Interaction of aminomethylated resorcinarenes with rhodamine B

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The interaction of aminomethylated resorcinarenes with a red xanthene dye, rhodamine B, was investigated in chloroform, methanol and chloroform–methanol solutions using UV-vis, NMR and fluorescence spectroscopy. Aminomethylated resorcinarenes **1** and **2** shift the rhodamine B equilibrium from the zwitterion to the lactone form unlike reference compounds **3** and **4**, which do not contain tertiary amino groups at the upper rim, giving an example of how supramolecular hosts can influence the equilibrium of rhodamine B isomers.

Introduction

Probing host–guest binding and molecular recognition events using fluorescent dye molecules has proven to be a very sensitive and useful technique, and numerous examples of the complexation of fluorescent guests can be found in the literature.[1] A typical example is the formation of an inclusion complex in aqueous solution, where the hydrophobic interactions act as a driving force to induce complexation, which is often accompanied by an increase[2] or decrease[3,4] in the fluorescence intensity resulting from a change in the microenvironment of the dye. Different host molecules, such as cyclodextrins,[2,5–7] cucurbiturils,[7,8] and water-soluble calixarene,[4,5,7,9] and resorcinarene[3,10] derivatives have been used in these studies.

Inclusion of non-fluorescent guests can be monitored using fluorescent probes, for example substituted 3*H*-indole with cyclodextrins,[11] or pyrene labeled guests with phosphonate cavitands[12] or pyrogallarene capsules.[13] When the use of fluorescent guests or probes is not feasible, host molecules can be covalently modified using fluorescent groups, resulting in fluorescence sensing multifunctional host molecules, such as coumarin functionalized cavitand crown ethers[14] or calixarenes.[15]

Rhodamine B, a strongly red xanthene dye, has been commonly used in dye lasers[16] and as a fluorescent label in biological staining.[17] The equilibrium of rhodamine B isomers, *i.e.* red zwitterion and a colorless lactone form (Scheme 1), has been an intensive target of research during the past fifty years due to the need to understand the complicated behavior of the dye in solution,[18] in the solid state,[19] and on catalyst coated surfaces.[20] Different optical properties of the isomers have already been utilized in an ammonia fluorosensor application.[21] The equilibrium of the rhodamine B base isomers depends, among other things, on the hydrogen bonding ability and self-organization of the solvent, where protic solvents favor the zwitterion and aprotic solvents favor the lactone form.[22] However, in a contradicting study, rhodamine B base was found to exist as a zwitterion in chloroform.[23] The equilibrium of rhodamine B hydrochloride salt lies strongly on the zwitterion side in protic solvents as well as in aprotic solvents, such as acetonitrile and chloroform, even though there has been some ambiguity whether the strong red color observed in chloroform results from the absorption of the zwitterion or from the cation form (Scheme 1).[22]

Resorcinarenes are a widely studied group of supramolecular hosts with a shallow and conformationally flexible binding cavity at the upper rim, which is readily available for versatile chemical modifications to introduce structural rigidity and selectivity to the binding properties.[24] Aminomethylation of resorcinarenes using Mannich condensation[25,26] extends the upper rim of the macrocycle with tertiary amino groups, which can be protonated by acidic compounds. Aminomethylated resorcinarenes and their salts have been observed to complex neutral organic guests, such as acetonitrile, formaldehyde and alcohols.[27,28] The size of the amine used in the aminomethylation can vary from simple diethylamine to bulky cyclic structures, which enable the complexation of rather large, chiral ammonium cations,[29] or tetramethylammonium cations with their counter anions.[30]

In the current research we have investigated the interaction of aminomethylated resorcinarenes **1–2** (Scheme 2) and their reference compounds **3–4** with rhodamine B in solution using spectroscopic methods. Special attention is paid to the effect of the aminomethylated resorcinarenes to the rhodamine B equilibrium in protic and aprotic solutions, since there are only a very few examples of such research in aprotic environments.[23] The long alkyl chain resorcinarenes **1** and **2** were chosen as target compounds due to their known ability to form self-assembled monolayers,[31,32] which could have further been utilized in designing functional monolayers.

Results and discussion

Synthesis and characterization of hosts 1–4

Mannich condensation of undecylresorcinarene with 5–10 equivalents of formaldehyde and 4 equivalents of diethylamine or 9-(methylaminomethyl)anthracene in ethanol afforded hosts **1** and **2**, respectively, in crown conformation.

