\Phi_n$) were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system ($\lambda^{ex} = 325$ nm).

2.2. Synthesis

General synthetic procedure for YK-1 and YK-2: To a THF solution of BfCzQ-1 under an Ar atmosphere was added ethereal solution of organolithium (2.5 equivalent BuLi or PhLi) at $-108$ °C over 15 min. After stirring for 15 min at room temperature, the reaction was quenched with saturated NH$_4$Cl solution. The solvent was evaporated, and the residue was extracted with CH$_2$Cl$_2$. The organic extract was washed with water. The CH$_2$Cl$_2$ extract was evaporated, and the residue was chromatographed on silica gel (CH$_2$Cl$_2$ : AcOEt = 3 : 1 as eluent) to give YK-1 or YK-2 with recovery
(25% or 34%) of quinone BfCzQ-1.

7-Butyl-3-(dibutylamino)-7-hydroxy-7,8-dihydro-6H-benzofuro[2,3-c]carbazol-6-one (YK-1):
Yield 7%. FT-IR (ATR): $\tilde{\nu} = 3263, 1598 \text{ cm}^{-1}$; $^1\text{H NMR (400 MHz, CDCl}_3$: $\delta = 0.74–1.66$ (m, 23H), 3.38–3.42 (t, 4H), 6.69 (s, 1H), 6.86 (d, $J = 7.2 \text{ Hz}$, 1H), 7.29 (m, 2H), 7.47–7.52 (m, 1H), 8.18–8.20 (m, 2H), 8.94 (s, -NH) ppm.

3-(Dibutylamino)-7-hydroxy-7-phenyl-7,8-dihydro-6H-benzofuro[2,3-c]carbazol-6-one (YK-2).
Yield 9%. FT-IR (ATR): $\tilde{\nu} = 3391, 1607 \text{ cm}^{-1}$; $^1\text{H NMR (400 MHz, acetone-}d_6$: $\delta = 1.00$ (6H, t), 1.42–1.48 (m, 4H), 1.66–1.74 (m, 4H), 3.51 (t, 4H), 6.75 (d, $J = 2.2 \text{ Hz}$, 1H), 7.05 (dd, $J = 2.2$ and 9.0 Hz, 1H), 7.21–7.31 (m, 5H), 7.45–7.48 (m, 2H), 7.52 (d, $J = 7.6 \text{ Hz}$, 1H), 8.29 (d, $J = 8.5 \text{ Hz}$, 1H), 8.36 (d, $J = 9.3 \text{ Hz}$, 1H), 11.1 (s, -NH) ppm.

3. Results and Discussion

As shown in Scheme 1, the benzofuro[2,3-c]carbazoloquinol YK-1 and YK-2 were obtained by the reaction of the quinone BfCzQ-1 with BuLi and PhLi, respectively, as organolithium reagents (RLi). It is well known that the addition of organometallic reagents to quinones yields not only quinols but also hydroquinones as a by-product, that is, both the 1,2-addition and the reduction of the quinoid skeleton by organometallic reagents proceed competitively.\(^{16-18}\) For the reduction of the quinoid skeleton in this case, the corresponding hydroquinone BfCzHQ-1 was produced in situ but was readily reoxidized by atmospheric oxygen during work-up of the reaction mixture, resulting in recovery of the starting quinone BfCzQ-1. On the other hand, for the 1,2-addition of the
organolithium reagents to the quinone BfCzQ-1, the counter anions (R−) preferentially attack the 7-carbonyl carbon than the 6-carbonyl in spite of the similar steric hindrance of the two carbonyls, leading to the production of 7-R-7-hydroxy derivatives YK-1 and YK-2. The fact indicates that the conjugated linkage of the electron-donating dibutylamino group to the 6-carbonyl group makes the 6-carbonyl carbon less electrophilic than the 7-carbonyl carbon. As a result, this 1,2-addition produces the quinols YK-1 and YK-2 because the counter anions (R−) preferentially attack the relatively electrophilic 7-carbonyl carbon of BfCzQ-1.19

