RESEARCH ARTICLE

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Modulating Aryl Azide Photolysis: Synthesis of a Room-Temperature Phosphorescent Carboline in Cucurbit[7]uril Host

Xujun Qiu, Yichuan Wang, Sonja Leopold, Sergei Lebedkin, Ute Schepers, Manfred M. Kappes, Frank Biedermann, and Stefan Bräse**

Cucurbit[7]uril (CB7), a supramolecular host, is employed to control the pathway of photolysis of an aryl azide in an aqueous medium. Normally, photolysis of aryl azides in bulk water culminates predominantly in the formation of azepine derivatives via intramolecular rearrangement. Remarkably, however, when this process unfolds within the protective confinement of the CB7 cavity, it results in a carboline derivative, as a consequence of a C—H amination reaction. The resulting carboline caged by CB7 reveals long-lived room temperature phosphorescence (RTP) in the solid state, with lifetimes extending up to 2.1 s. These findings underscore the potential of supramolecular hosts to modulate the photolysis of aryl azides and to facilitate novel phosphorescent materials.

1. Introduction

Organic azides, due to their rich nitrogen content and propensity for transformation under various reaction conditions, have held a prominent place in the annals of chemistry since their discovery in 1864.[1] Their utility spans a wide range of reactions such as 1,3-dipolar cycloaddition,[2] Staudinger/aza-Wittig reaction,[3] and C—H insertion.[4] The photolysis of aryl azides is a basis for important functionalization methods in chemical biology.[5]

From a mechanistic standpoint, aryl azide photolysis involves the expulsion of a nitrogen molecule and the formation of a highly reactive singlet nitrene intermediate. The latter can undergo one of three distinct reaction pathways.[6] The first involves amination of an X—H bond (X = C, N, O, or S). The second pathway entails an intramolecular rearrangement to ketenimines, which are subsequently open for nucleophilic insertion, yielding azepine derivatives. The third pathway entails an intersystem crossing to triplet nitrenes, which can then dimerize to azobenzenes. To control such diverse reactivity of nitrenes is a fascinating but challenging problem for chemists.

An application of supramolecular hosts as "reaction vessels" represents a promising approach to modulating the photoreaction pathways of aryl azides. This concept of supramolecular catalysis has been successfully demonstrated for supramolecular entities such as macrocycles,[7] capsules,[8] and cages.[9] Its essence lies in the creation of a microenvironment that influences the direction of the reaction through a variety of non-covalent interactions.[10] The hosts also provide a selective encapsulation of reagents.[11]

Cucurbit[*n*]urils (CB*n*), a class of glycoluril-based supramolecular hosts, stand out owing to their high affinity, particularly for cationic guests, in aqueous solutions.[12] Their pumpkin-shaped structure offers a well-defined hydrophobic cavity that can encapsulate molecules of different sizes to form 1:1,[13] 1:2,[14] or 1:3[15] host–guest complexes. This adaptability positions CB*n* as promising candidates for modulating chemical reactions. Indeed, several reactions have been conducted within the CB*n* host

X. Qiu, Y. Wang, S. Bräse
Institute of Organic Chemistry (IOC)
Karlsruhe Institute of Technology (KIT)
Kaiserstrasse 12, 76131 Karlsruhe, Germany
E-mail: braese@kit.edu

S. Leopold, U. Schepers
Institute of Functional Interfaces (IFG)
Karlsruhe Institute of Technology (KIT)
Kaiserstrasse 12, 76131 Karlsruhe, Germany

S. Lebedkin, M. M. Kappes, F. Biedermann
Institute of Nanotechnology (INT)
Karlsruhe Institute of Technology (KIT)
Kaiserstrasse 12, 76131 Karlsruhe, Germany
E-mail: frank.biedermann@kit.edu

M. M. Kappes
Institute of Physical Chemistry
Karlsruhe Institute of Technology (KIT)
Kaiserstrasse, 76131 Karlsruhe, Germany

S. Bräse
Institute of Biological and Chemical Systems–Functional Molecular Systems (IBCS-FMS)
Karlsruhe Institute of Technology (KIT)
Kaiserstrasse 12, 76131 Karlsruhe, Germany

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cavities, including the azide-alkyne cycloaddition,[16] Diels–Alder reaction,[17] and photodimerization.[18] Notably, even a partial confinement of (large) reagent molecules by CB*n* can greatly accelerate the rate of a specific reaction.[19]

In this study, we employed the unique properties of the cucurbit[7]uril host to selectively modulate the photolysis reaction of an aryl azide in an aqueous environment. Furthermore, the controlled photoreaction product carboline was applied in fabricating room temperature phosphorescence (RTP) materials for potential oxygen sensing.

