STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Mechanism of the Self-Assembly of Donor—Acceptor Triads Based on Cobalt(II) Porphyrin Complex and Fullero[60]pyrrolidine, According to Data Obtained by Spectroscopic and Electrochemical Means

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Received June 28, 2019; revised June 28, 2019; accepted September 17, 2019

Abstract—Kinetics and equilibriums for reactions between cobalt(II) 5,10,15,20-(tetra-4-isopropylphenyl)21H,23H-porphyrin (CoTIPP) and 1-methyl-2-(4-(1H-imidazole-1'-yl)phenyl)- and 1-methyl-2-(pyridine-4'-yl)-3,4-fullero[60]pyrrolidines (ImC₆₀ and PyC₆₀, respectively) resulting in the formation of donor acceptor (ImC₆₀)₂CoTIPP/(PyC₆₀)₂CoTIPP supramolecular triads are studied. The chemical structure of the triads is identified by means of UV, visible, IR, ¹H NMR spectroscopy; their redox behavior is studied via cyclic voltammetry. It is shown that the formation of triads is accompanied by a shift in the redox potentials of the precursors, testifying to interactions between the π -systems of the donor and acceptor. It is concluded that the obtained results should be considered in further studies of donor—acceptor systems with predictable stability for photovoltaic cells.

Keywords: cobalt(II) porphyrin, fullero[60]pyrrolidines, supramolecular system, spectral properties, kinetics and thermodynamics of formation

DOI: 10.1134/S0036024420060060

INTRODUCTION

Metal—pyridine/imidazole complexation is often used to obtain supramolecular systems with specific properties [1]. This approach is employed in creating photoactive porphyrin—containing systems [2]. The axial coordination of ligands containing fullerene fragments by metal porphyrins allows us to obtain supramolecules capable of the photoinduced separation of opposite charges, a fundamental process needed for both natural photosynthesis and the conversion of solar energy [3]. Metal porphyrins act as donor platforms in such supramolecular systems [4]. Most studies are performed for porphyrin/phthalocyanine fullerene systems, where the electron donors are zinc porphyrins/phthalocyanines [5–10].

A promising approach for expanding the options in designing photoactive supramolecular systems is to use porphyrin/phthalocyanine complexes of other metals [11–16], including cobalt [17–20]. The authors of [11] have used ruthenium phthalocyanine as a donor platform for obtaining supramolecules with fullerenes. Using ruthenium(II) phthalocyanines instead of the corresponding zinc(II) complexes

allows us to suppress energy loss and undesirable charge recombination. Employing aluminum porphyrin allows us to obtain supramolecules, where additional electron donors and acceptors can be covalently bonded to the central aluminum atom. In a triad obtained in [12], tetraphenylethylamine (TPE), an additional electron donor, was bonded covalently, and the ImC₆₀ acceptor was bonded via coordination bonds. It was shown that this triad is capable of stagewise light-induced charge separation, first between TPE and aluminum(III) porphyrin (AlP) up to the formation of $(TPE)^{\bullet+}$ - $(AlP)^{\bullet-} \leftarrow ImC_{60}$, and then to the final state with charge separation, $(TPE)^{\bullet+}$ -AlP \leftarrow $Im(C_{60})^{\bullet-}$, with a lifetime of 25 ns. Interestingly, both states with charge separation are characterized by high energies: 2.14 and 1.78 eV, respectively. The authors therefore believed this triad was promising for the field

The authors of [13] have performed a spectroscopic study of the self-assembly of magnesium(II) 5,10,15,20-(tetraphenyl)-21H,23H-porphyrin (MgTPP) with ImC_{60} . The formation of the $(ImC_{60})MgTPP$

of artificial photosynthesis and photovoltaics.

diad with a fairly high stability constant of (1.5 ± 0.3) × 10⁴ L mol⁻¹ was detected, but the expected $(ImC_{60})_2MgTPP$ triad was not observed. The $(ImC_{60})MgTPP$ diad was capable of photoinduced charge separation; the rate of direct electron transfer was characterized by a constant of $k_{CS} = 1.1 \times 10^{10} \text{ s}^{-1}$ and charge recombination constant of $k_{CS} = 8.3 \times 10^7 \text{ s}^{-1}$.

