catalysts

Synergistic Effect in Zinc Phthalocyanine – Nanoporous Gold Hybrid Materials for Enhanced Photocatalytic Oxidations

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Supporting Information

ESI-1: Supplementary data for the characterization of the npAu disk

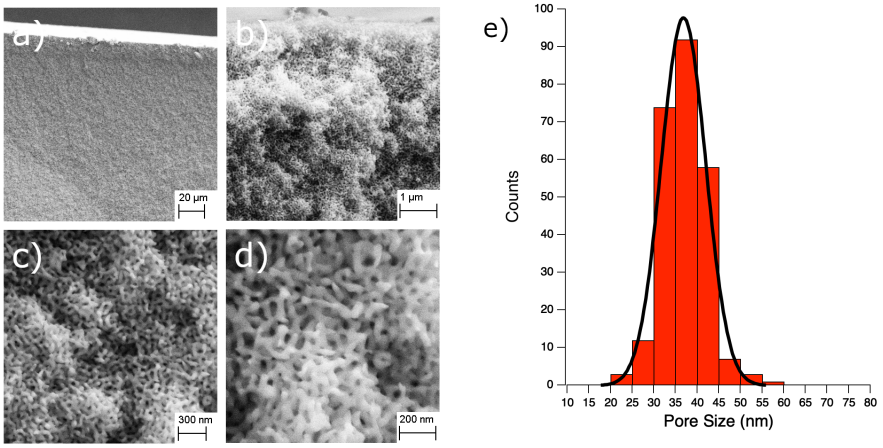

Figure S1. Representative SEM images of a ZnPc functionalized npAu disk showing the breaking edge with a magnification of (**a**) 1000; (**b**) 20000; (**c**) 50000; (**d**) 100000. Corresponding pore size distribution shows a Gaussian-distribution and is shown in (**e**).

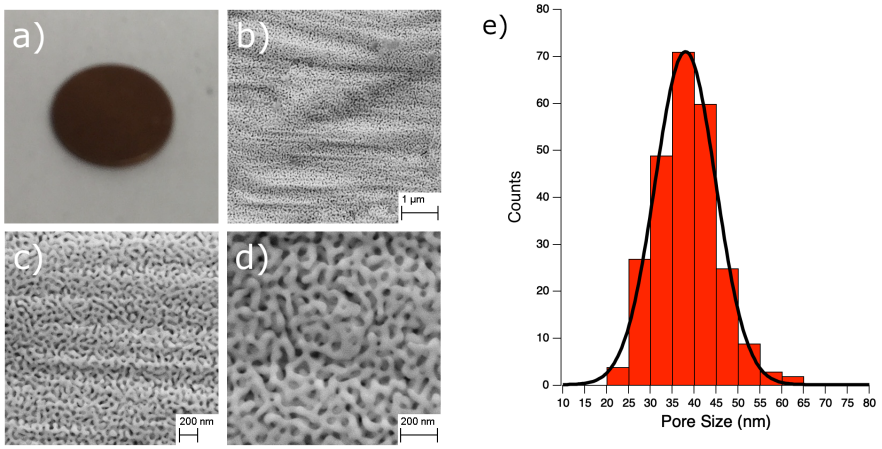

Figure S2. Representative optical image of a ZnPc functionalized npAu disk with a diameter of 5 mm in (**a**) and representative SEM images of a npAu disk showing the surface with a magnification of (**b**) 20000; (**c**) 50000; (**d**) 100000. Corresponding pore size distribution shows a Gaussian-distribution and is shown in (**e**).

