Fluorene-based macromolecular nanostructures and nanomaterials for organic (opto)electronics

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1. Introduction

Since the discovery of poly-(p-phenylenevinylene) (PPV) as the representative for conjugated polymers (CPs)

Nanotechnology not only opens up the realm of nanoelectronics and nanophotonics, but also upgrades organic thin-film electronics and optoelectronics. In this review, we introduce polymer semiconductors and plastic electronics briefly, followed by various top-down and bottom-up nano approaches to organic electronics. Subsequently, we highlight the progress in polyfluorene-based nanoparticles and nanowires (nanofibres), their tunable optoelectronic properties as well as their applications in polymer light-emitting devices, solar cells, field-effect transistors, photodetectors, lasers, optical waveguides and others. Finally, an outlook is given with regard to four-element complex devices via organic nanotechnology and molecular manufacturing that will spread to areas such as organic mechatronics in the framework of robotic-directed science and technology.
Figure 1. Diverse fluorene derivatives (F-I, II, III, IV and V) and a typical (oligo-) poly(dialkylfluorene) (F-VI).

in 1990 [1], polymer semiconductors consisting of CPs and stacked polymers [2] have attracted significant attention because of their remarkable electroluminescent and semiconducting features [3]. In the last two decades, various functions of plastic devices have been demonstrated, including polymer light-emitting diodes (PLEDs) [4,5] for commercial flat panel displays and white solid lighting sources, polymer solar cells (PSCs) [6,7], polymer thin-film transistors [8–11], polymer lasers [12–15], polymer photodetectors [16–19], polymer memory for information storage [20–25] and others [26–28]. In this area, the basic open question pertaining to commercialization is to fabricate low-cost, stable and high-performance thin-film devices. Beyond the device structure and interface, function and structure-directed molecular designs have been explored at molecular scale in the last two decades. The molecular design of CPs via covalent engineering has involved fruitful efforts to achieve various functional active layers that include carrier injecting or transporting materials, electroluminescent materials, high-mobility materials, electrically bistable materials, photosensitive materials and other active materials under the guidance of the energy-level diagram in physics, lighting up the road ahead towards commercialization. However, obstacles on the road to commercialization still exist in this area. If possible, to sustainable progress, the organic electronics industry should overcome several issues such as the expensive vacuum deposition techniques, low yield rate of products and short lifespan through the introduction of new technology. Furthermore, nanoelectronics together with printing electronics, green electronics [29], and flexible, stretchable and wearable textile electronics represent that area of organic electronics that has become a significant interdisciplinary area that captures the attention of many. Against this background, it has become increasingly important to introduce new versatile approaches with greater degrees of freedom, accelerating the progress in plastics electronics. Recently, nanotechnology has been making an impressive impact on organic electronics and will revolutionize organic optoelectronics in the future. Here, we focus on the progress in polyfluorene (PF)-based polymer semiconductor nanostructures to demonstrate how to push plastics electronics forwards.

As one of the most important \( \pi \)-CP semiconductors, PFs have attracted most attention in the last two decades owing to their inherent merits such as high photoluminescence (PL) quantum yields, excellent thermal and chemical stability, tunable molecular configurations and being commercially available [30,31]. The multi-levelled molecular substructures of PF derivatives, such as dialkylfluorenes (F-I), heterofluorenes (F-II) [32–34], fused or curved fluorenes (F-III) [35], diarylfluorenes (F-IV) [36,37] and spirofluorenes (F-V) [38,39] (figure 1), have become an ideal platform to demonstrate the four-element principle that contains the p-n covalent design (also called the D-A design) [40–43], steric design [44,45], conformation and topology design [15,46–48] and supramolecular interaction [25,31,49,50]. Previously, many efforts have been made to clarify low-energy green emission bands (also called g-bands) in PF-based electroluminescent
devices [51,52], and the complex polymorphic morphologies included the amorphous state, liquid crystalline and semicrystalline phases, β-phase, which has a ‘planar zigzag’ or 21 helix conformation [53,54], and networks [55,56] of PF molecular arrangement in solution, film and gel [57,58]. Recently, PF-based nanomaterials have become the new-generation polymer semiconductors for organic electronics. Nano approaches have not only extended PFs into biomedicine [59], but have also enabled them to be used in nanoelectronics and nanophotonics [60,61], and in thin-film electronics [62]. In this review, we will focus on the advances in the PF-based zero- and one-dimensional nanostructures for organic devices to summarize the recent efforts that have been made via nano-engineering.

2. Nano approaches to organic electronics

With regard to molecular and polymer engineering, nano approaches that can be traced back to Richard Feynman in 1959 have advanced the power not only of tools such as the scanning electron microscope (SEM), transmission electron microscope (TEM), scanning tunnelling microscope, atomic force microscope (AFM), X-ray diffraction (XRD) and others, but also sophisticated nanofabrication methods such as electron beam lithography, soft lithography, scanning probe lithography (SPL) and others [63–67]. Nanotechnology has become one solution to keep up with the challenge of electronics from Moore’s law, resulting in the generation of nanoelectronics. Nanofabrications have made it possible to miniaturize devices in the last several decades. On the other hand, organic electronics has offered an alternative for fabricating low-cost, large-area, flexible and nano-level devices. Therefore, a combination of nanotechnology and organic electronics—the so-called organic nanoelectronics—provides a new platform to improve the performance and stability of organic devices via nano-engineering, such as by constructing multi-dimensional nanomaterials and oriented thin films, which could be divided into two key levels: organic nanodevices and nanostructured thin-film organic devices (figure 2). Nano approaches, which involve nanofabrication and manufacture, nano-characterization and nano-manipulation, are powerful at the scale of ICs, device structures, interfaces between electrodes and semiconductors, and electrodes. Moreover, nanofabrication has provided the possibility of fabricating nanodevices that can realize active single molecules in contact with nanoelectrodes, and has enabled state-of-the-art models to be made that improve our understanding of the behaviour of excitons or carriers at the single molecular scale [68,69]. Nanobuilding blocks make diverse nanosystems and versatile nanocomposites, offering greater degrees of freedom to control energy transfer, charge separations and other optoelectronic properties by the control of thin-film morphology. Among them, semiconducting polymer nanoparticles have not only been rapidly developed into applications such as biosensors, imaging, drug delivery and therapy [70–73], but have also been applied to eco-friendly organic thin-film nanoelectronics and energy conversion and storage. One more appealing virtue of nano approaches over others lies in the affordability of this powerful method to manufacture green and eco-friendly solution-processed organic devices. Nanoparticle suspensions as printing inks offer the opportunity to fabricate organic devices using aqueous processing, high-throughput inkjet printing or roll-to-roll printing techniques [74–78]. Besides, organic semiconducting nanowires show great promise for integrated device networks because they can function as device components for logic, memory and sensing applications and interconnects [79]. Organic fluorescent nanofibres are an ideal platform for photonic devices such as lasers and optical waveguides and amplifiers in nanophotonics owing to subwavelength confinement effects [80]. In particular, optical and optoelectronic organic devices on fibres are suitable for cost-effective integration into textiles [81–84]. Nanostructures on wafers or electrodes are important for packaging chips and superstructured devices. Nanoscale ultrathin films often serve as the interface to adjust the energy diagram in organic devices. Oriented thin films improve mobility and realize polarized electroluminescence (EL). Distributed feedback (DFB) structures from nanopatterned thin films are a great benefit for organic injection lasers [85]. Nanoporous thin films hold great promise for gas, chemical or biosensors with regard to the improvement of their sensitivity. Bulk heterojunction PSCs have intrinsic nanostructured polymer
Figure 2. Generation of organic nanoelectronics through convergence between nanotechnology and organic electronics and the methods of preparation of PF-based nanoparticles and nanowires.

thin films for application in high-performance devices [86]. Organic nanosystems from fully conjugated block copolymers offer a new solution for solar cells [87,88]. Self-assembly of p-n fully conjugated diblock copolymers can achieve nanostructured thin films with two ordered independent channels of electrons and hole. Thin-film nanoelectrodes such as nanocarbons (carbon nanotube and graphene) or silvers are a promising alternative to ITO (indium tin oxide) for organic flexible and stretchable electronics with the feature of enhanced light extraction [22,89–91]. CP nanobuilding blocks and superstructured thin films mark the entry into a new realm in plastics electronics.

