Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

to accompany

A potent colorimetric and fluorogenic phosgene probe based on dual photophysical processes: PET attenuation and ICT reversal

Ankita Gangopadhyay, † Ajit Kumar Mahapatra*, †

† Department of Chemistry, Indian Institute of Engineering Science and Technology (formerly Bengal Engineering and Science University) Shibpur, Howrah, West Bengal 711103, India.

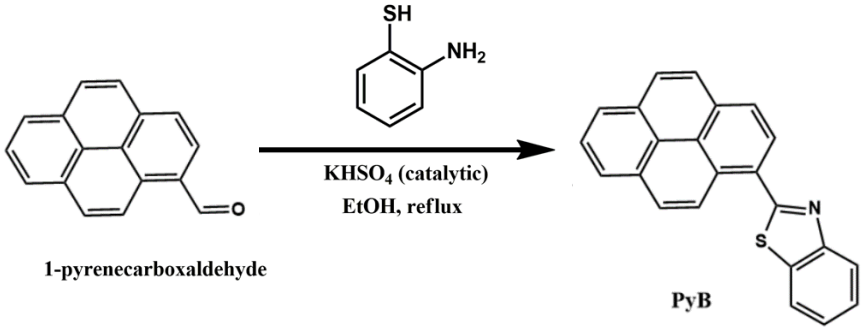
*Corresponding author. Fax: +91 33 26684564; Tel: +91 33 2668 4561;

E-mail: mahapatra574@gmail.com (A. K. Mahapatra)

Contents

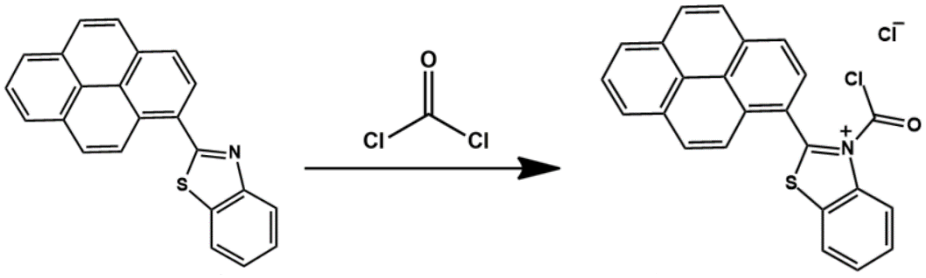
1. Synthesis of **PyB**

To a well stirred solution of 1-pyrenecarboxaldehyde (460 mg, 2 mmole) in absolute ethanol (15 mL) was added 312 mg (2.5 mmole) of 2-aminothiophenol. The reaction mixture was heated above 80℃ followed by the addition of a catalytic amount of potassium bisulphate. Within minutes a pale-yellow precipitate was found to appear. The reaction was allowed to continue for 1.5 hours after which it was taken off the heating bath and let cool. The precipitate was collected via suction filtration and washed three times with cold ethanol to afford pure **PyB** (572 mg, yield ~ 85%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 6.63-6.66 (m, 1H), 6.78 (d, 1H, J= 6.0 Hz), 6.94 (q, 1H, J= 7.2 Hz), 6.97 (d, 1H, J= 0.8 Hz), 7.22 (d, 1H, J = 2.0 Hz), 7.54 (d, 1H, J= 1.6 Hz), 8.09 (t, 1H, J= 12.0 Hz), 8.16 (q, 2H, J=18.0 Hz), 8.28-8.35 (m, 2H), 8.38 (d, 2H, J= 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (TMS, ppm): 114.71 (1C), 115.12 (1C), 115.51 (1C), 116.12 (2C), 117.27 (2C), 122.04 (1C), 123.35 (1C), 123.93 (1C), 124.58 (1C), 125.07 (1C), 125.87 (1C), 126.90 (2C), 128.32 (1C), 128.77 (2C), 129.54 (1C), 130.50 (2C), 135.26 (1C), 142.98 (1C). (ESI (+)-HRMS (m/z): **[M]**$^{+}$ calculated for **$C_{23}H_{13}NS$**: **335.0769**, found: **335.0842**)



2. Isolation of **PAPyB**

PyB (120 mg, 0.52 mmole) was dissolved in 5 mL $CHCl_3$ followed by addition of triphosgene/TEA (10 equivalent). The reaction mixture was stirred at room temperature with regular monitoring via TLC until no reactant remained. Upon completion of the reaction the mixture was dried under vacuum and then column chromatography performed on silica gel using chloroform/methanol (1/1) as eluent to afford **PAPyB** (152 mg, yield ~ 73%). ^{1}H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.70 (t, 2H, J= 12.0 Hz), 7.85 (t, 2H, J= 12.4 Hz), 7.93 (q, 3H, J= 7.2 Hz), 8.21 (t, 1H, J= 4.4 Hz), 8.29 (d, 4H, J= 7.2 Hz), 9.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (TMS, ppm): 77.81 (2C), 84.59 (1C), 88.79 (1C), 103.19 (2C), 117.39 (1C), 122.04 (1C), 123.64 (2C), 124.82 (2C), 125.87 (1C), 126.90 (1C), 129.26 (2C), 130.56 (2C), 135.26 (1C), 142.98 (1C), 150.40 (1C), 163.51 (2C), 173.85 (1C). (ESI (+)-HRMS (m/z): **[M]**$^{+}$ calculated for **$C_{24}H_{13}ClNOS^{+}$**: **398.0401**, found: **398.0467**; [**M + 2**]$^{+}$ calculated: **400.0372**, found: **400.0362**).



