Micellar (Photo-)Catalysis driven by IR-Active Semiconductor Surfactants

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Abstract: In micellar catalysis, one uses aggregates formed by surfactants as nanoreactors for performing chemical reactions. A special class of tailor-made surfactants containing catalytically active sites opens new perspectives in micellar catalysis. Little is known about the combination of such surfactants with photocatalysis. Molecular semiconductors are presented, which simultaneously have amphiphilic properties and are made of a hydrophilic fullerenol head group attached to dye molecules as the hydrophobic entity. The first generation of those surfactants produces reactive oxygen species (ROS) when exposed to light in the UV/Vis range. The concept of the current paper is that one can drive the photocatalytic process also using low-energy photons in the near-infrared region. For this purpose, NIR-active dye molecules were selected and attached to the fullerenol head. It is shown that a fullerenol - aminostilbene compound representing the second generation of semiconductor surfactants fulfills all requirements. It forms aggregates in water that are catalytically active. Moreover, two-photon experiments with λ = 780 nm were performed, indicating successful ROS production and, thus, photocatalytic activity.

Introduction

Green chemistry is an approach that aims to minimize the environmental impact of chemical processes and products. This is achieved by designing chemical products and processes that are inherently safer and more sustainable, with a focus on reducing or eliminating the use of hazardous substances, conserving resources, and reducing waste.^[1] The E-factor, or environmental factor,^[2] is a metric used in green chemistry to evaluate the efficiency of chemical processes in waste generation. The lower the E-factor, the more efficient the process is considered to be, as it generates less waste for each unit of product produced. The synthesis of fine chemicals is connected to a high E-factor, where micellar catalysis can lead to major improvements because the amount of solvents used in synthesis has a significant contribution.

Micellar catalysis has emerged as an innovative strategy to achieve sustainable and efficient chemical processes. Micelles are aggregate structures formed by surfactant molecules when they are dissolved in a suitable solvent, most importantly water, and they have a hydrophobic core and a hydrophilic shell. However, surfactants are much more than molecules forming aggregates, which Sorrentini et al. nicely argued.^[3] Using micelles as reaction media for catalytic transformations provides several advantages, including higher reaction rates, selectivity, reusability of the catalyst, and reduced environmental impact due to using less toxic solvents. The vision of micellar catalysis is that someday, only water as a solvent will be needed and that it can be applied to synthesize almost arbitrary fine chemicals.

The confined environment provided by micelles is beneficial for many types of catalysis, as nicely summarised by Scarso et al. in 2022,^[4] particularly for activating hydrophobic substrates that are inaccessible or poorly soluble in aqueous solvents. The hydrophobic domains of the micelles can extract and concentrate the hydrophobic substrate within them, bringing it closer to the catalytic sites. The so-called hydrophobic effect is significant in micellar catalysis, as has been discussed recently by Lipshutz.^[5] Conversely, the micelles' hydrophilic shell can mediate the reactive species' formation and stabilize the intermediates and products. Micelles as reaction media have been applied to various types of catalysis, including metal-catalyzed, enzymatic, and photochemical reactions.^[6] For example, micellar solutions have been used as media for Pd-catalysed C-C coupling reactions and Suzuki-Mivaura cross-coupling reactions,^[7] Ru-catalysed asymmetric hydrogenation ketones, Rh-catalysed of hydroformylation reactions, and various oxidation reactions.^[8] Micellar solutions have also been used for photochemical reactions, such as the photochemical synthesis of cyclic carbonates. An exciting perspective was presented by Tang et al. in 2022. Micellar catalysis is highly suitable for performing cascade catalysis.^[9] The micelles' size and shape can substantially affect the kinetics and selectivity of the reaction.

