Supplementary Materials for

The *p*-Metal Porphyrins: From Specificity of Properties to Application in Medicine, Catalysis, and Optoelectronics

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Table S1. The rate constants and the activation parameters of the MgPs dissociation in *tert*-butanol – trifluoroacetic acid[1,2]

Complex	C_{acid} 10^3, mol/L	k_{obs}, s^{-1}	Activation energy, kJ/mol	Activation entropy, J/(mol K)
Chlorophyll	0.2	1.14 ± 0.06	56 ± 2	117 ± 8
	2.0[a]	0.0036	-	-
Mg proto-porphyrin	0.2	0.50 ± 0.03	51 ± 1	134 ± 4
Mg meso-porphyrin	0.2	2.4 ± 0.1	43 ± 2	159 ± 6

[a] C_{CH_3COOH} 10^3, mol/L in ethanol

1. Drobisheva A.N., Karmanova L.P., Berezin B.D. *Zhurnal Fizicheskoi Khimii* **1977**, *51*, 1344-1348.
2. Berezin B.D., Drobisheva A.N. *Zhurnal Fizicheskoi Khimii* **1970**, *44*, 2804-2809.

Table S2. The kinetic parameters of the MPs dissociation in the concentrated sulphuric acid

Complex	*T*, K	k 10^4, L/mol s	Activation energy, kJ/mol	Activation entropy, J/(mol K)
(Cl)InTPP	298	0.36 10^{-2}	75 ± 11	-125 ± 32
	333	0.09 ± 0.01		-
	343	0.176 ± 0.01		
	353	0.42 ± 0.03		
(AcO)TlTPP	343	0.074	117 ± 12	-340 ± 36
	353	0.195		
	357	0.479		
	360	0.575		
	363	0.661		
$(OH)_2$SiTPP	298	2.0 10^{-4}	78	-140
	348	0.016		
	353	0.020		
	358	0.032		
$(Cl)_2$GeTPP	323	14 ± 2[a]		
	333	55 ± 10[a]		

[a] k 10^4, L^2/mol^2 s

Table S3. The kinetic stability (numerical *k* values at 298 K) of the main-group *meso*-tetraphenylporphin complexes in the concentrated sulphuric acid

Complex	$C_{H_2SO_4}$, mol/L	$k\ 10^4$, s^{-1}	Complex	$C_{H_2SO_4}$, mol/L	$k\ 10^4$, s^{-1}
(OH)AlP	[a]	stable	$(OH)_2$SiP	17.85	0.0040
(AcO)GaP	17.48	0.120	$(Cl)_2$GeP	[a]	0.200
(Cl)InP	17.60	0.065	$(Cl)_2$SnP	[a]	0.030
(OAc)TlP	17.53	0.390	$(OAc)_2$PbP	[a]	stable

[a]100%, monohydrate

Table S4. Methods for the synthesis, isolation and purification of complexes of H_2TPP and H_2TPC with *p*-metals

Complex	Complex-forming agent	Solvent	*T*, °C	Selection method	Purification method
(Cl)AlTPP	$AlCl_3$	Py	120	Precipitation by AcOH and H_2O adding	Double chromatography, Al_2O_3, $CHC1_3$
(OH)AlTPP	$AlCl_3$	PhOH	500	Extraction in $CHCl_3$, washing with water	Double chromatography, Al_2O_3, $CHC1_3$
(AcO)GaTPP	$Ga(AcO)_2(OH)$	PhOH	500	Extraction in $CHCl_3$, washing with water	Chromatography, $A1_2O_3$, $CHCl_3$
(AcO)TlTPP	$Tl(AcO)_3$ in TGF	$CHCl_3$:TGF 5:1	313	Solvent evaporation	Chromatography, $A1_2O_3$, $CHCl_3$
$(OH)_2$SiTPP	$SiCl_4$	Py[a]	458	Extraction in $CHCl_3$, washing with water	Double chromatography, Al_2O_3, $CHC1_3$
Cl_2GeTPP	$GeCl_4$	quinoline	510	Extraction in hexane	Chromatography, $A1_2O_3$, $CHCl_3$
$(Cl)_2$SnTPP	$SnCl_2$	DMF	150	Precipitation by H_2O adding	Double chromatography, Al_2O_3, $CHC1_3$
(Cl)InTPP	} $InCl_3$	Phenol	190	Extraction in $CHCl_3$, washing with water	Chromatography, $A1_2O_3$, $CHCl_3$
(Cl)InTPC		Phenol	190	Extraction in $CHCl_3$, washing with water	Chromatography, $A1_2O_3$, $CHCl_3$, then C_2H_5OH-1% AcOH

