Supporting Information

Photocatalytic Proton Reduction by a Computationally Identified, Molecular Hydrogen-Bonded Framework

Catherine M. Aitchison, Christopher M. Kane, David P. McMahon, Peter Spackman, Angeles Pulido, Xiaoyan Wang, Liam Wilbraham, Linjiang Chen, Rob Clowes, Martijn A. Zwijnenburg, Reiner Sebastian Sprick, Marc A. Little, Graeme M. Day, and Andrew I. Cooper

a. Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool L7 3NY, U.K.
b. Computational Systems Chemistry, School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.
c. Leverhulme Research Centre for Functional Materials Design, University of Liverpool, Liverpool, L7 3NY, U.K.
d. Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

† These authors contributed equally to this work

This PDF file includes:

Materials and Methods
Figures S1 to S70.
Tables S1 to S9.

Table of Contents:
1.0 Computational Methods
2.0 Experimental Methods
3.0 Crystal Structure Prediction Data
4.0 Experimental Data
5.0 Supplemental References
1. Computational Methods

1.1. Crystal Structure Prediction (CSP) Methodology

Crystal structure prediction was performed using a quasi-random sampling procedure, as implemented in our in-house Global Lattice Energy Explorer (GLEE) software (version 2). Molecules were generated via a conformation search in Maestro using the OPLS2005 forcefield (no cutoff and a dielectric of 1.0) using a mixed torsional/low-mode search with a maximum of 10000 steps allowed. Conformers with an energy less than 35 kJ mol$^{-1}$ above the lowest energy structure and with an RMSD of greater than 0.3 Å were retained. Each unique conformer was re-optimized using density functional theory (DFT) at the B3LYP GD3BJ/6-311G** level of theory using Gaussian09. Redundant conformers with an RMSD < 0.3 Å were eliminated. These molecular geometries were then held rigid throughout crystal structure generation and lattice energy minimization.

Trial crystal structures were generated with one molecule in the asymmetric unit in each of the 25 most common space groups based on statistics gathered from looking at non-polymeric $Z' = 1$ organic molecular crystal structures reported in the Cambridge Structure Database. (International space group numbers: 1, 2, 4, 5, 7, 9, 13, 14, 15, 18, 19, 20, 29, 33, 43, 56, 60, 61, 76, 86, 88, 96, 145, 148, 169). With a target of 10000 valid minimizations per space group.

Initial crystal generation involves a low-discrepancy sampling of all structural variables within each space group: unit cell lengths, angles, molecular positions and orientations within the asymmetric unit. Space-group symmetry was then applied, and a geometric test was performed for overlap between molecules. Molecular clashes were removed by lattice expansion. Lattice energy calculations were performed with using DMACRYST2.1.0 with atom–atom repulsion and dispersion interactions modelled with the FIT intermolecular potential, in conjunction with a spline. Electrostatic interactions were modelled using an atomic multipole description of the molecular charge distribution (up to hexadecapole on all atoms) from the B3LYP/6-311G**-calculated charge density using a distributed multipole analysis (version 2). Charge–charge, charge–dipole and dipole–dipole interactions were calculated using Ewald summation; all other intermolecular interactions were summed to a cut-off between molecular centres-of-mass (15 Å for pyrene, 20 Å for TPhP and 25 Å for all others). For each structure multiple rigid lattice energy minimizations were performed. During the initial lattice energy minimization point-charges obtained from a MULFIT fit of atomic charges to the molecular electrostatic potential generated from the B3LYP/6-311G**-distributed multipole analysis atomic multipoles were used in conjunction with a pressure of 0.1 GPa and a VDW cutoff that was increased by 10 Å. For all subsequent steps, multipoles at the hexadecapole level were used without pressure. Minimization cycles were continued until at least 3 minimizations had been performed and the structure had stopped changing (as indicated by an F-value < 1).

Initial clustering within each conformer was performed within each individual spacegroup. Initially, all structures within a lattice energy window of 1.0 kJ / mol and within a density window of ±0.05 g cm$^{-3}$ from the reference structure were compared. This was performed for all unique structures. The initial clustering of the data was performed using powder x-ray diffraction patterns generated by platon (wavelength 0.7 Å and a two-theta range of 20°) using a constrained dynamic time-warping algorithm (with a constraint that the offset between patterns < 10 lots of 0.02 two-theta) to compare pairs of structures.
were considered a match when the Euclidean distance between the powder patterns (normalized by area) was < 10.0 (units?). This was followed by clustering structures within 1.0 kJ / mol and ±0.01 g cm\(^{-3}\) with the COMPACK\(^{[98]}\) algorithm using 30 molecule molecular clusters, a distance tolerance of 40 % and a maximum value of the RMSD30 of 0.4 Å. A final clustering across space groups was performed using the constrained dynamic time-warping algorithm powder XRD analysis using a lattice energy window of 1.0 kJ / mol and with a density window of ±0.01 g cm\(^{-3}\). No clustering was performed between conformers.

1.2. Property calculations

Accessible surface area calculations were performed using Zeo++,\(^{[99]}\) using the high accuracy setting with the channel and probe radius set to 1.2 Å using 10000 Monte-Carlo samples.

1.3. Structure matches

RMSD30 between experimental and computed structures were calculated with Mercury.\(^{[100]}\)

1.4. Stacking analysis

Planar stacking analysis was performed using bespoke code tailored for this purpose, using molecular planes of best fit (PBFs). The PBF of a molecule is calculated from the principal components of the molecule, taken via singular value decomposition (SVD) i.e. \( M = U \Sigma V^\ast \) where \( M \) is the matrix of atomic positions in the molecule. SVD yields the principal components of the molecule, which can be sorted by their corresponding singular values \( \Sigma \). The least significant principal component \( N \) corresponds to the plane normal, and once atomic positions are projected onto this plane via dot product \( N \cdot x \) a bounding rectangle may be evaluated using the remaining two principal components by finding the extrema of the atomic positions when projected onto this plane.

Overlap between molecular PBFs may be calculated by projecting one molecular PBF onto the plane of the other, and calculating the area of intersection of their corresponding quadrilaterals in this plane. More useful than the raw area, though, is the ratio of the area of intersection to the total area of the PBF. Thus, 'overlap' corresponds to:

\[
\begin{align*}
P_1' &= P_1 \cdot n_2 \\
A_\cap &= P_1' \cap P_2 \\
overlap &= \frac{A_\cap}{A_2}
\end{align*}
\]

Two PBFs \( P_1 \) and \( P_2 \) are said to be ‘stacked’ when they satisfy all of the following criteria:

1. The smallest angle between their plane normals \((n_1, n_2)\) is less than 25 degrees,
2. The distance between the two plane centroids is less than 8.0 Å,
3. The smallest angle between the vector from centroid \( c_1 \) to centroid \( c_2 (c_{12}) \) and normal \( n_1 \) is less than 30 degrees.
4. The closest distance between the two planes (i.e. projection of \( c_{12} \) in \( n_1 \)) is less than 6.0 Å.
5. The overlap (as specified above) between the two planes is more than 30\%.
The PBFS are then added to a 'stack' of other planes if that plane stacks with one of the existing planes (according to the above criteria) and it is facing approximately the same direction as the stack (the angle between the average of the plane normals in the stack and the candidate plane normal less than 30 degrees).

To what degree these stacks are facing the same direction (i.e. the co-directionality) of the stacks can then be measured by comparison of the average direction of the stacks, and crystal structures with no stacks, or where the maximum stack size was less than 4 were considered 'unstacked'.

For all of the stacking analysis, all molecules whose centroids were within 35 Å of the asymmetric unit centroid were considered. The code for this analysis is available upon request.

3.5. DFT potential calculations
The vertical ionization potential (IP) and electron affinity (EA) of TBAP, TPhP and TPyP were calculated using a ΔDFT approach. First the ground state geometry of each as an isolated molecule was optimized using the B97-3c approach by Grimme and co-workers.[64] Next the energy of each of the molecules in its neutral (E(N)), cation (E(N-1)) and anionic (E(N+1)) state were obtained from single-point calculations using the B3LYP functional[80–83] and the 6-31G** basis-set.[84,85] Finally, IP and EA were calculated from:

\[
\begin{align*}
\text{IP} &= -(E(N) - E(N-1)) - 4.44 \\
\text{EA} &= -(E(N+1) - E(N) - 4.44
\end{align*}
\]

Where all energies are in eV and the subtraction by 4.44 converts the calculated IP and EA from the vacuum to the standard hydrogen electrode scale. The B3LYP single-point calculations were performed using Gaussian16[86] and employed the PCM solvation model[87] to describe the aqueous environment of the molecules near the molecular solid – solution interface. The B97-3c calculations were performed using Turbomole 7.3[88] and employed no solvation model.

