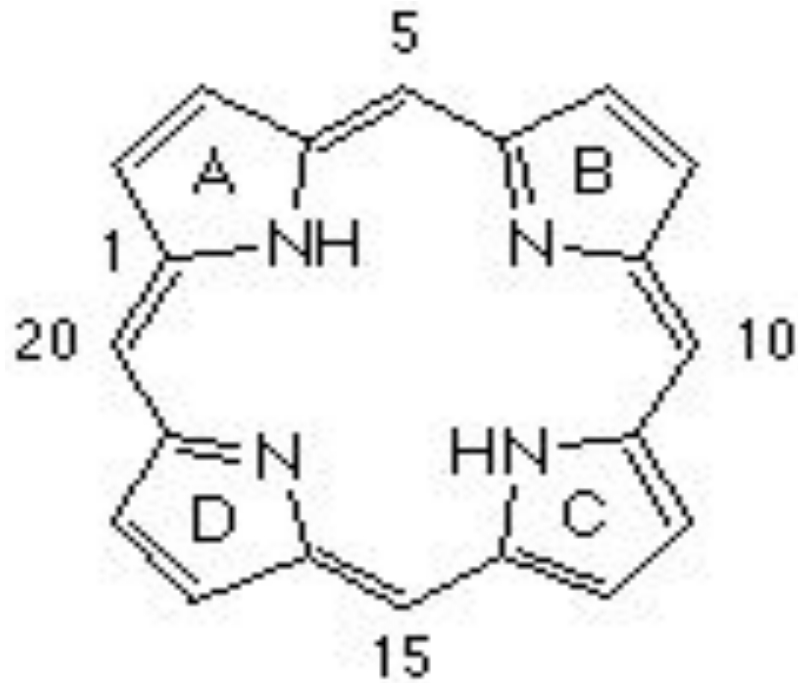
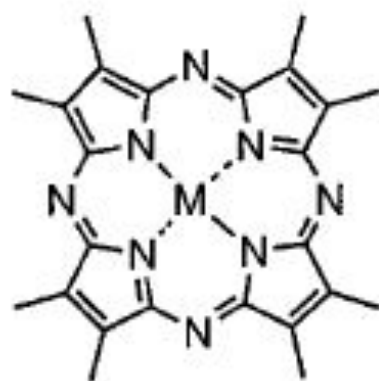


# Порфирины

# Порфирины

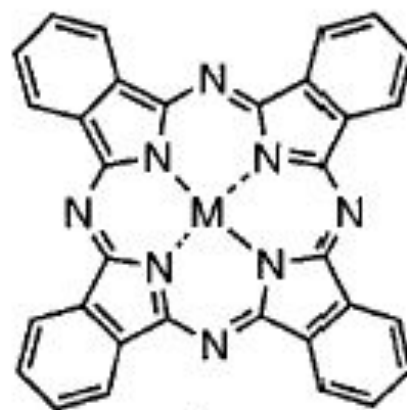


**Porphyrin**



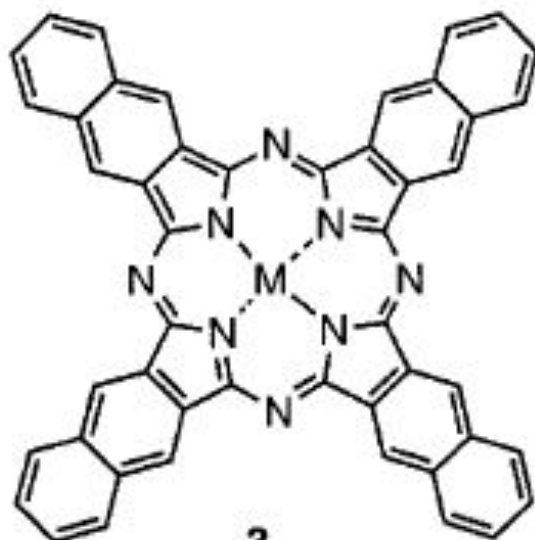
1

Porphyrazine



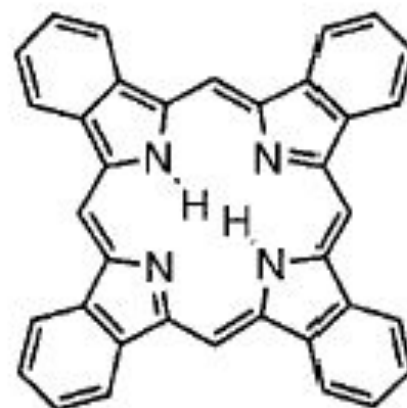
2

Phthalocyanine



3

Naphthocyanine



4

Tetrabenzoporphyrin

# Порфирины

**Гем** (от греч. haima — кровь), небелковая часть гемоглобина

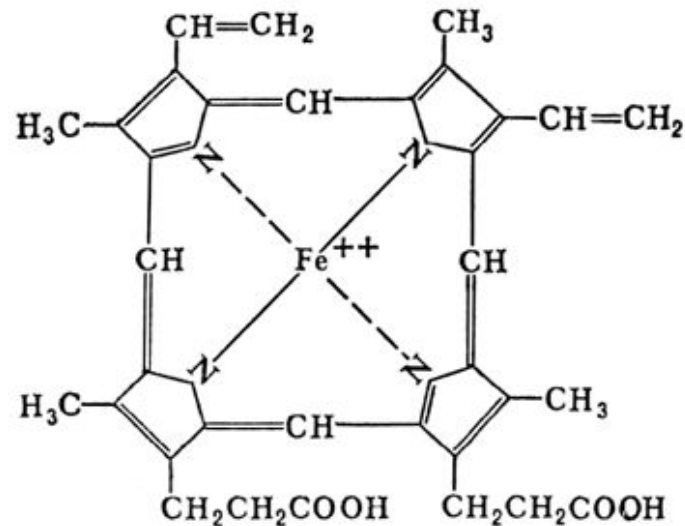
Функции в организме:

перенос  $O_2$  из органов дыхания к тканям

за счет координации с Fe (оксигенация);

перенос  $CO_2$  из тканей в органы дыхания

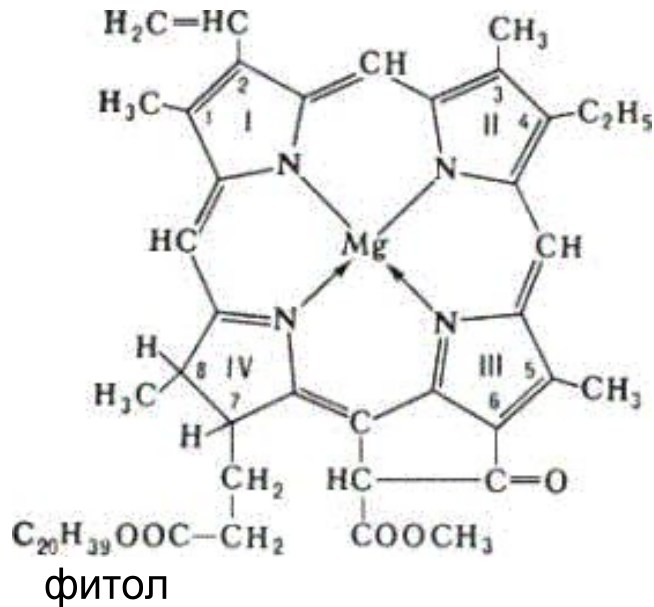
в результате реакции  $CO_2$  с  $NH_2$ -группами глобина (карбгемоглобин)



**Цитохромы**, сложные железосодержащие белки:

клеточное дыхание, фотосинтез, митохондриальное окисление

# Порфирины

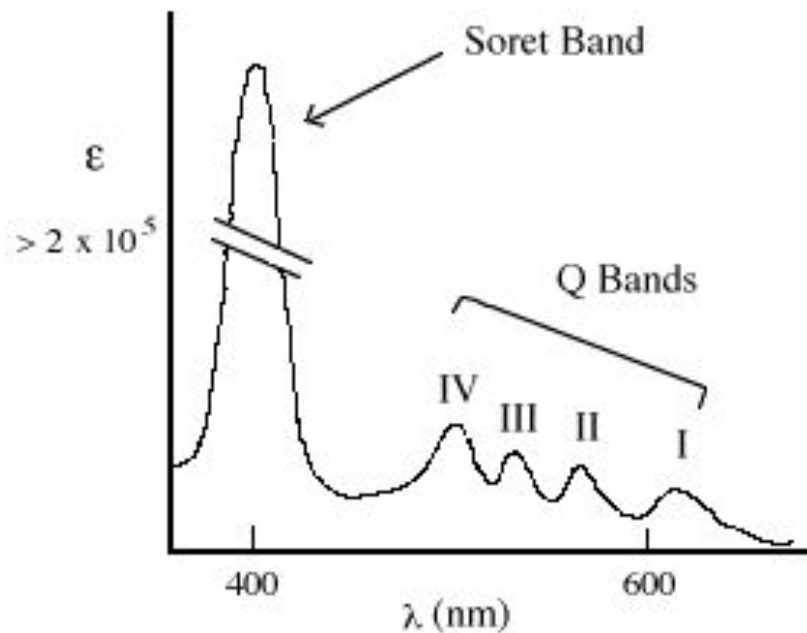


Поглощая квант света, молекула Хлорофила переходит в возбуждённое состояние (длительность жизни синглетного возбуждённого состояния около  $10^{-9}$  сек), которое может переходить в долгоживущее триплетное возбуждённое состояние с длительностью жизни до  $10^{-3}$  сек. Возбуждённые светом молекулы Хлорофилла способны переносить электрон от молекулы-донора к молекуле-акцептору.

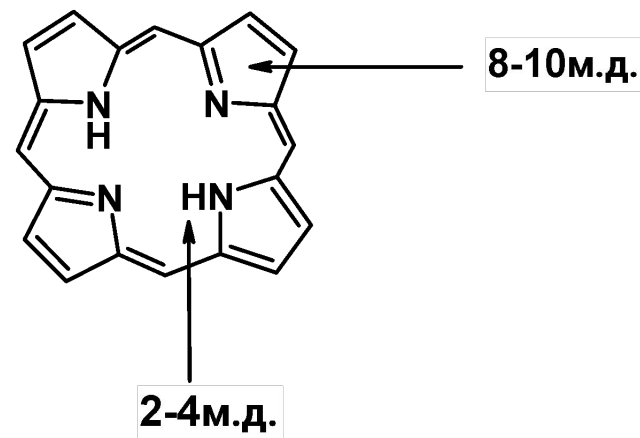
**Входит в состав хлорофилла** - зелёный пигмент растений, с помощью которого они улавливают энергию солнечного света и осуществляют фотосинтез. Локализован в особых клеточных структурах — хлоропластах или хроматофорах и связан с белками и липидами мембран.

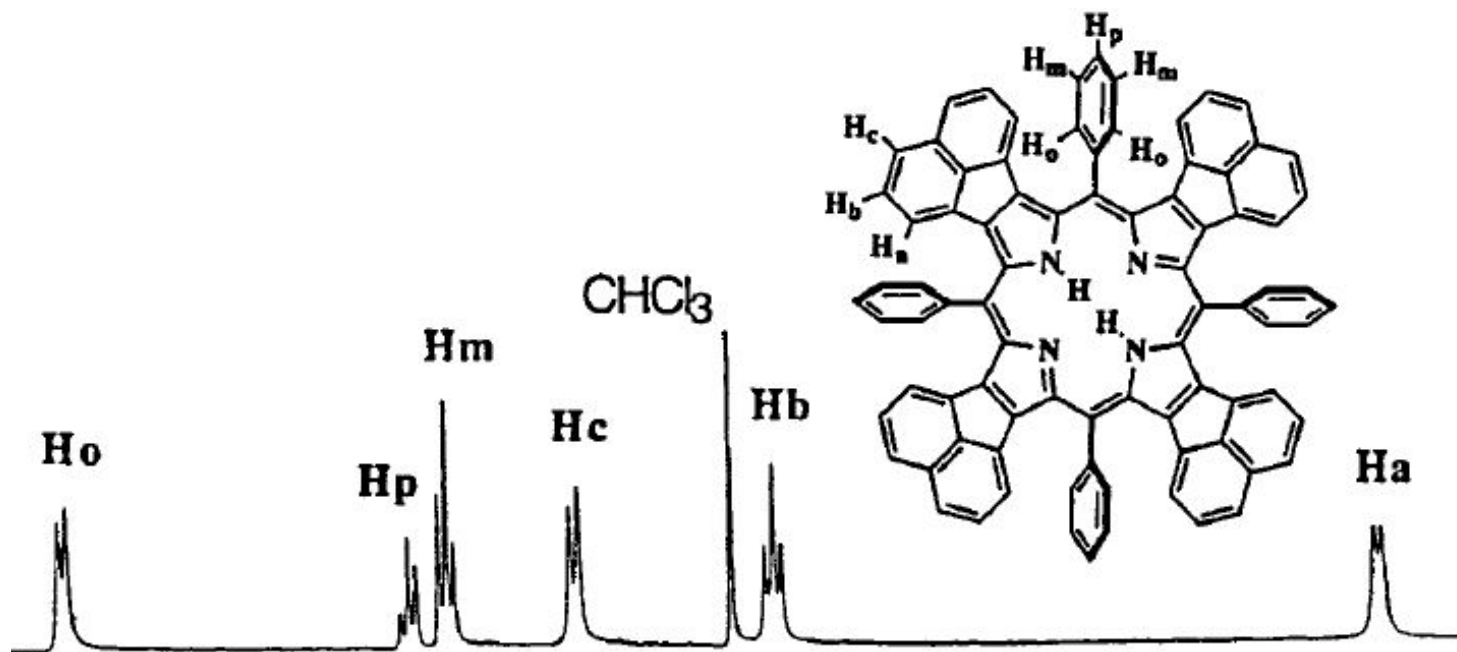
Свет, поглощаемый Х., вызывает в клетках также др. фотобиологические явления: индуцирует генерацию электрического потенциала на мембранах хлоропластов, влияет на движение одноклеточных организмов (фототаксис) и т.д

