Advances in supramolecularly assembled nanostructures of fullerenes and porphyrins at surfaces

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Dedicated to Professor Osamu Ito on the occasion of his retirement

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ABSTRACT: The ‘bottom-up’ strategy is an attractive and promising approach for the construction of nanoarchitectures. Supramolecular assemblies based on non-covalent interactions have been explored in an attempt to control surface properties. In this minireview, we focus on advances made in the past three years in the field of scanning tunneling microscopy (STM) on supramolecular assembly and the function of porphyrins, phthalocyanines, and fullerenes, non-covalently bound on metal single crystal surfaces. Well-defined adlayers, consisting of porphyrin and phthalocyanine for the design of supramolecular nanoarchitectures, supramolecular traps of C_{60} on hydrogen bond networks, a unique approach for controlling molecular orientation by a 1:1 supramolecularly assembled film consisting of C_{60} and the related derivatives and metallooctaethylporphyrins, and nanoapplications of fullerenes, either induced by tip manipulation or driven by thermal fluctuations at surfaces, were clearly visualized by STM. Copyright © 2007 Society of Porphyrins & Phthalocyanines.

KEYWORDS: supramolecular assembly, scanning tunneling microscopy, fullerenes, porphyrins, phthalocyanines, metal single crystal surface, electrochemistry, ultrahigh vacuum.

INTRODUCTION

Porphyrins provide an extremely versatile synthetic base for a variety of material applications in many disciplines of chemistry and physics, such as optoelectronics, electrochemistry, catalysis, data storage and solar cells [1-8]. It is well-known that porphyrins and related derivatives are included in metalloproteins as active centers, ‘hemes’. To understand their role and electrochemical properties such as dioxygen storage, a research on porphyrin thin films is one of the attractive fields in electrochemistry [9-12]. Since the late 1970’s, thin films of metalloporphyrin and metallophthalocyanine derivatives have been studied intensively due to the interest in electrocatalytic reactions, such as the reduction of O_{2} to develop efficient fuel cells; such reactions occur primarily at graphite electrodes [12-16]. However, thus far not much attention has been paid to the adlayer structure of these porphyrins. Formation and characterization of ordered adlayers of porphyrin and phthalocyanine molecules at electrolyte-electrode interfaces are therefore important in understanding the mechanism of O_{2} reduction.

On the other hand, covalently linked porphyrin-fullerene C_{60} dyads were used as one of the artificial photosynthetic models in the mid 1990’s [17-19]. Because fullerenes are known as one type of acceptor with strong \( \pi \)-electron accepting ability, they are considered to be suitable building blocks.
for the construction of three-dimensional molecular architectures [20]. Subsequently, the non-covalent interaction between C₆₀ and porphyrin cyclic dimer [21, 22] and C₆₀ and palladium-linked bis-porphyrin was reported [23]. Currently, fullerene-porphyrin supramolecular assemblies have been studied extensively to generate photocurrents as well as to elucidate their unique photophysical and photochemical properties [2-8, 24, 25]. Since establishing the concept for supramolecular chemistry [26-28], self-assembly of organic molecules has recently gained considerable attention as a key technique for the ‘bottom-up’ fabrication of nano-scale functional structures [26-33]. For example, self-assembled porphyrin trimers and graphitic nanotubes are attractive materials for surface patterning [34] and molecular electronics [35]. Research on programmed DNA assembly, the so-called ‘DNA-origami’ [36] and ‘DNA-nanotile’ [37-40], has also been an attractive topic. A new concept of biosensing to achieve multiplexed detection was proposed by using combinatorial self-assembly of DNA-nanotiles to direct the self-assembly of fluorescently labeled molecular probes into combinatorial encoding arrays [40].

In recent years, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been widely accepted as powerful tools for understanding the structure of adsorbed layers of molecules on metal surfaces at the atomic scale, both in ultrahigh vacuums (UHV) [41-44] and in aqueous solutions [45-51]. High-resolution STM has made it possible to directly determine packing arrangements and even internal structures of adsorbed organic molecules. Furthermore, it has been demonstrated that in situ STM makes it possible to monitor, with atomic or molecular resolution, a wide variety of electrode processes such as the adsorption of water-soluble inorganic and organic species and underpotential deposition of metal ions [45-48]. For the construction of supramolecular assembled nanoarchitectures, the appropriate modifications for concepts of solution-based supramolecular chemistry are necessary to further extend supramolecular assembly technique on substrates. Therefore, molecular level visualization is very important to fully understand, not only the interaction between substrate and adsorbates, but also the influence of electronic properties of adsorbed ligands on non-covalent bonds. Supramolecular assemblies based on non-covalent interactions such as dipole-dipole, hydrogen bonding and metal-ligand coordination on metal surfaces, have also been explored in an attempt to control surface properties [43, 44].

In this minireview, we focus on the molecular assemblies of functionalized molecules such as porphyrins, phthalocyanines and fullerenes, non-covalently bound on metal single crystal surfaces, because those molecules are important building blocks for the construction of nanostructures. This article primarily focuses on our own experimental results, obtained on Au single crystal electrodes in aqueous electrolyte solutions under electrochemical conditions, in addition to several published results from other groups in the last three years.

**Porphyrin and phthalocyanine adlayers**

*Single component adlayers.* Adlayer structures of porphyrin and phthalocyanine derivatives have been previously studied, mostly in UHV using STM on various metal surfaces [52-60]. Lippel et al. reported the first STM images of a copper(I) phthalocyanine (CuPc) adlayer on Cu(100) [52]. Gimzewski and coworkers investigated copper(II) 5,10,15,20-tetrakis(3,5-di-t-butylphenyl)porphyrin (CuTBPP) on Cu(100), Au(110), and Ag(110) in UHV [53, 54] and found that the packing arrangement of CuTBPP depends on the metal substrate used. Hipps and coworkers reported various MPC’s (M; Cu [55, 56], Co [55, 56], Ni [57], Fe [57], VO [58]) and metallotetraphenylporphyrins (MTPP) [59, 60] on reconstructed Au(111) and found that the brightness of the center spot of Pc or TPP is dependent on the active center metal. The difference in contrast between the metal ions in STM images was explained in terms of the occupation of the d₄ orbital. As listed above, STM imaging of hydrophobic MPC or MTPP molecules was successful in UHV.

STM has also been utilized in understanding the structure of adlayers of water-soluble porphyrin molecules in aqueous solutions [46, 61-70]. Highly ordered arrays of free-base 5,10,15,20-tetrakis(N-methylpyridinium-4-yl)porphyrin (H₄TMPyP) molecules were formed on the iodine-modified (I-) Au(111) [61-63], I-Ag(111) [64], I-Pt(100) [65], and S-modified Au(111) [66] electrodes. However, the ordering of a free-base porphyrin array directly attached to a bare Au(111) surface at an electrochemical interface was subsequently reported by He et al. [67, 68]. Potential manipulation plays a significant role in controlling the surface mobility of tetrakis(4-pyridyl)porphyrin (H₄TPyP) molecules [67]. Tao et al. also investigated the adlayers of three water-soluble molecules, iron(III) protoporphyrin, zinc(II) protoporphyrin, and protoporphyrin(IX), on the graphite basal plane in aqueous solutions with both STM [69, 70] and AFM [69]. Similar adlayer structures were formed using these three molecules, although the internal structures obtained by in situ STM were significantly different [69].

