



Highly bluish-white light emissive and redox active conjugated poly-N-phenyl anthranilic acid polymer fluoroprobe for analytical sensing



K. Rohini Das^a, M. Jinish Antony^{a,*}, Shinto Varghese^b

^a Research and PG Department of Chemistry, Centre for Sustainable Chemistry, St. Thomas College (Autonomous), Affiliated to University of Calicut, Thrissur, 680 001, Kerala, India

^b Technical Research Centre, Indian Association for the Cultivation of Science (IACS), Kolkata, 700 032, India

HIGHLIGHTS

- An efficient redox type fluorescent and conjugated poly-N-phenyl anthranilic acid (PNPA) was synthesised via chemical oxidative polymerisation of N-phenyl anthranilic acid (NPA) using FeCl₃ as oxidising agent in ethanol medium.
- The intense bluish-white light emission of polymer PNPA-H in sulphuric acid was quenched upon the addition of oxidising analytes like Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ ions.
- The fluorescence quenching concentration has been determined from three independent methods like naked eye fluorescence detection, UV-visible spectroscopy and spectrofluorometry.
- The limit of detection (LOD) for naked eye fluorescence quenching was found to be 0.75 μM, 0.5 μM, and 25 μM for MnO₄⁻, Ce⁴⁺ and Cr₂O₇²⁻ respectively.
- The sensitivity of the fluorescence was highest for MnO₄⁻ ions and least for Cr₂O₇²⁻ ions from stern-volmer plots.

ARTICLE INFO

Keywords:

Fluorescence quenching
Naked eye detection
Conjugated polymer
Poly-N-Phenyl anthranilic acid
Colorimetric sensors

ABSTRACT

An efficient fluorescent and redox type conjugated poly-N-phenyl anthranilic acid (PNPA) was synthesised via chemical oxidative polymerisation of N-phenyl anthranilic acid (NPA) using FeCl₃ as oxidising agent in ethanol medium. The polymer in sulphuric acid solution denoted as PNPA-H have highly intense bluish-white fluorescence. The intense bluish-white light emission of polymer was quenched upon the addition of oxidising analytes like Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ ions. The fluorescence quenching concentration at which the above three analytes oxidises the polymer were determined from three independent methods like naked eye fluorescence detection, UV-visible spectroscopy and spectrofluorometry. The mechanism of fluorescence quenching has been explained on the basis of the oxidation of diphenyl benzidine dicarboxylic acid repeating units of PNPA-H (in reduced form) into non-fluorescent diphenyl diquinoid dicarboxylic acid units (in oxidised form) by the oxidising analytes. The mole ratio plot of [analyte]/[polymer] against fluorescence intensity have revealed different stoichiometry for a particular analyte leading to quenching of fluorescence of polymer, which have striking influence on the redox potential of the analytes. The limit of detection (LOD) for naked eye fluorescence quenching was found to be 0.5 μM, 0.75 μM, and 25 μM for Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ respectively and sensitivity of quenching action was obtained highest for MnO₄⁻ ions and least for Cr₂O₇²⁻ ions from stern-volmer plots. The oxidised and non-fluorescent diphenyl diquinoid dicarboxylic acid units of PNPA-H have been reduced back to fluorescent diphenyl benzidine dicarboxylic units with reducing biomolecules like ascorbic acid, which indicate the redox reversibility of the system.

1. Introduction

Conjugated polymers have been extensively studied mainly due to its wide range of applications in sensors, optoelectronics, energy storage devices and display devices along with its ability to counterpart

conducting or semiconducting inorganic devices [1]. Applicative functions of conjugated polymers were mainly derived from chemical and physical properties such as chemically controllable electronic structure, electrical conductivity, optical properties, thermal properties and mechanical properties [2]. Conjugated polymers generally possess

* Corresponding author.

E-mail address: jinish06@yahoo.co.in (M.J. Antony).

<https://doi.org/10.1016/j.polymer.2019.121747>

Received 13 March 2019; Received in revised form 20 August 2019; Accepted 24 August 2019

Available online 27 August 2019

0032-3861/ © 2019 Elsevier Ltd. All rights reserved.

high light absorption and emission properties which mainly depend upon the polarization of their electronic structures [3]. The electrically or electrochemically switchable electrical conductivity (from insulating to semiconducting or conducting) and intrinsic redox states present in conjugated polymers were attractive and well-studied by many researchers [4–6]. Different type of sensors such as chemical sensor, electrode sensors and biosensor have been developed based on optical and electrical properties of conjugated polymers [7–12]. Signal amplification and trace level detection would be the most interesting features of conjugated polymer based sensors [13–15].

Fluorescent conjugated polymers have gathered very much attention because of their applications in the fields of fluorescent probes, smart polymer machines, fluorescent chemo sensor, fluorescent imaging, drug delivery carriers and so on [16–22]. Fluorescent polymers can be synthesised using fluorescent monomers or non-fluorescent monomers or fluorescent compounds as initiator or fluorescent compounds as chain transfer agents [23–26]. The responses for the fluorescent sensing action of conjugated polymers could be either turn off or turn on based upon quenching or Förster energy transfer or electron transfer or doping mechanisms [27,28]. Maiti, J. et al. developed polythiophene based fluorescent sensors for the detection of acids like HCl and metal ions like copper, cadmium and mercury based on the fluorescent quenching effect [29]. Kim et al. adopted Heck-Sonogashira protocol for the synthesis of sugar substituted poly (para-phenylene ethylene). These polymers were highly fluorescent and its light emission was quenched by mercury and lead ions by spin-orbit coupling [30]. The fluorescence sensing applications of intrinsically conducting polyaniline have not studied extensively mainly due to poor solubility. Therefore, development of fluorescent poly-aromatic amine systems with good solubility and different structural aspects would be challenging area to be addressed. Fang Liao et al. synthesised poly-ortho-phenylenediamines nanospheres via chemical oxidative polymerisation. Doping effect of these nano materials with hetero atoms was used as ultra-sensitive fluorescent detection system for Cu^{2+} , Ca^{2+} , Hg^{2+} and H_2O_2 [31]. Z. Wang et al. developed novel fluorescent probe for Pd^{2+} detection with the use of poly ortho-phenylenediamine nanospheres [32]. However, the naked eye fluorescence detection of analytes in solution by utilising the fluorescence quenching and redox properties of poly-diphenylamine derivatives have not explored exclusively.

In the present work, we have developed fluorescent poly-N-phenyl anthranilic acid (PNPA) polymer which has redox property to sense various oxidising agents in aqueous acidic medium. Chemical or biochemical colorimetric sensors working in aqueous media have an added advantage of non-toxic and universal solvent system for analytical applications. We have synthesised homopolymer of poly-N-phenyl anthranilic acid (PNPA) via chemical oxidative polymerisation using ferric chloride as oxidising agent in ethanol solvent. The structural characterisation of monomer and polymer have been carried out by nuclear magnetic resonance spectroscopy (^1H NMR) and fourier transform infrared spectroscopy (FT-IR). The powder X-ray diffraction studies have revealed intense crystalline peaks corresponding to monomer (NPA) and broad low intensity peaks corresponding to amorphous domain of polymer (PNPA). Thermogravimetric analysis revealed that polymer (PNPA) have more thermal stability than monomer (NPA) especially for higher temperatures. The good solubility of monomer and polymer in sulphuric acid and sodium hydroxide solutions enabled us to study absorption and emission properties in aqueous solutions. Fluorescence quenching of PNPA with analytes like Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions were studied by naked eye fluorescence detection, UV-visible absorption spectra and spectrofluorimetry. The redox reaction between reduced form of poly-N-phenyl of anthranilic acid (PNPA-H) and oxidising analytes have been contributed for the fluorescence quenching action. In short, we have developed an efficient redox active and fluorescent conjugated polymer based on poly-N-phenyl anthranilic acid and successfully demonstrated its use in quantitative sensing of analytes via fluorescent quenching.

2. Experimental

2.1. Materials and reagents

N-Phenyl anthranilic acid (97%) was purchased from LOBA chemicals and further purified by double recrystallization using acetone as solvent. Anhydrous FeCl_3 was purchased from Sigma Aldrich. Ammonium cerium (IV) sulphate dihydrate GR, potassium permanganate, potassium dichromate GR, acetone and concentrated H_2SO_4 (98%) were purchased from Merck chemicals, India. Double distilled ethanol and deionised water were used for synthesis and purification of polymer.

2.2. Measurements and instruments

NMR spectra of the samples were recorded using 400 MHz Bruker Avance III NMR Spectrophotometer in CDCl_3 solvent using TMS as internal standard. The FT-IR spectra of the samples were recorded by Shimadzu FT-IR spectrometer using KBr pellet method. The elemental analysis (CHN) of the samples were recorded by elemental vario EL III. Thermogravimetric analysis (TGA) of the samples were measured by PerkinElmer, Diamond TG/DTA in an inert atmosphere of nitrogen gas. Powder wide angle X-ray diffraction of the samples were measured using Anton Paar, TTK 450 diffractometer in the range of 2θ values between 3 and 80° . UV-Visible spectra of the samples were recorded by Shimadzu UV-Visible spectrometer in the range 200–800 nm with deionised water. Visible fluorescence emission of the polymer samples were checked using long UV light ($\lambda = 365$ nm) in Rotek UV inspection cabinet of 230 V. Specific viscosity (η_{sp}) of polymer was measured using Ostwald's U-tube viscometer by taking 0.25 % w/w of samples in ethanol. Fluorescence emission spectra of the samples were recorded in FluoroMax-4. Potentiometric titrations were performed using digital potentiometer of model ST. DPM 2V with input of $230 \text{ V} \pm 10\%$. Polymer molecular weight determination of the PNPA samples have been carried out using Ultraflex extreme MALDI-TOF/TOF from Bruker Daltonics using 2, 5-dihydroxy benzoic acid (DHB) matrix. The fluorescence quantum yield (Φ_f) was determined by a relative method by using quinine sulphate ($\Phi_f = 0.53$) in 0.1 M H_2SO_4 as reference. The optical density of the solutions kept have below 0.1 absorbance and excited at 366 nm. The quantum yield was calculated by using following equation.