In the case of TBAP the IP and EA values were also calculated using an alternative strategy, starting from the crystal structure. Here we first the experimental crystal structure of TBAP is energy minimized in a periodic DFT calculation using the B97-3c approach as implemented in Crystal17.[89] Subsequently, three cluster models were cut out of the DFT optimized crystal structure, corresponding to one monomer, one monomer (1C) with a molecule above and below it, as well as the phenyl groups of the laterally adjacent molecules (1C+, see Fig. S49), and an analogous structure with a tetramer in the centre (4C+). The IP and EA values of the three cluster models were calculated in the same way as for the isolated molecules discussed above, other than that in the last two cases we used the ONIOM QM/MM approach[90] and described the molecule (fragments) around the monomer and tetramer using the UFF forcefield.[91]

2. Experimental Methods
All reagents were obtained from Sigma-Aldrich, TCI Europe, Fisher, Manchester Organics, Alfa Aesar, and Combi-Blocks and used as received. Anhydrous solvents were purchased from Acros Organics and used without further purification. All gases for sorption analysis
were supplied by BOC at a purity of \( \geq 99.999\% \). Reactions were carried out under nitrogen atmosphere using standard Schlenk techniques.

**Nuclear Magnetic Resonance Spectroscopy**

NMR spectra were recorded on a Bruker 400 NMR spectrometer at 400 MHz (\(^1\)H) and referenced against the residual \(^1\)H signal of the solvent.

**Inductively Coupled Plasma Mass Spectrometry**

Samples were collected after photocatalysis by filtration, dried and digested in HNO\(_3\) with a microwave (Perkin Elmer Microwave Titan) using standard analytical procedures. ICP-MS measurements were performed on a Perkin Elmer ICP MS NexION 2000 and analyzed using external calibrations with Ge as the internal standard.

**Thermogravimetric Analysis**

TGA measurements were carried out using a TA Q5000IR analyzer with an automated vertical overhead thermobalance. Samples were heated at a rate of 5 °C min\(^{-1}\) unless otherwise stated.

**Single crystal X-ray Diffraction**

Single crystal X-ray data sets were measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-K\(\alpha\) radiation, \(\lambda = 0.71073\) Å, Kappa 4-circle goniometer, Rigaku Saturn724+ detector); at beamline 11.3.1, Advanced Light Source, Berkeley, USA, using silicon monochromated synchrotron radiation (\(\lambda = 0.7749\) Å, PHOTON II CMOS detector); or at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromated synchrotron radiation (\(\lambda = 0.6889\) Å, Pilatus 2M detector). Rigaku frames were converted to Bruker compatible frames using the programme ECLIPSE. Absorption corrections, using the multi-scan method, were performed with the program SADABS. For synchrotron X-ray data, collected at Diamond Light Source (\(\lambda = 0.6889\) Å) data reduction and absorption corrections were performed with xia2. Structures were solved with SHELXD, SHELXT, or by direct methods using SHELXS, and refined by full-matrix least squares on \(|F|^2\) by SHELXL interfaced through the programme OLEX2. Unless stated, all non-H atoms were refined anisotropically, and unless stated H-atoms were fixed in geometrically estimated positions and refined using the riding model. Supplementary CIFs, that include structure factors, are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

**Powder X-ray diffraction**

PXRD patterns were collected in transmission mode on samples held on thin Mylar film in aluminum well plates on a Panalytical Empyrean diffractometer, equipped with a high throughput screening (HTS) XYZ stage, X-ray focusing mirror, and PIXcel detector, using Cu-K\(\alpha\) (\(\lambda = 1.541\) Å) radiation. Diffraction patterns were measured over 2\(\theta\) range in 0.013° steps, for 15-60 minutes. For indexing, samples were loaded into borosilicate glass capillaries and PXRD patterns were recorded in transmission mode on a Panalytical Empyrean diffractometer, equipped with a sample spinner to improve powder averaging.

**Gas Sorption Analysis**

Surface areas were measured by nitrogen sorption at 77.3 K. Powder samples were degassed offline at 120 °C for 15 h, followed by degassing on the analysis port under vacuum, also at 100 °C. Isotherm measurements were performed using a Micromeritics 3flex surface
characterization analyzer, equipped with a *Cold-Edge technologies* liquid helium cryostat chiller unit for temperature control. For TBA\(\text{P-}\alpha\), BET surface areas were calculated over the relative pressure range 0.02 – 0.06. For TFP\(\text{PhP}\), the BET surface area was calculated over the relative pressure range 0.05 – 0.25.

**UV-Vis Measurements**

The UV-visible absorption spectra of the materials were recorded on a Shimadzu UV-2550 UV-vis spectrometer as powders in the solid-state. The band-gap of the materials was calculated via \(E (\text{eV}) = \frac{1243.125}{\lambda_g} (\text{nm})\). The solution spectra were recorded on an Agilent Cary 5000 UV-Vis-NIR spectrometer in DMSO solution.

**Water Sorption**

Water vapor isotherms were determined at 293 K using an IGA gravimetric adsorption apparatus (Hiden Isochema) with an anti-condensation system carried out in an ultrahigh vacuum system equipped with a diaphragm and turbo pumps.

**Scanning Transmission Electron Microscope**

STEM images were recorded on a Tescan S8000G with a TEM detector. Samples were dropped onto Agar Scientific holey carbon / Cu TEM grids from water suspensions. Unless otherwise stated images were recorded at 20 KeV with a current of 125 pA. Images were recorded in both Bright Field (BF) mode and High Angle Dark Field (HADF) mode.

**Static light scattering**

SLS measurements were performed on a Malvern Mastersizer 3000. Sample was dispersed in water by 10 minutes of ultrasonication and the resultant suspensions were injected into a stirred Hydro SV quartz cell, containing more water, to give a laser obscuration of 5 – 12%. Particle sizes were fitted according to Mie theory, using the Malvern ‘General Purpose’ analysis model, for non-spherical particles. A sample refractive index of 1.59, sample absorbance of 0.1 and solvent refractive index of 1.333 were used for fitting.

**Dynamic light scattering**

DLS measurements were performed on a Malvern Zetasizer Nano Particle Sizer, at 25 °C, in water and fitted using the Malvern ‘Generic latex’ standard operating procedure with solvent refractive index of 1.330 and viscosity 0.8872 cP.

**Synthesis of TBA\(\text{P}\):** TBA\(\text{P}\) was synthesized according to literature routes.\(^{[22]}\) Anal. Caled for \(\text{C}_{44}\text{H}_{26}\text{O}_8\): C, 77.41; H, 3.84; Found: C, 76.06; H, 3.80. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm}) = 8.20 (\text{s}, 4\text{H}), 8.15 (\text{d}, 8\text{H}, J = 8.0 \text{ Hz}), 8.07 (\text{s}, 2\text{H}), 7.84 (\text{d}, 8\text{H}, J = 8.0 \text{ Hz})\). HR-MS Calcd for \([\text{C}_{44}\text{H}_{26}\text{O}_8 + \text{H}]^{+}\): m/z = 683.1706, 684.1740, 685.1771; found: m/z = 683.1716, 684.1752, 685.1779.

**Synthesis of TPh\(\text{P}\):** TPh\(\text{P}\) was synthesized according to a literature route.\(^{[17]}\) Anal. Caled for \(\text{C}_{40}\text{H}_{26}\): C, 94.83; H, 5.17; Found: C, 94.36; H, 5.04. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm}) = 8.18 (\text{s}, 4\text{H}), 7.99 (\text{s}, 2\text{H}), 7.72 (\text{d}, J = 7.5 \text{ Hz}, 8\text{H}), 7.62 (\text{t}, J = 7.5 \text{ Hz}, 8\text{H}), 7.54 (\text{t}, J = 7.5 \text{ Hz}, 4\text{H})\).

**Synthesis of TPy\(\text{P}\):** 1,3,6,8-Tetrabromopyrene (1.04 g, 2 mmol), 4-pyridinylboronic acid (983 mg, 8 mmol), DMF (200 mL) and \(\text{K}_2\text{CO}_3\) (50 mL) were added to a flask and degassed by \(\text{N}_2\) bubbling for 30 minutes. \(\text{Pd}(\text{Ph}_3)\_4\) (40 mg, 0.035 mmol) was added and the solution was degassed for a further 10 minutes before heating to 145 °C for 48 hours. After cooling the
mixture was poured into water (1 L) and stirred for 30 minutes. The precipitate was collected by filtration and washed with water (100 mL), methanol (100 mL) and dichloromethane (100 mL) before drying under vacuum. The product was obtained as a green solid (986 mg, 1.92 mmol, 96 %). Anal. Calcd for C_{36}H_{22}N_{4}: C, 84.68; H, 4.34; N, 10.97; Found: C, 84.37; H, 4.31; N, 10.73. 1H NMR (400 MHz, Acetic acid-d_4): δ(ppm) = 9.08 (d, J 6.0 Hz, 8H), 8.41 (s, 4H), 8.36 (s, 2H), 8.17 (d, J 6.0 Hz, 8H). HR-MS Calcd for [C_{36}H_{22}N_{4} + H]^+: m/z =511.1923, 512.1954, 513.1985; found: m/z = 511.1922, 512.1957, 513.1993.

