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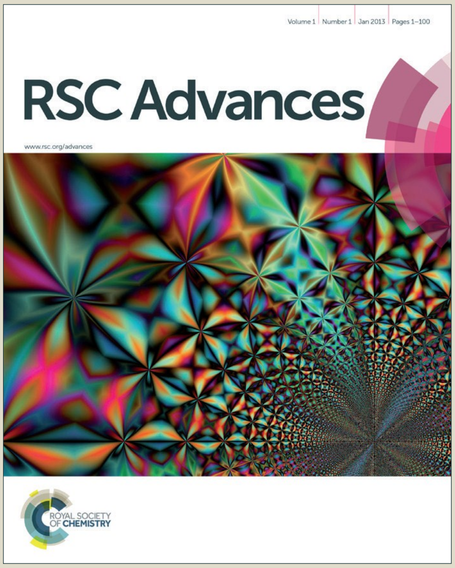

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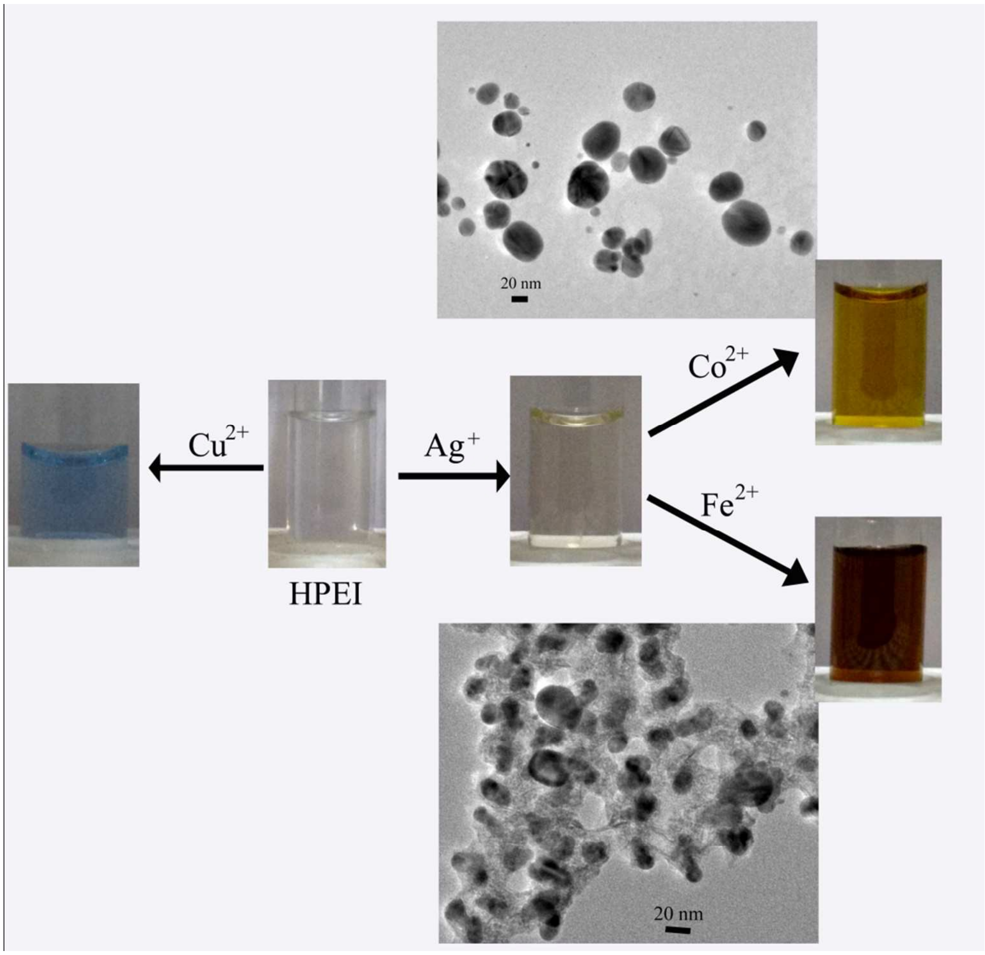
Hyperbranched polyethylenimine based multiple metal ions (Cu^{2+}, Co^{2+} and Fe^{2+}) sensor: Colorimetric sensing via coordination complex and silver nanoparticles formation

A commercially available HPEI polymer has been used as single colorimetric probe for selective colorimetric sensing of multiple metal ions in aqueous solution with distinguished color.



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Hyperbranchedpolyethylenimine based multiple metal ions (Cu^{2+}, Co^{2+} and Fe^{2+}) sensor: Colorimetric sensing via coordination or AgNPs formation

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Hyperbranched polyethylenimine (HPEI), an amine rich polymer, has been used as colorimetric probe for selective sensing of multiple metal ions (Cu^{2+}, Co^{2+} and Fe^{2+}) with clearly distinguishable color in aqueous solution. The selective coordination of Cu^{2+} with HPEI chelating amine induced visible color change from colorless to blue across wide pH range (pH 4.0 to 10.0). Other metal ions did not show any significant color change. Interestingly, addition of Co^{2+} and Fe^{2+} into HPEI in presence of silver ions (Ag^{+}) leads to the formation of strong yellow and brown color, respectively. The controlled studies suggest that Co^{2+} and Fe^{2+} undergoes oxidation and reduce the silver ions into silver nanoparticles (AgNPs). The strong surface plasmon resonance (SPR) vibration of AgNPs was responsible for yellow/brown color. UV-Visible studies showed strong absorption peak at 400 nm for Co^{2+} and broad absorption with λmax at 420 nm for Fe^{2+}. HR-TEM studies confirmed more uniformed spherical AgNPs for Co^{2+} with HPEI-Ag^{+} and polydispersed AgNPs aggregates for Fe^{2+}. The limit of detection of HPEI probe for Cu^{2+} is 0.25 μg/L and HPEI-Ag^{+} probe for Co^{2+} and Fe^{2+} is 40 and 30 μg/L, respectively. The practical application of HPEI probe for selective sensing of multiple metal ions with distinguishable color has been demonstrated in Whatman filter paper. Thus a simple commercially available HPEI has been successfully used for selective colorimetric sensing of biologically important Cu^{2+}, Co^{2+} and Fe^{2+} metal ions in aqueous medium.

