



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Synthesis, photophysical properties and spectroelectrochemical characterization of 10-(4-methyl-bipyridyl)-5,15-(pentafluorophenyl) corrole[☆]



Rhannanda C. Pivetta^a, Bruna L. Auras^a, Bernardo de Souza^a, Ademir Neves^a, Fábio S. Nunes^b, Leandro H.Z. Cocca^c, Leonardo De Boni^c, Bernardo A. Iglesias^{d,*}

^a Laboratório de Bioinorgânica e Cristalografia (LABINC), Departamento de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil

^b Departamento de Química, Universidade Federal Do Paraná, Cx. Postal 19081, 81531-980 Curitiba, PR, Brazil

^c Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

^d Departamento de Química, Universidade Federal de Santa Maria – UFSM, 97105-900 Santa Maria, RS, Brazil

ARTICLE INFO

Article history:

Received 29 June 2016

Received in revised form 15 August 2016

Accepted 10 September 2016

Available online 11 September 2016

Keywords:

Corroles

Trans-A₂B corroles

Photophysical properties

Photodynamic therapy PDT

ABSTRACT

The new bipyridyl-corrole dye 10-(4-methyl-bipyridyl)-5,15-(pentafluorophenyl)corrole, encompassing a coordinative methyl-bipyridine moiety (corrole **2**), was prepared starting from 5-(pentafluorophenyl) dipyrromethane and reacting it with methyl-bipyridyl-carboxaldehyde by Gryko's methodology. It was further characterized by spectroscopic and electrochemical methods. In addition, we investigated experimental photophysical properties, photostability, reactive oxygen species generation (ROS) and aggregation phenomena, which are relevant when selecting photosensitizers used in photodynamic therapy and many other applications. Photophysical properties have demonstrated that the corrole **2** dissolved in dichloromethane has a triplet quantum yield formation of about 51%. Fluorescence and internal conversion quantum yields of 4% and 45%, respectively, have also been determined in order to evaluate which could be was the main pathway of the excited state relaxation. Triplet state formation was also confirmed by measuring indirectly ¹O₂ generation. Additionally, quantum chemistry calculations indicated that the most probable intersystem-crossing pathway takes place through S₁-T₁, corroborating our rate equation model.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Corroles are tetrapyrrolic macrocycle, 18 π -electron Hückel aromatic compounds closely related to porphyrin with a direct pyrrole–pyrrole linkage lacking one methine bridge [1]. Description of the first method of corrole synthesis method was carried out by Johnson and Kay [2] in the late 1960s, motivated by the similarity of corroles to that of cobalt chelating corrin in vitamin B₁₂. A one-pot synthesis described by Gross and collaborators [3] in the 90's followed by remarkable development in the synthesis of

corroles, revolutionized the understanding of this unique tetrapyrrolic derivative.

With respect to their physico-chemical properties, corroles show relatively higher fluorescence quantum yields and molar absorptivities than the corresponding porphyrin macrocycles [4]. Moreover, the non-innocent nature of the corrole ligand in many coordination complexes is now well documented [5]. Their tri-anionic nature due to three inner nitrogen protons results in intriguing properties to corroles, which are significantly different from those of porphyrin macrocycles. In particular, the ability to stabilize relatively higher oxidation states of metals than those of the corresponding porphyrin complexes has increased the use of metalcorroles in catalytical processes [6]. During the last years, corroles have demonstrated potential applications in the field of photochemical sensors [7], artificial photosynthesis [8], material chemistry [9] and nano-biomedical applications [10].

Free-base corroles usually present lower stability under light and air than the porphyrin macrocycles [11]. This mainly originates

[☆] The authors state that the revised article "Synthesis, photophysical properties and spectroelectrochemical characterization of 10-(4-methyl-bipyridyl)-5,15-(pentafluorophenyl)corrole" is original and unpublished and is not being considered for publication elsewhere.

* Corresponding author.

E-mail address: bernardopgq@gmail.com (B.A. Iglesias).

from the electron-rich nature of corrole, reduced aromaticity and deformation of the macrocycles from planarity due to steric hindrance at the core. However, the tri-(pentafluorophenyl)-substituted corrole has been identified to be stable under oxidative degradation when in light and air due to the presence of electron withdrawing pentafluorophenyl groups at the *meso*-carbon and probably is a good choice when higher stability is desired. A few successful functionalizations of corroles reported in the literature shows significant effect on the electronic properties of the corrole macrocycle [12]. Functionalization of the aryl ring at the *meso*-position or in the *para*-position with a pentafluorophenyl is the most common and relatively easy modification [13]. Insertion of strategic aldehydes in this type of compounds, which contains coordinating groups such as pyridines [14] or bipyridines [15], can add new properties, thereby granting new possibilities into the corrole chemistry.

Therefore, partially inspired by the lack of literature reports on peripheral functionalization with coordinating ligands at the *meso*-carbon position of corrole, we report the successful direct 4-Mebpy-corrole conjugates (corrole **2**) obtained by cyclization between C₆F₅-dipyromethane with 4-(methylbipyridyl)-carboxaldehyde moiety.

The structure and electronic properties of this corrole derivative were investigated along with their electrochemical/spectroelectrochemical properties. In addition, we have performed a preliminary study of their photophysical properties, determining fluorescence, internal conversion and intersystem-crossing quantum yields. All these parameters were determined by employing Time-resolved fluorescence and Pulse Train Fluorescence (PTF) techniques. Furthermore, the most probable intersystem-crossing pathway, which occurs through S₁-T₁ transition, was also indicated by quantum chemistry calculations of spin-orbit coupling matrix elements using a CASSCF wavefunction. The present work indirectly explored the potential use of this chemically modified bipyridyl-corrole to be used in photodynamic therapy (PDT) studies.

