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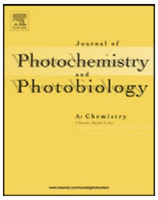

Selective fluoride ion recognition by a thiourea based receptor linked acridinedione functionalized gold nanoparticles

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ABSTRACT

The design and synthesis of acridinedione functionalized gold nanoparticles based PET anion sensor **6** is described. The sensor **6** employs simple aromatic thiourea as anion receptors and the fluorophore is the acridinedione moiety, which were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), UV–vis, steady-state and time-resolved fluorescence techniques. Upon selective recognition of F^- in acetonitrile, the fluorescence emission of **6** was quenched with significant changes in the absorption spectrum. These changes are ascribed due to the hydrogen bonding and deprotonation of the thiourea receptor of ADDTU-GNPs.

1. Introduction

The design and synthesis of systems that are capable of sensing various biologically and chemically important anions are currently of major interest, because anions play a fundamental role in chemical and biological processes [1–4]. Among various important anionic analytes, the fluoride ion is one of the most significant due to its role in dental care [5] and treatment of osteoporosis [6]. In order to selectively differentiate between biologically interesting anionic substrates of similar basicity and surface charge density, such as F^-, CH_3COO^-, and $H_2PO_4^-$, considerable efforts have been made to develop hydrogen-bonding donors/receptors containing urea [5], thiourea [6], amide [7–9], phenol [10–12], imidazole [13], or pyrrole [14] subunits involving different kinds of signaling mechanisms including internal charge transfer (ICT) [15,16], photoinduced electron transfer (PET) [17,18], metal-to-ligand charge transfer (MLCT)[19], excimer/exciplex formation [20], and tuning proton transfer [21] for fluorescence chemosensors.

In particular, the neutral anion receptors embracing the hydrogen-donor urea group have been extensively studied [22–26], in which the NH-anion hydrogen bond or anion-induced deprotonation of the NH groups was observed. To gain an insight into hydrogen-bond formation and neat proton transfer existing in the anion recognition process, Fabbrizzi et al. have investigated various colorimetric anion receptors containing NH binding sites and demonstrated that the deprotonation trend is enhanced by the increase in the acidity of the hydrogen-bond donors and basicity of the anions [27–29]. As the smallest and the most electronegative atom, the fluoride ion shows a very high affinity toward the N–H fragments of receptors containing a urea subunit and allows N–H deprotonation. Moran and co-workers, Gale and co-workers have reported acridinone-based anion sensors [30,31].

Acridinedione dyes (ADDs) have been reported as a new class of laser dyes with lasing efficiency comparable to that of coumarin-102 [32,33]. Interestingly, these dyes have been shown to mimic the NADH analogues to a greater extent because of their tricyclic structure, which is capable of protecting the enamine moiety [34]. It has been reported earlier by us that acridinedione thiourea chemosensor was excellent in specificity toward AcO^-, $H_2PO_4^-$, and F^- over other anions [35]. In this paper, we report the fluorescent chemosensor, thiourea based receptor linked acridinedione functionalized gold nanoparticles (ADDTU-GNPs). This chromophore, operated by PET mechanism, exhibits excellent specificity toward F^- over other anions.

2. Experimental

2.1. Materials

All chemicals used were of the highest purity available. Solvents used were of HPLC grade obtained from Qualigens (India) Ltd. All the anions used in this assay were in the form of their tetrabutylammonium (TBA) salts. Dimedone, 1, 2 phenylenediamine,

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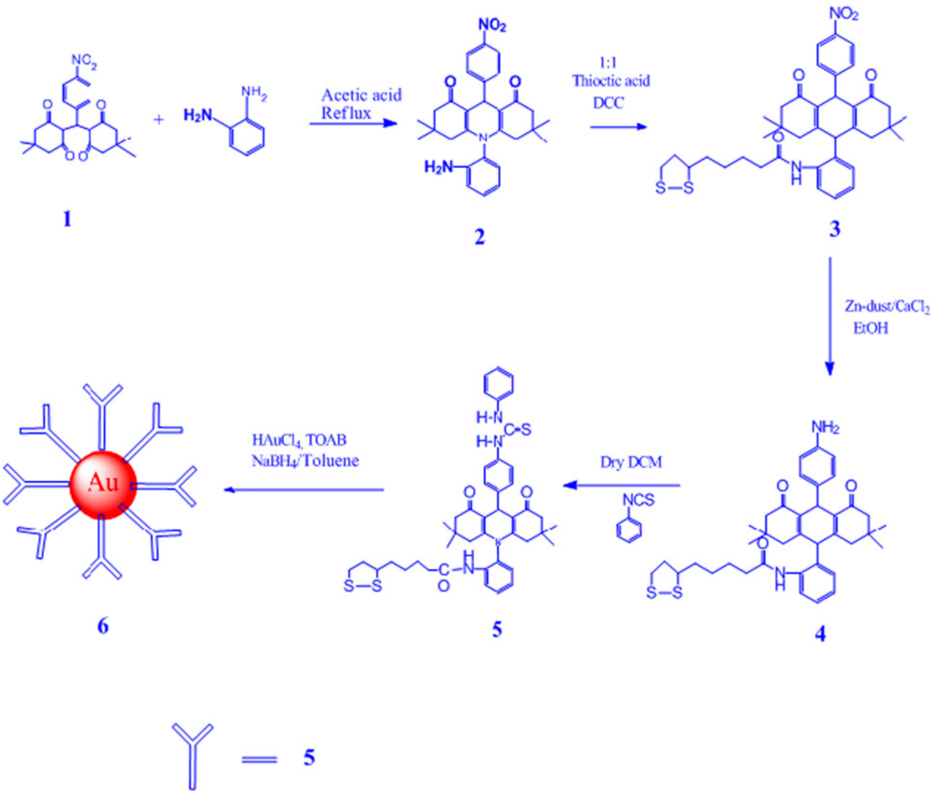


Scheme 1. Schematic illustration of synthesis and assembly of ADDTU-GNPs (**6**) via the reaction of HAuCl4 with ADDTU (**5**).

lipoic acid, DCC, sodium borohydride ($NaBH_4$), and tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$) were purchased from Sigma–Aldrich Chemicals Pvt., Ltd.

