

# Hierarchical organization of perylene-bisimides and polyoxometalates for photo-assisted water oxidation

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## Abstract

The oxygen in Earth's atmosphere is there primarily because of water oxidation performed by photosynthetic organisms using solar light and one specialized protein complex, photosystem II (PSII). High-resolution imaging of the PSII 'core' complex shows the ideal co-localization of multi-chromophore light-harvesting antennas with the functional reaction center. Man-made systems are still far from replicating the complexity of PSII as the majority of PSII-mimetics have been limited to photocatalytic dyads based on a 1:1 ratio of a light absorber, generally a Ru-polypyridine complex, with a water oxidation catalyst. Here we report the self-assembly of multi-perylene-bisimide chromophores (PBI) shaped to function by interaction with a polyoxometalate water-oxidation catalyst (Ru<sub>4</sub>POM). The resulting [PBI]<sub>5</sub>Ru<sub>4</sub>POM complex shows: a robust amphiphilic structure and dynamic aggregation into large 2D-paracrystalline domains, a red-shifted light-harvesting efficiency > 40%, and favorable exciton accumulation, with a peak quantum efficiency using 'green' photons ( $\lambda > 500$  nm). The modularity of the building blocks and the simplicity of the non-covalent chemistry offer opportunities for innovation in artificial photosynthesis.

Artificial Photosynthesis is a long-sought scientific dream for renewable energy applications<sup>1</sup>. Green plants, algae and photosynthetic bacteria stand as a formidable benchmark for solar energy conversion, while their emulation by man-made bio-inspired architectures still awaits a change of paradigm<sup>2,3,4</sup>. In this direction, the “quantasome hypothesis” was a decisive step forward for deciphering the function-vs-structure requirements of Natural Photosynthesis<sup>5,6</sup>. Since the earliest studies of Emerson and Arnold (1932)<sup>5</sup> and Park and Biggins (1964)<sup>6</sup>, the quantasome concept identifies the minimal photosynthetic unit responsible for the “quantum” solar energy conversion, taking place within the chloroplast membrane. This definition applies to photosystems (PS) II and I, working in tandem, being specialized for photo-oxidation and photo-reduction respectively<sup>2,3,5,6</sup>, that despite their structural and functional diversity, share the unique “quantasome” essentials: they both integrate a self-assembled light-harvesting antenna in combination with catalytic co-factors<sup>5,6</sup>. The need of a light-harvesting specialized unit is because solar light is a low-density energy source, with few photons hitting a square-nm per second (ca.10 photons nm<sup>-2</sup> s<sup>-1</sup>)<sup>7,8</sup>. Therefore, the extended cross-section and wavelength absorbance of multi-chromophore antennas (mainly chlorophylls) is meant to capture and accumulate enough photon excitation energy required for the chemistry to take place at the reaction center (RC)<sup>2,3</sup>. The light-harvesting units regulate the frequency of the photon conversion events according to the quantum flux (i.e. charge-separation in the range 10<sup>3</sup>-10<sup>4</sup> s<sup>-1</sup>), thus pushing the photosynthetic engine to its full capacity<sup>2,3</sup>. For this task, the number of pigments/chromophores composing the light-harvesting antenna exceeds by at least one order of magnitude that of functional centers of native photosystems<sup>5-9,10</sup>.

In PSII, ca. 30 core-chlorophylls surround the functional reaction center (PSII-RC) and trigger the quantized, four-flash photo-oxidation of water by the proximal Mn<sub>4</sub>CaO<sub>5</sub> oxygen evolving catalyst (PSII-OEC)<sup>9,10</sup>. In this asset, PSII is the most efficient photo-electrolizer built so far, converting solar light via a four-electron/four-proton oxidation mechanism (2H<sub>2</sub>O → O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup> E = 1.23V vs reversible hydrogen electrode, RHE)<sup>2,3,9,10</sup>, however with the one critical downfall of the fragile protein structure that undergoes photo-degradation with loss of the manganese co-factor<sup>2,3,9,10</sup>. Therefore, the engineering of a synthetic and robust PSII-analog is one formidable challenge of photocatalysis, and by far the most ambitious goal of Artificial Photosynthesis<sup>11-15</sup>.

Eluding the “quantasome” concept, the majority of PSII-mimetics have been limited to photocatalytic dyads based on a 1:1 conjugation of a light absorber (i.e. a Ru-polypyridine complex) with the water oxidation catalyst (WOC)<sup>11-15</sup>. The dyad arrangement rules out diffusion-limited electron transfer<sup>16-22</sup>, but equally favors intra-dyad back-recombination. Because recombination events are not counter-acted by a proximal light-harvesting antenna/exciton accumulation pool, photocatalysis by dyads is generally quenched at its initial take-off<sup>19-22</sup>. While the dyad provides a basic “embryo” of the photosynthetic apparatus, the quantasome model calls for a significantly different approach: the light-harvesting components, of selected type and number, together with their spatial organization need to be specifically optimized according to the WOC requirements, with the final aim to leverage its multi-electron transfer mechanism. On the other hand, sophisticated multi-chromophore architectures have been synthesized to mimic the natural light-harvesting antennas; however these are generally conceived as a self-standing unit, i.e. independently from a co-localized catalytic interface, and turn out to be plagued by inter-chromophore charge and energy transfer side-processes, i.e. competing with productive events involving the WOC moiety<sup>23,24</sup>.