2. Experimental

2.1. Materials

All reagents were of analytical grade and were purchased from Aldrich or national suppliers. Column chromatography was carried out using silica-flash 230–400 mesh from Aldrich. Analytical preparative thin-layer chromatography was performed on aluminum sheets (1.0 mm thick) Merck TLC silica-gel 60 F₂₅₄.

2.2. Physical measurements

Corrole analysis in a high resolution ESI-MS. (HRMS-ESI) was performed on a micrOTOF QII mass spectrometer (Bruker Daltonics, Billerica, MA). Mass spectra were performed with a methanolic solutions of concentration around 500 ppb with a flow of 180 μ L/min and at capillary of 3000 V–4500 V ¹H, ¹³C, ¹⁹F and COSY 2D NMR spectra were recorded with a Bruker Avance III spectrometer at 600.13 (¹H), 150.9 (¹³C) and 564.68 MHz (¹⁹F) respectively. CDCl₃ was used as solvent and TMS as the internal reference. The chemical shifts are expressed in δ (ppm) and coupling constants (*J*) are given in Hertz (Hz). The UV–vis absorption spectra were measured in the 1.0 mm optical path length of a quartz cuvette using a SHIMADZU UV-1800, with a concentration of about 50 μ M in dichloromethane solution. Fluorescence spectra and fluorescence quantum yields were measured in the 1.0 cm optical path length of a quartz cuvette using a HITACHI F7000 fluorimeter with a concentration 50 times

lower than the one used to measure the absorption. It was diluted to minimize re-absorption by the compound.

Cyclic voltammetry was carried out with an IVIUM CompactStat potentiostat/galvanostat. A gold disc electrode was employed in the measurements at 0.1 mol/L TBAPF₆ (tetrabutylammonium hexafluorophosphate as support electrolyte). Ag/AgNO₃ electrode ([Ag⁺] = 0.01 mol/L in MeCN solution of TBAPF₆ 0.1 mol/L) was used as reference (0.503 V versus SHE) and platinum wire was employed as auxiliary electrodes, respectively. Typical experiments were conducted with a mM concentration in dichloromethane solutions at room temperature. Spectroelectrochemistry measurements were performed with the IVIUM CompactStat potentiostat/galvanostat attached an Agilent 8453 diode-array spectrophotometer with about \approx 1 mmol/L complex and 0.1 mol/L of TBAPF₆ acetonitrile solutions. A three electrode system was used with a thin layer cell of 0.1 cm of internal optical path length. A platinum minigrid was used as transparent working electrode, in the presence of a small Ag/AgNO₃ reference electrode and a platinum auxiliary electrode. The compounds 2-(4-methylpyridin-2-yl)pyridine-4-carbaldehyde **1** and 2,3,4,5,6-(pentafluorophenyl)dipyromethane [16] were synthesized according to the literature.

2.3. Pulse train fluorescence technique

The experimental setup used to measure intersystem crossing rate of corrole **2** includes a frequency-doubled (532 nm), mode-locked and Q-Switched Nd:YAG laser. This laser system delivers a sequence of about 30 short pulses (100 ps FWHM) modulated by the Q-switched envelope (pulse train). The pulses in the train are separated approximately 13.2 ns. The laser characteristic output profile is shown in the Supplementary information section (ESI†, Section 6) with a repetition rate that can be chosen from 3 up to 800 Hz. In the present work, the repetition rate was set at 300 Hz, which delivered an output power of about 30 mW for the whole pulse train [17].

2.4. Electronic structure calculations

All calculations were performed by using the software ORCA, with default parameters unless stated otherwise [18]. The geometry for the corrole **2** and its other three tautomers were first optimized with DFT up to an energy change of less than 5.0×10^{-6} hartree, using the GGA functional PBE [19] and the triple zeta valence basis Def2-TZVP(-F) [20] at the potential of the solvent (dichloromethane), by using the COSMO approach [21]. To obtain a better long range interaction description, the atom-pairwise dispersion correction by Grimme with Becke-Johnson damping was also added [22]. The resolution of identity (RI) for the four center integrals was employed with the corresponding auxiliary basis. After geometry optimization, the frequencies for the normal modes were obtained and no negative energies were found, confirming that the structures were indeed a minimum. A TD-DFT calculation with COSMO corrections was performed to obtain the excited state wave functions and the transition oscillator strengths without TDA approximation [23] and using the same basis. In this part, we searched for the first 25 roots.

The spin-orbit coupling constants for **2** and the equivalent hydrogen substituted molecule were obtained from state-averaged CASSCF wave functions with energies corrected with NEVPT2, choosing a small active space of six electrons in six π -molecular orbitals (CAS(6,6)). Before the perturbation treatment, each averaged state had the orbitals relaxed by one step, as described on ORCA manual (option nev_canonstep = 3). In order to reduce the complexity of the problem, we have chosen the smaller Def2-SV(P) basis functions, also using COSMO to simulate solvent effects. The spin-orbit matrix elements were calculated by using the complete

Download English Version:

<https://daneshyari.com/en/article/4754224>

Download Persian Version:

<https://daneshyari.com/article/4754224>

[Daneshyari.com](https://daneshyari.com)