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{\eta}{\eta_R^2}$$

Where Q, I, η and O.D represents fluorescence quantum yield, integrated intensity, refractive index of the solvent and absorbance of the solution and subscript 'R' denotes to the reference fluorophore.

3. General procedure

3.1. Synthesis of poly-N-phenyl anthranilic acid (PNPA)

The recrystallized monomer N-phenyl anthranilic acid (0.5 g, 2.34 mmol) was dissolved in 15 ml double distilled ethanol. Anhydrous FeCl_3 (0.57 g, 3.52 mmol) dissolved in 5 ml ethanol was added to monomer solution at 30°C , and the polymerisation was allowed to proceed for 2 h without any disturbance. The blue polymer solution was precipitated into deionised water, filtered, and washed first with water and then many times with water-acetone mixture until the filtrate become colourless. The dark blue powder was dried in a vacuum oven at 60°C for 3 h. Yield = 0.382 g (76.4%). ^1H NMR (400 MHz, CDCl_3) δ : 7.471 (m, 6H, Ar-H), 6.323 (m, 8H, Ar-H. FT-IR (KBr, cm^{-1}): 3335, 3030, 1654, 1578, 1504, 1453, 1395, 1278, 1156, 745 and 694. Element analysis (anal., wt %): C, 63.42; H, 4.27; N, 5.79.

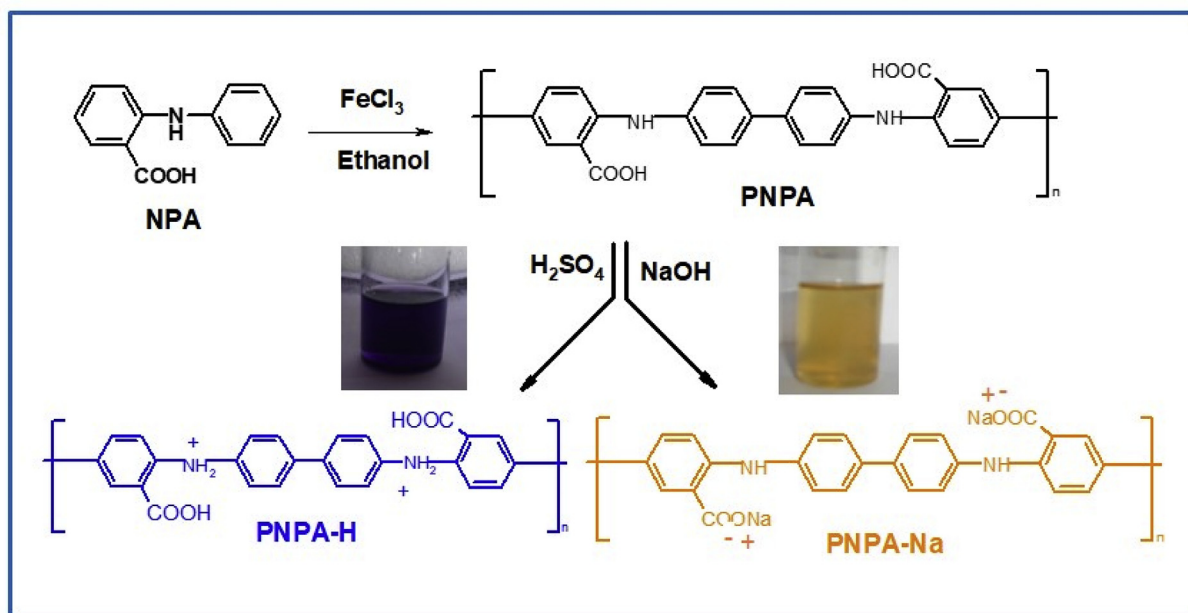


Fig. 1. Schematic representation of synthesis of PNPA using chemical oxidative polymerisation using FeCl₃. Photographs of PNPA in acid and basic media.

3.2. Preparation of PNPA-H (1×10^{-5} M) solution

Poly N-phenyl anthranilic acid (9.70 mg, 0.046 mmol) was dissolved in 10 ml of conc. H₂SO₄ (18 M) using sonicator. A light blue coloured solution of PNPA-H was obtained. PNPA-H solution (0.3 ml) was added to 100 ml standard flask and then made up to 100 ml using deionised water.

4. Results and discussion

Poly-N-phenyl anthranilic acid have been synthesised via chemical oxidative polymerisation of N-phenyl anthranilic acid using anhydrous ferric chloride as oxidising agent in ethanol solvent (see Fig. 1). The dark blue polymer powder obtained was soluble in organic solvents like acetone, ether, chloroform and ethanol. Although monomer and polymer were insoluble in water because of its nonpolar nature, however they are soluble in basic sodium hydroxide (~1–5 M) and also in sulphuric acid medium at moderate concentrations (~1–9 M) by dilution method. Poly N-phenyl anthranilic acid contain ionisable carboxylic acid group which loses its protons at basic pH to become carboxylate anionic side groups. On the other hand, polymer become protonated in acidic pH on the secondary amine group contained in the polymer backbone. Good solubility of the polymer in basic and acidic solution is due to the electrostatic attractive forces between polymer and solvent, which overcome the repulsive forces of the similar charged parts of polymer chains [33]. Poor solubility of unsubstituted polyaniline usually hampers the structural characterisation of polymer particularly in solution state. In the present case, the good solubility of monomer (NPA) and polymer (PNPA) in chloroform enabled us to do their structural characterisation by ¹H NMR spectra. The proton NMR spectra of NPA and PNPA recorded in CDCl₃ have shown in Fig. 2. The peak at 9.29 ppm of the monomer was assigned to the N-H proton [34]. The doublet present at 8.03–8.06 ppm was assigned to aromatic proton H_a. The downfield shift of this aromatic proton may be due to the presence of electron withdrawing group at its ortho position. The H_c proton and two H_f protons are overlapped and formed as a multiplet with chemical shift in the range 7.28–7.33 ppm. The multiplet in the range 7.20–7.25 ppm was assigned due to two H_e protons. The H_d proton show doublet in the range 7.21–7.23 ppm. Both H_b and H_g protons form a triplet due to the coupling of two neighbouring protons

in the region 7.11–7.15 ppm and 6.74–6.77 ppm respectively [35]. In the case of polymer, H₁, H₂ and H₃ protons present in substituted benzene have showed multiplet in the region 7.47–8.01 ppm in addition to solvent peak at 7.26 ppm. The benzenoid protons H₄, H₅ and H₆ also showed multiplet in the region 6.32–6.59 ppm, due to the coupling of neighbouring protons and also due to the overlapping of peaks. The triplet peaks corresponding to H_b and H_g protons of monomer were missing in the polymer sample which indicated the formation of polymer.

The monomer (NPA) and polymer (PNPA) were characterised by FT-IR spectroscopy by making thin pellets of samples with KBr powder (see Fig. 3a). The monomer showed characteristic strong peaks at 1665, 1576, 1503, 1438, 1324, 1255 and 1156 cm⁻¹ corresponding to C=O stretching, aromatic ring stretching, C=C stretching, carboxylic-OH bending, C-N stretching, C-O stretching and C-H stretching respectively [35,36]. The peaks at 745 and 694 cm⁻¹ were due to aromatic C-H out of plane bending vibrations, characteristic band of substituted phenyl rings [37,38]. The polymer PNPA have also shown characteristic peaks at 1654, 1578, 1504, 1453, 1395, 1278, 1158 cm⁻¹ corresponding to C=O stretching, aromatic ring stretching, C=C stretching, carboxylic-OH bending, C-N stretching, C-O stretching and C-H stretching respectively [35,39–43]. The structural difference of monomer and polymer was clearly evident from the C-N stretching, C-O stretching and carboxylic-OH bending which have different peak positions (see Fig. 3a). The polymer and monomer have shown characteristic peak of N-H asymmetric stretching and broad O-H stretching of carboxylic acid at 3335 cm⁻¹ and 3030 cm⁻¹ respectively [35,41]. Specific viscosity of monomer and polymer (PNPA) in ethanol solvent were measured using Ostwald's U-tube viscometer and its value was found to be 0.01 and 0.08 (± 0.005) respectively at 28 °C. The specific viscosity of polymer indicates that the formation of low molecular weight polymer rather than very high molecular weight polymer. MALDI-TOF analysis of the PNPA have been carried out using 2,5-dihydroxy benzoic acid matrix to find out the number of repeating units and to confirm polymer formation (see Fig. S1 in supporting information). The polymer molecular ions peaks of PNPA have been repeated at regular interval of m/z equal to 211 for molecular formula (C₁₃H₉NO₂)_n and an average 6–7 repeating units (mass between the range 832–1870 amu) were present. The other repeating peaks of equal mass difference corresponding to polymer adducts and fragmented peaks were also observed.

