Thermodynamically Controlled Self-Assembly of Covalent Nanoarchitectures in Aqueous Solution

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ABSTRACT The pursuit of methods for design and preparation of robust nanoarchitectonic systems with integrated functionality through bottom-up methodologies remains a driving force in molecular nanotechnology. Through the use of π-conjugated covalent bonds, we demonstrate a general substrate-mediated, soft solution methodology for the preparation of extended π-conjugated polymeric nanoarchitectures in low-dimensions. Based on thermodynamic control over equilibrium polymerization at the solid−liquid interface whereby aromatic building blocks spontaneously and selectively link, close-packed arrays composed of one-dimensional (1-D) aromatic polymers and two-dimensional (2-D) macromolecular frameworks have been prepared and characterized by *in situ* scanning tunneling microscopy. This methodology eliminates the necessity for severe conditions and sophisticated equipment common to most current fabrication techniques and imparts almost infinite possibilities for the preparation of robust materials with designer molecular architectures.

KEYWORDS: π-conjugated polymeric nanoarchitectures · "on-site" polycondensation · Schiff-base reaction · *in-situ* scanning tunneling microscopy (STM) · covalent self-assembly

The construction of sophisticated, supramolecular architectures through self-assembly[1−20] has attracted considerable attention as "bottom-up" nanotechnology over the past 10 years. Preparation of robust three-dimensional (3-D) nanostructured crystalline powders through metal−ligand complexation[11] or chemical reaction such as metal−organic frameworks (MOF)[16,17] and covalent organic frameworks (COF)[18−20] have been reported extensively. Selective intermolecular interactions have been widely exploited in solution-based chemistry for discrete supramolecular assemblies and for substrate supported 2-D assemblies in both solution and ultrahigh vacuum (UHV) conditions. Substrate supported systems are commonly self-produced through relatively weak noncovalent interactions such as van der Waals interactions, hydrogen bonds,[7−10,12−14] and $\pi-\pi$ stacking.[15] As expected, it has proven difficult to avoid unfavorable irreversible cross-linking which leads to formation of disordered 2- or 3-D nanostructures in substrate supported, covalently bonded molecular systems. Therefore, in ultrahigh vacuum (UHV) conditions,[3−6,21] successful preparative strategies have employed kinetically controlled, thermally activated reactions conducted at very low surface coverage in order to limit the supply of molecular building blocks. Although covalent 2-D frameworks have been achieved in UHV, alternative wet process methods based on self-assembly at the solid−liquid interface under ambient solution conditions remain an eagerly sought after bottom-up technology toward the construction of covalently bonded 2-D nanostructures. Irreversibility of the connecting reactions provides a general challenge for covalent self-assembly. In contrast, the existence of dynamic combination−recombination equilibrium between molecular building blocks enables self-organization processes to reach their most thermodynamically stable structure through iterations of trial and error.[7−12,22] Delicate self-organization induced by molecular dynamics and the robust toughness imparted by covalent bonding are thus typically perceived as a trade-off in extended molecular frameworks. To overcome this, we focused on equilibrium polycondensation reactions to connect building blocks in extended frameworks, specifically the use of aromatic primary amine and aromatic aldehyde units as

