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# Novel fluorescence quenching triad based on molybdenum(V) tetra-*p*-tolylporphyrin and substituted fullero[60]pyrrolidine

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**ABSTRACT:** With the aim of designing new photoactive donor–acceptor dyads, self-assembly in the (ethoxy)(oxo)(5,10,15,20-(4-methylphenyl)porphinato)molybdenum(V) (O=Mo(OEt)TTP)–2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl-methyl)pyrrolidino[60]fullerene (Py<sub>3</sub>F)-toluene systems was quantitatively studied using spectral methods (UV-vis, IR, <sup>1</sup>H NMR, mass spectrometry), chemical thermodynamics, and chemical kinetics. Interaction between O=Mo(OEt)TTP and pyridine (Py) proceeding as step equilibriums was preliminarily studied to model the processes above. The novel donor–acceptor triad based on O=Mo(OEt)TTP and Py<sub>3</sub>F is represented with both quantitative description of its formation and conformation of the chemical structure. Prospects for the study of the triad as a photosynthetic antenna imitator and an active layer in organic solar cells are substantiated by a fluorescence method. Along with this, it has been demonstrated that O=Mo(OEt)TTP is a good candidate for use as an optical and fluorescent chemosensor of volatile organic compounds and nitrogen bases — the building blocks of pharmaceuticals, food components and environmental pollutants.

**KEYWORDS:** molybdenum(V) porphyrin, pyridine, pyridyl substituted pyrrolidino[60]fullerene, donor–acceptor complexes, formation thermodynamics/kinetics, prospects in optoelectronics.

# INTRODUCTION

Chemical sensorics is an independent field of modern analytical chemistry. Though the first artificial sensor system was described in 1961 for odor analysis [1] and the history of electronic noses began in the 80s [2], creation and use of sensory systems is a very promising objective to this day. Currently, based on the principles of molecular recognition, scientists around the world are trying to obtain more complete information about the studied samples by modernization of analytical equipment. In this regard, chemical sensors that include optical, mass-sensitive, electrochemical and biosensors [3, 4] are convenient analytical tools.

A review by Meng et al. [5] highlights advances in electrochemical sensing based on 2D nanomaterials (graphene, phosphorene (BP) and transition metal dichalcogenides). The main achievements in the use of 2D nanomaterials are summarized for four different groups of analytes: gases, volatile organic compounds (VOCs), ions and biomolecules. A toluene suspension sensor based on CoPP-ZnO nanorods has been used for indoor environmental monitoring systems to detect very low concentrations of VOCs at an early stage of outgassing [6]. ZnO nanorods were functionalized with CoPP to add various adsorption sites for VOCs. Thin films of MoO<sub>3</sub>-based hybrids display sensitive properties to aldehyde gases [7]. Such hybrids with polypyrrole, polyaniline, as well as 5,10,15,20-tetrakis(N-methyl-4-pyridino)porphyrin show a distinct response to the adsorption of VOCs. New universal fluorescent sensors were synthesized based on sulfonated porphyrin

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(5,10,15,20-tetra(3-ethoxy-4-hydroxy-5-sulfonate) phenylporphyrin), which has showed excellent selectivity and sensitivity to molybdenum ions compared to competing ions in aqueous solutions [8]. Sensors based on  $\beta$ -octamethoxyporphyrin and  $\beta$ -octabutoxyporphyrin can act with respect to nitroaromatic compounds [9]. Porphyrin complexes are used for analysis of olive oils, gases, VOCs [10]. Numerous studies of solid-state receptors based on metalloporphyrins were reviewed by Paolesse *et al.* [11].

In recent years, applications of porphyrin complexes have expanded to nonlinear optics [12], liquid crystals [13], solar cells [14, 15], catalysts [16] and photodynamic therapy [17]. In our studies [18–21], metalloporphyrins as a group of potential gas-sensitive materials became a natural choice for the detection of VOCs due to their open reaction centers for axial ligation, their large spectral shifts during ligand bonding, and their intense absorbance in the UV-vis spectral region. Previously, we used toluene solutions of metalloporphyrins when studying the systems self-assembled *via* axial coordination with photoinduced electron transfer (PET) [22, 23].

