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A New Fluorescent Chemosensor for Cu^{2+} Based on a Dianthracene-Derivative

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Besides being of interest in photochemistry, photoinduced electron transfer (PET) is a process largely used in the design of fluorescent ion sensing molecules. One of the simplest systems is based on fluorescent aromatic groups linked to amino groups and proposed as possible fluorescent transition metal ion chemosensor [1]. In this case, the fluorescence of the fluorophore "ligths on" when the amino group is complexed. On the other hand, in the absence of metal ions, the fluorescence is quenched by a PET originating from the nitrogen lone electron pairs [2]. We prepared a new fluorescent chemosensor, abbreviated as Ant-NH-O-O-NH-Ant (shown in Fig. 1) in which the intramolecular PET is expected to be efficient. The chemosensor consists of a metal-binding dioxodiamino unit linked to two light-emitting anthracene fragments. This type of supramolecules when irradiated in methanol solution (conc. $1.89 \cdot 10^{-5}$ M.) at 368 nm displays a characteristic fluorescence spectrum for anthracene group with the most intensive band at 415 nm [Fig. 2(a)]. The emission is slightly enhanced upon coordination of such metal ions as $Ni^{2+}$and Zn^{2+} by the ligand fragment of the Ant-NH-O-O-NH-Ant molecule [Fig. 2(b) and (d)]. However, much higher intensity of emission is observed in the case of Cu^{2+} complex [see Fig 2(c)]. The fluorescence enhancement is presumably due to suppression of photoinduced fluorophore-to-metal electron-transfer mechanism.

The most important feature of the studied chemosensor is its fluorescence intensity *vs.* pH profiles (Fig. 3) which shows fluorescence switches for: uncomplexed species [Fig. 3(a)] and complexed one with Cu^{2+} [Fig. 3(b)] in MeOH/water solution (4:1, v/v). The fluorescence intensity/pH profiles have a similar shape, but not coincide. Thus, the displacement of the profile (b) of Cu^{2+} complex to pH value lower by about 1 unit reflects the higher solution stability for the system with the Cu^{2+} complexed ligand fragment compared with the free fragment [3].

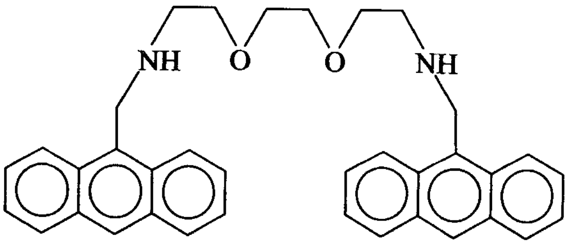

FIGURE 1 Diantracene-derivative, abbreviated as Ant-NH-O-O-NH-Ant

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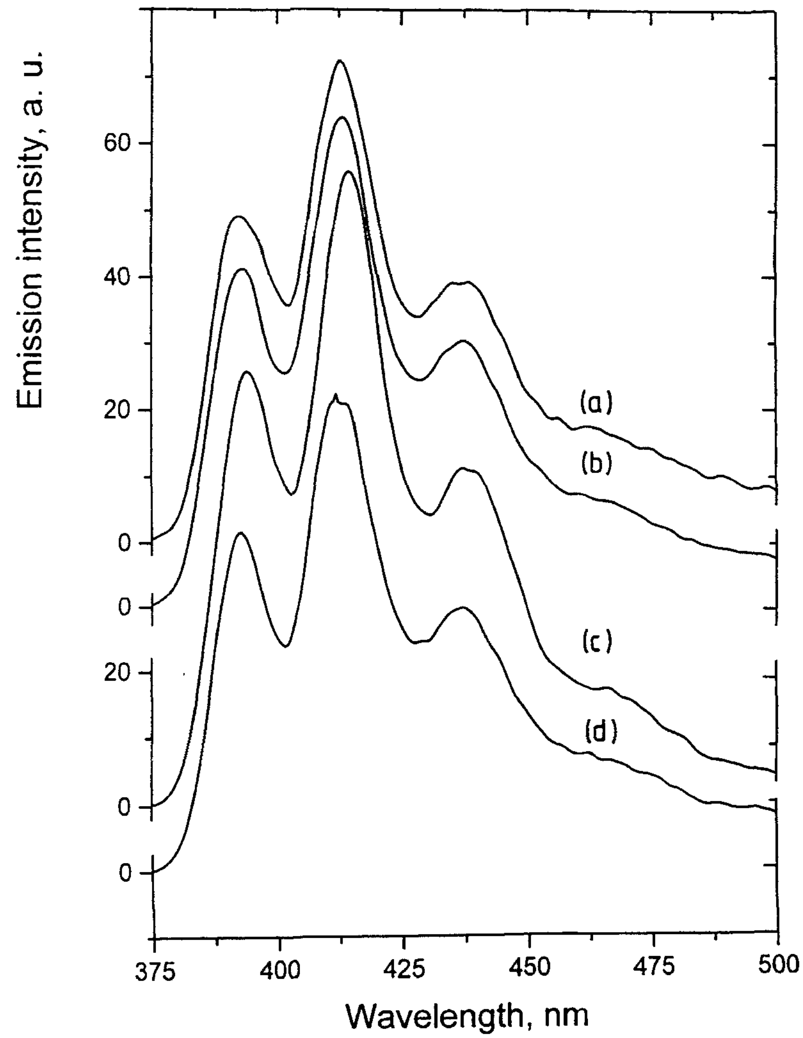

