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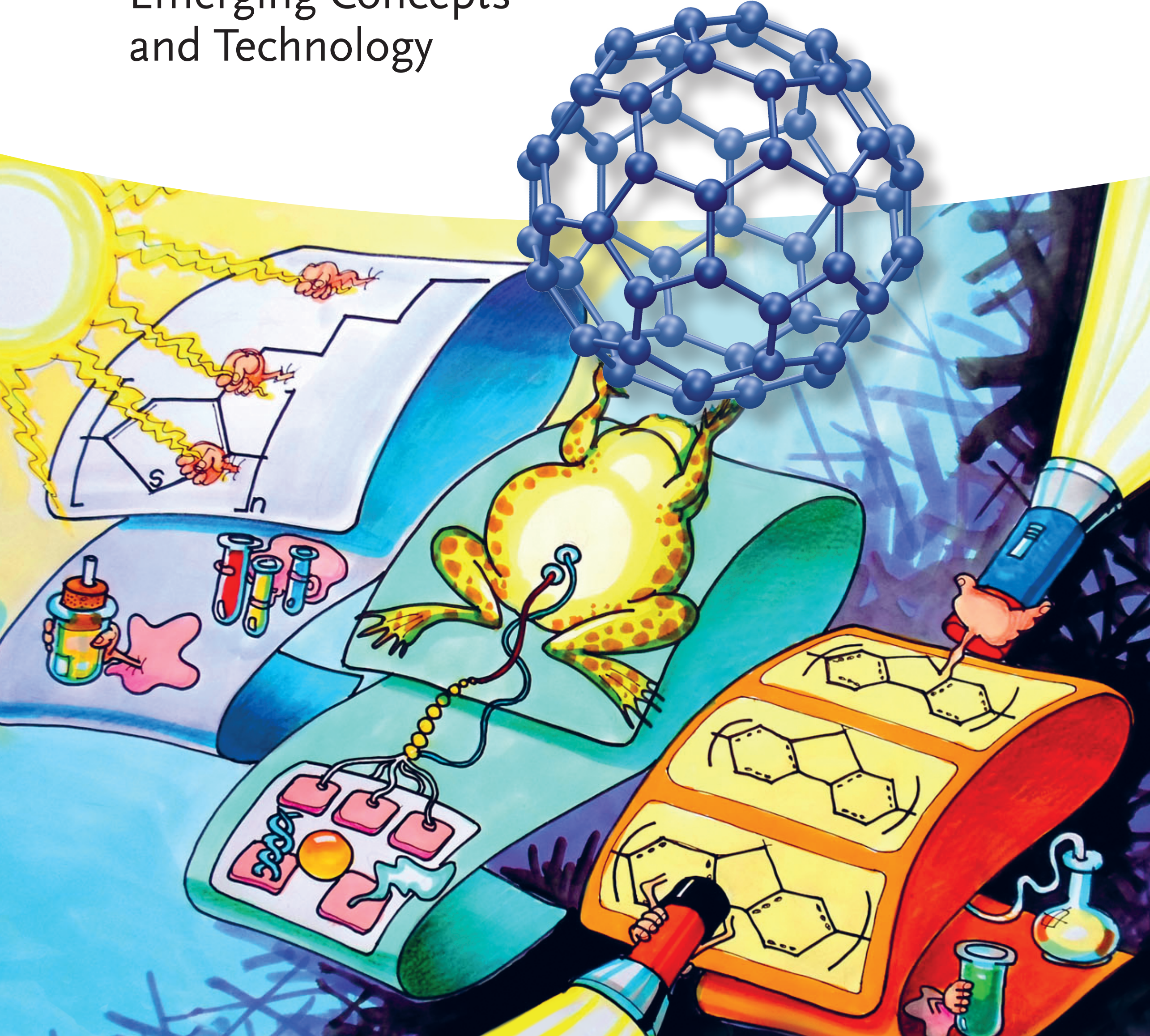
Organic Electronics

Emerging Concepts and Technology



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Contents

Preface

The goal of organic electronics, which uses thin films or single crystals of organic π-conjugated materials as semiconductors, is to enable technologies for large-area, mechanically flexible, and low-cost electronics. Intense research and development in organic electronics started in the 1990s, with the first demonstrations of light-emitting diodes, transistors, and solar cells based on organic semiconductors. Nowadays, organic electronic devices are becoming ubiquitous in our society. Displays based on organic light-emitting diodes are found in televisions, mobile phones, car stereos, and portable media players. Other devices, such as electrophoretic displays for electronic book readers and organic transistors for radio frequency identification tags, are expected to enter the market in the near future. In addition to the well-developed areas described above, exciting applications are envisaged in the field of organic bioelectronics, which takes advantage of the mixed ionic/electronic transport that can take place in organic electronic materials.

