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Blue–green LEDs from poly(phenylenevinylene) grafted with poly(ethylene imine): improved stability and coordination of transition metals

Iris Benjamin,[a,b] **Yair Avny,**[b] **Vadim N. Savvate'ev,**[c] **Dan Davidov**[c] **and Ronny Neumann***[a]

[a]*Casali Institute of Applied Chemistry,* [b]*Department of Organic Chemistry, and* [c]*Racah Institute Physics, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel*

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Light emitting diode devices prepared from poly(phenylenevinylene) grafted with poly(ethylene imine) show blue shifted spectra ($\lambda_{max}\approx$475–490 nm) proportional to the ratio of the grafted to ungrafted segmers and significantly (up to sevenfold) improved lifetimes; further coordination of transition metals led to increased electroluminescence intensity.

The realization of the technological advantages which conjugated polymers, notably of the poly(phenylvinylene) (PPV) family, offer compared to inorganic semiconductors especially in the field of light emitting diodes, LEDs,[1] will much depend on the ability to fabricate stable, long-lived devices of sufficient brightness and efficiency. While devices of sufficient brightness and efficiency across the visible spectrum and even beyond have already been described,[1] the typical lifetimes of such devices are apparently still insufficient for most applications. The specific mechanism of device failure may vary according to the method used to prepare the device and the specific operating conditions. In general, device failure modes include (a) destruction of the commonly used ITO anode,[2,3] already in the film preparation stage because of the formation of hydrohalic acid, which leads to diffusion of indium into the emitting polymer phase, a rise in current, localized heating and delamination at the ITO–PPV interface, (b) diffusion of oxygen from ITO or the atmosphere and degradation of PPV by photooxidation,[4–9] (c) oxidation of the low work function cathode *e.g.* Al, Mg in the presence of oxygen and humidity leading to delamination at the cathode–PPV interface[10–13] and (d) imperfections in the polymer films leading to short circuits, heating of the sample and finally carbonization.[14] Several directions of research have been suggested to help remedy these stability problems including use of a self-assembly technique for improved film homogeneity,[15] addition of intermediate layers at the electrodes to abate problems of diffusion and delamination,[16,17] replacement of ITO with polyaniline as anode,[18,19] use of soluble conjugated polymers[20,21] or methods where hydrohalic acids are not formed upon polymer conjugation[22] and operation in a pulsed mode with low duty cycles (instead of using a dc current) to decrease heating in the devices.[23,24]

Here, we describe chemical modifications which can be made to PPV in order to extend device lifetime. The approach taken has been to graft PPV with poly(ethylene imine) (PEI) so as to provide (a) better conjugated polymer–electrode interfaces, (b) capture of hydrohalic acid formed as result of the Lenz–Wessling method[25,26] used for PPV preparation through quaternization of amines and (c) use of additional complexation of transition or lanthanide metal ions by the poly(ethylene imine) graft to extend device lifetime presumably by separating PPV backbones, thus, reducing aggregation quenching and/or inhibition of radical type photooxidative degradation. Additionally, the grafted PPV:PEI polymers show shifted blue–green luminescence at 480–490 nm.

The generalized synthetic scheme for the preparation of poly(phenylenevinylene) (PPV) grafted with poly(ethylene imine), $NH_2(CH_2CH_2NH)_nH$ (PEI) is presented in Scheme 1. The precursor polymer of PPV was reacted with PEI ($n=3$ or *ca.* 45)† at various $z:b$ ratios.‡ Films were then formed on the desired substrate from the grafted precursor PPV and the final PPV:PEI films were obtained by heating to 220 °C under vacuum. The degree of grafting, *i.e.* the ratio $x:y$ was calculated from C, H and N elemental analysis of polymers.§ The absorption and photoluminescence spectra of PPV and PPV:PEI (Fig. 1) show that the addition of the graft, yielding $x:y$ ratios of *ca.* 20:1, significantly blue-shifted the peaks by 30 (photoluminescence) or 60 (electroluminescence) nm. Luminescence intensities (not shown) decreased only marginally by *ca.* 10–20% in PPV:PEI($x:y=20$). Higher degrees of grafting, *e.g.* $x:y\approx5$, formed from reaction conditions where $z:(b/n)=1$, led only to a further small hypsochromic shift of *ca.* 5 nm, but a much more dramatic decrease of *ca.* 70% in the luminescence intensity. The strong blue shift observed at $x:y$ ratios of *ca.* 20:1 in the PPV:PEI spectra can be attributed mostly to steric factors, *i.e.* prevention of π stacking between PPV chains, upon addition of the graft rather than reduction of the effective conjugation length since the maximum effective conjugation lengths in PPV are estimated to be *ca.* 10. This was surmised from the observation that a further increase in the degree of grafting and decrease in average conjugation lengths, *i.e.* from $x:y=$ *ca.* 20:1 to *ca.* 5:1, did not lead to a significant additional blue-shift, but instead, to a significant decrease in luminescence intensity.

