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A New Compound for Sequential Sensing of Picric Acid and Aliphatic Amines: Physicochemical Details and Construction of Molecular Logic Gates

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Abstract: Picric acid (PA) at low concentration is a serious water pollutant. Alongside, aliphatic amines (AAs) add to the queue to pollute surface water. Plenty of reports are available to sense PA with an ultralow limit of detection (LOD). However, only a handful of works are testified to detect AAs. A new fluorescent donor-acceptor compound has been synthesized with inherent intramolecular charge transfer (ICT) character that enables selective and sensitive colorimetric quantitative detection of PA and AAs with low LODs in non-aqueous as well as aqueous solutions. The synthesized compound is based on a hemicyanine skeleton containing

Introduction

Picric acid (PA) or trinitrophenol (TNP) is very well known because of its explosive nature at high concentrations and a major and notorious surface water pollutant at very low concentrations. Plenty of works are available to detect PA using various types of sensors, many of them with extremely low limit of detection (LOD). One example is the electron-rich oligofluor-anthene class of strongly fluorescent compounds that detect electron deficient Fe(III) ions and PA through fluorescence quenching mechanism via photoinduced electron transfer (PET).^[1] Such polymer and PET-based mechanism was also used to detect PA using donor-acceptor type polymer films, conjugated microporous polymers, lanthanide coordination polymers, azo-linked covalent organic polymers and polymer nanoparticles.^[2–7] Additionally, supramolecular materials were effectively used to detect PA with appreciable LODs. A recent

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two pyridenylmethylamino groups at the donor and a benzothiazole moiety at the acceptor ends. The detailed mechanisms and reaction dynamics are explained spectroscopically along with computational support. The fluorescence property of the detecting compound changes due to protonation of its pyridinyl centers by PA leading to quenching of fluorescence and subsequently de-protonation by AAs to revive the signal. We have further designed logic circuits from the acquired optical responses by sequential interactions.

report on the use of a Tröger's base structural motif using a 4amino-1,8-naphthalimide incorporated nitrogen-rich Zn(II) coordination polymer yielded good results.^[8] Host-guest based competitive binding controlled aggregation-induced emission (AIE) method came handy in detecting PA.^[9-17] Even carbon dotbased polypyrrole nanocomposites and sol-gel methods also proved beneficial for PA detection.^[18-25] Moreover, modern day metal-organic-frameworks (MOFs)^[26-38] and covalent-organicframeworks (COFs)^[39-41] were found to provide good sensor materials for PA in different solvents. There are numerous small molecule sensors as well to detect PA with low LOD.^[42-56] Zinc oxide nanomaterials and fluorescent quantum dots were also helpful in PA detection.^[57,58] The fluorescent outputs due to the sensing mechanisms were effectively used to prepare logic based devices in some cases.^[59,60]

Similarly, there are reports on the detection of aliphatic amines (AAs) with low LODs in various samples using different techniques. Self-stabilized micelles of fluorescent block copolymers were used to detect AA in surface water.^[61] An interpenetrated zinc-based coordination polymer could measure it in all the states of matter,^[62] and various polymer matrices were used to detect volatile AA.^[63] An armory of small molecules was also effectively used in AA sensing. Ranging from BODIPY fluorophores,^[64] zinc-based Schiff base complex,^[65] trifluoroace-tophenone-based dyes,^[66] certain diarylethenes,^[67] aminonaph-thalene anhydrides,^[68] perylene derivatives,^[69] extended distyrylbenzenes^[70] to bio-inspired diatoms derived from algae^[71] were used to detect AA efficiently.

