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A versatile synthetic strategy for nanoporous gold—organic hybrid materials for electrochemistry and photocatalysis

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ABSTRACT

Nanoporous gold (npAu) was employed as high surface area substrate for immobilization of redox- and photooxidative-active organic molecules. A two-step synthetic routine is demonstrated as a versatile and robust method for immobilization of various molecules. First, self-assembled monolayers (SAMs) of thiols containing an azide moiety were prepared on npAu substrates. Then, alkyne-modified ferrocene, tetrathiafulvalene, and zinc(II)phthalocyanine derivatives were covalently bound via the click reaction to this linker. Following the provided synthetic procedures high performance composite materials are generated for electrochemistry and photochemistry. The robust bonding between the organic functional group and the gold support provides stability even under strongly oxidizing conditions (applied potential or singlet oxygen).

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1. Introduction

In nanotechnology the modification of nanomaterials with functional groups is of increasing interest. Such hybrid-materials containing an organic functionality on the one hand and an inorganic substrate on the other hand are important in different fields of physics, chemistry, and electronics. Recently, porous gold–organic molecules hybrid-materials were employed for possible applications as biosensors^{1–4} (e.g., glucose or ATP detection) and also as actuator⁵ and high-strength composite materials.⁶ Key to these various applications is the high electrical conductivity of the material, its porosity increasing the surface area and thus sensitivity, as well as the unique optical and electronic properties generated by the nanostructure.^{5–7}

A substrate material, which became very popular in this context is nanoporous gold (npAu).⁴⁻⁹ This monolithic gold material exhibits a continuous 3D porous structure of nanosized gold ligaments and pores on the order of a few tens of nanometers. Based on a self-organization process of gold atoms during the preparation of the material by corrosion of an Au alloy (Au–Ag or Au–Cu) an extremely homogeneous porous structure is formed.¹⁰ About 70 percent of the material is void volume making the material penetrable for gases and liquids; hence, the entire surface of this gold sponge ($\sim 10 \text{ m}^2/\text{g}$) is exposed to the surrounding media. Since about ten years several publications reported on the high catalytic potential of the material for various reactions in gas and liquid phase.^{11–13} Accordingly, further engineering of surface reactivity by organic functional groups is an obvious approach for tailoring the surface chemistry and thus reactivity of the material for applications in catalysis, electrochemistry and sensors.

The most stable form for immobilization of an organic entity on a gold surface is the formation of a chemical bond between both partners. This concept is well established in the context of selfassembled-monolayers (SAMs) on gold substrates.^{14–16} Thiol or disulfide groups of the organic partner react with the gold surface forming a chemical bond. Common methods to functionalize nanoporous gold surfaces, hence, use molecules containing such groups (e.g., functionalized cysteine/lactase), attaching them directly to the surface.^{5,8,17} Alternative approaches use physical entrapment of glucose-oxidase in a sulfur containing polymer¹ (poly(3,4-ethylenedioxythiophene)) or binding of glucose-oxidase onto an already existing monolayer, which provides chemical reactivity in the form of acid-groups.³ Yet, a general synthetic route for immobilization providing a maximum of stability and

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reproducibility is missing. The motivation of our work, hence, is to establish and describe a general and versatile two-step synthetic approach: (A) the formation of a suitable SAM on the npAu surface and (B) binding the catalytic active entity to a specific linker molecule of the previously formed SAM. As compared to the direct synthesis of such functional thiols the proposed two-step approach bears several advantages (see also Ref. 16 for more details). (1) it generalizes the synthetic procedure (2) it enables the bonding of functionalities/catalysts, which are not available containing thiol moieties, making it a very versatile approach, (3) it takes advantage of the order of the preexisting SAM-smaller molecules show faster adsorption kinetics and, thus, less defects in the SAM (4) the synthesis of functionalized thiols is typically laborious (in case of sulfur containing molecules, peptides or proteins even a considerable challenge). Thiols also exhibit a distinct propensity to oxidation limiting their storage capability, which renders the synthesis of larger quantities of expensive thiols uneconomic. The described two-step procedure might, hence, be even the only suitable way of immobilization for many organic functionalities.

