

## Synthesis of Conjugates Based on Fullerene C<sub>60</sub> and *meso*-Tetraphenylporphyrins with Long Chain Substituents

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In this paper we report the synthesis of porphyrin-fullerene C<sub>60</sub> conjugates by reaction of Prato. Conjugates were determined by <sup>1</sup>H-, <sup>13</sup>C-NMR, IR, UV-vis spectroscopy and MALDI-TOF mass spectrometry.

**Keywords:** Porphyrin, fullerene C<sub>60</sub>, 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.<sup>[1-10]</sup>

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.<sup>[1]</sup> Application of water-soluble derivatives of fullerene in medicine is rather perspective.<sup>[2]</sup> Electron donors such as porphyrin, ferrocene, *N,N*-dimethylaminophenyl, ruthenium(II) trisbipyridine and tetrathiafulvarene, phthalocyanines and others<sup>[3-10]</sup> 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.<sup>[1,12]</sup>

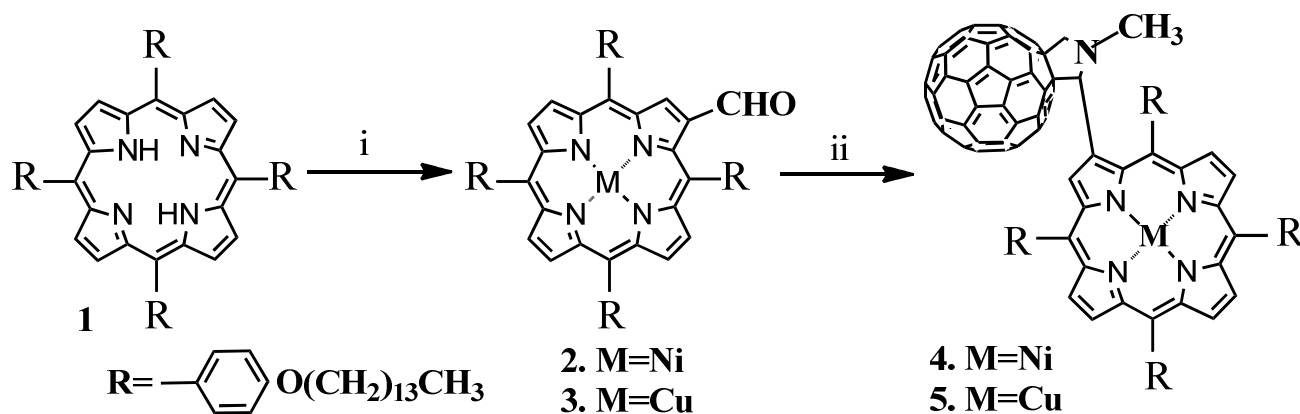
One of the most quickly developing directions is connected with the synthesis and study of fullerene-containing thermotropic liquid crystals (LC) - a new class of nanostructured materials. C<sub>60</sub> does not behave as a mesogenic unit. Two approaches have been developed for the preparation

of fullerene-containing liquid crystalline derivatives: in the first one (covalent approach),<sup>[13-19]</sup> C<sub>60</sub> is functionalized with liquid crystalline addends, whereas in the second one (non-covalent approach),<sup>[20-21]</sup> a supramolecular complex is formed between C<sub>60</sub> and mesogenic fragments. It was shown that mesomorphic derivatives of porphyrins can be chosen as mesogenic fragments.<sup>[2,22]</sup> To the beginning of our research the conjugates on the basis of covalent-associated conjugates of fullerene C<sub>60</sub> 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<sub>60</sub> and previously obtained *meso*-arylsubstituted porphyrins containing long chain alkyl groups.

Conjugates **4**, **5** were obtained by the method of Prato.<sup>[2]</sup> 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.<sup>[23]</sup> 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<sub>3</sub> in CHCl<sub>3</sub> 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 <sup>1</sup>H NMR, IR, UV-vis spectroscopy



**Scheme 1.** The synthesis of porphyrin-fullerene C<sub>60</sub> conjugates. i - 1) NiCl<sub>2</sub>/Cu(AcO)<sub>2</sub>, MeOH, CHCl<sub>3</sub>; 2) DMF and POCl<sub>3</sub>, CHCl<sub>3</sub>, ii - C<sub>60</sub>, *N*-methylglycine, toluene, argon.

and MALDI-TOF MS. The IR spectra show the bands at 1671 cm<sup>-1</sup> (**2**) and 1673 cm<sup>-1</sup> (**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 <sup>1</sup>H NMR spectrum of porphyrin **2** the formyl proton resonated as a distinctive singlet at  $\delta = 9.29$  ppm, whereas the signal of  $\beta$ -proton of the substituted pyrrole ring was observed at  $\delta = 9.30$  ppm. Formyl group causes downfield chemical shift of the signal of the neighboring  $\beta$ -proton due to the growth of the ring current as a result of +C-effect. Other  $\beta$ -protons have chemical shifts at  $\delta = 8.65$ -8.80 ppm.

The coupling reaction of aldehydes **2**, **3** with *N*-methylglycine and C<sub>60</sub> 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 <sup>1</sup>H, <sup>13</sup>C-NMR, IR, UV-vis spectroscopy, and MALDI-TOF MS.

In the UV-vis spectrum of **4** the Soret band ( $\lambda_{\max} = 426.5$  nm) is hypsochromically shifted if compared with that of formyl-porphyrin **2** ( $\lambda_{\max} = 432.5$  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<sup>+</sup> 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 <sup>1</sup>H NMR spectrum of **4** in CDCl<sub>3</sub> solution exhibits expected features with correct integration ratios:  $\delta = 5.30$  ppm (1H, s, NCH), 4.09, 4.12 ppm, (2H, m, NCH<sub>2</sub>), 2.75 ppm (3H, s, NCH<sub>3</sub>). The <sup>13</sup>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<sup>3</sup> fullerene carbon atoms (68.4, 77.72 ppm).

Thus, novel conjugates **4**, **5** were synthesized on the basis of the fullerene C<sub>60</sub> and *meso*-arylsubstituted porphyrin with long chain substituents.

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