An ‘artificial quantasome’ is reported herein, that is specifically designed for oxygen evolution by the template association of light-harvesting -perylenebisimides domains<sup>25-31</sup> with a polyoxometalate WOC, known as a bio-inspired analog of the PSII-OEC (Fig. 1a and Supplementary Fig. 1)<sup>16-18,32-37</sup>. To this aim, the bis-cationic N,N'-bis(2-(trimethylammonium)ethylene)perylene-3,4,9,10-tetracarboxylic acid bisimide (**PBI**) has been used in combination with the tetra-ruthenate polyanion, [Ru<sub>4</sub>(μ-O)<sub>4</sub>(μ-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(γ-SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]<sup>10-</sup>, **Ru<sub>4</sub>POM**, thus taking advantage of the complementary electrostatic interactions and hydrophobic properties of the molecular building blocks (Supplementary Fig. 1). This strategy points at the co-localization of PBI-based excitons with **Ru<sub>4</sub>POM**: the former provides one of the strongest and robust photo-generated oxidant using visible light ( $\lambda > 500$  nm,  $E(\mathbf{PBI}^{*'/\cdot-}) = 2.20$  V vs NHE)<sup>30,31</sup>; the latter works with low overpotential (300-350 mV), exceptionally wide pH-range of activity (pH = 1-7)<sup>32-37</sup>, ultra-fast photo-induced electron transfer (ps timescale)<sup>16-18,38-41</sup>, and well-defined water oxidation mechanism (> 4 electron oxidation)<sup>42</sup> in solution as well as on conductive nano-carbon supports including graphene<sup>33,34</sup>.

The “quantasome” assembly forms in water, with a definite **[PBI]<sub>5</sub>Ru<sub>4</sub>POM** stoichiometry, where each **Ru<sub>4</sub>POM** turns out to be caged within the surrounding walls of a five-fold PBI-corolla, (Fig. 1a and Supplementary Fig. 1). Converging evidence identifies the **[PBI]<sub>5</sub>Ru<sub>4</sub>POM** complex as the competent photosynthetic unit featuring: (i) a red-shifted, broad absorption cross-section, greatly improving the light harvesting efficiency of photoelectrodes (LHE >40%,  $\lambda = 500$  nm), (ii) favorable exciton accumulation and negligible excimeric loss; (iii) a robust amphiphilic structure by effect of the all-inorganic POM template; (iv) dynamic fluid-to-crystalline organization into two-dimensional (2D) patterns (**{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}**<sub>n</sub>, Fig. 1 and 2). The formation of 2D-arrays of the PBI-quantasomes sets a striking analogy with the PSII arrangement within the native photosynthetic membrane (Supplementary Fig. 2)<sup>43</sup>. Our results show the rendering of the PBI-quantasome 2D-phase onto nano-structured tungsten oxide photoelectrodes (**nanoWO<sub>3</sub>|{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}**<sub>n</sub>), confirming oxygen evolution using “green” photons ( $\lambda$  up to 560 nm), with quantitative faradaic yield (> 97 %) and quantum efficiency (IQE) up to 1.4 % in close analogy with PSII-bioelectrodes (Table 1).

## Results and discussion

**Characterization of the {[PBI]<sub>5</sub>Ru<sub>4</sub>POM}**<sub>n</sub> photosynthetic assembly. Intercalation of **Ru<sub>4</sub>POM** deca-anions into aqueous **PBI<sub>n</sub>** bundles ( $\pi$ - $\pi$  nano-stacks, Supplementary Fig. 1)<sup>25-31</sup> is probed in solution by conductometric and spectrophotometric titrations (25 – 100  $\mu$ M, in 2-20 mM phosphate buffer, pH 7, Supplementary Fig. 3), displaying sharp isosbestic points at  $\lambda = 465, 478, 522, 560$  nm and a 5:1 **PBI/Ru<sub>4</sub>POM** association stoichiometry, in compliance with electroneutrality requirements. The POM-induced exfoliation of **PBI<sub>n</sub>**, occurs with a progressive shift of Zeta Potential values ( $\zeta$ -Potential, Supplementary Fig. 4) from +20 mV to -37 mV, while Dynamic Light Scattering (DLS) analysis shows a corresponding shift of the size distribution, from 500 to 850 nm, indicating a major structural modification of the particles. Indeed, wide angle X-ray scattering (WAXS) measurements of aqueous **PBI<sub>n</sub>** (Fig. 1b Inset, bottom left corner, red trace) show a strong suppression and broadening of the prominent PBI peak at  $q = 17.6$  nm<sup>-1</sup> (ascribed to a  $\pi$ - $\pi$  interaction distance of  $2\pi/q = 3.57$  Å, Fig. 1b Inset, bottom left corner, blue trace) upon **Ru<sub>4</sub>POM** addition.