However, such an approach strongly depends on the step (B), the reaction between the catalytically active species and the preexisting SAM. This reaction has to fulfill the following conditions: mild reaction conditions avoiding thermal coarsening of the gold substrate, high reaction rates, and formation of a stable bond in various reaction media, also under applied electrochemical potentials. We, thus, opted for the copper(I) catalyzed reaction between an alkyne compound and an azide (linker in SAM) known as 'click-reaction' named by Sharpless in 2001.¹⁸ In order to demonstrate the versatility of our synthetic approach we synthesized exemplary organic molecules with the according moieties and tested the derived npAu/organic composites for applications in electrochemical environments and photo-catalysis. For the first application two different compounds were synthesized and immobilized onto npAu: redox-active ferrocene^{19,20} and tetrathiafulvalene.²¹ For the second application as a photocatalyst a zinc(II) phthalocyanine was synthesized and immobilized. This class of molecules (metallophthalocyanines) is an important (photo-) catalysts in industry for the photooxidation and oxidation of different substrates by the reaction with molecular oxygen.²²

2. Results and discussion

2.1. Synthesis

For the preparation of hybrid-materials consisting of ferrocene, tetrathiafulvalene, and phthalocyanine derivates (Fig. 2)



Fig. 1. Scanning-electron micrograph of a cross-section of a npAu disk.



Fig. 2. Structures of 11-azidoundecane-1-thiol 1 and the alkyne-substituted ferrocene, tetrathiafulvalene and phthalocyanine derivates 2–4.

immobilized on the surface of npAu the following reaction steps were carried out:

- 1. Preparation of npAu,
- 2. Synthesis of the linker 11-azido-1-undecanethiol 1,
- 3. Synthesis of the ferrocene, tetrathiafulvalene, and phthalocyanine derivates **2**–**4** containing alkyne groups,
- 4. Synthesis of tris(benzyltriazolylmethyl)amine (TBTA) **5** as copper ligand for the click-reaction,
- 5. Binding of linker 1 (and 1-octanethiol as a spacer) on npAu,
- 6. Binding of the alkyne-substituted compounds **2–4** via the click reaction at the modified npAu surface.

The preparation of the npAu substrate (step 1) was carried out following procedures described previously in Refs. 12,23. For the functionalization of 2-4, disks of a Au₃₀-Ag₇₀ alloy of about 6 mm diameter and 100 or 200 µm thickness were submersed in concentrated nitric acid for 24 h and 48 h, respectively, and subsequently dried in air. Scanning-electron micrographs of cross sections of these disks show the homogeneous porosity of the material (Fig. 1). In the following (step 2), the compound 11-azido-1-undecanethiol 1 was synthesized (Fig. S1, see Supplementary data for synthetic details and numbering). Starting with the commercially available 11bromo-1-undecanol 6, the intermediates 11-azido-1-undecanol 7, and 11-azido-1-undecanol,1-methanesulfonate 8 were synthesized as described in literature.²⁴ In an alternative pathway an intermediate component 11-azido-1-undecanol,1-thioacetate 9 was firstly obtained by nucleophilic substitution of 8 with potassium thioacetate. In a following step the component 1 could be obtained by using methanol/acetyl chloride instead of introducing gaseous HCl.²⁴

In step 3, the alkyne-substituted compounds **2–4** were synthesized. 1-Ferrocenyl-2-propyn-1-one **2** was obtained as described by Barriga et al.²⁵ starting from ferrocenecarbaldehyde **10** (Fig. S2). 4-carboxytetrathiafulvalene, propargylester **3** was synthesized starting with the basic compound tetrathiafulvalene **12** up to the intermediate tetrathiafulvalene-4-carboxylic acid **15** by following the pathway of Garin et al.²⁶ The alkyne terminated TTF product was prepared in a two-step sequence from the previously reported 4-carboxytetrathiafulvalene.²⁶ First, the acyl chloride was synthesized by treating the carboxylic acid with oxalyl chloride and *N*,*N*-dimethylformamide. Afterward the esterification was achieved by addition of propargyl alcohol and *N*,*N*-diisopropylethylamide (Fig. S3) to obtain **3**.

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Fig. 3. Schematic illustration of the attachment of the alkyne-substituted compounds **2**–**4** to npAu; (a) immobilization of the linker **1** and a spacer molecules (1:3) (SAM formation), (b) functionalization with active species **2**–**4** using the click-reaction, (c) nanoporous gold system with a specific functionality.

Next (part of step 3), 2,9,16,23-tetrakis(4-hex-5-yn-oxy)phthalocyanine-zinc(II) **4** was synthesized after modification of a procedure reported by Quinton et al.²⁷ and Meder et al.²⁸ (Fig. S4). Zn(II) was selected instead of Mn(II) the as central metal ion because zinc(II)phthalocyanine exhibits under irradiation a high singlet oxygen quantum yield.²⁹ Tris(benzyltriazolylmethyl)amine (TBTA, step 4) **5** was formed in a click reaction from tripropargylamine **19** and benzyl azide **20** in a procedure described by Chan et al. (Fig. S5).³⁰

After synthesis of these various compounds the two-step immobilization (steps 5 and 6, cf. Fig. 3) was carried out as follows. The first step (5) is the formation of a self-assembled monolayer (SAM) on the nanostructured gold material containing two different types of molecules, (1) a linker molecule **1** with an azide terminated group and (2) a shorter 'spacer' 1-octanethiol without any functional group at the other end of the C-chain. The latter alkanethiol, acting as diluent spacer, was added in a 3:1 ratio with respect to the linker molecule in order to avoid mutual steric hindrances of the space-filling active molecules **2–4** on the surface of npAu.

