TOPICAL REVIEW

Programmed self-assembly of large $\pi$-conjugated molecules into electroactive one-dimensional nanostructures

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Abstract
Electroactive one-dimensional (1D) nano-objects possess inherent unidirectional charge and energy transport capabilities along with anisotropic absorption and emission of light, which are of great advantage for the development of nanometer-scale electronics and optoelectronics. In particular, molecular nanowires formed by self-assembly of $\pi$-conjugated molecules attract increasing attention for application in supramolecular electronics. This review introduces recent topics related to electroactive molecular nanowires. The nanowires are classified into four categories with respect to the electronic states of the constituent molecules: electron donors, acceptors, donor–acceptor pairs and miscellaneous molecules that display interesting electronic properties. Although many challenges still remain for practical use, state-of-the-art 1D supramolecular nanomaterials have already brought significant advances to both fundamental chemical sciences and technological applications.

Keywords: self-assembly, nanowires, electronics, optoelectronics, supramolecule

1. Introduction

$\pi$-Conjugated molecules have attracted increasing attention for their potential applications in organic electronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photoconductors (OPCs) and organic photovoltaics (OPVs). In comparison with their inorganic counterparts, organic semiconductors have advantages such as light weight, flexibility and availability of simple and inexpensive fabrication processes of large samples. Another characteristic of organic semiconductors is their anisotropic electrical conductivity, which contrasts the typical three-dimensional (3D) electrical transport in inorganic semiconductors. In organic materials, charge carriers travel through overlapped $\pi$-electron clouds of molecules; therefore, organization of molecules into a desired configuration is important for device performance. Nanowires composed of $\pi$-conjugated molecules are an example of such organization and are possible candidates for effective energy and charge transporting media. Such nanowires are expected to serve as nanoscale electronic components, which may lead to the miniaturization of electronic devices. Various supramolecular nanowires have been reported including fibers, rods, tapes, tubes and coils [1]. However, the electronic and optoelectronic functions of these nanowires have not been sufficiently characterized yet, that is, the field of supramolecular electronics is still in its infancy.

This review presents recent topics on programmed self-assembly of $\pi$-electronic molecules into 1D nanostructures. Since the research field of supramolecular nanomaterials is very broad, these topics are limited to (i) 1D nano-objects formed from $\pi$-conjugated molecular
building blocks, which support electronic and optoelectronic applications, and (ii) 1D nano-objects constructed by a spontaneous assembly of molecules, rather than by lithographic or nano-fabrication processes. This article focuses on the 1D nano-objects reported within the last 7 years; the topics reported before 2005 are covered in excellent reviews on supramolecular electronics [2–4]. The molecular nanowires are further classified into four categories according to electronic states and combinations of the building-block molecules: electron donors (section 3), electron acceptors (section 4), donor–acceptor pairs (section 5) and other 1D nano-objects that display interesting electronic properties (section 6).

2. How to prepare 1D molecular assemblies in general

For molecules having a large aromatic core, $\pi-\pi$ interaction is primarily important for assembling molecules [3, 5]. Discotic molecules tend to stack on top of one another to form columns via $\pi-\pi$ interaction, which provides transport channels of energy and charge carriers. Attachment of side chains to the $\pi$-conjugated core is effective to change the solubility, polarity and dipole moment of the molecules. Asymmetric modification of $\pi$-conjugated cores by substituents of different hydrophobicities/hydrophilicities sometimes results in the formation of well-defined intriguing nano-objects such as tubes and coils [1]. Other important interactions for self-assembly are hydrogen bonding [6], metal coordination, interionic [7], sulfur–sulfur and other interactions. Solvent, concentration and temperature conditions are also important factors. The simplest method of self-assembly is heat-and-cool or condensation of a solution. If the solubility is so high that no precipitation occurs, a binary solvent is often used, that is, the addition of a ‘poor’ solvent into a solution of a ‘good’ solvent by rapid dispersion, phase transfer and vapor diffusion promotes the assembly of molecules with particular morphologies [8].

3. 1D assemblies from electron donors

3.1. Hexabenzocoronenes

Hexa-peri-hexabenzocoronene (HBC) can be regarded as the smallest graphene fragment consisting of 13 fused benzene rings, and has a tendency to form a herringbone molecular packing configuration [9]. Wu et al reported that chemical modification of HBC with long alkyl chains results in the formation of discotic liquid-crystalline materials that exhibit high charge-carrier mobilities [10]. Concerning 1D objects, hexa-dodecyl-HBC 1a forms several-hundred-micrometer-long, birefringent fibers owing to its high self-aggregation capability when drop-cast from a toluene solution ([1a] = 10$^{-4}$ M, figures 1(a) and (b)) [11]. The dimensions slightly depend on the solvent, but the morphology is uniform within the drop-cast film, where the columnar alignment coincides with the microfiber axis. On the other hand, HBC bearing branched side chains (1b) typically forms much shorter fibers when drop-cast from tetrahydrofuran (THF) solution. Nevertheless, centimeter-long, crystalline fibers could be grown by very slow evaporation of the solvent. By dipping into solutions with a higher concentration (10$^{-1}$ M) and slowly evaporating the solvent, uniaxially oriented fibers were deposited on the substrate (figure 1(c)).

Thinner fibers were obtained from the amphiphilic HBC 2, carrying two dodecyl chains on one side and two imidazolium ion-appended alkyl chains on the opposite side of the HBC core (figure 2(a)) [12]. Slow addition of ethanol into a dimethyl sulfoxide solution of 2 results in the formation...
of nanofibers with a uniform diameter of \(~6\) nm, which is about two times as large as the lateral size of \(2\) (figure 2(b)). The hydrophobic units are most likely placed in the inner part of the fiber, while the hydrophilic ion moieties cover the surface. Interestingly, the diameters of the nanofibers of \(2\) can be influenced by the solvent from which they are precipitated. For example, drop casting of the aqueous solution of \(2\) and slow evaporation afford regular fibers with diameters ranging from 200 to 300 nm (figure 2(c)). Slow diffusion of hexane into an aqueous solution of \(2\) yields a precipitate composed of uniform fibers with diameters of 10–15 nm and lengths of up to several micrometers (figure 2(d)).

