

Supporting Information

Plastic scintillators with PMP as unique fluorophore for efficient neutron/gamma pulse shape discrimination

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General conditions and materials

Part I: Preparation of materials

Part II: FTIR analysis

Part III: ^1H NMR spectra of compounds **1**

General conditions and materials

NMR spectra. Solvents for NMR spectroscopy were dried over molecular sieves. NMR spectra were recorded on 500 MHz Bruker spectrometers. Proton (^1H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sex, sextet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved and *br* indicates the signal in question is broadened.

FTIR absorption spectra were recorded on a Perkin Elmer Spectrum Two spectrometer with an ATR accessory (total attenuated reflection). FTIR absorptions are observed by bands and are given in cm^{-1} .

Size Exclusion Chromatography (SEC): Polymers were characterized on a SEC system operating in CH_2Cl_2 eluent at $27.5\text{ }^\circ\text{C}$ fitted with two styrene / divinylbenzene copolymer columns. A differential refractometer was employed as the detector. The instrument operated at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ and was calibrated with narrow linear poly(methyl methacrylate) (PMMA) standards. Molecular weights (M_n, M_w) and dispersity (D_M) were calculated using GPL50 Agilent software.

Thermogravimetric analyses (ATG) were performed on a Perkin Elmer TGA 7 (alumel, nickel and perkalloyl calorimeter). Samples were heated from 50 to 900 degrees Celsius with a heating speed of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, under a stream of nitrogen.

UV-Visible spectra were recorded on a Perkin Elmer Lambda Bio 20, 40, 40P UV-Vis spectrophotometer.

Fluorescence emission spectra were recorded on a Perkin Elmer LS 50B/55 spectrometer. The excitation source is a xenon lamp. The data were processed using the FL Winlab software.

Radioluminescence spectra were recorded with a Horiba Jobin Yvon Fluoromax-4P device monitored with FluorEssence software. The excitation light was shut down and in the center of the experiment chamber, a $^{90}\text{Sr}/^{90}\text{Y}$ β emitting source (33.3 MBq, 01/26/2015) was placed

close to the scintillator, opposite to the emission detection cell. Betas were deposited into one face of the scintillator, which initiated the photoluminescence of the entire material. Spectra were acquired with an integration time of 0.1 s/nm, and slits were adjusted to give ca. 10,000 counts at the maximum of the signal. An EJ-200 plastic scintillator with same dimensions was used as the reference material. Integration of the spectra gave the corresponding light output against EJ-200

Characterization of the neutron/gamma discrimination performance. The plastic samples were coupled with optical grease to a Hamamatsu H7195 photomultiplier tube assembly which was biased at -1600 V. The samples were wrapped with a teflon reflector, except on the face in contact with the photomultiplier window. The samples were exposed to an AmBe source with an activity of 370 MBq, emitting approximately 20000 neutrons/s and 12000 4.4-MeV gamma-rays/s. Signals from the photomultiplier were sent to a FASTER CARAS digital electronics board (developed at LPC Caen within the FASTER project), with the following characteristics: bandwidth 100 MHz; 500-MSamples/s, 12-bit digitizer; input range 2 V; input impedance 50 Ω ; baseline correction. The digitized and baseline-corrected signals were recorded event by event and the charge integration for neutron/gamma discrimination was performed offline. The calibration of the total scintillation light was performed with a 5-kBq ^{22}Na source.

Part I: Preparation of materials.

Multigram scale procedure for the synthesis of 3-mesityl-1-phenyl-4,5-dihydro-1H-pyrazole (1)

Step 1: In a dry Schlenk tube, mesitylmethylketone (1 eq, 128 mmol) and *N,N*-dimethylformiminium chloride (1 eq, 128 mmol) were introduced in dry acetonitrile (500 mL) under argon. The reaction mixture was stirred at reflux (110 °C) for 1 h. After cooling down the reaction mixture to r.t., the solvent was removed under vacuum. The crude product containing α,β -unsaturated ketone and β -ammonium ketone was directly engaged in the second step.

¹H-NMR of the crude shows a 4:1 ratio between ammonium **4** and α,β -unsaturated ketone **5**.

