



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaThrough-space electronic communication of zinc phthalocyanine with substituted [60]Fullerene bearing O₂N_xaza-crown macrocyclic ligandsBahram Ghanbari ^{a,*}, Leila Shahhoseini ^a, Niloofar Mahlooji ^a, Parisa Gholamnezhad ^a, Zahra Taheri Rizi ^b^a Department of Chemistry, Sharif University of Technology, Tehran, Iran^b Research Institute of Petroleum Industry, Tehran, Iran

ARTICLE INFO

Article history:

Received 1 May 2016

Received in revised form 13 August 2016

Accepted 16 August 2016

Available online 18 August 2016

Keywords:

[60]Fullerene

Zinc phthalocyanine

Aza-crown

Fluorescence

Quenching

ABSTRACT

Two new macrocyclic ligands containing 17- and 19-membered O₂N₃-donor aza-crowns anchored to [60]Fullerene were synthesized and characterized by employing HPLC, electrospray ionization mass (ESI-MS), ¹H and ¹³C NMR, UV–vis, IR spectroscopies, as well as powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) in solid state. TGA measurements revealed that upon linking each of these macrocycle rings to [60]Fullerene, the decomposition point measured for [60]Fullerene moiety was increased, indicating on the promoted stability of [60]Fullerene backbone during binding to these macrocyclic ligands. Moreover, the ground state non-covalent interactions of [60]Fullerene derivatives of O₂N_x (x = 2, and 3) aza-crown macrocyclic ligands namely, L¹–L⁴ with zinc phthalocyanine (ZnPc) were also investigated by UV–vis absorption, steady state and time resolved fluorescence spectrophotometry in *N*-methyl-2-pyrrolidone (NMP). The calculation of Stern-Volmer constants (*K*_{SV}) indicated on existence of an efficient quenching mechanism comprising of the excited singlet state of ZnPc in the presence of L¹–L⁴. The observation of an appropriate correlation between decrease in fluorescence intensity and lifetime parameters led us to propose the occurrence of a static mechanism for the fluorescence quenching of ZnPc in the presence of L¹–L³. The binding constants (*K*_{BH}) of L¹–L⁴/ZnPc were also determined applying the fluorescence quenching experiments. Meanwhile, the incompatibility of both *K*_{SV} and *K*_{BH} values found for L⁴ was also described in terms of structural features using DFT calculations using the B3LYP functional and 6-31G* basis set.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Among the eminent subjects of the current worldwide research, study on donor-acceptor molecular assemblies is of central topics for light-to-electricity and light to fuel conversion as well as for the purpose of investigation on artificial photosynthetic systems [1–5]. In molecular systems combining various donors and [60]Fullerene acceptors, photoinduced electron transfer and energy transfer have been widely investigated applying mainly their electrochemical and photophysical properties [6–9].

After the initial discovery in 1984, [60]Fullerene and higher fullerenes display a remarkable chemical feature, that is the chemical functionalization of fullerenes [10]. Chemical functionalization of the fullerene cage can be easily achieved, allowing the introduction of various functional groups which can help to both control and manipulate the fullerene molecules and tune the properties of the resulting hybrid compounds. On one hand, the combination of fullerene cages with those of other interesting materials, such as photoactive and/or electroactive units [11] and recently macrocyclic units [12] are diverse strategies which can enhance and tune the physicochemical properties

of the resulting fullerene-containing compound. On the other hand, macrocyclic units anchored to [60]Fullerene could be useful for creating fullerene/transition-metal complexes. Besides, as good electron donors and also excellent light acceptors, transition-metal complexes are largely ideal candidates to association with the fullerene cages to create photoactive donor-acceptor dyads for green energy production. Numerous researches have been directed to assess the performance of fullerene/transition-metal complexes as components of solar cell assemblies [13,14]. Molecular assemblies comprising of [60]Fullerene and transition metal complexes in separate molecules could potentially yield unique compounds which display the properties of their single molecular structures as well as diversified properties. Based on the chemical nature of the transition metal and the type of the fullerene-transition metal linkage, these compounds are potentially applicable in various fields [11]. Correspondingly, the application of such dyads containing [60]Fullerene derivatives as the electron acceptor with diverse donors, such as tetracene, tetrathiafulvalene, chlorines, amine, porphyrins, and ferrocenes, has drawn certain attention of researchers to donor–acceptor interactions.