Introduction

Cobalt (Co^{2+}), iron (Fe^{2+}) and copper (Cu^{2+}) are important transition metal ions that plays significant role in human health, animals and plants. Co^{2+} is an essential micronutrient for animals and plants, and an important component of vitamin B_{12} and other biological compounds.[1] However, deficiency of Co^{2+} can cause anaemia, slow down of growth and loss of appetite.[2] Also higher contamination of Co^{2+} with environmental water can have severe effects on both humans and animals.[3] Co^{2+} at higher concentration is highly toxic to humans and can induces several diseases and disabilities that include asthma, decreased cardiac output, cardiac enlargement, heart disease, lung disease, dermatitis and vasodilation.[4] Fe^{2+}, the most abundant metal ions in plants and human body, plays a trivial role in metabolism, catalysis, oxygen transport and as a cofactor in many enzymatic reactions.[5] The imbalance of Fe^{2+} can induces several diseases including anaemia, heart disease, liver damage and diabetes.[6-8] Similarly, Copper (Cu^{2+}) is a third essential transition metal ions after zinc and iron for human health and is an important cofactor for many enzymes in the biological process.[9-11] However, it is highly toxic for many human organisms at higher concentration because it may promotes the generation of reactive oxygen species (ROS).[12] The ROS strongly interfere with cellular signalling process and cause damage to cell structures or provoke apoptosis.[13-16] Further, high concentration of Cu^{2+} may also induce gastrointestinal disorder, as well as damage liver and kidney.[17] The increase of Cu^{2+} concentration in the neuronal cytoplasm might produce several other diseases like Alzheimer's, Parkinson's, and amyotrophic lateral sclerosis.[18,19] The selective binding of Cu^{2+} with the histidine-rich regions of the Prion Protein lead to mis-folding and protein fibrilization.[20] According to the U.S. Environmental Protection Agency (EPA), the limit of Cu^{2+} ions level in drinking water is 1.3 mg/L which is approximately 20 μM.[21] The increased use of copper in electronic device manufacturing, industrial and agricultural process makes Cu^{2+} contamination with environmental water is a serious problem.[22] Thus developing methods for continuous monitoring and detecting the concentration levels of Co^{2+} Fe^{2+}, and Cu^{2+} in environmental water sample is imperative for the benefit of human health.

Traditional detecting methods such as inductively coupled plasma atomic emission spectrometry, atomic absorption spectroscopy and electrochemical methods are required sophisticated instrumentation, tedious sample preparation and high cost.[23-26] In contrast, colorimetric sensor that offer

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Electronic Supplementary Information (ESI) available: Absorption spectra, interference studies, digital images and HR-TEM images are included. See DOI: 10.1039/x0xx00000x naked-eye detectable visible color change upon interaction with metal ions are having several advantages such as simple operation, cost-effective, robustness and on-site monitoring.[27-32] Several Schiff base and naphthalimide based chemosensors have been synthesized for selective colorimetric sensing of Cu^{2+} ions.[33-37] Surface functionalized noble silver nanoparticles (AgNPs) with specific organic linkers have also been reported as Cu^{2+} colorimetric sensors.[38-41] Mostly molecular materials predominantly Schiff bases and rarely surface functionalized noble nanoparticles based optical sensors have been reported for Fe^{2+}/Fe^{3+}.[42-48] However, colorimetric sensors for Co^{2+} metal ions are rarely reported. Coumarin-conjugated thiocarbanohydrazone colorimetric sensor was developed by Debabrata Maity et al.[49] Cheal Kim group reported Schiff base colorimetric sensor for Co^{2+}.[50] Triazole-carboxyl functionalized AgNPs and glutathione functionalized Ag nanorods have also been reported for selective sensing of Co^{2+} ions.[51,52] Recently, we have developed phenolic chelating ligand functionalized AgNPs for selective sensing of Co^{2+} ions in water.[53] Nevertheless, a single probe that can detect more than two metal ions are scarcely reported.[43,54-56] Thus developing a single colorimetric probe that can exhibit multiple metal ions sensing in aqueous solution is highly challenging.

Herein, we have demonstrated highly selective colorimetric sensing of Cu^{2+}, Fe^{2+} and Co^{2+} ions using commercially available hyperbranchedpolyethylenimine (HPEI) in aqueous medium. Addition of Cu^{2+} into HPEI solution produced visible color change (colorless to blue color) via selective coordination with chelating amine functionality. The selective colorimetric change for Cu^{2+} ions can be observed clearly across wide pH range (pH 4 to 10). Other metal ions did not show significant color change. Addition of Co^{2+} and Fe^{2+} ions into HPEI polymer in presence of Ag^+ converted colorless solution into yellow and dark brown color, respectively. The mechanistic studies indicate that oxidation of Co^{2+} and Fe^{2+} reduces silver ions into AgNPs selectively and produced yellow/ brown color due to strong surface plasmon resonance (SPR). Absorption studies showed strong absorption peak at 400 nm for Co^{2+} and slightly broad absorption with λ_{max} at 420 nm for Fe^{2+}. Importantly, both solution colours and absorption are clearly distinguishable. HR-TEM studies confirmed the formation more uniform sized of AgNPs for Co^{2+} and polydispersed AgNPs aggregates for Fe^{2+}. The concentration dependent studies showed linear enhancement of absorption intensity with increase of Cu^{2+}, Co^{2+} and Fe^{2+} concentration. To demonstrate the practical applicability of HPEI probe, selective colorimetric sensing of Cu^{2+}, Co^{2+} and Fe^{2+} have been performed on Whatman filter paper that also exhibited clear distinguishable color for three metal ions. Thus a simple HPEI colorimetric probe exhibited selective multiple metal ions sensing with clearly distinguishable color via coordination or oxidation induced AgNPs formation.

Experimental Section

Poly(ethylenimine), ethylenediamine branched (Hyperbranchedpolyethylenimine) (number average molecular weight, Mn =600, weight average molecular weight, M_w = 800), poly(vinylalcohol) (PVA), poly(acrylicacid) sodium salt (PAA) were purchased from Sigma-Aldrich and used as received. Metal salts ($Cr_2(SO_4)_3$, $Al(NO_3)_3$, $FeSO_4$, $CoCl_2$, $NiCl_2$, $Cu(OAc)_2$, $Zn(OAc)_2$, $Ca(NO_3)_2$, $Mg(OAc)_2$, $Cd(OAc)_2$, $HgCl_2$, $Pb(NO_3)_2$, $AgNO_3$) were obtained from Ranbaxy India. Aqueous metal salt solution (10^{-3} M) for colorimetric sensing studies was prepared using Milli-Q water.

