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N,N-Diphenylanilino-heterocyclic aldehyde-based chemosensors for UV-vis/NIR and fluorescence Cu(II) detection†

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Herein, three *N,N*-diphenylanilino-heterocyclic aldehyde probes (**5**, **6** and **7**) are synthesized, characterized and their sensing behaviour against metal cations tested. Acetonitrile solutions of the three probes show an intramolecular charge-transfer band in the 360–420 nm range due to the presence of an electron donor *N,N*-diphenylanilino group and an electron acceptor aldehyde moiety. Besides, all three probes are moderately emissive with bands in the 540–580 nm range in acetonitrile. The chromo-fluorogenic behaviour of the three probes in acetonitrile in the presence of selected metal cations is assessed. Of all the metal cations tested only Cu(II) induces marked colour and emission changes. In this respect, addition of Cu(II) cations to solutions of the probes induces the appearance of NIR absorptions at 756 nm for **5**, at 852 nm for **6** and at 527, 625 and 1072 nm for **7**. Besides, Cu(II) induces a marked quenching of the emission of the three probes. The observed spectral changes are ascribed to the formation of 1 : 1 probe-Cu(II) complexes in which the metal cation interacts with the acceptor part of the chemosensors. In addition, the limits of detection determined using UV-visible and fluorescence titrations are in the 0.21–5.12 μM range, which are values lower than the minimum concentration prescribed by the World Health Organization (WHO) guideline for drinking water for copper (30 mM). Besides, probe **7** is used for the detection of Cu(II) in aqueous environments using SDS anionic surfactant.

1. Introduction

In recent years, the development of new chromo-fluorogenic molecular chemosensors for biologically active metal ions has been extensively investigated because of their potential applications in life sciences, medicine, chemistry, and biotechnology.[1] These chromo-fluorogenic probes are generally formed by two components covalently linked, namely the binding site and the reporter unit. Interaction of transition metal cations with the binding site can induce a rearrangement of the π-conjugated system of the reporter unit, which may be reflected in colour and/or emission changes. However, the covalent linking of highly selective binding sites with reporter units requires, in most cases, great synthetic efforts in order to achieve certain selectivity to the guest and to impart the desired functionality in terms of color and/or emission changes upon coordination. In order to minimize synthetic requirements, recently, the preparation of simple chemical species that integrated binding sites into the structure of certain dyes or fluorophores has deserved great attention.[2]

On the other hand, copper is the third cation in abundance in human bodies besides zinc and iron. Cu(II) plays an important role in biological and environmental areas as an essential trace element for both plants and animals, including humans.[3] In addition, copper plays a key role in copper-containing enzymes in different catalytic and physiological processes.[4,5] Based on research findings, it has been suggested that copper deficiency can increase the risk of developing coronary heart disease,[6] while excessive concentrations of this cation lead to variation in brain function.[7] It has also been reported that a disturbance in Cu(II) levels results in human genetic disorders like,Wilson's disease[8] and Menkes syndrome.[9] Moreover, Cu(II) could lead to detrimental effects by causing oxidative stress and disorders associated with neurodegenerative diseases[10] such as Parkinson's,[11]

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Alzheimer's,[12] prion,[13] and Huntington's diseases[14] and metabolic disorders such as obesity and diabetes.[15] Taking into account the above-mentioned facts, several analytical methods for Cu(II) detection such as photometric measurements,[16] inductively coupled plasma emission or mass spectroscopy (ICP-ES, or ICP-MS),[17] atomic absorption spectroscopy (AAS),[18] anodic stripping voltammetry (ASV),[19] and total reflection X-ray fluorimetry (TXRF)[20] have been used. However, these techniques involve complicated procedures, and require high cost instrumentation, and trained personnel.

Owing to the significant physiological relevance and associated biomedical implications, there is a considerable interest in developing highly selective chemosensors for real time detection of Cu(II) in environmental and biological samples.[21] Moreover, very recently, the development of Cu(II) chromo-fluorogenic chemosensors with a marked optical response (changes in colour or in fluorescence) in the NIR zone (700–1100 nm) has deserved great attention.[22] Compared with UV-visible light, the NIR region has many advantages such as the possibility of reduced interferences of background absorption, fluorescence and light scattering. However, despite these interesting features, NIR probes for the sensing of cations are still scarce.[23]

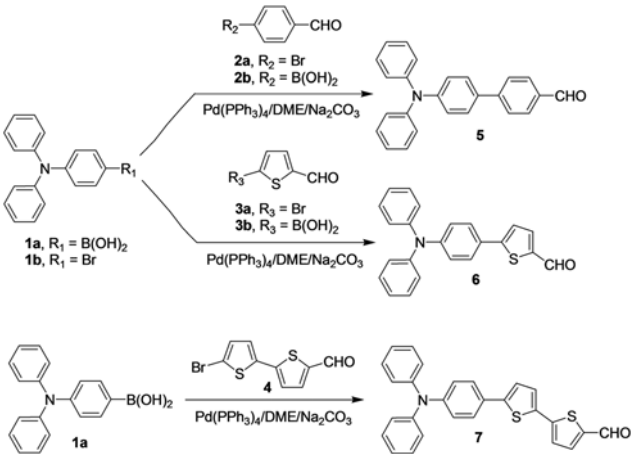
From another point of view, heterocyclic aldehydes are versatile building blocks that can further react to yield a diversity of more complex molecules.[24] Heterocyclic aldehydes can be synthesized following different methods such as Vilsmeier formylation, metalation followed by addition of DMF, Vilsmeier–Haack–Arnold reaction, Stille, Suzuki and Sonogashira cross couplings and Clauson–Kaas reactions.[25] Heterocyclic aldehydes prepared by these procedures can subsequently be used for the synthesis of more complex push–pull π-conjugated heterocyclic systems intended for several applications such as nonlinear optics (SHG, TPA), optical chemosensors, fluorescent probes, heterogeneous catalysts, OLEDs, and DSSCs, and in the synthesis of functionalized heterocyclic-based unnatural amino acids.[26]

Motivated by previous studies by us,[27] we decided to further explore the potential use of *N*,*N*-diphenylanilino-heterocyclic aldehydes, bearing aryl and thienyl spacers as optical probes, for the detection of cations. In particular, we report herein the synthesis, characterization and sensing studies toward metal cations of three chromo-fluorogenic probes (**5**, **6** and **7**) based on the *N*,*N*-diphenylanilino-heterocyclic aldehyde skeleton. Interaction of the three probes with Cu(II) induced the appearance of absorption bands in the NIR zone and a remarkable quenching of the fluorescence.

