

## Supporting Information

# Fluorescent Polymeric Ionic Liquids for the Detection of Nitroaromatic Explosives

Sayali V. Shaligram, P. P. Wadgaonkar and Ulhas K. Kharul\*

Polymer Science and Engineering Division  
CSIR-National Chemical Laboratory  
Dr. HomiBhabha Road, Pune- 411008 (INDIA)  
Phone: +91-20-25902180, Fax: +91-20-25902618  
Email: [uk.kharul@ncl.res.in](mailto:uk.kharul@ncl.res.in)

### Synthesis of PBI-BuI

PBI-BuI was synthesized by polycondensation reaction of DAB (3,3'-diaminobenzidine) and 5-*tert*-butyl isophthalic acid as reported earlier.<sup>1</sup> A three-necked round bottom flask equipped with a mechanical stirrer, N<sub>2</sub> inlet and CaCl<sub>2</sub> drying tube was charged with 600 g of PPA (polyphosphoric acid), 20 g (0.18668 mol) of DAB and temperature was elevated to 140 °C. After dissolution of DAB, 0.09334 mol of 5-*tert*-butyl isophthalic acid (20.743g) was added; temperature was raised to 170 °C and maintained for 5 h under constant flow of N<sub>2</sub>. The temperature was further raised to 200 °C and maintained for 12 h. The polymer was obtained by precipitation in water. It was crushed, washed thoroughly with water, kept in 10% NaHCO<sub>3</sub> for 16 h; followed by water wash. It was soaked in acetone for 16 h and dried in vacuum oven at 100 °C for 3 days. Further purification by dissolving in DMAc (3% w/v) and reprecipitation in water yielded yellow colored fibrous polymer (yield of purified polymer = 98%). Its inherent viscosity ( $\eta_{inh}$ ) was determined at the polymer concentration of 0.2 g/dL in H<sub>2</sub>SO<sub>4</sub> at 35 °C. It was found to be 1.4 dL/g.

### Synthesis of polymeric ionic liquids (PILs)

The *N*-substitution of PBI was carried out in dry DMSO by preparing sodium salt of PBI-BuI, followed by addition of the aralkyl halide. Typically a three-necked round bottom flask equipped with N<sub>2</sub> balloon and a septum was charged with 300 mL of dry DMSO, 10 g of PBI-BuI, 2.1 equivalents of NaH and stirred at ambient temperature for 24 h. The reaction mixture was then heated at 80 °C for 3 h. At this stage, a deep blood red color developed after the complete dissolution of PBI-BuI. The solution was allowed to cool to the ambient temperature and 2.1 molar equivalents of aralkyl halide, either 9-(chloromethyl)anthracene (An) or 2-(bromomethyl)pyrene (Py) dissolved in 10 mL of dry DMSO was added in a dropwise manner over a period of 15 minutes. The reaction mixture was precipitated indicating formation of the *N*-substituted PBI-BuI. The reaction mixture was stirred further at the ambient temperature for 12 h in order to allow complete dissolution and then was slowly poured into the stirred water. The precipitated polymer was washed several times with water and dried in a vacuum oven at 100 °C for 7 days.

The *N*-quaternization of thus obtained *N*-substituted PBI-BuI was carried out using 4-*tert*-butylbenzyl bromide (Bz). Typically, to a 3-necked round bottom flask, were charged 300 mL of dry DMSO, 10 g of *N*-substituted PBI-BuI, 2.5 equivalents of 4-*tert*-butylbenzyl bromide and the

reaction mixture stirred under dry N<sub>2</sub> atmosphere at the ambient temperature for 12 h. The reaction mixture was further heated at 80 °C for 12 h. After attaining ambient temperature, the obtained polymer was precipitated in a mixture of toluene and acetone (1:1 v/v). The golden yellow fibrous precipitate was dried at 80 °C for 24 h. It was further purified by dissolving in DMF and reprecipitating in the toluene: acetone (1:1 v/v) mixture. Obtained polymer after vacuum drying was purified by dissolving in DMF and reprecipitation in the mixture of toluene and acetone (1:1). The yield of this reaction was 94%. The inherent viscosity ( $\eta_{inh}$ ) of PILs was determined at the polymer concentration of 0.2 g/dL in DMSO at 35 °C. It was found to be 3.3 dL/g for [DPyDBzPBI-BuI][Br] was, while for [DAnDBzPBI-BuI][Br] it was 3.1 dL/g.

