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# NEW PHTHALOCYANINE-FULLERENE DYADS FOR SOLAR CELLS

Aurel DIACON[1], Edina RUSEN[2], Cristian BOSCORNEA[3], Andreea Mădălina PANDELE[4], Corneliu CINCU[5]

*În această lucrare este prezentată sinteza şi caracterizarea de noi antene fotoreceptoare formate din ftalocianine şi fulerenă $C_{60}$, pentru fabricarea de celule solare.*

*Ftalocianinele de zinc au fost alese ca potenţiale antene datorită stabilităţii lor chimice, a fluorescenţei ridicate şi a proprietăţilor semiconductoare. Alegerea fullerenei $C_{60}$ este datorată proprietăţii de acceptor de electroni superioară oricărui material natural implicat în fotosinteză cât şi datorită stabilităţii sale şi energiei de reorganizare scăzute.*

*Diadele obţinute au fost caracterizate prin spectroscopie IR, RAMAN, UV-VIS şi fluorescenţă. Rezultatele prezintă o importantă diminuare a fluorescenţei, ce poate fi explicată printr-un mecanism de transfer între colorant şi acceptor.*

*The paper reports on the synthesis and characterization of new phthalocyanine-fullerene $C_{60}$ based light-harvesting antennas for the fabrication of solar cells.*

*Zinc phthalocyanine dyes (ZnPc) have been chosen as potential antennas because of their high chemical stability, high photoluminescence quantum yield, and their semiconductive properties. The choice of the fullerene $C_{60}$ is due to its acceptor properties, superior to any natural compound involved in photosynthesis and to its high stability and low reorganization energy.*

*The obtained dyads have been characterized through IR, Raman, TGA, UV-VIS, and fluorescence spectroscopy. The results show high quenching of the fluorescence that can be explained by a transfer mechanism between the dye and the acceptor.*

**Keywords:** phthalocyanine, $C_{60}$ dyads, light-harvesting antenna

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[1] PhD student, Department of Science and Engineering of Polymers, University POLITEHNICA of Bucharest, Romania, e-mail: aurel_diacon@yahoo.com

[2] Lecturer, Department of Science and Engineering of Polymers, University POLITEHNICA of Bucharest, Romania

[3] Lecturer, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania

[4] Student, Department of Science and Engineering of Polymers, University POLITEHNICA of Bucharest, Romania

[5] Prof., Department of Science and Engineering of Polymers, University POLITEHNICA of Bucharest, Romania

## 1. Introduction

World's demand for energy is constantly increasing. Faced with this impending colossal need, many researchers are pointing to the sun as a necessary source of energy. The challenge remains how to harness that energy in a cost-effective, environmentally friendly way.

For billions of years, plants have been achieving precisely this thing, by means of photosynthesis, in which light's energy is used to split water, subsequently producing oxygen and building sugars. Sunlight is absorbed and converted to electrochemical potential energy by photoinduced electron transfer in the reaction center. The light is not absorbed directly by the protein that carries out the reaction, but instead, an antenna gathers the sunlight and transfers the resulting excitation energy to the reaction center (chlorophylls) through an energy transfer process.

The mimicry of the natural photosynthesis by artificial system holds the promise for cheap, environmentally friendly energy generation. Among the mechanisms employed to mimic this natural process it is the incorporation of artificial light-harvesting antennas into molecular electron-donor-acceptor systems that are prone to convert the excitation energy into an electrochemical potential or chemical energy in the form of a long-lived charge separation state [1-3] Fullerenes ($C_{60}$) have been chosen as the acceptor component in many artificial light-harvesting systems [4, 5], due to their superior electron acceptor properties.

Porphyrins are among the most studied light-harvesting molecules due to their role in the natural photosynthesis. Phthalocyanines, characterized by an outstanding chemical and light stability, are used both as electron-donor and electron-acceptor moieties [6].