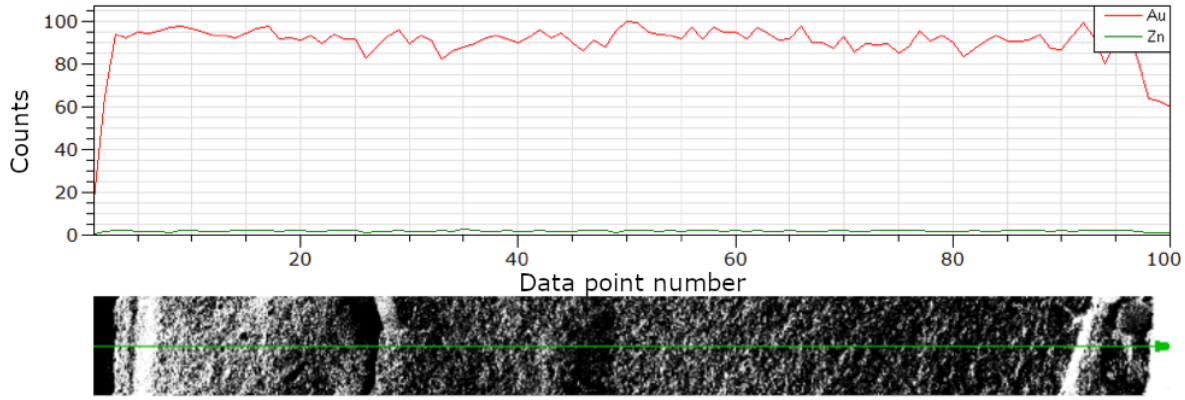

Figure S3. EDX line scan on the breaking edge of a npAu disk after the two-step functionalization with the azide **1** and the photosensitizer ZnPc **3** showing the ratio of the elements Zn and Au (top) and the corresponding SEM image (bottom) with the position of the line scan (length 333 µm).

ESI-2: Supplementary data for the characterization of the npAu powder

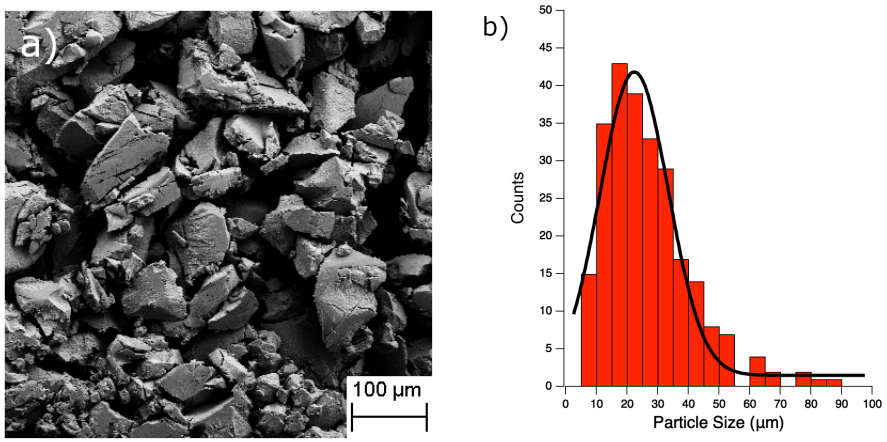

Figure S4. Representative SEM images of the npAu powder modified with the linker azidothioate **1** and functionalized with the ZnPc **3** with a magnification of 200 (**a**) to determine the particle size. Corresponding particle size distribution shows a Gaussian-distribution and is shown in (**b**).