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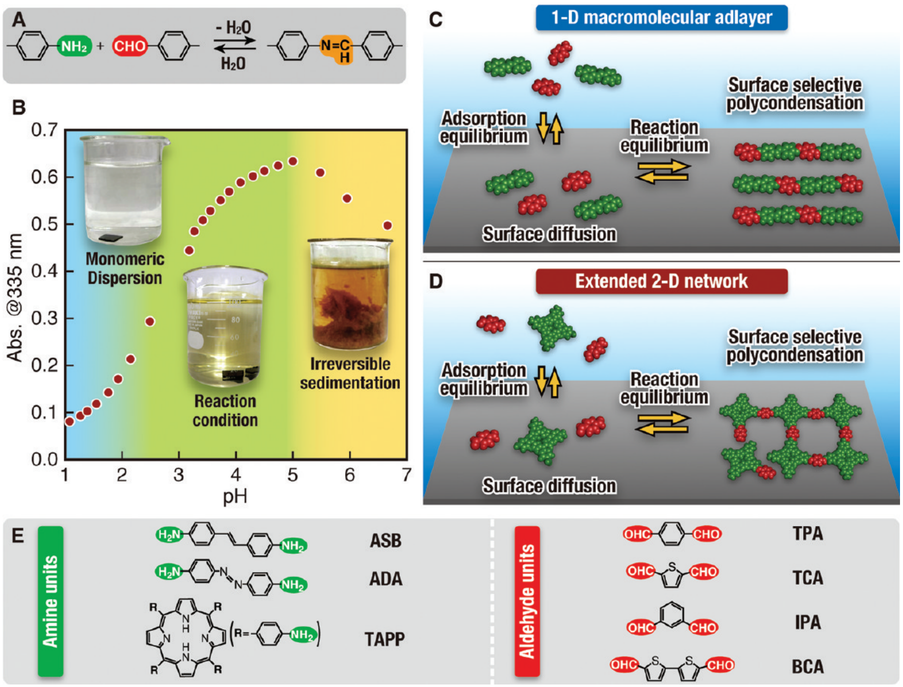

Figure 1. Self-assembly of π-conjugated macromolecular nanoarchitectures at the liquid−solid interface. General reaction scheme of Schiff base coupling reaction (A); representative pH-dependent absorbance plot (B) of an aqueous solution consisting of 100 μM ASB and 100 μM TPA with inset photos of pH-dependent solution conditions; schematic representation of the soft solution process used to construct 1-D (C) and 2-D (D) π-conjugated macromolecular nanoarchitectures; and the chemical structure list of molecular building blocks with corresponding acronyms used herein (E). Molecular building blocks are connected covalently by a surface selective polycondensation reaction induced by delicate control of adsorption and reaction equilibria.

complementary reactive substituents for aromatic Schiff-base (also known as imine or azomethine) coupling (Figure 1A).[23−27] Owing to its high facility as a coupling reaction, the Schiff-base reaction remains one of most prevalent in organic chemistry[19,21,23−27] and has been widely applied not only for synthesis of discrete supramolecules, but also for the construction of two-dimensional[21,25] and three-dimensional nanoarchitectures.[19] Recently, the Schiff-base coupling between aromatic trialdehyde and aliphatic diamine precursors was successfully applied in UHV and revealed pronounced kinetic effects on the polymer structure formed, including highly branched structures.[21]

It is not well-known, however, that aromatic Schiff base formation[23,24] between primary amines and aldehydes can be achieved spontaneously even in soft solution conditions, such as aqueous media at room temperature, and that the coupling reactions are essentially reversible in spite of covalent bonds. For instance, when 4,4′-diaminostilbene dihydrochloride (ASB) and terephthaldicarboxaldehyde (TPA) are mixed in water at basic pH values relative to pK_a at room temperature, the reaction proceeds immediately with irreversible sedimentation of an oligomeric product. At acidic pH values below pK_a of the primary amino group, the reaction results in a monomeric dispersion as the equilibrium shifts from "Schiff base formation" to "breakdown" due to protonation of the primary amino groups (Figure 1B and Supporting Information, Figure S2). The reversibility and thermodynamic control of this solution reaction encouraged us to extend the conventional process of molecular self-assembly in 2-D from noncovalently bonded systems to covalently bonded ones. Figure 1C shows conceptually the construction of extended covalently linked, π-conjugated macromolecular architectures through surface-mediated selective polycondensation.

