ChemCatChem
Research Article
doi.org/10.1002/cctc.202301162
Chemistry Europe
European Chemical Societies Publishing
www.chemcatchem.org

Perfluoralkyl/Rose Bengal Functionalized Janus Silica Nanoparticles for Photocatalytic Transformations with Singlet Oxygen

Omid Pourshiani,[a, b] Zeno Romero,[a] Nasim Ganji,[b] Tim Herrendorf,[a] Andreas Seifert,[c] Anna Demchenko,[d] Marc H. Prosenc,[a] Wolfgang Kleist,[a] Michael Kopnarski,[d] Babak Karimi,*[b, e] and Werner R. Thiel*[a]

A Janus mesoporous silica material with an imidazolium-based ionic liquid and perflouroalkyl motifs was synthesized using hollow Stöber particles. Its morphology, chemical composition and surface properties were characterized by N_2 physisorption analysis, scanning and transmission electron microscopy, elemental mapping, thermogravimetric and elemental analysis, and solid state NMR spectroscopy. The Janus nanoparticles have independent faces with fluorophilic and hydrophilic properties suitable for interaction with oxygen and Rose Bengal, which is a known photosensitizer for singlet oxygen generation. The catalytic activity of these Janus particles was evaluated in a series of transformations using singlet oxygen. They provide the desired products in high yield and selectivity.

Introduction

Performing reactions with high atom efficiency as well as minimum pollution and energy consumption is a prerequisite for the future of chemical syntheses. Consequently, green technologies, including photochemistry and electrochemistry, have been strongly developed during the last decade.[1] In this line, photosensitization to generate singlet oxygen ($^1O_2$) from triplet oxygen ($^3O_2$) under light irradiation has attracted attention.[2] $^1O_2$ is a reactive oxygen species (ROS)[3] that is widely used for the synthesis of fine chemicals and of biologically or pharmacologically active compounds.[4] In addition to chemistry, it also plays an important role in photodynamic therapy.[5] Since the generation of $^1O_2$ requires a photosensitizer, numerous light-absorbing molecules have been examined for this purpose. These include dyes based on transition metals[6] as well as metal-free dyes. The pioneering work in this area dates back to the 1940s when G. O. Schenck, inspired by nature, applied chlorophyll as a natural pigment for a light-driven transformation.[7] Subsequently, a wide range of organic dyes were investigated in this context.[8] These dyes can generate $^1O_2$ from $^3O_2$ with high efficiency under mild conditions. Rose Bengal (**RB**), for example, a xanthene-type dye, absorbs green light and efficiently generates $^1O_2$.[9] However, the majority of the reported photosensitizer systems work in solution, which raises the problem of recyclability and requires additional steps to separate them from the products. On the other hand, aggregation of the photosensitizer molecules in solution is another issue of this strategy, as such aggregated species usually have much lower performance in $^1O_2$ generation efficiency than the monomers.[10] Therefore, the development of reusable heterogeneous photosensitizers by immobilizing light-absorbing molecules on suitable supports in an appropriate concentration and dispersion is highly desirable.[11]

Anisotropic Janus materials, which have two distinct faces with different chemical functions have recently found widespread applications for example in catalysis.[12] They allow for example the adaption of catalysts to bi- or tri-phasic systems by stabilizing so-called Pickering emulsions. We have recently synthesized a series of heterogeneous silica- and PMO-based (PMO = periodic mesoporous organosilica) Janus-type catalysts and applied them in various chemical transformations.[13]

In a heterogeneously catalyzed reaction comprising of a liquid (substrate, solvent), a solid (catalyst) and a gas-phase

---

[a] Dr. O. Pourshiani, Z. Romero, T. Herrendorf, Dr. M. H. Prosenc, Prof. Dr. W. Kleist, Prof. Dr. W. R. Thiel
Fachbereich Chemie, RPTU Kaiserslautern-Landau
Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany
E-mail: thiel@chemie.uni-kl.de
Homepage: https://chem.rptu.de/ags/ag-thiel

[b] Dr. O. Pourshiani, Dr. N. Ganji, Prof. Dr. B. Karimi
Department of Chemistry
Institute for Advanced Studies in Basic Sciences (IASBS)
Prof. Sobouti Boulevard, Zanjan 45137-66731, Iran
E-mail: karimi@iasbs.ac.ir
Homepage: http://www.iasbs.ac.ir/~karimi/karimi.htm

[c] Dr. A. Seifert
Technische Universität Chemnitz, Fakultät für Naturwissenschaften
Institut für Chemie, Professur für Polymerchemie
Straße der Nationen 62, 09111 Chemnitz, Germany

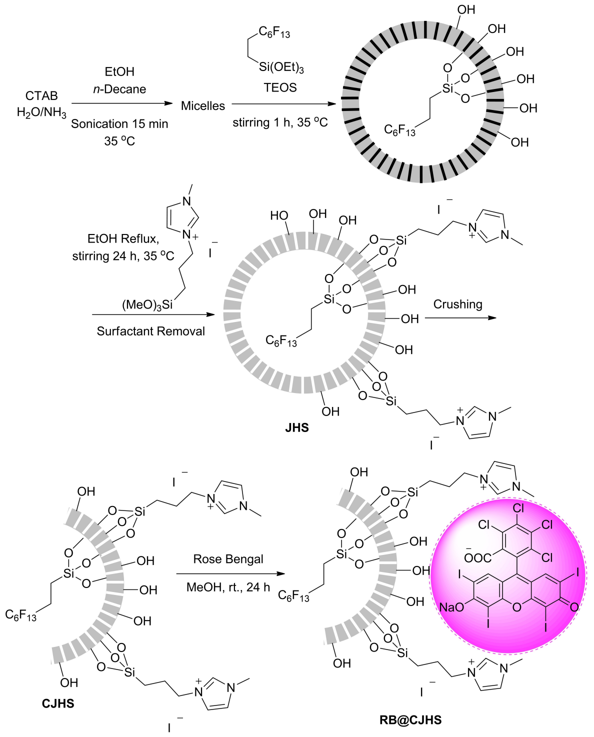
[d] Dr. A. Demchenko, Prof. Dr. M. Kopnarski
Institut für Oberflächen und Schichtanalytik (IFOS)
Trippstadter-Str. 120, 67663 Kaiserslautern, Germany

[e] Prof. Dr. B. Karimi
Research Center for Basic Sciences & Modern Technologies (RBST)
Institute for Advanced Studies in Basic Sciences (IASBS)
Prof. Sobouti Boulevard, Zanjan 45137-66731, Iran

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202301162

(substrate), the reaction rate strongly depends on the solubility of the gas in the liquid phase and on the accessibility of the catalytically active sites by the substrates. Inspired by the excellent tunability of Janus-type mesoporous materials, we asked ourselves whether it was possible to optimize a typical catalytic three-phase reaction by cleverly combining surface functionalities. In this context, the solid catalyst should both enhance the diffusion of oxygen and carry the photosensitizer to generate singlet oxygen ($^1O_2$). The reactants, together with a solvent, form the third phase. Such a system ensures at the same time the easy separation as well as the recyclability of the catalyst.

