

Structure of a Supramolecular Water Copolymer

Joseph F. Woods,^{a,‡} Kai Zhang,^{a,b,‡} Joëlle Peterschmitt,^c Olivier Blacque,^a Céline Besnard,^c Gustavo Santiso-Quinones,^d Laura Samperisi,^d Andreas Vargas Jentzsch,^e Michel Rickhaus^{*a,b}

^aDepartment of Chemistry, University of Zurich, 8057, Zurich, Switzerland

^bDepartment of Organic Chemistry, University of Geneva, 1205, Geneva, Switzerland

^cLaboratoire de Cristallographie, University of Geneva, 1211, Geneva, Switzerland

^dELDICO Scientific AG, 4123, Allschwil, Switzerland

^eSAMS Research Group, University of Strasbourg, Institut Charles Sadron, CNRS, 67200, Strasbourg, France

[‡]These authors contributed equally.

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ABSTRACT: The use of water as a solvent to facilitate supramolecular polymerization is well documented, however, it is rare that water acts as a monomer that undergoes polymerization. We report the copolymerization of water with a saddle-shaped porphyrinoid macrocycle, carpyridine, which allows for linearly stacked, eclipsed columns within formed 2D nanosheets. Self-assembling carpyridine monomers from solutions with different extents of wetness allow for the formation of nanosheets on surface that appear identical by microscopy. Structural analysis through electron diffraction reveals fundamental changes in the local organization. Under dry conditions, carpyridine stacks are formed through π - π interactions between curved surfaces whereas in solutions containing greater quantities of water, a hydrogen-bonded water-to-carpyridine-core network is propagated throughout perfectly linear columns. The observed wet phase can be interconverted to a dry one through vapor annealing, indicating an accessible energy surface of polymorphism.

The impact of water upon the capability of a monomer to self-assemble is well-known and carefully considered in supramolecular chemistry.¹⁻³ Self-assembly can be promoted or prevented by the presence of water or even prompt a change of assembly mode upon its addition.⁴⁻⁷ When employed as a solvent or a co-solvent for polymerization, water often exploits the hydrophobic character of monomers to organize matter in a manner that excludes the aqueous media or affects the strength of a hydrogen bond.⁸⁻¹² An alternative manner to facilitate or disrupt assembly is through direct coordination of the water molecules to specific sites on the assembling monomer, such as a group capable of forming hydrogen bonds.¹³⁻¹⁵

The affinity of water to bind to the monomer varies in each case, however, it is important to acknowledge that even in low quantities, water may have a drastic effect upon the polymerization.^{16,17} This is particularly notable in systems where multiple, weaker interactions are at play.^{18,19} The role of water is often speculated upon or implied in supramolecular polymerization as direct evidence of its precise involvement is difficult to obtain.²⁰ Herein, we present, to the best of our knowledge, the first known case for copolymerization of a porphyrinoid macrocycle and water that is supported with crystallographic evidence.

Carpyridines are porphyrinoids that our group have used to exert control over self-assembly processes by leveraging molecular curvature to govern weak interactions, resulting in the formation of columnar assemblies within 2D nanosheets and 1D fibers.^{6,21,22} Incorporation of negative curvature within the molecule limits the extent of rotational and translational freedom individual units have when aggregated into linear columns (**Figure 1**, left).^{6,22} These systems are weakly organized which permits modulation of the crystallinity from crystal into soft systems by simply trimming or expanding the sidechains by one or two carbons. The heteroatom-rich core is not

engaged in binding and is not a driver for the assembly. We rationalized that this vacancy could act as a preorganized framework to host water at the expense of π - π interactions (**Figure 1**, right). Tuning the crystallinity well enough should consequently allow for probing of the organization of the units within the polymer.

We sought to prepare a more rigidified system through restriction of the disorder typically associated with flexible alkyl sidechains at the periphery of the macrocycle. Retaining a six-carbon count in the sidechain was ideal for assembly but cyclization and planarization into an aryl ring (phenyl) would remove significant disorder. Rationalization that the aromatic sidechain would likely favor a coplanar arrangement with the carbazole and strengthen the shape-governing effect.^{21,22} In addition, the phenyl rings provide an opportunity for further π - π interactions that rigidify and rectify the self-assembled structure. This should make such a system suitable for diffractive analyses, such as micro-electron diffraction (μ -ED), to identify the assembly packing mode.

