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Research Article

Targeted identification of cyanide and fluoride ions utilizing dansyl-derived fluorescent probes: a deprotonation-driven sensing mechanism

Gonçalo Pedro [a,b], Frederico Duarte [a,b], Igor Lourenço [a], Georgi M. Dobrikov [c,*], Atanas Kurutos [c,d,**], Luz Fernandes [a], Elvira Gaspar [a], Hugo M. Santos [a,b], José Luis Capelo-Martinez [a,b], Elisabete Oliveira [a,b], Carlos Lodeiro [a,b,***]

[a] LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
[b] PROTEOMASS Scientific Society, 2825-466 Costa de Caparica, Portugal
[c] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria
[d] University of Chemical Technology and Metallurgy, 8 St. Kliment Ohridski blvd, 1756 Sofia, Bulgaria

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ABSTRACT

In this study, we present the detection of hazardous cyanide (CN^-) and fluoride (F^-) anions using six dansyl-derived fluorescent probes (**L1–L6**) specifically designed for rapid and highly sensitive detection in organic media. Through a combination of UV–Vis absorption and fluorescence titrations in acetonitrile, all ligands exhibited a distinct and selective "turn-off" fluorescence response upon exposure to CN^- and F^-, while remaining unresponsive to common halides such as Br^- and Cl^-. Quantitative analysis using HypSpec confirmed a consistent 1:1 binding stoichiometry across the series, with **L4** emerging as the top performer, displaying low limits of detection of 2 μM and 4 μM for CN^- and F^-, respectively, and association constants (Log Kass) of 6.37 for CN^- and 5.66 for F^-. NMR and LC–MS titration studies further revealed a deprotonation-based recognition mechanism, with CN^- inducing proton abstraction at sub-stoichiometric levels, while F^- required up to 10 equivalents. The high affinity and rapid responsiveness of these dansyl-based systems establish them as potent fluorescent tools for the non-invasive, real-time monitoring of the toxic anions cyanide and fluoride in organic-based samples.

1. Introduction

Fluorescent molecular probes have garnered significant interest in recent years owing to their exceptional qualities in analytical applications, including life sciences research, biomedical areas, and environmental monitoring [1,2]. These sensors are highly valued for their exceptional sensitivity, rapid response times, and non-invasive detection capabilities [3–5]. Among them, the dansyl fluorophore stands out, offering several key advantages, including high fluorescence quantum yields, a substantial Stokes shift that minimizes the risk of self-absorption, and emission within the visible region [6,7]. Additionally, its sulfonyl group allows for synthetic versatility, enabling simple incorporation into diverse molecular structures and sensing systems. This structural adaptability facilitates the design of highly selective probes, allowing for precise detection of target analytes, reinforcing their relevance in bioanalytical chemistry and environmental monitoring [3–5].

The detection of anions in aqueous and organic media has become increasingly relevant in the aforementioned fields. In particular, cyanide (CN^-) and fluoride (F^-) have garnered significant attention due to their profound impact on human health and the environment. Cyanide, a potent toxin that disrupts cellular respiration, poses severe risks to both human life and ecosystems [6]. Conversely, while fluoride is beneficial in controlled amounts for dental health, excessive exposure can lead to adverse effects such as dental and skeletal fluorosis [7]. Moreover, cyanide and fluoride share key characteristics, including high basicity,

* Corresponding author.
** Corresponding author at: Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 9, 1113 Sofia, Bulgaria.
*** Corresponding author at: LAQV-REQUIMTE, Chemistry Department, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.
E-mail addresses: Georgi.Dobrikov@orgchm.bas.bg (G.M. Dobrikov), Atanas.Kurutos@orgchm.bas.bg (A. Kurutos), cle@fct.unl.pt (C. Lodeiro).

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which leads to deprotonation, as well as a strong affinity for Lewis acids [8]. Due to these similarities, some detection systems exhibit low selectivity, leading to optical responses to both F^- and CN^- in the same sensor [9,10]. As a result, the development of highly selective and sensitive chemosensors for these anions remains a critical area of research.

