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1,2,3-Triazolyl functionalized thiophene, carbazole and fluorene based A-*alt*-B type π -conjugated copolymers for sensitive and selective detection of aqueous and vapor phase nitroaromatics (NACs)

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A series of highly emissive π -conjugated A-*alt*-B type copolymers (**P1-P3**), appended with 1,2,3-triazole moiety, have been synthesized via Suzuki polymerization. The well-defined and soluble π -conjugated copolymers have been characterized by multinuclear NMR spectra as well as tetradetector GPC studies, showing molecular weight (M_n) in the range of 16.4-20.1 kDa with polydispersity indices of 1.25-1.42. The synthesized emissive π -conjugated polymer probes have been explored as fluorescent chemosensor for nitroaromatic compounds (NACs) in solution, vapor and contact mode. The detailed photophysical and sensing studies have been studied to understand the insight of polymer-NACs interaction, inducing selective fluorescence quenching of the π -conjugated polymer probes, through photoinduced electron transfers (PET) mechanism. All the polymeric probes (**P1-P3**) are highly reversible in nature with NACs, and can be reusable for multiple times. The limit of detection of the probes towards nitroaromatics is found to be in the range of 120-200 ppb with high degree of association constant in the order of 10⁴ M⁻¹. Furthermore, test paper kits have also been fabricated demonstrating trace detection of picric acid by naked eye, making it as a practical means for a quick, easy and inexpensive way of on-site detection of NAC based explosives.

Introduction

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Detection of explosives has gained enormous interest for national security. Most of the explosive materials are also recognized as toxic contaminants for environmental pollution.1-⁵ Use of explosives in a large scale in the recent years has prompted the scientific community to develop novel sensing materials for rapid, sensitive and selective detection of explosives both in air and solution for the homeland security and environmental concern.⁶⁻⁸ Mostly used explosive materials are nitro-rich compounds such as 2,4,6-trinitrotoluene (TNT), picric acid (PA), 2,4-dinitrotoluene (DNT) and 3,5trinitroperhydro-1,3,5-triazine (commonly known as RDX).9-11 Thus the development of new materials for the easy, rapid, sensitive, selective, economic and trace detection of NACs for the purpose of preventing environmental pollution is in high demand. Nitroaromatic vapor is also hazardous and cause weakness, anaemia, respiratory headache. disorders. carcinogenicity, skin irritation and liver injury.1-5 There are numbers of commercial sophisticated instrumental methods such as gas chromatography(GC) coupled with different detectors,¹²⁻¹³ high performance liquid chromatography

(HPLC),14-15 ion mobility spectrometry (IMS),16-17 Raman or surface enhanced Raman scattering, surface Plasmon resonance,¹⁸⁻¹⁹ energy dispersive X-ray diffraction,²⁰⁻²¹ neutron activation analysis,²² electron capture detection,²³ and cyclic voltammetry²⁴⁻²⁶ are being used for the detection of trace NAC explosives for long times. However, each approach has its own drawbacks. Bulky instrumentation, operational inconvenience, analysis cost and test speed of detection restrict its broad applications. In the recent years, design and development of novel and simple fluorescent chemosensors for selective detection of NACs have been acknowledged much more attention, due to its quick response to the analytes, operational simplicity, high sensitivity and selectivity, cost-effectiveness and synthetic ease. Therefore, the interest in developing simple and highly sensitive optical fluorescent chemosensory probes for the selective and easy recognition of NACs is high in demand.

Electron-withdrawing nature of the nitro groups on the aromatic ring in NACs lower down the energy of the empty π^* orbitals, and thereby making nitroaromatic compounds as good electron acceptors. This property of the nitroaromatics has been exploited for its detection by the p-type fluorescent chemosensory probes.²⁷⁻²⁸ A number of fluorescent probes for detection of nitroaromatics have been developed by various groups. Most of the fluorescent chemosensors for detection of NACs are based on small molecule chemosensors, gels, nanoparticle, nano-fibers and MOFs.²⁹⁻⁴⁵ However, compared to the small molecular organic chemosensor, *p-type* π -conjugated polymer based probe possesses several important advantages.

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The electron rich nature of the π -conjugated polymer, makes them a potential candidate for the detection of NACs explosive with high efficiency, and has been received much attention in the recent years. The high sensitivity of the electron rich π conjugated polymers originates from the fast and facile exciton migration along the entire polymer chain as a result of *molecular wire* effect as demonstrated by Swager and coworkers.⁴⁶⁻⁴⁷ Taking the advantage of *molecular wire* effect, various conjugated polymer based detection probes have been developed by different group for NACs detection. In the recent past, significant efforts have been focused on the design and construction of electron rich p-type π -conjugated polymers to detect electron-deficient nitroaromatic compounds.⁴⁸⁻⁶¹

In a previous work, we have demonstrated the role of directly attached 1,2,3-triazole to the thiophene unit towards NACs detection.⁶² Herein, we report facile and easy synthesis of highly luminescent A-alt-B type π -conjugated copolymers with appended 1,2,3-triazole moiety through Suzuki polymerization. The 1,2,3-triazole functional moiety attached via -CH₂-O-CMe₂-to the thiophene unit plays a crucial role in enhancing the detection ability towards NACs. The detail photophysial and spectroscopic studies of the synthesized polymer robes have been carried out showing remarkable trace detection of NACs with high sensitivity and efficiency through fluorescence quenching.