The present work deals with new studies on the preparation of porphyrin-based donor-acceptor complexes capable of PET for solution-processed organic solar cells (OSCs), as well as with search for and study of new chemical VOC sensors based on porphyrin complexes. We represent the synthesis, electron-optical properties, stability, as well as quantitative thermodynamic/kinetic data on self-assembly of both a triad based on (ethoxy) oxo(5,10,15,20-(tetra-4-methylphenyl)porphinato) molybdenum(V) (O=Mo(OEt)TTP)-2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl-methyl)pyrrolidino[60] fullerene ( $Py_3F$ ) (Fig. 1) and axial pyridine complexes of O=Mo(OEt)TTP. Optical characteristics under controlled conditions (toluene,  $C_{\text{O=Mo(OEt)TTP}}$ ,  $C_{\text{Py}_2\text{F}}$ ,  $C_{\text{Py}}$ ,  $\lambda_{\text{work}}$ , the temperature, time) were obtained by measuring the UV-vis spectra of Mo(V) complex in pure toluene and in toluene-Py/Py<sub>3</sub>F mixtures. Testing for photoinduced electron transfer (PET) availability by the fluorescence method is described.

# EXPERIMENTAL

#### Synthesis

(*Ethoxy*)oxo(5,10,15,20-(*tetra*-4-*methylphenyl*) porphinato)molybdenum(V), O=Mo(OEt)TTP (1). The complex was synthesized as a derivative of H<sub>2</sub>TPP (TPP is 5,10,15,20-tetraphenylporphine dianion) [22]: H<sub>2</sub>TTP (0.01 g, 0.015 mmol) and MoO<sub>3</sub> (0.009 g, 0.06 mmol) were reacted for 4 h in boiling phenol (0.8 g) at 454 K. The complex was isolated in solid form *via* vacuum distillation of phenol and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> and twice chromatographed on an Al<sub>2</sub>O<sub>3</sub> column using CH<sub>2</sub>Cl<sub>2</sub> and then a 4:1 CH<sub>2</sub>Cl<sub>2</sub>:ethanol mixture. The



Fig. 1. The chemical structures of the compounds studied.

solid complex was obtained with a yield of 60% after precipitation from the solution. Found: C 72.81; H 4.96; N 6.91; O 3.85; Mo 11.47; Anal. Calcd for C<sub>50</sub>H<sub>41</sub>N<sub>4</sub>O<sub>2</sub>Mo: C 72.72; H 5.01; N 6.78; O 3.87; Mo 11.62; UV-vis  $(CH_2Cl_2, \text{ fresh solution}), \lambda_{max}, (nm) (\log \varepsilon): 620.0 (4.35),$ 580.0 (4.39), 453.0 (5.27), 345.0 (4.58); IR (KBr). µmax (cm<sup>-1</sup>): vibrations of benzene rings 684, 723 ( $\gamma$  C–H), 1069, 1184 (δ C–H), 1516, 1493 (v C=C), vibrations of pyrrole rings 796 (γ C–H), 1020 (C<sub>3</sub>–C<sub>4</sub>, ν C–N, δ C–H), 1340 (v C-N), 1402 (v C=N), -CH<sub>3</sub> 1379, 1465, Mo-N 431, Mo-O 525, Mo=O 948; IR (CsBr),  $\mu_{max}$  (cm<sup>-1</sup>): 639, 631, 596, 571, 555, 521, 441, 432, 404, 346, 295, 261, 243, 211; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm), J (Hz): 8.38 (br. s, 8H<sub>β</sub>), 8.04 (s, 8H<sub>α</sub>, Ph), 7.77 (s, 8H<sub>m</sub>, Ph), 3.70 (q, 2H<sub>-CH<sub>2</sub></sub>, -OC<sub>2</sub>H<sub>5</sub>), 2.77 (s, 12H<sub>-CH<sub>2</sub></sub>), 1.24 (t, 3H<sub>-CH<sub>2</sub></sub>, J = 9,  $-OC_2H_5$ ; MS (MALDI-TOF), (m/z): 782.925  $[M-OEt]^+$ , 785.997  $[M-OEt+3H]^+$  (the  $[M-OEt]^+$  signals for Mo stable isotopes see Supporting information).