2. Results and discussion

Synthesis and characterization of the probes

Aldehydes **5**, **6** and **7**, functionalized with *N*,*N*-diphenylanilino as a donor group and different π-spacers (benzene and thiophene) were designed in order to study the effect of the heterocyclic π-bridges (*i.e.* length and electronic nature) on the optical properties and selectivity and sensitivity of the prepared probes. Thiophene spacers were selected due to their excellent charge-transfer



Scheme 1 Synthesis of probes **5**, **6** and **7**.

properties and high thermal and photophysical stability.[24–26] In fact, compared with benzene derivatives, thiophenes offer a more effective conjugation and a lower energy for charge transfer transitions[28] due to their smaller resonance energy (thiophene, 29 kcal mol^{-1}; benzene, 36 kcal mol^{-1}).[29] On the other hand, *N*,*N*-diphenylanilino was chosen as the donor group due to its well-known photophysical properties and its significantly higher thermo- and photophysical stability compared to its *N*,*N*-dialkylaniline analogues.[30,31]

The synthetic protocols used to obtain probes **5**, **6** and **7** are shown in Scheme 1, following well-known procedures reported elsewhere.[25b,c,26a,c,d,32] The Suzuki coupling was selected as the method of synthesis due to well-known advantages of this coupling procedure (*i.e.* availability of the reagents, mild reaction conditions unaffected by the presence of water, tolerability of a broad range of functional groups and formation of non-toxic and easily removable inorganic by-products from the reaction mixture) compared to other coupling methods.[33]

Two different pairs of coupling components were used in order to determine the influence of the structure of the boronic acids as well as the brominated compounds on the yield of the Suzuki–Miyaura coupling reaction. Thus, probes **5**, **6** and **7** were prepared by Suzuki coupling with 4-(diphenylamino)phenylboronic acid **1a** and (hetero)aromatic brominated aldehydes **2a**, **3a** and **4** (*via* a) or using 4-bromo-*N*,*N*-diphenylaniline **1b** and heterocyclic boronic acids **2b** and **3b** as coupling components (*via* b).

According to Table 1, aldehydes **5** and **6** synthesised *via* a were obtained in higher yields (95–96%), compared to those observed *via* b (42–84%). These results are not unexpected

Table 1 Yields, UV-visible and fluorescence data for *N*,*N*-diphenylanilino aldehydes **5**, **6** and **7** in acetonitrile solutions

	Yield (%)		UV/Vis		Fluorescence		
	Via a	*Via* b	λ_{max} (nm)	log ε	λ_{em} (nm)	Φ_F	Stokes' shift (nm)
5	95	84	367	4.53	554	0.01	187
6	96	42	398	4.43	559	0.02	161
7	88	—	419	4.32	577	0.22	158

bearing in mind that in the Suzuki–Miyaura coupling the boronic acid is the nucleophilic coupling component and the aryl halide is the electrophilic coupling part. Therefore, boronic acids functionalized with electron donor groups are activated for the coupling reaction, and electron acceptor groups would activate the (hetero) aryl halides (*via* a).

The synthesis of aldehyde **6**, using the Suzuki coupling reaction with 4-(diphenylamino)phenylboronic acid as one of the coupling components in a 75% yield, was previously described.[34] Using another approach, when 4-iodophenyldiphenylamine was used as a coupling reagent for the preparation of aldehyde **6**, a 92% yield was obtained.[35] However, in this last paper 4-iodophenyldiphenylamine was prepared with an overall yield for the two steps of 53%. The synthetic procedure (though a Suzuki coupling) described in this paper is a clear alternative to the published methods because it uses commercially available coupling components and allows the preparation of **6** in a one-step process with a 96% yield (by means of *via* a).

On the other hand, compound **7** was previously synthesized using the Stille or Suzuki coupling reactions. The synthesis that used Stille couplings presented fair yields (68% and 74%)[36,37] and used, in both cases, toxic stannates as precursors. **7** was also prepared following the Suzuki coupling with 4-(diphenylamino)phenylboronic and 5-iodo-2,2′-bithiophenyl-5-carboxaldehyde in a 91% yield.[36b] In this case, the iodine precursor was also prepared from 2,2′-bithiophenyl-5-carboxaldehyde with an overall yield of 81% for aldehyde **7**. Besides, more recently, probe **7** was prepared using the Suzuki coupling reaction between 4-iodophenyldiphenylamine and 5′-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-[2,2′]-bithiophenyl-5-carboxaldehyde. In this case, 4-iodophenyldiphenylamine was prepared by a Ullmann coupling reaction involving copper catalyzed iodoarylation of diphenylamine with 1,4-diiodobenzene (overall yield of 34% for **7**).[38] Using our synthetic methodology, we were able to obtain probe **7** in a higher yield compared to the methods described above. Compound **7** was synthesized with an 88% yield in a one-step synthetic process through Suzuki coupling, using as precursors commercially available 4-(diphenylamino)phenylboronic and 5-bromo-2,2′-bithiophenyl-5-carboxaldehyde (*via* a).

