Electronic Supplementary Information for *Chemical Communications*

Blue Emitting Polyaniline

Debangshu Chaudhuri and D. D. Sarma*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore,
INDIA. Fax: +91-80-2360 1310; Tel: +91-80-2293 2945;
E-mail: sarma@sscu.iisc.ernet.in

Synthesis of Blue Emitting Polyaniline (LPBX_3, X = F, Cl and Br)

Undoped PANI (EB) was synthesized in the 50% oxidized form by oxidative polymerization of aniline in aqueous HCl solution using $(NH_4)_2S_2O_8$, at 0-5 ˚C and subsequent dedoping in 0.5 M aqueous NaOH solution. All subsequent reactions were carried out in a controlled atmosphere glove box (MBraun LABSTAR), where the moisture and O_2 levels were maintained below 5 ppm. Deprotonation of the amine N was carried out by treating undoped PANI (0.1812 g, 1 mmol) with 2 ml of 2.5 M (5 mmol) solution of *n*-butyl lithium (*n*BuLi) in *n*-hexane. To ensure complete deprotonation, excess *n*BuLi was used and the reaction mixture was allowed to equilibrate for 36 h at room temperature (300 K). Lithiated PANI (LPAN) thus obtained is yellowish-brown in color. It was washed with copious amount of dry *n*-heptane, and subsequently reacted with boron-trihalide (2-fold molar excess) to form LPBX_3. Freshly distilled BF_3-diethyl ether was used as the source of BF_3; BCl_3 and BBr_3 were used as a 1 M solution in dry heptane and dichloromethane, respectively. The complexation reaction was carried out overnight at 300 K. The light green colored product (LPBX_3) was washed with dry *n*-heptane, and pumped overnight. LPBX_3 dissolves readily in DMSO to give a bright-yellow colored solution.

Synthesis of reprotonated LPAN (rLPAN) and Leucoemeraldine Base (LB)

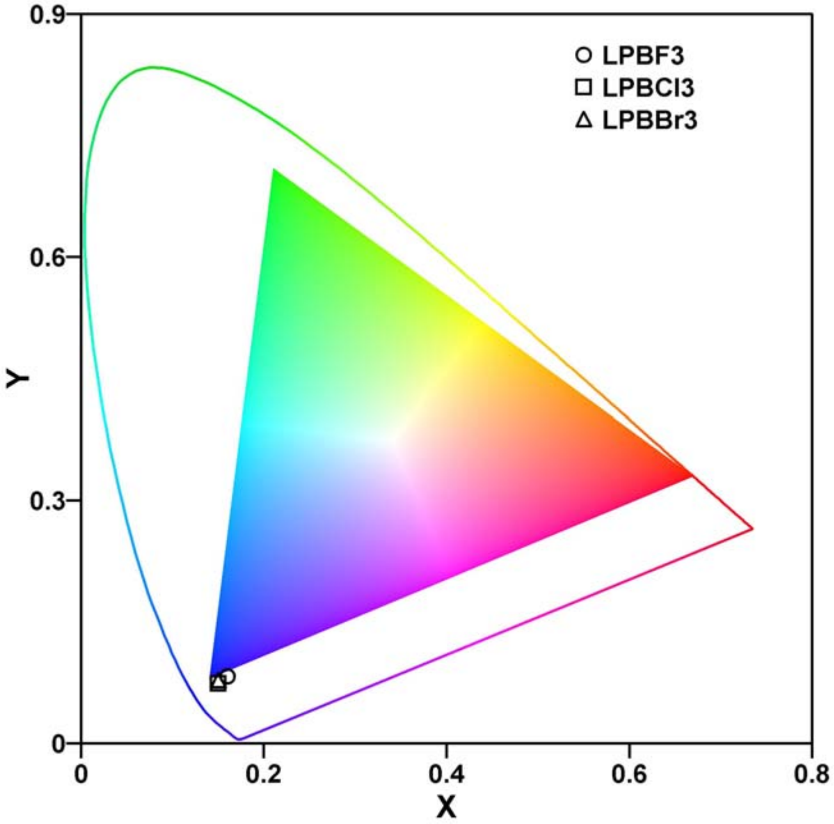
Reprotonation of LPAN was carried out by slow addition of double-distilled water in a mixture of LPAN in *n*-heptane. The reprotonation is spontaneous and the grayish-white rLPAN powder thus formed, was separated by centrifugation, repeatedly washed in deaerated water, and dried in dynamic vacuum for 10 hrs at 50 ˚C.

