

# Self-assembly of insulated molecular wires of a water-soluble cationic PPV and anionic dendrons

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**Insulated molecular wires of poly(phenylenevinylene) (PPV) were prepared by wrapping the conjugated backbones with dendrons through a noncovalent approach. It was found that electrostatic interaction between the quaternary ammonium groups of PPV-1 and the carboxylate moieties in dendrons induced the packing of dendrons along PPV-1 conjugated backbones. Absorption and emission spectroscopic examinations in solution and solid film indicated that the PPV-1 backbones adopted a more planar and isolated conformation in the complexes. Furthermore, interchain interactions in the complexes could be greatly reduced, improving the quantum yield of PPV-1.**

insulated molecular wires, self-assembly, water-soluble conjugated polymer, dendron

In recent years, conjugated polymers have received increasing attention in view of their unique physical properties arising from the  $\pi$ -electron delocalization structure and potential applications to flexible electronic devices<sup>[1]</sup>. Given the relatively high charge mobility along the individual polymer chain, conjugated polymers are gaining commercial importance in photovoltaic cells<sup>[2,3]</sup>, light-emitting diodes<sup>[4]</sup>, photodetectors<sup>[5]</sup>, thin film field-effect transistors<sup>[6]</sup> and sensors<sup>[7-9]</sup>. However, the interchain interactions between the conjugated polymers would modify the optical and electronic behavior, thus having unfavorable effects on applications. This makes it a challenging subject to find facile and convenient approaches to decrease and block these interactions. Conjugated polymers are often portrayed as “molecular wires”<sup>[10]</sup>, and the structure described as “insulated molecular wires” (IMWs) has attracted considerable interest for accessing the goal described above. The approaches to this structure include the encapsulation of conjugated backbones<sup>[10,11]</sup> through a protective sheath, preventing cross-talk or short-circuit between conjugated polymer chains and enhancing the chemical stability and luminescence efficiency<sup>[10-12]</sup>. Hitherto, several intriguing strategies have been developed to fabri-

cate IMWs, thus illustrating the broad appeal of this concept.

One strategy for IMWs is threading the conjugated  $\pi$  system through insulating macrocycles to form a pseudopolyrotaxane or polyrotaxane. The macrocycles used as the hosts for encapsulating are cyclophanes<sup>[13]</sup>, cyclodextrins<sup>[14-16]</sup> and ring-shaped inorganic nanocluster<sup>[17]</sup>. The rod-like guests could be inserted into the cavities provided by these materials and the threading process is driven by the noncovalent interactions between the host and guest. An alternative strategy for fabricating IMWs is to wrap the conjugated backbone with natural helical polymers to form polymer-polymer complexes. The helical polymers would provide axial cavities along the helix and encapsulate the molecular wires inside the cavities. However, most examples of this kind of complexes involve just two natural polysaccharides: amylose<sup>[18]</sup> and schizophyllan<sup>[19,20]</sup>.

Dendronized conjugated polymer is also a typical form of the IMWs structure, in which the conjugated

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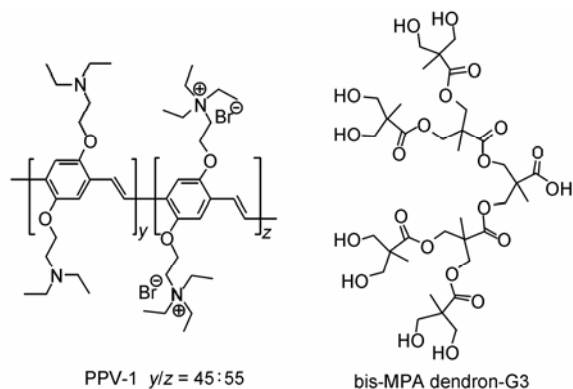
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backbones are encapsulated by covalent attaching dendrons laterally to its backbones. Therefore, dendrons with lots of regularly branched substituents densely pack along the conjugated backbones, and stretch out to generate a molecular cylinder. For example, dendronized poly(p-phenylenes)<sup>[21]</sup>, polyfluorenes<sup>[22,23]</sup>, poly(phenylenevinyls)<sup>[24–26]</sup>, poly(phenyleneethynylenes)<sup>[12,27]</sup> and polythiophenes<sup>[28]</sup> have been prepared by using various chemical synthesis methods. However, for this strategy, the synthesis process is tedious and often limited by the steric hindrance of the dendrons.

