# Synthesis and Properties of π-Conjugated Compounds

# Based on Carbazole or Thiophene

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# Contents

**Chapter 3    Substituent Effects on Photophysical Properties of Thienylanthracenes**

**General Introduction**

Organic electronic devices have attracted much attention because their properties can be easily tuned by suitable molecular design and they can be produced on a large scale at low prices.[1]

There are many reports on the organic materials for preparing electronic devices, such as printable circuits,[2] organic light-emitting diodes (OLEDs),[3] organic field-effect transistors(OFETs),[4] solar cells, and organic memories.[1b]  Especially, OLEDs have already been commercially available as a next-generation display substituted for liquid crystal display (LCD), because OLEDs are easier to make the devices thinner and the electrical power consumption lower than LCD.   Therefore, OLEDs are useful for not only displays but also other applications such as lighting apparatus.[5]

Electron-conducting polymers such as poly(phenylenevinylene) (PPV),[6] poly(p-phenylene),[7] poly(vinylcarbazole) (PVK),[8] and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS)[9] are well-known as examples of organic materials for electronic devices.

poly(phenylenevinylene)
(PPV)

poly(p-phenylene)

poly(vinylcarbazole)
(PVK)

poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
(PEDOT-PSS)
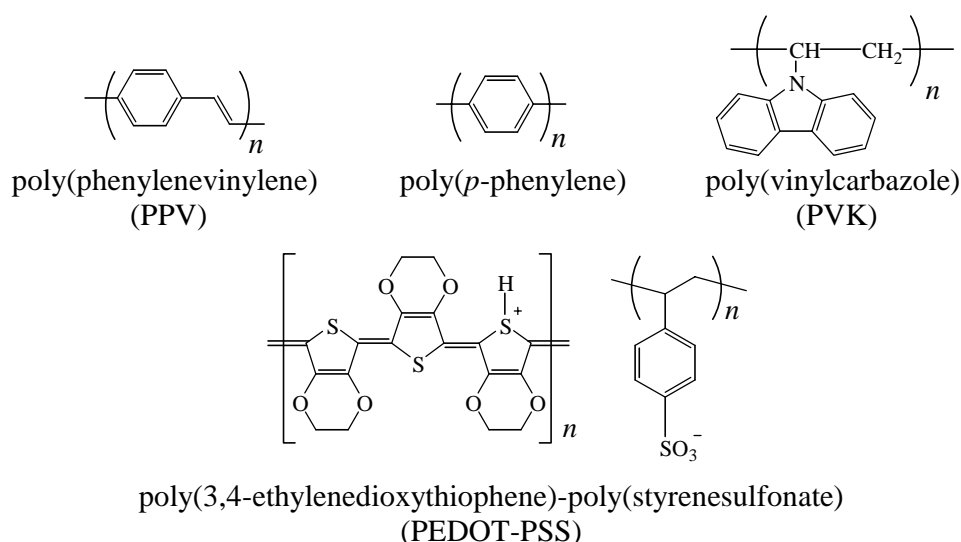
The properties of these polymers are highly dependent on their conformation.[10,11] Therefore, the control of their conformation and high-order structure is important for the

development of new materials. The synthesis and electronic properties of many polymers possessing high stability and specific conformation have been widely investigated.[11] However, the relationship between the structures and properties arising from π-stacked conformation in these polymers has been hardly clarified except for DNA.[12]

Among these polymers, the carbazole-based polymers such as poly(vinylcarbazole) show high hole-transporting properties and photoconductivity.[13] These polymers have also attracted much attention, since they can easily form relatively stable radical cations (holes), various substituents can be easily introduced into the carbazole nuclei, carbazole-containing compounds exhibit high thermal and photochemical stability as well as high durability of glassy state, and carbazole is a cheap material.[14]

PVK is relatively rigid, since the motion of the main chain and side groups is severely restricted due to the bulkiness of carbazole groups. PVK has a glass transition temperature of 227 ˚C, which is one of the highest among the vinyl polymers, and exhibits excellent thermal stability up to at least 300 ˚C.[15]

PVK is soluble in common organic solvents such as benzene, toluene, chloroform, and tetrahydrofuran. PVK is a useful material, since both vacuum deposition method and spin coat method are available for the device fabrication. Many attempts have been done to improve the characteristics of PVK.[16]

The UV absorption spectra of dilute solutions and thin films of PVK are very similar to each other.[17] This observation indicates that the interaction between the chromophores of PVK is small in the ground state. The analysis of electronic transitions of the polymers has been also reported.[18] The fluorescence spectra of PVK in dilute solutions are broad and structureless, and consist of two components of $\lambda_{max} = 420$ nm and 380 nm.[19] The former is attributed to the so-called sandwich-like excimer and the latter to another excimer of partially eclipsed configuration.[20] These excimer formation processes strongly affect the properties of electronic devices based on PVK.

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(Therefore), many experiments have been made to clarify the energy transfer from the light-excited chromophores to the carrier-generation sites in PVK-related polymers.[21] Yokoyama et al. reported the relationship between the hole-transporting mobility and the excimer formation in carbazole derivatives; the hole mobility of carbazole derivatives is decreased with an increase in the quantum yield of excimer fluorescence.[10] They have presumed that the excimer-forming sites are the same as the carrier-trapping sites.[22] This presumption was also supported by the fact that the hole-transporting mobility of *trans*-1,2-bis(carbazolyl)cyclobutane/polycarbonate system (chromophore concentration [Cz] = 2 mM cm$^{-3}$) without excimer formation is higher than that of PVK ([Cz] = 5 mM cm$^{-3}$).[23] Ledwith et al. reported that the carbazole-containing polymers exhibit no excimer emission except when the carbazole units are directly attached to the main chain of polymers.[11]

However, the carbazole rings of PVK generally have various conformations when the carbazole moieties are directly attached to the main chain. The cyclophane structures in which the relative arrangement of two carbazole chromophores is fixed more rigidly are suitable for the elucidation of relationship between the structures and properties in the excimer formation in PVK. The clarification of the excimer formation process is very important for the design of new polymers possessing high charge-generation efficiency and charge-mobility by photo-excitation.

Therefore, I investigated the preparation, characterization, and photophysical properties of carbazole-containing cyclophanes (carbazolophanes). Furthermore, we also investigated the properties of carbazolophanes bearing other aromatic rings at the carbazole *N*-position, in order to clarify the effects of aromatic rings on the electronic and photophysical properties of carbazolophanes. Chapter 1 describes the preparation, characterization, and photophysical properties of various carbazolophanes (Chart 1).
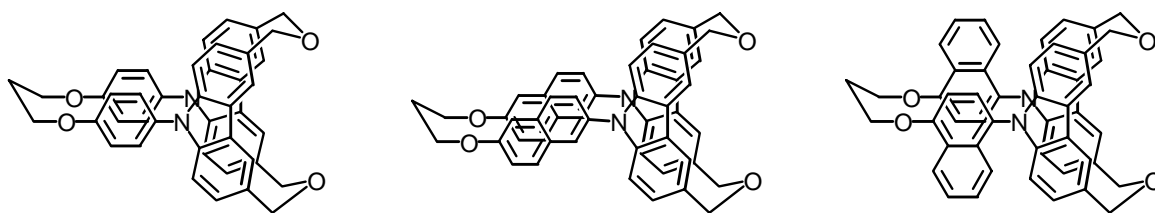
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Chart 1. Carbazolophanes.

Oligothiophenes containing a specific number of thiophene units have been widely used for various applications,[24] because they show high conductivity and unique optical properties.[25] Diarylethene derivatives based on thiophene have attracted much attention as photo-memories and photo-switches because of the reversible and efficient photochromic properties.[26] Oligothiophenes are important as a building-block of new materials with various properties, since their physical properties can be finely tuned by the chain length and terminal substituents.[27] PEDOT-PSS, a typical thiophene-containing material for organic electronic devices, is useful, since the spin coat method is available for the device fabrication.[10] Furthermore, PEDOT-PSS shows high conductivity, provides the smooth surface on ITO, and enables the charge injection and high compatibility between neighboring layers.[10]

Kim et al. reported the formation of black spots (non-luminescence part) in the OLEDs using polyfluorene/PEDOT-PSS.[28] The black spots were considered to arise from the electrochemical reactions including the reduction of PEDOT/PSS and the oxidation of ITO. Therefore, the replacement of PEDOT/PSS by other materials possessing higher conductivity and stability is necessary for the improvement of device lifetime and stability. Nitrogen atom-containing compounds such as triphenylamine and carbazole commonly show high charge-transporting ability as well as high thermal and chemical stability.[29] Thus, these compounds have been reported as hole-transporting materials for organic electronic devices. OLEDs based on oligomers or polymers containing thiophene and carbazole show moderate

device properties.[30] Thiophene-carbazole-containing compound are useful materials, since both vacuum deposition method and spin coat method are available for the device fabrication using these materials. Therefore, we investigated the photophysical properties of the compounds containing both carbazole and thiophene connected directly to obtain the information leading to the improvement of devices. Chapter 2 describes the preparation, characterization, and photophysical properties of some *N*-thienylcarbazoles (Chart 2).
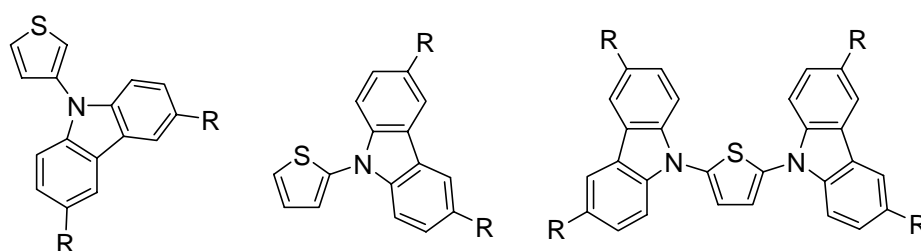
Chart 2. *N*-thienylcarbazoles.

Condensed polycyclic compounds are also interesting as building-blocks of electronic devices. Anthracene derivatives have been widely researched due to their unique photo- and electrochemical properties.[31] Anthracene shows 30% of fluorescence quantum yield and 70% of intersystem crossing[32] from the excited singlet state, and also gives [4 + 4] cyclic adducts.[33] Although anthracene is the first compound used for OLEDs, the device performance was not enough due to the problems of its photophysical and photochemical properties.[34]

However, they have recently attracted much attention as the light-emitting diodes and organic thin film transistors, since the problems such as intermolecular stacking was overcome and the charge-transport properties were improved.[35,36] Blue organic light-emitting diodes using anthracene derivatives bearing bulky substituents at 9- and 10-positions were reported recently.[37]

Furthermore, donor-acceptor-linked compounds containing anthracene and thiophene moieties were investigated as the model compounds for the intramoleculer energy and charge transfer. The interaction between the anthracene and thiophene moieties of these compounds is quite small in the ground state. However, the fluorescence of these compounds is composed of two component whose fluorescence quantum yields are dependent on the temperature. This result suggests the contribution of twisted intramolecular charge transfer (TICT) state.[38] The combination of thiophene and anthracene is expected to provide the high conductivity and moderate fluorescence quantum yields.[39] Therefore, we investigated the photophysical properties of the compounds containing both anthracene and thiophene connected directly to obtain the information on the improvement of devices.

Chapter 3 describes the preparation, characterization, and photophysical properties of some thienylanthracenes (Chart 3).
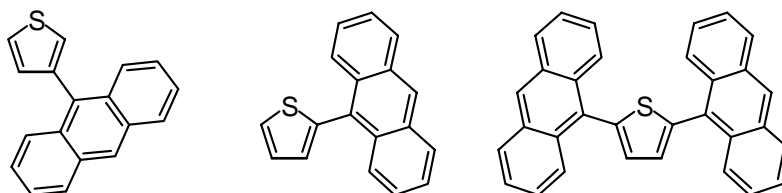


Chart 3. Thienylanthracenes.

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# Chapter 1

## Synthesis and Photophysical Properties of Carbazolophanes
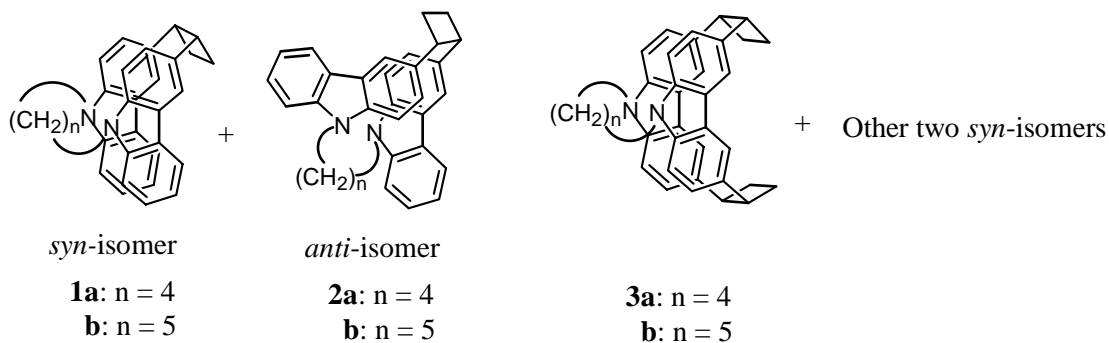
**Abstract**

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.

## 1.1 Introduction

Carbazole is the constituent of poly(*N*-vinylcarbazole) which is well-known as photoconductor, and 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 one of desirable compounds for the elucidation of the relationship between the chromophore arrangement and fluorescence properties.

Dioxa[3.3](3,6)carbazolophane, first synthesized among carbazolophanes 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, 5) were successfully prepared from the corresponding vinyl compounds (Scheme 1-1).[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, 5) by the photoreaction of α,ω-bis(3,6-divinyl-*N*-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.

*syn*-isomer      *anti*-isomer

**1a**: n = 4        **2a**: n = 4        **3a**: n = 4
**b**: n = 5         **b**: n = 5         **b**: n = 5

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 give desired carbazolophane **4**, only giving polymeric products.

Hence, I was stimulated to prepare **5**, in which cyclobutane rings are replaced by -CH$_2$OCH$_2$- units. Cyclophanes possessing cyclobutane rings are generally unstable towards UV lights, mainly due to the cleavages of cyclobutane ring(s), to give precursor vinyl compounds. Actually, some cyclophanes, especially *syn*-isomers, underwent partial decomposition even during the measurement of emission spectra. Our research group recently reported that the use of a –CH$_2$OCH$_2$– linkage instead of cyclobutane ring obviously enhanced the photostability of some cyclophanes including phenanthrene.[7] Furthermore, –CH$_2$OCH$_2$– linkages have an advantage that they can rule out the formation of stereoisomers. Carbazolophane **5** is expected to be readily prepared by the intramolecular etherification of precursor tetrol **13**.

In addition to **5**, the synthesis of carbazolophanes **6** and **7** 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. These properties may also depend on the difference in the bridging positions between **6** and **7**.

In this thesis, I describe the preparation, characterization, and photophysical properties of these carbazolophanes in detail.



**4**        **5**        **6**        **7**
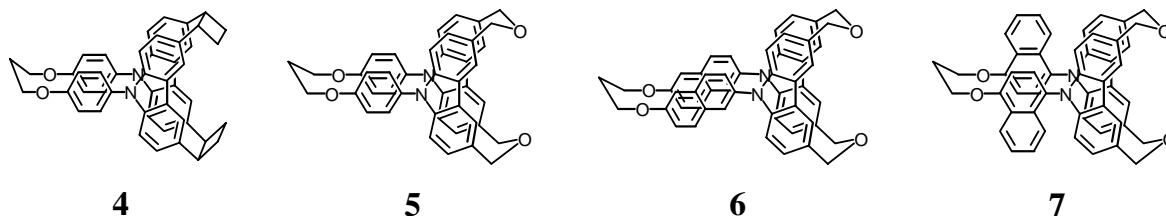
## 1.2 Results and Discussion

### 1.2.1 Synthesis of Carbazolophanes

The synthetic sequences of tetrols **13**, **19**, and **25**, which are the precursors of **5**, **6**, and **7**, respectively, are illustrated in Schemes 1-2, 1-3, and 1-4, respectively.

The palladium-catalyzed coupling reaction[8] of carbazole with dibromide **9**, prepared from 1,3-dibromopropane and 4-bromophenol under basic conditions, was successfully accomplished by using $Pd(dba)_2$ and $(t\text{-}Bu)_3P$ to give **10** in a moderate yield (Scheme 1-2). The bromination of **10** with $Br_2$ in $CCl_4$ afforded **11**, which were transformed into tetraldehyde **12** by lithiation and subsequent treatment with DMF. The conventional $NaBH_4$-reduction of **12** in EtOH yielded **13**.

The reaction of carbazole with dibromide **15**, prepared from 1,3-dibromopropane and 6-bromo-2-naphthol, in the presence of $Pd(dba)_2$ and $(t\text{-}Bu)_3P$ successfully gave **16** in a manner similar to **10** (Scheme 1-3). The bromination of **16** was attempted under conditions similar to that of **10**. However, the naphthalene rings as well as the carbazole rings were subjected to bromination, affording a complex mixture including **18** as a major product. Other various bromination conditions failed to give desired tetrabromide **17** as a main product. Thus, the preparation of carbazolophane **6** has not been accomplished at this stage.

In the preparation of **22**, the copper-catalyzed Ullmann coupling reaction[9] was employed, since the palladium-catalyzed coupling reaction failed to give **22**. The treatment

of carbazole with dibromide **21**, prepared from 1,3-dibromopropane and 4-bromo-1-naphthol, in the presence of copper and $K_2CO_3$ gave **22** in a moderate yield. The bromination of **22** with NBS in DMF successfully afforded **23**, in contrast with **16**; no bromination on the naphthalene rings was observed. Tetrabromide **23** was transformed into tetraldehyde **24** by lithiation and subsequent treatment with DMF. The reduction of **24** by $NaBH_4$ in EtOH yielded **25**.

The intramolecular etherification of **13** toward **5** was carried out in the presence of pyridinium *p*-toluenesulfonate as acid catalyst under high-dilution condition (ca. $1 \times 10^{-4}$ M). The reflux in 1,2-dichloroethane resulted only in the formation of insoluble polymeric products instead of desired **5**. In contrast, the reaction in dichloromethane at room temperature for 10 days successfully afforded **5** in 16% yield. After purification by silica gel column chromatography and GPC, carbazolophane **5** was isolated as a single product.

The intramolecular etherification of **25**, performed for 5 days in a manner similar to **5**, successfully afforded **7** in 23% yield. Carbazolophane **7** was also isolated as a single product by purification using silica gel column chromatography.

### 1.2.2 Structures of Carbazolophanes

The structures of carbazolophanes **5** and **7** obtained were definitely characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **5** showed a quite simple pattern consistent with its symmetry (Figure 1-1). Five sets of aromatic proton signals (three for carbazole and two for benzene rings) are observed, and they are generally high-field shifted compared to those of precursor **13**, indicating that the two *N*-phenylcarbazole chromophores are well overlapped with each other and subjected to their shielding effect. The benzyl protons were split into two broadened doublets, in contrast with those observed as a sharp singlet in **13**, indicating the formation of cyclic structure and dynamic behavior of -$CH_2OCH_2$- linkages. The number of signals in ^{13}C NMR spectrum is also consistent with

the structure of **5**.

The $^1$H NMR spectral pattern of **7** is similar to that of **5** (Figure 1-2).   The carbazole protons are generally high-field shifted compared to those of precursor **25**, suggesting that the two carbazole moieties are well overlapped with each other.   The benzyl protons are observed as two broadened doublets.   These observations apparently support the formation of cyclophane framework.   For the naphthalene rings, H2 and H3 protons are remarkably high-field shifted relative to **25**, 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 are overlapped with each other.

The single crystals of **5** and **7** suitable for the X-ray crystallographic analysis were obtained by recrystallization from hexane and dichloromethane.

The ORTEP drawing of **5** is illustrated in Figure 1-3.   The two carbazole rings are favorably overlapped, as already suggested by the $^1$H NMR spectrum.   The benzene ring is rather twisted relative to the carbazole ring, and the dihedral angle is about 50˚.   The distance between the two nitrogen atoms of carbazoles is 4.57 Å.

The ORTEP drawing of **7** is illustrated in Figure 1-4.   The two carbazole rings are well overlapped.   The naphthalene rings are only partially overlapped, as suggested by the $^1$H NMR spectrum.   The dihedral angle between the naphthalene ring and carbazole ring is about 60˚, which is larger than that in **5**.   This is probably ascribed to the steric repulsion between the naphthalene protons and carbazole protons.   The distance between the two nitrogen atoms of carbazole is 4.61 Å, slightly longer than that in **5**.   The steric repulsion between the two naphthalene rings may increase the distance between the two carbazole rings.

### 1.2.3 Electronic, Photophysical, and Electrochemical Properties of Carbazolophanes

**Absorption Spectra**

Figure 1-5 shows the absorption spectrum of carbazolophane **5** in cyclohexane at room temperature along with those of **10** and *N*-(4-methoxyphenyl)carbazole (**26**) for the comparison.

The absorption spectrum of **10** is quite similar to that of **26**, indicating that the two carbazole rings of **10** are not sufficiently close to each other and their interaction is almost negligible in the ground state. In contrast, the absorption spectrum of carbazolophane **5** exhibits considerable broadening and slight red shift relative to **10** and **26**. 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]

The absorption spectra of **5**, **10**, and **26** were also measured in polar acetonitrile (Figure 1-6). The spectra obtained resemble those in cyclohexane. These absorption spectra appear to be almost independent of solvents.

The absorption spectra of carbazolophane **7**, reference compound **22**, and *N*-(4-methoxy-1-naphthyl)carbazole (**27**) possessing naphthalene rings instead of benzene rings measured in cyclohexane and acetonitrile are illustrated in Figures 1-7 and 1-8.

The spectral shape of **27** is rather different from that of **26**. The 4-alkoxynaphthalene moiety appears to perturb the electronic state of carbazole. The absorption spectrum of **22** is quite similar to that of **27**, as in the case of **10** and **26**. In contrast, the absorption spectrum of carbazolophane **7** exhibits considerable broadening and red shift relative to **22** and **27**, indicating the electronic interaction between the carbazole rings. The broadening in **7** is more remarkable than that in **5**. The electronic effect of 4-alkoxynaphthalene moiety on carbazole seems to be larger than that of benzene moiety.

**Fluorescence Spectra**

The fluorescence spectra of carbazolophane **5** were measured in cyclohexane and acetonitrile at room temperature and are depicted in Figure 1-9. The fluorescence spectra of **10** and **26** are also shown in Figure 1-9.

The fluorescence spectra of **10** and **26** in cyclohexane are composed of vibrational structures and again resemble each other. These spectra are characteristic of the carbazole monomer fluorescence, suggesting that the interaction between the two carbazole rings is small in the excited state in **10**, and intramolecular excimer is not formed.

On the contrary, carbazolophane **5** exhibited red-shifted broad emission without vibrational structures with a maximum at 425 nm in cyclohexane. The peak shift from the 0–0 transition band of monomer fluorescence of **26** 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. The maximum wavelength ($\lambda_{max}$) is slightly red-shifted compared to carbazolophane **3a** 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 that this emission originates from carbazolophane **5**.

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 **10** and **26** in acetonitrile. As reported in the literature, 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 *N*-arylcarbazole with an unsubstituted

phenyl group shows almost no solvent effects.[12]   It is noteworthy that **10** and **26** carrying an electron-donating methoxy group exhibit such a solvent effect.   This behavior may result from the difference of dipole moment between the excited state and the ground state.

Figure 1-10 illustrates the fluorescence spectra of **7**, **22**, and **27** bearing naphthalene rings in cyclohexane and acetonitrile.

Surprisingly, the spectrum of **27** in cyclohexane is rather broadened and red-shifted compared to that of **26**.   The vibrational structures characteristic of carbazole monomer almost disappear in **27**.   These observations can be tentatively explained as follows.   Since the $S_1$ energy of carbazole is lower than that of naphthalene, the fluorescence of **27** shows a character of carbazole rather than naphthalene.   However, the interaction with naphthalene brings the remarkable broadening and red shift.   The spectra of **22** and **27** in cyclohexane are quite similar to each other, as in the case of **10** and **26**.   In **22**, intramolecular excimer is not formed.

Carbazolophane **7** in cyclohexane exhibits broad emission similar to **5**, though it is blue-shifted relative to **5** ($\lambda_{max}$ = 409 nm).   This emission is also interpreted as excimer fluorescence of carbazole.   The blue shift may result from the increased distance between the two carbazole rings due to the steric repulsion between the naphthalene rings.

In acetonitrile, carbazolophane **7** also exhibits a broad fluorescence ($\lambda_{max}$ = 415 nm), which is slightly red-shifted compared to that in cyclohexane.   The spectra of **22** and **27** in acetonitrile are further red-shifted and broadened compared to those in cyclohexane, as in the case of **10** and **26**.

**Fluorescence Lifetime and Quantum Yield**

The fluorescence decay functions of **5** and **10** bearing benzene rings and **7** and **22** bearing naphthalene rings were measured in degassed cyclohexane at 298 K by means of the nanosecond single-photon-counting method.   The decay functions were analyzed (by the

deconvolution method) as a single-exponential function or a sum of double-exponential functions (Eq. 1).


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


Table 1-1 lists the fluorescence lifetimes ($\tau$) and the ratio of each decay component just after excitation ($A_1$, $A_2$).

Figure 1-11 shows the typical fluorescence decay functions of **10**, excited at 280 nm and monitored at 350 nm.    This decay profile was satisfactorily analyzed as a single-exponential function with a lifetime of 8.34 ns.    On the contrary, 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. However, the ratio is too small to discuss in further detail (ca. 2%).

It is noteworthy that the difference in fluorescence lifetimes between **5** and **10** is relatively small, in spite of the remarkable difference in their spectral shape; **5** provides excimer fluorescence, while **10** gives monomer fluorescence.

Figure 1-12 shows the typical fluorescence decay functions of **22**, excited at 280 nm and monitored at 420 nm.    This decay profile was satisfactorily analyzed as a single-exponential function with a lifetime of 6.43 ns.    The decay profile of carbazolophane **7** was also fitted to a single-exponential function with a lifetime of ca. 7 ns.    The difference in fluorescence lifetimes between **7** and **22** is quite small, as in the case of **5** and **10**; it is smaller than that between **5** and **10**.    The fluorescence lifetimes of **7** and **22** bearing naphthalene rings are shorter than those of **5** and **10**, respectively.    The naphthalene rings of **7** and **22** affect the fluorescence lifetimes as well as the spectra.

The fluorescence quantum yields ($\Phi_f$) of **5**, **10**, **7**, and **22** were determined in degassed

cyclohexane at room temperature by using 1-naphthylamine (1-NA) as a standard ($\Phi_f = 0.465$). Based on $\Phi_f$ and $\tau_f$, the radiative rate constant ($k_f$) and nonradiative rate constant ($k_{nr}$) were determined (Eq. 2 and 3).

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

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

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

Similar tendencies were observed for **7** and **22**; the $\Phi_f$ of **7** is only about 1/10 of **22**, and the $k_f$ of **7** is less than 1/10 of that of **22**. The $\Phi_f$ of **7** and **22** is slightly larger than that of **5** and **10**, respectively. The $k_f$ of **7** and **22** is also larger than that of **5** and **10**, respectively, since the $\tau_f$ of **7** and **22** is shorter than that of **5** and **10**. The naphthalene rings on the nitrogen atoms apparently affect the properties of carbazole in the excited singlet state.

**Phosphorescence Spectra**

The total emission spectra, phosphorescence spectra, and excitation spectra of **5** and **10** were measured in MP (methylcyclohexane/isopentane (4/1)) at 77 K. These spectra are shown in Figure 1-13 along with those of *N*-ethylcarbazole as a reference.

The fluorescence spectra of **5** and **10** at 77 K appear to be essentially the same as those measured at room temperature; **5** exhibits broad structureless excimer fluorescence, while **10** gives monomer fluorescence with vibrational structures. The vibrational structures of **10** are

more sharpened compared to those at room temperature.  The peak positions in **10** are slightly red-shifted relative to *N*-ethylcarbazole.

The phosphorescence spectrum of **10** 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.  These emissions of **5** are remarkably different from the monomer phosphorescence in **10** or *N*-ethylcarbazole.  They 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 **10**.  Thus, it is concluded that **5** forms excimer in both singlet and triplet excited states.

The phosphorescence lifetimes of **5** and **10** were 5.2 and 5.3 sec, respectively.  These lifetimes are of the same order as that of *N*-methylcarbazole (7 sec).[14]

The total emission spectra, phosphorescence spectra, and excitation spectra of **7** and **22** measured in MP (methylcyclohexane/isopentane (4/1)) at 77 K are shown in Figure 1-14 along with those of 1-methoxynaphthalene as a reference.

