A versatile heterogeneous photocatalyst: nanoporous gold powder modified with a zinc(II) phthalocyanine derivative for singlet oxygen [4 + 2] cycloadditions

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Abstract

Nanoporous gold was functionalized with a photosensitizer, a zinc(II) phthalocyanine derivative. Such systems are active for the generation of reactive singlet oxygen which can be used for photocatalytic oxidation reactions. This study aims to demonstrate the versatility of such an approach, in terms of substrates and the employed solvent, only possible for a truly heterogeneous catalytic system. The activity of the hybrid system was studied for [4 + 2] cycloadditions of three different types of dienes and a total of eight substrates in two organic solvents and once in water. The highest activity was measured for 1,3-diphenylisobenzofuran, which is also highest in terms of sensitivity for the reaction with $^1\text{O}_2$. Trends in conversion could be anticipated based on reported values for the rate constant for the reaction of $^1\text{O}_2$. In almost all cases, an amplification of the conversion by immobilization of the sensitizer onto nanoporous gold was observed. The limiting case was ergosterol, which was the largest of all substrates with a van-der-Waals radius of about 2.1 nm. Additional factors such as the limited lifetime of $^1\text{O}_2$ in different solvents as well as the hampered diffusion of the substrates were identified.

Graphic abstract

Keywords Photooxidation · Nanoporous gold · Phthalocyanine · Singlet oxygen · Heterogeneous photocatalyst

1 Introduction

The generation of oxygenated compounds by reactive singlet oxygen ($^1\text{O}_2$) is an important step in organic synthesis [1, 2]. About 30 years ago, its use for the synthesis of natural products has emerged and was since then developed further [3]. $^1\text{O}_2$ can be generated chemically [4] or by direct excitation with light [5]. Due to the spin forbidden nature

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of this process the most common and practical way of $^1\text{O}_2$ generation is by photosensitization [6]. Indeed, this method is quite common in nature [7]. Here, the photosensitizer is first excited by light and undergoes intersystem crossing (ISC), followed by transfer of the energy to molecular (triplet) oxygen resulting in the formation of singlet oxygen (see also Eqs. 1–3). This singlet oxygen can be used in the synthesis of oxygenated compounds by reaction of carbon or heteroatomic double bonds resulting in endoperoxides ([4 + 2] cycloadditions), dioxetanes ([2 + 2] cycloaddition), hydroperoxides (Schenck ene reaction), and many more [3, 8].

This synthetic route is quite attractive as it only requires molecular oxygen, (visible) light, and a suitable photosensitizer such as phthalocyanine derivatives (ZnPc) [9–11]. This process consists of the following photophysical steps in solution:

First (Eq. 1), after excitation of ZnPc and formation of the excited singlet state (${}^1\text{ZnPc}^*$) intersystem crossing (ISC) occurs resulting in the excited triplet state (${}^3\text{ZnPc}^*$). Second (Eq. 2), the spin allowed triplet – singlet energy transfer from ${}^3\text{ZnPc}^*$ to triplet oxygen under formation of singlet oxygen occurs. In the last step (Eq. 3), singlet oxygen is reacting with the substrate. Singlet oxygen is a short lived and metastable compound but can diffuse and be used as a reactive compound. The photosensitizer (ZnPc 1) is absorbing in the visible region of light at $\lambda \sim 680$ nm with high extinction coefficients of $\epsilon_{680} \sim 140,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Fig. 1a).

Typically, the photosensitizer is dissolved in the reaction medium to enable diffusion and reaction of the singlet oxygen and the substrate. For practical application, it

is, however, useful to prepare heterogeneous catalysts by chemical attachment of the sensitizer to suitable supports such as inorganic silanes [12, 13]. In this way, the heterogeneous catalyst can be physically separated from the reaction medium and more easily applied into various reactor concepts.

