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PAPER

Anthracene-resorcin[4]arene-based capsules: Synthesis and photoswitchable features†

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Herein we present the synthesis and the photochemical behavior of several new hemicarcerands containing anthracene units as photoactive species. By means of NMR investigations of compounds **9** and **11** the dimerization mode was revealed as a 9,10-9′,10′-dimerization, classically known from anthracene. Nevertheless only compound **11** could be converted to the opened form upon irradiation with 300 nm. Reopening of compounds **9** and **10** could not be achieved so far either by heating or by irradiation.

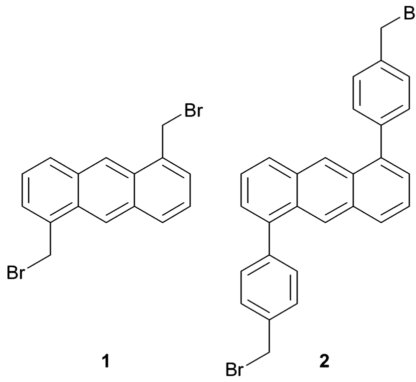
Introduction

Supramolecular chemistry is a highly fascinating research field, which was recognized publicly in 1987 by awarding the Nobel prize to Pederson, Lehn and Cram.[1] Calixarenes as a class of organic macromolecules are interesting and versatile representatives of this area. They are distinguished by their vase shaped cavity, straightforward accessibility and by the broad range of possible chemical functionalizations.[2] In addition they exhibit a strong tendency to coordinate charged as well as neutral guests *e.g.* small molecules. Resorcinarenes are one subtype of the calixarenes and are build up from the name-giving resorcinol.[3] They are extensively described in the literature in the form of their oxygen-bridged derivatives, the cavitands, to form a variety of supramolecular assemblies.[4] For many years we have undertaken research on the more flexible oxygen-methylated analogues.[5] Thereby we have also focused on the attachment of the resorcinarene scaffold to photochromic units like anthracene. Anthracene is well known to undergo a [4 + 4] cycloaddition with itself upon UV irradiation.[6] The back reaction can be conducted by irradiation with light of another wavelength or by thermal treatment of the sample. In 2004 Schäfer *et al.* published the attachment of two anthracenes on 1,3-alternate positions of the resorcinarene and utilized the photochromic behavior of the anthracene units to modulate the accessibility of the cavity.[5a–e] The authors demonstrated that upon irradiation the intramolecular dimeric form of the anthracenes was formed and they could revert the cycloaddition by means of heating the sample to 60 °C. Based on this work two dimeric capsules consisting of two resorcinarenes and two anthracene units were synthesized and their properties as switchable molecular containers were examined.[5f] Both molecules can be closed upon irradiation with UV light as expected. However the reopening of the capsules could not be achieved either by heating or by irradiation. The photochemical behavior of anthracene depends in a decisive manner on the type as well as the positions of substituents on the anthracene core.[6,7] Therefore and to reduce the sterical demand on the photoactive positions 9 and 10 we decided to switch from the 9,10-functionalized anthracenes to their 1,5-derivatized homologues as building blocks for photochromic hemicarcerands.

Results and discussion

Synthesis and characterization

Recently we reported the synthesis of several 1,5-functionalized anthracenes by means of Kumada coupling starting from 1,5-dichloroanthracene (two of them, **1** and **2**, are shown in Scheme 1).[8]



Scheme 1 Anthracene building blocks for the synthesis of supramolecular systems.[8]

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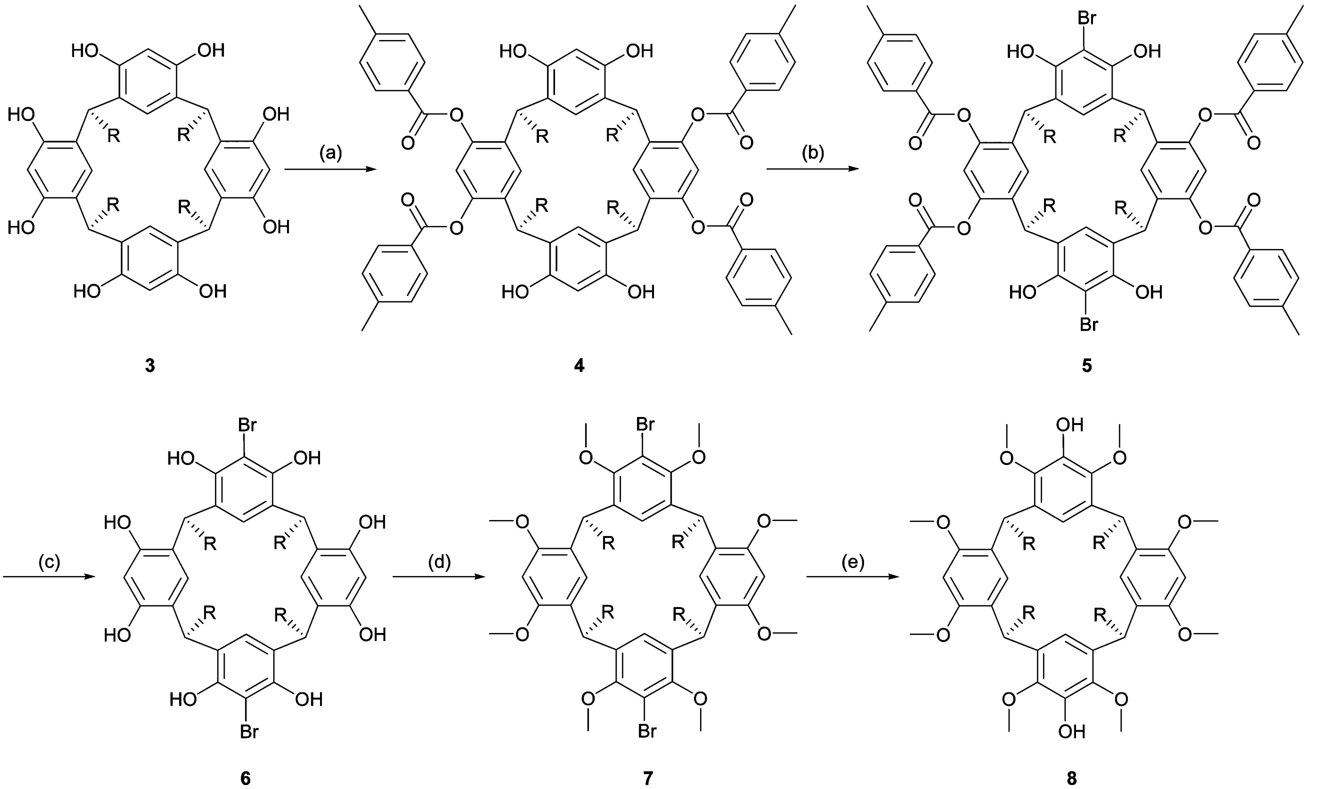
† Electronic supplementary information (ESI) available: ^{1}H-NMR spectra and ESI-MS spectra of compounds **8**, **9**, **10** and **11**; Optimized cartesian coordinates of all mentioned structures; Structure of **9** and **11**. See DOI: 10.1039/c1ob06030a



