Supporting Information

The Effect of the Stoichiometry in the Supramolecular Chirality Transfer to Zinc Bisporphyrins Systems

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Materials

All syntheses were carried out using chemicals as purchased from commercial sources unless otherwise noted. All commercial solvents and chemicals were of reagent grade quality and were used without further purification except as noted. Dichloromethane was deacidified by passing through a short column of aluminium oxide 90 active, neutral (Merck). When required, dried and deoxygenated solvents supplied by Sigma-Aldrich Solvent Purification System (SPS-200-6) were used. Thin-layer chromatography (TLC) and flash column chromatography were performed with DC-Alufolien Kieselgel 60 F254 (Merck). (*1R,2R*)-DACH and (*1S,2S*)-DACH were bulb to bulb distilled and DABCO was sublimed prior to use.

Titration experiments

CD spectra were recorded in a Chirascan instrument HP Compaq PC. UV-visible spectra were recorded on a UV-2401/2501 PC spectrophotometer and in a Chirascan instrument HP Compaq PC.

CD and UV-visible titrations were performed by adding solutions containing the ligand to a solution of the zinc-porphyrin in either a 1mm or 1cm path cuvette by using microliter syringes. In all cases the zinc-porphyrin was present in the guest solution at the same concentration as that in the cuvette to avoid dilution effects. Deacidified dichlorometane was used as solvent for the CD and UV-visible titrations. CD and UV-visible scanning conditions were as follows: scanning rate = 50 nm per min, bandwidth = 1 nm, response time= 0.5 s, accumulations = 1 scan.

Computation of the titration data. Estimating equilibrium constants and pure UV-vis and CD spectra of the different species involved in consecutive binding equilibria.

Introduction

SPECFIT/32[TM] is a sophisticated, multivariate data analysis program for modeling and fitting a variety of equilibrium titration 3D data sets that are obtained from multi-wavelength spectrophotometric measurements. Such 3D data set consist of simultaneous measurements of Absorbance (Ellipticity) vs Wavelength as a function of an independent variable, the concentration of the titrant (ligand). The details of the software and the related non-linear algorithms can be found in the literature (see ref.10 in the manuscript).

SPECFIT/32[TM] software was used for the simultaneous calculations of the stability constants and the corresponding UV-vis or CD spectra of the pure **4**:Zn-bisporphyrin 1:1 sandwich and 2:1 open complexes. We used 3D data obtained from multiwavelength spectrophotometric titrations (UV-vis and CD) in which the concentration of the porphyrin (host) was maintained constant and the concentration of the ligand (guest) was incrementally increased. After each addition of guest, a new spectrum was acquired. To avoid the dilution of the host solution the titrating guest solutions' were prepared using the solution of the host as the solvent. To cover a wide range of guest concentrations it was necessary to prepare several solutions with different concentrations.

The experimental 3D titration data set is directly imported into the SPECFIT/32[TM] software as a single file in .csv format specifying the total concentrations of host and guest in solution for each spectrum. Next, a binding *model* that can be justified by the eigenvector factor analysis of the data set automatically performed by SPECFIT/32[TM] or more importantly by the chemical nature of the system under study is postulated. SPECFIT/32[TM] uses the Newston-Raphson method to solve the speciation equilibria for complexometric equilibria. In the model various states of complexation are specified in terms of indices (stoichiometry) and overall stability constants (β_{xy}). The contribution of a species to the observed spectrum must be indicated by setting the species as colored. In the case at hand, the postulated model was for two titrable components (M, L) involved in four different stoichiometric states. Two free states, M_1L_0 and M_0L_1 and two complexes M_1L_1 and M_1L_2. By convention, the first species is denoted as a metal ion. M and L can be considered as possible titrants (variable concentration during the experiment). As mentioned above, we held the concentration of M at a fixed value. For the UV-vis titrations all species except M_0L_1 (diamine **4**) are colored and may contribute the observed spectrum. For the CD titrations, however, only the two complexes, M_1L_1 and M_1L_2, were considered as colored species. The colored species can also be assigned known spectra which are held as constant during the fit. The stability constants β_{xy} may also be specified as fixed values.

Molar absortivity scaling is based on the initial concentrations of the components, which may differ for each supplied spectrum in the titration series data set. Each scan is a separate speciation calculation experiment based on the current parameter set from the global minimization routine.

