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Singlet oxygen stimulus for switchable functional organic cages
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Molecular cages 1a and 2a incorporating a 9,10-diphenylanthracene (DPA) chromophore were synthesized through a templated ring-closure metathesis approach that allows variation in cavity size through the introduction of up to three different pillars. Reversible Diels–Alder reaction between the DPA moiety and photogenerated singlet oxygen smoothly converted 1a and 2a to the corresponding endoperoxide cages 1b and 2b, which are converted back to 1a and 2a upon heating. Endoperoxide formation constitutes a reversible covalent signal that combines structural changes in the interior of the cage with introduction of two additional coordination sites. This results in a large modulation of the binding ability of the receptors attributed to a change in the location of the preferred binding site owing to the added coordination by the endoperoxide oxygen lone pairs. Cages 1a and 2a form complexes with sodium and cesium whose association constants are modified by 4–20 fold for Na+ and 200–450 fold for Cs+ upon conversion to 1b and 2b. DFT calculations show that in the anthracene form, cages 1a and 2a can bind 2 metal cations in their periphery so that each cation is coordinated by 4 oxygens and one amine nitrogen, whereas the endoperoxide cages 1b and 2b bind cations centrally in a geometry that favors coordination to the endoperoxide oxygens.

Introduction

Molecular cages represent a versatile class of molecules that recognize and bind guests within a confined space defined by the structural parameters imposed by their molecular constituents.1–3 Compared to open or flexible receptors, they exhibit unique abilities for selective guest sequestration, sensing, transport (drug delivery) or transformation (nanoreactor, catalyst).4

Recently, switchable metalallocages emerged as attractive nano-objects able to tune on demand their chemical structures and therefore their binding abilities.5,6 The reversible changes within hosts then allow an in situ modulation of guest binding constant,7 with some examples of guest catch-and-release.8,9,10,11 This emerging area aims to implement reversibility in molecular sequestration to further advances in catalysis as well as biomedical and environmental applications.

Currently, the stimuli-response metalallocages rely on known switches based on photo-reactions5 or redox reactions6 under light/heat or electrochemical control. To extend the possibilities of adjustable cages, we envisioned that the molecular reversible [4π + 2π] reaction between anthracene and singlet oxygen could be a new switch available under smooth conditions with potential biomedical applications.7 In addition, we proposed that the covalently modified organic cage can benefit from the temporary presence of the endoperoxide functional group as an additional endo binding site. To the best of our knowledge, no example of the use of endoperoxides as a recognition feature has been reported.

In comparison to metalallocages whose efficient preparation exploits self-assembly by directed coordination but limits the functionalization of the cavity, organic cages require multi-step synthesis but can be decorated with various endo functional groups. With regards to switchable covalent organic containers, only two studies by Houk and co-workers described hemiacetal functionalization of benzene derivatives by size complementarity. Nonetheless, despite significant progress benefiting from the development of click and dynamic covalent chemistry,9 the synthetic access to organic covalent cages and the modulation of their structure...
and properties using an external stimulus remains a significant challenge.

Herein, we explore the reversible addition of singlet oxygen to 9,10-diphenylanthracene (DPA) as a molecular switch for the reversible tuning of the binding properties of a molecular cage. In particular, we aim to tune the guest localization within a polytopic cage depending on its switch state. Diphenylanthracene is well known for its ability to smoothly react with singlet oxygen ($^{1}\text{O}_2$) to form stable 9,10-endoperoxides whose thermal cycloreversion is also highly efficient and affords the parent anthracene chromophore.$^{7,10}$ The process involves the $[4\pi + 2\pi]$ reaction in which light is used to *in situ* generate $^{1}\text{O}_2$ through energy transfer from $^{3}\text{[DPA]}^*$ or through the use of an external photosensitizer. To date, this reversible reaction on DPA was mainly employed for the sensing or delivery of $^{1}\text{O}_2$ with a few reports of fatigue over several cycles.$^{11,13}$

Although anthracene-based receptors and containers$^{13}$ exist (some of which exploit the reversible dimerization of anthracenes),$^{14}$ there has been no investigation of the use of the $^{1}\text{O}_2$ addition/cycloreversion reaction to reversibly tune their binding properties, except for the pseudo-rotaxane developed by Smith$^{15}$ for a near-infrared dye catch-and-release system. To this end, cages 1a and 2a were designed to incorporate a DPA unit and two podand pillars for the complexation of metallic cations (Fig. 1). The sequential reactivity of cyanuric chloride towards substitution is used to incorporate two different lengths of the polyether chain ($n = 2, 4$). The corresponding endoperoxides 1b and 2b exploit a photo-triggered molecular change in structure and coordination number that significantly modifies their allosteric binding properties.

