Synthesis and characterization of dicyanoanthracene-tethered β-cyclodextrins

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The synthesis of 6-*O*- and 2-*O*-(9,10-dicyanoanthracene-2-methyl)-β-cyclodextrin (1 and 2) is described. Binding affinities with several aromatic sulfonate guests (6–10) are determined using fluorescence quenching results. The apparent Stern–Volmer constants, which are the sums of dynamic and static (binding) components, are adjusted by subtracting those obtained in the presence of 1-adamantanecarboxylate (AD–CO_2^-) which have just a dynamic term. Quenching constants with 9,10-dicyanoanthracene-2-sulfonate (4) and 9,10-dicyanoanthracene-2,6-disulfonate (5), and binding constants with β-CD are determined for comparison. The results show that the C6 tethered host binds better than the C2 host, which binds as well as does β-CD. Dynamic quenching accounts for at least 10% of the total even with strongly bound guests. The properties of these hosts are compared with a DCA-capped β-CD (3) (DCA = dicyanoanthracene).

Cyclodextrins (CDs) form complexes with small organic molecules in aqueous solution.[1] Cyclodextrin derivatives often show enhanced binding capability as well as new catalytic properties.[2] We are interested in attaching β-CD to photochemical sensitizers. We have studied anthraquinone[3] and benzophenone[4] derivatives of β-CD. Irradiation of these compounds results in hydrogen abstration from the CD by the triplet carbonyl moieties. Other photosensitizers which have been attached to CDs include flavin,[5] porphyrin[6] and rose bengal.[7] These compounds show enhanced photooxidation, photoreduction and photooxygenation, respectively, of certain bound substrates. Our recent focus has been on dicyanoanthracene as a sensitizer because of its desirable photophysical properties: its singlet excited state is a strong one-electron oxidant and a poor H-atom abstractor. We have reported the synthesis and binding affinity of a 9,10-dicyanoanthracene-capped β-CD (**3**).[8] The capped CD suffered in two respects: (i) it was isolated as a mixture of A,C- and A,D-regioisomers and (ii) the attachment is made *via* two sulfonate ester bonds which are hydrolytically labile. Here we report the synthesis of two DCA-derivatized β-CDs linked by ether bonds (Fig. 1), and we show they exhibit stronger binding of aromatic guests than does the capped-β-CD.

Experimental

^1H and ^{13}C NMR spectra were obtained with a GE QE-300 spectrometer. UV–VIS spectra were obtained with a Beckman DU-70 spectrophotometer. Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected. Combustion analysis was performed by Desert Analytics. Preparative high performance liquid chromatography was performed on a Waters 244 system equipped with a UV absorption detector (254 nm), using a Whatman Magnum 20 ODS column. Analytical HPLC was performed on a Waters 600E system equipped with a variable wavelength absorption detector set at 254 nm. The analysis of the ether regioisomers was carried out with a Whatman ODS-3 analytical column, using a linear gradient program (20–60% aq. CH_3CN, 40 min).

Fluorescence binding studies in water were carried out with a SLM-Aminco SPF-500C spectrofluorometer thermostatted at 25 °C. For a typical binding determination 1 ml aliquots of the