2.2. *Experimental methods*

Absorption spectra were recorded on a Agilent 8453 diode array spectrophotometer. Fluorescence spectral measurements were carried out using a Perkin-Elmer MPF-44B fluorescence spectrophotometer, interfaced with PC through RISHCOM-100 multimeter. ^1H NMR, ^{13}C NMR spectra were recorded with BRUKER-SF300 (300 MHz) instrument, with TMS as internal standard (chemical shift in δ ppm). Elemental analysis was carried out using a EURO EA Elemental analyzer. For HR-TEM studies, a drop of dilute suspension was placed on a carbon-coated copper grid and the solvent was allowed to evaporate. Specimens were imaged on a JEOL 300 kV high resolution transmission electron microscopy. FT-IR spectra were recorded with NICOLET-6700 instrument.

2.3. *Synthesis of acridinedione thiourea derivative (ADDTU)*

The synthetic procedure is shown in Scheme 1. The reaction of tetraketone **1** and 1,2-phenylenediamine in acetic acid on reflux afforded nitroacridinedione **2**. A mixture of **2** and lipoic acid in dry dichloromethane with dicyclohexylcarbodiimide (DCC) on reflux, afforded the acridinedione derivative **3**. A mixture of **3**, Zn-dust and $CaCl_2$ in ethanol on reflux, afforded the amino acridinedione derivative **4** [36]. An equimolar mixture of **4** and phenyl isothiocyanate in dichloromethane on reflux, afforded acridinedione thiourea derivative (ADDTU) **5**. The residue was recrystallised from a mixture (9:1) of $CHCl_3$ and methanol to yield yellow crystals of ADDTU.

2.3.1. *Preparation of 2,2′-(4-nitrobenzylidene) bis (5,5-dimethylcyclohexane-1,3-dione) (**1**)*

To a mixture of dimedone (5.0 g, 36 mmol in aq. methanol) was added 4-nitrobenzaldehyde (2.7 g, 18 mmol) and the mixture was warmed until the solution became cloudy. The (4-nitrobenzylidene)bis dimedone started to separate out. The reaction mixture was diluted with water (250 mL) and allowed to stand overnight; the tetraketone **1** was collected by filtration, dried and recrystallised from methanol.

Yield: 6.9 g (94%).

M.P.: 182–184 °C (Lit. [17] M.P. 188–190 °C).

2.3.2. *N-[4-{3,3,6,6-Tetramethyl-10-(2-thioctinoylamino phenyl)-3,4,6,7,9,10-hexahydro-1,8 (2H, 5H)-acridinedione-9-yl}-phenyl]-N′-phenyl thiourea (**5**)*

A mixture of aminoacridinedione **4** (1.0 g, 1.55 mmol) and phenyl isothiocyanate (0.037 g, 2.7 mmol) in dry dichloromethane (20 mL) was refluxed for 24 h under nitrogen atmosphere. After completion of the reaction, as indicated by TLC, the mixture was concentrated and the solid obtained was filtered and dried under vacuum. The thiourea derivative **5** was purified by column chromatography over silica gel using 2% methanol in chloroform as an eluent.

Yield: 0.90 g (75%), M.P. 172–174 °C.

IR (KBr) cm^{-1}: 3244, 3309, 2923, 1625, 1494.

^1H NMR (DMSO-d_6, 300 MHz): δ (in ppm) 1.08 and 1.10 (2 s, 12H, gem-dimethyl), 1.35–1.71 (m, 6H, S–CH–CH_2–CH_2–CH_2–CH_2–CO–), 1.81 (m, 1H, S–C*H*–), 2.15–2.20 and 2.60–2.65 (2d, 4H, J = 16.1 Hz, C_4 and C_5–CH_2), 2.24 (t, 2H, S–CH–CH_2–CH_2–CH_2–CH_2–CO–), 2.20 (s, 4H, C_2 and C_7–CH_2), 2.30 (t, 2H, S–CH_2-), 3.30 (m, 2H, S–CH_2–CH_2–CH–CH_2), 5.81 (s, 1H, C_9–*H*), 6.80–7.50 (m, 12H, Ar-*H*), 9.10 (s, 1H, N*H*), 9.79 and 9.85 (2 s, 2H, 2 NH thiourea) [Fig. S1].