2. Results

2.1. Photolysis of Aryl Azide 1 in Bulk Water

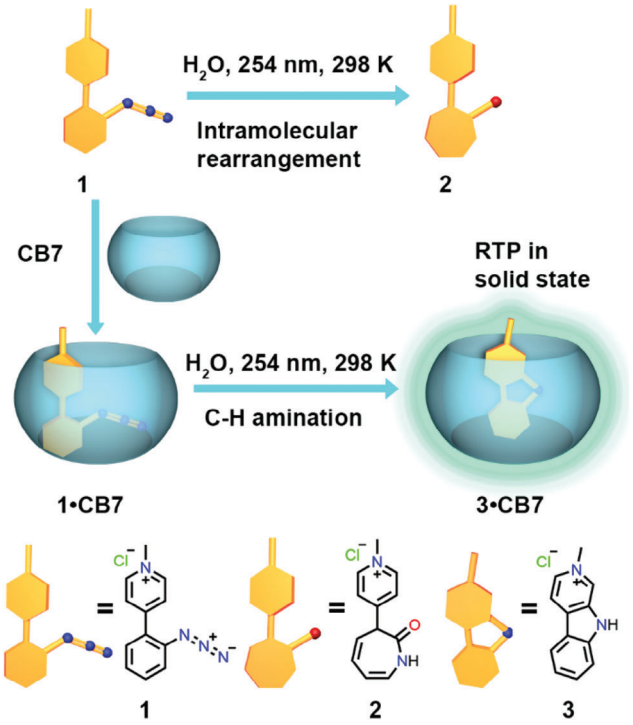
The pathways of photolysis of aryl azides are influenced by a variety of factors, including the nature of the substrates, solvents, and additives, the wavelength of light and temperature. Azepine derivatives are often the primary reaction product when the ortho position is substituted with an electron-withdrawing moiety, particularly in the presence of a nucleophile.[20] Our model compound for photolysis was 4-(2-azidophenyl)-1-methylpyridin-1-ium chloride (**1**). It possesses a pyridinium salt in the ortho position, serving as an electron-withdrawing unit. The synthesis and characterization procedures for **1** can be found in the Supporting Information (Figures S1–S3, Supporting Information).

First, we tested the photoreaction of aryl azide **1** under UV light irradiation (254 nm) in organic solvents including dichloromethane, chloroform, and acetonitrile. In these solvents the photolysis resulted in forming colored species and polymeric precipitates, their characterizations can be seen in Figure S4 (Supporting Information). No distinctive NMR signals were observed as illustrated in Figure S5 (Supporting Information) for the photolysis in DMSO, suggesting formation of mixtures of various products along different reaction (and perhaps cross-reaction) pathways. Figure S6 (Supporting Information) illustrates possible initial reaction steps and intermediates in the photolysis of aryl azide **1**.

We then performed the photoreaction of aryl azide **1** in H_2O or in D_2O if time-dependent ^1H NMR spectroscopy was used to follow the reaction. New NMR peaks emerged upon irradiation, indicating the formation of new species (Figure S7, Supporting Information). The reaction was completed after roughly 8 min of irradiation, as no significant changes were observed in the NMR spectra afterward. This observation was confirmed by UV–vis spectroscopy, following a decrease in the absorbance at 254, 286, and 331 nm (Figures S8 and S9, Supporting Information).

Relatively sharp signals in the NMR and UV–vis spectra post-photolysis suggested one major product was formed. It was isolated by preparative chromatography in 42% yield. NMR characterization (Figures S10–S12, Supporting Information) confirmed this product as an azepine derivative **2**, in accordance with the aforementioned expectations for the reaction course (**Scheme** 1).