Since polyamines are known chelating agents, various transition or lanthanide metals were added to the PPV:PEI polymers at the polymer precursor stage. Interestingly, analysis of the degree of coordination after complexation and purification¶ by ICP–MS showed that for PEI ($n=3$) only lantha-

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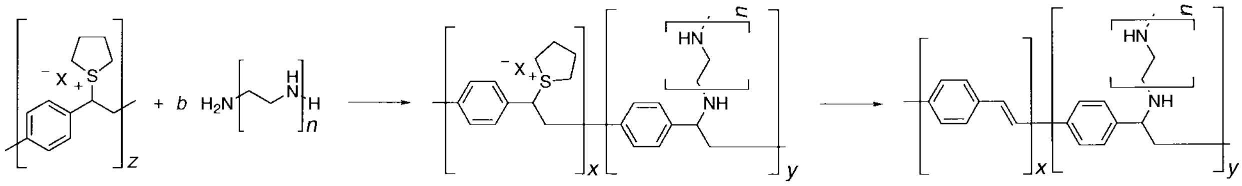
†PEI($n=3$) is triethylenetetraamine of 98% purity while PEI($n=45$) is a partially branched polymer [Aldrich 40,870–0; $M_n=1800$ (GPC), $M_W=2000$ (LS)].

‡In a typical procedure [$z:(b/n)=5$], PPV:PEI graft polymers were prepared by mixing 3.95 g of the precursor polymer of PPV, prepared by the usual Wessling–Lenz procedure, dissolved in 350 mL deionized water with 141 mg of PEI. For PEI($n=3$), triethylenetetraamine, the reaction was carried out at room temperature for 18 h, whereas for PPV:PEI($n=45$) the reaction was carried out at 50–55 °C for 4 days. After completion of the reaction, non-reacted PEI was removed by dialysis (12 000 dalton cutoff), the films spin cast and the final PPV:PEI graft polymers were obtained after heating to 220 °C for 12 h under vacuum.

§C, H, N elemental analysis of PPV:PEI polymers indicated that for a original $z:(b/n)$ ratio of 5, an $x:y$ ratio of 20:1 was obtained for PPV:PEI($n=3$) and a ratio of 22:1 was obtained for PPV:PEI($n=45$).

¶Complexation of transition metals by PPV:PEI was carried out by mixing the precursor polymer of PPV:PEI ($x:y\approx20$) obtained as described in ref. 16 with transition metal salts (MX) such as $CuBr_2$, $EuCl_3\cdot6H_2O$, $TbCl_3\cdot6H_2O$ or $La(NO_3)_3\cdot6H_2O$ where $n:MX=6$. After 2 h at room temperature, excess MX was removed by dialysis. The amount of transition metal complexed by pre-PPV:PEI was measured by ICP-MS before obtaining the final PPV:PEI:M graft polymers, by formation of spin cast thin films and heating to 220 °C for 12 h under vacuum.



Scheme 1 Reaction scheme for the preparation of PPV : PEI graft polymers.

