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Additional supporting information (SI)—STM results of as-deposited CA/3-HPLN films as well as CA/RA films, additional computational results and details, supplementary calculations regarding epitaxy considerations and dipolar moments, and structure coordinates—follows the references.

2D Cocrystallization from H-Bonded Organic Ferroelectrics

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Abstract

The synthesis of 2D H-bonded cocrystals from the room-temperature ferroelectric organics croconic acid (CA) and 3-hydroxyphenalenone (3-HPLN) is demonstrated through self-assembly on a substrate under ultrahigh vacuum. 2D cocrystal polymorphs of varied stoichiometry were identified with scanning tunneling microscopy, and one of the observed structural building blocks consists of

two CA and two 3-HPLN molecules. Computational analysis with density functional theory confirmed that the experimental (CA)₂(3-HPLN)₂ tetramers are lower in energy than single-component structures due to the ability of the tetramers to pack efficiently in two dimensions, the promotion of favorable electrostatic interactions between tetramers, and the optimal number of intermolecular hydrogen bonds. The structures investigated, especially the experimentally found tetrameric building blocks, are not polar. However, it is demonstrated computationally that cocrystallization can, in principle, result in heterogeneous structures with dipole moments that exceed those of homogeneous structures and that 2D structures with select stoichiometries could favor metastable polar structures.

Abbreviations: CA, croconic acid; 3-HPLN, 3-hydroxyphenalenone; STM, scanning tunneling microscopy; UHV, ultrahigh vacuum; DFT, density functional theory

For a long time since their discovery,^{1,2} hydrogen-bonded organic ferroelectrics (FEs) were sidelined by the perovskite FEs as being of little practical use. The recent discovery of room-temperature ferroelectricity in crystals of croconic acid (CA) has drawn renewed attention to hydrogen-bonded FEs.^{3,4} In the bulk crystalline form, CA, C₅O₅H₂, is an order-disorder-type FE,⁵ which exhibits a combination of the FE properties commensurate with those of its inorganic counterparts, for example, a low coercive field (14 kV/cm) and a large room-temperature polarization (21 μC/cm²), which are stable up to at least 125°C.^{3,4,6} The origin of ferroelectricity in CA is the resonance-assisted hydrogen (H)-bonding between the keto and enol forms $\text{--C=O}\cdots\text{HO--C=}$ $\leftrightarrow$ $\text{=C--OH}\cdots\text{O=C--}$, where the electric dipoles, which are mainly determined by the π -electron system, are reversed by an electric field via collective proton displacement in the H-bonds between molecules.⁴ Those β -diketone enol moieties, which are found in CA and other oxocarbons and related molecules such as 3-hydroxyphenalenone (3-HPLN),³ are likely a prototype for tautomerism-enabled ferroelectricity, as has been suggested by Horiuchi et al.⁷ The polarization in both CA and 3-HPLN is planar and parallel to the molecular planes,^{3,8} meaning that, in principle, both organics should be able to exhibit two-dimensional (2D) FE order.

An attractive strategy to engineer the potential energy surface for protons along the H-bond axis and to enhance the utility of organic materials is to form cocrystals. 2D organic cocrystals were first reported in 2002 by Hipps et al.⁸ and have since been studied both in ultrahigh vacuum (UHV)^{9–12} and at liquid-solid interfaces.^{13,14} A majority of the reported 2D organic cocrystals are hydrogen-bonded systems,^{10–12} but cocrystals based on van der Waals forces,^{13–15} dipolar interactions¹⁶ and ionic bonds¹⁷ were also reported. However, organics only rarely form cocrystals; only approximately 0.5% of crystals archived in the Cambridge Structural Database are cocrystals.¹⁸ Here, we report the successful synthesis of 2D H-bonded cocrystals from the room-temperature FE organics CA and 3-HPLN through self-assembly on a substrate under UHV. The distinct advantage of surface self-assembly is that it is a solvent-free approach,¹⁹ meaning that it eliminates the need to find the right solvent, which is often a critical complication in cocrystal synthesis especially if both of the components readily crystallize in the same solvent. Density functional theory (DFT) calculations, performed in parallel to the scanning tunneling microscopy (STM) studies, help identify details of the bonding patterns and tautomerization of the observed structures and predict conditions for the emergence of net polarization in the building blocks.

STM investigations were performed for structural characterization of CA- and 3-HPLN-containing 2D structures. STM images of 2D single-component networks of CA as well as 3-HPLN and of cocrystalline networks of varied stoichiometry, all grown on a Au(111) surface, are shown in Figure 1. Models of some of the observed structures are illustrated in Figure 2d. CA forms porous honeycomb networks (Figure 1a), which resemble those reported by us on Ag(111),³² with the difference being that on Au(111), the elementary building block is a trimer of CA (see the structure model in Figure 2d) whereas it is a dimer on Ag(111).³³ The 3-HPLN on Au(111), shown in Figure 1f, forms H-bonded 1D chains, which extend over hundreds of nanometers across the substrate surface, unimpeded by the presence of monatomic substrate steps. This bonding pattern, which we reported earlier^{21,22} and which is shown in Figure 2d, resembles the bulk crystal structure.³ The existence of such bulk-structure-like chains serves as evidence of weak interaction of the molecules with the substrate. On the more reactive Cu(111) surface, we observed more complex structures of 3-HPLN including trimer-based chiral networks²⁰ and π - π -stacked Kagome lattices.²¹ A comparison of the STM images in Figure 1a and f shows that 3-HPLN molecules clearly appear larger and more triangular, and thus, their apparent size and shape will help to identify them in cocrystalline networks later.

Figure 1. STM images of self-assembled 2D molecular structures on a Au(111) substrate. (a) CA; (b) CA/3-HPLN = 2:1, where $(\text{CA})_2(3\text{-HPLN})_2$ tetramers are shaded red and $(\text{CA})_2$ dimers are shaded green; (c,d) two network architectures of CA/3-HPLN = 1:1 that were found to coexist (packing polymorphism); $(\text{CA})_2(3\text{-HPLN})_2$ tetramers of different orientation are shaded blue and red in (d); (e) CA/3-HPLN at approximately 1:5; (f) 3-HPLN. Structural unit cells are highlighted in (b–d), where the cell in (c) corresponds to the simulation cell in the right hand side of Figure 2d.

If CA and 3-HPLN are combined together on the Au(111) surface by depositing CA first and 3-HPLN subsequently, they form ordered 2D cocrystalline networks such as those in the STM images in Figure 1b–e. Networks of different stoichiometry can be fabricated by varying the deposited amount of each species. Even without postdeposition annealing, STM images show structurally ordered cocrystalline islands containing both CA and 3-HPLN (see Figure S1 in the Supporting Information (SI)). Weak annealing of the samples at 65°C after deposition generally promotes island ripening and yields very large 2D cocrystals, which are limited in size only by the surface coverage. The cocrystals shown in Figure 1c and d are both 2D networks of a 1:1 stoichiometric ratio of CA/3-HPLN, which are found to coexist with similar frequency on the Au surface. The smallest building block of these networks is a tetramer containing two molecules of CA and two molecules of 3-HPLN. Structure models of this tetramer are shown in Figure 2a and c and will be discussed later. The unit cells of the 2D lattices are highlighted in the STM images. The unit cell of the 1:1 network shown in Figure 1c includes such a tetramer. The same tetramer is also the smallest building block of the second 1:1 network in Figure 1d, but what is different here is how the tetramers are arranged to form the 2D lattice, which is also referred to as packing polymorphism. Specifically, tetramers of two different orientations, highlighted red and blue, are stacked alternately, so that the structural unit cell here consists of two tetramers.

