Dansylated resorcinarenes

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Received (in Montpellier, France) 30th October 2006, Accepted 4th January 2007
First published as an Advance Article on the web 25th January 2007
DOI: 10.1039/b615772f

The synthesis, X-ray crystal structures and spectroscopic characterization (UV-Vis absorption and fluorescence emission) of regioselective tetradansylated resorcinarene **2** and octadansylated resorcinarene **3** are described. In solution, the resorcinarene backbone of **2** shows a boat conformation with C_{2v} symmetry, while the octasubstituted **3** shows at room temperature a time-averaged C_{4v} symmetry, which turns into stable boat conformation at low temperatures. The four hydroxyl groups of **2**, not present in **3**, form hydrogen bonds to the sulfoxide oxygens of the dansyl moieties and stabilize the C_{2v} conformation in solution. The X-ray crystal structures of **2** and **3** confirm the C_{2v} symmetry of both compounds in the crystalline state and revealed that the tetradansyl resorcinarene has two rather strong intramolecular O–H···O=S hydrogen bonds. In addition **2** forms a directly hydrogen-bonded dimeric assembly *via* four intermolecular O–H···O and O–H···O=S hydrogen bonds. In the solid state both **2** and **3** exhibit a multitude of intra- and intermolecular π–π interactions between the adjacent dansyl moieties and also with the aromatic parts of the macrocyclic skeleton. The absorption and fluorescence spectra of **2** and **3**, together with a reference compound, dansylphenolate **4**, were recorded. In chloroform, with the same dansyl concentration and absorption at excitation wavelength, fluorescence from **4** was clearly stronger than that from either **2** or **3**, an indication of excited-state dansyl–dansyl interactions in the dansyl substituted resorcinarenes. The absorption and emission bands of the dansyl units were gradually substituted by the absorption and emission bands of the protonated dansyl units when **2** and **3** were titrated with trifluoroacetic acid.

Introduction

Resorcinarenes,[1] are suitable building blocks of various supramolecular structures such as open inclusion complexes,[2] dimeric,[3] and hexameric,[4] capsules as well as nanotubes.[5] Alkylation and acylation of the resorcinarene hydroxyl groups have been used for the synthesis of cavitands, carcerands, hemicarcerands, and velcrands.[6] Resorcinarenes can be completely acylated and alkylated to esters and ethers,[7] and regioselectively acylated *via* partial acylation by using ester functions as protecting groups.[8] The cyclic array of hydrogen bonds does not exist in hydroxyl group persubstituted resorcinarenes and usually these molecules undergo a conformational change from crown (C_{4v}) to boat (C_{2v}).[9]

The photochemistry of the dansyl group and its interactions with cations and anions as well as its function as a light harvesting chromophore has been reported for several molecules such as calixarenes,[10] crown ethers,[11] dendrimers,[12] and cyclodextrins.[13] The dansyl substituent when covalently bound to a host molecule shows intense absorption bands in the near UV and a strong fluorescence in the visible region and is extensively used for sensing and labeling of proteins and macromolecules.[14] To the best of our knowledge, the spectroscopic characterization of the dansyl substituted resorcinarenes have not been reported. Here we report the synthesis and X-ray structures, supplemented by spectroscopic characterization (UV-Vis absorption and fluorescence emission) in solution, of tetradansyl resorcinarene **2** and octadansyl resorcinarene **3** in comparison to the monodansyl reference compound, dansyl phenolate **4**.

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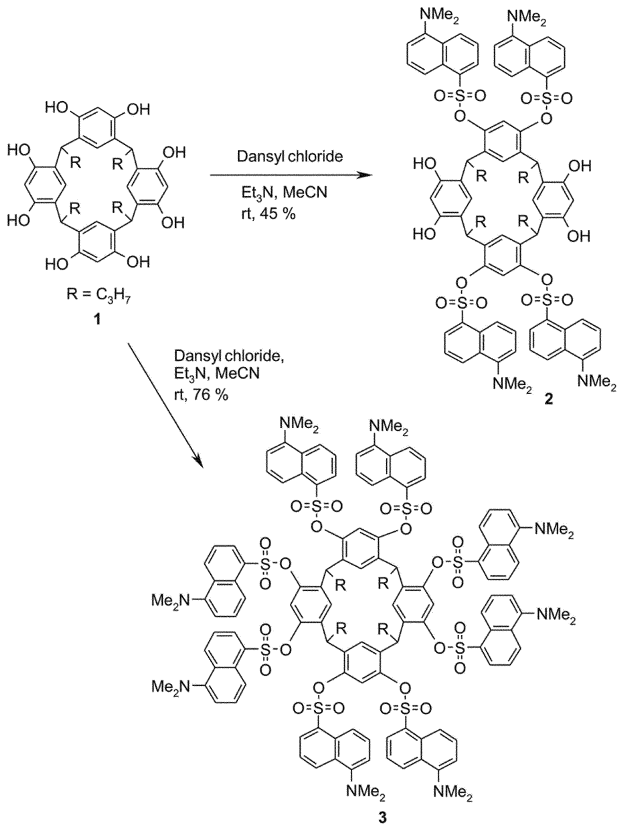
Results and discussion