HPEI colorimetric sensor studies

Aqueous solution of HPEI polymer was prepared by dissolving 0.25 g of HPEI in 100 mL of water. Aqueous solution of metal ions (10^{-3} M) was added into 2 mL of HPEI polymer solution and monitored the absorption and visible color change.

HPEI-Ag^+ colorimetric sensor studies

To the above prepared HPEI polymer solution (20 mL), silver nitrate (10^{-3} M, 2 mL) was added and stirred at room temperature solution. This solution was kept as stock solution under dark. The colorimetric sensor studies for various metal ions were performed by adding aqueous solution of metal salts (10^{-3} M) into HPEI solution (1 mL) and monitored the visible color change. The absorption spectra were recorded to support the color change.

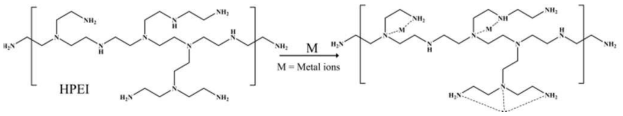
Characterization

The UV-visible measurements of the HPEI and HPEI-Ag^+ with different metal ions were performed in a Perkin Elmer model Lambda 1050. The size and morphology of AgNPs were investigated using high resolution transmission electron microscopy (HR-TEM). Samples for TEM measurements were prepared by placing a drop of NPs solution on the graphite grid and drying it in vacuum. Transmission electron micrographs were taken using JEOL JEM- 2100F operated at an accelerated voltage of 200 kV and an ultra high-resolution pole piece. The detection limit was calculated on the basis of the absorption titration. To obtain the slope, the change of absorption intensity (640 nm for Cu^{2+}, 400 nm for Co^{2+} and 418 nm for Fe^{2+}) was plotted against the concentration of metal ions.

Result and Discussion

Colorimetric sensor studies using HPEI

HPEI is an amine rich polyamine-imine polymer with metal chelating structure (Scheme -1). The good coordination character of amine coupled with chelating structure might promote coordination with transition metal ions. HPEI (0.25 g) was dissolved in water (100 mL). The pH of the as-prepared aqueous solution was 10.0. To investigate the colorimetric sensing, aqueous solution of different metal ions (10^{-3} M) was added into HPEI solution and monitored the absorption and visible color change. Interestingly, Cu^{2+} addition into HPEI solution selectively changed colorless solution to clear blue color (Fig. 1a). Addition of other metal ions into HPEI solution did not show any significant color change. Absorption studies of HPEI with Cu^{2+} showed a broad absorption peak around 650 nm (Fig. 1a). The appearance of longer wavelength absorption was responsible for blue color formation. It is noted that HPEI solution is colorless and did not show any absorption in the visible region. Other metal ions with HPEI also did not exhibit any absorption in the visible region. The concentration dependent studies of Cu^{2+} with HPEI are shown in Fig 1b. Addition of Cu^{2+} (10^{-4} M) leads to the appearance of longer wavelength absorption clearly. The increasing concentration of Cu^{2+} showed linear increase of absorption intensity. The interference studies of HPEI for Cu^{2+} (μM) in presence of different metal ions (10^{-3} M) confirmed the good selectivity (Fig. S1). Cu^{2+} addition into HPEI in presence of other metal ions have also produced the longer wavelength absorption that indicates other metal ions did not have significant interference on the Cu^{2+} colorimetric sensing.



Scheme 1. HPEI chemical structure and possible coordination with metal ion.

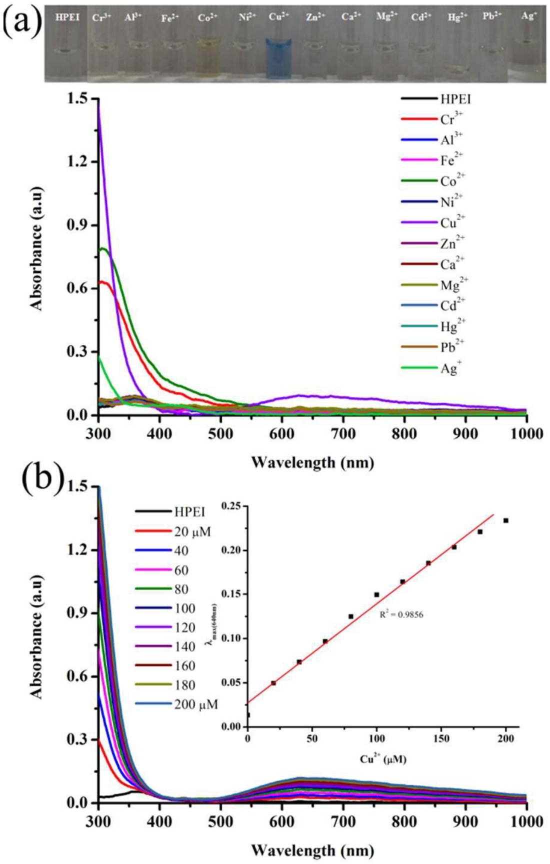


Fig. 1. (a) Digital image for color change and absorption spectra of HPEI with different metal ions (10^{-3} M) and (b) HPEI absorption Vs concentration of Cu^{2+} (pH = 10).

The pH of HPEI polymer solution was gradually decreased (8, 6, 4 and 2) by adding dilute HNO_3 to explore the colorimetric sensing of HPEI at wide physiological range. Interestingly, addition of Cu^{2+} to HPEI solution at pH 8.0 has also clearly exhibited blue color (Fig. S2). Similarly, pH 6.0 and 4.0 solution also showed clear blue color formation by adding Cu^{2+} ions. The absorption spectra of HPEI with Cu^{2+} at pH 8.0, 6.0 and 4.0 have also showed longer wavelength absorption (Fig. 2, S2). However, pH 2.0 polymer solution did not show any color change with Cu^{2+}. It was observed that the pH 4.0 polymer showed slightly reduced blue color intensity for Cu^{2+} relative to pH 8.0 and 10.0. This could be due to the protonation of free amine groups of HPEI at low pH might reduce their ability to coordinate with Cu^{2+} ions strongly. At pH 2.0, most of the amines might have protonated and hence it could not form any coordination complex with Cu^{2+} ions.