Scheme 2 Synthesis of the two-fold hydroxy-resorcinarene **8** (R = *iso*-butyl): (a) NEt_3, *p*-toluoyl chloride, CH_3CN, 26%; (b) NBS, acetone, 75%; (c) KOH, MeOH, H_2O, 74%; (d) NaH, MeI, DMF, 75%; (e) *n*-BuLi, $B(OMe)_3$, THF, H_2O_2 (30% in H_2O), NaOH, H_2O, 41%.

The molecules **1** and **2** are perfectly suited for the linkage to a resorcinarene *via* nucleophilic substitution, owing to their benzylic bromide functions. In addition Fages *et al.* reported that 1,5-functionalized anthracenes show a similar photochromic behavior like anthracene itself,[7] *i.e.* [4 + 4] cycloaddition *via* positions 9 and 10. Therefore the anthracenes **1** and **2** seem to be ideally suited for the synthesis of a photochromic, reversible hemicarcerand.

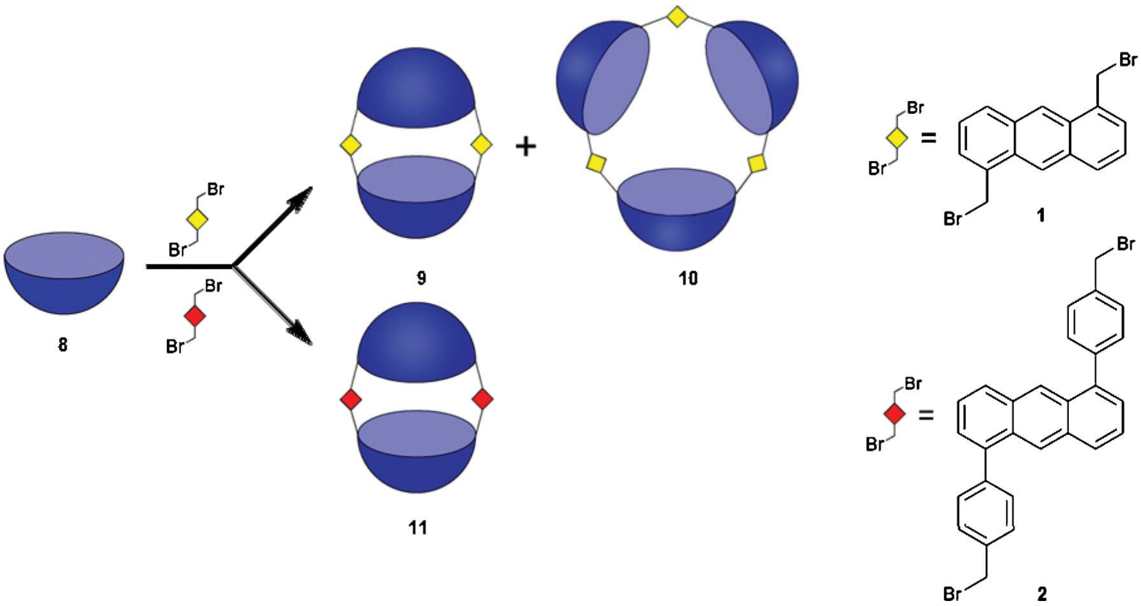
For the two-fold 1,3-functionalization of resorcinarene **3** a procedure that had already been reported before was applied (Scheme 2).[9]

The distal derivatization was realized by the introduction of four ester functions in a yield of 26%. Owing to the sterical demand of these groups the following bromination with NBS only took place on the two positions between the free hydroxy-functions and led to the dibrominated resorcinarene **5** in 75%. The esters were cleaved under basic conditions and the corresponding resorcinarene **6** was obtained with 74% yield. The methylation of the hydroxy-functions was performed under standard reaction conditions with methyl iodide and sodium hydride in DMF (75%). The subsequent formation of a boronic ester with oxidative work-up to yield the needed building block **8** for the hemicarcerand synthesis (41%) was adopted from Irwin *et al.*[10] However the reaction conditions were slightly modified, in particular the reaction times for the lithiation and the following quenching with trimethyl borate were extended (see experimental section). Though the synthesis of the corresponding cavitand was already described in 2000,[10] surprisingly compound **8** was not reported before.

The reactions between resorcinarene building block **8** and anthracenes **1** and **2** were performed in DMF with caesium carbonate as base to yield the dimeric capsules **9** and **11** as well as the trimeric capsule **10** (Scheme 3).

The capsules are directly obtained in one step instead of two consecutive reaction steps which is an advantage compared to our previous work whereby one tedious purification step *via* HPLC can be avoided. As normal for these kind of reactions the yields of the isolated products are rather low, since the formation of oligomer or polymer byproducts is inevitable. The reaction of the resorcinarene **8** with anthracene **2** afforded capsule **11** with the highest yield of 14%. Compounds **9** and **10** could only be isolated in yields of 4% and 2%, respectively. Compounds **9–11** have not been reported in the literature so far. In addition, **10** is, to the best of our knowledge, the first example of a photoreactive trimeric capsule based on calixarene units.

All compounds were characterized by means of NMR and high resolution mass spectrometry. Especially the NMR spectra in $CDCl_3$ reveal that the symmetry of the resorcinarene core unit is maintained not only in both dimers **9** and **11** but also in trimer **10**. Thus in all three cases the aromatic protons of the resorcinarene part can be assigned to three signals in the ^1H NMR spectrum exactly like for the starting macrocycle **8**. In addition the anthracene units in compounds **9** and **10** only show four distinctive aromatic signals. In the case of **11** two more signals are expected and observed in toluene-d_8 due to the protons of the additional phenyl rings. This indicates furthermore that the anthracenes are fixed symmetrically to each other.