The underlying chemical model and its nonlinear parameters are used to generate concentration profiles for each of the colored species, and the initial parameter estimates are then refined via the Levenberg-Marquardt procedure to minimize the least squares residuals between the 3D data set and the model system. The output from the global fitting procedures consists of: 1) the optimized model parameters and their standard errors; 2) the concentration

profiles of the colored and not colored species, 3) the absorptivity spectra for each colored species in the wavelength range of the 3D dataset. The predicted (calculated) molar absorptivity spectra are obtained after completion of the fitting procedure via a pseudo-inverse matrix methodology.

The advantages of utilizing SPECFIT/32$^{\text{TM}}$ for fitting multiwavelength 3D data sets include: 1) more reliable parameters are calculated than single-wavelength fits; 2) the ability to extract calculated spectra for intermediate complexes; 3) the ability to constrain fits with known molar absorptivity spectra and any or all of the stability constants.

Fitting methodology

The 3D UV-visible titration data (absorbance units) were analyzed using global multivariate factor analysis considering only three colored species (free bisporphyrin, 1:1 bisporphyrin@(1R,2R)-**4** sandwich complex and 1:2 bisporphyrin@(1R,2R)-**4** open complex). To minimize the number of variables in the fitting procedure the UV-vis spectra of free bisporphyrins were fixed. In addition, the stability constant of the 1:2 complex was estimated and fixed using the value K_{m} for the reference complex monoamine/monoporphyrin (see Figure 6 on the ESI, $K_{\text{m}} = 5 \times 10^4$ M^{-1} is the calculated microscopic constant for the interaction of a model primary monoamine, cyclohexylamine, with a model Zn-tetraarylporphyrin **5**), being $K_{12} = 4 \, K_{\text{m}}^2 = 1.0 \times 10^{10}$ M^{-1}, which was assumed to be identical for the three bisporphyrin@**4** systems. The remaining variables to be optimized during the fitting of the data are the stability constant of the 1:1 assembly and the UV-vis spectra of the 1:1 and 1:2 complexes. The calculated value for K_{11} is therefore based on the simultaneous fitting of the titration data for the formation of the sandwich and for its destruction.

We calculated the following values for the stability constants of the 1:1 sandwich complexes: $K_{11}(\mathbf{1a}) = 1.2 \pm 0.4 \times 10^6$ M^{-1}; $K_{11}(\mathbf{1b}) = 2.5 \pm 0.5 \times 10^5$ M^{-1}; $K_{11}(\mathbf{2}) = 2.5 \pm 0.2 \times 10^5$ M^{-1}. The fitting procedure returned the calculated spectra in molar absorptivity ε (M^{-1}cm^{-1}) of the different bisporphyrin complexes and also a speciation profile (as complexes concentrations,

$[ML_x]$) depending on the ligand **4** concentration. The K_{11} values calculated allowed determining the effective molarities EM (EM = K_{11}/K_m as shown in Scheme 1 in the manuscript) associated to these systems.

The spectral and binding parameters evaluated for the enantiomeric ligand, (1*S*,2*S*)-**4**, complexes were identical to those for (1*R*,2*R*)-**4** within experimental error.

The CD titration data (amplitude units or ellipticity units; θ(mdeg) = 32982 ΔA) of the three bisporphyrin@(1*R*,2*R*)-**4** systems, simultaneously recorded with the UV-visible data, were also analyzed using multivariate factor analysis. The whole series of experimental CD spectra recorded at 1nm intervals were fit to a binding model considering that the bisporphyrin is involved in three different stoichiometric states: a CD silent free state (not colored) and two CD active (colored) complexes with 1:1 and 1:2 bisporphyrin/**4** stoichiometries respectively. Fixing the stability constants of the 1:1 sandwich and the 1:2 open complexes to the values previously calculated from the UV-visible titration experiments, the only variables to be optimized during the fitting procedure were the CD spectra of the two active species, the 1:1 and 1:2 complexes.

For the three bisporphyrins, we obtained a remarkable good fit of the CD titration data to the theoretical curves at all the wavelengths. Figure 3d shows the fit of the experimental data to the theoretical curve in ellipticity (mdeg) units. The fitting procedure returned directly the calculated CD spectra for the complexes in molar circular-dichroism or delta epsilon $\Delta\varepsilon$ (M^{-1}cm^{-1}) units when the experimental input 3D data set was imported in amplitude units.

The spectral and binding parameters evaluated for (1*S*,2*S*)-**4** complexes were identical to those for (1*R*,2*R*)-**4** within experimental error, while the sign of the CD amplitude (A) value are opposite.

