How Water in Aliphatic Solvents Directs the Interference of Chemical Reactivity in a Supramolecular System

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Supplementary Information

Experimental details

All starting materials were obtained from commercial suppliers and used without prior purification. **Zn-1** was synthesized according to a previously reported procedure.[1] MCH and $CHCl_3$ used in the spectroscopic measurements were of spectroscopic grade and purchased from VWR and TCI respectively. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance 3 HD NanoBay spectrometer (^1H NMR 400 MHz, ^{13}C NMR 100 MHz) and measured in $CDCl_3$. ^1H and ^{13}C shifts are reported relative to the residual $CHCl_3$ signals at 7.26 ppm and 77.23 ppm, respectively. MALDI-ToF mass spectrometry was performed with a Bruker autoflex Speed. CD spectroscopy was performed on a Jasco J-815 CD spectrometer equipped with an MPTC-490 multicell holder. UV-Vis results were obtained with the JASCO J-815 CD spectrometer or a Jasco V-650 UV-Vis spectrometer. All measurements with the porphyrins were performed in screw-capped cuvettes (Hellma Analytics). UV-Vis measurements on the Michael reactions without porphyrins were performed in Teflon capped cuvettes without N_2 flow in the UV-Vis spectrometer. SLS data were collected in homemade air-tight, Teflon sealed screw-capped tubes. Water concentrations were determined in triplicate using a Mettler-Toledo C30 Coulometric KF Titrator with CombiCoulomat Frit KF reagent. Average values of the triplo are reported. SLS experiments were performed on an ALV Compact Goniometer System (CGS-3) Multi-Detector (MD-4) that was equipped with an ALV-7004 Digital Multiple Tau Real Time correlator, using a wavelength of 532 nm. Scattering angles between 35 and 150° were probed in steps of 5°. All SLS measurements were performed at 20 °C. AFM measurements were performed with an Asylum Research MFP-3D system in non-contact tapping mode. The obtained micrographs were processed with Gwyddion 2.52.

Column chromatography was performed a Biotage Isolera Spektra One Flash Chromatography system using KP-Sil Silica Gel SNAP column cartridges. HPLC-MS was performed with a Thermo Finnigan LCQ Fleet ion trap mass spectrometer equipped with a Surveyor PDA detector and Surveyor autosampler. Before analysis, the samples were separated on a reverse phase C18 column with an acetonitrile/water gradient with 0.1 % formic acid with a flow speed of 0.2 mL/min using Shimadzu SCL-10A pumps.

Association constants were determined using the Matlab code provided by Thordarson.[2] A 1:1 binding model was assumed.

Preparation dry solvents: Dry MCH and $CHCl_3$ were prepared by storing ambient MCH and $CHCl_3$ over 4 Å molecular sieves in a glove box for a minimum of 18 hours.

Preparation wet solvents: Wet MCH was prepared by stirring ambient MCH over a layer of water overnight. The MCH used for the sample preparation was pipetted from the phase-separated mixture.

Sample preparation titrations: A known amount between 1 and 2 mg of **Zn-1** or **H_2-1** was dissolved in 100 µL $CHCl_3$ and 900 µL MCH was added after the pink solid was dissolved. **NPrMal**, **PhSH**, **MA** and **MePip** stocks were prepared in MCH by dissolving a known amount of material in a known amount of solvent. These stocks were used to prepare samples of 10 µM **Zn-1** or **H_2-1** and the desired concentration of the additives. The samples were kept in Teflon-sealed vials and equilibrated overnight before measurement. Cuvettes with a path length of 1 mm were used for the experiments with **Zn-1** and **H_2-1**.

All dry samples were prepared and transferred to the screw-capped cuvettes in a nitrogen filled glove box.

The titrations of **Zn-Me** were performed in MCH sequentially adding aliquots of a stock solution containing a known amount of the piperidine catalyst and 1 µM **Zn-Me** to a 2.5 mL 1 µM solution of **Zn-Me** to achieve

a desired host-guest ratio. Spectra were collected immediately. Cuvettes with a path length of 1 cm were used.

Sample preparation SLS experiments: Samples were prepared in a similar way as described for the titrations. In addition, all solvents and stock solutions, except the porphyrin stock solution, were filtered through a 100 nm PTFE syringe filter before preparing the samples. After preparation of the samples in the desired compositions, the samples were filtered through a Whatman Puradisc 13 PTFE syringe filter with a 5.0 µm pore size. The first 1.5 mL of the filtrate was discarded, after which the remaining filtrate was collected in sample tubes. Samples were equilibrated overnight and measured in home-made Teflon-sealed, screw-capped sample tubes. Dry samples were prepared and transferred to the sample tubes in a nitrogen filled glove box.

Synthesis Zn-Me

This procedure was adapted from a previous report.[3]

Zn-1 (49.5 mg, 16 µmole) and MeI (41 µL, 0.659 mmole) were dissolved in THF (10 mL) under an argon atmosphere and cooled to 0 °C. Then, sodium hydride (30.3 mg, 0.758 mmole) in mineral oil (60 %) was added slowly to the reaction mixture. The mixture was left to stir and heat up to room temperature for 24 hours, after which the reaction was quenched with water (3 mL). Subsequently, the product was extracted into $CHCl_3$ (50 mL), after which the organic layer was washed with water and brine. The combined organic layers were then dried over $MgSO_4$, filtered and the solvent was evaporated to yield a purple solid. After column chromatography (SNAP KP-Sil 10g, $CHCl_3$-EtOAc, 0-100%), the product was obtained as a purple solid (35 mg, 69%). All NMR and MALDI-ToF data was in accordance with the previously reported results.[1]

Synthesis $H_2$1

Zn-1 (51.9 mg, 17 µmole) was dissolved in 20 mL $CHCl_3$ in a separatory funnel. The organic layer was washed with 10 mL 37% hydrochloric acid, upon which the solution turned green. The layers were separated and the aqueous layer was extracted with $CHCl_3$ until no green color could be observed in the aqueous phase anymore. Then, the combined organic layers were washed with saturated aqueous Na_2CO_3 solution, upon which the solution turned red. The organic layers were separated, and the aqueous layer was extracted with $CHCl_3$ until no color could be observed in that layer anymore. Subsequently, the combined organic layers were dried over $MgSO_4$, filtered and evaporated to yield the product as a purple solid (48.9 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (s, 8H, β-pyrrolic protons), 8.33 (d, 8H, ArH), 8.28 (d, 8H, ArH), 8.06 (s, 4H, NH), 7.11 (s, 8H, ArH), 4.12 (m, 16H, OCH_2), 4.02 (m, 8H, OCH_2), 1.98-1.12 (m, 120H, CH_2/CH), 0.99 (d, 36H, CH_3), 0.90 (d, 72H, CH_3), -2.76, (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.74, 153.69, 145.75, 135.67, 135.05, 134,94, 133.75, 125.69, 119.51, 99.67, 72.09, 67.85, 39.64, 37.82, 37.64, 36.69, 30.13, 30.00, 28.24, 25.00, 22.96, 22.87, 22.85, 19.86. MALDI-ToF analysis: Mass calc. 2964.21, mass observed: 2965.18 ($M+H^+$).

Synthesis Michael adduct

N-propylmaleimide (400 mg, 2.9 mmole), thiophenol (317 mg, 2,9 mmole) and Et_3N (9 mg, 72 µmole) were dissolved in 20 mL MeOH. The reaction was stirred at room temperature for 4 hours, after which the solvent was evaporated. After purification by column chromatography (KPSil 25g), the product was obtained as a yellow oil with quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (2H, M, ArH), 7.35, (3H, M, ArH), 4.00 (dd, 1H, CH_2), 3.38 (t, 2H, NCH_2), 3.13 (dd, 1H, CH_2), 2.70 (dd, 1H, CH_2), 1.53-1.40 (m, 2H, CH_2), 0.81 (t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.68, 174.73, 134.72, 130.50, 129.55, 129.50, 44.14, 10.91, 36.25, 21.05, 11.37. LC-MS: Mass calc. 249.08, mass observed: 250.18 ($M+H^+$).

^{1}H and ^{13}C NMR of H_2-1

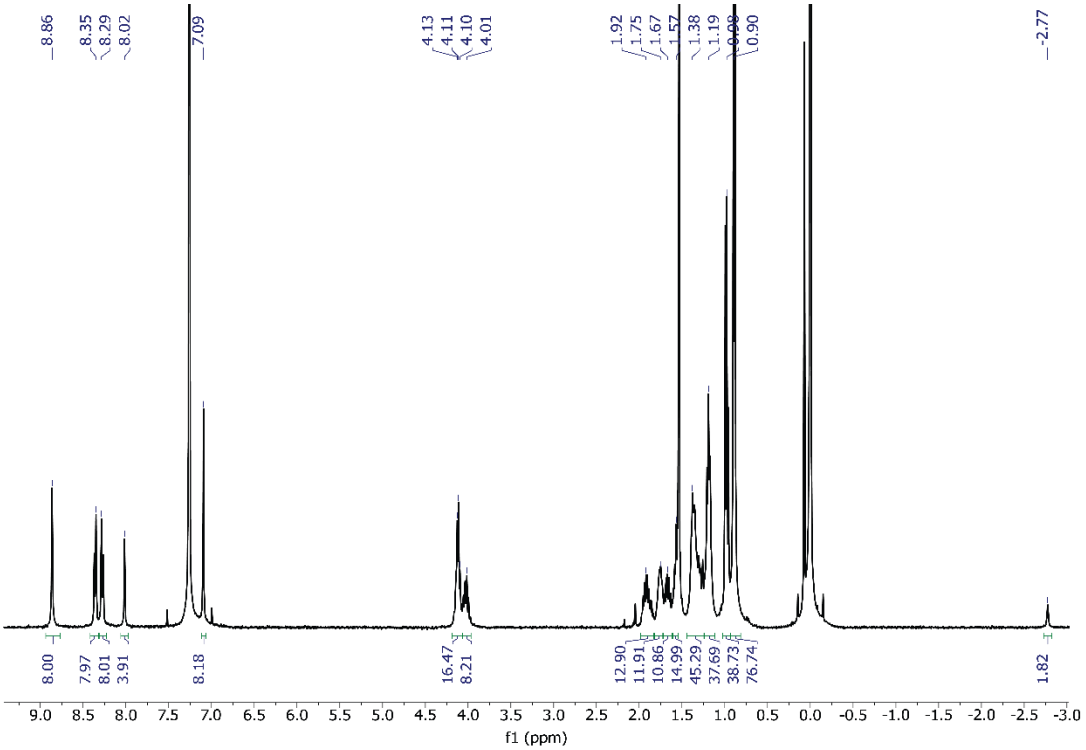

Figure S1 ^{1}H NMR spectrum of **H_2-1**.

