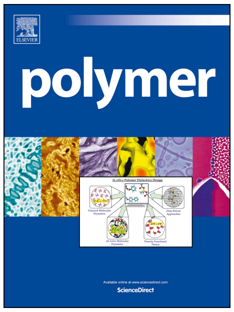

Catalytically active hybrid Polyurethane with tetraaniline pendant groups: Synthesis, properties and self assembly

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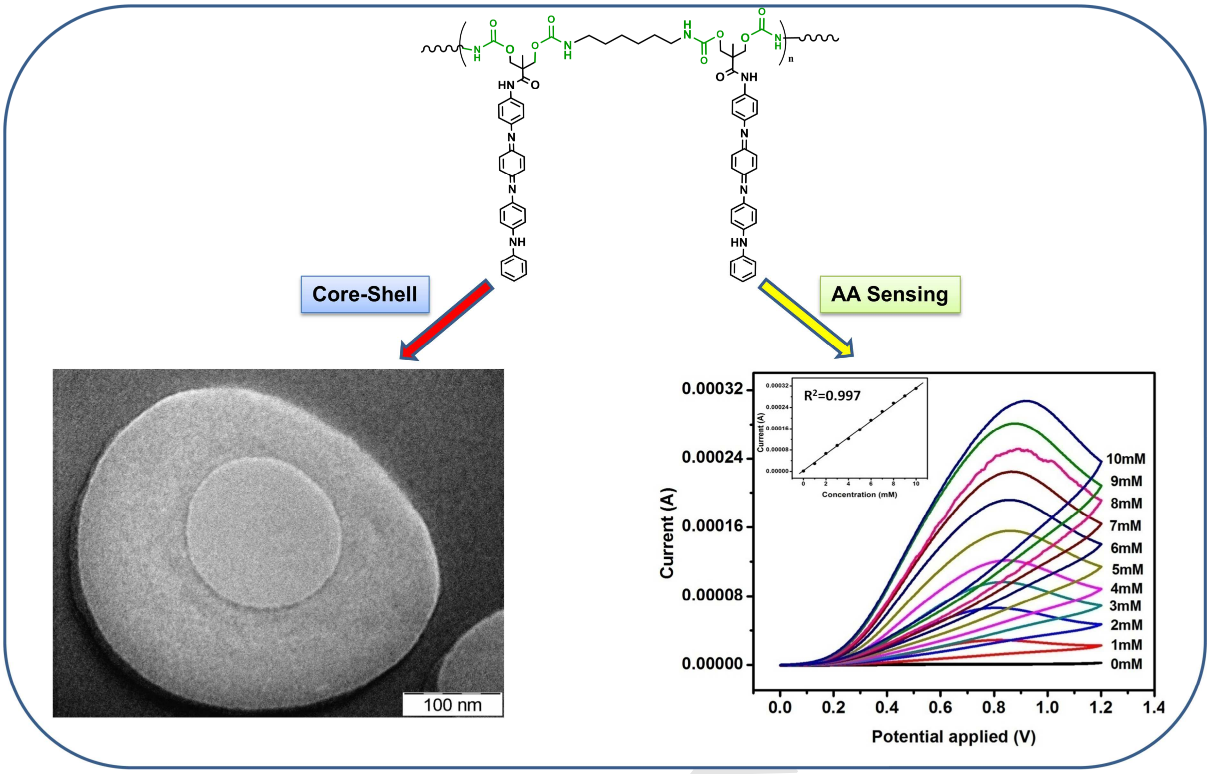
Core-Shell
AA Sensing
100 nm
R²=0.997
Concentration (mM)
Current (A)
0.00032
0.00024
0.00016
0.00008
0.00000
10mM
9mM
8mM
7mM
6mM
5mM
4mM
3mM
2mM
1mM
0mM
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Potential applied (V)

Catalytically active hybrid Polyurethane with tetraaniline pendant groups: Synthesis, properties and self assembly

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Abstract: For the first time we report a novel hybrid polyurethane synthesized from tetraaniline-diol (TAni-$(OH)_2$) and hexamethylene diisocyanate (HMDI) with pendant tetraaniline units on the back bone. The striking property of this unprecedented polyurethane is its electrochemical sensing of ascorbic acid and self assembly into core-shell type microstructures (microcapsules) in presence of aqueous acetic acid /n-octane interface. These microcapsules exhibited a wide range of pH responses in their absorption spectrum. The synthesized polyurethane containing pendant tetraaniline units showed good surface conductivity to the tune of 3.4×10^{-4} S/cm. The electrochemical investigation showed two single electron oxidations and two single electron reductions reversibly. We also investigated electrochemical sensing details of carbon paste electrode (CPE) fabricated with conducting polyurethane (TANI-PU) as ascorbic acid sensor (vitamin C, AA) in 0.2 M and p^H 7 phosphate buffer solution. The fabricated electrode is useful in sensing as low as 1 mM of ascorbic acid. Self-assembly property was probed by optical and TEM studies which established the core-shell structure of the assembled species. The self assembled microcapsules exhibited pH dependent doping and dedoping processes as established by UV-Vis study.

Keywords: tetraaniline, polyurethane, microcapsules, electrochemical sensing, cyclic voltammetry.

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1. Introduction:

Polyaniline (PANI) attracted considerable attention owing to its facile synthesis, excellent environmental stability, tunable electrical conductivity, and unique redox properties [1-3], with potential uses in energy storage applications [4-5] chemical sensors [6-10] supercapacitors [11]. Poor processability of PANI in common organic solvents rendered limited practical application in many fields [12]. Nevertheless, the untiring efforts by scientists worldwide put polyaniline back into track and enriched the field [13-16]. The scope for applications of polyaniline is widened by compositing with metal nanoparticles, metal oxides or carbon materials such as carbon nanotubes [17-19]. This new type of hybrid nanocomposite material may have numerous applications in nanotechnology, gas sensing, and catalysis. In recent years oligoanilines have attracted more attention due to their well-defined structure, easy functionalisation and most importantly for good processability in common organic solvents. Oligoanilines are model compounds of polyaniline (PANI) and they have similar redox property as polyaniline [20-26], with an edge of having better processability than PANI. Like polyaniline, oligoanilines (eg, tetraaniline, TAni) too exhibit three oxidation- states, namely, luecoemeraldine(LE), half oxidized emeraldine base(EB) and fully oxidized pernigraline (PE) and transition between each of them is possible either by chemical or electrochemical manipulations. Incorporation of these oligoanilines into the conventional polymers renders the latter into conducting and electroactive [27]. Wei and co-workers [28] prepared an electroactive and biodegradable polylactide- b-(ANI)5-bpolyactide(PLA-b-(ANI)5-b-PLA) film useful for tissue engineering. Polystyrene based, tetraaniline (TAni) terminated "star"-shaped polymer has been studied [29] for the electrochemical activity. Electrochromic properties have been studied [30] for poly(arylene ether sulfone) containing TAni. Electrochemical [31] and conductivity studies [32] on poly (methacrylamide) containing four and five aniline units have been reported. Of late, self assembly of oligoanilines has also become a focused area and few interesting reports are available [25, 26, 33, 34]. Few reports on synthesis and self assembly of oligoaniline containing polymers such as copolymers of PEG1500 [35], PEG750 [36], PEO [37] are known in literature.

Polyurethanes are versatile materials due to [38] their various applications as adhesives, elastomers, coatings for textiles/paper, foot wear, furniture/foams, packaging material, automotive finishes [38,39] and even as biomaterial [40] for catheters, peritoneal dialysis and infusion pumps to implanted pacemaker parts. To further widen its applications, there have been attempts to bring conductivity and electrochemical activity to this insulating polymer and recently this subject has been thoroughly reviewed [41]. There is no report available in literature in which tetraaniline is bonded via a –O-C(=O)-NH- (urethane) bond to give polyurethane. In this work first time we synthesized a polyurethane, TANI-PU with pendant tetraaniline units in the back bone using new diol made from tetraaniline [TAni-$(OH)_2$] with hexamethylene diisocyanate (HMDI). The results are presented and discussed below.

2. Experimental section:

2.1 Materials: Hexamethylene diisocyanate (HMDI), 2,2-bis(methoxyl)propionicacid(BMPA), dicyclohexylcarbodimide (DCC), dibutyltin dilaurate (DBTL), dimethylamino pyridine (DMAP), p-toluene sulphonic acid (PTSA), N-phenyl-p-Phenylene diamine, paraffin oil, fine graphite were procured from Aldrich Chemicals, USA and used as received. Aceticacid, n-octane, ferric chloride, hydrochloric acid, dry THF, acetone, dichloromethane, methyl ethyl ketone (MEK), N-methyl-2-pyrrolidone (NMP), methanol, and toluene were obtained from SD FINE chemicals, India, and were used as received. Isopropylidene-2,2-bis(methoxyl) propionicacid (compound-1) was prepared from literature [42]. Tetraaniline (TAni) was synthesized according procedure available in the literature [43]. The synthesis of TAni-$(OH)_2$ has been carried out according to the procedure depicted in Scheme-1 and is described below.

2.2 Synthesis of isopropylidene-2, 2-bis (methoxyl) propionicacid (compound-1)

To a stirred solution of B-MPA (10 g, 74.5 mmol) in 100 mL dichloromethane was added 2,2-dimethoxypropane (50 mL) and PTSA (catalytic amount, 10 mg) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 7 h. Then the reaction mixture was quenched with saturated sodium bicarbonate solution by bringing the pH to 7. The two layers were separated and the aqueous layer was extracted with dichloromethane. The combined dichloromethane fractions were dried over anhydrous Na_2SO_4. The dichloromethane was removed under reduced pressure. The compound 1 (9.54 g) was obtained as white crystals.

2.3 Synthesis of compound 2 and final compound TAni-$(OH)_2$

To a stirred solution of compound-1 [1 g, 1equivalent (eq.)], DCC (1.04 eq.) and DMAP (catalytic amount, 10 mg) in dry THF (30 ml) (for 30 min at 0^{o} C), tetraaniline (2.091 g, 1eq.) dissolved in dry THF (20 ml) was added slowly at room temperature under nitrogen atmosphere. After complete addition of tetraaniline (TAni), the mixture was stirred for another 10 h under nitrogen atmosphere. The blueish dicycloxylurea (DCU) precipitate was filtered off and the solvent was removed under reduced pressure. The pure compound 2 was isolated by column chromatography technique (silica gel 60–120 mesh, stationary phase) using 5% ethyl acetate in hexane. The product (2.994 g) was obtained as a blue colour powder.

The compound-2 was taken in 20 mL of methanol solvent and a catalytic amount of PTSA (10 mg) was added at 0^{0}C. The resulting mixture was stirred for 2.5 h under N_2 atmosphere. After completion of the reaction (monitored by TLC), the PTSA was neutralized by adding solid $NaHCO_3$ followed by filtration through sintered funnel under vacuum. The excess solvent was removed under reduced pressure and the crude reaction mixture was purified through column chromatography by eluting with pure ethyl acetate to obtain blue coloured TAni-$(OH)_2$ compound (1.5 g). The structure of the compound was confirmed by mass and NMR spectrum.

^{1}H NMR: (300 MHz, DMSO-d6): δ 8.31(s, 1H,-NH- CO-), δ 6.92(m, 3H, -Ar-), δ 6.54 (d, 4H, -Ar-), δ 6.31 (t, 1H,-Ar-), δ 6.21(m, 6H, -Ar-), δ 6.03(t, 2H, -Ar-), δ 4.07(s, 2H,-CH2-OH), δ 2.71(s, 4H, -CH2-O), δ 1.64(s, 3H, -C-CH3).

ESI-MS: m/z value at 482 (M+1 peak).

2.4 Preparation of Polyurethane with pendant tetraanilines (TAni-PU):

Synthetic scheme for TAni-PU is shown in Scheme-2 and the procedure is described below.