Figure 1. UV-visible and CD titration spectra (Soret region) of **1-2** with (*1R,2R*)-**4** in dichloromethane at 298K. The concentration of the bisporphyrin was maintained constant throughout the titration (1.2 x 10^{-5} M in a 1mm cuvette). a) **1a**. Number of equivalents of (*1R,2R*)-**4** added per dimmer bisporphyrin: 0, 1.1, 1.9, 16.5, 53.3, 204.2. b) **1b**. Number of equivalents of (*1R,2R*)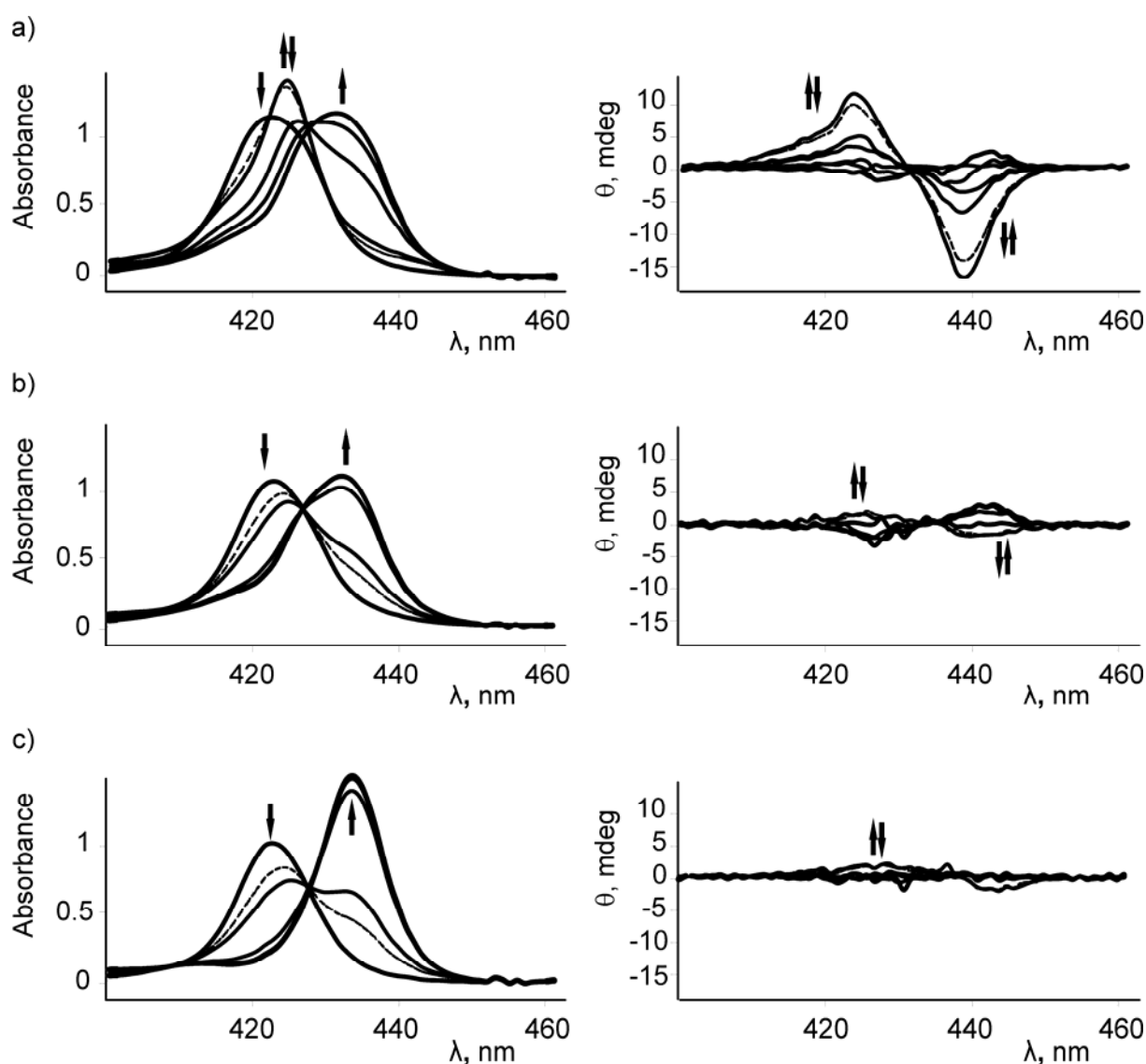-**4** added per bisporphyrin: 0, 1.1, 2.0, 14.7, 70.2, 228.9. c) **2**. Number of equivalents of (*1R,2R*)-**4** added per bisporphyrin: 0, 1.1, 1.9, 16.5, 53.3, 204.2.