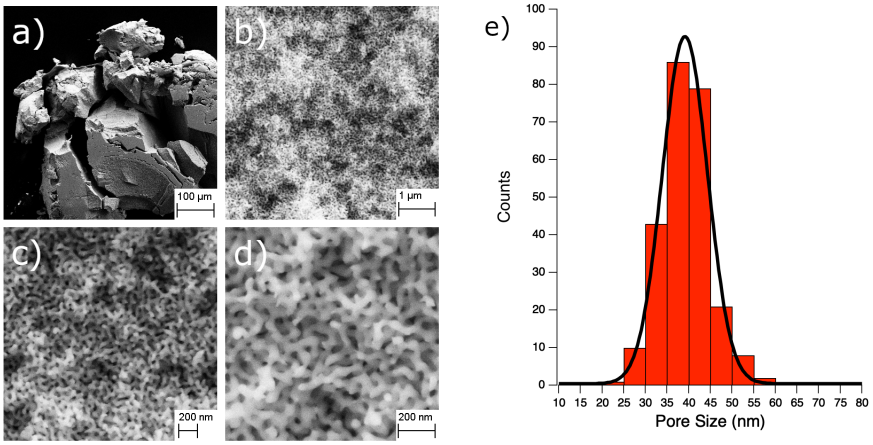

Figure S5. Representative SEM images of the npAu powder modified the linker azidothioate **1** and functionalized with the ZnPc **3** with a magnification of (**a**) 60; (**b**) 20000; (**c**) 50000; (**d**) 100000. Corresponding pore size distribution shows a Gaussian-distribution and is shown in (**e**).

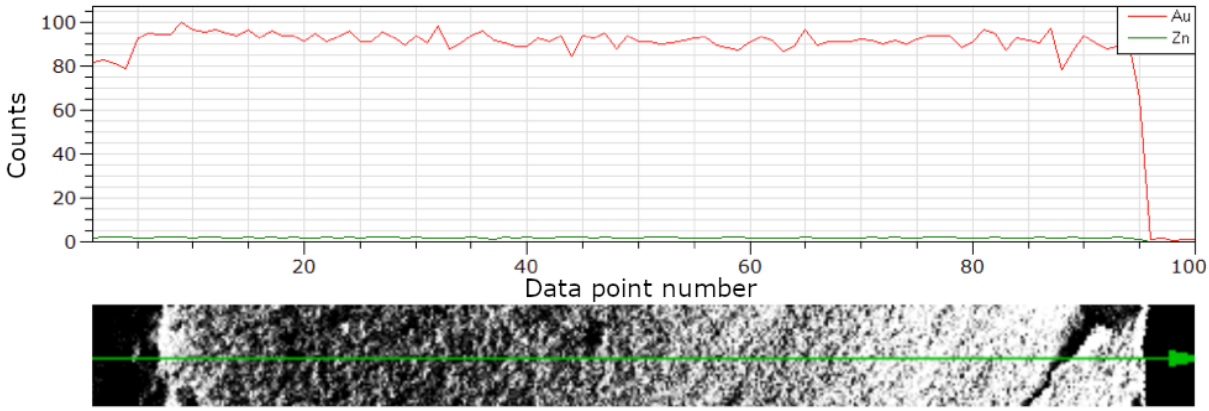

Figure S6. EDX line scan on the surface of a npAu powder particle modified with the linker azidothioate **1** and functionalized with the ZnPc **3** showing the ratio of the elements Zn and Au (top) and the corresponding SEM image (bottom) with the position of the line scan.

ESI-3: Supplementary data for the photooxidation of DPBF over npAu disks with and without an additional spacer molecule in the SAM

