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Local Solvent Acidities in β-Cyclodextrin Complexes with PRODAN Derivatives

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Abstract

The local solvent acidities (SA scale) of six 6-carbonyl-2-aminonaphthalene derivatives as β-cyclodextrin complexes in water are determined through fluorescence quenching. The local polarities (E_T^N scale) are determined through the shift of the emission center-of-mass. The apparent SA values reflect the solvent structure surrounding the guest's carbonyl group, whereas the apparent E_T^N values reveal the net polarity of the entire guest molecule. Comparison of these values affords greater insight into the structures of the host-guest complexes. Derivatives **1** and **5** show unusually large acidities indicative of highly exposed carbonyl groups. The remaining compounds give emission intensities pointing to shielded carbonyl groups. In this study PRODAN and its derivatives are functioning as dual channel sensors of their local environment.

Keywords

solvatochromism; host-guest complex; solvent acidity; PRODAN; β-cyclodextrin

Introduction

Small fluorescent molecules possessing charge-transfer emissive states are particularly useful as polarity probes. Among these fluorophores, PRODAN (6-propionyl-2-dimethyaminonaphthalene, **1**, Figure 1)[1] finds considerable use as a sensor, especially for lipid bilayers.[2-6] The Stokes shift of PRODAN is affected by specific H-bonding interactions in addition to the general effects of the solvent's polarity.[7-9] In fact, in correlating the solvatochromic shifts, using Catalán's solvent parameters, the coefficient for the polarity term (SPP) is only twice as large as the solvent acidity (SA) term.[10, 11] Although the amino group in PRODAN could potentially accept a H-bond, the carbonyl group is thought to be the dominant H-bond acceptor site for PRODAN's excited state.[12] The dependence of the emission maximum on both polarity and H-bonding complicates conclusions about the probe's immediate environment.[3, 11]

Recently we have shown that emission intensities of **1** - **6** (Figure 1) in a series of hydroxylic solvents correlate strongly with the solvent's H-bond donating abilities.[13] Specifically, the logarithm of the degree of quenching in the solvent is linearly related to Catalán's solvent acidity parameter for that solvent. The magnitude of the quenching is particularly pronounced with the carbonyl-twisted derivatives **3**, **4** and **6**. Because the Stokes shifts are a measure of the local polarity, we suggested that these compounds could act as dual channel chemosensors. In this paper we use PRODAN and the five derivatives as sensors of the local environment of a simple binding site; namely, the interior of a β-cyclodextrin (CD) cavity

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(Figure 1).[14, 15] This seven-unit glucose host molecule is known to form a 1:1 complex with PRODAN in aqueous solution.[16-18] Molecular modeling results suggest that PRODAN is oriented with its long axis parallel to the C_7 axis of β-CD with the dimethylamino group extending outward from the secondary face. The emission of the PRODAN/β-CD complex is blue-shifted by 20 nm and enhanced several fold in intensity. The solvatochromic shift has been attributed to the lower polarity of the cyclodextrin cavity relative to water, while the intensity increase has been thought to arise from the more rigid environment within the cavity that reduces the pathways for non-radiative relaxation back to the ground state. Such an increased rigidity is essentially an increase in the local viscosity. It is known that a large increase in viscosity can slow solvent relaxation around PRODAN to the point that it will exhibit dual emission from the locally-excited and intramolecular charge-transfer (ICT) states.[19] Smaller changes in viscosity have no effect on the solvatochromism.[20] Viscosity effects on emission intensity are common with fluorophores equipped with molecular rotors, especially those with twisted ICT states.[21] While an emissive TICT state has been proposed for PRODAN, [2, 22, 23] we have shown through the behavior of constrained derivatives that its excited state is planar, and therefore cannot be considered a molecular rotor.[24-26] In this paper the emission position and intensity for the βCD-bound PRODAN derivatives are attributed to changes in the H-bonding interactions with the surrounding water molecules.

