Electronic Supplementary Information

"Receptor Free" Inner Filter Effect Based Universal Sensor for Nitroexplosive Picric Acid Using Two Polyfluorene Derivatives in Solution and Solid State

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Caution! The nitroexplosive used in the experiment, particularly PA, TNT and RDX, are very explosives in nature and should be handled carefully in small amounts with suitable safety measurements.

1. Materials and Methods

Nitroexplosives namely, 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3dinitrobenzene (1,3-DNB) and 4-nitrotoluene (4-NT) were purchased from Sigma Aldrich Chemicals. 2,4,6-trinitrotoluene (2,4,6-TNT) and RDX were purchased from AccuStandard and used as received. Picric acid (PA) was obtained from Loba Chemie Pvt. Ltd. All other chemicals and reagents were bought from Merck and Alfa-Aesar, and were used without further purification. Milli-Q water was used everywhere in titration. ¹H NMR (400 and 600 MHz) and ¹³C NMR (100 and 150 MHz) spectra were recorded on Varian-AS400 NMR spectrometer and Bruker Ascend 600 spectrometer respectively. Photoluminescence spectra were taken on a Horiba Fluoromax-4 spectrofluorometer using 10 mm path length quartz cuvettes with a slit width of 3 nm at 298 K. Perkin Elmer Lambda-25 spectrophotometer was used to record absorption spectra. Edinburg Life Spec II instrument was used for execution of time-resolved fluorescence studies. Cyclic voltammograms were recorded using CH Electrocchemical instruments Model 700D series workstation. Gel Permeable Chromatography was carried out in THF using polystyrene as standard. Paper strip test was done by using Whatman qualitative filter paper grade 1.

2. Preparation of Stock Solutions

Stock solution of polymer PF1 and PF2 were prepared in THF solvent at a concentration of 1×10^{-4} M. Stock solution of other nitroaromatic compounds i.e. nitromethane (NM), phenol, 4-nitrophenol (4-NP), nitrobenzene (NB), were prepared at concentrations of 1×10^{-2} M. Stock solution of 2,4- dinitrophenol (2,4-DNP) was prepared in Milli-Q water at a concentration of 1×10^{-3} M. Stock solution of other nitroaromatics namely 4-Nitrotoluene (4-NT), 1,3-Dinitrobenzene (1,3-DNB), 2,4-Dinitrotoluene (2,4-DNT), 2,6-Dinitrotoluene (2,6-DNT), were prepared in HPLC grade THF at concentrations of 1×10^{-2} M. Stock solution of TNT and RDX were prepared at concentration of 1×10^{-2} M in 1:1 CH₃CN:MeOH. The absorption and fluorescence titrations were carried out in a quartz cuvette (1 cm \times 1 cm) after preparing various solution of PF1 (1.6 $\times 10^{-7}$ M) and PF2 (3.3 $\times 10^{-7}$ M) separately in 4:1 THF:HEPES (10 mM, pH=7) each containing different concentration of nitroaromatic

compounds. All the spectra were recorded at room temperature after thoroughly mixing of the resultant mixture.

3. Time-Resolved Decay Measurements

Lifetime decay measurements of PF1 (1.6×10^{-7} M) in the absence and presence of PA (66.6 $\times 10^{-6}$ M) were performed via pulse excitation of 375 nm and emission at 408 nm in 4:1 THF:HEPES (10 mM, pH=7). Similarly, Lifetime decay measurements of PF2 (3.3×10^{-7} M) in the absence and presence of PA (66.6×10^{-6} M) were performed via pulse excitation of 375 nm and emission at 415 nm in 4:1 THF:HEPES (10 mM, pH=7). The curves for PF1 and PF2 were fitted mono- and bi-exponentially respectively and the average life time was considered for uniformity in results. Table S1 and S2 in the supporting information file shows amplitude, lifetime of each component and average lifetime.

4. Preparation of Paper Strips

Whatman filter paper (70 mm diameter) was used to prepare fluorescent paper strips by dipping it into a solution of polymer (1×10^{-4} M) in THF followed by drying in air. The dried polymer coated test strip was cut into desired size ($1 \text{ cm} \times 1 \text{ cm}$) and used a portable PA detection purposes.