Scheme 3 Schematic depiction of the dimer and trimer capsule formation starting from diol **8** and anthracenes **1** and **2**, respectively. Blue bowl = dihydroxyresorcinarene **8**, reaction conditions: Cs_2CO_3, DMF, **9**: 4%, **10**: 2%, **11**: 14%.

Photochemistry

The absorption spectra of compounds **9–11** in degassed toluene solution are shown in Fig. 1.

All compounds show the typical anthracene pattern of absorption bands between 300 and 425 nm. **9** and **10** display very similar absorption spectra owing to the same anthracene unit. In contrast anthracene bands of **11** are broader and shifted by *ca.* 20 nm to longer wavelengths, due to the extension of the aromatic system. Anthracene dimerization occurs in all three cases upon irradiation with 350 nm light indicated by a decrease of the anthracene signals. The cycloaddition of capsule **9** is completed within 5 min where capsule **11** needs to be irradiated for 20 min before no further changes in the spectrum can be observed. Trimer **10** shows a decrease of the anthracene bands as well, however a complete disappearance could not be observed. This behavior is expected since the photochemical reaction between two anthracenes in one capsule still leaves one anthracene subunit unreacted. An intermolecular dimerization and thus a linkage of two trimers *via* the "free" anthracene can be excluded owing to the low sample concentration of *ca.* 10^{-4} M.

A thermal reversion of the cycloaddition could not be detected in all three cases even though the dimerized samples were heated over several hours at 100–120 °C. Higher temperatures *e.g.* 160 °C led to decomposition of the compounds.

After irradiation of the macrocycles **9** and **10** with 300 nm light the cycloaddition could also not be reversed. Instead of the recovery of the anthracene bands the absorption curves are just

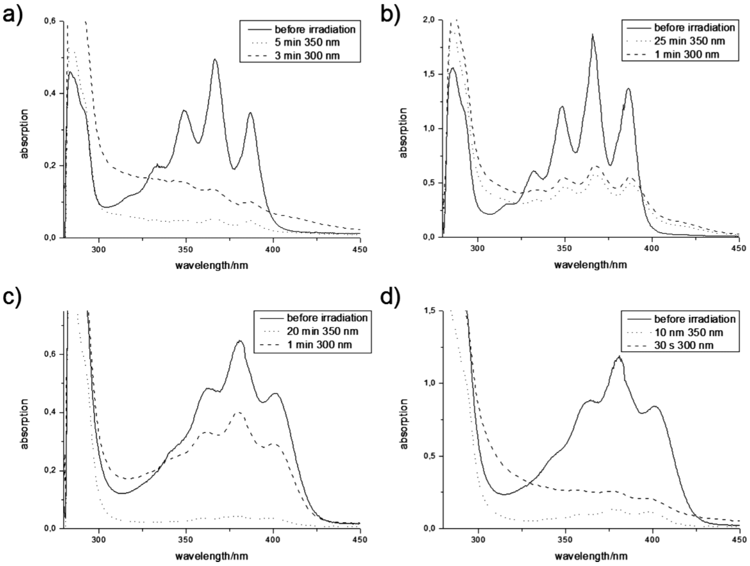


Fig. 1 UV/Vis spectra of compounds **9** (a), **10** (b) and **11** (c) in toluene and **11** in chloroform (d), $c = ca.\ 1 \times 10^{-4}$ mol L^{-1}.

lifted over the complete spectrum. This points to a decomposition of the compounds.

Compound **11** differs decisively from this behavior. Irradiation of the dimerized compound in toluene with 300 nm light leads to an increase of the anthracene bands to more than 60% of the starting intensity already after 1 min, indicating a reopening of the closed form. It is most likely that a complete reopening is not possible due to degradation processes with energy-rich 300 nm light which occurs upon further irradiation. This only leads to an increase of the absorption curve between 300 and 330 nm indicating decomposition of **11**.

An essential difference of the switching behavior occurs upon changing the solvent from toluene to chloroform. Dimerization can be conducted in chloroform just as in toluene by means of irradiation with 350 nm light indicated by the decreasing anthracene bands in the absorption spectrum (Fig. 1d). Remarkably, the cyclized form of **11** in chloroform cannot be reopened neither by heating nor by irradiation.

NMR experiments

Due to the high reactivity of **9** towards UV light the corresponding closed form of the capsule could be isolated and examined *via* NMR spectroscopy. A comparison of the ^{1}H NMR spectra of the open and the closed form points to a change in the symmetry of the resorcinarene units during the dimerization. Thus the methoxy functions display four singlets in the closed form instead of two singlets in the open form (for details see experimental part). New signals can be observed for the aromatic resorcinarene protons as well (Fig. 2, open: 3 signals, closed 5 signals). However, the signals that can be assigned to the anthracene part indicate a symmetrical arrangement of this photochromic unit in the dimerized form. The two doublets at 6.89 ppm and 6.91 ppm and the triplet at 6.73 ppm suggest that the anthracenes dimerized *via* positions 9 and 10. Other possible cycloadditions like the 9,10–1′,4′-dimerization would give rise to quite a different signal pattern.[7] As expected the photochemical reaction results in the disappearance of the signal of the directly involved protons at 8.37 ppm, due to the loss of aromaticity on the central anthracene ring in the cycloaddition. Instead these protons are shifted to higher field to give a singlet at 5.04 ppm. Summarizing the results obtained from the NMR spectrum of the closed form, dimerization of both anthracene units seems to occur between positions 9 and 10.

