Multichromophoric Cyclodextrins. 2. Inhomogeneous Spectral Broadening and Directed Energy Hopping

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A β-cyclodextrin bearing seven 2-naphthoyloxy chromophores is a good model for the study of the effect of the excitation wavelength on energy hopping among chromophores in well-defined positions, as in photosynthetic antennae. Absorption spectra, emission spectra, and excitation polarization spectra were recorded in a propylene glycol–dioxane glass at 200 K. Comparison is made with a bis(naphthoate) bichromophoric molecule. The parallelism between the increase of emission spectrum displacement and fluorescence anisotropy observed for the red edge of most vibronic bands, and especially for the 0–0 one, is established for the first time. It can be interpreted in terms of inhomogeneous spectral broadening due to solvation heterogeneity. The decrease of energy transfer that is observed upon red-edge excitation is evidence that energy hopping is not chaotic but directed toward lower-energy chromophores.

Introduction

The study of excitation energy transport among identical chromophores is of major interest for the understanding of light collection in natural and artificial systems; in particular, this process is relevant to the antenna effect involved in photosynthetic systems and in photochemical molecular devices.[1–4] Excitation energy transport has been extensively investigated in polymers having chromophores substituted at intervals along the chains (for reviews, see refs 5–7). In multichromophoric cyclodextrins, the position of the chromophores is much better spatially defined, and the limited number of chromophores in a circular arrangement is a distinct advantage for the interpretation of the photophysical results. In the first paper of this series,[8] we described the properties of β-cyclodextrins labeled with 7 or 14 naphthoyloxy chromophores: we analyzed excimer formation, and we showed how ultrafast hopping of excitation energy occurs between the chromophores with essentially randomly oriented transition moments.

In the present paper, attention is focused on spectral inhomogeneity and the resulting directed energy hopping as revealed by the excitation wavelength dependence of emission anisotropy. In the labeled β-cyclodextrin chosen for this investigation, CD7-(6), seven naphthoyloxy chromophores are covalently linked to the glucopyranose unit at position 6, i.e., on the primary face of the cyclodextrin (Figure 1). It is worth comparing the behavior of this multichromophoric cyclodextrin with that of a bichromophoric molecule containing two naphthoyloxy chromophores (NA-CX-NA) (Figure 1).

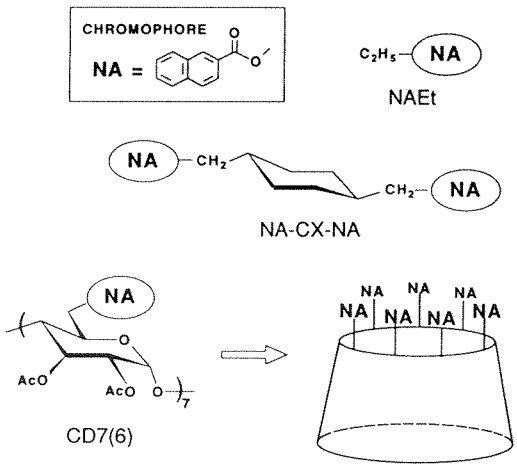

Figure 1. Chemical structure of the bichromophoric molecule NA-CX-NA and CD7(6). NA is the symbol of the 2-naphthoyloxy chromophore.

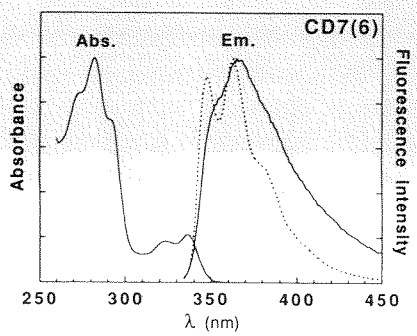

Figure 2. Absorption and corrected fluorescence spectra of CD7(6) in a mixture (9:1 v/v) of propylene glycol and 1,4-dioxane at 293 K (solid line) and 200 K (dotted line).

