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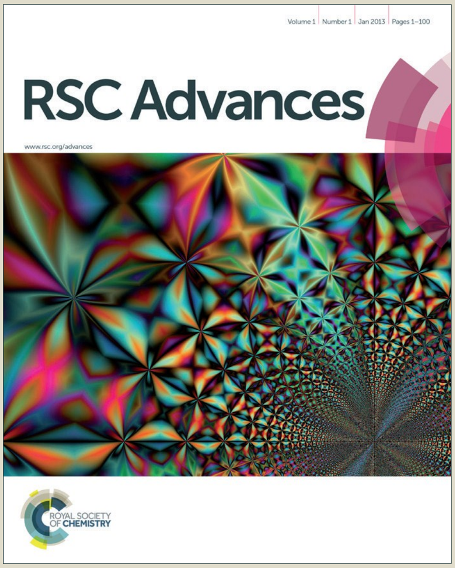

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ARTICLE

Aggregates of hydrazono-sulfonamide adduct as picric acid sensor

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Abstract: Novel hydrazono-sulfonamide adduct (**AVM**) was designed and synthesized. Due to inhibition of C=N isomerization at higher water content, adduct shows remarkable aggregation induced emission enhancement (AIEE) properties in THF:Water solvent system. The formation of nanoaggregates was confirmed by the transmission electron microscopy (TEM) analysis. Theoretical DFT calculations supported the observed photophysical changes. These aggregates of **AVM** act as selective and sensitive sensor for picric acid by fluorescence quenching mechanism. Efficiency of quenching process was calculated using Stern-Volmer equation. The detection limit was found to be 80 nM. In addition, contact mode detection using fluorescent test strips was developed to demonstrate the solid phase sensing of picric acid.

Introduction

Owing to strong acidity and high water solubility[1], picric acid (PA) is considering as a threat to human being and a great hazard to the environment.[2] Consequently, for the past several years, detection of picric acid has been a field of enormous interest to the researchers.[3] Due to explosive nature of PA and increasing the terrorist activities all over the world, it is necessary to develop sensitive and selective fluorescent probe for detection of PA. In spite of higher explosive nature of PA than other nitro aromatic compounds (NACs), development of sensors for detection of PA received lesser attention than development of sensors for other NACs. Several methods and materials such as metal complexes[4], ionic liquids[5], organic gels[6], polymers[7], metal-organic frameworks[8], and quantum dots[9] have been reported and useful for the detection of NACs. As fluorescent signalling involves simple instrumentation, high sensitivity, selectivity, fast response and importantly low cost, merits of fluorescent based detection of NACs among various other methods have been discussed in good number of publications.[10] Owing to the impact of PA, Kumar et al[11], Mukherjee et al[12], Tang et al[13], and others[14] have made significant contributions towards the preparation of various ensembles for the detection of PA.

Aggregation induced emission[15], which is exactly opposite to the concentration quenching or aggregation caused quenching, was first reported by Tang et al in 2001. In solution state, certain molecules are weakly emissive but emit highly in condensed phase or aggregated state.[16] In aggregation phenomenon, molecules tend to form highly emittive nanoparticles, which were effectively utilized as sensors for various analytes[17]. Restriction of intramolecular motion has been proven to be a primary reason for AIE of any luminogens. In addition, many of the reported probes for PA sensors were big molecules with high molecular weight, need costly raw materials for preparation, and involved multistep synthesis. Therefore, cost effective, highly-selective and sensitive small molecule based sensor for PA is still in demand. In our recent publication[18], we had disclosed novel method for the preparation of hydrazono-sulfonamide adduct using heterogeneous catalyst, which shows remarkable aggregation induced emission enhancement (AIEE) property. We said that the inhibition of C=N isomerization at higher water content was account for the observed AIEE character of adduct. In continuation of our previous work, we herein report a novel hydrazono-sulfonamide adduct **AVM** as fluorescent chemosensor for PA, which employs easy synthetic operation and shows superior priority towards PA over other NACs with high sensitivity, quenching constant and low detection limit. To the best of our knowledge, PA sensor using C=N isomerization concept is unprecedented.

