ARTICLES

Multichromophoric Cyclodextrins. 3. Investigation of Dynamics of Energy Hopping by Frequency-Domain Fluorometry

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A β-cyclodextrin labeled with seven naphthoyloxy chromophores was studied by steady-state and time-resolved fluorescence spectroscopy in order to get information on the dynamics of energy hopping between chromophores. The steady-state fluorescence anisotropy was recorded as a function of excitation wavelength in a mixture of methanol and ethanol at 110 K (rigid glass). The fluorescence anisotropy decay was obtained under the same conditions by the multifrequency phase-modulation technique upon excitation at 290 nm. The data were analyzed and interpreted on the basis of a theoretical model involving a unique rate constant for energy hopping between nearest neighbors. In particular, this model predicts a long-time leveling-off of the emission anisotropy at 1/7th of the fundamental anisotropy, which is confirmed by both steady-state and time-resolved data and thus indicates that there is no preferred mutual orientation between the chromophores. As regards the rate of energy hopping, an average value of 2×10^9 s^{-1} can be deduced from the comparison between the theoretical and experimental decays. This value is shown to be consistent with a dipole−dipole mechanism of energy transfer.

Introduction

Excitation energy hopping between chromophores is an important process occurring in the antennae pigments of photosynthetic units[1] and in antenna-based photomolecular devices.[2] For the understanding of fundamental aspects of energy hopping, it is of interest to study supramolecular systems containing a limited number of chromophores that are well spatially defined. In this respect, β-cyclodextrins labeled with chromophores offer distinct advantages.[3−5] They are also able to include species in their cavity, thus allowing to study the antenna effect, i.e., energy transfer from the antenna chromophores to an included acceptor.[6]

In the first two papers of this series,[3,4] we focused our attention on the photophysical properties of various β-cyclodextrins labeled with 7 or 14 2-naphthoyloxy chromophores. We showed that hopping of excitation energy occurred between the chromophores with essentially randomly oriented transition moments and was much faster than the intrinsic decay rate of the chromophores. Moreover, in a rigid glass, a decrease of energy transfer was observed upon red-edge excitation as a result of inhomogeneous broadening due to solvation heterogeneity; energy hopping was therefore shown to be not chaotic but directed toward lower-energy chromophores.

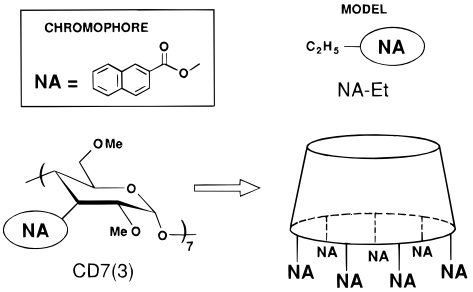

Figure 1. Chemical structure of the multichromophoric cyclodextrin CD7(3) and the model chromophore NA-Et (ethyl naphthoate).

The present paper deals with the dynamics of energy hopping as studied by time-resolved fluorescence anisotropy in the frequency domain. First, a simple theoretical model will be developed in order to derive an explicit expression for the fluorescence anisotropy decay curve which can be used to interpret the experimental decay data. Second, the experimental results obtained with the labeled β-cyclodextrin CD7(3) containing seven naphthoyloxy chromophores covalently linked to the glucopyranose unit at position 3, i.e., on the secondary face of the cyclodextrin (Figure 1) will be presented and compared to the theoretical predictions.