The progress of self-assembly of **1** together with the spacer 1octanethiol was monitored by cyclic voltammetry (CV, cf. Fig. 4). The electrolyte contains $K_3Fe(CN)_6$, which serves as a probe reagent. The reversible redox signals of the $K_3Fe(CN)_6$ appear at 360 mV (oxidation: $Fe^{2+} \rightarrow Fe^{3+}$) and 80 mV (reduction: $Fe^{3+} \rightarrow Fe^{2+}$), respectively, indicating the availability of free adsorption sites on the gold surface before the immobilization. Depending on the degree of formation of the monolayer the redox signals are decreasing. After three days no noticeable signals are visible any more, indicating that a monolayer is formed and the adsorption sites are blocked by the thiols 1-octanethiol and **1**.

In a subsequent copper(I) catalyzed reaction (step 6), active species (catalyst) containing the alkyne moiety **2–4** (cf. Fig. 2) were covalently bound to the azide terminated SAM (at room temperature, i.e., ~20 °C, total reaction time 24 h). In all 'click-reactions' tris(benzyltriazolylmethyl)amine (TBTA) **5** was added. Chidsey et al. showed that this compound acts as a co-catalyst to the copper during reaction (coordinating the Cu intermediates) and increases the reaction rate by a factor of up to 20.³¹

2.2. Redox active properties of the ferrocene and tetrathiafulvalene derivates 2,3 on the surface of npAu

The alkyne terminated ferrocene derivates **2** were bonded to the npAu surface according to above described procedure. The resulting ferrocene–npAu-system was characterized using cyclic voltammetry (Fig. 5a). The current density (related to the geometric surface of the catalysts) of the redox active molecule attached to the npAu electrode was nearly two orders of magnitude higher compared to the reference system on a planar gold surface. This encouraged us to extend this procedure to the synthesis of the tetrathiafulvalene derivate **3**. The possibility of a stepwise oxidation/reduction via the two oxidation states (TTF⁺ and TTF²⁺) makes



Fig. 4. Cyclic voltammograms (CV) of npAu after different periods of time during formation of a SAM (linker 1 and spacer octane-1-thiol, step 5). The CV was recorded in 0.1 M KCI (ACROS, p.A.) with 5 mM K₃Fe(CN)₆ (Merck, p.A.) versus Ag/AgCl and a scan rate of 10 mV/s. The characteristic oxidation (360 mV) and reduction (80 mV) signals of ferrocyanide decreases as a result of the formation of the SAM and the concomitant decrease of free adsorption sites.

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Fig. 5. Cyclic voltammograms of the electro-active species **2**,**3** on nanoporous gold substrate. (a) CV of ferrocene derivate **2**: the current density of the npAu electrode is higher than for the planar Au electrode by a factor of ~60. The CV was recorded in 0.1 M HClO₄ (Sigma Aldrich, ACS reagent 70%) versus a Ag/AgCl electrode with a scan rate of 10 mV/s. (b) CV of TTF bonded onto an npAu electrode and the flat gold substrate as reference. The current density of the npAu functionalized TTF-system is higher by a factor of 30 compared to the planar reference system. The CV was recorded in 0.1 M KCl (ACROS, p.A.) versus Ag/AgCl with a scan rate of 50 mV/s.

this molecule interesting for redox switches.²¹ Also in this case, the combination of the npAu electrode and tetrathiafulvalene derivate **3** is more sensitive (by a factor of ~30) as compared to the reference TTF-system on a planar gold surface (Fig. 5b). The electrochemical characterization of **2** and **3** dissolved in CH₂Cl₂ (not bound to the npAu electrode) is shown in Fig. S6 of the Supplementary data.