Experimental section

Materials and methods

Tosyl azide[19] was prepared by adopting method reported in the literature. Preparation and characterization data for Cu(BTC) MOF are presented in our reported protocol.[18] Unless stated otherwise, all solvents and chemicals were obtained from commercial sources and used without further purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel-G plates (Merck) using a mixture of petroleum ether (60-80 ˚C) and ethyl acetate (7:3) as the eluent. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Advance) 300 MHz instrument using TMS as an internal standard and $CDCl_3$ as solvent. Chemical shifts are

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expressed in parts per million (ppm) and the coupling constants (*J* values) are expressed in hertz (Hz). The following abbreviations are used to indicate spin multiplicities: s (singlet), m (multiplet). Elemental analyses were carried out with Perkin-Elmer 2400 series II analyzer. Melting points were determined using open capillaries and were uncorrected. Absorption measurements were carried out in Agilent single beam UV-Diode Array spectrophotometer. Fluorescence spectra were recorded in Agilent Cary Eclipse Fluorescence spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was recorded in LCQ Fleet, Thermo Fisher Instruments Limited, US. The morphological characterization of nanoaggregates was determined by using JEOL JEM-2010 Transmission Electron Microscopy. Single crystal XRD analysis was performed using 3-circle Bruker Apex X-Ray diffractometer. The slit width was 5 nm for both excitation and emission. HPLC grade solvents were used for photophysical measurements.

Preparation of aggregates

Stock solution of **AVM** was prepared in THF (10^{-4}M). An aliquot (1mL) of this stock solution was transferred to the volumetric flask. Appropriate amount of THF and water was added to the flask under vigorous stirring to get the 10^{-5}M THF:water mixtures with water fractions of 0-90%. The spectral analysis of the resultant mixtures was measured immediately.

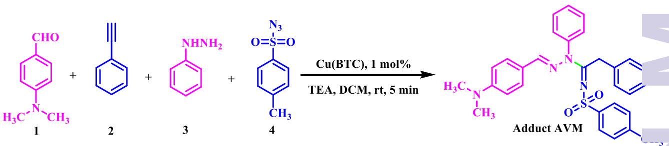
Caution! The nitroaromatic compounds used in this study, specially TNT and picric acid, are very powerful explosives. They must be handled with care and also in very small quantities.

Synthesis of probe AVM

Adduct **AVM** has been synthesized by following our recently reported protocol.[18] To the stirring mixture of *N,N*-Dimethylamino benzaldehyde **1** (1 mmol) and phenylhydrazine **3** (1 mmol) in DCM (3 mL) was added phenyl acetylene **2** (1 mmol), tosyl azide **4** (1 mmol) and activated Cu(BTC) MOF (1 mol%). To the above mixture, triethylamine (1.1 mmol) was added slowly. The whole reaction mixture was allowed agitated for 10 min at room temperature and then filtered to separate the catalyst from reaction mixture. To the filtrate was added petroleum ether and ethyl acetate mixture (1:1, 20 mL) and resulting mixture was stirred for 10 min. About 75% of solvent mixture was distilled off from filtrate under vacuum at 70 ˚C. The above crude product was cooled to 0 to 5 ˚C and triturated immediately in 5-8 min to afford light yellow solid which was collected by filtration. The recovered catalyst was thoroughly washed with DCM and air dried for 10 min before using it for next reaction. Isolated yield 80% (1.4g); Light yellow solid; mp 191-193 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 – 7.44 (m, 7H), 7.35 – 7.25 (m, 4H), 7.20 – 7.16 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 4H), 6.59 (d, *J* = 9.0 Hz, 2H), 4.95 (s, 2H), 2.98 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 151.8, 146.3, 141.6, 140.8, 136.6, 136.0, 129.9, 129.1, 129.1, 128.9, 128.7, 128.7, 128.4, 126.3, 125.9, 121.1, 111.6, 40.0, 36.9, 21.2; MS (ESI) m/z $[M+H]^+$: 511.2; Anal. Calcd for: $C_{30}H_{30}N_4O_2S$: C, 70.56; H, 5.92; N, 10.97%. Found C, 70.60; H, 5.87; N, 10.92%.