LB was prepared from EB by reduction using phenylhydrazine. Finely ground EB (0.5 g) was suspended and refluxed in 120 ml, 99% phenylhydrazine for 24 h at 120 ˚C, under nitrogen. The reaction mixture was filtered and washed exhaustively with methanol under a nitrogen atmosphere. The gray colored LB powder thus obtained was dried under dynamic vacuum at 80 ˚C.

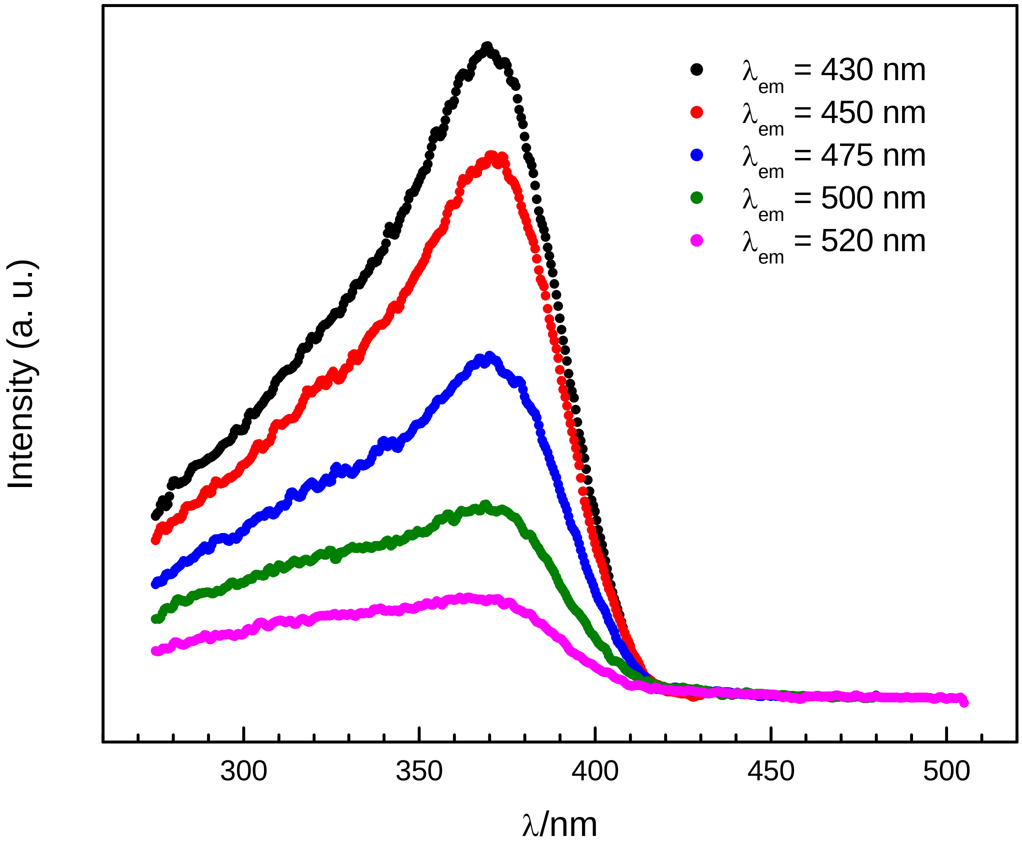
Experimental Details

All the absorption and photoluminescence studies were carried out with a solution of $LPBX_3$ and LB in dry DMSO. XPS measurements were performed on thin cast films of $LPBX_3$ using an Mg Kα (1253.6 eV) photon source in a commercial spectrometer manufactured by VSW, Scientific Ltd. The XPS spectra were referenced to the C 1*s* peak at 284.6 eV. For ^{11}B NMR (400 MHz) spectroscopy, samples were dissolved in dry d^6-DMSO. ^{13}C CP-MAS NMR spectrum (300 MHz) was recorded for solid rLPAN sample. The sample was spun at 4 and 7 KHz to identify the spinning side bands.