In light of the ongoing research for CN^- and F^- sensing probes, dansyl-derived compounds have been reported in the literature for specific binding of cyanide [11,12] and fluoride ions [13,14]. Recently, our group reported a novel dual chromophoric dansyl-acridine conjugate which was effective as a sensor for cyanide ions, operating through an acid-base anion sensing mechanism, where CN^- acts as a base. The system displayed altered photophysical properties in the presence of CN^-, while showing no significant response to other anions like F^-, Br^- and Cl^-. This interaction led to a "turn-on" effect in emission intensity and an increase in quantum yield to 29 %. Additionally, the authors thoroughly characterized the resulting species by calculating the stability constant, determining a log K_{ass} value of 4.23 [12]. Similarly, *Eunhye Jeong* et al. developed an ensemble system that combined an imidazolium-bearing dansyl-derived probe with a dicynovinyl substrate. Unlike traditional sensors, this system leverages the synergistic interaction between the two components to achieve selective and sensitive "turn-on" fluorescence detection of cyanide ions. With this system, the authors reported the formation of a supramolecular assembly upon the introduction of cyanide, explaining the high association constants achieved ($2.38 \times 10^8\ M^{-1}$). The system demonstrated exceptional sensitivity with a limit of detection (LOD) of 200 nM (5.2 ppb), making it one of the lowest LODs achieved for cyanide sensing to date [11].

Regarding fluoride ion detection, *Mongkholkaew* et al. developed a biphenolic-dansyl derivative that exhibited both colorimetric and fluorescence responses to fluoride ions with high selectivity over other anions. ^1H NMR analysis confirmed a deprotonation-based sensing mechanism, revealing an amide proton deprotonation. The sensor showed an association constant of $6.86 \times 10^5\ M^{-1}$ and a detection limit of 18 μM. Additionally a matrix was developed using a TLC plate and filter paper doped with the sensor, enabling rapid on-site fluoride detection by the naked eye [13]. Using an orcinol-dansyl derivative, *Kwanmuang* et al. designed a selective fluorescence probe for fluoride ion detection, achieving an association constant $4.5 \times 10^4\ M^{-1}$ with a 1:1 stoichiometry. This study revealed that fluoride binding induces deprotonation in the sensor, triggering internal charge transfer (ICT) processes that significantly alter the probe's photophysical properties [15].

To better contextualize the current study, Table 1 summarizes recently reported dansyl-based fluorescent probes for the detection of CN^- and F^- anions. This comparative overview highlights detection limits and sensing mechanisms across various solvent systems, enabling a clearer understanding of the advantages and limitations of current approaches.

Very recently, we have reported the synthesis and metal ion sensing of the six dansyl derivatives (L1 to L6) included in this communication (Fig. 1). All of them have been comprehensively characterized in different solvents, including DMSO, CH_3CN, EtOH, THF and $CHCl_3$ and their integration into low-cost and flexible dye-doped PMMA platforms [16]. To expand the applications, in this manuscript we have extended the investigations on their sensing properties in solution, upon the addition of several anions including Br^-, Cl^-, CN^- and F^-, where a turn-off emission response for CN^- and F^- was observed and elucidated. The studies included spectrophotometric and spectrofluorimetric studies, excited state life time measurements, and the interaction anion-probe by thermodynamic parameters (interaction constants). To complete the studies, compounds **L1** and **L4** have been explored after F^- and CN^- addition by NMR in solution. Furthermore, **L4** and **L6** were also studied by LC–MS analysis to further elucidate their binding profiles with CN^- and F^-.

2. Experimental section

2.1. Materials and methods

Reagents and solvents required for the photophysical experiments: acetonitrile (CH_3CN) (Merck Millipore, Darmstadt, Germany, 99.5 %, CAS 75-05-8); chloroform ($CHCl_3$) (Honeywell, Minneapolis, MN, USA, 99.0–99.4 %, CAS 67-66-3); diemthylsulfoxyde (DMSO) (Honeywell, 99.5 %, CAS 67-68-5); ethanol (EtOH) (Honeywell, 99.9 %, CAS 64-17-5); tetrahydrofuran (THF) (PanReac, Barcelona, Spain, 99.0 %, CAS 109-99-9); acetone (Honeywell, 99.5 %, 67-64-1); LUDOX® AS-30 colloidal silica (SiO_2, Sigma-Aldrich, 30 wt.% suspension in water, CAS 7631-86-9); Acridine Yellow G (Sigma-Aldrich, St, Louis, MO, USA, CAS 135-49-9); H_2O (Milli-Q ultrapure); Tetrabutylammonium bromide (Sigma-Aldrich, St, Louis, Mo, USA, CAS 1643-19-2); Tetrabutylammonium chlorine (Sigma-Aldrich, St, Louis, Mo, USA, CAS 1112-67-0); Tetrabutylammonium cyanide (Sigma-Aldrich, St, Louis, Mo, USA, CAS 10442-39-4); Tetrabutylammonium fluoride (Sigma-Aldrich, St, Louis, Mo, USA, CAS 22206-57-1).

