Supporting Information

Pyropheophorbide–Fullerene Dyad: Synthesis and Photochemical Properties

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Materials and equipment

The following commercially available materials were used in the work: methylpheophorbide *a* "raw" from Ivanovo State University of Chemistry and Technology, chloroform (chemically pure), dioxane (chemically pure), toluene (chemically pure), methanol (h.da), methylene chloride (chemically pure), 2,4,6-collidine (Acros organics, 98 %), silica gel (Acros organics, 40–60 μm, 60 Å), cross-linked polystyrene (Bio-Beads, SX-1), pyridine (chemically pure), *N*-methylglycine, osmium tetroxide, sodium periodate, Na_2SO_4, glacial acetic acid (chemically pure), trifluoroacetic acid (chemically pure). Purification of solvents: chloroform (chemically pure) and methylene chloride (chemically pure) was distilled over K_2CO_3; dioxane (chemically pure) was boiled over KOH for 4 hours, kept on metallic Na for 24 hours, and then distilled over metallic Na; pyridine (chemically pure) was kept over KOH for 24 hours and then distilled; toluene was kept over metallic sodium. The remaining substances were used without prior purification.

The rotary evaporator IKA RV-10 was used to evaporate the solvents. The ^{1}H NMR spectra were recorded on a Bruker AVANCE 50 (500 MHz) and Bruker AM-200 (200 MHz) spectrometer. Absorption spectra were recorded on a Cary-60 and Hitachi U-2900 spectrophotometer (UV-Vis), and stationary fluorescence spectra were recorded on a Cary-Eclipse spectrofluorometer. Matrix activated ionization (MAI) mass spectra were obtained using an Exactive Orbitrap high resolution mass spectrometer (ThermoFisher Scientific, Germany). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on an AXIMA Confidence MALDI TOF (Shimadzu) mass spectrometer with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix.

