

PORFIRINI

**Preddiplomski studij
Primijenjena kemija
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Studeni, 2024.

UVOD

- grčki “porphyryus” - purpurno
- **porfirini** – bojila ekstrahirana iz biljaka – indigo
- vrlo efikasna bojila – “Royal purple”
- 1897. u Njemačkoj se počinje proizvoditi sintetsko indigo bojilo
- puno jeftinije i pristupačnije
- stabilne boje do temperature 500 °C

Raznovrsna područja primjene:

- ligandi za metalne komplekse
- hemoglobin – transport kisika
- polimeri, solarne ćelije, materijali
- regulacija gena
- stanično disanje - hemi
- metabolizam željeza
- fotodinamska terapija
- sinteza hormona

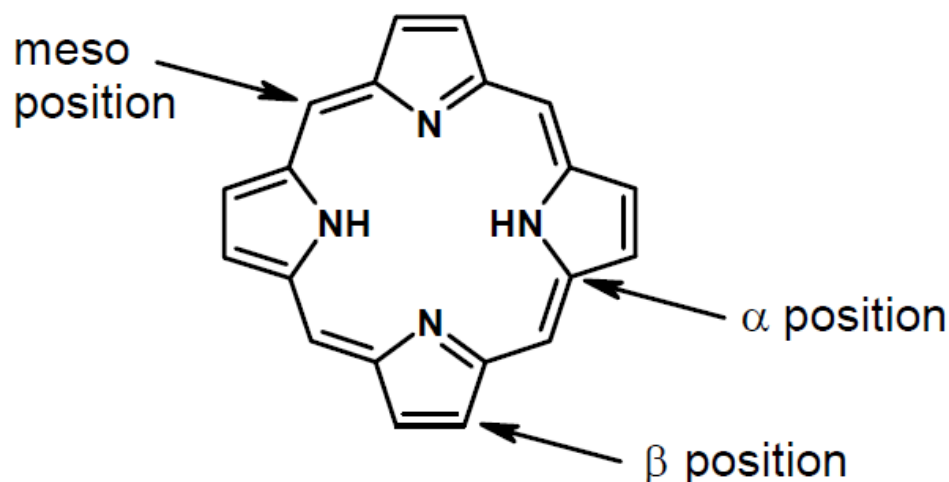


UVOD

- **porfirini** – derivati **porfina** koji imaju različite supstituente na vanjskom dijelu molekule
- mogu se vezati kao ligandi na metalne katione stvarajući metalne komplekse
- prirodni produkti prisutni u mnogim važnim biomolekulama i biološkim procesima (fotosinteza, kataliza)

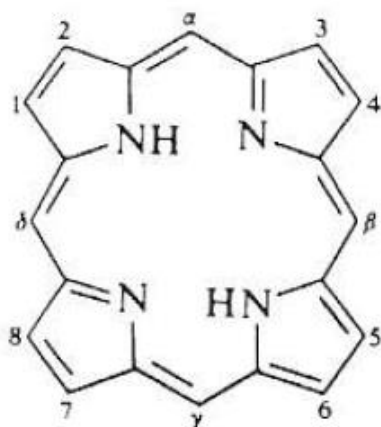
✓ aromatski makrociklički prsten sadrži 12 C atoma i 4 N atoma

✓ povezana 4 pirolna prstena metenskim mostovima

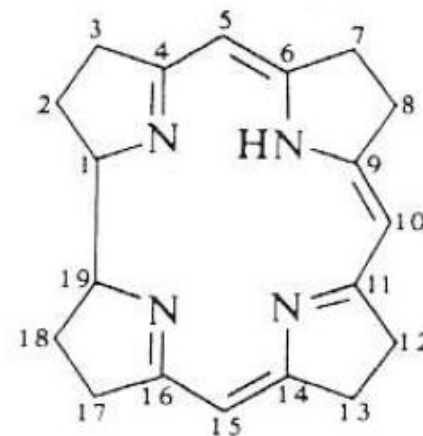
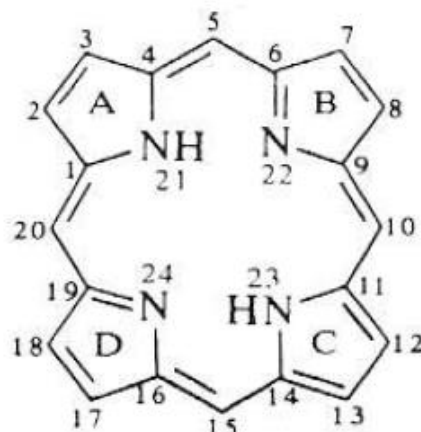


UVOD

Fischerova nomenklatura

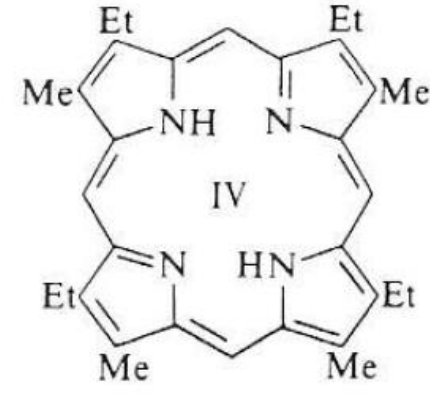
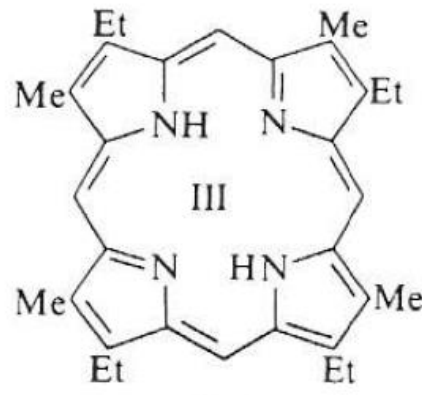
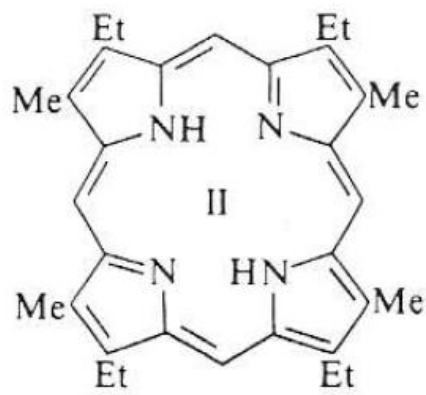
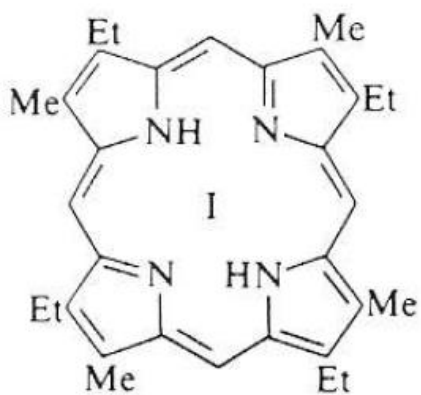


IUPAC-ova nomenklatura



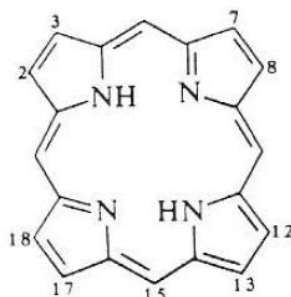
korin

4 moguća primarna tipa izomera:



etioporfirini I, II, III i IV

UVOD

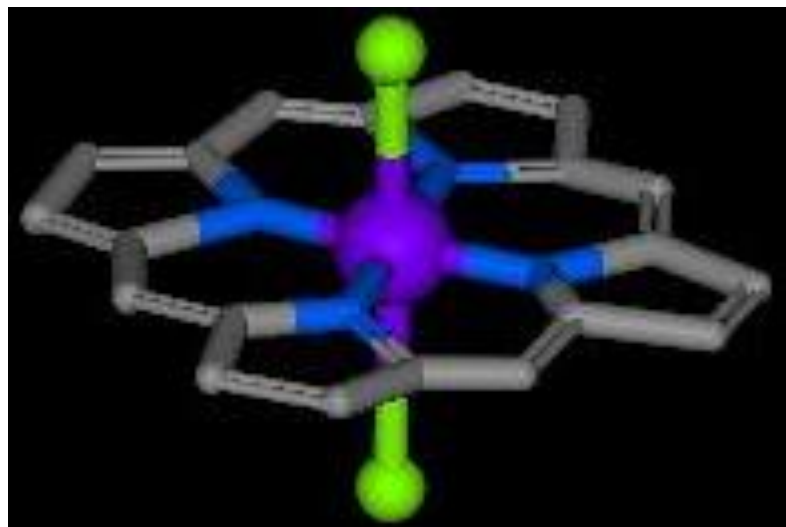
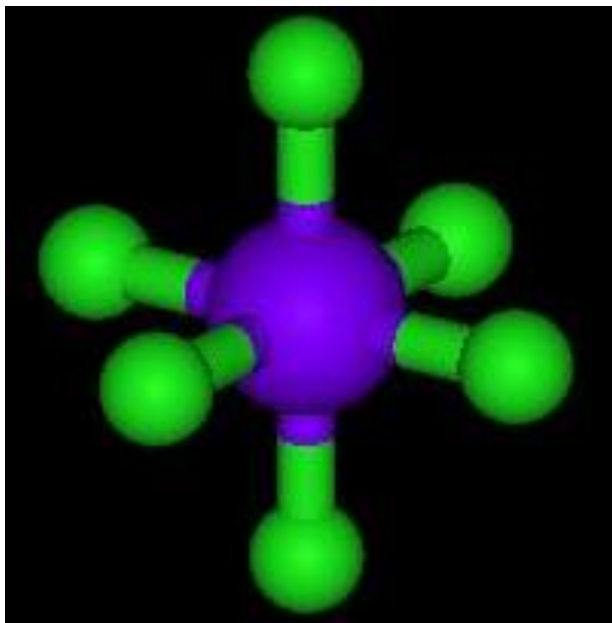


$P = CH_2CH_2CO_2H$
 $A = CH_2CO_2H$
 $V = CH=CH_2$
 $Ac = COMe$

<i>Porphyrin</i>	2	3	7	8	12	13	15	17	18
Octaethylporphyrin	Et	Et	Et	Et	Et	Et	H	Et	Et
Etioporphyrin-I	Me	Et	Me	Et	Me	Et	H	Me	Et
Etioporphyrin-III	Me	Et	Me	Et	Me	Et	H	Et	Me
Protoporphyrin-IX	Me	V	Me	V	Me	P	H	P	Me
Mesoporphyrin-IX	Me	Et	Me	Et	Me	P	H	P	Me
Deuteroporphyrin-IX	Me	H	Me	H	Me	P	H	P	Me
Hematoporphyrin-IX	Me	CH(OH)Me	Me	CH(OH)Me	Me	P	H	P	Me
Coproporphyrin-I	Me	P	Me	P	Me	P	H	Me	P
Coproporphyrin-III	Me	P	Me	P	Me	P	H	P	Me
Uroporphyrin-I	A	P	A	P	A	P	H	A	P
Uroporphyrin-III	A	P	A	P	A	P	H	P	A
Chlorocruoroporphyrin	Me	CHO	Me	V	Me	P	H	P	Me
Pemptoporphyrin	Me	H	Me	V	Me	P	H	P	Me
3,8-Diformyl-deuteroporphyrin-IX	Me	CHO	Me	CHO	Me	P	H	P	Me
3,8-Diacetyl-deuteroporphyrin-IX	Me	Ac	Me	Ac	Me	P	H	P	Me
Phylloporphyrin-XV	Me	Et	Me	Et	Me	H	Me	P	Me
Pyrroporphyrin-XV	Me	Et	Me	Et	Me	H	H	P	Me
Rhodoporphyrin-XV	Me	Et	Me	Et	Me	CO ₂ H	H	P	Me
Phylloerythrin	Me	Et	Me	Et	Me	CO-CH ₂		P	Me

