### Accepted Manuscript

Through-space electronic communication of zinc phthalocyanine with substituted [60]fullerene bearing  $O_2N_x$ Aza-crown macrocyclic ligands

Bahram Ghanbari, Leila Shahhoseini, Niloofar Mahlooji, Parisa Gholamnezhad, Zahra Taheri Rizi

 PII:
 \$1386-1425(16)30484-X

 DOI:
 doi: 10.1016/j.saa.2016.08.031

 Reference:
 \$AA 14617

To appear in:

Received date:1 May 2016Revised date:13 August 2016Accepted date:16 August 2016

Please cite this article as: Bahram Ghanbari, Leila Shahhoseini, Niloofar Mahlooji, Parisa Gholamnezhad, Zahra Taheri Rizi, Through-space electronic communication of zinc ph-thalocyanine with substituted [60]fullerene bearing  $O_2N_x$ Aza-crown macrocyclic ligands, (2016), doi: 10.1016/j.saa.2016.08.031

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# Through-Space Electronic Communication of Zinc Phthalocyanine with Substituted [60]Fullerene bearing O<sub>2</sub>N<sub>x</sub>Aza-Crown Macrocyclic Ligands

Bahram Ghanbari<sup>\*\*</sup>, Leila Shahhoseini<sup>a</sup>, Niloofar Mahlooji<sup>a</sup>, Parisa Gholamnezhad<sup>a</sup>, Zahra Taheri Rizi<sup>b</sup>

<sup>*a*</sup> Department of Chemistry, Sharif University of Technology, Tehran, Iran <sup>*b*</sup>Research Institute of Petroleum Industry, Tehran, Iran

Two new macrocyclic ligands containing 17- and 19-membered O<sub>2</sub>N<sub>3</sub>-donor aza-crowns anchored to [60]Fullerene were synthesized and characterized by employing HPLC, electrospray ionization mass (ESI-MS), <sup>1</sup>H and <sup>13</sup>C 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  $O_2N_x$  (x = 2, and 3) aza-crown macrocyclic ligands namely,  $L^1-L^4$  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  $L^1-L^4$ . 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  $L^1-L^3$ . The binding constants ( $K_{\rm BH}$ ) of  $L^1$ - $L^4$ /ZnPc were also determined applying the fluorescence quenching experiments. Meanwhile, the incompatibility of both  $K_{SV}$  and  $K_{BH}$  values found for  $\mathbf{L}^4$  was also described in terms of structural features using DFT calculations using the B3LYP functional and 6-31G\* basis set.

Keywords: [60]Fullerene; zinc phthalocyanine; aza-Crown; fluorescence; quenching

#### **1. Introduction**

Amongst 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 physiochemical 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  $\pi$ -electron aromatic macrocycles and perfectly capable to fit to the buckyball structure 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 donoracceptor 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  $\pi$ – $\pi$  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  $\mathbf{L}^1$  and  $\mathbf{L}^2$  (Fig. 1) as new [60]Fullerene derivatives [12] potentially capable to bind to various transition metal cations as ligands through their macrocycle rings [28].



Fig. 1. The structures of O<sub>2</sub>N<sub>2</sub> and O<sub>2</sub>N<sub>3</sub> aza-crown macrocyclic ligands

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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> 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 1cm×1cm 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<sup>-1</sup>). 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 -20V.

The HPLC measurements were carried out using  $C_{18}$  column and flow rate 0.8 mL min<sup>-1</sup> 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 $\theta$ ) 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  $O_2N_2$  and  $O_2N_3$ -azacrowns 1-4 were prepared according to the similar method reported before [30,31,32] shown in Scheme 1.



Scheme 1. The synthetic procedure for the preparation of  $L^1-L^4$ ; The reaction conditions were as follow: I. ethanol, reflux, 2 (for n=2) and 4 (for n=4) days, II. dry methanol, reflux, 20 min, III. stirring at room temperature, IV. toluene, reflux for 10 days.

The compounds were purified by using flash column chromatography; their purity was checked by <sup>1</sup>H and <sup>13</sup>C 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 separated yields of  $L^3$  and  $L^4$  were determined as 71, and 62%, respectively. The following analytical data was also found for:

#### *Macrocyclic derivative* $L^3$

Mass spectral parent peak for  $[M+H]^+$ , m/z 1746.6.

<sup>1</sup>H NMR: 2.40 (*broad s*, ArCH<sub>2</sub>NH), 2.61 (*t*, ArCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>), 2.72 (*t*, ArCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>), 3.83 (*s*, Ar-CH<sub>2</sub>N) 4.41 (*t*, OCH<sub>2</sub>), 6.92-7.31 (*m*, aromatic H)

<sup>13</sup>C NMR: 48.54 (ArCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>), 41.03, 48.90 (ArCH<sub>2</sub>NHCH<sub>2</sub>), 50.68 (Ar-CH<sub>2</sub>N), 67.05 (OCH<sub>2</sub>), 110.91, 120.66, 120.92, 125.32, 128.24, 128.46, 128.52, 129.06, 131.12, 131.38, 137.88, 143.10, 157.25 (*aromatic* C)

IR v (cm<sup>-1</sup>) 758, =C-H; 526, 1488, 1450 C=C;2846, 2937, C-H, 3392, N-H.