Organic semiconductors are integrated into well-defined nanostructures via nano approaches that either disperse in suspension or lie on the surface of, for example, a silicon wafer or ITO electrodes. Organic nanobuilding blocks in solution involve zero-, one-, two- and three-dimensional nanostructures with different sizes, shapes, composition, phases and architectures that can be re-assembled into nanostructured thin films or superstructured bulk materials. Controllable nanostructures on surfaces are more important to nanodevices, or systems on-chip or on-plastic, than irregular nanostructures in dispersions or suspensions. Nanostructures on surfaces include several types, such as nanopatterned, aligned or nanostructured thin films [92,93]. With regard to organic/polymer nanostructures, organic nanobuilding blocks are categorized into covalent organic nanostructures and supramolecular organic nanostructures. Zero-dimensional nanostructures are called nanodots, quantum dots, nanoparticles or nanospheres in the literature, depending on their different sizes. For example, conjugated
polymer nanodots or dots (CPDs) are the smallest in size, ranging from a few nanometres to several tens of nanometres; nanoparticles, by general description, from a few nanometres to hundreds of nanometres; and nanospheres can be larger, up to many hundreds of micrometres. One-dimensional nanostructures include nanorods, nanowires, nanofibres and nanotubes. Nanoscale manufacturing methods are categorized generally into ‘top-down’ fabrication and ‘bottom-up’ synthesis. The ‘top-down’ methods start from a bulk material that is subsequently ‘sculpted’ by lithography techniques to generate nanobuilding blocks. Bottom-up synthesis allows for the manufacture of nanostructures in the sub-10 nm range. Until now, there have been only a few reports on two-dimensional nanosheets of CPs, which are ideal advanced materials for solution-processed thin films that resemble low molecular weight semiconductors [94]. For CPs, three-dimensional crystalline nanostructures such as polyhedral nanocrystals [95,96] are more difficult to assemble than zero- or one-dimensional nanobuilding blocks. Nanopatterned, aligned or superlattice thin films are not described here owing to space limitations. Readers are referred to the reviews on various soft lithography or SPL techniques [97,98], electrochemical deposition [99] and mesoscale assembly [100]. Herein, several useful methods that have been exploited for conjugated polymer nanoparticles (CPNs) and nanowires or fibres are described in detail as follows.

For zero-dimensional nanostructures, we will introduce the following methods: mini-emulsion, micro-emulsion polymerization, re-precipitation and supramolecular assembly, which have been developed in the last few decades [71,73]. (i) Initially, CPNs were prepared via an emulsion technique that was described by Landfester and co-workers [101–104]. The polymer solution is added into surfactant-containing water, and the mixture is sonicated for a short time until a homogeneous size distribution of the droplets is obtained in the resulting mini-emulsion. Evaporating the organic solvent by gently heating the mixture gives a stable, aqueous dispersion of solid, narrowly distributed, polymer nanoparticles. The mini-emulsion method is suitable for submicrometre-sized nanoparticles with diameters in the range from several hundreds to 100 nm. This method can make multi-component nanoparticles, such as the binary blend of poly(9,9′-dioctylfluorene-co-bis-N,N′-phenyl-1,3-phenylenediamine) (PF-06) and poly(9,9′-dioctylfluorene-co-benzothiadiazole) (PF-04a, F8BT) that has been described by Scherf and co-workers [105] using a mini-emulsion procedure. (ii) Another approach based on a re-precipitation or injection method has also been applied to obtain nanoparticles [106]. The re-precipitation method involves rapid addition of a polymer solution (prepared with a water-miscible organic solvent) to water using a very dilute solution (less than 20 ppm) and brief sonication to improve mixing. Compared with CPNs prepared via the emulsion method, the diameter of CPN particles exhibited smaller size, which also produced an aqueous dispersion of nanoparticles with a diameter of less than 10 nm and consisting of a single polymer chain [107]. (iii) Currently, supramolecular self-assembly is a versatile tool to prepare nanoparticles by the design of amphiphilic, rod–coil or supramolecular CPs. An extensive pioneering structural study has been performed by Lee and co-workers [108,109], using a large variation of π-conjugated oligomers. The inherent characteristics of supramolecular self-assembly may exhibit predictable advantages such as a convenient preparation process, tunable properties and multi-functionality [70]. Solution-phase self-assembly of supramolecular CPs offers a powerful alternative to the thin-film techniques [55]. Recently, other emerging methods are being continually reported [110–112].

For one-dimensional nanostructures, CP nanowires and nanofibres have been prepared by a variety of methods, including dip-pen nanolithography (DPN) [113–115], electrospinning [116–118], template-assisted synthesis [119], soft template, vapour transport and deposition [120], and solution-phase self-assembly [121–124]. Controlling the dimensions (diameter or width \(d\), length \(L\)) of nanowires is a key issue in the development of advanced materials. The typical methods of producing CP nanofibres can be summarized as follows. (i) Electrospinning is a low-cost and useful top-down technique that uses electrostatic forces to produce one-dimensional nanostructures by means of plastic stretching that dates back to the 1930s. The electrospinning technique is compatible with popular textile manufacturing that permits processing of large volumes of polymers. The diameters of the nanofibres produced by the electrospinning methods
range from several tens of nanometres to micrometres [125–134]. However, in order to obtain well-defined nanofibres with a smooth surface, experimental conditions, such as solvents, concentration, molecular weight of CPs, the type of nozzles and collectors and so on, should be carefully controlled. Additives and auxiliaries with more solution-processable but optically inert compounds are often required for most CPs owing to their limited solubility and relatively poor viscoelasticity. Therefore, it is a significant challenge to obtain purified nanofibres by the electrospinning technique. Using non-solvents with a high boiling point and dielectric constant has proved beneficial to their processability for purified single-component nanofibres. In contrast to other methods, fibres prepared by this method may promote internal molecular orientation of the organic molecules by means of the applied electric field. On the other hand, one advantage of electrospinning synthesis is that it is suitable to construct multi-component nanofibres, facilitating the p/n or organic/inorganic hybrid. The morphologies of nanofibre textiles such as porous, hollow and core/sheath can be controlled by varying the external conditions, the unique nozzle or the spinneret structures. Xia and co-workers [127] reported that poly(2-methoxy-5(2′-ethyl)hexoxy-phenylenevinylene) (MEH-PPV) can be assembled into high-quality nanofibres using electrospinning techniques. Electrospun nanofibres of binary blends of CPs allow for tunable optical and electronic properties [135]. (ii) Hard templates [136] are widely employed in the synthesis of CP nanofibres [137]. In general, hard templates include a variety of ordered porous membranes such as anodized aluminium oxide (AAO) [138], silica, [139] nanochannel glass [140] or ion track-etched polymers [141]. This method does not require any specialized apparatus and is widely applicable across a range of organic materials [79]. For example, use of organic nanotubes and nanowires through the wetting of porous AAO membranes has been demonstrated to be a reliable method with flexible controllable critical parameters such as diameter, length, surface morphology and chemical composition [142]. The basic process of nanotubes is that a polymer solution is injected into the alumina template pores, where the driving force is the van der Waals interactions between the low-surface-energy solution and the high-surface-energy mesh walls. These strong adhesive forces are neutralized after the wetting layer has formed. Evaporation results in the trapping of the polymer material within the template pores. Kim et al. [143] have reported photo conductance in single bilayer nanotubes comprising PPV nanotube cores and carbonized PPV outer shells. (iii) Unlike conventional top-down techniques, soft templates are flexible tools to organize CPs into nanostructures. The extensively used templates include surfactant micelles and aggregates [144]. Surfactant molecules such as hexadecyltrimethylammonium bromide (CTAB) [145], sodium dodecylsulfate (SDS) [146], a triblock copolymer and (PEO)20–(PPO)70–(PEO)20 (Pluronic P123) have been explored as soft templates, acting as the segregates for nanostructures. Other useful soft templates for the synthesis of one-dimensional nanostructures include amphiphilic molecules, copolymers [147], liquid crystals, polymer nanofibres and self-assembled monolayers, biological molecules and macromolecular self-organized structures. Among them, biomolecules are useful for the self-assembly of nanofibres, such as DNA [148–150], proteins [151,152], lipid vesicles [153,154], fungi [155,156] and others. (iv) Molecular assembly is an alternative method of preparing nanofibres, nanowires or nanotubes by re-precipitation [157,158], solvent evaporation [159,160] or gelation [161,162]. For binary blending composites, controllable nano- or micro-phase separation enables them to assemble into nanowires [163,164]. Block copolymers are candidates for the preparation of nanowires via selective solvents [165–168]. Rod–rod copolymers also enable nanoscale phase separation in order to obtain a nanofibrillar morphology [169]. Supramolecular approaches are fascinating in terms of the improved quality of molecular assembly to form supramolecular polymer nanowires [170–172].