#### Estimation of degree of quaternization by Volhard's method

Bromide present in formed PILs was determined by Volhard's method,<sup>2</sup> in which 0.1 g of polymer in powder form was stirred in 25 mL of 0.01M AgNO<sub>3</sub> solution for 24 h. Excess of unreacted AgNO<sub>3</sub> was titrated with 0.01 M KSCN to deduce the amount of AgNO<sub>3</sub> consumed with bromide present in the polymer.

Fig. S1. shows the <sup>1</sup>H-NMR spectra of polymeric ionic liquids (PILs). The absence of a broad peak in the range of δ 13-14 (ascribed to imidazole N-H in the case of unsubstituted PBI-BuI) indicated that N-substitution reaction has quantitatively occurred.

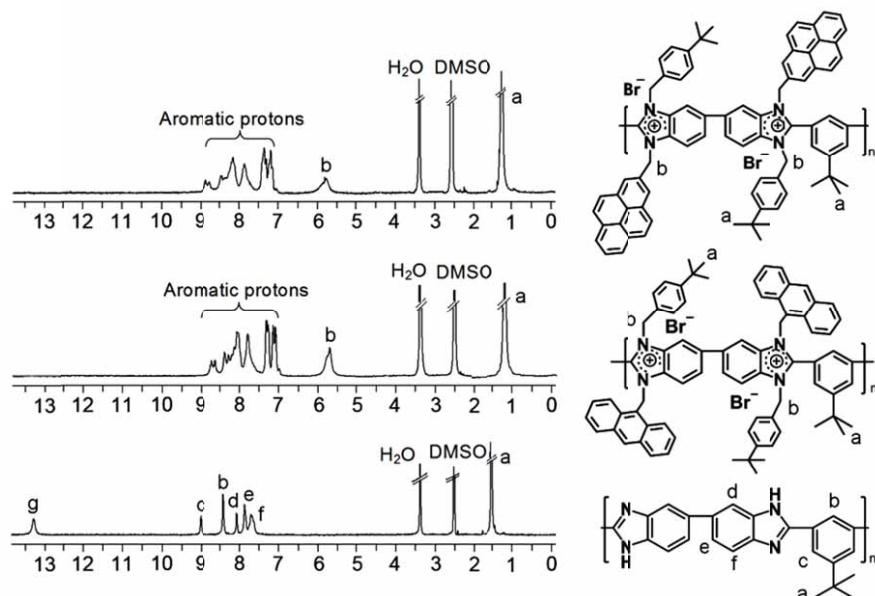


Fig. S1. <sup>1</sup>H-NMR spectra of polymeric ionic liquids (PILs).

**Fluorescence Quenching Study in Solution:** A 2 mL stock solution ( $1.0 \times 10^{-5}$  M) of the PILs was placed in a quartz cell of 1 cm width and quenchers ( $20 \times 10^{-6}$  M) solution was added gradually in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. For all measurement, PILs were excited at  $\lambda_{\text{ex}} = 350$  nm and their corresponding emission wavelength was monitored from  $\lambda_{\text{ex}} = 350$  nm. Both excitation and emission slit width were 1 nm for all the measurement. Relative fluorescence intensities were measured for solution of PILs in DMSO and analytes(PA, TNT and NB) were used as quenchers in DMSO. Analysis of the normalized fluorescence emission intensity ( $I_0/I$ ) as a function of increasing quenchers concentration ([Q]) was well described by the Stern-Volmer equation ( $I_0/I$ ) $-1 = K_{\text{sv}}x[Q]$ . The Stern-Volmer binding constant was calculated from the slope of the Stern-Volmerplot<sup>3</sup>.