In this flurry of works to detect PA and AA in different types of samples under various circumstances, a prominent lacuna is observed in using the same system to detect both of them sequentially. Moreover, very few of these reports have described the dynamics of PET or intramolecular charge transfer (ICT) elaborately to obtain a clear and deeper insight into the sensing mechanism. Since, the fundamental concept behind the detection of PA is exploiting its very strong acidic character and the strong basicity of the AAs, we could conceive an idea of synthesizing a sensitive organic compound bearing (i) donoracceptor property to exhibit ICT for fluorescence signaling, (ii) suitable prototropic centers to accept proton based on the pK_a values and (iii) good enough protonated form to allow a strong base to extract proton/s. Such a compound could be obtained from the hemicyanine family elaborately reported by Kabatc et al. $^{\scriptscriptstyle [72,73]}$ We adopted the protocol reported by Xu et al. $^{\scriptscriptstyle [74]}$ to synthesize 1 a (N,N-bis(pyridin-2-ylmethyl)aniline) and 1 b (4-(bis (pyridin-2-ylmethyl)amino)benzaldehyde) and added a benzothiazolium moiety to 1b to serve as the acceptor end, thereby to get the desired compound 1c ((E)-2-(4-(bis(pyridin-2-ylmethyl)amino)styryl)-3-ethylbenzo[d]thiazol-3-ium iodide) (Scheme 1). The synthetic method and characterization of 1c (Figure S1) are elaborately described in the supporting information. The compound 1c was designed to effectively detect PA as well as the AAs, using the same platform.

The pyridine moieties of 1c are mildly basic centers (pKa 7.2) that would attract proton from the extremely strong acid 2,4,6-trinitrophenol (TNP) or PA (pKa 0.42) selectively from a mixture of 2,4-dinitrophenol (DNP, pKa 4.09), 4-nitrophenol (NP, pKa 7.07), 2,4-dinitrotoluene (DNT, pKa 13.53) and 4-nitrotoluene (NT, pKa 11.27). Subsequently, the protonated 1c becomes a good acid for strong bases like the AAs (triethylamine (TEA, pKa 10.21), triisopropylamine (TIPA, pKa 11.06), diethylamine (DEA, pKa 10.58) diisopropylamine (DIPA, pKa 36) and methylamine (MA, pKa 10.63). The results were compared with dimethylaniline (DMA, pKa 5.15) and aniline (AN, pKa 4.6) bases as control. The sensitivity of 1c is appreciable with low LODs. We used the most popular colorimetric method of trace detection and explained the mechanism in detail. The previous reports greatly lacked the vivid elaboration of the dynamics of PET/ICT that we have showed here along with computational calculations supporting the experimental findings. Moreover, we used the sequential PA and AA detection method of 1c in developing interesting logic devices that may greatly aid computational detection. Although the initial experiments were performed in acetonitrile, we have shown that the tests are valid for aqueous samples as well. In addition, paper-strips could also be used to visually detect the color changes due to the interactions of 1 c with PA and AAs.

Results and Discussion

Selective sensing of PA by 1c

The possible selectivity of 1c toward TNP or PA over the other nitro compounds mentioned above, was examined from the changes in the spectroscopic signals of the probe due to titration with the additives (Figures S2 and S3). The absorption spectrum of 1c shows a clear change in character from an unstructured to a structured spectrum with an appreciable hypsochromic shift (Figure S2A). This indicates conversion of one form of $1\,c$ to another on interaction with PA (0–40 $\mu\text{M})$ in acetonitrile solution. The other nitro compounds practically do not affect the spectrum (Figures S2B-E). The fluorescence of 1 c gets remarkably guenched due to this process with a blue shift (Figure S3A) with no appreciable effect by the other nitroanalytes. We have presented several situations of selective effect of PA on 1c in acetonitrile solution in Figure 1. The figures demonstrate noticeable quenching of 1 c on addition of PA under various circumstances of the other nitroanalyte mixtures.

PA induces maximum quenching (about 92%) of the 1c fluorescence compared to the other nitroanalytes. Feeding the fluorescence intensities of 1c obtained at 588 nm in absence (I_0) and presence (I) of the various nitroanalytes to the Stern-Volmer equation: $I_0/I = 1 + K_{SV}[Q]$, where K_{SV} and [Q] are the quenching constant and the concentration of the quencher, respectively, we obtained a non-linear fitting with an upward offset for PA (Figure 2A). The other analytes produced linear fittings to the data. The non-linearity for PA indicates simultaneous static and dynamic quenching of 1 c, which could be due to hydrogen bonding interaction between 1c and PA before the dynamic proton transfer. From this non-linear curve fitting, modified Stern-Volmer equation:[75] using the



