The structural diversity of benzofuran resorcinarene leads to enhanced fluorescence.

Structural Diversity of Benzofuran Resorcinarene Leads to Enhanced Fluorescence


Abstract: An unexpected and previously unknown resorcinarene mono-crown with a fused benzofuran moiety in its macrocyclic core was obtained as a by-product from a bridging reaction of tetramethoxy resorcinarene with tetraethylene glycol ditosylate. The formation of the fused benzofuran moiety in the resorcinarene macrocycle resulted in a unique rigid and puckered boat conformation as shown by XRD studies in the solid state. The modification of the macrocycle was also observed to affect the photophysical properties in solution by enhancing the fluorescence brightness compared to a conventional resorcinarene macrocycle. The fluorescent properties enabled a unique detection of structural features, i.e. the rigid boat conformation with the conjugated benzofuran system and the more flexible crown bridge part, in solution.

Keywords: resorcinarene • calixarene • benzofuran • fluorescence • supramolecular chemistry • X-ray crystallography

Introduction

Resorcinarenes, a class of calixarene type macrocycles, have been widely investigated during the last few decades due to their advantageous features as concave host molecules, as well as, their versatile functionalization of the upper and lower rims leaving the aromatic cavity virtually intact during the synthesis.\[1\] Modifications affecting the upper rim of the resorcinarene core include, for example, the synthesis of cavitands, in which the resorcinarene macrocycle is rigidified into a fixed crown conformation by a covalent bridge between the neighboring phenolic hydroxyl groups,\[2\] as well as tetrabenzoxazine resorcinarenes, in which the resorcinol rings of the macrocycle and their hydroxyl groups form a benzoxazine ring with an amine.\[3\] However, these functionalizations still leave the actual macrocyclic core more or less intact affecting only the functional groups on the upper rim. Closely related pyrogallarene macrocycles, on the other hand, have shown inherent structural instability due to the ability of the aromatic rings to transform into lactone rings in dilute solutions.\[4\] Although the lactone structures were not successfully isolated and the lactone formation was exclusively stated as a property of pyrogallararenes, it proves that under certain conditions modification directly affecting the aromatic macrocyclic core is attainable.

An intriguing way to enhance the capacity of resorcinarenes in, for example, sensor applications is to functionalize them with a photoactive subunit,\[3, 4, 5\] as e.g. in dansylated fluorescent resorcinarenes\[3\] that have been exploited in sensing transition metals. Cavitand derivatives having either bulky fluorescent groups extending the walls of the cavity or flexible crown ether podand arms with a fluorescent moiety, have been demonstrated to work as fluorescent receptors for different metals\[7, 8\], anionic guests\[8\], and ammonium compounds\[9\], or function as molecular switches\[10\] or in biological applications to sense e.g. guanosine 5'-triphosphate\[11\].

Recently, by serendipity we succeeded to isolate a previously unknown resorcinarene by-product (1) from a reaction mixture of tetramethoxy resorcinarene bis-crown (3)\[12\] and mono-crown (2)\[13\] derivatives. To our surprise, the previously untouched resorcinarene core had one of the aromatic rings been replaced by a benzofuran moiety (Scheme 1) and, as at first observed with a naked eye under UV-light (366 nm, Figure S3), the benzofuran mono-crown derivative 1 showed intrinsic enhanced photophysical properties without having a separate fluorescent functionalization.

In this paper, we report the synthesis and discuss the possible reaction mechanism of the novel benzofuran mono-crown derivative 1. In addition, we report the structural characteristics arising from
the fused benzofuran ring that were observed both in the solid state and in solution by means of X-ray crystallography and 2D fluorescence measurements. The main focus of the fluorescence studies was to discover which structural features induce the enhanced fluorescence of the benzofuran resorcinarene mono-crown 1.

