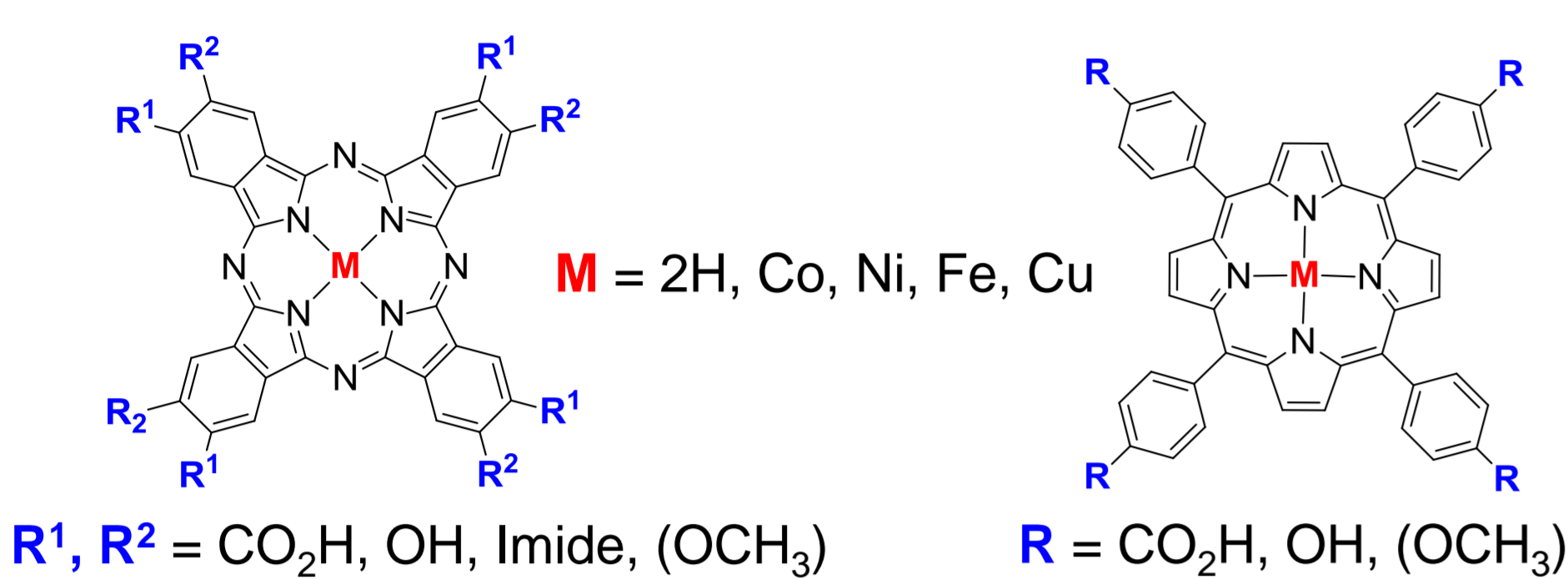


Introduction

Phthalocyanines, porphyrins and their appropriate metal complexes have been studied in great detail for many years. These compounds are well known for their tendency to form one-dimensional supramolecular architectures. Furthermore, they are distinguished by their high degree of aromaticity and their unique chemical and thermal stability. During the last two decades metallophthalocyanines and -porphyrins have gained special interest in the field of material sciences as they find application in non-linear optics, in optical data storage, as electrochromic substances, gas sensors, in photochemical and photovoltaic cells or in the therapy of cancer.^[1-5]