An important requirement for such supports is a high surface to volume ratio, exposing a large fraction of the functionalized surface, and, thus, sensitizer to the light. Simply, by structuring the support on the nanoscale, an amplification of the surface area is achieved by several orders of magnitude. Also, such nano-engineered materials show a number of exclusive physicochemical properties non-existent for materials either on larger (micro- and macroscopic) or smaller (molecular) scales. One interesting example of such a material is nanoporous gold (npAu) [14, 15]. This material is prepared by selectively etching Ag from Ag/Au alloys using concentrated nitric acid. A uniform nanoporous structure with identical interconnected nanometer-sized pores and gold ligaments across the entire volume is obtained (Fig. 1b). Dependent on the reaction conditions of the etching process, the pore sizes can range from around 7–70 nm in average diameter [16]. This support provides a high specific surface area of about $10 \text{ m}^2/\text{g}$ and exposes a large surface per volume to the irradiating light. Yet, it was also found to enhance the fluorescent signals of nearby phthalocyanines on the surface known as metal-enhanced fluorescence [17, 18]. This effect originates from the excitation of localized surface plasmon resonance (LSPR) of collective conduction-band electrons of the metallic support that can modify the quantum yield of adjacent fluorophores [19]. Two characteristic plasmon bands of npAu have been detected in optical transmission spectra (Fig. 1c). One at $\lambda \sim 490$ nm resulting from the resonant absorption of gold films is independent of nanopore sizes and dielectric surroundings. The other at $\lambda \sim 550$ – 650 nm arises from the excitation of localized surface plasmon resonance and shows a band shift with the nanopore sizes [20].

Fig. 1 Structure and corresponding optical spectrum for **a** the photosensitizer zinc(II) phthalocyanine **1** with peripheral propynoxy-substituents. **b** SEM image of nanoporous gold with pore sizes of

20–25 nm, and **c** corresponding transmission spectrum of a npAu foil with comparable pore sizes. All spectra were recorded employing DMF as solvent (ZnPc) or as dielectric environment (npAu)

Recently, we reported a hybrid system where a ZnPc derivative was immobilized on different shaped nanoporous gold supports as heterogeneous, monolithic systems, and coatings [16, 21, 22]. With these hybrid materials under irradiation with visible light a very efficient singlet oxygen formation compared to the same amount of ZnPc in solution was shown using 1,3-diphenylisobenzofuran (DPBF) as active singlet oxygen quencher. This effect is caused by the interaction of npAu and the immobilized ZnPc [21, 22].

However, central questions remain. As this system is heterogeneous, the reagents, i.e., the singlet oxygen as well as the substrate have to diffuse to one another to react. Does the reaction proceed mainly in the pores of the npAu? Also, the singlet oxygen is metastable and has a limited lifetime on the order of only a few μ s. While the system is truly heterogeneous and not limited by the solubility of the sensitizer, the lifetime of singlet oxygen is strongly dependent on the solvent [5, 23–26]. Which solvent provides a long enough lifetime to enable diffusion of the reactive oxygen? Last but not least, the strong suit of the $^1\text{O}_2$ oxidation of organic compounds is its versatility and applicability to a wide range of substrates bearing double bonds. Does the reaction in the hybrid system with singlet oxygen proceeds the same way as in solution?

Based on these questions we investigated the system of ZnPc immobilized on powdered npAu support for the oxidation of a variety of substrates, namely furan derivatives, anthracene derivatives, and 1,3-cyclohexadiene based structures, the largest substrate is ergosterol with a van-der-Waals diameter of about 2.1 nm. These substrates are commercially available to a reasonable price. By a [4 + 2] cycloaddition with singlet oxygen all of these substrates should be converted into their oxygenated counterparts. If the reaction proceeds as reported in the liquid phase, differences in reactivity should be attributed to the rate constant of the reaction between $^1\text{O}_2$ and the substrate (Eq. 3). We will also vary the

solvents from *N,N*-dimethylformamide (DMF) to acetonitrile (ACN) as well as water, enabling a singlet oxygen lifetime from 60 μ s down to below 1 μ s for water [5, 23–26]. Last but not least, the reusability of the catalyst will be tested. Overall, we seek to investigate the versatility of this heterogeneous ZnPc-npAu hybrid photocatalyst.

2 Results and discussion

2.1 Synthesis and characterization

Nanoporous gold powders (npAu) were prepared by leaching of Ag from a Au(30at%)Ag(70at%) master alloy in concentrated nitric acid. This procedure also dubbed free corrosion is known to result in npAu with pore sizes as small as 20 nm, depending on the temperature [27] and dealloying time (Fig. 1b) [16]. The monolithic shape of the starting alloy is retained while the corrosion proceeds and the Ag fraction is replaced by an open pore volume. In this way, npAu shaped in the form of disks with a macroscopic diameter of about 5 mm and a thickness of about 200 μ m were prepared. Fracturing by physical means was achieved using tweezers. The resulting powder was comprised of about 25 μ m large npAu particles (Figure S1).

