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ARTICLE

Fluorescent phenanthroimidazoles functionalized with heterocyclic spacers: synthesis, optical chemosensory ability and Two-Photon Absorption (TPA) properties

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Three series of fluorescent phenanthroimidazoles bearing heterocyclic spacers were synthesized in moderate to excellent yields and evaluated as optical chemosensors for ions as well as two-photon absorbing chromophores. Interaction of compounds **5**-**7** with anions and cations in acetonitrile and acetonitrile/H_2O (95:5) showed them to be selective receptors for several anions (AcO^-, CN^- and F^-) and cations (Fe^{3+}, Cu^{2+} and Pd^{2+}), with compound **7a** being the most sensitive receptor for Fe^{3+} and Cu^{2+}. On the other hand, compounds **5a**, **7b** and **7c** were the most sensitive receptors for AcO^-, CN^- and F^-. The binding stoichiometry between the receptors and the anions and cations was found to be 1:2 (ligand to anion/metal cation). The binding process was also followed by ^1H NMR titrations. The evaluation of the TPA properties of chosen phenanthroimidazoles **7a**-**c** by the two-photon induced fluorescent method revealed that compound **7c**, which contains a bithienyl spacer, exhibited the highest TPA cross-section (σ_2) value.

Introduction

π-Conjugated heterocyclic systems are versatile organic components for the preparation of several devices with application in nonlinear optics, DSSCs, supramolecular chemistry and others.[1]

During the last decades, experimental and theoretical studies have confirmed that in an organic push-pull system the substitution of a benzene ring by a heterocycle results in improved intramolecular charge transfer (ICT).[2a-p] Due to their electronic nature and low aromaticity, they can act efficiently as π-bridges as well as auxiliary donors (electron-rich heterocycles: *e.g.* thiophene, furan) or as auxiliary acceptors (electron-deficient heterocycles: *e.g.* imidazole, pyrazine). The main advantage of the CT chromophores with a D-π-A arrangement over other organic dyes is the well-defined and tuneable structures and predictable properties. The longest wavelength absorption maxima (CT band) and dipole moment can be modulated by alternating the A (acceptor), D (donor) and π-bridge.[2,3] Moreover, the optical and electronic properties of these heteroaromatic systems depends not only on the electronic nature of the aromatic rings, but also on the location of these heterocycles in the system. In fact, the presence of heterocycles containing N, O and S atoms such as electron rich heterocycles (thiophene, pyrrole, furan), electron deficient azines (pyridine, phenanthroline) and azoles (imidazole, thiazole, oxazole) in a particular system may contribute to enhanced photophysical properties, especially increasing the fluorescence efficiency.[2]

Additionally, inclusion of heterocycles can promote higher polarizability as well as thermal and chemical stabilities,[4] while also constituting a site for further modification (acid/base and coordination properties). For example, heterocyclic systems containing chelating groups have the ability to act as both the recognition unit for anions and cations, as well as the signalling unit, since variation of their absorption/fluorescence properties can happen during the recognition event.[5] Generally, π-conjugated heterocyclic systems increase intramolecular electron delocalisation, enhancing photophysical properties. With careful design, the inclusion of heterocycles can optimize analyte recognition while simultaneously leading to higher fluorescence and, therefore, higher sensitivity.[2]

The design and synthesis of selective chromo-fluorogenic sensors for anions, cations and neutral molecules is an interesting and exciting field of research with many recent developments,[6] such as the possibility of using colorimetric/fluorimetric probes to sense both anions and cations in aqueous solution.[7]

Trivalent metal cations play important roles in biological processes. Therefore, their detection is an interesting topic of research in supramolecular chemistry. For example, iron is the most abundant transition metal in cellular systems. More specifically, Fe^{3+} is an essential element in the growth and

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development of living systems as well as in many biochemical processes at cellular level,[8] and its deficiency is associated with several diseases (anemia, hemochromatosis, diabetes, Parkinson´s and dysfunction of heart, pancreas and liver.[9] Palladium is widely used as catalyst in organic synthesis and the development of novel systems for its easy detection is especially important; a high level of residual palladium (typically 300-2000 ppm) is often found in the resultant products, which can be a health hazard.[10] Finally, the development of optical chemosensors for Cu^{2+} has also received great attention because it is as an essential trace element, playing a critical role as a catalytic cofactor for many metalloenzymes and transcriptional events.[11] An alteration of intracellular copper ion homeostasis can cause oxidative stress and neurodegenerative disorders including Alzheimer's, Parkinson's, Wilson's, Menkes' diseases and amyotrophic lateral sclerosis.[9a-b,12] Selective recognition of anions is also a very active topic of research and among the anions of biological, clinical, environmental, and waste management interest, fluoride is of particular importance due to its established role in dental care and treatment of osteoporosis. Due to the toxicity of the cyanide anion, highly harmful to the environment and human health, there is also an interest to develop new and more selective chemosensors for this analyte.[6a-b,6d-f,7a]

Very recently, several reports on phenanthroimidazole derivatives as chemosensors were found in the literature, but the derivatives reported in the present manuscript differ from the previously reported by using different π-spacers of heterocyclic nature, namely oxygen and sulphur five-membered heterocycles (furan and thiophene). Such heterocycles contribute to the overall photophysical properties and provide additional binding sites for certain ions.[13]

In the last two decades, novel two-photon-active chromophores,[14] which play an important role in the current field of non-linear optical materials, have also attracted a large attention from chemists, material scientists and biophysicists. They are finding applications in 3D optical data storage, optical limiting, microfabrication, upconversion lasing, TPA probes, sensors, fluorescence imaging, two-photon microscopy (TPM), photodynamic therapy, photoactivation and drug delivery.[15]

A large quantity of studies concerning the synthesis, structure-property relationships and theory revealed the importance of certain straightforward structural motifs for TPA-active organic materials such as (D–π–A) dipoles, (D–π–D) and (A–π–A) quadrupoles, octupoles, etc. In general, the most important factors in the optimization of TPA properties are the efficiency of intramolecular charge transfer (ICT), conjugation length, molecular planarity, dimensionality of the charge-transfer network, and the donating and withdrawing abilities of the component moieties.[14] Despite extensive experimental and theoretical efforts, no single unified strategy for the construction of molecules with large TPA cross sections has yet emerged. Therefore, there still remains significant space for structural modification by incorporation of easily delocalizable π-excessive or π-deficient heterocycles (*e.g.* thiophene, furan, imidazole, etc.) which preserves the chemical and photochemical stabilities and additionally allows the fine-tuning of the electro-optical properties with the aim of producing strong fluorescence, an essential prerequisite for certain TPA-based applications.[14,16-18]

Imidazole based chromophores have received increasing attention recently due to their distinctive optical properties and excellent thermal stabilities making them versatile systems for several applications such as optical chemosensors,[17,19] and two-photon absorbing molecules,[17-18] among others.

Motivated by our previous studies,[16c,16g,19] as well as by the work reported by several groups,[16-18] we decided to explore the potential of fluorescent phenanthroimidazole derivatives as novel TPA chromophores and optical chemosensors for the detection of ions with environmental and medicinal interest. The functionalization of the imidazole core at position 4 and 5 by a fused planar phenanthrene moiety as well the introduction of extra UV-absorbing and fluorescent heterocycles at position 2 of the imidazole heterocycle was expected to provide additional binding sites for a variety of ions through the heterocycle donor atoms, as well as improved photophysical properties (*e.g.* TPA properties) and enhanced optical chemosensory ability. It was also intended to assess the influence of the structure in the TPA properties and chemosensing ability of anions and cations.

We report herein the synthesis, characterization and evaluation of the optical (linear and TPA) properties as well as the chemosensory ability of three new series of phenanthroimidazole derivatives **5**-**7** bearing an imidazole electro-deficient heterocycle fused with an emissive phenanthrene moiety in the central core, and different spacers with diverse electronic nature, constituted by thiophene and furan heterocycles.