The fullerene chemistry allows for different ways of attachment to chromophores; among the most frequently used are the Prato [7] and Bingel [8] reactions. Another technique for the functionalization of fullerene is offered by the click chemistry approach [9]. Although most of the used reactions are primary cycloadditions, fullerene also allows the reaction with organo-metallic derivates and other types of nucleophilic additions [10].

In a phthalocyanine-fullerene dyad, the role of the phthalocyanine is dual: first it is to function as an antenna and the second to act as a donor molecule once photoexcitated. Previous fullerene-phthalocyanine dyads have been synthesized [11, 12] involving usually the Prato reaction.

In this paper, we have exploited click chemistry method and nucleophilic addition of the amine group for the grafting on the fullerene. We also studied the optical properties of a fused dyad, compared to a dyad with a short spacer between the chromophore and fullerene $C_{60}$.

## 2. Experimental

### 2.1. Materials

Zinc acetate ($Zn(CH_3COO)_2$) (Merck), formamide (Acros), N-methylpyrrolidone (NMP) (Fluka), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Acros), methanol (Fluka, Chimopar), HCl (Chimopar), $Na_2S{\cdot}9H_2O$ (Aldrich), N, N-dimethylformamide (DMF), fullerene $C_{60}$ (99.9%) (Acros Organics), dichlorobenzene (DCB) (Sigma Aldrich), carbon disulfide ($CS_2$), sodium azide ($NaN_3$) (Aldrich), epichlorohydrin (Aldrich), acetone (Chimopar), diethyl ether (Fluka) were used as received. The zinc tetraamino phthalocyanine was synthesized based on previous work [13].

### 2.2. Methods

**a) Zinc tetranitro phthalocyanine synthesis:** In a three-neck round bottom flask, equipped with a mechanical stirrer, thermometer and reflux condenser, 17.3 g (0.1 mol) 4-nitro phthalodinitrile, 5 g (0.025 mol) $Zn(CH_3COO)_2$, 15 mL formamide (0.1 moli) and 40 mL N- methylpyrrolidone have been added, together with a small amount of DBU, with the role of catalyst. The reaction mixture has been heated under stirring at 50°C. After the beginning of the reaction the temperature was increased at 125°C, then at 150°C for 1h; after another 30 minutes at 170°C, the mixture has been cooled at 50°C and 50 mL of methanol were added under continuous stirring for 30 minutes. The hot mixture has been filtered and has been washed with methanol. The precipitate has been added to 100 mL of HCl 5%, heated for 30 minutes, filtered and washed with water. A blue-violet powder was obtained (9.9 g, 50% yield). The reactions through which the zinc tetranitro phtalocyanine and zinc tetraamino phatlocyanine have been synthesized are presented in Fig. 1.

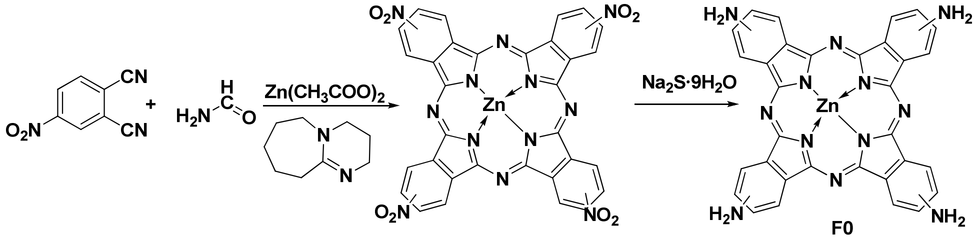

Fig. 1. Zinc tetraamino phthalocyanine synthesis (isomers mixture)

**b) Zinc tetraamino phthalocyanine (F0) synthesis:** In a three-neck round bottom flask, equipped with a mechanical stirrer, thermometer and reflux condenser, 9.9 g zinc tetranitro phthalocyanine and 55 mL N, N-dimethylformamide (DMF) have been added and the mixture has been stirred at 40$^{o}$C for 30 minutes to allow the dissolution of the dye. Then, a solution of $Na_2S\cdot9H_2O$ in 26 mL of water has been added. The mixture has been heated under stirring at 50-55°C for 6 h. The reaction mass has been cooled, diluted with 50 mL $H_2O$, filtered and washed with water. The precipitate was dissolved in 400 mL of HCl 2N and heated for 3 h at reflux, filtered to remove impurities and cooled at room temperature. The solution has been neutralized with NaOH, filtered, washed with water and dried. A green powder was obtained (5.8 g, 70% yield).