3. Rise in fluorescence intensity of **PyB** with phosgene addition

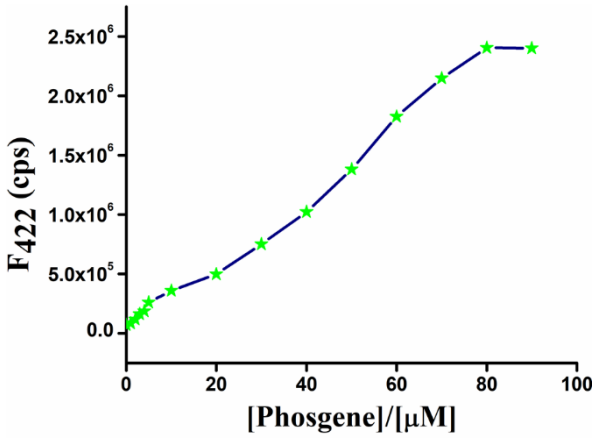


Figure S1: Plot of fluorescence intensity at 422 nm vs. concentration of phosgene (0- 90μM) in $CHCl_3$-acetone (1:1) at 25°C. (λ_{ex} = 400 nm, λ_{em}= 422 nm)

4. Calculation of Limit of Detection (LOD)

The calibration curve was derived from a plot of fluorescence intensity at 422 nm as a function of phosgene concentration. The regression equation was obtained for the part corresponding to lower phosgene concentrations (1.0−7.0 μM).

$$\text{LOD} = {}^{3\sigma}/_{k}$$

where k is the slope of the curve and σ stands for the standard deviation of the fluorescence intensity of **BB** in presence of phosgene.

$$F_{422} = 151140E + 3x - 156398.57143 \; (R^2 = 0.92536)$$

$$\text{LOD} = (3 \times 77849.33956) \div (151140E + 9) = 1.54 \text{ nM}$$

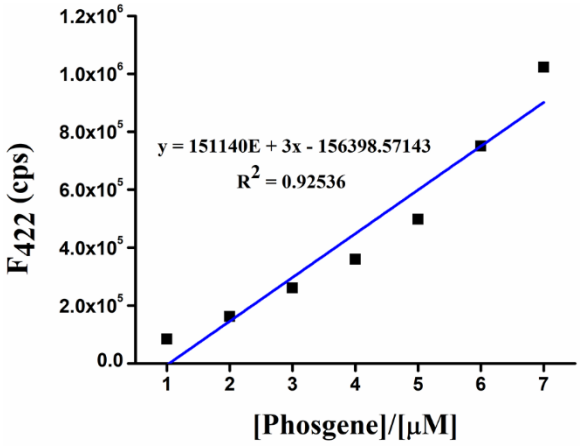


Figure S2. Calibration curve of fluorescence intensity of 10.0 μM of **PyB** as a function of phosgene concentration. (λ_{ex}= 400 nm, λ_{em}= 422nm).

5. Calculation of pseudo first order rate constant: k'

Measurement of the fluorescence enhancement of **PyB** (1.0µM) at 422 nm in presence of an excess of triphosgene (100.0 µM) containing added TEA led to the determination of the pseudo first order rate constant from the following equation: $\ln[(F_{max} - F_t)/F_{max}] = -k' t$

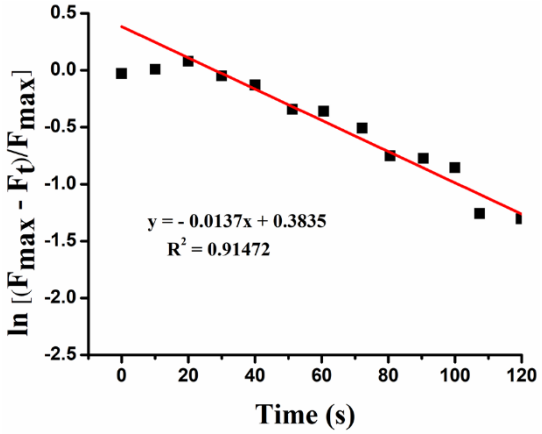


Figure S3. Pseudo first order kinetic plot of **PyB** (1.0 µM) in the presence of triphosgene/TEA (100 µM). (λ_{ex}= 400 nm, λ_{em}= 422 nm).

where F_t and F_{max} represent the fluorescence intensities at 430 nm at time t and the maximum value obtained upon completion of the reaction, respectively, and k' is the observed pseudo-first order rate constant which has been calculated to be 0.014 s^{-1} according to **Figure S3**.