Hill et al. reported the self-assembled nanotubes from the HBC amphiphile \(3a\), which bears two dodecyl chains on one side and triethylene glycol (TEG) chains on the other side (figure 3(a)) [13]. When a THF solution of \(3a\) ([\(3a\)] = 1 mg mL\(^{-1}\)) is heated to 50°C and then cooled to 30°C, a yellow-colored solution turns cloudy within a few hours. Scanning electron microscopy (SEM) of a THF suspension of self-assembled \(3a\) reveals the formation of fibrous assemblies with an extremely high aspect ratio of \(\geq 1000\) (figures 3(b) and (c)). Transmission electron microscopy (TEM) of the air-dried suspension of \(3a\) demonstrates that the tubes are straight and discrete with no branched structures and have a uniform diameter of 20 nm (figure 3(d)). The wall is 3 nm thick, and thus, the internal tube hollow is 14 nm in diameter. Indeed, when water is mixed into the THF solution of \(3a\) (20% \(v/v\)), both tubular and coiled objects are obtained. Considering the molecular structure of \(3a\), the nanotube consists of two single-layered graphitic tapes with bilaterally coupled 1D HBC columns. Here, the long alkyl chains are interdigitated to hold in the bilayer structure, whereas the hydrophilic TEG chains, located on the surface of the tape, suppress the formation of multilayer structures in a polar solvent such as THF.

X-ray diffraction (XRD) analysis reveals the detailed packing structure in the nanotubular wall [14]. For the XRD analysis, nanotubes of \(3b\) have a great advantage [15] because they can be aligned unidirectionally into a macroscopic fiber (figure 4(a)) [16]. As shown in figure 4(b), a 2D diffraction pattern is obtained, which clearly shows that the HBC units are \(\pi\)-stacked on top of each other and oriented perpendicular to the long axis of the macroscopic fiber. As illustrated in figures 4(d)–(f), the \(\pi\)-stacked columnar arrays of the HBC molecules are helically stranded, and the central axes of the helical HBC columns are tilted 45° relative to the longer axis of the tube. The phenyl groups adopt a cofacial orientation with a tilting angle of 27° relative to the HBC plane, which may determine the handedness of the helical chirality of the nanotube.

The HBC nanotubes turn electroconductive upon chemical oxidation [13]. Whereas the intact nanotube is an insulator, after oxidation with NOBF\(_4\), it shows an ohmic \(I–V\) profile. The conductivity decreases upon cooling, indicating that the oxidized nanotube is a semiconductor with a resistance of 2.5 MΩ at 285 K. The nanotubes show a clearly anisotropic conduction [16], where the resistivities at 298 K of the oriented macroscopic fiber of \(3b\) along (\(\rho_1\)) and across (\(\rho_1\)) the fiber axis are 20 and 140 Ω cm, respectively, and the ratio \(\rho_2/\rho_1\) increases from 7 to 35 upon cooling from 298 to 55 K. The anisotropy of charge transport is confirmed by flash-photolysis time-resolved microwave conductivity (FP-TRMC) [16] and electron spin resonance (ESR) measurements [17].

Yamamoto et al. studied the device properties of the nanotubes using a field-effect transistor (FET) setup [18]. Cast films of the nanotubes from \(3a\) acted as p-type FETs. The field-effect mobility (\(\mu_{\text{FET}}\)) and on-to-off current ratio (\(I_{\text{ON}}/I_{\text{OFF}}\)) were 1.3 \times 10\(^{-10}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 2800, respectively. In contrast, a thin film consisting of ill-defined, nontubular aggregates of \(3a\) displays poor \(\mu_{\text{FET}}\) and \(I_{\text{ON}}/I_{\text{OFF}}\) values of 2.8 \times 10\(^{-6}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 12, respectively. The FET properties show clear dependence on the length of the oligoether chains on the nanotube surface, where \(\mu_{\text{FET}}\) is higher for shorter oligoether chains (figure 3(a)). For example, at 298 K, \(\mu_{\text{FET}}\) of the nanotubes of \(3e\) is almost twice as large as that of \(3a\). This trend is more explicit at lower temperatures, where \(\mu_{\text{FET}}\) of the nanotubes of \(3e\) at 260 K is one order of magnitude greater than that of the nanotubes of \(3a\). The activation energy (\(E_a\)) evaluated for the nanotubes of \(3e\) (0.18 eV) is three times smaller than that of \(3a\) (0.48 eV).

Xiao et al. reported the contorted HBC (hexa-kata-hexabenzocoronene) compound 4 having 8 dodecylxoy chains (figure 5(a)), which forms a 1D crystalline fiber from its dodecane solution ([4] = 2 mg mL\(^{-1}\)) [19]. Each fiber is \(~200\) nm thick, implying that molecular strands of 5 nm diameter pack to form fibers (figure 5(b)). The nanowires were transferred into transistor devices using elastomer stamps, which behaved as p-type semiconductors with a carrier mobility of \(~0.02\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) (figure 5(c)).

