CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Supramolecular storage and controlled photorelease of an oxidizing agent using a bambusuril macrocycle

Authors: Edoardo Torti, Vaclav Havel, Mirza Yawer, Lucie Ludvíkova, Michal Babiak, Petr Klan, and Vladimir Sindelar

To be cited as: *Chem. Eur. J.* 10.1002/chem.201704948

Link to VoR: http://dx.doi.org/10.1002/chem.201704948

Supported by
ACES

WILEY-VCH

Supramolecular storage and controlled photorelease of an oxidizing agent using a bambusuril macrocycle

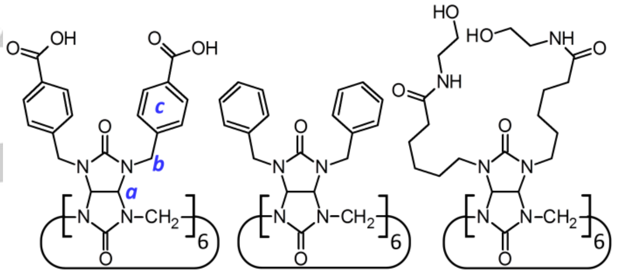
Edoardo Torti,[a]† Václav Havel,[a]† Mirza A. Yawer,[a] Lucie Ludvíková,[a] Michal Babiak,[b] Petr Klán,[a]* and Vladimir Sindelar[a]*

Abstract: Bambusuril inhibits oxidizing ability of peroxodisulfate by its complexation inside the macrocycle cavity. This dianionic agent can be released on demand from its stable 1 : 1 complex in water (log K_a = 6.9 M^{-1}) by addition of a more strongly bound anion, such as iodide (log K_a = 7.1 M^{-1}), which can also be delivered upon irradiation *in situ* from a 4-hydroxyphenacyl iodide derivative with a spatial and temporal precision. The peroxodisulfate ion liberated from the complex recovers its oxidizing properties and can be involved in subsequent chemical transformations.

Supramolecular chemistry offers unique opportunity to control and explore changes in the reactivity of guests upon their binding in host molecules. The complexation of guests inside a supramolecular receptor can mask their reactivity or, in contrast, the system can act as a catalyst to enhance it. Examples of both cases can be found in artificial and naturally occurring supramolecular systems.[1–5] In addition, supramolecular chemistry can provide encapsulation and targeted release of reactive species.[6–8] However, a report of masking reactivity of inorganic anion in water by the formation of host-guest complexes is absent in literature.

Bambusurils are a rapidly expanding family of macrocyclic anion receptors.[9–14] They offer high stability of anion complexes with large, more polarizable and less hydrated anions in organic solvent and also in water. Moreover, their properties can be fine-tuned by incorporating different substituents onto the glycoluril building block.[9,10,12,15] In this work, we used a chemical stability of these macrocycles and their ability to strongly bind anionic guests in water[12] to mask oxidative properties of the peroxodisulfate ($S_2O_8^{2-}$) ion and, subsequently, release this ion using external stimuli to oxidize a reactant present in an aqueous solution. Peroxodisulfate was selected for being a widely used oxidizing agent and a radical reaction initiator.[16–19]

In our investigation, 4-carboxybenzyl bambusuril derivative[12] (**BU1**, Figure 1) was used at first as the only available bambusuril soluble in water at the moment. ^{1}H NMR was used to study interaction between **BU1** and $S_2O_8^{2-}$ in water. On an NMR time scale, the inclusion of peroxodisulfate ion into **BU1** exhibited a slow chemical exchange rate. After addition of $S_2O_8^{2-}$ (0.5 equiv.), two sets of signals, one for an anion free macrocycle and the second for a complex, were found in the spectrum (Figure 2B). After further addition of $S_2O_8^{2-}$ (1.0 equiv. total), only the signals for the complex remained (Figure 2C). This indicates that the complex stoichiometry is 1 : 1 and that the complex is too stable to allow direct measurement of the association constant by NMR. Therefore, an isothermal titration calorimetry (ITC) was used to determine the association constant to be (3.1 ± 0.1) × 10^5 M^{-1} for the **BU1**·$S_2O_8^{2-}$ complex in aqueous phosphate buffer (0.1 M, pH 7.2). The stability of this complex is surprisingly high considering that the binding takes place in water and the anion bears two negative charges. The NMR spectra of the **BU1**·$S_2O_8^{2-}$ complex remain unchanged after one month, indicating its high stability under the experimental conditions used.



