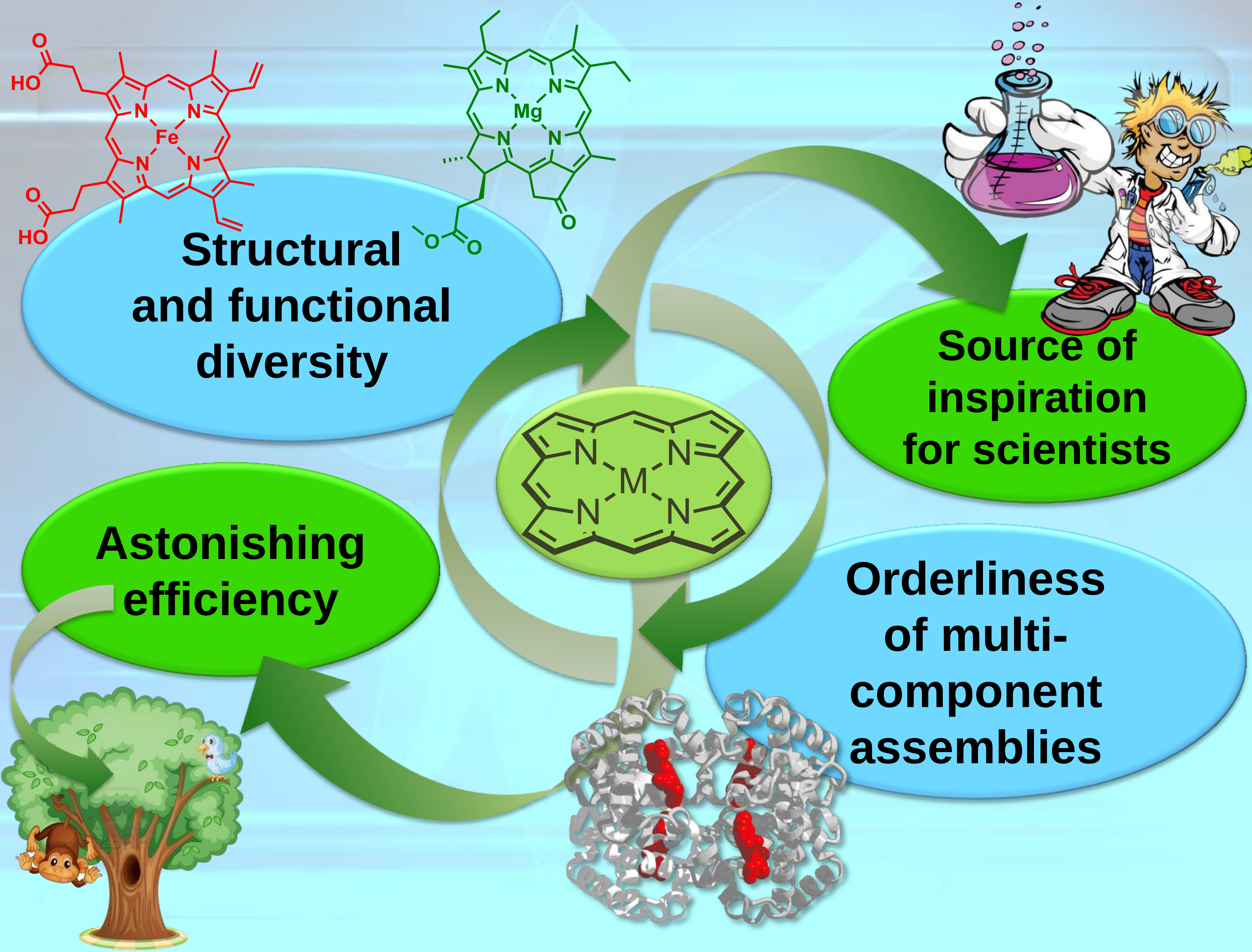
III Российский день редких земель

СЭНДВИЧЕВЫЕ КОМПЛЕКСЫ РЗЭ С ТЕТРАПИРРОЛЬНЫМИ ЛИГАНДАМИ - ВЛИЯНИЕ СИММЕТРИИ И "ПАЛУБНОСТИ" НА ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА

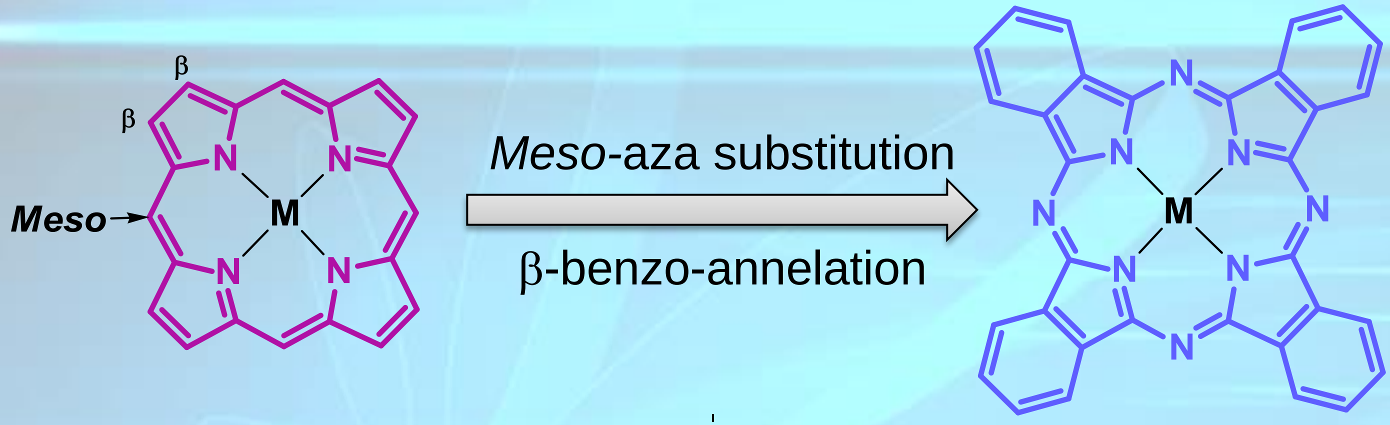
Горбунова Ю.Г.

Институт физической химии и электрохимии им. А.Н. Фрумкина РАН
Институт общей и неорганической химии им. Н.С. Курнакова РАН

20 февраля 2017 г., Новосибирск


Structural
and functional
diversity
Source of
inspiration
for scientists
Orderliness
of multi-
component
assemblies
Astonishing
efficiency

Tetrapyrrols around us



Functions of porphyrins in Nature

•Photosynthesis

•Biocatalysis

•Transfer of energy

•Transfer of electrons

Technological and industrial applications of phthalocyanines

•Dyes and pigments

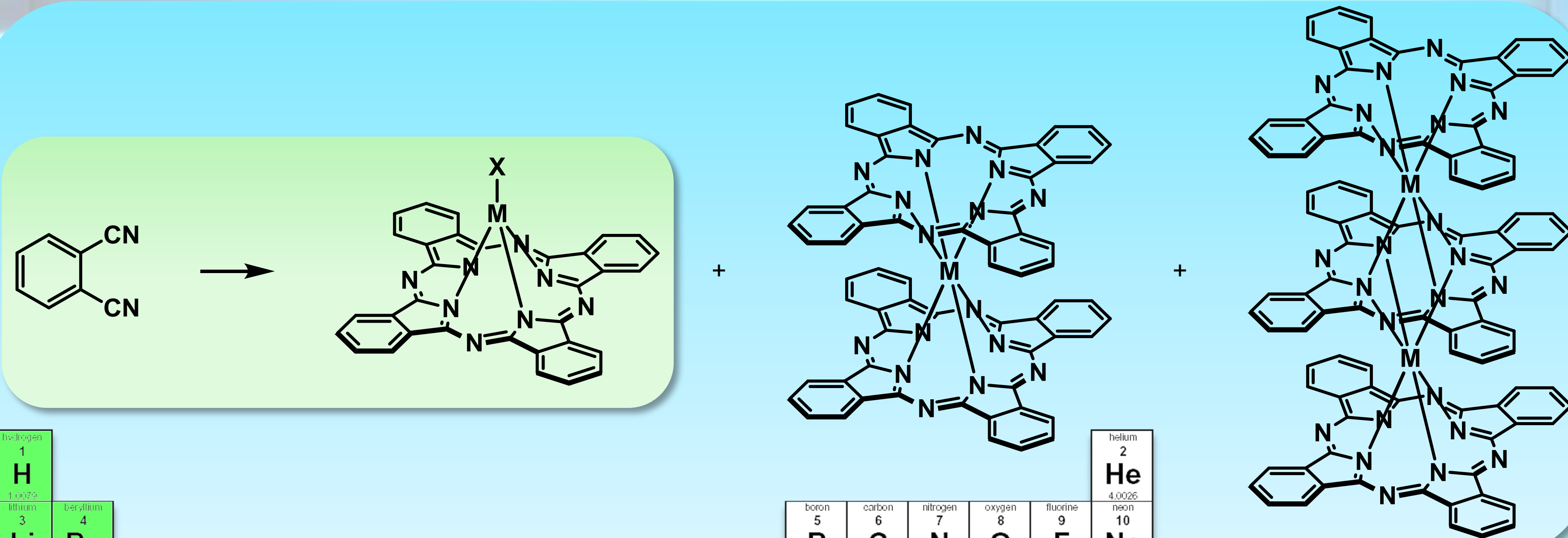
•Catalysis

•Photodynamic therapy

•Solar energy applications and electrochemistry

•Wöhrle D. *et al.*
Practical Applications of Phthalocyanines –
from Dyes and Pigments to Materials for Optical, Electronic and Photo-Electronic Devices
Macroheterocycles **2012**, *5* (3), 191

Periodic table of phthalocyaninates

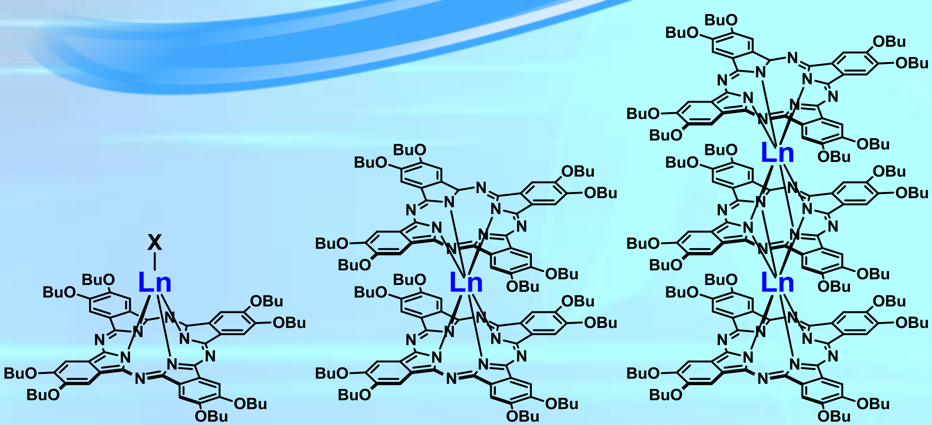


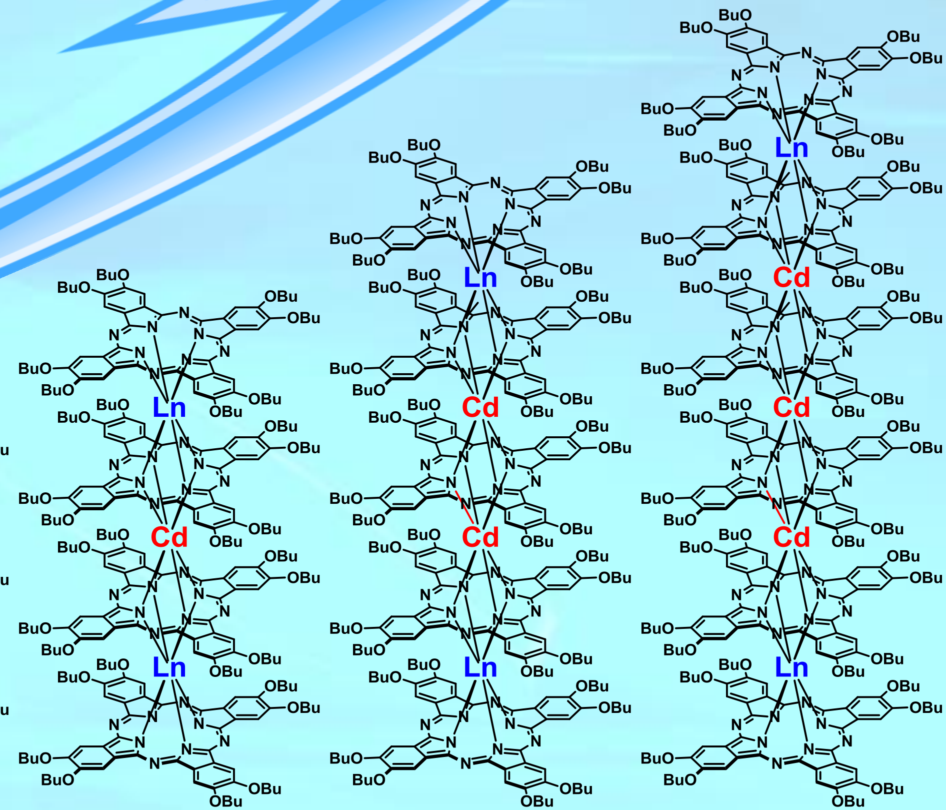
hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

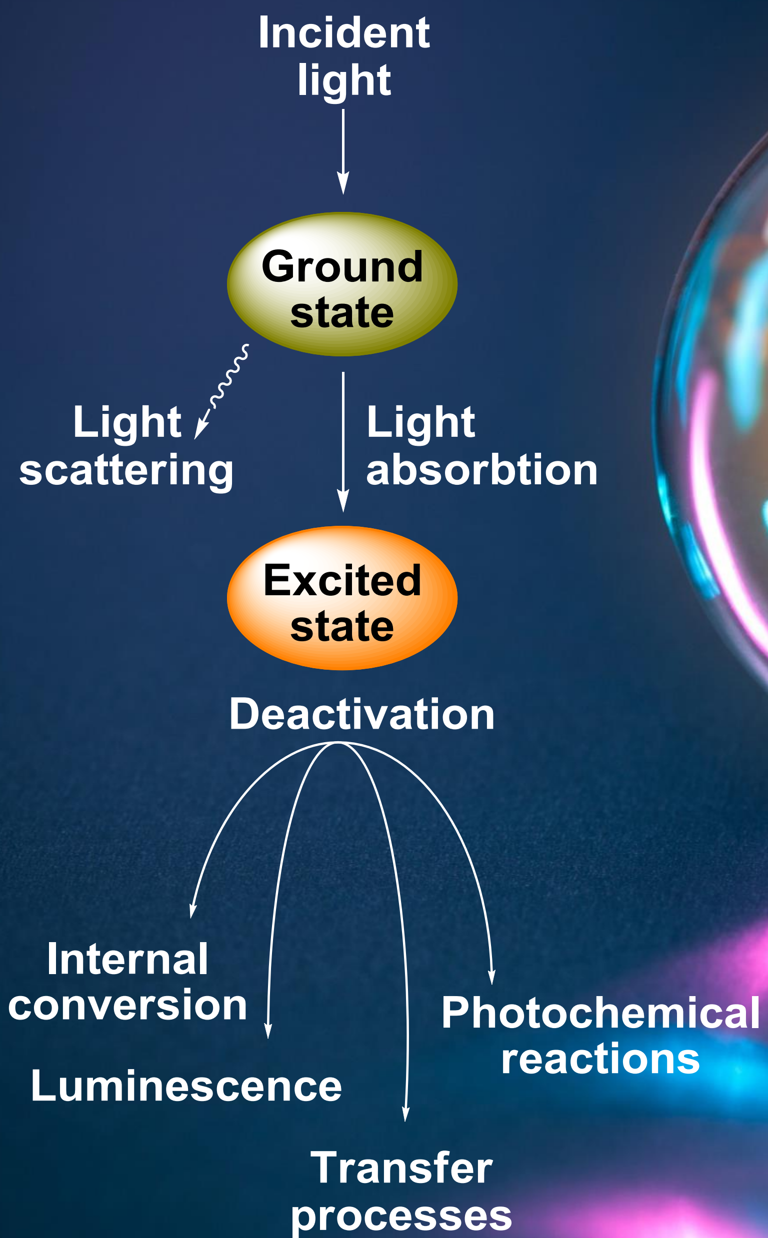
Filling in the gap between molecules and condensed phases