6. Calculation of fluorescence quantum yields

The fluorescence quantum yields of **PyB** and **PAPyB** were determined in EtOH with anthracene (φ = 0.27) as the fluorescence standard. The quantum yields were calculated using the following equation:

$$\varphi_S = \varphi_A \times \frac{F_S}{F_A} \times \frac{A_A}{A_S} \times \frac{\eta_S^2}{\eta_A^2}$$

where A_A and A_S are the absorbances of anthracene and sample solutions at the same excitation wavelength; F_A and F_S are the corresponding integrated fluorescence intensities of anthracene and sample solutions; η_A and η_S are the refractive indices of the respective solvents employed which in this case is EtOH for both measurements.

Species	**φ**
PyB	0.21
PAPyB	0.48

7. Selectivity profile of **PyB**

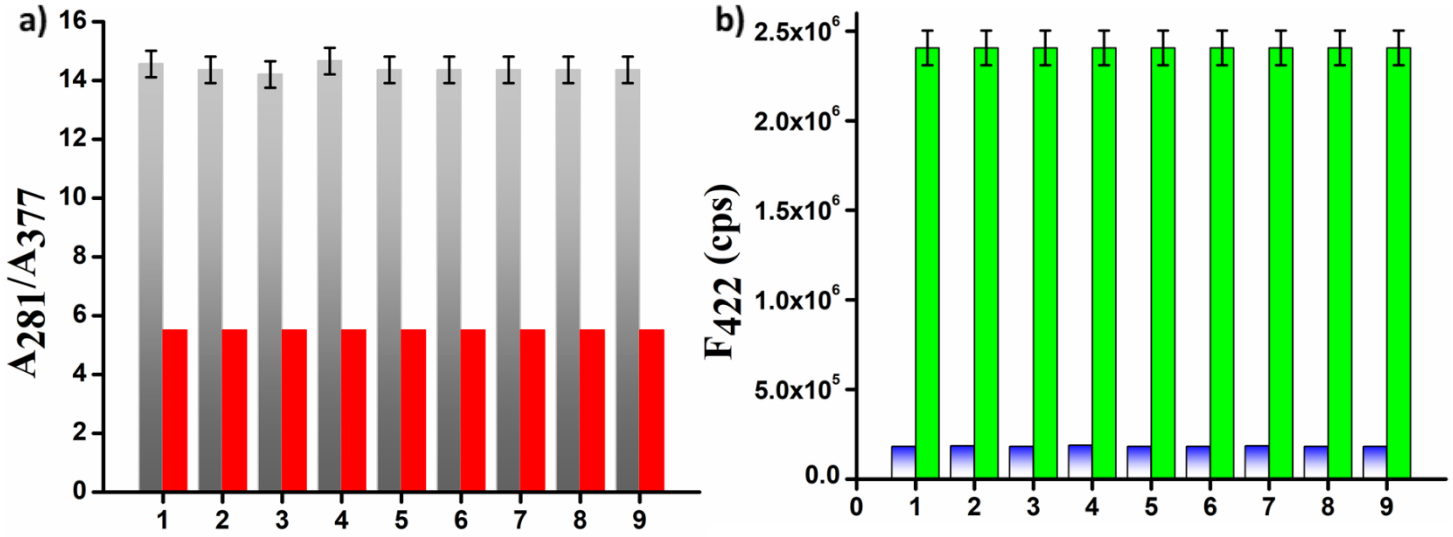


Figure S4. Selectivity profile diagram in bar representation with error bars included. **a)** Changes in ratio of absorbance recorded at 281 and 377 nm in $CHCl_3$-acetone (1:1) upon addition of excess of different species (50.0 µM): grey bars: **PyB** + other species; red bars: **PyB** + other species + phosgene (error amount 3.1%; Y error bars for both ± deviations). **b)** Changes in fluorescence intensity at 422 nm (λ_{ex} = 400 nm) under identical conditions: bicolour (blue and white) bars: **PyB** + other species; green bars: **PyB** + other species + phosgene (error amount 4.0%; Y error bars for both ± deviations). Legend: (1) HCl, (2) TFA, (3) TsCl, (4) CH_3COCl, (5) $POCl_3$, (6) $SOCl_2$, (7) $(COCl)_2$, (8) DCNP, (9) DCP.

8. Time dependent selectivity profile

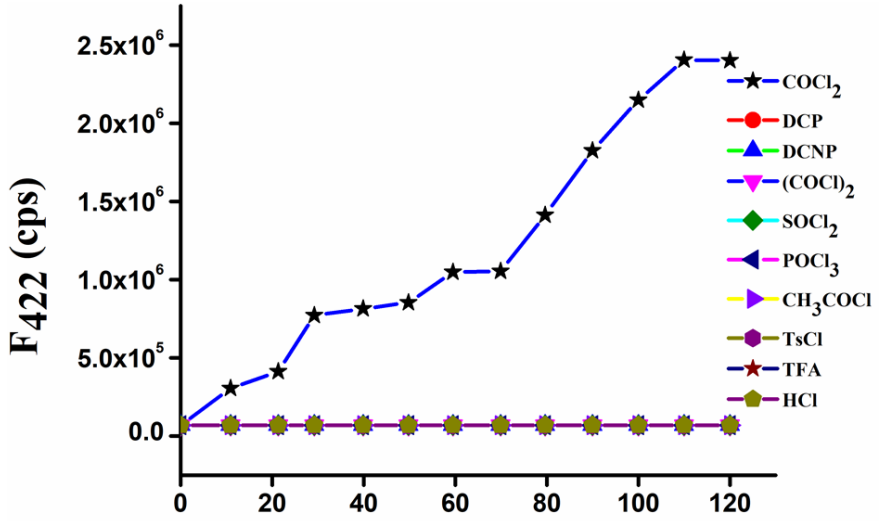


Figure S5. Time coursed observation of fluorescence emission of **PyB** (1.0 µM) at λ_{em}=422 nm (λ_{ex}= 400 nm) in presence of various analytes (50.0 µM).