The process of the cycloaddition of **11** could be investigated by means of NMR spectroscopy as well. The ^{1}H NMR spectrum of **11** in toluene before and after 25 min irradiation with 350 nm is shown in Fig. 3. The signal at 8.28 ppm which is ascribed to the anthracene protons in position 9 and 10 vanishes completely after irradiation with 350 nm. Instead a new singlet at 4.58 ppm appears for these protons indicating a symmetrical dimerization. This interpretation is supported by the signals in the aromatic area. The protons of the aromatic part of the resorcinarene can be assigned to three singlets just as before irradiation. In addition, the aromatic anthracene protons only show three signals and prove

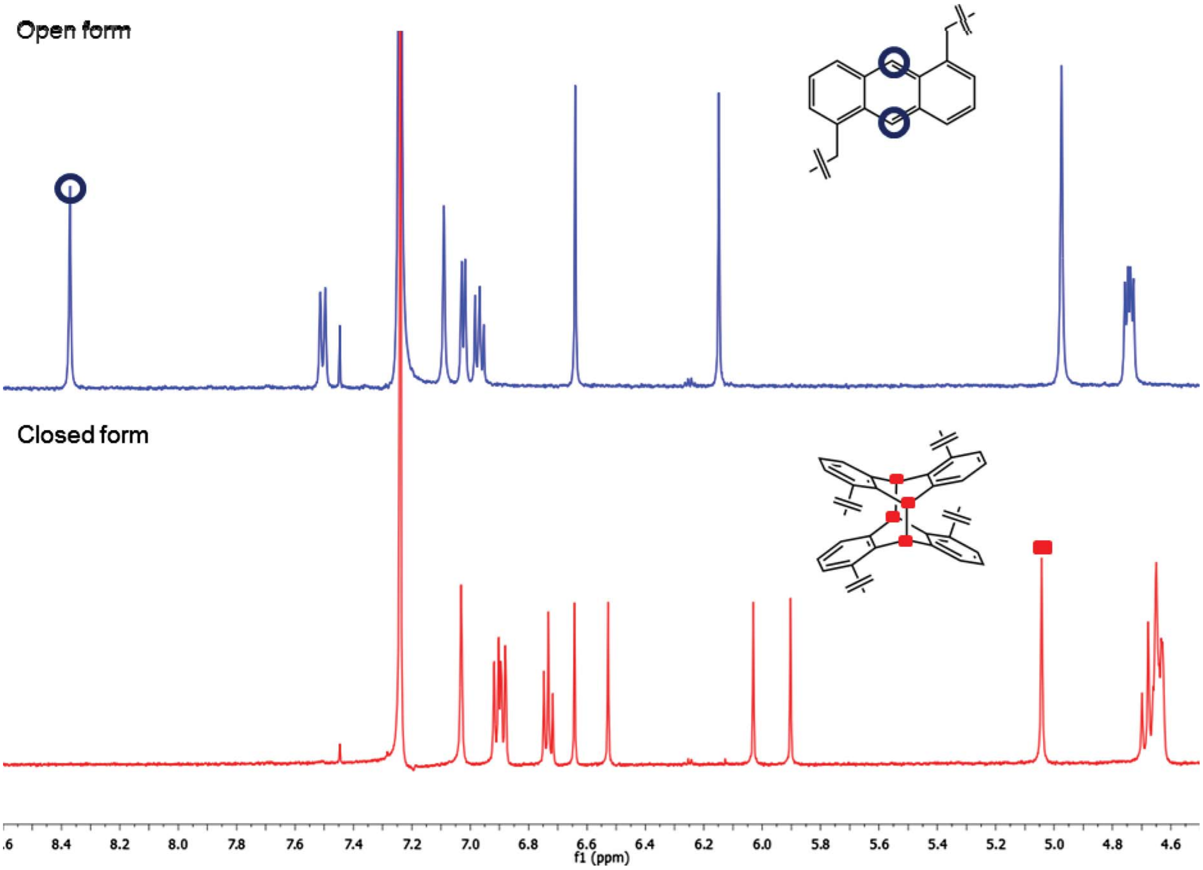


Fig. 2 NMR spectra of the open (blue) and closed form (red) of **9** in $CDCl_3$. The blue coloured circle in the upper spectrum represents the corresponding aromatic anthracene protons. In the closed form the protons at position 9 and 10 are shifted to a new signal at higher field (red rectangle).

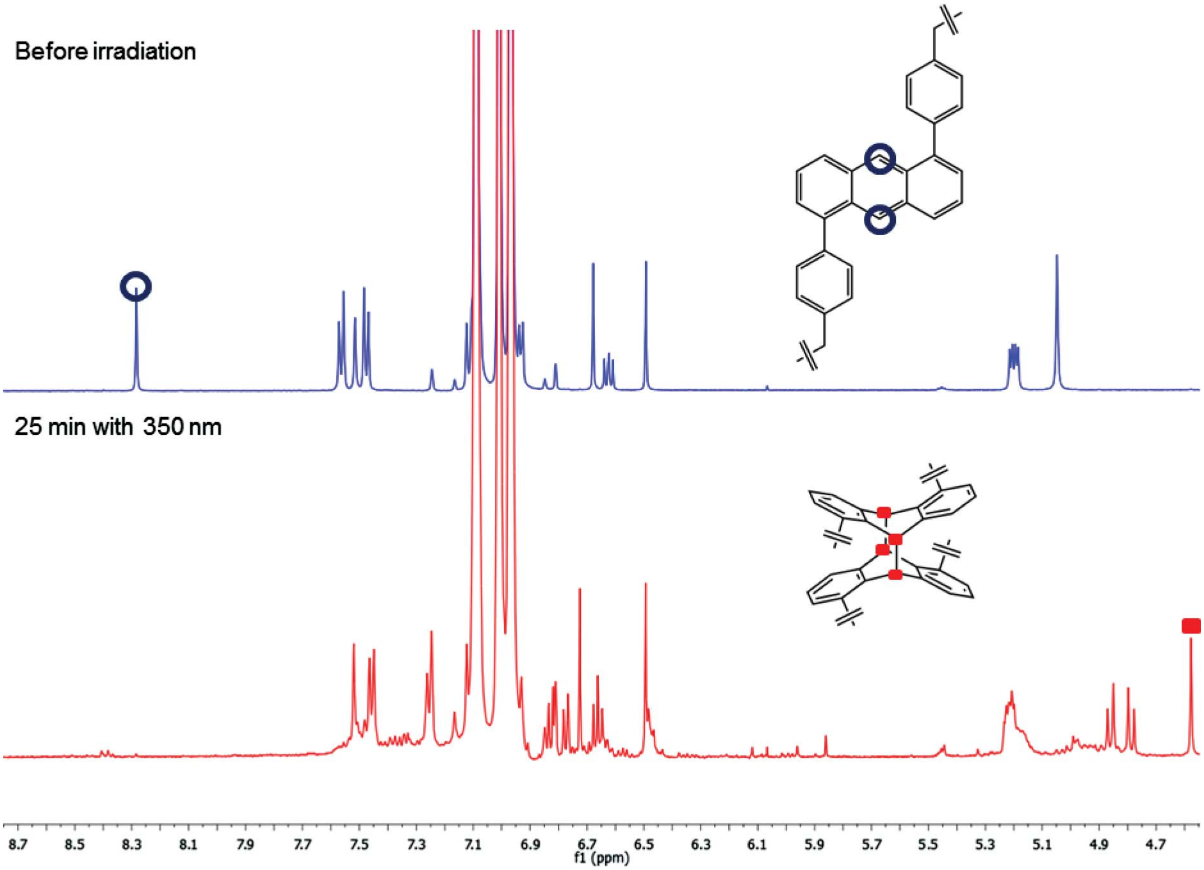


Fig. 3 NMR spectra of dimer **11** in toluene-d$_8$ before (top) and after 25 min irradiation with 350 nm light (bottom). In the upper spectrum two aromatic signals of the anthracenes are covered by the toluene-d$_8$ signal. Upon irradiation the signal for the protons at position 9 and 10 (blue circle) is shifted to higher field (red rectangle).

