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# Chiroptical Properties of Chiral Porphyrin Cages and their Host-Guest Complexes

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## Introduction

The amount of information trafficking on the internet nowadays is enormous and keeps increasing. Technologies for storing data have greatly changed over the years (**Figure 1**)[1]. The aim is to work towards more efficient data storage techniques that allow for faster processing, higher data densities and smaller storage devices.

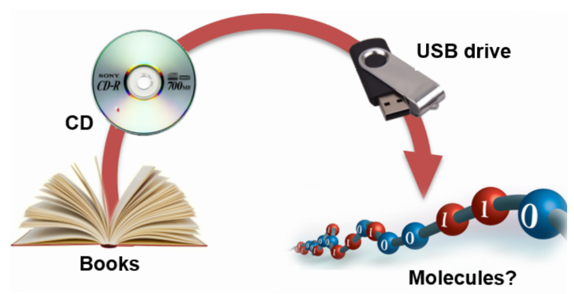



**Figure 1.** Data storage technology throughout the ages

This project is part of a program which aims to develop a molecular system which is able to write a binary code onto butadiene polymer chains. The system consists of a chiral porphyrin cagewhich moves along these chains. If a manganese ion is bound inside the porphyrin, the system is able to write chiral epoxides onto the chain ((R,R)-epoxide = digit 0; (S,S)-epoxide = digit 1, **Figure 2**)[2].

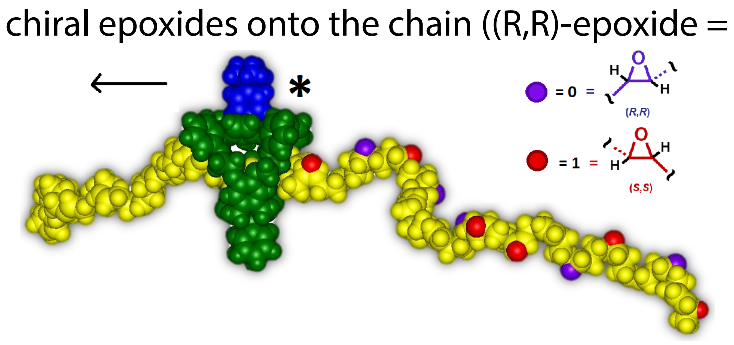


**Figure 2.** Processive catalytic system consisting of a chiral porphyrin catalyst (**MnI**) which builds in either (R,R)-epoxides (0) or (S,S)-epoxides (1).

## Aim

In this poster the separation and analysis of the binding properties of chiral nitroporphyrin cages are reported. This project aims at host-guest complexes of porphyrin cages with different chiral guests (**Figure 3**). Two types of cages are used, mononitro and trans-dinitro porphyrin cages. It is investigated whether the mono- and dinitro cages show enantioselective binding. The complexes have been characterized using vibrational circular dichroism (VCD).

