JOURNAL OF
Materials
CHEMISTRY

Synthesis and properties of crown ether containing poly(*p*-phenylenevinylene)

Hongwei Liu,[a] Shuai Wang,[a] Yanhong Luo,[a] Wenhong Tang,[a,b] Gui Yu,[a] Lin Li,[a] Chuanfu Chen,[a] Yunqi Liu[a] and Fu Xi*[a]

[a]*Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: xifu@infoc3.icas.ac.cn; Tel: +86-010-62557907; Fax: +86-010-62559373*
[b]*Department of Chemistry, Jilin University, Jilin 130023, P. R. China*

Received 4th July 2001, Accepted 3rd October 2001
First published as an Advance Article on the web 6th November 2001

A soluble PPV derivative (C-PPV) with high molecular weight, substituted with a crown ether in direct π-conjugation at the 2,3-position, has been synthesized *via* a modified Gilch route in good yield. The double layer LED based on C-PPV (ITO/C-PPV/Alq_3/Al) exhibits a high luminance of $730\ \mathrm{cd\,m^{-2}}$, and emits yellow–green light with an external EL quantum efficiency of 0.04%. The fluorescence attenuation of the polymer solution is found upon K^+, Na^+, or Li^+ binding. The AFM provides high-resolution images of C-PPV in thin films constructed from a very dilute solution in the absence and presence of metal ions. Worm-like images with well-defined width and height are observed only in the presence of K^+, which is in striking contrast to the individual ball shape of C-PPV molecules in the absence of K^+, or in the presence of Na^+, or Li^+. It was also observed that the worm-like images grew longer and longer as the solution of C-PPV in the presence of K^+ stood longer. These unique self-assembling features of the C-PPV molecules may be attributed to the complexation of K^+.

Introduction

Since the discovery of electroluminescence (EL) in poly(*p*-phenylenevinylene) (PPV),[1] conjugated polymers, such as poly(fluorene)s (PFs), poly(*p*-phenylene)s (PPPs), poly(thiophene)s (PTs) and their derivatives, have been extensively studied.[2–7] Their applications are varied in light-emitting diodes (LEDs), photovoltaic diodes, light-emitting electrochemical cells, and laser devices.[2–7] In the last few years, functionalized conjugated polymers have developed into a class of materials capable of detecting a large variety of metal ions, neutral and charged organic species which has potential application for the design of chemical sensors.[8] In particular, conjugated polymers such as poly(thiophene)s and poly(phenyleneethynylene)s bearing molecular recognizing groups, have been well exploited.[8,9] Today, PPV and its derivatives are still the most popular materials used in LEDs. The most commonly used substituents in PPV derivatives are alkoxy,[10,11] silyl[10,14,15] and phenyl[12,13,16,17,18] groups, while crown ether substituted groups are rarely found, except in the recent contributions from Babudri *et al.*[11] They reported the synthesis of low molecular weight poly(2,5-dialkoxy-1,4-phenylenevinylene) polymers with cyclic polyethereal alkoxy chains by a Stille cross-coupling reaction. An ion-selective crown ether is an excellent molecular sensory component.[8,9] Attachment of this group to a PPV does not reduce its basic function, but endows some new properties to the conjugated polymer. Recently, the 2,3-disubstituted derivatives of PPV, which exhibit considerably high performance, have attracted much interest owing to their ability at controlling the electronic properties of PPV *via* steric interaction of the side-substituted groups.[10,17,18] On the basis of all these studies, it is then postulated that PPV with crown ether units in direct π-conjugation at the 2,3-position is expected to exhibit new functional properties based on the electrical conductivity of the main chain and the cation-binding ability of the crown cavity.

In the present work we report the successful synthesis of a soluble PPV substituted with crown ether units in direct π-conjugation at the 2,3-position *via* a modified Gilch route (C-PPV, as shown in Scheme 1). The LED fabricated with C-PPV (ITO/C-PPV/Alq_3/Al) has been investigated. Moreover, the effects of metal cation binding on absorbance and fluorescence spectra, and the morphological structure of the polymer in thin films have also been depicted.