UVOD

- **porfirini** – planarna rigidna struktura
- metalni kompleksi – oktaedarska struktura
- vrlo stabilni spojevi, jako obojeni
- *N*-atomi na 4 strane oktaedra – ostaju dvije slobodne strane na dnu i vrhu – interakcija s drugim molekulama



UVOD

➤ važni prekursori u sintezi biološki važnih molekula

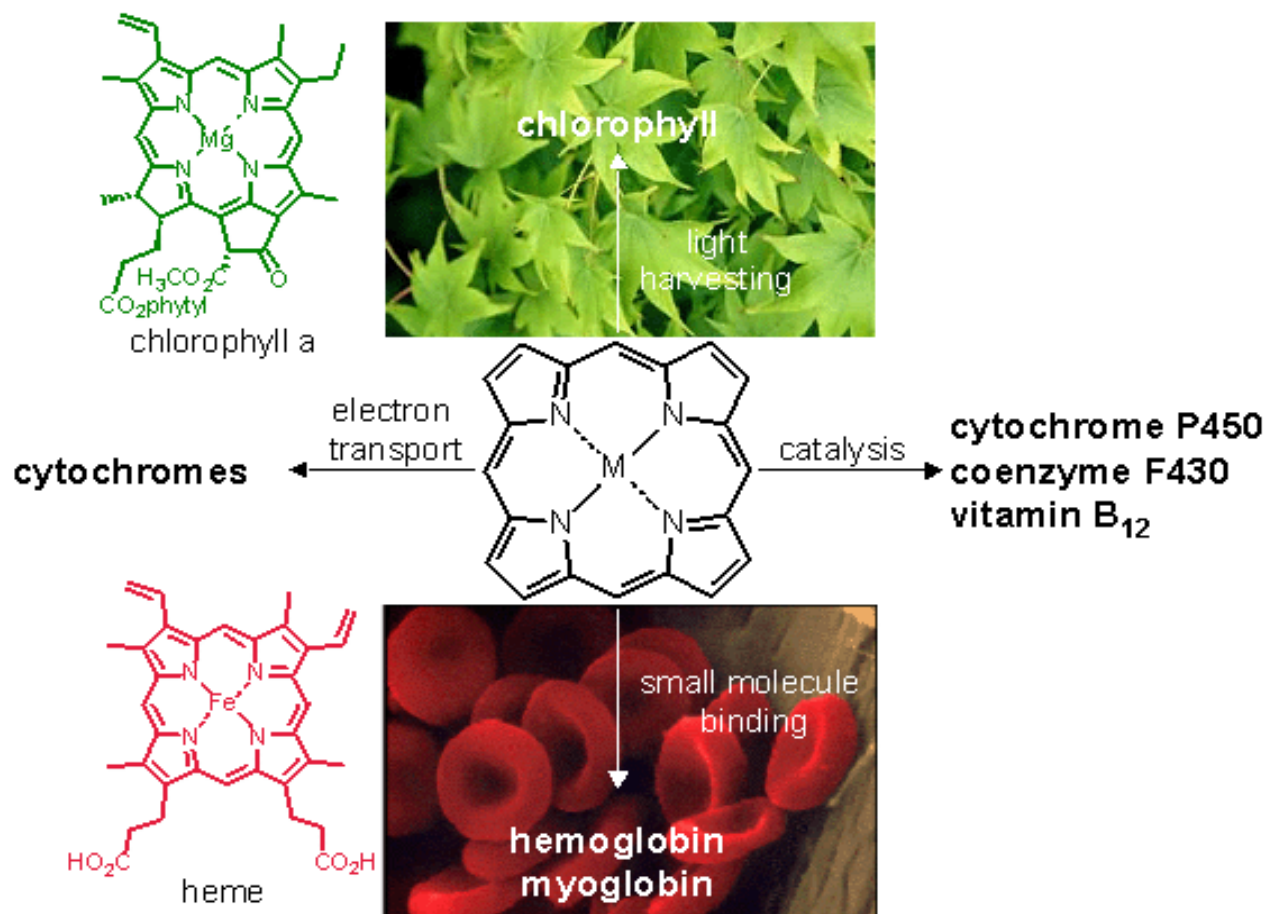
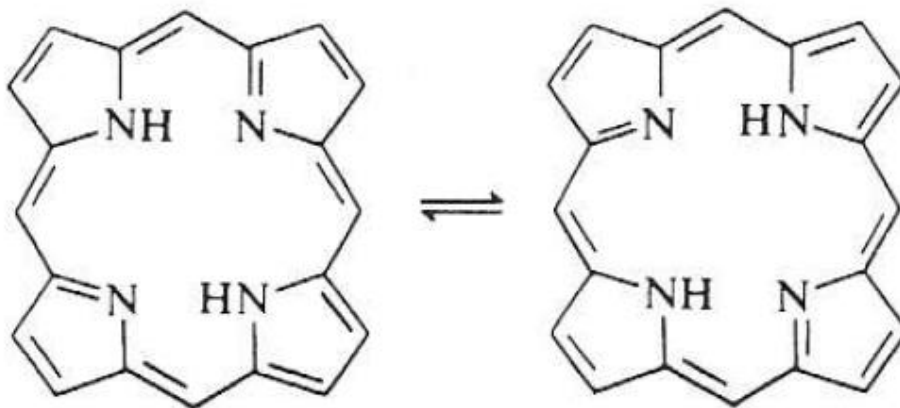


Figure 1. Diverse functions of metalloporphyrins in Nature

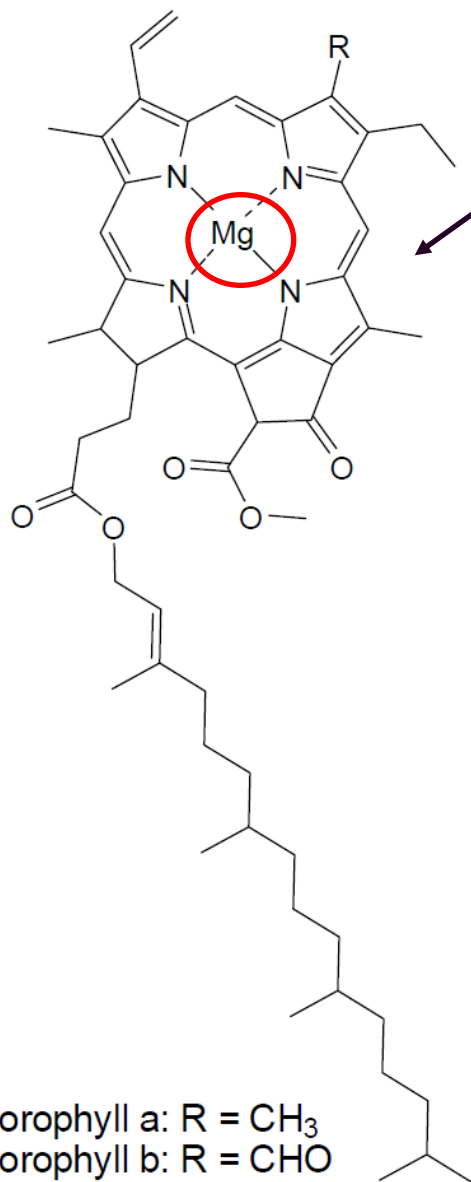
UVOD

- visoko konjugirani ciklički sustav
- mnogo rezonancijskih formi
- 18π delokalizirani sustav – aromatski spojevi
- **amfoliti** – ponašaju se i kao kiseline i baze

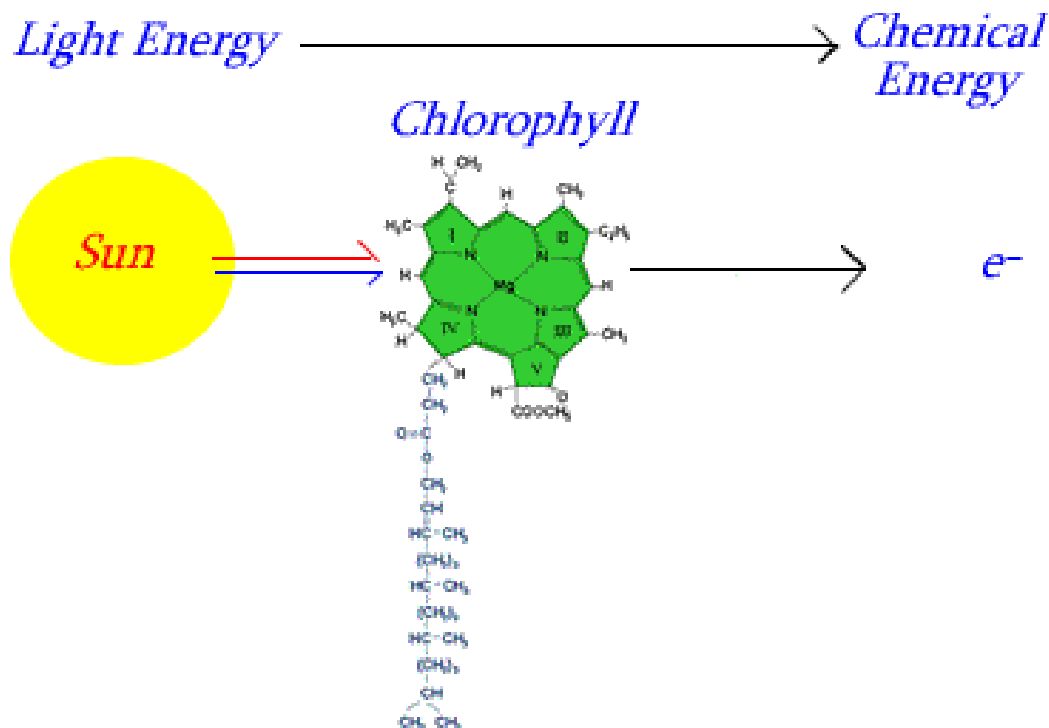
glavne tautomerne forme



BIOLOŠKI VAŽNI DERIVATI PORFIRINA

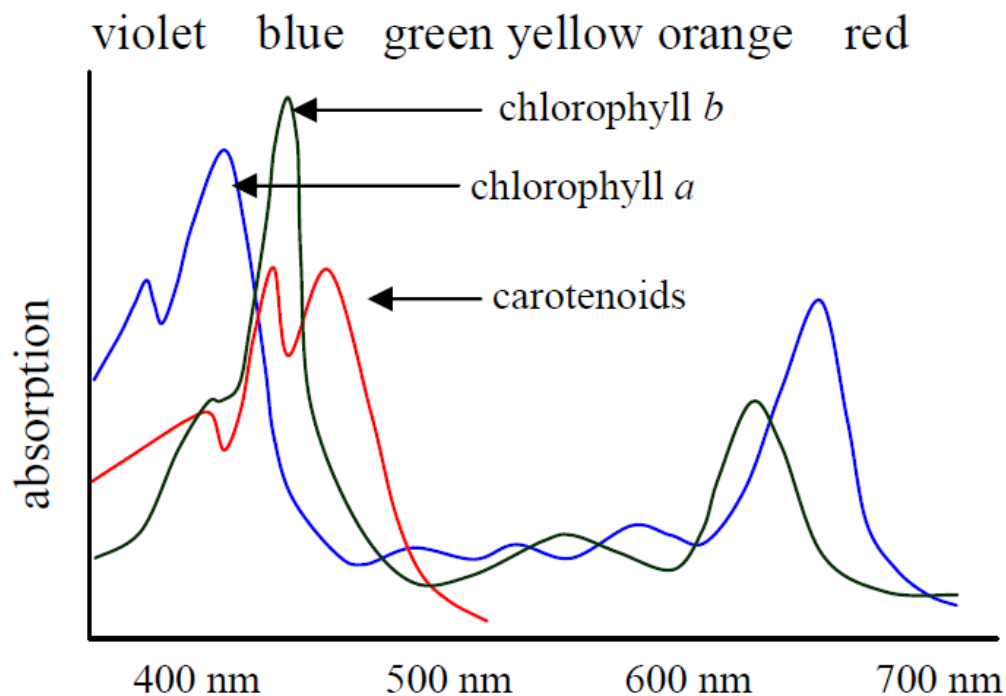


- **klorofil** – u zelenim biljkama, neophodan za fotosintezu jer pretvara sunčevu energiju u kemijsku – konjugirani sustav
- **klorini** – dihidro derivati