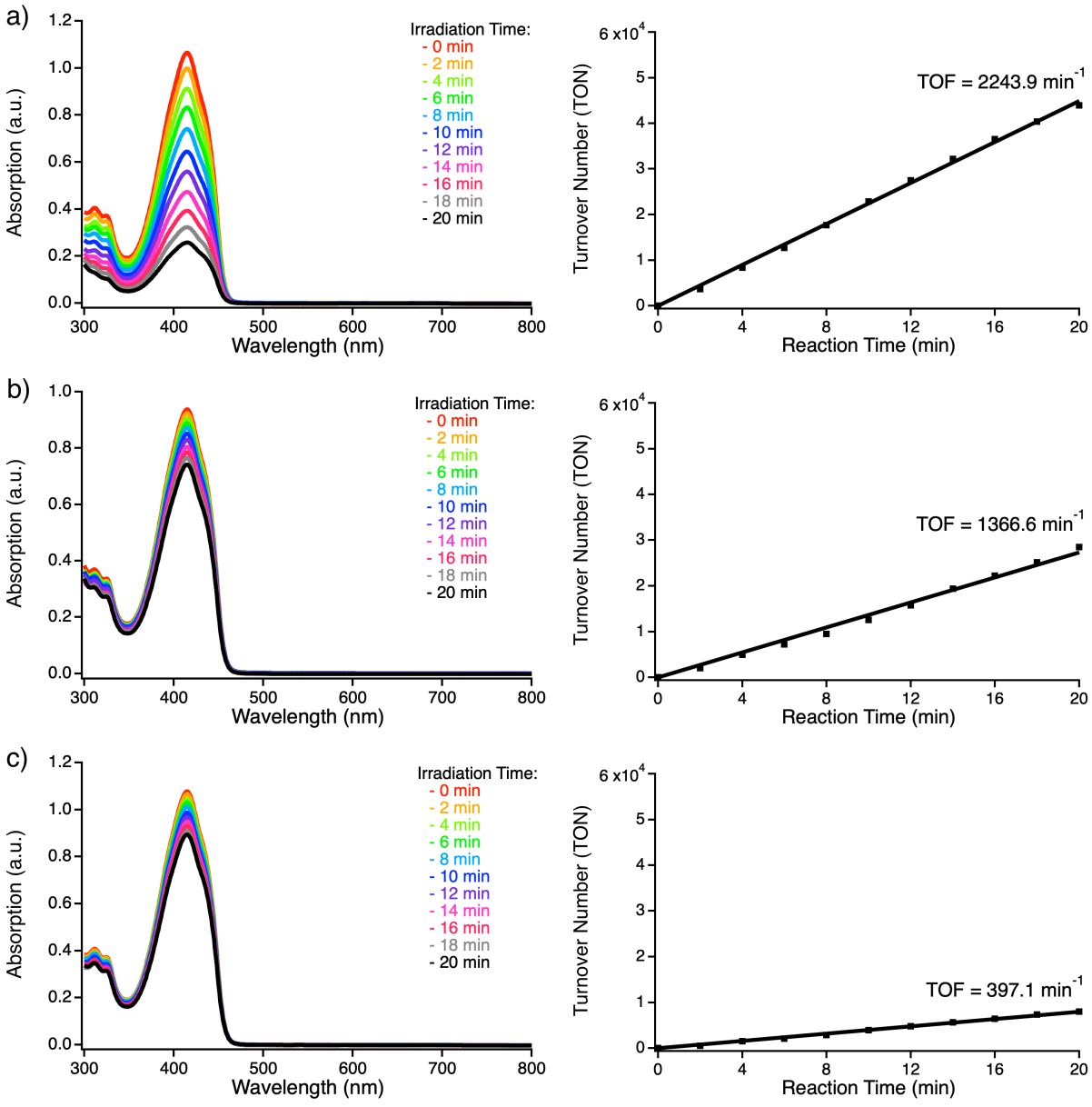

Figure S7. UV Vis spectra for the photooxidation of DPBF over (**a**) a npAu disk modified with the linker azidothioate **1** and functionalized with the ZnPc **3**; (**b**) a npAu disk with the liker azidothioate **1** in the presence of octanethiol as spacer (1:3) and functionalized with the ZnPc **3**. All photooxidations were performed under irradiation with a 550 nm cut-on filter. From the obtained number of converted DPBF, the turnover numbers (TON) were calculated using the illuminated photosensitizer amount of 8 x 10^{-11} mol and 3 x 10^{-11} respectively. (**c**) For comparison the photosensitizer **3** in solution with a concentration of 1 x 10^{-10} was measured. The values of a, b, c were plotted against the reaction time and the slope obtained by linear regression is the desired turnover frequency (TOF).

ESI-4: Supplementary data for the photooxidation of DPBF over npAu disks using different irradiation wavelengths