Results and discussion

Synthesis of phenanthroimidazoles 5-7

Aldehydes **2**-**4** bearing (hetero)aromatic groups with diverse electronic nature (aryl, thienyl, furyl) were used as precursors of phenanthroimidazoles **5**-**7** in order to evaluate the effect of the π-spacer (length, electronic nature and relative position of the heterocyclic moieties) on the optical (linear and TPA) properties and on the chemosensory ability (selectivity and sensitivity). Therefore, compounds **5**-**7** bearing a rigid phenanthroimidazole core and (hetero)aromatic π-bridges linked to position 2 of the imidazole were synthesized in moderate to excellent yields (53-89%, Table 1), through the Radziszewski reaction,[20] of 9,10-phenanthrenedione **1** with formyl precursors **2**-**4** and ammonium acetate in refluxing glacial acetic acid for 8 h, (Scheme 1). Compounds **5a**-**b** have been already reported by other investigators having in mind their preparation using different synthetic methodologies as well the study of their biological activity.[21a-c] Compounds **5**-**7**

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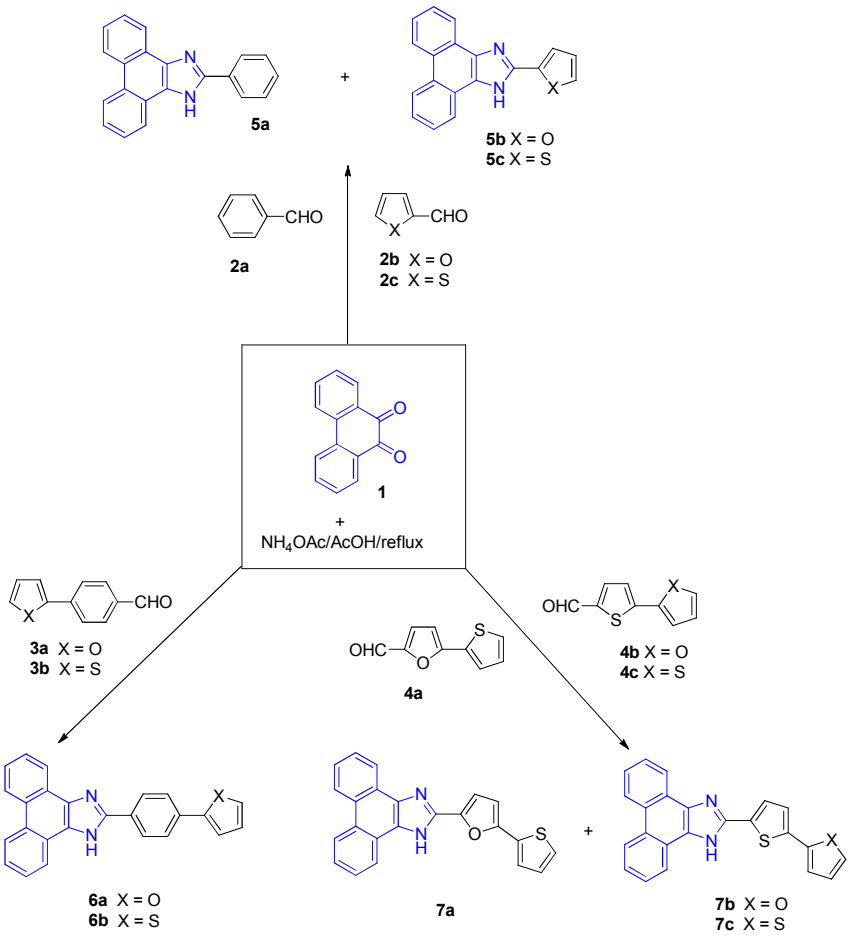
were characterized by the usual spectroscopic techniques (Table 1).



Scheme 1. Synthesis of phenanthroimidazoles **5**-**7**.

The ^{1}H NMR spectra of phenanthroimidazoles **5**-**7** exhibited broad singlets at about δ 13.44-13.67 ppm which were attributed to the NH of the imidazole. A broad correlation was observed between the electronic nature of the π-spacer and the chemical shift of the nitrogen proton of the imidazole ring in compounds **5**-**7**. From the data in Table 1, one may conclude that an increase in the chemical shift of the NH proton in the ^{1}H NMR spectra results from the substitution of a phenyl ring by thiophene or furan heterocycles bearing electronegative S and O heteroatoms (*e.g.* **5a** *versus* **5b** and **5c**) or by the introduction of a second heterocyclic ring at the π-bridge (*e.g.* **5c** *versus* **7b** and **7c**). IR spectroscopy was also used to identify the typical NH absorption bands in compounds **5**-**7** which appeared as sharp bands between 3122-3438 cm^{-1}.

Photophysical properties of phenanthroimidazoles 5-7

The photophysical properties (absorption and emission) of phenanthroimidazoles **5**-**7** were measured in ACN solutions and are presented in Table 1 and Figure 1.

Electronic absorption spectra of imidazole derivatives **5**-**7** in ACN solutions showed an intense lowest energy charge-transfer absorption band in the UV-visible region which can be ascribed to an intramolecular (ICT) transition. The position of this band depended on the π-spacer (length, electronic nature of the aromatic or heteroaromatic rings and relative position of the heterocyclic moieties on the π-bridge). Therefore, substitution of the phenyl ring in **5a** by the electron-rich thiophene heterocycle (*e.g.* **5c**) induced a batochromic shift of 23 nm. On the other hand, modification of the electronic nature as well as increasing the length of the π-spacer by introduction of furan or thiophene induced bathocromic shifts in the range of 28-31 nm, for imidazoles bearing phenylfuran (**6a**; λ_{max} = 340 nm) and phenylthiophene (**6b**; λ_{max} = 343 nm), compared to the phenyl derivative (**5a**; λ_{max} = 312 nm). As expected, substitution of the phenyl ring by a second heterocyclic ring in compounds **6a** and **6b** also induced a bathochromic shift of 41 nm (**7a**) or 42 nm (**7b**), as seen in Table 1 for compound **6b** *versus* **7c**.

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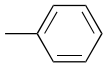
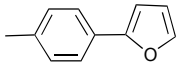
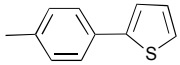
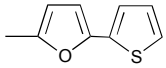
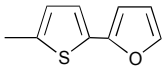
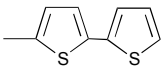
The position of the electron-rich five-membered heterocycles furan and thiophene on the π-bridges influenced the λ_{max} of the absorption band (*e.g* **7a**, λ_{max} = 371 nm *versus* **7b**, λ_{max} = 381 nm).

Table 1. Yields, IR absorption, ^{1}H NMR, UV-visible absorption and fluorescence data for phenanthroimidazoles **5**-**7** in acetonitrile solution.

Cpd.	π-spacer	Yield (%)	IR ν (cm^{-1})[a]	δ_H (ppm)[b]	UV/Vis		Fluorescence		
					λ_{max} (nm)	log ε	λ_{em} (nm)	Φ_F	Stokes' shift (nm)
5a		54	3122	13.44	312	4.7	389	0.38	77
5b		87	3438	13.67	312	4.5	394	0.31	82
5c		82	3236	13.53	335	4.5	396	0.55	61
6a		86	3437	13.48	340	4.4	410	0.90	70
6b		89	3246	13.51	343	4.6	423	0.79	80
7a		53	3438	13.59	371	4.6	427	0.70	56
7b		60	3423	13.63	381	4.6	445	0.41	64
7c		88	3168	13.59	385	4.7	455	0.50	70

[a] For the NH stretching band of the imidazole (recorded in KBr).
[b] For the NH proton of the imidazole (in DMSO-d_6).

