TOPICAL REVIEW

Paradigm shift from self-assembly to commanded assembly of functional materials: recent examples in porphyrin/fullerene supramolecular systems

Mao Li¹, Shinsuke Ishihara¹,², Qingmin Ji¹, Misaho Akada¹, Jonathan P Hill¹,² and Katsuhiko Ariga¹,²

¹ World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan
² Japan Science and Technology Agency, CREST, 1-1 Namiki, Tsukuba 305-0044, Japan

E-mail: LI.Mao@nims.go.jp and ARIGA.Katsuhiko@nims.go.jp

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Abstract
Current nanotechnology based on top-down nanofabrication may encounter a variety of drawbacks in the near future so that development of alternative methods, including the so-called bottom-up approach, has attracted considerable attention. However, the bottom-up strategy, which often relies on spontaneous self-assembly, might be inefficient in the development of the requisite functional materials and systems. Therefore, assembly processes controlled by external stimuli might be a plausible strategy for the development of bottom-up nanotechnology. In this review, we demonstrate a paradigm shift from self-assembly to commanded assembly by describing several examples of assemblies of typical functional molecules, i.e. porphyrins and fullerenes. In the first section, we describe recent progress in the design and study of self-assembled and co-assembled supramolecular architectures of porphyrins and fullerenes. Then, we show examples of assembly induced by external stimuli. We emphasize the paradigm shift from self-assembly to commanded assembly by describing the recently developed electrochemical-coupling layer-by-layer (ECC-LbL) methodology.

Keywords: self-assembly, commanded assembly, porphyrin, fullerene, layer-by-layer assembly

1. Introduction
Considerable advances in micro- and nanotechnologies have assisted creation of various miniature devices. Most successful devices rely on sophisticated fabrication involving ‘hard’ inorganic materials and top-down approaches for preparation of micro/nano systems from macroscopic objects. However, the current rate of miniaturization, which is expected to be governed by the so-called Moore’s law of top-down nanotechnology, will be slowed down quite soon due to the physical limits of device dimensions imposed by ultraviolet, electron/ion beam and soft x-ray lithographic techniques [¹, ²]. Therefore, development of alternative approaches, i.e. bottom-up approaches, has...
attracted considerable recent attention. These approaches rely heavily on spontaneous processes of self-assembly and/or self-organization [3–7].

The success of the bottom-up approach based on self-assembly might be indicated if we consider the bottom-up processes in biological systems. Evolution of the highly sophisticated structures contained in living creatures was initiated billions of years ago and is continuously developing. We know that the functions observed in biological systems possess excellent efficiencies and specificities. Highly evolved assemblies of various component molecules achieve advanced functionalities based on integrated actions. Therefore, some people believe that synthesis of bio-like assembled structures could become the ultimate strategy for nanotechnology.

For our part, we have undertaken a variety of research projects on self-assembly and made several findings in nanomaterial syntheses using self-assembled structures [8–10] and stimuli-responsive systems and materials [11–14]. However, only a few of them have so far resulted in practical technological development. Scientific accomplishments regarding self-assembly lag far behind those that have been evolved in nature. Spontaneous self-assemblies in biological systems are often surprisingly efficient and result in highly sophisticated functions that are difficult to mimic. Thus, the technology of artificial self-assembly is so far significantly inferior to that of biology. We suppose that strategies relying only on spontaneous self-assembly in synthetic systems might not be useful for developing functional materials and systems. One needs to add points of control to self-assembly processes to create potentially applicable technologies. Self-assembly controlled by commands from external stimuli could be a plausible strategy for the future of bottom-up nanotechnology.

In this review, we propose a paradigm shift from self-assembly to commanded assembly through several examples of assemblies of the archetypical functional molecules porphyrin and fullerene. Porphyrin and fullerene were selected for several reasons. They are both typical shape-defined molecular units, i.e. porphyrin is a planar molecule while fullerene is spherical. These molecules can be easily characterized by molecular-level analysis techniques such as scanning probe microscopy (SPM). While porphyrin is a typical electron donor, fullerene is an electron acceptor. Therefore, assembly of porphyrin and fullerenes in well-controlled nanostructures can create novel functional systems based on photoinduced electron transfer, which is a highly important subject in solar energy conversion.