### 3.2. Pentacenes

Pentacene is a representative molecule for organic FET applications due to its high field-effect hole mobility of
Figure 4. (a) A macroscopic fiber consisting of bundled nanotubes of 3b processed by using a glass hook. (b) 2D wide-angle x-ray diffraction (WAXD) image of a macroscopic fiber (4 mm in length and 0.2 mm in diameter) composed of the nanotubes of 3b oriented along the longer axis of the fiber. (c) X-ray diffraction profiles of the fiber at β-angles of 0 (red), 27° (green) and 45° (blue). (d–f) Schematics of the hierarchical self-assembled structures of 3b: (d) π-stacked columnar array, (e) bilayer wall, and (f) nanotube. (Reproduced with permission from [14] ©2008 American Chemical Society.)

Figure 5. (a) Molecular structure of HBC 4. (b) TEM images of fibers of 4 on a lacey carbon grid. (c) Schematic of an FET prepared from an isolated fiber of 4 and transistor characteristics measured by varying $V_g$ from 0 to –24 V in 4 V steps. (Reproduced with permission from [19] ©2006 American Chemical Society.)

>3.0 cm² V⁻¹ s⁻¹ for thin-film [20] and ~60 cm² V⁻¹ s⁻¹ for single-crystal devices [21]. However, only few examples of pentacene-based 1D nanostructures have been reported. This is possibly because pentacene tends to form a herringbone packing rather than cofacial π-stacks. To avoid the herringbone packing, Briseno et al introduced intermolecular S–S interactions and synthesized the hexathiapentacene 5 (HTP, figure 6(a)) [22]. Their thin-film transistors with a top-contact configuration exhibited a p-type behavior and hole mobilities of 0.005–0.04 cm² V⁻¹ cm⁻¹. Interestingly, HTP formed nanowires with typical lengths and diameters of dozens to hundreds of micrometers and 70–470 nm, respectively, by a heating-cooling process in benzonitrile ([5] = 1.2 mg mL⁻¹) [23]. Single wires displayed p-type FET characteristics with a mobility of 0.11 cm² V⁻¹ cm⁻¹ on average and 0.27 cm² V⁻¹ cm⁻¹ at most (figures 6(b) and (c)). Furthermore, a network of nanowires also exhibited p-type conductions with an average mobility of 0.017 cm² V⁻¹ cm⁻¹ even on a flexible poly(ethylene terephthalate) substrate.

Wakayama et al prepared nanowires by a thermal evaporation of 6,13-bis(methylthio)pentacene (BMTP 6: figure 7(a)) onto octadecyltrichlorosilane (OTS)-treated SiO₂/Si substrate [24]. Because of the S–S and S–Cπ interactions between SCH₃ substituents attached on both sides of pentacene, BMTP 6 orders in a slipped cofacial π-stacking along the a-axis of the unit cell (figure 7(b)). The nanowires, 30–150 nm in diameter and 1–5 μm long, possess a highly oriented structure with the (020) plane parallel to the substrate plane, displaying p-type behavior in both the bottom-gate and top-gate FET configurations.

3.3. Porphyrins

Porphyrin derivatives play important roles in biological systems such as photosynthesis (chlorophyll), oxygen transport (hemoglobin) and vitamin B₁₂ (cyanocobalamin). As an interesting example of self-assembled 1D nano-objects, Sugimoto et al reported a double-stranded helical structure of an achiral synthetic polymer such as poly(trimethylene iminium) (PTMI) mixed with zinc porphyrin (P₂Zn) having a
Figure 6. (a) Molecular structure and packing of HTP 5. (b) SEM image of a representative bottom-contact HTP nanowire device. The inset shows a magnified view of the HTP nanowire bridging the source-drain gold electrodes. (c) Transfer characteristics of an HTP single-nanowire transistor. The nanowire was cast from a dilute suspension in CHCl$_3$. (Reproduced with permission from [22, 23] ©2006 and 2007 American Chemical Society.)

Figure 7. (a) Molecular structure of BMTP 6. (b) Schematics of the BMTP wire. The long axis of the wire coincides with the \( \pi \)-stacking direction. The highly uniform diameter and straightness of the wire observed in the SEM image suggest a single-crystalline structure. (Reproduced with permission from [24] ©2007 American Chemical Society.)

C$_2$ chiral ligand (P$_{Zn}$ 7, figure 8) [25]. As a result of the hydrogen bond between the PTMI and 7 in a CHCl$_3$/CH$_3$CN mixed solvent (2/1 v/v), linear helical assemblies were formed with a width and average length of 2.3 and 86 nm, respectively. These dimensions agree well with the estimated length of PTMI from the polymerization degree (~62 nm estimated from the length of the repeating unit for an averaged degree of polymerization of 130).

Lazarenko et al performed macroscopic hierarchical surface patterning of tetraphenylporphyrin (TPP) trimers via self-assembly and dewetting processes [26]. Compound 8, which consists of three TPP moieties that are linked via amide bonds to a central benzene core, possesses a high tendency to form aggregates (figure 9(a)). After evaporation of a diluted CHCl$_3$ solution ([8] = 4.8 \times 10^{-6} M, 3-µl droplets) drop-cast on mica, very large domains (up to ~3 nm$^2$) were observed containing a highly ordered pattern of equidistant, nearly parallel, wire-like architectures with a line height of 4.5 ± 0.4 nm (figure 9(b)). Interestingly, when larger droplets were deposited under similar conditions ([8] = 4.8 \times 10^{-6} M, 10 µl), the longer evaporation time resulted in porphyrin

Figure 8. (a) Molecular structure of P$_{Zn}$ 7. (b) Schematics of the artificial double-helix from zinc porphyrin (ZnPor) 7 and achiral synthetic polymer PTMI. (Reproduced with permission from [25] ©2007 American Chemical Society.)