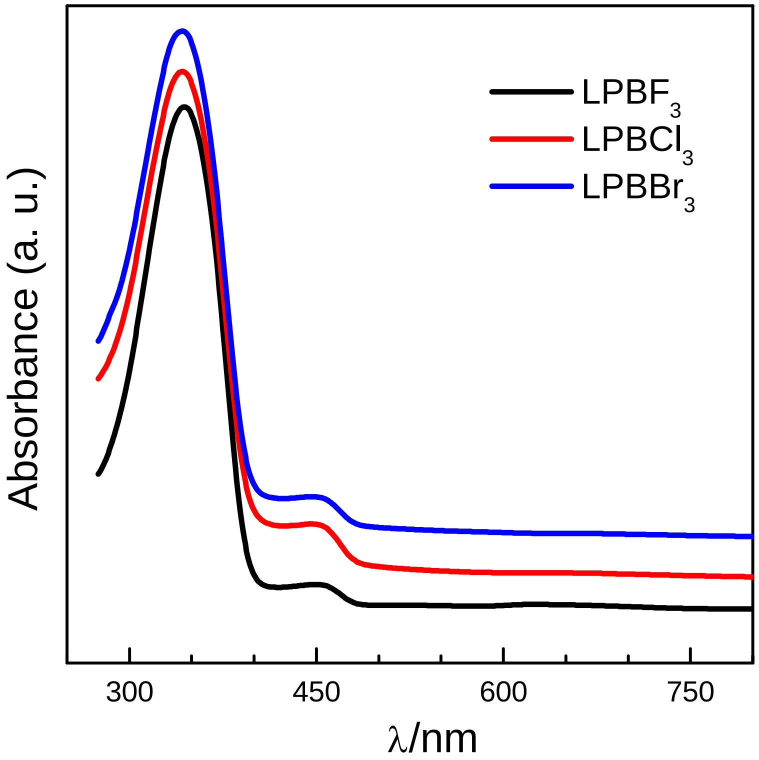
Internal PL efficiency of $LPBF_3$ was determined relative to that of LB by comparing the slopes of their respective I_{em} *vs.* A plots. I_{em} refers to total emission intensity, and is given by the area under the emission curve, when the sample is excited at λ_{ex}. A refers to value of absorbance at λ_{ex}. Therefore, by varying the concentration of the sample solution, the respective I_{em} *vs.* *A* plots were obtained. The experiments were carried out in the dilute limit, as suggested by the linearity of the I_{em} *vs.* *A* plots.



ESI 1 The CIE 1931 coordinates for the three LPBX_3 samples; LPBF$_3$ (0.16, 0.083), LPBCl$_3$ (0.15, 0.074) and LPBBr$_3$ (0.15, 0.078). The triangular gamut is drawn as per the National Television Standards Committee (NTSC) coordinates for pure red, blue and green. The NTSC coordinates for pure blue is (0.14, 0.08).