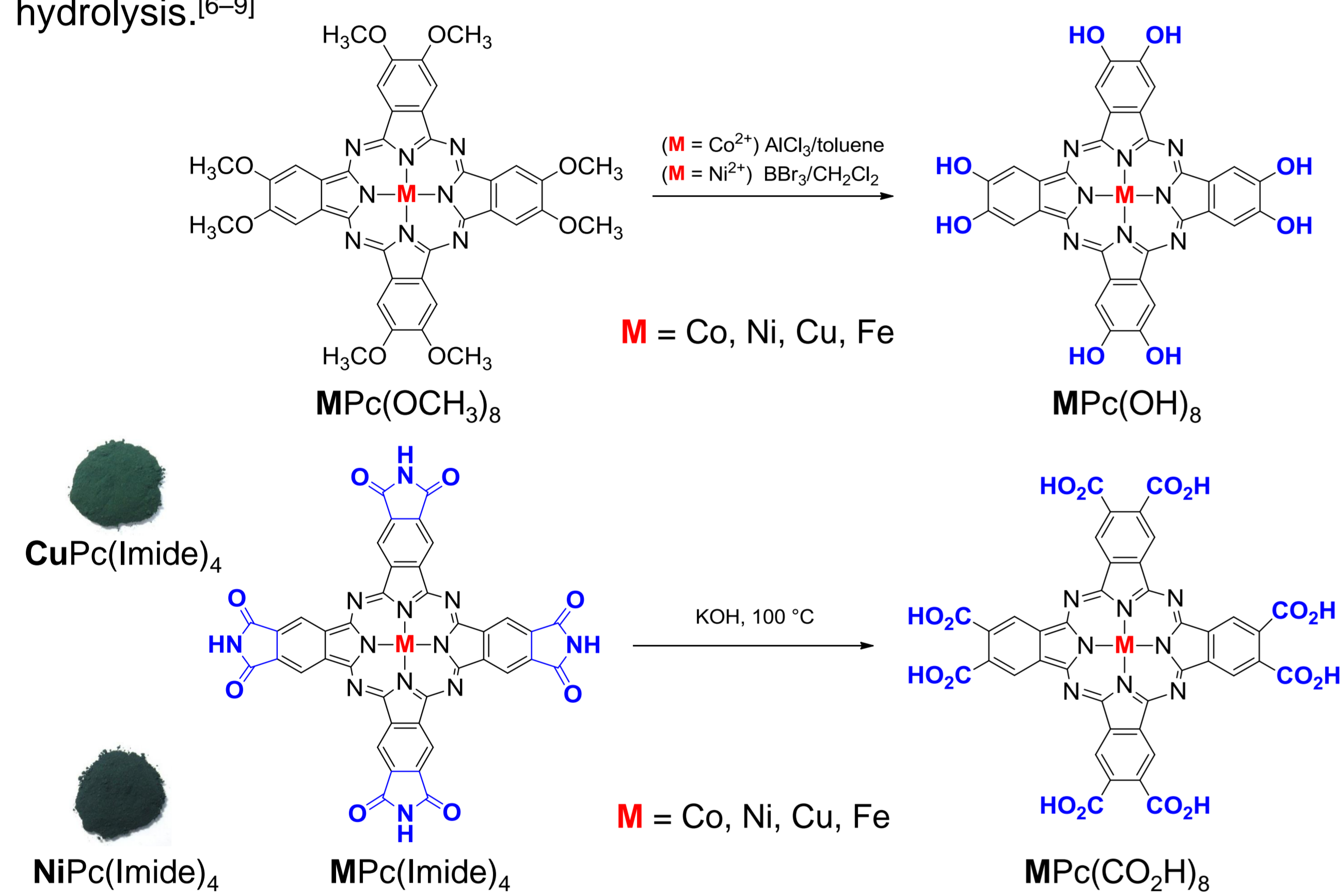
Motivation



One of the challenges of project SP2 is to synthesize magneto-active molecules, which have the possibility to generate networks formed by hydrogen bond interactions, when deposited on surfaces (e.g. Au(111)). This can be achieved by terminal modification of the phthalocyanine and porphyrin scaffold, using polar substituents, which provides hydrogen donor and/or acceptor functionalities. Here we report on the synthesis and characterization of various *p*-phenyl-substituted phthalocyanines and porphyrins ($R = CO_2H, OH$), the appropriate metal species (Co, Ni, Fe and Cu) and their use for magnetic response. In cooperation with SP1, SP6, SP7 and SP8 the arrangement of phthalocyanine and porphyrin monolayers based on the intermolecular hydrogen bond interactions should be determined via STM (scanning tunneling microscopy).