*Oxo*(5,10,15,20-(*tetra-4-methylphenyl*)*porphinato*)(*dipyridine*)*molybdenum*(V) *ethoxide*,  $[O=Mo(Py)_2TTP]^+$ *OEt*<sup>-</sup> (2). The complex was synthesized by the reaction of O=Mo(OEt)TTP with Py taken in molar ratio 1: 2 in toluene at 298 K. A solid sample of **2** was observed in nearly 100% yield by vacuum distillation of the solvent. UV-vis (toluene),  $\lambda_{max}$  (nm): 625.0, 584.0, 456.0; IR (KBr),  $\mu_{max}$  (cm<sup>-1</sup>): vibrations of benzene rings 723 (γ C–H), 1073, 1184 ( $\delta$  C–H), 1512 ( $\nu$  C=C), vibrations of pyrrole rings 798 ( $\gamma$  C–H), 1017 (C<sub>3</sub>–C<sub>4</sub>,  $\nu$  C–N,  $\delta$  C–H), 1335 ( $\nu$  C–N), 1407 ( $\nu$  C=N), –CH<sub>3</sub> 1384, 1464), Mo–N 431, Mo–O 522, Mo=O 945; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm), *J* (Hz): 8.1–7.9 (br. s, 8H<sub>β</sub>), 7.82, 7.64 (br. s, br. s, 8H<sub>0</sub>-Ph, 4H<sub>0</sub>-pyridine), 7.59 (br. s, 2H, H<sub>p</sub>-pyridine), 7.18–7.14 (m, 8H<sub>m</sub>-Ph, 4H<sub>m</sub>-pyridine), 3.70 (q, 2H<sub>-CH<sub>2</sub>-,</sub>  $-OC_{2}H_{5}$ ), 2.76 (s,  $12H_{-CH_{3}}$ ), 1.24–1.21(t,  $3H_{-CH_{3}}$ , J = 9,  $-OC_{2}H_{5}$ ).

2'-(*Pyridin*-4-*yl*)-5'-(*pyridin*-2-*yl*)-1'-(*pyridin*-2-*ylmethyl*)*pyrrolidino*[60]*fullerene*, *Py*<sub>3</sub>*F* (3). The compound was synthesized by the reaction between C<sub>60</sub> and azomethinilide in 1,2-dichlorobenzene by Dr. P. Troshin [24]. UV-vis (toluene);  $\lambda_{max}$  (nm) (log ε): 702.0 (2.88), 432 (3.72); IR (KBr),  $\mu_{max}$  (cm<sup>-1</sup>):1727, 1588, 1568, 1462, 1434, 1412, 1377, 1168, 1049, 996, 746, 693, 661, 598, 574, 548, 527, 481, 464, 402; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm), *J* (Hz): 9.04 (d, 1H<sub>m</sub>, *J* = 4.3, pyridine), 8.70 (d, 2H<sub>p</sub>, *J* = 5.5, pyridine), 8.66 (d, 1H<sub>m</sub>, *J* = 4.3, pyridine), 8.01 (d, 1H<sub>m</sub>, *J* = 5.3, pyridine), 7.95 (t, 4H<sub>o</sub>, *J*=7.3, pyridine), 7.74 (m, 1H<sub>m</sub>, pyridine), 7.56 (s, 1H<sub>-CH<sub>2</sub></sub>), 7.35 (m, 2H, CH Py), 6.17 (s, 1H<sub>-CH<sub>2</sub></sub>), 4.38 (d, 1H<sub>=CH-</sub>, *J* = 15.2), 4.07 (d, 1H<sub>=CH-</sub>, *J* = 14.7). The spectral characteristics coincide with the published data [25].

Oxo(5,10,15,20-(tetra-4-methylphenyl)porphinato) (di-(2'-(Pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyr *yl-methyl*)*pyrrolidino*[60]*fullerene*)*molybdenum*(V) ethoxide,  $[O=Mo(Py_3F)_2TTP]^+ OEt^-$  (4). The complex was synthesized by the reaction of O=Mo(OEt)TTP with Py<sub>3</sub>F taken in molar ratio 1: 2 in toluene at 298 K for 1.5 h. The solid for spectral studies was isolated by toluene vacuum distillation. UV-vis (toluene),  $\lambda_{max}$  (nm), (log  $\varepsilon$ ): 620.0 (4.35), 580.0 (4.39), 453.0 (5.27), 345.0 (4.58); IR (KBr),  $\mu_{max}$  (cm<sup>-1</sup>): vibrations of benzene rings 700, 729 (γ C–H), 1066, 1215 (δ C–H), 1541 (ν C=C), vibrations of pyrrole rings 798 (γC–H), 1018, 997 (C<sub>3</sub>–C<sub>4</sub>, νC–N, δ C-H), 1307 (v C-N); 1377 (v C=N), C<sub>60</sub> core vibrations 1434, 574, 527, 848, 824 (γ C–H, =CH–), Mo–N<sub>Pv<sub>2</sub>F</sub> 562, Mo-N 432; Mo-O 527, Mo=O 946, Py<sub>3</sub>F pyridine and pyrrolidine ring vibrations 1735, 1588, 1413, 1066, 1048, 746, 700, 599, 548, 481; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm), J (Hz): 8.67, 7.98 (d, d, 4H<sub>o</sub>, pyridin-4-yl, Py<sub>3</sub>F, 4H<sub>o</sub>, pyridin-2-yl, Py<sub>3</sub>F), 7.46 (s, 8H<sub>b</sub>, 8H<sub>o</sub>,), 7.4; 7.2 (m; s, 8H<sub>m</sub>,-Ph, 4H<sub>m</sub>-pyridin-4-yl, 8H<sub>m</sub>-pyridin-2-yl), 7.46 (s, 4H<sub>-CH-</sub>, Py<sub>3</sub>F), 5.15, 4.69 (s, s, 2H<sub>-CH-</sub>, Py<sub>3</sub>F, 2H<sub>-CH-</sub>, Py<sub>3</sub>F), 3.63 (br. s,  $2H_{-CH_{2}-}$ ,  $-OC_{2}H_{5}$ ), 2.76 (s,  $12H_{-CH_{2}-}$ Ph), 1.24 (s,  $3H_{-CH_{2}}$ ,  $-OC_{2}H_{5}$ ).