#### *Macrocyclic derivative* $L^4$

Mass spectral parent peak for  $[M+H]^+$ , m/z 1091.2

<sup>1</sup>H NMR: 1.95 (*broad s*, ArCH<sub>2</sub>N**H**), 2.08 (*m*, OCH<sub>2</sub>C**H**<sub>2</sub>), 2.73-2.80 (*t*, ArCH<sub>2</sub>NHC**H**<sub>2</sub>), 3.80 (*s*, Ar-C**H**<sub>2</sub>N) 4.03(*t*, OC**H**<sub>2</sub>), 6.89-7.29 (*m*, *aromatic* **H**)

<sup>13</sup>C NMR: 18.48 (OCH<sub>2</sub>CH<sub>2</sub>), 26.39 (ArCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>), 49.48, 49.82 (ArCH<sub>2</sub>NHCH<sub>2</sub>), 51.14 (Ar-CH<sub>2</sub>N), 67.17 (OCH<sub>2</sub>), 110.56, 11.03, 120.41, 128.06, 128.56, 130.84, 143.10, 157.27 (*aromatic* C)

IR v (cm<sup>-1</sup>) 758, =C-H; 526, 1488, 1450 C=C; 2846, 2937, C-H; 3392, N-H.

#### 2.4. Photophysical measurements

The quantum yields of the complexes,  $\mathbf{L}^{n}/ZnPc$  ( $\mathbf{L}^{1}-\mathbf{L}^{4}$ ), were recorded in NMP. The absorption and the emission intensities in the fluorescence spectra of  $\mathbf{L}^{n}/ZnPc$  were measured at fixed concentrations of ZnPc and variable concentrations of  $\mathbf{L}^{1}-\mathbf{L}^{4}$  ( $1.8\times10^{-5}$ ,  $3.6\times10^{-5}$ ,  $5.4\times10^{-5}$ ,  $7.2\times10^{-5}$ ,  $9\times10^{-5}$ ,  $1.1\times10^{-4}$  mol dm<sup>-3</sup>). Then, the absorption and emission intensities of ZnPc were employed as the standard fluorophore [33]. The other operative parameters as source of light, slit width, and cuvette were fixed during the measurements. Moreover, the absorption intensities were plotted against emission intensities and the slopes of these graphs were calculated for the complexes of  $\mathbf{L}^{n}/ZnPc$  as well as the standard sample. Employing these slopes and Eq. (1), the relative quantum yield for  $\mathbf{L}^{n}/ZnPc$  ( $\mathbf{Ø}_{\rm F}$ ) were calculated.

$$\emptyset_{\rm F} = \emptyset_{\rm F}^{\rm ZnP_{\rm C}} \frac{F \cdot A_{\rm ZnP_{\rm C}} \cdot n^2}{F_{\rm ZnP_{\rm C}} \cdot A \cdot n_{\rm ZnP_{\rm C}}^2} \qquad {\rm Eq.} (1)$$

where *F* and  $F_{ZnPc}$  are the slopes of  $\mathbf{L}^{\mathbf{n}}/\mathbb{Z}nPc$  and the standard samples, respectively. *A* and  $A_{ZnPc}$  represent the absorbance of the complexes of  $\mathbf{L}^{\mathbf{n}}/\mathbb{Z}nPc$  and  $\mathbb{Z}nPc$ , respectively, at the excitation wavelength (in 1% pyridine in toluene) while the quantum yield for the standard sample was  $\mathcal{O}_{F}^{ZnPc}=0.30$  [33] and *n* and  $n_{ZnPc}$  are correspondingly the refractive indices of the solvent applied for dissolution of the complexes of  $\mathbf{L}_{\mathbf{n}}/\mathbb{Z}nPc$  as well as the standard samples [34].

#### **3.** Results and Discussion

### 3.1. The synthesis and characterization of $L^3$ and $L^4$

The synthesis of  $L^3$  and/or  $L^4$  was accomplished by stirring the mixture containing 15 equivalent weight of 3 and/or 4 in the presence of one equivalent weight of [60]Fullerene in toluene at ambient temperature stirring for several days. The excess mole ratio of the

macrocycle:[60]Fullerene was applied to ensure the maximum derivatization capability of [60]Fullerene with **3** and/or **4** [35].

From the practical point of view, ESI-MS has been conventional as the method of choice for the mass spectrometric study on [60]Fullerene derivatives [36–38]. Recently, we successfully applied ESI-MS for the characterization of  $L^1$  and  $L^2$  [12]. In similar experiments based on the ESI-MS results obtained for  $L^3$  and  $L^4$ , the molecular ion [M+H]<sup>+</sup> afforded the main peak in the spectrum of  $L^3$  at m/z 1746.6 which indicated on a 3:1 mole ratio for **3**:[60]Fullerene in  $L^3$ .

In the meantime, a 1:1 mole ratio of 4:[60]Fullerene in  $L^4$  was found by observing the protonated molecular ion  $[M+H]^+$  at m/z 1091.2. Then, the purity of  $L^3$  was also checked by employing HPLC method in order to phase out the presence of any other mole ratios of 3:[60]Fullerene in  $L^3$  sample except for 3:1 mole ratio which was found in its mass spectrum. Basically, liquid chromatography (LC) is the most effective separation technique which is applicable for the separation of Fullerenes as well as their derivatives [39]. The chromatogram in Fig. 1S specifies the purity of  $L^3$  in terms of any other derivatives as by-product.

In conclusion, Table 1 summarizes the ratio of macrocycle:[60]Fullerene for  $L^1-L^4$  calculated by ESI-MS results.