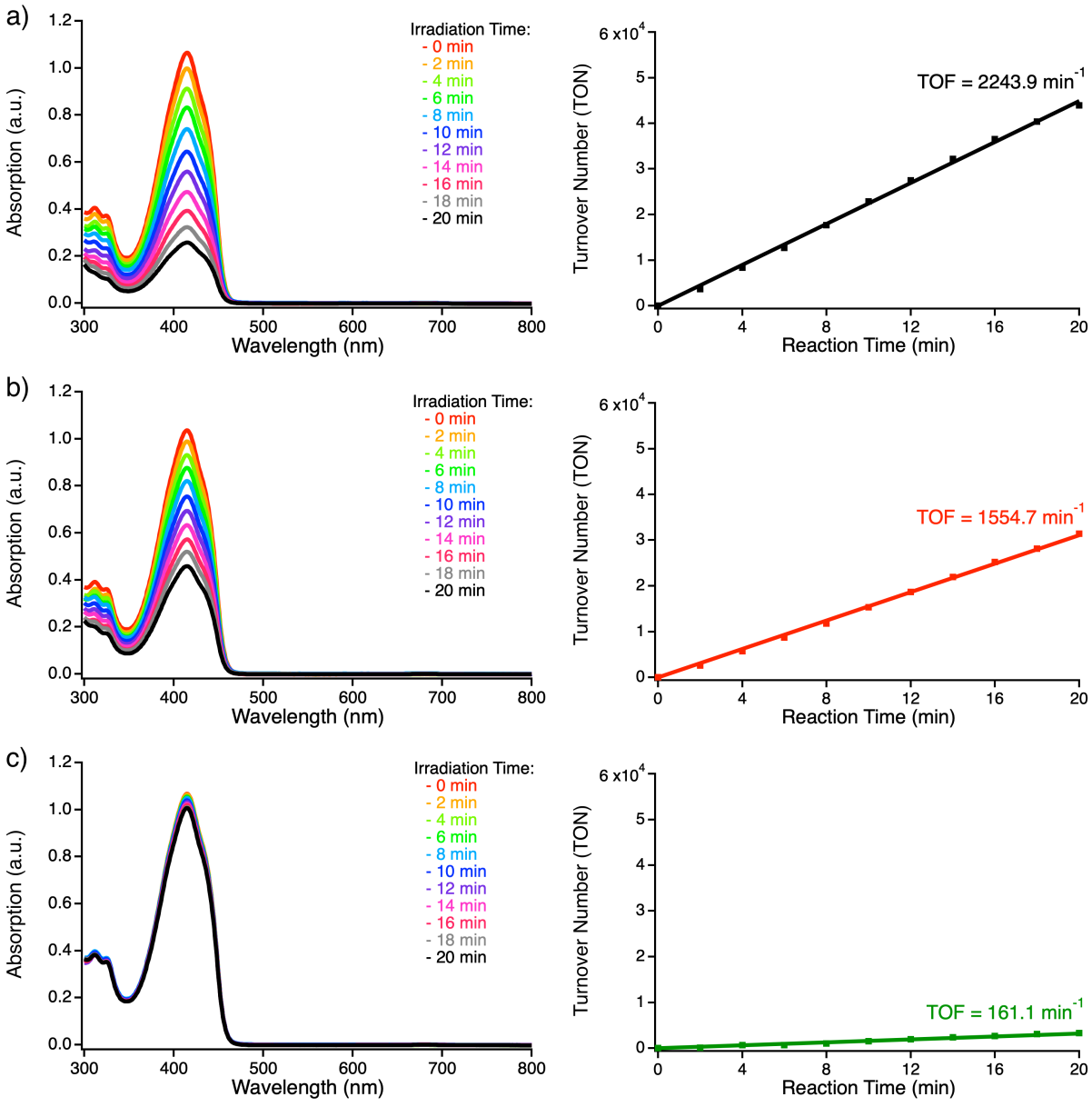

Figure S8. UV Vis spectra for the photooxidation of DPBF over a npAu disk modified with the linker azidotioate **1** and functionalized with the ZnPc **3** irradiated with (**a**) 550 nm cut-on filter; (**b**) 700 nm bandpass filter and (**c**) 550 nm bandpass filter. From the obtained number of converted DPBF, the turnover numbers (TON) were calculated using the illuminated photosensitizer amount of 8 x 10^{-11} mol. The values of a, b, c were plotted against the reaction time and the slope obtained by linear regression is the desired turnover frequency (TOF).