Results and Discussion

The absorption and fluorescence spectra of CD7(6) and NA-CX-NA are shown in Figures 2 and 3, respectively. A mixture (9:1 v/v) of propylene glycol and 1,4-dioxane was chosen for all the experiments because such a mixture forms a rigid and transparent glass upon cooling to 200 K. The absorption spectra of both compounds are almost identical and exhibit the low-energy band ($^1L_b \leftarrow {}^1A$) and the high-energy band ($^1L_a \leftarrow {}^1A$) that are characteristic of 2-substituted naphthalene derivatives. In contrast, the fluorescence spectra are somewhat different at room temperature: the fluorescence spectrum of CD7(6) exhibits

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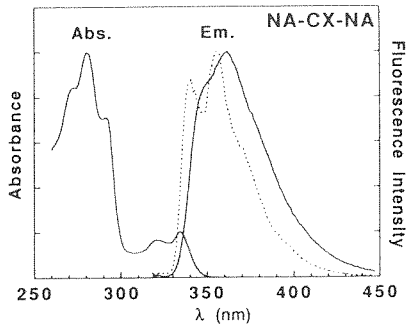

Figure 3. Absorption and corrected fluorescence spectra of NA-CX-NA in a mixture (9:1 v/v) of propylene glycol and 1,4-dioxane at 293 K (solid line) and 200 K (dotted line).

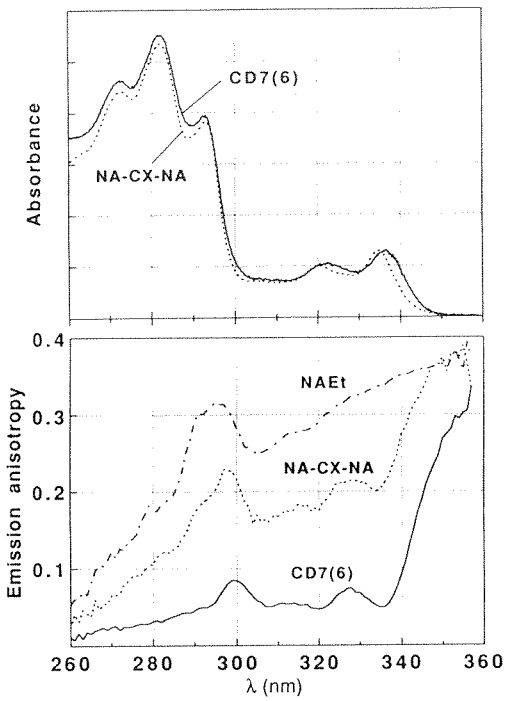

Figure 4. (bottom) Excitation polarization spectra in a rigid glass made of a mixture (9:1 v/v) of propylene glycol and 1,4-dioxane at 200 K (observation wavelength 380 nm). (top) Absorption spectra recorded under the same conditions.

a longer tail at high wavelengths due to excimer formation, as confirmed by time-resolved experiments,[8] while NA-CX-NA has been designed in such a way that no excimer can be formed because of the conformational constraints imposed by the cyclohexyl ring. In the rigid glass at 200 K, excimer formation is no longer possible in CD7(6), and the fluorescence spectra of both compounds become almost identical in shape and only slightly shifted with respect to one another.

The excitation polarization spectra (variations in emission anisotropy as a function of the excitation wavelength) of CD7(6) and NA-CX-NA in the rigid glass at 200 K are displayed in Figure 4 together with that of 2-ethyl naphthoate (NAEt). The latter is a good spectroscopic model (the chromophore is the same and does not undergo energy transfer), and its excitation polarization spectrum can be taken as a reference for the study of the effect of energy transfer on the spectra of CD7(6) and Na-CX-NA.

