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Photooxidation of organic sulfides in the presence of new metal(IV)porphyrinate-monocapped Fe(II)-, Ni(II) and Co(III)-centered pseudoclathrochelates

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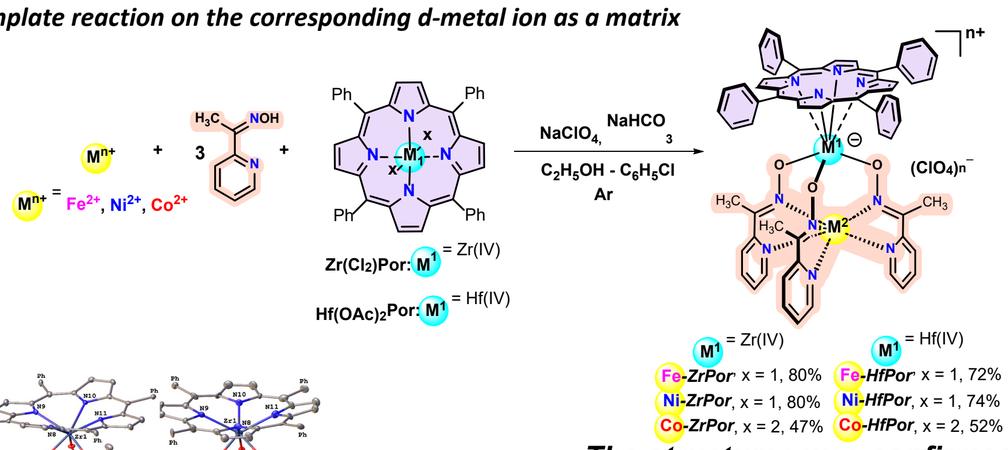
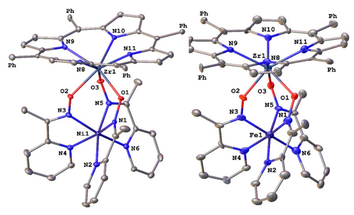
INTRODUCTION & AIM

The utilization of generated reactive oxygen species (ROS) allow selectively oxidation of organic substrates under mild reaction conditions, preventing the side reactions or their degradation, which meets the principles of «green chemistry». Metalloporphyrins and their analogs are well-known to be the excellent photosensitizers for effective formation of ROS. Varying the coordinated metals or introducing additional functional fragments can improve the photocatalytic properties of porphyrin photosensitizers. There we obtained and studied of new zirconium- and hafnium(IV)porphyrinate-monocapped Fe(II), Ni(II) and Co(III) tris-pyridineoximate as promising photosensitizers for photocatalytic oxidation.

SYNTHESIS

Direct template reaction on the corresponding d-metal ion as a matrix





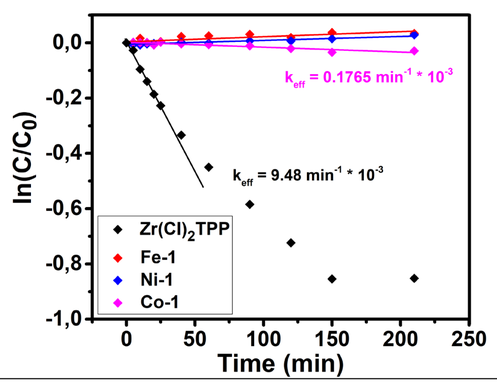
General view of the pseudoclathrochelate cations [Fe-1]+ (left) and [Ni-1]+ (rights) in Fe-1·CH_2Cl_2 and Ni-1·3$CHCl_3$

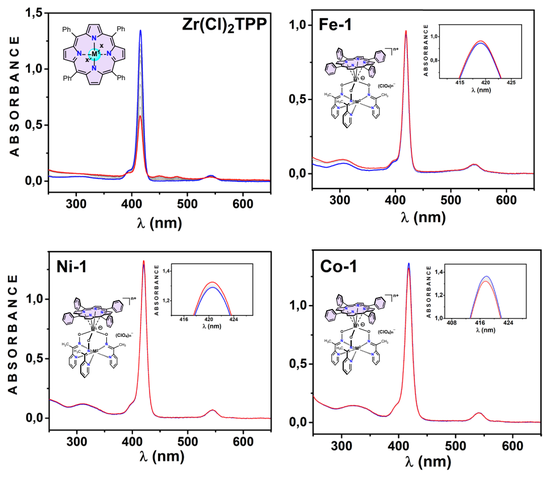
The structures was confirmed by:

