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Synthesis and Spectroscopic Properties of Porphyrin Derivatives of C60

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Synthesis and Spectroscopic Properties of Porphyrin Derivatives of C60

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Chemical synthesis of two C_{60} fullerene derivatives: with porphyrin (C_{60}-H_2P) and of the iodide salt of Zn porphyrin $(C_{60}\text{-}ZnP)^+I^-$ is described. Both compounds are soluble in several organic solvents, with a larger solubility observed for C_{60}-H_2P. Thin films obtained by solution drawing or by spinning techniques from C_{60}-H_2P solution in organic solvents or dissolved in a polymer matrix show a peculiar granular structure with regular submicron size particles. Their size of is a little smaller in polymer matrix. The solution UV–Vis absorption spectra exhibit typical bands which can be attributed to porphyrin and to the fullerene. A solvatochromic effect is observed in C_{60}-H_2P which shows a nonzero first hyperpolarizability β, most likely due to the charge transfer between fullerene and porphyrin.

Keywords Aggregation; fullerene C_{60}; Guterman model; nanoparticles; porphyrine; zinc porphyrin

Introduction

The discovery of a stable carbon aggregate composed of 60 carbon atoms [1], forming a truncated icosahedral structure of a diameter of 1 nm (C_{60}), resembling a regular golf ball in shape and later another one made of 70 carbon atoms (C_{70}), gave rise to a very important research on synthesis of these materials [2,3] studies of their properties and applications. These new classes of materials are commonly called fullerenes, as their chemical structures, particularly that of C_{60}, show some resemblance with the geodesic dome designed by the American architect Richard Buckminster Fuller for the world industrial exhibition in 1967 in Montreal, Canada. Very rapidly it was shown that these materials exhibit exceptional physico-chemical properties. For example C_{60} can be doped inside and outside the cage. Doping outside the cage with alkali ions gives a superconducting material [4].

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The π electron conjugation, leading to electron delocalization and as consequence, enhanced second hyperpolarizability γ attracted a lot of interest for these new materials for application in photonics, and particularly in nonlinear optics [5–9]. Another argument in favor of fullerenes is the absence of low energy C−H and O−H vibrations, present in organic polymers, whose harmonics absorb in the telecommunications window, the wavelength length range of targeted applications of organic NLO materials. Indeed, as it was shown by Kafafi *et al.*, the C_{60} material is perfectly transparent in near IR.

C_{60} may act as an electron accepting or electron donating molecule. It is a very useful property for practical applications. In particular it was used by Okada-Shudo *et al.* [10] in fabrication of artificial intramolecular charge transfer structures for second order NLO. This property of C_{60} is also used in photosensitizing organic materials, particularly for obtaining photorefractive properties [11] and for medical applications [12].

Another stable carbon aggregates were discovered later on, particularly the nanotubes [13,14] which exhibit very interesting properties and actually find a lot of practical applications [15]. Actually the whole family of these materials, including nanotubes, are known under the name of fullerenes.

However one of the most important problem encountered with C_{60} was the poor solubility of this molecule. Therefore a lot of chemical synthesis work was done in functionalizing it, using the active C=C bond. Also functionalizing fullerene with another molecule may bring another, interesting properties to the new compounds.