To continue our studies of the formation and properties of supramolecular systems based on cobalt complexes, this work presents data on the formation of donor–acceptor complexes based on cobalt(II) 5,10,15,20-(tetra-4-isopropylphenyl)21H,23H-porphyrin (CoTIPP) and 1-methyl-4-(1H-imidazole-1'-yl)phenylfullero[60]pyrrolidine (ImC₆₀)/1-methyl-2-(pyridine-4'-yl)-3,4-fullero[60]pyrrolidine (PyC₆₀). The data on the stability of these systems and their electrooptical/electrochemical properties can allow us to obtain of structure–property dependences that are required for continuing research in developing systems with predictable stability for photoelectrochemical cells.

EXPERIMENTAL

5,10,15,20-(Tetra-4-isopropylphenyl)21H,23H-por**phin** (H_2TIPP) was synthesized according to [21]. Pyrrole (3.39 g, 32 mmol) and 4-isopropylbenzaldehyde (4.74 g, 32 mmol) were consistently added dropwise to 100 mL of refluxing propionic acid with constant stirring. After aldehyde was added, the reaction mixture was refluxed for 30 min with stirring. The solution was cooled to room temperature and placed into a freezer for 12 h. The precipitate was filtered and washed using methanol (3 times, 10 mL each) and hot water (3 times, 30 mL each). The resulting purple crystals were dried in air and then in vacuum. The yield was 20.25%. (Absorption spectra in CHCl₃ (λ_{max} , nm): 420, 450, 515, 555, 670. ¹H NMR spectrum (CDCl₃), δ, ppm: -2.75 s.br. (2H, NH), 1.55 m (24H, CH₃), 3.29-3.24 m (4H, CH), 7.61 d (8H_m, J = 7.6 Hz), $8.14 \text{ d} (8 \text{H}_{o}, J = 7.84 \text{ Hz}), 8.87 \text{ s} (8 \text{H}_{e})$. Mass spectrum (MALDI TOF), m/z (I_{rel} , %): 782 (95) [M]⁺).

(5,10,15,20-(Tetra-4-isopropylphenyl)21H,23Hporphinato)cobalt(II), (CoTIPP), was obtained in the reaction between the corresponding porphyrin (64 mg, 0.082 mmol) and Co(AcO)₂ · 4H₂O (105 mg, 0.42 mmol) in refluxing dimethylformamide (DMFA) for 40 min. At the end of the reaction, the reaction mixture was cooled, and the products were extracted with chloroform. The solution in CHCl₃ was repeatedly washed with distilled water to remove DMFA. The solvent was partially distilled, and the product was chromatographed on a column filled with Al₂O₃ (Brockmann activity II) using chloroform as an eluent. The main orange zone corresponding to CoTIPP was obtained. The yield was 82%. (Absorbance spectra in toluene (λ_{max} , nm (log ϵ)): 415 (5.21), 531 (3.97), 615 (2.93). IR spectrum (KBr) ν, cm⁻¹: 377, 447, 503, 572, 717, 753, 799, 813, 837, 853, 1002, 1032, 1055, 1074, 1097, 1140, 1165, 1185, 1206, 1245, 1272, 1298, 1351, 1382, 1406, 1459, 1505, 1547, 1608, 1687, 1726, 1804, 1910, 2869, 2927, 2959, 3022. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.79 s (24H, CH₃), 4.73 s (4H, CH), 9.82 s (8H_m), 13.21 br. s. (8H_o), 16.06 br. s. (8H_β). Mass spectrum (MALDI TOF), m/z (I_{rel} , %): 840.05 (100) [M]⁺).

