Aggregation Induced Enhanced Emission (AIEE) Based Colorimetric and Selective Turn-on Fluorescent Sensor for Cyanide

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Short Report

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Abstract

We have prepared and reporting a new cyanide colorimetric and turn-on fluorescent chemo sensor L. Naked-eye colorimetric studies shows the prepared receptor is selectively sensing cyanide ion in acetonitrile medium. The sensor L shows very weak fluorescence in acetonitrile medium. The emission intensity of L gets reduced (quenching of fluorescence) upon addition of one equivalent of cyanide. Meanwhile further gradual addition of more than one equivalents of cyanide onto 1:1 cyanide complex of L shows remarkable fluorescence enhancement. The weakly emissive receptor L show drastic enhancement in fluorescence intensity upon addition of excessive cyanide ion which is mainly attributed due to the restriction of intramolecular rotation of 1:1 L•CN⁻ complex and intermolecular aggregation of host: guest complex. This enhanced fluorescence emission is attributed due to the aggregation induced enhanced emission (AIEE) is subsequently supported with UV-Vis, emission and ¹H-NMR spectroscopic studies. The preferential binding of cyanide by electron deficient receptor L through hydrogen bonding and anion···π interaction over benzene analogue of L is also analyzed with help of MEP surface analyses. To the best of our knowledge, this is the first example for selective colorimetric and turn-on cyanide sensor through AIEE mechanism. This type of fluorine rich organic material having such an aggregation enhanced emission properties in response to cyanide addition will be useful to construct the new type of material for various sensory applications.

Main Text

Development of simple and effective chemo sensors for selective detection of hazardous anions is really challenging area of research in the field of synthetic anion receptor chemistry. Further, designing a selective colorimetric sensor for a particular anion is even a complicated one since anions having different shapes and charges. Among the hazardous anions, cyanide ion is one of the most poisonous anions because trace amounts of its presence lead to deactivates many biological processes such the activity of cyto-c and cellular respiration.

Cyanide is extensively used in industries such as in metal mining and electroplating process. The extensive usage of cyanide in industry also increases the risk of environmental pollution. Giving the importance of design and sensing the cyanide ion, we have recently reported bipodal, tripodal based electron deficient selective colorimetric and turn-on fluorescent sensors for cyanide ion. Majority of these sensor systems are working through either charge transfer or electron transfer mechanisms. Thus, there are several chemo sensor systems for cyanide anion so far developed based on change in fluorescence emission intensity, naked-eye colorimetric detection of cyanide, displacement and chemodosimetric approaches.

It has been observed that several types of organic compounds were utilized as fluorescent sensors for detecting anionic species through aggregation induced enhanced emission (AIEE) phenomenon; whereas
upon binding of guest species, the emission of normal fluorophore would be quenched, in particular at higher concentration level.\textsuperscript{22-26} Unlike normal receptors, AIEE active receptors show minimal or zero relative emission in dilute condition. On the other hand it turned in to remarkable turn-on fluorescent receptors in the higher concentration. This enhanced fluorescent emission is mainly attributed due to the restriction of intramolecular rotation of 1:1 L\textendash CN\textsuperscript{−} complex and intermolecular aggregation of host: guest complex.

At this juncture, developing AIEE based receptor molecules which will helps us to open a window for new opportunity to selectively detect a particular anion at their lower concentration level. With the long term interest to develop new receptor molecules for selective cyanide ion detection, here in we are reporting a perfluro-hydrazone based organic synthetic receptor L, Scheme 1.

Instantly, we have tested the colorimetric responses of sensor L by adding tetrabutyl ammonium salts of various anions into the respective acetonitrile solution of L. Only the solution contains receptor L with cyanide and fluoride ions show immediate color change from colorless to faint brown and yellow respectively, figure 1 inset picture. In the respective UV-Vis spectrum a new absorption band is appeared in the visible region. Appearance of new absorption band in the visible region after addition of cyanide and fluoride into the acetonitrile solution of L which is support our naked-eye colorimetric finding of L with cyanide and fluoride. As evidenced from the naked eye experiment and UV-Vis spectra (figure 1 and inset picture), the receptor L is almost intact with other anions. There were no color changes or spectral changes observed for complex 1 upon addition of any other anions, which clearly suggesting that the complex 1 shows high selectivity towards azide anion, (see ESI).

