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Synthesis and properties of a novel porphyrin–fullerene triad assembled through donor–acceptor bonding

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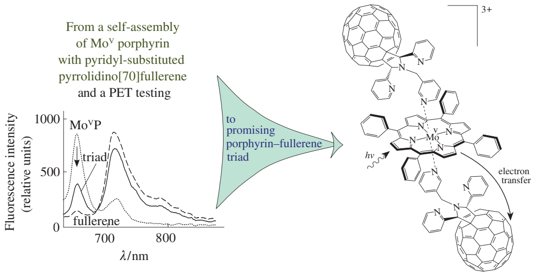
Complexation of (hydroxy)(oxo)(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) with 2′,5′-di(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[70]fullerene leading to a new donor–acceptor triad is characterized by quantitative description of the equilibrium and the reaction rate. The prospects of the triad as a photosynthetic antenna imitator and an active layer in solar energy conversion devices are substantiated.



A large number of organic photovoltaic cells comprising an active layer of electron donor and acceptor triad have been developed. Both small heterocyclic molecules, such as pyrrole or pyridine, and heterocyclic macrocycles, porphyrins and phthalocyanines, are used as donors. The fullerene derivatives appear most often as electron acceptors due to their unique ability to accumulate electrons with the formation of multianions.[1,2] Thus, polymer–fullerene solar cells with enhanced by several orders efficiency, *e.g.* based on conjugated poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] and C_{60}, were constructed in accordance with the concept of a bulk heterojunction.[3,4] The analogues based on C_{70} fullerene sometimes manifest much higher absorption in the electronic spectrum (see, *e.g*., refs. 4, 5).

Recent achievements and good prospects were described in terms of the field of donor–acceptor energy-saving systems based on porphyrins/phthalocyanines and C_{60} derivatives as electron donors and acceptors.[6] It was shown that the energy and electron transfer processes initiate from the singlet-excited state of the tetrapyrrole sensitizer to fullerene acceptor in the majority of the studied systems. Upon a lower probability of formation of the systems with the separated charges, the lifetime of the excited states is much higher in the case of the donor–acceptor porphyrin–fullerene dyads as compared to covalently linked systems.[7] There is one example of the zinc porphyrinate–C_{70} fullerene dyads,[8] in which the quenching of the zinc(II) porphyrin fluorescence by fullerene indicated the appearance of photo induced electron transfer. Since a central metal atom is involved in the formation of a molecular electronic structure, it is reasonable to anticipate an increase in the electron transfer in porphyrin complexes of other metals such as chromium, manganese, molybdenum and tungsten. Such complexes should display a hyper-type electronic absorption spectrum with additional bands assigned to charge transfer from porphyrin to metal, while zinc(II) porphyrins have normal-type UV-VIS spectrum.[9–11] A formal metal charge greater than two provides increased coordination ability along the axial axis of metal porphyrins thus improving the conditions for the fullerene acceptor coordination during the formation of porphyrin–fullerene dyads and triads. The stable donor–acceptor complex (1:1) with electron-optical properties promising for the use in photovoltaics and biomedicine was obtained by the reaction between (acetato)[octakis(*p-tert*-butylphenyl)tetraazaporphinato]-manganese(III) and 2′-(4-pyridyl)-5′-(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[60]fullerene.[12,13] Supramolecular architectures based on tin tetraphenylporphyrin and depsipeptide dendrons of different generations, including these exchanged for fullerene, on a Hamilton receptor are a good example of a tuneable excited-state deactivations upon photoexcitation.[14]

In this article, the synthesis, electron-optical properties and stability, as well as quantitative data on the thermodynamics and kinetics of the formation of a triad based on 2′,5′-di(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[70]fullerene **1** and (hydroxy)(oxo)(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) **2** are described (Scheme 1).[†] Complexation of compound **1** with two molecules of ligand **2** afforded the target triad **3**.[‡] The attention was focused on the first donor–acceptor triad involving a porphyrin complex of highly charged Mo^V and a fullerene derivative C_{70}, which has a higher order than C_{60}.