BIOLOŠKI VAŽNI DERIVATI PORFIRINA

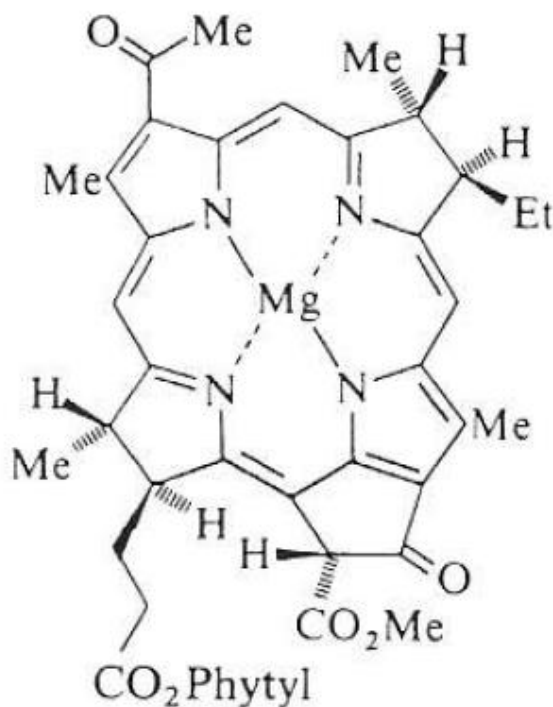
- **klorofil** – intenzivna elektronska apsorpcija
- konjugirani π -sustav porfirinskog prstena – fotoaktivne molekule
- karakteristična narančasto-crvena fluorescencija (600-650 nm)



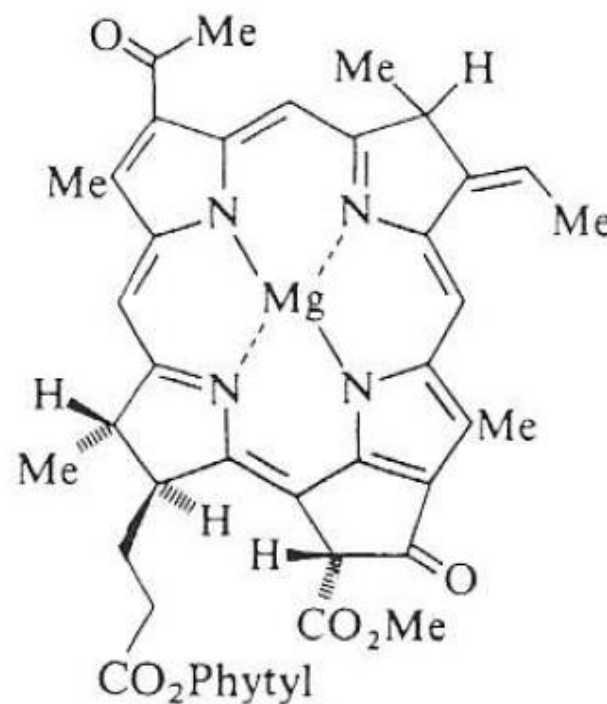
BIOLOŠKI VAŽNI DERIVATI PORFIRINA

- **bakterioklorofili** – pigmenti za fotosintetske procese kod različitih bakterija (*Thiorhodaceae*)

bakterioklorofil a



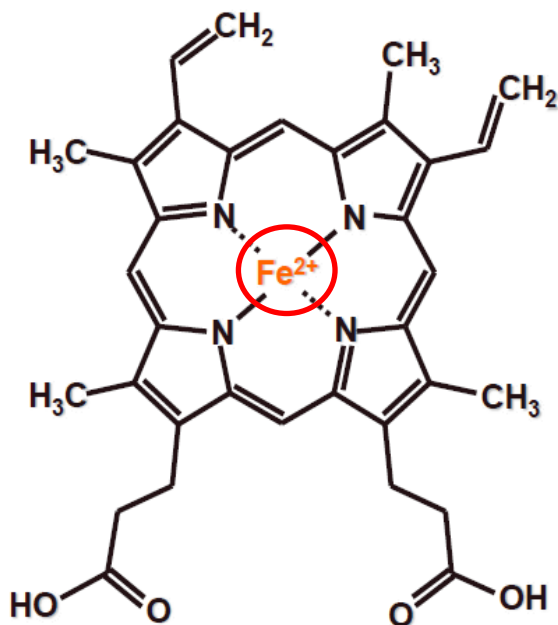
bakterioklorofil b



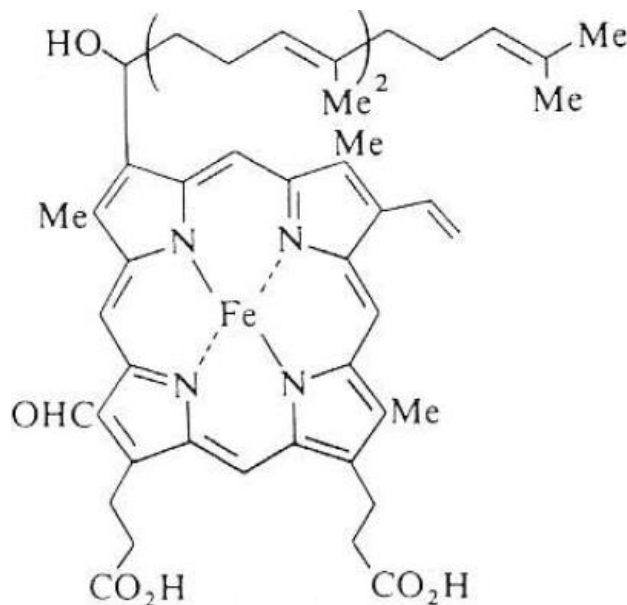
BIOLOŠKI VAŽNI DERIVATI PORFIRINA

- **hemi** – u hemoglobinu za transport kisika i procesu oksidativne fosforilacije (stanično disanje)
- Fe kompleks protoporfirina IX

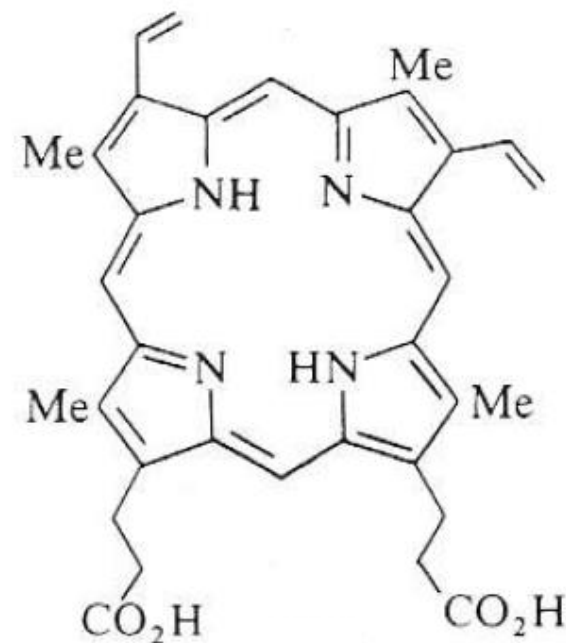
hem B



hem A

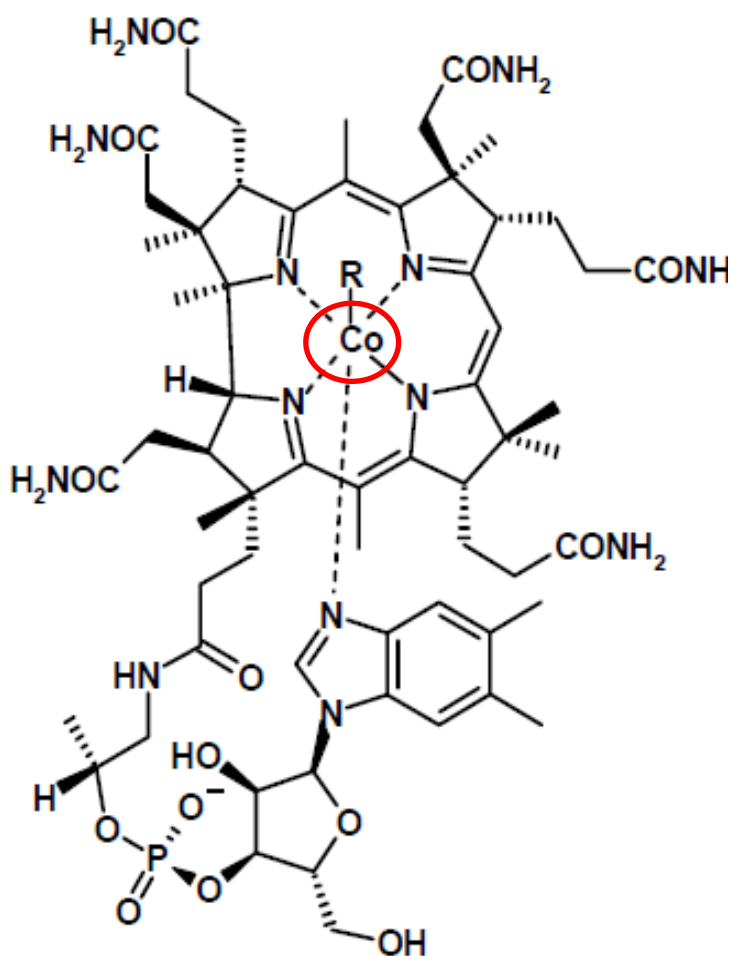


protoporfirin

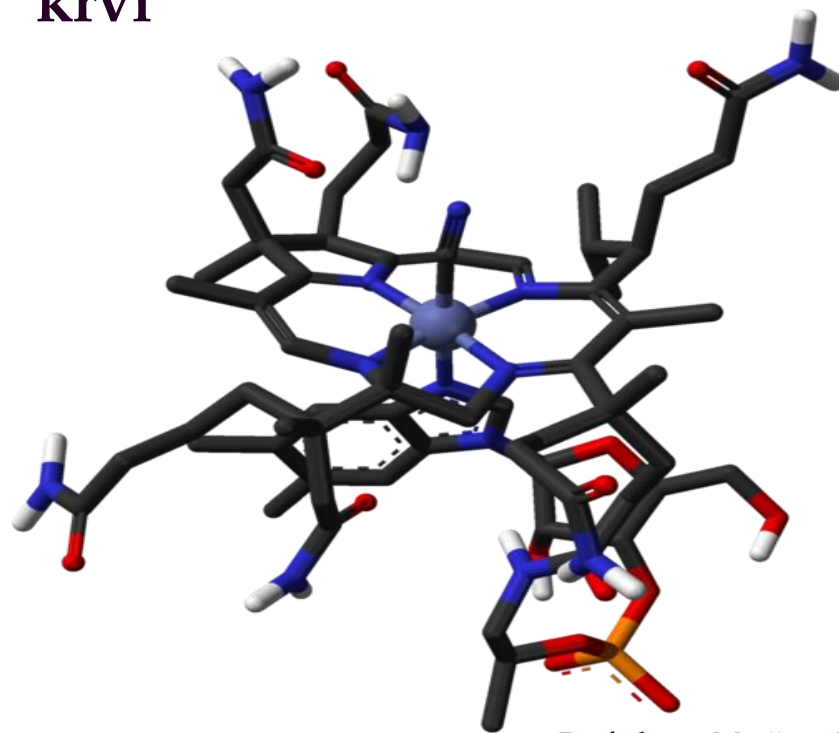


BIOLOŠKI VAŽNI DERIVATI PORFIRINA

- **vitamin B12** – kobalamin (korini – u odnosu na porfirine imaju jedan C atom manje – 15 atoma)

