Supporting information

CARBAZOLE-FUNCTIONALIZED COBALT(II) PORPHYRIN AXIALLY BONDED WITH C_{60}/C_{70} DERIVATIVES: SYNTHESIS, AND CHARACTERIZATION

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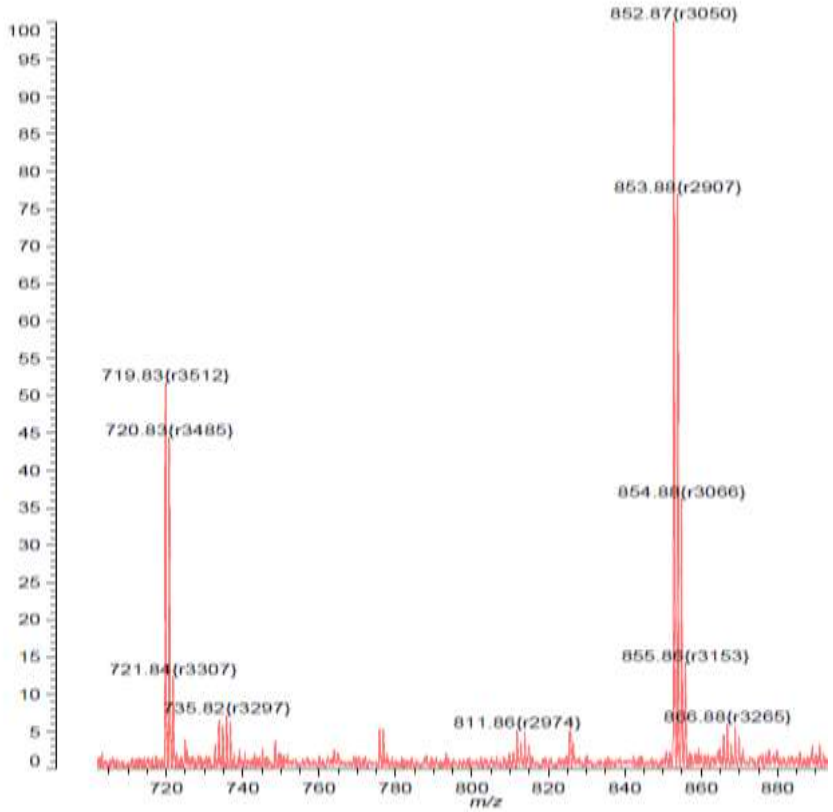
Synthesis of 1-N-methyl-2-(pyridin-4-yl)-3,4-fullero[60]pyrrolidine, PyC_{60}.

PyC_{60} was prepared according to a general procedure of fulleropyrrolidine synthesis developed by Prato and coworkers [Prato M., Maggini M., Giacometti C., et al. // Tetrahedron. 1996. V.52. №. 14. P. 5221. https://doi.org/10.1016/0040-4020(96)00126-3]. The changes in the procedure (the ratio of reagents, the reaction time, and the purification method) were done, which led to the increase in the yield of the product (Supplementary Information). UV-vis (toluene): λ_{max} (logε) = 312, 328, 433 (3.56) nm. IR (KBr) ν 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 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.71 (d, J 5.49 Hz, 2H, CH_{Py}), 7.82 (m, 2H, CH_{Py}), 5.02 (d, J 9.77 Hz, 1H, CH_2), 4.96 (s, 1H, CH_2), 4.31 (d, *J* 9.77 Hz, 1H, CH-N), 2.83 (s, 3H, CH_{Py}). MS (MALDI-TOF), m/z (rel. int.): 852.87 (100) $[M]^+$, 853.88 (77) $[M–H]^+$, 719.83 (53) $[C_{60}]^+$ (Fig. S1).

Figure S1. PyC_{60} MALDI TOF mass spectrum.



Although 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.