Figure 9. (a) Molecular structure of TPP trimer 8 and schematics of a columnar stack of 8. (b) AFM image (area 10 \times 10 \mu m$^2$), with the inset showing the cross section indicated in the AFM image. Inset shows the formation mechanism of the patterned lines. During the evaporation of the droplet (A \( \rightarrow \) B), the contact line is pinned several times, resulting in the formation of contact pinning lines (1, 2 and 3). After retraction of the solvent front, a thin film remains in which a pattern of thin lines is formed as a result of self-assembly and dewetting. (c) AFM image (area 95 \times 95 \mu m$^2$) of a line pattern on mica. Inset shows the formation mechanism of the patterned lines. The presence of aggregates preformed in solution hinders the retraction of the solvent front from 1 to 2, causing partial pinning of the contact line. In combination with the molecular self-assembly, this partial pinning results in an orientation and growth of linear aggregates orthogonal to the local solvent front; no contact pinning lines are observed. (Reproduced with permission from [26] ©2004 American Association for the Advancement of Science.)
Figure 10. Molecular structures of (a) \( P_{2n} \) polymer 9, (b) ladder-like supramolecular polymer 9 • Bipy\(_n\) formed upon addition of Bipy, and (c) single-stranded 9 • Bipy\(_n\).

\( \text{Ar} = m$\text{-C}_6\text{H}_4[\text{Si(C}_6\text{H}_{13}_1)_1]_2 \).

Figure 11. (a) Molecular structures of PDI 10a–10d. (b) SEM image of the self-assembled nanobelts of 10d. (c) \( I-V \) curves for a single nanobelt of 10d deposited across a pair of gold electrodes separated by 80 \( \mu \text{m} \). Open squares: in hydrazine vapor (140 ppm), solid squares: in air. (Reproduced with permission from [31] ©2007 American Chemical Society.)

4. 1D assemblies from electron acceptors

4.1. Perylene and naphthalene diimides

Perylene diimide (PDI) derivatives are one of the most widely used organic materials in various electronic and optoelectronic applications due to their high stability to temperature and light, as well as n-type charge transport properties. Balakrishnan et al reported the formation of nanowires and nanobelts. For example, nanobelts of propoxyethyl-PDI 10a can be formed by a rapid solution-dispersion method (figure 11(a)) [29]. Typically, a concentrated \( \text{CHCl}_3 \) solution of 10a ([10a] = 1 mM, 5–125 \( \mu \text{M} \)) is injected rapidly into methanol (MeOH, 5 ml), followed by immediate mixing with the pipette. SEM, TEM and atomic force microscopy (AFM) images reveal uniform crystalline nanobelts with an average thickness of 100 nm and a ratio of width to height of \( \sim \)4. The effect of the side chains on the morphology of the self-assembled objects has been studied with PDIs 10b and 10c having different alkyl substituents (figure 11(a)) [30]. \( N, N'\)-dodecyl-PDI 10b self-assembles into 1D nanobelts by phase-transfer self-assembly between excess of hexane and a concentrated \( \text{CHCl}_3 \) solution, due to the favorable \( \pi-\pi \) stacking of 10b. The nanobelts have an average width of 200 nm, and a length of a few tens of micrometers, leading to an aspect ratio of nearly 100. On the other hand, \( N, N'\)-nonyldodecyl-PDI 10c self-assembles to form isometric aggregates of \( \sim 200 \text{ nm} \) size in a binary solvent of water/MeOH (35/65 v/v). The spherical morphology of these molecular aggregates is consistent with a distorted \( \pi-\pi \)-stacking, which prevents the molecules from assembling into a 1D geometry. Che et al further investigated the self-assembly and charge transport property of asymmetric PDI 10d, having a branched alkyl chain on one side and a
polyoxyethylene chain on the other side (figure 11(a)) [31]. The self-assembly of 10d was induced through a solvent exchange process, in which the molecules were transferred from a ‘good’ solvent such as EtOH ([10d] = 0.5 mg ml⁻¹, 2 ml) into a ‘poor’ solvent such as water (2 ml) to yield ultralong nanobelts with a length greater than 0.3 nm and a width-to-thickness ratio of 10 (figure 11(b)). Electrical measurements on a single nanobelt, upon reduction by hydrazine vapor, showed an enhancement in electric current by 3 orders of magnitude compared with the current in the absence of the hydrazine vapor (figure 11(c)).

Yan et al synthesized self-assembled 1D nanofibers from multi-chromophore PDI [32]. A CH₂Cl₂/MeOH mixture (9/2 v/v) of propeller-shaped PDI trimer 11 (figure 12(a)) was allowed to slowly evaporate, resulting in an organization of 11 into thermodynamically stable nanofibers. Changing the solution concentration can control the diameters and the morphologies. For example, the concentrated solution ([11] = 50 µM) results in densely packed fibers, which are tens of micrometers long and have a high aspect ratio of 500 (figure 12(b)). As the concentration is lowered, thinner fibers are formed, and a 1 µM solution of 11 yields very thin fibers, with the diameter (4 nm) equal to the height of a single column of 11. The PDI plane is perpendicular to the axis of the fibers, as confirmed by polarized scanning confocal microscopy. A large red-shift in emission was observed from the nanofibers of 11 by total internal reflection fluorescence (TIRF) microscopy (figures 12(c) and (d)), indicating strong intermolecular electronic interaction and high structural order, which lead to large exciton diffusion lengths and high charge carrier mobilities.

Figure 12. (a) Molecular structure of PDI trimer 11. (b) AFM image of the nanofibers of 11 (diameters ∼100 nm). (c) TIRF image of self-organized fibers together with free molecules. (d) Emission spectra of red fibers with (green line) or without (red line) a green component and bulk absorption spectra (black line) of the solid sample. The spectra are normalized at the peaks. Excitation wavelength: 488 nm. (Reproduced with permission from [32] ©2005 American Chemical Society.)