The absorption spectra were recorded on a JASCO V-650 UV–Vis Spectrophotometer, and the fluorescence emission spectra on a Horiba Jobin-Yvon Scientific Fluoromax-4, using slit widths of 2 nm for every measurement. A correction for the absorbed light was performed when necessary. Lifetime studies were carried out on TemPro, Deltahub Nanoled of Horiba Jobin-Yvon, with a 390 nm Nanoled. All spectroscopic studies were performed using quartz cuvettes with a 10 mm optical path length. All analytical instruments were provided by PROTEOMASS-BIOSCOPE facility.

High-resolution mass spectrometry (HRMS) analyses were carried out at the Laboratory for Biological Mass Spectrometry – Isabel Moura (PROTEOMASS Scientific Society Facility) using an ultra-high-resolution ESI-Qq-TOF Impact HD mass spectrometer (Bruker Daltonics, Bremen, Germany). The compounds were dissolved in acetonitrile to a final concentration of 0.1 μg/mL and introduced by direct infusion into the electrospray ionization (ESI) source, operating in positive ion mode. Data were acquired in Multiple Reaction Monitoring

Table 1
Summary of dansyl-based fluorescent sensors for fluoride and cyanide detection.

Ref.	Probe type/Structure	Target Anion	Solvent	Mechanism	LOD
Jeong et al. 2019 [11]	Dansyl-imidazolium/dicyanovinyl ensemble	CN^-	HEPES: DMSO (2:8)	Supramolecular assembly	200 nM
Duarte et al. [12]	Dansyl–acridine conjugate	CN^-	CH_3CN	Acid–base (acridine deprotonation)	Not reported
Mongkholkaew et al. 2021 [13]	Biphenyl–dansyl derivative	F^-	DMSO	Acid–base (amide deprotonation)	18 μM
Miao et al. 2004 [14]	Peptido-calix[4]arene bearing four dansyl groups	F^-	CH3CN	H-bonding/interactions	Not reported
Kwanmuang et al. 2019 [15]	Orcinol–dansyl derivative	F^-	DMSO	Internal Charge Transfer (ICT) via OH deprotonation	Not reported

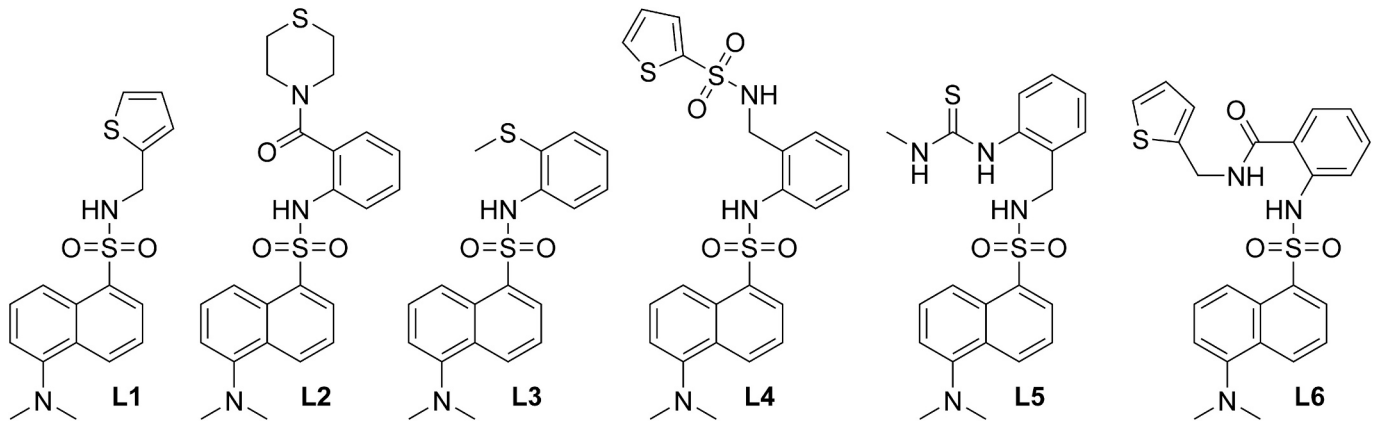

Fig. 1. Molecular structures of the dansyl-derived compounds L1-L6 under investigation.

