

Short Note

2,2'-(2,2'-Oxybis(ethane-2,1-diyl)bis(oxy))bis(N-(2,2'-bithiophen-5-ylmethylene)aniline)

Bruno Pedras ¹, Daniel Gallego ¹, Patrick Figueiredo ¹, J lio Dinis Nunes-Miranda ², Jos  Luis Capelo ^{1,2} and Carlos Lodeiro ^{1,2,*}

¹ REQUIMTE, Department of Chemistry, FCT-UNL, 2829-516 Monte de Caparica, Portugal

² BIOSCOPE Group, Physical-Chemistry Department, Faculty of Science, Campus Ourense, University of Vigo, 32004, Ourense, Spain

* Author to whom correspondence should be addressed; E-Mail: clodeiro@uvigo.es.

Received: 8 April 2010 / Accepted: 10 May 2010 / Published: 11 May 2010

Abstract: A new flexible fluorescent compound L derived from 1,5-bis(2-aminophenoxy)-3-oxapentane (**A**) has been synthesized by classical Schiff-base reaction between (**A**) and 2,2'-bithiophene carbaldehyde (**B**). The same synthesis was reproduced by a green methodology using an ultrasonication reaction in a classical sonication bath. The structure of the new compound was confirmed by elemental analysis, IR, ¹H-NMR, MALDI-TOF-MS and EI-MS-spectra, UV-vis and fluorescence emission spectroscopy.

Keywords: imine compounds; fluorescence chemosensors; 2,2'-bithiophene

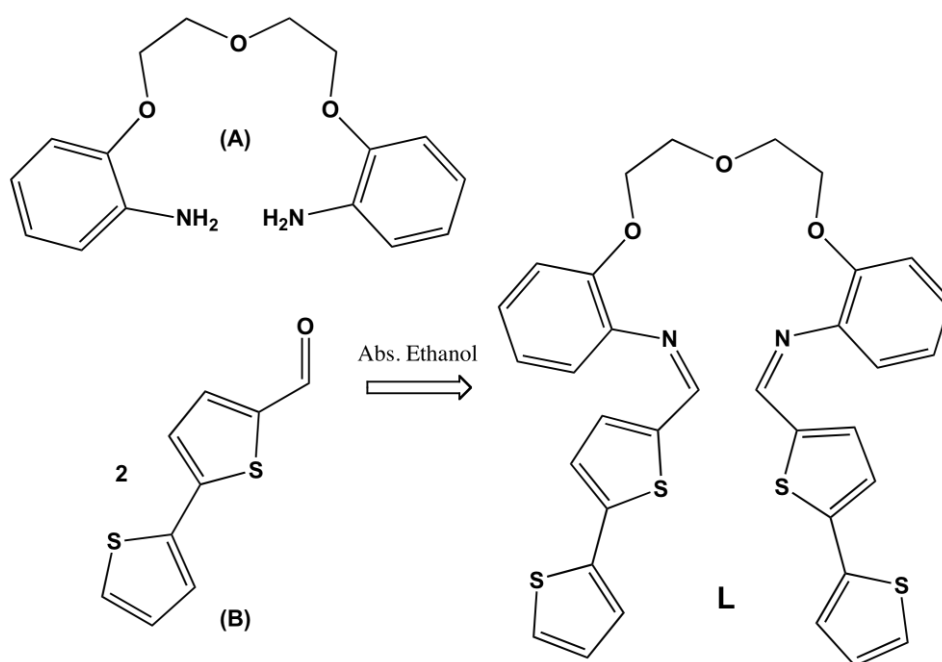
1. Introduction

In the field of fluorescence chemosensors [1] with potential applications as emissive sensing materials, different approaches have been followed for their synthesis [2–4]. A Schiff-base condensation is a classical reaction starting from a primary amine and an active carbonyl group as an easy way to obtain emissive compounds provided with the C=N donor-group [5,6].

Due to the interest of the above suggestion, we planned to synthesize a new emissive compound that combines together two sensing sites, which are a polyoxa chain provided with two phenolic units and two bithiophene chromophores. In the present note, we are reporting a simple method for synthesizing a bithiophene derivative, using classical Schiff-base condensation in ethanolic solution [7–10] and a green method using an ultrasound-assisted synthesis [11], which does not need any catalyst. The work-up procedure was very simple and convenient.

2. Experimental

A mixture of 0.5 mmol of 1,5-bis(2-aminophenoxy)-3-oxapentane (**A**) (0.144 g) and 1 mmol of 2,2'-bithiophene carbaldehyde (**B**) (0.194 g) was added to 50 mL of absolute ethanol, and kept under reflux for 4 h. After that time, the mixture was allowed to cool to room temperature, and a yellow precipitate was formed, which was filtered off and washed with diethyl ether (3 portions of 10 mL) and with cold absolute ethanol (3 portions of 10 mL). The yellow powder was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate, 3/7). The reaction was reproduced in the same solvent using a green methodology, employing a 1510 Branson ultrasonication cleaner bath during 2 h at room temperature with the same results. In order to reduce the quantity of residues, the reaction can be reproduced reducing the solvent employed (absolute ethanol) to 25 or 5 mL. In both cases, the reactants were reduced to 0.25 mmol and 0.5 mmol, and to 0.05 mmol and 0.1 mmol of the amine and the carbaldehyde precursors respectively.



Yield: 300 mg (94%).

EI-MS: m/z (rel. int%): 640.04 (100) ($[L]^+$)

MALDI-TOF-MS: m/z (rel. int%): 641.08 (95) $[L+H]^+$.