Functionalization of the npAu powder with the ZnPc derivative to obtain the npAu-ZnPc hybrid system was carried out in two-steps as developed by us (Scheme 1) [22]. Compared to a direct immobilization of thiol-substituted ZnPcs, the two-step approach offers several benefits. The synthetic effort can be significantly reduced while on the same time the long-time stability of the building blocks is higher than for thiol-substituted ZnPcs. In addition, the obtained SAMs prepared from alkanethiols usually exhibit a higher order compared to SAMs prepared from large macrocycles [28]. The surface of the npAu powder

Scheme 1 Schematic representation for the two-step functionalization of the npAu powder; formation of a self-assembled monolayer (SAM) on npAu with 6-azidothiophenyl-1-thioacetate **2** followed by copper catalyzed azide–alkyne cycloaddition (“click reaction”) with the ZnPc derivative **1**

was functionalized by a SAM of 6-azidohexyl-1-thioacetate **2**. Then the ZnPc derivative **1** was bound to the free azide groups of the SAM via copper catalyzed azide–alkyne cycloaddition (CuAAC). The successful formation of the triazole ring was studied by X-ray photoelectron spectroscopy (XPS) and is in good agreement with previous studies reported in the literature (Figure S2) [29]. After functionalization, the particle size and the porous structure of npAu remained unchanged. The employed alkyl chain length of the azidothioacetate and the peripheral side chains of the ZnPc derivative were selected because the obtained hybrid material with a distance of ~ 1.3 nm between npAu and ZnPc under irradiation exhibits a preferable coupling between the plasmonic states of npAu and the ZnPc to achieve the highest singlet oxygen generation [21]. The energy dispersive X-ray spectroscopy (EDX) measurements of all samples showed a homogeneous zinc distribution, which was confirmed by EDX mapping and line scan experiments as described before by us [22]. By inductively-coupled plasma mass spectrometry (ICP-MS) the amount of immobilized Zn was determined as ~ 350 μg per g hybrid catalyst.

The photooxidation reactions were conducted under oxygen by irradiation with visible light of 180 mWcm^{-2} (Figure S3). A 550 nm cut-on filter was used for simultaneous irradiation of the plasmon resonance of npAu between 550 and 650 nm and the Q-band of the immobilized ZnPc at 690 nm (Fig. 1), and to avoid irradiation at shorter wavelengths. After transmission spectra of npAu films the penetration depth of visible light in this material is only around 300 nm [16, 22]. This means that in the npAu–ZnPc powder system up to this depth, npAu and ZnPc can contribute by irradiation via their excited states to the generation of singlet oxygen for the photooxidation reactions. Therefore, considering

the ZnPc loading of $350\text{ }\mu\text{mol/g}$ and the employed hybrid catalyst quantity of 28 mg, the active and irradiated parts correspond to around 0.5 nmol ZnPc . A great excess of substrates of 10 or 5 μmol was employed which corresponds to a molar ratio of substrate:active ZnPc = 20.000:1 or 10.000:1, respectively. The consumption of the substrates over time was measured via UV–Vis spectroscopy and the turnover numbers (TON) and the turnover frequencies (TOF) were determined. It was found that after the TON graphs in every case the photooxidations obey a zero-order kinetic during the first minutes. Larger deviations were observed for prolonged use of the photocatalyst which might be due to photobleaching of the ZnPc **1** by singlet oxygen caused degradation. It is important to note that the unfunctionalized npAu powder or modified only by the azidothioate **2** under irradiation shows no generation of $^1\text{O}_2$.

