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Carbazole-Acenaphthene (Donor-Acceptor) based luminophores for picric acid detection: a combined experimental and theoretical study

Aravind Babu Kajjam, Kasturi Singh, R. V. Varun Tej and Sivakumar Vaidyanathan*

Department of Chemistry, National Institute of Technology,
Rourkela 769008, Odisha, India

*To whom correspondence should be addressed. Email: vsiva@nitrkl.ac.in (V. Sivakumar) Tel: +91-661-2462654;
Abstract:

In the present investigation, carbazole-Acenaphthene based Donor-Acceptor luminophores were designed and synthesized. All the luminophores were showing fluorescence quenching behavior towards nitroaromatics through complex formation. All the luminophores were used for the detection of picric acid (PA) based on fluorescence quenching. All the luminophores were showing highest quenching efficiency with PA, compared with other explosives like, 2, 4-dinitrophenol (2, 4-DNP), 4-nitrophenol (NP), benzoic acid (BA), and phenol (PH). Fluorescence quenching behavior was confirmed by $^1$H NMR, fluorescence and DFT studies. The time-resolved fluorescence results indicate that the dynamic quenching mechanism is involved in PA detection. The induced photo electron transfer (PET) from luminophore to PA was confirmed by NMR and DFT analysis. DFT calculations of luminophore with PA were also carried out to know the energy levels of the complex after addition of PA. In addition, detection limit, photographic detection of PA has been successfully demonstrated in solution and solid state (TLC plate). DFT calculations of luminophore with PA were also carried out to know the energy levels of the complex after addition of PA. The singlet and triplet energy states of the excited molecules were calculated through Time-Dependent Density Functional Theory (TD-DFT) calculations.

Key words: Chemosensor, Picric acid, DFT, TD-DFT.
Introduction:

Efficient design of luminophores has drawn significant interest in the identification of explosives in the field of environmental pollution control and better combat terrorism.\textsuperscript{1-2} This is an important challenge for national security, environmental protection and bio analysis applications in recent decades.\textsuperscript{3} The principal constituents of many explosives are various nitro aromatic compounds such as trinitrotoluene (TNT), 2, 4-dinitrophenol (2,4-DNP) and picric acid (PA). Detection of picric acid (PA) compared to other nitroaromatic compounds is very essential, as the explosive nature of PA has been used to prepare weapons such bombs and grenades. In addition, PA can cause damage to the skin, aggravation of the eyes, sickliness, cancer nature, lung damage and damage to respiratory organs.\textsuperscript{4} In the last two decades, a variety of strategies have been used to distinguish PA, for example, gas chromatography, mass spectrometry (GC-MS), particle versatility spectrometry (IMS), electrochemical techniques, surface-improved Raman spectroscopy, etc.\textsuperscript{5} Generally, electron deficient nitroaromatics are anticipated to quench the fluorescence through photo-induced electron transfer process for electron rich compounds, which constitutes a strong basis for their applications in the detection of explosives. However, these and exorbitant instrumental systems are difficult to manage and have restrictions for their practical applications. Alternatively, simple procedures were used to distinguish nitroaromatics that allow a few points of interest such as low cost, rapid reaction and high selectivity.\textsuperscript{6} In contrast to all simple techniques, fluorescence quenching is one of the most effective methods to detect nitroaromatic explosives.\textsuperscript{7-10}
To date, many scientists have been studying fluorescent organic molecules for the detection of nitroaromatics, including small molecular dyes, conjugated polymers, fluorescent metal-natural systems, metal organic frame works (MOFs), quantum dots, gold nanoparticles, conjugated polymers, and fluorescent molecular assemblies.\textsuperscript{11-12} Most of the reports available to identify nitroaromatics, however, lack of high selectivity, resulting in poor PA signal amplification. Till date, significant efforts have been made to synthesize a new and efficient organic luminophores (luminescent materials) that can detect PA (and nitroaromatics). Although, searching new luminescent materials with optical response (e.g. color changes or fluorescence varying) is still highly desirable because this type of detection has a fast response, high sensitivity, low cost, and simple sample preparation. It is well known that, imidazole derivatives are considered to be excellent luminogens and have been demonstrated to show excellent optical responses in the field of OLEDs (including ligand for Eu-complexes),\textsuperscript{13} biomedicine,\textsuperscript{14} supramolecular chemistry,\textsuperscript{15} coordination chemistry\textsuperscript{16} and CO\textsubscript{2} chemosensor.\textsuperscript{17} However, very few examples about imidazole-based materials were used as sensors for the detection of nitroaromatics.\textsuperscript{18} In addition, acenaphthene derivatives have verity of biological properties\textsuperscript{19} and widely used in pharmaceutical applications.\textsuperscript{20} Despite of fascinating spectrum of biological activities and luminogens properties in Acenaphthene group and imidazole linkages, integration of both the moieties in one chromophore and their effect on photophysical properties. In addition, to the best of our knowledge, there is no report on Acenaphthene based luminophores for PA sensing.