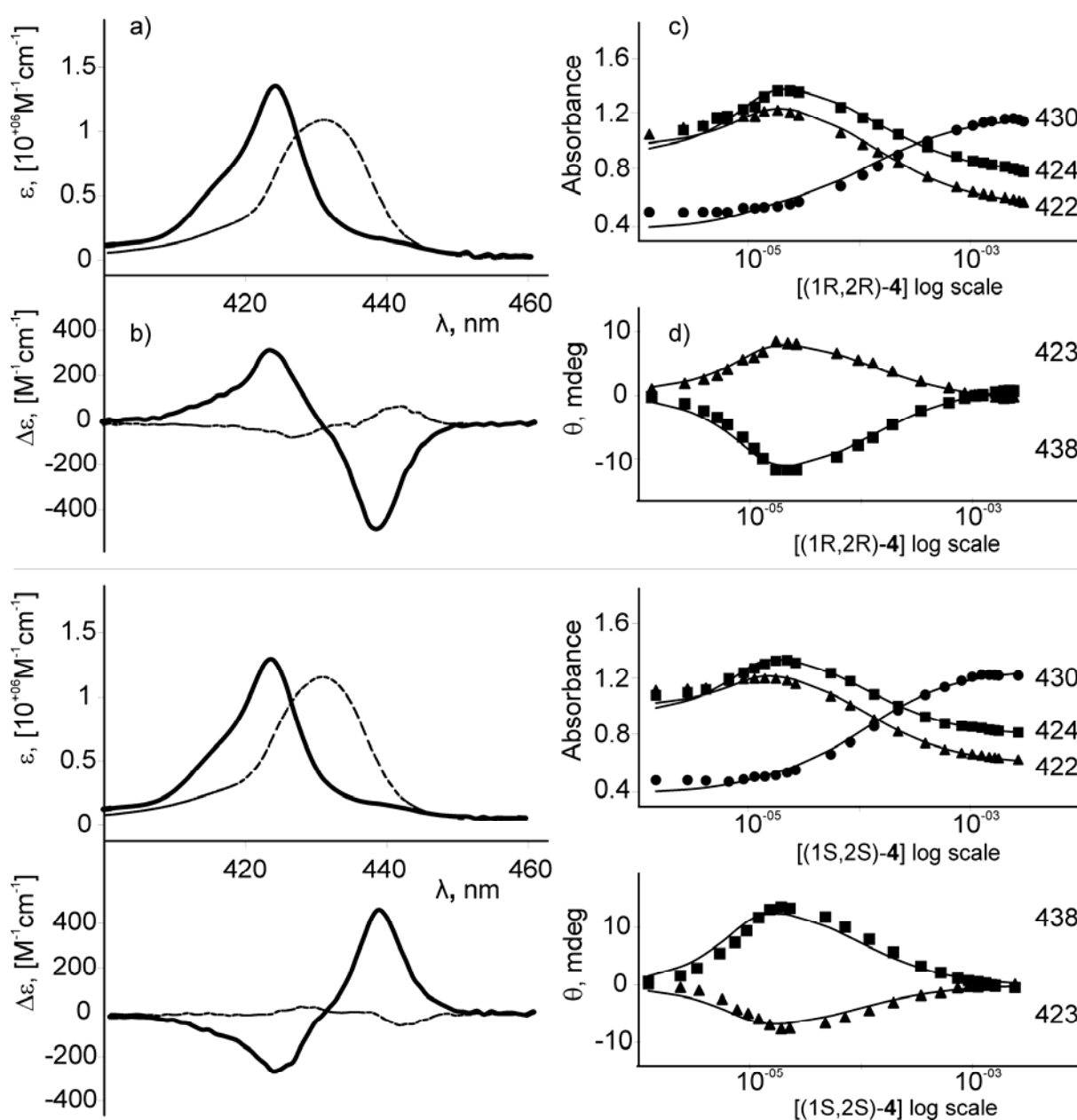
Figure 2. Calculated UV-visible spectra (a) and CD spectra (b) of the 1:1 (bold line) and 2:1 (dashed line) complexes formed between **1a** and (*1R,2R*)-**4** in dichloromethane at 298K. Fits of the titrations data at selected wavelengths to the theoretical binding model considering the bisporphyrin in three different stoichiometric states (free, 1:1 and 2:1 complexes). UV-visible at 422, 424 and 430 nm (c) and CD data at 423 and 438 nm (d). The figure below represent the same data for the titration of **1a** with (*1S,2S*)-**4**.
