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Soft-photoconversion using floating self-assembled crystalline films of porphyrin nanostructures

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Abstract

One of many evolved functions of biological cell membranes is to induce and regulate self-assembly of photoactive molecules into efficient light harvesting nanomaterials. Synthetic molecular assemblies at soft interfaces exhibit macroscale long-range order and so provide routes to biomimetic analogues that minimise concentration quenching. Here, we report the facile assembly of free-standing layered crystalline films of zinc(II) meso-tetrakis(4-carboxyphenyl)porphyrin nanostructures that exhibit significant photocurrents *in situ* at an electrified liquid | liquid interface. This methodology does not require acidic conditions, specialised amphiphilic porphyrins, or the use of additives or external stimuli. The assembly process is driven by an interplay between the hydrophobicity gradient at an immiscible aqueous | organic interface and optimised hydrogen bonding in the formed nanostructure. Highly-ordered interfacial nanostructures may provide a new paradigm for realisation of light-harvesting antennae in artificial photosynthetic technologies.

Photosynthetic organisms universally exploit antenna systems to capture high energy photons and funnel this excitation energy in the form of excitons toward a coupled reaction centre.^{1,2} There, the excitation energy is transformed into chemical potential in the form of a charge separated state.^{1,2} Self-assembled molecular antennae consisting of multi-layers of chromophores, such as porphyrins, can potentially function as high efficiency light harvesters due to their exceptionally high molar absorption coefficients ($10^5 \text{ cm}^{-1} \cdot \text{M}^{-1}$).³ However, to mimic the evolved nanomachinery in photoautotrophs and avoid “concentration quenching” of the excited state at disordered trap sites,³ the supramolecular packing of the individual chromophores within the antenna nanostructure must be precisely controlled and show long-range molecular order.

Molecular self-assemblies at “soft” liquid | air or immiscible liquid | liquid interfaces can exhibit the required macroscale long-range order.⁴ These soft interfaces are exceptionally smooth, and have no inherent defects leading to an unrivalled macroscale uniformity in molecule-interface interactions.^{5,6} By contrast, the grain boundaries, step defects and edge sites always present at solid | liquid interfaces can impede diffusion of adsorbed molecules, trapping them in local energy minima as molecules stick to defect sites.^{7,8} The uniform templating of adsorbed molecules at liquid | air or immiscible liquid | liquid interfaces has been exploited to create a variety of ordered porphyrin nanostructures,^{9–14} yet a facile and robust route to create films of layered crystalline porphyrin nanostructures has not yet been reported to the best of our knowledge.

Here we describe light harvesting nanomaterials made using readily available, hydrophilic symmetrically substituted porphyrins that work efficiently in mild pH conditions. Thus, we avoid acidic conditions (that would lead to the expulsion of the central metal ion),¹⁵ as well as the use of synthetically challenging and relatively expensive amphiphilic porphyrin molecules,¹⁶ and more complicated routes using additives (*e.g.*, divalent cations or surfactants)^{17–19} or external stimuli (*e.g.*, electric fields).^{20–22} The key design criteria for the porphyrin molecule is that it must possess a *meso*-substituent capable of hydrogen bonding, and at pH = pK_a conditions either the protonated or deprotonated form of the porphyrin (each present in a 1:1 ratio) must have a molecular charge of zero and adsorb at the liquid | liquid interface.

We chose zinc(II) *meso*-tetrakis(4-carboxyphenyl)porphyrin (ZnTPPc) as a prototypical model system (pK_a^{COOH} = 5.8)²³ to demonstrate this new means of self-assembly at an immiscible aqueous | organic interface. Simply contacting aqueous ZnTPPc solutions prepared in citrate buffer at pH 5.8 with a neat, immiscible organic phase of α,α,α ,-trifluorotoluene (TFT) lead to the immediate formation of free-standing films of porphyrin

nanostructures. We rationalise our findings using atomistic computer simulations of the hydrophobicity gradient at the immiscible aqueous | organic interface that show that the carboxylic acid-carboxylate hydrogen bonding in the formed nanostructure is maximised under the mild $\text{pH} = \text{pK}_a^{\text{COOH}}$ conditions. The presence of multi-layers with strong visible light absorption (due to the extended π - π conjugated electronic structure in porphyrin assemblies), and the crystalline macroscale long-range molecular order in the porphyrin nanostructure, suggested these films as ideal light-harvesting antennae in artificial photosynthetic technologies. To confirm this, we employed these nanostructures in a photoinduced interfacial electron transfer (PIET) arrangement between electron donor and acceptor species confined to the organic and aqueous phases, respectively. The energy absorbed by the nanostructure was used to create a highly energetic excited state that mediated electron transfer between the donor and acceptor molecules. *In situ* photocurrent transient measurements at a controllably electrified and LED illuminated liquid | liquid interface were as high as $20 \mu\text{A} \cdot \text{cm}^{-2}$, one order of magnitude higher than in previous studies.²⁴ Our findings clearly demonstrate that the ordered three-dimensional spatial arrangement of the individual porphyrin molecules in the nanostructure diminishes concentration quenching.

Results and discussion

Triggering the formation of interfacial nanostructures. The selective formation of ZnTPPc nanostructures at the interface between water and TFT was observed upon contacting the ZnTPPc aqueous solution (at pH 5.8) with neat TFT. A yellow/green colour was observed at the water | TFT interface within minutes, easily distinguishable from the purple colour of the bulk ZnTPPc aqueous solution, and associated with the formation of porphyrin interfacial nanostructures (Por-INs) (Fig. 1a,b and Supplementary Fig. 1). Self-

assembly was observed in a very narrow pH range around the pK_a of the carboxylic substituents ($pK_a^{\text{COOH}} = 5.8$).²³ At this pH, ZnTPPc in solution exists in a ratio of 1:1 between the fully protonated ($H_4[ZnTPPc]$) and fully deprotonated ($[ZnTPPc]^{4-}$) species. Molecular dynamics (MD) computer simulations indicate that the hydrophobic, neutral $H_4[ZnTPPc]$ species accumulates either at the interface, or even on the oil side of the interface (Fig. 1c,d and Supplementary Fig. 2), driven by the hydrophobicity gradient at the immiscible liquid | liquid interface. This interfacial layer acts as a template structure for the hydrophilic, anionic $[ZnTPPc]^{4-}$ species to adsorb *via* carboxylic acid-carboxylate hydrogen-bonding and π - π interactions (Fig. 1c). In this manner, a highly crystalline film of ZnTPPc nanostructures, stabilised by hydrogen bonding and π - π interactions, builds up layer-by-layer at the interface. Akin to the clathrate crystals of ZnTPPc developed by Goldberg and coworkers,^{25–29} the strength of each individual hydrogen bond or π - π interaction may be insubstantial, but the cooperative effect allows the net enthalpies of these multivalent interactions to cumulatively rival the strength of a covalent bond and stabilise the Por-IN. *Ex situ* scanning electron microscopy (SEM) images revealed the thickness of the floating film of ZnPor-INS to be approximately 135 ($\pm$ 5) nm (Fig. 1e).

Fig. 1 | Mechanism of formation of the porphyrin interfacial nanostructures. **a**, Chemical structure of fully protonated zinc(II) *meso*-tetrakis(4-carboxyphenyl)porphyrin ($H_4[ZnTPPc]$). **b**, Optical image of the robust adherence of the porphyrin interfacial nanostructures (Por-INS) to the interface after replacement of the buffer solution containing ZnTPPc with a buffer solution free of porphyrin. **c**, Representative computer structure of the water | α,α,α -trifluorotoluene (TFT) interface with $[ZnTPPc]^{4-}$ (red) and $H_4[ZnTPPc]$ (dark blue) introduced from the aqueous phase (water molecules not shown for clarity, TFT molecules are cyan). **d**, Computed potential of mean force or free energy profiles for translation of ZnTPPc and H_2TPPc molecules across the water | TFT interface, averaged over 10 ns of free molecular dynamics, with the carboxylate groups on the 4-carboxyphenyl-substituents either fully deprotonated, $[ZnTPPc]^{4-}$ (solid red line) and $[H_2TPPc]^{4-}$ (dotted red line), or fully protonated, $H_4[ZnTPPc]$ (solid blue line) and $H_4[H_2TPPc]$ (dotted blue line). Water occupies the $z < 0$ region and TFT the $z > 0$ region. **e**, Scanning electron microscopy (SEM) image of a film of ZnPor-INS transferred from the water | TFT interface to a copper grid with a holey carbon substrate. **f**, Distribution percentage of neutral $H_4[ZnTPPc]$ (blue line) and anionic $[ZnTPPc]^{4-}$ (red line) in the aqueous phase as a function of pH. The pK_a of the carboxylate groups on the 4-carboxyphenyl-substituents is pH 5.8, *i.e.*, the pH yielding a 50/50 mixture of $H_4[ZnTPPc]$ and $[ZnTPPc]^{4-}$.