The receptor L alone has no significance in its emission in the spectrum. The above synthesized receptor L shows relatively weak fluorescent emission in acetonitrile solution. When we excite the molecule at 260 nm, the sensor molecule L shows a weak mono fluorescence emission with two centered maxima at 309 nm and 417 nm in dry acetonitile. Further, upon 1:1 stocchiometric addition of cyanide and fluoride anion into the respective acetonitrile solution of L, the respective emission intensity is further quenched, figure 2. There were no considerable changes were observed with addition of other anions as tetrabutyammonium salts. As depicted in the figure 2, it is clear that upon UV illumination, the intensities of fluoride and cyanide complexes of L were quenched which will justify our obtained emission spectral data.

The binding efficiency of the receptor L towards fluoride and cyanide ion is estimated through emission titration. The emission titration was performed with monitoring the emission intensity of L at 309 nm and 417 nm upon addition of calculated amount of fluoride and cyanide ion into the acetonitrile solution of L. The emission intensity of receptor L at 309nm and 417nm are started to decrease upon addition of increasing amount of fluoride. Finally it has reached minimum, figure 3. Further we have calculated the stoichiometric ratio of this ligand-cyanide/fluoride host: guest system and it is found to be 1:1 by job's plot (ESI). The association constants and LoDs are calculated and tabulated in table 1.
Table 1.1

| Host | Guest    | \( R^2 \)  | Association Constant | Limit of Detection |
|------|----------|-------------|----------------------|--------------------|
| L    | Fluoride | 0.9962      | 2.405 \( \times 10^4 \) | 8 \( \times 10^{-6} \) M |
| L    | Cyanide  | 0.9954      | 1.494 \( \times 10^4 \) | 1 \( \times 10^{-6} \) M |

In order to check the trend of emission spectral changes upon addition of cyanide beyond the one equivalent, we have decided to continue the cyanide anion addition beyond 1 one equivalent i.e. up to 10 equivalents with gradual additions (in to 1:1 - L: cyanide complex), figure 4. Interestingly, it has been observed that the intensity of fluorescent spectrum of L: cyanide complex is started to increase upon gradual addition of cyanide and reached the maximum when 10 equivalents of cyanide is added. In addition, the emission spectrum also gets blue shifted from 417 nm to 471 nm (~57 nm), figure 5.

From this result, it is clear that initially the fluorescent intensity of L was quenched with 1 equivalent of cyanide, upon further additions of cyanide ion it is started to increase drastically. The detailed emission study suggesting that the excess addition of cyanide ion induce the per fluorinated receptor result in a receptor-anion aggregation lead to aggregation induces enhanced emission, AIEE.

The weakly emissive receptor L show drastic enhancement in fluorescence intensity upon addition of excessive cyanide ion which is mainly attributed due to the restriction of intramolecular rotation of 1:1 L-CN complex. The aggregation induced emission (AIEE) is also can be visualized from the naked-eye detection of cyanide complex when it is exposed under UV light, figure 6 inset picture. The association constant of this cyanide complex is found to be 2.5 \( \times 10^4 \) M\(^{-1}\) which is might higher than that of 1:1 complex (1.4 \( \times 10^4 \)M\(^{-1}\)) which also supports our proposed mechanism, table 1.

Solution state binding properties of L towards fluoride and cyanide is examined by \(^1\)H-NMR spectroscopy in deuterated dimethylsulfoxide (DMSO-\( d_6 \)). Fig. 7 shows the chemical shifts of \(-NH\) resonances of receptor L upon additions of fluoride and cyanide. Both the \(-NH\) resonances of sensor L are identified in the \(^1\)H-NMR spectrum with \( \delta \) values of 8.56 (amide-\( H-NH \)), and 8 11.10 (PF-Ar-\( H-NH \)). Most considerable chemical shifts are observed for amido proton (\( H-C=O-Ar-PF \)), and aromatic proton (PF-Ar-\( H-NH \)) is almost vanished due to the strong interaction between fluoride cyanide and receptor L, suggesting that they are providing the sites of interactions between the sensor L and fluoride/cyanide anions.