# Физические свойства порфиринов



*Typical UV-Visible absorption spectrum of a porphyrin*

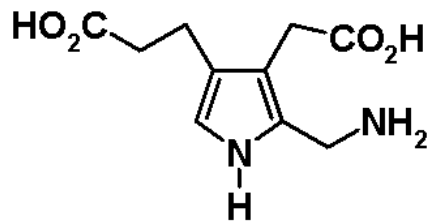




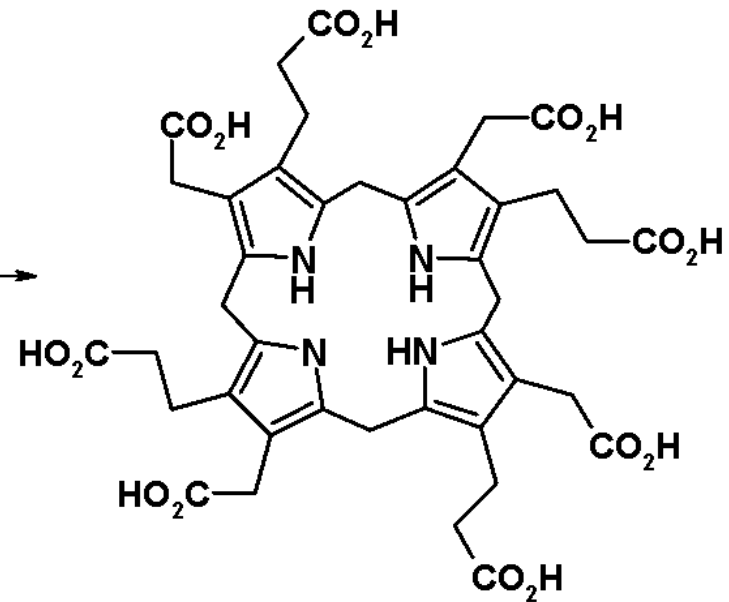
# Биосинтетические предшественники

конденсация глицина и янтарной кислоты

d-аминолевулиновая кислота



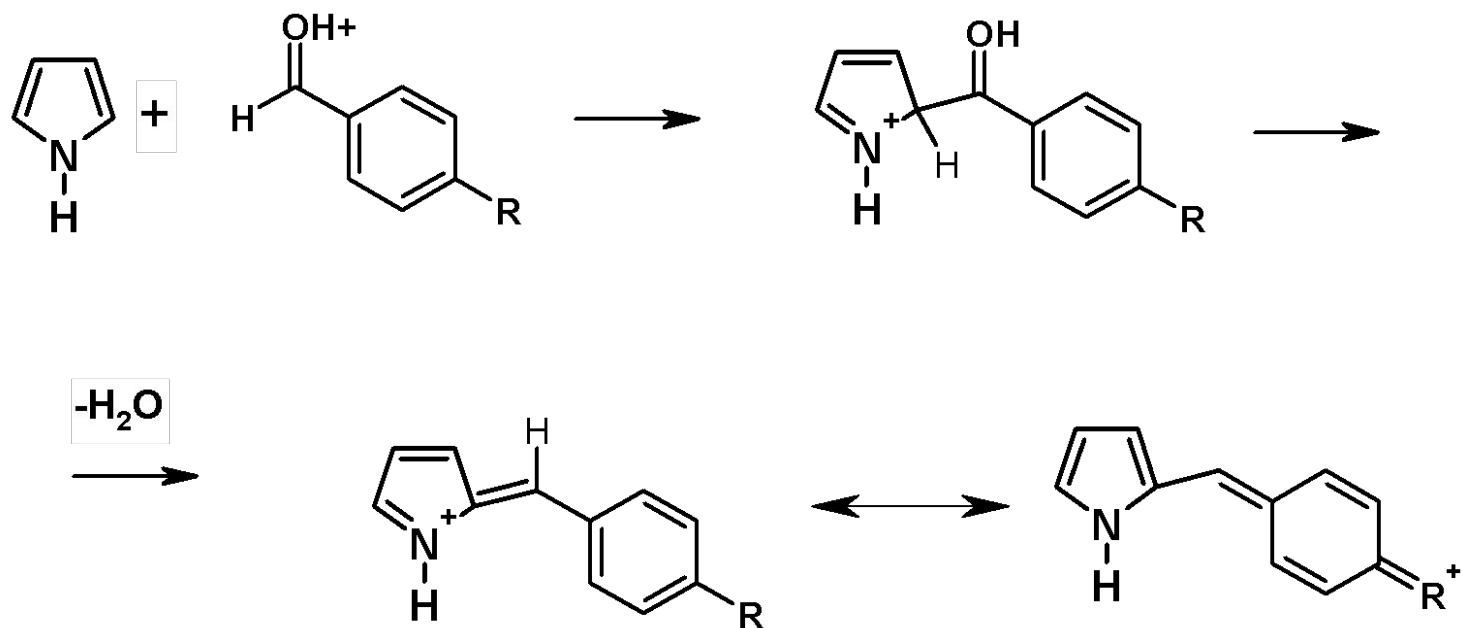
порфобилиноген



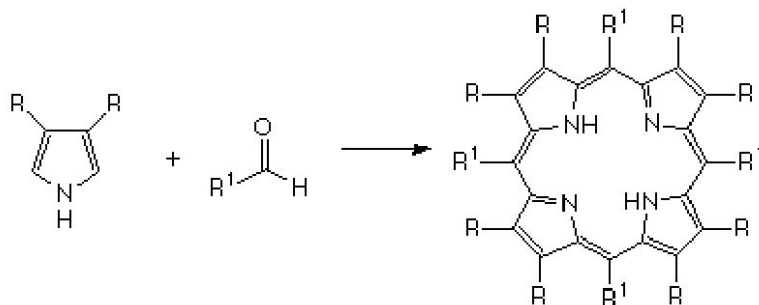
уропорфириноген



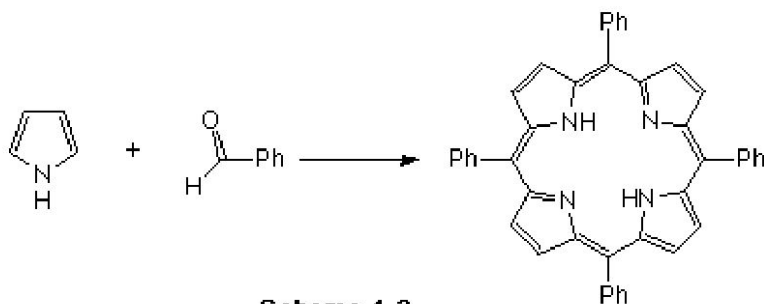
# Механизм реакции получения порфиринов



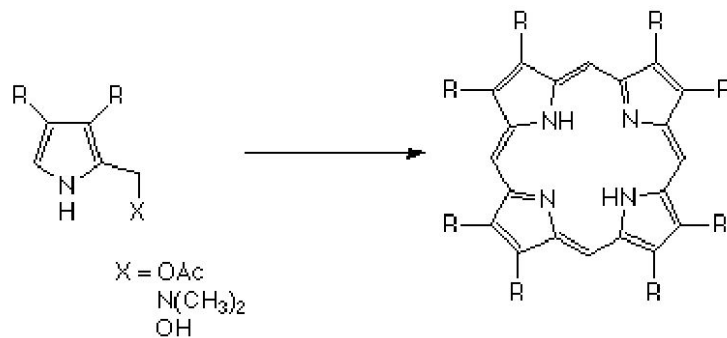
# Методы получения порфиринов



Scheme 1.1



Scheme 1.2

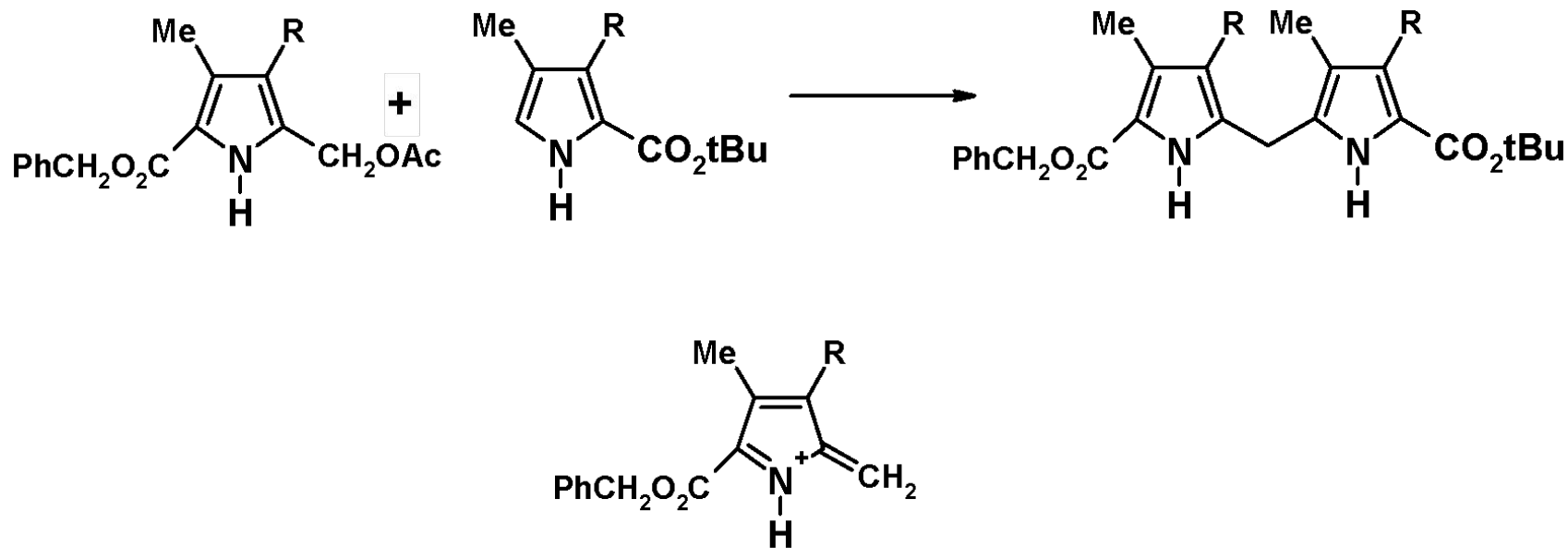


Scheme 1.3

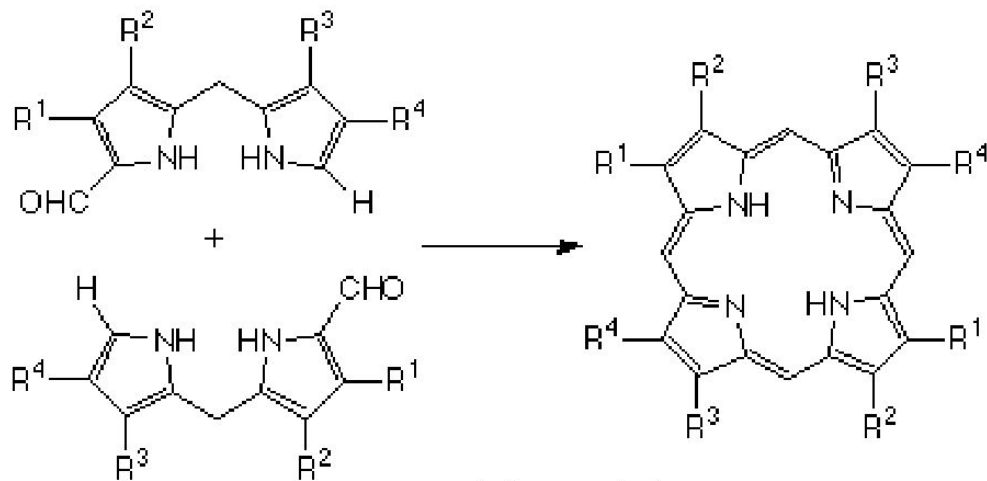
**Терамеризация  
пирролов в присутствии  
альдегидов**

**Конденсация  
ацетоксипирролов  
с аминопирролами**

# Методы получения дипирролов

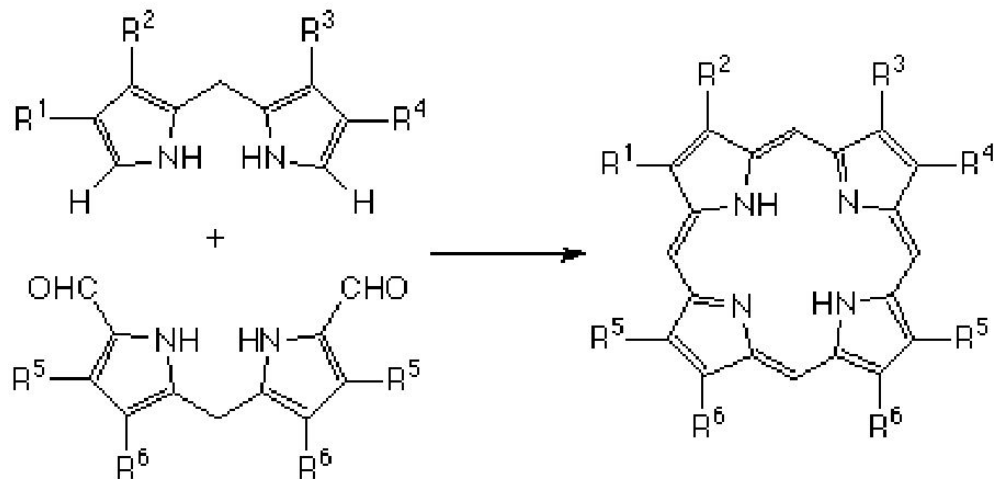


# Методы получения порфиринов



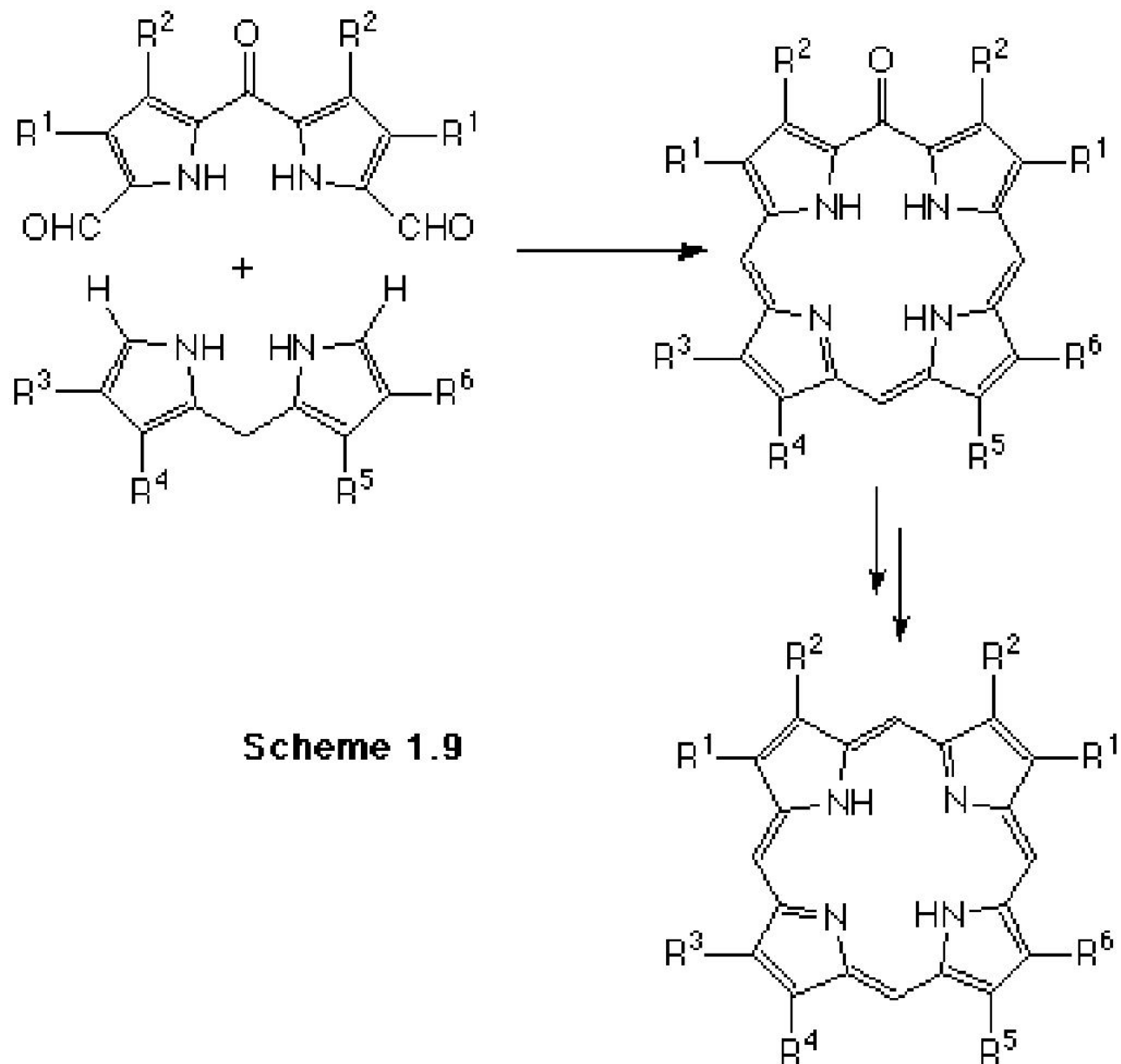
Scheme 1.7

**Самоконденсация  
дипирролов  
(MacDonald synthesis )**

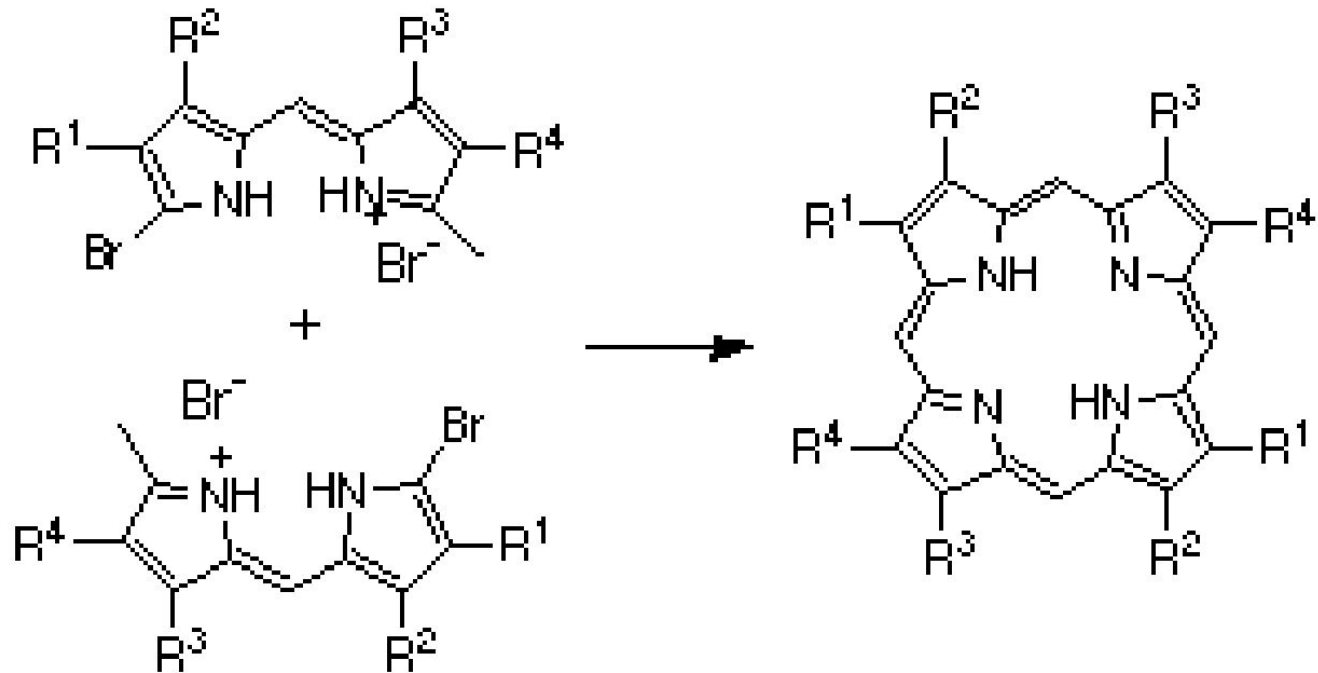


Scheme 1.8

# Методы получения порфиринов



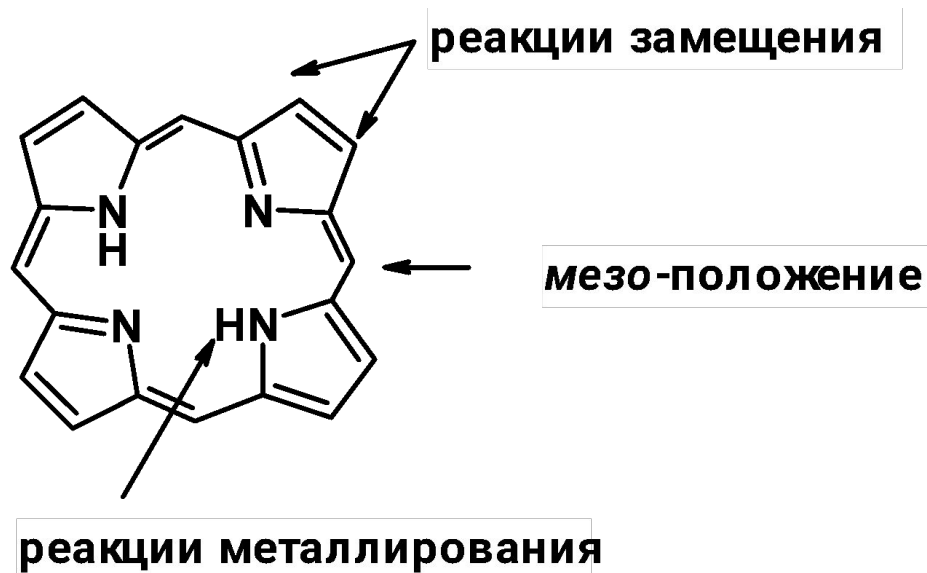
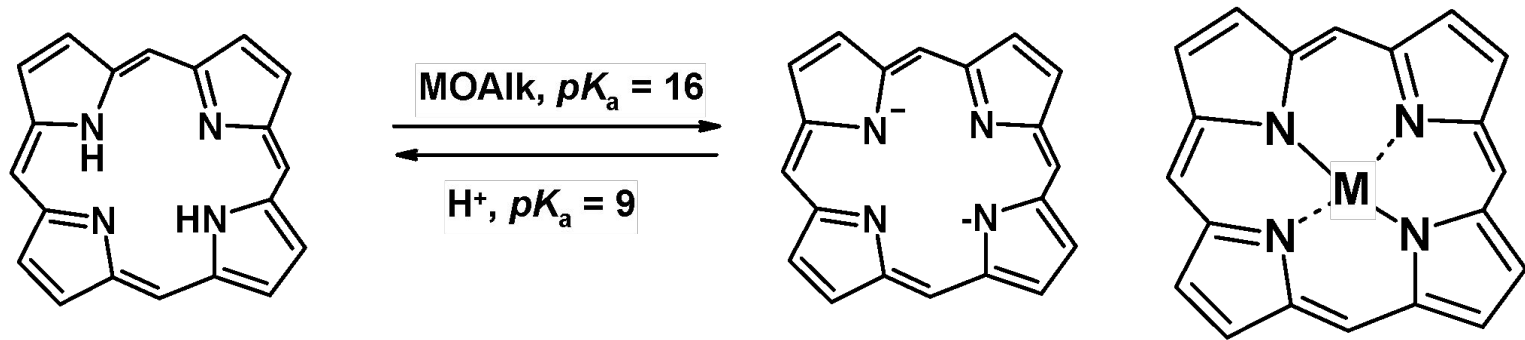
# Методы получения порфиринов

