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Optical properties of oligo(2,3-dioxyfunctionalized)naphthalenes

Kazunori Tsubaki,[a,*] Masaya Miura,[a] Asao Nakamura[b] and Takeo Kawabata[a]

[a] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

[b] *Faculty of Engineering, Shibaura Institute of Technology, Fukasaku, Minuma-ku, Saitama-shi, Saitama 337-8570, Japan*

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This paper is dedicated to the memory of the late Professor Kiyoshi Tanaka

Abstract—The properties of two series of oligo(2,3-dioxyfunctionalized)naphthalenes which are connected at the 1,4-positions, that is, methoxy derivatives **1**–**4** and derivatives that possess two pyrene groups on the central scaffolding oxygen functions **5**–**8**, are described. In **1**–**4**, the fluorescence quantum yields increased by about 20–80% as the number of naphthalene units increased. The intramolecular energy transfer quantum yields of **5**–**8** were around 20% regardless of the number of naphthalene units.

Recently, π-conjugated oligomers, which are mainly composed of five-membered hetero-aromatic rings, have received significant attention. Their properties, functions, and behaviors have been reported from a viewpoint of materials science.[1] Although the oligo(*para*-phenyl) skeletons are used as backbones for the rigid β-barrel motifs and/or characteristic properties,[2] oligonaphthalenes have received little attention despite their unique structural features. This is probably due to (1) the lack of effective synthetic methods and (2) the lack of coplanarity of neighboring naphthalenes.[3] We have developed an efficient synthesis for optically active oligonaphthalenes (from 2mer to 16mer).[4] Herein, we report the optical properties of two types of oligonaphthalenes (methoxy derivatives **1**–**4**[4b] and derivatives that possess two pyrene groups on the central scaffolding oxygen functions **5**–**8**[4b]) (Fig. 1).

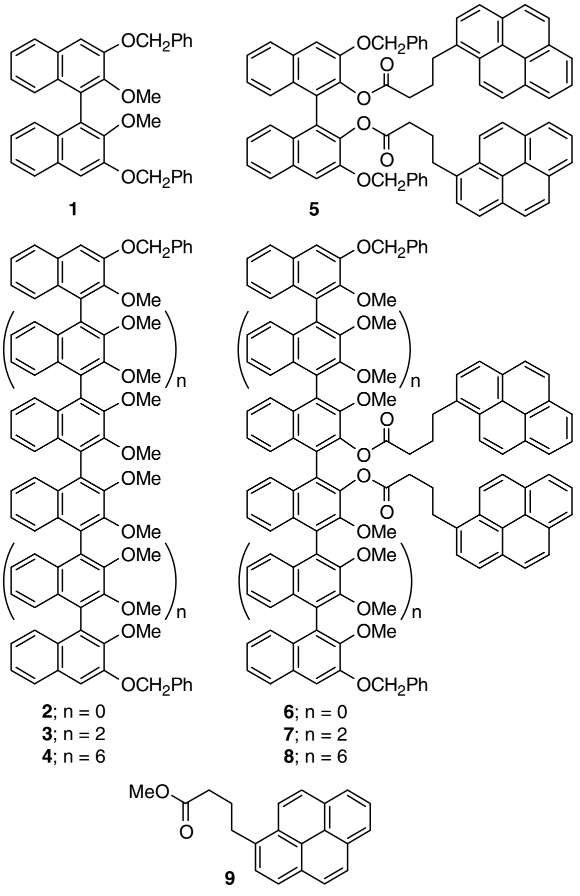

Figure 1.

Figure 2 and Table 1 show the UV–vis and fluorescence spectra and the photophysical properties of methoxy derivatives **1**–**4**. In the UV spectra (Fig. 2a), the absorption near 300 nm shifts to a longer wavelength as the number of naphthalene units increases. However, a very small shift was observed at the absorption band around 240 nm. The red shift at 300 nm is due to the coupling of the transition moments that are parallel to the minor

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[*] Corresponding author. Tel.: +81 774 38 3193; fax: +81 774 38 3197; e-mail: tsubaki@fos.kuicr.kyoto-u.ac.jp