Recently, two groups have reported PV cells using PDI-based nanofibers. Foster et al and Palermo et al presented PV devices incorporating PDI-substituted polyscyancyanide (PIC) materials with polythiophene- and polyfluorene-based conjugated polymers (figure 13(a)) [33, 34]. In those devices, the perylene units were arranged into chiral ‘helter-skelter’ arrays along the helical PIC backbone (figures 13(b) and (c)), resulting in highly rigid polymer chains with a persistence length of 76 nm [35]. A cast film of the fibers of 12 exhibited n-type FET behavior with an electron mobility of 10⁻³ cm²V⁻¹s⁻¹ [36]. The bulk heterojunction PV cells from 1:1 blends of 12 and poly(3-hexylthiophene) (P3HT) showed the overall power conversion efficiency of ~0.2% (figure 13(d)), which is a 20-fold improvement as compared with analogous blend architectures using the PDI monomer.

Wicklein et al reported that PDI organogelator 13 forms nanowires during the gelation process [37]. They created a nanostructured donor–acceptor interface by combining hydrogen bond-directed self-assembly of an n-type organogelator, PDI 13, with a p-type polymer, poly(vinyl-dimethoxynaphthalenobenzidine) (pDMDTBP) (figure 14(a)). The PV device with an inverted cell geometry (figure 14(b)) exhibited a short-circuit current (Jsc) of 0.28 mA cm⁻², an open-circuit voltage (Voc) of 390 mV, and a fill factor (FF) of 0.38, leading to a power conversion efficiency of 0.041% (figure 14(c)).

Kimizuka et al reported the self-assembly of naphthalene diimides (NDIs) back in 1995 [38], where coassembly of NDIs and melamines resulted in nanotubes. Six NDIs and six melamine molecules were complementarily connected by hydrogen bonds, and the resultant cyclic 12-mer stack formed tubules of 8 nm in diameter. Recently, Shao et al have reported that amphiphilic NDI self-assemblies to form a monolayer...
Figure 14. (a) Molecular structures of PDI 13 and pvDMTPD. (b) Device architecture with inverted cell configuration. FTO = fluorine-doped tin oxide, PEDOT = poly(3,4-ethylenedioxythiophene), PSS = poly(styrene sulfonate). (c) J–V plots under illumination with white light (AM 1.5 spectral conditions, 100 mW cm⁻²) for PV devices constructed from a PDI xerogel/pvDMTPD blend with an additional pvDMTPD layer. The compositions for the devices B1, B2, and B3 are 3:1, 1:1 and 1:3 (PDI:pvDMTPD wt%), respectively. (Reproduced with permission from [37] ©2009 American Chemical Society.)

nanoring that further stacks to give nanotubes [39]. The exceptional homogeneity in the structure and conformation of the constituent molecules led to a rapid energy migration within the nanotubular wall.

4.2. Fullerenes

C₆₀ fullerene and its derivatives are representative forms of nanocarbon; they are widely used as electron-accepting and electron-transporting components in organic FET and PV devices. There are several reports on the formation of nanowires from pristine C₆₀. Wang et al reported that a slow evaporation of a saturated m-xylene solution of C₆₀ ([C₆₀] = 1.4 g l⁻¹) on a silicon or glass substrate yields single-crystalline C₆₀ nanorods with the widths and lengths of 100–450 nm and 100 µm, respectively [40]. Sathish et al prepared C₆₀ nanowhiskers using a liquid–liquid interfacial precipitation method by mixing a saturated benzene solution of C₆₀ with isopropanol (IPA) [41]. Jin et al used a rapid and facile approach for the preparation of single-crystal C₆₀ nanorods with uniform submicron dimensions [42]. A toluene solution of C₆₀ (0.30 wt%) was dropped into IPA at a desired rate controlled using a syringe pump, yielding nanorods within a few minutes. All these single-crystalline nanowires have a face-centered cubic lattice. Geng et al reported exceptionally long C₆₀ nanowires with an orthorhombic lattice, grown from a 1,2,4-trimethylbenzene solution ([C₆₀] = 2 × 10⁻³ M). The nanowires were typically 100–500 nm thick and 0.2–1 mm long [43].

Attaching side chains to C₆₀ affords a variety of nanostructures depending on self-assembly conditions. Nakaniishi et al reported various types of self-assembled structure from the C₆₀ derivative with long alkyl chains (figure 15) [44, 45]. For example, compound 14a in 1-propanol yields 20-µm-long nanofibers. Tsunashima et al produced highly oriented nanofibers of 3,4,5-tris(dodecyloxy)benzamide-substituted fullerene derivative 14b by the Langmuir–Blodgett method (figure 15) [46]. The nanowires had a monolayer fibrous structure with a height of 1.2 nm, width of 8 nm, and length of 5–10 µm.

5. 1D assemblies from electron donor and acceptor pairs

One of the important subjects for optoelectronic applications using organic materials is how to arrange molecules with a desired configuration. An ideal configuration for organic photovoltaics consists of properly connected hole- and electron-transporting layers (p–n heterojunction), which are formed from electron-donating (D) and electron-accepting (A) molecular components, respectively, and lack either charge transfer (CT) complexation or macroscopic D/A segregation. As a strategy to prevent the macroscopic segregation, the use of covalently or noncovalently connected D–A modules has attracted increasing attention.

5.1. Hexabenzocoronene-acceptor dyads

Yamamoto et al synthesized photoconductive nanotubes by a controlled self-assembly of the HBC–trinitrofluorenone (TNF) covalent D–A dyad 15a (figure 16(a)) [47]. Those nanotubes have a coaxial configuration, in which a molecular layer of electron-accepting TNF laminated an electron-donating graphitic bilayer of π-stacked HBC (figure 16(b)). Such a structure creates an extremely wide interface for the spatially segregated redox couple, so that upon photoirradiation, the electrical conduction has an on/off ratio greater than 10⁴. The coaxial nanotubes are prepared
from a 0.12 mM THF solution of 15a, which is exposed to MeOH vapor at 25 °C. The resultant yellow-colored substance is composed of nanotubes with a uniform diameter and wall thickness of 16 and 3 nm, respectively. Interestingly, when the concentration of 15a in THF was only 10 times higher ([15a] = 1.2 mM), the diffusion of the MeOH vapor produced a dark-brown precipitate, which consisted of solid microfibers without a hollow space. In contrast with the coaxial nanotubes, the microfibers showed almost no photocurrent due to the alternate stacking of HBC and TNF moieties.

