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Photophysical properties of new anthracene-ended calix[4]resorcinols

Irina R. Knyazeva,*[a] Tatiana P. Gerasimova,[a] Ilya E. Kolesnikov,[b] Victor V. Syakaev,[a] Sergey A. Katsyuba[a] and Alexander R. Burilov[a]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 273 4872; e-mail: ihazieva@mail.ru*

[b] *Center for Optical and Laser Materials Research, St. Petersburg State University, Peterhof, 198504 St. Petersburg, Russian Federation*

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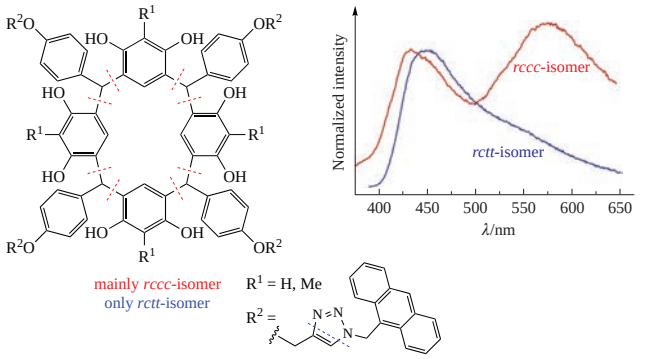
New calix[4]resorcinols with four anthracene-ended triazole-containing fragments as *rctt*- and *rccc*-diastereoisomers were obtained in two synthetic pathways, namely, by acid-catalyzed condensation of resorcinols with 4-{[1-(anthracen-9-ylmethyl)-1*H*-[1,2,3]triazol-4-yl]methoxy}benzaldehyde or by the *click* reaction of 9-(azidomethyl)anthracene with calix[4]resorcinols bearing four terminal acetylene moieties. The compounds obtained demonstrate dual emission in solid state with intensity of low energy band depending on calix[4]-resorcinol conformation. The emission in solutions is dominated by anthracene bands, with *rccc*-isomer showing additional low energy band.



Keywords: calix[4]resorcinols, click reaction, triazoles, anthracenes, emission.

Calix[4]resorcinols are macrocyclic products of acid-catalyzed condensation of resorcinols with aldehydes or acetals. The scientific interest towards them is caused by their unique reactivity features, in particular, the possibility of their easy modification by introducing various functionalized substituents affording more complex macromolecules capable of creating new supramolecular and coordination systems with unique properties.[1–3]