2.2 Reaction of $^1\text{O}_2$ with furan derivatives

The photooxidation of three furan derivatives was investigated. Furans are 1,3-heterodienes, in the presence of singlet oxygen they undergo [4 + 2]-cycloadditions at the double bond in 2,5-positions under formation of the unstable endoperoxides **3b–5b** which undergo further reactions to the final products (Scheme 2) [4, 37–39]. We selected 1,3-diphenylisobenzofuran (DPBF) **3a** because this compound exhibits a very high reactivity and sensitivity [6] against singlet oxygen [26, 40]. The reaction in DMF started immediately after irradiation, indicated by the decrease of the DPBF absorption at $\lambda = 415\text{ nm}$ by UV–Vis spectroscopy (Figure S4). Already after 10 min, full conversion of DPBF was observed (Fig. 2; Table 1). The same amount of ZnPc dissolved in solution resulted only to about 20% conversion

Scheme 2 **a** [4 + 2] Cycloaddition of $^1\text{O}_2$ to DPBF **3a**. The at first obtained unstable endoperoxide **3b** reacts further to 1,2-dibenzoylbenzene **3c** as final stable product. **b** The [4 + 2] cycloaddition of 2,5-diphenylfuran (DPF) **4a** with $^1\text{O}_2$ leads via the unstable endoperoxide **4b** to cis-1,2-dibenzoylbenzene **4c**. **c** The reaction of furfuryl alcohol **5a** with $^1\text{O}_2$ results via the thermally unstable endoperoxide **5b** in 5-methoxy-2(5H)-furanone **5c** and 5-methoxy-5-hydroxymethyl-2-furanone **5d**, as major reaction products

Fig. 2 **a** Photocatalytic conversion of DPBF **3a** (black) and DPF **4a** (blue) over time in DMF and **b** of FFA **5a** (gray) in ACN by oxidation with $^1\text{O}_2$ employing the ZnPc photocatalyst immobilized on npAu (bold line) and for comparison the same amount of ZnPc in solution (dashed line)

after the same reaction time. The synergistic effect between the npAu and ZnPc results, hence, in an increase of conversion by a factor of more than 5 [22].

The linear run of the conversion and TON, respectively, showed that the photooxidation follows zero-order kinetics until saturation effects become dominant. From the slope of the linear regime, a high turnover frequency of 1949 min^{-1} was calculated. This was the highest activity measured for

all substrates in this study and is reflected by the comparably high reaction constant ($5 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$) for the reaction of singlet oxygen with this substrate. Also 2,5-diphenylfuran (DPF) **4a** was investigated as chemical trap for detection of singlet oxygen (Scheme 2b) [4, 41]. The rate constant for the reaction of singlet oxygen with DPF is about $0.7 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ (Table 1). As expected, the conversion after 20 min is lower with 65% conversion and a corresponding TOF of 281.9 min^{-1} due to the lower rate constant (Figs. 2 and S5). Next, the oxidation of a further furan derivative, furfuryl alcohol (FFA) **5a** was studied (Scheme 2c). Again, the conversion set in right after irradiation and the decay of the signal at $\lambda = 221$ was detected (Figure S6). Even though a rate constant of the reaction in water was reported of about $1 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, the measured conversion in acetonitrile accounts to only 70% after 240 min and is, hence, much lower as for DPBF. As in the case of **3a**, the activities for the photooxidation of **4a** and **5a** with the ZnPc in solution are lower compared to the heterogeneous hybrid photocatalyst (Fig. 2).

2.3 Reaction of $^1\text{O}_2$ with anthracene derivatives

A further class of conjugated diene analogues are anthracene derivatives which bear at the 9,10-positions two double bonds with a high reactivity in chemical reactions (Scheme 3). Two anthracene derivatives which are also commercially available were now investigated for the reaction with $^1\text{O}_2$. 9,10-dimethylantracene (DMA) **6a** as well as 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA) **7a** which were also described as chemical traps for singlet oxygen [6, 33, 42–45]. DMA reacts selectively with singlet oxygen after a [4 + 2]-cycloaddition to form the 9,10-endoperoxide **6b** (Scheme 3). Right after starting the irradiation a decrease of the absorption at $\lambda = 379 \text{ nm}$ was observed by UV–Vis spectroscopy indicating the reaction with $^1\text{O}_2$ (Figure S7). After 60 min about 80% of DMA was converted to the corresponding endoperoxide. The same amount of ZnPc **1** in solution showed only a conversion of 25% during

Table 1 Summary of conversion of the various substrates by $^1\text{O}_2$ in the respective solvent (DMF: *N,N*-dimethylformamide, ACN: acetonitrile)

