Aggregation-Induced Improvement of Catalytic Activity by Inner-Aggregate Electronic Communication of Metal-Fullerene-Based Surfactants

Marius Kunkel,[a] Stefan Bitter,[a] Frank Sailer,[a] Rainer F. Winter,[a] and Sebastian Polarz*[a, b]

A paradigm for active constituents in (homogeneous) catalysis is that optimum performance requires maximum dispersion. Generally, aggregation results in a decline. This is a different case in supramolecular catalysis. A new concept based on surfactants equipped with functional heads is presented, which becomes a more active catalyst itself upon aggregation. The head group of the surfactants is composed of a diethylenetriamine-functionalized fullerene capable of coordinating to catalytically active metals like Co^{II}. The improvement of catalytic properties upon aggregation is demonstrated via electrocatalytic water-splitting reaction as a model system. Detailed electrochemistry studies were performed at concentrations below and above the critical aggregation concentration (*cac*). While isolated surfactant molecules represent only moderately active catalysts, drastic improvement of efficiency in the hydrogen evolution (HER) as well as in the oxygen evolution reactions (OER) were detected, once vesicular structures have formed. Self-organization of the surfactants leads to an increase in turnover frequencies of up to 1300% (HER). The strongly beneficial effect of aggregation arises from the favorable alignment of individual molecules, thus, facilitating intermolecular charge transfer processes in the vesicles.

In many cases, aggregation is seen as a major drawback for catalytic reactions since upon aggregation the number of accessible reactive centers is reduced and a maximum of dispersion, especially for heterogeneous systems was the goal to achieve. Research perspective changed and systems have been developed in which aggregation comes hand in hand with beneficial effects. The field of self-assembled compounds, the supramolecular chemistry gives rise to supramolecular catalysis. In micellar catalysis, the formation of aggregates is used to perform reactions at their interface with compounds that would otherwise not be combinable. It is also possible to use solvents that would normally not be suitable for such reaction. These aggregates can be formed by supporting compounds that do not take place in the reaction themselves or by the catalyst molecule.[1–3] The phrase supramolecular catalysis is manly known from reactions with enzymatic systems which can catalyze reaction via weak interactions within their structural motif. Furthermore, this field describes the assembly of small-molecule organic catalysts.[4–5] This very assembly of the catalyst influences the reactants in a way that reactive moieties are exposed and activated, intermediates or transition states are stabilized or that the reactivity is enhanced by increasing the local concentration of the reactants.[6–8] In this work, we present a new concept of supramolecular catalysis that does not influence the reactant's properties but the catalyst itself. This is achieved by a catalytically active surfactant. Surfactants are molecular compounds with amphiphilic properties, which form well-defined aggregates. Depending on concentration, individual surfactant molecules self-assemble into micelles, vesicles or liquid crystals. Recently, more and more papers describe advanced surfactants with properties beyond simple amphiphilic properties.[9–10] Our group has specialized in the synthesis of surfactants equipped with functional, metal-containing head groups,[11–14] and several examples of catalytically active surfactants have already been published by us.[2–3] Important preliminary work of relevance to the current work is centered on fullerene-based surfactants that evaluated their self-assembly behavior and the related beneficial effect of self-assembly on their properties.[15–17]

For our supramolecular catalyst system electrocatalytic water splitting was chosen as a model system as a rather simple electron transfer reaction regarding intermediates and transition state species that is well observable. For water splitting, huge efforts during the last decades were taken in exploring and developing different realizations of the water splitting reaction, resulting in H_2 (hydrogen evolution reaction; HER) and O_2 (oxygen evolution reaction; OER).[18–20] A lot of heterogeneous and homogeneous systems have been evaluated. In the field of homogeneous systems mostly rare earth and transition metal complexes are used and groups have developed and tailored the systems to achieve low over potentials and high turnover frequencies (TOF).[21–27] The turnover frequency, one factor that defines the efficiency of a catalytic system ranges from several to several thousand per second for reported