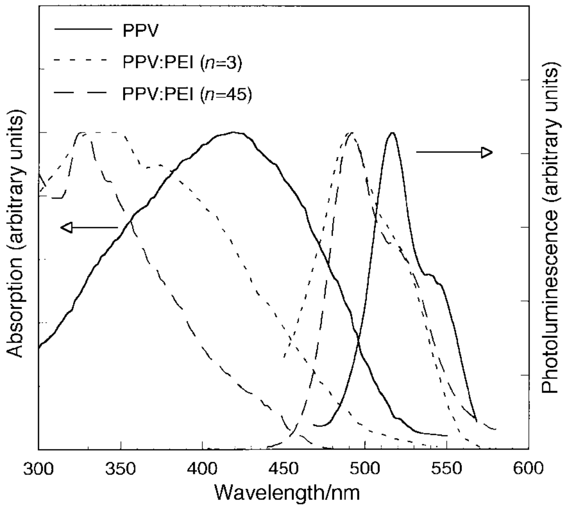


Fig. 1 UV–VIS absorption and photoluminescence spectra of PPV : PEI. Spectra were measured for PPV, PPV : PEI($n=3$, $x:y=20$) and PPV : PEI($n=45$, $x:y=22$). Films of thickness 227 ± 24 Å were deposited on quartz glass. For PL measurements, excitation wavelengths were 390 nm for PPV and 375 nm for PPV : PEI.

nide metals such as La^{III}, Tb^{III} and Eu^{III} were coordinated to 30% of the PEI ($n=3$) grafts, while first row transition metal cations (Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) were very poorly chelated (<0.1%). On the other hand, for PEI ($n \approx 45$), of all cations used only Cu^{II} was effectively coordinated at *ca.* 45% of the PEI grafts while other first row transition metal and lanthanide cations were poorly coordinated. Measurement of photoluminescence and electroluminescence in cases where coordination was successful, the latter in a ITO/PPV : PEI : M/Al configuration, showed that metal cation coordination had a considerable positive effect on the luminescence intensity without changing the spectra (Fig. 2). This effect was reproducible for 10 samples. Addition of transition metal salts to non-grafted PPV (PPV : M) had no effect on the spectra.

A typical current–voltage curve showing the effect of the PEI($n=3$, $x:y=20$) graft and lanthanide metal cation (Tb^{III}) complexation is shown in Fig. 3. The PPV : PEI devices have a threshold voltage of 4.5 ± 0.5 V depending on the specific sample. Metal cation complexation decreases the threshold voltage to *ca.* 2–3 V. Comparison of the electroluminescence intensity at a constant current, until device failure, for PPV : PEI($n=3$, $x:y=20$) and PPV : PEI($n=3$, $x:y=20$): Tb (Fig. 3 insert), reveals the positive effect of metal complexation on the device lifetime and electroluminescence intensity (Fig. 2). A series of similar experiments (internal comparison) under constant current and atmospheric conditions (non-encapsulated devices) leads to a comparison (Table 1) of lifetimes for various emitting polymer layers of PPV : PEI : M. It is observed that upon addition of long chain grafts, PEI ($n=45$), there is a six-fold increase in the device lifetime. The complexation of Cu^{II} yielded no further statistically significant increase. For PPV grafted with PEI($n=3$), the results were different. Here, the graft alone had no effect on the device lifetime, but further complexation of lanthanides increased the device longevity up to seven-fold. Importantly, again simple addition of lanthanide salts to non-grafted PPV (PPV : M) had no positive effect on the device lifetime. We propose the following preliminary explanations or hypotheses, for the observed results. For PPV : PEI($n=45$) the presence of PEI ($M_W=2000$) increases the device lifetime because (a) HCl formed in the thermal elimination process is easily captured by amine moieties in the grafted polymer by formation of quaternary ammonium adducts, thus preventing degradation of the ITO during the formation of the conjugated polymer and injection of In^{III} into the polymer and/or (b) the presence of the PEI grafts improves the adhesion at the electrode (mainly ITO)–polymer interfaces and less delamination may occur owing to the presence of the hydrophilic PEI grafts, therefore, leading to longer device lifetimes. Additional complexation of copper did not synergestically improve the device lifetime although the resulting brightness was somewhat higher. At similar brightness some further improvement in device lifetime can thus be expected. For PPV : PEI($n=3$), the presence of the low molecular weight graft alone did not suffice to hinder delamination or reaction with HCl. Rather, increased device lifetimes and luminescence intensity in PPV : PEI($n=3$) : M must be associated with a different mechanism. Again preliminarily, we assume that lanthanide chelation may have a steric effect, leading to separation of the PPV main chains

