Comprehensive structure–function correlation of photoactive ionic π-conjugated supermolecular assemblies: an experimental and computational study†

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We provide a structure–function relationship study of an organic crystalline photoconductor composed of oppositely charged ionic porphyrins. Nano to millimeter size crystals with well-defined morphology composed of stoichiometric amounts of meso-tetra(N-methyl-4-pyridyl)porphyrin (TMPyP) and meso-tetra(4-sulfonatophenyl)porphyrin (TSPP) were grown in a controlled and reproducible manner. The rod shaped TMPyP:TSPP monoclinic P2_{1}/c crystals have a pseudo-hexagonal cross section and their internal structure consists of highly organized molecular columns of alternating porphyrin cations and anions. Experimental characterization of the TMPyP:TSPP solid was performed using powder-XRD, AFM, SEM, DRS UV-visible, and photoconductivity measurements. For the first time the morphology of an ionic porphyrin solid is predicted. The TMPyP:TSPP crystals are non-conducting in the dark but become conductive with illumination. The n-type photoconductive response is significantly faster with excitation in the Q-band than with excitation in the Soret band. Quantum mechanical calculations were performed to determine the electronic band structure and density of states and to explain the photoconduction in TMPyP:TSPP. Based on these results we propose a model in which two types of photoconductivity occur: (1) band conduction which occurs at all excitation wavelengths and (2) hopping conductivity caused by metastable photoinduced defects that form primarily at higher energy excitations. This work combines the results from structural and theoretical studies and correlates them with electronic and optoelectronic properties thereby opening the road to the engineering of highly-organized functional materials from organic π-conjugated molecules.

Introduction

Organic molecular and nanostructured semiconductors possess unique photon absorption characteristics induced by their highly polarizable π-electronic structures. These characteristics make them particularly useful for developing novel optoelectronic devices such as light-emitting diodes, field-effect transistors, photo switches, sensors, solar cells, and memory devices.

Although organic nanostructured semiconductors have become viable alternatives to their well-established inorganic counterparts there is still a continuing need for research in controlling their composition and structure through synthetic strategies and processing since those factors determine the useful behavior of these materials. Consequently, good fundamental understanding of structure–property relationship is essential in designing and building high performance, stable, and durable molecular materials and is one of the main scientific challenges for advancing organic optoelectronic technology.

The work that we present here is a comprehensive structure–property correlation study of a model self-assembled organic semiconductor based on ionic porphyrin synthons using both experimentation and theory. The porphyrin supermolecular structures are synthesized reproducibly under chemically controlled conditions and their photoconductive properties are linked with their molecular organization and morphology. Theoretical calculations help explain the experimental photoconductivity measurements and make useful recommendations...
for structure modification to optimize charge transport properties in these π-conjugated systems. While there have been many papers reporting on optical, chemical, and electronic properties of binary ionic porphyrins, this is the first to combine structure determination, electronic band calculations, and experiment in a unified study.21,32–34 It is this combination of crystal structure, morphology, electronic structure, and photoconductivity that makes this study unique.

Porphyrins constitute an important category of conjugated organic semiconductors that structurally and functionally resemble natural light harvesting chromophores and have wide application in optical and electronic technologies. In particular, crystalline assemblies made from ionic forms of these tetrapyroles represent a novel class of robust materials that have been shown to be potentially useful as active components of solar cells,6,7,9,20 and photovoltaics.9,17,21 In addition, the elastic modulus of these porphyrinic structures is comparable to those reported for covalently bonded flexible polymeric systems making them excellent candidates for flexible optoelectronic devices.15,23,24

Free-base porphyrins and their metal derivatives substituted with ionic groups can form nano to micro-sized supermolecular crystalline assemblies in the form of rods, tubes, nanofibers, sheaves, sheets, spheres, and clovers via ionic self-assembly (ISA).15–18,25–34 In these structures, strong electrostatic attraction, π–π interactions, and hydrogen bonding direct molecular ordering and influence optical and charge transport properties of the supermolecular assemblies. The molecular arrangement of self-assembled porphyrin tectons is nearly always deduced from the solution electronic absorbance or Raman spectra of the ISA assemblies.

To date, no studies relating light response of electroactive ISA porphyrins and their crystal structures have been reported. These include nanorods of zwitterionic meso-tetra(4-sulfonatophenyl) porphyrin (TSPP) which displayed photoconductivity and exhibited rapid induced current on/off signal upon light exposure studied by Schwab37,38 and Riley.39 These authors proposed a qualitative model where the conduction occurred through a wide conduction band formed by strongly overlapping LUMOs of adjacent porphyrin molecules making up the nanorods, but were limited by the fact that the actual structure of the material has never been uniquely determined. Friesen et al. investigated electron transport in TSPP aggregates by employing Scanning Tunneling Microscopy (STM) imaging and Orbital Mediated Tunneling Spectroscopy (OMTS).15,40,41 The TSPP nanorods were found to be rectifying, exhibiting a dramatic increase in conductivity above +1 V bias which was ascribed to a band formed from the combined LUMOs of the porphyrin zwitterions.15,40–42 Shelnutt, Medforth, and coworkers reported that clovers-shaped nanocrystals composed of ZnTSPP43 and Sn(n) tetra(N-hydroxyethyl-4-pyridiniumyl)porphyrin44 are photoconductive and photocatalytic, producing H₂ gas when exposed to laser light.21 The photoconductivity of the Zn/Sn system was rationalized in terms of the energetics of molecular excitations (charge transfer excitons) occurring in the illuminated solid where the Sn(n) porphyrins acted as the acceptors and Zn(n) porphyrins as donors. But again, no crystal structure is known.

The molecular structure was determined for nanosheets composed of ZnTSPP and Sn(n)-tetra(N-methyl-4-pyridiniumyl) porphyrin. But, this material is not photoconductive.21 The lack of conductivity was attributed to severe slipped π–π stacking of the synths in the crystal framework resulting in no significant electronic interactions between the porphyrin ionic dimers.

Because molecular arrangement within the ionic porphyrin solid dictates the efficiency of carrier transport, an in-depth understanding and control of the growth mechanism, morphology, and crystallinity of the ensuing structures at the molecular level is critical. Accordingly, fundamental studies of structure–property relationships are essential for providing guidance for rational design and building of highly functional ISA porphyrin based devices.

The system of interest here is an ISA binary porphyrin system fabricated from stoichiometric metal free porphyrin tectons namely, meso-tetra(N-methyl-4-pyridyl)porphyrin, TMPyP, and meso-tetra(4-sulfonatophenyl)porphyrin, TSPP, Fig. 1. TMPyP:TSPP nano to millimeter size crystalline structures were grown in a controlled and reproducible manner using a nucleation and growth model developed by us earlier.32 This model accurately predicts the size distribution of molecular materials grown at a particular temperature and concentration.
thus allowing one to fabricate crystalline structures with predictable size and morphology. For the first time, millimeter size rod-like high quality TMPyP:TSPP crystals were grown in a relatively short time (less than 24 hours). A similar binary material reported earlier by Scheldt and coworkers required extremely long growth periods (excess of eighteen months) in a gel matrix yielding small crystalline plates. Consequently, it was not clear that the reported structure matched that of the nanorods reported here. The crystal structure of the TMPyP:TSPP solid reported in the current work has somewhat different unit cell parameters and a superior reliability factor than the crystal structure reported by Scheldt.