Synthesis of 2,5-di-(pyridin-2-yl)-3,4-fullero[70]pyrrolidine, Py_2C_{70}

Pyridine-2-carboxyaldehyde (15 mg, 0.14 mmol) and 2-picolylamine (15 mg, 0.14 mmol) dissolved in dichlorobenzene (3 ml) were added to the dichlorobenzene solution of C_{70} (100 mg, 0.12 mmol). The reaction mixture was heated at 180^0C for 15 min. Then the solvent was removed by vacuum distillation. The residue was dissolved with toluene and adsorbed on silica gel: the first zone is unreacted C_{70} (toluene as an eluent), and the second zone is Py_2C_{70} (toluene:methanol (20:1) as an eluent). The yield: 45 mg (45 %). UV-vis, toluene (λ_{max}, nm (logε)): 398 (4.91), 464 (4.23). IR (KBr) ν, cm^{-1}: 402, 437, 464, 534, 555, 569, 580, 622, 636, 641, 672, 690, 726, 746, 755, 770, 777, 794, 823, 833, 865, 910, 925, 996, 1047, 1089, 1127, 1147, 1219, 1256, 1293, 1321, 1376, 1412, 1427, 1441, 1472, 1493, 1513, 1571, 1590, 1753, 2850, 2920, 3008, 3050. ^{1}H NMR ($CDCl_3$): δ, ppm: 9.17 (d, J 5.40 Hz, 1H), 8.94 (d, J 5.20 Hz 1H), 8.77 (m, 1H), 8.36 (m, 1H), 8.16 (m, 1H), 7.95 (t, J 7.73 Hz, 1H,), 7.71 (m, 1H), 7.55 (m, 1H), 6.37 (s, 1H), 6.20 (s, 1H), 5.17 (s, 1H). MALDI-TOF MS, m/z: 1040.29 $[M]^+$.

Figure S2. Py_2C_{70} MALDI TOF mass spectrum.

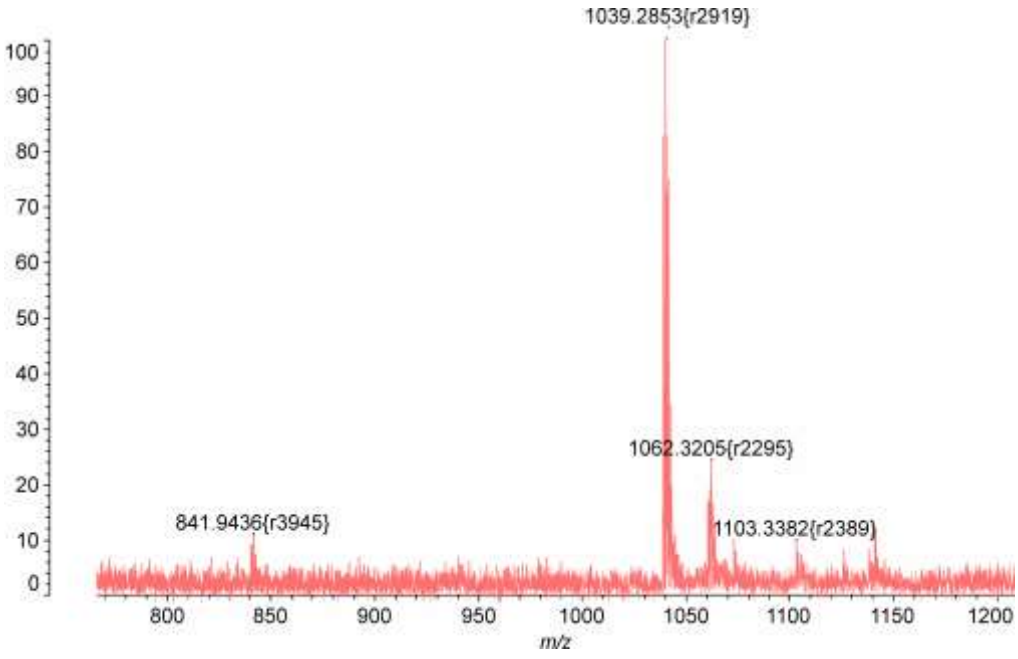


Table S1. UV-vis spectra of several *meso*-substituted porphyrins and cobalt porphyrins.

Compound	Solvent	Soret band λ, nm	*Q* bands λ, nm				ref
H_2TPP	toluene	419	514	548	592	648	[1]
H_2TIPP	$CHCl_3$	419	517	550	590	647	[2]
H_2TBPP	$CHCl_3$	421	518	554	590	649	[3]
5	toluene	423	517	551	593	649	this work
CoTPP	toluene	413	529	-	-	-	[4]
CoTIPP	toluene	415	531	615	-	-	[5]
CoTBPP	toluene	415	530	613	-	-	[3]
CoDTBCP	toluene	419	532	-	-	-	this work