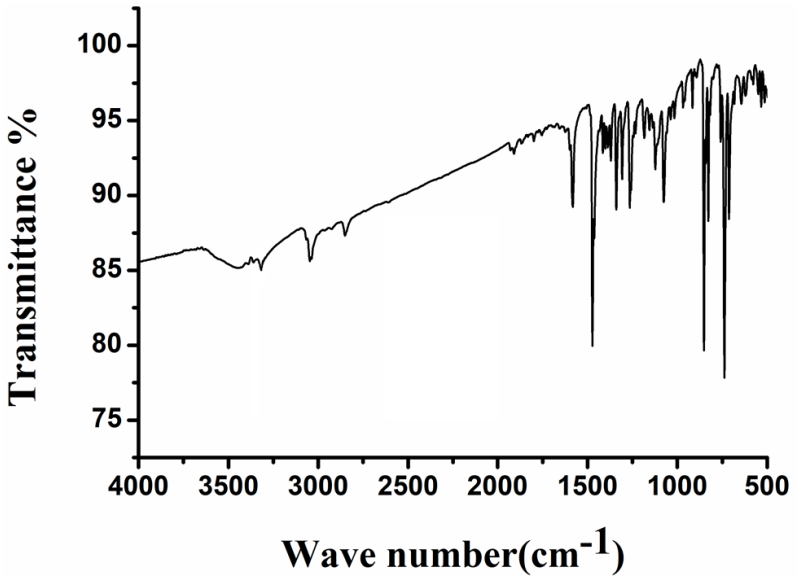


Figure S6. FTIR of **PyB**

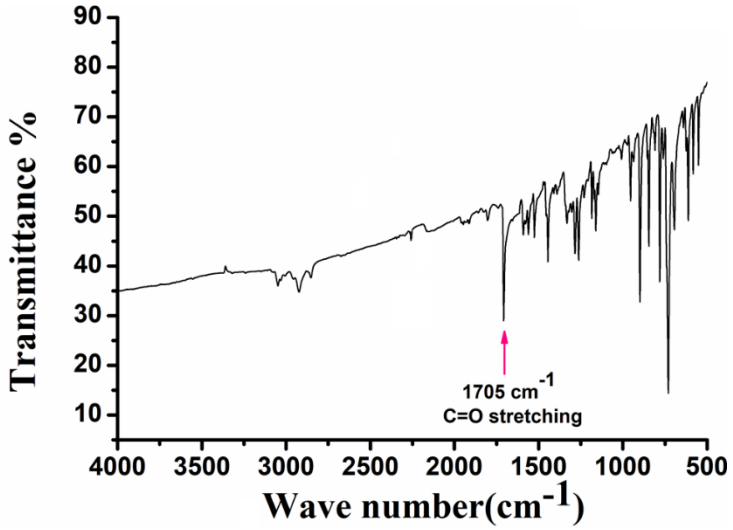


Figure S7. FTIR of **PAPyB**