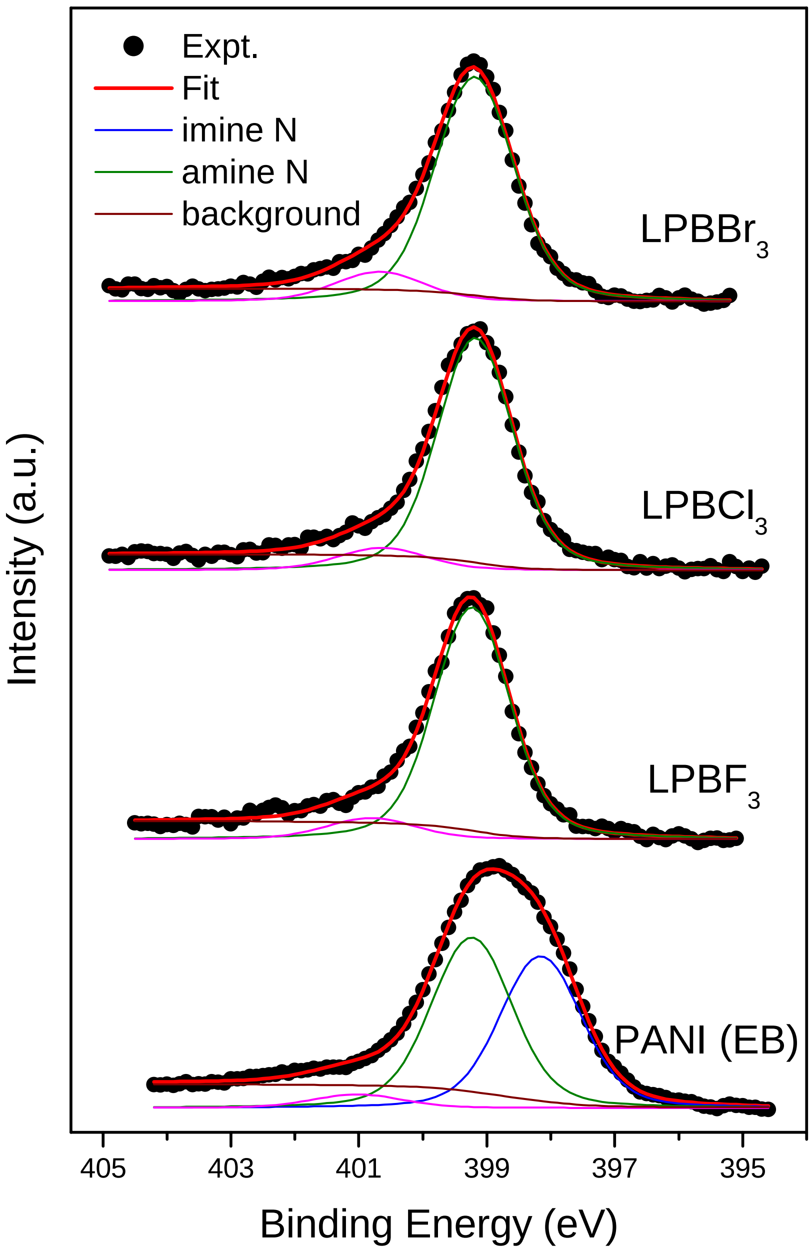


ESI 2 Different excitation spectra for $LPBF_3$ in DMSO were collected by changing the emission wavelength gradually from 430 to 520 nm. As can be seen from the figure, all the spectra are identical to each other. The absence of any intensity above 420 nm, clearly suggests that the electronic states corresponding to the absorption feature at 450 nm, do not play any role in the fluorescence decay of the excited state.

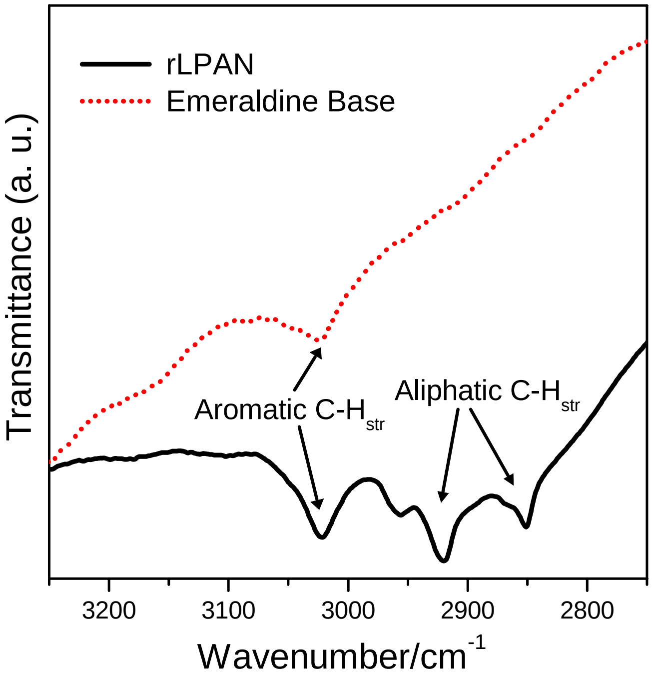


ESI 3 UV-visible absorbance spectra of LPBX_3 samples in dry DMSO. Absence of any absorption feature at 630 nm suggests a reduced backbone.