TAni-(OH) $_{2,}$ (0.480 g, 1eq.) was taken in methyl ethyl ketone (MEK) and NMP (3:1) solvent in a double neck round bottom flask. To this mixture, 0.214 g (1eq.) of hexamethylene diisocyanate was added. This mixture was kept in oil bath under N_2 atmosphere at 60°C. The total reaction mixture stirred over night at room temperature, until NCO became zero by which time polyurethane with tetraaniline pendants (TAni-PU) was formed. The polymer formation was conformed by IR, NMR spectroscopy. The obtained TAni- PU was doped with PTSA ($TAni_{inpolymer}$: PTSA = 1:2 ratio) by stirring in aqueous solution of PTSA and filtering the product.

^{1}H NMR: (300 MHz, DMSO-d6): δ 8.32 (s, -NH- CO- in urea groups), δ 6.8-6.1(m Ar-H), δ 4.85 (t, -CH_2-NH-CO methylene attach amide), δ 2.1(s, -CH_2-O), δ 1.84 (s, -CH_3 in TAni-(OH) 2), δ 1.9- 1.3 (m, -CH_2-).

MALDI-TOF(supp. Material): (THF mixed solvent) Average mol. Wt: 2913 with 142 m/z as fragmenting units. The polydispersity is 2.02 (GPC, THF).

2.5 Preparation of TAni-PU carbon paste electrode

The carbon paste electrode (CPE) was prepared by mixing 100 mg of TAni-PU, 150 mg of fine graphite powder and 100 µL of paraffin oil placed in an agate mortar, using a pestle to obtain homogeneous carbon paste. The homogeneous carbon paste was inserted into two open end Teflon tube with Φ = 5 mm. A copper wire (5 cm length) was inserted into the filled teflon tube to make electrical contact. Finally the bottom portion of teflon tube was cut with the help of scissors for the activated surface of CPE. This carbon paste electrode was used for cyclic voltammetry for electrochemical sensing of ascorbic acid.

2.6 Preparation of electroactive microcapsules of TAni-PU

Electroactive microcapsules were prepared by adopting closely related procedure [44]. Scheme-5 is the schematic diagram showing microcapsules formation. The synthetic procedure is given below.

Fine TAni-PU (about 2 mg) powder was dispersed in 4.0 ml of glacial acetic acid and mixed with 1.0 ml of n-octane. This mixture was shaken for 2 minutes and centrifuged at 4000 rpm for 7 min to remove undissolved particles. The supernatant liquid was collected into a dialysis bag and dialyzed in 1 L beaker which contained distilled water under constant stirring. The dialysis was repeated three times for every three hours with fresh distilled water, until the distilled water reached a pH value of 7. The product was analyzed by optical microscope and TEM.

2.7 Characterization methods

Characterization of TAni-PU powder and self assembled microcapsules were done by, FT-IR spectra (Perkin Elmer Spectrum-100 spectrometer using KBr pellet). Each sample was scanned 8 times with resolution, 4 cm^{-1} and averaged to obtain the spectrum. All the spectra were scanned within the range 400-4000 cm^{-1}. The ^{1}H NMR spectra were recorded in DMSO-d^{6} solvent using a Varian-Inova-300 MHz spectrometer. Chemical shifts (δ) are given in ppm with tetramethylsilaneas a standard. UV-Vis spectral measurements were carried out on a Spectro UV-Vis Double Beam PC-8 Scanning Auto cell, LABOMED INC. Thermo gravimetric analyses of polymer samples were carried out using TA Instruments (TGA Q500 V20.8, USA) from ambient to 700 ^{o}C under nitrogen atmosphere at a heating rate of 10 ^{o}C per minute. Differential scanning calorimetry analyses of polymer sample were carried out using TA Instruments (DSC Q100 EXFO Series 2000 USA). Powder X-ray diffraction patterns (XRD) of TAni and TAni-PU were recorded using Siemens/D-5000 diffractometer with Cu-K-apha radiation (l = 1.5406 Ǻ). The MALDI-TOF analysis of the TAni-PU was carried out on Shimadzu Biotech Axima with linear mode and a nitrogen laser (λ) 337 nm). The radiation target prepared from tetrahydrofuran (10mg/1ml THF) solution with 0.1% dithranol as matrix and sodium trifluoroacetate in THF. Cyclic voltammetry (CV) was performed using AUTOLAB-302N-potentiostat-galvanostat equipped with FRA32M module in a three-electrode electrochemical cell using SCE as the reference electrode and platinum wire as the counter electrode. A Pt electrode was used as working electrode (12 mm x12 mm) for above three materials (in DMF solvent). GC electrode was used as working electrode for microcapsules. Carbon paste electrode (CPE) was used for AA sensing. All the CV experiments were carried out in 1M H_2SO_4 solution with a scan rate of 100 mV/s. Conductivity of the powder of TAni-PU or TAni-$(OH)_2$ was measured by four probe method using 6220 constant current source and 2182A voltmeter (Keithley, Cleveland, Ohio, USA). Powders of these compounds were pressed into a disk of 13 mm diameter and about 1.5 mm thickness under a pressure of 120 Kg/cm^2 for conductivity measurements. Morphological studies for films were performed using Hitachi 3000N, scanning electron microscope operating at 10 kV. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample from possible charging. Optical microscopy (OM) of the microcapsules was observed by Olympus CKX41 microscope (inverted phase contrast tissue culture microscope with trinocular head and 4x, 10x, 20x and 40x objectives) (USA) instrument. TEM experiments were conducted on PHILIPS TECHNAI FE12 instrument at 120 kV after casting a drop of well dispersed dilute samples on copper grids.

3. Results and discussions:

3.1 Synthesis of hybrid polyurethane TAni-PU: Tetraaniline was functionalised with diol group using reaction sequence shown in scheme-1 and was characterized by FT-IR and ^{1}H

NMR spectroscopy. All the peaks are identified in NMR spectrum (Fig.S1 (a) supporting data) and ESI –mass spectrum (Fig.S2 supporting data) gave M+1 peak expected at 482. The functionalized diol was used for the synthesis of polyurethane TAni-PU which possesses pendant tetraaniline units (scheme-2). The synthesis of TAni-PU was carried out as described in experimental section. The formed TAni-PU was precipitated in large quantity of water and oven dried at 50 ^oC for 12 h. The product was characterized by FT-IR and UV-Vis spectroscopy as discussed below. Molecular weight of the polymer was estimated by MALDI-TOF as 2913. The difference between each peak is 142 m/z assignable to loss of urethane linkage, $-C(O)-NH-(CH_2)_6-NH-$ as shown Fig.S4 (supp. Material). The GPC found polydispersity is 2.02. The low molecular weight of the polymer is due to the bulky tetraaniline group that restricts the polymerisation.

3.2 FT-IR analysis

The diol, $TAni(OH)_2$ gave coupled (OH +NH) peaks (Fig.1) appearing as doublet at 3384 cm^{-1} and 3338 cm^{-1} , C-H stretching vibration at 2926 cm^{-1}, N-Q-N at 1596 cm^{-1} (B refers to benzenoid and Q refers to quinoid ring). The carbonyl stretching (in amide functionality) is seen at 1720 cm^{-1}. When doped with PTSA, the diol showed N-Q-N and N-B-N bands at 1574 cm^{-1}, 1507 cm^{-1} respectively with intense band at 1037 cm^{-1} attributable to SO_3^- anion**.** The peaks at 1306, 1158 and 801 cm^{-1} are due to C-N stretching vibration of secondary aromatic amine, aromatic-in-plane blending modes and C-H out of plane bending vibrations of ortho and para aromatic substituted benzene rings respectively. The spectrum was modified considerably for the polyurethane TAni-PU, particularly in 1700-1500 cm^{-1} region. There is overlap of peaks due to N-Q-N of tetraaniline segments and amide-II mode. The band due to N-B-N is clear and distinguishable at 1505 cm^{-1}. For doped polyurethane, N-Q-N (with amide-II) and N-B-N bands were observed at 1573 cm^{-1} and 1509 cm^{-1} respectively. The prominent peaks are listed in Table 1, with their assignments.

3.3 Electronic spectroscopy (UV-VIS)

UV–Vis electronic spectroscopy is a valuable tool for conducting polymers and their composites for identifying the conducting and insulating states. Electronic absorption spectra were recorded for all the samples in the range 250–900 nm. For this purpose TAni-PU and TAni-PU-doped powders were taken in DMF solvent (5 mg compound per 20 ml of DMF). The spectra are shown in Fig.2 (a) (data in Table 2)**.** For doped TAni-PU sample, the spectra showed bands at 589, 428 and 313 nm due to the presence of conducting TAni-PU-PTSA. The undoped (pure) polymer showed bands at 321 and 592 nm. The band 321 nm can be assigned to $\pi \rightarrow \pi^*$ transition of benzene rings and band at 592 nm can be ascribed to benzenoid to quinoid ($\pi_B \rightarrow \pi_Q$) excitonic transitions [45]. The new absorption band emerged at 428 nm in the PTSA doped sample is attributed to polaron → π^* [44].

3.4 Conductivity and Surface morphology

The interesting feature of the conducting polyaniline is its electronic conductivity and redox properties. Similar to the polyaniline, tetraaniline is also known for its electronic conductivity and reversible electron transfer property. For understanding its conducting behaviour, the pure TAni-$(OH)_2$ was also doped by PTSA. The conductivity as determined from its pressed pellet is 1.83 x10^{-3} S/cm, which is lower than conductivity of TAni-PTSA (8.0 x10^{-3} S/cm). The conductivity of doped polyurethane, TAni-PU is still lower, 3.42 x10^{-4} S/cm (Table 2). It is understandable that conductivity achieved by the TAni-$(OH)_2$-PTSA is found to be higher when compared to TAni-PU-PTSA system. This is believed to be due to the presence of urethane segments in TAni-PU system. Though the conductivity of the TAni-PU-PTSA system is lower than pure PAni or its composites [17, 18], the present investigation paves a way to impart conductivity to the otherwise insulating polyurethane to the tune of x10^{-4} S/cm.

The surface morphology of the undoped and doped TAni-PU polymer was examined by scanning electron microscopy. The microscopy revealed rough topology with fibres and granules surfacing on the top for the as prepared (undoped) TAni-PU. Interesting morphology changes occurs when the polymer is doped by PTSA. Regular and perfectly shaped spherical globules are developed after doping [Fig.3 (a), (b)]. The spherical globule formation took place because of hydrophobic nature of polyurethane particles and severe stirring conditions, the doped polymer transformed into spherical structure. The spherical structures, for example as shown in Fig.3 (c), (d) are found in different diameters in the range 0.15 um, 0.35 um, 0.44 um, 0.65 um and the biggest diameter is 1.1 um. These SEM probed particles are found to be in bigger size compared to TEM probed sample which is primarily due to low concentration and well dispersion by heavy sonication. These spheres are 96 nm, 130 nm [Fig.3, (e)] or slightly more 100 nm, 104 nm 150 nm or 168 nm [Fig.3 (f)].

TAni gave mixed sharp and broad XRD peaks (Fig.S3, supplementary material) suggesting that it is semi crystalline in nature. Based on closely related urethane compound [46], two peaks at $2\Theta = 19.687$ (d= 4.505 A^0) and $2\Theta = 26.47$ (d= 3.36 A^0) in the TAni difractogram can be assigned to periodicity parallel to the polymer chain. The latter peak is due to possible π-π stacking in TAni. Similarly TAni-PU gave new peaks (Fig. S3, supplementary material) along with some overlapping with TAni. The peak at $2\Theta = 20$ is due to the periodicity parallel to the polymer chain [47] and peak at $2\Theta = 23.57$ may be due to π stacking in the polymer [46].