TPP - 5,10,15,20-tetraphenylporphin
TIPP - 5,10,15,20-(tetra-4-isopropylphenyl)porphin
TBPP - 5,10,15,20-(tetra-4-*tert*-butylphenyl)porphin

[1] B. Ventura, L. Flamigni, G. Marconi, F. Lodato, D.L. Officer // New J. Chem. 2008, 32, 166–178.
[2] H. Dehghani, R. Sahba, M. Afrooz, H.Mollaei // J. Chinese Chem. Soc. 2010, 57, 690-695.
[3] N.G. Bichan, E.N. Ovchenkova, M.S. Gruzdev, T.N. Lomova // J. Struct. Chem. 2018, 59, 711-719.
[4] N.G. Bichan, E.N. Ovchenkova, V.A. Mozgova, N.O. Kudryakova, T.N. Lomova // Rus. J. Inorg. Chem. 2019, 64, 605–614.
[5] N.G. Bichan, E.N. Ovchenkova, V.A. Mozgova, N.O. Kudryakova, M. S. Gruzdev, T.N. Lomova // Rus. J. Phys. Chem. A. 2020, 94, 1159–1166.

Table S2. The chemical shifts of H_β and H_o in cobalt(II) porphyrins and their supramolecular systems with pyrrolidino[60]/[70]fullerenes.

Complex	**H_β, ppm**	**H_o, ppm**	ref
CoTPP	15.94 br.s.	13.16 br.s.	[1]
$(PyC_{60})_2$CoTPP*	13.50 br.s.	9.88 br.s.	[1]
CoTIPP	16.06 br.s.	13.21 br.s.	[2]
$(PyC_{60})_2$CoTIPP	14.31 br.s.	10.97 br.s.	[2]
CoTBPP	16.05 br.s.	13.24 br.s.	[3]
$(PyC_{60})_2$CoTBPP	14.62 br.s.	11.40 br.s.	[3]
CoDTBCP	16.29 br.s., 15.05 br.s.	12.11 br.s.	this work
$(PyC_{60})_2$CoDTBCP	14.42 m	10.09 br.s.	this work
(Py_2C_{70})CoDTBCP	16.01 br.s., 14.89 br.s.	12.08 br.s.	this work

[1] N.G. Bichan, E.N. Ovchenkova, V.A. Mozgova, N.O. Kudryakova, T.N. Lomova // Rus. J. Inorg. Chem. 2019, 64, 605–614.
[2] N.G. Bichan, E.N. Ovchenkova, V.A. Mozgova, N.O. Kudryakova, M. S. Gruzdev, T.N. Lomova // Rus. J. Phys. Chem. A. 2020, 94, 1159–1166.
[3] N.G. Bichan, E.N. Ovchenkova, M.S. Gruzdev, T.N. Lomova // J. Struct. Chem. 2018, 59, 711-719.

Figure S3. The transformation of the UV-vis spectrum of the CoDTBCP – 5.49 × 10^{-5} M PyC_{60} mixture in toluene at 298 K during 1000 seconds.

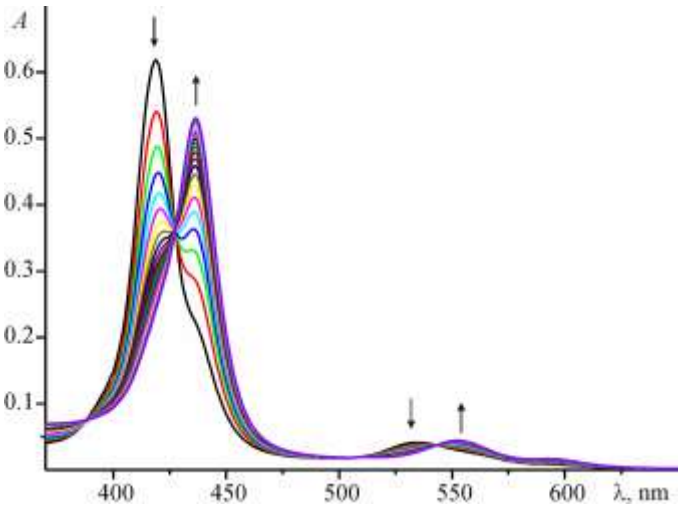


Figure S4. The plots of log(($A_0 - A_\infty$)/($A_\tau - A_\infty$) *vs* τ for the reaction of CoDTBCP with PyC_{60} in toluene at 298 K.