Synthesis and Characterization

The metallophthalocyanines are obtained via intermediate steps such as methoxy or imide substituted metallophthalocyanines. These are accessible in a one step cyclotetramerization reaction of functionalized phthalic anhydrides and benzodinitriles, respectively, with the corresponding metal salts in high boiling solvents or melts.^[5-8] The intermediates are converted to the final products by the reaction of boron tribromide or by hydrolysis.^[6-9]



After appropriate work-up, the thus obtained compounds were fully characterized by 1H and $^{13}C\{^1H\}$ NMR, IR and UV/Vis spectroscopy, elemental analysis as well as high resolution mass spectrometry.

The 1H NMR spectra of all four compounds show the expected resonance signals.

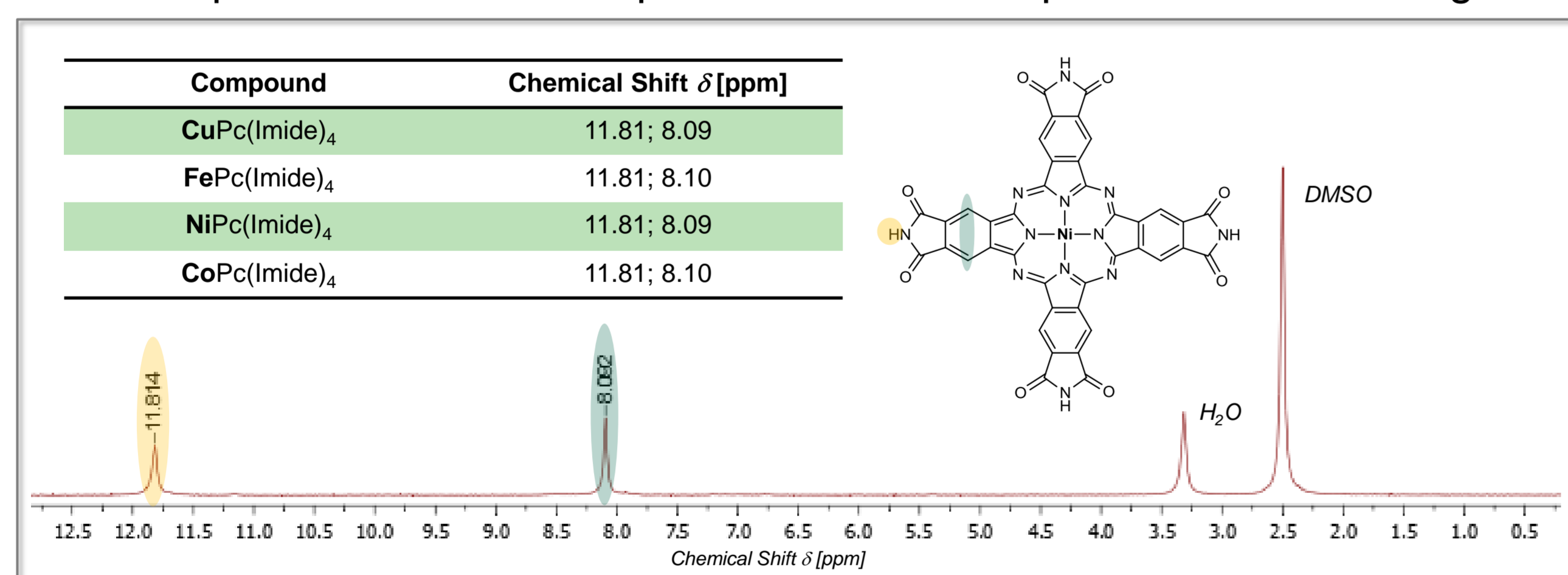


Fig. 1: Part of the 1H NMR spectrum of NiPc(Imide)₄ measured in DMSO-*d*₆.

