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

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Experimental Section

*(Hydroxy)(oxo)molybdenum(V) 5,10,15,20-tetraphenylporphyrinate **2***. Tetraphenylporphyrin (0.1 g, 0.16 mmol) was boiled with MoO_3 (0.076 g, 0.53 mmol) in phenol (0.8 g) at 181 °C for 4 h. After cooling the reaction mixture, the product was extracted with chloroform; the solution was repeatedly washed with warm distilled water to remove phenol, then dissolved in $CHCl_3$ and placed on the Al_2O_3 column. Double chromatography using $CHCl_3$ was performed. Pink and green zones were obtained, which were unreacted porphyrin and self-assembled complex, respectively. The yield of complex **2** was 60%. UV-VIS [$CHCl_3$, λ_{max}/nm (logε)]: 620.0 (2.94), 584.0 (2.92), 456.0 (3.78). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (s, 8H$_\beta$), 7.84 (s, 8H$_o$), 7.26 (m, 2H$_m$), 6.97 (t, 6H$_m$), 6.95 (m, 4H$_p$), 2.48 (s, 1H, OH). IR (KBr, ν/cm^{-1}): 701, 752 (γ C–H) (benzole); 1070, 1177 (δ C–H); 1484, 1596 (ν C=C); 800 (γ C–H, pyrrole); 1018 (C_3–C_4, ν C–N, δ C–H); 1336 (ν C–N); 1441 (ν C=N); 441 (Mo–N); 659 (Mo–O); 928 (Mo=O).

2,5-Di(2-pyridyl)-1-(3-pyridylmethyl)pyrrolidino[70]fullerene **1** was synthesized by the reaction between fullerene C_{70} and azomethine ylide in 1,2-dichlorobenzene by Dr. P. A. Troshin. UV-VIS [toluene, λ_{max}/nm (logε)]: 399 (4.08), 433 (3.75), 705 (2.72). IR (KBr, ν/cm^{-1}): 1304 (ν C–N), 1463 (ν C=N), 1096, 1148 (δ C–H) (pyridine); 1121, 996 (ν C–N) (pyrrolidine); 1433, 1147, 789, 685, 646, 573, 527, 462 (C_{70} skeleton).

Thermodynamic and kinetic experiments. The equilibrium constants and reaction rates for **1**+**2** self-assembling were determined spectrophotometrically for each composition of the reaction mixture *via* the molar ratio and excess concentration methods, respectively, according to the original author's one-step procedure. For this, measurements of the optical density for a series of solutions with a constant concentration of complex **2** ($1.06\ 10^{-5}$ M) and ligand **1** concentrations varying from $3.54\ 10^{-5}$ to $6.02\ 10^{-4}$ M were carried out at 462 nm both in the start of complex formation ($\tau = 0$) and during the one-way reaction. To avoid the formation of peroxides in a solvent medium, the **1/2** solutions in freshly distilled toluene were prepared immediately prior to use. Toluene (ECOS) was

dried with potassium hydroxide and distilled prior to use (T_b 110.6 °C). The water content determined by Fisher titration did not exceed 0.01%. Since ligand **1** has its own absorption spectrum, the UV-VIS spectra of the reaction mixtures was registered in the subtraction mode that took away the signal from the coordinated **1** part using as the zero line the spectrum of **1** of the same concentration as in the working solution. The solutions were thermostated at 298 ± 0.1 K in closed quartz cells in a special cell of a spectrophotometer.

Calculation of equilibrium constants and kinetic parameters. The equilibrium constants, *K* were calculated from the equation (1) derived for the three-component equilibrium system using the principle of detailed equilibrium and the Bouguer-Lambert-Beer law for a mixture of two colored compounds, *viz.*, the initial complex **2** and the product of its interaction with ligand **1.**

$$K = \frac{\frac{A_i - A_0}{A_\infty - A_0}}{1 - \frac{A_i - A_0}{A_\infty - A_0}} \left(C_{\mathbf{1}} - C^0_{\mathbf{2}} \frac{A_i - A_0}{A_\infty - A_0} \right)^{-n} \qquad (1)$$

where C^0_2, C_1 are initial concentrations of **2** and **1** in solution in toluene, respectively; A_o, A_i, A_∞ are absorbances of **2** solution (τ = 0 min), the equilibrium mixture with a certain concentration of **1** and the reaction product at the working wavelength, n is the number of coordinated molecules **1**.