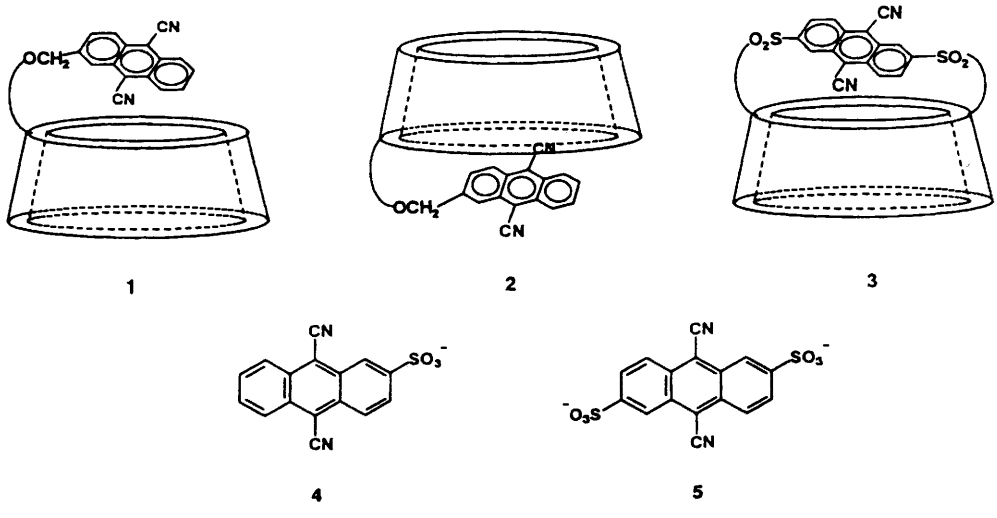

Fig. 1 Fluorophore structures

Table 1 ^{13}C Chemical shift differences for **1** and **2** *vs.* β-CD

Regioisomer	C	$\Delta\delta$(ppm)[a]
6-*O*-	1	+0.5
	5	−1.5
	6	+9.4
2-*O*-	1	−1.9
	2	+9.0
	4	−2.0

[a] A minus sign indicates an upfield shift.

fluorophore (*ca.* 10^{-4} M) were combined with varying aliquots of quencher (1–6 ml, *ca.* 10^{-3} M) and diluted to 10 ml with water. The blank was run first, then in order from the least concentrated to most concentrated to give ample equilibration time. Two excitation wavelengths were used for each binding study; intensities were obtained by integration of the emission spectra. Repeat experiments were conducted with quencher concentrations which should give $I_0/I - 1$ values evenly spaced from 0.33 to 2. In the competitive binding experiments the AD–CO_2^- concentration was 0.22 mM.

Dimethylacetamide (DMAC) was fractionally distilled from CaH_2 under N_2, and the fraction boiling at 163 °C and higher was collected. DMF was distilled from CaH_2 *in vacuo* (0.1 Torr). CuCN was freshly prepared from $CuSO_4$, KCN and $NaHSO_3$ before use.[9] β-Cyclodextrin (Amaizo) was dried at 100 °C at 0.1 Torr overnight before use, and it was recrystallized twice from H_2O and dried as above for use in binding studies.

The preparation of **5** is described elsewhere.[8] The amine quenchers were commercially available except 6-dimethylamino-2-naphthalene sulfonate (**7**) which was made by a modified literature method.[10] The aminonaphthalene sulfonates were recrystallized from aq. NaCl or aq. KCl, whereas the other amines were used without purification.

2-Methylanthraquinone (Aldrich) was reduced to 2-methylanthracene with Sn and Zn,[11] and the anthracene was brominated to give 9,10-dibromo-2-methylanthracene using standard methods.[12]

9,10-Dicyano-2-methylanthracene

9,10-Dibromo-2-methylanthracene (3.60 g, 10.3 mmol) and CuCN (6.60 g, 73.5 mmol) were suspended in DMAC (400 ml). The solution was heated by immersion into an oil bath preheated to 200 °C, and heating was maintained for 4 h. Most of the solvent was removed *in vacuo* (0.1 Torr). The residue was poured into water, and the mixture was stirred for 1 h and filtered with suction. The brown solid which was collected was digested with boiling 4 M HNO_3 (400 ml). The mixture was heated to boiling with stirring for 15 min. The hot acid solution was filtered with suction through a fritted glass funnel, washed with water and dried *in vacuo*. The solid was recrystallized from EtOH (250 ml) and toluene (50 ml) and then sublimed to give the dicyanoanthracene (1.58 g, 6.52 mmol, 63%), mp 236 °C (decomp.); ^1H NMR ($CDCl_3$) δ 2.57 (3 H, s, CH_3), 7.53 (1 H, d, $J_{3,4}$ = 8.8, 3-H), 7.70 (2 H, m, 6,7-H), 8.04 (1 H, s, 1-H), 8.19 (1 H, d, $J_{3,4}$ 8.8 Hz, 4-H), 8.30 (2 H, m, 5,8-H); ^{13}C NMR ($CDCl_3$) δ 22.4, 110.2, 111.2, 116.0, 116.1, 124.4, 125.9, 126.1, 126.2, 129.4, 129.8, 130.9, 131.5, 132.1, 132.5, 132.7, 140.8. Found: C, 84.22; H, 3.85; N, 11.48. Calc. for $C_{17}H_{10}N_2$: C, 84.28; H, 4.16; N, 11.56%.

