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# 1. Introduction

Supramolecular architectures based on carbon nanoforms  $(C_{60}, C_{70} \text{ derivatives})$  and porphyrins are of considerable interest. The combination of the specific properties of porphyrins and fullerenes in these systems often leads to a synergy effect, which makes these compounds unique and promising for use in various fields of science, technology, medicine, and biotechnology. Advances in the synthesis of fullerenes and tetrapyrrole macroheterocycles make it possible to obtain a number of supramolecular systems with a set of practically important properties.

There has been increasing interest in the synthesis of carbazole-functionalized porphyrins/phthalocyanines in recent decades.<sup>1–7</sup> The carbazole derivatives are a well-known class of aromatic heterocyclic compounds with high UV-vis absorption, efficient fluorescent emission and high photostability.<sup>8</sup> Due to



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Two supramolecular cobalt(II) porphyrin–fullerene systems,  $(PyC_{60})_2CoDTBCP/(Py_2C_{70})CoDTBCP$ , self-assembled *via* axial coordination of 1-*N*-methyl-2-(pyridin-4-yl)-3,4-fullero[60]pyrrolidine and 2,5-di-(pyridin-2-yl)-3,4-fullero[70]pyrrolidine by (5,15-bis[3,5-bis(*tert*-butyl)phenyl]-10,20-bis[4,6-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)pyrimidin-5-yl]porphinato)cobalt(II), respectively, were prepared and characterized for the first time. Target carbazole-functionalized cobalt(II) porphyrin was synthesized by direct metallation of the corresponding porphyrin that was in its turn obtained by tetra-substitution of 5,15-bis[4,6-dichloropyrimidin-5-yl]porphyrin with 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenol. All compounds synthesized were fully characterized by mass spectrometry and UV-vis, IR, and <sup>1</sup>H NMR spectroscopy. Chemical structure and spectral properties of the triad/dyad were additionally described using chemical thermodynamics, kinetics, and DFT calculations. The analysis of the geometric and electronic structures of the (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP FMOs in the ground state and the study of their femtosecond transient absorption spectra points to the existence of photoinduced electron transfer in the triad and dyad. The data obtained are required for further photoelectrochemical study of the triad/dyad and determining their potential in the building of photovoltaic devices.

their electron-donor properties and the ability to form charge transfer complexes they are used extensively in organic photovoltaics<sup>9</sup> and as a building block for optoelectronic materials.<sup>10</sup> Carbazole derivatives have been widely used in medicine too as active components in antitumor, antimicrobial, antihistaminic, antioxidative, anti-inflammatory, and psychotropic drugs.<sup>11–14</sup> For example, a variety of carbazole substituted compounds are a potential drug candidate for the treatment of chronic diseases,<sup>15,16</sup> Alzheimer's disease<sup>17</sup> and acute myeloid leukemia.<sup>18</sup>

Kimura and co-workers have synthesized carbazole-fused zinc phthalocyanine, studied the influence of the carbazole groups on the optical and electrochemical properties of phthalocyanines, and reported their performance in dye-sensitized solar cells (DSSCs) which show wide light-harvesting properties in the 400–800 nm range.<sup>19</sup> In the paper,<sup>20</sup> the series of zinc porphyrin based sensitizers containing carbazole groups in the *meso*-substituted porphyrin core were synthesized to investigate their performance in DSSCs. Theoretical calculations have revealed that the carbazole unit does not significantly affect the electronic properties of the dyes but crucially it helps in the suppression of the aggregation of the dyes on the TiO<sub>2</sub> surface, which leads to the higher conversion efficiency of the device.<sup>20</sup> Xu and co-workers have synthesized three dendritic



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#### Paper

carbazole-based porphyrins with intramolecular energy transfer properties and showed that these macromolecules could emit intense red light with high fluorescence quantum yields and so might be good candidates for photonic devices.<sup>21</sup> Carbazolefunctionalized iron porphyrin has been explored for its suitability as a catalyst for CO<sub>2</sub> electroreduction by immobilizing it inside the microporous CO<sub>2</sub>-absorbing material.<sup>22</sup>

There has only been one report on the synthesis of supramolecular fullerene systems based on carbazole-containing phthalocyanine complexes, where D'Souza and co-workers reported tetracarbazole-substituted zinc phthalocyanine axially coordinated to a phenylimidazole-functionalized fulleropyrrolidine.<sup>23</sup> It was established that the stability constant of this donoracceptor complex was an order of magnitude higher than that observed earlier for similar complexes due to the electronic effect induced by the carbazole entities. Also, this system exhibited photoinduced energy transfer from the carbazole to zinc phthalocyanine with a reasonable light-to-energy conversion efficiency in devices.<sup>23</sup> Cobalt(II) porphyrins (CoPs) can be considered as a good donor platform primarily because they are thermally/chemically/electro/photo stable and soluble in organic solvents. They show a strong absorbance in the visible region, rich redox chemistry, and the ability to form thermodynamically stable donor-acceptor complexes with organic Nbases due to the large coordination capacity of the central ion.<sup>24-28</sup> Self-assembly in the cobalt(II) porphyrin/phthalocyanine-pyridyl-substituted fulleropyrrolidine systems, leading to the formation of systems with photoinduced electron transfer (PET), has been established in earlier publications.<sup>27–30</sup>

Despite the fact that the results of femtosecond studies show shorter lifetimes (12  $\pm$  4 ps) for excited states of cobalt(II) porphyrins<sup>31,32</sup> compared with zinc porphyrins, CoPs are used as donor building blocks for charge transfer systems. Chargetransfer C<sub>70</sub>/C<sub>60</sub>-cobalt porphyrin cocrystals prepared by a solution-processable co-assembly strategy have been characterized by a collection of experimental and theoretical methods.<sup>33,34</sup> These supramolecular architectures, characterized by strong intermolecular interactions between the C<sub>60</sub>/C<sub>70</sub> and cobalt porphyrin, display a significantly high electrical conductivity and high hole mobility as well as an extraordinarily high thermal stability. As shown in ref. 35 and 36 using time-resolved spectroscopic measurements and theoretical calculations, the origin of the enhanced electrocatalytic activity of the graphene oxide (GO)-cobalt porphyrin hybrid complexes (Co<sup>II</sup>APFP) is provided by the formation of an generated chargeseparated state, GO<sup>-</sup>-(Co<sup>II</sup>APFP)<sup>+</sup>, undergoing fast charge recombination (<10 ps) between the  $GO^-$  and  $(CoAPFP)^+$ moieties, which is directly related to the quick neutralization of  $(Co^{\pi}APFP)^{+}$  and the reduction in the dead time of inactive Co<sup>m</sup>APFP after the electrocatalytic reduction reaction. Guldi et al.<sup>37</sup> have integrated single-wall carbon nanotubes (SWNTs), several water soluble pyrenes, and a number of water-soluble porphyrins including CoP into functional nanohybrids through the combination of associative van der Waals and electrostatic interactions. The photoexcitation of these nanohybrid systems with visible light leads to rapid intrahybrid charge separation



Fig. 1 Chemical structure of the compounds studied.

causing the reduction of the electron-accepting SWNT and, simultaneously, the oxidation of the electron-donating porphyrin. Transient absorption measurements confirm the formation of radical ion pairs displaying lifetimes in the microsecond range.<sup>37</sup>

Taking into account the interesting photophysical properties of both carbazole entities and porphyrins, we have synthesized for the first time a cobalt( $\pi$ ) porphyrin containing 3,5-di-*tert*butylphenyl and 4,6-di-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl) phenoxy)pyrimidyl *meso*-substituents, CoDTBCP, and its coordination complexes with pyridyl-substituted fullero[60]/[70] pyrrolidines, (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP/(Py<sub>2</sub>C<sub>70</sub>)CoDTBCP, for which we expect an improvement of the applied properties (Fig. 1). We also report here the peculiarities of the self-assembly of the donor-acceptor systems above and their geometric/electronic structures obtained by the methods of thermodynamics/ kinetics, UV-vis, NMR, IR, mass spectrometry and DFT calculations, respectively.