So far no suitable crystals could be obtained for single crystal X-ray analysis. Also the elemental analysis exhibit a large deviation from the calculated values.

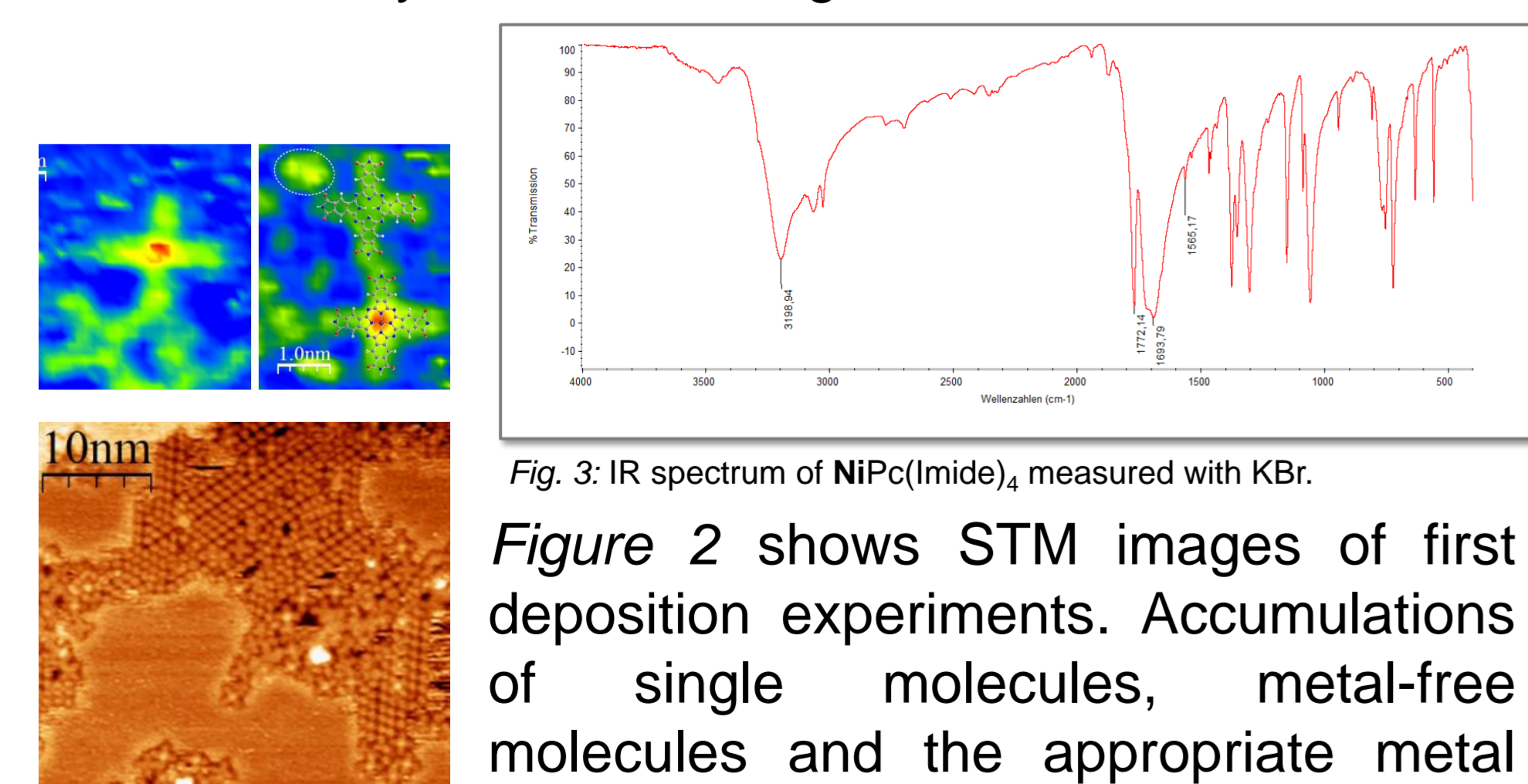


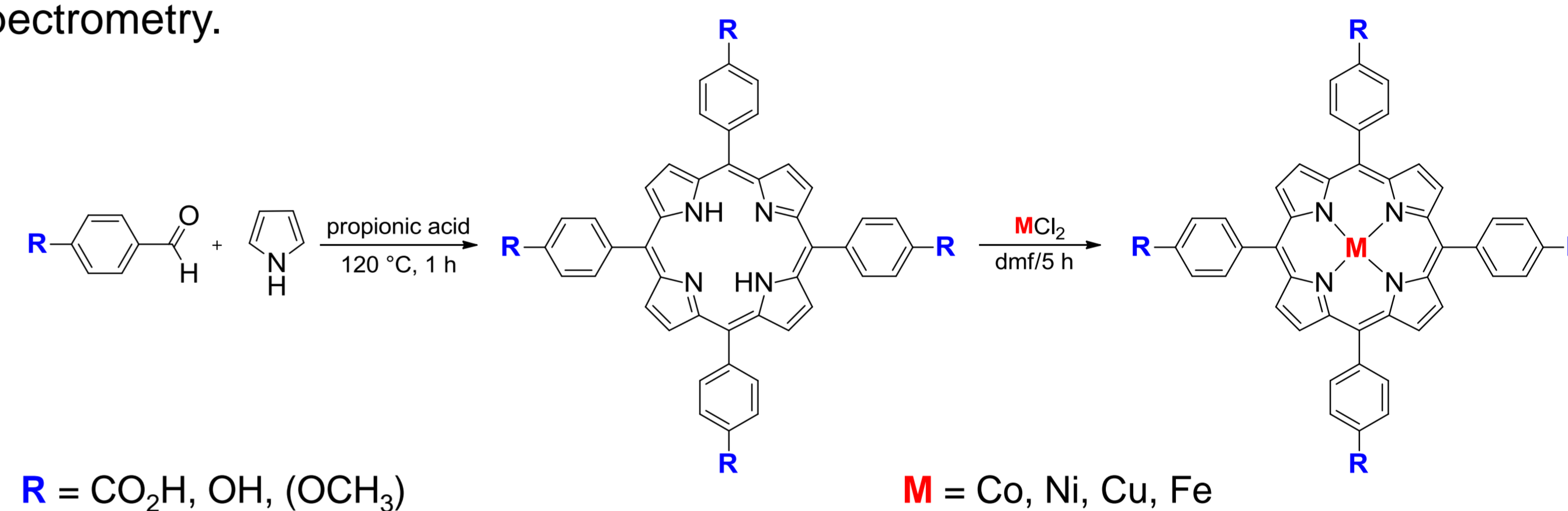
Fig. 3: IR spectrum of NiPc(Imide)₄ measured with KBr.

Figure 2 shows STM images of first deposition experiments. Accumulations of single molecules, metal-free molecules and the appropriate metal complex could be observed. There are still impurities detectable.

Fig. 2: STM images of FePc(Imide)₄Cl⁻.

From the IR spectra (Figure 3) characteristic CO and NH stretching frequencies can be observed. However, the compounds offer extremely poor solubility in common organic solvents, and hence a more precise characterization is very difficult. ESI-MS and APCI-MS measurements did not give any results.

The synthesis of the metalloporphyrins is realized via an intermediate step of the appropriate metal-free porphyrin systems. The corresponding functionalized aldehyde (*p*-R-C₆H₄-CHO) is reacted with pyrrole in propionic acid under reflux.^[10] Subsequent reaction with the respective metal salt MCl_2 in dmf produces the desired metal complexes.^[11] The resulting porphyrins exhibit a good solubility in common organic solvents, which simplifies a detailed characterization of the systems. After appropriate work-up, the thus obtained compounds were fully characterized by 1H and $^{13}C\{^1H\}$ NMR, IR and UV/Vis spectroscopy, elemental analysis as well as high resolution mass spectrometry.



