JOURNAL OF Materials CHEMISTRY
Feature Article

Substituted polythiophenes designed for optoelectronic devices and conductors

Mats R. Andersson,*[a] Olinga Thomas,[b] Wendimagegn Mammo,[b] Mattias Svensson,[b] Mathias Theander[c] and Olle Inganäs[c]

Departments of [a] Polymer Technology and [b] Organic Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[c] Laboratory of Applied Physics, Department of Physics and Measurement Technology (IFM), Linköping University, SE-581 83 Linköping, Sweden

Received 12th April 1999, Accepted 11th June 1999

Polythiophenes are a very versatile class of conjugated polymers. Substituted polythiophenes can be tailored for various applications by designing the side groups to give the polymer different desired properties. Our work on preparing polythiophenes designed to have high stability in the doped state is described. We also discuss our efforts on tuning the colour of the emission from polythiophenes for use in polymer light-emitting diodes. Design criteria for the synthesis of polythiophenes with high luminescence efficiency for use in light-emitting diodes and lasers are also described. Finally, the design of polythiophenes for use in photodiodes is discussed.

Introduction

The development of substituted conjugated polymers has been focused on several properties, to be tuned by molecular engineering. These substitutions are often chosen in order to enhance a property deemed attractive for application, but which may also be a property designed for extended hypothesis testing of basic physical and chemical concepts. Of course, both goals may be desired and might be attained in the same measure. As the shifting emphasis on applications has moved from electronic conductivity and electrochemical activity in the 1980's, towards use in polymer electronics in the 1990's,[1] one class of polymers has followed suit. This is the class of polythiophenes, the first among the soluble and fusible conjugated polymers. These were first prepared in a soluble form in the mid-eighties in several labs in the US,[2] Japan[3] and Finland more or less simultaneously. The focus was at this time that of electronic conductivity, and the combination with processability was the main new attraction of the new class of poly(3-alkylthiophenes). Since then a great variety of soluble polythiophenes have been prepared with an impressive range of properties.[1]

We have chosen to work with polythiophenes for several reasons. Polythiophenes are relatively stable, and thiophene monomers can be polymerised by a number of different routes which are well known.[4] The properties of the polymers can easily be varied by changing the substituents on the monomer. The polymer is still with us today, and is now designed for use in polymer electronics, diodes, light-emitting diodes, photodiodes and in lasers. We review some aspects of the synthesis and materials/device applications of these polymers.

The first area discussed is our work on the preparation of stable conducting polythiophenes. The stability of the doped polymer is crucial for use of the polymer as a conductor. We then discuss our work on colour tuning of the emission from substituted polythiophenes designed for use in polymer light-emitting diodes. Our work has been concentrated on achieving electroluminescence through the whole visible spectrum using different polythiophenes. We also present our efforts in preparing substituted polythiophenes with high luminescence efficiency for use in polymer light-emitting diodes and lasers, and present studies of the photophysics of these polymers. Finally, we highlight design of substituted polythiophenes for use in polymer photodiodes.

Synthesis of polythiophenes

Pure polythiophene without side chains is neither soluble nor fusible. Once the polymer is prepared it is not possible to further process the prepared films or powder. However side chains which give solubility and fusibility to the polymer can be attached to the repeating unit (the thiophene ring).[5] The most widely used side chains are straight alkyl chains (C_4 and longer). 3-Alkylthiophenes are normally prepared by nickel-catalysed coupling of 3-bromothiophene with Grignard reagents of alkyl halides.[6]

When 3-alkylthiophenes are polymerised, three different couplings can occur: head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) (Fig. 1). The properties of the polymers depend on the regioregularity of the polymers[7] and the size of the side chain. The regioregularity of soluble poly(3-alkylthiophenes) can be determined by ^{1}H NMR.[4]

Polymerisation of thiophenes can be carried out in many different ways and they have recently been excellently described by R. D. McCullough.[4] The most commonly used methods are the following:

- Electropolymerisation of the monomers has been widely used, mostly for the preparation of films of insoluble polymers. Polymerisation of 3-alkylthiophenes gives irregular polymers, with approximately 70% of the HT-coupling.[8]
- Grignard coupling of 2,5-diiodo-substituted 3-alkylthiophenes gives random polymers, with approximately 50–60% of the HT-coupling.[7]
- Polymerisation with $FeCl_3$[3] is simple and is generally known to give irregular polymers, approximately 70–80% HT,[4] although exceptions with regioselective polymerisation

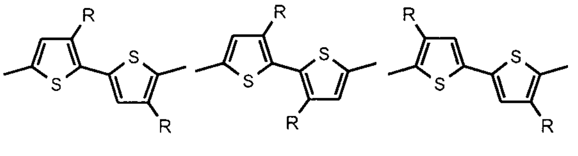


Fig. 1 Three possible couplings between two 3-alkylthiophenes along the polymer chain.

exist.[9–11] The formed polymers are in the doped state and must be dedoped before they become soluble and fusible.

- The McCullough method gives regioselective polymerisation and is based on a Grignard type of reaction.[12] The regioregularity is generally 98% HT.[4] Two other methods for preparing regioregular polymers following this procedure but using Suzuki[13] or Stille[14,15] coupling instead of Grignard coupling have also been developed. McCullough and co-workers have recently described a simplified method based on Grignard coupling.[16]
- Rieke has developed a method for preparing regioregular 3-alkylthiophenes using zinc and a special catalyst (Ni(dppe)Cl_2).[17] The HT content in the polymer is also generally 98% HT.[4]

All our polymers have been prepared by using $FeCl_3$ polymerisation of the monomers. This is a very simple polymerisation method but the drawback with the method is that the polymer must be carefully purified after polymerisation to remove the residual iron. We have shown that regioregular polymerisation is possible when polymerising 3-phenyl substituted thiophenes with $FeCl_3$.[9] The versatility of this technique for synthesising regioregular substituted poly(3-phenylthiophenes) has also been examined by us.[11]

Stable polythiophenes in the doped state

Undoped conjugated poly(3-alkylthiophenes) have a very low conductivity. The conductivity of poly(3-alkylthiophenes) depends on the regioregularity of the polymers. Poly(3-octylthiophene), P3OT (**1**), prepared by the $FeCl_3$-method and doped by $FeCl_3$ or iodine, has a conductivity of approximately 20–30 S cm^{-1}.[18] Thin films of regioregular poly(3-dodecylthiophene) have been reported to have a conductivity up to 1000 S cm^{-1} when doped by iodine.[4] The polymers are not processable (soluble or fusible) in the doped state.

