Electronic Supplementary Information

Self-Assembled via Axial Coordination Cobalt(II)porphyrin-Fulleropyrrolidine Triad with Photoinduced Electron Transfer

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Page

Figure S1. UV-vis spectra of PyC_{60} in toluene at 298 K. C_{PyC60} = 3.60 × 10^{-5} (*1*), 4.85 × 10^{-5} (*2*), 6.04 × 10^{-5} (*3*), 9.19 × 10^{-5} (*4*), 9.98 × 10^{-5} (*5*), 1.20 × 10^{-4} (*6*), 1.62 × 10^{-4} (*7*) M.

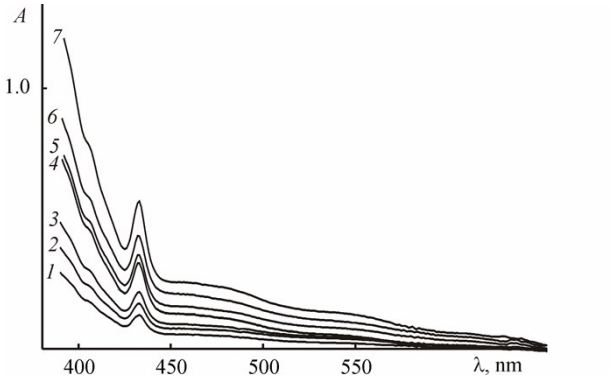


Figure S2. Plots of lg*I* vs lgC_{PyC60} for the reaction of PyC_{60} with $Co^{II}P$ at τ = 0.

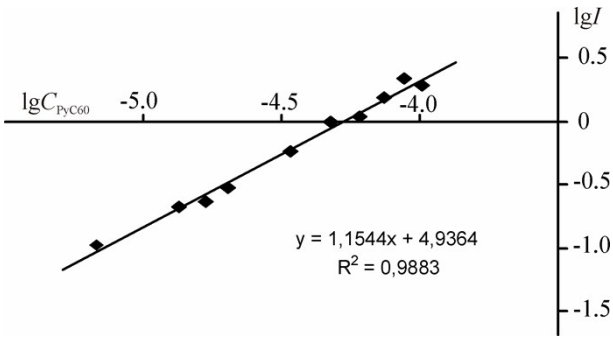


Figure S3. Plot of lgk_{ef} versus lgC_{PyC60} for the reaction of $Co^{II}P$ with PyC_{60} in toluene at 298 K.

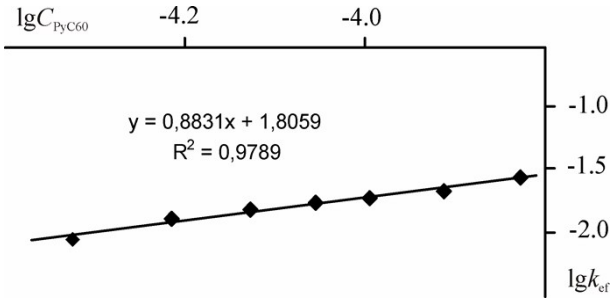


Figure S4. IR spectrum of $(PyC_{60})_2Co^{II}P$.