Control experiments and MD simulations demonstrated that the ZnTPPc and free-base H_2TPPc molecules are kinetically stable in solution at pH 5.8, and do not undergo spontaneous bulk aggregation in the concentration range studied (Supplementary Fig. 3). This indicates that the Por-INS form only by self-assembly *in situ* at the water | TFT interface. Furthermore, to achieve selective Por-IN formation, the pH of the aqueous buffer solution must be controlled across a narrow pH range $5.1 \leq \text{pH} \leq 6.1$ (Fig. 1f). More alkaline

conditions inhibit formation of the Por-INs because of electrostatic repulsion between tetra-anionic porphyrins. MD simulations show that the $[\text{ZnTPPc}]^{4-}$ species prefer to sit in water at a distance of $\sim 3\text{-}5\text{ \AA}$ above the interface due to their hydrophilic nature (Fig. 1d). Meanwhile, at more acidic conditions, spectroscopic measurements reveal simultaneous formation of a host of randomly structured aggregates in the bulk aqueous phase (Supplementary Fig. 4). This pH dependency of Por-IN formation indicates that cooperative H-bonding is prerequisite for self-assembly of an ordered film. Por-IN formation is not restricted to a single immiscible biphasic system, with control experiments showing that ZnPor-INs also form selectively at immiscible interfaces between water and 1,2-dichloroethane (DCE, Supplementary Fig. 5).

TEM and XRD analysis confirm the crystalline and layered nature of the porphyrin interfacial nanostructures. *Ex situ* transmission electron microscopy (TEM) images with corresponding selected area electron diffraction (SAED) analysis, and X-ray diffraction (XRD) patterns from ZnPor-INs were acquired after immobilization of the film on an amorphous hydrophilized glass substrate (Fig 2a-d). The diffraction pattern for ZnPor-INs (Fig. 2d) bears a striking resemblance to NAFS (nanofilm on a solid surface) structural models for liquid phase interfacial synthesis of highly ordered molecular nanosheets.³⁰ SAED and XRD estimate a 0.55-0.57 nm interplanar spacing between $\{110\}$ planes, with a $\sim 1.1\text{ nm}$ periodicity measured from HRTEM lattice fringes (Fig. 2a). The intense 220 reflection is consistent with a lack of layer-on-layer stacking order (due to non-registered stacking), but a highly crystalline nanosheet material is formed. The (200) reflections indicate strong axial coordination that is a distinct feature of layering along the *c*-axis normal to the support. Clearly discernible (*hk*0) reflections are consistent with a tetragonal unit cell with preferred growth orientation along the plane of the liquid | liquid interface (Fig. 2b,c).

Control experiments with H₂Por-INs demonstrate the key role of the central metal ion in enhancing the crystallinity of the film of porphyrin interfacial nanostructures. H₂Por-INs

grown in the same way also form a crystalline 2D layered material, and show a similar XRD pattern but with a more pronounced amorphous background and suppressed reflection intensity compared to the ZnPor-INs (Fig. 2e). A schematic representation of the crystalline and interdigitated layered clathrate-type structure of the ZnPor-INs is illustrated in Fig. 2f, which assumes interdigitation to account for the reduced unit cell spacing compared to a NAFS-1 or NAFS-2 tetragonal metal-organic nanosheet crystalline structure.

Fig. 2 | Characterisation of the ZnPor-INs and H₂Por-INs *ex situ* by transmission electron microscopy (TEM) and X-ray diffraction (XRD). (a) TEM image of the ZnPor-INs transferred from the water | TFT interface to a copper grid with a holey carbon substrate, taken at 185 k magnification. The profile of the lattice fringing shown on the right is taken from the area marked by the red box in the TEM image. (b) TEM image of ZnPor-INs, taken at 185 k magnification at an accelerating voltage of 300 kV and (c) the corresponding diffraction pattern with a 40 μm selected area aperture and camera length of 580 mm. (d) XRD pattern of the ZnPor-INs transferred to a silicon substrate. Patterns were acquired in ω -2 θ geometry and clearly discernible ($hk0$) reflections confirms a tetragonal unit cell and dominant c -axis layering. (e) XRD of the H₂Por-INs. (f) Schematic representation of the crystalline and layered clathrate-type structure of the ZnPor-INs. Black balls represent carbon, pink is zinc, blue are nitrogen, and green are oxygen.

Adsorption isotherms indicate that assembly is driven by hydrogen-bonding and π - π interactions between the tightly spaced porphyrins in the nanostructure. The interfacial concentration of porphyrin adsorbed to form the Por-INs was measured at equilibrium as a function of the solution concentration of ZnTPPc and H₂TPPc, respectively. Over the concentration range studied (0.5-100 μ M), ZnTPPc adsorption followed a Brunauer-Emmet-Teller (BET) isotherm behaviour, whereas H₂TPPc adsorption followed a linear isotherm behaviour (Fig. 3). Using the BET model for liquid phase adsorption reported by Ebadi *et al.*,³¹ the isotherm obtained for ZnTPPc adsorption was fit to Eqn. 1:

$$\Gamma = \Gamma_m \frac{K_1 C_{eq.}}{(1-K_2 C_{eq.})(1-K_2 C_{eq.} + K_1 C_{eq.})} \quad (1)$$

in which K_1 and K_2 are the *pseudo*-equilibrium constants of adsorption to form the first and second layers of the ZnPor-INs, Γ and Γ_m are the equilibrium and monolayer porphyrin surface concentrations, respectively, and $C_{eq.}$ is the equilibrium concentration of the porphyrin in solution. Non-linear fitting determined Γ_m as 13.08 (± 0.94) nmol·cm⁻², and K_1 and K_2 as 4.55×10^{-2} (± 0.25) and 8.79×10^{-3} ($\pm 2.21 \times 10^{-4}$) L· μ moles, respectively (95% confidence). Thus, the Gibbs free energy of adsorption ($\Delta G_{ads.}$) of ZnTPPc to form the first and second layers of the ZnPor-INs are 7.65 kJ·mol⁻¹ and 11.72 kJ·mol⁻¹, respectively. These positive values of $\Delta G_{ads.}$ suggest that the packing interactions between individual neutral H₄[ZnTPPc] species and the organic phase are not sufficient to form thermodynamically favourable assemblies, that is, the entropic cost of assembly outweighs the small enthalpic gain in free solution. This suggests that the assembly observed experimentally (Fig. 1b) is mediated by trapping of the Por-INs at the interface and driven by hydrogen-bonding and π - π interactions between the tightly spaced porphyrins in the nanostructure.

Fig. 3 | Adsorption isotherms obtained at 20 °C of ZnTPPc and H₂TPPc at the water | TFT interface. Inset: Adsorption isotherm data for ZnTPPc at the water | TFT interface, highlighting the Brunauer-Emmet-Teller (BET) behavior.

The difference in the adsorption isotherms for ZnTPPc and H₂TPPc further emphasises the influence of the metal centre during porphyrin interfacial adsorption. Previous studies at an aqueous | dodecane interface demonstrated that the adsorption of an oil-soluble metalloporphyrin was highly dependent on the nature of the central metal ion due to the different water coordination geometries around different metals.³² Thus, we used MD simulations to quantify the influence of the presence or absence of Zn²⁺, and the protonation state, on the adsorption of ZnTPPc and H₂TPPc at the water | TFT interface (Supplementary Fig. 6). For all model variants, the molecules were found to lie in the plane of the interface, with a dihedral angle between the porphyrin plane and the interface close to 0° which suggests that the difference in the adsorption behaviour stems from different supramolecular packing modes within the Por-INs. Assuming perfectly flat lying molecules, the theoretical monolayer concentration of the ZnPor-INs was calculated as 3.18×10^{14} molecules·cm⁻² (assuming the area of a single ZnTPPc molecule as 3.14 nm², calculated from its molecular surface). Experimentally the value obtained from the ZnTPPc absorption isotherm is an order

of magnitude greater at 4.76×10^{15} molecules·cm⁻². Therefore, the experimental surface coverage suggests that the monolayer surface concentration (Γ_m) corresponds to a layer of interdigitated molecules.