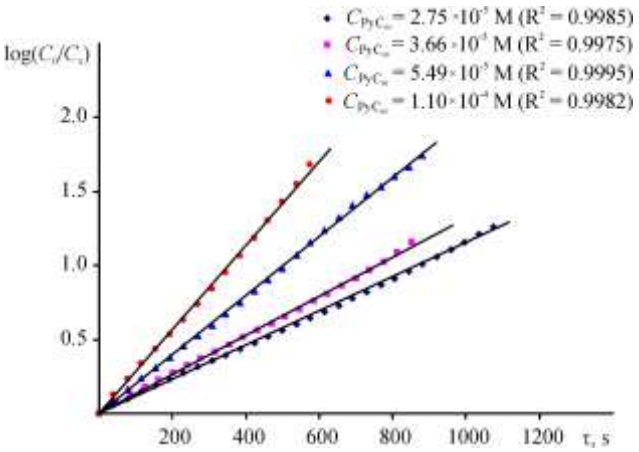


Figure S5. The plot of logk_{obs} *vs* log$C_{PyC_{60}}$ for the reaction of CoDTBCP with PyC_{60} in toluene at 298 K.

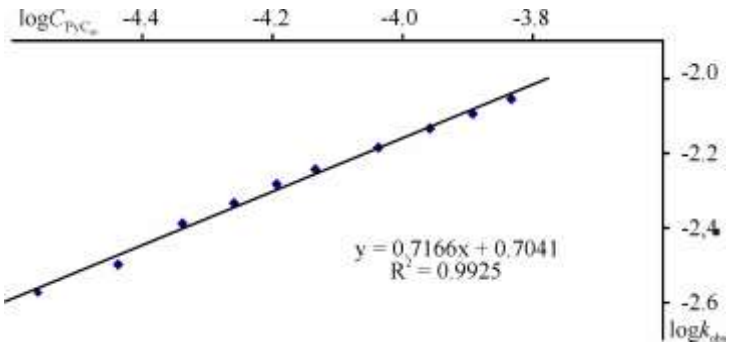


Figure S6. The plots of log((*A*$_0$ – *A*$_\infty$)/(*A*$_\tau$ – *A*$_\infty$) *vs* τ for the reaction of CoDTBCP with Py_2C_{70} in toluene at 298 K.

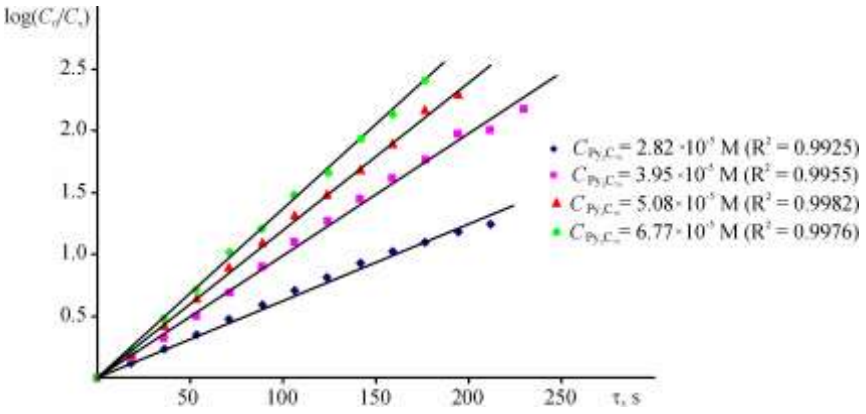


Figure S7. The plot of log*k*$_{obs}$ *vs* log$C_{Py_2C_{70}}$ for the reaction of CoDTBCP with Py_2C_{70} in toluene at 298 K.

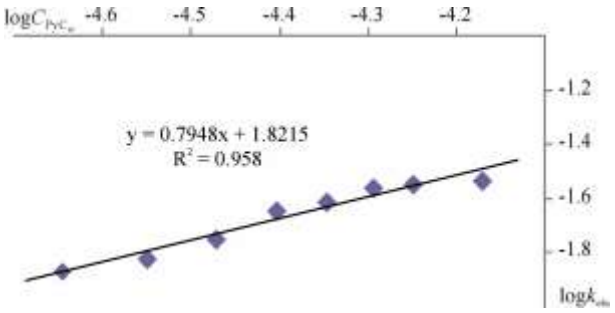


Figure S8. The IR spectra of CoDTBCP (black) and its triad with Py_2C_{70} (green) in KBr. Bands corresponding to vibrations of Py_2C_{70} are denoted with asterisks.

