Synthesis of Conjugates Based on Fullerene C_{60} and *meso*–Tetraphenylporphyrins with Long Chain Substituents

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In this paper we report the synthesis of porphyrin-fullerene C_{60} conjugates by reaction of Prato. Conjugates were determined by ^{1}H-, ^{13}C-NMR, IR, UV-vis spectroscopy and MALDI-TOF mass spectrometry.

Keywords: Porphyrin, fullerene C_{60}, conjugates, reaction of Prato.

In recent time the functionally substituted fullerenes are of the particular interest; a large number of publications in the world literature is devoted to the synthesis and study of these compounds.[1-10]

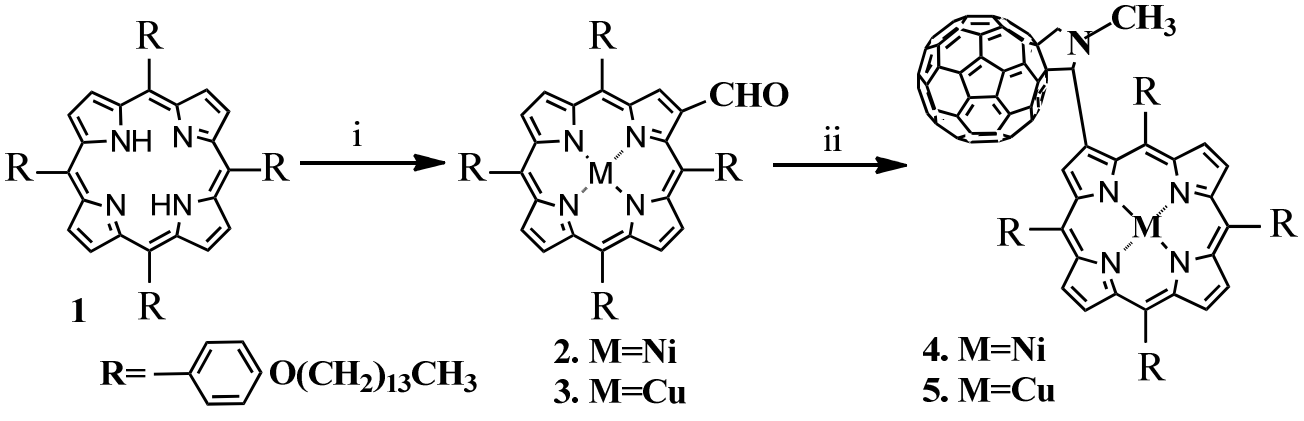
Fullerene derivatives have valuable properties and can find practical application in various fields of science and technology as a new chromatographic carriers, liquid crystals, catalysts, dyes, superfirm composites, various conductors, molecular ferromagnets.[1] Application of water-soluble derivatives of fullerene in medicine is rather perspective.[2] Electron donors such as porphyrin, ferrocene, *N*,*N*-dimethylaminophenyl, ruthenium(II) trisbipyridine and tetrathiafulvarene, phtalocyanines and others[3-10] have been employed to form fullerene - electron donor type dyads and also can find application in photovoltaic. Since fullerenes linked to porphyrins can produce a long-lived charge-separated state with a high quantum yield in comparison with other known types of donor-acceptor complexes, they are useful candidates to build molecular and supramolecular devices and artificial light energy harvesting systems with unique electronic and magnetic properties.[1,12]

One of the most quickly developing directions is connected with the synthesis and study of fullerene-containing thermotropic liquid crystals (LC) - a new class of nanostructured materials. C_{60} does not behave as a mesogenic unit. Two approaches have been developed for the preparation of fullerene-containing liquid crystalline derivatives: in the first one (covalent approach),[13-19] C_{60} is functionalized with liquid crystalline addends, whereas in the second one (non-covalent approach),[20-21] a supramolecular complex is formed between C_{60} and mesogenic fragments. It was shown that mesomorphic derivatives of porphyrins can be chosen as mesogenic fragments.[2,22] To the beginning of our research the conjugates on the basis of covalent-associated conjugates of fullerene C_{60} and mesogenic porphyrins have not been described in the literature.