Table 1. The calculated number of macrocyclic	c ligands linked to [60]Fullerene in $\mathbf{L}^{1}$ - $\mathbf{L}^{4}$
---	--

compound	mole ratio of
	aza-crown:[60]Fullerene
$L^1$	1:1 [12]
$L^2$	2:1 [12]
$\mathbf{L}^{3}$	3:1
$\mathbf{L}^{4}$	1:1

Moreover, TGA results (Fig. 2S) illustrated significant variations in thermal behaviour of  $L^3$  and  $L^4$  comparing with pristine [60]Fullerene. Fig. 2S generally showed no upsurge in weight due to added oxygen was experienced before weight loss begins for these samples. Besides, the recorded TGA curves for **3** and **4** represented two main weight-loss steps; 65-80% decomposition at 350-450°C and subsequent 20-35% decomposition at 450-800°C. Fig. 2S also displayed that decomposition of  $L^3$  consists of two steps of weight loss: 51% from 100 to 390 °C, and 49% from 460 to 590 °C. Similarly, TGA curve for  $L^4$  (Fig. 2S) demonstrated a 30% weight loss from 220 to 480 °C essentially assigned to the first major decomposition step of  $L^4$  (by comparison with TGA curve for **4**), following a 70% weight loss from 490 to 780 °C mainly assigned to the decomposition of [60]Fullerene backbone. Taking into account the abovementioned discussion for the comparison of TGA curve of  $L^3$  with  $L^4$  at <400°C (Fig. 2), it was found that more weight loss for  $L^3$  was observed than the corresponding curve for  $L^4$ . This was another indication of 3:1 mole ratio proposed for **3**:[60]Fullerene (in  $L^3$ ). The HF/3-21G optimized structure for 3:1 mole ratio of **1**:[60]Fullerene resulted in the structure shown in Fig. 3S.

Besides, These TGA curves indicated on significant differences in thermal behaviour of both  $L^3$ , and  $L^4$  with respect to the corresponding results for their paten macrocyclic ligands, 3, 4 as well

as [60]Fullerene. Meanwhile, the temperature of thermal decomposition reported for pure [60]Fullerene was 475 to 625 °C (mainly at 545 °C) [40] which was far from the observed value found for  $L^3$  as well as  $L^4$  (in Fig. 2S). The TGA results found for  $L^3$  and  $L^4$  were also consistent with our recent observation for  $L^1$  and  $L^2$  [12].

Comparing the thermal decomposition temperature of pure [60]Fullerene [41] in Table 2 with those found in Fig. 2S for  $L^3$  and  $L^4$  unveiled that [60]Fullerene moiety generally received more stabilization upon linking to 3 and 4.

Table 2.	Thermal	decomposition	temperature	obtained	for	free	and	the	bonded	forms	of
[60]Fuller	rene to 3 (	in $L^3$ ) and 4 (in )	$L^4$ )			)					

Decomposition Temperature (°C) for					
free [60]Eullerene in					
	$L^3$	$L^4$			
470 [41]	500-600	550-750			

The presence of [60]Fullerene backbone in  $L^3$  and  $L^4$  derivatives was also examined by employing powder X-ray diffraction (PXRD) analysis. The patterns of PXRD found for  $L^3$  and  $L^4$  were compared with the pattern of pristine [60]Fullerene in Fig. 4S.

The first three peaks in the XRD pattern of pristine [60]Fullerene powder shown in Fig. 4S were assigned to Bragg diffractions from (111), (220), and (311) crystal planes [42]. On one hand, the corresponding peaks of  $L^3$ , and  $L^4$  (in Fig. 4S) are much broader than those of the pristine [60]Fullerene powder. On the other hand, it should be noted that the peak indexed to (111) of [60]Fullerene in the XRD pattern of  $L^3$ , and  $L^4$  (in Fig. 4S) was blue-shifted from that in the XRD pattern of the [60]Fullerene. These evidence suggested that the interplanar distance of  $d_{111}$  was little larger in  $L^3$ , and  $L^4$  than that in the pristine [60]Fullerene powder. Furthermore,  $L^3$ , and  $L^4$  exhibit new diffraction patterns at 20 9.5° and 8.5° which furnish solid [60]Fullerene moiety of  $L^3$ , and  $L^4$  in various packing lattices.

The structures of  $L^3$  and  $L^4$  were also monitored by <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> (Fig. 4S).

In The next step, selected proton and carbon chemical shifts ( $\delta$ ) of  $L^3$  and  $L^4$  (shown in Fig. 5S) were collected in Table 3 and compared with the corresponding chemical shifts found for free macrocyclic ligands 3 and 4.

Table 3. The proton and carbon chemical shift changes ( $\Delta\delta$ ) recorded for  $L^3$  and  $L^4$  versus 3 and 4 in CDCl<sub>3</sub>

		Chemical shift of the hydrogen and carbon atoms					
Compound	ArCH <sub>2</sub> N	Ar <u>C</u> H <sub>2</sub> N	ArCH <sub>2</sub> NCH <sub>2</sub>	ArCH <sub>2</sub> NCH <sub>2</sub>	ArCH <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N	ArCH <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N	
L <sup>3</sup>	3.82	50.68	2.73	48.90*	2.63	48.54	
3	3.83	51.1	2.71	49.3	2.60	49.0	
Δδ (ppm)	-0.01	-0.42	0.02	-0.4	0.03	-0.82	
$\Delta_{\rm obs}$ (Hz)	-4	-168	8	-160	12	328	
$L^4$	3.80	51.14	2.79	49.82	2.75	49.48	

4	3.82	51.50	2.80	50.20	2.76	49.82*
Δδ (ppm)	-0.02	-0.36	-0.01	-0.18	-0.01	-0.32
$\Delta_{\rm obs}$ (Hz)	-8	-144	-4	-72	-4	-128

\* the least chemical shift value was considered (see the  ${}^{13}C$  NMR spectral assignment for  $L^3$ ).