Theory

The dynamics of electronic excitation energy hopping between the seven naphthoate chromophores of CD7(3) in a cyclic arrangement can be approximately described by the kinetic scheme shown in Scheme 1, where NA_i stands for the ith

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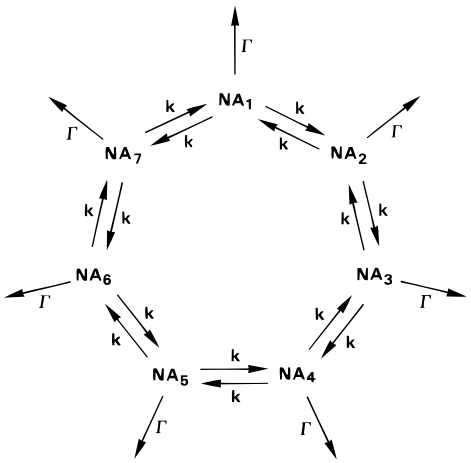
SCHEME 1



naphthoate chromophore ($i = 1, .., 7$), Γ is the (common) intrinsic decay rate, and k is the rate constant for energy hopping, supposed to occur only between nearest neighbors. The neglect of hopping between nonneighboring pairs is based on the rapid decrease with distance of both dipole−dipole and exchange mechanisms; hopping will therefore occur through the shortest paths, that is, between nearest neighbors. The assumption of a single rate constant for all neighboring pairs implies that a common distance and orientation holds for all of them, which is only an approximation. If the chromophore NA_1 is excited by light absorption at time $t = 0$, then the time evolution of the excitation probabilities obeys the master equation

$$\frac{d}{dt}\begin{bmatrix}\rho_1\\ \rho_2\\ \rho_3\\ \rho_4\\ \rho_5\\ \rho_6\\ \rho_7\end{bmatrix} = \begin{bmatrix} -(\Gamma+2k) & k & 0 & 0 & 0 & 0 & k \\ k & -(\Gamma+2k) & k & 0 & 0 & 0 & 0 \\ 0 & k & -(\Gamma+2k) & k & 0 & 0 & 0 \\ 0 & 0 & k & -(\Gamma+2k) & k & 0 & 0 \\ 0 & 0 & 0 & k & -(\Gamma+2k) & k & 0 \\ 0 & 0 & 0 & 0 & k & -(\Gamma+2k) & k \\ k & 0 & 0 & 0 & 0 & k & -(\Gamma+2k) \end{bmatrix} \times \begin{bmatrix}\rho_1\\ \rho_2\\ \rho_3\\ \rho_4\\ \rho_5\\ \rho_6\\ \rho_7\end{bmatrix} \quad (1)$$

subject to the initial condition

$$\begin{bmatrix}\rho_1(0)\\ \rho_2(0)\\ \rho_3(0)\\ \rho_4(0)\\ \rho_5(0)\\ \rho_6(0)\\ \rho_7(0)\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\\0\\0\\0\end{bmatrix} \quad (2)$$

The resolution of this system of differential equations yields (Appendix), with $q_i(t) = \rho_i(t)\exp(\Gamma t)$

$$\begin{bmatrix}q_1\\ q_2\\ q_3\\ q_4\\ q_5\\ q_6\\ q_7\end{bmatrix} = \begin{bmatrix}1/7\\ 1/7\\ 1/7\\ 1/7\\ 1/7\\ 1/7\\ 1/7\end{bmatrix} + \begin{bmatrix}0.286\\ 0.178\\ -0.064\\ -0.257\\ -0.257\\ -0.064\\ 0.178\end{bmatrix} \exp(-0.753kt) + \begin{bmatrix}0.286\\ -0.064\\ -0.257\\ 0.178\\ 0.178\\ -0.257\\ -0.064\end{bmatrix} \exp(-2.445kt) + \begin{bmatrix}0.286\\ -0.257\\ 0.178\\ -0.064\\ -0.064\\ 0.178\\ -0.257\end{bmatrix} \exp(-3.802kt) \quad (3)$$

giving, as could be expected, the attainment of an excited state equilibrium at long times, all chromophores being then equally likely to be in the excited state.