Step 2: In a Schlenk tube equipped with a condenser, the 4:1 mixture of **4** and **5** of **Step 1** and PhNHNH₂ (3 eq, 385 mmol) were introduced in a 1:1 mixture of degassed AcOH/H₂O (250 mL) under argon. The reaction mixture was stirred at 100 °C overnight. The product was extracted from the crude reaction mixture with pentane (5 x 100 mL). The combined organic layers were dried over MgSO₄. Solvent was removed under vacuum; 33.8 g of crude products were obtained, as a brown oil. The crude was purified by silica gel column chromatography (pentane/diethyl ether 98:2) to produce a yellowish solid, which was recrystallized in EtOH to afford 19.3 g of pure PMP (**1**), as a white solid with an overall yield of 57 % for the two steps).

¹H-NMR (500 MHz, C₆D₆, δ) 2.14 (s, 3H), 2.17 (s, 6H), 2.49 (t, *J* = 10.0 Hz, 2H), 3.28 (t, *J* = 10.0 Hz, 2H), 6.76 (s, 2H), 6.86 (t, *J* = 6.8 Hz, 1H), 7.23-7.28 (m, 4H) ppm. ¹³C-NMR (500 MHz, C₆D₆, δ) 20.2 (qx2), 21.1 (qx1), 36.5 (tx1), 48.4 (tx1), 113.7 (dx2), 119.5 (dx1), 128.8 (dx2), 129.4 (dx2), 131.0 (sx1), 136.8 (sx2), 137.8 (sx1), 147.6 (sx1), 150.9 (sx1) ppm. IR (neat, powder) ν = 2915, 2852, 1599, 1500, 1465, 1375, 1335, 1291, 1250, 1216, 1180, 1161, 1116, 1103, 1065, 1031, 996, 878, 857, 754, 745, 693, 662, 576, 509 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₈H₂₀N₂ [M+H]⁺ : 265.1700 ; found : 265.1705.

Preparation of plastics doped with compound 1

4-vinyltoluene was first distilled under vacuum and degassed (Freeze-Pump-Thaw method). Each plastic scintillator was prepared by dissolving under argon, a specific amount of PMP in a specific amount of 4-vinyltoluene in a glass polymerization tube, previously purged with

argon and sealed off under vacuum. Following this procedure, 0 g, 0.5 g, 1 g, 1.5 g, 2 g, 2.5 g, and 3 g of PMP were thus respectively dissolved under argon in 11.15 mL, 10.59 mL, 10.03 mL, 9.48 mL, 8.92 mL, 8.36 mL, and 7.80 mL of 4-vinyltoluene ($d = 0.897$), for the conception of the desired plastic scintillators doped with 0, 5, 10, 15, 20, 25, and 30 wt% of PMP, respectively. The tubes were then immersed in an oil bath equipped with a stirrer at 120 °C and the temperature was kept at 120 °C for 5 days. After 5 days, the tubes were slowly cooled to room temperature and the plastic scintillators were simply obtained by breaking the glass polymerization tubes carefully. The plastic scintillators were finally polished and sent for analysis.

