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Synthesis and Solid-State Fluorescence Properties of Structural Isomers of Novel Benzofuro[2,3-*c*]oxazolocarbazole-Type Fluorescent Dyes

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Structural isomers of novel benzofuro[2,3-*c*]oxazolo[4,5-*a*]-carbazole-type (**3a**) and benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole-type fluorophores (**4a**), which differ in the position of oxygen and nitrogen in the oxazole ring, and their *N*-alkylated (R = butyl, benzyl and 5-nonyl) carbazole derivatives (**3b**–**d** and **4b**–**d**) have been synthesized, and their photophysical properties in solution and in the solid state have been investigated. Considerable differences in the absorption and fluorescence spectra were observed between structural isomers in both states. In solution, the fluorophore **3a** exhibits much stronger absorption and fluorescence intensities than the fluorophore **4a**. However, the two isomeric fluorophores exhibit similar fluorescence intensities in the crystalline state. In solution, the dyes **3a**–**d** and **4a**–**d** exhibited almost the same absorption and fluorescence spectra in each compound series. On the other hand, their solid-state fluorescence excitation and emission spectra were quite different, and a drastic fluorescence enhancement was found to be caused by the *N*-alkylation of the fluorophores; the fluorophores **3d** and **4d** (R = 5-nonyl) with sterically hindered substituents exhibited strong solid-state fluorescence properties. Semi-empirical molecular orbital calculations (AM1 and INDO/S) and solid-state fluorescent spectral analyses have been carried out to elucidate the effects of the substituents and chromophore skeleton on the photophysical properties of the two isomers (**3** and **4**) both in solution and in the crystalline state. On the basis of the results of calculations and the spectral analyses, the relations between the observed photophysical properties and the chemical structures of the benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores are discussed.

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Introduction

Solid-state organic fluorescent dyes have received considerable attention because they are attractive materials not only for fundamental research on solid-state photochemistry,[1] but also for their possible applications in optoelectronics such as organic light-emitting diodes[2] and photoelectric conversion systems.[3] Many studies have been conducted on the correlation between solid-state fluorescence properties and molecular packing structures on the basis of the X-ray diffraction measurements. It has been revealed that strong intermolecular π-π interactions[1d,1e,4,10–13] or continuous intermolecular hydrogen bonding[3b,12] between neighbouring fluorophores is a principal factor of fluorescence quenching in the solid state. Consequently, the key point in designing new strong solid-state emissive fluorophores is to reduce the intermolecular interactions between fluorophores leading to fluorescence quenching. Recently, Yoshida et al. have reported that the introduction of substituents through a non-conjugated linkage to the novel heterocyclic quinol-type fluorophores can efficiently prevent the short π-π contact between the fluorophores in molecular aggregation states and cause a dramatic solid-state fluorescence enhancement.[4c] They also demonstrated that isomeric pairs of the heterocyclic quinol-type fluorophores exhibited surprisingly different absorption and emission properties both in solution and in the solid state.[4a,4b]

In this paper, we describe the synthesis of structural isomers of novel benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores **3a** and **4a**,[5] which differ in the position of oxygen and nitrogen in the oxazole ring, and their *N*-alkylated (R = butyl, benzyl and 5-nonyl) carbazole derivatives (**3b**–**d** and **4b**–**d**). Their absorption and fluorescence properties in solution and in the solid state are also reported. Semi-empirical molecular orbital calculations (AM1 and INDO/S) and solid-state fluorescent spectral analyses have been carried out to elucidate the effects of the substituents and chromophore skeleton on the photophysical properties of the two isomers (**3** and **4**) both in solution and in the crystalline state. On these bases, the relations between the observed photophysical properties and the chemical structures of the benzofuro[2,3-*c*]oxazolocarbazole-type fluorophores are discussed.

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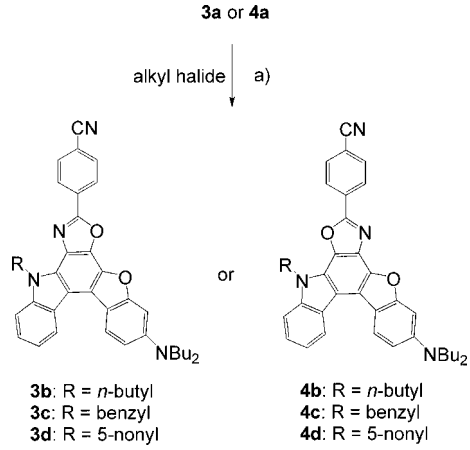
Results and Discussion

Synthesis of Benzofuro[2,3-*c*]oxazolocarbazole-Type Fluorophores (3a–d) and (4a–d)