Figure 1 also shows a CA-rich cocrystal of stoichiometric ratio CA/3-HPLN = 2:1 (Figure 1b) and a 3-HPLN-rich structure, where CA/3-HPLN is approximately 1:5 (Figure 1e). The 2:1 network is particularly interesting as it is composed of a $(\text{CA})_2(\text{3-HPLN})_2$ tetramer (shaded in red) as well as a CA dimer (green). It appears that in this structure, the excess CA forms dimers, which interact with the tetramers and thus form a continuous H-bonded cocrystalline phase. These CA dimers have been identified in an earlier study as the elementary building block of a single-component 2D network of CA on Ag(111).³² They would potentially be able to bind to the tetramers via H-bonds, using one of their –OH groups that is not already incorporated in the dimer, and via weaker van der Waals interactions.

The existence of the herringbone-like reconstruction of the surface underneath of the molecular networks, as seen in Figure 1c and d, is additional evidence for the relatively weak interaction of the molecular adsorbates with the Au(111) surface. Yet, there is an epitaxial orientation relationship between the networks and the surface. The tetramers are oriented on Au(111) such that an axis that connects the two CA molecules in the tetramer is aligned along the $\langle 0-10 \rangle$ direction of the substrate. Also, the CA dimers in the 2:1 network that are not part of the tetramers are oriented along this substrate direction. It is reasonable to assume that the epitaxial relationship is caused by the tendency to maximize the overlap of surface and adsorbate wave functions over a noble metal surface;²² in this case, a slight site preference of the oxygen atoms on the Au surface is likely.^{23,33}

Probing the details of the H-bonding pattern and the polarization state of the 2D networks experimentally is not feasible with current techniques. Therefore, we turn to a model based on DFT calculations, performed first on isolated molecular clusters in the gas phase and then on extended 2D networks. After considering the shape of the features in the STM image of the tetramer, we built an intuitive model for this basic building block

that maximizes the number of intermolecular H-bonds, as shown in Figure 2a, labeled “bowtie.” The binding energy of the planar bowtie tetramer was determined from molecular DFT calculations to be -2.29 eV per $\text{CA}_2(3\text{-HPLN})_2$, corrected for the basis set superposition error. The CA dimer illustrated at the top of Figure 2b plays a key role in the $\text{CA}_2(3\text{-HPLN})_2$ tetramer model and has already been determined to be a key building block in CA-containing supported structures.³² This CA dimer is in fact ~ 0.13 eV per molecule higher in energy (i.e., less stable) than the CA dimer shown below it in Figure 2b, which demonstrates nicely how such 2D networks can stabilize their molecular constituents in configurations that are otherwise metastable in the gas phase. We will use the latter, lower-energy dimer to construct the most stable models of the 2:1 CA/3-HPLN stoichiometry later in the text.

Figure 2. (a) Structural model of the $(\text{CA})_2(\text{HPLN})_2$ tetramers observed in the STM images; the three symmetry-inequivalent H-bonds are highlighted as h1, h2, and h3. (b) Two CA dimers from different CA isomers. The dimer on the top was used to construct the $(\text{CA})_2(\text{HPLN})_2$ tetramer. The dimer at the bottom was found to be the lowest in energy; see ref 32. (c) The lowest-energy models that were found of the $(\text{CA})_2(\text{HPLN})_2$ tetramer when (left) the entire structure was relaxed and (right) when the tetramer was constrained to lie perfectly flat. (d) The extended networks used to model CA (left), HPLN (middle), and the CA/HPLN structure from Figure 1c (right). The unit cells are illustrated by the faint gray lines.

The three symmetry-inequivalent H-bonds in the optimized, planar bowtie $\text{CA}_2(3\text{-HPLN})_2$ tetramer, labeled h1/h2/h3 in Figure 2a, measure 1.64 Å/ 2.35 Å/ 1.47 Å. The long distance of h2 suggests that it is not a very strong bond and inspired us to look closer at the DFT potential energy surface around the bowtie structure. It was found that the bowtie motif is energetically unstable, at least within DFT, with respect to, first, a tautomerization that assigns two hydroxyl groups to each 3-HPLN molecule like what is shown in the left model of Figure 2c and, second, to a bowtie motif built from a less stable conformational isomer of CA, as shown in the right model of Figure 2c. Both models, the “tautomer” and the “alt-bowtie,” were calculated as being more stable than the planar bowtie in Figure 2a using six density functionals, as described in the SI. The energy difference between the

bowtie and its isomeric tautomer/alt-bowtie models is $-0.17/-0.32$ eV per $\text{CA}_2(3\text{-HPLN})_2$, respectively. The most noticeable difference between them is the shorter average length of the H-bonds in the more stable isomers; the three symmetry-inequivalent H-bonds measure $1.65 \text{ \AA}/1.61 \text{ \AA}/1.65 \text{ \AA}$ in the tautomer and $1.50 \text{ \AA}/1.62 \text{ \AA}/1.63 \text{ \AA}$ in the planar alt-bowtie model. Furthermore, unconstrained structural optimizations show that the lowest-energy gas-phase geometries of the bowtie tetramer and its tautomer are not planar and buckle substantially out-of-plane, in this case by bending the CA dimer motif. Conversely, the alt-bowtie model prefers the planar geometry when allowed to relax out-of-plane. The energy of the bowtie tetramer drops by ~ 0.10 eV per $\text{CA}_2(3\text{-HPLN})_2$, and the energy of the tautomer drops by 0.17 eV per $\text{CA}_2(3\text{-HPLN})_2$ as a result of their buckling. The out-of-plane distortions, which effectively also shorten the H-bonds, allow the tautomer to become slightly preferred, by approximately 0.03 eV per $\text{CA}_2(3\text{-HPLN})_2$, over the alt-bowtie model. Our previous calculations for extended 2D networks of 3-HPLN on Ag(111) also showed that nonplanar geometries were energetically preferred.²⁰

Periodic DFT calculations were used next to build freely relaxed planar models of the experimentally observed CA/3-HPLN networks; the initial guesses were based on untautomerized CA and 3-HPLN molecules and do not include the substrate. The lowest-energy planar periodic network models that we found of CA, 3-HPLN, and the 1:1 CA/3-HPLN stoichiometry network from Figure 1c are shown in Figure 2d. During the geometry optimization of the 1:1 CA/3-HPLN network, the molecules spontaneously formed the tautomer, as could be expected considering the enhanced stability of the tautomeric molecular constituents over the bowties. Networks of the $\text{CA}_2(3\text{-HPLN})_2$ tetramer in the alt-bowtie configuration were also constructed by hand but were found to be higher in energy than the tautomerized networks by approximately 0.30 eV per $\text{CA}_2(3\text{-HPLN})_2$. For the 1:1 network built from the bowtie tautomer, we compute the binding energy, with respect to the isolated molecular constituents, to be -4.25 eV per $\text{CA}_2(3\text{-HPLN})_2$.

