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Covalent-bound conjugates of fullerene C_{60} and metal complexes of porphyrins with long-chain substituents

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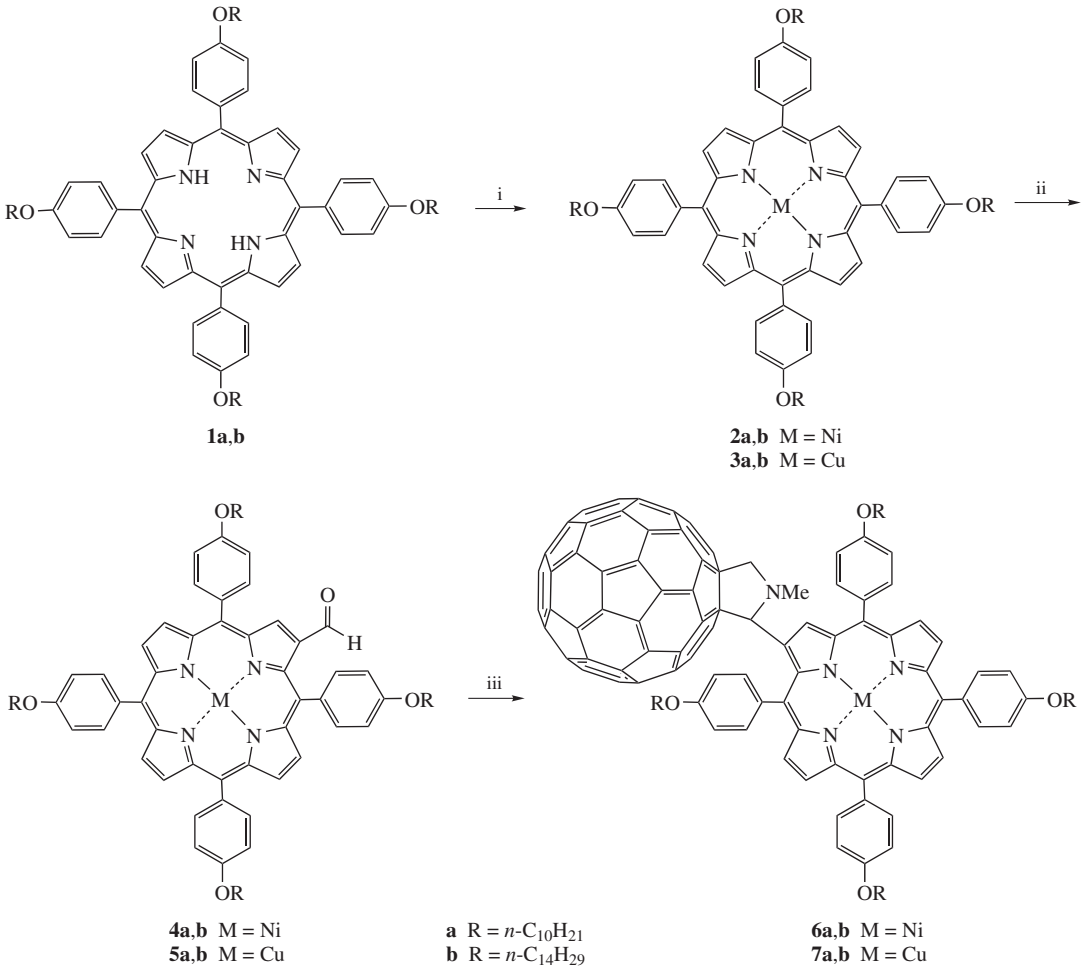
Conjugates of fullerene C_{60} and lipophilic *meso*-arylporphyrins with long-chain substituents were prepared using the Prato reaction.

