Supplementary Information

for

Morphological Families of Self-Assembled Porphyrin Structures and

their Photosensitization of Hydrogen Generation

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Materials

All porphyrins were obtained from Frontier Scientific and used without further purification. Purity was checked by proton NMR spectroscopy. Potassium tetrachloroplatinate(II) (K₂PtCl₄; 99.99%), L-ascorbic acid (99+%), triethanolamine (99+%), and methylviologen were purchased from Aldrich and used without further purification. Ethylenediamine tetraacetic acid (EDTA) was purchased from J.T.Baker. All the solutions used in the synthesis were prepared using ultrapure water from a Barnstead Nanopure water system and were filtered through 0.2-µm syringe filters to remove particles. Argon was purchased from Matheson Trigas.

Synthesis and Purification of Porphyrin Clovers

The porphyrin clover-like structures with different Zn(II) and Sn(IV) metal combinations ZnTPPS/SnT(N-EtOH-4-Py)P (Zn/Sn), ZnTPPS/ZnT(N-EtOH-4-Py) (Zn/Zn), SnTPPS/ZnT(N-EtOH-4-Py (Sn/Zn) and SnTPPS/SnT(N-EtOH-4-Py)P (Sn/Sn) were prepared by ionic self-assembly of porphyrin pairs. Typically, 1 mL of 210 μ M anionic porphyrin (e.g., ZnTPPS) solution and 1 mL of 210 μ M cationic porphyrin (e.g., SnT(N-EtOH-4-Py)P) solution were equilibrated to the desired temperature in a water bath. The solutions were then mixed and the temperature maintained for two hours. The clover suspension was then removed from the water bath and returned to room temperature.

XRD

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Samples of the clovers for XRD were prepared by depositing drops of the clover suspensions onto glass slides and air drying the slides. In some cases, XRD data spectra patterns were obtained from wet sample periodically as the sample was dried. XRD patterns were recorded on a Siemens D500 diffractometer using Ni-filtered Cu K_{α} radiation ($\lambda = 1.5418$ Å) in θ -2 θ scanning mode using a step size of 0.05° and a 90-second step time. Peak shifts and intensity differences in the XRD patterns of wet and dry samples of the 23° clovers suggest the presence of water molecules in the crystal lattice.

SEM

Samples for scanning electron microscopy (SEM) imaging were prepared by pipetting 50 µL of the precipitate onto Si wafers. After allowing precipitation for 2 minutes, excess solvent was wicked away using a Kimwipe tissue and the wafer was allowed to dry in air. SEM imaging was performed on a Hitachi S-5200 Nano scanning electron microscope operating at 2 keV.

Self-platinization of Porphyrin Clovers

Aqueous K₂PtCl₄ solution (20 mM) was prepared and equilibrated overnight. Ascorbic acid is unstable in water, so stock solutions (0.2 M) were freshly prepared before each reaction. For photocatalytic self-platinization of the clovers, 6 mL of the suspension of purified Zn/Sn clovers grown at a range of temperatures between 10 and 80° C (105 μ M in each porphyrin) was placed in a 20-mL glass vial and diluted with water to 10 mL. To this mixture, 150 μ L of the aged K₂PtCl₄ solution (20 mM) and 150 μ L of ascorbic acid solution (0.2M) were added. The Zn/Sn

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clover mixtures were irradiated with an incandescent lamp from a projector (0.1 W cm⁻¹) for one hour.