The successful implementation to the desired products can be observed via 1H NMR spectroscopy. The detected resonance signals can be assigned to the corresponding hydrogen atoms of molecules (A) Por(*p*-C₆H₄-OCH₃)₄, (B) Por(*p*-C₆H₄-OH)₄ and (C) Por(*p*-C₆H₄-CO₂H)₄. An influence of the functional groups on the chemical shift of the resonance signals of the aromatic hydrogen atoms can be observed.

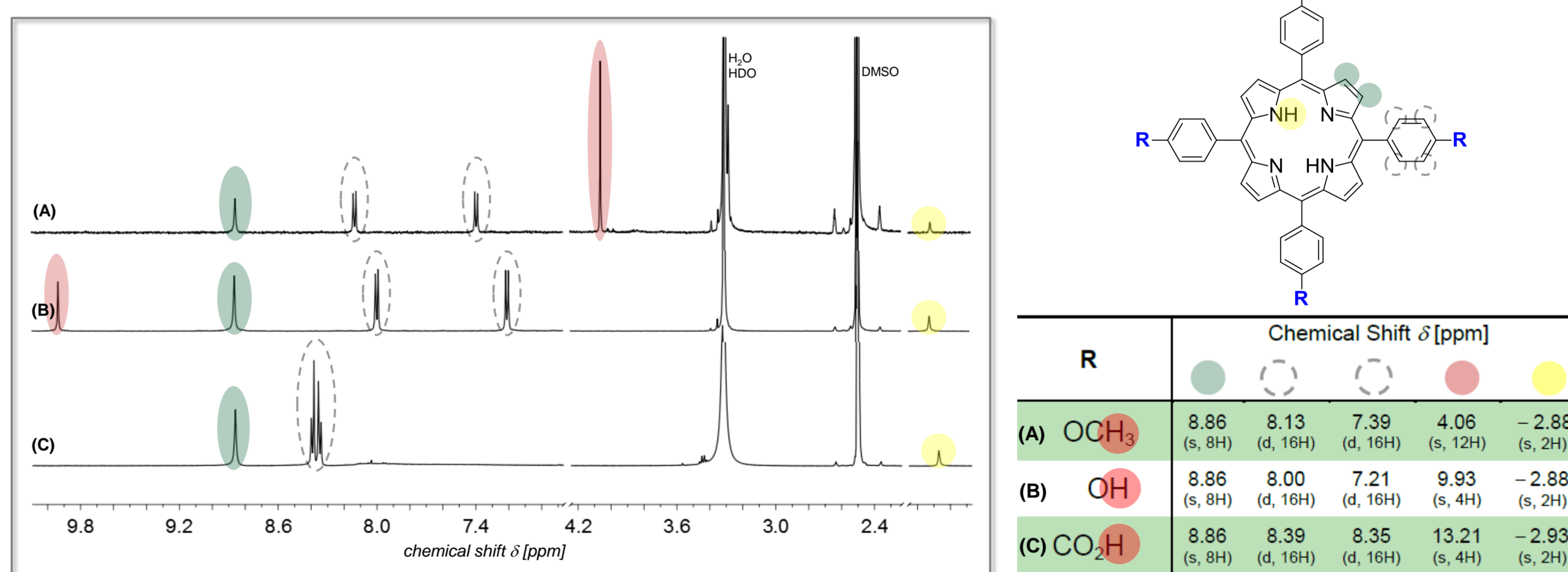


Fig. 4: Part of the 1H NMR spectrum of (A) Por(*p*-C₆H₄-OCH₃)₄, (B) Por(*p*-C₆H₄-OH)₄ and (C) Por(*p*-C₆H₄-CO₂H)₄ measured in DMSO-*d*₆.