The doping is normally done by treating the polymer films with an oxidising agent, commonly iodine or $FeCl_3$. Counterions are generated from the oxidant and must diffuse into the polymer, and neutralise the charges on the polymer chains. The long-term stability of the conductivity for the doped conjugated polymers is crucial for many applications. Unsubstituted, doped poly(thiophenes) are relatively stable but,[19,20] when all the thiophene rings are substituted to give processability in the undoped state, the stability of the doped polymer is drastically reduced.[21–23] The reduced stability leads to a quick loss of conductivity at higher temperatures (thermal dedoping).

The cause of thermal dedoping was much studied around 1990, and three main hypotheses were formulated. In one model, hypothesis A, the transition was a thermodynamical necessity given the thermochromic behaviour in the same class of polymers.[24] It was suggested that the conformational flexibility of the main chain, so evident in the thermochromism of the undoped polymer, must also be a limitation to the stability of the doped and planar geometry of the chain. In the competition between side chain mobility, main chain torsion and planar doped geometry, increased temperature with reduced conjugation length of the main chain would always force a thermal dedoping, due to the increase of the oxidation potential of the twisted polymer.[21,25] Attempts to modify this suggested mechanism by reducing the redox potential of the polymer failed, however. More emphasis was then put upon another aspect of the geometry of the doped state: the location of dopants with respect to the polythiophene backbone. It was suggested, in hypothesis B, that the location of the side chains would strongly interfere with the position of the dopants.[25] When the temperature increases, the conformational flexibility of the alkyl side chains drives the dopant out of the preferred geometry, and undoping occurs. From these concepts, a desired goal would be to prepare substituted polythiophenes with space for the dopants, where a low density of side chains would be high enough to render the polymer soluble but low enough not to interfere too strongly with the dopant.

Studies of the chemical changes occurring during thermal treatment of undoped P3OT (**1**) revealed, however, another aspect: the thermally treated sample would be partly insoluble, and would accumulate defects at the first methylene group in the alkyl side chains.[26] These defects were clearly shown by infrared spectroscopy, and could be explained as being due to the higher reactivity of the $-CH_2-$ structure, with crosslinking and carbonyl formation occurring at this site. To handle this mechanism, hypothesis C, which describes the thermal undoping as a chemical reaction, we would preferably remove the reactive structure.[27] It is in the light of these concepts that materials synthesis of copolymers was initiated, a successful route for obtaining enhanced stability.

Copolymerisation of 3-methylthiophene and 3-octylthiophene gives a polymer which has a higher stability towards thermal dedoping than homopolymers of 3-octylthiophene. These random copolymers were prepared by electrochemical[28] and Grignard[29] polymerisation methods. In addition, the amount of 3-methylthiophene was low when soluble polymer was prepared. Random copolymerisation of the monomers with the $FeCl_3$-method gives only a low yield of soluble polymer.

A better way to 'dilute' the concentration of side chains along the polymer backbone is to polymerise bithienyls or terthienyls with only one side chain. We have prepared and used the polymers shown in Fig. 2 to test the idea that fewer side chains more evenly distributed give polymers with an improved stability in the doped state.[30] Polymerisation of the dimers and trimers gives regiorandom polymers. For polymers **3**–**5** the monomers (the dimers and trimers) were constructed in such a way that no head-to-head linkage of alkyl substituted thiophene rings could be formed along the polymer backbone. The processability and the mechanical properties of the poly-

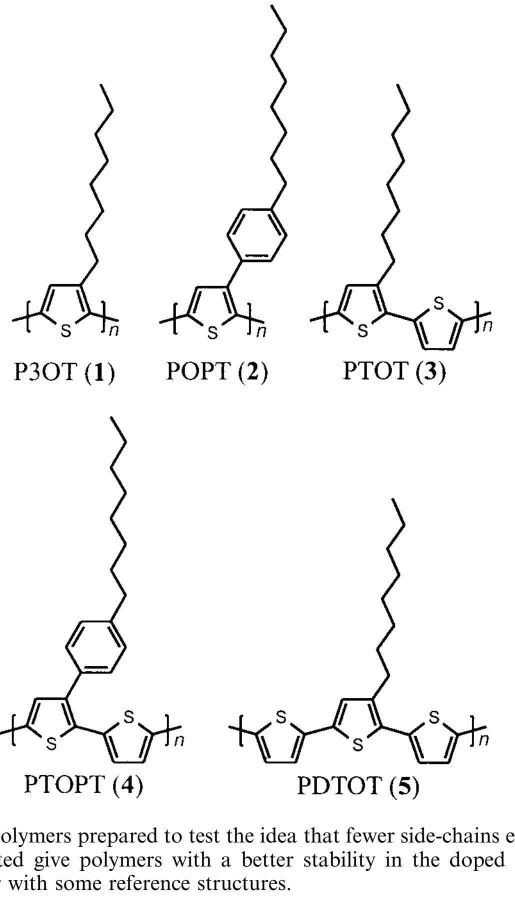


Fig. 2 Polymers prepared to test the idea that fewer side-chains evenly distributed give polymers with a better stability in the doped state, together with some reference structures.

mers should still resemble the properties of polymer P3OT (**1**) to be suitable for different applications.

Poly(3-(4-octylphenyl)thiophene), POPT (**2**), was prepared by Järvinen *et al.*,[27,31] and the P3OT (**1**) was obtained from Neste OY, both polymers having been prepared with $FeCl_3$. Isomerically pure monomer was later used to prepare POPT (**2**) with improved regioregularity.[9] The syntheses of the other polymers in Fig. 2 have been published elsewhere.[30,32]

The monomers were polymerised using $FeCl_3$ in chloroform. When the normal polymerisation procedure[3] was used, only low molecular weight products were formed from the bithienyls or terthienyls.[30] The normal polymerisation procedure is to add the monomer quickly to a suspension of $FeCl_3$ in chloroform and then to stir the mixture for some time. The molecular weight of the polymers could be increased by adding the $FeCl_3$ slurry slowly to the monomer dissolved in chloroform.[30] This gives a more soft and selective polymerisation and there is no large excess of $FeCl_3$ at the beginning of the polymerisation. This favours the growth of the polymer chains instead of the growth of new chains, and thus favours the production of high molecular weight products. The yield of soluble polymer after polymerisation depends on the structure of the monomer. PTOT (**3**) was prepared with a yield of 43%[30] which can be compared with the yield for PTOPT (**4**) (83%).[32] This is due to the removal of the reactive $-CH_2-$ group on the side chains attached directly onto the polythiophene backbone. The phenyl ring acts as a spacer and the benzylic hydrogen on the side chain becomes more stable. This prevents crosslinking during the polymerisation and the yield is increased.

