Blue emitting polyaniline†

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A family of stable polyaniline (PANI) derivatives exhibiting deep blue photoluminescence (PL) has been prepared. The synthetic strategy provides a unique way to functionalize the PANI backbone.

Two different advances in the science and technology of conjugated polymers are rapidly emerging as forerunners among the electrical and optical applications of the coming decade. These refer to making a class of polymers conducting, rendering flexible and foldable electronic circuits possible,[1] and making another class of polymers emit colors under various excitations, so that extraordinarily thin and flexible display panels become a reality.[2] We report a blue photoluminescence from a novel class of functionalized PANI, otherwise well known to be an archetypical conducting polymer.[3] While there have been a few reports on visible luminescence from the reduced form of PANI (leucoemeraldine base, LB),[4] our samples exhibit a distinct improvement over LB in terms of enhanced environmental stability and a much higher PL efficiency.

The serendipitous discovery of this interesting class of luminescent polymer had started with our attempts to carry out electron-doping of PANI, in contrast to the ubiquitous hole-doped conducting PANI. To achieve an n-doped PANI, we devised a synthetic strategy that proceeds with deprotonation of the amine N atoms (–NH–) in the polymer using *n*-butyl lithium (*n*BuLi), which is a very strong base.[5] However, the lithiated PANI (LPAN) thus obtained is extremely unstable and reacts exothermally with moisture. The next part of the synthesis was aimed to stabilize LPAN. Since the instability of LPAN is primarily because of its electron-rich N centers, we carried out a complexation of LPAN with electron-deficient boron trihalides (BX_3, X = F, Cl and Br) to form the final product ($LPBX_3$). Obviously, the last step involved in the synthesis negates the effect of n-doping, as the majority of negative charges doped into the polymer are pulled out by the BX_3 molecules. Consequently, $LPBX_3$ is non-conducting, but instead becomes stable and exhibits PL.

The PL emission and excitation spectra along with the respective UV–visible absorption spectra collected in dimethylsulfoxide (DMSO) are shown in Fig. 1(a). All the samples show an intense absorption at 340 nm, which is characteristic of the band gap in these systems. There is a second peak at 450 nm,[5] which is lower in intensity. The emission characteristics of the three samples are also identical. The emission maximum (λ_{em}) is at 430–440 nm. Fig. 1(b) shows the deep blue emission from a solution of $LPBF_3$ in DMSO, when excited using a light of 360 nm wavelength. The Commission Internationale de l'Eclairage (CIE) coordinates for the three samples are (0.155 ± 0.005, 0.079 ± 0.005).[5] These values are very close to the National Television Standards Committee (NTSC) coordinates for *pure blue* emission (0.14, 0.08).[6] In all cases, the excitation spectrum corresponding to the emission at 435 nm has a peak (λ_{ex}) at ~360 nm, and dies out below 420 nm. The fact that the absorption feature at 450 nm does not play any role in the fluorescence decay is confirmed by the fact that different excitation spectra corresponding to emission at wavelengths between 430 and 520 nm are identical to each other.[5]

The absence of any absorption feature between 500–900 nm suggests that in $LPBX_3$,[5] PANI is in a lower oxidation state than emeraldine base (EB). It is well known that in X-ray photoelectron spectroscopy (XPS), the N 1s core level chemical shifts are different for amine and imine N (399.3 ± 0.1 and 398.1 ± 0.1 eV, respectively).[7] The N 1s spectrum of $LPBF_3$ is shown along with that of EB in Fig. 2; the spectra for the other two samples are very similar to that of $LPBX_3$, as shown here.[5] It is evident that N 1s spectra of $LPBX_3$ samples are significantly narrower than that of EB. In order to quantify this observation and thereby understand the nature of these changes, we decompose the total N 1s spectrum

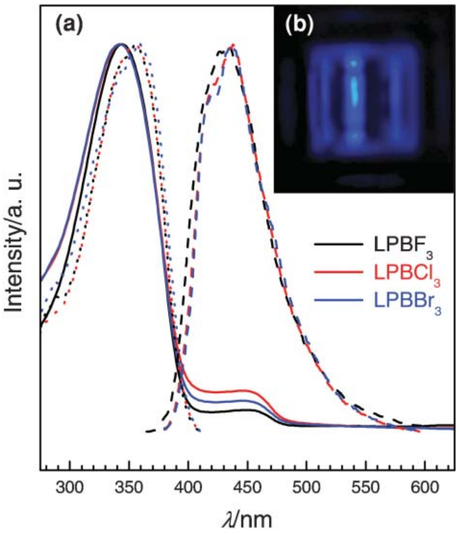

Fig. 1 (a) UV–Visible absorption spectra (solid lines), excitation spectra (λ_{em} = 435 nm, dotted lines) and emission spectra (λ_{ex} = 360 nm, dashed lines), for $LPBF_3$ (black), $LPBCl_3$ (red) and $LPBBr_3$ (blue). (b) Deep-blue emission from a solution of $LPBF_3$ in DMSO, upon exciting with a monochromatic beam (λ = 360 nm) from a xenon discharge lamp. The centrally emitted color can also be seen reflecting off the walls of the cuvette and beyond.

