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Luminescent Coordination Polymer-Fullerene Composite as Highly Sensitive and Selective Optical Detector for 2,4,6-Trinitrophenol (TNP)

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Highly sensitive and selective detection of TNP by a coordination polymer-fullerene (C_{60}) composite assembly has been reported through luminescence quenching and shifting of major emissive centre. The composite assembly shows high sensitivity even in very low concentration regions towards the detections of TNP with K_{SV} (quenching constant based on linear Stern-Volmer plot) value of 37.5×10^4 M^{-1}, which is the highest value known for any luminescence based selective TNP detector reported to date. The selectivity of TNP detection has been achieved in presence of other nitroaromatics such as 1,3-dinitro benzene (1,3-DNB), 1,4-dinitro benzene (1,4-DNB), 2,4-dinitro toluene (DNT), 4-nitrotoluene (NT) and nitrobenzene (NB) and common metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}.

Introduction

The rapid and selective detection of high energetic chemicals has become a major concern due to the increased use of these chemicals in terrorism as explosives.[1] Among the various explosive chemicals, nitroaromatics are the most widely used. Nitroaromatics are key energetic chemicals for the preparation of landmines and improvised explosive device (IED).[2] Considering all nitroaromatics, 2,4,6-trinitrophenol (TNP) is one of the most dangerous chemicals and its explosive nature is even stronger than 2,4,6-trinitrotoluene (TNT).[3] Owing to its high rate of thermal expansion under external stimuli, TNP has been used as an important ingredient in the manufacturing of explosives and rocket fuels.[1] On the other hand, TNP is widely used in fireworks, dyes, matches, glass, and leather industries. The mutagenic activities of TNP also cause harmful effect on human health such as irritant to skin/eye and damage the respiratory system.[4] Therefore, the selective detection of trace amount of TNP is of high significance for both security reasons and pollution control. However, highly sensitive and selective detection of TNP from other related nitroaromatics and common metal ions is a challenging task, considering the high electron affinity of nitroaromatics and metals ions resulting in fake responses.[5]

Recently, luminescence based detections of nitro explosives have been emerged as one of the most efficient and sensitive methods with many advantageous features over the trained canines or sophisticated instruments due to low cost, simple functioning processes and portability.[6] Luminescent based explosive detections have been attempted with variety of materials including conjugated organic polymers, supramolecular organic polymers, metal complexes and nano-materials.[7] Very recently, increasing investigations have been focused on the design of coordination polymers/metal-organic frameworks based luminescence detectors for nitro explosives.[8,9] In all of the reported coordination polymers based detectors used for selective detection of TNP are based on luminescence quenching.[9] It has been realized that only monitoring the decrease of emission intensity is usually insufficient for accurate and highly selective detections of a targeted chemicals, especially when more than one chemicals quench to a similar extent.[6] The pioneering work of Strano and co-workres using peptide secondary structure modulates single-walled carbon nanotube for selective detection of nitroaromatics employing both intensity-and wavelength-based signal transduction encouraged us to design a composite detector for TNP.[10] Monitoring the changes in both luminescence intensity and wavelength adds a new variable of signal transduction: from one-dimension (1D) to two-dimensions (2D), where both sensitivity and selectivity can be expected to increase along with minimization of fake responses.[6] Based on the above considerations, we have prepared a composite solution by mixing acetonitrile solution of C_{60} and a water solution of a one-dimensional coordination polymer (CP) with exposed carboxylate ion. The composite solution shows high intense visible blue emission on the exposure of UV light. The luminescence of composite shows quenching along with the change in main emissive centres in higher wavelength region in presence of trace amount of TNP. The selectivity of TNP detection has been achieved in presence of other nitroaromatics such as 1,3-dinitro benzene (1,3-DNB), 1,4-dinitro benzene (1,4-DNB), 2,4-dinitro toluene (DNT), 4-nitrotoluene (NT) and nitrobenzene (NB) and common metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}. It also shows high sensitivity even in very low concentration region (0 - 2.5 μM) towards the detections of TNP with K_{SV} (quenching constant) value of 37.5×10^4 M^{-1}, which is the highest value known for any luminescence based selective TNP detector reported to date. This is the first observation, to our knowledge, where coordination polymer-C_{60} composite are used for the detection of nitro explosives.