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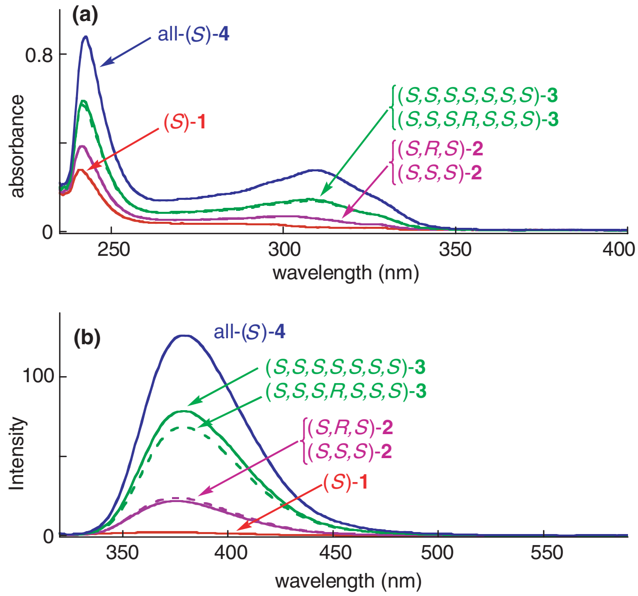

Figure 2. (a) UV–vis spectra of **1**–**4**: conditions, $CHCl_3$ 2.0×10^{-6} M, 25 °C, light path length = 10 mm. (b) Fluorescence spectra **1**–**4**: conditions, $CHCl_3$ 2.0×10^{-7} M, 25 °C, light path length = 10 mm, $\lambda_{ext} = 310$ nm.

Table 1. Photophysical properties and quantum yields of **1**–**4**

	$\lambda_{max,abs}$ ($\varepsilon \times 10^{-2}$)[a]	$\lambda_{max,em}$[b]	Stokes' shift	Φ_{fl}[c]
(*S*)-**1**	240.5 (1390), 282.5 (182)	367	84.5	0.20
(*S*,*S*,*S*)-**2**	241.5 (1920), 299.0 (338)	376	77	0.57
(*S*,*R*,*S*)-**2**	241.5 (1940), 300.0 (332)	377	77	0.62
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**3**	241.5 (2950), 307.0 (726)	379	72	0.83
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**3**	241.5 (2860), 307.0 (692)	379	72	0.76
All-(*S*)-**4**	242.5 (4400), 309.0 (1382)	379	70	0.82

[a] Conditions: $CHCl_3$ 2.0×10^{-6} M, 25 °C, light path length 10 mm.
[b] Conditions: $CHCl_3$ 2.0×10^{-7} M, 25 °C, light path length 10 mm, $\lambda_{ext} = 310$ nm.
[c] The fluorescence quantum yields were determined using a solution of quinine sulfate in 1 N H_2SO_4 as the reference standard ($\Phi_{fl} = 0.546$).

axis of the naphthalene ring (i.e., parallel to the rod of the corresponding molecule). In Figure 2b, the maximum wavelength of the emission ($\lambda_{ext} = 310$ nm) shifts to a longer wavelength. Since the extent of the red shift in the fluorescence spectra is smaller than that in the UV spectra, the degree of the Stokes' shift becomes smaller as the number of naphthalene units increases. Fluorescence quantum yield was largely dependent on the number of naphthalene unit.

Thus, the fluorescence quantum yields increase as follows: 20% for binaphthalene **1**, about 60% for quaternaphthalenes **2**, about 80% for octinaphthalenes **3**, and plateaus near 80% for hexadecanaphthalene **4** (Table 1). A simple explanation for this tendency is that the nonradiative processes are suppressed as the rigidity of molecules is enhanced. This is contrary to that reported by Lin and co-workers for the quantum yields of chiral 1,1′-binaphthol-based oligomers linked through their 6,6′-positions (from 4mer to 10mer). Lin et al. mentioned that the quantum yields of their compounds decreased as the number of naphthalene units increased (from 50% to 21%).[3c]

The circularly polarized fluorescence (CPL) spectra of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**3** was also measured.[5] In Figure 3, the CPL spectrum of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**3** is shown as well as the UV, fluorescence, and CD spectra. Circular anisotropy factor ($2(I_L - I_R)/(I_L + I_R)$) was about 0.05%, but a meaningful negative sense is obtained.