The present work is devoted to the synthesis of porphyrin-fullerene conjugates based on the fullerene C_{60} and previously obtained *meso*-arylsubstituted porphyrins containing long chain alkyl groups.

Conjugates **4**, **5** were obtained by the method of Prato.[2] Formylporphyrins with long alkyl substituents were used as aldehyde components. The *meso*-arylsubstituted porphyrin **1** was synthesized by the monopyrrole condensation method in soft conditions using pyrrole and 4-tetradecyloxybenzaldehyde with 40 % yield.[23] Based on the compound **1** Ni and Cu complexes were obtained (Scheme 1). Formylporphyrins **2**, **3** were synthesized by the Vilsmeier method using DMF and $POCl_3$ in $CHCl_3$ during 5-6 h, t = 60°C.

The structure of Ni and Cu complexes of 2-formyl-5,10,15,20–tetrakis-(*p*-tetradecyloxyphenyl)porphyrin (**2**, **3**) was determined by ^{1}H NMR, IR, UV-vis spectroscopy



Scheme 1. The synthesis of porphyrin-fullerene C_{60} conjugates. i - 1) $NiCl_2$/$Cu(AcO)_2$, MeOH, $CHCl_3$; 2) DMF and $POCl_3$, $CHCl_3$, ii – C_{60}, *N*-methylglycine, toluene, argon.

and MALDI-TOF MS. The IR spectra show the bands at 1671 cm^{-1} (**2**) and 1673 cm^{-1} (**3**), which correspond to the stretching vibrations of the aldehyde group. In the electronic absorption spectrum of compound **2** a bathochromic shift of the Soret band from 420 nm to 432.5 nm was observed, what confirms the formation of the formyl group. In the ^{1}H NMR spectrum of porphyrin **2** the formyl proton resonated as a distinctive singlet at δ = 9.29 ppm, whereas the signal of β-proton of the substituted pyrrole ring was observed at δ = 9.30 ppm. Formyl group causes downfield chemical shift of the signal of the neighboring β-proton due to the growth of the ring current as a result of +C-effect. Other β-protons have chemical shifts at δ = 8.65-8.80 ppm.

The coupling reaction of aldehydes **2**, **3** with *N*-methylglycine and C_{60} in toluene at reflux gave the pyrrolidine-linked porphyrin-fullerene dyads (**4**, **5**). The formation of the conjugate was controlled by TLC (hexane:toluene = 3:1, R_f = 0.75 (**2**), R_f = 0.80 (**3**)). Products **4**, **5** were isolated by column chromatography on silica gel (hexane:toluene = 3:1, hexane:chloroform = 3:1). The yields of compounds **4**, **5** are 20-25 %. The structures of dyads **4**, **5** were determined by spectroscopic analysis such as ^{1}H, ^{13}C-NMR, IR, UV-vis spectroscopy, and MALDI-TOF MS.

In the UV-vis spectrum of **4** the Soret band (λ_{max} = 426.5 nm) is hypsochromically shifted if compared with that of formyl-porphyrin **2** (λ_{max} = 432.5 nm). The absorption bands of the formyl group are not observed in the IR spectra of compounds **4** and **5**. MALDI-TOF MS spectrum exhibit the corresponding M^+ ion peak: (*m/z*) 2298 for **4** and intensive peaks *m/z* (a.u.): 1574.870 (66427), 1577.034 (14192), 1577.952 (24462), which correspond to the characteristic decomposition products. The ^{1}H NMR spectrum of **4** in $CDCl_3$ solution exhibits expected features with correct integration ratios: δ = 5.30 ppm (1H, s, NC*H*), 4.09, 4.12 ppm, (2H, m, NCH_2), 2.75 ppm (3H, s, NCH_3). The ^{13}C NMR spectrum for **4** shows a multiplicity of signals in the region at 159.80-113.12 ppm arising from fullerene, as well as four peaks assignable to the two pyrrolidine carbon atoms (69.4, 76.84 ppm) and two sp^3 fullerene carbon atoms (68.4, 77.72 ppm).

Thus, novel conjugates **4**, **5** were synthesized on the basis of the fullerene C_{60} and *meso*-arylsubstituted porphyrin with long chain substituents.

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