Synthesis and NMR investigations

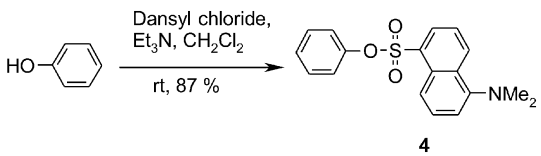
The reaction of resorcinarene **1** with dansyl chloride in acetonitrile (MeCN) in the presence of triethylamine (Et_3N) as base (1 : 4 : 4 molar ratio) resulted in tetradansylated resorcinarene **2** in moderate 45% yield. Corresponding reaction with equimolar amounts of the reagents per hydroxyl group (1 : 8 : 8; **1**–dansyl chloride–Et_3N) resulted in complete dansylation of resorcinarene **1** to give octadansylated resorcinarene **3** in 76% yield (Scheme 1).

As a reference for the spectroscopic characterizations of **2** and **3**, a model compound was prepared by the base-catalyzed acylation of phenol with dansyl chloride in CH_2Cl_2 giving dansyl phenolate **4** which was purified by column chromatography (Scheme 2).

The structure and composition of resorcinarenes **2** and **3**, as well as reference compound **4**, were confirmed by NMR



Scheme 1 Partial and complete dansylation of resorcinarene **1** by dansyl chloride.



Scheme 2 Synthesis of dansyl phenolate **4**.

spectroscopy, mass spectrometry, X-ray crystallography and elemental analysis. The ^{1}H NMR spectrum of resorcinarene **2** in acetone-d_6 at 303 K (Fig. 1) contains a doublet of doublets corresponding to the methine protons. The splitting of the signal is due to the coupling with the diastereotopic protons of the neighboring methylene groups that appear in turn as two well-separated multiplets. Also, the protons of the methylene groups more remote from the methine carbons appear as two well-separated multiplets. In addition, the spectrum of **2** contains a singlet for the methyl groups of the dansyl, four singlets for the aromatic protons of the resorcinol rings indicating the boat conformation, one singlet for the free OH-groups and four doublets and two overlapping triplets for the aromatic protons of the dansyl groups. This spectrum is in line with structure **2** as shown in Scheme 1 and indicates a C_{2v}-symmetric conformation of the resorcinarene skeleton. The resorcinarene skeleton of **2** contains four hydroxyl groups that can form hydrogen bonds to the sulfoxide groups of the dansyls and stabilize the boat conformation in solution at room temperature (Fig. 1). The ESI-TOF mass spectrum

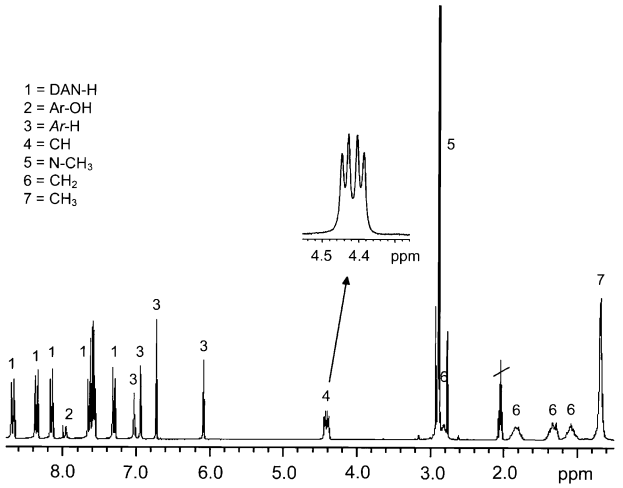


Fig. 1 ^{1}H NMR spectrum of resorcinarene **2** in acetone-d_6 at 303 K. Four singlets of the aromatic protons of resorcinol rings indicate a C_{2v}-symmetric conformation. Coupling with the diastereotopic protons of the methylene group causes the doublet of doublet for the methine protons. DAN stands for dansyl.

showed a major peak at m/z 1612.78 corresponding to the sodium adduct of **2**.

The ^{1}H NMR spectrum of the persubstituted octadansyl **3** (Fig. 2) in $CDCl_3$ at 323 K shows one sharp and one broad (at 6.5 ppm) overlapping signals for the aromatic protons of the resorcinarene skeleton. This is due to a fast dynamics of the resorcinarene skeleton resulting in a spectrum consistent with time-averaged C_{4v} symmetry. The dynamics is verified at 243 K where this signal splits into four separate peaks indicating the formation of the rigid C_{2v} boat conformation (Fig. 2). The ESI-TOF mass spectrum showed a major peak at m/z 2546.40 corresponding to the sodium adduct of **3**.

