Propylimidazole Functionalized Coumarin Derivative as Dual Responsive Fluorescent Chemoprobe for Picric Acid and Fe\(^{3+}\) Recognition: DFT and Natural Spring Water Applications

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Received: 3 November 2021 / Accepted: 24 March 2022 / Published online: 4 April 2022
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Abstract
A propylimidazole functionalized coumarin derivative (IPC) was fabricated for the first time and applied as a dual responsive fluorescent chemoprobe for sensitive and selective recognition of picric acid (PA) and Fe\(^{3+}\). Strong fluorescence quenching phenomena of the IPC were observed in H\(_2\)O/ACN (5/95, v/v) medium (\(\lambda_{\text{em}}=408\) nm) upon the additions of Fe\(^{3+}\) or PA. The fabricated dual responsive IPC offered good selectivity and sensitivity with the low limit of detection values (0.92 µM for PA and 0.22 µM for Fe\(^{3+}\)) lower than the acceptable amounts of Fe\(^{3+}\) and PA by the international official authorities. The validation study for the chemoprobe IPC for PA and Fe\(^{3+}\) was also performed. The interaction phenomena of IPC with PA and Fe\(^{3+}\) based on the findings of a range of experiments were considered and DFT computations were done to verify their recognition mechanisms. The sensing phenomena of IPC towards PA (1:1) and Fe\(^{3+}\) (3:1) were confirmed by the MALDI TOF–MS, FT–IR, \(^1\)H–NMR titration and Job's methods. Furthermore, the compound IPC was effectively applied as a fluorescent sensor for Fe\(^{3+}\) and PA detection in real natural spring water samples.

Keywords Fluorescent sensor · Picric acid · Iron · Coumarin · DFT · Natural water

Introduction
Fluorescent sensor technology has attracted extensive interest to researchers for trace analyte detection in recent years due to its advantages; such as operational/instrumental simplicity, portability, cost efficiency, excellent sensitivity/selectivity, ease of visual detection and fast signal processing [1–4]. Fluorescent organic substances have been extensively utilized for the design of fluorescent sensors/probes to recognize a wide range of environmentally and biologically important analytes like heavy metal ions/cations, anions, thiols, amino acids and nitroaromatic compounds [5]. Out of different nitroaromatic compounds, picric acid (PA; 2,4,6–trinitrophenol, TNP) is commonly utilized in blasting, manufacturing and chemical industries due to its better–quality explosiveness [6–9]. PA is known as a more influential secondary explosive substance than its structural related compounds like \(p\)–dinitrobenzene (\(p\)–DNB), 2,4–dinitrotoluene (DNT) and trinitrotoluene (TNT) and is also defined as a threat to public security and human health. Due to its extremely explosive nature, it could easily be employed by terrorists for illegal activities [10]. Moreover, it could induce fatal diseases like anemia, cancer, faintness, acute scratchiness and allergic reactions of the skin, eye irritation and damage to the functions of kidney and liver and does not degrade easily in nature [1, 11, 12]. On the other hand, highly sensitive and selective recognition of heavy metal ions in trace level with fluorescent organic compounds have been of great interest because of the fact that they have pivotal roles in various environmental and
biological processes. For instance, Fe$^{3+}$ has vital roles in many living systems like electron transfer, oxygen uptake and transportation. Its superabundance (hyperferremia) in the body would injure bio–systems and induces various failures of limbs such as the heart, liver and kidney; as a result of producing reactive oxygen species. In the meantime, its absence (hypoferremia) could result in a number of critical diseases such as diabetes, insomnia, anemia diseases, and it induces iron homeostasis that is an important matter for the progression of Parkinson’s, Huntington’s and Alzheimer’s diseases [13–16]. Thus; there is a great need to develop new analytical methodologies for the selective and sensitive recognition of PA and Fe$^{3+}$.

To date, several analytical methods have been developed for the recognition of PA and Fe$^{3+}$, for instance, inductively coupled plasma–optical emission spectroscopy (IPC–OES), ion chromatography (IC), atomic absorption spectroscopy (AAS), high–pressure liquid chromatography (HPLC), etc. These methods have some drawbacks, such as they have need sophisticated instruments, specialized personnel, laborious sample pre–treatment procedures and the usage of costly chemical reagents. To keep away from these drawbacks, fluorescent sensing systems have been recently developed due to their superior advantages mentioned above [8, 17–19]. However, the literatures based upon fabricating dual responsive fluorescent chemoprob for the recognition of both PA and Fe$^{3+}$ with high selectivity and sensitivity, are still rare [11, 20–22]. Therefore, the need is great for more fluorescent chemoprobes able to detect the PA and Fe$^{3+}$ in real–time and reliably.

