Dyes and Pigments 140 (2017) 469–479

Contents lists available at ScienceDirect

Dyes and Pigments

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

Electronic structure and NH-tautomerism of a novel metal-free phenanthroline-annelated phthalocyanine

Alexander G. Martynov [a, *], John Mack [b, **], Bokolombe P. Ngoy [b], Tebello Nyokong [b], Yulia G. Gorbunova [a, c], Aslan Yu. Tsivadze [a, c]

[a] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr., 31, Bldg. 4, Moscow, 119071, Russia
[b] Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa
[c] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr., 31, Moscow, 119991, Russia

ARTICLE INFO

Article history:
Received 6 December 2016
Received in revised form
30 January 2017
Accepted 31 January 2017
Available online 1 February 2017

Keywords:
Low-symmetry phthalocyanine
Phenanthroline
UV–Vis spectroscopy
TD-DFT
NH-tautomerism
^{13}C NMR

ABSTRACT

A novel low-symmetry $\mathbf{A_3B}$-type phthalocyanine annelated with a pyrazino[2,3-*f*]phenanthroline ring system and substituted with six solubilizing diisopropylphenoxy-groups (**1**) was synthesized by metal-free DBU-promoted cross-condensation of diiminoisoindolines derived from 4,5-bis(diisopropylphenoxy)phthalonitrile and pyrazino[2,3-*f*][1,10]phenanthroline-2,3-dicarbonitrile. The use of these particular precursors affords $\mathbf{A_3B}$ phthalocyanine in 15% yield, while cross-condensation of the corresponding dinitriles yields only trace amounts of the target compound. Comparative studies of the $\mathbf{A_3B}$-type phthalocyanine and its symmetrical octa(diisopropylphenoxy)-substituted counterpart **2** reveal striking differences in the Q band regions of their UV–visible absorption (UV–Vis) spectra, which could be readily rationalized through a comparison with calculated TD-DFT spectra. Since **1** can have two NH-tautomers with equivalent and non-equivalent NH-groups, and DFT calculations predict that the former tautomer is only 2.3 kcal/mol more stable than the latter one, a comprehensive analysis of ^{13}C NMR spectra was carried out through the application of ^{1}H–^{13}C HMBC and HSQC techniques. It demonstrated that only the tautomer with equivalent NH-groups is present in solution.

1. Introduction

The synthesis and characterization of low-symmetry phthalocyanines (Pc) has been the focus of considerable research in recent decades for several reasons [1–5]. Firstly, the combination of various substituted moieties to form Pc analogues enables the fine tuning of their optical and electrochemical properties to make them suitable for specific scientific and technological applications. Secondly, low-symmetry Pcs often have new properties, which are not observed in their fully-symmetrical counterparts. Among these properties are second-order non-linear optical (NLO) properties, which occur in non-centrosymmetric molecules and the enhancement of third-order nonlinear optical susceptibility [6]. Also, low-symmetry Pcs have charge-transfer properties upon photoexcitation, which is useful for solar energy applications [7–9]. Thirdly, an analysis of their photophysical properties through a comparison with the results of quantum-chemical modelling provides insights into the structure-property relationships of low-symmetry Pcs, and this can be used to guide the rational design of new compounds [2,10–13].

Low-symmetry Pcs bearing various anchoring substituent groups have also attracted considerable attention, since it enables the grafting of molecules onto the surfaces of photo- and electro-active materials [14,15], and the elaboration of multichromophoric assemblies that mimic natural photosynthetic systems [16]. Annelation of the Pc scaffold with a pyrazino[2,3-*f*]phenanthroline (Phen) moiety has resulted in the formation of novel class of low-symmetry molecules, which are expected to exhibit enhanced NLO properties [17] and have potential applications in organic solar cells and organic field-effect transistors [18]. It is anticipated that their properties can be further enhanced through the binding of metal ions at the peripheral Phen sites [19,20]. Herein, we report

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: Martynov.Alexandre@gmail.com (A.G. Martynov), J.Mack@ru.ac.za (J. Mack).

http://dx.doi.org/10.1016/j.dyepig.2017.01.072
0143-7208/