In the proposed mechanism based on the literature data,[6] aryl azide **1** loses N_2 to form the highly reactive singlet nitrene A (**Figure 1**). This intermediate then undergoes an intramolecular rearrangement to form 1,2-didehydroazepine C, which is subsequently attacked by a water molecule in a nucleophilic addition, resulting in the azepine derivative **2**.



Scheme 1. Modulation of the outcome of the photolysis of aryl azide **1**) by using cucurbit[7]uril (CB7). **2**) photolysis product in bulk water, and **3**) in a CB7 cage. Complex **3**•CB7 shows long-lived room temperature phosphorescence (RTP) in the solid state.

2.2. Host-Guest Studies of Aryl Azide 1 with CB7

Next, we hypothesized that the reaction pathway could be altered if aryl azide **1** was shielded from water by a macrocyclic host. Cucurbit[7]uril (CB7) was chosen as a promising candidate. The host-guest interactions between **1** and CB7 were probed by ^1H-^1H COSY NMR spectroscopy (Figures S13 and S14, Supporting Information). As illustrated in **Figure 2**a, the ^1H NMR spectra of **1** displayed significant changes upon addition of CB7 in a 1:1 molar ratio in D_2O. In particular, six sets of aromatic proton signals (b–e, g) from the aryl and pyridine groups shifted upfield substantially, indicating the encapsulation by CB7. The formation of a 1:1 host-guest complex **1**•CB7 was further confirmed by detection of a MALDI-MS peak at m/z 1346.28, corresponding to $[1+CB7\text{-}N_2\text{-}Cl]^+$ ions (Figure S15, Supporting Information) The binding strength of **1** and CB7 in water was assessed by UV–vis

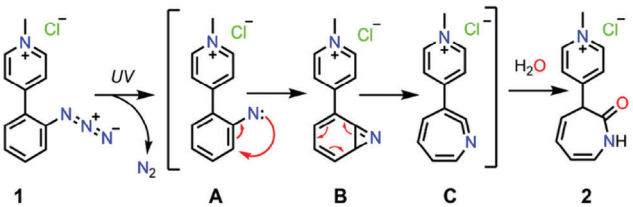


Figure 1. Proposed mechanism of photolysis of aryl azide **1** in water (H_2O). When photolysis is performed in D_2O, e.g., for ^1H NMR analysis, product **2** attains ND instead of NH as the structural fragment in the azepine ring.

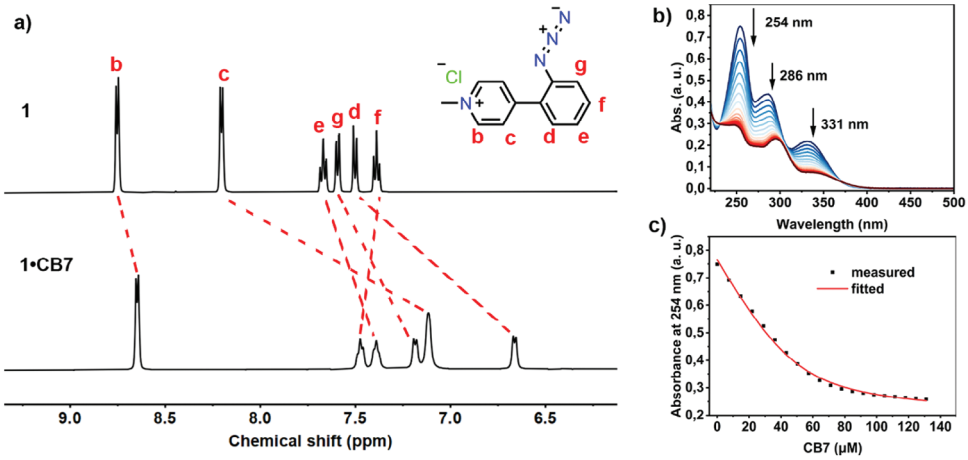


Figure 2. a) 1H NMR spectra (500 MHz, D_2O, 298 K) of 1 (2 mM) and of an equimolar mixture of 1 and CB7 (2 mM each). A zoom into the aromatic region is shown, for the full spectra see Figure S13 (Supporting Information), b) UV–vis titration spectra of 1 (50 μM) upon addition of CB7 (0–131 μM) in water at 298 K, and c) the corresponding binding isotherm fitted with a 1:1 host–guest binding model.

titration (Figure 2b; Figure S16, Supporting Information), following a decrease in absorbance at 254, 286, and 331 nm. The binding constant, K_a, was determined to be $(1.43 \pm 0.11) \times 10^5$ M^{-1} by fitting the binding isotherms (three replica measurements) to the 1:1 host-guest binding model (Figure 2c; Figure S17, Supporting Information).