A central question is whether the cocrystalline 2D networks are lower in energy than the single-component networks. To answer this question, we computed the energy difference corresponding to the formation of $2\text{CA}_n + 2(3\text{-HPLN})_n \rightarrow [\text{CA}_2(3\text{-HPLN})_2]_n$ and found it to be -0.75 eV per $\text{CA}_2(3\text{-HPLN})_2$ in favor of the heterogeneous network. This leads to the conclusion that cocrystallization in two dimensions is energetically favorable for CA and 3-HPLN. Moreover, a slightly off-rectangular simulation cell, with the angle between lattice vectors measuring 95° , was found to be lower in energy than a rectangular cell by roughly 0.2 eV per $\text{CA}_2(3\text{-HPLN})_2$, consistent with the experimental STM image in Figure 1c.

When one of the tetramers is removed from the $[\text{CA}_2(3\text{-HPLN})_2]_2$ simulation cell, the binding energy of the remaining tetramer decreases by 30% to -3.05 eV per $[\text{CA}_2(3\text{-HPLN})_2]_2$, which strongly suggests that interactions between tetramers, such as van der Waals and electrostatic attractions, are certainly not negligible. The computed dispersion correction that is used in the PBE-D3 functional, which we use here as a general indicator of the strength of the van der Waals forces in each structure, favors the mixed $\text{CA}_2(3\text{-HPLN})_2$ unit by 0.09 eV over the pure CA and 3-HPLN networks; this suggests that the presence of pores in the CA network and their absence in the $\text{CA}_2(3\text{-HPLN})_2$ network leads to stronger van der Waals interactions in the latter, mixed, network. More importantly,

however, visualization of the electrostatic potential (ESP) around isolated planar models of the bowtie and tautomeric tetramers (Figure 3a) suggests that the tetramers assemble in such a way that the regions with a negative ESP are in closest contact with regions of positive ESP in neighboring molecules. This qualitative argument explains the characteristic offset between the neighboring bowties in the STM image in Figure 1c and also explains the perpendicular stacking in the 1:1 network isomer in Figure 1d. Because the isomeric networks from Figure 1c and d are both closed-packed and are therefore likely to exhibit similar attractive van der Waals and electrostatic interactions between the tetramers, we did not explicitly study the network from Figure 1d via DFT.

Figure 3. (a) Computed ESP on the $\rho = 0.001$ atomic units (au) charge density isosurface around the bowtie and tautomer $(\text{CA})_2(\text{HPLN})_2$ models. (b) The lowest-energy model that was considered for the 2:1 CA/3-HPLN network and (c) an alternative model where the tetramer building blocks are broken up. (d) The gas-phase structure of the recurring trimer motif that makes up the network shown in (c); the computed dipole moment is shown alongside the structure. (e) Au(111) simulation cell over which a simple nontautomerized model of the 2:1 CA/3-HPLN network from (c) can be optimized (the top layer of the Au(111) surface is shown), and (f) the gas-phase structure and computed dipole moment of the untautomerized CA/HPLN motif from (d).

The H-bonding, closed-packing, and favorable ESP interactions are all preserved in the lowest-energy model that we considered of the 2:1 CA/3-HPLN network as well, which is

shown in Figure 3b. This model contains the same $\text{CA}_2(3\text{-HPLN})_2$ tetramers as those used in the 1:1 CA/3-HPLN model but has extra CA dimers inserted between the tetramers. The “extra” CA dimers adopt the previously mentioned lowest-energy CA_2 conformer, shown at the bottom of Figure 2b, which forms H-bonds that bridge nearby tetramers.

In all of the aforementioned planar network structures, whether they be based on the bowtie, the tautomer, or the alt-bowtie building blocks, the presence of an inversion symmetry element in the center of each tetramer forces the in-plane component of their dipole moments to be 0. This suggests that 2D networks of CA/HPLN bowtie motifs and/or CA dimers are unlikely to form a polarized state. We were also unable to locate a simple low-energy H-transfer mechanism that would polarize the tetrameric motifs, though they can be imagined. Because such H transfers along the H-bonds are the origin of FE behavior in pristine CA and 3HPLN, it is unlikely that these particular networks will exhibit FE behavior. We note, however, that the inversion center of symmetry can be removed in the 2:1 CA/3-HPLN 2D system by a simple modification of our structure model in Figure 3b that breaks up the tetrameric motif. Such a modification, illustrated in Figure 3c, is built from the model in Figure 3b by simply rotating one 3-HPLN molecule per bowtie motif by 180° so that each CA dimer, shaded with a rectangle, forms H-bonds with exactly one neighboring 3-HPLN molecule, shaded with a triangle. Such a broken symmetry network would still be consistent with our STM results and is a necessary first step toward fashioning a network with net electric polarization and perhaps ferroelectricity.

The proton arrangements along the ribbons of CA dimers are necessarily changed during this transformation, but the energy of the gas-phase network in Figure 3c does not change much; with our planar models, it was only 0.02 eV less stable per $\text{CA}_4(3\text{-HPLN})_2$ unit than the network in Figure 3b. This is significantly less than the 0.14 eV per $\text{CA}_2(3\text{-HPLN})_2$ unit energy difference that we observed from placing the $\text{CA}_2(3\text{-HPLN})_2$ tetramer over different binding sites on a crude two-layer Au(111) surface model, as shown in the SI. That means that within our calculations, the broken symmetry model from Figure 3c is energetically viable. The networks of the types shown in Figures 3b and c would possibly be indistinguishable in the STM images because the functional groups of the 3-HPLN cannot be located in the triangular-shaped appearance of the molecules.

The nontautomerized $\text{CA}_2(3\text{-HPLN})$ trimer motif that was used to initially construct the 2:1 CA/3-HPLN model network in Figure 3c is shown in Figure 3e and f. It was found that the motif does not tautomerize when its geometry is optimized over a simple Au(111) simulation cell that stretches the CA dimer chains slightly versus their optimal computed parameters in vacuum. The energy difference between it and the more stable tautomer in Figure 3d was found to be ~ 0.40 eV per $\text{CA}_2(3\text{-HPLN})$ unit on the surface, but it is worth noting that the projection of the building block’s computed dipole moment, 9.5 D, along the CA dimer axis is 6.6 D. This demonstrates that the dipole moment of heteromolecular structures consisting of CA and 3-HPLN can, in principle, be larger than that of, for example, the CA dimer (has a dipole of 0 D) and 3-HPLN molecular building blocks alone. It further illustrates that the formation of organic FE cocrystals might be feasible given the right constituents, stoichiometry, and dimensionality.