As an example, when the reaction for the Zn/Sn clovers is carried out in visible light (0.1 W cm⁻²) for 1 hour, SEM images of the Zn/Sn clovers (Fig. S6a, middle) show many small Pt nanoparticles (~10 nm) coating the surfaces due to photocatalytic seeding; the particles are small because the available Pt metal is distributed over many nucleation centres created on the surface of the CBI structures. In contrast, SEM images of the platinized Zn/Sn structures (not shown) have sparse large (up to ~150 nm diameter) globular Pt particles or dendrites after a reaction time of 1 hour in the dark. This is due to the lack of photocatalytic seeding as the available Pt is distributed over only a few spontaneously formed nucleation centres. Similar platinized clovers are obtained for the Sn/Zn, Zn/Zn, and Sn/Sn combinations (Fig. S6b-c, middle). In the case of the Sn/Zn clovers (Fig. S6b, middle, and Fig. S8), the Pt nanoparticles are very small, making them barely visible in the SEM images.

Fig. S9 shows SEM images for Pt growth on the Zn/Sn 70° clovers (shown in Fig. S7) after 3 hours in the dark and after 3 hours in visible light. For the light reaction, the clovers are heavily coated with small nanoparticles and some clusters of larger Pt particles. In contrast, the dark reaction gives a sprinkling of large Pt particles on the surface.

H₂ Evolution Reactions with Porphyrin Clover Suspensions and Solutions of the Constituent Porphyrins

Suspensions of the platinized clovers (6 mL) as prepared previously were centrifuged to

isolate the clovers. The precipate was then re-dispersed in 10 mL of aqueous triethanolamine (200 mM) at pH 3 in a 25 mL glass vial (Fisher) generating a suspension with a concentration at 63 µM in each porphyrin. MV was added (20 mM) and the glass vial was then sealed with a rubber septum, purged with argon for 10 minutes, and irradiated with a tungsten light source (0.1 W cm^{-2} measured at the outer wall of the vessel as determined by a bolometer (Model 201, Coherent)). The clovers were kept suspended during the reaction by stirring using a magnetic stirrer bar. Gas samples (50-100 µL) were taken from the 15 mL head space of the glass vial at time intervals (typically 24 h). The H_2 content was determined using a gas chromatograph (HP 5890 Series II) equipped with a 5-Å molecular sieve column and a thermal conductivity detector. The carrier gas was argon. Gas chromatograph was calibrated using argon with a known concentration of hydrogen (0.492 %). Note that hydrogen evolution data for the Zn/Sn clovers (with MV) shown in Fig. 7 were obtained with irradiance at 0.033 W cm⁻² and expanded by a factor of 3 to adjust to the 0.1 W cm⁻² irradiance of the other plots. This adjustment produces data consistent with other measurements performed for the Zn/Sn clovers at 0.1 W cm⁻² for shorter irradiation times.

Solutions of the constituent porphyrins for hydrogen generation experiments were prepared as follows: 10 mL of 63 μ M porphyrin solution was placed in a 25 mL glass vial, and 0.585 mg of ETEK Pt black (3 μ moles) was added, along with 298.5 mg of triethanolamine (giving a 200 mM solution) and 51.44 mg methylviologen (giving a 20 mM solution). The pH was then adjusted to 3.0 with 0.1 M HCl and the sample irradiated at 0.1 W cm⁻² using a tungsten lamp (ENX 3M) and projector. The amount of H₂ in the headspace was determined using the same method described for the clovers. Fig. S12 shows the H₂

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produced versus time for each of the constituent porphyrins at the same concentrations as in the clovers (63 μ M) and under the same solution conditions except for twice the MV concentration (to try to improve porphyrin stability) and the light intensity was 0.15 W cm⁻².

Methylviologen Reduction by Solutions of the Constituent Porphyrins

We also measured the rates of production of the blue (high pH form) of reduced methylviologen by the free porphyrins with the goal of understanding the variation in the rates of H₂ productions for the different clovers. Samples of the porphyrin solutions (5 μ M) were irradiated with visible light in the presence of EDTA or TEOA as an electron donor (200 mM) and MV (100 mM). The initial rates are presented in Table S1. The concentration of reduced methylviologen is measured by the change in absorbance at 600 nm near the peak of its radical anion band. Zn and Sn in T(N-EtOH-Py)P are far more active in photosensitizing the reduction of methylviologen than either metal in TPPS; Sn is more active than Zn in TPPS. Thus, this predicts that the Sn/Zn clovers will be most active, but this is not true for the initial rates (Fig. 7). In these considerations it is important to remember that the H₂ producing species at pH 3 is likely not the blue MV⁺⁻ anion but the colourless protonated radical MVH⁻²⁺.