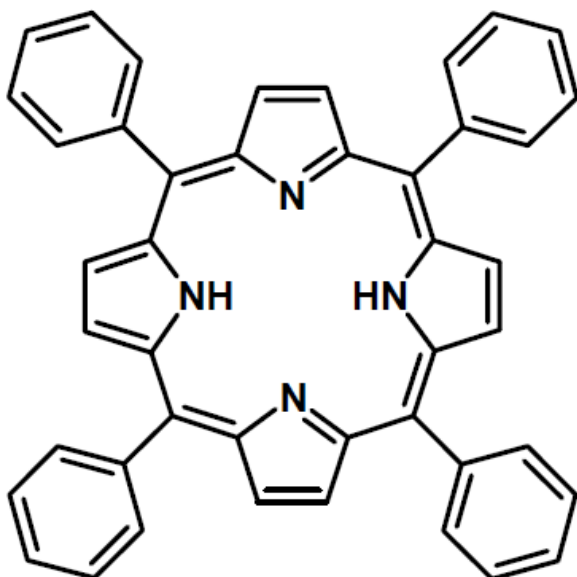


- ključna uloga u normalnom funkcioniranju mozga i živčanog sustava te nastajanju krvi

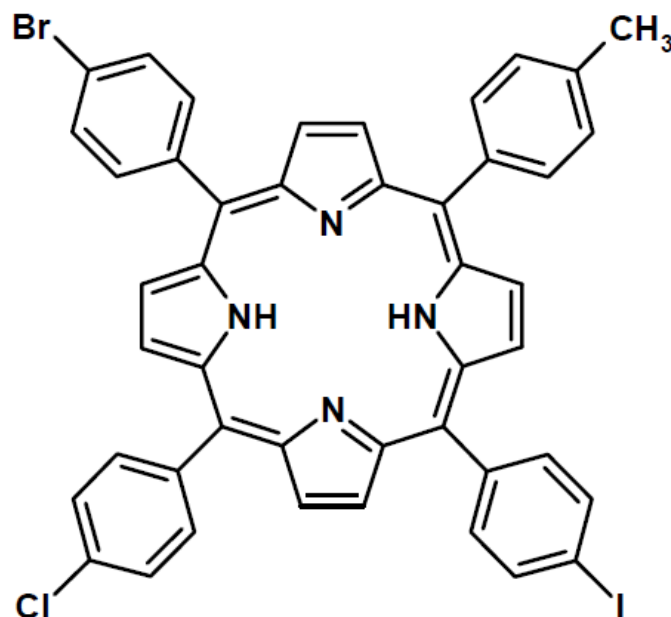


SINTETSKI PORFIRINI

- **porfirini druge generacije** – nisu prisutni u ljudskom tijelu ni u prirodnim produktima
- derivati najjednostavnijeg porfina
- porfirinski skelet – iz aldehida, pirola i sličnih prekursora
- **1936. prvi derivat** (Rothemund) – tetrafenilporfirin
- simetrični i asimetrični porfirini

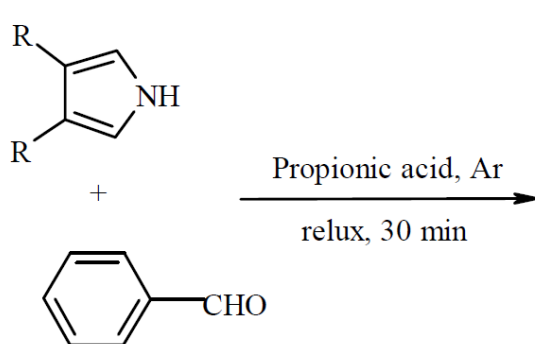


meso-tetraphenylporphyrin

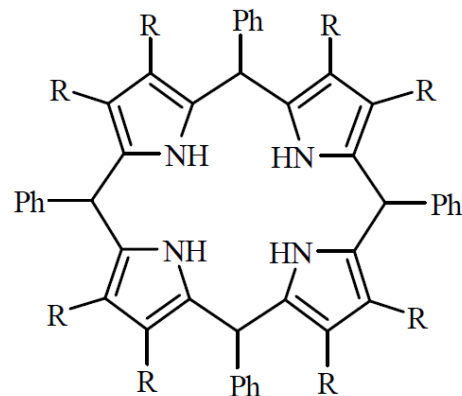


Asymmetric porphyrin

SINTETSKI PORFIRINI

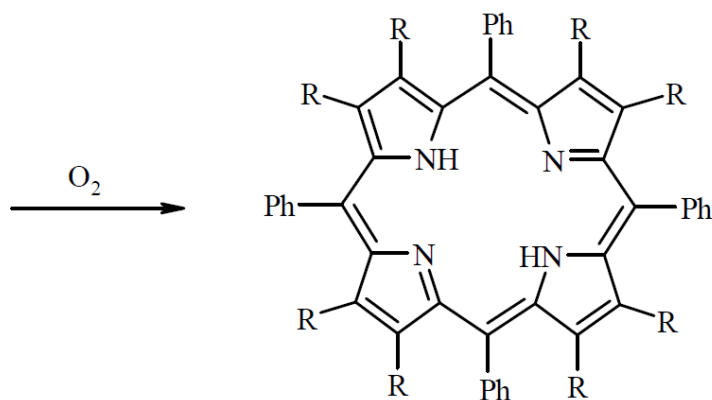


R = H, Me



R = H - meso-Tetraphenylporphyrinogen

R = Me - β -octamethyl-meso-tetraphenylporphyrinogen

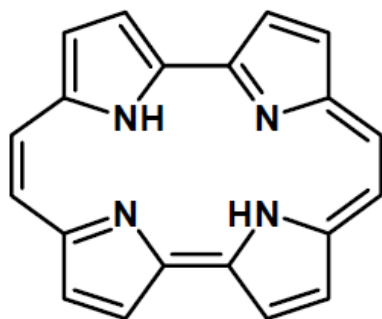


R = H - meso-Tetraphenylporphyrin

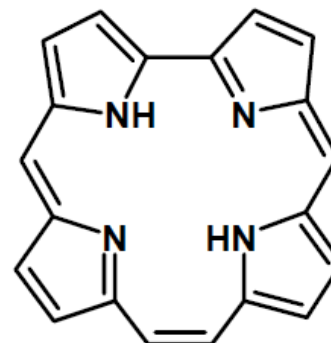
R = Me - β -octamethyl-meso-tetraphenylporphyrin

ANALOZI PORFIRINA

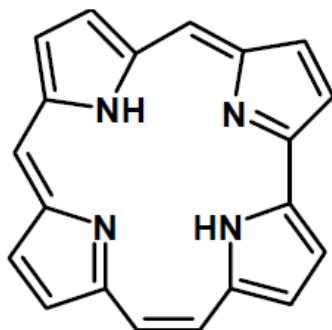
- konfiguracijski izomeri – metenski most na različitim položajima pirolnog prstena



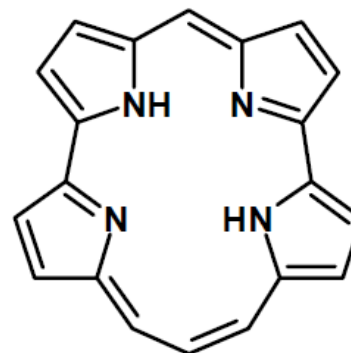
Porphycene



Corrphycene



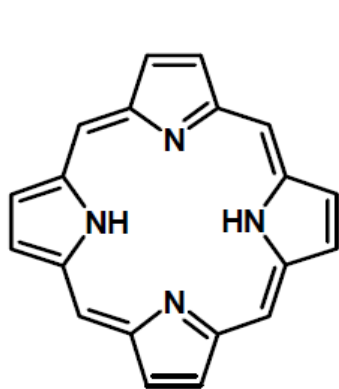
Hemiporphycene



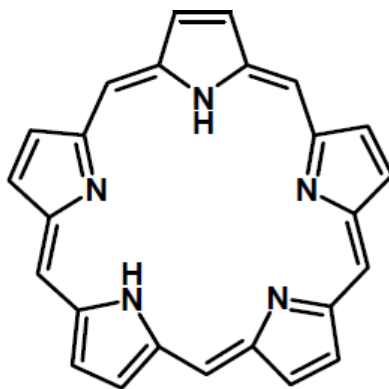
Isoporphycene

DERIVATI PORFIRINA

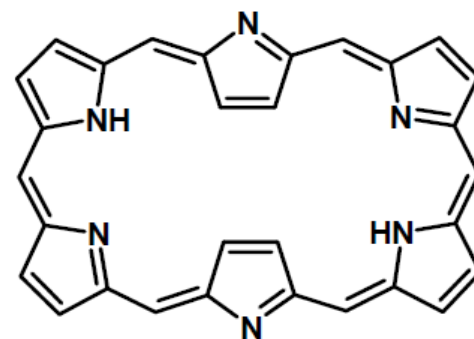
➤ makrociklički aromatski prsten s više C i N atoma