The molecular structures of both **Ru<sub>4</sub>POM** and **PBI** have a comparable axial length (1.8-2.1 nm, Supplementary Fig. 5) and complementary charge distribution localized at the peripheries of the longest dimension (see the calculated electrostatic potential map, MEP, in Supplementary Fig. 1), which supports an axial alignment of **PBI** and **Ru<sub>4</sub>POM** in their electrostatic assembly. *The resulting supramolecular assembly, [PBI]<sub>5</sub>Ru<sub>4</sub>POM, is thus envisaged as a POM-encapsulated super-complex, in which the inorganic polyanion templates a corolla-like arrangement of five surrounding PBIs* (Fig. 1a, and Supplementary Fig. 5); The co-axial localization of the PBI-corolla / POM building blocks is reminiscent of the PSII-core complex structure<sup>43</sup> (Supplementary Fig. 2) and is conveniently described as a “core-shell” cylindrical amphiphile, which, by effect of the large  $\pi$ -surface area of the PBI outer-walls, is expected to form higher order aggregates in water (Fig. 2a).<sup>44</sup> Indeed, small angle X-ray scattering (SAXS) measurements (Fig. 1b) suggest that a paracrystalline phase forms in solution arising from the close packing of the [PBI]<sub>5</sub>Ru<sub>4</sub>POM units. More in detail: (i) the slope of -1.90, obtained in the low-q regime power law fit, is consistent with self-assembly of [PBI]<sub>5</sub>Ru<sub>4</sub>POM into a 2D-lamellar superstructure, albeit with a broad defect dislocation (a slope of -2.00 is indicative of an ideal lamellar arrangement, Fig. 1b), and with an approximate thickness of 8.2 nm (Guinier approximation for infinite plate-like particles)<sup>45,46</sup>; (ii) the two correlation peaks in the mid-q scattering part, observed around 3 and 4 nm<sup>-1</sup> (Fig. 1b, top right corner), correspond to molecular d-spacings of  $2.3 \pm 0.3$  nm and  $1.7 \pm 0.6$  nm respectively (Supplementary Table 1), and are assigned to **Ru<sub>4</sub>POM**···**Ru<sub>4</sub>POM** distances due to its high electron density contrast.

Interpretation of the supramolecular organization of the building blocks in such bidimensional superstructure is complicated by their association hierarchy and even intrinsic dynamics (Supplementary Fig. 1). A plausible hypothesis, based on the SAXS fitting results and also considering the molecular dimensions of the [PBI]<sub>5</sub>Ru<sub>4</sub>POM unit (with an estimated average diameter of ca. 1.5-1.6 nm, Supplementary Fig. 5), is the following: we attribute the d-spacing of  $1.7 \pm 0.6$  nm to a **Ru<sub>4</sub>POM**···**Ru<sub>4</sub>POM** motif with intercalated **PBI** pairs at a  $\pi$ - $\pi$ -stacking distance of 0.3-0.4 nm, arising from an in-plane perpendicular alignment of the [PBI]<sub>5</sub>Ru<sub>4</sub>POM unit within the 2D-nanoplates (Fig. 2a and Supplementary Fig. 5). The d-spacing of  $2.3 \pm 0.3$  nm is instead ascribed to the mean distance between vertically diffracting planes within the nanoplates, in agreement with the long-axis dimension of **Ru<sub>4</sub>POM** (Fig. 2a). Atomic Force

Microscopy (AFM) imaging of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  confirms the 2D morphology of the nano-flakes, showing a broad size distribution and an average height of ca 9 nm (Supplementary Fig. 6). Noteworthy, micro-sized hexagonal-shaped crystalline aggregates formed over time (Fig. 2b), showing the expected UV-Vis signature of the PBI-quantasome (Supplementary Fig. 7). X-ray diffraction studies revealed a single crystal-like behavior with significant mosaicity in reciprocal space and a distinctive in-plane scattering pattern, corresponding to a strained hexagonal lattice (C2 cell, approx. dimensions  $a = 1.5$  nm,  $b = 2.0$  nm, see Fig. 1d and Supplementary Fig. 7). The high-density hexagonal-like arrangement of the PBI-quantasomes in the single crystallites is consistent with the postulated cylindrical shape and core-shell amphiphilic nature of the  $[\text{PBI}]_5\text{Ru}_4\text{POM}$  unit<sup>45,46</sup>, and could be considered as a thermodynamic sink of the 2D-lamellae dynamics. The coexistence of disordered packings, ordered arrays, and/or mixtures thereof, as found in the native thylakoid membrane (Supplementary Fig. 2), strengthens the high biomimetic appeal of the artificial PBI-quantasome<sup>43</sup>.

**Photo-catalytic water oxidation by  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$ .** The redox potential of the  $\text{PBI}^*/\text{PBI}^-$  couple is estimated as  $E(\text{PBI}^*/\text{PBI}^-) = +2.20$  V vs normal hydrogen electrode (NHE), Supplementary Fig. 8 and Fig. 9. The excited state  $\text{PBI}^*$  is thus expected to leverage multiple electron transfer from  $\text{Ru}_4\text{POM}$ , with oxidation features in the range 0.75 – 1.02 V, up to the catalytic water oxidation onset at 1.2 V vs NHE (Supplementary Fig. 8). Therefore, the driving force for electron transfer is significantly higher within the PBI-quantasome than with classical ruthenium polypyridine sensitizers ( $[\text{Ru}(\text{bpy})_3]^{3+/2+} = +1.26$  vs NHE)<sup>47</sup>, or with cerium ammonium nitrate (CAN) (+1.75 vs NHE), typically used for water oxidation catalysis<sup>47</sup>. Indeed, static quenching of the PBI excited-state emission occurs, levelling off at the expected 5:1 PBI/POM association stoichiometry ( $\text{PBI}$  10  $\mu\text{M}$ , in phosphate buffer, 20 mM, pH 7.0, Supplementary Fig. 9), while photo-induced oxygen evolution is confirmed in the presence of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) as terminal electron acceptor (Fig. 3a, Supplementary equations 6-10, energy diagram in Supplementary Fig. 10 and Supplementary Table 2). In all cases, oxygen evolution by the ternary  $\text{PBI}/\text{Ru}_4\text{POM}/\text{S}_2\text{O}_8^{2-}$  system is observed from the reaction solution that shows the spectroscopic footprint of the  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  aggregates ( $\text{PBI}$  100  $\mu\text{M}$ ,  $\text{Ru}_4\text{POM}$  added in

the range 3-60  $\mu\text{M}$ ,  $\text{S}_2\text{O}_8^{2-}$  1 mM, LED white lamp irradiation, 4.5 mW/cm<sup>2</sup>; Fig. 3a, Supplementary Table 2). Moreover, the oxygen evolution kinetics and yield, both reach a maximum plateau value at  $[\text{Ru}_4\text{POM}] \sim 20 \mu\text{M}$ , i.e. at the expected 5:1 PBI/Ru<sub>4</sub>POM stoichiometry (Figure 3a). *This result is consistent with the PBI-quantasome assembly being the competent photosynthetic unit responsible for oxygen evolution.* The PBI-quantasome proves to be exceptionally robust with respect to the Ru(bpy)<sub>3</sub><sup>2+</sup> benchmark as superimposable UV-Vis spectra are registered before and after oxygenic turnover (Supplementary Fig. 11).