This was our motivation to design a silica-based Janus material containing covalently bound perfluorocarbon chains (PFCs) on one side and an imidazolium based ionic liquid on the other side.[14] PFCs are not only extremely hydrophobic, but also show an inherently high oxygen solubility and transferring capacity.[15] While the use of fluoroalkyl groups to develop efficient homogeneous photocatalytic systems is an established strategy,[16] their potential as heterogeneous photosensitizers remained largely unexplored.[17] In the current study, we have employed a new approach by directly functionalizing the surface of a Janus support with fluorinated hydrocarbon chains. This innovative strategy aims to increase the concentration of dioxygen molecules surrounding the photosensitizer and thereby enhancing the overall efficiency of the photocatalytic system. Since Rose Bengal is an anionic compound, the grafting of the photosensitizer is achieved by electrostatic interactions with the imidazolium sites of the Janus material.



Scheme 1. Synthesis of the photocatalyst **RB@CJHS**.

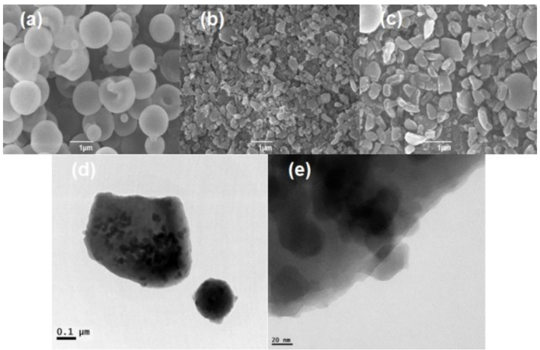


Figure 1. SEM images of **JHS** (a), **CJHS** (b), and **RB@CJHS** (c). TEM images of **RB@CJHS** with different magnifications (d and e).

Results and Discussion

To start this work, porous Janus hollow spheres (**JHS**) were synthesized in the first step by a modified Stöber process using tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (PFOTES) in a basic aqueous environment (Scheme 1). The resulting material **JHS** is decorated with perfluoroalkyl chains at the inner side of the spheres. Treatment of **JHS** with methyl-3-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium iodide (MTMSPII) immobilizes the ionic-liquid motifs on the outer side of the particles **JHS**. Then the spheres possessing two different sides were crushed to give **CJHS**. Finally, the iodide anions were exchanged against anionic Rose Bengal to furnish **RB@CJHS**.

The surface properties of the synthesized materials were investigated by N_2 physisorption analysis (see Table S3 in the SI). All samples show an H1-type hysteresis at higher relative pressure (P/P_0: 0.9–1), indicating the presence of some macropores in the shell (see Figures S1 and S2 in the SI). Interestingly, the specific surface area increases from 193 to 342 $m^3 \cdot g^{-1}$ by crushing the hollow silica spheres.

Figure 1 gives an impression of the morphology of the prepared materials. The SEM image of **JHS** shows mainly intact hollow particles with a rather uniform diameter in the range of 1.0 to 1.5 μm (Figure 1a). The presence of some wrinkled particles is a proof for the hollow structure. Crushing converts these hollow spheres into nano-sheets with a uniform wall thickness (approx. 150–200 nm) (Figure 1b). Analyzing the morphology of **RB@CJHS** by SEM and TEM further confirms the preparation of crushed Janus particles with different sizes (Figures 1c–1e).

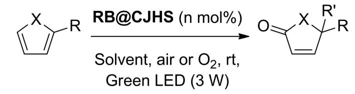
The solid-state ^{13}C, ^{29}Si CP-MAS and ^{19}F MAS NMR spectra of **RB@CJHS** are deposited in the SI (Figures S25–S27), too. The typical resonances detected by the high resolution ^{13}C NMR spectra of the organosilane precursors and **RB** are also observed in the solid-state ^{13}C CP-MAS NMR spectrum of **RB@CJHS**. The ^{29}Si CP-MAS NMR spectrum of **RB@CJHS** exhibits broad resonances at −110, −100, and −92 ppm, arising from Q^4 [$Si(OSi)_4$], Q^3 [$Si(OSi)_3(OH)$], and Q^2 [$Si(OSi)_2(OH)_2$] sites in the silica framework. Moreover, two signals at −66 and -57 ppm correspond to T^3 [$RSi(OSi)_3$] and T^2 [$RSi(OSi)_2(OH)$] species, providing solid evidence for the successful covalent incorporation of the organosilane precursors in the network (Figure S27).[13a,b] The ^{19}F MAS NMR spectrum of **RB@CJHS** presents the typical resonances of the PFOTES precursor. The loading of imidazolium groups incorporated into the Janus structure was measured by elemental analysis and calculated to be 0.8 $mmol \cdot g^{-1}$.

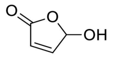
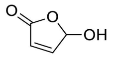
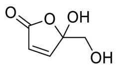
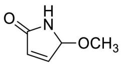
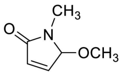
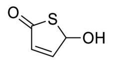
In the next step, the ability of the **RB@CJHS** material to act as a photocatalyst in several organic transformations with $^1O_2$ was investigated. The particular reactivity of $^1O_2$ in such transformations depends on different factors, including the type of substrate, solvent, temperature, etc. The reaction pathways that $^1O_2$ species usually take when they encounter olefins, dienes or aromatic structures include [4+2] and [2+2] cycloadditions as well as ene reactions.[18]