Part II. FTIR analysis

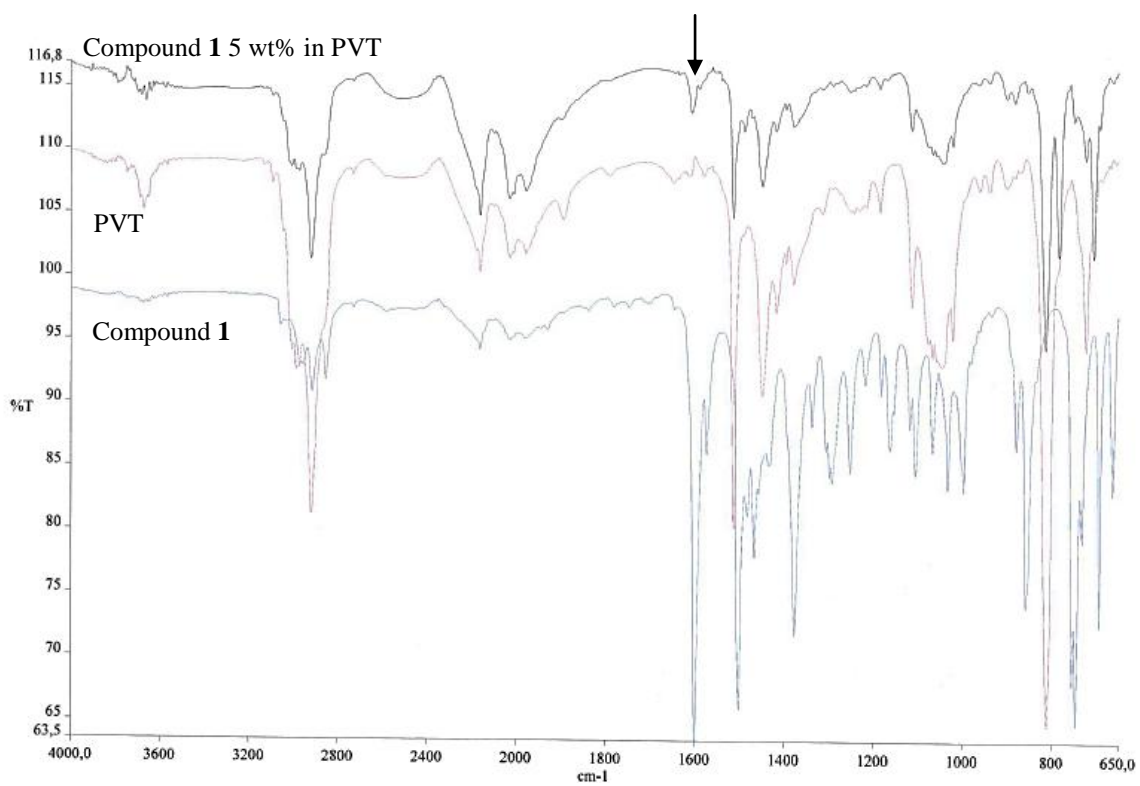


Figure S1. FTIR spectra of grinded PVT plastic containing 5 wt% of compound **1**, grinded pure