Synthesis

Di(acetate)(5,10,15,20-tetraphenylporphinato)lead(IV), $(AcO)_2$PbTPP + (5,10,15,20-tetraphenylclorinato)lead(II), PbTPC. $Pb(AcO)_2$ and H_2TPP were placed in a solvent (pyridine, dimethylformamide, or acetic acid) in a certain variable ratio (Table S5). The mixture was heated and refluxed until complete conversion. The latter was monitored by the disappearance of porphyrin absorption bands in the UV-vis spectrum of the mixture probe. The end of the reaction was achieved in about 60 minutes. When the reaction was carried out in the AcOH medium, complete conversion was observed during the first 30 minutes, then the spectrum of the reaction mixture passed into the one of H_2TPP. The solvent was removed by vacuum distillation. The solid residue was dissolved in chloroform and washed repeatedly with water to remove excess salt. The reaction product solution was chromatographed on a L40/250 Al_2O_3 column using chloroform. Two zones were observed: bright green and pink. The first zone was washed off the column with the mixture of chloroform - benzene in a volume ratio of 1: 1. The second one which was firmly held at the start was washed off with dimethylformamide. During chromatography of the product after synthesis in DMF with a mixture of chloroform - benzene (1: 1), the appearance of trace amounts of H_2TPP was observed in all cases, which were first washed off the adsorbent. The reaction product in an acetic acid medium is pure H_2TPP. The individuality of the compounds isolated from the green and pink zones was proved by thin layer chromatography on Silufol plates with chloroform - benzene (1: 1). **$(AcO)_2$PbTPP·Py**. UV-Vis (chloroform) λ_{max} nm: 650 sh, 605 sh, 584, 530 sh, 444, 345 sh, 310 (with alternating absorption intensity VII > VI > V > III > IV > II > I. IR (KBr) ν_{max} cm^{-1}: vibrations of pyrrole rings 798 (γ C-H), 976 (ν C-C, δ C-H, ν C-N), 1340 (ν C-N), 1440 (ν C=N), 1523 (vibrations of pyrrole rings in the plane); vibrations of benzene rings 704, 778 (γ C-H), 1072, 1159 (δ C-H), 2860, 2920 (ν C-H); pyridine frequencies 700, 1460, 1560; Pb-N_{Py} 405 and Pb-$N_{porphyrin}$ 450; symmetric and asymmetric stretching vibrations O-C-O 1655 and 1734. The frequencies ν C=C of benzene rings are not identified due to the absorption of Py in this region. Found: Pb 20.15, $C_{48}H_{34}O_4N_4Pb$·Py requires 20.37%. **PbTPC.** UV-Vis (chloroform) λ_{max} (lgε) nm: 652 (3.37), 609 (3.52), 551 (3.25), 516 (3.4), 466 (4.33), 419 (4.5), 355 (3.76). IR (KBr) ν_{max} cm^{-1}: vibrations of pyrrole rings 796 (γ C-H), 1000 (ν C-C, δ C-H, ν C-N), 1328 (ν C-N), 1440 (ν C=N), 1525 (vibrations of pyrrole rings in the plane); vibrations of benzene rings 704 and 752 (γ C-H), 1072 and 1176 (δ C-H), 1470, 1576 and 1592 (ν C=C), 2860, 2920 and 3020, 3080 (ν C-H); Pb-$N_{porphyrin}$ 416. ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 8.87, 8.89 (H_β); 8.16 (H_o); 7.73 (H_m); 7.73 (Hp). Found: Pb 24.74, $C_{44}H_{30}N_4Pb$ requires 25.2%.

Table S5. The yield of $Pb(AcO)_2$ - H_2TPP reaction products

Solvent	$Pb(AcO)_2$:H_2TPP mol: mol	Yield, %		
		PbTPC	$(AcO)_2$PbTPP Py	H_2TPP
Py	2:1	97.5	2.5	-
Py	5:1	97.0	3.0	-
Py	20:1	95.4	4.6	-
Py	30:1	96.0	4.0	-
AcOH	20:1	-	0	100
DMF	11:1	92.2	2.8[a]	5
Py	20:1[b]	92.9[б]	7.1[b]	-
Py	20:1[c]	100[c]	0[c]	-