Experimental

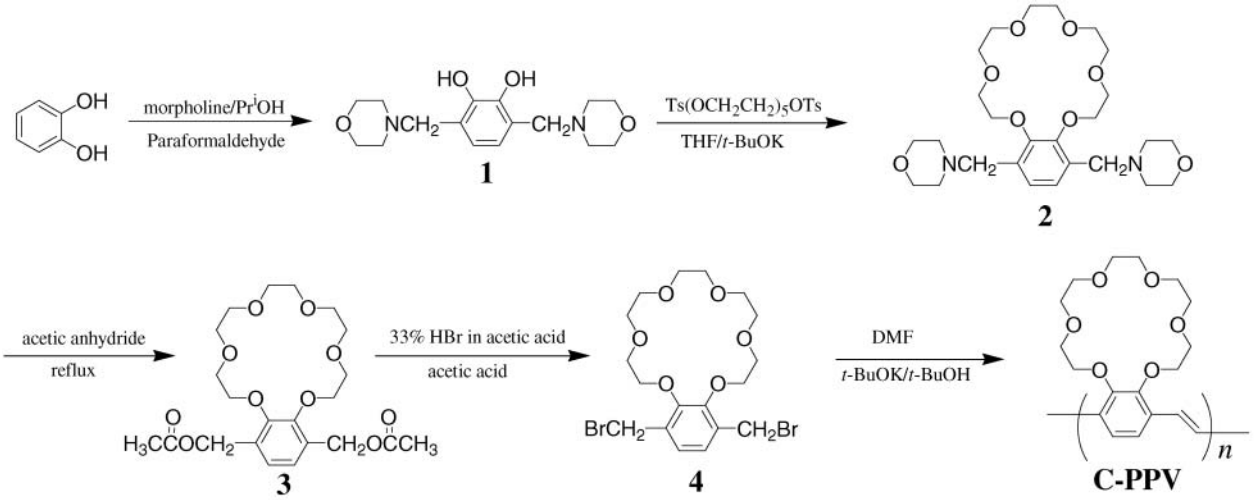
General

THF, DMF and *tert*-butanol were dried before use. All other reagents were used as supplied, without further purification. ^1H NMR spectra were recorded on a UNITY-200 spectrometer. Elemental analyses were measured with a Heraeus CHN-RAPID elemental analyzer. The molecular weight was detected by laser light scattering on DLS-700 and RM-102 instruments ($\lambda = 632.8$ nm, 25 °C in $CHCl_3$). IR spectra were taken on a Bruker EQUINOX55 spectrometer.

Light-emitting diodes (LEDs) were fabricated using C-PPV as emissive material, Alq_3 as an electron-transport layer, and the aluminum as the cathode. C-PPV film was spin-coated onto the ITO substrates (sheet resistance $30\ \Omega/\square$) from a chloroform solution ($2.3\ \mathrm{g\,ml^{-1}}$). The emitting area of the EL devices was $14\ \mathrm{mm^2}$. EL spectra were recorded on a Hitachi F-4500 Fluorescence Spectrophotometer with the LED devices forward biased. The power of EL emission was measured using a Newport 2835-C multifunction optical meter. Photometric units ($\mathrm{cd\ m^{-2}}$) were calculated using the forward output power. Current–voltage characteristics were measured with a Hewlett Packard 4140B semiconductor parameter analyzer. All the measurements were performed under ambient atmosphere at room temperature.

Absorption and PL were studied using a General TU-1201

DOI: 10.1039/b105905j



Scheme 1 Structure and synthesis of crown ether containing conjugated polymer C-PPV.

UV-vis Recording Spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer respectively. The concentration of C-PPV in $CHCl_3$ is 5 μM, and of the cation is 1.5×10^{-2} M in acetonitrile for KPF_6, $NaClO_4$, and $LiClO_4$ (then 3 ml of the polymer solution and 1 μm of the cation solution have an equimolar ratio of cation and crown ether groups).