Herein, a new propylimidazole functionalized coumarin compound, N–(3–(1H–imidazol–1–yl)propyl)–2–oxo–2H–chromene–3–carboxamide (IPC) was prepared and utilized as a dual responsive chemoprobe for the detection of PA and Fe$^{3+}$ with high selectivity by fluorescence quenching behaviors. It is important to point out that fluorescence sensors capable of dual determination of PA and Fe$^{3+}$ are scarce. The optical properties and responses of IPC towards PA and Fe$^{3+}$ in H$_2$O/ACN (5/95, v/v) media were determined. DFT computations were done to confirm the electronic and geometrical structural characteristics of IPC and its complexes. Moreover, IPC was used for the sensitive detection of PA and Fe$^{3+}$ in real natural spring water samples. The obtained results demonstrated that IPC is a good candidate for the determination of PA and Fe$^{3+}$. Furthermore, the binding mechanisms were performed as well.

**Materials and Methods**

**Chemicals and Instrumentations**

All chemical reagents and solvents were bought from commercial suppliers (Sigma Aldrich, Thermo Fisher Scientific and VWR International Chemicals) and used directly. Merck Milli–Q$^{®}$7003/05/10/15 water purification machine in our laboratory was used to obtain ultra high–quality water, 18.2 Ω.cm (Darmstadt, Germany). Nitroaromatic explosives [4–Nitrobenzoyl chloride (NBC), 3,5–Dinitrobenzoic acid (DNBA), 4–Bromo–3–nitrobenzoic acid (BNBA), 2,4–Dinitrotoluene (DNT), 1–Chloro–2,4–dinitrobenzene (CDNB), 2,5–Dibromonitrobenzene (DBNB), Nitrobenzene (NB) and 2,4,6–trinitrophenol (PA, picric acid) and chloro cation salts (K$^+$, Ag$^+$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$) were used under this study.

$^1$H–NMR spectra were gained on a Bruker–DPX 600 MHz (Massachusetts CA, USA) NMR spectrometers. Infrared spectra were recorded on a Spectrum–100 spectrometer with ATR accessory (Perkin Elmer Inc., MA, Wellesley, USA). Mass data were acquired on Bruker MicroflexTM LT MALDI TOF–MS system (Massachusetts, CA, USA). Fluorescence studies were recorded on an Agilent Technologies Cary Eclipse fluorescence spectrometry. pH Measurements were performed by using a benchtop pH–meter (Apera Instruments, Columbus, USA).

**Synthesis Protocol of IPC**

Briefly, the compound A was synthesized according to the previous literature [23]. Then, the compound A (107 mg, 0.517 mmol) was added to a solution of 1–(3–aminopropyl) imidazole (64.61 mg, 0.517 mmol) in acetonitrile (MeCN, 10.0 mL). The reaction mixture was stirred at rt for 2h, and then the precipitated occurred. The obtained product was filtered by washing several times with MeCN (Scheme S1).

Yield: 30 %; FT–IR (ATR*solid) (ν, cm$^{-1}$): 3139, 3026, 2981 and 1724; $^1$H NMR (DMSO–d$_6$, 600 MHz): δ (ppm) 8.73 (s, 1H), 8.66 (s, 1H), 8.58 (s, 2H), 7.90 (d, 1H), 7.71 (t, 2H), 7.58 (s, 1H), 7.47 (s, 1H), 4.17 (t, 2H), 2.74 (t, 2H), 2.02 (m, 2H); Calculated MALDI TOF–MS: C$_{16}$H$_{15}$N$_3$O$_3$: 297.11, Found MALDI TOF–MS: 298.526.

**Fluorescence Studies of IPC**

For the fluorescence sensing studies, 1×10$^{-2}$ M stock solution of the chemoprobe IPC was prepared and then it was diluted to 50 μM in H$_2$O/ACN (5/95, v/v) media. The stock solutions of nitroaromatic explosives (NBC, DNBA, BNBA, DNT, CDNB, DBNB, NB and PA) and metal ions (K$^+$, Ag$^+$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$) were prepared as 1×10$^{-2}$ M. The spectra of PA and Fe$^{3+}$ were gathered from the emission region of 340–800 nm ($\lambda_{em}$=380 nm, $\lambda_{em}$=408 nm, slit widths 10.0 and 20.0 nm). Titration plots were constructed by plotting the emission intensities at 408 nm. For the selectivity studies, the same equivalents of 7
kinds of nitroaromatic explosives (50.0 eqv.) and 8 kinds of metal ions (50.0 eqv.) were employed by the chemoprobe IPC solution. The validation study for the chemoprobe IPC for PA and Fe$^{3+}$ was performed and all measurements were done at least three times.

**Computational Studies**

The molecular structures and HOMO/LUMO levels of the IPC and its complexes (IPC–PA and IPC–Fe$^{3+}$) were gained with the gas phase, by using DFT computations through the employ of Gaussian-09 \[B3LYP/LANL2DZ (for \text{PA and Fe}^{3+})\] and 6–31G \((d,p)\) (for C, H, N, O) and GaussView–5.0.8 software packages (Gaussian, Inc., Wallingford CT, UK).