Table S1: Initial	rates of production	of reduced MV	in µmoles/hour.
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T(N-EtOH-4-Py)P		TPPS		
Sn	Zn	Sn	Zn	
17	22	2.2	<1	
8.5	14	1.3	<1	
2.3	4.0	<1	<1	
	T(N-Et Sn 17 8.5 2.3	T(N-EtOH-4-Py)P Sn Zn 17 22 8.5 14 2.3 4.0	T(N-EtOH-4-Py)P TPPS Sn Zn Sn 17 22 2.2 8.5 14 1.3 2.3 4.0 <1	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

TEOA, pH 3 data not available as MVH^{2+} is colourless at pH 3.



Figure S1. Structures grown from solutions of SnTPPS and ZnT(N-EtOH-4-Py)P at different temperatures: (a) 10, (b) 23, (c) 60,and (d) 80 ⁰C.



Figure S2. Structures grown from solutions of ZnTPPS and SnT(N-EtOH-4-Py)P at different temperatures: (a)10, (b) 20, (c) 40, (d) 60, (e) 70, and (f) 80^{0} C



Figure S3. Structures grown from solutions of ZnTPPS and ZnT(N-EtOH-4-Py)P at different temperatures: (a)10, (b) 23, (c) 60, and (d) 80 °C.



Figure S4. Structures grown from solutions of SnTPPS and SnT(N-EtOH-4-Py)P at different temperatures: (a)10, (b) 23, (c) 60, and (d) 80 0 C.



Figure S5. X-ray diffraction patterns for the Zn/Sn CBI structures (ZnTPPS and SnT(N-EtOH-4-Py)P) synthesized at 23° C (dark blue) and 70° C (light blue). Low angle patterns are also shown for the 23° structures when wet (dark cyan) and air dried (dark pink). Samples for XRD measurements were prepared either by depositing the clover powder (dried by mild heating) onto glass slides (VWR) or Si wafers or by depositing a drop of a suspension of the 'wet' clovers onto the glass slide and allowing them to air dry.



Figure S6. SEM images of the structures pepared at room temperature for all four combination of Zn(II) and Sn(IV) in the two porphyrins (left), the corresponding unwashed clovers after platinization for one hour with ascorbic acid as electron donor (middle), and the washed clovers after two weeks of continuous hydrogen generation (right): Zn/Sn (a), Sn/Zn (b), Zn/Zn (c), and Sn/Sn (d).



Figure S7. SEM images of 70[°] Zn/Sn CBI structures showing the clovers before platinization and use in the hydrogen generation experiments.



Figure S8. High magnification SEM image of the unwashed photocatalytically platinized Sn/Zn clovers

(expansion of Fig. S6b, center).



Figure S9. SEM images of the platinized $Zn/Sn 70^{\circ}$ structures after 3 hours in the dark (a) and after 3 hours of exposure to white light (b).



Figure S10. SEM image of the platinized Sn/Zn clovers after two weeks of continuous hydrogen generation (expansion of Fig. S6b, right).



Figure S11. SEM images of pieces of the platinized 70[°] Zn/Sn CBI structures after the hydrogen generation experiments. Note that in this case the large (~30 μ m) clovers were broken into smaller pieces (the dark material in the image) by agitation from stirring during hydrogen generation. The Pt nanoparticles are the light material in the image. Not much breakage of the clovers is observed for the small room temperature clovers (*c.f.*, Fig. S6, right).



Figure S12. Hydrogen generated by free porphyrins at the same concentrations as in the clovers as a function of irradiation time by white light at 0.15 W cm⁻².