(MRM) mode, targeting specific precursor ions across the *m/z* range of 80–1300. The collision energy in the collision cell was maintained at 1 eV to minimize fragmentation and preserve intact precursor ions. Instrument settings were as follows: capillary voltage 4500 V, end plate offset −500 V, charging voltage 2000 V, corona current 4000 nA, nebulizer gas pressure 0.4 bar, dry gas flow 4.0 L/min, and drying temperature 180 °C.

2.2. Spectrophotometric and spectrofluorimetric measurements

The spectroscopic characterizations and titrations were performed using stock solutions of the compounds (ca. 10^{-3} M), prepared by dissolving the appropriate amounts of each compound **L1**–**L6** in acetonitrile, chloroform, dimethyl sulfoxide, tetrahydrofuran, and ethanol. The studied solutions were prepared by appropriate dilution of the stock solutions up to 10^{-5}–10^{-6} M. Titrations of compounds **L1**-**L6** were carried out in acetonitrile by the addition of microliter amounts of standard anion solutions of Br^-, Cl^-, CN^- and F^- in acetonitrile. The complexation constants for the interaction of ligands **L1** to **L6** in the presence of CN^- and F^- ions were calculated using the *HypSpec* software [17]. Luminescence quantum yield of compounds **L1**–**L6** was measured using a solution of Acridine Yellow [ϕ = 0.37] [18,19] in ethanol as a standard. All measurements were performed at 298.0 K at the BIOSCOPE-PROTEOMASS facilities, LAQV-REQUIMTE.

2.3. Determination of the detection and quantification limits

Determination of the detection limit (LOD) and quantification limit (LOQ) began with ten independent measurements of a solution containing the selected probe, without the addition of any analyte (referred to as yblank). The LOD and LOQ were then calculated using the following standard formulas [20,21].

- LOD = y_{dl} = yblank +3std, where y_{dl} = signal detection limit and std. = standard deviation.
- LOQ = y_{dl} = yblank +10std, where y_{dl} = signal detection limit and std. = standard deviation.

The final step involved the determination of the minimal detectable and quantified concentration of anion by titration with the ligands.

2.4. NMR studies

The chemical identities of all free ligands and after the additions of tetrabutylammonium cyanide and tetrabutylammonium fluoride respectively, were confirmed by a combination of ^{1}H NMR, ^{13}C NMR, DEPT-135, 2D-COSY, 2D-HSQC, 2D-HMBC, and 2D-NOESY NMR spectroscopic techniques. Utilizing 5 mm tubes on a Bruker Avance II+ 600 and a Bruker AVANCE NEO 400 MHz spectrometers (Institute of Organic Chemistry with Centre of Phytochemistry-Bulgarian Academy of Sciences/NMR Centre), the ^{1}H NMR and ^{13}C NMR spectra were acquired in CD_3CN at 293.0 K, with spectrometer operating frequencies of 600.13/400.13 MHz and 150.92 MHz, respectively. The ^{1}H NMR and ^{13}C NMR spectra were standardized to the tetramethylsilane (TMS) signal, δ = 0.00 ppm. Chemical changes were quantified with a precision of 0.01 ppm (ppm). The coupling constants (*J*) were given with an accuracy of 0.1 Hz. The spin multiplicity in the ^{1}H NMR is represented by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and m = multiplet. MestreNova v. 15.0 from Mestrelab Research S. L. was utilized to process the raw NMR data files.

3. Results and discussion

The sensorial ability of dansyl derivatives **L1**-**L6** towards Br^-, Cl^-, CN^- and F^- ions in acetonitrile was evaluated by titrating the free ligands with small aliquots of the corresponding anions. The absorption and emission spectra were recorded at 298.0 K until stabilization, revealing that all derivatives detect only CN^- and F^- except **L1**, which responds solely to F^- (Fig. 2).

As the spectral behavior was similar between ligands, **L4** was selected as a representative example. Titrations with the other ligands are presented in Supplementary Material (Figs. S2–S11). Fig. 2 displays the absorption and emission changes, respectively, upon incremental addition of CN^- and F^- in acetonitrile. As the concentration of CN^- or F^- increases, the 307 nm (CN^-) and 303 nm (F^-) absorption bands grow, while the 375 nm and 378 nm bands diminish slightly; simultaneously, emission at 520 nm (CN^-) and 531 nm (F^-) is progressively quenched.

