

Synthesis and Photophysical Properties of *N*-Arylcarbazolophanes

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Two carbazolophanes bearing benzene or naphthalene rings on the nitrogen atoms of carbazole were successfully synthesized by the intramolecular etherification of the precursor tetraols, and their photophysical properties were investigated in detail based on the absorption spectra, fluorescence spectra, fluorescence lifetimes, quantum yields, phosphorescence spectra, and transient absorption spectra. It was concluded that the carbazolophane bearing benzene rings forms carbazole excimer in both excited singlet and triplet states, while the carbazolophane bearing naphthalene rings forms carbazole excimer only in the excited singlet state and has a locally excited state of naphthalene in the excited triplet state. These results are reasonably explained by the relationship of excitation energies between carbazole and benzene (or naphthalene) and their arrangement such as the extent of overlap. The introduction of aromatic rings on the carbazole nitrogen atoms was found to affect the electronic and photophysical properties of carbazolophanes sensitively.

Carbazole is a constituent of the well-known poly(*N*-vinylcarbazole) as photoconductor. The photophysical properties of its dimer model compounds[1] and polymers[2] have been extensively investigated. A cyclophane composed of carbazoles, namely carbazolophane, in which the relative arrangement of two carbazole chromophores is fixed more rigidly, is a desirable compound for the elucidation of the relationship between chromophore arrangement and fluorescence properties. Dioxa[3.3](3,6)carbazolophane, the first carbazolophane synthesized by Tani et al., was found to adopt anti conformation, leading to small overlap between the carbazole rings and therefore, the absence of excimer fluorescence.[3]

We have synthesized cyclobutane-fused [2.*n*]cyclophanes possessing various aromatic hydrocarbons by the intramolecular [2 + 2] photocycloadditions of bis(vinylaryl)alkanes.[4] This synthetic method is usually suitable for the preparation of syn isomers; in some cases, syn isomers are exclusively obtained. By using this method, [2.*n*](3,9)carbazolophanes **1** and **2** ($n = 4$ and 5) were successfully prepared from the corresponding vinyl compounds (Chart 1).[5] These carbazolophanes displayed fluorescence spectra different from one another, depending on their structures: for instance, **1a** afforded broad emission assigned as sandwich excimer fluorescence, whereas **2a** gave monomer fluorescence with vibrational structures. Recently, we have succeeded in the preparation of triply-bridged [2.2.*n*](3,6,9)carbazolophanes **3** ($n = 4$ and 5) by the photoreaction of α,ω-bis(3,6-divinyl-9-carbazolyl)alkanes.[6] These carbazolophanes **3** adopted syn conformation exclusively and suffered from no isomerization into anti conformation, since two carbazole nuclei are fixed more rigidly by two cyclobutane rings and an oligomethylene linkage, although carbazolophanes **3** were composed of three isomers based on the configuration of cyclobutane rings and their separation was extremely difficult.

Introduction of aromatic rings at the N-position of carbazole is expected to modify the carbazole-based π-conjugated system, such as the wavelength and intensity of absorption and/or fluorescence spectra. Thus, the preparation of triply-bridged carbazolophane **4** possessing benzene rings was attempted by the intramolecular [2 + 2] photocycloaddition of the corresponding vinylcarbazole derivative. However, this photoreaction failed to provide desired carbazolophane **4**, only giving polymeric products.

Hence, we were stimulated to prepare **5**, in which cyclobutane rings are replaced by $-CH_2OCH_2-$ units. Cyclophanes possessing cyclobutane are generally unstable towards UV light, mainly due to cyclobutane ring cleavage, to give precursor vinyl compounds. Actually, some cyclophanes, especially syn isomers, underwent partial decomposition even during the measurement of emission spectra. Recently, we reported that the use of a $-CH_2OCH_2-$ linkage instead of cyclobutane ring significantly enhanced the photostability of some cyclophanes including phenanthrene.[7] Furthermore, $-CH_2OCH_2-$ linkages have an advantage that they can rule out the formation of stereoisomers. Actually, carbazolophane **5** was readily prepared as a single isomer by the intramolecular etherification of precursor tetraol and isolated as a stable product.[7b] In addition to **5**, the synthesis of carbazolophane **6** bearing naphthalene rings instead of benzene rings was also carried out, in order to clarify the effects of aromatic rings at the carbazole N-position on the electronic and photophysical properties of carbazolophanes. Here, the preparation, characterization, and photophysical properties of these carbazolophanes **5** and **6** are described in detail.

Results and Discussion

Synthesis and Characterization. Since the details for the synthesis of **5** have been reported in previous literature,[7b] only the synthesis of **6** is described here. The synthetic sequence of **6** is illustrated in Scheme 1.

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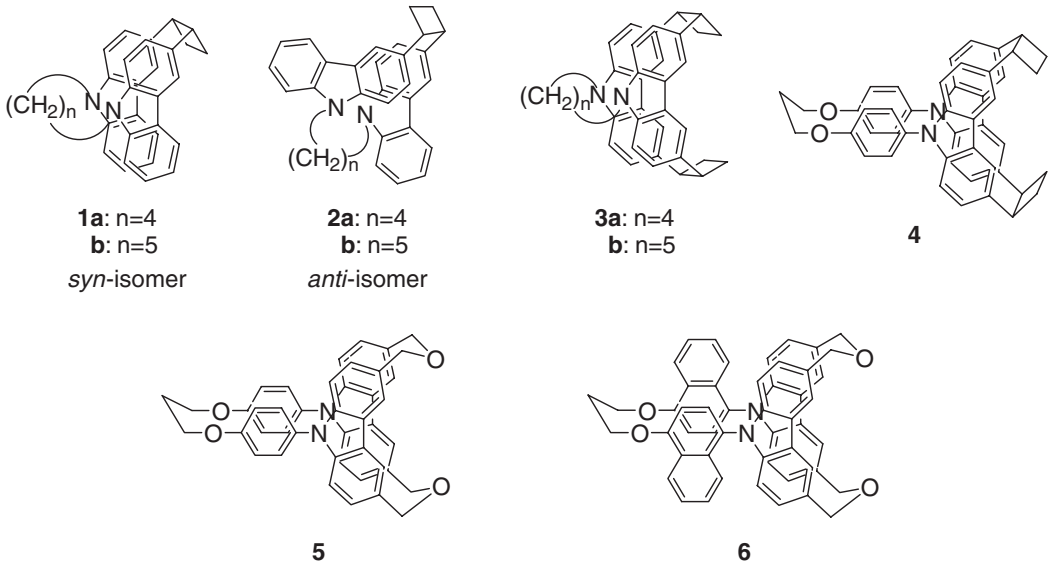
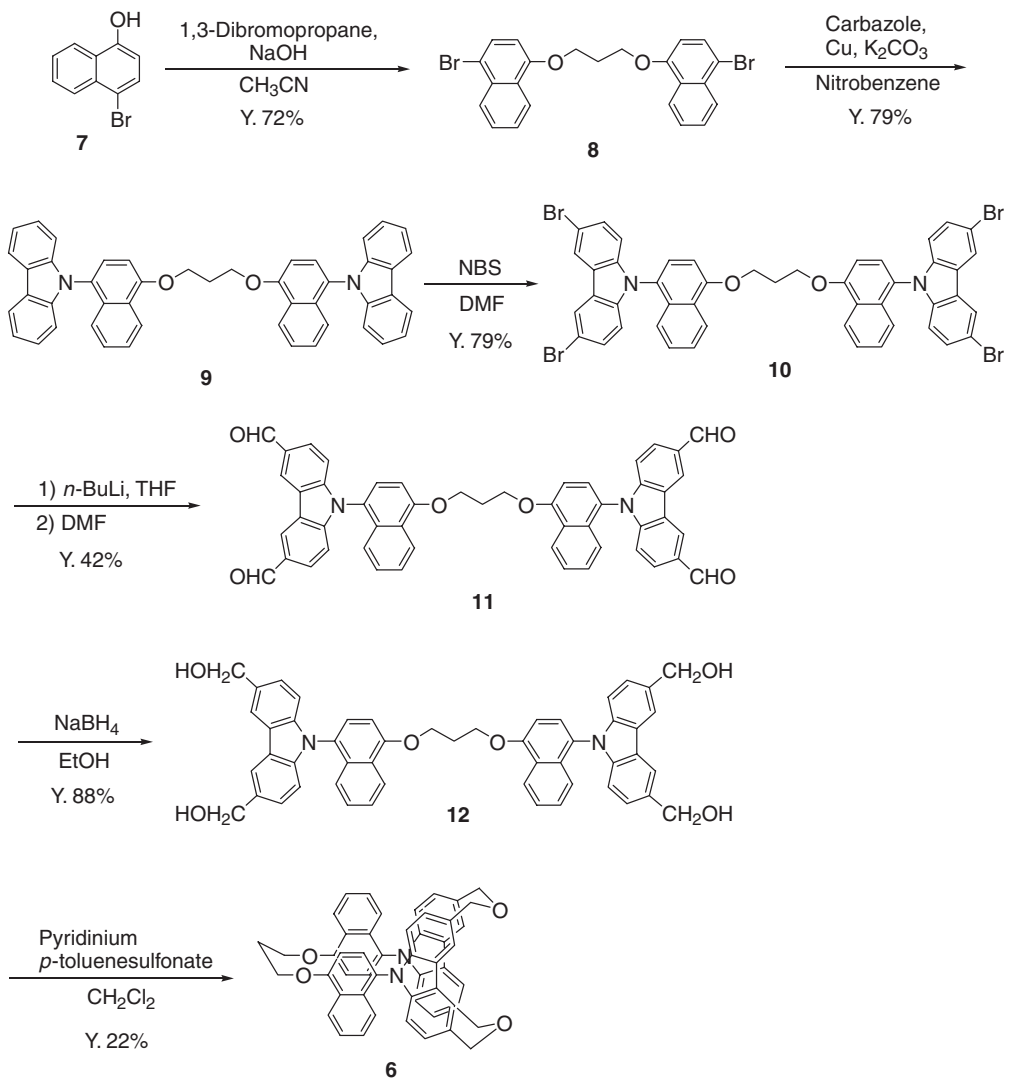