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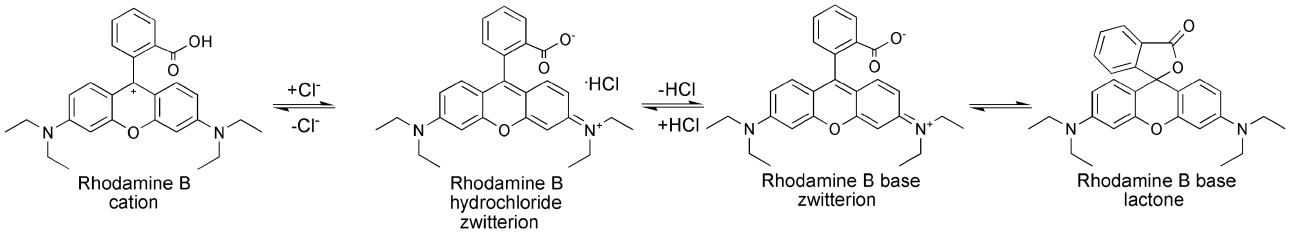
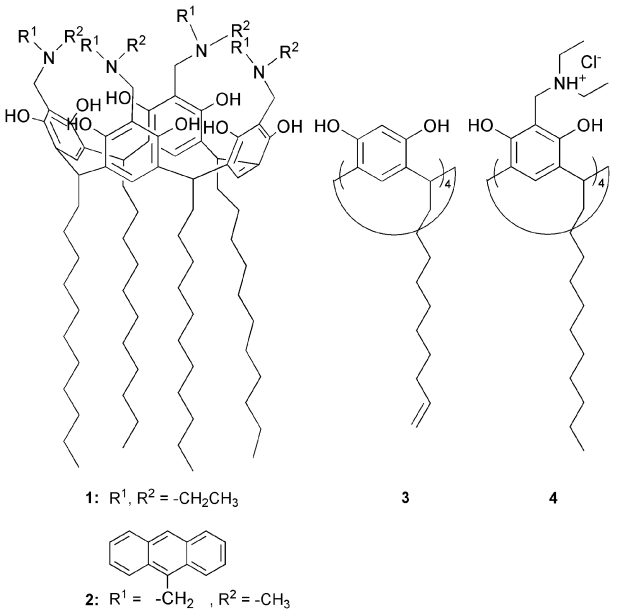


Scheme 1 The equilibrium of rhodamine B isomers.



Scheme 2 Structures of aminomethylated resorcinarenes **1–2** and reference compounds **3–4**.

The conformation was confirmed by the ^{1}H NMR spectra, where only one sharp aromatic proton signal arising from the resorcinarene core was observed. The starting material, undecylresorcinarene, has a hydrogen bonded upper rim that keeps the molecule in the crown conformation, which after aminomethylation is further supported by nitrogen atoms participating in the hydrogen bonding array, as illustrated in single crystal X-ray structures of closely related compounds which show how the array of intramolecular hydrogen bonds extends and rigidifies the binding cavity of the host.[26,27,33]

Reference compound **3** was synthesized according to the literature procedure[34] and compound **4** by heating the host **1** at reflux with 5 eq. of aqueous HCl in ethanol and removing the solvent under vacuum. The compound **3** was chosen as a reference compound instead of undecylresorcinarene because of its potential as a starting material for sulfur-functionalized resorcinarenes[32] or for self-assembling monolayers on Si surfaces.[35] The results of the NMR experiments show that the length of the alkyl chain or double bond functionality did not have any observable effect on the interaction with rhodamine B.

^{1}H NMR spectroscopy

The interaction of aminomethylated resorcinarenes **1–2** with rhodamine B hydrochloride was investigated in $CDCl_3$ by titrating samples of rhodamine B with **1** and **2**. The acquired ^{1}H NMR spectra were compared with the spectrum of pure rhodamine B hydrochloride and the spectrum of rhodamine B base in lactone form.

Addition of compound **1** induces dramatic changes in the rhodamine B signals (Fig. 1), indicating a transformation of the rhodamine B zwitterion into the lactone form. In addition, the aromatic proton signal of **1** is shifted from 7.10 to 7.30 ppm, value which corresponds to the aromatic proton signal of reference compound **4** (Fig. 2). This indicates that compound **1** is protonated and the simultaneous decrease in the resolution of the upper rim proton signals at 1 : 1 ratio with rhodamine B suggests that **1** has an equilibrium between protonated and deprotonated forms and potentially some interaction with rhodamine B.