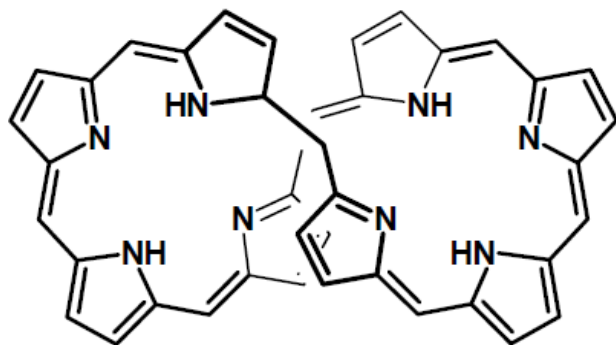
Porphyrin



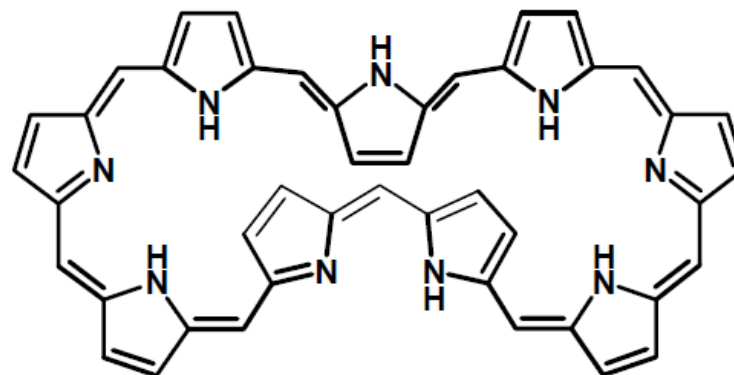
Pentaphyrin



Hexaphyrin

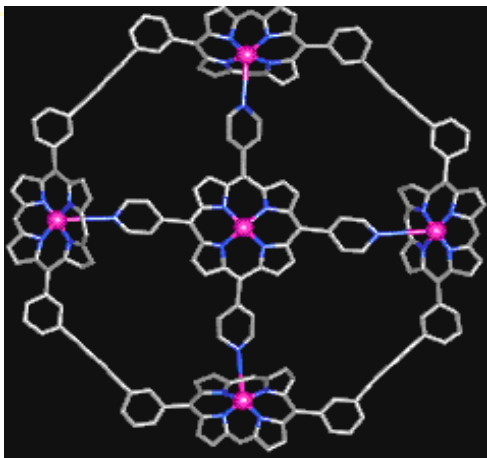


Octaphyrin

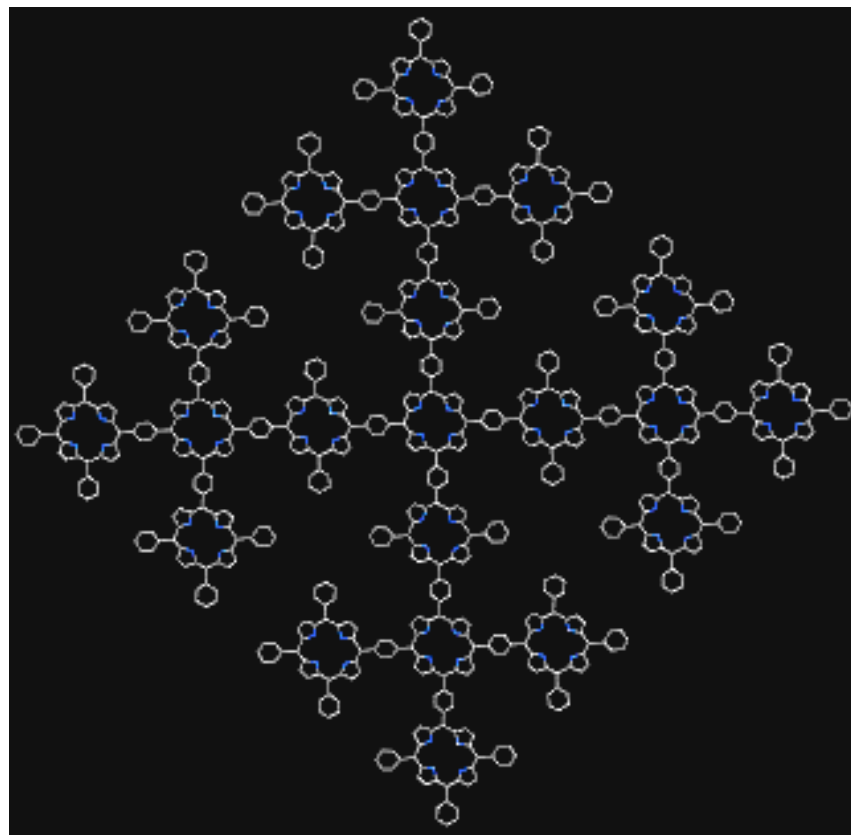
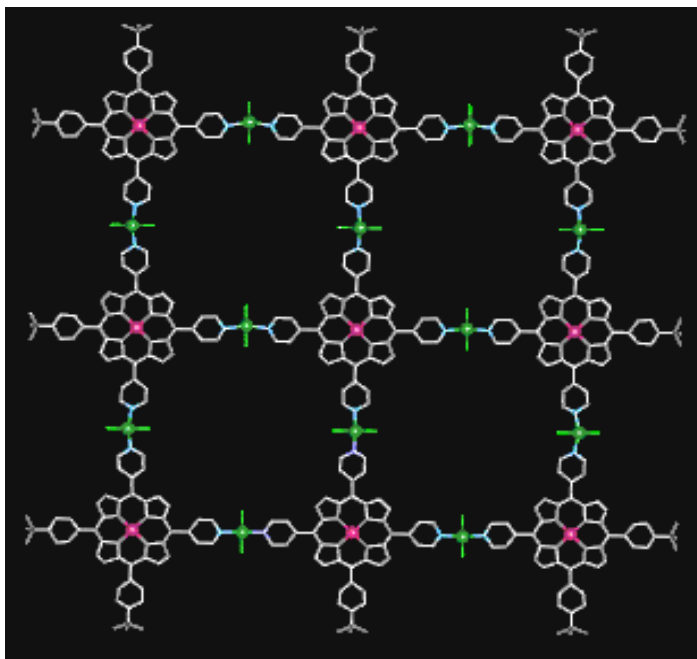


Nonaphyrin

DERIVATI PORFIRINA

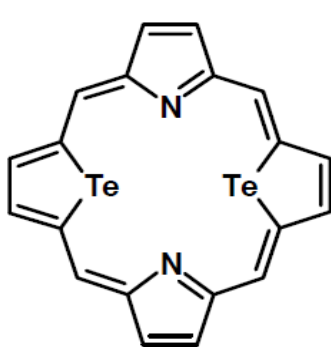


- makrociklički aromatski prsten s više C i N atoma

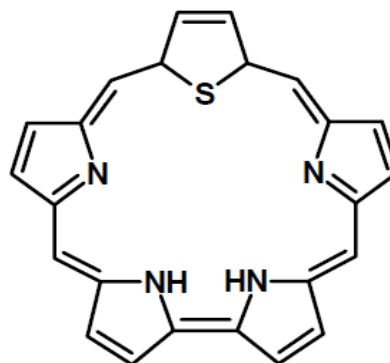


DERIVATI PORFIRINI S HETEROATOMIMA

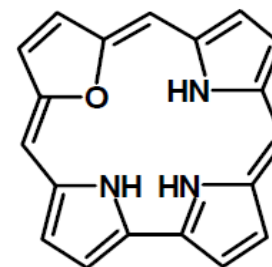
➤ makrociklički aromatski prsten s više C i N atoma



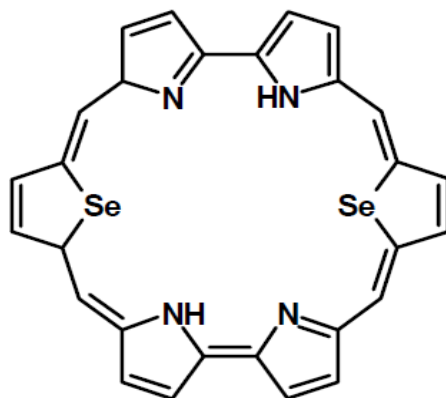
Ditelluraporphyrin



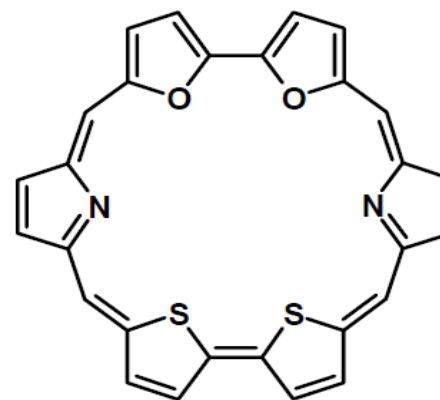
Thiasapphyrin



Oxacorrole



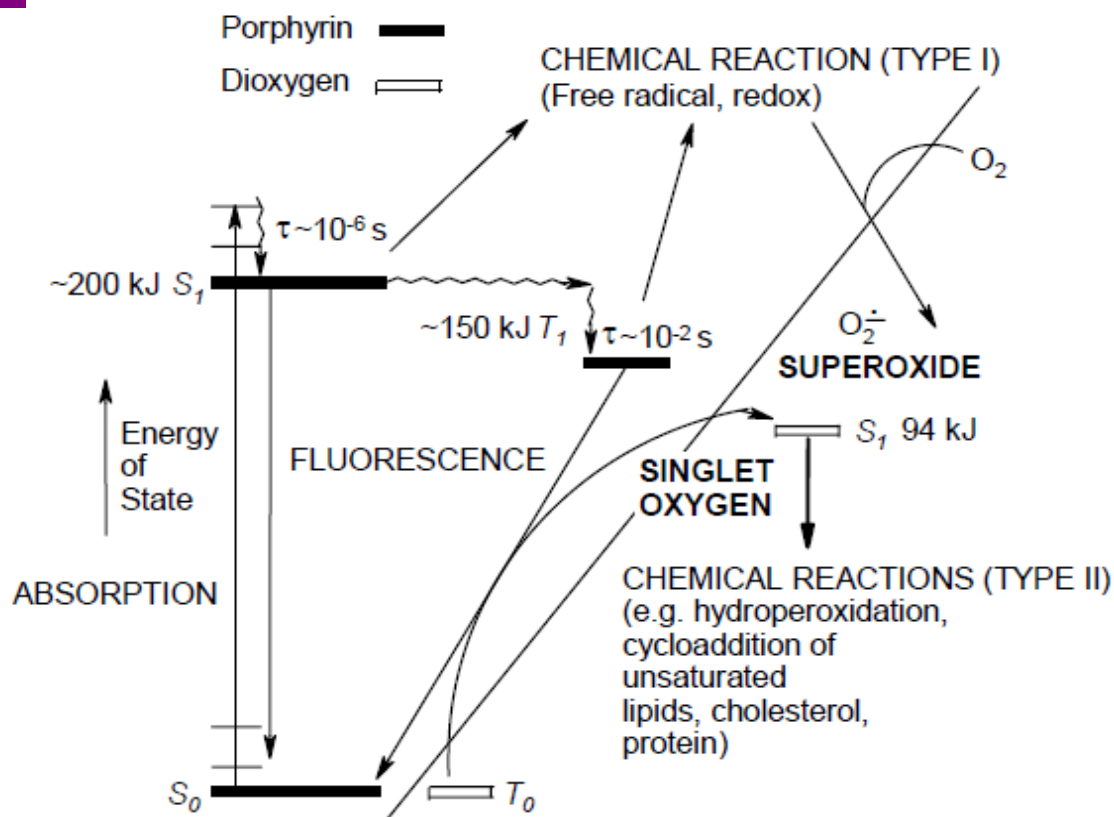
Diselenarubyrin



Dioxadithiarubyrin

PRIMJENA: FOTODINAMSKA TERAPIJA

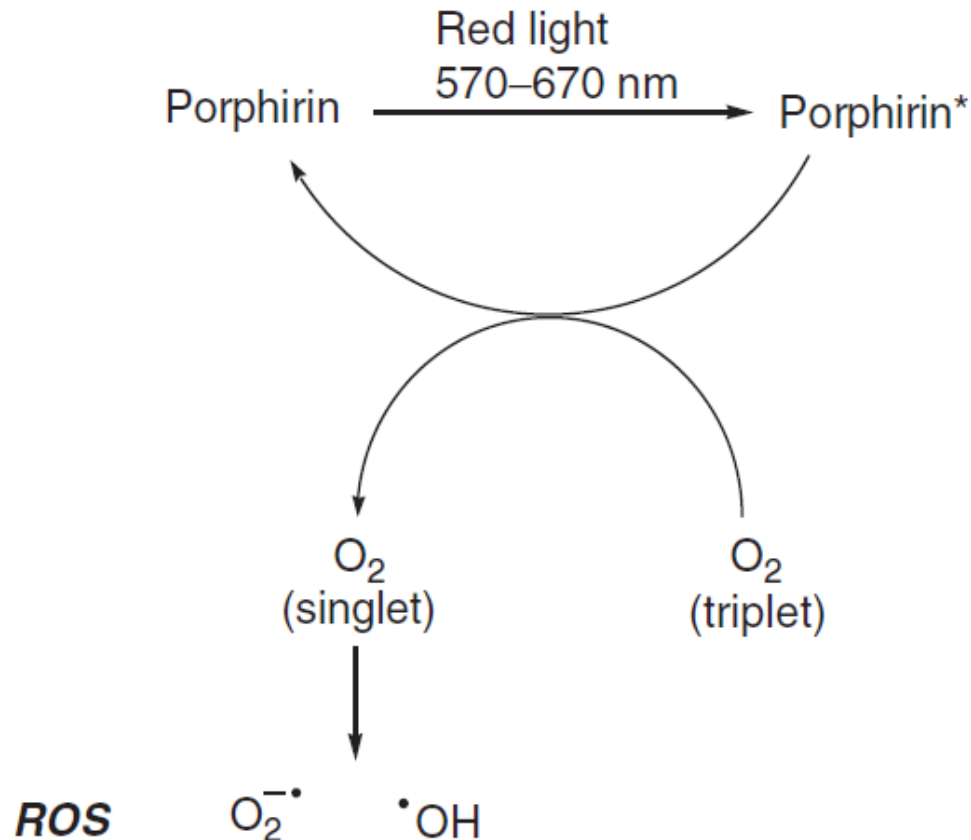
Ova vrsta terapije bazira se na sposobnosti molekula da apsorbiraju svjetlo koje nije štetno (vidljiv dio UV spektra) te da na taj način prijeđu u molekulu koja ima određenu antitumorsku aktivnost. Takve se molekule nazivaju fotosenzibilizatori (PS).