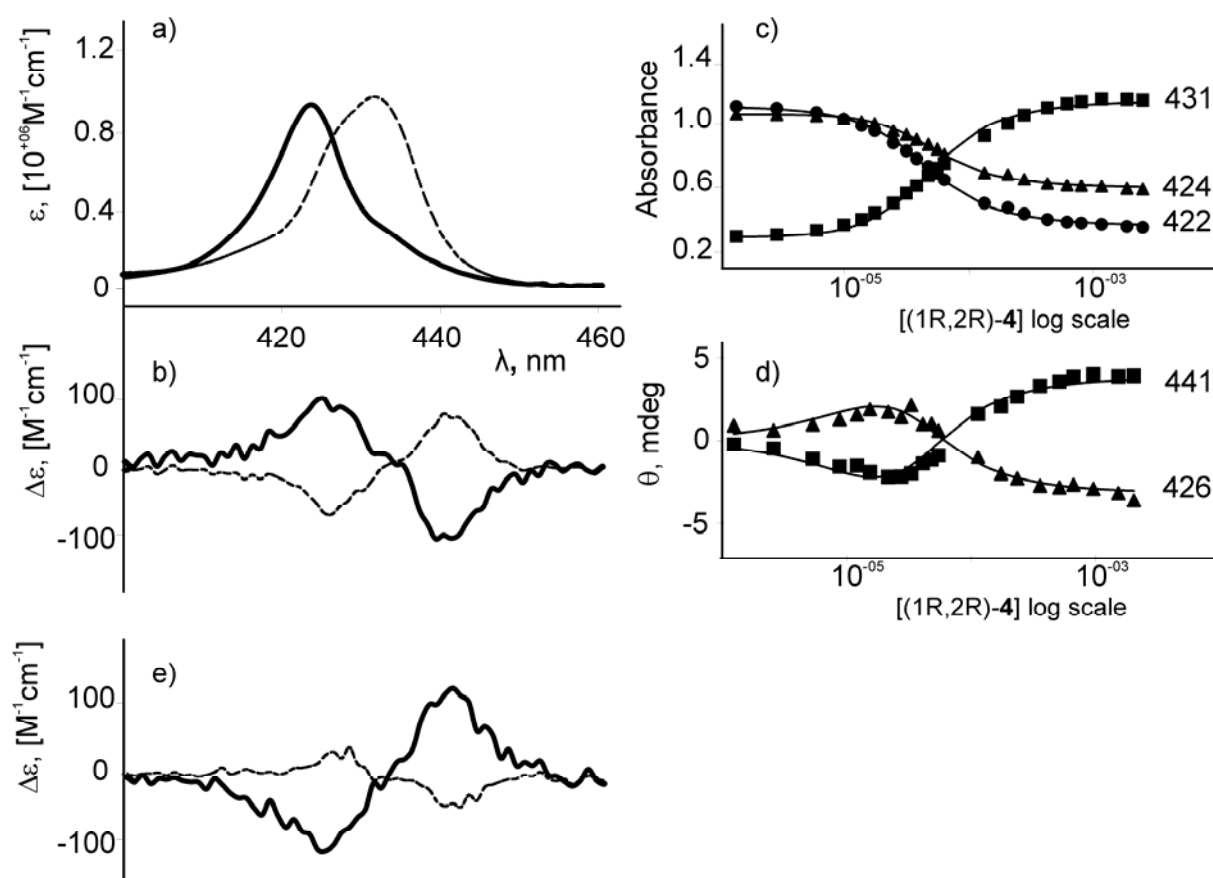
Figure 3. Calculated UV-visible spectra (a) and CD spectra (b) of the 1:1 (bold line) and 2:1 (dashed line) complexes formed between **1b** and (*1R,2R*)-**4** in dichloromethane at 298K. Fits of the titrations data at selected wavelengths to the theoretical binding model considering the bisporphyrin in three different stoichiometric states (free, 1:1 and 2:1 complexes). UV-visible at 422, 424 and 431 nm (c) and CD data at 426 and 441 nm (d). Calculated CD spectra of the 1:1 (bold line) and 2:1 (dashed line) complexes formed between **1b** and (*1S,2S*)-**4** (e).