Results and discussion

Synthesis and Characterization

The π -conjugated polymer having thiophene, fluorene, carbazole units are one of the most studied π -conjugated emissive polymers in the recent time as polymer based fluorescence sensing probes due to their strong and tunable emission with high quantum yield. The use of thiophene, fluorene, carbazole units itself remains very limited due to its tendency to from aggregates under high concentration or in the solid state leading to fluorescence quenching. There is always a challenge to prevent such aggregation. However, by introducing long chain alkyl groups at suitable position on the polymer backbone, one can restrict such aggregation. Electron-donating groups are always preferred because of their ability to increase the electron density on the conjugated polymer backbone and thereby enhancing the electron-transfer ability towards the electron-deficient NACs. Another way to increase the sensing behavior is by incorporating the dipolar units such as 1,2,3triazole unit (5 Debye)⁶³⁻⁶⁴ as a pendant group. The triazole unit was favored to take the advantage of facile supramolecular interaction with the nitroaromatics providing a straight forward route to enhance the sensory response of π -conjugated polymer towards NACs by tuning electronic property of the polymer backbone.65-67

The key starting precursor, 2,5-dibromo functionalized 1,2,3-triazole appended thiophene monomer (4) was synthesized from 3-methylthiophene involving stepwise bromonation, cycloaddition and hydration respectively as outlined in scheme 1 (and scheme S1 in ESI⁺). The

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characterization and purity of the monomer (4) were determined by multinuclear NMR and mass spectrometric analyses (ESI⁺). ¹H NMR of **4** in CDCl3 shows two multiplets at 7.39-7.37 and 7.30-7.28 ppm for the phenyl protons. The thienyl protons resonate at 6.88 ppm as singlet. The signal for triazolyl proton overlaps with multiplets of the aromatic protons. The (Th)CH₂-O- (Th = thienyl) and $-CH_2$ -Ph (Ph = phenyl) protons resonate at 5.53 and 4.15 ppm respectively, whereas the six methyl protons resonate as singlet at 1.46 ppm. ¹³C{¹H}NMR confirms the formation of triazole unit by showing resonance at 119.7 ppm for the "C-H" of the triazole ring. The other aromatic carbons resonate in the range of 152.7-128.1. Formation of 4 was further confirmed by HRMS study by showing the molecular ion peak (M+H)⁺ at 471.9539. Another key precursors, the diboronic ester functionalized carbazole, fluorene and thiophene monomers (M1, M2 and M3) for Suzuki polymerization were obtained by borylation of the dibromoderivatives (6, 8 and 10) on treatment with *n*-BuLi followed by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2addition of dioxaborolane (iPrO-Bpin) in dry THF at -78 °C with 68-78% yield (Scheme S2 in ESI⁺).⁶⁸⁻⁶⁹ The dibromo-derivatives (6, 8 and 10) were synthesized from the commercially available carbazole, fluorene and 3-bromothiophene respectively following the previously reported methods (ESI⁺). Characterization and purity of the monomers (M1-M3) were determined by multinuclear NMR and mass spectrometry analyses (ESI⁺).

To access the corresponding A-alt-B type copolymers (P1-P3), the poly-condensation of analytically pure monomers 4 and M1/M2/M3 was carried out in degassed THF using aqueous potassium carbonate as base and Pd(PPh₃)₄(2 mol%) as catalyst following Suzuki coupling polymerization protocol as outlined in Scheme 2. The polymerization reaction was carried out under refluxing condition with vigorous stirring for 48 h under inert atmosphere. The crude polymers were isolated by precipitation in methanol from their concentrated CHCl₃ solution. It was further purified through Soxhlet extractor using MeOH, followed by hexanes to remove the oligomers and catalyst residue. Finally, the well-defined copolymers were obtained from subsequent extraction in distilled chloroform. The synthesized π -conjugated A-*alt*-B type copolymers with long alkyl groups are readily soluble in common organic solvents such as THF, toluene and chlorinated solvents and exhibits strong blue, cyan and yellow fluorescence emission respectively in solution. Interestingly, all the synthesized A-alt-B type copolymers exhibit appreciable amount of fluorescence even in solid state (as thin film).

The synthesized π -conjugated polymers were unambiguously characterized by multinuclear NMR, FTIR and tetradetector Gel Permeation Chromatography (GPC). ¹H NMR spectrum (in CDCl₃) of the polymer **P1** exhibits multiplets in the Published on 11 September 2020. Downloaded by Cornell University Library on 9/12/2020 9:11:46 PM.

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region of 8.40-8.32 and 7.76-7.62 ppm for the carbazole protons. The triazole proton resonates as broad singlet at 7.45 ppm. The signal for phenyl and thienyl proton overlaps and resonate as multiplets in the range of 7.19-7.05 ppm. The (Th)CH₂-O- (Th = thienyl) protons resonate at 5.28 ppm as broad singlet, whereas the -N-CH₂(heptyl) protons of the heptyl groups attached to 9-position of carbazole and -CH₂Ph protons resonate at 4.40-4.25 ppm as multiplet. The remaining heptyl protons appear in the region of 1.95 to 0.86 ppm. The aromatic carbons of P1 resonate at 143.2-120.0 ppm, whereas the alkyl carbons resonate in the range of 59.3-14.1 ppm. The characteristic resonance for "C-H" in triazolyl ring is observed at 119.6 ppm in ¹³C{¹H} spectra. The FTIR spectroscopy further confirms the existence of 1,2,3-triazole unit by showing bands at 1635 and 1458 cm⁻¹, characteristic for triazole moiety. Similar characteristic observation was noted in ¹H and ¹³C {¹H} NMR spectra for the polymers P2 and P3. The formation of the polymers was further confirmed by tetradetector Gel Permeation Chromatography as shown in Fig. 1a. The numberaverage molecular weights (M_n) of the well-defined π conjugated polymers (P1-P3) are found to be in the range of 16.4-20.1 kDa with the very good polydispersity indices of 1.25-1.42 respectively (Table 1). The molecular weight of the synthesized *p*-type π -conjugated copolymers (**P1-P3**) is high enough to explore efficient sensing properties towards nitroaromatics.