Chart 1.



Scheme 1.

Since **9** was not obtained by the palladium-catalyzed coupling reaction,[8] the copper-catalyzed Ullmann coupling reaction[9] was employed; the treatment of carbazole with dibromide **8**, prepared from 1,3-dibromopropane and 4-bromo-1-naphthol, in the presence of copper and K_2CO_3 gave **9** in a moderate yield. The bromination of **9** with NBS in DMF successfully afforded **10**; no bromination of the naphthalene rings was observed. Tetrabromide **10** was transformed into tetraaldehyde **11** by lithiation and subsequent treatment with DMF. The reduction of **11** by $NaBH_4$ in EtOH yielded **12**.

The intramolecular etherification of **12** toward **6** was carried out in the presence of pyridinium *p*-toluenesulfonate as acid catalyst under high-dilution (ca. 4×10^{-4} M), in a manner similar to **5**. The reaction in dichloromethane at room temperature for 5 days afforded **6** in 22% yield. After purification by silica gel column chromatography and GPC, carbazolophane **6** was isolated as a single product.

Carbazolophane **6** obtained was characterized by ^{1}H and ^{13}C NMR spectroscopy. Similar to carbazolophane **5**, the carbazole protons are generally high-field shifted compared to those of precursor **12**, suggesting that the two carbazole moieties are well overlapped with each other and subjected to shielding effects. The benzyl protons were split into two broadened doublets, in contrast with those observed as a sharp singlet in **12**, indicating the formation of a cyclic structure and dynamic behavior of $-CH_2OCH_2-$ linkages. For the naphthalene rings, H2 and H3 protons are remarkably high-field shifted relative to **12**, while the other protons are hardly shifted. This behavior suggests the partial overlap of the naphthalene rings; only the six-membered rings including H2 and H3 overlap each other. The number of signals in the ^{13}C NMR spectrum is also consistent with the structure of **6**.

Absorption Spectra. Figure 1 shows the absorption spectrum of carbazolophane **5** in cyclohexane at room temperature along with those of 1,3-bis(4-(9-carbazolyl)phenoxy)propane (**13**) and *N*-(4-methoxyphenyl)carbazole (**14**) for comparison. The absorption spectrum of carbazolophane **5** exhibits considerable broadening and slight red shift relative to **13** and **14**. These observations indicate that the two carbazole nuclei electronically interact with each other in the ground state. These broadening and peak shifts can be explained by Kasha's exciton coupling theory.[10] In contrast, the absorption spectrum of **13** is quite similar to that of **14**, indicating that the two carbazole rings of **13** are not sufficiently close to each other and their interaction is almost negligible in the ground state. The absorption spectra of **5**, **13**, and **14** in acetonitrile were similar to those in cyclohexane.

Figure 2 shows the absorption spectra of carbazolophane **6**, reference compound **9**, and *N*-(4-methoxy-1-naphthyl)carbazole (**15**) possessing naphthalene rings in cyclohexane. The absorption spectrum of carbazolophane **6** also exhibits considerable broadening and red shift relative to **9** and **15**, indicating the electronic interaction between the two carbazole rings. The broadening in **6** is more remarkable than that in **5**. The electronic effect of the 4-alkoxynaphthalene moiety on carbazole seems to be larger than that of 4-alkoxybenzene moiety, as also demonstrated by the difference in the spectral shape between **14** and **15**. The absorption spectrum of **9** is quite similar to that of **15**, as in the case of **13** and **14**.

