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Indirect approach for CN^- detection *via* Cu^{2+} induced turn-off sensor: Using novel AIEE fluorophore with logic gate and antimicrobial application

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A novel chromone based effectual molecular receptor S has been synthesized according to the excited state intramolecular proton transfer (ESIPT) and are shown the remarkable aggregation-induced emission enhancement (AIEE) in aqueous medium. S1 can be observed as fluorescent sensor for relay recognition of Cu^{2+} and CN^- in aq. medium (10 mM HEPES buffer pH-7.4). Additionally the S1 was mimic as the function of a sequential logic circuit at molecular level based on “On–Off–On” sensing behavior by the inputs of Cu^{2+} and CN^-. Further both S1 and S1-Cu^{2+} complex shows the antimicrobial activities against fungi: *Bipolaris oryzae* and *Rhizoctonia solani* using agar well diffusion method.

1. Introduction

Cyanide has been incessantly of apprehension all above the world due to high toxic nature and extensive use in industrial applications, such as silver or gold extraction from composite ores, metallurgy, acrylic fiber manufacturing and herbicide production [1–3]. Endorsement of toxic CN^- could conclude *via* exposure to skin, absorption by lungs and also from polluted drinking water and contaminated food [4]. Undesirably, prolonged CN^- exposure induces pain, irritation, nervous damage and trace amount can be lethal due to interruption of mitochondrial electron transport chain by interdepending with cytochrome *c* oxidase and causes cellular asphyxiation [5,6]. The appalling concentration of CN^- within the blood of fire victims has been recommended to be between 23 and 26 mM [7,8]. Colorimetric and fluorimetric methodologies were recently studied for the prompt and simple selective recognition of many analysts including CN^- [9–15]. To reduce the interfering anions such as F, AcO and H_2PO_4 [16,17] chemodosimeters take lead the unique nucleophilicity of CN^- to appreciate recognition *via* bond-formation reaction between B–CN [18,19] or C–CN [20–23] bonds. Moreover due to high binding affinity of CN^- with transition metal ions is another significant method for CN^- sensing [24–26]. Furthermost of the chemodosimeters and metal based probe essential to be functioned either in mixed organic or in pure organic solvents due to poor solubility of chemosensors and weaken the nucleophilic addition reaction in presence of water. Thus far, reports concerning for CN^- sensors in complete aqueous system have been limited. Development of aggregates emit based chemosensor in aqueous medium has prompted much concern in recent years. Tang's et al. in 2001 reported “aggregation induced emission enhancement” (AIEE) phenomenon, which is precisely opposite to the aggregation caused quenching (ACQ) effect [27]. Since, AIEE luminogens properties have been intensively deliberate, containing variations of proposed mechanism and potential applications such as bio/chemosensors organic light-emitting diodes (OLEDs) [28], two-photon absorption (2PA) [29], materials and drug delivery [30]. Chromone derivatives drill an important component of pharmacophores and show a significant domain of pharmacological and biochemical actions such as antibacterial [31], antifungal [32], anticancer [33] etc.

Here we reported a novel cromone based fluorophores due to the optical properties for Cu^{2+} and CN^-. Further; we envisioned that aggregates of chromone derivative (aqueous medium) undergo disaggregation in the presence of Cu^{2+} and ensemble Cu^{2+} complexes aggregates with CN^- due to high copper–cyanide affinity,

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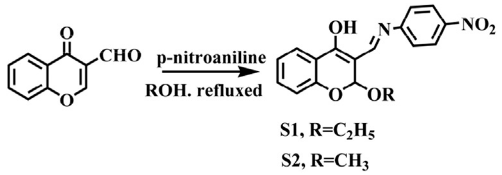

Scheme 1. Synthesis of S1 and S2.

which show fast, selective response and lead to alteration in the photophysical properties of supramolecular aggregates. Moreover we applied this sensing system as logic gate behavior as well as antimicrobial activity, proposed their auspicious prospect in biological and environmental science.

2. Experimental section

2.1. Chemical and instrumentation

All chemicals and solvents (MeOH, EtOH) were purchased from Sigma–Aldrich. Both solvent were distilled under reduced pressure ($CaCl_2$ as drying) and stored on molecular sieve. The elemental analysis (for CHNS) was supported by using vireo MICROV3.1.1 instrument. For UV-Vis spectra, Specord S600 Thermo-Scientific PC double beam spectrophotometer (path length 1 cm) and for fluorescence spectra Horiba RF-5301PC (path length 3 cm) used with standard quartz cell. The NMR spectra were documented in JEOL 400 MHz spectrophotometer by using TMS as an internal standard. CHI760E Electro analyser three-electrode cell with glassy carbon as working electrode, $Hg/HgCl_2$ as reference electrode, Pt wire as counter electrode and 0.1 M tetrabutylammonium hexafluorophosphate (nBu_4NPF_6) as supporting electrolyte were used for electrochemical study.