3. Polyfluorene-based nanostructures

PF-based nanomaterials via nano approaches facilitate aqueous solution processing that has a dramatic advantage over bulk molecular processing [71,73]. There are two major kinds of nanostructures that have been dealt with in many reports, including zero-dimensional
nanoparticles (or nanospheres) and one-dimensional nanofibres (nanorods, or nanowires, nanoribbons). PF-based nanoparticles have extended the application of PF-based materials to biosensors and imaging [173–180] and organic nanodevices. PF-based nanoparticles have served as state-of-the-art semiconducting nanomaterials for applications in organic devices [62,181], in which nanostructured thin films improve the efficiency of PSCs and electroluminescent PLEDs. PF-based nanofibres or nanowires are suitable for nanophotonics and nanoelectronics. In this section, we demonstrate nanobuilding blocks using PFs as a typical example that will be highlighted with regard to nanostructures, and their thin films as well as their applications in organic electronics.

(a) Polyfluorene-based zero-dimensional nanostructures

PF-based nanoparticles have been reported to be produced by several typical methods, including mini-emulsion, emulsion polymerization, re-precipitation and supramolecular assembly, as outlined in figure 3. The initial PF-based nanoparticles of PF-01c (PF2/6), PF-01d (PF1112) and PF-02 (Me-ladder-type poly(para-phenylene); Me-LPPP) were prepared via the mini-emulsion method by Landfeater et al. [104]. The sizes of the CPNs range from 50 to 250 nm. Emulsion polymerization is another conventional method to fabricate CPNs with high molecular weight and monodispersity, which is a facile modified procedure compared with mini-emulsions. However, the key technique is in selecting suitable surfactants and emulsion systems. Liu and co-workers [185] reported that PF-04a (F8BT) CPNs obtained by Suzuki coupling emulsion polymerization in an oil-in-water system using Tween 80 are ideal surfactants. Recently, an excellent study by Kuehne et al. [111] demonstrated that the highly monodisperse nanoparticles of PF-01f (PFO-co-F2/6), PF-04a (F8BT) and PF-15 could be prepared via Suzuki–Miyaura dispersion polymerization using a surfactant mixture of poly(1-vinylpyrrolidone-co-vinyl acetate), Triton X-45 and 1-propanol, which these monodisperse particles readily self-assemble into photonic crystals that exhibit a pronounced photonic stopgap. Nanoparticles of PF-07 and PF-09a-d have been reported via Knoevenagel and Sonogashira coupling emulsion polymerization, respectively [182–184]. Re-precipitation is an alternative method for obtaining hydrophobic nanoparticles, which was first employed for producing PF-based nanoparticles, as reported by McNeill and co-workers [191]. They used re-precipitation methods to prepare nanoparticles of PFO (PF-01a) and PF-06 dispersed in water without any surfactants. Single-component nanoparticles produced via this method exhibited smaller size, such as diameters of 5–10 nm, than those produced by mini-emulsion methods. Meanwhile, the introduction of supramolecular moieties or strong polar groups as oligofluorenes or PFs offers a versatile platform to synthesize nanoparticles via supramolecular assembly. Tagawa and co-workers [199] reported self-condensed nanoparticles of oligofluorenes (PF-12a) with water-soluble side chains. Nanoparticles have radii of 20–100 nm in tetrahydrofuran (THF)-H2O solution. Liu and co-workers [198] recently developed a novel kind of core–shell structure nanospheres from amphiphilic diblock copolymers of PF-11. Yang and co-workers [196,197] reported amphiphilic oligo- and PFs of PF-3a, 3b, 12b that can assemble into nanoparticles as a fluorescent probe for the mercury ion. Meijer and co-workers [202,203] focused on self-assembled fluorescent nanoparticles based on π-conjugated fluorene oligomers of PF-14b-e in water. Takeuchi and co-workers [201,204] reported on oligofluorene-based electrophoretic nanoparticles of PF-13 with diameters of approximately 95 nm from dynamic light scattering (DLS) analysis. The β-cyclodextrin-functionalized fluorene copolymer (PF-03c) nanoparticle was designed and prepared for organic molecule sensing and cell labelling [192]. Photosensitizer-doped PF-17b was prepared [173] by using a re-precipitation method. These tetraphenylporphyrin ( TPP)-doped PF-23 nanoparticles are stable and have a uniform size of 50 nm, with observed efficient intraparticle energy transfer from PF-17b to TPP and enhanced two-photon excitation singlet oxygen generation efficiency in the TPP-doped PF-17b nanoparticles.

PF-CPNs can be further functionalized by cross-linking, blending, encapsulation and surface modification (figure 4), which have more advantages over the precursor nanoparticles for
Figure 3. The chemical molecular structures of oligofluorenes or PFs for nanoparticles: PF-02 and 01d from [104]; PF-01a and 06 from [177]; PF-01e and 15 from [111]; PF-07 from [182]; PF-09a, 09b and 9c from [183,184]; PF-04a from [111,185]; PF-04c from [186]; PF-04e, 08a and 08b from [187,188]; PF-10a from [189]; PF-01b from [190]; PF-01c from [191]; PF-03c from [192]; PF-03d and 3e from [193]; PF-04b from [194]; PF-10b from [195]; PF-16 from [176]; PF-17a from [180]; PF-17b from [173]; PF-04a and PF-05 or PF-01f and PF-02 from [163]; PF-3a, 3b and 12b from [196,197]; PF-11 from [198]; PF-12a from [199]; PF-18 from [200]; PF-13 from [201]; and PF-14b–14e from [202]. (Online version in colour.)

application in biomedicine, thin-film electronics and energy devices. For example, the chemical modification of PF-based CPNs such as by covalent cross-linking processes afforded them more robustness and mechanical stability [205]. In this context, several fascinating aspects to focus on are nanoparticle chemistry and physics processes, with many prospects for practical applications. Tuncel and co-workers [206] reported a cross-linked nanostructure using the precursor particles of
PF-03d and 3e via an in situ click reaction synthesis (covalent). Liu and co-workers [194] described the dendritic cross-linking of PF-04b modified with azide groups via a copper-free click reaction in an oil-in-water mini-emulsion.

