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Catalytic Activity of Macroion–Porphyrin Nanoassemblies

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Supporting Information

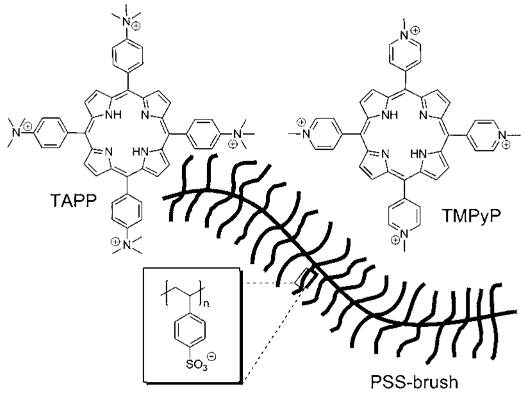
ABSTRACT: A new type of catalytically active self-assembled nanostructures in aqueous solution is presented. Polyelectrolyte–porphyrin nanoscale assemblies consisting of anionic cylindrical poly(styrene sulfonate) brush molecules and cationic tetravalent *meso*-tetrakis(4-*N*-methyl-pyridinium)porphyrin (TMPyP) or *meso*-tetrakis-(4-(trimethyl-ammonium)phenyl)-porphyrin (TAPP), respectively, exhibit up to 8-fold higher catalytic activity with regard to light induced iodide oxidation than the corresponding porphyrins without polymeric template. This is particularly interesting because a general concept rather than a specific binding motif is exploited. The approach introduced here hence is attractive due to its facility and versatility and bears potential, for example, in light harvesting and energy conversion.

In this study, we present a new type of catalytically active self-assembled nanostructures in aqueous solution which consist of ionic polymer brushes and oppositely charged porphyrins and show substantially higher catalytic activity than the non-assembled porphyrins. Self-assembling processes are ubiquitous throughout biology, realizing a variety of architectures and functions thus far unseen in synthetic systems. Self-assembly has therefore received a lot of attention in chemistry, physics and nanoscience and its potential includes applications ranging from carrier systems over molecular motors to nanoelectronics.[1] One of the key compounds in natural systems is porphyrin, which plays an essential role in photosynthesis and oxygen transport. In synthetic systems, porphyrins are interesting for catalysis,[2] light harvesting,[3] and photodynamic cancer therapy.[4] However, for the design of functional synthetic structures, the nanoscale supramolecular arrangement of porphyrins has yet to be fully exploited.[5] The supramolecular organization is particularly promising, because in their biologic functionality, porphyrin molecules never occur individually but in nanoassemblies with peptides and other molecules. Therefore, the goal of this study is to elucidate the catalytic activity of ionic porphyrins in supramolecular nanoscale assemblies with charged synthetic polymers, specifically, a macroion–porphyrin system that exhibits its functionality in aqueous solution. The great advantage of choosing the electrostatic interaction of ionic porphyrins with macroions for supramolecular association is that it makes the system versatile and custom-designable; that is, we herein investigate a general concept rather than a specialized structure relying on specific binding motifs.

Self-assembly based on amphiphilicity,[1b,d,6] hydrogen bridging or metal coordination yields a variety of interesting structures.[7,8] Supramolecular concepts have also been applied to catalysis, for example, as enzyme mimics based on coordination chemistry and hydrogen bridging,[4,9] acting by creating cage-like, allosteric or dissymmetric sites through well-designed local binding motives or by bringing two reacting species into close proximity. Yet, hydrogen-bridged associates are often unstable in polar solutions or require the complex synthesis of specific architectures and binding motifs, so it is appealing to use the concept of "electrostatic self-assembly" to interconnect macroions and oppositely charged organic molecules into supramolecular nanostructures. Previously, we showed that this concept leads to well-defined supramolecular nanoparticles of various shapes in aqueous solution.[10] While those studies focused on structural aspects, we herein report for the first time the functionality of this type of electrostatically self-assembled nanoparticles, specifically their catalytic activity.