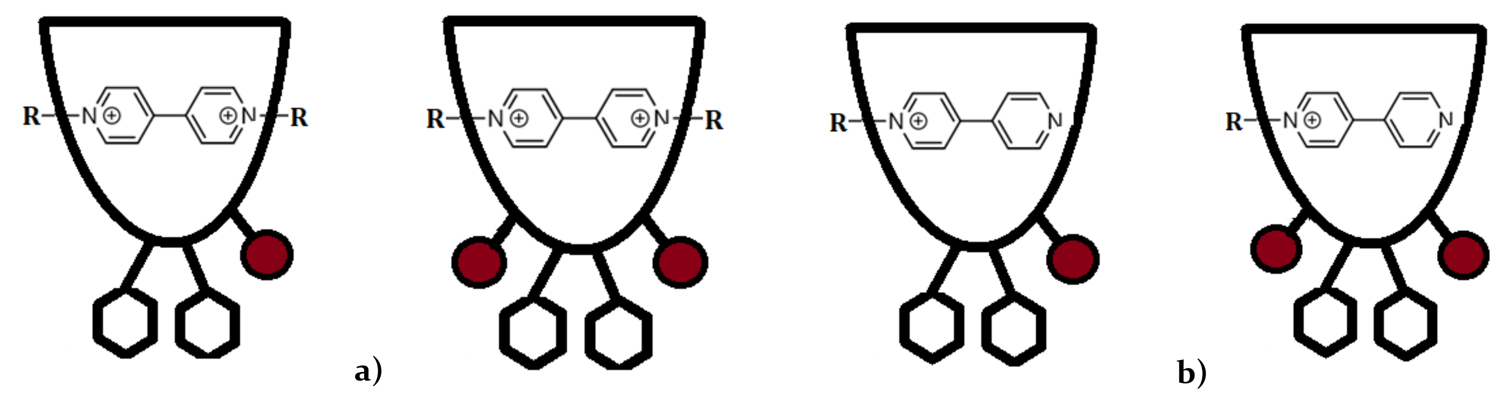
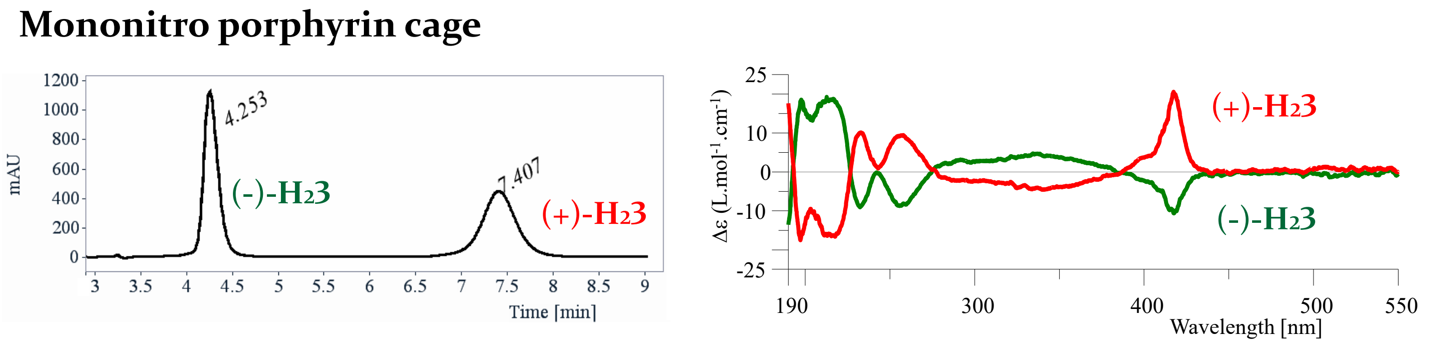