Finally, substitution of the furan by a thiophene in the π-spacer also induced bathochromic shifts in the range of 3-23 nm due to the enhancement of their charge-transfer properties. These results are not unexpected, and can be explained by a combination of the bathochromic effect of sulphur and the partial increase of aromatic character of the thiophene heterocycle compared to furan, which allows an increase of conjugation.[22] The relative fluorescence quantum yields for phenanthroimidazoles **5**-**7** were determined by using 10^{-6} M solutions of DPA in ethanol as standard (Φ_F = 0.95).[23] As noted in Table 1, compounds **5**-**7** exhibited good to excellent emissive properties with relative fluorescence quantum yields between 0.31 and 0.90. The planarity of the fused phenanthroimidazoles **5**-**7**, the usually high quantum yields of imidazole derivatives as well as the extent of these π-conjugated systems all contribute to these results.[19,24] The position of λ_{em} depended also on the π-spacer (length, electronic nature of the aromatic or heteroaromatic rings and relative position of the heterocyclic moieties on the π-bridge) following the same trend described above for the absorption properties (Table 1). Therefore, bathochromic shifts in the emission bands were observed by substitution of aryl by heteroaryl groups on the spacers as well as by increase of the π-spacer due to the addition of five-membered heterocycles. Noteworthy is also the effect of the heteroatom of the five membered heterocycles. π-Spacers bearing furan generally had higher relative fluorescence quantum yields compared to the corresponding thiophene π-spacers (e.g. **6a**; Φ_F = 0.90 *versus* **6b**; Φ_F = 0.79 and **7a** Φ_F = 0.70 *versus* **7c**; Φ_F = 0.50). Furan derivatives do not suffer from the heavy atom effect observed in thiophene-based fluorophores, thus, they tend to exhibit stronger luminescence. For example, compound **6a** (0.90) showed a great enhancement of the quantum yield, compared with that of **7b** (0.41) due to the quenching of fluorescence associated with the heavy atom induced spin-orbit coupling by the sulphur atoms, which gives rise to a very efficient intersystem crossing mechanism that lowers the emission.[22,25-26] Compounds **5**-**7** showed moderate to good Stokes' shifts in the range of 56-82 nm.

Having in mind these photophysical properties, derivatives **5**-**7** could be potential candidates as fluorescent chemosensors and TPA chromophores due to the high fluorescence quantum yields, important for maximization of the response in the analysis of very dilute samples.

Two-photon absorption of phenanthroimidazoles 7a-c

Given the high fluorescent quantum yields, the two-photon absorption (TPA) cross-sections (σ_2) of phenanthroimidazole derivatives could be determined by investigating the two-photon induced fluorescence using the well-established method described by Xu and Webb.[27] Rhodamine 590 (Rhodamine 6G) was employed as the reference,[28] for measurements of the TPA properties of the selected imidazoles **7a**-**c**. The TPA spectra were recorded in the 750-850 nm spectral range using ethanol solutions (*ca*. 1.0 × 10^{-4} M) of the chosen phenanthroimidazoles **7a**-**c** (Table 2) and the

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corresponding two-photon absorption cross-sections were found to lie between 1.5 and 5.3 GM.

Figure 1. Acetonitrile solutions of phenanthroimidazoles **5**-**7**: (top) naked-eye colour; (down) visualization under a UV lamp at 365 nm.

A prospective study of the TPA properties of phenanthroimidazoles **7a**-**c** showed that the position of the furan and thiophene on the π-bridge lead to marked differences on the two-photon absorption cross-sections (σ_2) values. Therefore, compound **7b**, in which the thiophene heterocycle is directly linked to the electron-deficient imidazole ring, exhibited an almost 3 times higher σ_2 (4.3 GM) compared to **7a** (σ_2 = 1.5 GM) (Table 2). On the other hand, comparison between phenanthroimidazoles **7b** and **7c** showed that replacing a thiophene heterocycle by a furan also increased the σ_2 value of **7c** compared to **7b**. In both cases the results obtained for σ_2 follow the same trend described for the linear optical (absorption and emission properties) described above.

At first sight it seems strange that the two-photon absorption cross-section for compound **7a** is less than half that for molecules **7b** and **7c** given the very similar chemical structure. However, one point worth keeping in mind is that two-photon absorption is a third order nonlinear effect and within the unsold approximation the second hyperpolarizability is proportional to the fourth moment of the electron distribution in the HOMO state.[29] As molecule **7a** has the furan moiety closed to the imidazole, one expects the extent of the π-electron density to be partially localized around the more central oxygen atom in **7a**, leading to lower values of the higher moments in the π-electron distribution. In contrast, for molecule **7b**, the furan moiety is at the far end, creating a less central π-electron distribution and consequently somewhat greater second hyperpolarizability. In the case of molecule **7c** with two thiophene moieties, one would also expect a wider π-electron distribution.

Spectrophotometric/spectrofluorimetric titrations and chemosensing studies of phenanthroimidazoles 5-7 with anions and metallic cations

The modification of imidazole through the introduction of extra UV-absorbing and fluorescent heterocycles within its structure was expected to provide additional binding sites for a variety of ions through the heterocycle donor atoms, as well as improved photophysical properties for the chemosensing studies.

Furthermore, these modifications provide an opportunity to assess the influence of the structure on the chemosensing ability of anions and cations.

Table 2. Photophysical and two-photon absorption properties of imidazoles **7a**-**c** in ethanol.

Cpd.	π-spacer	λ_{max} (nm)	λ_{em}[a] (nm)	Φ_F	σ_2[b] (GM)
7a		372	426	0.78	1.5
7b		382	444	0.42	4.3
7c		385	455	0.47	5.3

[a] Emission maximum wavelength excited at the single photon absorption maximum.

[b] Two-photon absorption cross-section given in GM at an excitation wavelength of 750 nm, 1 GM = 1 x 10^{-50} cm^4 s $photon^{-1}$.

Several studies have demonstrated that imidazole derivatives are good binding groups for the coordination of anions.[19,30] In fact, the coordination ability of the imidazole group depends on the acidity of the NH proton that can be modulated,[31] for example by the presence in the structure of easily delocalizable heteroaromatic rings, such as thiophene and furan. On the other hand, the presence in the imidazole nucleus of two nitrogen atoms, one of them with a free electron pair, also supports the coordination of metal cations by this heterocycle.[19,32]

Therefore, we decided to design and synthesize several phenanthromidazoles bearing different π-spacers (constituted by furan and thiophene heterocycles) in order to modulate their photophysical properties having in mind also their application as optical chemosensors for specific anions and metal cations.

The interaction of phenanthroimidazoles **5**-**7** with anions (AcO^-, F^-, Cl^-, Br^-, CN^-, NO_3^-, BzO^-, $H_2PO_4^-$, HSO_4^-) and metal cations (Cu^{2+}, Cd^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+}) with biological, environmental and analytical relevance, was evaluated through spectrophotometric and spectrofluorimetric titrations in ACN and ACN/H_2O (95:5) solutions.

A preliminary test was carried out by addition of up to 50 equiv of each ion to the solutions of compounds **5**-**7**. Noticeable changes occurred in the colour of the solutions (from pale yellow to dark yellow) for compound **7c** upon interaction with CN^- and for **7b** with CN^- and F^- anions. Subsequent spectrophotometric titrations of phenanthroimidazoles **7b** and **7c** in acetonitrile with CN^- and F^- revealed a trend in the UV-vis spectra: the intensity of longest wavelength absorption band (at 380 and 386 nm, respectively) decreased progressively upon addition of CN^- and F^- (**7b**) or upon addition of CN^- (**7c**), with the simultaneous growth of a new red-shifted absorption band located at 404/405 and 417 nm, respectively. Simultaneously, there was also the appearance of a new absorption band located at about 300 nm for compounds **7b** and **7c** after the interaction with CN^- and F^- (Figure 2 and Figures S1-S2 in supplementary information). This observation can be

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explained by the interaction of the anions with the electron-withdrawing part of the molecule.