In conclusion, our studies show that CA and 3-HPLN cocrystallize as 2D crystals in a solvent-free approach when confined by a substrate. Computational analysis has confirmed that the experimental $(\text{CA})_2(3\text{-HPLN})_2$ tetramer networks are lower in energy than the single-component networks; the best structural models maximize the H-bonding and electrostatic interactions between $(\text{CA})_2(3\text{-HPLN})_2$ tetramers and CA_2 dimers. While the lowest-energy models have no net dipole moment nor any obvious low-energy intermolecular H-transfer mechanisms to create one, it was demonstrated that compound clusters that are only slightly higher in energy can have net polarization that is considerably larger than the polarization of individual CA or 3-HPLN molecules and that 2D networks based on these clusters are still consistent with our STM results. The importance of this study is also in the exploratory solvent-free test of the miscibility of two organic FEs and their ability to cocrystallize. An example where the ability of the constituents to cocrystallize could be ruled out by STM is CA and the directly related oxocarbon rhodizonic acid (see SI Figure S2 for STM images). The surface-supported cocrystallization could thus become a quick and versatile test to identify miscible constituents and inform solution-based cocrystallization. This is a departure from existing approaches and could potentially accelerate the discovery of new materials and will enable the rational design of organic FE cocrystals, which quickly become prohibitively complex to investigate using heuristic-guided approaches. We hope that this work will encourage the search for cocrystalline organic H-bonded systems, particularly those that are prone to forming networks that may remove any visible inversion centers and exhibit ferroelectricity in 2D.

Experimental Procedures

The experimental investigation was performed in UHV at a base pressure of 1×10^{-10} millibars. A gold metal substrate of (111) orientation was prepared in situ by repeated cycles of Ar^+ ion sputtering and subsequent annealing at approximately 600°C . Characteristic for the clean Au(111) surface is the herringbone surface reconstruction, which was checked with STM. The herringbone reconstruction is easily visible in the STM images in this study as ripples underneath of the molecular adlayers. In the vacuum system, the molecules were thermally evaporated from a home-built four-pocket Knudsen cell onto the substrates, which were held at room temperature during the film growth. The deposition rate was about 0.03–0.5 monolayers per minute, depending on the desired coverage. For cocrystallization, CA was always deposited first at submonolayer coverage, followed by 3-HPLN deposition. After film growth, the samples were transferred in situ into an Omicron low-temperature STM where they were imaged at a 77 K substrate temperature. The STM was operated with electrochemically etched tungsten tips.

DFT calculations on isolated CA/3-HPLN clusters in the gas phase were carried out using the ADF software package.^{24,25} The revPBE functional^{26,27} corrected with a post-SCF dispersion term²⁸ (revPBE-D3) was used to compute the geometries and energy values discussed in the main text; the calculations used a triple- ζ Slater-type basis set with polarization functions (TZP) from the ADF basis set library. The revPBE-D3 findings were checked with other density functionals, and further computational details on the molecular calculations are given in the SI. Periodic DFT calculations on the extended network models

were performed using the VASP software package.²⁹ The PBE density functional³⁰ was also used in conjunction with a post-SCF dispersion correction²⁸ (PBE-D3, as implemented with the IVDW = 12 tag in the VASP input file). The numbers cited in the main text were computed with the PBE-D3 method, and the projector augmented wave (PAW) method was employed to treat the core states.³¹ A plane-wave basis set with an energy cutoff of 600 eV was used for isolated organic networks and 500 eV for surface/adsorbate systems. Further computational details on the periodic calculations, on calculations with different functionals, and the setup for the surface/adsorbate systems are provided in the SI.

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Supporting Information for:

2D Co-Crystallization From H-Bonded Organic Ferroelectrics

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Section S.1: Experimental Results	S2
Section S.2: Computational Details	S3
Section S.3: Supplementary Calculations – Epitaxy Considerations and Dipole Moments of Molecular Motifs	S4
Section S.4: Structural Coordinates of Molecular Clusters -- XYZ format	S6
Section S.5: Structural Coordinates of Periodic Networks -- POSCAR format	S10

Section S.1: Experimental Results

An STM image of as-deposited croconic acid and 3-HPLN on Au(111) without annealing post-deposition is shown in Figure S1. It is clear that already here, co-crystalline structures containing both types of organics are formed. However, comparison with post-annealed structures shows that this annealing improves the long-range order in the films, whereas thermally induced Ostwald ripening increases the size of the co-crystalline islands.

Figure S1: STM image of 3-HPLN and CA as grown at room temperature. CA was deposited first, followed by 3-HPLN. Tunneling parameters: -0.5 V, 300 pA. [13]

An example where supported organics did not co-crystallize is shown in Figure S2. Here, croconic acid and the related rhodizonic acid have been deposited at room temperature. CA has been deposited first. Phase separation of both species is clearly observed, and the network structure of each phase is identical to those structures observed for homogeneous films of CA and RA.

Figure S2: STM image of croconic acid, CA, and rhodizonic acid, RA on Au(111), showing phase separation of both species. No co-crystallization was observed here. The structural phase of the CA lattice is consistent with the network observed for pristine CA on Au(111), as shown in the main article in Figure 1a.

Section S.2: Computational Details

The ADF software package [1, 2] was used for the Density Functional Theory (DFT) calculations on isolated CA/HPLN clusters in the gas phase. The ADF calculations were carried out using, first, the revPBE functional [3,4] corrected with the post-SCF dispersion term developed in Grimme's research group, the DFT-D3 functional [5]. The BLYP [6,7] and B3LYP [8] functionals, with and without dispersion corrections, were also used to complement the revPBE-D3 findings. The numbers which are cited in the text are taken from the revPBE-D3 calculations. The basis functions on all of the atoms consisted of a triple-zeta–Slater–type basis set with polarization functions (TZP) from the ADF basis–set library. The core shells up to 1s were kept frozen for C, N, and O. The basis set superposition error (BSSE) was obtained using the Counterpoise method [9], and all of the binding energies discussed in the text include the BSSE corrections.

Periodic DFT calculations were performed using the VASP software package [10]. The PBE density functional [11] was used in conjunction with DFT-D2 [5] and DFT-D3 methods (as implemented with the IVDW=10 and IVDW=12 tags, respectively, in the VASP input file) to account for dispersion. The numbers cited in the main text were computed with the PBE-D3 method. The projector augmented wave (PAW) method was employed to treat the core states [12]. A plane-wave basis set with an energy cutoff of 600 eV was used for isolated organic networks and 500 eV for surface/adsorbate systems. The Monkhorst-Pack scheme was used to generate *k*-point grids, which resulted in an energy convergence of less than 0.04 eV per formula unit with, for example, a 3x3x1 *k*-point grid for the simulation cells containing two tetramers, or a 5x5x1 *k*-point grid for the Au(111) simulation cell shown in Figure 4d of the main text. A vacuum thickness of at least 15 Å was used to model all of the 2D networks. The preliminary surface calculations were carried out with PBE-D3 over two-layer slabs, constrained to mimic the Au-Au distances which occur with the bulk crystal experimental lattice constant.