Results and Discussion

Synthetic route for the preparation of adduct **AVM** is outlined in S**cheme 1**. Adduct was fully characterized by NMR, ESI-MS and elemental analysis. Single crystals of **AVM** were obtained by slow evaporation of solution of **AVM** in ethyl acetate and pet ether solvent mixtures (Figure 1 and CCDC 1404294). X-ray diffraction analysis revealed that adduct is crystallised in the monoclinic crystal system with the *P21/c* space group. The crystallographic parameters of adduct are provided in table 1. From the crystal structure, it was found that both the imines are in *E* configurations. Adduct is highly soluble in common organic solvents such as THF, chloroform, dichloromethane, etc. and insoluble in water. We envisaged that **AVM** could be weakly emissive because of active C=N isomerization, which can be arrested in aggregated state.[18, 20]



Scheme 1. Synthesis of adduct **AVM**

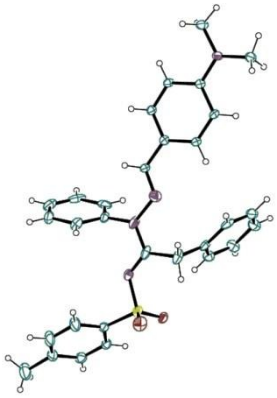


Figure 1. ORTEP diagram of **AVM**

We screened photophysical properties of adduct **AVM** using UV-Vis and fluorescence spectroscopy techniques in THF and THF:water mixtures by maintaining the concentration 1 × 10^{-5} M. The UV-vis spectrum (Supporting Information) of adduct **AVM** in THF shows absorption maxima at 354 nm. When water (90% volume fraction) was added to THF solution of **AVM**, absorption band was slightly red shifted to 371 nm with the appearance a *leveling-off* long wavelength tail due to Mei scattering effect, which confirms the formation of nanoparticles.[21] Photoluminescence (PL) spectrum of **AVM** in THF and THF:water mixtures are shown in Figure 2. As depicted in Figure 2, **AVM** is weakly emissive when it is dissolved in THF and exhibits emission band at 435 nm. When 10 to 50 % of water was added, the PL intensity gradually increased with shift in wavelength from 434 to 460 nm. At the same time, PL intensity of 60, 70 and 80 % water fractions were decreased. In contrast, PL intensity of 90 % water fractions reached maximum and emission maxima located at 438 nm. Similar kind of spectral changes was frequently observed for compounds with AIEE properties, but the reason remains unclear.[22] We assumed that the inhibition of C=N isomerization could be the primary reason for the observed spectral changes. Because of C=N isomerization of **AVM** was weakly emissive in THF solution, when water was added C=N isomerization gets blocked causing suppression of non-radiative decay from excited state.[18] After the addition of water, solute molecules can aggregate into various kinds of nanoparticle suspensions: crystal particles and amorphous particles.[22f] The former leads to an enhancement in the PL intensity, while the latter leads to a reduction in intensity. Thus, the measured overall PL intensity data depends on the combined actions of the two kinds of nanoparticles. However, it is difficult to control the formation of nanoparticles in high water content. Thus, the measured PL intensity often shows no regularity in high water content. Transmission electron microscopy (TEM) further confirmed the formation of spherical nanoparticles (Figure. 3a).