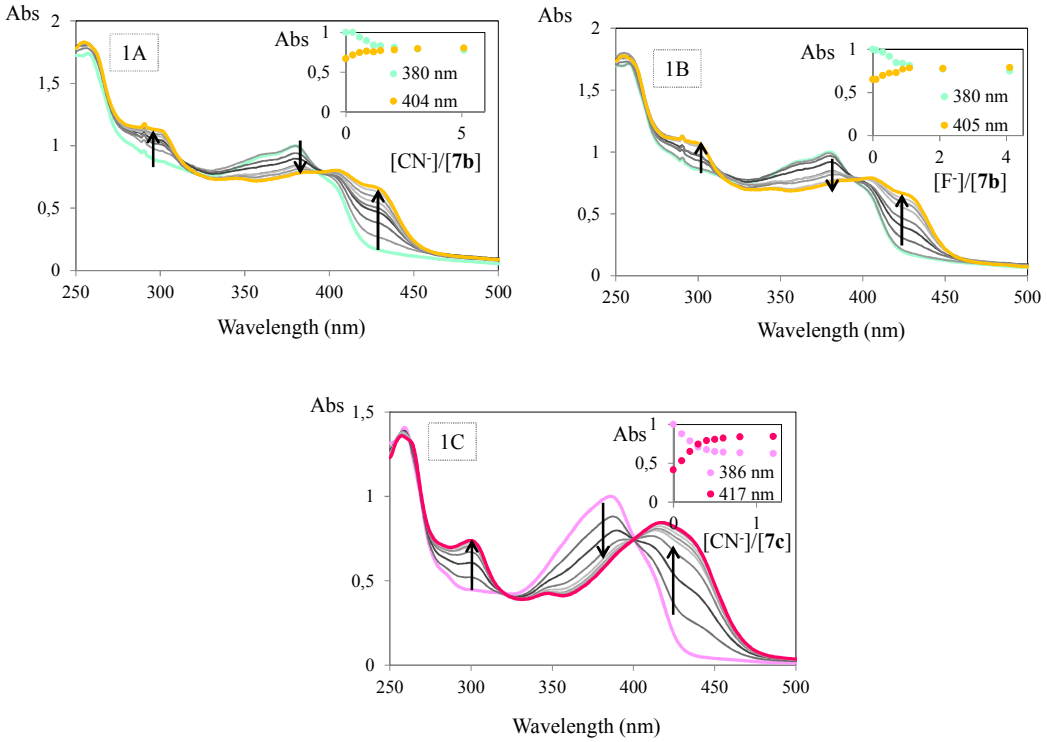

Figure 2. Spectrophotometric titrations of **7b** (1A, 1B) and **7c** (1C) with addition of increasing amounts of CN^- and F^- in ACN. The inset represents the normalized absorption a 380 and 404 nm (1A); 380 and 405 nm (1B) and 386 and 417 nm (1C) ([**7b**-**c**] = $1x10^{-5}$ M, T = 298 K).

Regarding the fluorimetric response, a preliminary test was also carried out by addition of up to 50 equiv of each ion to the acetonitrile solutions of compounds **5**-**7**. Noticeable changes occurred in the fluorescence of the solutions for compounds **5**-**7** upon interaction with several anions (AcO^-, F^-, CN^-) and cations (Cu^{2+}, Pd^{2+} and Fe^{3+}). Consequently, spectrofluorimetric titrations of phenanthroimidazoles **5**-**7** in acetonitrile with the ions described above were also performed. Spectrofluorimetric titrations of phenanthroimidazoles **5**-**7** in acetonitrile with CN^- and F^- and AcO^- revealed the same trend in the emission spectra: the intensity of longest wavelength emission band (between 389 and 455 nm) decreased progressively upon addition of CN^- (**5b**-**c**, **6a** and **7a**-**c**) or upon addition of F^- (**5**-**7**), with the simultaneous growth of a new red-shifted emission band. In Figure 3, representative examples are shown, namely the spectrofluorimetric titrations of phenanthroimidazole **7c** with F^- and CN^- in which the intensity of the emission band centred at 456 nm was reduced (a chelation enhanced quenching, CHEQ effect), and a new red-shifted emission band appeared at 516 nm due to a fluorescence enhancement upon chelation effect (CHEF). An isoemissive point was also observed at 493 nm. In the case of F^-, 2.8 equivalents were necessary to achieve a plateau, while for CN^- 3.2 equivalents were required.

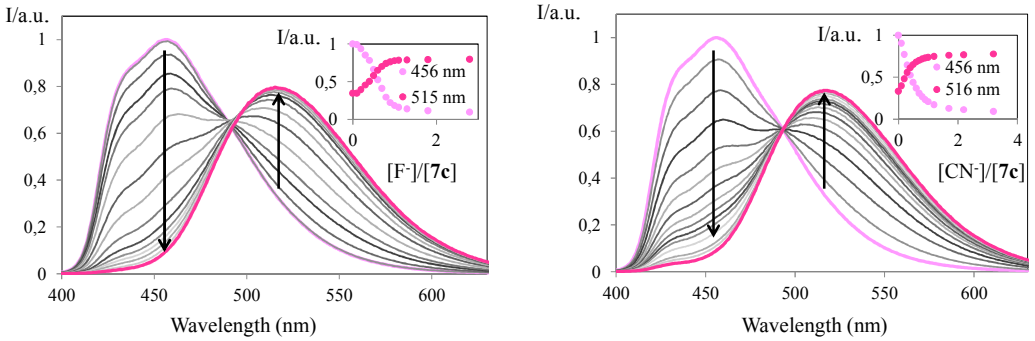

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Figure 3. Spectrofluorimetric titrations of **7c** with addition of increasing amounts of CN^- (right) and F^- (left) in ACN. The inset represents the normalized emission ([**7c**] = 1x10^{-5} M, T = 298 K).

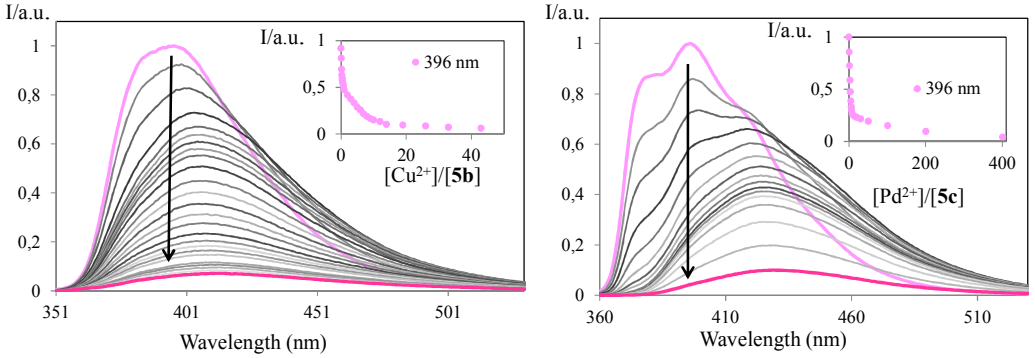

Figure 4. Spectrofluorimetric titrations of **5b** and **5c** with addition of increasing amounts of Cu^{2+} and Pd^{2+}, respectively, in ACN. The inset represents the normalized emission ([**5b**] = [**5c**] = 1x10^{-5} M, T = 298 K).

Comparison between the spectrofluorometric titrations of compounds **5**-**7** showed that the only difference was the number of equivalents necessary to quench at least 90% of the initial fluorescence intensity of each phenanthroimidazole solution. The number of equivalents for each anion was as follows: CN^-: 13.3 equiv. for **5b**, 23.6 equiv. for **5c**, 53 equiv. for **6a**; 5.5 equiv. for **7a**; 3.5 equiv. for **7b** and 3.2 equiv. for **7c**; F^-: 10 equiv. for **5a**, 3.1 equiv. for **5b**, 3 equiv. for **5c**, 42 equiv. for **6a**; 3 equiv. for **6b**, 2.3 equiv. for **7a**; 1.1 equiv. for **7b** and 2.8 equiv. for **7c**; AcO^-: 86 equiv. for **5a**, 310 equiv. for **5b**; 123 equiv. for **5c**; 120 equiv. for **7a** and 92 equiv. for **7c**. Therefore, the most sensitive receptors for CN^-, F^- and AcO^- were imidazoles **7c** (3.2 equiv.), **7b** (1.1 equiv.) and **5a** (86 equiv.) respectively, due to the smaller number of equivalents need to achieve 90% of fluorescence quenching.