Based on the spectrophotometric titration data (Figures 1 and S1, Online Supplementary Materials), equilibrium was instantaneously

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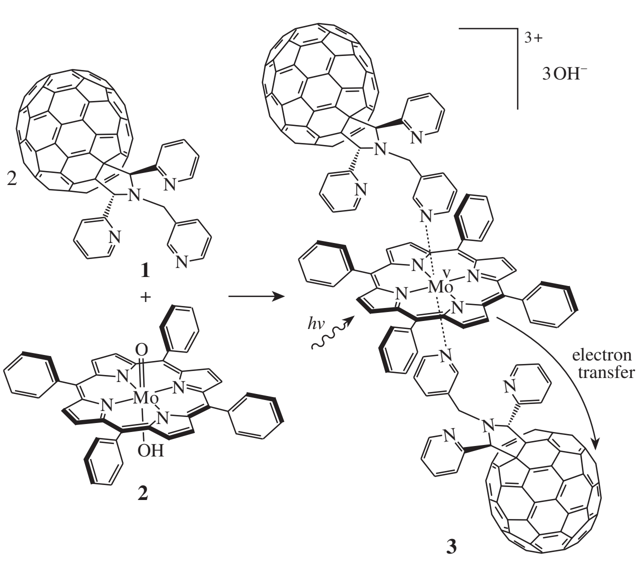
[†] *2′,5′-Di(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[70]fullerene* **1** was synthesized by cycloaddition of azomethine ylide at C_{70} in 1,2-dichlorobenzene.[15] (Hydroxy)(oxo)(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) **2** was synthesized by the reaction of 5,10,15,20-tetraphenylporphyrin and MoO_3 in boiling phenol[16] (see Online Supplementary Materials).

[‡] *(5,10,15,20-Tetraphenylporphinato)[2′,5′-di(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[70]fullerene]molybdenum(V) trihydroxide* **3** was synthesized in a quantitative yield by the reaction between compounds **1** and **2** in toluene at 25 °C for 3 h. The solid for spectral studies was isolated by vacuum removal of the solvent. UV-VIS (toluene, λ_{max}/nm): 463, 592, 633. IR (KBr, ν/cm^{-1}): 2922, 2848, 2362, 1631, 1586, 1570, 1541, 1470, 1433, 1376, 1335, 1282, 1245, 1215, 1188, 1147, 1121, 1097, 1049, 1019, 996, 964, 930, 859, 827, 790, 766, 752, 729, 711, 700, 686, 663, 638, 612, 599, 588, 562, 554, 544, 527, 512, 480, 463, 512, 398, 382, 377. The stoichiometry of complex **3** agrees with the data on thermodynamics and kinetics of its synthesis.



Scheme 1

settled in the reaction mixtures **1**–**2**–toluene for all the compositions studied. This fact is indicated by a decrease in the intensity of the band assigned to charge transfer from porphyrin to molybdenum atom at 462 nm upon increasing the concentration of fullerene **1** (the isosbestic point was chosen at 478 nm). The data shown in Figure S1 allow one to calculate the stoichiometry of compounds **1** and **2** as 2 : 1 and the numerical value of the equilibrium constant (formation constant, stability constant) as 2.94×10^7 dm^6 mol^{-2}. Thus, the experiment reveals the presence of self-organization in the **1**–**2**–toluene system and a quantitative level of the formation of the stable donor–acceptor (1 : 2) porphyrin–fullerene triad. For comparison, some similar Mo$^{\mathrm{V}}$ porphyrin–fullerene triads and dyads are characterized by stability constants: **2**·L1 ($K_{\mathrm{total}} = 2.27\times10^8$ dm^6 mol^{-2})[17] > > **2**·L2 (1.97×10^4 dm^3 mol^{-1}),[18] where L1 is 2′-(4-pyridyl)-5′-(2-pyridyl)-1′-(3-pyridylmethyl)pyrrolidino[60]fullerene and L2 is 2′-(4-pyridyl)-5′-(2-pyridyl)-1′-(2-pyridylmethyl)pyrrolidino-[60]fullerene, respectively. Note that there are two possible coordination patterns, in which nitrogen atom of either 4-pyridyl, or 3-pyridyl substituent in a fullerene-containing ligand may be involved. Maximal *K* value of 8.4×10^4 dm^3 mol^{-1} among the dyads of analogous zinc porphyrin pyrrolidino[60]fullerene complexes with different numbers of pyridyl moieties and modes of Zn$^{\mathrm{II}}$ coordination was obtained.[19] The binding constant of 5.1×10^4 dm^3 mol^{-1} for porphyrin–[60]fullerene dyad assembled through Watson–Crick hydrogen bonds in CH_2Cl_2 obtained by steady-state fluorescence spectroscopy[20] does not exceed the above value.