The purpose of this book is to cover recent developments in emerging topics of organic electronics, such as organic bioelectronics, spintronics, light-emitting transistors, and advanced structural analysis, to provide a large readership with a general overview of the enormous potential of organic electronics. We are convinced that the topics covered in this book will gain much momentum in the coming years.

This book will benefit different categories of readers such as graduate students, postdoctoral fellows, experienced researchers in organic electronics, and scientists active in fields close to organic electronics such as organic chemistry, bio and bio-inspired materials, and thin film engineering. Although rather focused on novel aspects, and therefore not offering a complete picture of organic electronics, we believe this book will become a useful reference for graduate students and postdoctoral researchers. For educational purposes, the book will constitute a perfect complement for academic graduate courses in organic electronics.

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Nanoparticles Based on π-Conjugated Polymers and Oligomers for Optoelectronic, Imaging, and Sensing Applications: The Illustrative Example of Fluorene-Based Polymers and Oligomers

Irén Fischer and Albertus P.H.J. Schenning

1.1

Introduction

Nanoparticles based on π-conjugated polymers and oligomers have received considerable attention for optoelectronic and biological applications due to their small size, simple preparation method, and their tunable and exceptional fluorescent properties [1–7]. Nanoparticles are appealing for optoelectronic devices such as organic light-emitting diodes (OLEDs) [8,9], organic photovoltaic devices (OPVs) [10], and organic field-effect transistors (OFETs) [11] to gain control over the morphology of the active layer that plays a crucial role in the device performance. For example, in OPVs exciton dissociation occurs only at the interface of the donor and acceptor materials. Therefore, it is critical to control the donor–acceptor interface in order to optimize charge separation and charge migration to the electrodes [12,13]. The most common way to increase the interfacial area is by blending donor and acceptor materials making bulk heterojunction solar cells [14]. This necessary control over nanomorphology can be achieved by using nanoparticles to generate the active layer of the device [15]. Furthermore, the development of stable and fluorescent nanoparticles is interesting when combined with printing techniques to achieve large-area patterned active layers [6].

Nanoparticles based on π-conjugated systems show excellent fluorescence brightness, high absorption cross sections, and high effective chromophore density, which makes them attractive for imaging and sensing applications [1–5]. Fluorescence-based methods for probing biomolecular interactions at level of single molecules have resulted in significant advances in understanding various biochemical processes [16]. But there is currently a lack of dyes that are sufficiently bright and photostable to overcome the background fluorescence and scattering within the cell [17,18]. In addition, the photostability of the chromophore is critical for single-molecule imaging and tracking [19].

Here, an overview of the recent advances of nanoparticles based on fluorene oligomers and polymers is presented. We have chosen the illustrative example of fluorene-based π-conjugated systems to restrict this chapter but still show all aspects

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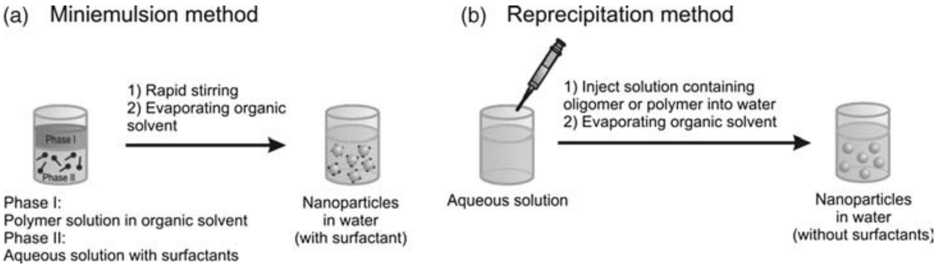

Figure 1.1 Schematic representations of the preparation of the nanoparticles (a) by using the miniemulsion method and (b) by using the reprecipitation method.

of nanoparticles based on π-conjugated polymers and oligomers. The fluorene moiety is a very favorable building block for π-conjugated systems because of its high and tunable fluorescence, high charge carrier mobility, and good solubility in organic solvents [20–24]. Furthermore, a large variety of fluorene-based polymers and oligomers can be created due to easy synthesis procedures [25,26]. Most organic nanoparticles for optoelectronic applications are prepared by the so-called miniemulsion method (Figure 1.1a) [27,28]. In this process, the π-conjugated system is dissolved in an organic solvent and then added to an aqueous solution containing surfactants. Stable nanoparticles are formed after sonication and evaporation of the organic solvent. The diameter of the nanoparticles can be reduced by increasing the surfactant concentration in the water solution or decreasing the polymer concentration in the organic solvent [29]. Nanoparticles in water for imaging and sensing applications are mostly prepared by the reprecipitation method in which a π-conjugated polymer or oligomer dissolved in THF solution is rapidly injected into water and subsequently sonicated (Figure 1.1b) [30,31].