BU1 **BU2** **BU3**

Figure 1. Compounds used in the study.

We were unable to obtain a crystal structure of the **BU1**·$S_2O_8^{2-}$ complex, therefore, we replaced **BU1** with a relatively similar benzyl-substituted bambusuril **BU2** (Figure 1) because its complexes with anions readily crystallize. Indeed, crystals of the **BU2**·$(NH_4)_2S_2O_8$ complex were prepared by mixing a **BU2** solution in CH_2Cl_2 with a solution of ammonium peroxodisulfate in methanol, and then diethyl ether vapors were allowed to slowly diffuse into the mixture. The X-ray structure of the complex (Figure 3) showed that the guest occupies an off-center position where only one end of the anion is located in the center of the **BU2** cavity, forming hydrogen bonds with both sets of the methine protons. The end of $S_2O_8^{2-}$ located in the portal of the macrocycle is bound less tightly than that inside the macrocycle which is apparent from its higher disorder, visualized by the thermal ellipsoid model (Figure 3A). It is also apparent from the CPK model (Figure 3B) that the benzyl groups on the **BU2** portals are not able to cover the negative end of $S_2O_8^{2-}$ pointing out of the macrocycle. In the next step, we investigated the possibility of releasing the bound peroxodisulfate from **BU1** in an aqueous solution. Iodide was used as a competitive ion, and the peroxodisulfate release was followed by ^{1}H NMR because the **BU1** complexes of these two

---

[a] E. Torti, Dr. V. Havel, Dr. M. A. Yawer, L. Ludvíková, Prof. P. Klán, Prof. V. Sindelar
Department of Chemistry & RECETOX,
Faculty of Science, Masaryk University
Kamenice 5, 625 00 Brno, Czech Republic
E-mail: klan@chemi.muni.cz, sindelar@chemi.muni.cz
[b] M. Babiak
CEITEC - Central European Institute of Technology and National Centre for Biomolecular Research, Masaryk University,
Kamenice 5, 625 00 Brno, Czech Republic

† Author Contributions: E.T. and V.H. contributed equally.

Supporting information for this article is given via a link at the end of the document.

10.1002/chem.201704948

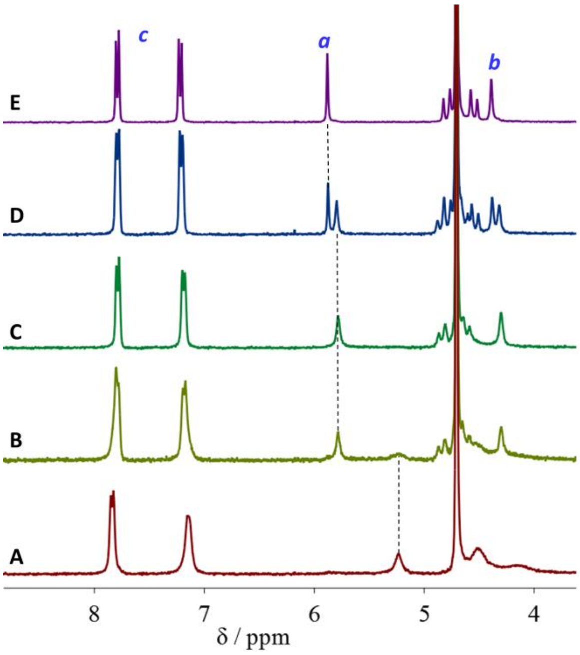


Figure 2. Stacked ^{1}H NMR spectra (D_2O, 500 MHz, 30°C, K_2DPO_4 20 mM, pH = 7.1) of (A) anion free **BU1** (1 mM), **BU1** (B) after addition of 0.5 equiv. and (C) 1.0 equiv. of $(NH_4)_2S_2O_8$, (D) 1.0 equiv. of $(NH_4)_2S_2O_8$ + 0.5 equiv. of TMAI, and (E) 1.0 equiv. of $(NH_4)_2S_2O_8$ + 1.25 equiv. of TMAI. The equivalents of ions are referred to **BU1**.