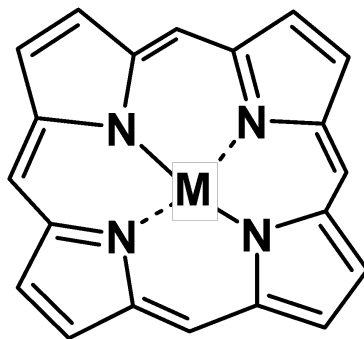


**Scheme 1.4**

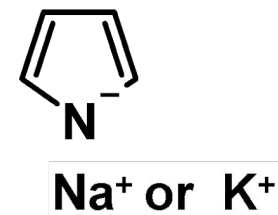
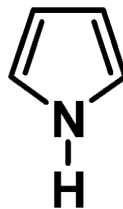
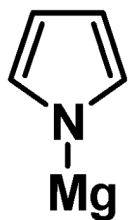
**Developed by Fischer**

# Химические свойства порфиринов



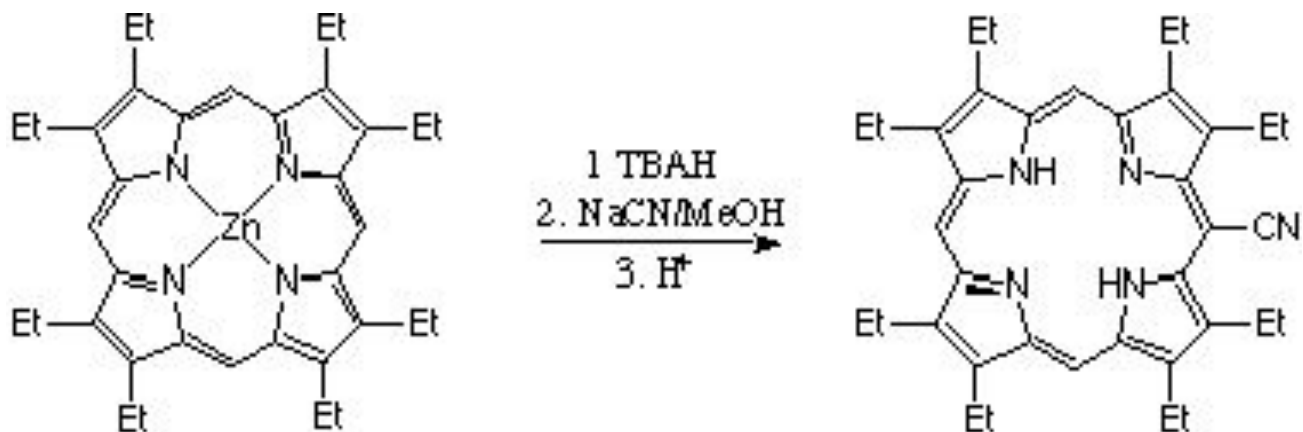


**Fe, Zn, Cu, Ni, Ru, Mg, Rh**



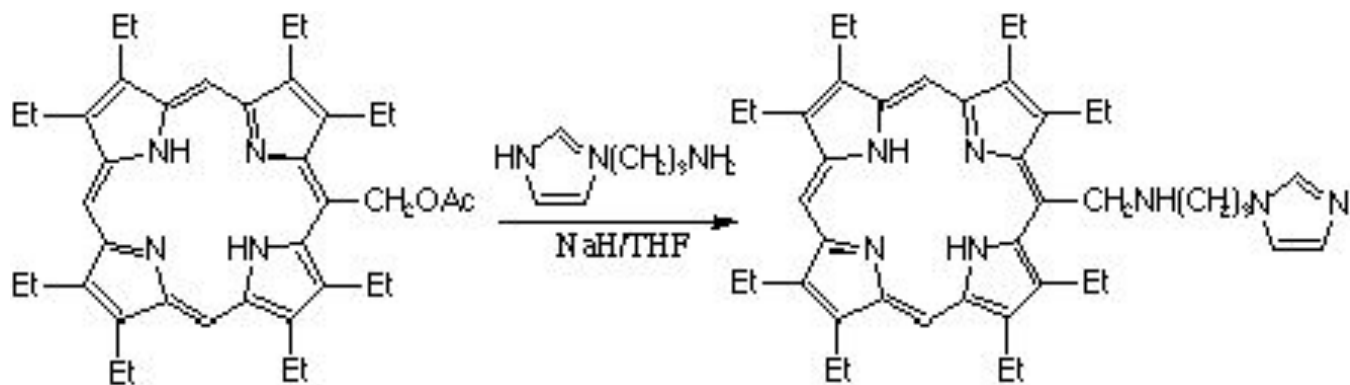


# Химические свойства порфиринов



Scheme 1

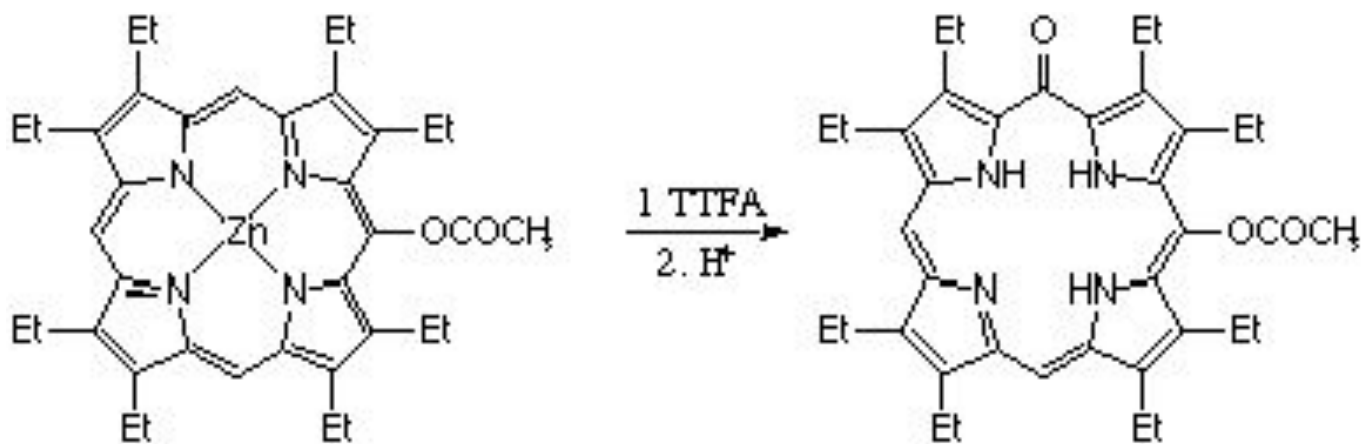
tris(p-bromophenyl)ammoniumyl hexachloroantimonate  
(TBAH)



Scheme 3

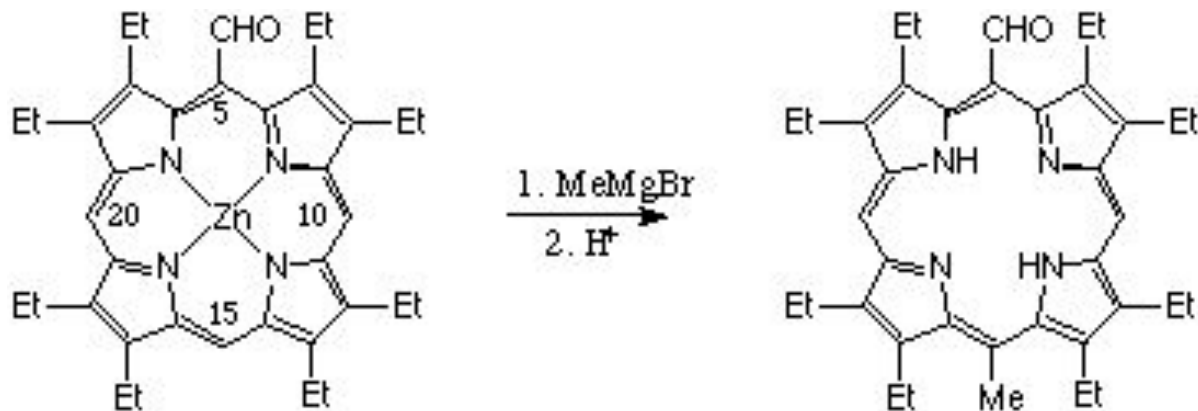
# Химические свойства порфиринов

thallium(III) trifluoroacetate

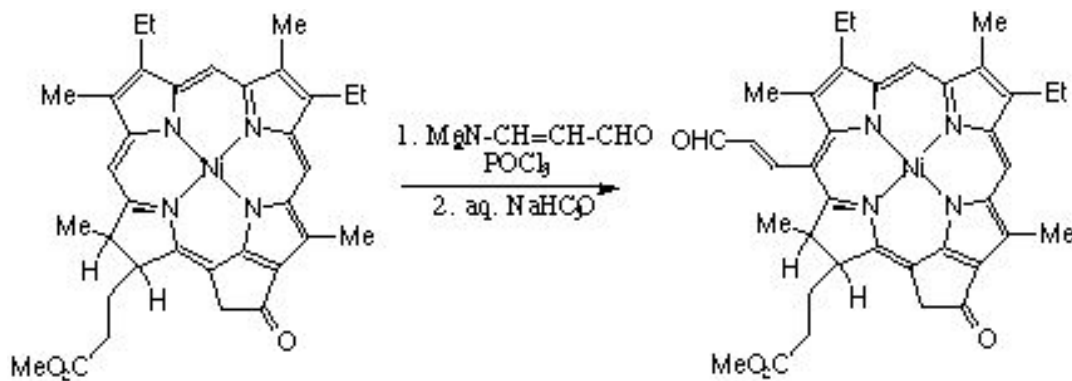


Scheme 4

# Химические свойства порфиринов



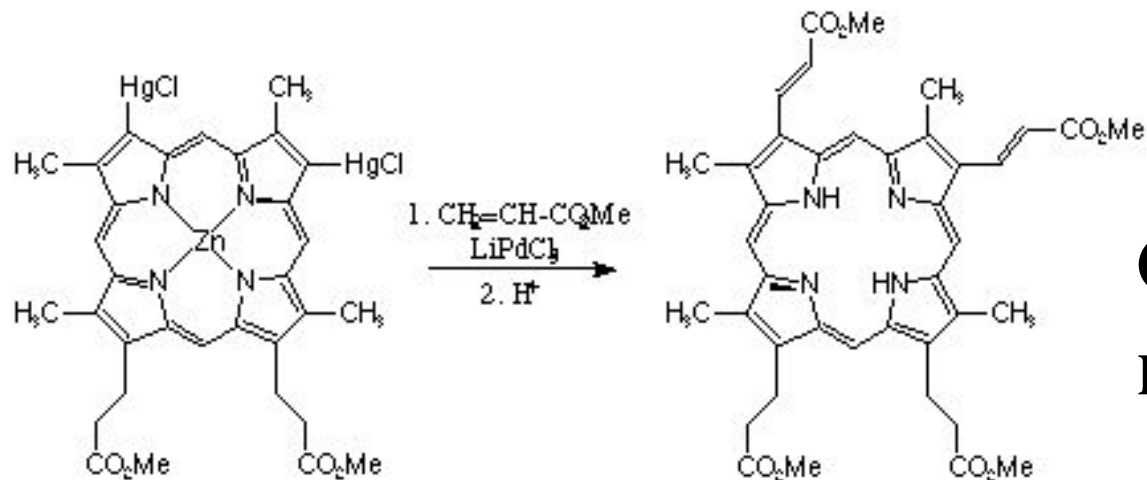
Scheme 5



Scheme 6

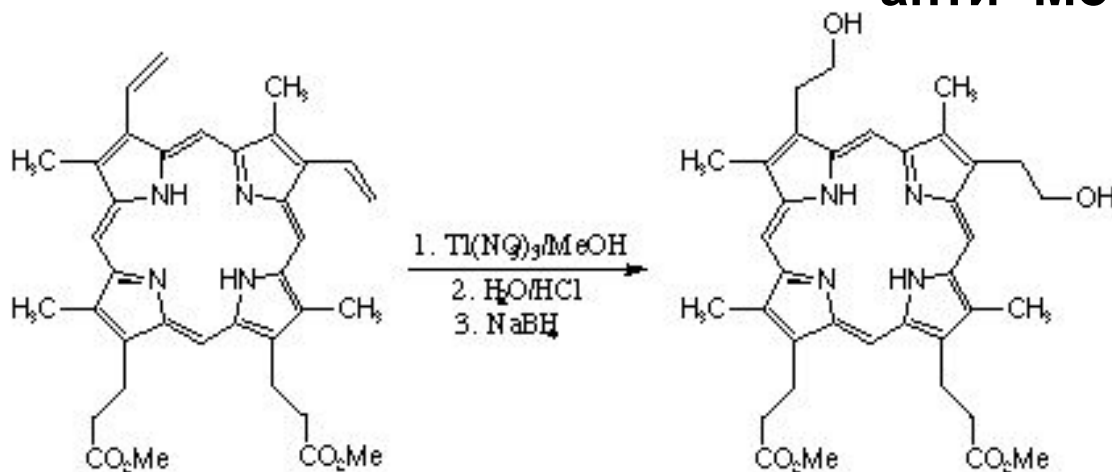
**Реакция  
Вильсмейера**

# Химические свойства порфиринов



Scheme 7

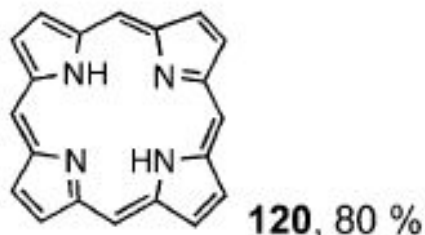
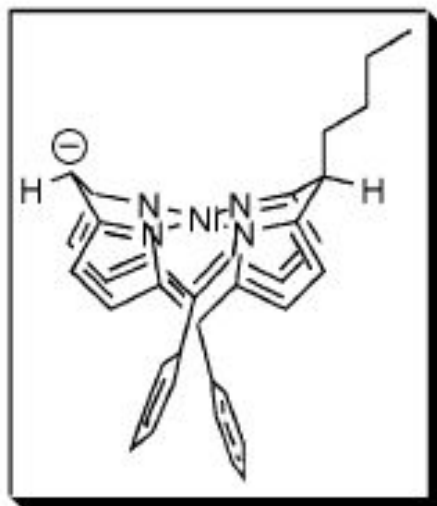
**Cross-coupling  
reaction**



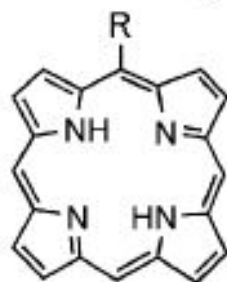
Scheme 8

**Гидроксилирование  
анти-Марковников**

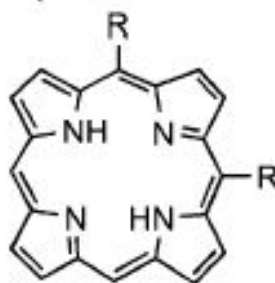
# Химические свойства порфиринов



1. THF, x RLi, 30 min  
2. H<sub>2</sub>O, DDQ



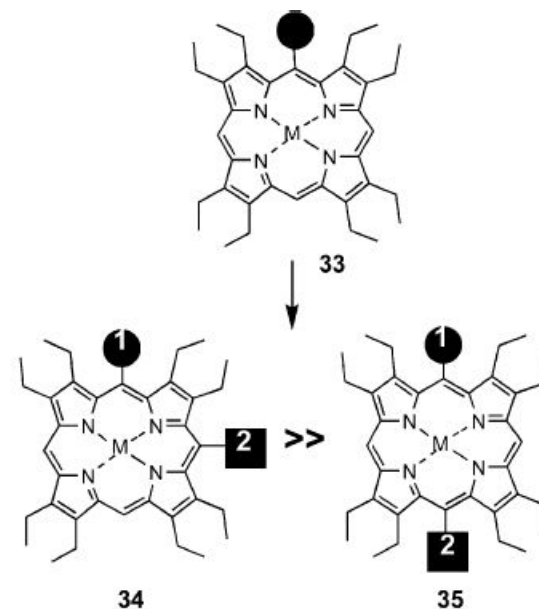
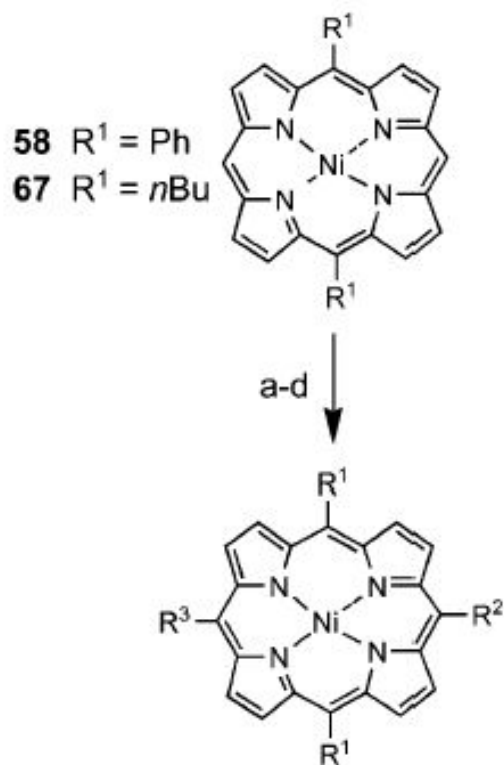
**121** R = *t*Bu, 4 %  
**122** R = *n*-hexyl, 48 %  
**123** R = Ph, 17 %  
**124** R = *n*Bu, 48 %  
**125** R = 2-MeO-Ph, 17 %