Using the unit cell parameters obtained from the TMPyP:TSPP crystal structure, crystal morphology, or habit, was predicted by applying two different analytical models, the Bravais–Friedel–Donnay–Harker (BFDH) model and attachment energy model. The predicted habit is in excellent agreement with the experimental structural morphology of TMPyP:TSPP observed by microscopic techniques (AFM, and SEM). This is the first example of utilizing crystal structure in predicting the morphology of an ionic porphyrin solid.

In the dark the TMPyP:TSPP crystals are nearly insulating but upon exposure to light they become conductive. The induced conductivity was evaluated as a function of laser wavelength (blue to red region) and laser power. The photoconductive response was found to be significantly different for excitation in the Q-band and the Soret band regions. DFT calculations were carried out to explain the experimental photoconductivity measurements. The conduction process is related to the molecular structure and organization of ionic porphyrin tectons within the TMPyP:TSPP crystalline assemblies. Based on the presented structure–function relationship data, guidelines for developing novel ionic porphyrin based nanostructures with optimal charge transport properties are proposed using periodic simulations.

### Experimental section

#### Materials

Porphyrin starting materials: *meso*-tetra(4-sulfonatophenyl)-porphyrin dihydrochloride, ([H$_2$TSPP]·2HCl), *meso*-tetra(N-methyl-4-pyridyl)porphyrin tetrachloride, [H$_2$TMPyP]·Cl$_4$, and tetrasodium *meso*-tetra(4-sulfonatophenyl)porphyrin, Na$_4$[H$_2$TSPP], were purchased from Frontier Scientific (99% purity) and used without further purification. NaOH (J. T. Baker) and HCl (Fisher Scientific), acetonitrile (J. T. Baker), methanol (Decon Labs Inc.), and KBr (J. T., Baker) were all reagent grade. Millipore water (18 MΩ) was used in all preparations. The porphyrin stock solutions (1000 µM) were made by dissolving the porphyrin solid in water and were used within two weeks’ time. Sodium hydroxide solution (2 mM) and 1 M HCl were used to adjust the pH of the porphyrin solutions.

#### Synthesis of TMPyP:TSPP crystals

Desupersaturation experiments were performed in a batch reactor in a temperature controlled Brinkmann bath as previously described. Aqueous solutions of the individual porphyrins (10 µM, neutral pH) were made at the required concentration, preheated to 333 K, and mixed together at which point different amounts of an organic solvent, acetonitrile or methanol, were introduced to the mixture. The precipitation reaction was allowed to proceed for about 20 hours according to this reaction:

\[
\text{TSPP}^{4-} + \text{TMPyP}^{4+} \rightarrow \text{TMPyP:TSPP}_{(s)}
\]

After the TMPyP:TSPP solid crystallized, small aliquots of suspension were withdrawn for crystallographic, spectroscopic, conductivity, and microscopic analysis. It important to add that the TMPyP:TSPP crystals remain stable under UHV conditions for prolonged periods of time during TEM and selected area electron diffraction data collection. In addition, the XPS spectra of the crystals showed no visible changes with heating up to 140 °C.

**AFM**

Samples for imaging were prepared by depositing 2 drops of a solution containing the TMPyP:TSPP solid on a freshly cleaved mica surface (SPI supplies Inc.) mounted on a metallic disk. Images were obtained with a Bruker Multimode 8 Atomic Force Microscope using RTESPA tips (silicon cantilever with driving frequency of 300 MHz and force constant of 40 N m$^{-1}$). TAP 150 tips (Antimony doped silicon tips having a resonance frequency of 150 kHz and a force constant of 5 N m$^{-1}$) were used both in tapping and PeakForce Quantitative Nanoscale Mechanical (QNM) imaging modes.

**SEM**

Porphyrin samples were deposited on glass coverslips (10 mm diameter, Ted Pella Inc.) from solution and allowed to dry in vacuum overnight. The glass pieces were attached to a double stick electrically conductive carbon tape affixed to an aluminum SEM stub and was coated with a thin layer of gold (5–6 nm). A small amount of silver paint was used at the edges of cover slip for better conductivity. Scanning electron microscopy images were obtained with a FEI Quanta 200F SEM at 10 mm working distance and 30 kV beam energy. The instrument working pressure was $10^{-6}$ Torr.

**Optical microscopy**

A drop of TMPyP:TSPP solution was placed on a glass microscope slide and a cover glass was slipped on top of to spread the liquid and immobilize the motion of the porphyrin crystals. Images of the crystals were obtained with and without a polarized light using the Leitz Aristoplan Fluorescence Microscope.

**X-ray diffraction**

Suitable TMPyP:TSPP single-crystals were selected and cut to smaller dimensions. A needle-like crystal 0.004 mm × 0.006 mm × 0.061 mm was used for the X-ray crystallographic analysis. A Bruker D8 VENTURE single crystal diffractometer equipped with a Ga METALJET X-ray source (1.341398 Å) and Photon 100 detector was used for data collection. Temperature was...
maintained at 105(±2) K. A total of 2094 frames were collected. The total exposure time was 56.30 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33146 reflections to a maximum θ angle of 66.76° (0.8 Å resolution), of which 6977 were independent (average redundancy 4.751, completeness = 99.11%, Rint = 8.18%, Rsig = 9.34%) and 4493 (64.40%) were greater than 2σ(I). The measured cell constants are based upon the refinement of the XYZ-centroids of 465 reflections above 2σ(I) with 12.82° < 2θ < 102.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.764. SHELXTL-2014/5 software was used for structure solution and APEX3 v2016.1-0 (Bruker AXS, Inc.) was used for cell refinement computation. The details of data collection and structural refinement are summarized in Table S1 (ESI†). The atomic coordinates and equivalent isotropic displacement parameters are given in Table S2 (ESI†). The interatomic bond angles are given in Table S3 (ESI†), the selected interatomic distances are summarized in Table S4 (ESI†), and the anisotropic atomic displacement parameters are in Table S5 (ESI†). The crystallographic information file ( cif file) is available in ESI.†

UV-visible diffuse reflectance spectroscopy (DRS)

The TMPyP:TSPP solid was isolated by filtering a suspension of crystals through a 0.1 μm pore size, 47 mm Teflon filter membrane from Membrane Solutions using a Millipore vacuum filtration setup followed by drying of the solid. DRS samples were prepared by grinding a small amounts of solid TMPyP, TSPP, and TMPyP:TSPP with KBr such that the final concentration of the porphyrin was about 0.2% in each of the three specimen. The powders were pressed loosely in a metal anvil cell outfitted with a 1 cm quartz window. Reflectance spectra were collected using the ThermoFisher Bio 260 UV-vis Spectrophotometer equipped with an ISA-220 integrating sphere. The Kubelka–Munk transform was used on the absorbance data.

Fluorescence spectroscopy

Laser-induced steady state emission spectra were collected with a home-built luminescence spectrometer outfitted with a Coherent Model 0222-583-00, 408 nm (~2 mW) cw-diode laser. Details of the experimental setup are described elsewhere. The width of the sample tube was 2 mm (O.D.) and the laser beam diameter at sample was 25 μm. Luminescence spectra of the free-base monomers of TMPyP and TSPP, a 1 : 1 molar ratio physical mixture of the monomers, and that of TMPyP:TSPP composite were measured. No change in the luminescence intensity was observed for all the samples during data collection indicating that no material photodecomposition took place. All spectra were corrected based on calibration with an Ocean Optics calibrated light source.