The building blocks used in this study are displayed in Chart 1. The macroion component is anionic poly(styrene sulfonate) with the architecture of a cylindrical brush molecule (PSS-brush). It consists of a polymeric backbone with (shorter) polymeric side chains that force the molecule to adopt a wormlike shape instead of a flexible polymer coil structure. This results in a "bottle brush" with 12 nm diameter and 100 nm length.[11] These polyelectrolytes are combined with cationic tetravalent *meso*-tetrakis(4-*N*-methyl-pyridinium)porphyrin (TMPyP) or *meso*-tetrakis(4-(trimethyl-ammonium)phenyl)-

Chart 1. Building Blocks Used in This Study: Cylindrical Polystyrene Sulfonate Brushes Are Combined with Cationic Tetravalent Porphyrins into Nanoscale Assemblies in Solution



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porphyrin (TAPP). For structure formation, aqueous solutions of both components are mixed.

Figure 1a displays the morphology of the structure resulting at a charge ratio (that is, a molar ratio of positive charges on the porphyrin to negative polyelectrolyte sulfonate groups) of *l* = 0.4, as analyzed by atomic force microscopy (AFM). Networks of interconnected polymer brushes result, which is a similar morphology to the TAPP/PSS-brush case reported previously.[12] Inter-brush aggregate formation in solution was also proven by dynamic light scattering (DLS) as shown in Figure 2.

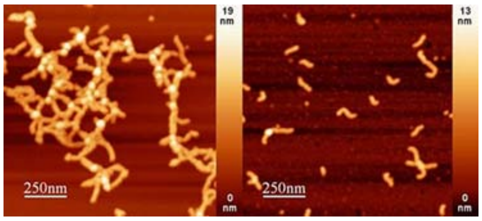


Figure 1. Atomic force microscopy (AFM) of aTMPyP/PSS-brush sample with a charge ratio of *l* = 0.4 deposited onto a mica surface: (a) sample prepared in aqueous solution, (b) sample prepared in aqueous solution with *c*(iodide) = in 0.01 mol L^{-1}.

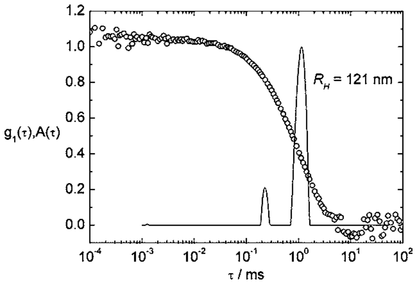
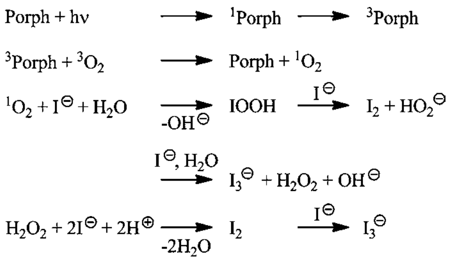


Figure 2. Dynamic Light Scattering of aTMPyP/PSS-brush sample with a charge ratio of *l* = 0.4; electric field autocorrelation function $g^1(\tau)$ and distribution of relaxation times $A(\tau)$; aggregates with a hydrodynamic radius of R_H = 121 nm form.

Networks with an average hydrodynamic radius of R_H = 120 nm result for *l* = 0.4, while depending on the porphyrin/polymer charge ratio, the size of these network-like assemblies varies between R_H = 40 and 160 nm for $0 \leq l \leq 0.8$ (see Supporting Information).[13] The light induced oxidation of iodide is chosen as model reaction for catalysis (Scheme 1). Scheme 2 depicts the system under investigation schematically.