Spectroscopic investigation of the effect of nanostructure formation on the electronic structure of the interfacial porphyrins. Comparison of the *in situ* UV/vis absorption spectra of both ZnTPPc and H₂TPPc in solution with that of the corresponding Por-INs within the Soret band region are shown in Figs. 4a,b. The full spectra are shown in Supplementary Fig. 7, with the absorption maxima (λ_{max}) of the Soret and Q bands summarised in Supplementary Table 1. The λ_{max} value of the Soret band for the ZnPor-INs is slightly blue-shifted (422 to 413 nm), while for the H₂Por-INs slightly red-shifted (414 to 419 nm). Perturbation of the electronic absorption spectra in terms of shifts of the Soret and Q absorption bands, and spectral broadening of the Soret band, clearly indicate the presence of domains with slight variations in the geometric arrangements of the porphyrins within the nanostructure at the interface. Analogous to ZnTPPc in solution, the ZnPor-INs display two Q bands, indicating that the porphyrin ring remains metallated with Zn²⁺ upon nanostructure formation, and thus retains the *D*_{4h} symmetry typical of single ZnTPPc molecules. The H₂Por-INs display four Q bands, again indicating that the porphyrin ring retains the *D*_{2h} symmetry typical of single H₂TPPc molecules. In solution, one main peak centred at 422 nm was deconvoluted from the experimental spectrum of ZnTPPc (Fig. 4a). This peak represents the B(0,0) transition, indicating the monomeric nature of ZnTPPc under these experimental conditions. The latter is consistent with the adherence of ZnTPPc in solution to the Beer-Lambert law across an extensive concentration range (Supplementary Fig. 3), and with previous studies.³³ Best fits in all other instances required multiple peaks, each related to different vibronic transitions, revealing the co-existence of monomers and dimers in solution

for H₂TPPc (Fig. 4b) and domains with slight variations in the geometric arrangements of the porphyrins within the Por-INs.

Fig. 4 | Spectroscopic characterisation of the ZnPor- and H₂Por-INs by *in situ* UV/vis absorbance and steady-state fluorescence, and *ex situ* Raman spectroscopy. Deconvolution of the Soret absorbance bands for **a**, ZnTPPc in solution and the ZnPor-INS and **b**, H₂TPPc in solution and the H₂Por-INS. Comparison of the fluorescence emission spectra of **c**, ZnTPPc in solution and the ZnPor-INS for an excitation wavelength (λ_{exc}) of 418 nm and **d**, H₂TPPc in solution and the H₂Por-INS for λ_{exc} of 413 nm. **e**, Comparison of the Raman spectra of films of ZnPor- and the H₂Por-INS transferred from the water | TFT interface to a silicon substrate (see Supplementary Table 2 for peak assignments).

In situ steady-state fluorescence spectra were measured for a series of excitation wavelengths (λ_{exc}) spanning the Soret bands of both ZnTPPc and H₂TPPc in solution, and their corresponding Por-INS (Fig. 4c,d and Supplementary Figs. 8 and 9). Comparison of the emission profiles of ZnTPPc in solution and the ZnPor-INS shows that the Q(0,0) transient is slightly blue-shifted and Q(0,1) transition slightly red-shifted upon nanostructure formation

(Fig. 4c). By contrast, the spectra of the H₂Por-INs were red-shifted in comparison to the spectra for H₂TPPc in solution, consisting of a peak at 654 nm and much less intense peak at ~710 nm (Fig. 4d). The dependencies of the emission profiles on λ_{exc} across the Soret band mirrored the *in situ* UV/vis spectroscopy findings, confirming the monomeric or dimeric nature of the porphyrins in solution and presence of domains with slight variations in the geometric arrangements of the porphyrins within the Por-INs. Furthermore, the retention of fluorescence emission after nanostructure formation demonstrates how the crystalline long-range molecular order in the nanostructure leads to diminished concentration quenching, a key attribute when designing light-harvesting antennae in artificial photosynthetic technologies.

Since ZnTPPc self-assembles in mild pH conditions, expulsion of Zn²⁺ was avoided, as confirmed by analysis of the effect of nanostructure formation on the vibrational modes of the ZnPor- and H₂Por-INs by *ex situ* Raman spectroscopy (Fig. 4e). Prominent differences between the two are entirely consistent with previous comparisons of metallo- and free-base 4-carboxyphenyl-substituted porphyrin Raman spectra (see Supplementary table 2).^{34,35} The retention of Zn²⁺ increases the inter-system crossing (ISC) rate constant, k_{ISC} , due to the heavy atom effect, increasing the probability of the forbidden S₁ → T₁ transition. From the T₁ state, relaxation may occur *via* phosphorescence or charge transfer. The long-lived (up to millisecond) excited triplet state lifetimes provides sufficient time for the excited state to efficiently interact with ground state quencher molecules,³⁶ and is exploited herein to achieve photoconversion at a controllably electrified and LED illuminated liquid | liquid interface as described below.

Enhancing photoconversion by an order-of-magnitude at electrified aqueous | organic interfaces with floating ZnPor-INs. The concept of photo-induced interfacial electron transfer (PIET) mediated by ZnPor-INs between redox species chemically confined to

different sides of a liquid | liquid interface is illustrated in Fig. 5a. The multi-layers of porphyrin in the ZnPor-INs floating at the interface function as high efficiency light harvesters. Upon illumination, the generated triplet excited state is reductively quenched by electron transfer from decamethylferrocene, and the ground state regenerated by hole transfer from O₂. This charge separation is accompanied by an electrical photocurrent through an external circuit. Optimal functionalisation of the liquid | liquid interface with photoactive species is vital as PIET only involves those photosensitisers specifically adsorbed at the interface. Photocurrent transients associated with the rate of PIET were measured as 9 $\mu\text{A}\cdot\text{cm}^{-2}$ at 0 V and 20 $\mu\text{A}\cdot\text{cm}^{-2}$ when the aqueous phase was polarised 0.5 V with respect to the organic phase. The magnitude of the photocurrents increase substantially at 0.5 V due to the increase in the rate of interfacial electron transfer and the suppression of shunt resistances associated with the competitive transfer of cationic by-products (decamethylferrocenium cations) across the interface. The photocurrents generated with the ZnPor-INs of $\sim 20 \mu\text{A}\cdot\text{cm}^{-2}$ are an order of magnitude greater than those under similar conditions ($< 1 \mu\text{A}\cdot\text{cm}^{-2}$) with ZnTPPc molecules adsorbed at the interface.^{24,37} This step-change in photoconversion efficiency demonstrates the feasibility of using these highly ordered molecular assemblies in photosynthetic technologies.

Fig. 5 | Soft-photoconversion at the interface between two immiscible liquids. **a**, Schematic of “soft-photoconversion”; converting light energy to chemical energy using dye-sensitised electrified liquid | liquid interfaces. The donor species (D) is decamethylferrocene and the acceptor species (A) is O_2 . The ZnTPPc triplet excited state in the crystalline, layered ZnPor-INS undergoes reductive quenching by decamethylferrocene, with O_2 regenerating the ground state. Thus, light energy is converted to chemical energy in the form of the oxidised donor (D^+) and reduced acceptor (A^-) spatially separated on either side of the water | TFT interface. Photocurrent transients were measured **b**, at 0 V and **c**, at a positive polarisation of the interface (0.5 V), at pH 5.8 and 5 mM decamethylferrocene in the TFT phase. The ZnPor-INS floating at the water | TFT interface were illuminated with an LED (470 nm at $50 \text{ mW}\cdot\text{cm}^{-2}$) controlled by the potentiostat. The water | TFT interface was electrified using a specialised 4-electrode electrochemical cell (CE_w and CE_o are the counter electrodes in the water and TFT phases, respectively, and RE_w and RE_o are the reference electrodes in each phase).