Fluorescence energy transfer (FRET) in nanoparticles is an important tool to study their nanomorphologies for solar cells [32–34], tune their colors in OLEDs [35,36], and exploit them for sensing applications [37,38]. For an efficient energy transfer process, the emission spectrum of the donor should overlap with the absorption spectrum of the acceptor and the donor and acceptor need to be in close proximity, as the process highly depends on the distance between the donor and the acceptor (Eq. (1.1)) [39].

The Förster energy transfer rate (k_{DA}) for an individual donor–acceptor pair separated by a distance R is given by

$$k_{\mathrm{DA}}(t) = \frac{1}{\tau_{\mathrm{D}}}\left(\frac{R_0}{R}\right)^6, \tag{1.1}$$

where R_0 is the Förster radius and τ_{D} is the natural lifetime of the donor in the absence of acceptors.

In the first part of this chapter, nanoparticles based on fluorene polymers and their application in optoelectronic devices, biosensing, and imaging will be discussed. In the second part, nanoparticles based on fluorene oligomers will be described. Water-soluble fluorene-based polyelectrolytes [40–43] and so-called hybrid nanoparticles [44,45] are beyond the scope of this chapter.

1.2
Nanoparticles Based on Fluorene Polymers

1.2.1
Optoelectronic Applications

1.2.1.1 Characterization of Nanoparticles

Most polyfluorene-based organic nanoparticles for optoelectronic applications are prepared by the so-called miniemulsion method [27,28]. The sizes of polyfluorene-based particles prepared by this method range typically between 50 and 500 nm [29]. Recently, small particles were prepared by *in situ* metal-catalyzed polymerization of a bifunctional diacetylene fluorene in aqueous miniemulsion yielding particles of around 30 nm [46]. This new method provides access to stable particles with sizes small enough for the preparation of ultrathin films [47], and is not limited to polymers with a high solubility in organic solvents [46]. The emission wavelength of the polyfluorene nanoparticles in comparison with the polymer in chloroform was shifted from blue to green and the quantum yield was decreased, which is normally seen for π-conjugated polymer films (Figure 1.2). Interestingly, copolymerization of a perylene diimide dye equipped with two acetylene functionalities with the fluorene moiety could also be carried out *in situ* in the aqueous solution. The emission wavelength could be varied from blue for the pure fluorene polymer to red for 2% incorporated perylene diimide dye in the copolymer due to (partial) energy transfer. The emission spectra and the quantum yields of the nanoparticles in aqueous solution were found to resemble the solution-cast film

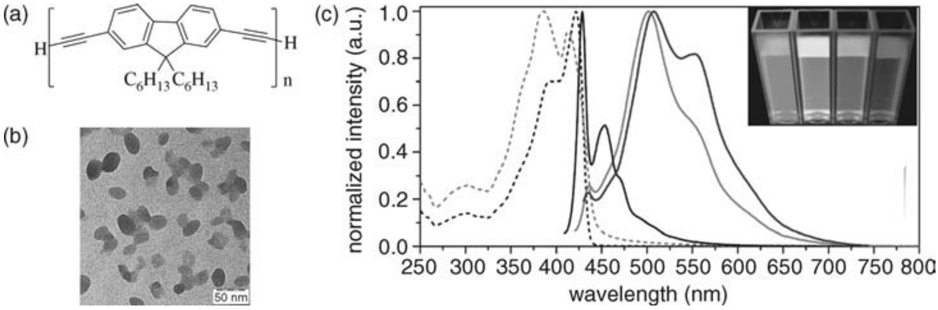

Figure 1.2 (a) Chemical structure of the fluorene–acetylene polymer. (b) Transmission electron microscopy (TEM) image of fluorene nanoparticles. (c) Absorption (dashed line) and fluorescence (solid line) spectra of aqueous dispersions (light gray), chloroform solutions (black), and thin films (dark gray) of polyfluorene nanoparticles. The inset shows the photograph of dilute polymer dispersion with 0, 0.1, 0.2, and 0.8% incorporated perylene diimide dye. (Reprinted with permission from Ref. [46]. Copyright 2009, American Chemical Society.)

samples showing that the morphology in the nanoparticles is not changed during drop casting (Figure 1.2) [46].