As it is evident from the data in Table 3, the maximum value of  $\Delta_{obs}$  recorded for proton and carbon atoms of -CH<sub>2</sub>- groups near by the nitrogen groups were 12 and 328 Hz, respectively. Such values are much greater than that expected for the solvation effect. In conclusion, these  $\Delta_{obs}$  were increased as the result of the covalent bonding of the nitrogen donor groups with [60]Fullerene. Similar features have previously been reported for some complexes of [60]Fullerene with a series of aromatic hydrocarbons and methylpyridines [43,44].

#### 3.2. UV-vis and fluorescence investigations

In the following experiments the interaction of  $L^1-L^4$  ( $L^n$ ) with ZnPc was studied in NMP since we found NMP as the good solvent for dissolution of  $L^n$ . Besides, previous spectroscopic reports [45] have presented that the aggregation of [60]Fullerene in their NMP solutions proceeds at the concentration range >0.05×10<sup>-2</sup> g cm<sup>-3</sup> which was fairly higher than the selected concentrations in our experiments. The first evidence on the interaction of  $L^n$  with [60]Fullerene in NMP was observed employing UV-vis spectrophotometry shown in Fig. 2.





Wavalenght(nm.)



Fig. 2. The UV–vis titration of  $L^{1}$ - $L^{4}$  with ZnPc in NMP as solvent, keeping the concentration of ZnPc fixed at 7x10<sup>-6</sup> mol dm<sup>-3</sup>; the concentration of  $L^{n}$  increased (from bottom to top) for:  $L^{1}$  1.8x10<sup>-5</sup>, 3.6x10<sup>-5</sup>, 5.4x10<sup>-5</sup>, 7.2x10<sup>-5</sup>, 9x10<sup>-5</sup>, 1.1x10<sup>-4</sup> mol dm<sup>-3</sup>;  $L^{2}$  and  $L^{3}$  1.25x10<sup>-5</sup>, 2.5x10<sup>-5</sup>, 3.7x10<sup>-5</sup>, 5.0x10<sup>-5</sup>, 6.2x10<sup>-5</sup>, 7.5x10<sup>-5</sup>, 8.7x10<sup>-5</sup> mol dm<sup>-3</sup>,  $L^{4}$  0.9x10<sup>-4</sup>, 1.9x10<sup>-4</sup>, 2.8x10<sup>-4</sup>, 3.7x10<sup>-4</sup>, 4.6x10<sup>-4</sup>, 5.6x10<sup>-4</sup> mol dm<sup>-3</sup>.

Although not very inclusive, but the most prominent spectral change in the spectra of  $L^n/ZnPc$  was typically due to an insignificant spectral change in the UV region of the  $L^n$  spectrum. For instance, a red shift in 335-nm band of  $L^n$  was perceived in Fig. 2.

Since ZnPc is a well-known fluorophore towards [60]Fullerene [46], fluorescence spectroscopy was hired to study these interactions. The large molar extinction coefficients found for ZnPc with respect to [60]Fullerene in the visible UV-vis spectral region allowed us to excite preferentially the ZnPc, although the ZnPc concentration was much lower than [60]Fullerene. It was observed that fluorescence of ZnPc at 679 nm, upon excitation at 340 nm (i.e., Soret absorption band), was diminished gradually by addition of various concentration of  $L^1-L^4$  in NMP medium. Typically, the fluorescence spectral changes for ZnPc upon addition of  $L^n$  solution are shown in Fig. 3.





Fig. 3. The steady state fluorescence spectral variation of ZnPc ( $7x10^{-6}$  mol dm<sup>-3</sup>) in the presence of **L**<sup>n</sup> in NMP medium; the applied concentrations of **L**<sup>n</sup> were described in the caption of Fig. 2.

The emission peak of the phthalocyanines at 679 nm agreed fairly well with the reported values in the literature for other phthalocyanines [47]. Employing the method of continuous variation,

Job's plots (Fig. 4) for  $L^1-L^4$  were fundamentally established 1:1 stoichiometry for these interactions.



In the next step, the binding constants for these complexes ( $K_{BH}$ ) were estimated according to a modified Benesi-Hildebrand equation Eq (1) [48]:

$$\frac{F_0}{(F_0 - F)} = \frac{1}{A} + \left[ \left( \frac{1}{K_{BH}} \right) \left( \frac{1}{[L^n]} \right) \right]$$
Eq. (1)

In Eq (1),  $F_0$  and F denote on the fluorescence intensity of ZnPc without and with  $\mathbf{L}^n$  (Fig. 3); A is a constant associated with the difference in the emission quantum yield of the complexed and uncomplexed ZnPc. Four typical BH fluorescence plots of  $\mathbf{L}^n$ /ZnPc systems were shown in Fig. 5.