The photoabsorption and fluorescence spectra of BfCzQ-1, YK-1, and YK-2 in 1,4-dioxane are shown in Fig. 2, and their optical data are summarized in Table 1. The photoabsorption spectra demonstrated that BfCzQ-1, YK-1, and YK-2 show two photoabsorption bands (photoabsorption maximum wavelength (λmax(abs) = 400 nm and 482 nm for BfCzQ-1, λmax(abs) = 396 nm and 437 nm for YK-1, and λmax(abs) = 401 nm and 435 nm for YK-2) with moderate molar extinction coefficients (εmax = 7400 M−1 cm−1 and 10800 M−1 cm−1 for BfCzQ-1, 14300 M−1 cm−1 and 5900 M−1 cm−1 for YK-1, and 17100 M−1 cm−1 and 8400 M−1 cm−1 for YK-2, respectively) in the range from 350 nm to 550 nm, which are assigned to the π-π* transition on the benzofuro[2,3-c]carbazoloquinone skeleton for BfCzQ-1 and the benzofuro[2,3-c]carbazoloquinol skeleton containing the dibutylamino group for YK-1 and YK-2, respectively. In addition, BfCzQ-1 showed a feeble and broad photoabsorption band (λmax(abs) = 613 nm, εmax = 2200 M−1 cm−1) in the range of 600 nm to 800 nm, which is assigned to the n-π* transitions on the quinone skeleton, that is, the carbonyl groups. In the corresponding fluorescence spectra, YK-1 and YK-2 exhibit a fluorescence band with a fluorescence maximum
wavelength ($\lambda_{\text{max}}$) of 516 nm and 523 nm, respectively, in the range of 450 nm to 650 nm. Thus, this result clearly indicates that due to the non-conjugated linkage of the substituents ($R = \text{Bu}$ and Ph) to the chromophore skeleton, the photoabsorption and fluorescence spectra of YK-1 and YK-2 resemble very well each other. Consequently, it was found that the effect of the substituents at the 7-position on the optical properties of the benzofuro[2,3-$c$]carbazoloquinol derivatives is negligible. Moreover, the fluorescence quantum yields ($\Phi_{\text{fl}}$) of YK-1 and YK-2 are 0.28 and 0.24, respectively, indicating moderate fluorescence properties. However, BfCzQ-1 did not show any observable fluorescence band. The significant fluorescence quenching of BfCzQ-1 is attributed to the promoted intersystem crossing (ISC) from singlet to triplet excited states by the two carbonyl groups in the conjugated $\pi$-system, as explained by El-Sayed’s rule.$^{20,21}$ On the other hand, YK-1 and YK-2 having one carbonyl group in the partially disconnected $\pi$-conjugated system may cause the relaxation of El-Sayed’s rule, resulting in the fluorescence emission.

The electrochemical properties of YK-1 and YK-2 were investigated by CV in acetonitrile containing 0.1 M tetraethylammonium perchlorate ($\text{Et}_4\text{NClO}_4$). The potentials were internally referenced to ferrocene/ferrocenium (Fc/Fc$^+$). The cyclic voltammograms of YK-1 and YK-2 are shown in Fig. 3, and their electrochemical data and the HOMO and LUMO energy levels are summarized in Table 2. YK-1 and YK-2 showed an irreversible oxidation at $-0.29$ V and $-0.28$ V, respectively, while any obvious reduction wave did not appear within the potential window. The HOMO energy levels ($-[E_{\text{onset}}^{\text{ox}} + 4.8]$ eV) versus vacuum level were estimated from the onset potentials ($E_{\text{onset}}^{\text{ox}} = -0.40$ V for YK-1 and $-0.39$ V for YK-2) of the oxidation waves, and the LUMO
energy levels were estimated from the $E_{\text{onset}}^{\text{ox}}$ and intersections (optical energy gap: $E_g^{\text{opt}} = 2.58$ eV for YK-1 and 2.55 eV for YK-2) of the photoabsorption and fluorescence spectra in 1,4-dioxane. Thus, the HOMO and LUMO energy levels were $-4.40$ eV and $-1.82$ eV for YK-1 and $-4.41$ eV and $-1.86$ eV for YK-2, respectively. Consequently, the HOMO and LUMO energy levels of YK-1 and YK-2 resemble very well each other, indicating that the effect of the substituents (R) at the 7-position on the electrochemical properties of the benzofuro[2,3-c]carbazoloquinol derivatives is negligible.