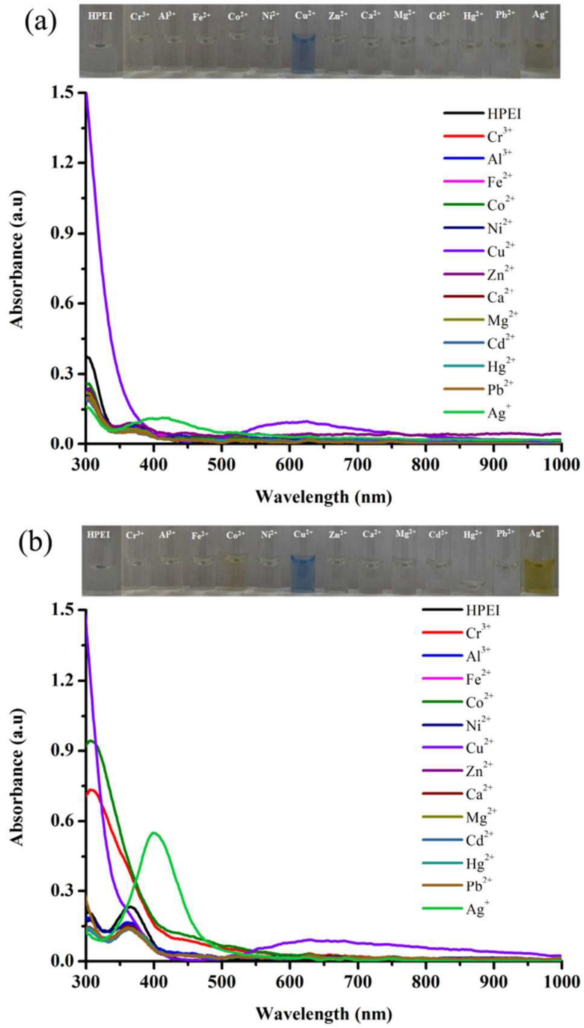


Fig. 2. Digital image for color change and absorption spectra of HPEI with different metal ions at pH (a) 4.0 and (b) 6.0.

Addition of silver ions (Ag^+) into HPEI solution at pH 10.0 did not show any color formation (Fig. 1a). However, light yellow color to clear yellow color formation was observed upon reducing pH of HPEI solution from 10.0 to 6.0 along with Ag^+ (Fig. 2, S2). Further acidification (pH 4.0 and 2.0) produced only very light yellow color. The clear yellow color appearance at pH 6.0 could be due to the formation of AgNPs. Absorption studies of HPEI with silver ions at different pH showed a clear absorption peak at 400 nm for pH 6.0 sample (Fig. 2b). A weak slightly broad absorption was observed around 400 nm for pH 4.0 and 8.0 sample. HPEI-Ag$^+$ at pH 10.0 did not show any absorption in the visible region. The strong absorption at 400 nm suggests the formation of AgNPs. Noble metal nanoparticles such as silver (Ag) and gold (Au) are known to exhibit strong absorption in the visible region due to surface plasmon resonance vibration (SPR).[57] AgNPs with spherical shape generally exhibit absorption peak between 390 – 440 nm. HR-TEM studies of Ag$^+$ added HPEI sample at pH 6.0 clearly confirmed the formation of poly-dispersed spherical AgNPs with size range between 8-25 nm (Fig. 3a). HPEI-Ag$^+$ at pH 10.0 did not show any AgNPs formation and support the absorption studies (Fig. 3b). It has been reported that polyethylenimine can reduce silver ions into AgNPs in the acidic conditions whereas it remains as silver ions in basic condition and formaldehyde reduction produced silver nanoclusters (AgNCs).[58-59]

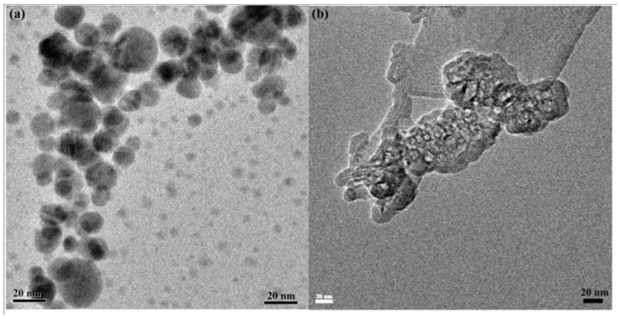


Fig. 3. HR-TEM images of HPEI-Ag$^+$ at pH (a) 6.0 and 10.0.

Colorimetric sensing of Co^{2+} and Fe^{2+} by HPEI-Ag$^+$

Addition of Co^{2+} and Fe^{2+} into HPEI polymer solution did not show significant color change across basic to acidic condition. Absorption spectra also did not show any characteristic absorption peak in the visible region (Fig. 1). However, addition of Co^{2+} and Fe^{2+} into HPEI in presence of Ag$^+$ under ambient condition (air equilibrated solution) produced clear yellow and dark brown color from a colorless solution, respectively (pH = 10.0, Fig.4). The light yellow color of HPEI-Ag$^+$ solution at pH 8.0 has also been converted to intense yellow and dark brown color by Co^{2+} and Fe^{2+} addition (Fig. 4). Other metal ions addition into HPEI-Ag$^+$ did not show any significant color change. The clear yellow color of HPEI-Ag$^+$ at pH 6.0 was further intensified with Co^{2+} whereas Fe^{2+} addition again produced dark brown color (Fig. 4). However, addition of Co^{2+}/Fe^{2+} into HPEI-Ag$^+$ at pH 2.0 and 4.0 did not show any color change. Further it was observed that strong yellow color formed by Co^{2+} addition into HPEI-Ag$^+$ at different pH (6.0 to 10.0) was quite stable (more than two weeks). The dark brown color of HPEI-Ag$^+$ obtained by Fe^{2+} addition settle down slowly depend on the pH of the medium. At pH 10.0, the dark brown color settles down within 5 minutes whereas it was stable for 30 minutes at pH 8.0. The dark brown color of pH 6.0 sample was stable for 1 h and then slowly settles down. Thus AgNPs produced from HPEI-Ag$^+$ with Co^{2+} and Fe^{2+} metal ions not only showed different color but it also showed different stability.

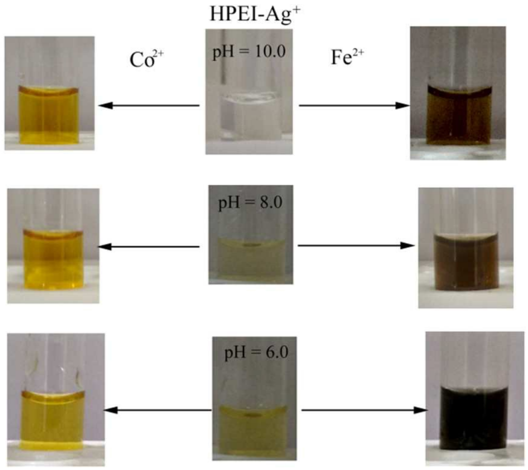


Fig. 4. Digital images of HPEI-Ag$^+$ color changes upon addition of Co^{2+} and Fe^{2+} at different pH.