Substrate	Solvent	k_t [$10^8 \text{ L mol}^{-1} \text{ s}^{-1}$]	Conversion
DPBF 3a	DMF	5 (in CH_3OH) [30]	100% after 10 min
DPF 4a	DMF	0.7 (in CH_2Cl_2) [31]	65% after 20 min
FFA 5a	ACN	1 (in H_2O) [32]	70% after 240 min
DMA 6a	DMF	1.33 (in ACN) [33]	80% after 60 min
ABDA 7a	DMF/ H_2O	0.1 (in H_2O) [34]	18%/1% after 60 min
α -Terpinene 8a	ACN	1 (in CHCl_3) [35]	85% after 120 min
ERGO 9a	ACN	0.3/0.1 (CHCl_3 /Pyridine) [35]/[36]	75% after 240 min
1,3-CHD 10a	ACN	0.07 (in CHCl_3) [35]	40% after 360 min

The rate constants for the reaction of the particular substrate with $^1\text{O}_2$ are given according to literature results (solvent). The error bar is typically stated with $\pm 10\%$

Scheme 3 a [4+2] cycloaddition of $^1\text{O}_2$ to DMA **6a**, resulting in the formation of the endoperoxide **6b** as final stable product [33]. b The reaction of the anthracene derivative 9,10-anthracenediyl-

bis(methylene)dimalonic acid **7a** (ABDA) towards $^1\text{O}_2$ under formation of the endoperoxide **7b**

Fig. 3 Photocatalytic conversion of DMA **6a** (black) and ABDA **7a** (blue) over time in DMF by oxidation with $^1\text{O}_2$ employing the ZnPc photocatalyst immobilized on npAu (bold line) and for comparison the same amount of ZnPc in solution (dashed line)

this time frame. As for the furan derivatives, this reflects an increase of conversion by a factor of 4 due to the synergistic effect of the sensitizer and the npAu support (Fig. 3).

The conversion of the other anthracene derivative 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA) **7a** by reaction with singlet oxygen was studied in DMF as well as in aqueous solution (Scheme 3b). Using water as a solvent is preferable in the context of green chemistry. However, the problem is the low solubility of most substrates and the limited lifetime of singlet oxygen in this medium as also discussed below. Since ABDA is appreciably soluble in water it is, however, important to be studied as a benchmark. Right after irradiation a decrease of absorption at $\lambda = 379$ nm was detected indicating the reaction of ABDA with $^1\text{O}_2$ (Figure S8). As expected, based on the lower reaction constant by about an order of magnitude in comparison to DMA, the conversion of

ABDA was determined to 18% in DMF and even lower at only 1% in water after 60 min of irradiation (Fig. 3). Assuming a zero-order kinetic and a linear increase of the TON during the first 20 min, TOF values of 53.2 min^{-1} in DMF and 9.01 min^{-1} in water were determined.

2.4 Reaction of $^1\text{O}_2$ with 1,3-cyclohexadienes

A further interesting class of 1,3-dienes which react with $^1\text{O}_2$ by [4+2] cycloadditions are 1,3-cyclohexadienes such as 1,3-cyclohexadiene [35], α -terpinene, and ergosterol. For example, α -terpinene **8a** reacts with $^1\text{O}_2$ forming ascaridole **8b** (Scheme 4a). This was at first studied in the pioneering work of Schenck using chlorophyll as sensitizer [46–48]. Again, right after irradiation a decay of the UV–Vis signal at $\lambda = 267$ nm was observed, indicating the reaction of α -terpinene with sensitized $^1\text{O}_2$ (Figure S9). After 120 min a conversion of about 85% was reached, corresponding to a TOF of about 185.3 min^{-1} (Fig. 4). The same amount of photosensitizer in solution showed a conversion of about 45%. Even though this is still an increase by a factor of 2 due to the synergistic effect of the npAu, it is considerably lower as overserved for the furan and anthracene derivatives.