### 2. Experimental section

#### Synthesis

**3,6-Di-***tert***-butyl-9***H***-carbazole (1).** Carbazole (5.0 g, 0.03 mol) and anhydrous  $AlCl_3$  (4.0 g, 0.03 mol) were dissolved in  $CH_2Cl_2$  (100 mL). When the mixture was cooled to 0 °C, the solution of

*tert*-BuCl (6.6 mL, 0.06 mol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added slowly. After that, the ice-bath was removed and the resulting mixture was stirred for 24 h at room temperature. Then, the mixture was poured into water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to afford the crude products, which were twice recrystallized from hexane giving 4.5 g (54%) of a white solid, mp: 233.0–235.0 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  = 8.07 (2 H, s, Ar-H), 7.84 (1 H, s, NH), 7.46 (2 H, d, Ar-H), 7.32 (2 H, d, Ar-H), 1.45 (18 H, s, –CH<sub>3</sub>). MALDI-TOF-MS, *m/z*: calc. 279.2, found: 280.0 [M + H]<sup>+</sup>.

3,6-Di-tert-butyl-9-(4-methoxyphenyl)-9H-carbazole (2). 3,6-Di-tert-butyl-9H-carbazole (2.8 g, 0.01 mol), 1-iodo-4methoxybenzene (2.5 g, 0.011 mol), Cu<sub>2</sub>O (3.0 g, 0.021 mol), and dimethylacetamide (15 mL) were mixed in a flask under an argon atmosphere and heated to 160 °C in an oil bath for 24 h. Then, the mixture was cooled to the room temperature and filtered. The filtrate was poured into 200 mL CH<sub>2</sub>Cl<sub>2</sub> and washed 5 times with water. The organic layer was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The product was purified by chromatography (silica gel, hexane) giving 3.2 g (83%) of a white solid, mp: 162.0–164.0 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm):  $\delta = 8.14$  (2 H, s, Ar-H), 7.45–7.42 (4 H, m, Ar-H), 7.24 (2 H, d, Ar-H), 7.08 (2 H, d, Ar-H), 3.91 (3 H, s, –OMe), 1.46 (18 H, s, –CH<sub>3</sub>). MALDI-TOF-MS, *m/z*: calc. 385.5, found: 386.3 [M + H]<sup>+</sup>.

4-(3,6-Di-tert-butyl-9H-carbazol-9-yl)phenol (3). A solution of boron tribromide (BBr<sub>3</sub>) (0.86 mL, 8.9 mmol) in 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise into a solution of 3,6-di-tert-butyl-9-(4-methoxyphenyl)-9H-carbazole (2.3 g, 6.0 mmol) in 40 mL of dry CH<sub>2</sub>Cl<sub>2</sub> at room temperature. After being stirred at room temperature for 24 h, the mixture was slowly poured into H<sub>2</sub>O (200 mL) and stirred for 1 h. The organic phase was separated and the compound from the water phase was extracted in CH<sub>2</sub>Cl<sub>2</sub> until the phase became colorless. Both CH<sub>2</sub>Cl<sub>2</sub> solutions were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was chromatographed on silica gel with hexane/  $CH_2Cl_2$  (1:3) as the eluent affording 2.0 g (90%) of a white solid, mp: 198.0–200.0 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  = 8.13 (2 H, s, Ar-H), 7.45 (2 H, d, Ar-H), 7.43 (2 H, d, Ar-H), 7.24 (2 H, d, Ar-H), 7.03 (2 H, d, Ar-H), 1.46 (18 H, s, -CH<sub>3</sub>). MALDI-TOF-MS, *m*/*z*: calc. 371.5, found: 372.1 [M + H]<sup>+</sup>.

5,15-Bis[3,5-bis(tert-butyl)phenyl]-10,20-bis[4,6-dichloropyrimidin-5-yl] porphyrin (4). A solution of 3,5-bis(tert-butyl)phenyldipyrromethane (0.5 g, 1.89 mmol) and 4,6-dichloropyrimidine-5-carbaldehyde (0.34 g, 1.89 mmol) in dichloromethane (500 mL) was deoxygenated by purging with argon for 15 min. Boron trifluoride etherate (0.02 g, 0.19 mmol) was added *via* syringe, and the solution was stirred under argon and protected from light for 1 h at room temperature. *p*-Chloranil (0.454 g, 1.89 mmol) was added, and the mixture was refluxed for 1 h. The solvent was removed and the residue was purified by chromatography (silica gel, dichloromethane) yielding porphyrin as a purple solid (0.445 g, 53%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\varepsilon$ ) 420 (5.82), 516 (4.47), 549 (3.79), 592 (3.83), 649 (3.60). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta = 9.05$  (8 H, s, H<sub>6</sub>), 8.76 (2 H, d, *J* = 4.8 Hz,

Ar-H), 8.59 (2 H, d, J = 4.8 Hz, Ar-H), 7.29 (4 H, s, Ar-H), 1.51 (36 H, s, -CH<sub>3</sub>), -2.50 (2 H, s, NH). MALDI-TOF-MS, m/z: calc. 982.94, found: 983.05 [M + H]<sup>+</sup>. This compound was prepared under the same conditions as the literature procedure.<sup>38</sup>

5,15-Bis[3,5-bis(tert-butyl)phenyl]-10,20-bis[4,6-(4-(3,6-di-tert*butyl-9H-carbazol-9-yl)phenyl)pyrimidin-5-yl]porphyrin* (5). solution of 4 (17.15 mg, 0.0175 mmol) and 3 (39.05 mg, 0.24 mmol) in 10 mL dry DMF was prepared, and K<sub>2</sub>CO<sub>3</sub> (117 mg, 0.83 mmol) was added. The mixture was stirred for 48 hours at 60 °C. Then it was cooled and poured into 50 mL dichloromethane. The organic layer was washed with distilled water and dried over MgSO<sub>4</sub>. The drying agent was filtered off, and the filtrate was evaporated. Column chromatography (silica/DCM: EtAO 10:1), (silica/DCM: heptane 4:1), ( $Al_2O_3$ / DCM:EtAO 10:1) was performed. The yield was 71.3%, 42 mg. UV-vis (toluene)  $\lambda_{\text{max}}$  nm (log  $\varepsilon$ ): 423 (5.78), 517 (4.77), 551 (4.41), 594 (4.23), 650 (4.04). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 8.90 (4 H, s, H<sub>b</sub>), 8.89 (4 H, s, H<sub>b</sub>), 8.10 (2 H, s, Ar-H), 7.80-7.98 (24 H, m, Carb-H), 7.07-7.35 (22 H, m, Ar-H), 1.99 (36 H, s, -CH<sub>3</sub>), 1.46 (36 H, s, -CH<sub>3</sub>), 1.28 (36 H, s, -CH<sub>3</sub>), -2.54 (2 H, s, NH). MALDI-TOF-MS, m/z: calc. 2323.20, found: 2324.05 [M + H]<sup>+</sup>.

(5,15-Bis[3,5-bis(tert-butyl)phenyl]-10,20-bis[4,6-(4-(3,6-di-tertbutyl-9H-carbazol-9-yl)phenyl)pyrimidin-5-yl]porphinato)cobalt(11) CoDTBCP. The reaction of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (42 mg, 0.1686 mmol) with 5 (40.0 mg, 0.0172 mmol) was carried out in dimethylformamide (10 mL) with heating for 10 min. Reaction completion was monitored by TLC until no traces of the starting material were detected. The reaction mixture was cooled and diluted with water. Products were extracted into chloroform and purified by flash chromatography (Al<sub>2</sub>O<sub>3</sub>/CHCl<sub>3</sub>). The yield was 30.8 mg (77%). UV-vis (toluene)  $\lambda_{max}$  nm (log  $\varepsilon$ ): 419 (5.32), 532 (4.11). IR [(KBr),  $\nu_{\text{max}}/\text{cm}^{-1}$ ]: 3049  $\nu$ (C-H); 2963, 2854  $\nu$ (C-H) of tert-butyl groups; 1732; 1593 v(C=N); 1556, 1506, 1479, 1459, 1419, 1364, 1330  $\nu$ (C=C); 1295  $\nu$ as(=C-O-C-); 1260, 1201  $\nu$ (C-N); 1091; 1020  $\nu$ s(=C-O-C-); 930, 862, 798, 746, 728, 704, 661, 635, 611, 567, 513; 472 v(Co-N); 400. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 16.29 (4 H, br s, H<sub>β</sub>), 15.05 (4 H, br s, H<sub>β</sub>), 12.11 (4 H, br s, Ar-H), 10.86 (2 H, s, Ar-H), 9.41 (2 H, s, Ar-H), 7.76 (12 H, m, Carb-H), 7.55-7.17 (8 H, m, Ar-H), 6.88 (12 H, m, Carb-H), 6.39 (5 H, m, Ar-H), 5.97 (3 H, m, Ar-H), 2.47 (36 H, s, -CH<sub>3</sub>), 1.59-1.42 (36 H, m, -CH<sub>3</sub>), 1.16 (36 H, s, -CH<sub>3</sub>). MALDI-TOF-MS, *m/z*: calc. 2378.1, found: 2378.57 [M]<sup>+</sup>.