First, we examined the $^1O_2$-based oxidation of a series of five-membered heterocycles with **RB@CJHS** as a photocatalyst. Among these substrates, furfural was efficiently converted to 5-hydroxy-2(5*H*)-furanone (HFO) under the reaction conditions shown in Table 1 (entry 1). This reaction most likely proceeds *via* a [4+2] cycloaddition reaction generating an endo-peroxide intermediate (Scheme S4, SI). In the past, several photocatalytic routes have been reported for the preparation of HFO, which is a key synthon for the synthesis of pesticides, insecticides, alkaloids and other biologically active products.[19] However, most of these methods have limitations, such as the use of inappropriate or harmful light sources, poor recyclability of the photosensitizer, high temperatures, long reaction times or tedious product work-up. Therefore, the highly efficient synthesis of HFO in our system using a supported photosensitizer and just a green LED under mild reaction conditions in combination with a short reaction time is an important progress in this field. **RB@CJHS** was also applicable for the photooxidation of 2-furoic acid to HFO in high yield in just 30 min (Table 1, entry 2). Treatment of 5-(hydroxymethyl)furfural (5-HMF), a bio-based building block for the preparation of various high-value chemicals,[20] under modified conditions (0.15 mol% of **RB@CJHS**, *i*PrOH:H_2O (1:1), 20 h) provided 5-hydroxy-5-(hydroxymethyl)-furan-2(5*H*)-one (H^2MF) in good yield and selectivity (TOF = 23 h^{-1},Table 1, entry 3). An interesting protocol for this important transformation was discovered by Kappe *et al.*[21] using homogeneous **RB** afforded H^2MF, which gave an excellent TOF of 600 h^{-1} in a continuous flow system. While acknowledging the significant achievements in this report, the use of a high-power light source (60 W), high oxygen pressure (17.2 bar O_2), and the potential photodegradation and non-recyclability of homogeneous RB[22] are notable shortcomings, which are avoided in our catalyst system. The method presented here also worked well for the photochemical oxidation of pyrrole derivatives. The corresponding 5-methoxy lactams were obtained in high yield and selectivity (Table 1, entries 4 and 5). This result is also of great value with respect to the rather limited number of studies on the reactivity of $^1O_2$ toward pyrrolic compounds.[23] However, attempts to extend this approach to the oxidation of 2-thiophene carboxylic acid with $^1O_2$ were not successful (Table 1, entry 6).

To evaluate the benefit of the perflouroalkyl chains, we compared the activity of **RB@CJHS** (TOF = 3300 h^{-1}) in the oxidation of furfural with a similar material containing octyl chains instead of $(CH_2)_2(CF_2)_5CF_3$ groups. The alkyl-based catalyst showed lower activity (2 h, 90% yield) (TOF = 750 h^{-1}) than **RB@CJHS** under the given reaction conditions, highlighting the substantial role of the fluorinated alkyl groups, which we assign to an increase of oxygen solubility in close proximity to the

Table 1. Substrate scope for the oxidation of five membered heterocycles with $^1O_2$ using **RB@CJHS** as the photosensitizer.[a]



Entry	Substrate	Cat. (mol%)	Solvent	t (h)	Product	Yield (%)
1	furfural	0.06	CH_3OH	0.5		>99[b]
1	2-furoic acid	0.06	CH_3OH	0.5		>99[b]
3	5-HMF	0.15	*i*PrOH:H_2O (1:1)	20		70[c]
4	pyrrole	0.09	CH_3OH	0.5		96[c]
5	*N*-methylpyrrole	0.09	CH_3OH	1		70[c]
6	2-thioph carboxylic acid	0.06	CH_3OH	1		0[c]

[a] reaction conditions: substrates (1 mmol), cat.: **RB@CJHS**, with the given molar amount of **RB**), r.t., solvent (5 mL), ambient pressure, isolated yields. [b] with air balloon [c] with oxygen balloon.

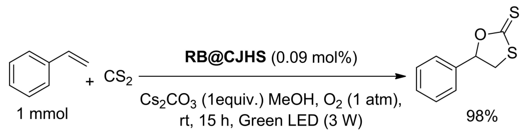
photosensitizer. To elucidate and highlight the influence of the extraordinary structure of the **RB@CJHS** catalyst on its capability in catalyzing the mentioned reactions, we prepared two other catalysts including RB supported on a simple silica sample and RB supported on a silica sample bearing imidazolium ionic liquid groups, and investigate their efficiency on photooxidation of furfural to HFO as a model reaction. Both catalysts were more sluggish than **RB@CJHS**, and after 6 h just 13 % (TOF = 36 h^{-1}) and 45 % (TOF = 125 h^{-1}) yield were obtained for the RB supported on the simple silica and RB supported on silica bearing imidazolium ionic liquid groups, respectively. It seems that the special arrangement of the **RB@CJHS** structure with imidazolium groups on one side and perfluorocarbon groups on the opposite side and the synergism and cooperation between them play an essential role in the present photocatalytic system.

Table S1 in the SI compare the present system with several previously reported photoorganocatalytic systems for the photooxidation of different five-membered heterocyclic compounds. The results demonstrate that our system is superior and comparable to previously reported systems in terms of sustainability, versatility, simplicity of apparatus design, and efficiency.

These results encouraged us to investigate the efficiency of **RB@CJHS** in the photooxidation of some aromatic compounds.[24] Anthracene endo-peroxide could be obtained after 24 h of irradiation of anthracene in the presence of 0.15 mol% of **RB@CJHS** in acetonitrile solution under an atmospheric pressure of oxygen in 80 % yield (Table S2 in the SI). The photo-induced dearomatization of electron-rich *para*-alkyl phenols leading to *para*-peroxyquinols is a key step in the total synthesis of some natural products.[25] With **RB@CJHS** (0.25 mmol), the photo-oxygenation of 2,4,6-trimethylphenol led to 80 % of 4-hydroperoxy-2,4,6-trimethylcyclohexa-2,5-dienone after 24 h in a 1 : 1 mixture of water and acetonitrile (Table S3 in the SI).

The regioselective synthesis of 1,3-oxathiolane-2-thiones by a photochemical difunctionalization of styrenes[26] was introduced by Yadav *et al.* in 2016. The conventional protocols that are available for the synthesis of these compounds, including the ring opening of oxiranes, suffer from some drawbacks. The probably most important issue in these reactions is the formation of regioisomers.[27] With **RB@CJHS** as the photosensitizer and styrene as the substrate, 5-phenyl-1,3-oxathiolane-2-thione was obtained in 98 % yield under an atmospheric pressure of dioxygen as the sole product (Scheme 2).

RB-type photocatalysts have also shown excellent activity in the α-functionalization of *N*-aryl tetrahydroisoquinolines through a sp^3 C–H bond activation, followed by reaction with a carbon nucleophile. This is a powerful method for C–C bond formation that leads to α-substituted compounds with interesting biological and pharmaceutical activities.[11,28] **RB@CJHS** exhibited excellent photocatalytic activity in the cross-dehydrogenative coupling reaction of *N*-aryl tetrahydroisoquinolines **1 a,b** with the nitroalkanes **2 a,b** under green LED irradiation, as shown in Table 2, entries 1–3. In addition, coupling reactions of the same substrate with trimethylsilyl cyanide (**3**) and ethyl diazoacetate (**4**) gave rise to the desired products in good to excellent yields (Table 2, entries 4–6). Such reactions typically occur *via in-situ* formation of an iminium intermediate, which is susceptible to attack by nucleophiles (Scheme S5 in the SI).



Scheme 2. Synthesis of 5-phenyl-1,3-oxathiolane-2-thione using **RB@CJHS** as the photosensitizer.