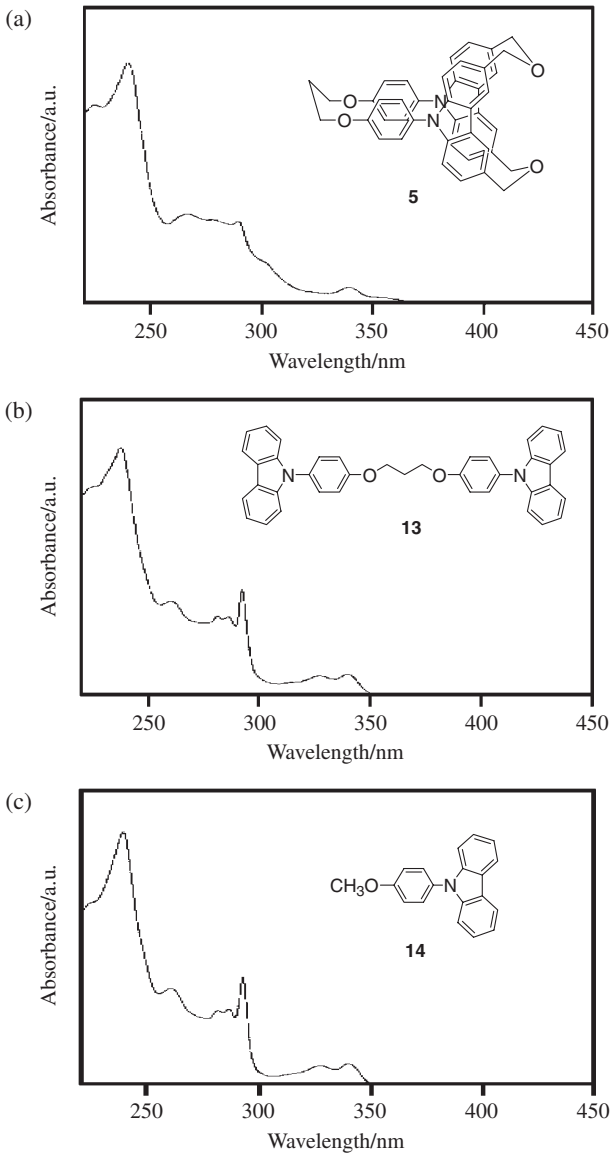


Figure 1. Absorption spectra of (a) **5**, (b) **13**, and (c) **14** in cyclohexane at room temperature.

Fluorescence Spectra. Figure 3 depicts the fluorescence spectra of carbazolophane **5** in cyclohexane and acetonitrile at room temperature along with those of **13** and **14**.

Carbazolophane **5** exhibited red-shifted broad emission with a maximum at 425 nm in cyclohexane, in contrast with **13** and **14** providing vibrational structures characteristic of the carbazole monomer fluorescence. The peak shift from the 0–0 transition band of monomer fluorescence of **14** is about 5200 cm^{-1}. The large peak shift is characteristic of excimer fluorescence for most aromatic compounds.[11] Therefore, it is reasonable to assign the broad structureless emission observed for **5** to the intramolecular excimer fluorescence of carbazole, as reported for the related carbazolophanes.[5,6,12] The maximum wavelength (λ_{max}) is slightly red-shifted compared to carbazolophane **3a** ($\lambda_{max} = 417$ nm) with no phenyl group on the nitrogen atoms of carbazole rings.[6] The fluorescence excitation spectra, on monitoring the broad emission, were in good agreement with the absorption spectrum, obviously indicating

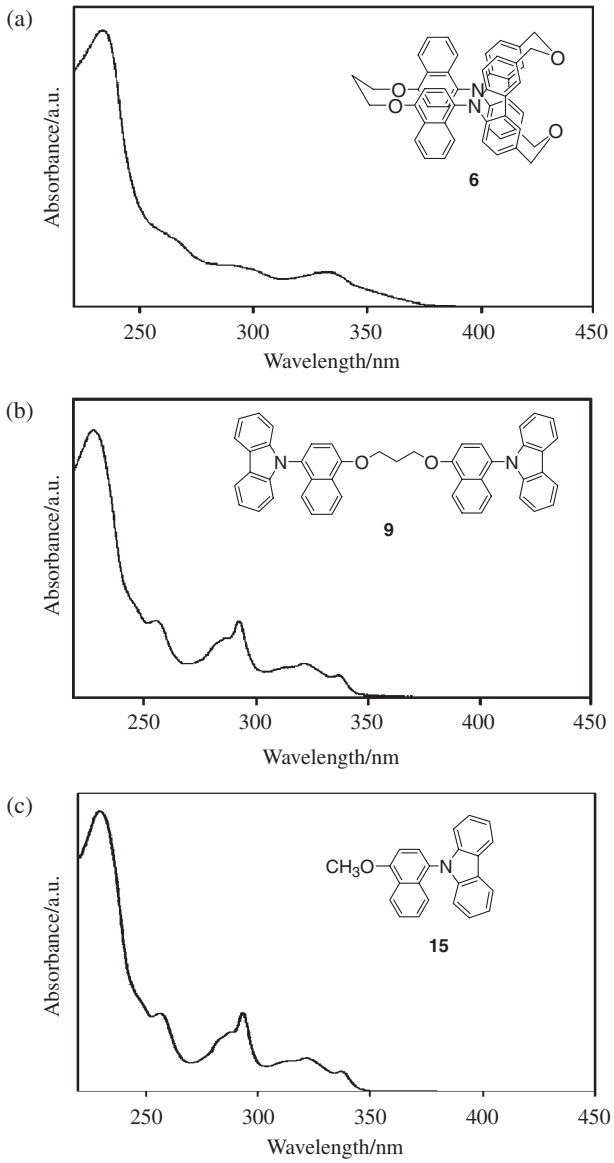


Figure 2. Absorption spectra of (a) **6**, (b) **9**, and (c) **15** in cyclohexane at room temperature.

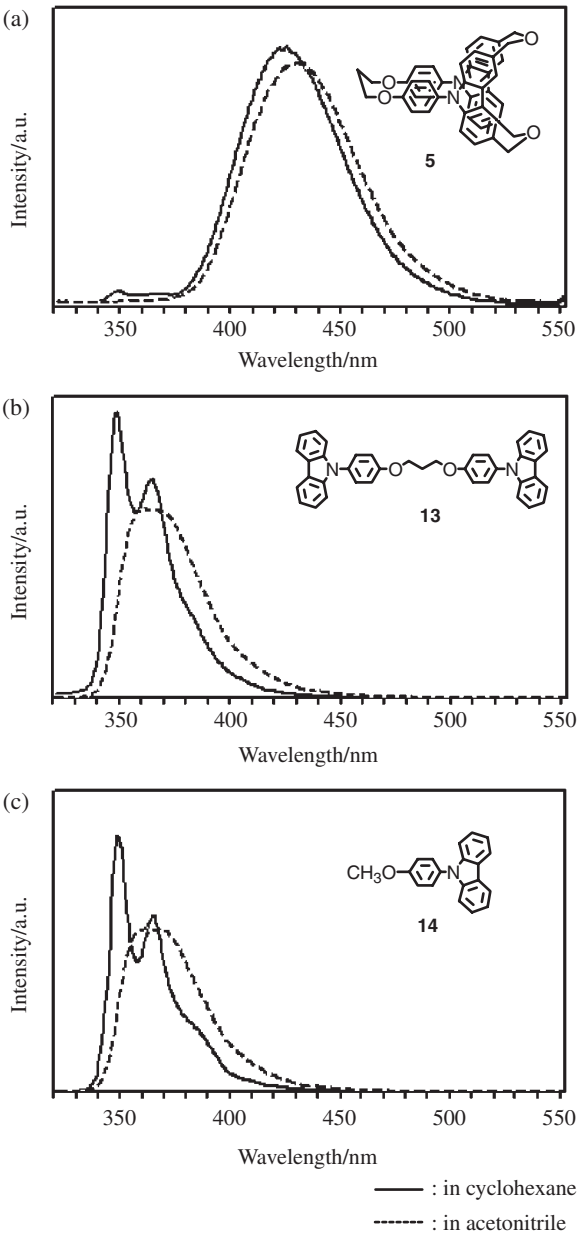


Figure 3. Fluorescence spectra of (a) **5**, (b) **13**, and (c) **14** upon 280-nm excitation in cyclohexane (solid line) and acetonitrile (dotted line) at room temperature.

that this emission originates from **5**. The spectrum of **13** is quite similar to that of **14**, suggesting that the interaction between the two carbazole rings is small in the excited state in **13**.