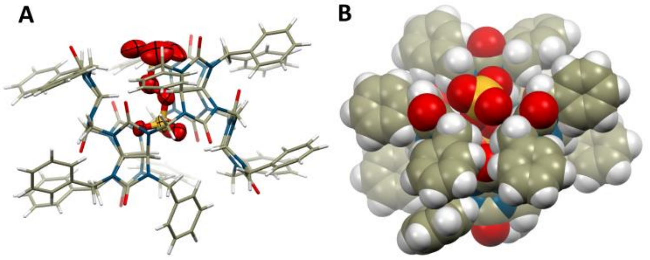


Figure 3. X-ray crystal structure of a **BU2**·$(NH_4)_2S_2O_8$ complex. (A) Side view of the complex with a guest depicted in thermal ellipsoid setting (80% occupancy) and (B) space-filling model displaying an open portal of **BU2** allowing a view to the bound peroxodisulfate anion. Solvent molecules, counterions and disordered parts of the complex were omitted for clarity. Color coding: O, red; S, yellow; C, gray; N, blue; H, white.

different anions exhibit different chemical shifts of the macrocycle signals in their spectra (Figure 2D). Only a slight excess of iodide (1.25 equiv.) was required for the quantitative release of peroxodisulfate from this complex (Figure 2E).

To find whether peroxodisulfate encapsulated inside **BU1** loses its oxidizing properties, a simple Fe^{2+}/Fe^{3+} redox system was chosen because the $Fe^{2+} \rightarrow Fe^{3+}$ reaction can be monitored by absorption spectroscopy. This redox system is a part of Fenton's and Fenton-like reagents comprising H_2O_2 or peroxodisulfate ($S_2O_8^{2-}$) ions, respectively, as oxidants. It is commonly used to oxidize contaminants in waste waters and finds applications also in molecular biology.[20–22] The Fe^{3+} ion in water has a characteristic absorption band centered in the region of 250−400 nm[23] where Fe^{2+} does not absorb.[24] Unfortunately, an intensive absorption band corresponding to Fe^{3+} ion appeared when Fe^{2+} salt was added to the **BU1**·$S_2O_8^{2-}$ complex, indicating that the macrocycle is not able to mask the peroxodisulfate reactivity. We hypothesize that the reaction is assisted by the attraction of Fe^{2+} ions by negatively charged carboxylate groups in close proximity to the portal of receptor and the bound guest. Moreover, the 4-carboxybenzyl substituents on **BU1** should not be able to fully prevent the approach of a substrate nearby of the guest as it is apparent from the crystal structure of an analogous **BU2** macrocycle (Figure 3B).

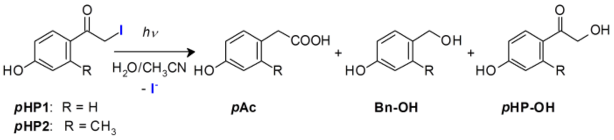
To test whether the substituents on the macrocycle influence the reactivity of encapsulated $S_2O_8^{2-}$, we prepared a new water-soluble bambusuril **BU3** by transformation of recently developed dodecakis(5-carboxypentyl)bambusuril[15] into its 2-hydroxyethylamide derivative. The flexible and sterically demanding alkylamide substituents provide **BU3** with a good solubility even in unbuffered water, reduce undesired repulsion of anionic guests and negatively charged substituents, and facilitate a hydrogen bonded structure between the substituents to hinder undesired reaction of Fe^{2+} with its peroxodisulfate complex. NMR titration and ITC experiments revealed that **BU3** forms an inclusion complex with $S_2O_8^{2-}$ ion of 1 : 1 stoichiometry (K_a = (8.3 ± 0.1) × 10^6 M^{-1} in pure water; Figure S23 and S28).