5. Detection Limit Calculations

Various solutions of PF1 (1.6×10^{-7} M) in 4:1 THF:HEPES (10 mM, pH=7) each containing PA (2.33 µM, 2.00 µM 1.66 µM, 1.33 µM, 1.0 µM, 0.66 µM, 0.33 µM, 0.0 µM) were prepared separately and emission spectrum was recorded for each sample. Similarly, Various solutions of PF2 (3.3×10^{-7} M) in 4:1 THF:HEPES (10 mM, pH=7) each containing PA (2.33 µM, 2.00 µM 1.66 µM, 1.33 µM, 1.0 µM, 0.66 µM, 0.33 µM, 0.0 µM) were prepared separately and emission spectrum was recorded for each sample. A calibration curve was obtained for both PF1 and PF2 separately, between the emission intensity maxima and the concentration of PA to get a regression curve equation. The limit of detection (LOD) was evaluated from the equation $3\sigma/k$, where σ is the standard deviation (SD) in the emission intensity for the blank polymer solution in the absence of PA and K is the slope of the calibration curve.

6. Calculations for photoluminescence quantum yield

The quantum yield of polymers PF1 and PF2 were determined in THF using quinine sulphate ($\Phi_r = 0.54$ in 0.1M H₂SO₄) as reference material. The following equation³⁴ was employed for calculations.

$$\Phi_{\rm s} = \Phi_{\rm r} \left(A_{\rm r} F_{\rm s} / A_{\rm s} F_{\rm r} \right) \left(\eta_{\rm s}^2 / \eta_{\rm r}^2 \right)$$

where, s and r represents the sample and reference, respectively, A denotes the absorbance, F is the relative integrated fluorescence intensity and η is used for refractive index of the medium used.

7. Cyclic Voltammetry Studies

CV measurements were performed using a CH Instruments 760D electrochemical workstation at a scan speed of 50 mV/s. A three-electrode cell with platinum wire counter electrode, glassy carbon working electrode and Ag/Ag⁺ reference electrode was used. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was used as supporting electrolyte and Fc⁺/Fc was used as reference. A thin film of polymer was casted from 10 μ L, 1 mM solution in DCM on the glassy carbon working electrode and the measurements were performed at room temperature under inert atmosphere.



Scheme S1: Structures of various nitroexplosive compounds used in the experiments.

Table S1: Fluorescence lifetime decay of each component and their fractions.

Sample	τ_1	%	χ²
	(ns)		
PF1	0.551	100	1.093
PF1-PA	0.548	100	1.047

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Table S2: Fluorescence lifetime decay of each component and their fractions.

Sample	τ_1	%	τ_2	%	χ²	$ au_{avg}$
	(ns)		(ns)			(ns)
PF2	0.599	94.104	2.637	5.896	1.126	0.719
PF2-PA	0.596	94.585	2.838	5.415	1.105	0.717







Fig. S6 ¹H NMR spectra of PF2.



	Distribution Name	Mh (Daltons)	Mw (Daltons)	MP (Daitons)	Mz (Daltons)	Mz+1 (Daltons)	Rolydispersity	Mz/Mw	Mz+1/Mw
1		2039	5681	2333	13065	22008	2.785763	2.299872	3.873988

Fig. S7 GPC chromatogram of polymer PF1.

Broad Unknown Relative Chromatogram 150.00 4798-100.00 50.00 0.00- Δ NV -50.00--100.00--150.00--200.00-200 16.00 18.00 4.00 6.00 8.00 10.00 1200 14.00 20.00 Minutes Peak Table

	Broad Unknown Relative Peak Table													
	Distribution Name	Mh (Daitons)	Mw (Daltons)	MP (Daitons)	Mz (Daitons)	Mz+1 (Daltons)	Rolydispersity	Mz/Mw	Mz+1/Mw					
1		6630	24199	4798	76488	118339	3.649713	3.160826	4.890288					

Fig. S8 GPC chromatogram of polymer PF2.



Fig. S9. Image of PF1 and PF2 under UV-light before and after addition of PA.



Fig. S10 Stern-Volmer plot obtained at lower concentration of PA for PF1.



Fig. S11 Stern-Volmer plot obtained at lower concentration of PA for PF2.



Fig. S12 Fluorescence intensity of PF1 in 4:1/THF:HEPES buffer (pH=7, 10 mM) *vs* PA concentration.

LOD= $3 \times \text{S.D./k}$ LOD = $3 \times 1375.02/(3724.2 \times 10^7)$ = 110 nM or 25.2 ppb



Fig. S13 Fluorescence intensity of PF2 in 4:1/THF:HEPES buffer (pH=7, 10 mM) vs PA concentration.