Figure 1. Comparison of the photoluminescence (PL) intensity of 1 c in acetonitrile (A) in the presence of PA, DNP, NP. DNT and NT; (B) before and after the addition of the nitroanalytes (80 μ L, 1 mM) separately followed by the addition of the same amount of TNP: the brown, red and pink bars represent the PL intensities of 1 c, on adding the various nitroanalytes to 1 c and the subsequent addition of PA (80 μ L, 1 mM) to the mixture (I. DNP, II. DNT, III. NP and IV. NT; (C) on gradual addition of the nitroanalytes to 1 c. The samples were excited at 505 nm.



Scheme 1. Structure of (E)-2-(4-(bis(pyridin-2-ylmethyl)amino)styryl)-3-ethylbenzo[d]thiazol-3-ium iodide (1 c).

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Figure 2. (A) Stern-Volmer plots of the quenching of **1 c** on interaction with the nitroanalyte quenchers, (B) comparison of the extent of quenching of **1 c** fluorescence by the nitro analytes and (C) gradual quenching of **1 c** by PA compared to the other nitro analytes.

 $I_0/I = Ae^{k[PA]} + B = 1.29e^{0.0594[PA]} - 0.93$, we obtain the static quenching constant (k) as 5.94 x 10⁴ M⁻¹ that reinforces the hypothesis of hydrogen bond interaction. Linear fitting to the Stern-Volmer equation for the other nitroanalytes shows collisional interaction with **1c** without any static interaction. 92% quenching percentage of PA (Figure 2B) signifies absolute specificity of **1c** to PA, which is also observed from Figure 2C.

We calculated the binding constant of PA with **1 c** using the Benesi-Hildebrand equation:^[76]

$$\frac{1}{I_0 - I} = \frac{1}{K(I_0 - I_{min})[PA]} + \frac{1}{(I_o - I_{min})}$$
(1)

where, *K* is the binding constant and I_0 , I_{min} and *I* are the fluorescence intensities of **1c** without, at the maximum and varying PA concentrations, respectively. The plot of $1/(I_0 - I)$ vs. 1/[PA] gives a linear fit (Figure S4) from where the binding constant was calculated to be $2.72 \times 10^5 \text{ M}^{-1}$ that establishes strong binding between the species. A plot of $(I_{max} - I)/(I_{max} - I_{min})$ vs. Iog[PA] (Figure S5) gives a linear fit to the raw data yielding the LOD of PA by **1c** in acetonitrile solution from the intercept on the x-axis.^[42] The LOD was calculated from, ([PA]×MWPA)/1000 multiplied by 10⁹ to get the value in ppb), where MWPA is the molecular weight of PA. The LOD, 363 ppb (equivalent to 1.59 μ M), is quite low in this case. This is very competitive with the existing LOD data in the literature as provided in Table S1A.

Recovery of PA-quenched fluorescence of 1 c by the AAs

The protonated form of 1c due to interaction with PA should be deprotonated by the strong AA bases, such as, TEA, TIPA, DEA, DIPA and MA, while the aromatic amines, such as, DMA and AN, shall remain undetected due to their low pK_a. Hence, the quenched fluorescence of **1c** by PA is supposed to be restored by the AAs as we found and depicted in Figure 3. MA behaves slightly differently as its sensitivity to the protonated **1c** develops above 36 μ M (Figure 3E). The fascination of **1c** towards the AAs over the aromatic ones is remarkable as we could recover ~90% of the PA-quenched fluorescence (Figure 3H). The calculated LOD of **1c** for the AAs is 27 μ M in acetonitrile. This LOD value is quite comparable to the existing AA sensing data using various other systems (Table S1B). There is a clear bathochromic shift of the emission spectrum of the quenched **1c** on interacting with the AAs and hence, the change in color of the solution is visible by naked eyes (Figure 4A). Experiment on paper strips is also successful which helps in making the application handy (Figure 4B). It is note-



Figure 3. (A–D) Restoration of the PA quenched PL of 1 c by AAs (TEA, TIPA, DEA and DIPA, respectively), (E) MA starts reviving the fluorescence above 36 μ M concentration (refer to inset), and (F, G) effects of DMA and AN on the quenched PL of 1 c. The insets show that DMA and AN are insensitive even up to 72 μ M. (H) comparison of percentage recovery of 1 c emission by the amines (up to 36 μ M).