2.3. Photolysis of Aryl Azide 1 within CB7 Cavity

Furthermore, we conducted the photolysis of **1** caged by CB7 (2 mM each) under the same conditions as for **1** in bulk water. The reaction process was first tracked by ^{1}H NMR. New sets of ^{1}H NMR peaks (b-h in blue color) emerged during irradiation, which are distinct from the signals of azepine derivative **2** (Figure S18 and S19; **Figure 3**a (i–iii)). A single peak b at ≈8.92 ppm was observed without coupling with any other peak in the ^{1}H-^{1}H COSY NMR spectra (Figure S20, Supporting Information), which suggests desymmetrization of the pyridinium moiety. Signals at 8.68 ppm (c) and 8.28 ppm (d) were observed as coupled peaks. The reaction was completed in ≈10 min as no changes in the ^{1}H NMR peaks were observed afterward. After that, amantadine, a competitive guest with a high binding constant with CB7, was added to the solution to expel the reaction product **3** from its complex with CB7 (Figure 3a; Figures S21 and S22, Supporting Information). Compound **3** was then isolated by preparative chromatography in 95% yield. Its analytical data (Figures S23–S26, Supporting Information) coincided with that of the carboline derivative shown in Figure 3b and reported earlier.[21]

By comparison with the typical ^{1}H NMR shifts induced by CB7 (de)complexation (Figure 3a), we concluded that in complex **3**•CB7 the aryl ring of **3** (e–h, Figure 3a (iv)) is fully encapsulated within the CB7 cavity while the pyridine ring (b–d, Figure 3a (iv)) resides near one of the portal areas of CB7.

The above results demonstrate that in bulk water the photolysis of **1** proceeds via a ring expansion pathway, primarily controlled by solvolysis (Figure 1), as described in the literature.[20] However, when **1** is encapsulated within the hydrophobic CB7 cavity, a water attack is prevented. Thus, upon the irradiation, the singlet nitrene intermediate **A**, generated from **1** after loss of N_2, likely transforms into isocarboline intermediate **D** by an intramolecular insertion. The intermediate **D** then rearomatizes through an exothermic 1,5-hydrogen shift to carboline **3** (Figure 3b).[22]

The photolysis of **1** caged by CB7 was also examined with UV–vis spectrometry and fluorometry, using the same samples as for ^{1}H NMR. As demonstrated in Figure 3c and Figures S27 and S28 (Supporting Information), we observed an initial increase in absorption peaks during the irradiation period, which reached a stable plateau after ≈10 min. The emergence of new peaks at 254, 308, and 375 nm indicates the formation of carboline **3**. The conversion to **3** is also accompanied by a substantial enhancement in fluorescence, which also stabilized after 10 min of irradiation (Figure 3d).

The binding constant of complex **3**•CB7 was determined as $(3.14 \pm 0.16) \times 10^5$ M^{-1} via UV–vis titration (Figures S29 and S30, Supporting Information) and is thus comparable to that for **1**•CB7 (see above).

We also attempted the photolysis of aryl azide **1** in CB6 and CB8. However, due to the smaller cavity size, CB6 is not able to encapsulate aryl azide **1** (Figure S31, Supporting Information). As for the CB8, we performed the photolysis aryl azide **1** within CB8 in the 1:1 and 2:1 binding model (Figures S32 and S33, Supporting Information). The LC-MS results (Figure S34, Supporting Information) suggest the formation of carboline product **3** as well as other byproducts.