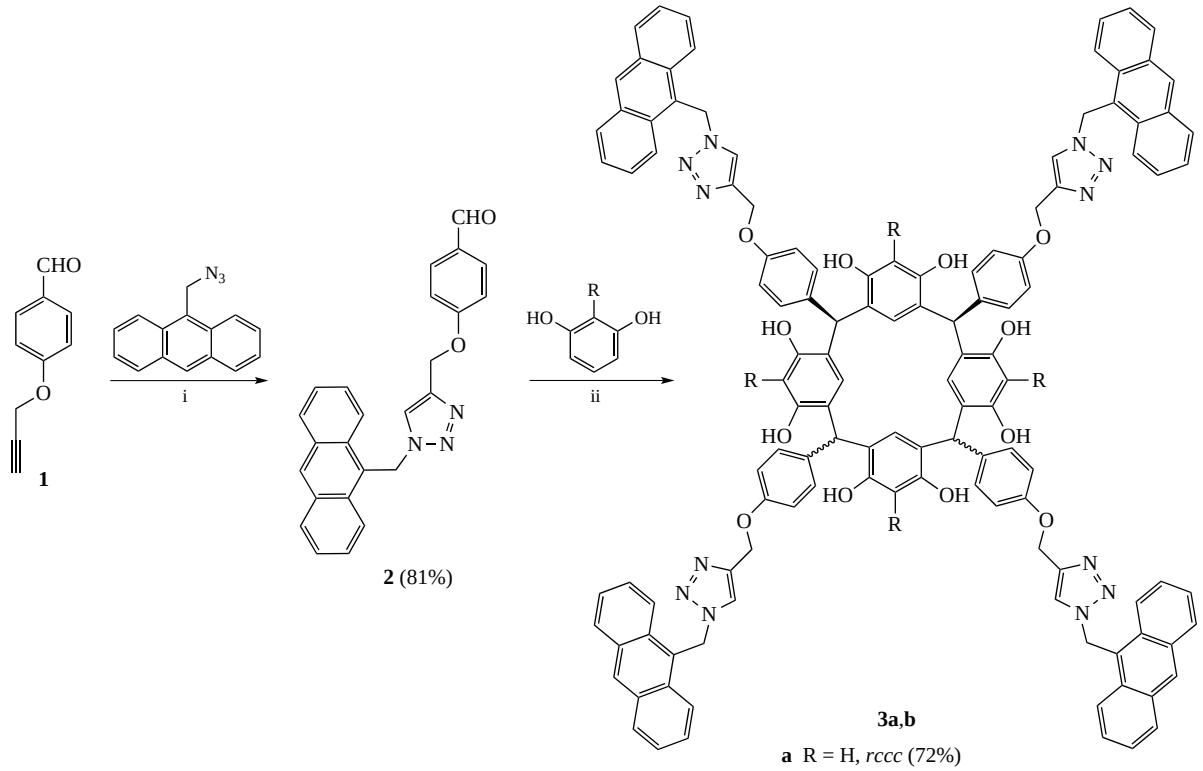
Calixarenes containing anthracene units have been found to serve as effective receptor systems for recognizing various ions and neutral molecules. For example, those with two anthracene moieties coupled with the calixarene matrix through azo- or imine bonds are selective chemosensors toward divalent metal ions such as Cd^{2+}, Cu^{2+}, Fe^{2+} (refs. 4, 5) and Ca^{2+}.[6] Antracenyl-containing azacrown calix[4]arene conjugate can act as an 'off–on' fluorescent indicator for detection of potassium ions.[7] Calix[4]arenes bearing two anthryl subunits linked to the lower rim by triazole(-ium) bridges (synthesized *via* the click reaction) are sensitive fluorescence sensors for selective recognition of picric acid[8] and nucleoside triphosphates.[9] The calixarene platform would determine the relative position of fluorophore moieties that can affect the emission properties of the latter similar to published conformation-controlled emission for tetraphenylethene-embedded pillar[5]arene.[10] The specific packing of anthracene-containing compounds can also lead to formation of excimers and appearance of additional emission that can be affected by aggregation[11,12] or pressure.[13,14]

Our investigations are focused at developing the one-step synthesis of new functionalized calix[4]resorcinols by acid-catalyzed condensation of various aldehydes or acetals, as well as vinyl phosphonates, with resorcinol and its derivatives.[15–18] In this work for the obtaining of novel calix[4]resorcinols with four anthracene-ended triazole-containing fragments, a new functionalized benzaldehyde, namely, 4-{[1-(anthracen-9-ylmethyl)-1*H*-[1,2,3]triazol-4-yl]methoxy}benzaldehyde, was introduced into the acid-catalyzed condensation with resorcinols. We also showed that the same macrocyclic products could be obtained by the click reaction of 9-(azidomethyl)anthracene with previously obtained calix[4]resorcinol derivatives equipped with four terminal alkyne groups. Both synthetic pathways are based on the efficient click approach with the use of the $CuSO_4 \cdot 5H_2O$/sodium ascorbate catalytic system and lead to the different calixarene diastereoisomers. It has been revealed that the obtained diastereomers demonstrate different photophysical properties.