The fluorescence spectra of **7** and **22** at 77 K appear to be essentially the same as those measured at room temperature; **7** exhibits broad structureless excimer fluorescence, while **22** shows a fluorescence different from simple carbazole monomer fluorescence, suggesting the interaction of carbazole with naphthalene.

The phosphorescence spectrum of **22** exhibits vibrational structures, which are similar to those of 1-methoxynaphthalene, not *N*-ethylcarbazole, as is evident from the wavelength. 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 energy of 1-methoxynaphthalene ($E_{T1}$ = 250 kJ/mol) is lower than that of carbazole ($E_{T1}$ = 294 kJ/mol), in contrast with their $S_1$ ($E_{S1}$ = 374 kJ/mol for 1-methoxynaphthalene; $E_{S1}$ = 347 kJ/mol for carbazole).[15,16] This behavior is different from that for **10**. In **10**, 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 **7** is also similar to that of 1-methoxynaphthalene, indicating the monomer phosphorescence of naphthalene, as in the case of **22**. Due to the lower $T_1$ level of 1-methoxynaphthalene than carbazole, the phosphorescence should have a naphthalene-like character. In **7**, two naphthalene rings are not sufficiently overlapped with each other, as demonstrated by $^1$H NMR spectrum and X-ray crystallography. Hence, it is quite reasonable that **7** afforded naphthalene monomer phosphorescence, not excimer phosphorescence. Thus, **7** provided excimer fluorescence of carbazole and monomer phosphorescence of naphthalene, reflecting the relationship of excitation energy between carbazole and naphthalene and their arrangement (the extent of overlap). The phosphorescence lifetimes of **7** and **22** were 0.8 and 1.7 sec, respectively. The latter is comparable to that of 1-methoxynaphthalene (2 sec).


**Transient Absorption Spectra**

The transient absorption spectra of **5**, **10**, **7**, and **22** were obtained at several delay times after laser pulsing at 308 nm in degassed cyclohexane at 293 K.

The spectra of **5** and **10** are illustrated in Figure 1-15 along with those of *N*-ethylcarbazole as a reference.

The spectra of *N*-ethylcarbazole with a sharp maximum around 400 nm are assigned to the triplet-triplet (T–T) absorption. The spectral behavior of **10** is quite similar to that of *N*-ethylcarbazole. Thus, the transient absorptions of **10** are obviously ascribable to the T–T absorption of carbazole moiety. Their lifetimes are almost on the same order (**10**: 170 μs; *N*-ethylcarbazole: 340 μs), although their decay functions could not completely be 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 **10** and *N*-ethylcarbazole. Hence, it is apparent that the absorptions observed for **5** are not local triplet species of carbazole. Probably, these absorptions are derived from the triplet excimer, as suggested by the phosphorescence spectrum.

The spectra of **7** and **22** are illustrated in Figure 1-16 along with those of **27** (and 1-methoxynaphthalene) as a reference.

The spectra of **27** exhibit a rather sharp band with a maximum of ca. 430 nm and a broad band around 500–800 nm. The shape and position of the former band are similar to those of the T–T absorption for 1-methoxynaphthalene rather than *N*-ethylcarbazole. The broad band in the longer wavelength region, which is observed in neither 1-methoxynaphthalene nor *N*-ethylcarbazole, probably originates from the interaction between carbazole and naphthalene. On the whole, the spectra of **27** are regarded as the T–T absorption of a naphthalene-like character rather than a carbazole-like character, with including the interaction between both chromophores. These observations are consistent with the relationship of excitation energy between carbazole and naphthalene. The spectra of **22** and **7** are also similar to those of **27**, although the band in the shorter wavelength region is slightly broadened in **7**. Thus, both **22** and **7** essentially show the T–T absorption of *N*-(4-alkoxy-1-naphthyl)carbazole moiety.

## Electrochemical Properties

The electrochemical properties of **5**, **7**, **10**, and **22** were investigated by cyclic voltammetry (CV) in benzonitrile. Their voltammograms are shown in Figure 1-17. Both carbazolophanes **5** and **7** showed reversible redox waves, whereas **10** and **22** showed rather

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irreversible waves.　The irreversible behavior of **10** and **22** indicates that the resulting cation radicals are relatively unstable, probably due to the absence of substituents at the reactive 3- and 6-positions of carbazole.　The reversible processes of **5** and **7** in contrast with **10** and **22** apparently result from the stabilization of cation radicals by the –CH$_2$OCH$_2$– linkages at the 3- and 6-positions of carbazole.

Both **5** and **7** showed two sets of redox waves, in contrast with one oxidation wave in **10** and **22**.　The two sets of waves in **5** and **7** indicate that the two carbazole moieties are not oxidized concurrently, but oxidized at different potentials; the interaction between the two carbazole moieties is larger than that in **10** and **22** due to the almost parallel arrangement with a suitable distance in the cyclophane framework.　As apparently demonstrated by the oxidation potentials, both **5** and **7** are higher in the electron-donating property than **10** and **22**. This is probably because the resulting cation is stabilized by the delocalization of positive charge over the two *N*-arylcarbazole moieties in **5** and **7**.　Carbazolophane **7** is less easily oxidized than **5**, suggesting that the distance between the two carbazole moieties in **7** is slightly larger than that in **5**, leading to the smaller interaction.

### 1.3 Conclusion

Two novel carbazolophanes **5** and **7** bearing aromatic rings on the nitrogen atoms were successfully prepared by the intramolecular etherification of precursor tetrols **13** and **25**, respectively, in the presence of acid catalyst.　The synthesis of carbazolophane **6** has not been accomplished.　The structures of **5** and **7** were distinctly characterized by ^{1}H NMR spectra and X-ray crystallographic analysis, which indicate that the two carbazole moieties are well overlapped with each other in both **5** and **7**, and the naphthalene rings are only partially overlapped in **7**.

Both **5** and **7** provided broadened and red-shifted absorption spectra compared to those of reference compounds **10** and **22**.　Both **5** and **7** exhibited excimer-like fluorescence with a

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maximum at 425 and 409 nm, respectively, at room temperature.

The photophysical properties of carbazolophanes **5** and **7** were investigated in further detail and compared with those of reference compounds **10** and **22**; the fluorescence lifetime, quantum yield, phosphorescence spectra, and transient absorption spectra were disclosed.

The radiative rates ($k_f$) of carbazolophanes **5** and **7** are less than 1/10 of those of reference compounds **10** and **22**, respectively, while the nonradiative rates ($k_{nr}$) of **5**, **7**, **10**, and **22** are of the same order. The radiative rates ($k_f$) of **7** and **22** bearing naphthalene rings are slightly larger than those of **5** and **10** 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, **7** 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. These spectra also suggest the triplet carbazole excimer. The transient absorption spectra of **7** 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 **27**.

From these observations, it is concluded that **5** forms carbazole excimer in the excited triplet state as well as the excited singlet state. In contrast, **7** forms carbazole excimer only in the excited singlet state and naphthalene monomer in the excited triplet state. These results are reasonably explained by the relationship of excitation energy between carbazole and benzene (or naphthalene) and their arrangement (the extent of overlap). The introduction of aromatic rings on the carbazole nitrogen atoms sensitively affects the electronic and photophysical properties of carbazolophanes.

## 1.4 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 an F-4500 spectrophotometer. These spectra were obtained in cyclohexane (spectroscopic grade) with a quartz cell of 10 mm optical path. GPC was performed with a JAI LC-918 R/U Recycling Preparative HPLC using JAIGEL-1H and 2H columns.

The fluorescence lifetimes ($\tau_f$) were obtained with a time-correlated single-photon counting (TCSPC) fluorometer (Edinburgh Analytical Instruments FL900CDT).

A nanosecond pulsed discharge lamp (pulse width ~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 ($\Phi_f$) 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.

$$\Phi_{fX} = \frac{F_X \, A_{ST} \, n_X^2}{F_{ST} \, A_X \, n_{ST}^2} \Phi_{fST} \tag{4}$$

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 $\Phi_f$ walue ($\Phi_{fST} = 0.47$) of 1-aminonaphthalene in cyclohexane was used as a standard solution.

Phosphorescence spectra and lifetime ($\tau_p$) 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 ~17 ns) were 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 the freeze-pump-thaw method.

**Preparation of 10**

A mixture of **9**[17] (13.7 g, 35.5 mmol), carbazole (12.5 g, 74.5 mmol), Pd(dba)$_2$ (0.82 g, 1.42 mmol), ($t$-Bu)$_3$P (0.72 g, 3.55 mmol), and $t$-BuONa (10.2 g, 106 mmol) in dry toluene (30 mL) was refluxed for 39 h. After addition of water (150 mL), the mixture was extracted with diethyl ether (three time) and toluene (three times). The combined organic phase was washed with brine (three times), dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **10** (14.1 g, 25.2 mmol, 71%) as white powder. Mp 194–195 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 8.15 (4H, d, $J$ = 7.6 Hz), 7.47 (4H, d, $J$ = 8.9 Hz), 7.42-7.26 (12H, m), 7.15 (4H, d, $J$ = 8.9 Hz), 4.34 (4H, t, $J$ = 6.0 Hz), 2.42 (2H, m). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 158.10, 141.29, 130.37, 128.59, 125.83, 123.06, 120.26, 119.63, 115.58, 109.65, 64.63, 29.33.

**Preparation of 11**

To a solution of **10** (1.10 g, 1.97 mmol) in carbon tetrachloride (250 mL) was added bromine (0.80 mL, 15.4 mmol) at 0 °C. After stirring at room temperature for 5 h, 5% aqueous NaHSO$_3$ solution (250 mL) was added to the mixture, which was extracted with chloroform (three times). The combined organic phase was successively washed with aqueous NaHCO$_3$ solution (once) and water (twice), dried over anhydrous MgSO$_4$, and

concentrated under reduced pressure.    The residue was recrystallized from toluene to give **11** (1.41 g, 1.61 mmol, 82%) as white crystals.    Mp 125–126 ˚C.    ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 (4H, s), 7.48 (4H, d, $J$ = 8.2 Hz), 7.39 (4H, d, $J$ = 8.6 Hz), 7.17 (4H, d, $J$ = 8.2 Hz), 7.15 (4H, d, $J$ = 8.6 Hz), 4.33 (4H, t, $J$ = 5.1 Hz), 2.42 (2H, m).    ^{13}C NMR (125 MHz, CDCl$_3$): δ 158.48, 140.24, 129.37, 129.27, 128.41, 123.65, 123.15, 115.74, 112.80, 111.37, 64.58, 29.24.

**Preparation of 12**

    To a three-neck flask containing **11** (1.72 g 1.97 mmol) was added dry THF (200 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 (7.6 mL, 12.0 mmol) was added to the solution, and the mixture was stirred for 30 min at the temperature.    After addition of DMF (1.86 mL, 24.0 mmol) in dry THF (20 ml), the reaction mixture was stirred at room temperature for 2 h.    The reaction was quenched by adding 5% aqueous ammonium chloride solution (100 mL).    The organic phase was separated, and the 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 purified by column chromatography (silica gel, toluene/ethyl acetate) to afford **12** (0.51 g, 0.76 mmol, 38%) as white powder.    Mp 135–136 ˚C.    ^{1}H NMR (500 MHz, CDCl$_3$): δ 10.16 (4H, s), 8.73 (4H, s), 8.01 (4H, d, $J$ = 8.2 Hz), 7.47 (4H, d, $J$ = 8.6 Hz), 7.41 (4H, d, $J$ = 8.2 Hz), 7.22 (4H, d, $J$ = 8.6 Hz), 4.37 (4H, t, $J$ = 5.1 Hz), 2.46 (2H, m).    ^{13}C NMR (125 MHz, CDCl$_3$): δ 191.51, 159.11, 145.71, 130.22, 128.56, 128.30, 127.98, 124.22, 123.22, 115.97, 110.77, 64.63, 29.19.

**Preparation of 13**

    A mixture of **12** (0.30 g, 0.45 mmol) and NaBH$_4$ (0.25 g, 6.6 mmol) in ethanol (70 mL)

was stirred at 30 °C for 5 h.   The mixture was diluted with water (70 mL), and neutralized by a small amount of acetic acid.   After ethanol was evaporated under reduced pressure, the residue was extracted with ethyl acetate (three times).   The combined organic phase was washed with water (twice), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure, to give **13** (0.24 g, 0.35 mmol, 80%) as white powder.   This compound was used for the following reaction without further purification.   Mp > 300 °C.   ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (4H, s), 7.43 (4H, d, $J$ = 8.6 Hz), 7.39 (4H d, $J$ = 8.2 Hz), 7.29 (4H, d, $J$ = 8.2 Hz), 7.16 (4H, d, $J$ = 8.6 Hz), 4.86 (8H, s), 4.35 (4H, t, $J$ = 5.1 Hz), 2.41 (2H, m).   ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.19, 141.31, 136.64, 132.50, 128.45, 125.79, 123.05, 119.35, 115.67, 109.89, 66.01, 29.71.

## Preparation of Carbazolophane 5

To **13** (0.19 g, 0.28 mmol) suspended in $CH_2Cl_2$ (300 mL) was added pyridinium *p*-toluenesulfonate (0.72 g, 2.82 mmol).   The mixture was stirred at room temperature for 10 days.   After the solution was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, toluene/dichloromethane) and GPC (polystyrene, chloroform) to give **5** (0.03 g, 0.047 mmol, 16%) as white powder.   Mp > 300 °C.   ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (4H, s), 6.95 (4H, d, $J$ = 8.2 Hz), 6.89 (4H, d, $J$ = 8.2 Hz), 6.83 (4H, d, $J$ = 8.6 Hz), 6.65 (4H, d, $J$ = 8.6 Hz), 5.00 (4H, bd), 4.77 (4H, bd), 4.27 (4H, t, $J$ = 5.1 Hz), 2.17 (2H, m).   ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.04, 139.53, 130.81, 127.33, 126.38, 125.70, 123.20, 121.69, 114.94, 108.93, 75.47, 62.48, 31.18.   HRMS: *m/z* calcd for $C_{43}H_{34}N_2O_4$: 642.2519; found: 642.2523.

## Preparation of 15

A mixture of 6-bromo-2-naphthol (6.64 g, 29.8 mmol) and NaOH (1.43 g, 35.7 mmol) was refluxed in acetonitrile (300 mL) for 1 h.   After addition of 1,3-dibromopropane (2.0 g,

9.91 mmol), the mixture was further refluxed for 39 h.   After addition of water (150 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.   The residue was washed with a small amount of ethanol to afford pure **15** (2.79 g, 5.74 mmol) as white powder.   ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.90 (2H, s), 7.64 (2H, d, $J$ = 8.8 Hz), 7.57 (2H, d, $J$ = 8.6 Hz), 7.48 (2H, d, $J$ = 8.8 Hz), 7.17 (2H, d, $J$ = 8.9 Hz), 7.13 (2H, s), 4.31 (4H, t, $J$ = 6.1 Hz), 2.40 (2H, m).

**Preparation of 16**

A mixture of **15** (2.50 g, 5.14 mmol), carbazole (1.81 g, 10.8 mmol), Pd(dba)$_2$ (0.12 g, 0.21 mmol), ($t$-Bu)$_3$P (0.10 g, 0.51 mmol), and $t$-BuONa (1.48 g, 15.4 mmol) in dry toluene (50 mL) was refluxed for 21 h.   After addition of water (60 mL), the mixture was extracted with diethyl ether (three time) and toluene (three times).   The combined organic phase was washed with brine (three times), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure.   The residue was purified by column chromatography (silica gel, hexane/ toluene) to afford **16** (3.24 g, 4.92 mmol, 96%) as white powder.   ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.16 (4H, d, $J$ = 8.6 Hz), 7.94 (4H, d, $J$ = 8.8 Hz), 7.81 (2H, d, $J$ = 9.0 Hz), 7.61 (2H, d, $J$ = 8.6 Hz), 7.41 (8H, m), 7.30 (8H, m), 4.43 (4H, t, $J$ = 5.9 Hz), 2.49 (2H, m).

**Preparation of 21**

A mixture of 4-bromo-1-naphthol (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 **21** (14.2 g, 29.3 mmol) as white powder. Mp 137.9-138.5 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.29 (2H, d, *J* = 8.4 Hz), 8.16 (2H, d, *J* = 8.4 Hz), 7.64 (2H, d, *J* = 8.3 Hz), 7.60 (2H, m), 7.50 (2H, m), 6.73 (2H, d, *J* = 8.3 Hz) , 4.43 (4H, t, *J* = 6.1 Hz) , 2.57 (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$_2$O$_2$: C, 56.82; H, 3.73%. Found: C, 56.50; H, 3.70%.

**Preparation of 22**

A mixture of **21** (7.00 g, 14.4 mmol), carbazole (6.01 g, 35.9 mmol), K$_2$CO$_3$ (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 **22** (7.52 g, 11.4 mmol, 79%). Mp 136.8-137.7 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.46 (2H, d, *J* = 8.4 Hz), 8.18 (4H, d, *J* = 8.2 Hz), 7.54 (2H, d, *J* = 7.9 Hz), 7.50 (2H, m), 7.30 (10H, m), 7.14 (2H, d, *J* = 8.3 Hz), 7.06 (2H, d, *J* = 8.1 Hz), 6.98 (4H, d, *J* = 7.1 Hz) , 4.63 (4H, t, *J* = 6.0 Hz), 2.73 (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$_2$O$_2$·1/2H$_2$O: C, 84.53; H, 5.28; N, 4.19%. Found: C, 84.52; H, 5.27; N, 4.19%.

**Preparation of 23**

To a solution of **22** (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 **23** (0.14 g, 0.14 mmol, 81%). Mp 261.4-263.3 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.47 (2H, d, $J$ = 8.1 Hz), 8.25 (4H, s), 7.51 (4H, m), 7.41 (4H, d, $J$ = 8.7 Hz), 7.34 (2H, m), 7.03 (4H, m), 6.84 (4H, d, $J$ = 8.6 Hz), 4.64 (4H, t, $J$ = 5.7 Hz), 2.74 (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 24**

To a three-neck flask containing **23** (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 the 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 **24** (0.51 g, 0.66 mmol, 42%) as white powder. Mp 192.2-193.4 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ 10.16 (4H, s), 8.79 (4H, s), 8.53 (2H, d, $J$ = 8.1 Hz), 7.95 (4H, d, $J$ = 8.6 Hz), 7.58 (4H, m), 7.39 (2H, m), 7.12 (4H, d, $J$ = 8.8 Hz), 7.05 (4H, m), 4.69 (4H, t, $J$ = 5.8 Hz), 2.79 (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 25**

A mixture of **24** (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 **25** (0.33 g, 0.42 mmol, 88%) as white powder. This compound was used for the following reaction without further purification. Mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (2H, d, $J = 8.5$ Hz), 8.19 (4H, s), 7.51 (4H, m), 7.32 (2H, m), 7.32 (4H, d, $J = 8.4$ Hz), 7.09 (2H, d, $J = 9.4$ Hz), 7.05 (2H, d, $J = 8.3$ Hz), 6.95 (4H, d, $J = 8.2$ Hz), 4.86 (8H, s), 4.65 (4H, t, $J = 5.8$ Hz), 2.74 (2H, m). HRESIMS $m/z$ 801.2943 (calcd for $C_{51}H_{42}N_2O_6Na$ 801.2935).


**Preparation of Carbazolophane 7**

To **25** (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 **7** (0.04 g, 0.057 mmol, 23%) as white powder. Mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (2H, d, $J = 8.3$ Hz), 8.00 (4H, s), 7.62 (2H, d, $J = 8.4$ Hz), 7.53 (2H, t, $J = 7.6$ Hz), 7.39 (2H, t, $J = 7.6$ Hz), 6.83 (4H, d, $J = 8.3$ Hz), 6.59 (4H, d, $J = 8.4$ Hz), 6.20 (2H, d, $J = 8.4$ Hz), 6.04 (2H, d, $J = 8.4$Hz), 5.06 (4H, br d), 4.75 (4H, br d), 4.45 (4H, m), 2.43 (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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*syn*-isomer

**1a**: n = 4
**b**: n = 5

*anti*-isomer

**2a**: n = 4
**b**: n = 5

+ Other two *syn*-isomers

**3a**: n = 4
**b**: n = 5

Scheme 1-1

**8**

1.3-dibromopropane,
NaOH
$\overrightarrow{CH_3CN}$

**9**   Y. 62%

Carbazole
$\overrightarrow{Pd(dba)_2, (t\text{-}Bu)_3P,}$
$t\text{-}BuONa, toluene$

**10**   Y. 71%

$\overrightarrow{\dfrac{Br_2}{CCl_4}}$

**11**   Y. 82%

1) *n*-BuLi, THF
2) DMF

**12**   Y. 38%

$\overrightarrow{\dfrac{NaBH_4}{EtOH}}$

**13**   Y. 80%

Pyridinium
*p*-toluenesulfonate
$\overrightarrow{CH_2Cl_2}$

**5**   Y. 16%

Scheme 1-2

**14**

1.3-dibromopropane,
NaOH
CH₃CN

**15**  Y. 58%

Carbazole

Pd(dba)₂, (*t*-Bu)₃P,
*t*-BuONa, toluene

**16**  Y. 96%

**17**

+

**18**

**19**

**6**
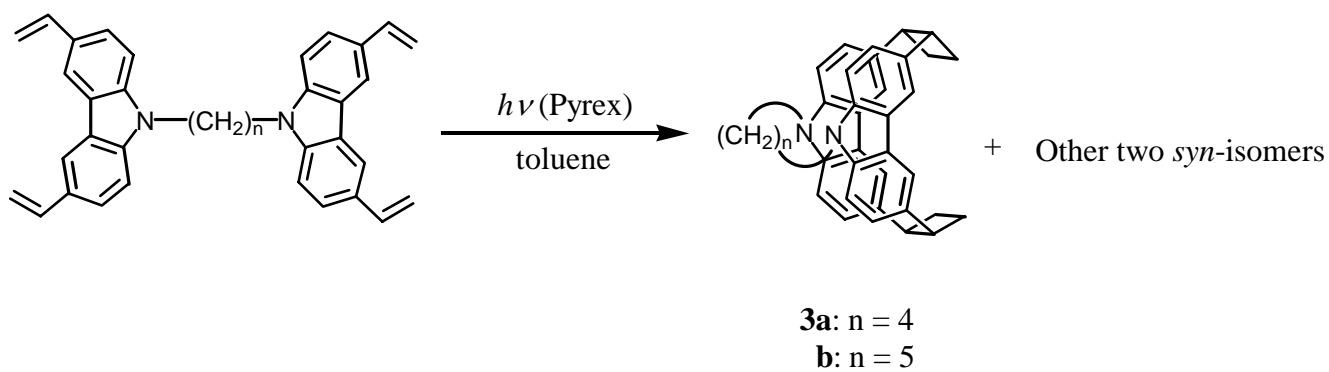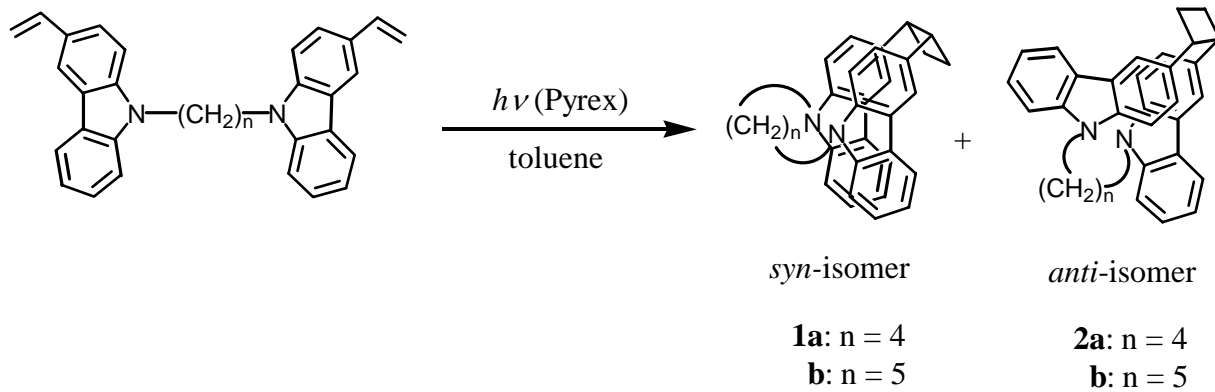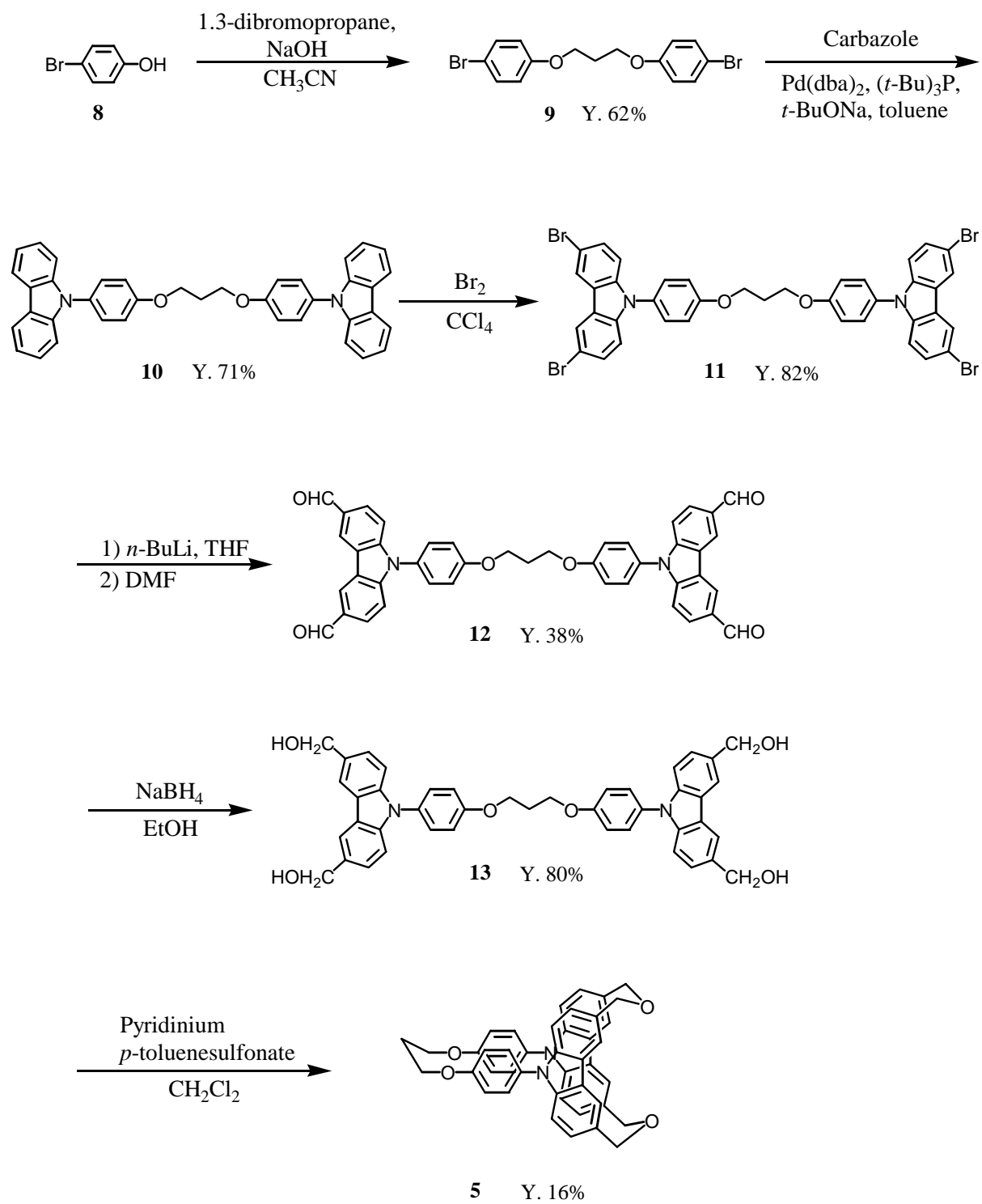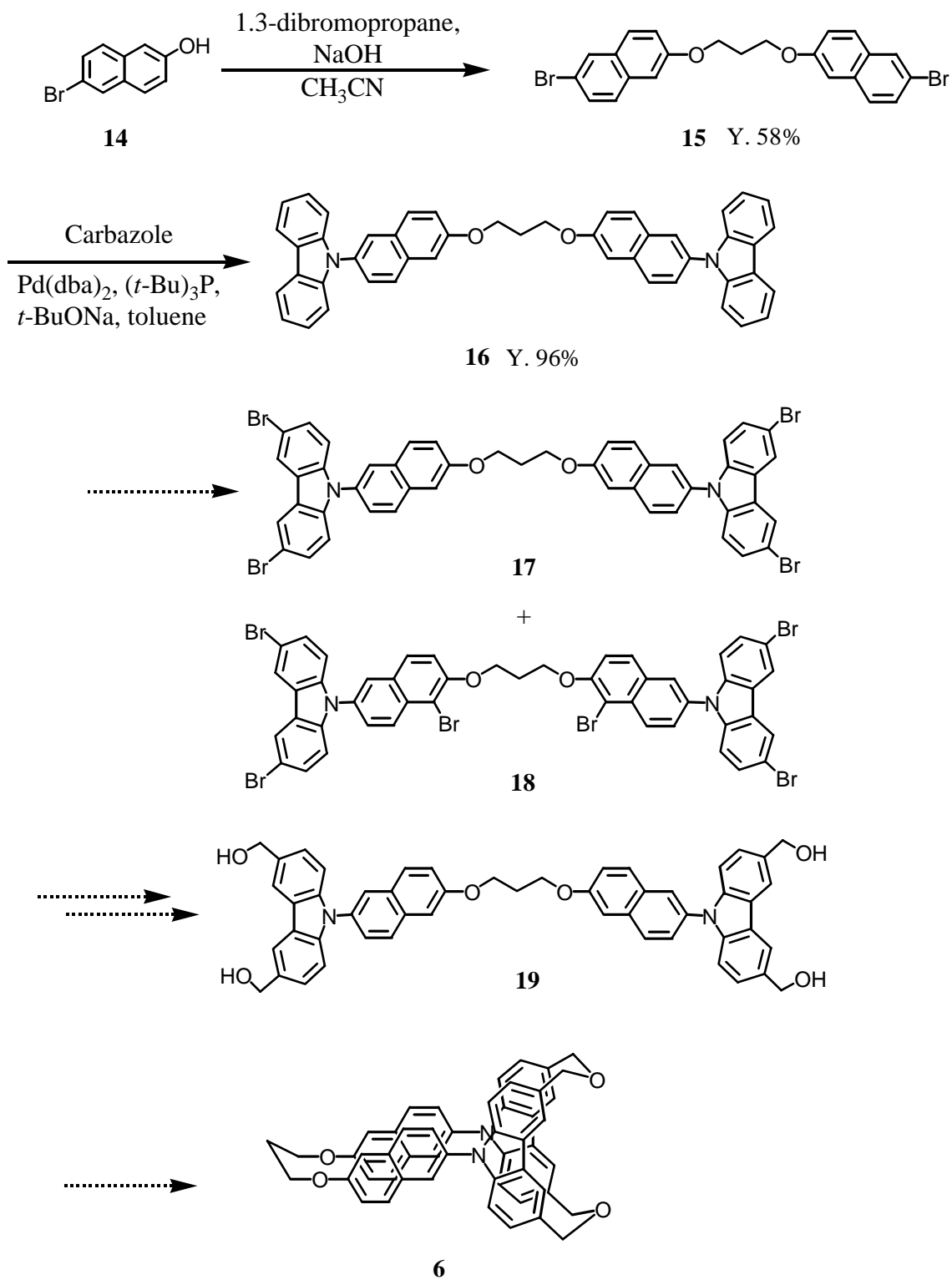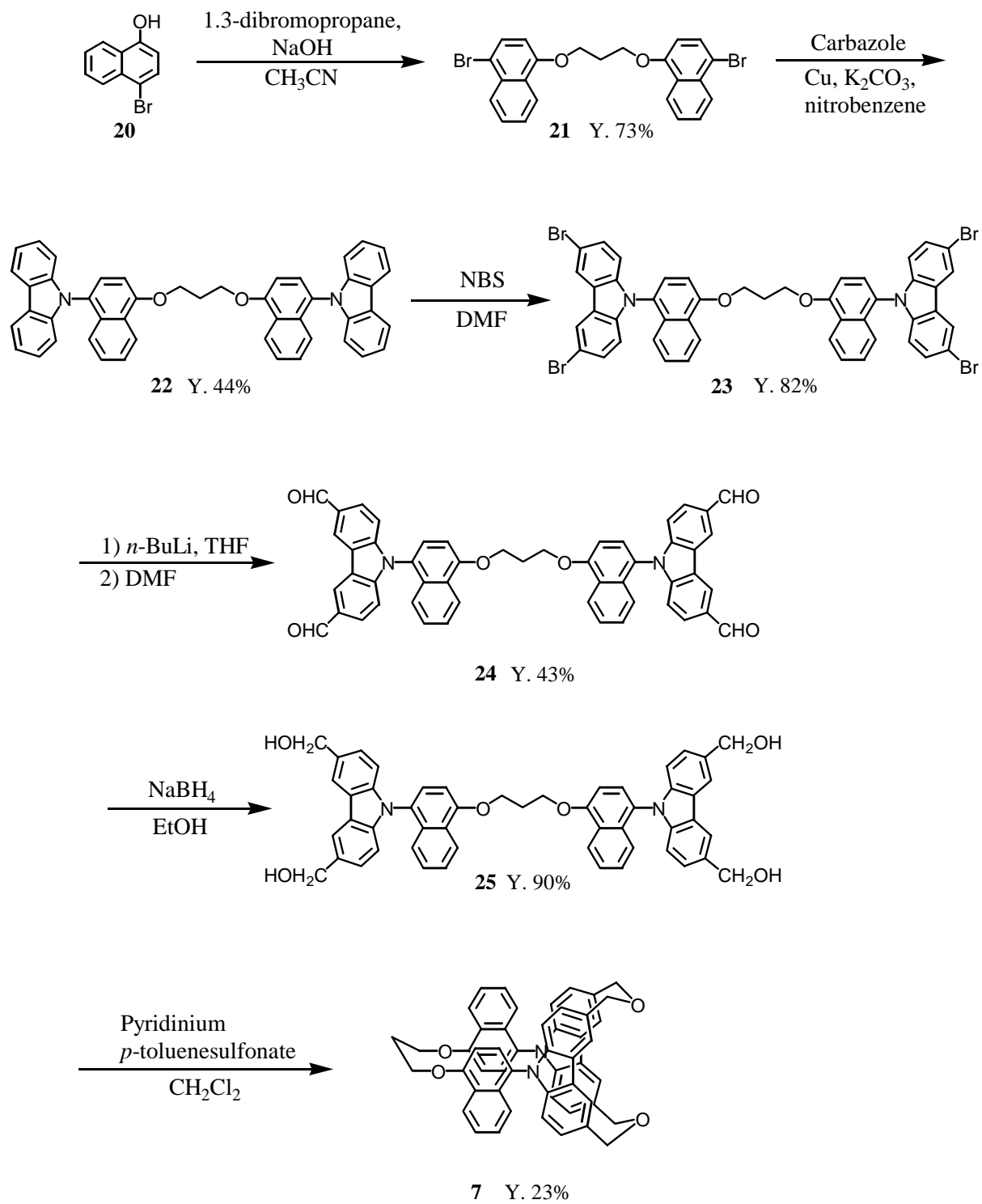
Scheme 1-3