**126** R = *n*hexyl, 61 %  
**127** R = Ph, 43 %  
**128** R = *n*Bu, >95 %

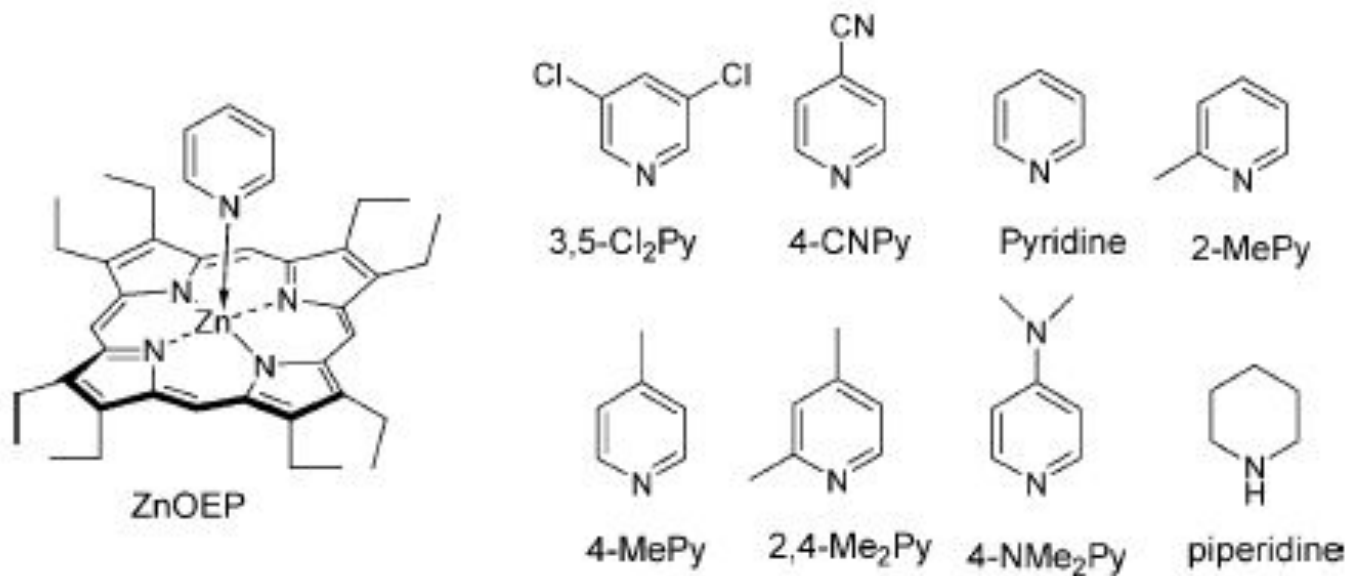
# Химические свойства порфиринов

**Scheme 9. One-Pot Two-Step Reaction of 5,15-Disubstituted Nickel(II) Porphyrins with  $R^2Li/R^3I^a$**



	$R^1$	$R^2$	$R^3$	yield (%)
<b>68</b>	Ph	<i>n</i> Bu	<i>n</i> Bu	92
<b>69</b>	Ph	Ph	<i>n</i> Bu	90
<b>70</b>	Ph	Bu	$CH_2CH_2CH_2CH_2I$	79
<b>71</b>	Ph	Ph	$CH_2CH_2CH_2CH_2I$	71
<b>72</b>	Ph	Bu	$CH_2CH_2CH_2CH_2OH$	48
<b>73</b>	Ph	Ph	$CH_2CH_2CH_2COOEt$	52
<b>74</b>	Ph	Ph	$CH_2CH_2CH_2CN$	80
<b>75</b>	<i>n</i> Bu	Ph	$CH_2CH_2CH_2CN$	62
<b>76</b>	Ph	Ph	$CH_2CH_2CH_2CH_2Br$	24

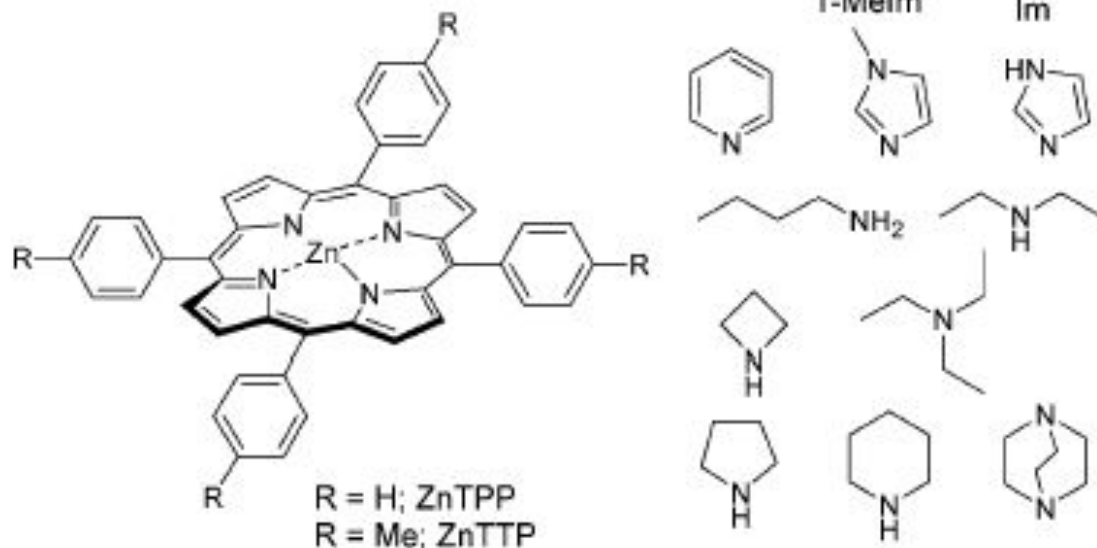
# Монокоординация пиридинов



**Table 1.** Association constants of ZnOEP with pyridine derivatives<sup>7a</sup>

Run	Porphyrin	Ligand <sup>b</sup>	pK <sub>a</sub> <sup>c</sup>	log <i>K</i>	<i>K</i> (M <sup>-1</sup> )
1	ZnOEP	3,5-Cl <sub>2</sub> Py	0.67 <sup>d</sup>	2.10	1.26 × 10 <sup>2</sup>
2	ZnOEP	4-CNPy	1.90	3.01	1.02 × 10 <sup>3</sup>
3	ZnOEP	Pyridine	5.17	3.37	2.34 × 10 <sup>3</sup>
4	ZnOEP	2-MePy	5.96	1.84	6.93 × 10 <sup>1</sup>
5	ZnOEP	4-MePy	6.00	3.67	4.68 × 10 <sup>3</sup>
6	ZnOEP	2,4-Me <sub>2</sub> Py	6.74	2.25	1.78 × 10 <sup>2</sup>
7	ZnOEP	4-NMe <sub>2</sub> Py	9.71 <sup>d</sup>	4.66	4.57 × 10 <sup>4</sup>
8	ZnOEP	Piperidine	11.1	4.55	3.56 × 10 <sup>4</sup>

# Монокоординация аминов

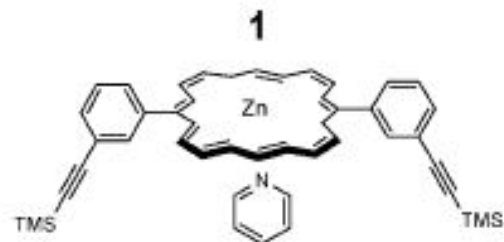
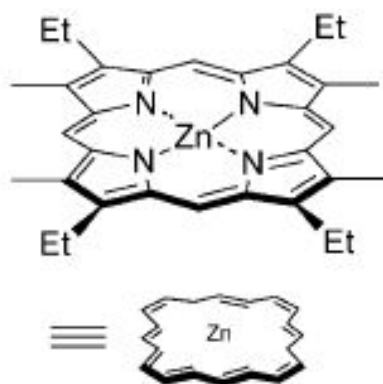


**Table 2.** Association constants of ZnTPP and ZnTTP with amines<sup>a</sup>

Run	Porphyrin	Ligand	pK <sub>a</sub> <sup>b</sup>	log K	K (M <sup>-1</sup> )	Solvent	Reference
1	ZnTTP	Pyridine	5.17	3.52	3.3 × 10 <sup>3</sup>	Toluene	8
2	ZnTTP	1-Melm	7.06	4.66	4.6 × 10 <sup>4</sup>	Toluene	8
3	ZnTPP	1-Melm	7.06	4.73	5.4 × 10 <sup>4</sup>	Toluene	9
4	ZnTPP	Im	6.99	4.73	5.4 × 10 <sup>4</sup>	Toluene	10
5	ZnTTP	<i>n</i> -BuNH <sub>2</sub>	10.64	4.4	2.5 × 10 <sup>4</sup>	Toluene	8
6	ZnTTP	Et <sub>2</sub> NH	10.8	3.15	1.4 × 10 <sup>3</sup>	Toluene	8
7	ZnTPP	Et <sub>3</sub> N	10.72	1.1	1.3 × 10 <sup>1</sup>	Benzene	11
8	ZnTTP	Azetidine	11.29	5.51	3.2 × 10 <sup>5</sup>	Toluene	8
9	ZnTTP	Pyrrolidine	11.3	3.32	2.1 × 10 <sup>3</sup>	Toluene	8
10	ZnTTP	Piperidine	11.1	4.84	6.9 × 10 <sup>4</sup>	Toluene	8
11	ZnTPP	Dabco <sup>c</sup>	8.60, 2.90	5.2	1.6 × 10 <sup>5</sup>	Benzene	11



# Дитопная координация пиридинов

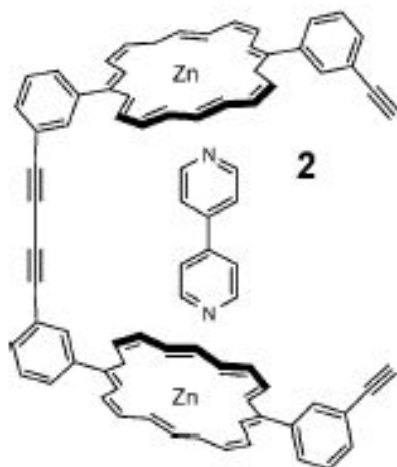


Py:  $K = 5 \times 10^3 \text{ M}^{-1}$

$\log K = 3.70$

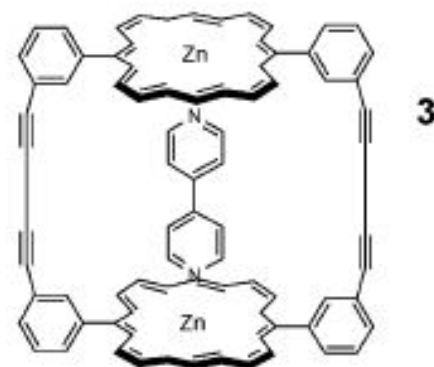
Bipy:  $K = 8 \times 10^3 \text{ M}^{-1}$

$\log K = 3.90$



Bipy:  $K = 6 \times 10^6 \text{ M}^{-1}$

$\log K = 6.78$

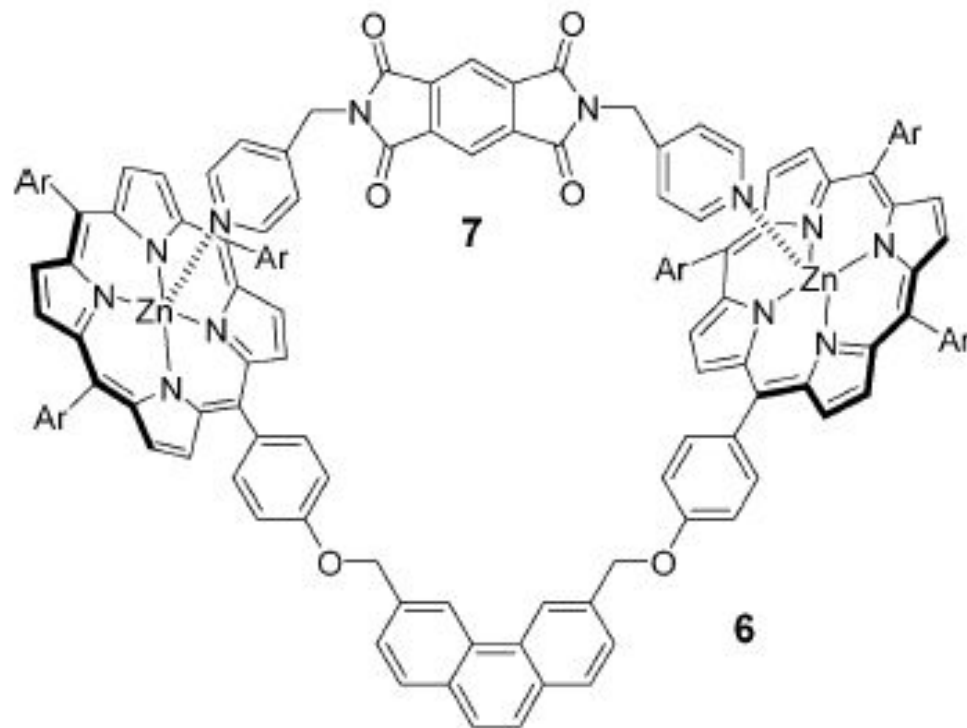


Bipy:  $K = 1 \times 10^9 \text{ M}^{-1}$

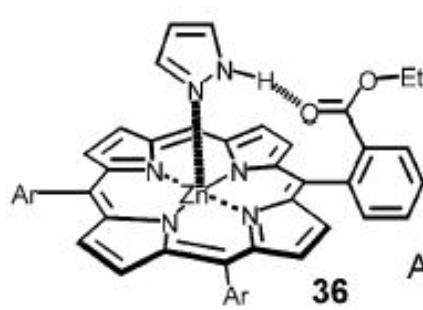
$\log K = 9$

$\text{CH}_2\text{Cl}_2, 303 \text{ K}$

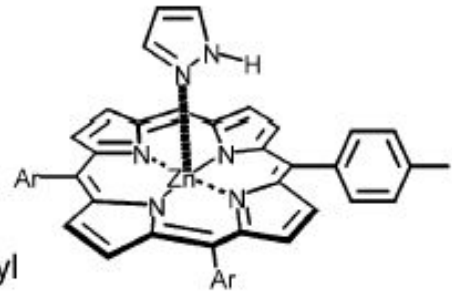
# Дитопная координация пиридинов



$K = 2.6 \times 10^6 \text{ M}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ , UV-vis  
 $\log K = 6.41$



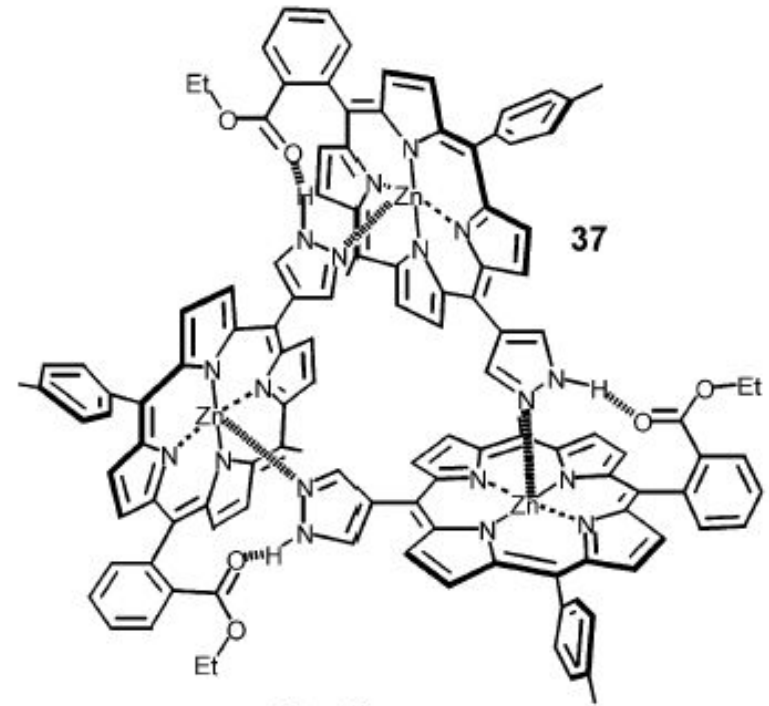
Ar = 4-tolyl



$K = 5.1 \times 10^4 \text{ M}^{-1}$ ,  $\log K = 4.71$

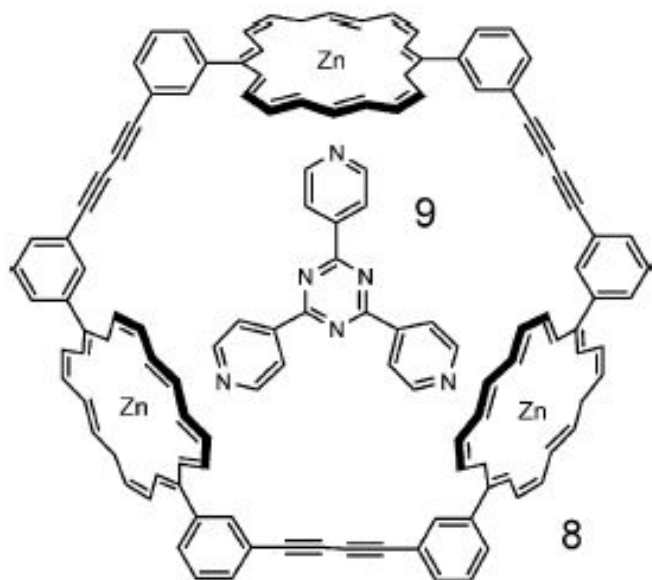
$K = 3.5 \times 10^3 \text{ M}^{-1}$ ,  $\log K = 3.54$