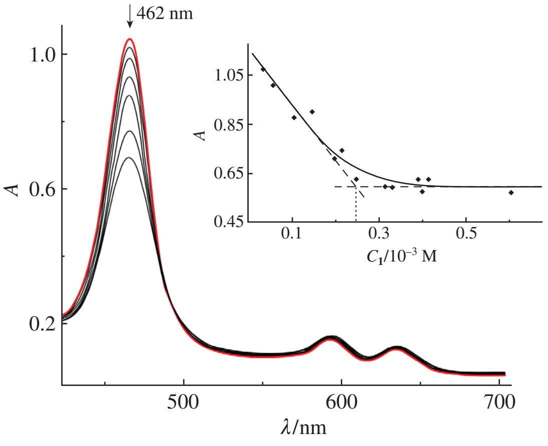


Figure 1 Changes in the UV-VIS spectrum of Mo$^{\mathrm{V}}$ complex **2** (1.06×10^{-5} M, upper line) in toluene upon the increase in the concentration of ligand **1** (3.54×10^{-5}–6.02×10^{-4} M). Inset is a plot of absorbance at 462 nm *vs.* concentration of ligand **1**.

However, a slow irreversible process is observed in the equilibrium mixtures, which according to kinetic studies was characterized by the effective rate constants k_{obs} and the first and zero (~0.2) orders towards Mo$^{\mathrm{V}}$ complex and ligand **1**, respectively (see Online Supplementary Materials, Table S1, Figure S2). The rate constant k [$k = k_{\mathrm{obs}}(C_{\mathbf{1}})^0$] that is independent of the concentrations is $(3.38\pm0.32)\times10^{-4}$ s^{-1}. The slow one-way reaction is accompanied by only a slight (1–4 nm) bathochromic shift of long-wavelength absorption maxima in UV-VIS spectrum of the reaction mixtures, which indicates that the chromophore remained practically unchanged (Figure S3). Taking into account the rapid preceding equilibrium involving possible formation of heptacoordinated complex **3′**, we performed kinetic calculations (Scheme 2), whose results were in good agreement with the spectral data.

$$\begin{tikzcd}
\mathrm{O{=}Mo(OH)(TPP)} \arrow[r, shift left, "\substack{2\mathrm{Py_3Ful}\\ \mathbf{1}\\ \mathrm{H_2O},\ K}"] & {[\mathrm{Mo(OH)(Py_3Ful)_2(TPP)}]^{2+}\cdot 2\mathrm{OH}^-} \arrow[l, shift left] \\
\mathbf{2} & \mathbf{3'} \arrow[dl, "k"] \\
{[\mathrm{Mo(TPP)(Py_3Ful)_2}]^{3+}\cdot 3\mathrm{OH}^-} & \\
\mathbf{3} &
\end{tikzcd}$$

Py$_3$Ful is tripyridyl fullerene ligand **1**
TPP is tetraphenylporphin dianion

Scheme 2

The additional spectral studies were undertaken to support the conclusion of porphyrin fullerene triad formation (for more details, see Figure S4, Online Supplementary Materials). A bathochromic shift in the UV-VIS spectrum with a charge transfer band at 463 nm (in toluene) characterizes the triad as a molybdenum(V) complex of porphyrin. New signals with frequencies of coordinated ligand **1** oscillations are detected in its IR spectrum (the published data[21] for uncoordinated **1** are given in parentheses): 1433 (1430), 1147 (1134), 790 (795), 686 (674), 638 (642), 573 (578), 527 (533), 463 (458) (C_{70} skeleton), 1335 ($\nu_{\mathrm{C-N}}$, pyridine);[22] 1121 and 996 ($\nu_{\mathrm{C-N}}$, pyrrolidine),[23] 480 (Mo–N$_{\mathrm{Py}}$).[24] These bands are absent in the spectrum of the starting **2**. The triad formation as a result of substitution of ligands along the axial axis is reflected in the IR spectra by the disappearance of signals with frequencies of 659 and 927 cm^{-1} corresponding to the vibrations of the Mo–O and Mo=O bonds, respectively, in the initial **2** (Figure S4).