To clarify whether the nanotube of 15a, fully covered by TNF, is indeed optimum for the efficient photocurrent generation, coaxial nanotubes with smaller TNF densities were prepared as shown in [48]. Despite the diameter and wall thickness have uniform values of 22 and 3 nm, respectively. In FET measurements, a cast film of nanotubes of 15b exhibits both n- and p-type charge transport properties with the electron ($\mu_e$) and hole ($\mu_h$) mobilities of 1.1 × 10^{-5} cm^2 V^{-1} s^{-1} and 9.7 × 10^{-7} cm^2 V^{-1} s^{-1}, respectively. The ambipolar charge transport character of the nanotube of 15b results in an explicit PV output with $V_{OC} = 0.46$ V (figure 17(b)), as evaluated using a dedicated PV device with a lateral channel. Furthermore, coassembly of 15b and 3a (figure 3(a)) gives a nanotubular structure at any molar ratio of 15b to 3a (figure 17(a)). In FET measurements of this structure, $\mu_e$ decreases gradually as the mole fraction of 15b decreases from 100 to 60%, and falls abruptly at lower mole fractions (figure 17(c), green). On the other hand, $\mu_h$ monotonically increases as the mole fraction of 15b decreases (figure 17(c), blue). Importantly, $V_{OC}$ in the PV output (figure 17(c), red) is maximized at a point where $\mu_h$ and $\mu_e$ are well balanced with one another (mole fraction of 15b in the range of 60–75%, yellow region in figure 17(c)). The relative power conversion efficiency is maximized at the mole content of 15b of 25%. At this concentration, the incident photon to current conversion efficiency (IPCE) peaks at ∼2% when the material is excited at its absorption maximum (360 nm).

If the density of the electron acceptors on the nanotube surface can be controlled by external stimuli, rather than by a coassembly of two HBC components (figure 17(a)), the photoconducting properties of the nanotubes can be modulated continuously. Dithienylethene (DTE), one of the representative photochromic molecules, is suitable
for this purpose, because only the closed-form DTE can act as an electron acceptor for HBC. Controlled self-assembly of HBC–DTE covalent dyad [5c (figure 16(a)) yields a coaxial nanotube, where the molecular layer of photochromic DTE densely covers the graphite-like bilayer of columnarly assembled HBC units [50]. Isomerization of the DTE pendants by irradiation with UV-visible light leads to a change in the efficiency of the photoinduced HBC-to-DTE electron transfer, thereby giving rise to an alternation of the photocarrier generation yield. Consequently, nanotubes with open- and closed-form DTE exhibit different photoconductivities. Furthermore, photoisomerization of the DTE pendants allows for the continuous modulation of the photoconductivity in the nanotube.

5.2. Hydrogen-bonded oligo(phenylene vinylene)–perylene diimide pairs

Hydrogen bonds can be applied to the construction of a D/A heterojunction at the molecular level. Schenning et al and Würthner et al produced a supramolecular p–n heterojunction using oligo(phenylene vinylene) (OPV 16) and bay-substituted perylene dimides (PDI 17, figure 18(a)) [51, 52]. Supramolecular OPV–PDI–OPV units initially formed via hydrogen bonding and subsequently self-assembled into chiral stacks by π–π interactions, yielding several-μm-long, 7-nm-thick helical nanofibers (figures 18(b) and (c)). Fluorescence quenching of OPV and PDI in the fiber can be related to photoinduced OPV-to-PDI electron transfer. By means of femtosecond transient photoabsorption spectroscopy, radical cation species of OPV were observed at 1450 nm upon excitation of the OPV moiety at 450 nm, strongly indicating that photoinduced charge separation takes place within a few picoseconds, while subsequent charge recombination occurs within 60 ps. Photovoltaic devices (glass/ITO/PEDOT:PSS/16–17–16/LiF:Al) were prepared with a 100-nm-thick layer of the 16–17–16 complex from methylecyclohexane on a PEDOT:PSS-coated indium tin oxide (ITO) substrate. A typical diode behavior was observed with V_{OC} = 0.74 V and J_{SC} = 2.6 μA cm^{-2}. When these molecules formed a supramolecular p–n heterojunction, ambipolar charge transport properties were observed by FET measurements (figure 18(d)) [53], and μ_{h} and μ_{e} of the cast film were determined as 2 × 10^{-7} and 1.5 × 10^{-7} cm² V^{-1} cm^{-1}, respectively. In contrast, a cast film prepared from a mixture of OPV and PDI without hydrogen-bonding units showed no FET activity due to CT complexion of OPV and PDI moieties.

5.3. Porphyrin–C₆₀ pairs

Porphyrin derivatives can incorporate guest molecules, and, in some cases, form supramolecular 1D fibers. Yamaguchi et al reported ‘supramolecular peapods’ composed of a linear P₂₃ nanotube and a fullerene such as C₆₀ or C₇₀ [54]. They were synthesized by the fullerene-triggered unidirectional supramolecular polymerization of an acyclic P₂₃ dimer (18) having six carboxylic acid (CO₂H) moieties (figure 19(a)). Compound 18 bears large [G4]-poly-(benzyl ether) dendritic wedges, which should resolve the solubility problem of carboxylic acid-appended metalloporphyrins and allow easier visualization by TEM. Typically, a 1,1,2,2-tetrachloroethane (TCE) solution of a mixture of 18 (1.2 × 10^{-5} M) and C₆₀ (2.4 × 10^{-5} M) is heated at 120 °C and then allowed to stand at 40 °C for 4 days. TEM observation of the resulting mixture showed the presence of 1-μm-long fibers with a uniform diameter of 15 nm (figures 19(b) and (c)). A virtually identical TEM image was observed when C₇₀ was used in place of C₆₀.