The long-term stability of the conductivity of the polymers was then examined by measuring the thermal dedoping of thin doped films (0.5–1 μm). Each film was cast on a glass slide coated with four gold electrodes and thereafter doped with $FeCl_3{\cdot}6H_2O$[33] in acetonitrile. $FeCl_3$ is known to be one of the dopants giving the highest stability of doped poly(3-alkylthiophenes).[2,34] The stability of the different polymers was measured as the conductivity decay at 110 °C in air, as shown in Fig. 3. Thin films were used to avoid diffusion phenomena and to achieve short measuring times. The stability measurements on thin films were made by Dr Q. Pei in Linköping.

Compared to P3OT (**1**), the thermal stability of the conductivity of the other polymers is clearly improved. PDTOT (**5**), which is the most stable polymer, has the lowest ratio of side chains on the polymer backbone. The stability decreases with increasing ratio of side chains, as is shown for copolymers of 3-methylthiophene and 3-octylthiophene.[28] The stability is also increased when a phenyl ring is used as a 'spacer' between the polymer backbone and the flexible side chain, giving a more rigid backbone. The stability seems to depend on how much space is available for the counterion, the rigidity of the polymer backbone and the reactivity of the side groups. The detailed mechanism for the dedoping is not known. The space requirement is also demonstrated by the observation that larger counterions decrease the stability of doped P3OT (**1**).[25]

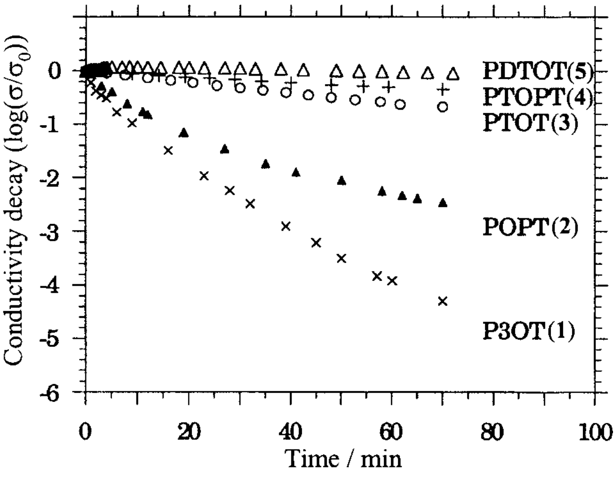


Fig. 3 Conductivity decay of thin doped ($FeCl_3$) films of the prepared polymers at 110 °C in air.

PTOPT (**4**) was selected for a more extensive study because of its stability, processability and mechanical properties. The melting interval for PTOPT (**4**) was found to be 195–205 °C when measured with a melting point microscope. Although PDTOT (**5**) was the most stable, it has too low a molecular weight which gives too low a melting interval (85–95 °C) and makes it impossible to prepare free standing films of this polymer. Free standing films of PTOPT (**4**) and P3OT (**1**) with a thickness of 43 μm were prepared. The films were doped by treating them with 1 M $FeCl_3{\cdot}6H_2O$ in acetonitrile for 24 h.[30,33] The conductivity of the films at room temperature measured with the four probe technique was 60 S cm^{-1} for PTOPT (**4**) and 32 S cm^{-1} for P3OT.

To compare the stability of free standing films of similar thickness of different conducting polymers, the half-time ($t_{1/2}$) of the initial conductivity for the films of P3OT (**1**) and PTOPT (**4**) was measured. The time it takes for the films to lose half of the initial conductivity at 150 °C in air was found to be 0.20 h for P3OT (**1**) and 4.3 h for PTOPT (**4**). This can be compared with polyaniline films doped with H_2SO_4 and toluene-*p*-sulfonic acid which exhibit a half-time of 18 and 3.2 h, respectively at similar conditions and similar film thickness.[35] Thermal degradation of doped polypyrrole films with toluene-*p*-sulfonate as the counterion shows a $t_{1/2}=25$ h at 150 °C in air with the same film thickness.[36]

From this it is clear that the stability of doped PTOPT (**4**) is much higher than that of doped P3OT (**1**) and that PTOPT (**4**) is approximately as stable as poly(aniline) doped with toluene-*p*-sulfonate. When the polymers are compared, it is important to remember that poly(aniline) and poly(pyrrole) are not processable as is PTOPT (**4**). Processable films of doped poly(aniline) have been prepared[37] but the structure resembles poly(aniline) doped with toluene-*p*-sulfonate and thus has probably approximately the same stability as doped PTOPT (**4**).

We note that recent work verifies the validity of this approach by investigations of infrared spectra of the doped state in similarly designed polythiophenes.[38] However, detailed studies of dopant–polymer geometry in stable and unstable doped substituted polythiophene systems remain to be performed and are hampered by the absence of efficient structural methods suitable for these disordered materials.

Colour tuning of polythiophenes for use in light-emitting diodes

Conjugated polymers can be used as the active layer in polymer light-emitting diodes (PLEDs). This was first discovered in 1990 when undoped poly(*p*-phenylenevinylene) was sandwiched between two different electrodes.[39] Today PLEDs are usually constructed as shown in Fig. 4.

The most widely used polymers in PLEDs are pure or substituted poly(*p*-phenylenevinylenes). We have chosen to use polythiophenes as the emitting layer in the diodes.

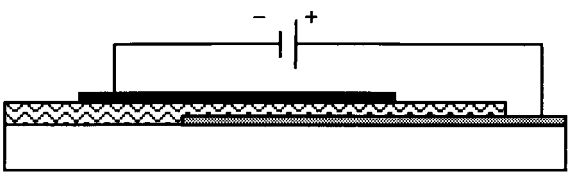


Fig. 4 Cross section of a polymer light-emitting diode. The layers from the top are: Al/Ca, polymer (50–100 nm), indium-tin-oxide and glass.

Uncharged polythiophenes are stable and it should therefore be possible to make stable diodes from these polymers. The properties of the polymer can easily be changed by varying the ratio and size of the side groups; in particular it should be easy to prepare different emission colours. In this way, desired properties of the diodes prepared from the polymers can be achieved.