 $LOD{=}3\times S.D./k$

LOD = $3 \times 1739.66/(2378.1 \times 10^7)$ = 219 nM or 50.1 ppb

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Publication	Material Used	Detection Limit	Selectivity	Sensing Mechanism	Medium Used
Present Manuscript	Conjugated Polymers	110 × 10 ⁻⁹ M (25.2 ppb) And 219 × 10 ⁻⁹ M (50.1 ppb)	Selective	IFE	THF:H ₂ O
J. Am. Chem. Soc. 2017 , 139, 5437–5443	Poly(β-aminoacrylate)s	3.87 μM for P1a2d and 0.12 μM for P1b2d	Not studied	AIE	THF/water
J. Am. Chem. Soc. 2017 , 139, 2421–2427	Conjugated Covalent Organic Frameworks	-	Not Selective	-	CH ₂ Cl ₂
ACS Appl. Mater. Interfaces 201 7, 9, 13415–13421	polyimide covalent organic framework	0.25 μM	Selective	Electron Transfer And IFE	C ₂ H ₅ OH
ACS Omega 2017 , 2, 4424–4430	Conjugated Polyelectrolyte	295 nM	Selective	IDA	H ₂ O
ACS Sens. 2016, 1, 1070–1077	Conjugated Polymer	57.8 nM	Selective	IFE and PET	THF:H ₂ O
<i>J. Mater. Chem. A,</i> 2015 , <i>3</i> , 92–96	Covalent-organic polymer	About 1 ppm	Selective	Electron transfer	CH ₃ OH
J. Mater. Chem. A, 2014, 2, 15560– 15565	polydiacetylene	0.11 ppm (0.48µM)	Selective	Electron transfer	CH ₃ OH
<i>Macromolecules</i> 2014 , 47, 4908–4919	poly(dipropargyl amine)s	1µM	Not selective	Energy transfer	THF:H ₂ O
<i>Polym. Chem.</i> , 2014 , <i>5</i> , 5628–5637	Poly(acrylate)	2.5 ppm	Not selective	Electron transfer	THF:H ₂ O
<i>RSC Adv.</i> , 2013 , <i>3</i> , 8193–8196	Poly(arylene ynonylene)	1 ppm	Not studied	-	THF:H ₂ O
<i>Macromolecules</i> 2013 , <i>46</i> , 3907–3914	Poly(aroxycarbonyltriazole)s	Upto 1µg/mL	Not studied	-	THF:H ₂ O
Macromol. Rapid Commun. 2013 , 34, 796–802	Polytriazole	9 × 10 ⁻⁸ M	Not studied	Energy transfer	THF:H ₂ O
<i>Macromolecules</i> 2011 , <i>44</i> , 5977–	Poly(silylenevinylene)s	Upto 1ppm	Not studied	Electron and/or	THF:H ₂ O

detection.	

5986				energy transfer	
Macromol. Rapid Commun. 2010 , 31, 834–839	Poly(silylenevinylene)	Upto 1ppm	Not studied	-	THF:H ₂ O
<i>Macromolecules</i> 2009 , <i>42</i> , 9400- 9411	Conjugated Polyelectrolyte	0.17 ppm (0.72 μM)	Not studied	-	THF:H ₂ O
J. Am. Chem. Soc. 2003, 125, 3821- 3830	Polymetalloles	Not reported	Not selective	Electron- transfer	THF

Table S4: A comparative study of some sensors developed for picric acid detection based on IFE mechanism.

Publication	Material	Stern-	Limit of	Portable	IFE
	Used	Volmer	Detection	Test	Correction
		Constant	(LOD)	Strip	$(E_{obs}-E_{corr})$
		(K _{sv})			(%)
Present	Conjugated	$5.1 \times 10^4 \text{ M}^{-1}$	$110 \times 10^{-9} M$	Prepared	77.39
Manuscript	Polymers	and	(25.2 ppb)		and
		$5.0 \times 10^4 \text{ M}^{-1}$	And $210 \times 10^{9} M$		71.05
			$219 \times 10^{5} M$ (50.1 nnb)		
ACS Appl. Mater.	Boron Nitride	$2.0 \times 10^4 \text{ M}^{-1}$	140 nM	Not	33.83
Interfaces 2018.	Ouantum			Shown	
10, 7315-7323	Dots				
New J. Chem.,	copper	$2.5 \times 10^4 \text{ M}^{-1}$	190 nM	Not	~20
2018 , <i>42</i> , 7223-	nanoclusters			Shown	
7229					
Analytica	carbon dots	$3.8 \times 10^4 \text{ M}^{-1}$	30 nM	Not	30.03
Chimica Acta				Shown	
2018 , 1013, 63-70					
ACS Appl. Mater.	covalent	$1.0 \times 10^{7} \text{ M}^{-1}$	250 nM	Not	Not
Interfaces 2017,	organic			Shown	Performed
9, 13415-13421	framework				
ACS Sens. 2016,	Conjugated	$1.0 \times 10^5 \text{ M}^{-1}$	57 nM	Shown	Not
1, 1070-1077	Polymer				Performed
ACS Appl. Mater.	Polymer	-	26 nM	Not	Not
Interfaces 2016,	Nanoparticles			Shown	Performed
8, 21700-21709					
Analyst 2016 ,	carbon dots	0.0052 μM ⁻¹	200 nM	Not	Not
141, 2676–2681				Shown	Performed
Talanta 2016 ,	carbon	1.0 ×10 ⁵ M ⁻¹	28 nM	Not	Not
161, 875–880	nanodots			Shown	Performed