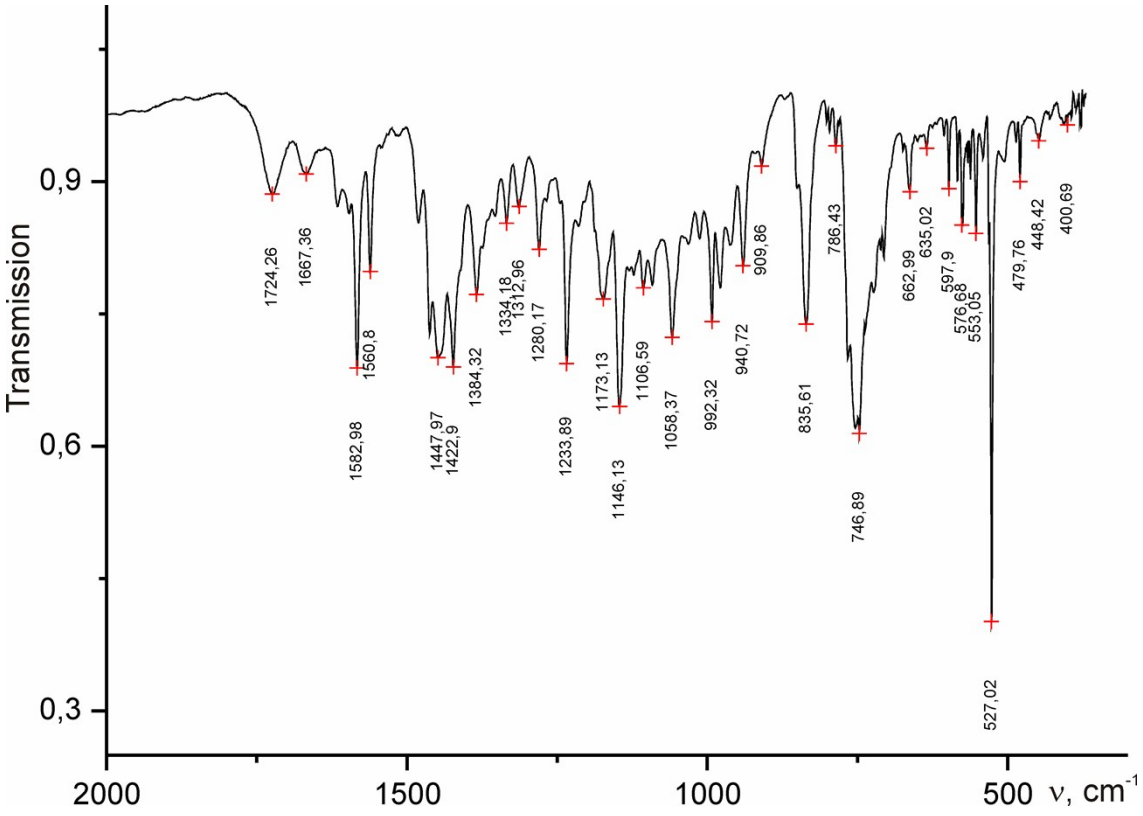
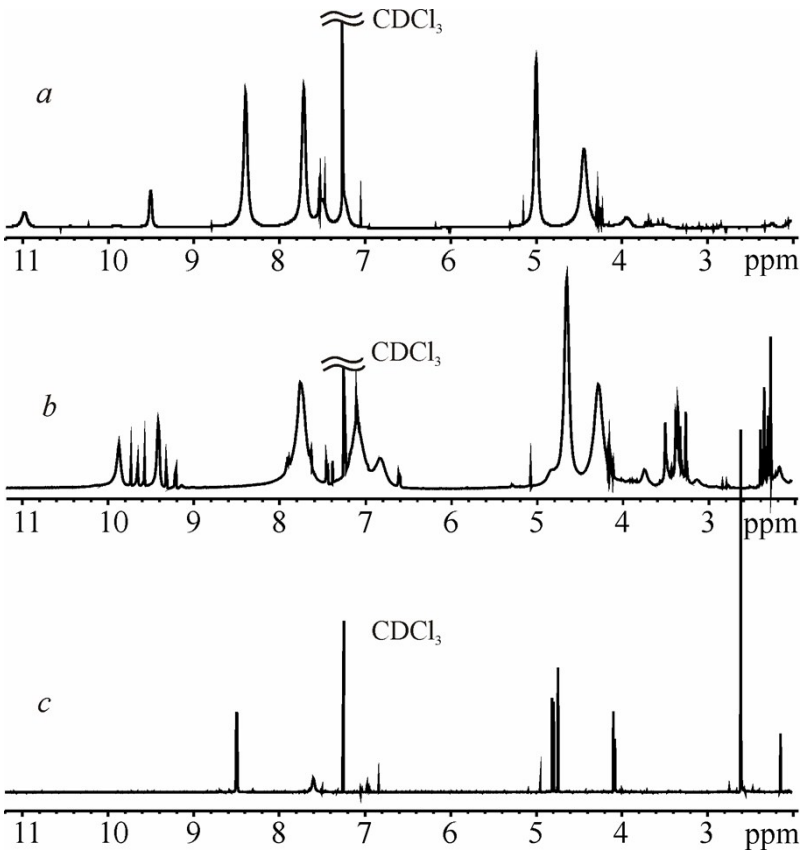


Fig. S5. ^1H NMR spectra of compounds $Co^{II}P$ (a), $(PyC_{60})_2Co^{II}P$ (b) and PyC_{60} (c) in $CDCl_3$.