The reaction rate constants for various concentrations of **1** were calculated from the formal first-order equation under the condition of an excess of **1** towards **2**:

$$k_{obs} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty} \qquad (2)$$

where A_0, A_τ, and A_∞ are the absorbances of the reaction mixture at the working wavelength at the start of the reaction, τ after the beginning and when the reaction is completed.

Optimization of the *K* and k_{obs} values and the determination of the mean square deviations were carried out by the method of least squares using the Microsoft Excel program. The relative error in the determination of *K* and k_{obs} did not exceed 26% and 10%, respectively.

Equipment. UV-VIS, IR, ^{1}H NMR and emission spectra were recorded on UV-VIS Agilent 8453, VERTEX 80v, Bruker Avance III-500, AvaSpec-2048 (Avantes, Holland). The fluorescence spectra were recorded in a thermostated cell based on the Peltier element at 298 K. The irradiator Ivolga OMS-1 equipped with the monochromator LM-4 (Lumex, Russia) was used as the light source.

Table S1 Effective rate constants k_{obs} of the reaction in the system **1**–**2**–toluene at 298 K, depending on the concentration of **1**.

C_1 10^4, M	($k_{obs} \pm \delta k_{obs}$) 10^4, s^{-1}
0.35	2.7 ± 0.2
0.59	3.0 ± 0.3
1.06	3.3 ± 0.4
1.98	3.9 ± 0.4
2.48	4.0 ± 0.3

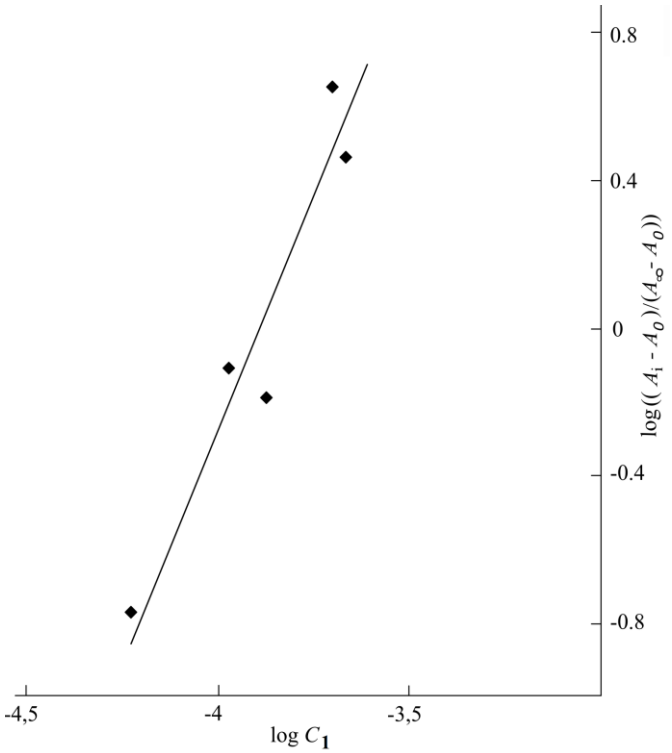

Figure S1 The plot of $\log(A_i - A_0)/(A_\infty - A_0))$ *vs.* $\log C_1$ for the reaction of **2** and **1** in toluene upon the **1** concentration in the range from 3.54 10^{-5} M to 6.02. 10^{-4} M. $R^2 = 0.864$.