### Investigation of $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$ Transient States by Time-Resolved Spectroscopy:

Oxygen evolution implies that photoexcitation of the PBI-quantasome triggers sequential  $\text{PBI}_5(\text{e}^-)\cdot\text{Ru}_4\text{POM}(\text{h}^+)$  charge-separation events, leading to multi-hole accumulation at the WOC site, up to the formation of the high valent oxygen evolving intermediate (formally  $\text{Ru}_4\text{POM}(\text{nh}^+)$ , Supplementary Fig. 10)<sup>42</sup>. This multi-state mechanism<sup>42</sup> is encoded within the quantasome unit, where the number of PBI photo-sensitizers per WOC offers a definite advantage for collecting excitation energy to power sequential electron transfer .

Femtosecond transient absorption (fsTA) spectroscopy was used to probe the unique excited-state dynamics resulting from  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$ , when compared to aqueous  $\text{PBI}_n$ , (Figure 3b and Supplementary Fig. 12). The fsTA spectra of the  $\text{PBI}_n$  reference (100  $\mu\text{M}$  in phosphate buffer, 20 mM, pH 7), following a 530 nm laser pulse, display a sharp ground-state bleaching at 500 nm, and formation of the singlet excited state ( $^1*\text{PBI}_n$ ) absorption maxima at 590, 700, 850, and 950 nm (Supplementary Fig. 12). Both time resolved multiple wavelength analysis and global fitting (GloTarAn software package,) reveal a monoexponential, short-lived decay for  $^1*\text{PBI}_n$  ( $^1*\text{PBI}_n$  coexists with a minor component stemming from monomeric  $^1*\text{PBI}$  featuring a lifetime of > 4 ns).

In line with previous studies, the 263 ps lifetime ( $k = 3.8 \times 10^9 \text{ s}^{-1}$ , Supplementary Fig. 12) reflects charge recombination following a non-resolvable symmetry-breaking charge separation<sup>23,24,30,31</sup>.

Very different transient dynamics emerge from  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (Fig. 3b). At a first glance, the PBI-centered singlet excited state  $^1*\text{PBI}\cdot\text{Ru}_4\text{POM}$  featuring maxima at 430, 550, 710, and 870 nm is seen to transform, within less than 25 ps, into a new transient species showing positive

absorption in the near-IR region at 750, 820 and 990 nm (Fig 3b), that indicates the formation of the **PBI<sup>-</sup>** radical anion, readily identified by comparison with spectroelectrochemical evidence (Supplementary Fig. 8). Moreover, a closer look at the early timescale shows the population of an intermediate state, that still retains the signature of the former excited state, but whose 990 nm maximum infers its definite charge-transfer character. We can conclude that upon photoexcitation, the PBI-quantasome undergoes a three-states cascade where the **\*PBI•Ru<sub>4</sub>POM** singlet excited state decays to a charge transfer excited state **\*(PBI<sup>(δ-)</sup>•Ru<sub>4</sub>POM<sup>(δ+)</sup>)** followed by formation of a **PBI(e<sup>-</sup>)•Ru<sub>4</sub>POM(h<sup>+</sup>)** charge-separated state (Fig. 3c), as indicated by an appreciable sharpening of the 990 nm maximum marker (detection of **Ru<sub>4</sub>POM(h<sup>+</sup>)** at pH 7 is hampered by its low extinction coefficient<sup>32-37</sup>). Ultra-fast energy transfer and charge separation within the PBI-quantasome also explains the fluorescence quenching observed upon its formation (Supplementary Fig. 9).

At variance with the **PBI<sub>n</sub>** reference, fitting of the **{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>** fsTA results, on the femto-to nanosecond timescales, were realized for a sequential “three-species” model (Fig. 3d). In the cascade, the localized PBI singlet excited state (state 1, 1.4 ps lifetime,  $k_1 = 7.1 \times 10^{11} \text{ s}^{-1}$ ) decays to an intermediate charge transfer state (state 2, 25 ps lifetime,  $k_2 = k_{cs} = 4.0 \times 10^{10} \text{ s}^{-1}$ ) which ultimately affords the fully stabilized, charge-separated state (state 3, 1050 ps lifetime,  $k_3 = k_{cr} = 9.5 \times 10^8 \text{ s}^{-1}$ ) whose decay to the ground state is about two orders of magnitude slower than its formation (Fig. 3c).