2.3. Photocatalytic properties of the phthalocyanine derivate 4 on the surface of the npAu

As mentioned before, zinc(II)phthalocyanine (ZnPc) is an active photocatalyst sensitizer in photooxidations. By excitation of the sensitizer in presence of oxygen $O_2(^{3}\Sigma_{g}^{-})$, singlet oxygen $(O_2(^{1}\Delta_{g}))$ is obtained followed by energy transfer to triplet oxygen, which is responsible for the photooxidation (Scheme 1). One example is the well-known photooxidation of (S)-(–)-citronellol, which results in

⁰Sens
$$\xrightarrow{h\nu}$$
 ¹Sens^{*} \xrightarrow{ISC} ³Sens^{*}

 $^{3}\text{Sens}^{*}$ + $O_{2}(^{3}\Sigma_{g})$ \longrightarrow $^{0}\text{Sens}$ + $O_{2}(^{1}\Delta_{g})$

Scheme 1. Generation of singlet oxygen $(O_2(^1\Delta_g))$ based on a photosensitizer (Sens) system.

the two peroxides as ene-products (Scheme 2). The peroxides can be converted to rose oxide.²² The photooxidation of (S)-(-)-citro-nellol finally to rose oxide is an industrial process in annual multi-ton quantities employing Rose Bengal as photosensitizer.



Scheme 2. Photocatalytic oxidation of (S)-(-)-citronellol catalyzed by ZnPc.

The photo-oxidative activities of ZnPc 4 on npAu were determined by measuring the oxygen consumption over time for the oxidation of citronellol (molar ratio citronellol to $ZnPc=10^4$:1) in a photoreactor under irradiation with visible light.²² The oxygen consumption in the dark is negligible. Under irradiation employing the pure nanoporous gold no oxygen was consumed. By functionalization of the nanoporous gold with the phthalocyanine 4 a reproducible conversion of ~37% citronellol ($c_0=0.5$ mmol; 25 mg npAu, 6 mm in diameter) over 24 h was measured (Fig. 6). The conversion of citronellol to the peroxides was confirmed by using gas chromatography and mass spectrometry (GC-MS). For comparison, a flat gold surface (1.8×1.8 cm) was modified with the ZnPc as well. No oxygen consumption at all was detected indicating that the amount of the dye on the planar gold surface is too low, and therefore a dye-functionalization on planar surfaces is not suitable for this application. As a benchmark of this system we quantified the amount of Zn (which means ZnPc 4) immobilized on the gold surface. The amount of $\sim 5 \times 10^{-8}$ mol ZnPc on 25 mg npAu was confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES). In a homogeneous photooxidation (in the absence of npAu) no oxygen consumption was detected using the same amount of ZnPc in solution $(5 \times 10^{-8} \text{ mol in } 50 \text{ mL})$ indicating a positive influence of the nanoporous gold. It can be speculated that this enhanced activity is related to the unique electronic and optical properties of the npAu, e.g., a plasmonic effect.^{32,33} For a more detailed insight further investigations are required, which are in progress. Also, we detect that only a fraction of the ZnPc 4 provided in solution (corresponding to 1/3 of a monolayer) was actually immobilized onto the substrate (~ 0.01 of a monolayer determined by ICP-MS). This deviation might be explained by the



Fig. 6. Photooxidation of citronellol (0.5 mmol in 50 mL ethanol) in the presence of a npAu disk (m=25 mg; thickness of 100 µm; irradiated area of 19 mm²) functionalized with the ZnPc derivate **4**. The squares indicate pressure drops measured by the instrument. The dotted line represents the deduced conversion of citronellol as a guide for the eve.

multifunctionality of the ZnPc molecule potentially binding to more than one azide group on the npAu surface. In this context, for future investigations Zn(II)phthalocyanines with only one acety-lene functionality should be synthesized.

3. Conclusions

The aim of this study was to demonstrate a versatile and reproducible synthetic approach for a stable immobilization of different organic molecules onto a highly porous gold substrate, namely the nanoporous gold. The open porosity of the monolithic nanostructure in conjunction with its high electrical conductivity makes it an ideal candidate for applications in catalysis and electrochemistry. Electrochemically and photochemically active molecules were used to demonstrate the potential of such systems. In a first step, a suitable SAM with reactive azide units was bound onto the npAu substrate serving as a stable platform for further functionalization with the reactive molecules (catalyst). We presented an alternative and more easy binding of an azide-linker as well as the successful immobilization of three compounds containing alkyne functionalities for potential sensor and photocatalytic applications. The redox active species (ferrocene- and tetrathiafulvalene derivates) on npAu and the ZnPc-npAu system for photooxidation of citronellol showed very appreciable activity. In both cases the activity of the nanoporous gold derived system was superior to reference systems on planar gold substrates, owing to its nanoporosity and, thus, increased surface area. In the case of the electrochemical active system, the sensitivity could be enhanced by nearly two orders of magnitude. The immobilized photocatalyst on the planar gold surface showed no detectable reactivity, while the ZnPc-npAu-system reaches almost 40% conversion of 0.5 mmol citronellol even though the size of the sample and irradiated geometric area, respectively, was ~ 20 times smaller than that of the planar substrate. The finding that the ZnPc-npAu showed even higher conversion than the same amount of ZnPc dissolved in the reaction medium indicates an enhancement from the nanoporous gold substrate possibly by surface plasmons. The demonstrated synthetic routine provides a versatile tool for generating high performance organic/npAu composite materials with a robust chemical bond between the organic functionality and the Au substrate.