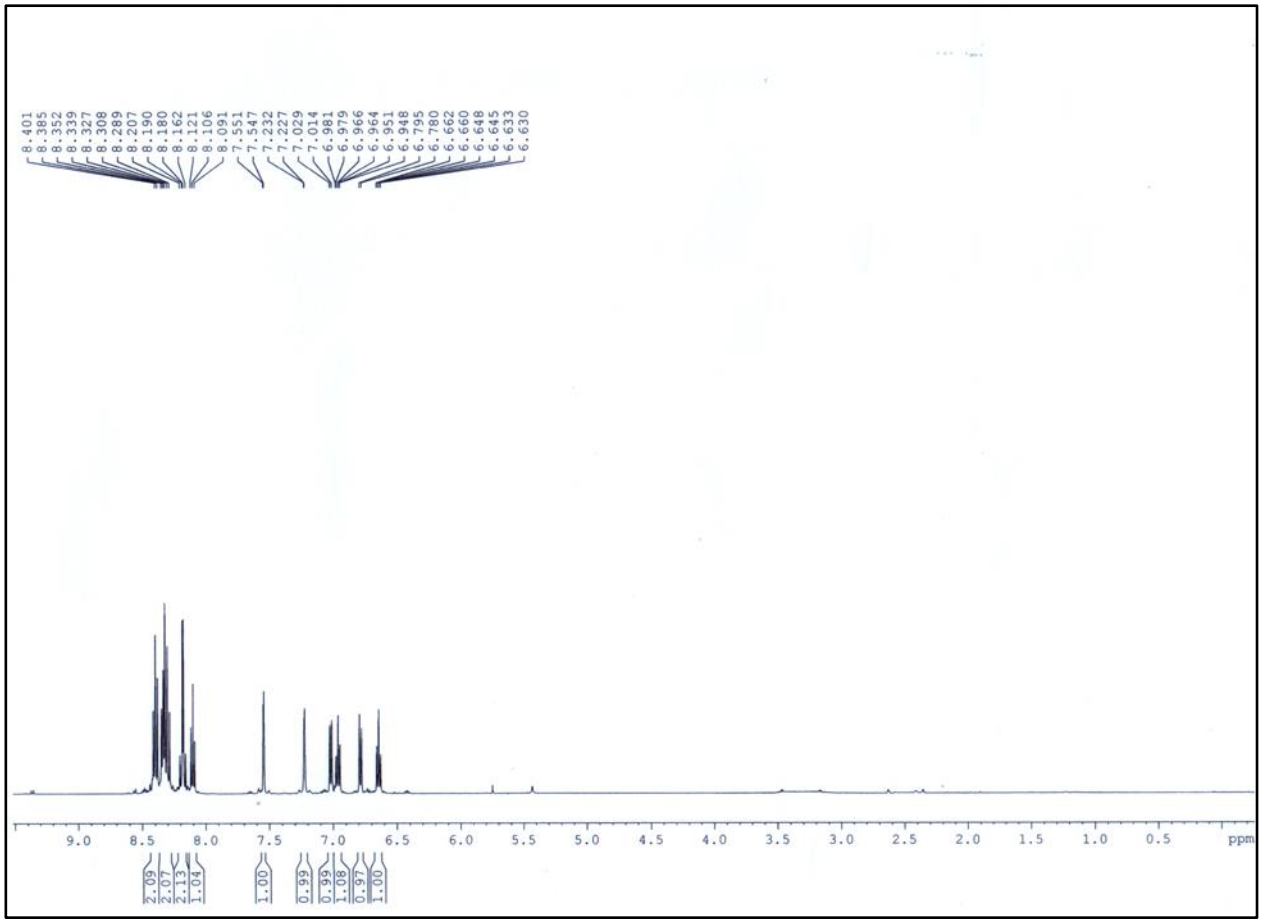


Figure S8: ^{1}H NMR of **PyB** in $CDCl_3$

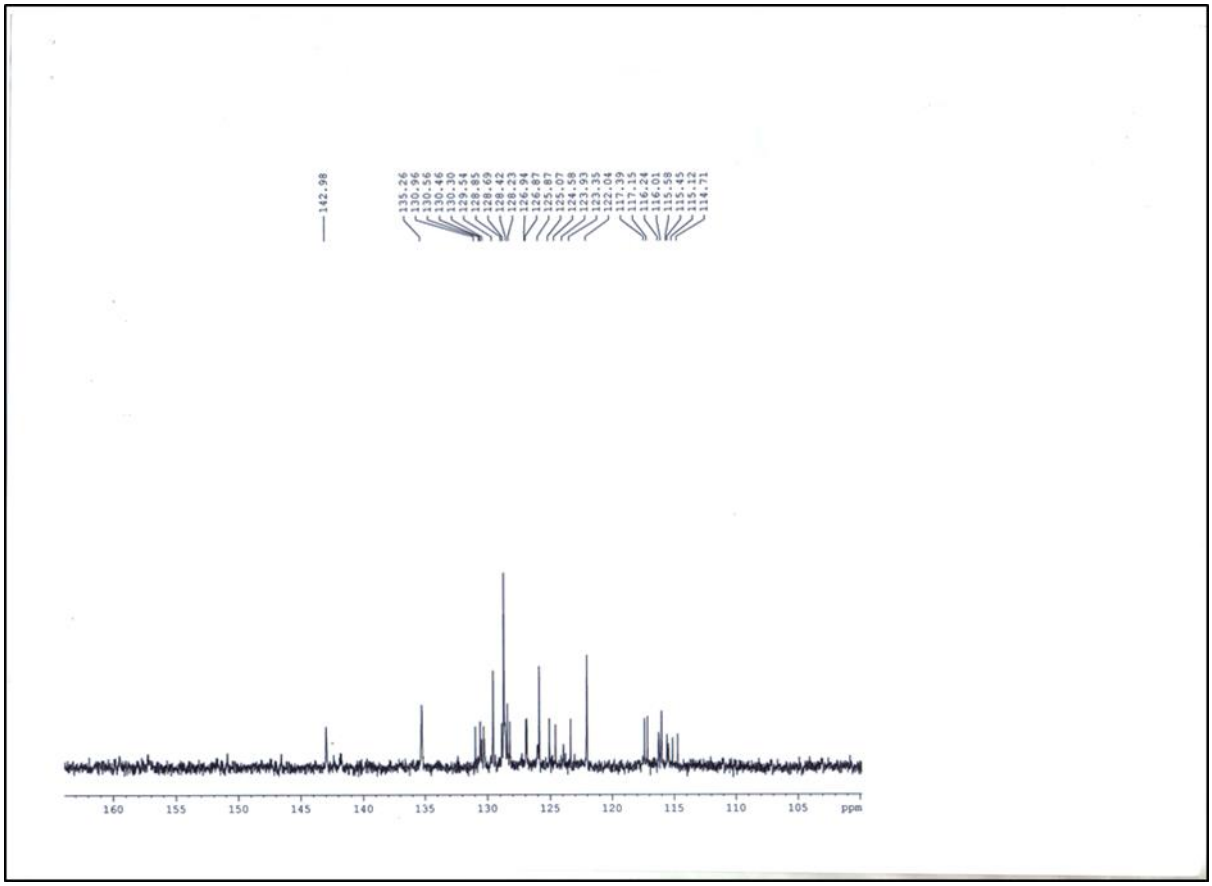