In the rigid glass, i.e., in the absence of rotational motion of the chromophores, the emission anisotropy values of NAEt observed at high excitation wavelengths are close to the theoretical limit of 0.40 pertaining to collinear absorption and emission transition moments in the first band ($^1L_b \leftarrow {}^1A$) that is mainly short axis polarized. The gradual decrease in emission anisotropy as the excitation wavelength is decreased is due to vibronic coupling with the strong ($^1B_b \leftarrow {}^1A$) band, which occurs at ca. 240 nm. Emission anisotropy rises again at the 0–0 transition of the second band ($^1L_a \leftarrow {}^1A$), which is also mainly short axis polarized: from the anisotropy ratio of the 0–0 transitions of $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ bands, the angle between the respective transition moments is estimated to be 16°, which is equal to the theoretical value computed for 2-naphthol.[9] Below 290 nm, the monotonous decrease of anisotropy toward negative values is again a result of vibronic coupling with the strong $^1B_b \leftarrow {}^1A$ band, long axis polarized.[10] The overall polarization pattern is identical to that observed for other 2-substituted naphthalenes with strongly conjugating groups.[10]

The excitation polarization spectra of CD7(6) and NA-CX-NA show values of emission anisotropy lower than NAEt. Since the rotational motions of the chromophores are frozen in the rigid glass, such a depolarization effect is solely due to nonradiative electronic energy transfer, i.e., energy hopping between chromophores. In fact, an emitting chromophore that is indirectly excited by energy transfer is likely to have its emission transition moment oriented differently from that of the directly excited one. The extent of depolarization effect in CD7(6) and in Na-CX-NA can be interpreted as follows. Since the energy hopping process is much faster than the chromophore intrinsic decay, as previously demonstrated in the first paper of this series,[8] the probability that the emitting chromophore is the directly excited one is 1/2 in Na-CX-NA and 1/7 in CD7(6). The steady-state emission anisotropy of the directly excited chromophore is at most 0.4, whereas the indirectly excited ones have a lower contribution; if they are randomly oriented, this contribution is negligible. In fact, in the case of randomly oriented chromophores undergoing efficient energy transfer, the acceptor steady-state anisotropy is expected to be close to zero.[11] Invoking the additive property of anisotropy, one has $r = \sum_i f_i r_i$, where f_i is the fraction of light emitted by the ith species, with anisotropy r_i. In the present case, owing to the rapidity of transfer,[8] an excited-state equilibrium is rapidly attained, each chromophore contributing with 1/2 to the global intensity in NA-CX-NA and 1/7 in CD7-(6). If the indirectly excited naphthoates have essentially unpolarized emission ($r_i \approx 0$), the expected overall anisotropy is 0.4/2 = 0.2 in NA-CX-NA and 0.4/7 = 0.4/7 = 0.057 in CD7-(6). In fact, the anisotropy measured upon excitation in the first absorption band, except in the long-wave edge of the absorption spectrum (see below), i.e., in the range 310–355 nm, is close to 0.2 in NA-CX-NA and 0.06 in CD7(6), which is consistent in both cases with a model of fast energy hopping between chromophores with essentially randomly oriented chromophores.

It should be emphasized that when increasing the excitation wavelength beyond 335 nm, the emission anisotropy drastically increases, thus indicating a gradual decrease of energy-transfer efficiency. At the very red edge (≈ 350 nm) there is a complete lack of energy transfer. Such a red-edge effect was first observed by Weber[12,13] (and is called the Weber effect for this reason). It is also noticed that the increase in emission anisotropy at wavelengths ranging from 320 to 328 nm (long-wave edge of the second vibronic band) is significantly steeper for NA-CX-NA and CD7(6) than for NAEt. Furthermore, the maximum of emission anisotropy around 300 nm (i.e., at the long-wave edge of the second electronic band) is located at higher wavelengths for NA-CX-NA and CD7(6) than for NAEt. One can thus speak of a *vibronic red-edge effect* displayed here for the first time.[14]