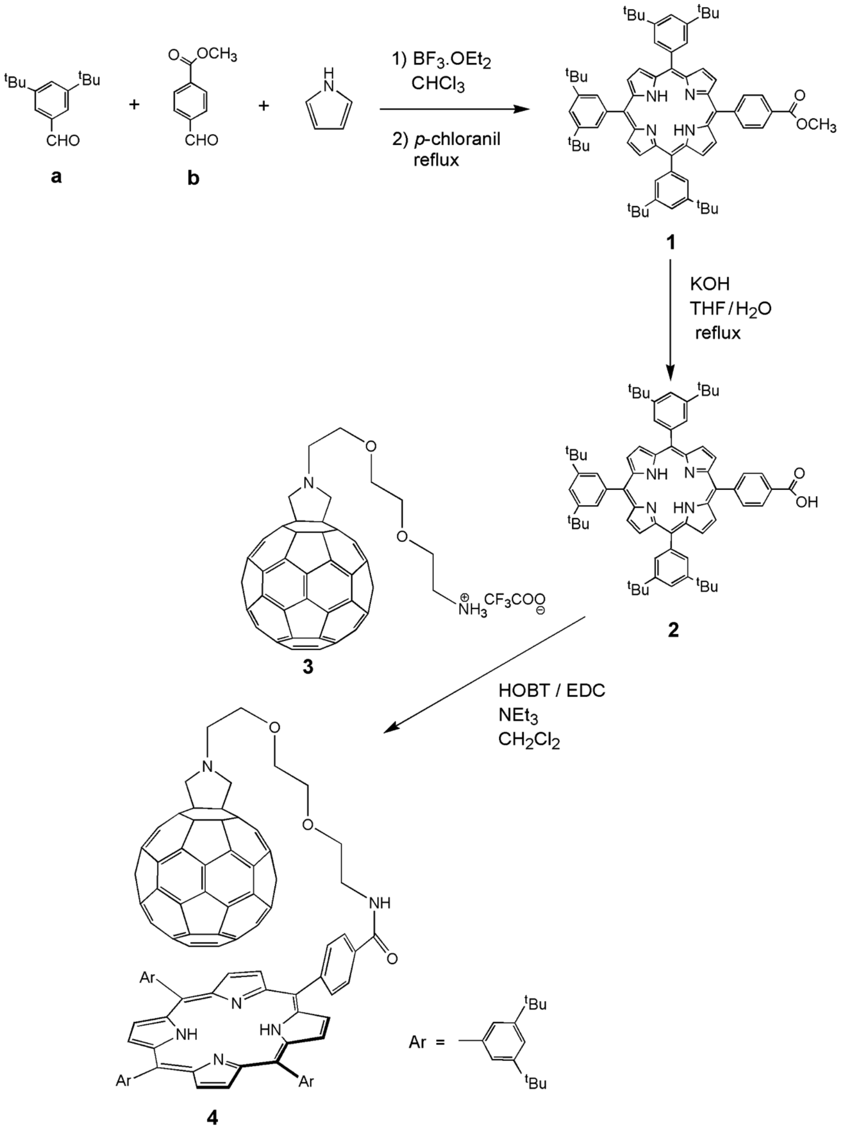
In this paper we describe the chemical synthesis of the C_{60}-porphyrin complexes and their spectroscopic properties. Porphyrin is one of the most studied and interesting molecule. The porphyrin ring is the basic part of chlorophyll with magnesium as central atom, present in all vegetables and leafs and playing a fundamental role in photosynthesis, i.e., transformation of CO_2 and water into glucose and oxygen. Similarly important role in living organisms play heme, in which the central atom is iron. Heme molecule is an important constituent of hemoglobin. Because of a strong absorption in the visible and the photosensitizing property porphyrin is also considered as a good candidate for solar energy conversion [16–18]. We have chosen two porphyrins, one with zinc as central atom and the second one with hydrogen (cf. Schemes 1 and 2).

Chemical Synthesis

The chemical routes for obtaining both compounds are shown in Scheme 1 (C_{60}-H_2P) and in Scheme 2 (C_{60}-ZnP).

Synthetic Part

Aldehyde **b** and all other reagents and solvents were obtained from Fluka, Sigma-Aldrich and J. T. Baker, and used without further purification. Mass spectra were taken with the PESCIEX API 1 (MS-ES) spectrometers. Infrared spectra were recorded on a Jasco FTIR-200 spectrometer using KBr powder (DRIFT system). ^{1}H-NMR spectra were recorded on a Jeol (400 MHz) and on a Varian Gemini-200 (200 MHz) at room temperature in $CDCl_3$. ^{13}C-NMR spectra were recorded on a Varian Gemini-200 (50 MHz) at room temperature in $CDCl_3$. Chemical shifts are