In acetonitrile, carbazolophane **5** also displays a broad fluorescence spectrum quite similar to that in cyclohexane. The maximum position (429 nm) is slightly red-shifted compared to that in cyclohexane. Intriguingly, a significant red-shift, loss of vibrational structures, and broadened band are observed for the fluorescence spectra of **13** and **14** in acetonitrile. As reported in the literature,[13] some *N*-arylcarbazoles bearing naphthalene, phenanthrene, and 4-cyanobenzene exhibit red-shifted and broadened fluorescence in polar solvents due to the twisted intramolecular charge-transfer (TICT) state, while a carbazole with an unsubstituted phenyl group shows almost no solvent effects. It is noteworthy that **13** and **14** carrying an electron-donating alkoxy group exhibit such a solvent effect.

Figure 4 illustrates the fluorescence spectra of **6**, **9**, and **15** in cyclohexane and acetonitrile. Carbazolophane **6** in cyclohexane exhibits broad emission ($\lambda_{max} = 409$ nm) similar to **5**, though it is blue-shifted relative to **5**. This emission is also interpreted as excimer fluorescence of carbazole. The spectra of **9** and **15** in cyclohexane, similar to each other, are rather broadened and red-shifted compared to that of **13** and **14**. This observation is probably due to the interaction between the carbazole and naphthalene moieties.

In acetonitrile, carbazolophane **6** also exhibits a broad fluorescence ($\lambda_{max} = 415$ nm), which is slightly red-shifted compared to that in cyclohexane. The spectra of **9** and **15** in acetonitrile are further red-shifted and broadened compared to those in cyclohexane, as in the case of **13** and **14**.

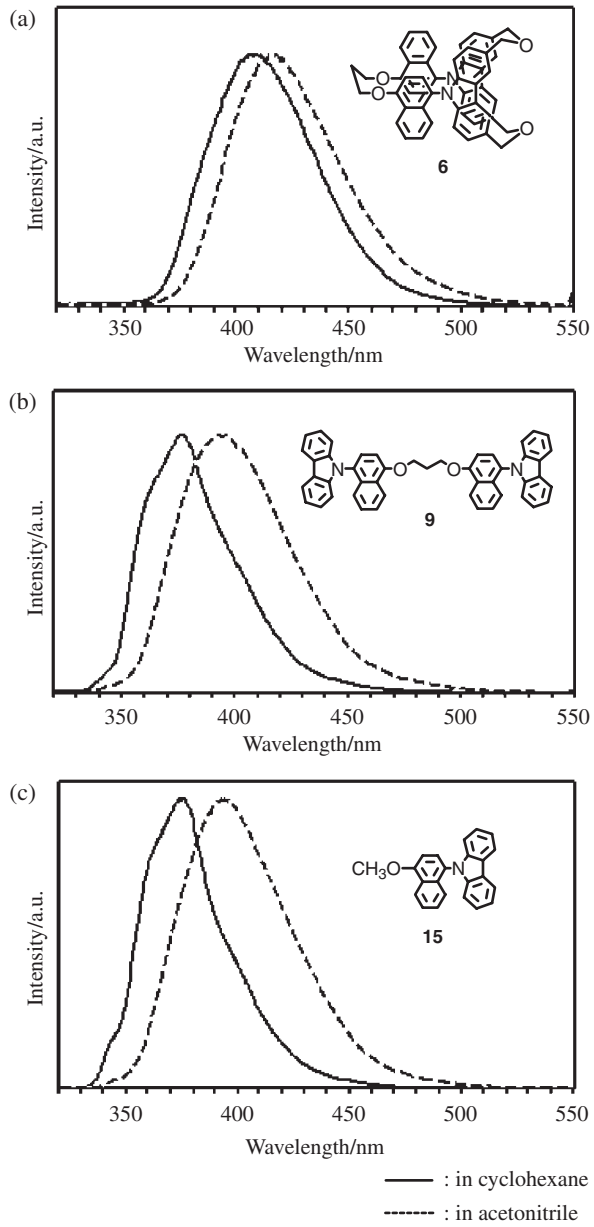


Figure 4. Fluorescence spectra of (a) **6**, (b) **9**, and (c) **15** upon 280-nm excitation in cyclohexane (solid line) and acetonitrile (dotted line) at room temperature.

Fluorescence Lifetimes and Quantum Yields. The fluorescence decay functions of **5**, **6**, **9**, and **13** were measured in degassed cyclohexane at 298 K by means of nanosecond single-photon-counting. The decay functions were analyzed by deconvolution as a single-exponential function or a sum of double-exponential functions (eq 1).

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

Table 1 lists the fluorescence lifetimes (τ) and the ratio of each decay component just after excitation (A_1 and A_2).

While the fluorescence decay profile of **13** was satisfactorily analyzed as a single-exponential function with a lifetime of 8.34 ns, carbazolophane **5** (monitored at 423 nm) afforded not only the major component with a lifetime of 10.2 ns, but also the minor component with a lifetime of 2.4 ns. Such short-life component was also detected when monitored at 470 nm. The origin of this species is unrevealed at the present stage, but the ratio is too small to discuss in further detail (ca. 2%). It is noteworthy that the difference in fluorescence lifetimes between **5** and **13** is relatively small, in spite of the remarkable difference in their spectral shape; **5** provides excimer fluorescence, while **13** gives monomer fluorescence.

Table 1. Fluorescence Lifetime of **5**, **6**, **9**, and **13** in Cyclohexane at 298 K

	Em/nm	τ_1/ns	%	τ_2/ns	%	χ^2
5	423	2.39	2.5	10.2	97.5	1.063
	470	1.88	2.5	10.2	97.5	1.170
13	350	8.34	—			1.214
	400	8.34	—			1.121
6	380	7.25	—			1.183
	410	7.16	—			1.102
	450	7.09	—			1.073
9	360	6.44	—			1.076
	420	6.43	—			1.013

Table 2. Fluorescence Quantum Yield (Φ_f), Fluorescence Lifetime (τ_f), and Radiative Rate (k_f) of **5**, **6**, **9**, and **13** in Cyclohexane at Room Temperature

	Φ_f	Φ_{nr}	τ_f/ns	$k_f/10^7\,s^{-1}$	$k_{nr}/10^7\,s^{-1}$
5	0.035	0.97	10.2	0.34	9.5
13	0.39	0.61	8.34	4.7	7.3
6	0.047	0.95	7.16	0.66	13
9	0.48	0.52	6.43	7.5	8.1

The fluorescence decay profiles of **6** and **9** were satisfactorily analyzed as a single-exponential function with lifetimes of ca. 6.4 and ca. 7.1 ns, respectively. The difference in fluorescence lifetimes between **6** and **9** is smaller than that between **5** and **13**. The fluorescence lifetimes of **6** and **9** bearing naphthalene rings are shorter than those of **5** and **13**, respectively. The naphthalene rings of **6** and **9** not only broaden the fluorescence spectra but also shorten the fluorescence lifetimes.

The fluorescence quantum yields (Φ_f) of **5**, **6**, **9**, and **13** were determined in degassed cyclohexane at room temperature by using 1-naphthylamine as a standard ($\Phi_f = 0.465$). Based on Φ_f and τ_f, the radiative rate constant (k_f) and nonradiative rate constant (k_{nr}) were determined (eqs 2 and 3).

$$k_f = \Phi_f/\tau_f \quad (2)$$

$$k_{nr} = \Phi_{nr}/\tau_f = (1 - \Phi_f)/\tau_f \quad (3)$$

These parameters are summarized in Table 2. The quantum yield of carbazolophane **5** is only about 1/10 as much as that of **13**. Thus, the radiative rate of **5** is less than 1/10 of that of **13**, since the fluorescence lifetime of **5** is slightly longer than that of **13**. The much lower radiative rate of **5** indicates that the excimer emission of **5** is partially forbidden, as suggested in some related carbazolophanes.[12] In contrast, the nonradiative rates of **5** and **13** are on the same order.