[a] M. Kunkel, S. Bitter, F. Sailer, R. F. Winter, Prof. S. Polarz
Department of Chemistry
University of Konstanz
Universitätsstrasse 10
78457 Konstanz (Germany)
E-mail: sebastian.polarz@uni-konstanz.de
[b] Prof. S. Polarz
Institute of Inorganic Chemistry
Leibniz-University Hannover
Callinstrasse 9
30167 Hannover (Germany)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202000412

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systems. A special challenge for such systems is the performance in pure aqueous system being stable as well as active. Catalytic systems of different facets with nickel, cobalt, copper and more are known to literature.[28–34] Although we do not want to compete with established systems we chose to combine a water soluble surfactant system with controlled self-assembly to enhance its catalytically activity via aggregation presenting a new way of improving such systems.

In the current work, we aim at developing a system, which is equipped with moieties that are capable of effecting electrocatalytic water splitting,[28,35] but with a fullerene-based surfactant design. Particular focus is on the role of self-assembly on catalytic activity.

The major synthesis steps leading to our target system are depicted in Figure 1a. The asymmetrical, pentachlorinated C_{60} (**1**)[36] is reacted with dodecylamine to obtain the penta-alkylated compound (**2**). Diethylenetriamine is then attached to the remaining hemisphere to obtain the ligand modified species (**3**). It is used as a ligand for complexation of cobalt(II) chloride to obtain the final product (**4**) (see Supporting Information for detailed synthesis procedure and characterization, Figure S1). Figure 1b,**c** shows the characteristic signals for the organic ligand before (**3**) and after coordination to cobalt (**4**) in electrospray ionization time of flight mass spectrometry (ESI-TOF MS). Successful coordination of Co^{II} ions was also proven by UV/Vis spectroscopy, which, in addition to the absorption of the fullerene core, showed the d-d transition band of a Co(II) triamine chelate with a maximum at 480 nm (Figure S1).

The amphiphilic properties of (**4**) were investigated by recording concentration dependent surface tension γ(c). The corresponding plot shows a shape, (see Figure 1d), which is typical for surfactants. The minimal surface tension reached is about 39 mN/m. The position of the kink in the γ(c) curve indicates that aggregation commences at a concentration *cac* of approximately 0.2 mM. Aggregation has also been confirmed