In order to calculate the fluorescence anisotropy, further assumptions are required. If the orientation of the chromophores is at random and uncorrelated, then the hop of energy from a given chromophore to the next entails a major decrease of anisotropy. Indeed, detailed calculations for two-chromophore systems[7] show that the contribution of the indirectly excited chromophore is very small for all times. In a cyclic hepta-chromophoric system with nearest-neighbor interactions, while the exact calculation is wanting, the same conclusions should hold, because the directly excited molecule has only two neighbors, and the remaining four chromophores are attained only after two or more hops, that is, after almost complete depolarization. More precisely, in a two-chromophore system, ignoring the contribution of the indirectly excited chromophores leads to an error of less than 2%.[7] In the heptachromophoric cyclodextrin, there are six indirectly excited chromophores but those which are excited after two or three hops have an extremely small contribution; in other words, only the two nearest neighbors of a directly excited chromophore should be considered and the error on the emission anisotropy should not exceed 4% when their contribution is ignored. Finally, assuming that the contribution of the indirectly excited chromophores to the overall fluorescence anisotropy $r(t)$ is negligible,

$$r(t) = r_0 q_1(t) = r_0\{1/7 + 0.286[\exp(-0.753kt) + \exp(-2.445kt) + \exp(-3.802kt)]\} \quad (4)$$

where r_0 is the fundamental anisotropy. This simple model thus predicts a triple-exponential decay with equal amplitudes, plus a constant term $r_0/7$ that gives a leveling-off at long times. As regards the steady-state anisotropy, it is given by

$$\bar{r} = r_0\left[\frac{1}{7} + 0.286\left(\frac{1}{1+0.753\frac{k}{\Gamma}} + \frac{1}{1+2.445\frac{k}{\Gamma}} + \frac{1}{1+3.802\frac{k}{\Gamma}}\right)\right] \quad (5)$$

If $k \gg \Gamma$, a rapid excited state equilibrium is attained and $\bar{r} = r_0/7$; on the other hand, if $k \ll \Gamma$, the excitation remains on the initial chromophore during the lifetime and $\bar{r} = r_0$.

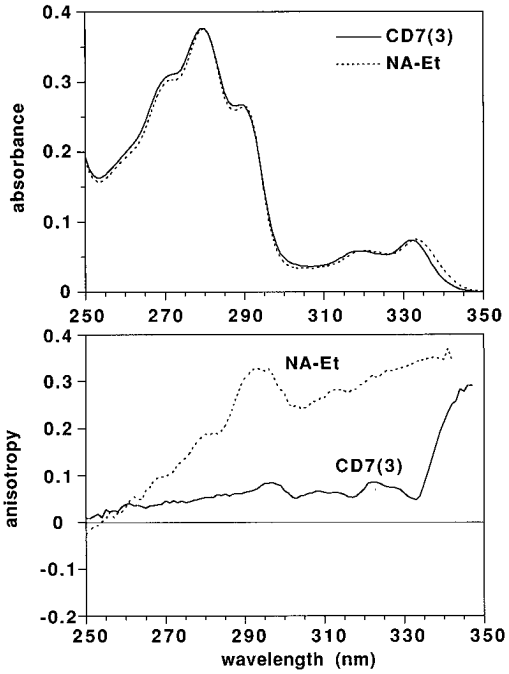


Figure 2. Absorption spectra (top) and excitation polarization spectra (observation wavelength: 380 nm) (bottom) of the multichromophoric cyclodextrin CD7(3) and the model chromophore NA-Et in a mixture of ethanol and methanol (9:1 v/v) at 110 K.

Supposing now that a fraction f of the heptachromophoric molecules does not undergo energy hopping owing to inhomogeneous broadening, the time-resolved and steady-state anisotropies will be given by

$$r(t) = fr_0 + (1-f)r_0\{{}^1/_7 + 0.286[\exp(-0.753kt) + \exp(-2.445kt) + \exp(-3.802kt)]\} \quad (6)$$

$$= r_0\{({}^1/_7 + {}^6/_7 f) + 0.286(1-f)[\exp(-0.753kt) + \exp(-2.445kt) + \exp(-3.802kt)]\}$$