#### Materials

All chemicals, solvents and chromatographic materials were obtained from Sigma-Aldrich and Acros Organics and were used as received. The purity of  $C_{60}$  and  $C_{70}$  was quoted as 99.9% and 98.6% by weight, respectively. Details of the PyC<sub>60</sub> and Py<sub>2</sub>C<sub>70</sub> synthesis together with the MALDI-TOF mass spectra (Fig. S1 and S2, ESI†) are given in the ESI.† They were prepared according to a general procedure of fulleropyrrolidine synthesis developed by Prato<sup>39</sup> and Troshin (with coworkers).<sup>40</sup>

We changed the procedure (the ratio of reagents, the reaction time, and the purification method) somewhat, which led to an increase in the yield of the product.

#### Methods

Kinetics. The kinetics of the slow CoDTBCP reaction with PyC<sub>60</sub>/Py<sub>2</sub>C<sub>70</sub> in toluene at 298 K were studied spectrophotometrically using the method of superfluous concentrations. The UV-vis spectra were recorded with an Agilent 8454 UV-visible spectrophotometer. The upper concentration limit of fullerene was determined by its solubility in toluene. Absorbance measurements were carried out for the solution series at a constant concentration of CoDTBCP (3.86  $\times$  10<sup>-6</sup> M) appropriate for observing the porphyrin Soret band with different additions of PyC<sub>60</sub>/Py<sub>2</sub>C<sub>70</sub>. The PyC<sub>60</sub>/Py<sub>2</sub>C<sub>70</sub> spectra with concentrations the same as in the stock solution were used as a zero line. The first order rate constant values,  $k_{obs}$ , were calculated using the equation  $k_{obs} = 1/\tau \cdot \ln((A_0 - A_\infty)/(A_\tau - A_\infty)))$ , where  $A_0, A_\tau$ , and  $A_{\infty}$  are the absorbance values at a working wavelength for CoDTBCP, a reaction mixture at  $\tau$  time and a reaction product. The relative error in  $k_{obs}$  determination did not exceed 10%.

**Thermodynamics.** The equilibrium constant values for the reaction between CoDTBCP and  $PyC_{60}/Py_2C_{70}$  in toluene were calculated using the equation for a three-component equilibrium system with two colored components:

$$K = \frac{(A_{i} - A_{0})/(A_{\infty} - A_{0})}{1 - (A_{i} - A_{0})/(A_{\infty} - A_{0})} \cdot \frac{1}{(C_{\text{Fullerene}}^{0} - C_{\text{CoDTBCP}}^{0} \cdot (A_{i} - A_{0})/(A_{\infty} - A_{0}))}$$

here,  $C_{\text{Fullerene}}^{0}$  and  $C_{\text{CoDTBCP}}^{0}$  are initial concentrations of PyC<sub>60</sub>/ Py<sub>2</sub>C<sub>70</sub> and CoDTBCP in toluene, respectively; and  $A_0$ ,  $A_i$ , and  $A_{\infty}$  are absorbance values at a working wavelength of an initial complex, an equilibrium mixture at a definite fullerene concentration, and a reaction product. The relative error in *K* determination did not exceed 30%.

NMR, IR and mass spectroscopy. <sup>1</sup>H NMR spectra were recorded with a Bruker Avance III-500 NMR spectrometer using deuterochloroform (CDCl<sub>3</sub>) as a solvent. IR spectra were recorded with a VERTEX 80v spectrometer in KBr. In order to record the IR spectra of donor–acceptor complexes, we prepared the solid residue of dyad/triad by removing the solvent in vacuum. Mass spectra were obtained using a Shimadzu Confidence spectrometer. Samples were put on the target in 2,5-dihydroxybenzoic acid (DHB) matrices.

*DFT calculations.* DFT calculations for CoDTBCP and PyC<sub>60</sub>/ Py<sub>2</sub>C<sub>70</sub> were performed using the PC GAMESS v.12 program package.<sup>41</sup> The electronic structures of CoDTBCP and PyC<sub>60</sub>/ Py<sub>2</sub>C<sub>70</sub> were studied using Density Functional Theory with the B3LYP functional and the def2-SVP basis set.<sup>42</sup> The influence of intramolecular dispersion interactions on the molecular structure was explored using the dispersion corrections introduced by Grimme *et al.* (D3).<sup>43</sup> Geometric optimization of the porphyrin–fullerenes was carried out without limitation in symmetry. Harmonic vibration frequencies were calculated at the same theory level in order to characterize the stationary points as true minima, representing equilibrium structures on potential energy surfaces. The spin multiplicity for the Co atom in  $(PyC_{60})_2CoDTBCP$  and  $(Py_2C_{70})CoDTBCP$  is a doublet and singlet, respectively. The Unrestricted Hartree–Fock (UHF) calculation was used in the case of  $(PyC_{60})_2CoDTBCP$ . The UCSF Chimera<sup>44</sup> and ChemCraft 1.8<sup>45</sup> were used to analyze results and molecular graphics.

*Femtosecond laser photolysis setup.* The output of a Ti:Sapphire oscillator (800 nm, 80 MHz, 30 fs, "Tsunami", Spectra-Physics, USA) was amplified using a regenerative amplifier ("Spitfire Pro", Spectra-Physics, USA). The repetition rate of the amplified laser pulses was set at 100 Hz. This frequency is small enough to eliminate permanent bleaching of the sample and at the same time corresponds to the maximum performance of the registration system.

The amplified pulses (800 nm, 100 Hz, 1.5 mJ, 40 fs) were split into two beams. One of the beams was attenuated to  $1-2 \mu J$  and focused into a nonlinear optical crystal ( $\alpha$ -BBO) to produce the second harmonic radiation which was used as a pump pulse. The pump pulse had a Gaussian pulse shape centered at a wavelength of 400 nm, 50 fs duration, and 100 nJ pulse energy. This energy is optimal for obtaining a signal of sufficient amplitude, and at the same time is small enough to exclude nonlinear processes in the sample.

The second beam was attenuated to 0.8 mJ and directed to a non-collinear optical parametric amplifier ("Topas-white", Light Conversion, Lithuania) whose radiation (900 nm, 3 5 fs, 10  $\mu$ J) was attenuated to 1  $\mu$ J and focused into a thin quartz cell with pure H<sub>2</sub>O to produce a supercontinuum probe pulse. The supercontinuum probe pulse was attenuated and spectrally filtered from excess radiation at a wavelength of 900 nm and had a smooth spectrum in the wavelength range of 380–850 nm and negligible energy (~1 nJ) to exclude its influence on the observed signal.

The pump and probe pulses were delayed relative to each other by a computer-controlled delay line in the range of 0–500 ps, with a resolution from 3.3 fs to 1 ps. The pulses were then attenuated, recombined, and focused onto the flow sample cell. The pump and probe light spots had diameters of 300 and 120  $\mu$ m, respectively. The relative polarizations of the pump and probe beams were adjusted to 54.7° (the magic angle).

The experiments were carried out at 278 K. The circulation rate in the flow cell was fast enough to avoid multiple excitations in the sample volume and was 8 mL min<sup>-1</sup>. Pure dry argon was fed into the flow system to avoid contact of the sample solution with air.

The supercontinuum probe signal out of the sample was dispersed using a polychromator ("Acton SP-300", Roper Scientific, USA) and detected using a CCD camera ("Newton", Andor, USA). Transient absorption spectral changes  $\Delta A(t, \lambda)$  were recorded within the range of 380–850 nm. The measured spectra were corrected for group delay dispersion of the supercontinuum using the procedure described previously.<sup>46,47</sup> The zero time delay between pump and probe pulses was determined in control experiments by recording the signal of a non-resonant coherent burst from pure de-aerated toluene.