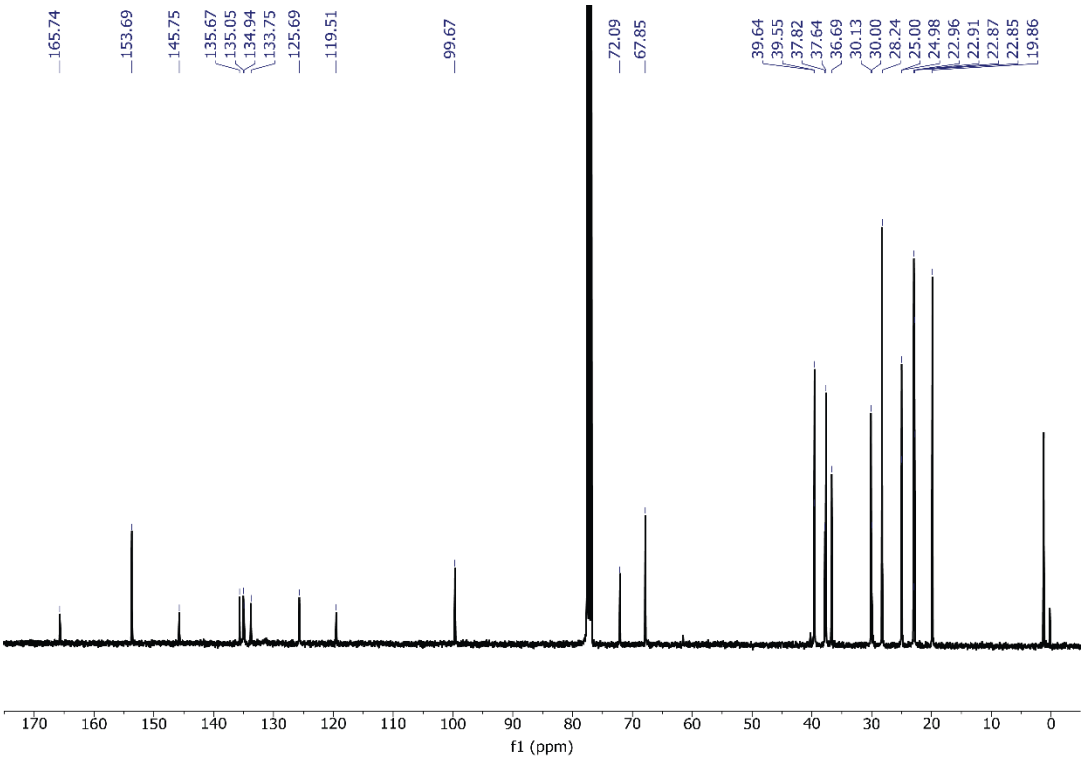

Figure S2 ^{13}C NMR spectrum of **H_2-1**.

^{1}H and ^{13}C NMR of MA

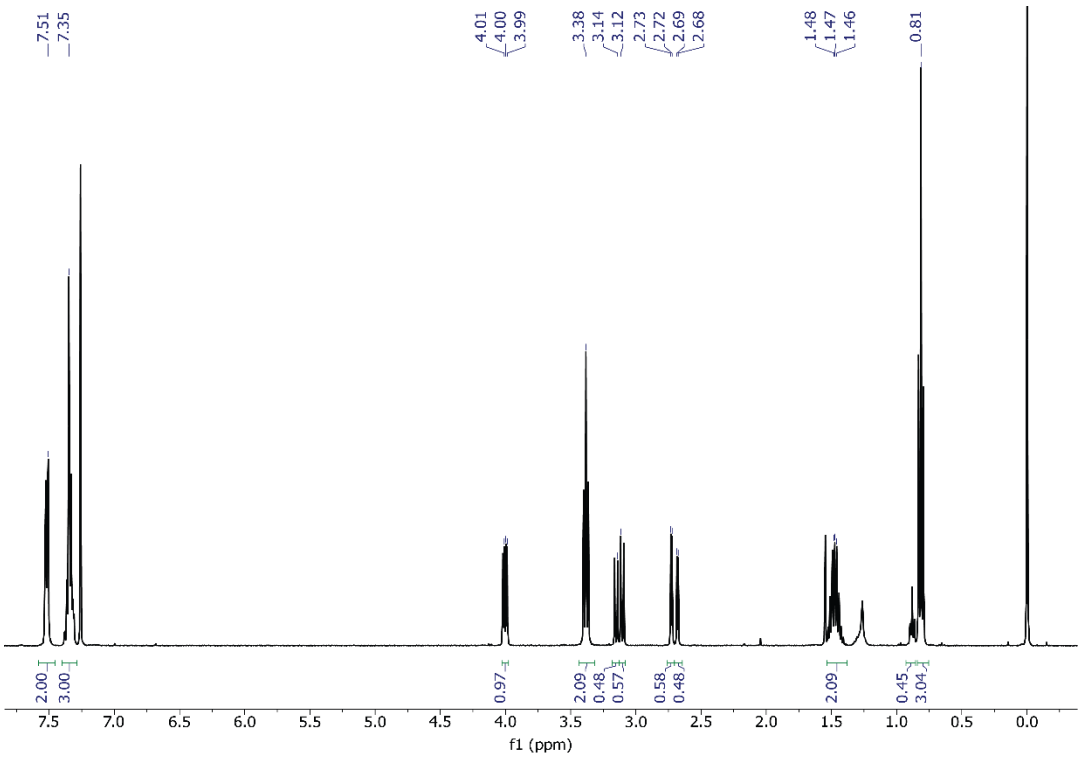

Figure S3 ^{1}H NMR spectrum of **MA**.

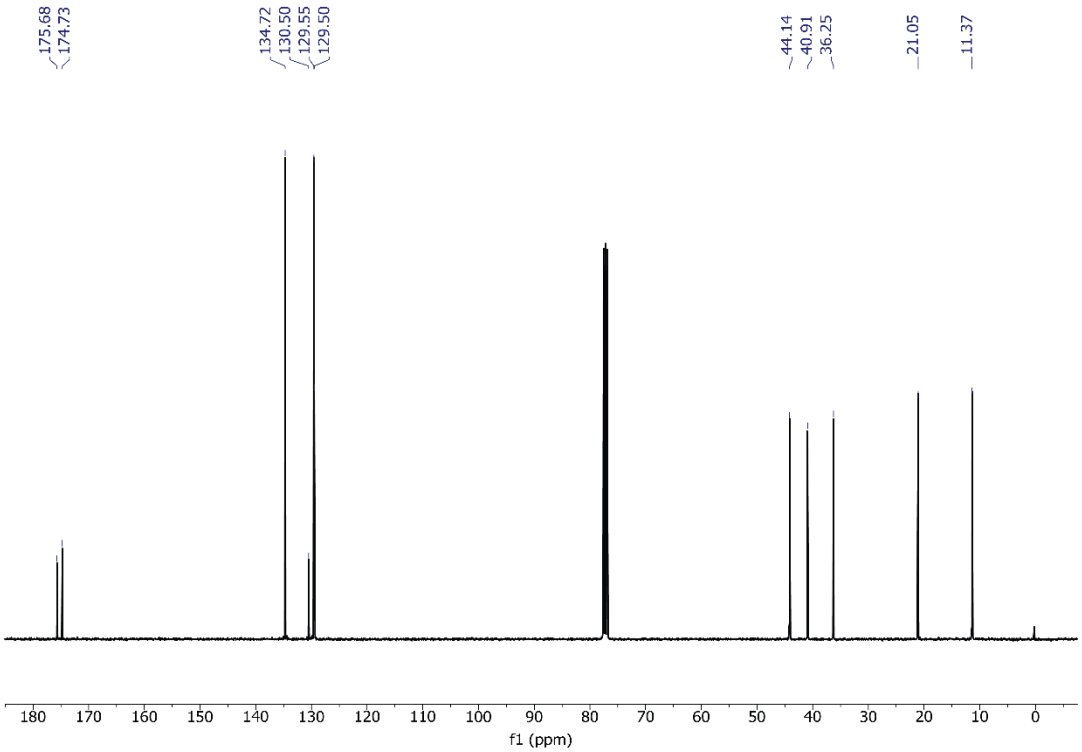

Figure S4 ^{13}C NMR spectrum of **MA**.