To further elucidate these ligand–anion interactions and quantify their binding strengths, we determined the stability constants using the HypSpec program [17]. Furthermore, the determination of the detection and quantification limit parameters of both compounds towards both has been fulfilled. The association constants, LOD and LOQ are included in Table 2. The stability constants indicate the formation of mononuclear species for CN^- and F^- in all cases, with **L4** presenting the highest association constants for F^- and CN^-, with values of Log K_{ass} = 5.66 ± 0.01 and 6.37 ± 0.01, respectively. The lowest detectable and quantifiable amounts were determined for **L2** and **L4** (2.0 μM and 4.0 μM).

To explore solvent effects on sensing behavior, additional titration studies were performed for the ligands with higher binding constants, **L4** and **L6**, in $CHCl_3$, THF, EtOH and DMSO, which yielded consistent results between the two ligands (Figs. S12–S13). In THF, a response similar to that observed in acetonitrile was recorded with full quenching at 2 equivalents. However, in the other solvents, complete emission quenching was only observed upon addition of 10 equivalents of the

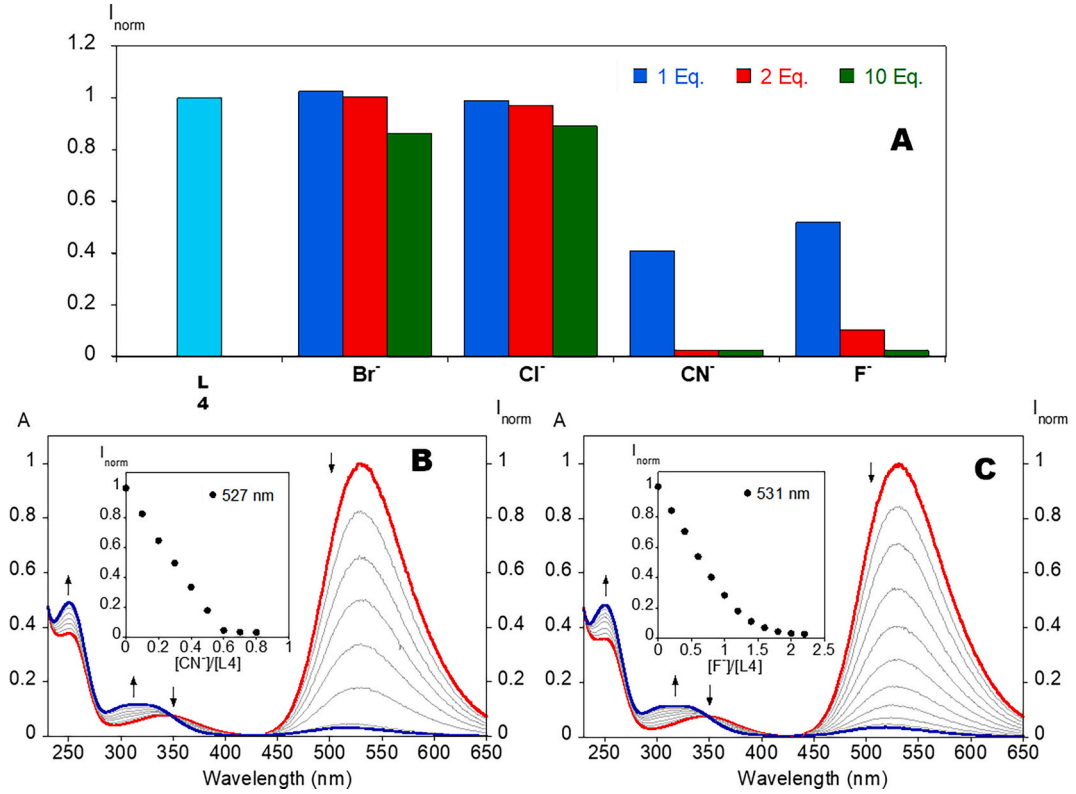

Fig. 2. (A) Maximum emission intensities of **L4** after the addition of 1.00, 2.00, and 10.00 equivalents of Br^-, Cl^-, CN^- and F^-. Spectrophotometric and spectrofluorometric titrations of dansyl derivative **L4** with increased additions of CN^- (B), and F^- (C) in CH_3CN. The inset represents the emission intensity as a function of $[CN^-]/[\mathbf{L4}]$ and $[F^-]/[\mathbf{L4}]$ respectively. [**L4**] = 20 μM, λ_{exc}L4 = 337 nm, T = 298.0 K).