Pre- and post-processing of nanoparticles involve physical processes, doping, nanocomposites and blending. In particular, nanocomposites will be crucial for their use in light-emitting and photovoltaic applications [156]. Nanoparticles offer a unique system to dope, blend or use composite binary or ternary polymers or active molecules to construct multi-component nanoparticles that can further blend with each other to investigate the interparticle interactions. Mixed-phase particles of PF-01b (PFO) with obvious features of $\beta$-phase emission have been obtained via a swelling physical post-process of a nanoparticle suspension using either water-miscible solvent THF or toluene [190]. Doped nanoparticles offer ideal models to investigate energy transfer-mediated fluorescence. McNeill and co-workers [207] investigated the CPs of PF-01a (PDHF) doped with PF-06 (PFPV), PF-04a (F8BT) and MEH-PPV. Doped PF-based nanoparticles prepared via re-precipitation tend to be spherical with a size of less than 30 nm; they are estimated to contain 100–200 polymer molecules per nanoparticle. The introduction of a dopant with a concentration of less than 10% has no apparent effect on particle size and morphology. However, re-precipitation is not an effective method to control the size of particles and phase separation compared with mini-emulsion. The mini-emulsion method was successfully applied in polymer blends to precisely manipulate the dimensions of phase separation in a range from 30 to 500 nm [105,163,208]. The major reason lies in the driving force of the formation of nanoparticles obtained via re-precipitation being mostly attributed to hydrophobic interaction and $\pi-\pi$ stacking. But surfactants in the mini-emulsion approach probably help arrest particle growth and prevent agglomeration, which affords better size control [73,209]. This assumption was confirmed by many previous studies by Grey and co-workers [210], who observed that the mini-emulsion technique allows for greater control of the particle size of PF-05 (PFB)/PF-04a (F8BT) nanoparticles than re-precipitation. Moreover, PF-05
(PFB)/PF-04a (F8BT) produced using an aqueous re-precipitation approach exhibited very large size. They investigated p/n (D/A) polymer blend nanoparticles (1:1 w/w) of PF-05 (PFB)/PF-04a (F8BT) with nominal sizes of 58 and 100 nm using the scanned probe and single particle spectroscopy techniques. PL spectra of 58 and 100 nm PF-05/F8BT nanoparticles show efficient energy transfer from the PF-05 (PFB, donor) component to the PF-04a (F8BT, acceptor) component, which is independent of particle size. It is reasonable to deduce that nanoparticles are phase segregated into discrete PF-05/F8BT nanodomains of the order of 20–40 nm for both particle sizes. Pressure-dependent nanoparticle PL spectra support this hypothesis where line-shape maxima of each component red-shift in a similar manner owing to high molecular packing in the single nanodomains. An interparticle mixture is another way to adjust mixture components, which exhibit dramatically different properties from nanocomposites [211]. Li and co-workers [212] described a binary internanoparticle solution of PFO and MEH-PPV to detect radicals using synergy fluorescence. Tuncel and co-workers [213] investigated non-radiative resonance energy transfer in hybrid nanoparticles of PF-01a (PDHF) and MEH-PPV. They checked the two different types of mixtures, that is, interparticle blending and intraparticle nanocomposites. Nanocomposites in intra-nanoparticles have been proved to be made of PF-01a (PDHF) as the core and MEH-PPV as the shell. The highest energy transfer efficiency, recorded to be 35%, is obtained from the last system, in which a PF layer is sequentially formed on MEH-PPV nanoparticles.

Encapsulation, surface modification and supramolecular functionalization of nanoparticles allow for the selective connection with biomolecules. PF-based nanoparticles that are encapsulated by silica shells exhibited higher fluorescence brightness with the additional benefit of improving photostability, facilitating the introduction of bio- or functional groups [191]. PF-04a (F8BT) has been co-assembled with polystyrene (PS)-bearing carboxylic acids as attachment points for post-functionalization by Chiu and co-workers [214,215]. In this way, the surface modification of CPNs affords specific targeting that minimizes non-specific adsorption and biocompatibility. Wang et al. [216] observed that the amphiphilic cellulose nanoaggregates as the soft template for PF-01b (PFO) nanoparticles showed biocompatibility properties. Schenning and co-workers [217] developed pre- and post-functionalization of self-assembled π-conjugated fluorescent organic nanoparticles of PF-14a with precise surface properties suitable for various applications, including imaging and sensing for dual targeting. Liu and co-workers [186] reported hybrid poly(ethylene glycol) (PEG/PF-04b) CPNs via transfer of the hydrophobic polymer into water using a short-chain PEG, resulting in an improved fluorescence quantum yield of 46%.

Nanoparticles offer an alternative to adjust the electronic structures beyond molecular design. Organic nano-objects have a greater degree of freedom to alter themselves than organic molecules. CPDs exhibit amplified energy transfer with high efficiency observed (roughly 50% efficient at 2% acceptor doping and more than 90% efficient at 6% acceptor doping) owing to the special exciton diffusion [218]. Compared with other CPNs, PF-based CPNs have advantages such as high-efficiency fluorescence quantum yields, photostability and easy modification. The advantages of PF-suspended nanoparticles over polymer solutions have been systematically demonstrated by the McNeill group. PF-based CPNs generally have a quantum yield level of 10–20% in suspension or dispersion [191,207]. The highest fluorescence quantum yields of PF-01b (PFO)-suspended nanoparticles have been determined to be as high as 40% [219]. Mixed-phase nanoparticles of PF-01b (PFO) have more advantages, such as narrow, red-shifted fluorescence spectra and increased fluorescence quantum yield (ΦPL, 35%), over their counterparts in the glassy phase (21%) [190]. This result is in contrast to thin films, where the glassy-phase and β-phase PF-01b (PFO) were found to exhibit similar ΦPL. This contributes to efficient energy transfer from the glassy polymer to the β-phase polymer, which dramatically decreases at the non-radiative decay rate. PF-based CPDs also have excellent multi-photon fluorescence [177,220]. Two-photon action cross sections (λem = 770 nm) are as high as 1.4 × 10⁴ for PF-01a (PDHF) and 2.0 × 10⁵ GM for PF-06 (PFPV) [177]. The model of a three-dimensional random walk simulation was proposed by the McNeill group with excitons and acceptor dyes confined to the interior of a sphere [221]. McNeill and co-workers [219] investigated the fluorescent nanoparticles of PF-01b (PFO) using single particle fluorescence imaging and kinetic studies, covering superior features such as higher emission rates.
(10^8 s^{-1}), no blinking and excellent photostability with as many as 10^9 or more photons emitted per nanoparticle. Nanoscale three-dimensional tracking of PF-04a (F8BT) nanoparticles exhibited high absorption cross sections, high radiative rates and low or moderate aggregation quenching, resulting in extraordinarily high fluorescent brightness [220].