IDE preparation and treatment

Gold interdigitated electrodes (IDEs) (UC Santa Barbara Nano-fabrication Facility) with a spacing of 500 nm were used for the conductivity experiments. The Au electrodes were fabricated on top of a 400 nm thick SiO2 layer supported on a p++ doped silicon chip. TMPyP:TSPP crystals were deposited on the IDEs by casting a drop of liquid suspension onto the IDE, allowing the solution to remain an hour, and then removing the excess fluid by wicking the IDE with a Kimwipe. The IDE was then examined under an optical microscope to determine if a sufficient amount of the porphyrin crystals were present on the IDE surface and the process was repeated until an acceptable number of rods had been deposited.

Photoconductivity measurements

Action spectrum, time dependence, I–V curves, and field effect experiments were measured in an in-house designed vacuum chamber with a base pressure <5 mTorr and equipped with a temperature controlled sample stage (Fig. 2). Prior to all measurements, the samples were heated to 348 K under vacuum for at least 12 hours. Source-drain biases (VSD) were applied using a Data Translation DT9812 data acquisition system (DAQ). The current was measured using a Keithley 427 current amplifier and recorded by the DT9812 DAQ. Gate voltages (VG) were applied using a Keithley 246 high voltage supply. Variable power 405, 445, 473, and 671 nm diode lasers and a 632.8 nm HeNe laser were used. These wavelengths were selected on the basis of the absorbance maxima of the electronic spectrum of the solid TMPyP:TSPP. The laser beams were focused down to a 1 mm diameter spot size. Laser power was monitored during all experiments using a calibrated photodiode. Illumination experiments were performed using a Measure Foundry (Data Translation, Inc.) program designed to control and record the VSD and record the time, current, and photodiode signal.

Fig. 2 Schematics of an in–house designed vacuum chamber and electronic components layout used for performing the photoconductivity experiments. The vacuum chamber base plate has several electrical feed throughs for: VSD and IGD measurements (A), thermocouple and a resistive heater (B), and temperature controlled sample stage (C). The plate also has a (D) vacuum outlet (D) and a cooling line (E). In the bottom left corner is an optical microscope image of a gold IDE overlaid with the TMPyP:TSPP rods.
Current–time \((I-t)\) curves were collected by applying \(V_{\text{SD}} = 2\ \text{V}\) and \(V_{G} = 0\ \text{V}\) while recording the current. A baseline was measured in the dark for 500 s, and then the sample was illuminated with either 445 nm or 671 nm irradiation until saturation current was reached. Illumination was then terminated but measurement of the current continued for at least 30 min. All experiments were performed at 298 K. It should be noted that there was considerable variation in persistent current lifetime from one IDE preparation to another, but the value of \(\beta\) did not depend on sample preparation.

Models and methods

Crystal growth model

Controlled growth of the TMPyP:TSPP crystals was achieved using a crystal size distribution prediction model reported earlier.\(^{42}\) Although this model was developed for binary porphyrin synthesis, it can be applied for controlling the growth of organic crystalline supermolecular structures in general. The model assumes a homogenous nucleation in the crystallization process of a binary porphyrin structure based on classic nucleation theory and incorporates Chiang and Donohue’s growth formula for multicomponent precipitation crystallization.\(^{45}\) The rate of nucleation, \(J\) (number of nuclei per unit time per unit volume) is expressed in the form of an Arrhenius equation,

\[
J = A \exp \left( \frac{-4\beta\gamma_{\text{CL}} V_{m}^{2}}{27\pi^{2}k_{d}^{3}T^{2}(\ln S)^{2}} \right)
\]

and the growth rate, \(R_{G}\), is defined as,

\[
R_{G} = \left( 1 + \frac{2k_{t}}{k_{d}} C \right) - \sqrt{1 + \frac{4k_{t}}{k_{d}} C + \frac{k_{t}}{k_{d}} C_{\text{eq}}^{2}}
\]

where \(\gamma_{\text{CL}}\) is the interfacial tension between crystal and solution (\(\text{N}\ \text{m}^{-1}\)); \(k\) is the Boltzmann constant (\(\text{J}\ \text{K}^{-1}\)); \(T\) is the temperature in Kelvin; \(V_{m}\) is the volume of the growth unit (\(\text{m}^{3}\)); \(x\) is the volume shape factor; \(\beta\) is the surface shape factor; \(S\) is the relative supersaturation; \(k_{d}\) is the mass transfer coefficient; \(C\) is the concentration of the solute in the bulk of the solution and \(k_{t}\) is the integration rate constant. The above formulas predict that higher temperature and lower concentration as well as changes in solubility will dramatically affect the nucleation rate and, therefore, the final size of the crystals. Using these guidelines we succeeded in reproducibly growing high quality, controlled size crystals of TMPyP:TSPP. This is the first time such large crystals of any rod or tube shaped crystal of ISA porphyrin have been reported.

Crystal habit

The morphology (shape, size and dimensional aspect ratios) of TMPyP:TSPP molecular crystals was predicted using the Bravais–Friedel–Donnay–Harker\(^{46–48}\) and the attachment energy \((AE)\)\(^{49–51}\) computational methods. The BFDH simulation calculates only the geometry of the crystal, \(i.e.,\) the interplanar distances \((d_{hkl})\) and their orientation. This simple model identifies the important faces in the growth process when only minimal crystal structure information is available. It does not take into account any chemical interactions and does not always reproduce the experimentally observed morphology.\(^{46–48}\)

The \(AE\) method, which explicitly includes the presence of chemical bonding within the crystal, was also used in modeling the TMPyP:TSPP morphology. In this model, the attachment energy \((E_{\text{att}})\) is defined as the energy per mole of molecules released when a new layer is attached to the surface of the crystal.\(^{42,53}\) \(E_{\text{att}}\) is computed as:

\[
E_{\text{att}} = E_{\text{latt}} - E_{\text{slice}}
\]

where \(E_{\text{latt}}\) = lattice energy of the crystal, \(E_{\text{slice}}\) = energy of a growth slice of thickness \(d_{hkl}\). Thus, faces which have higher \(E_{\text{att}}\) grow faster and have lower morphological importance. The attachment energies were calculated using semi empirical \(ab\ initio\) method and the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field.\(^{54}\) Calculated \(E_{\text{att}}\) is an average of the surfaces with Miller indices \([hkl]\) and \([-h-k-l]\). The physical faces possess minimum energy and are oriented in accordance with Gibbs–Wulff construct.\(^{55–57}\) It is important to note that the accuracy with which the predictive models can duplicate the crystal morphology depends most importantly on the quality and completeness of the crystallographic data.

Molecular modeling

Calculations on isolated \([\text{H}_{2}\text{TMPyP}]^{4+}, [\text{H}_{2}\text{TSPP}]^{4-}\) ions and neutrally charged \([\text{H}_{2}\text{TMPyP}]^{4+}:\text{H}_{2}\text{TSPP}]^{4-}\) binary molecule were performed using density functional theory (DFT) with Gaussian 09 package.\(^{58}\) B3LYP hybrid functional\(^{59–61}\) with 6–311++G(d,p) basis set\(^{62}\) is used for all calculations. The geometries all molecules are obtained from the crystal structure and are used with no further optimization. Molecular electrostatic potential (MEP) surfaces were plotted using the GaussView09 program\(^{58}\) and values for the isosurfaces are denoted in the figure captions.