By plotting  $F_0/(F_0-F)$  (relative fluorescence intensity) versus  $1/[\mathbf{L}^n]$ ,  $K_{BH}$  values were obtained for various  $\mathbf{L}^1 - \mathbf{L}^4/\mathbb{Z}nPc$  complexes shown in Table 4.

system	$K_{\rm BH},{\rm dm^3mol^{-1}}$	quantum yield ( $\emptyset_F$ )
L <sup>1</sup> /ZnPc	16925 (±349)	0.12
L <sup>2</sup> /ZnPc	15153 (±662)	0.14
L <sup>3</sup> /ZnPc	11249 (±377)	0.13
L <sup>4</sup> /ZnPc	2714 (±221)	0.16
[60]Fullerene/ZnPc	33880 (±933)	0.10

Table 4. The calculated  $K_{\rm BH}$  values and the respective quantum yield of  $L^1 - L^4 / ZnPc$  by fluorescence spectrophotometry

 $K_{\rm BH}$  values calculated in Table 4 revealed that the rise in the fluorescence quenching efficiency observed for  $L^1-L^4$ , subsequently led to increase in the magnitude of  $K_{\rm BH}$ . This can be attributed to the fact that the rigidity of the phthalocyanine molecule results in tight binding of  $L^1-L^4$  to [60]Fullerene in  $L^1-L^4/ZnPc$ .

The calculated quantum yields of  $L^1-L^4/ZnPc$  in NMP are also presented in Table 4. As evident from Table 4, the calculated quantum yields found for  $L^1-L^4/ZnPc$  were typically  $\emptyset_F \sim 0.1$  which were not significantly different from the measured quantum yields found for [60]Fullerene/ZnPc. Basically, the quantum yield can change due to variation in the rate of nonradiative decay and/or due to conformational transformations in the fluorophore [49]. Evidently, it has already been reported that light induced energy or electron transfer reactions occurred in self-assembled supramolecular ZnPc/[60]Fullerene as donor-acceptor systems [49]. As a general phenomenon, the competition between the energy and electron transfer processes is characteristically a solventdependent photophysical behavior occurred for donor-[60]Fullerene molecular complex [50].

Therefore, in the present investigation the quenching phenomenon can be ascribed to the photoinduced energy transfer from ZnPc to [60]Fullerene.

#### 3.2.1. Mechanistic Studies

As it was seen in Fig. 3, the emission intensity of ZnPc was reduced as the concentration of  $L^n$  was increased. The spectral changes finally reached a plateau, indicating that the fluorescence quenching was evidently induced by the interaction of  $L^n$  with ZnPc. For this reason, in our fluorescence experiment for  $L^n/ZnPc$  interactions, the Soret absorption band of ZnPc was employed as the source of excitation wavelength. Applying similar experiments for particular designed supramolecules containing [60]Fullerene, Yin [51] and Guldi [52] showed that the second excited singlet state of the ZnPc was deactivated by the following mechanism [52]:

<sup>0</sup>phthalocyanine + 
$$h\nu \rightarrow$$
 <sup>2</sup>phthalocyanine<sup>\*</sup>  $\xrightarrow{\text{internal conversion}}$ 

<sup>1</sup>phthalocyanine<sup>\*</sup>  $\xrightarrow{\text{energy transfer to [60]Fullerene}}$ <sup>0</sup>phthalocyanine/<sup>3</sup>[60]Fullerene<sup>\*</sup>

Fluorescence quenching processes are fundamentally divided into two categories: static and dynamic quenching [49]. Since the quencher should diffuse to the fluorophore during the lifetime of the excited state, the rate of a dynamic quenching process is practically controlled by the diffusion rate of these two chemical species. However, the formation of a ground-state non-fluorescent complex or the presence of a sphere of effective quenching is crucial for a typical quenching process with static quenching mechanism. Whilst, dynamic quenching processes occur as a result of the collision between a ground-state and an excited-state fluorophore quencher follow by the formation of a transient complex [49].

In this work, both of the steady-state and time resolved fluorescence quenching data were studied following Stern–Volmer (SV) Eqs. (2) and (3) [49]:

$$F_o/F = 1 + k_q^{SS} \cdot \tau_o [Q] = 1 + K_{sv} [Q] \qquad \text{Eq. (2)} \tau_o/\tau = 1 + k_q^{TR} \cdot \tau_o [Q] = 1 + K_{sv} [Q] \qquad \text{Eq. (3)}$$

In Eqs. (2) and (3),  $F_o$  and F denoted on the fluorescence intensities in the absence and presence of the quencher, respectively,  $k_q$  was the bimolecular quenching rate constant,  $K_{sv}$  defined as the Stern-Volmer quenching constant and [Q] was the concentration of the quencher.  $\tau_o$  and  $\tau$  were the average fluorescence lifetimes of the fluorophore ZnPc in the absence and presence of the quencher Q, respectively. The superscripts SS and TR on  $k_q$  defined the quenching constants for the steady state and time-resolved experiments, correspondingly.

In our experiments, the fluorescence emission of ZnPc was reduced from  $F_o$  to F in the presence of different concentrations of quencher, e.g.  $\mathbf{L}^n$ . Fig. 6 displays the Stern-Volmer plots of the quenching processes of ZnPc by  $\mathbf{L}^n$ .



Fig. 6. The Stern-Volmer (SV) plots from steady state fluorescence emission intensity for ZnPc in the presence of  $L^{1}-L^{4}$  in NMP at 25°C

The plots in Fig. 6 demonstrate the linearity of  $F_o/F$  curves to the quencher concentration  $L^n$ . Basically, it is important to note that observation of a linear Stern-Volmer plot does not necessarily verify that collisional quenching of fluorescence was occurred since the static quenching also gave rise to linear Stern-Volmer plots [49]. The static and dynamic quenching could be recognized by their different reliance on and/or viscosity, temperature or rather by lifetime measurements.