(*Chloro*)*oxo*(5,10,15,20-(*tetra*-4-*methylphenyl*) *porphinato*)*molybdenum*(V), *O=Mo*(*Cl*)*TTP* (5). The complex was synthesized as described in [26]. The dichloromethane solution of O=Mo(OEt)TTP was kept for 1.5 h under laboratory lighting. Yield ~100%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$  (nm), (log ε): 678.0 (4.09), 632.0 (4.01), 502.0 (4.69), 419.0 (4.78), 399 (4.82); IR (CsBr); µmax (cm<sup>-1</sup>): 642, 620, 596, 571, 560, 522, 464, 439, 432, 416, 405, 432, 277, 226, 212, 199; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 8.24 (br. s, 8H<sub>β</sub>, Ph), 8.00 (br. s, 8H<sub>o</sub>, Ph), 7.80 (s, 8H<sub>m</sub>, Ph), 2.81 (s, 12H <sub>-CH<sub>3</sub></sub>).

## Thermodynamics/kinetics of self-assembly in the Mo<sup>v</sup> porphyrin — N-base systems

Equilibria and rates of the 1 reaction with  $Py/Py_3F$ were studied spectrophotometrically by the molar

ratio and excess concentration methods, respectively. Solutions of 1, Py and Py<sub>3</sub>F in freshly distilled toluene were prepared immediately before use to avoid the formation of peroxides in the solvent medium. The absorbance of the solutions with constant 1 concentration of  $5.9 \times 10^{-6}$  M and base concentrations from  $4.13 \times 10^{-4}$ to 11.38 M and from  $1.38 \times 10^{-5}$  to  $9.9 \times 10^{-5}$  M for Py and Py<sub>3</sub>F, respectively, was measured at the working wavelength of 450 nm at the initial moment of time  $(\tau = 0)$  and throughout the duration of the experiment. The solutions were thermostated with an error of  $\pm 0.1$  K at 298 K in closed quartz cells in a special cell of the spectrophotometer. Spectrophotometric titration data in the concentration and time fields (time-dependent spectrophotometric titration method [27]) were used to determine equilibrium constants, rates of one-way reactions, and equilibration time in one experimental series. Equilibration time was determined from the minimum error in the numerical value of the equilibrium constant calculated at different  $\tau$  values.

С

Pyridine of pure analytical grade was dried for 2 days over KOH grains and then distilled off (bp  $115.3 \,^{\circ}$ C). Toluene was dried over KOH and distilled off before use (bp  $110.6 \,^{\circ}$ C). Water content determined by Fischer titration did not exceed 0.01%.

The equilibrium constants of two-way reactions were determined by Eq. (1), derived using the law of mass action and the Bouguer–Lambert–Beer law, the mathematical expression of which was written for a mixture of two colored compounds, **1** and the product of its reaction with  $Py/Py_3F$ .

$$K = \frac{(A_{\rm i} - A_{\rm 0})/(A_{\rm \infty} - A_{\rm 0})}{1 - (A_{\rm i} - A_{\rm 0})/(A_{\rm \infty} - A_{\rm 0})} \cdot \frac{1}{(C_{\rm L}^{0} - C_{\rm MP}^{0} \cdot (A_{\rm i} - A_{\rm 0})/(A_{\rm \infty} - A_{\rm 0}))^{\rm n}}$$
(1)

Here  $C_{MP}^{0}$  and  $C_{L}$  are the initial concentrations of 1 and Py/Py<sub>3</sub>F in toluene, respectively;  $A_0$ ,  $A_i$  and  $A_{\infty}$  are the absorbance at the working wavelength of solutions of 1 at  $\tau = 0$ , an equilibrium mixture at a definite Py/Py<sub>3</sub>F concentration, and the reaction products, respectively; *n* is the number of Py/Py<sub>3</sub>F molecules involved in the reaction.