Abstract in Finnish:

Results and Discussion

Synthesis

The synthesis protocol established for the preparation of resorcinarene mono-crown derivative 2 by a nucleophilic reaction of tetramethoxy resorcinarene with one equivalent of tetraethylene glycol ditosylate in the presence of anhydrous Cs₂CO₃ in DMF at 90 °C, was also shown to produce a previously unknown resorcinarene mono-crown derivative 1 as a by-product in addition to the earlier reported resorcinarene mono- 2 and bis-crown 3 derivatives (Scheme 1). The ratio of the three resorcinarene crown derivatives 1–3 was determined to be 2:3:5, respectively, and the isolated yield of the by-product 1 was 5.2% (Table 1, entry 1). The unusual structure of compound 1 with benzofuran ring as a part of the resorcinarene skeleton was characterized by means of NMR spectroscopy (¹H, ¹³C, HMBC and HMQC), mass spectrometry (accurate mass, ESI⁺) and X-ray crystallography, which revealed the unexpected formation of the benzofuran unit inducing an elongated conjugated system with the alternating σ- and π-bonds into the resorcinarene macrocycle (highlighted in Scheme 1).

Synthesis conditions, namely the reaction temperature and media, and the influence of the base and the bridging reagent were taken under consideration in order to study the factors affecting the formation of the benzofuran fused macrocyclic structure in more
A. Formation of a DMF radical in the presence of a base

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{N} \quad \text{CH}_2 & \quad \text{-e} \\
\text{MeO} & \quad \text{OH} \\
\text{MeO} & \quad \text{-H} \\
\text{MeO} & \quad \text{O} \\
\text{MeO} & \quad \text{O} \\
\text{MeO} & \quad \text{O} \\
\end{align*}
\]

B. Formation of benzofuran ring via radical mechanism

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
\text{Cs}_2\text{CO}_3 & \quad \text{-H}\text{+} \\
\text{MeO} & \quad \text{O} \\
\text{MeO} & \quad \text{-H}_2 \\
\text{MeO} & \quad \text{O} \\
\text{MeO} & \quad \text{O} \\
\end{align*}
\]

Scheme 2. Proposed reaction mechanism for the benzofuran ring formation via a radical pathway.\cite{10,20}

detail (Table 1). Using the aforementioned conditions and allowing tetramethoxy resorcinarene and Cs$_2$CO$_3$ to react about 60 min in the specified solvent before the addition of one equivalent (entries 1, 2, 4 and 5) of tetraethylene glycol ditosylate, were set as a standard procedure. The reaction was quenched after one day and the product outcome was analyzed.

When the reaction was performed in DMF at a lower temperature of 60 °C (entry 2), only the formation of bis-crown derivative 3 was observed. The same result was also obtained in acetonitrile at refluxing temperature. Excluding the bridging unit from the reaction resulted in deprotonation of the resorcinarene hydroxy groups, and only a mixture of unreacted tetramethoxy resorcinarene and its deprotonated form was obtained. When the reaction was performed with two equivalents of tetraethylene glycol ditosylate (entry 3), the bis-crown derivative 3 was clearly the major product and only a very small amount of the mono-crown derivative 2 formed as a minor product. These observations indicate that solvent (DMF) and a higher reaction temperature together with the 1:1 ratio of the starting compounds are the enabling factors on the formation of the benzofuran derivative 1.

The exceptional benzofuran ring formation within the resorcinarene skeleton led us to speculate the possible reaction mechanism in more detail. Recent literature presents numerous methods for the synthesis of benzofurans by the formation of the furan ring via intramolecular cyclization of various benzene derivatives.\cite{15} These include the formation of the furan ring from \textit{ortho}-substituted phenol derivatives e.g. by Pd(II)-catalyzed cyclization of \textit{o}-alkenyl or \textit{o}-alkynyl phenols\cite{16}, acid catalyzed dehydration of \textit{o}-hydroxybenzyl ketones\cite{17} or via Pd(II)-mediated Sonogashira cross-coupling of \textit{o}-halophenols with alkynes.\cite{18} However, while considering the possible reaction pathways for the benzofuran ring formation within the resorcinarene skeleton that lacks an electron deficient \textit{\beta}-carbon atom at the \textit{ortho} substituent (Scheme 1), the only conceivable alternative seems to be a radical reaction mechanism initiated by DMF radicals. Although DMF is generally considered to be an inert solvent it was recently shown that DMF radicals readily form in the presence of a base, (Scheme 2).\cite{19} Therefore, we anticipated that under the applied basic reaction conditions some DMF radicals form and a radical reaction mechanism based on an earlier proposition by Katrizky \textit{et al.}\cite{20} takes place (Scheme 2). As such, it is proposed that upon deprotonation by Cs$_2$CO$_3$ base, the resorcinarene phenoxide B forms a radical C in the presence of a DMF radical. The radical C then loses H to form the \textit{ortho}-quinonoid derivative D, which upon tautomerization gives the vinylphenol E. Although the exact reaction mechanism of the ring closure is not yet known, it has been suggested that the intramolecular dehydrocyclization occurs via the addition of the hydroxyl group across the alkenyl side chain to give the intermediate F, which finally upon loss of H$_2$ leads to the formation of the benzofuran derivative G.\cite{20,21}