Compounds **5**, **6** and **7** were characterized by spectroscopic techniques (see Table 1 for UV-visible and fluorescence data). The most distinctive signals in the ^{1}H NMR spectra for probes **5**, **6** and **7** were those corresponding to the aldehyde protons at *ca.* 9.86–10.05 ppm. FT-IR spectroscopy was also used in order to identify the typical band of the carbonyl group in aldehydes **5**, **6** and **7** that appeared in the 1656–1698 cm^{-1} range.

Photophysical studies in acetonitrile solutions. The photophysical properties (absorption and emission) of the three *N*,*N*-diphenylanilino-heterocyclic aldehyde derivatives were studied in acetonitrile (Table 1). Electronic absorption spectra of heterocyclic aldehydes **5**, **6** and **7** in acetonitrile solutions showed an intense absorption band in the UV-visible region, in the 360–420 nm range, which can be attributed to an intramolecular charge-transfer (ICT) transition as a consequence of the presence of an *N*,*N*-diphenylanilino electron donor moiety directly linked to (hetero)aromatic bridges functionalized with

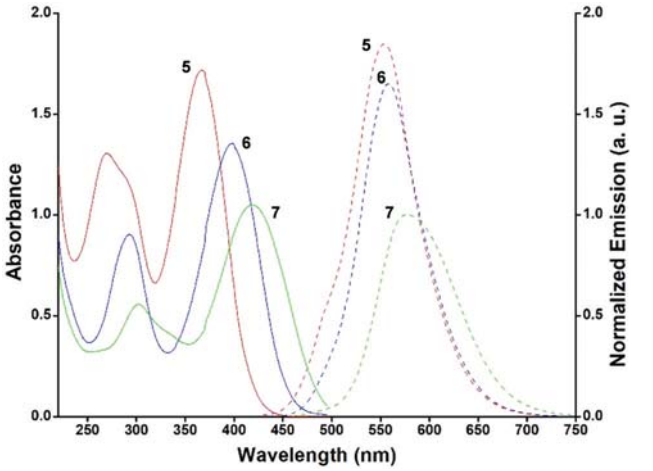


Fig. 1 UV/Vis (solid lines) and fluoresence (dashed lines) spectra of the three probes in acetonitrile. Red lines: **5** (λ_{ex} = 367 nm); blue lines: **6** (λ_{ex} = 398 nm); green lines: **7** (λ_{ex} = 419 nm).

the aldehyde electron acceptor group (see Fig. 1). The wavelengths of the ICT absorption bands of the three probes were directly related with the π-spacer (length, and electronic nature of the aromatic or heteroaromatic rings). In this respect, a less effective conjugation and a higher energy for charge transfer transitions due to the higher resonance energy of the phenyl ring in probe **5** accounted for the lower wavelength of the ICT band (367 nm). On the other hand, the presence of one (probe **6**) or two (probe **7**) thiophene heterocycles induced an increase in the ICT character, which was reflected in redshifted wavelengths of the absorption bands (398 and 419 nm for **6** and **7**, respectively). These facts are clearly related with the more effective conjugation, lower energy for the ICT transition and smaller resonance energy of thiophenes when compared to benzene derivatives.[25,29]

The three probes are weakly to moderately emissive upon excitation in the maximum of the corresponding absorption bands (see also Table 1). Upon excitation, the three probes showed broad unstructured emission bands in the 550–580 nm range (Fig. 1). The relative fluorescence quantum yields were determined by using 10^{-6} M solutions of 9,10-diphenylanthracene (DPA) in ethanol as standard (Φ_F = 0.95).[39] Probes **5**, **6** and **7** exhibited low to moderate fluorescence quantum yields in acetonitrile (Φ_F = 0.01–0.22, Table 1). Besides, all probes showed large Stokes' shifts from 158 to 187 nm (Table 1 and Fig. 1). The large Stokes' shifts presented by **5**–**7** are a desired feature for fluorescent probes because it allows an improved separation of the light inherent to the matrix and the light dispersed by the sample.[40]

To further characterize the ICT nature of the absorption and emission bands and to understand the solvent relaxation mechanism of probes **5**, **6** and **7**, fluorescence solvatochromism measurements were performed.[41] As it has been reported that, upon excitation of fluorophores with D–π–A (donor–π–acceptor) structures, an intramolecular charge transfer (ICT) occurs and this process is expected to be sensitive to solvent changes. In fact, the emission spectra of the ICT fluorophores have been reported to shift in response to the changes of the solvent

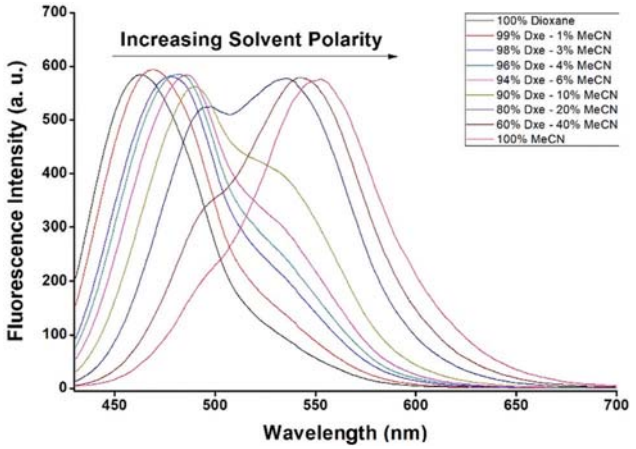


Fig. 2 Emission band shifts of probe **5** in different dioxane-acetonitrile mixtures.