Table 1: Crystal data and structure refinement parameters of **AVM**

Parameters	AVM
Formula	$C_{30}H_{30}N_4O_2S$
Formula Weight	510.2
Crystal System	Monoclinic
Space Group	*P21/c*
a/Å	13.4218(17)
b/Å	10.5641(11)
c/Å	19.169(3)
α/°	90
β/°	106.172(7)
γ/°	90
$V/Å^3$	2610.4(6)
Z	4
Temperature (K)	100
D, g/cm^3	1.308
μ (Mo-Kα)mm^{-1}	0.160
F(000)	1086
Size (mm)	0.08 × 0.15 × 0.25
θ range (°)	1.6 – 25.0
Reflection collected	19348
R1[a] [I > 2σ(*I*)]	0.0671
wR2[b] [I > 2σ(*I*)]	0.1817
Goodness-of-fit	1.10

[a] $R1 = \Sigma|F_o - F_c| / \Sigma|F_o|$; [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2] / w(F_o^2)^2]^{1/2}$

The ground state geometry of the **AVM** was optimized using a density functional theory (DFT) method using B3LYP/6-31G basis sets. The DFT calculations were carried out using the Gaussian 09 program.[23] The ground state optimized geometries and absorption behaviours of the corresponding transitions of the compounds were obtained from time dependant (TD) DFT using above mentioned functional and basis set. DFT optimized structure indicates similar *E* configuration for both the imine groups in the gas phase which is same as crystal structure of adduct (Figure 4b). The frontier molecular orbital diagram (Figure 4a) shows that the highest occupied molecular orbital (HOMO) is mainly delocalized on *N*,*N*-dimethyphenyl moiety indicating the n-π* transition. Lowest unoccupied molecular orbital (LUMO) are delocalized on *N*,*N*-dimethyphenyl and sulfonyl groups. The calculated energy gap between HOMO and LUMO is 3.9 eV.

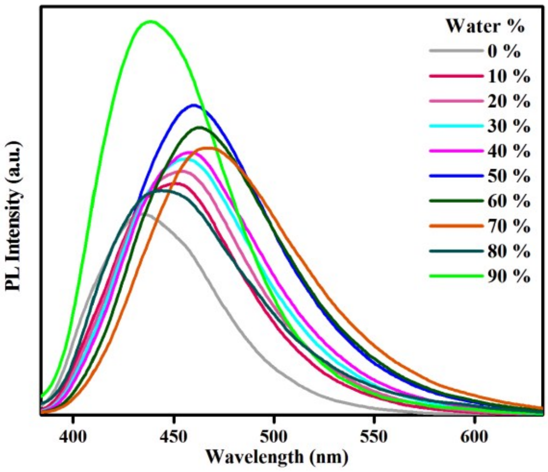


Figure 2. PL spectrum of **AVM** (1×10^{-5} M) in THF:water mixtures

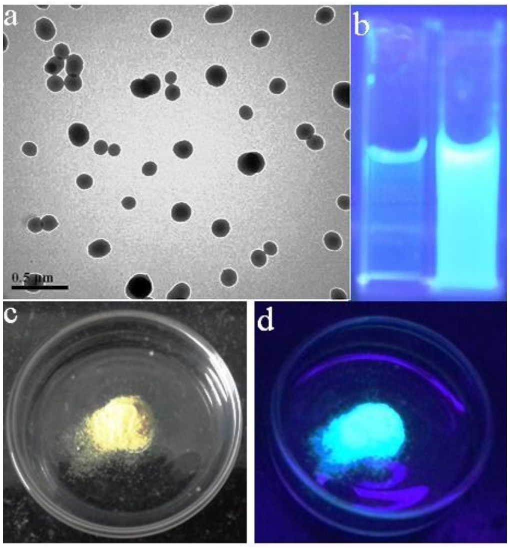


Figure 3. TEM image of nano-aggregates for 90% water fraction (a), color change in 0 and 90% water fraction (b) under UV irradiation, solid state emission in day light (c) and UV light, 365 nm (d)