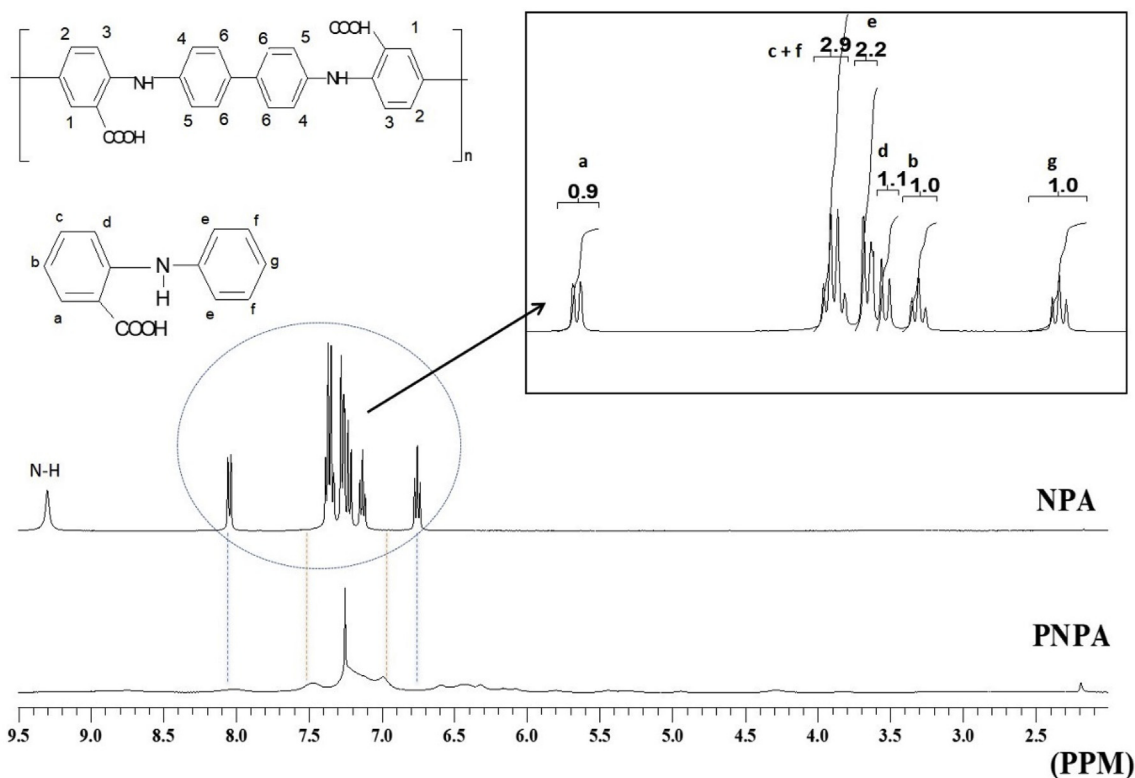


Fig. 2. ^1H NMR spectra of NPA and PNPA in CDCl_3 with enlarged peaks of NPA shown as inset.

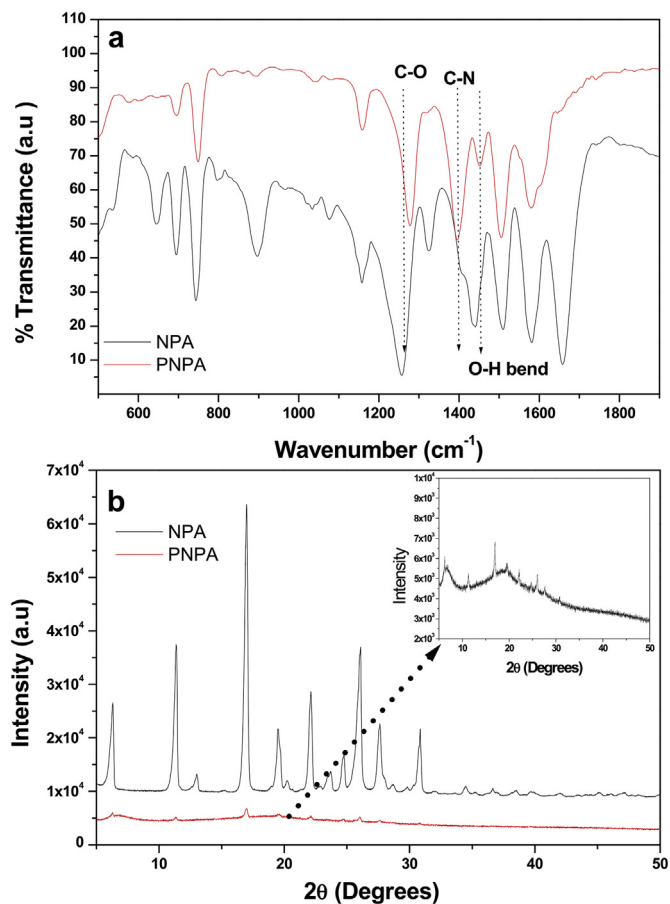


Fig. 3. (a) FT-IR spectra of NPA and PNPA (b) Powder WXR diffraction of NPA and PNPA with enlarged diffraction of PNPA as inset.

The powder X-ray diffraction studies provide information regarding the amorphous, crystalline or semicrystalline nature of the samples. X-ray diffraction pattern of monomer N-phenyl anthranilic acid (NPA) and poly-N-phenyl anthranilic acid (PNPA) were shown in Fig. 3b. The recrystallized monomer N-phenyl anthranilic acid have shown sharp crystalline peaks at 2θ values 6.5 , 11.4 , 17.13 , 19.5 , 22.1 , 26.0 , 27.6 and 30.7° . However, single crystal XRD is necessary to see the molecular packing in NPA which will be done later. Poly-N-phenyl anthranilic acid (PNPA) samples do not have sharp crystalline peaks; instead they show less intense broad peaks (see inset for expanded diffractogram of PNPA). The polymer has shown lower angle peak centred at $2\theta = 6.1^\circ$, which corresponds to the organized polymer domains. The presence of less intense peak as well as broad peaks in the 2θ range 17 – 30° showed the weak interchain interactions and amorphous nature of the polymer similar to parallel and perpendicular periodicity of polymer chain in polydiphenylamine and polyaniline [42,44–48]. Thermal stability of monomer and polymer were recorded by thermogravimetric analysis by heating the samples in nitrogen atmosphere up to 700°C . The monomer have shown 10% weight loss at 218°C and then a sudden weight loss of 50% was observed on increasing temperature to 250°C (see Fig. S2 in supporting information). The polymer have shown 10% weight loss at 232°C and then slowly losses 50% weight on increasing temperature to 333°C . The thermal stability for polymer was higher than monomer especially for higher temperature [40–43,49].

The good solubility of the monomer and polymer in sodium hydroxide solution enabled us to record the UV–visible absorption spectra in basic aqueous medium. The absorption spectra of polymer and monomer at different concentration have been recorded in sodium hydroxide denoted by PNPA-Na and NPA-Na respectively (see Fig. 4a and Fig. S3 in supporting information). Dark blue coloured PNPA changes to yellowish brown solution upon the addition of sodium hydroxide, whereas colourless NPA do not change its colour. Two peaks were observed for both NPA and PNPA at 288 nm and 339 nm corresponding to benzenoid (π - π^*) and extended π - π^* transition of

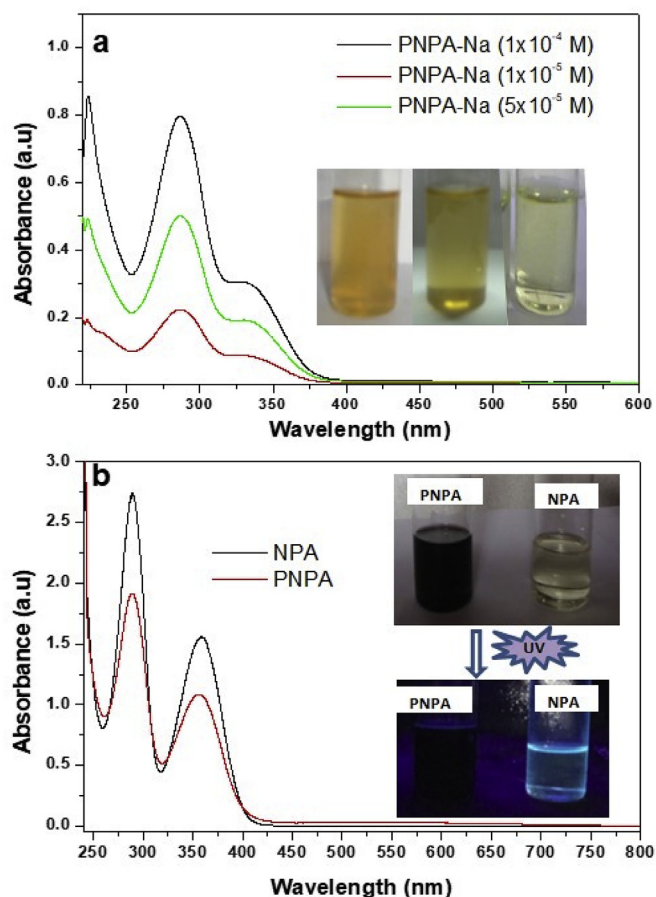


Fig. 4. UV-visible absorption spectra of (a) different concentration of PNPA-Na in sodium hydroxide solution (2 M) is shown with photographs (b) PNPA and NPA in chloroform solvent along with photographs in the absence and presence of UV light.