Spectra and titration curves of Zn-Me with various piperidine catalysts

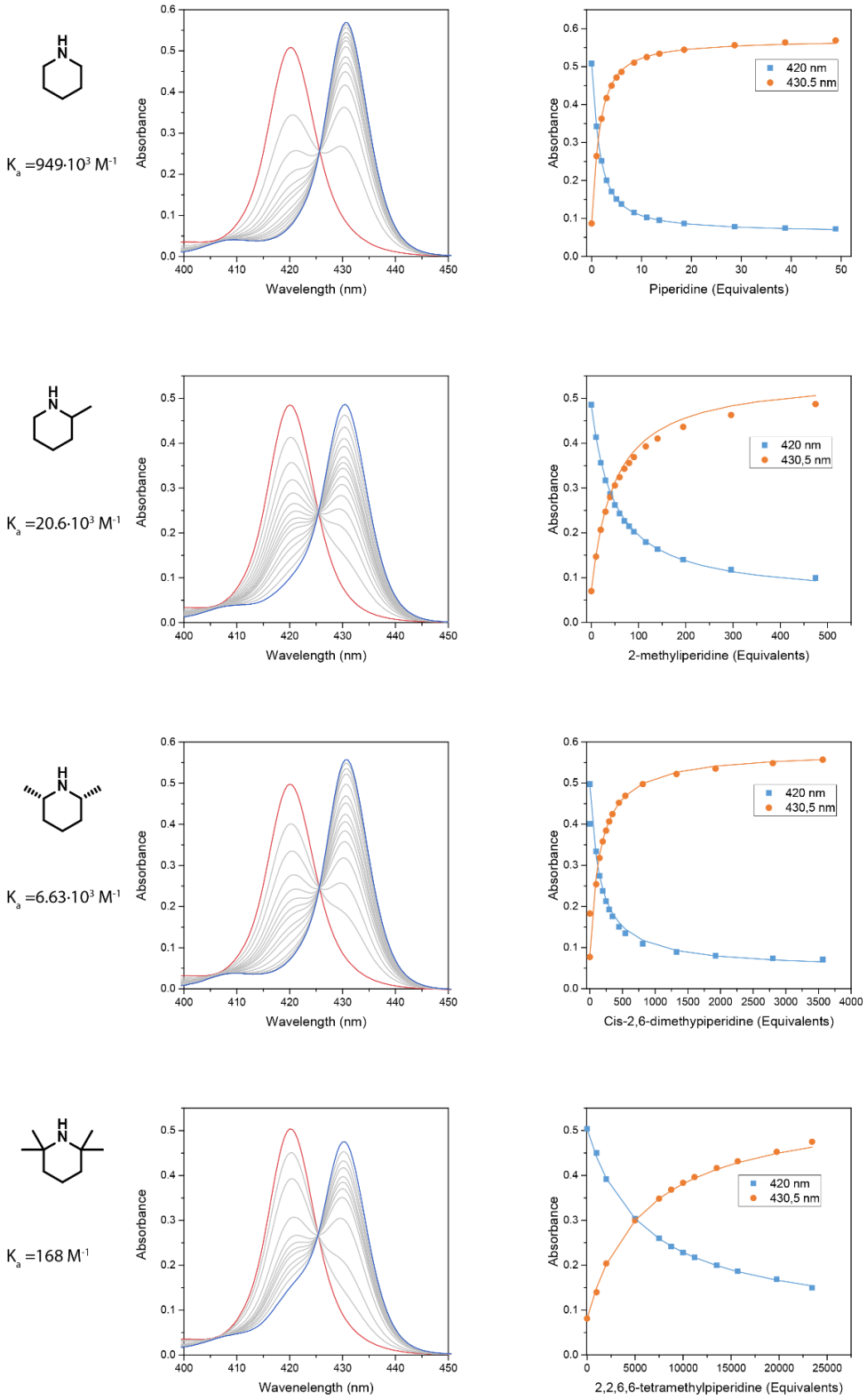

Figure S5 Spectra and titration curves of 1 µM **Zn-Me** measured in MCH with the different piperidine based catalysts. The blue spectra indicate the spectra without ligand and the red spectra indicate the spectra with maximum amine concentration.

Time dependent CD spectra of Zn-1 in the reaction mixture in dry, ambient and wet MCH

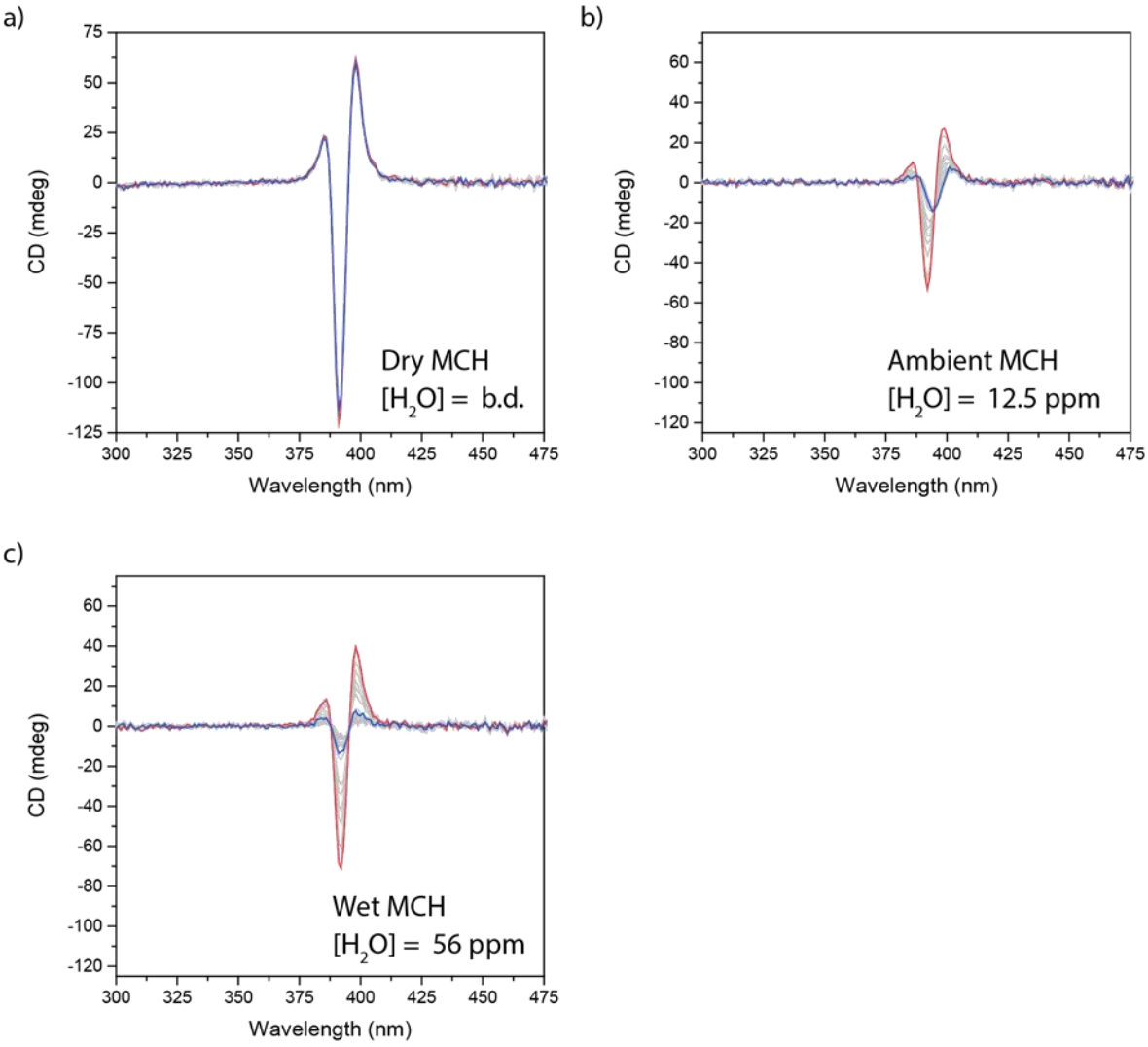

Figure S6 Selection of CD spectra for samples with 10 µM **Zn-1** and 0.5 mM **Me2Pip**, 4 mM **NPrMal** and 4 mM **PhSH** in dry (a), ambient (b) and wet (c) MCH, collected together with the UV-Vis spectra shown in Figure 2 in the main text and Figure S7 in the Supporting Information. In the dry sample, the concentration of water is below the detection limit of the Karl-Fisher titrator. The red spectra indicate the first collected spectrum and the blue spectrum indicate the last collected spectra, corresponding to the last time point in Figures 2b, 2d and S7b.

Time-dependent UV-Vis results of Zn-1 in the Michael reaction mixture in wet MCH

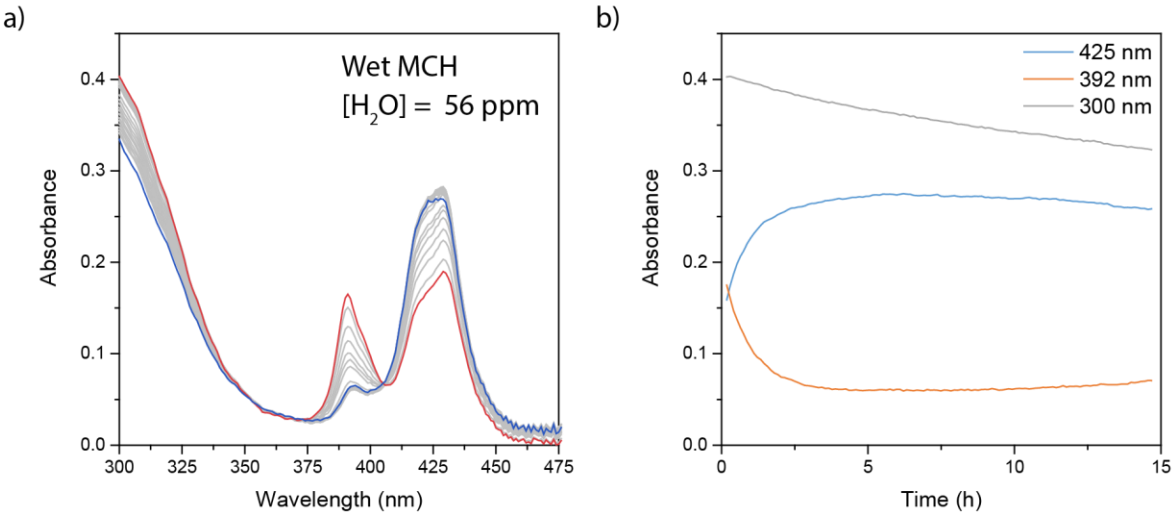

Figure S7 a) Selection of UV-Vis spectra of a solution of 10 µM **Zn-1** with 0.5 mM **MePip** and 4 mM **NPrMal** and **PhSH** in wet MCH between 0 (red spectrum) and 15 hours (blue spectrum) of the measurement. b) Time dependency of the absorbance at 300 nm, 392 nm, and 425 nm.