The surface morphology of the thin films was studied by Tapping Mode Atomic Force Microscope (Nanoscope IIIa AFM, Digital Instruments Inc., USA). C-PPV thin films were fabricated by spin coating from a chloroform solution ($0.016\ mg\ ml^{-1}$) in the absence and presence of KPF_6 (1.5×10^{-2} M in acetonitrile).

Synthesis

3,6-Bis(morpholin-4-ylmethyl)catechol (1). A mixture of paraformaldehyde (6 g, 0.2 mol) and morpholine (17.4 g, 0.2 mol) in isopropyl alcohol (70 ml) was refluxed until it was homogeneous. The resulting solution was cooled to room temperature, and to this solution catechol (11 g, 0.1 mol) in isopropyl alcohol (50 ml) was added. The mixture was stirred for 72 h at room temperature, and then filtered. The solid was recrystallized from ethanol to give the product as white crystals (mp 177–178 °C, 14 g, 45%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.65 (t, 8H, CH_2), 3.75–3.82 (m, 12H, CH_2), 6.56 (s, 2H, ArH), 8.6 (br, 2H, OH).

3′,6′-Bis(morpholin-4-ylmethyl)benzo-18-crown-6 (2). To a solution of 3,6-bis(morpholin-4-ylmethyl)catechol (**1**) (12.32 g, 40 mmol) in tetrahydrofuran (500 ml) under nitrogen was added potassium *tert*-butoxide (10 g, 89 mmol). After the solution had been stirred for 1 h at room temperature, pentaethylene glycol ditosylate (23.36 g, 42.8 mmol) in tetrahydrofuran (100 ml) was added dropwise. The mixture was stirred at room temperature for 18 h, and then refluxed for 6 h. The reaction mixture was cooled, filtered, and concentrated under reduced pressure to 50 ml. The resulting solution was partitioned between chloroform and water. The organic layers were separated and the aqueous phase was extracted with chloroform. The combined organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by silica chromatography (eluent: ethyl acetate). A white solid was obtained (mp 70–72 °C, 7.42 g, 36.2%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 (t, 8H, CH_2), 3.52 (s, 4H, Ar-CH_2), 3.68–3.74 (m, 20H, CH_2), 3.87 (t, 4H, CH_2), 4.19 (t, 4H, CH_2), 7.03 (s, 2H, ArH); elemental anal. Calcd for $C_{26}H_{42}O_8N_2$: C, 61.17; H, 8.23; N, 5.49. Found: C, 60.90; H, 8.05; N, 5.74%.

3′,6′-Bis(acetoxymethyl)benzo-18-crown-6 (3). A mixture of (**2**) (7.4 g, 14.5 mmol) and acetic anhydride (200 ml) was refluxed for 60 h, and then concentrated under reduced pressure to 10 ml, and partitioned between chloroform and water. The aqueous layer was extracted with chloroform, and the combined organic layer was washed with water, dried and concentrated. The residue was purified by silica chromatography (eluent: ethyl acetate–petroleum ether 1 : 1). A white solid was obtained (mp, 57–59 °C, 5.4 g, 81.8%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.08 (s, 6H, CH_3), 3.64–3.74 (m, 12H, CH_2), 3.89 (t, 4H, CH_2), 4.22 (t, 4H, CH_2), 5.15 (s, 4H, Ar-CH_2), 7.09 (s, 2H, ArH); elemental anal. Calcd for $C_{26}H_{32}O_{10}$: C, 57.89; H, 7.02. Found: C, 57.84; H, 7.02%.

3′,6′-Bis(bromomethyl)benzo-18-crown-6 (4). A mixture of (**3**) (2.78 g, 5 mmol), 33% hydrogen bromide–acetic acid (10 ml) and acetic acid (10 ml) was stirred for 2 h at room temperature, then poured into water, neutralized with a solution of sodium hydrogen carbonate, and extracted three times with chloroform. The combined organic layer was washed with water, dried and concentrated. The residue was purified by silica chromatography (eluent: ethyl acetate–petroleum ether 1 : 2). A white solid was obtained (mp, 113–115 °C, 2.8 g, 92.2%). ^1H NMR (200 MHz, $CDCl_3$): δ 3.69–3.76 (m, 12H, CH_2), 3.95 (t, 4H, CH_2), 4.32 (t, 4H, CH_2), 4.54 (s, 4H, Ar-CH_2), 7.09 (s, 2H, ArH); elemental anal. Calcd for $C_{18}H_{26}O_6Br_2$: C, 43.37; H, 5.22. Found: C, 43.54; H, 5.49%.