**Natural Spring Water Analysis**

Natural spring water samples were collected from local water resources in Konya City. The samples were analyzed without sample pre–treatment; just they were centrifugated at 10.000 rpm for 3 min. 3 mL of the IPC sensing solution (50 μmol.L$^{-1}$) was transferred into quartz–cuvette, and then 15.0 μL sample was added into this solution. Afterward, the standard addition method was applied with the addition 15 μL of PA or Fe$^{3+}$(0.10 and 0.20 μmol.L$^{-1}$). After the adding of PA or Fe$^{3+}$ into the solution of chemoprobe IPC, their fluorescence intensities were recorded. The recovery and the standard deviation (RSD) values were calculated for the analytical evaluation. All the fluorescence measurements were performed at least three times and the statistical calculations were done.

**Results and Discussion**

**Fabrication and Characterization of IPC**

IPC was obtained as a white solid and well-characterized using FT–IR, $^1$H–NMR and MALDI TOF–MS techniques (Fig. S1–S3). $^1$H NMR spectrum shows α–hydrogen of coumarin and aliphatic peaks of propylimidazole groups clearly. In addition, 298.526 (m/z) was observed which corresponded to IPC (chemical formula: C$_{16}$H$_{15}$N$_3$O$_3$) in the mass spectrum. (Scheme 1)

**Fluorescence Sensing Studies of IPC**

The effect of different solvents on the emission intensity of IPC was studied. For this purpose, the emission intensities were obtained upon excitation at 330 nm for the chemoprobe IPC prepared in acetonitrile (ACN), methanol (MeOH), ethanol (EtOH), dimethylformamide (DMF), water (H$_2$O), and dimethylsulfoxide (DMSO) (Fig. S4). The maximum fluorescence of IPC was achieved at 408 nm as it was prepared in ACN. The influence of water percentage used in ACN on the fluorescence response was also studied for the IPC, IPC–PA and IPC–Fe$^{3+}$. The differentiation of emission intensities between the chemoprobe IPC and its complexes were the most appropriate when the both volume ratio of ACN/H$_2$O was 95/5. Thus, the solvent media of H$_2$O/ACN (5/95, v/v) was employed for the further fluorescence measurements under this study.

To reveal the sensing ability of chemoprobe IPC, its response towards a pool of analytes including different nitroaromatic explosives (NBC, DNBA, BNBA, DNT, CDNB, DBNB, NB and PA) and metal ions (K$^+$, Ag$^+$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$) was determined in H$_2$O/ACN (5/95, v/v) media (Figs. 1 and 2), with the help of fluorescence experiments. As seen from these figures, the chemoprobe IPC demonstrated high emission intensity at 408 nm upon excited at 330 nm. The chemoprobe IPC depicted dramatic “turn off” responses towards both PA explosive (Fig. 1a) and Fe$^{3+}$ (Fig. 2a) over other studied analytes, within 30 seconds. Subsequently, emission titration studies of IPC were performed with the increasing concentrations of PA (0–20.0 equiv.) (Fig. 1b) and Fe$^{3+}$ (0–20.0 equiv.) (Fig. 2b). Upon the adding of PA into a solution of chemoprobe IPC (50 μM), the emission intensity progressively quenched due to the π–π stacking and deprotonation phenomena \[24\] and it arrived at a minimum intensity level after the adding of 20.0 equiv. of PA. On the contrary, after the addition of different amounts of Fe$^{3+}$, the emission intensity of IPC was quenched because of the paramagnetic quenching effect with the transferring of energy and/or electron, which is known as "ligand–metal charge transfer mechanism (LMCT)". The fluorescence intensity reached a stable value after the concentration of Fe$^{3+}$ reached 20.0 equiv. (Fig. 2b) \[16, 25, 26\].

From the findings of fluorescence titration studies, the detection limits (LOD) of chemoprobe IPC for PA and Fe$^{3+}$ were computed by fluorescence alterations on the basis of 3σ/k equation; where "σ" is the deviation of the blank
emission intensity and "k" is the slope of the linear calibration graph. They were found to be 0.92 µM for PA and 0.22 µM for Fe³⁺, which is less than the daily uptake level of iron ion (2 mg.L⁻¹) suggested by the WHO [16]. These titration data were also employed to compute the association constants (log K) of IPC–PA and IPC–Fe³⁺ complexes, and they were found to be 6.72×10² M⁻¹ for PA and 3.62 M⁻¹/³ for Fe³⁺ on the basis of Benesi–Hildebrand equation (Fig. 3) [27–29]. Thus, these findings recommended that the chemoprobe IPC has a great potential of recognition quantitatively unidentified concentrations of PA or Fe³⁺ and could be utilized for the sensitive recognition of PA and Fe³⁺ in H₂O/ACN (5/95, v/v) media. The sensing properties of the chemoprobe IPC are also comparable to those of some dual–responsive fluorescent probes for PA and Fe³⁺, which reveals that our chemoprobe system has significant improvements (Table 1).