The dominant approach to micellar catalysis is encapsulating a catalyst or substrate within the core of the micelle. Scarso et al. looked in 2020 at the aspect of designer surfactants used for micellar catalysis. Reviewing the extensive literature on micellar catalysis, one sees that relatively few reports on surfactants containing the catalytic site covalently attached to it.^[4-5]

Among the different forms of catalytic activity, photocatalysis is highly attractive. Most reports in the literature apply solid-state semiconductors such as TiO2 as the photocatalyst.[10] Light absorption produces exciton pairs, electrons in the conduction band with high reduction potential, and holes in the valence band with high oxidation potential. These photogenerated charge carriers can react with multiple species, inducing photoreduction and oxidation. Huge attention was devoted to the water-splitting reaction into H₂ and O₂ by photocatalysis.^[10] Water splitting is an intermolecular process and requires the transfer of two electrons and two protons. Processes involving the transfer of only one electron are much easier to achieve and occur with higher yield before the full water-splitting reaction. The resulting compounds are different, so-called reactive oxygen species (ROS) such as hydroxyl radicals OH•, the superoxide ion O2^{-*}, or singlet oxygen ¹O₂. It should be noted that, compared to pure inorganic materials, less literature exists on so-called molecular semiconductors.

Molecular semiconductors typically feature an extended π system; examples exist in the literature on polymeric or low molecular weight cases.^[11] Many of those molecular semiconductors are used in photovoltaics and rarely for photocatalysis. It is well known from these studies that not only the molecular architecture determines the optoelectronic properties, but the aggregation of the molecules is equally important as charge carrier transport extends intermolecular distances. One would expect that the combination of micellar catalysis and photocatalysis represents a promising concept.

However, almost no publications exist on micellar photocatalysis, and if they exist, they report the encapsulation of semiconductor nanoparticles in aggregates formed by classical surfactants.^[12] A possible explanation for the described lack is that knowledge is scarce about surfactants that are molecular semiconductors simultaneously. Recently, we showed that fullerenol-dyad compounds represent powerful semiconductor surfactants.^[13] An important step was that we learned how to realize a Janus-type modification of C₆₀.^[14] As reported by Kuvvchko et al.^[15] it is possible to obtain with high selectivity C60Cl6 from the chlorination of C60 with ICI. The chlorine atoms are adjacent to each other and five of them react readily with almost any primary amine compounds. The succeeding hydroxylation under one-pot conditions results in modifying the pristine hemisphere with 19±3 OH groups. The analysis of the amphiphilic properties of fullerenol compounds containing π -conjugated systems like acridines showed unambiguously surfactant properties resembling those of lipids. Ref.^[13a] reports in detail about the molecular semiconductor properties of fullerenol-dyad surfactants. The transfer of photogenerated charge carriers from tail to head was studied by experimental (optical and photoluminescence spectroscopies, photo-conductivity studies, etc.), and theoretical methods (DFT calculations). Most importantly, the activity as a photocatalytic material was probed. It could be shown that the semiconductor surfactants are capable of the photoreduction of carbon dioxide inserted into a vesicular solution.

The photochemical activation of the surfactants mentioned in our previous publications required UV or Vis-light.^[13] Here, we want to introduce a novel compound active in photocatalysis under irradiation with light of lower energy in the near-infrared (NIR) region. Our motivation to develop such a system is that the preferred light source for driving photocatalysis is the sun. A notable portion of the energy is present in the tail of the blackbody radiation curve at wavelengths $\lambda > 750$ nm.

Results and Discussion

Surfactant Molecular Structure and Vesicle Formation

The compounds were prepared according to the previously reported method for fullerenol surfactants containing alternative hydrophobic tail groups.^[14] The hexachlorinated fullerene $C_{60}Cl_6$ is reacted in a one-pot reaction with five equivalents of the primary

amine group $R-NH_2$ followed by the hydroxylation reaction (**Scheme 1**). The hydroxylated hemisphere of C₆₀ represents the hydrophilic head group (blue), and the five attached organic dyes form the hydrophobic part of the molecule (red).



Scheme 1. Synthesis of different fullerenol surfactant-dyad compounds.

The compounds FuDy-1,2,3 were already reported in previous publications and serve here as reference systems.^[13] The π -conjugated rest in FuDy-4,5 was selected according to its suitability as a constituent in two-photon absorption systems reported in the literature.^[16] FuDy-4,5 were characterized by standard techniques which have also been used for other fullerenol-surfactants in the past (see the experimental part given in the Supporting Information).^[13-14, 17] As will be shown later, FuDy-4 containing amino-stilbene is the most important compound of the current study. Therefore, its amphiphilic properties will be described in more detail.