**Scheme 1-4**
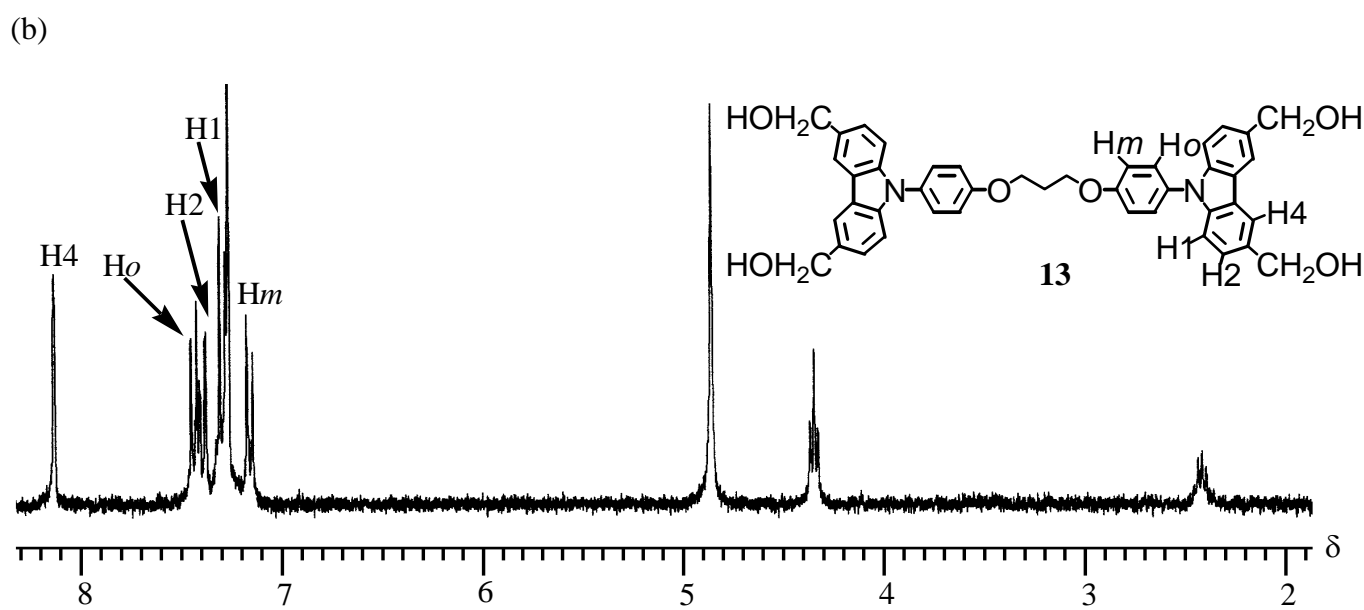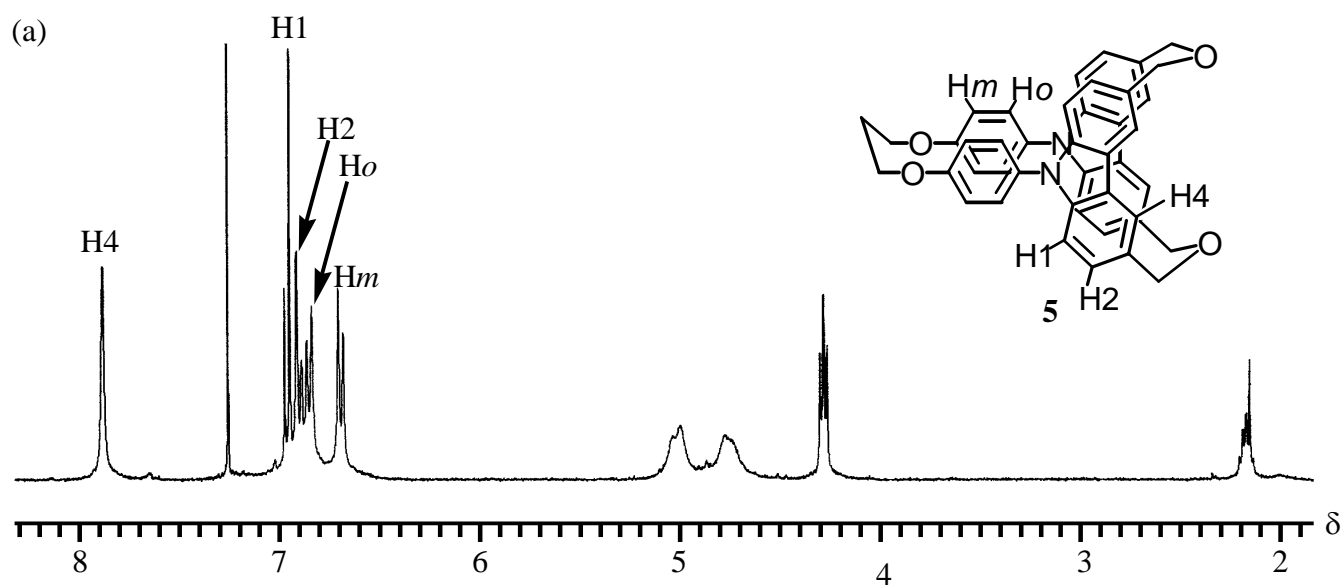
Figure 1-1. $^1$H NMR spectra of (a) **5** and (b) **13** in CDCl$_3$.

(a)
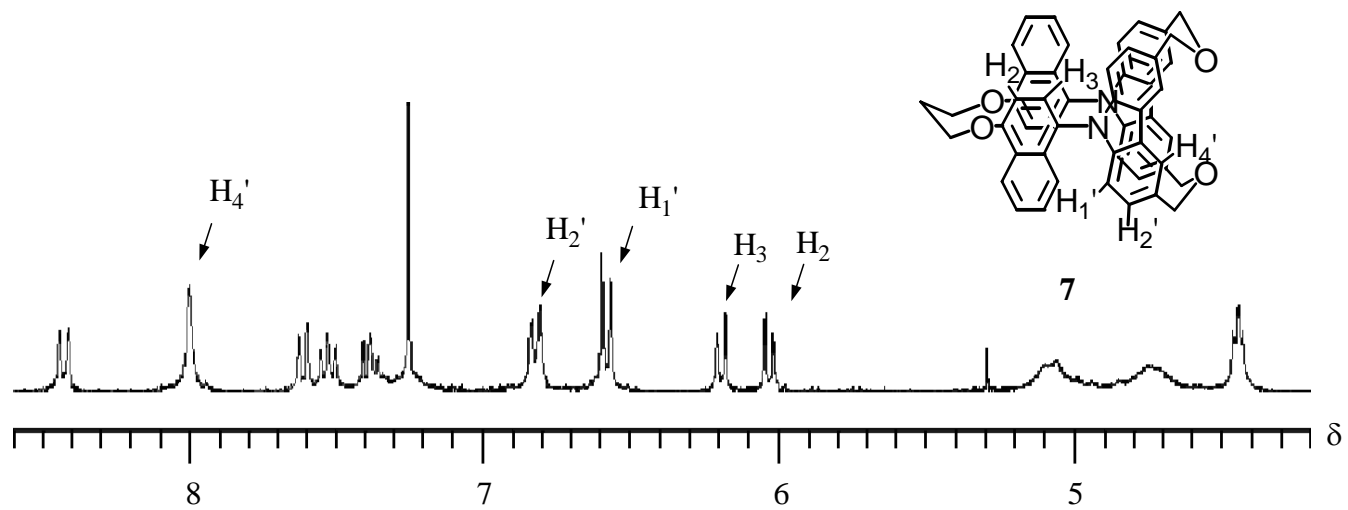


(b)
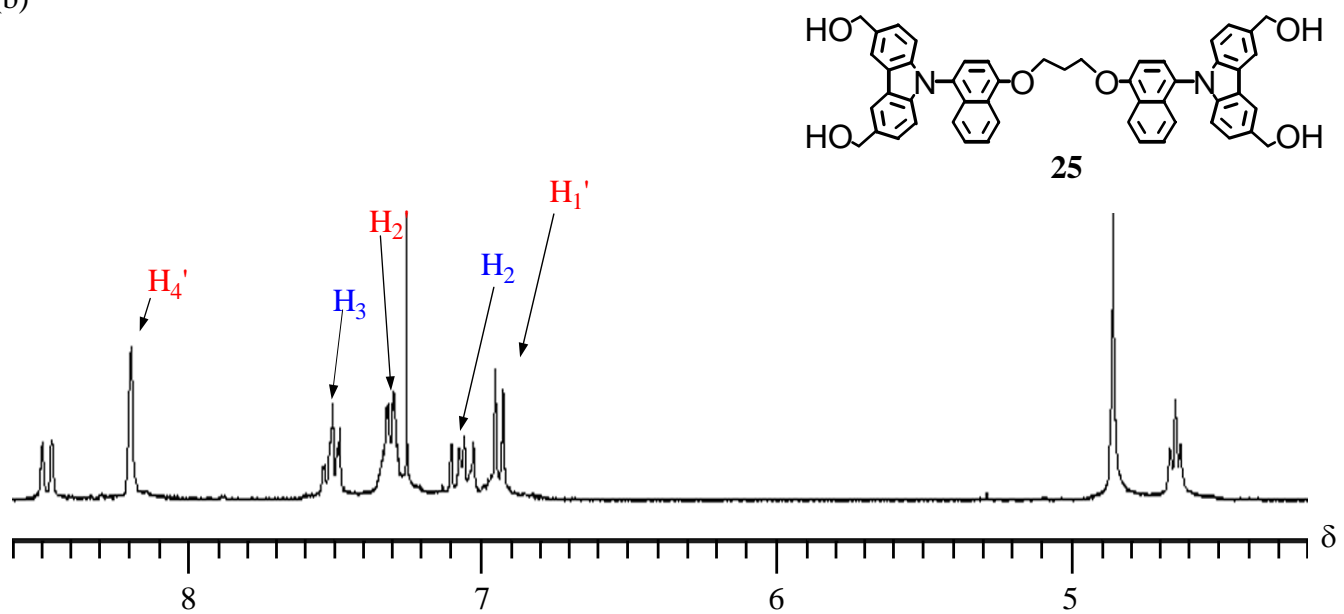


Figure 1-2. $^1$H NMR spectra of (a) **7** and (b) **25** in CDCl$_3$.

top view



side view



4.57 Å
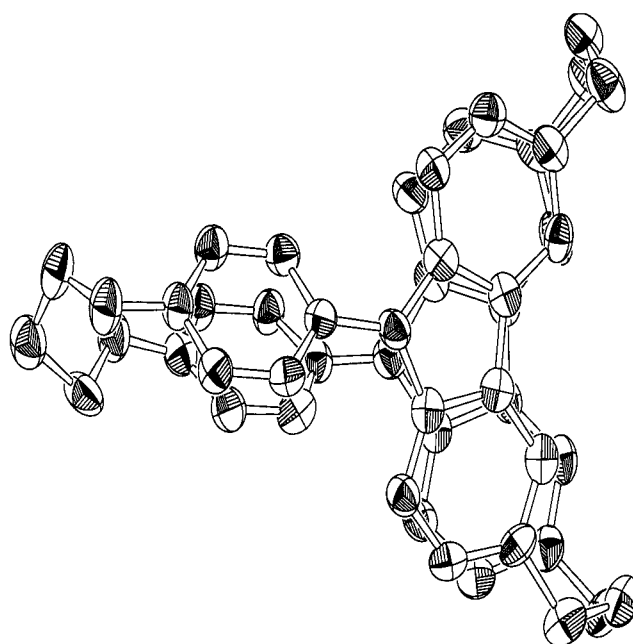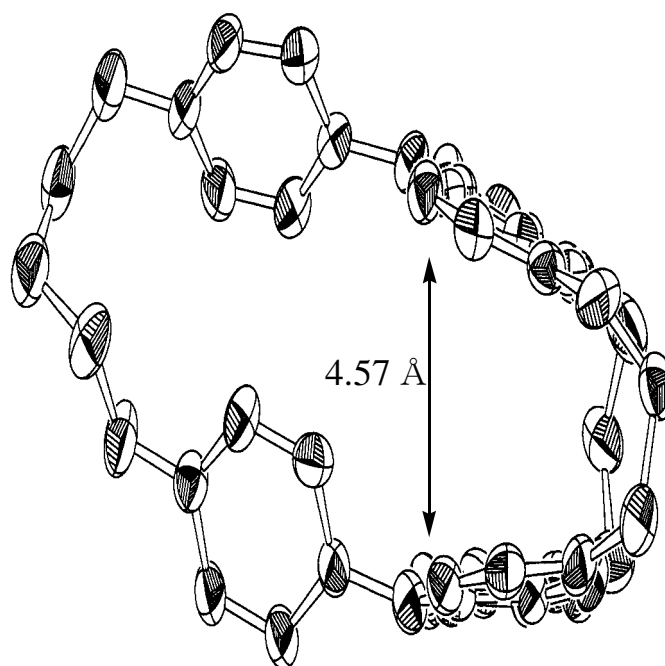
Figure 1-3.  ORTEP drawing of **5**.

top view



side view



4.61 Å
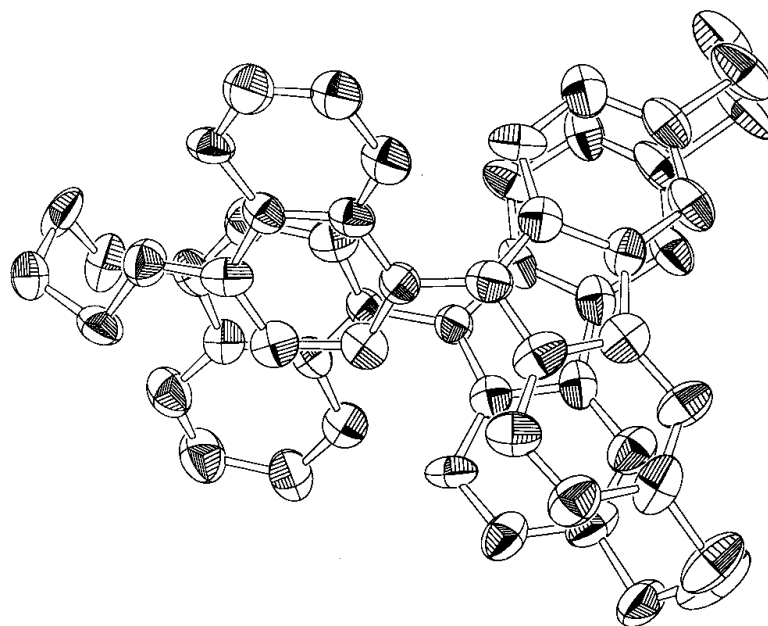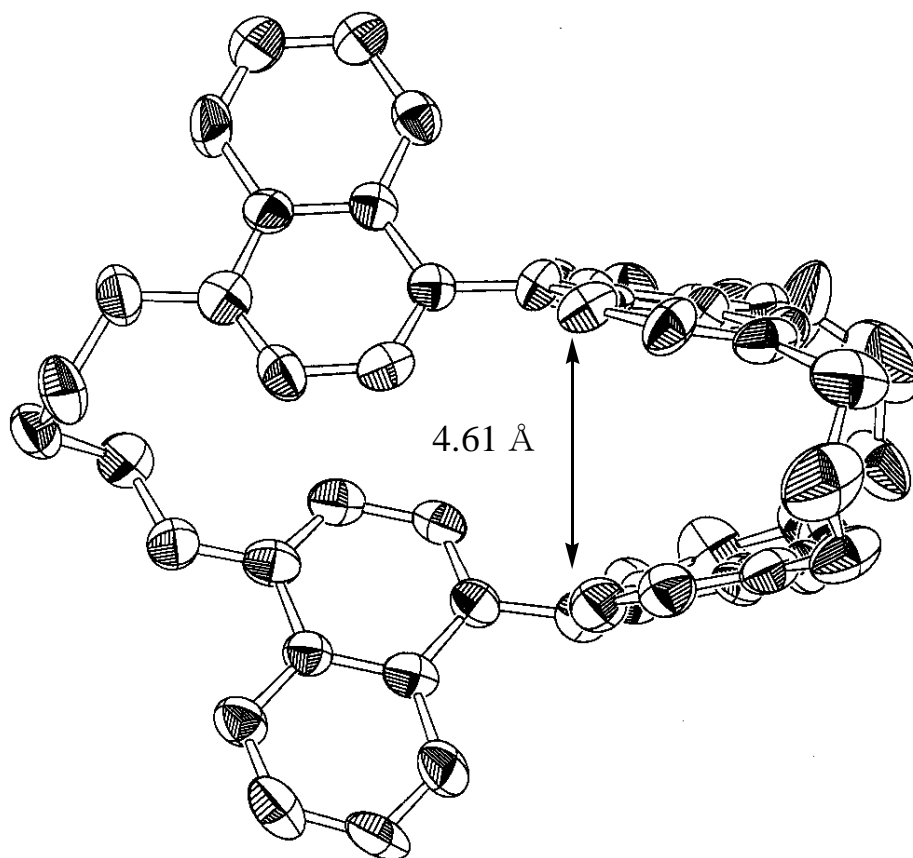
Figure 1-4. ORTEP drawing of **7**.

(a)

(b)

(c)
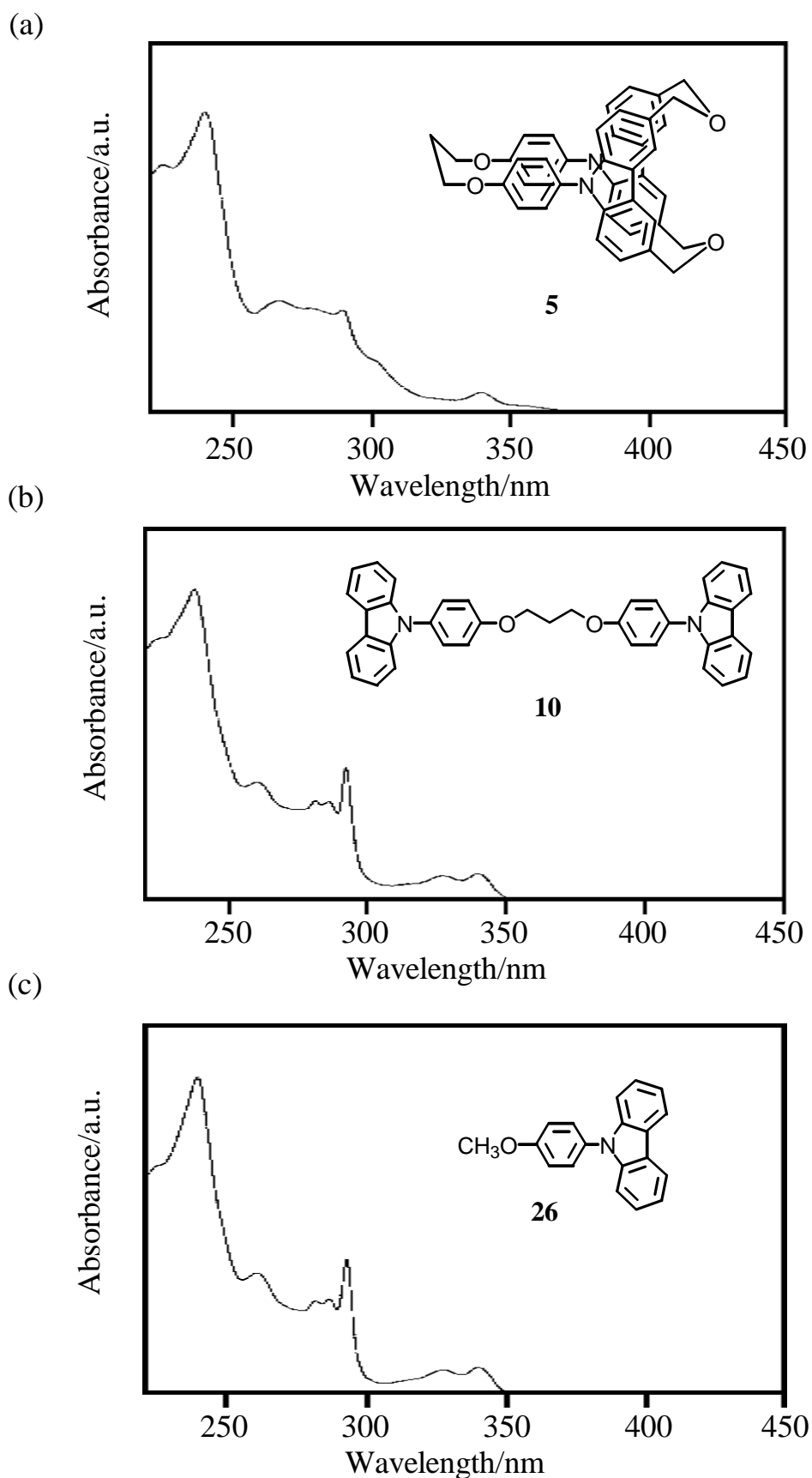
Figure 1-5. Absorption spectra of (a) **5**, (b) **10**, and (c) **26** in cyclohexane at room temperature.
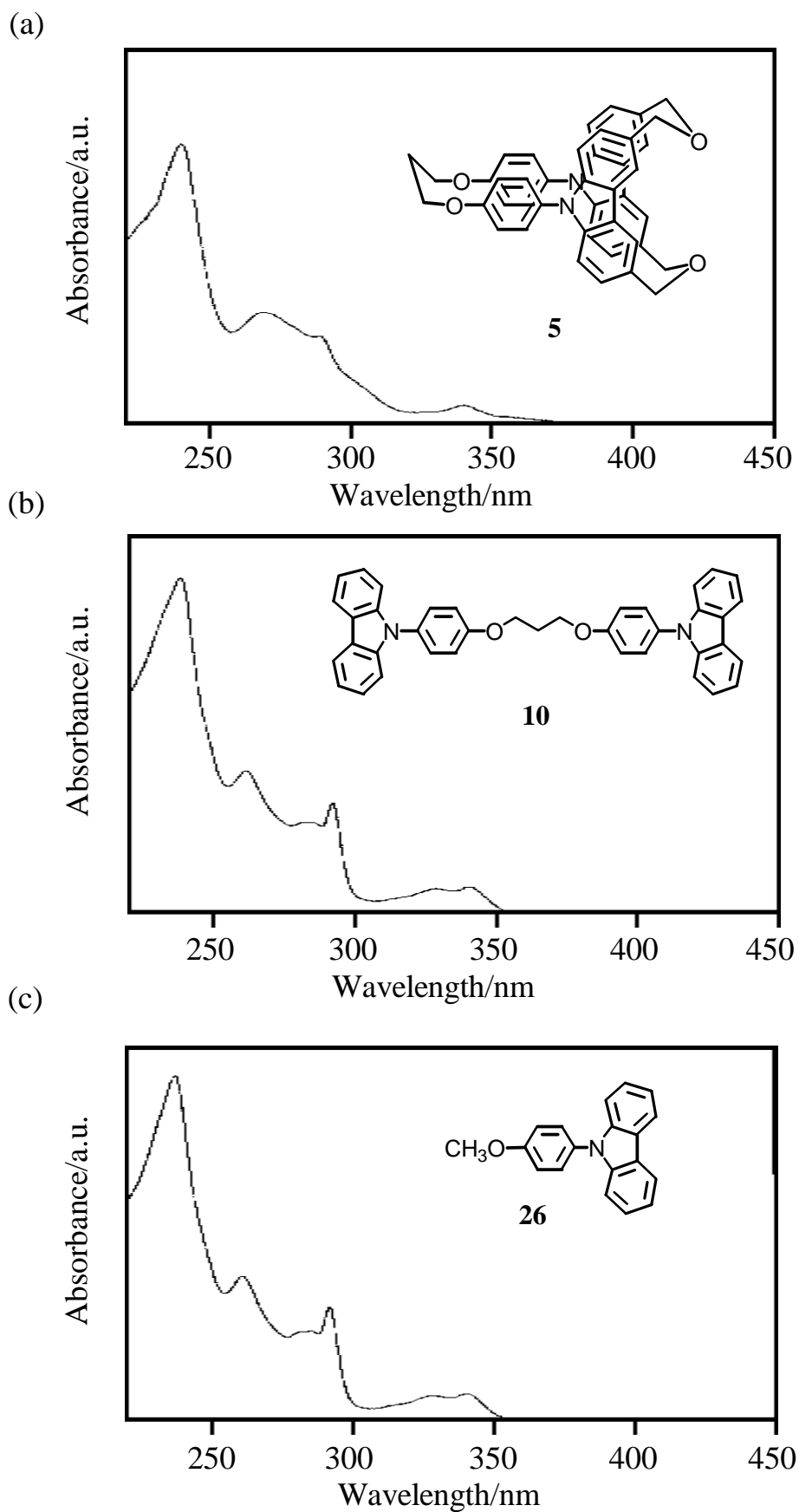
Figure 1-6. Absorption spectra of (a) **5**, (b) **10**, and (c) **26** in acetonitrile at room temperature.

