

## Cyclotetraazocarbazole – a multichromic molecule†‡

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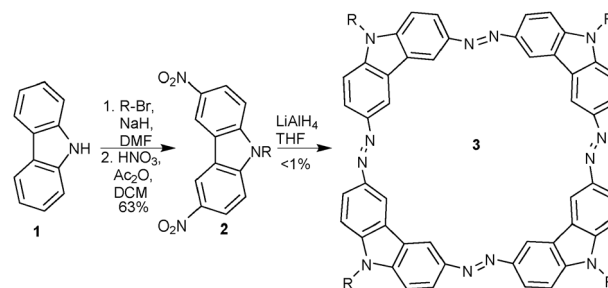
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A macrocyclic cyclotetraazocarbazole was prepared. Surprisingly, during the investigation of its photochromic behavior a drastic color change from yellow to green upon irradiation in chlorinated solvents was observed, which was temperature dependent and could also be induced by acid/base addition. With these three inputs an integrated molecular logic gate including an OR, a NOT and an AND function was build.

Controlling function at the molecular level opens immense possibilities in all areas of science, but also in our day-to-day life.<sup>1,2</sup> Therefore, we initiated a research program for the preparation of multiphotochromic macrocyclic switches based on the azobenzene scaffold.<sup>3</sup> These structures offer the possibility to access multiple different isomers,<sup>4</sup> which allow creation of higher order switches with more than two states, as we could recently show.<sup>5</sup> Additionally, the cyclic arrangement<sup>6</sup> forces the geometry to deviate from the preferred planarity. Ideally, a bowl-shaped structure will be adopted allowing the creation of a molecular gripper.<sup>7,8</sup> Unfortunately, the macrocyclic cyclotrisazobiphenyl switches prepared so far by our group were too flexible due to the rotability around the biphenyl unit to allow the efficient build-up of a cavity by *E* → *Z* transformation.<sup>4</sup> To overcome this limitation it was envisioned to bridge the biphenyl unit to block rotation. As a bridging unit the *N*-Alkyl group was chosen, as it allows attachment of solubilizing groups without creating stereochemical issues leading to a cyclooligoazocarbazole target structure.

In a first attempt to prepare such an azocarbazole macrocycle a stepwise strategy *via* Mills reactions (condensation of an aromatic amine with a nitroso compound)<sup>9,10</sup> was planned. Unfortunately, the Mills reaction was not successful and none of the desired azocompounds were observed. Therefore, the strategy was changed and a reductive coupling of 3,6-dinitrocarbazole (2) envisioned (Scheme 1).<sup>11</sup> Firstly, carbazole (1) was substituted with 1-bromododecane. Secondly, it was nitrated at the favored 3,6-positions.



Scheme 1 Synthesis of macrocycle 3 (R = C<sub>12</sub>H<sub>25</sub>).

This transformation led to the literature known 3,6-dinitro-9-dodecyl-9H-carbazole (2).<sup>12,13</sup> Finally, macrocycle 3 could be isolated from a one-pot reaction using LiAlH<sub>4</sub> as a reducing agent in <1% yield (Scheme 1). The major products of the final cyclization were linear polymers. Isolation of the cyclic product turned out to be difficult and could finally be achieved by column as well as recycling gel permeation chromatography.

In order to test our initial hypothesis to create a molecular switchable container a sample of macrocycle 3 was irradiated in chloroform with UV-light at 302 nm (hand held UV-lamp: UVP, 3UV-38 3UV Lamp, 8 Watt). Surprisingly, the color of the solution changed from yellow to a deep green and finally to almost colorless (Fig. 1).

To quantify this unexpected color change the process was followed by UV/VIS-spectroscopy (Fig. 2). Initially, an increase in the maximum at 420 nm could be observed after irradiation for 2 min. Further irradiation at 302 nm led to a decrease in the maximum at 420 nm but an appearance of a new absorption band at 570 nm. When irradiation was continued, the absorption

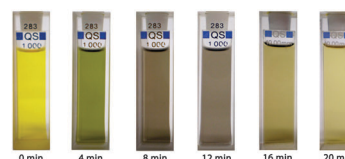


Fig. 1 Color change when macrocycle 3 was irradiated with UV-light ( $3 \times 10^{-5}$  M solution in CHCl<sub>3</sub>).

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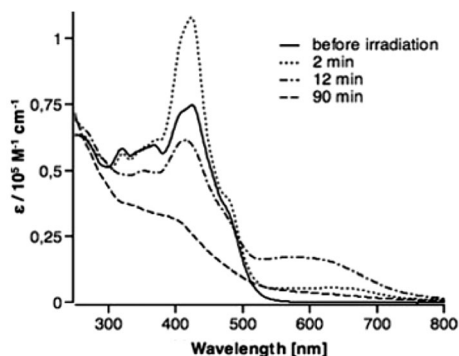


Fig. 2 UV/VIS-spectra of macrocycle 3.