**Figure 3.** Complexes of mono- and trans-dinitro porphyrin cages with a) viologen and b) bipyridinium guests.

## Separation

**Mononitro porphyrin cage**




**Trans-dinitro porphyrin cage**

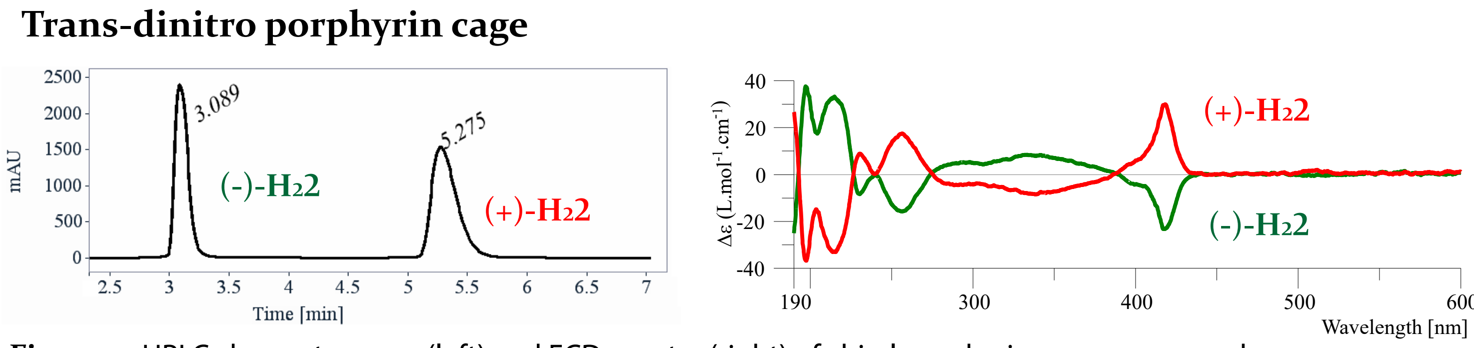
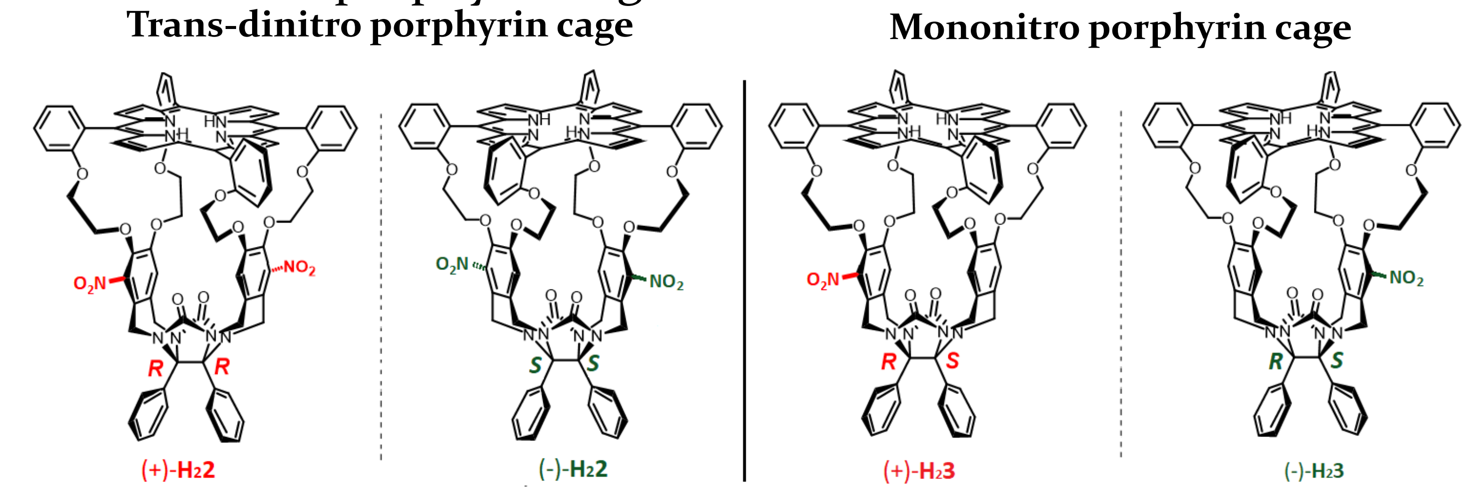