The networks were optimized with the following procedure. Simulation cells were first built by hand such that they appeared to match up with the experimental images as best as they could. The atomic coordinates in these constructed cells were optimized and then the lattice vectors were manually increased and decreased until the nearest potential energy minimum was thought to be found.

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Section S.3: Supplementary Calculations – Epitaxy Considerations and Dipole Moments of Molecular Motifs

Figure S3. Illustrations of the simple models that were used for the proposed 2:2 CA:3-HPLN stoichiometry model adsorbed over a two-layer slab of Au(111). The top layer of the Au(111) substrate is shown to illustrate the position of the CA atoms with respect to the nearest Au atoms. The lowest-energy model was built in order to minimize as many Au-O distances as possible, since it seems to be more favorable for the O atoms to lie directly over an Au site.

In Figure S3, we show a simple model of the 2:2 CA:3-HPLN stoichiometry model adsorbed over a two-layer slab of Au(111). This model was built to get a rough estimate of the corrugation energy of a CA/HPLN network on an Au(111) substrate. The tetramers were found to tautomerize spontaneously during geometry optimizations of the atoms in the CA/HPLN tetramer, like they do in the gas-phase networks. In Figure S4, we show a more tightly-packed model of the 2:2 CA:3-HPLN stoichiometry adsorbed over a four-layer slab of Au(111). The tetramers were again found to tautomerize spontaneously during a geometry optimization and they were found to flatten even when the starting geometry of the adsorbed tetramers were buckled like they are in the optimized gas-phase molecular and network geometries.

Figure S4. Atomistic structure of a higher-coverage 2:2 CA:3-HPLN stoichiometry model adsorbed over a four-layer slab of Au(111).

As described in the main text, the tetramers were also used to build the most stable model of the 2:1 CA:3-HPLN network (Figure 3b from the main text). But a broken symmetry structure that doesn't use the tetramer building block (Figure 3c from the main text) is also possible and is energetically competitive. Networks with larger simulation cells that contain both the tetramers and the broken-symmetry fragments can also be imagined and may have a comparable energy, but those are not considered here.

The broken-symmetry 2:1 CA:3-HPLN model was the only CA/HPLN network with which we were able to find a non-tautomerized model that remained stable during geometry optimization on an Au(111) substrate (but it is noted that the non-tautomerized structure is less energetically stable than the tautomerized structure).

In Figure S5, we show the computed dipole moments of different motifs that can be used to model the broken-symmetry 2:1 CA:3-HPLN stoichiometry as described in the main text. The Figure S5a and S5b models correspond to the change in dipole moment of the motif after transferring a single H atom from one CA molecule to another in the tautomerized network model from Figure 3c of the main text. The Figure S5c model is the same model which is described in Figure 3e and 3f of the main text.

Figure S5. The computed dipole moments of the trimer $\text{CA}_2(3\text{-HPLN})$ motifs that can be used to build the broken-symmetry 2:1 CA:3-HPLN networks, as shown in Figure 4 of the main text. a) The building block that was used to build the network shown in Figure 3c of the main text. b) A similar building block as the one shown in part a, but where one H atom is moved from one CA molecule to the other. c) The non-tautomerized building block used to build the models shown in Figure 3e and 3f of the main text.

Section S.4: Structural Coordinates of Molecular Clusters -- XYZ format

Bowtie CA₂HPLN₂ tetramer – Planar Constraint

70

C	4.787637971	12.935011578	9.999999825
C	5.782136301	11.811181360	9.999999869
C	5.637276659	14.219797913	9.999999851
C	7.083965889	13.775524058	9.999999909
C	7.096273600	12.335642643	9.999999917
C	13.964321307	13.420018639	10.000000175
C	12.969700549	14.543472761	10.000000131
C	13.114815236	12.135276248	10.000000149
C	11.668058600	12.579478129	10.000000091
C	11.655509657	14.019614269	10.000000083
C	11.679158683	5.822522882	10.000000127
C	11.724847993	4.410071245	10.000000136
C	10.550918898	3.672945867	10.000000095
C	9.282301799	4.322612689	10.000000043
C	9.231465432	5.754571671	10.000000033
C	10.455288126	6.495648839	10.000000076
C	7.964483607	6.413460527	9.999999981
C	7.906830597	7.899694231	9.999999971
C	10.369147722	7.954167903	10.000000065
C	9.152905292	8.605941101	10.000000015
C	9.464071074	22.032928040	9.999999957
C	9.515279015	20.600961237	9.999999967
C	8.291638421	19.859507089	9.999999924
C	10.782434568	19.942385702	10.000000019
C	11.954552610	20.699242109	10.000000060
C	11.906644163	22.110713910	10.000000051
C	10.684148171	22.766806918	10.000000000
C	10.840751744	18.455933765	10.000000029
C	8.378215679	18.400961439	9.999999934
C	9.594480726	17.749378533	9.999999985
C	7.067591319	20.532301974	9.999999873
C	7.021528082	21.944810060	9.999999864
C	8.195244171	22.682283978	9.999999905
C	6.792164212	5.656842840	9.999999940
C	6.839765028	4.245434202	9.999999949
C	8.062087984	3.589044961	9.999999999
O	3.569954607	12.844062296	9.999999778
O	5.420388794	10.565464847	9.999999862
O	8.151933270	11.537299405	9.999999962
O	8.068990331	14.556655543	9.999999943
O	5.258411314	15.381777185	9.999999830
O	15.182053939	13.511531428	10.000000222
O	13.331877038	15.789509422	10.000000139
O	10.600220811	14.818148689	10.000000039
O	10.683196681	11.798283982	10.000000058
O	13.493431911	10.973174963	10.000000170

O	11.558621600	8.599848662	10.000000108
O	6.769851171	8.476660681	9.999999924
O	7.188600718	17.755114440	9.999999892
O	11.977482974	17.879205477	10.000000076
H	6.190706205	9.825523120	9.999999895
H	9.057211060	11.987877247	9.999999994
H	12.561426607	16.526445840	10.000000105
H	9.694548026	14.368009096	10.000000006
H	12.603653837	6.399224158	10.000000160
H	12.691086286	3.903770603	10.000000176
H	10.584156789	2.581119212	10.000000102
H	9.122250162	9.686062524	10.000000009
H	11.440189976	9.576106663	10.000000098
H	12.909511395	20.172929110	10.000000100
H	12.835418582	22.683266123	10.000000084
H	10.642068115	23.858438234	9.999999993
H	9.625188435	16.669136016	9.999999991
H	7.307297773	16.778921637	9.999999902
H	6.143221430	19.955351268	9.999999840
H	6.055139402	22.450861874	9.999999824
H	8.161678394	23.774126101	9.999999898
H	5.837261097	6.183139512	9.999999900
H	5.910851616	3.673146102	9.999999916
H	8.103869771	2.497422231	10.000000000