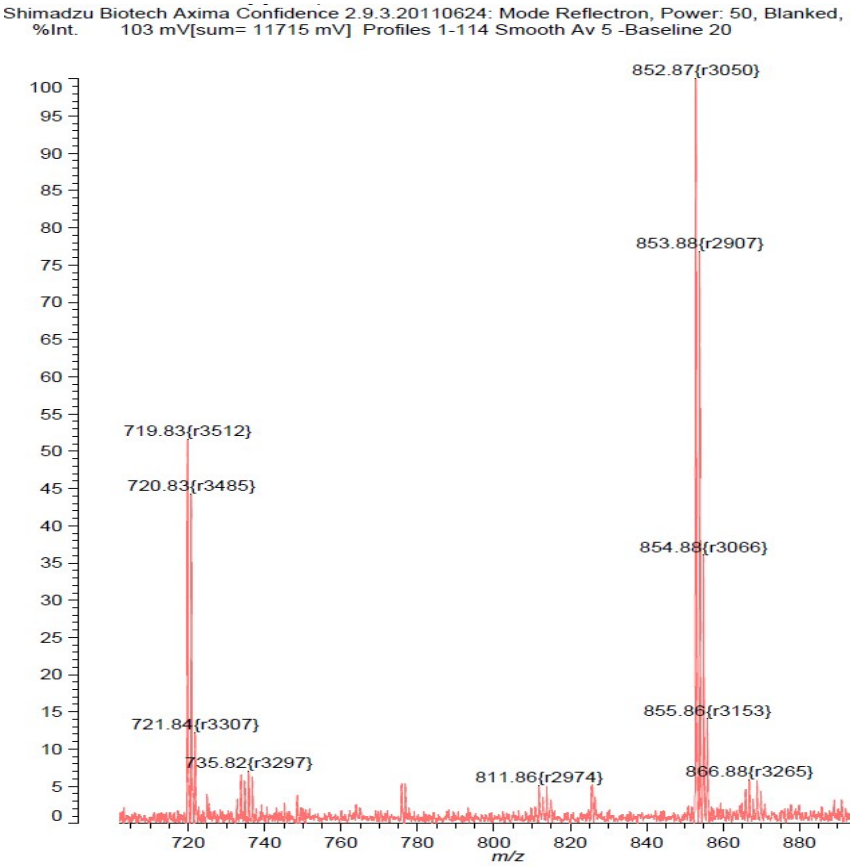
Synthesis of (2,3,7,8,12,18-hexamethyl,13,17-diethyl,5-(2-pyridyl)porphinato)cobalt(II), $Co^{II}P$

$Co(AcO)_2 \cdot 4H_2O$ (47.0 mg, 0.19 mmol) and (2,3,7,8,12,18-hexamethyl,13,17-diethyl,5-(2-pyridyl)porphyrin H_2P (20.0 mg, 0.04 mmol) were reacted in boiling dimethylformamide (10 ml) for 40-50 min. Completion of the reaction was monitored by TLC, until no traces of starting material were detected. The reaction mixture was cooled, after dilution with water the products were extracted into chloroform and purified by flash chromatography ($Al_2O_3/CHCl_3$). The red zone display on the chromatogram corresponding to $Co^{II}P$.

Synthesis of 1′-N-methyl-2′-(pyridin-4-yl)pyrrolidino[3',4':1,2][60]fullerene, PyC_{60}

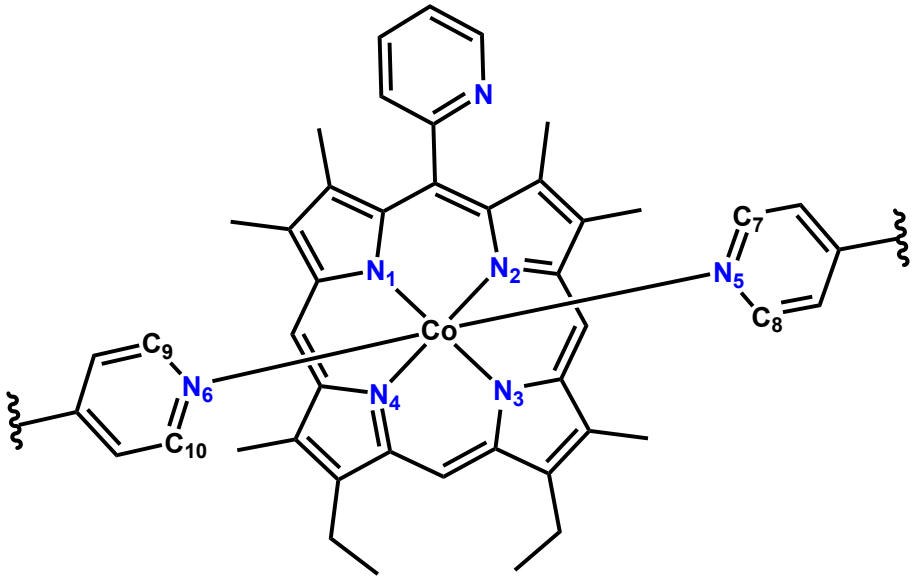
A solution of 100 mg (0.14 mmol) of C_{60}, 80 mg (0.70 mmol) of pyridine-4-carboxaldehyde and 43 mg (0.48 mmol) of N-methylglycine in 90 ml of toluene was stirred at reflux temperature for 2 h. Then the solvent was removed in vacuo. The formation of PyC_{60} was monitored by TLC and UV-Vis of the reaction mixture by the appearance of absorption with λ_{max} = 433 nm [M. Prato, M. Maggini, C. Giacometti, G.Scorrano et al. *Tetrahedron*, 1996, **52,** 5221; P.A. Troshin, S.I. Troyanov, G.N. Boiko, R.N. Lyubovskaya et al. *Fullerenes, nanotubes, and carbon nanostructures*, 2004, **12,** 413]. The reaction mixture was purified by column chromatography on Al_2O_3 (elution with the mixture of toluene- ethyl acetate (20:1)). Yield: 0.64 mg (52%).