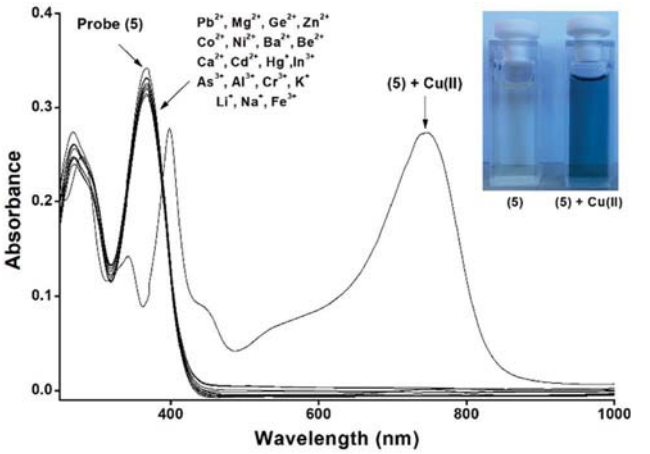


Fig. 3 UV-visible spectra of probe **5** in acetonitrile (1.0×10^{-5} mol L^{-1}) alone and in the presence of 10 eq. of selected metal cations. The inset shows the change in colour of acetonitrile solutions of probe **5** alone and in the presence of Cu(II) cations.

polarity.[42] Taking into account the above-mentioned facts, we measured the emission of probe **5** in different dioxane-acetonitrile mixtures ranging from pure dioxane to pure acetonitrile. The obtained results are depicted in Fig. 2. As could be seen, upon increasing the relative solvent polarity (water as standard for the polarity of 1.000) from 0.164 (pure dioxane) to 0.460 (pure acetonitrile),[43] the emission maximum shifted from 463 to 552 nm. Besides, a progressive increase of acetonitrile content in the mixture induced moderate shifts of the emission of probe **5**. The obtained shifts could be ascribed to a solvent relaxation process. In this respect, the strong dipole–dipole interaction between the probe in its excited state and the surrounding solvent molecules induced a decrease in the emission energy that was reflected in the observed redshifted bands. The photophysical features of the three probes were also investigated in ethanol (see Table S1 in the ESI†).

UV-visible absorption studies in the presence of cations

After the photophysical characterization of aldehyde-functionalized probes **5–7** their sensing behaviour in acetonitrile in the presence of selected metal cations was evaluated. Fig. 3 shows the UV-visible absorption spectra of probe **5** in acetonitrile (1.0×10^{-5} mol L^{-1}) alone and in the presence of 10 eq. of selected metal cations. As could be seen, probe **5** presents an absorption band centred at 367 nm that remained unchanged in the presence of Pb(II), Mg(II), Ge(II), Ca(II), Zn(II), Co(II), Ni(II), Ba(II), Cd(II), Hg(II), Fe(III), In(III), As(III), Al(III), Cr(III), Ga(III), K(I), Li(I) and Na(I). However, a remarkable response was obtained upon Cu(II) addition, which induced the appearance of a marked redshifted absorption centred at 756 nm together with a marked colour change from colourless to green (see Fig. 3).

Then, UV-visible changes of acetonitrile solutions of probe **5** (5.0×10^{-5} mol L^{-1}) in the presence of increasing amounts of Cu(II) cation was studied. The obtained set of UV-visible spectra is shown in Fig. 4. As could be seen, addition of progressive amounts of Cu(II) induced a gradual decrease of the absorption at 367 nm and the appearance of a new sharp band at 756 nm (see Fig. 4). It is also remarkable the appearance of two isosbestic

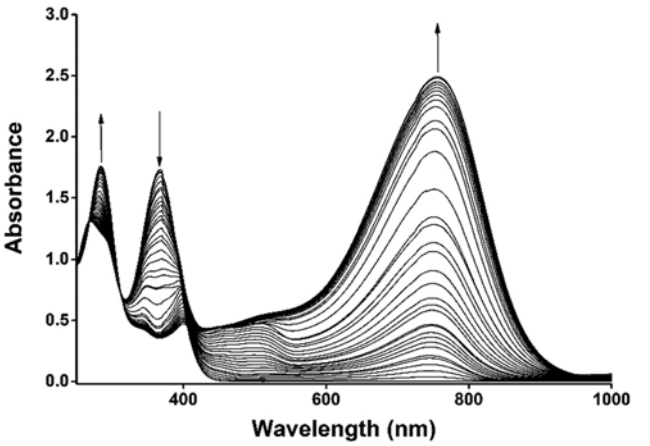


Fig. 4 UV-visible titration profile of probe **5** in acetonitrile (5.0×10^{-5} mol L^{-1}) upon addition of increasing amounts of Cu(II) cation (from 0 to 10 eq.).

points at 315 and 420 nm that indicated the formation of only one species between probe **5** and Cu(II) cations. Moreover, from the titration profile a limit of detection for Cu(II) of 1.60 μM was determined (see ESI,† Fig. S3).

Nearly the same response was obtained for probes **6** and **7**. Again, of all the cations tested, only Cu(II) induced remarkable changes in the UV-visible spectra which consisted of the appearance of redshifted absorptions in the NIR zone at 852 and 1072 nm for probes **6** and **7**, respectively (see ESI,† Fig. S1 and S2). UV-visible titration profiles of probes **6** and **7** upon addition of increasing amounts of Cu(II) cation were also obtained. As could be seen in Fig. 5, addition of increasing quantities of Cu(II) cation to acetonitrile solutions of probe **6** induced a progressive decrease of the absorption centred at 398 nm together with the growth of a band at 852 nm. This is reflected in a colour change from faint yellow to brownish-red. Besides, during the course of the titration, isosbestic points appeared at 305, 360 and 440 nm. From the titration profile (see ESI,† Fig. S4) a limit of detection for Cu(II) of 5.12 μM was determined using probe **6**.