$$\bar{r} = r_0\left[{}^1/_7 + {}^6/_7 f + 0.286(1-f)\left(\frac{1}{1+0.753\frac{k}{\Gamma}} + \frac{1}{1+2.445\frac{k}{\Gamma}} + \frac{1}{1+3.802\frac{k}{\Gamma}}\right)\right] \quad (7)$$

the presence of a fraction of molecules not undergoing energy transfer will thus imply the increase of the steady-state anisotropy, and in particular the increase beyond $r_0/7$ of the constant term corresponding to the long time plateau of the time-resolved anisotropy. Note that the fraction f is a function of the excitation wavelength, taking its highest values at the red edge of the vibronic bands.[4]

Results and Discussion

A solution of CD7(3) in ethanol−methanol (9:1 v/v) was prepared and cooled down to 110 K. At this temperature, the solvent mixture forms a glass and the rotational motion of the chromophores is thus frozen. Nevertheless, the fluorescence polarization spectrum (shown in Figure 2, together with the absorption spectrum) clearly shows a depolarization effect with respect to the model chromophore NA-Et. This excitation polarization spectrum was shown, in our previous paper,[3] to be consistent with excitation energy hopping between chromophores with essentially randomly oriented transition moments at a rate much higher than the chromophore intrinsic decay rate.

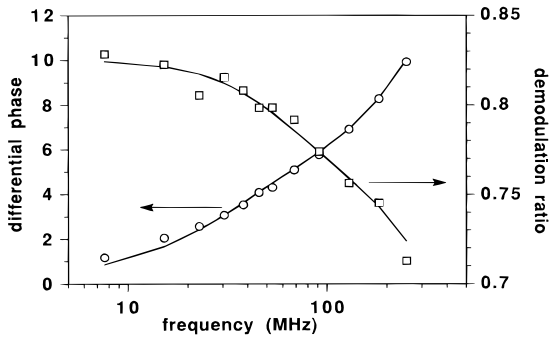


Figure 3. Measurements by differential polarized phase-modulation fluorometry (excitation at 290 nm) for the multichromophoric cyclodextrin CD7(3) in a mixture of ethanol and methanol (9:1 v/v) at 110 K: variations in the differential phase and the demodulation ratio as a function of modulation frequency (see Experimental Section for conditions). The solid line is the best fit using eq 8; the values of the relevant parameters are given in Table 1 for $r_0 = 0.30$ (fixed).

The increase in emission anisotropy observed for the red edge of the 0−0 band (and most of the vibronic bands) reveals less efficient energy transfer, which was interpreted in terms of inhomogeneous spectral broadening due to solvation heterogeneity.[4]

Under the same conditions, a time-resolved fluorescence anisotropy experiment was performed by the multifrequency phase/modulation technique.[8] The phase shift and relative modulation of both vertical and horizontal components of the fluorescence emission upon excitation by vertically polarized light at 290 nm were recorded as a function of modulation frequency from 5 to 250 MHz. The results are shown in Figure 3.

Data analysis for the total fluorescence intensity shows that the fluorescence decay is very close to a single exponential ($\tau = 14.9$ ns); the fractional intensity of a second component (0.35 ns) is less than 1%.

Nonlinear least-squares analysis of the anisotropy measurements was performed with special care. No satisfactory fit could be obtained with a triexponential function with equal preexponential factors, plus a constant (reduced chi-square = 46), as predicted by the theory (eq 4), which means that some assumptions in the model are not valid (in particular the existence of a single rate constant for transfer *(vide infra)*). It was then natural to attempt a fit with a sum of exponentials (plus a constant) without constraining the preexponential factors to be equal, but these factors and the decay times will not have any physical significance. It turned out that a fit with a sum of two exponentials plus a constant was satisfactory, and no significant improvement of the chi-squared value was found when using a sum of three exponentials (plus a constant). The experimental emission anisotropy decay can thus be written in the following form:

$$r(t) = r_0[a_1 \exp(-t/\theta_1) + a_2 \exp(-t/\theta_2) + a_3] \quad (8)$$

with $a_1 + a_2 + a_3 = 1$.