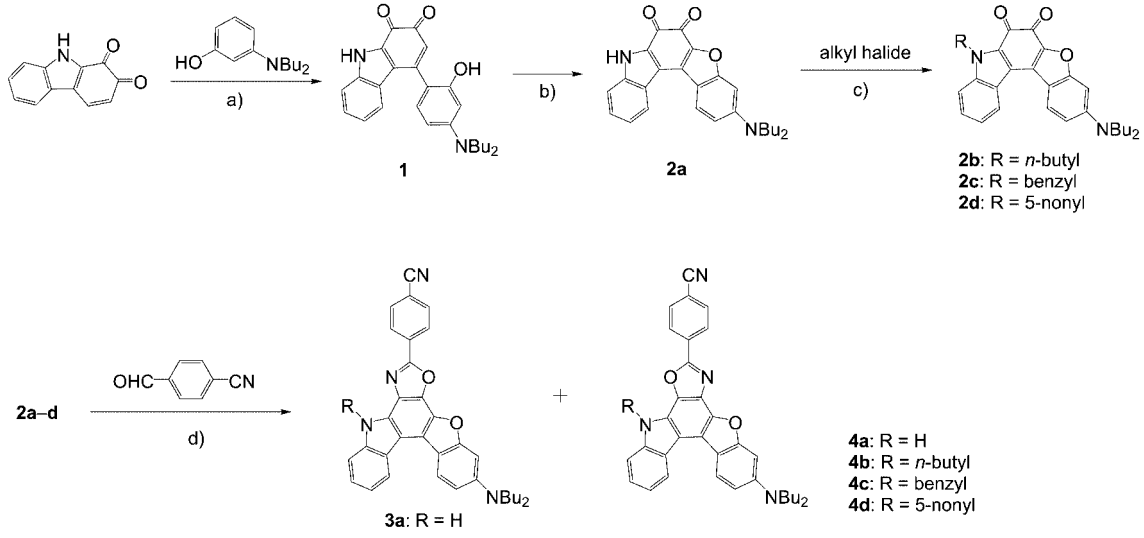
We first prepared the starting heteropolycyclic quinones **2** as shown in Scheme 1. Carbazole-1,2-dione was prepared according to the published procedure.[6] Compound **1** was obtained by the reaction of carbazole-1,2-dione with *m*-(dibutylamino)phenol in the presence of $CuCl_2$. Next, the intramolecular oxidative cyclization of **1** using $Cu(OCOCH_3)_2$ gave the quinone **2a**.[5] The *N*-alkylated quinones **2b–d** were obtained by the reaction of **2a** with the corresponding alkyl halide using sodium hydroxide. The quinone **2a** was allowed to react with *p*-cyanobenzaldehyde to give the structural isomers of oxazolocarbazole-type fluorophores **3a** and **4a**. This is the first report for the preparation of an isomeric pair of the oxazole compounds under these conditions using ammonium acetate. In this reaction, NH_3 resulting from CH_3COONH_4 in the initial stage is acting as the nucleophilic reagent to the 6- and/or 7-carbonyl carbon. In this case, NH_3 preferentially attacks the 7-carbonyl carbon rather than the 6-carbonyl in spite of the similar steric hindrance of the two carbonyls. It was considered that the conjugated linkage of the dibutylamino group to the 6-carbonyl group would make the 6-carbonyl carbon less electrophilic than the 7-carbonyl carbon, so that the nucleophilic reagents (NH_3) would preferentially attack the electrophilic 7-carbonyl carbon. As a result, this reaction afforded preferentially the compound **3a**. On the other hand, we found that the reaction of the *N*-alkylated quinones **2b–d** with *p*-cyanobenzaldehyde afforded preferentially the compounds **4b–d** because of the increased steric hindrance of the 7-carbonyl group. As shown in Scheme 2, the reaction of **3a** with the corresponding alkyl halide using sodium hydride gave **3b–d** in high yields. With **4a** under the same conditions, *N*-alkylated compounds **4b–d** were also obtained in high yields. These compounds were completely characterized by ^1H NMR, IR and elemental analysis. A comparison of the observed and calculated UV/Vis spectra for compounds **3** and **4** provided powerful evidence for the identification of the structures **3** and **4** as described later on.



Scheme 2. Synthesis of fluorophores **3** and **4**. a) **3b**: iodobutane, NaH, acetonitrile, r.t., 5 h, 82%; **3c**: benzyl bromide, NaH, acetonitrile, r.t., 10 h, 79%; **3d**: 5-bromononane, NaH, acetonitrile, r.t., 24 h, 74%; **4b**: iodobutane, NaH, acetonitrile, r.t., 2 h, 89%; **4c**: benzyl bromide, NaH, acetonitrile, r.t., 2 h, 82%; **4d**: 5-bromononane, NaH, acetonitrile, r.t., 12 h, 70%.

Spectroscopic Properties of 3a–d and 4a–d in Solution

The absorption and fluorescence spectroscopic data of **3a–d** and **4a–d** in solution are summarized in Table 1, and the spectra of **3a** and **4a** in 1,4-dioxane are shown in Figure 1. The effect of *N*-alkylation of the carbazole ring on the photophysical properties of **3** and **4** was negligible, so



Scheme 1. Synthesis of fluorophores **3** and **4**. a) $CuCl_2$, DMSO, 50 °C, 1.5 h, 32%; b) $Cu(OCOCH_3)_2$, DMSO, 80 °C, 1.0 h, 63%; c) **2b**: iodobutane, aq Na_2CO_3, *N*-methyl-2-pyrrolidinone, 90 °C, 10 h, 23%; **2c**: benzyl bromide, aq. KOH, Bu_4NBr, toluene, reflux, 12 h, 31%; **2d**: 5-bromononane, aq. KOH, Bu_4NBr, toluene, reflux, 10 h, 26%; d) CH_3COOH, CH_3COONH_4, 90 °C, 1–4 h, 55% for **3a**, 16% for **4a**, 62% for **4b**, 63% for **4c**, 15% for **4d**.

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that the absorption and fluorescence spectra of the fluorescent dyes **3a**–**d** or **4a**–**d** resemble each other very well in each compound series. The fluorophores **3a**–**d** exhibit intense absorption bands at around 430 nm and 350 nm and a single intense fluorescence band at around 540 nm in 1,4-dioxane. The fluorescence quantum yields (Φ) of the fluorophores **3a**–**d** in 1,4-dioxane were almost 100%. On the other hand, the fluorophores **4a**–**d** exhibit a weak absorption band at around 430 nm and an intense absorption band at around 360 nm with a shoulder at 390 nm and a relatively weak fluorescence band at around 550 nm (Φ = 0.17%) in 1,4-dioxane. The absorption maxima of **3a**–**d** and **4a**–**d** are little affected by changing the solvent from 1,4-dioxane to acetone, while fluorescence maxima show a large bathochromic shift. Therefore, the Stokes shift value in polar solvents becomes larger than that in nonpolar solvents. A significant dependence of the fluorescence quantum yield on the solvent polarity was also observed: the Φ value of **3a** is reduced to ca. 16% with increasing polarity going from 1,4-dioxane to acetone, whereas for **4a**, an increase in solvent polarity causes a large bathochromic shift and a drastic decrease in the fluorescence intensity. Stokes shift values for

Table 1. Absorption and fluorescence spectroscopic data of **3a**–**d** and **4a**–**d** in solution.

Entry		Solvent	Absorption λ_{max} [nm] (ε_{max} [$dm^3\,mol^{-1}\,cm^{-1}$])	Fluorescence λ_{max} [nm]	Φ [%]	SS[c] $\Delta\lambda_{max}$ [nm]
1	**3a**	cyclohexane	460 (–), 431 (–)[a]	505, 472	–[a]	12
2			410 (–), 348 (–)[a]			
3		1,4-dioxane	428 (25900), 350 (27300)	539	0.99	111
4		THF	429 (24100), 350 (27100)	582	0.48	153
5		acetone	427 (24700), 349 (26200)	617	0.16	190
6	**3b**	cyclohexane	469 (21600), 438 (24400)	513, 480	0.99	11
7			415 (16600), 355 (28600)			
8		1,4-dioxane	430 (26300), 354 (32000)	535	0.99	105
9	**3c**	cyclohexane	466 (20500), 435 (24300)	512, 478	0.92	12
10			412 (16800), 353 (29400)			
11		1,4-dioxane	427 (23200), 353 (27900)	534	0.98	107
12	**3d**	cyclohexane	471 (18400), 439 (21200)	515, 482	0.99	11
13			416 (14500), 355 (26500)			
14		1,4-dioxane	430 (24000), 359 (30900)	534	0.99	104
15	**4a**	cyclohexane	442 (–), 390 (–), 360 (–)[a]	513, 484	–[a]	42
16		1,4-dioxane	430 (4700), 390[sh], 359 (60200)	575	0.17	145
17		THF	430 (5900), 390[sh], 359 (69200)	623	0.02	193
18		acetone	430 (5600), 390[sh], 357 (72000)	–[b]	–[b]	–[b]
19	**4b**	cyclohexane	446 (5400), 397 (19000)	521, 492	0.35	46
20			375 (24500), 362 (41900)			
21		1,4-dioxane	430 (4500), 390[sh], 362 (50300)	576	0.17	146
22	**4c**	cyclohexane	442 (4000), 394 (12300)	519, 489	0.32	47
23			376 (15600), 361 (31900)			
24		1,4-dioxane	430 (4500), 390[sh], 362 (55700)	575	0.16	145
25	**4d**	cyclohexane	445 (4200), 398 (18000)	522, 492	0.35	47
26			375 (23000), 361 (52400)			
27		1,4-dioxane	430 (4400), 390[sh], 362 (49000)	579	0.17	149