9,10-Dicyano-2-bromomethylanthracene

9,10-Dicyano-2-methylanthracene (1.00 g, 4.12 mmol) was dissolved with heating in CCl_4 (250 ml). A solution of Br_2 (780 mg, 4.88 mmol) in CCl_4 (30 ml) was added dropwise while the reaction was heated at reflux and irradiated with a 150 W halogen floodlamp. Irradiation and reflux were maintained for another 2 h. Most of the CCl_4 was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2. The solution was washed with 5% aq. $NaHSO_3$ and with 5% aq. $NaHCO_3$, dried over $CaCl_2$, and concentrated *in vacuo*. The product was purified by sublimation (> 200 °C, 0.1 Torr) giving the bromomethyl derivative, mp 229–231 °C (1.12 g, 3.49 mmol, 85%). Purification also could be achieved by recrystallization from EtOH and toluene: ^1H NMR ($CDCl_3$) δ 4.71 (2 H, s, CH_2Br), 7.85 (3 H, m, 2,6,7-H), 8.45 (4 H, m, 1,4,5,8-H); ^{13}C NMR ($CDCl_3$) δ 32.3, 111.7, 111.8, 115.8, 115.9, 125.3, 126.3, 126.4, 127.3, 130.2, 130.3, 131.1, 132.1, 132.5, 132.8, 139.9, 148.2. Found: C, 63.47; H, 2.72; N, 8.75. Calc. for $C_{17}H_9BrN_2$: C, 63.57; H, 2.82; N, 8.72%.

6-*O*- and 2-*O*-(9,10-Dicyanoanthracene-2-yl)methyl-β-cyclodextrin (1 and 2)

9,10-Dicyano-2-bromomethylanthracene (1.00 g, 3.11 mmol) was dissolved in DMF under N_2. NaOH (623 mg, 15.6 mmol) was dissolved in MeOH (25 ml). β-CD (6.00 g, 5.29 mmol) was dissolved in a second portion of DMF. Methanolic NaOH (5.0 ml) was added to the β-CD solution, and some of the solvent (*ca.*, 20 ml) was removed by vacuum distillation (0.1 Torr). The two DMF solutions were then combined under nitrogen and allowed to stir for 1 h at room temperature. The solution was poured into acetone (1500 ml), and the precipitate was collected by suction filtration and dried *in vacuo*. The ether regioisomers were separated using preparative reverse phase HPLC. 2-*O*-isomer: (42.1 mg, 0.031 mmol, 1.0%), t_R = 22.7 min; ^{13}C NMR [$(CD_3)_2SO$] δ 60.3, 72.4, 72.8, 73.4, 80.6, 81.8, 82.0, 82.6, 100.4, 102.3, 110.9, 116.0, 123.6, 126.0, 126.2, 130.8, 130.9, 131.0, 131.4, 131.6, 131.7, 131.8, 131.9, 135.8, 136.1, 141.4; UV $\lambda_{max}(H_2O)$/nm 361 (log ε 2.7), 380 (2.9), 405 (2.8), 428 (2.7). Found: C, 50.90; H, 5.99; N, 2.08. Calc. for $C_{59}H_{78}O_{35}N_2 \cdot 1H_2O$: C, 50.86; H, 5.79; N, 2.01. 6-*O*-isomer: (123.4 mg, 0.090 mmol, 2.9%), t_R = 23.4 min; ^{13}C NMR [$(CD_3)_2SO$] δ 60.4, 69.8, 71.1, 71.8, 72.6, 72.7, 73.5, 82.0, 82.3, 102.5, 103.0, 110.5, 110.7, 116.0, 122.6, 126.0, 126.1, 130.6, 130.9, 131.0, 131.1, 131.2, 131.9, 131.3, 131.7, 135.2, 135.4, 142.1; UV $\lambda_{max}(H_2O)$/nm 363 (log ε 2.9), 381 (3.1), 395 (3.0), 418 (3.0). Found: C, 50.55; H, 5.81; N, 1.98. Calc. for $C_{59}H_{78}O_{35}N_2 \cdot 1H_2O$: C, 50.86; H, 5.79; N, 2.01%.

9,10-Dicyanoanthracene-2-sulfonic acid, potassium salt (4)

This compound was prepared using the procedure for 9,10-dicyanoanthracene-2,6-disulfonic acid.[8] ^1H NMR [$(CD_3)_2SO$] δ 8.00 (2 H, m, 6,7-H), 8.13 (1 H, d, $J_{3,4}$ 7.8 Hz, 3-H), 8.44 (3 H, m, 4,5,8-H), 8.62 (1 H, s, 1-H); ^{13}C NMR [$(CD_3)_2SO$] δ 110.6, 111.4, 115.8, 121.2, 125.7, 125.9, 128.9, 130.7, 131.2, 131.4, 131.6, 131.7, 149.3. Found: C, 55.39; H, 1.87; N, 8.07. Calc. for $C_{16}H_7N_2SO_3K$: C, 55.48; H, 2.04; N, 8.09%.