Before discussing the origin of the observed excitation-wavelength dependence of energy transfer, the concept of inhomogeneous spectral broadening or organic molecules in rigid polar media should be recalled (for a review see ref 15). Each electronic state of moderately large and rigid chromophores consists of an almost continuous manifold of vibrational sublevels. Absorption and emission spectra could therefore be almost structureless. However, many of the vibrational modes are not active, neither in absorption nor in emission. Therefore, in some cases a clear vibrational structure is observed. Even in these

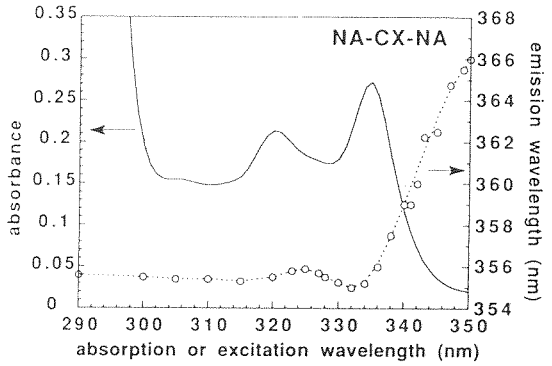

Figure 5. Absorption spectrum of NA-CX-NA in a mixture (9:1 v/v) of propylene glycol and 1,4-dioxane at 200 K and variations in the emission maximum as a function of the excitation wavelength (broken line).

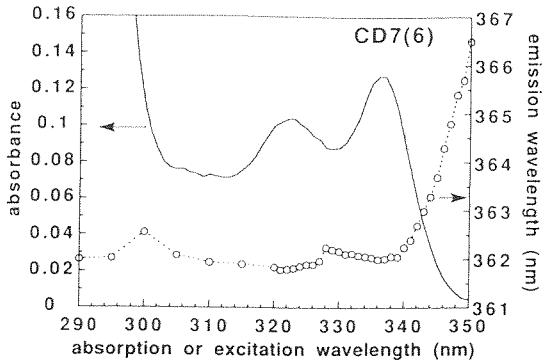

Figure 6. Absorption spectrum of CD7(6) in a mixture (9:1 v/v) of propylene glycol and 1,4-dioxane at 200 K and variations in the emission maximum as a function of the excitation wavelength (broken line).

cases, the width of each vibronic band is much larger than the homogeneous line width; this may partly due to the presence of low-frequency modes,[16] but the width is usually dominated by the phenomenon of inhomogeneous broadening, that is, by a distribution of solute–solvent configurations that leads to a distribution of homogeneous spectra. When the interaction is strong, and many configurations are possible, the spectra may become completely blurred. When only a small number of solvation subclasses is possible, as in Shpolskii matrices,[17] the global spectrum consists of the superposition of a few homogeneous ones. In this case, if the excitation bandwidth is smaller than the homogeneous band spacing, a given homogeneous population will be selected and a homogeneous narrow-line emission spectrum occurs. Even if the absorption appears to be broad under moderate resolution, narrow-line emission, though not strictly homogeneous, can be obtained in some cases.[18] Usually, however, there is an almost continuous distribution of solvates, and perfect selection of a homogeneous subclass is not feasible. Nevertheless, use of intense narrow band (laser) excitation allows the selective modification of a subpopulation, this forming the basis of the hole-burning technique.[19]

Focusing the excitation on the red edge of the absorption will favor the more stabilized configurations, and a red shift of the fluorescence spectrum results if the solvent is rigid, as in frozen solutions or polymer matrices.[20–24] Furthermore, if the absorption spectrum shows distinct vibrational structure, this should also occur at the red edge of each vibronic. (Selection of high-energy configurations at the blue edge of the vibronics may also be possible, but only if these are well separated.) This edge-excitation red shift disappears in fluid solutions where a dynamic equilibrium exists among the various solvation sites, but it is still observable if the solvent reorientation relaxation competes with the fluorescence decay; in this case there is a correlation with the well-known time-dependent spectral shift.[22c,25,26]

If vibronic bands are well separated, the red-edge effect recurs at every vibronic band, as discussed above for the experimental anisotropy. The corresponding effect for the fluorescence spectrum was observed long ago by Galley and Purkey[21] and more recently by others.[27] This prompted us to seek for the variations of the emission maximum versus excitation wavelength for NA-CX-NA and for CD7(6) in the propylene glycol–dioxane glass at 200 K. It was indeed observed that, upon excitation at the red edge, the emission maximum of NA-CX-NA is red-shifted by 12 nm (Figure 5). CD7(6) exhibits the same trend but with a smaller red shift (4–5 nm) (Figure 6). In both cases, a distinct vibronic effect is observed.