In the next step, the ability of **BU3** to hinder $S_2O_8^{2-}$ from reactions with other species was tested (Figure S10). A solution of **BU3** in a slight excess (5.73 × 10^{-5} M) and $Na_2S_2O_8$ (3.54 × 10^{-5} M) were dissolved in water to assure complete encapsulation the anion inside the macrocycle. Upon the addition of $FeSO_4$ (7.10 × 10^{-5} M) into the solution, the absence of an absorption band characteristic for Fe^{3+} indicated that **BU3** shields $S_2O_8^{2-}$ from its reaction with ferric ion.

A guest encapsulated inside **BU3** can be released by addition of a competing guest with a higher affinity towards the macrocycle itself. In this case, iodide was added to the solution (with above described composition) and the course of the $S_2O_8^{2-}/I^-$ exchange and Fe^{2+} oxidation was followed by absorption spectroscopy. A significant increase in the absorbance was observed upon addition of iodide, clearly indicating the oxidation of Fe^{2+} to Fe^{3+} (Figure S12). This competing iodide ion used to facilitate the peroxodisulfate release can be added directly to the solution or it can be released photochemically on demand from a suitable substrate with advantage of a spatial and temporal control over the reaction.[25] To design a photoremovable protecting group (photocage) to release the iodide ion, we chose the 4-hydroxyphenacyl (*p*HP) group which has been demonstrated to liberate a wide variety of anions.[26–29] Such a chromophore is water-soluble, and the leaving groups are usually efficiently (Φ = 0.1−1.0) and rapidly (k_{obs} = (7−100) × 10^8 s^{-1}) released upon irradiation with UV light. The photoreaction is based on a photo-Favorskii rearrangement to give phenylacetic acid as the major side-product.

10.1002/chem.201704948

Two *p*HP derivatives, ***p*HP1** and ***p*HP2** (Figure 1 and Scheme 1), were synthesized from the corresponding acetophenones employing their bromination by $CuBr_2$ in the first step,[30] followed by Finkelstein reaction (SI).



Scheme 1. Photochemistry of *p*HP derivatives.

Both compounds possess similar absorption maxima at ~290 nm, tailing off to 350 nm (Figure S2). The exhaustive irradiation of both *p*HPs in the presence of anion-free **BU3** in an argon-purged D_2O/CD_3CN (1 : 1) mixture using light from a Xe lamp filtered through a Pyrex filter (>290 nm) gave quantitative amounts of iodide (>91% in all cases), determined as a 1 : 1 complex with **BU3** by NMR (Figure S7 and S8). Three photoproducts were identified in the irradiated mixtures of ***p*HP1** and ***p*HP2**. In addition to typical photo-Favorskii rearrangement products, 4-hydroxyphenylacetic acid derivatives (***p*Ac**, 50 and 38% yields for ***p*HP1** and ***p*HP2**, respectively),[30,31] and 4-hydroxybenzyl alcohol derivatives (**Bn-OH**, 12 and 17% yields, respectively) that often accompany this rearrangement,[32] photosolvolysis (hydrolysis) products, 4-hydroxyphenacyl alcohols, were produced in 36 and 30% yields, respectively (***p*HP-OH**) (Scheme 1, Table S2, Figure S3 and S4). Photosolvolysis has also been already reported in the case of simple phenacyl derivatives[33] as well as of 4-hydroxyphenacyl derivatives, although in very low chemical yields.[34] Furthermore, photochemical behavior of ***p*HP1** after excitation was studied by picosecond pump-and-probe and nanosecond transient spectroscopies (SI). The mixture of tautomeric triplet state forms of ***p*HP1** was detected possessing an average lifetime of ~30 ns (the individual triplet-state forms could not be separated under experimental conditions), which is analogous to photobehavior of 4-hydroxyacetophenone.[35] We hypothesize that the heterolytic cleavage occurs from the triplet state, which is analogous to the reaction of 2-hydroxyphenacyl moieties.[36] We also detected a persistent phenacyl radical after excitation of ***p*HP1** at 266 nm, which is formed probably from the singlet excited state via homolytic cleavage.[37,38]