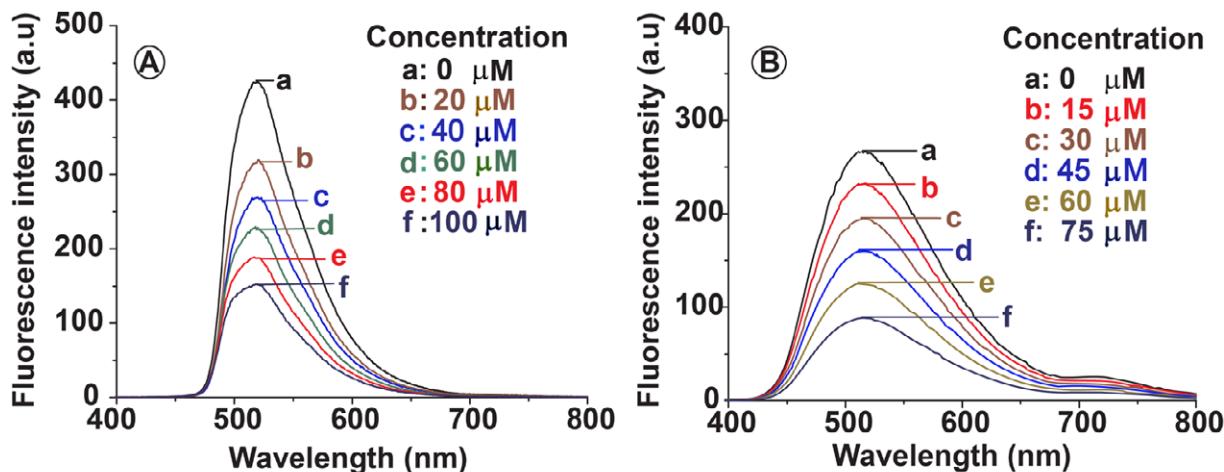


Fig.S2. Fluorescence emission spectra of PILs A: [DPyDBzPBI-BuI][Br], B: [DAnDBzPBI-BuI][Br] in the presence of different concentrations of nitrobenzene in DMSO ( $\lambda_{\text{ex}} = 350$  nm). This figure shows that with increase in the concentration of analyte, there is no change in the nature of emission spectra, except a gradual decrease in emission intensity. The Stern–Volmer binding constants for NB were calculated to be  $K_{\text{sv}} = 1.78 \times 10^4 \text{ M}^{-1}$  ([DPyDBzPBI-I][Br]),  $K_{\text{sv}} = 1.59 \times 10^4 \text{ M}^{-1}$  ([DAnDBzPBI-I][Br]).

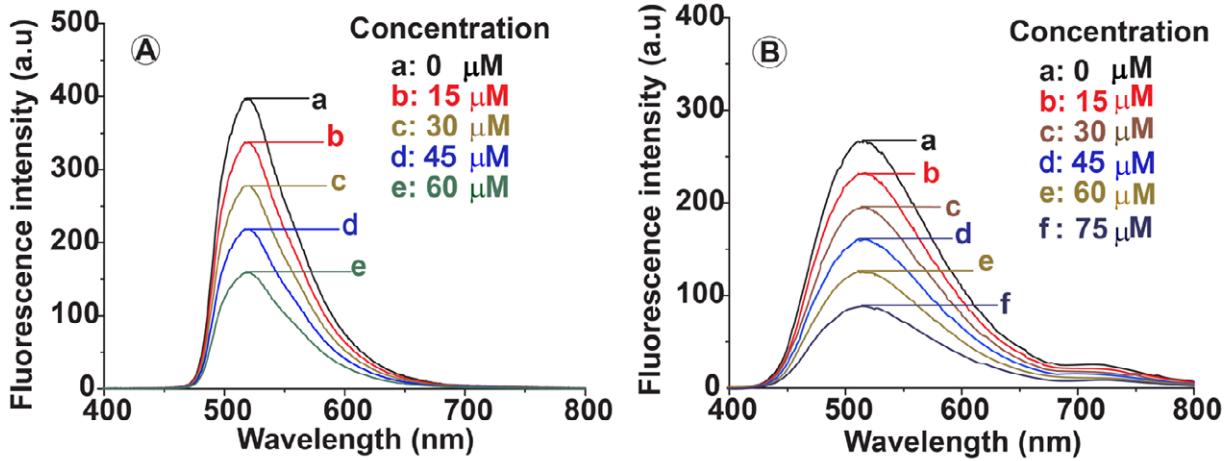


Fig.S3. Fluorescence emission spectra of PILs A: [DPyDBzPBI-BuI][Br], B: [DAnDBzPBI-BuI][Br] in the presence of different concentrations of TNT in DMSO ( $\lambda_{\text{ex}} = 350$  nm). The intensity decreased with the increase in concentration of TNT. The Stern–Volmer binding constants for TNT were calculated to be  $K_{\text{sv}} = 2.50 \times 10^4 \text{ M}^{-1}$  ([DPyDBzPBI-I][Br]),  $K_{\text{sv}} = 1.88 \times 10^4 \text{ M}^{-1}$  ([DAnDBzPBI-I][Br]).