To further verify the proposed mechanism for the formation of a benzofuran ring, the standard synthesis procedure was repeated at 60 °C and at 90 °C in the presence of potassium ferricyanide (0.9 \textit{equiv} entries 4 and 5 in Table 1), which is known to act as \textit{“one-electron abstractor”} that transforms the deprotonated hydroxyl groups into radicals.\cite{22} The reaction with the radical initiator produced only a small amount (yield < 2%) of benzofuran monocrown 1 at 60 °C, but at 90 °C a slight increase in the yield (6.1%) was observed supporting the idea of a possible radical mechanism.

Figure 1. Representative structure (I) of the highly distorted boat conformation of the resorcinarene macrocycle: (a) front and (b) side views highlighting the up-shift of the methine plane. Hydrogen atoms have been removed for clarity.

3
Structural properties

Single crystal X-ray diffraction studies revealed the structural and conformational properties of the benzofuran fused resorcinarene 1 in solid state. Single crystals were grown by slow evaporation at 8 °C from acetonitrile (I), chloroform-ethanol (II), chloroform-methanol (III), and ethanol (IV) solutions of 1. The resorcinarene benzofuran mono-crown 1 has no symmetry in the resorcinarene cavity, which is composed of three structurally different units (Scheme 1, A-D). In all four structures the resorcinarene skeleton is in a highly twisted boat conformation with a twist angle of 29–31° (Table S2, Figure S1).

Similarly to the resorcinarene mono-crown derivative 2, one end of the cavity is enclosed by a crown ether bridge connecting two adjacent aromatic rings (C-D), while the other end is defined by a horizontal aromatic ring having a free hydroxyl group (B) available for intermolecular hydrogen bonding. The center of the cavity is outlined by two upright aromatic rings (A and C), the other being the benzofuran ring (A) fused into the resorcinarene framework (Figure 1). In comparison to the boat conformations of the bis-crown[12] 3 and mono-crown[13] 2 derivatives, the resorcinarene skeleton of 1 is severely distorted due to the 180° rotation of the lower rim ethyl groups about the methine bridge (C14) as it takes part in forming the benzofuran ring. This causes the methine bridge (C14) to shift 2.40–2.79 Å up from the methine plane (C21-C28-C7, Figure 1a). The distortion of the resorcinarene skeleton is best seen by the inclination of the horizontal aromatic unit B by 30–33° from the methine plane (Figure 1b), while the conformational parameters of the other three aromatic units (A, C and D) agree well with the typical boat conformation having the dihedral angles of 106–118° for the upright aromatic rings (A and C) and 167–177° for the horizontal aromatic ring (D) (Table S2).

The conformation of the resorcinarene skeleton is very similar in all the four structures (Figure S1), indicating a rigid conformation in which the conjugated system formed by the benzofuran moiety and three aromatic rings is fixed. Notable change is seen in the crown ether bridge as it takes part in solvent binding either in an endo- or exo-cavity mode, which is seen as the outward or inward configuration of the crown ether bridge with respect to the cavity (Figure 2). In the endo-cavity binding a solvent guest is included in the crown pocket by intermolecular hydrogen bonding to the crown ether oxygen (I and III). Similar weak intermolecular interactions prevail in the exo-cavity binding (II and IV), but in this case the solvent molecule is located outside the resorcinarene cavity and the crown ether bridge is bent into the cavity making the average crown pocket diameter of 5.45–5.60 Å distinctly smaller than that of ~ 6.26 Å of the outward bent crown ether bridge.