3.5 Thermal characteristics

TGA profiles of TAni-$(OH)_2$ and TAni-PU (undoped state) are shown in Fig. 4(a) along with the starting material TAni and data is collected in Table-3. TGA data such as initial decomposition temperature (T_{1on}), first step final degradation (T_{1max}), second degradation onset (T_{2on}), final degradation (T_{2final}) and % wt remaining at 700 ^{o}C are given in the table. The starting material TAni showed three step decomposition pathways between 207-375 ^{o}C (first), 380-512 ^{o}C (second) and 520-700 ^{o}C (third). The three stage losses are due to the disintegration of TAni chain, similar to literature observation[48]. From the derivative curve of the TGA profile, the maximum losses of the mass occur at 345 ^{o}C, 483 ^{o}C and 645 ^{o}C respectively for the three degradations. TAni-$(OH)_2$ also degraded in three steps as suggested by its derivative curve (Table 6, Figure 4) and these occur at lower temperatures than TAni. The onset of the first degradation is at lower temperature (125 ^{o}C) which we presume due to the loss of amide functional group containing two hydroxyl groups. The second and third degradations are similar to TAni. TANi-PU showed a three-step decomposition profile with an initial decomposition temperature starting around 150 ^{0}C which is presumably due to scission of urethane bond between TAni and –(CH_2)- groups. The latter weight losses are due to degradation of TAni chain. TGA analysis on doped TANi-PU suggested the loss of doped PTSA in the range 250-320 ^{0}C. The thermal stability (temperature at 5wt% loss) of the TAni-PU (202 ^{0}C) is higher than TAni-$(OH)_2$ (153 ^{0}C).

The compounds TAni, TAni-$(OH)_2$ and TAni-PU (undoped) were also characterized by DSC technique (Fig. 4(b) ,Table-3). The DSC curve showed that there is a glass transition temperature (T_g) for the oligomers TAni and TAni-$(OH)_2$ at 78.4 ^{0}C and 44.9 ^{0}C respectively. The curves also exhibited exothermic peaks suggesting on set of decomposition at 136 ^{0}C and 131 ^{0}C respectively. The glass transition further decreased to 41 ^{0}C in the polymer TAni-PU due to the introduction more flexible -(CH_2)- segments. The curve also exhibited a well-resolved melting peak at 72 ^{0}C for TAni-PU. The polymer did not show any decomposition trend upto 150 ^{0}C, like its oligomeric precursors.

3.6 Redox properties

Cyclic voltammetry (CV) is widely used to characterize the electrochemical properties of conducting polyaniline. TAni, TAni-(OH)$_2$ and TAni-PU were characterized by cyclic voltammetry (CV) using a three-electrode electrochemical cell(data in Table 2). As shown in Fig. 5, two oxidation peaks at 0.286 (peak1) and 0.540V (peak 2) observed for TAni**.** This result is similar to the results observed in literature [37, 49], which displayed two reversible oxidation peaks corresponding to two one-electron-transfer processes. A reduction peak in the middle is also observed and attributable to impurities (benzoquinone). TAni-(OH)$_2$ was also investigated for the electrochemical activity. Similar two step electrochemical oxidations for TAni-(OH)$_2$ was observed as shown in Fig. 5. The first and second oxidation takes place at lower potential 0.249, at 0.445 V which suggests easy oxidation. Similarly the first and second oxidation peaks for TAni-PU are observed at 0.246 V and 0.445 V, very close to TAni-(OH)$_2$. The peak current of TAni is higher compared to TAni-(OH)$_2$ and which in turn is higher when compared to TAni-PU. This is due to increasing the aliphatic groups in TAni-(OH)$_2$ or backbone of TAni-PU. The oxidation peaks correspond to the transitions from leucoemeraldine base (LEB) to emeraldine base (EB) oxidation state and EB to pernigraniline (PA) oxidation state, respectively. The molecular structures of TAni-PU in various oxidation states are shown in Scheme 3.

3.7 Ascorbic acid sensing

Ascorbic acid (vitamin C, AA) is a naturally occurring organic compound which is mainly present in many food-stocks like fruits and vegetables. AA is a mild reducing agent, antioxidant and prevents many diseases. Some authors reported sensing behavior of AA by polymeric systems [50-55] due to its technological and biological importance. Electrochemical method is reliable and rapid for AA determination. In this work we have demonstrated the practical application of the new polyurethane TAni-PU as modified electrode for electrochemical sensing of AA. A modified electrode (carbon paste electrode, CPE) was prepared by taking fine graphite powder, TAni-PU and paraffin oil, as described in experimental section. The CPE exhibited one oxidation peak at 0.59 V and a reduction peak at 0.296 V [Fig. 6(a)] in 1M sulphuric acid. In presence of high background current from graphite, the two oxidation waves and two reduction peaks of pure TAni-PU coalesce to give single redox couple. Fig. 6(b) shows cyclic voltammograms of modified CPE at different AA concentrations (1-10 mM) in 0.2 M and pH 7.0 phosphate buffer solutions at 100 mV/s. One oxidation peak observed at 0.8 V. By increasing the concentration of AA, the peak current also increased. There is a linear relationship established between peak current versus concentration of AA (in inset, R= 0.997 and n= 11). The mechanism of sensing by TAni-PU is shown in Scheme- 4. The oxidation of AA to dehydroascorbic acid involves transfer of two electrons. AA is oxidized to dehydroascorbic acid losing two electrons and two protons, which are received by TAni-PU (EB) and result in concomitant reduction of TAni species into leucoemeraldine-PU (LE-PU). The LE-PU is externally oxidized to EB-PU state and is ready for the use in next cycle. To the best of our knowledge, the present TAni-PU system is first electrocatalytic polyurethane known in the literature that is useful for sensing AA.

3.8 Self assembly of TANI-PU into shells with liquid core:

The interesting property of TAni-PU, noticed by us, is its self assembly into core-shell type microspheres (microcapsules). The polymer forms thick shell around liquid core such as n-octane. Tetraaniline segments in TAni-PU are amphiphilic which are composed of a hydrophobic benzene ring and a hydrophilic amino group. In the self-assembly process, they can orderly aggregate into a nanostructure driven by hydrogen bonding and pi–pi stacking [56]. As shown scheme-5, when TANi-PU dissolved in glacial acetic acid was mixed with n-octane [scheme-5(a)], shaken and dialyzed, various sizes of microcapsules were formed [schem-5(b)]. Acetic acid and n-octane form two phases (water and oil). TAni-PU dissolves in acetic acid and also gets doped. When shear force, such as shaking is applied (1 minute, in the present case) on the system, the two phases break to form emulsion with different globule sizes of n-octane followed by immediate formation of shell by TANi-PU on the outer surface of n-octane.

The optical micrographs of the sphere s after dialysis are shown in Fig. 7. The TEM pictures are shown in Fig. 8 (a-f). TEM analysis on the microcapsules showed that the shell thickness and size of the capsules is varying. For example, Fig. 8(d) shows that the microcapsule is really a sphere with shell (TAni-PU) thickness of 50 nm and the liquid core (n-octane) diameter is about 180 nm. Fig. 8 (e) shows uniform sphere with about 60 nm thick shell with 233 nm core. Fig. 8 (f) is an egg-shaped capsule with thicker shell of 50-120 nm and a core of 165 nm. If the stirring/shaking is done for longer periods and vigorous, smaller and uniform sized microspheres are formed.

FT-IR spectrum of the microcapsules showed band at 1702.46 cm^{-1}. Gradual decrease in the intensity of the peaks in the range 1598-1500 cm^{-1} for TAni-PU doped and for final microcapsules was observed; this is caused due to doped TAni-PU-ES state. A strong band is observed at 1668 cm^{-1} in microcapsules spectrum [44], indicating that carboxylic anions are present in the microcapsules, as counter ions.

The microcapsules exhibited pH dependent changes in their visible spectra. As shown in Fig. 2(b) (Inset), the blue microcapsule dispersion turned violet when exposed to ammonia solution and regained its green colour when exposed with an acid. This suggests that doping-dedoping process is still retained in microcapsules. UV-VIS data of microcapsules showed main peaks at 315 and 602 nm. These have been assigned to $\pi \rightarrow \pi^*$ transitions of benzenoid rings and exciton bands. In doped microcapsules main bands are showed at 318, 425 and 638 nm which are assigned to the $\pi \rightarrow \pi^*$, polaron- π^* and π-polaron transitions respectively. The adsorption band observed in TAni-D at 769 nm is absent in the UV-spectra of TAni-PU-D and microcapsules. This is because TAni is monodisperse with definite molecular weight, we could calculate the amount acid needed for the full doping. The same amount of acid was not sufficient for full-fledge doping of polymers TAni-PU or its microcapsules. Hence we could not see the shift of 638 nm band to 769 nm. The UV-Vis data is collected in Table 2.

CV of core-shells on GC showed, one oxidation and a reduction peaks at 0.392, 0.291 V respectively as shown in Fig. 9. The oxidation peak correspond to the transitions from leucoemeraldine base (LEB) to emeraldine base (EB) oxidation state, further oxidation to pernigraline state is not achievable suggesting a thick, compact and rigid core-shell structure.

4. Summary and Conclusions

The amino group in tetraaniline has been successfully functionalized with a diol group and characterized. A new and hybrid polyurethane with pendant tetraaniline units has been synthesized from the new diol and HMDI. The new polyurethane is conducting to the level of 10^{-4} S/cm when doped with PTSA and also undergo two oxidations and subsequent reductions electrochemically. This novel material, in the form of a modified carbon paste electrode can sense ascorbic acid electrochemically in 0.2 M and pH 7.0 phosphate buffer. In this article new electroactive TAni-PU based core-shell microcapsules in a simple one-pot method is also described; microcapsules are prepared in a facile way by self-assembly of acetic acid dissolved-TAni-PU and n-octane. Optical microscopy (OM) of the resulting dispersion conformed that the microstructures are microspheres with TAni-PU as shell and n-octane core. TEM study further proved that the shells formed by TAni-PU are rather thick (50-60 nm) with a 180 nm core of n-octane. This investigation provided further insight into methods to prepare core-shell microcapsules and offer potential application in encapsulation, drug delivery and coatings.

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REFERENCES:

[1] D.K. Moon, M. Ezuka, T. Maruyama, K. Osakada, T. Yamamoto, Macromolecules 26 (1993) 364–369.

[2] A.G. MacDiarmid, Angew. Chem. Int. Ed. 40 (2001) 2581–2590.

[3] A.J. Heeger, Angew. Chem. Int. Ed. 40 (2001) 2591–2611.

[4] K. Wang, J. Huang, Z. Wei, J. Phys. Chem. C 114 (2010) 8062 – 8067.

[5] D. Belanger, X.M. Ren, J. Davey, F. Uribe, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 2923–29.

[6] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, J. Am. Chem. Soc. 125 (2003) 314.

[7] B. Mates, M. Anderson, J. Conklun, H. Reiss, R. Kauer, Synthetic Metals 55 (1993) 36.

[8] E.S. Matveena, R.D. Collega, Synthetic Metals 76 (1996) 127.

[9] S. Koul, S.K. Dhawan, S. Chandra, R. Chandra, Indian Journal of Chemistry 36A (1997) 901.

[10] S.K. Dhawan, D. Kumar, M.K. Ram, S. Chandra, D.C. Trivedi, Sensors & Actuators B 40 (1997) 99.

[11] Y.G. Wang, H.Q. Li, Y.Y. Xia. Adv. Mater 18(2006) 2619 –2623.

[12] P.J. Kinlen, B.G. Frushour, Y. Ding, V. Menon, Synth Met. 101 (1999) 758 –761.

[13] J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein, A.G. MacDiarmid, J. Am. Chem. Soc. 113 (1991) 2665.

[14] R. Paulina, C.S. Rodolfo, V.D. Rafael, Synthetic Metals 162 (2012) 794 –799.

[15] K.R. Reddy, K.P. Lee, A.I. Gopalan, Ali Md Showkat, Polym. Adv. Technol. 18 (2007) 38–43.

[16] S. Prakash, C.R.K. Rao, M. Vijayan, Electrochimica Acta 53 (2008) 5704–5710.