Similar tendencies were observed for **6** and **9**; the Φ_f of **6** is only about 1/10 of **9**, and the k_f of **6** is less than 1/10 of that of **9**. The Φ_f of **6** and **9** is slightly larger than that of **5** and **13**,

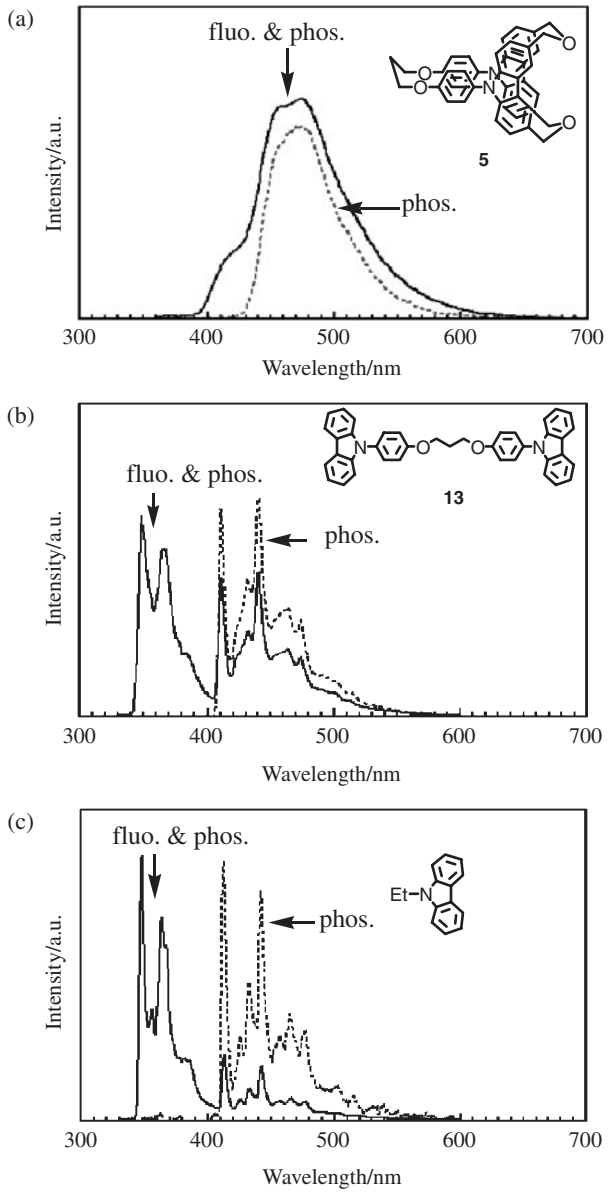


Figure 5. Total emission spectra (solid line) and phosphorescence spectra (dotted line) of (a) **5**, (b) **13**, and (c) *N*-ethylcarbazole upon 320-nm excitation in MP (4:1) at 77 K.

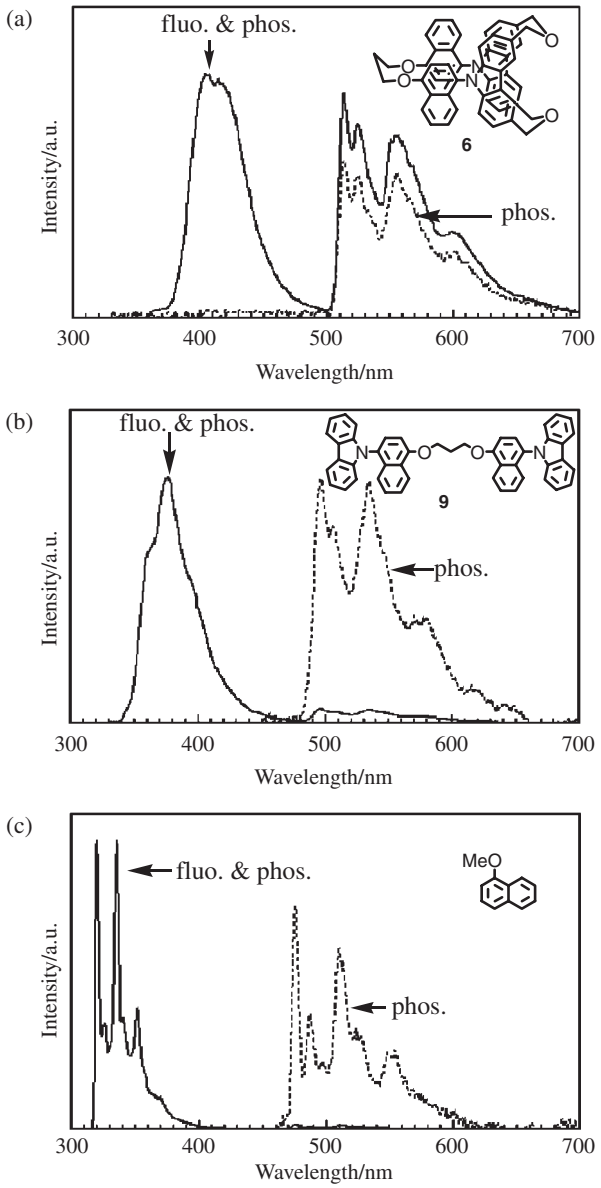


Figure 6. Total emission spectra (solid line) and phosphorescence spectra (dotted line) of (a) **6**, (b) **9**, and (c) 1-methoxynaphthalene upon 320-nm excitation in MP (4:1) at 77 K.

respectively. The k_f of **6** and **9** is also larger than that of **5** and **13**, respectively, since the τ_f of **6** and **9** is shorter than that of **5** and **13**. The naphthalene rings on the nitrogen atoms apparently increases the k_f values; they reduce the forbidden character in the excimer emission.

Phosphorescence Spectra. Figure 5 shows the total emission spectra and phosphorescence spectra of **5**, **13**, and *N*-ethylcarbazole in MP (methylcyclohexane/isopentane (4/1)) at 77 K.

The phosphorescence spectrum of **13** exhibits vibrational structures similar to those of *N*-ethylcarbazole, although the 0–0 transition band is slightly red-shifted. Hence, this phosphorescence is attributed to the local emission of a triplet carbazole moiety (monomer phosphorescence of carbazole). On the other hand, **5** shows a broad structureless band with a maximum at 474 nm. Similar broad phosphorescence was also observed in 2-methyltetrahydrofuran (MTHF) matrix. As described in the literature,[12d] these emissions of **5** are assignable to the phosphorescence from triplet carbazole excimer, although the difference in the peak positions between the fluorescence and phosphorescence bands in **5** is smaller than the difference in the 0–0 transition bands between the monomer fluorescence and phosphorescence in **13**. Thus, it is concluded that **5** forms excimer in both singlet and triplet excited states. The phosphorescence lifetimes of **5** and **13** were 5.2 and 5.3 s, respectively, which are of the same order as that of *N*-methylcarbazole (7 s).[14]

Figure 6 shows the total emission spectra and phosphorescence spectra of **6**, **9**, and 1-methoxynaphthalene measured in MP at 77 K.