### c) Fused fullerene/phthalocyanine dyads

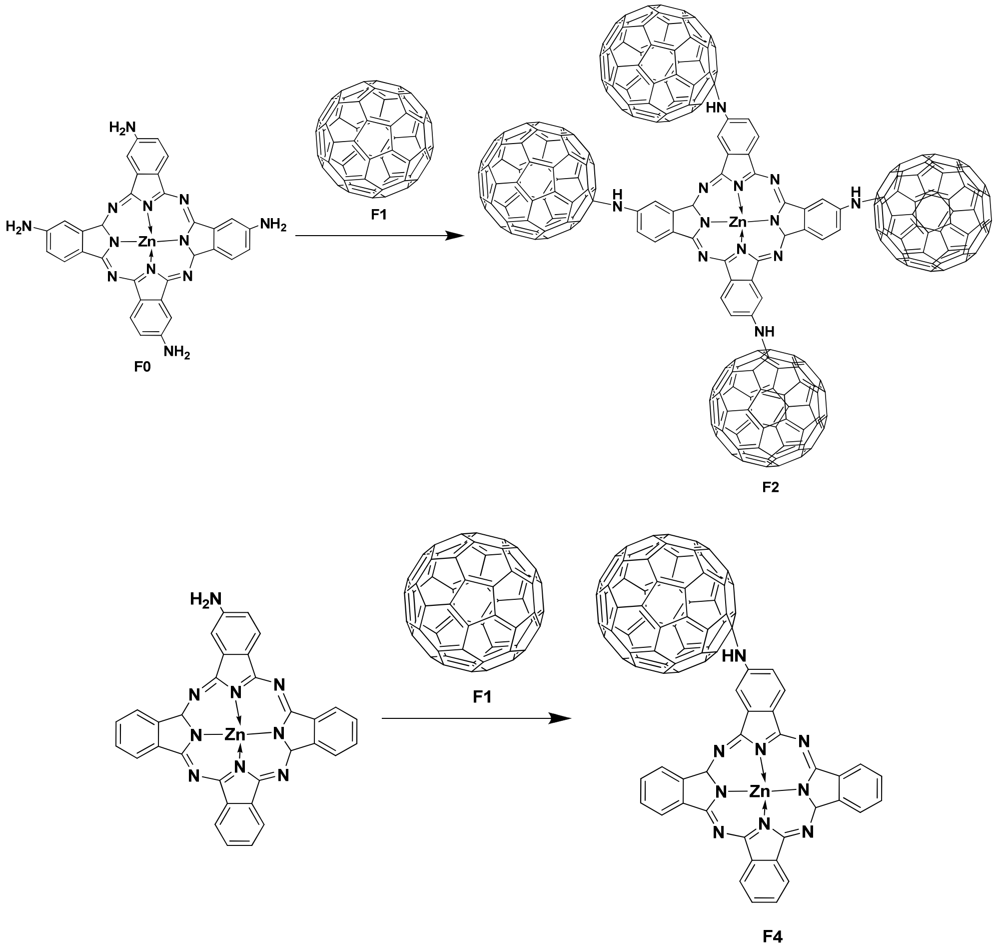

Fig. 2. F2, F4 fused dyad synthesis (possible structures)

**Synthesis of F2 (Fig. 2)**: 0.05 g zinc tetraamino phthalocyanine, 0.025 g fullerene $C_{60}$ (F1) and 15 mL of dichlorobenzene have been introduced in a round bottom flask. The mixture has been stirred at 80°C, under nitrogen, for 48 h. After being cooled at room temperature, the reaction mixture has been precipitated in acetone, filtered, washed with $CS_2$ to remove the excess fullerene and dried. A dark blue powder was obtained (0.07 g)