As we have seen in previous publications,[13, 17-18] the amphiphilic behavior of fullerenol-based surfactants is distinct from classical surfactants. Fig. 1a shows concentrationdependent surface tension measurements. Such an S-curve is not unusual for surfactants, and it is classically interpreted as such that first, the water-air interface is populated, leading to a decrease in surface tension. When the monolayer coverage is reached, micellization/ aggregation occurs, and the respective concentration can be identified by the turning point in the curve (c \approx 1 mM for FuDy-4). The surface tension value at saturation (γ_{sat} \approx 57 mN/m) indicates that something is different here compared to conventional surfactants for which γ_{sat} \approx 30-40 mN/m, depending on the type of surfactant. Two factors can rationalize the high value for FuDy-4, respectively the low decrease compared to the pure water-air interface. (a) the terminal dimethyl amino group is more polar than an alkyl chain, leading to a lesser decrease in the surface energy. (b) the more dense the packing of surfactants on the water-air interface is, the lower will be γ_{sat} . The five organic groups in the FuDy surfactants are not only very bulky, they are also stiff due to the π -conjugation. The shape of FuDy-4, for instance, is close to cylindrical (Fig. 1b). Despite the large fullerenol head group, the packing parameter is slightly larger than 1. As a result, FuDy-4 cannot pack very efficiently at the water-air interface, preventing further decrease of the interfacial energy. γ_{sat} remains relatively high.



Figure 1. (a) Concentration-dependent surface tension measurement of FuDy-4 in water at T = 25° C. (b) Molecular structure of FuDy-4 determined from molecular mechanics calculations, and schematic representation of the concentration-dependent aggregation process. (c) Aggregate size D_H (= hydrodynamic diameter) determined from DLS measurements; c = 1mM (grey hashes), 0.5mM (grey circles), 0.25 mM (grey triangles), 0.125 mM (grey squares), 0.0625 mM (black hashes), 0.015 mM (black triangles), 0.008 mM (black circles), 0.0004 mM (black squares). (d) Concentration dependency of the aggregate size. TEM micrographs of aggregates formed by FuDy-4 in water at c = 0.01 mM (e; scalebar = 100 nm) and 0.1 mM (f; scalebar = 100 nm). (g) Liquid-cell TEM of vesicular structures formed by FuDy-4 in water at c = 0.1 mM (scalebar = 25 nm).

Dynamic light scattering (DLS) was performed to investigate at which concentration the surfactant forms aggregates in solution. One can see from Fig. 1c that at a concentration way beyond the supposed critical aggregation concentration (cac), there are not only aggregates, but these aggregates are significantly larger than a micelle. The size of a micelle is typically twice the molecular extension of the surfactant (≈ 6 nm in the case of FuDy-4). Depending on concentration (Fig. 1d), we find aggregates ranging from 40 to 100 nm in size according to DLS. Based on the surfactant's large packing parameter and considering the hydrophobic groups' stiffness, one can expect that FuDy-4 forms vesicular structures. The latter can be confirmed by transmission electron microscopy (TEM) under cryogenic conditions shown in Fig. 1e. One sees "hollow" objects with a relatively broad polydispersity in diameter in the range of 20-50 nm. The aggregates are confined by two rims, one inside the vesicle and one outside, indicating a surfactant double layer forming (Fig. 1b).

The surfactants FuDy-1,2,3^[13a] behave similarly to FuDy-4, but there is one distinct difference. When one increases the concentration of FuDy-1, for instance, the size of the vesicular aggregates ($D_H \approx 50$ nm) remains constant, as shown in Supporting Information Fig. SI-1. It seems that FuDy-1 forms more vesicles when added to the solution, but the size of the vesicles remains unchanged. One can see from Fig. 1d that FuDy-4 behaves differently. According to DLS data (Fig. 1c,d) and TEM data (Fig. 1f), the aggregates' size increases when the surfactant concentration is larger. However, the increase in vesicle size is not linearly dependent on the surfactant

concentration. The formation of multi-layered vesicles can explain this effect. Liquid-cell TEM measurements (**Fig. 1g**) reveal that larger vesicles can even contain smaller ones. Once those multicomponent structures form, their size does not increase as much. The latter result is important because the type and degree of aggregation of a molecular catalyst can impact its catalytic activity.