1.2.1.2 **Nanoparticle Film Fabrication and Characterization**

Nanoparticle films deposited by spin coating onto glass substrates have been studied by Landfester *et al.* [48]. Layers of polyfluorene (PF2/6 and PF11112, Figure 1.3a) nanoparticles that were formed via the miniemulsion method were prepared. For particles of polyfluorenes (PF2/6), the particle structure can be well detected with atomic force microscopy (AFM) in the deposited layers. Annealing above the glass transition temperature resulted in coalescence of the particles, and larger structures were formed [48]. Due to the low glass transition temperature of PF11112, the particles combined and formed larger domains on the substrate already at room temperature. This method allows the construction of multilayer structures composed of alternating layers formed from an organic solvent and layers formed by deposition of aqueous polymer nanoparticles. In such a way, multilayers can be prepared from polymers that are soluble in the same solvent [48,49].

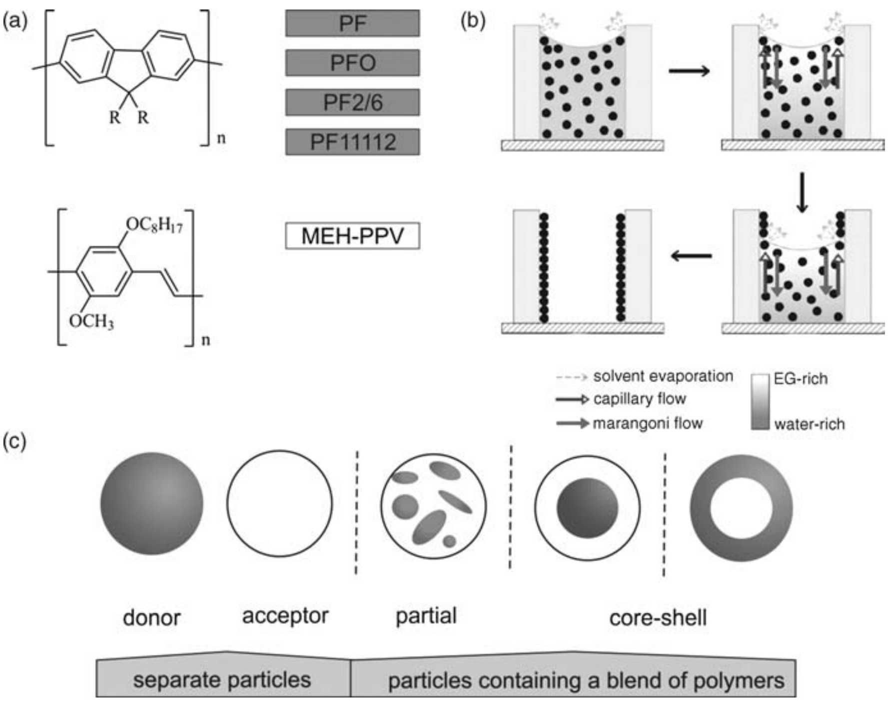

Figure 1.3 (a) Chemical structures of polyfluorenes (PF (R = hexyl), PFO (R = octyl), PF2/6 (R = 2-ethylhexyl), and PF11112 (R = 3,7,11-trimethyldodecyl)) and MEH-PPV. (b) Scheme for the solvent evaporation-induced self-assembly of organic particles on the substrates to form films from an aqueous solution containing ethylene glycol. (Reprinted with permission from Ref. [50]. Copyright 2010, American Chemical Society.) (c) Scheme to illustrate separate, partial, and core–shell nanoparticle structures.

The optical properties of poly(9,9-dihexyl)fluorene (PF) nanoparticle films have been studied in detail [51]. Via a so-called reprecipitation method, a rapid injection into water of a π-conjugated polymer dissolved in THF solution followed by sonication resulted in small nanoparticle (diameter 30 nm) dispersions, prepared without using surfactant. The nanoparticles were drop casted on a substrate to form a thin film and the film thickness was measured with AFM to be 35 nm for the nanoparticles, which corresponds to the diameters of the particles. Remarkably, the fluorescence quantum yield for films of the nanoparticles was $\Phi_{PL} = 68\%$, while drop-casted thin films of PF lacking nanoparticles displayed only a quantum yield in the range of $\Phi_{PL} = 23–44\%$, depending on the film thickness. Interestingly, the redshift in the emission wavelength is greatly reduced for the PF nanoparticle films compared to PF films. Nanoparticles offer an attractive alternative route to fabricate films compared to the conventional solution route since nanoparticles in the film state reveal almost identical properties than in the dispersion [51].

