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Synthesis of donor–acceptor systems based on the derivatives of chlorophyll *a* and [60]fullerene

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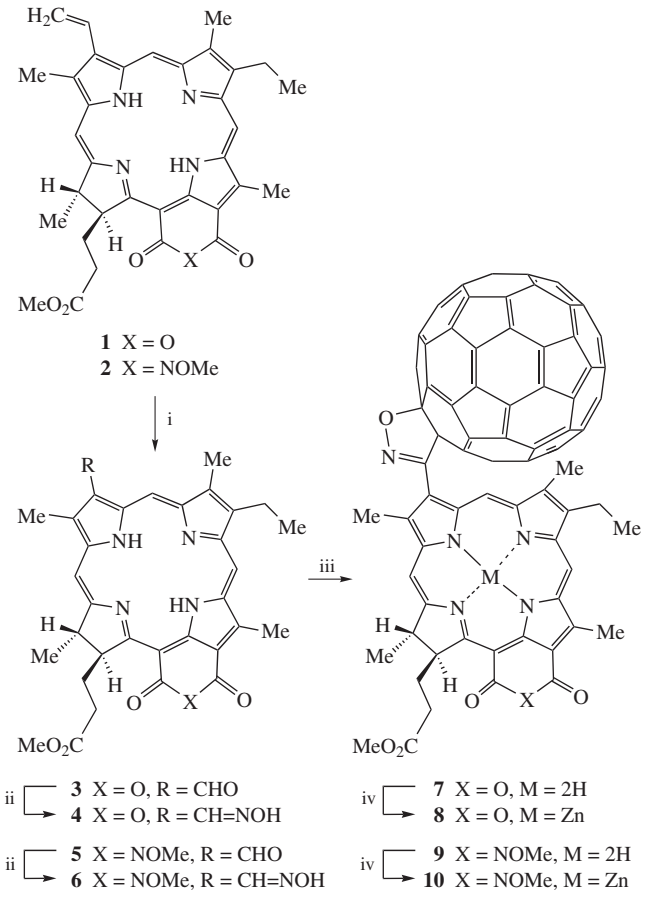
Isoxazoline-bound chlorin–fullerenes were synthesized in a yield of 80% from 3-hydroxyiminomethylchlorins and [60]fullerene (C_{60}) in the presence of diacetoxyiodobenzene under mild conditions.

Among the molecular ensembles that simulate particular steps of natural solar energy conversion,[1–4] the conjugates of chlorins with fullerenes occupy a special place.[5–12] These compounds are complementary in their properties. The conjugated system of double bonds in a chlorin macrocycle absorbs light over a wide range from UV to near IR radiation, and due to this fact chlorins can be used as light-collecting antennas. On the contrary, fullerenes weakly absorb light, but they are efficient electron scavengers. The photoinduced electron transfer in the chlorin–fullerene systems from the singlet excited state of a donor (chlorin) to the fullerene leads to a photoinduced charge-separated state, which simulates electron transfer in the process of photosynthesis. The covalent binding of fullerene in the vicinity of the chlorin macrocycle increases the life time of the charge-separated state in these donor–acceptor systems to 120 s at low temperatures.[9,11]

1,3-Dipolar cycloaddition is commonly used for the preparation of porphyrin and chlorin conjugates with fullerenes.[12,13] In this case, addition at the double bonds of fullerene occurs through the ylide, which is generated by condensation of *N*-methylglycine with formyl-substituted porphyrin or chlorin. However, this reaction demands severe conditions and provides moderate yields. Other modification of fullerenes by the addition of nitrile oxides with the formation of fullerene isoxazolines is also known.[14]

In this work, we synthesized the chlorin–fullerene systems with an isoxazoline spacer between a donor and an acceptor from 3-hydroxyiminomethylchlorins and C_{60} fullerene with the use of diacetoxyiodobenzene for the generation of nitrile oxide. The reaction proceeds at room temperature, and the yield of the target products is as high as 80%. As the initial chlorins, we used chlorophyll *a* derivatives, purpurin 18 **1** and chlorin p_6 *N*-methoxycycloimide **2** (Scheme 1), which contain anhydride and imide rings, respectively, conjugated with the main macrocycle to provide a bathochromic shift of the Q band from 665 nm, which is characteristic of chlorins, by 40–50 nm. A commonly used step in the modification of natural chlorins is the oxidation of the vinyl group at the 3-position of the macrocycle to an aldehyde group, which is a reaction center convenient for the subsequent transformations. The use of sodium periodate with catalytic amounts of osmium tetroxide for the production of formylchlorins is the most efficient and simple method.[15,16] This procedure provided access to 3-formylpurpurin 18 **3**[17] and chlorin p_6 *N*-methoxycycloimide **5**† (see Scheme 1). The appearance of a formyl group at the 3-position of a macrocycle causes a significant bathochromic shift of absorption maxima in their electronic spectra by 37–45 nm, as compared with those of initial **1** and **2**.