We subsequently investigated several water-insoluble porphyrin adlayers such as cobalt(II) porphine (CoP) [71], cobalt(II) octaethylporphyrin (CoOEP) [71], cobalt(II) tetraphenylporphyrin (CoTPP) [72],
cobalt(II) coordinated ‘picket-fence’ porphyrin (CoT$_{piv}$PP) [73] (these molecules are abbreviated as CoPor), and cobalt(II) phthalocyanine (CoPc) [74] (see Chart 1). We were successful in forming highly ordered molecular arrays of those molecules spontaneously on Au(111) surfaces by immersing Au(111) in benzene solutions containing those molecules. The enhancement of reductive current for O$_2$ reduction at those modified Au(111) electrodes compared to the bare Au(111) electrodes clearly shows that CoPor and CoPc adlayer catalyzes the reduction of O$_2$. By using rotating CoPor- or CoPc-modified Au(111) disk electrodes, it was indicated that the 2-electron reduction process of O$_2$ to H$_2$O$_2$ proceeded on the CoP-, CoTPP-, CoOEP-, and CoPc-modified Au(111) surfaces [50, 71-74]. High-resolution STM images for each adlayer on Au(111) are shown in Fig. 1. CoP formed highly ordered arrays following a slightly negative potential manipulation (see Fig. 1a). For the other adlayers, such as CoOEP, CoTPP and CoPc molecules, stable and highly ordered arrays were formed on the Au(111) surface. The adlayers were not dependent upon electrode potential at or near the H$_2$ evolution potential in HClO$_4$. The adlayer structures of CoOEP and CoTPP formed in benzene solutions were identical to those obtained in UHV [60, 75]. The CoOEP and CoTPP adlayers formed an incommensurate structure with respect to
the reconstructed Au(111) surface. For the CoT₉₀,PP, individual CoT₉₀,PP molecules were recognized to be square-shaped with four bright spots at the corners in the characteristic nanobelt array, whereas the ad-lattice was almost the same as that of CoTPP. Careful inspection revealed the presence of three small protrusions separated from each other in each bright spot, suggesting that they are tert-butyl groups in each CoT₉₀,PP molecule, as marked by white circles in Fig. 1d. The brightest one was assigned to the O₂-coordinated CoT₉₀,PP molecule. The state of O₂TPP adlayers on Ag(111). II (d₁₀₀) was distinctly observed in the solution phase. CoPc molecules formed three other adlayer structures following preparation from UHV by Lu et al. [55, 56]. However, we found that other adlayer structures following preparation from the solution phase. CoPc molecules formed three packing arrangements on Au(111) surface, i.e. one rectangular arrangement on reconstructed Au(111) and two hexagonal arrangements on Au(111)-(1 × 1), depending on the surface coverage [74]. Figure 1g shows a typical STM image for the CoPc adlayer with (3√3 × 3√3)R30˚ symmetry on Au(111)-(1 × 1) surface. The method of immersion into benzene solution was also consistent with that obtained in UHV [55-60]. Furthermore, we investigated the organization and hydrogen bonding network formation of carboxyphenyl porphyrin derivatives at electrochemical interfaces [76]. Our results demonstrate that the ordered arrays of monocarboxy- or tetracarboxy-substituted porphyrin derivatives formed on a Au(111) surface in acidic solution depend, to a remarkable extent, on the number of peripheral substituents (i.e. dimer and tetramer structures were formed for monocarboxy- or tetracarboxy-substituted porphyrin derivatives, respectively, by the variation of the applied potentials, see Fig. 1e,f). Electrochemical control of the self-assembly of porphyrin complexes is an effective method for constructing novel surface architectures. In the case of CoPc, the packing arrangement of CoPc on the reconstructed Au(111) surface was also consistent with that obtained in UHV by Lu et al. [55, 56]. However, we found other adlayer structures following preparation from the solution phase. CoPc molecules formed three packing arrangements on Au(111) surface, i.e. one rectangular arrangement on reconstructed Au(111) and two hexagonal arrangements on Au(111)-(1 × 1), depending on the surface coverage [74]. Figure 1g shows a typical STM image for the CoPc adlayer with (3√3 × 3√3)R30˚ symmetry on Au(111)-(1 × 1) surface. The method of immersion into benzene solution was further extended to a larger molecule such as 15-crown-5-ether-substituted cobalt(II) phthalocyanine (CoCRPc) [77]. Each molecule was seen as propeller-shaped with the brightest spot at the center, with four additional bright spots at the corners of each CoCRPc molecule (see Fig. 1h). The ad-lattice of the CoCRPc array on Au(111) was determined to be p(8 × 4√3R-30˚). In the absence of Ca²⁺, four additional spots were observed at the corners, whereas in the presence of Ca²⁺, only two additional bright spots were observed at diagonal positions with respect to the Pc ligand, as a result of encapsulation of two Ca²⁺ ions by crown ether rings [77]. Furthermore, it was demonstrated by using Au(100)-(1 × 1) lattice that the relationship between crown moieties of CRPc and the underlying Au lattice is important in the trapping of Ca²⁺ ions in crown rings [78]. In contrast, adlayers containing other central metal ions, for example, CuTPP, NiTPP, ZnTPP, CuOEP, NiOEP, ZnOEP, CuPc, and ZnPc, were observed as a dark spot in the center both in UHV [55-60] and in solution [72, 74, 79-82]. Molecular resolution STM revealed a propeller shaped ad-molecule or circle shape with eight additional spots at the corners with its center imaged as a protrusion for Coᵢ and a depression for other metal ions. The CoPc or CoTPP molecules were easily identified by the strong tunneling current resulting from orbital mediated tunneling through the half-filled dₓ orbital of the Coᵢ ion (dₓ): a bright spot appeared at the center of each molecule, whereas Niᵢ(dₓ), Cuᵢ(dₓ) Znᵢ(dₓ²) ions have a fully filled dₓ orbital [55-60, 81]. The remarkable contrast in tunneling current afforded by the difference in electronic configuration of transition metal ions allows one to clearly distinguish between species for chemical identification at the molecular level. In the case of Znᵢ ion, we found the possibility of epitaxial growth of ZnPc layer from the solution phase. ZnPc molecules can be epitaxially assembled because of the attractive interaction between the electron donating pair in the Pc scaffold and the zinc ion. The formation of epitaxial layers of ZnPc molecules from benzene solutions was controllable by altering the immersion time [81].