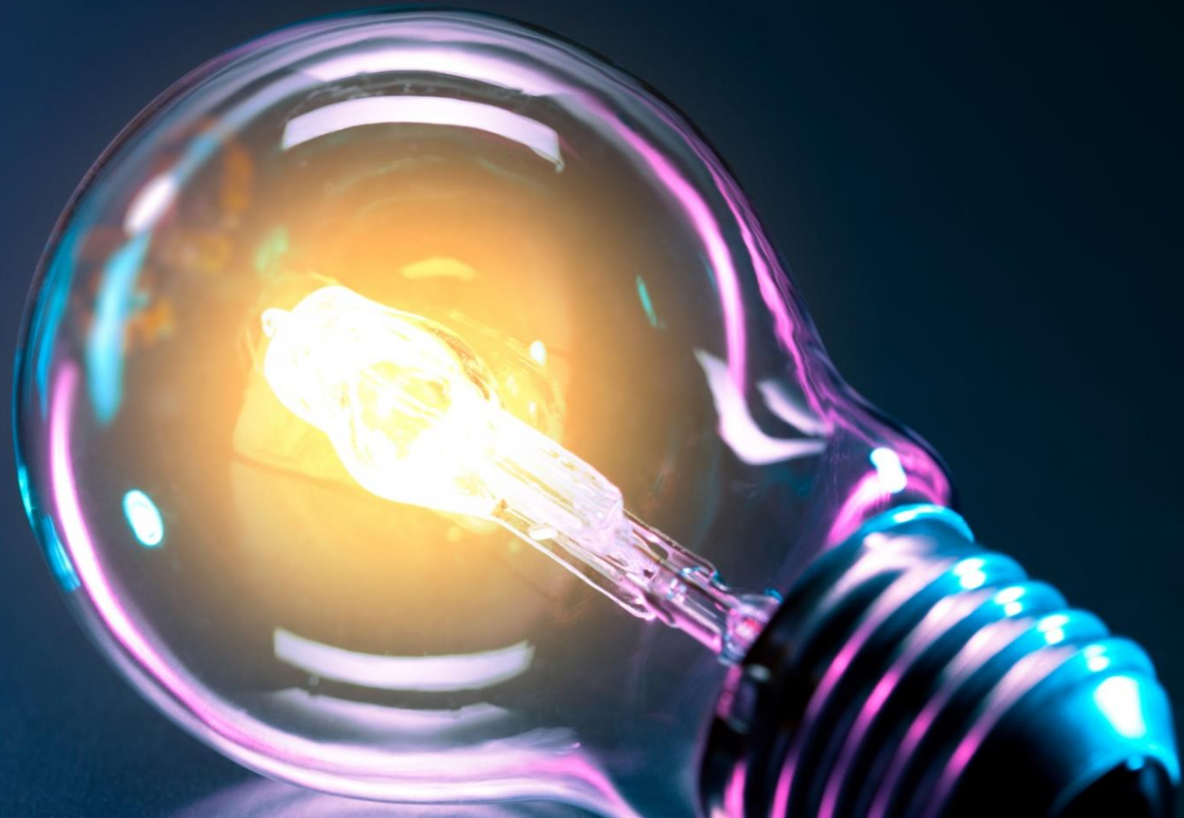
Enhancement of electrochemical, nonlinear optical and magnetic properties





Light-matter interaction: case of <u>medium</u> radiation intensity





$$\mathbf{P} = \chi^{(1)}\cdot\mathbf{E}$$

P – induced electrical polarization,

$\chi^{(1)}$ – *linear* susceptibility,

E – wave field

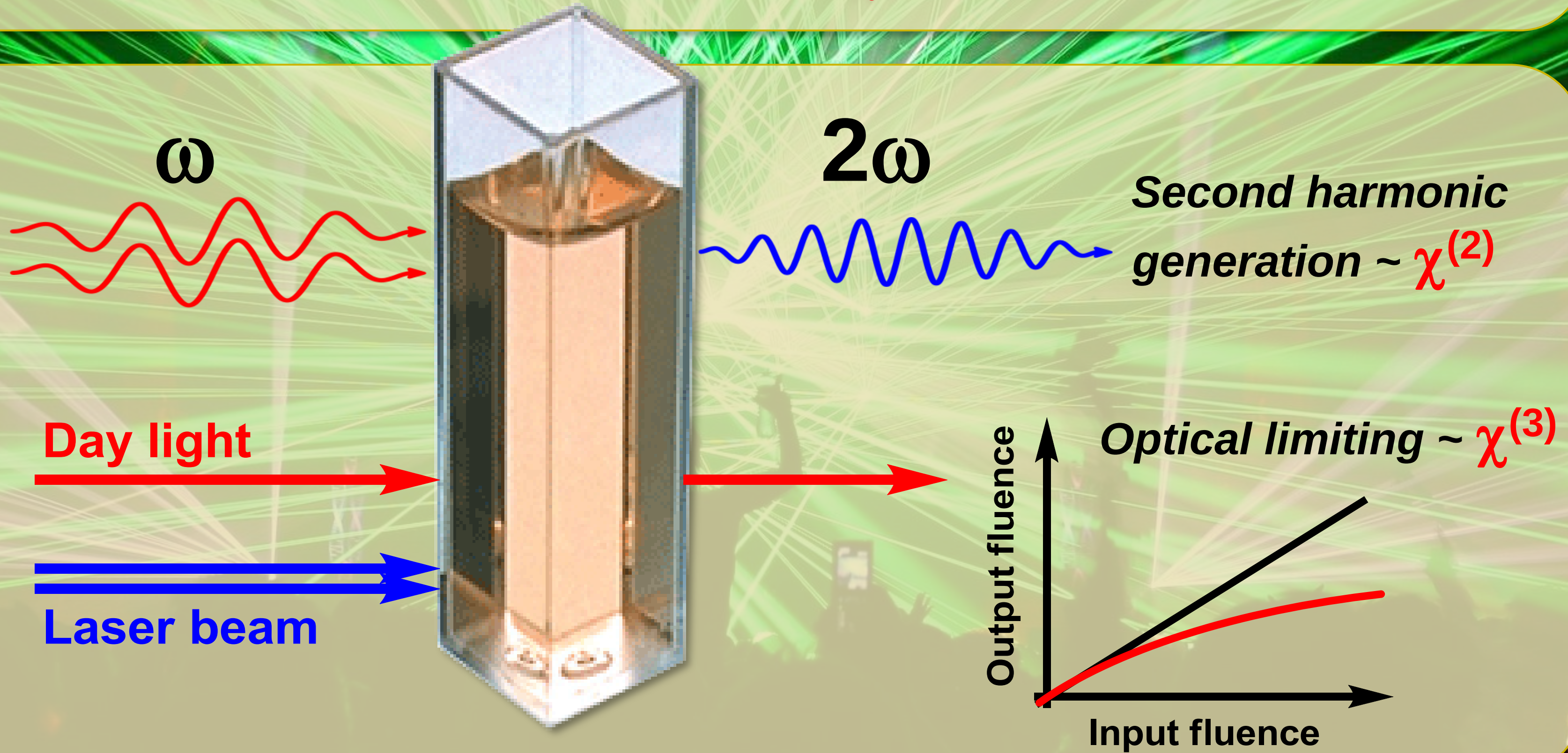
Light-matter interaction: case of strong radiation intensity

$$P = \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + \ldots$$

P – induced electrical polarization,

E – wave field, $\chi^{(1)}$ – *linear* susceptibility,

$\chi^{(2)}$ – *quadratic* susceptibility and $\chi^{(3)}$ – *cubic* susceptibility



Light-matter interaction: case of strong radiation intensity

$$P = \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + \ldots$$

P – induced electrical polarization,
E – wave field, $\chi^{(1)}$ – *linear* susceptibility,
$\chi^{(2)}$ – *quadratic* susceptibility and $\chi^{(3)}$ – *cubic* susceptibility

At molecular level

$$\chi^{(2)} \sim \beta$$

β - second-order hyperpolarizability

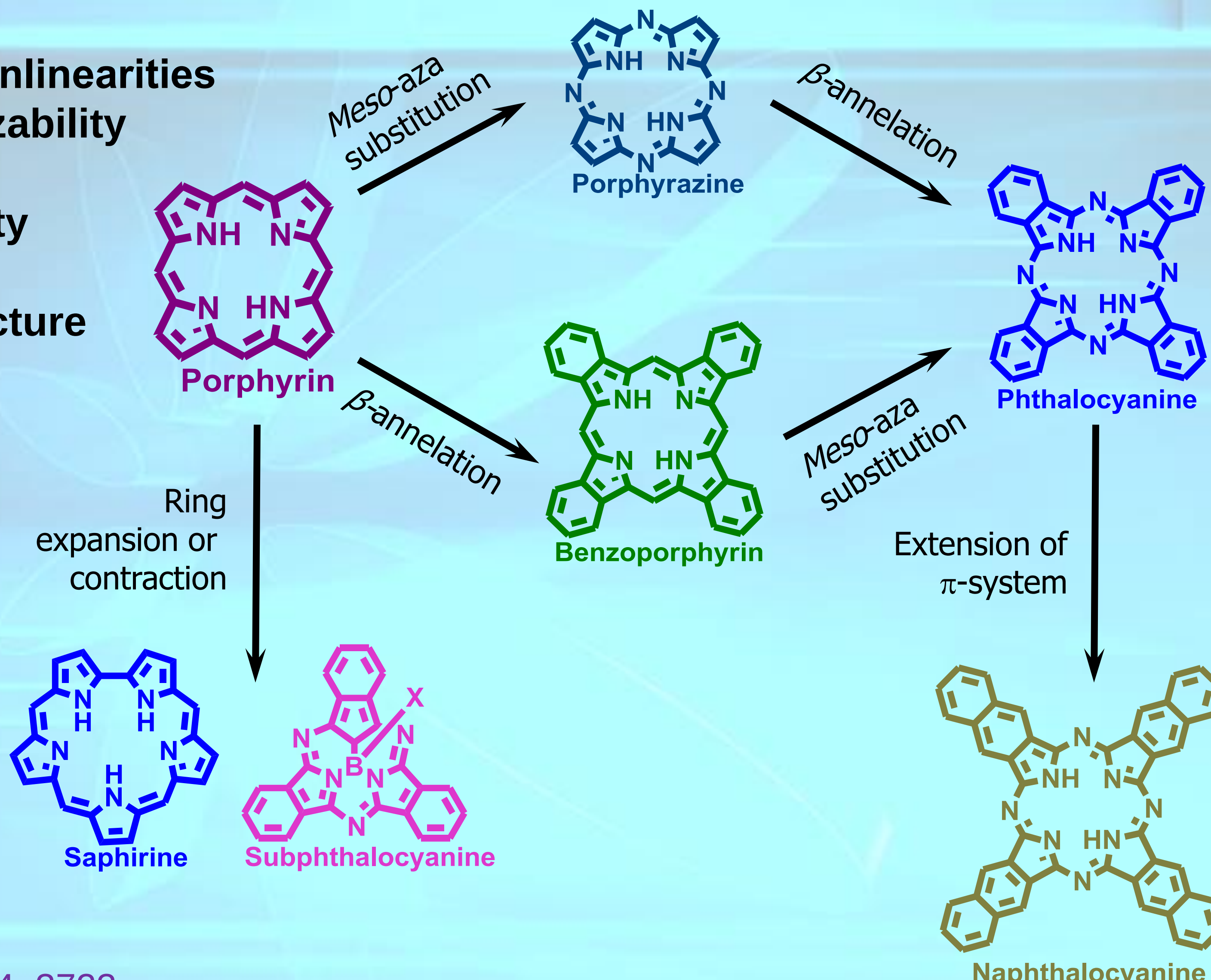
$$\chi^{(3)} \sim \gamma$$

γ - third-order hyperpolarizability

Compounds with high β and γ values are required for non-linear optical applications

Requirements for nonlinear optical materials

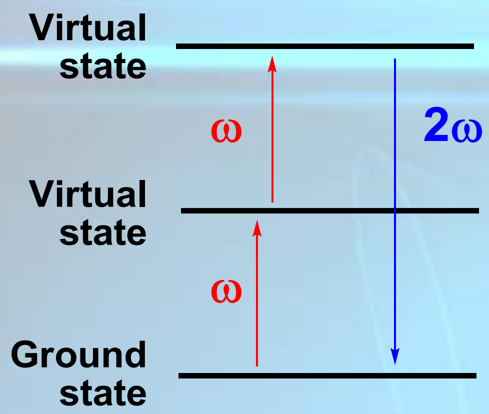
- **Large and fast nonlinearities due to high polarizability**
- **High photostability**
- **Tunability of structure and properties**
- **Facile processing**
- **Integration into optical devices**

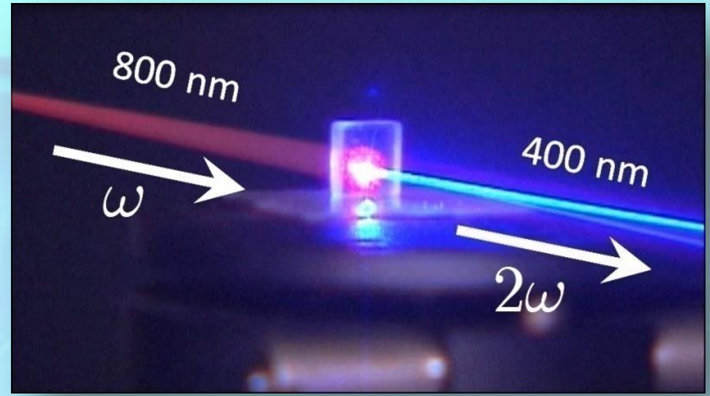


- *Chem. Rev.*, **2004**, 104, 3723.
- *J. Porphyrins Phthalocyanines*, **2009**, 13, 652.
- *Handbook of Porphyrin Science*, **2014**, vol. 2, pp. 271.