**Synthesis of compound F4 (Fig. 2):** 0.03 g zinc monoamino phthalocyanine, 0.03g fullerene $C_{60}$ (F1) and 15 mL of dichlorobenzene have been introduced in a round bottom flask. The mixture has been stirred at 80°C, under nitrogen, for 48 h. After being cooled at room temperature, the reaction mixture has been precipitated in acetone, filtered, washed with $CS_2$ to remove the excess fullerene and dried. A dark blue powder was obtained (0.06 g)

### d) Short spacer fullerene/phthalocyanine dyads

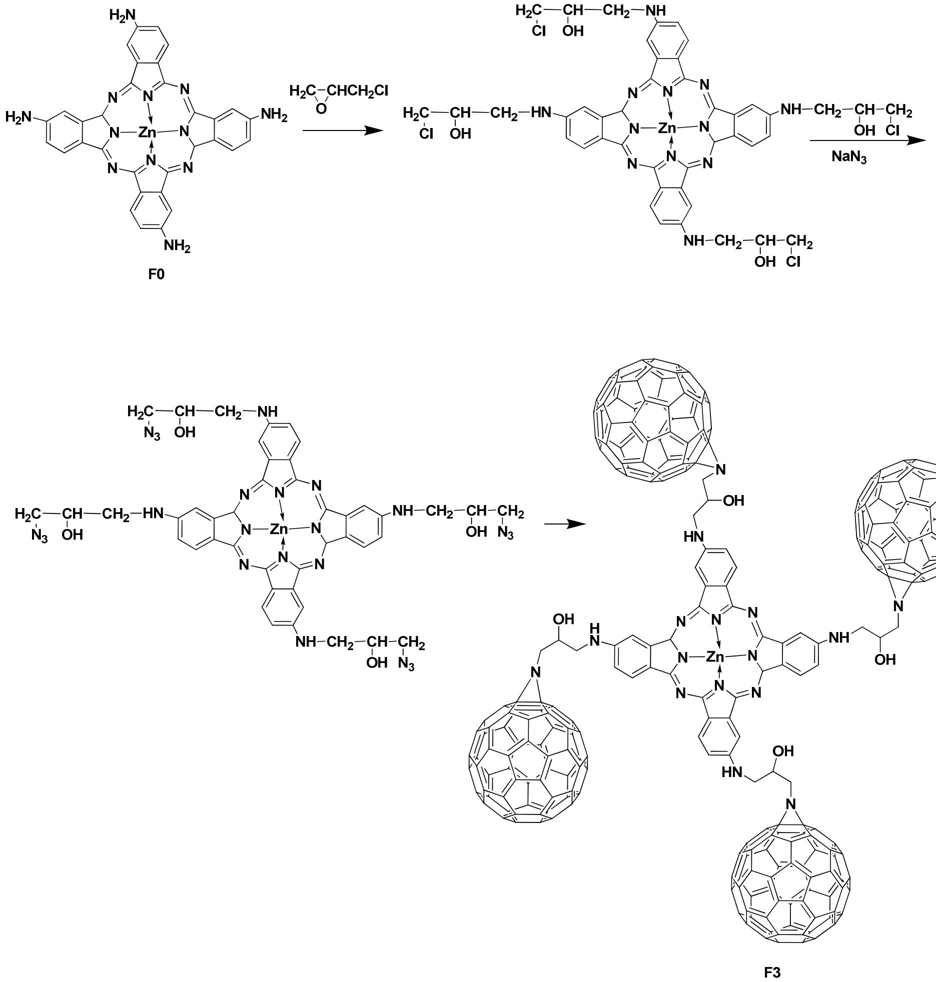

Fig. 3. Short spacer fullerene/phthalocyanine dyads (possible structures)

**Synthesis of compound F3 (Fig. 3):** 4 mL epichlorohydrin have been added to a solution of 0.5 g zinc tetraamino phthalocyanine in 50 mL DMF. The mixture has been stirred at 80°C for 24 h. The product has been precipitated in acetone and washed with diethyl ether. A blue powder has been obtained.