[a] Poor solubility. [b] Too weak. [c] Stokes shift value.

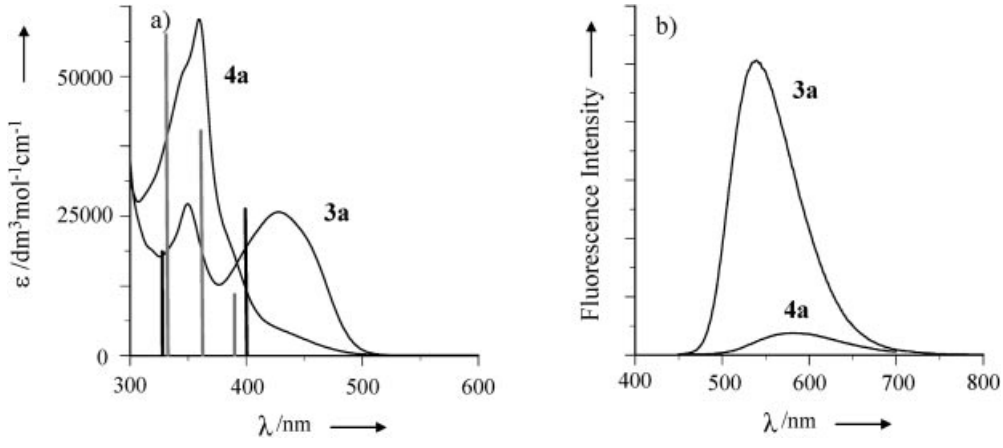

Figure 1. a) Absorption and b) fluorescence spectra of compounds **3a** and **4a** in 1,4-dioxane. The calculated absorption spectra of **3a** and **4a** are shown in black and gray lines, respectively.

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4a–**d** are large compared to those for **3a**–**d**. Similar spectral changes are generally observed for most fluorescent dyes whose dipole moments in the excited state are larger than those in the ground state. The Φ values of **3a**–**d** are greater than those of **4a**–**d**, suggesting that the degree of donor–acceptor conjugation for the former is larger than that for the latter owing to the conjugated linkage of the dibutylamino group to the cyano group in **3a**–**d**.

Electrochemical Properties of 3a–d and 4a–d

The electrochemical properties of **3a**–**d** and **4a**–**d** were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M Et_4NClO_4. As an example, the cyclic voltamograms of **3d** and **4d** are shown in Figure 2. These compounds give similar CV curves and show three oxidation waves at 0.32–0.36 V, 0.83–0.87 V and 0.98–1.01 V vs. Ag/Ag^+ (Table 2). The corresponding reduction waves appear at 0.26–0.29 V, 0.76–0.82 V and 0.91–0.96 V, and the half-wave potential ($E_{1/2}$) of these compounds are 0.29–0.33 V, 0.80–0.85 V and 0.95–0.99 V. The peak separations between oxidation wave and reduction wave were about 60–80 mV, showing that the electrochemical reactions are almost reversible. This implies that oxidised states of the fluorophores are stable, and the electron-transfer reactions are fairly fast.

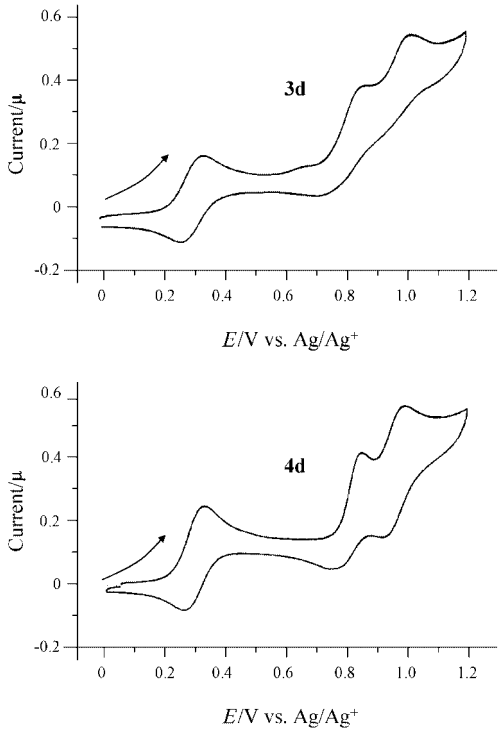

Figure 2. Cyclic voltammograms of compounds **3d** and **4d** in acetonitrile containing 0.1 M Et_4NClO_4 at a scan rate of 20 mV s^{-1}.

Semi-Empirical MO Calculations (AM1, INDO/S)

The photophysical and electrochemical properties of the compounds **3a**–**d** and **4a**–**d** were analyzed by using semi-empirical molecular orbital (MO) calculations. The molecular structures were optimized by using the MOPAC/AM1 method,[12] and then the INDO/S method[13] was used for spectroscopic calculations. The calculated absorption wavelengths and the transition characters of the first absorption bands are collected in Table 3. The observed and calculated absorption spectra of the compounds (Table 1 and Table 3) compare well with each other with respect to both the absorption wavelength and the absorption intensity, although the calculated absorption wavelengths are blue shifted. The deviation of the INDO/S calculations, giving transition energies greater than the experimental values, has been generally observed.[9] The calculations indicate that the longest excitation bands for both isomers **3** and **4** are mainly assignable to the transition from the HOMO to the LUMO, where the HOMO is mostly localized on the 3-(dibutylamino)benzofuro[2,3-*c*]oxazolocarbazole moiety, and the LUMO is mostly localized on the cyanophenyl moiety. The changes in the calculated electron density accompanying the first electron excitation are shown in Figure 3, which reveal a strong migration of intramolecular charge transfer from the 3-(dibutylamino)benzofuro[2,3-*c*]oxazolocarbazole moiety to the cyanophenyl moiety in all the dyes. In the longest excitation bands, the oscillator strength (*f*) of isomers **3a**–**d** are much larger than those of isomers **4a**–**d**, in good agreement with the experimental data. The values of the dipole moment in the ground state are 5.13–5.21 D for **3a**–**d** and 4.99–5.35 D for **4a**–**d**, and the differences between the dipole moments of the first excited (HOMO→LUMO) and the ground states ($\Delta\mu$) are 11.90–12.01 D for **3a**–**d** and 9.94–10.39 D for **4a**–**d**. In the second absorption band for **4a**–**d** (HOMO–1 → LUMO), the changes in the calculated electron density accompanying the first electron excitation represent a migration of intramolecular charge transfer from the carbazole moiety to the cyanophenyl moiety, corresponding to the shoulder of the

Table 2. Electrochemical properties of **3a**–**d** and **4a**–**d**.