Figures 4 and 5 show the UV–vis and fluorescence spectra of pyrene derivatives **5**–**9** and pictures of the fluorescence emission of **2** and **6** under UV light and natural light, respectively. The UV–vis spectra of pyrene derivatives **5**–**8** (Fig. 4a) in the 240–400 nm region are the simple sum of the spectra of the main skeletons **1**–**4** (Fig. 2a) and the spectrum (twice as intense) of side chain **9** (Fig. 4a). Thus, the naphthalene units and the pyrene units of **5**–**8** do not interact in the ground state.

Since pyrene side chain **9** barely absorbs the light at 310 nm, the naphthalene units can be excited with high selectivity at this wavelength. Furthermore, there is an

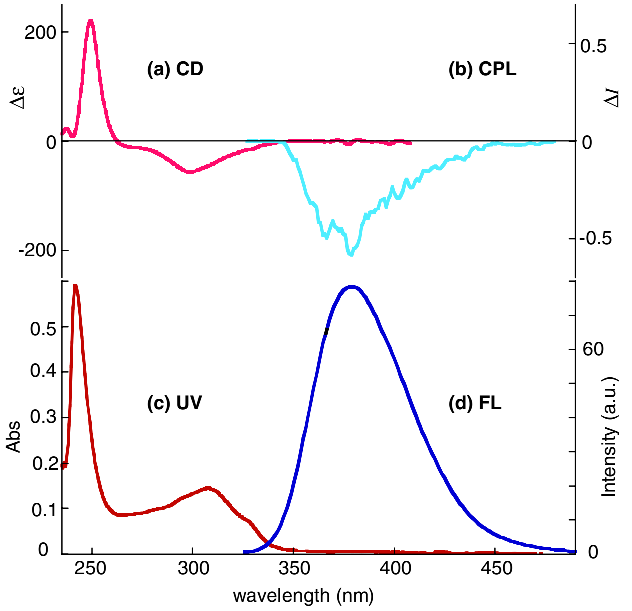

Figure 3. Spectra of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**3**. (a) CD spectrum: conditions, $CHCl_3$ 1.0×10^{-5} M, 25 °C, light path length 1 mm. (b) CPL spectrum: conditions, $CHCl_3$ 1.0×10^{-4} M, 25 °C, light path length 10 mm, $\lambda_{ext} = 280$ nm. $\Delta I = I_L - I_R$. (c) UV–vis spectrum: conditions, $CHCl_3$ 2.0×10^{-6} M, 25 °C, light path length 10 mm. (d) Fluorescence spectrum: conditions, $CHCl_3$ 2.0×10^{-7} M, 25 °C, light path length 10 mm, $\lambda_{ext} = 310$ nm.

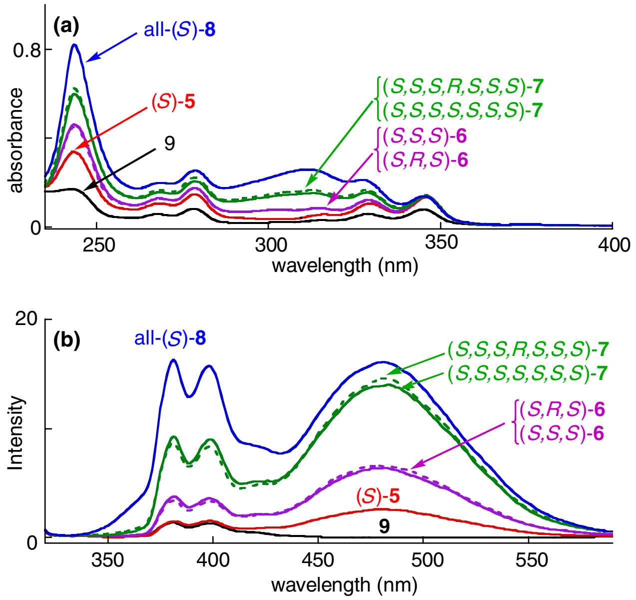

Figure 4. (a) UV–vis spectra of **5**–**9**: conditions, $CHCl_3$ 2.0×10^{-6} M, 25 °C, light path length 10 mm. (b) Fluorescence spectra **5**–**9**: conditions, $CHCl_3$ 2.0×10^{-7} M, 25 °C, light path length 10 mm, $\lambda_{ext} = 310$ nm.