Mass spectra

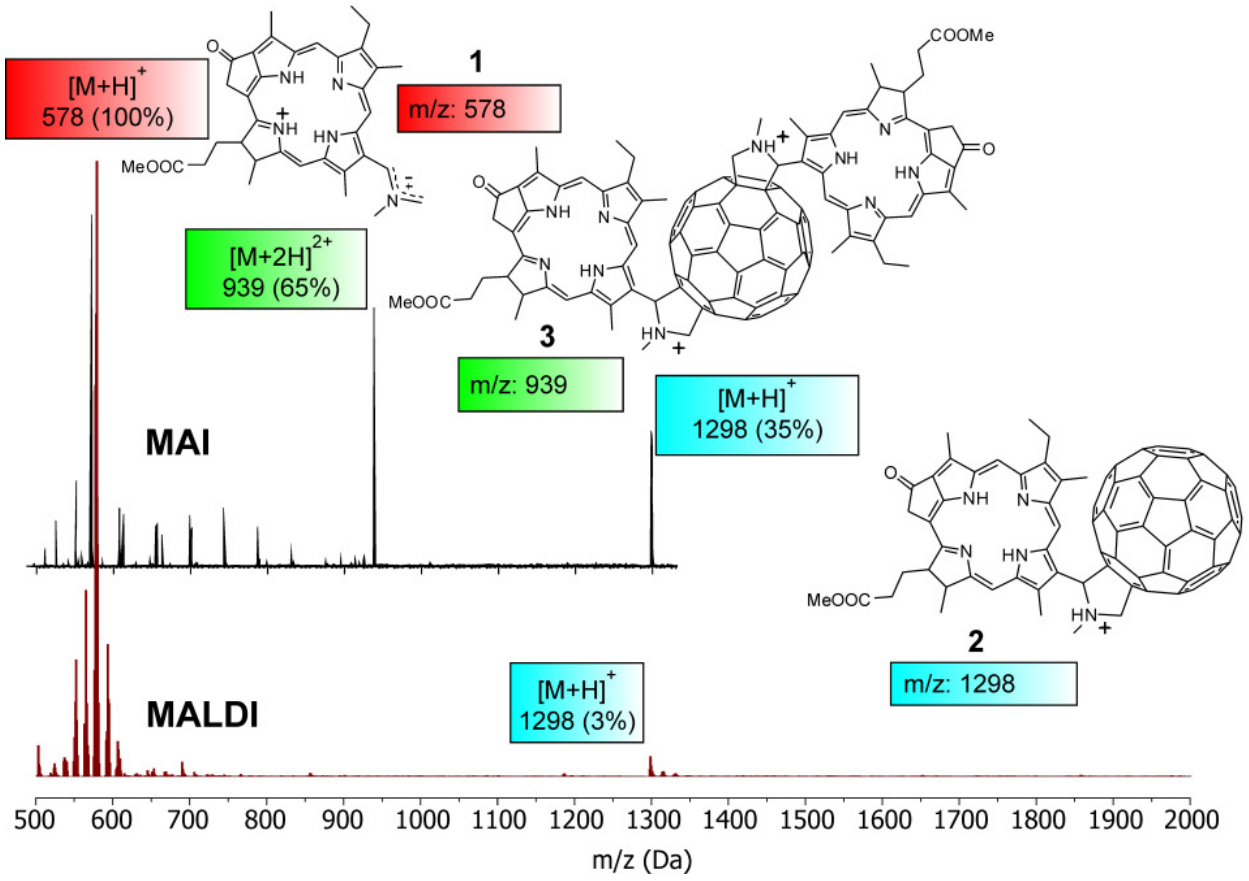

Figure S1. The **red line** is the MALDI mass spectrum of the mixture **2** and **3**. The **black line** is the MAI mass spectrum of the mixture **2** and **3**.

[1]H NMR spectra

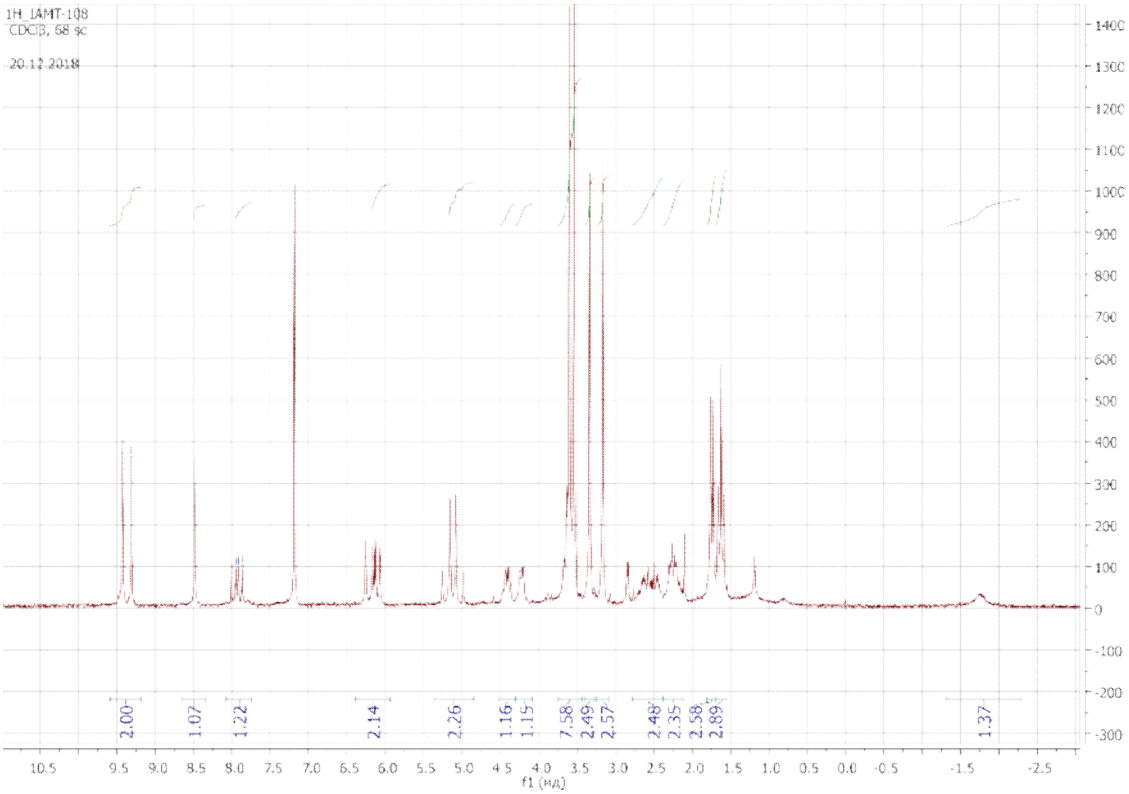

Figure S2.[1]H NMR spectrum of methylpyropheophorbide *a* in chloroform.