Prior to irradiation, the binding of porphyrin to the polyelectrolyte is evident from the size increase in static and dynamic light scattering and the network formation observed in AFM, but also from the different heights of the brush networks in Figure 1a which correspond to parts of loaded and unloaded brushes. Further proof is the difference in the UV−vis absorption spectra of the brush−porphyrin and the pure porphyrin that is evident when comparing the upper black curves in Figures 3a and 3b, respectively (see also combined plot in the Supporting Information). The spectral change (shift in absorption maximum from λ = 422 to 427 nm and change in peak shape) occurs because for the previously molecularly dissolved porphyrin mutual π−π interaction is induced when they attach to the oppositely charged polyelectrolyte. Below charge stoichiometry, all porphyrin molecules bind to the polyelectrolyte, that is, the number of porphyrin molecules per styrene sulfonate units is equal to 1/4 of the charge ratio *l*, for *l* = 0.4 corresponding to about 4000 porphyrin molecules per one cylindrical polymer brush molecule (degree of polymerization: $P_{w,\,total} \approx 4 \times 10^4$).

Scheme 1. Reaction Scheme of the Model Reaction for Catalysis



$$\mathrm{Porph} + h\nu \longrightarrow {}^1\mathrm{Porph} \longrightarrow {}^3\mathrm{Porph}$$

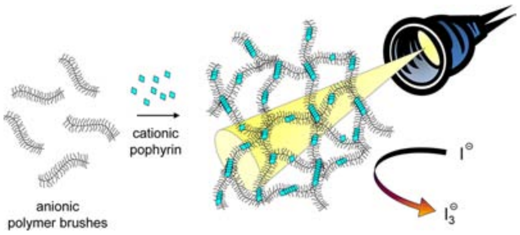
$$ {}^3\mathrm{Porph} + {}^3\mathrm{O_2} \longrightarrow \mathrm{Porph} + {}^1\mathrm{O_2}$$

$$ {}^1\mathrm{O_2} + \mathrm{I}^{\ominus} + \mathrm{H_2O} \xrightarrow[-\mathrm{OH}^{\ominus}]{} \mathrm{IOOH} \xrightarrow{\mathrm{I}^{\ominus}} \mathrm{I_2} + \mathrm{HO_2}^{\ominus}$$

$$\xrightarrow{\mathrm{I}^{\ominus},\ \mathrm{H_2O}} \mathrm{I_3}^{\ominus} + \mathrm{H_2O_2} + \mathrm{OH}^{\ominus}$$

$$\mathrm{H_2O_2} + 2\mathrm{I}^{\ominus} + 2\mathrm{H}^{\oplus} \xrightarrow[-2\mathrm{H_2O}]{} \mathrm{I_2} \xrightarrow{\mathrm{I}^{\ominus}} \mathrm{I_3}^{\ominus}$$

Scheme 2. Schematic Representation of Supramolecular Structure Formation and Photocatalysis As Investigated in This Study



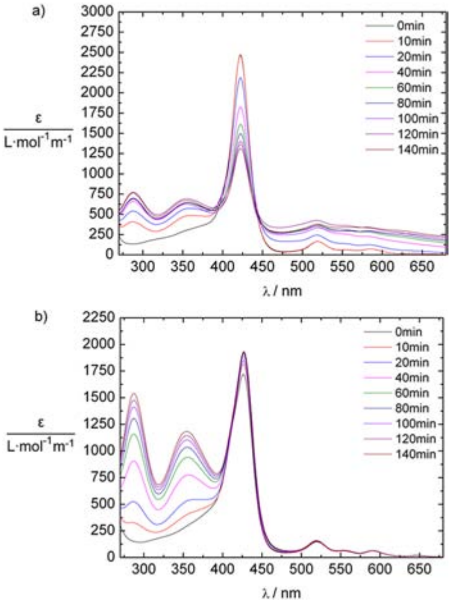


Figure 3. UV−vis absorption spectra in dependence on irradiation time for (a) TMPyP without polyelectrolyte and (b) a TMPyP/PSS-brush sample with a charge ratio of *l* = 0.4; both in iodide solution with *c*(iodide) = in 0.01 mol L^{-1}. The bands at λ = 353 nm and at λ = 287 nm indicate the faster tri-iodide formation with the nanoassembly as catalyst.