X-Ray crystal structures

The tetradansylated resorcinarene **2** crystallizes in a boat conformation (Fig. 3). Due to the bulky dansyl groups the position of the free hydroxyl groups is too far away from the adjacent resorcinol oxygens to allow intramolecular hydrogen bonding that are usually required for the crown conformation. Instead two intramolecular hydrogen bonds are formed to sulfonyl oxygens (S=O···O distances 2.781(9) and 2.798(8) Å, Fig. 3, top). The resorcinol rings containing unsubstituted hydroxyl groups are almost parallel (4.2° dihedral angle and 4.9 Å centroid-to-centroid distance) while the sulfonylated rings are nearly coplanar (172.7° dihedral angle between the resorcinol rings).

All four dansyl groups are in a propeller-like orientation beside the core resorcinarene leaving enough space for intermolecular hydrogen bonds. Indeed, two molecules of **2** form directly hydrogen bonded dimeric assemblies where two out of four intermolecular hydrogen bonds form between opposing hydroxyl groups (O···O distance 2.802(9) Å) and the other two are between opposing sulfonyl oxygen and hydroxyl groups (S=O···O distance 2.874(8) Å, Fig. 3, bottom). Due to the boat conformation, the cavity of the resorcinarene is

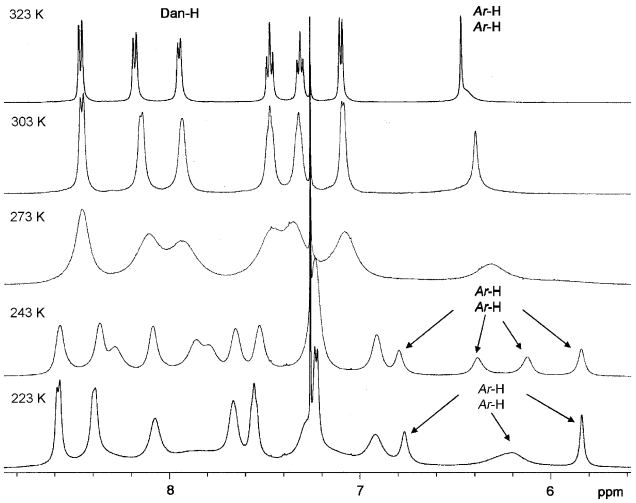


Fig. 2 ^{1}H NMR spectrum of resorcinarene **3** in $CDCl_3$ at different temperatures. At 323 K the compound shows two overlapping signals for the aromatic protons which broaden as the temperature is reduced and finally splits into four singlets at 243 K to confirm a C_{2v} symmetry conformation. The single peak at higher temperatures can be explained as a result of the fast dynamics resulting in the time-average C_{4v} symmetry.

very small and there is no room for a possible guest molecule inside the dimeric assembly.

In the structure **2** intramolecular edge-to-face π–π interactions show close proximity of the dansyl group and aromatic resorcinol rings of the resorcinarene skeleton. The shortest carbon to ring centre distance between carbons of resorcinol rings and dansyl moieties are 3.65 and 3.84 Å. Unlike in octadansyl resorcinarene **3** (see below) the dansyl groups in **2** are not packed close to each other, hence no intramolecular π–π interactions were detected between dansyl groups. However, in solution the π–π interactions of the dansyl groups affect the photoactive properties of both **2** and **3** by quenching of the fluorescence of the dansyl group (below).

As in **2**, the octadansylated resorcinarene **3** with a twofold crystallographic symmetry also assumes a boat conformation in the solid state (Fig. 4, top) because there are no possibilities for intramolecular hydrogen bonds and due to the arrangement of the bulky dansyl groups. The boat conformation is described by the dihedral angles between opposite resorcinol rings, which are 1.6 and 144.3° and the distances between the parallel resorcinol ring centers, 5.03 Å. In this case bulky dansyl moieties are bent beside and above of the upper part of the resorcinarene skeleton covering half of the molecule. Due to the spatial proximity, the dansyl groups show intramolecular π–π interactions with each other and with the resorcinol rings. One acetonitrile molecule is located at the lower rim between the four hydrophobic alkyl chains and its nitrogen atom is pointing towards the interior of the alkyl chain cage. Similar inclusions of a solvent molecule or an anion at the lower rim have been reported earlier for numerous resorcinarene crystal structures.[3,15]

Reference compound **4** gave suitable single crystals for X-ray analysis from propanol–CH_2Cl_2 solution (Fig. 4, bottom). Also in this case the π–π interactions affect the crystal packing. The phenyl group of the molecule is offset face-to-face stacked with the phenyl group of another nearby molecule, the distance between the centre of the aromatic ring and the nearest carbon atom of the adjacent group being 3.54 Å. In addition the phenyl group is edge-to-face stacked with aromatic part of the dansyl group of the same nearby molecule, the shortest distance between the carbon of the phenyl group and the centroid of the dansyl part being 3.95 Å. Two CH···O═S hydrogen bonds are detected between the methyl hydrogens of the amine and oxygens of the sulfonyl group [distance 3.141(3) Å] (Fig. 4, bottom right).