Entry		E_{pa}^{ox} [V] (vs. Ag/Ag^+)	E_{pc}^{ox} [V] (vs. Ag/Ag^+)	ΔE_p [mV]	$E_{1/2}$ [V]
1	**3a**	0.36, 0.87, 1.00	0.29, 0.82, 0.93	70, 50, 70	0.33, 0.85, 0.97
2	**3b**	0.34, 0.85, 0.98	0.27, 0.77, 0.91	70, 80, 70	0.31, 0.81, 0.95
3	**3c**	0.34, 0.87, 0.99	0.28, 0.81, 0.94	60, 60, 50	0.31, 0.84, 0.97
4	**3d**	0.33, 0.83, 0.99	0.27, 0.76, 0.93	60, 70, 60	0.30, 0.80, 0.96
5	**4a**	0.33, 0.88, 1.01	0.26, 0.82, 0.96	70, 60, 50	0.30, 0.85, 0.99
6	**4b**	0.32, 0.87, 0.98	0.26, 0.81, 0.93	60, 50, 50	0.29, 0.84, 0.96
7	**4c**	0.33, 0.88, 1.00	0.26, 0.81, 0.95	70, 70, 50	0.30, 0.85, 0.98
8	**4d**	0.32, 0.85, 0.99	0.26, 0.78, 0.92	60, 70, 70	0.29, 0.82, 0.96

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observed spectra. The differences in the dipole moments ($\Delta\mu$) between the second excited and ground state for **3a**–**d** or the third excited and ground state for **4a**–**d** (HOMO → LUMO+1) are 3.81–4.30 D and 3.06–3.31 D, respectively, where a moderate migration of charge transfer from the 3-(dibutylamino)benzofuro[2,3-*c*]oxazolocarbazole moiety to the cyanophenyl moiety is also observed in all the dyes. The oscillator strengths for the second excited band for **3a**–**d** are much smaller than those for the third excited band for **4a**–**d**, also in good agreement with the experimental data. These calculations indicate that both isomers **3** and **4** have similarly large dipole moments in their excited states, which ex-

Table 3. Calculated absorption spectra for the compounds **3a**–**d** and **4a**–**d**.

Entry		μ [D][a]	Absorption (calcd.) λ_{max} [nm]	f [b]	CI component[c]	$\Delta\mu$ [D][d]
1	**3a**	5.21	400	0.95	HOMO → LUMO (77%)	11.90
2			328	0.61	HOMO → LUMO+1 (45%)	3.81
3					HOMO–1 → LUMO (14%)	
4	**3b**	5.20	404	0.92	HOMO → LUMO (78%)	12.01
5			330	0.64	HOMO → LUMO+1 (46%)	4.17
6					HOMO–1 → LUMO (17%)	
7	**3c**	5.14	402	0.90	HOMO → LUMO (78%)	11.97
8			329	0.64	HOMO → LUMO+1 (44%)	4.13
9					HOMO–1 → LUMO (17%)	
10	**3d**	5.13	406	0.91	HOMO → LUMO (78%)	11.96
11			330	0.64	HOMO → LUMO+1 (46%)	4.30
12					HOMO–1 → LUMO (17%)	
13	**4a**	5.28	386	0.22	HOMO → LUMO (57%)	10.39
14			360	0.69	HOMO–1 → LUMO (64%)	7.32
15			333	1.00	HOMO → LUMO+1 (67%)	3.18
16	**4b**	5.35	391	0.18	HOMO → LUMO (57%)	10.15
17			362	0.72	HOMO–1 → LUMO (65%)	8.16
18			334	0.98	HOMO → LUMO+1 (69%)	3.06
19	**4c**	4.99	391	0.17	HOMO → LUMO (56%)	9.99
20			361	0.70	HOMO–1 → LUMO (65%)	7.97
21			334	1.00	HOMO → LUMO+1 (69%)	3.17
22	**4d**	5.01	396	0.15	HOMO → LUMO (57%)	9.94
23			363	0.73	HOMO–1 → LUMO (65%)	8.64
24			336	0.93	HOMO → LUMO+1 (70%)	3.31

[a] The value of the dipole moment in the ground state. [b] Oscillator strength. [c] The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component. [d] The difference in the dipole moment between the excited and the ground states.

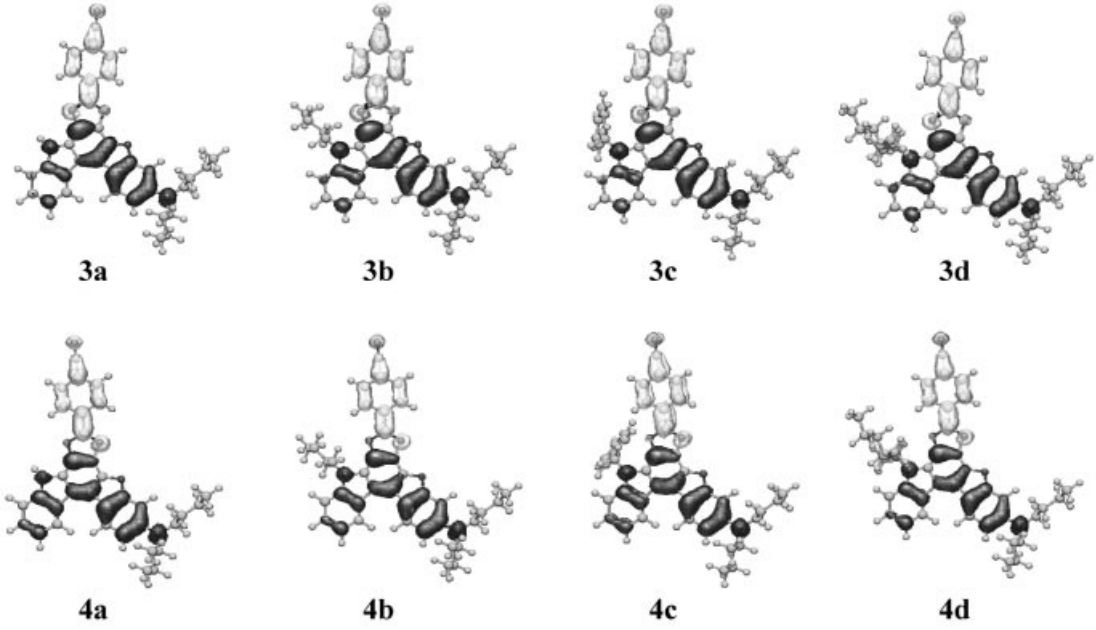

Figure 3. Calculated changes in electron density accompanying the first electronic excitation of **3a**–**d** and **4a**–**d**. The black and white lobes signify decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change.