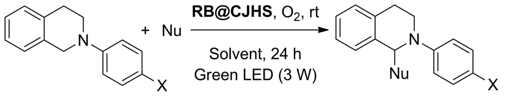
With these results in hand, it seemed reasonable to extend the α-functionalization of *N*-aryl tetrahydroisoquinolines to multicomponent reactions that involve a sp^3 C–H bond functionalization of a tetrahydroisoquinoline at the α-position with an isocyanide and a carboxylic acid. Photochemical versions of such transformations have been reported in the past.[29] In the presence of **RB@CJHS**, the reactions proceeded smoothly at room temperature and the desired α-aminoamide products were achieved in moderate to good yields (Table 3). It is interesting to note that in the case of α-functionalization of *N*-aryl tetrahydroisoquinolines, almost all reactions inherently required longer reaction times to achieve satisfactory product yields (or a steady conversion) compared to other photo-induced $^1O_2$-mediated oxidative transformations in this study. Taking into account that *N*-aryl tetrahydroisoquinolines have a tertiary amine functionality similar to DABCO, which is a well-known $^1O_3$ quenching agent, it is plausible that the longer reaction times are a result of a partial quenching of $^1O_2$ by the isoquinoline.[30] It is also very important to mention that the contribution of *in*-situ generated superoxide anions in the reaction involving *N*-aryl tetrahydroisoquinolines cannot be neglected. The proposed mechanism for these reactions involves the nucleophilic attack of isocyanides and carboxylic acids on iminium intermediates, followed by a rearrangement to the final α-aminoamides (Scheme S5, S6 in the SI).

The recyclability of **RB@CJHS**, which is an important factor for a practical application, was evaluated for the photooxidation of furfural in methanol solution at ambient temperature and air pressure. The catalyst efficiency for the conversion of furfural to HFO was screened after 1 h with GC analysis. After this time, the solid catalyst was filtered off, washed thoroughly with EtOH, dried overnight at 60 °C and was directly reused in the next run. Figure 2 summarizes the results of five consecutive cycles, revealing no significant loss in the activity of the catalyst.

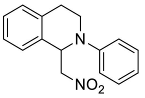
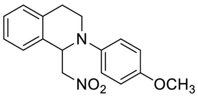
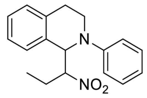
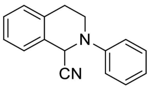
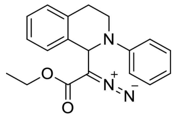
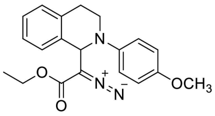
Conclusions

In summary, Janus nanoparticles containing imidazolium-based ionic liquid groups on one side and highly hydrophobic fluorinated octyl groups on the other side could be obtained by the initial preparation of hollow spheres using a modified Stöber process followed by crushing to nanosheets. Decoration of the imidazolium functionalized side with Rose Bengal resulted in the heterogeneous photocatalyst **RB@CJHS**. This

Table 2. Substrate scope for the α-functionalization of *N*-aryl tetrahydroisoquinolines with carbon nucleophiles using **RB@CJHS** as the photosensitizer.



1a: X = H, 1b: X = OCH_3
Nu = 2a: CH_3NO_2, 2b: $C_3H_7NO_2$
3: TMSCN, 4: $C_4H_6N_2O_2$

Entry	Reactants	Nu	Solvent	Product	Yield (%)[a]
1	1a	2a	EtOH		88[b]
2	1b	2a	EtOH		92[b]
3	1a	2b	EtOH		55[b]
4	1a	3	CH_3CN		80[c]
5	1a	4	CH_2Cl_2		84[b]
6	1b	4	CH_2Cl_2		90[b]

Reaction conditions: substrate (0.5 mmol), **RB@CJHS** (0.6 mol% of **RB**), r.t., solvent (5 mL). [a] Isolated yield. [b] Nu (5 mmol). [c] TMSCN (3 mmol).

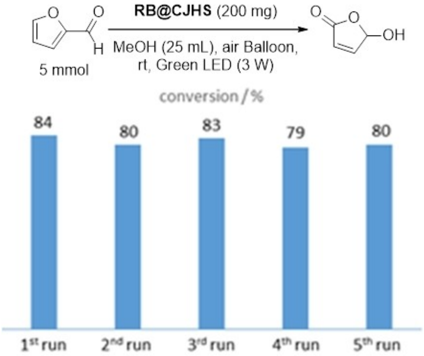


Figure 2. Recyclability study for the photocatalyst **RB@CJHS**.

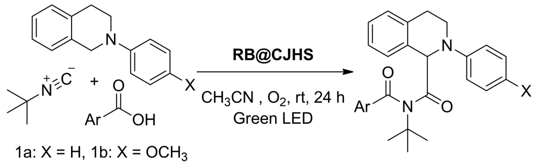
Janus material is able to catalyze a wide range of photochemical transformations with $^1O_2$, providing the desired products in good to excellent yield and with high selectivity by simple irradiation with a green LED. Comparison with an alkyl functionalized congener suggests that the fluorinated octyl motifs act as oxygen carriers. A recyclization study proved that **RB@CJHS** can be applied in a series of runs without significant loss of activity. We currently are exploring further applications of **RB@CJHS** in reactions with singlet oxygen and carry out mechanistic investigations.

Experimental Section

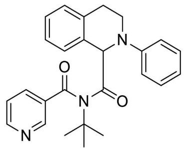
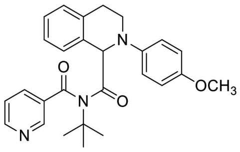
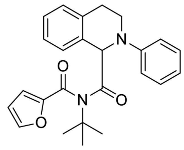
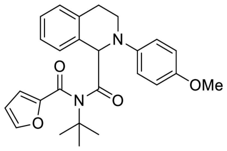
Synthesis of 1-methyl-3-(3-trimethoxysilyl)propyl)-1*H*-imidazol-3-ium iodide (MTMSPII): The ionic liquid **MTMSPII** was prepared by reacting 0.804 mL (10 mmol, 0.821 g) of *N*-methylimidazole and 2.06 mL (10 mmol, 2.9017 g) of 3-iodopropyltrimethoxysilane in a two-neck flask containing 30 mL of dry toluene under a nitrogen atmosphere using a Schlenck line technique. The resulting mixture was refluxed for 24 h. After this time, the reaction mixture was allowed to cool to room temperature and then the toluene phase was decanted off, leaving the solid product. Finally, the ionic liquid was washed with dry *n*-pentane (5×15 mL) to remove the unreacted starting materials and obtain pure MTMSPII (97 % yield).