0.2 g of $NaN_3$ has been added to a solution of 0.4 g epichlorohydrin derivate in 50 mL DMF. The mixture has been stirred at 80°C for 24h. The product has been precipitated in water and separated by centrifugation, then washed with acetone and diethyl ether. A blue power has been obtained.

0.045 g azide derivate has been added to a solution of 0.030 g fullerene $C_{60}$ in 15 mL DCB. The mixture has been stirred, under nitrogen, at 80°C for 24h. The product has been precipitated in diethyl ether, filtered, washed with $CS_2$ to remove the excess fullerene and dried. A dark blue powder has been obtained.

## 2.3. Characterization

The Raman spectra have been registered on a DXR Raman Microscope from Thermo Scientific with a 780 nm laser. The laser beam has been focused with the 10x objective.

The UV/VIS spectra have been recorded using a V-500 Able Jasco spectrophotometre. The 3D fluorescence spectra have been registered using a FP-6500 Able Jasco spectrofluorometer.

The TGA analysis has been performed on Q500 TA Instruments equipment, under nitrogen atmosphere, using a heating rate of 10 °C/min from room temperature to 600 °C.

The infrared absorption spectra have been recorded at room temperature with a Nicolet 6700 FTIR spectrometer in the range of 4000-400 $cm^{-1}$.

## 3. Results and discussions

The first step of the study was the characterization of F0 by IR and RAMAN spectroscopy, since synthesis method used is original. The IR spectra have shown signals at: 3326 $cm^{-1}$ ($NH_2$), 3209 $cm^{-1}$ ($NH_2$), 1604 $cm^{-1}$ (C-N), 1487-1400 $cm^{-1}$ (C-C aromatic), 1300-1400 $cm^{-1}$ (C-H) which correspond to literature data [14].

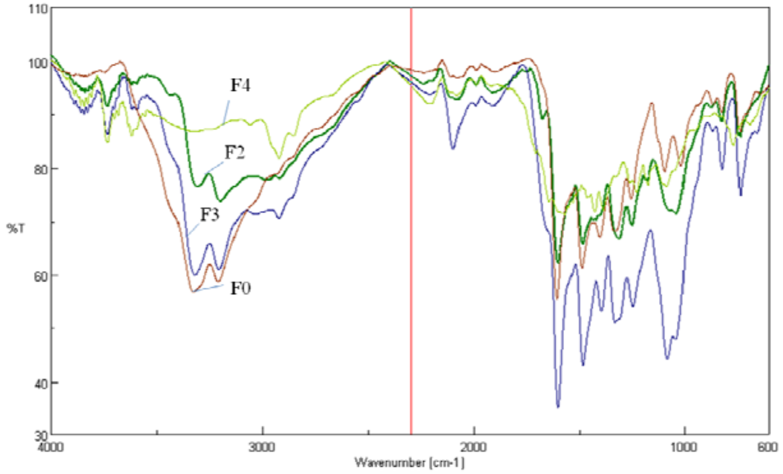

Fig. 4. IR spectra for F0, F2, F3 and F4

For the compound F3, the intermediates were characterized using IR spectroscopy. For the epichlorohydrin derivate, signals at 3326 $cm^{-1}$ ($NH_2$), 3209 $cm^{-1}$ ($NH_2$), 1604 $cm^{-1}$ (C-N), 1487-1400 $cm^{-1}$ (C-C aromatic), 1300-1400 $cm^{-1}$ (C-H), 650 $cm^{-1}$ (C-Cl) have been registered. For the azide derivate, the signal characteristic for the N≡N vibration at 2200 $cm^{-1}$ has been obtained in the IR spectra.