FIGURE 2 Fluorescence emission spectra of Ant-NH-O-O-NH-Ant in methanol ($1.89 \cdot 10^{-5}$ M): (a) uncomplexed and complexed with: (b) Ni^{2+}, (c) Cu^{2+}, (d) Zn^{2+}. The excitation wavelength λ_{exc} = 368 nm

The fluorescence of the chemosensor is quenched due to the thermodynamically favoured PET between the binary aliphatic nitrogen (binary amine) and the excited chromophore (*Ant). Increasing the oxidation potential of the binary amine due to complexation prevents this PET and regenerates the fluorescence of Ant-NH-O-O-NH-Ant [4].

Noticeably, only Cu^{2+} among studied 3d divalent cations, including Ni^{2+} and Zn^{2+} had a distinct effect on the light-emitting properties of the chemosensor. A pH value can be chosen within the interval delimited by the profile of Cu^{2+}[Fig. 3(b)]. Thus, the MeOH/water solution containing Ant-NH-O-O-NH-Ant was adjusted to pH 4.7 with CH_3COOH/CH_3COO^- buffer. The above solution was titrated with solutions of $Ni^{2+}$and Zn^{2+}, Addition of more than 1 equivalent of metal ions had influence only slightly the emission intensity in the case of nickel(II) and

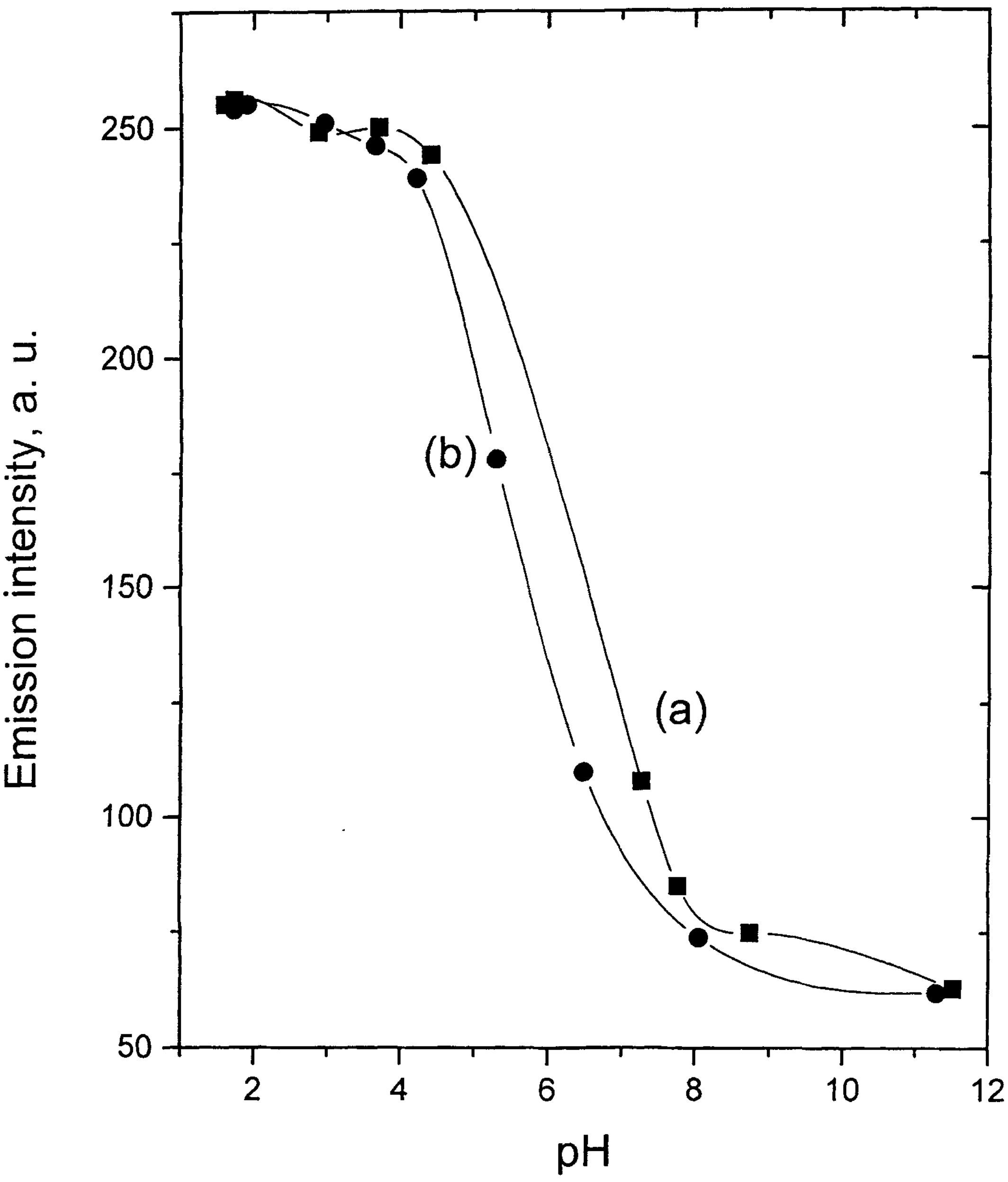

FIGURE 3 pH dependence of the fluorescence intensity for solutions containing Ant-NH-O-O-NH-Ant: (a) uncomplexed and (b) complexed with Cu^{2+}. The curves serve as guides to the eye