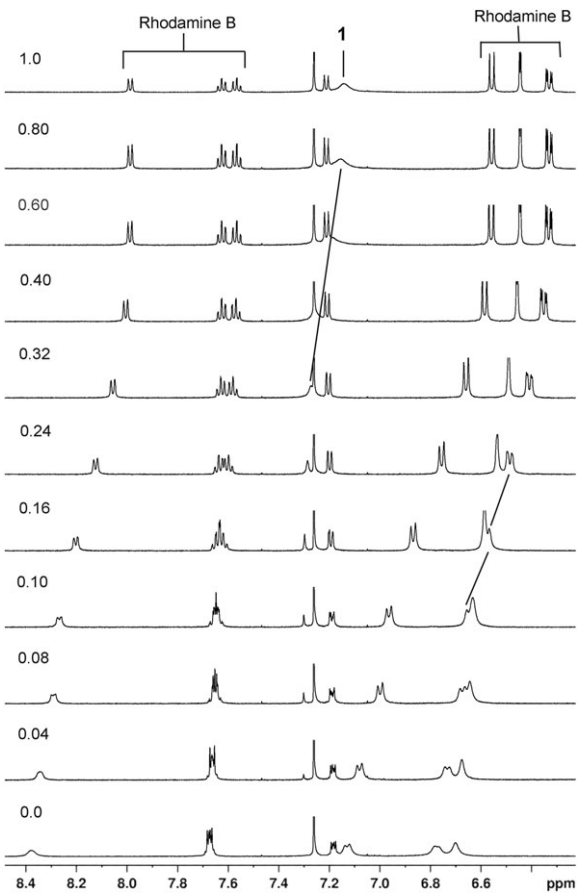


Fig. 1 NMR titration of rhodamine B hydrochloride in $CDCl_3$ with **1** showing lactonization of rhodamine B. Additions as molar equivalents.

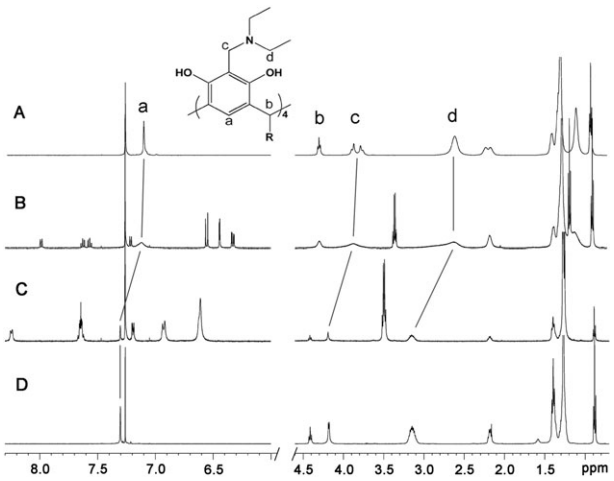


Fig. 2 ^{1}H NMR spectra in $CDCl_3$ of (**A**) **1**, (**B**) **1** with 1 eq. of rhodamine B hydrochloride, (**C**) **1** with 10 eq. of rhodamine B hydrochloride, (**D**) **4**, showing a downfield shift of the aromatic proton signal of **1** and broadening of the upper rim signals upon the addition of rhodamine B.

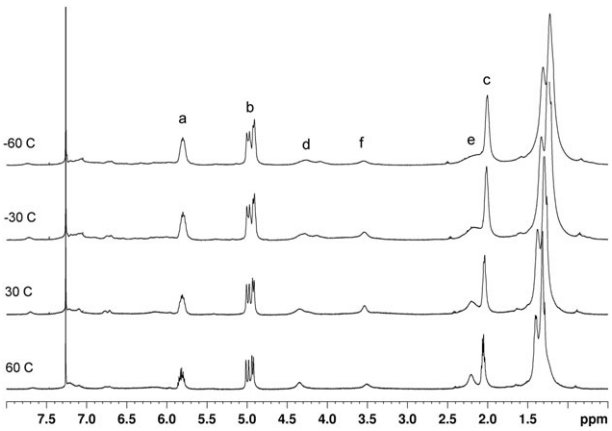


Fig. 3 ^{1}H NMR spectra of compound **3** with 1 eq. of rhodamine B hydrochloride in $CDCl_3$ at −60, −30, 30 and 60 °C. The resolution of the resorcinarene signals **a** (–C*H*═CH_2), **b** (–CH═C*H*$_2$), **c** (–C*H*$_2$CH═CH_2), **d** (Ar–C*H*) and **e** (Ar–CHC*H*$_2$) is increased at 60 °C and decreased at −60 °C, **f** from rhodamine B (–N–C*H*$_2$CH$_3$).

Rhodamine B lactonization was also observed in the presence of **2**, and the aromatic proton signal arising from the host's resorcinarene core was shifted downfield from 6.95 to 7.03 ppm at 1 : 1 ratio of rhodamine B. After addition of excess rhodamine B, the signal was covered under broad signals of the anthracene moieties. Even though the overlapping of proton signals made the analysis of the NMR spectra more complicated, compound **2** was chosen for further study because of the possibility of the aromatic anthracene moieties binding *via* π–π interaction to the rhodamine B molecule, and because of the fluorescence properties of the anthracene substituents. The reference compounds **3** and **4** do not induce rhodamine B lactonization, which proves, as expected, that the tertiary amino groups at the upper rim of resorcinarenes **1–2** are required for lactonization.