Herein, we present a facile strategy to prepare IMWs by wrapping the conjugated polymer with dendrons through noncovalent interactions. To study the viability of this approach, a water-soluble cationic conjugated polymer, poly{2,5-bis[3-(N,N,N-triethylammonium)-1-oxapropyl]-1,4-phenylenevinylene}-dibromide (PPV-1) was chosen as a model molecular wire, and an anionic dendron, polyester-8-hydroxyl-1-carboxyl bis-MPA dendron, generation 3 (bis-MPA dendron-G3), was used as the protective shell. The chemical structures of PPV-1 and the dendron are shown in Figure 1. It is expected that upon the introduction of bis-MPA dendron-G3 into aqueous PPV-1 solution, electrostatic interaction between these two components results in the packing of dendrons along the PPV-1 conjugated backbones, leading to the formation of IMWs.



**Figure 1** Chemical structures of PPV-1 and bis-MPA dendron-G3.

## 1 Experimental

### 1.1 Materials

Polyester-8 (and 16)-hydroxyl-1-carboxyl bis-MPA dendron, generation 3 (and 5) (bis-MPA dendron-G3, bis-MPA dendron-G5) were purchased from Aldrich and used as received. THF was purified by distillation from

sodium in the presence of benzophenone. All other chemicals were commercially obtained with satisfied purity and used as received. Poly{2,5-bis[3-(N,N,N-triethylammonium)-1-oxapropyl]-1,4-phenylenevinylene}-dibromide (PPV-1) was synthesized following the reported procedures<sup>[29]</sup>.

### 1.2 Synthesis

**1,4-Bis[(N,N-diethylamino)hydrochloride]-1-oxapropyl]-2,5-dichloromethane-benzene (monomer).** Briefly, 2-chlorotriethylamine hydrochloride (10.8 g, 0.062 mol) and anhydrous  $K_2CO_3$  (35.0 g, 0.25 mol) were added to 150 mL acetone. After purging with Ar for 15 min, 1,4-dihydroquinone (3.0 g, 0.027 mol) was added, and then the reaction mixture was refluxed for 3 d with stirring under  $N_2$  atmosphere. After cooling to room temperature, the precipitates were filtered off, and the resulting filtrate was evaporated under reduced pressure. The obtained residue was poured into water, and extracted with ether, and then the organic fractions were washed with aqueous NaOH solution (10%), water and brine, and dried with  $MgSO_4$ . A pale-yellow oil product 1,4-bis[(N,N-diethylamino)-1-oxapropyl]-benzene (**1**) was obtained after evaporating the solvent. Yield: 89%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.81 (s, 4H, Ar-H), 4.00 (t, 4H,  $OCH_2CH_2N$ ), 2.84 (t, 4H,  $OCH_2CH_2N$ ), 2.62 (q, 8H,  $N(CH_2CH_3)_2$ ), 1.05 (t, 12H,  $N(CH_2CH_3)_2$ ).