Photoinduced electron transfer is the fundamental basis of photochemical reactions such as those observed in energy conversion, catalytic, photosynthetic, and biological systems [15–17]. Photophysics and photochemistry of excited states in organic molecules have provided a synthetic approach to a deeper understanding of solar energy conversion in green plants and is expected to aid the development of new technologies to address global energy demands and environmental issues [18–20]. Mimicking natural photophysical processes, improvement of electron transfer efficiency through chemical modification of a variety of compounds is an attractive area of research. Inspired by natural photosynthetic reaction centers, which contain chlorophyll dyes as electron donors and quinones as electron acceptors, the three-dimensional (3D) electron-accepting fullerenes in combination with porphyrins are undoubtedly among the most popular artificial building blocks; they have been used for electron transfer studies in supramolecular systems owing to their rich electron transfer processes and distinguishing electronic properties [21–25].

This review article highlights the recent progress made in the design and study of self-assembled and co-assembled supramolecular architectures of porphyrin and fullerene. In the first part, we discuss supramolecular self-assembly through \( \pi-\pi \) stacking interactions, hydrogen bonding, metal-mediated coordination, and electrostatic attractions for control of their structure. In the latter part, we show examples of commanded assembly induced by external stimuli, to demonstrate the paradigm shift from self-assembly to commanded assembly.

2. Single-component self-assembly

2.1. Porphyrin assembly

Owing to their panel-like shape that facilitates stacking or pinning together and their ease of synthesis and flexible design of chromophore structure and properties, porphyrins have long been regarded as attractive building blocks for organic nanostructures including 1D, 2D and 3D, on-substrate, polymeric, and on-nanoparticle constructions [26–29].

Self-assembled 2D structures of porphyrin derivatives have been a prime target for observations by SPM, including scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Rojas et al observed that molecules of 2H-tetraphenylporphyrin (2H-TPP) form a 2D network on Ag(111), driven by attractive intermolecular interactions [30], while the surface migration barriers are comparatively small and charge transfer to the adsorbed molecules is minimal. On the contrary, a significant charge transfer is observed in 2H-TPP/Cu(111), resulting in repulsive forces between the molecules that prevent the formation of a molecular adlayer network. It was shown that the limiting factor in the formation of self-assembled networks is the nature of frontier orbital overlap and adsorbate-interface electron transfer. Schwab et al fabricated nanorods with a diameter of 3.8 ± 0.3 nm and a length of 0.8 ± 0.4 \( \mu m \) by aggregation of the diacid form of tetrakis(4-sulfonatophenyl)porphine (TPPS) in acidic aqueous solutions on hydrophilic (mica) and hydrophobic (polystyrene and graphite) substrates [31]. Hu et al developed an effective and facile method for self-assembling porphyrin molecules into hollow hexagonal nanoprisms with uniform size and shape and controllable aspect ratio [32].

Hill et al completed an analysis of 2D structures of a porphyrin derivative (figure 1) [33], which result in a hatch-like structure with linear arrays of the molecules arranged approximately orthogonally under the strong influence of hydrogen bonding interactions involving phenolic protons and porphyrin imino nitrogen atoms. Hydrogen bonding interactions are also responsible for the surface...
adsorbed structures with modulation by the underlying substrate lattice. At submonolayer substrate coverage, the molecules exhibit a variety of structural motifs. There is a tendency toward the formation of cyclic trimeric species through hydrogen bonding, which are surface-mobile and can act as precursors in the formation of a Kagomé 2D porous network structure. However, more than one trimer unit structure is possible because of the asymmetry of the molecular conformation so that self-assembly of this unit into extended structures is interrupted. Both macrocyclic and ring-open forms of the trimer are commonly observed. Hill et al also described an unusual ‘mixed’ conformation of tetraphenylporphyrin in a 2D crystal lattice mismatch of tetraphenylporphyrin molecules [34].

Otsuki et al reported monolayer arrays of a series of meso-tetra-substituted porphyrins containing octadecyloxy and carboxyl (or pyridyl) groups on a highly oriented pyrolytic graphite (HOPG) surface at the liquid/solid interface [35]. Various patterns determined by the intricate interplay between directional hydrogen bonding interactions and packing forces, including molecule–molecule and molecule-substrate interactions, demonstrated the possibility of programmed surface patterning using porphyrins incorporating directional intermolecular interaction sites. Nishiyama et al investigated the sequential hydrogen bonding layer-by-layer (LbL) assembly of carboxyphenyl-substituted porphyrin on Au(111) by low-temperature STM [36]. This method enabled the rational design and construction of a wide range of thin-film structures, as well as control of electronic properties.