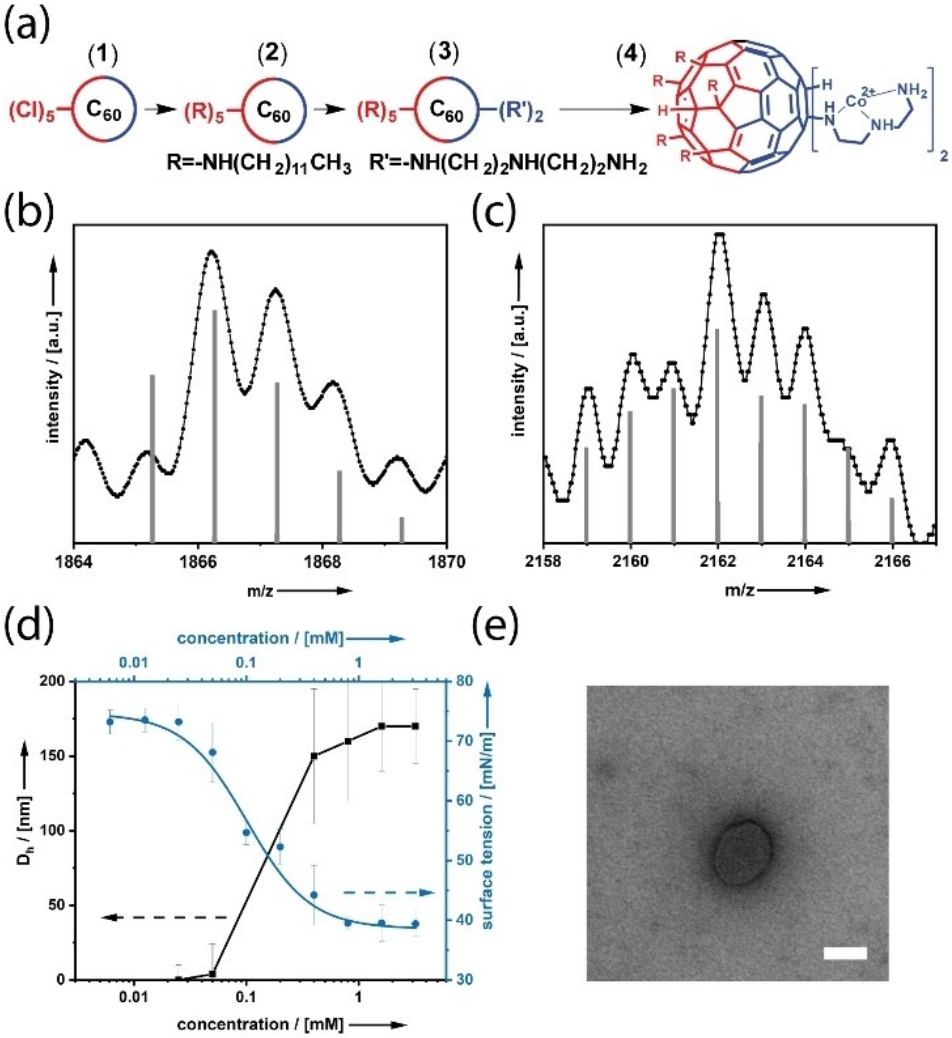

Figure 1. (a) Synthesis scheme for amphiphilic metal-fullerene-based catalyst (**4**). (b) ESI-TOF MS data of the organic ligand (**3**; black dots) and simulation of the molecular ion peak $[M]-(H^+)+(H_2O)=1866.23$ g/mol (grey bars) and (c) of the surfactant (**4**; black dots) and simulation of the molecular ion peak $[M]+(Cl^-)+(H_2O)=2161.98$ g/mol (grey bars). (d) Concentration-dependent aggregate size (black) and surface tension (blue). (e) TEM micrograph of a vesicle formed by (**4**) above the *cac*; scalebar = 100 nm.

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by dynamic light scattering (DLS). The aggregate sizes determined from DLS are shown in Figure 1d. There were no aggregates found at low concentration, and above *cac* aggregates with a hydrodynamic diameter $D_H = 150$ nm (Figure S2) appear. Analysis of these aggregates using transmission electron microscopy (TEM; Figure 1e) confirms that surfactant (**4**) forms hollow, bilayer vesicular structures rather than micelles. In these aggregates the polar metal-fullerene complex, which serves as head group to the surfactant, align side by side at the outside of the bilayer. This general structuration was reported before for fullerene-based surfactants.[15,17] That this alignment is indeed the case a zetapotential measurement was performed. The measurement shows a high positive potential of +60 mV confirming this circumstance.

As a prototype reaction, electrocatalytic water splitting was used and the influence of catalyst self-assembly on the catalytic activity was evaluated with cyclic voltammetry (CV). First studies were performed at concentrations distinctly below the *cac* as the reference state at a threshold concentration of 0.025 mM of (**4**) in aqueous solution (pH = 7) (Figure 2).

The pure organic compound (**3**) is, as expected, catalytically inactive. The redox behavior of the solution in the presence of the Co-containing surfactant (**4**) is significantly different. There are strongly increased currents at onset potentials of $\eta_{0.5} = +1940$ mV for OER and $\eta_{0.5} = -740$ mV for HER at $j = 0.5$ mA/cm^2, which are both accompanied by strong gas formation. The voltammogram of (**4**) displays a partially reversible reduction signal at a $E_{max} = +20$ mV, which is a feature belonging to the fullerene-based ligand. Furthermore, it contains an oxidation at $E_{max} = +1600$ mV which can be assigned to the Co(II) to Co(III) oxidation, which features indirect reversibility.