**Results and discussion**

**Synthesis and characterization of switchable DPA cages**

The synthetic pathway selected to prepare DPA-based containers incorporating three (1a) or two (2a) different pillars (Schemes 1 and 2). It relies on the selective sequential aromatic nucleophilic substitution of cyanuric chloride by different amine nucleophiles.$^{16}$ Cation-templated ring-closure metathesis (RCM) adapted from the “magic ring” method$^{17}$ was chosen to perform the final macrocyclization. Reports of molecular containers prepared using RCM are relatively scarce, with some examples employing hydrogen-bonds$^{18}$ or coordination chemistry$^{19}$ to template ring closure. Hydrogenation of the double bonds then affords the desired organic cages containing three pillars.

Both containers 1a and 2a were prepared from diamine 3. The synthesis of 1a (Scheme 1) relies on the one-pot formation of macrocycle 6 through two successive substitutions of cyanuric chloride by 3 at 20 °C, then diamine 5 at 40 °C (60% overall yield). Attempts to achieve the third macrocyclisation using a third diamine failed, resulting in oligomerization and insoluble products. Therefore, the final macrocyclization was undertaken according to the strategy described in Scheme 1. Substitution of the two triazine moieties in 6 by monoamine 7 at 90 °C led to bis-allyl compound 8 (92% yield). Ring-closing metathesis (95% yield) in the presence of NaBARF (1 equiv., BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) followed by hydrogenation of the olefin (99% yield) allowed the isolation of pure container 1a. In the absence of sodium cations, oligomerization of the bis-allyl macrocycle was instead observed.
The larger cage 2a was synthesized through two successive ring-closure metatheses to form a symmetric pseudo crown-ether (Scheme 2). In a one-pot reaction, cyanuric chloride (2 equiv.) underwent two successive substitutions, first by diamine 3 at 20 °C, followed by monoamine 7 at 35 °C (51% overall yield). The third substitution on each triazine moiety was achieved with amino-alcohol 9 at 70 °C (76% yield) to afford compound 10. The first RCM was successfully achieved without the use of NaBArF as template in 71% yield and it was followed by a quantitative hydrogenation to give macrocycle 11. Finally, two allyl groups were introduced on the alcohol substituents (68% yield) and a second RCM, templated by NaBArF (1 equiv., 65% yield) provided compound 2a after hydrogenation.

After purification by column chromatography, both cages 1a and 2a were isolated as cage compounds without any traces of oligomeric or dimeric macrocycles which are potential side-products from a divergent ring-closure metathesis, that was prevented by the controlled use of NaBArF as an efficient template (see ESI†). Although single crystals suitable for crystallographic analysis could not be obtained, the structures and composition of 1a and 2a were confirmed by mass spectrometry and VT-NMR studies. At 20 °C, the NMR signals of 1a and 2a are complicated by significant signal broadening attributed to the presence of rotamers originating from the restricted rotation around the C(s-triazine)–N(2,4,6-amino substituents) bonds and to the different polymer conformers.

$^1$H VT-NMR (toluene-$d_8$, 293–373 K) allowed clear identification of the two cages by showing sharp signals for the polymer structure of the two pillars and the typical signature of DPA at higher temperatures. The absorption and emission properties of 1a and 2a ($f_{\text{max}}$, 378 nm = $12 \times 100 \, \text{M}^{-1} \, \text{cm}^{-1}$, $\phi_p = 0.95$, $\tau = 6.0 \, \text{ns}$ in degassed dichloromethane) are similar to those of the parent DPA chromophore and show no appreciable solvatochromic behavior. Slow conversion of 1a and 2a to the corresponding endoperoxides 1b and 2b could be achieved by direct irradiation in O$_2$-saturated dichloromethane solutions, but this was found to be much faster when using a triplet photosensitizer such as methylene blue to generate $^1$O$_2$ (Fig. 2a). The use of a high boiling point solvent (propylene carbonate, 15 mol% methylene blue) allowed repeated interconversion between the DPA and endoperoxide forms by visible-light irradiation at 20 °C (2 h) to form 1b and 2b, followed by heating (140 °C, 1 h) to revert to 1a and 2a, respectively (Fig. 2b). Under these conditions, a fatigue of 10% is observed, possibly due to the oxidation side-products from anthracene that can occur during cycloreversion or resulting from the limited solubility of the compounds in propylene carbonate.\(^7\)\(^{22}\)