Concentrated HCl (20 mL) was added to the paraformaldehyde (1.38 g), **1** (2.53 g, 8.22 mmol) and acetic acid (10 mL) mixture at  $0^\circ C$ . The solution was saturated with HCl gas for 30 min. Then the mixture was stirred at room temperature for 15 h. After evaporating the solvents under the reduced pressure, the residue was then added to 50 mL methanol, filtered and washed with ethyl acetate. Then the solid was recrystallized with ethanol and the monomer was obtained. Yield: 34%.  $^1H$  NMR ( $D_2O$ ):  $\delta$  6.94 (s, 2H, Ar-H), 4.52 (s, 4H,  $CH_2Cl$ ), 4.26 (t, 4H,  $OCH_2CH_2N$ ), 3.50 (t, 4H,  $OCH_2CH_2N$ ), 3.20 (q, 8H,  $NH^+(CH_2CH_3)_2 \cdot Cl^-$ ), 1.20 (t, 12H,  $NH^+(CH_2CH_3)_2 \cdot Cl^-$ ). Anal. Calcd. for  $C_{20}H_{36}Cl_4N_2O_2$  (478.32) (%): C, 50.22; H, 7.59; N, 5.86. Found (%): C, 49.88; H, 7.61; N, 5.85.

**Poly{2,5-bis[3-(N,N,N-triethylammonium)-1-oxapropyl]-1,4-phenylenevinylene}-dibromide (PPV-1).** *t*-BuOK (2.85 g, 0.025 mol) in THF (25 mL) was added dropwise at room temperature to 100 mL THF solution of the monomer (1.41 g, 2.95 mmol). The mixture was stirred under  $N_2$  atmosphere for 24 h to yield a shiny red solution. Then, the reaction mixture was evaporated un-

der reduced pressure, and the residue was poured into water. The solid was filtered and washed with distilled water repeatedly. After drying under vacuum, orange-red product poly{2,5-bis [3-(N,N,N-diethylamino)-1-oxapropyl]-1,4-phenylenevinylene} (PPV) was obtained. Anal. Calcd. for  $(C_{20}H_{32}N_2O_2)_n [(332.48)_n]$  (%): C, 72.25; H, 9.70; N, 8.43. Found (%): C, 70.31; H, 9.38; N, 8.08. And then the polymer was fractionized successively with THF and chloroform through Soxhlet extraction. To prepare water-soluble PPV derivatives, the component extracted from chloroform was quarternized by adding EtBr into PPV solution in chloroform. The mixture was stirred at 46°C for 5 d and reddish precipitate was afforded. The solid was filtered, washed with ether and dried under vacuum, and PPV-1 was obtained.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  7.4–7.2 (Ar-H and trans vinyl protons), 4.7 ( $\text{OCH}_2\text{CH}_2\text{N}$ , overlapping  $\text{H}_2\text{O}$ ), 3.75 ( $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.37 ( $\text{NCH}_2\text{CH}_3$ ), 1.21 ( $\text{N}^+(\text{CH}_2\text{CH}_3)_3\cdot\text{Br}^-$ ), 1.18 ( $\text{N}(\text{CH}_2\text{CH}_3)_2$ ). The level of quarternization was estimated to be 55% by  $^1\text{H}$  NMR spectrum (The integrated area proportion of  $\delta$  1.18/ $\delta$  1.21 = 43/80).

### 1.3 Complex preparation

Aqueous stock solutions of PPV-1 and dendron were prepared in pure water ( $1.5 \times 10^{-3}$ ,  $2.5 \times 10^{-3}$  and  $2.5 \times 10^{-3}$  mol/L for PPV-1, bis-MPA dendron-G3 and bis-MPA dendron-G5, respectively). The dendron/PPV-1 complexes were prepared by adding aqueous dendron stock solution into a dilute aqueous PPV-1 solution with the given concentration, and then the mixed solution was incubated for 6 h at room temperature. The apparent pH value of the complex solution is around 4.5.