Particular attention was paid to the "coherence spike" or "coherent artifact", which is observed at initial delays during the overlap of pump and probe pulses and complicates the analysis of the measurement results at delays of <70 fs. The problem of the resonance signal of a chromophore molecule in solution for the "coherent spike" time window was analyzed in accordance with ref. 48.

# 3. Results and discussion

#### Synthesis and characterization of CoDTBCP

Fig. 2 shows the synthetic route for the target cobalt( $\pi$ ) porphyrin bearing peripherally 3,5-di-*tert*-butylphenyl and bulky 4,6-di-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenoxy)pyrimidyl substituents (CoDTBCP). The presence of the *tert*-butyl groups in CoDTBCP facilitates its high solubility in most organic solvents. The free base porphyrin 5 (Fig. 2) used as the starting

material for CoDTBCP was prepared by tetra-substitution of 4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenol (3) with 5,15-bis[4,6dichloropyrimidin-5-yl]porphyrin (4). Compound 3 was in turn synthesized by the treatment of 3,6-di-tert-butyl-9H-carbazole (1) with 1-iodo-4-methoxybenzene, and Cu<sub>2</sub>O in dimethylacetamide to obtain 3,6-di-tert-butyl-9-(4-methoxyphenyl)-9Hcarbazole (2), the further treatment of which by boron tribromide in CH<sub>2</sub>Cl<sub>2</sub> at room temperature leads to the formation of 3. Compound 4 was obtained by reaction of 3,5-bis(tertbutyl)phenyldipyrromethane with 4,6-dichloropyrimidine-5carbaldehyde in CH<sub>2</sub>Cl<sub>2</sub> under an argon atmosphere for 15 min with the further addition of boron trifluoride etherate and *p*-chloranil. Identification of the chemical structure of the compounds synthesized was achieved using standard spectral techniques: UV-vis, IR, <sup>1</sup>H NMR spectroscopy and MALDI-TOF mass spectrometry (Experimental section). Spectral analysis is consistent with their proposed structures.

The UV-vis absorption spectra of the free base, **5** and CoDTBCP were recorded in toluene at the room temperature. The corresponding  $\lambda_{\text{max}}$  values reported in Table S1 (ESI<sup>†</sup>) were

(*i*) 1-Iodo-4-methoxybenzene, Cu<sub>2</sub>O, DMAC, 160°C, 24 h, argon atmosphere
(*ii*) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temperature for 24 h, and then stirred with H<sub>2</sub>O for 1h
(*iii*) CH<sub>2</sub>Cl<sub>2</sub>, argon atmosphere for 15 min, then was added boron trifluoride etherate and *p*-Chloranil
(*iiii*) K<sub>2</sub>CO<sub>3</sub>, DMF, 60°C, 48 h
(*iiiii*) Co(AcO)<sub>2</sub>·4H<sub>2</sub>O, DMF, 153°C, 10 min

Fig. 2 Scheme of the CoDTBCP synthesis.

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compared with other *meso*-substituted porphyrins and their complexes with cobalt. The free-base porphyrin, 5 exhibits a well-defined strong Soret band at 423 nm and four weaker *Q*-bands between 517 and 649 nm, which is consistent with the literature data.<sup>24,49,50</sup> The CoDTBCP spectrum, with the Soret and *Q* bands at 419 nm and 532 nm, respectively, is slightly hypsochromically shifted compared with the free base. The four *Q* bands of free porphyrin turn into a single band in agreement with the insertion of cobalt in the porphyrin core. The UV-vis CoDTBCP spectrum, being similar to those for porphyrin complexes of cobalt(n) (Table S1, ESI†), describes the substance under consideration as tetra-coordinated cobalt(n) porphyrin. The CoDTBCP solid and toluene solution is stable at room temperature for a long time.

The CoDTBCP chemical structure was confirmed by IR and <sup>1</sup>H NMR spectroscopy data. The disappearance of N-H proton signals (-2.54 ppm) of 5 in the <sup>1</sup>H NMR spectrum of CoDTBCP shows that the metalloporphyrin was successfully synthesized (Experimental section). The CoDTBCP IR spectrum obtained from KBr pellets contains the characteristic vibrations signals of the porphyrin macrocycle and the carbazole moieties. The absorption bands in the range of 2854-2963 and 1364 cm<sup>-1</sup> correspond to the stretching and deformation C-H vibrations in the *tert*-butyl groups. The  $\nu$ (C–H) frequency at 3049 cm<sup>-1</sup> suggests the presence of the aromatic benzene rings in CoDTBCP. The intense bands at 1593 and 1260, and 1201 cm<sup>-1</sup> are assigned to the  $\nu$ (C=N) and  $\nu$ (C-N) vibrations, respectively. The characteristic vibrations of  $\nu_{as}$  (=C-O-C-) and  $\nu_s$  (=C-O-C-) were observed at 1295 cm<sup>-1</sup> and 1020 cm<sup>-1</sup>, respectively. The frequencies of the aromatic  $\nu$ (C=C) are in the range from 1459 to 1556 cm<sup>-1</sup>. The peaks of the cobalt( $\pi$ ) porphyrin in the region of 513–930 cm<sup>-1</sup> are caused by vibrations of the macrocycle skeleton. The weak signal at  $472 \text{ cm}^{-1}$  is observed in the range of stretching vibrations of Co-N bonds.<sup>51</sup> This signal is absent in the IR spectrum of free base, 5.

The paramagnetic character of CoDTBCP was determined by <sup>1</sup>H NMR spectroscopy. The chemical shifts in the <sup>1</sup>H NMR spectra of the cobalt(n) complexes with different substituted porphyrins are summarized in Table S2 (ESI†). CoDTBCP having the Co<sup>II</sup> ground state configuration 3d<sup>7</sup> exhibits the signals

of the β-protons as two broad singlets at 16.29 and 15.05 ppm (Experimental section). The signals of the phenyl *ortho*-protons in the 3,5-di-*tert*-butylphenyl substituents appear as a broad singlet at 12.11 ppm. Phenyl and carbazole fragment protons in the 4,6-di-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenoxy)pyrimidyl groups resonate in the 8.18–5.94 ppm range. The signals in the 2.47–1.16 ppm range correspond to the *tert*-butyl group protons. Thus, the <sup>1</sup>H NMR spectrum clearly demonstrates the paramagnetic nature of the sample indicating the Co( $\pi$ ) complex.

#### Self-assembly of the porphyrin-fullerene systems

The self-assembly of the donor–acceptor complexes based on CoDTBCP and  $PyC_{60}/Py_2C_{70}$  was studied by means of spectral methods and chemical thermodynamics/kinetics. The spectral analysis of the CoDTBCP reaction with fullero[60]/[70]pyrrolidine has allowed the determination of different stoichiometric mechanisms of  $PyC_{60}$  and  $Py_2C_{70}$  coordination. In the case of  $PyC_{60}$ , the two-stage process leading to the triad,  $(PyC_{60})_2$ . CoDTBCP, and the one-stage formation of  $(Py_2C_{70})$ CoDTBCP were respectively observed.

Spectral analysis of the CoDTBCP reaction with PyC<sub>60</sub> has allowed the detection and description of the fast equilibrium and slow two-way reaction of PyC<sub>60</sub> coordination simultaneously due to using the original method for information collection during spectrophotometric titration at  $\tau = 0$  and over time (time-dependent titration<sup>52</sup>). The spectral changes during the transformation of CoDTBCP with PyC<sub>60</sub> in toluene solution at zero time, namely in the first stage, are shown in Fig. 3a. The bonding of PyC<sub>60</sub> to CoDTBCP in the first stage is characterized by both a gradual decrease of the intensity at 419 nm in the CoDTBCP spectrum and the appearance of the new band at 436 nm in the form of a shoulder. One PyC<sub>60</sub> molecule is bonded by CoDTBCP, as followed from the slope of the log *I*-log *C*<sub>PyC60</sub> dependence (Fig. 3a).