the 9,10–9′,10′ cycloaddition. In case of a different cyclization *e.g.* between positions 9,10 and 1′,4′ the spectrum would give rise to a more complex signal pattern. Much smaller signals mainly in the aromatic area, point to a reaction competitive to the 9,10–9′,10′ dimerization. However, due to the low intensity they cannot be assigned so far. In comparison to the 9,10–9′,10′ dimerization such a side reaction seems to be much less significant.

In principle dimerization in CDCl$_3$ shows the same behavior upon irradiation as in toluene-d$_8$. However, a complete analysis of the NMR spectrum is complicated due to the fact that a chlorination of **11** by irradiation in chloroform took place as well. By means of ESI mass spectrometry the capsule mass plus one chlorine atom could be detected after 20 min irradiation in chloroform. Therefore some unforeseen radical processes obviously took place. These side reactions could be a possible explanation for the non-reversible switching behavior in chloroform in contrast to toluene. Owing to this chloroform is not a suitable solvent for this kind of investigation. Higher masses due to an intermolecular reaction could not be observed either in chloroform or toluene.

Theoretical calculations

At the moment no crystallographic structure information is available for compounds **9–11**. To get at least some insight into the overall molecular shape and especially into the dimensions available for potential guest molecules we examined one conformation isomer of **11** with KS-DFT calculations. We focused on **11** since this is the only compound that shows the desired reversible switching behavior. The DFT-calculations were conducted for the derivative of **11** wherein the *iso*-butyl groups are exchanged against methyl functions.

Because of **11**'s comparatively large number of atoms we chose as theoretical method the BP86[11a,11b] local density functional in combination with the Stuttgart-Dresden pseudo potentials and associated double zeta quality basis set,[12] SDD, without polarization functions (thereby reducing significantly the number of used basis functions). Although neglecting polarization functions is normally not advisable we checked that missing polarization functions have no effect on the structurally important phenyl–arene dihedral angles (by comparing the BP86-D/SDD and RIMP2/def2-TZVP equilibrium structures of the model compound α-phenylnaphthalene) and no significant effect on internuclear distances (carbon–carbon internuclear distances are underestimated at maximum by 1.5 pm with respect to the RIMP2/def2-TZVP optimized structure; we expect no larger errors for internuclear distances in the resorcinarene unit of **11**). Overall, the BP86/SDD method seems to be accurate enough for the purpose of estimating structural parameters of **11**.

A priori it was unclear if there are attractive non-bonding interactions between **11**'s anthracene units and maybe even between the phenylene rings bonded to the anthracene units. Therefore we re-optimized the obtained BP86/SDD stationary point using the BP86-D/SDD method (the BP86/SDD method in combination with Grimme's empirical vdW-correction[13a,13b] for KS-DFT). Unfortunately, a (numerical) normal coordinate analysis for this BP86-D/SDD stationary point is computationally very expansive (as the used ORCA programme[14] has no analytical second derivatives implemented) and was therefore omitted. Additionally, also the normal mode analysis of the BP86/SDD stationary point turned out to be impossible because of an internal error of the used Gaussian03 programme[15] (too many ECP integrals in the programme part for calculation of the Hessian). Nevertheless, we are optimistic that both structures shown in Fig. 4 are local minima on their respective potential energy surfaces as we observed no negative eigenvalues of the approximate Hessians obtained during the structure optimization.

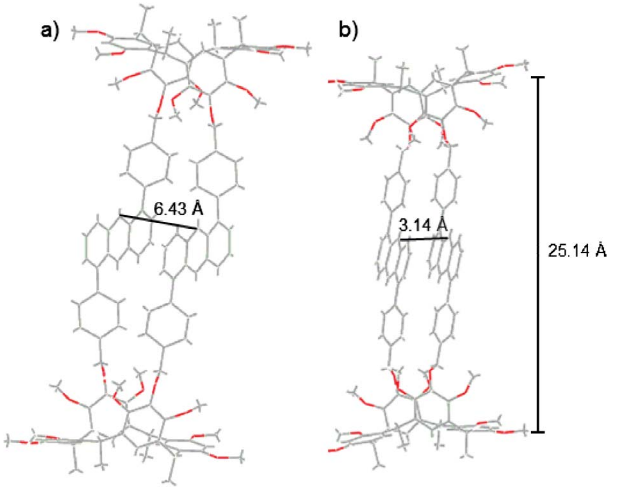


Fig. 4 Stick representations of the obtained (a) BP86/SDD (no dispersion correction) and (b) BP86-D/SDD (with dispersion correction) stationary point, respectively.

Fig. 4 shows stick representations of the obtained stationary points: on the left hand side without dispersion correction and on the right hand side with dispersion correction. In the conformation isomer obtained from the dispersion corrected BP86-D calculation the parallel oriented anthracene units are roughly at right angle with the phenyl ring planes of the resorcinarene while in the BP86 conformation isomer this dihedral angle is only approx. 45 degrees. The whole molecule is of roughly cylindrical shape with a length of approximately 25.14 Å. Without the dispersion correction the distance between the two planes containing the anthracene carbon nuclei is approximately 6.43 Å and with dispersion correction it shrinks to approximately 3.14 Å. Taking the carbon atom's van der Waals radius of 1.70 Å into account the space between the anthracene units available for a guest has a diameter of roughly 4.73 Å in the structure without dispersion correction while in the structure with dispersion correction no space at all is available. In the BP86 calculation without dispersion correction there are no attractive but (Pauli) repulsive forces between the anthracene subunits. Therefore this theoretical conformation isomer will be more or less similar to the structure of **11** containing a not too large guest between the anthracene subunits. The structure obtained from the dispersion-corrected BP86 calculation should be nearly identical to pure **11**'s equilibrium structure in the gas phase or solid state.