**Figure 4.** HPLC chromatograms (left) and ECD spectra (right) of chiral porphyrin cage compounds

## Compounds

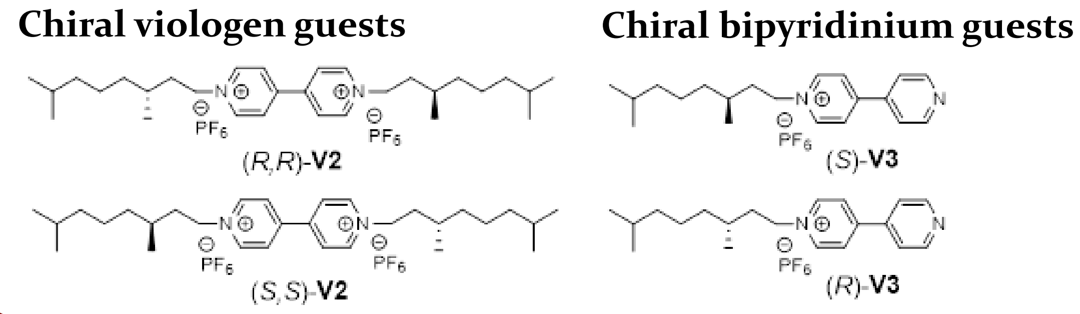
**Hosts:** Chiral porphyrin cages

**Trans-dinitro porphyrin cage** | **Monitro porphyrin cage**




**Guests:**

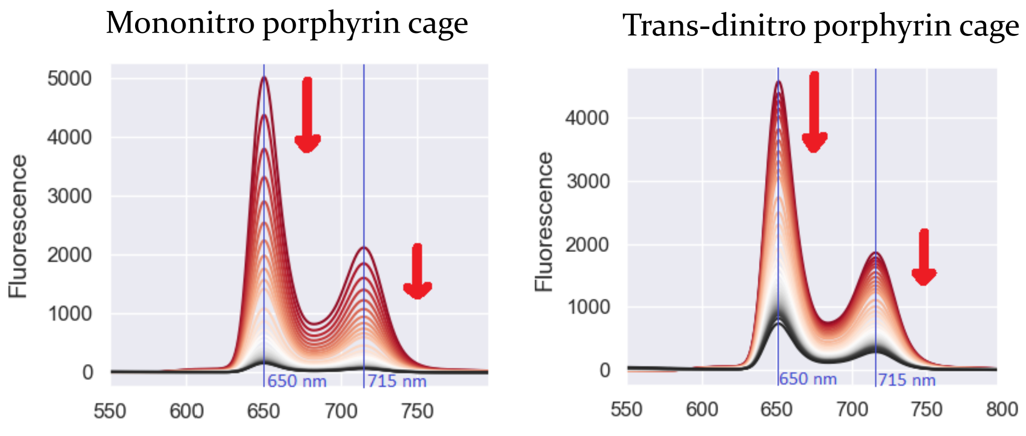
**Chiral viologen guests** | **Chiral bipyridinium guests**