The following slow interaction leading to equilibrium in the CoDTBCP-PyC<sub>60</sub> systems of all compositions taken is accompanied by the gradual decrease in the absorption at 419 nm together with the appearance of the new Soret band 436 nm. The intensity ratio of the *Q*-bands is also varied so that the form of the spectrum becomes typical of six-coordination cobalt



Fig. 3 UV-vis spectrum transformations during the titration of CoDTBCP with PyC<sub>60</sub> ( $C_{PyC60} = 0 \div 1.47 \times 10^{-4}$  M) in toluene at  $\tau = 0$  (a) and  $\tau = \infty$  (b). Inset: Plots of log *I* vs. log  $C_{PyC60}$  at  $\tau = 0$  (a) and  $\tau = \infty$  (b).

Table 1 Chemical structure, formation reaction equations and corresponding equilibrium/rate constants for (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP<sup>a</sup>



complexes.<sup>53</sup> One PyC<sub>60</sub> molecule participates in the reaction second stage, which follows from the tan  $\alpha$  numerical value of the slope  $\log I - \log C_{PvC60}$  (Fig. 3b). The reaction reversibility is confirmed experimentally by diluting mixtures with respect to the PyC<sub>60</sub> concentration. The isosbestic points are observed during the transformation of the UV-vis spectra (Fig. S3, ESI<sup>+</sup>). The equilibrium in the mixtures studied is established within 700–1200 seconds depending on the  $PyC_{60}$  concentration. Fig. S3 (ESI<sup>†</sup>) shows the UV-vis spectrum transformations typical of the reaction mixtures at  $C_{\rm PvC60}$  between 2.75  $\times$  10<sup>-5</sup> and 1.47  $\times$  $10^{-4}$  M. Thus, the formation of the donor-acceptor triad can be represented as two successive two-way reactions with corresponding equilibrium constants (Table 1). As indicated above, the second equilibrium is established over time, which allows measurement of the reaction rate constants  $(k_{2obs})$  (Table 2). The first orders with respect to CoDTBCP (Fig. S4, ESI<sup>†</sup>) and  $PyC_{60}$  (Fig. S5, ESI<sup>†</sup>) are determined and the  $k_2$  and  $k_{-2}$  rate constants of the direct and inverse reaction are calculated (Table 1).

Table 2 Rate constants of the CoDTBCP reaction with the second molecule  $\mbox{PyC}_{60}$  in toluene at 298 K

$\frac{C_{\rm PyC60} \times 10^5,  M}{2.75}$	$(k_{ m 2obs}\pm\delta k_{ m 2obs}) imes$ 10 $^3$ , s $^{-1}$	
	$2.67\pm0.09$	
3.66	$3.15\pm0.20$	
4.58	$4.06\pm0.13$	
5.49	$4.60\pm0.12$	
6.41	$5.20\pm0.19$	
7.33	$5.71\pm0.24$	
9.16	$6.54 \pm 0.26$	
11.0	$7.33 \pm 0.44$	
12.8	$7.98 \pm 0.36$	
14.7	$8.81\pm0.47$	

The coordination of one  $Py_2C_{70}$  molecule with CoDTBCP giving the donor-acceptor dyad,  $(Py_2C_{70})$ CoDTBCP, which is accompanied by the UV-vis spectrum change (Fig. 4) proceeds as a one-stage reversible process (see the reaction equation in Table 1). The formation of the five-coordination cobalt( $\pi$ ) porphyrin complex over time is characterized by both the gradual intensity decrease of the band at 419 nm and the appearance of the shoulder near 437 nm with the preservation of the isosbestic points at 401, 427 nm. The reaction rate constants ( $k_{obs}$ ) are shown in Table 3.

The first order with respect to CoDTBCP was determined during the kinetic measurements (Fig. S6, ESI<sup>†</sup>). The straightline dependence of  $\log k_{obs} vs. \log C_{Py2C70}$  indicates that the reaction order with respect to  $Py_2C_{70}$  is close to unity (Fig. S7, ESI<sup>†</sup>). The rate constants of the direct (*k*) and inverse reactions,



Fig. 4 Transformation in the UV-vis spectrum of the mixture of CoDTBCP and  $2.82\,\times\,10^{-5}$  M  $Py_2C_{70}$  in toluene at 298 K over 600 seconds.

Table 3 Rate constants for the reaction of CoDTBCP with  $\text{Py}_2\text{C}_{70}$  in toluene at 298 K

$C_{ m Py2C70} imes10^5$ , M	$(k_{ m obs}\pm\delta k_{ m obs}) imes 10^2,{ m s}^{-1}$
2.26	$1.36\pm0.11$
2.82	$1.50\pm0.03$
3.38	$1.78\pm0.09$
3.95	$2.24\pm0.13$
4.51	$2.42\pm0.04$
5.08	$2.75\pm0.12$
5.64	$2.82\pm0.13$
6.77	$2.93\pm0.24$

 $(k_{-})$  were found by optimization of the dependence in Fig. S7 (ESI<sup>†</sup>) and as ratio k/K (Table 1), respectively. To construct the titration curve (Fig. 5) and calculate K (Table 1) for the reaction between CoDTBCP and Py<sub>2</sub>C<sub>70</sub>, solutions were maintained until the end of the slow reactions. The one Py<sub>2</sub>C<sub>70</sub> molecule participates in the equilibrium that follows from the numerical value of the slope of the straight line in the coordinates log *I*-log *C*<sub>Py2C70</sub>, tan  $\alpha$  0.85 (Fig. 5b).

In this way, the CoDTBCP–fullero[60]/[70]pyrrolidine mixtures in organic solvent are self-organizing systems suitable for obtaining the fullerene-containing coordination complexes with various stoichiometries. The donor–acceptor complexes,  $(PyC_{60})_2CoDTBCP$  and  $(Py_2C_{70})CoDTBCP$ , exhibit moderately high stability, which follows from the *K* values being much higher than one. Comparison of the numerical values  $K_1$  and *K* (Table 1) shows that their stability is commensurate within the margin of error but  $(Py_2C_{70})CoDTBCP$  stays coordinationally saturated in comparison with intermediate  $(PyC_{60})CoDTBCP$ .

#### Chemical structure of porphyrin-fullerene systems

The formation of  $(PyC_{60})_2$ CoDTBCP and  $(Py_2C_{70})$ CoDTBCP was also monitored by the change in IR and <sup>1</sup>H NMR spectra. The formation of  $(PyC_{60})_2$ CoDTBCP was accompanied by a change in the signal intensity ratios of the macrocycle  $\nu$ (C=N),  $\nu$ (C=C) and  $\nu$ (C-N) vibrations in the triad IR spectrum compared with CoDTBCP (Fig. 6). A high-frequency shift of these signals was also observed. The signals of  $\nu$ (C=N),  $\nu$ (C=C) and  $\nu$ (C-N) appear at 1596, 1560 cm<sup>-1</sup> and 1261, and 1208 cm<sup>-1</sup> respectively. The frequencies of the C-H stretching vibrations of the *tert*-butyl groups remain unchanged due to their distant location from the macrocycle plane. The new signals at 2921, 2784, 1463, 1334, 1314, 1179, 1162, 909, 767, 707, 663, 598, 574, 553, 541, 527, 504, 448, 427, and 402 cm<sup>-1</sup> assigned to the vibrations

Fig. 5 Spectrophotometric titration curve (a) and plot of log / vs. log  $C_{Py_2C_{70}}$  (b) for the reaction of CoDTBCP with  $Py_2C_{70}$  at  $\tau = \infty$ .

 $\log C_{\text{Py}_2\text{C}_n}$ -5.5



Fig. 6 IR spectra of CoDTBCP (black) and its triad with  $PyC_{60}$  (red) in KBr. Bands corresponding to vibrations of  $PyC_{60}$  are denoted with asterisks.

of coordinated PyC<sub>60</sub> appear in the IR spectrum of the triad (Fig. 6, red line). The signals at 1179, 574, and 527  $\text{cm}^{-1}$ correspond to the vibrations of the  $C_{60}$  moiety in PyC<sub>60</sub><sup>54</sup> and their positions are unchanged in the spectrum of the triad. The  $PyC_{60}$  frequencies in the  $(PyC_{60})_2$ CoDTBCP spectrum assigned to vibrations of the pyridine and pyrrolidinyl rings are shifted by 1–5 cm<sup>-1</sup> compared with those of free PyC<sub>60</sub>. The appearance of the new low-intensity signal at 427 cm<sup>-1</sup> presumably corresponded to the Co– $N_{PyC_{60}}$  bond  $^{51}$  and the shift of the  $\nu ({\rm Co–N})$ signal to 479 cm<sup>-1</sup> also confirms the formation of the supramolecular systems. The mentioned shift is probably related to the Co axial displacement due to the appearances of PyC<sub>60</sub> in the triad structure. Really, the quantum chemical calculations below show that the Co atom is displaced from the macrocycle plane respectively by 0.20 Å and 0.55 Å in (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP, respectively.