Table 2
Stability association constants and limits of detection and quantification in acetonitrile at room temperature.

Compounds	Anion (A)	Association constants ($LogK_{ass}$)	L: A	LOD (μM)	LOQ (μM)
L1	F^-	3.66 ± 0.01	1:1	80	240
L2	F^-	4.49 ± 0.01	1:1	4	8
	CN^-	4.79 ± 0.01	1:1	2	4
L3	F^-	4.14 ± 0.01	1:1	8	16
	CN^-	4.60 ± 0.01	1:1	3	5
L4	F^-	5.66 ± 0.01	1:1	4	8
	CN^-	6.37 ± 0.01	1:1	2	4
L5	F^-	4.04 ± 0.01	1:1	12	16
	CN^-	4.91 ± 0.01	1:1	4	8
L6	F^-	5.36 ± 0.01	1:1	6	14
	CN^-	5.76 ± 0.02	1:1	4	8

anion.

From **L1** to **L3**, each receptor presents only a single N—H proton, which limits the density of hydrogen-bond donors, resulting in comparably low association constants. In contrast, **L4** to **L6** incorporate two or three N—H sites and are linked via a flexible —CH_2— spacer. This combination not only increases the number of potential binding sites for cyanide and fluoride but also enhances conformational flexibility, facilitating the anion access and thereby increasing their overall binding constants. Comparing **L4** to **L6**, the results suggest that the NH-bearing moiety modulates the acidity of the NH protons, and consequently affects the binding affinity for CN^- and F^-. Sulfonamide **L4** exhibits the highest association constants due to its —SO_2—NH— unit that is strongly electron-withdrawing, lowering the N—H pK_a. In **L6**, the amide group still withdraws electron density and supports hydrogen bonding, but to a lesser degree than the sulfonyl group. By contrast, thiourea **L5** exhibits the lowest association constants among the group. Although its NH protons are intrinsically strong hydrogen-bond donors, in our system they could be prone to intramolecular hydrogen bonding, raising the N—H pK_a and hindering the deprotonation.

The proposed mechanism underlying the detection of these anions involves a deprotonation, where primarily the anions function as a base, deprotonating the amine groups in the molecule. This hypothesis aligns with the observed results, where the constant is consistently higher for the CN^- compared to the F^-, attributed to the cyanide ion being a stronger base. This is further supported by detailed NMR studies of **L4**, where the addition of 1 equivalent of CN^- led to the disappearance of the NH proton signals at 6.08 ppm (amide) and 7.88 ppm (sulfonamide), as well as the conversion of the benzyl CH_2 doublet at 3.91 ppm into a singlet at 3.95 ppm (Fig. 3). In contrast, F^- required up to 10 equivalents to induce similar spectral changes, suggesting a weaker interaction. No new signals appeared in the ^{19}F NMR spectrum, confirming that no covalent C—F bonds are formed, however the NH resonances shift upon addition of CN^- or F^-. To confirm ligand–anion binding, LC–MS analyses of **L4** and **L6** after treatment with CN^- and F^- (Figs. S14–S19) revealed new peaks corresponding exclusively to 1:1 ligand–anion adducts, with no evidence of higher-order species, thus providing evidence of 1:1 complex formation. Together, these results confirm that CN^- and F^- act as bases in a deprotonation-driven sensing mechanism, with CN^- acting more strongly, which is consistent with its higher binding constant in all the ligands.

