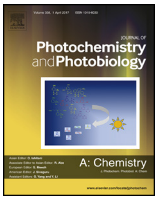
Journal of Photochemistry and Photobiology A: Chemistry 348 (2017) 41–46

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



A novel fluorene-derivative Schiff-base fluorescent sensor for copper (II) in organic media

Fabiane dos Santos Carlos[a], Marcelo Carpes Nunes[a], Leonardo De Boni[b], Guilherme Sippel Machado[c], Fábio Souza Nunes[a],*

[a] Departamento de Química, Universidade Federal do Paraná, Cx. Postal 19081, 81531-980 Curitiba, PR, Brazil
[b] Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP, Brazil
[c] Centro de Estudos do Mar, Universidade Federal do Paraná, Pontal do Paraná, Cx. Postal 61, 83255-976, PR, Brazil

ARTICLE INFO

Article history:
Received 31 May 2017
Received in revised form 7 August 2017
Available online 12 August 2017

Keywords:
Fluorescence
Sensor
Copper(II)
Fluorene
6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione
2-formylpyridine

ABSTRACT

A new Schiff-base sensor containing fluorene was synthesized and investigated for determination of metal ions in dimethylsulfoxide solutions. Fluorescence was quenched upon coordination, showing selectivity for Cu(II) over Mn(II), Fe(III), Ni(II), Pd(II), Zn(II), Ca(II), Hg(II), Na(I) and K(I) in a concentration range of 1.00 to 10.0×10^{-7} mol L^{-1}. Good results were observed for sensor 1 derived from 2-formylpiridine. Benesi-Hilderbrand formalism indicates that the most abundant species formed have 2:1 (metal/ligand) ratio with a calculated biding constant of 1.74×10^{12} L^2 mol^{-2} in good agreement with the Stern-Volmer constant K_{SV} at 2.26×10^{12} L^2 mol^{-2}. The limit of detection (*LOD*) for Cu(II) was found to be 0.037 μmol L^{-1} with a relative standard deviation (*RSD*) of 3.19% in the copper(II) concentration range of 3.00 to 7.00×10^{-7} mol L^{-1}.

1. Introduction

The search for chemical sensors for metal ions has recently been increasing due to their potential applications in many areas such as analytical chemistry, biology and environmental sciences. Sensors are attractive due to their high selectivity, sensitivity and low cost, particularly to essential or hazardous metal ions such as Fe, Cu, Zn, Hg and Cd, for example [1–3].

Copper is an essential element in biological systems as it plays key roles within the cell, but it is also a pollutant and can produce risk of intoxications when in high concentrations in the environment [4].

Copper concentration in the environment comes from natural occurrence, mining activities and industrial discharges. Literature presents some fluorescent sensors for copper ion, with varying degrees of sensitivity, selectivity, applicable conditions of use and difficulty of preparation [5–22].

As part of our continuing effort to study coordination chemistry of polyfunctional ligands, we have developed a new luminescent sensor 1 (Scheme 1) using the photoinduced electron transfer (PET) principle [9].

Fluorene was chosen as fluorophore due to its established photophysical properties [23–27]. Sensor 1 was prepared by connecting diaminodiamide ligand to two equivalents of 2-formylpyridine. As a Schiff base, this ligand forms stable complexes with transition metal ions. However, it has never been reported as a fluorescent sensor. The diaminodiamide unit has interesting coordination properties, but few papers on appending fluorescent groups to this diaminodiamide ligand have been reported [23,28–30].