Thermal properties of the polymers are essential to investigate the stability of the polymers. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed to determine the thermal properties of the polymers, **P1-P3**. TGA was carried out in nitrogen atmosphere at heating rate of 10 °C/min from RT to





| Table 1 Chara Polymer | Table 1 Characterization data for P1 - P3 Polymer Mn (kDa) Mw (kDa) ^a PDI ^a | | | | |
|---|--|------|------|-----|--|
| P1 | 16.4 | 21.9 | 1.34 | 340 | |
| P2 | 18.4 | 26.2 | 1.42 | 342 | |
| P3 | 20.1 | 25.1 | 1.25 | 360 | |
| ^a Obtained from GPC (gel permission chromatography), ^b Calculated | | | | | |
| from TGA studies. ^c Polymer decomposition temperature. | | | | | |

700 °C to find out the thermal stability of the polymers. The onset point of decomposition (T_d) was determined from the temperature at 5% weight loss. The decomposition

| Polymer _ | Absorbance (nm) | | Emission (nm) | | | Stoke's shift (cm ⁻¹) | |
|-----------|--|---------------------------|----------------|--------|----------------|-----------------------------------|-------|
| | Solution λ _{max} (ε x 10 ⁻⁴) | Solid λ _{max} | Solution | | Solid | Solution | Solid |
| | | | λ_{em} | Ф (%)ª | λ_{em} | | |
| P1 | 325 (2.11) | 333 | 458 | 18 | 467 | 8935 | 8616 |
| P2 | 391 (2.15) | 397 | 464, 489 | 20 | 488 | 5125 | 4697 |
| P3 | 406 (2.03) | 419 | 551 | 19 | 566 | 6481 | 6198 |

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temperatures of the polymers (**P1-P3**) was found to be 340 °C, 342 °C and 360 °C respectively as shown in Figure S17. All the new polymers exhibit good thermal stability, suitable for applications in explosive detections. Noticeable glass transition temperature was not observed for the polymers during DSC analysis.

Photophysical properties

Excellent solubility of the synthesized A-alt-B type copolymers allowed us to evaluate the photophysical properties of the polymers with UV-vis and fluorescence spectra. The photophysical properties of the synthesized π -conjugated copolymers were conducted in CHCl₃ in 2×10⁻⁵ M concentration as depicted in Fig. 2. In solution phase, polymer P1 exhibits a well resolved intense absorption at λ_{max} of 325 nm with ϵ values of 2.11 x 10⁴ M⁻¹cm⁻¹, which is attributed to the π - π * transition through the π -conjugated backbone. The λ_{max} for **P2** and **P3** are red shifted by 66 and 81 nm respectively compared to that of polymer **P1** suggesting higher degree of π -conjugation in fluorene-alt-thiophene and thiophene-alt-thiophene based copolymers with relatively lower optical band gap. In thin film (made by spin coating on quartz substrate), the absorption maxima of the polymers P1, P2 and P3 were observed at 333, 397 and 419 nm respectively. The π -conjugated polymers P1 and P2 exhibit strong blue to cyan emission centered at 458 nm (λ_{ex} =325 nm) and 464 nm (λ_{ex} =391 nm) for **P1** and **P2** respectively. For P2, a shoulder at 489 nm along with strong emission at 464 nm was also observed.⁷⁰⁻⁷¹ Interestingly, polymer P3 shows a strong yellow emission at λ_{em} of 551 nm. The photoluminiscent quantum yields (Φ) of the polymers are in the range of 18 - 20% in THF as measured by relative method with quinine sulphate (in 0.1M sulphuric acid) as reference.⁷² The solid state (as film) photophysical studies of the polymers were also inspected. More interestingly, all the A-alt-B type copolymers are highly emissive in blue to yellow spectral region even as thin film showing λ_{em} at 467, 488 and 566 nm respectively with Stoke's shift in the range of 4697-8935 cm⁻¹. A red shift by ca. 6-13 nm (in absorption spectra) and 9-24 nm (in PL spectra), relative to that in solution state, was observed presumably due to the enlarged π -conjugation of the polymer backbone in solid state. The relevant photophysical data of the polymers are tabulated in Table 2.

Detection of nitroaromatics

The excellent and intense emission properties and favorable HOMO-LUMO energy levels of the highly soluble copolymers **P1**, **P2** and **P3** prompted us to explore the potential applicability as a chemosensors towards the detection of nitroaromatic (NAC) compounds utilizing the fluorescence emission as a measure of polymer-nitroaromatics interaction. Nitroaromatics are electron deficient in nature and can undergo strong π - π interaction with the electron rich *p*-type aromatic rings. The high stability and the electron rich π -conjugated backbone of the synthesized A-*alt*-B type copolymers make a supreme candidate for sensing of nitroaromatic explosives through the fluorescence quenching taking the advantage of molecular wire effect of the π -conjugated polymers.