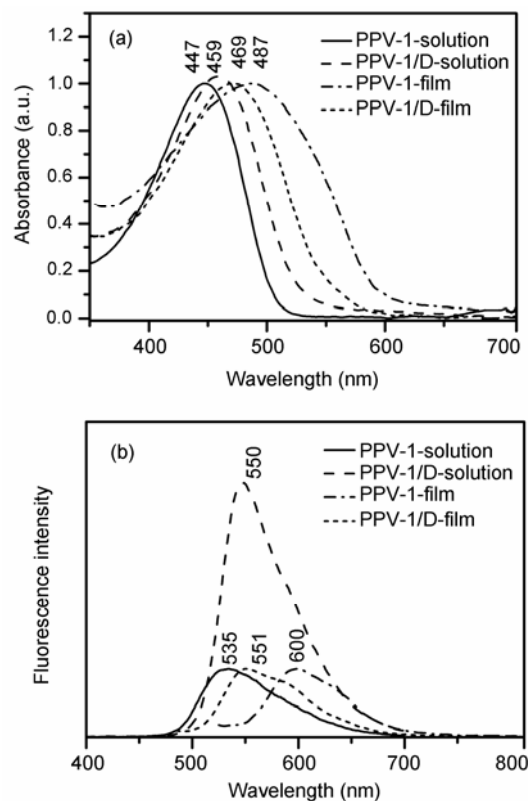
### 1.4 Measurements

UV-Vis absorption and emission spectra were collected by using a Hitachi 3010 UV-Vis spectrometer and an LS 55 fluorescence spectrometer (PerkinElmer), respectively.  $^1\text{H}$  NMR spectra were carried out on a JNM-ECA600 spectrometer (JEOL). Elemental analyses were performed on a CE-440 elemental analyzer.

## 2 Results and discussion

### 2.1 Absorption and emission spectra of PPV-1/bis-MPA dendron-G3 complexes

Figure 2 compares the absorption and emission spectra between PPV-1 and its mixture with bis-MPA dendron-G3 in solutions and solid films. In the absence of



**Figure 2** Absorption (a) and emission (b) spectra of PPV-1 and its mixture with bis-MPA dendron-G3 in aqueous solutions and solid films. Excited wavelength: 366 nm.  $[\text{PPV-1}] = 3.0 \times 10^{-4}$  mol/L,  $[\text{bis-MPA dendron-G3}] = 3.0 \times 10^{-3}$  mol/L. The absorption and emission intensity of the solid films was normalized to that of PPV-1 in solution for comparison.

bis-MPA dendron-G3, PPV-1 in water exhibits an absorption maximum at 447 nm, which was attributed to the conjugated  $\pi$ -backbone of the polymer. The absorption maximum is red-shifted to 459 nm upon addition of bis-MPA dendron-G3 into PPV-1 solution. The smaller but obvious shift (by 12 nm) is associated with an increase in the effective conjugation length of PPV-1, demonstrating that the interaction between PPV-1 and bis-MPA dendron-G3 will force the PPV-1 backbone to adopt a more planar conformation. Due to the fact that PPV has a relative rigid backbone, the conformation change is relatively smaller in comparison with that of the other more flexible conjugated polymers, such as polythiophene derivative<sup>[19]</sup>.

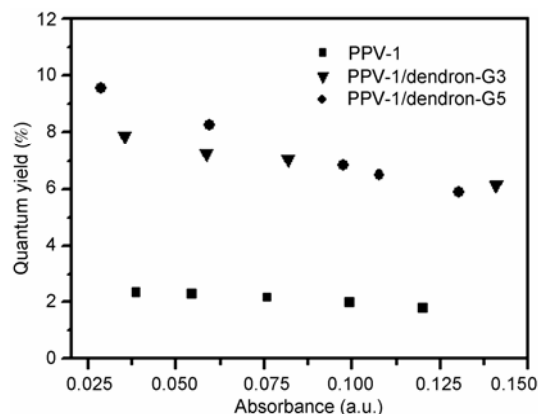
Emission spectra were also recorded to monitor the conformational transition and interchain interaction of the conjugated polymer backbones. As shown in Figure 2(b), upon addition of bis-MPA dendron-G3, an emission maximum of 535 nm is red-shifted to 550 nm, along with a pronounced enhancement in intensity.