Figure 4. Calculated UV-visible spectra (a) and CD spectra (b) of the 1:1 (bold line) and 2:1 (dashed line) complexes formed between **2** and (*1R,2R*)-**4** in dichloromethane at 298K. Fits of the titrations data at selected wavelengths to the theoretical binding model considering the bisporphyrin in three different stoichiometric states (free, 1:1 and 2:1 complexes). UV-visible at 422, 426 and 436 nm (c) and CD data at 426 and 443 nm (d). Calculated CD spectra of the 1:1 complex formed between **2** and (*1S,2S*)-**4** (e).
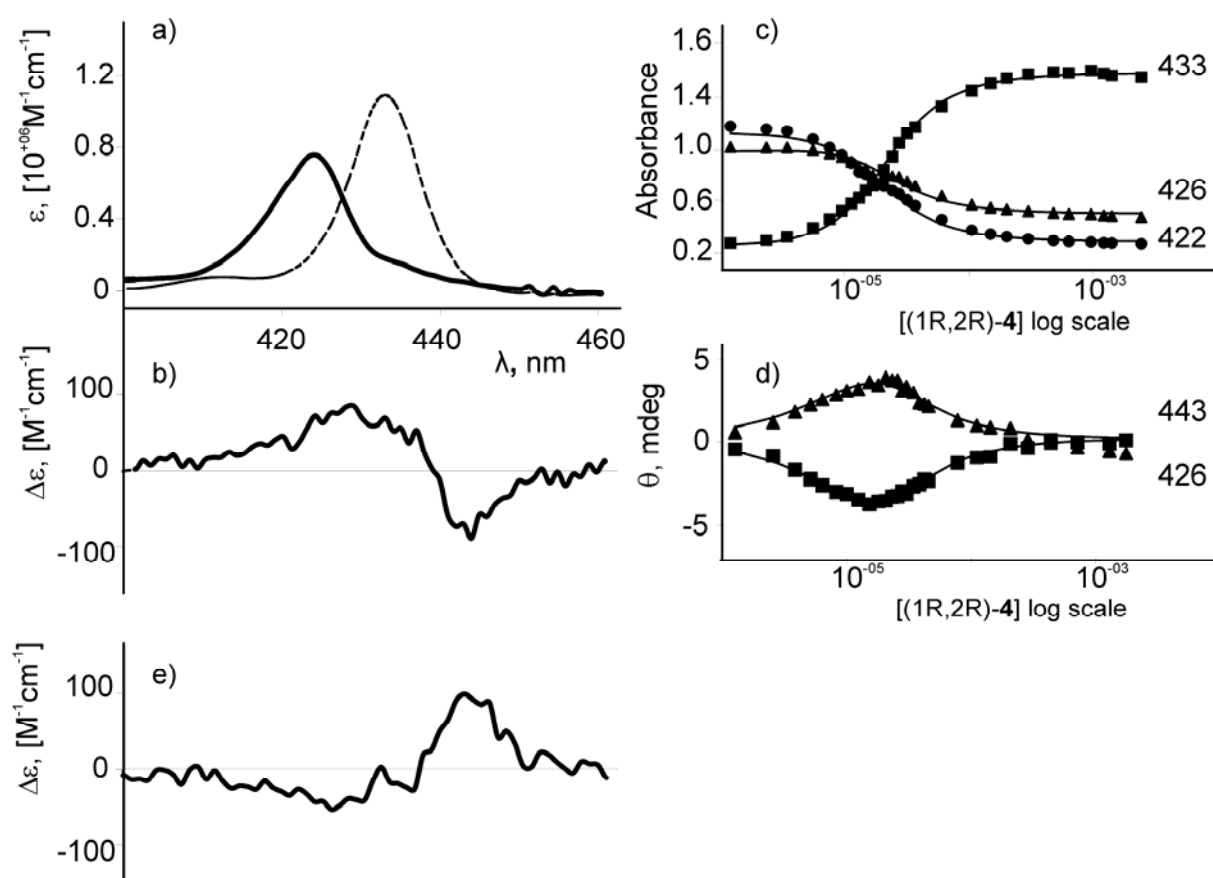
Figure 5. UV-visible and CD titrations of **1a** and the corresponding Zn-tetraarylporphyrin **5** with (*R*)-1-cyclohexylethylamine (*R*)-**6** in dichloromethane at 298K. The concentration of the host was maintained constant throughout the titration (1.0 x 10^{-6} M in a 1cm cuvette). a) **1a**. Number of equivalents of (*R*)-**6** added per bisporphyrin: 0, 10, 20, 30, 40, 50, 60, 80, 100, 135, 190, 365, 668, 2293, 5350, 15508. b) **5**. Number of equivalents of (*R*)-**6** added per porphyrin: 0, 3, 37, 77, 89, 101, 123, 143, 171, 196, 219, 239, 298, 415, 702, 1250.
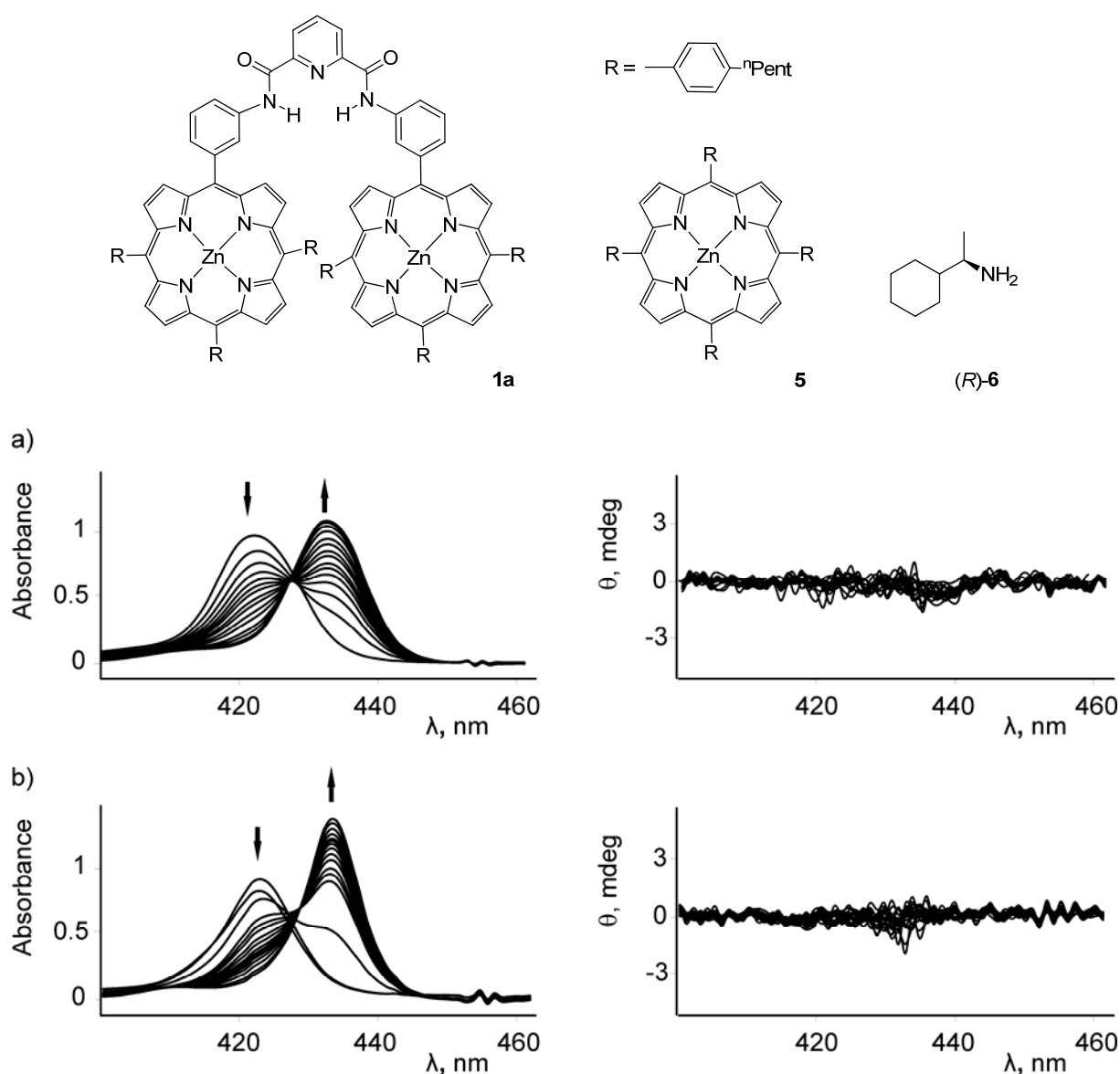
Figure 6. UV-visible titration (Q bands) of the Zn-tetrarylporphyrin **5** with cyclohexylamine **7** in dichloromethane at 298K. The concentration of the host was maintained constant throughout the titration (1.1 x 10^{-4} M in a 1mm cuvette). Number of equivalents of **7** added per porphyrin: 0, 0.2, 0.38, 0.56, 0.73, 0.9, 1.06, 1.21, 1.51, 1.78, 2.04, 2.28, 2.50. Analysis of the binding isotherm with a 1:1 binding model gave a microscopic association constant for the reference interaction in dichloromethane of $K_m = K_{11} = 5 \pm 2$ x 10^4 M^{-1}.
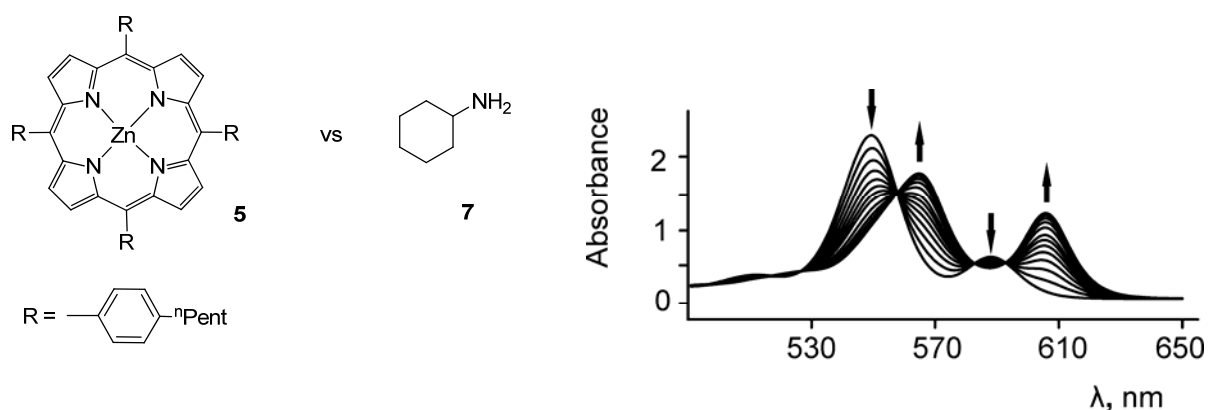