Figure S9: ^{13}C NMR of **PyB** in $CDCl_3$

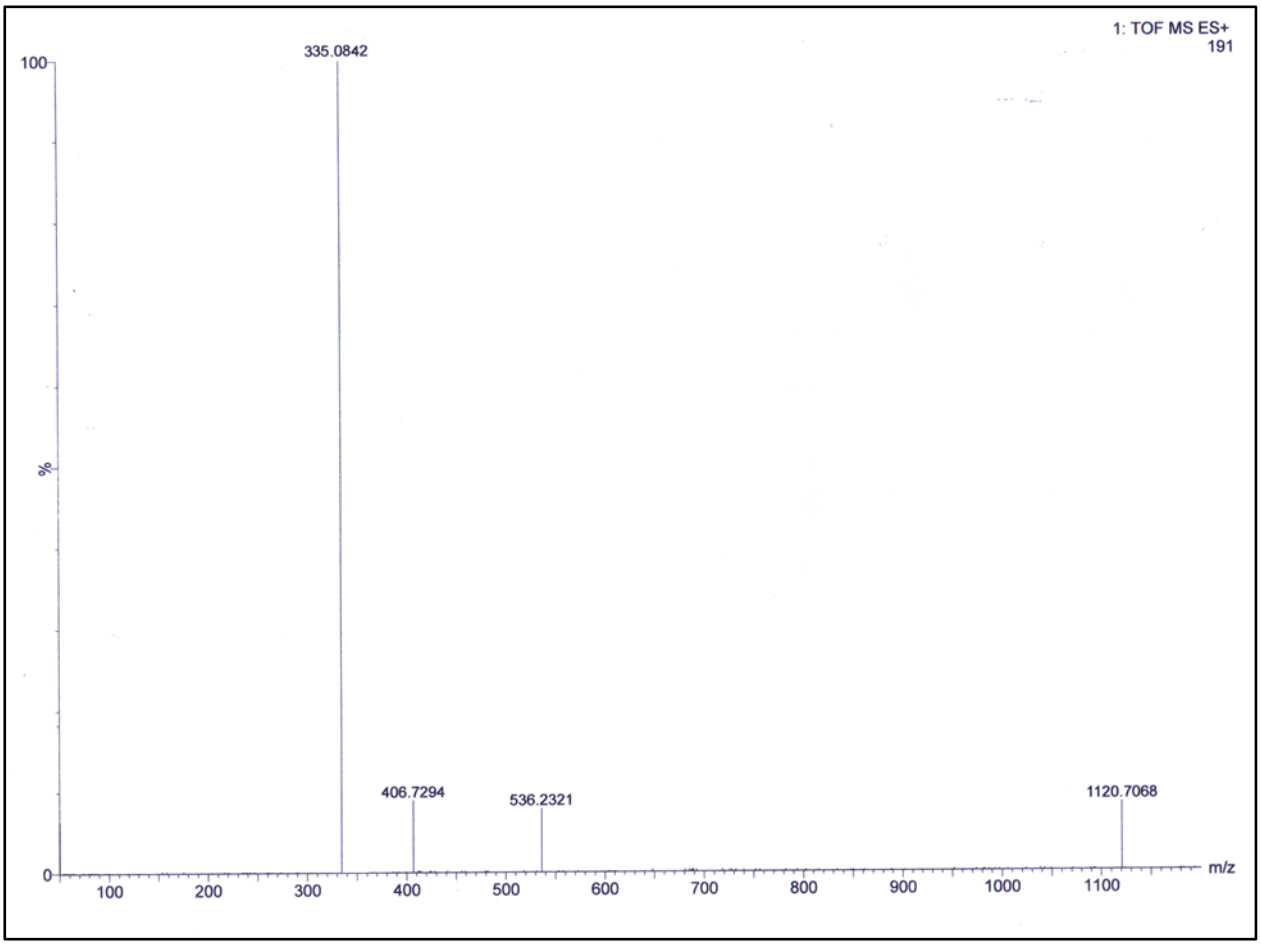


Figure S10: ESI-MS of **PyB**