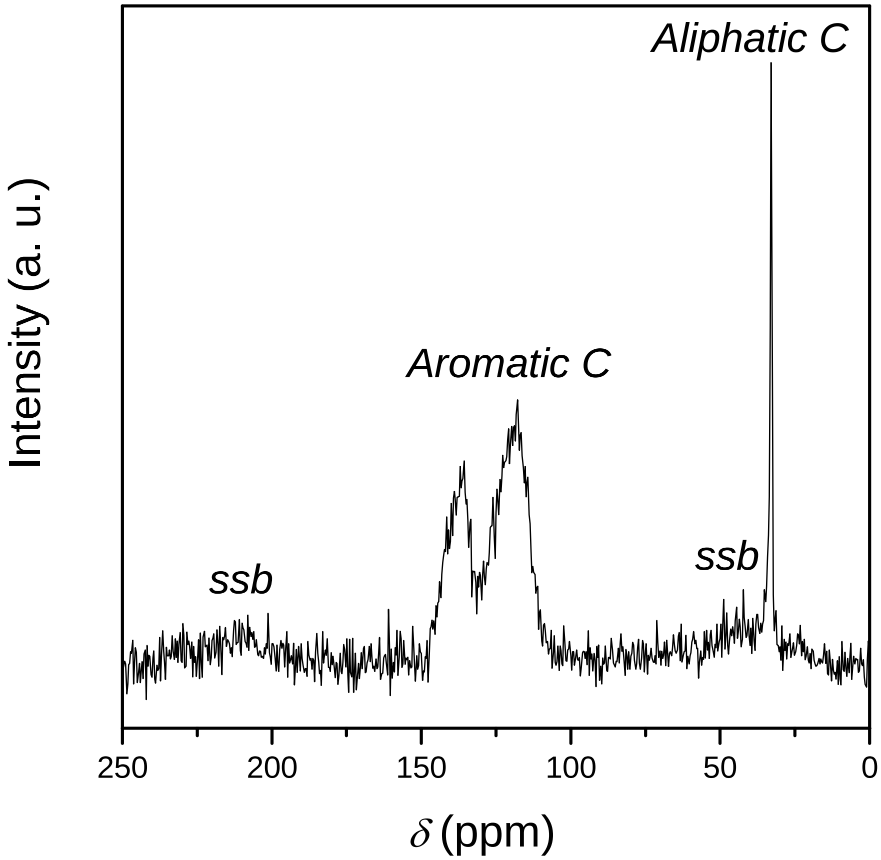
The absorption spectrum of protonated Leucoemeraldine, a feature appears at ~440 nm. We believe the weak intensity feature at 450 nm in the spectra of our samples is due to a partial complexation of BX_3 at amine N sites. We have found that by reducing the reaction time in the 2nd step of LPBX_3 synthesis, this peak could be reduced to a negligible intensity. This, however, does not affect the photoluminescence to any extent.



ESI 4 N 1*s* XPS spectra for the undoped PANI (EB) and the LPBX_3 samples. The feature corresponding to imine N (at 398.2 eV), clearly visible in the case of EB, is absent in all the LPBX_3 samples, suggesting its reduced state. Also see Table 1.

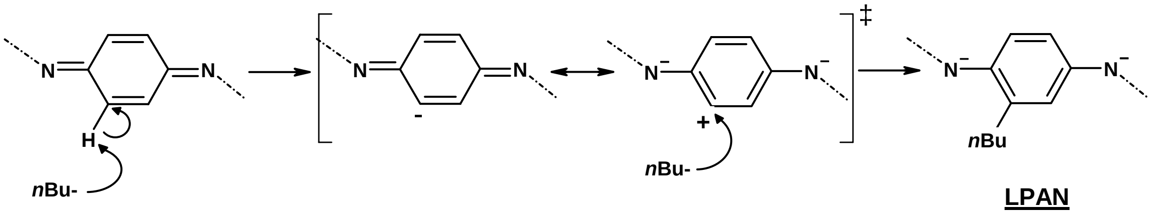


ESI 5 FTIR spectra of rLPAN and emeraldine base (EB) in the region of C-H stretching frequency. The C-H stretching of the aromatic rings can be seen in both the samples at 3020 cm^{-1}. However, in the spectrum of rLPAN, additional features appear in the region of aliphatic C-H stretching (2850 to 2950 cm^{-1}).