275 K,  $\text{CH}_2\text{Cl}_2$ , UV-vis

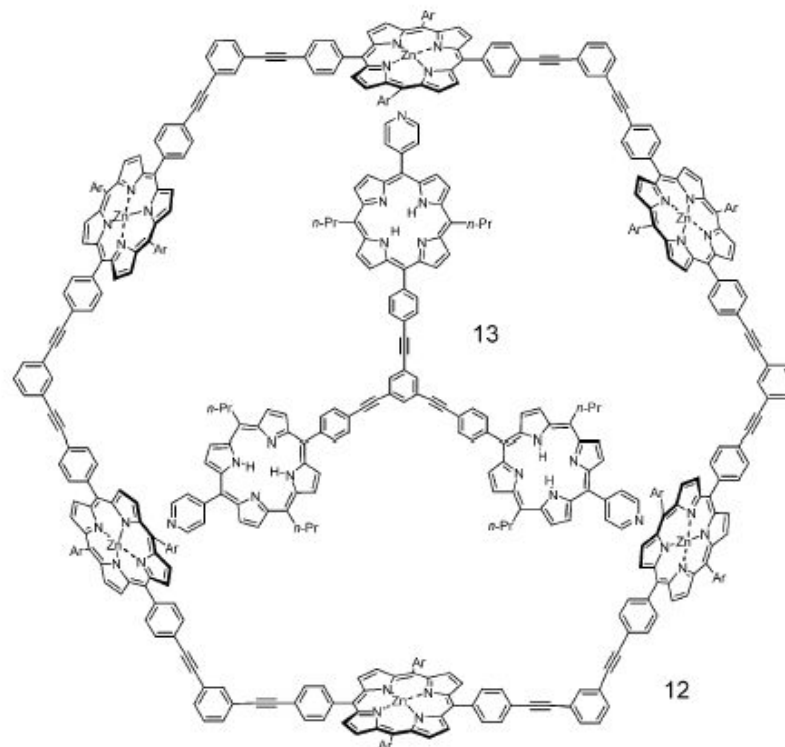


$K = 2.3 \times 10^{15} \text{ M}^{-2}$ , 275 K,  $\text{CH}_2\text{Cl}_2$ , UV-vis

# Политопная координация пиридинов

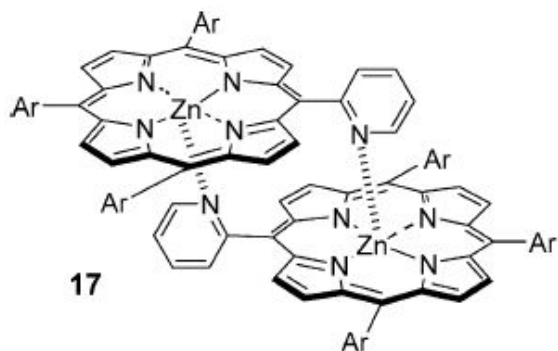


$K = 10^{10} \text{ M}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ , 303 K  
 $\log K = 10$



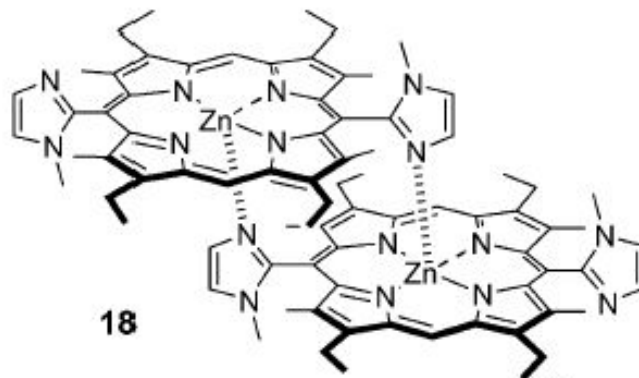
$K = 2.6 \times 10^9 \text{ M}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ , 293 K, UV-vis  
 $\log K = 9.41$

# Димеры порфиринов



Ar = 3,5-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup>, and others

concentration  $5.2 \times 10^{-5}$  M, CH<sub>2</sub>Cl<sub>2</sub>, rt



dimer was observed under conditions:  $10^{-9}$  M, CHCl<sub>3</sub>

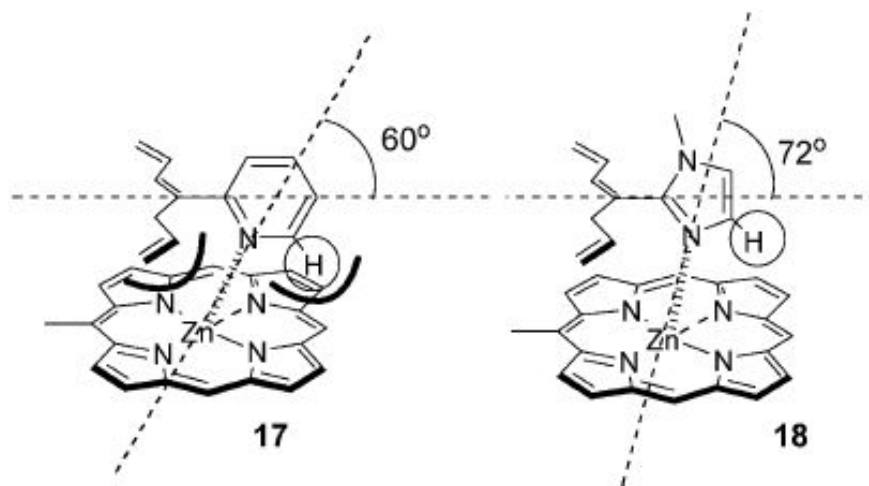
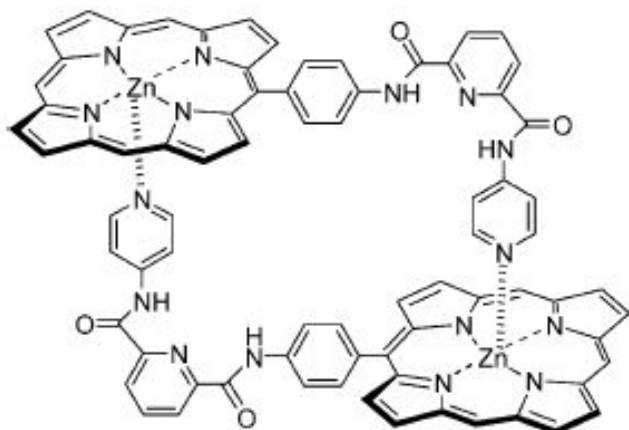
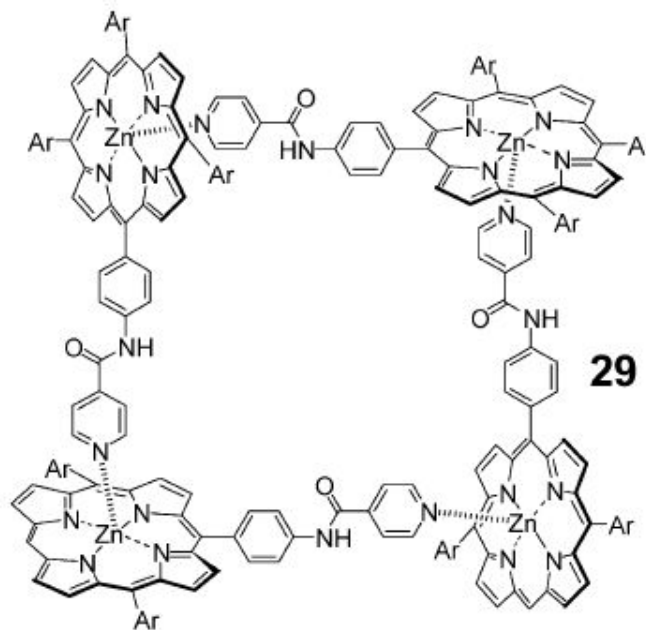


Figure 13. Comparison of coordination angle of dimers 17 and 18.

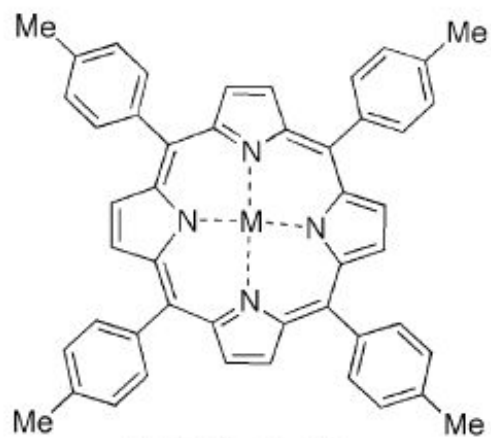
# Димеры порфиринов



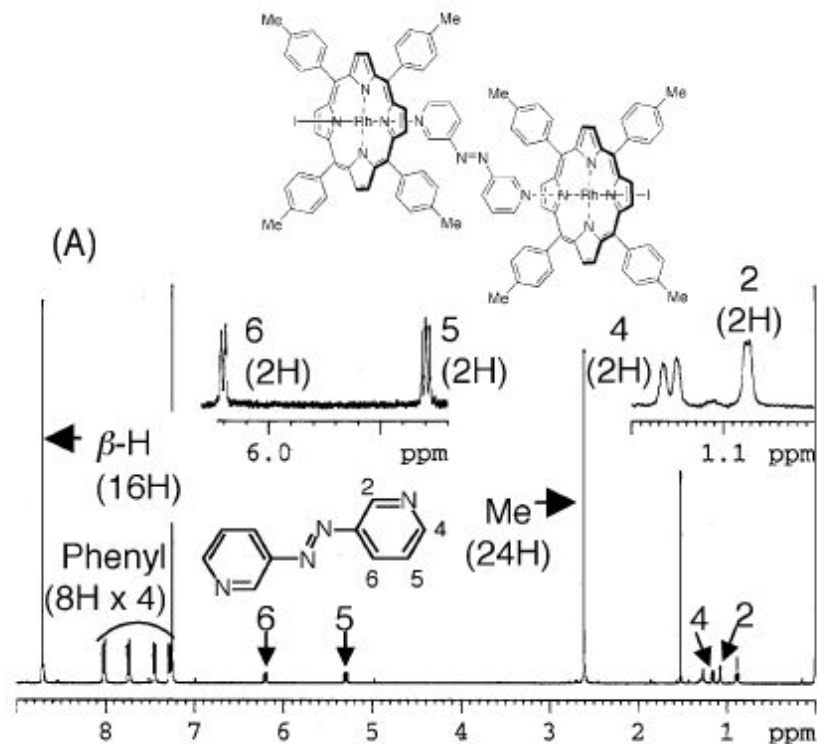
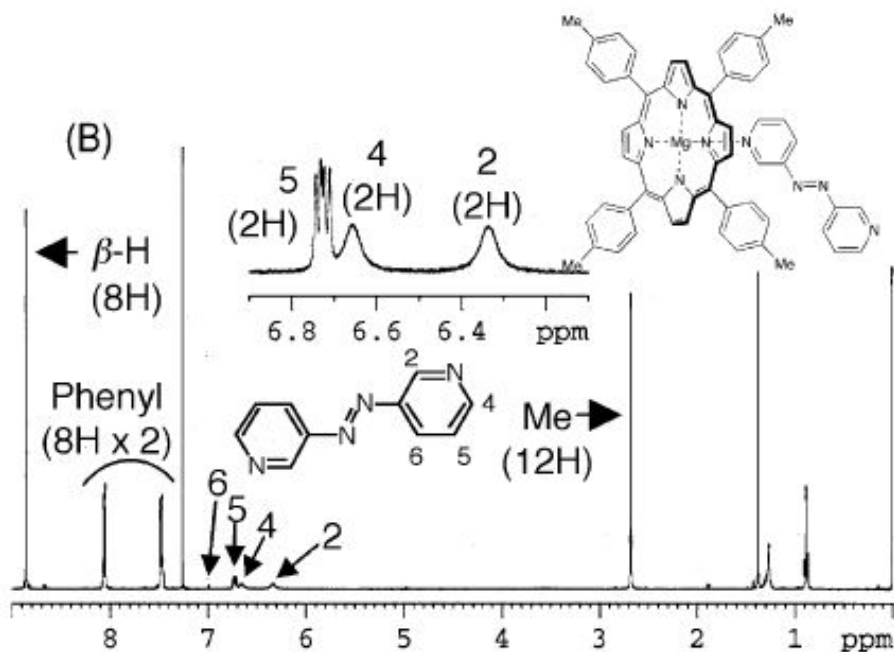
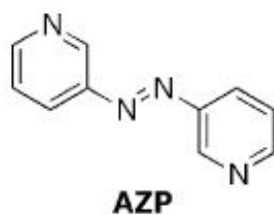
$K > 10^8 \text{ M}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ , UV-vis **21**  
 $\log K > 8$



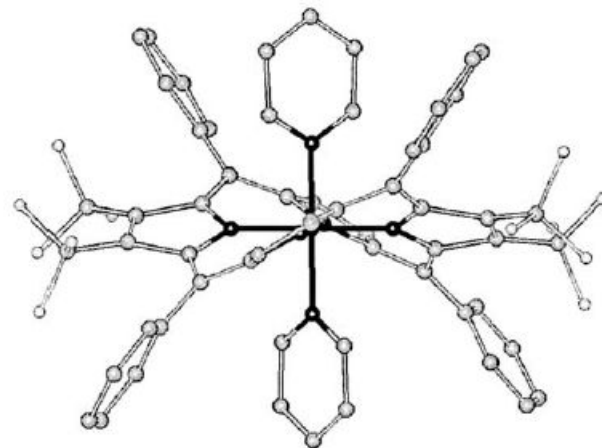
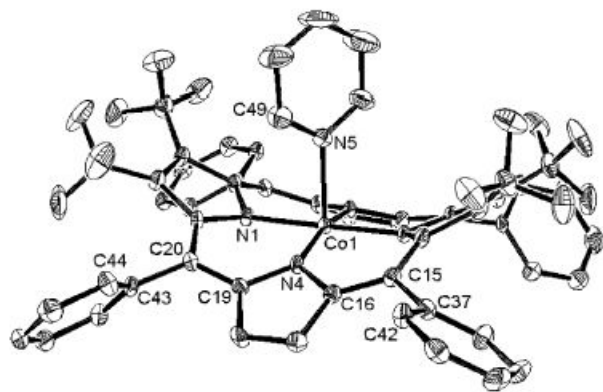
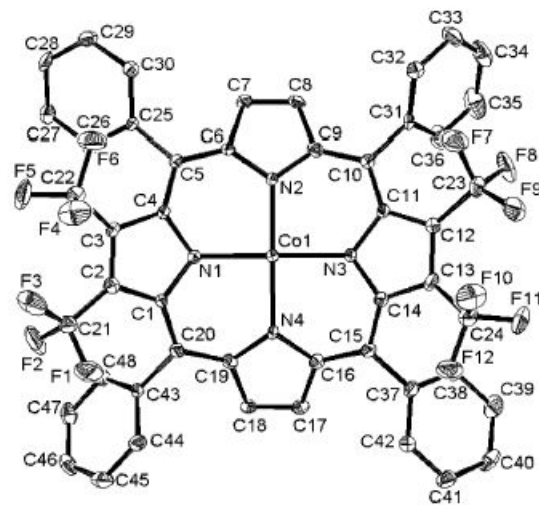
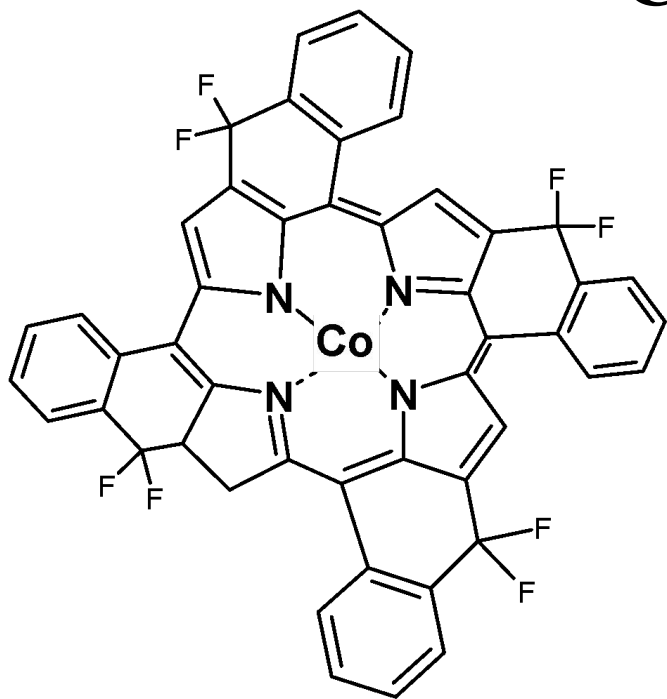
$K = 9 \times 10^{12} \text{ M}^{-3}$  in  $\text{CH}_2\text{Cl}_2$ , UV-vis/NMR **29**