Porphyrin-fullerenes possess unique photophysical and electrochemical properties and are the promising objects for nanotechnology and for the preparation of extra-hard composites, conductive materials, liquid crystals, bioactive compounds and pharmaceuticals.[1–8] The hydrophobic properties of fullerenes facilitate their transport through the lipid bilayer of the cell membrane, whereas functionalisation of fullerene with derivatives of photoactive tetrapyrrole compounds opens a way to create pharmaceutical products for the PDT of cancer.[9] Conjugates based on fullerenes and porphyrins are used in studies on intramolecular photoinduced electron transfer and in simulations of artificial photosynthetic sites; in this case, the life time of a state with separated charges in such systems is by a few orders longer than that in other known types of donor-acceptor systems.[10–12] The presence of long-chained substituents in the porphyrin molecules changes considerably their properties and enhances their capability to undergo self-organisation,[13] which makes them suitable for photovoltaics and optoelectronics. Such conjugates may be of interest in the synthesis of new materials for light-conducting systems.

This study deals with a synthesis of covalent-bound porphyrin–fullerene conjugates based on fullerene C_{60} and *meso*-aryl-substituted porphyrins with long-chain substituents.

The Prato reaction was the one of choice for our purpose, since it affords fullero[1,2]pyrrolidines by 1,3-cycloaddition of



1a,**b**

2a,**b** M = Ni
3a,**b** M = Cu

4a,**b** M = Ni
5a,**b** M = Cu

a R = *n*-$C_{10}H_{21}$
b R = *n*-$C_{14}H_{29}$

6a,**b** M = Ni
7a,**b** M = Cu

Scheme 1 *Reagents and conditions*: i, $NiCl_2$, DMF, 6 h or $Cu(OAc)_2$, CH_2Cl_2, MeOH, 4 h; ii, DMF, $POCl_3$, CH_2Cl_2, 6 h, Ar; iii, C_{60}, *N*-methylglycine, toluene, Ar, 20 h.

azomethine ylides (generated from α-amino acids and aldehydes) to a fullerene.[1] Variation within the aldehyde component makes it possible to synthesize fulleropyrrolidines with various substituents at the pyrrolidine ring. Herein, we used mono-β-formyltetraphenylporphyrins with long-chain alkyl substituents at the *para*-positions of phenyl groups as the aldehyde component.

The starting *meso*-aryl-substituted porphyrins **1a**,**b** were obtained in 40% yield by monopyrrole condensation from pyrrole and the corresponding 4-alkoxybenzaldehydes.[14] Metal complexes with Ni (**2a**,**b**) and Cu (**3a**,**b**) were obtained from compounds **1a**,**b** (Scheme 1).† The copper complexes of porphyrins were obtained in 95% yield in CH_2Cl_2 and MeOH. In the case of nickel complexes, the reaction in CH_2Cl_2 and MeOH gave lower yields (70%), so it was subsequently carried out by refluxing in DMF.

The Vilsmeier formylation[15,16] of metal complexes **2** and **3** was performed in dichloromethane by heating for 5–6 h. The yields of formylporphyrins **4** and **5** were 55–60%. The metal complexes of formylporphyrins thus obtained were characterised by IR, UV, ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry.† The IR spectra contained bands at 1671 cm^{-1} for compound **5a** and 1673 cm^{-1} for compound **4a**, which correspond to the stretching vibrations of the aldehyde group conjugated with the aromatic ring. The electronic absorption spectrum of compounds **4a**,**b** showed a bathochromic shift of the Soret band from 418 to 432 nm. The ^{1}H NMR spectrum of porphyrin **4a** contained a signal of formyl group proton at δ 9.32 and a signal of the adjacent β-proton at δ 9.30. The formyl group causes a downfield chemical shift of this β-proton due to an increase in the ring current owing to the +C-effect. The other β-protons have chemical shifts in the region of δ 8.65–8.80.

The addition of fullerene C_{60} to formylporphyrins **4** and **5** was carried out by refluxing with *N*-methylglycine in anhydrous toluene for 20 h under argon. The yields of compounds **6** and **7** were 20–25%. Unlike the original porphyrin, the resulting conjugates were brown. The presence of long-chain substituents in a porphyrin ensures a good solubility of porphyrin–fullerene dyads in dichloromethane, which simplifies considerably the subsequent study of the resulting compounds.