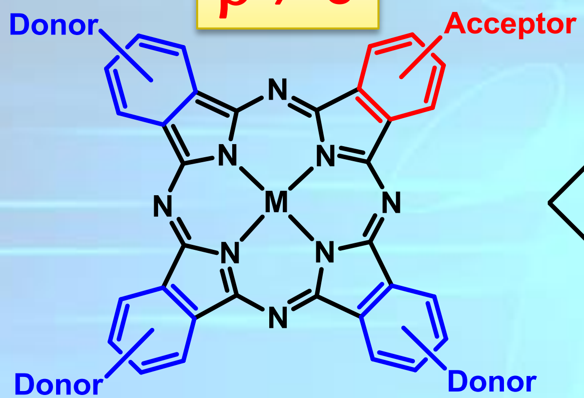
$\chi^{(2)}$

Second-harmonic generation (SHG)



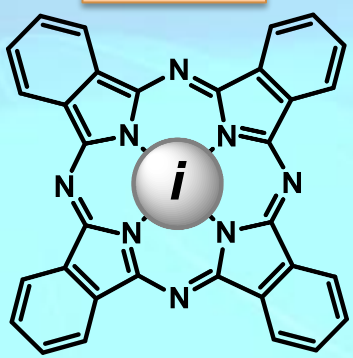


$\beta \neq 0$

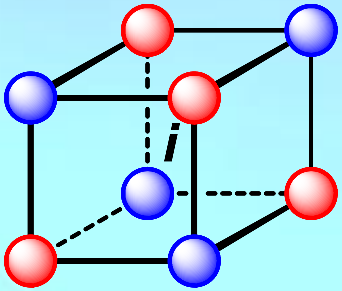


"Push-Pull" molecules

$\beta = 0$



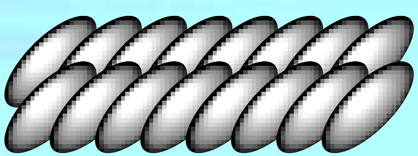
$\beta \neq 0$



Octupolar molecules

Easily to obtaine!

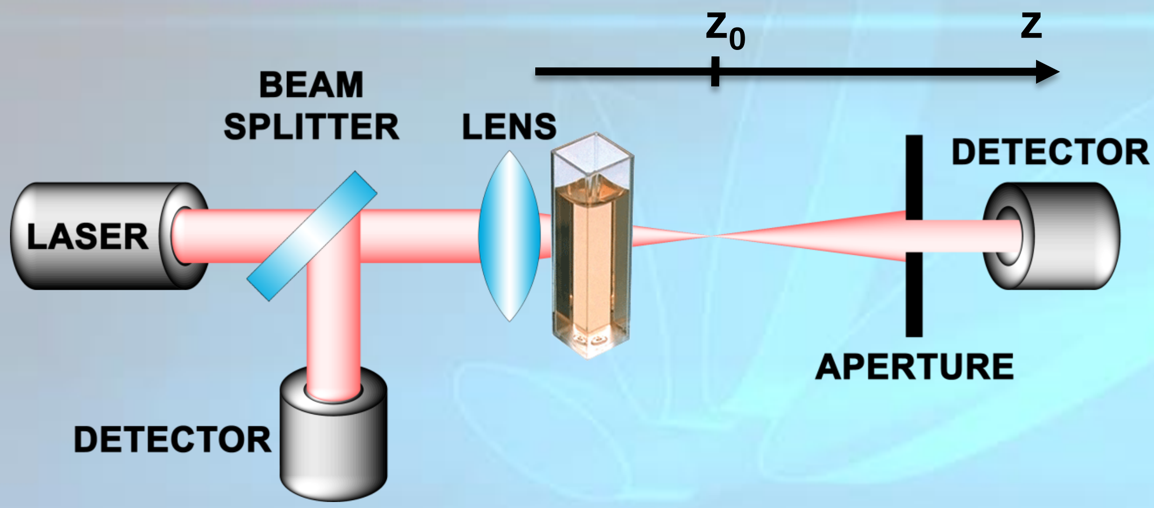
$\beta \neq 0$

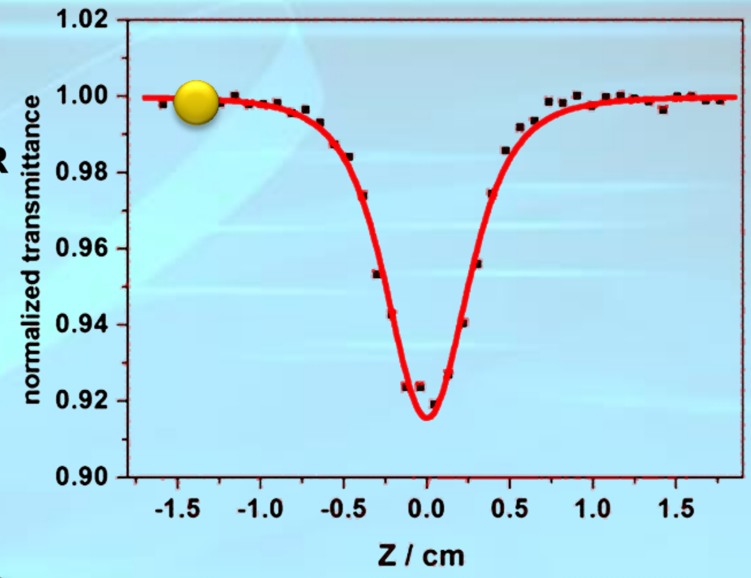


Lowering of local symmetry via formation of films and aggregates
(type of aggregates is important!)

$\chi^{(3)}$

Z-scan technique:
measurement of third-order NLO properties

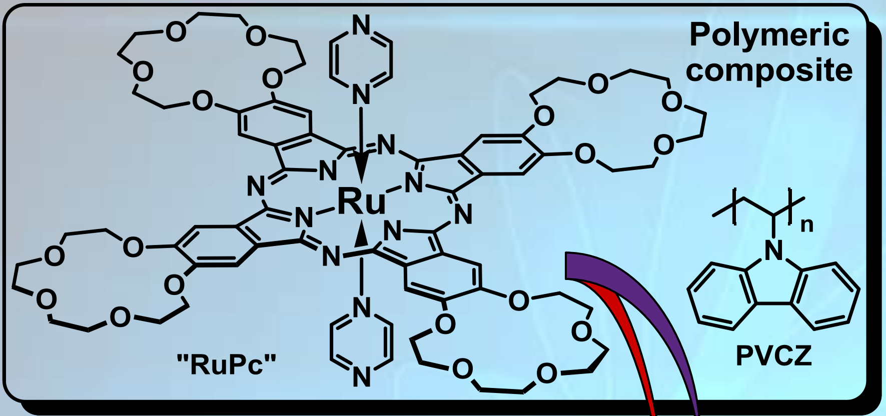




•http://www.holmarc.com/images/z_scan2.jpg

$\chi^{(3)}$

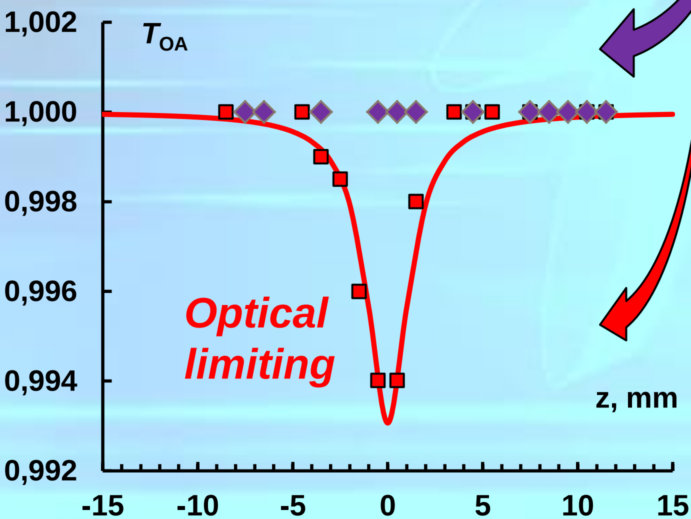
The role of self-assembly in NLO properties of polymeric composites based on Ru(II) complex



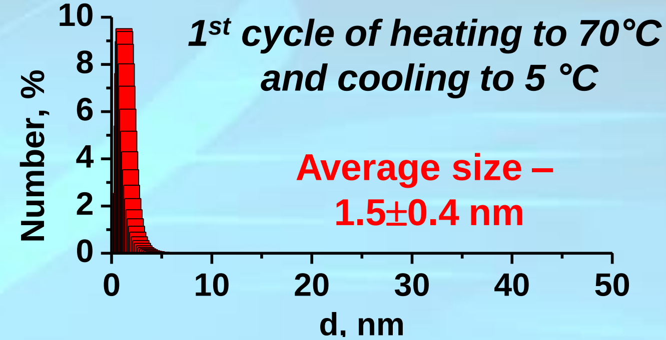
Prepared from <u>fresh</u> solution of RuPc in TClE

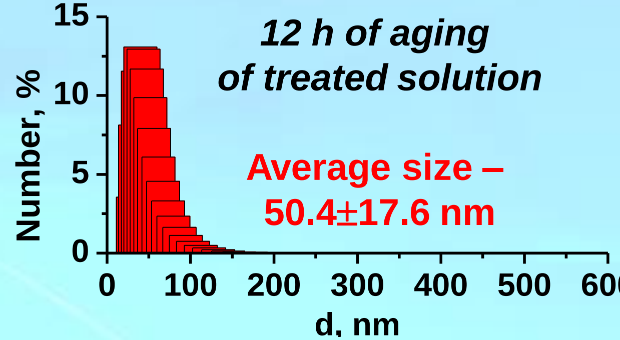
Prepared from <u>thermally treated and aged</u> solution of RuPc in TClE

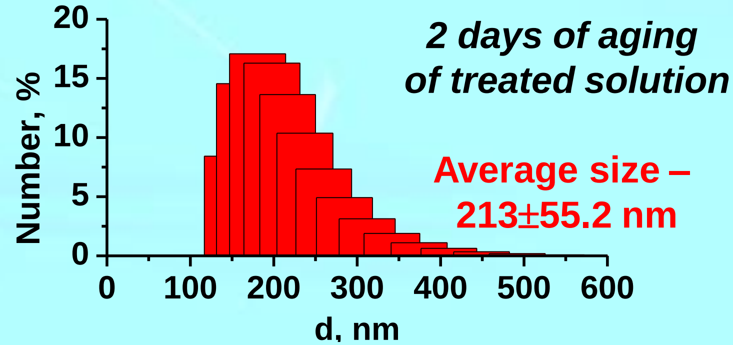
Z-scan using 1030 nm femtosecond laser (pulse 217 fs)



DLS measurements in TClE



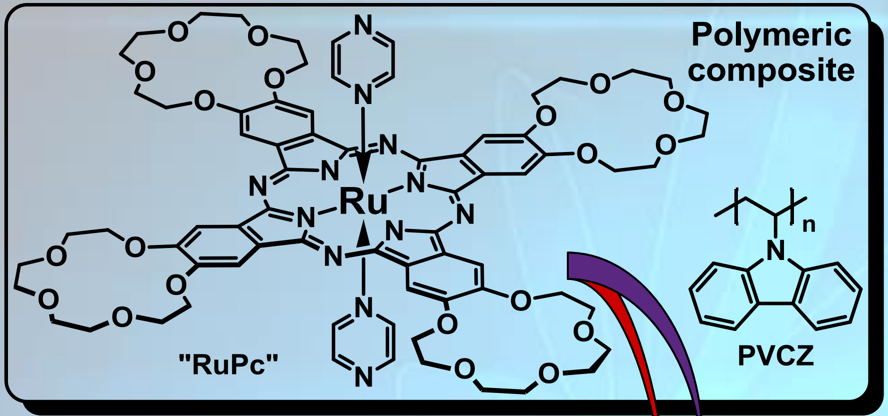




•*J. Mater. Chem. C*, **2015**, 3, 6692.

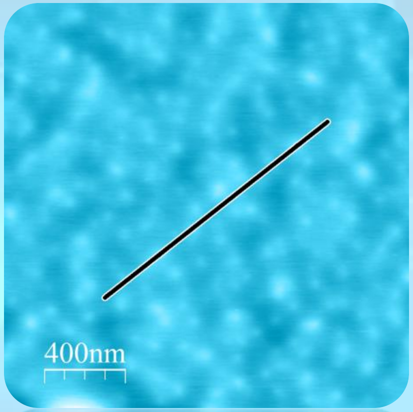
The role of self-assembly in NLO properties of polymeric composites based on Ru(II) complex

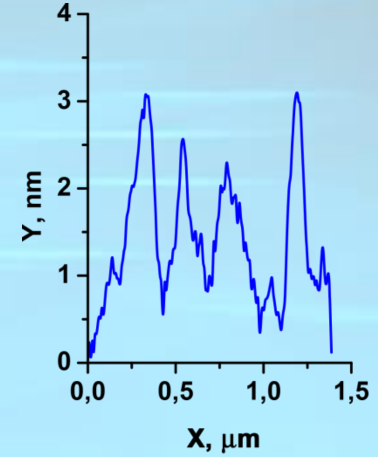
$\chi^{(3)}$



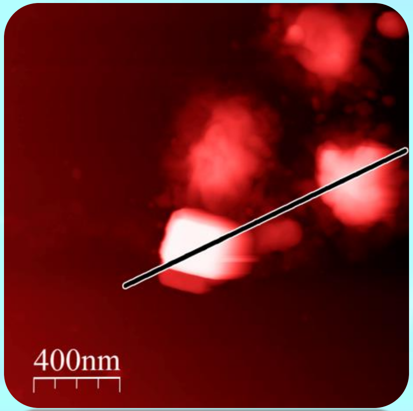
AFM measurements of cast films on mica prepared from solutions in TClE

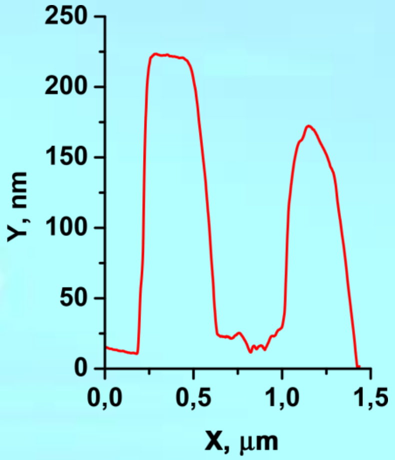
Prepared from <u>fresh</u> solution of RuPc in TClE



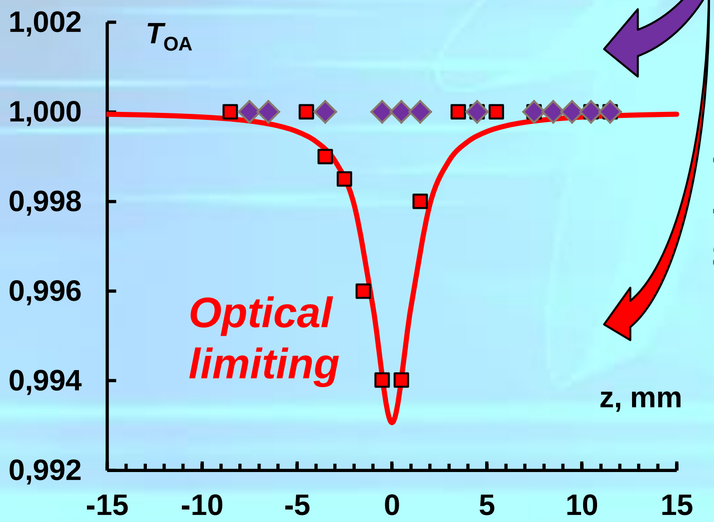


Prepared from <u>thermally treated and aged</u> solution of RuPc in TClE





Z-scan using 1030 nm femtosecond laser (pulse 217 fs)