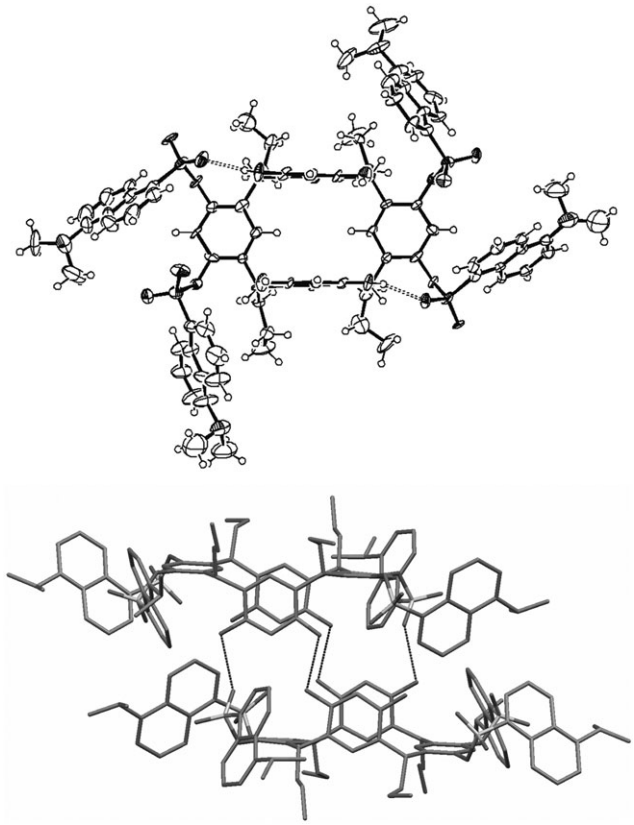


Fig. 3 ORTEP-plot (top) presentation of X-ray crystal structure of tetra-substituted resorcinarene **2**. Dimeric assembly of **2** (bottom). Intermolecular hydrogen bonds are shown as dotted lines and hydrogen atoms are omitted for clarity. Solvent molecules are omitted for clarity.

Absorption and fluorescence properties

The absorption and fluorescence spectra in chloroform with the same dansyl concentrations for **2**, **3** and **4** are shown in Fig. 5. The reference compound **4** in chloroform exhibits intense absorption bands in the near UV spectral region (λ_{max} = 350 nm) and a strong fluorescence band in the visible region (λ_{max} = 514 nm) where also the respective bands of resorcinarene **3** were observed, *i.e.* no spectral shifts were observed in the absorption and fluorescence bands between the resorcinarene **3** and reference compound **4**. The absorption and fluorescence bands of resorcinarene **2** are however slightly redshifted.

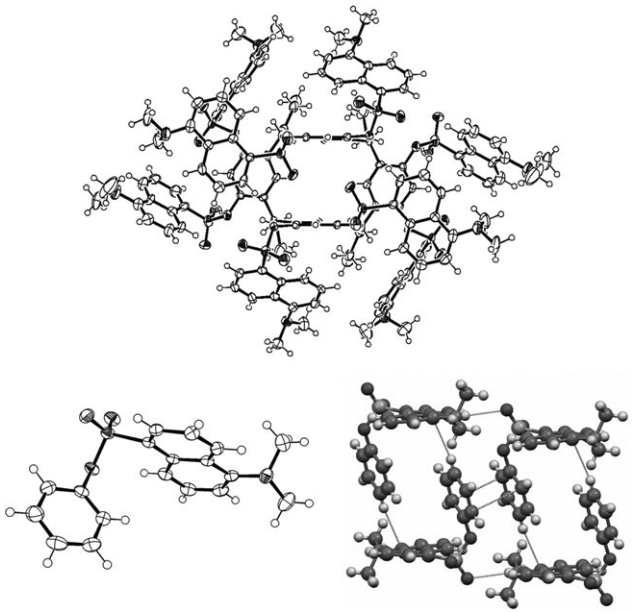


Fig. 4 Top view of the X-ray crystal structure of completely dansylated resorcinarene **3** (ORTEP-plot, presentation). ORTEP-plot of the X-ray crystal structure of reference compound **4** (bottom left) and crystal packing showing the C–H···π and π–π interactions and C–H···O═S hydrogen bonds (bottom right). All solvent molecules are omitted for clarity.

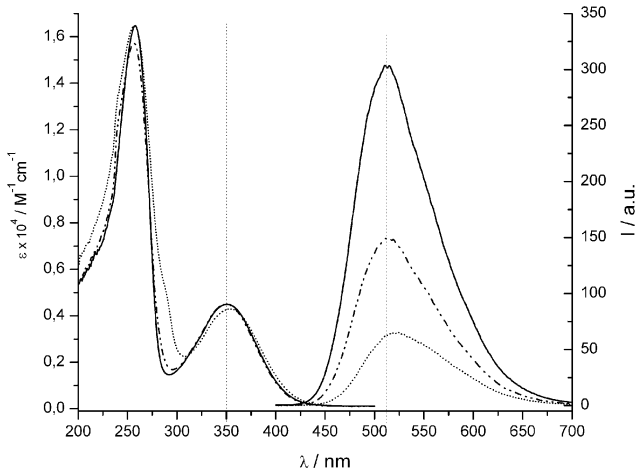


Fig. 5 Absorption and fluorescence spectra (λ_{exc} = 350 nm) of resorcinarene **2** (··· at 2.5 × 10^{-5} mol L^{-1}), **3** (· ·– at 1.25 × 10^{-5} mol L^{-1}) and **4** (— at 1.0 × 10^{-4} mol L^{-1}) in chloroform.