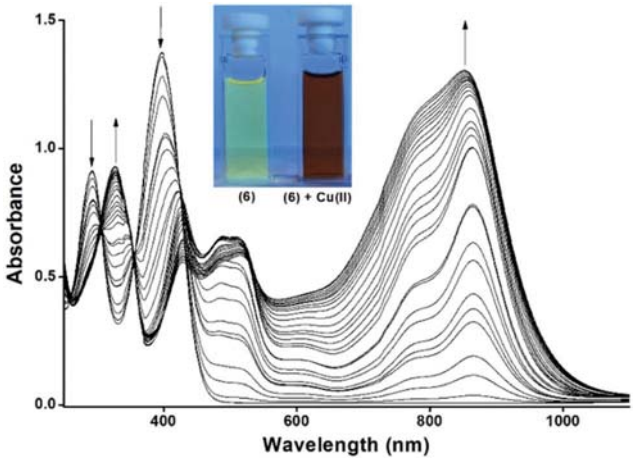


Fig. 5 UV-visible titration profile of probe **6** in acetonitrile (5.0×10^{-5} mol L^{-1}) upon addition of increasing amounts of Cu(II) cation (from 0 to 10 eq.). The inset shows the change in colour of acetonitrile solutions of probe **6** alone and in the presence of Cu(II) cations.

Dealing with probe **7**, addition of increasing amounts of Cu(II) cation induced the progressive appearance of a main absorption band in the NIR zone at 1072 nm together with the gradual decrease of the band at 419 nm (see Fig. 6). In addition, the colour changed from faint yellow to deep violet. Again, the appearance of isosbestic points at 275, 340, 370 and 450 nm indicated the presence of only one equilibrium in the interaction of probe **7** with Cu(II) cations. Finally, from the titration profile shown in Fig. 6, a limit of detection for Cu(II) of 2.14 μM was found (see ESI,† Fig. S5). The obtained limits of detection of Cu(II) for probes **5**, **6** and **7** are lower than the minimum concentration prescribed by the World Health Organization (WHO) guideline for drinking water (30 mM).[44]

In order to assess the mode of coordination between probes **5**–**7** and Cu(II) cations, Job's plots were measured. Moreover, the strength of coordination was studied *via* the evaluation of the

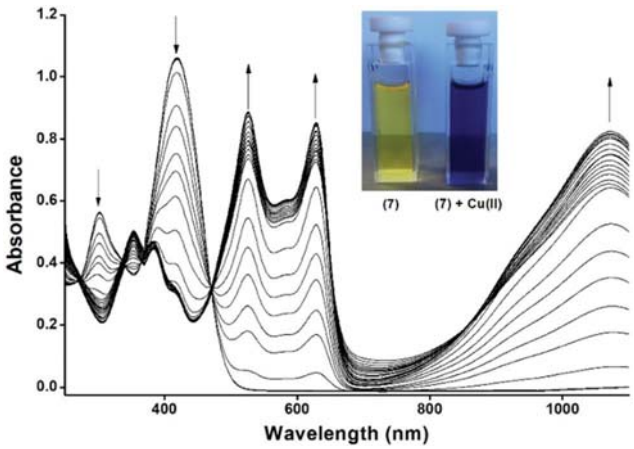


Fig. 6 UV-visible titration profile of probe **7** in acetonitrile (5.0×10^{-5} mol L^{-1}) upon addition of increasing amounts of Cu(II) cation (from 0 to 10 eq.). The inset shows the change in colour of acetonitrile solutions of probe **7** alone and in the presence of Cu(II) cations.

Table 2 Logarithms of the stability constants measured for the interaction of probes **5**, **6** and **7** with Cu(II) cations in acetonitrile

	5	**6**	**7**
$\log K_a$	5.39 ± 0.09	5.40 ± 0.12	6.50 ± 0.24

corresponding stability constants, which were determined by UV-visible spectroscopic titrations between probes **5**, **6** and **7** and Cu(II) using the Benesi–Hildebrand equation (Table 2).[45] The Job's plot obtained for probe **5** and Cu(II) cations (see Fig. 7) clearly indicated the formation of 1 : 1 stoichiometry complexes. The same results, namely formation of 1 : 1 complexes, were obtained for the interaction of probes **6** and **7** with Cu(II) cations (see ESI,† Fig S6 and S7). In order to assess if Cu(II) coordination with probes **5**–**7** was responsible for the generation of NIR bands, titrations of the complexes with EDTA were carried out. In this respect, addition of increasing amounts of EDTA to acetonitrile solutions of Cu(II)-**5**, Cu(II)-**6** and Cu(II)-**7** complexes induced the progressive disappearance of the NIR bands and the UV-visible spectra of the free probes were obtained (see ESI,† Fig. S8 and S9). These facts clearly pointed out that the observed chromogenic changes (generation of NIR bands) were due to Cu(II) coordination with probes **5**–**7**.

Moreover, the appearance of redshifted UV-visible bands upon coordination of **5**–**7** with Cu(II) cations suggested the participation of the acceptor part of the probes in the interaction with copper. Taking into account this fact, *i.e.* interaction of Cu(II) cations with the electron acceptor aldehyde group in **5**–**7**, one should expect very similar stability constants for all three probes. However, although the stability constants for probes **5** and **6** are quite similar (see Table 2), that found for **7** is significantly larger. This indicates that the presence of phenyl or thienyl rings, in probes **5** and **6**, as linkers of the *N*,*N*-diphenylaniline donor group with the electron acceptor aldehyde moiety seems to have a negligible effect on the strength of the coordination with Cu(II) cations. On the other hand, the presence of two electronically connected thienyl