Aggregation-dependent, catalytic ROS quenching

The literature documents that fullerenol molecules are capable of catalytic ROS quenching.^[19] Therefore, we briefly discuss this feature before the photochemical investigations will be mentioned. The mechanisms for the ROS-quenching were investigated in depth in a paper by Ghao, Zhao et al.^[20] The superoxide radical O_2^{-*} is decomposed to O_2 , the hydroxy radical OH• reacts to water H₂O, and hydrogen peroxide H₂O₂ results in $O_2/$ H₂O. Here, we concentrate on the superoxide quenching pathway, which can be monitored by a nitroblue tetrazolium (NBT) assay.^[21] O_2^{-*} is generated from phenazine methosulfonate and nicotinamide adenine dinucleotide + H (NADH).^[22] The ROS quenching efficiency as a function of concentration is compared in **Fig. 2**.

FuDy-4 is obviously active in the ROS quenching mechanism, but there are important differences to the known FuDy-1 system.^[13b] The efficiency of ROS quenching scales linearly with concentration in the case of FuDy-1. This is expected because, the more of the surfactant is present, the more vesicles are forming in solution (see above). Surprisingly, FuDy-4 is much more effective at much lower concentrations.



Figure 2. The ROS (superoxide) quenching efficiency of different FuDy surfactants (1 = circles; 4 = squares) depending on the surfactant concentration was determined from an NBT assay.

The maximum ROS quenching efficiency is reached at c = 0.025 mM and remains constant afterward. This means that the surfactants added above this point do not contribute any more to the catalytic decomposition. We believe this is due to the unusual aggregation of FuDy-4 described in the previous section. Because the diffusion length of the superoxide radical is low, it is hypothesized that only the surfactants on the external surface of the vesicles are the active catalysts. Considering that **Fig. 2** reflects **Fig. 1d**, it means that all FuDy-4 surfactant molecules located in the intra-vesicular aggregates (**Fig. 1b**) are deactivated because of the particular aggregation behavior of this surfactant.

The dual functionality (catalytic ROS deactivation and production) of semiconductor FuDy surfactants was studied in more detail in ref.^[13b], whereas here, the wavelength-dependency of the photocatalytic activity is the focus.

Photochemical Activity

As described before,^[13] FuDy-1,2,3 are capable of superoxide generation by 1-photon absorption of light in the UV and Vis regions of the electromagnetic spectrum. **Fig. 3a** shows a simplified Jablonski diagram of the processes. The absorption of light excites an electron from the highest occupied molecular orbital (HOMO), located at the dye residues, to orbitals with coefficients involving the fullerenol head. Charge separation occurs, and the electron can be transferred to the π^* acceptor orbitals of molecular oxygen, forming ${}^{1}\text{O}_{2}^{-*}$. If one wants to use the sun as a light source to drive the photocatalytic process, one sees from **Fig. 3b** that the lower energy region ($\lambda > 650$ nm) does not correspond to any absorption features and, thus, is not active for ROS generation (**Fig. 3c**). The latter was confirmed by exciting the surfactants FuDy-1,2,3 with different wavelengths ($\lambda_{exc} = 450$, 532, 630 nm) and probing for superoxide formation using an NBT assay. Only λ_{exc} = 450nm (E_{exc} = 2.76 eV) is sufficient for generating superoxide, which indicates that excitation to the LUMO-2 (lowest unoccupied molecular orbital; **Fig. 3a**) is necessary for successful charge transfer. Although FuDy-2,3 absorb in this region, excitation with green light is insufficient for the photocatalytic reaction. All three surfactants produce no ROS species under irradiation with red light (**Fig. 3c**).