The value r_0 of emission anisotropy at time zero was either left as a floating parameter or fixed to be 0.30, which is the value found at 290 nm for the model compound 2-ethylnaphthoate (NA-Et) (see Figure 2). The results are reported in Table 1 and show minor differences between the two sets of fitting parameters. Therefore, the value of $r_0 = 0.30$, together with the relevant values of a_1, a_2, a_3, θ_1 and θ_2 given in Table 1, will be used in the rest of the paper.

It is of interest to use these values to calculate the steady-state anisotropy $\bar{r}$ for comparison with that obtained from the

TABLE 1: Data Analysis of the Time-Resolved Anisotropy Experiment in Ethanol−Methanol (9:1 v/v) at 110 K[a]

r_0	a_1	θ_1 (ns)	a_2	θ_2 (ns)	a_3	χ_R^2
0.30	0.713 ±	0.177 ±	0.100 ±	3.55 ±	0.187 ±	1.431
(fixed)	0.005	0.004	0.005	0.44	0.004	
0.253	0.68 ±	0.25 ±	0.108 ±	4.67 ±	0.214 ±	0.991
	0.01	0.03	0.005	0.95	0.007	

[a] The values given in this table correspond to the best fit using $r(t) = r_0 [a_1 \exp(-t/\theta_1) + a_2 \exp(t/\theta_2) + a_3]$, with $a_1 + a_2 + a_3 = 1$.

steady-state experiment. $\bar{r}$ is obtained by integration over the fluorescence decay which is approximated to a single exponential with a lifetime $\tau = 14.9$ ns:

$$\bar{r} = r_0\left[\frac{a_1}{1+\tau/\theta_1} + \frac{a_2}{1+\tau/\theta_2} + a_3\right] \tag{9}$$

The value obtained in this way is 0.064, which is in good agreement with the experimental value: 0.062 ± 0.005.

Let us examine now the limiting value of $r(t)/r_0$. The theory (eq 4) predicts $r(\infty)/r_0 = 1/7 = 0.143$ while the experimental value is 0.187 for $r_0 = 0.3$ (Table 1). This value is thus significantly larger than the theoretical one, and the question arises as to whether the mutual orientations of the chromophores are not completely at random. Before trying to answer this question, let us calculate the expected value of r at 334 nm which is close to the 0−0 transition and at which no significant red-edge effect exists. At this wavelength, the excitation polarization spectrum of NA-Et yields $r_0 = 0.34$. Then, the value of r expected from the anisotropy decay parameters (eq 8) with $\tau = 14.9$ ns is 0.073 which is significantly larger than the experimental value 0.051. This observation prompted us to suppose that the experimental decay at 290 nm contains a contribution from molecules that do not undergo energy transfer because of possible residual red-edge effect (290 nm lies indeed in the red-edge of a vibronic band of the second electronic band-($^1L_a \leftarrow A$)). Let us note f the fraction of these molecules. $r(t)$ is then given by

$$\begin{aligned} r(t) &= fr_0 + (1-f)r_0[\alpha_1 \exp(-t/\theta_1) + \alpha_2 \exp(t/\theta_2) + \alpha_3] \\ &= r_0[\alpha_3 + f(1-\alpha_3) + \alpha_1 \exp(-t/\theta_1) + \alpha_2 \exp(t/\theta_2)] \end{aligned} \tag{10}$$

As the experimental decay was analyzed using eq 8, comparison between eqs 8 and 10 leads to $f = (a_3 - \alpha_3)/(1 - \alpha_3)$. Assuming that there is no preferred mutual orientation between the chromophores, α_3 is taken to be 1/7. Hence, for $a_3 = 0.187$, f is equal to 0.052, i.e., about 5%. Therefore, a small fraction of molecules not undergoing energy transfer can account for the difference between the experimental and theoretical values of $r(\infty)/r_0$.