The sterol ergosterol (ERGO, (22*E*)-Ergosta-5,7,22-trien-3 β -ol) **9a** is a biological precursor of vitamin D₂. This compound contains a 1,3-conjugated double bond within the sterol backbone and a single double bond at the side chain (Scheme 4b). Due to the higher reactivity of the conjugated double bond in the reaction with $^1\text{O}_2$, the endoperoxide **9b** was isolated as main reaction product [49–51]. Right after starting the illumination a decrease of the absorption at $\lambda = 282$ nm indicates the reaction with $^1\text{O}_2$ (Figure S10). A reaction constant for the reaction of ERGO with $^1\text{O}_2$ of about $0.2 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ is about one order of magnitude lower as the one for the reaction with α -terpinene [35, 49]. This is reflected by a lower conversion of only 80% after 240 min (Fig. 4). Most interestingly, for ergosterol no increase of conversion was detected when the photosensitizer was bound

Scheme 4 **a** [4+2] cycloaddition of $^1\text{O}_2$ to α -terpinene **8a**, resulting in the formation of the endoperoxide ascaridole **8b** as final stable product. **b** Reaction scheme for the addition of $^1\text{O}_2$ to ergosterol **9a** under formation of the endoperoxide **9b** as main product and the

hydroperoxide **9c** as side product. **c** Addition of $^1\text{O}_2$ to 1,3-cyclohexadiene **10a** leading to the endoperoxide **10b** followed by conversion to 4-hydroxycyclohex-2-en-1-one **10c** by cleavage of the peroxide

Fig. 4 Photocatalytic conversion of α -terpinene **8a** (black), ergosterol **9a** (blue), and 1,3-cyclohexadiene **10a** (gray) over time in ACN by oxidation with $^1\text{O}_2$ employing the ZnPc photocatalyst immobilized on npAu (bold line) and for comparison the same amount of ZnPc in solution (dashed line)

to npAu. This fact can be explained by the large van-der-Waals diameter of ERGO of 2.1 nm and the comparably low diffusion coefficient of only about $1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ as also discussed below.

A structurally more simple hydrocarbon with a conjugated double bond in 1,3-position is 1,3-cyclohexadiene **10a**. It undergoes also [4+2]-cycloaddition under formation of the corresponding endoperoxide **10b**, which reacts further to compound **10c** by cleavage of the peroxide (Scheme 4c) [52, 53]. The degradation of 1,3-cyclohexadiene sets in right after irradiation (Figure S11). However, the measured conversion was only 40% after 360 min, which is the lowest of all studied 1,3-cyclohexadienes (Fig. 4). This can be expected

based on the comparably low electron density in the absence of donating substituents at the 1,3-positions, reflected by the reaction constant of only $0.07 \cdot 10^8 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Table 1). Noteworthy, in this case, the increase of conversion due to immobilization of the ZnPc still was a factor of 2 as also observed in the case of α -terpinene.

2.5 Influence of the solvents: O_2 lifetime vs diffusion

A discussion of the observed conversions and activities, respectively, must involve the lifetime and diffusion length of the excited singlet oxygen as well as the diffusion of the substrates. Mass transport becomes increasingly important when dealing with heterogeneous catalysts [54, 55]. The intrinsic lifetime of $^1\text{O}_2$ in the absence of a chemical reaction is limited by its deactivation to the triple state by energy transfer to solvent vibrations (physical quenching) [36, 56]. Typical values reported are 14 μs for DMF [26], 30–60 μs for ACN [2, 23, 24], and only 0.2–4 μs for water [25]. Based on a diffusion constant for O_2 in water of $2 \cdot 10^{-9} \text{ m}^2/\text{s}$ (it scales inversely proportional with the viscosity of the solvent) [57] the average diffusion length of $^1\text{O}_2$ during its lifetime can be estimated to vary from 20 nm in water up to 150 nm in DMF and 513 nm in ACN. Considering a pore diameter of the npAu of 25 nm this means that the reaction is restricted to the pore volume of the npAu in case of water and extends only shortly into the solution in case of ACN and DMF. This is an important aspect when further developing this concept of a heterogeneous catalyst. While the nanoporous structure provides a high surface to volume ratio and a large fraction of surface

per area it is limited by the diffusion of singlet oxygen into the reaction medium. Structuring the npAu in terms of micrometer sized particles did not only improve the fraction of illuminated sensitizer [22] but also increases the macroscopic surface area of the material. Nevertheless, the measured conversion using the ZnPc **1** immobilized onto the npAu was at least as high as the conversion using the same amount in solution. This effect was lowest for ERGO **9a** (factor of 1) and highest for DPBF **3a** (factor of 5). Besides the reaction constant of this reaction (Table 1) the diffusion of the substrate towards the npAu surface has to be considered. Here, the diffusion coefficient is dependent on the molecular size and van-der-Waals radius, respectively. It can vary by orders of magnitude from $1.4 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for a molecule such as cyclohexene [58], down to a value of about $1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ calculated for ergosterol **9a** in water based on the Stokes–Einstein equation. In the latter case the conversion is, thus, hampered by the slow diffusion of the molecule towards the macroscopic surface of the npAu.