Ordered organic nanoparticle films of PFO and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) can be obtained by solvent evaporation-induced self-assembly (Figure 1.3a and b) [50]. By proper introduction of a second solvent such as ethylene glycol into the solution, a so-called Marangoni flow in the opposite direction of the capillary flow can be achieved, counterbalancing the transportation of nanoparticles toward the contact line by the capillary flow (Figure 1.3b) [50]. Consequently, the self-assembly of nanoparticles on the substrate is controlled by the nanoparticle–substrate and nanoparticle–nanoparticle interactions [50]. During the drying process of the solution, a uniform film of the nanoparticles can be achieved on the substrate without any additives. The technique could be an alternative for conventional thin-film processing techniques such as spin coating that require viscous solutions.

1.2.1.3 **OLEDs**

Mixed organic nanoparticles can be prepared either as separate polymer particles or as particles containing a blend of polymers (Figure 1.3c). Tuncel and coworkers constructed different bicomponent nanoparticles, separate, mixed, and core–shell particles, composed of PF as an energy donor and MEH-PPV as an energy acceptor (Figure 1.3) to investigate which morphology resulted in efficient energy transfer [35]. Separate particles are achieved by the preparation of PF and MEH-PPV nanoparticles separately using the reprecipitation method and subsequent mixing. Due to the long distance in solution between donor and acceptor particles, no energy transfer is observed. Mixed particles are made by mixing PF and MEH-PPV prior to nanoparticle formation. In this case, the donor and acceptor polymers are at close distance and energy transfer is observed. Core–shell particles of PF and MEH-PPV were prepared by first injecting one polymer stock solution into water and subsequently adding the second polymer. The formation of core–shell nanoparticles was verified by the observation of energy transfer. Interestingly, the highest energy transfer efficiency (up to 35%) was observed for the core–shell structure in which the PF is located at the periphery of the nanoparticles.

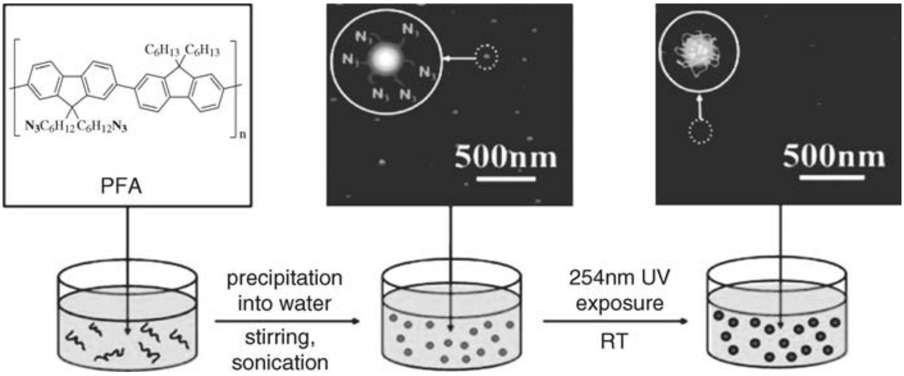

Figure 1.4 Schematic representation of the preparation of the shelled architecture of the conjugated polymer nanoparticles exhibiting white emission. (Reprinted with permission from Ref. [52]. Copyright 2011, American Chemical Society.)

Organic dyes have also been used as energy acceptors in order to tune the emission wavelength of aqueous self-assembled nanoparticles [36]. Negatively charged polyfluorene nanoparticles (PF2/6) made by the miniemulsion method using an ionic surfactant showed effective excitation energy transfer from the nanoparticles to surface-bound cationic fluorescent rhodamine dye. Such studies not only are interesting for tuning the emission wavelength in optoelectronic applications such as OLEDs but could also be interesting for future sensing in water [36]. White-emitting conjugated polymer nanoparticle dispersions have been used for application in OLEDs [52]. Polyfluorene nanoparticles containing azide as cross-linkable group have been made by the reprecipitation method (Figure 1.4). After cross-linking with UV light, mechanically stable particles with a cross-linked shell were obtained in which the core and shell have different energy levels, with the core emitting in the blue and the shell emitting green-yellow [52]. By controlling the shell formation, the energy transfer process between the energy donor core and energy acceptor shell can be tuned to generate white emissive particles. Based on these particles, an OLED could be constructed showing white light electroluminescence.