Figure 4. Visual change of color of 1 c on application of PA and TEA in sequence (A) in acetonitrile solution and (B) on paper strips.

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worthy to mention here that **1c** is insensitive to the AAs in absence of PA as shown by its practically unchanged fluorescence intensity (Figure S6).

Analysis by time-resolved fluorescence up-conversion spectroscopy

To have a deeper insight to the phenomenon of selective sensing, we present the findings from time-resolved ultrafast fluorescence up-conversion spectroscopy. The excited state decay dynamics of pristine **1c**, **1c** with PA and **1c** with PA and **TEA** (representative AA) were investigated in a much shorter time scale. All the measurements were carried out with 400 nm pump beam and the decay traces were probed at the emission wavelength of **1c**, i.e., 588 nm. A comparison of dynamics (at the emission probe position) for all the samples is shown in Figure 5. Interestingly, faster decay kinetics is observed for **1c**-PA complex compared to pristine **1c**. The decay profile at 588 nm fits well with the single exponential component for **1c**, bi-exponential components for **1c**-PA and tri-exponential components for **1c**-PA.

As mentioned earlier, ultrafast ICT controls the excited state dynamics of 1 c which decays within 70 ps. For 1 c-PA, the timeresolved fluorescence data were fitted with a bi-exponential routine decaying in 1 and 55 ps, respectively. Reduction in decay time of the longer component suggests decrease in the



Figure 5. Femtosecond fluorescence up-conversion decay curves of (A) 1 c, (B) 1 c-PA and (C) 1 c-PA-TEA (λ_{abs} :400 nm and λ_{em} : 588 nm).

Table 1. Fitting parameters of femtosecond fluorescence up-conversion			
decay of 1 c with PA and TEA under different circumstances. The subscript			
'g' represents growth component and a _i 's are the weightage of the			
respective components.			

Sample	τ_1 [ps]	a ₁	τ_2 [ps]	a ₂	$ au_{3g}$ [ps]	a ₃
1c	70	1	-	-	-	-
1c-PA	55	0.75	1	0.25	-	-
1c-PA-TEA	39	0.62	2.8	0.08	22	0.30

ICT and the faster component signifies a new non-radiative channel for electron transfer from 1c to PA, which circumstantially caused the reduction of ICT in 1c. The fluorescence up-conversion measurement is in well accordance with the substantial quenching of the ICT fluorescence of 1c due to interaction with PA or, in other words, because of the complex formation. However, as seen in the steady state fluorescence study with added TEA to the PA-quenched emission of 1c, the time-resolved decay components responded alike. The electron transfer process becomes slower and a new growth component of 22 ps appears that signifies reasonable back electron transfer to 1c, thus recovering the quenched fluorescence. The apparent 39 ps decay of the ICT state gets reinforced by the back donation of EA.

Sensing capability of 1 c in water

The same process becomes more beneficial if replicated in water sample. Since, both the additives, PA or the AAs, are potential pollutants for surface water, hence we attempted their selective detection in aqueous medium using the same technique. **1c** is extremely sensitive to the environment pH and shows distinct phases of spectral shifts due to deprotonation at higher pH (Figures S7A and B). The shift in the emission maximum plateaued around pH = 7.2 (Figure S7C). This inherent pH sensitivity of **1c** is exploited by PA and AAs in selective sensing. We dissolved **1c** in water using acetonitrile (2%) as co-solvent and tested with PA and aliphatic amines. The results were similar to the non-aqueous solutions as depicted in Figure S8A–E. The LODs for **1c** in aqueous medium were **3** and 44 μ M, respectively for PA and the AAs.