Synthesis of the poly(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]-docosa-1(18),19,21-trien-19,22-ylenevinylene) (C-PPV). A solution of potassium *tert*-butoxide (1.02 g, 9 mmol) in *tert*-butanol (6 ml) was added dropwise under nitrogen to a stirred solution of (**4**) (600 mg, 1.2 mmol) in DMF (18 ml) over a period of 30 min at room temperature. The mixture was stirred for 24 h, and precipitated with methanol–water (1 : 1). The precipitate was collected, washed with water, methanol, and dried. The crude polymer was purified by dissolving in chloroform and then precipitating from methanol. The process was repeated twice. After drying under vacuum, the resulting polymer was obtained as an orange–red solid (170 mg, 42%).

^1H NMR (200 MHz, $CDCl_3$): δ 3.65–4.16 (m, 20H, CH_2), 7.36–7.56 (m, 4H); elemental anal. Calcd for $(C_{18}H_{24}O_6)_n$: C, 64.28; H, 7.14. Found: C, 63.83; H, 7.11%; IR (cm^{-1}): 2933, 2867, 1648, 1492, 1436, 1127, 1065, 945, 882, 819, 764.

Results and discussion

The synthesis of C-PPV was carried out according to Scheme 1. The catechol was converted to 3,6-bis(morpholin-4-ylmethyl)-catechol (**1**) by the Mannich reaction.[19,20] 3′,6′-Bis(morpholin-4-ylmethyl)benzo-18-crown-6 (**2**) was synthesized from (**1**) and pentaethylene glycol ditosylate in THF in the presence of potassium *tert*-butoxide. Acetification of (**2**) with acetic anhydride by reflux gave 3′,6′-bis(acetoxymethyl)benzo-18-crown-6 (**3**). Instead of the conversion of the diol prepared from saponification of the diacetate (**3**) into (**4**) with CBr_4 and PPh_3, a convenient method was employed to obtain 3′,6′-bis(bromomethyl)benzo-18-crown-6 (**4**), *i.e.*, the monomer (**4**) could be obtained in a high yield by treatment of compound (**3**) with 33% hydrogen bromide–acetic acid in acetic acid at room temperature. The polymerization of monomer (**4**) was carried out *via* a modified Gilch route.[21] The solvent used in the polymerization is an important factor for the solubility of the resultant polymers. When THF, dioxane and xylene or a mixture of xylene and *tert*-butanol were used, the polymers obtained always exhibited very poor solubility in common organic solvents. However, when DMF was employed as the solvent, the C-PPV afforded was soluble in $CHCl_3$. The crude polymer was purified by precipitation from methanol twice, and then the C-PPV was obtained as an orange–red solid with a yield of 42%. The purified polymer was confirmed by IR, ^1H NMR and elemental analysis. The element analysis data (C, 63.83; H, 7.11; Br, <0.3%) are in agreement with that (C, 64.28; H, 7.14%) calculated for $(C_{18}H_{24}O_6)_n$. The very low content of bromide implies a high degree of conversion. In fact, the laser light scattering reveals that the average molecular weight (M_w) of C-PPV is 8.69×10^4, which is much higher than the crown ether containing PPV at the 2,5-position ($M_w = 1880$) prepared by Babudri *et al.*[11] Thermogravimetric analysis (TGA) shows that the polymer exhibits good thermal stability, and the onset of thermal decomposition under nitrogen is around 402 °C. The differential scanning calorimetry (DSC) measurements show a glass transition at 76 °C.