Absorption studies of HPEI-Ag$^+$ (pH = 8.0) with different mental ions have also showed different absorption for Co^{2+} and Fe^{2+} (Fig. 5). Co^{2+} addition showed strong absorption at 400 nm whereas Fe^{2+} addition in to HPEI-Ag$^+$ broad absorption with λ_{max} at 420 nm. At pH 10.0, HPEI-Ag$^+$ with Co^{2+} exhibited clear absorption peak at 400 nm whereas Fe^{2+} showed broad absorption without a clear peak (Fig. S3). The broad absorption without a clear peak could be due to the faster settlements formed AgNPs. HPEI-Ag$^+$ with Co^{2+} at pH 6.0 has also exhibited clear strong absorption at 400 nm (Fig. S4). Co^{2+} addition strongly enhanced the absorption intensity without altering the λ_{max}. Fe^{2+} addition again showed broad absorption with λ_{max} at 418 nm. The strong yellow or brown color with clear absorption in the range between 400 to 440 nm indicates the formation of AgNPs. HR-TEM studies of HPEI-Ag$^+$ (pH = 10) which is a colorless solution did not show any AgNPs formation (Fig. 3). Co^{2+} addition into HPEI-Ag$^+$ (pH = 10.0) lead to the formation of spherical AgNPs in the size range between 10-25 nm (Fig. 6). HR-TEM studies further indicate that Co^{2+} ions could coordinate with HPEI amines and forms spherical micron sized particles (Fig. S5). The presence of smaller AgNPs has also clearly been seen on the HPEI-Co^{2+} polymer microspheres. Fe^{2+} addition into HPEI-Ag$^+$ (pH = 10.0) that produced dark brownish color showed the formation of polydispersed AgNPs aggregates with different shape (Fig. 6c,d, S6). Spherical, nanorod and other morphologies of AgNPs with 10-40 nm size could be observed. Further the HR-TEM suggests that AgNPs are completely trapped in the polymer matrix. The formation of AgNPs with different size, shape and aggregate was responsible for different color with Co^{2+} and Fe^{2+}. HPEI-Ag$^+$ at pH 6.0 showed the formation of poly-dispersed spherical AgNPs (Fig. 3). However, addition of Co^{2+} induced the formation of nearly uniform sized spherical AgNPs (5-10 nm) that strongly enhanced the absorption intensity (Fig. 6b). Hence the HR-TEM studies indicate that HPEI in presence of Ag$^+$ facilitate the oxidation of Co^{2+} and Fe^{2+} and reduction silver ions into AgNPs.

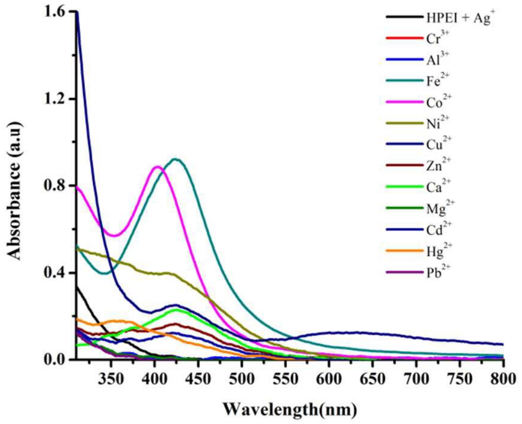


Fig. 5. Absorption spectra of HPEI-Ag+ with different metal ions (10^{-3} M) at pH 8.0.

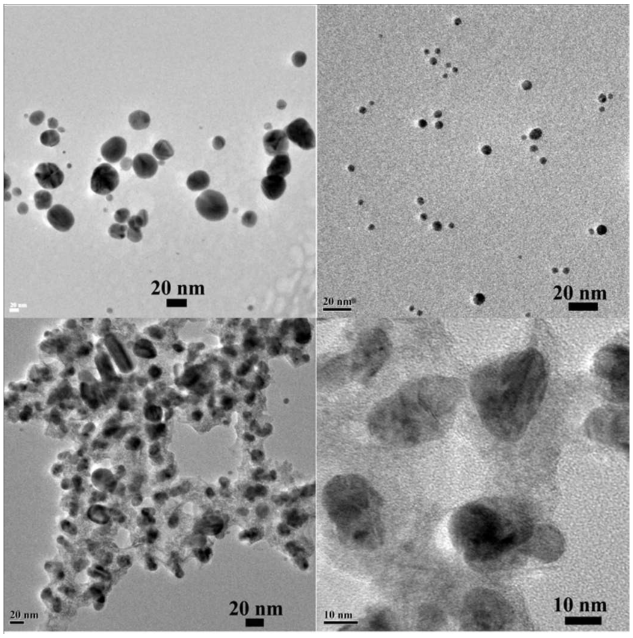


Fig. 6. HR-TEM images of HPEI-Ag$^+$ after the addition of Co^{2+} at pH (a) 6.0, (b) 10.0 and Fe^{2+} addition at pH 10.0 (c,d).

HPEI-Ag$^+$ at pH 8.0 was chosen as representative example to perform the concentration dependents studies. The concentration dependent studies of Co^{2+} and Fe^{2+} with HPEI-Ag$^+$ is shown in Fig. S7a. HPEI-Ag$^+$ showed a very weak broad absorption around 400 nm. Addition of Co^{2+} (10^{-4} M) leads to the formation of strong absorption peat 400 nm immediately. Further addition showed linear increase of absorption intensity without changing the λ_{max} with concentration of Co^{2+}. Addition of Fe^{2+} into HPEI did not show immediate increase of absorption intensity (Fig. S7b). However, subsequent addition exhibited enhancement of intensity with red shift of absorption peak to 418 nm. The limit of detection calculation indicate that HPEI-Ag$^+$ probe can detect Co^{2+} and Fe^{2+} in aqueous solution up to 40 and 30 μg/L, respectively. The interference studies of HPEI-Ag$^+$ for Co^{2+} and Fe^{2+} (μM) in presence of different metal ions (10^{-3} M) demonstrate the high selectivity (Fig. 7, S8-9). Addition of Co^{2+} into HPEI-Ag$^+$ in presence of other metal ions clearly produced strong yellow color and absorption at 400 nm. Similarly, addition of Fe^{2+} into HPEI-Ag$^+$ has also produced brownish color in presence of other metal ions. It is noted that the color was lightened in presence of other metal ions but still produced clear brown color. The interference studies indicate that HPEI-Ag$^+$ has strong selectivity for Fe^{2+} in presence other metal ions (S9). Addition of Fe^{2+} (0.3 equivalent to Co^{2+}) into HPEI-Ag$^+$ with Co^{2+} increased the intensity with small red shift, however, equal amount of Co^{2+} (1:1 to Fe^{2+}) was required to induce a small blue shift in the absorption. Interestingly, HPEI-Ag$^+$ produced strong reddish solution in presence of both Fe^{2+} and Co^{2+} that is different from Fe^{2+} addition into HPEI-Ag$^+$ or Co^{2+} addition into HPEI-Ag$^+$. Further, absorption spectra also showed small red (400 to 412 nm for Fe^{2+} addition) or blue shift (420 to 410 nm) in the λ_{max} with peak broadening (red