Further comparison between eqs 8 and 10 allows us to determine $\alpha_1 = 0.752$ and $\alpha_2 = 0.105$, and to calculate the expected value for the steady-state anisotropy at 334 nm by means of the following relation

$$\bar{r} = r_0\left[\frac{\alpha_1}{1+\tau/\theta_1} + \frac{\alpha_2}{1+\tau/\theta_2} + \frac{1}{7}\right]$$

where $r_0 = 0.34$, θ_1 and θ_2 are taken from Table 1 (0.177 and 3.55 ns, respectively), and $\tau = 14.9$ ns. The final result is $\bar{r} = 0.059$ which is in better agreement with the experimental value of 0.051 ± 0.005. Such a satisfactory agreement confirms the validity of the assumption that $r(\infty)/r_0$ is 1/7, i.e. there is no preferred mutual orientation between the chromophores.

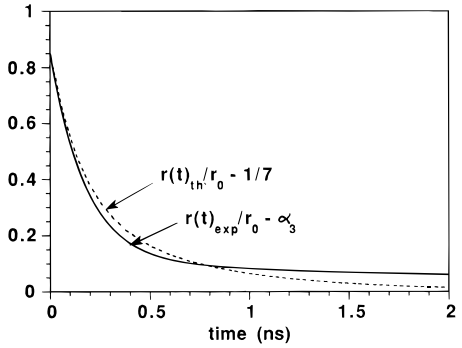


Figure 4. Comparison between the experimental and theoretical decays of emission anisotropy (see text).

As regards the rate constant for energy hopping, it is of interest to estimate it from Förster's theory[9] by means of the well-known relation

$$k = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6$$

where R is the interchromophoric distance and R_0 is the isotropic critical radius given by

$$R_0 = 0.2108[\kappa^2 \Phi_0 n^{-4} \int_0^\infty I(\lambda)\, \epsilon(\lambda) \lambda^4\, \mathrm{d}\lambda]^{1/6}$$

with R_0 in angströms, where κ^2 is the orientational factor, Φ_0 the donor fluorescence quantum yield, n the average refractive index of the medium in the wavelength range where spectral overlap is significant, $I(\lambda)$ the normalized fluorescence spectrum of the donor, $\epsilon(\lambda)$ the acceptor absorption coefficient (in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$), and λ the wavelength in nanometers.

Despite the fact that the assumption of dynamic averaging regime is not valid in a rigid medium, we take the orientation factor κ^2 equal to the dynamic average, i.e., 2/3, because only an order of magnitude is searched. With the quantum yield $\Phi_0 = 0.48$,[3] and $n = 1.36$, the value of R_0 is found to be 14 Å. The average interchromophoric distance being about 8 Å, the value predicted by Förster's theory is 1.9×10^9 s^{-1}.

Comparison is desirable between the experimental anisotropy decay and the theoretical decay in order to obtain a best fit value of k appearing in eq 4. In order to get rid of the residual red-edge effect at 290 nm, the best fit is searched for

$$r(t)/r_0 - \alpha_3 = \alpha_1 \exp(-t/\theta_1) + \alpha_2 \exp(t/\theta_2) = 0.752 \exp(-t/0.177) + 0.105 \exp(-t/3.55)$$

by using the theoretical relation

$$r(t)/r_0 - 1/7 = 0.286[\exp(-0.753kt) + \exp(-2.445kt) + \exp(-3.802kt)]$$

The comparison is displayed in Figure 4. The best fit value of k is $(2.0 \pm 0.1) \times 10^9$ s^{-1}.

The difference in shape between the experimental and theoretical decays arises from several causes. First, the model assumes a single rate constant for all neighboring pairs, which is not exact, because a distribution of distances, although narrow, should exist, and also because not all pairs have the same mutual orientation. A second cause is the presence of inhomogeneous broadening—in this work, it was rationalized as a fraction of molecules not undergoing hopping, but more realistically it implies a distribution of rate constants.