Direct synthesis of metalloporphyrin at Ag(111) was reported by Gottfried et al. [83, 84]. This group prepared free base H₂TPP adlayer on Ag(111) in UHV, then Co was further deposited at the adlayer. XPS results indicated that Co ion can be coordinated to a porphyrin ring [83]. This method was effective for Zn-metalation to H₂TPP adlayer by Zn deposition [84]. Very recently, direct observation of iron-metalation into a free-base porphyrin array were independently reported by two groups [85, 86]. Auwärter and coworkers succeeded in directly observing Fe-metalation at H₂TPyP array on Ag(111) in UHV [85]. Buchner et al. also showed iron-metalation with H₂TPP array formed on Ag(111) by using UVH-STM [86]. In both cases, each H₂TPyP or H₂TPP molecule appeared as brighter spots in the high-resolution STM image after the deposition of iron on those adlayers, suggesting that the metalation of the Fe atom occurred at the H₂TPyP and H₂TPP adlayers on Ag(111). The precise control of function (such as dioxygen reduction activity) is determined by the method of direct coordination of various metal ions.

**Structure-controlled binary arrays.** Porphyrins are also well-known as suitable building components to construct two- or three-dimensional self-organized
multiarrays [87-94]. Self-assembly of complementary subunits via non-covalent interactions such as hydrogen bonds and metal-ligand coordination is an attractive approach to the controlled oligomerization of monomers to form large supramolecular architectures [91-94]. The binary system consisting of porphyrin and phthalocyanine will aid in understanding the supramolecular design of nanoarchitectures. Hipps and coworkers found the formation of well-ordered regions with an entirely new structure with 1:1 composition of cobalt(II) hexadecafluoro phthalocyanine (F16CoPc) and NiTPP on Au(111) by vapor-phase deposition in UHV [95]. F16CoPc and NiTPP molecules were distinguished from each other by the difference in brightness of central metal ions between F16CoPc and NiTPP molecules. The remarkable contrast in tunneling current afforded by the difference in electronic configuration of transition metal ions allows one to clearly discriminate between species for chemical identification at the molecular level. When CoPc and NiTPP molecules were deposited on Au(111), the binary adlayer consisting of CoPc and NiTPP revealed a densely packed, apparently well-defined structure, which is compositionally disordered [96]. Hipps et al. concluded that the formation of 1:1 composition of F16CoPc and NiTPP is explained by the ability of the two types of molecules to interlace due to the up-to-4 kJ.mol⁻¹ attractive energy for each close-approach fluorine-hydrogen intermolecular interaction and the reduced repulsive interaction between F16CoPc molecules because of the increase of spacing forced by NiTPP units. They also investigated CoPc and CoTPP mixed system on Au(111). The electronic structure (state) between CoPc and CoTPP was differentially identified in the alternate binary CoPc and CoTPP array by STM and the orbital-mediated tunneling spectra measurements [97].

Another system, a bimolecular array consisting of CoPc and CuTPP, was examined both on the Au(111) and Au(100) surfaces by immersing the surfaces in benzene solutions [98, 99]. We found that an alternate mixed layer consisting of CoPc and CuTPP was formed on reconstructed Au(100)-(hex) but not on reconstructed Au(111), suggesting that the supramolecular assembly consisting of two chemical components also depends upon the crystallographic orientation of Au [98]. In this case, the terrace of Au(111) was completely covered with two different phases: a disordered region and a highly ordered region consisting of CuTPP, whereas the stripes composed of alternate bright and dark lines were observed on Au(100)-(hex) (see Fig. 2a). The difference in brightness at the centers of CoPc and CuTPP molecules is clearly explained by the difference in the mode of occupation of d orbitals, as described by Hipps and coworkers [55, 56, 96]. Subsequently, we found that a similar two-component supramolecular adlayer consisting of CoPc and CuTPP was formed on Au(111) following the different modification condition [99]. It is likely that the adsorbate-substrate interaction is much weaker on Au(111) than on Au(100)-(hex). The formation of the stripe structure was independent of the crystallographic orientation, while the corrugation periodicity of reconstruction for the underlying substrate is quite different from Au(111) and Au(100). One possibility is that the difference in π-electron donating ability between CoPc and CuTPP might play a significant role for the alternate stripe formation. We believe that the molecular assembly in this system is somewhat weak and dominated by van der Waals interactions. A bimolecular system consisting of CuOEP and CoPc on Au(111) was also examined by our group at the electrochemical interface [100]. In the case of the bimolecular array consisting of CuOEP and CoPc, it has a π(9 × 3√7R-19.1°) and its mirror structure, π(9 × 3√7R-40.9°), were alternately formed on the Au(111) terrace. Furthermore, we attempted to control the domain size and composition by changing the potential scan at a slow rate to a slightly cathodic potential. In this case, one-dimensional (1D) molecular chains of CuOEP were clearly observed as dark gaps between bright rows consisting of two or three CoPc molecular rows, as shown in Fig. 2b, with the result that the structure changed drastically upon this potential manipulation [100]. In this system, the surface mobility and the molecular reorganization of CuOEP and CoPc were accelerated by variation of electrode potential. The surface charge density at the electrochemical interface would contribute not only to the interaction between molecule and substrate but also to the interaction between molecules. Such a precise and unique control
of electrochemical interfaces is of great interest for exploring further applications of the porphyrin and phthalocyanine molecular assembly.

**Double- and triple-deckers.** In recent years, adlayers of several sandwich compounds such as the bis-phthalocyanine double-decker complexes of Y, Ce, Pr, La, and Er, have been investigated at the liquid-solid interface (mainly on HOPG in 1-phenyloctance) [101-107]. Possible future applications for these rare earth complexes include their use as organic field-effect transistors, liquid crystals, chemical sensors [108] and especially, molecular memory of surfaces, as has been proposed by Lindsey and coworkers [109]. In the case of double-decker heterodimers, several groups have reported a unique property of molecular rotation [110-113]. This rotation can be controlled by coordination to specific functional groups within the molecule [110-112] or by the redox properties of the rare earth central metal [113]. Thus, it is very important to understand the formation of double- or triple-decker adlayers by rotation control and electrochemical properties. We very recently reported the adlayer of 15-crown-5-ether-substituted Pc and tetraphenyl porphyrin (TPP) triple-decker complex coordinated by EuIII, TPP/CRPc/CRPc on a Au(111) surface to create a three-dimensional functional molecular architecture [114]. A unique molecular assembly and new surface properties of TPP/CRPc/CRPc was found as a result of the adsorption orientation and electrochemical potential variation on the Au(111) surface. As can be seen in Fig. 3a,b, a characteristic well-ordered domain of 2:1 sandwich complex consisting of phthalocyanines and tetraphenylporphyrin was found on a Au(111) surface in HClO₄ by *in situ* STM, indicating that a highly ordered array was formed by alternately arranging two different molecular orientations, as illustrated in Fig. 3c. This finding is applicable to “bottom-up” nano-fabrication of the surface by controlling the molecular orientation and the rotation of the ligands.