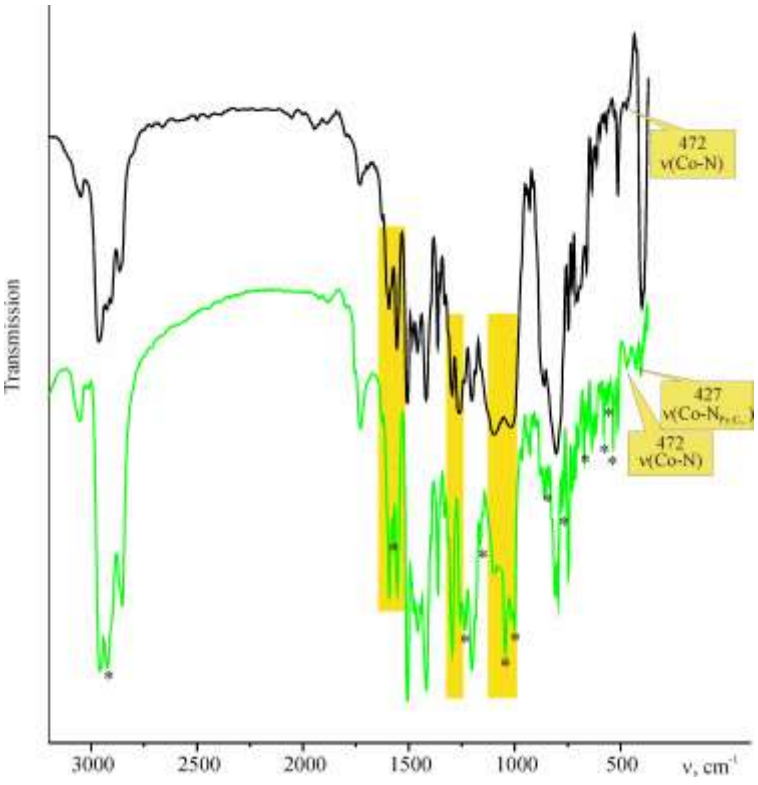


Figure S9. The ^{1}H NMR spectrum of CoDTBCP (*a*), its triad, (PyC_{60})$_2$CoDTBCP (*b*), and its dyad, (Py_2C_{70})CoDTBCP (*c*) in $CDCl_3$.