Next, we focussed on the surfactants FuDy-4,5 because they contain a π -conjugated constituent, which, according to the literature, is capable of an energy upconversion process. Fig. 3d shows the UV/Vis absorption spectra of the compounds. The full spectra from 200-800 nm are shown in Supporting Information. FuDy-5 has an absorption band (λ_{max} = 714nm) that extends into the NIR region. When we exposed FuDy-5 to red light, we saw a steady change in the color of the solution, and the peak at λ_{max} = 714nm vanished (see Supporting Information Fig. SI-2). FuDy-5 is actually quite effective in the production of ROS, but unfortunately singlet oxygen ${}^{1}O_{2}$ is generated. ${}^{1}O_{2}$ initiates the phototruncation of the hydrophobic unit in FuDy-5 according to the pathway reported by Matikonda et al. on the non-amphiphilic heptamethine cyanine.^[23] The auto-destruction pathway disgualifies FuDy-5, and it is not considered any further.

Fig. 3d shows the UV/Vis spectrum of FuDy-4. Compared to FuDy-1 (Fig. 3a) its adsorption edge is shifted even more to higher energies (λ_{max} = 340 nm; see Supporting Information Fig. SI-3). Because the adsorption band of the stilbene derivative is in the UV, it is expected that the same accounts for FuDy-4. The weak tail from 400-450 nm is due to the spectroscopic features of the fullerenol group. Consequently, even the excitation of FuDy-4 with blue light (λ = 450 nm) does not cause any ROS production. What happens if red light is used?

Fig. 3e contains a series of different UV/Vis spectra. The spectrum of FuDy-4 after irradiation with red light (λ_{max} = 640 nm) for 24h showed no difference from when the surfactant was kept for 24h under dark conditions. This means that the surfactant is stable under irradiation and potential ROS formation. As a second reference experiment, we have treated a solution containing only NBT for 24h with red light. The characteristic absorption band at (λ_{max} = 262 nm) represents the intact, unreacted NBT molecule. The NBT molecule is stable and produces no ROS species. When we mix FuDy-4 and NBT and keep it for 24h in the dark, the spectral features are superposed, and one can conclude from the constant intensity of the band at λ_{max} = 262 nm that there is no reaction of NBT with FuDy-4.

The situation changes when red light is applied. The signal at $\lambda_{max} = 262$ nm has decreased in intensity (**Fig. 3e,f**), and the spectral range from $\lambda = 250-350$ nm resembles that of FuDy-4. A broad absorption pattern with a maximum at $\lambda_{max} = 568$ nm can be observed, which we assign to the NBT-formazan species, showing the reaction of NBT with the superoxide molecule. The latter results indicate that FuDy-4 could potentially show low energy photocatalysis we sought for. $\lambda = 640$ nm as an excitation source is still in the Vis region of the electromagnetic spectrum. Furthermore, it is documented in literature^[24] that two-photon processes benefit from high light intensities. Using our self-made LED reactor it is not surprising that we observe sufficient ROS formation only after 24 h. What happens if we expose the system to a high dose of NIR light?



Figure 3. (a) Simplified Jablonski-Diagram; fullerenol-dyad orbitals and energy levels (left); possible optical transitions (middle); HOMO of molecular oxygen and the photoreduction process (right). (b) UV/Vis absorption spectra of FuDy-1 (squares), FuDy-2 (circles), and FuDy-3 (triangles) compared to the terrestrial solar spectrum (yellow line). (c) Results of the NBT essay for investigating the superoxide formation of FuDy-1 (squares), FuDy-2 (circles) and FuDy-3 (triangles) irradiated with blue light, green light and red light. (d) UV/Vis absorption spectra of FuDy-4 (squares) and FuDy-5 (triangles). (e) UV/Vis spectra of a NBT-assay as a reference (squares), of FuDy-4 in water as a reference (circles) and of NBT in presence of FuDy-4 (triangles). The samples were either irradiated with red light ($\lambda = 640$ nm) for 24h (red) or were kept in the dark (black). (f) For better visibility of the changes, the graph shows the difference between the absorption of the FuDy-4/NBT mixture under dark and irradiated conditions.