Periodic modeling

Calculations on the TMPyP:TSPP crystal were performed using the Vienna \(ab\ initio\) Simulation Package (VASP)\(^{63,64}\) version 5.2 and with extended Hückel tight binding (EHTB)\(^{65–69}\) method. VASP calculations were done using the Perdew–Burke–Ernzerhof (PBE)\(^{70}\) exchange–correlation functional with plane-wave basis set and projector augmented wave (PAW)\(^{71,72}\) potentials. A plane-wave energy cutoff of 450 eV was applied. TMPyP:TSPP X-ray crystal structure unit cell parameters were used for all calculations. The water molecules in the crystal structure \((\text{vide infra})\) were removed in the periodic calculations to determine the electronic properties of only the binary porphyrin (TMPyP:TSPP) nanostructures. No further optimizations of the crystal structure were done. Self-consistent field (SCF) calculations were carried out with a \(k\)-point grid of \(9 \times 6 \times 4\) in the irreducible Brillouin zone (BZ) of the monoclinic cell using the Monkhorst and Pack (MP) method.\(^{73}\) All DFT calculations were performed with dispersion corrected
vdW-DF functional\(^{74,75}\) of Klimes, Langreth and Lundqvist \textit{et al.} which takes into account the non-local nature of electron correlation. This functional is the optB88-vdW GGA functional\(^{76}\) with PBE potentials. It was previously reported\(^{77}\) that calculations with dispersion corrected vdW-DF functional yields better geometries and properties when compared with experiment than with conventional DFT functionals.

It is well documented that DFT underestimates the band gap and inadequately describes band structure in a variety of systems.\(^{78-80}\) EHTB is a semi-empirical method which has been used as alternative for reliable band structure calculations if the structure being modeled is well defined.\(^{81-83}\) Also EHTB is inexpensive compared to DFT calculations. Especially, EHTB calculations remain valuable in evaluating the salient electronic structural features of materials for which crystal structures are known. Here we performed EHTB calculations using the virtual nano lab-atomistic toolkit (VNL-ATK) software package\(^{84}\) on the TMPyP:TSPP crystal structure. The off-diagonal elements of the Hamiltonian are evaluated with the Wolfsberg–Helmholtz formula. Numerical integrations over the symmetry-unique section of the Brillouin zone of the crystal structure of TMPyP:TSPP were performed using a set of 76 \(k\)-points. Calculated matrix data was then used to plot the Density of states (DOS) and band structure. Using the band structure, the effective masses of electrons and holes at Gamma point (\(\Gamma\)) of the Brillouin zone were obtained.

### Result and discussion

#### Controlled TMPyP:TSPP crystal growth

Rod like TMPyP:TSPP crystals were formed reproducibly in a 1:1 stoichiometric tecton ratio in a neutral pH solution by a procedure described earlier.\(^{32}\) At this hydrogen ion concentration, the TMPyP and TSPP ions are in their free-base form (or protonation state) and their respective charges are +4 and −4. The charges on TMPyP and TSPP ions are further confirmed by molecular electrostatic potential (MEPs) mappings (Fig. 1 and Fig. S1, ESI\(^{†}\)) from DFT calculations on [H\(_4\)TMPyP]\(^+\), [H\(_2\)TSPP]\(^−\) ions and [H\(_4\)TMPyP]\(^+\)·[H\(_2\)TSPP]\(^−\) binary molecular structures. The MEP mappings show that most of the positive density is concentrated on the four pyridyl rings of [H\(_4\)TMPyP]\(^+\) and the negative density is concentrated on the four sulfonate groups in TSPP (Fig. 1). More interestingly, this is also true for the TMPyP:TSPP binary structure (Fig. S1, ESI\(^{†}\)). The MEP mapping of TMPyP:TSPP indicates that charge distribution is mostly localized within the binary structure with little charge transfer between the two ions, thus confirming the electrostatic nature of the binding between TMPyP and TSPP ions.

Grown in an aqueous environment at low porphyrin concentrations (5 \(\mu\)M) and elevated temperature (323 K) the average rod length was \(\sim 50 \mu\)m. Once formed these ionic crystals are nearly insoluble in water: \(3.1 \times 10^{-9}\) mol L\(^{-1}\) at 293 K and \(6 \times 10^{-8}\) mol L\(^{-1}\) at 343 K. For comparison solubility of saturated aqueous solution of AgCl is about \(1.3 \times 10^{-5}\) mol L\(^{-1}\). To increase the size of the crystals we used our predictive model which proposes lowering both the nucleation and growth rate by increasing the solubility of the ISA solid.\(^{32}\) Higher solubility of the product should reduce both the interfacial tension and supersaturation, two factors that strongly influence the final size of the crystals (see equations in Experimental section). Increased dissolution of TMPyP:TSPP was achieved by adding methanol or acetonitrile to the reaction mixture (see ESI,\(^†\) Fig. S2). Table 1, summarizes the dramatic changes in the nucleation rate with relatively minor increases in solubility of the ISA solid. Addition of 20\% of acetonitrile (by volume) to the reaction mixture increased the solubility of the TMPyP:TSPP solid by a factor of 5 while the nucleation rate is reduced by a factor of \(10^{10}\) compared to when water alone was used as the reaction medium. Methanol co-solvent yielded the same solubility and nucleation rate trends as the ACN, although the values were less dramatic. The final steps taken in optimizing the crystal size included adjusting the reaction temperature and tecton concentration.

The comparison of the size distribution of TMPyP:TSPP crystals produced in 20\% acetonitrile at 60 \(^{\circ}\)C with the predicted size range is illustrated in Fig. 3. The simulated histogram represented by solid red bars parallels the experimental (hollow bars) data very well, validating the accuracy of the predictive model. The purple TMPyP:TSPP crystals can be easily observed under a polarizing optical microscope as long uniform rods (inset in Fig. 3) averaging about 1 mm in length. The ISA rod-like crystals synthesized previously were at most 20 \(\mu\)m long.\(^{32}\) By using our predictive model we are able to controllably engineer porphyrin structures to a much greater length (~1 mm) while maintaining the same aspect ratio as those only a few hundred nm long.

It should be mentioned that TMPyP:TSPP crystals synthesized in three different solvent environments all have identical composition, tecton protonation state, and powder XRD patterns (Fig. S3, ESI\(^{†}\)). The stoichiometry of the porphyrin synthons as well as the protonation state of their pyrrole nitrogens were examined by X-ray photoelectron spectroscopy (XPS) as a routine analysis but are not presented here. For XPS data of the TMPyP:TSPP crystals prepared in water refer to our earlier study.\(^{32}\)

#### Crystal structure

High quality TMPyP:TSPP crystals prepared in 20\% ACN were used for the crystallographic measurements. The space group for TMPyP:TSPP crystal structure was determined to be monoclinic \(P2_1/c\) (No. 14) with cell constants \(a = 8.3049(11)\) Å,
same space group but somewhat different unit cell. In the previous report, small blue crystalline sheets or prisms were grown by slow diffusion in a propylene glycol gel for over 1.5 years.35

The crystal structure of TMPyP:TSPP presented here is consistent with 1:1 stoichiometry of ionic tectons in the nanorod as was previously determined.1 The a axis is the long (primary growth) axis in the rods. Fig. 4a depicts a projection down the crystallographic a axis in which the viewer sees molecules composed of half each the [H2TMPyP]+4 and the [H2TSPP]−4 ion because the molecular slab in that crystal direction in not flat (see Fig. 4b). There are five water molecules per porphyrin ion pair and they are located in the channels between the molecular stacks (only the oxygens are shown in Fig. 4).