ESI-5: Supplementary data for the photooxidation of DPBF over npAu powder using different irradiation wavelengths

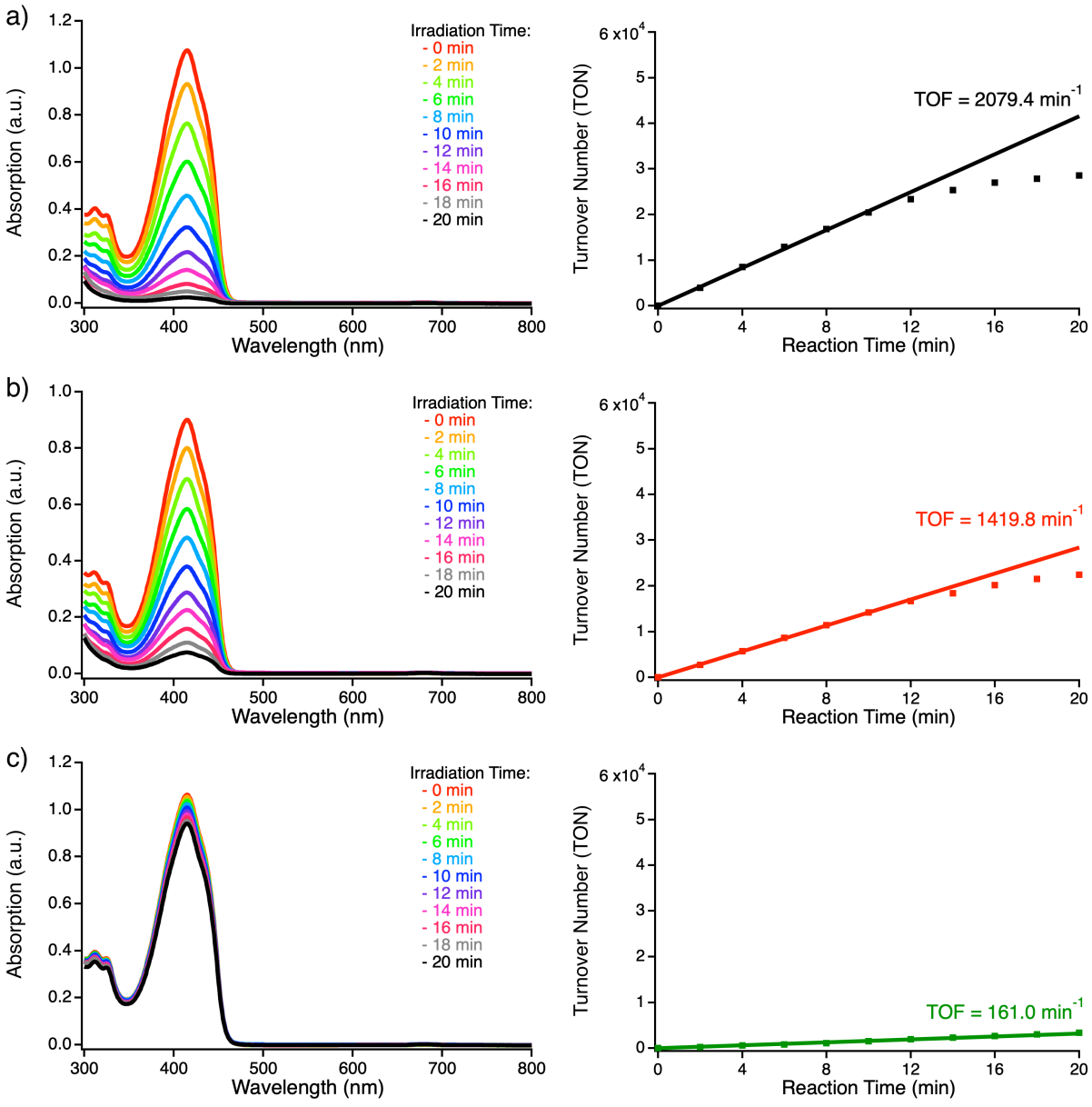

Figure S9. UV Vis spectra for the photooxidation of DPBF over a npAu powder modified with the linker azidothioate **1** and functionalized with the ZnPc **3** irradiated with (**a**) 550 nm cut-on filter; (**b**) 700 nm bandpass finlter and (**c**) 550 nm bandpass filter. From the obtained number of converted DPBF and the turnover numbers (TON) from the npAu disks, the illuminated photosensitizer amount was calculated to as 1.6 x 10^{-10} mol. The values of a, b, c were plotted against the reaction time and the slope obtained by linear regression is the desired turnover frequency (TOF).