The spontaneity and selectivity of the polycondensation reaction between building blocks bearing connecting units, even under conditions at which the solution reaction does not occur, are the key concept of this methodology. To achieve surface-selective polycondensation through physical adsorption, the selection of solution conditions and substrates is crucial. Initial assessment of the synthetic strategy involved the preparation of more simple π-conjugated polymeric systems, shown here to spontaneously form on the surface in homogeneous solution. Here, the solution pH was carefully selected for each combination of molecular building blocks and set at a slightly acidic value relative to the pK_a of the molecules bearing primary amino units, resulting in protonation and scarce inhibition of the reaction in the homogeneous solution. Chemically inert and hydrophobic iodine-modified Au(111) (I/Au(111)) was selected as a

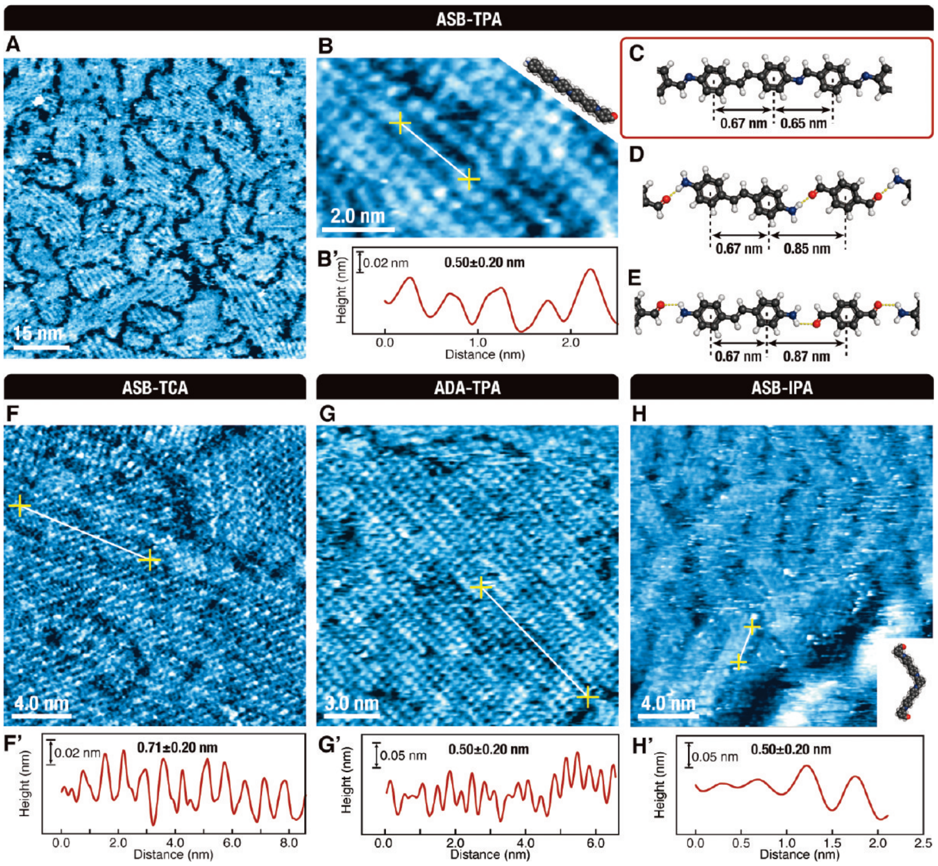

Figure 2. Highly ordered adlayers of linear 1-D π-conjugated aromatic polymers. Representative *in situ* STM images (A, B, F−H), corresponding connection models (C−E) and cross sections (B′, F′, G′, and H′) of close-packed arrays of 1-D π-conjugated aromatic polymers formed by polycondensation of building blocks (100 μM) from aqueous solutions (1 mM KI) on iodine-modified Au(111) surfaces. Combination systems: ASB-TPA (A and B), ASB-TCA (F), ADA-TPA (G), and ASB-IPA (H). The appropriate pH was selected for each combination, namely 2.49, 2.48, 3.01, and 4.00 for ASB-TPA, ASB-TCA, ADA-TPA, and ASB-IPA, respectively. The cross sections were obtained at the locations marked by the lines.

substrate to readily enable spontaneous adsorption, self-organization, and subsequent bond formation between relatively large organic molecules.[22] Weak adsorption (physisorption) allows for high molecular mobility on the surface and/or dynamic adsorption−desorption equilibrium even at room temperature.