conjugated phenyl rings in reduced amine [50,51]. The absorption spectra of NPA and PNPA in organic solvent like chloroform have shown two absorption maxima at 290 nm and 358 nm corresponding to benzenoid and extended π - π^* transition respectively (see Fig. 4b) [52]. The absorption corresponding to oxidised quinoid unit (above 620 nm) was absent in the polymer structure [40,53]. The UV-visible absorption spectra of NPA and PNPA in sulphuric acid denoted as NPA-H and PNPA-H have shown sharp benzenoid peak at 254 nm and broad absorption band with vibronic peaks at 363, 387 and 404 nm corresponding to protonated conjugated polymer structure (see Fig. 5 and Fig. S4 in supporting information) [37]. It was interesting to see a blue shift of 20 nm in basic conditions and red shift of 50 nm in acidic conditions with respect to absorption obtained for 358 nm peak in chloroform. Concentration dependant absorption spectra of polymer PNPA-H in sulphuric acid have been recorded for different concentrations of polymer by varying its concentrations from 1.0×10^{-4} to 4.6×10^{-6} M (see Fig. 5). The PNPA-H have not shown any shift in peak position with change in concentration. The fluorescence emission of blue coloured polymer (PNPA-H) at different concentration have been checked in dilute sulphuric acid by irradiating solutions under UV light ($\lambda = 365$ nm) in dark chamber. The polymer solutions have intense bluish-white fluorescence and the intensity of the bluish-white fluorescence of the polymer samples decrease with decrease in concentration (see photographs in Fig. 5). In acidic environment PNPA is protonated, the polymer structure becomes more rigid because of the repulsion of charges and conjugation, which result in the stronger fluorescence intensity. The UV-visible spectroscopy shows that the onset of the π - π^* conjugated peak for the PNPA-H in acid medium, PNPA-Na in basic medium and PNPA in chloroform were at 440 nm, 375 nm and 410 nm respectively, which indicate the change in conjugation. Fluorescence quantum yield (Φ_f) of the polymer solution has been quantified as $0.38 \pm 5\%$ by a comparative method using quinine sulphate as reference at an excitation wavelength of 365 nm. Monomer (NPA) have shown weak green fluorescence in chloroform, bluish-white fluorescence in sulphuric acid and no fluorescence in sodium hydroxide solution. The polymer (PNPA) has intense bluish-white fluorescence in sulphuric acid, no visible emission in chloroform and sodium hydroxide solution.

The light emission of polymer solutions are very sensitive and

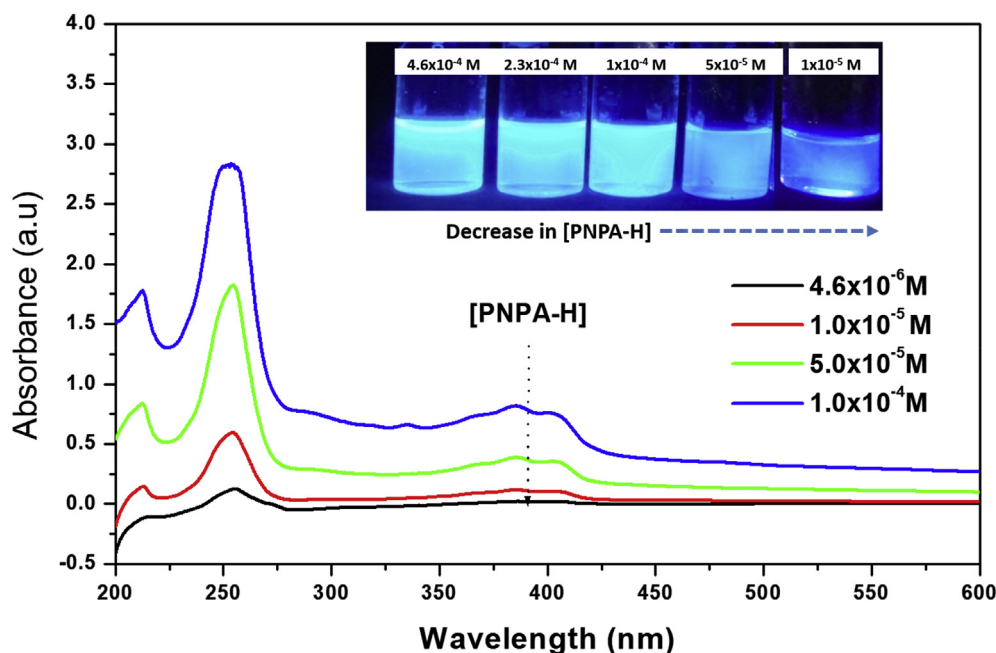


Fig. 5. Concentration dependant UV-visible spectra of PNPA-H in sulphuric acid. Fluorescence images of PNPA-H for different concentration is shown as photographs.

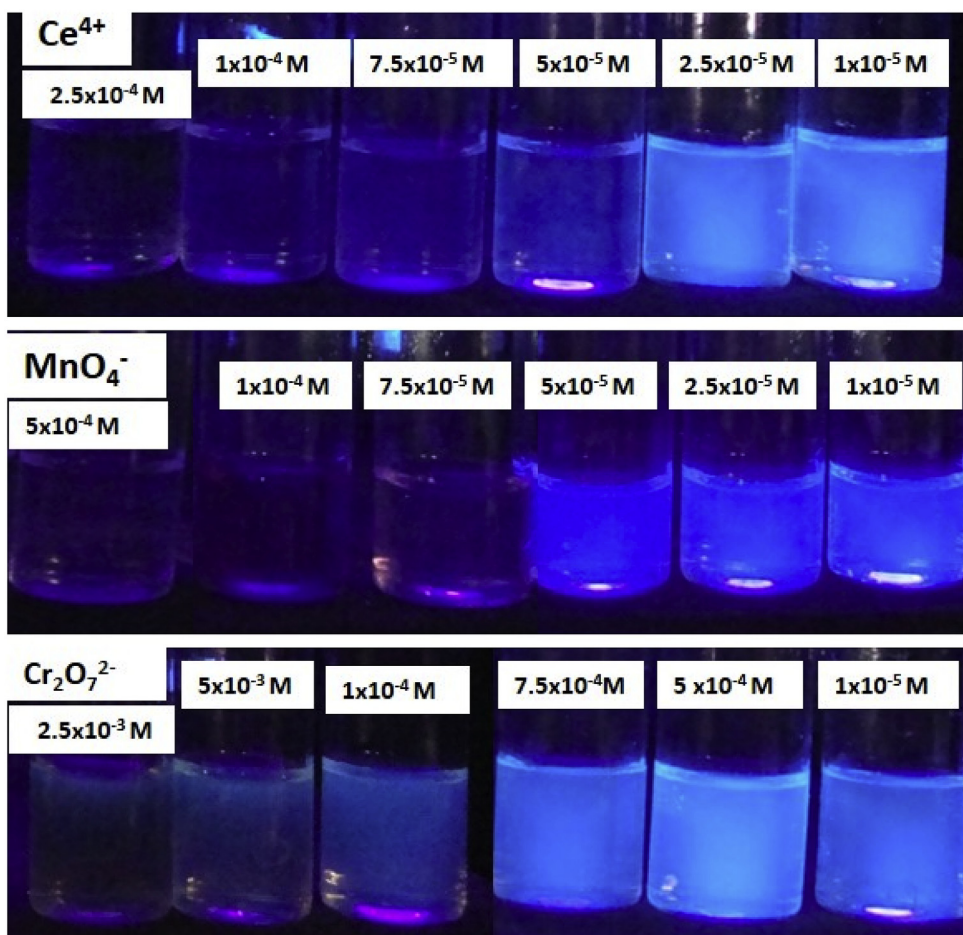


Fig. 6. Fluorescence quenching studies of PNPA-H with different concentration of analytes like Ce^{4+} , KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ by colorimetric detection.

detection of specific ions, atoms or small molecules in trace level is possible by fluorescent intensity change or colorimetric sensing [54,55]. Different anions and cations such as Ce^{4+} , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, Cu^{2+} , Co^{2+} , Hg^{2+} and molecules such as glucose, urea, ascorbic acid were randomly added to the bluish-white light emitting polymer solution of PNPA-H to check any change in fluorescence signal. Strong oxidising agents such as cerium ammonium sulphate dihydrate, potassium permanganate and potassium dichromate solutions instantly quenched the bluish-white fluorescence of polymer. A systematic concentration depended studies have been carried out to find actual concentration at which fluorescence quenching was observed by adding the solution of analytes. For this purpose, concentration of aqueous salt solutions of Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions were systematically varied in the concentration range from 1×10^{-2} M to 1×10^{-5} M and the polymer concentration was fixed as 1×10^{-5} M (see Fig. 6). Naked eye fluorescence quenching was observed on and above 5×10^{-5} M, 7.5×10^{-5} M and 2.5×10^{-3} M for Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ respectively. The [analyte]/[polymer] mole ratio for which fluorescence quenching was obtained for $[\text{Ce}^{4+}]/[\text{PNPA-H}]$, $[\text{MnO}_4^-]/[\text{PNPA-H}]$ and $[\text{Cr}_2\text{O}_7^{2-}]/[\text{PNPA-H}]$ were 5, 7.5 and 250 respectively. The limit of detection (LOD) of analytes for simple naked eye fluorescence detection have been found to be 0.5 μM , 0.75 μM and 25 μM for Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions respectively, by setting the lowest naked eye emissive polymer concentration as 1×10^{-7} (see Fig. S5 in supporting information).