Herein, we report a series of new conjugated imidazole derivatives (Acenaphtho[1,2-d]imidazole (electron deficient center) moiety and carbazole (electron rich center) moiety as an efficient sensor material for selective detection of trace amounts of picric acid at ppb levels. As shown in scheme 1, six new luminophores were successfully prepared, namely 8-(4-(9H-carbazol-9-yI)phenyl)-7-
phenyl-7H-acenaphtho[1,2-d]imidazole (AC-1), 8-(4-(9H-carbazol-9-yl)phenyl)-7-p-tolyl-7H-acenaphtho[1,2-d]imidazole (AC-2), 8-(4-(9H-carbazol-9-yl)phenyl)-7-(9,9-diethyl-9H-fluoren-2-yl)-7H-acenaphtho[1,2-d]imidazole (AC-3), 8-(4-(9H-carbazol-9-yl)phenyl)-7-(3-(trifluoromethyl)phenyl)-7H-acenaphtho[1,2-d]imidazole (AC-4), 8-(4-(9H-carbazol-9-yl)phenyl)-7-(4-(trifluoromethyl)phenyl)-7H-acenaphtho[1,2-d]imidazole (AC-5), 3-(8-(4-(9H-carbazol-9-yl)phenyl)-7H-acenaphtho[1,2-d]imidazol-7-yl)benzonitrile (AC-6). Herein, we present a detailed account of their photophysical, electrochemical, theoretical analysis. Fluorescence quenching was performed on various explosives such as benzoic acid (BA), phenol (PH), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and picric acid (PA). Photophysical, electrochemical and PA detection mechanisms have been verified by density functional theory calculations. A single step method shown in Scheme 1 (supporting information) was used to obtain the Acenaphthene-imidazo derivatives connected by different conjugation units such as benzene, toluidine, fluorene, 4-(trifluoromethyl)phenyl, 3-(trifluoromethyl)phenyl and benzonitrile at N1 position. All the luminophores were have donor-acceptor (D–A) structures, which contain elementary units of electron donating carbazole and electron-accepting Acenaphthene-imidazole group. The only difference in the luminophores was different conjugation units on N1 position. The reaction of the corresponding aldehyde to the ketone in the presence of ammonium acetate produced desired target luminophores with good yields (supporting information). The molecular compositions of the yellowish-orange luminophores were unambiguously established by $^1$H, $^{13}$C NMR, high resolution mass spectrometry measurements and some of them were crystallographically characterized. Finally, these Acenaphthene-imidazo luminophores were used for detecting nitroaromatics. Fortunately, these luminophores (good selectivity and high sensitivity) can be used for PA detection in both solution and contact mode (TLC Plates).
**Fig. 1** Chemical structures of Acenaphthene-imidazo based luminophores (top) quenchers used for chemo sensors (down).
Scheme 1. Synthetic procedure of the designed luminophores.
Results and Discussion:

The single crystal analysis of AC-1 and AC-2 were carried out to understand the structural properties like bond angles and bond lengths of luminophores. Fig. 2 shows the ORTEP diagram of AC-1 and AC-2 luminophores and the corresponding refinement parameters, bond lengths and bond angles were tabulated in Table-ST1-ST5. An attempt has been made to crystallize the other luminophores (AC-3-AC-6), however, the attempts were failed.