Synthesis of crushed Janus hollow spheres (CJHSs): To prepare the Janus hollow spheres, 0.644 g (1.76 mmol) of CTAB were added to a 500 mL round bottom flask containing 215.6 mL of deionized water and 0.4 mL of aqueous ammonia (25 w%). The mixture was then stirred at room temperature. A solution containing 128 mL of EtOH and 0.5 mL (0.365 g) of *n*-decane was prepared in another flask and then transferred into the above solution under vigorous stirring. The resulting mixture was ultrasonicated at 35 °C for

Table 3. Substrate scope for the multi component reaction of *N*-aryl tetrahydroisoquinolines, isocyanides and carboxylic acids with $^1O_2$ using **RB@CJHS** as the photosensitizer.



1a: X = H, 1b: X = OCH_3
2a: Ar = 3-pyridyl, 2b: Ar = 2-furyl

Entry	1	Ar	Product	Yield (%)[a]
1	1a	3-Pyridyl		70
2	1b	3-Pyridyl		56
3	1a	3-Furyl		80
4	1b	3-Furyl		60

Reaction conditions: *N*-aryl-tetrahydroisoquinolines (0.25 mmol), *tert*-butyl isocyanide and carboxylic acids (0.3 mmol), **RB@CJHS** (0.6 mol% of **RB**), CH_3CN (5 mL). [a] Isolated yield.

15 min. Then 0.39 mL (1 mmol) of PFOTES and then 4.26 mL (19.2 mmol) of TEOS were added dropwise to the above solution under a nitrogen atmosphere. After 1 h, 744.6 mg (2 mmol) of **MTMSPII** dissolved in 1 mL of dry EtOH were added to the reaction flask to immobilize the ionic liquid groups on the outer surface of the formed spheres. After 24 h, the white solid was separated from the solution by centrifugation. The synthesized material was transferred into a 250 mL round bottom flask containing 120 mL of EtOH and 0.25 mL of conc. HCl (37 %). The obtained suspension was stirred at 60 °C for 6 h to remove the CTAB template. The template removal process was repeated at least twice to ensure the complete extraction of CTAB from the porous structure. The resulting Janus material (2.15 g) was collected by centrifugation (5 min at 5000 rpm), washed with EtOH several times and dried overnight in an oven at 60 °C.

The prepared Janus hollow spheres were completely crushed through a mild grinding method using mortar and pestle for 30 min to increase the accessibility of the active sites at the inner and outer surfaces. The loading of the ionic liquid units calculated by elemental analysis was found to be 0.8 mmol·g^{-1}.

Synthesis of the Rose Bengal catalyst (RB)@CJHS: **RB@CJHS** was prepared as follows: First, 1.00 g of the synthesized **CJHS** was dispersed in 20 mL of MeOH using ultrasonication for at least 30 min. Then 0.03 g (0.0294 mmol) of the sodium salt of Rose Bengal was dissolved in 30 mL of MeOH and the obtained pink-colored solution was added dropwise to the **CJHS** suspension. The reaction mixture was vigorously stirred at room temperature for 24 h, then filtrated and the solid residue washed with MeOH (4×10 mL). The solid was further washed with H_2O (3×10 mL) and then washed again with MeOH (3×10 mL) to ensure the removal of RB species that had no electrostatic interaction with the ionic liquid moieties of the Janus material. The resulting pink-colored powder was dried overnight in an oven at 60 °C. The loading of RB molecules immobilized on the surface of the Janus material was studied by solid state UV-Vis spectroscopy of **RB@CJHS**, as well as by UV-Vis spectroscopy of the mother liquor and the washing solution and calculated to be 0.0163 mmol·g^{-1}.

Photooxidation of furfural to 5-hydroxy-2(5*H*)-furanone using the RB@CJHS photocatalyst: The singlet oxygen-induced photooxidation of furfural to 5-hydroxy-2(5*H*)-furanone was taken as a model reaction for [4+2] cycloaddition reactions catalyzed by **RB@CJHS**. It was performed as follows: 96.085 mg (1 mmol) of furfural, 20 mg (0.06 mol% of RB loading) of **RB@CJHS** and 5 mL of MeOH were transferred into a reaction flask charged with a magnetic stirring bar and a balloon filled with air. The reaction mixture was sonicated for a few minutes and then stirred under low-power green LED irradiation (3 W, 500 nm) at room temperature for 30 min. After this time, the solid catalyst was separated by centrifugation. After removing the solvent under reduced pressure, the crude product was obtained, and its purity was quantified by NMR spectroscopy.

Photo-mediated difunctionalization of styrene to 5-phenyl-1,3-oxathiolane-2-thione using the RB@CJHS photocatalyst: For the photo-mediated difunctionalization of styrene, 60 μL (1 mmol) of carbon disulfide was added to a solution of Cs_2CO_3 (1 equiv., 0.326 g) in MeOH (5 mL). The reaction flask was sealed and the mixture was stirred at room temperature for 3 h to prepare the cesium methylxanthate intermediate. Then, 115 μL (1 mmol) of styrene and 50 mg of **RB@CJHS** were added to the suspension. The reaction mixture was ultrasonicated for a few minutes and then stirred under an O_2 atmosphere and green LED irradiation (3 W, 500 nm). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by centrifugation, and the filtrate was extracted using EtOAc and H_2O. Finally, the organic layer was dried on magnesium sulfate, and the solvent was evaporated using a rotary evaporator and the crude product was purified by flash column chromatography on silica gel (*n*-hexane:ethyl acetate 20:1). The purity of the final product was determined by NMR spectroscopy.

α-Functionalization of *N*-aryl-tetrahydroisoquinolines with nitroalkanes in the presence of the RB@CJHS photocatalyst: 0.5 mmol of the *N*-aryl-tetrahydroisoquinoline, 5.0 mmol of a nitroalkane, 100 mg of **RB@CJHS** and 5 mL of EtOH were charged in a reaction vessel equipped with a magnetic stirring bar and balloon of oxygen (1 atm). The resulting mixture was stirred under the irradiation of a green LED (3 W, 500 nm) at room temperature for 24 h. After this time, the catalyst was separated from the reaction mixture by centrifugation. The solvent was evaporated under reduced pressure and the crude product was purified using flash column chromatography on silica gel (*n*-hexane:ethyl acetate 20:1) to afford the desired products.

α-Functionalization of *N*-aryl-tetrahydroisoquinolines with ethyl diazoacetate or trimethylsilyl cyanide using the RB@CJHS photocatalyst: The **RB@CJHS** catalyzed coupling of *N*-aryl-tetrahydroisoquinolines with ethyl diazoacetate or trimethylsilyl cyanide was carried out using a procedure similar to that for the functionalization with nitroalkanes, albeit with some changes concerning the solvent and amount of catalyst to obtain the desired products in high yield and selectivity. The conditions for these reactions are summarized in Table 2 in the manuscript.