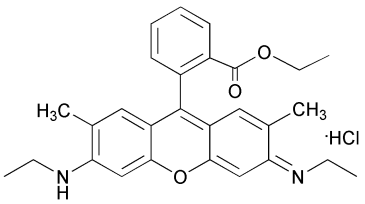
Addition of rhodamine B hydrochloride into a sample of **4** does not change the spectrum of the host at all, whereas addition of rhodamine B hydrochloride into a sample of **3** significantly reduces the resolution of all signals of host **3** and rhodamine B compared with the spectra of the pure components. This indicates that the system involves unspecified binding events close to the NMR timescale, which were further studied by varying the temperature of the sample between −60 and 60 °C (Fig. 3). At 60 °C the resolution is partially restored for the signals of **3**, especially at the lower rim, but for the rhodamine B signals no significant change was observed. The interaction was too vague to be specified but it is likely to involve the free hydroxyl groups at the upper rim of resorcinarene **3**, which could hydrogen bond to various functional groups of rhodamine B, and π–π interaction between aromatic rings of rhodamine B and **3**.

The ability of compound **1** to interact with rhodamine B hydrochloride in protic solvent was investigated by measuring a sample of **1** with rhodamine B hydrochloride in deuterated methanol. Protic solvents are known to shift the rhodamine B equilibrium towards the zwitterion form, which is thought to result from the ability of a protic solvent to stabilize the rhodamine B zwitterion through hydrogen bonding.[22] Chemical shifts of rhodamine B hydrochloride proton signals when 1 equivalent of **1** is added (Table 1) correspond quite accurately to the chemical shifts of rhodamine B base in methanol-d_4. The solubility of compound **1** in methanol is poor by itself, but the addition of rhodamine B improves the solubility of **1** by protonation of the nitrogens since sufficient amount of **1** was dissolved in the solvent to induce deprotonation in rhodamine B hydrochloride.

Based on the NMR experiments, the observed interaction between aminomethylated resorcinarenes **1–2** and rhodamine B hydrochloride is an obvious example of an acid–base interaction, where compounds **1–2** act as a base, and rhodamine B hydrochloride acts as an acid, and the result of this interaction is the lactonization of rhodamine B. However, the additional changes in the NMR spectra of **1** mentioned earlier indicate that there could be π–π interaction between the aromatic ring structure of rhodamine B and the aromatic part of resorcinarene, or interaction between the amino or acid groups of rhodamine B and the upper rim of the resorcinarene as observed with compound **3**. To reveal these interactions and eliminate the effect of lactonization in the spectra, rhodamine 6G (Scheme 3), which is an esterified analog of rhodamine B and therefore incapable of forming a lactone ring structure, was mixed with **1** in $CDCl_3$. The resulting NMR spectra did not show any changes in the chemical shifts of rhodamine 6G

Table 1 Comparison of the proton chemical shifts of pure rhodamine B hydrochloride, rhodamine B hydrochloride with 1 eq. of **1** and pure rhodamine B base (zwitterion) in methanol-d_4

	RhB·HCl	RhB·HCl + **1** (1 : 1)	RhB base
–NCH$_2$C*H*$_3$ (12 H)	1.31	1.29	1.29
–NC*H*$_2$CH$_3$ (8 H)	3.68	3.65	3.66
Xanthene-*H* (2 H)	6.97	6.91	6.90
Xanthene-*H* (2 H)	7.03	6.99	6.99
Xanthene-*H* (2 H)	7.14	7.28	7.28
Phenyl-*H* (1 H)	7.41	7.25	7.24
Phenyl-*H* (2 H)	7.82	7.62	7.62
Phenyl-*H* (1 H)	8.34	8.09	8.09



Scheme 3 Rhodamine 6G.

or aromatic proton signal of **1**, which was slightly surprising since protonation of **1** by rhodamine 6G hydrochloride could have been expected. Therefore we can conclude that rhodamine B hydrochloride has a much better ability to protonate compound **1** than rhodamine 6G, and changes in the spectra of rhodamine B hydrochloride in the presence of **1** in aprotic solvent are induced by lactonization, not by deprotonation.