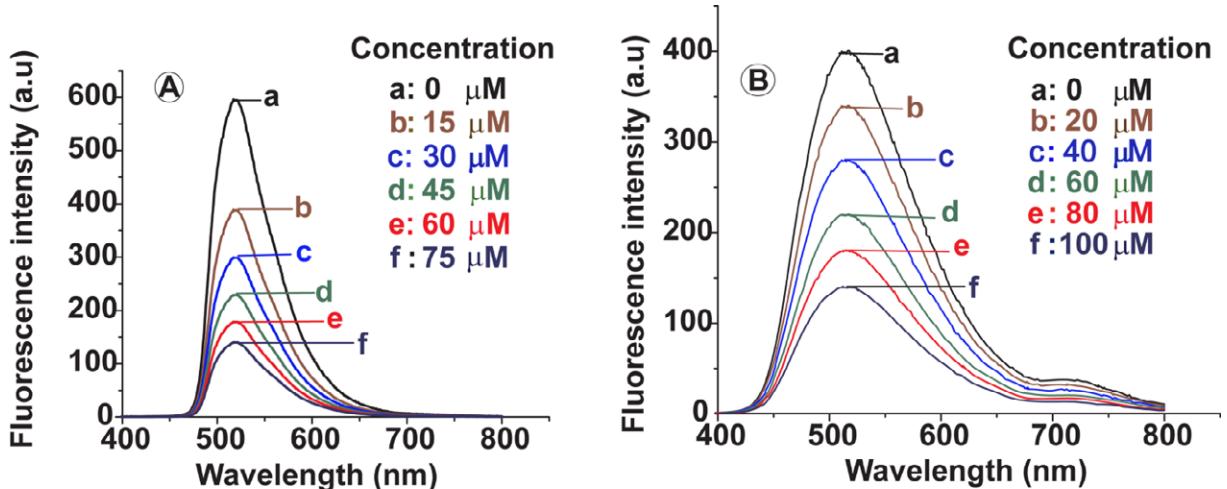


Fig.S4. Fluorescence emission spectra of PILs A: [DPyDBzPBI-BuI][Br], B: [DAnDBzPBI-BuI][Br] in the presence of different concentrations of PA in DMSO ( $\lambda_{\text{ex}} = 350$  nm). With an increase in concentration of PA, a decrease in intensity was as observed in earlier cases of NB and TNT. The Stern–Volmer binding constants for PA were calculated to be  $K_{\text{sv}} = 3.25 \times 10^4 \text{ M}^{-1}$  ([DPyDBzPBI-I][Br]),  $K_{\text{sv}} = 2.03 \times 10^4 \text{ M}^{-1}$  ([DAnDBzPBI-I][Br]).

**Solid-State Fluorescence Quenching Study:** For this study, the PIL films were prepared by solution casting method using 0.5% (w/v) DMAc solution at 80 °C for 18 h under dry conditions. After evaporation of the solvent, formed thin film was peeled off from the glass plate and kept in the vacuum oven at 80 °C for a week in order to ensure complete removal of the solvent. For quenching, a desiccator was used, in which a petri-dish that contained 5mL of nitrobenzene was placed. The polymer film was introduced in a desiccator after about 30 min. For other TNT and PA the solid state analysis was carried out in small glass vial saturated with explosive vapors.