Conclusions

The defect-free nature of the water | organic interface provides an ideal platform to self-assemble interfacial nanostructures with unique structural arrangements. In this Article, we report the self-assembly of free-floating interfacial nanostructures of zinc *meso*-tetrakis(4-carboxyphenyl)porphyrin. The nanostructures are stabilised by cooperative hydrogen bonding and, due to the templating interaction of the interface with adsorbed porphyrin molecules, possess a crystalline, layered structure. This approach uniquely harnesses the difference in

hydrophobicity between the neutral protonated and tetra-anionic non-protonated versions of the porphyrin at pKa conditions, combined with the introduction of a hydrophobicity gradient to trigger interfacial self-assembly. We open a new avenue to porphyrin nanostructure formation under mild experimental conditions without the need for acidic pH, designer amphiphilic porphyrin molecules, aggregation-inducing additives or external triggers. The macroscale long-range molecular order and diminished concentration quenching of these photoactive nanostructures facilitates their application in next generation photocatalytic, photovoltaic, opto-electronic and sensor devices. In this regard, the feasibility of using such nanostructures for light collection and harvesting was demonstrated *in situ* by measuring photocurrents associated with photoinduced interfacial electron transfer across the water | TFT interface, with an order-of-magnitude increase in photoconversion efficiency achieved in comparison to previous studies. The ability to isolate the photoactive film at the liquid-liquid interface provides an elegantly simple system for future exploration of photo-induced electron transfer at electrified soft interfaces to gain the fundamental insights necessary to realise a new approach to solar energy conversion entirely based on a self-assembled system.

Experimental Methods

Chemicals. All reagents were used as received without further purification. *Meso*-tetrakis(4-carboxyphenyl)porphyrin (H₂TPPc, ≥98%) and its zinc(II) derivative (ZnTPPc, ≥98%) were obtained from Porphychem. Lithium hydroxide (LiOH, ≥98%), citric acid (H₃Cit, ≥99.5%), decamethylferrocene (97%), and 1,2-dichloroethane (DCE, ≥99.0%) were purchased from Sigma-Aldrich, and α,α,α-trifluorotoluene (TFT, ≥99%) from Acros Organics. All aqueous solutions were prepared using Milli-Q® deionized water (18.2 MΩ). Aqueous solutions of ZnTPPc were prepared by directly dissolving the solid in the lithium citrate buffer pre-adjusted to the desired pH, followed by sonication of the solution for three minutes. Initially,

H₂TPPc was insoluble in the buffer at neutral pH. Therefore, the solid was dissolved first in LiOH and the pH subsequently adjusted with H₃Cit. The ionic strength of each lithium citrate buffer solution containing either porphyrin was maintained at 10 ($\pm$ 2) mM.

Characterisation. The films of Por-INs were gently transferred to a silicon substrate for SEM, XRD and Raman characterisation, or an Agar Scientific TEM grid (Holey Carbon film 300 Mesh Cu) for TEM imaging, by bringing the solid supports into contact with the interface. Prior to imaging, the samples were sequentially rinsed with water and TFT, and dried under a stream of nitrogen gas. TEM images were acquired on a Thermo Fisher double aberration corrected Titan Themis, spot size 6, on a Gatan Oneview detector. SEM images were obtained on a FEI Quanta 650 FEG high resolution SEM. X-ray diffraction patterns (XRD) were acquired in θ -2 θ geometry with a Phillips Xpert PW3719 diffractometer using Cu K α radiation (λ = 0.15418 nm, operation voltage 40 kV, current 40 mA). Patterns were also acquired in ω -2 θ geometry using a PANalytical X'pert PRO XRD. UV/vis absorbance spectra were collected in a Thermo Scientific Evolution 60S UV/vis spectrophotometer with illumination provided by a Xenon light source (accuracy $\pm$ 0.8 nm). Steady-state fluorescence experiments were performed in a LS 55 Perkin Elmer Fluorescence spectrometer. The experimental configuration implemented to obtain UV/vis and steady-state fluorescence spectra of the Por-INs is illustrated in Supplementary Fig. 10. Raman measurements were carried out using a Horiba Jobin Yvon T64000 spectrometer equipped with a nitrogen cooled CCD detector. The laser wavelength was 532 nm with a power of 13 mW. Raman spectra were obtained in 10 acquisitions of 30 seconds duration.

Adsorption isotherms. Vials containing biphasic systems of ZnTPPc or H₂TPPc in lithium citrate buffer (10 mM ionic strength, pH 5.8) at different initial bulk concentrations and TFT as the organic phase were prepared and left to stand for 24 hours. After this time, the Por-INs formed and all remaining unadsorbed porphyrin in the bulk aqueous phase was extracted by

thoroughly rinsing with porphyrin-free buffer solution. The solutions containing unadsorbed porphyrin were collected and analysed by UV/vis absorbance spectroscopy to quantify the porphyrin concentration therein (final bulk concentration). By subtracting the final from the initial bulk concentrations, the surface concentration (number of moles adsorbed per geometric area of aqueous | organic interface) was determined. All quantifications were performed using a calibration curve.

Molecular dynamics simulations. Simulations of interfacial adsorption and assembly were performed using a pre-equilibrated water | TFT interface, consisting water and TFT regions with 4000 water molecules and 1226 TFT molecules, respectively. Full details are provided in the Supplementary Information.

Photocurrent transient measurements at an electrified aqueous | organic interface.

Photocurrent measurements with a DC illumination were performed using the LED driver provided by Metrohm Autolab in conjunction with a PGSTAT204 in a 4-electrode configuration as presented in Supplementary Fig. 11. The overlap of the emission spectrum of the LED with the absorption spectra of ZnTPPc, H₂TPPc and their respective Por-INs is presented in Supplementary Fig. 12. The determination of the photon flux at the electrified liquid | liquid interface as a function of the LED driving current is outlined in Supplementary Fig. 13.

Data availability. The authors declare that all data supporting the findings of this study are available within the article and its Supplementary Information files and from the corresponding author upon request.

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Author information

Contributions

A.F.M.-O. and M.D.S. conceived and designed the experiments. D.L.C. performed and analysed the molecular dynamics computer simulations. C.O.D. acquired and processed the X-ray diffraction data. A.S. acquired and analysed the high-resolution TEM and SAED experiments. G.H. and M.D. acquired and analysed the steady-state fluorescence and Raman

characterizations. A.F.M-O. and M.D.S. wrote the manuscript and all authors commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Soft-photoconversion using floating self-assembled crystalline films of porphyrin nanostructures

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Supplementary Figures and Tables

Supplementary Fig. 1 | Methodology of porphyrin interfacial nanostructure formation.

a, Aqueous solutions of ZnTPPc or H₂TPPc were typically prepared with 50 μ M porphyrin present. Critically, the pH of the aqueous solution was adjusted using a 10 mM ionic strength lithium citrate buffer to match the pK_a of the 4-carboxyphenyl substituents (pK_a^{COOH} = 5.8). Subsequently, aqueous solutions at pH 5.8 were contacted with α,α,α -trifluorotoluene (TFT), leading to a well-defined aqueous | organic interface. Note the top phase is the aqueous phase.

b, Upon contact, the clear formation of porphyrin interfacial nanostructures (Por-INS) was immediately seen visually as a yellow/green complexion (image taken after one hour of contact).

c, To isolate the Por-INS at the interface, the upper 50% of the volume of the aqueous phase was carefully removed by a pipette and replaced with porphyrin-free lithium citrate buffer. This procedure was repeated until no porphyrin was detectable in the aqueous phase by UV/vis spectroscopy. The Por-IN film remained intact and stable, with no re-dissolution observed after 1 day.

Supplementary Fig. 2 | Molecular dynamic studies demonstrating the layer-by-layer formation of the porphyrin interfacial nanostructures at the water | TFT interface. a, Density (ρ) profiles mimicking the situation at pH 5.8 ($= \text{pK}_a^{\text{COOH}}$), averaged over 10 ns of molecular dynamics. The simulation consists of 16 fully deprotonated $[\text{ZnTPPc}]^{4-}$ molecules (red lines) and 16 fully protonated $\text{H}_4[\text{ZnTPPc}]$ molecules (black lines). The density profiles of water (blue line) and TFT (green line) are also shown. **b,** A simulation snapshot of the water | TFT | water density profile with 16 $[\text{ZnTPPc}]^{4-}$ (red) and 16 $\text{H}_4[\text{ZnTPPc}]$ (blue) molecules present in the aqueous phase. **c,** The density profile and **d,** simulation snapshot of the water | TFT | water density profiles for H_2TPPc adsorption, averaged over 10 ns of molecular dynamics.