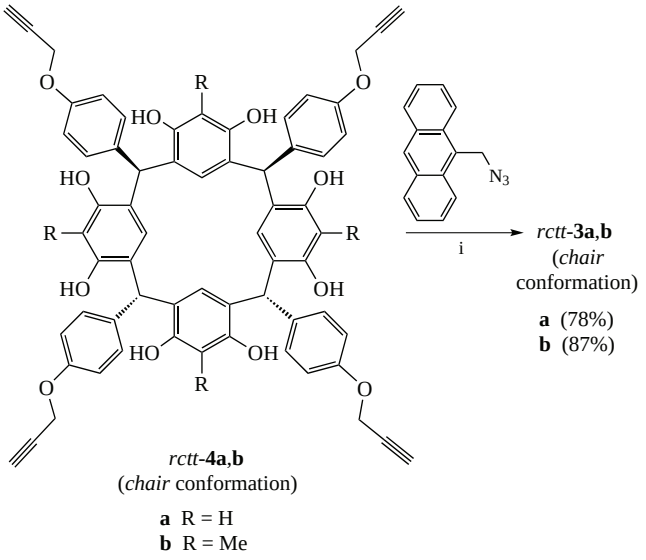
Initially, the Cu-catalyzed click reaction between 4-propargyl-oxybenzaldehyde[19] **1** and 9-(azidomethyl)anthracene[20] afforded new 4-{[1-(anthracen-9-ylmethyl)-1*H*-[1,2,3]triazol-4-yl]-methoxy}benzaldehyde **2** (Scheme 1). The subsequent acid-catalyzed condensation of aldehyde **2** with resorcinol and 2-methylresorcinol in $CHCl_3$ in the presence of trifluoroacetic acid gave the corresponding calix[4]resorcinols **3a**,**b**.

Importantly, in the case of resorcinol, the *rccc*-**3a** diastereoisomer in the *cone* conformation was obtained in a yield of 72% (see Scheme 1). When 2-methylresorcinol was used, the *rccc*-**3b** in the *cone* conformation was predominantly formed in 67% yield along with 12% of the minor *rctt*-**3b** isomer in the *chair* conformation. Due to their different solubilities, both products were separated by sequential recrystallization from acetone and ethanol.

Products with the similar compositions were alternatively obtained by the click reaction of previously synthesized *rctt*-diastereoisomers of calix[4]resorcinols **4a**,**b**[16] (*chair* conformation) having four propargyl groups with 9-(azido-methyl)anthracene (Scheme 2). The reactions proceed with the retention of the conformational features of the initial macrocycles,



Scheme 1 *Reagents and conditions*: i, $CuSO_4 \cdot 5H_2O$ (cat.), Na-ascorbate, THF, H_2O, argon, 60–65 °C, 24 h; ii, CF_3CO_2H, $CHCl_3$, argon, 45–50 °C, 24 h.



Scheme 2 *Reagents and conditions*: i, $CuSO_4 \cdot 5H_2O$, Na-ascorbate, THF, H_2O, 60–65 °C, 18 h.

and as a result, only *rctt*-diastereoisomers of the corresponding calix[4]resorcinins **3a**,**b** are formed. It should be noted that macrocyclic products obtained according to Scheme 1 are not available by protocol from Scheme 2, and *vice versa*, excluding calixresorcinol *rctt*-**3b**.

The structures of all synthesized compounds were confirmed by NMR (^{1}H, ^{13}C, HSQC, HMBC) and IR spectroscopy, mass spectrometry (MALDI-MS) and elemental analysis. Calix[4]-resorcinols are known to exist as four diastereoisomers with *rccc*-, *rcct*-, *rctt*- *and rtct*-configurations of substituents and in 1,2-*alternate*, 1,3-*alternate*, *cone* and *chair* conformations[21] depending on reaction conditions, nature of substituents and functional groups present in the molecule. In our case, each group of signals in the NMR spectra of compounds *rccc*-**3a** and *rccc*-**3b** appears as a single peak, which indicates the existence of a highly symmetrical *cone* conformation with *rccc*-configurations of substituents in the solutions. The ^{1}H and ^{13}C NMR spectra of compounds *rctt*-**3a** and *rctt*-**3b** in the *chair* conformation with *rctt*-configurations of substituents display doubling of their proton and carbon signals for the resorcinol fragments; this attests to the different, vertical (*v*) and horizontal (*h*), arrangements of opposite resorcinol rings with respect to the macrocyclic plane as was the case for analogous calix[4]-resorcinol derivatives in our previous publications (for details, see refs. 16–18, 22, 23).