IR spectroscopy has been used as first investigation technique in order to study the chemical linking of F0 to the $C_{60}$ in the case of all the dyads (Fig. 4). The characteristic signals for the amino group and the phthalocyanine were present in the spectra.

Another investigation technique used to characterize the dyads has been the RAMAN spectroscopy. The characteristic peaks for F0 in RAMAN spectroscopy are: 700-900 $cm^{-1}$ macrocycle ring stretching vibration [15], bending vibrations of the C-H groups 1000 to 1300 $cm^{-1}$ and 1500 $cm^{-1}$ for the symmetric $NH_2$ deformations [16]. For all the dyads, a change has been noticed in the interval 600-800 $cm^{-1}$, compared to the phthalocyanine spectrum. The change consists in an increase of the intensity at $\approx$ 750 $cm^{-1}$. This could be explained by the increase of the C-C bonds number; this corresponds to one of the characteristic signals of the fullerene (772 $cm^{-1}$). The other characteristic peaks are similar to those for the F0 compound, with small shifts in the response. The RAMAN signals corresponding to the fullerene-$C_{60}$ are at 275 $cm^{-1}$, 496 $cm^{-1}$, 772 $cm^{-1}$ and 1467 $cm^{-1}$ (Fig. 5).

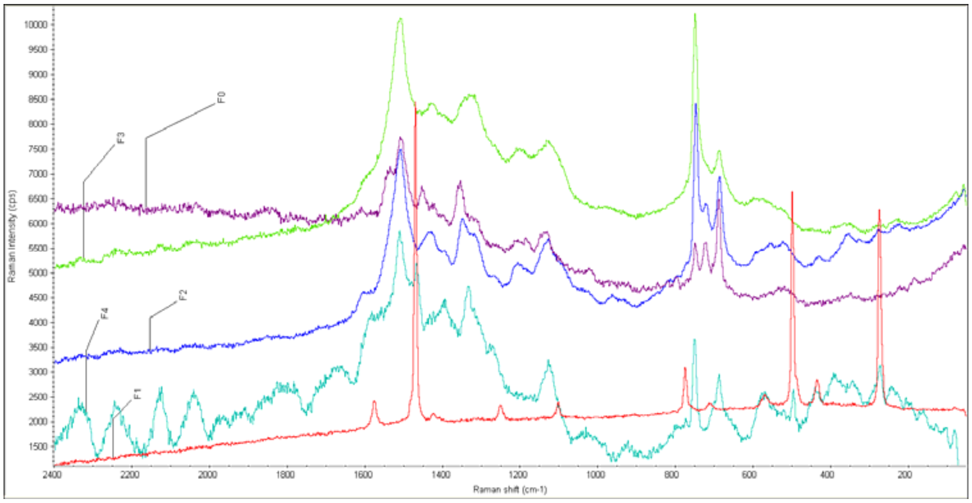

Fig. 5. RAMAN spectra for F0, F1, F2, F3, F4

In the case of UV-VIS spectroscopy (Fig. 6), characteristic for F0 is the absorption at 717 nm corresponding to the Q band, compared to the fullerene which has characteristic absorbance only in the UV range at 295 nm and 394 nm. By comparing the absorption of the F2, F3 and F4 dyads, we noticed a different degree of modification with fullerene, resulting from the modification of the absorption intensity of each moiety. Considering that the intensity is directly proportional with the concentration of the excited components, the ratio between the intensity of the peaks corresponding to the absorption of the fullerene moiety and the Q band intensity decreases in the order F4>F2>F3. There was also a small bathochromic shift in the Q band absorption value compared with the F0, which is due to the loss of symmetry of the phthalocyanine moiety.