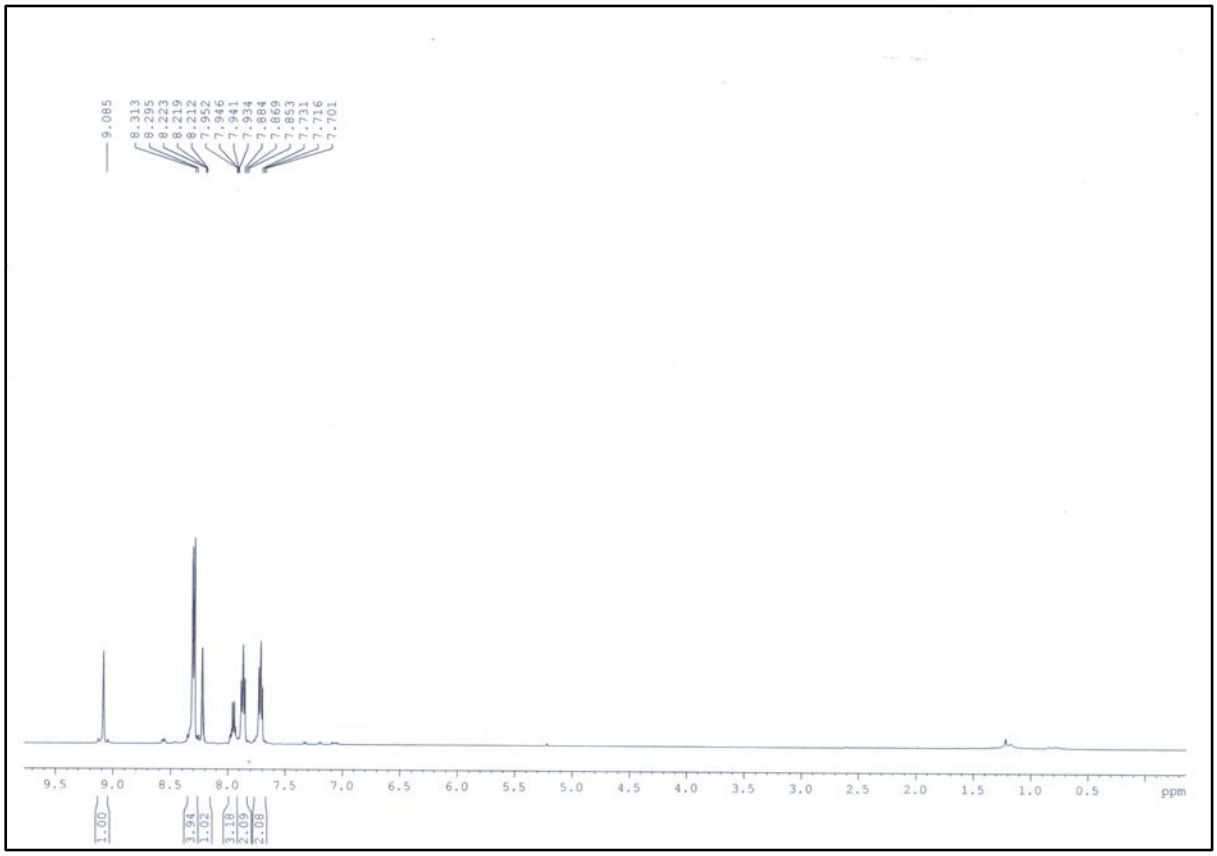


Figure S11: ^{1}H NMR of **PAPyB** in $CDCl_3$

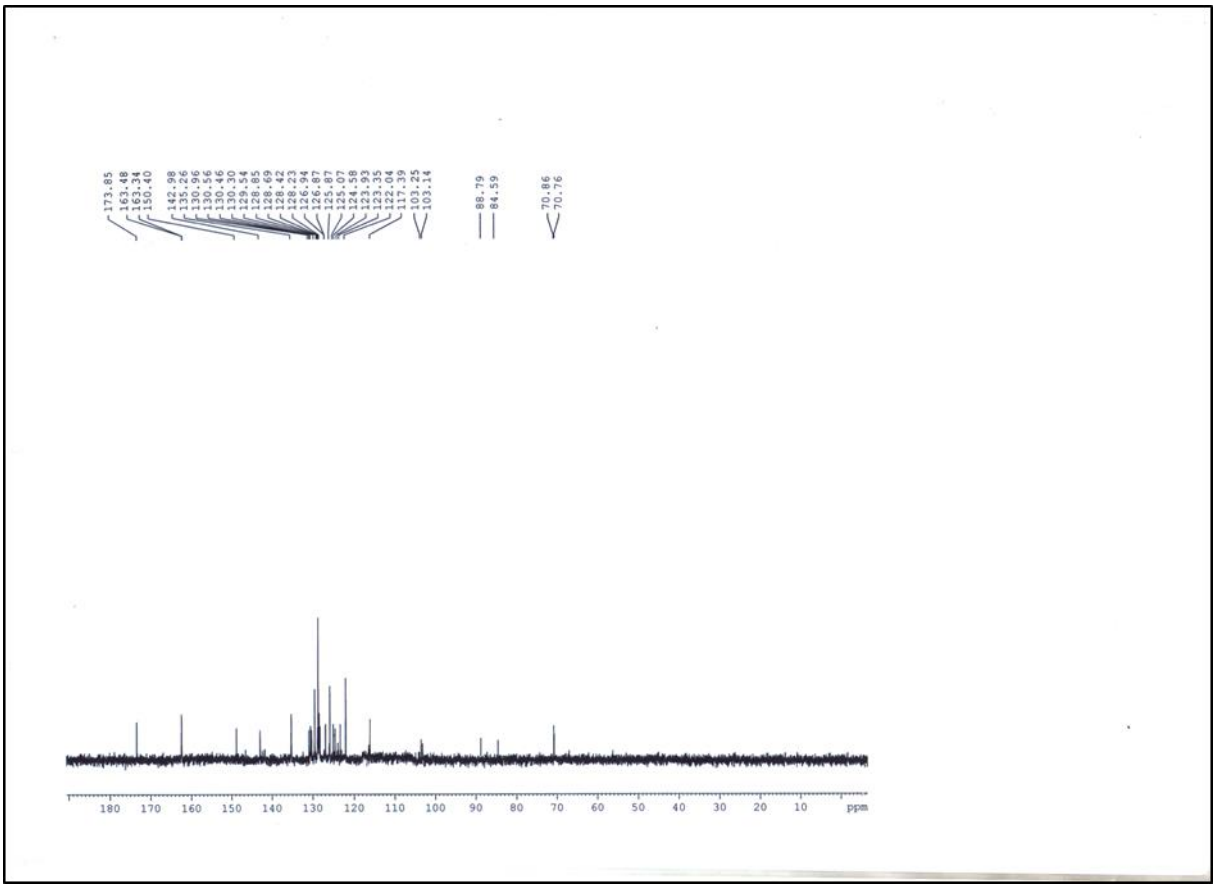