However, the model is semiquantitatively obeyed, if a small contribution from inhomogeneous broadening is allowed for.

The value of k is surprisingly in very good agreement with that estimated by Förster's theory, despite the latter being a crude approximation because the distributions of distances and mutual orientations of the chromophores have not been taken into account. Therefore, although Dexter's exchange mechanism for energy transfer[10] cannot be excluded since the flexible link of the chromophores allows them to approach each other at a distance smaller than 5 Å, it is reasonable to consider that the energy hopping process is mainly governed by Förster's dipole−dipole mechanism.

Conclusion

Dynamics of energy hopping between seven chromophores in a circular arrangement has been theoretically studied under the assumption of a unique identical rate constant for energy hopping, supposed to occur only between randomly oriented nearest neighbors. The overall fluorescence anisotropy is found to be a triple-exponential decay with equal amplitudes, plus a constant term which is 1/7th of the fundamental anisotropy r_0.

Steady-state and frequency-domain fluorescence anisotropy experiments are in good agreement with a long-time leveling-off of the emission anisotropy at $r_0/7$, thus confirming that there is no preferred mutual orientation between the chromophores.

As regards the dynamics of energy hopping, the difference between the experimental and theoretical anisotropy decay curves can be explained by the approximations made in the model. In particular, the distributions of distances and mutual orientations of the chromophores have not been taken into account. Nevertheless, an average value of the rate constant for energy hopping can be determined and is consistent with a predominant dipole-dipole mechanism of transfer.

Further studies with cyclodextrins labeled with chromophores on the primary face, i.e., at a closer distance than in the present investigation, will be undertaken. Much faster energy hopping is indeed expected and should involve both dipole−dipole and exchange mechanisms. Furthermore, Monte-Carlo simulations are in progress for a better theoretical description of excitation energy hopping among randomly oriented chromophores; the preliminary results show that a distribution of tranfer rate constants should be considered instead of a single average rate constant.

Experimental Section

Materials. The synthesis of CD7(3) was previously described.[3] Commercially available methanol and ethanol (spectroscopic grade) were used without further purification.

Methods. The UV−vis absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. Steady-state fluorescence anisotropies, defined as $r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2\,I_{\perp})$, (where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities observed with vertically polarized excitation light and vertically and horizontally polarized emissions, respectively) were measured with a SLM 8000 C spectrofluorometer. The G-factor method[11] was used to correct the data for instrumental response.

Low-temperature spectra (110 K) were performed with an Oxford DN1704 cryostat with windows; specially made 1 cm × 1-cm strain-free quartz cuvettes were used for the sample.

Time-resolved fluorescence measurements were obtained with the multifrequency phase fluorometer at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana−Champaign. The light source is a mode-locked Nd-YAG laser, (Coherent 700) which synchronously pumps a rhodamine 6G dye laser. Data were collected until the standard deviation of each phase and modulation measurements were below 0.2 and 0.004 for the phase and modulation, respectively. A special low-temperature cryostat was built for this experiment that allow the measurement of two cuvettes by rotation of the low-temperature dewar. The lifetime measurement were obtained using *p*-terphenyl (1.05 ns) as a reference. The reference was at room temperature. The temperature control of the low-temperature dewar was better than 1 °C during the entire measurement.

Analysis of the data was performed using the Globals Unlimited software (Beechem and Gratton).