OLEDs have also been made based on PFO and poly(*p*-phenylene vinylene) (POPPV, Figure 1.5) blended nanoparticles by Foulger and coworkers in which

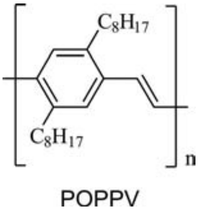

Figure 1.5 Chemical structure of POPPV.

color tuning of the electroluminescence from blue to green was achieved by energy transfer from the PFO energy donor to the POPPV energy acceptor [53]. To the nanoparticle dispersion, a binder (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), PEDOT:PSS) was added to prevent electrical shorts before spin coating onto the transparent indium tin oxide (ITO) anode forming the active layer of the OLED (Figure 1.5) [54]. The inherent lack of solubility of POPPV in organic solvents has hampered its application in devices but by creating mixed particles this polymer could be applied in OLEDs [53]. These nanoparticle dispersions can most likely be printed into devices through high-throughput manufacturing techniques (e.g., roll-to-roll printing) [53].

To study the fluorescence of F8BT particles, Barbara and coworkers measured electrogenerated chemiluminescence of single immobilized nanoparticles [55] by using a newly developed single-molecule spectroelectrochemistry technique [56]. Electrochemiluminescence from 25 nm sized immobilized nanoparticles was observed, which shows that this technique serves as a powerful method to obtain information about particle environments [55].

It is well known that the blue emission of polyfluorenes as an emission layer in OLEDs frequently changes into a yellow emission band at 500–550 nm, as a result of fluorenone defects [57–59]. This property has been used to create yellow emissive nanoparticles based on fluorene copolymers in which fluorenone moieties were introduced [60,61]. Nanoparticles could be prepared in aqueous solution of 2,7-poly(9,9-dialkylfluorene-*co*-fluorenone) (PFFO) by the miniemulsion process using cellulose acetate butyrate (CAB) as a surfactant (Figure 1.6a) [60]. Interestingly, nanoparticles with four main size classes, namely, 500, 150, 50, and 5 nm, could be produced showing a size-dependent emission with a yellow to blue color shift (Figure 1.6b). Most likely in the smaller particles, the formation of the yellow excimer emission is suppressed due to reduction of the interaction and order between the polymer chains [60]. The PFFO nanoparticles were revealed to be suitable for inkjet printing and successfully used to print photoluminescent patterns using a very low amount of PFFO (Figure 1.6c) [61]. This nanoparticle suspension shows the properties of inks commonly used in inkjet printing processes as well as being easy to handle and use as a stable, nonhazardous solvent [61].

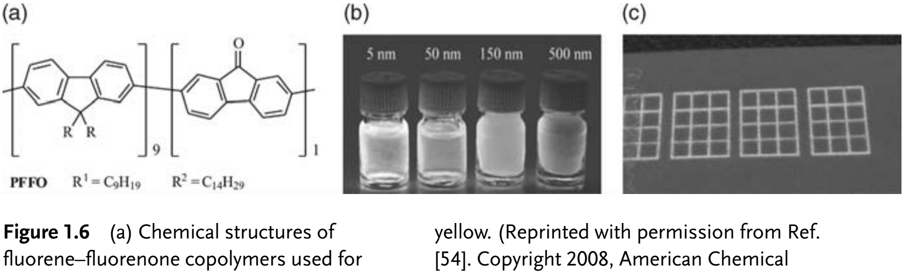

Figure 1.6 (a) Chemical structures of fluorene–fluorenone copolymers used for nanoparticle preparation (R^1 [60]) and inkjet printing (R^2 [61]). (b) Nanoparticle size-dependent emission varying from blue to yellow. (Reprinted with permission from Ref. [54]. Copyright 2008, American Chemical Society.) (c) Inkjet printed patterns under UV light. (Reproduced with permission from Ref. [61].)