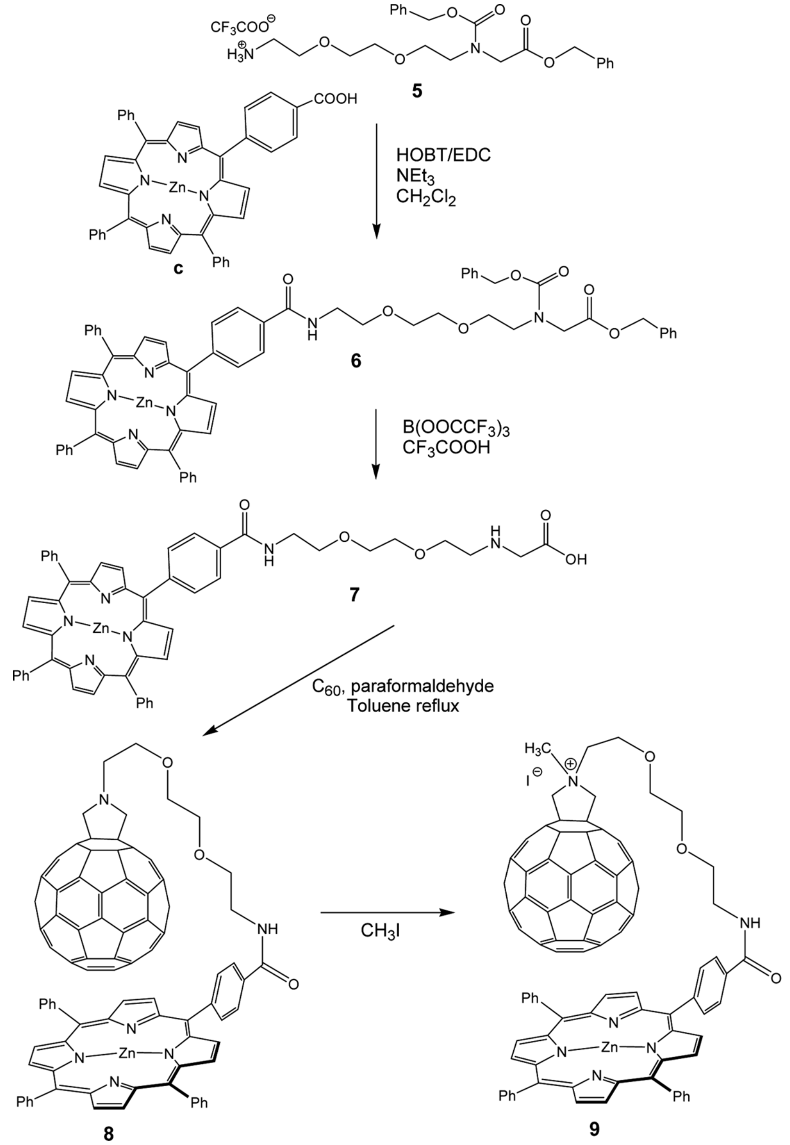


Scheme 1. Sequence of chemical reaction leading to synthesis of C_{60}-H_2P molecule.

given in parts per million (δ) relative to TMS. UV/Vis absorption spectra were recorded with a Perkin-Elmer Lambda 20 UV/Vis spectrophotometer.

The N-(3,6-dioxaoctan-1-ammonium trifluoroacetate)-fulleropyrrolidine **3** was prepared according to reported procedures in the literature [19]. The porphyrin **1** was prepared using the Lindsey conditions reported in the literature [20,21], The aldehyde **a** [22], the porphyrin **c** [23] and the salt **5** [24] were prepared according to the literature.

Porphyrin (1). To a solution of pyrrole (0.56 mL, 0.008 mol) with the aldehyde **a** (1.31 g, 0.006 mol) and the aldehyde **b** (0.33 g, 0.002 mol) in 800 mL of chloroform



Scheme 2. Sequence of chemical reaction leading to synthesis of C_{60}-ZnP molecule.

was added the $BF_3 \cdot OEt_2$ acid catalyst (0.83 mL of a 3.2 M solution in chloroform). The reaction mixture was stirred at room temperature under N_2 for 1 h. Then (1.48 g, 0.006 mol) of the oxidant *p*-chloranil was added, and the mixture was stirred under reflux for 1 h more. After cooling to room temperature the acidic solution was neutralized by addition of triethylamine (0.37 mL) and the solvent was evaporated. The product was purified by column chromatography (pure hexane following by CH_2Cl_2/hexane 1:1) to afford the compound **1** as a violet solid.

1: $C_{70}H_{80}N_4O_2$ (MW 1009.4), yield: **21%** (420 mg, 0.42 mmol). Analytical data were identical with the reported data [25].

Porphyrin (2). A solution of **1** (240 mg, 0.238 mmol) and of KOH (272 mg, 4.76 mmol) in THF/water (25/10 mL) was stirred under reflux for 5 days. The violet organic phase was decanted from the colourless aqueous phase, and the THF was evaporated. The residue was dissolved in dichloromethane and washed 2 times with a saturated solution of NH_4Cl and with distilled water. The organic phase was dried over Na_2SO_4 and the solvent was evaporated under vacuum. The crude residue was purified by column chromatography (pure CH_2Cl_2 following by EtOAc/MeOH 9:1) to afford the compound **2** as a violet solid.

2: $C_{69}H_{78}N_4O_2$ (MW 995.4), yield: **88%** (210 mg, 0.211 mmol). Analytical data were identical with the reported data [26].