Results

The synthesis of 2-bromomethyl-9,10-dicyanoanthracene, necessary for the attachment of the dicyanoanthracene group to the β-CD, was accomplished through cyanation of 9,10-dibromo-2-methylanthracene followed by benzylic bromination. Reaction of the mono sodium salt of β-CD and the bromomethyl DCA derivative according to the method of D'Souza[13] gave a 3:1 ratio of the 6-*O*- and 2-*O*-derivatives, which were separated by preparative HPLC. The two regioisomers were assigned on the basis of their ^{13}C NMR spectra.[14] Alkyl substitution at a glucose C2-OH in β-CD gives rise to a downfield shift for C2 (relative to the C2 resonance in β-CD), and upfield shifts for the neighbouring C1 and C4, whereas substitution at a C6-OH gives rise to downfield shifts for C6 and C1 and an upfield shift for C5.[15] The observed chemical shift differences for the carbons in the affected glucose unit are given in Table 1.

The binding properties of **1** and **2** and several aromatic sulfonate guests were elucidated by fluorescence quenching studies. The absorption properties of the DCA moiety allowed

Table 2 Stern–Volmer and binding constants of several aromatic sulfonates with β-CD, **1**, **2** and **3**

	Stern–Volmer constants[a]					Binding constants[a]			
Quencher/guest	**1**	**2**	**3**	**4**	**5**	β-CD	**1**[e]	**2**[e]	**3**[f]
6	540	320	280	120	60	110	430	200	160
	(110)[b]	(120)	—				(20)[d]	(38)	(43)
7	3 700[c]	2 000	480	230	180	1 300	3 240	1 710	250
	(460)	(290)	—				(12)	(14)	(48)
8	750	620	250	240	130	360	490	360	10
	(260)	(260)	—				(35)	(42)	(96)
9	12 000	4 400	—	1 200	640	3 500	9 200	2 800	—
	(2 800)	(1 600)					(23)	(36)	
10	5 200	4 200	—	320	190	2 900	4 020	3 020	—
	(1 180)	(1 180)					(23)	(28)	

[a] In $dm^3\ mol^{-1}$. [b] Numbers in parentheses are the apparent Stern–Volmer constants in the presence of AD–CO_2^-. [c] ± 600, the standard deviation and/or linear regression errors of all other values are less than 10%. [d] Numbers in parentheses are the percentage dynamic component. [e] Subtracting the K_{SV} term from AD–CO_2^- competition results. [f] Subtracting the K_{SV} term from **4**.

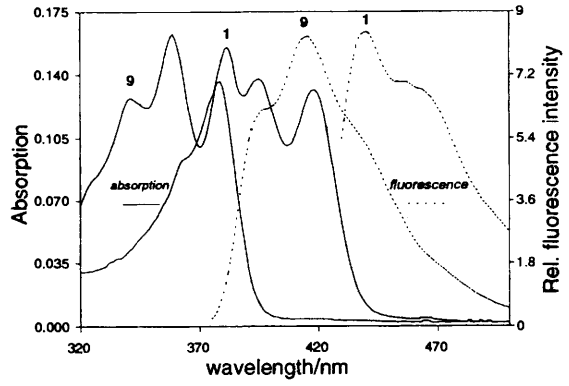

Fig. 2 Absorption and fluorescence spectra of **1** and **9**

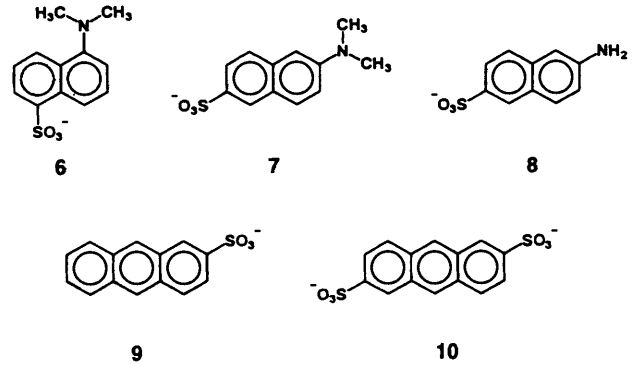

Fig. 3 Quencher/guest structures

for selective excitation of the host even in the presence of the anthracene sulfonates (Fig. 2).