Similar packing motifs to resorcinarene bis- and mono-crown derivatives are observed including self-assembly either to self-inclusion dimer pairs composed of enantiomers of opposite inherent chirality (I, II and IV) or to solvent mediated hydrogen bonded dimer pairs (III). The closest packing into ordered crystal lattices is realized via weak intermolecular hydrogen bonding, CH–aromatic, aromatic–aromatic and CH–O interactions (Figure S2).

Spectroscopic properties

The effects of the rigid and puckered boat conformation, as well as the effect of the extended conjugated system to the photophysical properties of the benzofuran mono-crown 1 were further investigated in solution by fluorescence spectroscopy. THF was selected as the solvent due to its aprotic nature.

Absorption spectra

The UV-Vis absorption spectra of the benzofuran mono-crown 1, as well as the mono-crown derivative 2, and 2,3-benzofuran[23] (BF) selected as reference samples, were measured (Figure 3). The
absorption spectrum of 2,3-benzofuran resembles the one presented in the literature. Mono-crown derivatives 1 and 2 exhibit the same spectral features: two main absorption bands, one at 284 (2) and 290 nm (1) and a shoulder at 325–350 nm. The slight shift (6 nm) in the maximum absorption band of 1 is due to a bathochromic shift i.e. red shift caused by the longer conjugated system. In addition, unlike 2,3-benzofuran and mono-crown derivative 2, benzofuran mono-crown 1 possesses another shoulder around 450 nm. The absorption coefficients (ε, Table 2) of the benzofuran mono-crown derivative 1 at wavelengths of 340 and 375 nm (307.40 and 86.75 M⁻¹ cm⁻¹, respectively) are multiple times higher than the ones obtained for the mono-crown derivative 2 (4412.88 and 15.70 M⁻¹ cm⁻¹) and for 2,3-benzofuran (18.95 and 2.29 M⁻¹ cm⁻¹). However, at the wavelength of 290 nm the absorption coefficient of 2 (4412.88 M⁻¹ cm⁻¹) is slightly higher than the absorption coefficient of 1 (4300.02 M⁻¹ cm⁻¹). These results indicate that benzofuran ring fused into the macrocycle increases the absorbance at the wavelength range higher than 300 nm and somewhat reduces it at the wavelength range lower than 300 nm. The increase in the conjugation degree of the macrocycle 1 causes the observed spectrum shifts and also explains the growth of absorbance.

Fluorescence spectra

Steady-state emission spectra of benzofuran mono-crown derivative 1 were measured with three different excitation wavelengths of 290, 340 and 375 nm still using mono-crown 2 and 2,3-benzofuran as reference samples (Figure 4, Figure S4). The emission maxima are expressed in Table 2. The multiple emission maxima with various excitation wavelengths indicate that the solution contains various types of emitting components. Potentially these components are in dynamic exchange, for example because of complexation with the solvent molecules. The emission properties of 2,3-benzofuran (18.95 and 2.29 M⁻¹ cm⁻¹), respectively) are multiple times higher than the absorption coefficient of benzofuran (18.95 and 2.29 M⁻¹ cm⁻¹).

Table 2: Photophysical characteristics of resorcinarene derivatives 1, 2 and 2,3-benzofuran Bf.