(a)

(b)

(c)
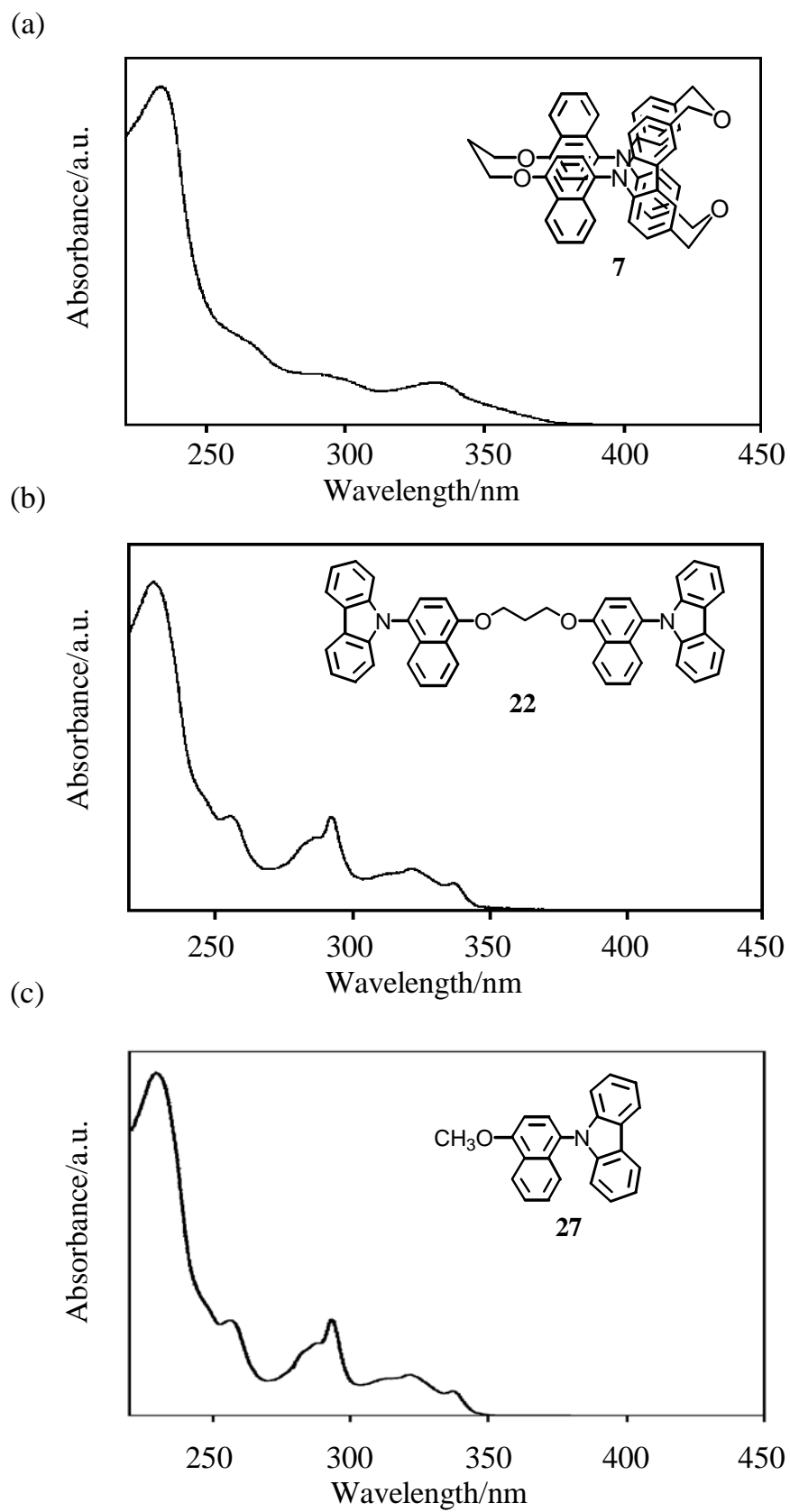
Figure 1-7. Absorption spectra of (a) **7**, (b) **22**, and (c) **27** in cyclohexane at room temperature.

(a)



(b)



(c)
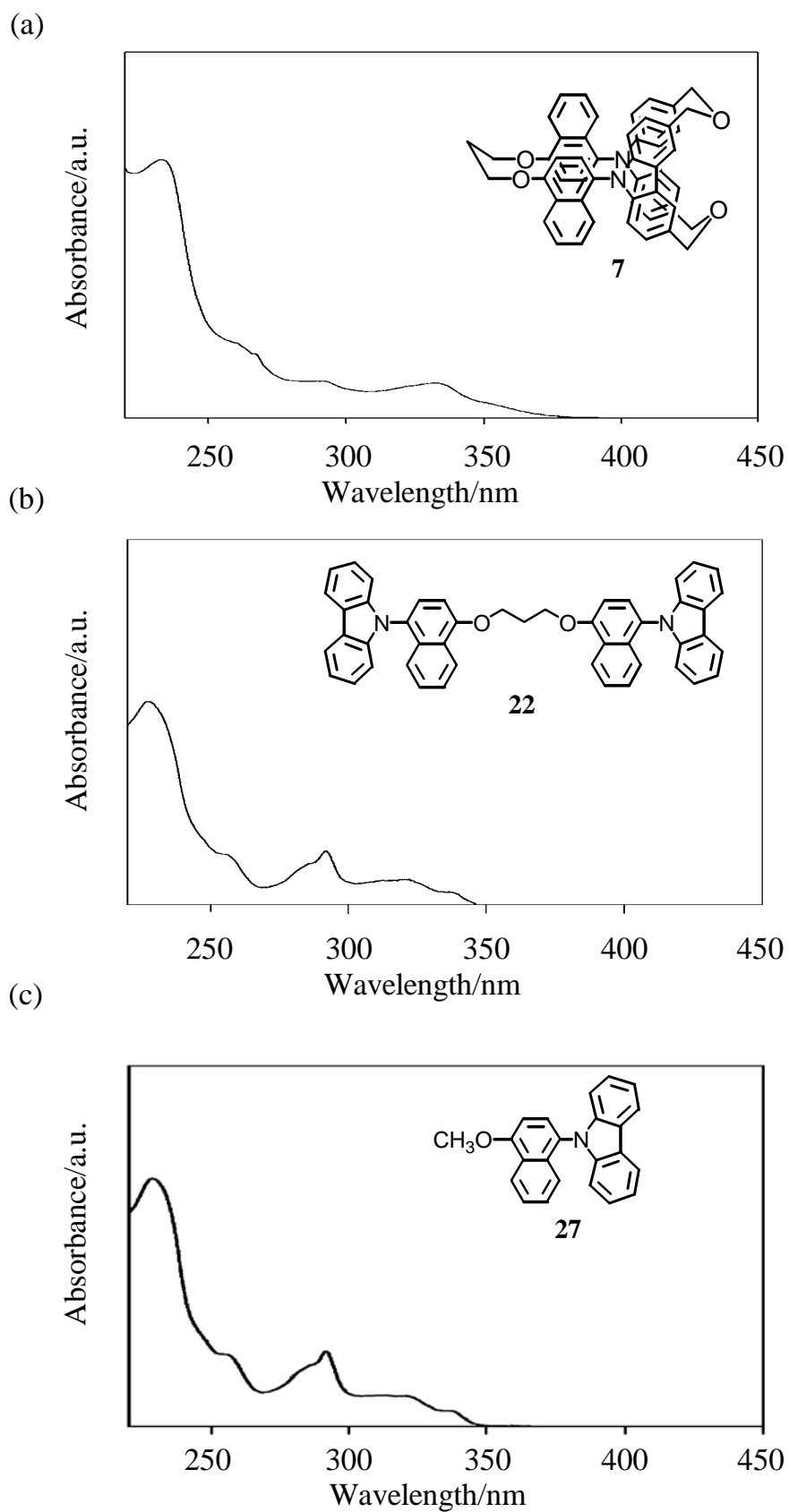


Figure 1-8. Absorption spectra of (a) **7**, (b) **22**, and (c) **27** in acetonitrile at room temperature.
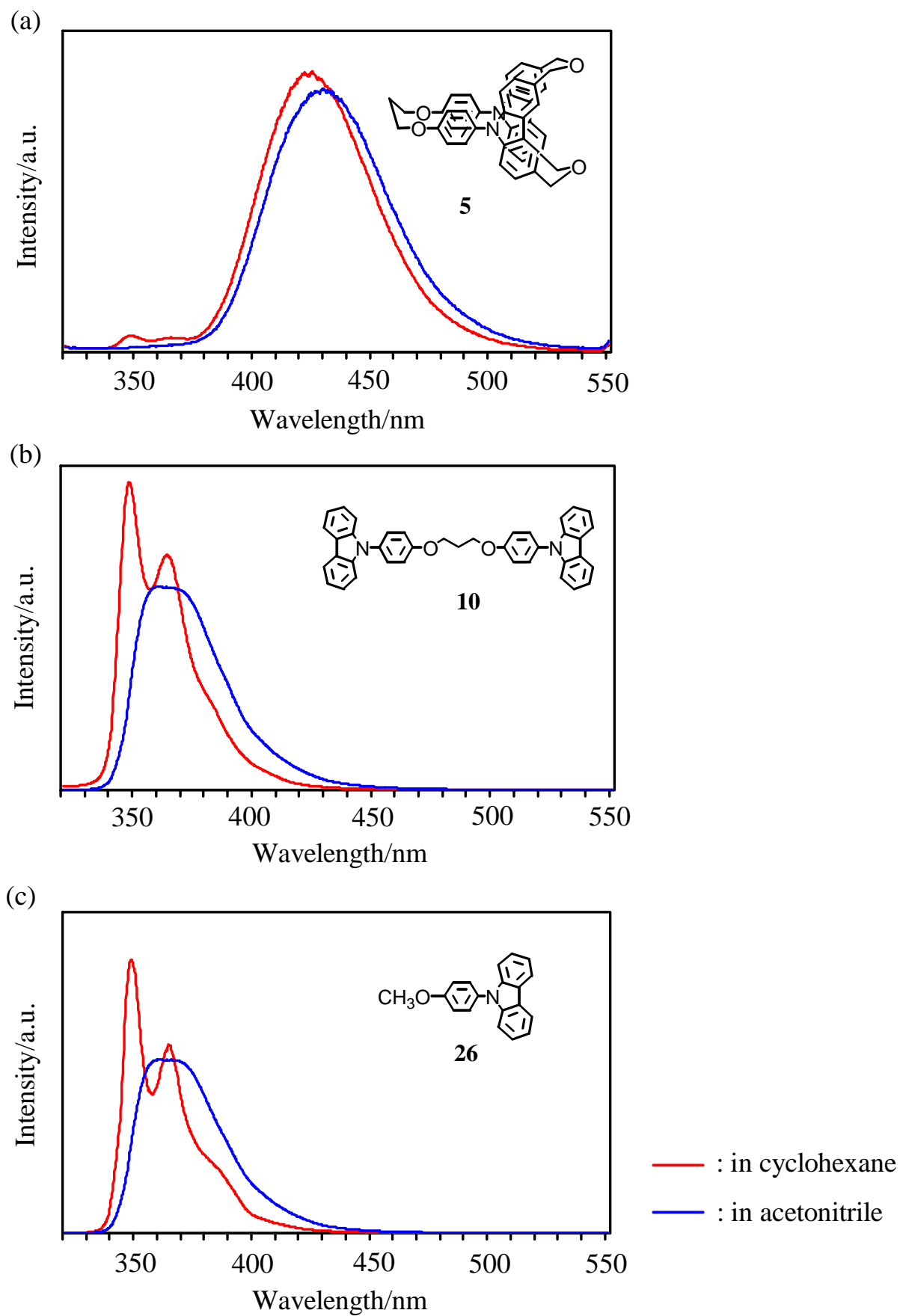
Figure 1-9. Fluorescence spectra of (a) **5**, (b) **10**, and (c) **26** on 280-nm excitation at room temperature.
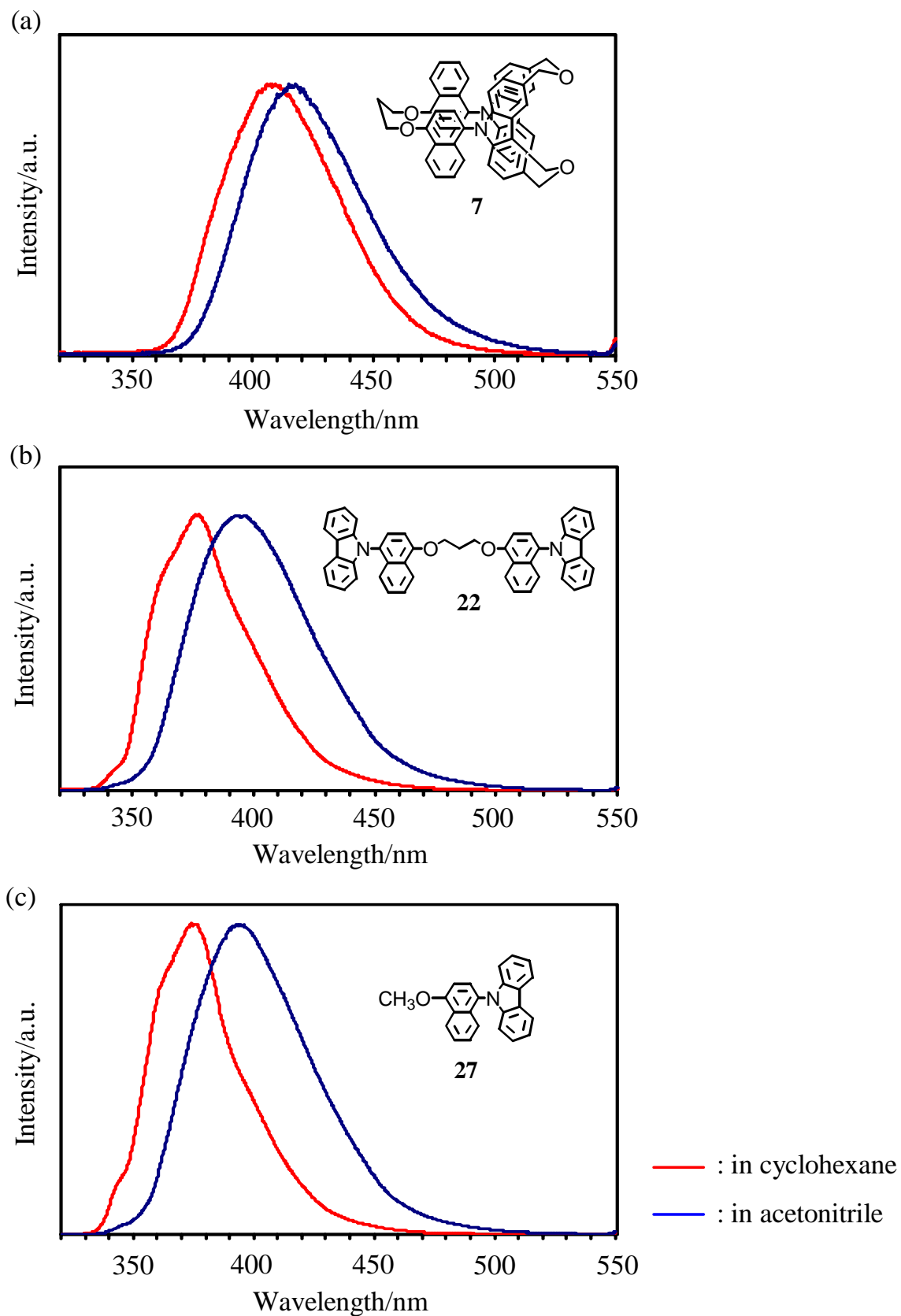
Figure 1-10. Fluorescence spectra of (a) **7**, (b) **22**, and (c) **27** on 280-nm excitation at room temperature.

Table 1-1. Fluorescence Lifetime of **5**, **7**, **10**, and **22** in Cyclohexane at 298 K

|  | Em / nm | $\tau_1$ / ns | % | $\tau_2$ / ns | % | $\chi^2$ |
|---|---|---|---|---|---|---|
| **5** | 423 | 2.39 | 2.5 | 10.2 | 97.5 | 1.063 |
|  | 470 | 1.88 | 2.5 | 10.2 | 97.5 | 1.170 |
| **10** | 350 | 8.34 | - |  |  | 1.214 |
|  | 400 | 8.34 | - |  |  | 1.121 |
| **7** | 380 | 7.25 | - |  |  | 1.183 |
|  | 410 | 7.16 | - |  |  | 1.102 |
|  | 450 | 7.09 | - |  |  | 1.073 |
| **22** | 360 | 6.44 | - |  |  | 1.076 |
|  | 420 | 6.43 | - |  |  | 1.013 |

Table 1-2. Fluorescence Quantum Yield ($\Phi_f$) and Fluorescence Lifetime ($\tau_f$) of **5**, **7**, **10**, and **22** in Cyclohexane at Room Temperature

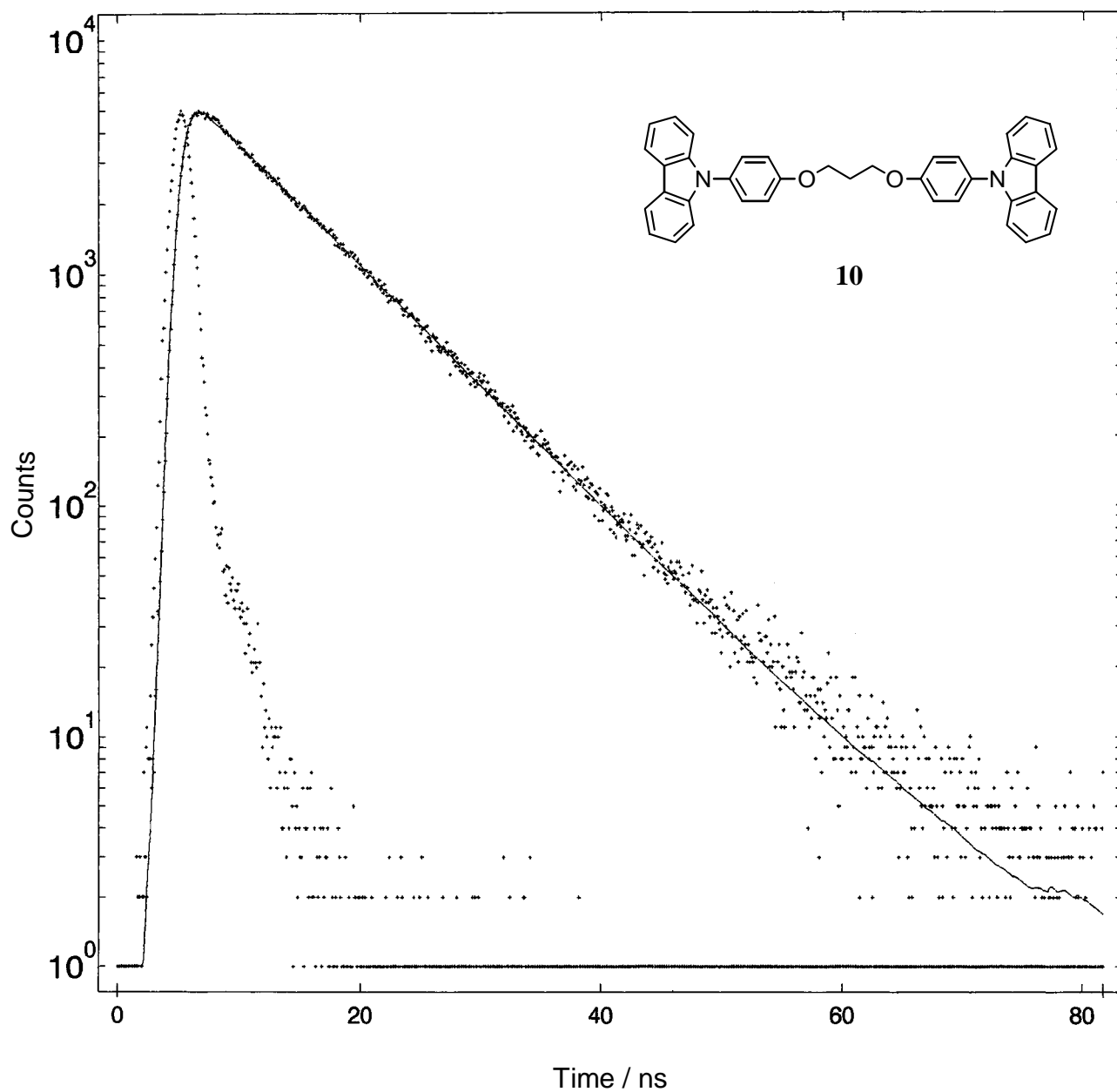|  | $\Phi_f$ | $\Phi_{nr}$ | $\tau_f$ /ns | $k_f$ /$10^7$s$^{-1}$ | $k_{nr}$ /$10^7$s$^{-1}$ |
|---|---|---|---|---|---|
| **5** | 0.035 | 0.97 | 10.2 | 0.34 | 9.5 |
| **10** | 0.39 | 0.61 | 8.34 | 4.7 | 7.3 |
| **7** | 0.047 | 0.95 | 7.16 | 0.66 | 13 |
| **22** | 0.48 | 0.52 | 6.43 | 7.5 | 8.1 |
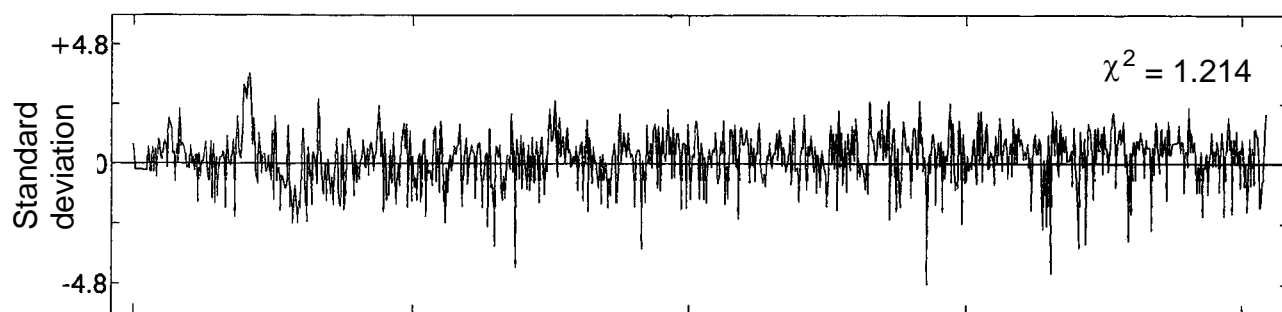
Figure 1-11. Fluorescence decay function of **10** in cyclohexane at 298 K
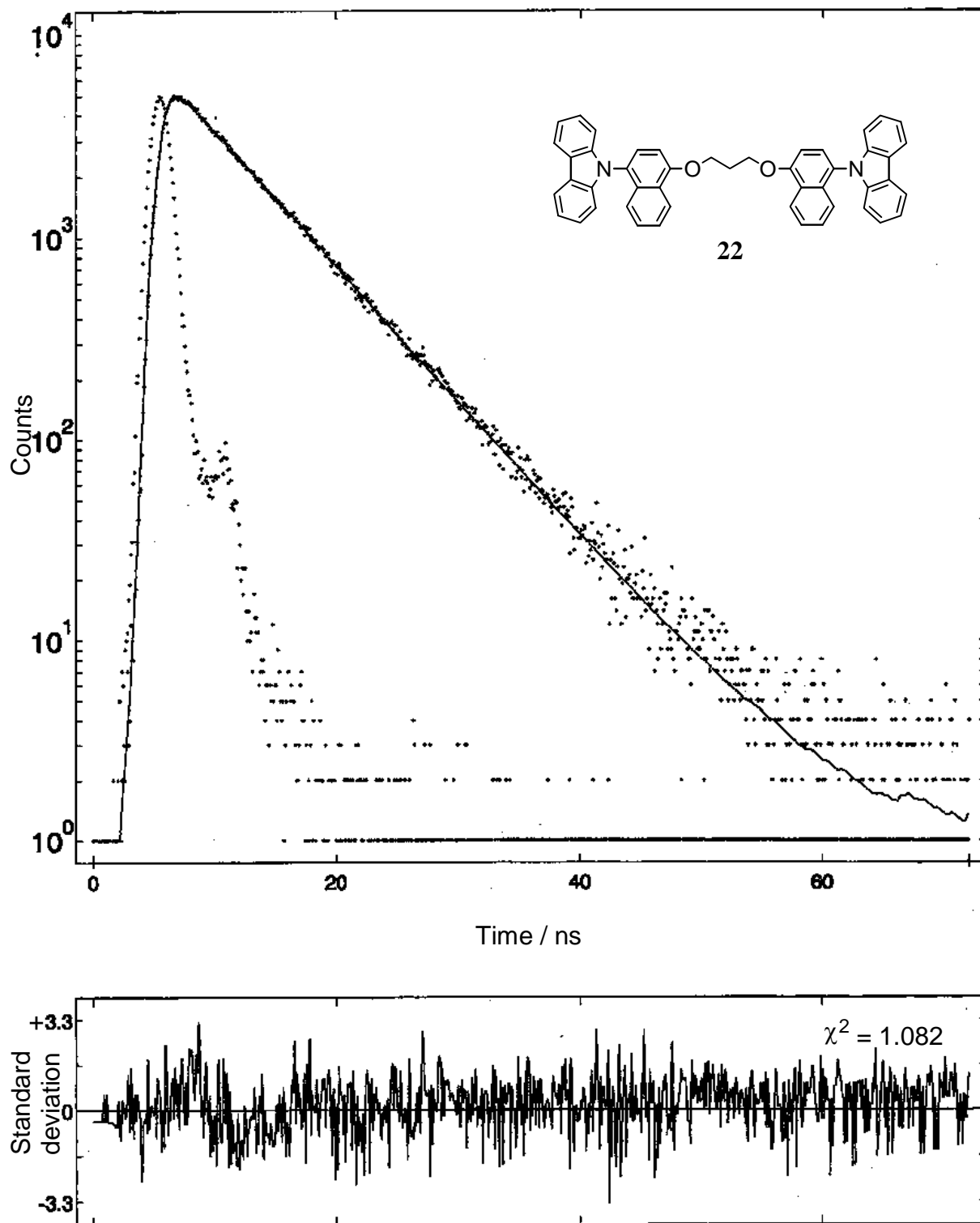excited at 280 nm and monitored at 350 nm.