Current densities remain unchanged on repetitive cycling, thus confirming that the homogeneous catalyst (**4**) is the catalytically active species and no decomposition product like colloidal cobalt. X-ray spectroscopy (EDX) coupled scanning electron microscopy (SEM) analysis revealed that no cobalt is precipitated on the electrode for (**4**) (Figure S3). The surface of the electrode is clean with absolutely no Co-containing residues caused by adsorption of the catalyst or decomposition. In particular, metallic Co nanoparticles cannot be found anywhere. As a reference experiment, analogous experiments using a $CoCl_2$ solution have been performed (Figure S3a). Not only could we not see comparable electrocatalytic activity, but also the electrode is now covered by Co-nanoparticles. Furthermore, repetitive cycling of $CoCl_2$ shows several changes of the system over time. In essence, it can be excluded that any other compound than the metal-surfactant is responsible for the electrocatalytic activity. In order to quantify the catalyst's properties in more detail, the turnover frequency was calculated, assuming a pseudo-first-order catalytic model (see Supporting Information equation 1, Figure S4).[32,37–40] Evaluation of the data results in $TOF(OER)_{2000mV} = 57 \pm 10\ s^{-1}$ and $TOF(HER)_{800mV} = 25 \pm 10\ s^{-1}$, which indicates a medium activity compared to other electrocatalysts known to literature ranging from several to a maximum of several thousand per second.[28–34] The Randles-Sevcik plot depicted in Figure 2 shows a linear increase of the current density with the square root of the scan rate *v* for OER, indicating a diffusion controlled process. However, the value of current density for HER decreases with increasing *v*, which indicates that the catalytic process is kinetically slow giving rise to the assumption that the fullerene ligand is involved in the reaction. As the cyclic voltammograms of (**4**) do not show a wave for cobalt(II) to

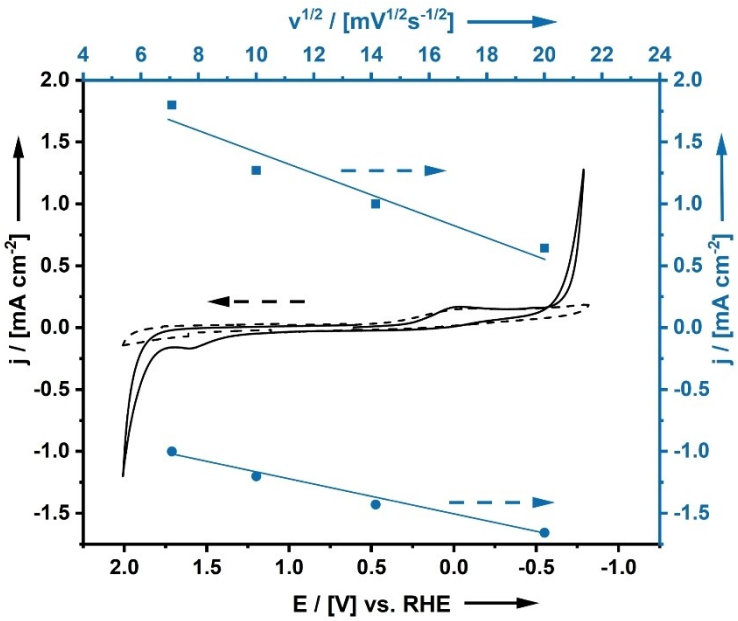

Figure 2. CV measurement (black) and Randles-Sevcik plot (blue; OER = circles; HER = squares of (**4**) at 0.025 mM compared to the CV of the organic ligand (**3**; dashed line).