Figure S6. MALDI TOF mass-spectra of the PyC_{60}.



Although the PyC_{60} is expected to give one signal in MALDI TOF mass-spectrum with m/z corresponding to the formula $C_{68}H_{10}N_2$ (calc. m/z 854.0) it gives the signal with m/z 719.83, corresponding to the $[C_{60}]^+$. It is expected that this signal are formed under the conditions of mass-spectrum registration.

Table S1. The basic structural parameters (bond lengths, angles, NBO atomic charges (*q*)) of the $(PyC_{60})_2Co^{II}P$ optimized structure (B3LYP-D3/6-31G (d,p)).



	Bond length, Å		Angle, grad		*q*, e⁻
Co–N(1)	2.043	**N(1)–Co–N(2)**	89.98	**Co**	1.299
Co–N(2)	2.060	**N(2)–Co–N(3)**	91.23	**N(1)**	-0.637
Co–N(3)	2.094	**N(3)–Co–N(4)**	89.50	**N(2)**	-0.644
Co–N(4)	2.084	**N(4)–Co–N(1)**	91.27	**N(3)**	-0.640
Co–N(5)	2.288	**N(1)–Co–N(3)**	178.38	**N(4)**	-0.639
Co– N(6)	2.263	**N(2)–Co–N(4)**	178.48	**N(5)**	-0.497
		N(1)–Co–N(5)	91.55	**N(6)**	-0.491
		N(2)–Co–N(5)	88.45		
		N(3)–Co–N(5)	89.57		
		N(4)–Co–N(5)	91.99		
		Co–N(5)–C(7)	114.63		
		Co–N(5)–C(8)	118.83		
		N(1)–Co–N(6)	87.48		
		N(2)–Co–N(6)	91.02		
		N(3)–Co–N(6)	91.41		
		N(4)–Co–N(6)	88.17		
		Co–N(6)–C(9)	118.88		
		Co–N(6)–C(10)	120.10		

Figure S7. TDDFT spectrum of the PyC_{60} (B3LYP-D3/6-31G (d,p), PCM(toluene)).

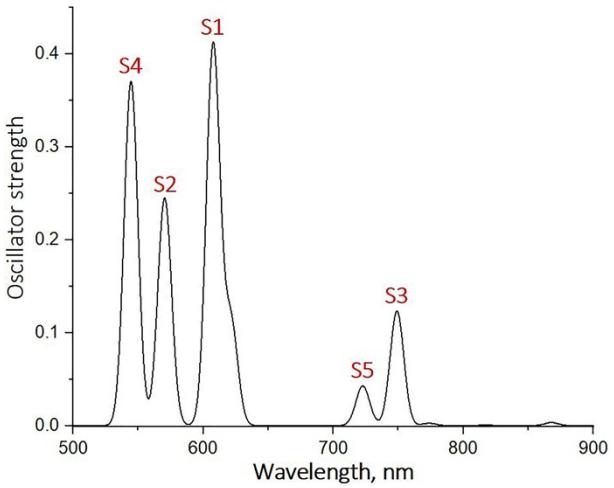


Table S2. Theoretically calculated spectral characteristics of the PyC_{60} in toluene and corresponding oscillator strengths (*f*) (B3LYP-D3/6-31G (d,p)).

State	Transition	Energy, ev	*f*
S1	H-1 L	2.041	0.41
S2	H-1 L+8	2.174	0.25
S3	H-2 L	1.665	0.12
S4	H-3 L	2.278	0.23
S5	H-2 L+2	1.716	0.04

Table S3. The photocurrent density* of system Ti|film|0.5 M Na_2SO_4|Pt.