Experimental

Compounds **1** - **6** were prepared previously and sublimed under vacuum before use.[24, 25, 27] β-Cyclodextrin was a gift from Amaizo and was recrystallized twice from water and dried *in vacuo* at 100°C before use. Solvents used for photophysical characterization were spectrophotometric grade. Fluorescence emission data were collected using a fiber optic system with a 300W light source monochromated to 365 nm with a bandpass of 5 nm and a high sensitivity Ocean Optics Maya CCD detector. Absorption spectra were obtained from the same fiber optic system with a miniature deuterium/tungsten light source. Binding isotherm data were generated from the emission spectra of a series of aqueous solutions in which the fluorophore concentration was held constant and the β-CD concentration was varied. The following procedure was typical: 5 μL of a stock solution of fluorophore (ca. 5 mg/10 mL MeOH) and a variable volume (0 to 500 μL) of a stock solution of β-CD (ca. 500 mg/ 25 mL H_2O) were diluted to 5 mL with H_2O and stirred for 4 hours before recording the emission spectrum. Reference solutions of the same concentration of fluorophore in MeOH and EtOH were also prepared. The relative molar absorptivities of the fluorophore in H_2O, MeOH and EtOH and of the fluorophore/β-CDcomplex in H_2O were determined by the method of standard additions. The electronic noise was subtracted from the raw emission data, and the abscissa scale was converted to wavenumbers before subsequent mathematical treatment. Emission intensity values were determined through numerical integration of the intensity *vs.* cm^{-1} data, $I(\tilde{\nu})$, between 26300 cm^{-1} (380 nm) and 13300 cm^{-1} (750 nm). The emission center of mass ($\tilde{\nu}_{CM}$) was determined from equation 1.

$$\tilde{\nu}_{CM} = \frac{\int I(\tilde{\nu}) \cdot \tilde{\nu} d\tilde{\nu}}{\int I(\tilde{\nu}) d\tilde{\nu}} \quad (1)$$

Plots of the integrated intensity, I_{int}, *vs.* [β-CD] were fit to equation 2 using non-linear least squares. Here I_L is the limiting intensity of the plot and hence the intensity of the fluorophore/β-CD complex, while fH_2o is the emission factor ratio between the fluorophore solvated in water and complexed with β-CD. This factor accounts for differences in the absorption at the excitation wavelength (365 nm) and in the relative quantum yields (equation 3).

$$I_{int} = \frac{I_L \left(f_{H_2O} + K\left[\beta - CD \right] \right)}{1 + K\left[\beta - CD \right]} \quad (2)$$

$$f_{H_2O} = \frac{\varepsilon_{H_2O} \cdot \Phi_{H_2O}}{\varepsilon_{complex} \cdot \Phi_{complex}} \quad (3)$$

The integrated emission intensities of **1** - **6** in MeOH and EtOH give the emission factor ratios f_{MeOH} and f_{EtOH} (equation 4) after correcting for the different indices of refraction (η).

$$f_{ROH} = \frac{I_{ROH}}{I_L} \cdot \frac{\eta^2_{ROH}}{\eta^2_{water}} = \frac{\varepsilon_{ROH} \cdot \Phi_{ROH}}{\varepsilon_{complex} \cdot \Phi_{complex}} R = Me, Et \quad (4)$$

Rearranging equation 4 gives the ratios of the relative quantum yields of the complex *vs.* water, methanol and ethanol, respectively (equation 5)

$$\frac{\Phi_{complex}}{\Phi_{ROH}} = f_{ROH}^{-1} \frac{\varepsilon_{ROH}}{\varepsilon_{complex}} R = H, Me, Et \quad (5)$$

The apparent solvent acidities in the complexes are determined through equation 6. The slope m is determined using the two points on the plot of $-\log(\Phi_{ROH})$ vs. SA where the intensities of the fluorophore in the reference solvents bracket that of the complex (equation 7)

$$SA_{app} = SA_{ROH} - \frac{\log \left(\Phi_{complex} / \Phi_{ROH} \right)}{m} \quad (6)$$

$$m = \frac{\log \left(\varepsilon_{ROH} / I_{ROH} \eta^2_{ROH} \right) - \log \left(\varepsilon_{R'OH} / I_{R'OH} \eta^2_{R'OH} \right)}{SA_{ROH} - SA_{R'OH}} \quad (7)$$