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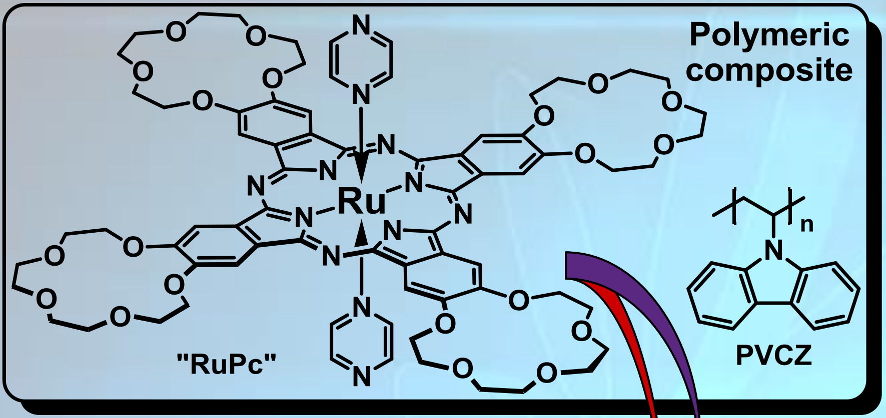
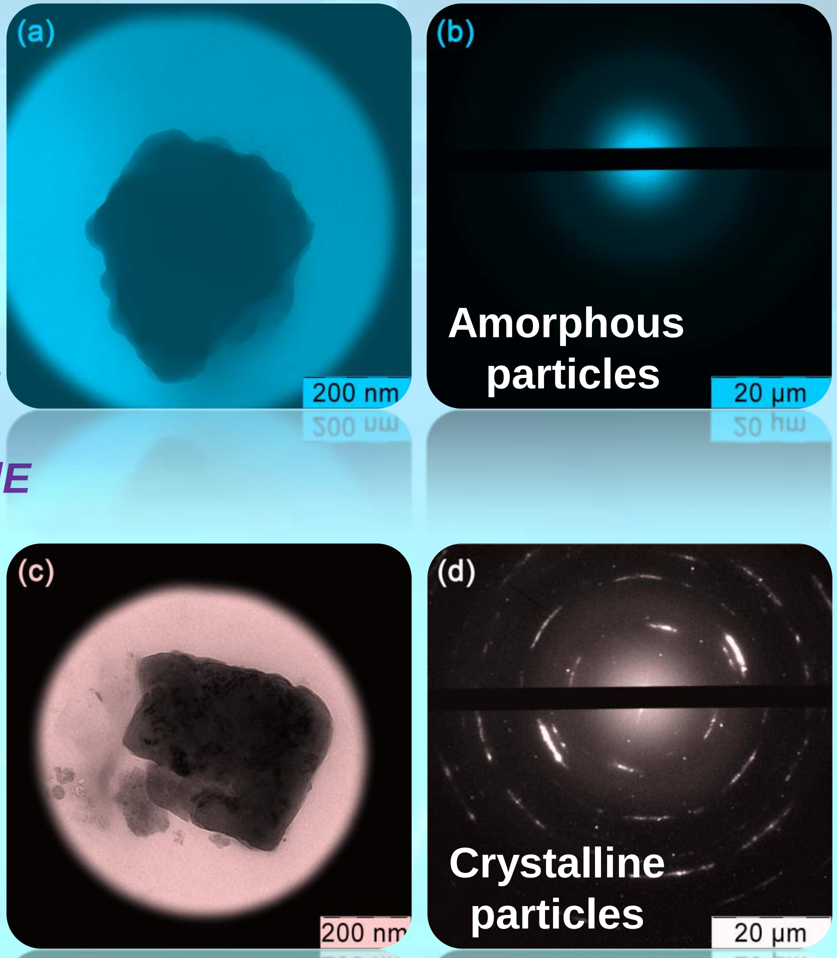
The role of self-assembly in NLO properties of polymeric composites based on Ru(II) complex

$\chi^{(3)}$



TEM measurements of cast films on graphite prepared from solutions in TClE



Prepared from <u>fresh</u> solution of RuPc in TClE

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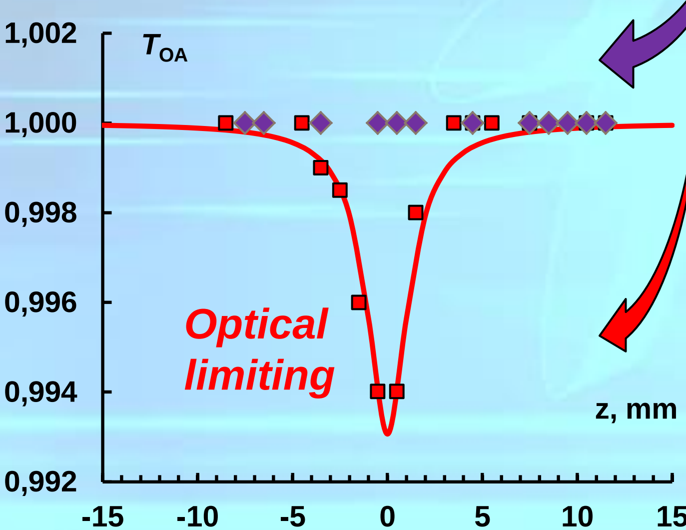
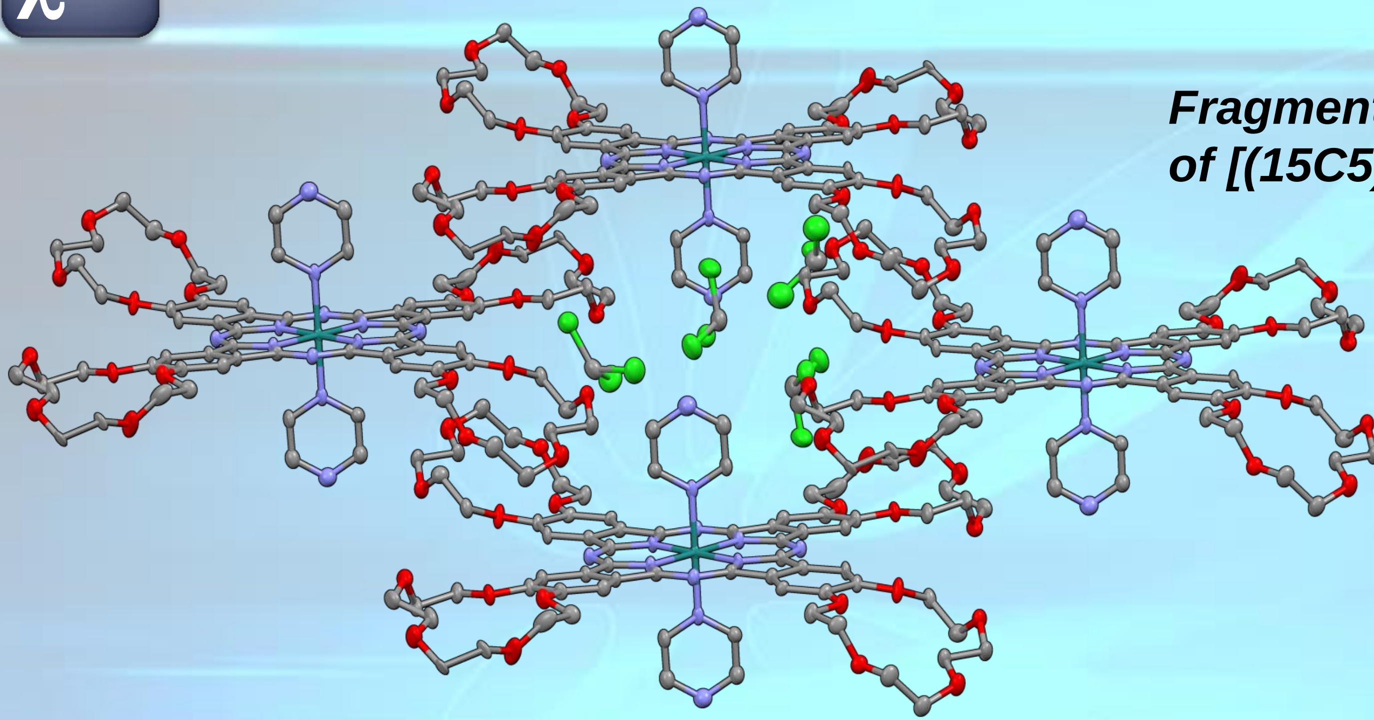
Z-scan using 1030 nm femtosecond laser (pulse 217 fs)



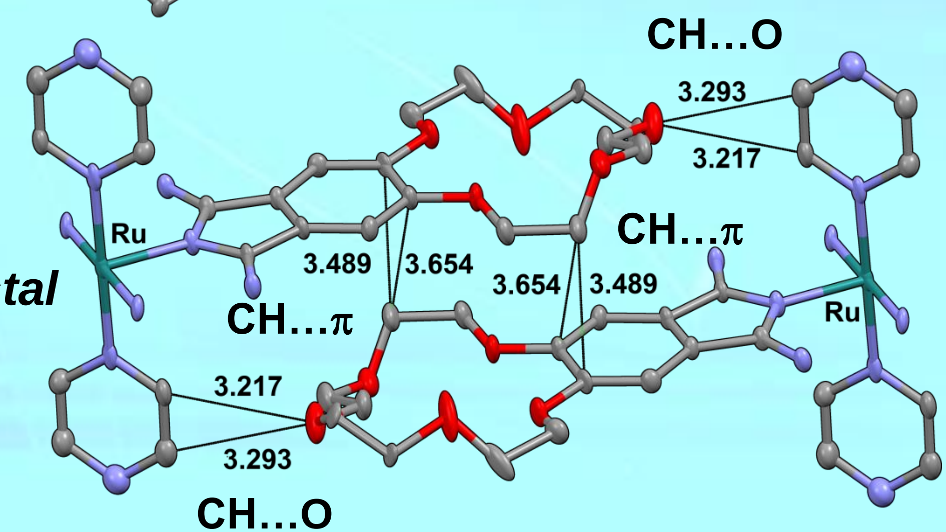
•*J. Mater. Chem. C*, **2015**, 3, 6692.

$\chi^{(3)}$

X-Ray structure of $[(15C5)_4Pc]Ru(Pyz)_2$



Fragment of crystal packing of $[(15C5)_4Pc]Ru(Pyz)_2$

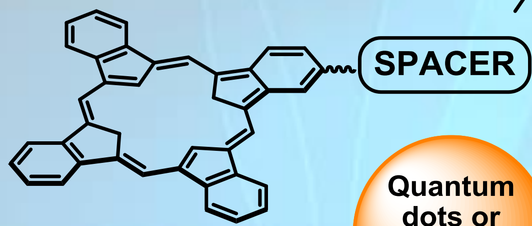


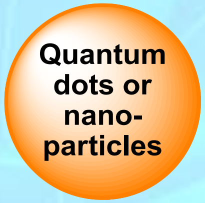
Some of contacts, found in crystal lattice of $[(15C5)_4Pc]Ru(Pyz)_2$

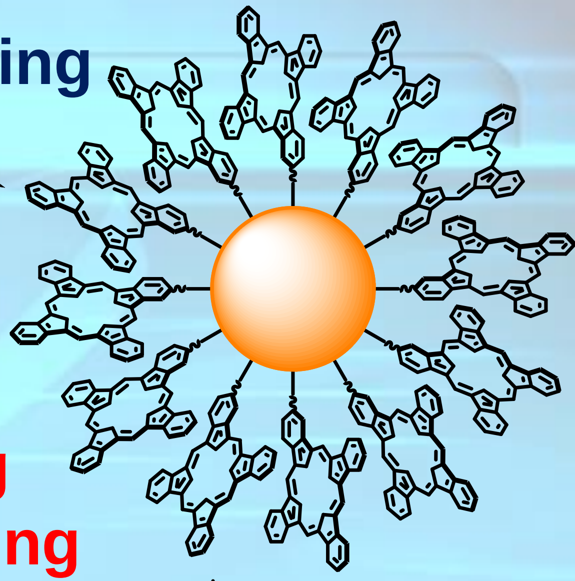
•*J. Mater. Chem. C*, **2015**, 3, 6692.

