



## Novel non-covalent supramolecular systems based on zinc(II) bis(dipyrromethenate)s with fullerenes

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### ARTICLE INFO

#### Article history:

Received 20 March 2018

Received in revised form 31 July 2018

Accepted 11 August 2018

Available online 12 August 2018

#### Keywords:

Zinc(II) bis(dipyrromethenate)s

Fullerenes

Non-covalent

Supramolecular systems

Fluorescence

### ABSTRACT

This paper presents the results of UV/vis, fluorescence, FT-IR, DOSY, and DFT study of a novel non-covalent supramolecular systems based on zinc(II) bis(dipyrromethenate)s ( $[Zn_2L_2]$ ) with  $C_{60}$ . It was found that zinc(II) bis(dipyrromethenate) forms stable supramolecular  $\pi$ - $\pi$ -complexes ( $[Zn_2L_2(C_{60})_4]$ ) with  $C_{60}$ . DFT calculations revealed stable complexation between  $[Zn_2L_2]$  and  $C_{60}$ . The  $[Zn_2L_2(C_{60})_4]$  LUMO energy levels are predominantly spread on the  $C_{60}$  unit and the HOMO energy levels are mainly spread on the  $[Zn_2L_2]$ . The photoinduced electron transfer testing by the substantial fluorescence quenching of the  $[Zn_2L_2]$  by non-covalently bonded  $C_{60}$  gives the positive result that shows prospects of the studying  $[Zn_2L_2(C_{60})_4]$  as the active layers in solar energy conversion devices.

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### 1. Introduction

Fullerenes are remarkable electron acceptors. It is common to consider fullerenes are electron-deficient polyene systems rather than aromatic molecules. Extensive three-dimensional spherical form of fullerene molecules facilitates delocalization of charges along their entire structure and provides unique opportunities for stabilization of charged particles [1,2]. In addition, fullerenes possess unique electrochemical and characteristic spectral properties [3,4]. Special attention is attracted to the search and receipt of supramolecular systems based on various nature fullerenes [5,6]. This is due to the fact that complexes can be used to create photosynthetic and photonic devices [7–9]. Effective complexation with a molecular ligand is feature of supramolecular chemistry of fullerenes. Host-guest systems are one of the typical and often obtained supramolecular systems based on fullerenes. Various host molecules have been designed in recent past, for example, carbon nanotubes [10], crown ethers [11,12], calixarenes [13], cyclodextrins [14]. On the other hand, porphyrins [15–19] and phthalocyanines [20,21] are often used as receptors for fullerenes covalent binding. Porphyrin (phthalocyanine) – fullerene covalent systems are good platforms for creating alternative photosynthetic reaction centers. This is due to the high electron-donor ability of extended conjugated macrocyclic  $\pi$ -systems of porphyrins and phthalocyanines [22,23]. A large

number of papers are devoted to the studies of covalently bound porphyrin-fullerene complexes [24–26]. Their study was an important step in understanding the mechanism governing photoinduced electron transfer in molecular systems [23,27]. However, the supramolecular assembly of non-covalent fullerene-containing systems is another rapidly developing approach for the photoactive components production. This method has the advantages of synthesizing covalent porphyrin-fullerene systems. Ease of implementation is one of the main advantages. Therefore, the search of powerful  $\pi$ -electron-donor systems capable of interacting with fullerene molecules due to  $\pi$ - $\pi$  interactions is an important task. From this point of view, a new class of luminophores based on zinc(II) bis(dipyrromethenates) ( $[Zn_2L_2]$ ) is of considerable interest. It is important to note that the data on supramolecular complexes of  $[Zn_2L_2]$  with fullerenes are absent in modern literature. However,  $[Zn_2L_2]$  having intense luminescent properties are promising building blocks for creating molecular architectures with charge separation.

Binuclear helicates ( $[Zn_2L_2]$ ) are luminescent dyes with intense and clear absorption spectra and high sensitivity of fluorescence characteristics to the medium properties. It was shown earlier that  $[Zn_2L_2]$  form stable supramolecular complexes of the composition  $[Zn_2L_2X_n]$  (X is an aromatic molecular ligand) due to  $\pi$ -stacking of aromatic systems of helicate dipyrromethene domains and X molecules [28–30]. The  $\pi$ -stacking efficiency, luminophore polarization, and components mobility in supramolecular complex increase the probability of nonradiative transitions in the excited state. Thus, creating of the capable of

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