Formation of porphyrin 3D structures through self-assembly processes has also been investigated. Indelli et al implemented the self-assembly of new molecular boxes based on 2 + 2 porphyrin metallacycles and ditopic chromophoric units using N,N’-dipyridyl perylene bisimides to give two discrete multichromophoric self-assembled structures with high stability [37]. Wang et al reported the first synthesis of porphyrin nanotubes using ionic self-assembly of two oppositely charged porphyrins in aqueous solution [38]. A significant advantage of the ionic self-assembly approach is the ability to vary molecular subunits (tectons) to introduce desired functionality. They also demonstrated that other synthetic approaches can yield porphyrin nanostructures by ionic self-assembly [39]. Specifically, phase-transfer reactions are used to generate porphyrin nanofiber bundles by the phase-transfer ionic self-assembly of water-soluble porphyrins with water-insoluble porphyrins. Hoeben et al investigated assembled structures of oligo(p-phenylene vinylene) (OPV)-appended porphyrins containing all trans-vinylene (either hydrophilic or lipophilic) or amide linkages.
Various self-assembling motifs of porphyrin-related compounds with polymer, dendrimer and nanoparticle. (lipophilic) in supramolecular arrangements. They presented a way to achieve the required degree of organization and so guarantee that subsequent excitation transfer steps occur with high efficiency.

Polymers and nanoparticles provide a self-assembly medium for porphyrin-related compounds in various assembly motifs as exemplified in figure 2. Verma et al demonstrated charge-carrier generation in the exciton-coupled charge-transfer complex between J-aggregates of 5,10,15-triphenyl-20-(3,4-dihydroxyphenyl) porphyrin and surface of TiO$_2$ nanoparticles. The large exciton binding energy and ultrafast exciton decay processes (about 200 fs) are the limiting factors for the exciton-harvesting route. In such systems, the coupling strength dictates the conversion efficiency of charge-neutral exciton states to charge-separated states. The exciton dissociation at the interface is increased through the strong binding energy (catechol-TiO$_2$), and thus strong coupling promotes electron transfer (< 80 fs) at the interface. Saito et al developed strategies for single-walled carbon nanotube (SWNT) separation as useful nanoscale building blocks. Long-lived charge-separated states are attained upon photoexcitation of the supramolecular nanohybrids. This method opens a new strategy toward the extraction of large-diameter SWNTs without destruction of the π-conjugated system within SWNTs and the development of efficient light energy conversion.

2.2. Fullerene assembly

Fullerene is a spherical molecule possessing high electron-affinity, low reorganization energy in the electron-transfer processes, long-lived charge-separated states, and high carrier mobility. Construction of shape-defined fullerene assemblies could lead to developments of dimensional and confinement materials in composites for photoconversion processes.

Nakanishi et al reported formation of 1D arrays of fullerene derivatives. This example demonstrates the possibility of self-assembling nanowires in a predictable way by using tailored fullerenes. The formation of a planar array of 1D structures, epitaxially oriented along the HOPG lattice by fullerene derivatives bearing long alkyl chains, has been confirmed. The distance between adjacent nanowires can be regulated at the nanometer scale by the molecular design. The fullerene nanowires were grown by a simple process, i.e. spin-coating of chloroform solutions of the alkylated fullerene derivatives onto freshly cleaved HOPG. The C$_{60}$ moieties are organized in a zigzag fashion within the lamellae and the spacing between lamellae is determined by the alkyl chain length. The C$_{60}$ moieties are electroactive, opening the way to address individual C$_{60}$ molecules and to investigate the conductivity of individual (polymerized) nanowires.

One of the pioneering examples of fullerene 3D assemblies was demonstrated by Zhou et al who reported formation of bilayer vesicle structures composed entirely of fullerene derivatives. A fullerene penta-substituted with phenyl rings possesses a stable cyclopentadienide anion that converts the highly hydrophobic fullerene into an amphiphile. The potassium salt of the pentaphenyl fullerene in water formed stable spherical vesicles with an average hydrodynamic radius and a radius of gyration of about 17 nm. Rigid and well-defined structures of the hydrophobic moiety may lead to well-controlled design of vesicular structures. The relatively non-toxic nature of modified fullerene might be advantageous for applications in drug delivery systems. As Nakanishi et al demonstrated,
self-assembly of alkyl-tail-attached fullerene derivatives in various solvents gives nanofibers, nanosheets, spheres, or flower-like nano-objects [55–58]. Fulleropyrrolidines functionalized with multi(alkyloxy)phenyl groups exhibit thermotropic polymorphism and were investigated for their high carrier mobilities [59]. These materials showed an electron mobility of $\sim 3 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ in their highly ordered, compactly packed mesophase.