UV-vis spectroscopy

Rhodamine B hydrochloride presents an intense absorbance maximum at 552 nm in $CHCl_3$ with a shoulder at 516 nm and additional bands in the UV region at 353, 307, 282 and 261 nm, whereas the lactone form presents only UV absorbance bands at 317, 278, and 242 nm (Fig. 4). Titration of rhodamine B hydrochloride solution in chloroform with increasing amounts of **1** or **2** showed a rapid decrease in the intensity of the rhodamine B absorbance maximum at 552 nm and bleaching of the pink color indicating a shift in the rhodamine B equilibrium from the zwitterion to the lactone form. The effect is comparable to that observed by Barra *et al*. in a study of rhodamine B with erythromycin A.[23]

Bleaching was more effective with host **1** than with host **2** when the same amount of host solution was added to the sample (Fig. 5), which contradicts our preliminary idea that the aromatic anthracene moieties of **2** would enhance interaction with the dye. Job's method[36] was used to determine the stoichiometry of the investigated interaction and it was found to be 1 : 2 (host–RhB) for both **1** and **2**, which indicates that one host molecule is able to deprotonate two rhodamine B molecules.

Reference compounds **3–4** did not induce rhodamine B lactonization, but addition of **3** to rhodamine B solution shifted the absorbance maximum 1 nm to longer wavelength,

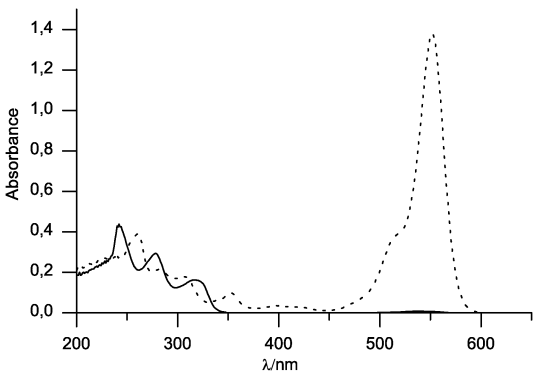


Fig. 4 Absorption spectra of rhodamine B hydrochloride (dotted line) and rhodamine B base in lactone form (solid line) at 1×10^{-5} M concentration in chloroform.

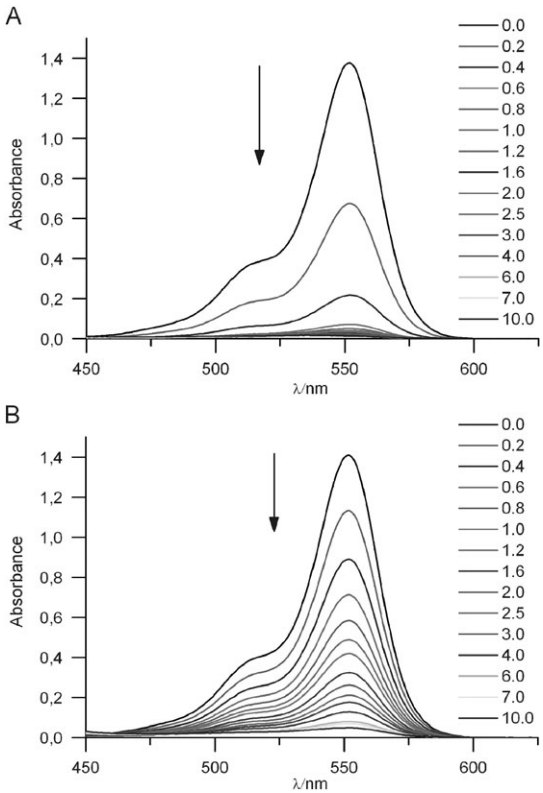


Fig. 5 UV-vis titration of rhodamine B hydrochloride in $CHCl_3$ with (A) **1** and (B) **2**. Additions as molar equivalents.

which is an indication that a cation form of rhodamine B, which exists in acidic conditions,[18] is stabilized in the presence of **3**. In addition, a rhodamine 6G sample was titrated with **1** in $CHCl_3$, but no change in the absorbance spectra of the dye was observed, which together with the NMR experiments confirms that rhodamine 6G does not interact with aminomethylated resorcinarene **1**.

The ability of the aminomethylated resorcinarenes to interact with rhodamine B in protic solvent was also investigated with UV-vis spectroscopy. Rhodamine B hydrochloride samples were titrated with compounds **1–2** in $CHCl_3$–MeOH (1 : 1), and instead of bleaching, an 8 nm blue shift was observed, which corresponds to the peak of zwitterionic rhodamine B base in the same conditions.

The ability of **1**, which was observed to be a stronger lactonizing compound, and reference compound **3** to extract rhodamine B into hexane phase from water phase was examined using hexane–water extraction. Rhodamine B hydrochloride is insoluble in hexane, whereas the long aliphatic chains of resorcinarenes **1** and **3** make them very soluble in non polar organic solvents, but insoluble in water. An aqueous solution of rhodamine B was stirred with a hexane solution of **1** or **3**, and after separation of the phases, the decrease in the rhodamine B absorbance in the water phase was used to calculate the amount of the dye transported. Compound **1** did not transport any rhodamine B but compound **3** transported 15.2 ± 0.9% when the rhodamine concentration was ten times higher than the host concentration. The results show that resorcinarene **3**, which has an open binding cavity,

aggregates with rhodamine B as depicted in the NMR experiments and therefore has better ability to transport rhodamine B than **1**. In case of compound **1** the interaction between **1** and rhodamine B is mainly acid–base interaction and requires that the components are in the same phase.