Fig. 2 (a) Solution state (solid line) and solid state (dotted line) UV-vis spectra for the polymers **P1** -**P3** in CHCl₃ with a concentration of $\sim 10^{-5}$ M. (b) Solution and solid state (spin coated on quartz plate from CHCl₃ solution of polymers) PL spectra for the polymers at 28 °C. (c) Photograph of polymer **P1**, **P2** and **P3** in chloroform under 365 nm light)

To investigate the optimum concentration in which fluorescence quenching through self-aggregation of the π conjugated polymeric probes through π - π stacking is minimal, the concentration dependent emission spectra as well as dynamic light scattering (DLS) studies have been carried out. Polymer concentrations are reported as moles of repeating unit per litre. With increasing concentration from 10⁻⁵ to 10⁻³ M in CHCl₃, the emission intensity for **P1-P3** decreased significantly (Figure S19). The emission intensity of the probes also started

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to decrease when the solution was diluted to 10^{-6} M. DLS studies of the polymer probes were inspected by varying the concentration, ranging from 10^{-3} to 10^{-5} M. The average aggregate size (D_H) of 8-15 nm for the three polymer probes confirmed the negligible self-aggregation and the presence of mainly unimers of the polymeric probes in relatively dilute solution of ca. 10^{-5} M in CHCl₃ (Figure S20). Henceforth, the sensing application was explored in the concentration of 10^{-5} M to avoid the self-aggregation behaviour of the probes.



Fig. 3 Emission quenching of polymer **P2** towards different nitroaromatics and non-nitroaromatics in CHCl₃. Toluene: TOL, 1,2-dichlorobenzene: DCB, Nitrobenzene: NB, Nitrotoluene: NT, Nitrobenzoic acid: NBA, p-Hydroxy nitrobenzene: HNB, 2,4-Dinitrophenol: DNP, 2.6-Dinitrobenzene:DNT, Picric acid: PA. Analyte concentration: ~10⁻⁵ M, polymer concentration: ~1 x 10⁻⁵ M in CHCl₃.

Polymers probes P1-P3 were treated with various nitroaromatic compounds such as nitrobenzene, nitrotoluene, nitrobenzoic acid, p-hydroxynitrobenzene, 2,4-dinitrophenol, 2,6-dinitrotoluene and picric acid. Solution state fluorescence quenching of the polymer probes were witnessed by treating of polymer probe in chloroform with known concentration of nitroaromatic compounds. However, there is no effect on change of fluorescence intensity upon addition of other aromatic compounds, such as toluene and dichlorobenzene even in excess equivalent, demonstrating selectivity of the polymer probes as chemosensing probes towards nitroaromatics. Due to the electron deficient nature of the nitroaromatics, the electron transfer process between the electron rich fluorophore and the electron deficient NAC molecule becomes facile and the fluorescence intensity is readily quenched upon gradual addition of nitroaromatics. Fig. 3 represents the fluorescence quenching profile of polymers P2, upon the addition of various analyte solution of ca. 10⁻⁵ M concentration to the solution of polymer probes ($^{1} x 10^{-5} M$). The different percentage of quenching was observed with different nitroaromatics for all the three copolymers. Interestingly, the percentage of quenching was significantly higher for picric acid, having the highest number of nitro group

than the other nitroaromatics. Hence, the polymer probecting selectively recognize the picric acid^Oarmong⁹/the^{CO}other nitroaromatics. The relative emission quenching ability of various electron deficient nitroaromatics towards **P1-P3** probes are summarized as bar diagram in Fig. 4. It is interesting to observe that the percentage of quenching for the NACs is significantly higher for the fluorene-*alt*-thiophene based copolymer (**P2**) than the carbazole-*alt*-thiophene and thiophene-*alt*-thiophene based copolymers (**P1** and **P3**). This clearly demonstrates that the π -conjugated polymer backbone of fluorene-thiophene unit and the dipolar triazole unit facilitates supramolecular interaction between the polymer probe and the nitroaromatics inducing fluorescence quenching (*vide supra*).



Fig. 4 Percentage of emission quenching for **P1–P3** towards different nitroaromatics (NACs) and non-nitroaromatic compounds in CHCl₃.



Fig. 5 Fluorescence titration upon incremental addition of PA (concentration range of ~ 1.1×10^{-5} M to ~ 1.2×10^{-4} M) to P2 polymer probe (~ 1×10^{-5} M in CHCl₃) with visual change in fluorescence.

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To investigate the insight of quenching phenomenon and to analyze the mechanistic interaction between the chemosensory probes and nitroaromatics analyte, the fluorescence titration has been carried out towards various nitroaromatics in ca. 10⁻⁵ M concentration in CHCl₃. The intensity of the fluorescence band centred at 458, 464 and 551 nm were dramatically decreased for the polymers P1, P2 and P3 respectively, upon the incremental addition of picric acid (Fig. 5 for P2). The fluorescence quenching was clearly visible with naked eye under the illumination of 365 nm light The fluorescence lifetime studies have also been investigated for both the probes at different concentrations of picric acid to study the mode of the interaction. The fluorescence lifetime values of P2 (Table S1, Fig. 6) was found to be invariant at different concentration of picric acid, suggesting static mechanism of fluorescence quenching. Similar observation was also witnessed for P1 and P3 probes.