So far, shape control of nanostructures has been achieved by using the three fundamental strategies of crystallization/precipitation, template synthesis, and amphiphilic assembly. Although approaches based on amphiphilic self-assembly often require attachment of large functionless groups, the crystallization method of micro-object formation through precipitation from solution utilizes pristine C$_{60}$ molecules. The crystallization and precipitation from appropriate solvents and/or at an interface could be the most promising method for the formation of crystals with well-defined shapes of pristine fullerene components. This strategy has been used for shape-defined fullerene assembly as seen in the formation of fullerene nanowhiskers [60–62]. As shown in figure 5, interfacial precipitation of C$_{60}$ by the addition of poor solvents into C$_{60}$ saturated solutions provides various morphologies of 2D crystals of C$_{60}$ [63, 64]. The results demonstrate controlled formation of 2D nanosheets of various shapes (hexagons, rhombi, and mixed polygons)—all from pristine C$_{60}$ molecules—by a very simple solvent treatment. In addition, a water-triggered shape change is observed from 2D nanosheets to 1D nanostructures by treatment with water. This technically innovative concept represents a new methodology for fullerene-based bottom-up nanotechnology.

3. Multicomponent self-assembly

Supramolecular structures consisting of fullerene (C$_{60}$) and porphyrin subunits are particularly attractive for the fabrication of functional nanomaterials, given the potential light-harvesting and photoinduced electron transfer properties of their constituents [65–68]. Only utilization of the functions of both components, porphyrin (electron-donor) and fullerene (electron-acceptor), might enable us to construct materials and systems for efficient photoelectron conversion. Therefore, co-assembly of porphyrin and fullerene units within the same nanostructures is a crucial step for advanced functionalities. Multicomponent self-assembly has been investigated through various molecular interactions.

3.1. Molecular assembly

Weak interactions such as van der Waals interactions are commonly used for the formation of assembled structures. Fathalla et al designed and constructed a novel water-soluble porphyrin–fullerene C$_{60}$ nanorod by the self-assembly of pristine C$_{60}$ and a double-sided porphyrin projecting four β-cyclodextrins from each face (figure 6) [69]. β-Cyclodextrin moieties encapsulate pristine C$_{60}$ in a 2 : 1 stoichiometry, yielding nanorods both in solution and solid state. Zhou et al fabricated supramolecular columnar liquid crystals composed of porphyrin and fullerene, which attained a highly ordered homeotropic alignment by simple thermal annealing [70] (figure 7). It was suggested that C$_{60}$ is sandwiched between two porphyrin cores due to the strong donor–acceptor interactions, and that the dominant factors for achieving large-area uniform homeotropic alignment are the film thickness and cooling rate from the melt. Homeotropically aligned columnar phases are expected to provide an efficient electron/ hole transport pathway along the column. This conceptual demonstration provided an insight into fabrication of defect-free large-area blended
Figure 6. Formation of porphyrin–fullerene nanorods by self-assembly of pristine C$_{60}$ and a double-sided porphyrin projecting β-cyclodextrins.

Figure 7. Formation of a supramolecular columnar liquid crystal composed of porphyrin and fullerene.

thin films with directed molecular arrangement. Hasobe et al constructed fullerene-encapsulated hexagonal porphyrin nanorods [71, 72] (figure 8). These nanorods, composed of fullerenes (C$_{60}$, C$_{60}$ derivatives and C$_{70}$) and zinc meso-tetra(4-pyridyl)porphyrin [ZnP(Py)$_4$], are formed with the aid of a surfactant, cetyltrimethylammonium bromide (CTAB), in a dimethylformamide/acetonitrile mixture. Fullerene-ZnP(Py)$_4$ rod-modified electrodes exhibited efficient light energy conversion properties, such as a power conversion efficiency of 0.63% and an incident photon to current conversion efficiency (IPCE) of 35%, which are superior to those of the ZnP(Py)$_4$ tube.

Electrostatic and related interactions play an important role in many supramolecular assemblies. D’Souza et al assembled exotic supramolecular triads and tetrads as photosynthetic reaction center mimics of a ‘special pair’ dimer linked to one or two acceptors [73]. A cofacial porphyrin dimer that can operate as the special-pair donor was formed through the potassium-ion-mediated electrostatic dimerization of meso-(benzo-[15]crown-5)porphyrinatozinc. The dimer was then self-assembled with functionalized fullerenes through axial coordination and complexation with crown ether-alkyl ammonium cation, resulting in donor–acceptor pairs. In the assembled systems, efficient forward electron transfer from the singlet excited zinc porphyrin dimer to the fullerene entity was accomplished as well as a relatively slow reverse electron transfer. This was an important step in photosynthetic light energy conversion.
The same research team also reported photoinduced electron-transfer processes in cis- and trans-functionalized bis-18-crown-6 porphyrins that had been self-assembled with fullerences functionalized with pyridine or alkylammonium cation entities [74]. The charge-separation rates and quantum yields were higher for the 1:2 porphyrin:fullerene conjugates as compared to the earlier reported 1:1 porphyrin:fullerene conjugates using the same binding methodologies. The experimentally determined charge-separation rate constants from nanosecond transient absorption studies were 2–3 orders of magnitude lower than the charge-separation rate constants in other reports, suggesting the occurrence of charge recombination in the Marcus inverted region, as well as charge stabilization in the studied conjugates.