$\chi^{(3)}$ Composite materials for optical limiting

Binding of Pc with
QD or NP



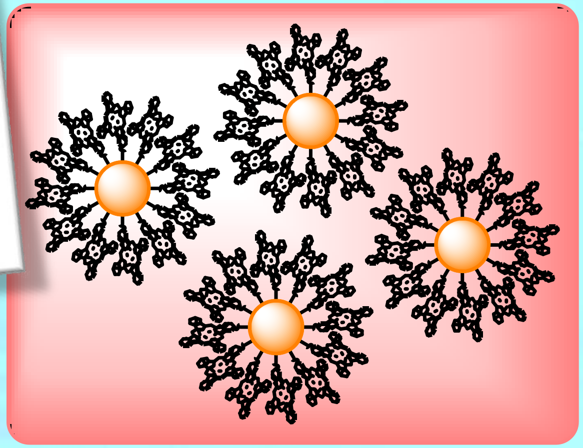




Improving optical limiting characteristics

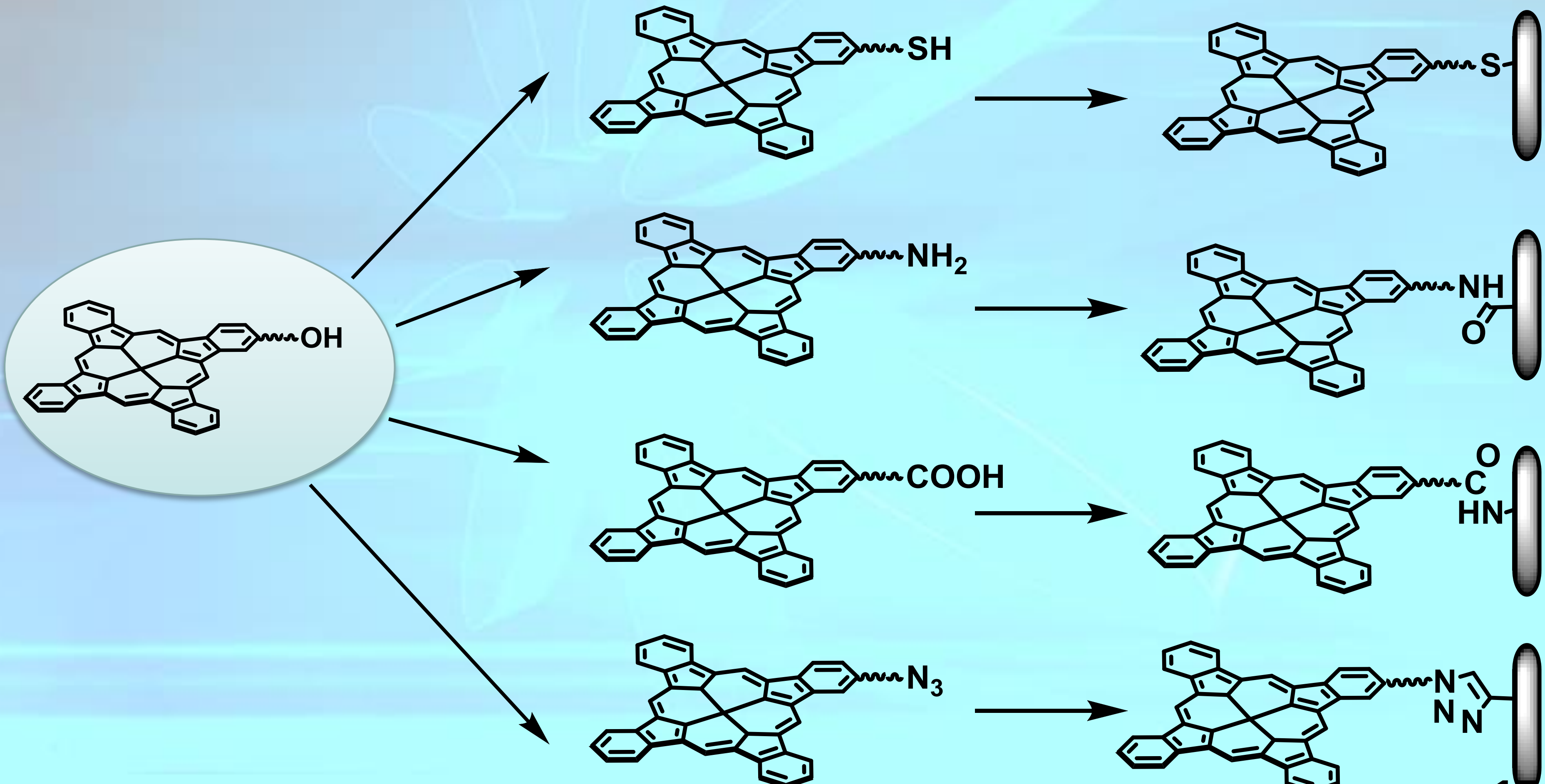
Incorporation
into polymer matrix

Prof. Tebello NYOKONG
Rhodes University
South Africa

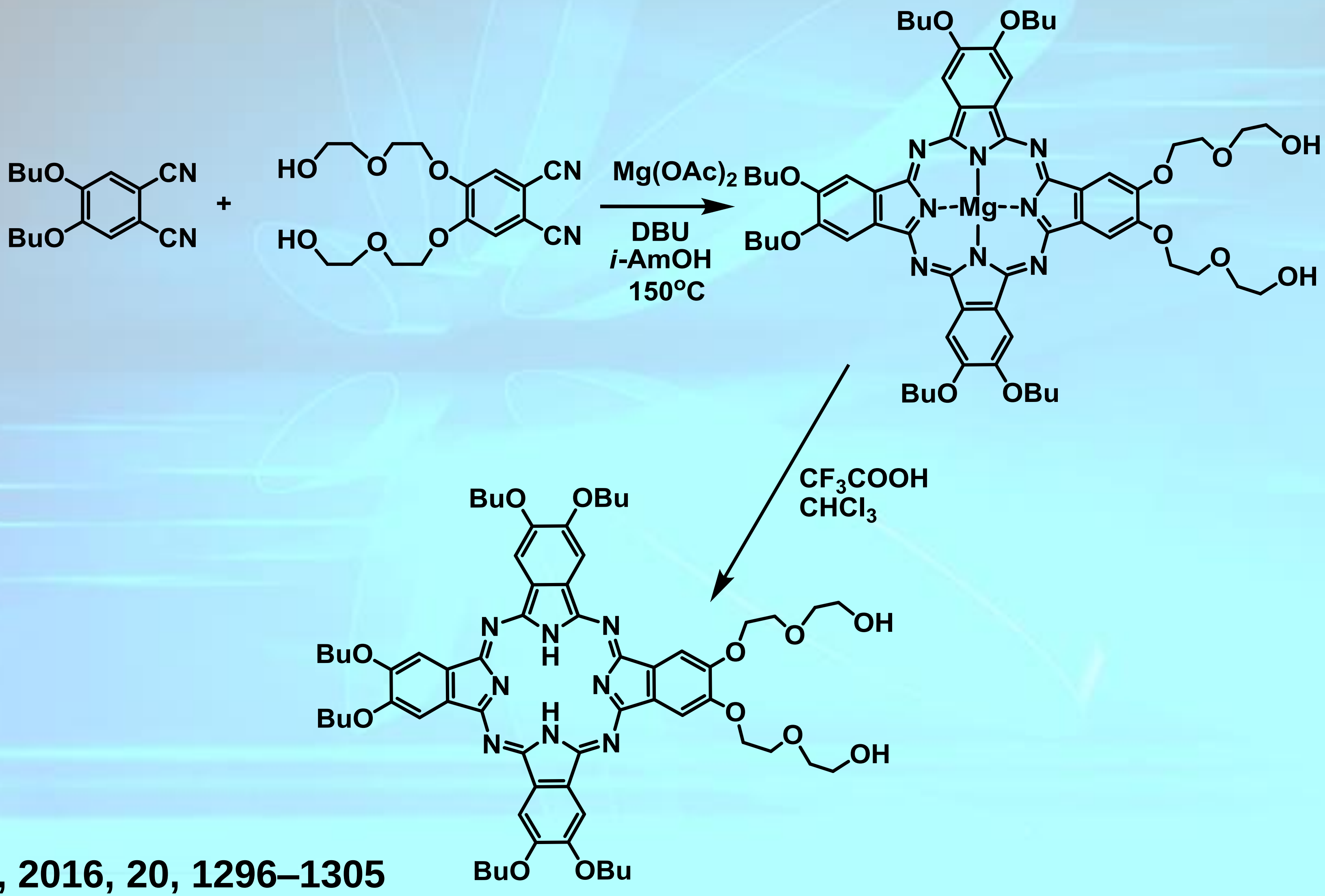


QD: CdSe, CdTe, etc.
Polymers: PMMA, PBC, etc.

Grafting of pthalocyanines into nanomaterials – enhancement of NLO properties



Synthesis of target unsymmetrical phthalocyanine

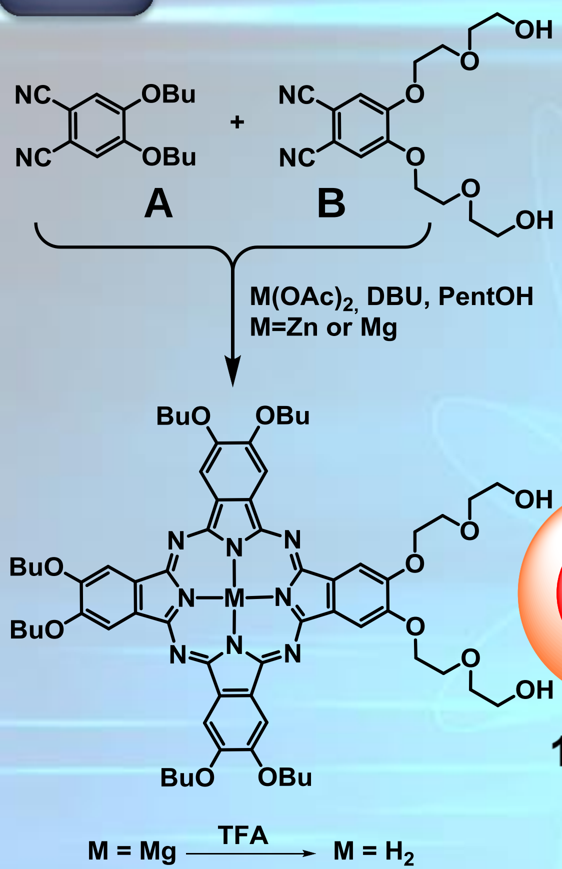


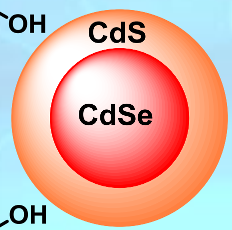
JPP, 2016, 20, 1296–1305

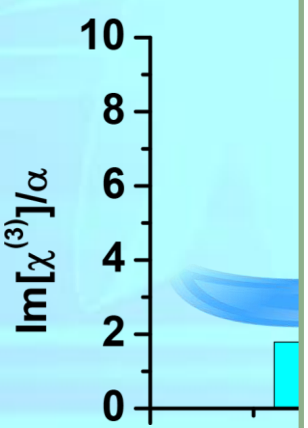
Composite materials for optical limiting

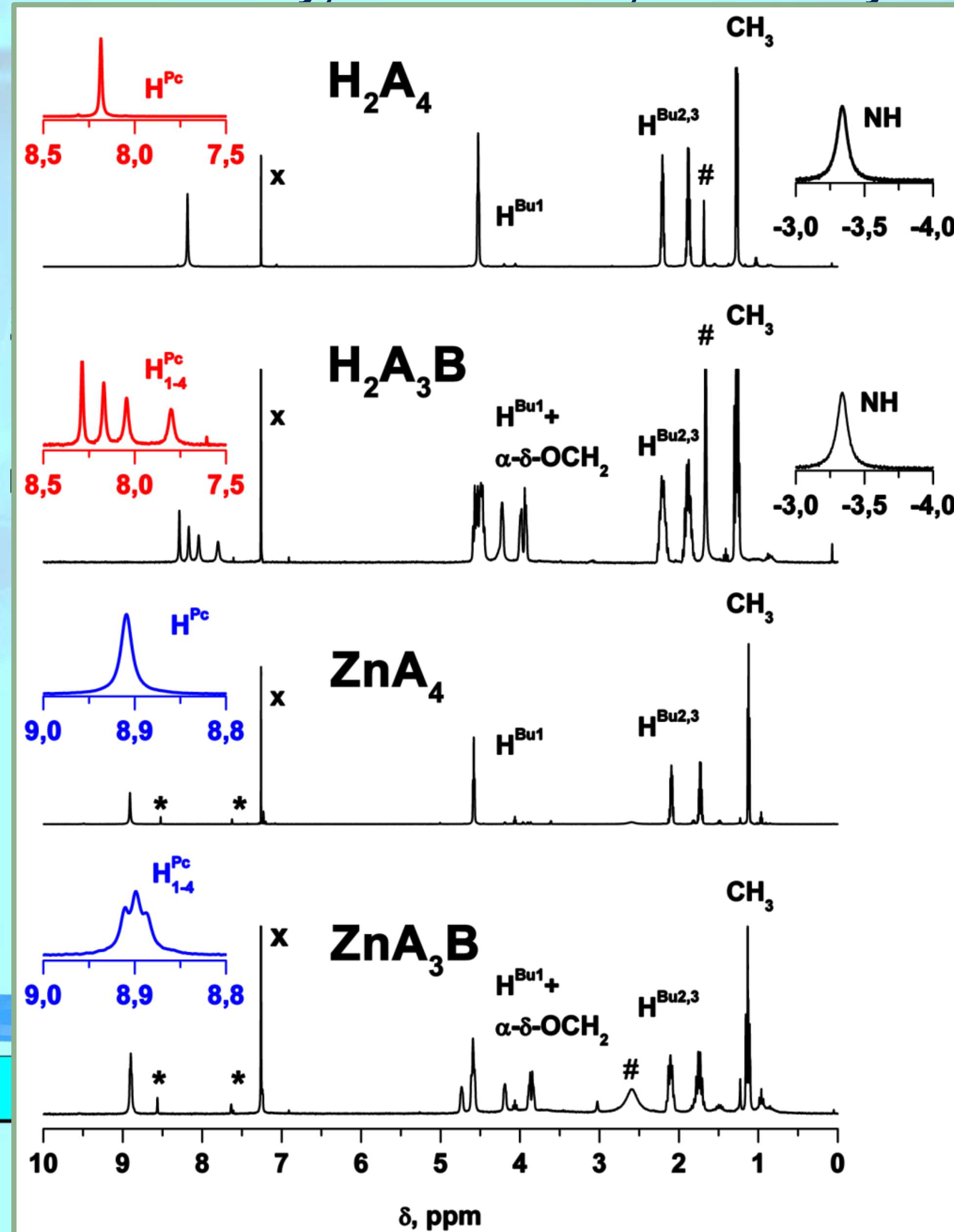
Collaboration with Rhodes University, South Africa, Prof. T. Nyokong