**Fig. 2** ORTEP Diagrams of AC-1 and AC-2 luminophores (50% probability ellipsoids; H atoms and co-crystallized solvent molecules are omitted). N atoms blue in color. (CCDC 1568852(AC-1) and CCDC 1568853 (AC-2)).

All the luminophores exhibited nearly identical absorption (Fig. 3a, Table 1) and emission behaviors (Fig. 3b), except for a slight red-shifting tendency in the luminophores as a result of the introduction of different conjugated group on N1 position. In Figure 3a, the absorption spectrum of luminophores displays four well defined absorption peaks were observed. The strong absorption peaks at ~290, ~325 ~340 nm, can be assigned to π-π* transition and other weak absorption peaks around 400-450 nm, can be assigned to n-π* transitions, respectively.21,22 The UV-Vis absorption
titrations were performed to get quantitative idea of the interaction of PA to the luminophores at room temperature (Fig. S24- S29). While increasing the PA concentration to the luminophores there is slight increase in the absorption peaks were observed. Indicating the formation of ground state complex between luminophores and PA via charge transfer transition. When dilute solutions of luminophores are treated with PA, the solutions are immediately changed to colorless from yellow under UV light.

![UV-Visible absorption spectra and Emission spectra](image)

**Fig. 3** a) UV-Visible absorption spectra (inset images under UV-lamp). b) Emission spectra (inset CIE plot) of synthesized luminophores.

**Table 1.** Photophysical and CIE chromaticity values of all luminophores (AC—AC-6).

| Luminophore | λ_{abs}(nm) | λ_{em}(nm) | PLQY (Φ) (%) | Lifetime (μs) | CIE coordinates (x, y) |
|-------------|-------------|------------|--------------|---------------|------------------------|
| AC-1        | 293, 325, 339, 411 | 556 | 15.2 | 1.12 | 0.37, 0.46 |
| AC-2        | 291, 326, 340, 410 | 558 | 11.6 | 2.37 | 0.42, 0.52 |
| AC-3        | 309, 422 | 547 | 10.5 | 1.72 | 0.36, 0.48 |
| AC-4        | 274, 335, 351, 394 | 564 | 14.3 | 1.24 | 0.43, 0.51 |
| AC-5        | 281, 325, 339, 415 | 566 | 16.5 | 2.15 | 0.46, 0.51 |
| AC-6        | 280, 325, 340, 416 | 571 | 19.1 | 1.36 | 0.45, 0.52 |
The florescence spectra of the luminophores showing intense yellowish emission at 547-571 nm (Fig. 3b) with corresponding excitation wavelength (Table 2). Sensing behavior of all the luminophores were done in THF (1×10^{-6} M) with different nitro-containing compounds such as phenol (PH), benzoic acid (BA), 2,4-dinitrophenol (2,4-DNP), 4-nitrophenol (4-NP), and picric acid (PA) (Fig. S30 – S34). The fluorescence spectral changes were observed upon addition of PA. Figure 4a, shows the decreasing intensity of the luminophore with increasing PA concentration.

To evaluate the quenching efficiency of the luminophores, fluorometric analysis of the luminophores with PA data were transformed to Stern-Volmer plot. The quenching constant was calculated by using Stern–Volmer equation:

\[
\frac{I_0}{I} = 1 + K_{SV} [Q]
\]

where, I_0 and I are the PL intensities before and after the addition of PA, [Q] is the quencher concentration and K_{SV} is the Stern–Volmer or quenching constant (Figure 4b).