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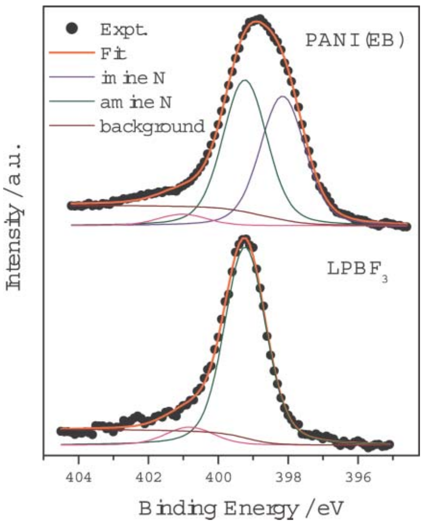
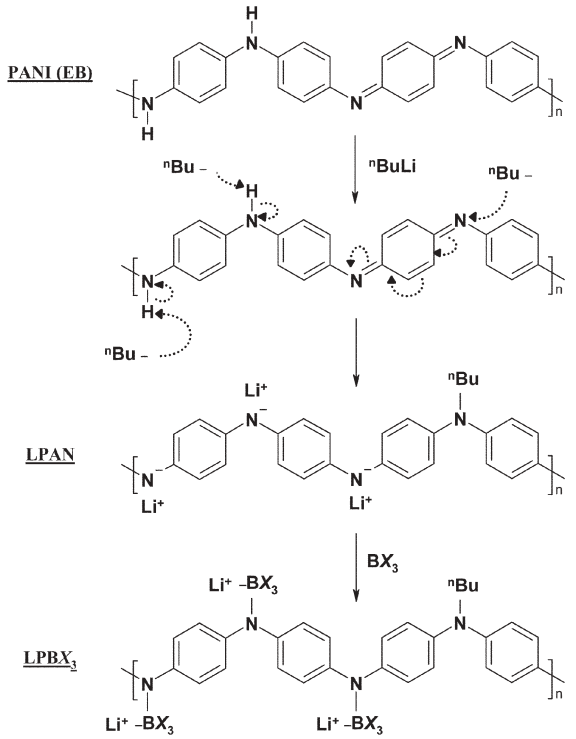


Fig. 2 The XPS N 1s spectra for thin films of undoped PANI (EB) and LPBF$_3$. The results of a least-squared-error fitting are also shown. The imine component appearing at 398.2 eV (blue curve) in undoped PANI is absent in the case of LPBF$_3$.

in terms of component spectra. The N 1s spectrum of EB requires dominantly two components of roughly equal intensity with peaks of the corresponding component spectra appearing at 399.2 (amine N) and 398.2 eV (imine N), as shown in Fig. 2. Along with the ever-present smoothly increasing background contribution arising from inelastic scattering of photoelectrons, we also needed to include a weak intensity component spectrum with a peak at about 400.7 ± 0.1 eV (see Fig. 2), in order to obtain a very good description of experimental spectra.[5] In the case of EB, the ratio of amine to imine N is 1 : 0.91, which agrees well with its 50% oxidized state. However, in case of LPBX$_3$, the spectral analysis unambiguously establishes a complete absence of the imine component, as shown in Fig. 2 for LPBF$_3$. Therefore, with the help of XPS we are able to establish that in LPBX$_3$, PANI is in the fully reduced form.

At this stage, it is important to attempt an understanding of the reduction mechanism of PANI during the formation of LPBX$_3$. There are clearly two steps involved in the synthesis of LPBX$_3$. In the first step, EB reacts with excess *n*BuLi to form LPAN, and in the next step, LPAN reacts with BX$_3$. We believe that the reduction takes place in the first step of the reaction. In Scheme 1, we present a possible mechanism for the reduction. In the first step of the reaction, excess *n*BuLi plays a dual role: on one hand it acts as a strong base that deprotonates the amine N to generate N^- Li+ species. Simultaneously, it also acts as a nucleophile that attacks one of the imine N, initiating a rearrangement of the π-electrons that eventually converts the quinoid ring to a benzenoid type, as shown in the first step of Scheme 1. Therefore at the end of the first step, all the 6-membered rings in LPAN are reduced to the benzenoid form. During the same step, one of the imine N is converted to amine form (–NR–, where R is the *n*-butyl group), while the other imine N becomes indistinguishable from the two deprotonated amine N atoms. In the second step of the reaction, BX$_3$ complexes with the three negatively charged (deprotonated amine) N, forming a $[N–BX_3]^-$ Li^+ kind of species. Thus, in LPBX$_3$, all the N atoms are converted to amine form. The fact that XPS is not able to differentiate between N–R and N–BX$_3$ species could mean that the electron density around the N atom is similar in both the species and, therefore, that the two kinds of amine N have very close binding energies. This suggests that there should be a significant charge transfer from the N to the B atom, making the latter highly negatively charged.