**TTP(Mg):** M = Mg  
**TTP(Zn):** M = Zn  
**TTP(Rh):** M = Rh-I



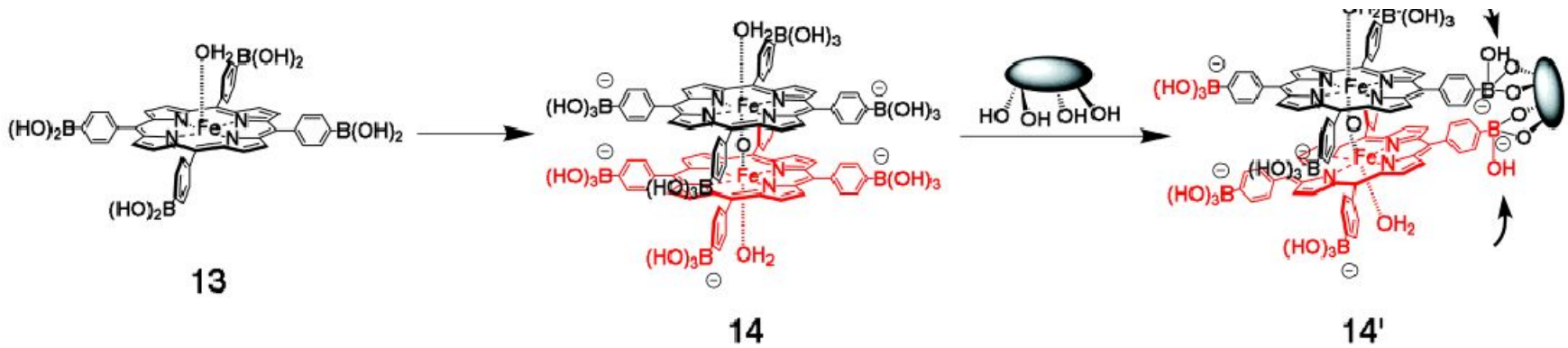
# Со- порфирин



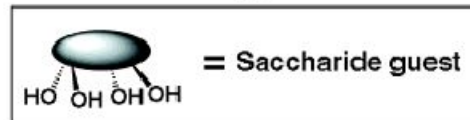
1 (Py)<sub>2</sub>



# Fe- порфирин



14



# Ce- порфирин

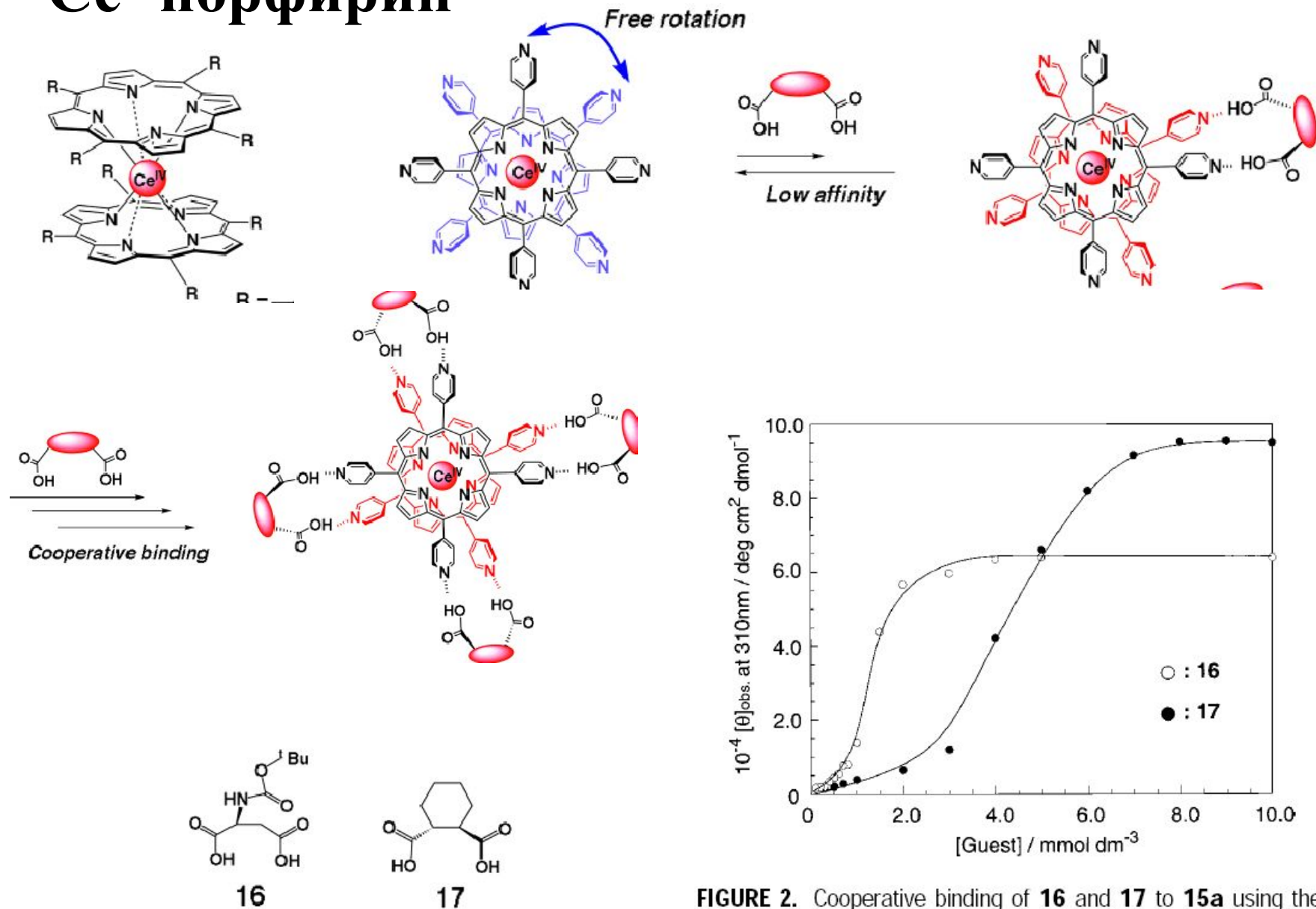


FIGURE 2. Cooperative binding of **16** and **17** to **15a** using the hydrogen-bonding interaction.<sup>37</sup>

# Порфирин + ДНК

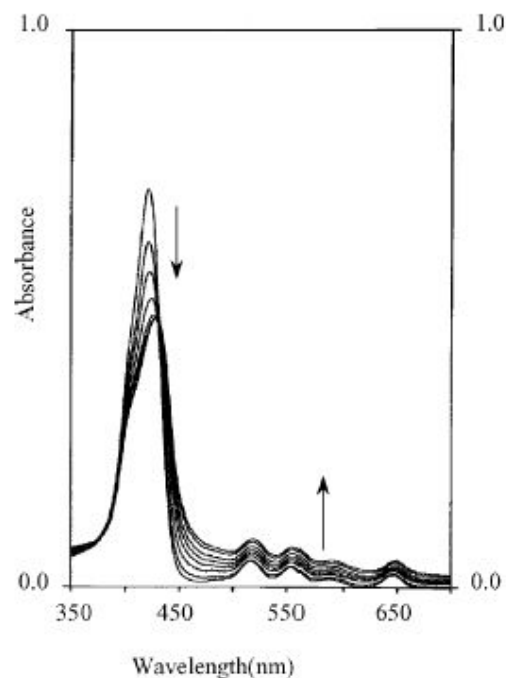
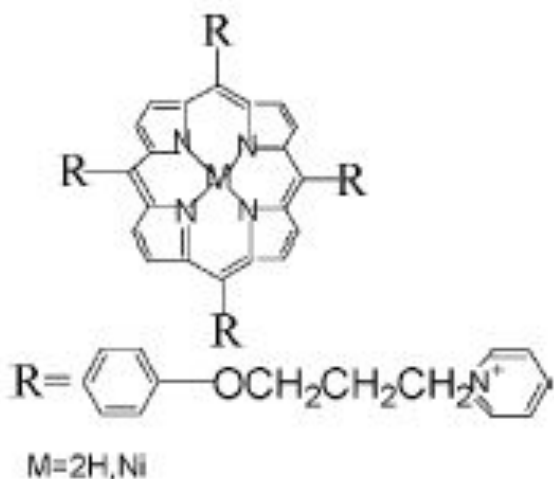


Fig. 1. Absorption spectra of TPYP ( $5.8 \mu M$ ) in the absence (top) and presence of calf thymus-DNA ( $1.6 \mu M$ ,  $3.2 \mu M$ ,  $4.8 \mu M$ ,  $6.4 \mu M$ ,  $8.0 \mu M$ ,  $9.6 \mu M$ ,  $11.2 \mu M$ ,) in phosphate buffer pH 7.0 ( $I = 0.15 M NaCl$ ). Arrow shows that the absorbance changes upon increasing DNA concentration.

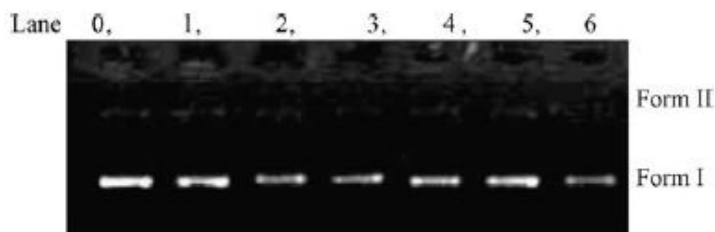
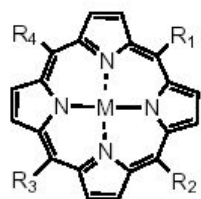


Fig. 8. Interaction of supercoiled pBR322 DNA by porphyrin TPYP TPYP(Ni) and  $12 \mu L$  reaction mixtures contained  $40 ng$  of plasmid DNA. Lane 0: DNA alone; lane 1: DNA + TPYP ( $1 \mu M$ ); lane 2: DNA + TPYP ( $5 \mu M$ ); lane 3: DNA + TPYP ( $10 \mu M$ ); lane 4: DNA + TPYP(Ni) ( $1 \mu M$ ); lane 5: DNA + TPYP(Ni) ( $5 \mu M$ ); lane 6: DNA + TPYP(Ni) ( $10 \mu M$ ).



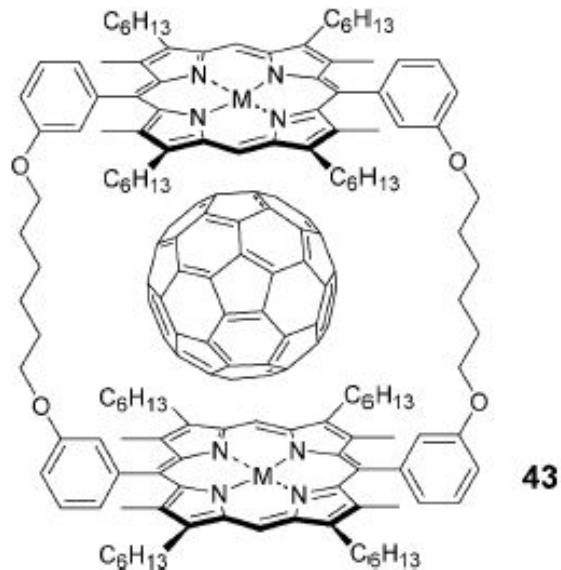
abbreviation	substituent	—R
TPPS	M = 2H; R <sub>1-4</sub> =	
TPPC		
TPPP		
TMPyP		
TMPTP		
BPPTP	M = 2H; R <sub>1,3</sub> = R <sub>2,4</sub> =	
TPPTP	M = 2H; R <sub>1,2,3</sub> = R <sub>4</sub> =	
ZnTDCSPP	M = Zn; R <sub>1-4</sub> =	
ZnTMPyP	M = Zn; R <sub>1-4</sub> =	
PdTMPyP(4)	M = Pd; R <sub>1-4</sub> =	
PdTMPyP(2)	M = Pd; R <sub>1-4</sub> =	
PdTMPyP(3)	M = Pd; R <sub>1-4</sub> =	

tum yields of the triplet states ( $\Phi_T$ ) and of the singlet oxygen generation ( $\Phi_\Delta$ ) of protein-bound porphyrins

tizer	$\Phi_T$	$\Phi_\Delta$
CSPP <sup>a</sup>	0.96	0.74
CSPP/HSA <sup>a</sup>	—	0.76
/histone <sup>c</sup>	0.76 <sup>b</sup> , 0.79 <sup>f</sup>	0.57 <sup>d</sup> , 0.64 <sup>f</sup>
/HSA <sup>f</sup>	$\leq 0.2$	<0.1
PS <sup>f</sup>	0.66	0.66
PS/HSA <sup>f</sup>	1.0	0.77
S <sub>1</sub> <sup>e</sup>	0.21	—
S <sub>1</sub> /HSA <sup>e</sup>	0.10	—
S <sub>2</sub> <sup>e</sup>	0.17	—
S <sub>2</sub> /HSA <sup>e</sup>	0.18	—
S <sub>3</sub>	0.17 <sup>e</sup> , 0.46 <sup>f</sup>	0.34 <sup>f</sup>
S <sub>3</sub> /HAS	0.18 <sup>e</sup> , 0.43 <sup>f</sup>	0.32 <sup>f</sup>
S <sub>3</sub> <sup>f</sup>	0.51	0.36
S <sub>3</sub> /HSA <sup>f</sup>	0.62	0.51

<sup>a</sup> ref. 11; <sup>b</sup> ref. 12; <sup>c</sup> ref. 13; <sup>d</sup> ref. 14; <sup>e</sup> ref. 15; <sup>f</sup> ref. 16

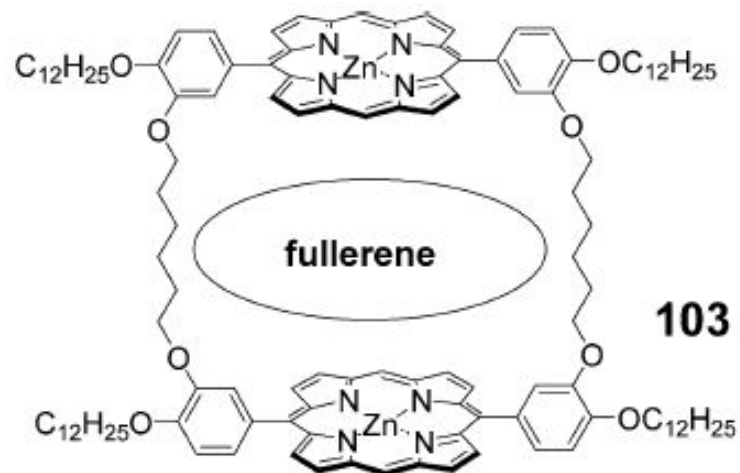
# Порфирин + фуллерен



**Table 6.** Association constants of porphyrins **43** with fullerenes<sup>a,57</sup>

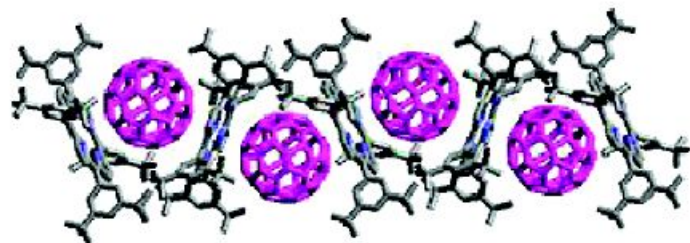
Run	Porphyrin <b>43</b>	Fullerene	log <i>K</i>	<i>K</i> (M <sup>-1</sup> )
1	M=2H	C <sub>60</sub>	5.9	7.9×10 <sup>5</sup>
2	M=2H	C <sub>70</sub>	7.2	1.6×10 <sup>7</sup>
3	M=Co(II)	C <sub>60</sub>	6.3	2.0×10 <sup>6</sup>
4	M=Co(II)	C <sub>70</sub>	7.1	1.3×10 <sup>7</sup>
5	M=Rh(III)	C <sub>60</sub>	7.4	2.5×10 <sup>7</sup>
6	M=Rh(III)	C <sub>70</sub>	8.0	1.0×10 <sup>8</sup>
7	M=Ni(II)	C <sub>60</sub>	5.4	2.5×10 <sup>5</sup>
8	M=Ni(II)	C <sub>70</sub>	6.3	2.0×10 <sup>6</sup>
9	M=Cu(II)	C <sub>60</sub>	5.7	5.0×10 <sup>5</sup>
10	M=Cu(II)	C <sub>70</sub>	6.7	5.0×10 <sup>6</sup>
11	M=Ag(II)	C <sub>60</sub>	5.1	1.3×10 <sup>5</sup>
12	M=Ag(II)	C <sub>70</sub>	6.5	3.2×10 <sup>6</sup>
13	M=Zn(II)	C <sub>60</sub>	5.8	6.3×10 <sup>5</sup>
14	M=Zn(II)	C <sub>70</sub>	7.3	2.0×10 <sup>7</sup>

<sup>a</sup> Conditions: 298 K, benzene, UV-vis.

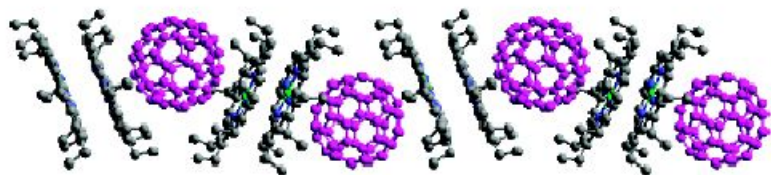


$K = 1.1 \times 10^5 \text{ M}^{-1}$	$K = 7.9 \times 10^5 \text{ M}^{-1}$	$K = 1.3 \times 10^7 \text{ M}^{-1}$
logK 5	logK 5.9	logK 7.1

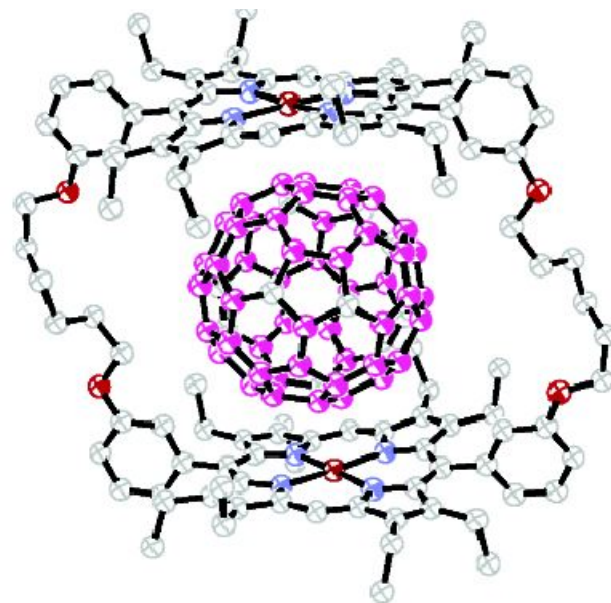
toluene/THF (1:1), 298 K, UV-vis



**FIGURE 2.** Zigzag alternating  $C_{60}$  and  $H_2TPP$  moieties in  $H_2T_{3,5}$ -di-*t*-butylPP· $C_{60}$ .<sup>6</sup> Solvate molecules have been omitted for clarity.