A different behavior is usually observed for electrostatic assemblies of **Ru<sub>4</sub>POM** with ruthenium polypyridine sensitizers, where ultra-fast recombination precludes the observation of photo-induced charge separation<sup>38-40</sup>. In contrast, a long-lived charge-separated state within the PBI-quantasome is likely favored by electron delocalization along the  $\pi$ -backbone of the **{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>** system after photo-induced injection<sup>21</sup>. Furthermore, the PBI-quantasome puts down deactivation processes (symmetry-breaking charge separation, SB-CS, and excimeric emission) generally arising from a multi-chromophore arrangement<sup>23,24</sup>. In this notion, ultra-fast electron-injection by **Ru<sub>4</sub>POM** outcompetes unproductive inter-chromophore charge/electron transfer<sup>23,24</sup>. *We can conclude that the PBI-quantasome is shaped to funnel the exciton energy towards the productive pathway of hole-formation at the catalytic site, by increasing the*



*probability of charge separation per unit time (light-harvesting/antenna effect) so to match the slower-boundary of the four-electron mechanism required for oxygen evolution.*

**Wiring of {[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub> onto photoanodes.** The wiring of a fully integrated photosystem (light-harvesting antenna + RC) has been previously demonstrated by loading the native PSII enzyme on mesoporous Indium Tin Oxide electrodes (*meso*-ITO|PSII, Table 1)<sup>48</sup>. Oxygenic photocurrent is observed for the bio-electrode, showing a peak Incident Photon to Current Efficiency (IPCE = 0.125 %) at 680 nm (i.e. the excitation wavelength of the PSII-chlorophyll primary electron donor, P680\*). This result is still unrivalled by synthetic photoanodes that generally show very low IPCE profiles at irradiation wavelengths  $\lambda > 500$  nm<sup>48,49</sup>. Engineered n-type semiconductor photoanodes have been recently reported to operate with IPCE values of ca 30-60% at  $\lambda < 450$  nm, dropping to zero at  $\lambda > 465$  nm. Implementation of sensitized interfaces responding to low energy photons (green and yellow light) might be envisaged via fabrication of multijunction dye sensitized cells, where each dye should operate within its optimal spectral range thus maximizing solar light harvesting and photocurrent generation.<sup>50-53</sup>

Building on the PBI-quantasome advantage, the {[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub> motif has been transferred onto a nanostructured tungsten oxide photoanode (*nano*WO<sub>3</sub>, ca. 1.5  $\mu$ m film thickness) to accomplish water splitting via regenerative photoelectrochemical cell (PEC) technology, (Table 1)<sup>48-53</sup>. *Nano*WO<sub>3</sub> shows a suitable conduction band potential, at approximately 0.3 V vs. RHE, similar to the redox potential of the quinone acceptors in PSII<sup>48</sup>. The photocatalytic onset for water oxidation is observed at ca. 0.74 V vs. RHE at  $\lambda < 420$  nm (potentials are referred to RHE for benchmarking with literature data). Both the photoanode fabrication and PEC experiments were performed in aqueous medium at pH 3 (1 mM HClO<sub>4</sub> / 0.1 M NaClO<sub>4</sub>), which guarantees the optimal WO<sub>3</sub> film stability.<sup>54</sup>

The resulting photoelectrode (*nano*WO<sub>3</sub>|{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>,) shows the UV-Vis footprint of {[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>, (Supplementary Fig. 13), together with a high surface-area/nano-morphology (AFM images in Fig. 4a), and GISAXS scattering curves / 2D-intensity maps that nicely correspond to the expected hierarchical organization of the photocomplex (compare the scattering profile of Fig. 4b,c with Fig. 1b).

The  $\text{nanoWO}_3\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photoanode (exposed area of  $1.5 \text{ cm}^2$ ) was probed in the potential range from 0.50 to 0.91 V vs RHE at 20 mV/s scan rate, under irradiation by a solar simulator (AM 1.5 G light, 1 sun,  $100 \text{ mWcm}^{-2}$ ) at  $\lambda > 450 \text{ nm}$  to avoid the direct excitation of the semiconductor layer. Compared to the dark scan ( $J < 5 \mu\text{A cm}^{-2}$ , dashed line in Fig. 4d), the photocurrent response is indicative of fast hole scavenging and catalysis by  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (solid line, Fig. 4d), featuring the onset potential close to the saturation plateau of  $> 40 \mu\text{A cm}^{-2}$ , respectively at  $< 0.60 \text{ V}$  and  $0.91 \text{ V}$ , i.e. with a cathodic shift of ca  $0.15 \text{ V}$  with respect to the bare  $\text{nanoWO}_3$  electrode and far below the expected thermodynamic limit for oxygen evolution ( $E(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V vs. RHE}$ ). Noteworthy, the incident photon to current conversion efficiency (IPCE) profile confirms that the action spectrum of the photoanode overlaps with the absorption features of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (Fig. 4e): the peak value of IPCE = 0.50 % corresponds to the expected absorption maxima (470 - 490 nm range) and values of IPCE up to 0.40 % are maintained at  $\lambda > 500 \text{ nm}$ , where  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  shows a broad absorption tail (Fig. 4e). These results stem from a favorable optical density (ca. 0.2) of  $\text{nanoWO}_3\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (roughness factor of ca. 150), with a maximum Light Harvesting Efficiency ( $LHE(\lambda) = 1 - 10^{-A(\lambda)}$ ) of the order of 40 % (Supplementary Fig. 13). A considerable absorption shift for  $\lambda > 500 \text{ nm}$  is observed with respect to the classical PBI-sensitized electrode (the LHE at 540 nm being ca. twice that of the  $\text{nanoWO}_3|\text{PBI}_n$  electrode black curve in Supplementary Fig. 13). Therefore the resulting Internal Quantum Efficiency (IQE) (calculated as Absorbed Photon to current Conversion Efficiency, APCE (%) = IPCE (%) / LHE) turns out to be ca. 1.3%, being constant in the 470-540 nm wavelength range (Supplementary Fig. 14).