The fluorescence and the Stern–Volmer plots (I_0/I vs. PA concentration) of all the luminophores (AC-1-AC-6) were presented in Fig. 4 and S35-S39. The Stern–Volmer constant of all the luminophores was found to be in the range of 9.16×10^4 – 2.43×10^5 M^{-1} (Table ST6), which is comparable to the reported values. It has been shown that, Stern-Volmer plots (Fig. 4b) gave curves bending upward (due to a super amplified quenching effect), suggesting that when the PA concentration increased, the emission (luminescence) quenching becomes more efficient. The linear Stern-Volmer curve was observed when the PA concentration was relatively low (insert in Fig. 4b). The remaining luminophores (AC-2-AC-6) florescence spectra with PA and Stern-Volmer plots have been mentioned in supplementary information. Compare to all the luminophores, the quenching constant of AC-2 and AC-6 has higher than those of some PA
reported sensors (refer Table ST6 in SI). This may be related to the highest LUMO (-1.769 eV, Table 3) level of the AC-2, and the electrons are easily transferred from AC-2 to PA. Similarly, the \( K_{SV} \) values of AC-1, AC-3, AC-4 and AC-5 can also calculated to be, \( 1.26 \times 10^5 \), \( 1.2 \times 10^5 \), \( 9.16 \times 10^4 \) and \( 1.14 \times 10^5 \) M\(^{-1}\), respectively (Table ST6 in SI). To determine the quenching mechanism of the luminophore, it is necessary to measure the lifetime of the luminophores. Lifetime measurement data of all the luminophores (AC1-AC6) were summarized in the supporting information (Fig. S39 and Table ST7). In all cases the decay of luminophore in chloroform solution was bi-exponentially fitted, and the average lifetime of the luminophores were in the range of 2.59-6.64 ns. However, after the addition of the quencher (PA) to the luminophore, a reduction in the lifetime has been observed. (Fig. S40- S42, Table ST7). This shows dynamic quenching by transferring electrons from the luminophore to the quencher molecule after the addition of PA.\(^{24a}\) In addition, the digital photograph (Fig. 10) clearly shows that, the fluorescence color has changed from orange to colorless. Interestingly, the quenching efficiency of all luminophores toward picric acid were found in the range of 83-95%, indicates effectiveness to detect PA over other nitroaromatics (Fig. 5a clearly shows that, the PA quenching efficiency of AC-6 and AC-2 has higher compared to other luminophores. The quenching behavior of AC-6 with different explosives was shown in Fig. 5b.) Similarly, the the quenching efficiencies of AC-1, AC-2, AC-3, AC-4 and AC-5 can also calculate to be, 84, 90, 84, 88 and 83% respectively (Fig. 5a). Quenching phenomena and their luminescence efficiency plots of remaining luminophores (AC-1- AC-5) with other explosives were mentioned in supporting information (Fig. S43-S46). It is clearly indicating that, the sensitivity of these luminophores to PA is high compared to all other explosives.
**Fig. 4a)** Change in the fluorescence of AC-1 upon the addition of PA. b) Stern–Volmer plots of AC-1 using PA as a quencher. Inset: Stern–Volmer plots at lower concentration region of PA.

**Fig. 5a)** Fluorescence quenching efficiencies of all luminophores in PA. b) Fluorescence quenching efficiencies of AC-6 towards different analytes.

The PA detection limit can be done by measuring the fluorescence of luminophores (AC-1 - AC-6, 10^{-4} M) in THF with PA solution (10^{-6} M). The corresponding fluorescence intensity as a function of added PA was plotted and shown in Fig 6. The detection of PA detection limit (DL) can be calculated by using following equation.24b
\[ DL = C_L \times C_T \] 

\[ (C_L = \text{concentrations of luminophore}; \ C_T = \text{concentrations of PA at which a steep decrease is observed}). \] The detection limits of currently synthesized luminophores are in the range of 50 - 450 ppb, (Table ST6) respectively has better sensitivity than most of the small molecular fluorescent PA sensors previously reported (for more examples, Table ST23 in the SI). \(^{25}\) Compare to all luminophores, AC-2 has highest sensitivity towards PA indeed. This may be because, AC-2 with methyl as an electron donating group more easily interacts with electron deficient PA than the others. \(^{25c}\)

**Fig. 6** Fluorescence intensity of luminophores as a function of PA concentration.

Fig. 7, demonstrates the feasible PA detection mechanism owing to the strong acid behavior of PA, it can easily transfer acidic proton to basic functional group in the luminophore. Because of the presence of basic N atom on luminophore imidazole ring, it can strongly interact with acidic PA that leading to the fluorescence quenching. The \(^1\)H NMR technique was also used to clarify the interaction between luminophore and PA. As shown in Fig. 7, the shift of PA proton signal in
the NMR spectra confirms the formation of complex with Acenaphthene-imidazo nitrogen and PA. The proton signal of AC-2 luminophore was moved up field from 8.16 ppm to 8.12 ppm after addition of PA excess, supporting the strong electrostatic interaction between PA and AC-2 luminophore. The results showed that the PET process could play a major role in the fluorescence sensing of AC-2 luminophore towards PA. $^1$H NMR spectra of the remaining Acenaphthene-imidazo derivatives with PA are shown in the supporting information (Fig. S48-S51).