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plains well our finding that the fluorophores show a large bathochromic shift of their fluorescence maxima in polar solvents, and that the Stokes shift values for both isomers **3** and **4** in polar solvents are much larger than those in nonpolar solvents. Consequently, the HOMO and LUMO energy levels of the isomers **3** and **4** resemble each other very well, in good agreement with the experimental data (absorption maximum and CV peaks). The calculations also reveal that a strong migration of intramolecular charge transfer from the donor moiety to the acceptor moiety for **3**, with the conjugated linkage of the dibutylamino group to the cyano group, leads to intense absorption and fluorescence properties. In addition, the effects of *N*-alkylation of the carbazole ring on electronic structures of these dyes were negligible. Therefore, the absorption and fluorescence spectra and the CVs of **3a**–**d** or **4a**–**d** resemble each other very well within each compound series.

Spectroscopic Properties of 3a–d and 4a–d in the Solid State

Interesting results have been obtained from the photophysical properties of **3a**–**d** and **4a**–**d** in the solid state. Figure 4 shows that the optical properties of the fluorophores **3a**–**d** or **4a**–**d** are similar in solution but quite different in the crystalline state. In order to investigate the difference in the solid-state photophysical properties among **3a**–**d** or **4a**–**d**, we have measured the fluorescence excitation and emission spectra of the crystals. As shown in Figure 5, the fluorophores **3c** and **3d** exhibit a stronger fluorescence band than the other compounds in the crystalline state. The fluorescence quantum yield increases in the order of **3d** (Φ = 0.22%) > **3c** (Φ = 0.20%) > **4d** (Φ = 0.17%) > **4c** (Φ = 0.13%) > **4b** (Φ = 0.11%) ≈ **3b** (Φ = 0.10%) >> **4a** (Φ = 0.03%). The fluorescence of **3a** was strongly quenched in the solid state and the precise evaluation of the quantum yield of **3a** was difficult. The wavelengths of the fluorescence excitation and emission maxima of **3a** (λ_{ex} = 508 nm, λ_{em} = 566 nm) and **4a** (λ_{ex} = 505 nm, λ_{em} = 562 nm) are substantially red-shifted (by 48 nm and 63 nm and 61 nm and 49 nm) compared with those in cyclohexane, respectively. On the other hand, the emission maxima of **3d** (λ_{em} = 562 nm) and **4d** (λ_{em} = 536 nm) show a blue shift with intense fluorescence comparable to those of **3a** and **4a**, respectively. Surprisingly, the Φ values of **4d** in 1,4-dioxane and in the solid state were almost the same. These results demonstrate that the *N*-alkylation of fluorophores can effectively prevent the intermolecular π–π interaction[1d,1e,4–13] and intermolecular hydrogen bonding[3b,12] between fluorophores in the molecular aggregation state, and thus, cause a dramatic enhancement in the solid-state fluorescence. However, the fluorescence enhancement and the blue shift of **3d** were relatively small compared to those of **4d**. This may imply that the intermolecular π–π interaction is liable to be formed in the crystals of strong donor–acceptor-type fluorophores.

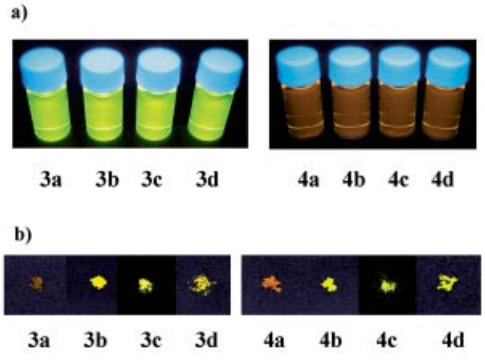

Figure 4. Fluorescence properties of **3a**–**d** and **4a**–**d**, a) in 1,4-dioxane and b) in the solid state.

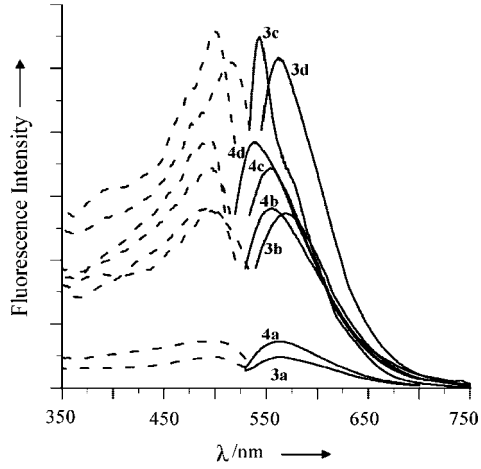

Figure 5. Solid-state excitation (···) and emission (−) spectra of the crystals of **3a**–**d** and **4a**–**d**. [λ_{ex} (nm), λ_{em} (nm)] = [508, 566], [502, 567], [502, 545], [515, 562], [505, 562], [495, 556], [498, 555], and [497, 536] for **3a**, **3b**, **3c**, **3d**, **4a**, **4b**, **4c**, and **4d**, respectively.

Conclusions

We have synthesized structural isomers of novel benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type (**3a**) and benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole-type fluorophores (**4a**), which differ in the position of oxygen and nitrogen in the oxazole ring and their *N*-alkylated (R = butyl, benzyl and 5-nonyl) carbazole derivatives (**3b**–**d** and **4b**–**d**). Their absorption and fluorescence properties in solution and in the solid state were studied. The isomers showed a marked difference in the degree of the donor–acceptor conjugation leading to quite different absorption and fluorescence spectra in solution. Intensely fluorescent compounds in the solid state have been prepared by the *N*-alkylation of the carbazole ring while retaining excellent photophysical properties. It is confirmed that the introduction of sterically hindered substituents on the carbazole ring of the chromophores **3** and **4** can efficiently prevent the short π-π contact between the fluorophores in the molecular aggregation states and cause a dramatic solid-state fluorescence enhancement. In addition, we have obtained new useful information concerning the solid-state fluorescence: the intermo-

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lecular π–π interaction is strongly formed in the crystals of the donor–acceptor-conjugated fluorophores. Studies of dye-sensitized solar cells (DSSCs) using these fluorophores are in progress and will be reported in the next paper.