Discussion | Free energy profiles (PMF) for the porphyrins at the water | TFT interface (Fig. 1d) demonstrate that the charged $[\text{ZnTPPc}]^{4-}$ or $[\text{H}_2\text{TPPc}]^{4-}$ species, being more hydrophilic, have a free energy minimum approximately 4 to 5 Å from the interface itself, while the neutral $\text{H}_4[\text{H}_2\text{TPPc}]$ or $\text{H}_4[\text{ZnTPPc}]$ molecules lie closer to the interface or on the TFT side of the interface. From the free energy profiles it can be seen that the porphyrins are only weakly bound to the interface, with desorption (into the aqueous layer) free energies of $\sim 24 \text{ kJ}\cdot\text{mol}^{-1}$ and $\sim 48 \text{ kJ}\cdot\text{mol}^{-1}$ for the charged and neutral species, respectively. A significantly higher barrier exists ($>200 \text{ kJ}\cdot\text{mol}^{-1}$) for the penetration of these molecules into the TFT layer, indicative of their highly hydrophilic nature. Meanwhile, the neutral porphyrins are both somewhat hydrophobic, with a lower barrier to enter the TFT layer. For $\text{H}_4[\text{H}_2\text{TPPc}]$ the desorption free energy (into the TFT layer) is similar to that for the charged porphyrins (into the aqueous phase). This difference in the location of charged and neutral molecules affects the assembly of porphyrin molecules at the interface (Supplementary Fig. 2). Due to their more hydrophobic nature, the neutral porphyrins reside on the aqueous-TFT interface, forming an interfacial layer. The charged porphyrins partially adsorb onto this, with the neutral molecules acting as a template for the formation of the multilayer porphyrin interfacial nanostructures (Por-Ins).

Supplementary Fig. 3 | Investigating the tendency of ZnTPPc and H₂TPPc molecules in the bulk aqueous solution to dimerise or aggregate as a function of porphyrin concentration. UV/vis absorption spectra of aqueous solutions of increasing concentrations of **a**, ZnTPPc (2 to 100 μM) and **b**, H₂TPPc (2 to 100 μM) in lithium citrate buffer (10 mM ionic strength, pH 5.8). Insets: The increase in absorbance as a function of porphyrin concentration. Dimerisation free energies were determined using potential of mean force (PMF) calculations. PMF calculations were performed between both deprotonated and protonated **c**, ZnTPPc and **d**, H₂TPPc molecules to mimic (i) highly alkaline pH conditions with predominantly the anionic [ZnTPPc]⁴⁻ or [H₂TPPc]⁴⁻ species present, (ii) pK_a^{COOH} conditions with 1:1 ratios of [ZnTPPc]⁴⁻ - H₄[ZnTPPc] or [H₂TPPc]⁴⁻ - H₄[H₂TPPc] species in solution, and (iii) pH conditions with predominately H₄[ZnTPPc] or H₄[H₂TPPc] molecules present in the range of 1 > pH < 5.

Discussion | For ZnTPPc, no deviation from the Beer-Lambert Law was observed as determined from the linear dependence of the absorbance of the Q band at 597 nm with increasing ZnTPPc concentration in solution (Supplementary Fig. 3a). Although a linear range of 2 – 100 μM is shown in Figure Supplementary Fig. 3a, this was seen to extend as far as 500 μM (data not shown). Previous studies by Pasternack *et al.* have also concluded that ZnTPPc remains in a non-aggregated monomeric form at pH 6.8, *i.e.*, at pH values more alkaline than pK_a^{COOH}, even in an aqueous solution with 10-times the ionic strength investigated herein.¹ This ability to resist dimerisation, or more extensive aggregation, in aqueous solutions is attributed to the penta-coordination of the zinc atom in ZnTPPc, with a water molecule occupying the axial position.^{2–5} The axial water ligand prevents close approach of porphyrin molecules. More subtly, axial coordination of metalloporphyrins leads to the metal ion being displaced from the porphyrin ring plane.⁶ The latter may have a disruptive effect on the π -electron density distribution within the core of the macrocycle, weakening the Van der Waals interactions responsible for dimer or higher aggregate formation with other porphyrin monomers.

In comparison, free-base porphyrins, such as H₂TPPc,^{7,8} and metalloporphyrins with a coordination number of four, such as CuTPPc, that lack hydration in the axial position^{1,3,9} dimerises and aggregate rapidly in aqueous solutions at pH values more alkaline than pK_a^{COOH} in the presence of added electrolyte. Even modest amounts of added electrolyte will reduce the coulombic barrier to the close approach of other ionic species, such as another anionic H₂TPPc molecule, thereby leading to dimerisation and aggregation at a certain concentration of H₂TPPc in solution. The latter has been reported as >10 μ M in 10 mM ionic strength buffer or > 1 μ M with 100 mM of added electrolyte.⁸ In broad agreement with these previous findings, we see a deviation from linearity of the absorbance of the Q band at 518 nm with increasing H₂TPPc concentration in solution (Supplementary Fig. 3b). The latter is indicative of H₂TPPc dimer formation for concentrations >10 μ M in 10 mM ionic strength lithium citrate buffer at pH 5.8. However, under these conditions no higher aggregates of H₂TPPc are formed, *i.e.* no spectral broadening or blue or red-shifting of the Soret or Q bands was observed, and no H₂TPPc aggregates were visible to the eye in solution.

For ZnTPPc the dimerisation free energy (taken to be the depth of the minimum at $r \sim 4$ Å) varies significantly with the protonation state of the molecule, with the dimerisation free energy for the H₄[ZnTPPc] - H₄[ZnTPPc] pair being approximately three times that of the other combinations (Supplementary Fig. 3c). The increased stability of the H₄[ZnTPPc] - H₄[ZnTPPc] pair compared to the others may be due to stronger hydrophobic interactions. The latter is in agreement with the kinetic instability of the neutral porphyrin species, experimentally observed to precipitate rapidly for pH conditions across the range of $4.0 \leq \text{pH} \leq 5.5$ (see Supplementary Fig. 4). Across this pH range, the steric influence of the axial water molecule alone is no longer sufficient to prevent the close approach of two H₄[ZnTPPc] species due to minimisation of electrostatic repulsion, leading to stronger hydrophobic interactions. The PMF calculations show significant structure with a number of minima spaced $\sim 2\text{-}3$ Å apart. These may arise due to water molecules interacting with the zinc centre. Such structure is much less apparent for H₂TPPc (Supplementary Fig. 3d), which lacks the zinc centre. For this case the dimerisation free energy is higher than for ZnTPPc and is less influenced by the protonation states of the molecules. Again, this finding fits with the experimentally observed deviation of H₂TPPc from the Beer-Lambert law due to rapid dimerisation in aqueous solutions (Supplementary Fig. 3b), even at pH values $\geq pK_a^{COOH}$ where ZnTPPc remains in monomeric form.

Supplementary Fig. 4 | Investigating the tendency of the porphyrin molecules in the aqueous solution to aggregate: influence of pH. UV/vis absorbance spectra of aqueous solutions of 50 μM ZnTPPc at pH conditions **a**, more acidic and **b**, more alkaline than $\text{pK}_a^{\text{COOH}}$ (= pH 5.8). Identical experiments were performed with 50 μM H_2TPPc at pH conditions **c**, more acidic and **d**, more alkaline than $\text{pK}_a^{\text{COOH}}$. The pH of each aqueous solution was adjusted using citric acid and LiOH. The ionic strength at each pH condition was maintained at 10 ($\pm$ 2) mM. Insets: The Q-band region of the ZnTPPc and H_2TPPc UV/vis absorbance spectra.