The UV-visible absorption spectra of polymer and polymer + analyte solutions were recorded to find any changes in absorption spectra of PNPA-H by the addition of analytes. The absorption spectra of polymer were taken at the concentration limit where naked eye

fluorescence quenching was observed (see Fig. 7a and b). In the case of analytes like Ce^{4+} and MnO_4^- ions, absorption at 388 nm was vanished completely upon the increasing analyte concentration to 5×10^{-5} M and 5×10^{-5} M respectively. In addition to that, the absorbance of the benzenoid peak present at 280 nm was suppressed considerably indicating the changes in the benzenoid structure. In the case of dichromate + polymer mixture, a strong light absorption of potassium dichromate at 380 nm region hampered our efforts to note changes in absorbance (see Fig. S6 in supporting information).

Emission spectra of polymer and polymer + analytes have been recorded using spectrofluorometer to get the quenching concentration from the changes in fluorescence intensity. The range of polymer and analyte concentrations selected for spectrofluorometric studies were the same as that used for naked eye fluorescence detection and UV-Visible absorption studies. The quenching of fluorescence of PNPA-H obtained from spectrofluorimetry for Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions were at concentrations equal to 1×10^{-4} M, 7.5×10^{-5} M and 2.5×10^{-3} M respectively (see Fig. 8 and Fig. S7 in supporting information). Fluorescence intensity changes of polymer obtained after the addition of different analyte concentrations have been plotted against [analyte]/[polymer] mole ratio (see Fig. 9 and Fig. S7 in supporting information). The analyte/polymer mole ratio for $\text{Ce}^{4+}/\text{PNPA-H}$, $\text{MnO}_4^-/\text{PNPA-H}$ and $\text{Cr}_2\text{O}_7^{2-}/\text{PNPA-H}$ for quenching action were obtained as 8, 4.5 and 100 respectively, via extrapolating the straight line to x-axis. The accuracy of sensing action in naked eye fluorescence detection and uv-visible absorption spectra would be slightly variable especially at very low concentration were due to the difficulty in judging the visibility of fluorescence and low absorbance, respectively. On the other hand, spectrofluorometer is a highly sensitive instrument which can measure

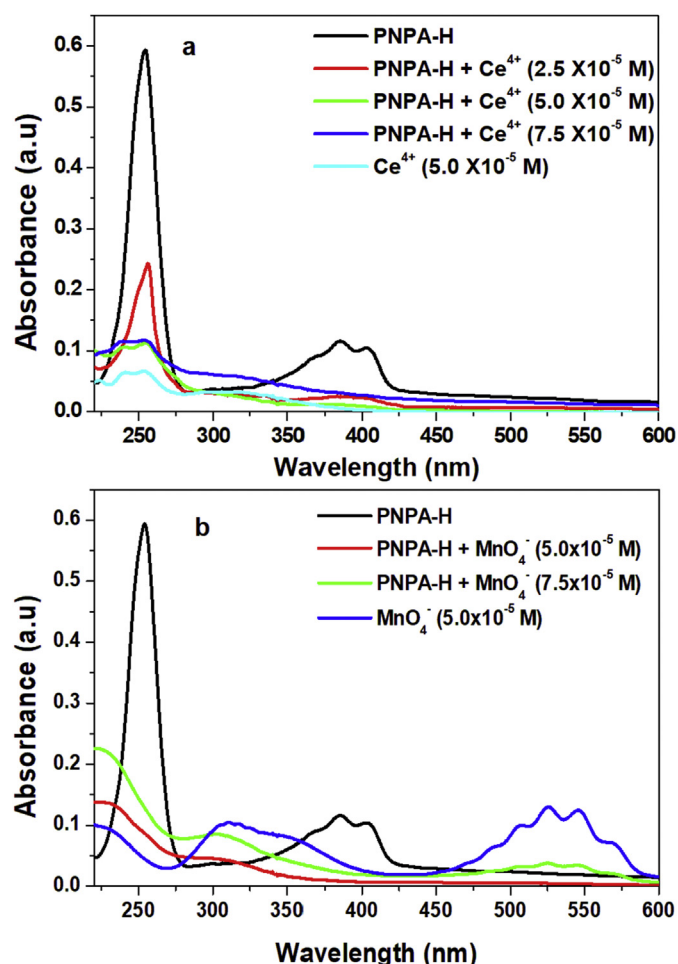


Fig. 7. UV-Visible absorption spectra of (a) Polymer + Ce^{4+} ions in solution and (b) Polymer + MnO_4^- ions in solution.

fluorescence signal even at very low concentration (up to nanomolar concentration) of polymer + analyte mixture. The fluorescence intensity changes of PNPA-H + analyte mixture plotted against different analyte concentrations (μM) were shown supporting information S8. Calibration curve shows that linear range of response was fairly straight with higher coefficient of determination (r^2) and low p-value (< 0.05), which suggests that model was fairly fitted with good precision. Moreover the three independent techniques provided reasonably good agreement for the fluorescence quenching action of analytes within the experimental limit.

The mechanism of fluorescence quenching was proposed based on the oxidising action of analytes on PNPA-H in reduced form (see Fig. 10). The oxidising power of analytes in solution can be obtained from the standard reduction potential (E°) of $\text{Ce}^{4+}/\text{Ce}^{3+}$ (+1.44 V), $\text{MnO}_4^-/\text{Mn}^{2+}$ (+1.51 V), and $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ (1.36 V) in acid medium [56–58]. The first step of the oxidation of N-phenyl anthranilic acid in redox titration is an irreversible step that results in the formation of colourless diphenyl benzidine dicarboxylic acid (reduced), which upon oxidation forms violet-red diphenyl diquinone dicarboxylic acid (oxidised) [59–63]. The standard redox potential for reduced (colourless) and oxidised forms (violet-red) of N-phenyl anthranilic acid dimer was found to be 1.08 V [60,64]. The blue coloured polymer (PNPA-H) synthesised for the present studies also contain diphenyl benzidine dicarboxylic acid repeating units in the reduced form, however which upon further oxidation becomes non-fluorescent diquinone structure (see Fig. 10). The [analyte]/[polymer] mole ratio at which fluorescence quenching observed was lowest for MnO_4^- ions (7.5) and highest for $\text{Cr}_2\text{O}_7^{2-}$ solutions (250) from spectrofluorimetry. The high $[\text{Cr}_2\text{O}_7^{2-}]$

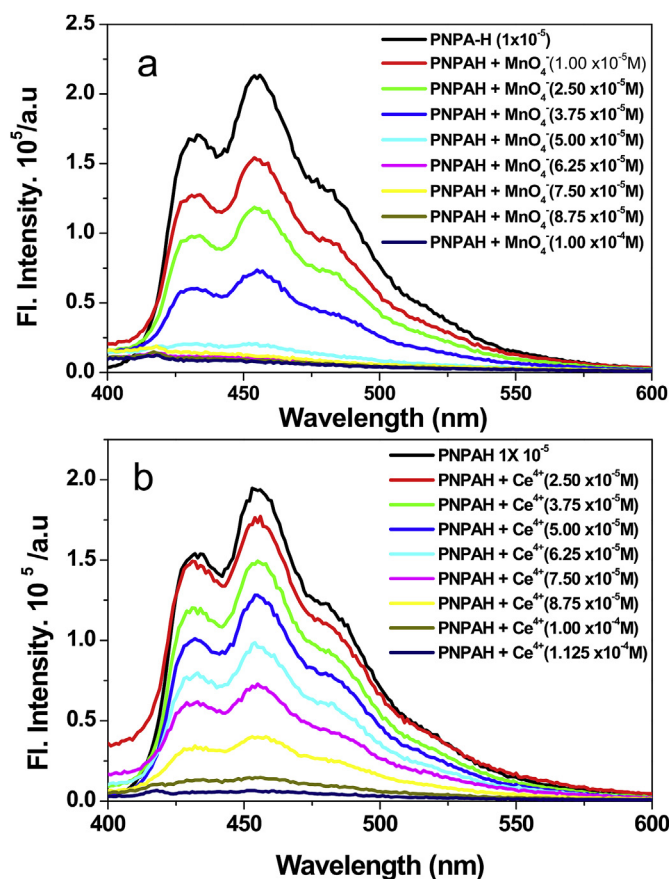


Fig. 8. Emission spectra of (a) Polymer + MnO_4^- ions in solution and (b) Polymer + Ce^{4+} ions in solution.