The fluorescence intensity of the reference compound **4** is clearly higher than that of the resorcinarene derivatives **2** and **3**. The intermolecular hydrogen bonding involving the sulfonic oxygen of the dansyl group and the hydroxyl groups of the resorcinarene core might have a role to play in the slight redshifting and reduced fluorescence emission of the resorcinarene **2** given that the dansyl concentration are the same as in resorcinarene **3**. The fact that the monosubstituted dansyl phenolate **4** shows about two times stronger fluorescence (scaled to same absorbance and same dansyl concentrations in solution) than the multisubstituted resorcinarenes **3** suggests strong intramolecular excited-state interactions taking place in the resorcinarene core. Quenching of fluorescence in dansyl resorcinarenes may be due to the efficient couplings of the exited singlet states to the low-frequency vibrational modes of the resorcinarene structures.[16] A more probable explanation is the excited-state energy transfer between the dansyls of the resorcinarenes resulting in reduced emission.[10a] These processes were not studied here, but will be the focus of a subsequent study using femtosecond fluorescence spectroscopy.

It is known that the absorption and fluorescence properties of the dansyl group are very sensitive to acid because of the protonation of the nitrogen in the dansyl unit at low pH.[10a,12,17] Upon addition of trifluoroacetic acid, the absorption of compounds **2**, **3** and **4** (at 260 and 350 nm) decreases continuously. A new absorption peak appears at 288 nm with a shoulder at 323 nm which gains intensity with addition of the acid. These new absorption peaks correspond to the protonated dansyl unit. Two isosbestic points observed at 270 and 313 nm indicate an A to B transformation of dansyls to protonated dansyls. The behavior is similar to that Valeur *et al.*[10a] observed with dansylated calixarenes and Vögtle *et al.*[12] with dansylated dendrimers. Different fluorescence measurements of the acid titration of compounds **2**, **3** and **4** were done with excitation at λ_{exc} = 350 nm (λ_{max}), and λ_{exc} = 313 nm (isosbestic point). The fluorescence of all the compounds with both excitation wavelengths decreases with an increase in trifluoroacetic acid concentration. The decrease in the fluorescence emission of the compounds with excitation at the isosbestic point is proof that the protonation of the dansyl group is responsible for this behaviour. The absorption and fluorescent spectra of the acid titration of resorcinarene **3** in chloroform are shown in Fig. 6.

The solubility limitations of the resorcinarenes (not soluble in polar solvents) limit their potential applications as sensors. Vögtle *et al.*[12] reported a study on dendrimers where the energy transfer occurred from dansyl units to the eosin dye. The resorcinarenes are not capable of complexing the eosin dyes due to the large size of the eosin dyes and the lack of electron donor atoms in the resorcinarene skeleton. Resorcinarenes are, however, known to complex tetraalkylammonium ions.[15c] The effect of this complexation in the fluorescence emission of the octadansylated resorcinarene **3** was investigated by titrating tetramethylammonium bromide in water with the resorcinarene **3** in chloroform. The formed complex is more soluble in chloroform than the free octadansyl resorcinarene **3** and the complexation has an effect on the photophysics of the dansyl groups. The non-polar wet chloroform layer was then measured. The addition of the tetramethylammonium bromide had no influence on the absorption behaviour but the fluorescence intensity shows a concentration dependent decrease with increasing tetramethylammonium bromide concentration as shown in Fig. 7.

Conclusion

The dansylation of resorcinarene **1** resulted in partially and completely substituted resorcinarenes **2** and **3** depending on

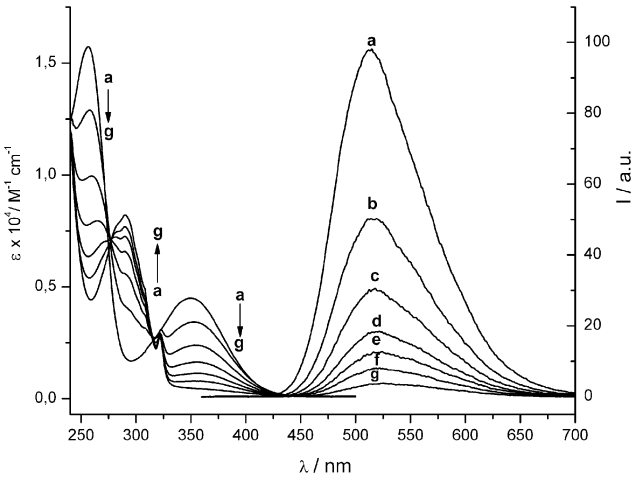


Fig. 6 Absorption and fluorescent titration of resorcinarene **3** with trifluoroacetic (TFA) acid in chloroform, [**3**] = 1.25×10^{-5} mol L^{-1}, [TFA] = 1.0×10^{-3} mol L^{-1}, λ_{exc} = 313 nm (isosbestic point). From a–g: 0, 0.8, 1.6, 2.4, 3.2, 4.0, 6.0, 8.0 equiv.