[17] K.R. Reddy, B.C. Sin, K.S. Ryu, J.Ch. Kim, Ch. Hoeil, Y. Lee, Synthetic Metals 159 (2009) 595–603.

[18] K.R. Reddy, K.P. Lee, A.I. Gopalan, Colloids and Surfaces A: Physicochem. Eng. Aspects 320 (2008) 49–56.

[19] K.R. Reddy, K.P. Lee, A. I. Gopalan, Min Seok Kim, Ali Md showkat, Young Chang Nho, J Polym Sci Part A: Polym Chem 44(2006) 3355–3364

[20] A.G. MacDiarmid, Synth Metals 84 (1997) 27.

[21] R.H. Baughman, J.F. Wolf, H. Eckhart, L.W. Shacklette, Synth Metals 25 (1988) 121.

[22] Y. Cao, S.Z. Li, Z.J. Xue, D. Guo, Synth Metals 16 (1986) 305.

[23] Z. Wei, Ch.F.J. Faul, Macromol. Rapid. Commun. 29 (2008) 280.

[24] A.G. MacDiarmid, Y. Zhou, J. Feng, Synth Met. 100 (1999) 131.

[25] Y. Wang, H.D. Tran, L. Liao, D. Xiangfeng, R.B. Kaner, J. Am. Chem. Soc. 132 (2010) 10365.

[26] S.P. Surwade, A. Srikanth Rao, D. Vineet, N. Manohar, S. Jain, S. Ammu, S.K. Manohar, J. Am. Chem. Soc. 131 (2009) 12528.

[27] A. Ravi, T. Appa Rao, C.R.K. Rao, R. Narayan, B. Sreedhar, J. Appl. Polym. Sci. 131 (2014) 40794.

[28] L. Huang, J. Hu, L. Lang, X. Wang, P. Zhang, X. Jing, X. Wang, X. Chen, P.I. Lelkes, A.G. MacDiarmid, Y. Wei, Biomaterials 28 (2007) 1741.

[29] D.H. Han, L.P. Yang, X.F. Zhang, C.Y. Pan, Eur. Polym. J. 43 (2007) 3873.

[30] D. Chao, X. Jia, H. Liu, L. He, L. Cui, C. Wang, E.B. Berda, J. Polym. Sci. Part A: Polym. Chem. 49 (2011) 1605.

[31] R. Chen, B.C. Benicewicz, Macromolecules 36 (2003) 6333.

[32] S. Liu, Z.T. Kaizheng, Y. Zhang, Y. Zhu, T.X. Xu, Mater. Lett. 59 (2005) 3715.

[33] Z.D. Zujovic, C. Laslau, T.S. Jadranka, Chem. Asian. J. 6 (2011) 791 – 796.

[34] Y. Zhao, E. Tomsk, J. Wang, Z. Morvkova, A. Zhigunov, J. Stejskal, M.Trchova, Chem. Asian J. 8 (2013) 129 – 137.

[35] L. Huang, J. Hu, L. Le, X. Chen, Y. Wei, X. Jing, Macro. Rapid. Commun. 28 (2007) 1559.

[36] J. Hu, X. Zhuang, L. Huang, L. Le, X. Chen, Y. Wei, J. Xiabin, Langmuir 24 (2008) 13376.

[37] Z. Yang, X. Wang, Y. Yang, Y. Liao, Y. Wei, X. Xie, Langmuir 26 (2010) 9386.

[38] G. Oertel, Polyurethane handbook. Hanser, New York (1985) 629.

[39] M. Szycher, Handbook of polyurethanes. CRC, Massachusetts (1999) 696.

[40] D.K. Chattopadhyay, K.V.S.N. Raju, Prog. Polym. Sci. 32 (2007) 352.

[41] T. Gurunathan, C.R.K. Rao, R. Narayan, K.V.S.N. Raju, J. Mater. Sci. 48 (2013) 67–80.

[42] K.G. Priyanka, A.K. Mishra, K. Sasidhar, N. Ramanuj, K.V.S.N. Raju, J .Appl. Pol .Sci. 126 (2012) 2024–2034.

[43] W.J. Zhang, J. Feng, A.G. MacDiarmid, A.J. Epstein, Synth. Met. 84 (1997) 119.

[44] L.V. Wei, F. Jiangtao, Y. Wei, Ch.F.J. Faul, J. Mater. Chem. B. 2 (2014) 4720 – 4725.

[45] Z. Shao, P. Rannou, S. Sadki, N. Fey, D.M. Lindsay, Ch.F.J. Faul, Chem. Eu. J. 17 (2011) 12512.

[46] U.U. Chinwe, R. Patrice, P.B. Benjamin, O.T. James, Ch.F.J. Faul, J. Mater. Chem. C 1 (2013) 6428 – 6437.

[47] Y. Wang, D.T. Henry, D. Xiangfeng, R.B. Kaner, J. Am. Chem. Soc. 132 (2010) 10365.

[48] K.Basavaiah, A.V. Prasada Rao, e-journal of chemistry 9 (2012) 1175 –1180.

[49] L. Chen, Y. Yu, H. Mao, X. Lu, W. Zhang, Y. Wei, Mater Lett. 59 (2005) 2446 –2450.

[50] A. Malinauskas, R. Garjonyte, R. Mazeikiene, I. Jureviciute, Talanta 64 (2004) 121–129.

[51] Ch.H. Tsao, S.T. Lin, L.C. Yeh, C.A. Chen, H.Y. Huang , Z.Y. Nian, H.H. Chen, J.M. Yeh, Polymer 53 (2012) 4373–4379.

[52] P. Saithip, P.M. Johannes, P. Ditsayut, L. Tanom, T. Adisorn, Electrochimica Acta 133 (2014) 294–301.

[53] A. Ambrosi, A. Morrin, M.R. Smyth, A.J. Killard, Anal. Chim. Acta. 609 (2008) 37–43.

[54] V.L. Reena, J.D. Sudha, K.N. Rohini, K.S. Neethu. J .Appl. Polym. Sci. 131 (2014) 40936.

[55] S. Chen, L. Xu, Y. Yang, B. Li, J. Hou, Anal. Methods 3 (2011) 2374–2378.

[56] Y. Zhao, J. Stejskal, J. Wang, Nanoscale 5 (2013) 2620.

Table-1: FT-IR data of different precursors and polymers

Characteristic Absorption Bands	Peak position (cm^{-1})				
	TAni	**TAni-(OH)$_2$**	**TAni-PU-U**	**TAni-PU-D**	**microcapsules**
N-H Str. Vibrations	3381	3338	3325	3324	3436
C-H stretching Vibrations	3025	2926	2851-2927	2851-2928	2934
Amide I(C=O) stretching Vibrations	--	1720	1706	1696	1722
Amide II (δ_{N-H} + γ_{C-N} + γ_{C-C})	--	--	1573	1573	1498
γ_{C-N}	1289	1300	1300	1310	1388
Amide III	--	--	1172	1154	1100
Amide-iv	--	--	748	750	802
Amide-V	--	--	694	694	663
Carboxylate anion	--	--	--	--	1663

Table-2: UV-Vis, conductivity and electrochemical data

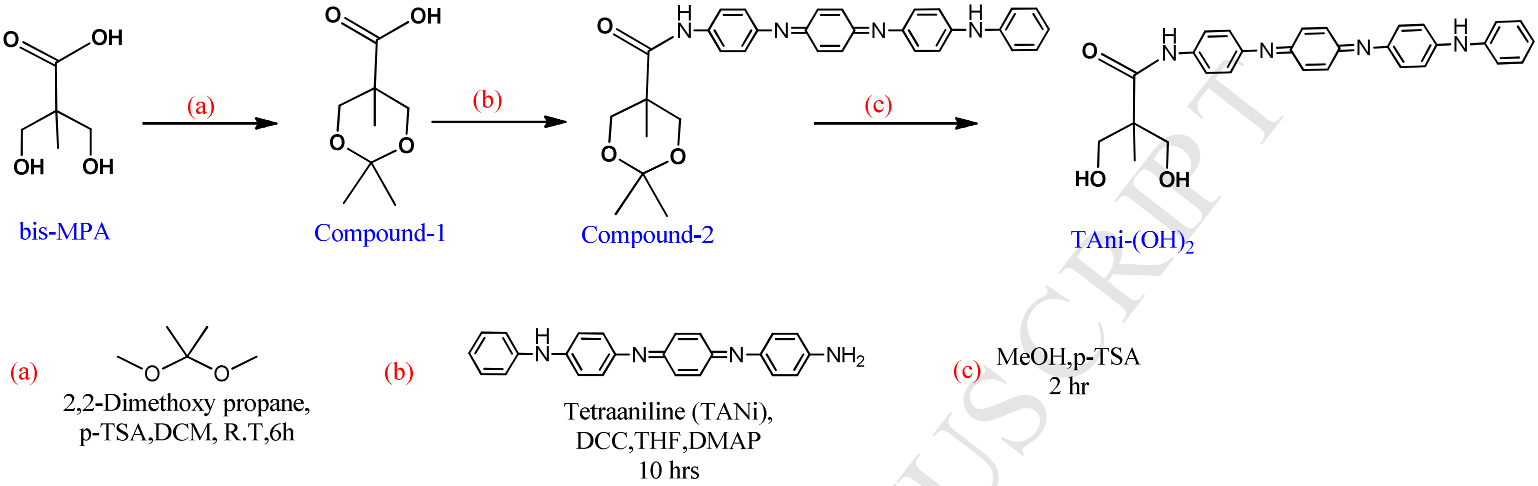
Sample	**UV-Vis (λ_{max},nm)**	**Conductivity(S.cm^{-1}) (Measured as pellet)**	**CV**			
			Oxd1	Oxd2	Red1	Red2
TAni-U	317, 595	--	--	--	--	--
TAni-D	317, 421, 595, 769	8.0 x10^{-3}	0.286	0.540	0.211	0.474
TAni(OH)$_2$-U	--	--	--	--	--	--
TAni(OH)$_2$-D	--	1.83 x10^{-3}	0.246	0.445	0.180	0.368
TAni-PU-U	321, 592	--	--	--	--	--
TAni-PU-D	313, 428, 589	3.42 x10^{-4}	0.245	0.445	0.188	0.394
Microcapsules as prepared	314, 422, 608	--	0.392	--	0.291	--
Microcapsules with NH$_3$	315, 602	--	--	--	--	--
Microcapsules With HCl	318, 425, 638	--	--	--	--	--
CPE	--	--	0.587	--	0.296	--