The porphyrin–fullerene conjugates were characterised by IR, UV, ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry. † A hypsochromic shift of the Soret band to 426 nm was observed for compounds **6a**,**b** in their electronic spectra.

The MALDI-MS spectrum of conjugate **7b** displayed a peak at *m*/*z* 2302.151 corresponding to the molecular ion as well as more intense peaks characteristic of the respective fragmentation products at *m*/*z* 1580.162 and 719.993.

In summary, the Prato reaction was found suitable to synthesize new conjugates based on fullerene C_{60} and nickel and copper complexes of *meso*-aryl-substituted porphyrins with long-chain substituents.

† IR spectra were recorded on a Bruker Equinox 55 Fourier spectrometer (Germany). NMR spectra were recorded on a Bruker MSL-300 pulse Fourier spectrometer (Federal Republic of Germany) with a working frequency of 300 MHz; measurements were carried out in the δ scale using TMS as the internal reference and $CDCl_3$ as the solvent. Electronic spectra were recorded in dichloromethane using a Jasko UV-7800 spectrophotometer. Mass spectra were obtained using the MALDI-MS method on a Bruker Ultraflex TOF/TOF instrument. TLC was performed on Silufol UV-254 plates (Kavalier) in the following systems: dichloromethane (system A), dichloromethane–hexane, 1 : 3 (system B) and toluene–hexane, 1 : 3 (system C). Chemical purification of the compounds was carried out in open columns with G 60 silica gel (Sigma).

General procedure for the preparation of nickel complexes of porphyrins **2a**,**b**. Nickel chloride (52 mg, 0.403 mmol) was added to porphyrin **1a** (50 mg, 0.040 mmol) in DMF (5 ml) and the mixture was refluxed for 6 h. The reaction mixture was diluted with 250 ml water and extracted with dichloromethane (30 ml); the solvent was removed *in vacuo*. Compound **2a** was eluted with system B and recrystallised from a chloroform–methanol mixture. Yield 95%. R_f 0.95 (system A). Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 418 (792), 526 (98).

Nickel complex of 5,10,15,20-tetra(4-tetradecyloxyphenyl)porphyrin **2b**. Yield 95%. R_f 0.95 (system A). Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 418 (798.3), 525 (93).

General procedure for the preparation of copper complexes **3a**,**b**. Copper acetate (73 mg, 0.401 mmol) in 5 ml methanol was added to porphyrin **1a** (50 mg, 0.040 mmol) in 20 ml dichloromethane. The reaction was carried out for 4 h with stirring at room temperature. The solvent was removed *in vacuo*; the residue was dissolved in dichloromethane and filtered to remove inorganic salts. The product was recrystallised from a chloroform–methanol mixture. Copper complex of 5,10,15,20-tetra-(4-decyloxyphenyl)porphyrin **3a**. Yield 95%. R_f 0.85 (system A). Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 416.5 (444), 539 (62.7).

Copper complex of 5,10,15,20-tetra(4-tetradecyloxyphenyl)porphyrin **3b**. Yield 95%. R_f 0.85 (system A). Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 416.5 (436), 539 (71).

General procedure for the synthesis of mono-β-formyltetraarylporphyrins **4** *and* **5**. The Vilsmeier complex prepared from $POCl_3$ (0.84 ml, 0.01 mmol) and DMF (0.60 ml, 0.012 mol) at 0 °C was added to a solution of the nickel complex of porphyrin **2a** (0.060 g, 0.046 mmol) in dichloromethane (5 ml). The reaction was carried out for 6 h at 40 °C. Then the reaction mixture was treated with a NaOH solution (pH 8–9) and extracted with dichloromethane; the extract was repeatedly washed with water to a neutral pH and concentrated *in vacuo*. Compound **4a** was eluted with system B and recrystallised from a chloroform–methanol mixture.