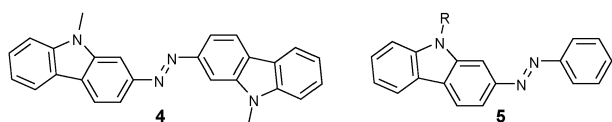


Fig. 3 Linear azocarbazoles 4 and 5.

decreased in the whole visible area of the spectrum. The latter behavior was most probably due to the decomposition of macrocycle 3 because the process was no longer reversible. If irradiation was stopped after 10 min, the green color was stable for days in an open flask. Analysis by  $^1\text{H}$  NMR spectroscopy only showed a broadening of the signal excluding the possibility of isomerization. However, attempts to isolate the green species on silica gel restored immediately the initial yellow color and produced a  $^1\text{H}$  NMR spectrum identical to that of the starting compound. In order to elucidate if this unanticipated property results due to the macrocyclic arrangement or the special features of the carbazoles two additional azocarbazole substrates were prepared, the bisazocarbazole 4 (ref. 14) and the azophenylcarbazole 5 (Fig. 3; see ESI† for synthesis details).

When a solution of dimer 4 in chloroform was irradiated with UV-light a similar effect was observed in the absorbance spectrum. The color changed from yellow to light green and a new absorption band at 610 nm was observed. Also, the absorption of 4 decreased in the whole visible area, when irradiation was continued. Irradiation of azocarbazole 5 with UV-light, however, led only to a very small new absorption band at 540 nm. No increase of the primary absorption band at 390 nm could be observed at the beginning of

the irradiation process. The color of the solution did not undergo any visible change. Nevertheless, the absorption of the solution of azocarbazole 5 also decreased in the whole visible area of the spectrum while longer irradiation with UV-light illustrated decomposition.

It is known that  $\text{CHCl}_3$  upon irradiation with X-rays loses a Cl radical which ultimately forms HCl.<sup>15</sup> It has been reported that carbazole itself can upon irradiation abstract Cl atoms from chlorinated compounds.<sup>16</sup> In the case of 3–5 protonation could result in the observed color change from yellow to green. The photoformation of HCl could be observed not only in chloroform, but also in 1,2-dichloroethylene and dichloromethane, which indicates a different mechanism from the simple decomposition of  $\text{CHCl}_3$  to phosgene and HCl as described above. No color change was observed in non-chlorinated solvents such as THF. A similar photoreaction was reported for other heterocycles such as  $\beta$ -carbolines,<sup>17</sup> or indoles.<sup>18</sup> It is proposed that the main process is an electron transfer from singlet-excited carbazole to  $\text{CHCl}_3$  via an exciplex formation.

As expected from this proposition the addition of HCl to a solution of macrocycle 3, dimer 4 or azocarbazole 5 yielded a colored HCl salt showing strong pH dependence (Fig. 4). The addition of sodium hydroxide to the acidic solutions led to the free base and a color change back to yellow. Upon adding diluted HCl to macrocycle 3 or dimer 4, the initial absorbance band increased first, and a new red shifted absorbance band occurred similar to irradiation with UV-light. Based on these observations it is proposed that first a carbazole unit and secondly the azo unit are protonated. The latter protonation led to the new red shifted absorbance band. The fact that no increase of the initial absorption band for azocarbazole 5 could be observed when irradiating with UV-light or when adding diluted HCl to a solution was a strong indication that only the azo unit was protonated. Additional  $^1\text{H}$  NMR titration experiments revealed the appearance of one additional signal ( $\sim 7.9$  ppm), which vanished upon treatment of the sample with  $\text{D}_2\text{O}$ . A second peak ( $\sim 8.0$ ) emerged on further addition of HCl before the signals broadened considerably (see ESI† for details). The protonation of azo units and the accompanied red shift were described in the literature for different aminoazobenzenes.<sup>19</sup> Methyl yellow is also reported to undergo a color change when irradiated in the presence of chlorinated compounds.<sup>20</sup>

As such an acid–base equilibrium should show temperature dependence, protonated samples of 3, 4 and 5 were heated. Remarkably, an irradiated solution of macrocycle 3 in chloroform