Results and Discussion

In this investigation PRODAN and derivatives function as sensors of the solvent acidity of hydroxylic media. In particular, the quenching of **1** - **6** is related to the H-bonding ability of the media, and it is expressed by an apparent SA value on Catalán's SA scale.[13] The fluorophores sense their local solvent acidity as they are bound to β-CD. Fluorescence titrations of **1** - **6** with β-CD gave hyperbolic binding isotherms characteristic of 1:1 complexes. Figure 2 shows a typical plot with **6** and β-CD together with the intensities of the same concentrations of **6** in ethanol and methanol. The limiting intensity (I_L) of the titration corresponds to the emission of the fluorophore in the β-CD complex, and it is determined by fitting the binding isotherm to equation 2. This fitting function has the binding constant (K) and an emission factor ratio (f_{H_2O}, equation 3) as parameters in addition to I_L. In reality, only two parameters are needed to fit the binding isotherm. The emission factor ratio could have been expressed in terms of the limiting intensity ($f_{H_2O} = (I_o/I_L)*(\varepsilon_{complex}/\varepsilon_{water})$ because the intensity of the free fluorophore (I_o, without added β-CD) and the molar absorptivites of the bound and free fluorophore are determined experimentally. However, this approach would propagate the use of the I_o value in the best-fit analysis. Because all of the PRODAN derivatives suffer the greatest quenching in water,

the I_o value has the largest relative uncertainty. Indeed, for the twisted PRODAN derivatives, **3**, **4** and **6**, the free fluorophore is quenched by an order of magnitude or more compared to the bound fluorophore. Also, aggregation of the more hydrophobic derivatives, especially **2**, **3** and **4**, make the measurement of I_o problematic.[13] Because of the problems with relying only on f_{H_2O} for determining the relative quantum yield of the complex, the emission factor ratios for the fluorophore in ethanol and methanol were also determined as references. The fluorescence intensity of the bound fluorophore typically lies between the intensities in these solvents. In all cases the relative quantum yield of the complex was calculated through interpolation using the f_{ROH} values that bracket that of the complex.

The relative quantum yield of the fluorophore in the β-CD complex is translated to an apparent solvent acidity through equation 6. This equation is derived from our previous work that showed an empirical linear relationship between the logarithm of the relative quenching and the solvent acidity parameter of Catalán. The slope of the line segment (*m*, equation 7) between the bracketing reference solvents is used in interpolating the apparent solvent acidity in the complex. The solvent acidity values for the six complexes are collected in Table 1 together with the respective binding constants. The range of apparent acidity values is large considering the structure similarity of the fluorophores. The lowest value (0.42) is nearly that of ethanol (0.40), and the highest value (0.91) is closer to that of water (1.062) than methanol (0.605). The binding affinities correlate poorly with the apparent solvent acidities.

The apparent solvent acidities offer added insight into the structure of the host-guest complex. In particular, these values reveal the nature of the H-bonding environment in the immediate proximity of the carbonyl group. A small value indicates a restricted water structure, while a large value indicates a less-perturbed water structure. A restricted water structure implies that the carbonyl group is relatively hidden from the bulk water. Both of the *t*-butyl derivatives, **3** and **4**, and the seven-membered ring derivative, **6**, give SA_{app} values reflecting a relatively less-water-accessible carbonyl group. On the other hand, PRODAN and the six-membered ring derivative, **5**, have exposed carbonyl groups according to the SA values. The large difference between the SA_{app} values for **5** and **6** is surprising since their structures differ only by a methylene group.

Complexation of the fluorophore with β-CD not only enhances the emission intensity, but it also blue-shifts the emission maximum. Such a change results from both H-bonding interactions and polarity effects with the solvent. Reichardt's E_T^N solvent polarity parameter reflects both of these terms, and not surprisingly, the emission maximum for PRODAN shows a strong linear correlation with E_T^N.[28-30] Figure 3 and Table 2 show that derivatives **2** - **6** behave similarly. The line segments for **3** and **4** are truncated because the emission data in water are blue-shifted due to aggregation and are not included in the plots. These plots show good linear fits and a narrow range of slope values.