To examine photoinduced electron transfer (PET) in triad **3** synthesized, the fluorescence emission of initial **2** and triad based on it was studied. The emission spectra ($\lambda_{\mathrm{exc}} = 435$ nm) of molybdenum(V) porphyrin, pyrrolidino[60]fullerene, and porphyrin–fullerene triad in toluene are shown in Figure 2.

High intensity of band at 456 nm ($\log\varepsilon = 3.78$, for more details, see Online Supplementary Materials) in complex **2** UV-VIS spectrum and considerably lower quantum yield of fullerene fluorescence as compared with metal porphyrins[25] allow one to display in the same plot the fluorescence emission spectra of compound **2** and pyrrolidino[60]fullerene of concentrations that differ from each other by an order of magnitude. The decrease more than 50% in the fluorescence emission of the initial **2** was observed due to addition of ligand **1**. This may be an evidence of photoinduced electron transfer in porphyrin–fullerene triad **3**, which is alike a primary charge separation in a photosynthetic antenna. Analogous effect of substantial quenching of the fluorescence emission in toluene was described for porphyrin–fullerene

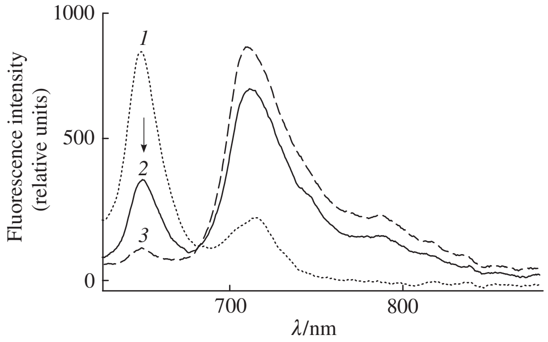


Figure 2 Fluorescence spectra (in toluene) of (*1*) complex **2** (λ_{exc} = = 435 nm, C_0 = 1.06×10^{-5} M), (*2*) triad **3** in the presence of compound **1** (C_1 = 1.45×10^{-4} M), (*3*) free compound **1** (C_1 = 1.45×10^{-4} M).

dyads, in which the two chromophores were linked by a bicyclic bridge.[26]

In conclusion, the thermodynamics and kinetics of self-assembly process and spectral properties of a novel porphyrin–fullerene triad assembled *via* donor–acceptor bonding were studied. The triad was obtained using molybdenum(V) porphyrin and pyridyl-substituted pyrrolidino[70]fullerene as electron donor and acceptor, respectively, which is a useful means of constructing self-assembled PET systems for optoelectronics. Being coordinatively unsaturated, the central atom in molybdenum(V) porphyrin is capable of strong bonding on the axial axis. The [70]fullerene derivative differs from the [60]fullerene analogues by a higher absorption in UV-VIS spectrum, *e.g.* in toluene log$\,\varepsilon$ are 3.75 (at 433 nm) for compound **1**, 3.48 (at 430 nm) for 1′-(picoline-2-yl)-2′,5′-di(2-pyridyl)pyrrolidino[60]fullerene[27] or 3.58 (at 432 nm) for 2′-(4-pyridyl)-5′-(2-pyridyl)-1′-(2-pyridylmethyl)pyrrolidino[60]fullerene).[18] Substituted pyrrolidino[70]fullerene is a strong ligand forming donor–acceptor complex (1:2) of increased stability (K = 2.94×10^{7} dm^{6} mol^{-2}) with molybdenum(V) porphyrin, which displays the effect of quenching fluorescence of the latter.

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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.2018.07.029.

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