2.4. Photophysical Properties of Carboline 3 with CB7

Bright blue fluorescence of aqueous solutions of **3** and **3**•CB7 at ca. 460 nm is characterized by quantum yields, Φ_{FL}, of 77% and 90% and lifetimes of 21.9 and 25.4 ns, respectively (Figures S35 and S36, Supporting Information). With such parameters, they may find utility as blue fluorescent labels. In a test experiment,

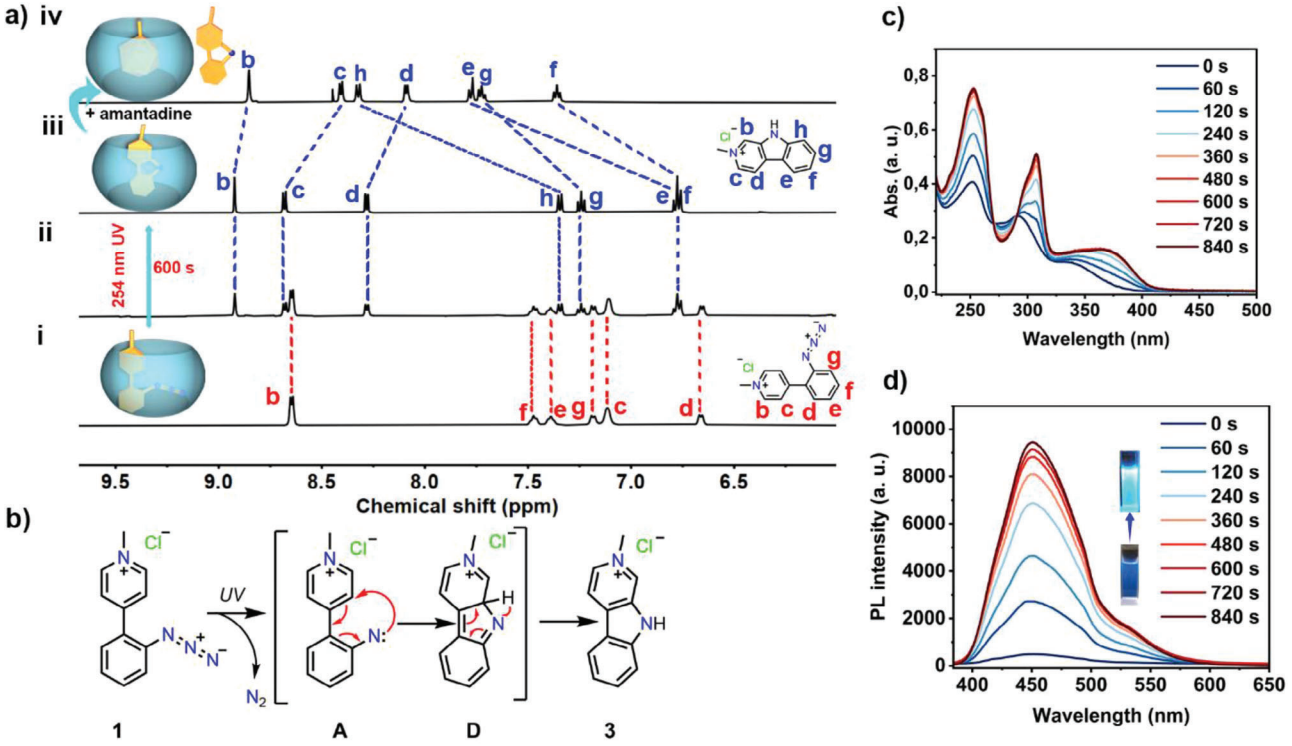


Figure 3. a) 1H NMR spectra of i) an equimolar ratio of 1 and CB7 (each 2 mM) in D_2O, after UV–light irradiation for ii) 120 s and iii) 600 s, and iv) after addition of amantadine as a CB7-sequestering guest; b) Proposed mechanism for the photolytic formation of carboline 3 in the CB7 cavity; c) UV–vis spectra of an equimolar reaction mixture of 1 and CB7 (each 2 mM) in water during the photolysis reaction with the 254 nm UV light source. Aliquots were taken at the specified time intervals and diluted to 50 μM prior to the UV–vis measurements; d) corresponding fluorescence spectra of the reaction mixture, which were obtained after dilution to 50 μM at 308 nm light excitation. The inset shows photographic images of the reaction mixture in a cuvette prior to and after 600 s UV light exposure.

carboline **3** produced fluorescent staining of HeLa cells as visualized by confocal microscopy (Figure S37, Supporting Information).