Experimental Section

General: Melting points were measured with a Yanaco micro melting point apparatus (MP model). IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer by the ATR method. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer, and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields (Φ) were determined with a Hamamatsu C9920–01 instrument equipped with a CCD by using a calibrated integrating sphere system (λ_{ex} = 325 nm). Cyclic voltamograms were recorded in 0.1 M Et_4NClO_4 in acetonitrile with a three-electrode system consisting of Ag/Ag^+ as the reference electrode, a Pt plate as the working electrode and a Pt wire as the counter electrode, by using a Hokuto Denko HAB-151 potentiostat equipped with a functional generator. Elemental analyses were recorded with a Perkin–Elmer 2400 II CHN analyzer. ^{1}H NMR spectra were recorded with a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed with silica gel (KANTO CHEMICAL, 60 N, spherical, neutral).

Preparation of 4-[4-(Dibutylamino)-2-hydroxyphenyl]-9*H*-carbazole-1,2-dione (1): To a solution of 9*H*-carbazole-1,2-dione[11] (1.20 g, 6.09 mmol) and $CuCl_2$ (0.82 g, 6.09 mmol) in DMSO (30 mL) was added *m*-(dibutylamino)phenol (1.40 g, 6.33 mmol) with stirring at 50 °C. After further stirring for 1.5 h, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate = 3:1 as eluent) to give **1** (0.80 g, yield 32%) as a blue powder, m.p. 190–191 °C (decomposition). ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 0.99 (t, 6 H), 1.39–1.46 (m, 4 H), 1.62–1.70 (m, 4 H), 3.39 (t, 4 H), 5.88 (s, 1 H), 6.38–6.41 (m, 2 H), 6.99–7.03 (m, 1 H), 7.20–7.52 (m, 4 H), 8.38 (s, 1 H, -OH), 11.54 (s, 1 H, -NH) ppm. IR (KBr): $\tilde{\nu}$ = 3310, 3232, 1607 cm^{-1}. UV/Vis (1,4-dioxane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 482 (6000), 409 (7300) nm. $C_{26}H_{28}N_2O_3$ (416.58): calcd. C 74.97, H 6.78, N 6.73; found C 74.78, H 6.82, N 6.71.

Preparation of 3-(Dibutylamino)-8*H*-5-oxa-8-azaindeno[2,1-*c*]fluorene-6,7-dione (2a): A solution of **1** (0.8 g, 1.92 mmol) and $Cu(OCOCH_3)_2$ (0.35 g, 1.92 mmol) in DMSO (10 mL) was stirred at 80 °C for 1 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate = 3:1 as eluent) to give **2** (0.50 g, yield 63%) as a black powder, m.p. 222–223 °C (decomposition). ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.00 (t, 6 H), 1.41–1.50 (m, 4 H), 1.67–1.74 (m, 4 H), 3.53 (t, 4 H), 6.72 (d, J = 2.44 Hz, 1 H), 7.04 (dd, J = 2.44 and 9.28 Hz, 1 H), 7.26–7.55 (m, 3 H), 8.17–8.23 (m, 2 H), 11.50 (s, 1 H, -NH) ppm. IR (KBr): $\tilde{\nu}$ = 3242, 1587 cm^{-1}. UV/Vis (1,4-dioxane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 613 (2200), 482 (10800), 400 (7400) nm. $C_{26}H_{26}N_2O_3$ (414.50): calcd. C 75.34, H 6.32, N 6.76; found C 75.14, H 6.22, N 6.62.

Preparation of 8-Butyl-3-(dibutylamino)-8*H*-5-oxa-8-azaindeno[2,1-*c*]-fluorene-6,7-dione (2b): To a solution of **2a** (0.60 g, 1.45 mmol), toluene (100 mL), tetrabutylammonium bromide (0.47 g, 1.45 mmol) and potassium hydroxide (40% in water, 0.08 g, 1.45 mmol) was added dropwise iodobutane (0.67 g, 3.62 mmol) with stirring at reflux. After further stirring for 10 h under reflux, the solvent was removed, and the residue was extracted with CH_2Cl_2. The organic extract was washed with water, dried and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **2b** (0.16 g, yield 23%) as a black powder, m.p. 189–190 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 0.94–1.02 (m, 9 H), 1.29–1.80 (m, 12 H), 3.51 (t, 4 H), 4.62 (t, 2 H), 6.72–6.76 (m, 1 H), 7.03–7.07 (m, 1 H), 7.31–7.37 (m, 1 H), 7.42–7.49 (m, 1 H), 7.62–7.64 (m, 1 H), 8.18–8.27 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 1601 cm^{-1}. UV/Vis (1,4-dioxane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 630 (2400), 492 (17100), 404 (7800) nm. $C_{30}H_{34}N_2O_3$ (470.60): calcd. C 76.57, H 7.28, N 5.95; found C 76.27, H 7.34, N 5.91.

Preparation of 8-Benzyl-3-(dibutylamino)-8*H*-5-oxa-8-azaindeno-[2,1-*c*]fluorene-6,7-dione (2c): To a solution of **2a** (1.00 g, 2.41 mmol), toluene (200 mL), tetrabutylammonium bromide (0.78 g, 2.41 mmol) and potassium hydroxide (40% in water, 0.14 g, 2.41 mmol) was added dropwise benzyl bromide (1.03 g, 6.03 mmol) with stirring at reflux. After further stirring for 12 h at reflux, the solvent was removed, and the residue was extracted with CH_2Cl_2. The organic extract was washed with water, dried and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate = 5:1 as eluent) to give **2c** (0.38 g, yield 31%) as a black powder, m.p. 213–215 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.00 (t, 6 H), 1.43–1.50 (m, 4 H), 1.67–1.73 (m, 4 H), 3.54 (t, 4 H), 5.94 (s, 2 H), 6.76 (d, J = 2.40 Hz, 1 H), 7.06 (dd, J = 2.40 and 9.28 Hz, 1 H), 7.24–7.64 (m, 8 H), 8.23–8.32 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 1598 cm^{-1}. UV/Vis (1,4-dioxane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 620 (2100), 488 (13900), 405 (7400) nm. $C_{33}H_{32}N_2O_3$ (504.62): calcd. C 78.55, H 6.39, N 5.55; found C 78.50, H 6.33, N 5.52.