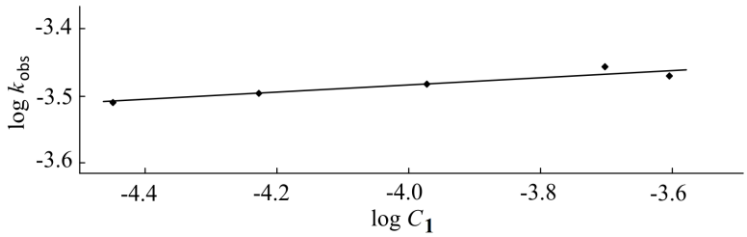

Figure S2 The plot of $\log k_{obs}$ *vs.* $\log C_1$ for the reaction of **2** and **1** in toluene at 298 K. $R^2 = 0.993$.

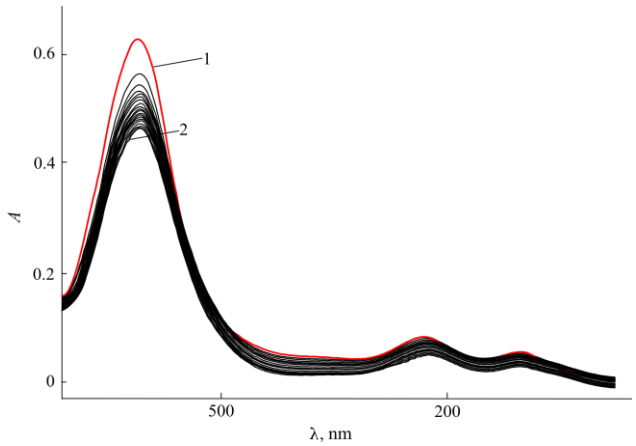

Figure S3 UV-VIS spectra of compound **2** in the molybdenum(V) porphyrinate – pyridyl-substituted pyrrolidino[70]fullerene – toluene system upon **1** concentration of 3.89×10^{-4} M: (*1*) immediately after the preparation of the mixture and (*2*) in 24 h (lower line). Intermediate lines correspond to time points up to 24 h.

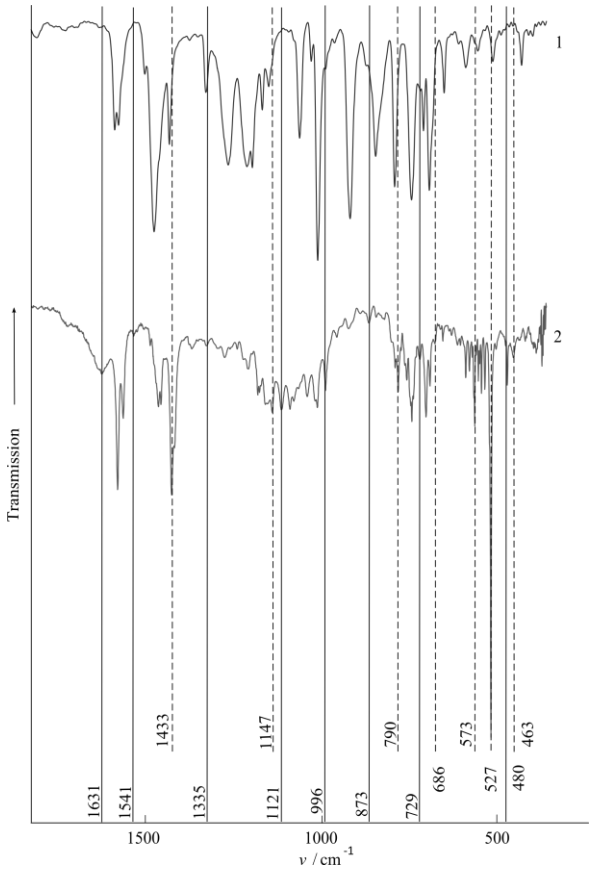

Figure S4 IR spectra: (*1*) starting **2** and (*2*) the product **3** of its reaction with ligand **1**.