These observations indicate that the PPV-1 backbones become more planar and more isolated and the IMW may be formed during the complexation with bis-MPA dendron-G3, resulting in the reduction of interchain interactions. These results are similar to those reported for polysaccharide encapsulated IMWs<sup>[19,20]</sup>.

Comparison of both absorption and emission spectra between PPV-1 and its mixture with bis-MPA dendron-G3 in solutions and solid films further supports the conclusion above. For PPV-1 alone, both absorption and emission maximum in the films show a distinct red shift (by 40 and 65 nm, respectively) in comparison with those of the solutions, suggesting the strong interchain aggregation of PPV-1 in the films. Whereas for the PPV-1/bis-MPA dendron-G3 complex, a slight change between the spectra of the solution and the solid film was detected, especially for emission spectrum with only 1 nm red shift and a slight increase in bandwidth. It is known that for conjugated polymers, there is a strong tendency to form aggregates via  $\pi$ - $\pi$  interactions in the solid state, which will lead to a red shift or low-energy band gap of emission spectrum. However, upon the introduction of bis-MPA dendron-G3, the aggregation of PPV-1 backbones was prohibited by the bulky dendritic substituents even in the solid film, and thus the emission maximum of PPV-1 in the complex film is blue-shifted to 550 nm in comparison with that of pure PPV-1 film (600 nm). The finding clearly demonstrates that PPV-1 is well wrapped by bis-MPA dendron-G3 through electrostatic interaction and thus can reduce the interchain interaction effectively.

## 2.2 Quantum yield of the PPV-1/dendron complexes

As discussed above, the luminescence activity of PPV-1 increases remarkably in the existence of bis-MPA dendron-G3. To quantitatively illustrate the changes of luminescence ability of PPV-1 wrapped with dendrons, the quantum yields ( $\phi_{FL}$ ) of PPV-1 and its complex with bis-MPA dendron-G3 were evaluated by referring to quinine sulfate solution<sup>[30]</sup>. Figure 3 shows the quantum yields of PPV-1 and its complexes with bis-MPA dendron-G3 (G5) in aqueous solutions. It was observed that the quantum yield of PPV-1 alone was extremely low (2.4%) in a dilute solution. In the existence of bis-MPA dendron-G3, the quantum yield of PPV-1 increased dramatically to 7.9%, and stayed at 5.3% even as the solution was concentrated to that with the absorbance of 0.25. These observations indicate that electrostatic interaction



**Figure 3** Fluorescence quantum yields ( $\phi_{FL}$ ) of PPV-1 and its complexes with bis-MPA dendron-G3 and bis-MPA dendron-G5 in aqueous solutions. Excited wavelength: 366 nm. The molar ratios of PPV-1 to bis-MPA dendron-G3 and bis-MPA dendron-G5 are 1:10 and 1:5, respectively.  $[PPV-1] = 5 \times 10^{-6} - 4 \times 10^{-5}$  mol/L.

between the quaternary amino groups of PPV-1 and the carboxylate moieties of the dendrons resulted in efficient wrapping of PPV-1 conjugated backbones with the dendrons, and the formation of a dendron-insulated sheath around the PPV-1 backbones. This kind of interaction can increase the distance between two individual polymer chains remarkably, and thus reduce the interchain interaction, exhibiting the increase of quantum yield.