Figure 3b displays the change in absorption spectra for the polymer−porphyrin assemblies in the iodide solution upon irradiation, as compared to the case of the pure porphyrin in iodide solution shown Figure 3a. The bands at λ = 353 nm and

λ = 287 nm indicate tri-iodide formation according to Scheme 2. It is evident that these bands increase much more rapidly in the sample with polyelectrolyte brushes than in the sample without. Hence, the presence of polymer does indeed influence the catalytic activity. The photosensitized reaction includes the formation of the porphyrin triplet state and transfer of energy to triplet oxygen, leading to $O_2(^1\Delta_g)$ formation. The "iodide method" is based on the reaction of I^- with $O_2(^1\Delta_g)$ so that the amount of photoproduced I_3^- is proportional to the amount of $O_2(^1\Delta_g)$.[14] Figure 4a considers the behavior in more detail by showing the dependence of the iodide absorption at λ = 353 nm as a function of time. Evidently, at the start of the reaction, the solution without polymer forms tri-iodide slightly faster than the solutions with polymer, while in the following, the tri-iodide concentration is substantially higher in the cases with polyelectrolyte and for the l = 0.4 sample it is about twice as high when the concentration change levels off. Thus, over the course of the whole reaction time, the polymeric template enhances the catalytic performance of the porphyrin.

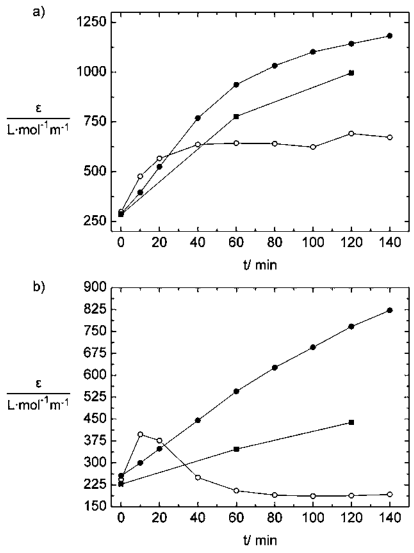


Figure 4. Kinetics of tri-iodide formation: extinction coefficient ε at λ = 353 nm versus irradiation time for (a) open circles, TMPyP without brush; black circles, a TMPyP/brush sample with a charge ratio of l = 0.4 (corresponding to data in Figure, 3); black squares, charge ratio of l = 0.6 and (b) open circles, TAPP without brush; black circles, a TAPP/brush sample with a charge ratio of l = 0.4; black squares, charge ratio of l = 0.6.