Figure 1-12. Fluorescence decay function of **22** in cyclohexane at 298 K excited at 280 nm and monitored at 420 nm.
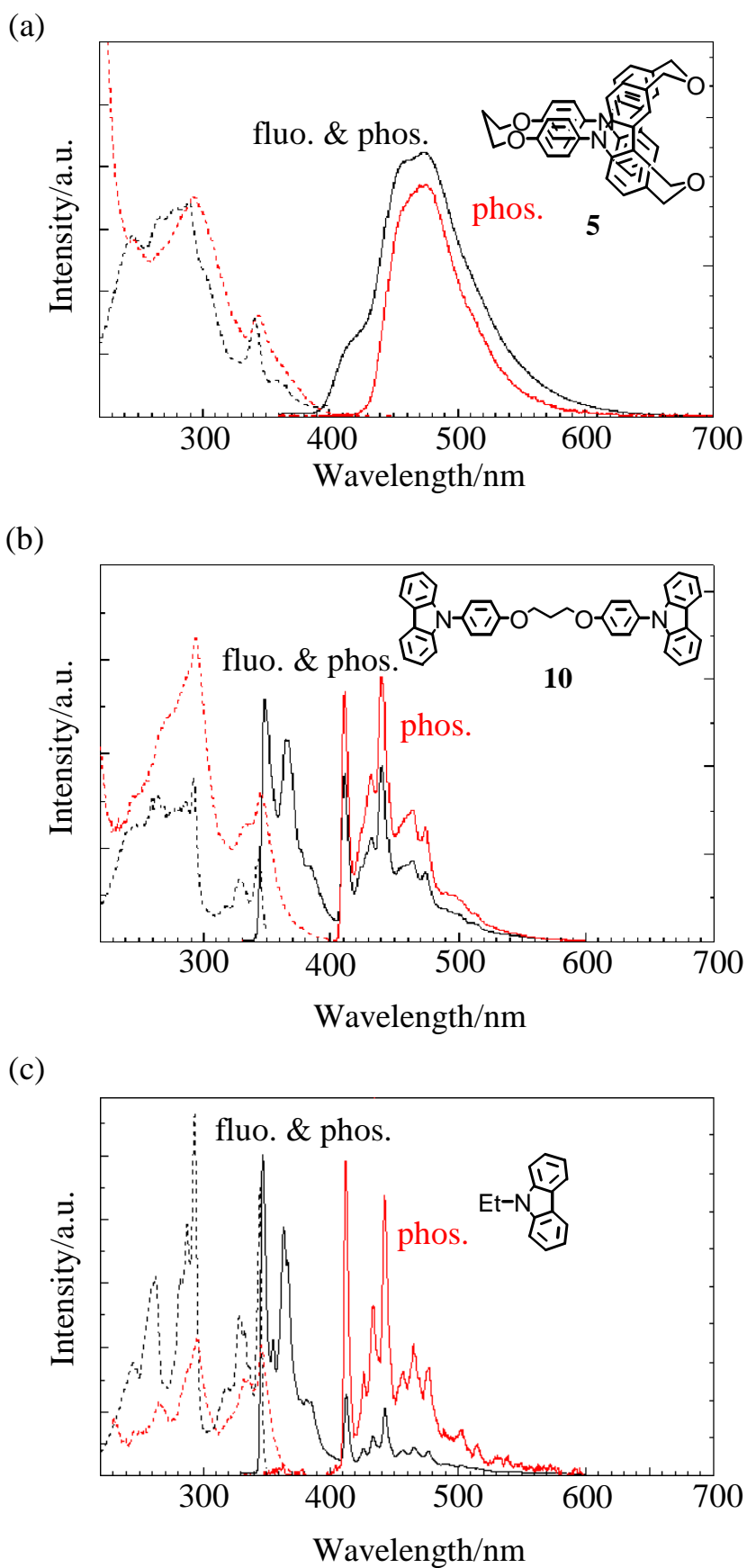
Figure 1-13. Phosphorescence spectra of (a) **5**, (b) **10**, and (c) *N*-ethylcarbazole upon 320-nm excitation in MP (4:1) at 77 K.
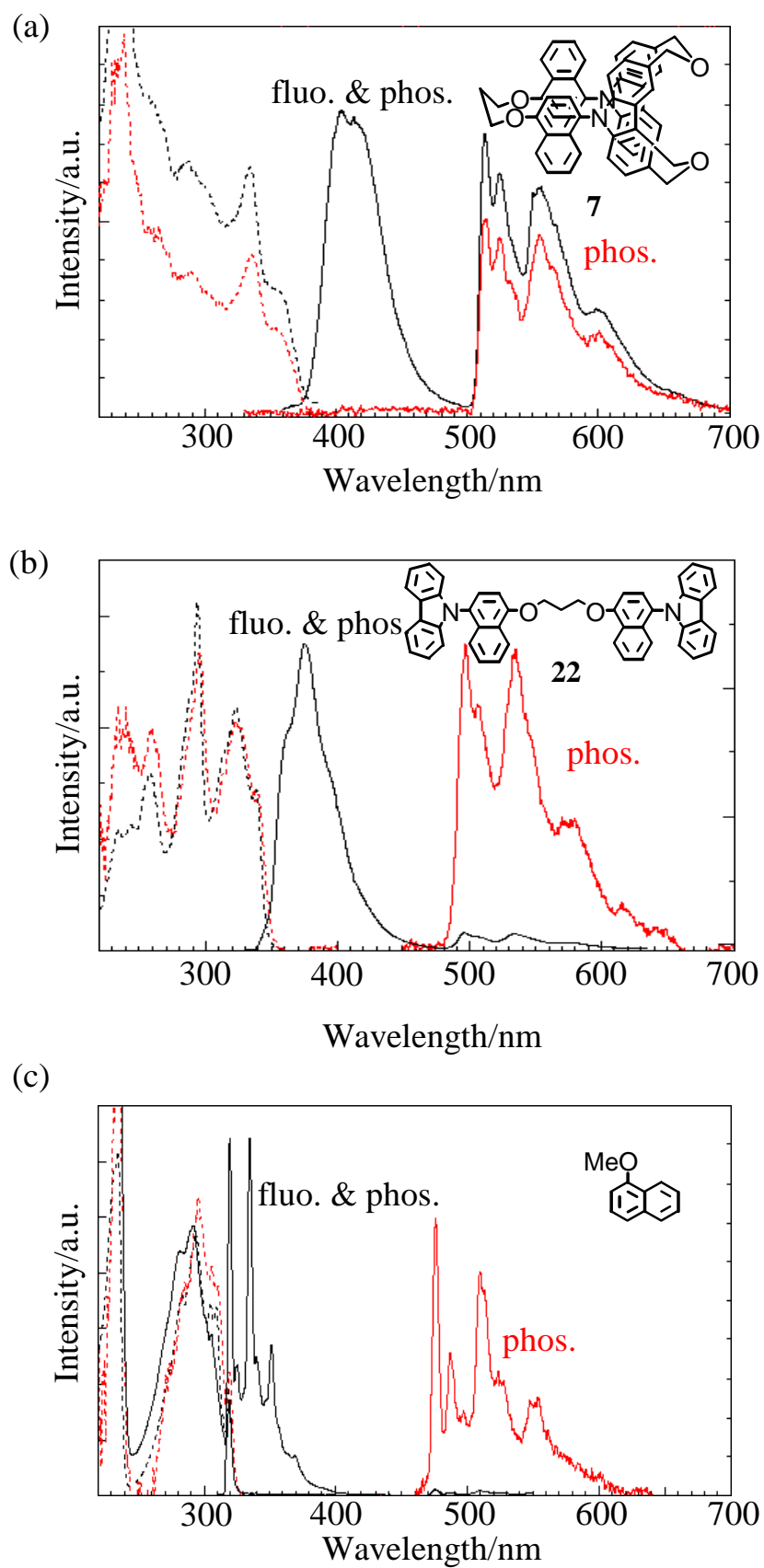
Figure 1-14.  Phosphorescence spectra of (a) **7**, (b) **22**, and (c) 1-methoxynaphthalene upon 320-nm excitation in MP (4:1) at 77 K.
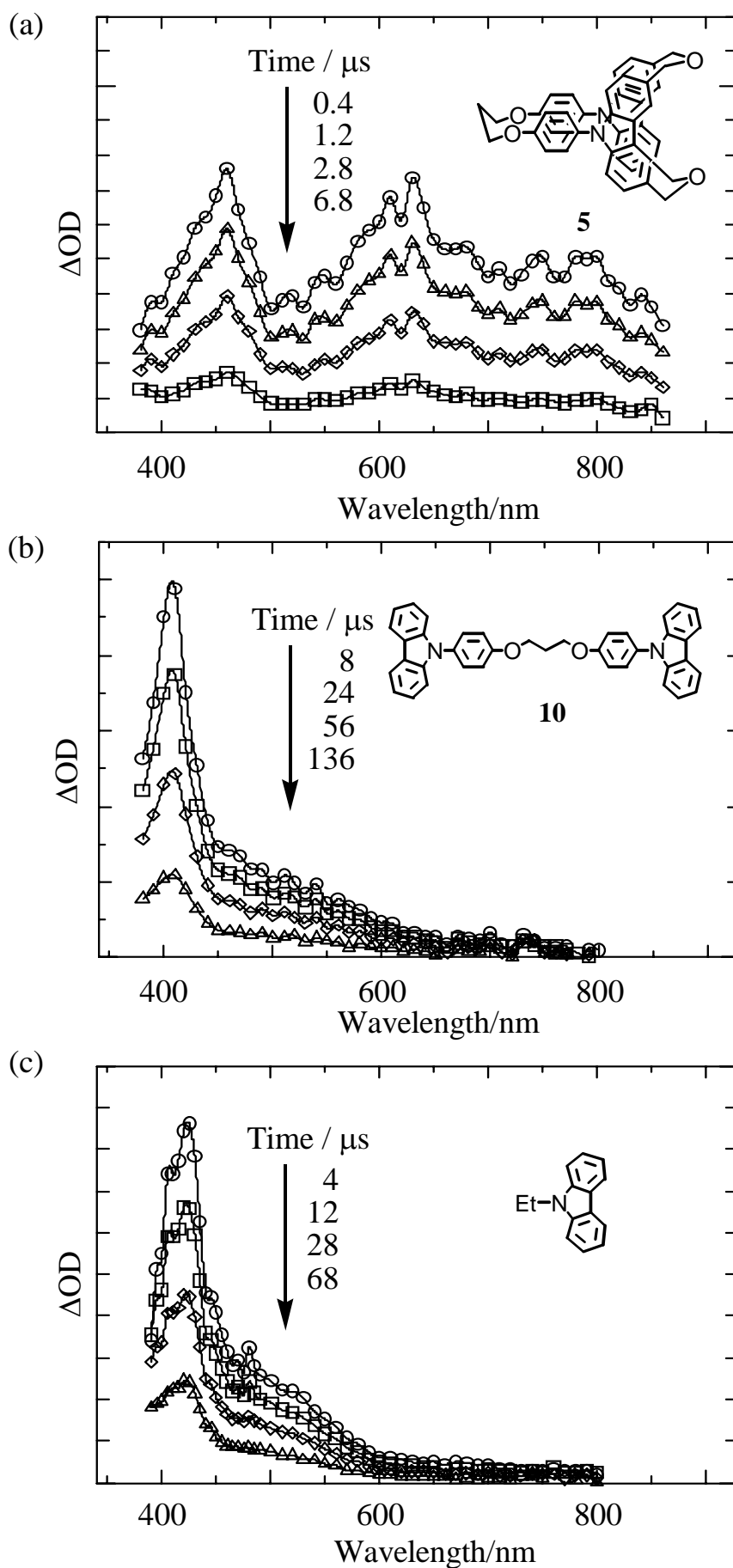
Figure 1-15. Transient absorption spectra of (a) **5**, (b) **10**, and (c) *N*-ethylcarbazole upon 308-nm excitation in cyclohexane at 293 K.
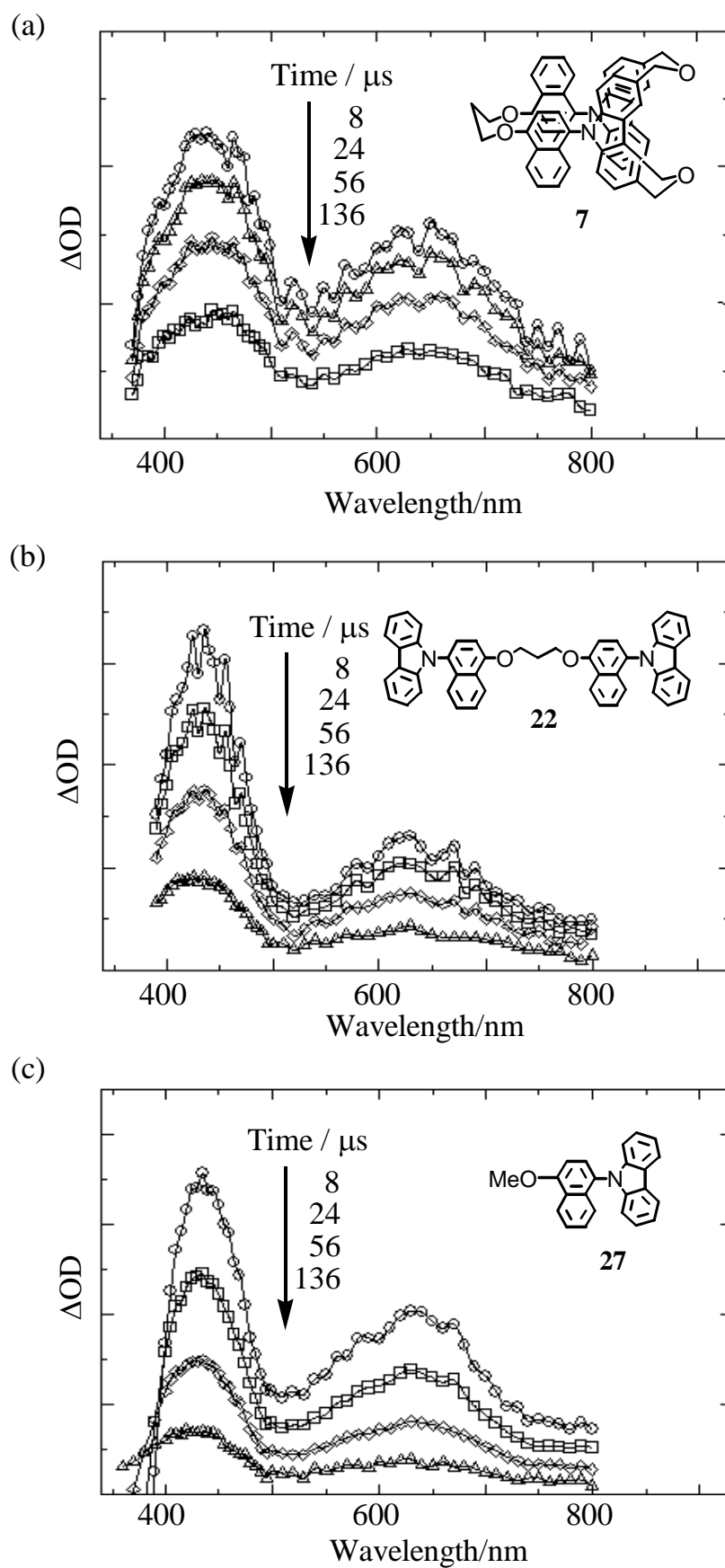
Figure 1-16.  Transient absorption spectra of (a) **7**, (b) **22**, and (c) **27** upon 308-nm excitation in cyclohexane at 293 K.
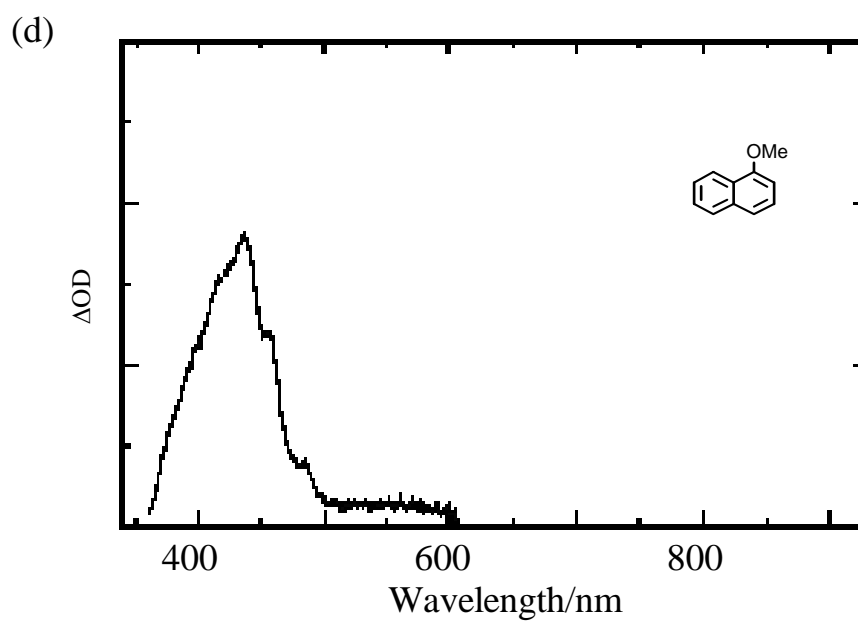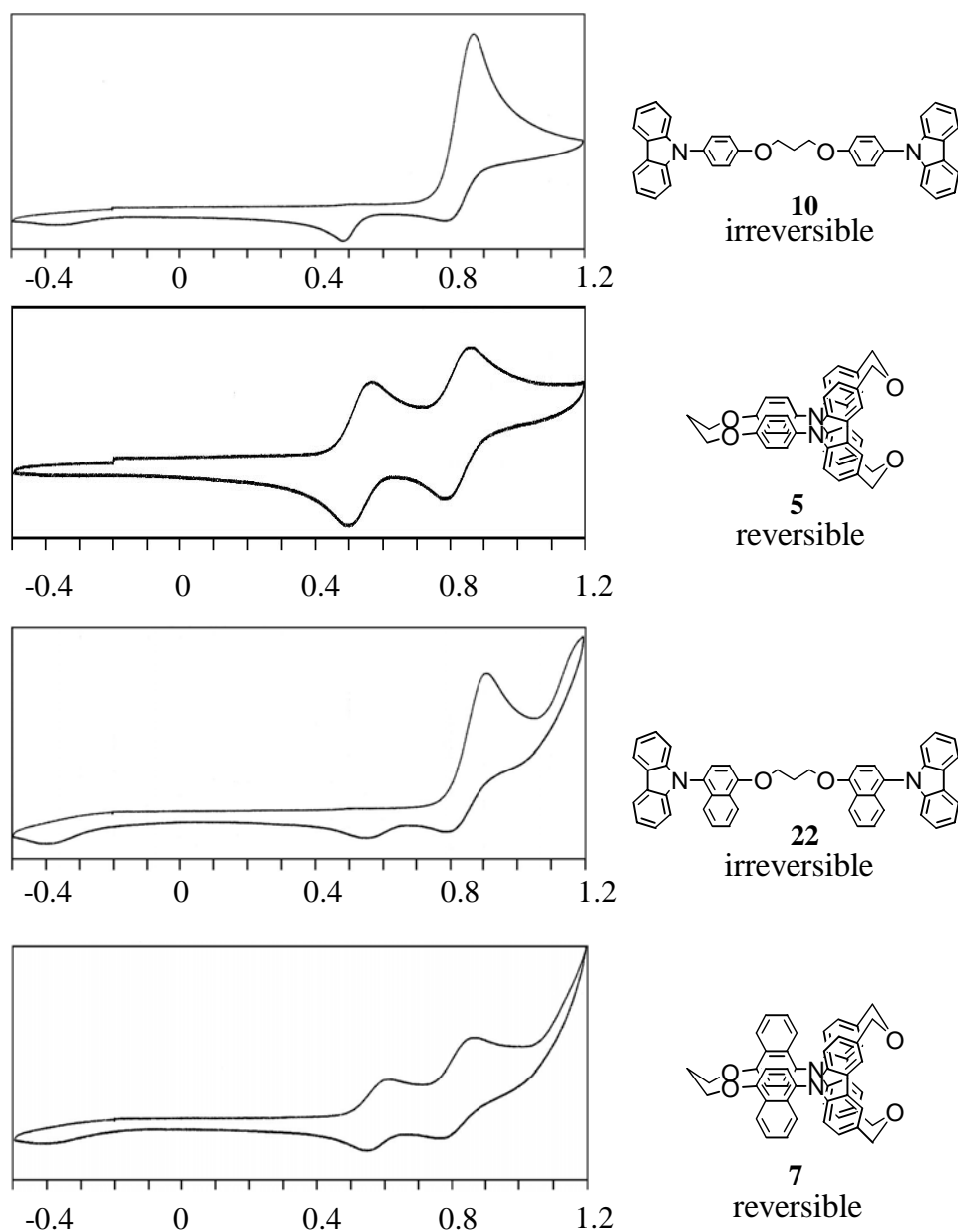
Figure 1-16. Transient absorption spectra of (d) 1-methoxynaphthalene upon 308-nm excitation in cyclohexane at 293 K.

-0.4  0  0.4  0.8  1.2

**10**
irreversible

-0.4  0  0.4  0.8  1.2

**5**
reversible

-0.4  0  0.4  0.8  1.2

**22**
irreversible

-0.4  0  0.4  0.8  1.2

**7**
reversible

(vs Fc/Fc$^+$ (Bu$_4$NPF$_6$) in benzonitrile, Scan rate 200 mV/s)

Figure 1-17. Cyclic Voltammograms of (a) **10**, (b) **5**, (c) **22**, and (d) **7**.

Table 1-3. Redox Potentials of **10**, **5**, **22**, and **7**

|     | $^1E_{1/2}$/V | $^2E_{1/2}$/V |
| --- | --- | --- |
| **10** | 0.813 [a)] | - |
| **5**  | 0.476 | 0.763 |
| **22** | 0.848 [a)] | - |
| **7**  | 0.521 | 0.761 |

a) $^1E_{OX}$ due to the irreversible process.

# Chapter 2

## Substituent Effects on Photophysical Properties of *N*-Thienylcarbazoles

**Abstract**

*N*-Thienylcarbazoles consisting of carbazole(s) and thiophene connected directly were synthesized by Ullmann condensation, 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. The electronic and photophysical properties of a series of *N*-thienylcarbazoles were first clarified and compared to one another. The characters of both ground and excited states of carbazole moiety are much more affected by a 2-thienyl group than a 3-thienyl group.

## 2.1 Introduction

Carbazole and thiophene are important heteroaromatic compounds from the aspects of constructing functional materials such as organic light-emitting materials, photoconductors, and so on.[1] For instance, these heterocycles have been used as building-blocks for hole-transport and light-emissive materials or host materials for triplet emitters in OLEDs.[2,3] As one of the most fundamental compounds containing carbazole and thiophene, *N*-(2-thienyl)carbazole (**2a**) has been prepared,[4] but its photophysical properties are unknown. 2,5-Bis(*N*-carbazolyl)thiophene (**3a**) is also known in the literature,[5] but its photophysical properties are not clarified, although those of 5,5'-bis(*N*-carbazolyl)-2,2'-bithiophene are disclosed.[6] Surprisingly, *N*-(3-thienyl)carbazole (**1a**) has been unknown in the literature. Thus, we were prompted to investigate and compare the electronic and photophysical properties of **1a–3a** systematically. In addition, the properties of **1b–3b**[7] bearing *tert*-butyl groups at the 3- and 6-positions of carbazole ring(s) were also investigated and compared with those of **1a–3a**. The *tert*-butyl groups are expected to increase the solubility of compounds, facilitate the characterization, and enhance the stability of compounds in both neutral and cation radical states. As a result of systematic investigation, we have found that their photophysical properties remarkably depend on the substitution positions of thiophene.



**1a** (R= H)
**1b** (R= *t*Bu)

**2a** (R= H)
**2b** (R= *t*Bu)

**3a** (R= H)
**3b** (R= *t*Bu)
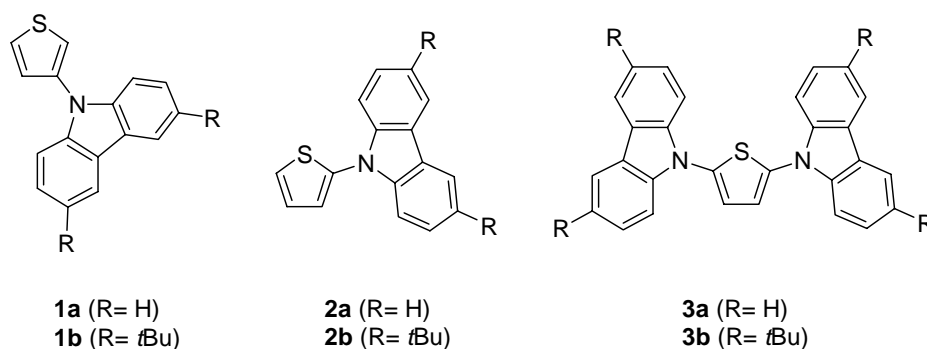
## 2.2 Results and Discussion

### 2.2.1 Synthesis of *N*-Thienylcarbazoles

*N*-(3-Thienyl)carbazole (**1a**) was prepared by the copper-catalyzed Ullmann condensation of 3-bromothiophene and carbazole, in a manner similar to **2a** and **3a** (Scheme 2-1). It was characterized by $^1$H and $^{13}$C NMR and other spectroscopies. In the $^1$H NMR spectrum of **1a**, three sets of double doublets for the thiophene protons were observed in addition to the carbazole proton peaks, while the thiophene protons of **3a** with a higher symmetry were observed as a singlet peak in contrast with **1a** and **2a**. The numbers of $^{13}$C NMR peaks of **1a** and **3a** were 10 and 8, respectively, in consistent with their structures.

All of **1b–3b** bearing *tert*-butyl groups were also prepared by the copper-catalyzed Ullmann condensation of the corresponding bromothiophene derivatives and 3,6-di-*tert*-butylcarbazole in a manner similar to **1a–3a** (Scheme 2-1).

### 2.2.2 Electronic, Photophysical, and Electrochemical Properties of *N*-Thienylcarbazoles

### Absorption and Fluorescence Spectra

The absorption spectra of **1a–3a** and **1b–3b** were measured in cyclohexane and acetonitrile at room temperature. The absorption spectra of **1a–3a** exhibit absorption bands characteristic of carbazole derivatives, a sharp and intense band at ca. 295 nm and vibrational structures around 300–350 nm (Figure 2-1). Among **1a–3a**, the spectrum of **1a** is the most similar to that of *N*-ethylcarbazole. The spectrum of **2a** is slightly broadened on the whole. This result suggests that the electronic property of ground state (S$_0$) of carbazole moiety is more perturbed by the 2-thienyl substitution than the 3-thienyl substitution. In **3a**, the spectrum is further broadened and the spectral shape around 300–350 nm is quite different from the others. These observations may be partly due to the intramolecular interaction between the two carbazole moieties in a conjugated system. The absorption spectra of **1a–3a** in acetonitrile were quite similar to those in cyclohexane. The absorption spectra of

**1b**–**3b** are quite similar to those of **1a**–**3a**, though slightly red-shifted (ca. 3–5 nm) relative to **1a**–**3a**. The two *tert*-butyl groups at 3- and 6-positions do not have significant effects on the electronic properties of these compounds.