Photoluminescence of **3** in solid state is also of interest, in view of long-lived ("ultralong") phosphorescence reported for some carbazoles that are structurally closely related to carbolines.[23] It can be enhanced by CB*n* hosts, as a result of impeding nonradiative relaxation processes.[24] We applied lyophilization as a gentle solidification method to obtain solid (amorphous) samples of **3**•CB7 (1:1) and **3**•CB7+*β*-CD (1:1:1), where *β*-cyclodextrin (*β*-CD) was added as a photophysically neutral matrix compound[25] partially separating **3**•CB7 molecules from each other. These were compared with a polycrystalline sample of **3**. A similar blue fluorescence as in the solutions (except the shift to λ_{max} = 490 nm in crystalline **3**) was found for the above samples with Φ_{FL} = 20%, 49%, and 79% for **3**, **3**•CB7, and **3**•CB7+*β*-CD, respectively, under normal conditions (**Figure 4**a; Figures S38–S40, Supporting Information).

Besides the blue fluorescence, **3**•CB7 and **3**•CB7+*β*-CD demonstrated a minor green long-lived phosphorescence (λ_{max} ≈ 520 nm); however, only in vacuum or oxygen-free gas atmosphere (Figure 4b,c). Its quantum efficiency was estimated by comparison to the fluorescence as 3% for **3**•CB7 and 7% for **3**•CB7+*β*-CD (at 295 K). The quenching by O_2 developed within 2–3 min (gas/vacuum handling time), affected only the phosphorescence (reduced by a factor of ≈30 in air), was reversible and detectable already at 5 mbar O_2 pressure (Figure 4d; Figure S41, Supporting Information). This high sensitivity to O_2 apparently relates to the solid structure of **3**•CB7 and **3**•CB7+*β*-CD: as typical lyophilized materials they contain a large volume fraction of open pores (evidenced by SEM images in Figure S42, Supporting Information), likely hierarchically structured from micro- to nanosized ones and providing for an efficient gas exchange within the whole structure.[26]

The quenching obviously also benefits from the very long phosphorescence lifetimes. The corresponding decay curves were measured for **3**•CB7 and **3**•CB7+*β*-CD in vacuum at 295 K up to t ≈ 5 and 13 s (Figure 4c). They deviate from the monoexponential ones, especially in case of **3**•CB7. The multiexponential fit gives lifetimes within 0.12–1.2 s and 0.78–2.1 s, respectively (Figures S43 and S44, Supporting Information). The substantially longer and narrower lifetimes in **3**•CB7+*β*-CD may be attributed to a more homogeneous local environment of **3**•CB7 molecules due to the addition of *β*-CD as a matrix compound. Quenching of electronically excited states by molecular oxygen can generate singlet oxygen which in part relaxes radiatively (typically with a very low probability), resulting in a weak but characteristic emission band at about 1275 nm.[27] Indeed, such emission was detected from lyophilized **3**•CB7+*β*-CD irradiated at 375 nm in air (Figure S45, Supporting Information).

We note that crystalline **3** shows the long-lived phosphorescence as well, but only at temperatures below ≈150 K (Figure S46,