1-Methyl-2-(pyridine-4'-yl)-3,4-fullero[60]pyrrolidine (PyC₆₀) was synthesized according to [22]. (Absorption spectra in toluene (λ_{max} , nm): 312, 328, 433. IR spectrum (KBr) v, cm⁻¹: 404, 431, 448, 479, 504, 527, 553, 574, 598, 635, 664, 707, 737, 767, 785, 824, 840, 910, 940, 989, 1034, 1067, 1083, 1109,1123, 1179, 1215, 1246, 1268, 1314, 1334, 1409, 1430, 1463, 1561, 1595, 1736, 2783, 2845, 2920, 2948. ¹H NMR (CDCl₃), δ , ppm: 2.83 s (3H), 4.96 s (1H), 4.31 d (1H, J = 9.77 Hz), 5.02 d (1H, J = 9.77 Hz), 7.82 m (2H), 8.71 d (2H, J = 5.49 Hz). Mass spectrum (MALDI TOF), m/z (I_{rel} , %): 853 (99) [M–H]⁺, 854 (76) [M]⁺).

1-Methyl-2-(4-(1H-imidazole-1'-yl)phenyl)fullero[60]-pyrrolidine (ImC₆₀) was synthesized according to [22]. C₆₀ (100 mg, 0.14 mmol), 4-(1H-imidazole-1-yl)benzaldehyde (120 mg, 0.70 mmol), and N-methylglycine (40 mg, 0.45 mmol) were mixed in 90 mL of toluene at the boiling point for 2 h; the solvent was then removed by vacuum distillation. The reaction mixture was chromatographed on Al₂O₃ column (Brockmann activity II) using toluene as an eluent for the first zone of unreacted C_{60} , methanol for unreacted aldehyde, and a toluene-ethyl acetate (4:1) mixture for the third zone containing ImC_{60} . The yield was 51%. (Absorption spectra in toluene (λ_{max} , nm): 312, 329, 434. IR spectrum (KBr) v, cm⁻¹: 376, 399, 430, 464, 476, 527, 544, 553, 562, 566, 575, 583, 599, 606, 617, 656, 694, 706, 727, 737, 746, 759, 767, 771, 789, 802, 833, 842, 863, 901, 908, 962, 1018, 1033, 1053, 1091, 1099, 1107, 1143, 1151, 1163, 1179, 1215, 1233, 1243, 1259, 1282, 1301, 1320, 1333, 1357, 1367, 1429, 1447, 1463, 1483, 1521, 1540, 1610, 2328, 2346, 2779, 2839, 2919, 2946, 3114. ¹H NMR (CDCl₃), δ, ppm: 2.82 s (3H), 4.29 d (1H, J = 4.28 Hz), 5.00 m (2H), 7.17 m (1H), 7.32 t (1H, J = 1.35 Hz), 7.48 d (1H, J =8.41 Hz), 7.90 m (2H).) Mass spectrum (MALDI TOF), m/z (I_{rel} , %): 920.75 (100) [M]⁺).

Toluene (EKOS) was dried over potassium hydroxide and distilled before use ($t_{\text{boil}} = 110.6^{\circ}$ C). The content of water determined via Karl Fischer titration did not exceed 0.01%.

Kinetics of the reversible reaction of CoTIPP with ImC_{60}/PyC_{60} in toluene were studied spectrophotometrically at 298 K in the 5.88×10^{-5} to 1.57×10^{-4} M (ImC_{60}) and 4.38×10^{-5} to 1.17×10^{-4} M (PyC_{60}) ranges of concentration using the excess concentration technique. The CoTIPP and ImC₆₀/PyC₆₀ solutions in freshly distilled toluene were prepared immediately before use to avoid the formation of peroxides in the solvent medium. Absorbance was measured for a series of solutions with a constant CoTIPP concentration $(6.28 \times 10^{-6} \text{ M})$ and a variable concentration of substituted fullerene at a working wavelength of 415 nm immediately after mixing the reagents. The UV–Vis spectrum of the reacting system was obtained using the spectrum of ImC₆₀/PyC₆₀ at the same concentration as in the working solution as the zero line. The solutions were thermostatted at 298 ± 0.1 K in closed quartz cuvettes inside a special spectrophotometer accessory. The reaction rate constants were calculated according to the equation

$$k_{\rm eff} = (1/\tau) \ln((A_0 - A_\infty)/(A_\tau - A_\infty)),$$

where A_0 , A_{τ} , A_{∞} are the values of the reaction mixture's absorbance at time points 0, τ , and the end of the reaction.