The fluorescence spectra of **1a**–**3a** in cyclohexane at room temperature are also shown in Figure 2-1. The spectrum of **1a**, showing vibrational structures characteristic of carbazole derivatives, is quite similar to that of *N*-ethylcarbazole. The spectrum of **2a** is slightly broadened. Noticeably, the spectrum of **3a** is remarkably red-shifted and broadened without vibrational structures. The fluorescence spectra in polar acetonitrile are red-shifted and broadened relative to those in cyclohexane. This behavior suggests the CT character in the excited singlet state, as observed in some other *N*-arylcarbazoles.[8] All the fluorescence excitation spectra were in good agreement with the corresponding absorption spectra, obviously indicating that these emissions originate from compounds **1a**–**3a**. The fluorescence spectra of **1b**–**3b** are quite similar to those of **1a**–**3a**, though slightly red-shifted (ca. 3–5 nm) relative to **1a**–**3a**. The photophysical properties of these compounds are not significantly affected by the two *tert*-butyl groups.

**Fluorescence Lifetime and Quantum Yield**

The fluorescence quantum yields and lifetimes of **1a**–**3a** are listed in Table 2-1.

Table 2-1. Fluorescence Quantum Yields and Lifetimes of **1a**–**3a** in Cyclohexane at Room Temperature

|  | $\Phi_f$ | $\tau_f$ / ps | $k_f$ / $10^7$ s$^{-1}$ [a)] |
|---|---|---|---|
| *N*-EtCz | 0.43[b] | 14400[b] | 3.0 |
| **1a** | 0.13 | 3210 | 4.03 |
| **2a** | 0.014 | 381 | 3.67 |
| **3a** | 0.0063 | 60.6 | 10.3 |

[a)] $k_f = \Phi_f / \tau_f$.  [b)] In MTHF. Ref. 9.

As seen from Table 2-1, both fluorescence quantum yields and lifetimes decrease in the order of *N*-ethylcarbazole, **1a**, **2a**, and **3a**. These observations indicate that the property of excited singlet state ($S_1$) of carbazole moiety is also much more affected by the 2-thienyl substitution than the 3-thienyl substitution. Especially, the disubstitution at both 2- and 5-positions of thiophene drastically modifies the character of $S_1$ of carbazole. The decrease of fluorescence quantum yields in **1**–**3** relative to *N*-ethylcarbazole may be partially due to the effect of sulfur atom of thiophene, since the fluorescence quantum yield of *N*-phenylcarbazole (0.33 in hexane, 0.40 in acetonitrile)[8c] is rather similar to that of *N*-ethylcarbazole.

**Phosphorescence Spectra**

The phosphorescence spectra of **1a**–**3a** in 3-methylpentane at 77 K are entirely different from one another, as shown in Figure 2-2. Compound **1a** provided a phosphorescence with vibrational structures similar to *N*-ethylcarbazole[10] and a long lifetime ($\tau_p$ = 4.8 s). The excited triplet state ($T_1$) of carbazole moiety is also relatively unaffected by the 3-thienyl group. In **2a**, quite weak and broad phosphorescence was observed with a maximum around 500 nm.[11] The phosphorescence lifetime of **2a** ($\tau_p$ = 170 μs) was much shorter than those of **1a** and **3a**. A 2-thienyl group also remarkably modifies the character of $T_1$ state of carbazole. In **3a**, similar broad phosphorescence was observed, and the lifetime ($\tau_p$ = 8 ms) was much shorter than that of **1a** but longer than that of **2a**.

**Transient Absorption Spectra**

The transient absorption spectra of **1a**–**3a** were obtained at several delay times after laser pulsing at 308 nm in degassed cyclohexane at 293 K (Figure 2-3).

The spectra of **1a** exhibit a sharp band with a maximum around 400 nm similar to *N*-ethylcarbazole, although the lifetime is slightly shorter than that of *N*-ethylcarbazole. This band is probably due to the T-T absorption of carbazole moiety. The spectral features of **2a**

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and **3a** are obviously different from that of **1a**, and their lifetimes are shorter than that of **1a**. Both **2a** and **3a** exhibit rather red-shifted and broad bands. The spectra of **3a** are especially broadened and the lifetime is shorter than that of **2a**. These observations apparently indicate the interaction between the thiophene and carbazole moieties of **2a** and **3a** in the $T_1$ state. This result also supports that the 2-thienyl group modifies the character of $T_1$ state of carbazole effectively.


**Electrochemical Properties**

The electrochemical properties of **1a**, **3a**, and **1b–3b** were investigated by cyclic voltammetry (CV) in benzonitrile. Their voltammograms are shown in Figure 2-4. Compounds **1a**, **1b**, and **2b** showed one set of redox waves, whereas **3a** and **3b** showed two sets of redox waves, corresponding to the numbers of electron-donating carbazole units. The redox processes of **1a**, **2b**, and **3a** are rather irreversible, while those of **1b** and **3b** are reversible. The irreversible behavior of **1a**, **2b**, and **3a** indicates the low stability of the resulting cation radicals. The instability of the cation radicals of **1a** and **3a** is probably due to the absence of substituents at the reactive 3- and 6-positions of carbazole. The reversible redox processes of **1b** and **3b** in contrast with **1a** and **3a** apparently result from the presence of *t*-butyl groups at the 3- and 6-positions of carbazole; the *t*-butyl groups enhance the electron-donating property of carbazole and the stability of its cation radical. In the cation radical of **2b** bearing *t*-butyl groups, some reaction may take place at the reactive 5-position of thiophene residue. The oxidation potentials of **3b** are less positive than that of **1b**. This observation is ascribed to the presence of two electron-donating carbazole units and the resulting extended delocalization of π-electron system.


**2.2.3 Molecular Orbital Calculation**

The molecular orbital calculations of **1a-3a** were performed on the basis of AM1

method for analyzing the fact that their electronic and photophysical properties are much more affected by a 2-thienyl group than a 3-thienyl group (Figure 2-5). The HOMO of **1a** shows a node between the carbazole moiety and the sulfur atom of thiophene ring. On the contrary, the HOMOs of **2a** and **3a** show no node between the carbazole moiety and the sulfur atom of thiophene ring. These results suggest that the electronic and photophysical properties are affected by a 2-thienyl group.

## 2.3 Conclusion

The *N*-thienylcarbazoles were synthesized by Ullmann condensation of bromothiophene and carbazole derivatives, 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. The electronic and photophysical properties of **1a–3a** and **1b–3b** were first clarified and compared to one another. 2-Thienyl groups more affect the characters of both excited singlet and triplet states of carbazole moiety than 3-thienyl groups. These results provide a guidance for the construction of new OLED materials and so on.

### 2.4 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 an F-4500 spectrophotometer. These spectra were obtained in cyclohexane (spectroscopic grade) with a quartz cell of 10 mm optical path. GPC was performed with a JAI LC-918 R/U Recycling Preparative HPLC using JAIGEL-1H and 2H columns.

The fluorescence lifetimes ($\tau_f$) were obtained with a time-correlated single-photon counting (TCSPC) fluorometer (Edinburgh Analytical Instruments FL900CDT). A nanosecond pulsed discharge lamp (pulse width ~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 (Figure 2-6, 2-7, 2-8).

The fluorescence quantum yield ($\Phi_f$) 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.

$$\Phi_{fX} = \frac{F_X \, A_{ST} \, n_X^2}{F_{ST} \, A_X \, n_{ST}^2} \Phi_{fST} \tag{4}$$

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 $\tau_f$ value ($\tau_{fST} = 0.47$) of 1-aminonaphthalene in cyclohexane was used as a standard solution.

Phosphorescence spectra and lifetime ($\tau_p$) 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 ~17 ns) were 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 the freeze-pump-thaw method.


**Preparation of 9-(3-Thienyl)carbazole (1a) (General Procedure)**

A mixture of 3-bromothiophene (0.50 g, 3.07 mmol), carbazole (0.34 g, 2.04 mmol),

$K_2CO_3$ (0.71 g, 5.11 mmol), and Cu (0.20 g, 3.07 mmol) in nitrobenzene (7 mL) was stirred at

180 ˚C for 42 h. After cooling to room temperature, $CHCl_3$ (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/hexane) to afford

**1** (0.33 g, 1.32 mmol, 64%). Mp 79.9–80.2 ˚C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.14 (2H, d,

$J$ = 7.8 Hz), 7.57 (1H,dd, $J$ = 3.4 Hz, 1.8 Hz), 7.48 (1H, dd, $J$ = 1.8 Hz, 1.4 Hz), 7.46–7.43

(4H, m), 7.34(1H, dd, $J$ = 3.4 Hz, 1.4 Hz), 7.31–7.28 (2H, m). ^{13}C NMR (125 MHz,

CDCl$_3$): δ 140.9, 135.8, 126.2, 126.0, 125.4, 123.2, 120.2, 120.0,119.4, 109.9. Anal. Calcd

for $C_{16}H_{11}NS$: C, 77.07; H, 4.45; N, 5.62. Found: C, 77.07 ; H, 4.39 ; N, 5.56.


**9-(2-Thienyl)carbazole (2a)**[4]

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.10 (2H, m), 7.43 (4H, m), 7.38 (1H, m), 7.30 (2H, m),

7.18 (2H, m).


**2,5-Bis(9-carbazolyl)thiophene (3a)**

Mp 227.2–227.4 ˚C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.17 (4H, d, $J$ = 7.9 Hz), 7.67

(4H, d, $J$ = 8.2 Hz), 7.54 (4H, m), 7.38 (4H, m), 7.34 (2H, s); ^{13}C NMR (125 MHz, CDCl$_3$):

δ 141.70, 126.42, 124.55, 123.59, 123.18, 121.26, 119.98, 110.41; Anal. Calcd for $C_{28}H_{18}N_2S$: C, 81.13; H, 4.38; N, 6.76.  Found: C, 80.76 ; H, 4.57 ; N, 6.73.

### 3,6-Di-*tert*-butyl-9-(3-thienyl)carbazole (1b)

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.11 (2H, d, $J$ = 1.8 Hz), 7.53 (1H, dd, $J$ = 4.9, 3.3 Hz), 7.47 (2H, dd, $J$ = 8.4, 1.8 Hz), 7.42 (1H, dd, $J$ = 3.3, 1.1 Hz), 7.37 (2H, d, $J$ = 8.4 Hz), 7.32 (1H, dd, $J$ = 4.9, 1.1 Hz), 1.46 (18H, m)

### 3,6-Di-*tert*-butyl-9-(2-thienyl)carbazole (2b)[7]

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.09 (2H, d, $J$ = 2.0 Hz), 7.48 (2H, dd, $J$ = 8.7, 2.0 Hz), 7.38 (2H, $J$ = 8.7 Hz), 7.33 (1H, m), 7.15 (2H, m), 1.48 (18H, m).

### 2,5-Bis(3,6-di-*tert*-butyl-9-carbazolyl)thiophene (3b)

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.12 (4H, s), 7.55 (8H, m), 7.21 (2H, s), 1.48 (36H, m).

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11  With a rotating chopper, the emission of **2a** at 77 K was not observed, but it is reasonable to assign the broad emission around 500 nm to the phosphorescence instead of the fluorescence, because its lifetime was 170 µs, which is too long for fluorescence, and **3a** also provided similar phosphorescence.
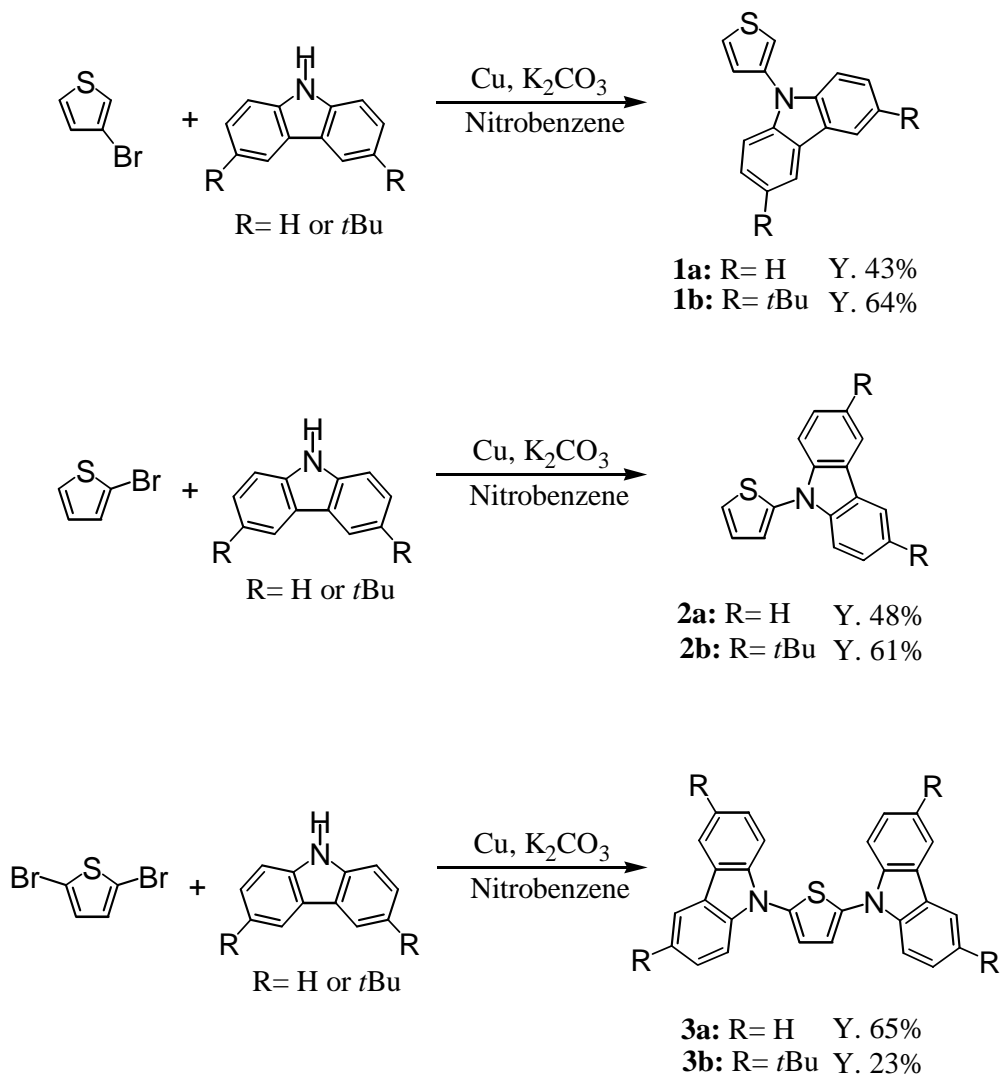
Scheme 2-1. Synthesis of *N*-Thienylcarbazoles **1a-3a** and **1b-3b**.
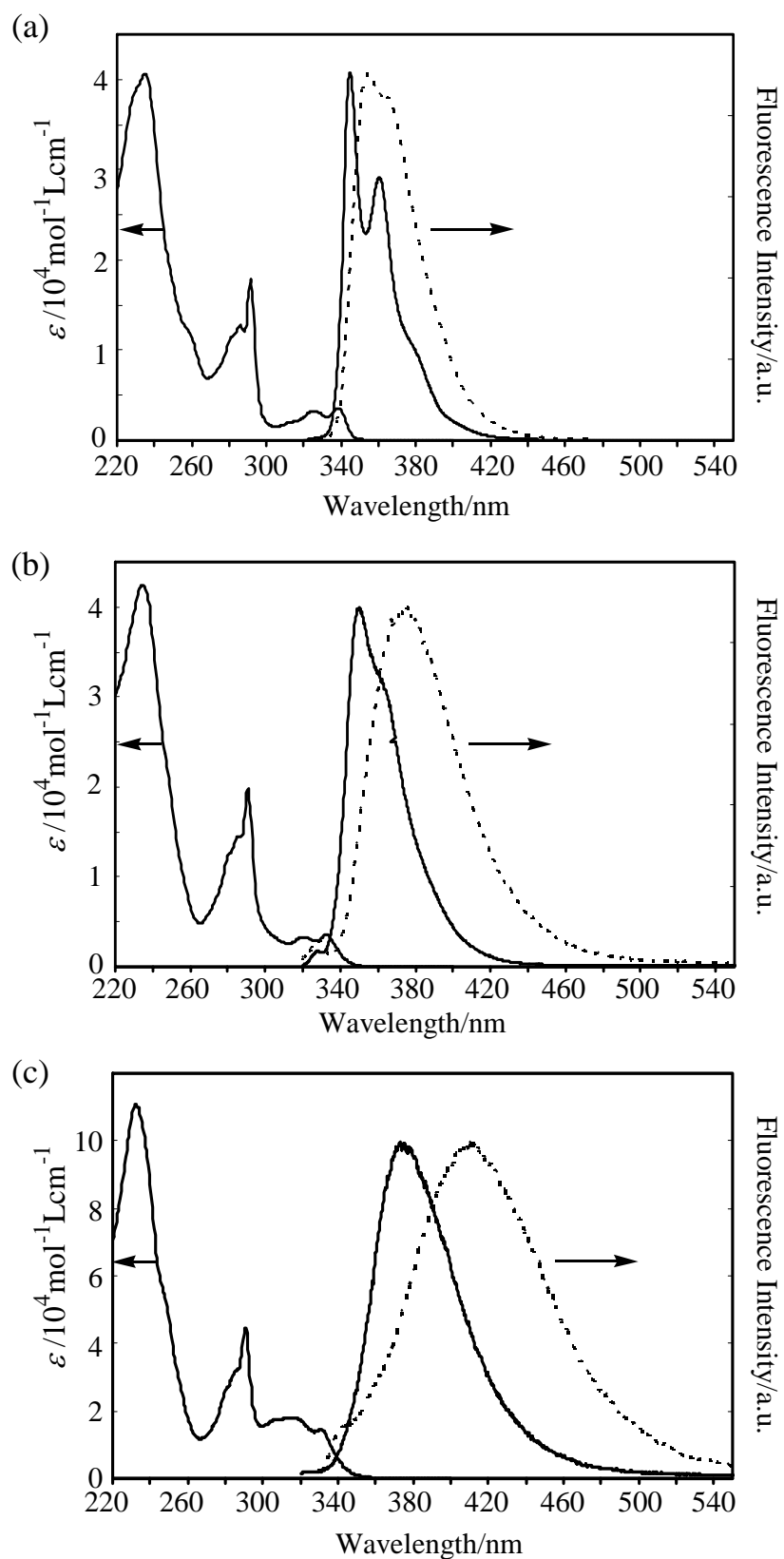
Figure 2-1. Absorption spectra in cyclohexane and fluorescence spectra ($\lambda_{ex}$ = 300 nm) in cyclohexane (solid line) and acetonitrile (dotted line) of (a) **1a**, (b) **2a**, and (c) **3a** at room temperature.
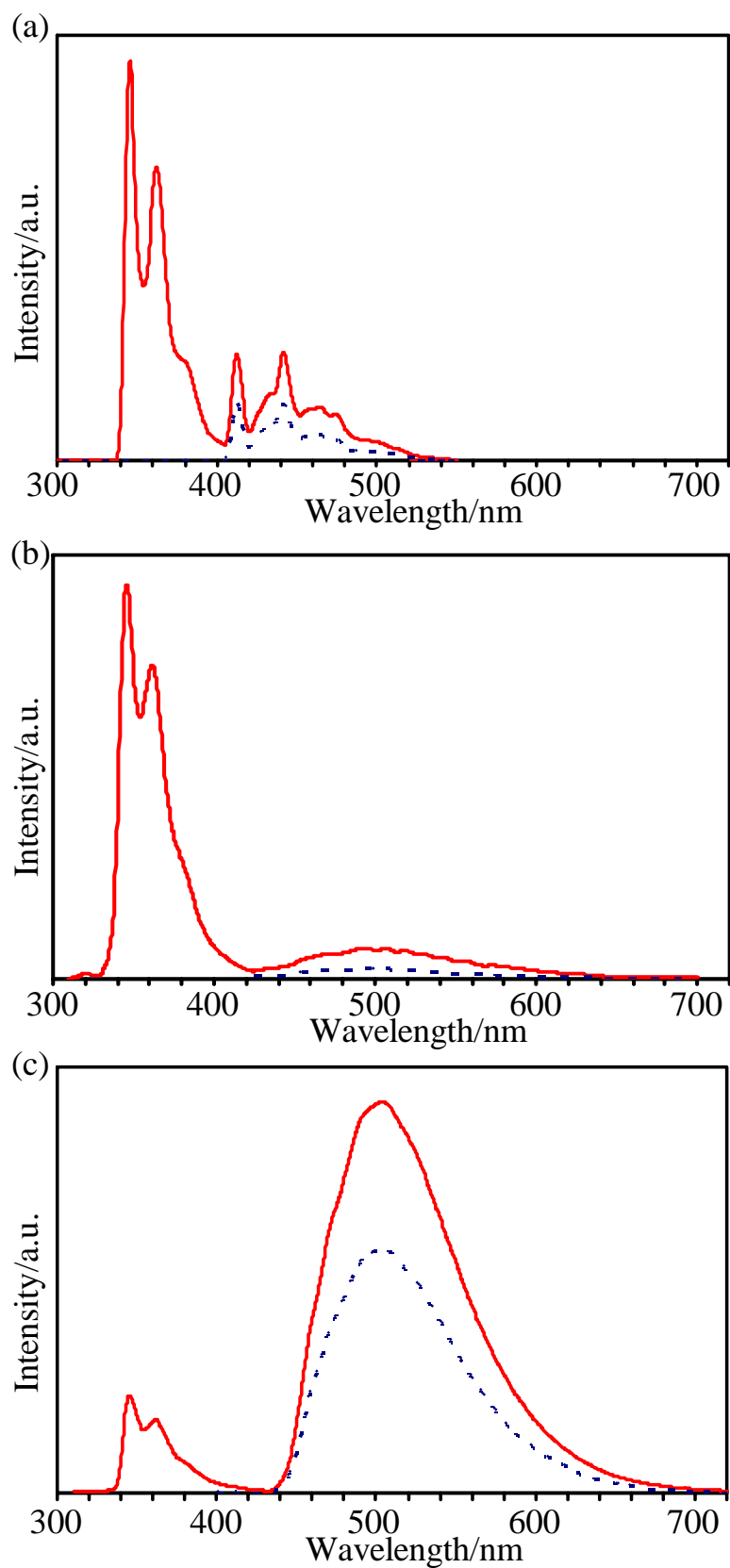
73

Figure 2-2. Total emission (solid line) and phosphorescence spectra (dotted line) of (a) **1**a, (b) **2**a, and (c) **3**a in 3-methylpentane at 77 K ($\lambda_{ex}$ = 300 nm).
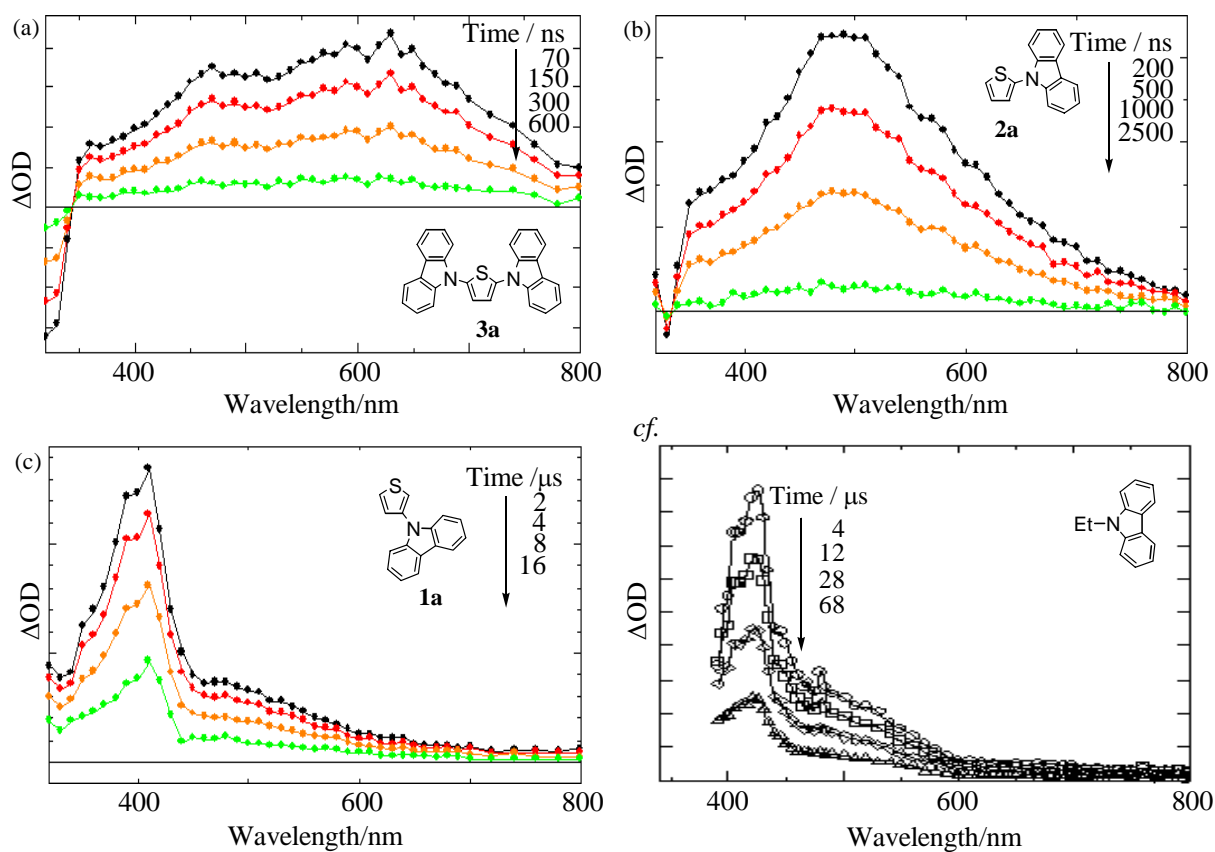
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Figure 2-3. Transient absorption spectra of (a) **3a**, (b) **2a**, (c) **1a**, and (d) *N*-ethylcarbazole upon 308-nm excitation in cyclohexane at 293 K.
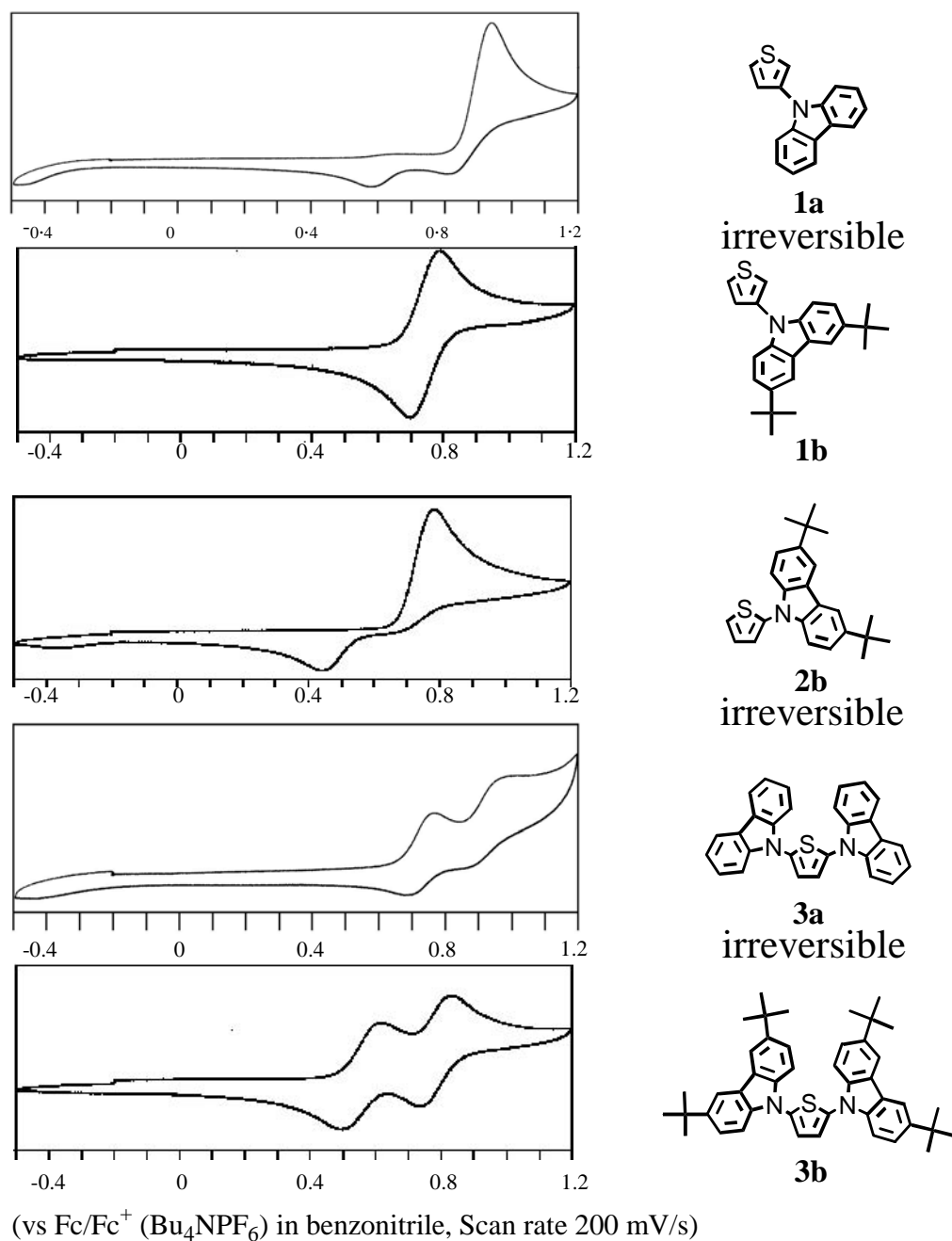
(vs Fc/Fc$^+$ (Bu$_4$NPF$_6$) in benzonitrile, Scan rate 200 mV/s)

Figure 2-4. Cyclic Voltammograms of (a) **1a**, (b) **1b**, (c) **2b**, (d) **3a**, and (e) **3b**.