^1H NMR (CDCl_3): δ = 8.6 (s, 2H, N=C-H); 7.3–6.9 (m, C-H, Ar); 4.2 (t, 4H, CH_2); 4.0 (t, 4H, CH_2) ppm.

IR (cm^{-1}): 3068 (C-H, Ar), 2926 and 2872 (C-H, Alq), 1659 (C=N), 1609, 1583, 1547 and 1505 (C=C, Ar), 1127 (C-S), 1047 (C-O, Alq).

Elemental analysis: Calcd for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_3\text{S}_4 \cdot 0.5\text{H}_2\text{O}$: C, 62.85; H, 4.50; N, 4.30; S, 19.75. Found: C, 62.95; H, 4.60; N, 4.05; S, 19.80%.

Uv-vis (Absolute ethanol, $[L] = 9.3 \times 10^{-6}$ M, $\lambda_{\max}$ 360 nm; ε ($M^{-1}cm^{-1}$): 29760.

Fluorescence Emission (Absolute ethanol, $[L] = 9.3E^{-6}$ M): $\lambda_{\max}$ 452 nm.

Acknowledgements

We would like to thank Xunta de Galiza (Spain) for project 09CSA043383PR and the University of Vigo, Vicou for projects INOU UVIGO/VICOUC/K914-122P64702/2009 and UVIGO/VICOUC/K912-122P64702/2009. Thanks to the FCT-MCTES/FEDER (Portugal) through national projects POCI/QUI/55519/2004 and PDTC/QUI/66250/2006. B. P thanks FCT/Portugal for the PhD Grant SFRH/BD/27786/2006. C.L. and J.L. thank Xunta de Galicia for the Isidro Parga Pondal Research Program.

References

1. Czarnik, A.W. Chemical Communication in water using Fluorescent chemosensors. *Acc. Chem. Res.* **1994**, 27, 302-308.
2. Lodeiro, C.; Pina, F. Luminescent and chromogenic molecular probes based on polyamines and related compounds. *Coord. Chem. Rev.* **2009**, 253, 1353-1385.
3. Cozzi, P.G.; Dolci, L.C.; Garelli, A.; Montati, M.; Prodi, L.; Zaccheroni, N. Photophysical properties of Schiff-base metal complexes. *New J. Chem.* **2003**, 27, 692-697.
4. Si, S.H.; Chen, F.R.; Zhou, Y.F.; Wang, J.N.; Zhang, H.; Xu, J.G. Enhanced fluorescence sensing of hydroxylated organotins by a boronic acid-linked Schiff-base. *Chem. Commun.* **2009**, 4179-4181.
5. Vázquez, M.; Bermejo, R.M.; Sanmartín, J.; García-Deibe, A.M.; Lodeiro, C.; Mahía, J. Metal complexes with a chiral N4 symmetrical Schiff base. Crystal structures of the ligand and its Cu(II) and Ni(II) "mono-helicates". *J. Chem. Soc. Dalton Trans.* **2002**, 870-877.
6. Lodeiro, C.; Capelo, J.L. Metal ion interaction of two new tritopic N2O3 macrobicycles with B15C5 moieties in acetonitrile solution. *J. Incl. Phen. Mac. Chem.* **2004**, 49, 249-258.
7. Lodeiro, C.; Lima, L.C.; Parola, A.J.; Seixas de Melo, J.S.; Capelo, J.L.; Covelo, B.; Tamayo, A.; Pedras, B. Intramolecular excimer formation and sensing behaviour of new fluorimetric probes and their interactions with metal cations and barbituric acids. *Sensors Act. B Chem.* **2006**, 115, 276-286.
8. Pedras, B.; Santos, H.M.; Fernandes, L.; Covelo, B.; Tamayo, A.; Bértolo, E.; Capelo, J.L.; Avilés, T.; Lodeiro, C. Sensing metal ions with two azomethine-thiophene pincer ligands (NSN): Fluorescence and MALDI-TOF-MS applications. *Inorg. Chem. Commun.* **2007**, 10, 925-929.
9. Fernandes, L.; Boucher, M.; Fernández-Lodeiro, J.; Oliveira, E.; Nuñez, C.; Santos, H.M.; Capelo, J.L.; Nieto-Faza, O.; Bértolo, E.; Lodeiro, C. Exploiting anionic and cationic interactions with a new emissive imine-based b-naphthol molecular probe. *Inorg. Chem. Commun.* **2009**, 12, 925-912.
10. Pedras, B.; Fernandes, L.; Oliveira, E.; Rodríguez, L.; Raposo, M.M.M.; Capelo, J.L.; Lodeiro, C. Synthesis, characterization and spectroscopic studies of two new Schiff-base bithienyl pendant-armed 15-crown-5 molecular probes. *Inorg. Chem. Commun.* **2009**, 12, 79-85.

10. Pedras, B.; Oliveira, E.; Santos, H.; Rodríguez, L.; Crehuet, L.; Avilés, T.; Capelo, J.L.; Lodeiro, C. A new tripodal poly-imine indole-containing ligand: Synthesis, complexation, spectroscopic and theoretical studies. *Inorg. Chim. Acta* **2009**, *362*, 2627-2635.
11. Lodeiro, C.; Capelo, J.L. Beyond the Analytical Chemistry. In *Ultrasound in Chemistry. Analytical Applications*; Capelo, J.L., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp. 129-148.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an Open Access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).