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cobalt(I) reduction, which would be expected at approximately −400 mV versus RHE, but solely a ligand reduction. This is consistent with the fullerene-DETA ligand acting as a non-innocent ligand similar to the work presented by Thompson *et al.* or Haddad *et al.*[31,41–42] Different from the mentioned literature the ligand is not likely to be protonated and is not catalytically active alone, excluding a metal-assisted ligand-centered as well as a only ligand-centered mechanism. It is more likely to be a metal-centered mechanism supported by the ligand. While the reaction takes place at the cobalt itself, the fullerene-DETA acts as electron reservoir for the reaction with the fullerene being an efficient electron mediator as reported for a nickel complex (Figure S5a).[43] The release of water from the initial complex results in the catalytically active species. The fullerene-DETA ligand is reduced in a one electron reduction, followed by the coordination of a proton to the metal center. A further reduction is followed by the reaction with a proton to release hydrogen. The detailed mechanism needs to be further evaluated with calculations. The mechanism for OER follows another pathway. According to the presence of the cobalt oxidation wave the mechanism might feature a Co (IV) intermediate (Figure S5b).[44–45]

The central issue of this work is unravelling the dependency of the catalytic properties on the level of aggregation. Consequently, we performed analogous electrochemical investigations at various concentrations, including c > *cac* and a threshold concentration of 0.8 mM of an aqueous solution of (**4**) at which the defined vesicular aggregates are present (Figure 3a).

As long as the surfactant concentration remains below *cac*, there is only an insignificant change in OER and HER-related current density at 2000 mV and −800 mV, respectively (Figure 3a blue). However, Figure 3a (black) displays that the concentration dependent current density increases tremendously stronger above the c > *cac* than below. Whereas, the systems showed to be a medium active catalyst at 0.025 mM