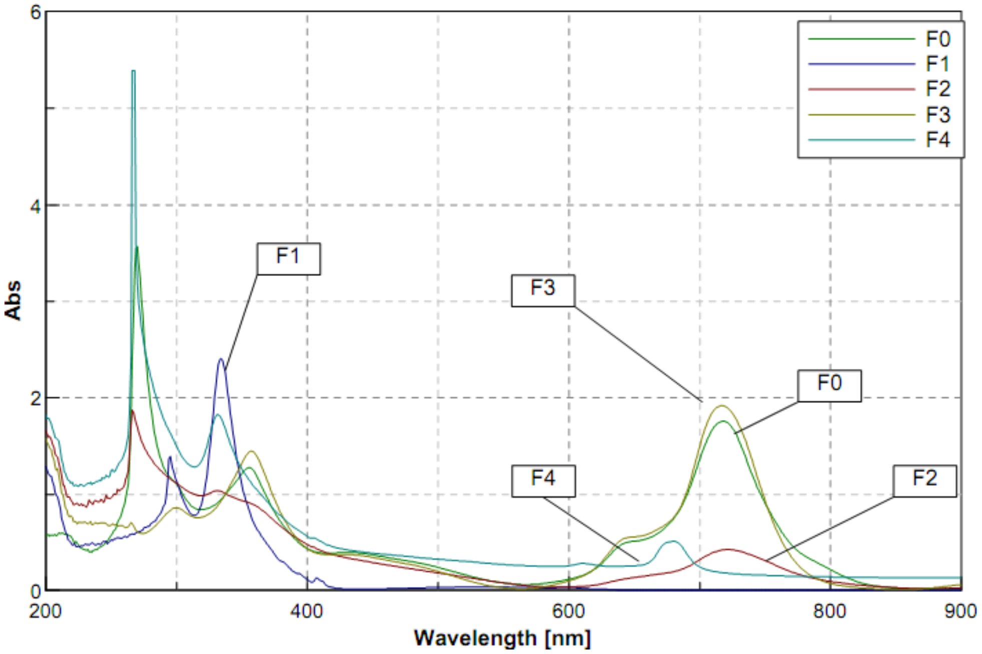

Fig. 6. UV-VIS spectra for F0, F1, F2, F3 and F4

In order to further study the optical properties of the dyads, the next step for their characterization was fluorescence spectroscopy. Using this technique, the wavelength of the emitted light on the irradiation of a sample with a monochromatic light is recorded (emission spectra). The 3D spectra are obtained by recording all the emission spectra for an interval of excitation wavelengths. In the present case, the fluorescence modification gives an insight into the interactions between the phthalocyanine and fullerene moieties since a donor-acceptor interaction is usually coupled with a fluorescence quenching.

In the fluorescence spectra recorded for the compound F0, the most important signal is in the emission range of 730-770 nm for an excitation wavelength of 700-750 nm. The same characteristics are present for F3, with a quenching of the fluorescence. In contrast, for F2 and F4, new signals are observed. In the case of F2, for an excitation wavelength of 280-440 nm, the compound emits in the range of 500-570 nm and 800-880 nm. For F4, the conservation of the emission at 800-880 nm was noticed.