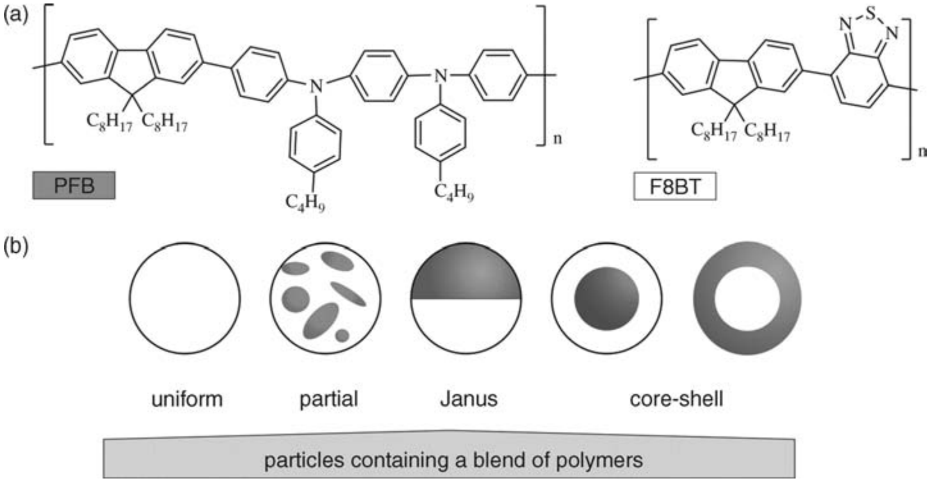

Figure 1.7 (a) Chemical structures of PFB (donor) and F8BT (acceptor). (b) Schematic illustration of the nanomorphology of particles containing a blend of polymers. The mixed nanoparticles could form uniform mixed, partial mixed, Janus-like, or core–shell structures.

1.2.1.4 **Solar Cell Applications**

As we have seen, particles containing a blend of polymers can have different nanomorphologies such as uniform mixed, partial mixed, Janus-like, or core–shell supramolecular structures (Figure 1.7). The nanomorphology of poly(9,9-dioctylfluorene-*co*-bis-*N*,*N*-(4-butylphenyl)-bis-*N*,*N*-phenyl-1,4-phenylenediamine) (PFB) and F8BT nanoparticles containing a blend of polymers (weight ratio 1 : 1) prepared via the miniemulsion method has been extensively studied [32–34]. These polymers were chosen because photoinduced charge transfer occurs between F8BT (electron acceptor) and PFB (electron donor), which is an important process in organic solar cell devices that highly depend on the local environment [62–65]. This intermixing of these two polymers can be studied by interchain exciplex emission. Neher and coworkers investigated thin films of mixed particles by photoluminescence (PL) spectroscopy detecting the presence of PFB-rich and F8BT-rich domains [32]. It was concluded that PFB/F8BT blend nanoparticles form Janus-like structures. Later, direct imaging of these nanoparticles could be achieved by scanning transmission X-ray microscopy (STXM) compositional maps [33]. These studies indicated that these nanoparticles separate into core–shell nanomorphology, with an F8BT-rich core and a PFB-rich shell (Figure 1.7) [33]. Recently, Gao and Grey prepared small ($\sim$58 nm) and large ($\sim$100 nm) PFB/F8BT nanoparticles that were studied by single-particle PL spectroscopy to determine the particle morphology [34]. Size-independent efficient energy transfer from PFB (donor) and F8BT (acceptor) in PFB/F8BT blend nanoparticles was observed but no exciplex emission. These data suggest that the nanoparticles phase segregated in domains with the sizes of $\sim$20–40 nm [34].

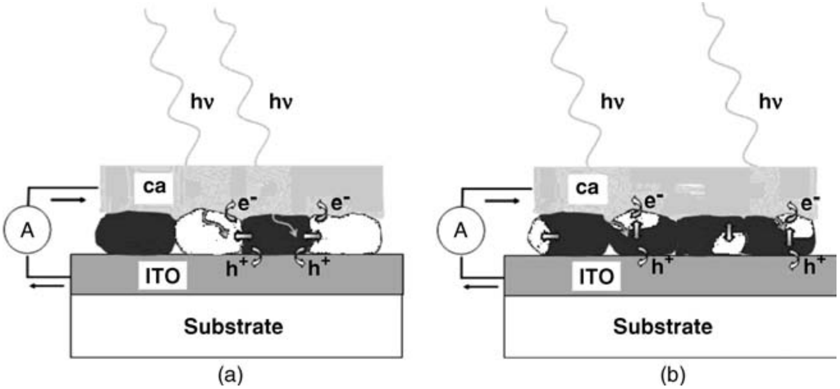

Figure 1.8 Schemes of solar cell devices based on separate particles (a) and a mix of polymers in each particle (b). (Reprinted with permission with Ref. [67]. Copyright 2004, American Chemical Society.)