zinc(II) ions [Fig. 4(a) and (b)]. When the same solution was titrated with Cu^{2+}, fluorescence has increased linearly after the addition of 0.5 equivalent of copper [Fig. 4(c)]. In general, this reflects the well known greater stability of Cu^{2+} complexes with amine ligands compared with $Ni^{2+}$and Zn^{2+}, in agreement with the Irving-Williams series [5]. This suggests a way to discrimi-

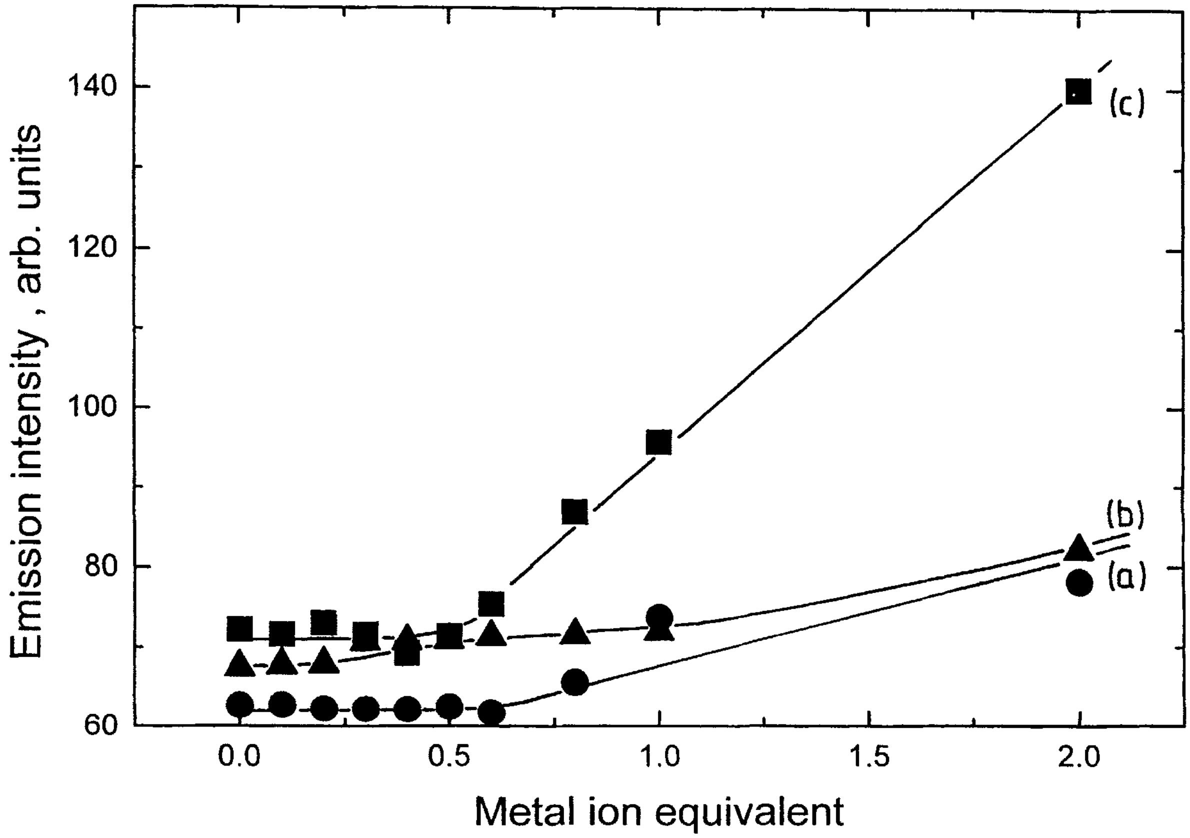

FIGURE 4 Spectrofluorimetric titration of the Ant-NH-O-O-NH-Ant chemosensor by: (a) Ni^{2+}, (b) Zn^{2+} and (c) Cu^{2+} in an MeOH / water solution (4:1, v / v), buffered at pH 4.7 with acetate buffer. The curves serve as guides to the eye

nate between Cu^{2+} and Ni^{2+}(or Zn^{2+}) using the studied fluorescent chemosensor.

The new class of PET chemosensors was tested. We used them for discrimination of $Cu^{2+}$and Ni^{2+} (or Zn^{2+}) cations. In our further studies we focused our attention on immobilization of the same chemosensors in silica xerogel. We expect that this system could be used as a recognition phase in an optical sensor [6].

Acknowledgements

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