Scheme 1 *Reagents and conditions*: i, OsO_4/$NaIO_4$, dioxane; ii, NH_2OH·HCl, pyridine; iii, $PhI(OAc)_2$, C_{60}, toluene; iv, $Zn(OAc)_2$, methanol.

3-Hydroxyiminomethyl-3-devinyl-13,15-N-*methoxycycloimide of chlorin* p_6 *methyl ester* **6**. Electronic spectrum [λ_{max}/nm (I_{rel})]: 420, 516, 556, 664, 724 (1 : 0.009 : 0.17 : 0.007 : 0.35). ^{1}H NMR ($CDCl_3$) δ: 9.68 (s, 1H, 5-H), 9.48 (s, 1H, 10-H), 9.30 (s, 1H, CH=N), 8.54 (s, 1H, 20-H), 8.29 (s, 1H, N–OH), 5.26 (m, 1H, 17-H), 4.96 (m, 1H, 18-H), 4.38 (s, 3H, N–OMe), 3.82 (s, 3H, 12-Me), 3.61 (s, 3H, CO_2Me), 3.48 (q, 2H, 8^1-CH_2, *J* 7 Hz), 3.39 (s, 3H, 2-Me), 2.99 (s, 3H, 7-Me), 2.85 (m, 1H, 17^1-CH_2), 2.55 (m, 2H, 17^2-CH_2), 2.10 (m, 1H, 17^1-CH_2), 1.71 (d, 3H, 18-Me, *J* 7 Hz), 1.69 (t, 3H, 8^2-Me, *J* 7 Hz), –0.12 (s, 2H, NH). MS, *m*/*z*: 595.5 [(M^+ – OMe) + 2H], 609.5 [M^+ – Me], 625.5 [M^+ + H]. Fluorescence spectrum (λ_{fl}/nm): 738.

† For characteristics of compounds **4** and **5**, see Online Supplementary Materials.

3-Hydroxyiminomethylchlorins **4** and **6** were prepared by the treatment of 3-formyl derivatives **3** and **5** with hydroxylamine hydrochloride in pyridine. A hypsochromic shift of an absorption maximum to 715 or 724 nm was observed in the electronic spectrum of chlorin **4** or **6**, as compared with those of initial **3** or **5**.

The condensation of compounds **4** and **6** with fullerene C_{60} in toluene was carried out in the presence of diacetoxyiodobenzene at room temperature to afford dyads **7**‡ and **9** in 82 and 80% yields, respectively. The mass spectrum of chlorin–C_{60} dyad **7** showed a molecular ion at *m*/*z* 1315.9. A peak at *m*/*z* 1345.7 due to $[M^+ + 2H]$ and a fragment at *m*/*z* 1315.7 corresponding to $[M^+ – OMe]$ were present in the spectrum of dyad **9**. The electronic spectra of dyads **7** and **9** exhibited a small hypsochromic shift of absorption maxima to 712 and 720 nm, respectively, as compared to those of oximes **4** and **6**. The zinc complexes of dyads **8** and **10** were synthesized by the treatment of compounds **7** and **9** with zinc acetate in a chloroform–methanol mixture. In the electronic spectra of dyads **8** and **10**, a further shift of absorption bands from 712 to 690 nm or from 720 to 698 nm, respectively, was observed.

The fluorescence emission spectra of synthesized dyads **7** and **9** were measured on the irradiation of their solutions in chloroform ($C = 1.2\times10^{-5}$ mol dm^{-3}) at $\lambda_{ex} = 514$ nm. The spectrum of compound **9** exhibited a band at 734 nm due to the fluorescence of a donor (the chlorin p_6 *N*-methoxycycloimide residue in the dyad) (Figure 1). In this case, a decrease in the fluorescence signal intensity of chlorin in the dyad, as compared with the emission intensity of initial compound **6**, was detected; this is indicative of the deactivation of the singlet state of chlorin by fullerene. An analogous pattern of fluorescence quenching was observed in dyad **7**. Note that, in the case of the zinc complexes **8** and **10**, a decrease in the fluorescence intensity of the chlorin component was more pronounced.

Thus, based on purpurin 18, chlorin p_6 13,15-*N*-methoxycycloimide and fullerene C_{60}, we obtained previously unknown photoactive dyads **7** and **9** and their zinc complexes **8** and **10**, which may be of interest as photosynthetic model systems.