Figure 5. Pictures of the oligonaphthalenes under (a) natural light and (b) UV light. Conditions: $CHCl_3$, 2.0×10^{-6} M.

effective overlap of the donor (naphthalene units) emission (Fig. 2b, 330–460 nm) and the acceptor (pyrene units) absorption (Fig. 4a, 320–360 nm). When pyrene derivatives **5**–**8** are irradiated at 310 nm, the fluorescence does not come from the naphthalene units, but is from the pyrene units (in Fig. 4b, the peaks at 381 and 399 nm are attributed to the pyrene monomer emission and that at ca. 480 nm is assigned to the pyrene eximer emission). This result demonstrates that an effective intramolecular energy transfer occurs from the naphthalene units to the pyrene units.[6] The difference in the emitting chromophore can be detected by the naked eye (Fig. 5). Under UV lamp (for TLC plate) irradiation, methoxy quaternaphthalenes **2** and pyrene ester **9** produce dark blue emissions, whereas the pyrene derivative **6** gives a bright celestial blue light.

Table 2 overviews the photophysical properties as well as the quantum yield of the energy transfer of the pyrene series. The nearly constant energy transfer quantum yields (20–25%) does not support direct through-space energy transfer from discrete naphthalene units to the pyrene units. Instead, it implies that the energy transfer proceeds via the following two steps: (1) an effective and fast through-bond energy transfer from an excited naphthalene unit to an adjacent naphthalene unit, (2) a through-space energy transfer (Förster type) from the naphthalene with a pyrene side chain to the pyrene unit. These steps are followed by the formation of pyrene excimer. This mechanism predicts that, if the total energy-transfer efficiency is determined by the second step, the efficiency is independent of the number of the naphthalene units. The mechanism also predicts that the intensity of the fluorescence emission from the pyrene groups increases in proportion to the number of the naphthalene units. These predictions are supported by the data.

In conclusion, the optical properties of oligo(2,3-dioxy-functionalized)naphthalenes, which are connected at their 1,4-positions, are more than just the sum of the discrete naphthalene units. These properties can be produced by coupling the transition moments that run parallel to the minor axis of the naphthalene ring. Studies on new and known functions of other oligonaphthalenes, which control all the axis chiralities, and the types and alignments of the functional groups on side chains are currently underway.

Table 2. Photophysical properties and quantum yields of **5**–**8**[a]

	$\lambda_{max,abs}$ ($\varepsilon \times 10^{-2}$)[a]	$\lambda_{max,em}$[b]	Φ_{fl}[c]
(*S*)-**5**	243.5 (1690), 316.0 (275), 329.5 (525), 346.0 (661)	381.0, 398.0, 482.0	0.18
(*S*,*S*,*S*)-**6**	243.5 (2300), 314.5 (419), 329.0 (606), 346.0 (692)	381.0, 398.0, 482.0	0.23
(*S*,*R*,*S*)-**6**	243.5 (2250), 314.5 (412), 329.0 (594), 345.5 (675)	381.0, 399.0, 479.0	0.24
(*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**7**	243.5 (3370), 313.0 (853), 328.5 (871), 345.5 (768)	381.0, 399.0, 483.0	0.24
(*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**7**	243.5 (3130), 312.5 (819), 328.5 (823), 345.5 (704)	381.0, 398.0, 483.0	0.25
All-(*S*)-**8**	243.5 (4110), 311.5 (13,000), 327.0 (1050), 345.0 (690)	381.0, 398.0, 481.0	0.21

[a] Conditions: $CHCl_3$ 2.0×10^{-6} M, 25 °C, light path length 10 mm.

[b] Conditions: $CHCl_3$ 2.0×10^{-7} M, 25 °C, light path length 10 mm, $\lambda_{ext} = 310$ nm.

[c] The fluorescence quantum yields were determined by using a solution of quinine sulfate in 1 N H_2SO_4 as the reference standard ($\Phi_{fl} = 0.546$).

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