Performance metrics for  $\text{nanoWO}_3\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  are reported in Table 1, for benchmarking against relevant photoelectrode configurations<sup>48,55,56</sup>. Inspection of the APCE values ranks the  $\text{nanoWO}_3\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photoanode at the top position in the series, with ca. a twofold enhancement compared to  $\text{nanoITO}|\text{PSII}$  or to  $\text{nanoWO}_3|\text{PBI}|\text{IrOx}$ , and outperforming by ca. *one-order of magnitude* the state-of-the art sensitized photoanodes based on  $\text{Ru}_4\text{POM}$  (cfr 1.3 % vs 0.11-0.39 %, Table 1). Continuous oxygen production at the  $\text{nanoWO}_3\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photoanode has been monitored by a generator-collector bipotentiostatic set-up, showing an overall faradaic yield  $> 97 \%$  ( $\lambda > 455 \text{ nm}$ , 0.91 V applied

bias vs RHE, for 15 min, Supplementary Fig. 15). The kinetic advantage of the integrated  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photo-complex is further confirmed by the turnover frequency value (TOF) obtained under Controlled Potential Electrolysis (CPE) and solar irradiation (see conditions in Table 1), approaching the bio-electrode performance (Table 1)<sup>48</sup>.

## CONCLUSIONS

In summary, the biomimetic potential of the PBI-based quantasome builds on the photophysics of the individual sensitizer–catalyst components and relies on their organization in a dynamic 2D array. Understanding how the quantasome assembly, spanning a broad range of time and length scales, correlates with photosynthetic functionality may provide opportunities for mimicking nature.

### Methods:

Synthetic procedures, characterization experiments, photophysical and kinetic analysis, and protocols for the quantification of O<sub>2</sub> evolution, are described in Supplementary Information.

**Photoanode fabrication.** Deposition of tungsten oxide onto fluorine doped tin oxide (FTO) electrodes was performed by spin coating a WO<sub>3</sub> colloidal paste (6 s at 600 rpm followed by 20 s at 2000 rpm) onto a portion of the active area of cleaned FTO slides and sintering at 550°C for 30 min to obtain a monoclinic nanocrystalline WO<sub>3</sub> layer: six layers of WO<sub>3</sub> were deposited with this procedure and, for the last layer, the sintering time was prolonged to 45 min, followed by activation in H<sub>2</sub>SO<sub>4</sub> and finally by sintering for further 45 min. *nano*WO<sub>3</sub>| $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photoanodes were then obtained by soaking into a 1 mM solution of **PBI**(PF<sub>6</sub>)<sub>2</sub> in acetonitrile at 50°C for 6 h, rinsed with ethanol, dried in N<sub>2</sub> flow and then exposed to Ru<sub>4</sub>POM (9 mM aqueous solution in NaClO<sub>4</sub> 0.1 M, pH 3) by 15 minutes soaking, followed by rinsing with milliQ water and drying in N<sub>2</sub> flow.

The  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  loading on *nano*WO<sub>3</sub> has been determined upon dissolution of the electrode surface layer, by analysis of the ruthenium content via Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), and by Uv-Vis quantification of the **PBI** released in

solution. In these experiments, the ruthenium content was found  $4.34 \pm 0.23$  nmol/cm<sup>2</sup> while the **PBI** chromophore turned out in the range 16-20 nmol/cm<sup>2</sup>, which is close to the expected stoichiometry ratio. The long-term stability of the **nanoWO<sub>3</sub>{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>** is hardly addressable in the present construction set that would instead require a precise engineering of the surface adhesion properties together with a three-dimensional reconstruction of the photosynthetic lamellae into a 3D-interlocked pattern. In the adopted configuration, the photoelectrode suffers from delamination and material-leaching occurring under oxygen evolution regime and leading to a ca 60% photocurrent loss after few minutes of irradiation. Besides the photocurrent drop occurring within the first 100 s, the photoanode achieves operational stability, coupled to photogenerated oxygen evolution up to 1 h (Supplementary Fig. 15). Notheworthy, **{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub>** arrays are very robust, and fast electron transfer to the encapsulated polyoxometalate is instrumental for dye photoprotection.

**Data availability.** The data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant source data are available from the corresponding authors upon request.

**Acknowledgments:** This work was supported by the Italian Ministero dell'Istruzione, Università e Ricerca (FIRB RBAP11C58Y, PRIN-2010N3T9M4), Universities of Padova, and Trieste, INSTM, the Seventh Framework Programme [FP7/2007–2013] under grant agreement no. 310651 (SACS project).

**Author contributions:** Z.S., E.P., F.R. did the synthesis and characterization experiments; M.Bu. and H.A. conducted the WAXS and SAXS structural investigation; N.M. isolated and characterized the hexagonal crystalline aggregates, N.M. and N.D. conducted the X-Ray diffraction analysis, K.D. and D.M.G. designed and analyzed the fsTA studies, G.A.V. and G.L. optimized the oxygenic activity and photocurrent performance; S.B., S.C., C.A.B. conducted the PEC experiments; A.S. analyzed the solution and PEC results, M.B. and M.P. designed the experiments and wrote the paper.