The absorption and photoluminescence (PL) spectra of C-PPV thin film prepared by spin coating from a chloroform solution onto quartz substrates are shown in Fig. 1. The UV-vis spectrum of the polymer shows a maximum absorption peak around 458 nm that can be attributed to the π–π* electron transition associated with the π-conjugated polymer backbones. The energy gap between the HOMO and the LUMO, taken from the edge of the absorption spectrum (526 nm), is estimated to be 2.36 eV. The polymer exhibits a strong yellow–green emission around 534 nm when an excitation at 410 nm is applied.

The double layer LED based on C-PPV (the thickness of the polymer films about 70 nm) fabricated with a configuration of ITO/C-PPV/Alq_3/Al shows a yellow–green emission with a maximum at 534 nm, which closely resembles the PL spectrum of C-PPV thin film (Fig. 1). This means that the same excitations are involved in both cases. Fig. 2 shows the current–voltage and luminance–voltage characteristics of the double layer LED. The LED shows that the turn-on voltage for both current and emissive light is around 12 V, and the luminance of the device reaches 730 cd m^{-2} at 22.9 V and 9 mA. The external EL quantum efficiency of the device is measured to be 0.04%, which is similar to that of 0.03% fabricated with phenyl-substituted PPV[16] when aluminium is employed as the cathode (this is higher than that of 0.015% reported by Babudri *et al.* based on alkoxy-substituted PPV).[11]

The conjugated crown ether containing polymer C-PPV has the ability to bind metal ions (K^+, Na^+, and Li^+) in solution, which can be demonstrated by the change of fluorescence spectra. The measurements were carried out with a dilute solution of C-PPV (5×10^{-6} M) in chloroform and different molar ratios (0, 0.25, 0.5, 0.75, 1, 2, 3, 4, 6) of cation to crown ether unit were employed. It is observed that the solutions of polymer C-PPV display unchanged absorbance spectra in the presence of K^+, Na^+, or Li^+, relative to the maximum absorption band at 442 nm in the absence of metal ions. While in the case of fluorescence spectra, the fluorescent intensity decreases as the molar ratio of K^+, Na^+, or Li^+ increases compared with the emission bands at 490 and 525 nm in the absence of metal ions with the excitation at 440 nm. Fig. 3 shows the fluorescence spectra of C-PPV in chloroform in the absence and presence of K^+. The emission of C-PPV has been dramatically reduced to near background level when the molar ratio of K^+ to the crown ether unit is 6. At the same time, the maximum emission appears at 525 nm, which may be attributed to the formation of excimers.[22] The fluorescence attenuation is the result of electron-transfer from the excited polymer to the analyte K^+.[23] In addition, it is found that the C-PPV does not have obvious selectivity to K^+, Na^+ or Li^+.

Atomic Force Microscopy (AFM) is employed to reveal the effect of the cation ion on the morphology of conjugated polymer C-PPV since AFM is a powerful surface technique that can be used to obtain high-resolution images of the surface

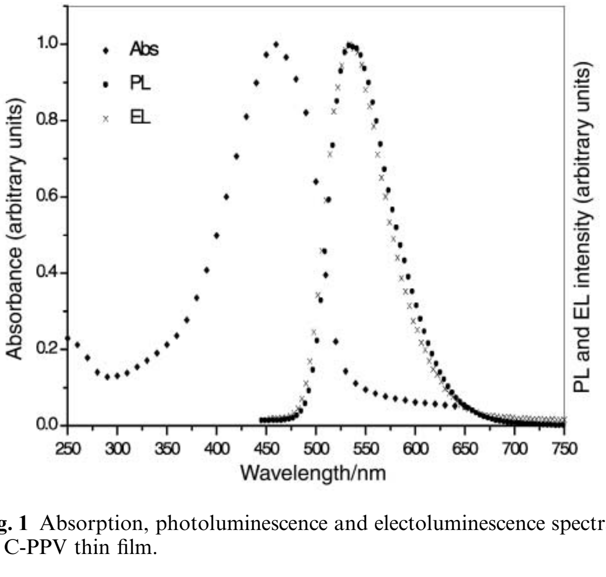


Fig. 1 Absorption, photoluminescence and electoluminescence spectra of C-PPV thin film.