$\chi^{(3)}$



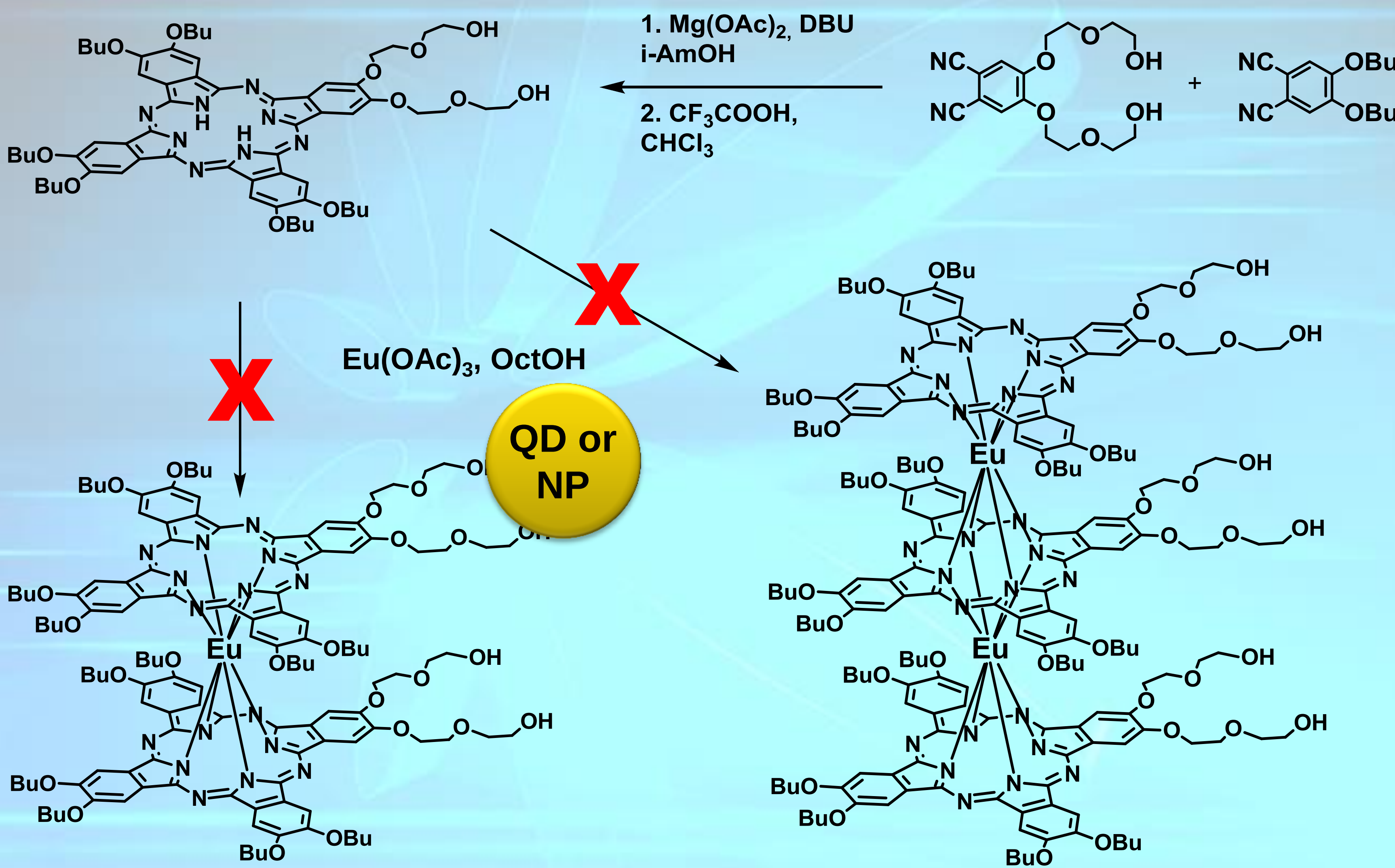




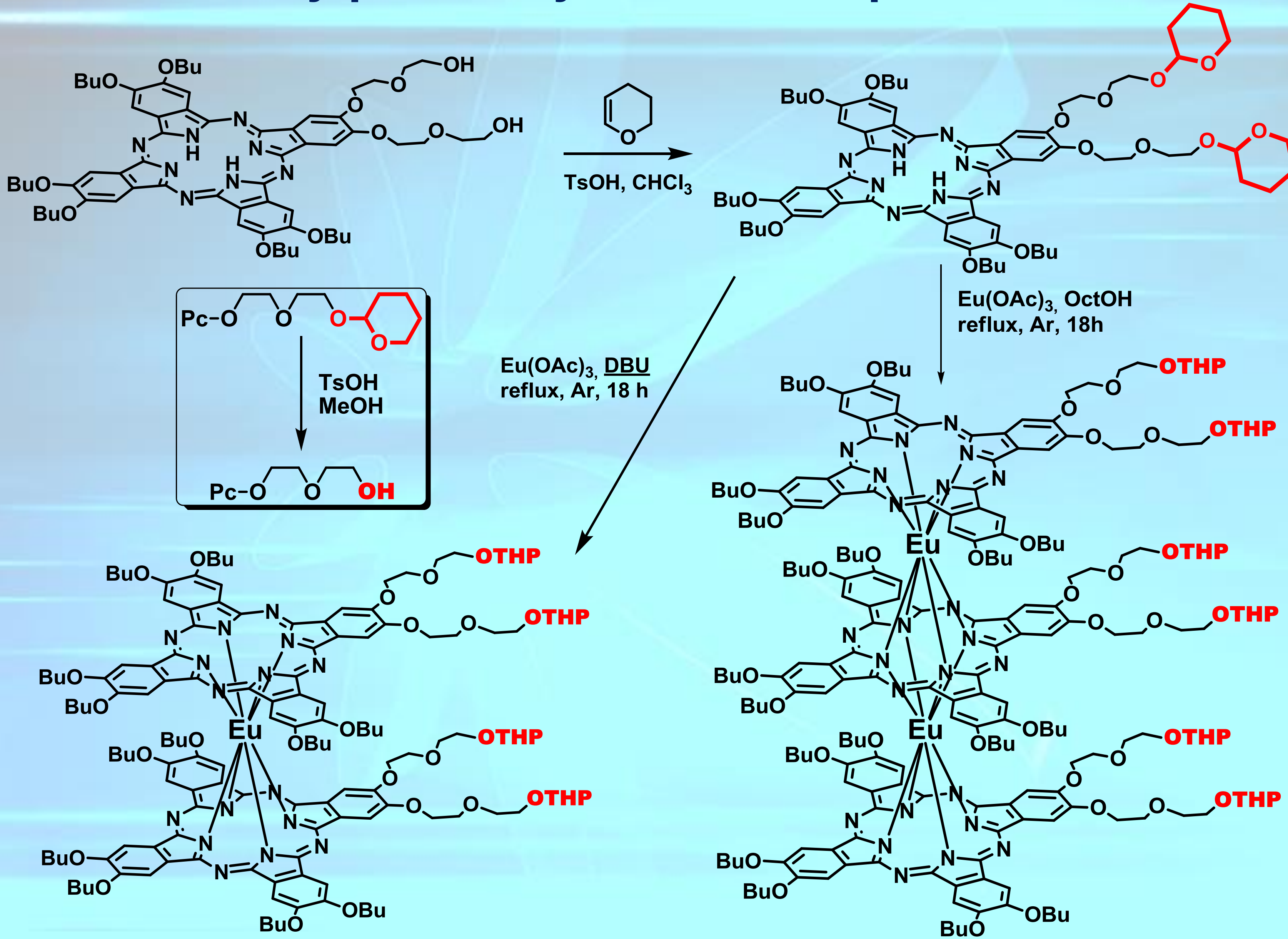


JPP, 2016, 20, 1296–1305

Joint project between Russian Academy of Sciences and Rhodes University – with group of Prof. Tebello Nyokong

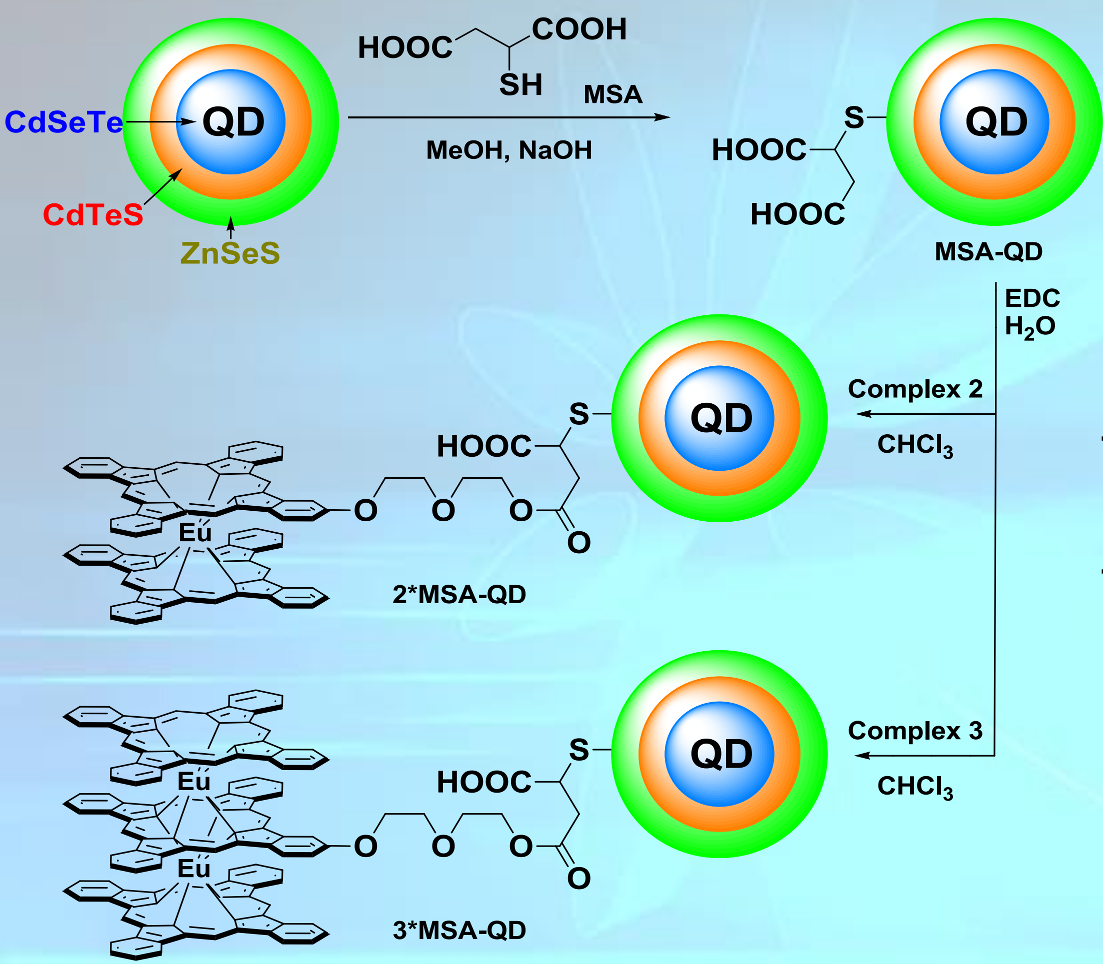


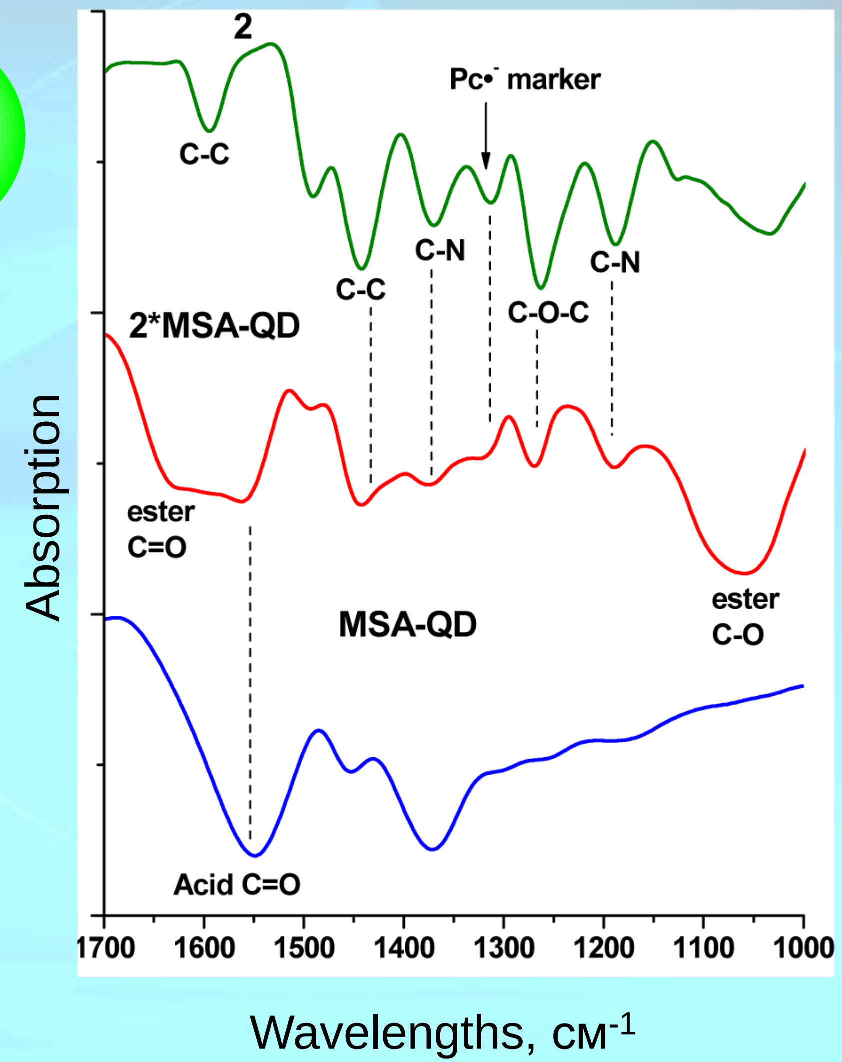
Novel hybrid optical limiters based on nanocomposites, formed by phthalocyanines and quantum dots



Oluwole D. O., Yagodin A. V., Mhkize N. C. et al. // Chem.- A Eur. J., **2017**, online