Table-3: TGA and DSC Data of TAni, TAni-$(OH)_2$ and TAni-PU

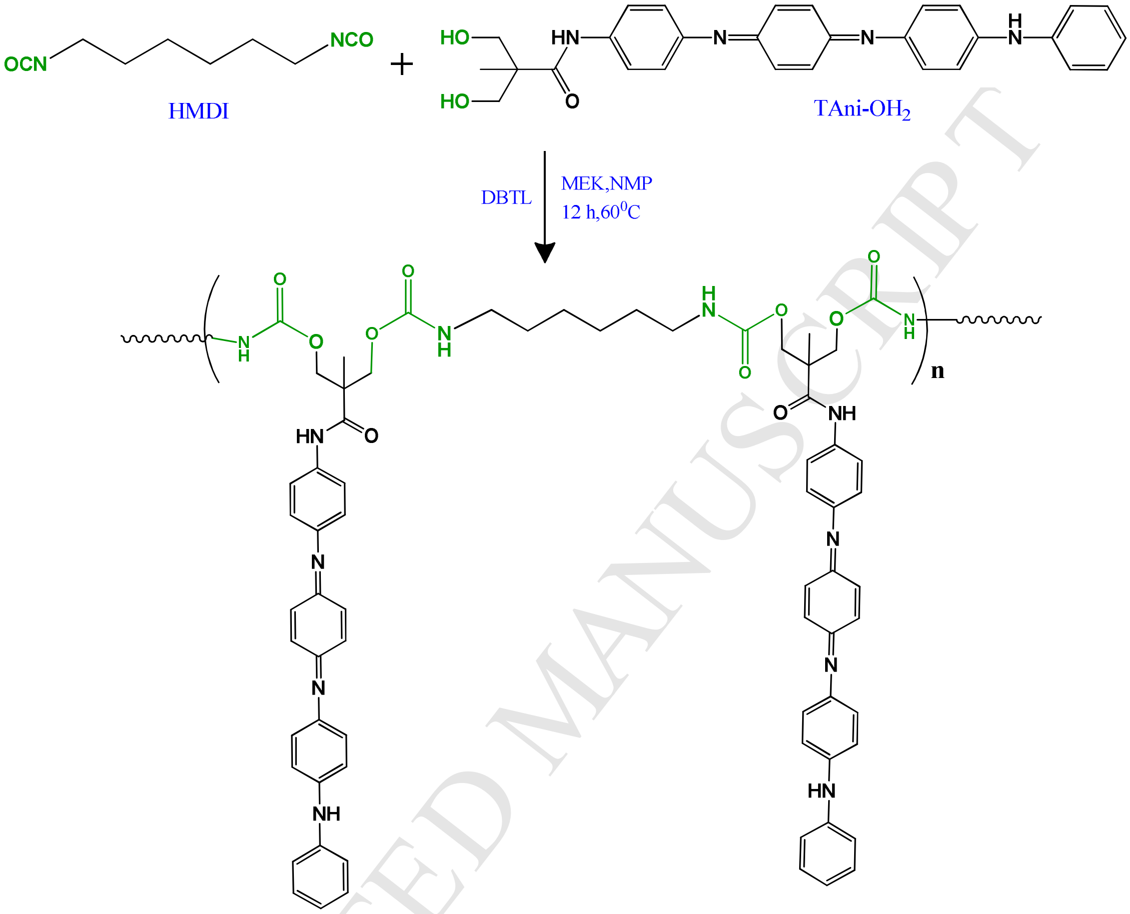
	TGA								DSC	
Sample	**T_{1ON} -T_{1final} (^{o}c)**	**T^*_{1MAX} (^{o}c)**	**T_{2ON}- T_{2final} (^{o}c)**	**T^*_{2MAX} (^{o}c)**	**T_{3ON}- T_{3final} (^{o}c)**	**T^*_{3MAX} (^{o}c)**	**Wt % at 700 ^{o}c**	**Thermal stability temp (^{o}c) (5% loss)**	**Tg (^{o}c)**	**Melting(m) decompose(d)**
TAni	207-375	345	389-533	483	550-650	645	29.0	295	78.4	136 (d)
TAni-$(OH)_2$	125-310	227	325-420	287	420-500	395	20.5	153	44.9	131 (d)
TAni-PU	150-291	279	300-425	374	430-500	450	18.5	202	41.0	72 (m)

T*= Temperature from derivative curve

Scheme: 1 Chemical Synthesis of TAni-(OH)$_2$

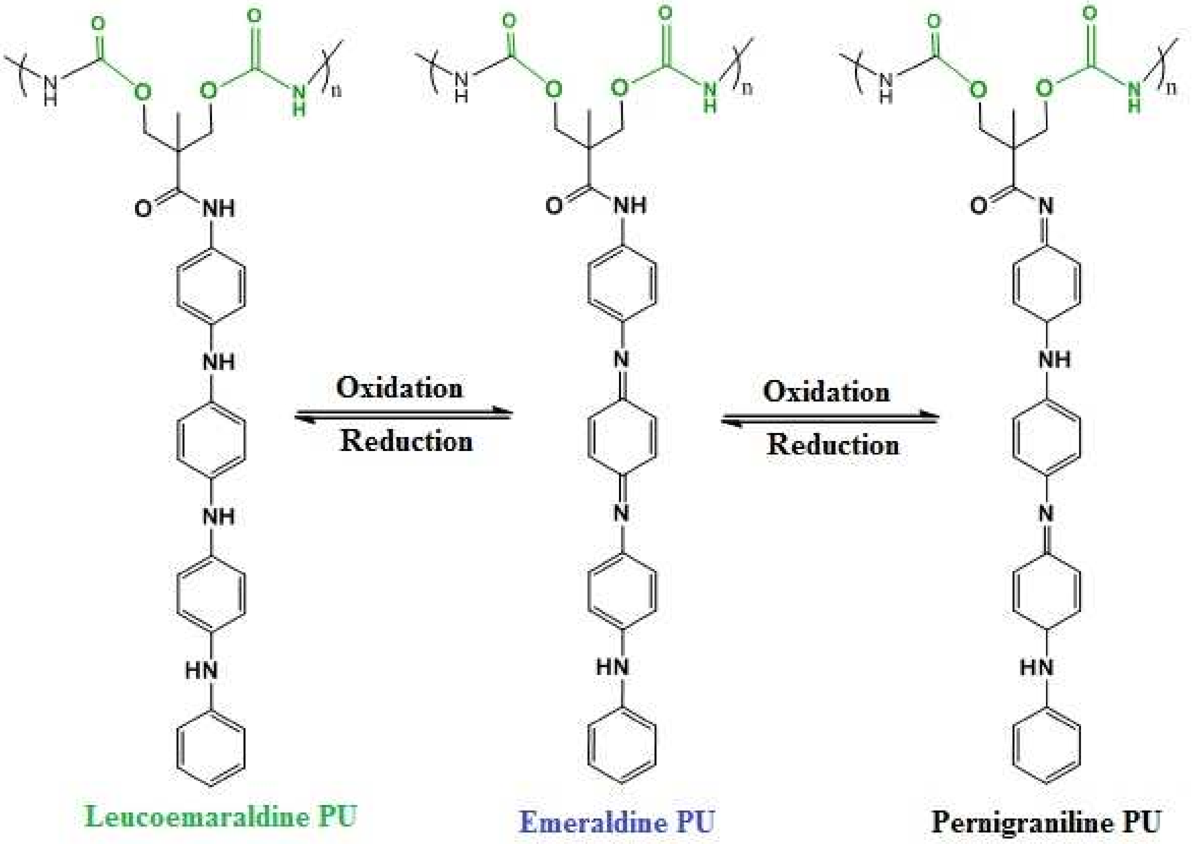


Scheme: 2 Chemical Synthesis of TAni-PU

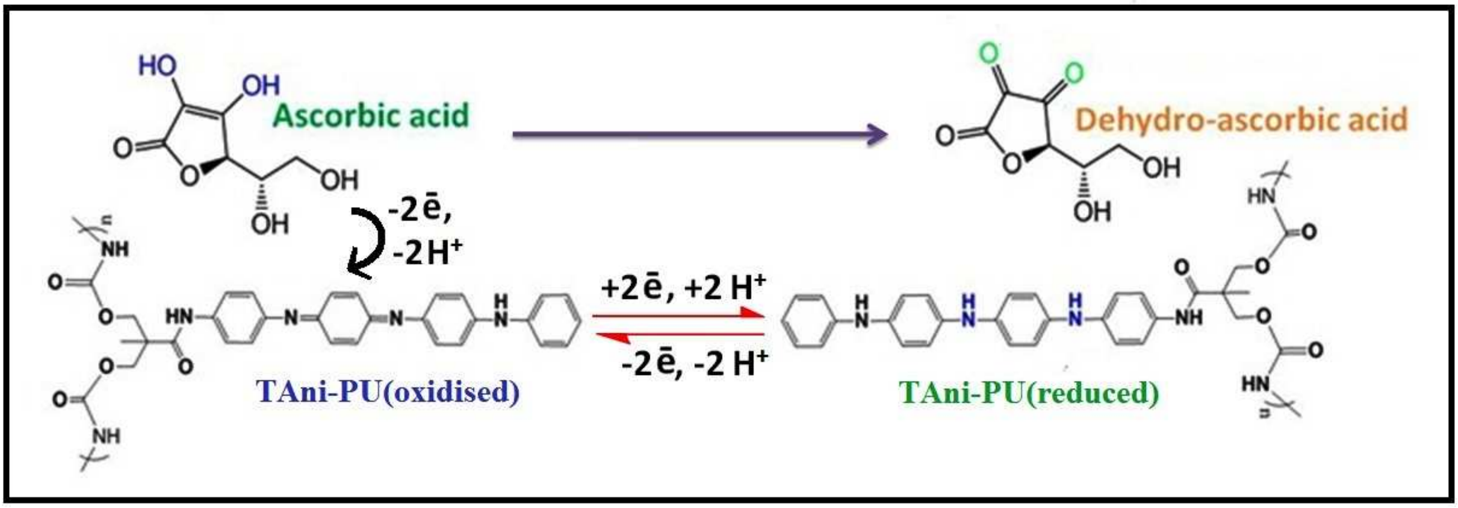


TAni-OH$_2$ Containing Polyurethane-urea (TAni-PU)

Scheme: 3 molecular structures of TAni - PU in various oxidation states



Scheme: 4 sensing behaviour of AA by TAni-PU



Scheme: 5 Schematic diagram of the TAni-PU microcapsules formation.