Titanium electrode with natural oxide film	j_{ph}^1, μA cm^{-2}	j_{ph}^2, μA cm^{-2}	j_{ph}^3, μA cm^{-2}	j_{ph}^4, μA cm^{-2}	j_{ph}^5, μA cm^{-2}	j_{ph}^6, μA cm^{-2}	j_{ph}^{avg}, μA cm^{-2}
NOF	0	0	0	0	0	0	0
$Co^{II}P$ ($C_{Co^{II}P}$ = 1.80 × 10^{-5} M)	118.92	112.90	115.11	119.28	117.65	116.28	116.69
PyC_{60} (C_{PyC60}= 1.47 × 10^{-4} M	95.19	97.71	96.35	99.13	95.13	95.12	96.58
$(PyC_{60})_2Co^{II}P$ ($C_{Co^{II}P}$ = 1.80 × 10^{-5} M, C_{PyC60} = 1.47 × 10^{-4} M)	289.93	287.52	288.03	283.38	285.77	287.61	287.04

* j_{ph}= *i*/S, here *i*- photocurrent, μA; S- the surface area of the modified electrode illuminated by monochromatic UV light (365 nm).
[1-6] - number of experiment

Figure S8. Cyclic voltammogram of the PyC_{60} (a), $Co^{II}P$ (b) and $(PyC_{60})_2Co^{II}P$ (c) in CH_2Cl_2 containig 0.1 M $(n\text{-}Bu)_4NClO_4$ supporting electrolyte. Scan rate: 100 mV s^{-1}.

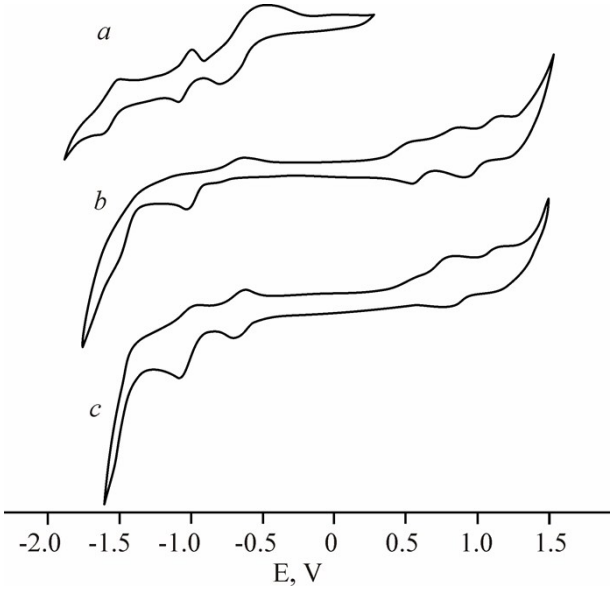


Table S4. Redox potentials, free-energy changes for charge separation (ΔG_{CS}) and recombination (ΔG_{CR}) for the $(PyC_{60})_2Co^{II}P$ in CH_2Cl_2.

Compound	$E_1^D{}_{ox}$	$E_2^D{}_{ox}$	$E_{1/2}(D^{\bullet+}/D)$	$E_1^A{}_{red}$	$E_2^A{}_{red}$	$E_{1/2}(A/A^{\bullet-})$	$-\Delta G_{CR}$, eV	$-\Delta G_{CS}$, eV
$(PyC_{60})_2Co^{II}P$	0.80	1.17	0.74	-0.64	-1.02	-0.58	1.32	0.72

$-\Delta G_{CR} = E_{1/2}(D^{\bullet+}/D) - E_{1/2}(A/A^{\bullet-})$ [a]
$-\Delta G_{CS} = E_{0\text{-}0} - (-\Delta G_{CR})$ [a]

[a] A. Bagaki, H.B. Gobeze, G. Charalambidis, A. Charisiadis, C. Stangel, V. Nikolaou, A. Stergiou, N. Tagmatarchis, F. D'Souza and A.G. Coutsolelos, *Inorg. Chem*., 2017, **56**, 10268-10280.

$E_1^D{}_{ox}$ – the first oxidation potential of electron donor ($Co^{II}P$).
$E_2^D{}_{ox}$ – the second oxidation potential of electron donor.
$E_{1/2}(D^{\bullet+}/D)$ – the potential for the first oxidation process of the donor.
$E_1^A{}_{red}$ – the first reduction potential of electron acceptor (PyC_{60}).
$E_2^A{}_{red}$ - the second reduction potential of electron acceptor.
$E_{1/2}(A/A^{\bullet-})$ – the potential for the first reduction process of the acceptor.