**Crystallization of Other TBAP Phases**

500 mg of as-synthesized TBAP were covered by DMF, N,N-dimethylacetamide, or N-methyl-2-pyrrolidone (40 mL) in a large vial. The mixture was sonicated for 10 min. and left overnight so all remaining undissolved material settled at the bottom of the vial. The supernatant solutions from each dipolar aprotic solvent were filtered into 5 2.5 mL vials using a 0.45 µm PTFE syringe filter to remove any particulates. The vials were closed with a plastic cap that each had a whole bore into it. These 5 vials from each solvent were then placed into larger 15 mL vials with 2 mL of each anti-solvent (CHCl_3, acetone, THF, 1,4-dioxane, ethyl acetate) and were then capped tightly. Vapor diffusion of the anti-solvents into the TBAP solutions were carried out for several days until the vials were nearly full of solvent and in most cases, crystal growth had occurred. These crystals were then analyzed by single crystal x-ray diffraction. For unit cell and full collection results, see Table S5. The solvents N-methyl-2-pyrrolidone and N,N-dimethylacetamide lead to 1:4 solvates, which featured complementary hydrogen bonding motifs between the crystallization solvent and carboxylic acid group of TBAP (SI, Fig. S16-17), rather than TBAP-α, but second TBAP polymorphs can also be isolated by heating a DMF/EtOH solution at 90 °C.[109]

**Time-Correlated Single Photon Counting Experiments**

TCSPC experiments were performed on an Edinburgh Instruments LS980-D2S2-STM spectrometer equipped with picosecond pulsed LED excitation sources and a R928 detector, with a stop count rate below 3%. An EPL-375 diode (λ = 370.5 nm, instrument response 100 ps, fwhm) was used as the light source. Suspensions were prepared by ultrasonicing the materials in water. The instrument response was measured with colloidal silica (LUDOX HS-40, Sigma-Aldrich) at the excitation wavelength. Decay times were fitted in the FAST software using suggested lifetime estimates.

**Synthesis of Pt Nanoparticles**

Pt nanoparticles were synthesized according to a modified literature procedure.[110] H_2PtCl_6 (0.9 mL, 8 wt. % solution) was added to water (36 mL). Water (464 mL) was heated to 95 °C and the H_2PtCl_6 solution was added with stirring followed by 0.05 wt. % citric acid / 1 wt. % trisodium citrate dihydrate aqueous solution (11 mL) followed by sodium borohydride (37 mg) in 0.05 wt.% citric acid / 1 wt. % trisodium citrate dihydrate aqueous solution (11 mL). The solution was stirred at 100 °C for 10 minutes before cooling to room temperature.

**Hydrogen Evolution Experiments**

A flask was charged with the photocatalyst (25 mg), aqueous ascorbic acid solution (0.1 M, 25 mL), and sealed with a septum. The resulting suspension was ultrasonicated until the photocatalyst was dispersed before degassing thoroughly by N_2 bubbling for 30 minutes. The stirred reaction mixture was illuminated with a 300 W Newport Xe light source (Model: 6258, Ozone free) for the time specified at a fixed distance under atmospheric pressure. The Xe light source was cooled by water circulating through a metal jacket. Gas samples were taken with a gas-tight syringe and run on a Bruker 450-GC gas chromatograph equipped with
a Molecular Sieve 13X 60-80 mesh 1.5 m × \( \frac{1}{8} \)” × 2 mm ss column at 50 °C with an argon flow of 40 mL min\(^{-1}\). Hydrogen was detected with a thermal conductivity detector, referencing against standard gases with known concentrations of hydrogen. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. The rates were determined from a linear regression fit and the error is given as the standard deviation of the amount of hydrogen evolved. No hydrogen evolution was observed for aqueous ascorbic acid solutions under \( \lambda > 420 \) nm illumination in absence of a photocatalyst. Where stated, platinum was added to the photocatalyst by either in situ photodeposition of H\(_2\)PtCl\(_6\) (8 wt. % solution in water) or pre-loaded onto samples by sonication in aqueous suspension of Pt nanoparticles followed by evaporation of water under reduced pressure.

**Carbon Monoxide Production Experiments**

Borosilicate crimp top vials (Agilent Technologies, 10 mL, 23 × 46 mm) were charged with 5 mg of the photocatalyst and transferred to a Chemspeed Accelerator SWING platform for liquid transfer. Degassed aqueous ascorbic acid solution (0.1 mL) and degassed stock solution of H\(_2\)PtCl\(_6\) were loaded into the system and the whole system was flushed with nitrogen for 4 hours. Liquids were automatically dispensed into the vials and the vials were capped under inert conditions by the system. The vials were then ultrasonicated for 10 minutes before illumination with an Oriel Solar Simulator 94123A (1 Sun, classification IEC 60904-9 2007 spectral match A, uniformity classification A, temporal stability A, 1600 W Xenon lamp, 12 × 12 in. output beam, Air ass 1.5G filter, 350-1000 nm) and continuous dispersion of the photocatalyst on a Stuart roller bar SRT9.. After photocatalysis, the samples were measured on a Shimadzu GC-2010 plus equipped with a BID detector using a HS-20 headspace auto-sampler and sampling from the headspace of the vial. Helium was used as the carrier-gas and the gases were separated on a 5 Å Molseive capillary column. The gas amounts were calculated by referencing against standard gases with known concentrations of hydrogen and CO. Hydrogen and CO dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen and CO was neglected in the calculations.

**Deuterium Labelling Experiments**

high-density acid (440 mg) was dissolved in D\(_2\)O (25 mL). TBAP-\( \alpha \) (25 mg) was dispersed in this solution by ultrasonication before degassing thoroughly by N\(_2\) bubbling for 30 minutes. The mixture was placed in a quartz vessel and sealed in a reactor under nitrogen. The sample was illuminated with a 300 W Newport Xe light source (Model: 6258, Ozone free) for the time specified at a fixed distance under atmospheric pressure. The Xe light source was cooled by water circulating through a metal jacket. Gas samples from the 1.3 mL headspace of the reactor were analyzed at the time periods specified by a customized HPR-70 batch sampling system from Hiden Analytical using a HAL3F/301 triple filter Mass Spectrometer with a Faraday detector for analysis.

**External Quantum Efficiencies**

EQEs were measured using LEDs controlled by an IsoTech IPS303DD power supply. The platinum loaded photocatalysts (12 mg) were suspended in aqueous ascorbic acid (0.1 M, 8 mL). An area of 8 cm\(^2\) was illuminated and the light intensity was measured with a ThorLabs S120VC photodiode power sensor controlled by a ThorLabs PM100D Power and Energy Meter Console. The external quantum efficiencies were estimated using the equation below:
\[ EQE = 2 \times \frac{\text{moles of hydrogen evolved}}{\text{moles of incident photons}} \times 100\% \]

**Photocurrent Measurements**

Chronoamperometric measurements were carried out on an EC-Lab SP-200 (Bio-Logic Science Instruments SAS) in a three-electrode-cell system with a FTO coated glass slide as the working electrode, Ag/AgCl\(_2\) electrode (-0.35 V vs standard hydrogen electrode) as the reference electrode, platinum wire as the counter electrode. The photocatalyst was dispersed in acetone (1 mg mL\(^{-1}\)) and 100 µL were added to 100 µL of Nafion 117 (5 wt. % in a mixture of lower aliphatic alcohols and water). This mixture (30 µL) was drop-casted onto an FTO glass working electrode. The sample was then dried under in a fume hood overnight at room temperature. A three-electrode-cell system containing an aqueous sodium sulfate solution (0.01 M) was purged with N\(_2\) for 10 minutes. The measurement was performed by illuminating the front of the working electrode with a solar simulator (1 Sun, Oriel Instruments LSH-7320 (IEC ABA certified)).

### 3. Crystal Structure Prediction Data

**Table S1**: Intramolecular energies of unique TPhP conformers after gas-phase optimization at B3LYP/6-311G** GD3BJ level of theory

| Structure | Conformer | B3LYP/6-311G** energy (Hartree) | GD3BJ optimized energy (Hartree) | \( E_{\text{Intra Rel}} \) (kJ / mol) |
|-----------|-----------|-------------------------------|---------------------------------|-----------------------------|
| TPhP      | 2         | -1540.5132178                 |                                 | 0.00                        |
| TPhP      | 3         | -1540.5128241                 |                                 | 1.03                        |
| TPhP      | 1         | -1540.5127850                 |                                 | 1.14                        |
| TPhP      | 4         | -1540.5121309                 |                                 | 2.85                        |