Figure 7. UV-visible titration (Soret region) of the Zn-tetraarylporphyrin **5** with DABCO **3** in dichloromethane at 298K. The concentration of the host was maintained constant throughout the titration (2.1 x 10^{-5} M in a 1mm cuvette). Number of equivalents of **3** added per porphyrin: 0, 0.14, 0.28, 0.41, 0.54, 1.05, 1.57, 2.11, 3.26, 3.70, 7.86. Analysis of the binding isotherm with a 1:1 binding model gave a microscopic assiciation constant for the reference interaction in dichloromethane of $K_m = K_{11}/2 = 8.5$ x 10^4 M^{-1}.
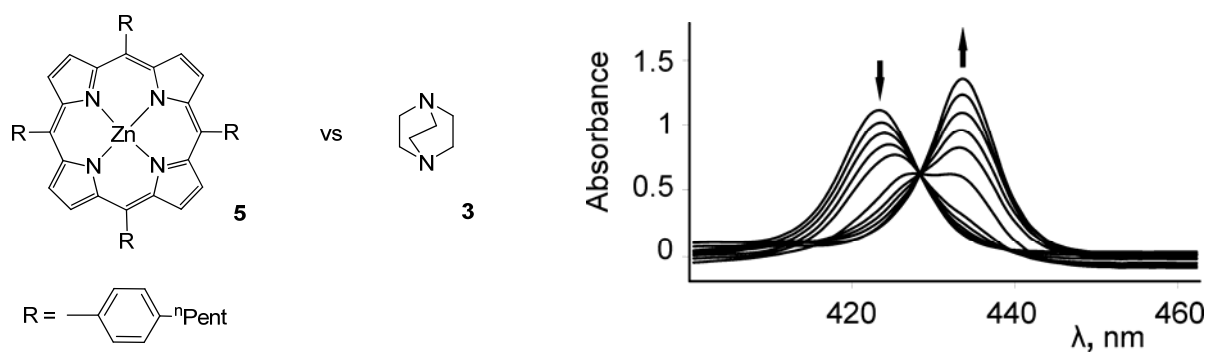
Figure 8. UV-visible titration (Soret region) of **1b** with DABCO **3** in dichloromethane at 298K. The concentration of the host was maintained constant throughout the titration (1.6 x 10^{-6} M in a 1cm cuvette). Number of equivalents of **3** added per bisporphyrin: 0, 0.3, 0.5, 0.8, 1.0, 1.3, 4.2, 9.9, 75, 140, 330, 638, 1743, 50370.

The titration curve for the destruction of the sandwich complex was analyzed by curve fitting as a simple two-state equilibrium, assuming that the concentration of free **1b** is negligible after one equivalent of DABCO has been added. If we assume that the sandwich complex is 1:1 DABCO@**1b**, by determinig $K_{11\approx12}$ we can directly obtain an estimate for K_{11} using $K_{11} = K_{21}/ K_{11\approx12} = 4\ K_{m}^{2}/K_{11\approx12} = 1.2 \times 10^{7}\,\mathrm{M}^{-1}$.