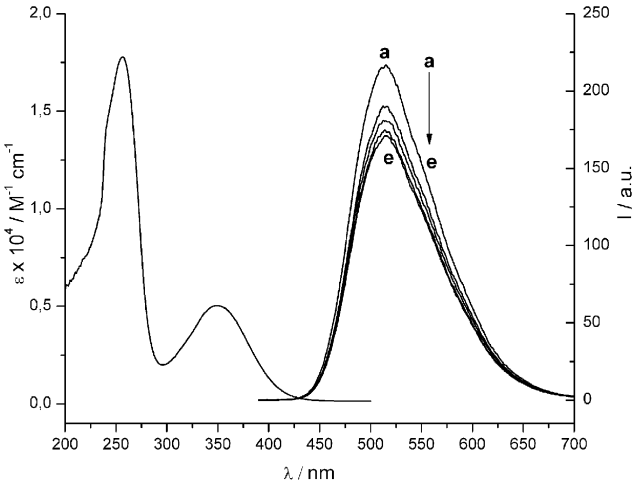


Fig. 7 Absorption and fluorescent titration of octadansylated resorcinarene **3** in chloroform with trimethylammonium bromide (TMA-Br) in H_2O, [**3**] = 1.25×10^{-5} mol L^{-1}, [TMA-Br] = 1.0×10^{-3} mol L^{-1}, λ_{exc} = 350 nm (λ_{max}). From a–e: 0, 0.8, 1.6, 3.2, 4.0 equiv.

the ratio of the used starting compounds; resorcinarene, dansyl chloride and the base. Resorcinarene **2** adopts a boat conformation in solution and in solid state while resorcinarene **3** adopts a time-averaged C_{4v} symmetry due to fast dynamics of the resorcinarene skeleton at room temperature in solution that stabilizes to rigid C_{2v} symmetry at low temperatures and in the solid state. The relative fluorescence intensity increases with the increase in number of dansyl units in the resorcinarenes but is clearly less than the intensity of the reference compound **4**. This indicates excited state interactions of the dansyl groups in **2** and **3** resulting in quenching of the fluorescence. Direct conversion of the dansyl to the protonated form was observed on acid titration with trifluoroacetic acid leading to a decrease in the absorption and fluorescence spectra of all the compounds. Complexation of tetramethylammonium bromide had a slight effect on the fluorescence but not on the absorption behaviour of octadansylated resorcinarene **3**.

Experimental

General remarks

Melting points were determined with a Mettler Toledo FP62 capillary melting point apparatus and are uncorrected. Elemental analyses were carried out with a Varian ELIII elemental analyzer. Absorbance measurements were performed using a CARY 100 Conc. (UV-visible) Spectrophotometer and a PERKIN ELMER LS 50 B Luminescence Spectrometer for fluorescence measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C assignments were mainly based on HMQC and HMBC 2D correlation spectra. All signals are expressed as δ values in ppm using residual solvent signal as internal standard. *J* values are given in Hz. The mass spectra were carried out with a Micromass LCT ESI-TOF mass spectrometer and VG Auto Spec. EI (Electron Impact) ion source spectrometer.