The first solar cell containing polyfluorene nanoparticles was prepared by Neher and coworkers [66]. PFB (electron donor)/F8BT (electron acceptor) mixed nanoparticles from 1 : 1 weight mixtures in chloroform or xylene were prepared via the miniemulsion method. For the organic solar cells, the polymer dispersions were spin coated onto glass that was covered with transparent ITO electrode. Afterward, the Ca/Al cathode was evaporated onto the particle monolayer. Remarkably, the external quantum efficiency (EQE) was almost unaffected by the solvent from which the particles were synthesized. Furthermore, the efficiency of 1.7% is among the best reported for 1 : 1 weight ratio of PBT/F8BT layers spin coated from xylene, but below the efficiency reported [64] for layers spin coated from chloroform [66]. In a more detailed study, solar cell devices containing separate particles and mixed particles of PFB/F8BT in a weight range of 5 : 1 to 1 : 5 have also been studied (Figure 1.8) [67]. Particles retained their spherical shape after spin coating, leading to low efficiency in the solar cells. Therefore, the spin-coated layers were annealed to 150 °C for 2 h, which led to the flattening of nanoparticles and a more homogeneous surface [67]. Solar cells prepared from annealed separate nanoparticle dispersions showed the highest efficiency of approximately 2% with the highest concentration of PFB (weight ratio 5 : 1). Interestingly, solar cells from mixed PFB/F8BT particles revealed efficiency of up to 4% for F8BT-rich mixed particles (weight ratio 1 : 2). This efficiency is among the highest value reported for PFB/F8BT blended solar cells [64]. The authors propose that the differences between separate and mixed particles in device performance are due to the different dimensions of phase separation in layers of separate or mixed particles (Figure 1.8). In layers of separate particles, the efficiency is determined by the probability that excitons are formed at the interface of two phases and dissociate into free carriers [67]. Due to the rather small exciton diffusion length of the F8BT phase, the F8BT polymer particles need to be surrounded and in direct contact by PFB particles to ensure dissociation of

F8BT excitons [67]. In contrast, the efficiency of solar cells containing both polymers in mixed nanoparticles is determined by the probability that both kinds of charge carriers on a mixed particle can be extracted to the corresponding electrode [67].

Snaith and Friend have developed multilayer structures for OPVs of polymers that are originally soluble in a common solvent by depositing PFB/F8BT (weight ratio 1 : 1) nanoparticles and spin coating them with a thin polymer film of F8BT [68]. Highly uniform films of nanoparticles on ITO glass were obtained by the so-called electroplating method. Unfortunately, the device performance was only 0.4% due to the excess of isolating surfactant blocking charge transfer.

1.2.2
Imaging and Sensing Applications

1.2.2.1 Characterization of Nanoparticles

Nanoparticles in water for imaging and sensing applications are mostly prepared by the reprecipitation method in which a π-conjugated polymer dissolved in THF solution is rapidly injected into water and subsequently sonicated [30,31]. During nanoparticle formation, a competition exists between aggregation and chain collapse of the π-conjugated polymers. Therefore, the size of the nanoparticles, from a few nm (a single, collapsed conjugated polymer chain) to 50 nm, can be controlled by the polymer concentration in THF solution [69]. For example, F8BT nanoparticles possess a diameter of around 10 nm after injection of a diluted stock solution and around 25 nm after injection of a concentrated stock solution [70]. The absorption of the nanoparticles is usually blueshifted compared to a solution of the polymer in a good solvent due to an overall decrease in conjugation length upon nanoparticle formation (Figure 1.9). The fluorescence spectra of the nanoparticles

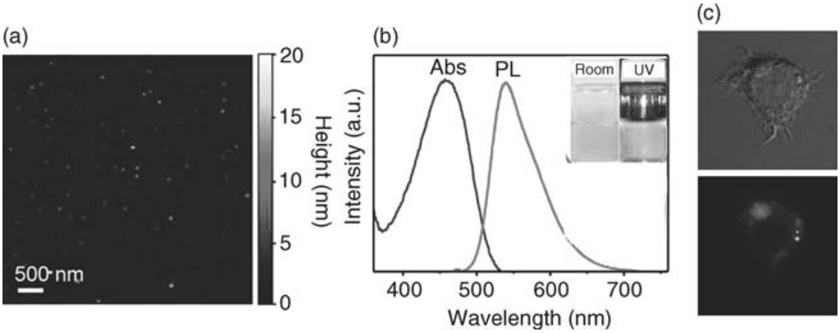

Figure 1.9 (a) AFM image of F8BT nanoparticles. (b) The absorption and emission ($\lambda_{ex} = 475$ nm) spectra of F8BT nanoparticles suspended in water. The inset shows the nanoparticles suspended in water under room light and UV light illumination. (Reprinted with permission from Ref. [71]. Copyright 2009, American Chemical Society.) (c) Differential interference contrast (DIC) image (top) and fluorescence image (bottom) of macrophage cells with F8BT. (Reprinted with permission from Ref. [70]. Copyright 2008, American Chemical Society.)