D’Souza et al. constructed a biomimetic bacterial photosynthetic reaction ‘special center’ complex using cofacial zinc phthalocyanine dimer as electron donor and fullerene as electron acceptor by employing well-defined self-assembly methods (figure 9) [75]. Potassium-ion-induced dimerization of the crown-ether-substituted peripheries was employed for the supramolecular dimerization of zinc phthalocyanines. The dimer was further self-assembled with C_{60} analogs through a two-point non-covalent binding involving axial coordination and crown ether-alkyl ammonium cation complexation, and the photoinduced electron transfer within the supramolecular donor–acceptor conjugate was investigated. Unlike the previously reported porphyrin analog, the present cofacial phthalocyanine dimer-based model system exhibited superior electron-transfer properties, including formation of a long-lived charge-separated state, clearly delineating the role of the cofacial phthalocyanine dimer in stabilizing the charge-separated state in donor–acceptor systems.

Because metal porphyrin derivatives are highly capable of coordination linkage, metal coordination is often used to assemble porphyrin-related molecules. Jintoku et al. fabricated J-type ordered aggregates of a low-molecular-weight zinc porphyrin derivative [76]. Subsequent integration of a pyridylated fullerene derivative leads to coordination and orientation onto the porphyrin aggregates. This system achieves unusually high efficiency in fluorescence quenching for one-to-one mixtures of the donor and acceptor.
the Stern–Volmer constant and association constant of this system are 2520 and 56 times higher, respectively, than those of the corresponding non-assembled system. D’Souza et al reported a self-assembled supramolecular triad as a model to mimic the light-induced events of the photosynthetic antenna–reaction center, i.e. ultrafast excitation transfer followed by electron transfer ultimately generating a long-lived charge-separated state [77]. For the construction, the antenna mimicking boron dipyrin was placed between the electron donor, zinc porphyrin, and electron acceptor (C$_{60}$) to modulate the kinetics of the photochemical events. Nanosecond transient absorption studies revealed the lifetime of the charge-separated state to be $\sim$100 $\mu$s, the longest ever reported for these type of antenna-reaction center mimics, indicating an improved charge stabilization as a result of a different arrangement of the antenna, donor, and acceptor entities of the supramolecular triad.

Jakob et al studied the structure-function relationships in a rotaxane of free-base porphyrin rotaxanes and zinc porphyrin analogous systems [78]. They suggested that the changes in rotaxane conformation combined with the variation in the solvent properties strongly affect the thermodynamic parameters of the relevant electron transfer, establishing a structure-medium-function correlation in mechanically interlocked supermolecules. Megiatto et al prepared a new class of [2]catenanes containing zinc(II)-porphyrin and/or fullerene as appended groups by Cu(I) template methodology and ‘click’ 1,3-dipolar cycloaddition chemistry [79]. This work illustrates the concept that supramolecular techniques can efficiently lead to complex 3D nanostructures containing electron donor and acceptor moieties, whose photoexcitation can produce long-lived states with a long-distance charge separation.

Wessendorf et al unambiguously demonstrated electronic communication in rigid electron donor–acceptor nanohybrids formed through hydrogen bonding [80]. The hydrogen bonding pattern is the Hamilton receptor/cyanuric acid motif. Spacers with good electron transfer properties facilitate electron transfer along the supramolecular bridge and, in addition, cause an increase in the apparent association constants. Gadde et al assembled a novel bis(zinc porphyrin)-fullerene supramolecular triad through complementary hydrogen bonding between a diacetylamidopyridine and uracil motifs [81]. Picosecond time-resolved emission and nanosecond transient absorption studies of kinetics of electron transfer and the electron-transfer products revealed that the positioning of the porphyrin with respect to the fullerene influences the kinetics of charge-separation and charge-recombination events. Yu et al designed a 2-ureido-4[1H]-pyrimidinone-bridged hydrogen-bonded complex between porphyrin and fullerene [82]. The assemblies exhibited intra-assembly photoinduced electron transfer via the quadruple complementary hydrogen bonds. Relatively rigid assemblies prevent the porphyrin and fullerene from any intra-assembly collisions, where the quadruple complementary hydrogen bonds play crucial roles in mediating the intra-assembly.