<table>
<thead>
<tr>
<th>λmax (nm)</th>
<th>Sample</th>
<th>ε (M⁻¹ cm⁻¹)</th>
<th>λmax (nm)</th>
<th>Φ</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td>290 nm</td>
<td>1</td>
<td>4300.02</td>
<td>332</td>
<td>0.087</td>
<td>375.5 (100%)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4412.88</td>
<td>319</td>
<td>0.065</td>
<td>287.7 (77%)</td>
</tr>
<tr>
<td></td>
<td>Bf</td>
<td>92.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>340 nm</td>
<td>1</td>
<td>307.40</td>
<td>448</td>
<td>0.020</td>
<td>6.150 (100%)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49.81</td>
<td>465</td>
<td>0.024</td>
<td>1.201 (20%)</td>
</tr>
<tr>
<td></td>
<td>Bf</td>
<td>18.95</td>
<td>360</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>375 nm</td>
<td>1</td>
<td>86.75</td>
<td>452</td>
<td>0.0061</td>
<td>0.5265 (100%)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15.70</td>
<td>477</td>
<td>0.013</td>
<td>0.2053 (39%)</td>
</tr>
<tr>
<td></td>
<td>Bf</td>
<td>2.29</td>
<td>468</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Φ2=0.065), whereas at the excitation wavelengths of 340 nm (Φ2=0.020 and Φ2=0.024) and 375 nm (Φ2= 0.0061 and Φ2=0.013) they were almost negligible. At the excitation wavelength of 290 nm the quantum yield of mono-crown 2 is approximately 75% of the quantum yield of 1. A similar trend was also observed with the time-resolved lifetime measurements as the fluorescence lifetime for derivative 2 (τ = 1.48 ns) was 83% of the fluorescence lifetime of benzofuran mono-crown derivative 1 (τ = 1.79 ns, Figure S5a, Table S4). Samples were excited at 290 nm and decays were monitored at 340 nm. The rigid conjugated structure of mono-crown 1 causes the reduction of the non-radiative pathways which enhances the fluorescence quantum yield compared to mono-crown 2. For the same reason the mono-crown 1 shifts the emission maxima toward red compared to mono-crown 2. However, to the contrary of measurement with the excitation wavelength of 290 nm, at excitation wavelengths of 340 and 375 nm the quantum yields favored the mono-crown derivative 2 over the derivative 1. The quantum yields were 20% higher at the excitation wavelength of 340 nm, and more than two times higher at 375 nm for mono-crown 2. To ensure that such sizeable difference exists, time-resolved fluorescence lifetime measurements were conducted. Samples were excited at 377 nm and decays were monitored at 440 nm. The averaged fluorescence lifetimes obtained for the derivative 1 (τave = 0.91 ns) and derivative 2 (τave = 1.93 ns) correlate well with the ratio of the quantum yields at the excitation wavelength of 375 nm (Figure S5b, Table S4). The reason for the observed phenomena is probably electron or energy transfer between the benzofuran moiety

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and the aromatic rings, or an intermolecular proton transfer since in the literature it has been observed that the solvent, pH, and the substitution pattern cause variations to the fluorescence spectra with similar structural features. More specific studies of the reasons, however, are out of the scope of this paper.

Brightness

The quantum yield does not take the concentrations of the samples into account whereas brightness values are calculated from quantum yields and absorption coefficients and are thus concentration dependent. In fact, the brightness values confirm the visual observations under UV light (366 nm); benzoﬂuran ring clearly increases the fluorescence brightness of compared to the mono-crown derivative 2 (Table 2, Figure S3). At the excitation wavelength of 290 nm the brightness of the benzoﬂuran mono-crown derivative 1 is about 20% higher than that of the mono-crown derivative 2 and at the excitation wavelengths of 340 and 375 nm the brightness of the derivative 1 is signiﬁcantly higher (80 and 60%, respectively).

EEM spectra

Emission/excitation matrix (EEM) spectra for the benzoﬂuran mono-crown derivative 1 and 2 were measured to study in more detail, which structural features affect the ﬂuorescence. As expected based on the basic ﬂuorescence measurements three separate ﬂuorescence signals were observed in the EEM spectrum (Figure 5). The shapes of the ﬂuorescence signals at the excitation wavelengths of 300–320 and 330–350 nm are beautifully round, but the third ﬂuorescence signal (exc. wavelengths 360–400 nm) differs notably from the other two signals as it has a stretched oval shape. The two round ﬂuorescence signals suggest homogeneity and rigidity in certain parts of the structure being most likely caused by the aromatic and the benzoﬂuran rings of the macrocycles.

As observed in the solid state structures, the formation of the benzoﬂuran ring forces the resorcinarene core into a highly distorted and rigid boat conformation. As such, conformational interconversion of the benzoﬂuran mono-crown 1 macrocycle is not possible making the structure spectacularly homogenous on that part, and causing the roundness of the two ﬂuorescence signals. Similar phenomenon is also observed with mono-crown 2. Even though it lacks the additional rigidity brought by a benzoﬂuran moiety, the bridging and lack of intramolecular hydrogen bonds favour the boat conformation in the solid state and in solution.