Red–green–blue (RGB) and white colours are important for thin-film light-emitting devices. Until now, the emission colours of PF-based CPNs have covered the entire RGB visible range (including white) via doping, nanocomposites, co-assembly or blending [176,219]. Takeuchi and co-workers [201,204] reported the tunable colour emissions of oligofluorene-based nanoparticles PF-13a-d through fluorescence resonance energy transfer (FRET) by doping 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-pyran or a cationic dye, 4-(4-diethylaminostyryl)-N-methylpyridinium iodide. Near-infrared fluorescent particles are useful to circumvent interference from autofluorescence in biological tissues. Demir and co-workers [222] have carried out comparison studies and found that the quantum efficiency of small NPs (up to 30 nm in diameter, high fluorescence quantum efficiency of Φ_{PL} = 68%) of PF-01a significantly surpass the efficiency observed for solid-state thin films without forming nanoparticles (Φ_{PL} = 23%). Emission intensity obviously depends on the film thickness. Relatively larger CPNs (up to 70 nm in diameter) exhibit a comparatively lower fluorescence quantum efficiency of Φ_{PL} = 43% that is lower, typically in the range of 23–44%, than for smaller particles of 30 nm. This low quantum efficiency is closely related to the lower emission from the interchain aggregate species in the PF thin films.

With regard to use in thin-film devices, deposition of CPs in suspension onto electrode substrates, such as silicon and ITO, typically by spin-coating, dip-coating or drop-coating, is necessary. Solution-processed nanoparticles with low viscosity are amenable to being printed into devices through low-cost and high-throughput inkjet or roll-to-roll printing techniques [78,81]. Jagannathan et al. [223] demonstrated that organic nanoparticles are suitable for low-cost printing procedures. Particularly, aqueous-based nanoparticle dispersions are more compatible with green and eco-friendly manufacturing techniques. With respect to organic, low molecular weight devices with multi-layered device structure engineering, it is difficult to fabricate multi-layered polymer thin films without being assisted by other methods owing to the miscible components in the typical wet-processing procedures. With regard to the multi-layered device, the first PF-based CPN film used as an emitting layer in PLEDs was the ladder-type PF-02 (m-LPPP) reported by List and co-workers in 2003 [181]. For PF-02 (m-LPPP) nanoparticles of different sizes, ranging from 69 to 154 nm, they did not observe a significant difference in optoelectronic properties such as PL and Φ_{PL} before and after the use of nanoparticles. In fact, the optoelectronic properties of most CPs are extremely sensitive to chemical defects, impurities and solid-state packing effects. They used nanoparticles with a diameter of 94 nm for the fabrication of devices with a configuration of ITO/PEDOT: PSS/m-LPPP nanoparticles without SDS/Al, ITO/poly(ethylene dioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS)/m-LPPP nanoparticles with SDS/Al or ITO/PEDOT:PSS/bulk m-LPPP nanoparticles/Al. The comparison study found a maximum brightness of 145 cd m^{-2} at 8 V and without surfactant effects owing to doping favourable for the space-charge-assisted current injection, which was better than the corresponding bulk device. Meanwhile, polymer nanoparticle-based devices would exhibit more robustness via an irreversible covalent cross-linking process to achieve excellent morphological stability. Fréchet and co-workers [211] explored site isolation for white light-emitting devices. Site isolation of cross-linking nanoparticles through encapsulating procedures led to the suppression of undesired energy transfer between chromophoric emitters by blending two nanoparticles as the light-emitting ‘inks’. The EL properties of these cross-linked nanoparticles in solid films were evaluated in a very simple device architecture, glass/ITO/PEDOT-PSS (40 nm)/emissive layer (65 nm)/BCP (40 nm)/LiF (1 nm)/Al (100 nm). The EL spectra of devices fabricated from either blue or red nanoparticles showed emission peaks around 498 and 598 nm, respectively. For the devices made from blends of these two nanoparticles, near-white emission with Commission Internationale de l’Eclairage (CIE) coordinates of (0.40, 0.42) is achieved. The turn-on voltage was 6.7 V and the device had a maximum brightness of 260 cd m^{-2} and maximum external quantum efficiency
(EQE) of approximately 1% [224]. Using this strategy, device performance could be enhanced by combining improvements in the quantum efficiency of the emitters with an increase in carrier mobility in order to limit series resistance [225]. Work in these directions with nanoparticle-based systems containing highly emissive phosphors and high-mobility charge transporting moieties is currently in progress. Water-dispersible PF-03d/03e nanoparticles with a cross-linked shell, reported by Tuncel and co-workers [193], realized colour-tunable emission and controllable photometric properties via photochemical cross-linking. They used a re-precipitation method to obtain white-emitting CPNs with diameters of 500 nm, which are prepared in different sizes by varying the concentration of polymer; the emission kinetics are tuned by controlling the shell formation. PF derivatives containing azide groups are selected that can be decomposed under UV light to generate highly reactive species, which greatly facilitate the inter- and intra-cross-linking of polymer chains to form shells. These results show that PF-03e nanoparticles can be used as white luminophores that cover a significant interval of the visible region. The CIE 1931 chromaticity coordinates of the spectra are (0.28, 0.34) at 6 V, (0.27, 0.33) at 6.5 V, (0.26, 0.31) at 7 V, (0.24, 0.23) at 7.5 V and (0.20, 0.10) at 8.5 V. The colour-rendering index of these sources is 66.35, indicating a moderate colour-rendering performance. The cool white light sources are generated by controlling the cross-link time. Demir and co-workers [226] achieved white-emitting PFs with a high colour-rendering index. PF-03e emitters collectively generate a very broad down-converting PL at longer wavelengths across the entirety of the visible spectrum, yielding high colour-rendering indices up to 91. Demir and co-workers [227] investigated the origin of high-quality white light emission from a hybrid organic/inorganic light-emitting diode using azide-functionalized PFs. Foulger and colleagues [228] described the preparation of hybrid nanoparticles composed of poly(2,5 dioctyl-1,4 phenylenevinylene), a green emitter (λ = 505 nm), and PF-01b (PFO), a blue emitter (λ = 417 nm). The aqueous-based nanoparticle dispersion composed of these two CPs is stable to aggregate and can be employed in the construction of PLEDs. The colour characteristics of the EL for the devices can be tuned by exploiting the Forster resonance energy transfer between the polymers within a particle, while suppressing energy transfer between the particles.

The PSCs also have been improved dramatically in the framework of bulk heterojunction, irregular nanoscale architecture. However, one obstacle on the road to commercialization in this area was precisely controlled phase separation of the D/A material in active single thin films. Blended CPNs are excellent model systems for understanding bulk heterojunction interface characteristics, and have also demonstrated promise for optoelectronic and sensing applications [62]. For this purpose, Scherf and co-workers [62] constructed the first PSCs based on nanoparticles to control multi-component phase separation at the nanoscale [62]. Preliminary studies on nanoparticles containing a blend of PF-05 (PFB) and PF-04b (F8BT) revealed that the efficiency of PSCs based on these particles is not dependent on the solvent used in the mini-emulsion process. An EQE of approximately 4% is attained for a device made from polymer-blended nanoparticles containing PF-05 (PFB) and PF-04b (F8BT) at a weight ratio of 1:2 in each individual nanosphere. Neher and co-workers [105] continually studied the effects of different ratios of PF-05 (PFB) and PF-04b (F8BT) on solar cell efficiency under a fixed length scale of phase separation. They presented a detailed discussion on the properties of PSCs based on polymer nanoparticles. Two different types of mixing in intra-particles or among inter-particles were compared. As a result, they found that an EQE of approximately 4% was obtained for a device made from intraparticles containing PF-05 (PFB) and PF-04b (F8BT) at a weight ratio of 1:2 in each individual nanosphere. Dastoor and co-workers [229] investigated multi-layered PSCs using a water-based, PF-based nanocomposite particle suspension as printing ink. They checked the effect of surfactant on performance, revealing successful migration away from the particle interface. The nanoparticles were fabricated from 1:1 blends [230]. They investigated the blending of nanoparticles with a z-average particle size of 51.9 ± 1.3 nm using SEM and DLS. They optimized the polymer domain size to maximize both charge separation and transport. The EQEs of the five-layer nanoparticulate devices were approximately twice those obtained for bulk PF-05 (PFB)/PF-04b (F8BT) blends [231] and significantly greater than those presented
previously for PF-based CPN devices. The most efficient five-layer nanoparticle devices with the configuration of ITO/PODET: PSS/PF-05 (PFB) and PF-04b (F8BT) nanoparticles/Al exhibited a power conversion efficiency (PCE) of 0.39% with an open-circuit voltage ($V_{oc}$) of 0.77 (0.37), $J_{sc}$ (mA cm$^{-2}$) of 1.81 (0.16), fill factor (FF) of 0.28 (0.26) and PCE of photovoltaic cells under AM1.5 illumination. They proved that tone can manipulate the composition of core–shell nanoparticles, which enables effective electron and hole transport. For a comparison of the integrated short circuit currents obtained from the EQE spectra with the short circuit currents obtained under AM1.5 conditions, the devices had $V_{oc}$ (V) of 1.09 (1.16), $J_{sc}$ (mA cm$^{-2}$) of 0.70 (0.63), FF of 0.27 (0.25) and PCE (%) of 0.20 (0.18). They demonstrated that it is now possible to build PF PSC devices from aqueous dispersions of nanoparticles that are more efficient than the corresponding bulk heterojunction devices by controlling both nanoparticle morphology and interparticle interactions.