The quenching behaviour due to the polymernitroaromatics supramolecular interaction was also analyzed in detail by the Stern-Volmer (SV) equation $I_0/I = 1 + K_{SV}[Q]$,⁷³ where I and I_0 are the fluorescence intensities in the presence and absence of the quencher [Q] respectively and K_{SV} is the Stern-Volmer rate constant. Upon treatment with different concentration of picric acid, a linear SV plot was obtained for the polymer probe (P2) having fluorene-alt-thiophene unit as shown in Fig. 7a. The decrease in the fluorescence intensity with the linear SV-plot suggests for static fluorescence quenching of the conjugated polymer probes in the presence of NACs. The K_{SV} value was found to be in the order of nitrobenzene (NB) < nitrotoluene (NT) < nitrobenzoic acid (NBA) < p-hydroxy nitrobenzene (HNB) < 2,4-dinitrophenol (DNP) < 2,6dinitrotoluene (DNT) <picric acid (PA). The higher K_{SV} value for PA $(6.40 \times 10^4 \text{ M}^{-1})$ and thus the higher percentage of quenching compared to other NACs could be attributed to the higher sensitivity of the fluorophore towards PA (Fig. 7b). It is noteworthy to mention that the quenching rate constant towards the picric acid is higher for P2 than that for the other polymer probes P1 and P3 (Figure S27 and S28). As expected, this result also indicates that the sensory responses towards the



Fig. 7 a) The Stern-Volmer plot for **P2**. b) Comparison of association constants of **P1-P3** for different nitroaromatics (1: NB, 2: NT, 3: NBA, 4: HNB, 5: DNP, 6: DNT, 7: PA).



emission at λ_{em} of 464 nm against the concentration of PA) for evaluation of LOD for sensing PA by **P2**.

different nitroaromatics by the polymer **P2** is highly sensitive than the probes **P1** and **P3**, as also observed from the relative

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percentage of quenching described in Fig. 4 (vide infra). Moreover, the limit of detection $(LOD)^{74}$ of polymer **P2** for nitroaromatics is found to be in the range of 900 to 525 nM (206-120 ppb) with the lowest value for picric acid (Fig. 8). While under the similar set of experimental condition, the polymer **P1** and **P3** shows *ca*.10-100 times less sensory responses towards the different nitroaromatic compounds.

| Table 3 Electrochemical data and HOMO and LUMO energy levels of | | | | | | |
|---|--------|--------|--------------------------|-------------------------------------|--|--|
| P1, P2 and P3. | | | | | | |
| Polymer | Eox. V | Еномо. | ELUMO. (eV) ^b | Eg ^{opt} (eV) ^c | | |

| Folymer | Lox, V | (eV) ^a | | Lg · (EV) | |
|---------|--------|-------------------|-------|-----------|---|
| P1 | 0.67 | -4.96 | -2.15 | 2.81 | |
| P2 | 0.90 | -5.19 | -2.61 | 2.58 | |
| P3 | 0.74 | -5.03 | -2.77 | 2.26 | _ |
| | | | | | |

^aFrom the onset of the oxidation potential, and using the equation, E_{HOMO} (eV) = [$E^{cx}_{onset} - E_{ox(ferrocene)}$] - 4.80. ^b($E_{LUMO} = E_{HOMO} + E_g^{opt}$). ^c E_g^{opt} from solid state absorption spectra.



PL quenching of fluorophore (**P2**) in the presence of PA. (ext. = excitation, r = radiative, nr = non-radiative).

It is assumed that the favorable HOMO-LUMO energy levels of the polymer probes, facile dipole-dipole and π - π interactions with the electro deficient nitroaromatic analytes play a synergistic effect inducing fluorescence quenching. The cyclic voltammetric experiments of these π -conjugated copolymers were conducted to investigate the electrochemical properties of the polymers and to evaluate the HOMO and LUMO energy levels. The cyclic voltammograms of thin film, drop-casted onto glassy carbon disc electrode from the DCM solutions of the polymers were shown in Figure S44. The cyclic voltammetric measurement was carried out in dry CH₃CN using nBu₄NPF₆ (0.1 M) as supporting electrolytes, glassy carbon disc working electrode, Pt wire counter electrode and Ag/AgCl reference electrode under argon atmosphere. The onset oxidation potentials of P1-P3 were located at 0.67, 0.90 and 0.74 V respectively. HOMO energy levels of P1-P3 were calculated as -4.96, -5.19 and -5.03 eV respectively from the onset oxidation potentials considering the known reference level for ferrocene (4.80 eV below the vacuum level) according to the equation; E_{HOMO} (eV) = [E^{ox}_{onset} - E^{ox}_(ferrocene)] - 4.80.⁷⁵⁻⁷⁸ Whereas, the E_{LUMO} energy levels of P1-P3 were evaluated as -2.15, -2.61 and -2.77 eV respectively using the relation, $E_{LUMO} = E_{HOMO} + E_g^{opt}$.⁷⁹⁻⁸¹ The optical band gaps (Egopt were estimated by considering the equation, $E_g{}^{opt}$ =1240/ $\lambda_{cut\text{-off}}$ ($\lambda_{cut\text{-off}}$ is the edge of the solid state

absorption spectra), and were found to be -2.81, -2,58 and -2,26 for P1, P2, and P3 respectively. The electrochemical data are summarized in Table 3. The LUMO of the analyte (PA) lies at -3.89 eV. The higher energy levels of LUMO of the polymer probes than that of NACs facilitates electron transfer from the polymer probes (P1-P3) to the electron deficient NACs and induces photo-induced electron transfer (PET) followed by reverse electron transfer to the HOMO of the probe in a nonradiative process, resulting in fluorescence quenching as depicted in Fig. 9.7-8 To understand further, the HOMO-LUMO energy levels were also calculated by Density Functional Theory (DFT) using B3LYP functional and polarized 6-31 G/ basis set for the model monomer systems (Figure S48-50).82-86 The extent of fluorescence quenching is relatively less for the other nitroaromatics (such as NT, DNP, and DNT) having the LUMO energy levels relatively higher in the range of -3.48 to -2.91 eV.³¹ Thus, the probes show higher sensitivity in recognizing picric acid over other nitroromatics.