Some relatively strong bands at 1590, 794, 672, 642, 578 and 534 cm<sup>-1</sup>, which are unique for C<sub>70</sub>,<sup>55</sup> are present unchanged in the (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP IR spectrum (Fig. S8, ESI†). The bands assigned to vibrations of pyridine and pyrrolidinyl rings of the Py<sub>2</sub>C<sub>70</sub> are shifted by 1–4 cm<sup>-1</sup> in the dyad IR spectrum compared with free Py<sub>2</sub>C<sub>70</sub>. With respect to vibrations of the macrocyclic ligand, the  $\nu$ (C=N),  $\nu_{as}$ (=C-O-C-), and  $\nu$ (C-N) signals undergo the largest shift (Fig. S8, ESI†) when the transition from the CoDTBCP spectrum to the (Py<sub>2</sub>C<sub>70</sub>)-CoDTBCP spectrum takes place and the new low-intensity signal at 427 cm<sup>-1</sup> corresponding to the Co-N<sub>Py2C70</sub> bond appears.

The addition of  $PyC_{60}$  and  $Py_2C_{70}$  to the CoDTBCP solution in CDCl<sub>3</sub> (Fig. 5a) is accompanied with a shift of the signals of CoDTBCP protons located in the macrocycle or in close proximity to it in the strong field (Fig. 7). The signals of the  $(PyC_{60})_2$ CoDTBCP  $\beta$ -protons are displayed as a broad multiplet

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0.5

a

log/

0.2

-0.2

-0.6



Fig. 7 The informative fragment of the <sup>1</sup>H NMR spectra of CoDTBCP (a), and its triad  $(PyC_{60})_2CoDTBCP$  (b), and dyad  $(Py_2C_{70})CoDTBCP$  (c) in CDCl<sub>3</sub>.

and shifted to 14.15 ppm. These signals remain as two broad singlets shifted upfield to 16.01 and 14.89 ppm in the (Py<sub>2</sub>C<sub>70</sub>)-CoDTBCP spectrum (Fig. 7c). The signals of the phenyl ring ortho-protons in the 3,5-di-tert-butylphenyl substituents are also shifted upfield when the donor-acceptor complexes are formed. Their most noticeable shift occurs in the case of (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP (Table S2, ESI<sup>+</sup>). The upfield shift of the PyC<sub>60</sub>/Py<sub>2</sub>C<sub>70</sub> protons in the spectra of the coordination complexes (Fig. S9, ESI<sup>+</sup>) indicates the reduced de-shielding by the macrocycle ring current arising in the macroring in a magnetic field, which clearly points to axial ligation of the substituted fullerenes to the central atom. The magnitude of the shift depends on the distance of the protons from the porphyrin ring, therefore the pyridyl protons in  $(PyC_{60})_2$ CoDTBCP and the pyrrolidinyl protons in (Py2C70)CoDTBCP display a shift indicating that coordination occurs via these groups. These conclusions agree well with the IR spectroscopy data above concerning the deformation of the coordination centers in (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP leading to a decrease in the macrocycle aromaticity. The observed  $\pi$ -stacking between the carbazole fragments and the fullerene moieties (see below) also supports this idea.

#### DFT calculations

To examine the geometric and electronic structures of  $(PyC_{60})_{2-}$ CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP (Fig. S10, ESI<sup>†</sup>), theoretical calculations were carried out. The CoDTBCP is energetically favorable for the axial bonding of two substituted C<sub>60</sub> molecules but only one Py2C70 molecule. This stoichiometric difference may be because one of the CoDTBCP carbazole moieties obstructs the coordination center, which hinders coordination of a second Py<sub>2</sub>C<sub>70</sub>. The cobalt(II) ion has an octahedral and pyramidal environment in (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)-CoDTBCP, respectively. The average value of the Co-N<sub>PvC60</sub> and Co-N<sub>Pv2C70</sub> bond length is 2.283 Å and 2.315 Å, respectively, which is in agreement with the bonding energy (Table S3, ESI<sup>†</sup>). The formation of (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP is accompanied by the macrocycle deviation from planarity by  $2.86^{\circ}$  and  $2.77^{\circ}$ , respectively. An interesting feature is that the carbazole fragments in the dyad and triad take part in  $\pi$ -stacking with the fullerene moieties. The fullerene residue in

both coordination complexes orients one carbazole fragment. The deviation from coplanarity between the carbazole moiety aromatic plane and the plane of the nearest hexagonal ring of the fullerene in  $(Py_{C_{60}})_2$ CoDTBCP is from  $20.3^{\circ}$  to  $44.1^{\circ}$ . This deviation in  $(Py_2C_{70})$ CoDTBCP is  $15.4^{\circ}$ . The distance between the carbazole moieties and the hexagonal rings of two  $C_{60}$  moieties is 3.280 Å and 5.001 Å, of one  $C_{70}$  moiety is 3.574 Å.

DFT calculations show that the HOMO and LUMO are localized on the electron donor porphyrin and the electron acceptor fullerene, respectively, which may shed light on the nature of the charge transfer states.<sup>56-58</sup> Calculation of the (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP/(Py<sub>2</sub>C<sub>70</sub>)CoDTBCP electronic structure has given a very interesting result, namely the presence of intramolecular photoinduced electron transfer (PET) clearly arising from the data in Fig. 8. The HOMO-3 and HOMO-2 of both coordination complexes are localized on the carbazole moieties, while HOMO and HOMO-1 are localized on the macrocycle. However, the LUMO and LUMO + n are completely localized in the C<sub>60</sub> and C<sub>70</sub> moieties. Using frontier molecular orbital (FMO) analysis of (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP and (Py<sub>2</sub>C<sub>70</sub>)-CoDTBCP, the strong electronic interaction of the  $PyC_{60}$ / Py<sub>2</sub>C<sub>70</sub> moiety with CoDTBCP (Fig. 8) is revealed. Besides, the electronic interaction due to PET between CoDTBCP as the electron donor and  $PyC_{60}/Py_2C_{70}$  as the acceptor (Fig. 9) is established. Similar behavior was observed by us for the other coordination dyads/triads.<sup>24,25,27-29</sup> The high values both stability constant and HOMO-LUMO gap of (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP compared with (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP (Fig. 9) may indicate a greater efficiency of PET in the triad (see section "Transient absorption spectroscopy").

#### Transient absorption spectroscopy

Femtosecond transient absorption measurements were performed at the excitation wavelength of 400 nm corresponding to CoDTBCP excitation. De-aerated toluene was used as a medium because it is stable under strong laser irradiation and demonstrates good solubility of the compound being studied. The transient absorption spectrum of CoDTBCP contains the negative peak at 521 nm, corresponding to the ground state bleaching, and the positive peaks at 430, 552 and 578 nm, corresponding to the excited state (Fig. S11, ESI†). The time profile of CoDTBCP absorbance at 430 nm can be well fit using three exponential decay components with different lifetimes. Two short lifetimes distinguishable in Fig. S11 (ESI†), at 0.99 and 3.18 ps, are the main contributors, while a small but discernible long lifetime component 16.76 ps is in the tail of the whole decay profile.

The femtosecond transient absorption spectra of  $(PyC_{60})_2$ . CoDTBCP and  $(Py_2C_{70})$ CoDTBCP at different delay times in toluene are shown in Fig. 10 and 11, respectively. These were using to determine the charge separation/charge recombination constants. The femtosecond transient spectrum of triad/ dyad largely resembles that of CoDTBCP, where only small shifts of the bands are observed. The negative peaks at 407, and 522 nm and the positive peaks at 432, and 572 nm are revealed upon excitation of  $(PyC_{60})_2$ CoDTBCP. The negative peak at



Fig. 8 Frontier molecular orbitals of (PyC<sub>60</sub>)<sub>2</sub>CoDTBCP (a) and (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP (b).