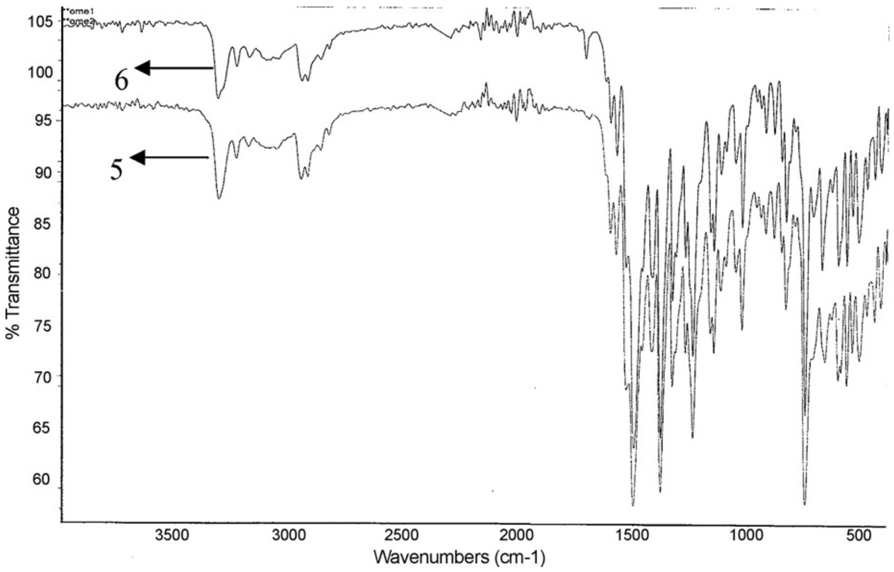


Fig. 1. FT-IR spectra of (**5**) ADDTU, (**6**) ADDTU-gold nanoparticles (No S–H stretching band at ca. 2560 cm^{-1} can be observed in the IR spectrum of **6**). A comparison of the FT-IR spectra of ADDTU-GNPs resembles that of **5**. $NaBH_4$ reduces the disulfide moieties of lipoic acid as well as enables the formation of metallic gold nuclei, which leads to the formation of S–Au bond to produce **6**.

^{13}C NMR (DMSO-d_6, 300 MHz): δ (in ppm) 21.6, 22.6, 24.5, 26.3, 27.2, 27.9, 29.3, 30.6, 32.3, 49.6, 54.4, 112.3, 112.9, 120.4, 122.4, 123.5, 124.3, 125.1, 128.4, 128.5, 135.9, 144.3, 149.1, 168.0, 179.5, 195.1 [Fig. S2].

Analysis: Found (calculated for $C_{44}H_{50}N_4O_3S_3$): C, 67.71 (67.83), H, 6.51 (6.46), N, 7.29 (7.19) EI-MS: 797[M+H_2O+H].

*2.3.3. Synthesis of gold nanoparticles capped with ADDTU (ADDTU-GNPs) (**6**)*

The synthesis of monolayer-protected clusters (MPCs) adopts modification of the method reported by Brust et al. [37]. To a stirred solution of tetraoctylammonium bromide (0.068 g,) in toluene (5 mL) was added dropwise an aqueous solution of hydrogentetrachloroaurate-(III) hydrate (11 mg, 0.028 mmol), and the mixture was stirred for 20 min. The reaction mixture was washed with distilled water (10 mL) several times, and the organic layer was separated. A solution of ADDTU (10 mg, 0.0072 mmol) in toluene (2 mL) was added to the above solution, and the resulting mixture was stirred for 30 min. An aqueous solution (3 ml) of sodium borohydride (11 mg, 0.28 mmol) was added dropwise, and the mixture was stirred for a further period of 3 h. The organic layer was washed with water and diluted with methanol (250 mL). It was kept in a refrigerator, and the precipitate obtained was further purified by dispersion in toluene and then centrifugation after the addition of methanol (10 mL). This process was repeated twice to remove any unbound thiol. The residue obtained was redispersed in 5 mL of toluene and used as stock solution. No S–H stretching band at ca. 2560 cm^{-1} can be observed in the IR spectrum of **6**. A comparison of the FT-IR spectra of ADDTU-GNPs resembles that of **5** (Fig. 1) as reported by Yan-Li et al. [38] and Velu et al. [39].

3. Results and discussion

3.1. Absorption studies

The absorption and emission maximum of acridinedione dyes in acetonitrile solution are centered around 380 and 430 nm, respectively. The peak at 380 nm is attributed to the intramolecular charge transfer from the nitrogen to the carbonyl oxygen in the acridinedione moiety and the emission at 430 nm to that of the local excited (LE) state [32–34,40–42]. In this study, acridinedione thiourea (**5**) exhibits a band at 360 nm in acetonitrile Fig. 2A. The anion-binding ability of ADDTU (**5**) with the anions F^-, Cl^-, Br^-, I^-, $HSO_4{}^-$, $ClO_4{}^-$, AcO^-, $H_2PO_4{}^-$, and $BF_4{}^-$ in acetonitrile were investigated using UV–vis and steady-state fluorescence techniques. It can be noted that, upon the addition of anions (except F^-), no noticeable absorption spectral changes occurred Fig. 2B (AcO^-, $H_2PO_4{}^-$ (inset)). On the other hand, upon addition of F^-, the absorption spectrum is dramatically affected (Fig. 2C) due to the deprotonation of the ADDTU thioctic amide hydrogen with associated enhancement in the push-pull character of the ICT transition, which is reflected in the increased absorbance at 375 nm. A similar result with OH^- ion confirms the deprotonation of ADDTU thioctic amide hydrogen providing evidence for the above observation. The inset of Fig. 2C represents a lower concentration of F^-, no significant change was observed.

*3.2. Emission spectral studies of ADDTU (**5**) with anions*

The relative decrease in the fluorescence intensities without shift in the emission maximum of an acetonitrile solution of the ADDTU scaffolds in the presence of various anions are represented in (Fig. 3). The hydrogen bonding interaction of the AcO^-, $H_2PO_4{}^-$, and F^- with thiourea (TU) brings out a decrease in the oxidation potential of the receptor, which triggers the PET from TU to the relatively electron deficient ADD moiety, and this causes the fluorescence to be quenched [19]. It can be noted that, upon addition of all other the anions, no noticeable spectral changes were observed (Fig. S3).