Tautomer CA₂HPLN₂ tetramer – Planar Constraint

70

C	4.845061600	12.773166100	0.000000000
C	5.930387231	11.851288275	0.000000000
C	7.270323287	12.354622422	0.000000000
C	7.487770604	13.766950642	0.000000000
C	6.394862566	14.639999796	0.000000000
C	5.074768988	14.141981564	0.000000000
C	8.363273605	11.434693426	0.000000000
C	8.116803841	10.057472266	0.000000000
C	6.794815604	9.563674935	0.000000000
C	5.720753624	10.442451183	0.000000000
C	8.866193071	14.255084838	0.000000000
C	9.937067707	13.355610814	0.000000000
C	9.723798225	11.971983446	0.000000000
O	9.026223493	15.571259002	0.000000000
O	10.701742848	11.079502614	0.000000000
O	11.234533478	16.928888123	0.000000000
C	12.487981358	16.878104155	0.000000000
C	13.434212570	18.071363269	0.000000000
C	14.857811163	17.480075536	0.000000000
C	14.701090551	15.986382609	0.000000000
C	13.313199422	15.692036517	0.000000000
O	13.130417739	19.254040325	0.000000000
O	15.919642745	18.094105754	0.000000000

O	15.666991619	15.139101844	0.000000000
O	12.722195047	14.500206273	0.000000000
O	13.206092806	12.011423500	0.000000000
C	14.172071742	11.164245828	0.000000000
C	14.015520881	9.670536851	0.000000000
C	15.439148471	9.079403077	0.000000000
C	16.385253110	10.272788289	0.000000000
C	15.559947073	11.458789615	0.000000000
O	15.743121838	7.896770055	0.000000000
O	17.638719002	10.222079559	0.000000000
O	12.953707930	9.056452056	0.000000000
O	16.150830497	12.650656136	0.000000000
O	19.846312691	11.579916178	0.000000000
C	20.006552553	12.896005247	0.000000000
C	21.385050490	13.384004678	0.000000000
C	21.602675917	14.796301555	0.000000000
C	20.509840809	15.716367249	0.000000000
C	19.149286856	15.179223346	0.000000000
C	18.935813628	13.795659314	0.000000000
C	22.477863485	12.510837437	0.000000000
C	23.798015172	13.008700526	0.000000000
C	24.027887381	14.377486106	0.000000000
C	22.942666900	15.299484799	0.000000000
C	20.756458313	17.093558452	0.000000000
C	22.078500609	17.587201673	0.000000000
C	23.152457232	16.708297371	0.000000000
O	18.171404745	16.071826616	0.000000000
H	13.284442713	13.661153899	0.000000000
H	15.588571499	13.489796220	0.000000000
H	8.962256107	9.369461364	0.000000000
H	6.622708937	8.486752400	0.000000000
H	4.696786311	10.062343703	0.000000000
H	10.946134912	13.749998827	0.000000000
H	11.647546270	11.468538392	0.000000000
H	22.295329419	11.436535710	0.000000000
H	24.636722824	12.311489864	0.000000000
H	25.048943910	14.765321283	0.000000000
H	17.926695442	13.401421915	0.000000000
H	17.225719129	15.682759724	0.000000000
H	19.911085071	17.781666640	0.000000000
H	22.250731875	18.664101855	0.000000000
H	24.176467708	17.088286674	0.000000000
H	6.577252894	15.714329184	0.000000000
H	4.235983625	14.839095984	0.000000000
H	3.824052658	12.385208962	0.000000000
H	18.873037326	11.252755332	0.000000000
H	9.999382255	15.898418831	0.000000000

Alt-Bowtie CA₂HPLN₂ tetramer – Planar Constraint

70

C	11.156060865	6.046522355	0.000000000
C	10.915151750	4.654399710	0.000000000
C	9.616001302	4.170217978	0.000000000
C	8.506010291	5.064081170	0.000000000
C	8.748032535	6.475584677	0.000000000
C	10.094687630	6.955023312	0.000000000
C	7.640471789	7.377718109	0.000000000
C	7.903441625	8.828669910	0.000000000
C	10.319143411	8.402466378	0.000000000
C	9.244629383	9.287971001	0.000000000
C	9.587212097	21.347225220	0.000000000
C	9.346729635	19.935526236	0.000000000
C	8.000633387	19.454788116	0.000000000
C	10.455198465	19.034539464	0.000000000
C	11.757100064	19.538428491	0.000000000
C	11.995957616	20.929635113	0.000000000
C	10.930623376	21.818781527	0.000000000
C	10.193620535	17.583479461	0.000000000
C	7.777651557	18.007292769	0.000000000
C	8.852973342	17.122849034	0.000000000
C	6.938306947	20.362117682	0.000000000
C	7.177710814	21.754392284	0.000000000
C	8.476335189	22.239879326	0.000000000
C	6.337980852	6.875255639	0.000000000
C	6.097588725	5.484266766	0.000000000
C	7.162034236	4.593954262	0.000000000
C	13.362482549	14.434021319	0.000000000
C	12.122733734	13.751811814	0.000000000
C	12.359311444	12.309810579	0.000000000
C	13.862149320	12.080664068	0.000000000
C	14.502468492	13.478055459	0.000000000
C	5.734975868	14.103231772	0.000000000
C	5.972149475	12.661095674	0.000000000
C	4.732799220	11.977972487	0.000000000
C	3.592188504	12.933564751	0.000000000
C	4.231885616	14.331610159	0.000000000
O	11.596149952	8.794691544	0.000000000
O	6.920264675	9.668112149	0.000000000
O	6.501048924	17.613890291	0.000000000
O	11.177754719	16.744906609	0.000000000
O	10.893624796	14.235742366	0.000000000
O	11.475079606	11.432752212	0.000000000

O	14.419233949	10.994425695	0.000000000
O	15.695072327	13.756330435	0.000000000
O	13.593825137	15.740630231	0.000000000
O	6.619158866	14.980487056	0.000000000
O	2.399519421	12.654715169	0.000000000
O	4.502061252	10.670989413	0.000000000
O	7.201938683	12.178230257	0.000000000
O	3.673801010	15.417598567	0.000000000
H	12.177562306	6.425950924	0.000000000
H	11.758703378	3.962807547	0.000000000
H	9.427032435	3.094413755	0.000000000
H	9.427501858	10.361154613	0.000000000
H	11.662087830	9.805939493	0.000000000
H	12.594212216	18.839940169	0.000000000
H	13.021189740	21.301935939	0.000000000
H	11.110892256	22.896097543	0.000000000
H	8.671031105	16.049552530	0.000000000
H	6.436273980	16.603124137	0.000000000
H	5.917275162	19.981578048	0.000000000
H	6.333466930	22.445069254	0.000000000
H	8.664175913	23.315829913	0.000000000
H	5.501700534	7.574797772	0.000000000
H	5.071906842	5.113064553	0.000000000
H	6.980579666	3.516791099	0.000000000
H	12.733386913	16.261122403	0.000000000
H	10.911832530	15.278137145	0.000000000
H	7.183731138	11.136087616	0.000000000
H	5.363032310	10.151239480	0.000000000