Synthesis began through functionalization at the 3- and 6-positions of the carbazole with a phenyl ring was sought to prepare a more electron rich system (**Scheme 1**). Phenylboronic acid was reacted with 3,6-dibromocarbazole *via* a Suzuki cross-coupling with Pd(PPh₃)₄ to provide 3,6-diphenylcarbazole **1**. This was then subjected to bromination and subsequent Miyaura borylation conditions. Suzuki-Miyaura cross-coupling of one equivalent of the diboronic ester **3** with an initial half an equivalent of dibromopyridine, followed by sequential addition of a further half equivalent yielded the desired phenylated carpyridine, **2H-Car-Ph**, in an improved yield of 21% compared to alkyl derivatives. UV-vis and fluorescence emission spectroscopy in toluene (**Figure S7**) returned the expected optical profiles of a carpyridine but also showed a red-shift in maxima compared to the previous alkyl derivatives. The shift of the

Water alters local organisation

Columnar arrangements of carpyridines depend on the presence of water. Left: carpyridines are rotationally locked by curvature but slip translationally due to π - π stacking. Right: intercalated water moves the carpyridine π -surfaces apart which enables eclipsed stacking. Curvature still restricts rotation.

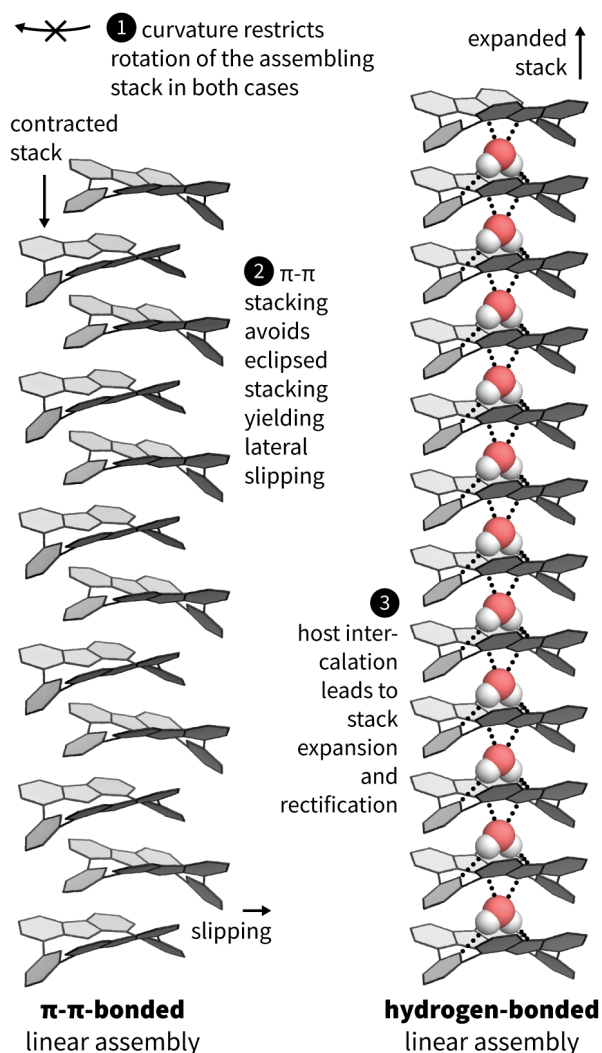
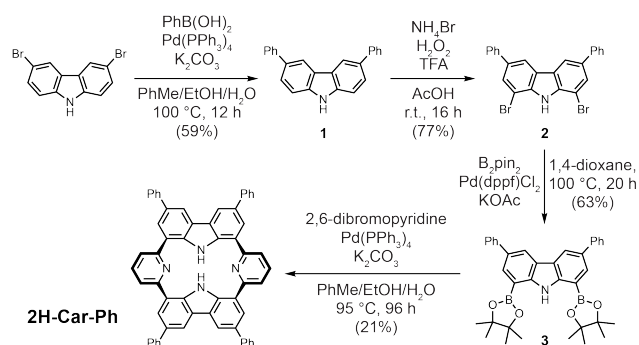


Figure 1. Different columnar arrangements of carpyridines are possible depending on the presence of water. Left: crystal structure of **2H-Car-Ph** grown from toluene/methanol, right: μ -ED (r.t.) of **2H-Car-Ph** nanosheets grown from wet toluene.

maxima to lower energies of 319 nm and 380 nm in the absorption spectrum indicated coupling between the carbazole and benzene ring systems. **2H-Car-Ph** exhibited a moderately strong fluorescence quantum yield of 50% from a single band at 397 nm.