**Table S2**: Intramolecular energies of unique TPyP conformers after gas-phase optimization at B3LYP/6-311G** GD3BJ level of theory

| Structure | Conformer | B3LYP/6-311G** energy (Hartree) | GD3BJ optimized energy (Hartree) | \( E_{\text{Intra Rel}} \) (kJ / mol) |
|-----------|-----------|-------------------------------|---------------------------------|-----------------------------|
| TPyP      | 2         | -1604.6599613                 |                                 | 0.00                        |
| TPyP      | 1         | -1604.6595763                 |                                 | 1.01                        |
| TPyP      | 3         | -1604.6595299                 |                                 | 1.13                        |
| TPyP      | 4         | -1604.6589253                 |                                 | 2.72                        |
**Table S3**: Intramolecular energies of unique TBAP conformers after gas-phase optimization at B3LYP/6-311G**\(^*\) GD3BJ level of theory

| Structure | Conformer | B3LYP/6-311G** energy (Hartree) | GD3BJ optimized | \(E_{\text{Intra Rel}}\) (kJ / mol) |
|-----------|-----------|---------------------------------|-----------------|-------------------------------|
| TBAP      | 4         | -2295.0673444                   |                 | 0.00                          |
| TBAP      | 5         | -2295.0673436                   |                 | 0.00                          |
| TBAP      | 8         | -2295.0673403                   |                 | 0.01                          |
| TBAP      | 2         | -2295.0673379                   |                 | 0.02                          |
| TBAP      | 21        | -2295.0672834                   |                 | 0.16                          |
| TBAP      | 26        | -2295.0672705                   |                 | 0.19                          |
| TBAP      | 24        | -2295.0672304                   |                 | 0.30                          |
| TBAP      | 25        | -2295.0669601                   |                 | 1.01                          |
| TBAP      | 30        | -2295.0669329                   |                 | 1.08                          |
| TBAP      | 33        | -2295.0669202                   |                 | 1.11                          |
| TBAP      | 36        | -2295.0669064                   |                 | 1.15                          |
| TBAP      | 34        | -2295.0669051                   |                 | 1.15                          |
| TBAP      | 1         | -2295.0668732                   |                 | 1.24                          |
| TBAP      | 45        | -2295.0668693                   |                 | 1.25                          |
| TBAP      | 13        | -2295.0668528                   |                 | 1.29                          |
| TBAP      | 6         | -2295.0668503                   |                 | 1.30                          |
| TBAP      | 46        | -2295.0668453                   |                 | 1.31                          |
| TBAP      | 14        | -2295.0668338                   |                 | 1.34                          |
| TBAP      | 19        | -2295.0668242                   |                 | 1.37                          |
| TBAP      | 22        | -2295.0668203                   |                 | 1.38                          |
| TBAP      | 3         | -2295.0668157                   |                 | 1.39                          |
| Crystal Structure | Expt Structure | RMSD30 (Å) | E_rel (kJ / mol) |
|-------------------|---------------|------------|-----------------|
| "100120030197931" | TPhP          | 0.464      | 26.6            |
| "102420030139213" | TBAP          | 1.016      | 57.2            |
| "100220030072916" | TPyP          | 0.673      | 0.0             |

**Figure S1.** Packing diagrams of the a) lowest and b) second lowest energy crystal structures in the spike centered at 0.75 g/cm3 on the TBAP CSP landscape.
4. Experimental Data

4.1 Material Characterization

Figure S2. Overlay of the crystal structures of the predicted structure of TPhP (red) with the 100K single crystal structure (blue).
Figure S3. (a) Displacement ellipsoid plot from the single crystal structure, TPyP-α; TPyP shown in entirety along [100]; ellipsoids displayed at 50 % probability level. Crystal packing in the single crystal structure, TPyP-α, showing interdigitated columnar packing of TPyP molecules along (b) [100] and (c) [010]. Crystal data for TPyP-α: CCDC # 1919802; Formula C_{36}H_{22}N_{4}; M = 510.57, monoclinic P2_1/n, yellow plate shaped crystal; a = 3.9510(2) Å, b = 10.9411(7) Å, c = 26.7651(14) Å, β = 91.814(5)°; V = 1156.43(11) Å³; ρ = 1.466 g/cm³; Z = 2; μ(Mo-Kα) = 0.088 mm⁻¹; F (000) = 532; crystal size = 0.27 x 0.08 x 0.06 mm; T = 100(2)K; 2347 unique reflections measured (1.522 < θ < 26.416), 2031 (I > 2σ(I)); R_1 = 0.0704 for observed and R_I = 0.0813 for all reflections; wR_2 = 0.1819 for all reflections; max/min difference electron density = 0.413 and -0.294 e·Å⁻³; data/restraints/parameters = 2347/0/182; GOF = 1.118. The X-ray crystal structure was refined as a two-component twin with a HKLF 5 file format and BASF refined to 0.106. X-ray data was detwinned using the TwinRotMat function Platon.
Figure S4. Overlay of the crystal structures of the predicted structure of TPyP (red) with the 100K single crystal structure (blue). The view is down the crystallographic a axis. The unit cell of the 100K single crystal structure is shown, with b-axis in green and c-axis in blue.
Figure S5. $^1$H NMR spectrum (400 MHz, DMSO-d$_6$) of TBAP after isolation. The inset shows the aromatic region with TBAP [8.20 (s, 4H, H$_{4,5,9,10}$), 8.15 (d, 8H, $^3$J$_{HH}$ = 8.0 Hz, H (ortho to –COOH)), 8.07 (s, 2H, H$_{2,7}$), 7.84 (d, 8H, $^3$J$_{HH}$ = 8.0 Hz, H (meta to –COOH)) ppm]. The signals at 2.50 and 3.33 ppm are DMSO and H$_2$O, respectively.
Figure S6. Displacement ellipsoid plot from the single crystal structure, TBAP·3.75(CHCl₃)·3(DMF); TBAP shown in entirety along [001] (left) and [010] right. Ellipsoids displayed at 50 % probability level and solvent has been omitted for clarity. Crystal data for TBAP·3(DMF)·3.75(CHCl₃): CCDC # 1919807: Formula C₄₄H₂₆O₈·3.75(CHCl₃)·3(C₃H₇NO); \( M = 1293.84, \) monoclinic \( C2/m, \) yellow needle shaped crystals; \( a = 29.369(3) \) Å, \( b = 27.773(3) \) Å, \( c = 3.8273(4) \) Å, \( \beta = 93.926(3)^\circ; \) \( V = 3114.5(6) \) Å³; \( \rho = 1.369 \) g/cm³; \( Z = 2; \) \( \mu (\text{Mo-K}_\alpha) = 0.190 \) mm⁻¹; \( F(000) = 1355; \) crystal size = 0.09 x 0.09 x 0.08 mm; \( T = 200(2) \) K; 9835 reflections measured (\( 2.781 < \theta < 26.367, \)) 3253 unique (\( R_{\text{int}} = 0.0383, \)) 2566 (\( I > 2\sigma(I) \)); \( R_1 = 0.0664 \) for observed and \( R_1 = 0.0761 \) for all reflections; \( wR_2 = 0.2442 \) for all reflections; max/min difference electron density = 0.59 and -0.27 e·Å⁻³; data/restraints/parameters = 3253/10/150; GOF = 1.156. This molecule was refined with OMIT cards for 2 reflections (110 and 530). In the crystal structure, there are large 1-D voids that contain disordered electron density that could not be accurately modelled. It was therefore necessary to use the SQUEEZE routine in Platon during the final refinement cycles.[112,113] SQUEEZE located two 649 Å³ voids which each had a disordered electron count of 289 e⁻. As a result, 6 DMF and 6 CHCl₃ solvent molecules were tentatively added to the unit cell atom count. Disordered electron density that could be located was modelled as severely disordered CHCl₃. The disordered CHCl₃ molecules were refined with bond distance restraints (DFIX, DANG and SADI in SHELX).
Figure S7. TGA of TBAP·x(DMF)·y(CHCl₃) after isolation.
Figure S8. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of TBAP·x(DMF)·y(CHCl$_3$) after isolation. The inset shows the aromatic region with TBAP [8.22 (s, 4H, PyH), 8.17 (d, 8H, $^3$J$_{HH}$ = 8.0 Hz, ArH (ortho to –COOH)), 8.09 (s, 2H, PyH), 7.86 (d, 8H, $^3$J$_{HH}$ = 8.0 Hz, ArH (meta to –COOH)) ppm], and DMF (7.96 ppm (-CHO)) signals. The signals at 2.50 and 3.33 ppm are H$_2$O and DMSO, respectively.
Figure S9. TGA of TBAP: x(Acetone) after solvent exchange of TBAP: x(DMF): y(CHCl₃) with acetone 10 times.
Figure S10. $^1$H NMR spectrum (DMSO-d$_6$) of TBAP·x(Acetone) after solvent exchange of TBAP·x(DMF)·y(CHCl$_3$) for 5 days. The integrated signal at 2.09 ppm corresponds to 2.61 eq. of acetone per TBAP. The signals at 2.50 and 3.33 ppm are H$_2$O and DMSO, respectively.
Figure S11. $^1$H NMR spectrum (DMSO-d$_6$) of activated TBAP after heating TBAP·x(Acetone) at 120°C for 2 hours showing no residual solvent remaining. The signals at 2.50 and 3.33 ppm are H$_2$O and DMSO, respectively.
Figure S12. Displacement ellipsoid plot from the single crystal structures of TBAP-α, recorded at 200 K, 300 K and 400 K; TBAP is shown in entirety along [001] and ellipsoids are displayed at 50% probability level. Crystal data for TBAP (200 K): CCDC # 1919804; Formula C_{44}H_{26}O_{8}; M = 682.69, monoclinic C2/m, yellow needle shaped crystals; a = 29.036(4) Å, b = 28.538(4) Å, c = 3.8714(5) Å, β = 91.979(8)°; V = 3206.0(7) Å³; ρ = 0.707 g/cm³; Z = 2; µ(λ = 0.7749 Å) = 0.058 mm⁻¹; F (000) = 708; crystal size = 0.160 x 0.050 x 0.050 mm; T = 200(2) K; 11767 reflections measured (1.53 < θ < 27.98), 3040 unique (R_int = 0.0518), 3040 (I > 2σ(I)); R₁ = 0.0442 for observed and R₁ = 0.0504 for all reflections; wR₂ = 0.1356 for all reflections; max/min difference electron density = 0.23 and -0.25 e•Å³; data/restraints/parameters = 3040/0/120; GOF = 1.071. This molecule was refined with OMIT cards for 2 reflections (110 and 530). Crystal data for TBAP (300 K): CCDC # 1919809; Formula C_{44}H_{26}O_{8}; M = 682.69, monoclinic C2/m, yellow needle shaped crystals; a = 29.09(4) Å, b = 28.61(4) Å, c = 3.928(6) Å, β = 91.87(2)°; V = 3268.2(7) Å³; ρ = 0.694 g/cm³; Z = 2; µ(λ = 0.7749 Å) = 0.057 mm⁻¹; F (000) = 708; crystal size = 0.160 x 0.050 x 0.050 mm; T = 300(2) K; 11570 reflections measured (1.53 < θ < 28.00), 3061 unique (R_int = 0.0714), 2583 (I > 2σ(I)); R₁ = 0.0481 for observed and R₁ = 0.0559 for all reflections; wR₂ = 0.1482 for all reflections; max/min difference electron density = 0.20 and -0.24 e•Å³; data/restraints/parameters = 3061/0/120; GOF = 1.079. This molecule was refined with OMIT cards for 2 reflections (110 and 530). Crystal data for TBAP (400 K): CCDC # 1919805; Formula C_{44}H_{26}O_{8}; M = 682.69, monoclinic C2/m, yellow needle shaped crystals; a = 29.16(9) Å, b = 28.69(8) Å, c = 3.998(13) Å, β = 91.92(5)°; V = 3343(17) Å³; ρ = 0.678 g/cm³; Z = 2; µ(λ = 0.7749 Å) = 0.056 mm⁻¹; F (000) = 708; crystal size = 0.160 x 0.050 x 0.050 mm; T = 400(2) K; 10220 reflections measured (1.529 < θ < 27.999), 3134 unique (R_int = 0.0442), 2480 (I > 2σ(I)); R₁ = 0.0375 for observed and R₁ = 0.0442 for all reflections; wR₂ = 0.1746 for all reflections; max/min difference electron density = 0.18 and -0.20 e•Å³; data/restraints/parameters = 3134/0/120; GOF = 1.111. This molecule was refined with OMIT cards for 2 reflections (110 and 530).
Figure S13. Crystal packing similarity search performed using the DMF/CHCl₃ solvated TBAP crystal structure recorded at 200 K (blue), and the desolvated TBAP-α recorded at 200 K (red); shown along b (left) and c (right); H atoms omitted for clarity. A close similarity in the eclipsed π-π stacking arrangement on pyrene cores and relative orientation of benzoic acid substituents is observed in these two structures.
Figure S14. (a) Extended crystal packing from the single crystal structure of TBAP at 200 K after solvent exchange by the $b$ axis. In the structure, the pyrene cores are oriented into offset, parallel stacks, separated by 3.48 Å. All hydrogen-bonding pairs from carboxylic acid groups are at a distance of 1.79 Å. (b) Crystal packing diagram of TBAP at 200 K after solvent exchange down the $c$ axis showing the 1-D empty pore structure. The empty, solvent-accessible space (1.4 Å probe radius, 0.1 Å grid spacing) makes up approximately 38.0% of the unit cell volume [$1219 \text{ Å}^3 (V_{\text{cell}} = 3206 \text{ Å}^3)$].
Figure S15. Powder diffraction profiles of all TBAP phases: TBAP-xCHCl₃-yDMF (generated from 100 K SCXRD data), TBAP-α at 200 K (generated from solvent exchanged 200 K SCXRD data), and empty TBAP-α post-sorption experiments (298 K, experimental data).
Table S5. Unit cell parameters for single crystals of TBAP, crystallized from DMF using different anti-solvents.