A linear relation between the emission and the excitation of the oval shape signal is 0.55 for 1 and 0.19 for 2 This ratio illustrates that the longer wavelength absorbing moieties of compound 1 and 2 have inhomogeneous broadening. As observed with the basic fluorescence measurement (λex = 375 nm) the signal is caused by the joint effect of the macrocycle and the crown ether bridge (Figure S6). The broadening together with the fluorescence characteristics of the signals are explained as the crown ether bridge is able to flip between the endo- and exo-positions while providing multiple coordination sites to the crown ether oxygens. The crown bridge ﬂexibility is also seen in the crystal structures (Figure 2) and in the 1H NMR spectrum as the multiplicity of the crown ether proton resonances.

Conclusions

The synthesis of resorcinarene mono- 2 and bis-crown 3 derivatives in DMF was observed to produce an exceptional benzoﬂuran mono-crown by-product 1, in which one of the aromatic rings was replaced by a benzoﬂuran moiety. The results of the synthesis studies suggest that the unexpected benzoﬂuran ring formation could happen via a radical pathway as the presence of a radical initiator potassium ferricyanide in the reaction showed a positive effect on the yield of benzoﬁuran resorcinarene mono-crown 1. The crystal structures revealed that the benzoﬂuran ring forces the resorcinarene skeleton into a highly distorted and rigid boat conformation, which is not observed with the previously studied resorcinarene mono- and bis-crowns.

The modified macrocycle structure has a signiﬁcant effect on the photophysical properties as the brightness of 1 was considerably enhanced compared to the structurally simpler mono-crown derivative 2. However, the benzoﬂuran moiety enables more interactions with the surrounding environment causing a decrease in the quantum yields compared to the mono-crown 2. The ﬂuorescence properties together with the rigid macrocyclic skeleton and the mobile bridge unit enabled the study of the structural characteristics by emission/excitation matrix measurements, which showed that the speciﬁc structural characteristics of the benzoﬂuran mono-crown derivative 1 can be observed not only in the solid state by the commonly used X-ray crystallography, but also in solution by spectroscopic methods.

Experimental Section

General
1H, 13C, HMQC and HMBC NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. Accurate ESI mass spectrum was measured with a Micromass LCT ESI-TOF instrument. The calibration was carried out using Leucine enkephalin as an inner standard. Melting point was obtained with a Stuart Scientific SMP3 melting point apparatus. Tetramethoxy resorcinarene was prepared according to literature procedures.14,15 Tetraethy glycol ditosylate was prepared from tetraethy glycol by a general toslylation reaction of hydroxyl groups using triethylamine as a base and dichloromethane as a solvent.15 All other reagents were commercial and used as received. DMF was distilled over Linde type 4 Å molecular sieves and stored over Bf bridge (103). The steady state absorption, fluorescence and excitation spectra of the samples were diluted in THF so that the absorption was sufficiently low (A < 0.07 at 290 and 375 nm) to prevent inner filter effect. The spectra were recorded using Perkin-Elmer LAMBDA 850 UV–Vis spectrophotometer and Varian Cary Eclipse fluorescence spectrophotometer. Excitation-emission matrix (EEM) fluorescence spectrum was obtained by concatenating emission spectra measured every 10 nm from 310 to 400 nm using excitation wavelengths ($\lambda_{ex}$) from 300 to 400 nm (10 nm intervals) with 0.5 s integration time and a 2.5 nm slit width. The Raman scattering peaks in the EEM spectrum were corrected with a method described by R. G. Zepp et al.16 1D emission and excitation spectra were measured using 290, 340 and 475 nm as excitation wavelengths and 340, 440 and 480 nm as emission wavelengths with 0.5 s integration time and a 2.5 nm slit width.