Scheme 1 A reaction mechanism proposed to explain the reduction of PANI (EB) during the synthesis of LPBX$_3$.

In order to validate the mechanism presented in Scheme 1, we have carried out a series of spectroscopic investigations. We carried out a careful reprotonation of LPAN with water, and characterized the product.[5] According to our hypothesis, one would expect LPAN to undergo complete protonation in water to form a fully reduced PANI derivative with an *n*-butyl chain tethered at one of the imine N sites. On the other hand, if there were no alkylative addition in the first step, reprotonation would be expected to give back PANI in the EB form. Fig. 3 shows the FTIR spectrum of reprotonated LPAN (rLPAN) compared to that of PANI in EB and LB[8] forms. In the spectrum of EB, the quinoid (Q) and benzenoid (B) ring deformations appear at 1593 and 1498 cm^{-1} (shown by solid arrows), respectively.[9] Upon reduction, the 1593 cm^{-1} peak becomes vanishingly small, as observed in the case of LB and rLPAN. Further, a small peak at 1379 cm^{-1} (marked by a dashed arrow) in the spectrum of EB, which corresponds to a characteristic stretching mode of the B–N=Q moiety, is also diminished in the spectrum of rLPAN. We have also studied the spectra of rLPAN and EB in the vicinity of 3000 cm^{-1}.[5] Both the samples exhibit the aromatic C–H stretching peaks at 3020 cm^{-1}; additionally in the case of rLPAN, aliphatic C–H stretching features of *n*-butyl group can be seen around 2850–2950 cm^{-1}. The attachment of an *n*-butyl group to the polymer backbone is further confirmed by ^{13}C CP-MAS NMR spectrum of rLPAN,[5] in which the ^{13}C resonance for the *n*-butyl group appears

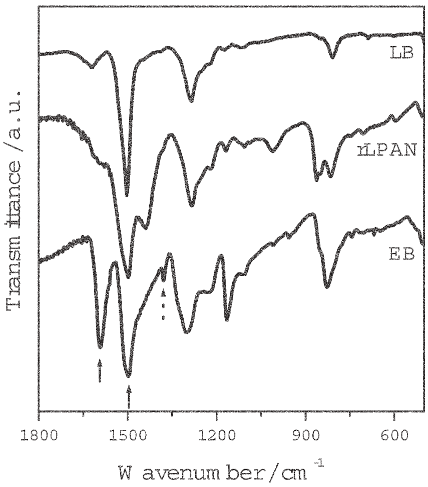


Fig. 3 FTIR transmission spectra for emeraldine base (EB), rLPAN and the fully reduced LB. The spectrum for LB has been taken from Ref. 7.

at 33 ppm. ^{1}H NMR of the rLPAN sample further establishes that an *n*-butyl group is bonded to the N atom.[5] The ^{1}H NMR spectrum shows 3 broad peaks at 6.95, 1.25 and 0.9 ppm in 16 : 5 : 3 ratio, for the aromatic, C(2) and C(3) methylene, and terminal –CH_3 group protons. The C(1) methylene protons, which is expected to appear at 3.6 ppm,[10] is masked by the water peak.

To understand the nature of interaction between BX_3 and the amine N, we studied the ^{11}B NMR spectra of $LPBX_3$ series of samples in d_6-DMSO.[5] As expected, the ^{11}B NMR in $LPBX_3$ show large chemical shifts with respect to free BX_3. In free BX_3, the ^{11}B resonance appears at +6.6, −29.2 and −22.7 ppm, while in $LPBX_3$, it shifts to 21.6, 42.8 and 42.9 ppm for X = F, Cl and Br, respectively.[11] It is evident from the large chemical shifts that the B site pulls out a considerable amount of negative charge from the N atom, making it similar to a neutral amine N, in agreement with the XPS results. Larger chemical shifts for $LPBCl_3$ and $LPBBr_3$ samples indicate a higher N to B charge transfer in these samples, and correlates well with the higher acidity of the corresponding Lewis acids. The width of ^{11}B resonance in $LPBF_3$ is much narrower (0.05 ppm) than that in $LPBCl_3$ (1.40 ppm) and $LPBBr_3$ (1.45 ppm). The extra broadenings in $LPBCl_3$ and $LPBBr_3$ samples are due to the rapid quadrupolar relaxation of ^{11}B nucleus caused by ^{35}Cl and ^{80}Br nuclei, which have a nuclear spin of 3/2. ^{19}F, being a spin ½ nucleus, has no quadrupolar moment and therefore does not influence the relaxation rate of the ^{11}B nucleus in $LPBF_3$.