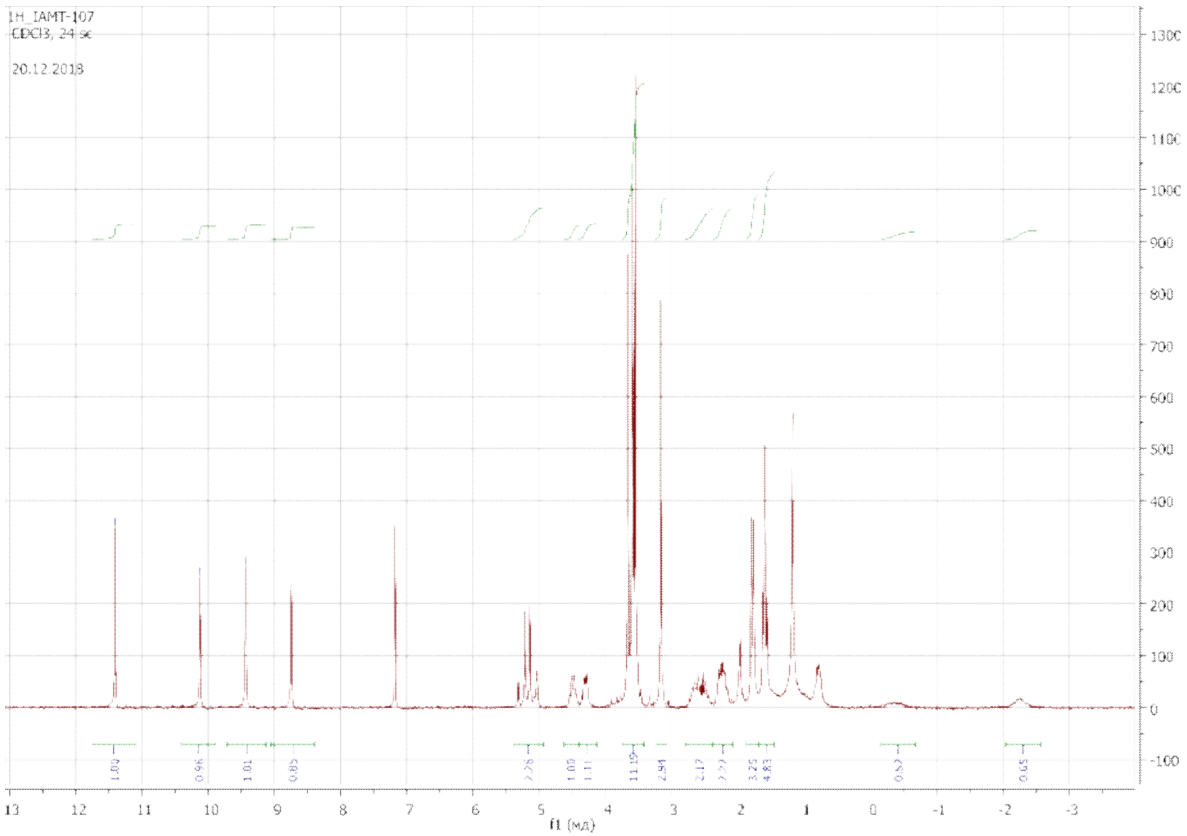

Figure S3.[1]H NMR spectrum of methylpyropheophorbide *d* in chloroform.