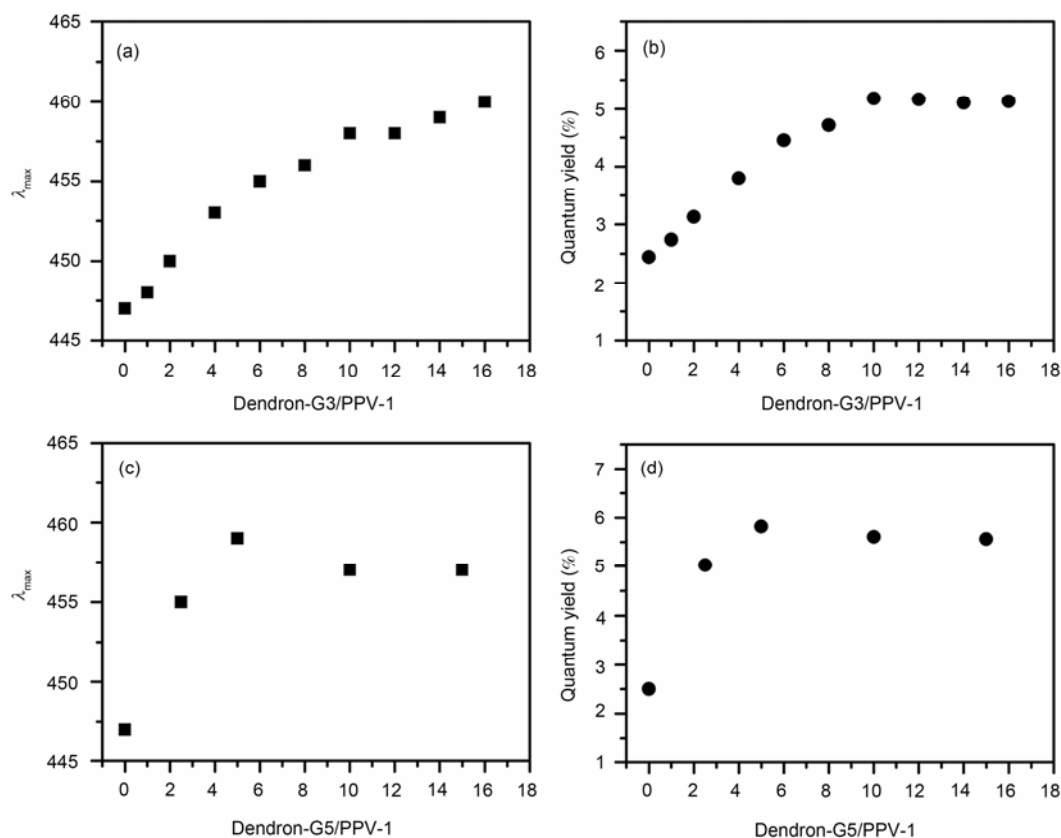
To further confirm this steric hindrance effect of dendrons on the PPV-1 interchain interaction, bis-MPA dendron-G5 with higher generation was also examined. It was found that the quantum yield of PPV-1 in the complex could further increase to 9.5% in a dilute solution even with lower molar ratio of dendron-G5 to PPV-1 (5:1). This result indicates that the larger the size of the dendron, the greater the distance between two individual PPV-1 polymer chains, the weaker the interaction between conjugated polymer chains.

Examinations on the quantum yields of PPV-1 and its complexes in solid films also supported the above conclusion. It was observed that PPV-1 had a quantum yield of 0.52% in the solid film, referring to 9,10-diphenylanthracene ( $2 \times 10^{-3}$  mol/L) in poly(methacrylate) film ( $\phi_{FL} = 0.83$ )<sup>[31]</sup>, whereas in the PPV-1/dendron complexes, the quantum yields were increased to 2.98% (with bis-MPA dendron-G3) and 3.80% (bis-MPA dendron-G5), respectively.

## 2.3 Optimization of the ratio of dendron to PPV-1 in the complexes

In order to characterize the properties of the PPV/den-





**Figure 4** Plots of absorption maximum ( $\lambda_{max}$ ) and fluorescence quantum yield of the bis-MPA dendron-G3/PPV-1 ((a),(b)) and bis-MPA dendron-G5/PPV-1 ((c),(d)) complexes against the molar ratio of dendron to PPV-1. [PPV-1] =  $5 \times 10^{-5}$  mol/L.