The optical and electrochemical properties of the benzofuro[2,3-c]carbazoloquinol derivatives YK-1 and YK-2 were analyzed using DFT and time-dependent DFT (TD-DFT) at the B3LYP/6-31G(d,p) level. The TD-DFT calculations indicated that for the lowest $S_0 \rightarrow S_1$ transition, the calculated $\lambda^{\text{abs-calcd}}$ are 377 nm and 430 nm for YK-1 and 382 nm and 437 nm for YK-2, which are mainly attributed to the transitions from the HOMO–1 to the LUMO (64% for YK-1 and 65% for YK-2) and the HOMO to the LUMO (65% for YK-1 and 66% for YK-2), respectively (Table 3). The corresponding oscillator strength ($f$) values are 0.47 and 0.07 for YK-1 and 0.46 and 0.08 for YK-2. For both YK-1 and YK-2, the HOMO are localized over the whole $\pi$-conjugated system, that is, 3-amino-benzofuro[2,3-c]carbazol-6-one skeleton, whereas the HOMO–1 are delocalized on the benzofuran and indole moieties. On the other hand, the LUMO are localized on the dibenzofuran-6-one moiety (Fig. 4). The calculated HOMO and LUMO energy levels were $-4.99$ eV and $-1.75$ eV for YK-1 and $-4.96$ eV and $-1.78$ eV for YK-2, respectively (Table 3). Thus, there are little difference in the calculated HOMO and LUMO energy levels between YK-1 and YK-2, resulting in the similar $E_g^{\text{calcd}}$ values ($3.24$ eV for YK-1 and $3.18$ eV for YK-2) to each other. Moreover, the DFT
calculations revealed that the HOMO and LUMO energy levels of \textbf{YK-1} and \textbf{YK-2} are higher than that (−5.18 eV and −2.88 eV) of \textbf{BfCzQ-1} (Figure S1). Actually, \textbf{YK-1} and \textbf{YK-2} in the solution are less stable which may lead to the oxidative decomposition due to the higher HOMO energy levels, although \textbf{YK-1} and \textbf{YK-2} are relatively stable in the solid state. Consequently, the DFT calculations are in good agreement with the experimental results from the CV and the photoabsorption and fluorescence spectral analyses.

4. Conclusions

We developed a new type of fluorescent dyes, benzofuro[2,3-\textit{c}]carbazoloquinol fluorophores, from the benzofuro[2,3-\textit{c}]carbazoloquinone chromophore. The optical and electrochemical properties of benzofuro[2,3-\textit{c}]carbazoloquinol fluorophores were successfully revealed by the experimental approach and the DFT calculations. Consequently, this work demonstrated the synthetic method of the novel quinol-type fluorophores from the corresponding quinone chromophore and their optical and electrochemical properties.

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Scheme 1. Synthesis of YK-1 and YK-2.

Figure 1. Chemical structures of BfCzQ-1 and quinol-type fluorophores YK-1 and YK-2.

Figure 2. (a) Photoabsorption spectra of BfCzQ-1, YK-1, and YK-2 in 1,4-dioxane. (b) Fluorescence spectra of YK-1 ($\lambda_{\text{ex}} = 437$ nm) and YK-2 ($\lambda_{\text{ex}} = 435$ nm) in 1,4-dioxane. Inset in (b) shows fluorescence color image (under 365 nm irradiation) of YK-2 in 1,4-dioxane.