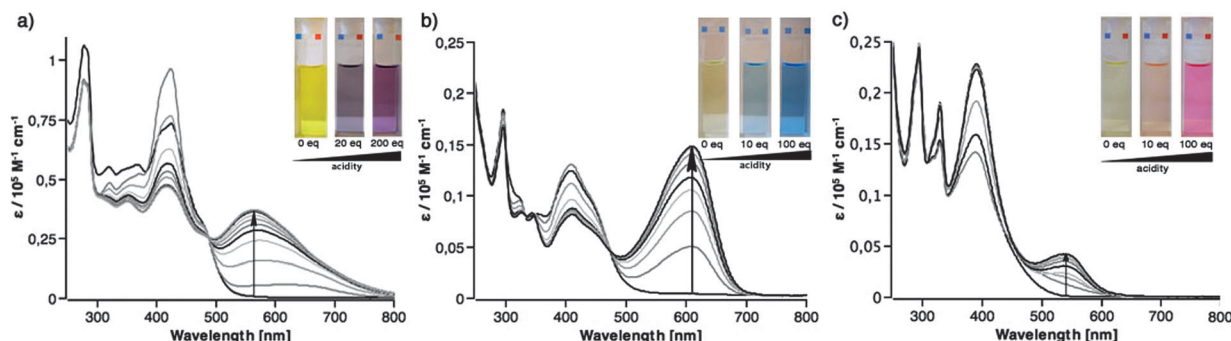
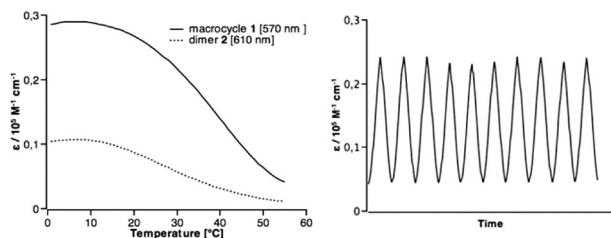
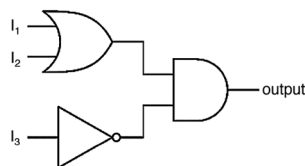


Fig. 4 UV/VIS-spectra of macrocycles 3 (a), 4 (b) and 5 (c) in  $\text{CHCl}_3$  when treated with 0.054 M HCl in methanol.



**Fig. 5** Temperature dependence of the absorption maximum at 570 nm of macrocycle **3** and at 610 nm of dimer **4** after irradiation with 302 nm (left); absorption of a solution of **3** at 570 nm in 10 heating and cooling cycles between 20 °C and 55 °C after irradiation with 302 nm (right).



UV = 1 when irradiated for 14 min at 302 nm  
 H<sup>+</sup> = 1 when 4.5 eq. HCl in MeOH added  
 temp. = 1 when heated > 45 °C  
 output = 1 when absorbance > 0.100

Input 1 UV	Input 2 H <sup>+</sup>	Input 3 temp.	Output 570 nm
1	0	0	1 (0.172)
0	1	0	1 (0.194)
0	0	1	0 (0.002)
1	1	0	1 (0.226)
0	1	1	0 (0.028)
1	0	1	0 (0.043)
1	1	1	0 (0.060)
0	0	0	0 (0.003)

**Fig. 6** Molecular logic gate [(UV OR H<sup>+</sup>) AND (NOT temp.)] based on **3** using an absorption at 570 nm as output ( $1 \times 10^{-5}$  M in CHCl<sub>3</sub>).

changed color from dark green to yellow when the temperature was increased from 0 to 55 °C, whereas the color of the solution of dimer **4** changed from light green to yellow. Hence, by changing the temperature it is possible to switch between the different absorbance spectra (Fig. 5). Interestingly, this thermochromism was only observed for azocarbazole **5** to a very small extent. The strongest change in the absorbance spectrum was observed between 10 °C and 40 °C. This temperature range makes these azocarbazoles potential indicators for applications in biology and medicine.

The switching process turned out to be reversible, as it was not accompanied by any decomposition when heated and cooled 10 times in a row. Reversibility of the transformation and stability over several days are other positive features of these systems.

The change of color due to multiple different stimuli makes the azocarbazoles suitable for sophisticated applications.<sup>21</sup> For instance, construction of an integrated molecular logic gate based on these features opens applications in physiology, medicine, biotechnology, as sensors or as diagnostic systems.<sup>22</sup> UV irradiation, addition of acid and change of temperature are the three logic inputs and the

absorbance band at 570 nm for macrocycle **3** or 610 nm for dimer **4** is the visible logic output of such a system (Fig. 6).

Several applications, for example electronic devices such as transistors, require such complex systems with more than two terminals.<sup>23</sup> Input and output were simply described “low” or “high”, respectively, as digital “0” and “1”. These simplifications allowed setting up a truth table. The logic array consists of several simpler logic gates including an OR, a NOT and an AND function. The combination of these logic gates described the functions performed by each of the two azocarbazoles in chloroform solution. Monitoring the absorbance band at 570 nm when a solution of macrocycle **3** in CHCl<sub>3</sub> was subjected to all possible input operations proved the principle. The absorbance perfectly corresponded to the output expected.

In summary macrocyclic as well as linear azocarbazoles were prepared. If the azo unit is flanked by two carbazoles a color change can be induced by different stimuli (UV irradiation in chlorinated solvents, pH and temperature). Based on this property an integrated molecular logic gate was realized. Further investigations to explore and apply azocarbazoles are ongoing.

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