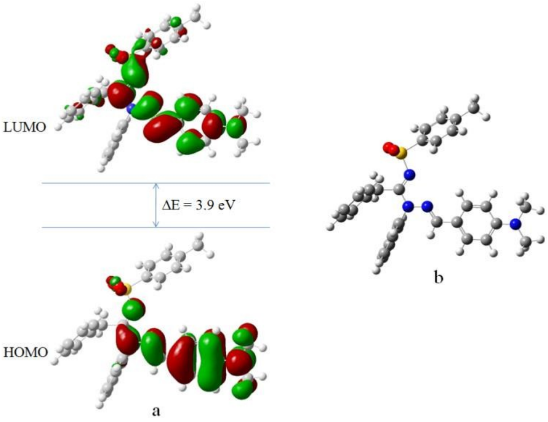


Figure 4. HOMO and LUMO energy levels of **AVM** calculated by TD-DFT/B3LYP/6-31G basis sets (a) and optimized geometry (b).

Picric acid detection

Highly emissive nature of **AVM** in condensed phase prompted us to explore possibility of its application as a sensor. In general, electron deficient NACs tend to interact with electron rich molecules and electron donating groups such as free amine and *N*,*N*-dialkyl or aryl amino group. Based on this concept several fluorescent sensors have been developed for NACs.[24] We hypothesized that **AVM** could act as a probe for NACs as it possesses *N*,*N*-dimethyl amino group. To confirm our hypothesis commenced our work using PA as model NAC. We used nanoaggregates of 50% and 90% water mixtures as picric acid probe along with pure THF solution of **AVM** for comparison.

Emission bands of pure THF solution of **AVM**, nanoaggregates of 50% and 90% water fractions were located at 434, 460, 438 nm when excited at corresponding absorption maxima. Fluorescence spectroscopic titration of nanoaggregates and pure THF solution of **AVM** with picric acid revealed that PL intensity of corresponding solution decreased with incremental addition of picric acid (Figure. 5). High emissive nature of nanoaggregates of 50% and 90% water fractions were completely quenched with 30 equivalents of picric acid, without any appreciable shift in the wavelength. However, pure THF solution of **AVM** needed 50 equivalents of picric acid for complete quenching which indicates the utility of nanoaggregates towards the sensing of PA compared to pure THF solution. During the addition of PA to the probe, colorless solution rapidly turned yellow (Supporting Information).

The data from fluorescence titrations were used to calculate the quenching constant using the Stern-Volmer equation,

$$I_0/I = 1 + K_{SV}[Q]$$

Where, I_0 and I are the PL intensities before and after addition of PA, [Q] is the quencher concentration and K_{SV} is the Stern-Volmer or quenching constant (Figure 5d).

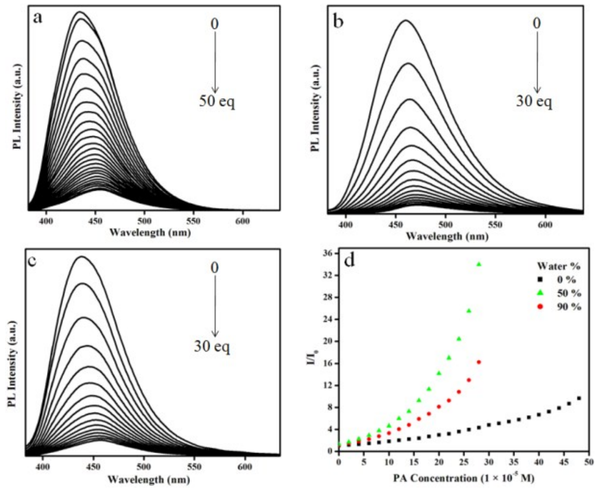


Figure 5. PL spectral changes of **AVM** (1×10^{-5} M) containing different concentration of PA in neat THF solution (a) and THF:water mixtures 50:50 (b), 10:90 (c), Stern-volmer plot (d)