The free-base porphyrin macrocycles are planar and form coherent columns (Fig. 4b) of alternating [H2TMPyP]+4 and [H2TSPP]−4 ions with their centers slightly offset relative to each other with an interplanar separation of 3.8 Å. The centroid to centroid distance is 4.15 Å. The phenyl sulfonyl and methyl pyridyl substituents on the porphyrin rings are rotated relative to the macrocyclic planes by 50.7° and adopt vertically parallel alignment within the macrocyclic columns (Fig. 4b) with a spacing of 4.15 Å between the phenyl rings and once again the interplanar distance is 3.8 Å.

Typically, π−π attraction between porphyrins leads to their aggregation in solution and crystalline phases resulting in a cofacial arrangement of the macrocycles that have their centers offset by approximately 3–4 Å along the pyrrole nitrogen–nitrogen axis.85,86 In these materials, two neighboring porphyrins are
parallel, with closest approach interplanar separation of 3.4–3.8 Å. In the ISA TMPyP:TSPP crystal, strong ionic attraction between the tectons plays the dominant role in their organization. The electron density, as seen from calculated MEPs (Fig. 1 and Fig. S1, ESI†), supports strong Coulombic attraction between alternating electron-deficient TMPyP and electron-rich TSPP molecular ions in what can be referred to as an ‘aromatic donor–acceptor interaction’.88 Although the π-orbital overlap between the ionic tectons is weak judging by the long interplanar distance of 3.8 Å, it importantly contributes to the overall columnar structure and stability of the TMPyP:TSPP supermolecular crystalline assembly.

**Morphology calculations**

Using the crystal structure parameters we obtained for TMPyP:TSPP crystals, their morphology was calculated employing both the BFDH and the AE methods. The AE model considers chemical bonding and has been rigorously tested for predicting morphologies of ionic and organic molecules.89 The calculated topographies of the TMPyP:TSPP system are depicted in Fig. 6. Both models predict rod cross sections with faces at 120°. However, the BFDH model predicts equilateral hexagon geometry whereas the AE model produces an elongated pseudo-hexagonal form.

It is gratifying to report that the crystal habit calculations correctly reproduced the experimentally observed pseudo-hexagonal topography of the TMPyP:TSPP rods shown in Fig. 5. In particular, the three dimensional rendering of AFM images of large TMPyP:TSPP rods, such as the one in Fig. 6b, reveal that the angles between its top face and the adjacent faces are nearly 120° (additional images of the TMPyP:TSPP crystals can be examined in the ESI†). Both the AFM and SEM images (Fig. 6) indicate that the (002) surfaces of the TMPyP:TSPP crystals are smooth and uniform while the (011) surfaces are stepped (e.g.; Fig. S4 and S5, ESI†). The numerous ISA rods examined were all pseudo-hexagonal, although few had symmetrical sides. (Fig. S4 and S5 in ESI†). It is obvious that the real crystals are much longer along the a axis that the models predict. We attribute this to the need for better parameterization in the COMPASS model for these materials.

The BDFH and the AE models showed that the most important morphological faces, are the {002} flat face and the {011} step and kink face as they make up most of the surface area of the TMPyP:TSPP crystal. The unequal {002} to {011} interplanar aspect ratio computed by the AE model is due to the higher face to face attachment energy leading to a faster crystal growth along the (001) direction. Also, as expected the {011} step and kink faces develop more rapidly (larger attachment energy) and have a smaller morphological importance compared to flat {002} face. This leads to the elongated hexagonal cross-section. AE calculations which include the facet area, attachment energy, and inter-planar distances in the TMPyP:TSPP crystals are summarized in Table S6, ESI†.

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**Fig. 5** Different calculated morphologies of TMPyP:TSPP crystal using: (a) BFDH theory showing view normal to the a crystallographic axis (long axis of the crystal); (b) BFDH theory displaying view normal to the b axis; (c) attachment theory with presenting normal to the a axis; (d) attachment theory showing view normal to b crystallographic axis.

---
Photoconductivity measurements

Absorbance, luminescence, and action spectra. Fig. 7a depicts overlaid UV-vis DRS spectra of the TMPyP:TSPP crystals and those of the parent synthons [H₂TMPyP]Cl₄ and Na₂[H₂TSPP]. The prominent Soret band present in each spectrum shows minimal shift of the maximum absorbance near 400 nm. Similarly, the Q bands of each molecular system have the same band profile and appear in almost the same region although with slightly different intensities. In Fig. 7b, the simulated spectrum of the TMPyP:TSPP crystals (obtained by addition of the TMPyP and TSPP free-base spectra) is compared to the actual UV-visible DRS spectrum of the TMPyP:TSPP crystals (normalized intensities). The absence of new absorption bands unique to the ISA species suggests a weak electronic interaction between the ionic tectons and, therefore, an absence of delocalized states within the rods that are accessible by photo-excitation. Thus, it appears that both porphyrins can be excited independently of the other. However, energy or charge transfer between molecules may still occur in states that are not photon accessible from the ground state; and, this concept is supported by the luminescence spectra. It is low energy states, like those from which the fluorescence occurs, that participate in the conduction process.

The luminescence spectrum of the TMPyP:TSPP rods is depicted in Fig. 7c. For comparison, the emission arising from an equimolar blend of the solid TMPyP and TSPP monomers...
(both in free-base forms) is also included in that figure. The intensity from the photoluminescence of the mixed porphyrins at 734 nm is dominated by the Q band emission from TMPyP. The solid state luminescence of TMPyP is similar to its emission spectrum in solution under neutral pH conditions.90 The TSPP free-base emission band from a powder sample is extremely weak (see Fig. S9 in the ESI†), unlike the fluorescence from the TSPP diacid in solution which is much more intense.30,91 The 807 nm emission band from the TMPyP:TSPP rods is very broad and red shifted relative to the luminescence originating from its monomers. This suggests that there are lower energy excited states that are unique to the ISA porphyrin system. The fact that the intensity of the luminescence does not increase with time eliminates the possibility that it originates from a photoinduced defect. Very recently, Natali and Scandola34 have demonstrated the presence of a low energy charge transfer state in zinc and free base TMPyP:TSPP dimers. From the electrochemical data they provide, the energy of the H2TMPyP:H2TSPP dimer can be estimated as 1.47 eV above the ground state. The observed luminescence (Fig. 7c) is a maximum at 1.49 eV, suggesting that its origin may indeed be a charge delocalized state.