The phosphorescence spectrum of **9** exhibits vibrational structures, which are similar to those of 1-methoxynaphthalene, not *N*-ethylcarbazole, as is evident from the peak positions. Hence, this phosphorescence is attributed to the local emission of a triplet naphthalene moiety (monomer phosphorescence of naphthalene). This observation is derived from the fact that the triplet (T_1) energy of 1-methoxynaphthalene ($E_{T1} = 250$ kJ mol^{-1}) is lower than that of carbazole ($E_{T1} = 294$ kJ mol^{-1}), in contrast with their S_1 ($E_{S1} = 374$ kJ mol^{-1} for 1-methoxynaphthalene; $E_{S1} = 347$ kJ mol^{-1} for carbazole).[15,16] This behavior is different from that for **13**, where monomer fluorescence and phosphorescence of carbazole were observed, since both S_1 and T_1 energies of carbazole are lower than those of benzene. The phosphorescence spectrum of **6** is also similar to that of 1-methoxynaphthalene, indicating the monomer phosphorescence of naphthalene, as in the case of **9**. Due to the lower T_1 level of 1-methoxynaphthalene than carbazole, the phosphorescence should have a naphthalene-like character. In **6**, two naphthalene rings are not sufficiently overlapped with each other, as demonstrated by the ^{1}H NMR spectrum. Hence, it is quite reasonable that **6** afforded naphthalene monomer phosphorescence, not excimer phosphorescence. Thus, **6** provided excimer fluorescence of carbazole and monomer phosphorescence of naphthalene, reflecting the relationship of excitation energies between carbazole and naphthalene and their arrangement (the extent of overlap). The phosphorescence lifetimes of **6** and **9** were 0.8 and 1.7 s, respectively. The latter is comparable to that of 1-methoxynaphthalene (2 s).

Transient Absorption Spectra. The transient absorption spectra of **5**, **6**, **9**, and **13** were obtained at several delay times after laser pulsing at 308 nm in degassed cyclohexane at 293 K.

Figure 7 illustrates the spectra of **5**, **13**, and *N*-ethylcarbazole. The spectra of *N*-ethylcarbazole with a sharp maximum around 400 nm are assigned to the triplet–triplet (T–T) absorption. The spectral features of **13** are quite similar to those of *N*-ethylcarbazole. Thus, the transient absorptions of **13** are obviously ascribable to the T–T absorption of carbazole moiety. Their lifetimes are almost on the same order (**13**: 170 μs, *N*-ethylcarbazole: 340 μs), although their decay functions could not be completely analyzed by first-order kinetics due to the T–T annihilation.

On the other hand, carbazolophane **5** exhibits remarkably different spectral features. It shows rather broad absorption bands over the range of 400–850 nm and two maxima around 450 and 630 nm. In addition, the lifetime (6 μs) is much shorter than those of the T–T absorption of **13** and *N*-ethylcarbazole. Hence, it is apparent that the absorptions observed for **5** are not due to the local triplet species of carbazole, but the triplet excimer, as suggested by the phosphorescence spectrum. Similar transient absorption bands have been reported in some other carbazolophanes.[12d]

Figure 8 shows the spectra of **6** along with those of **9** and **15**. The spectra of **6** exhibit a rather intense band with a maximum of ca. 450 nm and a broad band around 500–800 nm. These bands are also observed in **9** and **15**, although the former band is slightly broadened in **6**. The shape and position of the former band are similar to those of the T–T absorption for 1-methoxynaphthalene (Figure S1) rather than *N*-ethylcarbazole. The broad band in the longer wavelength region, which is

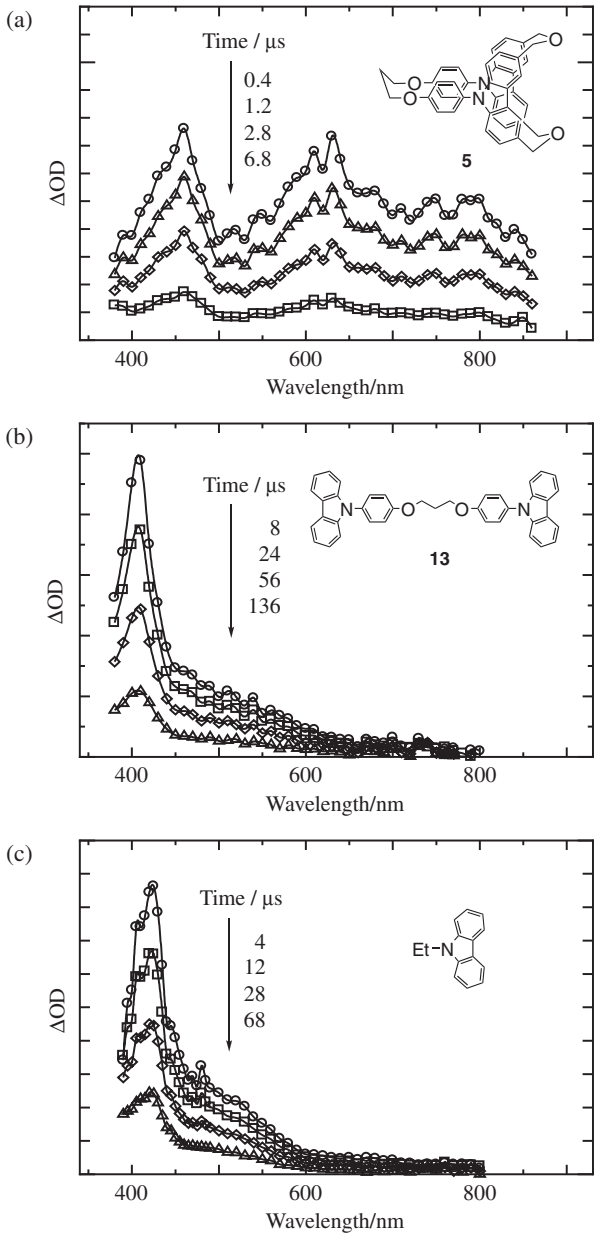


Figure 7. Transient absorption spectra of (a) **5**, (b) **13**, and (c) *N*-ethylcarbazole upon 308-nm excitation in cyclohexane at 293 K.

observed in neither 1-methoxynaphthalene nor *N*-ethylcarbazole, probably originates from the interaction between the carbazole and naphthalene moieties. On the whole, the spectra of **6** are regarded as the T–T absorption of a naphthalene-like character involving the interaction with the carbazole moiety. These observations are consistent with the relationship of excitation energies between carbazole and naphthalene.