The photorelease of iodide from ***p*HP2** (4.76×10^{-4} M) to replace $S_2O_8^{2-}$ (4.29×10^{-4} M) inside the **BU3** (4.31×10^{-4} M) cavity *in situ* in a D_2O/CD_3CN (1 : 1) mixture was followed by ^1H NMR. The signals at $\delta = 5.61$ and 4.93 ppm, characteristic for the **BU3**$\cdot S_2O_8^{2-}$ complex, were converted to the signals at 5.64 and 5.00 ppm, indicating the formation of a complex with I^- (Figure S9). We found that both the release of iodide and the exchange between I^- and $S_2O_8^{2-}$ in a complex were quantitative. The photoproducts and intermediates formed during irradiation did not interfere with the process: Both **BU3**$\cdot S_2O_8^{2-}$ and **BU3**$\cdot I^-$ complexes in a D_2O/CD_3CN mixture were found to be completely stable in the dark and under irradiation conditions used (SI).

Finally, the photochemically activated replacement of peroxodisulfate in the bambusuril complex by I^- in a H_2O/CH_3CN (99 : 1) mixture was established and reduction of the $S_2O_8^{2-}$ ion released in the presence of Fe^{2+} ions (to give Fe^{3+} ions) was observed. This experiment was performed to verify that the studied system can act as a photoactivatable Fenton-like reagent. Thus, a solution of **BU3** (8.64×10^{-5} M), sodium peroxodisulfate (8.59×10^{-5} M), $FeSO_4$ (1.71×10^{-4} M, 1 equiv.) and ***p*HP1** (9.50×10^{-5} M, 1.1 equiv.) was irradiated, and the extent of Fe^{2+} oxidation was followed by absorption spectroscopy (Fig S13). Because the absorption band of Fe^{3+} ions is a relatively weak and overlaps with those of ***p*HP1** and its photoproducts, we chose instead to visualize of the remaining Fe^{2+} ions using 1,10-phenanthroline (phen) as a $Fe(phen)_3^{2+}$ complex (ferroin), which exhibits a strong absorption band at 508 nm.[39] Thus, phen was added to the solution of ***p*HP1**, **BU3**/$S_2O_8^{2-}$ and $FeSO_4$ before and after irradiation. A remaining very weak signal of $Fe(phen)_3^{2+}$ in the thoroughly irradiated solution revealed that practically quantitative oxidation of Fe^{2+} to Fe^{3+} occurred (Figure 4). Similar results were obtained by repeating the experiment with ***p*HP2**. The chemical yields of I^- released and the extent of $Fe^{2+} \rightarrow Fe^{3+}$ oxidation are given in Table 1. It has to be mentioned that except for the *p*HP derivatives, all the other reactants either individually or in any mixture were found chemically inactive upon irradiation (SI) and that only the photorelease of iodide was responsible for the observed photochemical behavior of the system. The concentration ratios of the reactants used in this work were optimized for the highest chemical yields (see Supporting Information).

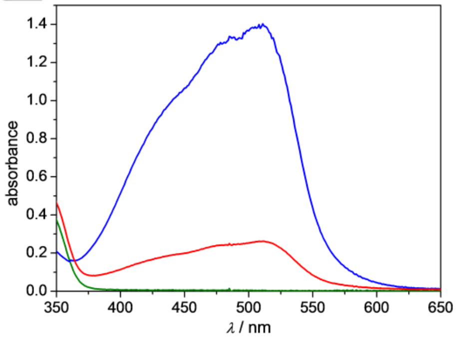


Figure 4. The absorption bands of $Fe(phen)_3^{2+}$ complexes obtained by addition of 1,10-phenanthroline (phen) to the irradiated and not irradiated solutions of $FeSO_4$ (1.7×10^{-4} M), $Na_2S_2O_8$ (8.6×10^{-5} M), **BU3** (8.6×10^{-5} M) and ***p*HP1** (9.5×10^{-5} M) in an argon saturated H_2O/CH_3CN 99:1 mixture. The absorption spectra of a blank solution (without $FeSO_4$; green), non-irradiated (blue) and irradiated (red; 10 min) samples are shown.