ESI-6: Supplementary data for the synthesis of 6-azidohexylthioate 1

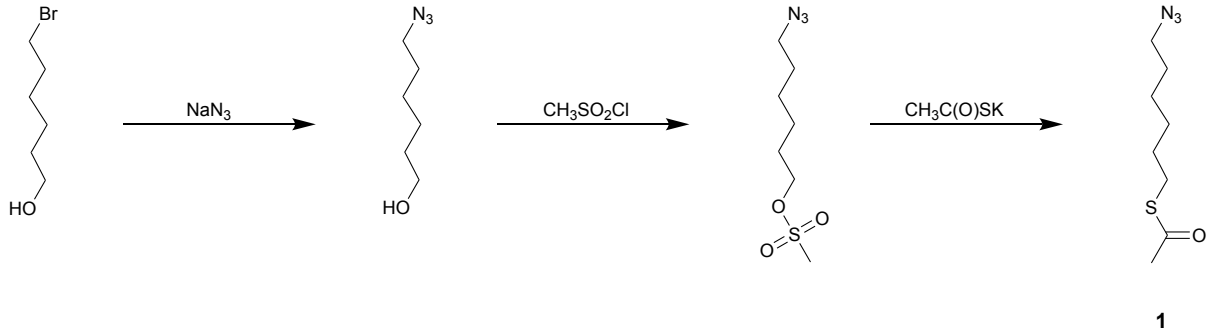

Figure S10. Synthesis scheme for the linker *S*-(6-azidohexyl)ethanethioate **1** starting from 6-bromo-1-hexanol via 6-azidohexan-1-ol and 6-azidohexyl methanesulfonate.

ESI-7: Supplementary data for the synthesis of the zinc(II) phthalocyanine derivative 3