2. Experimental

2.1. Preparations

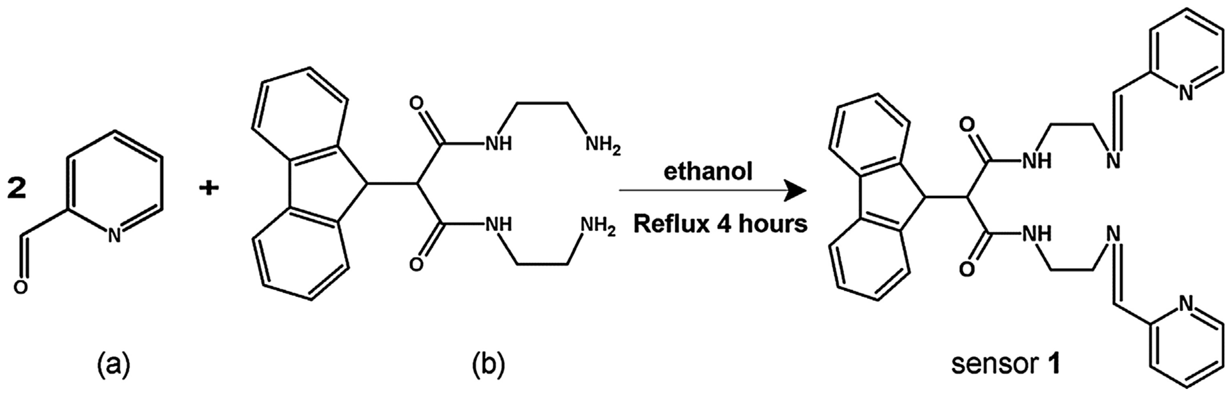
The chemicals used in this work were purchased from Sigma-Aldrich and used as supplied. 6-(9-fluorenil)-1,4,8,11-tetraazaundecano-5,7-dione was prepared as described elsewhere [23].

6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione-1,11-bis (2-iminepyridine), sensor 1 was synthesized according to the same procedure in one step as illustrated in Scheme 1. A 12.0 mmol solution of 2-formylpyridine (a in Scheme 1) in 50 mL of ethyl alcohol was slowly added to 6-(9-fluorenyl)-1,4,8,

---

* Corresponding author.
E-mail address: fsnunes@ufpr.br (F.S. Nunes).

http://dx.doi.org/10.1016/j.jphotochem.2017.08.022



Scheme 1. Synthesis of sensor 1.

11-tetraazaundecane-5,7-dione (1.76 g, 5.00 mmol) (b in Scheme 1) dissolved in 200 mL of ethanol under reflux. The system was refluxed for 4 h. After filtration, the product was recovered, washed with cold ethanol and dried under vacuum.

Sensor 1 is a light-yellow powder, yield of 52%, it decomposes to a dark-brown solid before melting at 161 °C at 768 mmHg. IR data in KBr (cm^{-1}): 3300 ($\nu OH + \nu NH$), 3061, 2944 ($\nu CH_{aromatic}$), 2854 ($\nu CH_{aliphatic}$), 1640, 1620 ($\nu C{=}O_{amide} + \delta NH_{amide}$), 1518 ($\nu C{=}C$), 747-730 $\pi C{=}C$. ^1H NMR δH in ppm in DMSO-d_6, 400 MHz, numbering refer to Supplementary material Fig. SM1: 7.707–8.079 (H1 to H4 of fluorene, m), 7.161–7.500 (H11 to H14 of pyridine rings, m), 2.586–3.170 (H6 and H9, m), 3.673–4.090 (m, H8); 8.631 (H7 and H10, m). ^{13}C NMR δ_C in DMSO-d_6, 400 MHz, numbering refer to supplementary mateiral Fig. SM2: 163.046 (C1), 127.427 (C4), 57.676 (C7), 144.416 (C9), 59.967 (C10), 119.821 (C12), 149.272 (C13), 126.963 (C14). Elemental analysis: Found C, 68.1; H, 5.7; N, 14.9%; molecular formula $C_{32}H_{32}N_6O_4$, requires C, 68.1; H, 5.2; N, 14.9%. HRMS ESI–MS (negative mode) at m/z: Found: $[M\text{-}H]^-$ 529.2285; molecular formula $C_{32}H_{31}N_6O_4$ requires $[M-H]^-$ 529.2352. Uv–vis data λ_{max} (DMSO): 269 nm and $\varepsilon_{max} = 1.27 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$; 262 nm and $\varepsilon_{max} = 4.22 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$. Fluorescence data λ_{max} (DMSO): 278 nm; emission λ_{max} at 307 nm, Stokes shift 29 nm, quantum yield at 11.5% and excited state lifetime at 2.5 ± 0.2 ns.