The validation parameters were calculated using the “Youden approach” and “Fisher and Dixon tests”. All of PA (0.00–20.0 eqv.) in H₂O/ACN (5/95, v/v) media (λex=330 nm, λem=408 nm) and (c) an illustration and photograph of fluorescence responses

\[ RSD(\%) = \frac{s}{\bar{x}} \]  

\[ RSD \text{ Horwitz(\%)} = 0.67 \times 2^{1-0.5 \times \log \, CA} \]
Afterward, the intermediate precision study was performed at a single concentration (10 or 20 µM) and single period (16 h, 20 h or 24 h) by two different analysts. As can be seen from Table S3, the HorRat ratios were determined <1. Besides, the Fisher test ($F$-test) was performed using Eq. (4). It is clearly seen that the obtained $F_{\text{calculated}}$ values are lower than the $F_{\text{critical}}$ value ($F_{\text{calculated}} < F_{\text{critical}}$). Thus, it has been determined that the proposed method is reproducible.

In addition, the robustness study of the fluorescence method was performed using the Youden approach. The diversifying conditions of this study were presented in Table S4. All conditions were determined with different factorial combinations (Ci) (Table S5). Pareto's graphs for PA and Fe$^{3+}$ (Fig. S5) were achieved using the Eq. (5). All conditions including storage time, type of water, before the analysis, solvent system, temperature of analysis (°C), nitrogen atmosphere, pH were notable, verifying the robustness of the fluorescence method.

For the parameter $3 = \frac{\left( C_2 + C_4 + C_6 + C_8 \right)}{4} + \frac{(C_1 + C_3 + C_5 + C_7)}{4}$

To use the chemoprobe IPC as a selective fluorescent sensor for PA and Fe$^{3+}$, the impacts of competing for nitroaromatic explosives (NBC, DNBA, BNBA, DNT, CDNB, DBNB, NB and PA) and metal ions (K$^+$, Ag$^+$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$) have been also studied. As seen from Fig. 4a, the emission quenching was observed for the mixtures of PA with other nitroaromatic explosives was similar to that stimulated by PA alone; therefore, the presence of competing explosives could not make interference with the recognition of PA. Likewise, the Fe$^{3+}$ sensing system in H$_2$O/ACN (5/95, v/v) media was not influenced by a pool of metal ions (Fig. 4b). The competition studies showed that the fluorescence response of the chemoprobe

$$RQ_{\text{calculated}} = \left| \bar{x}_{n} - \bar{x}_{n+1} \right| / \left( \bar{x}_{\text{highest}} - \bar{x}_{\text{lowest}} \right)$$

$$F_{\text{calculated}} = s_a^2 / s_b^2$$

$$3 = \frac{\left( C_2 + C_4 + C_6 + C_8 \right)}{4} + \frac{(C_1 + C_3 + C_5 + C_7)}{4}$$
Fig. 3 Plots of the fluorescence intensity of chemoprobe IPC versus (a) PA and (b) Fe$^{3+}$ concentrations and Benesi–Hildebrand of the chemoprobe IPC towards PA and Fe$^{3+}$ in H$_2$O/ACN (5/95, v/v) media ($\lambda_{ex}=330$ nm, $\lambda_{em}=408$ nm)

Fig. 4 Relative emission intensity alterations (selectivity studies) of IPC (50 µM) in the presence of higher concentrations of common interfering (a) nitro aromatic explosives (NBC, DNBA, BNBA, DNT, CDNB, DBNB, NB and PA) and (b) metal ions (K$^+$, Ag$^+$, Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Al$^{3+}$ and Fe$^{3+}$) in H$_2$O/ACN (5/95, v/v) media ($\lambda_{ex}=330$ nm, $\lambda_{em}=408$ nm)

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Scheme 2  Schematic presentation of the sensing mechanisms for the interactions of IPC with PA and Fe^{3+}

Fig. 5  The findings of IPC, IPC–PA and IPC–Fe^{3+} by DFT/B3LYP/LANL2DZ.
IPC toward PA or Fe$^{3+}$ was not interfered with the studied competing analytes; therefore, IPC could be used as a "turn–off" fluorescent chemoprobe for the recognitions of both PA and Fe$^{3+}$.

The response time is another critical parameter for a newly designed chemoprobe in real applications. As seen from Fig. S6, the fluorescence quenching for PA and Fe$^{3+}$ occurred only within just 30 seconds, and their fluorescence intensities were reached equilibrium at the same response time. Thus, a response time was decided on 30 seconds for the following experiments and the chemoprobe IPC depicted an excellent response time towards PA and Fe$^{3+}$ respecting the formerly developed a lot of fluorogenic dual chemoprobes [11, 20–22].