3.3. Time-resolved fluorescence studies of ADDTU with anions

The complexation between anions and ADDTU has been investigated by the time-resolved fluorescence technique. Figs. S4–S6 present the fluorescence decay of ADDTU at different concentration of anions was monitored at 430 nm, respectively, in acetonitrile. In the absence of anion, ADDTU (**5**) exhibited triexponential decay with lifetimes of 0.52, 0.91 and 3.1 ns (with amplitudes of 16%, 70% and 14%, respectively). The triexponential decay data suggests the presence of three distinct species. Upon the addition of F^-, $H_2PO_4{}^-$ and AcO^- to ADDTU, The fluorescence decay exhibited triexponential behaviour with decreasing lifetimes of 0.25, 1.2 and 3.0 ns

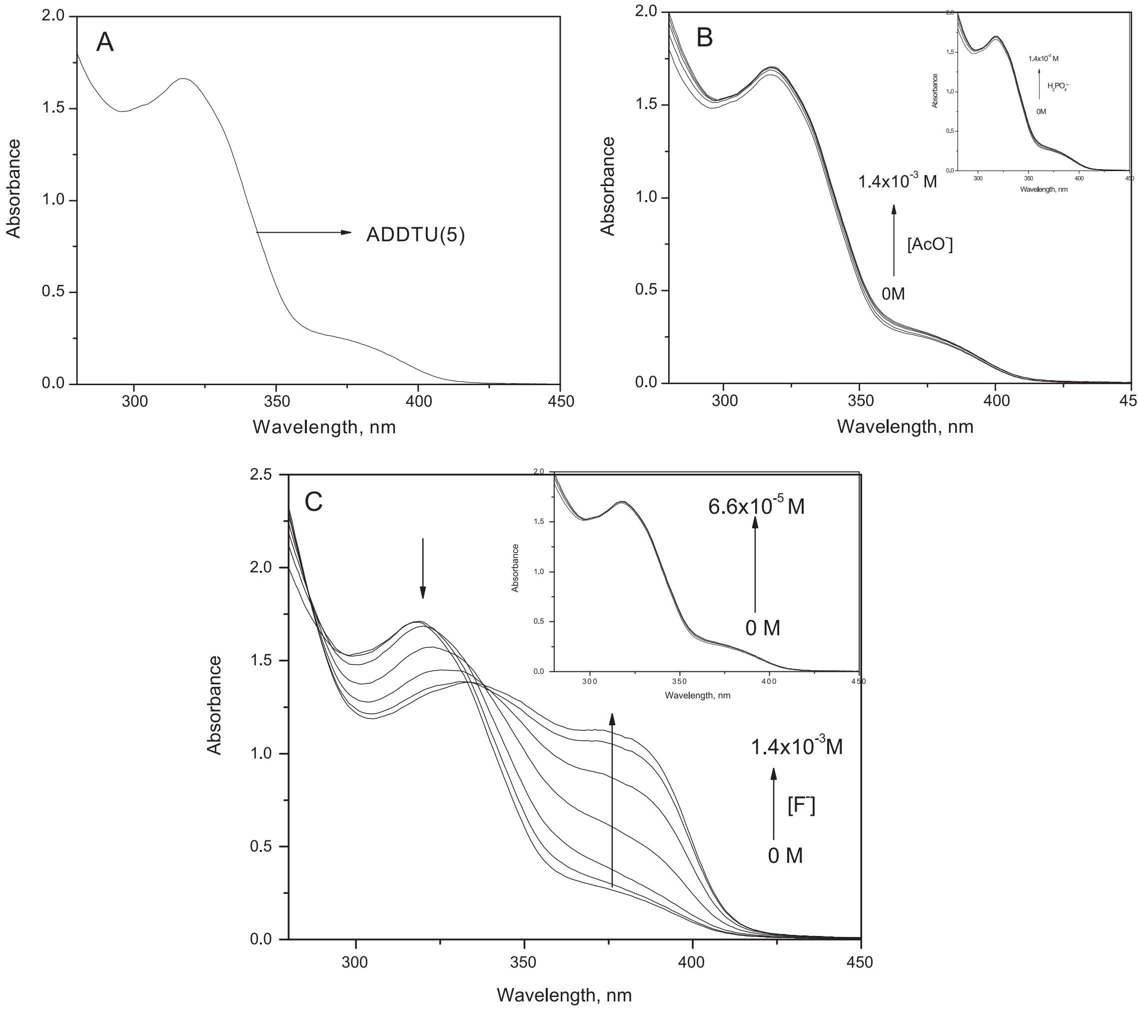


Fig. 2. The absorption spectra in acetonitrile of (A) ADDTU; (B) upon addition of AcO$^-$ (the inset of B represents addition of $H_2PO_4^-$, where no significant change was observed). (C) Upon addition of F$^-$.

for F$^-$ (with amplitudes of 5%, 71% and 24%); 0.24, 1.2 and 3.1 ns for $H_2PO_4^-$ and 0.26, 1.2 and 3.2 (for AcO$^-$ at monitored 430 nm). The relative abundance of all these species (ADDTU with $H_2PO_4^-$ and AcO$^-$) remained more or less unaffected. The decrease in the lifetime was attributed to the PET between the TU and ADD in ADDTU–anions complex. The variation in the fluorescence lifetime of ADDTU on addition of anions, in acetonitrile, was observed as presented in Table ST1.