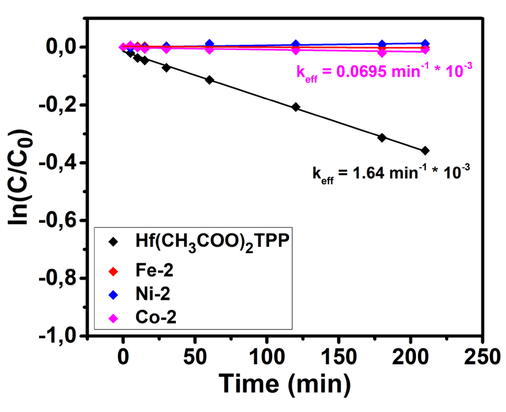
- ***Elemental analysis***
- ***^{1}H and ^{13}C{1H} NMR***
- ***MALDI-TOF mass***
- ***UV-vis spectra***
- ***X-ray diffraction (XRD) (for the iron and nickel(II) pseudocloathrochelates)***

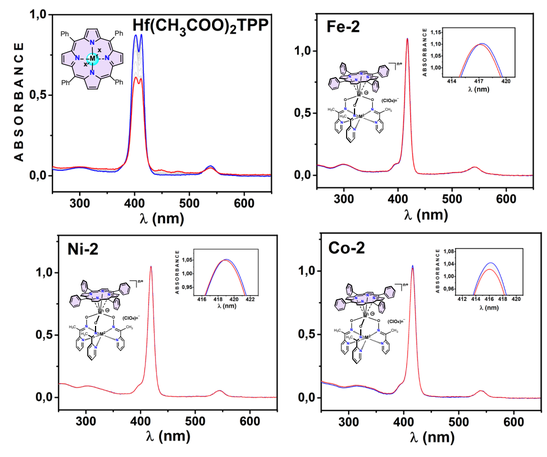
PHOTOSTABILITY STUDY

Change in the absorption intensity of porphyrins upon irradiation with blue light (3W, 430 – 505 nm) in a DCM/MeOH 2/1





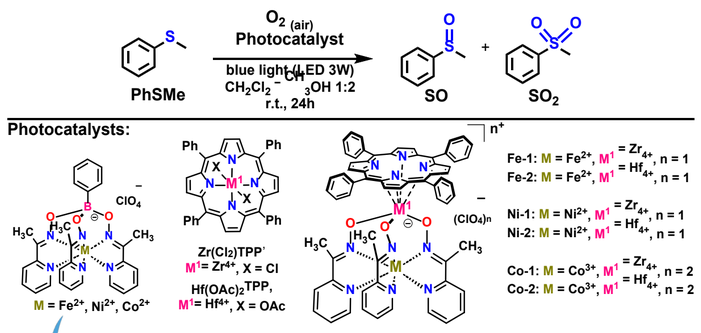


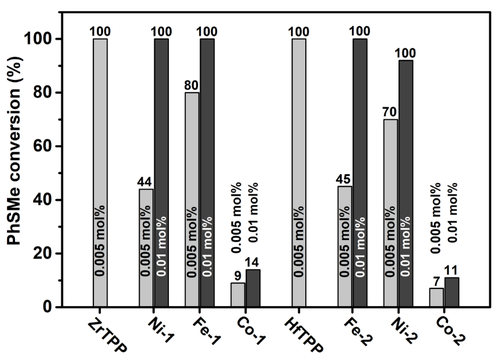


Photodegradation kinetics

PHOTOCATALYSIS

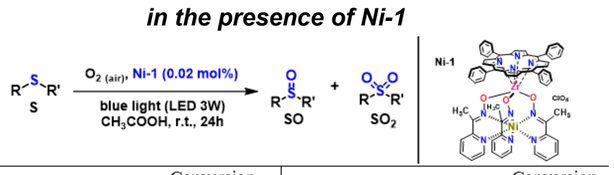
Photooxidation of thioanisole as a model substrate upon irradiation with blue light (3W, 430 – 505 nm) in a DCM/MeOH 2/1