3.2. Assembly with materials

Although supramolecular complexes with small numbers of component molecules are useful for investigation of fundamental phenomena in solution, these systems are usually far from practical use. Therefore, assembly of porphyrin and fullerene functions within materials including organic polymers and inorganic nanomaterials may be beneficial for various purposes.

Fukuzumi et al constructed an organic photovoltaic system using supramolecular complexes of porphyrin dendrimers with fullerenes [83, 84]. By changing the dendrimer’s structure and generation, optimization of efficiency in light energy conversion might become possible. Hasobe et al similarly demonstrated that multi-porphyrin polymer arrays of porphyrin-peptide oligomers with fullerene showed remarkable enhancement in the photoelectrochemical performance [85]. In their system, a broader photosresponse in the visible and near-infrared regions was achieved by increasing the number of porphyrin units in α-polypeptide structures. A power conversion efficiency of 1.3% was attained using composite clusters of a porphyrin–peptide octamer and fullerene. Formation of a molecular assembly between fullerene and multi-porphyrin arrays with a polypeptide backbone controls the electron transfer efficiency in the supramolecular complex. These facts may be essential for the light-energy conversion.

Charvet et al developed photoconductive films of domain-segregated self-assembled nanowires with tailorable dimensions from block copolymers appended with well-controlled segregation of electron donor and acceptor moieties [86] (figure 10). Films of the resulting nanowires exhibit remarkably high charge mobility and can be fabricated by simple drop-casting into a device structure, which allows persistent sequential photocurrent switching. High contrast in the transmission electron microscopy (TEM) images is due to amphiphilic segregation of the chromophoric groups within the nanostructures with dark regions corresponding to fullerene-rich domains. Flash photolysis time-resolved microwave conductivity upon excitation with a 355 nm laser pulse provided an overall conductivity as high as 6.4 $\times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, and an overall charge mobility as high as 0.26 cm$^2$ V$^{-1}$ s$^{-1}$ was calculated. The nanowire films led to the observation of persistent photocurrent switching with sharp on/off responses upon alternating white light irradiation and darkness for nanowires assembled on gold gap electrodes. These 1D nanostructured organic materials are interesting candidates for applications in photovoltaic or electronic devices and provide insight into the preparation of functional organic materials.

Hasobe et al [87, 88] reported novel organic solar cells prepared using quaternary self-assembly of porphyrin (donor) and fullerene (acceptor) dye units by clustering with gold or TiO$_2$ nanoparticles. They demonstrated a remarkable enhancement in the photoelectrochemical performance, as well as broader photosresponse in the visible and infrared relative to the reference systems. The solar cells exhibited an incident photon-to-photocurrent efficiency of 54% and a power conversion efficiency of 1.5%, which is 45 times
higher than that of the reference system consisting of the single components of porphyrin and fullerene. The design of such ‘host’ structures on porphyrin-coated nanoparticles provides a variety of ways for further development of more efficient light energy conversion systems by modulating the surface structure. Hayashi et al developed a strategy to construct a multiple electron transfer system composed of organic/inorganic ternary composites (porphyrin, zinc oxide nanoparticles, reduced graphene oxide) on a semiconducting surface. Hayashi et al designed a systematic series of indium tin oxide (ITO) electrodes chemically modified with SAMs of porphyrin and/or fullerene is a useful way to develop photoconversion devices. Yamada et al designed a systematic series of indium tin oxide (ITO) electrodes chemically modified with SAMs of porphyrins and porphyrin–fullerene dyads on an ITO electrode without impairing the respective donor–acceptor components [89]. The hierarchical electron transfer cascade system exhibited remarkably high photocurrent generation with an incident-photon-to-current efficiency of about 70%.

Modification of electrodes with self-assembled monolayers (SAMs) of porphyrin and/or fullerene is a useful way to develop photoconversion devices. Yamada et al designed a systematic series of indium tin oxide (ITO) electrodes chemically modified with SAMs of porphyrins and porphyrin–fullerene dyads [90]. The results clearly demonstrate that utilization of fullerene as electron acceptors linked with porphyrin chromophores on ITO electrodes is highly promising for the construction of artificial photosynthetic systems. Cho et al reported an unusually high performance from photovoltaic cell based on a C60 metal cluster-porphyrin dyad SAM on an ITO electrode. A quantum yield of up to 19.5% was calculated from the number of photons absorbed by the chromophores [91].

Similar approaches have been reported by many other researchers [92–99].