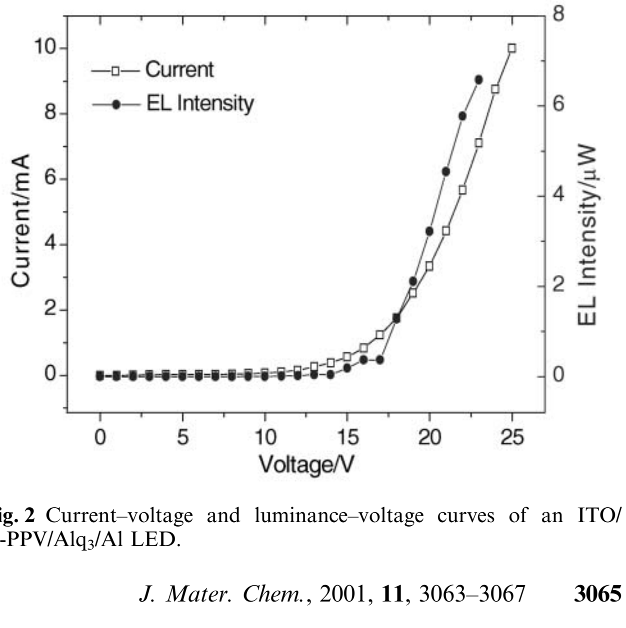


Fig. 2 Current–voltage and luminance–voltage curves of an ITO/C-PPV/Alq_3/Al LED.

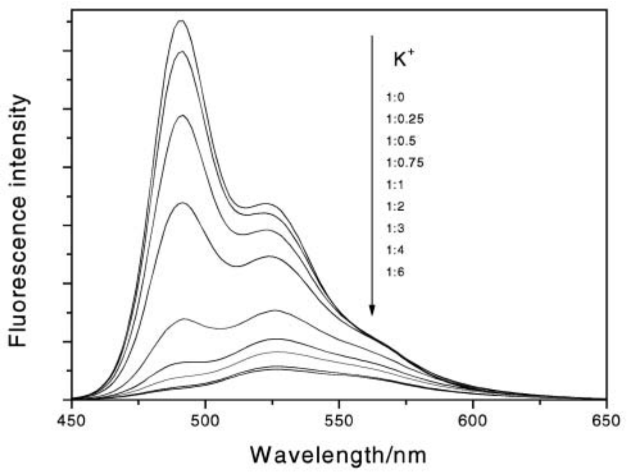


Fig. 3 Fluorescence spectra of C-PPV in solution in the absence and presence of K$^+$.

of organic films.[24,25] Fig. 4(a)–(f) show AFM images of C-PPV films on silicon substrate fabricated by spin coating from a very diluted chloroform solution (0.016 mg ml^{-1}) in the absence and presence of 6 equiv. of K$^+$. Fig. 4(a) shows an image of C-PPV molecules in the absence of K$^+$. The particles have apparent diameters of 18–38 nm, and average height of 2 nm. Taking into account the size and shape of the AFM tip, the vertical resolution of AFM images is much better than the lateral resolution. The obtained diameters usually need to be corrected due to the AFM tip broadening effect.[26] As a result, the true diameter of these particles might be smaller than the apparent diameters. It can be estimated that in such a very dilute solution most of the small particles might be the single C-PPV molecules, while some larger particles may consist of several single C-PPV molecules which could be the result of molecule aggregation.

On the contrary, worm-like morphological features are observed when the films are in the presence of K$^+$ as shown in Fig. 4(b)–(f). Before the films were fabricated the solution of C-PPV in the presence of 6 equiv. K$^+$ had been left to stand over different periods of time. It was observed that the worm-like images grow longer and longer as the solution of C-PPV in the presence of K$^+$ stood longer. The apparent average width is about 16 nm which becomes smaller than the average diameter of the particles shown in Fig. 4(a), and the height is about 1.7 nm. This C-PPV molecule self-organization to form worm-like structures is mainly considered to be owing to metal ions of K$^+$ inducing a conformational change of the polymer. The binding of the metal ions in the crown ether rings make these macrocycles and the polymer backbone more rigid, favoring their π-stacking interaction with each other and advantaging the elongation of worm-like structures. On the other hand, it is worth mentioning that: the AFM images of the molecule of C-PPV are mainly isolated from each other in the form of the individual particles in the presence of Na$^+$ or Li$^+$, similar to that in the absence of K$^+$ as shown in Fig. 4(a). Only in the presence of K$^+$ does the molecule of C-PPV have the evident proclivity to self-assemble in definite extension forming chain-like assemblies with well-defined width and height.