In this article, we present selective detection of TNP using coordination polymer-C_{60} composite along with the mechanistic investigation of the selectivity.

Experimental Section

Materials

The chemicals needed for the synthesis of the coordination polymer, $Zn(NO_3)_3.6H_2O$ (Sigma-Aldrich, 98%), trans-3-(3-Pyridyl)acrylic acid (Sigma-Aldrich, 99%), triethyl amine (Sigma-Aldrich, 99.5%) and fullerene-C_{60} (Sigma-Aldrich, 99.5%) were used as received. The chemical used for the detection experiments, acetonitrile (99.8%), 2,4,6-trinitrophenol (TNP) (98%), 1,3-dinitrobenzene (1,3-DNB) (97%), 1,4-dinitrobenzene (1,4-DNB) (98%), 2,4-dinitrotoluene (DNT) (97%), 4-nitrotoluene (NT) (99%) and nitrobenzene (NB) (99%), were used as received from Sigma-Aldrich without further purification. The water used was double distilled and filtered through a Millipore membrane.

Synthesis and characterizations

The CP has been synthesized based on earlier reported procedure.[11] The powder XRD patterns of the synthesized CP is being entirely consistent with the simulated XRD pattern generated based on the structures determined using the single-crystal XRD data of CP reported by Wang and Co-workers. (see ESI, Fig. S1).[11] The composite assembly was prepared by mixing 100 mL C_{60} solution in acetonitrile (5 μM) and 200 mL CP solution (1 mM) in water followed by ultrasonic agitation for 30 min. The morphologies and the sizes of composite were investigated using scanning electron microscope (QUANTA FEG250, FEI).

Optical Measurements

The photoluminescence properties of composite were investigated at room temperature. Photoluminescent spectra were measured using a Fluorolog Horiba Jobin- Yvon spectrofluorometer. The analytes were added using micro pipette into quartz cuvette containing 2 mL composite solution. UV-Vis spectra of analytes in mixed solvent (acetonitrile and water in 1:2 volume ratio) were studied using Shimadzu UV-2600 UV-Vis spectrophotometer.