Finally, the stability and thermodynamic parameters of the studied bambusuril complexes in aqueous phosphate buffer (0.1 M, pH 7.2) or in pure water was determined using isothermal titration calorimetry (ITC; Table 2). The binding of peroxodisulfate with both bambusuril derivatives (**BU1** and **BU3**) is characterized by an exceptionally high enthalpy which is compensated by a high entropic penalty. This is one of the largest compensations reported for the interaction of an anion and an artificial macrocycle.[40] Our results also reveal that the removal of electrostatic repulsion from bambusuril has a substantial influence on its binding affinity. Stability of the **BU3**·$S_2O_8^{2-}$ complex is higher by more than one order of magnitude when compared with that of the parent carboxyalkyl derivative. Such differences in the complex stabilities can be one of the reasons why the oxidation ability of $S_2O_8^{2-}$ is suppressed in the presence of **BU3** and not **BU1**.

Table 1. Yields of iodide released and Fe^{2+} oxidized upon irradiation of argon-saturated solutions of ***p*HP1** and ***p*HP2.**

	conversion [%][a]	I^- released [%][a]	Fe^{2+} oxidized [%][b]
***p*HP1**	100	>91	79[c]
***p*HP2**	100	>91	82[d]

[a] Solutions of **BU3** (5.1×10^{-4} M) and ***p*HP1** or ***p*HP2** (5.6×10^{-4} M, 1.1 equiv.) in a D_2O/CD_3CN (1 : 1) mixture irradiated for 10 minutes using a 1000-W Xe lamp. The reaction conversion (the consumption of *pHP* derivatives) and the yields of iodide released as a complex with **BU3** were estimated using ^{1}H-NMR. [b] The concentrations of Fe^{2+} ions was determined in the presence of 1,10-phenanthroline using absorption spectroscopy. Solutions of either [c] ***p*HP1** or [d] ***p*HP2** in a H_2O/CH_3CN (99 : 1) mixture irradiated in the presence of **BU3**, $Na_2S_2O_8$ and $FeSO_4$ (the molar ratios: 1.1 : 1 : 1 : 2).

Table 2. Yields of iodide released and Fe^{2+} oxidized upon irradiation of argon-saturated solutions of ***p*HP1** and ***p*HP2.**

host	guest	K_a/M^{-1}	$\Delta H°$/kJ mol^{-1}	$T\Delta S°$/kJ mol^{-1}
BU1	$K_2S_2O_8$	$(3.1 \pm 0.1) \times 10^5$	−96.4 ± 5.5	−64.6
	TMAI	$(1.8 \pm 0.1) \times 10^6$	−80.5 ± 1.8	−44.2
BU3	$K_2S_2O_8$[a]	$(8.3 \pm 0.1) \times 10^6$	−95.5 ± 2.8	−55.3
	TMAI	$(1.3 \pm 0.1) \times 10^7$	−69.0 ± 1.6	−27.8
	TMAI[a]	$(1.3 \pm 0.1) \times 10^7$	−66.1 ± 2.1	−24.9

All experiments were performed in triplicate using independently prepared solutions. The guest (1 mM) and host (0.1 mM) solutions were prepared in either phosphate buffer (0.1 M, pH 7.2) or [a] in pure water.

In conclusion, we prepared the first neutral water soluble bambusuril macrocycle **BU3**. We showed that peroxodisulfate reactivity is inhibited inside the **BU3** cavity and its targeted release and oxidation potential recovery via a photochemical release of a competing anion can be achieved. Despite a large interest in binding of anions in water in recent years, the best neutral receptors interact with inorganic anions only on milimolar concentrations, and stimuli responsive complexes of this kind has not been reported yet. Our host-guest complex with ability to strongly bind and release simple oxidizing anionic agent on demand in water represents the first example of such a system, which could be used in many applications, including radical polymerization or chemical footprinting of proteins.[19,41,42] In addition, the complex between the **BU3** macrocycle and peroxodisulfate with submicromolar stability in water is the most stable assembly ever reported for inorganic dianionic guests and artificial receptors in this medium.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported by the Czech Science Foundation (V.S.: 13-15576S, P.K.: GA13-25775S) and the Ministry of Education, Youth and Sports of the Czech Republic (LQ1601, LO1214, and LM2015051). We acknowledge the CF X-ray diffraction and Bio-SAXS supported by the CIISB research infrastructure (LM2015043 funded by MEYS CR). The authors thank to Peter Štacko for fruitful discussions and help with the photochemical experiments.