Fluorescence spectroscopy

The effect of **1** in rhodamine B hydrochloride fluorescence spectrum was investigated in $CHCl_3$. Rhodamine B hydrochloride has an emission maximum at 580 nm, but in the presence of compound **1**, the maximum is shifted to 558 nm, and the emission intensity is decreased close to the values observed for rhodamine B base. Furthermore, rhodamine B lactonization was confirmed as an appearance of a new emission band at 487 nm at excitation wavelength 286 nm, which corresponds to the maximum absorption of resorcinarene core and rhodamine B lactone. With 350 nm excitation, which corresponds to the absorption of rhodamine B hydrochloride, the emission intensity was very low. The fluorescence spectra of rhodamine B hydrochloride, rhodamine B base (lactone form) and a sample of rhodamine B with 1 equivalent of **1** at 286 nm excitation are presented in Fig. 6.

Host **2**, which contains four anthracene units connected by $–CH_2–N(CH_3)–CH_2–$ bridges to the upper rim, has fluorescence maxima at 395, 418 and 442 nm wavelengths in $CHCl_3$. Tertiary nitrogen atoms next to anthracene are known to cause fluorescence quenching by PET (photoinduced electron transfer) processes.[37] When acid was added to the sample of **2** in chloroform, the fluorescence intensity was increased. After 1 equivalent of HCl was added, the increase of intensity was roughly 70% accompanied by a 1–2 nm red shift of the fluorescence bands, and after 10 equivalents of HCl were added, the increase was 95%. The observed increase is likely induced by protonation of the nitrogens, which hinders PET and therefore promotes fluorescence. When rhodamine B hydrochloride was added to the sample of **2**, the fluorescence intensity of **2** was first increased as well (~25%), but after addition of more than 1 eq. of rhodamine B, the fluorescence intensity was decreased, which probably indicates that rhodamine B absorbance becomes a dominating factor (Fig. 7).

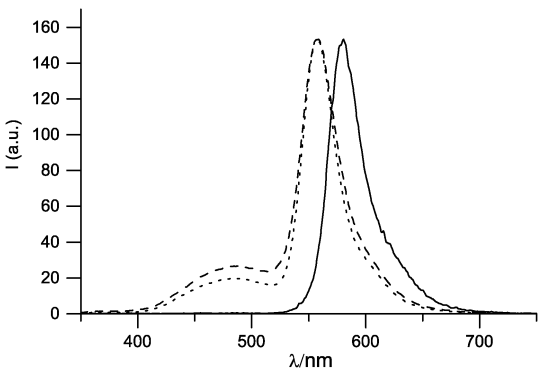


Fig. 6 Fluorescence spectra of rhodamine B hydrochloride (solid line), rhodamine B base in lactone form (dotted line) and rhodamine B hydrochloride with 1 eq. of host **1** (dashed line) in $CHCl_3$ at 286 nm excitation. Concentration 5×10^{-6} M, intensity values are normalized to rhodamine B base intensity.

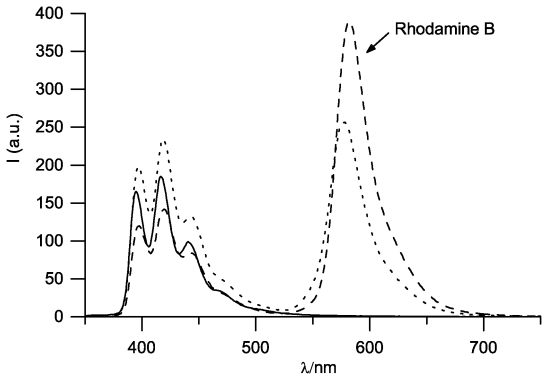


Fig. 7 Fluorescence spectra of host **2** (1×10^{-5} M in $CHCl_3$) at 258 nm excitation with addition of rhodamine B hydrochloride 0 eq. (solid line), 1 eq. (dotted line) and 2 eq. (dashed line).

Conclusions

The interaction of rhodamine B hydrochloride with aminomethylated resorcinarenes was investigated in solution using spectroscopic methods. In aprotic media, aminomethylated resorcinarenes **1–2** transformed the rhodamine B equilibrium from the zwitterion into the lactone form. Since lactonization was not observed in the presence of compounds **3–4**, we can conclude that the tertiary amine groups at the upper rim of resorcinarenes **1–2** induce lactonization by acting as a base. Lactonization was more effective with host **1** than host **2** based on the UV-vis titration, and the stoichiometric ratio was found to be 1 : 2 (host : RhB) determined by Job's method. In protic media, rhodamine B base as a zwitterion was observed.