Notably, the π-conjugated polymers synthesized here are composed solely of aromatic units carrying no bulky side groups or ionic groups, which are usually indispensable for increasing solubility and avoiding stacking in a homogeneous medium.[26,28] Moreover, these π-conjugated aromatic polymers are candidate systems for molecular wires in nanoelectronics applications due to their previously reported electrical transport properties.[27]

RESULTS AND DISCUSSION

Highly ordered adlayers of π-conjugated polymers in the presence of aromatic diamines and dialdehydes were observed by *in situ* STM (Figure 2). Extended, mosaic patchlike ordered domains of π-conjugated linear polymer arrays fully covering the surface were reproducibly observed for almost all combinations of the building block molecules bearing two primary amino units, ASB and 4,4′-azodianiline (ADA), and those bearing two aldehyde units, TPA and 2,5-thiophenedicarboxaldehyde (TCA), as shown in Figure 2 panels A, B, and F−H. In contrast, no molecular adlayer was observed for unitary molecular systems. The presence of a nearly continuous molecular layer and associated chain termination at phase boundaries affirms polymer formation through surface propagation rather than sedimentation of polymeric species from the solution (see Figure 2A and Supporting Information, Figure S4).

Typical high-resolution STM images (Figure 2A,B) clearly revealed that each domain consisted of parallel lines where the aligned spots in each domain are assigned to the benzene rings in an extended π-conjugated polymer chain. Each feature in the STM images shows a good agreement with corresponding structural models in both stretched and flat orientations both in terms of size and conformation. As expected for a covalent linkage between monomer units, the observed packing

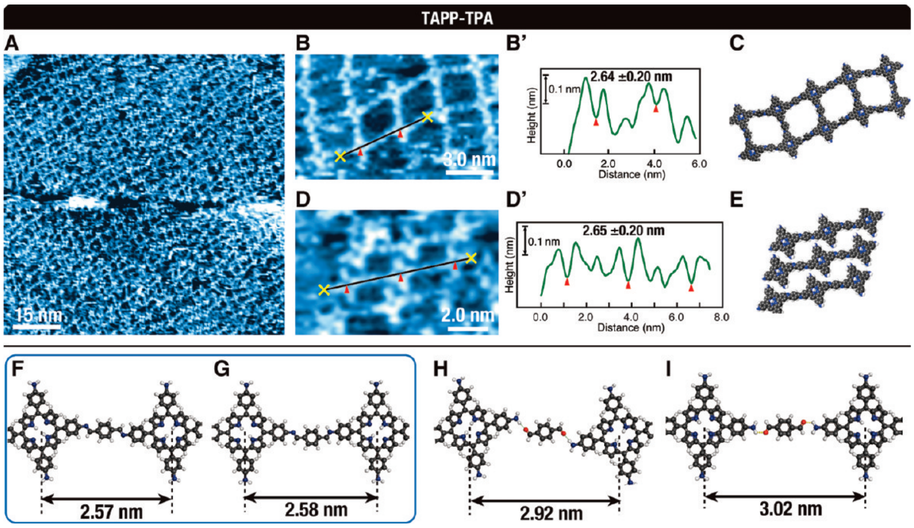

Figure 3. Structural variation and polymorphism of 2-D π-conjugated macromolecular frameworks. Representative *in situ* STM images (A, B, and D), cross sections (B′ and D′) and corresponding models (C and E) of covalently bonded macromolecular nanoarchitectures consisting of TAPP–TPA and connection models for Schiff-base bonding (F and G) and hydrogen boding (H and I). Typical compositions of the aqueous reaction solutions were 88 mM $NaClO_4$ with 0.12–0.37 μM TAPP and 20 μM TPA. The appropriate pH was selected for each combination, namely 3.52. The cross sections were obtained at the locations marked by the lines.