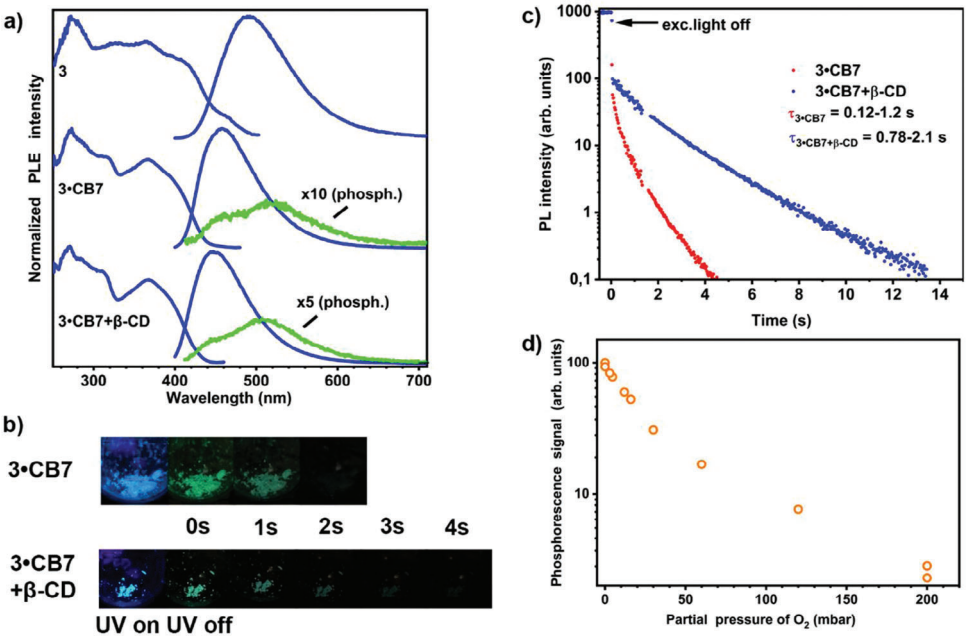


Figure 4. a) Fluorescence excitation and emission spectra (solid blue lines, left and right, respectively) of 3, 3●CB7 (1:1), and 3●CB7+β-CD (1:1:1) under normal conditions (at 295 K). Phosphorescence spectra (solid green line) for 3●CB7 and 3●CB7+β-CD in vacuum or in inert gas. b) Photographic images of 3●CB7 and 3●CB7+β-CD in vacuum, captured during and after exposure to 365 nm UV light. c) Phosphorescence decay curves of 3●CB7 and 3●CB7+β-CD in vacuum. d) The total phosphorescence signal of 3●CB7+β-CD as a function of the partial pressure of oxygen. The values at 0 mbar and 200 mbar were measured twice, at the beginning and end of the variation of O_2 (air) pressure, and thus indicate the reproducibility of the measurements.

Supporting Information). In line with previous observations,[24] the CB7 host apparently restricts nonradiative electronic relaxation channels in the photoexcited carboline guest molecule and thus promotes the PL, particularly the long-lived RTP emission.

Mechanical compression of the lyophilized samples under vacuum into firm pellets was pursued to suppress the pore structure and oxygen gas intake. Such a pellet was prepared from lyophilized **3**●CB7+β-CD evacuated in a pellet die and pressed at 20 kN cm^{-2}. The obtained pellet demonstrated RTP under normal conditions (in air) with parameters comparable to the initial **3**●CB7+β-CD material in vacuum or in an inert gas.

The oxygen sensitivity of the lyophilized phosphorescent compounds, as described above, is reminiscent of O_2-reduced PL in some metal–organic framework compounds investigated as oxygen sensors.[28] Accordingly, our results suggest carbolines as phosphorescent emitters and cucurbiturils as their hosts for oxygen-sensing applications.

3. Conclusion

To summarize, this study proposes a novel method to control the photolysis of an aryl azides in aqueous media using cucurbiturils (CBn) as a reaction chamber. The method was showcased with 4-(2-azidophenyl)-1-methylpyridin-1-ium chloride (**1**) and CB7. However, based on the mechanistic considerations, we expect that it can be extended to many other suitable combinations of CBn and aryl azides (see the additional aryl azides structures in Figure S47, Supporting Information). Namely, the hydrophobic environment within the cucurbituril cavity effectively guards photoreaction intermediates from a solvent (water) attack. This, together with the cavity confinement, steers the photoreaction of **1** toward generation of a carboline derivative with an excellent selectivity. In contrast, when the photolysis is carried out in bulk water, the dominant pathway involves ring opening and rearrangement, leading to the formation of an azepine derivative. The host-directed photolysis may thus provide an alternative to traditional methods of carboline synthesis, which typically rely on a metal catalyst.[29] Furthermore, the observation of long-lived RTP from the carboline derivative, when complexed with CB7, marks another exciting function of the cucurbituril cavity as a protective environment for luminescent guest molecules. This result will be of interest for producing RTR materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

aryl azide, cucurbiturils, host-guest interactions, oxygen sensing, photolysis, RTP

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