dron complexes and find an optimal ratio of dendrons to PPV-1, we screened the absorption and emission spectra of the complexes by keeping PPV-1 in a certain concentration and varying the content of the dendrons. It was found that with increasing concentrations of bis-MPA dendron-G3, the absorption maximum of PPV-1 kept red-shifting from 447 to 460 nm as the molar ratio of dendron to PPV-1 ( $r$ ) changed from 0 to 16 (Figure 4(a)). Simultaneously, the emission maximum was also red-shifted from 535 to 550 nm along with the increase in intensity, which attained a constant maximum value around  $r = 10:1$ . Above the point of  $r = 10:1$ , addition of bis-MPA dendron-G3 did not lead to further changes of the emission spectrum (i.e., the fluorescence quantum yield of the complexes). Therefore,  $r = 10:1$ , beyond the inflexion point shown in Figure 4(b), was chosen for investigating the properties of the complex to insure that

the PPV-1 backbones have been wrapped with bis-MPA dendron-G3 completely. Similarly, the optimal ratio of bis-MPA dendron-G5 to PPV-1 was determined as 5:1, which was lower than that of the bis-MPA dendron-G3/PPV-1 complex, originating from the fact that the bulky size of bis-MPA dendron-G5 was favorable for blocking PPV-1 interchain interaction with respect to bis-MPA dendron-G3.

### 3 Conclusion

In conclusion, we have developed a facile approach to fabricate PPV IMWs by wrapping water-soluble cationic PPV-1 conjugated backbones with anionic bis-MPA dendrons through electrostatic interaction. We hope that this reliable and flexible method based on ionic self-assembly will offer a simple way to the preparation of supramolecular IMWs.

1 Hoeben F J M, Jonkheijm P, Meijer E W, et al. About supramolecular assemblies of  $\pi$ -conjugated systems. *Chem Rev*, 2005, 105: 1491–1546

2 Granström M, Petritsch K, Arias A C, et al. Laminated fabrication of polymeric photovoltaic diodes. *Nature*, 1998, 395: 257–260