The reaction rate constants for various concentrations of  $Py_3F$  were calculated from the formal first-order Equation (2) under the condition of an excess of  $Py_3F$  with respect to **1**:

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

Here  $A_0$ ,  $A_{\tau}$  and  $A_{\infty}$  are the absorbance of the reaction mixture at the working wavelength at moments of time 0,  $\tau$ , and at the end of the reaction.

The relative error in the  $K/k_{obs}$  values determined by the least squares method did not exceed 23/10%. A numerical value of *n* in Eq. (1) was determined from the  $\log I - \log C_{\text{Py/Py}_3\text{F}}$  dependence, where *I* is  $A_i - A_0/A_{\infty} - A_i$ . The reaction order with respect to Py/Py\_3F was determined from the  $\log k_{\text{obs}} - \log C_{\text{Py/Py}_3\text{F}}$  plot.

#### Equipment

The elemental analysis of C, H, N, O was carried out on a FlashEA analyzer. The elemental analysis of Mo was completed by a Clever C–31 X-ray fluorescence spectrometer under the following conditions: voltage 45 kV, current 400  $\mu$ A, without filter, time 60 s, air, anode of X-ray tube rhodium. The UV-vis, IR, <sup>1</sup>H NMR, and mass spectra were recorded on a UV-vis Agilent 8453 spectrophotometer, a VERTEX 80v spectrometer, an AVANCE-500 spectrometer, and a Shimadzu AXIMA Confidence mass spectrometer, respectively. The fluorescence spectra were recorded in a temperature-controlled cell based on a Peltier element at 298 K. A Volga OMS-1 instrument (Lumix, Russia) with an M-4 monochromator (Lumix, Russia) was used as a light source.

# **RESULTS AND DISCUSSION**

#### Synthesis and characterization

Synthesis of molubdenum(V) porphyrin complexes by a reaction between porphyrin and an inorganic Mo derivative in boiling phenol ends with the phenoxy ligated complex (O=Mo<sup>V</sup>(OPh)P) in which axial OPh is transformed during chromography [28]. Final O=Mo(OH)P is observed if H<sub>2</sub>TPP is used and a weak acid added to the chromatography solvent. The ethanol addition instead of an acid was used to obtain the Mo complex with H<sub>2</sub>TTP (see Experimental section), which led to O=Mo(OEt)TTP (1). 1, 2, and 4 are characterized by "hyper-type" UV-vis spectra (Experimental section) with the additional charge transfer band at 453 nm compared with the closed-shell  $d^0$  or  $d^{10}$  central ions [29]. Such spectrum is typical of the porphyrin complexes of the metal ions in configurations  $d^1$  to  $d^6$  [28]. The IR spectrum of 1 shows the characteristic vibration signals of the pyrrole and benzene rings, the -CH<sub>3</sub> groups, Mo-N, Mo-O and Mo=O bonds (Fig. S1). It is known that the M=O frequency in oxometal(V) porphyrins O=M(X)P (M = Mo, W, Re) is subject to *cis*- and *trans*effects from the change of equatorial and axial ligand, respectively [30]. Improvement of electron-donor properties of H<sub>2</sub>TTP and –OEt in 1 causes a decrease in the Mo=O signal frequency by about 20 cm<sup>-1</sup>, as well as its intensity compared to H<sub>2</sub>TPP derivatives, for example, with O=Mo(OH)TPP [31] in which the axial ligands was shown to occupy the trans-positions. Signal broadening in the <sup>1</sup>H NMR spectrum (Fig. 2a) points to the presence an unpaired electron on the d orbital in the paramagnetic complex 1 [32, 33]. Electron configuration  $(d^{1})$  is confirmed for porphyrin molybdenum(V) complexes



**Fig. 2.** <sup>1</sup>H NMR spectra (in CDCl<sub>3</sub>) of O=Mo(OEt) TTP (a), the product of its reaction with Py,  $[O=Mo(Py)_2TTP]^+OEt$  (b), and the product of its reaction with Py<sub>3</sub>F,  $[O=Mo(Py_3F)_2TTP]^+OEt$  (c).

by the resolved EPR spectra [34–37]. Nonetheless the  $-O-CH_2-CH_3$  proton signals are distinctly displayed at 3.70 and 1.24 ppm (Experimental section). A single peak in the 1 mass spectrum (see Experimental section and Fig. S2 in the Supporting information) corresponds to molecular ion without OEt axial ligand. This is not surprising given the well-known fact that weak-field ligands are almost always absent in the molecular ions of axially coordinated porphyrin complexes [28].