Computational study

To elucidate the mechanism of interaction of **1c** with PA in more detail, we performed density functional theory (DFT) based computational studies using the Gaussian 09 program package.^[77] B3LYP hybrid functional and 6–31G basis set were used for the calculations. The calculated HOMO-LUMO energy levels for the various nitroanalytes are shown in Scheme 2A, which portrays that the quenching efficiency is superior for PA



Scheme 2. Calculated energy levels of (A) 1 c and the different nitroanalytes and (B) effect on the energy levels due to the 1 c-PA complex formation. The black and red lines represent the HOMOs and LUMOs of the species.

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over the others due to the comfortable positioning of the LUMO (-3.51 eV) with respect to that of 1 c (-2.85 eV) making the PET process lucid. The LUMO energies of the other nitroanalytes are higher and unsuitable for efficient fluorescence quenching due to PET. As described earlier, PA attaches to 1 c through strong hydrogen bonding to the prototropic centers stabilizing the LUMO facilitating PET (Scheme 2B). The HOMO-LUMO energy gap of 1 c and 1 c-PA complex are 2.77 and 3.63 eV, respectively which explains the hypsochromic shift of 1 c upon gradually addition of PA.

Confirmation of hydrogen bonding interaction of the analytes with 1 c

To consolidate the strong hydrogen bonding interaction of PA with the dangling pyridine moieties of 1c to form the 1c-PA complex as predicted before and supported by the theoretical results, we examined the effect of viscosity and temperature on the molecular motion and hence the ICT emission of 1c. The intensity of 1c fluorescence intensifies considerably in the comparatively rigid medium provided by glycerol and lower temperature (Figure S9). The apparent rigidity presumably restricts the C-N and C-C bond rotations. We confirmed this observation from variable temperature (VT) ¹H-NMR spectroscopy. It was observed that upon increasing the temperature from 25 °C to 90 °C, the H_i proton (δ =6.86) is more deshielded indicating higher rotational motion of C–N bond (Figure 6A). ¹H-NMR titration of **1 c** illustrated that successive addition of PA shifts the pyridine protons $(H_{er}, H_{fr}, H_{ar}, H_{h})$ and the methylene proton (H_m) downfield (Figure 6B). This observation clearly reflects protonation of the pyridine nitrogen atoms. The upfield shift of the H_i proton is due to the breaking of the hydrogen bonds between the pyridine nitrogen and the H_i proton of the anilinic ring upon gradual addition of PA. No distinct ¹H NMR signal for the tertiary N-atom indicates that it does not get protonated in the process and hence, the sensing mechanism proceeds through 1:2 host-quest binding. We found confirmation for such binding in a Job's plot that we constructed for the 1c-PA conjugate formation (Figure S10). The relative change in absorbance showed a break at mole fraction ~0.65 indicating 1:2 host-guest stoichiometry.

Construction of logic devices from the acquired results

The exhilaratingly selective sensing capability of PA and the AAs by **1c** tempted us to apply the concept in preparing molecular logic gates. The optical responses in combination with the chemical retorts were converted to binary 0 s and 1 s after application of proper threshold to a particular optical output channel. A dual input single output IMPLICATION logic gate was designed on the unimolecular platform of **1c**, considering the absorption values received at the 505 nm channel (Figure S2A). In the IMPLICATION logic designing, signal from 40 μ M PA addition was considered as 'Input A', simultaneously any of the amines, TIPA/DIPA/TEA/DEA (36 μ M) could



Figure 6. (A) VT ¹H-NMR spectra (selected region) of 1 c (solvent = DMSO-d₆) and (B) ¹H-NMR titration of (a) 1 c upon gradual addition of (b) 0.5 equiv., (c) 1.0 equiv. and (d) 3.0 equiv. PA in DMSO-d₆. The inset shows the assigned protons of 1 c for convenience.

be utilized as 'Input B'. The absorption values always remained above the threshold except for the situation of solitary PA. In presence of PA only the output response was OFF that designated the binary value 0. Furthermore, considering the emission responses at 588 nm another IMPLICATION logic gate could be designed considering the same device and same chemical inputs. In this logic designing signal from 10 μ M **1 c** was coupled to the optimum concentrations of the 'Input A' (40 μ M) and 'Input B' (36 μ M), respectively (Figure 7A).