![Fig. 3](image)

*Fig. 3.* (a) Typical STM image (30 × 30 nm²) and (b) a height-shaded plot of TPP/CRPc/CRPc molecular array formed on Au(111) obtained at 0.80 V vs. RHE in 0.05 M HClO₄. (c) Proposed structural model of an alternately arranged superstructure of in the adlayer of TPP/CRPc/CRPc. Reprinted with permission from reference 114, copyright © 2007 Wiley-VCH
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Host-guest interface using hydrogen bonding architectures. Several interesting nanoarrays were also found in UHV environment. Hydrogen bond-based network structures provide a potential pathway to the design of host-guest interfaces, because the cavity size can be controlled through careful selection of the component molecules. For example, the formation of a self-assembled bimolecular network through hydrogen bonds by co-adsorption of perylene tetra-carboxylic di-imide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) on Ag/Si(111)-(√3 × √3)R30° in UHV was reported by Theobald et al. [115]. The substrate, Ag deposited on Si(111), is one of the suitable surfaces for adsorption of organic molecules such as fullerenes, phthalocyanine, and naphthalene tetracarboxylic di-imide (NTCDI) in UHV environment, as those molecules diffuse freely on the deposited surface and form islands in which the order is predominantly governed by intermolecular interactions. The framework provides a regular array of identical nanoscale traps in which further deposited molecules nucleate cluster growth. Such network arrays could recognize selectively fullerenes C_{60} or C_{84} as guest molecules [115, 116] and it was demonstrated that the seven C_{60} molecules were included in a 2D open honeycomb network whereas three C_{84} molecules were trapped in the cavity. According to a recent study on adlayers composed of those components, a similar host-guest function was also found on Au(111) [117]. The bimolecular network consisting of melamine and PTCDI on Au(111) was formed by elevating the temperature (see Fig. 4a,b). Supramolecular traps of C_{60} molecules occurred at the template of the bimolecular network consisting of melamine and PTCDI. The cluster size of C_{60} depends upon the coverage of C_{60}. When the coverage is lower than 0.1 monolayers, an open hexamer is predominantly formed in the bimolecular network array, as shown in Fig. 4c. At higher coverage, the hexamers transform to heptamers and C_{60} molecules attach over the top of the bimolecular network through further C_{60} deposition (see Fig. 4d), as illustrated in Fig. 4e.

Reutt-Robey and coworkers reported that a unique supramolecular assembly of C_{60} on the adlayer of acridine-9-carboxylic acid (ACA) formed on Ag(111) in UHV [118, 119]. Because ACA molecules can form several adlayers depending on the coverage on Ag(111) [119], the adlayer structure of C_{60} in the supramolecular assembled layer is also dependent on the ACA adlayers. For example, when 0.65 ML of C_{60} is added to the ACA adlayer of the initial coverage of 0.3 ML, adlayers with chiral structures and linear arrangements of C_{60} were predominantly formed on Ag(111) as shown in Fig. 5a. Close-up views of C_{60} arrays on chiral and linear structures are shown in the high-resolution STM images of Fig. 5b,c. Each C_{60} molecule positions on the central portion of each ACA trimer in the chiral structure consisting of alternately arranged ACA trimers as a “pinwheel” shape (with the (2√21 × 2√21R ± 10.9°) symmetries), whereas C_{60} molecules are located on the linearly-arranged ACA adlayer. The subtle control of the coverage plays a significant role in the formation of supramolecular pattern.

It is a very attractive and effective method to use hydrogen bonding for two-dimensional networks or arrays of porphyrins at surfaces. For example, Lei et al. reported that highly ordered arrays of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (H_{2}TCP) and copper(II) 2,3,9,10,16,17,23,24-octakis(carboxyl)phthalocyanine (CuPc8C) were for-
med on HOPG by the coadsorption of stearic acid and 1-iodooctadecane, respectively, under ambient conditions [120]. Because 2D hydrogen bonds of porphyrin and Pc were stabilized by the presence of those alkane derivatives, the alkane derivatives contribute the minimization of surface free energy in a 2D system. Furthermore, as reported by Otsuki et al., 5,10-bis(4-carboxyphenyl)-15,20-bis(4-octadecyl-oxyphenyl)porphyrin was found to form dimer rows at the dichlorobenzene-HOPG interface, suggesting that the adlayer structure is determined by directional hydrogen-bonding interactions between nearest neighbor molecules [121].

In contrast, on Au(111), the supramolecular nanostructures composed of carboxyphenyl-substituted porphyrins can be precisely controlled by the conformation selective assembly [122]. Supramolecular assembly using porphyrin derivatives has also been investigated to potentially fabricate precisely-controlled molecular wires. Yokoyama and coworkers showed that selective aggregation of porphyrin derivatives are rationally controlled by tuning the dipole-dipole interactions between molecules [123]. They found that CN-substituted (3,5-di-t-butylphenyl)porphyrin derivative (TBPP) molecules could produce supramolecular aggregates such as trimers, tetramers, and one-dimensionally extended wire-like structures on Au(111) at low temperatures (63 K) in UHV. Dipole-dipole interactions between CN moieties is a key factor for molecular assembly of TBPP. A similar selective assembly was also formed by carboxyphenyl porphyrins [122]. A remarkable difference between CN- and COOH-moieties in TBPP derivatives is the variation of intermolecular interactions between porphyrin derivatives. For example, one-carboxyphenyl-substituted TBPP molecules form a dimer structure through hydrogen bonding between two molecules (see Fig. 6a), whereas one CN-substituted TBPP molecules arrange in clusters of trimers. The supramolecular selective assembly of 5,15-bis(4-carboxyphenyl)-10,20-bis(3,5-di-t-butylphenyl)porphyrin (trans-BCaTBPP) with a long, straight wire was found on the Au(111) surface by sequential hydrogen bonding between carboxyphenyl groups (see Fig. 6b), while the isolated supramolecular wires were formed by cyanophenyl-substituted TBPP molecules [123]. In the case of cis-BCaTBPP, the supramolecular assemblies depended upon the coverage. At low coverage, cis-BCaTBPP forms tetramers the same as cis-CN-substituted TBPP molecules, as shown in Fig. 6c. Increasing the coverage, the condensed structure of cis-BCaTBPP composed of a zigzag arrangement appeared on the Au surface. The supramolecular nanostructures on the surfaces can be precisely controlled by the conformation selective assembly. In addition, it was very recently reported that linear \( \text{C}_60 \) arrays were formed on the supramolecular assembled trans-BCaTBPP wires on Au(111) [124]. As reported by the same authors, trans-BCaTBPP forms linearly arrays on Au(111), as shown in Fig. 6d. However, linear arrays of opened nanopore structures consisting of trans-BCaTBPP molecules were formed, i.e. a lateral shift of the supramolecular wires which is accompanied by a partial change in the conformation of trans-BCaTBPP was caused by deposition of \( \text{C}_60 \) molecules. High-resolution STM images revealed that each \( \text{C}_60 \) molecule was located on the open...