**Fig. 7** $^1$H-NMR spectra of AC-2 with PA in CDCl$_3$. 
Fortunately, a good quality AC-5-PA single crystal was grown using the slow vapor diffusion method (a dichloromethane solution of AC-5 and PA was used) and later X-ray diffraction study was performed for the hybrid crystal. The ORTEP diagram of the AC-5 with picric acid was shown in Fig. 8. Fig. 8 and crystal data clearly indicates that the complex formed by the transfer of picric acid protons to the imidazole group. The Table ST11 clearly shows that, there is a strong N-H-O interaction between imidazole moiety (N2) and oxygen atom (O46) picrate ion. The detailed bond lengths, bond angles and the hydrogen bonds of the AC-5-PA tabulated in Table- ST8-ST11.
Fig. 9 ORTEP Diagram of AC-6 with Picric acid (left). Wire and stick structures of AC-6 with Picric acid by using Diamond software (solvent molecules is vomited) (right). N atoms blue, F atoms in green and O atoms in red in color.

Although, the single crystal of AC-6-PA was obtained (Fig. 10), but the quality of the diffraction and fitting is comparatively not good. The detailed crystal information of AC-6-PA was given in supplementary information (Fig. S53, Table ST12-ST14).

It is well known that during preparation and packaging of explosive devices, the partial explosive contamination on clothing, human body, and other materials in the ambience has been observed. In such cases, the contamination of the explosive chemical can be easily checked by contact mode. To ensure that, TLC plates are prepared by spotting a THF solution of luminophores on TLC. All the luminophores have orange emission in TLC plates and it becomes non-emissive, when PA solution is absorbed by the luminophore (Fig. 10 down). Fluorescence-quenching phenomenon is observed by addition of PA solution under UV lamp, (Fig. 10 top).
Fig. 10 Images of solution (top) with luminophores under UV light before and after adding PA. Images of TLC plates (down) observed by luminophores under UV light before and after adding the PA.

Electrochemical analysis:

The electrochemical properties of the luminophores were measured by cyclic voltammetry (CV). All the luminophores were electrochemically stable and there was one reversible or quasi-reversible redox peak observed for each molecule under CV conditions (Fig. 11). The reversible one-electron oxidation process around 1.10–1.39 eV was derived from the acenaphtheneimidazole moiety. These obtained results suggest that all the compounds possess good hole as well as electron transporting properties. There is little difference in the LUMO of all compounds, which would be attributed to the conjugation and substitution of the group, whereas, the HOMO energy levels are located in same range and there is no difference among them. Compare with all the materials AC-6 has shown low band gap due to the presence of electron withdrawing cyanide (CN)
group on meta position of the benzene ring and is correlating with the photoluminescence data.

The detailed electrochemical data of the synthesized luminophores were tabulated in Table 2.

![Cyclic voltammetry diagram of acenaphthene based luminophores.](image)

**Fig. 11.** Cyclic voltammetry diagram of acenaphthene based luminophores.

**Table 2.** Electrochemical analysis of luminophores.

| Ligand | $E_{\text{ox}}$ (V) | $E_{\text{red}}$ (V) | HOMO (eV) | LUMO (eV) | Band Gap (eV) |
|--------|---------------------|----------------------|-----------|-----------|---------------|
| AC1    | 1.107               | -1.329               | -5.507    | -3.071    | 2.436         |
| AC2    | 1.301               | -1.108               | -5.701    | -3.292    | 2.409         |
| AC3    | 1.399               | -1.540               | -5.799    | -2.860    | 2.939         |
| AC4    | 1.138               | -1.168               | -5.538    | -3.232    | 2.306         |
| AC5    | 1.127               | -1.107               | -5.527    | -3.323    | 2.234         |
| AC6    | 1.107               | -1.077               | -5.507    | -3.323    | 2.184         |

$E_{\text{onset}}$ = the onset reduction potentials; $E_{\text{onset}}$ = the onset oxidation potentials; $E_{\text{LUMO}} = -e(E_{\text{onset red}} + 4.4)$; $E_{\text{g}} = $ band gap = $E_{\text{HOMO}} - E_{\text{LUMO}}$.