In the course of lifetime measurements for these interactions, it was establish that the emission decay of  $\mathbf{L}^{1}$ - $\mathbf{L}^{4}$  at 340 nm (Fig. 7) was conveniently fitted to the first order reaction rate.



Fig. 7. The time profile for the emission of ZnPc,  $L^1-L^4/ZnPc$  systems at 340 nm.

The Stern-Volmer ( $K_{SV}$ ) and quenching rate constants ( $k_q^{SS}$ , and  $k_q^{TR}$ ) found for  $L^1-L^4/ZnPc$  were presented in Table 5.

Table 5. The calculated values of  $k_q^{SS}$ ,  $k_q^{TR}$  and  $K_{SV}$  using steady-state and time-resolved fluorescence experiments for the interactions of various  $L^n/ZnPc$  systems estimated in NMP at 298 K.

	$K_{\rm SV}^*$ , dm <sup>3</sup> mo	l <sup>-1</sup> calculated in	$k_q$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>		
system	steady-state experiments	time-resolved experiments	$k_q^{SS}$	$k_q^{TR}$	
L <sup>1</sup> /ZnPc	28297(±6854)	26270(±6516)	$5.8 \times 10^8$	$5.4 \times 10^8$	
$L^2/ZnPc$	29406(±1973)	27334(±8587)	$6.1 \times 10^8$	$5.6 \times 10^8$	
L <sup>3</sup> /ZnPc	24727(±2765)	23590(±3273)	$5.1 \times 10^8$	$4.9 \times 10^8$	

L <sup>4</sup> /ZnPc	3750(±724)	27338(±2024)	$7.7 \text{x} 10^7$	$5.6 \times 10^8$
[60]Fullerene/ZnPc	73681(±7567)	-	$1.5 \times 10^{9}$	-

\*The calculated value of  $\tau_0$  for ZnPc was 48.5 µs.

The results in Table 5 together with the observation of a parallel decrease in both fluorescence intensity and lifetime parameters (i.e.,  $F_0/F = \tau_0/\tau$ ) pointed out the occurrence of static quenching for the fluorescence emission of ZnPc in the presence of  $\mathbf{L}^n$ . The aforementioned fluorescence quenching phenomenon is primarily attributed to involvement of a static  $\pi-\pi*$  charge transfer process considering a static quenching mechanism. Conversely, the incompatibility of  $K_{SV}$  values found for  $\mathbf{L}^4$  (comparing the steady-state and time-resolved results in Table 4) waived the static fluorescence quenching mechanism.

#### 3.3. Theoretical Calculations

In order to collect structural data to evaluate poor  $K_{SV}$  value found for  $L^4/ZnPc$  (Table 4), the geometry of  $L^4$  was typically explored by DFT calculations using the B3LYP functional and 6-31G\* basis set [53,54]. In order to find the most stable connection mode through O<sub>2</sub>N<sub>3</sub>-donor groups of **3**, and **4** to [60]Fullerene backbone, the number of connecting atoms were altered and the optimized systems were shown in Fig. 6S.

Fig. 5S revealed that major electronic difference expected from these structural modes could be originated from their total electron withdrawing effect of the nitrogen groups.

Table 6 displays the relative energies (calculated by B3LYP/6-31G\* method) as well as the enthalpy values (calculated by HF/3-21G method) for *a-d* linking modes (in Fig. 6S) of **3** and **4** to [60]Fullerene in  $L^3$  and  $L^4$ .

name		The connection mode to [60]Fullerene	Relative Energy calculated by B3LYP/6-31G* method (kcal mol <sup>-1</sup> )	Enthalpy of reaction calculated by HF/3-21G method (kcal mol <sup>-1</sup> )
	a	A	-21.0	-35.8
<b>T</b> 3	b	В	-17.1	-34.3
L	С	A,B	-7.6	771.9
	d	A,B,C	0	109.8
	а	А	-122.3	-1.8
<b>T</b> 4	b	В	-119.3	13.5
L	С	A,B	-113.0	831.1
	d	A,B,C	0	105.8

Table 6. The B3LYP/6-31G\* optimized relative energies for various modes of linking of **3** and **4** to [60]Fullerene in  $L^3$  and  $L^4$ .

The data in Table 6 demonstrates that although the best chance for linking of  $O_2N_3$ -donor azacrown **3** and **4** to [60]Fullerene is connection through one nitrogen, but the calculated relative energy differences among *b*-*c* modes were not very significant for  $L^4$ . Table 6 also showed that

there could be different linking modes of types *a* or *b* modes available to  $\mathbf{L}^3$  while linking through *c* mode for  $\mathbf{L}^4$  might be the decisive reason for the observed reduced  $K_{SV}$  value found for  $\mathbf{L}^4$ /ZnPc (Tables 4 and 5). In conclusion, having higher number of electron withdrawing nitrogen groups on 4 linked to [60]Fullerene (by accepting *a* mode) could resulted in lower  $K_{SV}$  value for  $\mathbf{L}^4$  with respect to  $\mathbf{L}^3$ .

In order to visualize the geometry and the electronic structures of  $L^3$  and/or  $L^4$ /ZnPc dyads, their ground states were optimized by B3LYP/6-31G\* level with Gaussian 03. As shown in Fig. 8 (panels **a-f**), all of the dyads revealed stable structures on the Born-Oppenheimer potential energy surface with no steric constraints between the donor and acceptor entities.