Determination of the extinction coefficient of CoPor(*p*-C₆H₄-CO₂H)₄ in methanol.

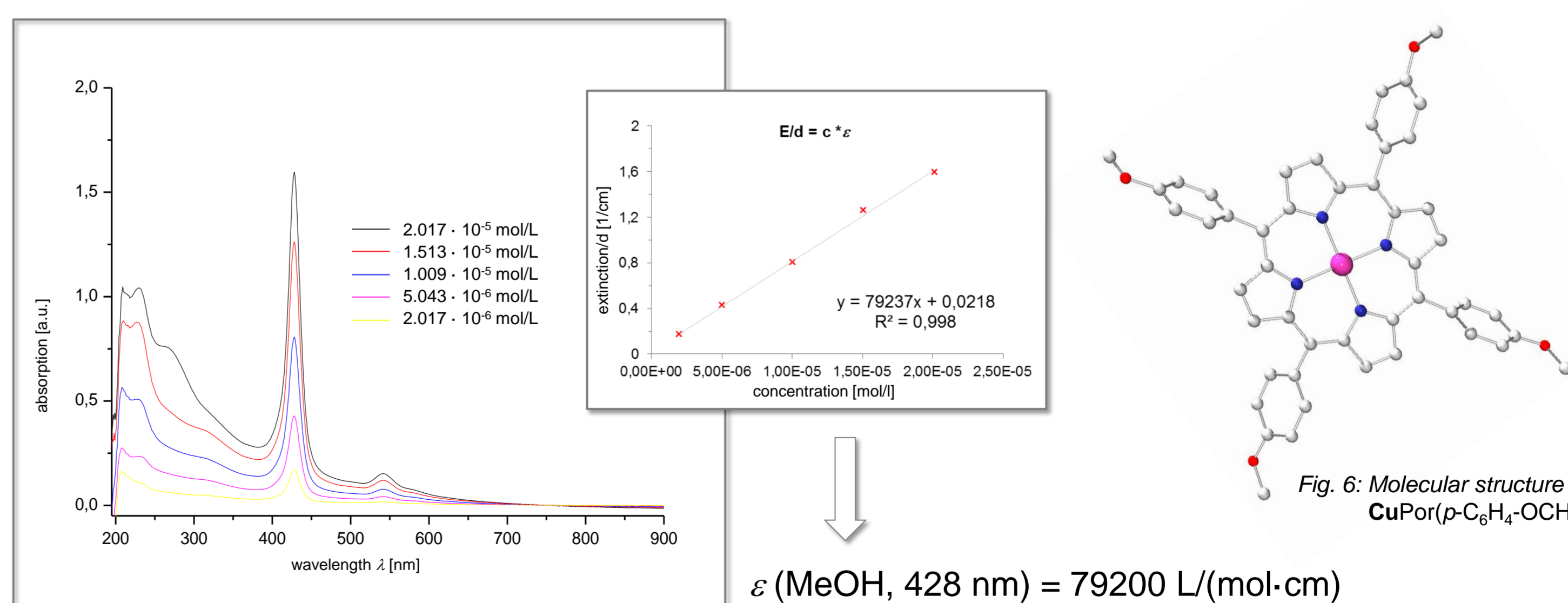
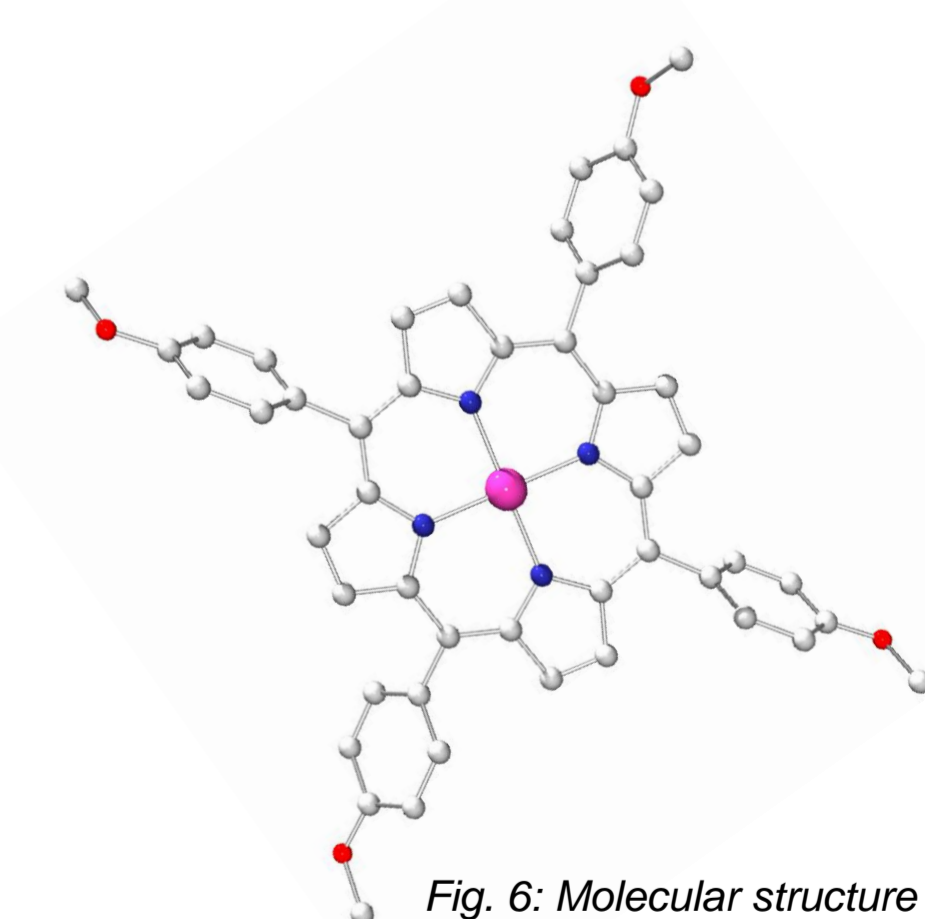