The fluorescence titrations of **1** - **6** with β-CD gave limiting solvatochromic shifts corresponding to the emission of the β-CD complex. Using the linear fits from Figure 3, these shifts are converted to apparent E_T^N values, and they are collected in Table 3. The range of the values is rather narrow: less than 0.10. The values indicate polarities that are closer to MeOH (0.762) than to H_2O (1.00) or EtOH (0.654). They are consistent with other experimental determinations of the polarity of the β-CD cavity.[31] For example, the fluorescence lifetime of the 2-naphthol/ β-CD complex (7.2 ns) lies between the lifetimes for 2-naphthol in methanol (5.9 ns) and ethanol (8.9 ns), but is significantly greater than the lifetime in water (4.8 ns).[32]

The comparison between the apparent E_T^N and SA values sheds light on the nature of the fluorophore/β-CD complex. While the E_T^N scale and the SA scale are close in magnitude, they do not allow for direct comparison. The latter can be made by converting the apparent values to a percentage of the range between the values for ethanol and water. The results of these conversions are also shown in Table 3 along with the differences between the percentage values. Interpretation of these results requires understanding the factors that determine the apparent E_T^N and SA values. The E_T^N values depend in part on polarity effects experienced by the entire molecule, whereas SA values only depend on H-bonding with the carbonyl group. If the rescaled E_T^N and SA values are close, then the polarity effects on the molecule and the H-bonding effects on the carbonyl are similar. However, Table 3 shows that values are different suggesting that the carbonyl groups do not experience the same net environment as do the molecules. This behavior is consistent with axial inclusion of the naphthalene groups resulting in one end being buried in the less polar cavity while the other end is exposed to bulk water. The high acidities compared to the net polarities for PRODAN and **5** are consistent with inclusion complexes where the carbonyl groups, not the dimethyl amino groups, extend out from the secondary face. Derivatives **2** and **3** containing a piperidine ring give complexes that experience a relatively polar environment overall but show poor H-bonding with the carbonyl, especially with **3**. These data suggest that the piperidine ring inhibits penetration into the β-CD cavity and that it is exposed to the solvent while the carbonyl group is hidden despite the fact that the piperidine group is more hydrophobic than the carbonyl groups, especially in the case of **2**. The *tert*-butyl group in **3** and **4** and the seven-membered ring in **6** give rise to strongly and deeply included carbonyl groups as shown by the large binding constants and the relatively low apparent polarities and acidities.

Conclusions

The dual sensor capability of PRODAN and derivatives towards H-bonding interactions and solvent polarity has been demonstrated for guest-host complexes with β-cyclodextrin. Integrated emission intensities report on the H-bonding donating ability of the solvent surrounding the carbonyl group, whereas emission center-of-mass values are indicative of the polarity felt by the entire guest molecule. Together these values offer greater insight into the average structures of the bound complexes.