Fig. 10 Change in chemical shift of the protons in P2 in ^{1}H NMR titration in CDCl₃ on incremental addition of PA (* = residual CHCl₃).

The static fluorescence quenching, as confirmed by fluorescence life time measurements and Stern-Volmer plot (vide infra), allowed us to examine the supramolecular interaction between the π -conjugated polymeric probe and the electron deficient NACs by ¹H NMR spectroscopic titration studies. The ¹H NMR titration for the polymer probe P2 has been investigated with incremental addition of picric acid (PA) (Fig. 10). The thienyl, fluorenyl and triazolyl protons experienced a gradual shift upon incremental addition of picric acid due to supramolecular complexation. Most interestingly, the triazolyl proton (H_e) experienced down field shift by 0.02 ppm presumably due to hydrogen bonding with nitro groups of NAC molecules, whereas the thienyl (H_d) and fluorenyl aromatic protons (H_a, H_{a'}, H_b, H_{b'}, Hc, Hc') were slightly up fielded suggesting π - π intermolecular interactions between the fluorene-thiophene unit of P2 probe and the aromatic ring of PA.^{31,34,39} Similar results were obtained for other polymer

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probes (P1 and P3) during the NMR titration with PA as

Fig. 11 a) Quenching of fluorescence intensity of thin film samples of **P2** upon exposure to PA vapor by varying exposure time. b) Superiority of **P2** over **P1** and **P3** as indicated by relative quenching efficiency (in %) as a function of the exposure time to picric acid vapor.

The excellent 'turn-off' sensing behaviour of the probes (P1-P3) towards NACs motivated us to explore their practical application of the polymer probes for on-site detection of picric acid. The potential utility of the sensing probes toward PA was investigated in solid state by making a thin film of all the synthesized A-alt-B type copolymers. Thin films of the probes were casted from chlorobenzene solution (5 mg in 1 ml chlorobenzene) onto quartz plates through spin coating at a rate of 1200 rpm. The sensory response of polymer thin films towards nitroaromatics was carried out by the decrease in fluorescence intensity of polymer thin films upon increasing of the exposure time with the vapor of picric acid in atmospheric pressure (Fig. 11a). It was observed that after exposing the polymer film for about 200 s, the fluorescent intensity was diminished by 91% for P2, while for P1 and P3 the quenching was relatively lower to 53% and 48% respectively (Fig. 11b), demonstrating superiority of P2 probe over the others. To

demonstrate the reusability of the probe, the film was exposed to vapor of picric acid for 200 s followed by repeated washing with ethanol:water mixture and drying under hot air. The emission spectra were recorded for the polymer film before and after washing out the picric acid analyte. The whole process was repeated for multiple times. The initial fluorescence intensity was significantly regained and the quenching efficiency of 85% was observed even after multiple cycles of exposure to the picric acid, indicating its reusability and stability of the polymer film (Fig. 12, Figure S35-S36).

The successful repeatability studies of the polymer film towards picric acid vapor, encouraged us to explore the ability of the sensing probes for detecting trace picric acid present as contamination in water. Nitroaromatics are well known as toxic and hazardous contaminants to environment results polluting soil and drinking water.¹⁻⁵ The percentage of fluorescence quenching was determined after dipping the polymer (P2) film into the aqueous samples of picric acid varying concentration (Figure S34). The study reveals that the fluorescence emission intensity is significantly quenched by ca. 64% when the concentration of the picric acid is reached to 100 µM. Moreover, similar results were observed for the other polymer films as depicted in Figure S32-S33, with slightly less detection efficiency. The scanning electron microscopic (SEM) image analyses of the polymer probe samples (prepared by drop casting of 5 x 10⁻⁴ M chloroform solution on aluminum substrate) were conducted in presence and absence of picric acid and its derivative to understand the change in surface morphology. The sensing probes (free P1, P2 and P3) showed porous film like surface morphology which is essential to be a good nitroaromatic sensor (ESI⁺). The porous morphology of the probes changed to irregular shape morphology upon treatment with picric acid in FESEM analysis as shown in Figure S45-S47. The Energy Dispersive X-ray (EDX) line analysis showed the presence of bromine while treating with the derivative of



Fig. 12 Cycles of emission quenching and recovery by exposing the probe film to PA vapor for 200 s demonstrating reusability.

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PA (2,4,6-trinitrophenyl 3-bromobenzoate), further confirming

the formation of polymer:NAC adduct.

In recent days, contact mode approach has received great attention for real time application in practical field to find the trace amount of nitroaromatics explosive residue. Therefore, to demonstrate its practical applicability, the filter paper (Whatman 42) test strips were dipped into a concentrated chloroform solution of the polymer probes and dried under reduced pressure. Picric acid crystals were placed on the polymer coated test strips for 10-15 s. To visualize the contact mode responses of nitroaromatics, the polymer coated strips were illuminated under 365 nm light with the appearance of black spots on the contact area with picric acid. The visual change in the fluorescence intensity of the polymer coated film strip provides an easy way to detect nitroaromatics. To demonstrate the trace detection of NAC analytes in solution state, different concentrations (10⁻³–10⁻⁹ M) of picric acid in chloroform were prepared and 2 μL of each solution was spotted on each freshly prepared test paper strip (Fig. 13). The visual colour change in fluorescence responses with different concentration of PA were recorded upon exposure to 365 nm light exhibiting dark black spot of PA. The black spots were found to be prominent for the concentrated analyte solution and faded upon dilution. Remarkably the minimum detection limit of the picric acid by the naked eyes is even up to 10⁻⁹ M level for polymer P2, showing an excellent chemosensor for the instant visual detection for practical application in detecting trace amount of picric acid in solution as well as in vapor phase. Similar experiment was also carried out for the polymer P1 and P3 (Figure S37-S38).