Time-dependent UV-Vis result of Zn-1 with PhSH and NPrMal in dry MCH

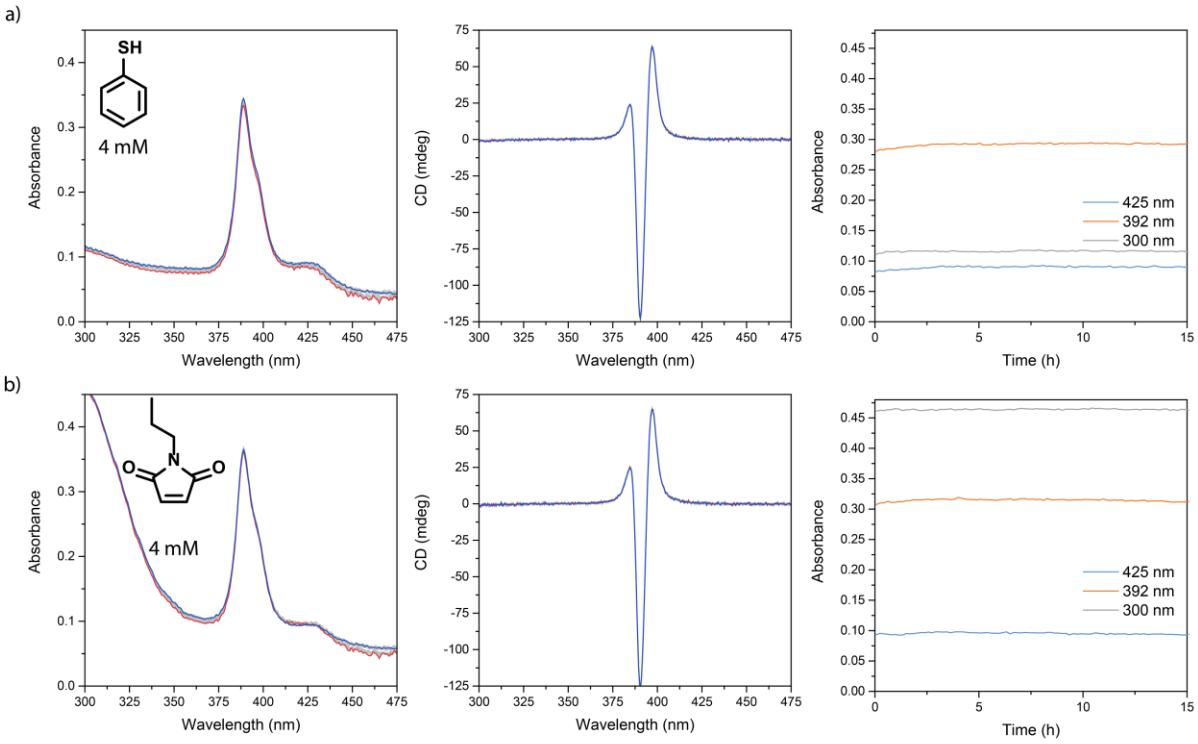

Figure S8 Selection of UV-Vis spectra (left panels) and simultaneously collected CD spectra (middle panels) of samples of 10 µM **Zn-1** with 4 mM **PhSH** (a) and 4 mM **NPrMal** (b) in dry MCH ([H_2O]=9.0 ppm). The spectra were collected between 0 hours (red spectrum) and 15 hours (blue spectrum) after sample preparation. The right panels show the time dependency of the absorbance at 300 nm, 392 nm and 425 nm, which is extracted from the spectra collected at various time points.

UV-Vis and CD spectra titrations of Zn-1 with combinations of PhSH, NPrMal and MePip in dry MCH

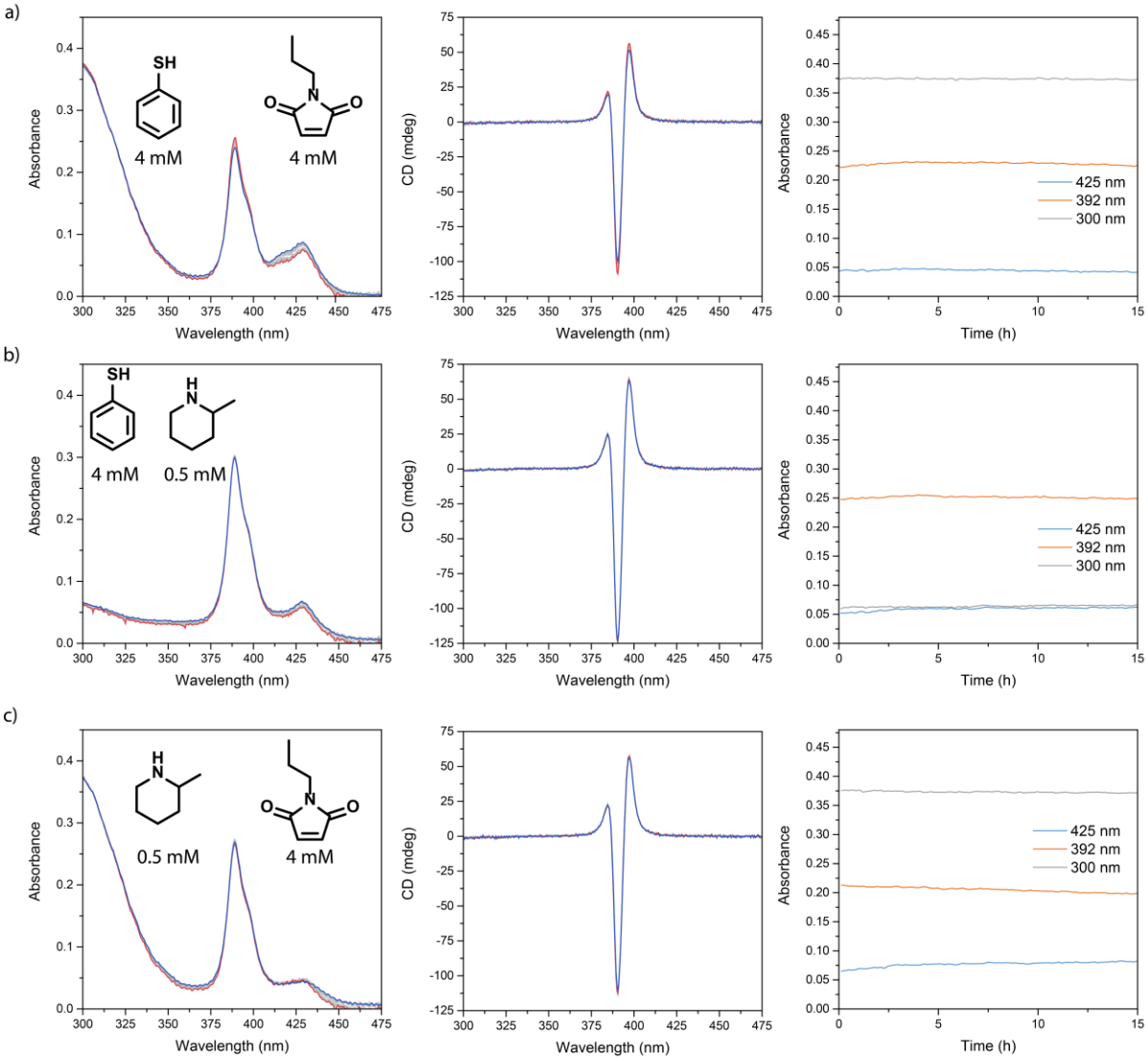

Figure S9 Selection of UV-Vis spectra (left panels) and simultaneously collected CD spectra (middle panels) of samples of 10 µM **Zn-1** with 4 mM **PhSH** and 4 mM **NPrMal** (a), 4 mM **PhSH** with 0.5 mM **MePip** (b) and 4 mM **NPrMal** with 0.5 mM **MePip** in ambient MCH ([H_2O]=9.0 ppm). The spectra were collected between 0 hours (red spectrum) and 15 hours (blue spectrum) after sample preparation. The right panels show the time dependency of the absorbance at 300 nm, 392 nm and 425 nm, which is extracted from the spectra collected at various time points.