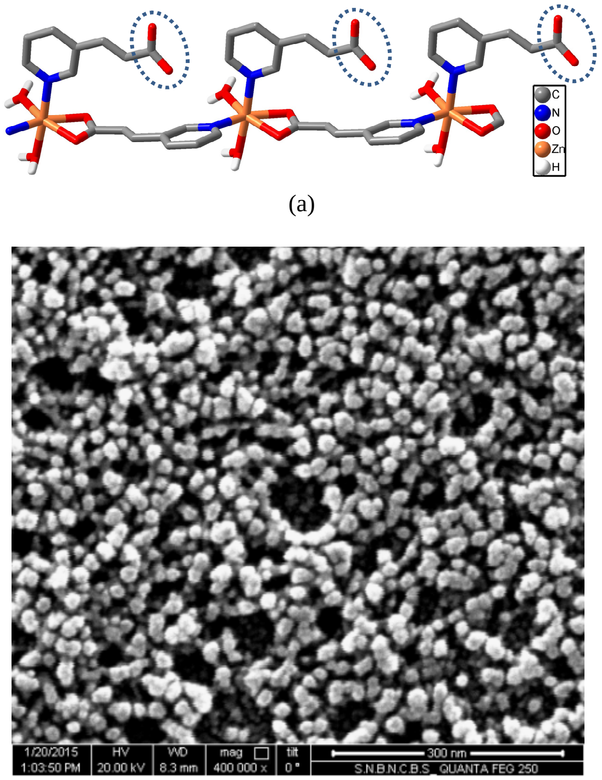
Results and Discussion

Structure and morphology

The coordination polymer (CP) used for the preparation of the composite assembly has one dimensional structure with non-bonded exposed carboxylate group, $[Zn(L)_2(H_2O)_2]$ (L = 3-(3-pyridyl acrylate) (Fig. 1a). This non-bonded exposed carboxylate groups have an important role for the formation CP-C_{60} composite through the interaction between electron rich CP (donor) and electron deficient C_{60} (acceptor). The composite mixture has been analysed using scanning electron microscopy (SEM) by drop casting in silicon wafer (Fig. 1b). The SEM image shows the presence of homogenous assembly with particle sizes in nano regime (~10-25 nm).

Nitroaromatics Detections

The solution of composite assembly exhibited strong emission centered at 394 nm along with a shoulder at 457 nm upon excitation at 314 nm (see ESI, Fig. S2). The strong emission bands observed at 394 can be assigned to transitions based on assembly centered which has been formed between the interaction of the electron rich exposed carboxylate group of the CP and electron deficient C_{60}.



(a)

(b)

Fig. 1. (a) View of one dimensional structure with two different type of organic ligands based on the bonded and exposed carboxylate in $[Zn(L)_2(H_2O)_1]$ (L = 3-(3-pyridyl) acrylate) (hydrogen atoms of ligands are not shown for clarity). The dotted circle shows the position of exposed carboxylate. (b) SEM image of the composite.

The originality of the composite centered emission has been confirmed by comparing with the individual emission of the CP and C_{60} separately upon excitation at 314 nm (see ESI, Fig. S3). The modification of the emission spectra of the composite from the CP and C_{60} are, probably, due the modification of the electronic state through the interactions. To explore the ability of the composite solution to detect a trace amount of nitroaromatics, luminescence quenching titrations were performed with the incremental addition of analytes (nitroaromatics) to the composite solution. Figure 2 shows changes in the luminescence intensity with the increasing addition of TNP (upto 30 μM). The visible bright blue emission of the composite on UV exposure vanished upon the addition of the TNP, which quenched nearly 99% of the initial luminescence intensity (based on the emission centered at 394 nm). In addition to this, the main emission peak centre also shifted to 457 nm from 394 after the addition of 7.5 μM of TNP. The luminescence quenching can be clearly detected at as low as 0.25 μM concentration which is equivalent to 56 ppb of TNP (see ESI, Fig. S4). The luminescent titration of the composite has compared with the pure CP and C_{60} in presence of TNP (see ESI, Fig. S5). These results indicate the composite is much superior for detection in terms of quenching and shifting of main emission peak position.

Similar luminescence quenching titrations were also performed with other nitroaromatics such as 1,3-dinitro benzene (1,3-DNB), 1,4-dinitro benzene (1,4-DNB), 2,4-dinitro toluene (DNT), 4-nitrotoluene (NT) and nitrobenzene (NB) (see ESI, Fig. S6 – S10). The quenching of the composite emission (at 394 nm) in the case of all analytes after addition of 10 μM of analytes is shown in figure 3 as bar diagram.

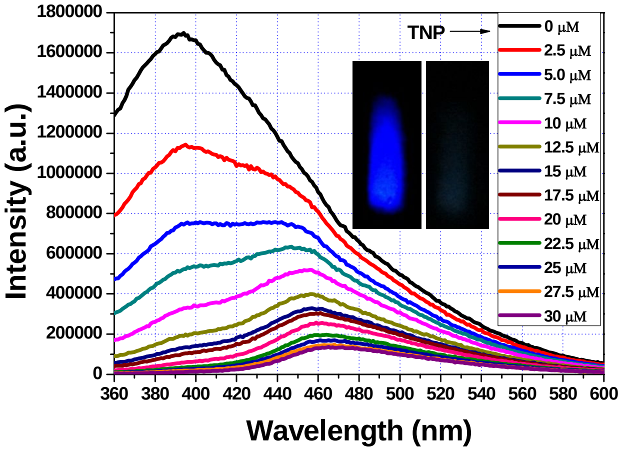


Fig. 2. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of TNP (λ_{ex} = 314 nm). Final concentration of TNP in the medium is indicated in the legend. Inset: photograph showing the original blue luminescence of the composite solution and the quenched one in presence of 30 μM TNP.