4. Commanded assembly

As demonstrated by several examples of the previous sections, immobilization of self-assembled structures of porphyrin and fullerene onto the surfaces of devices such as electrodes has become a crucial process in the development of photoelectron-transfer devices. Self-assembly methods required for these immobilization processes are somewhat different from those of self-assemblies in solution. Self-assembly should be conducted using controlled methods. Functional moieties should be immobilized on the device surfaces with defined thickness, controlled orientation and arrangement, and with well-specified areal distributions. Functional units should be fixed with the required thickness and orientation only at the required positions, which must be controlled under external commands. In addition to the SAM strategy, Langmuir–Blodgett (LB) [100, 101] and LbL assembly [102, 103] techniques have been widely used for thin-film assemblies of various functional units, some of which are not available for vapor deposition methods under high vacuum. The SAM technique can be applied to a wider range of substances, but it is not a useful method for multilayer fabrication. The LB technique is an elegant way to build up multilayer structures, although it suffers from the requirement of rather expensive instrumentation and it is not applicable to many kinds of non-amphiphilic materials. Unlike these two methodologies, LbL assembly is a simple and inexpensive process for multilayer formation and allows different types of materials to be incorporated in the film structures. LbL assembly can be regarded as a versatile bottom-up nanofabrication technique that is very useful for immobilization of functional organic units for photoelectronic devices. In this section, after a brief introduction of the LbL method, we describe several examples of LbL approaches for assemblies of porphyrin and fullerene functional units. We also introduce a novel thin-film preparation technique that can be operated by external commands.

In many cases, LbL assembly is conducted through electrostatic interactions. The assembly mechanism of the LbL method is quite simple. Relatively high concentrations of substances in solution lead to excess adsorption of the substances where charge neutralization and resaturation lead to charge reversal. Alternation of the surface charge results in the continuous assembly of positively and negatively charged materials affording a great freedom in the number of layers and layering sequence. The only required equipment is beakers and tweezers. Owing to the simplicity of the procedure, this methodology has been rapidly adopted by various research communities. In addition to polymeric materials including synthetic polymers [104, 105], biopolymers [106, 107], and inorganic colloidal objects [108, 109], small organic molecules such as dyes and molecular assemblies [110, 111] can be immobilized into thin layers by using this method. Because driving forces for assembly can be expanded to other interactions including
coordination [112, 113], hydrogen bonding [114, 115], biospecific recognition [116, 117], and formation of charge transfer complexes [118] and stereo-complexes [119, 120], various kinds of organic functional molecules can be incorporated to the films through supramolecular interactions.

Photoelectronic properties such as charge separation and photocurrent generation are also an attractive target for LbL assemblies. Guldi et al reported a unique effect of molecular structure on the efficiency of photoinduced charge separation in LbL films of a porphyrin–fullerene dyad molecule [121] (figure 11). In that porphyrin–fullerene dyad, porphyrin and fullerene moieties are bridged through a short rigid spacer. LbL assembly was conducted with charged polyelectrolytes. A base layer of poly-((diallyl-dimethylammonium) (PDDA) was deposited onto the hydrophobic surface of an ITO electrode by simple hydrophobic interactions (i.e. step 1). Next, the electrostatically driven deposition of poly-(sodium-4-styrenesulfonato) (PSS) yielded the PDDA/PSS precursor layer. On the precursor layer, deposition of PSS and porphyrin–fullerene dyad, for up to 12 times, led to the systematic stacking of sandwich layers. In response to visible light irradiation, injection of electrons into the ITO conduction band occurred directly from the photochemically generated radical pair and indirectly through electron transport mediated by suitable electron carriers.

Ikeda et al reported multilayer assemblies comprising fullerene and porphyrin layers formed using the LbL method through the formation of a homohexacalix[3]arene-[60]fullerene 2 : 1 complex (figure 12) [122]. On an ITO electrode, an appropriate SAM structure was first prepared to create a surface with a relatively high density of anionic charges. The cationic complex of fullerene and calixarene was then deposited so that fullerene molecule could be directly assembled. Anionic polyelectrolytes containing porphyrin units as pendant groups were adsorbed onto the thus-formed cationic surface. Photocurrent of the assembled film was measured in a 0.1 M Na2SO4 solution containing 50 mM ascorbic acid as a sacrificial electron donor. In this system, the photocurrent flow from the porphyrin units to the C60 units and from the C60 units to the electrode was demonstrated.