**DFT analysis:**

**Frontier molecular orbital properties:**

The optimized structures of all the luminophores (AC-1-AC-6) were shown in Fig. 12. To understand the photophysical properties of these luminophores, the frontier molecular orbital
energies, as well as the HOMO and LUMO contour plots of investigated materials were plotted in Fig. 13 and ST15. Table 3 reveals the calculated HOMO-LUMO levels and their energy levels (singlet and triplet). The Table ST15 shows small differences in the electron density distributions (population) of the HOMOs of all the compounds which are all mainly localized on the carbazole and little on acenaphthene group. However, unlike in the case of HOMOs, the six studied materials have shown a great difference in the electron density distribution of the LUMOs. For AC-1 to AC-3, the LUMO is primarily contributed from the acenaphthene group of the molecule as well as a little contribution on imidazole moiety. Compared with AC-1 to AC-3, the absence of the hetero atoms in these molecules does not have a great influence on the electron density distribution of the LUMO. In contrast, the introduction of the CF$_3$ and CN group has a great influence on the electron density distributions of the LUMO. Additionally, different substitution positions of the CF$_3$ group also show little difference in the LUMO electron density distributions. For example, when the CF$_3$ moiety is attached to the para-position of the phenyl ring of the molecule, the LUMO is localized more on the phenyl ring of the molecule when compared to its meta substituted analogue. Here, it should be noted that the electron density distributions of the LUMOs for luminophore with the CF$_3$ group are quite different from those without CF$_3$ group. While, the electron density distributions of the LUMOs for molecules with the CF$_3$ group are more like those with CN group, suggesting that the CF$_3$ and CN group have a great influence on the electron density distributions of the LUMO. The different types of molecular orbital will absolutely influence the electronic transition character upon excitation, which will be further explained in detail in the electronic absorption spectra. The detailed theoretical absorption spectra and their corresponding singlet energy levels of all luminophores explained in SI (Fig. S59 and Table ST16)
Fig. 12 Optimized structures of acenaphthene based luminophores.

Table 3. Theoretical data of all luminophores (AC-1 –AC-6) and luminophores with PA.

| Compound | HOMO (eV) | LUMO (eV) | HOMO-1 (eV) | LUMO+1 (eV) | Band gap (eV) | Singlet (eV) | Triplet (eV) |
|----------|-----------|-----------|-------------|-------------|---------------|--------------|--------------|
| AC-1     | -5.071    | -1.801    | -5.489      | -1.036      | 3.270         | 2.6657       | 2.0658       |
| AC-1+PA  | -5.466    | -2.594    | -5.800      | -2.412      | 2.872         | -            | -            |
| AC-2     | -5.042    | -1.768    | -5.469      | -0.998      | 3.274         | 2.6654       | 2.0659       |
| AC-2+PA  | -5.297    | -3.006    | -5.712      | -2.706      | 2.291         | -            | -            |
| AC-3     | -5.043    | -1.769    | -5.472      | -1.269      | 3.274         | 2.6668       | 2.0698       |
| AC-3+PA  | -5.422    | -2.515    | -5.756      | -2.379      | 2.07          | -            | -            |
| AC-4     | -5.200    | -1.934    | -5.594      | -1.302      | 3.266         | 2.6882       | 2.0651       |
| AC-4+PA  | -5.379    | -3.197    | -5.778      | -2.882      | 2.182         | -            | -            |
| AC-5     | -5.198    | -1.970    | -5.600      | -1.365      | 3.227         | 2.675        | 2.0662       |
| AC-5+PA  | -5.361    | -3.201    | -5.754      | -2.884      | 2.160         | -            | -            |
| AC-6     | -5.217    | -2.041    | -5.613      | -1.904      | 3.175         | 2.6532       | 2.0531       |
| AC-6+PA  | -5.417    | -3.285    | -5.811      | -2.957      | 2.132         | -            | -            |
Fig. 13. Energy level diagram of the luminophores (AC-1 – AC-6)