**Table 1** Comparison of the chemoprobe IPC with some reported studies towards PA and Fe$^{3+}$

| chemoprobe | recognition process | solvent system | LOD (M) | binding constant (M$^{-1}$) | application | ref. |
|------------|---------------------|----------------|---------|-----------------------------|-------------|------|
| [Cd$_2$(NTB)$_2$(DPP)·(DMA)$_2$]$_4$DMA | turn–off fluorescence (ICT) | DMSO | 0.098 × 10$^{-6}$ (for PA) 4.90 × 10$^{-6}$ (for Fe$^{3+}$) | 9.73 × 10$^4$ (for PA) 3.49 × 10$^3$ (for Fe$^{3+}$) | yes | [21] |
| [Eu(L)$_2$(H$_2$O)]BrH$_2$O | turn–off fluorescence (ICT) | H$_2$O/EtOH (25/75, v/v) | 6.90 × 10$^{-7}$ (for PA) 3.60 × 10$^{-7}$ (for Fe$^{3+}$) | 4.65 × 10$^5$ (for PA) 1.42 × 10$^5$ (for Fe$^{3+}$) | yes | [20] |
| MOF [{Co$_3$(phen)$_2$(HL)$_2$·(H$_2$O)$_2$}]$_n$ | turn–off fluorescence (RET) | H$_2$O | 1.79 × 10$^{-6}$ (for Fe$^{3+}$) 3.35 × 10$^{-6}$ (for PA) | 8.50 × 10$^3$ (for Fe$^{3+}$) | yes | [32] |
| MOF La(TPT)(DMSO)$_2$·H$_2$O | turn–off fluorescence (RET) | EtOH | 47.6 × 10$^{-6}$ (for PA) 3.35 × 10$^{-6}$ (for PA) | 9.89 × 10$^4$ (for PA) 1.36 × 10$^4$ (for Fe$^{3+}$) | , | [33] |
| IPC | turn–off fluorescence (ICT) | H$_2$O/ACN (5/95, v/v) | 0.92 × 10$^{-6}$ (for PA) 0.22 × 10$^{-6}$ (for Fe$^{3+}$) | 6.72 × 10$^2$ (for PA) 3.62 (for Fe$^{3+}$) | yes | this study |

**Binding Mechanisms of IPC Towards PA and Fe$^{3+}$**

To understand the binding stoichiometry of the complexes between IPC and PA/Fe$^{3+}$, the MALDI TOF–MS, FT–IR and Job’s plot methods were applied. The stoichiometric ratios of chemoprobe IPC toward Fe$^{3+}$ were found to be 3:1. To determine the binding stoichiometry of IPC–Fe$^{3+}$ complex, Job’s plot study was performed (Fig. S7). The fluorescence intensities at 408 nm are graphed against the molar fractions of the chemoprobe IPC. The maximum spot was monitored at a mole fraction of 0.75 for Fe$^{3+}$ and this result has shown that it was 3:1 stoichiometry of the binding mode of IPC–Fe$^{3+}$. In addition, it is clearly observed that the N–H peak of the chemosensor IPC, which was present at 3259...
nm, disappeared in the infrared spectrum of the complex. The C=O peak of the chemosensor IPC was shifted from 1722 nm to 1709 nm (Fig. S8). Also, the MALDI TOF–MS data also confirms the 3:1 of binding stoichiometry between the chemoprobe IPC and Fe³⁺, because the peaks at m/z= 298.526 and m/z= 944.219 correspond to the [chemoprobe IPC + H⁺] and [chemoprobe IPC + Fe³⁺ + H⁺], respectively (Fig. S9) (Scheme 2). The stoichiometric ratios of chemoprobe IPC towards PA were found to be 1:1 (Fig. S7). To understand the binding stoichiometry of IPC–Fe³⁺ complex, Job's plot study was performed. The maximum spot was monitored at a mole fraction of 0.5 for PA and this result has shown that it was 1:1 stoichiometry of the binding mode of IPC–PA. Also, ¹H–NMR measurements were performed to obtain an insight into the interaction mechanism between IPC and PA. As depicted in Fig. S10, the slight peak was shifted up–field in the presence of PA. Therefore, the formation of π–π stacking and the intermolecular H–bonds between IPC and PA caused the quenching of fluorescence intensity [6, 24]. (Scheme 2) 

**Theoretical Computations**

Theoretical computations of the chemoprobe IPC and its complexes have been done to obtain their HOMO–LUMO energy levels. The orbital energies were computed using Gaussian–09 [B3LYP/6–31G (d,p) (for IPC and IPC–PA) and LANL2DZ (for IPC–Fe³⁺)] and GaussView–5.0.8 software packages. To confirm the suggested interaction pathway of the chemoprobe IPC toward PA, a DFT calculation was performed based on the reported study [6]. The optimal structure of IPC–PA displayed intermolecular hydrogen bonding between IPC and PA due to π–π interactions (Fig. 5). As depicted in Fig. 5, the computed energy gaps between HOMO and LUMO orbitals of IPC, IPC–PA and IPC–Fe³⁺ were found as 3.32, 2.19 and 0.7 eV, respectively, showing good interactions. Therefore, these findings revealed that the interaction of IPC towards PA and Fe³⁺ stabilizes the systems as evident from the lower HOMO–LUMO energy gaps of the complexes compared to IPC (Fig. 5).