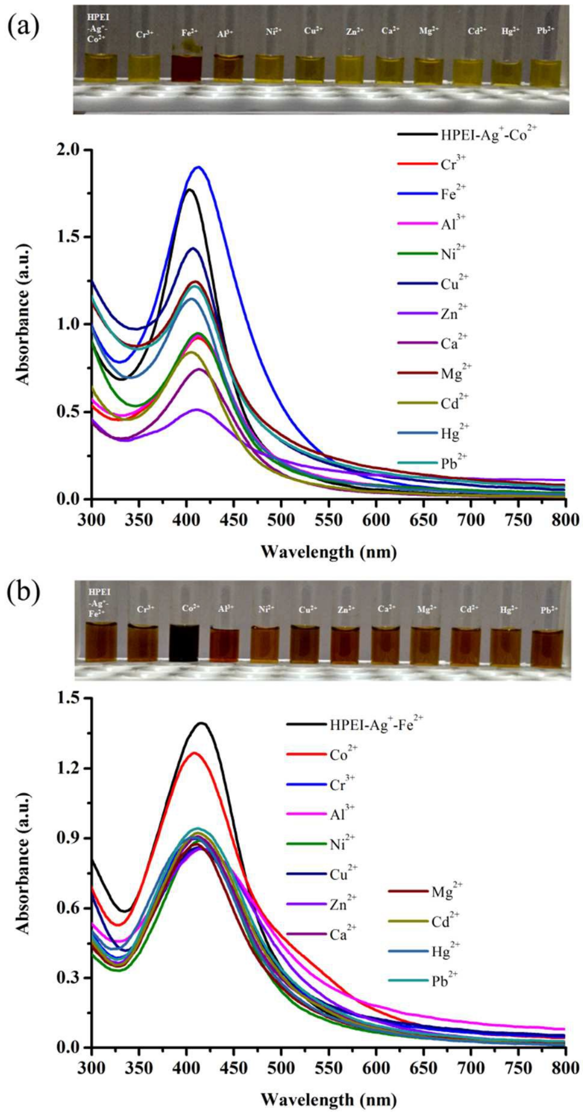
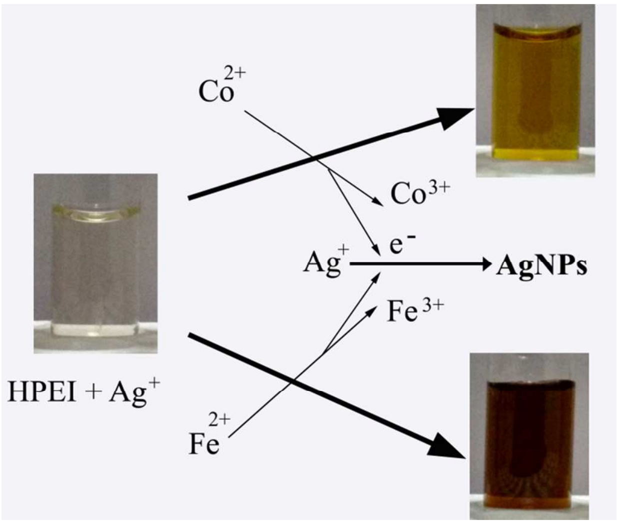


Fig. 7. Selectivity studies of HPEI-Ag+ for (a) Co2+ (μM) and (b) Fe2+ (μM) in presence of different metal ions (mM).

shift of $\lambda_{cut\text{-}off}$). Hence, although HPEI-Ag^+ exhibit high selectivity for Fe^{2+}, it can also be used as colorimetric probe for detecting Co^{2+} metal ions.

To get the insight on the mechanism of Co^{2+} and Fe^{2+} colorimetric sensing by HPEI-Ag^+, controlled studies were performed. It is noted that Co^{2+} and Fe^{2+} addition into HPEI polymer alone did not show any visible color or absorption in the visible region. However, Co^{2+}/Fe^{2+} addition into HPEI in presence of Ag^+ under ambient condition lead to the appearance of clear yellow/dark brown color due to the formation of AgNPs which was confirmed by absorption and HR-TEM studies. The same experiment was performed under N_2 atmosphere. Interestingly, Co^{2+} and Fe^{2+} addition under inert condition did not produce any color that indicates Ag^+ ions have not been reduced into AgNPs (Fig. S10). However, removing N_2 atmosphere and bringing the reaction medium into normal condition resulted in the formation of yellow and dark brown color immediately. Further it was observed that Co^{3+} or Fe^{3+} addition into HPEI-Ag^+ did not produce any color. Similarly, direct addition of Co^{2+} or Fe^{2+} into Ag^+ (10^{-4} or 10^{-3} M) without HPEI polymer under ambient condition has also not showed characteristic color formation. Interestingly, addition of HPEI polymer into Co^{2+}/Fe^{2+} with Ag^+ solution leads to formation of yellow/dark brownish color. Other water soluble polymer such as poly(vinylalcohol) (PVA) and poly(vinylpyrrolidone) (PVP) was used to confirm the significance HPEI polymer. Addition of Co^{2+}/Fe^{2+} into PVA-Ag^+ or PVP-Ag^+ aqueous solution did not produce any significant color that indicates the importance of amine rich HPEI polymer for the reduction of Ag^+ to AgNPs (Fig. S11). These studies indicate that Co^{2+}/Fe^{2+} undergoes oxidation in presence of HPEI polymer, Ag^+ and oxygen in air that reduces silver ions into AgNPs (Scheme 2). However, to induce Co^{2+}/Fe^{2+} oxidation, Ag^+, HPEI and oxygen are required. It appears that it might be a synergistic effect of all three components (Ag^+, HPEI, air) for the oxidation of Co^{2+}/Fe^{2+} and reduction of Ag^+ into AgNPs. It is noted that Co^{2+}/Fe^{2+} oxidation will lead to the formation another stable oxidation state of these metal ions (Co^{3+}/Fe^{3+}). Importantly, both Co^{2+} and Fe^{2+} induced AgNPs showed distinguishable color with different absorption and suggest that HPEI-Ag^+ probe can be used to detect Co^{2+} and Fe^{2+} ions in aqueous solution.