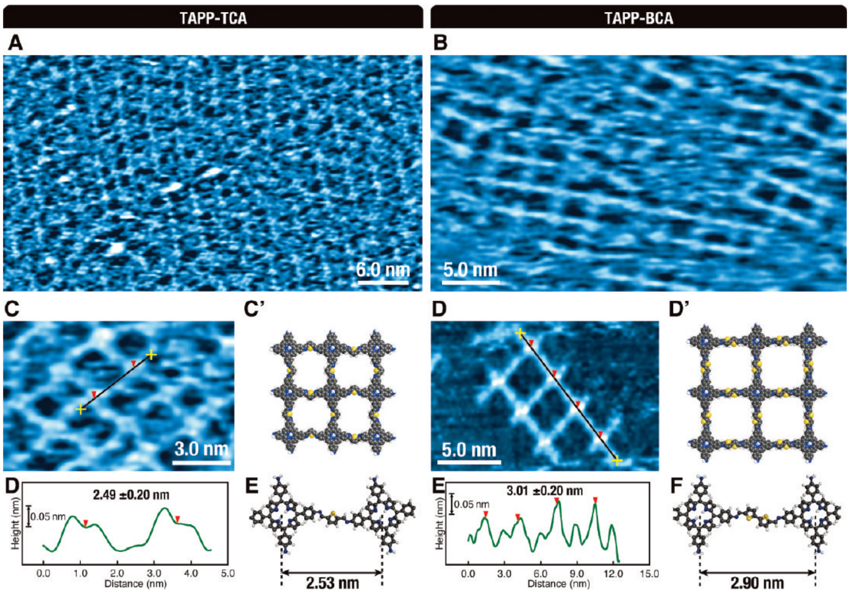

Figure 4. Structural variation of 2-D π-conjugated macromolecular frameworks. Representative *in situ* STM images (A–D), corresponding mesh models (C′ and D′), cross sections (E and G), and covalent connecting models (F and H) of covalently bonded macromolecular nanoarchitectures consisting of TAPP–TCA (A, C, C′, E, and F) and TAPP–BCA (B, D, D′, G, and H′). Various 2-D frameworks were produced under similar conditions as TAPP–TPA (Figure 3). The appropriate pH was selected for each combination, namely 3.52 and 3.50 for TAPP–TCA and TAPP–BCA, respectively. The cross sections were obtained at the locations marked by the lines.

periodicity of the linear polymers, ASB-TPA and ADA-TPA was 0.50 ± 0.20 nm (Figure 2 B, B′, G, G′). By comparing the modeled interaction length in the case of ASB-TPA polymer, the distance between covalent bond and hydrogen bond estimated were 0.65 and 0.85 nm, conclusively proving that formation of covalent bond but not hydrogen bond. In addition, the fact that the constant periodicity observed (Figure 2B, B′) strongly supports the covalent model (Figure 2C), because the models based on hydrogen bond conection (Figure 2D, E) should give an alternately shifted corrugation. Occasionally, a second adlayer on the arrays was also observed (Supporting Information, Figure S5). The degree of polymerization, estimated from domain lengths along the direction of the polymer chain, revealed individual polymer chains commonly composed