**Additional information** Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to M.B. and M.P.

**Competing interests:** the authors declare no competing interests.

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## Figure captions

**Fig. 1. Characterization of the  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photosynthetic assembly.** **a**, Figurative representation of the  $[\text{PBI}]_5\text{Ru}_4\text{POM}$  building-block [ $\text{Ru}_4\text{POM}$  = blue framework;  $\text{PBI}$  = red (aromatic body) and grey (alkylammonium tails) framework], shown as a core-shell cylindrical amphiphile [cartoon:  $\text{PBI}$  shell = red cylinder,  $\text{Ru}_4\text{POM}$  = blue cylinder]. **b**, Small angle x-ray scattering (SAXS) data for  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (blue) formed upon mixing 20 mM  $\text{PBI}$  with stoichiometric amounts of  $\text{Ru}_4\text{POM}$  in 20 mM phosphate buffer, pH 7. The y-axis label  $I(q)$  is scattered intensity. The low- $q$  Porod slope of -1.9 indicates the formation of a defected 2D lamellar super-structure. Two disordered correlation peaks are visible in the mid- $q$  regime (black arrows): a peak-fitting (red line in the top inset) links these peaks to corresponding d-spacings of  $1.7 \pm 0.6$  nm and  $2.3 \pm 0.3$  nm; the coherent domain size of the 1.7 nm d-spacing is significantly lower than the one corresponding to 2.3 nm, suggesting that the two peaks are caused by two different structural motifs, in-plane and out-of-plane, respectively (see Supplementary Table 1). Inset, bottom left corner: Wide angle x-ray scattering (WAXS) measurements of 40 mM  $\text{PBI}$  before (red trace) and after (blue trace) the addition of 10 mM  $\text{Ru}_4\text{POM}$  in water, compared to the theoretical  $\text{Ru}_4\text{POM}$  formfactor scattering (black dotted traces) calculated using CRY SOL.

**Fig. 2. Hierarchical organization of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photosynthetic aggregates.** **a**, Multi-scale model representation (cartoon version) of the cylinders packing into stacked nano-lamellae, where the mean molecular out-of-plane distance corresponds to  $2.3 \pm 0.3$  nm, causing the first correlation peak in the scattering data (Fig.1b) Note that the building-blocks are not necessarily confined into each lamella. The zoom-in shows a single lamellar plane, built from the parallel alignment of the cylinders with a mean in-plane distance of  $1.7 \pm 0.6$  nm. Estimated dimensions of the building-block and center-to-center distances of the  $\text{Ru}_4\text{POM-PBI//PBI-Ru}_4\text{POM}$  supramolecular motif within a lamella are reported in Supplementary Fig. S5. **b**, Reciprocal space map of a hexagonal-shaped, laminar crystalline aggregates of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  (single-crystal like behavior with mosaicity of about  $10\text{-}15^\circ$ ), separating over time from the solution (upper left right corner – scale bar denotes 25  $\mu\text{m}$ ); indexing of the in-plane reflections (see white cubes) yields a strained hexagonal unit-cell (see Supplementary Fig. S7 for reflection

labels). A simplified model of the packing arrangement in a single crystallite, shown in the lower right corner.

**Fig. 3. Femtosecond transient absorption (fsTA) dynamics of oxygenic  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$**  **a.** Plot of evolved  $\text{O}_2$  (left axis, black plot) and of the initial rate of  $\text{O}_2$  production (right axis, red plot) versus the  $\text{Ru}_4\text{POM}/\text{PBI}$  ratio; the error bars are given from the maximum deviations in experiments run in triplicate. Inset: Oxygen evolution kinetics, with  $[\text{PBI}] = 100 \mu\text{M}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 1 \text{ mM}$ ,  $\text{Ru}_4\text{POM}$  (3.0 - 60  $\mu\text{M}$ ) in 20 mM phosphate buffer, pH 7, upon irradiation with a LED white lamp (4.5  $\text{mW}/\text{cm}^2$ ). **b.** Temporal evolution and transient dynamics of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$ : differential absorption spectra of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  with  $[\text{PBI}] = 100 \mu\text{M}$  and  $[\text{Ru}_4\text{POM}] = 60 \mu\text{M}$  recorded in phosphate buffer (20 mM, pH 7) with several time delays between 2 ps (red) and 3300 ps (blue) obtained upon femtosecond flash photolysis (530 nm) in the range 400-750 nm. The inset displays the differential absorption spectra in the range 800-1200 nm showing the peak shaped absorption at 990 nm ascribed to the PBI radical anion transient (Supplementary Fig. 8). **c.** kinetic model used to fit / deconvolve the excited state surfaces of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  at pH 7 via GloTarAn with states 1-3 as described in the main text. **d.** deconvoluted transient absorption spectra in the visible range, associated via GloTarAn analysis to states 1 (black), 2 (grey), and 3 (orange) according to the kinetic model in **c**; inset shows the time evolution of state population. In Fig. 3b and 3d, the data in the interval 520-560 nm are not reported due to interference with laser excitation.

**Fig. 4: Characterization of  $\text{nanoWO}_3|[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  photoanodes.** **a.** AFM image of  $\{[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  on  $\text{nanoWO}_3$  at different magnification, showing a smooth and uniform texture with a porous substructure in the nanometer scale. **b.** GISAXS scattering intensities along vertical cuts at  $q_H = 0 \text{ nm}^{-1}$  (see white box in c), showing a distinct PBI inherent scattering (peak a) for the POM-free,  $\text{nanoWO}_3|\text{PBI}$  electrode that is i) strongly reduced for  $\text{nanoWO}_3|[\text{PBI}]_5\text{Ru}_4\text{POM}\}_n$  and ii) accompanied by the formation of a broader correlation peak (peak b) corresponding to the  $\text{Ru}_4\text{POM}-\text{Ru}_4\text{POM}$  scattering centres with intercalated,  $\pi-\pi$  PBI doublets (see Figure 1b for comparison). **c.** 2D scattering-images of the corresponding GISAXS scattering intensities. **d.** Photocurrent density (solid line) versus dark current density

(dashed line) as a function of the applied potential (oxidative scan up to 0.90V vs RHE, scan rate 20 mV sec<sup>-1</sup>) under simulated solar irradiation (AMG 1.5, 1 Sun, with a cut-off filter at 450 nm), in aqueous HClO<sub>4</sub> pH 3, 0.1 M NaClO<sub>4</sub>; counter electrode: Pt wire; reference electrode: Ag/AgCl. The potential values were then converted to the reversible hydrogen electrode (RHE) according to the equation: E(RHE) = E(Ag/AgCl) + 0.197 + 0.059 x pH. **e**, Action spectrum of the *nano*WO<sub>3</sub>|{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub> photoanode showing the incident photon to current conversion efficiency (IPCE, red squares) as a function of the irradiation wavelength and overlapped with the absorption spectra of the *nano*WO<sub>3</sub>|{[PBI]<sub>5</sub>Ru<sub>4</sub>POM}<sub>n</sub> photoanode (black solid line).