Stern-Volmer plot (I_0/I vs. PA concentration) is presented in Figure 4d. The Stern-Volmer constant of the quenching process was found to be 1.0×10^5 M^{-1} which is comparable to the reported values.[11h, 12a, 25] Higher quenching constant indicates the effective interaction between probe and PA, which is further supported by the spectral overlap between absorption spectrum of PA and emission spectrum of probe in the wavelength region 381 – 491 nm (Supporting Information). Linearity in the lower concentration PA from Stern-Volmer plot (Supporting Information) indicates the involvement of static quenching mechanism. However, at higher concentration of PA, the plot bent upward due to super amplified quenching effect.[26] Nanoaggregates of 50% water fraction shows higher sensing performance than 90% water fraction, which may due to polymer packing in the former is looser than in the latter and the looser packing allows voids to interact with more PA molecule.[13c]

The turn-off mechanism (Figure. 6) may be explained by the electron transfer and/or energy transfer mechanism[11a, 27,] between picrate ion and **AVM** adduct. The proton NMR spectral studies shows the presence of PA, shift the sensor peak positions to the downfield (Figure. 7), which further confirms the electrostatic interaction between sensor and PA.[14c] The aromatic protons near to the $-NMe_2$ group was shifted to the downfield, thus confirms the $-NMe_2$ group is the receptor site. In addition to PA, we screened other NACs 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 1,4-dintrobenzene (DNB), 4-nitrobenzene (NB), 1,4-dintrophenol (DNP), 4-nitrophenol (NP), 4-nitrobenzoic acid (NBA), and benzoquinone (BQ) with probe (Figure 8). Noticeably, the selectivity is very high toward PA compared to other NACs. Nanoaggregates of **AVM** offer more diffusion channels for the exciton to migrate, allowing them to be more quickly annihilated by picric acid.[29]

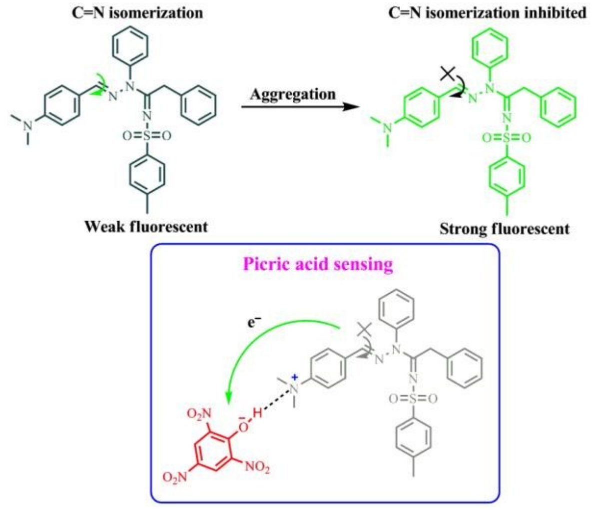


Figure 6. Sensing mechanism

Detection limit[30] was calculated using the equation 3σ/slope, where σ is the standard deviation. The detection limit was found to be 80 nM, which is almost comparable to the reported values.[14i, 31] To explain the merits of this work, we demonstrated the solid phase detection of PA using test strips. Test strips were prepared by using TLC plate coated by dipping it into the solution of **AVM** adduct. The coated strips were dried under vacuum and then used for the detection PA. The emission nature of test strips was quenched when it comes in contact with PA. The quenching confirms the solid phase interaction between probe and PA (Figure 9).