In presence of these nitroaromatics, luminescence quenching is much lower than the TNP along with the no change of the main emissive centre. The variation of I/I_0 (I_0 and I are luminescence intensity in absence and presence of analytes) with concentration of the analytes shows non-linear behaviour for TNP and nearly linear behaviour for other nitroaromatics (Inset of figure 3).

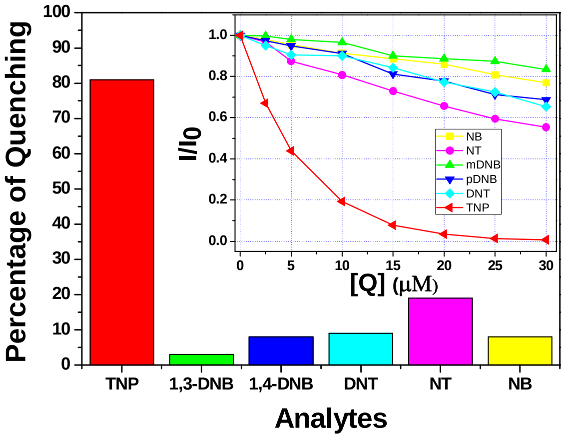


Fig. 3. Percentage of luminescence quenching with respect of composite emission (**at 394 nm**) with 10 μM of different analytes. Inset shows plot of fraction of luminescence intensity of the composite **(at 394 nm)** vs concentration of analytes. I_0 and I are luminescence intensity in absence and presence of analytes, respectively. Note the very high quenching for TNP.

To understand the sensitivity for the detection of TNP, the Stern-Volmer plots were used to calculate the quenching constants of the analytes using the SV equation $(I_0/I) = K_{SV}[A] + 1$, where I_0 and I are the luminescence intensities before and after the addition of the analyte, [A] is the molar concentration of the analyte and K_{SV} is the quenching constant. At low concentration (upto 2.5 μM) of TNP a linear increase in (I_0/I) was observed (Fig. 4). With the increasing concentration of TNP, SV plot diverged from linearity and began to bend upwards (Fig. 5). The linear variation at lower concentration are mainly due to static quenching, whereas the steep curves at higher concentration are presumably due to dynamic quenching. The static quenching can be accredited due to the ground state interaction between TNP and the composite. The dynamic quenching is mainly due to the energy and electron transfer processes between TNP and the composite. Fitting of linear plot allows determination of the quenching constants (K_{sv}) to be 37.5 $\times 10^4$ M^{-1}. The very high observed K_{sv} values revealed extremely high sensitivity, which made the composite one of the best sensitive luminescence based detector for TNP.

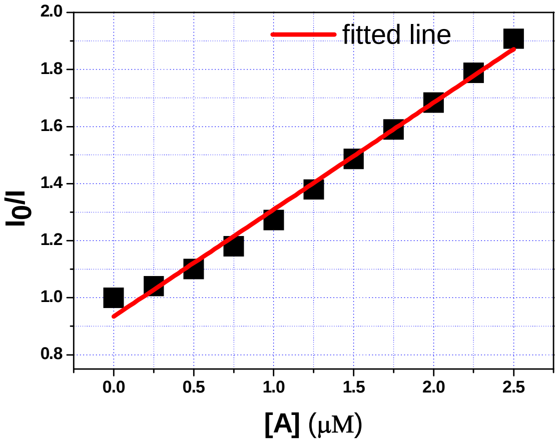


Fig. 4. Plot of I_0/I of composite solution **(at 394 nm)** vs concentration of TNP in lower concentration range of TNP (upto 2.5 μM). I_0 and I are luminescence intensity in absence and presence of TNP, respectively. The linear fit is shown as red line.