Apparent Stern–Volmer (SV) quenching constants for **1** and **2** were obtained by titrating the DCA fluorescence with added guests **6**–**10**, plotting $(I_o - I)/I$ *vs.* [guest], where I_o is the intensity in the absence of added agents, and determining the slopes through linear regression. The titrations were repeated in the presence of AD–CO_2^-. Association constants between β-CD and guests **6**–**10** were determined by titrating the guest fluorescence with β-CD, plotting $(I - I_o)/[\beta\text{-CD}]$ *vs.* I, and determining the slopes through linear regression. The association constant is the absolute value of the slope. Stern–Volmer constants also were determined for **4** and **5**. The Stern–Volmer and the association constants are reported in Table 2.

The fluorescence quenching results were interpreted within a simple model system where guest molecules quench the host fluorescence through random encounters (dynamic quenching) or through complexation (static quenching). If quenching in the complex is nearly complete, then the observed fluorescence derives only from the unoccupied host fluorophores which suffer quenching by random encounters with the free guest. The unoccupied host concentration depends upon its binding affinity with the guest as well as the host and guest concentrations. The Stern–Volmer relationship for a system with dynamic and static quenching components has been derived previously,[16] and is shown in eqn. (1).

$$\frac{I_o - I}{I} = [Q]\cdot(K + K_{SV} + K\cdot K_{SV}\cdot[Q]) \qquad (1)$$

The above expression assumes low absorption (< 0.1) and irradiation at an isosbestic point for the host fluorophore and its complex with Q (guest/quencher). The limiting slope as [Q] approaches zero is the sum of the binding constant (K) and the dynamic Stern–Volmer constant ($K_{SV} = \tau_f\cdot k_q$, where τ_f is the fluorescent lifetime of the fluorophore in the absence of Q and k_q is the rate constant for solution quenching).

The binding constant was estimated by determining the K_{SV} (dynamic) term and subtracting it from the apparent Stern–Volmer constant (Table 2). Four approximations of K_{SV} were obtained: Stern–Volmer constants for two related DCA derivatives, **4** and **5**, and Stern–Volmer constants for **1** and **2** in the presence of AD–CO_2^- (Table 2).

Discussion

The Williamson ether synthesis technique was successful in attaching the dicyanoanthracene moiety to β-CD, albeit in low isolated yield and as a mixture of 6-*O*- and 2-*O*-regioisomers. D'Souza[14] has shown this method to be effective for the regioselective substitution at the 2-*O*-position, as it relies on the greater acidity of the C2-OH than either the C3 or C6-OH. The electron-deficient nature of the DCA group is likely responsible for the non-selectivity, and we are currently investigating the origin of this discrepancy.

Fluorescence quenching studies were used to determine which host provided for optimal guest binding. The guests used in this assay are water-soluble; they possess large hydrophobic surface areas and bind strongly to β-CD; they orient longitudinally in the CD cavity with the sulfonate group extending from the secondary face;[17] and they are able to quench the excited DCA moiety *via* electron transfer.[18] Binding constants were extracted from the apparent Stern–Volmer constants by subtracting an estimated value for the dynamic quenching component.

Four estimates of the dynamic quenching component were determined: two by competition with a non-quenching, strongly-bound guest (AD–CO_2^-), and two from water-soluble DCA sulfonates. AD–CO_2^- has a high binding affinity for

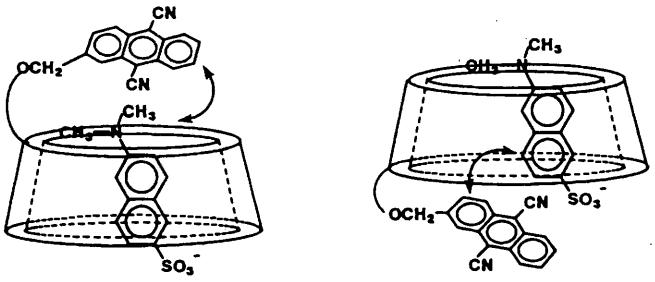

Fig. 4 Hydrophobic stabilization in DCA-tethers

β-CD (K = 40 000[19] at 25 °C, pH 7.2), and probably a higher affinity for **1** or **2**. The presence of a sufficient concentration of AD–CO_2^- results in complete consumption of the fluorophore as a complex with AD–CO_2^-, and the DCA moiety will be quenched only by random encounters. The DCA sulfonates do not possess a binding site, and therefore quenching occurs only *via* dynamic encounters. The DCA sulfonates also differ from **1** and **2** with respect to their electronic structures, which are altered by the sulfonate group(s), and their charge (anion and dianion *vs.* neutral).