Time-dependent UV-Vis & CD result of Zn-1 with PhSH and NPrMal in ambient MCH

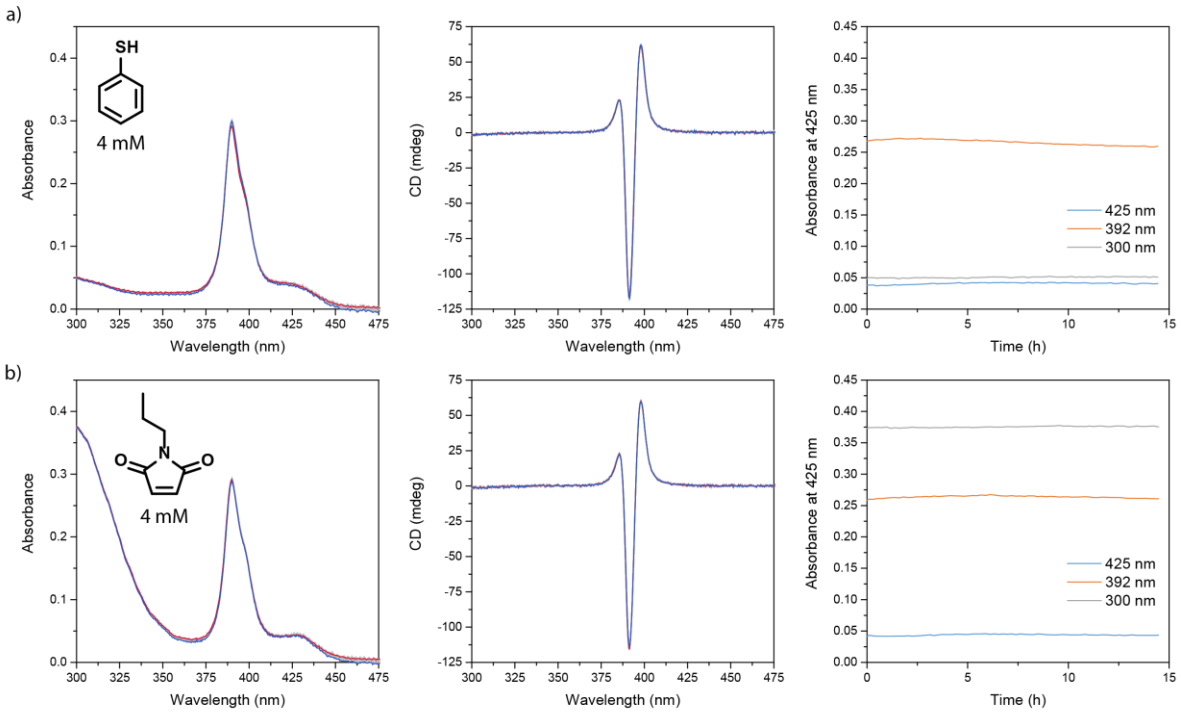

Figure S10 Selection of UV-Vis spectra (left panels) and simultaneously collected CD spectra (middle panels) of samples of 10 µM **Zn-1** with 4 mM **PhSH** (a) and 4 mM **NPrMal** (b) in ambient MCH ([H_2O]=12.5 ppm). The spectra were collected between 0 hours (red spectrum) and 15 hours (blue spectrum) after sample preparation. The right panels show the time dependency of the absorbance at 300 nm, 392 nm and 425 nm, which is extracted from the spectra collected at various time points.

UV-Vis and CD spectra titrations Zn-1 with combinations of PhSH, NPrMal and MePip in ambient MCH

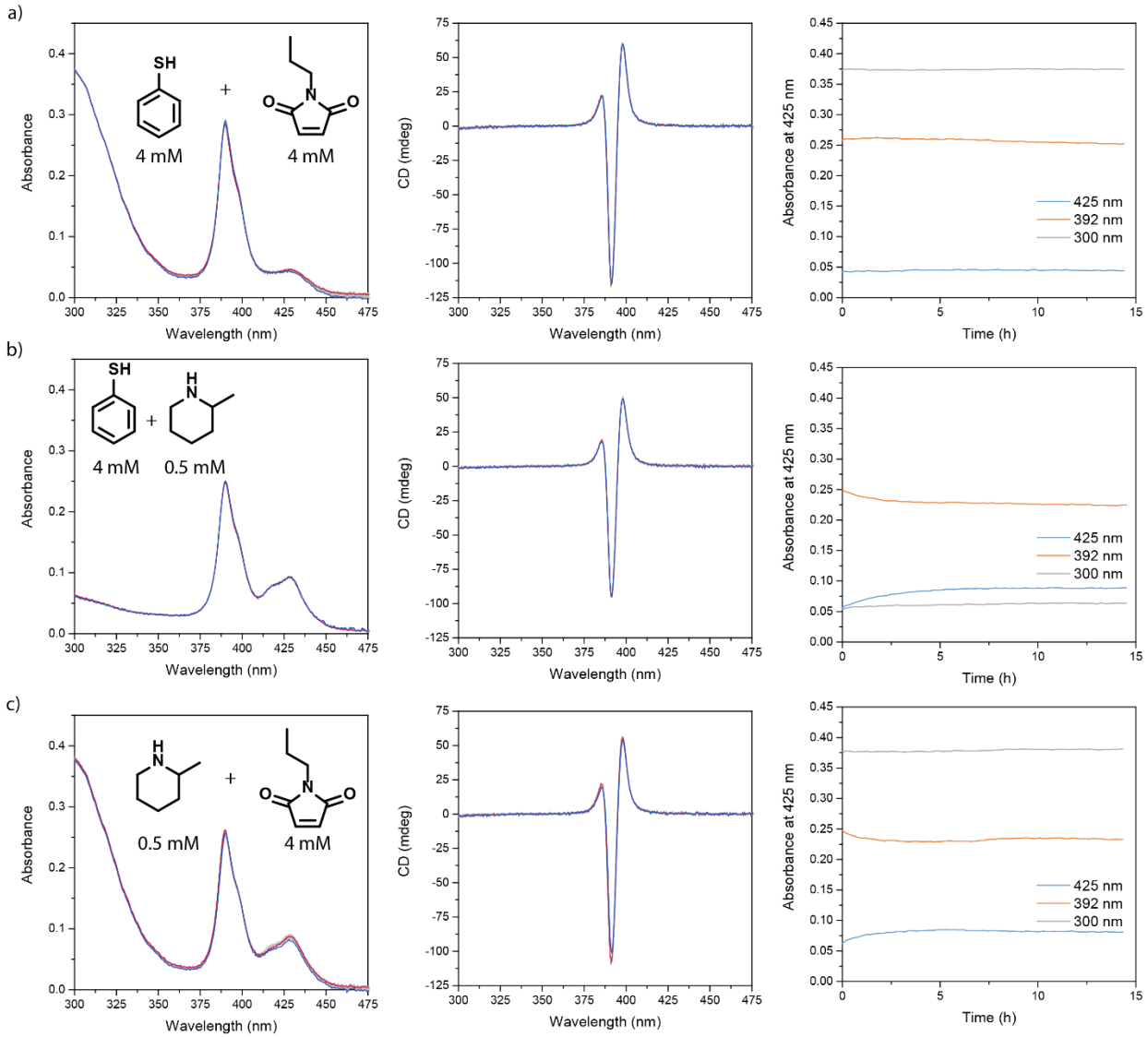

Figure S11 Selection of UV-Vis spectra (left panels) and simultaneously collected CD spectra (middle panels) of samples of 10 µM **Zn-1** with 4 mM **PhSH** and 4 mM **NPrMal** (a), 4 mM **PhSH** with 0.5 mM **MePip** (b) and 4 mM **NPrMal** with 0.5 mM **MePip** in ambient MCH ([H_2O]=12.5 ppm). The spectra were collected between 0 hours (red spectrum) and 15 hours (blue spectrum) after sample preparation. The right panels show the time dependency of the absorbance at 300 nm, 392 nm and 425 nm, which is extracted from the spectra collected at various time points.