$]/[\text{PNPA-H}]$ mole ratio reveals that potassium dichromate was a weak oxidising analyte ($E^\circ = +1.36$ V) for PNPA-H in comparison to other analytes. Other two analytes ($\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$) have more positive standard reduction potential than $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ and thus they reacted with PNPA-H at low analyte/PNPA-H mole ratio. The fluorescence intensity ratio (I_0/I) plotted against concentration of analyte was shown in Fig. S9 in supporting information, where I_0 and I are the intensity of transmitted light in the absence and presence of analyte. The plots have shown a curve with positive deviation from straight line which indicates static quenching. This may be because of the formation of non-fluorescent complex formation for higher [analyte]/[polymer] mole ratio. One of the requirement for Stern-Volmer theory is that the donor concentration should be low, so that the donor molecules do not influence each other [65,66]. We have calculated the slope of curve manually using the equation, slope = $\Delta Y/\Delta X$ by taking two concentrations from the curve and the slope of the curve for MnO_4^- , Ce^{4+} and $\text{Cr}_2\text{O}_7^{2-}$ ions were 3.73×10^5 , 9.41×10^4 and $5.00 \times 10^3 \text{ M}^{-1}$ and the sensitivity of different analytes follow the order $\text{MnO}_4^- > \text{Ce}^{4+} > \text{Cr}_2\text{O}_7^{2-}$.

Reversibility and the redox behaviour of PNPA-H have been checked by adding reducing biomolecules like ascorbic acid to the oxidised non-fluorescent form of polymer in solution. The standard reduction potential (E°) value for dehydroascorbic acid (DHA)/ascorbic acid (AsA) was reported to be -0.066 V [67]. Ascorbic acid was added to the polymer at the concentration in which fluorescence was just quenched by analytes (1×10^{-4} M for Ce^{4+} , 7.5×10^{-5} M for MnO_4^- , and 2.5×10^{-3} M for $\text{Cr}_2\text{O}_7^{2-}$). The fluorescence was reappeared on the addition of ascorbic acid at concentrations 5×10^{-4} M, 2.5×10^{-4} M and 1×10^{-2} M respectively for Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ solutions respectively (see Fig. 10). Although system was reversible, slight excess oxidant or reductant concentration was required to quench or reappear

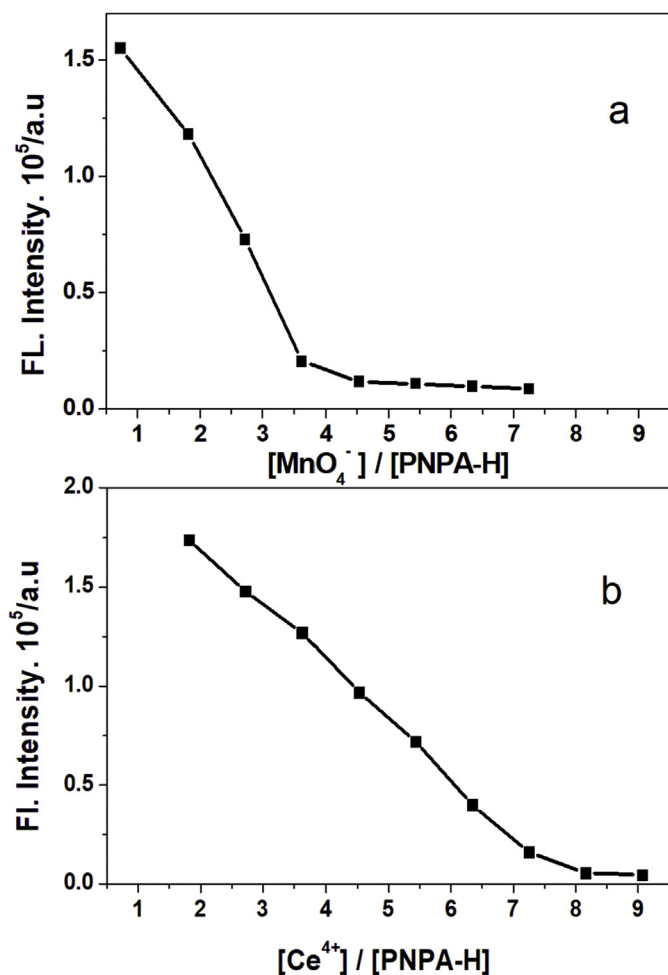


Fig. 9. Mole ratio plots of (a) Polymer + Ce⁴⁺ ions in solution and (b) Polymer + MnO₄⁻ ions in solution.

the fluorescence which may be due to the polymeric structure in which variable levels of oxidation or reduction can take place. The changes in the UV-visible spectra of polymer + analyte mixtures by adding ascorbic acid was also checked (see Fig. S10 in supporting information). Polymer + analyte + ascorbic acid mixture have an absorbance at 265 nm which indicates the reformation of benzenoid structure in PNPA-H. However, peak which was responsible for blue light emission at 388 nm was not clearly visible due to the broad absorption of other reduced ions of analytes, slight excess ascorbic acid and low concentration PNPA-H in the final mixture. Direct synthesis of oxidised quinoid form of PNPA using stronger oxidising agents are currently in progress, which could be directly used for sensing action of reducing biomolecules. The potentiometric titrations of the polymer (PNPA-H) against the analytes (fixed polymer and analyte concentration as 1×10^{-5} M) have been carried. The change of potential with respect to volume ($\Delta E/\Delta V$) plotted against volume of analyte have typical nature of potentiometric redox titration curve (see supporting information S11). The concentration of analyte calculated from first derivative plot of potentiometric titration was relatively in good agreement with quenching concentration of analyte obtained from other methods.

A naked eye fluorimetric titration of analytes has been carried out using PNPA-H solution to demonstrate its potential application as fluorescent indicators especially at very low concentration of analytes (see Fig. S12 in supporting information). The concentrations of polymer and analytes taken was comparable (1×10^{-5} M) for fluorimetric titration and the [analyte]/[polymer] mole ratio at which fluorescence quenching observed was found to be relatively in good agreement with

other methods. We have also studied the effect of interfering analytes, especially mild oxidising agents like FeCl₃, CuSO₄, NaWO₄ and Pb(NO₃)₂ on the fluorescence intensity of PNPA-H using naked eye detection test. It has been found that these analytes have no effect on fluorescence of PNPA-H. (See Fig. S13 in supporting information). We have also checked the combined effect of these analytes separately with Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ and it has been noted that FeCl₃, CuSO₄, NaWO₄ and Pb(NO₃)₂ do not interfere the polymer-analyte reaction. This also indicated highly sensitive nature of poly N-phenyl anthranilic acid towards strong oxidising agents like Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻. In a nutshell, the redox reaction between conjugated fluorescent PNPA-H and analytes which leads to quenching of bright bluish white fluorescence have been used for sensing applications.

5. Conclusions

Chemical oxidative polymerisation of N-Phenyl anthranilic acid was successfully accomplished using anhydrous ferric chloride as oxidising agent in ethanol medium. An efficient bluish-white light emitting poly-N-phenyl anthranilic acid (PNPA-H) was utilized for the sensing of analytes like Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ solutions. The important outcomes of the present investigation are as follows. i) The formation of polymer (PNPA) was confirmed by ¹H NMR spectroscopy, FT-IR spectroscopy, elemental analysis and MALDI-TOF mass spectroscopy. ii) Powder X-ray diffraction studies have revealed the highly crystalline nature of monomer and amorphous nature of polymer. iii) Thermal stability of polymer was found to be much higher than monomer. iv) UV-visible absorption spectra of polymer in sodium hydroxide solution (PNPA-Na) and in sulphuric acid solution (PNPA-H) have shown marked differences in absorption spectra. v) The polymer have shown broad band with vibronic peaks at 363, 387 and 404 nm in sulphuric acid medium and which was mainly responsible for bluish-white light emission. vi) The bluish-white emission of PNPA-H was quenched by oxidising analytes like Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ ions, which was quantified by three independent methods like colorimetric sensing, UV-Vis absorption spectra and fluorescence emission spectroscopy. vii) Ce⁴⁺, MnO₄⁻ and Cr₂O₇²⁻ have shown different [analyte]/[polymer] mole ratio for fluorescence quenching, which was correlated with difference redox potential viii) The oxidation reaction reduced diphenyl benzidine units of polymer to oxidised diquinoid units by oxidising analytes was responsible for fluorescence quenching. ix) The reversibility of redox reaction was confirmed by the reappearance of fluorescence by the addition of reducing biomolecules like ascorbic acid. x) The limit of detection of analytes for naked eye fluorescence quenching of PNPA-H for Ce⁴⁺, MnO₄⁻, and Cr₂O₇²⁻ ions were 0.5 μM, 0.75 μM and 25 μM respectively and sensitivity was obtained highest for MnO₄⁻ ions and lowest for Cr₂O₇²⁻ ions. In short, we have developed novel method for the detection of oxidising analytes like potassium dichromate, potassium permanganate and cerium ammonium sulphate by the utilization of poly N-phenyl anthranilic acid (PNPA-H) as a redox fluoroprobe.