For checking the activity of the system in the NIR region, a femtosecond laser system (Chameleon Ultra II, Coherent, US) at a wavelength of λ = 780 nm, repetition rate of 80 MHz, and power of 200 mW was used as a light source and the samples were placed in a commercial two-photon microscope (MPM200, Thorlabs Inc., US), immobilized between two coverslips. The activity was investigated ROS-production bv а dichlorofluorescein-H diacetate (DCFH-DA) assay.[25] Because this assay is based on observing the fluorescence of 2,7dichlorofluoresceine as the product after reaction with the ROSspecies, it is important to investigate the photoluminescence properties of FuDy-4 first.

One sees two effects when comparing the fluorescence spectrum of FuDy-4 to the spectrum of aminostilbene as a reference. The fluorescence of FuDy-4 is strongly red-shifted ($\lambda_{em,max} = 549$ nm). A reasonable explanation is the formation of exciplexes. Intra- and inter-molecular stacks of the π -conjugated systems are possible because there are five dye groups attached to each fullerenol head in an oriented way (see **Fig. 1b**, **3a**), and because of the aggregation into the vesicular state in which the single surfactant molecules are very close to each other. As a result, the formation of an exciplex becomes facilitated, an adduct between two aminostyrene entities, one in the excited state. The

fluorescence of such exciplexes are shifted significantly to lower energy.^[26] However, the latter effect is rather of academic interest because one also sees from **Fig. 4a** that the fluorescence intensity of FuDy-4 is magnitudes smaller in comparison to the pristine aminostilbene. The fluorescence signal of FuDy-4 is almost quenched, which is consistent with the aforementioned highly effective separation of the photogenerated charge carriers (h⁺, e⁻) in the excited FuDy molecule. Although FuDy-4 shows a fluorescence in a similar region than the fluorescence of 2,7-dichlorofluoresceine ($\lambda_{em,max} = 525$ nm), it will not interfere negatively with the measurements that follow.

Fig. 4b-d shows a series of fluorescence microscopy images of an aqueous dispersion containing FuDy-4 (c = 2 mM). The first image shows the sample before irradiation with NIR light. The surfactant aggregates appear as red objects. The irradiation of the sample with ultrashort NIR light clearly induces the formation of ROS species which can be seen from the green fluorescing zones extending from the surfactant aggregates. A movie illustrating the effect even better is given in the Supporting Information. Data were taken for 30s and from different positions in the sample. **Fig. 4f** shows the intensity of the fluorescence of 2,7-dichlorofluoresceine as a function of time. There is an almost linear increase of ROS generation.



Figure 4. (a) Fluorescence spectrum of aminostilbene (grey) as a reference and the vesicular aggregates of FuDy-4 (black). Multiphoton fluorescence microscopy images of an DCFH-DA assay containing FuDy-4 irradiated at λ = 780 nm for t = 0s (b), 3s (c), and 6s (d). (e) Change of the fluorescence intensity due to the increasing formation of 2,7-dichlorofluoresceine because of ROS production by FuDy-4 (black) and pristine aminostilbene as a reference (grey).

As a reference, we have also performed the same measurement using pristine aminostilbene instead of the surfactant. As expected, no ROS formation occurred. The latter experiment proves the unique functionality of FuDy-4.

Conclusion

Molecular semiconductors with surfactant properties comprising a fullerenol head group and dye molecules as "tails" show photocatalytic activity as an additional function. As a proof of concept reaction, the generation of reactive oxygen species (ROS), respectively the formation of the superoxide radical has been selected. Like classical solid-state catalysts, the optoelectronic properties of the semiconductor surfactants determine which wavelength can be used to drive the photocatalytic process. Radiation in the Vis to UV region of the electromagnetic spectrum is sufficient for a one-photon process, which leads to electron-hole separation first, followed by the photoreduction reaction. However, the energy of "green" and particular "red photons" is too low unless the surfactant is equipped with a special dye residue. The fullerenol-dyad compound containing aminostilbene can produce superoxide when it is exposed to red and even to NIR light via a 2-photon process.

In classical semiconductor science, for solar cells but also in photocatalysis, one aims at maximizing the photon yield with the sun as the most sustainable light source. One can do this by a multijunction architecture, the combination of different semiconductors whose band-gap covers a broader spectral range. We believe that the novel NIR-active surfactants enable a unique chance to transfer the multijunction concept to micellar catalysis. The current study proves that surfactants characterized by a multi-wavelength photocatalytic activity are available. In a micelle or a vesicle, it should be possible to mix those different surfactants and obtain a system that can use almost the entire spectrum of the sun.