The Stern–Volmer constants in Table 2 reveal several interesting trends for the dynamic component models. First, the quenching constants with **4** are up to twice as large as those with **5**. Although these differences could be due to their differing LUMO energies, we believe that they arise from the greater electrostatic repulsion with **5** and the negatively-charged guests, all of which bear at least one sulfonate group. The quenching constants for **4** are very similar to those for **2** in the presence of AD–CO_2^-. The significant exception to this trend occurs with anthracene-2,6-disulfonate (**10**), where the quenching rate is much lower with **4**. Again, this difference can be explained in terms of the greater electrostatic repulsion between an anion (**4**) and dianion (**5**) than between two anions. The quenching constants for **1** and **2** under competitive binding conditions are nearly identical with **6**, **8** and **10**, but not with **7** and **9**, where **1** provides greater K_{SV} constants. Because the AD–CO_2^--filled β-CD portion is, in one sense, a large substituent on the DCA moiety, the K_{SV} terms for (**1**)·(AD–CO_2^-) and (**2**)·(AD–CO_2^-) should be similar. Several explanations for the quenching behaviour with **7** and **9** are possible. The argument that AD–CO_2^- may not completely inhibit the formation of the fluorophore/quencher complex is unlikely because AD–CO_2^- probably binds more strongly than either **7** or **9** (*vide supra*), and because the Stern–Volmer constant in the presence of 0.88 mM AD–CO_2^- (×4 increase) is unchanged in the case of **1** with **9**. Given that **9** forms a 2:2 complex with β-CD[20] and that AD–CO_2^- forms a 2:1 complex with β-CD,[21] we propose that **9** (and likewise **7**) forms a ternary structure with (**1**)·(AD–CO_2^-). The greater K_{SV} term for **1** with AD–CO_2^- is due to the added static component of the ternary complex. This hypothesis is being investigated currently. Because of the constancy of the K_{SV} terms for (**2**)·(AD–CO_2^-), they seem to offer the most reasonable estimate for the dynamic quenching component.

The estimated binding constants in Table 2 show a clear trend. **1** Binds **6** 2.1-fold, **7** 1.8 fold, **8** 1.3-fold, **9** 3.3-fold and **10** 1.3-fold more strongly than **2**. **1** Binds **6** 3.9-fold, **7** 2.5-fold, **8** 1.3-fold, **9** 2.6-fold and **10** 1.3-fold more strongly than β-CD. The greater binding strengths of **1** is ascribed to the greater hydrophobic stabilization resulting from the axial orientation and directional inclusion from the 2° face of the guests (Fig. 4). The binding strengths of **1** and **2** do not differ greatly with poorly bound guests and with **10** which places hydrophilic sulfonate groups at either end of the CD cavity thereby minimizing any added hydrophobic stabilization.

The binding data also reveal significant differences between the DCA-tethered β-CD and the DCA-capped β-CD. **2** Binds nearly as well as β-CD, and much better than **3**. These results are interpreted by considering the cap or tether as a perturbation on the β-CD structure. The perturbation can alter the potential energy of the unbound host and/or the host–guest complex. If the appended group 'pushes out' internal water molecules in the free host, then the potential energy of the free host is lowered and the binding constant becomes smaller.[22] On the other hand, if the appended groups prevent full penetration of the guest, then the potential energy of the complex increases, also resulting in poorer binding. Because of the long span of the DCA moiety, disruption of internal waters is small in **1**, but larger in **2** since the 2° face is wider. The poor binding ability of the **3** likely derives from poor guest penetration. Inoue and co-workers have reached similar conclusions with diphenylmethane and diphenyl ether caps.[22]

Conclusions

The synthesis of two regioisomeric DCA-tethered β-CDs has been carried out. Several aromatic guests bind strongly with these hosts resulting in static quenching of the DCA fluorescence. Quenching data from **4** and from competitive binding with AD–CO_2^- can be used to extract binding constants from the apparent Stern–Volmer constants. **1** Binds guests more strongly than **2**, which binds as strongly as β-CD. **1**, **2** And β-CD bind more strongly than does **3**. Dynamic quenching of the unbound host with guests accounts for at least 10% of the apparent Stern–Volmer constant, and may be a factor in using these hosts to control reactions resulting from photoinduced electron transfer. Of the three DCA-derivatized β-CDs, the C6-tether is the best candidate for study as an electron-transfer photosensitizer. We are currently investigating other structures with the hopes of maximizing the ratio of binding to dynamic quenching.

Acknowledgements

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