3.4. *HR TEM studies*

The HR TEM sample of **6** was prepared by drop-casting a dilute suspension on a carbon-coated copper grid. Images are presented in (Fig. 4). Three-dimensional approach in TEM images indicates that ADDTU (**5**) is anchoring on the surface of the gold nanoparticles (GNPs). The size of GNPs was found to be an average diameter of 3.2 nm. The GNPs are assumed to be spherical; the number of ADDTU molecules capping with one gold nanoparticle of size 3.2 nm can be estimated, if the foot print area of the ADDTU molecule is 0.657 nm^2. This shows that forty-nine ADDTU molecules are capping with the nanogold particle having a total surface area of 32.15 nm^2. In this study, it has been estimated that the number of gold atoms in the nanoparticle as 992.55 using the density of nanogold (58.01 atoms/nm^3) by adopting a tight-packed spherical model suggested by Murray and co-workers [43]. The surface area of the nanogold particle obtained in our study is 32.15 nm^2. Using the hexagonally close packed surface density of nanogold (13.89 atoms/nm^2); we could estimate the number of gold atoms on the surface of nanogold to be 566. (Detailed calculation and data given in the supplementary data.)

3.5. *Absorption studies of ADDTU-GNPs (**6**)*

In general, the absorption and emission maxima of acridinedione dyes in acetonitrile solution are centered around 380 and 430 nm, respectively. In this study, acridinedione thiourea-GNPs exhibited two sets of bands; absorption band in the UV region is characteristic of functionalized ADDTU molecules (360 nm) in acetonitrile and a broad band in the visible region (529 nm), which is attributed to the surface plasmon resonance (SPR) absorption for the stabilized gold nanoparticles **6** (Fig. 5A).

3.6. *Selective fluorescence signaling of fluoride anion by ADDTU-GNPs (**6**)*

The ability of the ADDTU-GNPs to sense anions AcO$^-$, $H_2PO_4^-$ and F$^-$ was investigated. No significant change was observed in the longer wavelength absorption and emission spectra of ADDTU-GNPs on the addition of AcO$^-$ and $H_2PO_4^-$ in acetonitrile as shown in Figs. 5B, 7A and S7A. This indicates that there is no interaction between these anions and ADDTU-GNPs in the ground state and excited state. On the other hand, upon addition of F$^-$ the absorp-

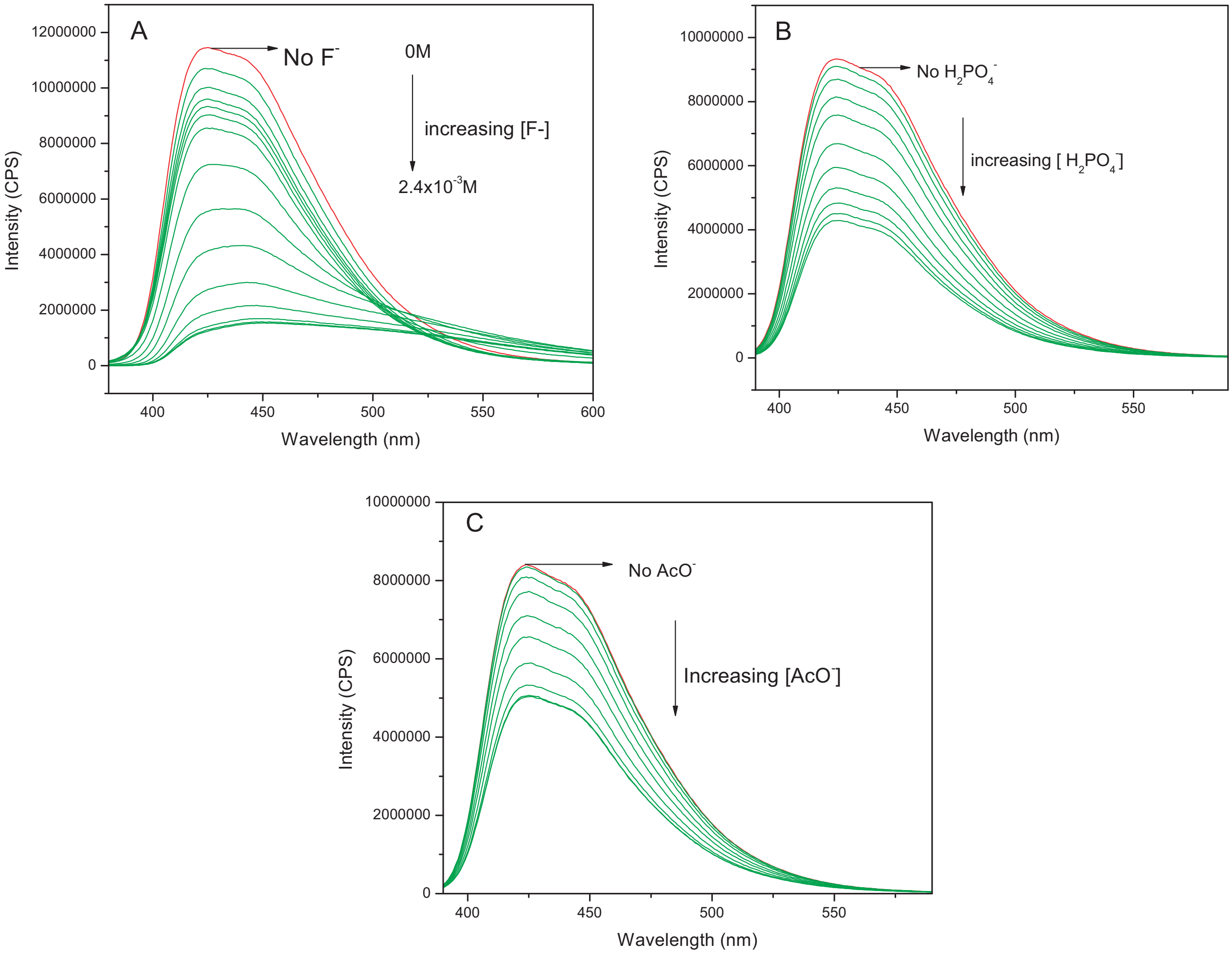


Fig. 3. The fluorescence emission spectra of **5** upon addition of (C) F^-, (D) $H_2PO_4^-$, (E) AcO^- (0–2.4 × 10^{-3} M) in acetonitrile, showing the quenching of fluorescence emission upon anions recognition.