Shirakawa et al presented C₆₀-assisted organogel formation in a porphyrin derivative bearing hydrogen-bonding
sites [55]. When C_{60} (3.0 mM) was added to a benzene or toluene solution of amide-appended porphyrins 19 ([19] = 6.1 mM, figure 20(a)), a gel consisting of 1D fibers has formed, as revealed by SEM and TEM (figures 20(b) and 20(c)). Computational modeling studies indicate that the porphyrin planes are warped so that they can contact C_{60} as much as possible (figure 20(d)). As a result, four amide groups in the C_{60}-including side form straight hydrogen-bonding bridges with the amide groups of another porphyrin, whereas four amide groups in the opposite side form bent hydrogen-bonding bridges with those in the next porphyrin. The 1D aggregate of hexameric 19 provides three cavities large enough to entrap C_{60} and two cavities, which are too small to accept C_{60}.

Self-assembly of the porphyrin–C_{60} dyad was reported by Georgakilas et al [56]. This group studied how C_{60} derivatives, having an ionic part, assemble depending on the slight structural differences. Spheres and nanorods are formed in water depending on the side chain appendage of the fullerene spheroid. Nanotubes were observed only for C_{60} bearing a TPP moiety, and their diameter and length were 30 and 500 nm, respectively. They further investigated the molecular arrangement in the nanotubular wall, and estimated that the porphyrin–porphyrin stacking configuration is more stable than the interlayered configuration of porphyrin and C_{60}.

Hizume et al synthesized a series of amphiphilic porphyrin–C_{60} dyads and assembled them into nanometer-sized objects. Dyad 20a (figure 21), having an ester linker between P_{Zn} and C_{60} and four TEG chains on the other side of P_{Zn}, forms multilamellar vesicles in water. The vesicles have a diameter of several hundred nanometers and contain stacked P_{Zn} and C_{60} units that form CT complexes [57]. Owing to the strong CT interaction, the vesicles are very stable in water and tolerant towards membrane lysis with detergents. Next, Hizume et al changed the linker structure and number of TEG chains. Free base porphyrin–C_{60} dyad 20b (figure 21) with its racemic mixture formed a spherical assembly with an average diameter of 300 nm [58]. Interestingly, when the dyad was optically separated, its enantiopure substance self-assembled to form nanofibers with a typical length of 10 μm. More intriguingly, the chiroselectively formed nanofibers display ambipolar charge transport properties with μ_{h} and μ_{e} of 0.14 and 0.10 cm^{2} V^{-1} s^{-1}, respectively. These values are remarkably high and even better than those reported for top-class organic materials in a D/A heterojunction. Self-assembled nanotubes from amphiphilic P_{Zn}–C_{60} dyads 20c and 20d (figure 21) have recently been reported in [59]. Although they differ from the previous compound only in the linker part, they assemble in quite different molecular configurations and geometries. Dyad 20c forms nanotubes with a diameter of 32 nm and a wall thickness of 5.5 nm even in a racemic mixture. As a result of the segregated stacking of D (P_{Zn}) and A (C_{60}) moieties in the bilayer wall, the nanotubes exhibit remarkable photoconduction and photovoltaic responses. In contrast, dyad 20d, under identical self-assembly condition to that of dyad 20c, yields nanotubes with a diameter of only 7.5 nm, and their wall consists of monolayers of alternately stacked P_{Zn}/C_{60} moieties. As a result of the alternating D/A geometry, those nanotubes exhibit very poor photoelectric properties.

5.4. Porphyrin–perylenes and naphthalene diimide dyads

Van der Boom et al investigated the self-assembly and photochemical properties of covalently linked zinc porphyrin–PDI and phthalocyanine–PDI dyads. For example, zinc tetraphenylporphyn (TPP_{Zn}) appended with four bay-substituted PDI 21 (figure 22(a)) self-assembles into ordered photosensitive organic nanoparticles, which not only exhibit characteristic properties of antenna-reaction center complex, but also demonstrate efficient charge carrier transport within the nanoparticles [60]. Dynamic light scattering measurements on a 10^{-4} M solution of 21 in toluene shows that 21 forms large soluble nanoparticles with a diameter of 150 ± 30 nm. AFM shows cone-shaped structures with an average height and diameter of 30–50 nm and 100–150 nm, respectively (figure 22(b)). In the aggregates, the PDI moieties most likely stack on top of one another, presumably at a van der Waals contact distance of about 3.5 Å, while the TPP_{Zn} moieties occupy sites in every other layer, with an interlayer Zn–Zn distance of about 7 Å (figure 22(c)). Photoexcitation of the nanoparticles results in a charge separation within 3.2 ps to form TPP_{Zn}PDI^{-},PDI^{+} radical ion pairs. The generated electron rapidly migrates through PDI molecules, as evidenced by magnetic effects.

Li et al reported a covalent zinc phthalocyanine (ZnPc)–PDI derivative 22 (figure 23(a)) [61]. The ZnPc–PDI...
Figure 21. Molecular structures of amphiphilic \( \text{PZn-C}_{60} \) dyads 20a, 20c, 20d, free-base porphyrin–\( \text{C}_{60} \) dyad 20b, and resultant self-assembled nanostructures (Reproduced with permission from [57], [58], and [59] ©2004 The Royal Society of Chemistry and ©2010 and ©2012 American Chemical Society.)