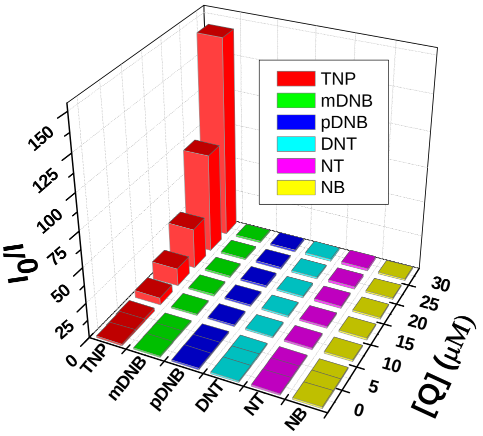


Fig. 5. Plot of I_0/I of composite solution **(at 394 nm)** vs concentration of analytes in higher concentration range of analytes (upto 30 μM). I_0 and I are luminescence intensity in absence and presence of analyte, respectively. Note the steeped non-linear behavior in the case of TNP.

Motivated by very high luminescence quenching of the composite solution in presence of TNP, we thought to check the selectivity for TNP in the presence of other nitroaromatics. In a specially designed experiment protocol, the luminescence spectrum of the composite solution was recorded, to this 1 μL of 0.01 M acetonitrile solution of

1,3-DNB was added sequentially in two equal portion (0.5 µL in each portion) followed by 1 µL of 0.01 M acetonitrile solution of TNP in similar way and the corresponding emissions were monitored. The 1,3-DNB was added initially, but the addition of 1,3-DNB showed very little effect on luminescence intensity. On the other hand, the addition of acetonitrile solution of TNP, gave significant luminescence quenching, with the quenching efficiency of TNP remaining unaffected, even through further addition sequences (see ESI, Fig. S11). Similar results were obtained upon addition of acetonitrile solutions of other nitroaromatics followed by TNP to the composite solution (see ESI, Fig. S12-S15). The results can be easily visualized by plotting the percentage of luminescence intensity versus volume of analyte added (Figure 6). The stepwise decrease in luminescence intensity clearly demonstrates high selectivity of the composite solution for TNP in presence of other nitroaromatics.

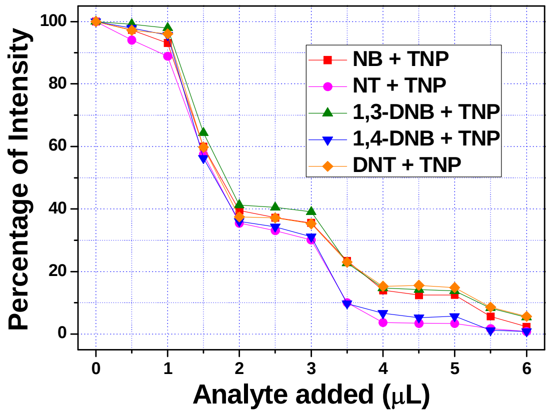


Fig. 6. Decrease in percentage of luminescence intensity upon the addition of acetonitrile solutions of different nitroaromatics followed by TNP.

To check the selectivity for TNP in presence of common metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+} Fe^{3+}, the similar luminescence experiments have been carried out by adding 1 µL of 0.01 M aqueous solution of metal ion followed by 1 µL of 0.01 M actonitrile solution of TNP (see ESI, Fig. S16-S20). The results also show high selectivity for TNP in presence of these metal ions (Fig. 7).