**Natural Spring Water Application**

In the last part of the study, the applicability of the developed fluorescence chemoprobe system for the recognition of PA or Fe³⁺ in natural spring water samples was tested. For real water sample measurements, the samples were spiked with known concentrations (0.10 and 0.20 mol.L⁻¹) of PA or Fe³⁺, according to the standard addition method. After the adding of PA or Fe³⁺ into the solution of chemoprobe IPC, their fluorescence intensities were recorded. The findings were given in Table 2, and the recovery values of PA and Fe³⁺ were between 90.89 and 104.71% with the lower relative standard deviation (RSD) values. Thus, these findings revealed that the chemoprobe IPC system could specifically and accurately labor to recognize PA or Fe³⁺ in natural spring waters.

**Table 2** Fluorescence detection of PA and Fe³⁺ in natural spring waters by IPC

|                  | PA spiked (μmol·L⁻¹) | PA determined (μmol·L⁻¹) | recovery (%) | RSD (%) (n=3) |
|------------------|----------------------|--------------------------|--------------|---------------|
| ultra pure water |                      |                          |              |               |
| 0.00             | 0.0153 ±0.0003        | 98.03                    | 1.64         |
| 0.10             | 0.1133 ±0.0031        | 93.01                    | 2.70         |
| 0.20             | 0.2059 ±0.0040        | 95.28                    | 1.94         |
| natural spring water –1 |       |                          |              |               |
| 0.00             | 0.0331 ±0.0010        | 99.88                    | 2.09         |
| 0.10             | 0.1262 ±0.0025        | 93.01                    | 1.99         |
| 0.20             | 0.2373 ±0.0032        | 102.10                   | 1.35         |
| natural spring water –2 |       |                          |              |               |
| 0.00             | 0.0047 ±0.0001        | 99.13                    | 2.42         |
| 0.10             | 0.1038 ±0.0025        | 99.13                    | 2.42         |
| 0.20             | 0.2141 ±0.0072        | 104.71                   | 3.37         |
| Fe³⁺ spiked (μmol·L⁻¹) |                |                          |              |               |
| ultra pure water |                      |                          |              |               |
| 0.00             | 0.0005 ±0.00001       | 99.88                    | 2.12         |
| 0.10             | 0.1004 ±0.0027        | 99.88                    | 2.12         |
| 0.20             | 0.1903 ±0.0040        | 94.91                    | 2.12         |
| natural spring water –1 |       |                          |              |               |
| 0.00             | 0.0120 ±0.0003        | 97.53                    | 1.90         |
| 0.10             | 0.1095 ±0.0021        | 97.53                    | 1.90         |
| 0.20             | 0.1938 ±0.0046        | 90.89                    | 2.36         |
| natural spring water –2 |       |                          |              |               |
| 0.00             | 0.0160 ±0.0003        | 90.89                    | 2.36         |
| 0.10             | 0.1184 ±0.0042        | 102.35                   | 3.52         |
| 0.20             | 0.2036 ±0.0064        | 93.76                    | 3.16         |
Conclusion

In summarize, a new of dual–responsive fluorescence chemoprobe (IPC) based on propylimidazole functionalized coumarin structure for the recognition of PA and Fe3+ has been successfully developed. The IPC revealed "on–off" fluorescence responses towards PA and Fe3+ at 408 nm within only 30 seconds in H2O/ACN (5/95, v/v) media. The LOD values for PA and Fe3+ were found to be 0.92 µM and 0.22 µM, respectively, which are satisfactorily low to permit the recognition of these analytes in realistic applications. The stoichiometry of the complexes [IPC–PA (1:1) and IPC–Fe3+ (3:1)] was identified by MALDI TOF–MS, FT–IR, 1H–NMR titration and Job’s plot experiments. The binding mechanism of IPC toward PA or Fe3+ was also supported by the DFT computation study. Furthermore, the chemoprobe IPC was employed for detecting PA or Fe3+ in natural spring waters with good recovery values. Therefore, these promising findings will make a great contribution to researchers studying nitroaromatic explosives and metal ions in different systems.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-022-02936-z.