The colour of the light emitted from the PLEDs is directly dependent on the conjugated polymer used in the diode. The electroluminescence spectrum from a polymer is usually almost identical to the photoluminescence spectrum from a film of the polymer. Several groups have used molecular engineering to tune the colour of the electroluminescence. The colour of the emission is directly dependent on the extent of the conjugation along the π-system. Short conjugation gives blue-shifted emission and long conjugation gives red-shifted emission from the polymer. The length of the conjugation can be varied in different ways. A widely used method is to use different copolymers with conjugated and non-conjugated segments.[40–44] Block copolymerisation of different thiophene monomers to give regiospecific thiophene polymers has also been used combined with the regiospecific head-to-head homopolymer of 3-octylthiophenes and of 3,4-dioctylthiophene.[45]

We have chosen to control the conjugation along the polymer backbone by adding different substituents on the repeating unit.[32] This is motivated by our studies of thermochromism in the poly(3-alkylthiophenes), where a temperature dependent bandgap is found to be caused by a temperature dependent geometry of the main chain. We have attempted to lock in the geometry typical of the high temperature by positioning side chains of the right character and density on the main chain. If the repeating unit is kept small, the ease of synthesis of the monomer increases. Substituents in the 3- or both 3- and 4-positions on the thiophene rings give steric interactions between the side groups and the adjacent thiophene ring and/or the side group attached to the adjacent thiophene ring. Large substituents lead to a large dihedral angle between the rings and short conjugation along the polymer backbone. Using different amounts and different sizes of substituents on the repeating unit, we have been able to control the size of the conjugation. The regioregularity is also important for the conjugation along the polymer backbone. A large degree of head-to-head coupling in the polymer gives a shorter conjugation and blue-shifted emission as compared to a regioregular head-to-tail coupled poly(3-alkylthiophene). We have prepared and used the polymers shown in Fig. 5 to achieve electroluminescence over the whole visible spectrum.[32]

We can evaluate these polymers using the photoluminescence of their films, and find that we can span the full length of the visible spectrum, see Fig. 6. When calculating the chromatic co-ordinates for the polymers we find that we cover only part of the chromatic space (Fig. 7) in an arc spanning from the deep red to blue. No deep green colours are available in this family of polymers. The broad emission spectrum prevents us from obtaining the clear greens. There are major variations in the photoluminescence efficiency between these different polymers, as discussed below.

Most of the devices use cathodes prepared by sequential Ca and Al evaporation. Characterisation is done immediately upon fabrication, as the cathode will eventually be consumed in air, where we do the measurements. We must include a layer of evaporated molecules, the oxadiazole PBD (2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole), in diodes with high bandgap polythiophenes, between the polymer and the metal electrode in order to balance charge injection. This molecule is also emitting in these devices, and we therefore have a strong element of the PBD photoluminescence spectrum in the polythiophene devices emitting in the blue–green range. The most extreme case of light emission from the PBD molecule is found in blends of PBD and PTOPT (4) which

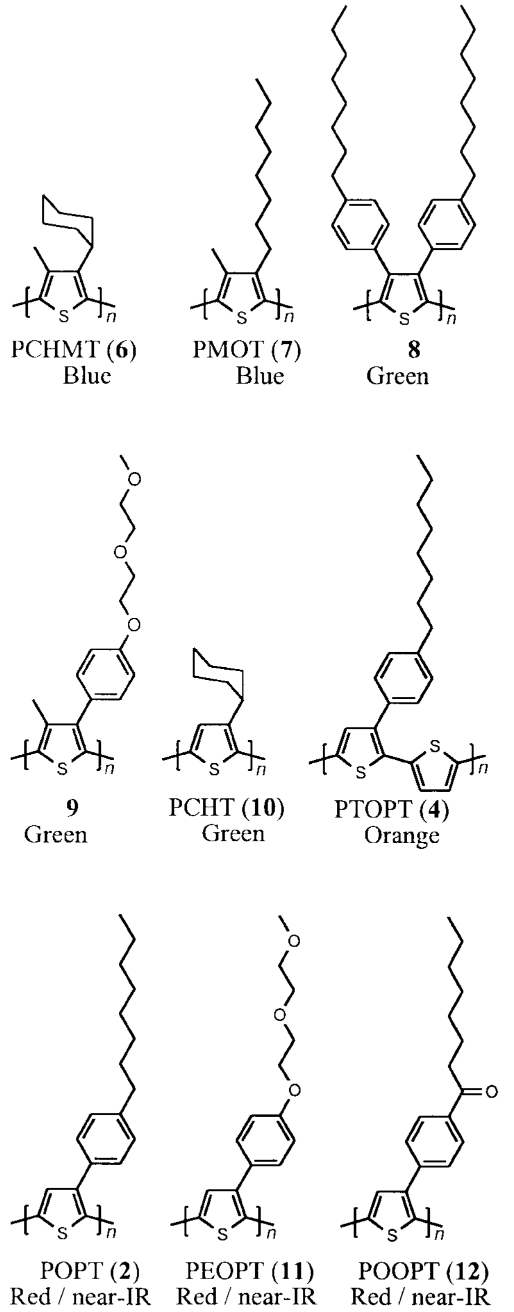


Fig. 5 Prepared polymers and luminescence colour, covering the whole visible spectrum.

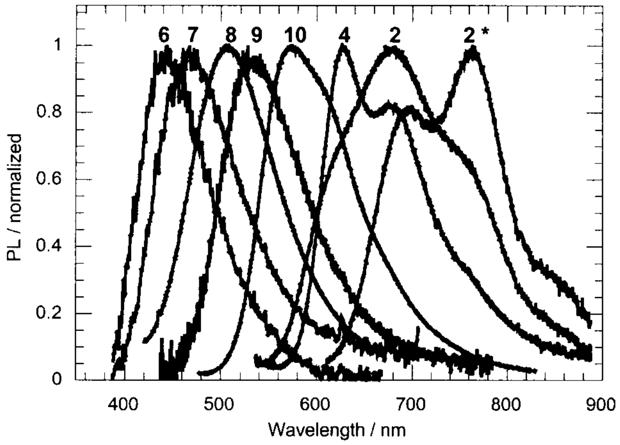


Fig. 6 Photoluminescence spectra from spin-coated films of some of the polymers. *The same film treated with chloroform vapour in room temperature.

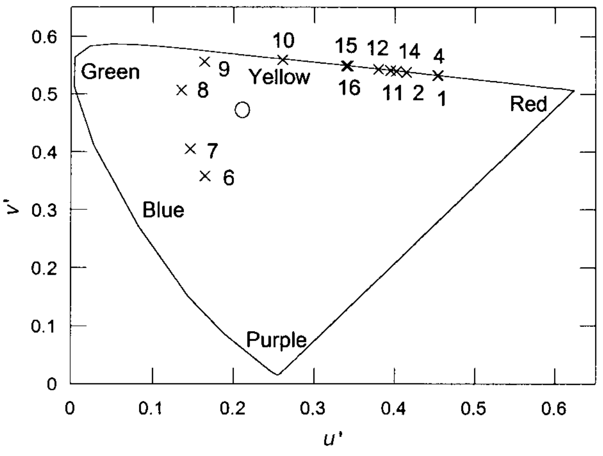


Fig. 7 Chromatic co-ordinates for the polymers and the white spot (o).

can be designed to give maximum emission in the UV range.[46] White emission can also be found from such devices. The full emission spectrum of some of these PBD–polythiophene devices cannot be explained even by a linear addition of emission from the PBD or the polythiophene layer. A third peak observed in the PBD–PTOPT (PBD–**4**) devices we attribute to a new indirect transition at the interface between PBD and PTOPT (**4**); a hole in PTOPT (**4**) recombines with an electron in PBD. A related emission, but now found in a PBD–PMOT (PBD–**7**) structure, drains the emission from the two layers. This emission can be located at the interface PBD/PMOT (PBD/**7**) by applying interference modelling and we have named such emission routes electroplexes, as they will not show up in photoluminescence but are only visible in electroluminescence from the devices.[47]

It is therefore through three different routes that light might be obtained in the devices with PBD–polythiophenes of high bandgap. Interestingly, the quantum efficiency of electroluminescence in these devices can be much higher than the quantum efficiency of photoluminescence in the polythiophene; as more than one route for emission is available this does not contradict the orthodoxy in the field, of 1/4 photoluminescence efficiency setting the upper limit for electroluminescence efficiency.