Nakon osvjetljavanja PS molekule iz osnovnog stanja prelaze u singletno pobuđeno stanje te prelaskom u osnovno stanje emitiraju energiju (npr. fluorescenciju) što je važno kod detekcije (fotodijagnoze). ISC prijelazom PS može prijeći u pobuđeno tripletno stanje pa povratkom u osnovno stanje dolazi do fosforescencije.

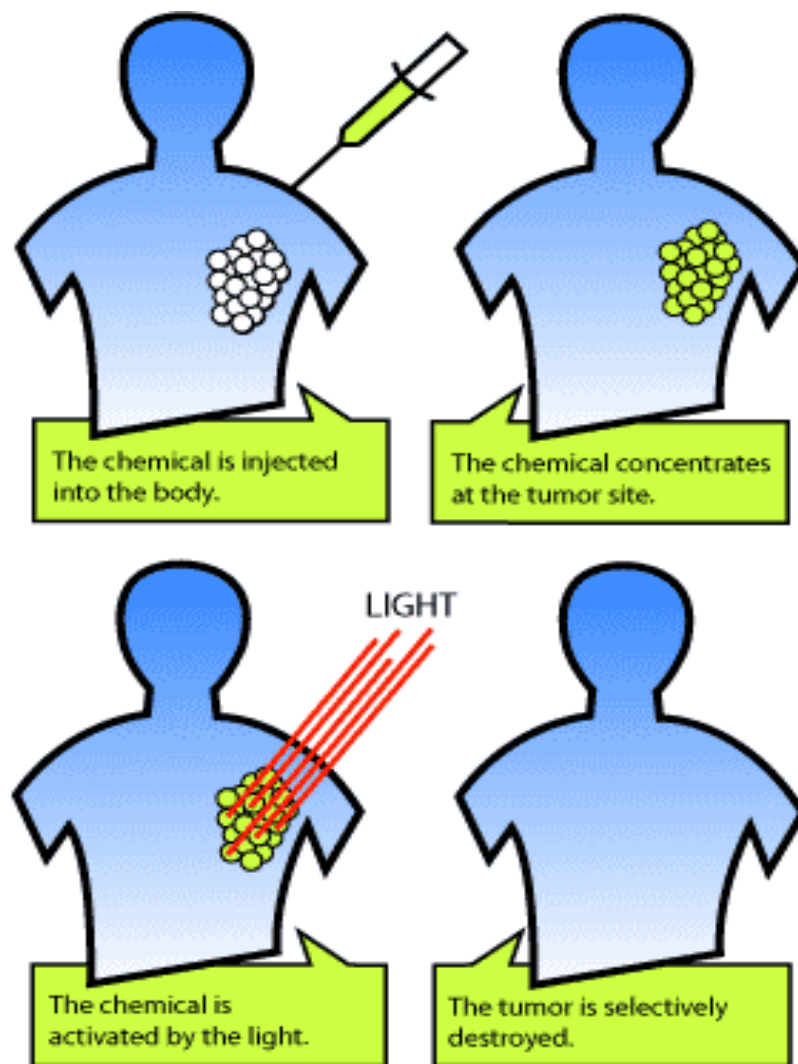
PRIMJENA: FOTODINAMSKA TERAPIJA

- generiranje ROS-a – oksidativni mehanizam
- u praksi se koristi već više od 20 godina i to najčešće za liječenje raka kože ali u posljednje vrijeme i za druge vrste za tumora.



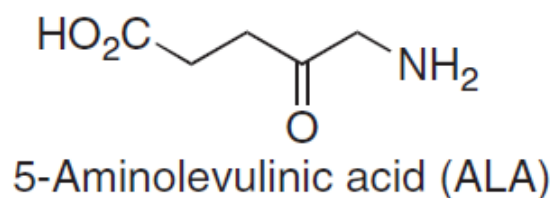
PRIMJENA: FOTODINAMSKA TERAPIJA

Nakon doziranja s fotoaktivnim agensom, osvjetljavanje ciljanog tumorskog tkiva vrši se optičkim difuzorom za lokalnu aktivaciju. Ova je metoda minimalno invazivna jer okolno zdravo tkivo nije osjetljivo na svjetlost.

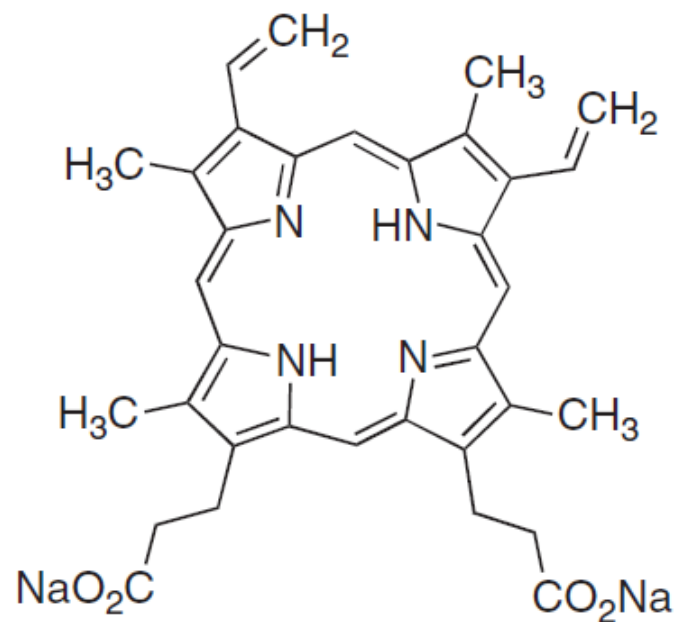


Biosinteza porfirina

Alternativni način liječenja ovom metodom uključuje biosintetski prekursor za sintezu protoporfirina, 5-aminolevulensku kiselinu. Otežavajuća okolnost može biti transport svjetla do mjesta tumora.



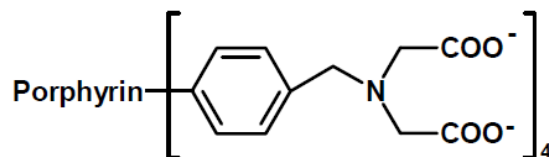
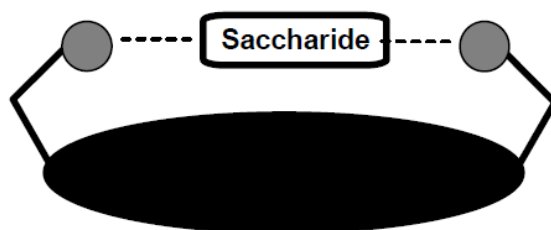
Biosynthesis



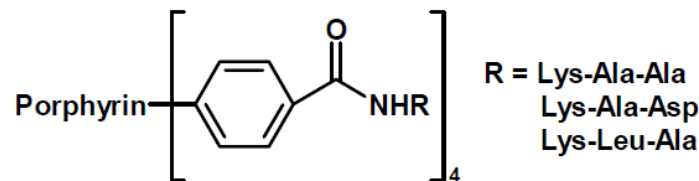
Protoporphyrin IX (PPIX)

RECEPTORI ZA UGLJIKOHIDRATE

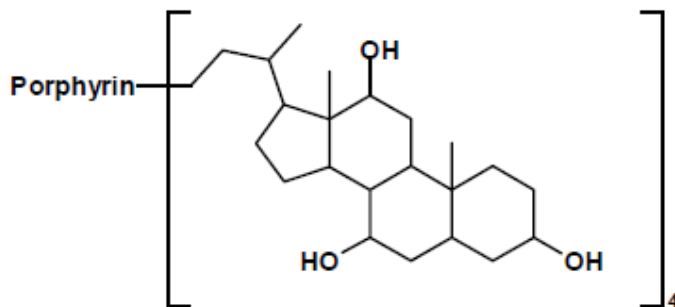
- **bioanalitika** – prepoznavanje ugljikohidratnih dijelova u bioanalitima



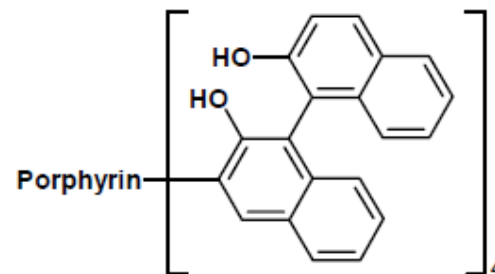
Porphyrin-octacarboxylate



Porphyrin aminoacid conjugate



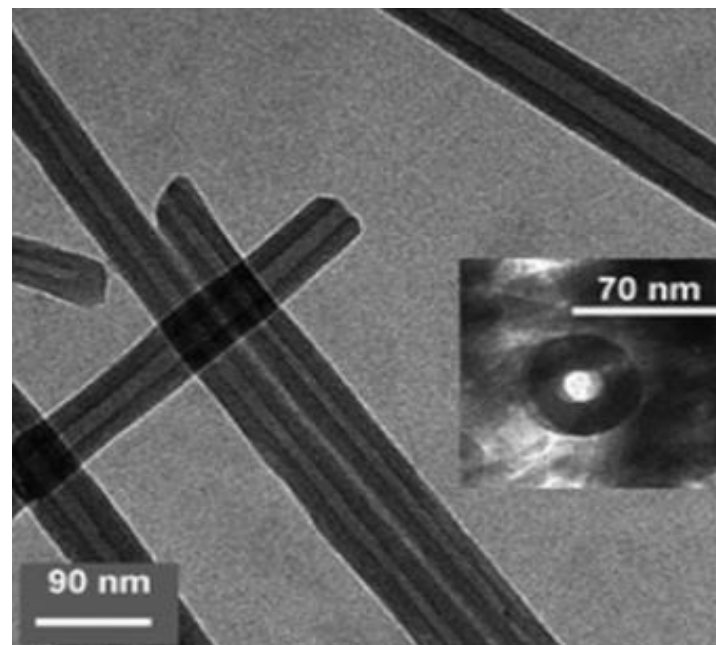
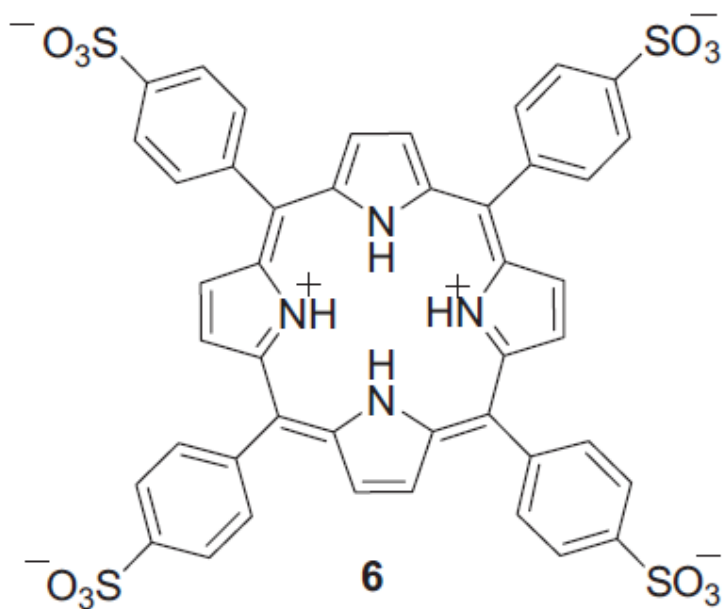
Porphyrin steroid conjugate