| Solvent system        | DMF/CHCl₃   | DMF/Acetone | DMF/THF    | DMF/Dioxane | DMF/Ethylacetate |
|-----------------------|-------------|-------------|------------|-------------|------------------|
| **Space group**       | C2/m        | C2/m        | C2/m       | C2/m        | C2/m             |
| **a (Å)**             | 29.036(4)   | 29.5275(2)  | 29.623(2)  | 29.5282(3)  | 29.5810(2)       |
| **b (Å)**             | 28.538(4)   | 27.2338(3)  | 27.1349(10)| 27.3644(5)  | 27.1691(5)       |
| **c (Å)**             | 3.8714(5)   | 3.764       | 3.7664(2)  | 3.7650(1)   | 3.7637(1)        |
| **α(°)**              | 90          | 90          | 90         | 90          | 90               |
| **β(°)**              | 91.979(8)   | 94.993(1)   | 94.810(5)  | 94.460(1)   | 94.915(1)        |
| **γ(°)**              | 90          | 90          | 90         | 90          | 90               |
| **V (Å³)**            | 3206.0(7)   | 3015        | 3017       | 3033        | 3014             |
| **T (K)**             | 200         | 100         | 100        | 100         | 100              |
| **Collection**        | Full        | Unit Cell   | Unit Cell  | Unit Cell   | Unit Cell        |
|                       | collection  |             |            |             |                  |
Figure S16. Displacement ellipsoid plot from the single crystal structures of TBAP∙4(DMA), TBAP is shown in entirety along [001], and ellipsoids are displayed at 50% probability level. Crystal data for TBAP∙4(DMA) (100 K): CCDC # 1919806; Formula 4(C₄₄H₂₆NO), C₄₄H₂₆O₈; M = 1031.13, triclinic P₁, yellow needle shaped crystals; a = 7.1765(2) Å, b = 12.6174(4) Å, c = 14.4481(4) Å, α = 98.264(3)º, β = 92.099º, γ = 99.768(3)º; V = 1273.40(7) Å³; ρ = 1.345 g/cm³; Z = 1; μ(λ = 0.6889 Å) = 0.088 mm⁻¹; F (000) = 546; crystal size = 0.063 x 0.027 x 0.020 mm; T = 100(2)K; 15655 reflections measured (1.383 < θ < 25.503), 4996 unique (R_int = 0.0680), 3639 (I > 2σ(I)); R₁ = 0.0636 for observed and R₁ = 0.0821 for all reflections; wR₂ = 0.2011 for all reflections; max/min difference electron density = 0.42 and -0.25 e•Å³; data/restraints/parameters = 4996/0/351; GOF = 1.044.
Figure S17. Displacement ellipsoid plot from the single crystal structures of TBAP-4(NMP), TBAP is shown in entirety along [001], and ellipsoids are displayed at 50% probability level. Crystal data for TBAP-4(NMP) (100 K): CCDC # 1919808; Formula 4(C₅H₉NO), C₄₄H₂₆O₈; M = 1079.17, triclinic P₁, yellow needle shaped crystals; a = 7.2283(3) Å, b = 13.0283(6) Å, c = 14.3638(7) Å, α = 99.572(4)°, β = 91.962(4)°, γ = 100.785(4)°; V = 1307.3(1) Å³; ρ = 1.371 g/cm³; Z = 1; μ(λ = 0.6889 Å) = 0.088 mm⁻¹; F(000) = 570; crystal size = 0.07 x 0.01 x 0.01 mm; T = 100(2)K; 13145 reflections measured (1.397 < θ < 22.502), 3665 unique (R_int = 0.0988), 2466 (I > 2σ(I)); R₁ = 0.0835 for observed and R₁ = 0.1137 for all reflections; wR² = 0.2516 for all reflections; max/min difference electron density = 0.77 and -0.25 e•Å³; data/restraints/parameters = 3665/0/365; GOF = 1.069.
Figure S18. TGA plot for TBAP-α, recorded after activation at 120 °C under dynamic vacuum. TGA was recorded under N₂ gas flow and the sample was heated at a ramp rate 10 °C/min.
Figure S19. N₂ sorption isotherms for batches 1, 2, and 3 of TBAP-α, recorded at 77 K (closed symbol for adsorption points, open symbols for desorption points). The apparent $S_A^{BET}$ for TBAP-α batches 1, 2, and 3 are 2001, 2270, 2074 m² g⁻¹, respectively.
Figure S20. Le Bail fit for TBAP-α batch 1. Final observed (red), calculated (black) and difference (blue) PXRD profiles for Le Bail refinement ($R_{wp} = 7.936\%$, $R_p = 5.452\%$, $\chi^2 = 2.598$) of TBAP-α recorded post-gas sorption ($a = 29.219(6) \text{ Å}$, $b = 28.591(5) \text{ Å}$, $c = 3.913(1) \text{ Å}$; $\beta = 91.86(2)^\circ$; $V = 3267(1) \text{ Å}^3$, $C2/m$).
Figure S21. Le Bail fit for TBAP-α batch 2. Final observed (red), calculated (black) and difference (blue) PXRD profiles for Le Bail refinement ($R_{wp} = 6.939\%$, $R_p = 4.507\%$, $\chi^2 = 6.621$) of TBAP-α batch 2, recorded after activation of the acetone solvate at 120 °C under dynamic vacuum ($a = 29.055(2)$ Å, $b = 28.594(1)$ Å, $c = 3.9268(2)$ Å; $\beta = 91.89(1)^\circ$; $V = 3259.7 (3)$ Å$^3$, $C2/m$).
Figure S22. Le Bail fit for activated TBAP-α batch 3. Final observed (red), calculated (black) and difference (blue) PXRD profiles for Le Bail refinement ($R_{wp} = 7.598\%$, $R_p = 4.686\%$, $\chi^2 = 7.248$) for TBAP-α batch 3, recorded after activation of the acetone solvate at 120 °C under dynamic vacuum ($a = 29.078(3)$ Å, $b = 28.606(2)$ Å, $c = 3.9240(2)$ Å; $\beta = 91.90(2)$°; $V = 3262.3(4)$ Å³, $C2/m$).
### 4.2 Photocatalysis experiments