**2** and **4** synthesized by treatment of **1** with an excess of Py and  $Py_3F$  in toluene (Experimental section) are stable and can be isolated in a solid form for spectral identification. Samples of the reaction products for recording the IR spectra were obtained by solvent vacuum distillation from a reaction mixture of the composition



**Fig. 3.** The UV-vis spectra and the titration curves (in the insets) of O=Mo(OEt)TTP ( $C = 5.9 \times 10^{-6}$  M) with pyridine in toluene.  $C_{\text{Py}}$ , M: 1 - 4.13 × 10<sup>-4</sup>, 2- 1.24 × 10<sup>-2</sup> (a), 3 - 1.24 × 10<sup>-2</sup>, 4 - 11.38 (b).

corresponding to the point equivalence during titration when the entire source complex 1 was titrated (detailed consideration is represented below). The 2/4 IR spectrum retains signals typical of 1. However, insignificant highfrequency shifts of the benzene ring vibration signals are observed. The signals corresponding to the pyrrole rings are shifted to the low frequency range and their intensity decreases markedly in the entire spectral range (Fig. S1). The range of "fingerprints" from 600 to 1400 cm<sup>-1</sup> changes dramatically with splitting of signals in the 4 IR spectrum. The low-frequency signal at 527 cm<sup>-1</sup> increases

noticeably, which indicates porphyrin macrocycle deformation due to additional coordination of two molecules of 3. New signals with vibration frequencies of coordinated Py and Py<sub>3</sub>F are presented in the IR spectra of 2 and 4, respectively (Table S1 and Fig. S1b and c). 2/4 <sup>1</sup>H NMR signals in the characteristic regions of chemical shifts are shown in Fig. 1b and c. Overlapping signals assigned to 2/4 H<sub>B</sub>, H<sub>o</sub>, H<sub>m</sub> of both the macrocycle and the Py/Py<sub>3</sub>F at the spectral region from 7.1 ppm to 8.7 ppm were observed. The upfield shifts of both the  $H_{\beta}$  and  $H_{\alpha}$ , H<sub>m</sub> signals indicate weakening of the de-shielding action of the ring current of the macrocycle on the mentioned protons. This means that the effect of OEt displacement in the second coordination sphere in <sup>1</sup>H NMR spectrum of 1 when Py/Py<sub>3</sub>F ligation takes place prevails over the one appearing from the base molecule in the coordination polyhedron of Mo. The significant or perceptible upfield shifts are displayed for the Py proton signals in the 2 spectrum compared with Py uncoordinated (Table S2). In the 4 spectrum, the signals of both 2-pyridyl and 4-pyridyl protons also shift similarly in the 3 spectrum (Table S2). The H signals of both varieties of -CH<sub>3</sub> groups located significantly far from the coordination center and macrocycle keep their position while the - $CH_2$ -OEt proton signal is shifted by 0.07 ppm in the 4 <sup>1</sup>H NMR spectrum.

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# Self-assembly of the molubdenum(V) porphyrin-pyridyl substituted [60]fullerene donor–acceptor triads

Thermodynamic/kinetic study of the reactions between **1** and Py was performed to both modeling of porphyrin– fullerene donor–acceptor complex formation and obtaining the parameters of **1** sensor ability towards Py. Characteristics of **1** as the chemosensor of Py, namely sensitivity, a relative optical response, and a minimum detection limit were obtained by spectrophotometric

**Table 1.** The equilibrium/rate constants,  $K_n/k_n$  of the simple reactions in the molubdenum(V) porphyrin – Py/Py<sub>3</sub>F systems, relative optical response,  $A_{opt}$ , and the Py/Py<sub>3</sub>F minimum detection limit,  $C_{min}$ .

Self-assembled system	Stage 1		Stage 2		A <sub>opt</sub>	$C_{\min}$ , M
	$K_1$ , L/mol	n	$K_2$ , L/mol	n		
<b>1</b> – Py	$3.78 \times 10^2$	1.14	10	0.93	0.2	0.002
$1 - Py_3F$	$4.56\times10^{7a}$	1.75	$4.70 \times 10^{-2 \text{ b}}$	0.44	0.2	0.00008
O=Mo(OH)TPP – Py <sup>d</sup>	$9.1 \times 10^{3}$	1.08	39.3	1.04		0.02
O=Mo(OH)TPP-Py <sub>3</sub> F	$1.97 \times 10^4$	~1	0.26 <sup>e</sup>	1 <sup>c</sup>		0.00003
O=Mo(OH)TPP-Py <sub>3</sub> F' <sup>f</sup>	$2.27 \times 10^{8  g}$	2.2 <sup>g</sup>	$0.159 \times 10^{-8}$ e	0.9°		0.00007
O=Mo(OH)TPP-Py <sub>3</sub> F" <sup>h</sup>	$2.94  imes 10^{7j}$	2	$3.38 \times 10^{-4  k}$	0.2°		0.0002