The observed strong binding towards cyanide/fluoride can be explained with the help of molecular electrostatic potential (MEP) maps of receptor L and their anionic complexes. The molecular electrostatic potential surface maps are generated by using MolView programmer, and the results are displayed in the figure 8.\(^{27}\) The blue color dominated regions in the MEP surface of L are electron deficient areas in which anion can bind through anion···\( \pi \) interactions. From the figure 8a, it is very clear that the fluoro-
substituted substituted benzene rings are holding positive clouds inside the aromatic ring (blue in color) and hence the respective pentafluoro substituted benzene rings became more positive which is a favorable condition for approaching anion towards electron deficient aromatic rings. Meanwhile on the other hand when we don't have electron withdrawing natured fluoro substitution on the phenyl rims the electrons are poised middle of the aromatic ring and those became more positive (deep red in color). This could not be the favorable conditions to approach a negatively charged anion, figure 8b.

In conclusion, We have prepared and reporting a new cyanide colorimetric and turn-on fluorescent chemo sensor L. Naked-eye colorimetric studies shows the prepared receptor is selectively sensing cyanide ion in acetonitrile medium. The sensor L shows very weak fluorescence in acetonitrile medium. The emission intensity of L gets reduced (quenching of fluorescence) upon addition of one equivalent of cyanide. Meanwhile further gradual addition of more than one equivalents of cyanide onto 1:1 cyanide complex of L shows remarkable fluorescence enhancement. The weakly emissive receptor L show drastic enhancements in fluorescence intensity upon addition of excessive cyanide ion which is mainly attributed due to the restriction of intramolecular rotation of 1:1 L•CN⁻ complex and intermolecular aggregation of host: guest complex. This enhanced fluorescence emission is attributed due to the aggregation induced enhanced emission (AIEE) is subsequently supported with UV-Vis, emission and ¹H-NMR spectroscopic studies. The preferential binding of cyanide by electron deficient receptor L through hydrogen bonding and anion···π interaction over benzene analogue of L is also analyzed with help of MEP surface analyses.

To the best of our knowledge, this is the first example for selective colorimetric and turn-on cyanide sensor through AIEE mechanism. The overall concept and results are depicted in the figure 9. This type of fluorine rich organic material having such an aggregation enhanced emission properties in response to cyanide addition will be useful to construct the new type of material for various sensory applications.

Declarations

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There are no conflicts to declare

Ethics approval/declaration Consent to participate

Not applicable

Consent to participate
Authors' contributions

Sudha Lakshminarayanan: Conceptualization, Methodology, Data collection, Writing - original draft; Kumaresan Murugesan, review & editing; Vanthana Jeyasingh: graphing, review & editing, Narayanan Selvapalam: Co-Supervision, Geetha Das - Supervision

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**Figures**
Figure 1

Absorbance spectra of sensor L in the presence of various anions. Inset picture: Naked-eye detection of cyanide and fluoride: (a) receptor, L (b) L + cyanide, (c) L + fluoride.
Figure 2

Stacked fluorescence emission spectra of L in the presence of various anions with excitation wavelength of 270 nm ($\lambda_{ex}$ = 260 nm). Inset picture: Under UV illumination: (a) receptor, L (b) L + cyanide, (c) L + fluoride.
Figure 3

Change in the fluorescence emission spectra of receptor L along with increasing concentration of fluoride anion addition in acetonitrile, (λex = 260 nm).
Figure 4

Change in the fluorescence emission spectra of receptor L along with increasing concentration of cyanide up to 1:1 stoichimetric (L to cyanide) anion addition in acetonitrile, (λex = 260 nm).
Figure 5

Change in the fluorescence emission spectra of sensor L upon addition of increasing concentration of cyanide anion, ($\lambda_{ex} = 260$ nm).
Figure 6

Aggregation induced enhanced emission: Inset picture: Under UV illumination: (a) receptor, and its cyanide complex.
Figure 7

Partial 1H-NMR spectra of receptor L and the chemical shifts of amide-NH-NH- and PF-Ar-NH-NH- resonances upon additions of fluoride and cyanide in DMSO-d6.
**Figure 8**

MEP surfaces of receptor L and its benzene analogue with cyanide ion.
**Figure 9**

Pictorial representation of AIEE based sensor system.

**Supplementary Files**

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