AFM micrographs of Zn-1 in dry and MCH*

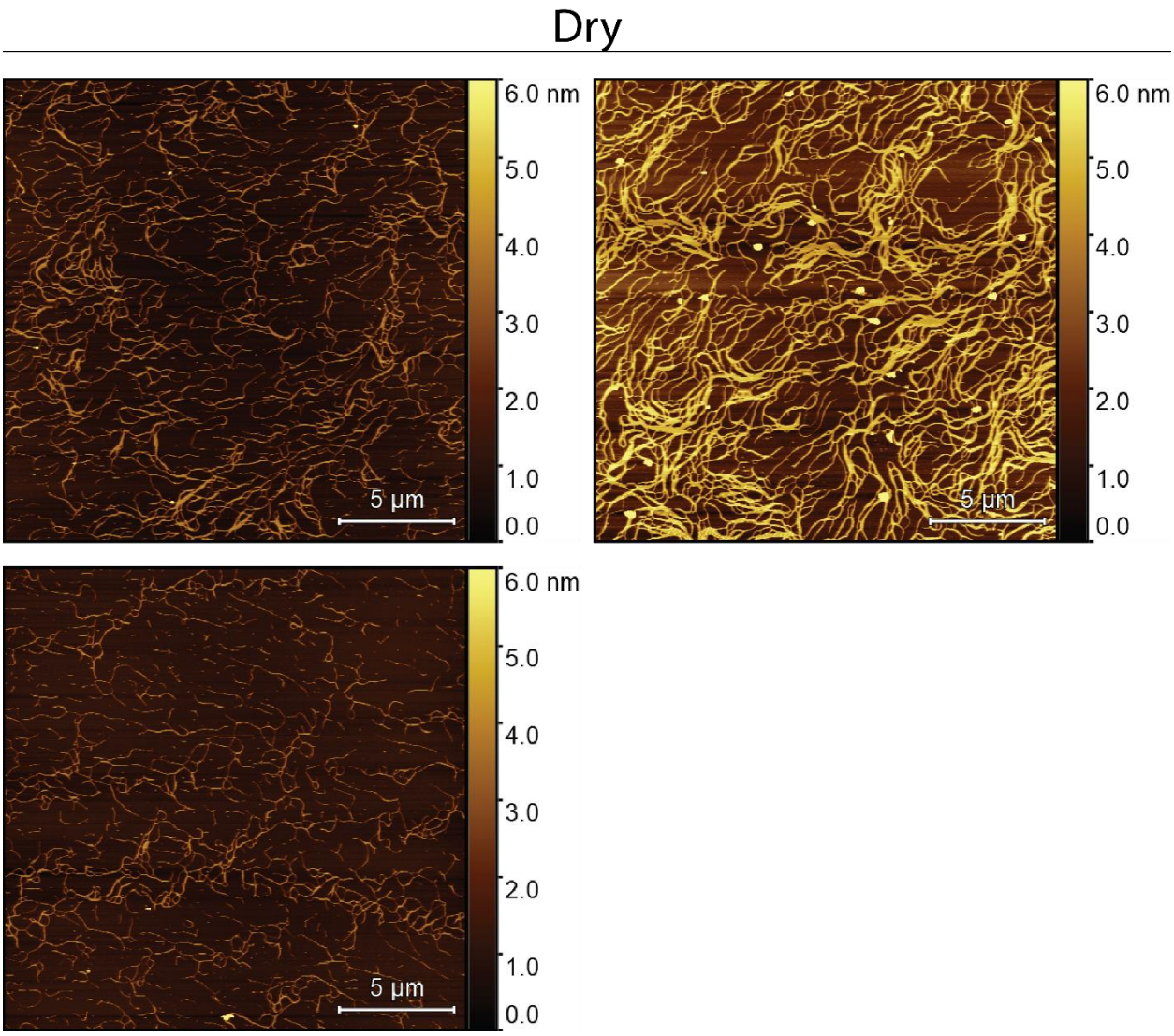

Figure S12 AFM micrographs of samples drop casted from solutions of 10 µM **Zn-1** in dry MCH*. [H_2O] = 20.0 ppm.

Ambient

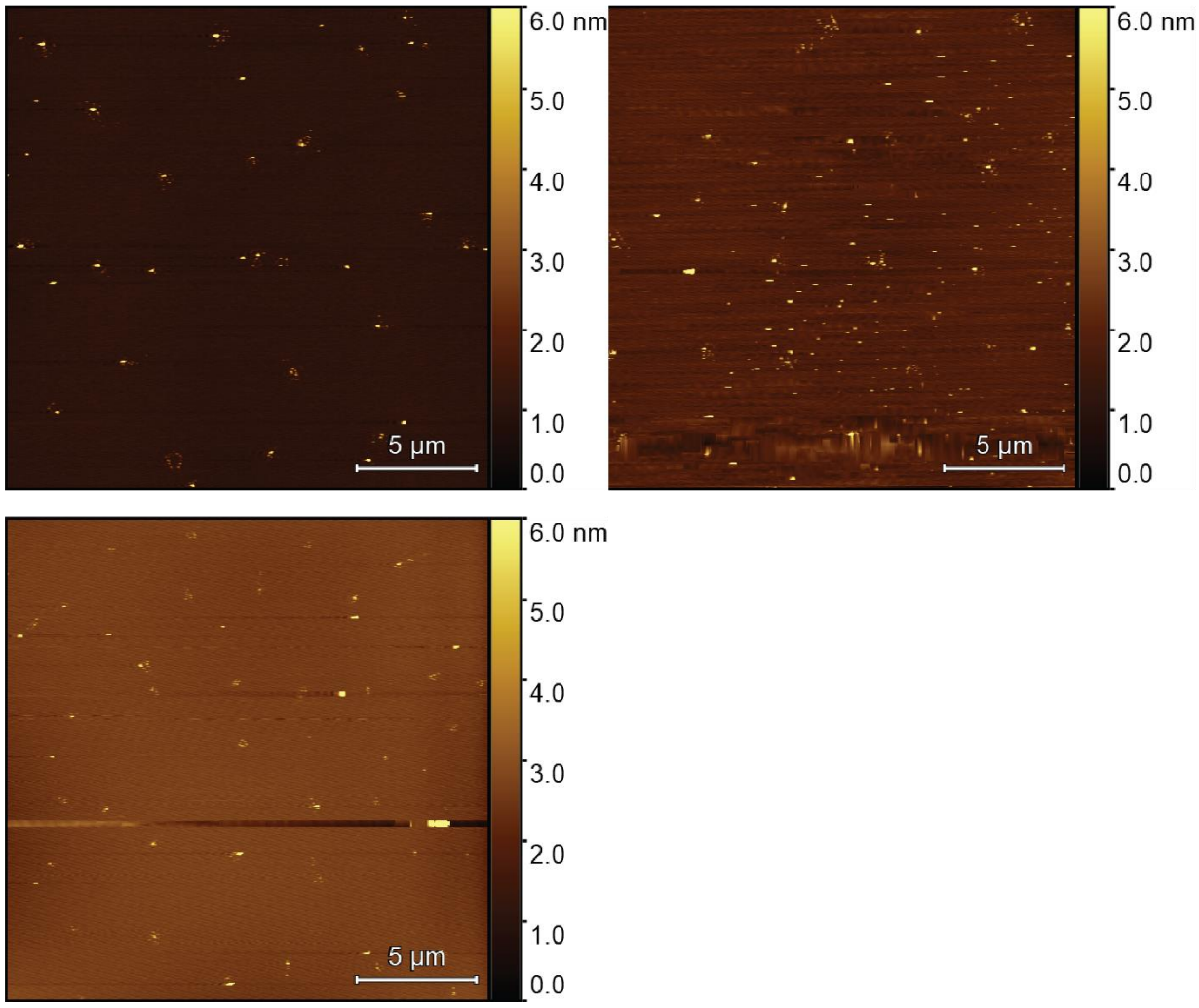

Figure S13 AFM micrographs of samples drop casted from solutions of 10 µM **Zn-1** in ambient MCH*. [H_2O] = 48.9 ppm.

SLS count rate at various concentrations of Zn-1

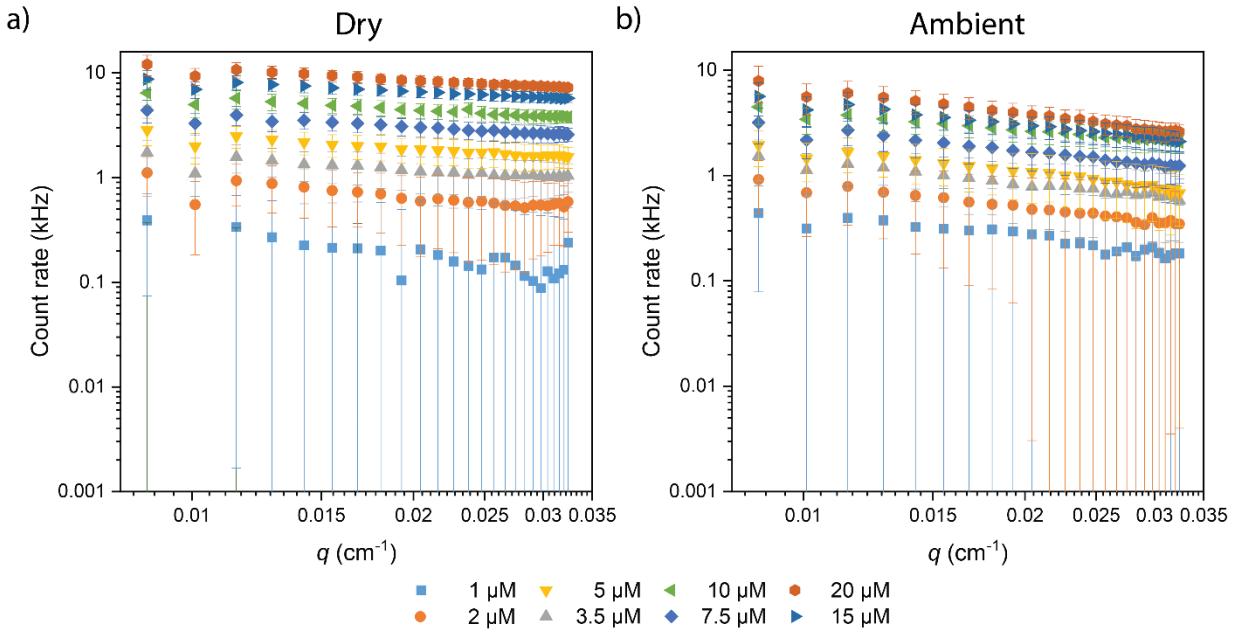

Figure S14 Light scattering count rates at various concentrations of 10 µM **Zn-1** in dry (a) and ambient (b) MCH*. In the dry samples, [H_2O] = 5.1 ppm and in the ambient samples, [H_2O] = 52.1 ppm.

Comparison SLS count rates at various concentrations and humidities

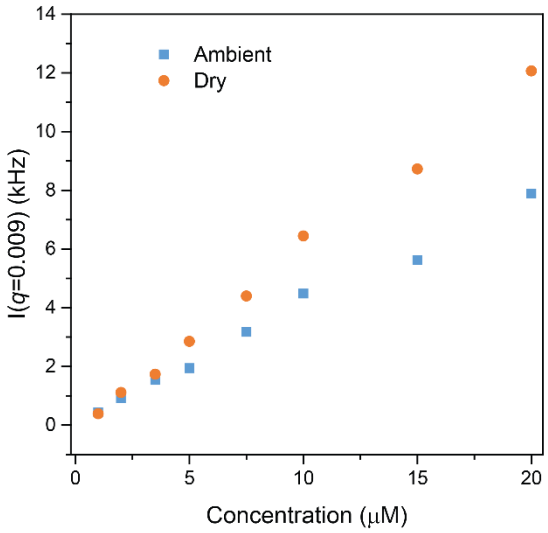

Figure S15 Light scattering count rates at q=0.009 cm^{-1} at various concentrations of 10 µM **Zn-1** in dry (circles) and ambient (squares) MCH*. In the dry samples, [H_2O] = 5.1 ppm and in the ambient samples, [H_2O] = 52.1 ppm. The linear increase indicates the polymer chains are in the dilute rather than semi-dilute regime.