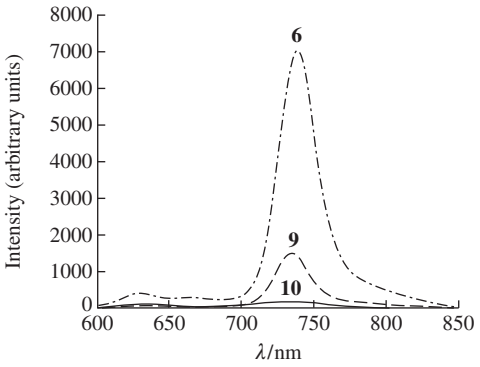


Figure 1 Fluorescence spectra of chlorin **6** and dyads **9**, **10** ($\lambda_{ex} = 514$ nm) in chloroform; concentration, 1.2×10^{-5} mol dm^{-3}.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.01.011.

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‡ *Chlorinofullerene* **7**: 10 mg (0.017 mmol) of the methyl ester of 3-hydroxyiminomethyl-3-devinylpurpurin 18 **4** and 27 mg (0.085 mmol) of diacetoxyiodobenzene were added to a solution of 12 mg (0.017 mmol) of fullerene in 8 ml of toluene. The reaction mixture was stirred for 20 min at room temperature; the solvent was evaporated *in vacuo*, and the target product was separated by chromatography on silica gel in chloroform–methanol (70 : 1). Yield 14 mg (82%). Electronic spectrum [λ_{max}/nm (I_{rel})]: 412, 507, 546, 650, 712 (1 : 0.08 : 0.20 : 0.06 : 0.40). ^{1}H NMR ($CDCl_3$) δ: 9.72 (s, 1H, 5-H), 9.64 (s, 1H, 10-H), 8.79 (s, 1H, 20-H), 5.26 (m, 1H, 17-H), 4.46 (q, 1H, 18-H, *J* 7 Hz), 3.85 (s, 3H, 12-Me), 3.66 (q, 2H, 8^1-CH_2, *J* 7 Hz), 3.64 (s, 3H, CO_2Me), 3.58 (s, 3H, 2-Me), 3.13 (s, 3H, 7-Me), 2.73 (m, 1H, 17^2-CH_2), 2.46 (m, 2H, 17^1-CH_2), 2.00 (m, 1H, 17^2-CH_2), 1.78 (d, 3H, 18-Me, *J* 7 Hz), 1.67 (t, 3H, 8^2-Me, *J* 7 Hz), –0.17 (s, 2H, NH). MS, *m*/*z*: 1315.9 $[M^+ + 2H]$. Fluorescence spectrum (λ_{fl}/nm): 726.

Zinc complex of chlorinofullerene **8**. Electronic spectrum [λ_{max}/nm (I_{rel})]: 425, 431, 639, 690 (1 : 0.13 : 0.12 : 0.53). MS, *m*/*z*: 1376.8 $[M^+]$.

Chlorinofullerene **9** was prepared analogously to compound **7**. Yield, 80%. Electronic spectrum [λ_{max}/nm (I_{rel})]: 419, 550, 660, 720 (1 : 0.22 : 0.07 : 0.40). ^{1}H NMR ($CDCl_3$) δ: 9.67 (s, 1H, 5-H), 9.59 (s, 1H, 10-H), 8.73 (s, 1H, 20-H), 5.35 (m, 1H, 17-H), 4.42 (q, 1H, 18-H, *J* 8 Hz), 4.36 (s, 3H, N–OMe), 3.87 (s, 3H, 12-Me), 3.67 (q, 2H, 8^1-CH_2, *J* 8 Hz), 3.66 (s, 3H, CO_2Me), 3.58 (s, 3H, 2-Me), 3.14 (s, 3H, 7-Me), 2.77 (m, 1H, 17^1-CH_2), 2.47 (m, 2H, 17^2-CH_2), 2.06 (m, 1H, 17^1-CH_2), 1.79 (d, 3H, 18-Me, *J* 8 Hz), 1.68 (t, 3H, 8^2-Me, *J* 8 Hz), –0.18 (s, 2H, NH). MS, *m*/*z*: 1315.7 $[(M^+ – OMe) + 3H]$, 1345.7 $[M^+ + 2H]$. Fluorescence spectrum (λ_{fl}/nm): 734.

Zinc complex of chlorinofullerene **10**. Electronic spectrum [λ_{max}/nm (I_{rel})]: 430, 569, 646, 698 (1 : 0.18 : 0.15 : 0.49). MS, *m*/*z*: 1408.8 $[M^+ + 2H]$.