2.6 Stability of the hybrid photocatalyst

A main motivation to use immobilized sensitizer on heterogeneous npAu is its reuse and recyclability. Simply the reaction medium can be refreshed after use as the sensitizer is not dissolved in the reaction medium. This, however, recommends a good stability of the sensitizer under reaction conditions. We investigated the stability of the hybrid photocatalyst for the oxidation of DPBF in DMF. Four times 5 μmol of DPBF was added after the conversion of 100% was achieved. After the fifth run 85% of the activity is still present (Fig. 5).

Fig. 5 Repeated photocatalytic conversion of DPBF **3a** over time in DMF by oxidation with $^1\text{O}_2$ employing the ZnPc photocatalyst immobilized on npAu

The slight decrease in activity is due to the photocatalytic degradation of the bound ZnPc by $^1\text{O}_2$ [59, 60]. This effect is much more pronounced in solution, when DPBF is added a second time to the solution of 0.5 nmol ZnPc, almost no photocatalytic activity was observed.

3 Conclusion

Hybrid systems of ZnPc immobilized on npAu are highly active for the generation of singlet oxygen which can be used for photocatalytic oxidation reactions. Exciting this hybrid system by irradiation with visible light, photooxidations with singlet oxygen are more efficient compared to the ZnPc dissolved in an organic solvent. The reason is that under irradiation energy transfer from localized plasmon resonance (LSPR) to the immobilized photosensitizer ZnPc contributes significantly to the formation of singlet oxygen [16, 21, 22]. We demonstrated now the scope of such an approach for [4 + 2] cycloadditions of eight different substrates of three different classes of 1,3-dienes. The conversions could be widely anticipated based on the reported values for the rate constant of the reaction with $^1\text{O}_2$. As this system is heterogeneous, it is not limited by the solubility of the sensitizer. The solubility of phthalocyanines in various solvents, especially in water, is an ongoing synthetic quest [61]. Besides functionalization with strongly hydrophilic substituents, immobilization is a viable strategy as we demonstrate. Solubility of the substrate and the singlet oxygen lifetime are limiting factors for the choice of solvent, though. Physical quenching of the singlet state by energy transfer to the solvent molecule reduces the lifetime of $^1\text{O}_2$ from 30 to 60 μs for acetonitrile to under 1 μs in water. This is particularly important for this heterogeneous system as the $^1\text{O}_2$ has to diffuse from the pores of the npAu into the solution. The conversion of ABDA **7a** which is soluble in water was only 1% after 60 min as compared to 18% in DMF under otherwise same conditions. The other benefit of immobilizing the ZnPc onto npAu is the enhancement of its activity. While this effect was independent of the solvent, we found differences for the various substrates. The largest molecule in this study ERGO **9a** did not show any increase in that matter which can be explained by a hampered diffusion from solution to the pores of the hybrid system. Overall, this approach of a synergistic photocatalytic system is versatile in terms of substrates and solvents. The challenge, however, is the limited mass transport and further design of the catalyst. Compared to a dissolved photocatalyst the advantage of the heterogeneous system npAu–ZnPc is that it can be filtered and used again or cleaned and then functionalized again with ZnPc.

4 Experimental section

4.1 Materials

6-Azidoethyl-1-thioacetate (**2**) [62–64] and 2,9,16,23-tetrakis(2-propyn-1-yloxy)phthalocyanine zinc(II) (**1**) were prepared as described elsewhere [65]. The co-catalyst tris(benzyl-triazolylmethyl)amine (TBTA) was obtained by literature procedures [66, 67]. Hydroquinone was obtained from Merck and $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (97%) from Aldrich. Ethanol (abs., reagent grade), THF (reagent grade, > 99.0%), DMF (analytical reagent grade, 99.5%), ACN (analytical reagent grade, > 99.5%), and HNO_3 (analytical reagent grade, 65 wt%) were received from VWR and used as obtained. The following substrates for photooxidations were used: 1,3-diphenylisobenzofuran (DPBF, > 95%, TCI), 2,5-diphenylfuran (DPF, > 98%, TCI), furfuryl alcohol (FFA, > 98%, TCI), 1,3-cyclohexadiene (1,3-CHD, > 97%, Fluka), α -terpinene (> 90%, TCI), ergosterol (ERGO, > 95%, TCI), 9,10-dimethylanthracene (DMA, > 98%, TCI), and 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA, 98%, Sigma–Aldrich). UV–Vis spectra of the ZnPc **1**, npAu and for the measurements of the photocatalytic oxidations were recorded on a UV-1600PC UV–Vis spectrometer from VWR.