(b) Polyfluorene-based one-dimensional nanostructures

A variety of PF derivatives that have been integrated into one-dimensional nanowires, nanofibres and nanotubes are outlined in figure 5. Various top-down and bottom-up methods such as nanoimprinting lithography (NIL) [248,249], DPN [250], electrospinning, AAO hard template methods, soft template methods and molecular assembly methods have been exploited by several groups such as List and co-workers, Jenekhe and co-workers, Chen and co-workers, Pisignano and co-workers, Redmond and co-workers as well as others. The nanopatterned and/or aligned one-dimensional nanostructures of PFs prove to be favourable for the polarized luminescence, optical subwavelength and lasing emission behaviours by means of electromagnetic confinement. PFs nanofibres and nanowires have been applied to nanophotonic devices, or thin-film devices, such as field-effect transistors (FETs), photodetectors, nanowires lasers and PLEDs, have been fabricated by the use of nanowire thin films, exhibiting excellent properties.

Electrospinning techniques have been developed for the fabrication of these PF nanofibres. Although this method is a simple and powerful tool for producing inorganic or polyolefin nanofibres, they are still faced with some problems because of the requirement for viscosity. The key factors that should be considered include high molecular weight, suitable solvents or blending matrices for the electrospinning process. Jenekhe and co-workers [232] first exploited PFO (PF-01b) binary composite nanofibres with the blends of MEH-PPV through a coaxial two-capillary spinneret. They found the content of MEH-PPV to be up to 44%, in which smooth nanofibres with diameters of 100–500 nm can be obtained, with either core–shell structures or continuous bundles according to TEM and SEM characterizations. In terms of PFO (PF-01b) with PVP (poly(vinylpyrrolidone)), undesirable short fibres are obtained only via co-electrospinning after the extraction of PVP in ethanol. Chen and co-workers [235] reported that benzyl triethylammonium chloride helps in the formation of uniform PFO (PF-01b)/PMMA fibres with an optimized salt concentration of 3 wt% using poly(methyl methacrylate) (PMMA) as the blending host. Porous nanofibres with diameters ranging from 250 to 750 nm have a core of PFO (PF-01b) and shell of PMMA using a single-capillary spinneret. The desirable nanofibres of PF-20 (PFQ)/PMMA, F8BT (PF-04a)/PMMA and PF-21 (PFTP)/PMMA can also be obtained under similar conditions. The molecular design can change the solubility and polarity of PFs, which leads to the variation in the microstructure of nanofibres. Rod–coil copolymers have the benefit of molecular weight or viscosity being high enough to improve the quality of the nanofibres. This group employed electrospun nanofibres of a series of fluorene-based rod–coil di- or triblock copolymers, including PF-24, PF31-36, that have reversible thermo-responsive luminescence characteristics, suggesting their potential use as sensor materials [241–243,251]. They found that the electrospun fibres of PFO (PF-01b)/PMMA have a core–shell structure but that the periodic aggregate domains in the fibres for PF-24/PMMA have additional cationic groups [236]. However, single-component fully CP nanofibres without any assistance from inert hosts are still challenging to explore. Pisignano and co-workers [60] obtained insights into using non-solvents with a high boiling point and dielectric constant, which improves
Figure 5. The chemical molecular structures of oligo- or PFs for nanofibres or nanowires: PF-19 from [61]; PF-20-25 from [60,232–238]; PF-26 from [60]; PF-27 from [239]; PF-28-30 from [240]; PF-28-30 from [240]; PF-29 from [241]; PF-29 from [242]; PF-36 from [243]; PF-37-39 from [244]; PF-40-41 from [245]; PF-42 from [246]; and PF-44-47 from [247].

Figure 5. The chemical molecular structures of oligo- or PFs for nanofibres or nanowires: PF-19 from [61]; PF-20-25 from [60,232–238]; PF-26 from [60]; PF-27 from [239]; PF-28-30 from [240]; PF-28-30 from [240]; PF-29 from [241]; PF-29 from [242]; PF-36 from [243]; PF-37-39 from [244]; PF-40-41 from [245]; PF-42 from [246]; and PF-44-47 from [247].

their processability, facilitating the realization of single-component CP fibres using electrostatic spinning. Also, the polymer side-groups can increase the steric hindrance and the conformational plasticity of viscous solutions. They chose the mixed solvents dimethyl sulfoxide and THF with a 1:15 v/v relative concentration to obtain electrosprun nanofibres of PF-22, PF-26 and F8BT (figure 6), with diameters ranging from 75 nm to 5 \( \mu m \).

To overcome the limitations of the electrospinning method, PF nanowires without any inert components have been fabricated via alternative hard template methods. AAO templates are another simple, low-cost and effective method for one-dimensional nanostructures with...
Figure 5. (Continued.)

the special apparatus to generate PFs nanowires that were reported by Redmond and co-workers [17,61,252–255]. A representative PF-19 (F8T2) nanowire has an average length of 15 μm and diameter of 200 nm. PFO (PF-01b) nanowires produced via melt-assisted pore template wetting exhibit semicrystalline morphology states with diameters of approximately 300 nm, lengths of up to several micrometres and well-defined end faces. Redmond and co-workers [253] modified a method that was called solution-assisted template wetting to acquire a PFO (PF-01b) nanowire with tailored pronounced β-phase morphology and a mean nanowire diameter of 232 nm. They investigated the β-phase nanowires of PFO (PF-01b) with strong axially polarized nanowire emission and measured the dichroic ratio to be up to 8.9 [256]. This versatile method is suitable for not only nanowires of various PFs such as PFO (PF-01b) and F8T2 (PF-19)
but also their nanotubes, in addition to the fluorene/anthracene copolymer [257] poly(N-vinylcarbazole) (PVK) and small-molecule pentacenes. PFO (PF-01b)-aligned nanotube arrays have a close packed density of $10^9 \text{ tubes cm}^{-2}$ by melt-assisted template wetting. Discrete individual nanotubes have diameters of 260 nm and wall thicknesses of 50 nm, in which polymer chains exhibit axial orientation and intrachain reorientation from the amorphous state to $\beta$-phase conformations, according to the joint characterization of optical spectroscopy, Raman spectra, XRD and polarization resolved PL [254]. However, there are rare explorations using other hard templates for polymer semiconductor one-dimensional nanostructures.