[a] yield of $(AcO)_2$PbTPP DMF, [b] in the dark, [c] in N_2

(Chloro)(5,10,15,20-tetraphenylporphinato)indium(III), (Cl)InTPP + (chloro)(5,10,15,20-tetraphenylchlorinato)indium(III), (Cl)InTPC. 1.5 g of phenol and 0.59 g (0.96 mmol) of H_2TPP were placed in a 50-ml pear-shaped flask equipped with a reflux condenser. The mixture was heated to reflux (230 °C) and then 0.55 g (2.49 mmol) $InCl_3$ was introduced into the flask. The synthesis was completed after 10 minutes (the time for which the maximum product yield is reached). The reaction mixture was cooled, dissolved in chloroform, and washed several times with warm water in a separator funnel to remove phenol. The chloroform solution was concentrated and loaded onto an Al_2O_3 column soaked in chloroform. Three zones were observed during chromatography with $CHCl_3$. The first and second zones (H_2TPP and (Cl)InTPP, respectively) were sequentially washed off with chloroform. Chloroform was distilled off. H_2TPP was used to synthesize other batches of complexes. The (C1)InTPP yield is 0.164 g (30%). The third zone ((C1)InTPC) was washed off with 10% ethanol solution of AcOH. An equal volume of $CHC1_3$ and water were added to the complex solution until the chloroform layer separated. (C1)InTPC transformed into chloroform was separated, washed with water, and distilled off. The (C1)InTPC yield is 0.06 g (10%). **(Cl)InTPP**. UV-Vis (chloroform) λ_{max} ($\varepsilon \cdot 10^{-5}$) nm: 420 (0.947), 520 (0.039), 559 (0.213), 599 (0.089), 628 (0.020). ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 9.07 (8H, H_β), 8.38 and 8.12 (8H, H_o), 7.80 (8H, H_m), 7.75 (4H, H_p). Found: In 15.0 ± 0.35, $C_{44}H_{28}N_4InCl$ requires 15.05. Melting point: it is stable when heated in air to 400 °C. Specific electrical conductivity $\sigma = 6\ 10^{-14}$ and $3\ 10^{-13}$ Ohm^{-1} cm^{-1} in air and in vacuum, respectively. (C1)InTPP is soluble in $CHC1_3$, DMF, DMSO, 12-18 M H_2SO_4; slightly soluble in ethanol, ether, insoluble in water. **(Cl)InTPC**. UV-Vis (chloroform) λ_{max} ($\varepsilon \cdot 10^{-5}$) nm: 427 (1.26), 525 (0.0637), 568 (0.0545), 599 (0.0812), 628 (0.180). (The spectrum completely coincides with the one of the substance obtained from H_2TPC and $InCl_3$ in phenol represented bellow.) ^{1}H NMR ($CDCl_3$, 298 K) δ_H ppm: 8.43 (d, 4H, C_4H_2N) and 8.45 (t, 6H,

C_4H_4N), 7.96 and 8.19 (8H, H_o), 7.70 (8H, H_m), 7.70 (4H, H_p). Found: In (14 ± 1), $C_{44}H_{30}N_4InCl$ requires 15.01. Melting point: it turns into (Cl)InTPP at 350 °C. Specific electrical conductivity $\sigma = 2\ 10^{-13}$ and $4\ 10^{-12}$ Ohm-1 cm-1 in air and in vacuum, respectively. Stability: dissociation rate constant *k* is $1.04\ 10^{-4}\ s^{-1}$ at 298 K in the AcOH – 2M H_2SO_4 mixture. (C1)InTPC is soluble in $CHCl_3$, ethanol, slightly soluble in AcOH, insoluble in water.

Counter synthesis

(Chloro)(5,10,15,20-tetraphenylchlorinato)indium(III), (Cl)InTPC. 1.5 g of phenol, 0.6 g (0.96 mmol) of H_2TPC, and 0.55 g (2.49 mmol) of $InC1_3$ were sequentially introduced in a pear-shaped flask with a capacity of 50 ml. The contents of the flask were refluxed at 230 °C for 10 minutes. Metalloporphyrin was extracted into chloroform, washed with warm water, and chromatographed on $A1_2O_3$ using an ethanol - chloroform mixture (1: 10 vol%). The yield of (C1) InTPC is 9.6%. When heated to 350 °C, the complex transforms into (C1)InTPP. (C1)InTPC is soluble in $CHC1_3$, ethanol, slightly soluble in AcOH, insoluble in water.

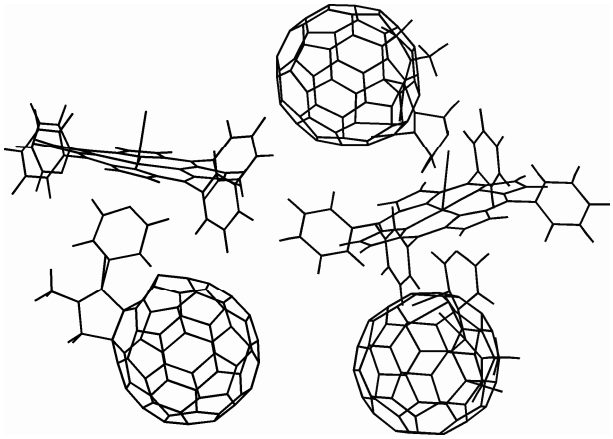

Figure S1. The optimized structure of the dyad (left) and the triad (right) based on indium(III) *meso*-teraphenylporphyrin and 1-methyl-2-(pyridin-4'-yl)-3,4-fullero[60]pyrrolidine

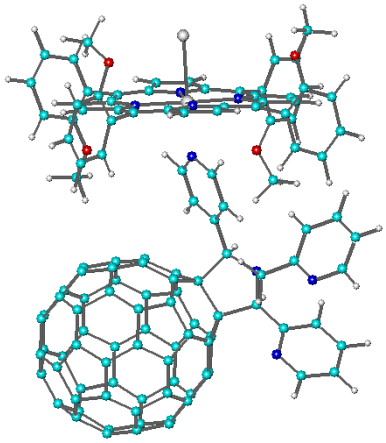

Figure S2. The optimized structure of the dyad based on *meso*-tetra(1-methyloxi)phenylporphin and 1-(pyridine-2-yl)methyl-2-(pyridin-4-yl)-5-(pyridine-2-yl)-3,4-fullero[60]pyrrolidine