Acknowledgments

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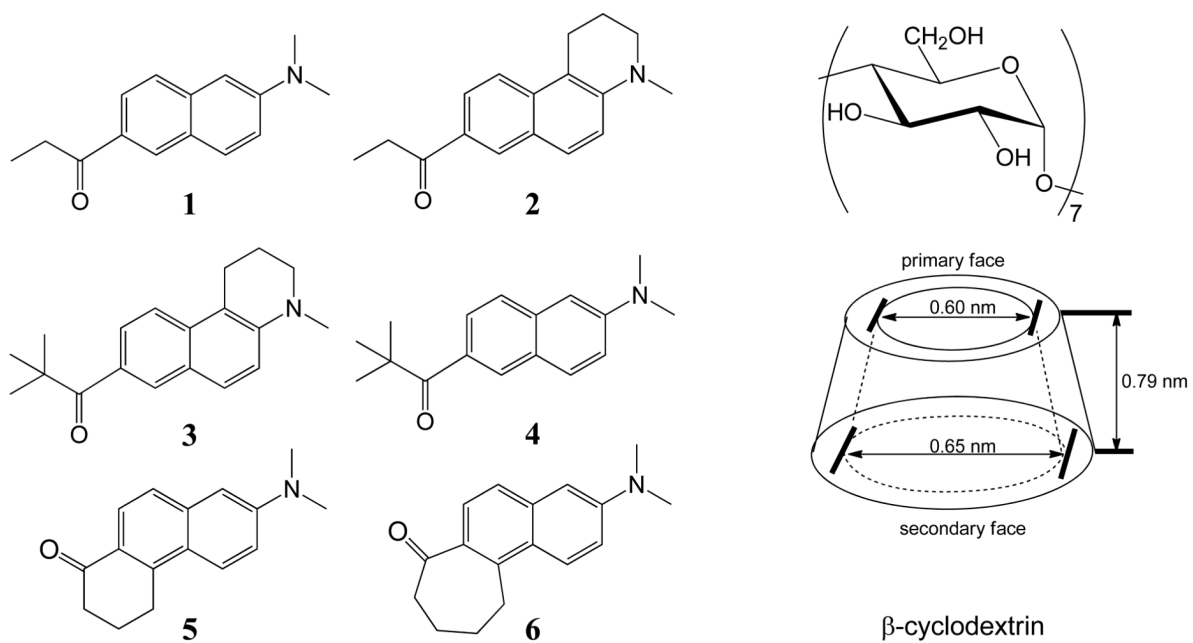
Figure 1.
Structures of PRODAN (**1**), PRODAN derivatives (**2**-**6**) and β-cyclodextrin.
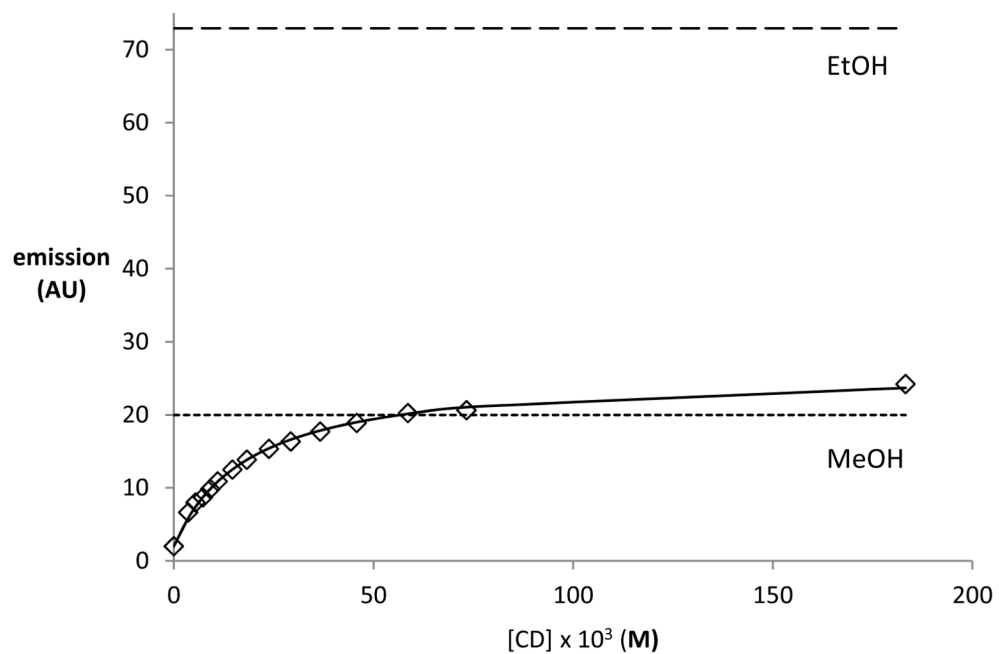
Figure 2.
Binding isotherm from the titration of **6** with β-CD and emission intensities of the same concentration of **6** in ethanol (— — —) and methanol (----).
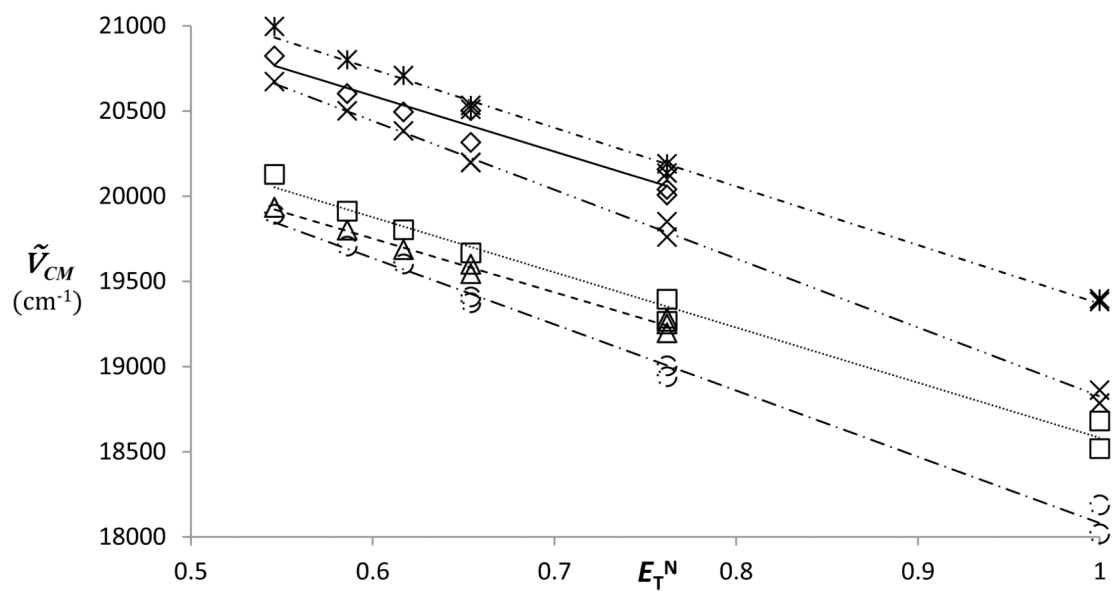
Figure 3.