**Fig. 5.** (a) Large-scale STM image of \( \text{C}_60 \) arrays on the ACA (coverage 0.75ML) adlayer on Ag(111). High-resolution STM images for (b and c) and (d and e) proposed models of \( \text{C}_60 \) arrays on chiral domain and linear domain, respectively. Reprinted with permission from reference 119, copyright © 2006 American Chemical Society.
nanopores, not on the center of each trans-BCaTBPP molecule (see Fig. 6e,f), suggesting that the opening of the nanopores results from the subtle balancing of substrate-molecule and molecule-molecule interactions.

Lin and coworkers reported the construction and control of various surface structures such as chirality, nano cavity, and network array by metal-organic coordination in UHV [44, 125-132]. They reported that terephthalic acid (TPA), 1,2,4-tricarboxylic benzoic acid (TMLA), 4,1',4',1''-terphenyl-1,4''-dicarboxylic acid (TDA) molecules easily undergo complexation with coadsorbed Fe [125, 126]. For example, a two-dimensional nanoporous network was formed on Cu(100) by the metal-organic coordination either between TPA and Fe or between TDA and Fe [125]. The tuning of 2D metal-organic networks using Fe and TPA or TDA is shown in STM images in Fig. 7a-c. An adlayer structure consisting of Fe and TPA was dependent upon the concentration of Fe, i.e. ladder-type structure with elongated cavities was dominantly formed on Cu(100) with a low concentration of Fe (Fig. 7a), whereas a trellis with a square unit cell and a cross-shaped cavity was found on complete 2D Fe-carboxylate reticulation (Fig. 7b). In the case of TDA, a higher analogue to networks obtained with TPA can provide the construction of 2D metal-organic coordination (Fig. 7c). Such network arrays composed of metal atoms and organic molecules could selectively recognize C₆₀ molecules as a guest molecule. As seen in the STM image shown in Fig. 7d, single C₆₀ (yellow spheres) could be linearly arranged on a ladder-type network with preferential occupation of available larger cavities (C₆₀ clusters are on areas with bare Cu substrate). The network cavities consisting of Fe and TPA accommodated single C₆₀ molecules, whereas either dimers or trimers of C₆₀ molecules were trapped in single cavities composed of Fe and TDA. This method has been applied to Co and TPA network formation on Au(111) [130, 131]. In addition, the symmetry of the evolving coordination networks is independent of the difference in metal substrate and in crystallographic orientation, which indicates that the metal-ligand coordination predominates over the substrate. The Co-coordination, which is rarely encountered in 3D metal-organic frameworks, is promoted on Cu(100) and Ag(111) by the strict confinement of a 2D environment [132]. Thus, selection of coordination metal, iron or cobalt, makes it possible to precisely control this kind of nanostructure.

**Fullerene and porphyrin supramolecular assembly.** It is known that porphyrins and fullerenes spontaneously attach to each other [25]. For example, MOEP and C₆₀ form a supramolecular assembly through the π-π interaction in cocrystallites with a ratio of 2 : 1 [133]. To control supramolecular assemblies between porphyrins and fullerenes during three-dimensional construction, layer-by-layer growth on metal surfaces must be used as a first step. Such a supramolecular assembly produced through π-π or donor-acceptor interaction would be useful for the design and organization of functional organic molecules on electrode surfaces. For example, individual CuPc molecules were observed on a highly ordered C₆₀ array formed on Au(111) in UHV [134]. Subsequently, we first reported a supramolecular assembled array of C₆₀ molecules on ZnOEP adlayer on Au(111) through a wet process, i.e. successive immersion into benzene solution containing ZnOEP and C₆₀ molecules and the adlayers were observed under the electrochemical environment [80]. As reported in several papers, the thin epitaxial film of C₆₀ on Au(111) was found to take two different close-packed structures, (2√3 × 2√3)R30° and the so-called “in-phase” (38 × 38), not only in UHV [135-137] but also in solution [138, 139]. The intermolecular distance between C₆₀ molecules was 1.0 nm in the adlayer of C₆₀ directly attached Au(111), whereas the intermolecular distances between the nearest neighbor C₆₀ molecules were found to be either 1.65 ± 0.07 or 1.40 ± 0.05 nm for directions of two molecular rows on the ZnOEP adlayer [80]. The adlayer structure of ZnOEP on Au(111) was identical to that of CoOEP on ZnOEP.
Au(111). The fact that the intermolecular distances between C₆₀ molecules are nearly equal to the distance between ZnOEP molecules indicates that each C₆₀ is located on the center above each ZnOEP molecule [50]. The identical structures of C₆₀ and C₇₀ were also observed on a NiOEP array formed on Au(111) [82]. However, the replacement reaction of the first adlayer of nickel(II) tetraphenylporphyrin (NiTPP) occurred upon adsorption of fullerene molecules as the second layer, suggesting that supramolecular assemblies of C₆₀ and C₇₀ are strongly influenced by the underlying layer of porphyrin, as shown in Fig. 8. The dependency on the underlying porphyrin layer for supramolecular assembly of fullerenes might be tentatively explained by the difference in interaction between porphyrin and fullerene. According to the density functional theoretical (DFT) calculation, the interaction energy between ZnTPP and C₆₀ was estimated to be -16 to -18 kcal.mol⁻¹ [140], whereas the interaction energy between ZnP and C₆₀ was -33.9 kcal.mol⁻¹ [141]. Because the adsorption energy of C₆₀ at the Au(111) surface is known to be 16~45 kcal.mol⁻¹ (average is approximately 31 kcal mol⁻¹) [142], this is consistent with the result of the displacement by C₆₀ at NiTPP layer on Au(111) during modification. It has been demonstrated that the stability of the first adlayer is an important factor in the surface design of host-guest selectivity of fullerenes on electrode surfaces [82].