These examples demonstrate the great potential of the LbL method for the construction of photoelectron transfer systems by assembling photosensitive electron donors and acceptors in the required layering sequence in thin films. This process is based on self-assembly phenomena that can occur spontaneously at the solution-solid interface. Therefore, these methods cannot offer a higher level of controllability such as determining the deposition area or assembly timing. Greater control can only be achieved from the device surface. In a next-generation methodology, LbL assembly driven by commands from substrates such as electrodes has to be invented. Recently, we proposed a novel LbL strategy called electrochemical-coupling layer-by-layer (ECC-LbL) assembly, which involves electrochemical reactions driven by electrical control signals from electrodes [123]. For this strategy, we selected N-alkylcarbazole dimerization as a coupling reaction (figure 13). This reaction can be performed through electrochemical stimuli from an electrode surface beneath the films without the use of additional reactants. In addition, electrochemical signals can reach the top layer in the films during the assembly since N-alkylcarbazoles and their dimers have large hole transport mobilities [124, 125]. Unlike other electropolymerizable precursors such as aniline and thiophene, the resulting di-N-alkylcarbazole is transparent to visible light [126], which is highly advantageous for certain optical or electrical applications.

For demonstration of ECC-LbL assembly, various carbazole derivatives carrying distinctive donor (porphyrin and fluorene) and acceptor (fullerene) moieties were used. Electrochemical coupling of N-alkylcarbazoles was performed using cyclic voltammetry (CV) apparatus to precisely control the layer thickness. As an example of ECC-LbL assembly, alternating layers of porphyrin and fullerene were prepared by CV sweeps. While continuous film growth was confirmed by monitoring the optical absorbance at 500 nm, the absorbance at 437 nm for the porphyrin Soret band exhibited a switching behavior. The latter feature revealed electronic interaction between porphyrin and fullerene in the nearby layers. The smooth surface morphology of this assembly was confirmed by AFM. Because these assemblies were conducted by electrical commands from the electrodes, we could make films at the required location with the required timing.

As an attractive potential application of the ECC-LbL films, photoelectronic performance was demonstrated using a prototype thin-film p–n heterojunction device with
Figure 13. ECC-LbL assembly by electrochemical \(N\)-alkylcarbazole dimerization driven by electrical signals from electrodes where electron donors (porphyrin and fluorene) and acceptor (fullerene) can be immobilized in controlled layer sequences.

Figure 14. Patterned display produced by ECC-LbL assembly.

An effective demonstration of the usefulness of commanded assembly would be area-selective patterned assembly. Demonstration of ECC-LbL in area-selective patterned mode \[127\] was conducted using a patterned ITO electrode with an ‘MAO’-shaped mask, where the three capital letters, M, A, and O, were positioned on different parts of the ITO layer on the same glass surface (figure 14). ECC-LbL assembly can operate at different areas so that each of the ITO parts could be individually turned on by connection to a working electrode. A fluorescent fluorene layer was first assembled on all the characters, and the patterned areas, M, A, and O, yielded a fluorescent display of MAO. Area-selective assembly of a non-fluorescent fullerene layer only on the M and A areas changed the message from MAO to O. The dimmed characters could be recovered by a further assembly of a fluorene layer, as seen by changes of the fluorescence display from O to MO and finally to MAO. Quenching of fluorescence from the fluorene (energy donor) layer by covering it with a fullerene (energy acceptor) layer was induced by efficient energy transfer at the interface of these two layers. The commanded-assembly ECC-LbL method can be employed on well-defined micro- and nanosized conductive material surfaces of arbitrary topography for device applications. Area-selective assembly in patterning mode can be performed by varying the spatial application of voltage. Therefore, commanded assembly can be coupled with the products of top-down nanotechnology such as miniaturized integrated circuits.

5. Future perspectives

In this review, we have summarized recent progress in the assembly of porphyrin and fullerene molecules. Assemblies of porphyrins and fullerenes were selected due to their...
is crucial in the development of our technology for practical applications—otherwise many outstanding achievements in materials’ self-assembly will remain simply as pure basic science. Electrochemical coupling layer-by-layer (ECC-LbL) assembly is highlighted as one of the possible methods of commanded assembly. The concept of this method is based on the simple combination of the well-known LbL assembly and a coupling reaction under command from an electrode. Only with this strategy can controlled assembly of optically and electronically functional units be performed with predetermined thickness, layer sequence, and location. ECC-LbL commanded assemblies should be considered as part of the larger family of techniques that include directed assembly and guided assembly. When the paradigm shift from self-assembly to commanded assembly has been successfully completed, molecular/material assembly can be promoted from a scientifically curiosity to a practically useful technology, which may help ameliorate the problems facing humanity.

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**Figure 15.** Paradigm shifts from self-assembly to guided and/or directed assembly, then commanded assembly.
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