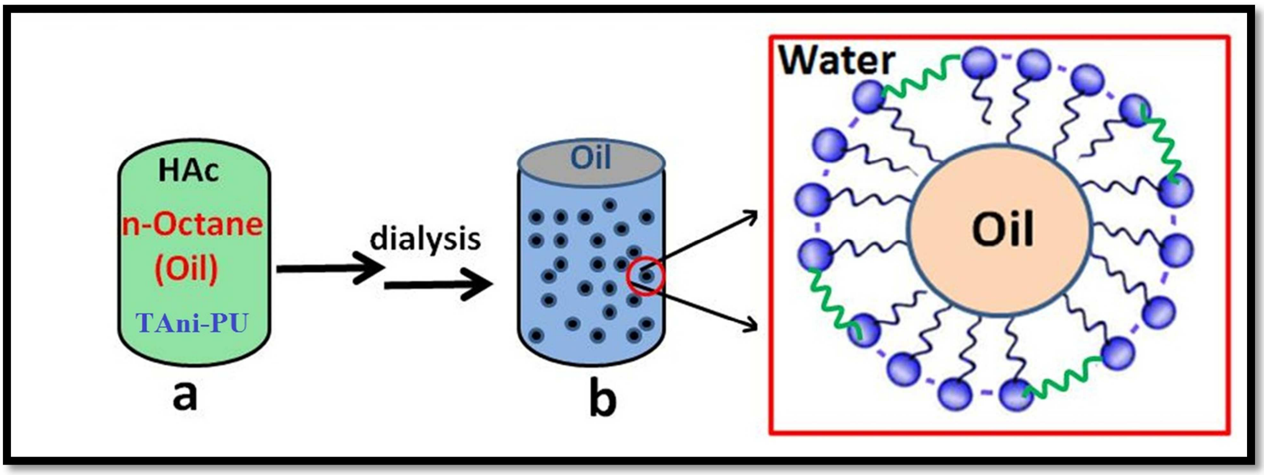


Fig.1: FT-IR spectra of different precursors and polymer

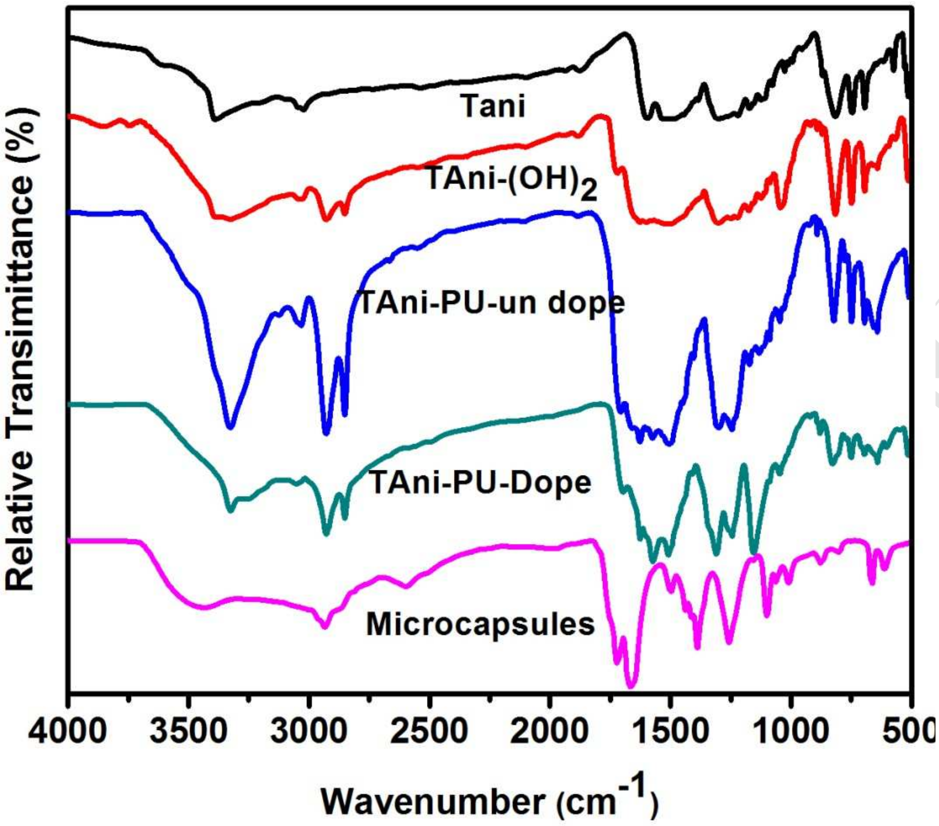


Fig.2: UV-Vis spectra of a) powder TAni-PU b) core-shell microspheres of TAni-PU

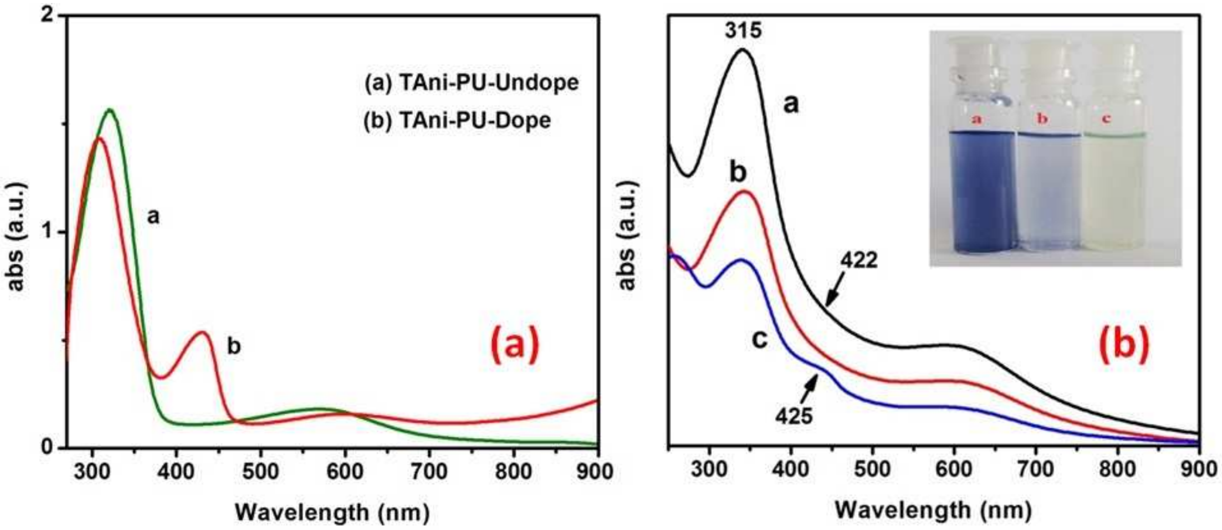


Fig.3: (a,b,c,d) Scanning electron micrographs (SEM) of doped powder of TAni-PU (e,f) TEM pictures of doped powder of TAni-PU.

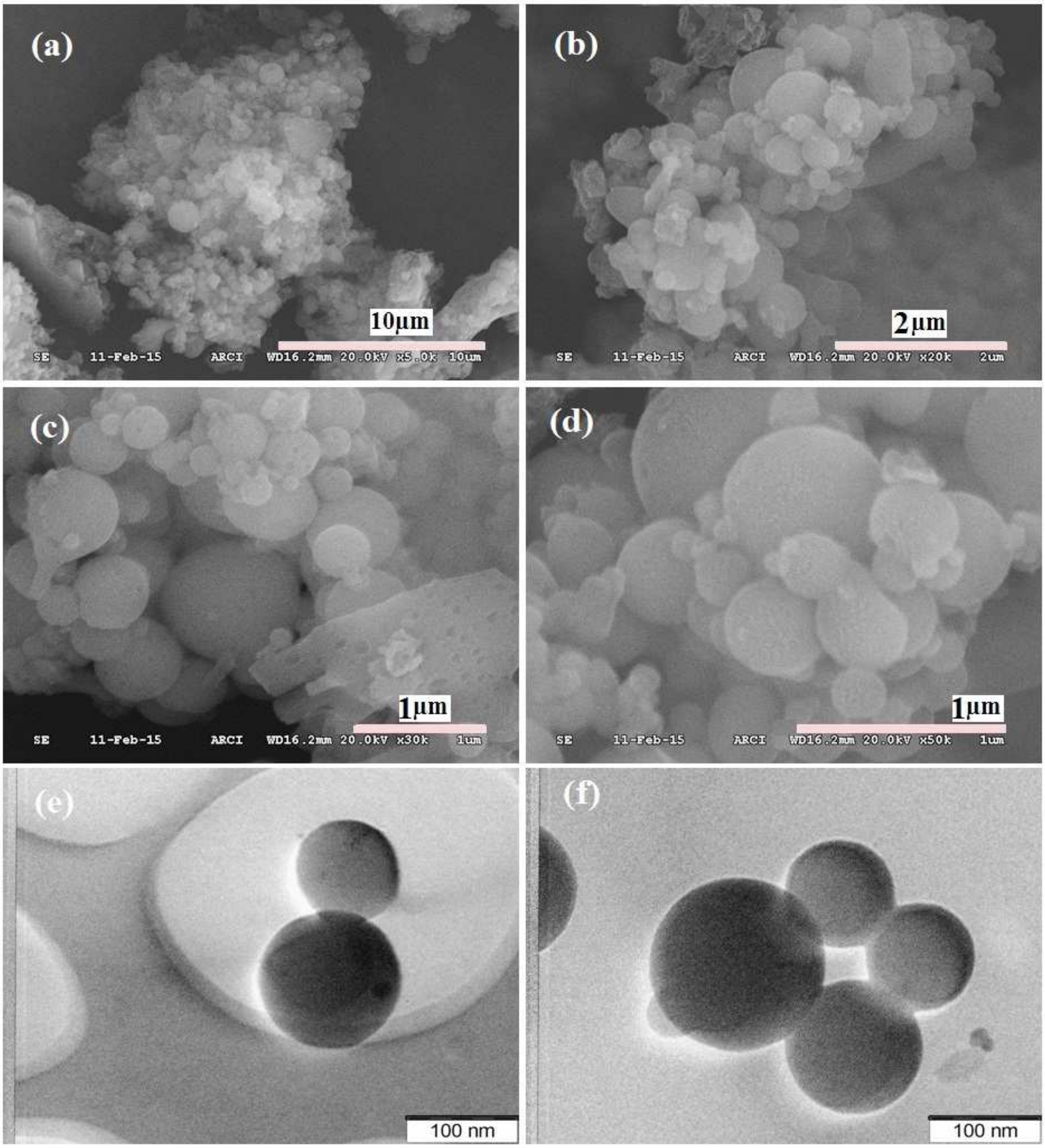


Fig.4: (A, B, C) TGA profiles (D) DSC profiles of precursors and polymer.

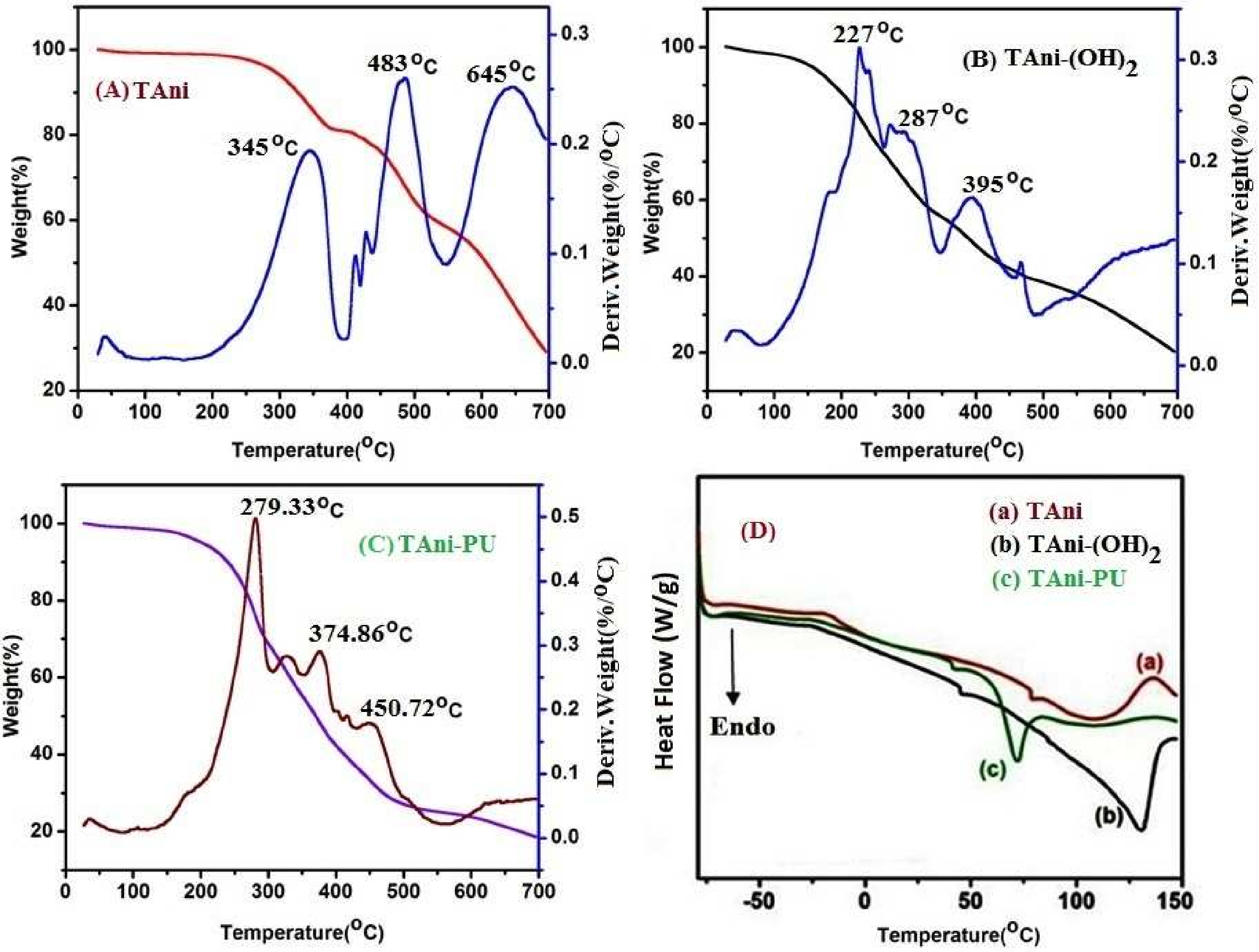


Fig.5: Cyclic voltammograms of precursors and polymer in DMF solvent (20 ml) with 5 ml of 1M HCl. The scan rate is 100 mV/s with Pt disc (2 mm) electrode.