Plots of $\tilde{\nu}_{CM}$ vs. E_T^N for **1-6** in hydroxylic solvents (**1**, ×, — •• —; **2**, ○, — • —; **3**, △, --- ; **4**, ◇, —; **5**, *, – • –; **6**; □, •••; iPrOH, BuOH, PrOH, EtOH; MeOH; H_2O)

Table 1

Effective solvent acidities (SA$_{eff}$) and binding constants (K) for **1** - **6** with β-CD.[a]

	1	**2**	**3**	**4**	**5**	**6**
SA$_{app}$	0.84 ±0.04	0.62 ±0.05	0.42 ±0.04	0.50 ±0.02	0.91 ±0.01	0.52 ±0.02
K × 10^{-3} (M^{-1})	3.1 ±0.1	6.3 ±1.3	1.3 ±0.1	10 ±1	3.2 ±0.6	5.2 ±0.2

[a]The uncertainties are standard deviations from multiple determinations.

Table 2

Best-fit slopes, standard errors and R^2 values for the plots of $\tilde{v}_{CM}$ vs. E_T^N in Figure 3.

	1	2	3	4	5	6
−slope (cm⁻¹)	4000	3900	3200	3300	3400	3200
error	80	130	100	340	90	150
R^2	0.998	0.992	0.989	0.938	0.996	0.987

Table 3

Apparent E_T^N values for the complexes of **1 - 6** with β-CD and comparison with the apparent SA values.

	1	2	3	4	5	6
E_T^N app	0.81 ±0.02	0.86 ±0.02	0.80 ±0.03	0.78 ±0.01	0.76 ±0.01	0.80 ±0.03
E_T^N app % of range [1,2]	45 ±7	59 ±7	43 ±8	36 ±3	32 ±1	41 ±7
SA_app % of range [1,3]	66 ±6	33 ±8	3 ±6	15 ±3	77 ±2	18 ±3
difference	21 ±13	−26 ±15	−40 ±14	−21 ±6	45 ±3	−23 ±10

[1] Expressed as a percentage of the range between the corresponding values for ethanol (0%) and water (100%)

[2] MeOH is 31%

[3] MeOH is 31%.