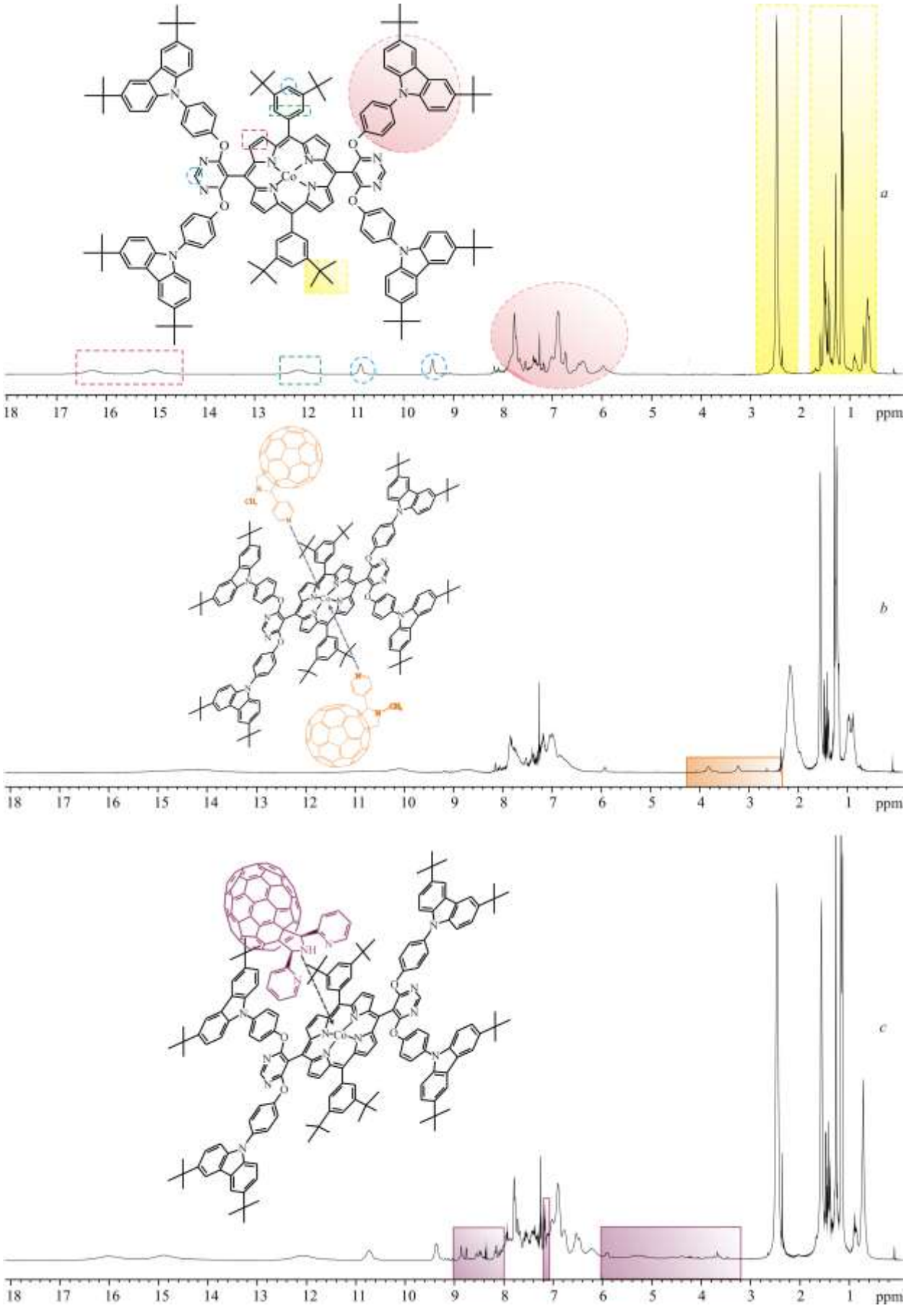
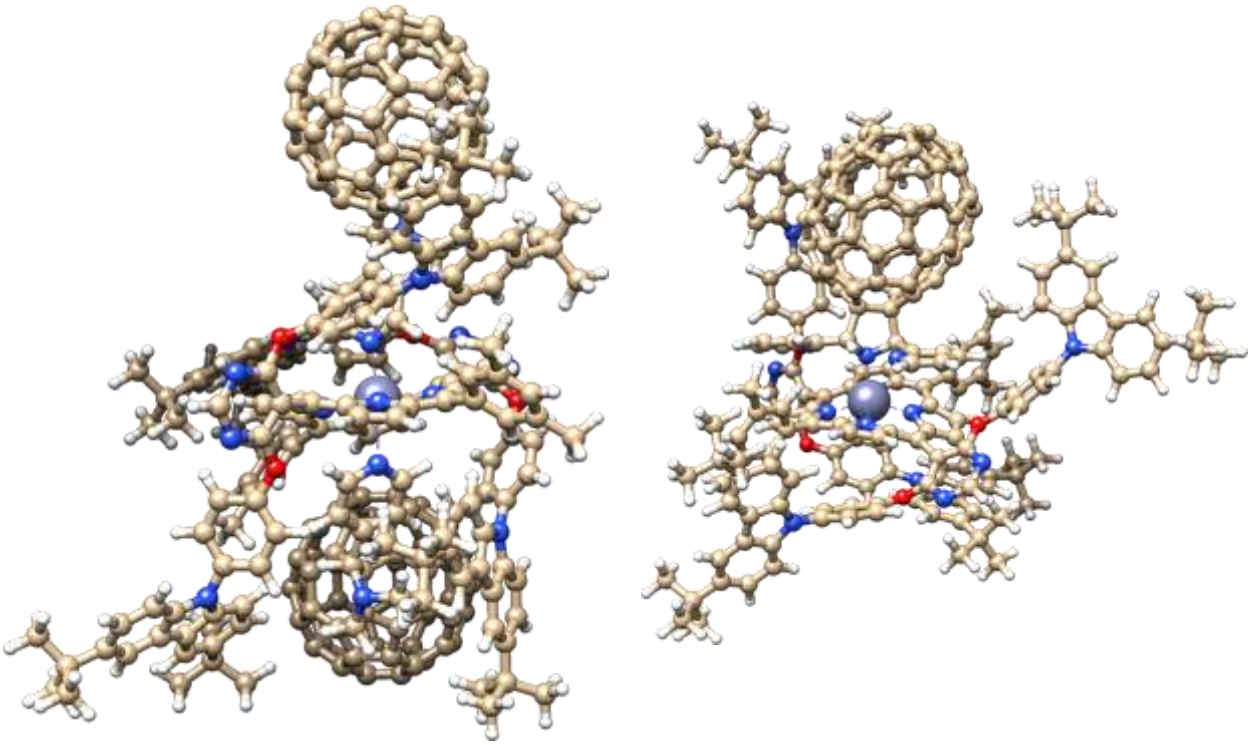
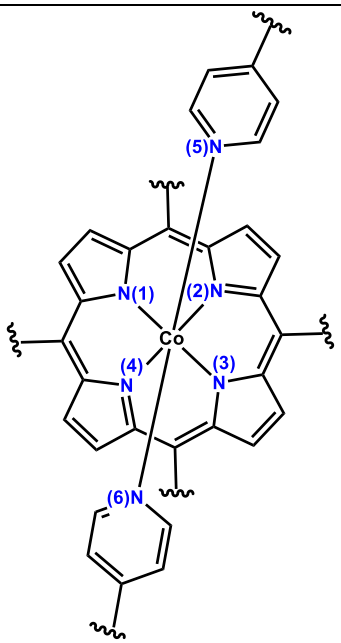