Preparation of 3-(Dibutylamino)-8-(5-nonyl)-8*H*-5-oxa-8-azaindeno-[2,1-*c*]fluorene-6,7-dione (2d): To a solution of **2a** (0.75 g, 1.81 mmol), toluene (100 mL), tetrabutylammonium bromide (0.58 g, 1.81 mmol) and potassium hydroxide (40% in water, 0.10 g, 1.81 mmol) was added dropwise 5-bromononane (0.94 g, 4.52 mmol) with stirring at reflux. After further stirring for 10 h at reflux, the solvent was removed, and the residue was extracted with CH_2Cl_2. The organic extract was washed with water, dried and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **2d** (0.25 g, yield 26%) as a black powder, m.p. 124–126 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 0.79 (t, 6 H), 0.83–0.93 (m, 4 H), 1.00 (t, 6 H), 1.18–1.50 (m, 12 H), 1.67–1.74 (m, 4 H), 3.53 (t, 4 H), 5.00–5.02 (m, 1 H), 6.75 (d, J = 1.96 Hz, 1 H), 7.05 (m, 1 H), 7.31–7.42 (m, 2 H), 7.79–7.81 (m, 1 H), 8.21–8.32 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}. UV/Vis (1,4-dioxane): λ_{max} (ε, L mol^{-1} cm^{-1}) = 621 (2200), 492 (16400), 406 (7600) nm. $C_{35}H_{44}N_2O_3$ (540.74): calcd. C 77.74, H 8.20, N 5.18; found C 77.71, H 8.20, N 5.12.

Preparation of 7-(4-Cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]-oxazolo[4,5-*a*]carbazole (3a) and 7-(4-Cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole (4a): A solution of **2a** (1.00 g, 2.41 mmol), *p*-cyanobenzaldehyde (0.32 g, 2.41 mmol) and ammonium acetate (3.72 g, 48 mmol) in acetic acid (30 mL) was stirred at 90 °C for 1 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (toluene/acetic acid = 5:1 as eluent) to give **3a** (0.70 g, yield 55%) as an orange powder and **4a** (0.20 g, yield 16%) as an orange powder.

Compound 3a: M.p. 295–296 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.03 (t, 6 H), 1.47–1.52 (m, 4 H), 1.70–1.78 (m, 4 H),

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3.54 (t, 4 H), 7.02–7.08 (m, 2 H), 7.41–7.44 (m, 1 H), 7.51–7.55 (m, 1 H), 7.80 (d, J = 8.28 Hz, 1 H), 8.06 (d, J = 8.56 Hz, 2 H), 8.51 (d, J = 8.56 Hz, 2 H), 8.55 (d, J = 8.76 Hz, 1 H), 8.71 (d, J = 8.04 Hz, 1 H), 11.49 (s, 1 H, -NH) ppm. IR (KBr): $\tilde{\nu}$ = 3427, 2227 cm^{-1}. $C_{34}H_{30}N_4O_2$ (526.63): calcd. C 77.54, H 5.74, N 10.64; found C 77.51, H 5.71, N 10.60.

Compound 4a: M.p. 303–304 °C (decomposition). ^1H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.03 (t, 6 H), 1.46–1.52 (m, 4 H), 1.70–1.78 (m, 4 H), 3.52 (t, 4 H), 7.01 (dd, J = 9.04 and 2.20 Hz, 1 H), 7.07 (m, J = 2.20 Hz, 1 H), 7.43 (m, 1 H), 7.54 (m, 1 H), 7.76 (d, J = 8.20 Hz, 1 H), 8.06 (d, J = 8.32 Hz, 2 H), 8.50 (d, J = 8.32 Hz, 2 H), 8.51 (d, J = 9.04 Hz, 1 H), 8.74 (d, J = 7.80 Hz, 1 H), 11.49 (s, 1 H, -NH) ppm. IR (KBr): $\tilde{\nu}$ = 3341, 2229 cm^{-1}. $C_{34}H_{30}N_4O_2$ (526.63): calcd. C 77.54, H 5.74, N 10.64; found C 77.48, H 5.51, N 10.51.

General Synthetic Procedure for 3b–d and 4b–d by the Reaction of 3a or 4a with Alkyl Halide: A solution of **3a** (or **4a**) in dry acetonitrile was treated with sodium hydride and stirred for 1 h at room temperature. Alkyl halide (iodobutane, benzyl bromide or 5-bromononane) was added dropwise over 30 min, and the solution was stirred at room temperature for 2–14 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was dried with $MgSO_4$, filtered and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **3b–d** (or **4b–d**). The following are synthetic procedures for **3b–d**.

Preparation of 9-Butyl-7-(4-cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole (3b): A solution of **3a** (1.0 g, 1.90 mmol) in dry acetonitrile was treated with sodium hydride (60%, 0.23 g, 5.70 mmol) and stirred for 1 h at room temperature. Iodobutane (1.75 g, 9.49 mmol) was added dropwise over 30 min, and the solution was stirred at room temperature for 5 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was dried with $MgSO_4$, filtered and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **3b** (0.91 g, yield 82%). M.p. 230–231 °C. ^1H NMR (400 MHz, [D$_3$]chloroform, TMS): δ = 1.00–1.03 (m, 9 H), 1.42–1.68 (m, 10 H), 2.00 (m, 2 H), 3.42 (t, 4 H), 4.92 (t, 2 H), 6.87 (dd, J = 8.70 and 2.20 Hz, 1 H), 6.92 (m, J = 2.20 Hz, 1 H), 7.37–7.41 (m, 1 H), 7.53–7.57 (m, 1 H), 7.77 (d, J = 8.21 Hz, 2 H), 8.10 (d, J = 8.22 Hz, 1 H), 8.33 (d, J = 8.21 Hz, 2 H), 8.42 (d, J = 8.70 Hz, 1 H), 8.62 (d, J = 7.73 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2163 cm^{-1}. $C_{38}H_{38}N_4O_2$ (582.73): calcd. C 78.32, H 6.57, N 9.61; found C 78.22, H 6.44, N 9.61.

Preparation of 9-Benzyl-7-(4-cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole (3c): A solution of **3a** (1.0 g, 1.90 mmol) in dry acetonitrile was treated with sodium hydride (60%, 0.23 g, 5.70 mmol) and stirred for 1 h at room temperature. Benzyl bromide (1.62 g, 9.49 mmol) was added dropwise over 30 min, and the solution was stirred at room temperature for 10 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was dried with $MgSO_4$, filtered and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **3c** (0.93 g, yield 79%). M.p. 253–254 °C. ^1H NMR (400 MHz, [D$_6$]-acetone, TMS): δ = 1.04 (t, 6 H), 1.47–1.53 (m, 4 H), 1.72–1.76 (m, 4 H), 3.51–3.56 (m, 4 H), 6.37 (s, 2 H), 7.03–7.07 (m, 3 H), 7.20–7.28 (m, 3 H), 7.39–7.54 (m, 3 H), 7.78 (d, J = 7.60 Hz, 1 H), 8.06 (d, J = 8.80 Hz, 2 H), 8.52–8.57 (m, 3 H), 8.76 (d, J = 7.60 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2229 cm^{-1}. $C_{41}H_{36}N_4O_2$ (616.75): calcd. C 79.84, H 5.88, N 9.08; found C 79.66, H 5.85, N 8.86.