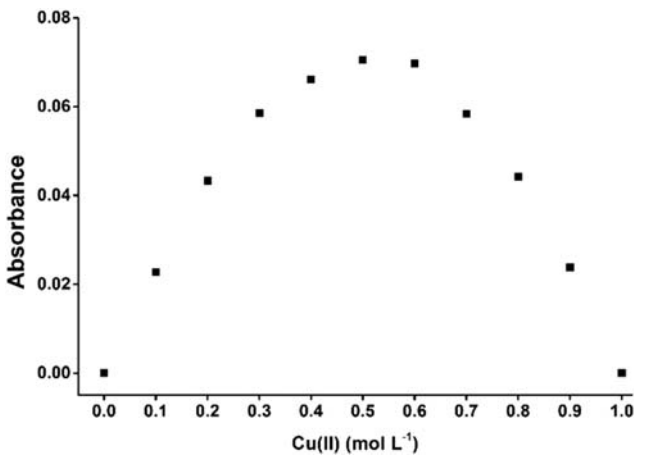


Fig. 7 Job's plot for probe **5** and Cu(II) in acetonitrile. Total concentration of **5** and Cu(II) of 2.0×10^{-5} mol L^{-1}.

heterocycles in probe **7** increased one order of magnitude the strength of the interaction with Cu(II) cations when compared to those obtained for **5** and **6**. This fact could tentatively be indicative of the involvement of the second thienyl heterocycle in binding Cu(II) or of a more extended conjugation in probe **7** when compared with **6** (with only one thienyl linker).

Fluorescence studies in the presence of cations

Having assessed the chromogenic behaviour of the three probes in the presence of selected metal cations, in this section we carried out studies of the fluorescence response toward the same targets. In this respect, excitation at 420 nm (*i.e.* an isosbestic point in the Cu(II)-**5** titration profile) of acetonitrile solution of **5** (5.0×10^{-5} mol L^{-1}) induced the appearance of a broad emission band centred at 554 nm (see Fig. 8). The response observed toward selected metal cations showed that only Cu(II) induced a progressive emission quenching (see also Fig. 8). From the emission titration profile obtained, a limit of detection of 1.98 μM for Cu(II) was determined (see ESI,† Fig. S10).

Nearly the same results were obtained for acetonitrile solutions (5.0×10^{-5} mol L^{-1}) of probes **6** and **7**, namely a marked quenching of the broad emission bands (at 559 nm after excitation at 440 nm for **6** and at 577 nm after excitation at 450 nm for **7**) after addition of increasing amounts of Cu(II) cation (see figures, ESI†). Again, from the titration profiles (see ESI,† Fig. S9 and S10), limits of detection of 0.21 and 2.50 μM were measured for probes **6** and **7**, respectively (see ESI,† Fig. S11 and S12).

Chromo-fluorogenic studies in the presence of cations in aqueous environments

Finally, we tested the possible use of probes **5**–**7** in aqueous environments because this is an essential issue for monitoring environmental, biological, and industrial samples. Unfortunately, the selective chromogenic response toward Cu(II) cations in acetonitrile was not observed in the presence of small amounts of water. In this respect, water content as low as 4% prevents the formation of the corresponding complexes between probes **5** and **6** and Cu(II) cations (see ESI,† Fig. S13 and S14). On the other hand, the chromogenic response of probe **7** in the presence of Cu(II) was observed even with *ca.* 7% of water (see ESI,† Fig. S17). The absence of response of probes **5** and **6** when water was used is ascribed to the high solvation energy of Cu(II) which is not energetically compensated by the moderate interaction of Cu(II) cations with the probes.

One common alternative used to overcome the strong solvation effects of metal cations, that impose a highly effective energetic barrier that inhibits sensing processes in aqueous solution, is the use of surfactants. The use of chemical probes embedded in micelles for the chromo-fluorogenic detection of analytes in water is a well stablished field. Several authors showed that selected binding sites and fluorophores can be arranged in micelles of surfactants allowing detection of metal cations in water by changes in fluorescence.[46]

Taking into account these facts, and considering that the chromogenic response of **7** toward Cu(II) cations was observed even with *ca.* 7% of water, we studied the fluorogenic response of this probe to metal cations in sodium dodecyl sulfate (SDS) (20 mM, pH 7.5)-acetonitrile 90 : 10 v/v solution. Probe **7** is weakly soluble in pure water but is completely solubilized in SDS (20 mM, pH 7.5)-acetonitrile 90 : 10 v/v mixture. This solubilisation could be ascribed to the inclusion of probe **7** into the inner hydrophobic core of the SDS micelles. SDS aqueous solution of probe **7** presented a marked emission band centred at 565 nm upon excitation at 450 nm. Addition of 10 eq. of Ba(II), Pb(II), Mg(II), Co(II), Ni(II), Be(II), Ca(II), Cd(II), In(III), As(III), Al(III), Cr(III), K(I), Li(I), and Na(I) induced negligible changes in the emission of probe **7**. As a clear contrast, in the presence of Zn(II) a moderate emission quenching (*ca.* 30% of the initial probe fluorescence) was observed. However, addition of Cu(II) induced a marked *ca.* 80% reduction in the emission intensity of the probe (see ESI,† Fig. S18). This emission quenching was ascribed to a proper SDS-assisted internalization of Cu(II) cations into the inner micellar core with subsequent interaction with probe **7**.

Once the selective response of probe **7** in SDS (20 mM, pH 7.5)-acetonitrile 90 : 10 v/v solution was assessed, the emission behaviour upon addition of increasing amounts of Cu(II) cation

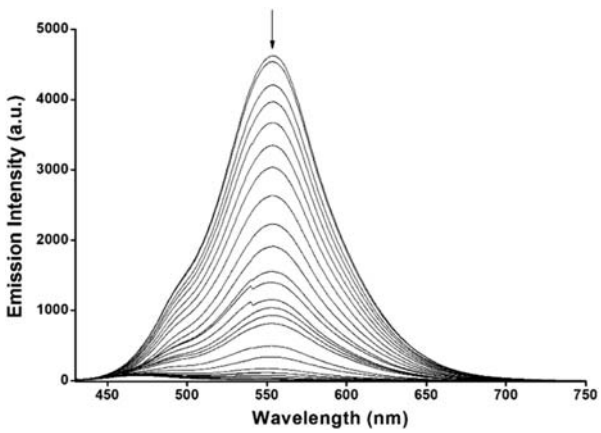


Fig. 8 Fluorescence titration profile of **5** in acetonitrile (5.0×10^{-5} mol L^{-1}) upon addition of increasing amounts of Cu(II) cation (from 0 to 10 eq.) (λ_{ex} = 420 nm).