Figure S10. The optimized structures of $(PyC_{60})_2$CoDTBCP (*a*) and (Py_2C_{70})CoDTBCP (*b*).



a *b*

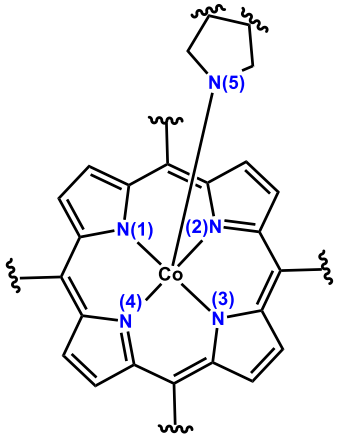
Table S3. The structural parameters (bond lengths, angles, and bonding energy (E_b)) of $(PyC_{60})_2$CoDTBCP and (Py_2C_{70})CoDTBCP.



$(PyC_{60})_2$CoDTBCP

	Bond length, Å		**Angle, °**	**E_b, kJ·mol^{-1}[a]**
Co–N(1)	2.056	**N(1)–Co–N(2)**	88.36	
Co–N(2)	2.037	**N(2)–Co–N(3)**	92.18	
Co–N(3)	2.016	**N(3)–Co–N(4)**	89.52	220
Co–N(4)	2.044	**N(4)–Co–N(1)**	89.09	
Co–N(5)	2.158	**N(1)–Co–N(3)**	169.55	

Co–N(6)	2.409	**N(2)–Co–N(4)**	174.72	
		N(1)–Co–N(5)	86.11	
		N(2)–Co–N(5)	81.37	
		N(3)–Co–N(5)	83.65	
		N(4)–Co–N(5)	93.84	
		N(1)–Co–N(5)	91.51	
		N(2)–Co–N(5)	91.71	
		N(3)–Co–N(5)	98.90	
		N(4)–Co–N(5)	92.99	



(Py_2C_{70})CoDTBCP

	Bond length, Å		**Angle, °**	***E*$_b$, kJ·mol^{-1}[a]**
Co–N(1)	2.055	**N(1)–Co–N(2)**	86.13	117
Co–N(2)	2.055	**N(2)–Co–N(3)**	87.39	
Co–N(3)	2.024	**N(3)–Co–N(4)**	88.32	
Co–N(4)	2.037	**N(4)–Co–N(1)**	87.50	
Co–N(5)	2.315	**N(1)–Co–N(3)**	161.34	
		N(2)–Co–N(4)	146.56	
		N(1)–Co–N(5)	90.36	
		N(2)–Co–N(5)	107.99	
		N(3)–Co–N(5)	108.29	
		N(4)–Co–N(5)	104.84	

[a]The bonding energy (E_b) was calculated as follows: $E_b = |E_{triad/dyad} - (E_{CoDTBC} + E_{PyC_{60}/Py_2C_{70}})|$.

Figure S11. Femtosecond transient absorption spectrum of CoDTBCP in toluene at the excitation wavelength of 400 nm (Insert: the time profile of transient peaks of CoDTBCP).