Fig. 5: UV/Vis absorption spectra of CoPor(*p*-C₆H₄-CO₂H)₄ in methanol.

In the UV/Vis spectrum the Soret band can be observed at 428 nm. In comparison to the metal-free compound, where four Q-bands can be observed, only one Q-band for the metalloporphyrin is found, which indicates successful metal complexation.



References and Acknowledgment

- [1] Dini D., Barthel M., Hanack M. *Eur. J. Org. Chem.* **2001**, 3759–3769. [2] Shirakawa *et al.* *J. Org. Chem.* **2003**, 68, 5037–5044. [3] Hanack M., Albert K. *et al.*, *Chem. Eur. J.* **2001**, 7, 2459–2465. [4] Yuksel F., Tuncel S., Ahsen V. *J. Porphyrins and Phthalocyanines* **2008**, 12, 123–130. [5] Plater M. J., Aiken S., Bourhill G. *Tetrahedron* **2002**, 58, 2415–2422. [6] Hanack M., Lang M. *Adv. Mater.* **1994**, 6, 819–833. [7] Sakamoto K., Ohno E. *Progr. in Organic Coatings* **1997**, 31, 139–145. [8] Ruf M., Lawrence A. M., Noll B. C. *Inorg. Chem.* **1998**, 37, 1992–1999. [9] Metz J., Schneider O., Hanack M. *Inorg. Chem.* **1984**, 23, 1065–1071. [10] Adler A. D. *J. Org. Chem.* **1967**, 32, 476. [11] Kumar A., Maji S., Dubey P., Abhilash G. J., Pandey S., Sarkar S. *Tetrahedron Lett.* **2007**, 48, 7287–7290.

We are grateful to the DFG for generous financial support.