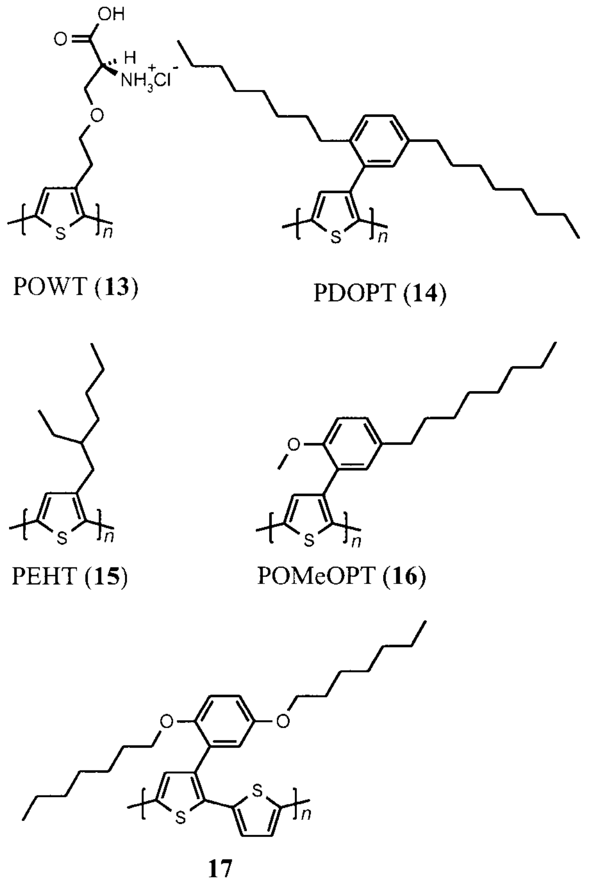
In the search for tuneable emission from PLEDs, POPT (**2**) has been used to demonstrate this possibility. Spin-coated films of POPT (**2**) are formed in a non-ordered state which can be ordered by solvent vapour treatment or by annealing.[48] This gives a red shift of the optical absorption and emission. The crystallinity in the film is increased during this ordering.[49] PLEDs prepared from POPT (**2**) emit red light but after annealing the diode the emission occurs in the near-IR range.[48]

The different properties of substituted polythiophenes with varying bandgaps have also been utilised in PLEDs with voltage controlled colours, with white light emission and in nanoPLEDs. Here we utilise phase separation in polymer blends to assemble the polythiophenes in small domains extending from cathode to anode. At low voltages all current will be injected into low bandgap polymers; at higher voltages injection into higher bandgap polymers is possible and is added to the light emission from the low bandgap materials. It is therefore possible to voltage control the colour of the PLED.[50] The mixing of these polymers can also be utilised to build white light emitting devices.[51] If we combine the luminescent polymer with a non-conjugated polymer and obtain a similar structure in the thin film devices, we can also prepare flexible nanoPLED devices.[52] In this way it is also possible to improve the voltage control of the colour. Diodes prepared from blends of three (red, green and blue emitting) conjugated polymers and an inert matrix have been constructed.[53]

Polythiophenes with high luminescence efficiency

The observation under UV light of photoluminescence from a polymer solution when drying out is a dull experience; as the solvent finally disappears, the luminescence intensity falls dramatically. This is particularly clear in the case of many poly(3-alkylthiophenes) where the photoluminescence efficiency drops by almost an order of magnitude upon deposition into thin films. It is clear that the close distance of the main chains in these solids is of great importance for the dramatic decrease of photoluminescence efficiency. We have therefore attempted to study the photoluminescence processes in solutions and in thin films in order to carefully analyse the mechanism of excitation decay in the substituted polythiophenes. In our search for highly luminescent polythiophenes we have examined and prepared several different polythiophenes and some of the polymers can be seen in Fig. 8.

Instead of using solvents to dilute the polymers they can be diluted in the solid state by blending the conjugated polymer in an inert polymer matrix.[54] The drawback with this method is that blends of two polymers normally phase segregate and the photoluminescence efficiency is not increased. Phase segregation can be avoided if there exist attractive forces between the two polymers. We have demonstrated an example of this when we prepared blends of POWT (**13**) with poly(acrylic acid). Attractive interactions between the substituted polythiophene and the matrix polymer here prevent phase separation, as investigated with infrared spectroscopy and scanning force microscopy.[55] The functional groups on POWT (**13**) form hydrogen bonds with poly(acrylic acid) and blends on a molecular level could be prepared. From these studies it is clear that interactions between the conjugated chains cause non-radiative recombination of the excited state on the chains; by suppressing these in the solid solution, we can enhance the photoluminescence yield from 4% in the homopolymer to 16%



POWT (**13**)

PDOPT (**14**)

PEHT (**15**)

POMeOPT (**16**)

17

Fig. 8 Polymers prepared for studying and improving the photoluminescence efficiency in the solid state.