tion spectrum is dramatically affected. The absorption at 300 nm decreases with the appearance of a new band centered at 375 nm with an isosbestic point at 321 nm (Fig. 6). The inset of Fig. 6 represents at lower concentration of F^-, where no significant change was observed.

Excitation at the isosbestic point shows fluorescence quenching (Fig. 7) with the increase in the concentration of F^-. The quenching of fluorescence in the presence of F^- is due to the photoinduced electron transfer (PET), which takes place between the anion receptor and the ADD moiety in the fluorophore. At lower concentration

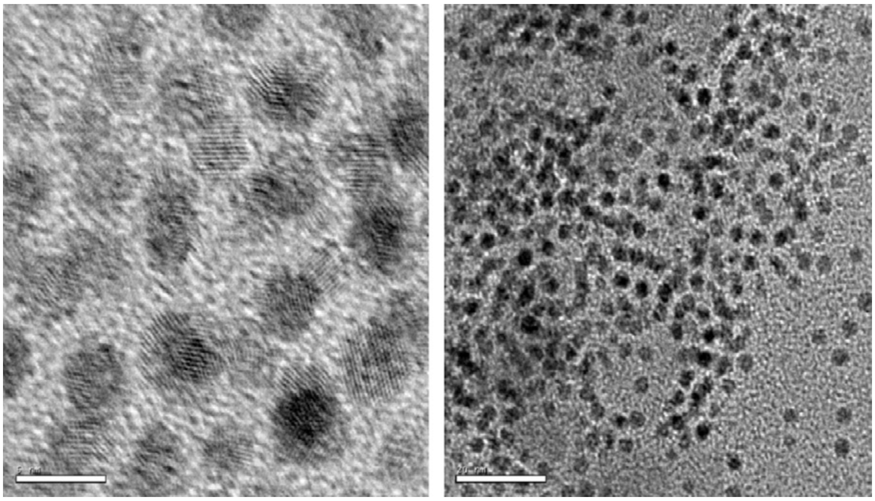


Fig. 4. Typical HR-TEM images of compound **6**.

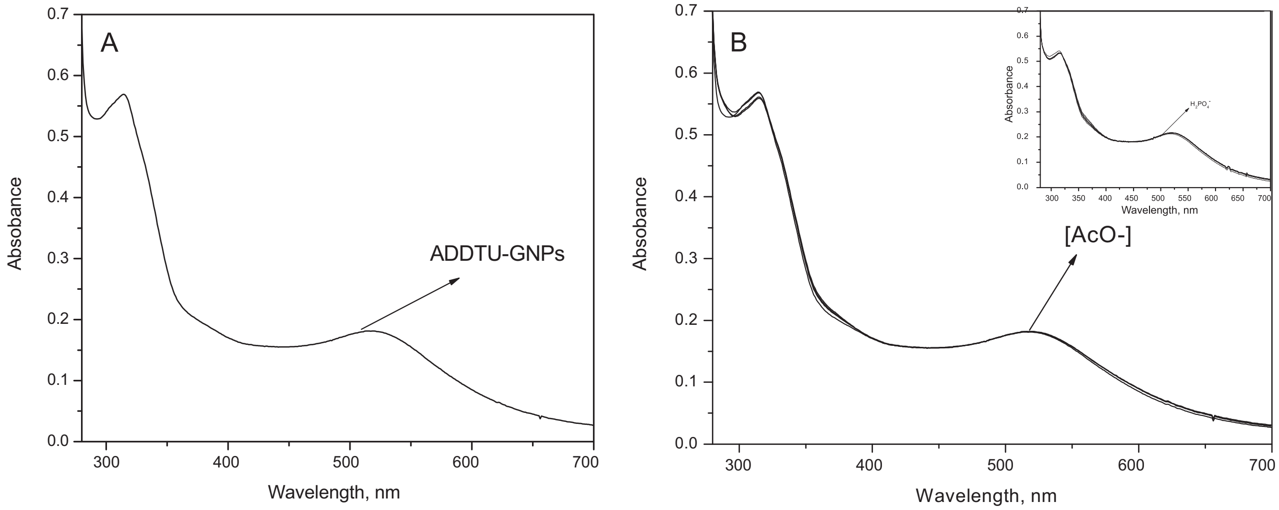


Fig. 5. UV–vis spectral changes observed for (A) ADDTU and (B) ADDTU-GNPs with addition of AcO^-, $H_2PO_4^-$ (inset)(0–2.4 × 10^{-3} M) in acetonitrile.