Figure S12: ^{13}C NMR of **PAPyB** in $CDCl_3$

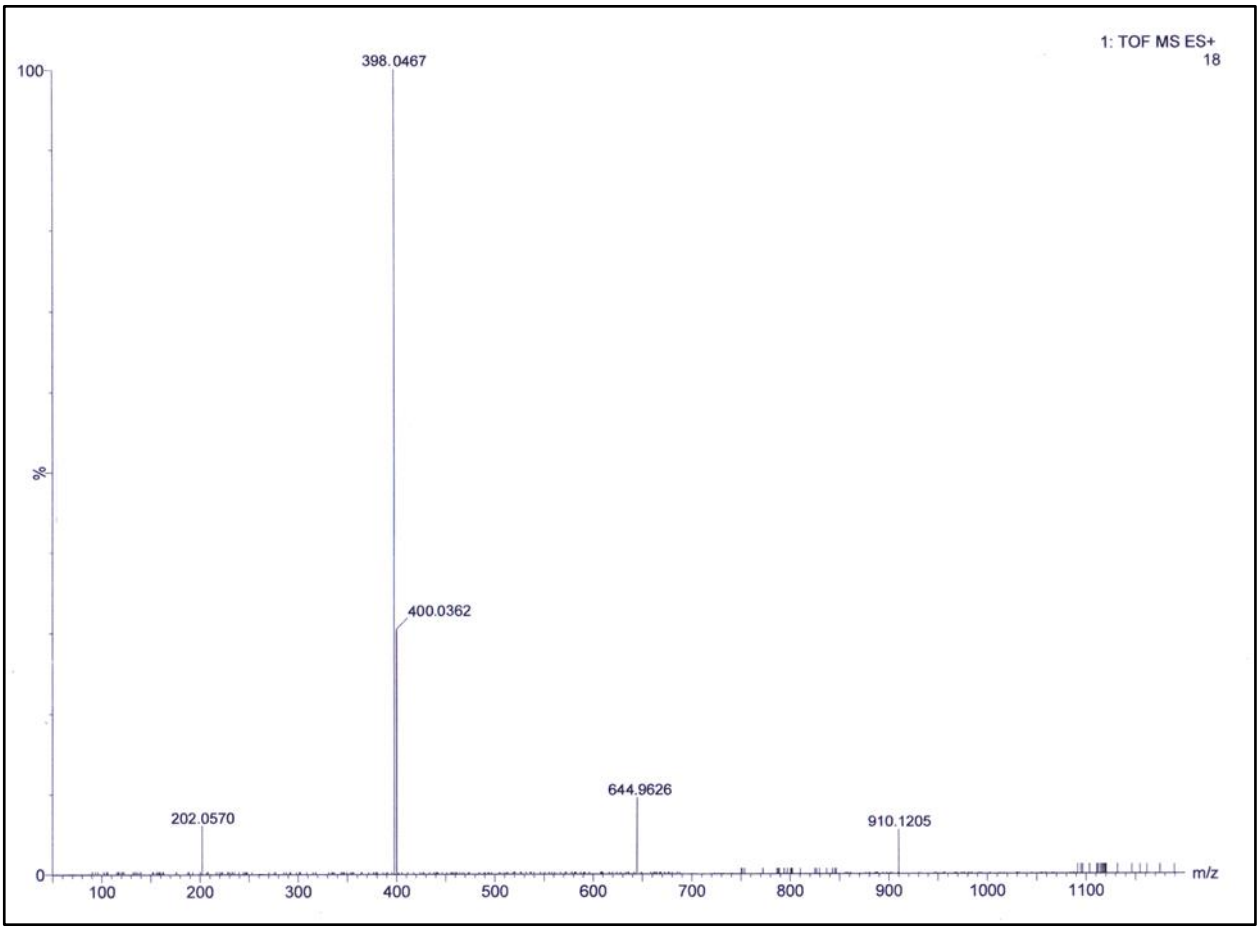


Figure S13: ESI-MS of **PAPyB**