Fig. 13 Visual appearance of **P2** coated filter paper before and after the drop casting of different concentrations of PA by contact mode method under illumination at 365 nm.

Conclusions

In conclusion, we have synthesized a series of highly emissive carbazole, fluorene and thiophene containing A-*alt*-B type π -conjugated copolymers appended with 1,2,3-triazolyl moiety *via* Suzuki polymerization. The synthesized polymers have been unambiguously characterized by various spectroscopic tools and their detail photophysical properties have been investigated. The triazolyl functionalized π -

conjugated polymers efficiently recognize electron Adeficient nitroaromatics both in solution and as Gold Gibble Through fluorescence quenching with high sensitivity and efficiency. The facile HOMO/LUMO energy levels and photophysical studies suggest static fluorescence quenching through PET mechanism by supramolecular complex formation between the polymer probe and NAC molecules, as manifested by ¹H NMR titration. All the polymers show high sensitivity towards picric acid exhibiting ppb level detection with binding constant in the order of 10⁴ M⁻¹. The sensing ability of the polymer probes towards trace NACs as filter paper strips has also been demonstrated for its practical utility as on-site detection kit by naked eye. Further development of the π -conjugated polymeric probes for detection of NAC explosives with enhanced sensitivity is underway.

Conflicts of interest

There are no conflicts to declare.

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Experimental Section

Syntheses

Pd(PPh₃)₄ was synthesized following the procedure described in the literature.⁸⁷ Details syntheses and characterization of Copper(II)-hydroxyapatite(Cu-HAP),⁸⁸ compounds **1**, **2**,⁸⁹ and the monomers **M1–M3** have been described in ESI⁺. Compounds **5**, **6**,⁹⁰ **7**, **8**,⁹¹ **9** and **10**⁹² were synthesized from the commercially available carbazole, fluorene and 3-bromo thiophene respectively following the previously reported methods.

Compound 3: Cu-HAP (1.2 g, 25 wt%) was added to a stirring mixture of 2-Methyl-4-(trimethylsilyl)-3-butyn-2-ol (4.5 g, 29.2 mmol), benzyl bromide (5.0 g, 29.2 mmol), TBAF (catalytic amount) and sodium azide (2.5 g, 37.9 mmol) in THF/H₂O (1:1) mixture at room temperature. The reaction mixture was stirred for 14 h and after that the progress of the reaction was monitored by TLC (hexane/ethylacetate eluent 4:1). After completion of the reaction, the desired product was separated by extraction with DCM from the reaction mixture. The product was obtained after concentration of the DCM solution as highly pure crystalline compounds with 76% yield (4.5 g). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.40-7.37 (m, 3H, phenyl), 7.34 (s, 1H, triazolyl), 7.29-7.27 (m, 2H, phenyl), 5.50 (s, 2H, -CH₂-Ph), 1.61 (s, 6H, -CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 134.1, 131.4, 129.1, 128.8, 128.1 (aromatic carbons), 120.7 (triazol –

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CH-), 73.4(-C(CH₃)₂), 54.2 (-CH₂-Ph), 27.1 (-CH₃). MALDI-TOF (m/z): C₁₂H₁₅N₃O, calculated value 218.539 (M+H)⁺, found 218.534 (M+H)⁺. Compound 4: То solution of 2,5-Dibromo-3а (bromomethyl)thiophene (2) (500 mg, 1.3 mmol), in anhydrous DMF (10 ml), tBuOK (240 mg, 2.0 mmol) and 2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol (357 mg, 1.6 mmol) were added at 0 °C. The reaction mixture was stirred at 90 °C for 12 h. After consumption of thiophene reaction was monitored by TLC, substrate (the nhexane:ethylacetate was used as the eluent) the reaction mixture was poured into cold water (200 ml), extracted with ethyl acetate (3 × 50 ml) and dried over anhydrous MgSO₄. The solvent was removed under diminished pressure and the residue was purified by column chromatography eluting with hexanes to afford a white solid with 78 % yield (470 mg). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.39-7.37 (m, 4H, phenyl, triazolyl), 7.30-7.28 (m, 2H, phenyl), 6.88 (s, 1H, thienyl), 5.53 (s, 2H, -CH₂-O-), 4.15 (s, 2H, -CH₂-), 1.46 (s, 6H, methyl protons). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 152.7, 139.7, 134.6, 131.0, 129.1, 128.8, 128.1,111.0, 109.2 (aromatic carbons), 120.7 (triazolyl -CH), 73.4, 59.6 (-CH2-O-), 54.2(-CH2-Ph), 27.1(-CH3). HRMS (m/z): $C_{17}H_{17}Br_2N_3OS,$ calculated value 471.9537 (M+H)+, found 471.9539 (M+H)+.