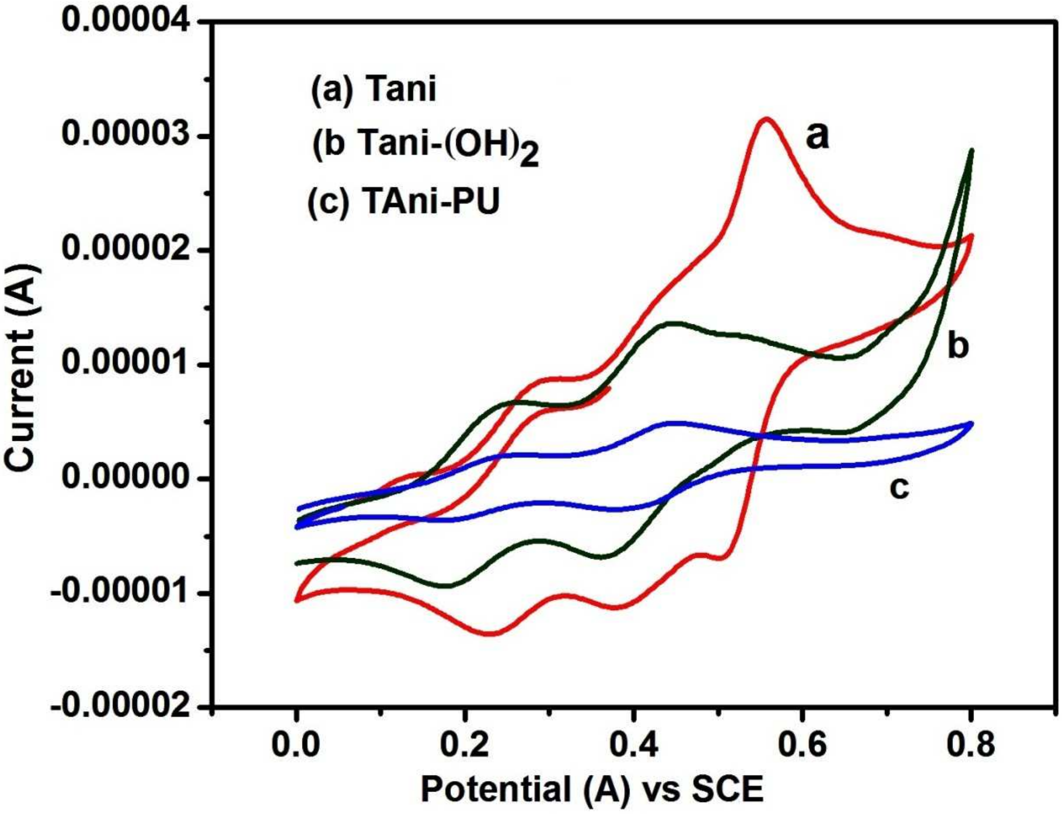


Fig.6: (a) CV of carbon paste electrode (CPE) made from powder TAni-PU (b) CVs obtained from the sensing of ascorbic acid at different AA concentrations using CPE.

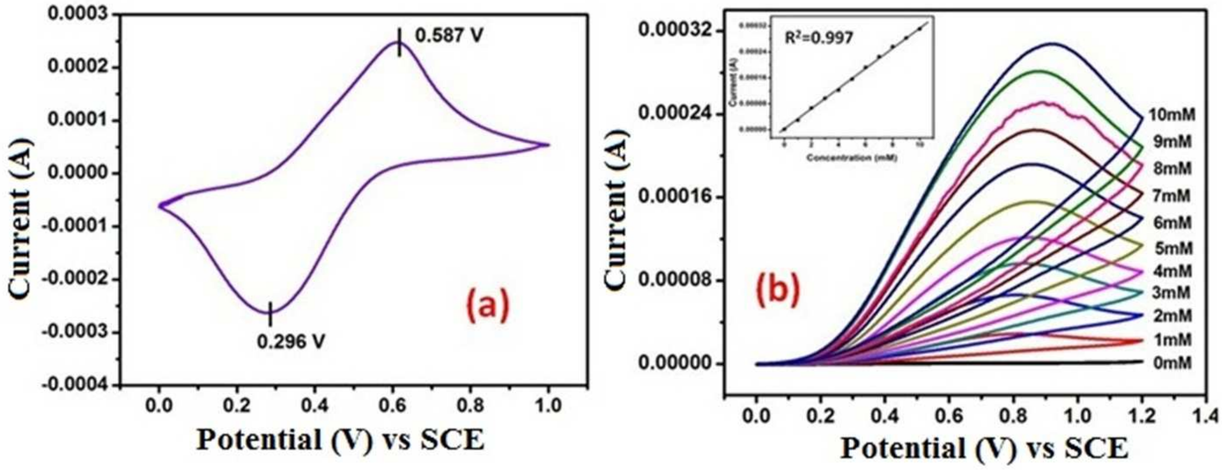


Fig. 7: Optical micrographs of microspheres at different magnifications.

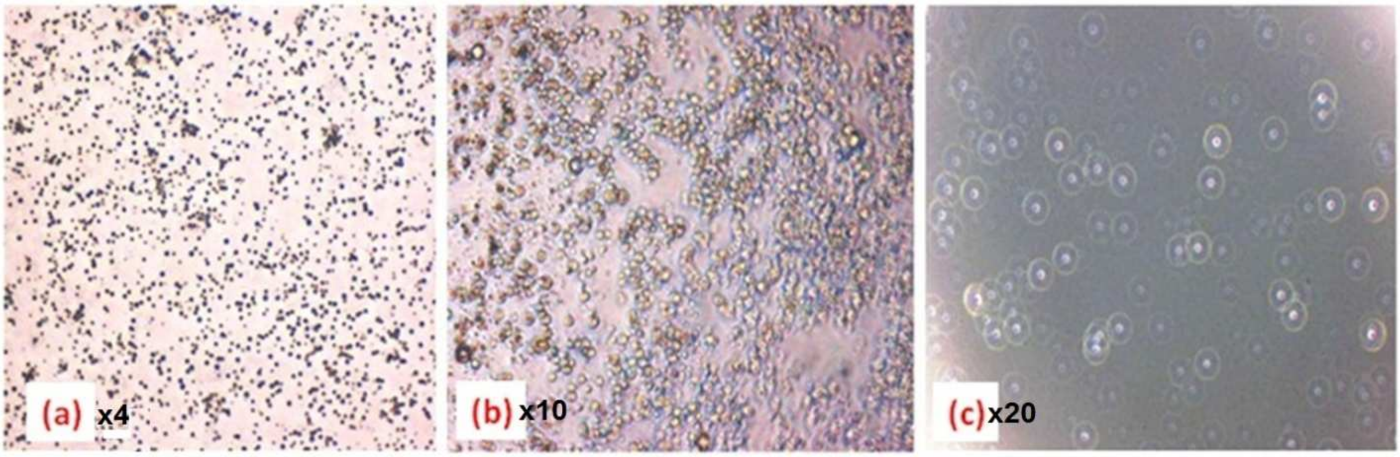


Fig.8: TEM pictures of core-shell microspheres/capsules.

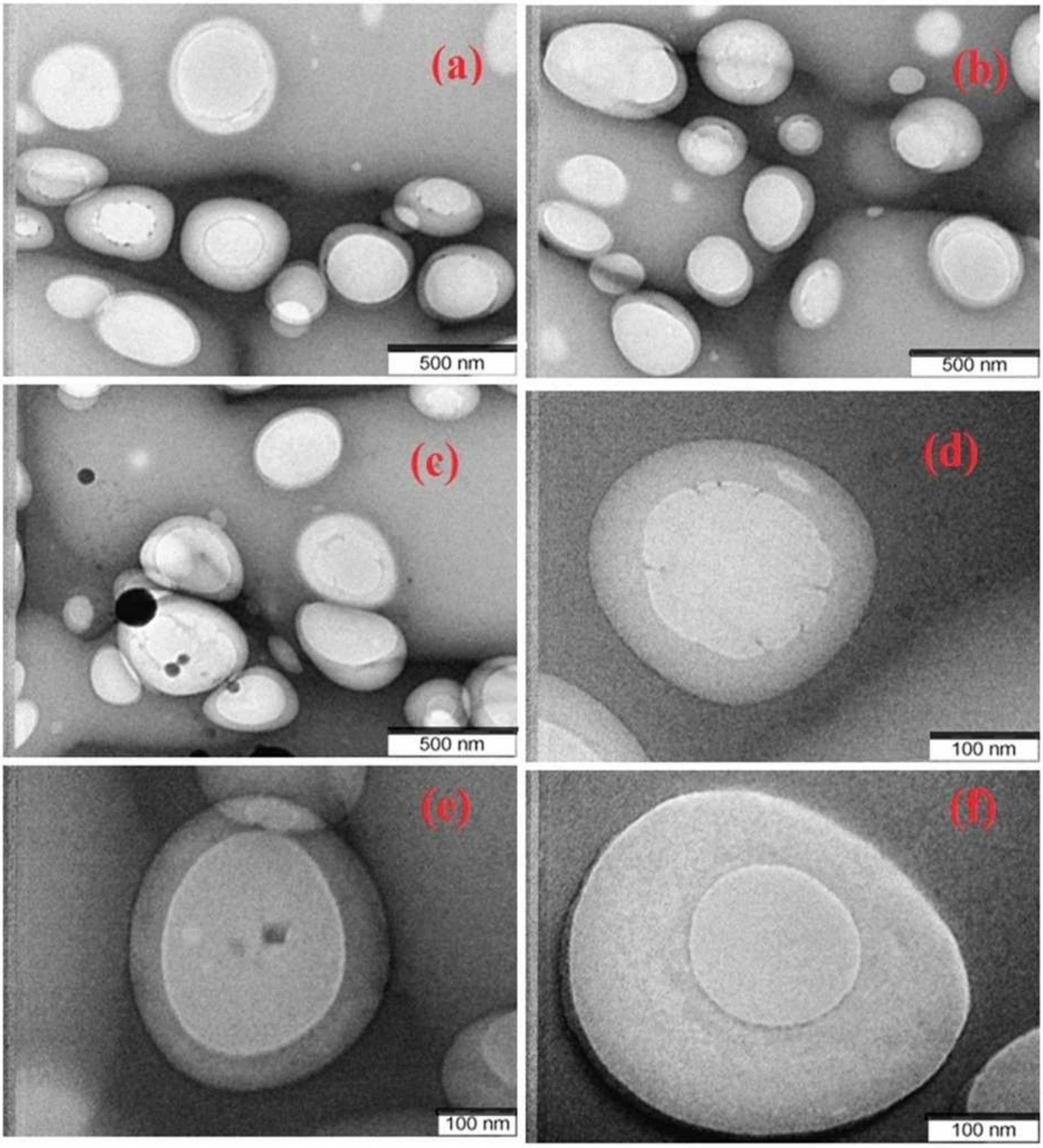
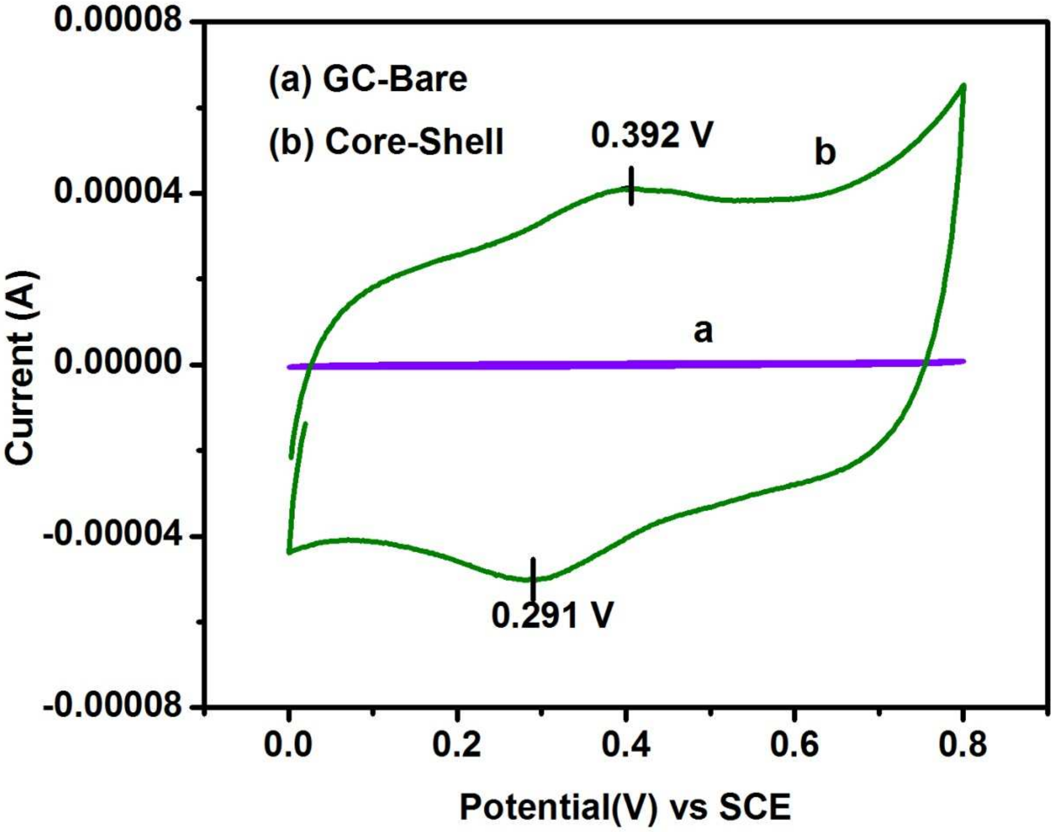