Due to the obvious changes that occurred also in the fluorescence of the solutions of compounds **5**-**7** upon interaction with Cu^{2+}, Pd^{2+} and Fe^{3+}, spectrofluorimetric titrations of phenanthroimidazoles **5**-**7** in acetonitrile with these cations were also performed. They revealed the same trend in the emission spectra: a progressive quenching of longest wavelength emission band, CHEQ effect, between 389 and 455 nm accompanied by a small red-shift of the emission band.

In the spectrofluorimetric titrations with Fe^{3+}, a strong decrease of the fluorescence intensity with an almost complete fluorescence quenching was observed for all phenanthroimidazoles except for **7b**. Imidazole **5c** exhibited a total quenching in the fluorescence in the presence of Pd^{2+}, whereas compounds **5b** and **7a**-**c** exhibited the same behaviour in the presence of Cu^{2+} (Figure 4). The quenching effect in the presence of Cu^{2+} can be attributed to an energy transfer quenching of the π* emissive state through low-lying metal-centered unfilled *d*-orbitals.[33] This result suggests the involvement of the metal ion with donor atoms, the N from the imidazole and the O or S from the pendant furan or thiophene.

Once again, comparison between the spectrofluorometric titrations of compounds **5**-**7** showed that the only difference was the number of equivalents of cations necessary to quench the initial fluorescence intensity of each phenanthroimidazole solution. The number of equivalents for each cation was as follows: Fe^{3+}: 112 equiv. for **5a**, 89 equiv. for **5b**, 199 equiv. for **5c**, 36 equiv. for **6a**; 65 equiv. for **6b**, 14 equiv. for **7a**; 56 equiv. for **7c**; for Cu^{2+}: 63 equiv. for **5b**; 3.7 equiv. for **7a**; 5.6 equiv. for **7b**, 44.2 equiv. for **7c**, and for Pd^{2+}: 401 equiv for **5c**. Therefore, imidazole **7a** was the most sensitive receptor for Fe^{3+} (14 equiv.) and Cu^{2+} (3.7 equiv.) in ACN solutions due to the smaller number of equivalents needed to achieve 90% of quenching of fluorescence. In Figure 4, representative examples of the spectrofluorimetric titrations of phenanthroimidazoles **5b** with Cu^{2+} and **5c** with Pd^{2+} are shown. The drastic effect of cation complexation is evident in the band centred at the wavelength of maximum emission at 396 nm for both compounds.

Having in mind the practical applications of compounds **5**-**7** in aqueous media, the chemosensory ability was also evaluated in mixtures of acetonitrile/H_2O (95:5). A strong decrease of the fluorescence intensity was observed for all derivatives in the spectrofluorimetric titrations with Fe^{3+}, Cu^{2+} and Pd^{2+} cations with an almost complete fluorescence quenching, leading to the selective fluorescent detection of Fe^{3+} for compounds **5a**, **6a** and **6b** and Cu^{2+} for derivative **7b**. However, a higher number of equivalents were necessary in order to obtain 90% quenching of fluorescence compared to the study in acetonitrile solutions. Thus, the number of equivalents for each cation was as follows: for Fe^{3+}: 139 equiv. for **5a**, 184 equiv. for **5b**, 254 equiv. for **5c**, 58 equiv. for **6a**, 267 equiv. for **6b**, 333 equiv. for **7a**; for Cu^{2+}: 140 equiv. for **5b**, 3 equiv. for **7a**, 307 equiv. for **7b**, 70 equiv. for **7c**; and for Pd^{2+}: 361 equiv for **5c** (see also Figures S3-S9 in supplementary information).

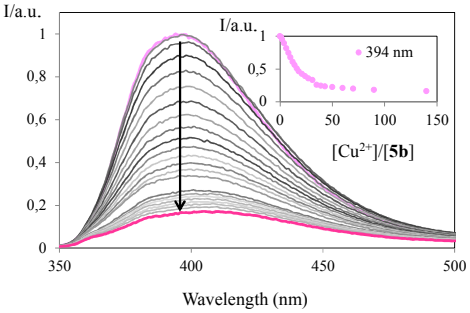

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Figure 5. Spectrofluorimetric titration of **5b** with addition of increasing amounts of Cu^{2+} in ACN/H_2O (95:5). The inset represents the normalized emission ([**5b**] = 1x10^{-5} M, T = 298 K).

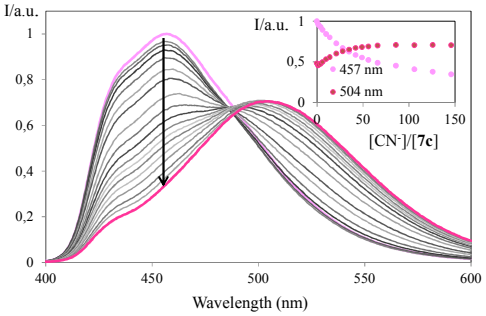

Figure 6. Spectrofluorimetric titration of **7c** with addition of increasing amounts of CN^- in ACN/H_2O (95:5). The inset represents the normalized emission ([**7c**] = 1x10^{-5} M, T = 298 K).

Overall, imidazole **7a** was the most sensitive towards Fe^{3+} (3 equiv.) and Cu^{2+} (58 equiv.) in acetonitrile/H_2O. Figure 5 shows a representative example of the spectrofluorimetric titration of phenanthroimidazole **5b** with Cu^{2+} where the drastic effect of cation complexation is evident in the band centered at the wavelength of maximum emission at 394 nm.

The spectrofluorimetric titrations of compounds **5**-**7** in acetonitrile/H_2O (95:5) resulted in a marked loss of sensitivity. Therefore, only compounds **5b**, **7a** and **7c** exhibited noticeable changes, upon interaction with cyanide, following the same trend observed in acetonitrile solutions, namely a strong decrease of fluorescence intensity (CHEQ effect) with the simultaneous growth of a new red-shifted emission band. The spectrofluorimetric titration of phenanthroimidazole **7c** is shown in Figure 6, as a representative example where the effect of the cyanide interaction is evident in the band centred at the wavelength of maximum emission at 457 nm. A strong quenching of the fluorescence followed by the formation of a new red-shifted band and a isoemissive point at about 490 nm, indicating the presence of two emissive species in solution.

^{1}H NMR titrations of phenanthroimidazoles with selected anions/cations

The sensory behaviour observed with the spectrophotometric and spectrofluorimetric titrations was also complemented by performing ^{1}H NMR titrations for compound **7a** with F^- and Cu^{2+}, as representative examples, in order to gain further insight into the binding mode between the receptor and the cations and anions under study. Due to the limited solubility of compound **7a** in deuterated acetonitrile, the titrations were carried out in DMSO-d_6 (Figure 7).

In DMSO-d_6, the signal of the imidazole NH appeared downfield at 13.6 ppm, which was further shifted downfield to 16.0 ppm (Δδ ~ 2.4 ppm) upon addition of up to 7.0 equiv. of fluoride, thus suggesting that the interaction is occurring at this site. The aromatic protons exhibited a slight upfield shift upon continued addition of fluoride until 7 equiv. This shielding effect is probably due the formation of the charge transfer complex between the anion and the receptor, resulting in an increase in the electron density in the system (Figure 7).

Titration of the same compound with Cu^{2+} resulted in the concomitant broadening of the NH signal at 13.6 ppm and the loss of resolution of the signals related to the aromatic protons, accompanied by a very subtle upfield shift. These findings can also corroborate the formation of the already mentioned charge transfer complex.

The binding stoichiometry of compounds **5**-**7** with selected anions/cations and the binding affinity were calculated by HypSpec software from the spectrofluorimetric titrations in acetonitrile and aqueous acetonitrile, and a 1:2 ligand:metal cation/anion stoichiometry is suggested (Table 3). The 1:2 stoichiometry of the complex formed between phenanthroimidazoles **5**-**7** and Fe^{3+} was also confirmed by spectrofluorimetry by the method of continuous variation for the 1:2 binding mode of **5c** with Fe^{3+}.

Table 3. Logarithm of association constants (K_{ass}) for the interaction of phenanthroimidazoles **5**-**7** with several anions/cations in acetonitrile (L:M or L:A stoichiometry suggested from HypSpec is 1:2).