Conclusions

In conclusion, this work presents the synthesis of a novel PPV derivative substituted with crown ether units, and the

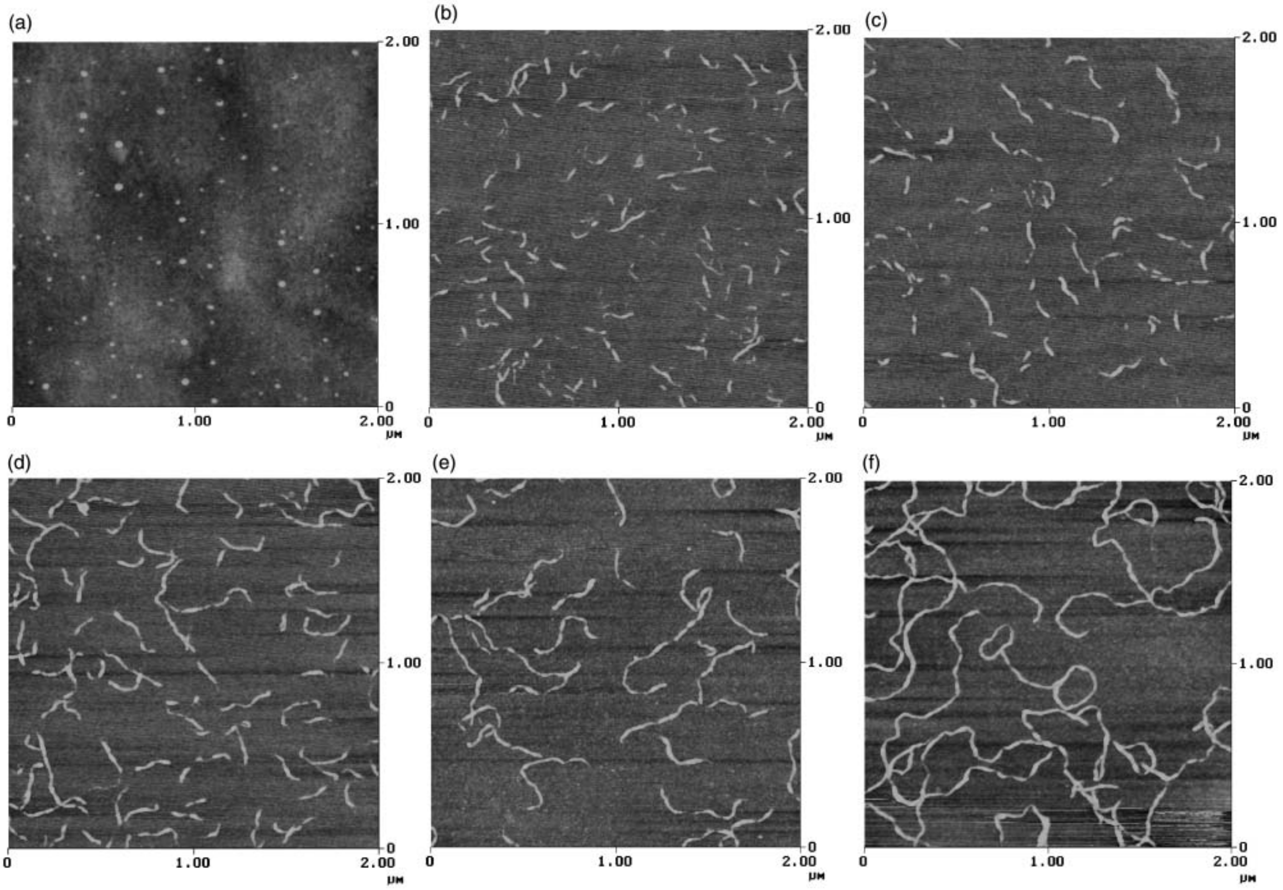


Fig. 4 AFM images of the C-PPV films made by spin-coating on silicon (a) in the absence of K$^+$, (b)–(f) in the presence of K$^+$. Before the films were fabricated the solution of C-PPV in the presence of 6 equiv. K$^+$ had been left to stand over different periods of time for (b) 0.5 h, (c) 6 h, (d) 24 h, (e) 12 days, and (f) 70 days.

performance of the polymer as an emissive material for LEDs. The crown ether containing PPV can bind metal ions in solution. It is found that the fluorescent intensity decreases as the molar ratio of K^+, Na^+, or Li^+ increases compared with that in the absence of metal ions with the excitation at 440 nm. Moreover, the AFM provides the morphology of the polymer thin films in the absence and presence of metal ions. Worm-like images are observed only in the presence of K^+. Further studies on the influence of different cation ions and conditions on these systems are in progress in order to gain an insight into the binding and self-assembly characteristics.

Acknowledgements

We are grateful to the support of National Natural Science Foundation of China (contract grant number: 29974034).

References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.

2 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.

3 M. D. McGehee and A. J. Heeger, *Adv. Mater.*, 2000, **12**, 1655.

4 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.

5 J. L. Segura, *Acta Polym.*, 1998, **49**, 319.

6 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.

7 F. Cacialli, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 159.

8 D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537 and references cited therein.