In future studies, it is planned to use the ROS species for oxidation catalysis. However, there is a further perspective. An important application of ROS species is in photodynamic therapy.^[27] Because photodynamic therapy involves among others the treatment of diseases inside the body, UV/Vis light is not ideal as it is absorbed by biological tissue. Thus, a semiconductor surfactant capable of generating ROS when irradiated within the transparency window of biological tissue (λ = 650 - 1350 nm) is of high interest in nanomedicine.

Supporting Information

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

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Entry for the Table of Contents



Interfacing photocatalysis and micellar catalysis can be realized by fullerenol-dye amphiphiles possessing semiconductor properties. Whereas the energy for the reaction is typically provided by one high energy photon, the special dyads shown here are capable of photocatalytic ROS production by 2-photon processes using NIR light.

Micellar (Photo-)Catalysis driven by IR-Active Semiconductor Surfactants

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SUPPORTING INFORMATION

Experimental Part.

Chemical Synthesis.

Synthesis of Hexachlorofullerene $C_{60}Cl_6$: The synthesis was carried out according to literature protocols of Kunkel et al.^[1] 200 mg (0.28 mmol) of C₆₀ was dissolved in 14 mL chlorobenzene and sonicated for 5 minutes. The solution was heated to 30°C and 0.6 mL (6.95 mmol) lodine monochloride was added in one portion. After addition of ICl the solvent was removed under vacuum. The remaining brown-red solid was purified by column chromatography (silica gel, eluent: toluene) to yield 72 % C₆₀Cl₆.

Synthesis of FuDy-1,2,3: The surfactants were prepared as reported in the literature.^[2] *Synthesis of FuDy-4*: 200 mg of C₆₀Cl₆ was dissolved in 8 mL chlorobenzene together with 533 mg (2.24 mmol; 8 eq.) N-(4-[2-(4-aminophenyl)ehtenyl]phenyl)-N,N-dimethylamine. 0.4 mL Tetrabutylammoniumhydroxide (TBAH; 40% in water) was added together with 40 mL water, 0.8g NaOH and 1.5 mL H₂O₂. The mixture was heated to reflux for 2 hours and afterward was cooled to room temperature. The reaction mixture was filtered and the phases were separated. The aqueous phase was reduced to volume of ~20 mL and 50 mL methanol was added. The precipitate was washed with methanol and diethylether to receive CST as brown solid with a yield of 37%. ATR-IR: v (cm⁻¹) = 3022, 2959, 2925, 2853, 2796, 1604, 1520, 1354, 1164, 1106, 1060, 962, 823; ESI-MS: [(OH)₂₆C₆₀(C₁₆H₁₇N₂)₅ Na]⁺ m/z = 2372.49 (2372.46); TGA: 37-220°C 13.1 %; 220-608°C 16.9 %; 608°C 51,4 %.

Synthesis of FuDy5: 200 mg C₆₀Cl₆ was dissolved in 8 ml chlorobenzene together with 242.2 mg (2.24 mmol; 8 eq.) 1,4-phenylendiamin. 0.4 mL Tetrabutylammoniumhydroxide (TBAH; 40% in water) was added together with 40 mL water, 0.8g NaOH and 1.5 mL H₂O₂. The mixture was heated to reflux for 2 hours and afterward was cooled to room temperature. The reaction mixture was filtered and the phases were separated. The aqueous phase was

reduced to volume of ~20 mL and 50 mL methanol was added. The brown Diaminophenylfullerene precipitate was washed with methanol and diethylether. 40 mg (0.025 mmol) of Diaminophenyl-Fullerene was mixed with 113 mg (0.15 mmol) of Quinolinium, 1-[(4-carboxyphenyl)methyl]-4-[3-[1-[(4-carboxyphenyl)methyl]-4(1*H*)quinolinylidene]-1-propen-1-yl]-, bromide, 36 mg (0.175 mmol) DCC and 21 mg (0.175 mmol) DMAP. The mixture was dissolved in 10 ml dimethylformamide and 10 ml chloroform and stirred at room temperature overnight. The solvent was evaporated and the resulting dark blue solid was solved in water (~150ml). The aqueous phase was extracted with hexane (3x 100 mL) and the solvent was removed.