C_{60}-H_2P (4). The fullerene derivative **3** (52 mg, 0.054 mmol) was dispersed in 6 mL of dichloromethane with 17 µL (0.113 mmol) of triethylamine and the mixture was stirred at room temperature for 30 minutes. The porphyrin derivative **2** (45 mg, 0.045 mmol) was dissolved in 12 mL of dichloromethane with the 1-Hydroxybenzotriazole hydrate HOBT (13 mg, 0.090 mmol) and the N′-(3-Dimethylaminopropyl)-N-ethylcarbodiimid Hydrochloride EDC (18 mg, 0.090 mmol). The mixture was then stirred at room temperature under N_2 for 30 min. Then the solution of **3** with NEt_3 was added to the solution of porphyrin **2** with HOBT/EDC and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the crude residue was purified by column chromatography (Toluene/EtOAc 2:3). The brown purple solid was dissolved in dichloromethane and precipitated by addition of methanol to afford the desired compound **4**.

4: $C_{137}H_{94}N_6O_3$ (MW 1872.3), yield: **89%** (74 mg, 0.040 mmol). ^{1}H-NMR 400 MHz ($CDCl_3$): δ 8.81 (t, J = 5.2 Hz, 2H, $H_{\beta 1}$), 8.77 (t, J = 5.2 Hz, 6H, $H_{\beta 2}$), 8.43 (d, J = 8.2 Hz, 2H, H_m), 8.32 (d, J = 8.2 Hz, 2H, H_o), 8.04 (d, J = 1.7 Hz, 2H, $H_{o'}$), 7.92 (d, J = 1.7 Hz, 4H, $H_{o''}$), 7.80 (t, J = 1.7 Hz, 1H, $H_{p'}$), 7.74 (t, J = 1.7 Hz, 2H, $H_{p''}$), 7.38 (bs, 1H, NH-CO), 4.05 (t, J = 6.6 Hz, 2H), 3.95 (s, 4H, H_{pyrr}), 3.88 (m, 8H), 3.29 (t, J = 6.6 Hz, 2H), 1.56 (s, 18H, tBu′), 1.47 (s, 36H, tBu″), −3.00 (bs, 2H, NH_{porph}). ^{13}C-NMR 200 MHz ($CDCl_3$): δ 167.6; 153.1; 148.6; 146.3; 145.9; 144.9; 144.6; 144.1; 143.8; 143.4; 142.8; 141.2; 141.1; 140.5; 140.1; 139.9; 138.1; 134.8; 134.3; 134.0; 131.4; 129.6; 128.9; 128.2; 125.4; 121.9; 121.5; 120.9; 117.8; 70.5; 70.1; 69.7; 69.4; 68.4; 54.6; 39.8; 35.1; 31.9; 29.7. ES-MS (Tetrahydrofuran): $m/z = 1873$ $[M + H^+]$. FT-IR: cm^{-1} 3917, 2951, 2875, 2710, 2351, 1788, 1676, 1600, 1473, 1360, 1263, 1128, 985, 918, 812, 737, 542.

Amino Ester (6). The salt **5** (180 mg, 0.332 mmol) was dispersed in 6 mL of dichloromethane with 115 µL (84 mg, 0.831 mmol.) of triethylamine and the mixture was stirred at room temperature for 30 minutes. The porphyrin derivative **c** (200 mg, 0.277 mmol) was dissolved in 12 mL of dichloromethane with the 1-Hydroxybenzotriazole hydrate HOBT (61 mg, 0.553 mmol) and the N′-(3-Dimethylaminopropyl)-N-ethylcarbodiimid Hydrochloride EDC (106 mg, 0.553 mmol). The mixture was then stirred at room temperature under N_2 for 30 min. Then the solution of **5** with NEt_3 was added to the solution of porphyrin **c** with HOBT/EDC and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the crude residue was purified by column chromatography (CH_2Cl_2/EtOAc 1:9) to afford compound **6** as a violet solid.