In the context of the present work, it is important to note that visible PL (λ_{em} = 400–430 nm) has previously been observed in LB samples.[4] However, the present series of samples have two distinct advantages over the pure LB. Upon comparing the internal PL efficiency in deaerated DMSO, we found that $LPBF_3$ exhibits a 6 times higher PL efficiency than pure LB.[5] At this stage, it is tempting to speculate that the bulky BX_3 groups and *n*-butyl chains, attached to the polymeric backbone at short and regular intervals possibly help in keeping the polymer chains apart, thereby preventing aggregate quenching of the PL intensity. Further, LB is known to be extremely unstable towards aerial oxidation. Since, the PL is entirely due to the reduced motifs of the polymer, oxidation leads to a drastic drop in the PL efficiency. We find that under ambient conditions $LPBX_3$ samples exhibit a much better stability against aerial oxidation. This could be attributed to the presence of several electron-withdrawing BX_3 attached to the backbone. While visible luminescence has also been seen in reduced polythiophenes[12] and polymers containing arylamine groups,[13] ours is the first report of a stable luminescence from a PANI derivative.

It is important to note here that the present reaction scheme may open out a rather general route to functionalize PANI with diverse properties. What we have been able to achieve in the first step of the reaction is to convert 75% of N atoms into N^- Li^+ species. These deprotonated N− species are strongly nucleophilic, and presumably a variety of functional groups can be attached to these sites, rendering PANI diversely useful. While in the present work, we have specifically attached BX_3 to the N^- sites, it will be interesting to explore other possibilities in the future.

To conclude, we report a novel class of blue-emitting polymer based on PANI. Using various spectroscopic characterization techniques, we conclude that PANI is in a reduced form that exhibits an enhanced stability and a higher PL efficiency than pure LB. A possible reduction mechanism has been discussed. The synthesis proceeds through a highly reactive intermediate (LPAN) that can provide a starting point for the synthesis of a variety of PANI derivatives.

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Notes and references

1 H. Sirringhaus, J. P. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. L-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig and D. M. DeLeeuw, *Nature*, 1999, **401**, 685; H. Sakaguchi, H. Matsumura and H. Gong, *Nat. Mater.*, 2004, **3**, 551.

2 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. Bredas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121; A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.

3 M. Reghu, Y. Cao, D. Moses and A. J. Heeger, *Phys. Rev. B: Condens. Matter*, 1993, **47**, 1758; D. Chaudhuri, A. Kumar, I. Rudra and D. D. Sarma, *Adv. Mater.*, 2001, **13**, 1548.

4 S. A. Chen, K. R. Chuang, C. I. Chao and H. T. Lee, *Synth. Met.*, 1996, **82**, 207; S. Kapelle, W. Rettig and R. Lapouyade, *Chem. Phys. Lett.*, 2001, **348**, 416.

5 See ESI† for synthetic procedure, characterization details, additional figures and tables.

6 Y. H. Kim, D. C. Shin, S. H. Kim, C. H. Ko, H. S. Yu, Y. S. Chae and S. K. Kwon, *Adv. Mater.*, 2001, **13**, 1690.

7 K. L. Tan, B. T. G. Tan, E. T. Kang and K. G. Neoh, *Phys. Rev. B: Condens. Matter*, 1989, **39**, 8070.

8 R. P. McCall, J. M. Ginder, J. M. Leng, H. J. Ye, S. K. Manohar, J. G. Asturias, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev. B: Condens. Matter*, 1990, **41**, 5202.

9 M. Trchova, J. Stejskal and J. Prokes, *Synth. Met.*, 1999, **101**, 840.

10 S. A. Chen and G. W. Hwang, *J. Am. Chem. Soc.*, 1994, **116**, 7939.

11 W. D. Phillips, H. C. Miller and E. L. Meutterties, *J. Am. Chem. Soc.*, 1959, **81**, 4496.

12 H. Mao and S. Holdcroft, *Macromolecules*, 1992, **25**, 554; R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70.

13 J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, *J. Am. Chem. Soc.*, 2003, **125**, 11808; T. H. Huang, W. T. Whang, J. Y. Shen, J. T. Lin and H. Zheng, *J. Mater. Chem.*, 2005, **15**, 3233.