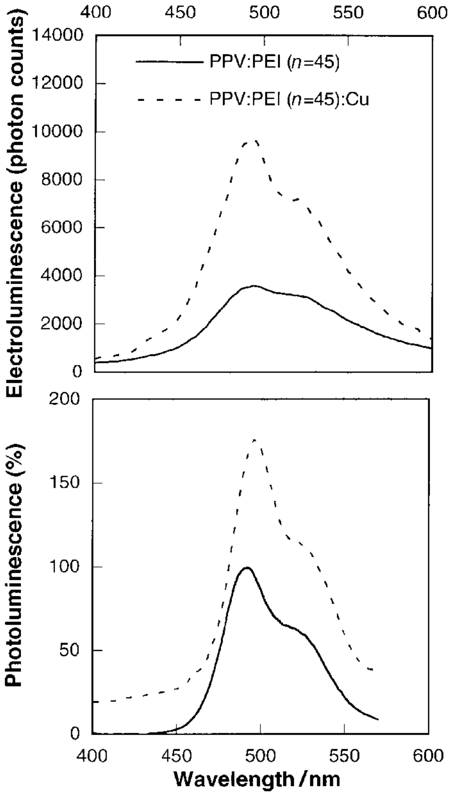


Fig. 2 Electroluminescence and photoluminescence spectra of PPV : PEI and PPV : PEI : M. Spectra were measured for PPV : PEI($n=45$, $x:y=22$) and PPV : PEI($n=45$, $x:y=22$) : Cu. For PL films of thickness 227 ± 24 Å were deposited on quartz glass, excitation wavelength = 375 nm. For EL, LEDs were prepared in the ITO/polymer/Al non-encapsulated configuration and operated under ambient conditions. The thickness of the polymer layer was 397 ± 42 Å, the electrode area was 20 mm^2, and devices were operated at 6 V dc. Almost the same results were obtained for PPV : PEI($n=3$ $x:y=20$) and PPV : PEI($n=3$, $x:y=20$) : Tb or Eu.

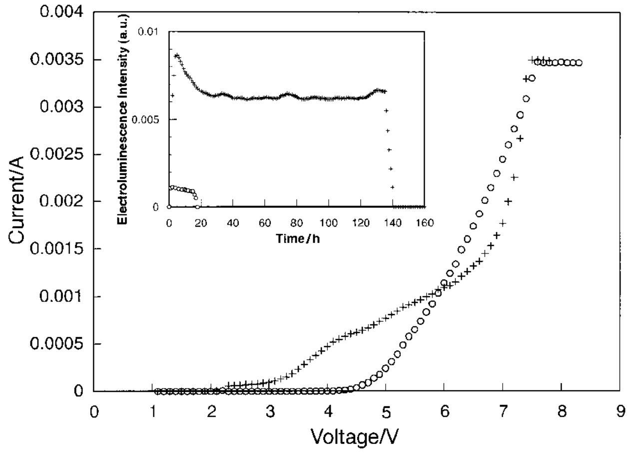


Fig. 3 Current–voltage curves and electrolumiscence intensity as a function of time for PPV:PEI(n=3, x:y=20) and PPV:PEI(n=3, x:y=20):Tb. LEDs were prepared in the ITO/polymer/Al non-encapsulated configuration and operated under ambient conditions. The thickness of the polymer layer was 397±42 Å, the electrode area was 20 mm^2. Lifetimes were measured under a constant current of 10 mA.