2.2. General procedure for experiments

The absorption spectra were examined by keeping the ligand concentration at 20 μM, while 5 μM used for emission spectra. The antagonism study used different interfering anions with CN in 4:1 ratio. The detection limit (LOD) was intended by perilously reported method (3σ/S) [23,24], where σ is the standard deviation of the blank solution and S is the slope of the calibration curve. For CV, distilled MeOH and nBu_4NPF_6 has been used on which S1 was dispersed (1 mmol scan rate 0.1 V s^{-1} and potential range −2.0 to +2.0 V). Further titrate ligand S1 with 1 mmol solution of Cu^{2+} & CN^- and observed the change in potential.

3. Result and discussion

3.1. Synthesis and characterization of ligand

For the synthesis of S1 the ethanolic solution of 3-formyl chromone (1 mmol) and *p*-nitroaniline (1 mmol) was mixed and refluxed. After completeness of reaction, yellow colored precipitate of ligand was formed within 40 min. The incorporation of solvent pointed out *in-situ* nucleophilic substitution reaction took place *via* solvent, which was confirmed by replacement of solvent system with *m*ethanol and found methoxy group integrated S2 (Scheme 1 and 2).

Characterization of S1; Yield: 89% Anal. Cal. ($C_{18}H_{16}N_2O_5$): C-63.52, H-4.74, N-8.23, O-23.51; Found: C-63.54, H-4.73, N-8.23; ^1H NMR ($CDCl_3$, 400 MHz): δ 12.17 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 9.3 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.81 (s, 1H), 3.96–3.89 (m, 1H), 3.78–3.70 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 182.7, 162.0, 156.3, 141.9, 140.0, 135.2, 126.6 (2C), 122.6, 122.4, 118.2, 116.3, 112.7, 106.3 (2C), 101.4, 55.7, 15.3; APCI-MS *m*/*z* (m+1) = 341.2 (calcd-341.11).

Characterization of S2; Yield: 93%. Anal. Cal. ($C_{17}H_{14}N_2O_5$): C-62.57, H-4.32, N-8.59, O-24.52.

Found: C-62.61, H-4.29, N-8.62; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.80 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 2H), 8.19 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 14.7, 8.1 Hz, 3H), 7.15 (dd, *J* = 17.5, 7.9 Hz, 2H), 5.85 (s, 1H), 3.40 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz): 181.4, 156.2, 145.32, 146.3, 143.9, 143.0, 135.7, 126.2, 122.9, 122.7, 118.8, 117.1, 109.1, 106.6, 101.6, 97.5, 55.5; APCI-MS *m*/*z* (m+1) = 327.1 (calcd-327.09).

Characterization of S1 & S2 is given in the ESI (Fig. S14-S19).

3.2. AIEE behavior and optimization of S1

To examine the AIEE properties of S1 employed MeOH as the decent solvent and water as poor solvent. S1 shows less molar absorptive band at 382 nm with very low intense emission band (Φ = 0.04) at 456 nm in pure MeOH solvent due to excited state intramolecular proton transfer (ESIPT) process along with isomerization of C=N at the excited state [34]. Clearly, upon altering the water system from methanol (up to 100%), the absorption and emission intensity was enhanced with red shift. The emission band shifted to 503 nm and reaches to the maximum, just about 13 folds (Φ = 0.53) greater than its molecularly discrete species in MeOH, indicates inhibition of ESIPT process and molecules gets aggregates with increasing water content (Fig. 1 and S1a).

Thus the specious enhancement in emission was prompted by aggregation, substantiating its AIEE behavior due to the restricted intramolecular motions. The aggregation procedure could be further assisted due to intermolecular hydrogen bonds formation (−N···-HO) between adjacent molecules [35–38]. Similarly in absorption spectra, red shift with large hypochromic shift at 395 nm was observed upon addition of water, due to aggregated process into the molecules, which was further proved by SEM (scanning electron microscopy) images in aqueous mixture (Fig. 1b). The preferred pH was sustained with dilute solutions of hydrochloric acid and sodium hydroxide. Remarkably, the absorption behavior of S1 practically remains constant between 6 and 9 pH ranges; on the other hand, the emission intensity is stable at 6–8 pH range due to protonation and deprotonation of −OH group (Fig. 2 & Fig. S1b). From above result shows the compatibility of S1 in pure aqueous medium at biological pH range, thus all analytical

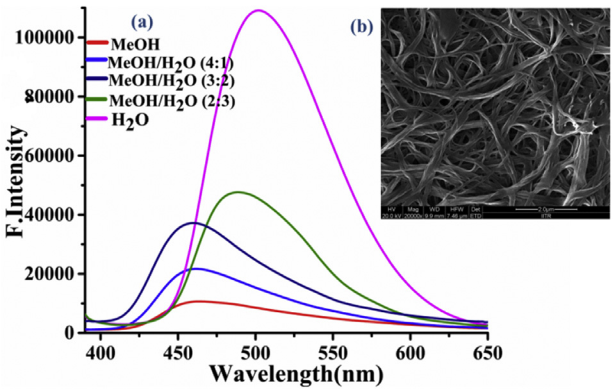

Fig. 1. (a) Variation in emission properties of S1 with consequent amount of water (aggregation induced fluorescence); (b) SEM image of S1 aggregates obtained in 100% aq. solution.