RB@CJHS-mediated multicomponent Ugi-type reaction of *N*-aryl tetrahydroisoquinolines with isocyanides and carboxylic acids: The α-functionalization/multicomponent Ugi-type reaction of *N*-aryl-tetrahydroisoquinolines with carboxylic acids and *tert*-butyl isocyanide was performed as follows: *N*-aryl-tetrahydroisoquinoline (0.5 mmol), carboxylic acid (0.6 mmol), *tert*-butyl isocyanide (0.6 mmol), **RB@CJHS** (50 mg), and acetonitrile (5 mL) were transferred into a 10 mL reaction flask. The reaction mixture was stirred under an O_2 atmosphere and green LED irradiation at room temperature for a specified time. The progress of the reaction was monitored by TLC. After completion of the reaction, the solid catalyst was separated from the reaction mixture, and the crude product was purified by column chromatography on silica gel using *n*-hexane:ethyl acetate as eluent.

Supporting Information

The authors have cited additional references within the Supporting Information (Ref. [31–39]).

Acknowledgements

The authors thank the research unit NanoKat at the RPTU Kaiserslautern-Landau for providing facilities and funding, as well as the Iran Science Elites Federation (ISEF) Grant No 11/66332 and Ministry of Science, Research and Technology of Iran (MSRT) for financial support of O.P. The authors acknowledge the AK Manolikakes in TU Kaiserslautern for providing some chemicals and also are grateful to Mr. Yannick Otto from the electronics workshop at the RPTU Kaiserslautern-Landau for his invaluable help. B.K. also greatly appreciates Alexander von Humboldt Foundation for donation of a George Forster Research Award no. Ref [3].4-1116632-IRN-GFPR. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

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: Rose Bengal · Janus material · Photosensitizer · Fluorinated hydrocarbons · Singlet oxygen

[1] a) K. D. Patil, *Trends Chem. Eng.* **2014**, *2*, 12–19; b) M. Sugiyama, K. Fujii, S. Nakamura, *Solar to Chemical Energy Conversion Theory and Application. Vol. 32*, Springer International Publishing, **2016**, pp. 1–34; c) L. Buzzetti, G. E. M. Crisenza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 3730–3747.

[2] a) K. Imato, K. Ohira, M. Yamaguchi, T. Enoki, Y. Ooyama, *Mater. Chem. Front.* **2020**, *4*, 589–596; b) J. Park, D. Feng, S. Yuan, H. C. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 430–435; c) P. Kubat, P. Henke, V. Berzediova, M. Stepanek, K. Lang, J. Mosinger, *ACS Appl. Mater. Interfaces* **2017**, *9*, 36229–36238.

[3] a) V. Dogra, C. Kim, *Front. Plant Sci.* **2020**, *10*, 1640–1648; b) I. Pibiri, S. Buscemi, A. P. Piccionello, A. Pace, *ChemPhotoChem* **2018**, *2*, 535–547.

[4] a) P. Esser, B. Pohlmann, H. D. Scharf, *Angew. Chem. Int. Ed.* **1994**, *33*, 2009–2023; b) M. Oelgemöller, C. Jung, J. Mattay, *Pure Appl. Chem.* **2007**, *79*, 1939–1947; c) M. Kleczka, D. But, D. Dylong, C. Fendinger, V. Marmann, C. Wartke, A. G. Griesbeck, *ChemPhotoChem* **2018**, *2*, 964–975; d) A. G. Griesbeck, M. Kleczka, A. de Kiff, M. Vollmer, A. Eske, S. Sillner, *Pure Appl. Chem.* **2015**, *87*, 639–647.

[5] a) R. Gao, X. Mei, D. Yan, R. Liang, M. Wei, *Nat. Commun.* **2018**, *9*, 1–11; b) V. Biju, *Chem. Soc. Rev.* **2014**, *43*, 744–764.

[6] a) C. K. Prier, D. A. Rankic, D. W. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; b) M. H. Shaw, J. Twilton, D. W. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926; c) A. G. Amador, T. P. Yoon, *Angew. Chem. Int. Ed.* **2016**, *55*, 2304–2306; d) Y. Zhang, Q. Wang, Z. Yan, D. Ma, Y. Zheng, *Beilstein J. Org. Chem.* **2021**, *17*, 2520–2542.

[7] G. O. Schenck, *Angew. Chem.* **1944**, *57*, 101–102.

[8] a) D. A. Nicewicz, T. M. Nguyen, *ACS Catal.* **2014**, *4*, 355–360; b) S. G. E. Amos, M. Garreau, L. Buzzetti, J. Waser, *Beilstein J. Org. Chem.* **2020**, *16*, 1163–1187; c) P. De Bonfils, E. Verron, C. Sandoval-Altamirano, P. Jaque, X. Moreau, G. Gunther, P. Nun, V. Coeffard, *J. Org. Chem.* **2020**, *85*, 10603–10616; d) D. P. Hari, B. Konig, *Chem. Commun.* **2014**, *50*, 6688–6699; e) J. H. Park, K. C. Ko, E. Kim, N. Park, J. H. Ko, D. H. Ryu, T. K. Ahn, J. Y. Lee, S. U. Son, *Org. Lett.* **2012**, *14*, 5502–5505; f) W. Schilling, Y. Zhang, P. K. Sahoo, S. K. Sarkar, S. Gandhi, H. W. Roesky, S. Das, *Green Chem.* **2021**, *23*, 379–387.

[9] a) G. R. Fleming, A. W. E. Knight, J. M. Morris, B. J. S. Morrison, G. W. Robinson, *J. Am. Chem. Soc.* **1977**, *99*, 4306–4311; b) T. Yamaguchi, Y. Sugiura, E. Yamaguchi, N. Tada, A. Itoh, *Asian J. Org. Chem.* **2017**, *6*, 432–435; c) J. Yang, D. Xie, H. Zhou, S. Chen, J. Duan, C. Huo, Z. Li, *Adv. Synth. Catal.* **2018**, *360*, 3471–3476; d) M. H. Stockett, C. Kjaer, S. Daly, E. J. Bieske, J. R. R. Verlet, S. Brøndsted Nielsen, J. N. Bull, *J. Phys. Chem. A* **2020**, *124*, 8429–8438.

[10] B. M. Estevao, F. Cucinotta, N. Hioka, M. Cossi, M. Argeri, G. Paul, L. Marchese, E. Gianotti, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26804–26812.