Table 1 PPV:PEI LED device lifetimes[a]

Emitting polymer	Device lifetime[b]/h
PPV	22±5
PPV:PEI(n=3, x:y=20)	18±3
PPV:PEI(n=3, x:y=20):Eu	135±8
PPV:PEI(n=3, x:y=20):Tb	122±10
PPV:PEI(n=45, x:y=22)	118±4
PPV:PEI(n=45, x:y=22):Cu	114±6

[a] LEDs were prepared in the ITO/polymer/Al non-encapsulated configuration and operated under ambient conditions. The thickness of the polymer layer was 397±42 Å, the electrode area was 20 mm^2, and devices were operated at a constant current of 10 mA. [b] Average of three measurements.

and reduced aggregation quenching. Other possibilities such as inhibition of photooxidative degradation by the complexed metal cation need also be considered. In the future, we believe that integration of the chemical modifications described herein, along with use of better suited electrodes, exclusion of oxygen and humidity, and operation in a pulsed mode, may lead to practical LED devices with commercially attractive lifetimes.

Acknowledgments

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References

1 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
2 H. Aziz and G. Xu, *J. Phys. Chem. B*, 1997, **101**, 2745.
3 S. Karg, M. Meier and W. Reiss, *J. Appl. Phys.*, 1997, **82**, 1951.
4 B. H. Cumpston and K. F. Jensen, *Trends Polym. Sci.*, 1996, **4**, 151.
5 B. H. Cumpston, I. D. Parker and K. F. Jensen, *J. Appl. Phys.*, 1997, **81**, 3716.
6 B. H. Cumpston and K. F. Jensen, *Synth. Met.*, 1995, **73**, 195.
7 J. Salbeck, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 1667.
8 S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott, *Appl. Phys. Lett.*, 1997, **70**, 2067.
9 F. Papadimitrakopoulos, X.-M. Zhang, D. L. Thomsen and K. A. Higginson, *Chem. Mater.*, 1996, **8**, 1363.
10 P. E. Burrows, V. Bulcovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty and M. E. Thompson, *Appl. Phys. Lett.*, 1994, **65**, 2922.
11 J. McElvain, H. Antoniadis, M. R. Hueschen, J. N. Miller, D. M. Roitman, J. R. Sheats and R. L. Moon, *J. Appl. Phys.*, 1996, **80**, 6002.
12 J. C. Scott, J. H. Kaufman, P. J. Brock, R. DiPietro, J. Salem and J. A. Goitia, *J. Appl. Phys.*, 1996, **79**, 2745.
13 J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, *Science*, 1996, **273**, 884.
14 V. N. Savvate'ev, A. V. Yakimov, D. Davidov, R. M. Pogreb, R. Neumann and Y. Avny, *Appl. Phys. Lett.*, 1997, **71**, 3344.
15 H. Hong, D. Davidov, Y. Avny, H. Chayet, E. Z. Faraggi and R. Neumann, *Adv. Mater.*, 1995, **7**, 846.
16 M. Meier, M. Cölle, S. Karg, E. Buchwals, J. Gmeiner, W. Riess and M. Schwoerer, *Mol. Cryst. Liq. Cryst.*, 1996, **283**, 197.
17 S. Karg, J. C. Scott, J. R. Salem and M. Angelopoulos, *Synth. Met.*, 1996, **80**, 111.
18 G. Yu, *Synth. Met.*, 1996, **80**, 143.
19 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477.
20 S. Doi, T. Kuwabara, T. Noguchi and T. Ohnishi, *Synth. Met.*, 1993, **57**, 4174.
21 D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, 1991, **58**, 1982.
22 S. Son, A. Dodabalapur, A. J. Lovinger and M. E. Galvin, *Science*, 1995, **269**, 376.
23 Y. Z. Wang, D. D. Gebler, L. B. Lin, J. W. Blatchford, S. W. Jessen, H. L. Wang and A. J. Epstein, *Appl. Phys. Lett.*, 1996, **68**, 894.
24 Y. Z. Wang, D. D. Gebler, K. D. K. Fu, T. M. Swager and A. J. Epstein, *Appl. Phys. Lett.*, 1997, **70**, 3215.
25 R. A. Wessling and R. G. Zimmermann, *US Pat.*, 3 401 142, 1968.
26 R. W. Lenz, C. C. Han, J. S. Smith and F. E. Karasz, *J. Polym. Sci., Polym. Chem.*, 1988, **26**, 3241.

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