Compound	Ion	log K_{ass}
5a	Fe^{3+}	12.1736±0.0451
	F^-	12.4992±0.1161
	AcO^-	13.9239±0.1191
5b	Fe^{3+}	12.0838±0.0258
	Cu^{2+}	13.1719±0.1503
	CN^-	12.5790±0.1187
	F^-	12.2937±0.1310
	AcO^-	13.3805±0.0635
5c	Fe^{3+}	12.2449±0.0306
	Pd^{2+}	12.6432±0.0313
	CN^-	12.3270±0.1243
	F^-	11.8473±0.1137
	AcO^-	12.9158±0.0431
6a	Fe^{3+}	12.9423±0.1326
	F^-	13.0154±0.1222
	CN^-	13.2450±0.2381
6b	Fe^{3+}	13.0096±0.0371
	F^-	12.4786±0.1660
7a	Fe^{3+}	12.1051±0.0355
	Cu^{2+}	12.1870±0.1071
	CN^-	12.6623±0.1145
	F^-	12.1950±0.1366
	AcO^-	14.1572±0.1229
7b	Cu^{2+}	12.4124±0.2351
	F^-	11.5732±0.1265
	CN^-	11.9672±0.1315
7c	Fe^{3+}	11.7641±0.0437
	Cu^{2+}	12.8135±0.1757
	CN^-	12.5009±0.1308
	F^-	12.4308±0.1287

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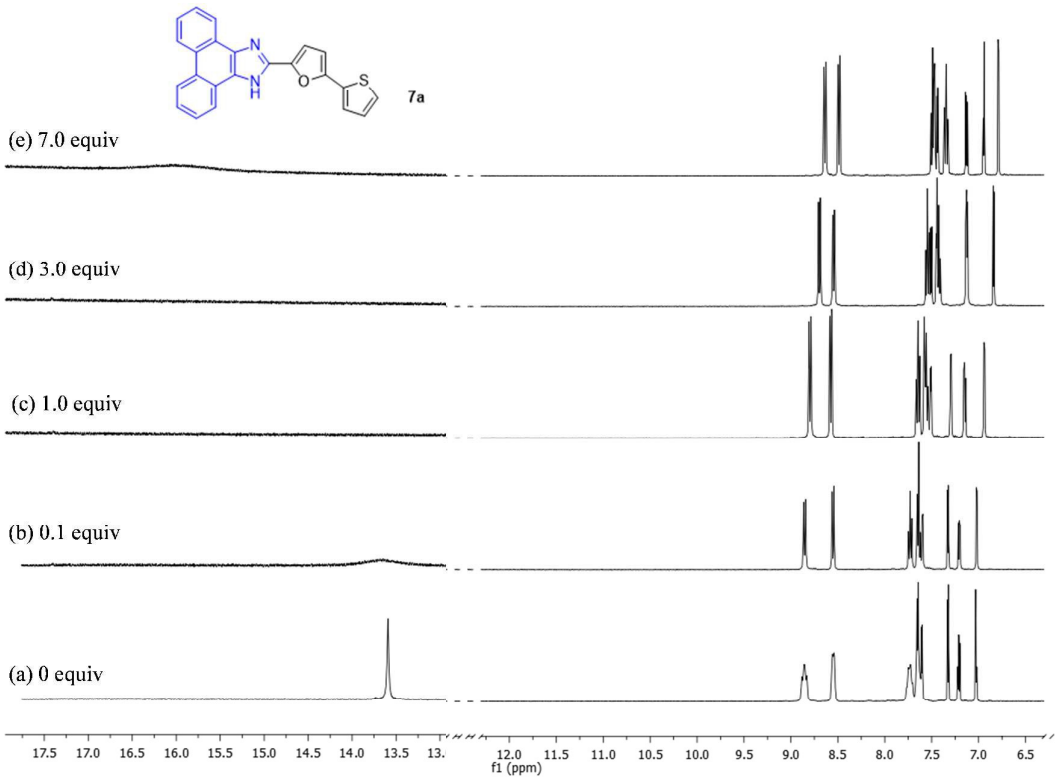

Figure 7. Partial ^{1}H NMR spectra of phenanthroimidazole **7a** (2.2 x 10^{-2} M) in DMSO-d_6 in the: (a) absence and presence of (b) 0.1, (c) 1.0, (d) 3.0 and (e) 7.0 equivalents of F^-.

Tentative structures of the complexes between compound **7a** (as representative example of the ligand) and F^- (as representative of anions), Cu^{2+} and Fe^{3+} (as representatives of cations) were included in the supplementary material (Figure S10 in supplementary information). The imidazole nucleus is quite versatile and may be involved in the complex formation either through hydrogen bonding of the NH to the fluoride or by coordination of the N with the lone electron pair to the metal cation (with a cooperative effect of the other heteroatoms in the structure).

Conclusions

The synthesis of a series of fluorescent phenanthroimidazoles bearing heterocyclic spacers (furan and thiophene) was achieved, having in mind their study as optical chemosensors for ions and as two-photon absorbing chromophores. The photophysical properties (absorption and fluorescence) were evaluated and the assessment of the TPA properties of chosen phenanthroimidazoles **7a**-**c** by the two-photon induced fluorescent method revealed that compound **7c** (containing a bithienyl spacer) exhibited the highest TPA cross-section (σ_2) value. The interaction of the synthesised compounds with anions and cations was explored in acetonitrile and acetonitrile/H_2O (95:5, v/v) solutions which revealed that higher sensitivity was achieved in acetonitrile solutions with some of the title compounds being selective and sensitive to AcO^-, CN^- and F^- and for Fe^{3+}, Cu^{2+} and Pd^{2+}. Phenanthroimidazole **7a** bearing a thiophenylfuranyl spacer was found to be the most sensitive receptor for Fe^{3+} and Cu^{2+}, while compounds **5a**, **7b** and **7c** were the most sensitive receptors for AcO^-, CN^- and F^-. The binding stoichiometry between the receptors and the anions and metal cations was calculated and found to be 1:2 (L:M or L:A). The binding process was also followed by ^{1}H NMR titration.

Experimental

Synthesis and characterization general

Reaction progress was monitored by thin layer chromatography (0.25 mm thick pre-coated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was carried out by silica gel column chromatography (Merck Kieselgel 60; 230-400 mesh). NMR spectra were obtained on a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H and 100.6 MHz for ^{13}C using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS and given in ppm). Mps were determined on a Gallenkamp apparatus. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. Mass spectrometry analyses were performed at the "C.A.C.T.I. -Unidad de Espectrometria de Masas" at the University of Vigo, Spain. All commercially available reagents were used as received. Dione **1** and aldehydes **2**-**3**, **4c** were commercially

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available and the syntheses of precursor aldehydes **4a**-**b** have been reported elsewhere.[32]

General procedure for synthesis of phenanthroimidazoles 5-7.
9,10-Phenanthrenedione **1** (1 mmol), heterocyclic aldehydes **2**-**4** (1 mmol), and NH_4OAc (20 mmol) were dissolved in glacial acetic acid (5 mL), followed by stirring and heating at reflux for 8 h. The mixture was then cooled to room temperature, ethyl acetate was added (15 mL) and washed with water (3 x 10 mL). After drying the organic fraction with anhydrous $MgSO_4$, the solution was filtered and the solvent was evaporated to dryness. Recrystallization from acetone/petroleum ether (40-60^{o}C) afforded the pure imidazole derivatives **5**-**7**.

2-Phenyl-1H-phenanthro[9,10-d]imidazole, 5a.[21a-c] Off white solid (115 mg, 54%). Mp: 316.6-317.3 ^{o}C. IR (KBr): ν = 3122, 3054, 1940, 1902, 1704, 1661, 1612, 1544, 1518, 1472, 1456, 1382, 1353, 1326, 1230, 1157, 1104, 1037, 750 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.50 (dt, J = 8.4 and 2.0 Hz, 1H, H-4'), 7.57 – 7.65 (m, 4H, H-3', H-5', H-5 and H-10), 7.70 – 7.77 (m, 2H, H-6 and H-9), 8.31 (dd, J = 7.2 and 1.2 Hz, 2H, H-2' and H-6'), 8.55-8.61 (m, 2H, H-4 and H-11), 8.82 – 8.87 (m, 2H, H-7 and H-8), 13.45 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 121.87, 121.97, 122.40, 123.71, 124.07, 125.12, 125.33, 126.12, 126.97, 127.04, 127.13, 127.51, 127.65, 127.67, 128.91, 129.21, 130.36, 136.96, 149.08 ppm.