Table 2-2. Redox Potentials of **1a**, **1b**, **2b**, **3a**, and **3b**

|  | $^1E_{1/2}$/V | $^2E_{1/2}$/V |
|---|---|---|
| **1a** | 0.89 [a)] | - |
| **1b** | 0.71 | - |
| **2b** | 0.75 [a)] | - |
| **3a** | 0.72 [a)] | 0.82 [a)] |
| **3b** | 0.52 | 0.75 |

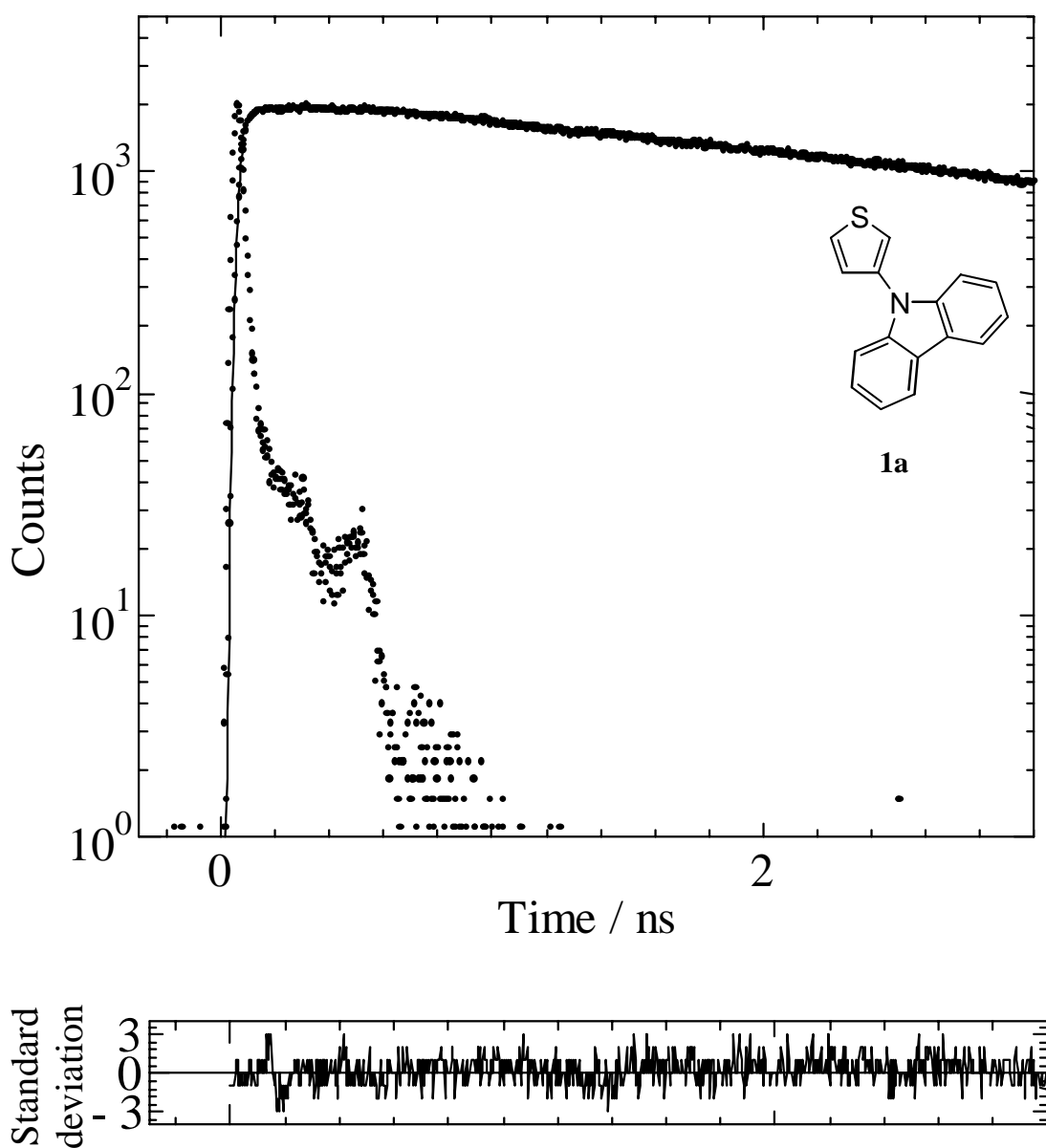a) $^1E_{OX}$ due to the irreversible process.

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Figure 2-5. Fluorescence decay function of **1a** in cyclohexane at 298 K excited at 266 nm and monitored at 345 nm.
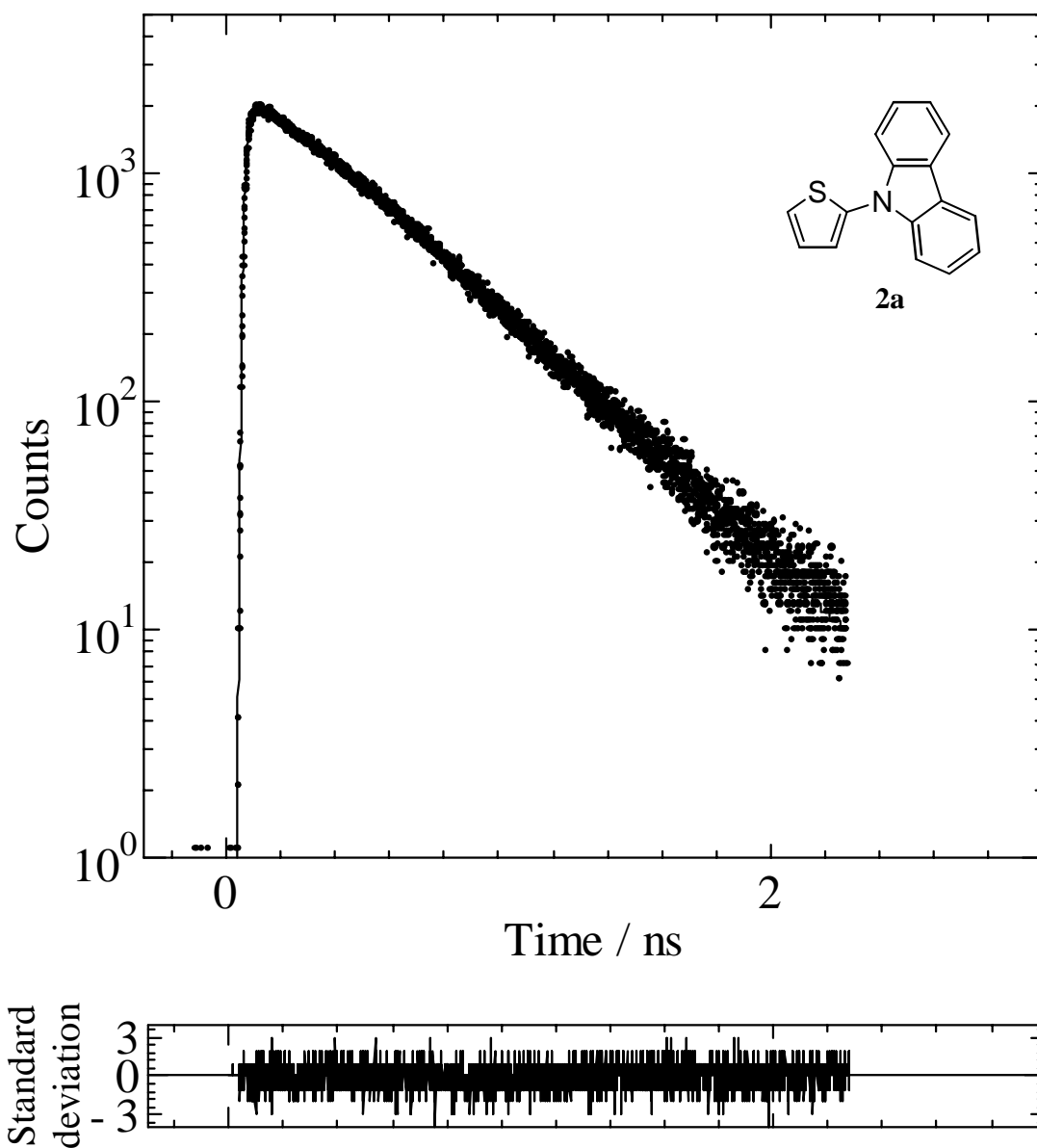
Figure 2-6. Fluorescence decay function of **2a** in cyclohexane at 298 K excited at 266 nm and monitored at 350 nm.
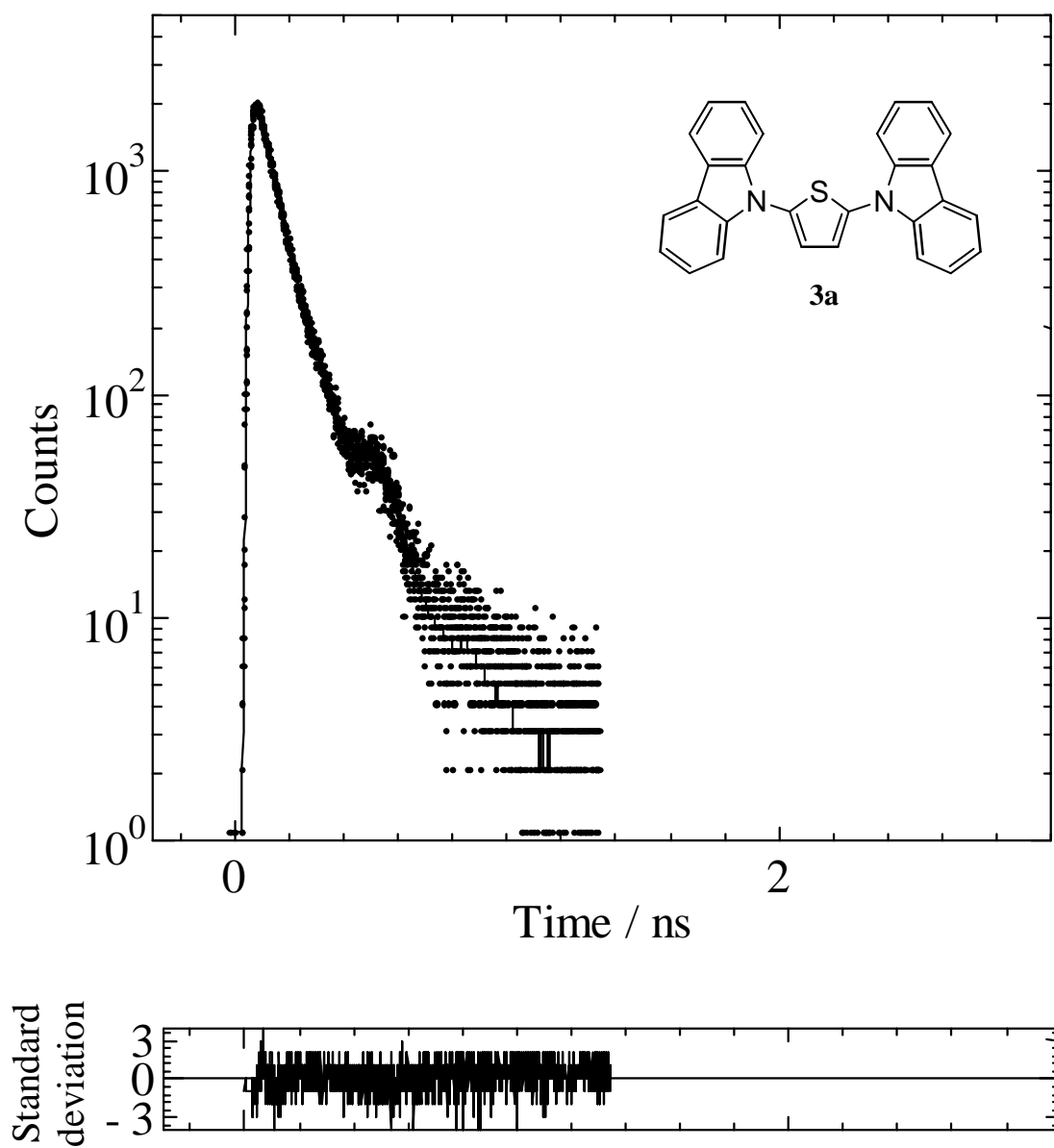
Figure 2-7. Fluorescence decay function of **3a** in cyclohexane at 298 K excited at 266 nm and monitored at 345 nm.

# Chapter 3

## Substituent Effects on Photophysical Properties of Thienylanthracenes

**Abstract**

The compounds containing both anthracene and thiophene connected directly were successfully synthesized by the palladium-catalyzed Suzuki coupling reaction, and their photophysical properties were investigated in detail based on the absorption spectra, fluorescence spectra, fluorescence lifetimes, quantum yields, and phosphorescence spectra. The electronic and photophysical properties of a series of thienylanthracenes were first clarified and compared to one another. 2-Thienyl groups more affect the characters of both excited singlet and triplet states of anthracene moiety than 3-thienyl groups.

**3.1 Introduction**

Various thiophene derivatives have been prepared for the wide application into organic electronic devices,[1] since they show characteristic properties such as high charge carrier mobility,[2] excellent thermal,[3] photochemical,[4] electrical stabilities, and high fluorescence quantum yields. Anthracene derivatives have also attracted much attention from the viewpoint of application into organic electronic devices because of their characteristics such as high fluorescence quantum yields[5] and high electron mobility due to the $\pi$-$\pi$ stacking structure.

By combining thiophene and anthracene, it is possible to construct new organic photofunctional materials. Actually some compounds containing both aromatics have been prepared and their properties examined.[6] However, there have been no reports on the systematic investigation of the substituent effects of thiophene onto anthracene or the opposite substituent effects. The clarification of such substituent effects is of great importance for the improvement of properties and the development of new compounds. We have clarified the substituent effect of thiophene onto carbazole nucleus as described in Chapter 2. We have found that the fluorescence of carbazole is significantly quenched when a 2-thienyl residue is attached to the nitrogen atom of a carbazole ring, whereas the fluorescence is hardly quenched when a 3-thienyl residue is substituted at the nitrogen atom of a carbazole ring. We were prompted to investigate whether the quenching effect of 2-thienyl group is effective for other aromatics. Thus, we have prepared a series of thienylanthracenes **1**–**3**, investigated their electronic and photophysical properties, and compared with those of thienylcarbazoles.



|  **1**  |  **2**  |  **3**  |
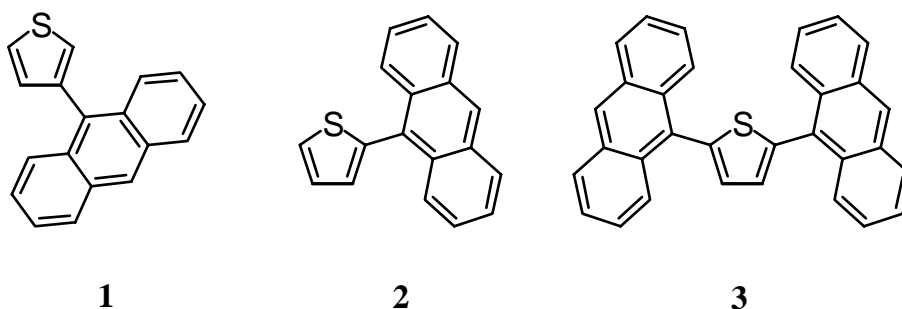
**3.2 Results and Discussion**

**3.2.1 Synthesis of Thienylanthracenes**

Scheme 3-1 illustrates the synthesis of **1**–**3**. Both **1** and **2** were prepared by the palladium-catalyzed Suzuki coupling reaction of 9-bromoanthracene and the corresponding thiophene boronic acid or boronic acid pinacol ester in a manner similar to that in the literature.[7] 2,5-Bis(9-anthryl)thiophene **3** was prepared by the Suzuki coupling of 2,5-dibromothiophene and 9-anthraceneboronic acid pinacol ester, since the preparation of 2,5-thiophenebisboronic acid was difficult. All of **1**–**3** were characterized by $^1$H and $^{13}$C NMR and other spectroscopies. In the $^1$H NMR spectra of **1** and **2**, three sets of peak for the thiophene protons were observed in addition to the five sets of peak for the anthracene protons, while the thiophene protons of **3** with a higher symmetry were observed as a singlet peak in contrast with **1** and **2**.

**3.2.2 Electronic and Photophysical Properties of Thienylanthracenes**

**Absorption Spectra**

The absorption spectra of **1**–**3** and anthracene measured in cyclohexane at room temperature are shown in Figure 3-1.

The absorption spectra of **1**–**3** exhibit absorption bands characteristic of anthracene; the weak vibrational structures around 325–420 nm and the intense, sharp absorption band at ca. 250 nm are attributed to the $S_0$–$S_1$ and $S_0$–$S_3$ transitions of the anthracene moiety, respectively. The $S_0$–$S_1$ bands of **1**–**3** are red-shifted relative to anthracene ($\lambda_{max}$ = 381 nm), indicating the extension of the $\pi$-conjugated system by the introduction of a thiophene ring. The red shift increases in the order of **1** ($\lambda_{max}$ = 397 nm), **2** ($\lambda_{max}$ = 400 nm), and **3** ($\lambda_{max}$ = 415 nm). These results indicate that the electronic property of the ground state ($S_0$) of anthracene moiety is more affected by the 2-thienyl substitution than the 3-thienyl substitution.

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**Fluorescence Spectra**

The fluorescence spectra of **1**–**3** and anthracene measured in cyclohexane and acetonitrile at room temperature are shown in Figure 3-1.

The spectrum of **1**, showing vibrational structures characteristic of anthracene derivatives, is most similar to that of anthracene, though slightly broadened. The spectrum of **2** is further broadened, showing almost no vibrational structures. The fluorescence intensity of **3** is extremely decreased with further broadening relative to **2**. These results indicate that the property of excited singlet state ($S_1$) of anthracene is also much more affected by the 2-thienyl substitution than the 3-thienyl substitution. The fluorescence intensities of **2** and **3** in acetonitrile are rather lower than those in cyclohexane. These tendencies are similar to those of the *N*-thienylcarbazoles described in Chapter 2.

**Fluorescence Quantum Yields and Lifetime**

The fluorescence quantum yields ($\Phi_f$) and lifetimes ($\tau_f$) of **1**–**3** in cyclohexane and acetonitrile are listed in Table 3-1. The details for the analysis of lifetimes are described in Experimental section.

Among **1**–**3**, the fluorescence lifetimes of **1** are by far the longest in both solvents and close to those of anthracene. The fluorescence lifetimes of **2** and **3** are shorter than those of **1** and on the same order. The fluorescence quantum yields decrease in the order of **1**, **2**, and **3** in both solvents. These results indicate that the property of excited singlet state ($S_1$) of anthracene is also much more affected by the 2-thienyl substitution than the 3-thienyl substitution. The fluorescence quantum yields of all of **1**–**3** in acetonitrile are lower than those in cyclohexane.

The quantum yields of intersystem crossing ($\Phi_{isc}$) of **1**–**3** were measured by photoacoustic spectroscopy for further clarification of the relaxation process of excited states. The quantum yields of internal conversion ($\Phi_{ic}$) were also calculated from the $\Phi_f$ and $\Phi_{isc}$

values.

The $\Phi_{ic}$ of **3** is significantly larger than that of **1** in both solvents.   The low fluorescence quantum yield of **3** relative to **1** is mainly due to the fast internal conversion process in **3** relative to the fluorescence emission process.   Interestingly, the ratio between $\Phi_{isc}$ and $\Phi_{ic}$ of **2** is remarkably dependent on the solvents; the $\Phi_{isc}$ is larger than $\Phi_{ic}$ in cyclohexane, whereas the $\Phi_{ic}$ is larger than $\Phi_{isc}$ in acetonitrile.   From these results, the low fluorescence quantum yield of **2** relative to **1** is due to the high $\Phi_{isc}$ in cyclohexane and the high $\Phi_{ic}$ in acetonitrile for **2**.

Table 3-1. Fluorescence Quantum Yield ($\Phi_f$) and Fluorescence Lifetime ($\tau_f$) of **1**–**3** in Cyclohexane and Acetonitrile at Room Temperature

| Compound | Solvent | $\tau_f$ /ps | $\Phi_f$ | $\Phi_{isc}$ | $\Phi_{ic}$ [a] | $k_f/$ $10^7$ s$^{-1}$ [b] | $k_{isc}/$ $10^7$ s$^{-1}$ | $k_{ic}/$ $10^7$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Anthracene | n [c] | 5300 | 0.30 | | | | | |
| | p [c] | 5800 | 0.27 | | | | | |
| **1** | CH | 4290 | 0.40 | 0.60 | ~0 | 9.3 | 13.9 | 0 |
| | MeCN | 4800 | 0.41 | 0.37 | 0.22 | 8.5 | 7.8 | 4.5 |
| **2** | CH | 307 | 0.02 | 0.86 | 0.12 | 6.5 | 279 | 40 |
| | MeCN | 119 | 0.005 | 0.23 | 0.76 | 4.2 | 191 | 639 |
| **3** | CH | 354 | 0.004 | 0.14 | 0.85 | 1.1 | 40.3 | 241 |
| | MeCN | 303 | 0.002 | 0.11 | 0.88 | 0.7 | 37.8 | 292 |

[a] $\Phi_{ic} = 1-(\Phi_f + \Phi_{isc})$.    [b] $k_f = \Phi_f /\tau_f$.    [c] n: non-polar solvent, p: polar solvent.

**Phosphorescence Spectra**

The phosphorescence spectra of **1**–**3** measured in ethanol at 77 K are shown in Figure 3-2. The phosphorescence spectra of **1**–**3** are broadened relative to anthracene and exhibit different spectral features.　These results indicate that the electronic properties of triplet state ($T_1$) of anthracene are affected by each thienyl substitution.

**3.3 Conclusion**

Thienylanthracenes were successfully synthesized by the palladium-catalyzed Suzuki coupling reaction, and their photophysical properties were investigated in detail based on the absorption spectra, fluorescence spectra, fluorescence lifetimes, quantum yields, and phosphorescence spectra.　The electronic and photophysical properties of **1**–**3** were clarified and compared to one another.　2-Thienyl groups more affect the characters of both excited singlet and triplet states of anthracene moiety than 3-thienyl groups.　These results provide a guidance for the construction of new OLED materials and so on.

## 3.4 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 an F-4500 spectrophotometer. These spectra were obtained in cyclohexane (spectroscopic grade) with a quartz cell of 10 mm optical path. GPC was performed with a JAI LC-918 R/U Recycling Preparative HPLC using JAIGEL-1H and 2H columns.

The fluorescence lifetimes ($\tau_f$) were obtained with a time-correlated single-photon counting (TCSPC) fluorometer (Edinburgh Analytical Instruments FL900CDT). A nanosecond pulsed discharge lamp (pulse width ~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 decay functions of **1**–**3** were measured in degassed cyclohexane and acetonitrile at 298 K by means of the nanosecond single-photon-counting method. The decay functions were analyzed (by the deconvolution method) as a single-exponential function or a sum of double-exponential functions (Eq. 1).

$$I(t) = A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right) + A_3 \exp\left(-t/\tau_3\right) \qquad (1)$$

Table 3-2 lists the fluorescence lifetimes ($\tau$) and the ratio of each decay component just after excitation ($A_1$, $A_2$, $A_3$).

Table 3-2.　Fluorescence Lifetime of **1**, **2**, and **3** in Cyclohexane and Acetonitrile at 298 K

| Sample | Solvent | $\tau_1$/ ps | % | $\tau_2$/ ps | % | $\tau_3$/ ps | % |
|--------|---------|--------------|---|--------------|---|--------------|---|
| **1** | CH | 4290 | - | | | | |
| | MeCN | 4800 | - | | | | |
| **2** | CH | 307 | - | | | | |
| | MeCN | 9.6 | 16.7 | 119 | 70.7 | 6300 | 12.6 |
| **3** | CH | 10 | 53.8 | 354 | 46.2 | | |
| | MeCN | 11 | 53.2 | 303 | 46.8 | | |

Figure 3-3 shows the typical fluorescence decay functions of **1**, excited at 350 nm and monitored at 395 nm in cyclohexane and excited at 350 nm and monitored at 400 nm in acetonitrile.　These decay profiles were satisfactorily analyzed as a single-exponential function with a lifetime of 4290 ps in cyclohexane and 4800 ps in acetonitrile.

Figure 3-4 shows the typical fluorescence decay functions of **2**, excited at 266 nm and monitored at 420 nm in cyclohexane and acetonitrile.　The decay profile in cyclohexane was satisfactorily analyzed as a single-exponential function with a lifetime of 307 ps.　On the contrary, the decay profile in acetonitrile consists of three components of 9.6 ps, 119 ps, and 6300 ps.　The major component (119 ps, 70.7%) was considered as the lifetime of **2** in acetonitrile.　The other minor components may be due to some impurities, but they are unrevealed at the present stage.

Figure 3-5 shows the typical fluorescence decay functions of **3**, excited at 266 nm and monitored at 455 nm in cyclohexane and acetonitrile.　The decay profiles of **3** in both solvents consist of two components of ca. 10 ps (ca. 53%) and ca. 300 ps (ca. 46%).　The component of ca.10 ps maybe arise from some impurities when considering the results for **2**.

The absolute fluorescence quantum yield ($\Phi_f$) of **1** was measured on Hamamatsu

Photonics integrating sphere. The fluorescence quantum yields ($\Phi_f$) of **2** and **3** were 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.

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

(2)

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 $\Phi_f$ value ($\Phi_{fST}$ = 0.40 in cyclohexane, $\Phi_{fST}$ = 0.41 in acetonitrile) of **1** was used as a standard solution.

The radiative rate constant ($k_f$) was determined based on the fluorescence quantum yield ($\Phi_f$) and fluorescence lifetime ($\tau_f$) (Eq. 3).

$$k_f = \Phi_f / \tau_f$$

(3)

The phosphorescence spectra and lifetime ($\tau_p$) 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 ~17 ns) were 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 the freeze-pump-thaw method.

## Preparation of Compound 1[7]

A mixture of 3-thiophene boronic acid (0.20 g, 1.56 mmol), 9-bromoanthracene (0.42 g, 1.63 mmol), $Na_2CO_3$ (0.17 g, 1.60 mmol), and $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol) in toluene/ ethanol (4/1) (50 mL) was stirred at 120 °C for 7 h.   After cooling to room temperature, the target compound was extracted with toluene (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/hexane) to afford **1** (0.21 g, 0.81 mmol, 51%).   Mp 118.0-118.8 °C.   ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (1H, s), 8.03 (2H, d, $J$ = 8.5 Hz), 7.78 (2H, d, $J$ = 8.5 Hz), 7.58 (1H, m), 7.46 (1H, m), 7.38 (4H, m), 7.23 (1H, m)   ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.42, 131.88, 131.29, 130.77, 130.73, 128.31, 126.72, 126.64, 125.48, 125.45, 125.13, 125.10.

## Preparation of Compound 2[7]

A mixture of 2-(2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.21 g, 1.00 mmol), 9-bromoanthracene (0.25 g, 0.97 mmol), $Na_2CO_3$ (0.16 g, 1.51 mmol), and $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) in toluene/ethanol (4/1) (50 mL) was stirred at 120 °C for 7 h.   After cooling to room temperature, the target compound was extracted with toluene (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/ hexane) to afford **2** (0.16 g, 0.60 mmol, 62%).   Mp 109.0-110.0 °C.   ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (1H, s), 8.03 (2H, d, $J$ = 8.3 Hz), 7.85 (2H, d, $J$ = 8.3 Hz), 7.60 (1H, m), 7.44 (4H, m), 7.21 (2H, m).