Bonifazi et al. synthesized Zn²⁺ porphyrin derivatives 1 and 2 (see Chart 2) and investigated supramolecular assemblies of C₆₀ on 1 and 2 arrays formed on Ag single crystal surfaces in a UHV environment [143]. Such π-conjugated molecules with tunable electronic properties are building blocks for the construction of functional materials with exceptional electrochemical and photophysical properties. C₆₀ molecules located precisely on top of the 3-cyanophenyl substituents, in a zinc porphyrin derivative 1 array, form a chainlike structure on the zinc porphyrin derivative 1-modified Ag(100) surface have especially exceptional properties as shown in Fig. 9a. The lateral displacements of C₆₀ molecules resulted from the manipulation of the STM tip. The black circle denotes a C₆₀ molecule that vanished during the repositioning operation. As illustrated in the proposed model (Fig. 9b), C₆₀ molecules are located precisely on top of the 3-cyanophenyl substituents in porphyrinatozinc dimer array on Ag(100). In the case of 2, two segregated domains, such as (2√3 × 2√3)R30˚ and a condensed phase composed of 2 were found on Ag(111) with the deposition of 0.14 ML of C₆₀ onto 0.85 ML of 2. The

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**Fig. 7.** High-resolution STM images of TPA-Fe coordination networks on Cu(100); (a) ladder-type structures with two distinct types of nanocavities (marked by A and B), where not all available carboxylate groups are involved in coordination bonding and (b) fully interconnected network with complete 2D reticulation, giving rise to square cavities (marked by C). (c) High-resolution STM image of 2D reticulated Fe-TDA open network with rectangular nanocavities. (d) High-resolution STM image of adsorption of single C₆₀ in Fe-TPA host networks. Inset: C₆₀-monomer accommodation in cavities of type-C network. (e-g) top-view models for C₆₀ adsorption in the cavities encountered in (d) with molecules drawn to scale. Reprinted with permission from reference 125, copyright © 2004 Nature Publishing Group

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**Chart 2.** Chemical formulae of Zn²⁺ porphyrin derivatives 1 and 2
unprecedented molecular assembly of 2 and C_{60} was caused by thermal annealing (453 K). The 2 adlayer recognizes the formation of hybrid 2-C_{60} assembly with a C_{60} paired line pattern as the main phase. The C_{60} molecules were arranged in vertically aligned pairs (intrapair C_{60}-C_{60} distance of 2.3 nm) with an intermolecular distance of about 6.0 nm, whereas the paired line pattern was repeated every 7.3 nm in the horizontal direction (see Fig. 9c). Thus, supramolecular assembly of C_{60} also depends on chemical structures in the underlying porphyrin layer or the crystallographic orientation of metal substrates [143].

The control of the supramolecular assembly of fullerenes has been extended to another system. Mena-Osteritz et al. synthesized macrocyclic oligothiophenes, C[12]T [144], and reported that a self-assembled adlayer of C[12]T on HOPG can be used as a veritable template to epitaxially grow 3D nanoarchitectures with C_{60} [145]. STM images allowed the investigation of unique 1:1 donor-acceptor complexes comprising a ring-shaped p-type and a spherical n-type semiconductor, under ambient conditions at room temperature. The electronic properties of the complexes were elucidated by means of scanning tunneling spectroscopy (STS), which showed interesting saturation behavior in the I-V curves [145].

We found that supramolecularly assembled layers of C_{60} were formed on both coronene- and perylene-modified Au(111) surfaces [146]. As reported in our previous papers, coronene formed a highly ordered array having a (4 × 4) symmetry on Au(111) [147, 148]. The adlayer structure of the C_{60} was found to be strongly influenced by the underlying organic layers, suggesting that the latter underlying organic adlayers play an important role in the process of the formation of the C_{60} molecular adlayer. The all-carbon (C_{2m}-C_{2n} type) fullerene dimers such as C_{60}C_{70} (C_{131}) molecules also formed a stable honeycomb-like array on the coronene-modified Au(111) surface, suggesting that the insertion of one C atom between C_{60} and C_{70} cages can alter the adsorption site of each cage. [149]. Epitaxial molecular assemblies for other fullerenes such as C_{50}, C_{46}C_{60} dumbbell-dimer (C_{120}), and C_{60}C_{70} cross-dimer (C_{130}) were also found on the coronene-modified Au(111) surface. The details of this experiment were reported in a separate paper [150].
Dendritic molecules appended with multiple zinc porphyrin units (DP$_m$; number of Zn$^{II}$ porphyrin moiety) and bipyridine compounds carrying multiple fullerene units (Py$_2$F$_n$; number of C$_{60}$ units) were synthesized by Aida and coworkers (see Chart 3) [151]. Such segregated arrays of multiple donor and acceptor units using a dendritic scaffold indicate a photoinduced charge separation. Some of the coordination complexes between DP$_m$ and Py$_2$F$_n$ were visualized by STM under UHV conditions. For example, DP$_{12}$ molecules were clearly observed as petal-like patterns with a uniform diameter of 7 nm, as shown in Fig. 10a, when a CHCl$_3$ solution containing DP$_{12}$ and Py$_2$F$_3$ was deposited on a Au(111) surface by pulse injection. High-resolution STM images also exhibited many bright spots at the periphery of DP$_{12}$ molecules, which are most likely fullerene clusters of Py$_2$F$_3$ (Fig. 10b). The pulse injection method has been already established for observing structures of supramolecular assemblies under UHV conditions at liquid nitrogen temperature. Several UHV-STM studies on covalently linked multi-porphyrins formed on Cu(100) have already been reported [152,153]. An interesting ferrocene-bridged zinc porphyrin macrocycle was synthesized by Shoji et al. [154]. This group succeeded in visualizing the single molecule of a supramolecular coordination assembly on Au(111) in UHV [155].

Control of molecular orientation of functionalized fullerenes. The approach of supramolecular assembly consisting of fullerene and MOEP is more effective for control of molecular orientation of asymmetrical functional fullerenes [50, 156, 157]. For example, open-cage fullerenes are attractive and important molecules for synthesis of a new endohedral fullerene encapsulating molecular hydrogen. Recently, Komatsu’s group succeeded in preparing H$_2$@C$_{60}$ and its dimer (H$_2$@C$_{60}$)$_2$ by a strategy of ‘molecular surgery’ in which the fullerene cage is opened and closed after insertion of H$_2$ gas [158, 159]. Subsequently, H$_2$@C$_{70}$ and 2H$_2$@C$_{70}$ molecules were also synthesized by the same method [160]. Because the open-cage fullerene derivative 3 (see Chart 4) has two carbonyl moieties, the electrochemical redox reaction is expected to be useful as a monitor reaction of the modified electrode surface. Figure 11a shows typical cyclic CVs of a well-defined Au(111) (dotted line) and 3 directly attached on a Au(111) electrode (red solid line) in 0.05 M H$_2$SO$_4$, recorded at a scan rate of 20 mV s$^{-1}$. For the Au(111) electrode directly modified with 3, broad redox peaks were observed at 0 and 0.85 V. In contrast, when the modification by ZnOEP was carried out before the adsorption of 3, a pair of characteristic redox peaks clearly appeared at 0 and 0.85 V during cathodic
and anodic scans, respectively. This result suggests that 3 was attached to the ZnOEP-modified Au(111) surface, and that carbonyl groups of 3 were oriented toward the solution phase. The CV profile drawn with a solid red line in Fig. 11a is strongly associated with the electrochemical redox reaction of >C=O to >C•-OH (and >C•-OH to >C=O) for two carbonyl groups in each molecule of 3. On the basis of the electronic charge calculated from the reductive peak area, the amount of transferred electronic charge is estimated to be ca. 15.8 μC.cm⁻². If two-electron reduction occurs on the 3/ZnOEP-modified Au(111) electrode, the value corresponds to the surface concentration of $(7.9 \pm 0.7) \times 10^{-11}$ mol.cm⁻². The electron transfer process is very slow as indicated by the CV profile shown in Fig. 11a. When potential switching was carried out at potentials negative than 0.85 V, no reduction peak at 0 V was observed. The STM image showed a completely disordered structure of 3 directly attached to the surface of Au(111), whereas highly-ordered arrays consisting of bright round spots were found on the ZnOEP-modified Au(111), as shown in Fig. 11b [50, 156]. This result suggests that the formation of a highly ordered adlayer of 3 plays a significant role in the control of molecular orientation. The adlayer structure of 3 on the ZnOEP-modified Au(111) surface was identical to that of C₆₀ on the Au(111) surface covered with highly ordered ZnOEP arrays.