4.2 Preparation of nanoporous gold powders

The npAu powder was prepared according to a modified published procedure [27, 68] by dealloying of Ag(70 at%)/Au(30 at%) alloy disks (diameter 5 mm, thickness 200 μm) in concentrated HNO_3 (50 mL, 65 wt%) for 24 h. The temperature was constantly held during the dealloying process at 5 °C using a cryostat. This ensured small pores and ligaments of about 21.7 ± 3.7 nm as determined from SEM. To stop the etching process, the samples were repeatedly washed with deionized H_2O and dried [16, 22, 69]. After dealloying the npAu disks were cautiously powdered by fragmentation with a metal tweezer.

4.3 Preparation of the npAu-ZnPc hybrid system

At first, SAMs were prepared by covering the npAu powder with an ethanolic solution (5 mL) of 6-azidoethyl-1-thioacetate (**2**, 1 mmol) for 72 h [22, 68]. After thoroughly washing with EtOH, in the second step the npAu powder with azide groups were reacted with a solution of the ZnPc derivative **1** (0.15 μmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (931.8 μg , 2.5 μmmol), TBTA (1.326 mg, 2.5 μmol), and hydroquinone (272.5 μg , 2.5 μmmol), dissolved in a THF/ H_2O mixture (5 mL, 3:1

v%) for another 72 h. Finally, any physisorbed material was removed from the hybrid catalyst by washing several times with THF.

4.4 Characterization methods

By inductively coupled-plasma mass spectrometry (ICP-MS, iCAP Q, Thermo Fisher Scientific GmbH) the quantity of immobilized ZnPc on npAu hybrid material was determined after dissolving 10 mg of them in ultrapure aqua regia (2 mL). Morphology of the samples including pore and ligament sizes of the npAu material and zinc distribution in the npAu-ZnPc hybrids were determined as described before by SEM and EDX [16, 22]. For XPS characterization, after mounting the samples were directly transferred to the XPS chamber of an ESCALAB250Xi instrument (Thermo Fisher Scientific, East Grinstead, UK) at the University of Oldenburg. The base pressure of the XPS chamber was $1 \cdot 10^{-9}$ – $2 \cdot 10^{-9}$ mbar. The spectra were fitted using the freely available version of XPSCasa.

4.5 Photocatalytic oxidations

Photocatalytic oxidations were carried out in a previously described self-built reaction setup consisting of a cylindrical 120 mL stainless steel tube with quartz windows and a water filter (Figure S3) [22]. For irradiation a 300 W Xe-arc lamp (LOT qd GmbH, Darmstadt, Germany) with a light intensity of 180 mWcm^{-2} was used. The irradiation source was equipped with a 550 nm cut-on filter from Andover for simultaneous irradiation of npAu and the immobilized ZnPc **1**. At first, the reaction vessel was filled with 100 mL of a solvent (DMF, ACN or H_2O) and then the powdered hybrid catalyst (28 mg) was added. Weak stirring with a magnetic stirrer was carried out throughout each experiment. The reaction vessel was flushed with O_2 at 25 °C for 10 min to achieve gas saturation of the solvent. Finally, 3, 5 or 10 μmol of a substrate dissolved in 500 μL of a solvent (DMF, ACN or H_2O) was added. The vessel was closed with a septum and irradiation started. At defined time intervals, aliquots for UV–Vis spectroscopy were taken out of the reactor via a syringe. The photocatalytic activity for every substrate was determined by the conversion over time and quantified by the respective turnover numbers (TON, [converted substrate] (mol)/[irradiated ZnPc] (mol)) and turnover frequencies (TOF, slope of the plot of TON versus reaction time (min^{-1})) [22].

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Declarations

Conflict of interest The authors declare that they have no conflicts of interests.

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