Keywords: bambusurils • anion recognition • macrocycles • supramolecular chemistry • self-assembly

Notes

‡ Crystal structure is available from https://www.ccdc.cam.ac.uk (CCDC 1566757).

[1] D. Coquière, A. de la Lande, O. Parisel, T. Prangé, O. Reinaud, *Chem. - Eur. J.* **2009**, *15*, 11912–11917.
[2] S. Liu, H. Gan, A. T. Hermann, S. W. Rick, B. C. Gibb, *Nat. Chem.* **2010**, *2*, 847–852.
[3] J. Su, X. Sheng, S. Li, T. Sun, G. Liu, A. Hao, *Org. Biomol. Chem.* **2012**, *10*, 9319.
[4] A. M. Klibanov, *Nature* **2001**, *409*, 241–246.
[5] M. C. Bewley, V. Graziano, J. Jiang, E. Matz, F. W. Studier, A. E. Pegg, C. S. Coleman, J. M. Flanagan, *Proc. Natl. Acad. Sci.* **2006**, *103*, 2063–2068.
[6] D. J. Cram, M. E. Tanner, R. Thomas, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1024–1027; *Angew. Chem.* **1991**, *103*, 1048–1051.
[7] P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* **2009**, *324*, 1697–1699.
[8] M. M. J. Smulders, J. R. Nitschke, *Chem Sci* **2012**, *3*, 785–788.
[9] J. Svec, M. Necas, V. Sindelar, *Angew. Chem. Int. Ed.* **2010**, *49*, 2378–2381; *Angew. Chem.* **2010**, *122*, 2428–2431.
[10] V. Havel, J. Svec, M. Wimmerova, M. Dusek, M. Pojarova, V. Sindelar, *Org. Lett.* **2011**, *13*, 4000–4003.
[11] J. Rivollier, P. Thuéry, M.-P. Heck, *Org. Lett.* **2013**, *15*, 480–483.
[12] M. A. Yawer, V. Havel, V. Sindelar, *Angew. Chem. Int. Ed.* **2015**, *54*, 276–279; *Angew. Chem.* **2015**, *127*, 278–281.
[13] M. Singh, E. Solel, E. Keinan, O. Reany, *Chem. - Eur. J.* **2015**, *21*, 536–540.
[14] M. Singh, E. Solel, E. Keinan, O. Reany, *Chem. - Eur. J.* **2016**, *22*, 8848–8854.
[15] V. Havel, M. Babiak, V. Sindelar, *Chem. - Eur. J.* **2017**, *23*, 8963–8968.
[16] S. Y. Jon, N. Selvapalam, D. H. Oh, J.-K. Kang, S.-Y. Kim, Y. J. Jeon, J. W. Lee, K. Kim, *J. Am. Chem. Soc.* **2003**, *125*, 10186–10187.
[17] W. V. Smith, *J. Am. Chem. Soc.* **1948**, *70*, 3695–3702.
[18] D. A. House, *Chem. Rev.* **1962**, *62*, 185–203.

[19] B. C. Gau, H. Chen, Y. Zhang, M. L. Gross, *Anal. Chem.* **2010**, *82*, 7821–7827.

[20] Y.-T. Lin, C. Liang, C.-W. Yu, *Ind. Eng. Chem. Res.* **2016**, *55*, 2302–2308.

[21] F. Pan, X. Zhong, D. Xia, X. Yin, F. Li, D. Zhao, H. Ji, W. Liu, *Sci. Rep.* **2017**, *7*, 44626.

[22] S. Hernández, J. K. Papp, D. Bhattacharyya, *Ind. Eng. Chem. Res.* **2014**, *53*, 1130–1142.

[23] M. Dinç, Ö. Metin, S. Özkar, *Catal. Today* **2012**, *183*, 10–16.

[24] L. Huang, X. Weng, Z. Chen, M. Megharaj, R. Naidu, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2014**, *117*, 801–804.

[25] P. Klán, T. Šolomek, C. G. Bochet, A. Blanc, R. Givens, M. Rubina, V. Popik, A. Kostikov, J. Wirz, *Chem. Rev.* **2013**, *113*, 119–191.