Discussion | As the pH becomes progressively more acidic than $\text{pK}_a^{\text{COOH}}$, the equilibrium is displaced towards the neutral $\text{H}_4[\text{ZnTPPc}]$ or $\text{H}_4[\text{H}_2\text{TPPc}]$ species relative to the anionic $[\text{ZnTPPc}]^{4-}$ or $[\text{H}_2\text{TPPc}]^{4-}$ species. As noted in Supplementary Figs. 3c and 3d, the $\text{H}_4[\text{ZnTPPc}]$ - $\text{H}_4[\text{ZnTPPc}]$ pair (or $\text{H}_4[\text{H}_2\text{TPPc}]$ - $\text{H}_4[\text{H}_2\text{TPPc}]$ pair) is stable due to strong hydrophobic interactions, leading to kinetic instability and rapid bulk aggregation. The latter explains the reduction in peak intensity and broadening of the Soret bands across the range of $4.0 \leq \text{pH} \leq 5.5$ for ZnTPPc and H_2TPPc in Supplementary Figs. 4a and 4c, respectively.

Supplementary Fig. 5 | Investigating the formation of porphyrin interfacial aggregates at the aqueous-organic interface: influence of the organic solvent. UV/vis absorbance spectra of **a**, ZnPor-INs and **b**, H₂Por-INs self-assembled as described in Fig. 1 for 24 hours with 50 μ M porphyrin in the aqueous phase and either an α,α,α -trifluorotoluene (TFT) or 1,2-dichloroethane (DCE) organic phase. The UV/vis spectra with each organic solvent were normalized to the maximum absorbance of the Soret bands of the ZnPor-INs ($\lambda_{\text{max}} = 414$ nm) or H₂Por-INs ($\lambda_{\text{max}} = 420$ nm), respectively. Insets: The Q-band region of the ZnPor- and H₂Por-INs UV/vis absorbance spectra.

Supplementary Fig. 6 | Simulations of the average angle of orientation, θ , of fully protonated (black lines) and fully deprotonated (red lines) **a**, ZnTPPc and **b**, H_2 TPPc molecules *versus* time at the water | TFT interface. Probability distributions of the angle of orientation, $P(\theta)$, of fully protonated (black lines) and fully deprotonated (red lines) **c**, ZnTPPc and **d**, H_2 TPPc molecules average over 10 ns of molecular dynamics (MD).

Discussion | Regardless of the presence of the zinc centre and protonation state, the molecules lie in the plane of the interface, with a dihedral angle between the porphyrin plane and the interface close to 0° . However, there is a significant degree of orientational freedom (Supplementary Fig. 6a,b), with all molecules adopting a range of orientations relative to the interface. This is reflected in the orientational angle probability distributions (Supplementary Fig. 6c,d) which have peaks at low ($<15^\circ$) angle but remain non-zero for all angles. These findings are in line with previous MD studies for the adsorption of symmetrically substituted hydrophilic porphyrin molecules to aqueous | hydrophobic phospholipid membrane interfaces that revealed the central porphyrin rings stay almost flat at the bilayer surface once equilibrium was reached.¹⁰ Thus, MD analysis strongly infers that the molecules primarily lie flat in the plane of the liquid | liquid interface.

Supplementary Fig. 7 | Comparison of the *in situ* UV/vis absorption spectra for **a**, ZnTPPc in solution *versus* ZnPor-INs and **b**, H₂TPPc in solution *versus* H₂Por-INs. The porphyrin aqueous solutions consisted of either 50 μ M ZnTPPc or H₂TPPc in lithium citrate buffer (10 mM ionic strength, pH 5.8). The Por-INs were self-assembled as described in Fig. 1 for 24 hours with either 50 μ M ZnTPPc or H₂TPPc in the aqueous phase. The *in situ* UV/vis absorption spectra of the Por-INs were normalized to the maximum absorbance of the Soret bands of ZnTPPc ($\lambda_{\text{max}} = 422$ nm) or H₂TPPc ($\lambda_{\text{max}} = 414$ nm) in solution, respectively. Insets: The Q band region of the *in situ* UV/vis absorption spectra.

Supplementary Table 1 | The absorption maxima (λ_{max}) of the Soret and Q bands of both ZnTPPc and H₂TPPc in 10 mM lithium citrate buffer solution (pH 5.8), and their corresponding Por-INs self-assembled at the immiscible water | TFT interface.

Porphyrin species	Absorption peaks (nm)				
	Soret	Q(1,0)		Q(0,0)	
ZnTPPc in solution	422 (11)	557		596	
ZnTPPc interfacial nanostructures	413 (35)	563		604	
	Soret	Q(1,0) _y	Q(0,0) _y	Q(1,0) _x	Q(0,0) _x
H ₂ TPPc in solution	414 (15)	518	555	582	639
H ₂ TPPc interfacial nanostructures	419 (34)	517	552	593	648

^a Accuracy of the absorption maxima is ± 1 nm. ^b Values in the brackets are the full width at half maximum (FWHM) of the Soret bands. The latter are provided to highlight the extent of spectral broadening upon porphyrin nanostructure formation.

Discussion | The λ_{max} values of the Soret and Q bands in solution are within ± 2 nm of previously reported values for spectra of ZnTPPc¹¹ and H₂TPPc,^{7,12–15} respectively, recorded in comparable aqueous phases.

Supplementary Fig. 8 | *In situ* steady-state fluorescence spectra as a function of excitation wavelength ($\lambda_{\text{exc.}}$) for **a**, 50 μM ZnTPPc and **b**, 50 μM H₂TPPc in 10 mM lithium citrate buffer (pH 5.8), and **c**, ZnPor-INS and **d**, H₂Por-INS self-assembled as described in Fig. 1 for 24 hours with 50 μM ZnTPPc or H₂TPPc, respectively, in the aqueous phase.

Supplementary Fig. 9 | Two different emission regimes were observed for the *in situ* steady-state fluorescence spectra of the ZnPor-INS as a function of excitation wavelength ($\lambda_{\text{exc.}}$).

Discussion | *In situ* steady-state fluorescence spectroscopy was employed to investigate the effect of incident radiation falls within the Soret band (Kasha's rule). Thus, if a single species of uniform electronic structure was present, only the intensity of the emissions but not the emission spectra profiles should be affected by varying $\lambda_{\text{exc.}}$ within the Soret band. However, if a number of species with varying electronic structures were present, both the emission intensities and spectral profiles should vary significantly upon changing $\lambda_{\text{exc.}}$ within the Soret band. The latter would therefore be expected from a mixture of domains with slightly

different geometric arrangements of the porphyrin molecules due to their excitation at slightly different wavelengths. Quantitative comparison of emission intensities of ZnTPPc in buffer solution and the Por-INs was hampered by scattering due to the experimental configuration (Supplementary Fig. 10).

The emission profiles of 50 μM ZnTPPc in solution were independent of λ_{exc} across the Soret band indicating the presence of a monomeric ZnTPPc species only in solution (Supplementary Fig. 8a). A dependence of the emission profile of 50 μM H₂TPPc in solution on λ_{exc} across the Soret band was observed due to the co-existence of the monomer and dimer species in solution (Supplementary Fig. 8b). The latter was expected based on previous observations from in situ UV/vis spectroscopy (see Supplementary Fig. 3b). The emission profile of the ZnPor-INs was highly dependent on λ_{exc} across the Soret band. Two emission regimes were tentatively assigned, each potentially corresponding to distinct domains with slightly different geometric arrangements of the porphyrin molecules (Supplementary Figs. 8c and 9). The emission profile of the H₂Por-INs was independent of λ_{exc} across the Soret band (Supplementary Fig. 8d), suggesting either a single nanostructure of H₂TPPc was formed at the interface, or that any different domains in the nanostructure had very similar electronic structures.

Supplementary Table 2. Assignment of the bands observed in the Raman spectra of the ZnPor- and H₂Por-INs excited at 532 nm (the experimental data is presented in Fig 4e; note that the peak at 522 cm⁻¹ is due to the underlying silicon substrate).