Fig. 8. HOMOs and LUMOs of  $L^n/ZnPc$  dyads at various electronic states: (a)  $L^3/ZnPc$ , (b) HOMO of  $L^3/ZnPc$ , (c) LUMO of  $L^3/ZnPc$ , (d)  $L^4/ZnPc$ , (e) HOMO of  $L^4/ZnPc$ , (f) LUMO of  $L^4/ZnPc$  done by B3LYP/6-31G\* calculations.

As shown in Fig. 8b,c,e, and f , the calculated HOMOs for  $L^3$  and  $L^4/ZnPc$  were fundamentally located on ZnPc entity, while the LUMOs were fundamentally located on  $L^3$  and  $L^4$  entities. The so-called interactions recommended  $L^1-L^3/ZnPc$  as potent fluorophore candidates for detection of metal ions by fluorescence spectrophotometry through their appended macrocycle rings which were of our ongoing research theme.

#### Conclusions

Fluorescence spectrophotometry was applied as an efficient method to detect non-covalent interaction of ZnPc with [60]Fullerene derivatives bearing aza-crown macrocycles,  $\mathbf{L}^{1}$ - $\mathbf{L}^{4}$ . The existence of an efficient quenching mechanism by reducing excited singlet state of ZnPc in the presence of  $\mathbf{L}^{1}$ - $\mathbf{L}^{4}$  in NMP was observed. Comparing the steady state and time resolved fluorescence results, a notable correlation between decrease in the fluorescence intensity and the lifetime parameters which confirmed on the occurrence of a static mechanism for the fluorescence quenching of ZnPc in the presence of  $\mathbf{L}^{1}$ - $\mathbf{L}^{3}$ . Meanwhile, the poor Stern-Volmer constant ( $K_{SV}$ ) measured for  $\mathbf{L}^{4}$  was also described according to a structural feature using DFT calculations.

#### Acknowledgment

Financial supports from Research Office of Sharif University of Technology and Iran National Science Foundation are appreciated.

#### References

- [1] A.M. Sanders, T.J. Magnanelli, A.E. Bragg, J.D. Tovar, Journal of the American Chemical Society 138 (2016) 3362–3370.
- [2] M.A. Lebedeva, T.W. Chamberlain, P.A. Scattergood, M. Delor, I.V. Sazanovich, E.S. Davies, M. Suyetin, E. Besley, M. Schröder, J.A. Weinstein, A.N. Khlobystov, Chemical Science (2016).
- [3] C.B. KC, F. D'Souza, Coordination Chemistry Reviews 322 (2016) 104–141.
- [4] G.-J. Huang, M.A. Harris, M.D. Krzyaniak, E.A. Margulies, S.M. Dyar, R.J. Lindquist, Y. Wu, V.V. Roznyatovskiy, Y.-L. Wu, R.M. Young, M.R. Wasielewski, The journal of physical chemistry. B 120 (2016) 756–765.
- [5] G.D. Blanco, A.J. Hiltunen, G.N. Lim, C.B. KC, K.M. Kaunisto, T.K. Vuorinen, V.N. Nesterov, H.J. Lemmetyinen, F. D'Souza, ACS applied materials & interfaces 8 (2016) 8481–8490.
- [6] Y. He, Y. Li, Physical chemistry chemical physics PCCP 13 (2011) 1970–1983.
- [7] Y. Matsuo, in: F. Huang, H.-L. Yip, Y. Cao (Eds.), Polymer Photovoltaics, Royal Society of Chemistry, Cambridge, (2015) 78–100.
- [8] A. Mohajeri, A. Omidvar, Physical chemistry chemical physics PCCP 17 (2015) 22367– 22376.
- [9] P. Luo, P.-L. Karsenti, B. Marsan, P.D. Harvey, Inorganic chemistry 55 (2016) 4410-4420.
- [10] P. Li, P. Song, Q. Zhou, C. Du, Y. Ding, L. Xia, Journal of Luminescence 177 (2016) 325– 330.
- [11] M.A. Lebedeva, T.W. Chamberlain, A.N. Khlobystov, Chemical reviews 115 (2015) 11301–11351.
- [12] B. Ghanbari, P. Gholamnezhad, M. Hatami, J Therm Anal Calorim 118 (2014) 1631–1637.
- [13] S.-H. Lee, C.T.-L. Chan, K.M.-C. Wong, W.H. Lam, W.-M. Kwok, V.W.-W. Yam, Journal of the American Chemical Society 136 (2014) 10041–10052.

- [14] C. Dragonetti, A. Colombo, M. Fontani, D. Marinotto, F. Nisic, S. Righetto, D. Roberto, F. Tintori, S. Fantacci, Organometallics 35 (2016) 1015–1021.
- [15] A. Ray, K. Santhosh, S. Bhattacharya, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 135 (2015) 386–397.
- [16] A. Ray, K. Kundu, K. Kundu, S.K. Nayak, S. Bhattacharya, Journal of Molecular Liquids 220 (2016) 92–100.
- [17] A. Ray, S. Bhattacharya, Chemical Physics Letters 651 (2016) 66–71.
- [18] A. Ray, S. Banerjee, A.K. Bauri, S. Bhattacharya, Chemical Physics Letters 646 (2016) 119–124.
- [19] A. Ray, S. Banerjee, S. Ghosh, A.K. Bauri, S. Bhattacharya, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 152 (2016) 64–69.
- [20] A. Ray, S. Bhattacharya, Chemical Physics Letters 639 (2015) 183–188.
- [21] C.B. Kc, G.N. Lim, P.A. Karr, F. D'Souza, Chemistry A European Journal 20 (2014) 7725–7735.
- [22] A. Ray, H. Pal, S. Bhattacharya, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 117 (2014) 686–695.
- [23] H. Geng, X.-F. Zhang, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 139 (2015) 13–19.
- [24] G. Bottari, G. de La Torre, D.M. Guldi, T. Torres, Chemical reviews 110 (2010) 6768– 6816.
- [25] A. Ray, S. Chattopadhyay, S. Bhattacharya, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 79 (2011) 1435–1442.
- [26] H.M. Rhoda, M.P. Kayser, Y. Wang, A.Y. Nazarenko, R.V. Belosludov, P. Kiprof, D.A. Blank, V.N. Nemykin, Inorganic chemistry (2016).