The equilibrium of the reaction between CoTIPP and ImC_{60}/PyC_{60} in toluene was studied at 298 K in the 1.46×10^{-6} to 1.31×10^{-4} M (PyC₆₀) and 1.37×10^{-6} to 1.57×10^{-4} M (ImC₆₀) ranges of concentration via time-dependent spectrophotometric titration using the molar ratio technique. Equilibrium constants *K* were determined according to the equation

$$K = \frac{(A_{\rm i} - A_0)/(A_{\infty} - A_0)}{1 - (A_{\rm i} - A_0)/(A_{\infty} - A_0)} \times \frac{1}{(C_{\rm L}^0 - C_{\rm CoTIPP}^0)(A_{\rm i} - A_0)/(A_{\infty} - A_0))},$$

where $C_{\rm L}^0$ and $C_{\rm CoTIPP}^0$ are the initial concentrations of L (PyC₆₀/ImC₆₀) and CoTIPP in toluene, respectively; A_0, A_i, A_∞ are the absorbance values of CoTIPP, the equilibrium mixture at the given concentration of L, and the reaction product. The relative error in estimating *K* did not exceed 25%. The reaction stoichiometry was determined as the slope of line log $I-f(\log C_{\rm L})$, where $I = (A_i - A_0)/(A_\infty - A_i)$.

UV–Vis, IR, NMR, and mass spectra were recorded using an Agilent 8453 spectrophotometer; VERTEX 80v and Bruker Avance III-500 spectrometers; and a Shimadzu Confidence mass spectrometer, respectively.

Electrochemical measurements were made at 298 K under anaerobic conditions in a three–electrode cell using a PI-50-Pro-3 pulse potentiostat with the PS Pack 2 software. Voltammetric curves were measured at the potential sweep rate of 100 mV/s. The working and auxiliary electrodes were a platinum electrode and platinum wire, respectively. The reference electrode was a saturated calomel electrode. The electrochemical properties of CoTIPP, PyC_{60}/ImC_{60} , and donor–acceptor triads based on them were studied with freshly prepared solutions in methylene chloride with addition of the background electrolyte (0.1 M (n-Bu)₄NClO₄) under an argon flow.

RESULTS AND DISCUSSION

Spectral analysis of the synthesized CoTIPP and fullero[60]pyrrolidines (ImC₆₀, PyC₆₀) reliably characterizes their chemical structures. The UV–Vis spectra of fullero[60]pyrrolidines manifest characteristic absorption in the range of 430 nm [22, 23]. The spectrum of CoTIPP, a complex of cobalt(II), contains a Soret band $(1a_{1g} \rightarrow 2e_u)$ at 415 nm and a *Q*-band $(1a_{1g} \rightarrow 1e_u)$ at 531 nm [24].

The reaction of CoTIPP with ImC₆₀ was studied via spectrophotometry. Two equilibria can be detected for processes that occur as a result of interaction between CoTIPP and ImC₆₀. The first is established instantaneously after the reagent solutions are poured together, and the second is observed over time at a measurable rate. Using an approach based on spectrophotometric time-dependent titration (the data on spectrophotometric titration are processed at $\tau = 0$ and ∞ after the slow reaction is over for all mixture compositions) allows us to describe quantitatively both equilibria and the rate of the second stage of the reaction. The scheme of the formation of supramolecular porphyrin-fullerene complexes of CoTIPP and ImC₆₀ is shown in Fig. 1.

The evolution of spectra as a result of interaction between CoTIPP and ImC_{60} at the first stage (at the zero timepoint) are shown in Fig. 2. At the first stage after equilibrium is established at all compositions of the reaction mixture, the subsequent slow interaction in the CoTIPP-ImC₆₀ system is accompanied by a gradual drop in the intensity of Soret band absorption at 415 nm and the appearance of a new band at 436 nm. The dynamics of the spectrum clearly confirms the formation of a hexacoordinated cobalt complex [25]. The second equilibrium in the cobalt(II) porphyrin-substituted fullerene system is established depending on the fullerene concentration on average for 10-15 minutes (Fig. 3). The stoichiometry of the forming donor-acceptor systems of CoTIPP with ImC_{60} at the first and second stages was determined from the linear $\log I - \log C_{ImC_{60}}$ dependences. The slope $(\tan \alpha)$ of these lines at the first and second stages is 1.02 and 1.27, respectively. The reaction equations, numerical values of equilibrium constants, and overall constant of stability (of formation) (β) of the $(ImC_{60})_2$ CoTIPP triad are presented in Table 1.