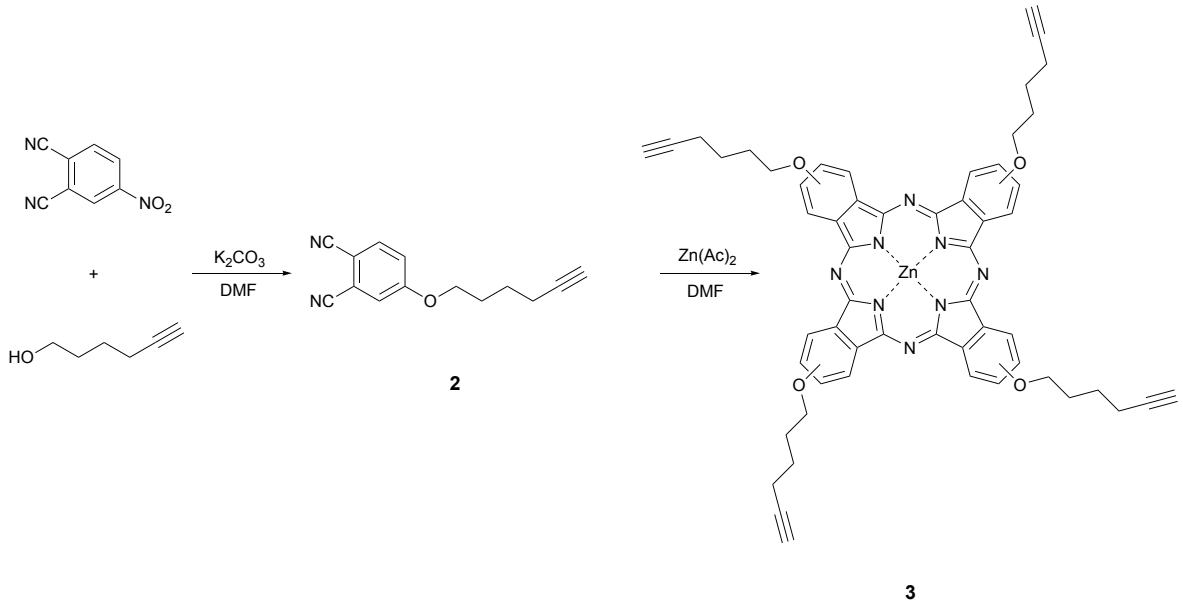

Figure S11. Synthesis scheme for the photosensitizer 2,9,16,23-Tetrakis(4-hex-5-ynoxy) phthalocyanine-zinc(II) (ZnPc) **3**.

The phthalocyanine **3** was prepared by mixing **2** (224.3 mg, 1 mmol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (66 mg, 0.3 mmol) with three drops of DMF. Then the mixture was reacted in a microwave (350 W) for 10 minutes. The dark mixture was allowed to cool and methanol was added to suspend the product which was collected by centrifugation. Then the complex was purified by extraction with methanol in a Soxhlet extractor resulting in a dark green compound (157 mg, 16.3%). ^{1}H-NMR (200 MHz, DMF-d_7, ppm): δ 9.34-9.24 (m, 4H, Ar-H), 9.04-8.88 (m, 4H, Ar-H), 7.88-7.76 (m, 4H, Ar-H), 4.78-4.54 (m, 8H, CH_2-O-), 2.60-2.44 (m, 8H, CH_2), 2.36-2.29(m, 4H, -C≡CH), 2.26-2.16 (m, 8H, CH_2), 2.08-1.86 (m, 8H, CH_2). IR: (KBr, ν [cm^{-1}]): 3276 (-C≡CH), 2935, 2910, 2867, 2840 (C_{aryl}-H/C_{alkyl}-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/C_{aryl}-C_{alkyl}), 1120, 1092 (C-H/C-C), 634 (Pc-Ring). MS: (ESI^+, DMF) *m/z*: 961 $[M+H]^+$; (ESI^-, DMF) *m/z*: 995 $[M-Cl]^-$, 879 $[M-C_6H_9]^-$, 914 $[M-C_6H_9+Cl]^2$, 977$[M-OH]^-$ UV-vis (DMF, λ (nm)): 354, 680.

ESI-8: Supplementary data for the photocatalytic setup for DPBF oxidation

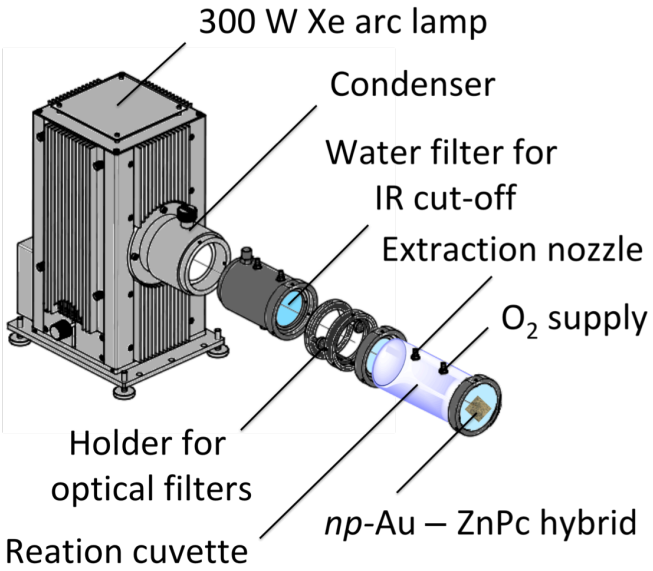

Figure S12. Schematic representative of the photocatalytic setup modified from [1] with permission from LOT qd GmbH, Darmstadt, Germany. For illumination a scientific lightsource from LOT qd GmbH equipped with a 300 W Xe arc lamp was used.