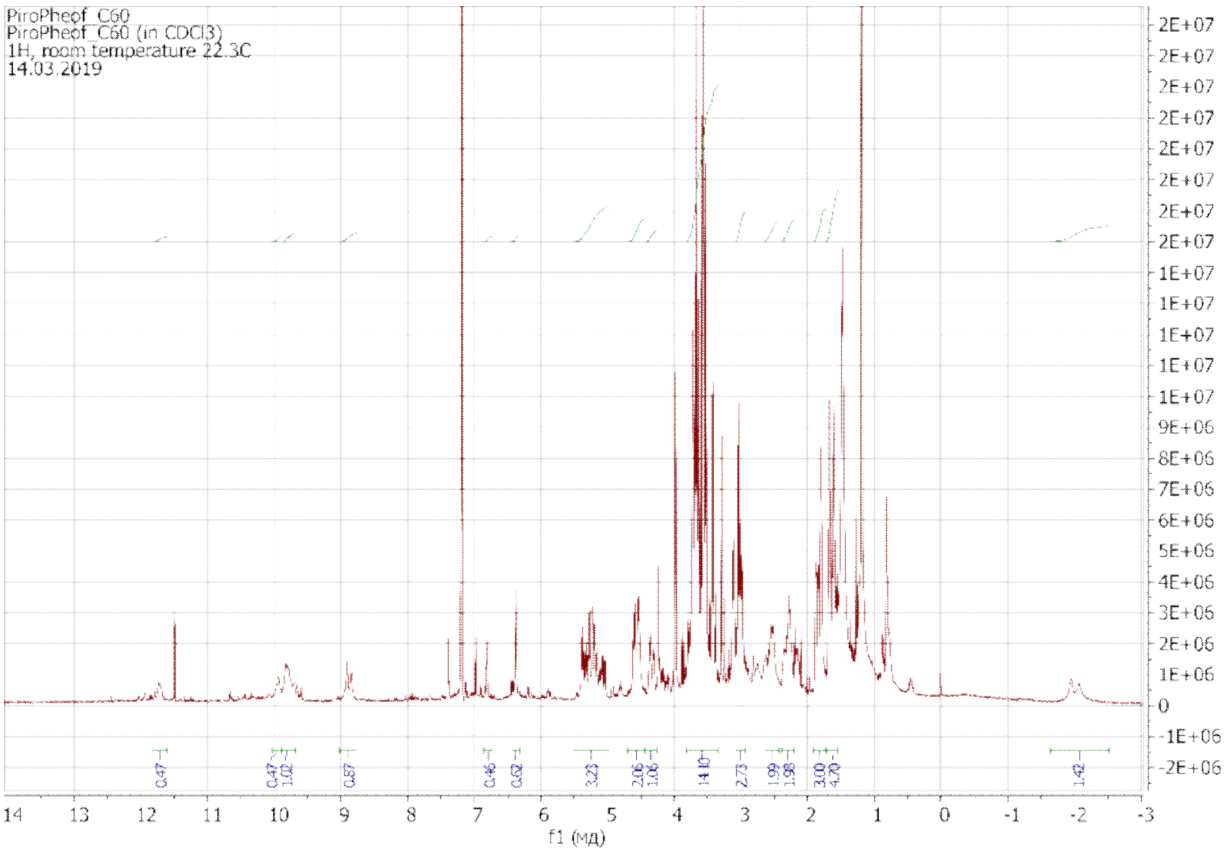

Figure S4. ^{1}H NMR spectrum of the methyl ether α,β-3-((2'R,S)-*N*-methyltetrahydro[60]fullereno[*c*]N-methylpyrrol-2-yl)-3-diethylene pyropheophorbide *a* in chloroform with trace content of CF_3COOD.

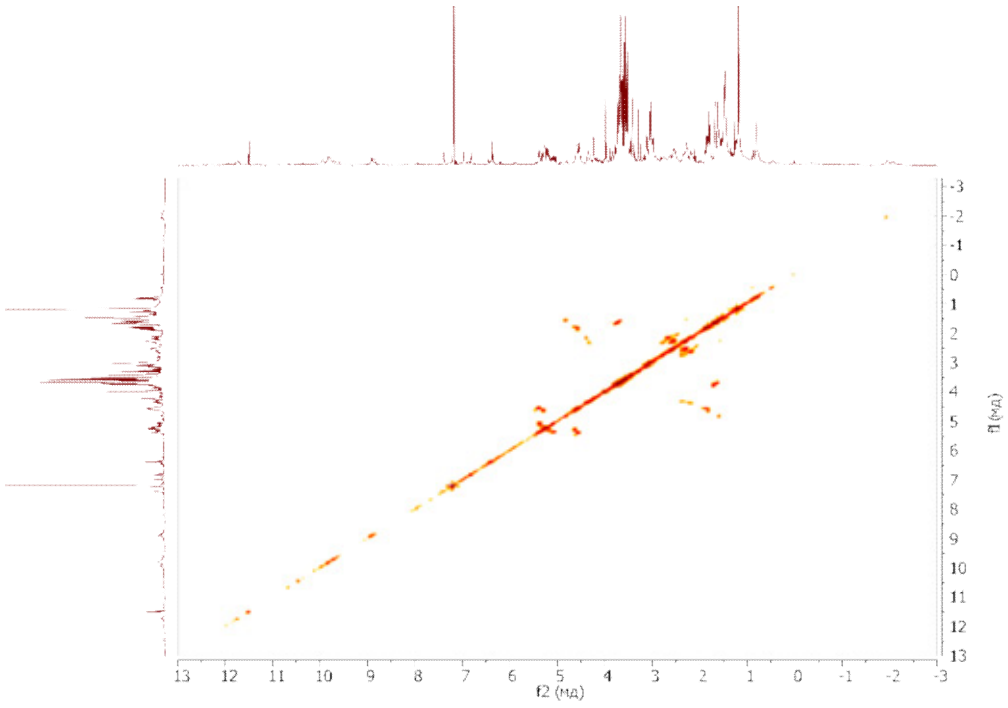

Figure S5. ^{1}H-^{1}H COSY NMR spectrum of the methyl ether α,β-3-((2'R,S)-*N*-methyltetrahydro[60]fullereno[*c*]N-methylpyrrol-2-yl)-3-diethylene pyropheophorbide *a* in chloroform with trace content of CF_3COOD.