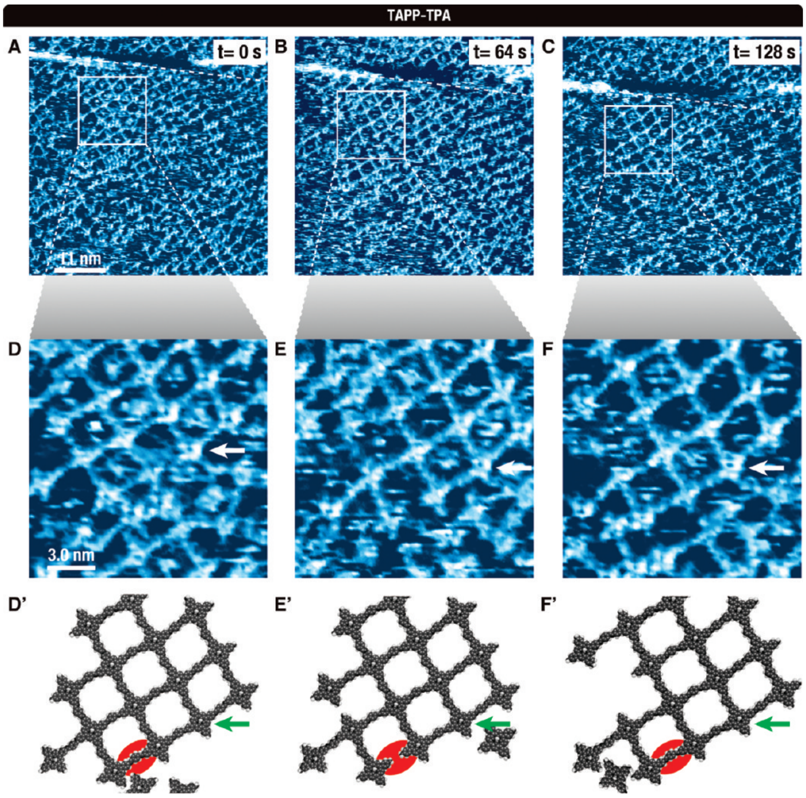

Figure 5. Real-space imaging of covalent bond formation/cleavage dynamics on the equilibrium reaction. Sequential (A–C) and zoomed (D–F) images acquired in the same location and corresponding structural models (D′–F′) clearly demonstrate covalent bond formation/cleavage dynamics. The irregular TAPP unit, denoted by arrows, provides a position marker in a changing molecular framework where the covalent bond marked by red circles in models revealed "connected", "disconnected" and "connected" forms in D, E, and F, respectively.

of several tens (approaching a maximum of one hundred) of benzene units (see Supporting Information, Figure S3).

Interestingly, when meta-substituted building molecule, isophthalaldehyde (IPA) was used with ASB, a domain consisting of zigzag lines was observed (Figure 2H). The twist angle (*ca.* 120°) was consistent with the corresponding model with a flat orientation. These representative examples clearly demonstrate the synthesis of π-conjugated aromatic polymers with high molecular weight achieved through carefully conducted "on-site" successive polymerization on a surface. The thermodynamic reaction of Schiff base bonding is generally regulated by concentration and pH. The equilibrium reaction at marginal conditions is easily influenced by the nature of the surface. The hydrophobic nature of the I/Au(111) surface is advantageous in terms of higher surface concentration by physical adsorption rather than that in the solution. Moreover, the hydrophobic (lipophilic) surface pushes the equilibrium toward dehydration for the polycondensation, similar to the addition of an organic solvent to an aqueous solution shifting the equilibrium toward bond formation.

Following the successful "on-site" successive polycondensation of π-conjugated 1-D polymeric systems, the ability to apply this synthetic methodology toward the fabrication of 2-D π-conjugated supramacromolecular frameworks was pursued (Fig. 1D). As compared to chain polymerization such as polyacetylene, polyaniline, polypyrrole, and polythiophene initiated by local bias[29] or electrochemical control,[30] surface-mediated successive polymerization enables the preparation of sophisticated nanostructured materials by varying the number and relative arrangement of predefined reaction points, as in the case of molecular systems based on noncovalent bonding. 5,10,15,20-Tetrakis(4-aminophenyl) porphyrin (TAPP), which provides four possible linkages to other molecules, in combination with a series of bifunctional connector molecules, generated several 2-D macromolecular mesh frameworks (Figures 3 and 4 and Supporting Information, Figure S7). In each case, individual TAPP units are interconnected *via* molecular linkers through π-conjugated covalent bonds. In all combinations, various configurations of macromolecular mesh frameworks, including square, distorted square, and an argyle pattern, were observed along with various irregular structures.