[11] a) D. Valverde, R. Porcar, D. Izquierdo, M. I. Burguete, E. Garcia-Verdugo, S. V. Luis, *ChemSusChem* **2019**, *12*, 3996–4004; b) X. Li, Y. Li, Y. Huang, T. Zhang, Y. Liu, B. Yang, C. He, X. Zhou, J. Zhang, *Green Chem.* **2017**, *19*, 2925–2930; c) Y. Chu, N. Corrigan, C. Wu, C. Boyer, J. Xu, *ACS Sustainable Chem. Eng.* **2018**, *6*, 15245–15253; d) P. Li, G. W. Wang, *Org. Biomol. Chem.* **2019**, *17*, 5578–5585; e) Y. Huang, Z. Xin, W. Yao, Q. Hu, Z. Li, L. Xiao, B. Yang, J. Zhang, *Chem. Commun.* **2018**, *54*, 13587–13590; f) S. M. Soria-Castro, B. Lebeau, M. Cormier, S. Neunlist, T. J. Daou, J. P. Goddard, *Eur. J. Org. Chem.* **2020**, *2020*, 1572–1578; g) R. Radjagobalou, J. F. Blanco, L. Petrizza, M. Le Bechec, O. Dechy-Cabaret, S. Lacombe, M. Saveb, K. Loubiere, *ACS Sustainable Chem. Eng.* **2020**, *8*, 18568–18576; h) C. Mendoza, N. Emmanuel, C. A. Paez, L. Dreesen, J. C. M. Monbaliu, B. Heinrichs, *ChemPhotoChem* **2018**, *2*, 890–897; i) B. Tambosco, K. Segura, C. Seyrig, D. Cabrera, M. Port, C. Ferroud, Z. Amara, *ACS Catal.* **2018**, *8*, 4383–4389; j) V. Blanchard, Z. Asbai, K. Cottet, G. Boissonnat, M. Port, Z. Amara, *Org. Process Res. Dev.* **2020**, *24*, 822–826.

[12] a) A. Walther, A. H. E. Müller, *Soft Mater.* **2008**, *4*, 663–668; b) A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194–5261; c) C. Marschelke, A. Fery, A. Synytska, *Colloid Polym. Sci.* **2020**, *298*, 841–865; d) Z. Peng, J. Huang, Z. Guo, *Nanoscale* **2021**, *13*, 18839–18864; e) X. Li, L. Chen, D. Cui, W. Jiang, L. Han, N. Niu, *Coord. Chem. Rev.* **2022**, *454*, 214318.

[13] a) M. Vafaeezadeh, P. Lösch, P. Breuninger, C. Wilhelm, S. Antonyuk, S. Ernst, W. R. Thiel, *ChemCatChem* **2019**, *11*, 2304–2312; b) M. Vafaeezadeh, C. Wilhelm, P. Breuninger, S. Antonyuk, S. Ernst, W. R. Thiel, *ChemCatChem* **2020**, *12*, 2695–2701; c) M. Vafaeezadeh, J. Schaumlöffel, A. Lösch, A. De Cuyper, W. R. Thiel, *ACS Appl. Mater. Interfaces* **2021**, *13*, 33091–33101; d) M. Vafaeezadeh, W. R. Thiel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206403; e) M. Vafaeezadeh, W. R. Thiel, *Chem. Eur. J.* **2023**, *29*, e202204005.

[14] a) B. Karimi, N. Ganji, O. Pourshiani, W. R. Thiel, *Prog. Mater. Sci.* **2022**, *125*, 100896; b) B. Karimi, D. Enders, *Org. Lett.* **2006**, *8*, 1237–1240; c) B. Karimi, F. Mansouri, H. Vali, *Green Chem.* **2014**, *16*, 2587–2596; d) B. Karimi, B. Ghaffari, H. Vali, *J. Colloid Interface Sci.* **2021**, *589*, 474–485.

[15] a) C. A. Fraker, A. J. Mendez, C. L. Stabler, *J. Phys. Chem. B* **2011**, *115*, 10547–10552; b) J. G. Riess, *Artif. Cells Blood Subst. Biotechnol.* **2005**, *33*, 47–63.

[16] a) M. A. Revuelta-Maza, S. Nonell, G. De La Torre, T. Torres, *Org. Biomol. Chem.* **2019**, *17*, 7448–7454; b) E. Çelenk Kaya, S. Ersoy, M. Durmuş, H. Kantekin, *Heterocycl. Comm.* **2018**, *24*, 259–265; c) Y. Que, Y. Liu, W. Tan, C. Feng, P. Shi, Y. Li, H. Xiaoyu, *ACS Macro Lett.* **2016**, *5*, 168–173; d) A. Abate, R. Dehmel, A. Sepe, N. L. Nguyen, B. Roose, N. Marzari, J. K. Hong, J. M. Hook, U. Steiner, C. Neto, *J. Mater. Chem. A* **2019**, *7*, 24445–24453.

[17] S. Pushalkar, G. Ghosh, Q. Xu, Y. Liu, A. A. Ghogare, C. Atem, A. Greer, D. Saxena, A. M. Lyons, *ACS Appl. Mater. Interfaces* **2018**, *10*, 25819–25829.

[18] a) C. S. Foote, *Acc. Chem. Res.* **1968**, *1*, 104–110; b) A. R. Reddy, M. Bendikov, *Chem. Commun.* **2006**, 1179–1181; c) A. Eske, B. Goldfuss, A. G. Griesbeck, A. de Kiff, M. Kleczka, M. Leven, J. M. Neudörfl, M. Vollmer, *J. Org. Chem.* **2014**, *79*, 1818–1829; d) A. G. Griesbeck, B. Goldfuss, C. Jäger, E. Brüllingen, T. Lippold, M. Kleczka, *ChemPhotoChem* **2017**, *1*, 213–221.

[19] a) Y. Morita, H. Tokuyama, T. Fukuyama, *Org. Lett.* **2005**, *7*, 4337–4340; b) J. M. Carney, R. J. Hammer, M. Hulce, C. M. Lomas, D. Miyashiro, *Synthesis* **2012**, *44*, 2560–2566; c) Z. Yan, W. Wei, H. Xun, S. Anguo, *Chem. Lett.* **2012**, *41*, 1500–1502; d) H. Nsubuga, C. Basheer, H. A. S. Al-Muallem, A. N. Kalanthoden, *J. Environ. Chem. Eng.* **2016**, *4*, 857–863; e) D. K. Chauhan, V. R. Battula, A. Giri, A. Patra, K. Kailasam, *Catal. Sci. Technol.* **2022**, *12*, 144–153.

[20] a) X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, *ACS Catal.* **2014**, *4*, 2175–2185; b) J. F. Bai, M. F. Cheng, H. Z. Lu, M. B. Hou, Y. A. N. G. Yu, J. Y. Wang, M. D. Zhou, *J. Fuel Chem. Technol.* **2022**, *50*, 418–427.

[21] T. S. A. Heugebaert, C. V. Stevens, C. O. Kappe, *ChemSusChem* **2015**, *8*, 1648–1651.