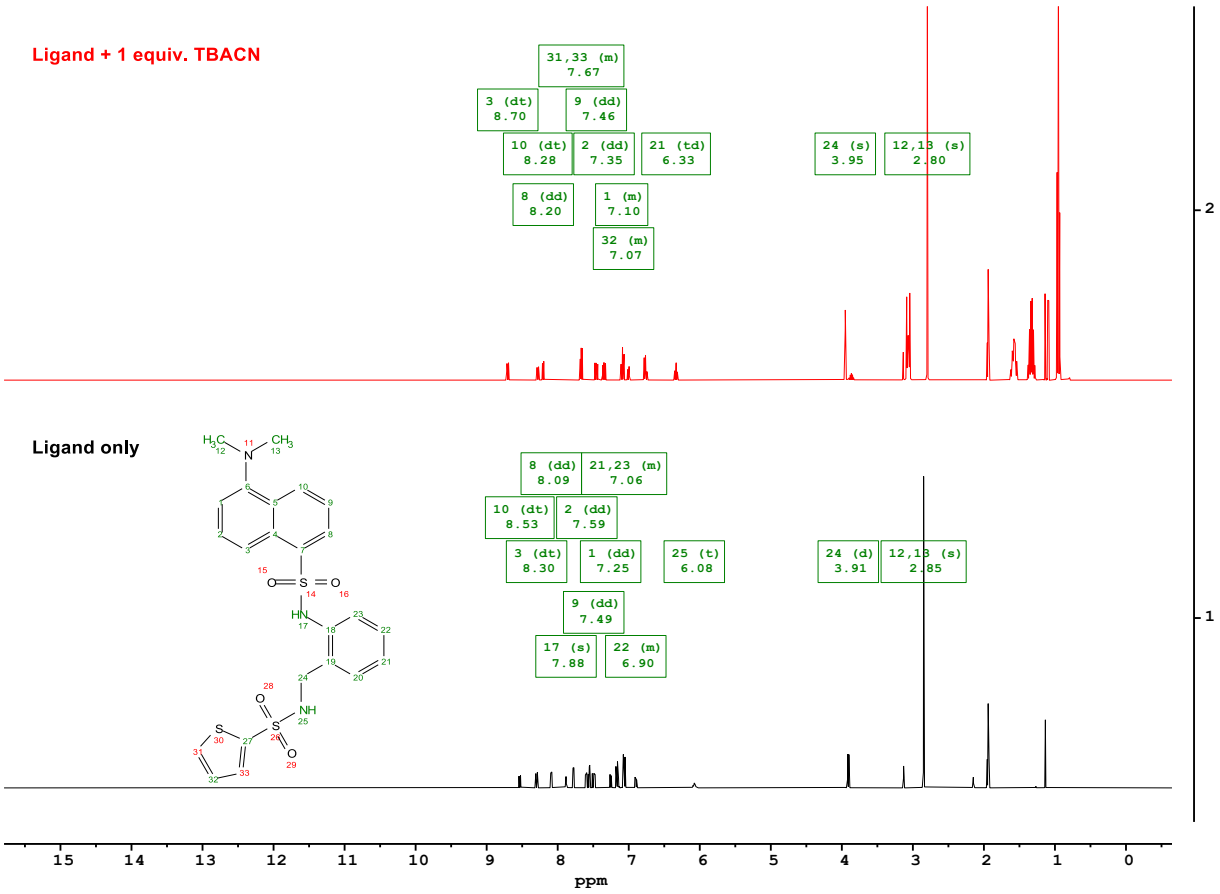

Fig. 3. Stacked ^{1}H NMR spectra of L4 at increasing concentrations of CN^{-} in CD_3CN.

4. Conclusions

The anion-sensing behavior of the dansyl-based ligands **L1–L6** were investigated in acetonitrile towards Br^{-}, Cl^{-}, CN^{-} and F^{-}. The spectroscopic titrations revealed, that all ligands selectively respond to CN^{-} and F^{-}, with **L1** exhibiting exclusive sensitivity to F^{-}. Solvent-variation studies on **L4** and **L6** in THF, EtOH, $CHCl_3$ and DMSO demonstrated behavior consistent to that in acetonitrile. Among the studied derivatives, **L4** exhibits the strongest interaction with both anions, as confirmed by a combination of UV–Vis and fluorescence spectroscopy, stability constant analysis, LOD/LOQ determination, NMR techniques and LC–MS studies. The observed spectral changes along with the NMR and LC–MS evidence support a deprotonation-driven sensing mechanism, where CN^{-} acts as a stronger base than F^{-}, consistent with its higher binding affinity, leading to a 1:1 ligand-anion binding stoichiometry. In comparison with the reported dansyl-based probes summarized in Table 1, **L4** provides a versatile and sensitive system, enabling dual CN^{-}/F^{-} detection with low limits of 2 μM and 4 μM, respectively, through a deprotonation-driven turn-off mechanism, while maintaining consistent performance across five common organic solvents. These findings highlight the potential of dansyl derivatives as selective and responsive fluorescent probes for basic anions in organic media, particularly for cyanide detection.