Absorption and Fluorescence Spectra

Electronic absorption, fluorescence and excitation spectra of dyad **2** obtained under the conditions described in the literature[1] with sequential separation by gel permeation and sorption chromatography.

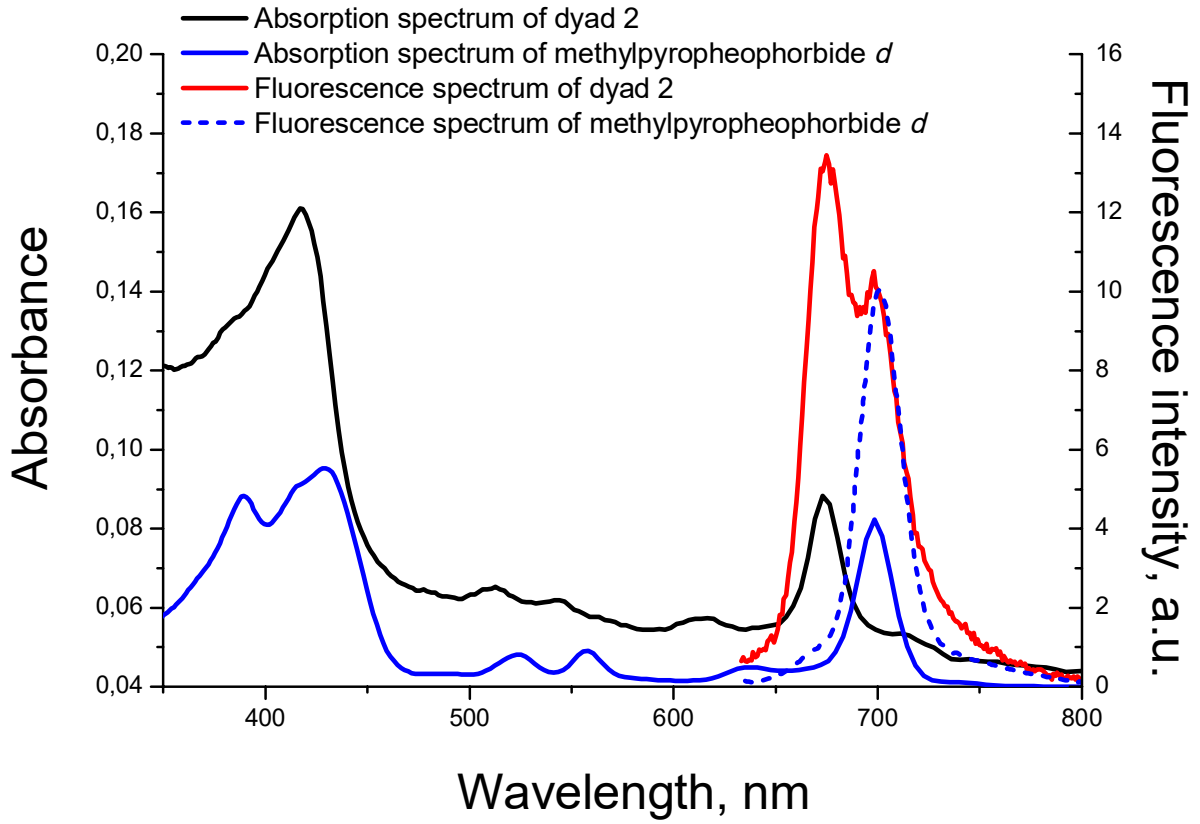

Figure S6. The **black solid line** is the absorption spectrum of **2**, **the red solid line** is the fluorescence spectrum of **2**. The **blue solid line** is the absorption spectrum of methylpyropheophorbide *d*, the **blue dashed line** is the fluorescence spectrum of methylpyropheophorbide *d*.