Section S.5: Structural Coordinates of Periodic Networks -- POSCAR format

1:1 CA:HPLN Periodic and Planar Network --- POSCAR format

C O H

1.0000000000000000

19.40400 0.00000 0.00000

-2.07081 23.66958 0.00000

0.00000 0.00000 20.00000

C O H

72 28 40

Direct

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0.3401263009315016	0.5442762624006647	0.5000000000000000
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0.4079512837695347	0.4656459533540556	0.5000000000000000
0.4090701422951852	0.5256651269951007	0.5000000000000000
0.7600368337392851	0.5143396343526163	0.5000000000000000
0.7103287065087756	0.4621749040121657	0.5000000000000000
0.7162598040153583	0.5644190207111208	0.5000000000000000
0.6425176694875034	0.5408140239589301	0.5000000000000000
0.6413623805437680	0.4807894362904293	0.5000000000000000
0.6322055161280176	0.8039171667451370	0.5000000000000000
0.6438831257399187	0.8630275315772664	0.5000000000000000
0.5883333677076266	0.8958909046055510	0.5000000000000000
0.5192204962284279	0.8708275447928031	0.5000000000000000
0.5073038226839017	0.8106518980360988	0.5000000000000000
0.5649764251433709	0.7774423310134608	0.5000000000000000
0.4380346095819618	0.7852682112358238	0.5000000000000000
0.4276999387548415	0.7241052846810732	0.5000000000000000
0.5517706388321244	0.7164695668624503	0.5000000000000000
0.4840642740486416	0.6913325327735649	0.5000000000000000
0.5313391658194391	0.1355499199083781	0.5000000000000000
0.5438967428122012	0.1956823242741095	0.5000000000000000
0.4866117669237440	0.2292920809621464	0.5000000000000000
0.6133812002897443	0.2206203536177966	0.5000000000000000
0.6683302328801020	0.1861864705734817	0.5000000000000000
0.6559709220072421	0.1270618113290354	0.5000000000000000
0.5886105810639037	0.1023183165865262	0.5000000000000000
0.6242478076831759	0.2817342199671984	0.5000000000000000
0.5003677662552093	0.2902073226120194	0.5000000000000000
0.5682720966245256	0.3149139849247504	0.5000000000000000
0.4191517146766941	0.2032774937053503	0.5000000000000000
0.4068706186830937	0.1442268861187799	0.5000000000000000
0.4620337443626212	0.1109500625313800	0.5000000000000000
0.3826864640234859	0.8192856262297710	0.5000000000000000
0.3943803672752182	0.8784587289229648	0.5000000000000000
0.4615527757094142	0.9036436664298648	0.5000000000000000
0.8329848649914169	0.9446508173837245	0.5000000000000000
0.9067703713095412	0.9681837456688456	0.5000000000000000
0.9176999559442933	0.7053814862411443	0.5000000000000000
0.9058439755723455	0.6462837339509733	0.5000000000000000

0.9613027772020430	0.6133178064792304	0.5000000000000000
0.7892952683996839	0.9947963031032572	0.5000000000000000
0.8390581337416521	0.0469069191455418	0.5000000000000000
0.9079745410124644	0.0282161130213225	0.5000000000000000
0.9362156281224969	0.2883602165902559	0.5000000000000000
0.9251969482465086	0.2272505966201948	0.5000000000000000
0.8813716591976686	0.3228990965234502	0.5000000000000000
0.8938865642083229	0.3820157327225644	0.5000000000000000
0.0304757515401377	0.6382581285512785	0.5000000000000000
0.9849923115922934	0.7317321384418847	0.5000000000000000
0.9983284924155242	0.7926928648459253	0.5000000000000000
0.2094597429034053	0.9647956953653463	0.5000000000000000
0.1404785603580336	0.9833345704962397	0.5000000000000000
0.0425669435440597	0.6984214096884998	0.5000000000000000
0.1118950522407616	0.7236899944091277	0.5000000000000000
0.1671371835302153	0.6895584247211133	0.5000000000000000
0.1552714842279102	0.6303941992114233	0.5000000000000000
0.0880411537240633	0.6053280585180190	0.5000000000000000
0.1223612309548301	0.7848458542141259	0.5000000000000000
0.0660881585555799	0.8177180622494973	0.5000000000000000
0.2590593520935016	0.0170046694531649	0.5000000000000000
0.2152167120531843	0.0670924938267490	0.5000000000000000
0.1414811537924763	0.0433386248194054	0.5000000000000000
0.1304538096962347	0.3053545596991469	0.5000000000000000
0.1428976326664753	0.3643931994488483	0.5000000000000000
0.0878358554927701	0.3977763050748635	0.5000000000000000
0.0184718692305594	0.3733041491130678	0.5000000000000000
0.0057517879986335	0.3131846014491231	0.5000000000000000
0.0629324979507899	0.2794668957525772	0.5000000000000000
0.0490275984893884	0.2185664709728528	0.5000000000000000
0.9810744947272383	0.1939681759647058	0.5000000000000000
0.9613017131840209	0.4066468063089772	0.5000000000000000
0.2270509616379996	0.4906225137279847	0.5000000000000000
0.3235343056562527	0.5940283467304681	0.5000000000000000
0.4628237572797929	0.5631988467159701	0.5000000000000000
0.4600162963217542	0.4363501811612096	0.5000000000000000
0.3133575409316833	0.3916549434126821	0.5000000000000000
0.8234426065328364	0.5159655610451281	0.5000000000000000
0.7268380574930191	0.4124086906634972	0.5000000000000000
0.5876461253284546	0.4432425296004254	0.5000000000000000
0.5905839241793984	0.5702606963015384	0.5000000000000000
0.7369671735534382	0.6147933242088612	0.5000000000000000
0.6071076053726330	0.6873474262303390	0.5000000000000000
0.3629303349006392	0.7011802212471778	0.5000000000000000
0.4452834648742439	0.3196153873196010	0.5000000000000000
0.6891720850296252	0.3044378269383117	0.5000000000000000
0.9587471370827956	0.9387854725451916	0.5000000000000000
0.8121532131976608	0.8943034447703226	0.5000000000000000
0.9430393667278025	0.8218668999674250	0.5000000000000000
0.7258953394344303	0.9932574123497062	0.5000000000000000
0.8226036217490176	0.0966915568409235	0.5000000000000000
0.9617540463817846	0.0656922654027454	0.5000000000000000
0.8602356685716757	0.2046353331147301	0.5000000000000000
0.2261620093441792	0.9150777479384615	0.5000000000000000