If the attractive interaction between the anthracene units is not disturbed by a guest or a solvent the precoordination between the anthracenes may lead to a preferred dimerization between positions 9 and 10. This could be an explanation for the fact that dimerization of capsule **11** mainly leads to a symmetrical dimer as proven by NMR-experiments shown in the last section.

Optimized cartesian coordinates of all mentioned structures are given in the ESI.†

Conclusions

In conclusion, we present the synthesis of three new macrocyclic capsules based on resorcinarene units and anthracene linkers. All three compounds dimerize upon irradiation with 350 nm but only capsule **11** can be reopened by means of exposure to 300 nm light in toluene to more than 60%. Investigation of the dimerization behavior in NMR indicates that both compounds, **9** and **11**, dimerize "classically" *via* positions 9 and 10 as known from anthracene itself.

This is the first example in the literature where the shape of an anthracene-calixarene-based capsule like **11** can be switched reversibly by irradiation at different wavelengths. In addition, the closed form is stable at room temperature and even at elevated temperatures since a thermal back reaction was never observed. Our future objective is to improve the efficiency of the reopening and to investigate the effects of dimerization on the coordination of smaller molecules. Since the shape of the inner cavity of **11** can be controlled by light a number of interesting applications, *e.g.* light-driven reactions or host–guest interactions inside the supramolecular system, are thinkable.

Experimental section

General remarks

All commercially available compounds were purchased from Acros, Alfa Aesar or Sigma-Aldrich and were used without further purification. Dibromoresorcinarene **7** needed for the synthesis of **8** was synthesized according to literature.[9] Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (0.040–0.063 mm, Macherey–Nagel). All HPLC separations were conducted on a Kontron Instruments system using an UV/VIS detector (observing at 280 nm and 365 nm) and a silica gel column from Machery–Nagel.

NMR spectra were recorded on a 500 MHz NMR spectrometer (Bruker, DRX500). Spectra were referenced to solvent peaks ($CDCl_3$ = 7.24 ppm (^1H), 77.0 ppm (^{13}C), DMSO-d_6 = 2.49 ppm (^1H), 39.52 ppm (^{13}C), CD_2Cl_2 = 53.80 ppm (^{13}C), toluene-d_8 = 7.09 ppm (^1H), acetone-d_6 = 29.84 ppm). HRMS spectra were performed using a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer Bruker APEX III. Irradiations at 350 nm and 300 nm were carried out in a rayonet reactor. Absorption spectra were recorded with a Perkin-Elmer Lambda 40 spectrometer.

rccc-5,17-Dihydroxy-4,6,10,12,16,18,22,24-octa-*O*-methyl-2,8,14,20-tetra(*iso*-butyl)-resorcin[4]arene (8)

Before the reaction was started *rccc*-5,17-Dibromo-4,6,10,12,16,18,22,24-octa-*O*-methyl-2,8,14,20-tetra(*iso*-butyl)-resorcin[4]arene (**7**, 500 mg, 0.509 mmol, 1eq) was transferred into a flame dried flask and treated with dry THF (5 mL). The solvent was removed in vacuum and the residue was dried in vacuum for 45 min at 80 °C. This procedure was performed three times. The remaining solid (489 mg, 0.497 mmol, 1 eq) was dissolved in 30 mL dry THF, cooled to −78 °C (acetone, dry ice bath) and treated with n-butyllithium (1.27 mL, 2.04 mmol, 1.6 M in hexane, 4.1 eq). After 2 h stirring at this temperature freshly distilled trimethyl borate (0.29 mL, 2.5 mmol, 5.0 eq) was added, the cooling bath was removed and the mixture was stirred over night at room temperature. 6.0 mL of a 1 : 1 mixture of aqueous hydrogen peroxide (30%) and sodium hydroxide solution (3 M) were added under ice cooling on the next day. After the ice bath was removed the solution was stirred over night at room temperature (formation of a colourless solid). Afterwards aqueous sodium bisulfite solution (50 mL, 1 M) was carefully (!) added at 0 °C. The reaction mixture was extracted with ethyl acetate (3 × 40 mL), the combined organic phases washed with aqueous sodium bisulfite solution (2 × 40 mL, 1 M), saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), brine (1 × 40 mL) and dried over magnesium sulfate. After evaporation of the solvent the raw product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 7 : 3; raw product was dissolved in ethylacetate and adsorbed onto silica gel; R_f 0.10). Yield: 173 mg (0.202 mmol, 40%; corrected yield because a small amount of ethyl acetate could not be removed in vacuum); mp = 224 °C; δ_H (CDCl$_3$, [ppm]) = 0.89 (d, ^3J = 6.5 Hz, 24H, *iso*-butyl CH$_3$), 1.45–1.54 (m, 4H, *iso*-butyl CH), 1.65–1.70 (m, 8H, *iso*-butyl CH$_2$), 3.54 (s, 12H, OCH$_3$), 3.66 (s, 12H, OCH$_3$), 4.62 (t, ^3J = 7.6 Hz, 4H, Ar-CH-Ar), 5.26 (s, 2H, OH), 6.27 (s, 2H, ArH), 6.34 (s, 2H, ArH), 6.68 (s, 2H, ArH); δ_C (acetone-d$_6$, [ppm]) = 22.75, 22.78, 25.81, 33.55, 44.63, 55.83, 60.30, 96.40, 116.65, 125.66, 126.59, 133.42, 141.46, 143.64, 155.76; HRMS (ESI): *m*/*z* calc. for [$C_{52}H_{72}O_{10}$ + Na]$^+$: 879.50177; found: 879.50045.

Dimer 9 and trimer 10

1,5-Bis(bromomethyl)anthracene (**1**, 85 mg, 0.23 mmol, 1 eq) and *rccc*-5,17-dihydroxy-4,6,10,12,16,18,22,24-octa-*O*-methyl-2,8,14,20-tetra(*iso*-butyl)-resorcin[4]arene (**8**, 200 mg, 0.233 mmol, 1 eq) were dissolved in 20 mL dry DMF in a flame dried flask under argon and light exclusion. Caesium carbonate (1.52 g, 4.67 mmol, 20 eq) was added, the solution was stirred for 1 h at room temperature and afterwards 4 d at 60 °C. The mixture was filtered and the DMF was removed in vacuum. The residue was dissolved in dichloromethane (80 mL) and water (50 mL). After phase separation the aqueous phase was extracted with dichloromethane (2 × 50 mL). The combined organic phases were washed with water (2 × 80 mL) and brine (1 × 80 mL) and dried over magnesium sulfate. The dissolved crude product was adsorbed onto silica gel und purified by means of column chromatography (cyclohexane/ethyl acetate 85 : 15) and HPLC (cyclohexane/ethyl acetate 9 : 1, R_f = a) dimer **9**: 0.22, b) trimer **10**: 0.25). The reaction and the work up should be conducted under light exclusion! Yield a) dimer **9**: 8.0 mg (3.8 μmol, 4%), b) trimer **10**: 6.0 mg (1.9 μmol, 2%).