[1]Helaja J., Tauber A.Y., Abel Y., Tkachenko N. V, Lemmetyinen H., Kilpeläinen I., Hynninen P.H. *J. Chem. Soc., Perkin Trans. 1*, **1999**, 2403. https://doi.org/10.1039/a904817k

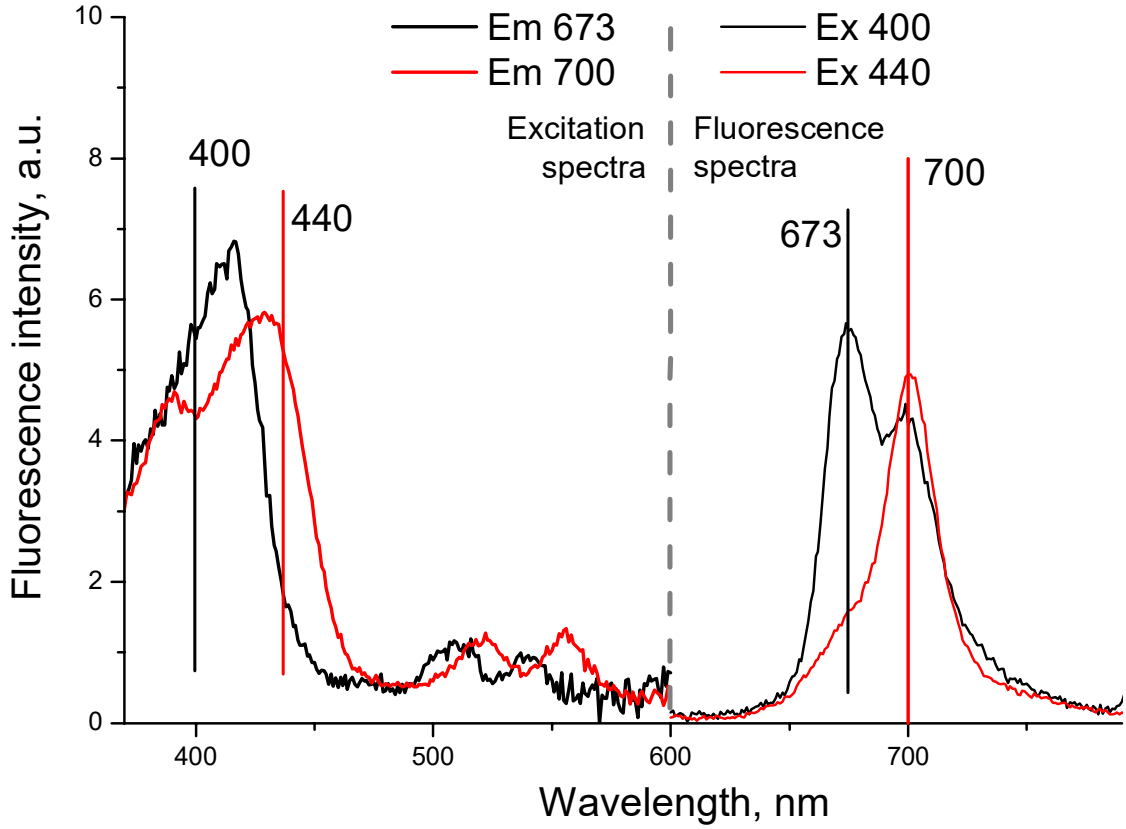

Figure S7. Excitation and fluorescence spectra of dyad **2**, obtained under the conditions described in the literature[2] In the range from 350 to 600 nm excitation spectra of **2**: **black line** - Em = 673 nm, **red line** - Em = 700 nm. In the range from 600 to 800 nm fluorescence spectra of **2**: **black line** - Ex = 400 nm, **red line** - Ex = 440 nm.

As it can be seen from the fluorescence and excitation spectra, the final fission product contains an admixture of methylpyropheophorbide *d*. Moreover, the calculation of the fluorescence quantum yield of the putative chromophore of unpurified dyad **2** with a maximum fluorescence at 673 nm showed a value of $4.97 \cdot 10^{-3}$, however, the fluorescence spectrum under identical conditions of the purified product (**2**) obtained by a modified method could not be detected.

On the basis of this fact we can conclude that dyad **2** has more than an order of magnitude lower quantum yield of fluorescence and the modified method allows us to obtain a dyad **2** with the lowest content of impurities of by-products structurally similar to methylpyropheophorbide.

[2]Helaja J., Tauber A.Y., Abel Y., Tkachenko N. V, Lemmetyinen H., Kilpeläinen I., Hynninen P.H. *J. Chem. Soc., Perkin Trans. 1*, **1999**, 2403.