From the practical point of view, phthalocyanines (Pcs) are the structural analogues of porphyrins which are planar 18 π-electron aromatic macrocycles and perfectly capable to fit to the buckyball structure

* Corresponding author.

E-mail address: ghanbari@sharif.edu (B. Ghanbari).

of fullerenes according their saddle-like macrocycle ring. Meanwhile they could experimentally act as light energy conversion systems. Associated to porphyrins, Pcs enjoy their advantage of having higher absorption around 700 nm which covers the maximum spectra received from the solar photon flux. Numerous systems bearing Pcs as electron donor and [60]Fullerene as electron acceptor have been reported and investigated by researchers during the past decade [15].

In order to identify and study on the charge transfer phenomenon of [60]Fullerene derivatives as the acceptor in donor-acceptor hybrids, spectroscopic techniques have been extensively used [16–19]. As a well-known donor-acceptor hybrid, [60]Fullerene-Pcs have been studied as charge transfer assemblies employing spectroscopic techniques [20–23]. Furthermore, photoactive supramolecular assemblies, in which both donor and acceptor moieties are non-covalently linked together, are principally attractive either as prototypes of the conversion of light into electric current or natural photosynthesis [24–26]. Basically, two mechanisms were introduced for electron transfer phenomena in [60]Fullerene-metallophthalocyanine and/or metalloporphyrin dyads [27]. In the first mechanism the covalent bonding guarantees linking of both donor-acceptor moieties while the other approach enjoys from supramolecular self-assembling of the aforesaid moieties by virtue of so-called interactions as H bonding, electrostatic interactions, metal – ligand coordination, and π - π plane-to-plane stacking of their aromatic rings [27].

On the other hand, a collection of bidentate and tridentate N-donor ligands have been shown to be chemically linked to the [60]Fullerene cage, including 2,2'-bipyridine, 1,10-phenanthroline, diazafluorene, dipyrromethene, and terpyridine. They were capable to bind simultaneously to various transition metal ions creating charged complexes [11]. To the best of our knowledge, however, there is no report on photochemical study of aza-crown derivative of [60]Fullerene with Pcs.

Recently, we reported **L**¹ and **L**² (Fig. 1) as new [60]Fullerene derivatives [12] potentially capable to bind to various transition metal cations as ligands through their macrocycle rings [28].

In the present work, we developed the synthesis of new [60]Fullerene derivatives, **L**³ and **L**⁴ (Fig. 1) to elaborate a systematic study on their basic photochemical behavior as electron acceptor in the presence of ZnPc as a well-known electron donor, in the course of a charge transfer process. Herein, the possibility of non-covalent interactions between **L**¹-**L**⁴ (Fig. 1) with ZnPc are investigated by employing various spectroscopic methods, e.g. absorption, steady state fluorescence and time-resolved fluorescence spectrophotometry in solution as well as DFT calculations.

2. Experimental

2.1. Materials and methods

[60]Fullerene (98%) and ZnPc were purchased from BuckyUSA and Sigma-Aldrich respectively. The other reagents were obtained in analytical and/or chemical grade from Merck without further purification.