521 nm and the positive peaks at 426, 550, and 575 nm are observed for  $(Py_2C_{70})CoDTBCP$ . Unfortunately, the conditions of the experiment (the spectral range of our instrument setup from 400 to 900 nm) do not allow detection of the transient band of  $PyC_{60}^{\bullet-}$  in the triad/dyad, which is apparent in the range from 950 to 1020 nm.<sup>37</sup>

The time constants for charge separation and charge recombination were obtained by fitting of the time profile of the 432 nm and 426 nm peaks for  $(PyC_{60})_2$ CoDTBCP and  $(Py_2C_{70})$ -CoDTBCP, respectively. The rise time of 0.82 ps for  $(PyC_{60})_2$ . CoDTBCP results in the rate of charge separation  $k_{CS} = 1.29 \times 10^{12} \text{ s}^{-1}$  suggesting the occurrence of ultrafast charge



**Fig. 9** Mechanism of PET in  $(PyC_{60})_2$ CoDTBCP and  $(Py_2C_{70})$ CoDTBCP (the HOMO-LUMO gap for  $(PyC_{60})_2$ CoDTBCP and  $(Py_2C_{70})$ CoDTBCP is 5.63, and 5.48 eV, respectively).

separation in the triad. However, the decay was found to be biexponential (Fig. 10b) with the time constants of 2.13 and 19.43 ps resulting in the rate of charge recombination  $k_{\rm CR} = 4.7 \times 10^{11} \, {\rm s}^{-1}$  and  $5.15 \times 10^{10} \, {\rm s}^{-1}$ , respectively. The rise time of

1.29 ps for (Py<sub>2</sub>C<sub>70</sub>)CoDTBCP results in  $k_{\rm CS} = 7.75 \times 10^{11} \text{ s}^{-1}$  while the biexponential decay with the time constants of 4.49 and 20.65 ps results in  $k_{\rm CR}$  values of  $2.2 \times 10^{11} \text{ s}^{-1}$  and  $4.84 \times 10^{10} \text{ s}^{-1}$ , respectively. These results indicate the existence of electron transfer from CoDTBCP to coordinated PyC<sub>60</sub>/Py<sub>2</sub>C<sub>70</sub> in the triad/dyad. The analysis of the  $k_{\rm CR}$  values shows not too large a lifetime for the radical ion-pairs of the triad/ dyad in toluene. The lifetime for excited states of cobalt( $\pi$ ) porphyrins can be changed by variation of the solvent properties.<sup>32</sup>

# 4. Conclusions

Carbazole-functionalized cobalt(II) porphyrin was synthesized for the first time to obtain its architectures with substituted fullerenes. Self-assembly in the mixtures of (5,15-bis[3,5-bis(*tert*butyl)phenyl]-10,20-bis[4,6-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl) pyrimidin-5-yl]porphinato)cobalt(II) and 1-*N*-methyl-2-(pyridin-4yl)-3,4-fullero[60]pyrrolidine or 2,5-di-(pyridin-2-yl)-3,4-fullero[70] pyrrolidine in toluene results in the porphyrin–fullerene coordination system of moderately high stability. The formation of the



Fig. 10 Femtosecond transient absorption spectrum of  $(PyC_{60})_2$ CoDTBCP in toluene at the excitation wavelength of 400 nm (a) and the time profile of the transient peaks of  $(PyC_{60})_2$ CoDTBCP (b).



Fig. 11 Femtosecond transient absorption spectrum of  $(Py_2C_{70})CoDTBCP$  in toluene at the excitation wavelength of 400 nm (a) and the time profile of the transient peaks of  $(Py_2C_{70})CoDTBCP$  (b).

triad,  $(PyC_{60})_2CoDTBCP$ , and the dyad,  $(Py_2C_{70})CoDTBCP$ , respectively, in the case of CoDTBCP–PyC<sub>60</sub> and CoDTBCP–  $Py_2C_{70}$  were established by thermodynamic/kinetic description of the self-assembly. This result was confirmed by IR and <sup>1</sup>H NMR spectroscopy methods and DFT calculation. The peculiarity of the chemical structure of the coordination complexes studied is the displacement of Co from the macrocycle plane not only in the dyad (0.55 Å) but also in the triad (0.20 Å), which is reflected in the corresponding IR and <sup>1</sup>H NMR spectra. DFT calculations and femtosecond investigations have confirmed the existence of photoinduced electron transfer in the triad and dyad. The data obtained are required for further study of both the  $(PyC_{60})_2CoDTBCP/(Py_2C_{70})CoDTBCP$  photoelectrochemical properties and their potential in the building of photovoltaic devices.

# Author contributions

E. N. Ovchenkova: conceptualization, formal analysis, writing – original draft, writing – review and editing; N. G. Bichan: methodology, investigation, writing – original draft, funding acquisition, writing – review and editing, M. S. Gruzdev: formal analysis, methodology, visualization, writing – original draft; A. A. Ksenofontov: formal analysis, writing – original draft, visualization; F. E. Gostev: methodology, investigation, writing – original draft; I. V. Shelaev: methodology, investigation, visualization; V. A. Nadtochenko: writing – review and editing, resources; T. N. Lomova: writing – review and editing, project administration, resources.

# Conflicts of interest

There are no conflicts to declare.

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# References

- 1 N. Balsukuri and I. Gupta, Dyes Pigm., 2017, 144, 223-233.
- 2 A. Ryan, B. Tuffy, S. Horn, W. J. Blau and M. O. Senge, *Tetrahedron*, 2011, **67**, 8248–8254.

- 3 N. Balsukuri, S. Das and I. Gupta, New J. Chem., 2015, 39, 482-491.
- 4 F. Loiseau, S. Campagna, A. Hameurlaine and W. Dehaen, *J. Am. Chem. Soc.*, 2005, **127**, 11352–11363.
- 5 S. A. Majeed, B. Ghazal, D. E. Nevonen, P. C. Goff, D. A. Blank, V. N. Nemykin and S. Makhseed, *Inorg. Chem.*, 2017, **56**, 11640–11653.
- 6 K. Laba, M. Lapkowski, D. L. Officer, P. Wagner and P. Data, *Electrochim. Acta*, 2020, **330**, 135140.
- 7 O. I. Koifman, T. A. Ageeva, I. P. Beletskaya, A. D. Averin, A. A. Yakushev, L. G. Tomilova, T. V. Dubinina, A. Y. Tsivadze, Y. G. Gorbunova, A. G. Martynov, D. V. Konarev, S. S. Khasanov, R. N. Lyubovskaya, T. N. Lomova, V. V. Korolev, E. I. Zenkevich, T. Blaudeck, C. von Borczyskowski, D. R. T. Zahn, A. F. Mironov, N. A. Bragina, A. V. Ezhov, K. A. Zhdanova, P. A. Stuzhin, G. L. Pakhomov, N. V. Rusakova, N. N. Semenishyn, S. S. Smola, V. I. Parfenyuk, A. S. Vashurin, S. V. Makarov, I. A. Dereven'kov, N. Z. Mamardashvili, T. S. Kurtikyan, G. G. Martirosyan, V. A. Burmistrov, V. V. Aleksandriiskii, I. V. Novikov, D. A. Pritmov, M. A. Grin, N. V. Suvorov, A. A. Tsigankov, A. Y. Fedorov, N. S. Kuzmina, A. V. Nyuchev, V. F. Otvagin, A. V. Kustov, D. V. Belykh, D. B. Berezin, A. B. Solovieva, P. S. Timashev, E. R. Milaeva, Y. A. Gracheva, M. A. Dodokhova, A. V. Safronenko, D. B. Shpakovsky, S. A. Syrbu, Y. A. Gubarev, A. N. Kiselev, M. O. Koifman, N. S. Lebedeva and E. S. Yurina, Macroheterocycles, 2020, 13, 311-467.
- 8 Y. Zhang, L. Wang, T. Wada and H. Sasabe, *Macromolecules*, 1996, **29**, 1569–1573.
- 9 K.-S. Kim, S. Jeong, C. Kim, J.-Y. Ham, Y. Kwon, B.-D. Choi and Y. S. Han, *Synth. Met.*, 2009, **159**, 1870–1875.
- 10 A. Bahy, M. Chemli and B. B. Hassine, *Tetrahedron Lett.*, 2013, 54, 4026–4029.
- 11 F.-F. Zhang, L.-L. Gan and C.-H. Zhou, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 1881–1884.
- 12 W.-W. Peng, L.-X. Zheng, C.-J. Ji, X.-G. Shi, Z.-H. Xiong and X.-C. Shangguan, *Chin. J. Nat. Med.*, 2018, **16**, 509–512.
- 13 N. Salih, J. Salimon and E. Yousif, *Arabian J. Chem.*, 2016, 9, S781–S786.
- 14 T. Aggarwal, Sushmita and A. K. Verma, *Org. Biomol. Chem.*, 2019, **17**, 8330–8342.
- 15 A. A. Pieper, S. L. McKnight and J. M. Ready, *Chem. Soc. Rev.*, 2014, **43**, 6716–6726.
- 16 T. Takeuchi, S. Oishi, T. Watanabe, H. Ohno, J.-I. Sawada, K. Matsuno, A. Asai, N. Asada, K. Kitaura and N. Fujii, *J. Med. Chem.*, 2011, 54, 4839–4846.
- 17 X. Wu, J. Kosaraju, W. Zhou and K. Y. Tam, ACS Chem. Neurosci., 2017, 8, 676–685.
- 18 M. M. Gallogly, H. M. Lazarus and B. W. Cooper, *Ther. Adv. Hematol.*, 2017, 8, 245–261.
- 19 M. Kimura, H. Suzuki, Y. Tohata, T. Ikeuchi, S. Yamamoto and N. Kobayashi, *Asian J. Org. Chem.*, 2017, **6**, 544–550.
- 20 C. Chitpakdee, S. Namuangruk, K. Suttisintong,
   S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk, K. Sirithip,
   V. Promarak and N. Kungwan, *Dyes Pigm.*, 2015, 118, 64–75.