The first order with respect to $(ImC_{60})CoTIPP$, and therefore to CoTIPP (quasiequilibrium), is determined by studying the slow direct reaction of the second equilibrium stage (Eq. (2) in Table 1). The effective rate constants are given in Table 2. The log k_{2eff} log $C_{ImC_{60}}$ dependence has a slope (order of the reaction with respect to the ImC₆₀ concentration) close



Fig. 1. Formation of supramolecular porphyrin-fullerene complexes of CoTIPP with ImC₆₀.



Fig. 2. Evolution of UV–Vis spectra of CoTIPP in toluene at 298 K with a growing ImC_{60} additive (from 0 to 1.57×10^{-4} M) in toluene at $\tau = 0$. Inset: corresponding spectro-photometric titration curve, obtained at a working wavelength of 415 nm.

to 1 (tan α = 0.90, R^2 = 0.99). The numerical value of rate constant k_2 for reaction (2), found by optimizing the log $k_{2\text{eff}}$ -log $C_{1\text{mC}_{60}}$ dependence, is 40.55 mol⁻¹ L s⁻¹.

The reaction between CoTIPP and 1-methyl-2-(pyridine-4'-yl)-3,4-fullero[60]pyrrolidine (PyC₆₀) was studied to determine the effect the chemical structure of fullero[60]pyrrolidines on the stability of donor-acceptor complexes based on cobalt(II) porphyrin. The reaction between CoTIPP and PyC₆₀ was



Fig. 3. Evolution of UV–Vis spectra of CoTIPP in toluene at 298 K with a growing ImC_{60} additive (from 1.37×10^{-6} to 1.76×10^{-4} M) in toluene at $\tau = \infty$ (when the reactions were completed). Inset: corresponding spectrophotometric titration curve, obtained at a working wavelength of 415 nm.

studied in a manner similar to the one used above, in toluene ($C_{CoTIPP} = 5.31 \times 10^{-6}$ M with $C_{PyC_{60}}$ being varied from 0 to 1.31×10^{-4} M). This reaction is also a successive two-stage coordination of PyC₆₀ molecules with the cobalt atom within the porphyrin complex (tan α for the log I-log $C_{PyC_{60}}$ linear dependences at the first and second stages is 1.17 and 1.06, respectively) resulting in the formation of a supramolecular 1 : 2 complex of (PyC₆₀)₂CoTIPP. The reaction equa-

Reaction equation	K_n , L/mol (log K_n)	$\beta = K_1 K_2, \mathrm{L}^2 \mathrm{mol}^{-2} (\log\beta)$
$CoTIPP + ImC_{60} \xleftarrow{K_1} (ImC_{60})CoTIPP (1)$	$(3.29 \pm 0.49) \times 10^4 (4.52)$	$(2.05 \pm 0.35) \times 10^9 (9.31)$
$(ImC_{60})CoTIPP + ImC_{60} \xleftarrow{K_2} (ImC_{60})_2CoTIPP$ (2)	$(6.23 \pm 0.61) \times 10^4 (4.79)$	
$CoTIPP + PyC_{60} \xleftarrow{K_{1}} (PyC_{60})CoTIPP (3)$	$(1.59 \pm 0.45) \times 10^4 (4.20)$	$(3.21 \pm 0.95) \times 10^9 (9.51)$
$(PyC_{60})CoTIPP + PyC_{60} \xleftarrow{K_2} (PyC_{60})_2CoTIPP (4)$	$(2.02 \pm 0.38) \times 10^5 (5.31)$	
$CoTPP + PyC_{60} \xleftarrow{K_1} (PyC_{60})CoTPP$	$(5.43 \pm 1.21) \times 10^4 (4.73)$	$(4.69 \pm 1.23) \times 10^9 (9.67)$
$(PyC_{60})CoTPP + PyC_{60} \xleftarrow{K_2} (PyC_{60})_2CoTPP [27]$	$(8.69 \pm 1.39) \times 10^4 (4.94)$	
$CoTBPP + PyC_{60} \xleftarrow{K_1} (PyC_{60})CoTBPP$	$(1.04 \pm 0.11) \times 10^4 (4.02)$	$(1.34 \pm 0.12) \times 10^{10} (10.13)$
$(PyC_{60})CoTBPP + PyC_{60} \xleftarrow{K_2} (PyC_{60})_2CoTBPP [28]$	$(1.21 \pm 0.32) \times 10^{6} (5.91)$	
$CoP + PyC_{60} \xleftarrow{K_1} (PyC_{60})CoP$	$(1.79 \pm 0.33) \times 10^4 (4.25)$	$(1.04 \pm 0.12) \times 10^{10} (10.02)$
$(PyC_{60})CoP + PyC_{60} \xleftarrow{K_2} (PyC_{60})_2CoP [18]$	$(5.76 \pm 0.60) \times 10^5 (5.76)$	
$CoP + Py_3C_{60} \xleftarrow{K_1} (Py_3C_{60})CoP$	$(9.30 \pm 0.80) \times 10^3 (3.97)$	$(5.58 \pm 0.16) \times 10^8 (8.75)$
$(Py_{3}C_{60})CoP + Py_{3}C_{60} \xleftarrow{K_{2}} (Py_{3}C_{60})_{2}CoP [19]$	$(6.0 \pm 1.2) \times 10^4 (4.78)$	