[22] a) E. Gianotti, B. Martins Estevão, F. Cucinotta, N. Hioka, M. Rizzi, F. Renò, L. Marchese, *Chem Eur. J.* **2014**, *20*, 10921–10925; b) C. Mendoza Gallego, N. Emmanuel, C. Pàez Martinez, L. Dreesen, J. C. Monbaliu, B. Heinrichs, *ChemPhotoChem* **2018**, *2*, 890–897.

[23] a) P. de Mayo, S. T. Reid, *Chem. Ind.* **1962**, 1576; b) H. H. Wasserman, A. H. Miller, *J. Chem. Soc. D Chem. Commun.* **1969**, *5*, 199–200; c) G. B. Quistad, D. A. Lightner, *J. Chem. Soc. D Chem. Commun.* **1971**, *18*, 1099–1100; d) W. Schilling, Y. Zhang, D. Riemer, S. Das, *Chem. Eur. J.* **2020**, *26*, 390–395.

[24] a) M. Klaper, P. Wessig, T. Linker, *Chem. Commun.* **2016**, *52*, 1210–1213; b) V. Martínez-Agramunt, E. Peris, *Inorg. Chem.* **2019**, *58*, 11836–11842; c) W. Fudickar, T. Linker, *Langmuir* **2010**, *26*, 4421–4428; d) Z. Yuan, S. Yu, F. Cao, Z. Mao, C. Gao, J. Ling, *Polym. Chem.* **2018**, *9*, 2124–2133; e) J. Zhu, J. Zou, J. Zhang, Y. Sun, X. Dong, Q. Zhang, *J. Mater. Chem. B* **2019**, *7*, 3303–3309.

[25] a) D. Magdziak, S. J. Meek, T. R. R. Pettus, *Chem. Rev.* **2004**, *104*, 1383–1430; b) S. P. Roche, J. A. Porco, *Angew. Chem. Int. Ed.* **2011**, *50*, 4068–4093.

[26] a) A. K. Yadav, L. D. S. Yadav, *Green Chem.* **2016**, *18*, 4240–4244; b) S. Firoozi, M. Hosseini-Sarvari, *Eur. J. Org. Chem.* **2020**, *2020*, 3834–3843.

[27] a) N. Kihara, Y. Nakawaki, T. Endo, *J. Org. Chem.* **1995**, *60*, 473–475; b) I. Yavari, M. G. Darjani, Z. Hossaini, M. Sabbaghan, N. Hosseini, *Synlett* **2008**, *6*, 889–891; c) W. Clegg, R. W. Harrington, M. North, P. Villuendas, *J. Org. Chem.* **2010**, *75*, 6201–6207.

[28] a) W. Guo, W. Fu, G. Zou, C. Xu, *J. Fluorine Chem.* **2012**, *140*, 88–94; b) J. X. Jiang, Y. Li, X. Wu, J. Xiao, D. J. Adams, A. I. Cooper, *Macromolecules* **2013**, *46*, 8779–8783; c) M. N. Gandy, C. L. Raston, K. A. Stubbs, *Chem. Commun.* **2015**, *51*, 11041–11044; d) M. R. Patil, J. Shah, A. V. Kumar, A. R. Kapdi, *Chem. Asian J.* **2020**, *15*, 4302–4306; e) G. Kumar, S. R. Dash, S. Neogi, *J. Catal.* **2021**, *394*, 40–49; f) T. Cai, B. Huang, H. Hu, C. Meng, J. Xu, X. Dong, J. He, Q. Zhao, *Dyes Pigm.* **2022**, *200*, 110156.

[29] a) G. Jiang, J. Chen, J. S. Huang, C. M. Che, *Org. Lett.* **2009**, *11*, 4568–4571; b) Y. Chen, G. Feng, *Org. Biomol. Chem.* **2015**, *13*, 4260–4265; c) L. A. Ho, C. L. Raston, K. A. Stubbs, *Chem. Eur. J.* **2018**, *24*, 8869–8874.

[30] a) E. Baciocchi, T. Del Giacco, A. Lapi, *Org. Lett.* **2004**, *6*, 4791–4794; b) A. Berlicka, B. König, *Photochem. Photobiol. Sci.* **2010**, *9*, 1359–1366.

[31] M. I. Burguete, R. Gavara, F. Galindo, S. V. Luis, *Catal. Commun.* **2010**, *11*, 1081–1084.

[32] H. Urakami, K. Zhang, F. Vilela, *Chem. Commun.* **2013**, *49*, 2353–2355.

[33] S. V. Vliet, J. G. H. Hermens, Y. Fu, L. Pfeifer, B. L. Fering, *Chem. Commun.* **2023**, *59*, 884–887.

[34] D. A. Lightner, G. S. Bisacchi, R. D. Norris, *J. Am. Chem. Soc.* **1976**, *98*, 802–807.

[35] J. K. Howard, K. J. Rihak, C. J. T. Hyland, A. C. Bissember, J. A. Smith, *Org. Biomol. Chem.* **2016**, *14*, 8873–8880.

[36] a) J. M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, *Acc. Chem. Res.* **2003**, *36*, 668–675; b) W. Fudickar, T. Linker, *Chem. Commun.* **2008**, 1771–1773; c) W. Fudickar, T. Linker, *J. Am. Chem. Soc.* **2012**, *134*, 15071–15082.

[37] a) W. Adam, S. G. Bosio, B. Fröhling, D. Leusser, D. Stalke, *J. Am. Chem. Soc.* **2002**, *124*, 8316–8320; b) D. Miranda, R. Capela, I. S. Albuquerque, P. Meireles, I. Paiva, F. Nogueira, R. Amewu, J. Gut, P. J. Rosenthal, R. Oliveira, M. M. Mota, R. Moreira, F. Marti, M. Prudêncio, P. M. O'Neill, F. Lopes, *ACS Med. Chem. Lett.* **2014**, *5*, 108–112.

[38] a) M. J. Cabrera-Afonso, S. R. Lucena, Á. Juarranz, A. Urbano, M. C. Carreño, *Org. Lett.* **2018**, *20*, 6094–6098; b) L. Péault, P. Nun, E. Le Grognec, V. Coeffard, *Chem. Commun.* **2019**, *55*, 7398–7401; c) J. Fischer, P. Nun, V. Coeffard, *Synthesis* **2020**, *52*, 1617–1624.

[39] G. C. Resende, E. S. Alvarenga, J. C. Galindo, F. A. Macias, *J. Braz. Chem. Soc.* **2012**, *23*, 2266–2270.

Manuscript received: September 15, 2023
Revised manuscript received: December 21, 2023
Accepted manuscript online: January 5, 2024
Version of record online: January 25, 2024