Conflicts of interest

There are no conflicts to declare under a "Conflicts of Interest"

Acknowledgement

We are thankful to Technical Research Centre (TRC, Project No. AI/1/62/IACS/2015), IACS, Kolkata for collaborative support. We acknowledge DST-FIST scheme and UGC-CPE scheme for instrumentation facilities offered in STC, Thrissur. We acknowledge STIC, Cochin for instrumental facilities such as NMR, elemental analysis, and thermo gravimetric analysis. RDK thankfully acknowledge KSCSTE for research fellowship for the period 2018–2019. JAM gratefully acknowledges his doctoral mentor Dr. M Jayakannan, Professor IISER, Pune for guidance

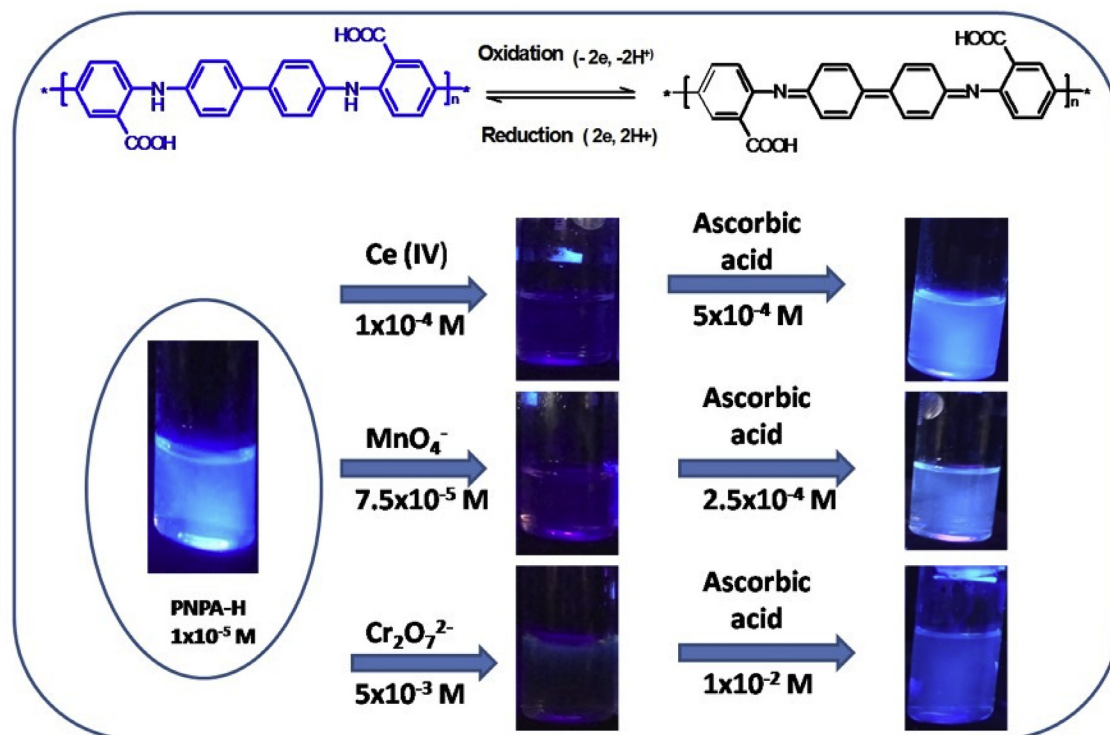


Fig. 10. Mechanism of fluorescence quenching and reappearance of PNPA-H on adding oxidising and reducing analytes with its photographs.

and support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.121747>.

References

- Y.Z. Long, M.M. Li, C. Gu, M. Wan, J.L. Duvail, Z. Liu, Z. Fan, Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers, *Prog. Polym. Sci.* 36 (2011) 1415–1442.
- C. Li, H. Bai, G. Shi, Conducting polymer nanomaterials: electrosynthesis and applications, *Chem. Soc. Rev.* 38 (2009) 2397–2409.
- S.W. Thomas, G.D. Joly, T.M. Swager, Chemical sensors based on amplifying fluorescent conjugated polymers, *Chem. Rev.* 107 (2007) 1339–1386.
- D.E. Kline, Thermal conductivity studies of polymers, *J. Polym. Sci.* 50 (1961) 441–450.
- D.E. Stilwell, Electrochemistry of conductive polymers, *J. Electrochem. Soc.* 136 (1989) 688.
- C. Basavaraja, N.R. Kim, E.A. Jo, D.S. Huh, Characterization and conductivity studies of nanocomposite films with polymer networks containing polyaniline-alginate/titanium dioxide, *Polym. Compos.* 31 (2010) 1754–1761.
- D.T. Mcquade, A.E. Pullen, T.M. Swager, Conjugated Polymer-Based Chemical Sensors, (2000).
- M. Gerard, A. Chaubey, B.D. Malhotra, Application of conducting polymers to biosensors, *Biosens. Bioelectron.* 17 (2002) 345–359.
- P. Anilkumar, M. Jayakannan, Hydroxyl-functionalized polyaniline nanospheres: tracing molecular interactions at the nanosurface via vitamin C sensing, *Langmuir* 24 (2008) 9754–9762.
- J. Bobacka, A. Ivaska, A. Lewenstam, Potentiometric ion sensors based on conducting polymers, *Electroanalysis* 15 (2003) 366–374.
- T.M. Swager, The molecular wire approach to sensory signal amplification, *Acc. Chem. Res.* 31 (1998) 201–207.
- B. Adhikari, S. Majumdar, Polymers in sensor applications, *Prog. Polym. Sci.* 29 (2004) 699–766.
- A.C. Partridge, M.L. Jansen, W.M. Arnold, Conducting polymer-based sensors, *Mater. Sci. Eng. C12* (2000) 37–42.
- C. Tan, M.R. Pinto, K.S. Schanze, Photophysics, aggregation and amplified quenching of a water-soluble poly(phenylene ethynylene), *Chem. Commun.* 2 (2002) 446–447.
- Q. Zhou, T.M. Swager, Fluorescent chemosensors based on energy migration in conjugated polymers: the molecular wire approach to increased sensitivity, *J. Am. Chem. Soc.* 117 (1995) 12593–12602.
- Q. Ye, F. Yan, D. kong, J. wang, X. Zhou, L. Chen, Synthesis and applications of fluorescent polymers as fluorescent probes, *Curr. Org. Chem.* 19 (2015) 1–1.
- A. Yamada, Y. Hiruta, J. Wang, E. Ayano, H. Kanazawa, Design of environmentally responsive fluorescent polymer probes for cellular imaging, *Biomacromolecules* 16 (2015) 2356–2362.
- S. Uchiyama, Y. Matsumura, A.P. De Silva, K. Iwai, Fluorescent molecular thermometers based on polymers showing temperature-induced phase transitions and labeled with polarity-responsive benzofurazans, *Anal. Chem.* 75 (2003) 5926–5935.
- L.J. Fan, Y. Zhang, C.B. Murphy, S.E. Angell, M.F.L. Parker, B.R. Flynn, W.E. Jones, Fluorescent conjugated polymer molecular wire chemosensors for transition metal ion recognition and signaling, *Coord. Chem. Rev.* 253 (2009) 410–422.
- A.P. De Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Signaling recognition events with fluorescent sensors and switches, *Chem. Rev.* 97 (1997) 1515–1566.
- L. Zou, Y. Wen, H. Zhang, J. Chai, X. Duan, L. Shen, G. Zhang, J. Xu, Highly sensitive fluorescence sensor based on electrosynthesized poly(Fmoc-L-serine) enables ultra-trace analysis of Cr2O7²⁻ in water and agro-product samples, *Sens. Actuators B Chem.* 277 (2018) 394–400, <https://doi.org/10.1016/j.snb.2018.09.046>.
- H. Zhang, G. Zhang, J. Xu, Y. Wen, W. Ding, J. Zhang, S. Ming, S. Zhen, Electrosynthesis, characterization and optical sensing application of amino acid functionalized polyfluorene, *Chin. J. Polym. Sci.* 34 (2016) 229–241, <https://doi.org/10.1007/s10118-016-1742-3>.
- J. Yuan, S. Wang, J. Shan, J. Peng, L. Wei, X. Xu, Formation and photoluminescence of fluorescent polymers, *Int. J. Polym. Sci.* 2010 (2010).
- F.S. Rodembusch, F.P. Leusin, L.B. Bordignon, M.R. Gallas, V. Stefani, New fluorescent monomers and polymers displaying an intramolecular proton-transfer mechanism in the electronically excited state (ESIPT). Part II. Synthesis, spectroscopic characterization and solvatochromism of new benzazolyvinylene derivatives, *J. Photochem. Photobiol. A Chem.* 173 (2005) 81–92.
- J.J. Yan, Z.K. Wang, X.S. Lin, C.Y. Hong, H.J. Liang, C.Y. Pan, Y.Z. You, Polymerizing nonfluorescent monomers without incorporating any fluorescent agent produces strong fluorescent polymers, *Adv. Mater.* 24 (2012) 5617–5624.
- Y. Sha, Q. Zhu, Y. Wan, L. Li, X. Wang, G. Xue, D. Zhou, Synthesis of polymer with defined fluorescent end groups via reversible addition fragmentation transfer polymerization for characterizing the conformations of polymer chains in solutions, *J. Polym. Sci. Part A Polym. Chem.* 54 (2016) 2413–2420.
- N. Li, Q. Xu, X. Xia, L. wang, J. Lu, X. Wen, A polymeric chemosensor for Fe³⁺ based on fluorescence quenching of polymer with quinoline derivative in the side chain, *Mater. Chem. Phys.* 114 (2009) 339–343.
- B.Y. Wang, X.Y. Liu, Y.L. Hu, Z.X. Su, Synthesis and photophysical behavior of a water-soluble coumarin-bearing polymer for proton and Ni²⁺ ion sensing, *Polym. Int.* 58 (2009) 703–709.
- J. Maiti, B. Pokhrel, R. Boruah, S.K. Dolui, Polythiophene based fluorescence sensors for acids and metal ions, *Sens. Actuators B Chem.* 141 (2009) 447–451.
- I.B. Kim, B. Erdogan, J.N. Wilson, U.H.F. Bunz, Sugar-poly(para-phenylene ethynylene) conjugates as sensory materials: efficient quenching by Hg²⁺ and Pb²⁺