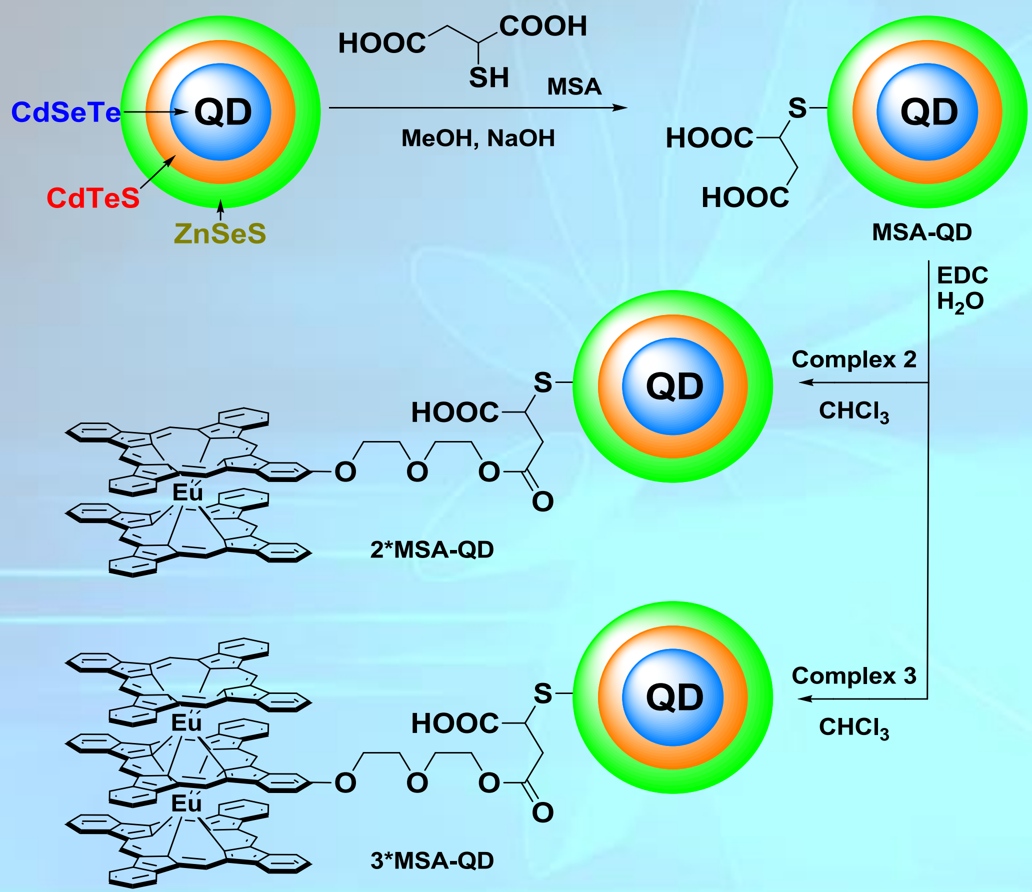
Conjugates with Quantum Dots

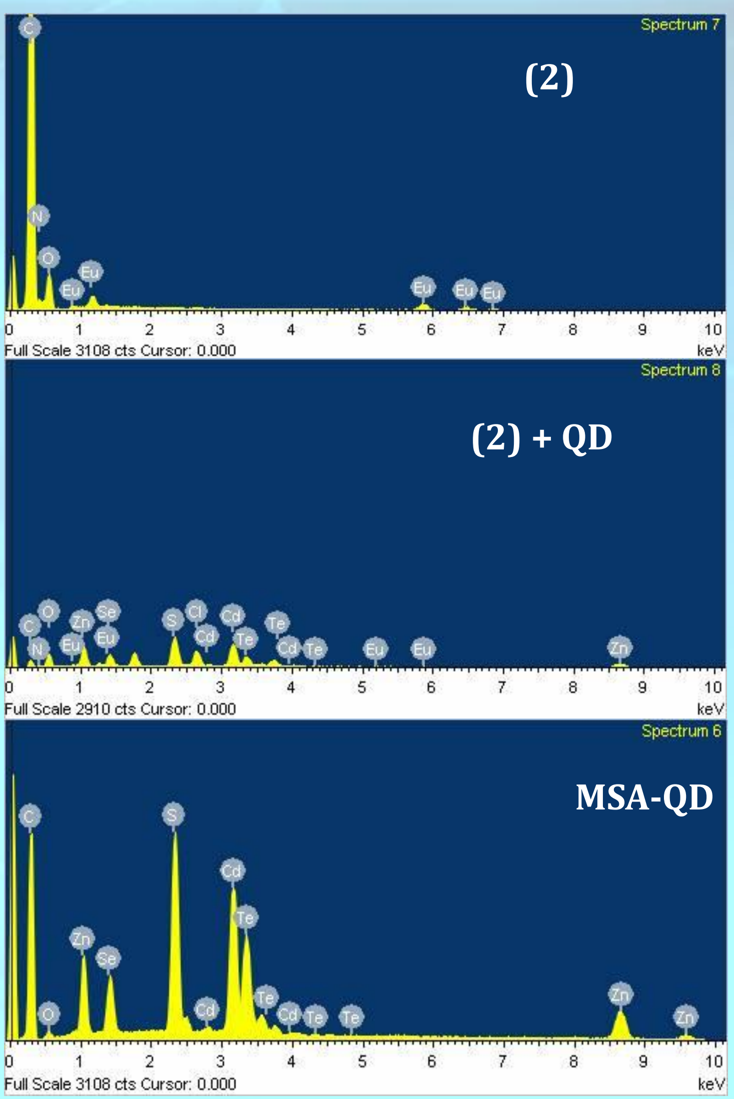




MSA - mercaptosuccinic acid
EDC - ethyl(dimethylaminopropyl)carbodiimide

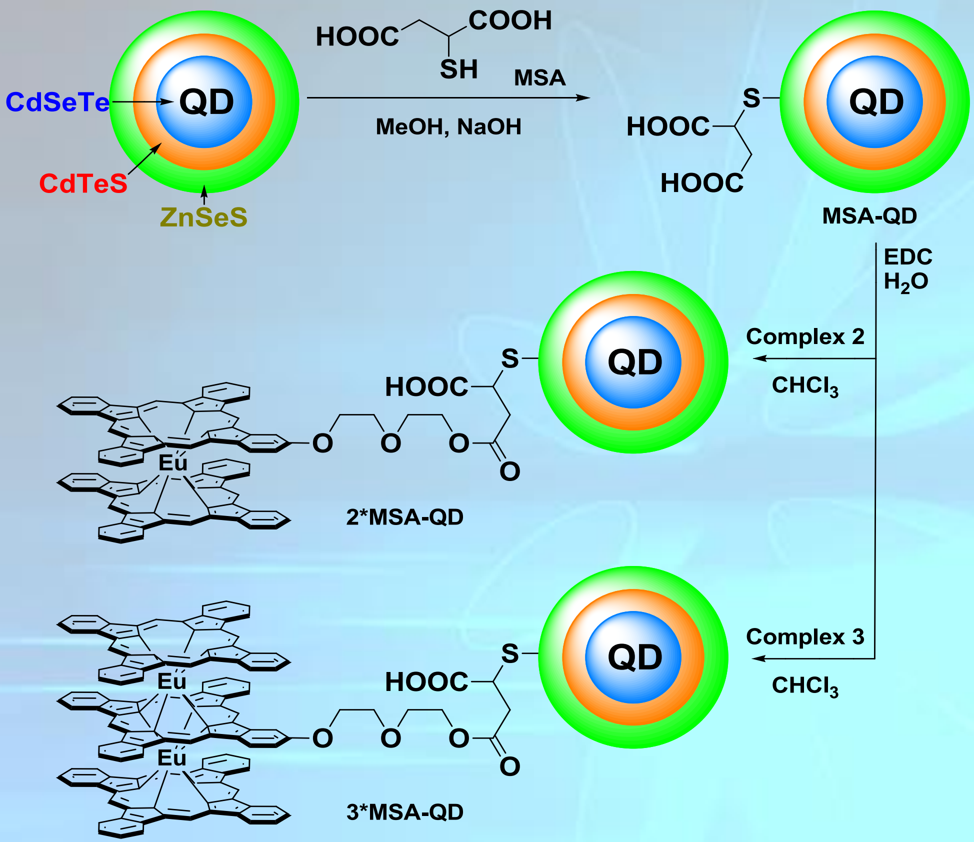
Conjugates with Quantum Dots

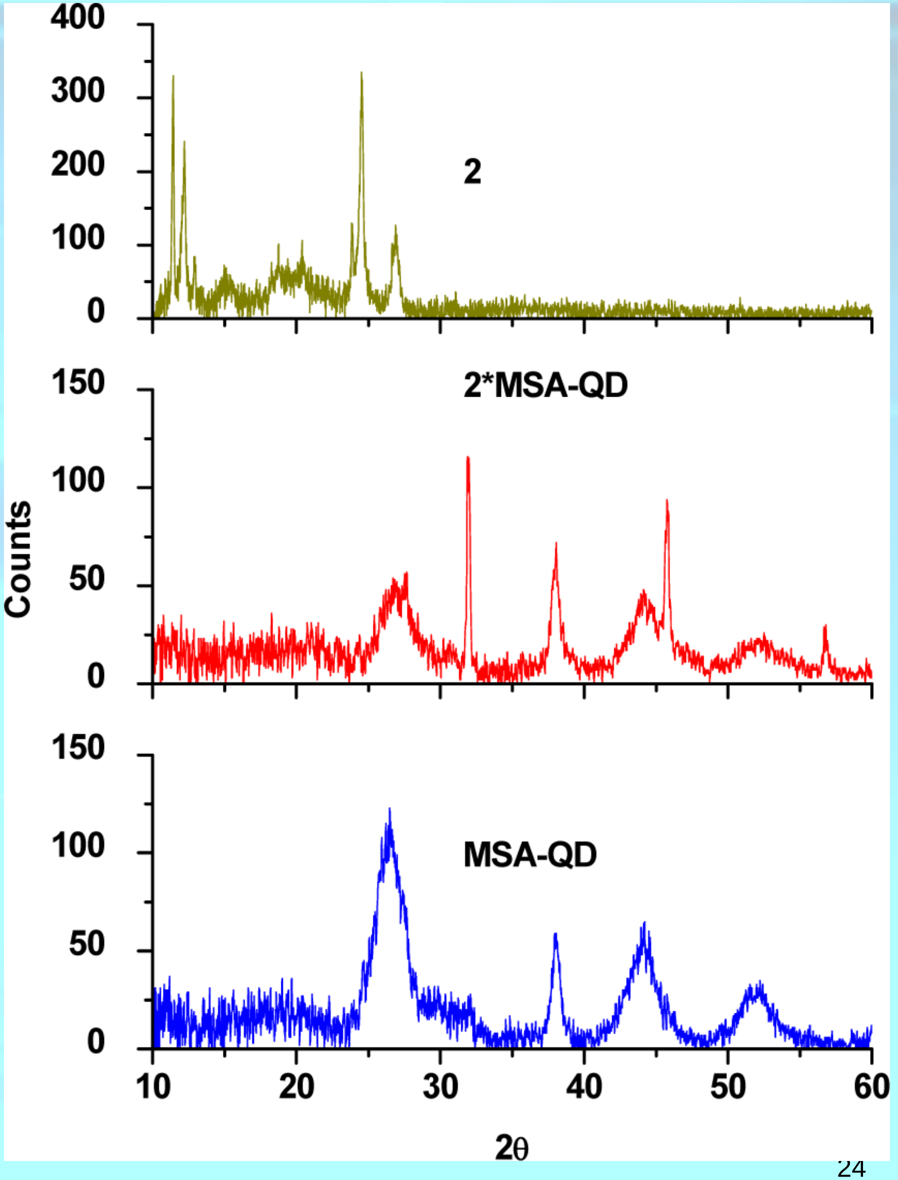




Oluwole D. O., Yagodin A. V., Mhkize N. C. et al. // Chem.- A Eur. J., **2017**, doi: 10.1002/chem.201604401

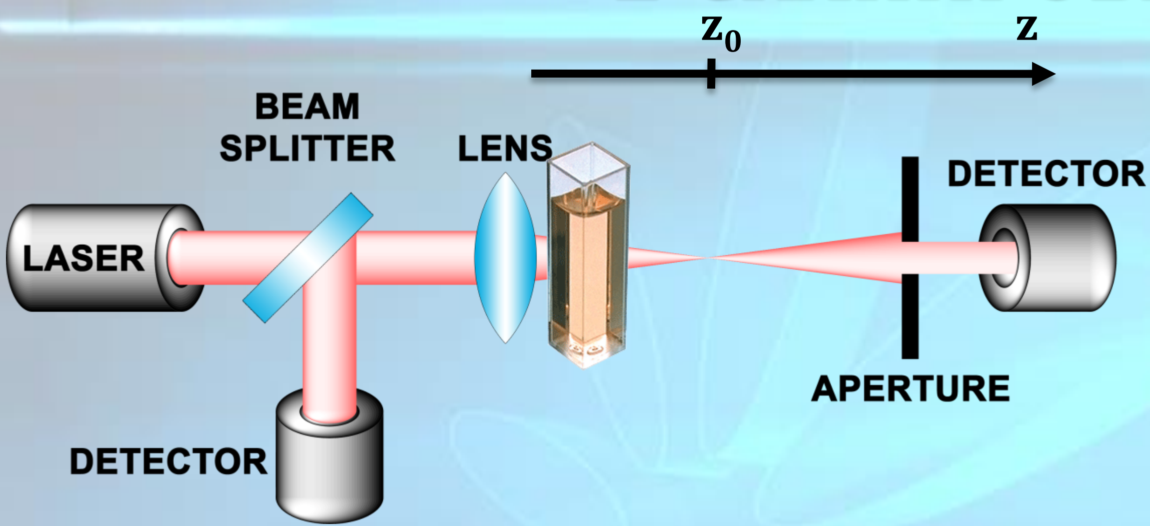
Conjugates with Quantum Dots

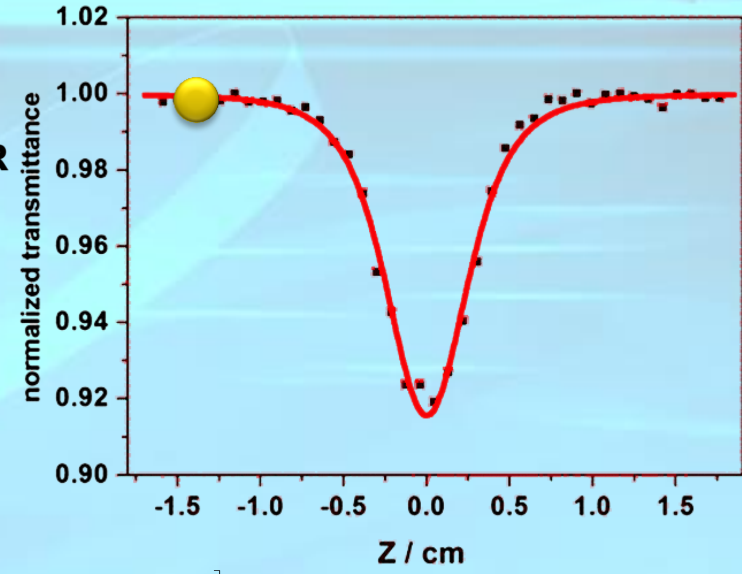


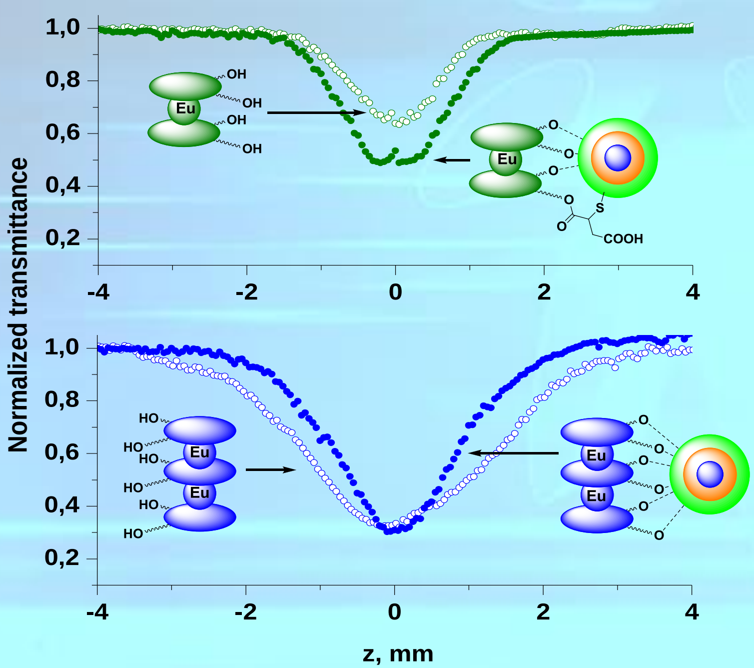


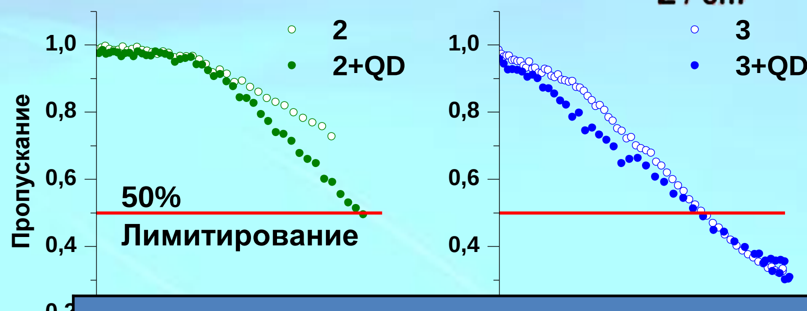
Oluwole D. O., Yagodin A. V., Mhkize N. C. et al. // Chem.- A Eur. J., **2017**, doi: 10.1002/chem.201604401

Z-СКАНИРОВАНИЕ



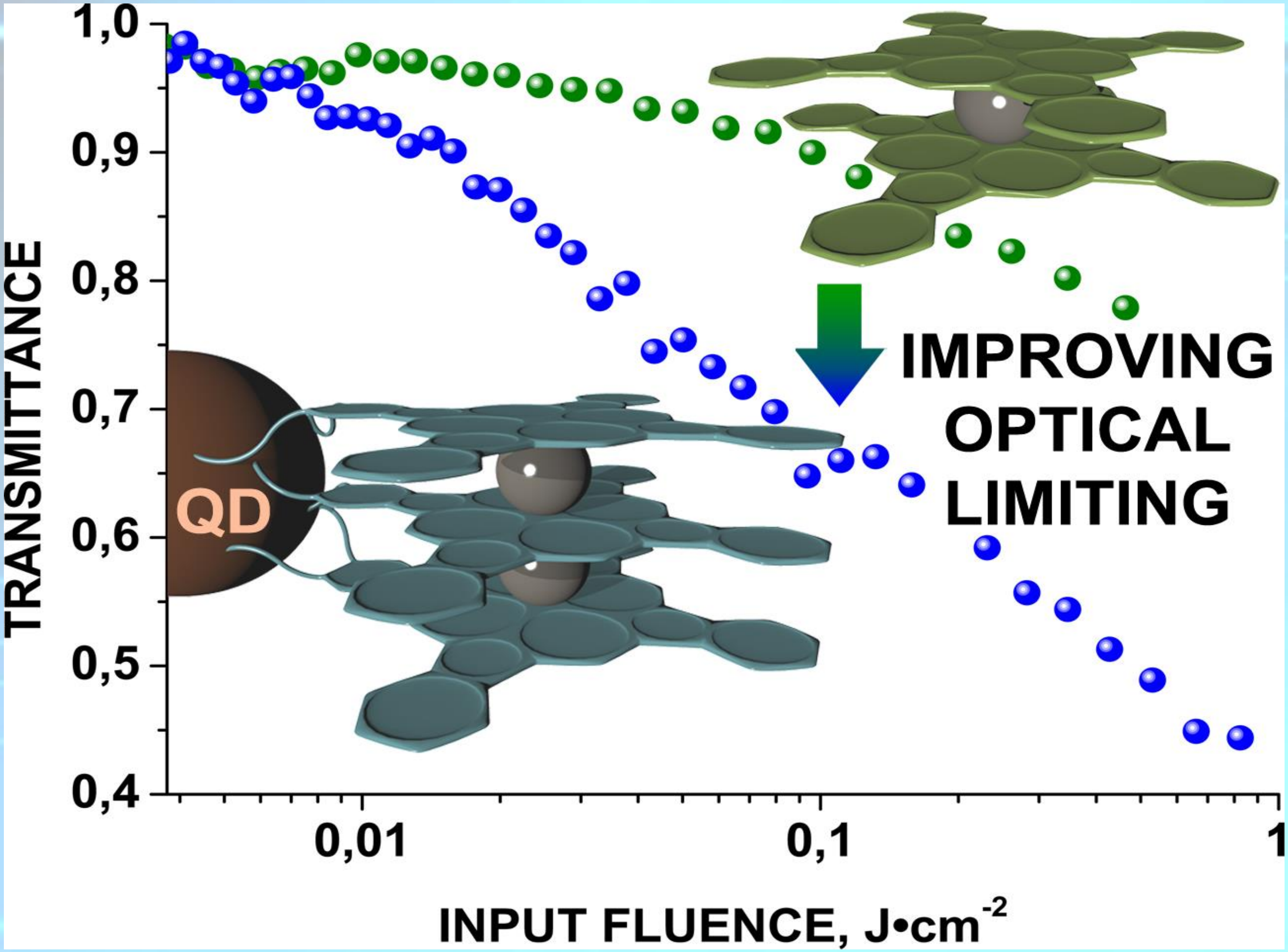






Соединение	I_{lim} (Дж·см$^{-2}$)
Complex 2	50% ограничение не достигается
Complex 2 + MSA*QD	2.00
Complex 3	0.57
Complex 3 + MSA*QD	0.42