[26] R. S. Givens, A. Jung, C.-H. Park, J. Weber, W. Bartlett, *J. Am. Chem. Soc.* **1997**, *119*, 8369–8370.

[27] R. S. Givens, C.-H. Park, *Tetrahedron Lett.* **1996**, *37*, 6259–6262.

[28] R. S. Givens, J. F. W. Weber, P. G. Conrad, G. Orosz, S. L. Donahue, S. A. Thayer, *J. Am. Chem. Soc.* **2000**, *122*, 2687–2697.

[29] R. S. Givens, M. Rubina, J. Wirz, *Photochem. Photobiol. Sci.* **2012**, *11*, 472.

[30] P. Sebej, B. H. Lim, B. S. Park, R. S. Givens, P. Klan, *Org. Lett.* **2011**, *13*, 644–647.

[31] K. Stensrud, J. Noh, K. Kandler, J. Wirz, D. Heger, R. S. Givens, *J. Org. Chem.* **2009**, *74*, 5219–5227.

[32] R. S. Givens, D. Heger, B. Hellrung, Y. Kamdzhilov, M. Mac, P. G. Conrad, E. Cope, J. I. Lee, J. F. Mata-Segreda, R. L. Schowen, et al., *J. Am. Chem. Soc.* **2008**, *130*, 3307–3309.

[33] W. Chai, A. Takeda, M. Hara, S.-J. Ji, C. A. Horiuchi, *Tetrahedron* **2005**, *61*, 2453–2463.

[34] R. S. Givens, M. Rubina, K. F. Stensrud, *J. Org. Chem.* **2013**, *78*, 1709–1717.

[35] Ĺ. Klíčová, P. Šebej, T. Šolomek, B. Hellrung, P. Slavíček, P. Klán, D. Heger, J. Wirz, *J. Phys. Chem. A* **2012**, *116*, 2935–2944.

[36] B. P. Ngoy, P. Šebej, T. Šolomek, B. H. Lim, T. Pastierik, B. S. Park, R. S. Givens, D. Heger, P. Klán, *Photochem. Photobiol. Sci.* **2012**, *11*, 1465.

[37] S. V. Jovanovic, J. Renaud, A. B. Berinstain, J. C. Scaiano, *Can. J. Chem.* **1995**, *73*, 223–231.

[38] W. U. Palm, H. Dreeskamp, *J. Photochem. Photobiol. Chem.* **1990**, *52*, 439–450.

[39] I. M. Kolthuff, T. S. Lee, D. S. Leussing, *Anal. Chem.* **1948**, *20*, 985–985.

[40] K. I. Assaf, M. S. Ural, F. Pan, T. Georgiev, S. Simova, K. Rissanen, D. Gabel, W. M. Nau, *Angew. Chem. Int. Ed.* **2015**, *54*, 6852–6856; *Angew. Chem.* **2015**, *127*, 6956–6960.

[41] J. W. H. Wong, S. D. Maleknia, K. M. Downard, *Anal. Chem.* **2003**, *75*, 1557–1563.

[42] S. D. Maleknia, K. M. Downard, *Chem. Soc. Rev.* **2014**, *43*, 3244.

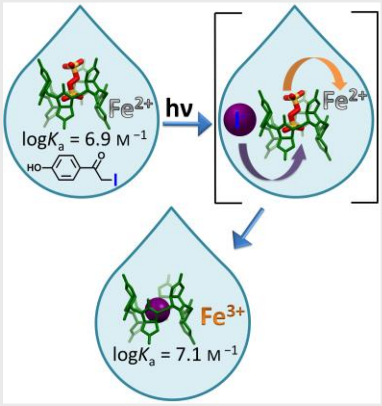
10.1002/chem.201704948

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Peroxodisulfate oxidation ability suppressed inside bambusuril macrocycle is restored upon photoinduced release of iodide into water solution.



Edoardo Torti, Václav Havel, Mirza A. Yawer, Lucie Ludvíková, Michal Babiak, Petr Klán, and Vladimír Sindelar**

Page No. – Page No.*

Supramolecular storage and controlled photorelease of an oxidizing agent using a bambusuril macrocycle