Figure 3. Cyclic voltammograms of (a) YK-1 and (b) YK-2 in acetonitrile containing 0.1 M Et$_4$NClO$_4$ at scan rate of 100 mV s$^{-1}$. The arrows denote the direction of the potential scan.

Figure 4. HOMO−1, HOMO, and LUMO of YK-1 and YK-2 in their optimized geometries derived from DFT calculations at the B3LYP/6-31G(d,p) level.
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Table 1. Optical data of BfCzQ-1, YK-1, and YK-2 in 1,4-dioxane

| Dye   | \( \lambda_{\text{max}} \text{abs}/nm (\epsilon_{\text{max}}/M^{-1} \text{cm}^{-1}) \) | \( \lambda_{\text{max}} \text{fl}/nm (\Phi_{\text{fl}}) \) |
|-------|-------------------------------------------------|-----------------|
| BfCzQ-1 | 400 (7400), 482 (10800), 613 (2200)             | 516 (0.28)      |
| YK-1  | 396 (14300), 437 (5900)                          | 523 (0.24)      |
| YK-2  | 401 (17100), 435 (8400)                          | 523 (0.24)      |

*Fluorescence quantum yields (\( \Phi_{\text{fl}} \)) were determined by using a calibrated integrating sphere system (\( \lambda^\circ = 325 \text{ nm} \)). *Too weak.

Table 2. Electrochemical data and HOMO and LUMO energy levels of YK-1 and YK-2

| Dye   | \( E_{\text{onset}}^{\text{ox}}/V \) | \( E_\text{g}^{\text{opt}}/eV \) | HOMO/eV | LUMO/eV |
|-------|-----------------------------------|---------------------------------|---------|---------|
| YK-1  | 0.40                              | 2.58                            | -4.40   | -1.82   |
| YK-2  | 0.39                              | 2.55                            | -4.41   | -1.86   |

*Onset \( (E_{\text{onset}}^{\text{ox}}) \) versus \( \text{Fc/Fc}^+ \) of the oxidation potential. *Optical energy gaps \( (E_\text{g}^{\text{opt}}) \) were determined from the intersections (480 nm for YK-1 and 486 nm for YK-2) of photoabsorption and fluorescence spectra in 1,4-dioxane. *HOMO energy levels \( (-\{E_{\text{onset}}^{\text{ox}} + 4.8 \} \text{ eV}) \) versus vacuum level were estimated from the \( E_{\text{onset}}^{\text{ox}} \) of the oxidation waves. *LUMO energy levels versus vacuum level were estimated from the \( E_\text{g}^{\text{opt}} \).

Table 3. Calculated HOMO and LUMO energy levels, HOMO-LUMO energy gaps, and photoabsorption data of YK-1 and YK-2

| Dye   | HOMO \text{calcd}/eV | HOMO-1 \text{calcd}/eV | LUMO \text{calcd}/eV | \( E_\text{g}^{\text{calcd}}/eV \) | \( \lambda_{\text{abs}}^{\text{calcd}}/\text{nm} \) (f) | Attribution |
|-------|---------------------|------------------------|----------------------|----------------------------|----------------------|----------------|
| YK-1  | -4.99               | -5.46                  | -1.75                | 3.24                       | 377 (0.47)           | H-1 → L (64%) |
|       |                     |                        |                      |                           | 430 (0.07)           | H → L (65%)    |
| YK-2  | -4.96               | -5.46                  | -1.78                | 3.18                       | 382 (0.46)           | H-1 → L (65%) |
|       |                     |                        |                      |                           | 437 (0.08)           | H → L (66%)    |

*HOMO-LUMO energy gap \( (E_\text{g}^{\text{calcd}}) = \text{LUMO}_\text{calcd} - \text{HOMO}_\text{calcd} \). *Oscillator strength. *H = HOMO, L = LUMO.