H ₂ Por-IN	ZnPor-IN	Assignment ^{a,b}
322	-	?
-	374	?
-	408	?
705	-	Phenyl
824	-	Phenyl
966	-	Phenyl
1005	1009	Phenyl, $\nu(\text{C}_\alpha\text{-C}_\text{M})$
-	1031	Phenyl
1086	1076	A _{1g} , $\delta_s(\text{C}_\beta\text{-H})$
1140	-	A _{1g} , $\nu(\text{C}_\alpha\text{-N})$
-	1179	Phenyl
1241	1243	$\nu(\text{C}_\text{M}\text{-}\Phi)$
1327	-	B _{1g} , $\nu_{\text{as}}(\text{C}_\alpha\text{-N})$
1364	-	A _{1g} , $\nu_s(\text{C}_\alpha\text{-N}) + \nu_s(\text{C}_\alpha\text{-C}_\beta)$
-	1354	A _{1g} , $\nu_s(\text{C}_\alpha\text{-C}_\beta) + \nu_s(\text{C}_\alpha\text{-N})$
1453	1450	B _{1g} , $\nu_{\text{as}}(\text{C}_\beta\text{-C}_\text{M})$
-	1496	B _{1g} , $\nu(\text{C}_\beta\text{-C}_\beta)$
1555	1550	A _{1g} , $\nu(\text{C}_\beta\text{-C}_\beta)$
1606	1605	Phenyl

^a ν represents bond stretching and δ represents bond bending. Subscripts s and as refer to the symmetric and asymmetric vibrations with respect to the pyrrole 2-fold axis for $\nu(\text{C}_\beta\text{-H})$, $\delta(\text{C}_\beta\text{-H})$, $\nu(\text{C}_\alpha\text{-N})$, or the methine 2-fold axes for $\nu(\text{C}_\alpha\text{-C}_\beta)$. Φ represents the phenyl group. ^b Assignments from references ¹⁶⁻¹⁹.

Discussion | Firstly, the peak at 322 cm⁻¹ for the H₂Por-INs is absent for the ZnPor-INs, with two peaks at 374 and 408 cm⁻¹ observed instead. Secondly, the single peak at 1354 cm⁻¹ for the ZnPor-INs is replaced by a doublet at 1327 and 1364 cm⁻¹ for the H₂Por-INs. Furthermore, as noted by Vlčková *et al.* when comparing surface-enhanced resonance Raman spectra (SERRS) of free-base and silver H₂TPPc species,¹⁸ a major distinguishing factor is a loss in intensity of the phenyl out-of-plane modes and a gain in intensity of the phenyl in-plane modes upon metalation. For example, bands at 705, 824 and 966 cm⁻¹, associated with π_3 , π_2 and π_1 phenyl ring out-of-plane modes (mode orders from Spiro and co-workers)^{20,21} are present in the H₂Por-IN spectra, but absent in the ZnPor-IN spectra. Additionally, the phenyl ring in-plane mode at 1179 cm⁻¹ present in the ZnPor-IN spectra is entirely absent in the H₂Por-IN spectra.

Supplementary Experimental Methods

***In situ* microscopy.** The films of Por-INs were very well adhered to the aqueous-TFT interface (see Fig. 1b). This attribute significantly facilitated their subsequent unambiguous *in situ* spectroscopic characterisation as it allowed the selective removal of the bulk porphyrin molecules from solution. The absorption or emission of light by the latter would otherwise greatly interfere with the selective *in situ* acquisition of UV/vis absorption or fluorescence emission spectra from the Por-INs.

Supplementary Fig. 10 | Schematic of the experimental configuration implemented to obtain *in situ* UV/vis absorbance and steady-state fluorescence spectra of the Por-INs.

Molecular dynamic simulations. Simulations of interfacial adsorption and assembly were performed using a pre-equilibrated water | TFT interface, consisting water and TFT regions with 4000 water molecules and 1226 TFT molecules, respectively. For the dimerisation free energy calculations two porphyrin molecules were placed in a box containing 4000 water molecules. The porphyrin and TFT molecules were modelled using the Generalised Amber Force Field²² and the TIP3P model was used for the water molecules. Charges on the zinc porphyrin unit were found using the Metal Center Parameter Builder.²³ Charges on the sidechains and TFT were determined from AM1-BCC calculations.^{24,25} Bonded potentials for the Zn atom were taken from the work of Lin and Wang.²⁶ Force field setup and parameterisation were performed using the Antechamber program in AmberTools (version 14). Full details of the force field, along with sample input files are detailed *vide infra*.

All simulations were performed using the LAMMPS molecular dynamics package.²⁷ The simulation temperature and pressure were 298 K and 1 atm, with temperature and pressure controlled using Nose-Hoover thermostat (relaxation time 0.2 ps) and barostats (relaxation 2 ps).²⁷ For interfacial simulations the box was allowed to vary in the *x* and *y* dimensions (the *z* box length was held fixed). Electrostatic interactions were evaluated using a particle-particle-particle-mesh sum.²⁸ For interface simulations convergence parameter $\alpha = 0.263 \text{ \AA}^{-1}$ and a reciprocal space grid of 36 x 36 x 80 was used, for simulations in bulk water $\alpha = 0.278 \text{ \AA}^{-1}$ and a reciprocal space grid of 40 x 40 x 40 was used. Van der Waals interactions were cut-off at 11 Å, with tail corrections applied to both energy and force. Adsorption and dimerization free energies were found using the Adaptive Biasing Force (ABF) method.^{29,30} To assist convergence the full *z* and *r* range were divided into 5 Å wide windows, with ABF used to generate the free energy profile in each window.

Force field details

Atom types. The atom names for the porphyrin are shown below (two rings are given explicitly, atom names for the other rings can be found by equivalence). For the free base the nitrogen atoms NA and NC are bonded to hydrogens (HA and HC)

Non-bonded parameters

[ZnTPPc]⁴⁺

Atom	Atom type	q / e	ε / kcal mol ⁻¹	σ / Å
C1A, C1B, C1C, C1D, C4A, C4B, C4C, C4D	ca	+0.498	0.086	3.40
C2A, C2B, C2C, C2D, C3A, C3B, C3C, C3D	ca	-0.275	0.086	3.40
H2A, H2B, H2C, H2D, H3A, H3B, H3C, H3D	ha	+0.165	0.015	2.60
NA, NC	nc	-0.710	0.170	3.25
NB, ND	nd	-0.710	0.170	3.25
CHA, CHB, CHC, CHD	cg	-0.249	0.086	3.40
ZN	ZN	+1.132	0.0125	1.96
C1E, C1F, C1G, C1H	ca	-0.162	0.086	3.40
C2E, C2F, C2G, C2H, C6E, C6F, C6G, C6H	ca	-0.166	0.086	3.40
H2E, H2F, H2G, H2H, H6E, H6F, H6G, H6H	ha	+0.101	0.015	2.60
C3E, C3F, C3G, C3H, C5E, C5F, C5G, C5H	ca	-0.109	0.086	3.40
H3E, H3F, H3G, H3H, H5E, H5F, H5G, H5H	ha	+0.148	0.015	2.60
C4E, C4F, C4G, C4H	ca	-0.124	0.086	3.40
C7E, C7F, C7G, C7H	c	+0.906	0.086	3.40
O1E, O1F, O1G, O1H, O2E, O2F, O2G, O2H	o	-0.834	0.210	2.96

H₄[ZnTPPc]

Atom	Atom type	q / e	ε / kcal mol ⁻¹	σ / Å
C1A, C1B, C1C, C1D, C4A, C4B, C4C, C4D	ca	+0.498	0.086	3.40
C2A, C2B, C2C, C2D, C3A, C3B, C3C, C3D	ca	-0.275	0.086	3.40
H2A, H2B, H2C, H2D, H3A, H3B, H3C, H3D	ha	+0.165	0.015	2.60
NA, NC	nc	-0.710	0.170	3.25
NB, ND	nd	-0.710	0.170	3.25
CHA, CHB, CHC, CHD	cg	-0.518	0.086	3.40
ZN	ZN	+1.132	0.0125	1.96
C1E, C1F, C1G, C1H	ca	-0.094	0.086	3.40
C2E, C2F, C2G, C2H, C6E, C6F, C6G, C6H	ca	-0.148	0.086	3.40
H2E, H2F, H2G, H2H, H6E, H6F, H6G, H6H	ha	+0.141	0.015	2.60
C3E, C3F, C3G, C3H, C5E, C5F, C5G, C5H	ca	-0.069	0.086	3.40
H3E, H3F, H3G, H3H, H5E, H5F, H5G, H5H	ha	+0.157	0.015	2.60
C4E, C4F, C4G, C4H	ca	-0.138	0.086	3.40
C7E, C7F, C7G, C7H	c	+0.652	0.086	3.40
O1E, O1F, O1G, O1H	o	-0.554	0.210	2.96
O2E, O2F, O2G, O2H	oh	-0.608	0.210	2.96
HE, HF, HG, HH	ho	+0.447	0	0