<sup>a</sup> $K_3$ , L<sup>2</sup>/mol<sup>2</sup>, <sup>b</sup> $k_4$ , s<sup>-1</sup>, <sup>c</sup>the reaction order with respect to a base, <sup>d</sup>The third stage with  $K_3 = 1.0$  L/mol and n = 1.26 was obtained [38], <sup>e</sup> $k_2$ , L/mol<sup>-1</sup>·s<sup>-1</sup> [39], <sup>f</sup>2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-yl-methyl)pyrrolidino[60]fullerene [22] <sup>g</sup> $K_1$ , L<sup>2</sup>/mol<sup>2</sup> and n for two parallel reactions, <sup>b</sup>2'-(pyridin-2-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-yl-methyl)pyrrolidino[70]fullerene [23], <sup>j</sup> $K_1$ , L<sup>2</sup>/mol<sup>2</sup>, <sup>k</sup> $k_2$ , s<sup>-1</sup>



Scheme 1. Mechanism of Py (a) and Py<sub>3</sub>F (b) bonding by O=Mo(OEt)TTP in toluene.

titration of the 1 solution by Py in toluene. Firstly, stability of 1 in toluene was established. Given the fact of axial ligand exchange in oxomolybdenum(V) porphyrins in chlorine-containing solvents [26], we have found that a dark green solution O=Mo(OEt)TTP in dichloromethane is unstable under laboratory lighting (Fig. S3). The product was identified by UV-vis spectroscopy as the chloro-oxo derivative, O=Mo(Cl)TTP. The charge transfer band at 453 nm in the 1 spectrum disappears and a characteristic peak of the chloro-oxo complex at 502 nm is formed together with all other peaks of the new complex (Experimental section). The UV-vis, IR (the signal assigned to the Mo-Cl vibrations appear at 226 cm<sup>-1</sup>), and <sup>1</sup>H NMR spectroscopy data (Experimental section and Fig. S3) show that the ethoxy-oxo complex was completely converted to the chloro-oxo complex (5). That is why the toluene medium was chosen for above mentioned titration. Optical response of 1 with respect to Py detected in two concentration ranges of the latter from  $4.13 \times 10^{-4}$  M to  $1.24 \times 10^{-2}$  M and from  $1.24 \times 10^{-2}$  M to 11.38 M an increase in the intensity of absorption band at 453 nm (Fig. 3a) and decrease in the intensity of the one with the additional bathochromic shifts of the absorption maxima (Fig. 3b), respectively.

Thus, a distinct optical response reflects not only the Py presence but the change in its content. The observed spectral changes indicate the presence of free coordination sites on the high-charged metal center. Quantitative parameters of two stages of self-assembly in the **1**–Py medium are shown in Table 1.

Taking into account step reaction stoichiometry and the decrease in the K value together with the UV-vis

absorption maxima changing at the stage 2, we can represent a 1–Py reaction scheme (Scheme 1) that does not contradict reaction thermodynamics and  $Mo^{5+}$  coordination chemistry. The maximum  $Mo^{5+}$ coordination number is achieved at the first stage [40], so the second Py molecule ligation passes as axial OEt substitution (Scheme 1). The coordination of Py with the O=Mo(OH)TPP includes three stages, which makes it possible to cover the range of lower concentrations [38]. Thus, the macrocycle periphery modifications changing the acceptor properties [41] have led to other reaction mechanism.

The equilibrium constants of Py coordination by molubdenum(V) porphyrins are several orders of magnitude higher than 1 L/mol (Table 1), which points to high affinity of these chemosemsors to the Py molecule and opens the prospect of obtaining new porphyrin–fullerene donor–acceptor dyads bonded *via* the pyridyl residue. In order to create systems with the PET properties for OSCs and photosynthetic antenna imitation, self-assembly in the 1–Py<sub>3</sub>F–toluene systems was studied. Self-assembly in this system proceeds according to the reactions with the equilibrium/rate constants  $K_3/k_4$  (Scheme 1) revealed from the data in Fig. 4 and taking into account the product chemical structure (see the previous section).