In addition to acid–base interaction, clear evidence of π–π interaction or inclusion-type complexation between hosts and the dye was not obtained, which may partly be due to the difficulty of observing weaker changes when lactonization of rhodamine B is taking place. However, compound **3** showed aggregation ability with rhodamine B, probably *via* π–π interaction or hydrogen bonding, which was observed in hexane–water extraction and ^{1}H NMR experiments.

Experimental

General

All chemicals and solvents were purchased from Sigma-Aldrich and they were used as received. NMR spectra were recorded with a Bruker Avance DRX (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometer at 30 °C. *J* values are given in Hz. ESI-MS spectra were measured with a Micromass LCT (ESI-TOF) instrument. Melting points were determined with a Stuart Scientific SMP3 and a Metler Toledo FP62 apparatus and are uncorrected. Elemental analyses were performed on a Vario EL III apparatus. UV-vis spectra were measured with a Varian Cary 100 Conc UV-vis spectrophotometer at RT using a 1 cm quartz cuvette, and fluorescence spectra with a Perkin Elmer Luminescence Spectrometer LS50B at RT using a 1 cm quartz cuvette.

NMR experiments

The ^{1}H NMR spectra were recorded in $CDCl_3$ or in CD_3OD at 500 MHz. The NMR titration was performed by adding

increasing amounts of compound **1** or **2** in $CDCl_3$ to an 8.7 mM solution of rhodamine B hydrochloride in $CDCl_3$ and recording the spectra.

UV-vis experiments

UV-vis titration was performed by adding increasing amounts of 1×10^{-3} M solution of **1** or **2** into 1×10^{-5} M solution of rhodamine B hydrochloride in $CHCl_3$ and recording the spectra. Titration experiments in $CHCl_3$–MeOH were performed identically.

Job plot samples were prepared by mixing 1×10^{-5} M solutions of rhodamine B hydrochloride and either **1** or **2** in $CHCl_3$ in different ratios (9 : 1, 4 : 1, 7 : 3, 3 : 2, 1 : 1, 2 : 3, 3 : 7, 1 : 4, 1 : 9) keeping the total concentration constant.

Extraction was performed by mixing 3 ml of 1×10^{-2} M rhodamine B hydrochloride in water and 3 ml of 1×10^{-3} M resorcinarene **1** or **3** in hexane for 1 h. On the following day the water phase was diluted 100 fold with water and analyzed using a UV-vis spectrophotometer. Blank samples were prepared identically as the actual samples but without resorcinarene in the hexane phase. The percent of rhodamine B transported was calculated by comparing the A_{354} of the sample against the A_{354} of the blank sample according to the equation

$$\text{transport}\% = [A_{354(\text{blank})} - A_{354(\text{sample})}]/A_{354(\text{blank})} \times 100\%.$$

Fluorescence experiments

Fluorescence spectra were recorded using 5 nm excitation and emission slits and a 350 nm emission filter for 258 and 286 nm excitation wavelengths, and a 390 nm emission filter for 350 nm excitation wavelength.

Acid titration of **2** in chloroform was performed by adding increasing amounts of 1×10^{-3} M HCl solution in $CHCl_3$ (prepared from conc. HCl) to a 1×10^{-5} M solution of **2** in $CHCl_3$ and recording the spectra at different excitation wavelengths (258, 386 and 350 nm). Titration with rhodamine B hydrochloride was performed identically.

Synthetic procedures

Aminomethylated resorcinarene **1** was prepared by Mannich condensation of formaldehyde and secondary amine into the resorcinarene aromatic ring.[25,26] Undecylresorcinarene (0.84 g, 0.76 mmol) was dissolved in a mixture of ethanol (22 ml) and 37% formaldehyde (0.28 ml, 3.76 mmol). Diethylamine (0.22 g, 3.0 mmol) was added dropwise under vigorous stirring. After the addition of amine the stirring was stopped and by next day crystals had grown. Crystals were filtered with suction and dried under vacuum to give **1** (0.94 g, 85%) as a pale powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, J = 7.0, 12H), 1.10 (t, J = 6.8, 24H), 1.27 (m, 64H), 1.37 (m, 8H), 2.17 (m, 8H), 2.59 (m, 16H), 3.81 (m, 8H), 4.28 (t, J = 7.9, 4H), 7.10 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 11.0, 14.1, 22.7, 28.3, 29.4, 29.74, 29.77, 29.82, 29.86, 29.87, 32.0, 33.4, 33.5, 46.4, 51.3, 107.8, 121.9, 124.0, 150.4, 153.0 ppm. MS (ESI-TOF) m/z 1446.20 $[M]^+$. Anal. calcd. for $C_{92}H_{156}N_4O_8$: C 76.40%, H 10.87%, N 3.87%. Found C 76.11%, H 10.66%, N 3.49%. Mp 82 °C.