0.0867268179145384	0.9457728101845220	0.5000000000000000
0.1871686420490732	0.8077142966080118	0.5000000000000000
0.3224448368079038	0.0186274437920346	0.5000000000000000
0.0893270232570842	0.0725352477805004	0.5000000000000000
0.2359620222342613	0.1174486836037474	0.5000000000000000
0.1040384439210840	0.1890853211812953	0.5000000000000000
0.3580788413267371	0.6581323567258082	0.5000000000000000
0.5130012280337510	0.5519618758431264	0.5000000000000000
0.6937543056782403	0.3474010008280644	0.5000000000000000
0.5374506606394363	0.4544978001123283	0.5000000000000000
0.6758263309897004	0.7779492243805706	0.5000000000000000
0.6967239936379457	0.8827950211892670	0.5000000000000000
0.5980214512073800	0.9418355537721226	0.5000000000000000
0.4743944307170125	0.6455562006376852	0.5000000000000000
0.5977313838381448	0.6450683621284767	0.5000000000000000
0.7213073469886382	0.2056932108539158	0.5000000000000000
0.6994236231236783	0.1008837330101855	0.5000000000000000
0.5789587245395253	0.0563491105369280	0.5000000000000000
0.5783965911585298	0.3606624440191197	0.5000000000000000
0.4547059831464892	0.3618848054556878	0.5000000000000000
0.3758318353486132	0.2295555014413040	0.5000000000000000
0.3539037251279211	0.1247886643165756	0.5000000000000000
0.4519166323293788	0.0650387534763723	0.5000000000000000
0.3298869738894084	0.7994068272559005	0.5000000000000000
0.3505700757173784	0.9042942535781364	0.5000000000000000
0.4707883054495667	0.9496385690991787	0.5000000000000000
0.9523489912977894	0.8641564644116144	0.5000000000000000
0.8741891446100993	0.7314651522933175	0.5000000000000000
0.8529596713027843	0.6265972208192636	0.5000000000000000
0.9515031601435595	0.5673812855622913	0.5000000000000000
0.8555929569784979	0.1616670394708350	0.5000000000000000
0.8283481857888901	0.3034886552440312	0.5000000000000000
0.8505047473294596	0.4082706786292718	0.5000000000000000
0.1919753186955759	0.8507446929333398	0.5000000000000000
0.0366308472155836	0.9570824426364553	0.5000000000000000
0.2199870965596133	0.7093356104240840	0.5000000000000000
0.1989948364443350	0.6044657180058621	0.5000000000000000
0.0786829294917979	0.5593410200833588	0.5000000000000000
0.0758781015133536	0.8634855782734263	0.5000000000000000
0.0118981820057442	0.0543479213517131	0.5000000000000000
0.9708460882292442	0.1482287134557509	0.5000000000000000
0.9710879248848840	0.4526072826493959	0.5000000000000000
0.1736798117279719	0.2789757199348344	0.5000000000000000
0.1959168555348256	0.3837286555627344	0.5000000000000000
0.0981038678361443	0.4436740797413634	0.5000000000000000
0.0945617469414870	0.1468108881883552	0.5000000000000000

2:1 CA:HPLN Periodic and Planar Network --- POSCAR format

C O H

1.0000000000000000

29.0000000000000000 0.0000000000000000 0.0000000000000000

9.2955000000000000 21.8988200000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 15.0000000000000000

C O H

92 48 48

Direct

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0.4816119083290916	0.1937287669135364	0.5000000000000000
0.4360065036764013	0.1839874136105757	0.5000000000000000
0.3467735221732804	0.4968823593065050	0.5000000000000000
0.4026580484865269	0.4622718255735282	0.5000000000000000
0.3241256019565949	0.4494505672622642	0.5000000000000000
0.3661220128910408	0.3884426210982186	0.5000000000000000
0.4117533337062759	0.3981129559668558	0.5000000000000000
0.1184621749909221	0.3993549635499662	0.5000000000000000
0.0745458125099041	0.3877211741543814	0.5000000000000000
0.0775535511975639	0.3280994888277107	0.5000000000000000
0.1245782390850768	0.2780084935098589	0.5000000000000000
0.1693139147493793	0.2896248912028888	0.5000000000000000
0.1656947119560995	0.3511143021463327	0.5000000000000000
0.2165181626307434	0.2393564933756425	0.5000000000000000
0.2613630683960686	0.2522197326473785	0.5000000000000000
0.2117908500703478	0.3613861055534854	0.5000000000000000
0.2584671302884032	0.3122848770706306	0.5000000000000000
0.2187178499572960	0.1794358871677003	0.5000000000000000
0.1745186807351996	0.1684465831099657	0.5000000000000000
0.1281167765463204	0.2167781485063807	0.5000000000000000
0.5237061482145323	0.1327063811178151	0.5000000000000000
0.9964100601433394	0.0836098992821189	0.5000000000000000
0.9416684235177196	0.1197821693875754	0.5000000000000000
0.9785341865939061	0.1921414890642002	0.5000000000000000
0.9320501026038404	0.1828553992008973	0.5000000000000000
0.8420885467610739	0.4988980674572825	0.5000000000000000
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0.8177394205741979	0.4526675151716120	0.5000000000000000
0.8600708916724076	0.3902993534582051	0.5000000000000000
0.9065866904473794	0.3995614392502435	0.5000000000000000
0.7308895536508099	0.1812689951050478	0.5000000000000000
0.7742609736198217	0.1940425202376922	0.5000000000000000
0.7701630423047758	0.2540851744410319	0.5000000000000000
0.7227967542804941	0.3033691049409383	0.5000000000000000
0.6786829007188254	0.2906291105743265	0.5000000000000000
0.6832873206044950	0.2287910551771552	0.5000000000000000
0.6311740625726852	0.3402136578292629	0.5000000000000000
0.5868991725940474	0.3263172105853052	0.5000000000000000
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0.6280960080006094	0.4005056960027330	0.5000000000000000
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0.4369164218856446	0.6825882399026197	0.5000000000000000

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0.3225442461604973	0.9524778290390875	0.5000000000000000
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0.9969244571275532	0.5854402407845672	0.5000000000000000
0.9410465036744837	0.6197687681756932	0.5000000000000000
0.9771395525822757	0.6939625485177106	0.5000000000000000
0.9316288789507753	0.6839794947977145	0.5000000000000000
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0.5732637188114041	0.8278498270854361	0.5000000000000000
0.6202208548484703	0.7778667713101847	0.5000000000000000
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0.6611216456797562	0.8509553107509176	0.5000000000000000
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0.1734426147129921	0.7940676296137718	0.5000000000000000
0.1775484458682387	0.7323790227021998	0.5000000000000000
0.1260072542951965	0.8439352074034319	0.5000000000000000
0.0814488122017275	0.8305140534374585	0.5000000000000000
0.1316997565394463	0.7215247964248205	0.5000000000000000
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0.0193420176724101	0.6330934674500742	0.5000000000000000
0.5222777057412381	0.5274171765365786	0.5000000000000000
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0.3902788898107885	0.2267023756007933	0.5000000000000000
0.4872452637585710	0.2437406684183137	0.5000000000000000
0.4356377586025151	0.4840011670895164	0.5000000000000000
0.4572762197085472	0.3551070079111509	0.5000000000000000
0.3605070573251925	0.3384121553285002	0.5000000000000000
0.2788267199090166	0.4602313756884500	0.5000000000000000
0.2071832692051543	0.4190238739831773	0.5000000000000000
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0.3242187003458338	0.5524530617964563	0.5000000000000000

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0.9837089334879972	0.2417725312649178	0.5000000000000000
0.9319551273949142	0.4835859022479386	0.5000000000000000
0.9521986790358122	0.3572099085248279	0.5000000000000000
0.8546867478327198	0.3407576545641303	0.5000000000000000
0.7729186092938612	0.4635103863271430	0.5000000000000000
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