It should be noted that an excitation-wavelength dependence at the long-wave edge of the absorption spectrum has been observed not only for spectral displacement but also for other parameters such as lifetime,[22a,24,28] quantum yield,[24] and apparent rotational rate.[28,29] Applications to the investigation of polymer rigidity and/or free volume[30] and to the study of biological systems[31] and excited-state reactions[32] have been developed.

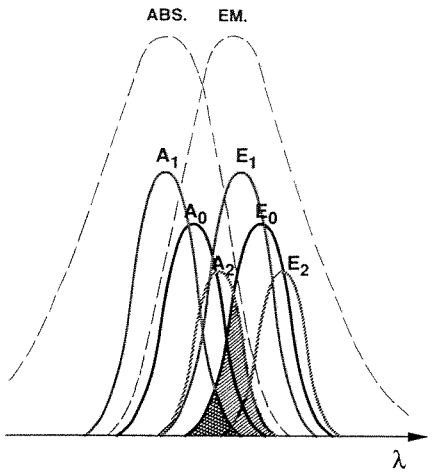

Figure 7. Illustration of the inhomogeneous spectral broadening and the resulting directed energy transfer. The efficiency of energy transfer depends on the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. The spectral overlap between the emission spectrum E_0 of an excited species (whose absorption spectrum is A_0) and the absorption spectrum A_2 of a solvate absorbing at higher wavelengths (cross hatched area + double cross hatched area) is larger that the spectral overlap with the absorption spectrum A_1 of a solvate absorbing at lower wavelengths (double cross hatched area).

It is shown in the present work for the first time that the variations of the emission maximum parallel those of the emission anisotropy at excitation wavelengths in the red edge of well-separated vibronic bands (Figures 4–6). The common origin of both phenomena is the inhomogeneous broadening of spectra, and the effect of this broadening on the efficiency of energy transfer, as revealed by the excitation-wavelength dependence of the emission anisotropy, will be now discussed. This problem has been the subject of several theoretical and experimental studies.[15,33–38] In a rigid polar solution of chromophores that are close enough to undergo nonradiative energy transfer, the probability of transfer from a chromophore in a given configurational state to a chromophore whose configurational state corresponds to a lower electronic transition frequency is greater than the probability of transfer to a chromophore with a higher electronic transition frequency. This is due to the smaller overlap in the latter case between the donor fluorescence and acceptor absorption spectra, as illustrated in Figure 7. In both mechanisms of transfer by dipole–dipole interactions[39] or exchange interactions,[40] the efficiency of transfer is indeed related to the spectral overlap. Therefore, the transfer from "blue" solvates to "red" ones is more probable than the reverse transfer. As back-transfer has a lower probability, one can speak of *directed nonradiative energy transfer*. This explains the lack of energy transfer upon red-edge excitation observed in NA-CX-NA and CD7(6): as the excitation wavelength increases beyond the absorption maximum, energy hopping from the directly excited chromophore becomes less and less probable because the proportion of "blue"

partners to which transfer is weak or impossible drastically increases. In other words, energy hopping is not chaotic but spectrally selective. Such a directed energy hopping may be of major importance in energy transport from the antenna to the reaction center in photosynthetic membranes.[36-38] Labeled cyclodextrins are good models for mimicking this process. Further studies using fast time-resolved spectroscopy will be undertaken with the aim at characterizing the time evolution of directed energy hopping.