The TMPyP:TSPP crystals are non-conducting in the dark but become conducting after illumination with laser radiation. Fig. 8 shows a comparison of the photoconductivity action spectrum with the UV-visible DRS spectrum of the TMPyP:TSPP crystals. The close similarities of the two spectra suggest that the number of electrons contributing to the photocurrent is directly proportional to the number of photons absorbed by the material. A further implication is that the mechanism of the immediate photoconductivity is the same whether excitation occurs in the Soret or the Q-band region. When the photoconductivity of the TMPyP:TSPP rods was examined as a function of laser power at 405 nm, 445 nm, and 671 nm excitation, a linear plot was obtained (Fig. S7 in ESI†). This linear power dependence of the photoconduction supports the conclusion that the number of electrons contributing to the photoconductivity is proportional to the number of photons absorbed. Moreover, the linearity shows that the mechanism of the photoconductivity does not change even at relatively high illumination intensity. The charge carriers in TMPyP:TSPP crystals were determined to be electrons based on the results of field-effect experiments where the photoconductivity was measured as a function of gate voltage (V_G). The measured source-drain current increased when V_G is positive and decreased when V_G is negative (see Fig. S8 in ESI†). This result is consistent with the behavior of n-type photoconductors where electrons are the primary charge carriers.39,92

Fig. 9a depicts a representative sample of the time dependent behavior of the TMPyP:TSPP rod photoconductivity at 25 °C using 671 nm and 445 nm excitation wavelengths. The time-dependent conductivity curve resulting from illumination with 671 nm laser light exhibits a very sharp rise in the photocurrent with the onset of illumination, followed by leveling off of the response, and then a steep drop in the signal when irradiation is terminated. The photoconductive response was prompt and reproducible with on/off illumination. The current vs. time curve which was obtained with excitation at 445 nm (Fig. 9b) shows a non-linear time dependence both upon illumination and when the light source is removed, signaling the presence of persistent photocurrent or persistent photocurrent, PPC. PPC is a photo-induced increase in the

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Fig. 8 Comparison of the UV-vis DRS spectrum of the TMPyP:TSPP rods and the photoconductivity action spectrum.

Fig. 9 Time dependence of the photoconductivity at TMPyP:TSPP acquired with a 671 nm laser illumination (a) and a 445 nm excitation (b) at room temperature.
electrical conductivity that persists after the illumination is switched off (thus retarding the recovery of the initial thermal equilibrium), often with very long time constants. The persistent photoconductivity decay observed in Fig. 9b can be fitted using the stretched exponential function:

\[ I(t) = I_{PPC} \exp \left( \left( \frac{t}{\tau} \right)^\beta \right) + I_{NPC}F(t) \]  

(5)

where \( I_{PPC} \) is the initial current (nA) from persistent photoconductivity; \( \tau \) is a weighted average lifetime (s); \( \beta \) is a stretching factor; \( I_{NPC} \) is the non-persistent photocurrent; and \( F(t) \) is a function describing the time dependence associated with \( I_{NPC} \), primarily arising from the time constant of the electronics used to measure the current. While analyzing the PPC data, only data obtained four seconds after illumination was terminated and beyond were considered. This was done to remove contributions from non-persistent photoconductivity (NPC). For a TMPyP:TSPP sample held at 25 °C (Table 2) having \( I_{PPC} = 1.22 \) nA the lifetime was 32881 s and \( \beta = 0.40 \). When the same sample was heated up to 100 °C (Table 2), \( \beta \) remained essentially unchanged while the value of \( \tau \) decreased dramatically indicating a thermally activated conduction process. We note that although the PPC and lifetimes varied for different samples, \( \beta \) was always 0.40 ± 0.04. For comparison the PPC observed in the zwitterionic TSPP nanorods fitted to the same function as in eqn (5) yielded \( \tau \) of 1500 s with \( \beta = 0.55 \).

Prompt and persistent photocurrent increased linearly with laser power with 445 nm excitation (see Fig. S10 in ESI†). The lifetime of the PPC decreases linearly with laser power (see Fig. S11 and Table S8 in ESI†) but the total decrease is small and the effect of 40 mW excitation is the same as a 6 °C temperature rise. It appears that the small decrease in the life time is due to a local heating by the laser.

**Periodic quantum mechanical simulations.** To further understand the electronic properties and to explain the photoconductive behavior of the TMPyP:TSPP rods, we performed periodic DFT calculations on its crystal structure. Water molecules were omitted from the calculations because they do not lie between the porphyrin stacks (Fig. 4) and should not interfere with the simulated band structure and electronic conduction along the \( a \)-axis of the crystal. Additionally, the \( \text{H}_2\text{O} \) molecules do not interact much with the porphyrin stacks based on the intermolecular distances. Hence, they should yield localized states much lower in the valence band or high in the conduction band which do not interfere with the photoconduction phenomena. As such, calculations performed on water free crystals should yield appropriate representation of the electronic structure in TMPyP:TSPP nanorods.

The calculated band structure and respective density of states (DOS) of crystalline TMPyP:TSPP are shown in Fig. 10. The projected density of states shows that the top of the valence band is populated by the contributions from TSPP and the bottom of the conduction band is populated by the TMPyP. There is also no mixing/hybridization of orbitals between TSPP and TMPyP ions in the vicinity of the band gap (Fig. 10a). The bandgap is calculated to be 0.90 eV. It has been reported⁷⁸–⁸⁰ that conventional DFT underestimates the bandgap and extended

### Table 2 Temperature dependence of photoconductivity of a TMPyP:TSPP sample under 445 nm, 21 mW laser irradiation

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>( I_{PPC} ) (nA)</th>
<th>( I_{PPC}/I_{NPC} )</th>
<th>( \tau ) (s)</th>
<th>( \beta )</th>
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</thead>
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<tr>
<td>25</td>
<td>1.22</td>
<td>2.83</td>
<td>32881</td>
<td>0.40</td>
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<tr>
<td>65</td>
<td>3.39</td>
<td>4.84</td>
<td>10473</td>
<td>0.38</td>
</tr>
<tr>
<td>100</td>
<td>4.32</td>
<td>7.08</td>
<td>1572</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Fig. 10 Projected density of states and band structure for the TMPyP:TSPP crystal computed from (a) DFT and (b) EHTB. The contributions from the TSPP is shown in green and that of TMPyP is depicted in red. The Fermi level \( (E_f) \) is set at zero in either method. The high symmetry points the Brillouin zone are as follows, \( \Gamma = (0,0,0), Z = (0,0,0.5), Y = (0,0.5,0), X = (0.5,0,0), A = (−0.5,0,0.5), E = (−0.5,0.5,0.5), B = (0,0,0.5) \). Brillouin zone is depicted in Fig. 11e.
Hückel tight binding (EHTB) method better estimates the band gap.\textsuperscript{81–83} The band structure and projected DOS of TMPyP:TSPP crystal obtained from EHTB calculations are depicted in Fig. 10b. The calculated EHTB bandgap is found to be 1.3 eV. The DOS and band structure obtained from EHTB correlates with the DFT result, but gives a somewhat different picture of tecton orbital mixing and band dispersion. Examining the band structure from either method shows little dispersion either at the top of the valence band or at the bottom of the conduction band. Comparative DOS obtained from DFT and EHTB calculations is presented in the ESI\textsuperscript{†} (Fig. S6). Together the DOS and band structure supports the experimental analysis from absorption spectra (vide supra) of TSPP, TMPyP, and TMPyP:TSPP structures that there is a minimal electronic interaction between the porphyrin species.