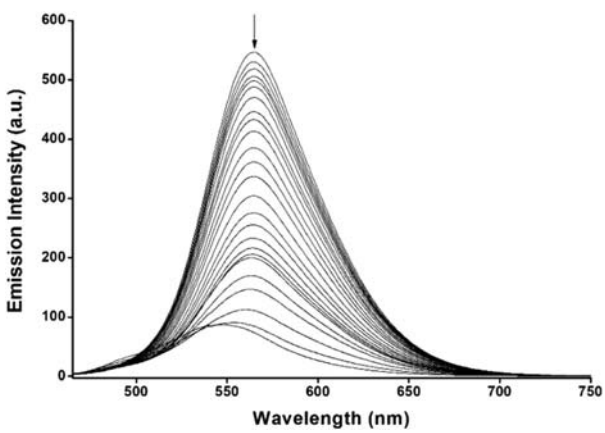


Fig. 9 Fluorescence titration profile of SDS (20 mM, pH 7.5)-acetonitrile 90 : 10 v/v solution of probe **7** (1.0×10^{-5} mol L^{-1}) upon addition of increasing amounts of Cu(II) cation (from 0 to 15 eq.) (λ_{ex} = 450 nm).

was tested. The obtained results are shown in Fig. 9. As could be seen, addition of increasing amounts of Cu(II) cation induced a progressive quenching of the emission band centred at 565 nm. From the titration profile (shown in the ESI,† Fig. S19) a limit of detection of 3.8 μM for Cu(II) was determined. This limit of detection is very similar to that obtained with **7** in acetonitrile (2.50 μM) which indicated a small reduction in probe sensitivity toward Cu(II) cations. These results clearly indicated that probe **7** could be used to detect Cu(II) in real aqueous samples, with remarkable selectivity and sensitivity, using an anionic surfactant such as SDS.

3. Conclusions

In summary, we described herein the synthesis (using the Suzuki coupling reactions), photophysical characterization and chromo-fluorogenic studies toward metal cations in acetonitrile of three heterocyclic aldehydes (**5**, **6** and **7**). The three probes presented intramolecular charge-transfer broad absorption bands in the 360–420 nm range due to the presence of *N*,*N*-diphenylanilino donor moieties, electronically conjugated with an aldehyde acceptor group through aryl or thienyl spacers. Besides, the probes are weakly to moderately emissive with fluorescence bands in the 540–580 nm range. Of all the cations tested, only Cu(II) induced the appearance of strong absorption bands in the NIR zone together with remarkable colour changes for the three probes. Besides, Cu(II) cations induced a marked emission quenching for the three probes. The observed colour/emission modulations were ascribed to the formation of 1 : 1 probe-Cu(II) complexes in which the metal cation interacts with the acceptor part of the probes. In addition, the limits of detection determined using UV-visible and fluorescence titrations are in the 0.21–5.12 μM range. This is below the minimum concentration prescribed by the World Health Organization (WHO) guideline for drinking water, which is set at 30 mM. Inclusion of probe **7** inside SDS micelles allowed Cu(II) detection in aqueous environments.

4. Experimental

Synthesis and characterization of the probes

Reaction progress was monitored by thin layer chromatography (0.25 mm thick pre-coated silica plates: Merck Fertigplatten Kieselgel 60 F_{254}), 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 an internal reference. The solvents are indicated in parentheses before the chemical shift values (δ relative to TMS and given in ppm). Melting points 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. Boronic acids **1a**, **2b** and **3b** and brominated derivatives **2a** and **3a** were commercially available. We have previously reported the synthesis of the precursor aldehyde **4**.[47]

General procedure for the synthesis of heterocyclic aldehydes 5, 6 and 7 (*via* a)

4-(Diphenylamino)phenylboronic acid **1a** (2.5 mmol) and aromatic or heterocyclic bromides **2a**, **3a** and **4** (1.9 mmol) were coupled in a mixture of DME (30 mL), ethanol (2 mL), aqueous Na_2CO_3 (2 mL, 2 M) and $Pd(PPh_3)_4$ (3 mol%) at 80 °C, by stirring under nitrogen. The reaction was monitored by TLC, which determined the reaction time (12 h). After cooling, the mixture was extracted with ethyl acetate (30 mL), a saturated solution of NaCl was added (15 mL) and the phases were separated. The organic phase was washed with water (3 × 20 mL) and with a 10% solution of NaOH (30 mL). The organic phase obtained was dried with anhydrous $MgSO_4$, filtered, and the solvent removed to give a crude mixture. The crude product was purified using column chromatography (silica gel, and chloroform as eluent) to afford the pure coupled products **5** (95%), **6** (96%) and **7** (88%).

4-(4′-(Diphenylamino)phenyl)phenyl-carbaldehyde (5). Yellow solid (168 mg, 95%). Mp: 113.6–114.1 °C. FTIR (CH_2Cl_2): ν = 3420, 3036, 2828, 2734, 1698, 1592, 1491, 1329, 1282, 1170, 816, 696 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.12 (dt, J = 7.2 and 1.2 Hz, 2H, 2 × H-4″), 7.18–7.21 (m, 6H, H-3′, H-5′, 2 × H-2″ and 2 × H-6″), 7.32 (dt, J = 7.2 and 1.2 Hz, 4H, 2 × H-3″ and 2 × H-5″), 7.55 (dd, J = 6.8 and 2.0 Hz, 2H, H-2′ and H-6′), 7.75 (dd, J = 6.8 and 2.0 Hz, 2H, H-3 and H-5), 7.95 (dd, J = 6.8 and 2.0 Hz, 2H, H-2 and H-6), 10.05 (s, 1H, CHO) ppm. ^{13}C NMR (DMSO-d_6): δ = 122.92 (C-3′ and C-5′), 123.33 (C-4″), 124.69 (C-2″ and C-6″), 126.66 (C-3 and C-5), 127.85 (C-2′ and C-6′), 129.26 (C-3″ and C-5″), 130.14 (C-2 and C-6), 132.53 (C-1′), 134.50 (C-1), 146.29 (C-4), 147.12 (C-1″), 148.21 (C-4′), 191.52 (CHO) ppm. Anal. calcd for $C_{25}H_{19}NO$: C, 85.90; H, 5.50; N, 4.00. Found: C, 85.79; H, 5.50; N, 3.80.