Part III: ^1H NMR spectra of compounds **1**

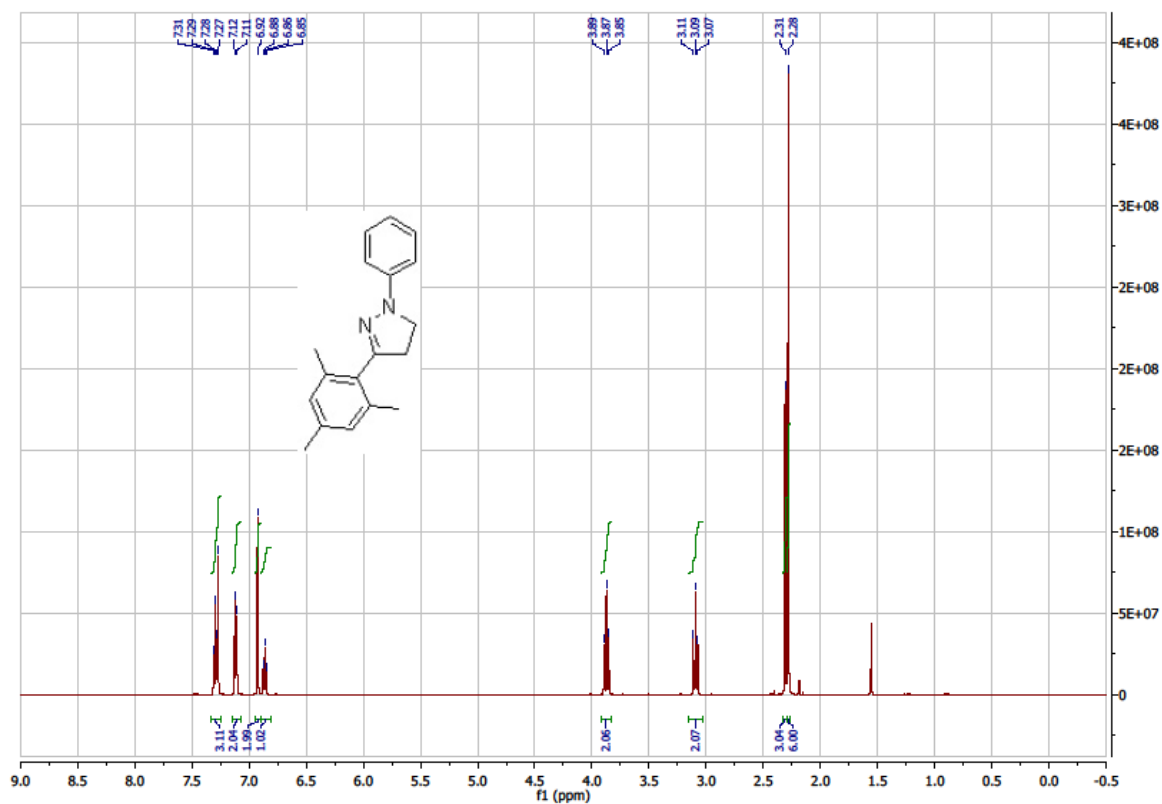


Figure S2. Compound **1** - ^1H NMR (CDCl_3 , 500 MHz)

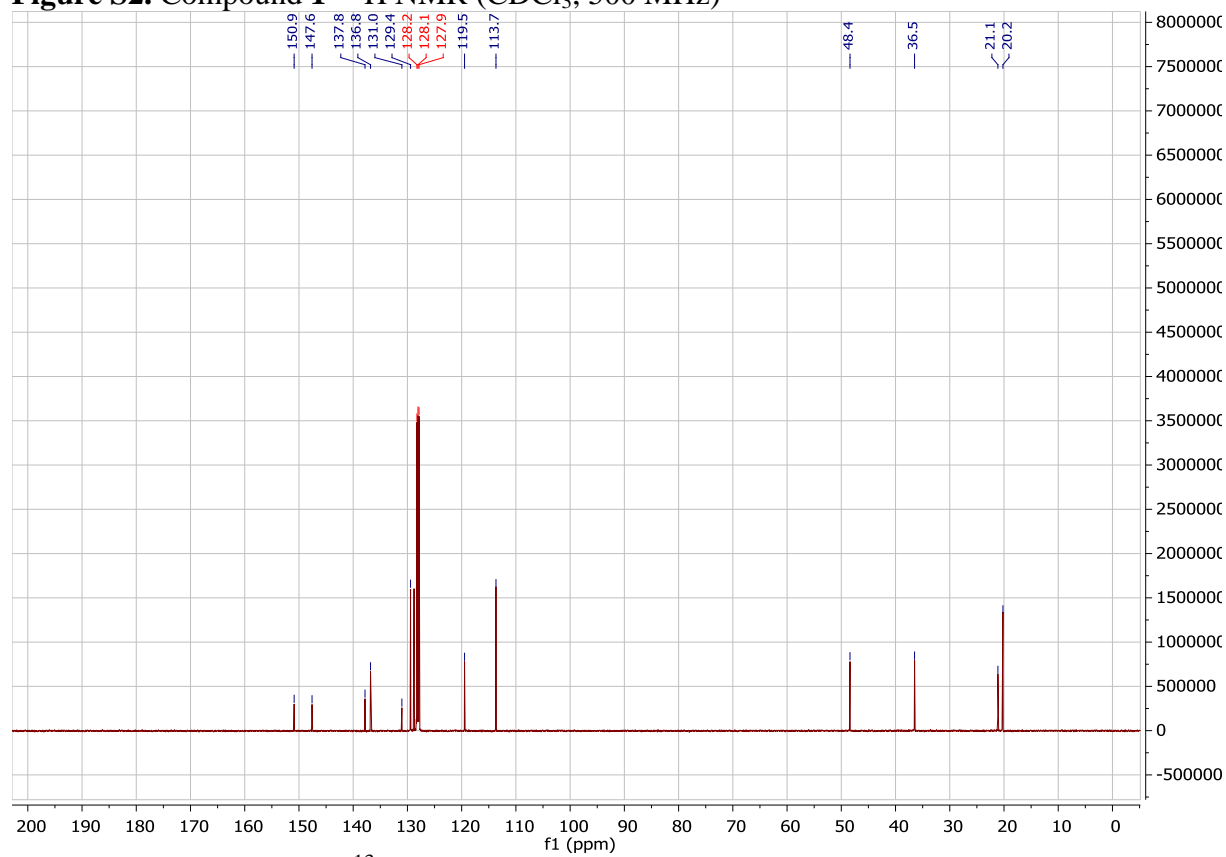


Figure S3. Compound **1** - ^{13}C NMR (C_6D_6 , 500 MHz)