## Tables

**Table 1.** Photoanode performance metrics and literature benchmark values. All experiments were performed under simulated solar irradiation (AM 1.5G, 1 Sun, cut-off filter at 450 nm.), in HClO<sub>4</sub> (pH 3), 0.1 M NaClO<sub>4</sub>; counter electrode: Pt wire; reference electrode: Ag/AgCl; potentials are then converted to Reversible Hydrogen Electrode, RHE, using the equation: E (V) vs RHE = E (V) vs Ag/AgCl + 0.197 + (0.0592×pH).

Photoanode	E vs RHE <sup>a</sup> (V)	J <sub>MAX</sub> <sup>b</sup> (μA cm <sup>-2</sup> )	TOF <sup>c</sup> (s <sup>-1</sup> )	IPCE <sup>d</sup> (%)	APCE <sup>e</sup> (%)	Reference
<i>nano</i> WO <sub>3</sub>  {[PBI] <sub>5</sub> Ru <sub>4</sub> POM} <sub>n</sub>	0.91	44	0.026 <sup>f</sup>	0.50 <sup>g</sup>	1.30 <sup>g</sup>	<i>this work</i>
<i>nano</i> ITO PSII <sup>h</sup>	0.94	0.3	0.030 <sup>i</sup>	0.12 <sup>j</sup>	0.70 <sup>j</sup>	48
<i>nano</i> WO <sub>3</sub>  PBI IrO <sub>x</sub> <sup>k</sup>	0.91	70	-	0.60 <sup>l</sup>	0.80 <sup>l</sup>	55
<i>nano</i> TiO <sub>2</sub>  [Ru(bpy) <sub>2</sub> (L)] Ru <sub>4</sub> POM <sup>m</sup>	0.54	14	0.003 <sup>n</sup>	-	0.11 <sup>o</sup>	56
<i>nano</i> TiO <sub>2</sub>  [Ru(dpbbpy)(L) <sub>1</sub> ] <sub>2</sub>  Ru <sub>4</sub> POM <sup>m</sup>	0.54	55	0.016 <sup>p</sup>	-	0.39 <sup>o</sup>	56

<sup>a</sup>Potential applied in controlled potential electrolysis under irradiation. <sup>b</sup>Maximum photocurrent density observed during the first anodic potential scan and irradiation. <sup>c</sup>Turnover frequency (TOF) determined from the equation TOF = [J<sub>MAX</sub>/(4×F×l<sub>WOC</sub>)]×FY/100, where J<sub>MAX</sub> is the maximum photocurrent density, F is the faraday constant = 96485 C mol<sup>-1</sup>, l<sub>WOC</sub> is the loading of the water oxidation catalyst, FY is the faradaic Yield of Oxygen production. <sup>d</sup>Incident Photon to Current conversion Efficiency (IPCE). <sup>e</sup>Absorbed Photon to Current conversion Efficiency (APCE) = IPCE(λ)/(1-10<sup>-A(λ)</sup>), where A(λ) is derived from the absorption spectra of the electrodes. <sup>f</sup>up to 0.050 s<sup>-1</sup> at 1.37 V vs RHE, with l<sub>WOC</sub> as the loading of Ru<sub>4</sub>POM = 4.34 nmol cm<sup>-2</sup>, determined by ICP-OES analysis, and considering the quantitative FY (>97%, Supplementary Fig. 15). <sup>g</sup>Values recorded at 490 nm. <sup>h</sup>Nanostructured Indium tin oxide (ITO) loaded with PSII; general conditions: pH 6.5 in 40 mM 2-(N-morpholino)ethanesulfonic acid (MES) electrolyte. <sup>i</sup>TOF calculated based on photocurrents obtained at 1.23 V vs RHE. <sup>j</sup>Recorded at 680 nm. <sup>k</sup>Dye sensitized WO<sub>3</sub> with spin coated IrO<sub>2</sub> nanoparticles; general conditions: HClO<sub>4</sub> pH 3, 0.1 M NaClO<sub>4</sub>, illumination under AM 1.5 G with a cut-off filter at 435 nm. <sup>l</sup>Recorded at 470 nm. <sup>m</sup>Dye sensitized *nano*-TiO<sub>2</sub> loaded with Ru<sub>4</sub>POM; general conditions: pH 5.8 in 80 mM Na<sub>2</sub>SiF<sub>6</sub>/NaHCO<sub>3</sub> buffer electrolyte containing NaClO<sub>4</sub> (200 mM), irradiation 455 nm (33 mW cm<sup>-2</sup>). <sup>n</sup>Calculated from the reported catalyst loading of 10 nmol cm<sup>-2</sup> and considering the measured FY of 90%. <sup>o</sup>Reported as internal quantum efficiency (IQE). <sup>p</sup>Calculated from the reported catalyst loading of 8 nmol cm<sup>-2</sup> and considering the experimental faradaic yield of 86%.