2.2. Apparatus

Elemental analyses were done in a Perkin-Elmer 2400 analyzer. Mass spectra were measured in a high resolution ESI–MS on a microTOF QII mass spectrometer (Bruker Daltonics, Billerica, MA) from dimethylsulfoxide solutions. ^1H and ^{13}C NMR spectra were recorded in a Bruker Avance HD spectrometer at 400 MHz, DMSO-d_6 was used as solvent and TMS as the internal reference. The chemical shifts are expressed in δ (ppm).

Electronic spectra in the UV–vis range (190–820 nm) were obtained on a diode array Hewlett-Packard 8452A or Varian Cary 50 spectrophotometer in dimethylsufoxide solutions using a 1.0 cm path length quartz cell.

Fluorescence measurements and fluorescence quantum yields were recorded in a 1.0 cm optical path length of a quartz cuvette using a Varian Cary Eclipse or Shimadzu RF5301-PC spectrofluorimeter with a concentration of $1 \times 10^{-5}\ mol\ L^{-1}$ to minimize the re-absorption. The equipment was set at 1.5 nm slit width and 600 $nm.min^{-1}$ scan rate for both excitation and emission spectra. The solutions were always purged with nitrogen prior to the measurements to avoid quenching by dioxygen molecules.

Fluorescence decay was measured employing femtosecond laser as excitation source. The samples were excited at 390 nm wavelength. The excitation wavelength was produced by a BBO thin crystal, which doubled in frequency the 780 nm delivered by a 150 fs CPA Ti:Sapphire laser. The excitation beam was filtered with a blue band pass, removing the IR (780 nm). After that, the laser beam was aligned and focused by a 15 cm convergent lens. The sample was positioned at 5 cm far from the focus in 2 mm fused silica cuvette, at this position the excited spot is about 1.5 mm of diameter, which helps to increase the fluorescence signal collected. The fluorescence was collected with a 1-mm core optical fiber positioned very close to the fluorescent spot. Also, between the sample and the optical fiber, a second optical filter is used to remove the excitation wavelength from the signal. The fluorescence is guided to a fast silicon detector with risetime of about 0.7 ns. The electrical signal, proportional to the fluorescence signal, is averaged during ten minutes with a 1 GHz digital oscilloscope. This procedure is repeated in three replicas by replacing the irradiated sample for a fresh one and recorded to further analyses. After the measurement, UV–vis spectrum was obtained to verify possible degradation due to the laser exposure. In addition to this measurement, the intrinsic electrical response time of the detector was also averaged during ten minutes and recorded to further analyses.

3. Results and discussion

3.1. Photophysics of the sensors

The photophysical and selectivity properties of sensor 1 was carried out in dimethylsulfoxide. Absorption and fluorescence spectra are in Fig. 1. UV–vis spectra show strong intraligand π–π^*

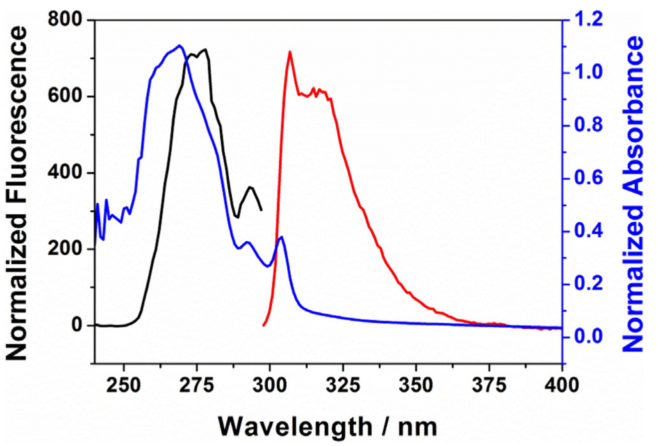


Fig. 1. Normalized Absorbance (blue line), excitation (black) and emission (red) spectra of sensor 1 in 10 $\mu mol\ L^{-1}$ dimethylsulfoxide solutions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)