Table 1. Equations of reactions between cobalt(II) porphyrin and fullero[60]pyrrolidines and the corresponding stability constants (β)

CoP = (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II); CoTBPP = 5,10,15,20-(tetra-4-tert-butylphenyl)-21H,23H-porphinato)cobalt(II); K_n is a stepwise equilibrium constant.

tions, numerical values of equilibrium constants, and overall constant of $(PyC_{60})_2$ CoTIPP stability are given in Table 1. The effective constants of the slow direct reaction of the second equilibrium stage (Eq. (4) in Table 1) are given in Table 2. The log k_{2eff} —log $C_{PyC_{60}}$ linear dependence is characterized by a tan α of 0.93 ($R^2 = 0.99$). The numerical value of rate constant k_2 for reaction (4) found using optimization of the log k_{2eff} —log $C_{PyC_{60}}$ dependence is 81.32 mol⁻¹ L s⁻¹.

The formation of supramolecular $(ImC_{60})_2CoTIPP/$ $(PyC_{60})_2$ CoTIPP triads is additionally confirmed by the data from IR and ¹H NMR spectroscopy and cyclic voltammetry. The IR spectrum of CoTIPP contains signals of the characteristic vibrations of macrocycle bonds, propyl substituents (in the range of 2950-2850, 1381 cm⁻¹), and a signal with the frequency of 446 cm⁻¹ characteristic of Co–N coordination bonds (Fig. 4a). When $(ImC_{60})_2CoTIPP/(PyC_{60})_2CoTIPP$ donor-acceptor triads form, new signals related to coordinated fullero[60]pyrrolidines appear, compared to the CoTIPP spectrum. To be specific, new signals appear in the IR spectrum of $(ImC_{60})_2CoTIPP$ at 2851, 2782, 1522, 1485, 1431, 1333, 1261, 1244, 1109, 1032, 963, 842, 771, 767, 747, 726, 657, 620, 599, 583, 553, 527, 487, 476 cm⁻¹ (Fig. 4c). The following signals correspond to vibrations of N-bonded PyC_{60} in the IR spectrum of $(PyC_{60})_2$ CoTIPP: 2786, 2329, 1429, 1335, 1282, 1268, 1232, 1163, 1060, 963, 909, 832, 767, 747, 737, 541, 486, 479, 451, 447 cm⁻¹. The frequencies of the vibration of propyl substituents of the macrocyclic ligand in the range of 2950– 2850 cm⁻¹ during the formation of donor–acceptor complexes fall by 1–3 cm⁻¹, compared to the initial CoTIPP. In the 440 to 460 cm⁻¹ range of the vibrations of cobalt–nitrogen bonds in the IR spectra of supramolecules, three signals are observed at frequencies of 443, 447, and 451 cm⁻¹ for the (PyC₆₀)₂CoTIPP triad. The broadening of the band at 447 cm⁻¹ is observed for (ImC₆₀)₂CoTIPP. All of these changes confirm the formation of donor–acceptor complexes.