[H₂TPPc]⁴⁻

Atom	Atom type	q / e	ε / kcal mol⁻¹	σ / Å
C1A, C1B, C1C, C1D, C4A, C4B, C4C, C4D	ca	+0.0417	0.086	3.40
C2A, C2B, C2C, C2D, C3A, C3B, C3C, C3D	ca	-0.0364	0.086	3.40
H2A, H2B, H2C, H2D, H3A, H3B, H3C, H3D	ha	+0.0639	0.015	2.60
NA, NC	nc	-0.355	0.170	3.25
HA, HC	hn	+0.166	0.016	1.069
NB, ND	nd	-0.247	0.170	3.25
CHA, CHB, CHC, CHD	cg	+0.151	0.086	3.40
C1E, C1F, C1G, C1H	ca	-0.162	0.086	3.40
C2E, C2F, C2G, C2H, C6E, C6F, C6G, C6H	ca	-0.166	0.086	3.40
H2E, H2F, H2G, H2H, H6E, H6F, H6G, H6H	ha	+0.101	0.015	2.60
C3E, C3F, C3G, C3H, C5E, C5F, C5G, C5H	ca	-0.109	0.086	3.40
H3E, H3F, H3G, H3H, H5E, H5F, H5G, H5H	ha	+0.148	0.015	2.60
C4E, C4F, C4G, C4H	ca	-0.124	0.086	3.40
C7E, C7F, C7G, C7H	c	+0.906	0.086	3.40
O1E, O1F, O1G, O1H, O2E, O2F, O2G, O2H	o	-0.834	0.210	2.96

H₄[H₂TPPc]

Atom	Atom type	q / e	ε / kcal mol ⁻¹	σ / Å
C1A, C1B, C1C, C1D, C4A, C4B, C4C, C4D	ca	+0.0417	0.086	3.40
C2A, C2B, C2C, C2D, C3A, C3B, C3C, C3D	ca	-0.0364	0.086	3.40
H2A, H2B, H2C, H2D, H3A, H3B, H3C, H3D	ha	+0.0639	0.015	2.60
NA, NC	nc	-0.355	0.170	3.25
HA, HC	hn	+0.166	0.016	1.069
NB, ND	nd	-0.247	0.170	3.25
CHA, CHB, CHC, CHD	cg	+0.151	0.086	3.40
C1E, C1F, C1G, C1H	ca	-0.094	0.086	3.40
C2E, C2F, C2G, C2H, C6E, C6F, C6G, C6H	ca	-0.148	0.086	3.40
H2E, H2F, H2G, H2H, H6E, H6F, H6G, H6H	ha	+0.141	0.015	2.60
C3E, C3F, C3G, C3H, C5E, C5F, C5G, C5H	ca	-0.069	0.086	3.40
H3E, H3F, H3G, H3H, H5E, H5F, H5G, H5H	ha	+0.157	0.015	2.60
C4E, C4F, C4G, C4H	ca	-0.138	0.086	3.40
C7E, C7F, C7G, C7H	c	+0.652	0.086	3.40
O1E, O1F, O1G, O1H	o	-0.554	0.210	2.96
O2E, O2F, O2G, O2H	oh	-0.608	0.210	2.96
HE, HF, HG, HH	ho	+0.447	0	0

Trifluorotoluene

Atom	Atom type	q / e	ϵ / kcal mol ⁻¹	σ / Å
C1	ca	-0.100	0.086	3.40
H1	ha	+0.139	0.015	2.60
C2, C6	ca	-0.134	0.086	3.40
H2, H6	ha	+0.142	0.015	2.60
C3, C5	ca	-0.081	0.086	3.40
H3, H5	ha	+0.151	0.015	2.60
C4	ca	-0.168	0.086	3.40
CF	c3	+0.687	0.109	3.40
F1, F2, F3	f	-0.238	0.061	3.118

Bonded parameters

Bond stretching and bond angle bending parameters for ZN atoms listed below. Other force field parameters are taken from the Generalized Amber Force Field.

Bond	k / kcal mol ⁻¹ Å ⁻²	r ₀ / Å
ZN-nc	56	2.07
ZN-nd	56	2.07

Angle	k / kcal mol ⁻² rad ⁻²	θ ₀ / degrees
nc-ZN-nc	31.1	180.0
nc-ZN-nd	31.1	90.0
nd-ZN-nd	31.1	180.0
ca-nc-ZN	47.65	126.5
ca-nd-ZN	47.65	126.5

Sample input files are available on request from the authors. For each simulated system (water-TFT interface with 1, 16, and 32 porphyrin molecules, each porphyrin dimer in water) a lammps input script and data file is included, along with parameter file containing GAFF parameters.

Photocurrent transient measurements. Photocurrent measurements using a DC illumination were performed in a specialised 4-electrode electrochemical cell, using the light emitting diode (LED) driver provided by Metrohm Autolab in conjunction with a PGSTAT204 in the configuration presented in Supplementary Fig. 11. The reference electrodes used were Ag/AgCl for the organic reference solution and Ag/AgCitrate for the aqueous electrolyte. The counter electrodes in each phase were Pt. The light source was a trifocal LED with a beam width of 18° and λ_{max} of 470 nm. The emission spectrum of the LED, as well as the absorption spectra of ZnTPPc, H₂TPPc and their respective Por-INs are presented in Supplementary Fig. 12. As clearly illustrated in Supplementary Fig. 12, a major advantage of porphyrin nanostructure formation is the broadening of the absorption spectrum, a highly desirable trait when designing nanomaterials for use in solar energy conversion.³¹ The broadening of the absorption spectra for ZnPor-INs and H₂Por-INs leads to a far greater overlap with the emission spectrum of the 470 nm LED in comparison to the aqueous solutions of ZnTPPc and H₂TPPc.

Supplementary Fig. 11 | Image of the 4-electrode electrochemical cell, with a schematic and image of the setup used for photocurrent transient measurements. (CE_w and CE_o are the counter electrodes in the water and TFT phases, respectively, and RE_w and RE_o are the reference electrodes in each phase).

Supplementary Fig. 12 | Overlaps between the emission of the blue LED and absorption of **a**, ZnTPPc and H₂TPPc in solution and **b**, their respective Por-INs.

The light intensity of the LED was controlled through the LED driver presented in Supplementary Fig. 11. This driver is a current source that converts an input voltage difference signal provided by the potentiostat to a current output signal directed to the LED. This conversion is performed using the Digital to Analog converter (DAC164) according to:

$$i_{\text{LED}} = \left(\frac{i_{\text{range}}}{V_{\text{range}}} \right) V_{\text{DAC164}} = \left(\frac{1000 \text{ mA}}{10 \text{ V}} \right) V_{\text{DAC164}} = (100 \text{ mA} \cdot \text{V}^{-1}) \cdot V_{\text{DAC164}}$$

where i_{LED} is the output driving current. For calculations, in order to convert this current to light intensity ($\text{mW} \cdot \text{cm}^{-2}$) and photon flux ($\# \text{ photons} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$), the LED intensity was calibrated using a photodiode located at a controlled distance from the light source. The calibration was performed knowing the responsivity (R) of the photodiode and the area of the electrified liquid-liquid interface using the following relationship:

$$P (\text{mW} \cdot \text{cm}^{-2}) = \frac{j_{\text{photodiode}} (\text{mA})}{\text{Area} (\text{cm}^2) \cdot R (\text{mA} \cdot \text{mW}^{-1})}$$

The photon flux at each driving current was calculated from the light intensity knowing that the energy of a photon with a wavelength of 470 nm is $4.226 \times 10^{-19} \text{ J}$. The results of these calculations are presented in Supplementary Fig. 13.

Supplementary Fig. 13 | a, Photocurrents measured from the calibration photodiode at each driving current applied to the LED driver, and the calculated light intensity provided by the blue LED. **b,** The calculated photon flux at the electrified liquid-liquid interface at each driving current applied to the LED driver.

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