Aminomethylated resorcinarene **2** was prepared by stirring a mixture of resorcinarene (0.3 g, 0.27 mmol), 9-(methylaminomethyl)anthracene (0.35 g, 1.6 mmol) and formaldehyde (2.0 ml, excess) in 10 ml of ethanol overnight. Yield 0.34 g (62%).^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.85 (t, J = 7.1, 12H), 1.18 (m, 72H), 2.03 (m, 8H), 2.21 (s, 12H), 3.95 (m, 8H), 4.08 (t, J = 7.3, 4H), 4.64 (m, 8H), 6.95 (s, 4H), 7.55 (m, 8H), 7.61 (m, 8H), 8.05 (m, 8H), 8.36 (m, 8H), 8.46 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) 14.1, 22.7, 28.2, 29.4, 29.67, 29.69, 29.71, 29.77, 29.9, 31.9, 33.4, 33.6, 41.2, 53.4, 55.1, 108.0, 121.8, 123.5, 124.0, 125.1, 126.6, 127.8, 128.4, 129.3, 131.2, 131.4, 150.4, 151.7 ppm. MS (ESI-TOF) m/z 2038.37 $[M]^+$. Anal. calcd. for $C_{140}H_{172}N_4O_8$: C 82.47%, H 8.50%, N 2.75%. Found C 82.54%, H 8.84%, N 2.79%. Mp 140 °C.

Resorcinarene **3** was synthesized according to the literature procedure.[34] To a mixture of resorcinol (4.0 g, 36.4 mmol) and 10-undecenal (7.5 ml, 36.1 mmol) in ethanol (125 ml), concentrated HCl (7.0 ml) was added dropwise under nitrogen atmosphere at 0–5 °C. The clear transparent mixture was stirred in an ice bath for 1.5 h and subsequently refluxed for 26 h. The product was precipitated from water, filtered with suction and dried under vacuum. The resulting yellowish powder was recrystallized from acetonitrile, purified by flash chromatography (SiO_2, eluent $CHCl_3$–MeOH, MeOH gradient from 0% to 10% v/v) and recrystallized again from acetonitrile–water. The resulting pale powder was filtered with suction and dried under vacuum. Yield 3.4 g (36%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (m, 32H), 1.38 (m, 16H), 2.04 (m, 8H), 2.21 (m, 8H), 4.30 (t, J = 7.5, 4H), 4.93 (m, J = 10 and 1.2, 4H), 5.00 (m, J = 17, 2.2 and 1.6, 4H) 5.81 (m, 4H), 6.12 (s, 4H), 7.20 (s, 4H), 9.29 (m, 4H), 9.60 (m, 4H) ppm.^{13}C NMR ($CDCl_3$, 126 MHz) δ 28.0, 29.0, 29.1, 29.50, 29.54, 29.7, 33.1, 33.3, 33.8, 102.9, 114.1, 123.9, 124.9, 139.2, 150.4, 150.6 ppm. MS (ESI-TOF) m/z 1039.96 $[M - H]^-$, m/z 519.48 $[M]^{2-}$. Anal. calcd. for $C_{68}H_{96}O_8 \cdot H_2O$: C 77.09%, H 9.32%. Found C 77.14%, H 9.46%. Mp > 300 °C.

Resorcinarene **4** was prepared by heating the compound **1** (0.2 g, 0.14 mmol) at reflux with 5 eq. of concentrated hydrochloric acid (59 µl, 0.68 mmol) in ethanol (50 ml) for 1 h and removing the solvent under vacuum. The resulting pale solid was dried under vacuum. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, J = 6.9, 12H), 1.27 (m, 64H), 1.40 (m, 8H), 1.40 (t, J = 7.2, 24H), 2.18 (m, 8H), 3.15 (m, 16H), 4.18 (d, J = 5.8, 8H), 4.41 (t, J = 7.8, 4H), 7.30 (s, 4H), 9.33 (s, 8H), 10.2 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ 8.9, 14.1, 22.7, 28.1, 29.4, 29.72, 29.76, 29.80, 29.81, 29.83, 32.0, 33.6, 34.8, 46.2, 47.8, 108.7, 125.6, 127.6, 151.2 ppm. MS (ESI-TOF) m/z 1446.00 $[M]^+$. Anal. calcd. for $C_{92}H_{160}N_4O_8Cl_4$: C 69.41%, H 10.13%, N 3.52%. Found C 69.38%, H 10.13%, N 3.27%. Mp 123 °C.

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