| Material          | Scavenger | pH\textsuperscript{a} | Pt Added (wt. %) | Pt Measured\textsuperscript{b} (wt. %) | HER\textsuperscript{c} (µmol h\textsuperscript{-1} g\textsuperscript{-1}) |
|-------------------|-----------|------------------------|------------------|-----------------------------------------|---------------------------------------------------------------|
| TBAP Amorphous    | Ascorbic Acid | 2.6                    | None             | < 0.01                                  | < 0.1                                                          |
| TBAP-α Batch 1    | Ascorbic Acid | 2.6                    | None             | < 0.01                                  | 59                                                            |
| TBAP Amorphous    | Ascorbic Acid | 2.6                    | 1\textsuperscript{d} | 0.24 ± 0.01                            | 6                                                             |
| TBAP-α Batch 1    | Ascorbic Acid | 2.6                    | 4\textsuperscript{d} | 1.27 ± 0.01                            | < 0.1                                                          |
| TBAP Amorphous    | Ascorbic Acid | 2.6                    | 4\textsuperscript{d} | 1.54 ± 0.12                            | 591                                                           |
| TBAP-α Batch 2    | Ascorbic Acid | 2.6                    | 4\textsuperscript{d} | 1.01 ± 0.01                            | 837                                                           |
| TBAP-α Batch 3    | Ascorbic Acid | 2.6                    | 4\textsuperscript{d} | 1.12 ± 0.02                            | 829                                                           |
| TBAP Amorphous    | Ascorbic Acid | 2.6                    | 1\textsuperscript{e} | 0.55 ± 0.01                            | 50                                                            |
| TBAP-α Batch 1    | Ascorbic Acid | 2.6                    | 1\textsuperscript{e} | 0.46 ± 0.01                            | 813                                                           |
| TPhP-α            | Ascorbic Acid | 2.6                    | 1\textsuperscript{d} | 0.54 ± 0.01                            | 2                                                             |
| TPyP-α\textsuperscript{f} | Ascorbic Acid | 2.6                    | 1\textsuperscript{d} | -                                       | 18                                                            |
| TBAP Amorphous    | Ascorbic Acid | 7                      | 1\textsuperscript{d} | -                                       | 3108                                                          |
| TBAP-α Batch 1    | Ascorbic Acid | 7                      | 1\textsuperscript{d} | -                                       | 156                                                           |
| TPhP-α            | Ascorbic Acid | 7                      | 1\textsuperscript{d} | 0.60 ± 0.02                            | 3                                                             |
| TPyP-α            | Ascorbic Acid | 7                      | 1\textsuperscript{d} | 0.91 ± 0.01                            | < 0.1                                                          |
| TBAP-α Batch 1\textsuperscript{f} | Triethylamine | 11.5                   | 1\textsuperscript{d} | -                                       | < 0.1                                                          |
| TPhP-α            | Triethylamine | 11.5                   | 1\textsuperscript{d} | 0.99 ± 0.01                            | 6                                                             |
| TPyP-α            | Triethylamine | 11.5                   | 1\textsuperscript{d} | 0.94 ± 0.02                            | 40                                                            |
| TBAP-α Batch 1    | Triethylamine | 7                      | 1\textsuperscript{d} | 0.18 ± 0.01                            | < 0.1                                                          |
| TPhP-α            | Triethylamine | 7                      | 1\textsuperscript{d} | 0.89 ± 0.01                            | < 0.1                                                          |
| TPyP-α            | Triethylamine | 7                      | 1\textsuperscript{d} | 1.01 ± 0.02                            | < 0.1                                                          |
| TBAP-α (MeCN:H\textsubscript{2}O)\textsuperscript{g} | Ascorbic Acid | 2.6                    | 1\textsuperscript{d} | 0.052 ± 0.001                          | 358                                                           |

\textsuperscript{a} Systems with pH 7 were adjusted using NaOH\textsubscript{(aq)} or HCl\textsubscript{(aq)}. \textsuperscript{b} Pt levels measured by ICP-MS; \textsuperscript{c} Hydrogen evolution rate over 5 hours, unless otherwise stated photocatalyst (25 mg) suspended in either aqueous ascorbic acid (25 mL, 0.1 M) or aqueous triethylamine (25 mL, 5 vol. %), λ > 420 nm, 300 W Xe light source; \textsuperscript{d} Pt loaded by photodeposition of H\textsubscript{2}PtCl\textsubscript{6} (aqueous solution, 8 wt. %); \textsuperscript{e} Pre-made Pt nanoparticles; \textsuperscript{f} Material partially or fully soluble in this system; \textsuperscript{g} TBAP (25 mg) and ascorbic acid (440 mg) in MeCN : water solution (9:1) (25 mL).
Figure S23. Three batches of TBAP-α (25 mg) loaded with 4 wt. % Pt, from photodeposition of H₂PtCl₆, dispersed in ascorbic acid solution (25 mL, 0.1 M) illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut off filter.
Figure S24. (A) Photocatalysis experiment of TBAP-α (black) and TBAP amorphous (red) (25 mg) loaded with 1 wt.% Pt, from photodeposition of H₂PtCl₆, dispersed in ascorbic acid solution (25 mL, 0.1 M) buffered to pH 7 by the addition of NaOH, illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut-off filter. The TBAP-α experiment was degassed by N₂ bubbling after 3 h. (B) PXRD spectra of TBAP-α before and after photocatalysis in buffered ascorbic acid.
Figure S25. Photocatalysis experiment of TBAP-α (black) and TBAP amorphous (red) (10 mg) loaded with 1 wt. % pre-made Pt nanoparticles dispersed in ascorbic acid solution (25 mL, 0.1 M) illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut off filter.
Photocatalysis experiment of tetraphenylpyrene (TPhP) (25 mg), tetrapyridylpyrene (TPyP) (25 mg) and tetraformylphenylpyrene (TFPhP) (25 mg) loaded with 1 wt. %, from photodeposition of H$_2$PtCl$_6$, dispersed in ascorbic acid solution (25 mL, 0.1 M) illuminated with a 300 W Xe light source fitted with a $\lambda > 420$ nm cut off filter. It should be noted that a significant proportion (aprox 50 wt. %) of TPyP had dissolved by the end of the experiment.
Figure S27. Photocatalysis experiment of tetraphenylpyrene (TPhP) (25 mg) and tetrapyridylpyrene (TPyP) (25 mg) loaded with 1 wt. %, from photodeposition of H₂PtCl₆, dispersed in water with TEA (25 mL, 5 vol. %) illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut off filter.
Figure S28. External quantum efficiencies and absorption profile of TBAP-α. The photocatalyst (12 mg) loaded with 1 wt. % Pt in an aqueous ascorbic acid solution (8 mL, 0.1 M) illuminated with LEDs at 420, 435, 470, and 595 nm (± 10 nm, fwhm) in a photoreactor with path length of 1 cm.
Figure S29. TBAP-α (25 mg) loaded with 1 wt. % Pt, from photodeposition of H₂PtCl₆, dispersed in D₂O (25 mL) containing ascorbic acid (0.1 M) illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut off filter. Partial pressures were measured by mass spectrometry.
Figure S30. GC Chromatograms of two photocatalysis experiments of TBAP-α. 5 mg of the photocatalyst in 5 mL aqueous ascorbic acid solution (0.1 M) were illuminated for 5 hours with a solar simulator (AAA solar simulator, 1 Sun). Hydrogen production (2.8 ± 0.03 µmol) and a small amount of CO (4.05 ± 0.22 nmol) were observed. Hydrogen production is observed while only a very small amount of CO is produced, which strongly indicates that the hydrogen production is not due to decomposition of the photocatalyst or ascorbic acid.
Figure S31. GC Chromatograms of two photocatalysis experiments of TBAP-α. 5 mg of the photocatalyst loaded with Pt (1 wt. %) in 5 mL aqueous ascorbic acid solution (0.1 M) were illuminated for 5 hours with a solar simulator (AAA solar simulator, 1 Sun). Hydrogen production (33.0 ± 0.71 µmol) and a small amount of CO (0.33 ± 0.03 nmol) were observed. Significant amounts of hydrogen are produced in presence of Pt, while only a very small amount of CO is produced, which strongly indicates that the hydrogen production is not due to decomposition of the photocatalyst or ascorbic acid.
Figure S32. $^1$H NMR spectrum (DMSO-$d_6$) of TBAP recorded after 110 hours of photocatalysis loaded with 1 wt. % Pt from an ascorbic acid solution (0.1 M) under visible light illumination ($\lambda > 420$ nm, 300 W Xe light source). Samples were collected by filtration and air dried before being dissolved in DMSO. The signals at 2.50 and 3.33 ppm are DMSO and H$_2$O, respectively.
**Figure S33.** PXRD patterns of amorphous TBAP recorded after drying the sample under dynamic vacuum at 120 °C (black, bottom) and recorded after 6 hours of photocatalysis, loaded with 1 wt. % Pt from an ascorbic acid solution (0.1 M) under visible light illumination ($\lambda > 420$ nm, 300 W Xe light source) (red, top). After photocatalysis experiments, the samples were collected by filtration and air dried before analysis.
Figure S34. UV-Vis spectra of TBAP-α, TBAP amorphous, TPhP and TPyP in the solid state.
Figure S35. PL Spectra of TBAP-α in DMSO solution ($\lambda_{\text{exc}} = 360$ nm and $\lambda_{\text{em}} = 451$ nm).
Figure S36. PL Spectra of TBAP-α in aqueous suspension ($\lambda_{\text{exc}} = 360$ nm and $\lambda_{\text{em}} = 451$ nm)
Figure S37. PL Spectra of TBAP amorphous in aqueous suspension ($\lambda_{\text{exc}} = 360$ nm and $\lambda_{\text{em}} = 451$ nm).
Figure S38. PL Spectra of TBAP-α in the solid-state ($\lambda_{\text{exc}} = 300$ nm and $\lambda_{\text{em}} = 510$ nm).
Figure S39. PL Spectra of TBAP amorphous in the solid-state ($\lambda_{\text{exc}} = 300$ nm and $\lambda_{\text{em}} = 510$ nm).
Figure S40. TCSPC measurement of TBAP in DMSO solution ($\lambda_{\text{exc}} = 370.5$ nm and $\lambda_{\text{em}} = 451$ nm, detector equipped with a $\lambda > 395$ nm band-pass filter.)
Figure S41. TCSPC measurement of Pt@TBAP-α in aqueous suspension ($\lambda_{\text{exc}} = 370.5$ nm and $\lambda_{\text{em}} = 451$ nm, detector equipped with a $\lambda > 395$ nm band-pass filter.)
Figure S42. TCSPC measurement of Pt@TBAP amorphous in aqueous suspension ($\lambda_{\text{exc}} = 370.5$ nm and $\lambda_{\text{em}} = 451$ nm, detector equipped with a $\lambda > 395$ nm band-pass filter.
Figure S43. TCSPC measurement of TBAP-α in aqueous suspension (λ<sub>exc</sub> = 370.5 nm and λ<sub>em</sub> = 451 nm, detector equipped with a λ > 395 nm band-pass filter.
Figure S44. TCSPC measurement of TBAP amorphous in aqueous suspension ($\lambda_{exc} = 370.5$ nm and $\lambda_{em} = 451$ nm, detector equipped with a $\lambda > 395$ nm band-pass filter.)
Figure S45. TCSPC measurement of TBAP-α in the solid-state ($\lambda_{\text{exc}} = 370.5$ nm and $\lambda_{\text{em}} = 510$ nm, detector equipped with a $\lambda > 495$ nm band-pass filter.)
Figure S46. TCSPC measurement of TBAP amorphous in the solid-state ($\lambda_{\text{exc}} = 370.5$ nm and $\lambda_{\text{em}} = 510$ nm, detector equipped with a $\lambda > 495$ nm band-pass filter.)
Figure S47. TCSPC measurement of TBAP-α and TBAP amorphous suspended in water and in ascorbic acid solution (0.1M), ($\lambda_{\text{exc}} = 404.5$ nm and $\lambda_{\text{em}} = 451$ nm).
Table S7. Estimated fluorescence lifetime times from time-correlated single photon counting experiments