Porphyrin binaphthol conjugate

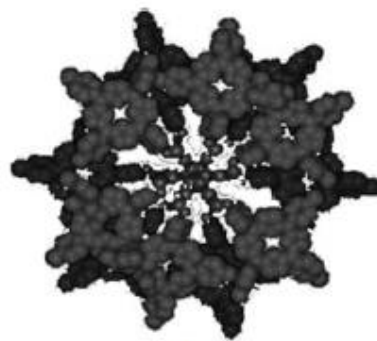
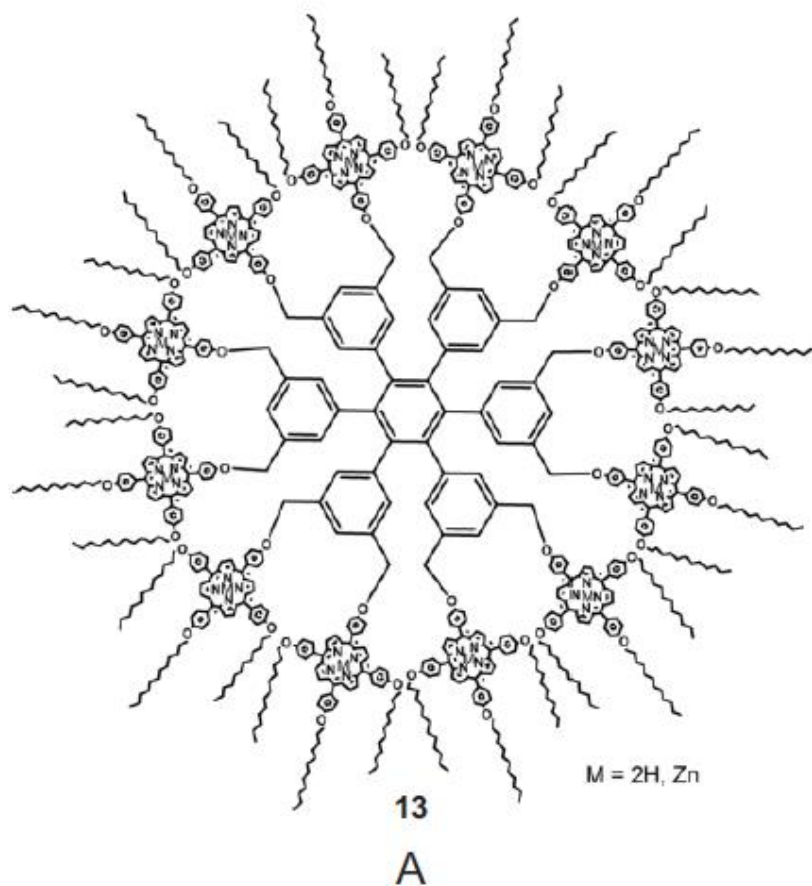
NANOMATERIJALI

- **molekularni materijali** – jedinstvena elektronska, magnetska i fotofizikalna svojstva



NANOMATERIJALI

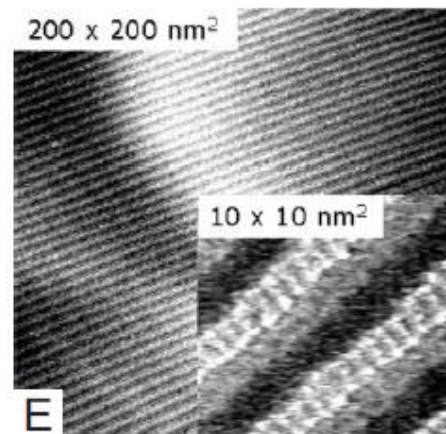
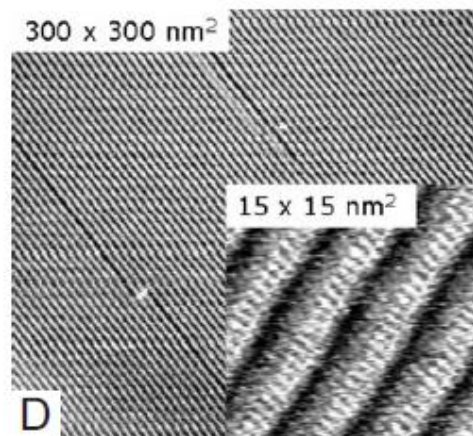
- **molekularni materijali** – jedinstvena elektronska, magnetska i fotofizikalna svojstva – solarne ćelije



B

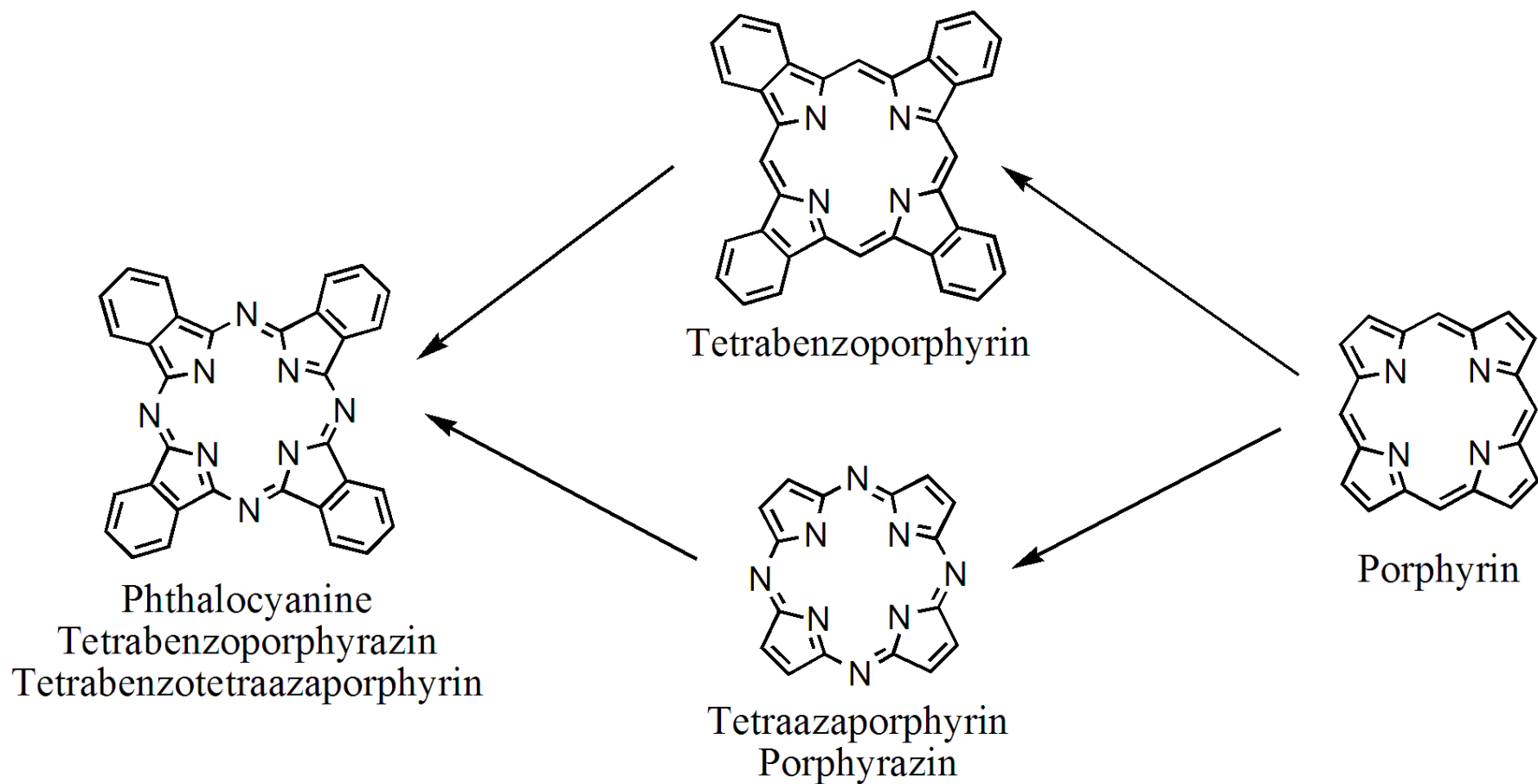


C



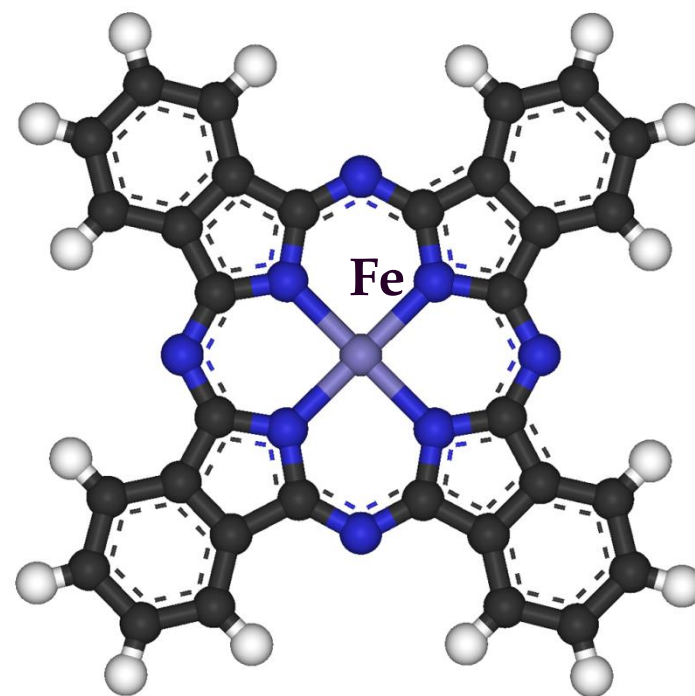
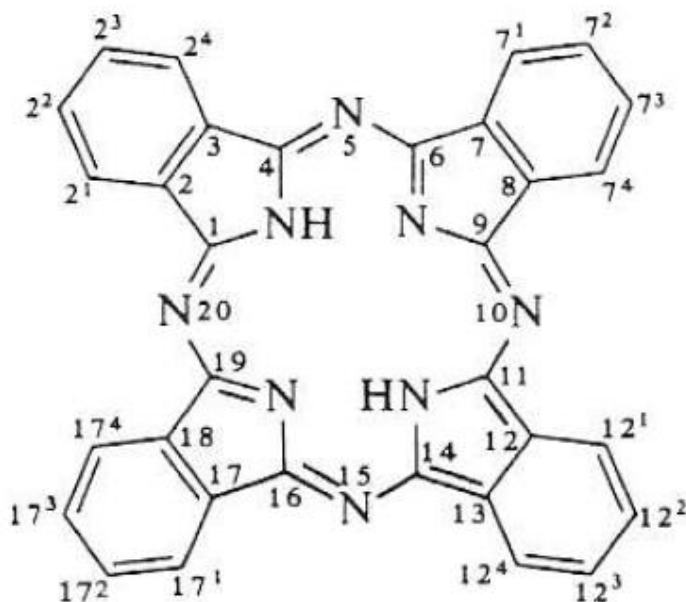
FTALOCIJANINI