Furthermore, dependency upon the adlayer structures of ZnOEP was found on reconstructed Au(100)-(hex) and unreconstructed Au(100)-(1 × 1) surfaces [157]. A hexagonally arranged ZnOEP array was formed on a Au(100)-(hex) surface, whereas a rectangularly arranged ZnOEP array was found on a Au(100)-(1 × 1) surface. The adlayer structure of ZnOEP was dependent upon the underlying Au atomic

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**Chart 4.** Chemical structures of open-cage C₆₀ and C₆₀Fc derivatives 3 and 4.
arrangements [157]. The voltammetric responses for the 3 on the ZnOEP-modified Au(100)-(hex) surface were similar to that on the ZnOEP-modified Au(111) surface, as shown in Fig. 11c. On the basis of the electronic charge calculated from the reductive peak area, the amount of transferred electronic charge was estimated to be ca. 16.2 μC.cm⁻², which is a similar value obtained at Au(111) electrode. For the 3 on the ZnOEP-modified Au(100)-(1 × 1) electrode, a pair of broad reduction and re-oxidation peaks was observed during the scan (Fig. 11e). Redox peak currents were smaller than those obtained at the reconstructed Au(100)-(hex) surface, suggesting that the molecular orientation of 3 was random on the ZnOEP-modified Au(100)-(1 × 1) surface. This difference in cyclic voltammograms is clearly reflected in STM images for the modified electrodes. Figure 11d shows a typical STM image of an adlayer of 3 formed on ZnOEP-modified Au(100)-(hex) in 0.05 M H₂SO₄. Highly ordered arrays consisting of bright round spots were observed over the entire surface of Au(100)-(hex). In contrast, a completely disordered structure was observed for the adlayer of 3 on the ZnOEP-modified Au(100)-(1 × 1) surface, as shown in Fig. 11f. Although several individual molecules of 3 could be distinguished under the present conditions, the ZnOEP-modified Au(100)-(1 × 1) surface was largely covered with aggregates of 3, as can be seen. These results indicate that the carbonyl groups of 3 were oriented toward the solution phase on the ZnOEP-modified Au(100)-(hex) surface because of the formation of a 1:1 supramolecular assembly with highly ordered ZnOEP arrays. When a polycrystalline Au electrode, such as a disk or a wire, was used as a substrate, the redox reaction was not evident even on the 3/ZnOEP system. This finding suggests that precise control of underlying ZnOEP adlayer structures with Au atomic structure is important to recognize the 3 present on them [157]. The clear enhanced redox peaks in the CV profile at the 3/ZnOEP-modified Au(111) and Au(100)-(hex) electrodes strongly support the conclusion that the orientation of 3 is controlled by the ZnOEP adlayer.

**Effect of central metal ions.** The supramolecular modification is also effective for control of the electron transfer reaction of ferrocene-linked fullerene (C₆₀Fc), 4 (see Chart 4) [161]. Because ferrocene is a typical redox species, it is a promising material for an electrochemical switching or sensing device. We investigated OEPs with several metals such as CoOEP, CuOEP, PdOEP, carbon FeClOEP and monoxide-coordinated Ru(CO)OEP as an underlying adsorbed layer. Figure 12a-f shows CVs of 4 on each MOEP-modified Au(111) electrode. Judging from the oxidative peak area, we calculated the electronic charges consumed during the oxidation. The electronic charge of redox reaction of ferrocene moiety on each adlayer is summarized in Table 1. The electronic charge of CuOEP consumed by the oxidation reaction of Fe to Fc²⁺ was estimated to be slightly lower than that of CoOEP, ZnOEP, and PdOEP. Furthermore, when FeClOEP and Ru(CO)OEP were used as an underlying adsorbed layer, different CVs were clearly obtained, as shown in Fig. 12e,f. The electrochemical response of the Fe moiety was poor at FeClOEP- and Ru(CO)OEP-modified Au(111) electrode, i.e., the redox peak currents observed around 0.80 V for these two adlayers were much smaller than those of ZnOEP-, CoOEP-, CuOEP- and PdOEP-modified Au(111) electrodes. These results for the FeClOEP- and Ru(CO)OEP-modified Au(111) electrode suggest that the surface was not fully covered with 4 molecules. Such metal ion dependence was found in the investigation of affinity between metalloporphyrin cyclic dimer and fullerene. According to a paper by Aida and coworkers, the association constants, \( K_{\text{assoc}} \) values for metalloporphyrin cyclic dimer of Co and Zn ions were greater than \( 10^7 \) M⁻¹, whereas the other three host molecules with other metal ions such as Ni, Cu, and Ag were inferior to the above host molecules \( (K_{\text{assoc}} < 10^7 \) M⁻¹) [162]. Recently, DFT calculations for other central metal ions were also reported by Basiuk [141]. DFT calculations for supramolecular interactions between metalloporphyrin and \( C_{60} \) showed that the interaction energy is strongly influenced by central metal ions. The decrease in the HOMO-LUMO gap energy of porphyrin framework is estimated to be found by supramolecular assembly of \( C_{60} \), as shown in Fig. 13. Although the electronic property of MOEP layers might also be affected by a gold surface, the difference in the HOMO-LUMO gap energy depending upon the central metal ions might be explained by the difference in electronic charge (or peak current) from the redox reaction of the Fc moiety.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ZnOEP</th>
<th>CoOEP</th>
<th>CuOEP</th>
<th>PdOEP</th>
<th>FeClOEP</th>
<th>Ru(CO)OEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q (μC.cm⁻²)</td>
<td>8.0</td>
<td>6.1</td>
<td>4.8</td>
<td>6.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Orientation of C₆₀Fc</td>
<td>ordered</td>
<td>ordered</td>
<td>ordered</td>
<td>ordered</td>
<td>disordered</td>
<td>disordered</td>
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Table 1. Electronic charge calculated from the oxidative peak area and \( C_{60} \)Fc adlayers based on the STM observation for each MOEP layer.
To understand the details of the interfacial phenomena, STM measurements were carried out in 0.1 M HClO\(_4\) for each case [161]. Hexagonal molecular packing arrangements were clearly observed by the same procedure for six different metal-coordinated OEPs (see Fig. 12g-l). Figure 12m-r shows typical STM images of the 4 arrays formed on ZnOEP-, CoOEP-, CuOEP-, PdOEP-, FeClOEP- and Ru(CO)OEP-modified Au(111) surfaces, respectively. As can be seen in Fig. 12g,p, 4 molecules were hexagonally arranged. Adlattices of 4 on the ZnOEP, CoOEP, CuOEP and PdOEP adlayers were almost identical to C\(_{60}\) on the ZnOEP adlayer. In contrast, Figure 12q,r shows typical large-scale STM images of 4 array on the FeClOEP- and Ru(CO)OEP-modified Au(111) surfaces. Although some ordered areas are visible, the entire surface was rough. Thus, the axial coordination of Cl and CO is likely to significantly affect the fullerene and porphyrin supramolecular assembly on metal surfaces, indicating that the coordination ligand in OEP faces the solution phase, in contrast with the Au(111) surface. The effect of the central metal ion in OEP on the formation of supramolecular assemblies with the 4 molecule was clearly demonstrated in the CV profiles and STM images. The same tendency was also found at supramolecular assembled layers with 3 [163]. Thus, based on the electrochemical results, MOEP adlayer plays an important role in not only suppression of the oxidative desorption of C\(_{60}\) but also the control of orientation of the C\(_{60}\) derivatives, because the fullerenes can be trapped in the “cup” consisting of ethyl moieties in the OEP scaffold.