Figure 7. Development of IMPLICATION, TRANSFER and AND logic gates.

Simultaneously, considering the 440 nm absorption channel (Figure S1A), a TRANSFER logic gate was designed with the same device and same chemical inputs (Figure 7B). TRANSFER gate is the combination of one NOT, two AND and one OR gate in a specific approach. In this logic gate the output channel is simply the reflection of the binary record of a particular input. Here, the output adopted binary 1 value ('ON' situation) for the situations where PA (Input A) was present, irrespective the presence or absence of Input B. Interestingly, the concentration dependent optical responses of 1 c-PA system could be utilized to mimic the truth table of a AND logic gate (Figure 7C). The initial emission of 1c at 588 nm turned OFF in presence of PA. Now considering this 1 c-PA system as the initial state, addition of 36 μ M MA left the active state as OFF. Whereas, further addition of another 36 μ M MA to this mixture (10 μ M 1 c, 40 μ M PA and 36 µM MA), turned the fluorescence ON at 588 nm. So, considering the 36 µM MA as both the inputs (Input A as well as Input B) a AND gate could be simply designed. Here, the output channel only adopted the 'ON state' in presence of both the inputs, i.e., a total 72 µM MA.

All single input-single output (YES, NOT, PASS 0 and PASS 1) opto-chemical logic gates could be easily designed based on the emission responses at 588 nm output channel, during the sequential interaction of 1c with "PA" and different amines. Considering 1c as the device and PA as the single chemical input, we designed a NOT gate. In addition, with the same device (1c) and same output channel (588 nm) we designed a PASS 1 logic gate, employing any of the amines as the single chemical input. Now, considering the 1c-PA chemical mixture as the initial system and TIPA/DIPA/TEA/DEA as the single chemical input a YES gate was fabricated. Further, with the same device (1c-PA) and same output channel (588 nm) a PASS 0 logic gate was mimicked with DMA/AN/MA as the single chemical input (Figure 8).

Accompanied with the binary logic function, the reversible and reproducible toggling of fluorescence ON-OFF states of **1 c** successively triggered by PA and different amines could be utilized to design a sequential "Erase-Read-Write-Read" type logic memory unit, ultimately to create molecular memory devices that are capable for storing and processing information. In the designing, the ON (1) and OFF (0) states were represented by the strong and less emission outputs at 588 nm



Figure 8. Construction of All single input-single output (YES, NOT, PASS 0 and PASS 1) opto-chemical logic gates.

channel, respectively. In the memory unit, chemical input PA was treated as the RESET key, simultaneously any of the amines, DIPA/TIPA/DEA/TEA could be employed as the SET key. Whenever the RESET input was high (R = 1), the existing '1' state would be erased and the '0' state will be written and memorized. In contrast, the system would write and memorize the binary state '1' as the SET input was high (S = 1). Most interestingly compared to the previously designed chemical triggered memory units,^[78,79] the versatility of this memory unit is expected to be much higher as the switching of 'ON-OFF' states of ADBTZ (reversibility cycle) could be repeated so many times without any performance breakdown (Figure 9).

Conclusion

We have synthesized a new fluorescent ICT probe for selective and sensitive colorimetric detection of PA over other nitroanalytes, as well as AAs over the aromatic ones. Both PA and the AAs are known to be environmentally hazardous even at appreciably low concentrations. The synthesized compound (1c) is capable to efficiently detect both pollutants with low LODs in non-aqueous as well as aqueous media. The detection is based on colorimetry and can be observed without any instrumental aid. The mechanism of sensing PA and AAs by 1c has been explained in detail spectroscopically. The fluorescence change of 1c is attributed to ICT/PET due to protonation of its pyridinyl centres by PA leading to quenching the fluorescence and subsequently de-protonation by AAs to revive the signal. We have explained the ultrafast dynamics of the process by fluorescence up-conversion spectroscopy supported by theoretical calculations. The results ensued us to develop different logic gates and memory device to incorporate the findings in suitable applications.

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Figure 9. Development of memory unit from the "Erase-Read-Write-Read" mechanism.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aliphatic amines · charge transfer · logic gates · picric acid · sensors

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