



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

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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 π - π -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 π -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 π -electron-donor systems capable of interacting with fullerene molecules due to π - π 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 π -stacking of aromatic systems of helicate dipyrromethene domains and X molecules [28–30]. The π -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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photoinduced charge transfer supramolecular structures based on the electron-donating $[Zn_2L_2]$ and electron-accepting fullerenes can lead to the effective photoactive molecular systems development for optoelectronics and photovoltaic devices.

In this paper, we present the first results of obtaining, experimental and theoretical studies of non-covalent supramolecular systems based on zinc(II) bis(dipyrromethenate) and C_{60} (Scheme 1).

2. Experimental

2.1. Materials and instrumentations

All commercial reagents and solvents were used without purification unless otherwise stated. The C_{60} (99.5%) has been purchased from Aldrich, USA.

FTIR spectra of the non-covalent supramolecular systems based on $[Zn_2L_2]$ with C_{60} were recorded on a VERTEX 80v spectrometer using KBr pellets from 4000 to 400 cm^{-1} .

The absorption and fluorescence spectra of samples in organic solvents were recorded on an SM 2203 (SOLAR) spectrofluorimeter. A solution of Rhodamine 6G in ethanol with the known fluorescence quantum yield (φ) equation of 0.94 was used as the standard for the φ determination [31].

The equation (Eq. (1)) for calculating the fluorescence quantum yield:

$$\varphi_x = \varphi_{st} (S_x/S_{st}) \cdot (A_{st}/A_x) \cdot (n_x/n_{st})^2 \quad (1)$$

where φ_x - fluorescence quantum yield of substance, φ_{st} - fluorescence quantum yield of the standard (Rhodamine 6G), S - integrated fluorescence intensity (area under spectrum), A - the absorbance at the excitation wavelength (480 nm), n - refractive index.

All NMR experiments were performed on a Bruker Avance III-500 NMR spectrometer equipped with a 5 mm probe using standard Bruker TOPSPIN Software. Temperature control was performed using a Bruker variable temperature unit (BVT-2000) in combination with a Bruker cooling unit (BCU-05) to provide chilled air. Experiments were performed at 298 K without sample spinning. Tetramethylsilane (TMS) was used as an internal standard. The two-dimension Diffusion Order Spectroscopy (2D DOSY) spectra were recorded with PGSTE pulse sequence using a bipolar gradient pulses and the insertion of a supplementary delay (LED) [32–35]. The PGSTE sequence was used with LED pulses, the bipolar gradient pulses for diffusion, two spoil gradients, a diffusion delay of 0.15 s, a total diffusion-encoding pulse width of 1.5 ms. For each of 16 gradient amplitudes, 16 transients of 16,384 complex data points were acquired.

Geometry optimization were performed on the basis of density functional theory with the CAMB3LYP [36] functional and the 6-31G (d,p) [37,38] basis set. The influence of intramolecular dispersion interactions on the structure was explored using the dispersion corrections introduced by S. Grimme (D3) [39]. Harmonic vibrational frequencies were computed at the same level of theory for S_0 state in order to characterize the stationary points as true minima, representing equilibrium structures on the potential energy surfaces. The polarizable continuum model (PCM) applying dielectric constants of toluene allowed evaluating solvation effects.

All DFT computations were performed by means of PC GAMESS v.12 program package [40]. The UCSF Chimera package [41] and ChemCraft 1.8 (<http://www.chemcraftprog.com>) were used for analyses of results and molecular graphics.

2.2. Synthesis of the $[Zn_2L_2]$

The synthesis, X-ray and elemental analysis, ^1H NMR, UV and IR spectroscopy data for complexes $[Zn_2L_2]$, and respective bis(dipyrromethene) dihydrobromides were described in previous works [42–45].

2.3. Synthesis of the $[Zn_2L_2(C_{60})_n]$

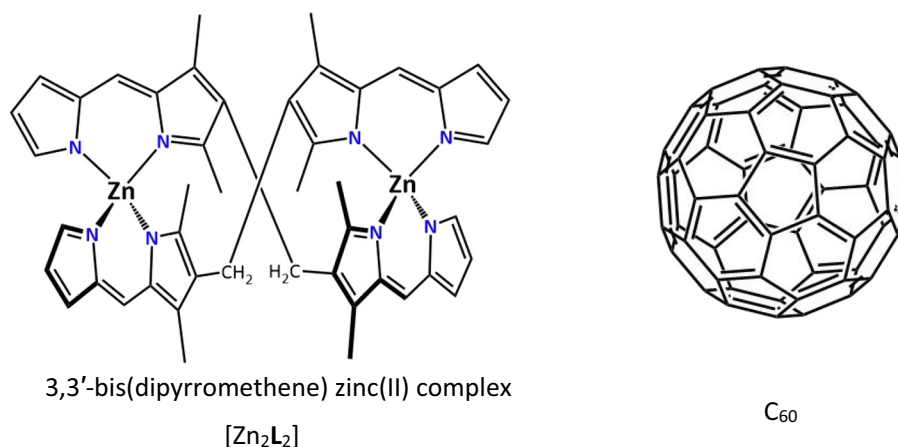
Crystalline samples formed by supramolecular complexes based on zinc(II) bis(dipyrromethenate)s and C_{60} were obtained by the slow crystallization from solutions in toluene ($[Zn_2L_2] = 4.6 \cdot 10^{-5}\text{ mol/L}$ and $c_{C_{60}} = 1.9 \cdot 10^{-4}\text{ mol/L}$) at a temperature about 300.15 K. The samples were withstand (over 24 h) to constant weight under vacuum to remove of residual weakly bound solvent.

FT-IR (KBr, cm^{-1}): $[Zn_2(L)_2(C_{60})_4]$: 2949 ($\nu(\text{CH}_3)$), 2920 ($\nu(\text{CH}_2)$), 2851 ($\nu(\text{CH}_2)$), 1600 ($\nu(\text{C}_\alpha\text{-C}_n)$), 1497 ($\nu(\text{C}_\beta\text{-C}_\beta)$), 1429 (C_{60}), 1389 ($\nu(\text{pyrrole})$), 1274 ($\nu(\text{pyrrole})$), 1182 (C_{60}), 1160 ($\nu(\text{C}_\beta\text{-C}_m\text{-C}_\beta)$), 1101 ($\delta(\text{C}_\beta\text{-H})$), 1035 ($\delta(\text{C}_\beta\text{-H})$), 983 (CH_3 rock), 922 (CH_3 rock), 886 (CH_3 rock), 854 ($\delta(\text{pyrrole})$), 797 ($\delta(\text{pyrrole})$), 747 ($\gamma(\text{C}_\beta\text{-H}) + \gamma(\text{C}_\alpha\text{-H})$), 726 ($\delta(\text{pyrrole})$), 691 ($\delta(\text{pyrrole})$), 577 (C_{60}), 527 (C_{60}), 454 (Zn-N).

3. Results and discussion

3.1. UV-vis absorption and fluorescence studies

Spectrofluorimetric studies showed that the weak blue shift (at 1 nm) of the $[Zn_2L_2]$ intense band maximum is observed in the electronic absorption spectrum when the $[Zn_2L_2]$ solution in toluene is titrated by C_{60} solution in toluene.



Scheme 1. The investigation objects.

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