We have found that the calix[4]resorcinols *rccc*-**3b** and *rctt*-**3b** with different conformations demonstrate different photophysical properties. Figure 1(*a*) represents the absorption spectra of the mentioned compounds measured in DMSO with the initial aldehyde **2**.

The absorption spectra of **2**, *rccc*-**3b** and *rctt*-**3b** in solution have a well-structured vibrational band of typical anthracene derivatives with peaks located at λ_{max} of 336, 352, 370 and 390 nm. The spectrum of *rccc*-**3b** contains additional band at 546 nm, which is absent in the spectra of **2** and *rctt*-**3b**. It should be mentioned that the UV spectra of another pair of *rccc* and *rctt*-isomers (*rccc*-**3a** and *rctt*-**3a**) also differ by the presence of additional low-energy band in the spectrum of the former (see Online Supplementary Materials, Figure S1). These low-energy bands are most probably associated with the close location of anthracene-ended triazole fragments in *rccc*-isomers (*vide infra*).

Emission spectra of the compounds have been recorded in solid state as well as in THF solution [Figures 1(*b*) and 2, respectively]. All compounds in the solid state demonstrate emission band with maximum at 425–450 nm related to anthracene. The initial aldehyde **2** demonstrates additional band at 530 nm which is much less intensive in the case of *rctt*-**3b** isomer (*chair* conformation). In contrast, the spectrum of *rccc*-**3b** isomer (*cone* conformation) contains a strong band at 580 nm. One of the possible explanation of these low energy bands is anthracene–anthracene or anthracene–triazole C–H···π interactions leading to an excimer emission due to close location

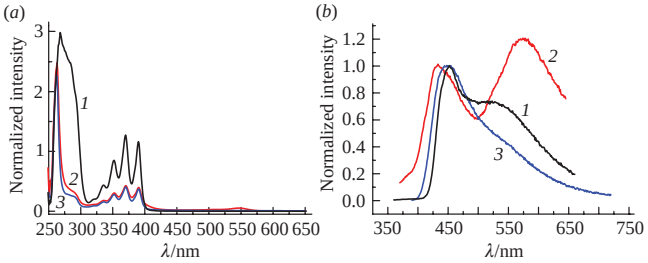


Figure 1 (*a*) Absorption spectra (C = 10^{-5} mol dm^{-3}) and (*b*) solid-state emission spectra of (*1*) aldehyde **2**, calix[4]resorcinols (*2*) *rccc*-**3b** and (*3*) *rctt*-**3b**.

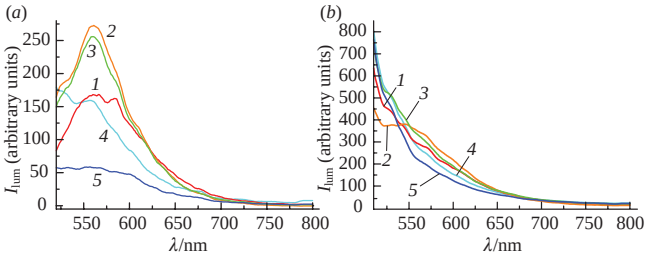


Figure 3 Emission spectra of (*a*) *rccc*-**3b** and (*b*) *rctt*-**3b** solutions in (*1*) THF, (*2*) THF:H_2O (4:1), (*3*) THF:H_2O (3:2), (*4*) THF:H_2O (2:3), (*5*) THF:H_2O (1:4); C = 10^{-4} mol dm^{-3}.

of these moieties in *cone* conformation which is avoided in *chair* conformation.[13,24–28] The molecules of aldehyde **2** most probably are arranged randomly in the solid state, although formation of similar pairs is not impossible but less likely, which leads to a decrease in the intensity of the corresponding band.