➤ *N*-supstituirani derivati porfirina



FTALOCIJANINI

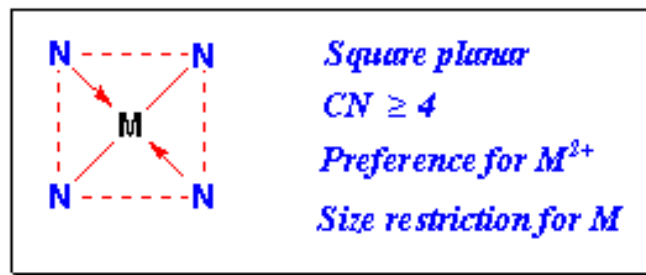
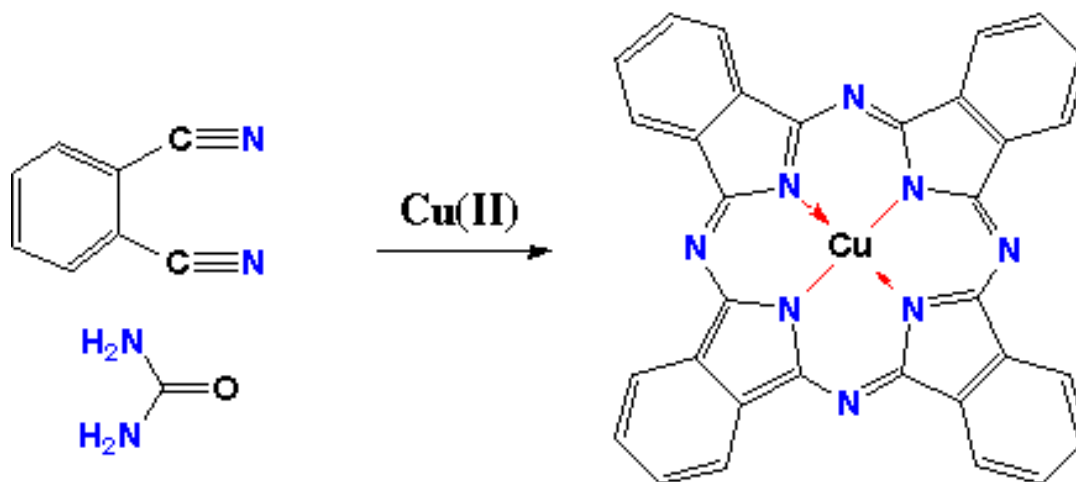
- otkriveni slučajno prilikom sinteze ftalimida
- metalni kompleksi, intenzivno obojeni
- bojila u tekstilnoj industriji



Cu(II)ftalocijanini

➤ jednostavna sinteza

Copper(II)phthalocyanine: A simple way to a complex molecule



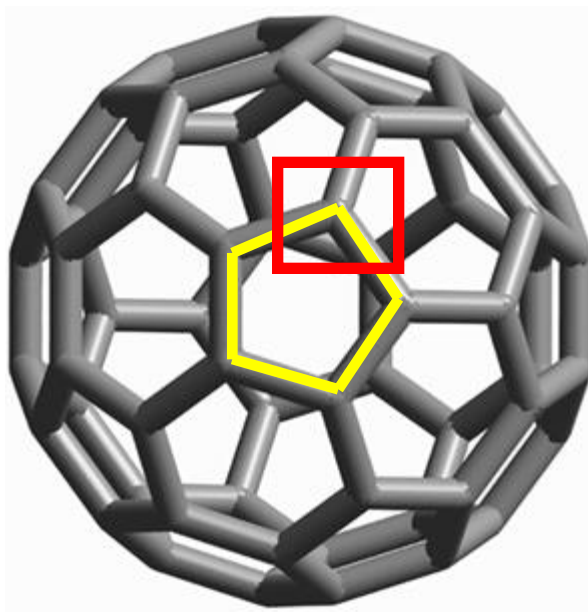
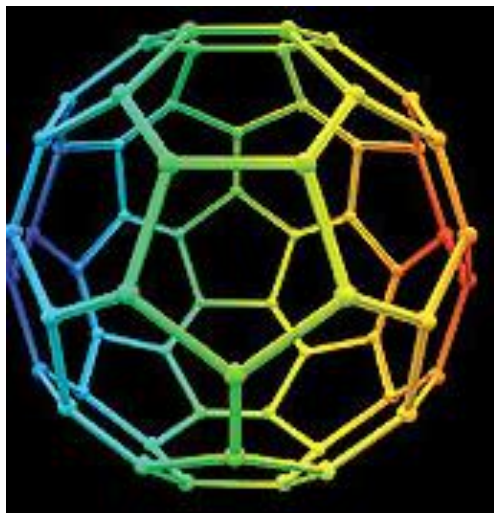
FULERENI

**Preddiplomski studij
Primijenjena kemija
Prof. dr. sc. Marijana Hranjec**

Studenii, 2022.

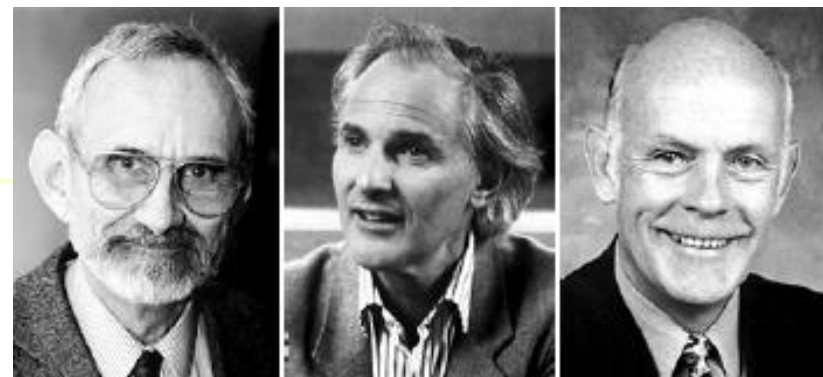
UVOD

- alotropi ugljika (dijamant, grafit) – aromatski spojevi
- poliedri sastavljeni od peterocikličkih i šesterocikličkih prstenova a u svakom uglu se spajaju tri stranice
- svaki ugljikov atom je sp^2 hibridiziran i vezan na tri druga C atoma
- trovalentni poliedarski sustav – oblik kugle





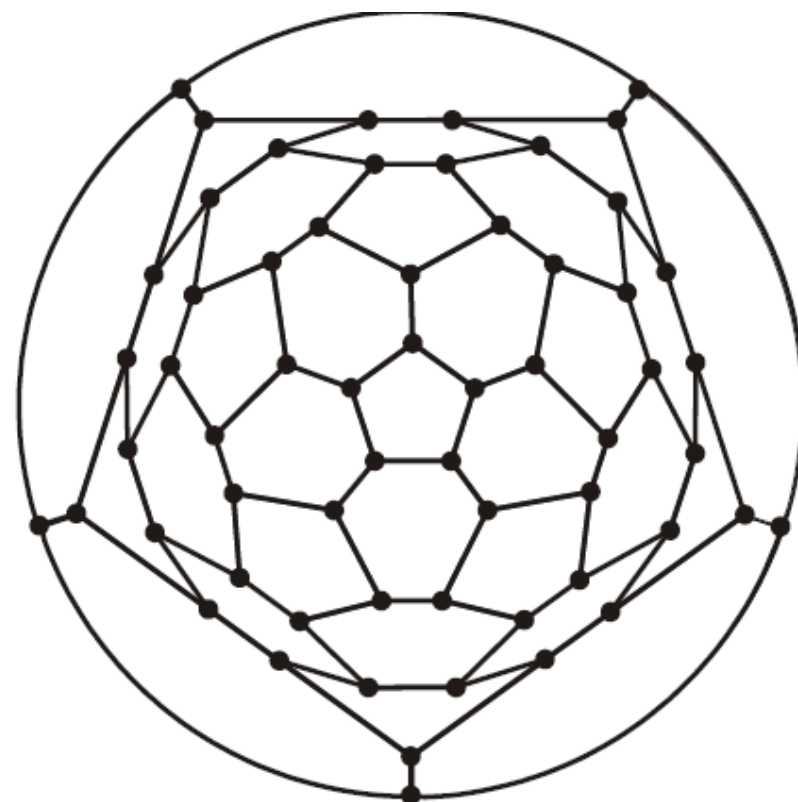
- 1985. R. F. Curl, H. W. Kroto i R. E. Smalley definirali strukturu molekule fullerena C_{60}
- 1996. Nobelova nagrada



Robert F. Curl Jr.

Sir Harold W. Kroto

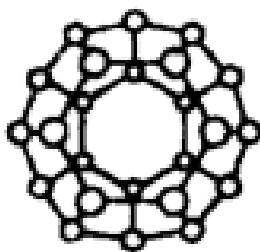
Richard E. Smalley



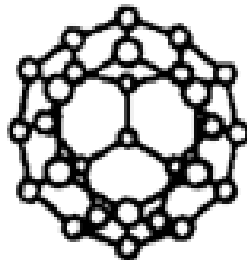
Buckminsterfullerene C_{60}

FULERENI

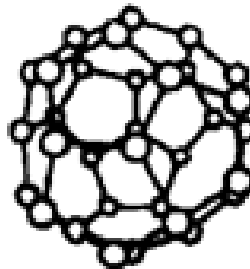
- najučestaliji fulereni su C_{60} i C_{70}
- stabilni spojevi - Kekule-ove strukture



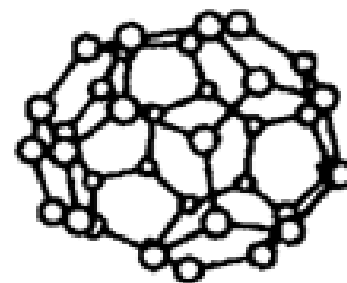
C_{24}



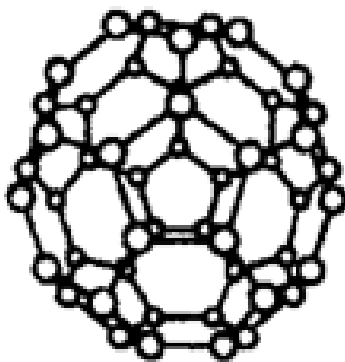
C_{28}



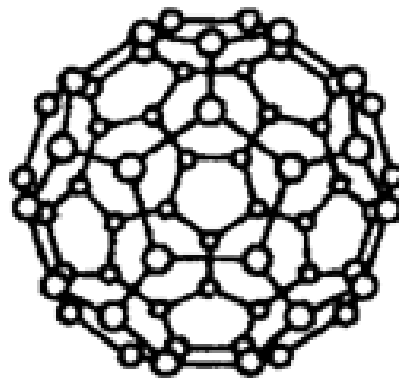
C_{32}



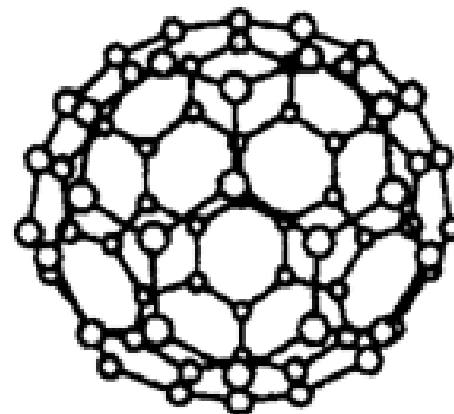
C_{36}



C_{50}



C_{60}



C_{70}

PRIMJENA

- nanocijevi – cilindrični fulereni
- superkonduktivne karakteristike
- vrlo male dimenzije