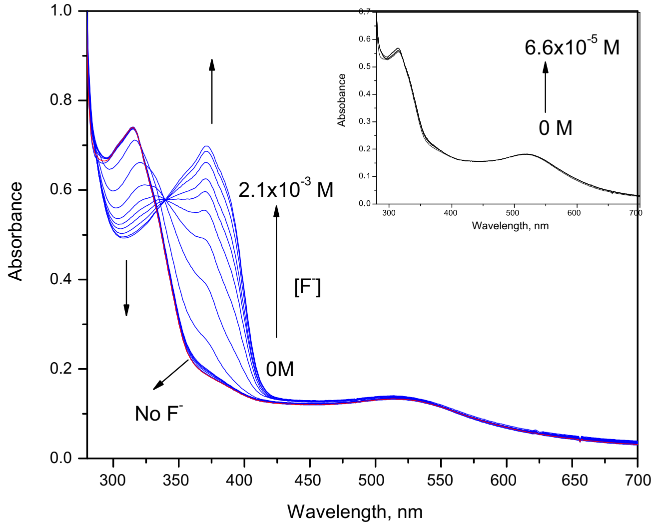


Fig. 6. UV–vis spectral changes observed for ADDTU-GNPs **6** with addition of fluoride anion (0–2.4 × 10^{-3} M) in acetonitrile.

of F^- (0–6.6 × 10^{-5} M), the hydrogen-bonding interaction predominates, while at higher concentration (6.6 × 10^{-5}–2.4 × 10^{-3} M) the deprotonation occurs at thiourea (TU) moiety in the fluorophore. Both the processes bring out a decrease in the oxidation potential of TU receptor, which triggers the PET from TU to the relatively electron deficient ADD moiety, and this causes the fluorescence quenching (Fig. 7B). Fig. 8 depicts the plot for the selectivity of **6** towards the anions. To confirm the hydrogen bonding interaction and deprotonation of ADDTU with F^-, the ^{1}H-NMR titration was carried out in $CDCl_3$ + DMSO-d6 (Fig. S8) at 25 °C. At lower concentration of F^- broadening with shift of the signals (–NH) were observed, which indicate the hydrogen bonding interaction of F^- with ADDTU; at higher concentration the complete disappearance of amide–NH proton peaks was observed similar to that of the earlier investigation [44,45]. The up-field shift of the aromatic proton attributed to the decrease in ring current by anion recognition [17].

When the ADDTU molecules were functionalized on gold nanoparticles, it was found that approximately 49 ADDTU molecules were bound to single nanoparticles. The presence of such a large number of molecules hinders, the approach of larger anions like phosphate and acetate, sterically. This facilitates the selectivity of the F^- ion interaction with ADDTU-GNPs as shown in the Scheme 2.

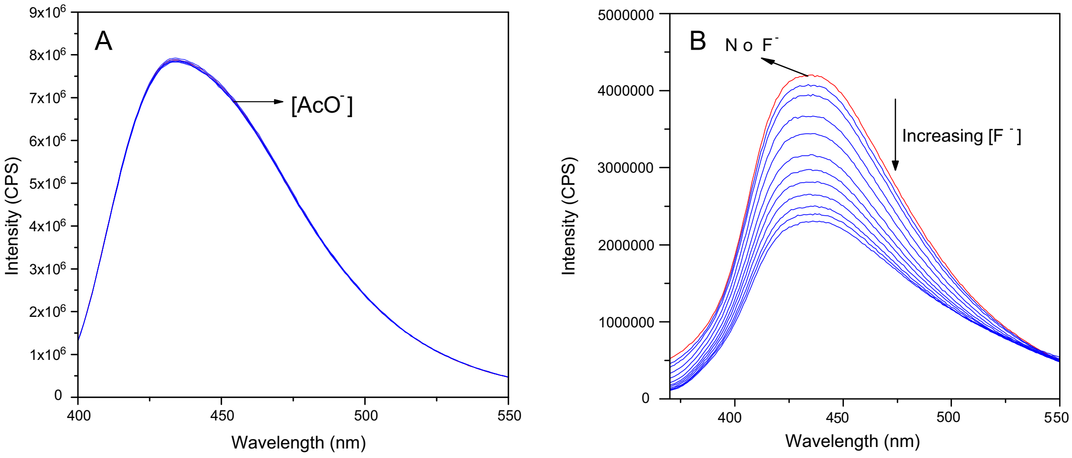


Fig. 7. (A) Addition of AcO^- did not alter the emission in acetonitrile. (B) Fluorescence emission spectra of **6** upon addition of fluoride anion (2.4 × 10^{-3} M), showing the fluorescence emission being quenched upon F^- recognition.

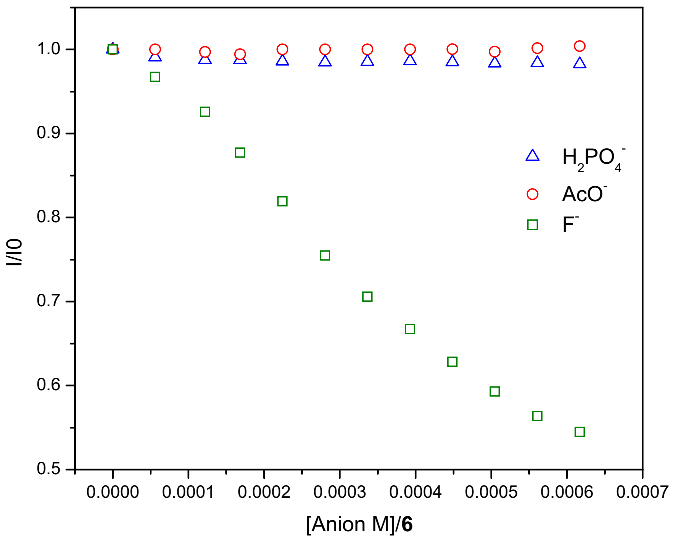


Fig. 8. Plot of I/I_0 versus the [anion]: **6**, which illustrates the selectivity for F^-, over $H_2PO_4^-$ and AcO^- ions.