Scheme 2. Proposed mechanism of Co^{2+} and Fe^{2+} colorimetric sensing of HPEI-Ag^+ via oxidation induced AgNPs formation.

The practical application of HPEI probe for selective colorimetric sensing of Cu^{2+}, Co^{2+} and Fe^{2+} in aqueous solution has been demonstrated using Whatman filter paper (Fig. 8). Aqueous solution of HPEI droplet was placed on a small piece of filter paper. Addition of different concentration of Cu^{2+} clearly produced blue color in the filter paper. Similarly, addition of Co^{2+} and Fe^{2+} into HPEI-Ag^+ soaked filter paper lead to the formation of yellow and dark brown color, respectively. The increasing Cu^{2+}, Co^{2+} and Fe^{2+} concentration lead to higher intensity of color.

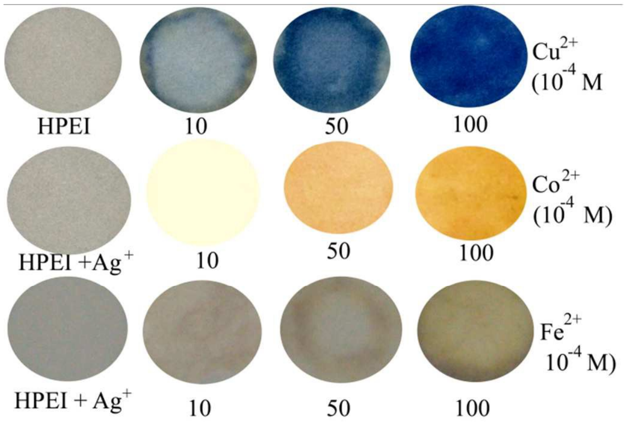


Fig. 8. Digital images of colorimetric sensing of Cu^{2+}, Co^{2+} and Fe^{2+} by HPEI probes using a Whatman filter paper.

Conclusion

In conclusion, we have demonstrated a highly selective colorimetric sensing of multiple metal ions (Cu^{2+}, Co^{2+} and Fe^{2+}) using commercially available HPEI polymer in aqueous medium. HPEI showed selective blue color appearance upon addition of Cu^{2+} ions via coordination with amine functionality of the polymer. Interestingly, the color change for Cu^{2+} could be observed across wide pH range (pH 4.0 to 10.0). Other metal ions did not show any characteristic color change with HPEI. Addition of Co^{2+} and Fe^{2+} into HPEI solution in presence of Ag^+ under ambient condition produced strong yellow and dark brown color, respectively. The controlled studies indicate that Co^{2+} and Fe^{2+} undergoes oxidation under ambient condition in presence of Ag^+ and HPEI polymer and reduces silver ions into AgNPs. The strong SPR phenomena of AgNPs produced color. The formation of AgNPs was confirmed by absorption and HR-TEM studies. The different color for Co^{2+} and Fe^{2+} was due to the change of AgNPs size, shape and aggregation. The limit of detection of HPEI probe for Cu^{2+} is 0.25 µg/L and HPEI-Ag^+ probe for Co^{2+} and Fe^{2+} is 40 and 30 µg/L, respectively. Interference studies confirm the high selectivity of HPEI colorimetric probe for Cu^{2+}, Co^{2+} and Fe^{2+}. Importantly, all three metal ions produced completely different and distinguishable color. The practical applicability of HPEI for selective colorimetric sensing of Cu^{2+}, Co^{2+} and Fe^{2+} has been demonstrated using a Whatman filter paper.