Author’s Contributions All authors contributed in the planning, editing and writing of the manuscript. SN KE: Resource, Methodology, Investigation, Software, Data curation. A K: Methodology, Investigation, Software, Data curation. FN A: Data curation, Writing-review and Editing. I Y: Data curation, Writing-review and Editing

Funding This study was supported by the KMU with the financial support (KMU BAP–Grant Numbers: 06–M–20, 02-YL-19 and 13-YL-15).

Data Availability The data sets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Consent to Participate Not applicable.

Informed Consent Informed consent was obtained from all individual participants included in the study.

Consent for Publication Not applicable.

Conflicts of Interest We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Software A licensed version of Gaussian-09 software is used in computational study

References

1. Sharma S, Dubey G, Sran BS et al (2019) Fabrication of a Hydrazone-Based Al(III)-Selective “Turn-On” Fluorescent Chemosensor and Ensuing Potential Recognition of Picric Acid. ACS Omega 4:18520–18529. https://doi.org/10.1021/acsomega.9b02132
2. Celestina JJ, Tharmaraj P, Sheela CD, Shakina J (2021) Anthracene based selective Co (II) colorimetric and fluorescent sensor for cytotoxicity studies and real sample analysis. J Lumin 239:118359. https://doi.org/10.1016/j.jlumin.2021.118359
3. Cai Z, Zhu R, Zhang S et al (2021) A highly sensitive and selective “turn off” fluorescent sensor based on water soluble copper nanoclusters for morin and temperature sensing. J Lumin 236:118108
4. Erdemir S, Malkondu S (2014) Novel “turn on” fluorescent sensors based on anthracene and carbazole units for Cu (II) ion in CH3CN-H2O. J Lumin 158:86–90. https://doi.org/10.1016/j.jlumin.2014.09.038
5. Saravana Kumar S, Selva Kumar R, Ashok Kumar SK (2020) An “Off–On–Off” type fluorescent chemosensor for the relay detection of Zn2+ and H2PO4− in aqueous environment. Inorgana Chim Acta 502:119348. https://doi.org/10.1016/j.ica.2019.119348
6. Pandith A, Kumar A, Lee YJ, Kim HS (2015) 9-Anthracencarboxamide fluorescent probes for selective discrimination of picric acid from mono- and di-nitrophenols in ethanol. Tetrahedron Lett 56:7094–7099. https://doi.org/10.1016/j.tetlett.2015.11.017
7. Roy B, Bar AK, Gole B, Mukherjee PS (2013) Fluorescent Trisimidazolium Sensors for Picric Acid Explosive. J Org Chem 78:1306–1310
8. Ahmed R, Ali A, Ahmad M et al (2020) Phenanthroimidazolide derivatives as Chemosensor for Picric Acid: A First Realistic Approach. New J Chem 44:20092–20100. https://doi.org/10.1039/D0NJ03422C. Volume
9. Li W, Zhou H, Nawaz MAH et al (2020) A pyrene monomide probe based fluorescent micelle sensor for the selective and sensitive detection of picric acid. Anal Methods 12:5353–5359
10. Li J, Zhuang X, Zhang N et al (2019) Synthesis and characterization of a luminescent Ni(II)-compound based on tpt and H2bdc detecting picric acid and chromate anions in aqueous. Inorganica Chim Acta 497:119096. https://doi.org/10.1016/j.ica.2019.119096
11. Arockiam JB, Ayyanar S (2017) Benzothiazole, pyridine functionalized triphenylamine based fluorophore for solid state fluorescence switching, Fe 3+ and picric acid sensing. Sensors Actuators B Chem 242:535–544. https://doi.org/10.1016/j.snb.2016.11.086
12. Rajalakshmi AV, Palanisami N (2020) Y-shaped ferrocene/non-ferrocene conjugated quinoxalines for colorimetric and fluorimetric detection of picric acid. Spectrochim Acta Part A Mol Biomol Spectrosc 228:117812
13. Hossain SM, Dam GK, Mishra S, Singh AK (2020) Nano-Molar Level Fluorogenic and Oxidation-State Selective Chromogenic Dual Reversible Chemosensor for Multiple Targets Cu2+/S2- and Fe3+/F− ion Sayed. New J Chem 44:15186–15194. https://doi.org/10.1039/D0NJ02777D
14. David CI, Bhuvanesh N, Jayaraj H et al (2020) Experimental and Theoretical Studies on a Simple S – S-Bridged Dimeric Schiff Base: Selective Chromo-Fluorogenic Chemosensor for Nanomolar Detection of Fe 2+ & Al 3+ Ions and Its Varied Applications. ACS Omega 5:3055–3072. https://doi.org/10.1021/acsomega.9b04294
15. Yun JY, Chae JB, Kim M et al (2019) A multiple target chemosensor for the sequential fluorescence detection of Zn2+ and S2– and the colorimetric detection of Fe3+/2+ in aqueous media and living cells. Photochem Photobiol Sci 18:166–176. https://doi.org/10.1039/c8pp00408k
16. Elmas SNK, Gunay IB, Genc HN et al (2020) A tetraoxacalix[2] arene[2]triazine based fluorogenic probe for the sensing of Fe3+: Computational and living–cell imaging applications. J Photochem Photobiol A Chem 403:112848. https://doi.org/10.1016/j.jphotchem.2020.112848
17. Li Y-J, Zhang Yun-Fei, Zhang You-Ming et al (2020) Tripodal naphthalimide assembled novel AIE supramolecular fluorescent sensor for rapid and selective detection of picric acid. Dye Pigment 181:108563
18. Parvathy PA, Dheepika R, Abhijnakrishna R et al (2020) Fluorescence quenching of triarylamine functionalized phenanthroline-based probe for detection of picric acid. J Photochem Photobiol A Chem 401:112780