Fig.9: CV of microspheres/capsules deposited on GC electrode.



Highlights of the article:

- Synthesized a novel hybrid polyurethane with tetraanilines as pendant groups
- Electrochemically active and conducting to the tune of 3.4 x 10^{-4} S/cm.
- The polymer can be reversibly oxidized and reduced similar to tetraaniline.
- First hybrid polyurethane to electrochemically sense ascorbic acid.
- Can self assemble into core-shell microspheres/capsules in presence of acetic acid/n-octane interface

Fig.S1: ^{1}H NMR spectra of (a) TAni(OH)$_2$ and TAni-PU.

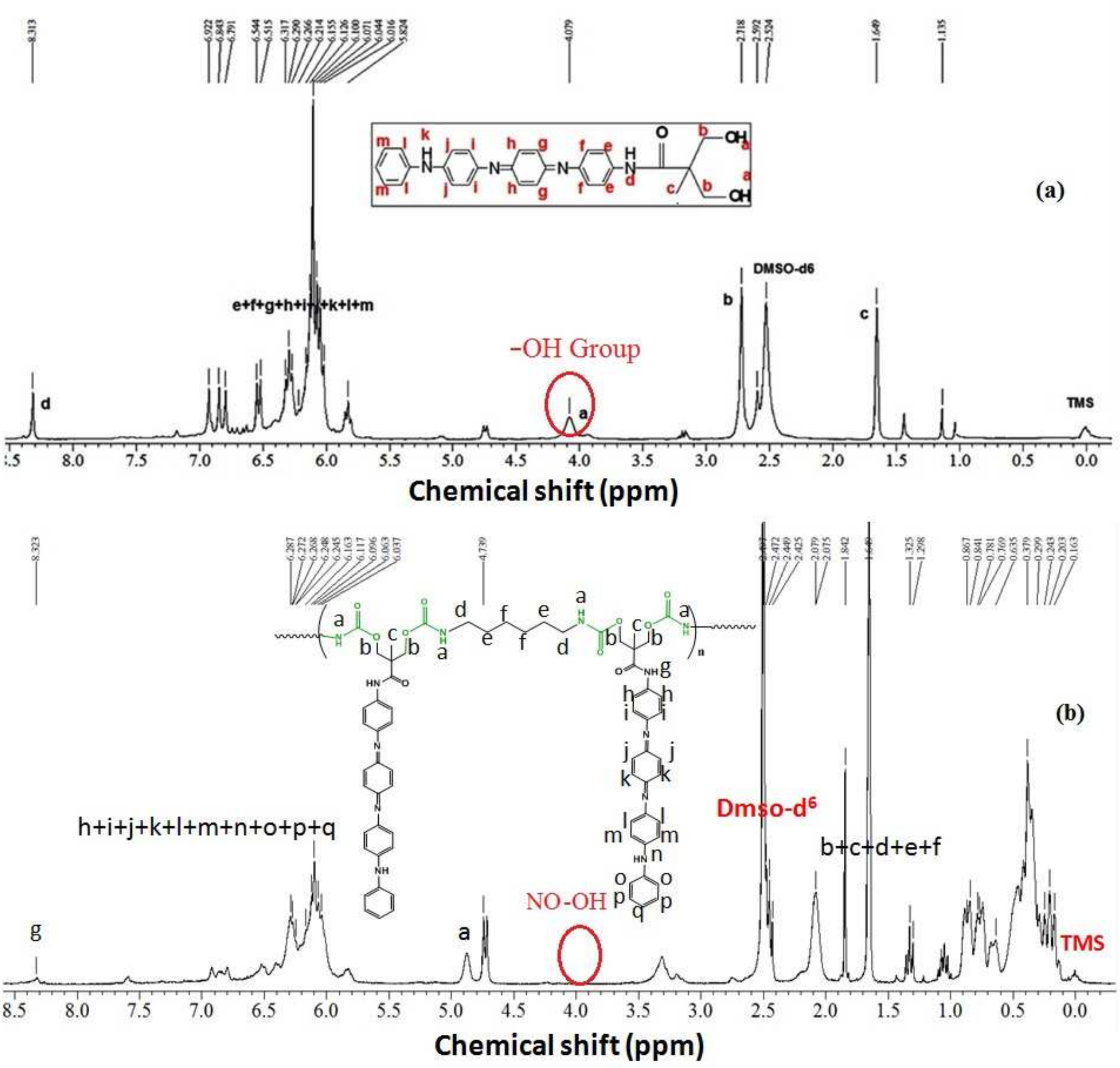


Fig.S2: ESI Mass spectrum of TAni(OH)$_2$.

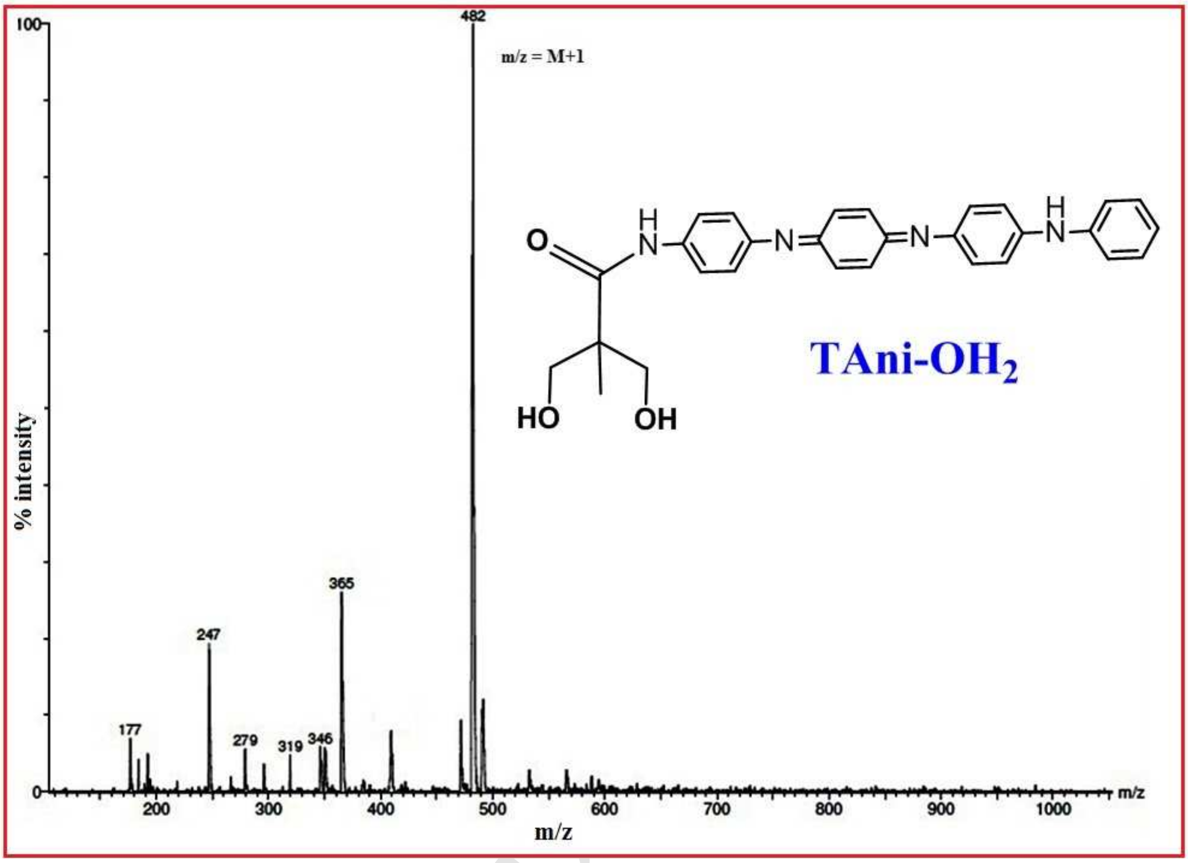


Fig.S3: XRD profiles of TAni and TAni-PU.

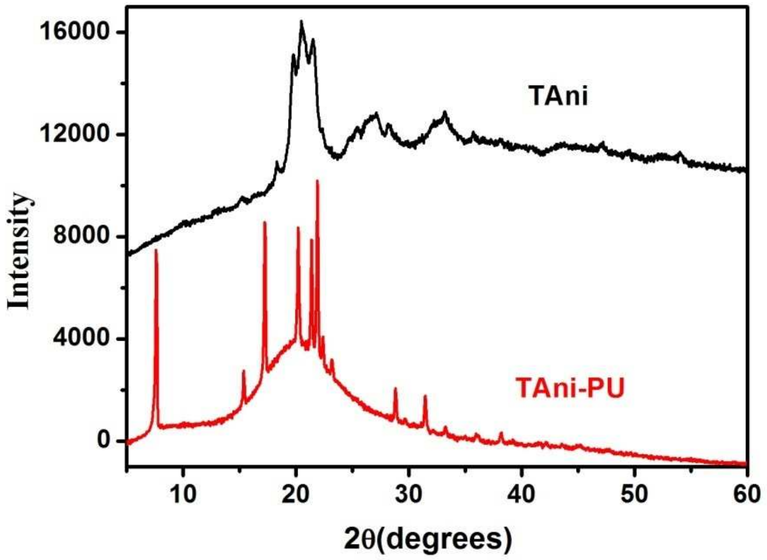


Table-S1: XRD Data of TAni and TAni-PU

S.NO	TAni		TAni-PU	
	2Θ(degree)	d(A^o)	2Θ(degree)	d(A^o)
1	--	--	7.61	11.60
2	--	--	15.36	5.76
3	18.32	4.83	17.21	5.14
4	19.68	4.50	20.09	4.41
5	20.54	4.31	21.40	4.14
6	21.48	4.13	21.88	4.05
7	26.47	3.36	23.57	3.77
8	28.60	3.11	28.52	3.12
9	32.38	2.76	31.42	2.84

Fig.S4: MALDI-TOF mass spectra of TAni-PU.