| Material   | Conditions       | λ_em (nm) | τ_1 (ns) | B_1 (%) | τ_2 (ns) | B_2 (%) | τ_3 (ns) | B_3 (%) | χ^2 | τ_avg (ns) |
|------------|-----------------|-----------|----------|---------|----------|---------|----------|---------|-----|------------|
| TBAP       | DMSO solution   | 451       | 0.032    | 3.928   | 0.857    | 14.195 | 2.044    | 81.877 | 0.950 | 1.80       |
| Pt@TBAP-α | water suspension| 451       | 0.094    | 3.007   | 0.414    | 5.668  | 2.148    | 91.324 | 0.970 | 1.99       |
| Pt@TBAP   | water suspension| 451       | 0.165    | 5.898   | 0.892    | 5.918  | 2.181    | 88.184 | 1.120 | 1.99       |
| TBAP-α     | water suspension| 451       | 0.054    | 1.824   | 0.341    | 6.247  | 2.142    | 91.929 | 1.085 | 1.99       |
| TBAP       | water suspension| 451       | 0.068    | 1.598   | 0.372    | 6.660  | 2.156    | 91.742 | 1.094 | 2.00       |
| TBAP-α     | Solid-state     | 510       | 0.018    | 15.872  | 0.107    | 15.716 | 1.991    | 91.062 | 1.482 | 1.38       |
| TBAP       | Solid-state     | 510       | 0.451    | 28.261  | 0.771    | 43.305 | 4.807    | 28.434 | 1.325 | 1.83       |

[a] Fluorescence lifetime times were obtained from fitting time-correlated single photon counting decays to a sum of three exponentials, which yield τ_1, τ_2, and τ_3 according to the equation:

\[ \sum_{i=1}^{n} (A_i + B_i \exp(-t/\tau_i)) \]

τ_{AVG} is the weighted average lifetime calculated as:

\[ \sum_{i=1}^{n} B_i \tau_i \]
Figure S48. Comparison of the IP and EA values of TBAP, TPhP and TPyP when modelled as isolated molecules immersed in water. Solution potentials for the reduction of protons to hydrogen and oxidation of ascorbic acid at pH 2.6, the likely pH of a 0.1 M ascorbic acid solution (left), and reduction of protons and oxidation of triethylamine at pH 11.5, the likely pH of a triethylamine solution, taken from the literature.[68]

Fig. S48 shows the predicted IP and EA values of TBAP and TPhP relative to those of the solution potentials relevant to the use of ascorbic acid as a hole scavenger and those of TPhP and TPyP for when using triethylamine instead. The two scenarios differ not only in scavenger but also in the pH of the resulting solution and hence the proton reduction potential is also different. All materials are predicted to have a very large driving force for proton reduction and reasonable driving force for the overall oxidation of ascorbic acid and triethylamine respectively. However, while TBAP and TPyP also have a small driving force for the intermediate oxidation step, this is predicted to be not true for TPhP. In the case of TPhP, the one-hole oxidation of ascorbic acid/triethylamine could thus act as an as an effective thermodynamic barrier to overall oxidation, which might be a contributing factor to the lower hydrogen evolution rates observed for TPhP when compared with TBAP/TPyP.
Table S8. Comparison between the experimental desolvated lattice parameters of TBAP-α and those obtained after an energy minimization using B97-3c (C2/m, 1x1x4 k-point grid, TOLINTEG 7 7 7 7 14, LDREMO=10). All cell lengths in Ångstrom, β in degrees and $V_{cell}$ in cubic Ångstrom.

|       | Exp.  | DFT   | Diff. (%) |
|-------|-------|-------|-----------|
| $a$   | 29.036| 28.993| -0.15     |
| $b$   | 25.538| 28.356| -0.64     |
| $c$   | 3.871 | 3.741 | -3.37     |
| $\beta$ | 91.179| 92.964| 1.07      |
| $V_{cell}$ | 3206.0| 3071.4| -4.2      |

Table S8 demonstrates that our periodic DFT calculation reproduces the lattice parameters of the desolvated TBAP-α well. The slight contraction of the DFT structure relative to the experimental structure is probably in part related to the fact that the experimental structure solved from diffraction data obtained at room temperature.