6: $C_{68}H_{56}N_6O_7Zn$ (MW 1134.60), yield: **40%** (150 mg, 0.133 mmol). ^{1}H-NMR 200 MHz ($CDCl_3$): δ 8.96–8.88 (m, 6H), 8.86–8.80 (m, 2H), 8.27–8.13 (m, 8H), 7.95–7.82 (m, 2H), 7.81–7.66 (m, 9H), 7.32–7.01 (m, 10H), 6.93 (t, J = 5.0 Hz, 1H), 5.01, 4.97 (s, 2H), 4.95, 4.87 (s, 2H), 4.08, 4.04 (s, 2H), 3.61–3.34 (m, 12H). ^{13}C-NMR 50 MHz ($CDCl_3$): δ 169.68, 166.95, 155.93, 155.65, 150.28, 150.21, 150.17, 149.66, 146.32, 146.21, 142.93, 136.19, 136.02, 135.16, 134.51, 132.56, 132.22, 132.10, 131.59, 128.49, 128.30, 128.08, 127.88, 127.77, 127.62, 127.51, 126.59, 124.92, 121.36, 121.22, 119.52, 70.21, 70.06, 69.80, 67.48, 67.36, 66.82, 50.22, 50.25, 48.12, 47.83, 39.41. ES-MS (Methanol): $m/z = 1070$ (M-Zn), 1074 (MH^+-Zn). FT-IR: cm^{-1} 3634, 3336, 3055, 2879, 1748, 1703, 1479, 1195, 998, 750, 707, 477.

Amino Acid (7). Equivalent amounts of boron tribromide (1.13 mL, 12 mmol) and trifluoroacetic acid (0.92 mL, 12 mmol) were mixed at 0°C in dichloromethane (15 mL) whereupon a precipitate was formed. The mixture was evaporated to dryness under reduced pressure. The residue was dissolved in trifluoroacetic acid (5 mL) and this solution was added directly to a solution of the amino ester **6** (240 mg, 0.2 mmol) in trifluoroacetic acid (10 mL) and stirred for 1 hour at room temperature. The solvent was evaporated and the boron compounds were removed by repeated evaporation with MeOH, yielding a green solid after precipitation with diethyl ether.

7: $C_{53}H_{44}N_6O_5Zn$ (MW 910.34), yield: **99%** (180 mg, 0.2 mmol). ^{1}H-NMR 200 MHz (CD_3OD): δ 8.87–8.73 (m, 8H), 8.32 (d, J = 8.2 Hz, 2H), 8.25–8.09 (m, 8H), 7.79–7.66 (m, 9H), 3.99–3.67 (m, 8H), 3.65–3.54 (m, 4H), 3.47 (t, J = 5.2 Hz, 2H). ^{13}C-NMR 50 MHz (CD_3OD): δ 168.52, 166.94, 149.53, 149.47, 149.39, 148.87, 146.53, 142.76, 133.76, 133.62, 132.44, 130,80, 130.60, 130.10, 127.62, 126.46, 125.50, 124.43, 120.22, 120.04, 118.30, 69.48, 69.42, 69.37, 69.30, 68.87, 67.90, 64.97, 64.91, 38.98, 38.53. ES-MS (Methanol): $m/z = 867$ (MNa^+-Zn). FT-IR: cm^{-1} 3555, 3062, 1677, 1549, 1485, 1430, 1196, 1136, 802, 713, 450. UV/Vis (CH_2Cl_2): $\lambda_{max} = 349$, 418, 435, 514, 550, 593, 651.

C_{60}-ZnP (8). A solution of amino acid **7** (51 mg, 0.056 mmol) in methanol (2 ml) was added to a mixture of C_{60} (128 mg, 0.177 mmol) and paraformaldehyde (118 mg, 3.9 mmol) in toluene (180 mL). The mixture was heated under reflux of toluene for 1 hour and 45 minutes. After evaporation of solvent, the crude material was purified by flash chromatography (toluene followed by toluene/AcOEt 8:2). The brown solid was dissolved in dichloromethane and precipitated by ethyl ether to afford compound **8**.

8: $C_{113}H_{44}N_6O_3Zn$ (MW 1598.99), yield: **33%** (30 mg, 0.019 mmol). ^{1}H-NMR 200 MHz ($CDCl_3$): δ 8.90–8.69 (m, 8H), 8.31–7.97 (m, 10H), 7.81–7.63 (m, 9H), 7.21 (bs, 1H), 4.44 (s, 4H), 4.06–3.47 (m, 10H), 3.37–3.18 (m, 2H). ES-MS (Tetrahydrofurane/Methanol): $m/z = 1537$ (masse without Zn) 1600 (MH^+). FT-IR: cm^{-1} 3301, 3052, 2923, 2792, 1659, 1485, 1342, 1114, 999, 757, 443. UV/Vis (CH_2Cl_2): $\lambda_{max} = 512$, 550, 590, 663.