The abovementioned hypothesis is confirmed by analysis of emission in solution. Whereas excitation at 380 nm leads to the ordinary anthracene emission in the spectra of **2**, *rccc*-**3b** and *rctt*-**3b** [Figure 2(*a*)], excitation at 500 nm leads to the appearance of an additional band at ~560 nm in the spectrum of *rccc*-**3b** exclusively [Figure 2(*b*)]. Being dissolved in THF, aldehyde **2** molecules are separated and do not form excimers, and anthracene fragments in *rctt*-**3b** isomer (*chair* conformation) are able to deviate from each other, whereas *rccc*-**3b** isomer (*cone* conformation) does not enable such separation. It should be mentioned that the emission spectra of *rccc*-**3a** and *rctt*-**3a** demonstrate the similar trend: being excited at 500 nm, *rccc*-isomer emits at ~530–540 nm (see Online Supplementary Materials, Figure S2). The integral quantum yields of emission φ for compounds **3a**,**b** when excited at 366 nm are 1–4%, for aldehyde **2** it is 22%. The bands near 550 nm appearing in the spectra of compounds *rccc*-**3a** and *rccc*-**3b** are very weak, namely, the φ value measured at λ_{exc} = 488 nm is lower than 0.01%.

Further evidence in favor of aggregation-induced origin of the low-energy emission is suggested by the analysis of spectra recorded in THF/H_2O mixtures of various compositions (Figure 3). All three compounds are insoluble in water, and an addition of the latter to THF presumably initiates self-aggregation of the solutes. The admixture of water in THF leads to rather moderate changes in the emission of the solutions of **2** (see Online Supplementary Materials, Figure S1). For *rccc*-**3b** and *rctt*-**3b**, the addition of one part of water to 4 parts of THF leads to an intensification of the emission band at ~560 nm, whereas a further increase in water content leads to quenching of emission. It should be mentioned that in *rctt*-**3b** the band appears as a weak shoulder.

In conclusion, new calix[4]resorcinols with four anthracene-ended triazole-containing fragments predominantly as *rccc*-diastereoisomers have been synthesized by the one-step acid-catalyzed condensation of resorcinols with new 4-{[1-(anthracen-9-ylmethyl)-1*H*-[1,2,3]triazol-4-yl]methoxy}-benzaldehyde obtained, in turn, by the Cu-catalyzed alkyne–azide cycloaddition (click reaction). The similar products were directly synthesized *via* the click reaction of 9-(azidomethyl) anthracene with calix[4]resorcinols equipped with four propargyl groups. In this case, only *rctt*-diastereomers of the corresponding calixarenes are formed, which is determined by the conformational features of the initial macrocycles.

Compounds **2**, *rccc*-**3a**,**b** and *rctt*-**3a**,**b** demonstrate emission both in solid state and in solutions. In the solid state dual emission has been observed with wavelength and intensity of low energy band depending on calix[4]resorcinol conformation. The low energy band most probably results from formation of anthracene–anthracene or anthracene–triazole C–H···π interactions leading to an excimer emission due to close location of latter in *cone* conformation.

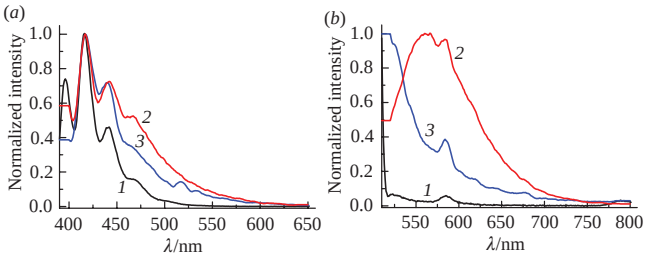


Figure 2 Emission spectra of (*1*) **2**, (*2*) *rccc*-**3b** and (*3*) *rctt*-**3b** in THF solution (C = 10^{-4} mol dm^{-3}), excitation wavelengths: (*a*) 380 and (*b*) 500 nm.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.033.

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