- ions, *Chem. Eur J.* 10 (2004) 6247–6254.
- [31] F. Liao, S. Yang, X. Li, L. Yang, Z. Xie, C. Hu, S. Yan, T. Ren, Z. Liu, Preparation of heteroatom doped poly(o-phenylenediamine) fluorescent nanospheres: tunable fluorescence spectrum and sensing performance, *Synth. Met.* 189 (2014) 126–134.
- [32] Z. Wang, F. Liao, Fluorescent probes for Pd²⁺ detection by poly(o-phenylenediamine) nanospheres with fluorescence enhancement, *Synth. Met.* 162 (2012) 444–447.
- [33] G. Kocak, C. Tuncer, V. Bütün, PH-Responsive polymers, *Polym. Chem.* 8 (2017) 144–176.
- [34] A. Miltojevic, N. Radulovic, Complete assignment of ¹H- and ¹³C-NMR spectra of anthranilic acid and its hydroxy derivatives and salicylic acid and its amino derivatives, *Facta Univ. – Ser. Phys. Chem. Technol.* 13 (2015) 121–132.
- [35] N. Rajendiran, T. Balasubramanian, Dual fluorescence of N-phenylanthranilic acid: effect of solvents, pH and β-cyclodextrin, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 68 (2007) 867–876.
- [36] K. Rajarajan, A. Anandhi, K.R.D. Reka, G. Madhurambal, Synthesis and characterization studies of diphenylamine picrate crystal – a non-linear optical material, *Int. J. Pharm. Chem. Biol. Sci.* 3 (2013) 480–487.
- [37] S.Z. Ozkan, I.S. Ereemeev, G.P. Karpacheva, T.N. Prudskova, E.V. Veselova, G.N. Bondarenko, G.a. Shandryuk, Polymers of diphenylamine-2-carboxylic acid: synthesis, structure, and properties, *Polym. Sci. Ser. B* 55 (2013) 107–115.
- [38] D.L. Pavia, G.M. Lampman, G.S. Kriz, *Introduction to Spectroscopy*, third ed., Thomson Learn. Inc., 2001, <https://doi.org/10.1006/jmra.1996.0145>.
- [39] C. Sivakumar, T. Vasudevan, A. Gopalan, T.C. Wen, Chemical oxidative polymerization and in situ spectroelectrochemical studies of a sulfonated aniline derivative by UV-visible spectroscopy, *Ind. Eng. Chem. Res.* 40 (2001) 40–51.
- [40] I.A. Sophia, G. Gopu, C. Vedhi, Synthesis and characterization of poly anthranilic acid metal nanocomposites, *Open J. Synth. Theory Appl.* 01 (2012) 1–8.
- [41] V. Chabukswar, A. Horne, S. Bhavsar, K. Mohite, Studies on synthesis and effect of dopants on conductivity and morphology of organically soluble poly(o-anisidine), *J. Macromol. Sci. Part A Pure Appl. Chem.* 49 (2012) 926–930.
- [42] M.J. Antony, M. Jayakannan, Polyaniline nanoscaffolds for colorimetric sensing of biomolecules via electron transfer process, *Langmuir* 27 (2011) 6268–6278.
- [43] S.Z. Ozkan, I.S. Ereemeev, G.P. Karpacheva, G.N. Bondarenko, Oxidative Polymerization of N-Phenylanthranilic Acid in the Heterophase System vol. 2013, (2013), pp. 63–69.
- [44] A.M. Showkat, X.T. Cao, D.W. Kim, M.R. Islam, K.T. Lim, Characterization of poly(diphenylamine)-gold nanocomposites obtained by self-assembly, *IOP Conf. Ser. Mater. Sci. Eng.* 77 (2015).
- [45] E.A. Zaragoza-Contreras, C.A. Hernández-Escobar, A. Estrada-Monje, T. Kobayashi, Synthesis of diphenylamine-co-aniline copolymers in emulsified systems using a reactive surfactant as the emulsifying agent and aniline monomer, *Synth. Met.* 214 (2016) 5–13.
- [46] L. Zhang, M. Wan, Y. Wei, Nanoscaled polyaniline fibers prepared by ferric chloride as an oxidant, *Macromol. Rapid Commun.* 27 (2006) 366–371.
- [47] K. Rohini Das, M. Jinish Antony, Synthesis and characterisation of water dispersible copolymer submicron spheres of poly-(phenylenediamine-co-N-sulfopropyl aniline) via random copolymerisation, *Polym. (United Kingdom)* 87 (2016) 215–225.
- [48] J.P. Pouget, M.E. Józefowicz, A.J. Epstein, X. Tang, A.G. MacDiarmid, X-ray structure of polyaniline, *Macromolecules* 24 (1991) 779–789.
- [49] A.A. Athawale, B.A. Deore, V.V. Chabukswar, Studies on poly(diphenylamine) synthesized electrochemically in nonaqueous media, *Mater. Chem. Phys.* 58 (1999) 94–100.
- [50] S.Z. Ozkan, G.N. Bondarenko, G.P. Karpacheva, Oxidative polymerization of diphenylamine-2-carboxylic acid: synthesis, structure, and properties of polymers, *Polym. Sci. Ser. A* B52 (2010) 263–269.
- [51] H.S.O. Chan, S.C. Ng, W.S. Sim, K.L. Tan, B.T.G. Tan, Preparation and characterization of electrically conducting copolymers of aniline and anthranilic acid: evidence for self-doping by X-ray photoelectron spectroscopy, *Macromolecules* 25 (1992) 6029–6034.
- [52] M. Liu, C. Yin, P. Chen, M. Zhang, S. Parkin, P. Zhou, T. Li, F. Yu, S. Long, Sp²CH---Cl hydrogen bond in the conformational polymorphism of 4-chloro-phenylanthranilic acid, *CrystEngComm* 19 (2017) 4345–4354.
- [53] A.V. Orlov, S.Z. Ozkan, G.N. Bondarenko, G.P. Karpacheva, Oxidative polymerization of diphenylamine: synthesis and structure of polymers, *Polym. Sci. Ser. A* B48 (2006) 5–10.
- [54] A. Balamurugan, M.L.P. Reddy, M. Jayakannan, Carboxylic-functionalized water soluble π-conjugated polymer: highly selective and efficient Chemosensor for Mercury(II) Ions, *J. Polym. Sci. Part A Polym. Chem.* 47 (2009) 5144–5157.
- [55] K. Kalyanasundaram, J.K. Thomas, Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems, *J. Am. Chem. Soc.* 99 (1977) 2039–2044.
- [56] G.G. Rao, G.S. Sastry, Titrimetric determination of ascorbic acid with cerium(IV) sulphate, *Anal. Chim. Acta* 56 (1971) 325–328.
- [57] Y.E. Yan, F.W. Schwartz, Oxidative degradation and kinetics of chlorinated ethylenes by potassium permanganate, *J. Contam. Hydrol.* 37 (1999) 343–365.
- [58] G.G. Rao, Potassium dichromate as an oxidimetric reagent, *Talanta* 13 (1966) 1473–1495.
- [59] W.S. Syrokomy, V.V. Stiepin, New oxidation—reduction indicators. I. Phenylanthranilic acid (o-Diphenylamine carbonic acid), *J. Am. Chem. Soc.* 58 (1936) 928–929.
- [60] K. Sriramam, Some observations on the redox behaviour of N-phenylanthranilic acid indicator in iron(II) titrations, *Talanta* 20 (1973) 383–390.
- [61] M. Kolthoff, L.A. Sarver, Properties of diphenylamine and diphenylbenzidine as oxidation-reduction indicators, *J. Am. Chem. Soc.* 52 (1930) 4179–4191.
- [62] E. Bishop, L.G. Hartshorn, Some observations on oxidation - reduction indicators of the benzidine, naphthidine and diarylamine types, *Analyst* 96 (1971) 26–36.
- [63] M. Lederer, F.L. Ward, The oxidation of the tolyl-anthranilic acids, *Anal. Chim. Acta* 6 (1952) 1–6.
- [64] H. Rashidi Nassab, A. Souri, A. Javadian, M.K. Amini, A novel mercury-free stripping voltammetric sensor for uranium based on electropolymerized N-phenylanthranilic acid film electrode, *Sens. Actuators B Chem.* 215 (2015) 360–367.
- [65] M. Hengchang, Z. Zhongwei, J. Yuanyuan, Z. Lajia, Q. Chunxuan, C. Haiying, Y. Zengming, Y. Zhiwang, L. Ziqiang, Triphenylamine-decorated BODIPY fluorescent probe for trace detection of picric acid, *RSC Adv.* 5 (2015) 87157–87167.
- [66] J. Keizer, Nonlinear fluorescence quenching and the origin of positive curvature in stern-volmer plots, *J. Am. Chem. Soc.* 105 (1983) 1494–1498.
- [67] H. Borsook, G. Keighley, Oxidation-reduction potential of ascorbic acid (vitamin C), *Proc. Natl. Acad. Sci.* 19 (1933) 875–878.