4. Experimental

4.1. General information

1-Ferrocenyl-2-propyn-1-one **2** (Fig. S2)²⁵ and tris(benzyl-triazolylmethyl)amine (TBTA) **5** (Fig. S5)³⁰ were prepared as described before. 11-Azido-1-undecanethiol **1** was synthesized as shown in Fig. S1. The starting material 11-bromo-1-undecanol **6** is commercially available (Sigma–Aldrich). The compounds 11-azido-1-undecanol, **7** and 11-azido-1-undecanol, **1**-methanesulfonate **8** were synthesized as described in literature.²⁴ The compounds 11-azido-1-undecanol, **1**-thioacetate **9** and 11-azido-1-undecanethiol **1** were synthesized as described in the Experimental part. The al-kyne-modified tetrathiafulvalene derivate **3** was synthesized following the general procedure reported by Garin et al.²⁶ up to compound tetrathiafulvalene-4-carbonyl chloride **16**; the synthesis of compound **3** is described in the experimental part (Fig. S3). The synthesis of metallo-phthalocyanine **4** (shown in Fig. S4) was similar to a procedure from D. Quinton et al.,²⁷ i.e., Meder et al.,²⁸ modifications are described in the Experimental part.

Reagent grade chemicals and solvents were used without further purification unless otherwise stated. All reactions were carried out under atmosphere of dry N₂. NMR spectra were recorded using *Bruker Avance DPX-200* spectrometer and *Bruker Avance NB-360* spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane using the residual CHCl₃ (7.26 ppm for ¹H, 77.0 ppm for ¹³C) signals as a reference. Low resolution mass spectra were measured on *Finnigan MAT 8200* or *Finnigan MAT 95* spectrometers for electron ionization (EI, 70 eV), and on a *Bruker Esquire-LC* spectrometer for electrospray ionization (ESI). High resolution MS-spectra (HRMS) were measured on a *Finnigan MAT 95* spectrometer (EI, 70 eV). Measured isotopic patterns of the M⁺ ions of all reported compounds were fully consistent with the calculated ones. Melting points were determined using capillary melting point apparatus and are uncorrected. *R*_f values were determined using 0.2 mm silica gel F-254 TLC cards. Flash chromatography (FC) was carried out using 230–440 mesh (particle size 36–70 µm) silica gel.

4.2. Preparation of the planar and nanoporous gold substrates

In all photochemical experiments nanoporous gold disks with a diameter of 6 mm and a thickness of 100 μ m were used, prepared by etching Ag-Au alloys (70 at% Ag, 30 at% Au) with 50 mL concentrated nitric acid (24 h, HNO₃, 65 wt %, OmniTrace EMD Chemicals). For functionalization of npAu with redox-active molecules 2,3 disks with 200 µm thickness were generated by corrosion in 50 mL concentrated nitric acid over 48 h. The master alloys were prepared in a procedure described before by us.¹¹ After washing with three times with 30 mL deionized water, the nanoporous gold samples were dried 24 h at ambient conditions. The residual silver content of the obtained material was below 1 at% as confirmed by AAS.²³ The npAu show reproducible pore sizes of ~ 40 nm (cf. Fig. 1). Different planar polycrystalline gold substrates were used as reference systems for comparison with the npAu-organic hybrid materials. In the electrochemical experiments gold foils with dimensions of ca. $10 \times 13 \times 0.5$ mm³ for immobilization of ferrocene derivate **2** and ca. $10 \times 10 \times 0.5$ mm³ for immobilization of tetrathiafulvalene derivate 3 were used. Before immobilization the gold substrates were cleaned by applying a potential of -1.8 V for 3 min in 0.5 M H₂SO₄. In case of immobilization of phthalocyanine derivate **4** a SiO₂-substrate (ca. 1.8×3.6 cm²) was sputtered with gold (Cressington Sputter Coater 108auto).

4.3. Organic functionalization of the nanoporous gold substrate

The nanoporous gold disk was immersed in an ethanolic solution (5 mL) containing 50 mM 11-azido-1-undecanethiol **1** and 150 mM 1-octanethiol (Sigma Aldrich, >98.5%) for 3 days at room temperature. The samples were washed immediately three times by dipping them in ethanol for 15 min removing the excessive linker **1** and the 1-octanethiol.