[27] V. Bandi, H.B. Gobeze, P.A. Karr, F. D'Souza, The Journal of Physical Chemistry C, 118

- (2014) 18969–18982.
- [28] B. Ghanbari, P. Gholamnezhad, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy 169 (2016) 202–207.
- [29] P.K. Zarzycki, H. Ohta, Y. Saito, K. Jinno, Chromatographia 64 (2006) 79-82.
- [30] K.R. Adam, L.F. Lindoy, H.C. Lip, J.H. Read, Journal of the Chemical Society Dalton Transactions 74 (1980).
- [31] L.G. Armstrong, L.F. Lindoy, Inorganic Chemistry 14 (1975) 1322–1326.
- [32] B. Ghanbari, N. Mahloojy, Fullerenes, Nanotubes and Carbon Nanostructures 22 (2014) 322–331.
- [33] P.S. Vincett, The Journal of Chemical Physics 55 (1971) 4131.
- [34] C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, 4th ed., Wiley-VCH, Weinheim, 2011.
- [35] B. Ghanbari, Z. Taheri, M. Shekarriz, S. Taghipoor, B. Mohajerani, M.S. Jamarani, Fullerenes, Nanotubes and Carbon Nanostructures 14 (2006) 315–319.

- [36] S.W. McElvany, M.M. Ross, J.H. Callahan, Accounts of Chemical Research 25 (1992) 162– 168.
- [37] R. Zouboulaki, E. Psillakis, Analytical Methods 8 (2016) 4821–4827.
- [38] L. Dunsch, U. Kirbach, K. Klostermann, Journal of Molecular Structure 348 (1995) 381– 384.
- [39] a. A. Astefanei, O. Núñez, M.T. Galceran, Analytica Chimica Acta, 882 (2015) 1–21, b. A. Carboni, R. Helmus, J.R. Parsons, K. Kalbitz, P. de Voogt, Journal of chromatography. A 1433 (2016) 123–130.
- [40] J.D. Saxby, S.P. Chatfield, A.J. Palmisano, A.M. Vassallo, M.A. Wilson, L.S.K. Pang, The Journal of Physical Chemistry 96 (1992) 17–18.
- [41] R.M. Nikonova, M.A. Merzlyakova, V.I. Lad'yanov, V.V. Aksenova, Russ. The Journal of Physical Chemistry 86 (2012) 1121–1127.
- [42] J.C. Scanlon, L.B. Ebert, The Journal of Physical Chemistry 97 (1993) 7138–7140.
- [43] S. Bhattacharya, A. Sharma, S.K. Nayak, S. Chattopadhyay, A.K. Mukherjee, The Journal of Physical Chemistry B 107 (2003) 4213–4217.
- [44] S. Bhattacharya, A.K. Bauri, S. Chattopadhyay, M. Banerjee, The journal of physical chemistry B 109 (2005) 7182–7187.
- [45] N. Yevlampieva, Y. Biryulin, E. Melenevskaja, V. Zgonnik, E. Rjumtsev, Colloids and Surfaces A: Physicochemical and Engineering Aspects 209 (2002) 167–171.
- [46] C.B. Kc, G.N. Lim, F. D'Souza, Nanoscale 7 (2015) 6813-6826.
- [47] F. Ghani, J. Kristen, H. Riegler, Journal of Chemical & Engineering Data 57 (2012) 439–449.
- [48] H.A. Benesi, J.H. Hildebrand, Journal of the American Chemical Society 71 (1949) 2703– 2707.
- [49] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer US, Boston, MA, 1999.
- [50] A. Ray, D. Goswami, S. Chattopadhyay, S. Bhattacharya, The journal of physical chemistry A 112 (2008) 11627–11640.
- [51] G. Yin, D. Xu, Z. Xu, Chemical Physics Letters 365 (2002) 232–236.
- [52] D.M. Guldi, T. Da Ros, P. Braiuca, M. Prato, Photochemical & Photobiological Sciences 2 (2003) 1067–1073.
- [53] V. Bandi, H.B. Gobeze, P.A. Karr, F. D'Souza, The journal of physical chemistry C 118 (2014) 18969–18982.
- [54] V. Bandi, S.K. Das, S.G. Awuah, Y. You, F. D'Souza, Journal of the American Chemical Society 136 (2014) 7571–7574.



### Highlights

Two new O<sub>2</sub>N<sub>3</sub>-donor aza-crowns anchored to [60]Fullerene were synthesized.

The steady-state and time resolved fluorescence quenching properties of  $L^{1}-L^{4}$  were studied.

The correlated decrease in both  $F_0/F$  and  $\tau_0/\tau$  suggested a static quenching for L<sup>1</sup>-L<sup>3</sup>/ZnPc.

The quenching was attributed to involvement of a static  $\pi - \pi *$  charge transfer process.

DFT calculations showed the relation between structural features and the observed  $K_{SV}$  values.