The weak dispersion that was observed in both VASP and EHTB band structure was mostly along the \( \Gamma - Y \) \( k \)-path in the Brillouin zone (Fig. 11b). The \( \Gamma - Y \) path corresponds to propagation along the long (\( a \)) axis of the TMPyP:TSPP crystal structure, which is also the \( \pi - \pi \) stacking axis of TMPyP and TSPP molecules (Fig. 4). Based on the band structure dispersion, crystal structure stacking and morphology, the electronic conduction in the nanorods is mostly expected to be along the stacking axis. It should be noted that both the phenyl and pyridyl substituents of TSPP and TMPyP molecules also exhibit \( \pi - \pi \) stacking along with the core porphyrin structure. Hence, we plotted the projected DOS of the TMPyP:TSPP as a function of \( \pi - \pi \) stacking and non-\( \pi - \pi \) stacking (–SO\(_3\) and –CH\(_3\) groups) atoms in Fig. S6 in ESI\textsuperscript{†} to elucidate the photoexcitation and conduction process.

It should be noted that unlike the DFT result, the EHTB show some near degeneracy of TSPP and TMPyP \( \pi \) structure in both the HOMO and LUMO region. Thus, there is the possibility of charge exchange within these bands.

Comparison of UV-visible DRS and photoconductivity action spectrum (Fig. 8) of TMPyP:TSPP rods showed no peaks unique to dimeric species. In other words, these spectra show that photoexcitation of the rods both in the Soret and Q-bands regions lead to electronic transitions from TSPP and TMPyP molecules distinctly. Consequently, if the rods are excited at a wavelength of 671 nm (1.85 eV), based on the computed band structure (Fig. 10a), the electrons should excite from both TSPP at \(-0.6 \text{ eV}\), and TMPyP at \(-1.3 \text{ eV}\) valence bands simultaneously to TSPP at \(+1.0 \text{ eV}\) and TMPyP at \(+0.5 \text{ eV}\) conduction bands respectively. Similarly, in the Soret region, photoexcitation with 445 nm (2.79 eV) wavelength, leads to electronic transitions from both TSPP at \(-0.6 \text{ eV}\) and TMPyP at \(-1.3 \text{ eV}\) valence bands simultaneously to TSPP at \(+2.1 \text{ eV}\) and TMPyP at \(+1.5 \text{ eV}\) conduction bands, respectively. It was found that quantum efficiency, electrons out per photon absorbed (see the action spectrum Fig. 8 obtained from photoexcitation at 445 nm is the same as with excitation with a 671 nm laser). Thus, the conductivity arises from relaxation to a band (or bands) below those to which absorption occurs – presumably the bands near \(+0.85 \text{ eV}\) in the extended Hückel computation (Fig. 10 and 11). The lowest unoccupied bands have only small dispersion, and they produce only meager conductivity – the quantum efficiency defined in terms of electrons out per electron impinging on a rod (not necessarily absorbed) is only about 0.1%. The greater dispersion in the conduction band relative to the valence band accounts for the electrons being the primary charge carrier for photoconductuation.

Fig. 11 shows the EHTB calculated band structures and respective Brillouin zones of TMPyP:TSPP crystal structures modified by changing the \( a \)-axis (which is also the \( \pi - \pi \) stacking axis) of the experimental unit cell (Fig. 4). Fractional atomic coordinates were used while generating the new structures, hence changing the \( a \)-axis of the crystal unit cell only shifts the \( x \)-coordinates of the atoms by a specified value. The length of the \( a' \) lattice parameter obtained from X-ray crystallography is 8.3 Å, which renders the TMPyP:TSPP interplanar/\( \pi \)-stacking distance of 3.84 Å. The band structures in Fig. 11 are obtained with \( a' \)-lattice parameters of 7.8, 8.3 and 8.8 Å from left to right respectively. Hence the \( \pi \)-stacking distances between porphyrins are 3.67, 3.84, 4.01 Å respectively.

The calculated band structures show that by modifying the stacking distance the band gap is almost invariant \(-1.25 \text{ eV}\) (Fig. 11a) to \(1.30 \text{ eV}\) (Fig. 11b) to \(1.27 \text{ eV}\) (Fig. 11c). But, the band dispersion increases significantly with reduced stacking distance. For example, in Fig. 11a–c between \(0.8–0.9 \text{ eV}\) (bottom of conduction band), significant change in band dispersion can be seen. The dispersion near \(0.85 \text{ eV}\) is about \(0.2 \text{ eV}\) for \(3.67 \text{ Å} \) stacking distance (Fig. 11a) and is reduced to \(0.1 \text{ eV}\) dispersion with \(3.84 \text{ Å}\) stacking (Fig. 11b). With \(4.01 \text{ Å}\) stacking distance (Fig. 11c), the bands are completely flat with no significant dispersion. Additionally the effective masses (\( m^* \)) obtained at the gamma point (\( \Gamma \)), Table S7 (ESI†), show that decreasing the \( \pi \)-stacking distance significantly decreases \( m^* \). For example, the highest occupied (valence) band has an effective mass reduction from \(-129.7 \text{ } m_e\) to \( -18.6 \text{ } m_e \) \((m_e = \text{mass of electron})\) when the stacking distance decreases from \(4.01 \text{ Å} \) to \(3.67 \text{ Å} \). Since carrier mobility (\( \mu \)) in a semiconductor is inversely proportional to the effective mass of the charge, lowering \( m^* \) results in better mobility. Hence, EHTB calculations show that if we can decrease the \( \pi \)-stacking distance between the porphyrins in ISA porphyrin crystals, much better carrier mobilities can be achieved.

One strategy to decrease the intermolecular ionic tecton spacing is to reduce the size of the cationic and anionic ring substituents. Both the \(-\text{SO}_3^-\) and \(-\text{N}^+\text{CH}_3\) are bulky groups and replacing them with smaller functionalities such as \(-\text{O}^-,\) \(-\text{COO}^-\) and \(-\text{NH}^+\) (pyridyl) will aid in reducing the approach distance between the porphyrin synthons and increase their \( \pi - \pi \) interactions.

Using a combination of experimental and computational techniques, we have shown that the TMPyP:TSPP nanorods can be synthesized in a controlled fashion and that they exhibit significant photoconductive properties. Quantum mechanical calculations have shown that the \( \pi - \pi \) stacking of porphyrin molecules is primarily responsible for photoconductivity in TMPyP:TSPP nanorods. The \( \pi - \pi \) stacking distance in the crystal structure is found to be 3.8 Å. Using quantum mechanical calculations, we have shown that by reducing the stacking...
distance between porphyrin ionic tectons in the crystal, we can increase the band dispersion, reduce the band gap ($E_g$), lower the effective masses ($m^*$) and therefore increase the mobility of charge carriers in the in ISA porphyrins. Therefore, if we can engineer a crystal structure with reduced porphyrin stacking distance, we can significantly improve the conduction properties of porphyrin based nanostructures.

While the calculated band structure provides insight into the electronic transitions responsible for the photoconductivity, it does not provide an explanation for the observed PPC shown in Fig. 9b. The observed lifetime associated with the PPC is on the order of hundreds of seconds and is therefore too long to be attributed to simple electron–hole recombination. Therefore, to fully understand the photoconductive behavior of the TMPyP:TSPP system, we propose a model describing the observed PPC.

Proposed model for photoconductivity. To explain the observed photoconductivity, we propose the following model, shown in Fig. 12. The nanorods exhibit two types of photoconductivity: band conductivity and hopping conductivity. The band conduction takes place as described above. Hopping conductivity occurs via the formation of photo-induced (meta-stable) defects (PIDs). We believe that these defects are small localized changes in the molecular structure or packing. The time scale of the measured PPC is much too long to be explained by a purely electronic phenomenon. These PIDs lie in between the valence and conduction bands and near the Fermi level of the gold electrodes. Electrons can be injected from the gold electrodes into a PID, at which point they travel along the length of the rod via a thermally excited hopping mechanism. The PIDs are only formed at higher energy excitations, which is why excitation at 671 nm doesn’t result in PPC while excitation at 445 nm does.