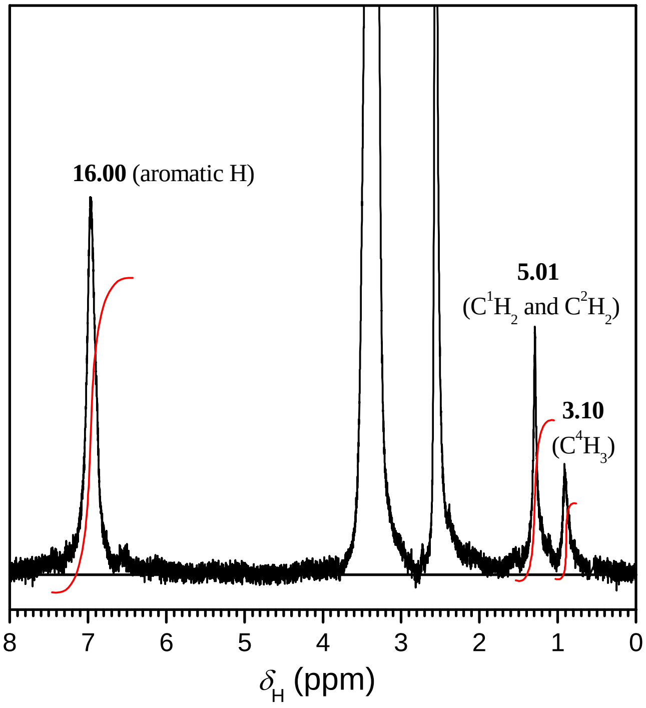


ESI 6 ^{13}C CP-MAS NMR spectrum (300 MHz) of reprotonated LPAN (rLPAN) acquired at a spinning speed of 7 KHz. The spinning side bands are marked as "*ssb*". A broad doublet of peaks between 100-150 ppm belongs to the aromatic C, while the aliphatic C of the *n*-butyl chain appears at 33 ppm.

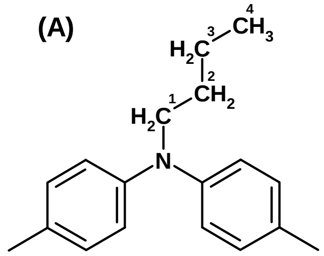
As per the mechanism suggested by us, the *n*-butyl group is bonded to a N atom in the final structure. The presence of *n*-butyl group in the sample has been confirmed by the FTIR and ^{13}C CP MAS NMR spectroscopy of the reprotonated LPAN (rLPAN) sample. However, there is a second possibility, as shown in the scheme below, which predicts a different final structure for LPAN with a *n*-butyl group attached to the ring C.



We find that the mechanism presented in the above scheme is not consistent with the ^{1}H NMR spectrum of rLPAN in d^6 DMSO.

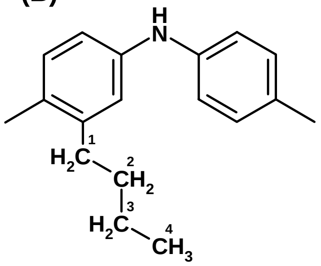


(A)



δ_H (aromatic, 16H) = 7 ppm
(C^1H_2, 2H) = 3.6 ppm
(C^2H_2 and C^3H_2, 4H) = 1.3-1.4 ppm
(C^4H_3, 3H) = 0.9 ppm

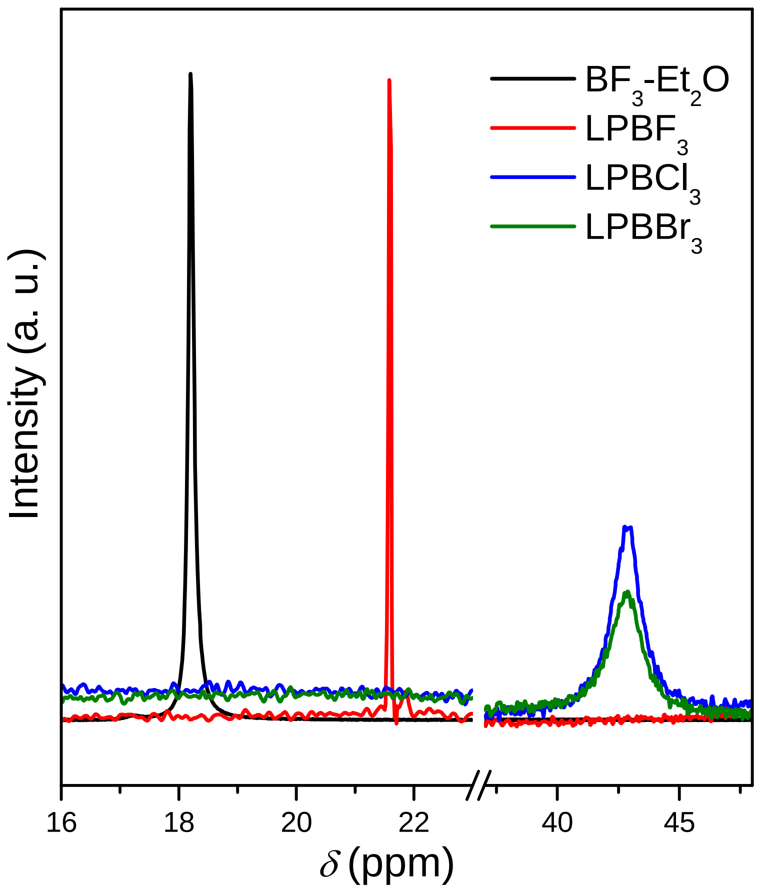
(B)