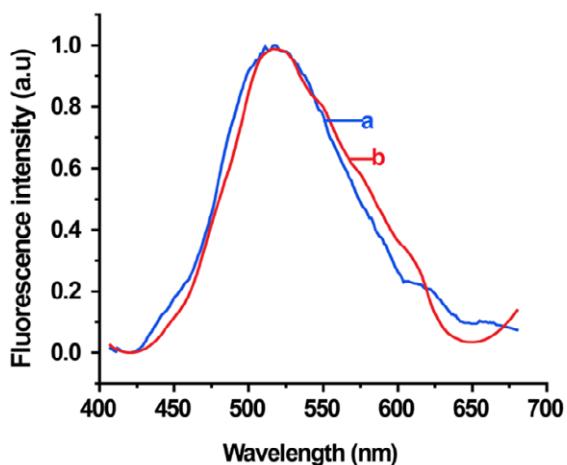


Fig. S5. Fluorescence emission spectra of a: [DPyDBzPBI-BuI][Br] and b: [DAnDBzPBI-BuI][Br] in film form (~ 12  $\mu$ m thick). Transforming PIL into a thin film form did not shift its emission wavelength than observed in the solution state.

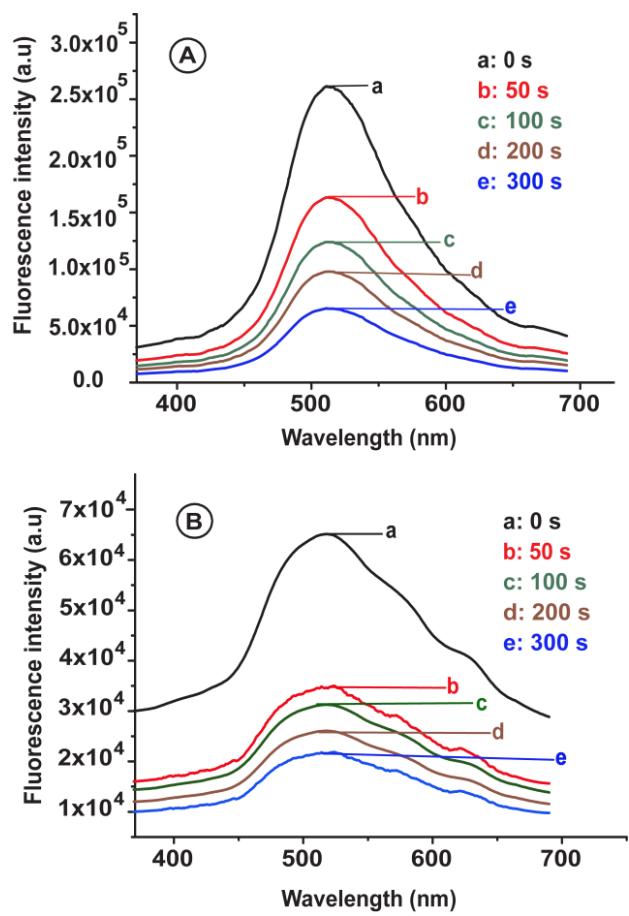


Fig. S6. Time dependent emission intensity PIL films A: [DPyDBzPBI-BuI][Br], B: [DAnDBzPBI-BuI][Br] upon exposure to the saturated vapors of NB.

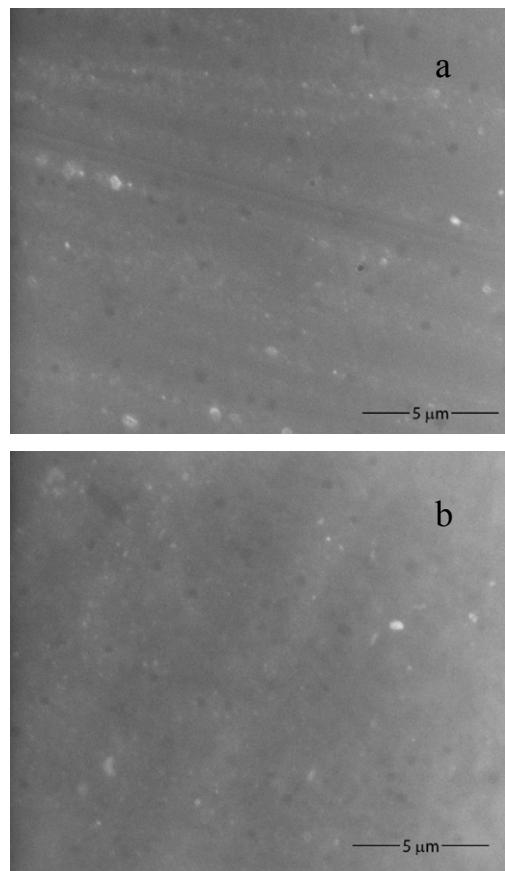


Fig. S7. SEM image of a: [DPyDBzPBI-BuI][Br] and b: [DAnDBzPBI-BuI][Br]. The morphology of PILs in dense films did not differ significantly and therefore does not seem to influence the fluorescence quenching efficiency of PILs.