<i>RSC Adv.</i> 2014 , <i>4</i> ,	tripyrenyl	$3.6 \times 10^4 \text{ M}^{-1}$	0.15 ppm	Not	Not
58077	truxene			Shown	Performed



Fig. S14. Photoluminescence spectra showing the effect of various nitro analytes (66.6×10^{-6} M) on fluorescence emission of PF1 (1.6×10^{-7} M) in 4:1/THF:water.



Fig. S15. Photoluminescence spectra showing the effect of various nitro analytes (66.6×10^{-6} M) on fluorescence emission of PF2 (3.3×10^{-7} M) in 4:1/THF:water.



Fig. S16 Bar diagram depicting effect of various metal ions (66.6×10^{-6} M) on the fluorescence intensity of PF1 (1.6×10^{-7} M).



Fig. S17 Bar diagram depicting effect of various anions (66.6×10^{-6} M) on the fluorescence intensity of PF1 (1.6×10^{-7} M).



Fig. S18 Bar diagram depicting effect of metal ions (66.6×10^{-6} M) on the fluorescence intensity of PF2 (3.3×10^{-7} M).



Fig. S19 Bar diagram depicting effect of various anions (66.6×10^{-6} M) on the fluorescence intensity of PF2 (3.3×10^{-7} M).



Fig. S20 Emission spectra of PF1 (1.6×10^{-7} M) with TNT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S21 Emission spectra of PF1 (1.6×10^{-7} M) with 2,4-DNT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S22 Emission spectra of PF1 (1.6×10^{-7} M) with 2,6-DNT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S23 Emission spectra of PF1 (1.6×10^{-7} M) with 1,3-DNB (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S24 Emission spectra of PF1 (1.6×10^{-7} M) with 4-NT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S25 Emission spectra of PF1 (1.6×10^{-7} M) with RDX (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S26 Emission spectra of PFBT $(3.3 \times 10^{-6} \text{ M})$ with phenol $(93.3 \times 10^{-6} \text{ M})$ followed by addition of PA (93.3×10^{-6} M) in DMSO.



Fig. S27 Emission spectra of PF1 (1.6×10^{-7} M) with NB (66.6×10^{-6} M) followed by addition of PA (66.6 \times 10⁻⁶ M).



Fig. S28 Emission spectra of PF1 (1.6 \times 10⁻⁷ M) with NM (66.6 \times 10⁻⁶ M) followed by addition of PA (66.6 \times 10⁻⁶ M).



Fig. S29 Emission spectra of PF2 $(3.3 \times 10^{-7} \text{ M})$ with TNT $(66.6 \times 10^{-6} \text{ M})$ followed by addition of PA $(66.6 \times 10^{-6} \text{ M})$.



Fig. S30 Emission spectra of PF2 (3.3×10^{-7} M) with 2,4-DNT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S31 Emission spectra of PF2 (3.3×10^{-7} M) with 2,6-DNT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S32 Emission spectra of PF2 $(3.3 \times 10^{-7} \text{ M})$ with 1,3-DNB $(66.6 \times 10^{-6} \text{ M})$ followed by addition of PA $(66.6 \times 10^{-6} \text{ M})$.



Fig. S33 Emission spectra of PF2 (3.3×10^{-7} M) with 4-NT (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S34 Emission spectra of PF2 (3.3×10^{-7} M) with RDX (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S35 Emission spectra of PF2 (3.3×10^{-7} M) with phenol (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S36 Emission spectra of PF2 (3.3×10^{-7} M) with NB (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S37 Emission spectra of PF2 (3.3×10^{-7} M) with NM (66.6×10^{-6} M) followed by addition of PA (66.6×10^{-6} M).



Fig. S38 UV-Visible spectrum of PF1 (1.6×10^{-7} M) with the increasing concentration of PA.



Fig. S39 UV-Visible spectrum of PF2 $(3.3 \times 10^{-7} \text{ M})$ with the increasing concentration of PA.