## Fluorescence titrations

**Chiral viologen guests**

Mononitro porphyrin cage | Trans-dinitro porphyrin cage




**Chiral bipyridinium guests**

Mononitro porphyrin cage | Trans-dinitro porphyrin cage

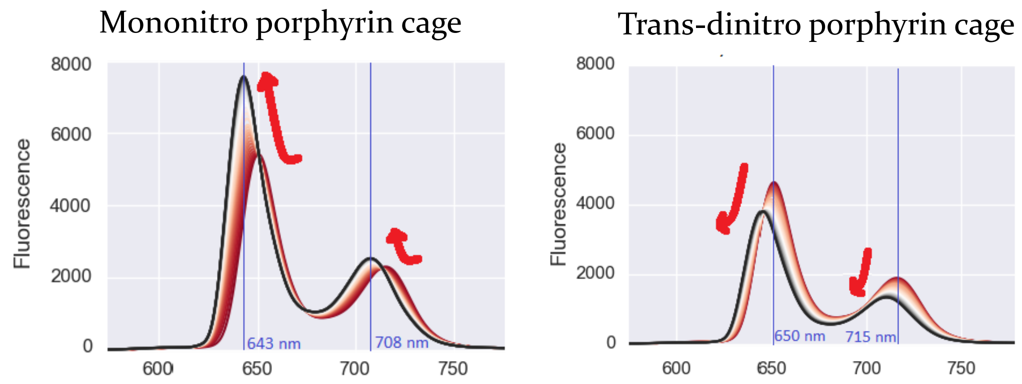



**Figure 5.** Fluorescence titrations of chiral porphyrin cages with chiral guests.

## VCD

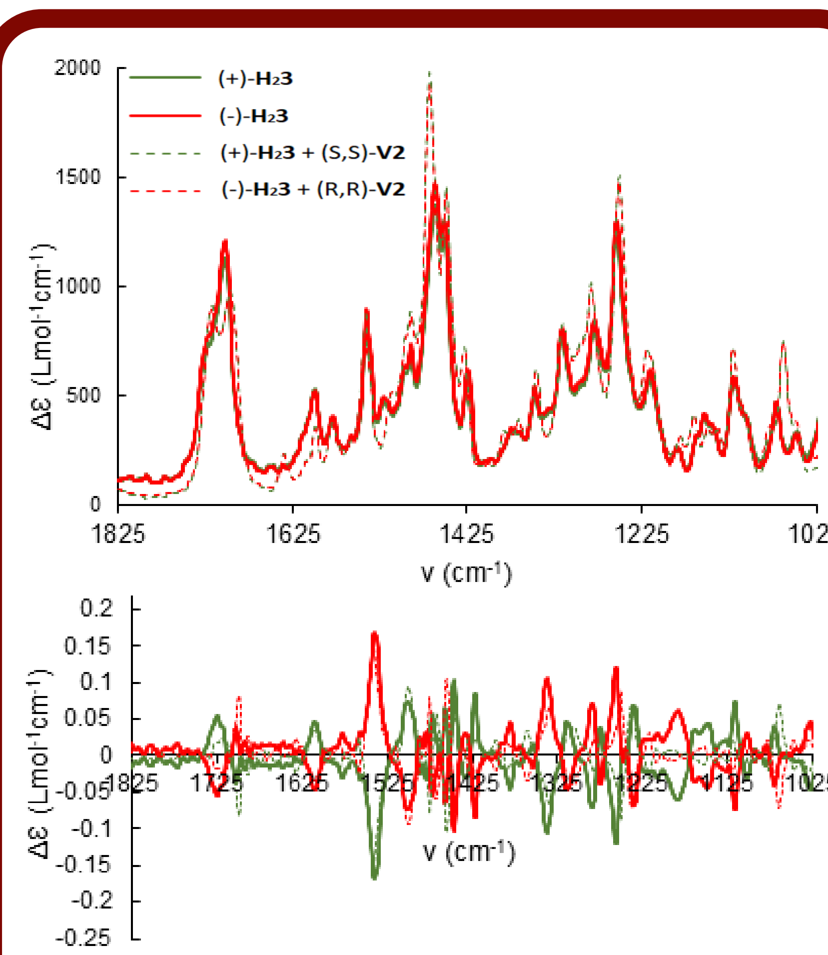



**Figure 6.** (Top) IR spectrum and (bottom) VCD spectrum of the mononitro porphyrin cage with the viologen guests.

## Results

**Table 1:** Association constants and reaction Gibbs free energies for complexes of mono- and dinitro cages with chiral viologen[a] and bipyridinium guests[b].

| *Host* | *Guest* | $K_a$ ($*10^4$ $M^{-1}$) | $\Delta_r G$ (kJ/mol) |
|---|---|---|---|
| (+)-$H_2$3 | | | |
| | (S,S)-**V2** | 215 ± 7 | -36.15 ± 0.08 |
| | (R,R)-**V2** | 351 ± 9 | -37.36 ± 0.07 |
| | (S)-**V3** | 57 ± 7 | -32.82 ± 0.32 |
| | (R)-**V3** | 32 ± 1 | -31.42 ± 0.10 |
| (-)-$H_2$3 | | | |
| | (S,S)-**V2** | 262 ± 12 | -36.63 ± 0.11 |
| | (R,R)-**V2** | 323 ± 19 | -37.15 ± 0.15 |
| | (S)-**V3** | 40 ± 1 | -31.95 ± 0.09 |
| | (R)-**V3** | 31 ± 1 | -31.34 ± 0.08 |
| (+)-$H_2$2 | | | |
| | (S,S)-**V2** | 10.8 ± 0.7 | -28.74 ± 0.16 |
| | (R,R)-**V2** | 8.5 ± 0.5 | -28.12 ± 0.15 |
| (-)-$H_2$2 | | | |
| | (S,S)-**V2** | 9.4 ± 0.2 | -28.38 ± 0.06 |
| | (R,R)-**V2** | 10.6 ± 0.6 | -28.69 ± 0.14 |

*a) Association constants obtained from triplo fluorescence titrations by following the change in intensity at 650 nm and b) at 643 nm. Titration executed at 25 °C, in 1 : 1 (v/v) chloroform : acetonitrile.*

## Conclusion

The mono- and trans-dinitro porphyrin cages do not show significant enantioselective binding of chiral viologen and chiral bipyridinium guests, but cages with more bulky substituents do[3].

References

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2. Thordarson, P., Bijsterveld, E.J.A., Rowan, A.E., Nolte, R.J.M., *Nature* **2003**, 424 (6951), 915-918.
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