CRediT authorship contribution statement

Gonçalo Pedro: Writing – review & editing, Visualization, Investigation, Formal analysis. **Frederico Duarte:** Writing – review & editing, Visualization, Investigation. **Igor Lourenço:** Writing – review & editing, Visualization, Investigation. **Georgi M. Dobrikov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis. **Atanas Kurutos:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Funding acquisition, Formal analysis. **Luz Fernandes:** Writing – review & editing, Visualization, Investigation. **Elvira Gaspar:** Writing – review & editing, Visualization, Resources. **Hugo M. Santos:** Writing – review & editing, Visualization, Validation, Resources, Investigation, Formal analysis. **José Luis Capelo-Martinez:** Writing – review & editing, Visualization, Validation, Resources, Funding acquisition. **Elisabete Oliveira:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Carlos Lodeiro:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: "Carlos Lodeiro role as member of the editorial Board had no involvement in the peer review of this article and had no access to information regarding its peer review. Full responsibility for the editorial process for this article was delegated to another journal editor." If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2025.115290.

Data availability

Data will be made available on request.

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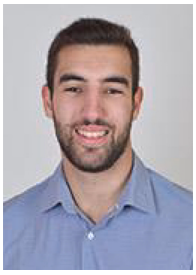
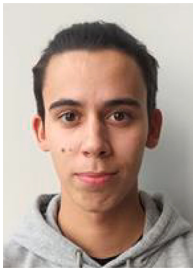


Gonçalo Pedro, PhD student of the Chemistry Programme at the NOVA FCT – Chemistry Department, University NOVA of Lisbon. Graduated in Applied Chemistry in 2023. Is being supervised by Prof. Carlos Lodeiro (NOVAFCT), Prof. Elisabete Oliveira (NOVAFCT) and Prof. Atanas Kurutos (Bulgaria Academy of Science – Bulgaria). GP has published 2 research papers. ORCID: 0009-0005-2399-0232.

Frederico Duarte, Last year PhD student of the Sustainable Chemistry Programme at the LAQV-REQUIMTE, NOVA FCT – Chemistry Department, University NOVA of Lisbon. Graduated in Applied Chemistry in 2019. Is being supervised by Prof. Carlos Lodeiro (NOVAFCT), Prof. Elisabete Oliveira (NOVAFCT) and Prof. Cristian Cuerva (Complutense University of Madrid - Spain). FD has published 18 research papers. ORCID: 0000-0001-5274-7139.

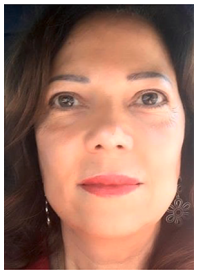


Igor Lourenço, Second year Master Student in the Bioorganic Chemistry Course at the NOVA FCT – Chemistry Department, University NOVA of Lisbon. Graduated in Applied Chemistry in 2024. Is being supervised by Prof. Carlos Lodeiro (NOVAFCT), and Prof. Elisabete Oliveira (NOVAFCT). IL has published 1 research paper. ORCID: 0009-0004-0169-0207.

Georgi M. Dobrikov, Associate Professor at the Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences. GD has published 54 research papers. ORCID: 0000-0003-0437-2162.

Atanas Kurutos, Associate Professor, affiliated with the Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences and University of Chemical Technology and Metallurgy. AK has published 51 research papers. ORCID: 0000-0002-6847-198X.

Luz Fernandes, Research Technician at the LAQV-REQUIMTE Laboratory, got the PhD by the NOVA University Lisbon in 2016. LF has published 15 research papers. ORCID: 0000-0003-0457-1575.



Elvira Gaspar, Assistant Professor at the Chemistry Department, LAQV-REQUIMTE, NOVA FCT, NOVA University Lisbon. EG has published 27 research papers. ORCID: 0000-0001-8906-4809.

Hugo M. Santos, Assistant Researcher at the Chemistry Department, LAQV-REQUIMTE, NOVA FCT, NOVA University Lisbon. HS has published 148 research papers. ORCID: 0000-0002-6032-8679.

José Luis Capelo-Martinez, Full Professor at the Chemistry Department, LAQV-REQUIMTE, NOVA FCT, NOVA University Lisbon. JLC has published 318 research papers. ORCID: 0000-0001-6276-8507.

Elisabete Oliveira, Assistant Researcher at the Chemistry Department, LAQV-REQUIMTE, NOVA FCT, NOVA University Lisbon. EO has published 94 research papers. ORCID: 0000-0002-8339-4820.

Carlos Lodeiro, Full Professor at the Chemistry Department, LAQV-REQUIMTE, NOVA FCT, NOVA University Lisbon. CL has published 338 research papers. ORCID: 0000-0001-5582-5446.