Preparation of 7-(4-Cyanophenyl)-3-(dibutylamino)-9-(5-nonyl)-benzofuro[2,3-*c*]oxazolo-[4,5-*a*]carbazole (3d): A solution of **3a** (1.0 g, 1.90 mmol) in dry acetonitrile was treated with sodium hydride (60%, 0.23 g, 5.70 mmol) and stirred for 1 h at room temperature. 5-Bromononane (1.62 g, 9.49 mmol) was added dropwise over 30 min, and the solution was stirred at room temperature for 24 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH_2Cl_2 and washed with water. The organic extract was dried with $MgSO_4$, filtered and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **3d** (0.92 g, yield 74%). M.p. 156–158 °C. ^1H NMR (400 MHz, [D$_6$]-acetone, TMS): δ = 0.72 (t, 6 H), 0.85–0.90 (m, 4 H), 1.03 (t, 6 H), 1.26–1.51 (m, 12 H), 1.68–1.74 (m, 4 H), 3.50 (t, 4 H), 4.95–4.98 (m, 1 H), 6.96–7.00 (m, 2 H), 7.39–7.52 (m, 2 H), 7.95–8.05 (m, 3 H), 8.50–8.52 (m, 3 H), 8.74 (d, J = 7.56 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2227 cm^{-1}. $C_{43}H_{48}N_4O_2$ (652.87): calcd. C 79.11, H 7.41, N 8.58; found C 78.81, H 7.64, N 8.28.

General Synthetic Procedure for 4b–d by the Reaction of 2b–d with *p*-Cyanobenzaldehyde: A solution of **2b** (or **2c** or **2d**), *p*-cyanobenzaldehyde and ammonium acetate in acetic acid was stirred at 90 °C for 2–4 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/*n*-hexane = 5:1 as eluent) to give **4b** (or **4c** or **4d**).

Preparation of 9-Butyl-7-(4-cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole (4b): A solution of **2b** (0.20 g, 0.42 mmol), *p*-cyanobenzaldehyde(0.06 g, 0.42 mmol) and ammonium acetate (0.66 g, 8.50 mmol) in acetic acid (30 mL) was stirred at 90 °C for 2 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/*n*-hexane = 5:1 as eluent) to give **4b** (0.15 g, yield 62%) as a yellow powder. M.p. 282–283 °C. ^1H NMR (400 MHz, [D$_6$]chloroform, TMS): δ = 1.00–1.04 (m, 9 H), 1.40–1.54 (m, 6 H), 1.66–1.72 (m, 4 H), 2.02 (m, 2 H), 3.42 (t, 4 H), 4.72 (t, 2 H), 6.89 (dd, J = 9.04 and 2.20 Hz, 1 H), 7.00 (m, J = 2.20 Hz, 1 H), 7.40–7.44 (m, 1 H), 7.55–7.60 (m, 2 H), 7.86 (d, J = 8.28 Hz, 2 H), 8.43 (d, J = 9.04 Hz, 1 H), 8.46 (d, J = 8.28 Hz, 2 H), 8.70 (d, J = 7.84 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2227 cm^{-1}. $C_{38}H_{38}N_4O_2$ (582.73): calcd. C 78.32, H 6.57, N 9.61; found C 78.35, H 6.45, N 9.60.

Preparation of 9-Benzyl-7-(4-cyanophenyl)-3-(dibutylamino)benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole (4c): A solution of **2c** (1.00 g, 1.98 mmol), *p*-cyanobenzaldehyde(0.26 g, 1.98 mmol) and ammonium acetate (3.05 g, 39.6 mmol) in acetic acid (300 mL) was stirred at 90 °C for 3 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/*n*-hexane = 5:1 as eluent) to give **4c** (0.77 g, yield 63%) as a yellow powder. M.p. 272–274 °C. ^1H NMR (400 MHz, [D$_6$]DMSO, TMS): δ = 0.97 (t, 6 H), 1.38–1.43 (m, 4 H), 1.58–1.62 (m, 4 H), 3.35–3.38 (m, 4 H, overlap peak of dissolved water in [D$_6$]DMSO), 6.12 (s, 2 H), 6.94–7.07 (m, 2 H), 7.15–7.47 (m, 7 H), 7.91 (d, J = 7.32 Hz, 1 H), 8.13 (d, J = 8.76 Hz, 2 H), 8.44–8.49 (m, 3 H), 8.70 (d, J = 7.32 Hz, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2230 cm^{-1}. $C_{41}H_{36}N_4O_2$ (616.75): calcd. C 79.84, H 5.88, N 9.08; found C 79.79, H 5.70, N 9.26.

Preparation of 7-(4-Cyanophenyl)-3-(dibutylamino)-9-(5-nonyl)-benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole (4d): A solution of **2d** (0.20 g, 0.37 mmol), *p*-cyanobenzaldehyde(0.05 g, 0.37 mmol) and ammonium acetate (0.57 g, 7.40 mmol) in acetic acid (30 mL) was

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stirred at 90 °C for 4 h. After the reaction was complete, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH_2Cl_2/*n*-hexane = 5:1 as eluent) to give **4d** (0.035 g, yield 15%) as a yellow powder. M.p. 219–221 °C. ^{1}H NMR (400 MHz, [D_6]acetone, TMS): δ = 0.71 (t, 6 H), 0.85–0.90 (m, 4 H), 1.03 (t, 6 H), 1.27–1.52 (m, 12 H), 1.71–1.77 (m, 4 H), 3.52 (t, 4 H), 4.93–4.96 (m, 1 H), 6.98–7.08 (m, 2 H), 7.43–7.62 (m, 2 H), 7.90–8.08 (m, 3 H), 8.52–8.60 (m, 3 H), 8.80–8.83 (m, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 2222 cm^{-1}. $C_{43}H_{48}N_4O_2$ (652.87): calcd. C 79.11, H 7.41, N 8.58; found C 79.34, H 7.36, N 8.56.

Computational Methods: The semi-empirical calculations were carried out with the WINMOPAC Ver. 3 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made using the AM1 method.[11] All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine procedure (keyword EF). The experimental absorption spectra of the eight compounds were compared with their absorption data by the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic).[12] All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

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