The carpyridine was dissolved in dry toluene (13 ppm, determined via Karl-Fischer titration) to provide a 1 mM solution as water was perceived to hinder assembly formation.⁶ After heating and cooling back to room temperature, the solution was dropcasted onto a C/Cu



Scheme 1. Synthetic route towards **2H-Car-Ph**. The macrocyclization reaction follows an optimized procedure involving sequential addition of the 2,6-dibromopyridine to favor carpyridine formation.

transition electron microscopy (TEM) grid to determine the self-assembly capability on-surface. Examination of the sample under the TEM beam showed the presence of multi-micrometer long nanosheets that were notably thinner than those seen with the alkyl derivatives (**Figure 2**).

To assess whether the nanosheets were formed using regular toluene with a higher water content (101 ppm) due to storage under ambient conditions, further 1 mM solutions were prepared, dropcasted and visualized under the TEM (**Figure 2**). This revealed similar rectangular objects on surface with arguably smoother nanosheet edges and prompted questioning of whether assembly formation was possible in solvent that was deliberately wetted. A solution of the same concentration of **2H-Car-Ph** in wet toluene (334 ppm) was then prepared, which again provided nanosheets of similar thicknesses, lengths and well-defined edges (**Figure 2**). For all three conditions used to prepare **2H-Car-Ph** nanosheets, atomic force microscopy (AFM) was used to confirm the uniformity and height of the assemblies, which is in the range of tens to hundreds of nanometers, highlighting their multilayered nature (**Figure 2**).

Insights into the molecular structure within the nanosheets were provided from the selected area electron diffraction (SAED) patterns in TEM (**Figure 2**, **Figure S16**). Discrete diffraction spots and their spacings in two dimensions demonstrated that different compositions were observed depending upon the water content of the toluene within the **2H-Car-Ph** solutions. The SAED patterns with dry toluene provided different values ($7.6 \times 17.2 \text{ \AA}$) to those seen with regular and wet toluene ($4.2 \times 16.4 \text{ \AA}$ and $4.4 \times 16.2 \text{ \AA}$, respectively), suggesting that a different assembly is obtained when using dry toluene instead of regular or wet toluene. The stability of the nanosheets formed using dry toluene under the electron beam was noticeably greater than those prepared from regular or wet toluene.

Single crystals of **2H-Car-Ph** were grown from vapor diffusion of methanol into regular toluene to examine which structure is adopted in the macroscopic crystalline state and to deduce the degree of coplanarization within the molecular saddle. Lattice parameters were in agreement ($17.5 \times 7.6 \times 31.7 \text{ \AA}$) with the 2D parameters obtained from the SAED pattern with dry toluene and the carbazole and phenyl rings shared a similar plane, indicating a larger saddle

Dryness-dependent nanosheet formations

TEM reveals long, rectangular nanosheets of multimicrometer length and similar apparent morphology when dropcasted from toluene solutions of varying dryness

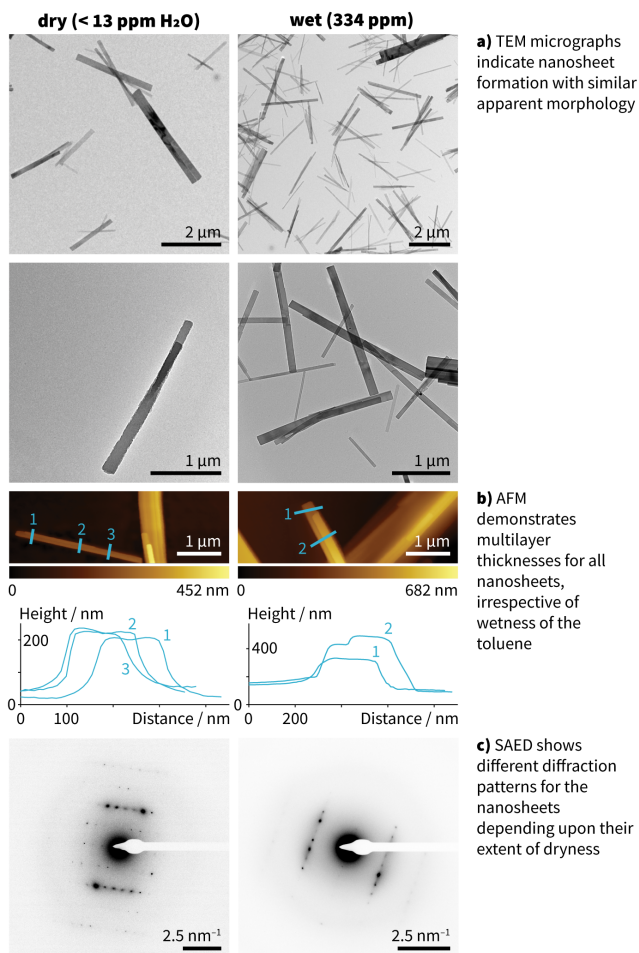


Figure 2. TEM micrographs, AFM images and height traces, and SAED patterns of **2H-Car-Ph** nanosheets from dry and wet toluene.