$(C_{60}$-ZnP$)^+I^-$ (9). A mixture of fulleropirrolidine **8** (30 mg, 0,019 mmol) and methyl iodide (4 mL, 64.25 mmol) was stirred at 80°C for 24 hours. After this time the methyl iodide in excess was remove by evaporation, the solid residue was washed with toluene, dissolved in dichloromethane and precipitated by ethyl ether to obtain compound **9**.

9: $C_{114}H_{47}IN_6O_3Zn$ (MW 1740.93), yield: **99%** (33 mg, 0.019 mmol). ES-MS (Tetrahydrofurane/Methanol): $m/z = 1611$ (M^+). Both compounds are partly soluble in common organic solvents. C_{60}-H_2P is soluble in dioxane at least 22 mg/ml (not more than 77.2 mg/ml), 1,1,2-trichloroethane, 1,2-dichloroethane, acetone, chloroform, DMF, DMSO. The iodide salt $(C_{60}\text{-ZnP})^+I^-$ issoluble in toluene (at least 21 mg/ml), and slightly in DMF and in dioxane. Insoluble in DMSO, and in acetonitrile.

Thin Film Formation

Because of poor solubility of the iodide salt, thin film formation ability was tested only for C_{60}-H_2P either in its pristine form or in blend with a polymer (PMMA). Two techniques were used:

- solution casting
- solution drawing

In all cases thin films of a granular form were obtained, as shown in Figures 1–2. The size of particles is typically of few hundreds of nanometers. It doesn't depend on the solvent used nor on the deposition conditions. A slightly smaller particles are obtained from C_{60}-H_2P dissolved in polymer (PMMA) (cf. Fig. 2). Apparently this ability to form well defined, regular nanoparticles is a property of this molecule and a finger print of a strong cohesion within this material, thus a strong interaction between the molecules. We note here that aggregation of porphyrin molecules was already reported either at higher solution concentrations [27] or by modifying environment (pH, polarity, etc.) [28–30]. Similar property can be expected for the second synthesized molecule, not tested in this study because of the already mentioned limited solubility.

UV-Vis Spectroscopy

Figure 3 shows absorption spectra of C_{60}-H_2P in different solvents. Well defined contribution of C_{60} absorption bands at 350 nm are seen as well as the porphyrin Soret (around 427 nm, except in 1,1,2-trichloroethane where it is red shifted to by about 30 nm) and four, weaker, Q bands in the wavelength range 500–700 nm [31].

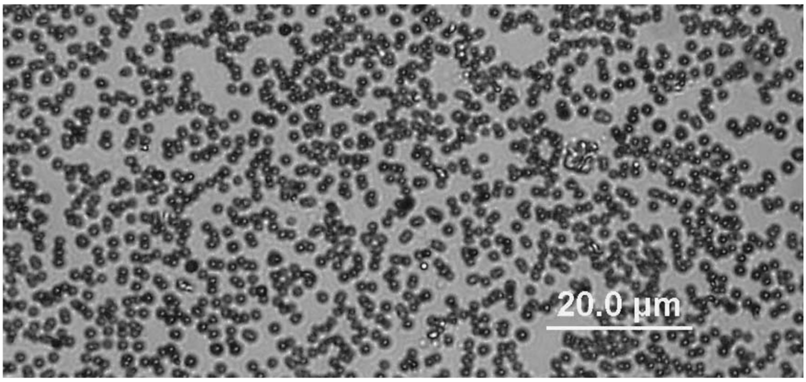


Figure 1. Optical microscope picture of thin film obtained by spin coating of C60-H_2P compound from 1,1,2-trichloroethane solution.

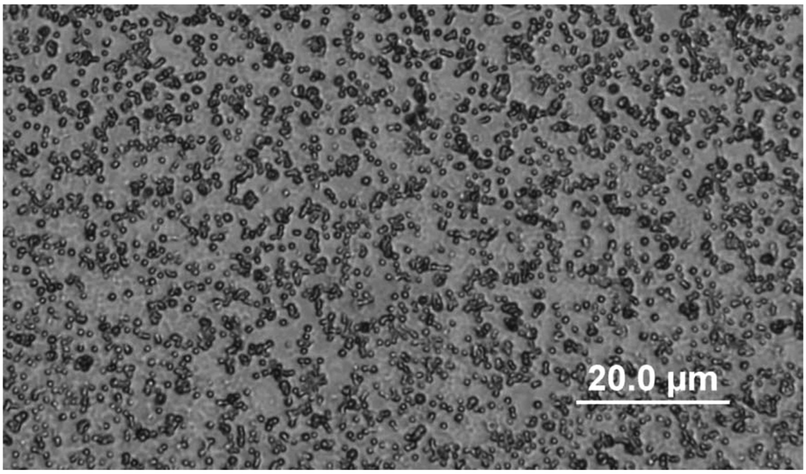


Figure 2. Optical microscope picture of thin film obtained by spin coating of C60-H_2P solution in PMMA. Here dioxane was used as solvent.