The ¹H NMR spectrum of CoTIPP is typical of paramagnetic complexes [26]. The signals of β -protons and *ortho*-protons of phenyl substituents are broadened singlets at 16.02 and 13.21 ppm, respectively. The signal of *meta*-protons of the phenyl ring

Table 2. Effective rate constants $(k_{2\text{eff}})$ of the reaction between (ImC₆₀)CoTIPP and ImC₆₀/(PyC₆₀)CoTIPP with PyC₆₀ in toluene at 298 K

$\frac{C_{\rm ImC_{60}} \times 10^5}{\rm M},$	$\frac{(k_{2\rm eff} \pm \delta k_{2\rm eff})}{\times 10^3, \rm s^{-1}}$	$C_{\rm PyC_{60}} \times 10^5,$ M	$(k_{2\rm eff} \pm \delta k_{2\rm eff}) \times 10^3, {\rm s}^{-1}$
5.88	6.41 ± 0.45	4.38	6.46 ± 0.60
7.83	8.09 ± 0.43	5.83	8.17 ± 0.23
9.80	9.75 ± 0.23	7.29	10.90 ± 0.82
11.80	11.90 ± 1.04	8.75	12.80 ± 0.79
13.70	13.70 ± 0.87	10.02	14.0 ± 0.94
15.70	15.30 ± 1.04	11.70	15.90 ± 1.05



Fig. 4. IR spectra of (a) CoTIPP, (b) ImC_{60} , and (c) $(ImC_{60})_2CoTIPP$ in KBr.

appears as a singlet at 9.82 ppm. The great distance between these protons and the central paramagnetic cobalt atom $(3d^7)$ does not result in its broadening. The signals corresponding to the protons of propyl substituents H_{-CH} and H_{-CH₃} also are observed as singlets at 4.73 and 2.79 ppm, respectively. The formation of the donor–acceptor (ImC₆₀)₂CoTIPP triad is accompanied by an upfield shift in the signals of βand *o*-protons (Table 3), just as when the donor platform in a supramolecule with PyC₆₀ is CoTPP [27]. Such changes in the ¹H NMR spectrum of the triad can be explained by the change in the effect of the ring current of the porphyrin ring due to the formation of supramolecules with fullero[60]pyrrolidines.

As seen in Table 1, the stability of the obtained supramolecules depends on the substituents in both the macrocycle and the fullero[60]pyrrolidine. The most stable donor-acceptor triads are $(PyC_{60})_2CoTBPP$ [28] and $(PyC_{60})_2CoP$ [18]. The

Table 3. Chemical shifts of H_{β} and H_{o} of cobalt porphyrin complexes and supramolecular systems with fullero[60]pyrrolidines

Complex	8H _β , ppm	8H _o , ppm
CoTIPP	16.06	13.21
(ImC ₆₀) ₂ CoTIPP	13.55	11.36
(PyC ₆₀) ₂ CoTIPP	14.31	10.97
CoTPP [27]	15.94	13.16
(PyC ₆₀) ₂ CoTPP [27]	13.50	9.88
CoTBPP [28]	16.05	13.24
(PyC ₆₀) ₂ CoTBPP [28]	14.62	11.40

presence of electron-donating alkyl substituents in the porphyrin ligand apparently stabilizes the donoracceptor supramolecules. The constants of the stability of supramolecules based on CoTPP and CoTIPP can be assumed to be comparable, allowing for the experimental error.

The rate constants of the formation of CoTIPPbased supramolecular complexes are approximately comparable with those of the formation of donor– acceptor porphyrin–based systems of $(PyC_{60})_2CoTBPP$ [28], $(PyC_{60})_2CoP$ [18], $(Py_3C_{60})_2CoP$ [19] containing donor substituents at the macrocycle periphery and exceed by four and eight times the constant for the $(PyC_{60})_2CoTPP$ triad.