PA(µM)	A _{ex}	A _{em}	I _{obs}	I _{corr}	I _{corr} /I _{obs}	I _{corr} /I _{corr,o}	E _{obs}	E _{corr}
					Correction		(%)	(%)
					factor			
					(CF)			
0.0	0.00327	-0.00035	1117560	1121318	1.003363	1	0	0
6.6	0.134571	0.098285	883766.4	1155488	1.307459	1.030473	20.92	-3.0473
13.3	0.260257	0.192205	670316	1128523	1.683569	1.006426	40.01968	-0.64258
20.0	0.392172	0.290904	505958.9	1110844	2.195523	0.99066	54.72646	0.934048
26.6	0.521551	0.385995	381816.6	1085495	2.842975	0.968053	65.8348	3.194731
33.3	0.657292	0.487313	283849.2	1060206	3.735102	0.9455	74.60099	5.450042
40.0	0.787289	0.581273	216180.1	1044953	4.833715	0.931897	80.65606	6.810312
46.6	0.924155	0.680701	158820.8	1007710	6.344947	0.898683	85.78861	10.13169
53.3	1.056392	0.774255	119473.1	983090.7	8.228554	0.876728	89.30947	12.32723
60.0	1.189109	0.870032	89895.4	962294.4	10.7046	0.858181	91.9561	14.18185
66.6	1.322754	0.962819	67334.48	935457.4	13.89269	0.834248	93.97487	16.57521

Table S4. IFE of PA on the fluorescence of PF1.

PA(µM)	A _{ex}	A _{em}	I _{obs}	I _{corr}	I_{corr}/I_{obs}	I _{corr} /I _{corr,o}	E _{obs}	E _{corr}
					Correction		(%)	(%)
					factor			
					(CF)			
0.0	0.006842	0.001354	742999.6	750043.7	1.009481	1	0	0
6.6	0.145425	0.091007	555744.7	729611	1.312853	0.972758	25.20255	2.724209
13.3	0.291972	0.185852	409644.4	710099.2	1.733453	0.946744	44.86613	5.325621
20.0	0.433255	0.276891	305668	692345.7	2.265025	0.923074	58.86027	7.692614
26.6	0.575615	0.368119	227674.9	674811.1	2.963924	0.899696	69.35733	10.03044
33.3	0.720185	0.459858	169103.4	657921.1	3.890644	0.877177	77.24045	12.28231
40.0	0.862995	0.550753	127194.5	647652.8	5.091831	0.863487	82.88095	13.65132
46.6	1.02185	0.649378	91055.99	623623.6	6.848792	0.83145	87.74481	16.85503
53.3	1.173185	0.745069	66709.42	607175.4	9.101794	0.80952	91.02161	19.048
60.0	1.320497	0.837099	49314.7	591254.5	11.98942	0.788293	93.36275	21.17067
66.6	1.465231	0.926808	36267.65	569559.3	15.70433	0.759368	95.11875	24.06319

Table S5. IFE of PA on the fluorescence of PF2.



Fig. S40 The normalised UV-Visible spectrum of PA, 2,4-DNP, 4-NP and the normalised fluorescence excitation and emission spectrum of PF1.



Fig. S41 The normalised UV-Visible spectrum of PA, 2,4-DNP, 4-NP and the normalised fluorescence excitation and emission spectrum of PF2.



Fig. S42 Comparison of quenching efficiency for 4-NP, 2,4-DNP and PA in 4:1-THF:HEPES (10 mM, pH=7.0) for PF1.



Fig. S43 Comparison of quenching efficiency for 4-NP, 2,4-DNP and PA in 4:1-THF:HEPES (10 mM, pH=7.0) for PF2.



Fig. S44 Stern-Volmer plot obtained at lower concentration of 2,4-DNP for PF1.



Fig. S45 Stern-Volmer plot obtained at lower concentration of 2,4-DNP for PF2.



Fig. S46 Cyclic voltammogram of PF1 (inset shows ferrocene peak).



Fig. S47 Cyclic voltammogram of PF2 (inset shows ferrocene peak).



Fig. S48 Calibration curve obtained for Polymer PF1.



Fig. S49 Comparison of ¹H NMR spectra of M2 before and after addition of PA.



Fig. S50 Comparison of ¹H NMR spectra of PF1 before and after addition of PA.





Fig. S51 Comparison of ¹H NMR spectra of PF2 before and after addition of PA.



Fig. 52 Comparison of IR Spectra of PF1 before and after addition of PA.



Fig. 53 Comparison of IR Spectra of PF2 before and after addition of PA.