The hopping rate between two sites $i$ and $j$, $\nu_{ij}$ can be described using the Miller–Abrahams model:

$$
\nu_{ij} = \nu_0 \exp \left( -\frac{2R_{ij}}{b} \right) \left( \frac{|e_j - e_i| + (e_j - e_i)}{2kB_T} \right)$$

where $R_{ij}$ is the distance separating sites $i$ and $j$ ($\text{Å}$); $\nu_0$ is the hopping attempt frequency ($\text{s}^{-1}$); $e_i$ and $e_j$ are the energies of
sites $i$ and $j$ respectively (eV), and $b$ is the localization radius of a charge carrier ($\text{Å}$).

As the concentration of metastable defects in the nanorods, $N$, increases, the average intersite distance, $a$ where $a = N^{-1/3} = \langle R_{ij} \rangle$, decreases, resulting in an increase in hopping rate ($\nu_{ij}$). The hopping rate is related to the drift mobility ($\mu_x$) by the expression:

$$\mu_x = \frac{ea^2\nu_{ij}}{k_B T}$$  \hspace{1cm} (7)

where $e$ is the elementary charge. The drift mobility is related to the conductivity ($\sigma$) of the system by the expression:

$$\sigma = n\mu_e$$  \hspace{1cm} (8)

where $n$ is the number of electrons. After the nanorods have been illuminated for a long period of time, on the order of thousands of seconds, an equilibrium concentration of metastable defects is reached and current levels off. When illumination stops, the concentration of metastable defects ($N$) begins to decrease. As $N$ decreases the distance $a$ increases, resulting in a decrease in mobility and subsequently a decrease in conductivity. This model is similar to one we have used to explain the ion induced persistent conductivity in another ISA porphyrin system.$^{95}$

The prompt photocurrent produced by irradiating the TMPyP:TSPP rods at 671 nm increases when the sample is heated. An Arrhenius plot of the NPC as a function of temperature yielded an activation energy ($E_A$) of 205 mV (see Fig. S12a, ESI†). This energy barrier can be associated with the electrons in the lowest state of the Q band crossing over into the conduction band. When the porphyrin crystals were illuminated with the 445 nm laser line, the PPC increased with increasing temperature while the nonpersistent current remained steady (Table 2). An Arrhenius plot of the PPC variation with temperature gave $E_A$ value of 165 mV (Fig. S12b in the ESI†). This activation barrier, we believe, is associated with a transition from the lowest excited bands of the rod to the ground state of a photoinduced defect.

In semiconducting materials where the stretched exponential function has been used to model the decay of the PPC, $\beta$ has been associated with the dimensionality of the charge transfer processes, where for a one-dimensional charge transport process has $\beta \leq 0.5$. In the TMPyP:TSPP material, $\beta = 0.40$, suggesting a one-dimensional charge transfer process. This is consistent with the hypothesis that conduction in these materials is facilitated via $\pi-\pi$ interactions. In the TMPyP:TSPP crystals, all of the $\pi-\pi$ interactions occur along the $a$-axis, or along the length of the nanorods.

**Conclusion**

A detailed study that correlates the crystal structure and photoconductivity of a binary TMPyP:TSPP porphyrin solid was presented. Variable size rod-like structures were synthesized in a controlled and reproducible manner by applying a previously developed nucleation and growth model and manipulating the solubility of the TMPyP:TSPP crystals in the solution. The observed pseudo-hexagonal morphology of the ISA crystals was readily reproduced by applying predictive models that utilized the crystal structure parameters obtained for porphyrin system. Predicting crystal habit may be useful in designing ISA crystals with specific geometric considerations.

The diffuse reflectance electronic spectrum of the TMPyP:TSPP solid was similar to co-added absorbance spectra of the TMPyP and TSPP free-base parent tectons. The absence of new absorption bands unique to the ISA species suggested that only weak electronic interaction exist between the ionic synthons and, therefore, there is an absence of delocalized photo-absorbing states within the rods. However, the luminescence spectrum indicates that the lowest excited states are different than those of the individual components. Similar features in the absorption and action spectra suggest that the number of electrons
contributing to the photocurrent is directly proportional to the number of photons absorbed by the material. Gate voltage experiments show that TMPyP:TSPP solid is an n-type conductor while quantum-mechanical simulations suggest that it has a direct band gap, thus making ISA porphyrin nanostructures good candidates for optoelectronic devices.

Based on the calculated band structure (both EHTB and DFT) it is apparent that the conduction is along the stacking direction (a crystallographic axis) of the crystal and is facilitated via π–π interactions. The dispersion within the bands is weak which is consistent with the observation of low quantum efficiencies as well as the lack of any unique bands in the DRS absorbance spectrum of TMPyP:TSPP.

The photoconductive response of TMPyP:TSPP was found to be significantly different for excitation into the Q and the Soret bands. The current vs. time excitation profile for the Soret band had a non-linear time dependence when the light source is removed, signaling the presence of persistent photocurrent or photoconductivity which has a life time on the order of hours. The PPC behavior can be rationalized by the presence of photo-induced metastable defects (PID) which allow for Miller–Abrahams hopping conductivity. The PPC decay can be modeled using a stretched exponential function. The value of β (stretching factor) obtained using this fit is consistent with a one-dimensional charge transfer process.

In general, this study provides a procedure to synthesize and controllably grow various organic nanostructures by modifying their reaction environment. Using computational modeling we have shown that the crystal structure can be used to predict the morphology and to better understand the conductive behavior of organic nanostructures.

**Abbreviation**

<table>
<thead>
<tr>
<th>Term</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>AE</td>
<td>Attachment energy model</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>BFDH</td>
<td>Bravais–Friedel–Donnay–Harker model</td>
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<tr>
<td>BPN</td>
<td>Binary porphyrin nanostructure</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
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<tr>
<td>DAQ</td>
<td>Data acquisition system</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<td>DOS</td>
<td>Density of states</td>
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<td>DRS</td>
<td>Diffuse reflectance spectroscopy</td>
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<tr>
<td>EHTB</td>
<td>Extended Hückel tight binding method</td>
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<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<td>IDE</td>
<td>Interdigitated electrodes</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<td>MP</td>
<td>Monkhorst and Pack method for k-space sampling</td>
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<td>NPC</td>
<td>Non-persistent photocurrent</td>
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<td>PAW</td>
<td>Projector augmented wave potentials</td>
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<tr>
<td>PBE</td>
<td>Perdew–Burke–Ernzerh of exchange–correlation functional</td>
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<tr>
<td>PID</td>
<td>Photo-induced metastable defects</td>
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<td>PPC</td>
<td>Persistent photoconductivity</td>
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<td>SCF</td>
<td>Self-consistent field</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TMPyP</td>
<td>Meso-tetra(N-methyl-4-pyridyl)porphyrin</td>
</tr>
<tr>
<td>TSPP</td>
<td>Meso-tetra(4-sulfonatophenyl)porphyrin</td>
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<td>UV-vis</td>
<td>Ultraviolet-visible spectrophotometry</td>
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<td>VASP</td>
<td>Vienna Ab initio Simulation Package</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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