**Tunable binding properties of cages**

The polyether chains in cages 1a and 2a are conducive to the binding of alkali metal cations.\(^{23}\) Preliminary studies were conducted in dichloromethane solution using soluble cations of different ionic radius, i.e. NaBArF (ca. 1.0 Å) and CsBArF (ca. 1.7 Å) to evaluate the (host : guest) complementary by monitoring the fluorescence emission of the DPA chromophore. In the case of 1a, the addition of Na$^+$ induced an initial decrease in fluorescence emission until 1 : 1 stoichiometry, followed by an increase in emission intensity to reach a value that is close to that of free 1a in deaerated solutions at a 1 : 2 stoichiometry (Fig. 3a, red curve). Instead, binding of Cs$^+$ resulted in a monotonic decrease of the fluorescence emission consistent with a 1 : 1 stoichiometry (Fig. 3b, red curve). Non-linear least-squares fitting of the binding isotherms to a 1 : 2 or a 1 : 1 model for Na$^+$ or Cs$^+$ respectively, allowed the extraction of the

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**Fig. 2** Reversible transformation between cages 2a and 2b monitored by absorption spectroscopy: (a) formation of cage 2b upon visible light irradiation of cage 2a (40 μM in propylene carbonate containing 1.5 μM methylene blue). (b) Fatigue cycles for the 2a/2b conversion in propylene carbonate in the presence of methylene blue as a photosensitizer. Cycloreversion is conducted by heating to 120 °C for 80–120 min.
binding constants for each cation. These are tabulated in Table 1, and evidence the very strong interactions between the cages and alkali metal ions (10–13 kcal mol$^{-1}$). Similar results were obtained with 2a, with the exception that a weaker 1 : 2 complex with Cs$^+$ could also be detected. Compared to 1a, the longer pillar in 2a results in a larger binding cavity that better accommodates both 1 : 1 and 1 : 2 complexes, resulting in a ca. 100- and 400-fold increase in the observed association constants for Na$^+$ and Cs$^+$, respectively.

In the case of the non-emissive endoperoxide cages 1b and 2b, an indirect fluorescence titration method was employed using cages 1a and 2a as competitive fluorescent indicators. The addition of one equiv. of 1b to a solution of 1a results in a shift of the binding isotherms for both Na$^+$ and Cs$^+$ as shown in Fig. 3 (blue curves), indicating that the binding of the cages is enhanced upon endoperoxide formation. Fitting of the binding isotherms using the previously determined values for the binding of 1a and 2a allows the determination of the association constants for endoperoxides 1b and 2b (Table 1). In the case of 1, formation of the endoperoxide results in the enhancement of the binding of the first Na$^+$, but not of the second cation, and in a ca. 20-fold increase in the binding of Cs$^+$. The situation is similar for 2, with the exception that the larger cage accommodates better the presence of two Na$^+$ cations in the endoperoxide form. The somewhat lower binding of Cs$^+$ by 2b vs. 2a is instead unexpected and counter to the general trend observed.

|                          | $K_{11}$ (M$^{-1}$) | $K_{12}$ (M$^{-1}$) | $K_{11}$ (M$^{-1}$) | $K_{12}$ (M$^{-1}$) |
|--------------------------|---------------------|---------------------|---------------------|---------------------|
| Na$^+$                   |                     |                     |                     |                     |
| 1a                       | $6 \times 10^8$     | $3 \times 10^5$     | $1 \times 10^7$     | —                   |
| 1b                       | $4 \times 10^9$     | $2 \times 10^6$     | $2 \times 10^8$     | —                   |
| 2a                       | $1 \times 10^{11}$  | $2 \times 10^9$     | $4 \times 10^8$     | $3.3 \times 10^6$   |
| 2b                       | $9 \times 10^{12}$  | $1 \times 10^9$     | $2 \times 10^7$     | —                   |

$^a$ Estimated errors: ±15%. $^b$ Host : guest stoichiometry is (1 : 1) or (1 : 2). $^c$ $<3 \times 10^6$.

Binding of the first metal cation in 1 or 2 defines two possible binding models (Fig. 4) as it may take place near the anthracene ring (a), where it could benefit from π–cation interactions and vicinal ether coordination, or near the triazine moieties (b). In the first case, we may expect that binding of the second cation induces a translation of the first ion to the opposite end of the cage to accommodate the second cation and reduce coulombic repulsion.