Z-СКАНИРОВАНИЕ



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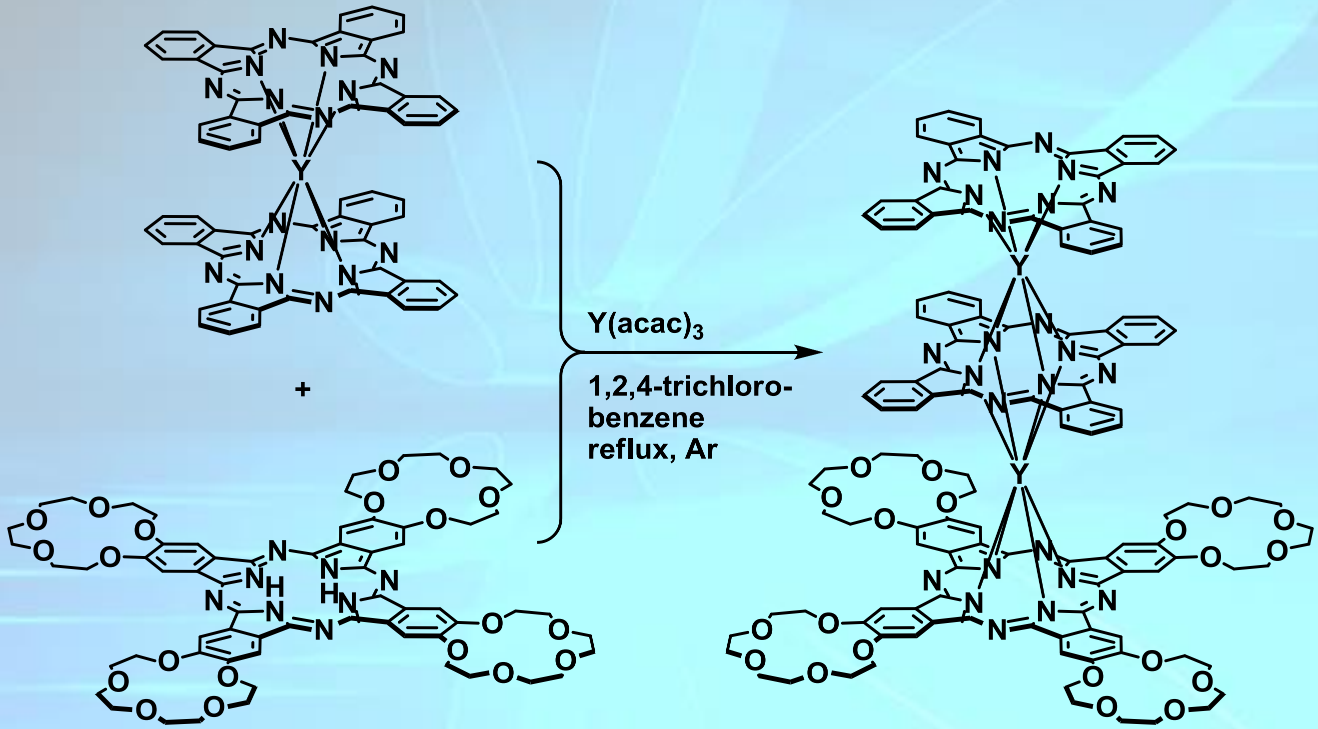
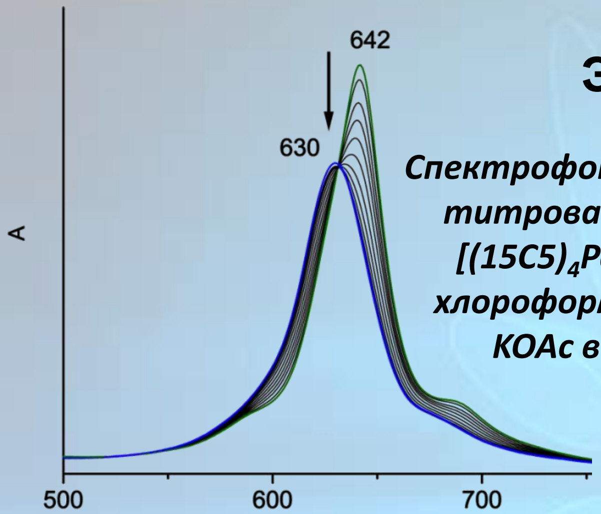
Шестипалубный комплекс



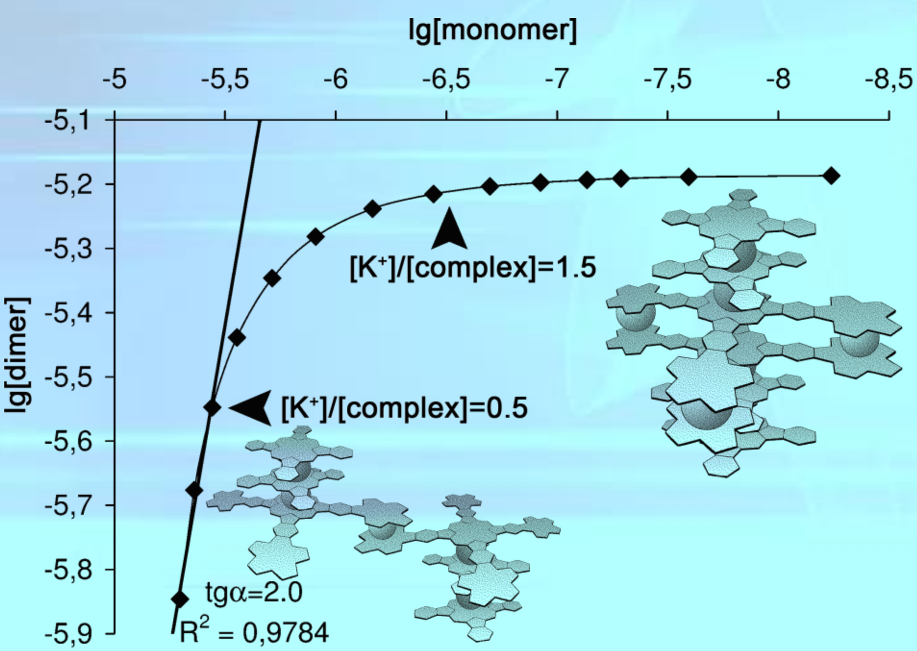
•Martynov A. G. *et al.*
Synthesis, Spectral Properties and Supramolecular Dimerisation of Heteroleptic Triple-Decker Phthalocyaninato Complexes with One Outer Crown-Substituted Ligand.
Inorg. Chim. Acta **2009**, *362* (1), 11

Супрамолекулярная димеризация трехпалубного комплекса

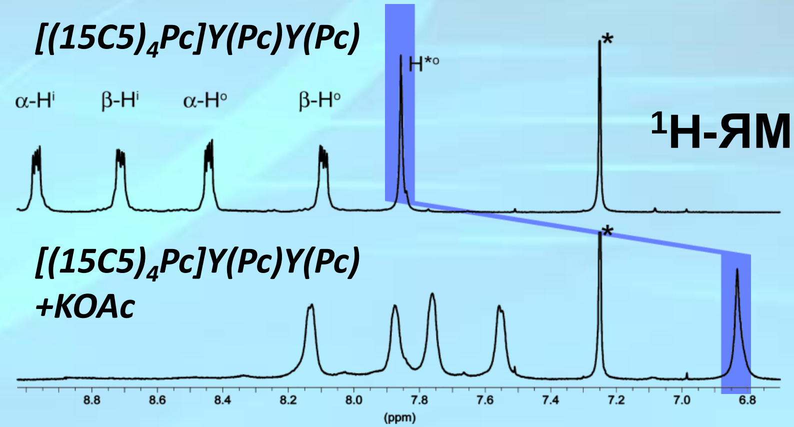


ЭСП

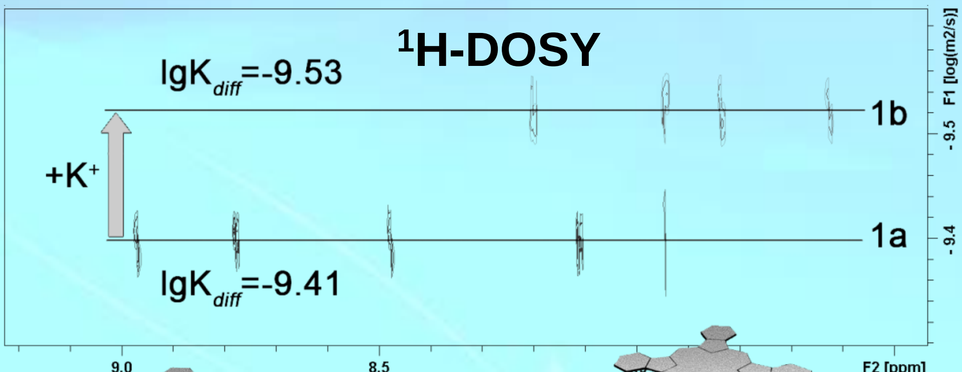
Спектрофотометрическое титрование раствора $[(15C5)_4Pc]Y(Pc)Y(Pc)$ в хлороформе раствором KOAc в метаноле

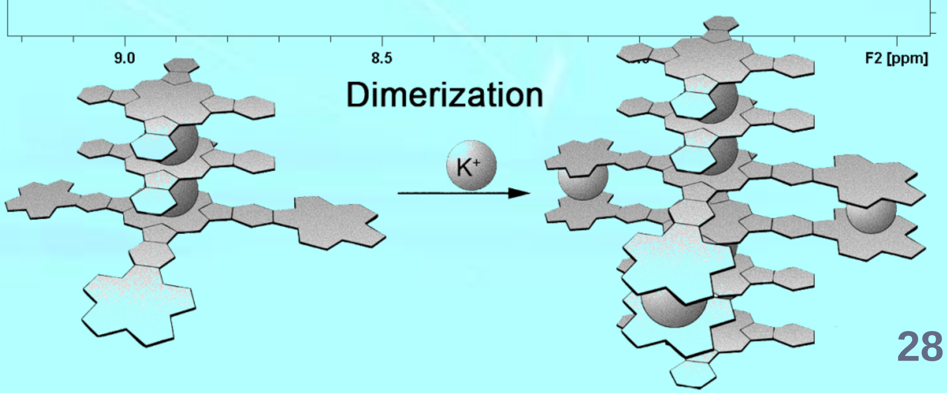


¹H-ЯМР

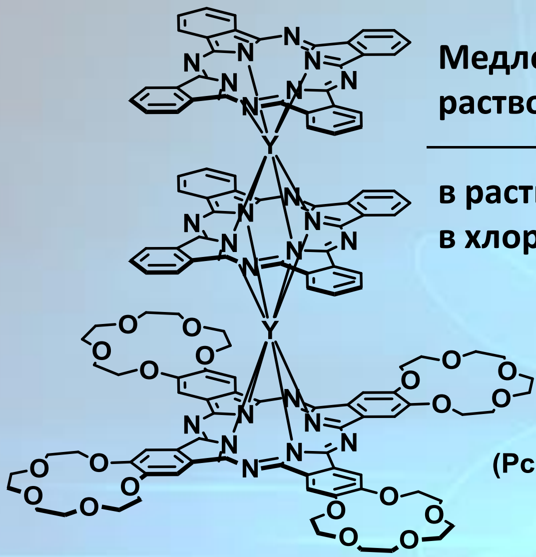


¹H-DOSY



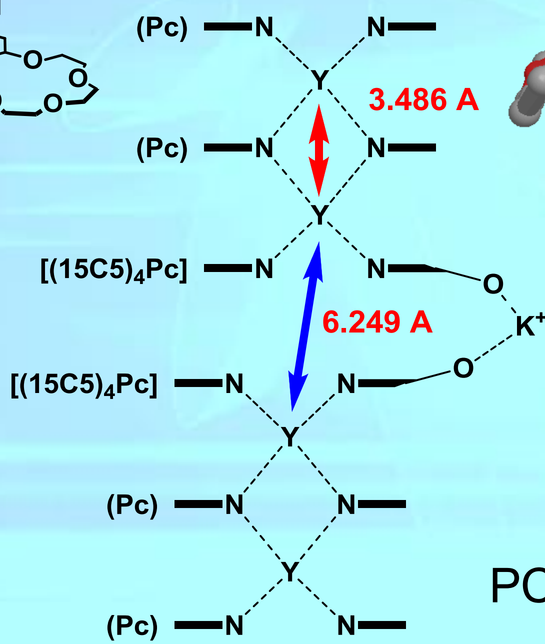


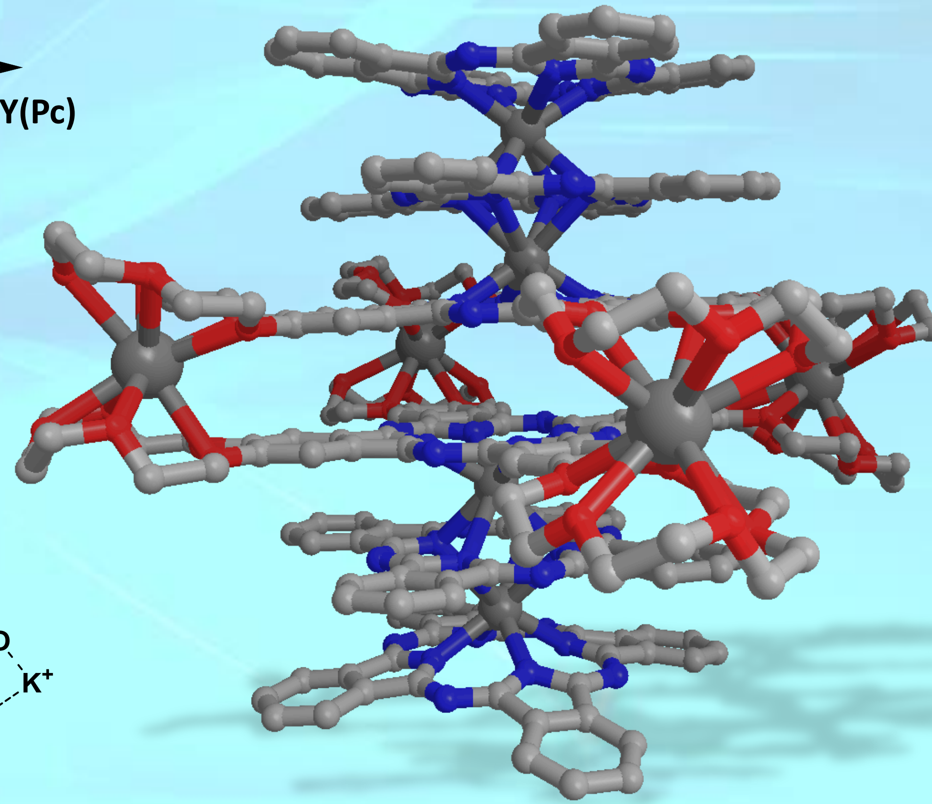
Первый пример структурно охарактеризованного супрамолекулярного шестипалубного комплекса



Медленная диффузия раствора $KBPh_4$ в CH_3CN

в раствор $[(15C5)_4Pc]Y(Pc)Y(Pc)$ в хлороформе





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Thank you
for
attention!