Synthesis of Quinolinium, 1-[(4-carboxyphenyl)methyl]-4-[3-[1-[(4-carboxyphenyl)methyl]-4(1H)-quinolinylidene]-1-propen-1-yl]-, bromide: The synthesis was performed according to the literature.^[3] A mixture of 4.77 mL (36 mmol) 4-methylquinoline an 6.45 g (30 mmol) 4-(bromomethyl)benzoic acid was stirred in anhydrous acetonitrile at 110 °C for 6h und nitrogen gas atmosphere to obtain compound 1. Acetonitrile was evaporated and the residue dissolved in 10 mL methanol. Afterwards up to 80 ml diethyl ether was added slowly to precipitate the product as a white solid. The precipitate was filtered, washed with diethyl ether and dried under vacuum. Yield of compound 1 was 69%. ¹H NMR (400 MHz, MeOHd4): δ 9.43 (d, J = 6.06 Hz, 1H), 8.60 (dd, J = 8.45 Hz, 1H), 8.38 (d, J = 8.91 Hz, 1H), 8.15 (t, J = 8.66 Hz, 1H), 8.09 (dd, J = 6.06 Hz, 1H), 8.05-8.00 (m, 3H), 7.40 (d, J = 8.72 Hz, 2H), 6.39 (s, 2H), 3.12 (s, 3H).

10 mmol (3.58 g) of compound 1 and 3.92 g (20 mmol) of N,N'-diphenylformanidine were dissolved in 20 ml acetic anhydride and stirred at 150 °C for 1h. After cooling to room temperature 200 mL diethyl ether were added slowly to precipitate compound 2. The precipitate was filtered as a brown solid, washed with diethyl ether and dried under vacuum. Yield of compound 2 was 84%. ¹H NMR (400 MHz, DMSO-d6): δ 9.39 (d, J = 6.61 Hz, 1H), 8.97 (d, J = 13.83 Hz, 1H), 8.49 (d, J = 6.75 Hz, 1H), 8.20 (d, J = 8.87 Hz, 1H), 8.04 (t, J = 9.10 Hz, 1H), 7.96-7.88 (m, 4H), 7.81 (t, J = 8.67 Hz, 1H), 7.72-7.64 (m, 2H), 7.53 (d, J = 7.40 Hz, 2H), 7.37 (d, J = 8.67 Hz, 2H), 6.29 (s, 2H), 6.07 (d, J = 13.98 Hz, 1H), 2.10 (s, 3H). A mixture of 1.089 g (3 mmol) compound 1, 1.266 g (3 mmol) compound 2 and 4.2 mL (30 mmol) triethylamine in 60 ml dichloromethane was stirred at room temperature for 24h. The solvents were evaporated and the residue dissolved in 5 ml methanol. Afterwards 400 ml

acetone was added slowly to precipitate compound 3 as a blue solid. The precipitate was filtered, washed with acetone and dried under vacuum to yield 41% of compound 3. ¹H NMR (500 MHz, DMSOd6): δ 8.83 (t, J = 13.44 Hz, 1H), 8.40 (m, 4H), 7.95-7.91 (m, 6H), 7.73-7.67 (m, 4H), 7.57 (t, J = 7.44 Hz, 2H), 7.38 (d, J = 8.40 Hz, 4H), 7.21 (d, J = 13.08 Hz, 2H), 5.81 (s, 4H).





Vesicles formed in water by FuDy-1 at different concentrations and their size determined from DLS measurements.

Fig. SI-2.



(a) UV-Vis spectrum of FuDy-5 (blue). Spectrum after irradiation of FuDy-5 with red light for 24h (blue).



(b) Time-dependent decay of the UV/Vis signal at λ = 730nm of FuDy-5 because of after irradiation with red light.



(c) Photograph of a solution of FuDy-5 in water before (right) and after with red light for 24h (left).

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