The electro-active compounds (ferrocene and tetrathiafulvalene derivates **2,3**) were attached subsequently in a reaction using 0.25 M of Fc or TTF alkyne derivatives, 0.1 M Cu[TBTA]PF₆, and 0.25 M hydroquinone (Sigma Aldrich, >99.0%) in 5 mL DMSO (Merck, p.A.)/H₂O 3:1 for 24 h. For the immobilization of the phthalocyanine derivate **4** a mixture of 5 mL THF (Merck, p.A.)/H₂O 3:1 was used as solvent. After immobilization, the samples were washed immediately three times by dipping them for 15 min in DMSO in the case of the Fc and TTF derivates **2,3** or in THF in the case of the phthalocyanine derivate **4**.

4.4. Determination of the phthalocyanine derivate 4 by inductively coupled plasma optical emission spectrometry (ICP-OES)

Subsamples (~10 mg of functionalized npAu) were weighed (balance Mettler MD-205) and transferred in Teflon TFM(R) HP120

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digestion vessels. 6 mL 14.4 mol/L nitric acid and 3 mL 10.2 mol/L hydrochloric acid were added. Closed vessels were subjected to a microwave-assisted digestion (ca. 210 °C for 40 min; MLS 1200 mega system, MWS GmbH, Leutkirch, Germany). Solutions obtained were clear, they were evaporated to near dryness by microwave action (2×40 min). Residues of ca. 0.5 mL each were determined gravimetrically, and 3 mL 0.5 mol/L nitric acid was added. The mixtures were subjected to a 10 min dissolution step in closed vessels under mild microwave action (250 W). Final volumes were calculated applying a residue density of 1.05. Two procedural blanks were run in the same sequence.

The Zn amount was measured by using a VARIAN Vista Pro. For the inductively coupled plasma optical emission spectrometry (ICP-OES) a radial plasma observation was used. The samples prepared as described above were diluted by a factor of two in 1% HNO₃.

4.5. Cyclic voltammetry with dissolved ferrocene and tetrathiafulvalene derivates 2,3

Cyclic voltammetry (CV) with dissolved substances was performed using a computer controlled *HEKA PG390* potentiostat in a three-electrode single-compartment cell (2.5 mL) with a platinum disk working electrode (diameter of 1.5 mm) and a platinum wire used as a counter electrode. A non-aqueous Ag/Ag⁺ secondary electrode (0.1 M TPAP+0.01 M AgNO₃ in MeCN) was used as the reference electrode. The samples were dissolved $1 \times 10^{\times 3}$ M in dry degassed MeCN containing 0.1 M Bu₄NClO₄ (TBAP) as supporting electrolyte. Ferrocene was taken as an electrochemical Ref. 34,35 with the potential $E_{1/2}^{ox}=0.38$ V versus saturated calomel electrode (SCE) for the Fc/Fc⁺ couple in TBAP/CH₂Cl₂.^{36,37} A CV scan of 1×10^{-3} M ferrocene solution was taken after each CV measurement for calibration purposes. Then the values of oxidation potentials were referenced to the Fc/Fc⁺ couple, recalculated, and reported versus Ag/AgCl (3 M KCl).

4.6. Cyclic voltammetry with ferrocene and tetrathiafulvalene derivates 2,3 immobilized on npAu

CV with immobilized substances was performed using a computer controlled *HEKA PG390* potentiostat in a three-electrode single-compartment cell (250 mL) with a gold wire used as a working electrode and a platinum counter electrode. An Ag/AgCl electrode (3 M KCl) was used as the reference electrode. CV samples were fixed with the gold wire and measured in water containing 0.1 M KCl or 0.1 M HClO₄ as supporting electrolyte. The values of oxidation potentials are reported versus Ag/AgCl.

4.7. Photooxidation of (S)-(-)-citronellol in organic solvents

Measurements for the photocatalytic activities were carried out as described at 25 °C in a 100 mL reaction vessel connected to a 50 mL gas burette.²² The vessel was irradiated with a 250 W quartz-halogen lamp of a slide projector, and the light intensity was adjusted to ~180 mW cm⁻². The reaction vessel was filled with 50 mL ethanol solutions containing the phthalocyanine derivate **4** immobilized on the nanoporous gold substrate (6 mm in diameter, 100 µm in thickness) or for the reference measurement the compound **4** dissolved in ethanol (5×10⁻⁸ mol). Then the apparatus was flushed with pure oxygen for 10 min, and 91 µL (0.5 mmol) citronellol was added to the vessel (molar ratio substrate to photosensitizer was 10⁴:1). After closing the apparatus, the reaction vessel was irradiated under intensive magnetic stirring, and the oxygen consumption over 24 h was recorded.