**Nanoapplications.** Fullerenes are often used as a model compound for the manipulation (guest molecule) of surface-supported supramolecular two-dimensional arrays both in UHV and in solution. Heckl’s group found that trimesic acid (TMA) forms two different structures on HOPG, a honeycomb lattice in the connection between the hexagons (cyclic hexamers) and a flower-like motif through hydrogen bonding between three TMA molecules between neighboring rings in UHV [164] and at the solid-liquid interface [165]. According to their study, it was found that the honeycomb lattice structures, whether hexagons or flower-like motif, were strongly influenced by organic solvents such as butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid and nonanoic acid [165]. Adlayer structures of TMA on HOPG surface depended on the solvent. Such cyclic hexamers stabilized by hydrogen bonding between three TMA molecules between neighboring rings in UHV [164] and at the solid-liquid interface [165]. According to their study, it was found that the honeycomb lattice structures, whether hexagons or flower-like motif, were strongly influenced by organic solvents such as butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid and nonanoic acid [165]. Adlayer structures of TMA on HOPG surface depended on the solvent. Such cyclic hexamers stabilized by hydrogen bonding among TMA molecules could act as a host network structure for guest molecules such as coronene [166] and C\(_{60}\) molecules [167]. In manipulation experiments with C\(_{60}\) molecules as a guest in the chicken wire structure,
the transfer from one cavity to an adjacent cavity was demonstrated.

Spillmann et al. reported that 2 molecules dominantly formed a hexagonal pattern by trimer formation, when 0.5-0.7 MLs of porphyrin 2 was deposited on Ag(111) [168]. Since the 3-cyanophenyl residues and the central porphyrin core hardly contribute to the tunneling current, each single porphyrin molecule appears as two bright lobes separated by 1.20 nm, which is consistent with the intramolecular distance between the 3,5-di(tert-butyl)phenyl substituents (center-to-center distance: 1.26 nm) in the crystal structure of 2. As reported by Yokoyama et al., it is suggested that the molecular assembly is driven by both van der Waals and dipole-dipole interactions involving the polar 3-cyanophenyl residues [123]. After further deposition of C₆₀ molecules, a lateral displacement of the C₆₀ molecules on the porphyrin network was found in the time-dependent STM images, as shown in Fig. 14a-c. To minimize the influence of the tip on the hopping process, all STM images were recorded under the condition of a high tunneling gap resistance (>100 GΩ). Driven by thermal fluctuations, single C₆₀ ad-molecules displace to neighboring pores as time proceeds. Furthermore, the conformational motion of the 3,5-di(tert-butyl)phenyl moieties in the porous network and self-repairing of a defect in the porous structure of 2 (dashed ellipse) were also found in those STM images. The same group subsequently reported the difference in mobility of single fullerene molecules between C₆₀ and C₇₀ [169]. The hopping rate of C₆₀ was $1 \times 10^{-3}$ s⁻¹ at coverage of 0.06, whereas that of C₇₀ was $9 \times 10^{-2}$ s⁻¹ at coverage of 0.01. The hopping rate also depends upon the coverage of fullerene on the porphyrin network.
Shirai et al. synthesized unique and attractive molecules, the so-called “nanocars” molecules consisting of an oligo(phenyleneethylenephenylene) “chassis” supporting four C_{60}-derived “wheels” (see Fig. 15a,b) [170, 171]. The motion of the “nanocar” depended upon the temperature. The “nanocar” remained effectively stationary on the surface at room temperature up to approximately 170 °C. The pivoting and translational motions of 5 were observed on a Au(111) terrace at approximately 200 °C, as seen in a sequence of STM images in Fig. 15c-f. The translational motion that occurred between pivoting was perpendicular to the axles, illustrating a directional preference relative to the molecular orientation. The observed movement of the nanocars indicated a new type of wheel-like rolling motion based on fullerene, as opposed to stick-slip or sliding translation. These molecules which include ‘nanotrails’ and ‘nanotrucks’ are promising materials for assisted small molecule transport across surfaces. Further investigations are expected for the development of attractive molecular motions.

**SUMMARY AND OUTLOOK**

This minireview primarily reported self-organization and supramolecular assembly of porphyrins, phthalocyanines, and fullerenes at surfaces using STM. The understanding of both intermolecular and molecule-substrate interactions in two-dimensionally self-organized films at the molecular level in UHV as well as in solution has been advanced considerably by the use of STM techniques in the past decade. The ‘bottom-up’ strategy is an attractive and promising approach for construction of nanoarchitectures. The understanding and the construction of the surface-supported supramolecular assembly have provided knowledge necessary for new surface design and patterning using characteristic molecular assemblies by non-covalent intermolecular interactions, such as dipole-dipole interactions, hydrogen bonding, electrostatic interactions, metal-ligand coordination and π-π interactions. To produce new functional materials and molecular devices based on the above knowledge, it is necessary to continue further exploration of the nanostructures at surfaces and the design of attractive molecules by organic synthesis in the future. However, as a next step, it is important to demonstrate a special function such as catalysis, photo-induced electron transfer, and conductivity (or hole-mobility) from the formation of nanostructures. The demonstration of the special functions by the formation of nanostructures must provide a “breakthrough” to the next stage of the ‘bottom up’ strategy.
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REFERENCES

3710.
148. Shi et al., unpublished results.