Soft templates not only enable the assembly of nanoparticles, but also are an alternative to nanowires or nanofibres. However, there are rare examples of PF nanowires or nanofibres being fabricated by this method. The selective functional surfactants or bioactive molecules are key to realizing controllable nanowires. PF nanowires of PF-27 have been organized via biomolecular templates such as DNA and amyloid proteins, which were employed by Inganas and co-workers [239]. PF-27 nanowires have the feature of in situ surface functionalization with DNA or amyloid, which has advantages such as biocompatibility over other methods.

Molecular assembly is a collection of promising chemical methods to generate PF nanowires. Until now, polymer semiconductors have had the ability to self-assemble into nanowires from solution. Masuhara and co-workers [258] enable hairy-rod PF2/6 (PF-01c) without any other non-covalent moieties to assemble into ordered fibril-like nanowires by the use of a laser beam on a glass substrate. Traiphol et al. [259] investigated the effects of concentration, substrate and solvent on the formation of PF2/6 (PF-01c) nanoribbons. The local structures and dimensions of the nanoribbons significantly vary with the type of solvent onto the SiO$_x$/Si substrate. The use of non-polar toluene as a solvent leads to the growth of nanoribbons with rather uniform width and height. The increase in solvent polarity and evaporation rate causes an increase in nanoribbon dimensions. Oligo- or PF-based rod–coil diblock copolymers of PF-37-42 have been observed to form nanowires and nanofibres with widths of several 10 nm, and chain packing in the assembled entities has been studied by AFM, XRD and theoretical modelling [244,245,259–265]. Rod–coil co-PFs of PF-42 enable morphological transformation through the variation of coil–segment fractions and the amount of immiscible solvent [246]. Recently, nanowire thin films have been obtained via nanoscale phase separation of fully conjugated block copolymers such as PF-28, 29 [266]. Supramolecular functionalization makes rod–coil block copolymers favourable as controllable and well-defined nanofibres. Chen and co-workers [267] reported the morphological transformation of rod–coil poly[2,7-(9,9-dihexylfluorene)]-$b$-poly (4-vinylpyridine) (PF-$b$-P4VP) from nanoparticles to nanowires. Verduzco and co-workers [247] demonstrated PF-based conjugated block copolymers with the linkage of supramolecular bonds as a potential way to obtain nanowires via supramolecular assembly. All hydrogen-bonded PFs (PF-44-46, PFO-UPy/PS-UPy blends, PFO-UPy/PEG-UPy and P3HT-UPy/PFO-UPy) exhibited submicrometre phase-separation behaviours with well-defined nanofibres. PFO-UPy/PEG-UPy was observed, with phase-separated domains roughly 300 nm in size. Its crystalline fibres have
fibre dimensions approximately 20 nm in width and lengths up to 200 nm. P3HT-UPy/PFO-UPy has similar fibril structures with dimensions of about 30 nm in width and 700 nm in length in P3HT-UPy/PFO-UPy blends.

Nanopatterning and alignment of luminescent nanofibres are the subjects of much research with respect to their wonderful photophysical properties such as polarized emissions for applications of electronics or photonics. Patterned light-emitting polymer nanofibres enable photonic crystals and DFB polarized emitters to be realized on one-dimensional organic nanostructures [60]. Pisignano and co-workers [60] exploited room-temperature nanoimprint lithography to generate imprinting of periodic nanofibres of PF-22, 26. In addition, the aligned electrospun fibres represent a strategic route to enhance the optical—electrical—magnetic sensitivity with potential application in sensors and actuators. The method of producing aligned nanofibres is the key technique that should be addressed. Several methods have been explored, including the use of an AFM tip, a rotating bobbin or drum technique, a two-strip collector and rectangular-frame metal electrodes. Chen and co-workers [236] used the mechanical stretching forces associated with electrospinning techniques to produce aligned nanofibres of PFO (PF-01b)/PMMA and aligned electrospun fibres of PF-34 (PF0t)/PMMA successfully. Dielectrophoretic self-assembly has been exploited to align PFO (PF-01b) nanofibres, which is described by Redmond and co-workers [268].

By carefully choosing the molecular structure of the PFs, nanofibres can generate full colour emissions [235]. Electrospun nanofibres of PFO (PF-1b)/PMMA exhibited blue emission of 440 nm, of PF-20 (PFQ)/PMMA green emission of 483 nm, of F8BT (PF-04a)/PMMA yellow emission of 540 nm and of PF-21 (PFPT)/PMMA red emission of 674 nm. They have enhanced luminescence characteristics according to the corresponding spin-coated films. Phase-separation behaviours in electrostatic spun fibres are obviously different from those of the spin-coating thin films, facilitating the set-up of new tuning tools for optical properties. Jenekhe and co-workers [232] found reduced efficiency of energy transfer from PFO (PF-01b) to MEH-PPV in blended nanofibres compared with bulk thin films, which is in sharp contrast to the blended nanofibres of MEH-PPV/poly(3-hexylthiophene-2,5-diyl) (P3HT). Blending nanofibres gives broad white light emission in the 400–650 nm region when the 28% and 50% blends occur. Electronic absorption spectra suggest more extended and oriented conformation along the fibre axis of both PFO (PF-01b) and PPV chains and better π—electron delocalization [232]. The solvent and composition also significantly affect the morphology and photophysical properties of electrospun nanofibres, together with internal waveguiding performance. Chen et al. [269] investigated ternary blending nanofibres produced from PFO (PF-01b)/poly(2,3-dibutoxy-1,4-phenylene vinylene) (DB-PPV)/PMMA using a single-capillary spinneret. An ellipsoidal domain for DB-PPV (10–40 nm) and fibre-like PFO (20–40 nm) in the PMMA was observed using chloroform, while both DB-PPV (10–20 nm) and PFO (20–30 nm) exhibited fibre-like properties using chlorobenzene when larger phase separation limited FRET. The emission colours from blue to red enable flexible achievement by controlling the electrospinning nanocomposites of PFs as hosts [234]. Nanofibre nanocomposites are an ideal platform to achieve controllable Förster-type energy transfer for white light-emitting devices. Achieving tunable white PL emission colour by changing the composition and controlling the degree of energy transfer was also demonstrated. White colour nanofibres of organic/inorganic hybrid materials have been electrospun by blending PF derivative PF-25 with organic dye-modified zeolite [233,238]. Polarization emission is an advantage of nanofibres with potential application in molecular light sources. Pisignano and co-workers [237] developed F8BT (PF-04a) nanofibres imprinted with a grating, with period matching having enabled an increase in the polarization ratio up to a factor of 2.4. PL polarization ratios of F8BT (PF-04a) fibres are increased up to a factor of 5 by the selection of THF solvents [270]. Alignment of the nanowires also resulted in the improvement of polarized emission. PF-34 (PF0t)/PMMA aligned nanofibres had polarized steady-state luminescence with a polarized ratio as high as 4, much higher than the non-woven electrospun fibres or spin-coated film [236]. It should be noted that the values are lower by about one order of magnitude and are still lagging behind the desirable oriented PFO (with values of up to 51).
Polymer semiconductor nanowires are of increasing interest with regard to nanoelectronics, nanophotonics, textile electronics and devices, and thin-film devices. Fluorene-based one-dimensional nanostructures have been explored for organic nanodevices such as organic FETs, photodetectors, optical waveguides, amplifiers and nanowire lasers, as well as thin-film PLEDs. Cavallini et al. [271] demonstrated that crystalline nanostripes of oligofluorene (PF-30) using nanolithography have obviously higher charge mobility than those in evaporated or spin-coated films. PF-30 nanowires have a field-effect hole mobility of $5 \times 10^{-5} \text{ cm}^2(\text{V s})^{-1}$. Redmond et al. [17] fabricated single-nanowire photodetectors with responsivities of approximately $0.4 \text{ mA W}^{-1}$ and an EQE of approximately 0.1%. The performances are comparable to those in single-inorganic-nanowire devices. Polymer semiconductor nanowires are fascinating waveguide structures with strong confinement. PF-based nanowires have enabled the achievement of optically pumped lasers by means of microcavity effects. Redmond and co-workers [61,255] showed that PFO (PF-01b) nanowires are suitable for application in active waveguiding devices, Fabry–Pérot microcavity and optically pumped lasers owing to their high solid-state luminescence quantum yield of up to 60% and large stimulated emission cross sections (approx. $10^{-15} \text{ cm}^2$). They achieved the first observation of optically pumped lasing in single nanowires of PFO (PF-01b) with single-mode excitonic laser action with a 0–1 emission peak (450–460 nm) and full width at half maximum (FWHM) of 1.4 nm (figure 7). When the excited energy of the laser ($355 \text{ nm, } 0.7 \text{ ns, } 1.25 \text{ kHz}$) is more than the energy threshold of 100 nJ (2.8 mJ cm$^{-2}$), nanowire lasers of PFO (PF-01b) exhibited stimulated emission with a super-linear increase of tip emission intensity versus pump energy. The threshold gain ($g_{th}$) was between 4100 and 2800 cm$^{-1}$,
similar to the stimulated emission in PFO (PF-01b) thin films. Pisignano and co-workers [60] exploited PF electrospun nanofibres for application in nanoscale optics. They assessed their waveguiding performance and emission tenability in the whole visible range and demonstrated the enhancement of the fibre forward emission. The propagation loss of waveguiding capability of PF-23 (F8BT) had a loss coefficient $\gamma$ of $3 \times 10^2 \text{ cm}^{-1}$, which is lower than the values reported for semicrystalline PFO (PF-01b) nanowires [61] and thin films (greater than $2 \times 10^3 \text{ cm}^{-1}$). PFO (PF-01b) nanowire thin films have been used for electrochemiluminescence (ECL) to investigate the mechanisms of charge carrier reactions [253]. Thin-film light-emitting electrochemical cells of PFO (PF-01b) nanowires exhibited ECL spectra with clearly resolved emission peaks at 444, 467 and 490 nm, consistent with the feature of pronounced PFO (PF-01b) $\beta$-phase morphology. PLEDs with a configuration of ITO/PEDOT: PSS/PFO (PF-01b) nanowire/Al have emission peaks at 439, 467, 497 and 530 nm, and a distinct turn-on voltage at approximately 3.4 V. Vohra et al. [83] fabricated thin-film PLEDs with a configuration of glass/ITO/PEDOT: PSS/F8BT (PF-04)-PEO fibres/PVK/Al, in which the active layer was F8BT (PF-04) nanofibres covered by PEO with a thickness of 100 nm and width of 700 nm. Devices with annealed nanofibres have a brightness of 2300 cd m$^{-2}$ at 6 V and a maximum EQE of 1.1%.