Figure 22. (a) Molecular structure of TPP\( \text{Zn-PDI} \) 21. (b) AFM image of nanoparticles of 21 on a CH\( _3 \)SiCl-treated quartz plate. (c) Schematic of self-assembled nanoparticle of 21. (Reproduced with permission from [60] ©2002 American Chemical Society.)

dyad 22 self-assembles into long fibrous structures in which the ZnPc and PDI moieties stack with the same components in an adjacent covalent building block (figure 23(b)). The smallest discernible fiber diameter in the image is about 5 nm, which is about the width of a single ZnPc–PDI\( _4 \) molecule (figure 23(c)). In this light-harvesting system, ultrafast energy transfer occurs from the aggregated peripheral PDI chromophores to the ZnPc core, followed by exciton migration between ZnPc chromophores within about 100 fs.

Recently, Tu et al. reported self-assembly of nanotubes from NDI–TPP–NDI bolaamphiphile 23 (figure 24) [62]. When the aqueous solution of 23, containing 10% MeOH, was aged for 2–3 days, well-organized, micrometer-long nanotubes formed with a diameter and wall thickness of 13.6 and 4.6 nm, respectively. A few nanotubes had larger diameters ranging from 21.6 to 70.2 nm with 2- to 7-fold thicker walls, indicating that multiwalled nanotubes were produced as well. During the assembly, bolaamphiphile 23 first organizes into monolayer rings, which then stack to form nanotubes. Owing to the presence of bicontinuous D–A arrays in the wall, the nanotube exhibits remarkable fluorescence quenching and faster fluorescence decay in comparison with the MeOH or trifluoroethanol (TFE) solution of free-base TPP, and even 23, indicating that photoinduced electron transfer takes place very efficiently in the nanotubular wall.

6. Other interesting topics on 1D assembly

Exciton migration properties in 1D assembly are mainly dependent on how molecules order in the nano-architectures, yet it is quite sensitive to small defects or disorder [63]. In particular, when 1D assembly is immobilized on a solid surface, exciton migration is significantly affected.
Figure 24. (a) Molecular structure of NDI–TPP–NDI bolaamphiphile 23. (b) Schematic of the self-assembly of 23. In an aqueous solution of 23 containing 10% MeOH, 23 self-assembles into monolayer nanorings, which further stack into nanotubes. In pure MeOH, or at pH 1 or 11 in an aqueous solution of 23 containing 10% MeOH, porphyrin-driven nonspecific aggregation occurs. TEM images show (top-right) nanotubes and nanorings and (bottom left) nonspecific aggregates (10% MeOH, pH 1), and a portion of the AFM image (bottom right) shows the supramolecular stacking of nanorings into nanotubes. (Reproduced with permission from [62] ©2011 American Chemical Society.)

Figure 25. Molecular structure of amphiphilic cyanine dye 24 and schematic of the self-assembled nanotube formed from 24. (Reproduced with permission from [64] ©2009 Nature Publishing Group.)

by disorder. To overcome this drawback, Eisele et al and von Berlepsch et al developed a drop-flow technique to immobilize self-assembled nanotubes formed from cyanine dye 27 (figure 25) and observed uniform excitation fluorescence from individual molecular nanotubes [64, 65]. The nanotube wall consists of a bilayer of 24, in which the cyanine moieties form J-aggregates inside the wall, while the inner and outer surfaces of the nanotube are covered by the hydrophilic sulfoxide ionic parts. Polarization-resolved fluorescence near-field scanning optical microscopy (NSOM) measurements revealed that, upon drop-flow treatment, the nanotubes are immobilized on the substrate surface without degradation in their morphology and optical properties. The NSOM images display a uniform supramolecular structure, both along individual nanotubes and between nanotubes in an ensemble. The authors mentioned that this is an excellent model system for the investigation of exciton transport in individual quasi-1D nanostructures, as well as for light harvesting and other optoelectronic applications in future solid-state devices.

Recently, Wei et al have reported a supramolecular linear p–n junction composed of two different graphitic nanotubes by a stepwise self-assembly of two kinds of HBCs having different electronic structures (figure 26) [66]. Firstly, 2, 2′-bipyridine-substituted HBC 25 is organized into a nanotubular assembly (NT25). Secondly, bundles of the resultant nanotubes are dispersed in acetone by complexation with copper(II) ions (NT25•Cu). Thirdly, fluorinated HBC (F-HBC, 26) is added to the dispersed NT25•Cu solution. Upon aging at 25 °C, F-HBC 26 starts to assemble at the edge of the nanotubular segment of 25 to form triblock nanotubes (block-NT25•Cu/NT26). A p–n junction is formed along the nanotube axis, and therefore, the nanotube exhibits efficient fluorescence quenching due to energy migration and subsequent charge transfer at the HBC/F–HBC interface. Furthermore, the lifetime of the charge carriers generated in the heterojunction nanotubes is five times longer than those for the nanotubes composed of a single component (HBC or F-HBC), indicating that the probability of the
charge recombination is reduced in the triblock nanotubes. Such self-assembled nanotubes, possessing electronically communicable 1D connection, are promising candidates for nanoscale conversion of light to electricity.

7. Summary and outlook

This review article presented various types of one-dimensional (1D) supramolecular assembly consisting of electron donors, acceptors and donor–acceptor pairs. These 1D nanarchitectures are electroactive, and exhibit charge transport properties, field-effect transistor outputs, photoconduction and photovoltaic response. These state-of-the-art 1D supramolecular nanomaterials bring significant advances to both fundamental chemical sciences and technological applications; however, the latter still require a technology of utilizing the nanoscale properties at the macroscopic level. These issues may shed light on a current limitation of the bottom-up strategy toward supramolecular electronics, and constitute an important subject worthy of further exploration.

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