19. Yan N, Song Jiale, Wang Fengyan et al (2019) Pyrenoviologen-based fluorescent sensor for detection of picric acid in aqueous solution. Chinese Chem Lett 30:1984–1988

20. Han Y, Zhao J, Yang H et al (2020) Synthesis of new fluorene compounds for highly selective sensing of picric acid, Fe3+ and L-arginine. J Mol Struct 1217:128395. https://doi.org/10.1016/j.molstruc.2020.128395

21. Roja SS, Shylaja A, Kumar R (2020) Phenothiazine-Tethered 2-Aminopyridine-3-carbonitrile: Fluorescent Turn-Off Chemosensor for Fe3+ Ions and Picric Acid. ChemistrySelect 5:2279–2283. https://doi.org/10.1002/slct.201904425

22. Shylaja A, Rubina SR, Roja SS, Kumar RR (2020) Novel blue emissive dimethylfuran tethered 2-aminopyridine-3-carbonitrile as dual responsive fluorescent chemosensor for Fe 3+ and picric acid in nanomolar detection limit. Dye Pigment 174:108062. https://doi.org/10.1016/j.dyepig.2019.108062

23. Li T, Wang L, Lin S et al (2018) Rational Design and Bioimaging Applications of Highly Specific “Turn-On” Fluorescent Probe for Hypochlorite. Bioconjug Chem 29:2838–2845. https://doi.org/10.1021/acs.bioconjchem.8b00430

24. Kundu BK, Pragti Reena et al (2019) Mechanistic and thermodynamic aspects of a pyrene-based fluorescent probe to detect picric acid. New J Chem 43:11483–11492. https://doi.org/10.1039/c9nj02342a

25. He W, Liu Z (2016) A fluorescent sensor for Cu2+ and Fe3+-based on multiple mechanisms. RSC Adv 6:59073–59080. https://doi.org/10.1039/c6ra09535f

26. Ma Y, Luo W, Quinn PJ et al (2004) Design, Synthesis, Physicochemical Properties, and Evaluation of Novel Iron Chelators with Fluorescent Sensors. J Med Chem 47:6349–6362

27. Aydin D, Nihan S, Elmas K et al (2021) An ultrasensitive "OFF – ON" fluorogenic sensor based on thiazole derivative for Zn 2+ : Food supplement, water and bio – imaging applications. J Photochem Photobiol, A Chem 419:113459

28. Nihan S, Elmas K, Karagoz A et al (2021) Fabrication and sensing properties of phenolphthalein based colorimetric and turn – on fluorogenic probe for CO 3 2- detection and its living – cell imaging application. Talanta 226:122166. https://doi.org/10.1016/j.talanta.2021.122166

29. Nihan S, Elmas K, Dinckan S et al (2021) A rhodamine based nanosensor platform for Hg 2 + sensing in near – perfect aqueous medium : Smartphone, test strip and real sample applications. J Photochem Photobiol, A Chem 421:113521

30. Wang K, Hu X-L, Li X et al (2021) Solvent induced two Cd-MOFs as luminescent sensors for picric acid, Fe3+ and Cr2O72-. J Solid State Chem 298:122128. https://doi.org/10.1016/j.jssc.2021.122128

31. Xu C, Huang H, Ma J et al (2018) Lanthanide(iii) coordination polymers for luminescence detection of Fe(iii) and picric acid. New J Chem 42:15306–15310. https://doi.org/10.1039/C8NJ02546K

32. Liu Y, Liu C, Zhang X et al (2019) Highly selective and sensitive detection of Fe3+, Al3+ and picric acid by a water-stable luminescent MOF. J Solid State Chem 272:1–8. https://doi.org/10.1016/j.jssc.2019.01.017

33. Zhang C, Yan Y, Pan Q et al (2015) A microporous lanthanum metal–organic framework as a bi-functional chemosensor for the detection of picric acid and Fe3+ ions. Dalt Trans 44:13340–13346. https://doi.org/10.1039/C5DT01065A

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