Although these bands seem to disappear completely in spectrum measured in of 1,1,2-trichloroethane, they are only strongly quenched in this solvent. This conclusion arises from Figure 4. The observed absorption spectra are in good agreement with the Gouterman four orbital model [32] (two HOMO and two LUMO), according to which the strong Soret band is due to the singlet – singlet transition between

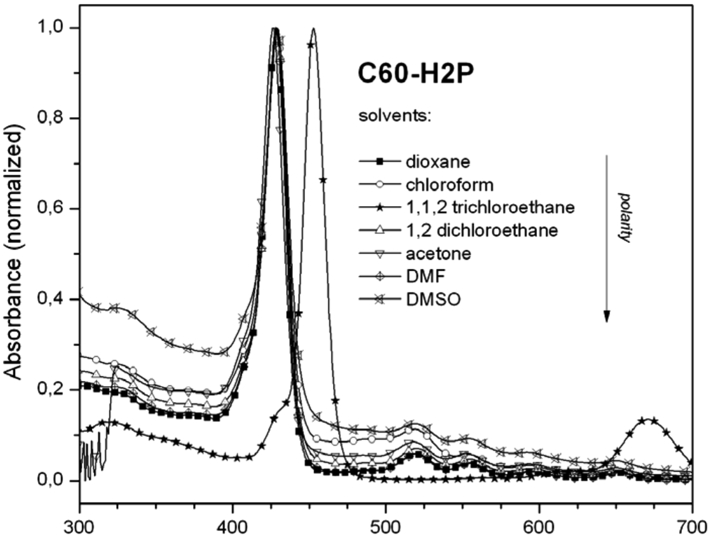


Figure 3. Optical absorption spectra of C_{60}-H_2P measured in solvents of increasing dipole moments (polarity), dioxane 0.4D (debye), chloroform 1.4D, 1,1,2-trichloroethane 1.7D, 1,2-dichloroethane 1.75D, acetone 2.7D, dimethylformamide (DMF) 3.8, dimethylsulfoxide (DMSO) 3.9D.

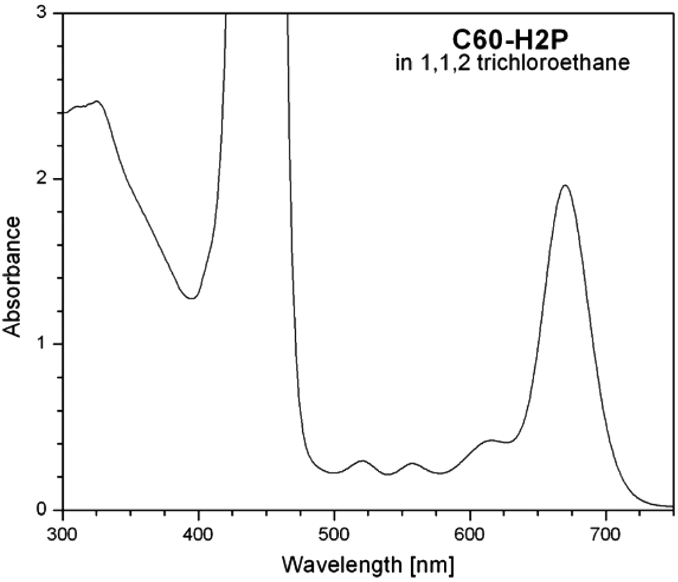


Figure 4. Absorption spectra in UV-*vis* wavelength range measured for C_{60}-H_2P compound in 1,1,2-trichloroethane measured in more concentrated solution then the spectrum shown in Figure 3.

the lowest (S_0) and the highest (S_2) states, whereas the weaker Q band arises from S_0 to S_1 transition. The observed several absorption bands in Q band are due the vibronic contributions. In the range 500–650 nm fullerene contributes to the absorption spectrum of the compound too. Central atom and the side groups influence the postion of both Soret and Q bands.