3 Günes S, Neugebauer H, Sariciftci N S. Conjugated polymer-based

- organic solar cells. *Chem Rev*, 2007, 107: 1324–1338
- 4 Burroughes J H, Bradley D D C, Brown A R, et al. Light-emitting diodes based on conjugated polymers. *Nature*, 1990, 347: 539–541
- 5 Friend R H, Holmes A B, Bradley D D C, et al. Photodetector device having a semiconductive conjugated polymer. US Patent, US5523555, 1996-6-4
- 6 Dimitrakopoulos C D, Malenfant P R L. Organic thin film transistors for large area electronics. *Adv Mater*, 2002, 14: 99–117
- 7 McQuade D T, Pullen A E, Swager T M. Conjugated polymer-based chemical sensors. *Chem Rev*, 2000, 100: 2537–2574
- 8 Rose A, Zhu Z, Madigan C F, et al. Sensitivity gains in chemosensing by lasing action in organic polymers. *Nature*, 2005, 434: 876–879
- 9 Hatchett D W, Josowicz M. Composites of intrinsically conducting polymers as sensing nanomaterials. *Chem Rev*, 2008, 108: 746–769
- 10 Frampton M J, Anderson H L. Insulated molecular wires. *Angew Chem Int Ed*, 2007, 46: 1028–1064
- 11 Cardin D J. Encapsulated conducting polymers. *Adv Mater*, 2002, 14: 553–563
- 12 Sato T, Jiang D L, Aida T. A blue-luminescent dendritic rod: Poly(phenyleneethynylene) within a light-harvesting dendritic envelope. *J Am Chem Soc*, 1999, 121: 10658–10659
- 13 Zhu S S, Carroll P J, Swager T M. Conducting polymetalloxanes: A supramolecular approach to transition metal ion sensors. *J Am Chem Soc*, 1996, 118: 8713–8714
- 14 Michels J J, O'Connell M J, Anderson H L, et al. Synthesis of conjugated polyrotaxanes. *Chem Eur J*, 2003, 9: 6167–6176
- 15 Terao J, Tang A, Anderson H L, et al. Synthesis of poly(paraphenylenevinylene) rotaxanes by aqueous Suzuki coupling. *Chem Commun*, 2004: 56–57
- 16 Wenz G, Han B H, Müller A. Cyclodextrin rotaxanes and polyrotaxanes. *Chem Rev*, 2006, 106: 782–817
- 17 Alam M A, Kim Y S, Aida T, et al. Directed 1D assembly of a ring-shaped inorganic nanocluster templated by an organic rigid-rod molecule: An inorganic/organic polyseudorotaxane. *Angew Chem Int Ed*, 2008, 47: 2070–2073
- 18 Frampton M J, Claridge T D W, Anderson H L, et al. Amylose-wrapped luminescent conjugated polymers. *Chem Commun*, 2008: 2797–2799
- 19 Li C, Numata M, Shinkai S, et al. Self-assembly of supramolecular chiral insulated molecular wire. *J Am Chem Soc*, 2005, 127: 4548–4549
- 20 Sakurai K, Uezu K, Shinkai S, et al.  $\beta$ -1,3-glucan polysaccharides as novel one-dimensional hosts for DNA/RNA, conjugated polymers and nanoparticles. *Chem Commun*, 2005: 4383–4398
- 21 Stocker W, Karakaya B, Schlter A D, et al. Ordered dendritic nanorods with a poly(p-phenylene) backbone. *J Am Chem Soc*, 1998, 120: 7691–7695
- 22 Marsitzky D, Vestberg R, Carter K R, et al. Self-encapsulation of poly-2,7-fluorenes in a dendrimer matrix. *J Am Chem Soc*, 2001, 123: 6965–6972
- 23 Tang H Z, Fujiki M, Zhang Z B, et al. Nearly pure blue photoluminescent poly{2,7-[9-(3,5-bis(benzyloxy)benzyloxy)benzyl]}-9-(3,6-dioxacyclohexyl)fluorine} in film. *Chem Commun*, 2001: 2426–2427
- 24 Bao Z, Amundson K R, Lovinger A J. Poly(phenylenevinylene)s with dendritic side chains: Synthesis, self-ordering, and liquid crystalline properties. *Macromolecules*, 1998, 31: 8647–8649
- 25 Tang R, Chuai Y, Cheng C, et al. Syntheses and electroluminescence properties of conjugated poly(p-phenylenevinylene) derivatives bearing dendritic pendants. *J Polym Sci Part A*, 2005, 43: 3126–3140
- 26 Kimura M, Sato M, Adachi N, et al. Poly(p-phenylenevinylene)s wrapped with 1,3,5-phenylene-based rigid dendrons. *Chem Mater*, 2007, 19: 2809–2815
- 27 Li W S, Jiang D L, Aida T. Photoluminescence properties of discrete conjugated wires wrapped within dendrimeric envelopes: “Dendrimer effects” on  $\pi$ -electronic conjugation. *Angew Chem Int Ed*, 2004, 43: 2943–2947
- 28 Malenfant P R L, Frchet J M J. Dendrimers as solubilizing groups for conducting polymers: Preparation and characterization of polythiophene functionalized exclusively with aliphatic ether convergent dendrons. *Macromolecules*, 2000, 33: 3634–3640
- 29 Gao Y, Wang C C, Wang H L, et al. Conjugated polyelectrolytes with pH-dependent conformations and optical properties. *Langmuir*, 2007, 23: 7760–7767
- 30 Lakowicz J R. *Principles of Fluorescence Spectroscopy*. 3rd ed. Heidelberg: Springer-Verlag, 2006
- 31 Bai H, Li C, Shi G Q. Pyrenyl excimers induced by the crystallization of POSS moieties: Spectroscopic studies and sensing applications. *ChemPhysChem*, 2008, 9: 1908–1913