Summary

Carbazolophane **6** bearing naphthalene rings on the nitrogen atoms was successfully prepared by the intramolecular etherification of tetraol **12** in the presence of acid catalyst in a manner similar to **5**, and distinctly characterized by ^{1}H and ^{13}C NMR spectra, which indicate that the two carbazole

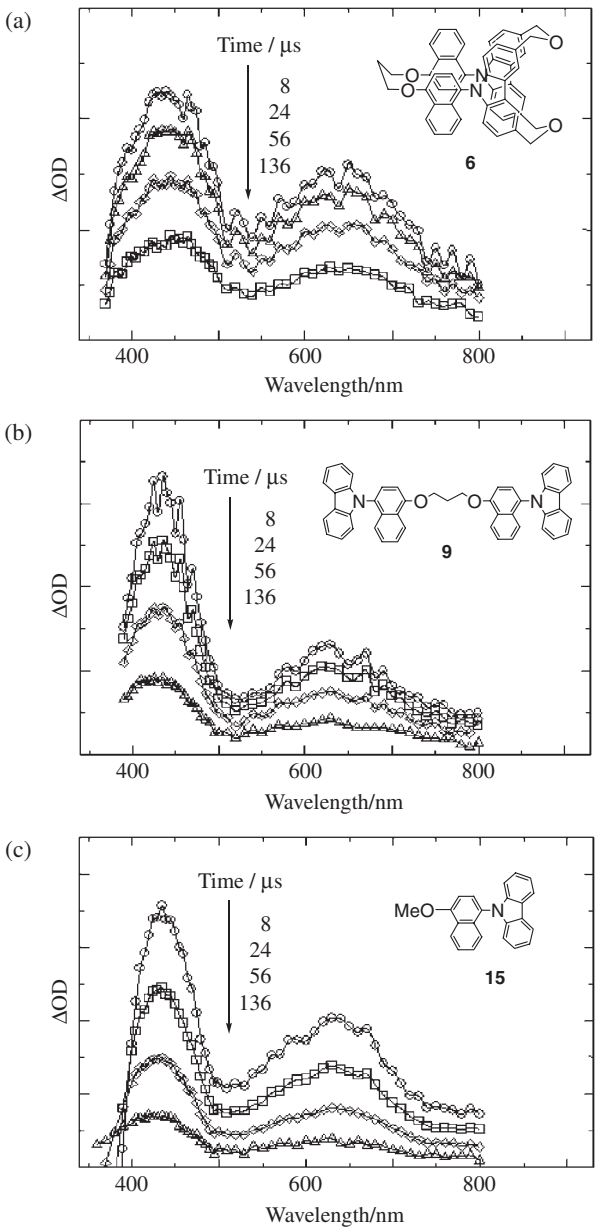


Figure 8. Transient absorption spectra of (a) **6**, (b) **9**, and (c) **15** upon 308-nm excitation in cyclohexane at 293 K.

moieties are well overlapped with each other and the naphthalene rings are only partially overlapped.

The electronic and photophysical properties of carbazolophanes **5** and **6** were investigated and compared in detail. Both **5** and **6** provided broadened and red-shifted absorption spectra compared to those of reference compounds **13** and **9**, and exhibited excimer-like fluorescence with a maximum at 425 and 409 nm, respectively, at room temperature.

The fluorescence quantum yields of **5** and **6** are only about 1/10 as much as those of **13** and **9**. The radiative rates (k_f) of carbazolophanes **5** and **6** are less than 1/10 of those of **13** and **9**, respectively, while the nonradiative rates (k_{nr}) of **5**, **6**, **13**, and **9** are of the same order. The radiative rates (k_f) of **6** and **9** bearing naphthalene rings are slightly larger than those of **5** and **13** bearing benzene rings, respectively.

At 77 K, **5** exhibited broad structureless phosphorescence, which is assignable to the emission from triplet carbazole excimer. On the contrary, **6** exhibited monomer phosphorescence of naphthalene with vibrational structures. This observation results from the lower T_1 level of 1-methoxynaphthalene than carbazole and the insufficient overlap between the two naphthalene rings.

The transient absorption spectra of **5** showed broad bands, which are remarkably different from the T–T absorption bands of carbazole, suggesting the triplet carbazole excimer. The transient absorption spectra of **6** showed the T–T absorption bands of a naphthalene-like character and the broad band due to the interaction between the naphthalene and carbazole moieties, similar to **15**.

From these observations, it is concluded that **5** forms carbazole excimer in both excited singlet and triplet states. In contrast, **6** forms carbazole excimer in the excited singlet state, whereas it has a locally excited state of naphthalene in the excited triplet state. These results are reasonably explained by the relationship of excitation energies between carbazole and benzene (or naphthalene) and their arrangement such as the extent of overlap. The introduction of aromatic rings on the carbazole nitrogen atoms sensitively affects the electronic and photophysical properties of carbazolophanes.

Experimental

General. NMR spectra were recorded on a JEOL λ-500 or JEOL AL-300 FT NMR spectrometer with tetramethylsilane as an internal standard. Absorption spectra were recorded on a HITACHI U-3210 spectrophotometer. Fluorescence spectra were measured on a HITACHI F-4500 spectrophotometer. These spectra were obtained in cyclohexane or acetonitrile (spectroscopic grade) with a 10-mm optical path quartz cell. GPC was performed with a JAI LC-918 R/U Recycling Preparative HPLC using JAIGEL-1H and 2H columns.

The fluorescence lifetimes (τ_f) were obtained with a time-correlated single-photon counting (TCSPC) fluorometer (Edinburgh Analytical Instruments FL900CDT). A nanosecond pulsed discharge lamp (pulse width ca. 1.0 ns, repetition rate 40 kHz) filled with hydrogen gas was used as the excitation light source. The fluorescence time profiles were analyzed by iterative reconvolution with the response function.

The fluorescence quantum yield (Φ_f) was determined from the fluorescence intensity (F), the absorbance (A) at the excitation wavelength, and the refractive index (n) of solvents by using the following equation.

$$\Phi_{fX} = \frac{F_X A_{ST} n_X^2}{F_{ST} A_X n_{ST}^2} \Phi_{fST} \quad (4)$$

where X and ST stand for sample and standard solutions, respectively. The absorbance of the sample solution was adjusted to be ca. 0.10 at excitation wavelength. The Φ_f value ($\Phi_{fST} = 0.47$) of 1-aminonaphthalene in cyclohexane was used as a standard solution.

Phosphorescence spectra and lifetime (τ_p) were measured on a HITACHI F-4010 spectrophotometer.

The transient absorption spectra were obtained by using a nanosecond laser flash photolysis system. A XeCl excimer laser (Lambda Physik, LEXtra 50; 308 nm, pulse width ca. 17 ns) was used as an excitation source. The monitoring light from a xenon lamp (Ushio, UXL-150D) was focused into a sample cuvette (SC) by two convex lenses. The transient signal was detected by a

photomultiplier tube (PMT) after passing through a monochromator (MC). The signal was recorded on a personal computer (CPU). In order to improve the signal to noise ratio (S/N) of the signal, the data averaging was carried out over 5 to 10 shots. The absorbance of each sample solution was adjusted to be ca. 0.7 at the excitation wavelength. All sample solutions were degassed by freeze–pump–thaw cycling.

Preparation of 8. A mixture of 4-bromo-1-naphthol (**7**) (22.3 g, 99.0 mmol) and NaOH (5.97 g, 149 mmol) was refluxed in acetonitrile (1000 mL) for 1 h. After addition of 1,3-dibromopropane (8.14 g, 40.3 mmol), the mixture was further refluxed for 62 h. After addition of water (500 mL), acetonitrile was removed under reduced pressure, and the residue was extracted with chloroform (three times). The combined organic phase was successively washed with aqueous NaOH solution (twice) and water (twice), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford pure **8** (14.2 g, 29.3 mmol, 72%) as white powder. Mp 137.9–138.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (2H, d, $J = 8.2$ Hz), 8.16 (2H, d, $J = 8.2$ Hz), 7.63 (2H, d, $J = 8.2$ Hz), 7.60 (2H, t, $J = 7.5$ Hz), 7.50 (2H, t, $J = 7.5$ Hz), 6.72 (2H, d, $J = 8.2$ Hz), 4.41 (4H, t, $J = 6.0$ Hz), 2.56 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.75, 132.92, 129.91, 128.25, 127.40, 127.27, 126.46, 122.78, 113.87, 105.87, 65.52, 29.75. Anal. Calcd for $C_{23}H_{18}Br_2O_2$: C, 56.82; H, 3.73%. Found: C, 56.50; H, 3.70%.