Table 1 Photoluminescence quantum efficiency (PL_{eff}) in solution and in films, UV–VIS absorption maximum (Abs_{max}) and photoluminescence maximum (PL_{max}) of films, molecular weight and the regioregularity for some of the presented polymers

Polymer	$PL_{eff}(CHCl_3)$	PL_{eff}(film)	Abs_{max}(film)/nm	PL_{max}(film)/nm	$\bar{M}_n$/g mol^{-1}	$\bar{M}_w$/g mol^{-1}	Regularity (HT)
P3OT (**1**)	0.27	0.04	506		35 000	110 000	0.70
POPT (**2**)	0.18	0.09 (0.03)[a]	482 (555)[a]	677 (764)[a]	8000	50 000	0.94
PTOPT (**4**)	0.27	0.05	513	627	9000	82 000	—
PCHMT (**6**)	0.013	0.008	303	442	26 000	72 000	—
PMOT (**7**)	0.046	0.022	326	468	42 000	91 000	—
8	0.011	0.010	346	504	21 000	63 000	—
9	0.038	0.028	380	532	16 000	48 000	—
PCHT (**10**)	0.27	0.09	405	574	6000	56 000	0.77
PEOPT (**11**)	0.20	0.08	476 (552)[a]	616 (783)[a]	7800	25 000	0.88
POOPT (**12**)	0.14	0.10	454 (555)[a]	638 (795)[a]	9400	27 000	0.85
PDOPT (**14**)	0.37	0.24	494, 532, 577	606, 659, 720	36 000	70 000	0.90
PEHT (**15**)	0.26	0.09	464	593			~0.70
POMeOPT (**16**)	0.29	0.11	470	590	46 000	160 000	0.90
17	0.31	0.04	510	598	24 500	105 000	—

[a] Annealed film.

in the solid polymer solution (and 26% in methanol).[55,56] Possible quenching processes in the solid state can therefore be formation of low luminescent excimers where the excitation is delocalised on more than one chain. Close packed chains also improve the mobility of the excitation. With high excitation mobility the chance of finding quenching sites is increased giving a low photoluminescence yield. The nature of the quenching sites is however unclear. The yield of the photoluminescence was measured with an integrating sphere.

Preventing close contact between conjugated chains should therefore be one of the goals when designing substituted polythiophenes for high photoluminescence efficiency. This has been successfully used in the synthesis of a polymer named PDOPT (**14**), where a dioctylphenyl group is attached to every thiophene ring.[56] From molecular structure simulations, we know that this structure should force the phenyl group to rotate *ca.* 90° out of the main chain plane. In this position, the two octyl side chains will be pointing outwards, to form molecular bumpers which force the main chains apart in all three dimensions. PDOPT (**14**) turned out to have a very high photoluminescence quantum efficiency in both solution and in film, see Table 1. The regioregularity of the polymer is also relatively high.

Polymers **15**–**17** (Fig. 8) have been designed to test the versatility of this technique to increase the photoluminescence efficiency by separating the conjugated chains. All of the polymers have lower photoluminescence efficiency in both solution and in the solid state compared to PDOPT (**14**). PEHT (**15**) has relatively low regioregularity but a relatively high photoluminescence efficiency compared to P3OT (**1**). This is due to the branched side chain which is bulky and separates the conjugated chains by a short distance and this is enough to improve the photoluminescence efficiency. The separation of the polymer chains in polymer **16** (POMeOPT) is less than for PDOPT (**14**) and the photoluminescence efficiency is clearly lower. Polymer **17** has a very low photoluminescence efficiency in the solid state although the polymer has groups separating the conjugated chains on every second thiophene ring (on average) along the polymer backbone. To achieve high photoluminescence efficiency in the solid state the conjugated chains must be separated, but this is not enough to achieve high efficiency. The polymers must also have high crystallinity which demands high order along the polymer chain. This is also supported by our observation that batches of PDOPT (**14**) which have lower photoluminescence efficiency also have lower crystallinity. The degree of vibronic structure in absorption as well as in emission spectra of PDOPT (**14**) also depends on the crystallinity. The polymer is partially crystalline and at a relatively high crystallinity the photoluminescence efficiency is high and the vibronic structure in absorption and emission is clear.[56] With relatively low crystallinity the photoluminescence efficiency is low and the vibronic structures have disappeared in the absorption and are less pronounced in the emission. X-Ray studies of PDOPT (**14**) show that the closest lattice spacing of the conjugated backbones is 10.8 Å in the crystalline phase.[57] This distance is more than twice the value for P3OT (3.8 Å)[1] and must be caused by the bulky side chains. Formation of excimers is therefore prevented when the polymer forms crystals in contrast to polythiophenes with straight alkyl side chains which have the lowest photoluminescence yield when the polymer is regular[58] and easily form crystals. In the poly(*p*-phenylenevinylene) family of conjugated polymers the size and the nature of the substituents are important for the photoluminescence efficiency but the crystallinity seems not to be important in achieving high photoluminescence efficiency in this system, in contrast to the polythiophene system.[59]

As can be seen in Table 1 the photoluminescence efficiencies for PCHMT (**6**) and PMOT (**7**) are very low. Fast photophysical measurements of photoluminescence and photoinduced absorption in combination with an integrating sphere measurement of the photoluminescence efficiency give the basic physical parameters. The lifetime is of the order of some 100 ps in these highly twisted polythiophenes, thus the excited state is rapidly drained by non-radiative processes[60] such as intersystem crossing and/or internal conversion into the ground state. This suggests that polythiophenes are not the best choice when preparing blue PLEDs.

Stimulated emission and lasing in polythiophenes

The presence of a Stokes shift in conjugated luminescent polymers has been used to great advantage in polymer lasers, as the red shifted stimulated emission will meet little self-absorption in these materials. There is a chance that photoinduced absorption can overlap with the stimulated emission, destroying then the possibility of building polymer lasers. This is happily not so in the PDOPT (**14**) polymer, which has stimulated emission in the red range, not overlapping to any major degree with photoinduced absorption.[61] This polymer has been integrated into a resonant cavity by utilising the melt processability of the polymer. Two dielectric mirrors designed to reflect well in the stimulated emission wavelength range of the polymer are coated with a properly chosen polymer film *via* spin coating, and these two mirrors are then melt sealed under slight heating and pressure. Optically flat sandwiches can be obtained over areas of several square centimetres with this technique; by adjusting the spin coating conditions we are able to prepare thicknesses of a half emission wavelength, as necessary for the microcavity conditions to apply. Another advantage with this assembly technique is that the flow of oxygen to the pump region now has to occur through the thin polymer film, and therefore this also acts to seal the device from photochemical degradation in combination with oxygen. When pumping this device with short laser pulses, stimulated emission is observed below a threshold of 2–2.4 μJ cm^{-2}, and a lasing phase transition then occurs as a microcavity mode is enhanced, leading to a power conversion efficiency increase of two orders of magnitude.[62]

Polythiophenes for photodiodes

The design of polymers for photodiode operation is determined by the mechanism of operation. If a single polymer layer is used in between two electrodes and optical absorption is creating excitons to be dissociated close to one electrode, or at defects in the polymer structure we would only focus on exciton and charge mobility. When using photoinduced charge transfer, as observed between conjugated polymers and the fullerene C60, we will need to design this interface, and to design the structures in which separate electron and hole transport occurs. This is certainly also relevant when designing polymer/polymer interfaces. When designing a polythiophene for photodiode applications we can focus on different aspects. First and foremost is of course the designing of the absorption properties, tuneable by control of torsion through steric hindrance as already demonstrated above. We are able to cover with absorption almost all of the visible spectrum, but do not (yet) extend far out into the infrared. To develop materials for polymer solar cells, we expect that this will be necessary in order to match the solar spectrum. We will always find that 1-D conjugated polymers give us a narrow absorption spectrum compared to a 3-D semiconductor; this forces us to reconsider the rules for solar cell design, if this is our objective. By doing this analysis we have demonstrated that the optimum for the single polymer bandgap is found in the 1.7–2 eV range, substantially higher than that found for 3-D semiconductors.[63] But within the same analysis we can demonstrate the 1-D polymers never have absorption spectra broad enough to match the solar spectrum; we therefore have to combine several polymers of different bandgap. Polymer blends are therefore of interest for polymer photodiodes with broad wavelength coverage.