High-resolution STM images (Figures 3 and 4) revealed the framework structures to be composed of TAPP molecules interconnected by covalently bonded linker molecules. Structural variations within the 2-D macromolecular frameworks were seen to depend on both the chemical structure of connecting molecules as well as linkage conformations. For example, the coexistence of square and parallelogram networks in the TAPP−TPA system revealed structural polymorphism due to flexibility in the structural frameworks despite their covalently bonded, cyclic structures (Figure 3B,C), whereas the TAPP−BCA system consistently exhibited a square mesh topology (Figure 4D,D′). In addition, small close-packed arrays of the linearly connected TAPP−TPA polymers were frequently observed together with patches of regular structures (Figure 3D,E). The frameworks, with their corresponding structural variations, extended over wide areas (Figure 3A) and demonstrated strong agreement with the corresponding model predictions. By again comparing the modeled interaction length in the case of covalent bond (2.57/2.58 nm, Figure 3F,G) *versus* hydrogen bond (2.92/2.83 nm, Figure 3H,I) formation, the observed intermolecular distances of 2.64−2.65 ± 0.2 nm cleary show the framework to comprise covalently linked molecular units as seen in Figure 3B,B′,D and D′.

Dynamic, real-space visualization of covalent bond breakage and formation within the framework was achieved through high-resolution imaging (Figure 5A−F). This direct observation of bond formation and dissociation clearly demonstrates the reversibility of this process and further supports its occurrence at the solid−liquid interface rather than in the solution. Interestingly, unconnected TAPP molecules were often observed as incorporated guests within the cavities of framework (Figure 5D−F).

CONCLUSIONS

The surface-mediated, solution-based synthetic methodology presented here introduces the unique concept of utilizing thermodynamic control of an equilibrium polymerization reaction toward preparation of robust, extended supramacromolecular networks and arrays. Although the specific example of Schiff-base coupling has been reported here, this concept can be generalized to the design and construction of various supramolecular systems through use of a wide array of equilibrium coupling reactions. In contrast to similar materials prepared under complex UHV conditions, materials constructed in this straightforward manner, essentially in a beaker with water, were robust and retained their structure to the molecular level following removal of the reaction solvent, drying, and even subsequent reintroduction to a solution environment (see Supporting Information, Figure S7). Since this solution-based process is not limited to planar 2-D surfaces, it can be readily applied to arbitrary 3-D micro- and macrostructured objects. In addition, the 2-D architectures constructed by this method could potentially serve as a surface template for subsequent 3-D growth of extended metal−organic or covalent-organic frameworks. These results pave the way to true "bottom-up" assembly of a vast array of solid-supported, designer supramolecular nanoarchitectures with potential utility as functional materials for applications including but not limited to electronics, solar and fuel cells, biosensors, separations, nanoporous membranes, and commercial coatings.

METHODS

Sample Preparation and Scanning Tunneling Microscopy. All chemicals were purchased and used without further purification. Atomically flat Au(111) facets formed on homemade single-crystal beads were used as a substrate. After being annealed with a hydrogen flame and quenched in ultrapure water, Au(111) samples were immersed in 10 mM KI aqueous solution to prepare iodine-modified Au(111) surfaces.[22] The samples were then transferred into the electrochemical STM cell filled with the prepared solutions. Electrochemical STM investigations[8,9,22] were carried out in the aqueous solutions using a Nanoscope E (Digital Instruments, Santa Barbara, CA). Tungsten STM tips were prepared by electrochemical etching in 1.0 M KOH and were subsequently coated with clear nail polish for minimization of residual faradic currents. Platinum wires were used as the reference and the counter electrodes. All STM images were obtained at open circuit potential in constant current mode. The calibration of the STM was carried out for each experiment tip using the atomic resolution lattices of Au(111) and HOPG. Dimensional analyses of intermolecular bond lengths were carefully decided by averaging a series of images, which were collected at same location with opposite scan derections to minimize the influence of thermal and mechanical drifting.

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Supporting Information Available: Schematic comparison of 3D crystallization and 2D network formation, pH-dependence of UV−vis spectra of an aqueous solution consisting of ASB and TPA, the evaluation of degree of polymerization from typical high resolution *in situ* STM image, schematic models of "on-site" growth of polymers, STM image with the cross-section of a secondary adlayer of ASB-TPA polymer arrays, *in situ* STM images, cross sections and corresponding models of structural variations of 2-D TAPP−TPA frameworks and typical *in situ* STM image of rehydrated two-dimensional frameworks after removal from reaction solution. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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