UV-Vis spectra of Zn-1 after filtering through various filters

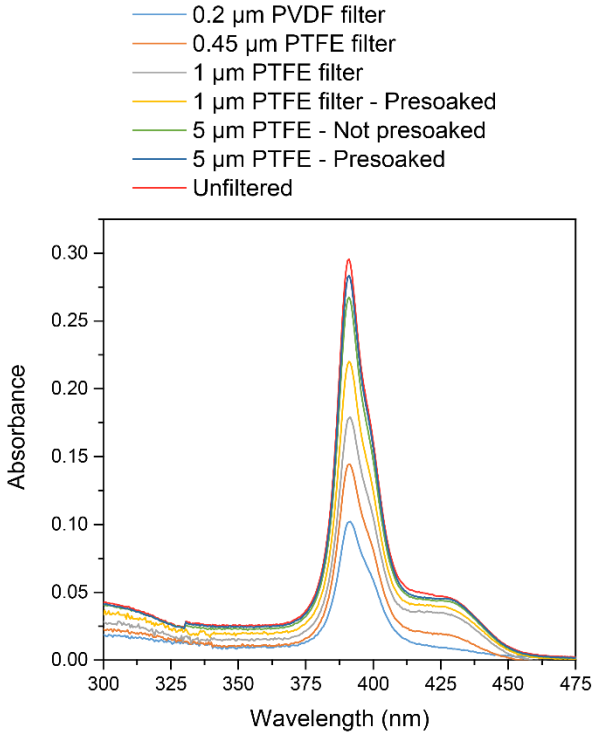

Figure S16 UV-Vis spectra of 10 µM solutions of **Zn-1** in ambient MCH* after filtering through various filters. The 0.2 µm and 0.45 µm filter were not washed and presoaked with the **Zn-1** solution before collection of the filtrate. For the 1 µm and 5 µm filters, both cases are shown. As can be seen, presoaking the filters with 1.5 mL **Zn-1** solution decreases adsorption to the filters and the presoaked 5 µm filters pass almost all **Zn-1** material.

Titration results of the titration of Zn-1 with MA in the absence and presence of MePip in ambient and dry MCH*

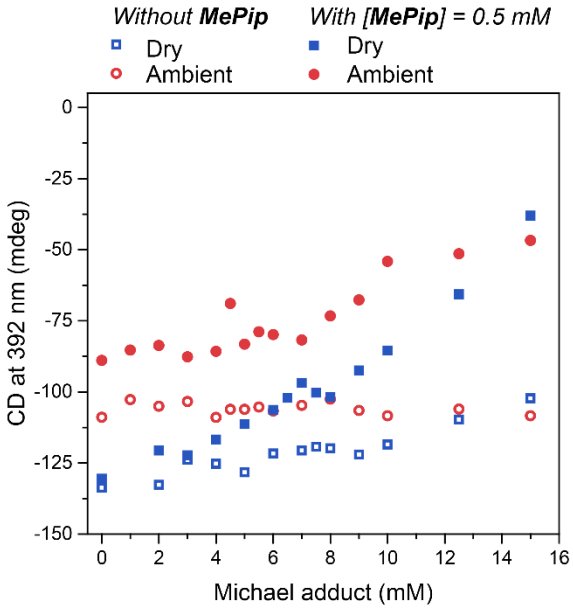

Figure S17 Titration results of the titration of 10 µM **Zn-1** with **MA** in dry ([H_2O] below detection limit of the Karl-Fisher titatrator) and ambient ([H_2O] = 13.8 ppm) MCH* in the presence and absence of 0.5 mM **MePip**.

Titration results of the titration of Zn-1 with NPrMal in the presence of PhSH in ambient and dry MCH*

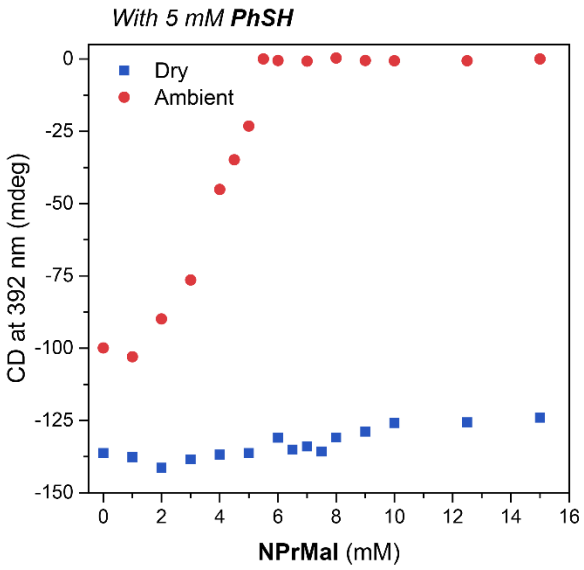

Figure S18 Titration results of the titration of 10 µM **Zn-1** with **NPrMal** in dry ([H_2O] below detection limit of the Karl-Fisher titatrator) and ambient ([H_2O] = 13.8 ppm) MCH* in the presence of 5 mM **PhSH**.

UV-Vis and CD spectra of the titrations Zn-1 with PhSH, NPrMal and MA in ambient MCH*

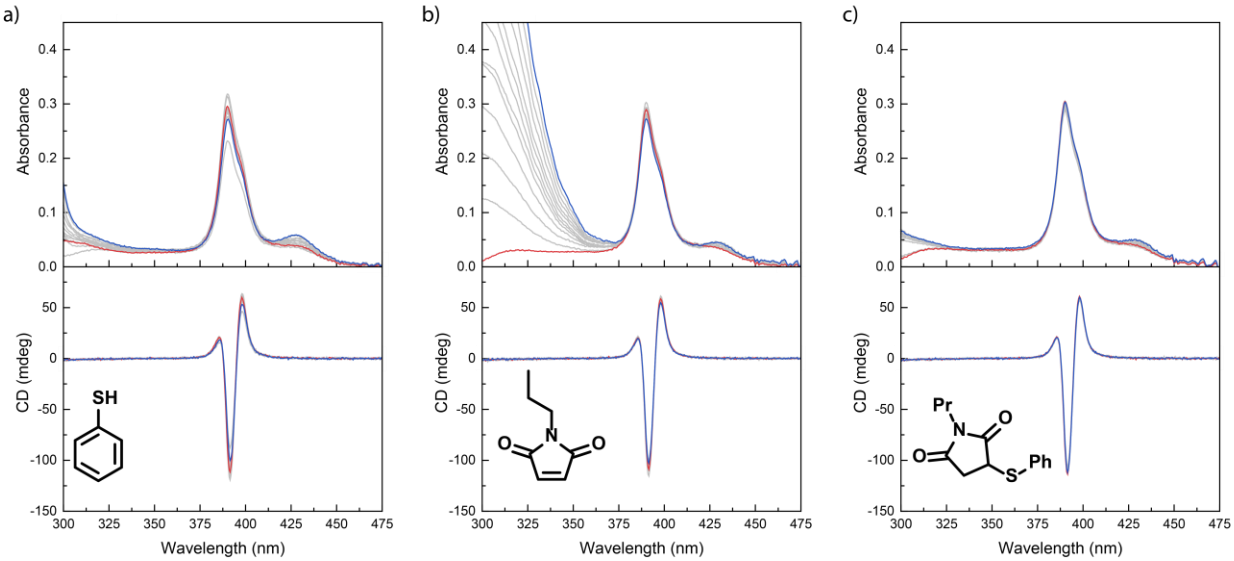

Figure S19 UV-Vis (top panels) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **PhSH**, **NPrMal** and **MA** in ambient MCH* and in the absence of **MePip**. From the spectra, the results given in Figure 4 in the main text and Figure S17 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra of the titrations Zn-1 with the PhSH, NPrMal and MA in the presence of 0.5 mM MePip in ambient MCH*