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Appendix

Equation 1 can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P} = \mathbf{K}\mathbf{P} \tag{A1}$$

where **P** is the excitation probability vector and **K** is the matrix of rate coefficients. Defining the auxiliary vector **Q**

$$\mathbf{Q} = \mathrm{e}^{\Gamma t}\mathbf{P} \tag{A2}$$

eq A1 becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{Q} = \mathbf{L}\mathbf{Q} \tag{A3}$$

where the matrix **L** is

$$\mathbf{L} = \begin{bmatrix} -2k & k & 0 & 0 & 0 & 0 & k \\ k & -2k & k & 0 & 0 & 0 & 0 \\ 0 & k & -2k & k & 0 & 0 & 0 \\ 0 & 0 & k & -2k & k & 0 & 0 \\ 0 & 0 & 0 & k & -2k & k & 0 \\ 0 & 0 & 0 & 0 & k & -2k & k \\ k & 0 & 0 & 0 & 0 & k & -2k \end{bmatrix} \tag{A4}$$

The solution of eq A3 is obtained as detailed in ref 12, the calculation of the eigenvalues and eigenvectors of matrix **L** being the main steps.

The eigenvalues λ_n ($n = 1, 2, ..., 7$) of the matrix **L** are the roots of the secular equation

$$|\mathbf{L} - \lambda\mathbf{U}| = 0 \tag{A5}$$

By making

$$x = -((\lambda/k) + 2) \tag{A6}$$

eq A5 becomes

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{A7}$$

The determinant of eq A7 is recognized as a cyclic determinant, or circulant,[13] and therefore eq A7 can be rewritten as

$$\prod_{n=1}^{7}(x + \omega_n + \omega_n^{6}) = 0 \tag{A8}$$

TABLE 2

n	1	2	3	4	5	6	7
x_n	−1.247	0.445	1.802	1.802	0.445	−1.247	−2
λ_n	$-0.753k$	$-2.445k$	$-3.802k$	$-3.802k$	$-2.445k$	$-0.753k$	0

where

$$\omega_n = e^{2\pi i n/7} \tag{A9}$$

and therefore the roots x_n are given by

$$x_n = -(\omega_n + \omega_n{}^6) = 2(-1)^{n+1} \cos\left(\frac{5n\pi}{7}\right) \qquad (n = 1, 2, ..., 7) \tag{A10}$$

From eqs A6 and A10, Table 2 is drawn.

There are therefore three double degenerate eigenvalues, the seventh eigenvalue being zero.

The rather lengthy calculation of the eigenvectors was done according to the procedure given in ref 12 for the case of degenerate eigenvalues.

References and Notes

(1) (a) *Antennas and Reaction Centers in Photosynthetic Bacteria*; Michel-Beyerle, M. E., Ed.; Springer Verlag: New York, 1985. (b) *The Photosynthetic Bacterial Reaction Center—Structure and Dynamics*; Breton, J., Vermeglio, H., Eds.; Plenum Press: New York, 1988.

(2) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: New York, 1990.

(3) Berberan-Santos, M. N.; Canceill, J.; Brochon, J. C.; Jullien, L.; Lehn, J. M.; Pouget, J.; Tauc, P.; Valeur, B. *J. Am. Chem. Soc.* **1992**, *114*, 6427.

(4) Berberan-Santos, M. N.; Pouget, J.; Valeur, B.; Canceill, J.; Jullien, L.; Lehn, J.-M *J. Phys. Chem.* **1993**, *97*, 11376.

(5) Gravett, D. M.; Guillet, J.*J. Am. Chem. Soc.* **1993**, *115*, 5970.

(6) Jullien, L.; Canceill, J.; Valeur, B.; Bardez, E.; Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2438.

(7) Berberan-Santos, M. N.; Valeur, B. *J. Chem. Phys.* **1991**, *95*, 8048.

(8) Gratton, E.; Jameson D. M.; Hall, R. D. *Annu. Rev. Biophys. Bioeng.* **1984**, *13*, 105.

(9) Förster, Th. *Z. Naturforsch.* **1949**, *4a*, 321−327.

(10) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836−850.

(11) Chen, R. F.; Bowman, R. L. *Science* **1965**, *147*, 729.

(12) Berberan-Santos, M. N.; Martinho, J. M. G. *J. Chem. Educ.* **1990**, *67*, 375.

(13) Muir, T. *A Treatise on the Theory of Determinants*; Dover: New York, 1960.

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