topography. Propagating the crystal structure packing revealed an environment of antiparallel columnar arrays containing **2H-Car-Ph** molecules (**Figure 3**) with a slight lateral translational offset. The addition of the phenyl ring appeared to impose a heavy restriction upon both rotational and translational motion, more so than the rotational locking effect seen with alkyl carpyridines.²² The maximum value of permitted rotation is lowered to 0.45° between carpyridines and, crucially, significant contractions in the columnar width were realized such that **2H-Car-Ph** is only found in two distinct environments. Individual columns are then further rigidified through lateral CH- π interactions with neighboring columns and the presence of an additional toluene solvent molecule within the unit cell assists the expansion of the structure into three dimensions.

Determining the structure of the nanosheets formed from wet toluene relied upon using μ -ED (r.t.) with an ELDICO ED-1 diffractometer due to the sensitivity of the sample to the electron beam with other techniques. Carpyridines were observed in perfectly eclipsed

antiparallel columns and are reinforced through a hydrogen-bonding interaction with a co-assembling water molecule inserted in the central cavity of the macrocycle (**Figure 3**). The water molecule forces the carpyridine macrocycles to be 4.22 Å apart from one another (vs. 3.81 Å observed in dry samples) with connecting hydrogen bonds from the carbazole N-H groups to the oxygen of water (2.06 Å) and from the hydrogens of water to the pyridines of **2H-Car-Ph** (2.40 Å). This second hydrogen bond appears to be weaker due to the longer bond length. A single water molecule between two carpyridines appears to hold the structure together, overcoming the π - π interactions responsible for the assembly in dry toluene. This interaction nullifies any rotational or translational offsets and also alters the packing of the carpyridines such that voids form between columnar arrays (**Figure S33**). These voids are propagated throughout the structure, leading to porous 1D channels within the nanosheets that account for 14% volume of the unit cell.

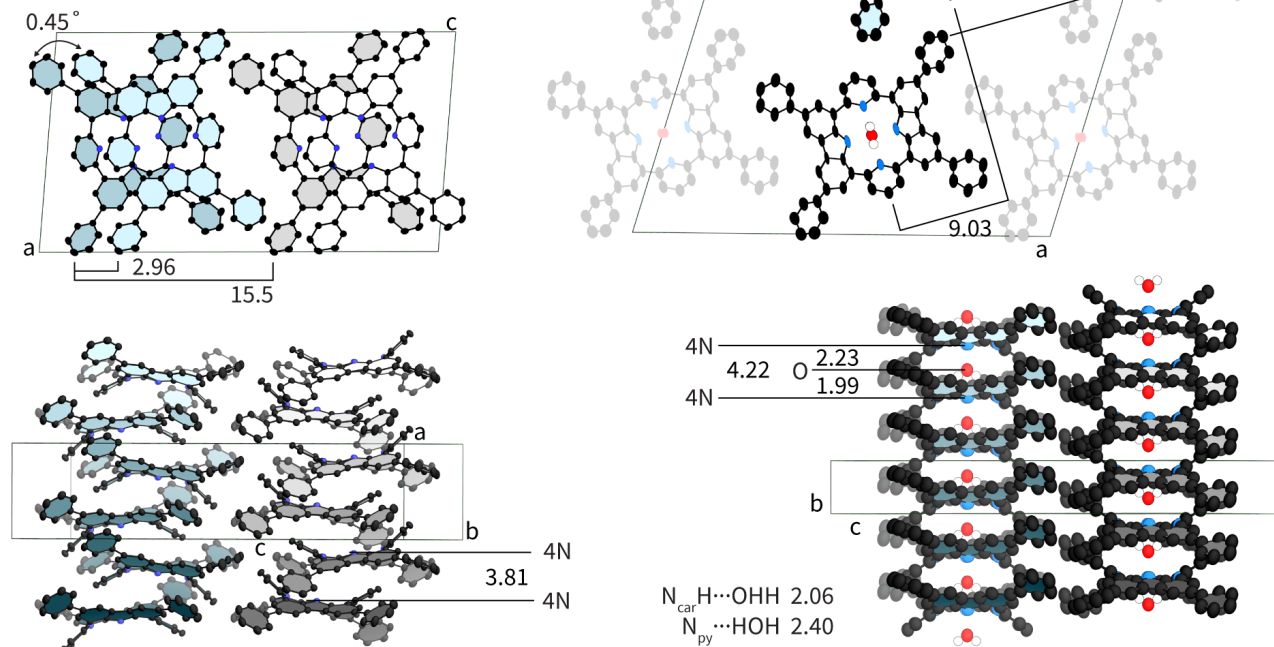
When examining the non-dried samples of **2H-Car-Ph** at low temperatures, cryo-ED (100 K) revealed a phase change to a structure that appears to exist in a form between dry and wet conditions. Carpyridines were seen to stack into slightly slipped antiparallel columns but with an intercalated water molecule between each macrocycle (**Figure S31**). The tripling of the unit cell along the stacking direction allows distinct carpyridine and water environments exist in the column due to small translational offsets, yielding an average rotation of 5.6° between carpyridines. Voids are found between carpyridine columns that lead to porous channels throughout the nanosheets but are less well defined compared to the structure obtained from μ -ED (r.t.). This reorganization at low temperature of the non-dried sample hints towards the existence of other semi-stable intermediate states. Conversion of the nanosheets formed under wet conditions to dry assemblies through annealing in dry toluene succeeded as evidenced by powder X-ray diffraction (PXRD). The inverse transformation, annealing dry nanosheets in water-saturated toluene did not result in a phase change, which we believe to be a consequence of the dry polymorph being overall more compact. Full dissolution into the monomeric state and drying does then allow access to the other polymorph.