Experimental Section

Materials. Propylene glycol from Aldrich (gold label) and 1,4-dioxane from Merck (spectroscopic grade) were used without further purification. The synthesis of CD7(6) was previously described.[8] NA-CX-NA was prepared according to the following procedure.

Synthesis of Na-CX-NA (1,4-Cyclohexanedimethanol-Dinaphthoyl Ester). A mixture of 1,4-cyclohexanedimethanol (144 mg, 1 mmol, cis/trans mixture in ratio 1/3 from Aldrich) and naphthoyl chloride (419 mg, 2.2 mmol) in dry pyridine (5 mL) was stirred for 24 h at 80 °C. After cooling and addition of water, the precipitate was collected and thoroughly digested and washed with CH_2Cl_2 to yield 265 mg of a nearly pure diester **I** [$R_f(CH_2Cl_2$/hexane 4/1) = 0.55]. The mother liquors were chromatographed on silica gel with the same eluent as above to yield 90 mg of the fast moving isomer **I** (R_f = 0.55) and 56 mg of the slower isomer **II** (R_f = 0.45). Recrystallization of the fractions **I** (R_f – 0.55) in chloroform yielded 200 mg of pure white crystals (186 °C). Recrystallization of the fractions **II** (R_f = 0.45) in a mixture of hexane–ether yielded 30 mg of pure white crystals (110 °C). The more abundant, higher melting diester was assumed to have the trans stereochemistry.[41] The other one, less abundant, lower melting isomer was assumed to have the cis stereochemistry.

I: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.62 (s, 2 H); 8.10–8.05 (dd, J = 1.7, 8.6 Hz, 2 H); 8.10–7.85 (m, 6 H); 7.65–7.50 (m, 4 H); 4.25 (d, J = 6.3 Hz, 4 H); 2.02 (m, 4 H); 1.9 (m, 2 H); 1.23 (m, 4 H). Anal. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24. Found: C, 79.53; H, 6.25. **II**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.62 (s, 2 H); 8.11–8.06 (dd, J = 1.6, 8.6 Hz, 2 H); 8.10–7.85 (m, 6 H); 7.65–7.50 (m, 4 H); 4.37 (d, J = 7.2 Hz, 4 H); 2.15 (m, 4 H); 1.7 (m, 6 H).

The stereochemistry of **I** was ascertained by comparison of ^{1}H-NMR and ^{13}C-NMR of **I** and **II**. The widths at half-height of the broad structureless multiplet arising from the methyne carbons of the cyclohexane ring were measured: $W_{1/2}$(**I**) = 22.1 Hz and $W_{1/2}$(**II**) = 18.8 Hz. This is in agreement with the larger coupling constant arising from H_{axial}–H_{axial} and H_{axial}–$H_{equatorial}$ coupling for both cyclohexane ring methyne in **I** compared to the average between one methyne with H_{axial}–$H_{equatorial}$ and H_{axial}–$H_{equatorial}$ coupling and the other with $H_{equatorial}$–H_{axial} and $H_{equatorial}$–$H_{equatorial}$ in **II**. Furthermore, ^{13}C-NMR chemical shifts (50.3 MHz, $CDCl_3$) for carbons of the cyclohexane ring arise at lower values in **I** (34.7 and 25.4 ppm) than in **II** (37.3 and 29.0 ppm), conforming to the trend observed for the *cis*- and *trans*-1,4-dimethylcyclohexanes.[42]

Spectroscopic Measurements. The UV–vis absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. Corrected fluorescence spectra and excitation polarization spectra were obtained with a SLM 8000 C spectrofluorometer. Steady-state fluorescence anisotropies defined as $r = (I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$ (where $I_\parallel$ and $I_\perp$ are the fluorescence intensities observed with vertically polarized excitation light and vertically and horizontally polarized emissions, respectively) were determined by the G-factor method.[43]

Low-temperature measurements (200 K) were performed in specially made 1-cm × 1-cm strain-free quartz cuvettes and with an Oxford DN1704 cryostat with quartz windows.

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