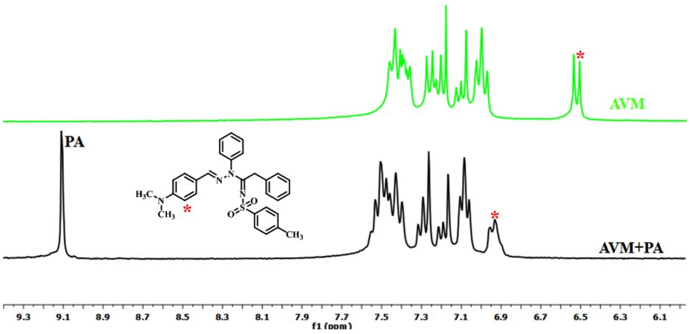


Figure 7. ^{1}H NMR spectra of **AVM** (green) and its PA complex (black) in $CDCl_3$

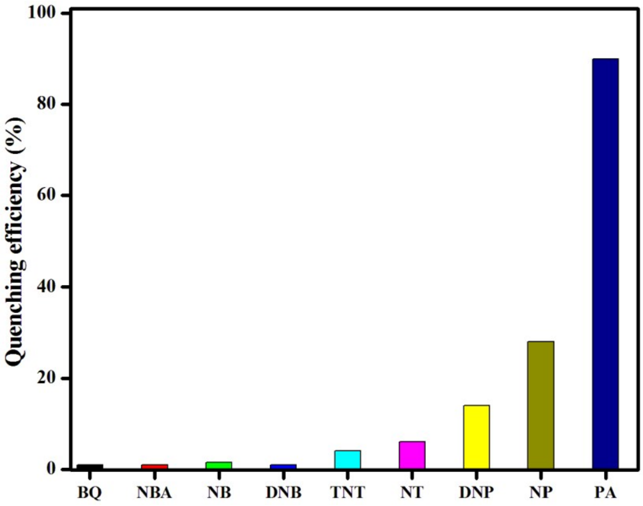


Figure 8. Relative fluorescence quenching of nanoaggregates of **AVM** upon addition of various NACs (30 eq) in THF:water (10:90) mixture

Figure 9. Test strips based detection of PA using UV light (365 nm), blank TLC plate (a), after coating **AVM** (b) and interaction with picric acid (c)

Conclusion

We have designed and synthesized novel hydrazono-sulfonamide (**AVM**) adduct using heterogeneous Cu(BTC) MOF catalyst in good yield. Aggregation study in THF:water system reveals that C=N isomerization is the main cause for observed spectral changes. Theoretical DFT calculations further confirmed this fact. Formation of nanoaggregates was confirmed by TEM analysis. Nanoaggregates of **AVM** adduct showed high sensitivity and selectivity towards PA compared to other NACs. Besides, low detection limit and high Stern-Volmer constant shows the efficiency of the quenching process. In addition, it was demonstrated that PA can be detected using the test strips made from TLC plates.

Acknowledgements

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Aggregates of hydrazono-sulfonamide adduct as picric acid sensor

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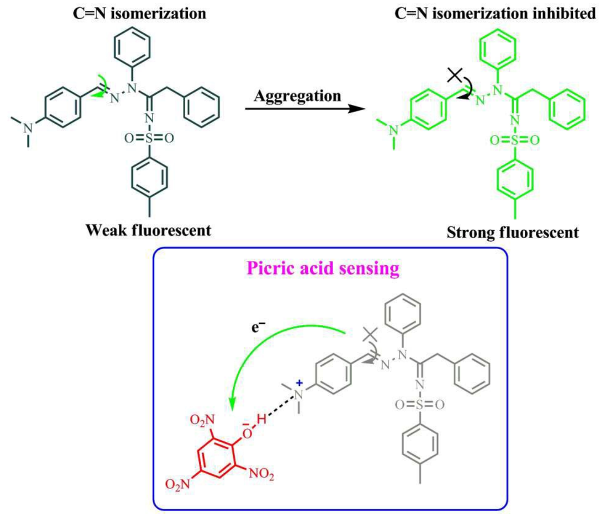
TOC GRAPHICAL ABSTRACT



The sensitive and seletive sensor for picric acid was developed using aggregates of novel hydrazono-sulfonamide adduct.