**Modelling**

To further understand the binding of Na$^+$ and Cs$^+$ in 1 and 2, possible 1 : 1 and 1 : 2 complexes were modeled using the Def2svp basis set in DFT B3LYP calculations to locate energy minima on the potential energy surface. The energies of these minima were then determined with greater precision using single point energy calculations at the post HF MP2(full)/Def2svp level. All calculations (geometry optimizations and single point energy) were performed using a polarizable continuum model to simulate solvent (see ESI‡ for details). The lowest energy structures found for Na$^+$ and Cs$^+$ complexes of 2a and 2b are shown in Fig. 5 (see ESI‡ for details).

The results show that, for the anthracene cages 1a and 2a, binding in the central position (Fig. 4a) is less favored than...
binding vicinal to the triazines (Fig. 4b), where coordination of the metal cation by the ether linkages and one of the amine lone pairs is possible. Interestingly, binding of the first cation induces a significant conformational change that disrupts the coordination geometry at the second site, in agreement with the pronounced negative cooperativity observed experimentally.

In the case of the endoperoxide cages $1b$ and $2b$, the preferred binding site is instead located near the endoperoxide site, where up to five oxygens can be coordinated (O–M’ distances $\leq$ sum of the van der Waals radii). This is consistent with the 10-fold greater anticooperativity observed in binding the second cation in $1b$ vs. $1a$ and in $2b$ vs. $2a$ ($M' = Na'$) since displacement of the first cation entails a loss in coordination by the endoperoxide oxygens. The calculations also show that binding of Cs’ by $1$ is significantly more favored when in the endoperoxide form $1b$ than by the anthracene form $1a$. This, however, is not the case for cage $2$ where the calculated difference in energy is instead very small. The reason for this becomes apparent upon closer inspection of the structures, which evidences that the tetramethylene segments in $1$ and $2$ are too long to allow optimal coordination of the centrally bound ion. This leads to the adoption of a $ggg$ conformation in $1b$–Cs’, where the central gauche conformation has a C–C torsional angle of 80°. In the case of $2b$, the two tetramethylene segments adopt $ggg$ and $ggg$ conformations with torsional angles for the central C–C bond of 69° and 89°, respectively. Therefore, despite the fact that both $1b$ and $2b$ bind Cs’ through the formation of five coordination bonds to nearby oxygen atoms, the torsional strain required to achieve this is greater in $2b$ vs. $1b$. In contrast, both $1a$ and $2a$ bind Cs’ near one of the triazines nitrogens ($d = 3.2$ Å) within a pseudo-crown ether cavity formed by four ether oxygens.

In light of the computational results described above, the fluorescence quenching behavior observed upon complexation of Na’ is intriguing. Quenching of emission in anthracene-containing organometallic complexes has been previously attributed to energy transfer from the excited anthracene chromophore to the ligated metal ion.6 However, we may discount such processes in $1a$–Na’ and $2a$–Na’ on the basis that unlike transition metal ions, sodium ions do not possess low-lying excited states. Similar energetic considerations rule out quenching by electron transfer, and collisional quenching would be expected to be similarly efficient for both ions in the case of sequential binding of the cations in the vicinity of the triazines (Fig. 4b). To solve this conundrum, we surmised that the low polarity of dichloromethane might favor the formation of relatively tight ion pairs, and that the quenching might in fact result from the proximity of the BARF counterion. To test this, we proceeded to examine the bimolecular Stern–Volmer quenching of 9,10-diphenylanthracene in THF by NaBARF, which evidenced moderately efficient quenching with a bimolecular quenching rate of $k = 8.6 \times 10^8$ M$^{-1}$ s$^{-1}$ (see ESI†). This suggests that ion pairing may indeed contribute to fluorescence quenching in host–guest complexes.

Conclusions

The covalent addition of singlet oxygen as reversible signal combines three distinct inputs: a structural change in the interior of the cage (Csp$^2$ → Csp$^3$), loss of anthracene aromaticity, and introduction of two oxygen atoms capable of providing new coordinating sites. This results in a large modulation of the binding ability of the receptors and also, according to molecular modeling studies, a change in the location of the preferred binding site owing to the added coordination by the endoperoxide oxygen lone pairs. The inside volume of the cages is well suited for binding first-row alkali metal cations, including Cs’ which is of interest as it is a common byproduct of nuclear fission.

Beyond the synthetic challenge of incorporating reversible covalent functionality in molecular receptors, the comparison of cages $1$ and $2$ also demonstrates how small geometrical variations in just one of three pillars may affect the binding ability and mechanism. This was possible thanks to the sequential substitution reactions in cyanuric chloride, which represents a valuable strategy for developing asymmetrical cages incorporating additional functionalities.

Conflicts of interest

There are no conflicts to declare.

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