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Notes and References

1 A. I. Stoica, M. Peltea, G. E. Baiulescu and M. Ionic, *J. Pharmaceut. Biomed.*, 2004, **36**, 653–656.
2 A. R. Khorrami, T. Hashempur, A. Mahmoudi and A. R. Karimi, *Microchem. J.*,2006, **84**, 75–79.
3 M. Gharehbaghi, F. Shemirani and M. D. Farahani, *J. Hazard. Mater.*,2009, **165**, 1049–1055.
4 D. G. Barceloux and D. Barceloux, *Clin. Toxicol.*, 1999, **37**, 201–216.
5 P. Aisen, M. Wessling-Resnick and E. A. Leibold, *Curr. Opin. Chem.Biol.*, 1999, **3**, 200–206.
6 E. L. Que, D. W. Domaille and C. J. Chang, Chem. Rev., 2008, **108**, 1517–1549.
7 C. Brugnara, *Clin. Chem.*, 2003, **49**, 1573–1578.
8 J. J. R. Fausto da Silva and R. J. P. Williams, The Biological Chemistry of the Elements, Oxford University, New York, 1992.
9 S. P. Wu, R. Y. Huang and K. J. Du, *Dalton Trans.*, 2009, **24**, 4735-4740.
10 E. D. Harris, *J. Nutr.*, 1992, **122**, 636−640.
11 J. Plastino, E. L. Green, J. Sanders-Loehr and J. P. Klinman, *Biochemistry*, 1999, **38**, 8204−8216.
12 P. Chen, E. I. Solomon, *J. Am. Chem. Soc.*, 2004, **126**, 4991−5000.
13 D. C. Radisky, D. D. Levy, L. E. Littlepage, H. Liu, C. M. Nelson, J. E. Fata, D. Leake, E. L. Godden, D. G. Albertson, M. A. Nieto, Z. Werb and M. J. Bissell, *Nature*, 2005, **436**, 123−127.
14 N. Houstis, E. D. Rosen, E. S. Lander, Nature, 2006, **440**, 944−948.
15 D. Trachootham, J. Alexandre, P. Huang, *Nat. Rev. Drug Discovery*, 2009, **8**, 579−591.
16 B. C. Dickinson and C. J. Chang, *Nat. Chem. Biol.*, 2011, **7**, 504−511.
17 R. Ninomiya, N. Koizumi, K. Murata, *Biol. Trace Elem. Res.*, 2002, **87**, 95−111.
18 E. Gaggelli, H. Kozlowski, D. Valensin, G. Valensin, *Chem. Rev.*, 2006, **106**, 1995−2044.
19 P. S. Donnelly, Z. Xiao, A. G. Wedd, *Curr. Opin. Chem. Biol.*, 2007, **11**, 128−133.
20 H. Kozlowski, D. R. Brown and G. Valensin, *Metallochemistry of neurodegeneration*, RSC Publishing: Cambridge, U.K., 2006.
21 D. J. Waggoners, T. B. Bartnikas and J. D. Gitlin, *Neurobiol. Dis.*, 1999, **6**, 221.
22 E. Forzani, H. Q. Zhang, W. Chen and N. Tao, *Environ. Sci. Technol.*, 2005, **39**, 1257.
23 A. R. Khorrami, A. R. Fakhari, M. Shamsipur and H. Naeimi, *Environ. Anal. Chem.*, 2009, **89**, 319-329.
24 M. Ghaedi, F. Ahmadi and A. Shokrollahi, *J. Hazard. Mater.*, 2007, **142**, 272-278.
25 A. Bottcher, T. Takeuchi, K. I. Hardcastle, T. J. Meade and H. B. Gray, *Inorg. Chem.*, 1997, **36**, 2498-2504.
26 K. S. Rao, T. Balaji, T. P. Rao, Y. Babu and G. R. K. Naidu, *Spectrochim. Acta Part B*, 2002 **57**, 1333-1338.
27 J. W. Liu and Y. Lu, *Chem. Commun.*, 2007, **46**, 4872-4874.
28 D. Karthiga and S. P. Anthony, *RSC Adv.*, 2013, **3**, 16765–16774
29 V. J. Sieben, C. F. A. Floquet, I. R. G. Ogilvie, M. C. Mowlem and H. Morgan, *Anal. Methods*, 2010, **2**, 484–491.
30 C. P. Han, L. Zhang and H. B. Li, *Chem. Commun.*, 2009, **24**, 3545-3547.
31 V. V. Kumar and S. P. Anthony, *AnalyticaChimicaActa*, 2014, **842**, 57–62.
32 N. Kaur and S. Kumar, *Tetrahedron*, 2011, **67**, 9233-9264.
33 V. K. Gupta, A. K. Singh, M. R. Ganjali, P. Norouzi, F. Faridbod and Naveen Mergu, *Sensors and Actuators B*, 2013, **182**, 642– 651.
34 H. Mu, R. Gong, Q. Ma, Y. Sun and E. Fu, *Tetrahedron Lett.*, 2007, **48**, 5525-5529.
35 Z. Xu, Y. Xiao, X. Qian, J. Cui and D. Cui, *Org. Lett.*, 2005, **7**, 889-892.
36 J. Huang, Y. Xu and X. Qian, *Dalton Trans.*, 2009, **10**, 1761-1766.
37 A. Kundu, P. S. Hariharan, K. Prabakaran and S. P. Anthony, *Sensors and Actuators B*, 2015 **206**, 524–530.
38 Y.-R. Ma, H.-Y. Niu, X.-L. Zhang and Y.-Q. Cai, *Chem. Commun*., 2011, **47**, 12643–12645.
39 C. J. Kirubaharan, D. Kalpana, Y. S. Lee, A. R. Kim, D. J. Yoo, K. S. Nahm and G. Gnana Kumar, *Ind. Eng. Chem. Res.,* 2012, **51**, 7441−7446.
40 L-J. Miao, J-W. Xin, Z-Y. Shen, Y-J. Zhang, H-Y. Wang and A-G. Wu, *Sensors and Actuators B*, 2013, **176**, 906– 912.
41 H. D. Song, I. Choi,S. Lee, Y. I. Yang, T. Kang, and J. Yi, *Anal. Chem.*, 2013, **85**, 7980−7986.
42 C-H. Chen, C. Choa, C-F. Wan and A-T. Wu, *Inorg. Chem. Commun.*, 2014, **41**, 88–91.
43 Y. W. Choi, G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee, G. R. You and C. Kim, *Sensors and Actuators B*, 2014, **194**, 343– 352
44 D. Weia, Y. Suna, J. Yina, G. Weia and Y. Du, *Sensors and Actuators B*, 2011, **160**, 1316– 1321
45 P. S. Hariharan, N. Hari and S. P. Anthony, *Inorg. Chem. Commun.*, 2014, **48** 1–4.
46 I. Grabchev, J.-M. Chevelon and X. Qian, *New J. Chem.*, 2003, **27**, 337–340.
47 Z.-Q. Liang, C.-X.Wang, J.-X. Yang, H.-W. Gao, Y.-P. Tian, X.-T. Tao and M.-H. Jiang, *New J. Chem.*, 2007, **31**, 906–910.
48 J. Zhan, L. Wen, F. Miao, D. Tian, X. Zhu and H. Li, *New J. Chem.*, 2012, **36**, 656–661
49 D. Maity and T. Govindaraju, *Inorg.Chem.*, 2011, **50**, 11282-11284.
50 G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee and C. Kim, Dalton Trans., 2014, 43, 6618-6622.
51 Y. Yao, D. Tian, and H. Li, *ACS Applied Mater & Interface*, 2010, **2**, 684.
52 H. K. Sung, S. Y. Oh, C. Park, and Y. Kim, *Langmuir*, 2013, **29**, 8978−8982.
53 V. V. Kumar and S. P. Anthony, *RSC Adv.*, 2014, **4**, 64717-64724.
54 E. J. Song, J. Kang, G. R. You, G. J. Park, Y. Kim, S. J. Kim, C. Kim, R. G. Harrison, *Dalton Trans.*, 2013, **42**, 15514–15520.
55 L. Meng, H-Y. Lu, R-L. Liu, J-D. Chen and C-F Chen, *J. Org. Chem.*, 2012, **77**, 3670−3673
56 P. S. Hariharan and S. P. Anthony, *AnalyticaChimicaActa*, 2014, **848**, 74-79.
57 P. Mulvany, *Langmuir*, 1996, **12**, 788-800
58 J. X. Dong, F. Qu, N. B. Li and H. Q. Luo, *RSC Adv.*, 2015, **5**, 6043–6050.
59 F. Qu, N. B. Li, and H. Q. Luo, *Langmuir*, 2013, **29**, 1199−1205.