Beyond nanoparticles and one-dimensional nanostructures such as nanowires, nanorods and nanotubes, topologically complex nanostructures of PFs have scarcely been reported, such as nano-helical configurations that resemble the configuration of DNA, branched nanofibres [272], Y-junctions [273], tetrapods, nano-rings [274] and dendritic superstructures that enable new functions and are of growing interest in the science and technology of organic devices. The reason is a lack of effective methodology to develop complex nanostructures, which are lagging behind their inorganic counterparts as they pose severe challenges. One solution to overcome these problems is to explore hierarchical self-assembly of supramolecular CPs, amphiphilic semiconducting polymers, rod–coil copolymers or fully conjugated block copolymers. The flexible transformation of PF nanostructures can be realized by the variation of segment fractions and special solvents. However, solution-phase self-assembly of CPs is not yet fully understood, and the supramolecular self-assembly of such pre-formed building blocks into extended nanostructures by the bottom-up approach remains a great challenge. Complex nano/microstructures require the introduction of top-down nanofabrication techniques such as photolithography, electron beam lithography [275,276], NIL, lithographically controlled wetting, SPL, DPN and proton beam writing. Room-temperature NIL enables DFB structures to be obtained for CP lasers [248,277]. The hierarchical superstructures could be acquired by the development of hybrid methods [278,279].

4. Summary and outlook

In summary, nano approaches offer a powerful toolbox to advance all aspects of organic devices, thereby bringing about an impressive revolution in organic electronics after molecular/polymer engineering and supramolecular approaches. CP nanostructures make organic devices more and more miniaturized, low cost, convenient, robust and functional. PF-based zero- and one-dimensional nanostructures have been fabricated and synthesized by a series of top-down and bottom-up methods, such as mini-emulsion, emulsion polymerization, re-precipitation and supramolecular assembly for nanoparticles; and electrospinning, AAO hard template, protein soft templates and molecular assembly for nanofibres, nanotubes or nanowires. PF-based nanoparticles make PLEDs and PSCs increasingly low cost, eco-friendly and suitable for high-throughput roll-to-roll or inkjet printing techniques. Diverse multi-component PF-based nanoparticles enable the easy and flexible achievement of tunable RGB colour, near infrared and white colour emission through the working of nanoparticle chemistry and nanocomposites. One-dimensional nanofibres or nanowires have extended the application of polymer semiconductors into nanoelectronics or nano-optoelectronics, as in FETs and photodetectors; nanophotonics, as in optical waveguide and nanowire lasers; textile electronics; and thin-film devices. PF-based nanofibres exhibit fascinating controllable energy transfer, polarized luminescence,
subwavelength optical features, such as microcavity effects, as well as solution processing. However, it is still a challenge to precisely control the sizes, shapes beyond a sphere, multiple composition, crystal phases and complex architectures such as Janus superstructures, which are key to making the ideal models to understand the structure–function relationship and to fabricating state-of-the-art advanced nanodevices. It should be noted that this framework is suitable for not only templates for other CPs, but also π-stacked polymers or macromolecules, which is a parallel area with a conjugated counterpart in plastics electronics.

Under the frameworks of the self-similar epistemology and cross-reference scenario between molecular and social societies, the ultimate structures of organic devices will possess the chemically precise and accurate molecular architectures that are waiting to be built up by molecular architects, as shown in figure 8. Electrons and their currents in these two-terminal framework devices resemble humans and their society, with humans living in building blocks and being inspired by external stimuli. Organic nanotechnology is a bridge between the molecular and macroscopic worlds, making organic devices more regular, rational, simple and controllable. Molecular engineering allows for the possibilities to produce covalent organic nanobuilding blocks with more well-defined structures, with more robustness, more functionality and selectivity. Molecular architects are facing many opportunities for the synergistic combination of top-down nano-manipulation with bottom-up molecular engineering techniques [280]. Semiconducting polymer nanoscale architectures have more emergent aspects that are waiting to be explored under the strategy of molecular manufacturing. Organic frame chemistry and materials will renew organic nanomolecular semiconductors [281,282]. Organic nanotechnology will keep pace with the trends of the awareness era, marked with intelligent robots that will be developed as a result of the information age owing to the extreme contradictions and requirements in human society. In view of this, robotic-directed science and technology will have many fascinating research areas that include recognition and artificial intelligence, information science and technology, mechanical manufacturing, electronic science and technology, materials and chemistry, physics and mathematics as well as philosophy. Under the impetus of plastics electronics, the future trends in organic mechatronics probably will be one frontier to progress with regard to organic intelligent robotics, as represented by the four element entities of matter–energy–information–awareness [31].

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References