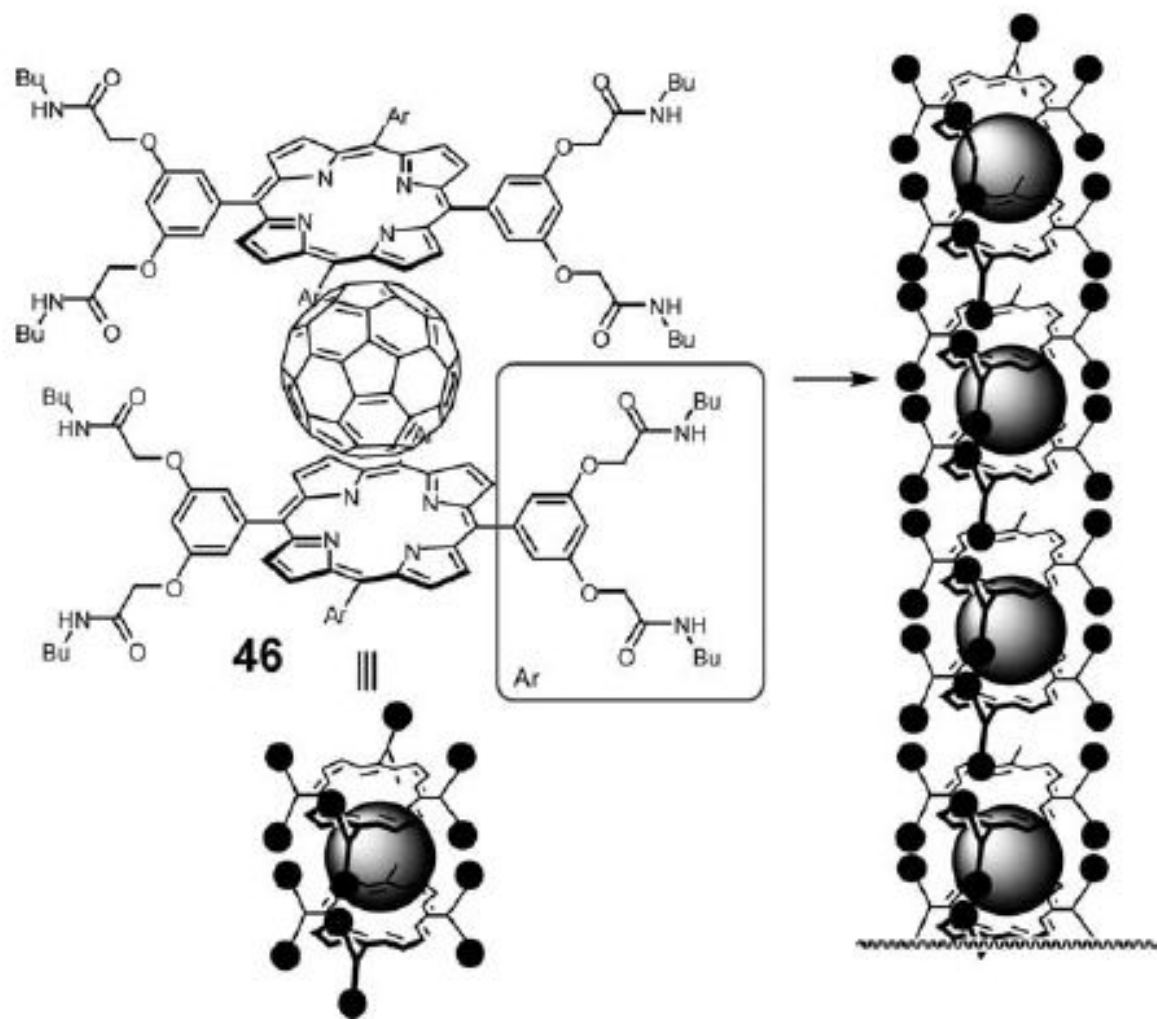


**FIGURE 3.** Zigzag alternating  $C_{60}$  and  $\{Co(OEP)\}_2$  moieties in  $2Co(OEP) \cdot C_{60} \cdot CHCl_3$ .<sup>7</sup> The solvate molecule has been omitted for clarity.



**FIGURE 5.** X-ray structure of  $C_{60}$  bound to a cyclic bisporphyrin host.<sup>19</sup>





**Figure 35.** Structure of octa-amide porphyrin **46** and its supramolecular aggregate in the presence of C<sub>60</sub>.<sup>59</sup>



# Ассоциация с участием водородных связей

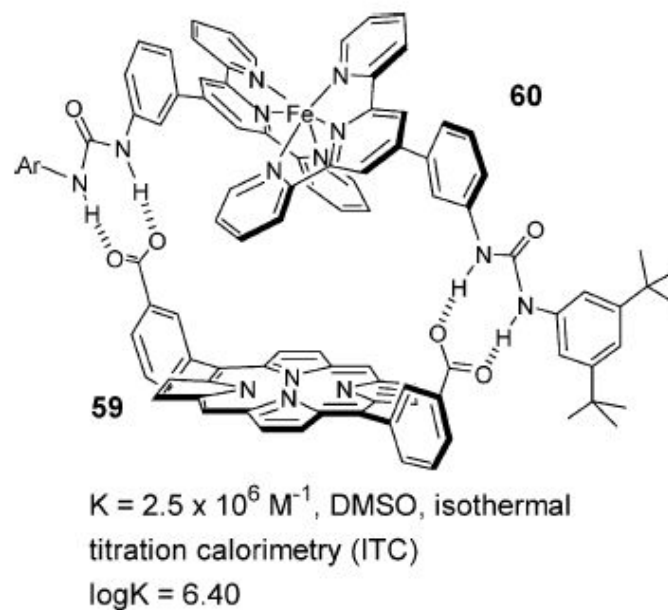
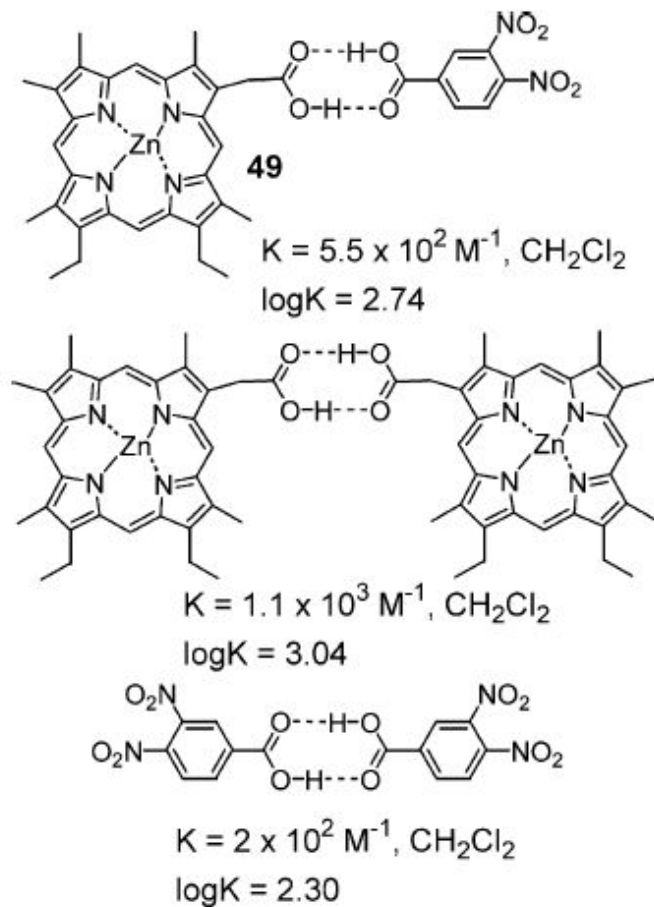
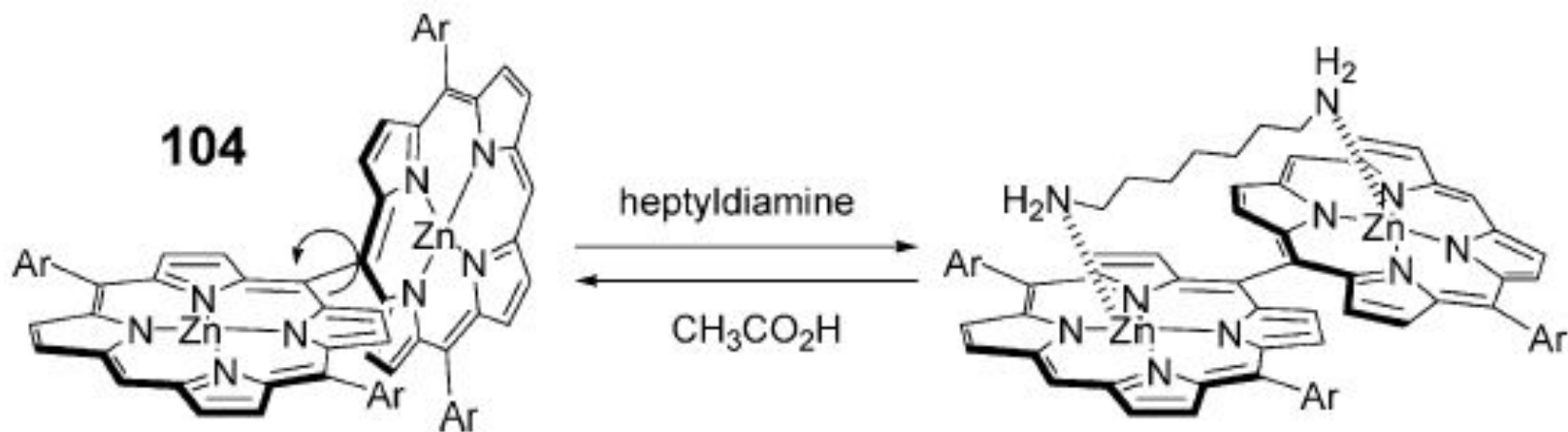


Figure 44. Porphyrin/ferrous terpyridine complex **59/60**.<sup>71</sup>

# Молекулярное переключение



# Молекулярное переключение

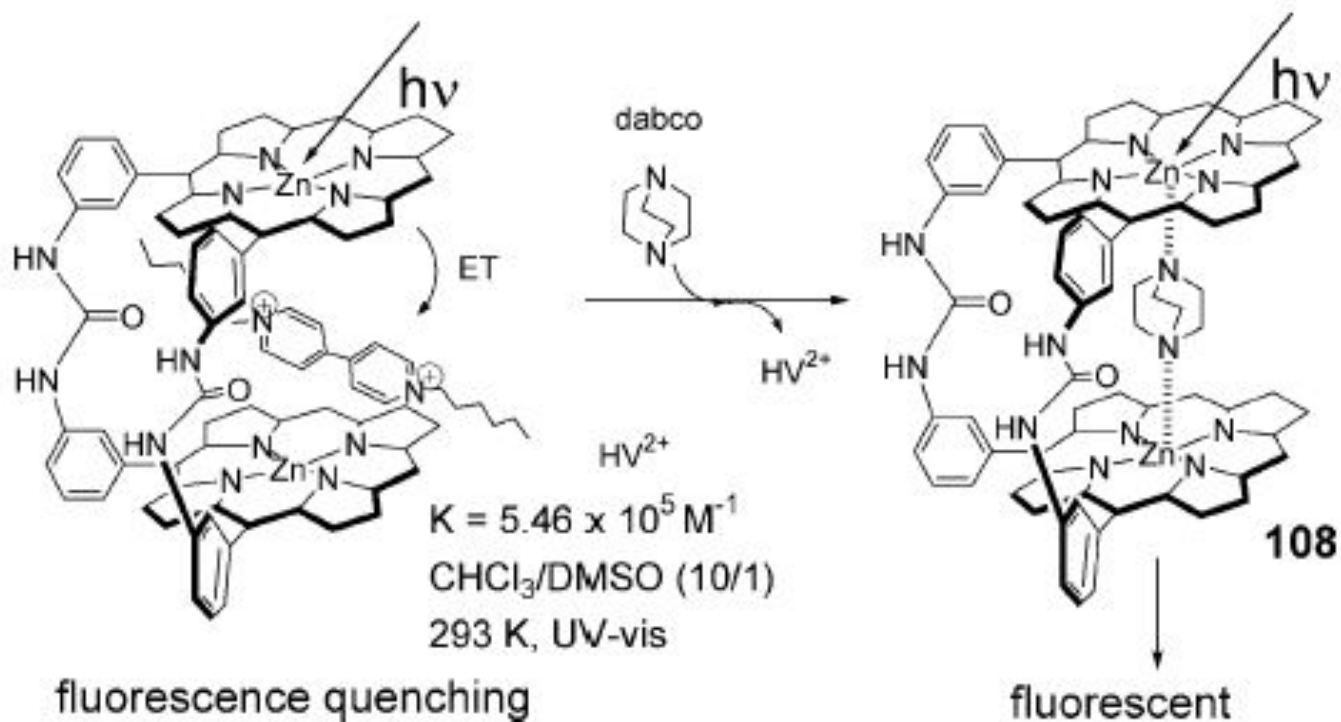


Figure 84. Dual-mode receptor of hexylviologen and dabco.<sup>144</sup>

# Полимеризация

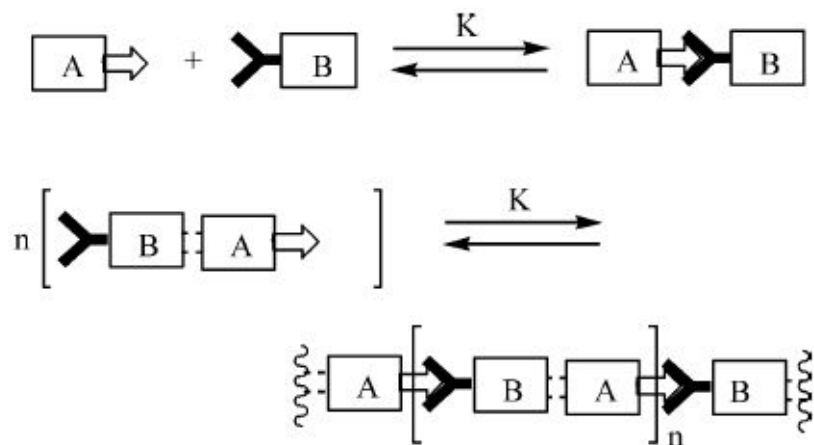
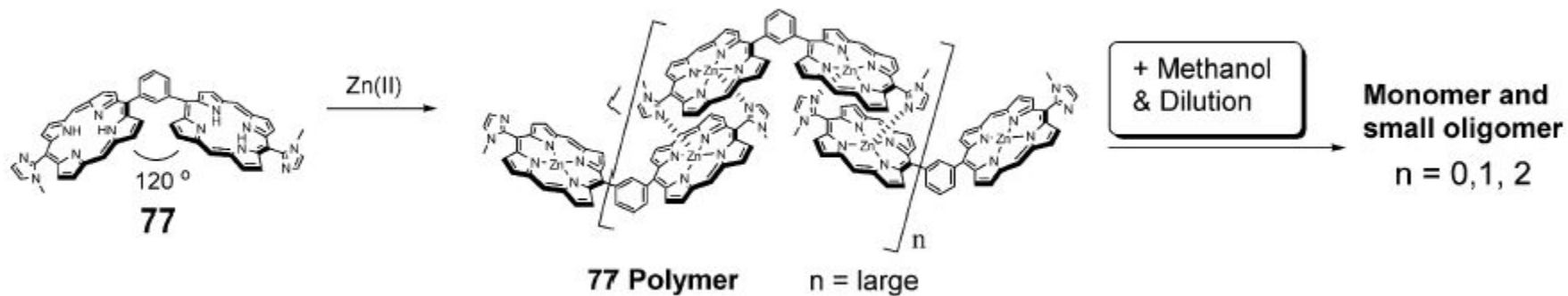
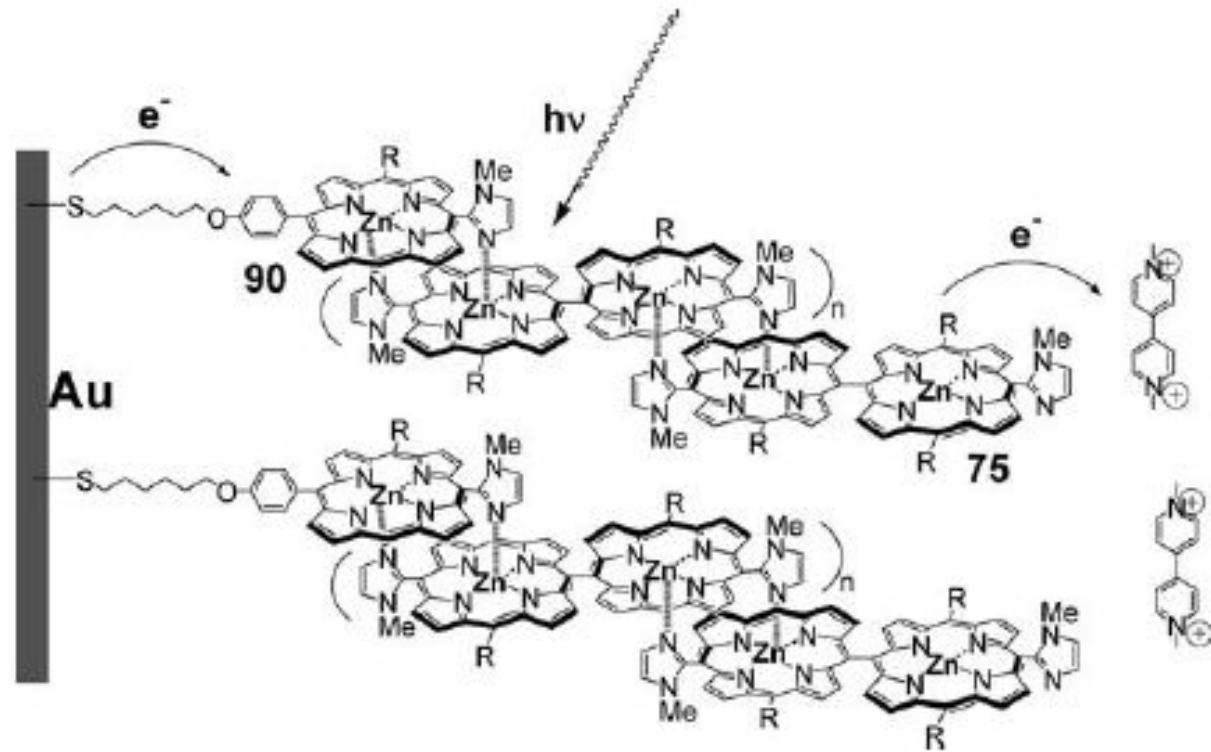


Figure 56. Schemes of formation of dimer and polymer.