- 21 T. H. Xu, R. Lu, X. P. Qiu, X. L. Liu, P. C. Xue, C. H. Tan, C. Y. Bao and Y. Y. Zhao, *Eur. J. Org. Chem.*, 2006, 4014–4020.
- 22 X.-M. Hu, Z. Salmi, M. Lillethorup, E. B. Pedersen, M. Robert, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *Chem. Commun.*, 2016, **52**, 5864–5867.
- 23 C. K. C. Bikram, N. K. Subbaiyan and F. D'Souza, J. Phys. Chem. C, 2012, 116, 11964–11972.
- 24 N. G. Bichan, E. N. Ovchenkova, M. S. Gruzdev and T. N. Lomova, J. Struct. Chem., 2018, 59, 711–719.
- 25 N. G. Bichan, E. N. Ovchenkova, N. O. Kudryakova and T. N. Lomova, *J. Coord. Chem.*, 2017, **70**, 2371–2383.
- 26 E. N. Ovchenkova, N. G. Bichan and T. N. Lomova, *Dyes Pigm.*, 2016, **128**, 263–270.
- 27 N. G. Bichan, E. N. Ovchenkova, N. O. Kudryakova, A. A. Ksenofontov, M. S. Gruzdev and T. N. Lomova, *New J. Chem.*, 2018, 42, 12449–12456.
- 28 E. N. Ovchenkova, N. G. Bichan, A. A. Tsaturyan, N. O. Kudryakova, M. S. Gruzdev, F. E. Gostev, I. V. Shelaev, V. A. Nadtochenko and T. N. Lomova, *J. Phys. Chem. C*, 2020, 124, 4010–4023.
- 29 N. Bichan, E. N. Ovchenkova, V. Mozgova, N. Kudryakova, M. Gruzdev and T. Lomova, *Russ. J. Phys. Chem. A*, 2020, 94, 1159–1166.
- 30 N. G. Bichan, E. N. Ovchenkova, A. A. Tsaturyan and T. N. Lomova, New J. Chem., 2020, 44, 11262–11270.
- 31 G. R. Loppnow, D. Melamed, A. R. Leheny, A. D. Hamilton and T. G. Spiro, *J. Phys. Chem.*, 1993, **97**, 8969–8975.
- 32 H. Z. Yu, J. S. Baskin, B. Steiger, C. Z. Wan, F. C. Anson and A. H. Zewail, *Chem. Phys. Lett.*, 1998, **293**, 1–8.
- 33 S. Zheng, J. Zhong, W. Matsuda, P. Jin, M. Chen, T. Akasaka,
   K. Tsukagoshi, S. Seki, J. Zhou and X. Lu, *Nano Res.*, 2018,
   11, 1917–1927.
- 34 T. Wakahara, P. D'Angelo, K. I. Miyazawa, Y. Nemoto, O. Ito, N. Tanigaki, D. D. C. Bradley and T. D. Anthopoulos, *J. Am. Chem. Soc.*, 2012, 134, 7204–7206.
- 35 S. Cho, J. M. Lim, J.-M. You, S. Jeon and D. Kim, *Isr. J. Chem.*, 2016, 56, 169–174.
- 36 J.-M. You, H. S. Han, H. K. Lee, S. Cho and S. Jeon, Int. J. Hydrogen Energy, 2014, 39, 4803–4811.
- 37 D. M. Guldi, G. M. A. Rahman, N. Jux, D. Balbinot, U. Hartnagel, N. Tagmatarchis and M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 9830–9838.
- 38 J. T. Groves and P. Viski, J. Org. Chem., 1990, 55, 3628-3634.
- 39 M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandona and G. Farnia, *Tetrahedron*, 1996, 52, 5221–5234.

- 40 P. A. Troshin, A. S. Peregudov, S. I. Troyanov and R. N. Lyubovskaya, *Russ. Chem. Bull.*, 2008, 57, 887–912.
- 41 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery Jr, *J. Comput. Chem.*, 1993, 14, 1347–1363.
  42 A. D. Backe, *J. Chem. Phys.* 1002, 00, 5610, 5652.
- 42 A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 43 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 44 E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch,
  D. M. Greenblatt, E. C. Meng and T. E. Ferrin, *J. Comput. Chem.*, 2004, 25, 1605–1612.
- 45 G. A. Zhurko, Chemcraft, Ver. 1.6., 2021.
- 46 S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann and N. P. Ernsting, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1999, **59**, 2369–2384.
- 47 I. V. Shelaev, F. E. Gostev, M. I. Vishnev, A. Y. Shkuropatov,
  V. V. Ptushenko, M. D. Mamedov, O. M. Sarkisov,
  V. A. Nadtochenko, A. Y. Semenov and V. A. Shuvalov, *J. Photochem. Photobiol., B*, 2011, **104**, 44–50.
- 48 A. L. Dobryakov, J. L. P. Lustres, S. A. Kovalenko and N. P. Ernsting, *Chem. Phys.*, 2008, 347, 127–138.
- 49 H. Dehghani, R. Sahba, M. Afrooz and H. Mollaei, J. Chin. Chem. Soc., 2010, 57, 690–695.
- 50 B. Ventura, L. Flamigni, G. Marconi, F. Lodato and D. L. Officer, *New J. Chem.*, 2008, **32**, 166–178.
- 51 F. E. Mabbs, Chem. Soc. Rev., 1993, 22, 313-324.
- 52 T. N. Lomova, M. E. Klyueva and M. V. Klyuev, Chemical Processes with Participation of Biological and Related Compounds: Biophysical and Chemical Aspects of Porphyrins, Pigments, Drugs, Biodegradable Polymers and Nanofibers, 2008, pp. 93–116.
- 53 Y. Terazono, B. O. Patrick and D. H. Dolphin, *Inorg. Chim. Acta*, 2003, **346**, 265–269.
- 54 M. C. Martin, X. Du, J. Kwon and L. Mihaly, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 173–183.
- 55 B. Chase, N. Herron and E. Holler, *J. Phys. Chem.*, 1992, **96**, 4262–4266.
- 56 A. M. El Mahdy, S. A. Halim and H. O. Taha, J. Mol. Struct., 2018, 1160, 415–427.
- 57 A. J. Stasyuk, O. A. Stasyuk, M. Solà and A. A. Voityuk, *Phys. Chem. Chem. Phys.*, 2019, 21, 25098–25107.
- 58 A. Ciammaichella, P. O. Dral, T. Clark, P. Tagliatesta, M. Sekita and D. M. Guldi, *Chem. – Eur. J.*, 2012, 18, 14008–14016.