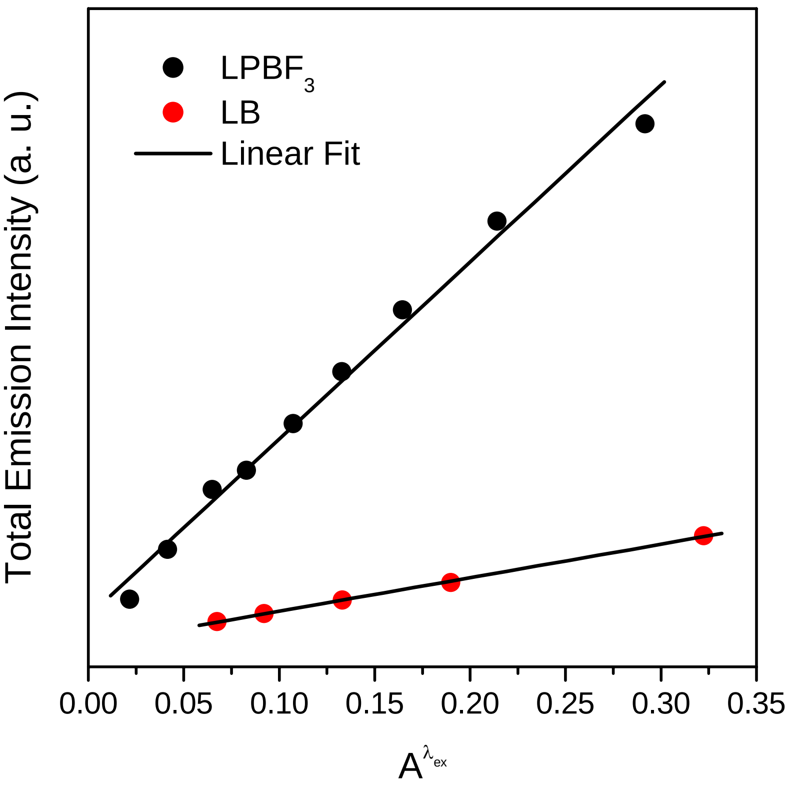
δ_H (aromatic, 15H) = 7 ppm
(C^1H_2, 2H) = 2.6 ppm
(C^2H_2, 2H) = 1.6 ppm
(C^3H_2, 2H) = 1.3 ppm
(C^4H_3, 3H) = 0.9 ppm

ESI 7 ^{1}H NMR spectrum of rLPAN. Three kinds of protons appear at 7, 1.3 and 0.9 ppm, in the ratio of 16:5:3. The chemical shifts and the ratios are in very good agreement with the structure (A), validating the mechanism suggested by us in Scheme 1. The signal of the methylene protons connected to the N (C^1H_2) is supposed to appear at 3.6 ppm, gets masked by the water peak (2.8-3.8 ppm).

rLPAN has negligible solubility in other solvents, and therefore the ^{1}H NMR could not be recorded in any other solvent.



ESI 7 ^{11}B NMR spectra (400 MHz) for BF_3-diethyl ether reference (black), $LPBF_3$ (red), $LPBCl_3$ (blue) and $LPBBr_3$ (green). The region between 23 to 37 ppm has not been shown.



ESI 8 Variation of the total emission intensity as a function of the absorbance at the respective excitation wavelengths, for LPBF$_3$ and LB samples. A linear dependence in both the cases ensures that the measurement was carried out in the dilute limit.

Sample	% Imine (398.2 eV)	% Amine (399.2 eV)	% Higher B. E. (400.7 ± 0.1 eV)
Undoped PANI	45.1	50.4	4.5
LPBF$_3$	0.0	90.5	9.5
LPBCl$_3$	0.0	90.0	10.0
LPBBr$_3$	0.0	87.3	12.7

Table 1 Contribution of various N species in the N 1*s* XPS spectra of the 4 samples, as obtained from a least-squared-error fitting procedure, is presented in the above table. For all the three LPBX_3 samples, amine N accounts for ~ 90% of the total spectrum.