Nickel complex of 2-formyl-5,10,15,20-tetra(4-decyloxyphenyl)porphyrin **4a**. Yield 0.034 mg (55%). Electronic spectrum, λ_{max}/nm ($\varepsilon \times 10^{-3}$): 432 (430.8), 539 (45.7), 584.1 (34). IR (ν/cm^{-1}): 1673. ^{1}H NMR, δ: 0.90–0.96 (t, 12 H, Me), 1.30–1.46 [m, 16 H, $(CH_2)_8$], 4.22–4.25 (t, 8 H, OCH_2), 7.52–7.73 (m, 12 H, *meso*-H_{Ar}), 7.84–7.90 (m, 4 H, *meso*-H_{Ar}), 8.68–8.78 (m, 6 H, pyrrole), 9.30 (s, 1β-H, pyrrole), 9.32 (s, 1H, CHO).

Nickel complex of 2-formyl-5,10,15,20-tetra(4-tetradecyloxyphenyl)-porphyrin **4b**. Yield 55%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 432 (410.6), 538.8 (45.7), 583.8 (32.2). IR (ν/cm^{-1}): 1673. ^{1}H NMR, δ: 0.89–0.92 (t, 12 H, Me), 1.24–1.42 [m, 26 H, $(CH_2)_{13}$], 4.17–4.22 (t, 8 H, OCH_2), 6.65–7.15 (m, 16 H, *meso*-H_{Ar}), 8.65–8.80 (m, 6 H, pyrrole), 9.28 (s, 1β-H, pyrrole), 9.30 (s, 1H, CHO).

Copper complex of 2-formyl-5,10,15,20-tetra(4-decyloxyphenyl)porphyrin **5a**. Yield 60%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 431 (717.9), 550 (73.4), 596 (56.7). IR (ν/cm^{-1}): 1671. MS (MALDI), *m*/*z*: 1376 [M$^+$ + 1].

Copper complex of 2-formyl-5,10,15,20-tetra(4-tetradecyloxyphenyl)-porphyrin **5b**. Yield 60%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 431 (295.6), 551 (33.1), 591 (22.3). IR (ν/cm^{-1}): 1674. MS (MALDI), *m*/*z*: 1601 [M$^+$ + 1].

General procedure for the synthesis of fullerene–porphyrin conjugates **6** *and* **7**. A mixture of formylporphyrin **4b** (40 mg, 0.030 mmol), *N*-methylglycine (80 mg, 0.902 mmol) and fullerene C_{60} (64 mg, 0.090 mmol) in toluene (50 ml) was refluxed for 20 h under argon. The solvent was removed and the product was eluted with system C. The solvent was removed *in vacuo* and product **6b** was recrystallised from a chloroform–methanol mixture.

For **6a**: yield 20%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 426 (390.1), 546 (57.5). ^{1}H NMR, δ: 5.38 (s, 1H, NCH), 4.29 (m, 2 H, NCH_2), 2.67 (s, 3 H, NMe). ^{13}C NMR, δ: 38.76 (NMe), 66.9 (NCH_2), 67.3 (NCH), 68.2, 75.9 (C_{sp^3}), 158.4–111.7 (C_{sp^2}).

For **6b**: yield 23%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 426 (382.7), 546 (59). ^{1}H NMR, δ: 5.30 (s, 1H, NCH), 4.09, 4.12 (d, 2 H, NCH_2), 2.75 (s, 3 H, NMe). ^{13}C NMR, δ: 38.7 (NMe), 66.9 (NCH_2), 67.0 (NCH), 67.4, 75.9 (C_{sp^3}), 159.80–113.12 (C_{sp^2}).

For **7a**: yield 21%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 426.5 (383.7), 546 (63.7). MS (MALDI), *m*/*z*: 1355.007 [M$^+$ – C_{60} – Cu], 719.454 [C_{60}^+].

For **7b**: yield 25%. Electronic spectrum [λ_{max}/nm ($\varepsilon \times 10^{-3}$)]: 426.5 (387.7), 546 (58). MS (MALDI), *m*/*z*: 2302.151 [M$^+$], 1580.162 [M$^+$ – – C_{60} – Cu], 719.993 [C_{60}^+].

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