Dimer 9. λ_{max}(toluene)/nm 283 (ε/dm^3 mol^{-1} cm^{-1} 4600), 292sh (3500), 316 (1100), 334 (2000), 349 (3500), 366 (4900) and 387 (3400); δ_H (CDCl$_3$, [ppm]) = 0.95 (dd, ^3J = 12.8 Hz, 6.3 Hz, 48H, *iso*-butyl CH$_3$), 1.54–1.64 (m, 16H, *iso*-butyl CH$_2$), 1.91–1.99 (m, 8H, *iso*-butyl CH), 3.21 (s, 24H, OCH$_3$), 4.02 (s, 24H, OCH$_3$), 4.74 (dd, ^3J = 9.5 Hz, 5.0 Hz, 8H, Ar-CH-Ar), 4.97 (s, 8H, anthracene-CH$_2$), 6.15 (s, 4H, ArH), 6.64 (s, 4H, ArH), 6.97 (dd, ^3J = 8.1 Hz, 6.8 Hz, 4H, anthracene-ArH), 7.02 (d, ^3J = 5.5 Hz, 4 H, anthracene-ArH), 7.09 (s, 4H, ArH), 7.50 (d, ^3J = 8.5 Hz, 4H, anthracene-ArH), 8.37 (s, 4H, anthracene-ArH); δ_C (CDCl$_3$, [ppm]) = 22.20, 23.72, 25.80, 26.90, 33.58, 44.29, 56.13, 60.48, 72.75, 95.47, 120.59, 123.13, 123.88, 126.66, 127.15, 128.61, 129.13, 129.32, 131.22, 131.81, 132.94, 145.49, 150.98, 155.10.

HRMS (ESI): *m*/*z* calc. for [$C_{136}H_{164}O_{20}$ + Na$_2$]$^{2+}$: 1081.58002; found: 1081.58112.

Trimer 10. λ_{max}(toluene)/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 15600), 292sh (11700), 317 (3100), 332 (6100), 349 (12100), 366 (18700) and 386 (13700); δ_H (CDCl$_3$, [ppm]) = 0.90 (d, ^3J = 5.8 Hz, 36H, *iso*-butyl CH$_3$), 0.95 (d, ^3J = 5.9 Hz, 36H, *iso*-butyl CH$_3$), 1.20–1.32 (m, 12H, *iso*-butyl), 1.50–1.53 (m, 12H, *iso*-butyl), 1.84–1.92 (m, 12H, *iso*-butyl), 3.11 (s, 36H, OCH$_3$), 3.92 (s, 36H, OCH$_3$), 4.73 (dd, ^3J = 8.9 Hz, 5.4 Hz, 12H, Ar-CH-Ar), 5.20 (s, 12H, anthracene-CH$_2$), 6.30 (s, 6H, ArH), 6.54 (s, 6H, ArH), 6.91 (dd, ^3J = 8.3 Hz, 6.9 Hz, 6H, anthracene-ArH), 7.07 (s, 6H, ArH), 7.16 (d, ^3J = 6.7 Hz, 6H, anthracene-ArH), 7.55 (d, ^3J = 8.5 Hz, 6H, anthracene-ArH), 8.56 (s, 6H, anthracene-ArH). δ_C (CDCl$_3$, [ppm]) = 22.41, 23.49, 25.74, 26.90, 33.03, 44.73, 56.08, 60.22, 72.92, 95.43, 120.44, 123.30, 124.32, 125.87, 126.92, 128.34, 129.11, 129.56, 131.68, 131.97, 133.30. 145.38, 150.70, 155.02.

HRMS (ESI): *m*/*z* calc. for [$C_{204}H_{246}O_{30}$ + Na]$^+$: 3198.76162; found: 3198.78411.

Dimer 11

Same procedure as for the synthesis of **9** and **10**. The used substances were: 1,5-bis(4-bromomethylphenyl)anthracene (**2**, 80 mg, 0.16 mmol, 1 eq), *rccc*-5,17-dihydroxy-4,6,10,12,16,18,22,24-octa-*O*-methyl-2,8,14,20-tetra(*iso*-butyl)-resorcin[4]arene (**8**, 133 mg, 0.155 mmol, 1 eq), caesium carbonate (1.01 g, 3.10 mmol, 20 eq). The reaction and the work up should be conducted under light exclusion! Yield: 27 mg (11 μmol, 14%); R_f 0.21 (cyclohexane/ethyl acetate 9 : 1); λ_{max}(toluene)/nm 283 (ε/dm^3 mol^{-1} cm^{-1} 13500), 292sh (8400), 341sh (2700), 362 (4800), 381 (6500) and 402 (4700); δ_H (CDCl$_3$, [ppm]) = 0.96 (d, ^3J = 6.4 Hz, 24H, *iso*-butyl CH$_3$), 1.00 (d, ^3J = 6.4 Hz, 24H, *iso*-butyl CH$_3$), 1.51–1.66 (m, 16H, *iso*-butyl CH$_2$), 1.92–2.00 (m, 8H, *iso*-butyl CH), 3.41 (s, 24H, OCH$_3$), 3.97 (s, 24H, OCH$_3$), 4.75 (dd, ^3J = 9.2 Hz, 5.6 Hz, 8H, Ar-CH-Ar), 4.83 (s, 8H, anthracene-CH$_2$), 6.16 (s, 4H, ArH), 6.58 (s, 4H, ArH), 6.73 (dd, ^3J = 8.3 Hz, 6.9 Hz, 4H, anthracene-ArH), 6.96 (d, ^3J = 6.5 Hz, 4H, anthracene-ArH), 7.13 (s, 4H, ArH), 7.33 (d, ^3J = 8.6 Hz, 4H, anthracene-ArH), 7.39–7.45 (m, 16H, anthracene-ArH), 8.14 (s, 4H, anthracene-ArH); δ_H (toluene-d$_8$, [ppm]) = 1.11 (d, ^3J = 6.4 Hz, 24H, *iso*-butyl CH$_3$), 1.14 (d, ^3J = 6.3 Hz, 24H, *iso*-butyl CH$_3$), 1.82–1.93 (m, 16H, *iso*-butyl CH$_2$), 2.24–2.32 (m, 8H, *iso*-butyl CH), 3.64 (s, 24H, OCH$_3$), 3.69 (s, 24H, OCH$_3$), 5.05 (s, 8H, anthracene-CH$_2$), 5.20 (dd, ^3J = 10.1 Hz, 4.6 Hz, 8H, Ar-CH-Ar), 6.49 (s, 4H, ArH), 6.62 (dd, ^3J = 8.3 Hz, 6.9 Hz, 4H, anthracene-ArH), 6.68 (s, 4H, ArH), 7.48 (d, ^3J = 8.0 Hz, 8H, anthracene-ArH), 7.52 (s, 4H, ArH), 7.56 (d, ^3J = 8.0 Hz, 8H, anthracene-ArH), 8.28 (s, 4H, ArH), two signals of the anthracene moiety are covered by the residual proton signals of toluene-d_8. δ_C ($CDCl_3$, [ppm]) = 11.09, 14.09, 22.38, 23.08, 23.32, 23.60, 25.76, 30.10, 33.38, 41.95, 44.34, 56.11, 60.54, 65.31, 74.13, 95.25, 120.46, 124.01, 124.37, 126.11, 126.91, 127.50, 127.83, 128.54, 128.84, 129.96, 131.28, 131.93, 137.29, 138.51, 139.84, 145.54, 150.73, 154.97.