Synthesis

Tetradansylated resorcinarene 2. To a solution of resorcinarene **1** (0.53 g, 0.81 mmol) in MeCN (20 ml), Et_3N (0.45 ml, 3.24 mmol) was added in one portion with vigorous stirring. A pink precipitate formed and the reaction mixture was stirred for 15 min. A solution of dansyl chloride (0.88 g, 3.24 mmol) in MeCN (25 ml) was added to the suspension in one portion and the reaction mixture was vigorously stirred to facilitate dissolution of the precipitate. The reaction mixture was stirred at room temperature for 72 h. The precipitate formed was filtered off, washed with MeCN (30 ml) and water (50 ml). The crude product was purified by column chromatography on silica using chloroform as eluent to give resorcinarene **2** (0.58 g, 45%) as a yellowish powder: mp 236 °C (Found C, 64.76, H, 5.78, N, 3.57. $C_{88}H_{92}N_4O_{16}S_4 \cdot 2H_2O$ requires C, 65.00, H, 5.95, N, 3.45%); λ_{max} ($CHCl_3$)/nm 260 (ε/M^{-1} cm^{-1} 16 500), 352 (4200); δ_H (500 MHz, acetone-d_6, Me_4Si, 30 °C) 0.69 (12 H, br, CH_2CH_3), 1.11 (4 H, m, CH_2CH_3), 1.34, (4 H, m, CH_2CH_3), 1.83 (4 H, m, $CHCH_2$), 2.76 (4 H, m, $CHCH_2$), 2.90 (24 H, s, $N(CH_3)_2$), 4.42 (4 H, dd, *J* 4.5 and 6.0, $CHCH_2$), 6.08 (2 H, s, Ar-*H*), 6.72 (2 H, s, Ar-*H*), 6.93 (2 H, s, Ar-*H*), 7.02 (2 H, s, Ar-*H*), 7.32 (4 H, d, *J* 7.25, Dan-*H*), 7.61 (8 H, m, Dan-*H*), 7.96 (4 H, br, s, Ar-O*H*), 8.15 (4 H, d, *J* 6.0, Dan-*H*), 8.36 (4 H, d, *J* 8.75, Dan-*H*), and 8.69 (4 H, d, *J* 8.5, Dan-*H*); δ_C (126 MHz, acetone-d_6, Me_4Si, 30 °C,) 14.4 (s), 21.7 (s), 36.1 (s), 38.05 (s), 45.7 (s), 114.2 (s), 116.7 (s), 119.7 (s), 120.4 (s), 124.4 (s), 126.6 (s), 129.5 (s), 129.8 (s), 130.8 (d), 131.3 (s), 132.8 (s), 133.6 (s), 138.6 (s), 145.9 (s), 153.0 (s) and 155.0 (d); *m*/*z* (ESI-TOF) 1590.80 $[M + H]^+$ (10%), 1612.78 $[M + Na]^+$ (100), 1628.17 $[M + K]^+$ (60).

Octadansylated resorcinarene 3. To a solution of resorcinarene **1** (0.15 g, 0.23 mmol) in MeCN (10 ml), Et_3N (0.26 ml, 1.85 mmol) was added in one portion with vigorous stirring.

A pink precipitate formed and the reaction mixture was stirred for 15 min. A solution of dansyl chloride (0.5 g, 1.85 mmol) in MeCN (20 ml) was added to the suspension in one portion and the reaction mixture was intensively stirred to facilitate dissolution of the precipitate. The reaction mixture was stirred at room temperature for 24 h. The precipitate formed was filtered off, washed with MeCN (30 ml) and water (50 ml). The crude product was purified by recrystallization from MeCN–CH_2Cl_2 (5 : 1). The precipitate was filtered off and dried to give resorcinarene **3** (0.44 g, 76%) as a yellowish powder: mp 242 °C (Found C, 63.89, H, 5.37, N, 4.18. $C_{136}H_{136}N_8O_{24}S_8 \cdot H_2O$ requires C, 64.28, H, 5.47, N, 4.41%); λ_{max} ($CHCl_3$)/nm 260 (ε/M^{-1} cm^{-1} 16 800), 350 (4600); δ_H (500 MHz, $CDCl_3$, Me_4Si, 30 °C) 0.54 (20 H, br s, CH_2CH_3), 1.35 (8 H, m, $CHCH_2$), 2.87 (48 H, s, $N(CH_3)_2$), 4.23 (4 H, t, *J* 7.4, $CHCH_2$), 6.39 (8 H, br, s, Ar-*H*), 7.11 (8 H, d, *J* 7.8, Dan-*H*), 7.32 (8 H, t, *J* 8.0, Dan-*H*), 7.46 (8 H, t, *J* 8.0, Dan-*H*), 7.90 (8 H, d, *J* 6.8, Dan-*H*), 8.08 (8 H, d, *J* 8.5, Dan-*H*), 8.48 and (8 H, d, *J* 8.5, Dan-*H*); δ_C (126 MHz, $CDCl_3$, Me_4Si, 30 °C,) 13.4 (s), 20.4 (s), 36.3 (d), 45.0 (s), 114.5 (s), 115.4 (s), 119.2 (s), 123.1 (s), 126.8 (s), 128.8 (s), 129.5 (s), 129.7 (s), 130.4 (s), 131.7 (s) 131.9 (s) and 157.3 (d); *m*/*z* (ESI-TOF) 2524.47 $[M + H]^+$ (30%), 2546.40 $[M + Na]^+$ (100), 2562.34 $[M + K]^+$ (15).