Then we might need to design the polymers for blending in the appropriate geometry. If combinations of conjugated polymers and acceptor molecules are to be used, we will need to consider the phase structure of such a blend and to tune the properties of the substituted polythiophene to obtain the desired morphology. The special case of C_{60} combined with polymers demonstrates this clearly. With PTOPT (**4**) we cannot make solid solutions of C_{60} at the level of 50%; in POMeOPT (**16**) this is feasible. The structure of the side groups on POMeOPT (**16**) resembles the structure of the solvent anisole (in which C_{60} is soluble) and is expected to compatibilize the polymer and C_{60}, as observed by force microscopy and infrared spectroscopy. Unfortunately, this POMeOPT–C_{60} (**16**–C_{60}) blend makes very poor devices; adding some PTOPT (**4**) now restores the diode functions and gives a photodiode with external quantum efficiencies of the order of 15%.[64] There is some nonlinearity in the response of photocurrent to varying incident light intensity, indicating that recombination and charge trapping can limit the response. This simple blending technique is adding two polymers with rather similar wavelength ranges of absorption, and does not help much to cover a broader spectrum of the solar spectrum.

In bilayer devices much can be clarified with respect to the photophysics of the polymer–C_{60} combination, and we have used the PEOPT–C_{60} (**11**–C_{60}) bilayers to study this physics. It turns out that the optical mode structures of these optically thin devices are determining for the performance; designing the layer geometry to constructively utilise this physics brings us to quantum efficiencies of 20% and better.[65] Depending on the geometry chosen we can reduce this number by a factor of four, should that be desired; what is more important is that conclusions on the efficiency of photoinduced charge transfer cannot be taken *prima facie* from diode studies, which also incorporate a great deal of multilayer optics aspects. The optimal geometry here is found when a maximum optical electrical field is located at the polymer/C_{60} interface.[66] Surprisingly, this modelling also reveals that most of the light giving photocurrent is absorbed in the C_{60} layer, with a minor contribution from the polymer layer.

With the help of some of these observations we can now start collecting more of the solar spectrum by adding different polymers into the polymer layer. This can be used to bring up the external quantum efficiency to 35–40%, in devices where light trapping into phase separated polymer films is also helping out.[67] Still we are barely covering the visible range of absorption with little coverage of the solar spectrum in the near-IR range.

Conclusion

Among the conjugated polymers, polythiophenes have been proven to be one of the most versatile classes for molecular engineering. Enhancement of conductivity and thermal stability, design of luminescence colours and efficiency for use in light emitting diodes and in photodiodes and photopumped lasers are demonstrated at this point.

Acknowledgements

These studies have been performed by a large number of collaborators including but not limited to Göran Gustafsson, Jan-Olov Nilsson, Peter Dyreklev, Qibing Pei, Magnus Granström, Magnus Berggren, Lucimara Stolz Roman, Lichun Chen, Leif Pettersson at Linköping University and Thomas Hjertberg, Olof Wennerström, Dennis Selse, Rolf Schmidt at Chalmers University of Technology. The work on soluble polythiophenes was initiated at Neste Oy by Jan-Erik Österholm, Jukka Laakso, Hannele Järvinen, with co-workers and our collaborators in the Nordic projects on these materials include Henrik Stubb, now at Åbo Akademi.

Present funding for photodiodes and polymer electronics comes from the Göran Gustafsson foundation, from the Swedish Research Council for Engineering Sciences (TFR), from the Swedish Foundation for Strategic Research (SSF) and from Chalmers University of Technology.

References

1 *Handbook of Conducting Polymers, 2nd edn.*, ed. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynholds, Marcel Dekker, New York, 1998.
2 K.-Y. Jen, G. G. Miller and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1986, 1346.
3 R. Sugimoto, S. Takeda, H. B. Gu and K. Yoshino, *Chem. Express*, 1986, **1**(11), 635.
4 R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93.
5 R. L. Elsenbaumer, K. Y. Jen and R. Oboodi, *Synth. Met.*, 1986, **15**, 169.
6 K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato and K. Suzuki, *Tetrahedron*, 1982, **38**, 3347.
7 H. Mao, B. Xu and S. Holdcroft, *Macromolecules*, 1993, **26**, 1163.
8 M. Sato and H. Morii, *Macromolecules*, 1991, **24**, 1196.
9 M. R. Andersson, D. Selse, M. Berggren, H. Järvinen, T. Hjertberg, O. Inganäs, O. Wennerström and J.-E. Österholm, *Macromolecules,* 1994, **27**, 6503.
10 I. Levesque and M. Leclerc, *J. Chem. Soc., Chem. Commun.*, 1995, 2293.
11 M. R. Andersson, W. Mammo, T. Olinga, M. Svensson, M. Theander and O. Inganäs, *Synth. Met.*, 1999, **101**, 11.

12 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.

13 S. Guillerez and G. Bidan, *Synth. Met.*, 1998, **93,** 123.

14 R. D. McCullough, P. C. Ewbank and R. S. Loewe, *J. Am. Chem. Soc.*, 1997, **119**, 633.

15 A. Iraqi and G. W. Barker, *J. Mater. Chem.*, 1998, **8**, 25.

16 R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.*, 1999, **11**, 250.

17 T.-A. Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.

18 J.-E. Österholm, J. Laakso, P. Nyholm, H. Isotalo, H. Stubb, O. Inganäs and W.-R. Salaneck, *Synth. Met.*, 1989, **28**, C435.

19 G. Tourillon and F. Garnier, *J. Electrochem. Soc.*, 1983, **130**, 2042.

20 J.-E. Österholm and P. Passiniemi, *Synth. Met.*, 1997, **18**, 213.

21 G. Gustavsson, O. Inganäs, J. O. Nilsson and B. Liedberg, *Synth. Met.*, 1988, **26**, 297.

22 M. T. Loponen, T. Taka, J. Laakso, K. Väkiparta, K. Suuronen, P. Valkeinen and J.-E. Österholm, *Synth. Met.*, 1991, **41**, 479.