4.8. Synthesis

4.8.1. Synthesis of 11-azido-1-undecanol,1-thioacetate (9). 1.46 g (5 mmol) 11-azido-1-undecanol,1-methanesulfonate 8 and 1.14 g (2 mmol) potassium thioacetate were dissolved in 50 mL DMF and stirred for 24 h at room temperature under an argon atmosphere. Afterward 300 mL water was added. The aqueous solution was extracted with ether for three times, and then the collected organic layers were washed with water for three times. The organic phase was dried by filtering over cotton wool. After removing the solvent and drying in vacuum the residue was purified by column chromatography (silica gel, CH₂Cl₂). Yield: 1.18 g (4.35 mmol, 87%). ¹H NMR (200 MHz, CDCl₃): δ =3.25 (t, ³*J*=6.9 Hz, 2H, CH₂N₃), 2.85 (t, ³*J*=7.2 Hz, 2H, CH₂S), 2.31 (s, 3H, CH₃), 1.59–1.52 (m, 4H), 1.44–1.19 (m, 14H). ¹³C NMR (200 MHz, CDCl₃): δ =196.3 (SOCCH₃), 51.7 (CH₂N₃), 30.9, 29.7, 29.6, 29.4, 29.3, 29.0, 26.9.

4.8.2. Synthesis of 11-azido-1-undecanethiol (1). Under argon at 0 °C 7 mL (95 mmol) acetyl chloride were added to 40 mL methanol. The solution was stirred for 30 min and then 1.14 g (4.2 mmol) 11azido-1-undecanol,1-thioacetate 9 in 10 mL methanol was added. Stirring was continued for 24 h. 300 mL of a saturated sodium bicarbonate solution was added. The mixture was extracted three times with 100 mL of diethyl ether and then washed with a sodium bicarbonate solution and water. The ether phase was washed with a sodium bicarbonate solution and water. The organic laver was separated and dried by filtration over cotton wool. The residue was dried again in vacuum and then purified by column chromatography (silica gel, CH₂Cl₂). The dark brown residue was distilled in vacuum to give an orange-yellow liquid. Yield: 608 mg (2.65 mmol, 63%). TLC (CH₂Cl₂): 0.74. ¹H NMR (200 MHz, CDCl₃): δ =3.24 (t, ³*I*=6.9 Hz, 2H, CH₂N₃), 2.56–2.45 (m, 2H, CH₂SH), 1.67–1.52 (m, 4H), 1.41–1.26 (m, 14H). ¹³C NMR (200 MHz, CDCl₃): δ =51.6 (CH₂N₃), 34.2, 29.6, 29.3, 29.2, 29.0, 28.5, 26.9, 24.8. IR (NaCl, Film): v=2927, 2854 (s, CH), 2095 (s, N₃), 1465 (m), 1349 (w), 1260 (m), 722 (w). MS (EI, 70 eV): *m*/*z*: 229 [M].

4.8.3. Synthesis of 4-carboxytetrathiafulvalene, propargylester (3). A heavy-walled Schlenk tube equipped with a wide bore Teflon stopcock was charged with 15 (0.1 g, 0.46 mmol) and THF (10 mL). Afterward DMF (10 µL) and oxalyl chloride (160 µL, 1.84 mmol) were added. The reaction mixture was stirred at 70 °C for 1 h and then at room temperature overnight. After concentration in vacuo, THF (5 mL) and propargyl alcohol (130 µL, 2.3 mmol) were added, followed by the slow addition of N-diisopropylamine (390 µL, 2.3 mmol). The reaction mixture was stirred for 1 h at room temperature and was concentrated in vacuo. The crude product was purified by flash chromatography (CH₂Cl₂) to afford red crystals. Yield: 0.14 g (0.36 mmol, 79%). Mp: 91 °C. *R*_f=0.65 (CH₂Cl₂). ¹H NMR (200 MHz, CDCl₃): δ 7.41 (s, 1H), 6.36–6.29 (m, 2H), 4.80 (d, ³J=2.44 Hz, 2H), 2.52 (t, ³J=2.44 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃): δ 158.39, 133.51, 127.42, 119.22, 118.72, 114.26, 107.11, 75.66, 53.04. MS (EI): m/z 286 (100) [M]⁺. HRMS (EI): m/z [M]⁺ calcd for C₁₀H₆O₂S⁺₄ 285.92507, found 285.92506. CV (vs Ag/AgCl, CH₂Cl₂): $E_{1/2}^{\text{ox1}}$ =0.42 V, $E_{1/2}^{\text{ox2}}$ =0.78 V.