HRMS (ESI): *m/z* calc. for $[C_{160}H_{180}O_{20} + (NH_4)_2]^{2+}$: 1228.68722; found: 1228.68891.

Irradiation of 9, 10 and 11

Solutions of **9**, **10** and **11** (c = *ca.* 1×10^{-4} mol L^{-1}) in toluene were filled into a quartz glass cuvette and degassed for 15 min by bubbling argon through the solution *via* cannula. The sealed sample was placed in a 350 nm photoreactor and irradiated. The closed forms were subsequently irradiated in a 300 nm photoreactor.

For NMR investigation of the dimerization process, dimer **11** was dissolved in chloroform ($c = 5.2 \times 10^{-4}$ mol L^{-1}) and toluene ($c = 6.2 \times 10^{-4}$ mol L^{-1}), respectively. The solutions were degassed for 15 min as described above with argon and irradiated in a sealed quartz glass cuvette (for the chloroform solution) or directly in a NMR tube (for the toluene solution). The process of the dimerization was checked by means of ^1H NMR measurements.

Closed form of **9** in chloroform

δ_H ($CDCl_3$, [ppm]) = 0.93 (t, ^3J = 5.7 Hz, 48H, *iso*-butyl CH_3), 1.43–1.49 (m, 8H, *iso*-butyl CH_2) 1.57–1.65 (m, 8H, *iso*-butyl CH_2), 1.87–2.00 (m, 8H, *iso*-butyl CH), 3.21 (s, 12H, OCH_3), 3.48 (s, 12H, OCH_3), 3.94 (s, 12H, OCH_3), 4.01 (s, 12H, OCH_3), 4.62–4.71 (m, 16H, Ar-CH-Ar, anthracene-CH_2), 5.04 (s, 4H, anthracene dimer-9,10-H), 5.90 (s, 2H, ArH), 6.03 (s, 2H, ArH), 6.53 (s, 2H, ArH), 6.64 (s, 2H, ArH), 6.73 (t, ^3J = 7.5 Hz, 4H, anthracene dimer-ArH), 6.89 (d, ^3J = 7.4 Hz, 4H, anthracene dimer-ArH), 6.91 (d, ^3J = 7.7 Hz, 4H, anthracene dimer-ArH), 7.03 (s, 4H, ArH).

Closed form of **11** in toluene

δ_H ($CDCl_3$, [ppm]) = 1.11 (dd, ^3J = 12.1 Hz, 6.1 Hz, 48H, *iso*-butyl CH_3), 1.80–1.91 (m, 16H, *iso*-butyl CH_2), 2.23–2.32 (m, 8H, *iso*-butyl CH), 3.55–3.63 (m, 24H, OCH_3), 3.65–3.72 (m, 24H, OCH_3), 4.58 (s, 4H, anthracene dimer-9,10-H), 4.79 (d, ^2J = 10.2 Hz, 4H, anthracene-CH_2), 4.86 (d, ^2J = 10.1 Hz, 4H, anthracene-CH_2), 5.15–5.24 (m, 8H, Ar-CH-Ar), 6.49 (s, 4H, ArH), 6.66 (t, ^3J = 7.5 Hz, 4H, anthracene dimer-ArH), 6.73 (s, 4H, ArH), 6.77 (d, ^3J = 7.6 Hz, 4H, anthracene dimer-ArH), 6.83 (d,^3J = 7.6 Hz, 4H, anthracene dimer-ArH), 7.25 (d,^3J = 7.9 Hz, 8H, anthracene dimer-ArH), 7.46 (d, ^3J = 7.7 Hz, 8H, anthracene dimer-ArH), 7.52 (s, 4H, ArH).

Closed form of **11** in chloroform

Owing to the complexity of the obtained spectrum a precise assignment of the signals is not possible.

Computational details

The BP86/SDD calculations were performed with the Gaussian03 programme[15] using the "ultrafinegrid" accuracy in numerical integration, automatically generated auxiliary basis set for charge density fitting, de-activated fast multiple method and standard convergence criteria in the SCF convergence and structure optimization, resulting in a relative accuracy of the electronic energy of 1×10^{-7} a.u. The structure optimization took place under constraint of C_i symmetry.

The BP86-D/SDD calculations were performed with the ORCA programme[14] using the "grid6, nofinalgrid" accuracy in numerical integration, the SV/J auxiliary basis set for charge density fitting (taken from the programme's internal basis set database), "scfconv7" SCF convergence criteria and standard convergence criteria in structure optimization, resulting in a relative accuracy of the electronic energy of 5×10^{-7} a.u. No symmetry constrained was used (not possible in the used programme version) but as the starting structure was C_i-symmetric the obtained equilibrium structure is also approximately C_i-symmetric.

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