Dansyl phenolate 4. A solution of dansyl chloride (1.0 g, 3.7 mmol) and Et_3N (2.1 ml, 14.8 mmol) in CH_2Cl_2 (10 ml) was added to solution of phenol (0.12 g, 1.2 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 20 h and the solvent was evaporated. The crude product was purified by column chromatography on silica using dichloromethane–ethyl acetate–*n*-hexane (1.5 : 1.5 : 1, v/v) as eluent to give reference compound **4** (0.34 g, 87%) (Found C, 65.07, H, 5.26, N, 4.29. $C_{18}H_{17}NO_3S \cdot 0.25H_2O$ requires C, 65.14, H, 5.31, N, 4.22%); λ_{max} ($CHCl_3$)/nm 260 (ε/M^{-1} cm^{-1} 16 800), 350 (4600); δ_H (500 MHz, $CDCl_3$, Me_4Si, 30 °C) 2.91 (6 H, s, $N(CH_3)_2$), 6.88 (2 H, m, Ar-*H*), 7.20 (3 H, m, Ar-*H*), 7.28 (1 H, d, *J* 7.8, Dan-*H*), 7.46 (1 H, t, *J* 7.5, Dan-*H*), 7.69 (1 H, t, *J* 7.5, Dan-*H*), 8.05 (1 H, d, *J* 6.0, Dan-*H*), 8.43 (1 H, d, *J* 7.8, Dan-*H*) and 8.62 (1 H, d, *J* 6.5, Dan-*H*); δ_C (126 MHz, $CDCl_3$, Me_4Si, 30 °C) 45.8 (s), 116.2 (s), 119.8 (s), 122.6 (s), 123.5 (s), 127.6 (s), 129.6 (s), 130.1 (s), 130.4 (s), 130.6 (s), 131.6 (d), 132.6 (s), 150.4 (s) and 152.7 (s); *m*/*z* (EI) 327 (M^+, 25%), 186 (7), 170 (100), 127 (15).

X-Ray crystallography

The data for **2**, **3** and **4** were recorded with a Nonius Kappa CCD using graphite-monochromated Mo-Kα radiation [λ(Mo-Kα) = 0.71073 Å)] and a temperature of 173.0 ± 0.1 K. The CCD data were processed with Denzo-SMN v0.95.373.[18] All structures were solved by direct methods (SHELXS-97),[19] and refinements based on F^2, were made by full-matrix least-squares techniques (SHELXL-97).[20] No absorption correction was applied. The hydrogen atoms were calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. In the structure of **2** the *R*-values and esds for bond lengths and angles are rather poor due to weakly diffracting poor quality crystals and severe disorder of solvent molecules. Acetonitrile molecule (occupancy factor 0.5) and disordered chloroform (occupancy factors 0.5 : 0.5) were refined isotropically. No hydrogen was determined for disordered chloroform. The anisotropic displacement parameters of C75, C76, N18 and O62 were fixed (EADP) with the respective parameters of C63, C64, N6 and O41. An electron density 1.06 e $Å^{-1}$ was found 1.4 Å away from acetonitrile molecule (C91). Residual electron density that could be assigned to two severely disordered chloroforms and an acetonitrile molecule were removed by SQUEEZE,[21] since no chemically reasonable model could be built for them. In the structure of **3**, acetonitrile molecules were refined isotropically with population parameters of 0.5 and 0.25, respectively. Disordered propanol molecule with occupancy factors 0.5 : 0.5 was refined

Table 1 Crystal data for **2**, **3** and **4**

Compound	**2**	**3**	**4**
Formula	$C_{88}H_{92}N_4O_{16}S_4 \cdot CHCl_3 \cdot 0.5CH_3CN$	$C_{136}H_{136}N_8O_{24}S_8 \cdot CH_3(CH_2)_2OH \cdot 1.5CH_3CN$	$C_{18}H_{17}NO_3S$
M_r	1729.79	2644.69	327.39
Crystal size/mm	0.10 × 0.10 × 0.20	0.10 × 0.10 × 0.25	0.82 × 0.75 × 0.60
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
a/Å	16.2474(7)	29.3447(9)	8.2180(4)
b/Å	16.2674(7)	22.6903(5)	11.3823(4)
c/Å	20.5931(7)	22.2725(7)	17.5254(9)
α/°	83.540(3)	90	90
β/°	76.736(3)	109.033(1)	101.113(2)
γ/°	71.072(2)	90	90
V/Å^3	5006.9(3)	14 019.2(7)	1608.6(1)
Z	2	4	4
D_c/Mg m^{-3}	1.147	1.253	1.352
μ/mm^{-1}	0.234	0.199	0.216
F(000)	1816	5576	688
θ-range/°	3.69–24.45	2.94–24.50	2.97–26.00
Refl. collected/unique/R_{int}	31 628/16 391/0.141	22 643/11 601/ 0.153	5830/3141/0.0287
Refl. ($I > 2\sigma(I)$) used in refinement/parameters	6033/1040	5201/853	2330/210
Goodness-of-fit on F^2	1.024	1.044	1.047
R/R_w	0.127/0.338	0.091/0.2217	0.0399/0.0831
Largest diff. peak, hole/e Å^{-3}	1.058, –0.807	0.725, –0.330	0.190, –0.398

isotropically and hydrogen atom of the hydroxyl group was not determined. Other X-ray data are presented in Table 1.

CCDC reference numbers 606001–606003.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615772f

Acknowledgements

K. R. wishes to acknowledge TEKES and the Academy of Finland (TEKES, 40476/01, AF 63018); N. K. B. the Graduate School of Bioorganic and Medicinal Chemistry; J. A. the Graduate School LASKEMO; A. Å. and M. N. the Academy of Finland (Proj. 211240) for financial support. Dr Volker Böhmer and Dr Myroslav Vysotsky, University of Mainz, Germany, are kindly thanked for their help on the NMR analysis of the dansyl resorcinarenes.

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