We can see that the reaction rate is most affected by the macrocycle substituents, and not by the chemical structure of fullero[60]pyrrolidines. Rate constants k_{-2} for processes (2) and (4) are 6.51 × 10⁻⁴ s⁻¹ (40.55 mol⁻¹ L s⁻¹/6.23 × 10⁴ L mol⁻¹) and 4.03 × 10⁻⁴ s⁻¹ (81.32 mol⁻¹ L s⁻¹/2.02 × 10⁵ L mol⁻¹). The ratio of rate constants of direct and reverse reactions (k_2 and k_{-2}) testifies to the acceptability of ignoring the reverse reaction in studying the kinetics of reversible processes at the second stage of reactions between CoTIPP and fullero[60]pyrrolidines (PyC₆₀, ImC₆₀).

(PyC₆₀)₂CoTIPP/(ImC₆₀)₂CoTIPP supramolecular systems and their components were studied via cyclic voltammetry. Fig. 5 shows cyclic voltammograms for PyC_{60} and ImC_{60} that have a similar shape and contain the three pairs of peaks characteristic of fullero[60]pyrrolidines [29, 30]. In the range of negative potentials, three fullerene reduction peaks (-0.66), -1.01, -1.60 V) and the corresponding oxidation peaks (-1.53, -1.02, -0.60 V) are observed for ImC₆₀, which agrees with the data in [12]. The CV of PyC_{60} was described in [27]. The CVs of donor-acceptor $(PyC_{60})_2CoTIPP/(ImC_{60})_2CoTIPP$ complexes are measured under the conditions of constant molar ratio corresponding to the equivalent point in the spectrophotometric titration experiment. The CVs of diads (Figs. 5c, 5d) in fact correspond to the sum of the peaks of CoTIPP and fullero[60]pyrrolidine. In the range of positive potentials, both diads have two peaks associated with the oxidation of their porphyrin part (0.85, 1.17 and 1.09, 1.32 V, respectively), while free CoTIPP is characterized by three oxidation peaks with potentials of 0.82, 0.95, 1.14 V. In the range of negative potentials, peaks are observed which correspond to processes occurring over the fullerene part of the diad. Analysis of the peak positions shows the formation of donor-acceptor complexes is accompanied by a shift in the redox potentials of both fullero[60]pyrrolidine and cobalt porphyrin, yet another confirmation of the formation of supramolecules and presence of interactions between the π -system of the donor and acceptor.



Fig. 5. Cyclic voltammograms of (a) $PyC_{60} (C_{PyC_{60}} = 4.03 \times 10^{-4} \text{ M})$; (b) $ImC_{60} (C_{ImC_{60}} = 5.2 \times 10^{-4} \text{ M})$; (c) $(PyC_{60})_2CoTIPP$; (d) $(ImC_{60})_2CoTIPP$ in methylene chloride with 0.1 M (*n*-Bu)_4NClO₄. The potential sweep rate is 100 mV/s.

CONCLUSIONS

Supramolecular $(ImC_{60})_2CoTIPP/(PyC_{60})_2Co-$ TIPP triads were obtained. The reactions of their formation were studied via chemical kinetics and thermodynamics. Spectral and electrochemical characteristics of these donor-acceptor complexes were described. The constants of $(PyC_{60})_2Co-$ TIPP/(ImC₆₀)₂CoTIPP stability were $(3.21 \pm 0.95) \times$ 10^9 and (2.05 ± 0.35) × 10^9 L² mol⁻², respectively. Correlation between the constants of the stability of cobalt porphyrin-based donor-acceptor systems (Table 1) and their chemical structure was considered. It was found that the rate of the process of supramolecule formation is most affected by the macrocycle substituents. The obtained data are required for further research of supramolecular systems with predictable stability for photovoltaic cells.

ACKNOWLEDGMENTS

This work was performed on equipment of the shared resource center of the Upper Volga Regional Center for Physicochemical Research, as part of the State Academies of Sciences program for studying the kinetics of the self-assembly of supramolecular triads, topic no. 0092-2014-0002. It was supported by the Russian Foundation for Basic Research and the Government of Ivanovo oblast, project nos. 18-43-370022 and 18-43-370023, ("Synthesis of the

CoTIPP paramagnetic complex" and "Synthesis and spectral and electrochemical characterization of triads.")

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Translated by M. Ehrenburg