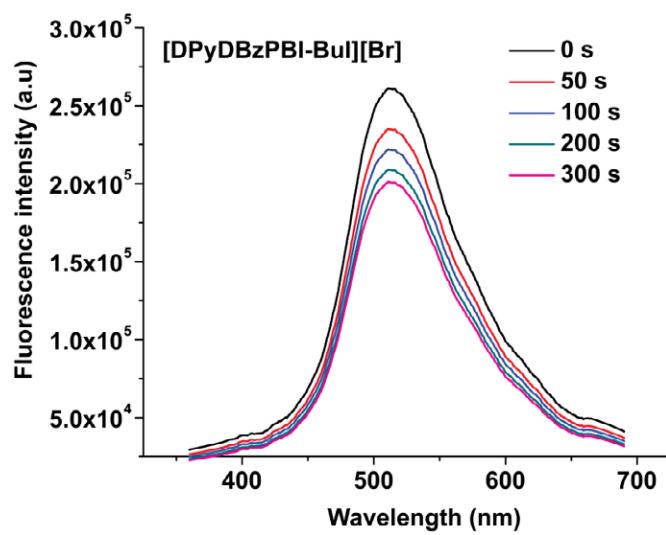


Fig. S8. The fluorescence quenching of thick film ( $\sim 40 \mu\text{m}$ ) of pyrene containing PIL by NB. The quenching after 50 s exposure time was calculated to be 11%; while it was 30% after 300 s.

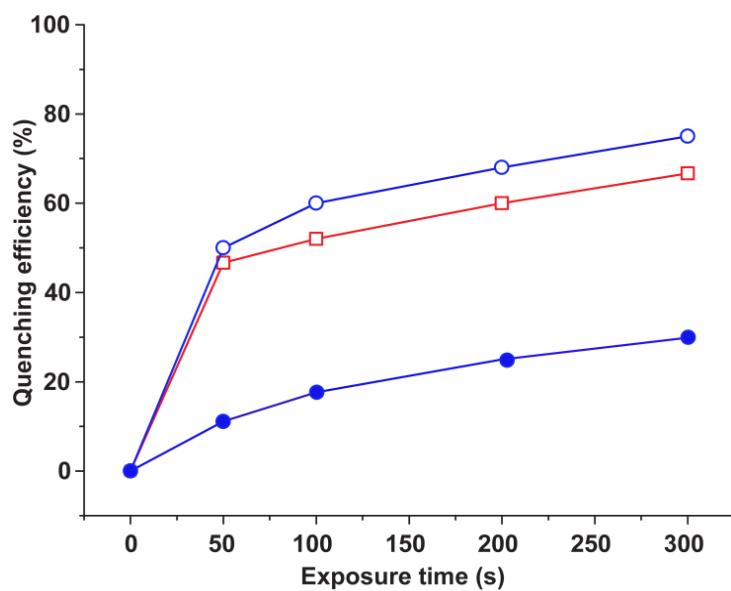


Fig. S9. Time dependent quenching of the PIL films  $\circ$ : [DPyDBzPBI-BuI][Br] (12  $\mu\text{m}$ ),  $\square$ : [DAnDBzPBI-BuI][Br] (12  $\mu\text{m}$ ) and  $\bullet$ : [DPyDBzPBI-BuI][Br] (40  $\mu\text{m}$ ) upon exposure to the saturated vapors of NB.

## **References**

- 1 S. C. Kumbharkar, M. Islam, R. A. Potrekar and U. K. Kharul, *Polymer*, 2009, **50**, 1403.
- 2 G. H. Jeffery, J. Bassett, J. Mendham, C. Denneyv, Vogel's Textbook of Quantitative Chemical Analysis,*British Library Cataloguing in Publication Data*, Fifth edn., 1989, pp. 355-356.
- 3 H. Gang, N. Yan, J. Yang, H. Wang, L. Ding, S. Yin, and Y. Fang *Macromolecules*, 2011, **44**, 4759.