# Фотоиндуцированный перенос электрона



**Figure 69.** Complementary coordination assembly of antenna porphyrins on gold surface.<sup>121</sup>

# Фотоиндуцированный перенос электрона

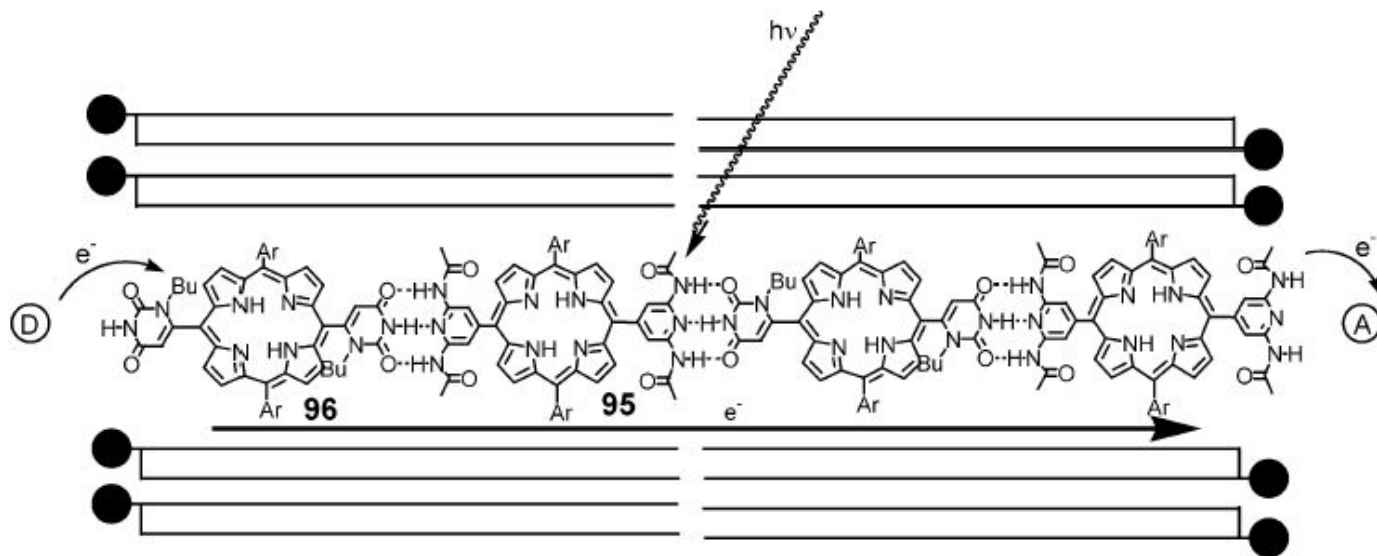


Figure 73. Photocurrent generation across the lipid bilayer membrane.<sup>126</sup>

$K_4Fe(CN)_6$

Table 1  
Abbreviations used for porphyrin compounds

Abbreviation	Name
ATPPS	5-(4'-Aminophenyl)-10, 15, 20-tris(4'-sulfonatophenyl) porphyrin
CoTRBP	<i>meso</i> -(Tetrapyridyl)porphyrinate cobalt(III) [bis-(bipyridine)(chloro)ruthenium(II)]
CPI	Coproporphyrin-I
<i>m</i> -BrTPPS <sub>4</sub>	<i>meso</i> -Tetrakis(3-bromo-4-sulfophenyl) porphyrin
OBTPPS	Octabromo-tetrakis(4-sulfonatophenyl) porphyrin
OEP	Octaethylporphyrin
<i>p</i> -NO <sub>2</sub> Bz-TPPS	<i>N</i> -4-Nitrobenzyl-tetrakis(4-sulfonatophenyl)porphyrin
( <i>p</i> -OH)TPP	Tetrakis(4-hydroxyphenyl)porphyrin
ProP	Protoporphyrin IX
TAPP	Tetrakis(4-aminophenyl)porphyrin
TCPP	<i>meso</i> -Tetrakis(4-carboxyphenyl) porphyrin
TMAP	<i>meso</i> -Tetrakis(4- <i>N</i> -trimethylaminophenyl)porphyrin
TMHPP	Tetrakis(3-methoxy-4-hydroxyphenyl) porphyrin
T(1-MPy)P	<i>meso</i> -Tetrakis(1-methylpyridinium-4-yl) porphyrin
TMPyP	Tetrakis(1-methyl-4-pyridyl)porphyrin
T(3-MPy)P	Tetrakis(3- <i>N</i> -methylpyridyl)porphyrin
T(4-MOP)PS <sub>4</sub>	<i>meso</i> -Tetrakis(4-methoxyl-3-sulfophenyl)porphyrin
TMOPP	Tetrakis(4-methoxylphenyl)porphyrin
TPP	Tetraphenylporphyrin
TPPS <sub>3</sub>	Tetraphenylporphyrin trisulfate
TPPS <sub>4</sub>	<i>meso</i> -Tetrakis(4-sulfophenyl)porphyrin
TPyP	<i>meso</i> -Tetra(4-pyridyl)porphyrin

# Аналитическая ХИМИЯ

# Спектрофотометрия

Spectrophotometric determination of metal ions with porphyrin reagents

Metal ion	Reagent	Condition	Absorption spectra		Range of determination	Interference
			$\lambda_{\max}$ (nm)	$\varepsilon$ ( $\times 10^5$ )		
Cu(II)	T(1-MPy)P	Complexation at pH 9, L-cysteine (room temp., 5 min) then acidify with H <sub>2</sub> SO <sub>4</sub>	423	3.9	6–60 $\mu\text{g}\cdot\text{l}^{-1}$	–
Cu(II)	TPPS <sub>3</sub>	pH 4 (100°, 1 min) then pH 2.5 with chloroacetic acid	434	4.8	6–60 $\text{ng}\cdot\text{l}^{-1}$	Zn
Cu(II)	TPP	Solubilised by Na-laurylsulfate at pH 4.7+NH <sub>2</sub> OH (100°, 3 min) then pH 0.6–1.2 with H <sub>2</sub> SO <sub>4</sub>	414	4.7	~140 $\text{ng}\cdot\text{l}^{-1}$	Ag, Hg(II), Zn > 10 $\mu\text{g}$ , Pd > 5 $\mu\text{g}$
Cu(II)	T(3-MPy)P	pH 6+NH <sub>2</sub> OH (100°, 7 min) then acidify with H <sub>2</sub> SO <sub>4</sub>	434	3.5	1–13 $\text{ng}\cdot\text{l}^{-1}$	Fe(III) and Pd
Cu(II)	TMAP	Complexation at pH 4.1–5.9+L-ascorbic acid	411	5.1	Up to 100 $\text{ng}\cdot\text{l}^{-1}$	Sn(II), I <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>
Cu(II)	p-NO <sub>2</sub> Bz-TPPS	pH 5 (90°, 7 min)	413	4.2	130 $\mu\text{g}\cdot\text{l}^{-1}$	Co(II), Pd, Fe(III) > 2 $\mu\text{g}$
Cu(II)	CPI	Complexation at pH 8 (90°, 10 min)	414	–	35–128 $\mu\text{g}\cdot\text{l}^{-1}$	–
Co(II)		+Imidazole or pyridine	380	–	–	–
Cd(II)	T(1-MPy)P	pH 9.8+Pb(II)+L-tryptophan	448	1.7	0.3–23 $\mu\text{g}\cdot\text{l}^{-1}$	Zn, Hg(II)
Zn(II)	TPPS <sub>4</sub>	pH 7.1+imidazole+Cd(II) (room temp., 30 min)	425	4.5	10–150 $\text{ng}\cdot\text{l}^{-1}$	Mn(II), Co(II) > 40 $\mu\text{g}\cdot\text{l}^{-1}$ Fe(III) > 70 $\mu\text{g}\cdot\text{l}^{-1}$
Zn(II)	TPPS <sub>4</sub>	pH 6+imidazole+Pb(II) (room temp., 30 min) then EDTA	421	4.7	Up to 100 $\mu\text{g}\cdot\text{l}^{-1}$	Cu, Co(II), Mn(II)
Zn(II)	TPP	Glacial acetic acid (room temp., 60–70 min)	551	0.14	Up to 200 $\mu\text{g}\cdot\text{l}^{-1}$	Cu
Zn(II)	TPPS <sub>4</sub>	pH 4.8+imidazole (stop-flow for 1 min)	424	–	Up to 2.5 $\mu\text{g}\cdot\text{l}^{-1}$	–
Zn(II)	TPPS <sub>4</sub>	pH 8–8.7+Mn(II)+NH <sub>2</sub> OH	413	2.8	–	Cd, Hg(II), Fe(III)
Pd(II)	TPPS <sub>4</sub>	pH 4+ascorbic acid (100°, 7 min) then pH 2.5	411	2.2	–	Cu, Hg(II)
Mg(II)	T(4-MPy)P	pH 9.1–10.6+8-quinolinol (100°, 60 min)	–	–	–	After dithizone separation
Bi(III)	p-NO <sub>2</sub> B <sub>2</sub> TAPS	pH 5.9+Cd(II) (35°, 2 min) then SDS	466	–	Up to 1.1 $\text{mg}\cdot\text{l}^{-1}$	–
Ag(I)	TPyP	(100°, 10 min)+ethanol, acidified with H <sub>2</sub> SO <sub>4</sub>	425	1.8	Up to 0.36 $\text{mg}\cdot\text{l}^{-1}$	–
Ni(II)	TPPS <sub>4</sub>	Complexation at pH 8–9+Cd(II)+imidazole (100°)	418	2.3	Up to 150 $\text{ng}\cdot\text{l}^{-1}$	–
Li(I)	OBTPPS	pH 11+EDTA+Mg(II)	490	2.0	7–700 $\mu\text{g}\cdot\text{l}^{-1}$	Hg(II)



# Потенциометрия

Potentiometric methods based on the use of porphyrin

Analyte	Electroactive component	Range of response, pX	Electrode matrix	Analysed sample	Ref.
Inorganic anions	SnTPP, CoTPP, InOEP	1–5	PVC	Water	[51]
Inorganic anions	GaTPP, GaOEP, InTPP, InOEP, TiTPP	2–5	PVC		[53]
Chloride	MnTPP, InTPP, MnOEP, InOEP		SR <sup>a</sup>	Human serum	[54]
NO <sub>2</sub> <sup>-</sup> , F <sup>-</sup>	CoTPP		Polysiloxane		[55]
Iodide	SnTAPP, H <sub>2</sub> TAPP	1–5	Carbon		[56]
Iodide	TPPS <sub>4</sub>	1–6	Ag	Edible seaweed	[57]
Iodide	MTAPP	1–4	Pt		[58]
SCN <sup>-</sup>	(FeTPP) <sub>2</sub> O	1–6	PVC	Urine	[52]
Salicylate	SnTPP	3–5	PVC	Serum, urine	[59]
Ni <sup>2+</sup>	H <sub>2</sub> TTP, HTMPP	1–6	PVC	Chocolate	[60]
Co <sup>2+</sup>	TPP	1–6	PVC		[61]

<sup>a</sup> SR, silicon rubber.

Table 4  
 Voltammetric determination involving the use of porphyrins<sup>a</sup>

Analyte	Electrode material	Modifier	Measuring technique	Analysed sample	Ref.
Organohalides	Graphite	CoTPP, CoTMOPP, CoOEP	SWV, CV	Aqueous sample	[62]
Sugars	Graphite paste	CuTPP	CV		[63]
Oxygen	Pt	FeTMHPP	Amperometry	LOD 27.5 nmol l <sup>-1</sup>	[64]
Oxygen	Au	CoTPPS <sub>4</sub> , CoTMPyP + βCD	CV, RRDE, RDE		[65]
Oxygen	Ag/colloid/PVA	CoTMPyP	CV		[66]
Hydrazine	Carbon paste	CuTPP	CV		[67]
Phenols	Glassy carbon	poly[MProP], M = Ni <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup>	CV		[68]
NO	Glassy carbon	NiTMHPP	CV		[69]
NO	Glassy carbon	NiTMHPP	CV, DVP		[70]
NO	Carbon fibre	NiTMHPP	Chronoamperometry	Solutions saturated with NO	[71]
NO	Carbon fibre	[NiTMHPP]poly	CV	Blood	[72]
NO	Carbon fibre	[NiTMHPP]poly	CV, DVP	Blood, single endothelial cells	[73]
NO	Carbon fibre	NiTMHPP	DVP	Rat brain, blood	[74]
NO	Carbon fibre	NiTMHPP	DVP	Rat brain, blood	[75]
NO	Glassy carbon	Haemoglobin	Amperometry		[76]
NO, NO <sub>2</sub> <sup>-</sup>	Vitreous carbon disk	Poly [FeProP], poly [FeTPPS <sub>4</sub> ], poly [FeTMPyP]	CV		[77]
NO <sub>2</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup>	Glassy carbon	CoTRBP/ZnTPPS <sub>4</sub>	CV		[78]
NO <sub>2</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup>	Vitreous carbon	CoTPyP	CV		[79]
Ni <sup>2+</sup>	Carbon or Pt	TMHP	CV	Water	[80]
Ni <sup>2+</sup>	Carbon fibre	[NiTMHPP]poly	DVP	Single biological cells	[81]
Ni <sup>2+</sup>	Carbon fibre	[NiTMHPP]poly	DVP	Single biological cells	[82]
Heavy metals, Cu <sup>2+</sup>	Glassy carbon	TPP	ASV	Tap water	[83]
Ace-toaminophen	Glassy carbon	NiTAPP	CV	Paracetamol	[84]
Alcohols	Glassy carbon	NiTMHPP	CV	Methanol solutions	[85]
DNA	Hg	TMAP	CV	Calf thymus DNA	[86]
DNA	Hg	CuTMAP	CV	Calf thymus DNA	[87]
DNA	Hg	NiTMPyP	CV, coulometry	Calf thymus DNA	[88]
Dopamine, neurotransmitters	Graphite	ZnProP	SWV, CV		[89]
Dopamine	Glassy carbon	CoTRBP	Amperometry, CV		[90]

<sup>a</sup> CV, cyclic voltammetry; DVP, differential pulse voltammetry; SWV, square wave voltammetry; ASV, anodic stripping voltammetry; RRDE, rotating ring disk electrode voltammetry; RDE, rotating disk electrode voltammetry.

Table 3  
Application of porphyrins in metal analysis by HPLC<sup>a</sup>

Analyte	Sample	Porphyrin	Column	Eluent	Ref.
Ni(II), Cu(II), Zn(II)	Bovine liver	TPP	Lichrosorb RP-18	Acetone/ACN	[103]
Cu(II), Pb(II), Zn(II), Cd(II)	Electroplating waste liquor, tin alloy	TPP	Micropak MCH-5	Methanol/H <sub>2</sub> O/chloroform	[96]
Y(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III)	Aqueous sample	TPP	TSK Gel ODS-80TH	Methanol/H <sub>2</sub> O/acetyloacetone/amine	[97]
Cu(II), Zn(II)	Tap water	THPP	Radial Pak C-18	Ethanol/H <sub>2</sub> O	[104]
Mn(II), Fe(III), Zn(II), Pd(II), Cu(II)	Peach leaves	<i>m</i> -BrTPPS <sub>4</sub>	Lichrosorb RP-18	ACN/H <sub>2</sub> O/TBABr	[105]
Co(II), Zn(II), Cu(II)	River water	<i>m</i> -BrTPPS <sub>4</sub>	Lichrosorb RP-18	ACN/H <sub>2</sub> O/TEAI	[98]
Co(II), Zn(II), Cu(II)	Tangerine skin, purple rice	<i>m</i> -BrTPPS <sub>4</sub>	Lichrosorb RP-18	ACN/H <sub>2</sub> O/TEAI	[99]
Cu(II), Zn(II), Mn(II), Co(II)	Aqueous sample	TCPP	Lichrosorb RP-18	ACN/acetate buffer	[107]
Co(II), Cu(II), Mn(II)	Tap water	TCPP	Bondapak C 18	Lactic acid/ACN/TBP	[112]
Cu(II), Zn(II), Fe(II), Mn(II)	Peach leaves	TPPS <sub>4</sub>	Lichrosorb RP-18	ACN/H <sub>2</sub> O/TBABr	[100]
Cu(II), Zn(II)	Peanuts	TPPS <sub>4</sub>	Shimpack CLC-ODS	Acetone/H <sub>2</sub> O/BTEACl	[108]
Mn(II), Zn(II), Cu(II)	Tea	TPPS <sub>4</sub>	Shimpack CLC-ODS	Acetone/H <sub>2</sub> O/BTEACl	[109]
Cu(II), Zn(II)	Peanuts	TPPS <sub>4</sub>	Shimpack CLC-ODS	ACN/H <sub>2</sub> O/BTEACl	[101]
Hg(II), Cd(II), Zn(II)	Waste water, silicate, corn samples	TPPS <sub>4</sub>	Silica gel cation exchanger	NaCl/tartaric acid	[110]
Co(II), Zn(II), Cu(II)	Tangerine skin, purple rice	T(4-MOP)PS <sub>4</sub>	Zorbax ODS	ACN/H <sub>2</sub> O/TEAI	[111]

<sup>a</sup> ACN, acetonitrile; TBABr, tetrabutylammonium bromide; TEAI, tetraethylammonium iodide; BTEACl, benzyltriethylammonium chloride; TBP, tributylphosphate.

# Хроматография

Table 6

Retention factors of selected amino acids on different protoporphyrin (ProP) and tetraphenylporphyrin (TPP) silica columns<sup>a</sup>

	Gly	His	Lys	Cys	Ser	Phe	Trp	Glu
H <sub>2</sub> TPP	0.1	0.3	0.1	0.1	0.1	0.5	2.4	0
H <sub>2</sub> ProP	0.1	1.0	1.2	0.2	0.1	1.5	10.5	0
ZnTPP	0.1	1.5	0.2	0.1	0.1	0.5	1.2	0
ZnProP	0.1	2.1	1.7	0.2	0.1	2.1	13.9	0
CuTPP	0.8	6.0	0.7	3.4	1.4	6.0	6.0	0
CuProP	0.1	4.1	2.2	0.3	0.1	8.7	109.0	0

<sup>a</sup> Mobile phase 50 mM phosphate buffer at pH 7.0; flow rate 1 ml min<sup>-1</sup>; detection UV 214 nm [115,121].

## Ник Лэйн

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Пигменты, которые под воздействием света превращаются в химические вещества, способны бороться с раком, слепотой и сердечно-сосудистыми заболеваниями. Возможно, именно здесь кроется объяснение слухов о происхождении вампиров.

Порфирины без иона металла (металлнесодержащие порфирины) переходят в возбужденное состояние при поглощении света определенной длины волны, их электроны перескакивают на орбиты с более высокой энергией. Возбуждение передается другим молекулам, имеющим подобный тип сцепления, особенно кислороду, приводя к появлению его синглетной формы и не менее опасных свободных радикалов. Иными словами, металлнесодержащие порфирины ускоряют выработку токсичных форм кислорода.

Применение порфиринов легло в основу

- фотодинамической терапии рака
- возрастной макулодистрофии зрения
- для лечения кожных заболеваний