5-(4′-(Diphenylamino)phenyl)thiophene-2-carbaldehyde (6)[34]. Green solid (83 mg, 96%). Mp: 120.2–121.0 °C. FTIR (CH_2Cl_2): ν = 3423, 1660, 1591, 1530, 1490, 1444, 1329, 1283, 1228, 1193, 1179, 804, 755, 696 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.07–7.17 (m, 8H, H-3′, H-5′, 2 × H-2″, 2 × H-4″ and 2 × H-6″), 7.29–7.33 (m, 5H, H-4 and 2 × H-3″ and 2 × H-5″), 7.52 (dd, J = 6.8 and 2.0 Hz, 2H, H-2′ and H-6′), 7.71 (d, J = 4.0 Hz, 1H, H-3), 9.86 (s, 1H, CHO) ppm. ^{13}C NMR (DMSO-d_6): δ = 122.24 (C-4″), 122.78 (C-4), 123.78 (C-3′ and C-5′), 125.06 (C-2″ and C-6″), 126.00 (C-1′), 127.13 (C-2′ and C-6′), 129.39 (C-3″ and C-5″), 137.66 (C-3), 141.19 (C-5), 146.84 (C-1″), 149.01 (C-4′), 154.40 (C-2), 182.45 (CHO) ppm.

5-(4′-(Diphenylamino)phenyl)-2,2″-bithiophene-5″-carbaldehyde (7)[36]. Orange solid (176 mg, 88%). Mp: 152.6–153.0 °C. FTIR (CH_2Cl_2): ν = 3424, 2362, 2094, 1656, 1490, 1453, 1382, 1329, 1276, 1225, 1050, 870, 797, 753, 695, 664 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.05–7.15 (m, 8H, H-3′, H-5′, 2 × H-2″, 2 × H-4″ and 2 × H-6″), 7.18 (d, J = 3.6 Hz, 1H, H-4‴), 7.25 (d, J = 4.0 Hz, 1H, H-3‴), 7.27–7.31 (m, 4H, 2 × H-3″ and 2 × H-5″), 7.33 (d, J = 4.0 Hz, 1H, H-4), 7.47 (dd, J = 8.8 and 2.4 Hz, 2H, H-2′ and H-6′), 7.68 (d, J = 3.6 Hz, 1H, H-3), 9.86 (s, 1H, CHO) ppm. ^{13}C NMR (DMSO-d_6): δ = 123.12 (C-4‴), 123.17 (C-3‴), 123.46 (C-3′ and C-5′),

123.73 (C-4), 124.80 (C-3), 126.61 (C-2″ and C-6″), 127.08 (C-2′ and C-6′), 127.23 (C-5), 129.39 (C-3″ and C-5″), 134.05 (C-5‴), 137.43 (C-4‴), 141.26 (C-2‴), 146.27 (C-1′), 147.24 (C-1″), 147.44 (C-2), 148.04 (C-4′), 182.40 (CHO) ppm.

General procedure for the synthesis of heterocyclic aldehydes 5 and 6 (*via* b)

4-Bromo-*N*,*N*-diphenylaniline **1b** (1.9 mmol) and boronic acids **2b** and **3b** (2.5 mmol), were coupled in a mixture of DME (30 mL), ethanol (2 mL), aqueous Na_2CO_3 (2 mL, 2 M) and $Pd(PPh_3)_4$ (3 mol%) at 80 °C, by stirring under nitrogen. The reaction was monitored by TLC, which determined the reaction time (12 h). After cooling, the mixture was extracted with ethyl acetate (30 mL), a saturated solution of NaCl was added (15 mL) and the phases were separated. The organic phase was washed with water (3 × 20 mL) and with a 10% solution of NaOH (30 mL). The organic phase obtained was dried with anhydrous $MgSO_4$, filtered, and the solvent removed to give a crude mixture. The crude product was purified using column chromatography (silica gel, and chloroform as eluent) to afford the pure coupled products **5**, and **6**, in 84 and 42% yield, respectively.

General methods

All cations, in the form of perchlorate salts, were purchased from Sigma-Aldrich Chemical Co., stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Solvents were dried according to standard procedures. Unless stated otherwise, commercial grade chemicals were used without further purification. All the photophysical experiments were performed with freshly prepared, air-equilibrated solutions at room temperature (293 K). UV-visible absorption spectra (200–1100 nm) were recorded using a JASCO V-650 spectrophotometer (Easton, MD, USA). Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer and fluorescence quantum yields were determined according to literature procedures using dilute solutions (1.0×10^{-5} M) of the compounds and 9,10-diphenylanthracene (DPA) in ethanol as fluorescence standard ($\Phi_F = 0.95$).[39]

Sensing measurements

Acetonitrile solutions of the three probes (1.0×10^{-5} mol L^{-1} for UV-visible measurements and 5.0×10^{-5} mol L^{-1} for emission studies) were prepared and stored in the dry atmosphere. Solutions of perchlorate salts of the respective cations (1.5×10^{-3} mol L^{-1}) were prepared in distilled acetonitrile and were stored under a dry atmosphere.

Conflicts of interest

There are no conflicts to declare.

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