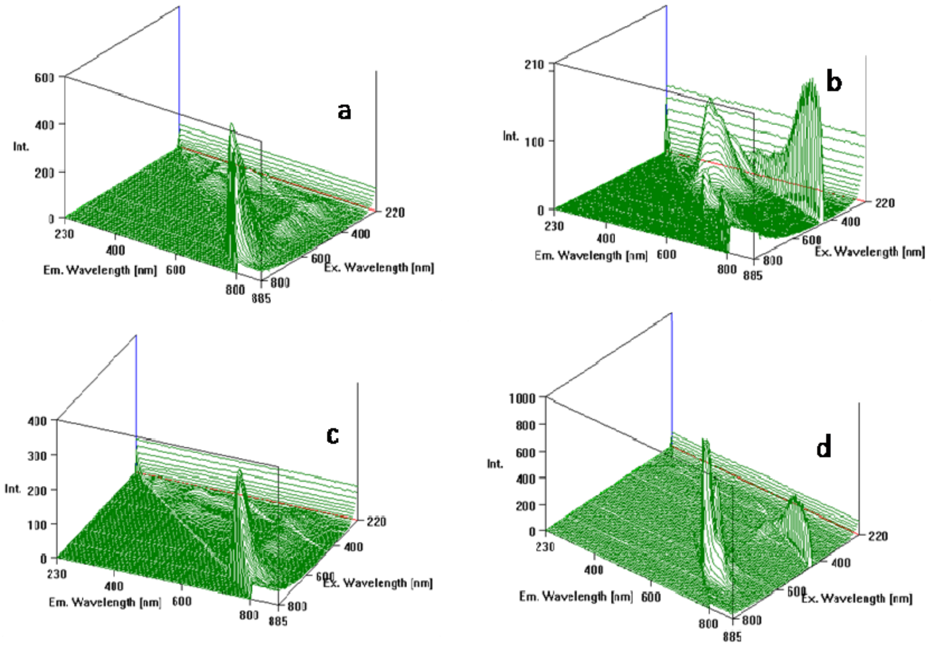

Fig. 7. Fluorescence 3D spectra for a) F0, b) F2, c) F3 and d) F4

Both the UV-VIS and the fluorescence spectroscopy prove an influence of the linkage of the $C_{60}$ upon the dyads spectroscopic properties.

TGA analysis has been used to study the thermal stability of the dyads (Fig. 8). High temperature stability has been obtained, which is normal for phthalocyanine [17], and the increase of the thermal resistance was directly proportional to the quantity of fullerene attached (noticed when comparing F2 to F4). The high stability of F0 may be due to its symmetry and the electron donor effect of the amino group, both elements that are disrupted in the case of F2. Although the addition of the $C_{60}$ should have had as a result an increasing of the thermal stability of the molecule, the symmetry and the electron-donor properties of the substituting groups on the phthalocyanine have a more important role in the overall stability of the dyad.

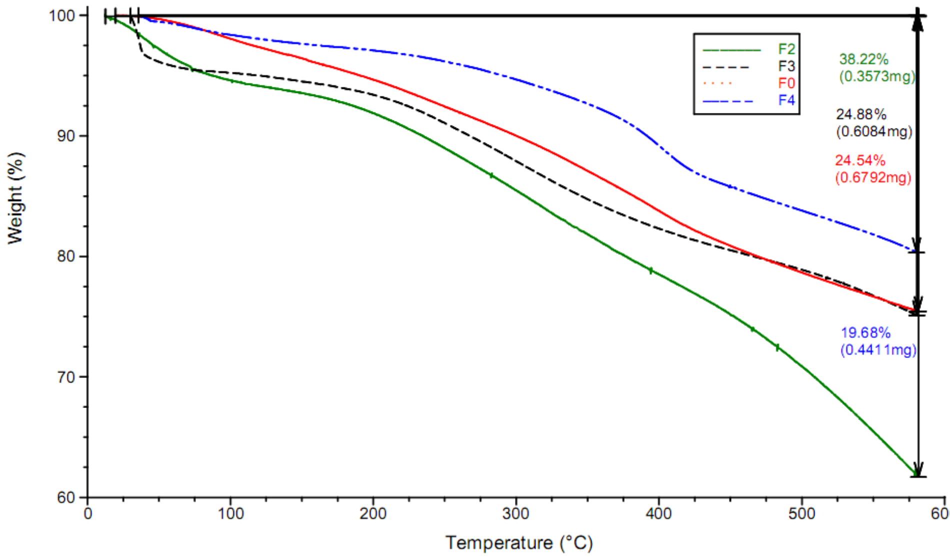

Fig. 8. TGA analysis F0, F2, F3 and F4

## 4. Conclusions

Dyads involving zinc phthalocyanine and fullerene $C_{60}$ have been synthesized. The fluorescence properties of the obtained dyads have been studied and quenching that may be due to transfer effect has been observed. The influence of the $C_{60}$ on the thermal stability of the dyads has been investigated and found not to be very important.

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