To understand this behavior, the aggregation status was further elucidated. In contrast to the catalysis literature referred to above, no specific local geometry was designed through placing of groups or cage synthesis. It is thus rather the assembly formation as such that controls the process; that is, we consider a nanoscale rather than a molecular effect. As mentioned, when mixing the aqueous solutions of both components, stable polymer brush–porphyrin networks result. In variance, in an aqueous iodide solution with a concentration of $c(I^-)$ = 0.01 mol L^{-1} networks almost completely disassemble while the porphyrin stays bound to the oppositely charged brush (catalysis is possible with both types of structures; see below). This is evident from the hydrodynamic radius changing from R_H = 121 nm for the network without added iodide to R_H = 32 nm in a solution with an iodide concentration of $c(I^-)$ = 0.01 mol L^{-1} (DLS see Supporting Information). Disassembly takes place due to screening of the electrostatic force in a solution of higher ionic strength.[12a] Results given in Figures 3 and 4 are for this case of iodide concentration. Hence, predominantly, binding of porphyrin to the polymer brush rather than a extended inter-brush connection determines the change in catalytic activity. More importantly, for this scenario, the assembly size remains more or less constant upon irradiation and tri-iodide production (R_H = (32–35) nm). This is in contrast to the sample without macroion under otherwise same conditions. In that sample, large aggregates with sizes larger than 1 μm form (DLS see Supporting Information), and these aggregates are undefined and also change over time. The latter is consistent with a previous report of a porphyrin catalysis.[15] Such aggregation is probably due to the interaction of the porphyrin with the iodide and tri-iodide. Thus, in the system presented here, it is the macroion that prevents such undesired porphyrin aggregation that hinders catalytic activity through electrostatic binding of the porphyrin to the polymer support. This also explains why the polymer-porphyrin assembly has the lower activity in the very beginning of the reaction: here, binding to the polymer brush or mutual porphyrin interaction reduces the accessibility of potentially active sites. In addition to the nanoscale self-assembly effect, a change in the microenvironment through association with the polyelectrolyte may also affect the catalytic activity. It is important to note that adding the corresponding monomer, benzosulfonate, instead of the polyelectrolyte does not cause any change in catalytic activity (see Supporting Information), emphasizing the importance of the macroion–counterion structure formation for the catalytic activity enhancement. Effects were also found for different iodide concentrations, where the range was determined by experimental accessibility and was 0.002 mol $L^{-1} \leq c(I^-) \leq$ 0.1 mol L^{-1}. At the lower of these iodide concentrations, porphyrin–polymer networks are present throughout the reaction.

To gain more insight, it was of interest to vary the porphyrin/polyelectrolyte charge ratio. No significant change in catalytic activity was found for small loading ratios $l \leq 0.3$. Within a range of $0.35 \leq l \leq 0.6$, an increase of the catalytic activity was observed, expressed the most for the l = 0.4 sample. For larger charge ratios ($l \geq 0.7$ or $l \geq 0.8$, depending on iodide concentration), assemblies—also without irradiation—are not stable in solution but precipitate. The porphyrin–polyelectrolyte sample with the loading ratio l = 0.4, hence, clearly shows the strongest influence; that is, for a certain given porphyrin concentration, there is an optimum amount of added polyelectrolyte.

Additionally, it is of importance whether polyelectrolyte-porphyrin assembly formation can also influence the catalytic activity for porphyrins other than TMPyP. For this purpose, TAPP, also a tetravalent cationic porphyrin but with a very different charge distribution (see Scheme 1), was applied. Tri-iodide absorption versus irradiation time is shown in Figure 4b. Evidently, the TAPP catalytic performance also improved in the polyelectrolyte–porphyrin assembly, whereas the mechanism creating the exact time dependence in the pure porphyrin sample seems to be more complex here. For l = 0.4, the final tri-iodide concentration is about 8-fold for the assembly sample, also after a (not shown) reaction time of several hours. This demonstrates the generality and applicability of the effect, a point that will be extended in future studies.[16]

In conclusion, we presented polyelectrolyte–porphyrin nanoassemblies that exhibit higher catalytic activity with regard to light induced iodide oxidation than do the corresponding porphyrins without polymeric template. This is particularly interesting, as the concept is basic and general, and no specific molecular architecture was designed to influence the reaction rate. Instead, the polymer serves as a nanoscale support avoiding uncontrolled porphyrin aggregation. As compared to covalent or more specialized supramolecular structures, the approach presented herein is attractive due to its facility and versatility. Various ionic porphyrins can be used; the polymer support will also allow the combination of different porphyrins in one assembly, wherein one type of porphyrin could potentially serve as a photosensitizer and the other type could serve as a catalyst, for example, to make use of a larger range of the solar spectrum in solar energy to chemical energy conversion. In addition, the nanoscale polymer brush or polymer brush network may provide desirable mechanical strength, catalyst recyclability and possibly also selectivity by modifying the porphyrin accessibility.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, further light scattering and further UV−vis results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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