3.7. *Time-resolved fluorescence studies*

The complexation between anions and ADDTU-GNPs has been investigated by the time-resolved fluorescence technique. Fig. 9 presents the fluorescence decay of ADDTU-GNPs at different concentration of F^- was monitored at 430 nm respectively in acetonitrile. In the absence of anion, ADDTU-GNPs (**6**) exhibited triexponential decay with lifetimes of 0.44, 1.20 and 4.22 ns (with amplitudes of 27%, 50% and 23%, respectively). The triexponential decay data suggests the presence of three distinct species. Upon the addition of AcO^- and $H_2PO_4^-$ to ADDTU-GNPs, there was no significant change in the fluorescence lifetime. On the other hand, upon addition of F^-, the fluorescence profile exhibited triexponential decay at lower and higher concentrations of F^-. The fluorescence decay exhibited triexponential behaviour with decreasing lifetimes of 0.25, 1.19 and 3.69 ns (with amplitudes of 25%, 50% and 25%, respectively, at monitored 430 nm). The relative abundance of both these species (free ADDTU-GNPs and ADDTU-GNPs with F^-) remained more or less unaffected. The decrease in the lifetime was

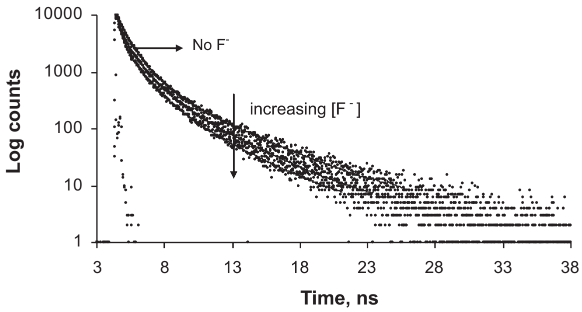
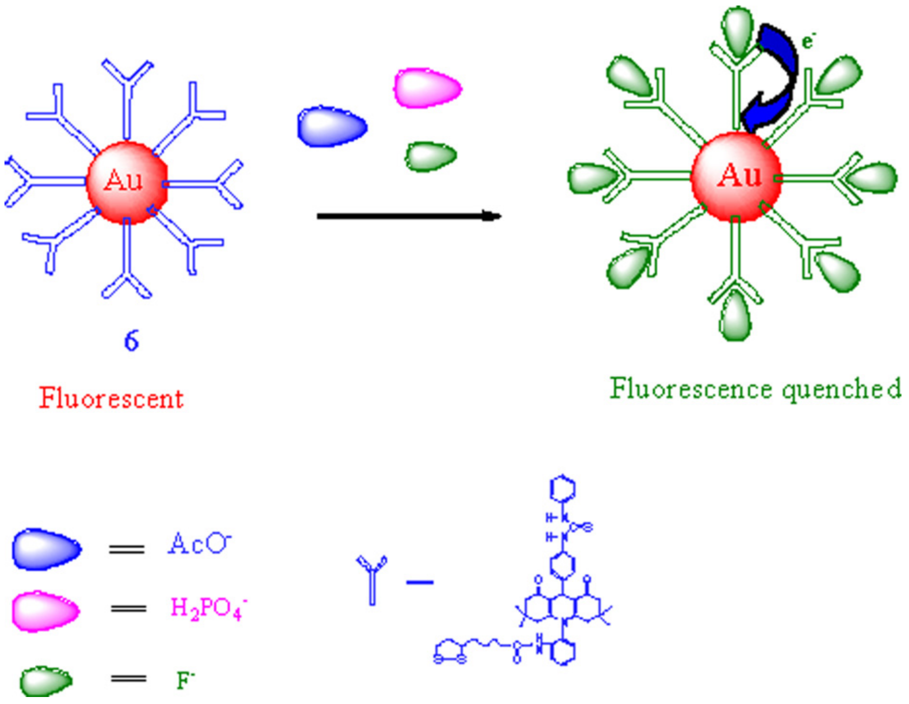


Fig. 9. Fluorescence decay profile of ADDTU-GNPs (**6**) with different concentration of F^- in acetonitrile; λ_{exc} = 375 nm and concentrations of F^- 0–1.3 mM. Fluorescence decay was monitored at 430 nm (A) in acetonitrile.



Scheme 2. The possible mechanism of the phenomenon of binding of the free ADDTU-GNPs with F^-, AcO^- and $H_2PO_4^-$.

Table 1
Fluorescence lifetime of ADDTU-GNPs on the addition of F^- in acetonitrile.

$[F^-]$ ($\times 10^{-5}$ M)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1 (%)	B_2 (%)	B_3 (%)	χ^2
0	0.44	1.20	4.22	27	50	23	1.24
98	0.25	1.16	3.5	22	50	28	1.20
130	0.25	1.08	3.12	28	43	29	1.40
170	0.25	1.19	3.69	25	50	25	1.38
190	0.25	1.16	3.4	33	45	22	1.00

attributed to the PET between the TU and ADD in ADDTU-GNPs–F^- complex. The variation in the fluorescence lifetime of ADDTU-GNPs on addition of F^-, in acetonitrile, was observed as presented in Table 1.

4. Conclusion

In summary, the chemosensors ADDTU and ADDTU-GNPs have TU receptor site, which play a key role in the selective fluorescence anion sensing. This investigation represents a ADDTU derivative as sensor for AcO^-, $H_2PO_4^-$ and F^-. Hydrogen bonding scaffolds with TU moiety of ADDTU results in the fluorescence quenching by PET mechanism. ADDTU-GNPs are highly selective towards F^- due to the steric nature of the cluster.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.10.025.

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