A quasi-equilibrium between 1 and  $Py_3F$  (Scheme 1) is observed according to the reaction thermodynamic/kinetic study (for the data see Table 1). The 1: 2 stoichiometry equilibrium (Fig. S5) is accompanied by the slow oneway reaction that ends with formation of 4 with *trans*position of two fullerene containing molecular ligands and OEt in the second coordination sphere. The reaction



**Fig. 4.** The UV-vis spectra and the titration curve (in the insets) for the reaction of **1** ( $C = 5.9 \times 10^{-6}$  M) with Py<sub>3</sub>F in toluene.  $C_{\text{Py}_3\text{F}}$  M:  $1 - 1.38 \times 10^{-5}$ ,  $2 - 9.9 \times 10^{-5}$  (a). UV-vis spectra of **1** in the toluene  $- 8.25 \times 10^{-5}$  M Py<sub>3</sub>F immediately after the preparation of the mixture (3) and after 24 hours (4) and the corresponding log $C_{\text{Py}_3\text{F}}$  - log $k_{obs}$  plot ( $R^2 = 0.983$ ) (in the insets). Intermediate lines correspond to current time points (b).

kinetic order with respect to Py<sub>3</sub>F is close to zero (Fig. 4, Table 1). The above processes are accompanied by band (453 nm) intensity increase with  $C_{Pv_{a}F}$  increasing and decreasing of this absorption together with the low absorption maximum shift in a blue region in time with all reaction compositions (Fig. 4). The thermodynamic and kinetic data in Table 1 show how the stoichiometric mechanism of the molubdenum(V) porphyrin-pyridyl substituted fullerene dyad/triad formation depends on a chemical structure of both macrocycle periphery and a fullerene-containing base. Thus, one can achieve the desired result, namely a different optical response on a different base concentration for semi-quantitative rapid analysis or increased affinity to a base by structural modification of donor-acceptor dyads/triads precursors.

#### Fluorescence behavior of the donor-acceptor triad

Fluorescence quenching of **1** in the donor–acceptor triad **4** in its *cis*-isomer form was confirmed experimentally (Fig. 5) in the O=Mo(OH)TPP–Py<sub>3</sub>F" donor–acceptor system studied earlier (Table 1) [23]. The electron acceptor (2'-(pyridin-2-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-yl-methyl)) pyrrolidino[70]fullerene) added at the concentration of  $1.45 \times 10^{-4}$  M displayed a decrease in fluorescence of the initial O=Mo(OH)TPP by more than 50%.



**Fig. 5.** Fluorescence spectra ( $\lambda_{exc} = 420 \text{ nm}$ ) of O=Mo(OEt)TTP ( $C = 5.57 \times 10^{-5} \text{ M}$ ) and the equilibrium porphyrin-fullerene mixtures in toluene at the Py<sub>3</sub>F concentration shown in the figure.

This effect in an excited fluorophore connected with an electron acceptor may be related to both PET and energy transfer (FRET) [42, 43]. To understand the fluorescence quenching motif, we turned to the results of the femtosecond transient absorption spectroscopy and DFTcalculation (the B3LYP+D3BJ/6-31G level of theory) performed for the donor-acceptor phthalocyaninefullerene analog with the Mn<sup>3+</sup> central ion [44]. The manganese(III) phthalocyanine-substituted fullerene radical ion-pair formation proven by the mentioned methods clearly indicates that observed quenching of manganese(III) phthalocyanine moiety fluorescence in the dyad by 1'-N-methy1-2'-(1H-imidazol-1-y1)phenylpyrrolidino[60]fullerene in toluene is connected with PET. Thus, the donor-acceptor triad description we address in our present study stimulates physicists to develop this field in OSCs design and the study of primary charge separation in natural photosynthesis.

## CONCLUSION

The synthesis *via* self-assembly of a novel fluorescence quenching donor–acceptor triad based on (ethoxy) oxo(5,10,15,20-(tetra-4-methylphenyl)porphinato) molybdenum(V) and 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl-methyl)pyrrolidino[60]fullerene for future use in both physical insight into a fluorescence quenching mechanism and in OSCs design as a photoactive layer was achieved together with its quantitative thermodynamic/ kinetic description. The new triad is characterized in its chemical structure, key spectral parameters, and ability to quench molybdenum(V) porphyrine fluorescence.

Investigation with respect to the coordination bonding of molecular pyridine by (ethoxy)oxo(5,10,15,20-(tetra-4methylphenyl)porphinato)molybdenum(V) was preliminarily performed for modeling the above triad formation and testing the molubdenum(V) porphyrin as a VOCs chemosensor in comparison with other similar structures. The advantage of (ethoxy)oxo(5,10,15,20-(tetra-4-methylphenyl)porphinato)molybdenum(V) as a new chemosensor is a different optical response on a different base concentration, which can be used for semiquantitative rapid analysis.

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## **Supporting information**

Figures S1–S5 and Tables S1–S2 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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