Furthermore, the calculated LUMO energy level of PA ($E_{\text{LUMO}} = -4.52$ eV) is between the calculated LUMO ($E_{\text{LUMO}} = -1.08$ eV) and HOMO ($E_{\text{HOMO}} = -4.99$ eV) energy levels of all luminophores (AC-1 – AC-6) Fig. 14 suggesting that the photo induced electron transfer (PET) process is the main possible contribution to the fluorescence quenching of luminophore by the addition of PA.
To understand the origin of PA sensitivity, the frontier molecular orbital of PA and AC derivatives (AC-1 – AC-6) were determined by density functional theory (DFT) computational studies based on B3LYP/6-31G basis set. Furthermore, the calculated LUMO energy level of PA ($E_{\text{LUMO}} = -4.58$ eV) is between the calculated LUMO ($E_{\text{LUMO}} = -1.76 – -2.04$ eV) and HOMO ($E_{\text{HOMO}} = -5.04 – -5.21$ eV) energy levels of AC luminophores (Fig. 14 and 15), suggesting the photo induced electron transfer (PET) process is the possible main contribution for the fluorescence quenching.  

The significant reduction in the electron density on the N atom upon binding of PA with luminophores indicates the charge transfer between PA and luminophore was observed (Fig. 15). Frontier Molecular Orbital (FMO) analysis further confirmed the internal charge transfer (ICT) process occurred after appendage of PA to luminophore, in all the cases HOMO localized on phenyl groups of luminophore unit and LUMO spread over on imidazole group of luminophore. In luminophore + PA (all luminophores) HOMO located over the moiety of luminophore unit whereas LUMO

**Fig. 14** Electron transfer process between luminophore (AC-1-AC-6) and PA.
spreads over only on PA. Thus, decrease in energy after binding of PA with luminophore clearly points out the formation of stronger charge transfer complex of luminophore with PA. The FMO orbitals of all luminophores with PA were shown in Fig.15. (FMO orbital of remaining luminophores (AC-2 to AC-6) with PA were shown in supporting information (Fig. S54-S58).

Fig. 15 Frontier molecular orbitals of AC-1 and AC-1 + PA obtained from the DFT calculations using Gaussian 09 program.

Conclusion:

In summary, we have reported six novel Acenaphthene-imidazole luminophores were designed and synthesized for the sensitive and selective detection of nitro aromatics by solution and solid state. To the best of our knowledge, these luminophores are first examples of acenaphthene imidazole based luminophores potential for the detection of trace amounts of picric acid. The detection limits of the all the luminophore in the range of 50-450 ppb. Fluorescence quenching of
all luminophores with PA has been studied with the help of emission,\(^1\) H NMR spectroscopy and single crystal XRD. Using DFT analysis, the HOMO-LUMO energy levels and emission properties of all luminophores were investigated theoretically. The chemosensing behavior of all the luminophores was confirmed by lifetime analysis and TD-DFT analysis. The lowest detection limit of AC-2 and AC-6 is attributed to PET effect, the easier transfer of electron from AC-luminophore to PA. Compared to all luminophores, AC-2 and AC-6 has a higher quenching efficiency towards PA.

**Experimental studies:**

**Materials:**

All the reagents were used as purchased without any further purification. All the operations involving air-sensitive reagents were performed under dry nitrogen atmosphere. The procedure for the synthesis of 4-(9H-carbazol-9-yl)benzaldehyde\(^1\) and the luminophores\(^2\) were adopted from the literature and modified accordingly.