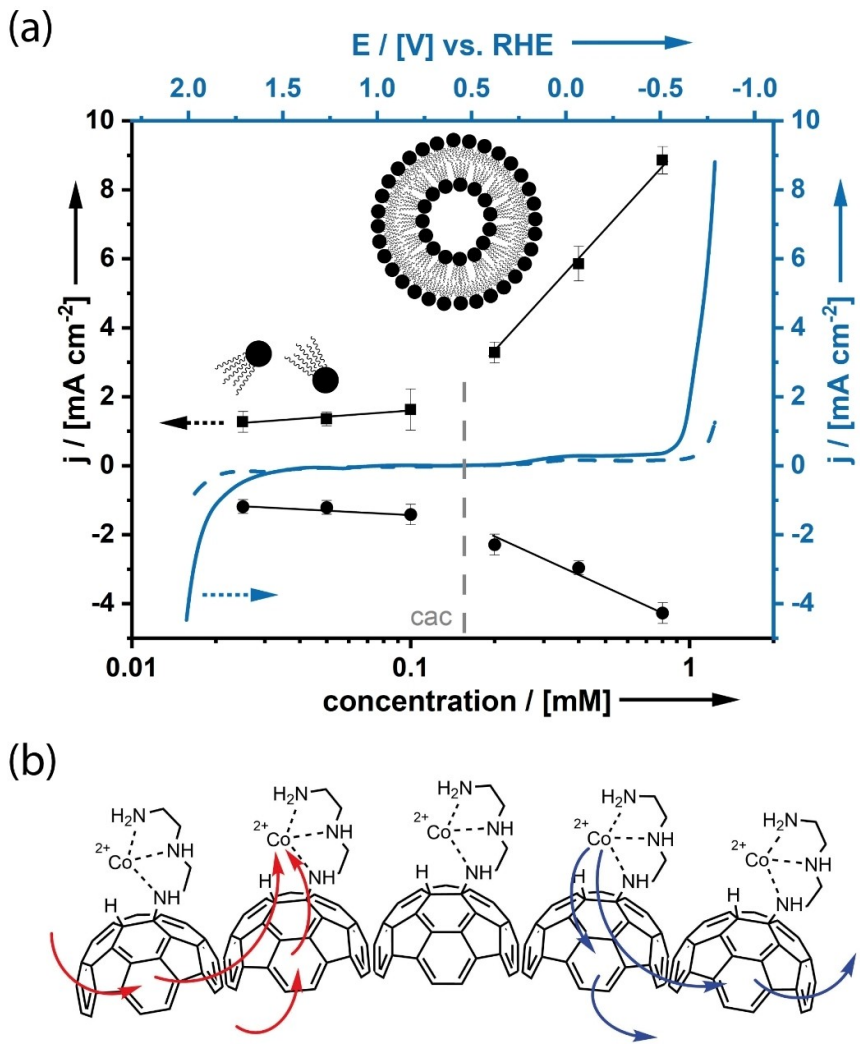

Figure 3. (a) Concentration-dependency of current density (black) for OER (circles) and HER (squares) below (left) and above (right) the *cac*. The grey dashed line marks the *cac*, when single surfactant molecules (left) assemble to vesicular aggregates (right). Linear sweep measurements (blue) of surfactant (**4**) below (0.025 mM) (dashed line) and above (0.8 mM) (solid line) *cac*. (b) Scheme showing the molecular structure of the vesicle surface and the proposed intra- and intermolecular charge transfer processes; (red arrows: reduction process; blue arrows: oxidation process).

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concentration, the concentration increase does not improve the system's activity a lot. The catalytic process seems to be rather ineffective. But after eventually reaching the *cac*, the situation changes. The system's performance instantly showed a drastic increase which continues with further increasing concentration. Speaking in numbers, doubling the concentration below the *cac* only results in an increase in current density by factor 1.1 whereas, doubling the concentration above the *cac* increases the current density by almost factor 2. This leads also in a change in turnover frequency. For concentrations above the *cac* the turnover frequency at -800 mV increases from $25 \pm 10\ s^{-1}$ to $346 \pm 10\ s^{-1}$ (Equation 1, Figure S6). This observed increase of 1300% compared to the turnover frequency determined for $c < cac$ obviously correlates with the self-assembly of the surfactant into vesicles (Figure 1d,e). This result is very astonishing considering that, in general, the mobility and accessibility of the catalytic centers should be lower in the aggregates, and, accordingly, activity should rather decrease or at the most remain constant at $c > cac$. Aqueous solution of fullerene based vesicles do not behave like nanoparticle systems[46–47] since a vesicle is a rather dynamic and permeable system. During the reaction, solvent molecules, reactant and product molecules can diffuse in and out the vesicular aggregate therefore, the number of accessible molecules for the reaction is not lowered but there is obviously an effect on the catalyst molecule upon aggregation. In addition to the turnover frequency, also the onset potential for OER decreases from $\eta_{0.5} = +1940$ mV to $\eta_{0.5} = +1720$ mV, while the onset potential for HER shifts from $\eta_{0.5} = -740$ to $\eta_{0.5} = -540$ mV (Figure 3a; Figure S6). The observed effect of enhanced catalytic activity can only be explained, if there is a cooperative effect between the individual surfactant molecules within the aggregate (Figure 3b). In fact, a change in the electronic situation upon aggregation can be observed. The emission of the single molecule diminishes completely upon reaching the *cac* when the system is excited at the fullerene core, but a new, heavily red shifted and broadened emission appears, that can be assigned to the aggregate state (Figure S7).

For the electron transfer reaction, our hypothesis (Figure 3b) is, that the vicinity and distinct orientation of the surfactant molecules with respect to each other in vesicle wall renders electron transfer from the ligand to the reactant more efficient and allows for intermolecular charge transfer processes in the aggregates.