2-(Furan-2'-yl)-1H-phenanthro[9,10-d]imidazole, **5b.**[21c] Light brown solid (205 mg, 87%). Mp: 275.5-275.8 ^{o}C. IR (KBr): ν = 3438, 3222, 3072, 1950, 1773, 1692, 1614, 1538, 1514, 1453, 1409, 1368, 1276, 1233, 1170, 1113, 1040, 1018, 754, 724 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 6.76 (dd, J = 3.2 and 1.6 Hz, 1H, H-4'), 7.23 (dd, J = 3.2 and 0.8 Hz, 1H, H-3'), 7.60 – 7.64 (m, 2H, H-5 and H-10), 7.69 – 7.72 (m, 2H, H-6 and H-9), 7.96 (dd, J = 1.6 and 0.8 Hz, 1H, H-5'), 8.53 (dd, J = 7.6 and 0.8 Hz, 2H, H-4 and H-11), 8.81 – 8.86 (m, 2H, H-7 and H-8), 13.67 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 109.30, 112.32, 121.86, 121.97, 122.30, 123.71, 124.04, 125.21, 125.38, 126.82, 126.94, 127.11, 127.15, 127.58, 127.71, 136.85, 141.63, 143.98, 145.80 ppm. MS (EI) *m/z* (%): 284 ([M]$^+$,100), 256 (12), 255 (33). HRMS: (EI) *m/z* (%) for $C_{19}H_{12}ON_2$; calcd 284.0950; found 284.0953.

2-(Thiophen-2'-yl)-1H-phenanthro[9,10-d]imidazole, **5c.** Beige solid (175 mg, 82%). Mp: 302.1-302.9 ^{o}C. IR (KBr): ν = 3236, 3073, 1948, 1683, 1614, 1564, 1487, 1456, 1411, 1363, 1294, 1239, 1193, 1166, 1123, 1077, 1041, 854, 714, 699 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.26 – 7.28 (m, 1H, H-4'), 7.59 – 7.65 (m, 2H, H-5 and H-10), 7.69 - 7.76 (m, 3H, H-5', H-6 and H-9), 7.92 (dd, J = 3.6 and 1.2 Hz, 1H, H-3'), 8.45 (d, J = 7.6 Hz, 1H, H-4), 8.50 (dd, J = 7.6 and 0.8 Hz, 1H, H-11), 8.81 – 8.87 (m, 2H, H-7 and H-8), 13.53 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 121.78, 121.88, 122.17, 123.72, 124.12, 125.17, 125.37, 125.78, 126.67, 127.08, 127.16, 127.31, 127.49, 127.69, 127.79, 128.21, 133.90, 136.73, 144.89 ppm. MS (EI) *m/z* (%): 300 ([M]$^+$, 100), 190 (11). HRMS: (EI) *m/z* (%) for $C_{19}H_{12}N_2S$; calcd 300.0721; found 300.0722.

2-(4'-(Furan-2''-yl)phenyl)-1H-phenanthro[9,10-d]imidazole, **6a**. Light brown solid (144 mg, 86%). Mp: 251.8-252.6 ^{o}C. IR (KBr): ν = 3434, 2108, 1643, 1455, 1429, 1355, 1283, 1156, 1006, 901, 841, 753, 720 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 6.65 – 6.66 (m, 1H, H-4''), 7.09 (d, J = 3.6 Hz, 1H, H-3''), 7.63 (dt, J = 8.0 and 1.2 Hz, 2H, H-5 and H-10), 7.74 (t, J = 8.0 Hz, 2H, H-6 and H-9), 7.82 (d, J = 1.6 Hz, 1H, H-5''), 7.93 (d, J = 8.4 Hz, 2H, H-2' and H-6'), 8.36 (d, J = 8.8 Hz, 2H, H-3' and H-5'), 8.57 – 8.58 (m, 2H, H-4 and H-11), 8.85 (d, J = 8.0 Hz, 2H, H-7 and H-8), 13.48 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 106.83, 112.35, 121.95, 122.33, 123.83, 124.05, 125.29, 126.61, 127.13, 127.65, 129.06, 130.77, 143.40, 148.71, 152.61 ppm. MS (EI) *m/z* (%): 360 ([M]$^+$, 100), 190 (9). HRMS: (EI) *m/z* (%) for $C_{25}H_{16}ON_2$; calcd 360.1263; found 360.1261.

2-(4'-(Thiophen-2''-yl)phenyl)-1H-phenanthro[9,10-d] imidazole**, 6b.** Yellow solid (105 mg, 65%). Mp: 216.4-217.3 ^{o}C. IR (KBr): ν = 3246, 3070, 2972, 1658, 1612, 1533, 1479, 1456, 1430, 1383, 1312, 1232, 1081, 1051, 754, 700 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.19-7.21 (m, 1H, H-4''), 7.60 – 7.67 (m, 4H, H-3'', H-5'', H-5 and H-10), 7.73 (t, J = 7.2 Hz, 2H, H-6 and H-9), 7.90 (dd, J = 8.4 and 1.6 Hz, 2H, H-2' and H-6'), 8.35 (dd, J = 8.4 and 1.6 Hz, 2H, H-3' and H-5'), 8.57 (d, J = 8.0 Hz, 2H, H-4 and H-11), 8.86 (d, J = 8.4 Hz, 2H, H-7 and H-8), 13.51 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 121.97, 123.91, 124.30, 125.30, 125.76, 126.25, 126.77, 127.11, 127.64, 128.67, 129.21, 134.34, 142.72, 148.62 ppm. MS (EI) *m/z* (%): 376 ([M]$^+$, 100). HRMS: (EI) *m/z* (%) for $C_{25}H_{16}N_2S$; calcd 376.1034; found 376.1030.

2-(2'-(Thiophen-2''-yl)furan-5'-yl)-1H-phenanthro[9,10-d] imidazole, **7a.** Dark yellow solid (116 mg, 79%). Mp: 285.8-286.4 ^{o}C. IR (KBr): ν = 3437, 2111, 1645, 1536, 1502, 1455, 1425, 1366, 1123, 994, 845, 755, 697 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.02 (d, J = 3.6 Hz, 1H, H-3''), 7.19 – 7.22 (m, 1H, H-4''), 7.32 (d, J = 3.6 Hz, 1H, H-4'), 7.60 (dd, J = 3.6 and 1.2 Hz, 1H, H-5''), 7.62 – 7.66 (m, 3H, H-3', H-5 and H-10), 7.72 – 7.75 (m, 2H, H-6 and H-9), 8.55 (m, 2H, H-4 and H-11), 8.83-8.89 (m, 2H, H-7 and H-8), 13.59 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 107.91, 111.75, 122.00, 123.93, 124.22, 125.40, 126.18, 127.14, 127.71, 128.27, 132.11, 141.18, 144.70, 149.53 ppm. MS (EI) *m/z* (%): 366 ([M]$^+$, 100), 338 (8), 337 (12). HRMS: (EI) *m/z* (%) for $C_{23}H_{14}ON_2S$; calcd 366.0827; found 366.0825.