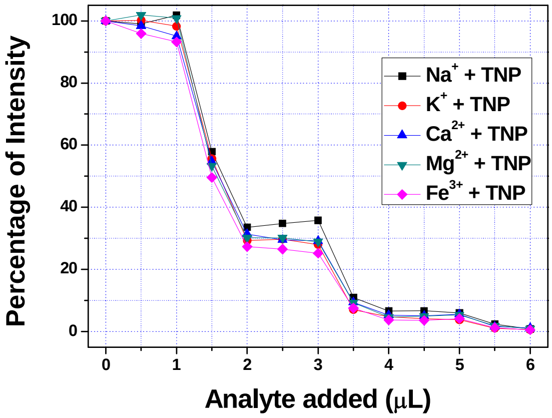


Fig. 7. Decrease in percentage of luminescence intensity upon the addition of water solutions of different metal ions followed by acetonitrile solution of TNP.

The very high sensitivity and selectivity for TNP indicate a strong molecular level interaction between CP and TNP. To visualize the fact, the possible selective molecular level interaction between CP and TNP are presented schematically in figure 8. Due to the presence of acidic phenolic hydrogen in TNP, it interacts with the CP through hydrogen bonding (O−H···O) and displaces the C_{60} from the position of the exposed carboxylate group of the CP. The displacement of the C_{60} along with the interaction of the TNP through hydrogen bonding, the composite assembly between CP and C_{60} disintegrate. On the hand, the interactions of all other nitroaromatics with the CP through exposed carboxylates are ruled out due to the absence of phenolic proton.

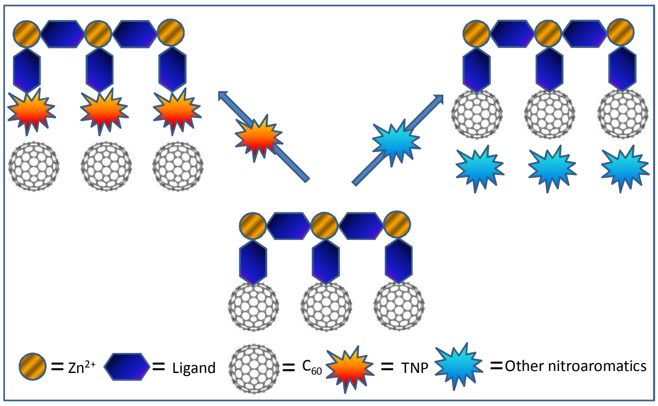


Fig.8. Schematic of interactions between C_{60} and CP in the composite assembly and the changes of interactions in the presence of TNP and other nitroaromatics.

To rationalize the observed luminescence quenching and its selectivity for TNP, the absorption spectra of all the analytes in solvent mixture are compared (see ESI, Fig. S21). In the case of all nitroaromatics except TNP, absorption bands are in much higher energy (lower wavelength) than the emission wavelength of the CP (414 nm). Whereas TNP has a broad absorption band (310-450 nm) which is overlapped to a good extent with CP emission centre (see ESI, Fig. S22). This overlap indicates the possibility of resonance energy transfer from the CP site to TNP. In addition to this, the presence of this absorption band (centered at 335 nm) indicates a possibility of electron transfer from the composite to TNP as the excitation energy (314 nm) is slightly higher than the absorption band. The close proximity between the CP and TNP through hydrogen bonding interactions enhances the possibility of the electron transfer as well as resonance energy transfer processes. The fully bonded ligands of the CP do not interact directly with TNP, which resulted in less quenching effect (at 457 nm) than the non-bonded ligand centerted one (at 414 nm). As a result, the bonded ligand centered emission has been emerged as main emissive centre in high concentration ranges of TNP. Beside this, the slight reductions of luminescence of the composite in presence other nitroaromatics are probably due to the direct absorption of the excitation energy (314 nm) as the absorption spectrums of these nitroaromatics show the presence of their absorption trails at 314 nm.