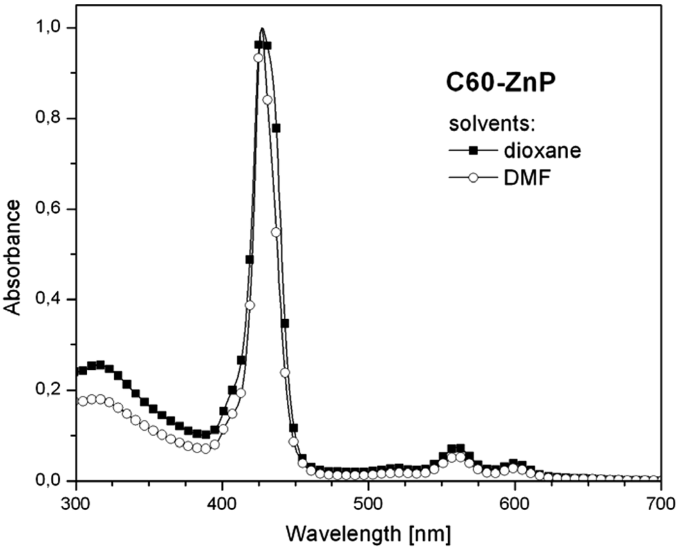


Figure 5. Optical absorption spectra of $[C_{60}\text{-ZnP}]^+I^-$ in two solvents: DMF and Dioxan.

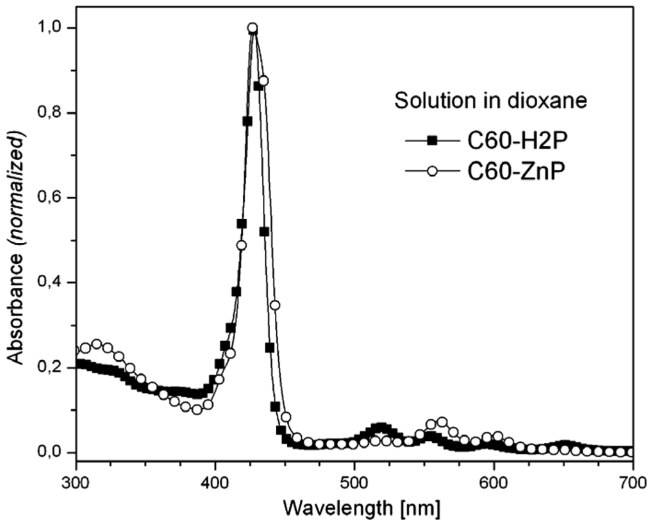


Figure 6. Comparison of optical absorption spectra of C_{60}-H_2P and $[C60\text{-}ZnP]^+I)$ in dioxane.

As already mentioned, we observe an important red shift of the porphyrin absorption spectrum between dioxane and 1,1,2-trichloroethane solution. Such a solvatochromic property is a finger print of nonzero first hyperpolarizability β which is proportional to the difference of dipolar moments at fundamental and first allowed excited state [33] and is used to determine this NLO hyperpolarizability [34]. As both molecules C_{60} and H_2P are centrosymmetric one can reasonably assume that a charge transfer occurs between them.

Figure 4 shows optical absorption spectra of $[C_{60}\text{-}ZnP]^+I^-$ in two solvents: DMF and dioxane. The absorption spectrum is very similar to that of C_{60}-H_2P with, similarly, contributions coming from C_{60} and ZnP. Also the harmonic replicas are present in the 500–700 nm wavelength range. Because of poor solubility of this molecule no absorption spectra for solution in 1,1,2-trichloroethane are available. Also no solvatochromic effect is observed in other solutions using the same solvents as in the case of C_{60}-H_2P. A slight, red shift is visible between absorption spectrum of $[C_{60}\text{-}H_2P]^+$ I^- and that of C_{60}-H_2P, as displayed in Figure 6.

Conclusions

We have synthesized two new C_{60} fullerene derivatives: with porphyrin (C_{60}-H_2P) and an iodide salt of Zn porphyrin $(C_{60}\text{-}ZnP)^+I^-$. First molecule shows better solubility than the second. Absorption spectra exhibit a strong Soret band and four Q bands, in agreement with the Gouterman four orbital model. A solvatochromic effect in C_{60}-H_2P is observed, with a red shift of about 30 nm of Soret band between 1,1,2-trichloroethane and several other solvens (dioxane, acetone, chloroform, DMF, DMSO…). This indicates that the molecule exhibit second order NLO properties. Solution cast thin films of C_{60}-H_2P are composed from regular submicron size particles. The size of the particles depends on the environment. When C_{60}-H_2P is dissolved in PMMA their size is reduced.

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