To assess whether association occurs in solution for **2H-Car-Ph**, variable temperature (VT) UV-vis experiments were performed in dry toluene. (**Figure S8**) There was no spectroscopic indication of aggregation as only linear changes were detected when changing temperature. There were no apparent changes to the absorption signatures in relation to the dryness of the toluene solution (dry, regular or wet), suggesting that polymerization does not occur in solution (**Figure S9**) at this concentration and temperature window. When titrating trifluoroacetic acid (TFA) into a toluene solution of **2H-Car-Ph**, a new band in the absorption spectrum at 430 nm evolved (**Figure S10**). However, no ordered structures were visualized with TEM (**Figure S17**). The addition of TFA made the crystallization process more favorable, but the obtained carpyridine-TFA crystal structures are clearly distinct from the ones discussed earlier. Notably the co-assembly by coordination to the TFA anion is clearly evidenced. This observation indicates that the spectroscopic observations are to be attributed to the coordination complex formation (**Figures S26** and **S27**) and not polymer formation.

Solid state structures

In the absence of water (< 13 ppm H₂O)

XRD and SAED reveal columnar contractions within shape-assisted stacks in the macroscopic crystalline state and in nanosheets formed from dry toluene



in the presence of water (334 ppm H₂O)

μ -ED and SAED patterns from structures grown from regular and wet toluene solutions indicate linear, eclipsed stacking arrangements between carpyridines with intercalated water molecules

Figure 3. Structure of **2H-Car-Ph** nanosheets in dry conditions, left, and in the presence of water, right. Hydrogen atoms are omitted for clarity.

Although there are reports of water facilitating the supramolecular polymerization of monomers,^{3,20,23,24} elucidation of water acting in such a precise manner within the repeating unit has not been achieved to our knowledge. There is no evidence of copolymerization with water in other alkylated carpyridine systems, however, it is known that phenyl rings can assist with water incorporation.^{25,26}

While **2H-Car-Ph** is arguably an ideal molecular system to study supramolecular copolymers with water, their observation was made possible due to the appropriate use of the relatively new technique of electron diffraction. Classical techniques either failed to resolve the structure or gave visually identical appearances, underpinning how important a careful analysis is required to reveal the local organization within a polymer.

The uncovered porous channels within the water-containing nanosheets pose an opportunity for host-guest chemistry, like gas adsorption. The discovery also presents the opportunity to utilize and tune carpyridines to become ligands that influence supramolecular ordering. Single crystal X-ray diffraction has also shown that π -extension of the carpyridine core increases the shape-assistance effect from a larger saddle to restrict the disorder in the formed columnar

stacks, adding weight to the shape-assisted self-assembly argument. Further π -extension and intercalation studies are currently in progress with the goal of expanding and unifying our observations to linear supramolecular polymers in solution in general.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* Michel Rickhaus, michel.rickhaus@unige.ch

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