Synthesis of Conjugates Based on Fullerene C$_{60}$ and meso-Tetraphenylporphyrins with Long Chain Substituents

Ekaterina S. Krutikova, Natal’ya A. Bragina, and Andrey F. Mironov
Lomonosov Moscow State Academy of Fine Chemical Technology, 119571 Moscow, Russia
@Corresponding author E-mail: e.s.krutikova@gmail.com

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, superfim 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 tetraithialfulvarene, phthalocyanines 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, $t = 60^\circ$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 $\delta = 9.29$ 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 $\delta$-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 $\text{C}_{60}$ 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 ($\lambda_{max} = 426.5$ 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 $\text{M}^+$ 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; $\delta = 5.30$ ppm (1H, s, NCH$_3$), 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 $sp^2$ fullerene carbon atoms (68.4, 77.72 ppm).

Thus, novel conjugates 4, 5 were synthesized on the basis of the fullerene $\text{C}_{60}$ and meso-arylsubstituted porphyrin with long chain substituents.

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