To prove the above mechanism, we have taken into consideration the luminescence quenching behaviour through the blocking of the exposed carboxylate ions by adding HCl. In a typically designed experiment, the luminescence spectrum of the composite solution was recorded, to this 10 µL of 0.1 M HCl solution was added and the corresponding emissions were monitored. As can be observed from figure 9, the emissive peak position shifted to 409 nm along with the reduction of luminescence intensity. This behaviour is the clear signature of breakdown of the CP-C_{60} composite and emerging of the non-bonded ligand as main emissive centre. Interestingly, further addition of 10 μL of 0.1 M HCl increased the luminescence intensity based on the non-bonded ligand emission (414 nm). This increase is probably due to the higher rigidity of the CP in presence of hydrogen ions through the interaction of CP *via* exposed carboxylate. As it can also been observed the luminescence quenching of 414 nm centered emission and the gradual shifting of the main emission peak to 457 nm with the incremental addition of 0.01 M actonitrile solution of TNP (0.5 to 5 μL) in the HCl mixed composite solution.

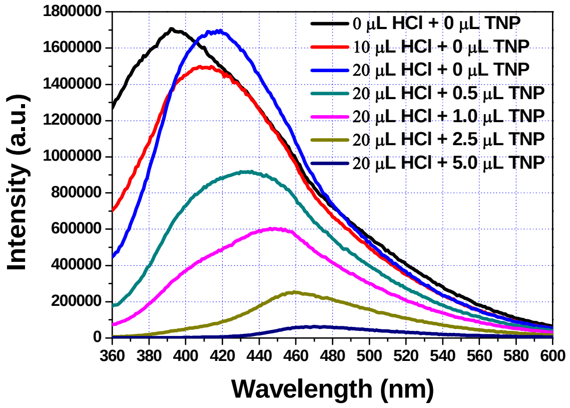


Fig. 9. Emission spectra of the 2 mL composite solution upon the incremental addition of 0.1 M HCl and 0.01 M acetonitrile solution of TNP (λ_{ex} = 314 nm). The final added volume of HCl and TNP solution in the medium is indicated in the legend.

The very high quenching constant (K_{SV}) for the detection of TNP in the present case encouraged us to compare with other state-of-art luminescence based TNP detectors reported for liquid medium (see ESI, table S1). Based on the comparison, the observed K_{sv} for TNP (37.5×10^4 M^{-1}) is highest value known for luminescence based selective TNP detector reported to date.

Conclusions

In conclusion, a highly luminescent coordination polymer-C_{60} composite assembly for highly sensitive and selective detection of the TNP has been reported through luminescence quenching and shifting of main emissive peak. The composite exhibited selective detection of TNP, even in the presence of other nitroaromatics and metal ions. The selectivity is ascribed to electron transfer as well as resonance energy transfer between TNP and the coordination polymer through molecular level interactions. The observation of very high quenching constant makes this composite one of the best detector for the detection of TNP in liquid medium.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of the experimental data and a table about the details of other luminescence based TNP detector. See DOI: 10.1039/c000000x/

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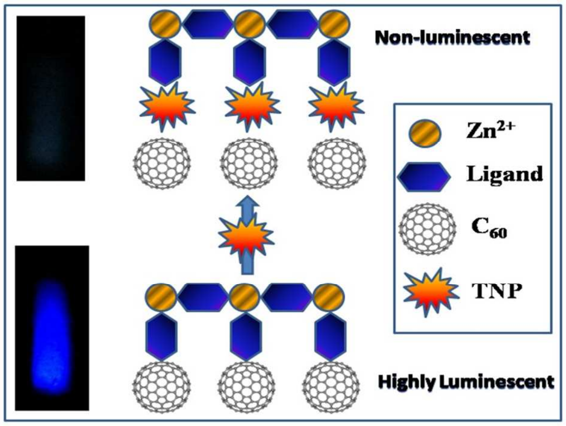

Text for TOC

Blue emitting coordination polymer-fullerene composite as highly sensitive and selective luminescent quenching based optical detector for 2,4,6-trinitrophenol.