UV-vis spectrophotometry was performed on a Rey Leigh UV-2601 equipped with thermo bath applying *N*-Methyl-2-pyrrolidone (NMP) at 25 °C. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker-ARX500 instrument at room temperature. Micro analytical measurements were performed on Truspec CHNS-Com Leco (USA). The fluorescence spectra was run on a Varian Cary Eclipse fluorescence spectrophotometer (Springvale, Victoria, Australia) equipped with 1 cm × 1 cm quartz cells and a xenon lamp which was applied for recording the fluorescence spectra. In these experiments, both of the excitation (340 nm) and emission (671 nm) bands were set at the slit width of 5 nm. TGA was recorded on STA instrument from Germany Linseis (gas flow 30 mL min⁻¹). Mass spectroscopic measurements were carried out on a ThermoFisher Scientific (Bremen, Germany) ion trap mass spectrometer (model LTQ, mass range *m/z* 10–2000) equipped with an electrospray ionization (ESI) interface. Instrument control, data acquisition and processing were conducted by the Xcalibur 2.0 SR2 software. Typical positive ESI-MS conditions were: capillary voltage – 2.0 kV and skimmer cone voltage – 20 V.

The HPLC measurements were carried out using C₁₈ column and flow rate 0.8 mL min⁻¹ with methanol-toluene (30/70 v/v) mixture as mobile phase. Based on the method of Jinno et al. [29], the eluent was monitored at 330, 206 nm since the absorbance associated with toluene at 254 nm would not interfere with the absorbance of [60]Fullerene.

The PXRD patterns were collected on X'Pert PRO MPD PANalytical Company using Cu K $\alpha_{1,2}$ (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2-theta (2 θ) range from 2° to 80°.

2.2. The synthesis of the parent aza-crown macrocyclic ligands **1**–**4**

The precursor dialdehydes as well as the respective O₂N₂ and O₂N₃-azacrowns **1**–**4** were prepared according to the similar method reported before [30,31,32] shown in Scheme 1.

The compounds were purified by using flash column chromatography; their purity was checked by ¹H and ¹³C NMR.

2.3. General procedure for the synthesis of **L**¹–**L**⁴

The [60]Fullerene-linked macrocyclic ligands **L**³ and **L**⁴ (Fig. 1) were synthesized using a general method shown in Scheme 1 employing the similar method reported before for the preparation of **L**¹ and **L**² [12] as follow: 1 g of **3** and/or **4** (in excess) was added to stirred solution of 0.2 g [60]Fullerene in 50 mL toluene under nitrogen atmosphere at ambient temperature. After 10 days, a dark brown solid product was filtered off and decanted several times with toluene to remove any unreacted starting materials. The dark brown-colored products were separated and used as the samples applied for the analyses. The

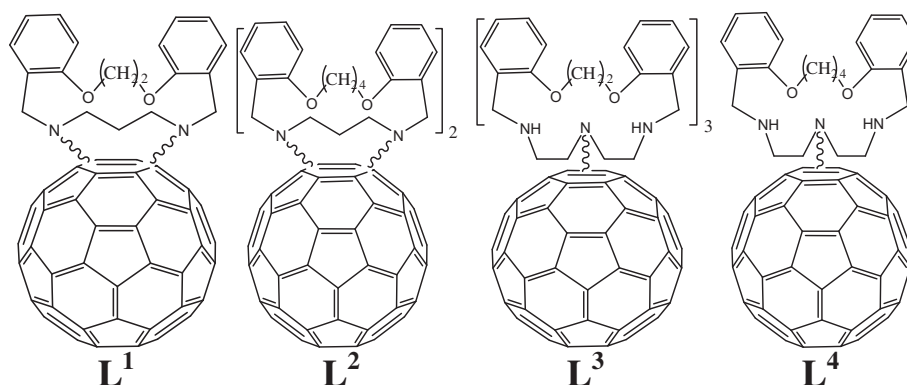


Fig. 1. The structures of O₂N₂ and O₂N₃ aza-crown macrocyclic ligands.

Download English Version:

<https://daneshyari.com/en/article/1229990>

Download Persian Version:

<https://daneshyari.com/article/1229990>

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