4.8.4. Synthesis of 4-(hex-5-yn-oxy)phthalonitrile (**18**). 200 μ L (1.84 mmol) 5-hexyn-1-ol and 266.9 mg (1.54 mmol) 4nitrophthalonitrile **17** were dissolved in 20 mL dry DMF under argon. The mixture was stirred for 15 min and then 360 mg (2.61 mmol) ground anhydrous potassium carbonate was added. 106 mg (0.77 mmol) potassium carbonate was further added after 3 h and again after 24 h. After 26 h, water was added to the reaction mixture. The brownish product was collected by centrifugation and rinsed with ethanol, and then it was washed with 3×20 mL of water, re-dissolved in toluene, and the solution dried over MgSO₄.

Evaporation of the solvent gave pure 4-(hex-5-yn-oxy)phthalonitrile as a light yellow solid. Yield: 102 mg (0.46 mmol, 30%). Mp: 97 °C. ¹H NMR (200 MHz, DMSO): δ 7.99–7.95 (Ar–H, m, 1H), 7.69-7.68 (Ar-H, m, 1H), 7.42-7.36 (Ar-H, m, 1H), 4.14-4.08 (CH₂−O−, t, ³*J*=6.9 Hz, 2H), 2.73−2.71 (−C≡CH, m, 1H), 2.24−2.16 (CH₂, m, 2H), 1.86-1.72 (CH₂, m, 2H), 1.62-1.51 (CH₂, m, 2H). IR (KBr), *v* [cm⁻¹]=3284 (−≡C−H), 3078 (C_{aryl}−H), 2962/2945/2866 (−CH₂), 2227 (−CN), 2114 (C≡C), 1603/1595 (C_{aryl}=C_{aryl}), 1309 (Carvl-O-Calkvl). MS: (EI, 70 eV) m/z (%): 224 (5) [M], 223 (10) [M-H], 144 (20) [M-C₆H₈], 127 (10) [M-C₆H₉O], 81 (90) [M-C₈H₃N₂O], 53 (60) [M-C₁₀H₇N₂O].

4.8.5. Synthesis of 2,9,16,23-tetrakis(4-hex-5-yn-oxy)phthalocyani*ne–zinc(II)* (4). 2,9,16,23-Tetrakis(4-hex-5-yn-oxy)phthalocyanine-zinc(II) was prepared by dissolving 100 mg (0.45 mmol) 4-(hex-5-yn-oxy)phthalonitrile **18** and 50 mg (0.27 mmol) anhydrous zinc acetate in 25 mL N,N-dimethylaminoethanol and heated at reflux temperature (135 °C) under argon for 15 h. The mixture was then allowed to cool and methanol was added to precipitate the product that was further collected by centrifugation. The complex was first purified by column chromatography over silica gel using DMF as eluent. DMF was removed under reduced pressure at 80 °C. The resulting product was then further purified by heating in methanol for 30 min. The solid was collected by centrifugation. Yield: 31.2 mg (32 μmol, 7%). ¹H NMR (200 MHz, DMF): δ 9.34–9.24 (Ar-H, m, 4H), 9.04-8.88 (Ar-H, m, 4H), 7.88-7.76 (Ar-H, m, 4H), 4.78-4.54 (CH2-O-, m, 8H), 2.60-2.44 (CH2, m, 8H), 2.36-2.29 (-C≡CH, m, 4H), 2.26-2.16 (CH₂, m, 8H), 2.08-1.86 (CH₂, m, 8H). IR: (KBr), *v* [cm⁻¹]: 3276 (−≡C−H), 2935/2910/2867/2840 (Carvi-H/Calkvi-H), 2109 (-C=C-), 1606 (-C=C- arom). 1487/ 1468 (C-H/C-N/C-C-), 1385/1336 (C-H/C-C/C-N), 1275 (C-H/ C-N), 1238 (C-H,C-N/Carvi-Calkyl), 1120/1092 (C-H/C-C), 634 (Pc-Ring). MS: (ESI, positive) (DMF): m/z: 961 [M+H]⁺; (ESI, negative) (DMF) m/z: 995 $[M-C1]^{-}$, 879 $[M-C_6H_9]^{-}$, 914 $[M-C_6H_9+C1]^2$, 977 $[M+OH]^-$ UV-vis (DMF) λ (nm): 354, 680 (for the UV-vis spectrum please see Fig. S7 in the Supplementary data).

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Supplementary data

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