23 Y. Wang and M. F. Rubner, *Synth. Met.*, 1991, **41**, 1103.

24 O.Inganäs, W. R. Salaneck, J. E. Österholm and J. Laakso, *Synth. Met.*, 1988, **22**, 395.

25 M. Granström and O. Inganäs, *Synth. Met.*, 1992, **48**, 21.

26 N. Ljungqvist and T. Hjertberg, *Macromolecules*, 1995, **28**, 5993.

27 H. Järvinen, J. Laakso, T. Taka, J.-E. Österholm, Q. Pei and O. Inganäs, *Synth. Met.*, 1993, **55**, 1260.

28 Q. Pei, O. Inganäs, J.-E. Österholm and J. Laakso, *Polymer*, 1993, **34**, 247.

29 R. L. Elsenbaumer, K. Y. Jen, G. G. Miller and L. W. Shacklette, *Synth. Met.,* 1987, **18**, 277.

30 M. R. Andersson, Q. Pei, T. Hjertberg, O. Inganäs, O. Wennerström and J.-E. Österholm, *Synth. Met.*, 1993, **55**, 1227.

31 Q. Pei, H. Järvinen, J.-E. Österholm, O. Inganäs and J. Laakso, *Macromolecules*, 1992, **25**, 4297.

32 M. R. Andersson, M. Berggren, O. Inganäs, G. Gustafsson, J. C. Gustafsson-Carlberg, D. Selse, T. Hjertberg and O. Wennerström, *Macromolecules*, 1995, **28**, 7525.

33 K. Väkiparta, J. Moulton, A. J. Heeger, P. Smith, H. Isotalo, H. Stubb and M. Loponen, *Synth. Met.*, 1991, **41**, 903.

34 Y. Wang and M. F. Rubner, *Synth. Met.*, 1990, **39**, 153.

35 Y. Wang and M. F. Rubner, *Synth. Met.*, 1992, **47**, 255.

36 V.-T. Truong, *Synth. Met.*, 1992, **52**, 33.

37 Y. Cao, P. Smith and A. J. Heeger, *Synth. Met.*, 1992, **48**, 91.

38 M. C. Magnoni, M. C. Gallazzi and G. Zerbi, *Acta Polym.*, 1996, **47**, 228.

39 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.

40 P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Nature*, 1992, **356**, 47.

41 A. B. Holmes, D. D. C. Bradley, A. R. Brown, P. L. Burn, J. H. Burroughes, R. H. Friend, N. C. Greenham, R. W. Gymer, D. A. Halliday, R. W. Jackson, A. Kraft, J. H. F. Martens, K. Pichler and I. D. W. Samuel, *Synth. Met.*, 1993, **57**, 4031.

42 A. Kraft, P. L. Burn, A. B. Holmes, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Synth. Met.*, 1993, **55**, 936.

43 G. G. Malliaras, J. K. Herrema, J. Wildeman, R. H. Wieringa, R. E. Gill, S. S. Lampoura and G. Hadziioannou, *Adv. Mater.*, 1993, **5**, 721.

44 Z. Yang, I. Sokolik and F. E. Karasz, *Macromolecules*, 1993, **26**, 1188.

45 R. E. Gill, G. G. Malliaras, J. Wildeman and G. Hadziioannou, *Adv. Mater.*, 1994, **6**, 132.

46 M. Berggren, M. Granström, O. Inganäs and M. Andersson, *Adv. Mater*., 1995, **7**, 900.

47 T. Granlund, L. A. A. Pettersson, M. R. Andersson and O. Inganäs, *J. Appl. Phys.*, 1997, **81**, 8097.

48 M. Berggren, G. Gustafsson, O. Inganäs, M. R. Andersson, T. Hjertberg and O. Wennerström, *Appl. Phys. Lett.*, 1994, **65**, 1489.

49 H. J. Fell, E. J. Samuelsen, M. R. Andersson, J. Als-Nielsen, G. Grübel and J. Mårdalen, *Synth. Met.*, 1995, **73**, 279.

50 M. Berggren, O. Inganäs, G. Gustafsson, J. Rasmusson, M. R. Andersson, T. Hjertberg and O. Wennerström, *Nature*, 1994, **372**, 444.

51 M. Granström and O. Inganäs, *Appl. Phys. Lett.,* 1996, **68**, 147.

52 M. Granström and O. Inganäs, *Adv. Mater.*, 1995, **7**, 1012.

53 M. Granström, M. Berggren, D. Pede, O. Inganäs, M. R. Andersson, T. Hjertberg and O. Wennerström, *Supramol. Sci.*, 1997, **4**, 27.

54 U. Lemmer, R. F. Mahrt, Y. Wada, A. Greiner, H. Bässler and E.O. Göbler, *Appl. Phys. Lett*., 1993, **62**, 2827.

55 M. Berggren, P. Bergman, J. Fagerström, O. Inganäs, M. R. Andersson, H. Weman, M. Granström, S. Stafström, O. Wennerström and T. Hjertberg, *Chem. Phys. Lett*., 1999, **304**, 84.

56 M. R. Andersson, M. Berggren, T. Olinga, T. Hjertberg, O. Inganäs and O. Wennerström, *Synth. Met*., 1997, **85**, 1383.

57 K. E. Aasmundtveit, E. J. Samuelsen, W. Mammo, M. Svensson, M. R. Andersson, L. A. A. Pettersson and O. Inganäs, submitted.

58 B. Xu and S. Holdcroft, *Macromolecules*, 1993, **26**, 4457.

59 M. R. Andersson, G. Yu and A. J. Heeger, *Synth. Met*., 1997, **85**, 1275.

60 M. Theander, O. Inganäs, W. Mammo, T. Olinga, M. Svensson and M. R. Andersson, submitted.

61 A. Ruzeckas, M. Theander, L. Valkunas, M. R. Andersson, O. Inganäs and V. Sundström, *J. Lumin*., 1998, **76&77**, 474.

62 T. Granlund, M. Theander, M. Berggren M. Andersson, A. Ruzeckas, V. Sundström, G. Björk, M. Granström and O. Inganäs, *Chem. Phys. Lett*., 1998, **288**, 879.

63 D. Godovsky and O. Inganäs, to be submitted.

64 L. S. Roman, M. R. Andersson, T. Yohannes and O. Inganäs, *Adv. Mater*., 1997, **9**, 1164.

65 L. S. Roman, W. Mammo, L. Pettersson, M. R. Andersson and O. Inganäs, *Adv. Mater*., 1998, **10**, 774.

66 L. A. A. Pettersson, L. S. Roman and O. Inganäs, *J. Appl. Phys.*, 1999, **86**, 487.

67 L. Chen, L. S. Roman, M. R. Andersson, D. M. Johansson and O. Inganäs, *J. Appl. Phys.*, in the press.

Paper 9/02859E