9 J. Kim, D. T. McQuade, S. K. McHugh and T. M. Swager, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)*, 2000, **41**, 32.

10 R. E. Martin, F. Geneste, R. Riehn, B. S. Chuah, F. Cacialli, R. H. Friend and A. B. Holmes, *Chem. Commun.*, 2000, 291.

11 F. Babudri, S. R. Cicco, L. Chiavarone, G. M. Farinola, L. C. Lopez, F. Naso and G. Scamarcio, *J. Mater. Chem.*, 2000, **10**, 1573.

12 D. M. Johansson, G. Srdanov, G. Yu, M. Theander, O. Inganäs and M. R. Andersson, *Macromolecules*, 2000, **33**, 2525.

13 S. Lee, B. Jang and T. Tsutsui, *Chem. Lett.*, 2000, 1184.

14 Z. Chen, W. Huang, L. Wang, E. Kang, B. J. Chen, C. S. Lee and S. T. Lee, *Macromolecules*, 2000, **33**, 9015.

15 T. Ahn, S. Song and H. Shim, *Macromolecules*, 2000, **33**, 6764.

16 J. Pei, W. Yu, W. Huang and A. J. Heeger, *Chem. Lett.*, 1999, 1123.

17 B. R. Hsieh, Y. Yu, E. W. Forsythe, G. M. Schaaf and W. A. Feld, *J. Am. Chem. Soc.*, 1998, **120**, 231.

18 W. C. Wan, H. Antoniadis, V. E. Choong, H. Razafitrimo, Y. Gao, W. A. Feld and B. R. Hsieh, *Macromolecules*, 1997, **30**, 6567.

19 W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, 1939, **61**, 2354.

20 D. L. Fields, J. B. Miller and D. D. Reynolds, *J. Org. Chem.*, 1964, **29**, 2640.

21 H. G. Gilch and W. L. Wheelwright, *J. Polym. Sci., Part A1*, 1966, **4**, 1337.

22 S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765.

23 J. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864.

24 J. Frommer, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1298.

25 J. Y. Josefowicz, N. C. Maliszewskyj, S. H. J. Idziak, P. A. Heiney, J. P. McCauley, Jr and A. B. Smith, III, *Science*, 1993, **260**, 323.

26 O. Cavalleri, C. Natale, M. E. Stroppolo, A. Relini, E. Cosulich, S. Thea, M. Novi and A. Gliozzi, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4630.