- ***No any photocatalytic activity***
- ***Highly active in photooxidation***
- ***Photolabile***
- ***Less active in photoreaction***
- ***Co(III) complexes have decreased photoactivity***
- ***All of them are robust under light***

Photocatalytic oxidation of organic sulfides in the presence of Ni-1



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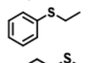
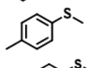
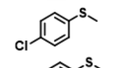
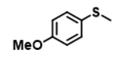
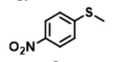
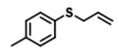
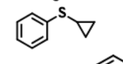
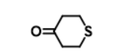
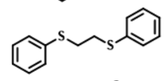
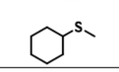
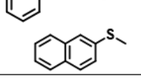
2		100	10		100
3		100	11		79
4		100	12		67
5		100	13		56
6		100	14		48
7		100	15		35
8		100	16		16

The substrate conversion was detected by the GC-MS or ^{1}H NMR method using o-DCB as an internal standard

Handmade 12-position photoreactor equipped with blue LED lamp (410–510 nm, 3W)

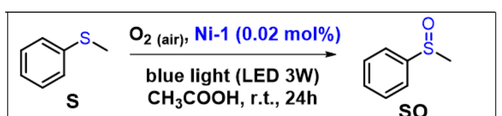
CONCLUSION

The highest photocatalytic activity even at low catalyst loading (0.01 mol%) was observed for the hybrid binuclear complexes with the encapsulated iron(II) and nickel(II) ions

Based on the data of scavengers, the main mechanism of the sulfoxidation in the presence of the binuclear complexes is single-electron transfer (SET).

SEARCHING FOR *ROS*

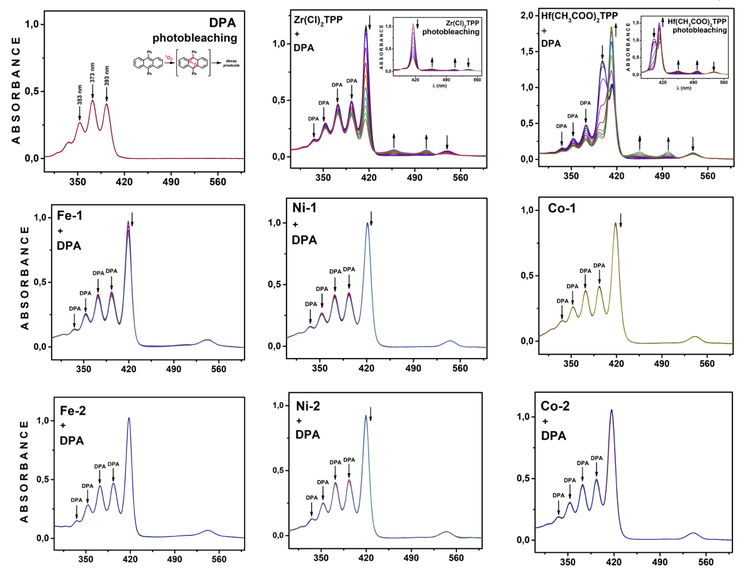
Photocatalytic oxidation of thioanisole in the presence of various scavenger using Ni-1 as the photocatalyst



Entry	Scavenger (*ca.*1 equiv.)[a]	Inhibited species or process	Conversion, %[b]
1	None	–	100
2	*i*-PrOH	$OH^·$ scavenger	100[c]
3	NaN_3	$^1O_2$ scavenger	100
4	DABCO	$^1O_2$ scavenger	81
5	$AgNO_3$	e^- scavenger	90
6	*p*-BQ	$O_2^{·-}$ scavenger	4
7	KI	h^+ deactivation	0

a – one or less equiv. of scavenger relative to the sulfide was used in the test depending on solubility in CH_3COOH; b – determined by ^{1}H NMR using o-dichlorobenzene as an internal standard; c – determined by GC-MS using o-dichlorobenzene as an internal standard

Photodegradation of DPA as selective $^1O_2$ scavenger (CH_2Cl_2 in the presence of porphyrin under blue light (3W, 410 – 510 nm) 1.5h



ACKNOWLEDGMENTS

Russian Science Foundation

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