General synthesis of polymers: Compound 4 (0.18 mmol) and M1/M2/M3 (0.18 mmol) were dissolved in 10 mL of distilled THF in a 100 mL Schlenk flask under argon atmosphere. The reaction flask was degassed three times via freeze-pump-thaw technique. In an another 100 mL Schlenk flask, K_2CO_3 (0.74 g, 5.35 mmol) was dissolved in 4 mL of mili-Q water and degassed by purging Ar through a needle for about 30 min. After that, the K₂CO₃ solution was transferred to the reaction mixture through a cannula. Next, Pd(PPh₃)₄ (4 mg, 0.0036 mmol, 2 mol%) was added to it and the reaction mixture was warmed to 65 °C for 72h while stirring. The colour of the reaction mixture turned to dark green during the course of the reaction. After cooling to room temperature, the solvent was concentrated to minimum volume of ca. 2 mL, and polymer was precipitated to a stirring methanol solution. After complete precipitation the methanol was removed and the brown colour polymer was washed another two times with methanol, followed by drying under vacuum. Next, the polymer was purified through Soxhlet extraction using distilled hexanes, methanol and at last collected in dry and distilled chloroform. The chloroform part was evaporated to get the dark greenish brown colored polymer. The polymers were finally purified by fractional precipitation in cold distilled hexanes from a concentrated dichloromethane solution to achieve well-defined and pure P1, P2 and P3 with yield of 58%, 62% and 55% respectively.

Polymer P1: ¹H NMR (600 MHz, CDCl₃): δ 8.40-8.32 (m, 2H, carbazole), 7.76-7.62 (m, 2H, carbazole), 7.45 (bs, 1H, triazolyl), 7.42-7.37 (m, 2H, carbazole), 7.19-7.05 (m, 6H, phenyl, thienyl), 5.28 (bs, 2H, -CH₂-O-), 4.40-4.25 (m, 4H, -N-CH₂-, -CH₂Ph), 1.95-1.88 (m, 2H, heptyl), 1.76-1.69 (m, 6H, heptyl), 1.28-1.25 (m, 10H, heptyl), 0.89-0.86 (heptyl). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 143.2, 141.4, 140.3, 139.8, 135.6, 134.7, 133.1, 131.9, 128.8, 128.1, 127.6, 125.6, 124.7, 123.5, 120.1, 120.0 (aromatic rings), 119.6 (-CH, triazole), 73.3 (-NCH₂, heptyl), 59.3 (-CH₂-O), 55.4(-CH₃), 54.1(-CH₃), 53.4, 40.6, 31.8,

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30.0, 29.2, 27.3, 23.9, 22.6(-CH2, heptyl), 14.1(-CH3, heptyl), UV-ivis (THF): λ_{max} (ϵ , M₋₁cm₋₁): 325 nm (2.11 × 10⁴) PU(dAdb39) λ_{eff} (λ_{eff}) 3498 (350). GPC: M_w = 21.9 kDa, M_n = 16.4 kDa, PDI = 1.34, T_d = 340 °C. **Polymer P2:** ¹H NMR (600 MHz, CDCl₃): δ 7.82-7.73 (m, 2H, fluorene), 7.59-7.53 (m, 4H, fluorene), 7.42 (bs, 1H, triazolyl), 7.35-7.27 (m, 6H, phenyl + thienyl), 5.52-5.51 (bs, 2H, -CH₂-O-), 4.44-4.42 (bs, 2H, -CH₂Ph), 2.08-2.03 (m, 4H, octyl), 1.76-1.74 (m, 6H, octyl), 1.12-1.10 (m, 25H, octyl), 0.82-0.79 (m, 6H, octyl). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 153.3, 151.8, 151.4, 143.2, 141.4, 140.3, 139.8, 135.6, 134.7, 133.1, 131.9, 128.7, 128.6, 127.9, 127.2, 126.0, 125.6, 124.7, 123.5, 120.1, 120.0 (aromatic rings), 119.6 (-CH, triazole), 59.3(-CH₂-O), 55.4, 54.1, 53.4, 40.6, 31.8, 30.0, 29.2, 27.3, 23.6, 22.6(-CH₂, octyl), 14.1(-CH₃, octyl). UV-vis (THF): λ_{max} (ϵ , M⁻¹cm⁻¹): 391 nm (2.15 × 10⁴), PL(CHCl₃): λ_{em} (λ_{ex}): 464, 489 (400). GPC: M_w = 26.2 kDa, M_n = 18.4 kDa, PDI = 1.42, T_d = 342 °C.

Polymer P3: ¹H NMR (600 MHz, CDCl₃): δ 7.37-7.29 (m, 5H, phenyl), 7.21 (bs, 1H, triazolyl), 7.04-6.98 (m, 2H, thienyl), 5.53-5.47 (m, 2H, -CH₂-O-), 4.24-4.19 (m, 2H, -CH₂-Ph), 2.60-2.46 (m, 2H, hexyl), 1.73-1.61 (m, 4H, hexyl), 1.31-1.25 (m, 12H, hexyl), 0.89-0.84 (m, 3H, hexyl). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 153.0, 143.4, 139.6, 134.8, 129.1, 127.8, 126.8, 125.4, 123.6 (aromatic rings), 119.8 (-CH, triazole), 61.0(-CH₂-O), 59.1, 54.1, 31.6, 30.7, 29.7, 29.0, 27.1, 23.4, 22.4(-CH₂, hexyl), 14.1(-CH₃, hexyl). UV-vis (THF): λ_{max} (ε, M⁻¹cm⁻¹): 406 nm (2.03 × 10⁴), PL(CHCl₃): λ_{em}(λ_{ex}): 551 (400). GPC: M_w = 25.1 kDa, M_n = 20.1 kDa, PDI = 1.25, T_d = 360 °C.

Caution: The permissible exposure limit of picric acid was strictly followed for sensing studies.

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