2-(2'-(Furan-2''-yl)thiophen-5'-yl)-1H-phenanthro[9,10-d]imidazole**, 7b.** Dark yellow solid (91 mg, 60%). Mp > 300 ^{o}C. IR (KBr): ν = 3583, 3423, 2362, 2340, 1639, 1478, 1407, 1262, 1155, 1016, 998, 765, 696 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 6.64-6.66 (m, 1H, H-4''), 6.92 (dd, J = 3.6 and 0.8 Hz, 1H, H-3''), 7.49 (d, J = 4.0 Hz, 1H, H-3'), 7.61 – 7.66 (m, 2H, H-5 and H-10),

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7.71- 7.75 (m, 2H, H-6 and H-9), 7.79 (d, J = 3.6 Hz, 1H, H-5''), 7.88 (d, J = 4.0 Hz, 1H, H-4'), 8.42 – 8.52 (m, 2H, H-4 and H-11), 8.82 – 8.88 (m, 2H, H-7 and H-8), 13.63 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 106.69, 112.44, 121.64, 123.70, 124.17, 125.12, 125.30, 125.51, 126.49, 127.06, 127.36, 127.57, 128.64, 132.28, 133.71, 136.86, 141.41, 143.14, 144.44, 148.26, 149.55 ppm. MS (EI) *m/z* (%): 366 ([M]$^+$, 100), 337 (17), 305 (8), 300 (10), 227 (9), 191 (9), 190 (29), 189 (8), 183 (9), 165 (12), 164 (11), 163 (14). HRMS: (EI) *m/z* (%) for $C_{23}H_{14}ON_2S$; calcd 366.0827; found 366.0830.

***2-(2',2''-Bithiophen-5'-yl)-1H-phenanthro[9,10-d]imidazole*, 7c.** Brown solid (138 mg, 88%). Mp: 258.6-259.1 °C. IR (KBr): ν = 3168, 1936, 1702, 1652, 1614, 1588, 1522, 1486, 1452, 1396, 1355, 1230, 1187, 1160, 1086, 1039, 931, 804, 752 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.14 – 7.16 (m, 1H, H-4''), 7.44 (d, J = 4.0 Hz, 1H, H-4'), 7.46 (dd, J = 3.2 and 0.8 Hz, 1H, H-3''), 7.59 (dd, J = 5.2 and 1.2 Hz, 1H, H-5''), 7.61 – 7.66 (m, 2H, H-5 and H-10), 7.71-7.76 (m, 2H, H-6 and H-9), 7.86 (d, J = 3.6 Hz, 1H, H-3'), 8.43 (d, J = 8.0 Hz, 1H, H-4), 8.51 (d, J = 8.0 Hz, 1H, H-11), 8.81 – 8.87 (m, 2H, H-7 and H-8), 13.59 (s, 1H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ = 121.79, 121.87, 122.07, 123.75, 124.15, 124.71, 124.81, 125.26, 125.49, 126.06, 126.56, 126.59, 127.14, 127.22, 127.55, 127.77, 128.55, 132.33, 136.07, 136.86, 137.63, 144.33 ppm. MS (EI) *m/z* (%): 382 ([M]$^+$, 100), 381 (8), 190 (7). HRMS: (EI) *m/z* (%) for $C_{23}H_{14}N_2S_2$; calcd 382.0598; found 382.0593.

Photophysical studies

All the photophysical experiments were performed with freshly prepared, air-equilibrated solutions at room temperature (293 K). UV-visible absorption spectra (200 – 700 nm) were recorded using a Shimadzu UV/2501PC spectrophotometer. Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer and fluorescence quantum yields were determined according to literature procedures using dilute solutions (10^{-6} M) of the compounds and 9,10-diphenylanthracene (DPA) in ethanol as fluorescence standard (Φ_F = 0.95).[23]

Two-photon absoprtion

TPA cross-sections (σ_2) were measured using the well-established two-photon induced fluorescence method with femtosecond laser pulses described by Xu and Webb.[23] A mode-locked Ti:Sapphire (Coherent Mira 900) was used as an excitation source with a central wavelength tuneable from 750 nm to 860 nm. The pulse duration (FWHM) was typically in the range of 100-125 fs while the energy per pulse ranged from 5-10 nJ. A 20-cm focal length plan-convex lens focused the incident light, polarized in the vertical direction, into a standard 1 cm cuvette that contained the sample. The distance between the incident beam and the front wall of the cuvette was approximately 1 mm. All samples were dissolved in methanol at a concentration of roughly 10^{-4} M.

The fluorescence resulting from the two-photon absorption was collected at right angles using a 5-cm focal length plano-convex lens to couple the fluorescence into a multimode fiber bundle connected to the entrance slit of a 0.3 m monochromator (Andor Shammrock). The resulting spectrum was captured using a cooled CCD camera (Andor Newton) and stored on a desktop computer.

The reported two-photon absorption cross-sections were determined by using a 10^{-4} M solution of Rhodamine 590 (Rhodamine 6G) in methanol as a standard. Absolute cross-sections have been measured for this compound for incident wavelengths in the range of 620 nm-1090 nm[28] and were used to calibrate our detection system. Specifically, the cross section of the sample, σ_s is given by

$$\sigma_s = \sigma_{ref}\left(\frac{C_{ref}\Phi_{ref}}{C_s\Phi_s}\right)\frac{\int F_{ref}}{\int F_s} \quad (1)$$

Here $C_{ref/s}$ represents the concentration of the reference (sample), $\Phi_{ref/s}$ the fluorescence quantum efficiency (assumed to be equal for one and two-photon absorption), while $\int F_{ref/s}$ indicates the total integrated area of the reference (sample) collected fluorescence. Makarov et al. estimate the relative uncertainty in their reported values for the absolute cross-sections of Rhodamine 590 as ±15%. Taking into account the small fluctuation in laser power registered over the course of the measurements as well as possible uncertainties in calculating the integrated fluorescent intensities, we conservatively place the overall uncertainty in our reported values as being ±15%.

Spectrophotometric and spectrofluorimetric titrations of compounds 5-7

Solutions of phenanthroimidazoles **5**-**7** (*ca*. 1.0 × 10^{-5} M) and of the organic and inorganic anions ($H_2PO_4^-$, CN^-, AcO^-, F^-, BzO^-, Br^-, Cl^-, HSO_4^-, NO_3^-) and cations (in the form of hydrated tetrafluorborate salts for Cu^{2+}, Ni^{2+} and Pd^{2+}, and perchlorate salts for Cd^{2+}, Cr^{3+}, Zn^{2+}, Hg^{2+}, Fe^{2+} and Fe^{3+}) under study were prepared in UV-grade ACN and ACN/H_2O (95:5) (ca. 1.0 × 10^{-2} to 1.0 × 10^{-3} M). Titration of the compounds with several anions and metallic cations was performed by the sequential addition of solutions of the ions to the imidazole derivative solution, in a 10-mm path length quartz cuvette and emission spectra were measured by excitation at the wavelength of maximum absorption for compounds **5**-**7** indicated in Table 1. The binding stoichiometry of the compounds **5**-**7** with selected anions and metal cations was determined by Hyperquad software.

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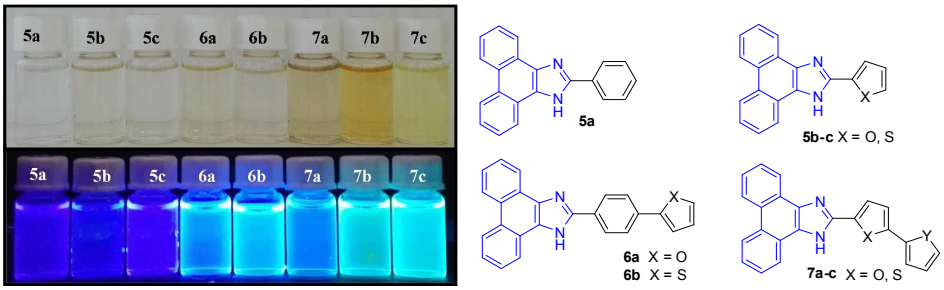
Table of Contents (TOC) entry

Fluorescent phenanthroimidazoles functionalized with heterocyclic spacers: synthesis, optical chemosensory ability and Two-Photon Absorption (TPA) properties

Rosa Cristina M. Ferreira, Susana P. G. Costa, Hugo Gonçalves, Michael Belsley, Maria Manuela M. Raposo



Fluorescent phenanthroimidazoles bearing heterocyclic spacers as novel optical chemosensors and Two-Photon Absorption chromophores