Figure S49. Structure of the 1C+ cluster model with the monomer described using DFT highlighted in blue.
Figure S50. Comparison of the IP and EA values of TBAP based on an isolated TBAP molecule optimized in the gas-phase (I), an isolated TBAP molecule taken from the DFT optimized TBAP-α crystal structure (II, 1C), a TBAP single molecule taken from the DFT optimized TBAP-α crystal structure surrounded by a molecule above and below it, as well as the phenyl groups of the laterally adjacent molecules, described using a forcefield (III, 1C+, see Fig. S49), and the analogous tetramer case (IV, 4C+). Solution potentials for the reduction of protons and oxidation of ascorbic acid at pH 2.6, the likely pH of a 0.1 M ascorbic acid solution, taken from the literature.[68]

Fig. S50 shows that the effect of packing on the predicted potentials of TBAP-α is very small, or at least when we make the assumption that the pores contain significant amounts of water. For all structural models it is predicted that there is a very large driving force for proton reduction and a reasonable driving force for the overall oxidation of ascorbic acid (A/H₂A). The intermediate one-hole oxidation of ascorbic acid (HA*/H₂A), which could act as an effective thermodynamic barrier to overall oxidation, is also in all cases predicted to be exergonic, though only by a small amount.
Figure S51. $N_2$ sorption isotherm for amorphous sample of TBAP recorded at 77 K (closed symbol for adsorption points, open symbols for desorption points).
Figure S52. Water uptake measurements for TBAP-α batch 1, and amorphous TBAP, recorded at 20.0 °C and up to 23.4 mbar (closed symbol for adsorption points, open symbols for desorption points).
Figure S53. PXRD data for activated TBAP-α and TBAP-α recorded after the water sorption isotherm shown in Fig. S52.
**Figure S54.** STEM images of TBAP amorphous with no (top), 1 wt. % (middle) and 4 wt. % (bottom) photodeposited Pt in BF mode (left) and HADF mode (right).
Figure S55. Size distribution of pre-made Pt nanoparticles in water by DLS. Average hydrodynamic diameter was calculated to be 13.17 nm (PDI = 0.329).
Figure S56. STEM images of TBAP-α (top) and TBAP amorphous (bottom) loaded with pre-made Pt nanoparticles in BF mode (left) and HADF mode (right).
**Figure S57.** TBAP-α with 1 wt. % Pt, STEM images in BF mode (top left) and HADF mode (top right) and SEM images at 1 KeV (bottom left) and 30 KeV (bottom right).
Figure S58. PXRD patterns for TPhP recorded before and after photocatalysis in ascorbic acid (blue) or TEA (pink). For reference, the simulated PXRD pattern of reported crystal structure of TPhP (CSD reference: YABBEL) is also shown.
**Figure S59.** $^1$H NMR spectrum (DMSO-$d_6$) of TPhP after sublimation (blue), after 24 hours visible light illumination ($\lambda > 420$ nm, 300 W Xe light source) in ascorbic acid solution (0.1 M) (red) and after 5 hours visible light illumination ($\lambda > 420$ nm, 300 W Xe light source) in TEA solution (5 vol. %) (green).
Figure S60. PXRD patterns for TPyP recorded before and after photocatalysis in ascorbic acid (blue) or TEA (pink). For reference, the simulated PXRD pattern TPyP-α is shown.
Figure S61. $^1$H NMR spectrum (acetic acid-d$_4$) of TPyP as synthesized (blue), after sublimation (red), after 24 hours visible light illumination ($\lambda > 420$ nm, 300 W Xe light source) in ascorbic acid solution (0.1 M) (green) and after 5 hours visible light illumination ($\lambda > 420$ nm, 300 W Xe light source) in TEA solution (5 vol. %) (purple).
**External Surface area Analysis**

It is important to consider the effect of external surface area of the photocatalysts; particle size analysis by static light scattering indicated that both TPhP-α and TPyP-α had smaller surface area weighted particle sizes than TBAP-α when suspended in water (SI, Figure S63 and Table S9) and that the former was also smaller in acidic solution. In addition, light transmission measurements for suspensions of the materials (SI, Figure S65) indicate that TPhP-α and TBAP-α have comparable dispersibilities and that TPyP-α was significantly more dispersible. In addition the amorphous TBAP sample was found to have particle sizes, intermediate between the three crystalline TBAP-α batches (Figure S62, Table S9) and to show similar dispersibility in ascorbic acid (Figure S65). Taken together these results show no strong correlation between the materials particle size or dispersibility and photocatalytic activity, and thus we conclude external surface area is not a dominant factor in these systems.
Figure S62. Size distribution of TBAP dispersed in water by SLS.
Figure S63. Size distribution of materials dispersed in water by SLS.
Figure S64. Size distribution of materials dispersed in ascorbic acid (0.1 M) by SLS.
Table S9. Sauter mean diameter of materials by SLS

| Material            | Dispersant            | $D_{[3,2]}$ (µm) |
|---------------------|-----------------------|------------------|
| TBAP-α Batch 1      | water                 | 15.52            |
| TBAP-α Batch 2      | water                 | 11.00            |
| TBAP-α Batch 3      | water                 | 9.25             |
| TBAP Amorphous      | water                 | 11.91            |
| TPhP                | water                 | 9.17             |
| TPyP                | water                 | 2.63             |
| TBAP-α Batch 1      | Ascorbic acid (0.1 M) | 10.13            |
| TBAP Amorphous      | Ascorbic acid (0.1 M) | 12.11            |
| TPhP                | Ascorbic acid (0.1 M) | 7.86             |
Figure S65. Light transmission measurements of materials dispersed in water (left) and ascorbic acid (right) over time. Scans were recorded every 30 mins with scan 1 occurring at t = 0 mins.
Figure S66. CSP landscapes for a) TPhP, b) TPyP and c) TBAP colored according to the presence (orange) or absence (blue) of extended π-stacked columns. Unstacked structures are plotted on top of stacked structures, so that stacked structures in the high energy / high density regions are hidden. d-f) Histograms of the energetic distributions of predicted crystal structures with and without stacking on the a) TPhP, b) TPyP and c) TBAP CSP landscapes.
Figure S67. Absorbance at 397 nm dependent on the concentration of TBAP in DMSO solution (left) and calculated extinction coefficient (right).
Figure S68. Photocurrent measurements of TBAP-α batch 1 loaded with preformed Pt nanoparticles and TBAP amorphous loaded with preformed Pt nanoparticles on FTO-glass under visible light (ABA solar simulator, 1 Sun). The area illuminated was 84 mm² and a bias voltage of -0.2 V was used.
Figure S69. TCSPC measurement of TPhP ($\lambda_{\text{exc}} = 404.5$ nm and $\lambda_{\text{em}} = 456$ nm) suspended in water and in ascorbic acid solution (0.1 M).
Figure S70. TCSPC measurement of TPhP (λ_{exc} = 404.5 nm and λ_{em} = 456 nm) and TPyP (λ_{exc} = 404.5 nm and λ_{em} = 508 nm) suspended in water and in 5 vol. % TEA solution.
Figure S71. (Top) Hydrogen evolution vs. time for TBAP-α (25 mg) loaded with 1 wt. % Pt, from photodeposition of H₂PtCl₆, dispersed in solution of ascorbic acid (0.1 M) in either water (black) or a (9:1) MeCN : Water mixture (red) illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut-off filter. (Bottom) PXRD of TBAP-α loaded with 1 wt. % Pt, after photocatalysis experiments performed in a solution of ascorbic acid (0.1 M) in a (9:1) MeCN : Water mixture, illuminated with a 300 W Xe light source fitted with a λ > 420 nm cut-off filter. After photocatalysis experiments, the samples were collected by filtration and air-dried before analysis.
5. Supplemental References

[92] Schrödinger, LLC. Release 2018-1. ConfGen, Schrödinger: New York, NY, 2018

[93] J. L. Banks, H. S. Beard, Y. Cao, A. E. Cho, W. Damm, R. Farid, A. K. Felts, T. A. Halgren, D. T. Mainz, J. R. Maple, R. Murphy, D. M. Philipp, M. P. Repasky, L. Y. Zhang, B. J. Berne, R. A. Friesner, E. Gallicchio, R. M. Levy, *J. Comput. Chem.* 2005, **26**, 1752. 1, 1128-1132.

[94] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 09, Rev. D.01. *Gaussian Inc., Wallingford, CT* 2016.

[95] A. J. Stone, *J. Chem. Theory Comput.* 2005, **1**, 1128.

[96] G. G. Ferenczy, P. J. Winn, C. A. Reynolds, *J. Phys. Chem. A* 1997, **101**, 5437.

[97] H. Sakoe, S. Chiba, *IEEE Trans. Acoust.* 1978, *ASSP*-**26**, 43.

[98] J. A. Chisholm, S. Motherwell, *J. Appl. Crystallogr.* 2005, **38**, 228.

[99] T. F. Willems, C. H. Rycroft, M. Kazi, J. C. Meza, M. Haranczyk, *Microporous Mesoporous Mater.* 2012, **149**, 134.
[100] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* 2008, 41, 466.

[101] S. Parsons, ECLIPSE 2004, The University of Edinburgh: Edinburgh.

[102] Bruker, *APEX II* 2009.

[103] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* 2015, 48, 3.

[104] G. Winter, D. G. Waterman, J. M. Parkhurst, A. S. Brewster, R. J. Gildea, M. Gerstel, L. Fuentes-Montero, M. Vollmar, T. Michels-Clark, I. D. Young, N. K. Sauter, G. Evans, *Acta Crystallogr. Sect. D Struct. Biol.* 2018, 74, 85.

[105] G. M. Sheldrick, *Acta Crystallogr. Sect. D Biol. Crystallogr.* 2010, 66, 479.

[106] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2015, 71, 3.

[107] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* 2015, 71, 3.

[108] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, 42, 399.

[109] Q. Yin, Y.-L. Li, L. Li, J. Lü, T.-F. Liu, R. Cao, *ACS Appl. Mater. Interfaces* 2019, 11, 17823.

[110] N. C. Bigall, T. Härtling, M. Klose, P. Simon, L. M. Eng, A. Eychmüller, *Nano Lett.* 2008, 8, 4588.

[111] A. L. Spek, *Acta Cryst* 2009, 65, 148.

[112] P. Van Der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* 1990, 46, 149.

[113] A. L. Spek, *Acta Crystallogr. Sect. C, Struct. Chem.* 2015, 71, 9.