**General information for Measurements:**

\(^1\) H NMR spectra were measured on a BRUKER AV 400 Avance-III (400 MHz) instrument with tetramethylsilane as the internal standard. All the luminophores and nitroaromatics were taken in \(10^{-4}\) M concentration. The absorption and photoluminescence (PL) excitation and emission spectra of the synthesized luminophores were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBAFLUOROMAX – 4P spectrophotometer, respectively. The absolute fluorescence quantum yield was measured with Edinburgh Spectrofluorimeter, FS5 with Integrating Sphere SC-30. Photoluminescence lifetime of the dyes were measured at 298 K with an Edinburgh Instruments FLS 980 based on the time correlated single photon counting technology upon the
corresponding excitation for all luminophores. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. Cyclic voltammetry experiments were performed in dimethylformamide solution containing 0.1 M tertbutyl ammonium perchlorate using Ag/AgCl as the reference electrode at a scan rate of 100 mV s\(^{-1}\) using an AUTOLAB 302N Modular potentiostat. The CIE color chromaticity coordinates of the phosphor were calculated from the emission spectral values by using MATLAB software. All the chemosensing analysis was done in THF solvent.

**Computational Details:**

The molecules under study were first optimized in the gas phase using density functional theory and the Becke three parameter Lee–Yang–Parr (B3LYP) form for the exchange–correlation potential and the 6-31G(d,p) basis set.\(^{30}\) All the structures were found to be in the minima of the potential energy surface as the normal mode of frequencies were all positive. After that the UV-Vis spectra calculations were done using Time Dependent-Density Functional Theory (TD-DFT)\(^{31}\) with gas phase optimized geometries. It is expected that the geometry of the molecule will change in the solvent phase in comparison to that of the gas phase, and hence the optimization of the geometries in the solvent phase has also been carried out. We found that there is no prominent change in the geometries of the molecules. As the UV-Vis experiment was done in the solution phase, we also calculated the UV-Vis spectra in the solvent phase by using the polarizable continuum model (PCM)\(^{32}\) approach within the TD-DFT methodology. Singlet and triplet energy calculations were performed by using the TD-SCF and B3LYP/6-31G(P) approach. All the calculations were carried out using the Gaussian09 W\(^{33}\) and Gaussian View suite of programs. The optoelectronic properties including FMOs, absorption and emission spectra were calculated using TD-DFT analysis.
Synthesis:

**Synthesis of 4-(9H-carbazol-9-yl)benzaldehyde:**

9H-carbazole (4.0 g, 23.92 mmol), 4-bromobenzaldehyde (5.2 g, 28.11 mmol), K$_2$CO$_3$ (13.20 g, 95.69 mmol), copper powder (3.04 g, 47.84 mmol) and dibenzo-18-crown-6 (0.63 g, 2.39 mmol) were dissolved in anhydrous DMF (50 mL) under nitrogen atmosphere and refluxed for 48 h. Then the mixture was cooled down to room temperature and filtered. The filtrate was poured into distilled water (300 mL) and stirred for 30 min. The crude product was collected by filtration and was purified by column chromatography (silica gel) eluting with a mixture of ethyl acetate:n-hexane (2:1; v/v) to give a light-yellow solid (4.5 g, 69%): $^1$HNMR (400 MHz) - δ 10.12 (s, 1H), 8.17–8.13 (m, 4 H), 7.78 (d, 2 H), 7.54–7.30 (m, 6 H);

**General procedure for the synthesis of luminophore:**

Acenapthequinone (5.5 mmol), 4-(9H-carbazol-9-yl)benzaldehyde (3.6 mmol), and an equivalent amount of aniline derivative C$_6$H$_5$NH$_2$R (R= H, m-CF$_3$, p-CF$_3$, m-CN, p-CH$_3$, diethylfluorene), together with ammoniumacetate (36 mmol) were dissolved in glacial acetic acid (15 ml) under nitrogen atmosphere and refluxed for about 24 h. The mixture was then poured in water and extracted with DCM. The extracted product was made into a crude product by adding silica gel. This crude was purified by column chromatography (silica gel) eluting with a mixture of ethylacetate : petroleum ether (3:7 v/v) to give a yellow or yellow-orange solid. The detailed NMR data were mentioned in the supporting information.

**Supporting Information:** The Supporting Information contains, Synthesis, Copies of NMR spectra, copies of Mass spectra, chemosensors data includes Photoluminescence spectra, lifetime
measurements, cyclic voltammetry analysis, Tables of single crystal data, Tables and images of DFT analysis. CIF files of single crystals. DOI:xxxxxxxxxxxxxxxx

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