Determination of the quantum yields was performed using the same fluorescence spectrophotometer and the excitation wavelengths were 290, 340 and 375 nm. The following standards were used: $p$-terphenyl in cyclohexane ($\Phi_0 = 0.93$) for the excitation wavelength of 290 nm,13 4,6-diamidino-2-phenylindole (DAPI) in water ($\Phi_0 = 0.043$) for the excitation wavelength of 340 nm,12 and coumarin 47 in ethanol ($\Phi_0 = 0.58$) for the excitation wavelength of 375 nm.13 Equation used to determine the quantum yields:

$$\Phi_F = \Phi_0 \frac{q_{ref}}{q_{sample}} \frac{A_{ref}/A_{sample}}{F_{ref}/F_{sample}}$$

where $\Phi_0$ = quantum yield of the reference compound, $q$ = refracting index of the solvent, $F$ = Integrated fluorescence intensity and $A$ = absorbance at the excitation wavelength.

Fluorescence decays of the samples in the sub-nanosecond and nanosecond time scales were measured using a time-correlated single photon counting (TCSPC) system consisting of a HydralHarp 400 controller and a PDL 800-D driver (PicoQuant GmbH). The samples were excited at 290 nm (spectral fwhm 20 nm) with the pulsed LED PLS 290-10 at a repetition frequency of 10 MHz and at 377 nm (spectral fwhm 1.3 nm) with the pulsed diode laser LDH-P-375 at a repetition frequency of 20 MHz driven by the PDL 800-D. The output power of the lasers were 5, 46 uW/cm2 and 0.554 mW/cm2 for 290 nm and 377 nm excitation, respectively. The interference filter was used to detect the emission at 340 nm and at 440 nm with a micro channel plate (MCP, R1564-07). The electrical signal obtained from the MCP detector is amplified by a pre-amplifier (PAM 102-M). The time resolutions of the experiments were determined to be approximately 600 ps for 290 nm and 80 ps for 375 nm (fwhm of the instrument response function (IRF)).

All measurements were carried out at room temperature and at ambient conditions.

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Crystal structure determination

The data were recorded on a Nonius Kappa CCD diffractometer equipped with an Apex II detector using graphite monochromated CuKα ($\lambda$=1.54178 Å) radiation at a temperature of 173.0 K. The data were processed with Denzo-SMN v0.97.63811 and absorption correction11 (multi-scan) was applied. The structures were solved by direct methods (SHELSXS-9710), and refinements based on F2 were made by full-matrix least squares techniques (SHELXL-9711). Hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms except for the hydroxyl and water hydrogen atoms, which were located from the difference Fourier map when possible. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 940314-940317. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Spectroscopic measurements

The steady-state absorption, fluorescence and excitation spectra of the samples were diluted in THF so that the absorption was sufficiently low (A < 0.07 at 290 and 375 nm) to prevent inner filter effect. The spectra were recorded using Perkin-Elmer LAMBDA 850 UV–Vis spectrophotometer and Varian Cary Eclipse fluorescence spectrophotometer. Excitation-emission matrix (EEM) fluorescence spectrum was obtained by concatenating emission spectra measured every 10 nm from 310 to 400 nm using excitation wavelengths ($\lambda_{ex}$) from 300 to 400 nm (10 nm intervals) with 0.5 s integration time, and a 2.5 nm slit width. The Raman scattering peaks in the EEM spectrum were corrected with a method described by R. G. Zepp et al.16 1D emission and excitation spectra were measured using 290, 340 and 375 nm as excitation wavelengths and 340, 440 and 480 nm as emission wavelengths with 0.5 s integration time and a 2.5 nm slit width.
Hey, they fluoresce!

Tiia-Riikka Tero, Kirsi Salorinne, Heli Lehtivuori, Janne A. Ihalainen and Maija Nissinen*… Page – Page

Structural Diversity of Benzofuran Resorcinarene Leads to Enhanced Fluorescence

A unique benzofuran ring modified resorcinarene derivative shows enhanced fluorescence properties compared to the conventional resorcinarene macrocycle of the mono-crown derivative.


Commercially available analogue of the benzofuran moiety of mono-crown derivative I.


The brightness values were calculated by multiplying quantum yields with absorption coefficients. The brightness of the mono-crown derivative 1 was set to 100% and the brightness of 2 is reported relative to that of 1.


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