Preparation of 9. A mixture of **8** (7.00 g, 14.4 mmol), carbazole (6.01 g, 35.9 mmol), K_2CO_3 (9.90 g, 72.0 mmol), and Cu (2.74 g, 43.0 mmol) in nitrobenzene (50 mL) was stirred at 190 °C for 52 h. After cooling to room temperature, chloroform (50 mL) was added, and the suspension was filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, toluene/ethyl acetate) to afford **9** (7.52 g, 11.4 mmol, 79%). Mp 136.8–137.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (2H, d, $J = 8.2$ Hz), 8.20 (4H, d, $J = 7.6$ Hz), 7.55 (2H, d, $J = 8.2$ Hz), 7.52 (2H, t, $J = 7.6$ Hz), 7.34–7.31 (6H, m), 7.30–7.27 (4H, m), 7.16 (2H, d, $J = 8.1$ Hz), 7.06 (2H, d, $J = 8.1$ Hz), 7.00 (4H, d, $J = 7.9$ Hz), 4.63 (4H, t, $J = 5.9$ Hz), 2.76–2.71 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.46, 142.88, 132.29, 127.99, 127.58, 127.01, 126.94, 126.49, 126.34, 123.70, 123.48, 123.04, 120.74, 120.04, 110.60, 104.89, 65.55, 29.95. Anal. Calcd for $C_{47}H_{34}N_2O_2 \cdot 1/2H_2O$: C, 84.53; H, 5.28; N, 4.19%. Found: C, 84.52; H, 5.27; N, 4.19%.

Preparation of 10. To a solution of **9** (0.12 g, 0.18 mmol) in DMF (20 mL) was added NBS (0.14 g, 0.79 mmol) at 0 °C. After stirring at room temperature for 3.5 h, water (15 mL) was added to the mixture, and the suspension was filtered. The solid was extracted with dichloromethane (three times), and the combined organic phase was successively washed with brine (twice), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, toluene) to afford **10** (0.14 g, 0.14 mmol, 79%). Mp 261.4–263.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (2H, d, $J = 8.6$ Hz), 8.25 (4H, s), 7.54 (2H, d, $J = 8.0$ Hz), 7.51 (2H, d, $J = 8.0$ Hz), 7.41 (4H, dd, $J = 1.8$, 8.7 Hz), 7.35 (2H, t, $J = 7.6$ Hz), 7.06–7.01 (4H, m), 6.85 (4H, d, $J = 8.7$ Hz), 4.64 (4H, t, $J = 5.8$ Hz), 2.76–2.73 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.85, 150.12, 141.78, 131.93, 129.85, 128.34, 127.56, 127.03, 126.73, 125.88, 124.10, 123.70, 123.14, 113.35, 112.33, 104.79, 65.56, 29.91. Anal. Calcd for $C_{47}H_{30}Br_4N_2O_2$: C, 57.94; H, 3.10; N, 2.88%. Found: C, 57.54; H, 3.16; N, 2.82%.

Preparation of 11. To a three-neck flask containing **10** (1.52 g, 1.56 mmol) was added dry THF (130 mL) under a nitrogen atmosphere. After the solution was stirred and cooled to −78 °C with a dry ice–acetone bath, 1.58 M *n*-butyllithium hexane solution (5.9 mL, 9.32 mmol) was added to the solution, and the mixture was stirred for 1 h at that temperature. After addition of DMF (1.2 mL, 15.6 mmol), the reaction mixture was stirred at room temperature for 2.5 h. The reaction was quenched by adding 5% aqueous ammonium chloride solution (130 mL). The organic phase was separated, and aqueous phase was extracted with toluene (three times). The combined organic phase was washed with water (three times), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was washed with acetone to afford **11** (0.51 g, 0.66 mmol, 42%) as white powder. Mp 192.2–193.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.16 (4H, s), 8.80 (4H, s), 8.53 (2H, d, $J = 8.5$ Hz), 7.95 (4H, d, $J = 8.6$ Hz), 7.61–7.57 (6H, m), 7.40 (2H, t, $J = 7.6$ Hz), 7.12 (4H, d, $J = 8.6$ Hz), 7.05 (2H, d, $J = 8.2$ Hz), 4.69 (4H, t, $J = 5.8$ Hz), 2.81–2.78 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.07, 156.33, 147.18, 131.57, 130.81, 128.73, 128.62, 127.59, 127.08, 126.99, 125.02, 124.78, 123.72, 123.41, 122.73, 111.69, 104.77, 65.63, 29.86. HRESIMS m/z 793.2275 (calcd for $C_{51}H_{34}N_2O_6Na$ 793.2309).

Preparation of 12. A mixture of **11** (0.37 g, 0.48 mmol) and $NaBH_4$ (0.27 g, 7.10 mmol) in ethanol (90 mL) was stirred at 30 °C for 1 h, and refluxed for 3.5 h. The mixture was diluted with water (20 mL), and neutralized by a small amount of acetic acid. After ethanol was evaporated under reduced pressure, the residue was extracted with ethyl acetate (twice). The combined organic phase was washed with water (twice), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure, to give **12** (0.33 g, 0.42 mmol, 88%) as white powder. This compound was used for the following reaction without further purification due to the extremely low solubility and instability. Mp >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (2H, d, $J = 8.5$ Hz), 8.20 (4H, s), 7.53–7.50 (4H, m), 7.33–7.31 (6H, m), 7.09 (2H, d, $J = 8.4$ Hz), 7.06 (2H, d, $J = 8.4$ Hz), 6.95 (4H, d, $J = 8.6$ Hz), 4.87 (8H, s), 4.66 (4H, t, $J = 5.8$ Hz), 2.77–2.72 (2H, m). HRESIMS m/z 801.2943 (calcd for $C_{51}H_{42}N_2O_6Na$ 801.2935).

Preparation of Carbazolophane 6. To **12** (0.19 g, 0.24 mmol) suspended in CH_2Cl_2 (600 mL) was added pyridinium *p*-toluenesulfonate (0.61 g, 2.43 mmol). The mixture was stirred at room temperature for 5 days. After the solution was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/dichloromethane) to give **6** (0.04 g, 0.054 mmol, 22%) as white powder. Mp >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (2H, d, $J = 8.4$ Hz), 8.01 (4H, s), 7.62 (2H, d, $J = 8.4$ Hz), 7.54 (2H, t, $J = 7.6$ Hz), 7.40 (2H, t, $J = 7.6$ Hz), 6.84 (4H, d, $J = 8.2$ Hz), 6.60 (4H, d, $J = 8.2$ Hz), 6.20 (2H, d, $J = 8.2$ Hz), 6.05 (2H, d, $J = 8.2$ Hz), 5.10 (4H, br), 4.73 (4H, br), 4.45 (4H, t, $J = 4.7$ Hz), 2.50–2.42 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.21, 141.16, 130.71, 130.23, 126.90, 126.74, 126.07, 125.98, 125.63, 124.78, 123.91, 123.68, 122.47, 121.65, 109.86, 104.73, 75.33, 61.93, 31.86. HRFABMS m/z 742.2826 (calcd for $C_{51}H_{38}N_2O_4$ 742.2832).

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Supporting Information

The transient absorption spectrum of 1-methoxynaphthalene

(Figure S1) is included in Supporting Information. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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