Intermolecular charge transfer is thus held responsible for improving electrocatalytic activity of the surfactant aggregates with respect that of dispersed surfactant molecules. If this hypothesis is correct, one would expect that a diminishing content of molecules (**4**) in the vesicle walls should also decrease its catalytic activity. It is known that sodium dodecyl sulfate (SDS) can also form vesicular structures[48–49] and it is totally inactive in the water splitting reaction. We therefore tried to use SDS as a co-surfactant in a mixture with surfactant (**4**); see Figure 4 insert. According to DLS, no SDS micelles are present in such mixtures and the size of the vesicles ($D_H =$ 143 nm) changes only insignificantly with respect to pure (**4**) (Figure S8a). Upon adding SDS to the catalytic system, the current at $+2000$ mV and -800 mV is lowered by approximately 30% (see Figure 4). This interpretation is also in line with the observed anodic shift of the onset potential of 45 mV for OER and a cathodic shift of 40 mV for HER (Figure S8b). In the mixed aggregates fewer molecules (**4**) are adjacent to each other and, therefore, intermolecular electronic communication as initiated by aggregation is rendered less efficient.

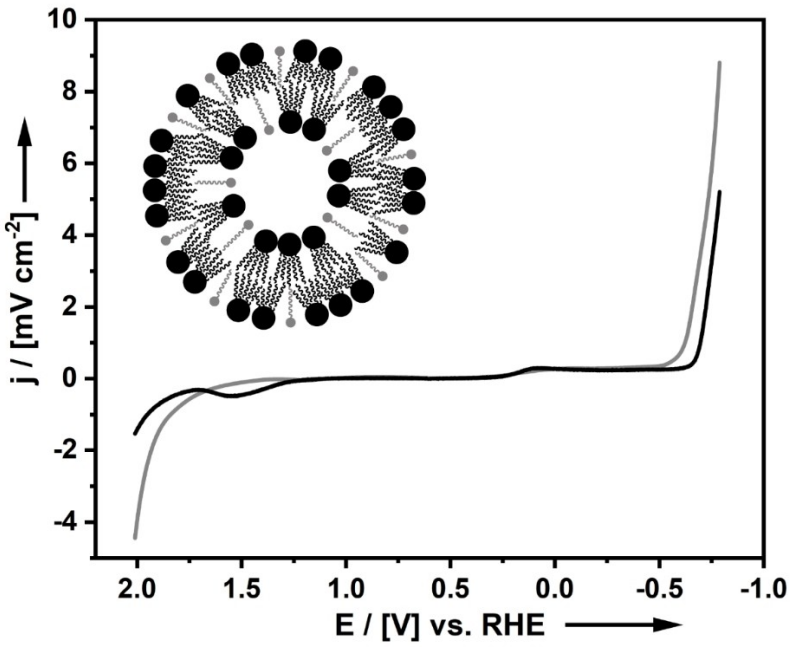

Figure 4. CV of (**4**) at c = 0.8 mM (grey) as a reference compare to the (**4**)/SDS mixed aggregates (black). Insert shows schematic illustration of a vesicle of (**4**; black) diluted with SDS (grey).

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Supramolecular catalysis give rise to new catalytic systems. In this work, we were able to show that aggregation of a surfactant based catalyst leads to a beneficial feature for electron transfer reactions like water splitting reaction as a model system and increases the system's performance. We present an amphiphilic cobalt-fullerene catalyst, which at concentrations below its *cac* shows an only medium catalytic activity in OER and HER at neutral pH in aqueous solution. The compound's catalytic activity, especially for HER increases tremendously at concentrations above *cac*, at which vesicular aggregates form. The onset potentials and current densities are improved and the turnover frequency increases by up to 1300%. Aggregation allows for intermolecular electron transfer and improves electronic communication within the system, leading to more efficient water splitting.

Supporting Information

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

Acknowledgements

The current research was funded by an ERC consolidator grant (I-SURF; project 614606). We further thank Stephan Siroky for his support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Fullerene · surfactant · self-assembly · catalysis · supramolecular chemistry · water splitting

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Manuscript received: March 9, 2020
Accepted manuscript online: March 16, 2020
Version of record online: April 6, 2020

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