## Preparation of Compound 3

A   mixture   of   2,5-dibromothiophene   (0.1   g,   0.41   mmol), 2-(9-anthranyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.27 g, 0.89 mmol), $Na_2CO_3$ (0.09 g,

0.85 mmol), and Pd(PPh$_3$)$_4$ (0.05 g, 0.04 mmol) in toluene/ethanol (4/1) (50 mL) was stirred at 120 ˚C for 24 h.    After cooling to room temperature, the target compound was extracted with toluene (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/hexane) to afford **3** (0.07 g, 0.16 mmol, 39%).    Mp 230.1-231.1 ℃.    $^1$H NMR (300 MHz, CDCl$_3$) δ 8.57 (2H, s), 8.18 (4H, d, *J* = 8.1 Hz), 8.07 (4H, d, *J* = 8.1 Hz), 7.55 (8H, m), 7.37 (2H, s).

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7   (a) B. Claudio, S. Anna, M. Giuseppe, S. Roberto, Masi. Francesco, PCT Int. Appl. **2002,** O 2002034746 A2 20020502.   (b) A. Courtin, E. Class, H. Erlenmeyer, *Helv. Chim. Acta* **1964**, *47*, 1748.
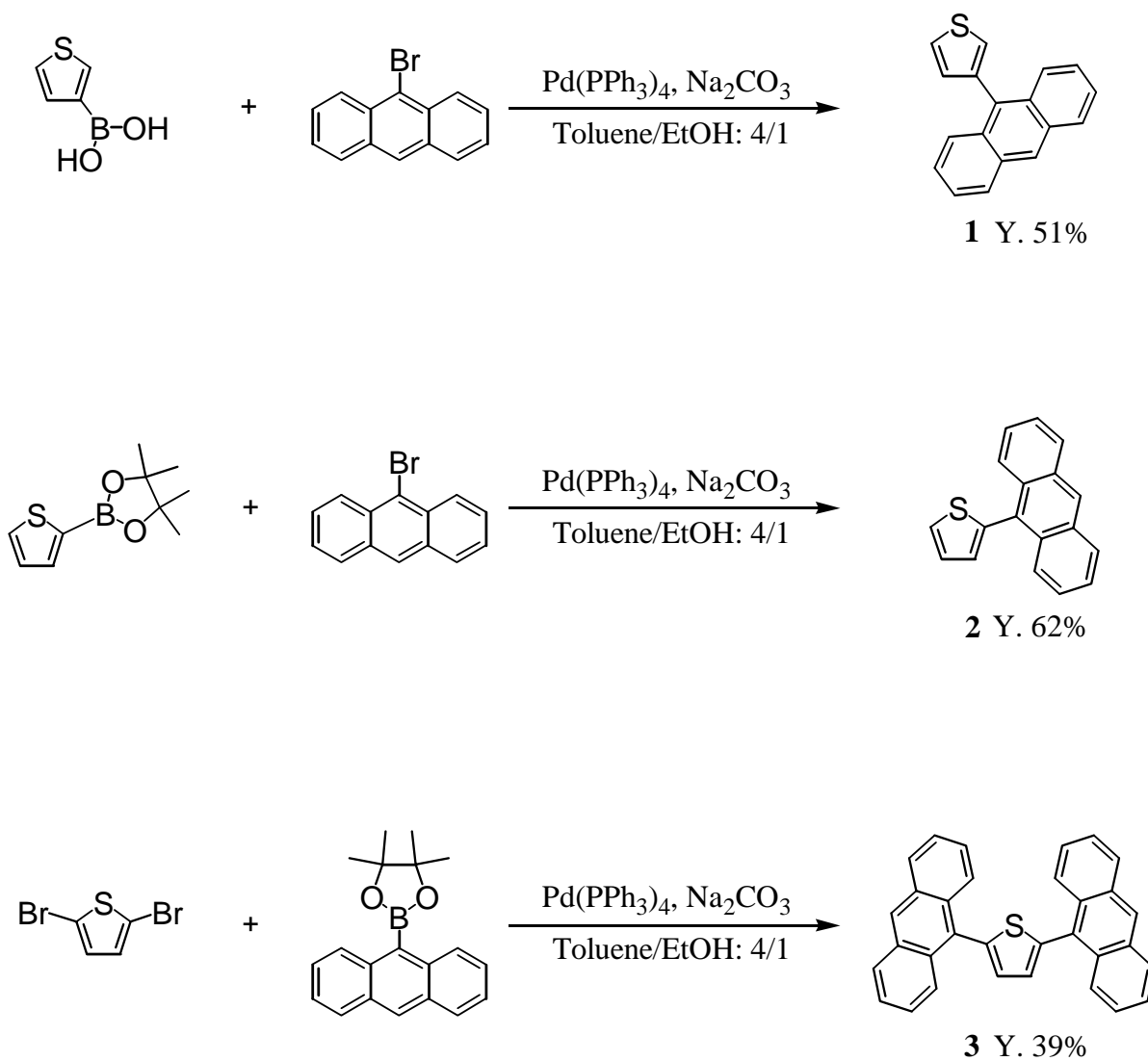
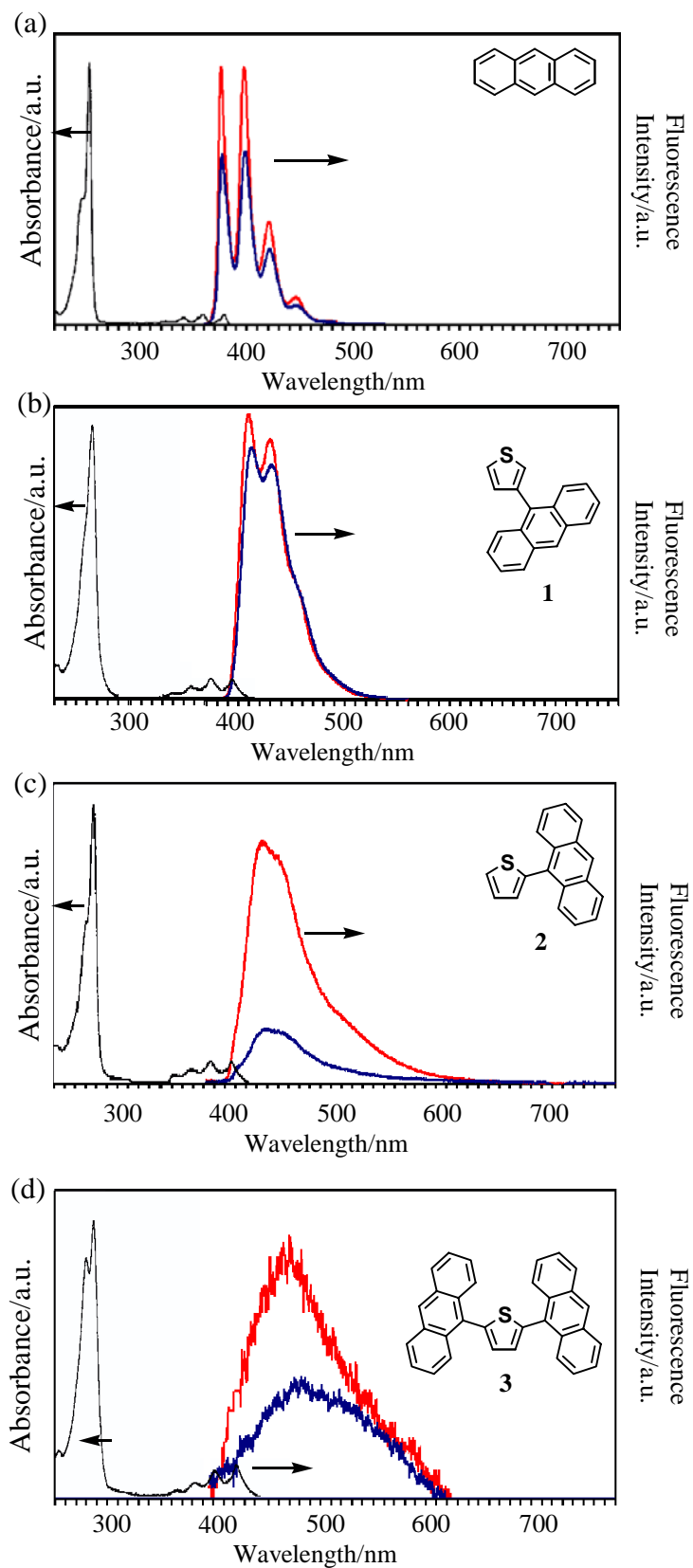Scheme 3-1. Synthesis of Thienylanthracenes **1-3**.

Figure 3-1. Absorption spectra in cyclohexane and fluorescence spectra ($\lambda_{ex}$ = 300 nm) in cyclohexane (red line) and acetonitrile (blue line) of (a) **1**, (b) **2**, and (c) **3** at room temperature.
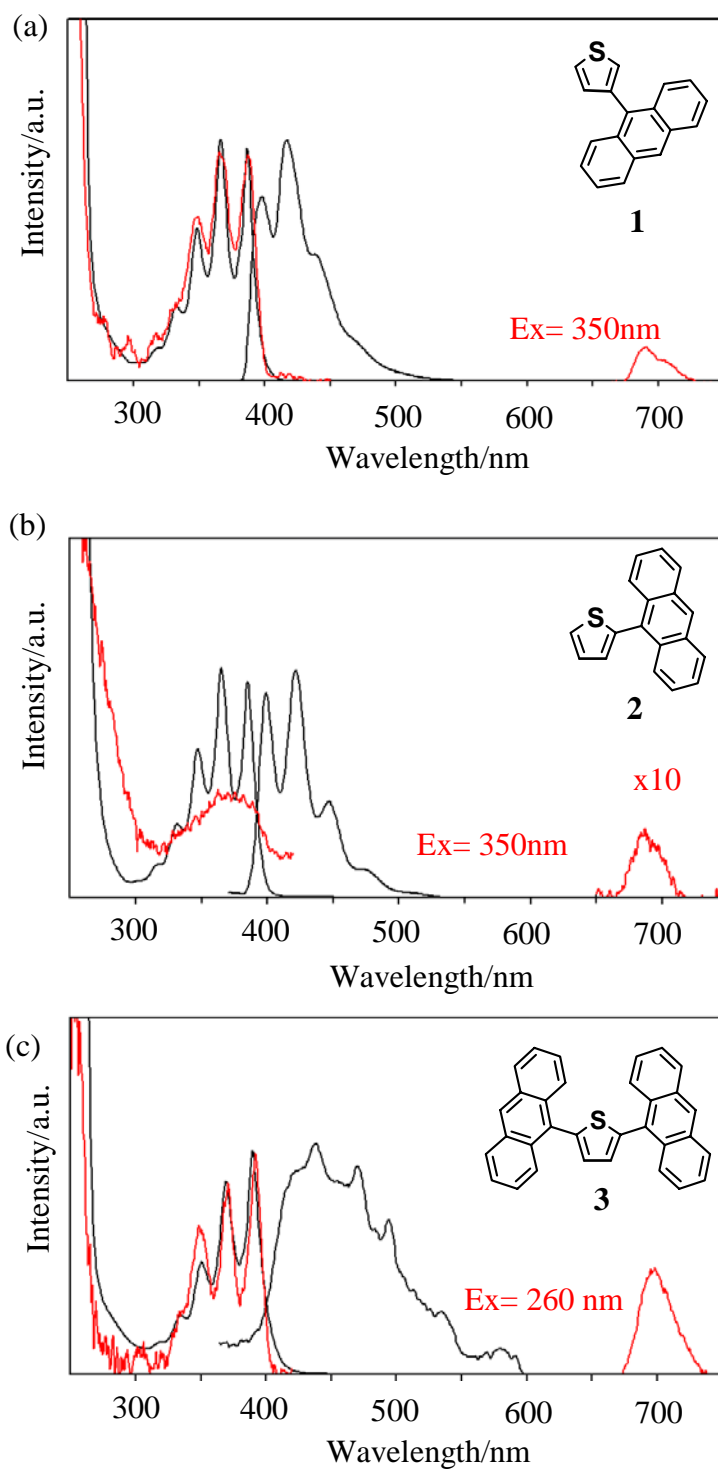
Figure 3-2. Total emission (black line) and phosphorescence spectra(red line) of (a) **1**, (b) **2**, and (c) **3** in EtOH at 77 K.
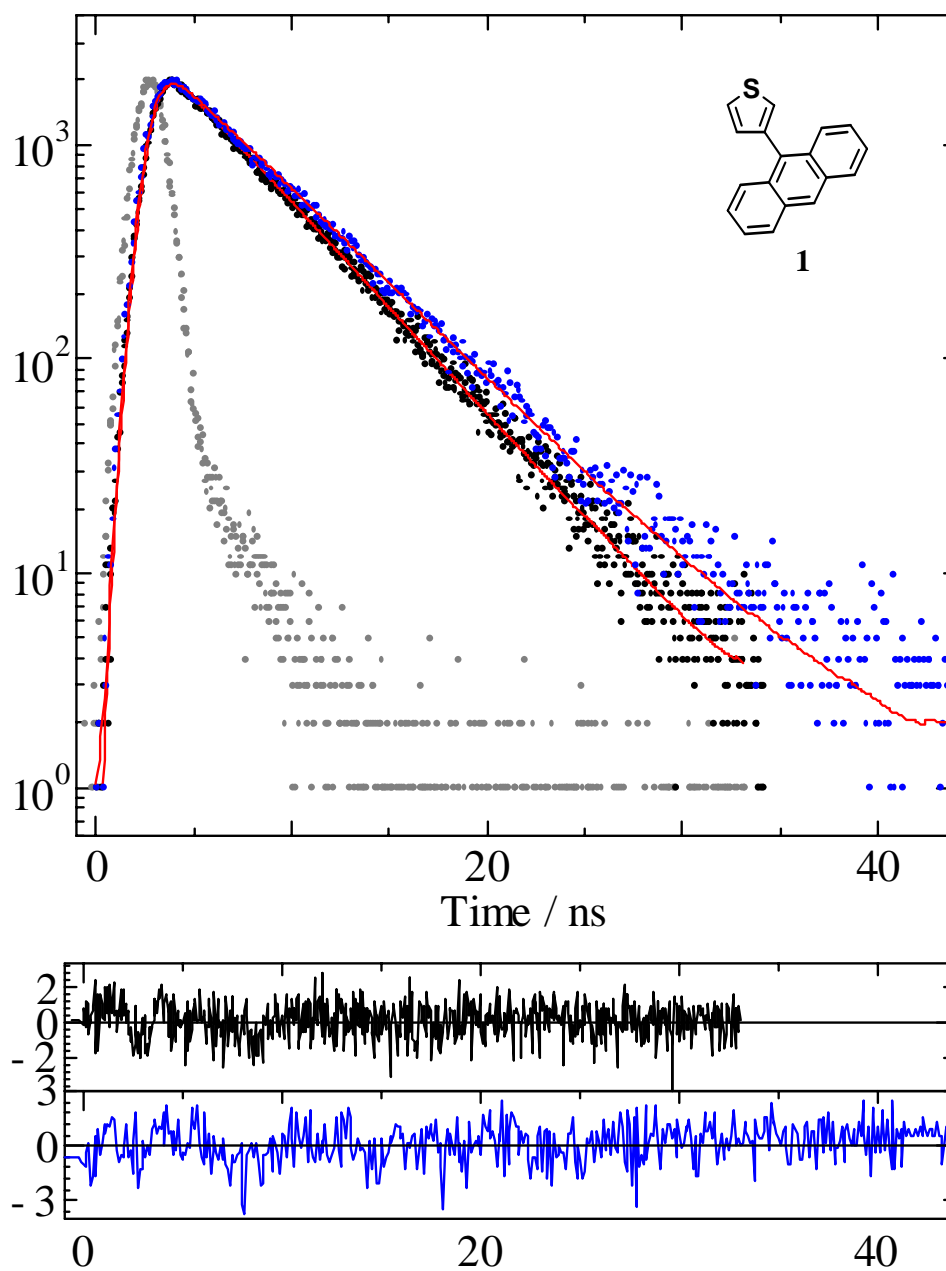
Figure 3-3. Fluorescence decay function of **1**, excited at 350 nm and monitored at 395 nm in cyclohexane and excited at 350 nm and monitored at 400 nm in acetonitrile.
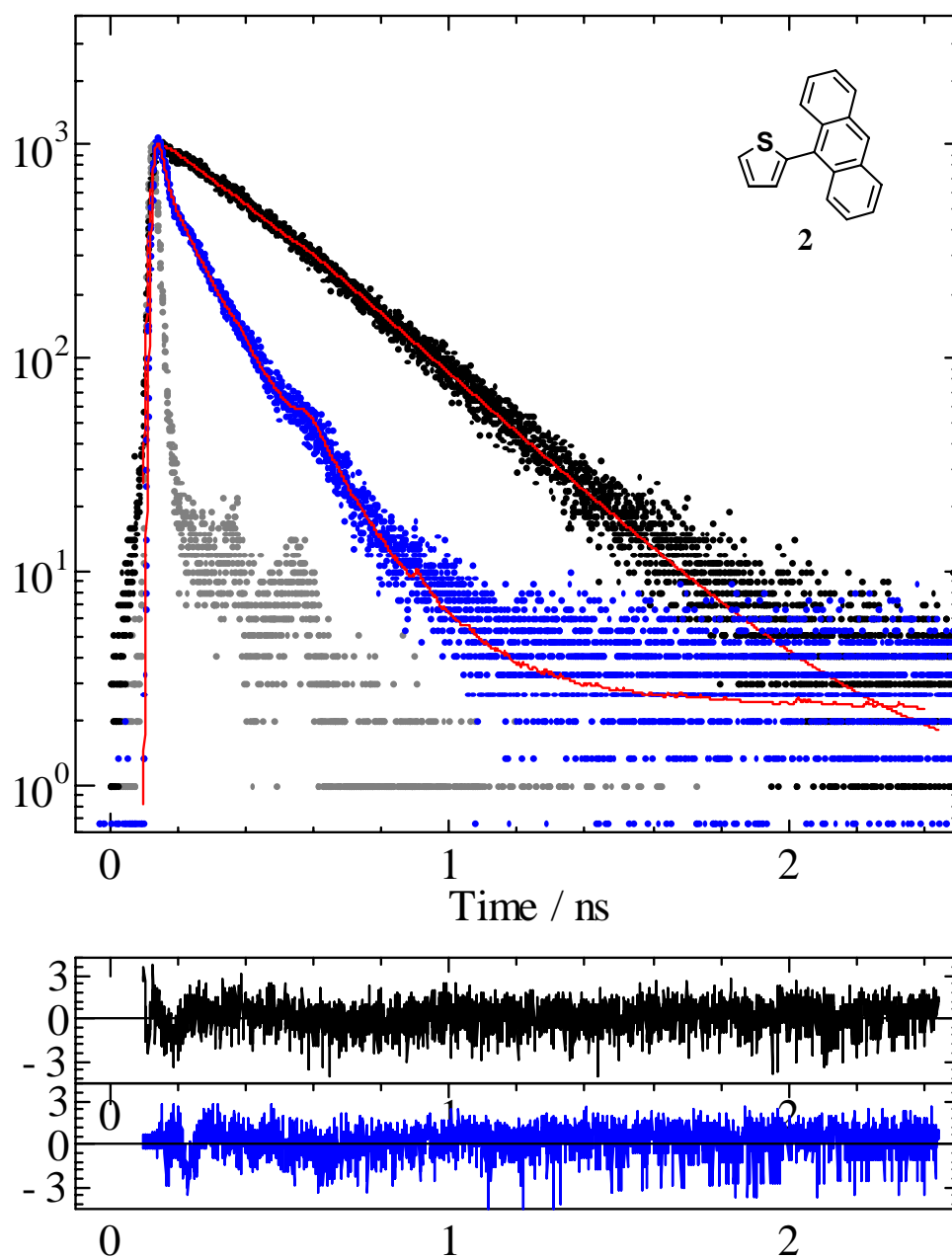
Figure 3-4. Fluorescence decay function of **2** in cyclohexane at 298 K excited at 266 nm and monitored at 420 nm.
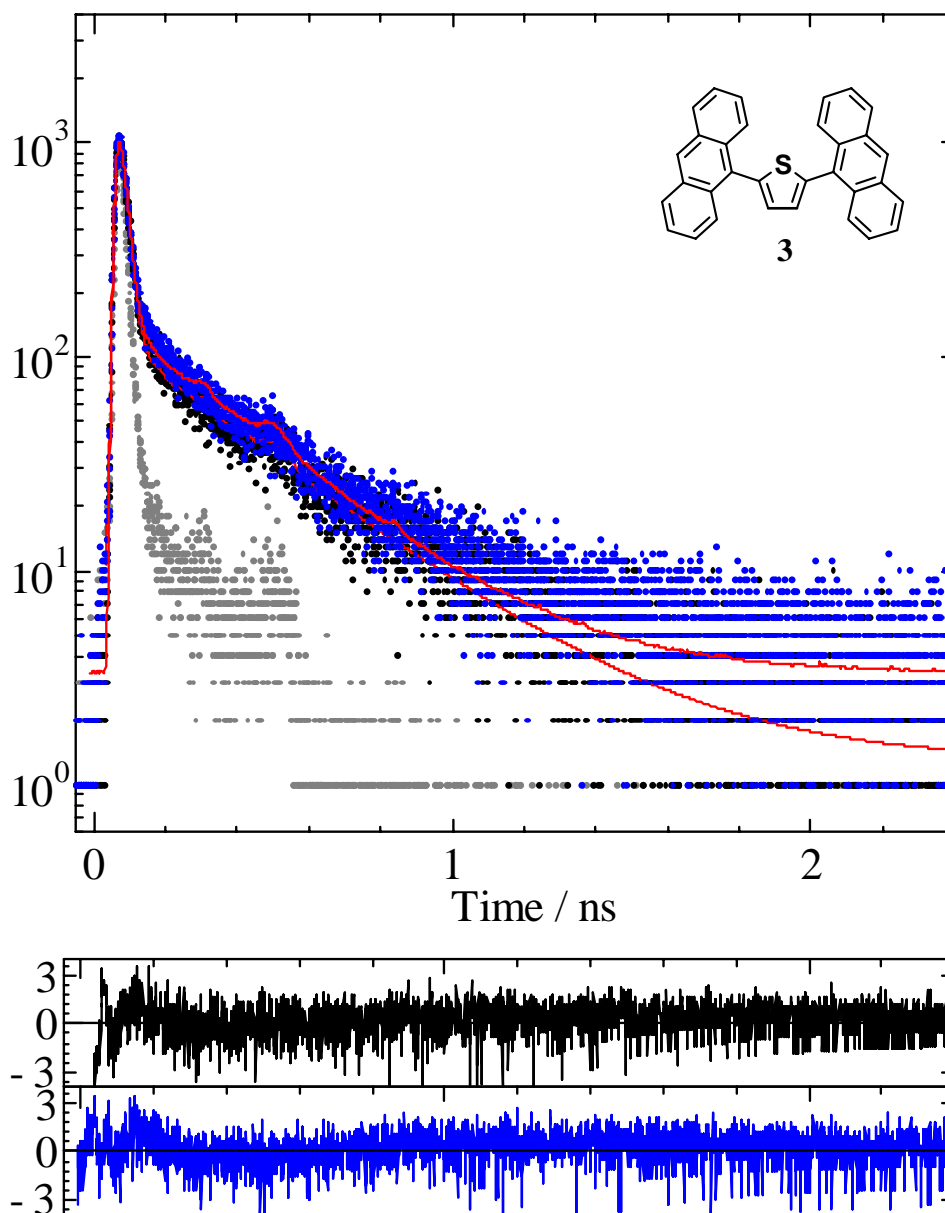
Figure 3-5. Fluorescence decay function of **3** in cyclohexane at 298 K excited at 266 nm and monitored at 455 nm.

**Concluding Remarks**

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. The carbazolophane involving benzene rings exhibited excimer fluorescence and excimer phosphorescence of carbazole, whereas the carbazolophane involving naphthalene rings showed excimer fluorescence of carbazole and monomer phosphorescence of naphthalene. 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. This result suggests that poly(vinylcarbazole)s and phosphorescence host materials for OLEDs having a variety of excited triplet states can be readily obtained by introduction of various aromatic rings on the carbazole nitrogen atoms.

A series of *N*-thienylcarbazoles consisting of carbazole(s) and thiophene connected directly were synthesized by Ullmann condensation, and their electronic and photophysical properties were investigated in detail based on the absorption spectra, fluorescence spectra, fluorescence lifetimes, quantum yields, phosphorescence spectra, and transient absorption spectra. The florescence of carbazole is highly quenched by the 2-thienyl group, while that is hardly quenched by the 3-thienyl group. Their electrochemical properties were also investigated by CV. The compound bearing two carbazole rings at 2,5-positions of thiophene showed highest electron-donating properties. Thus, the characters of both ground and excited states of carbazole moiety are much more affected by a 2-thienyl group than a 3-thienyl group.

A series of thienylanthracenes containing both anthracene and thiophene connected

directly were successfully synthesized by the palladium-catalyzed Suzuki coupling reaction, and their electronic and photophysical properties were investigated in detail based on the absorption spectra, fluorescence spectra, fluorescence lifetimes, quantum yields, and phosphorescence spectra.   In thienylanthracenes, the fluorescence quenching by the 2-thienyl group is much more remarkable than that by the 3-thienyl group, similar to *N*-thienylcarbazoles.

Regardless of aromatic rings, 2-thienyl groups quench the fluorescence and influence the characteristic of the aromatic compounds.   These results indicate that the 3-thienyl group is suitable for the construction of fluorescent materials, whereas the 2-thienyl group is suitable for the non-fluorescent materials.

**List of Publications**

**Original papers**

1    <u>H. Shimizu</u>, A. Kobayashi, S. Itoi, T. Yoshihara, S. Tobita, Y. Nakamura, J. Nishimura, **"**Substituent effects on photophysical properties of *N*-thienylcarbazoles," *Heterocycles* **2009**, *78*, 1265-1269.

2    <u>H. Shimizu</u>, Y. Kakinoya, K. Takehira, T. Yoshihara, S. Tobita, Y. Nakamura, J. Nishimura, **"**Synthesis and Photophysical Properties of *N*-Arylcarbazolophanes," *Bull. Chem. Soc. Jpn.* **2009**, *82*, 860-869.

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**Other publication**

1    <u>H. Shimizu</u>, Y. Nakamura, J. Nishimura, "Functionalization and transformation reaction of $C_{60}$ and CNT" in "Invention of Conjugated Electronic Structures: Synthesis, Functions and Applications," ed. by T. Hiyama, CMC, 2008, 86-97.

**List of Presentations**

1    Y. Nakamura, <u>H. Shimizu</u>, T. Yamazaki, Y. Kakinoya, J. Nishimura, "Synthesis and Properties of *N*-Arylcarbazolophanes," 85th Annual Meeting of the Chemical Society of Japan, Kanagawa University, Yokohama (March 26-29, 2005).

2    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, T. Yamazaki, Y. Takashima, J. Nishimura, "Synthesis and Properties of *N*-Arylcarbazolophanes," 35th Symposium on Structural Organic Chemistry, Osaka City University, Osaka (October 9-10, 2005).

3    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, K. Takehira, S. Tobita, J. Nishimura, "Preparation and Photophysical Properties of Various *N* –Arylcarbazolophanes," 86th Annual Meeting of the Chemical Society of Japan, Nihon University, Chiba (March 27-30, 2006).

4    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, Y. Takashima, J. Nishimura, "Synthesis and Photophysical properties of Various *N*-Arylcarbazolophanes," 51th Symposium on Kanto Branch of the Society of Synthetic Organic Chemistry, Saitama University, Saitama (May 12-13, 2006).

5    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, K. Takehira, S. Tobita, J. Nishimura, "Preparation and Photophysical Properties of Various *N*-Arylcarbazolophanes," The 2nd Gunma International Symposium on Chemistry (July 21, 2007).

6    Y. Nakamura, <u>H. Shimizu</u>, Y. Takashima, E. Takase, J. Nishimura "Synthesis and Properties of Carbazolophanes Bearing Siloxane Linkage," The Third International Symposium on Development of Silicon-based Functional Materials" Kiryu Gunma (November 30, 2007).

7    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, K. Takehira, S. Tobita, J. Nishimura, "Preparation and Photophysical Properties of Various *N*-Arylcarbazolophanes," 1$^{st}$ Symposium on Organic π-Electron systems, Tokyo (December 7-8, 2007).

8    Y. Nakamura, <u>H. Shimizu</u>, Y. Kakinoya, K. Takehira, S. Tobita, J. Nishimura,

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9    H. Shimiuz, Y. Nakamura, J. Nishimura "Design and synthesis of host materials for emitting layers in green OLED," 2nd Symposium of Kanto Branch of Chemical Society of Japan, Kiryu Gunma (September 18-19, 2008).