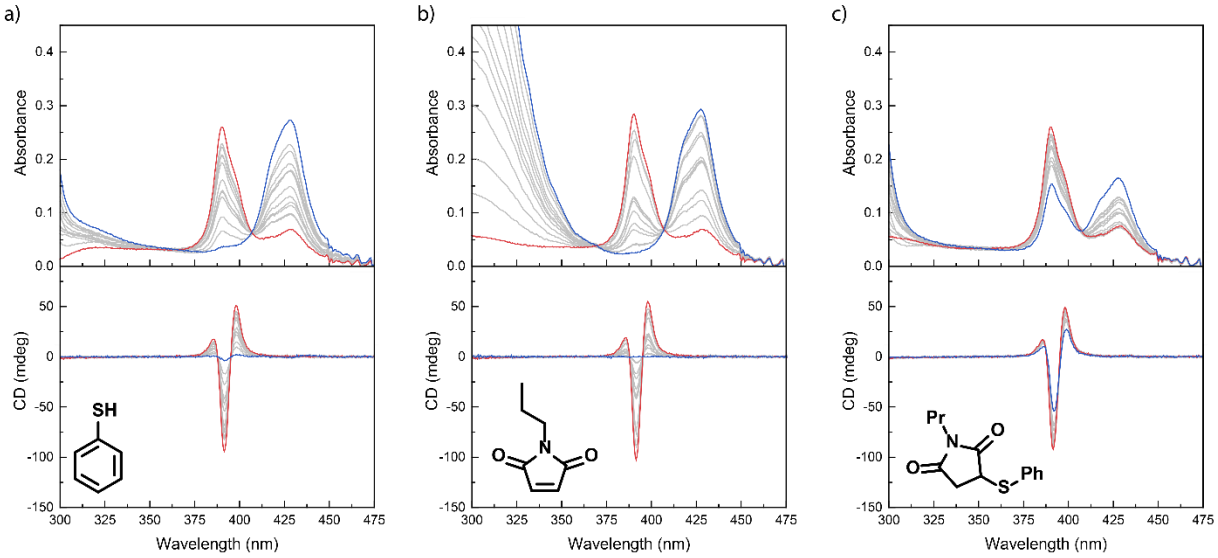

Figure S20 UV-Vis (top panels) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **PhSH**, **NPrMal** and **MA** in ambient MCH* and in the presence of 0.5 mM **MePip**. From the spectra, the results given in Figure 4 in the main text and Figure S17 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra of the titrations Zn-1 with NPrMal in the presence of 5 mM PhSH in ambient MCH*

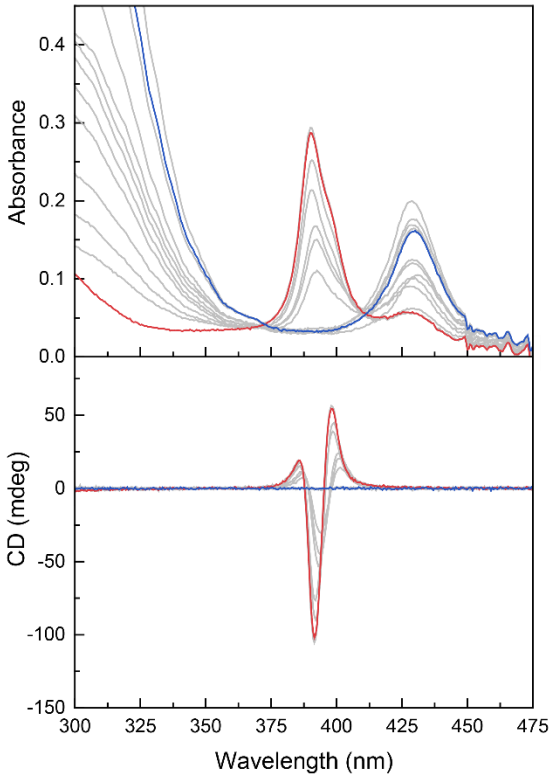

Figure S21 UV-Vis (top panel) and CD (bottom panels) spectra corresponding to the titrations of **Zn-1** with **NPrMal** in ambient MCH* and in the presence of 5 mM **PhSH**. From the spectra, the results given in Figure S18 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra of the titrations Zn-1 with PhSH, NPrMal and MA in dry MCH*

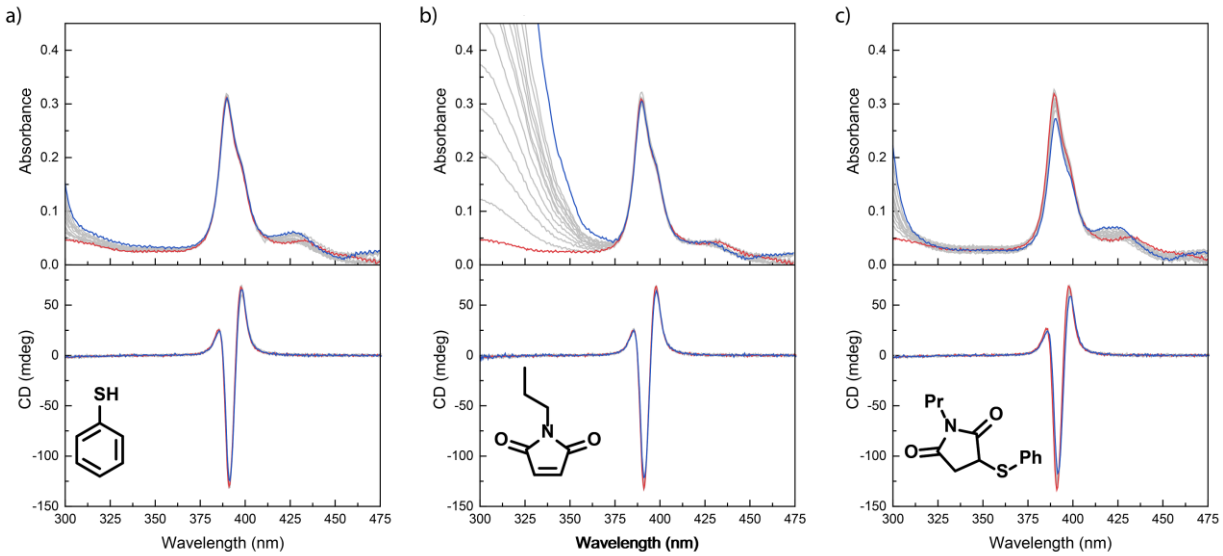

Figure S22 UV-Vis (top panels) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **PhSH**, **NPrMal** and **MA** in dry MCH* and in the absence of **MePip**. From the spectra, the results given in Figure 4 in the main text and Figure S17 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra of the titrations Zn-1 with the PhSH, NPrMal and MA in the presence of 0.5 mM MePip in dry MCH*

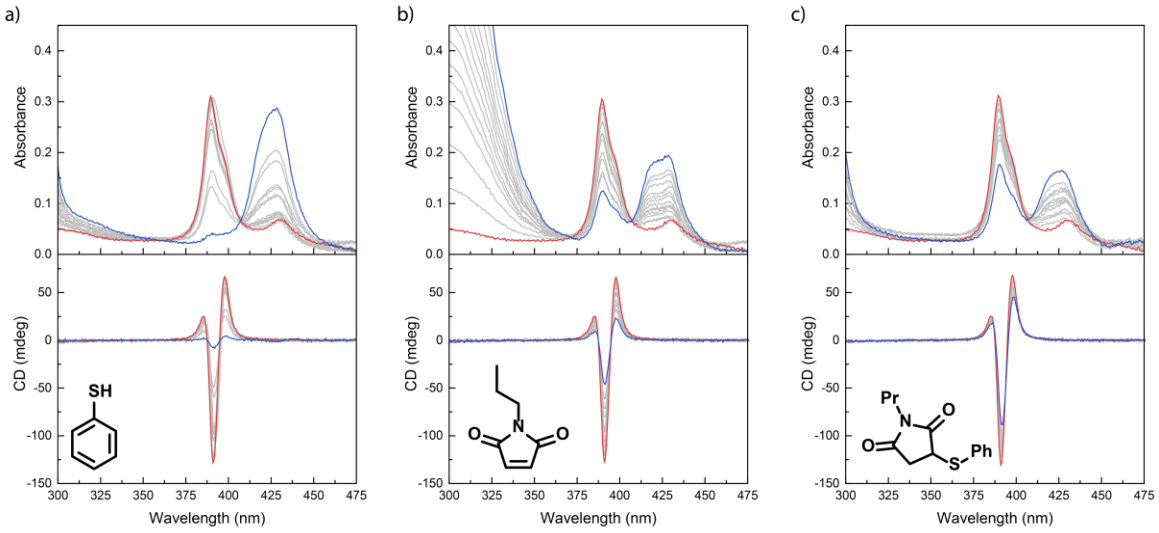

Figure S23 UV-Vis (top panels) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **PhSH**, **NPrMal** and **MA** in dry MCH* and in the presence of 0.5 mM **MePip**. From the spectra, the results given in Figure 4 in the main text and Figure S17 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra of the titrations Zn-1 with NPrMal in the presence of 5 mM PhSH in dry MCH*

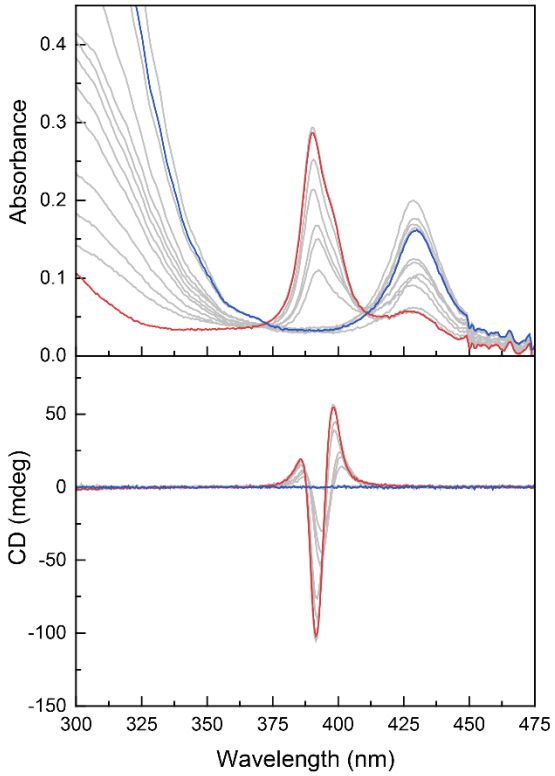

Figure S24 UV-Vis (top panel) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **NPrMal** in dry MCH* and in the presence of 5 mM **PhSH**. From the spectra, the results given in Figure S18 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis and CD spectra titrations Zn-1 and Me4Pip and pyridine with NPrMal, PhSH and MA

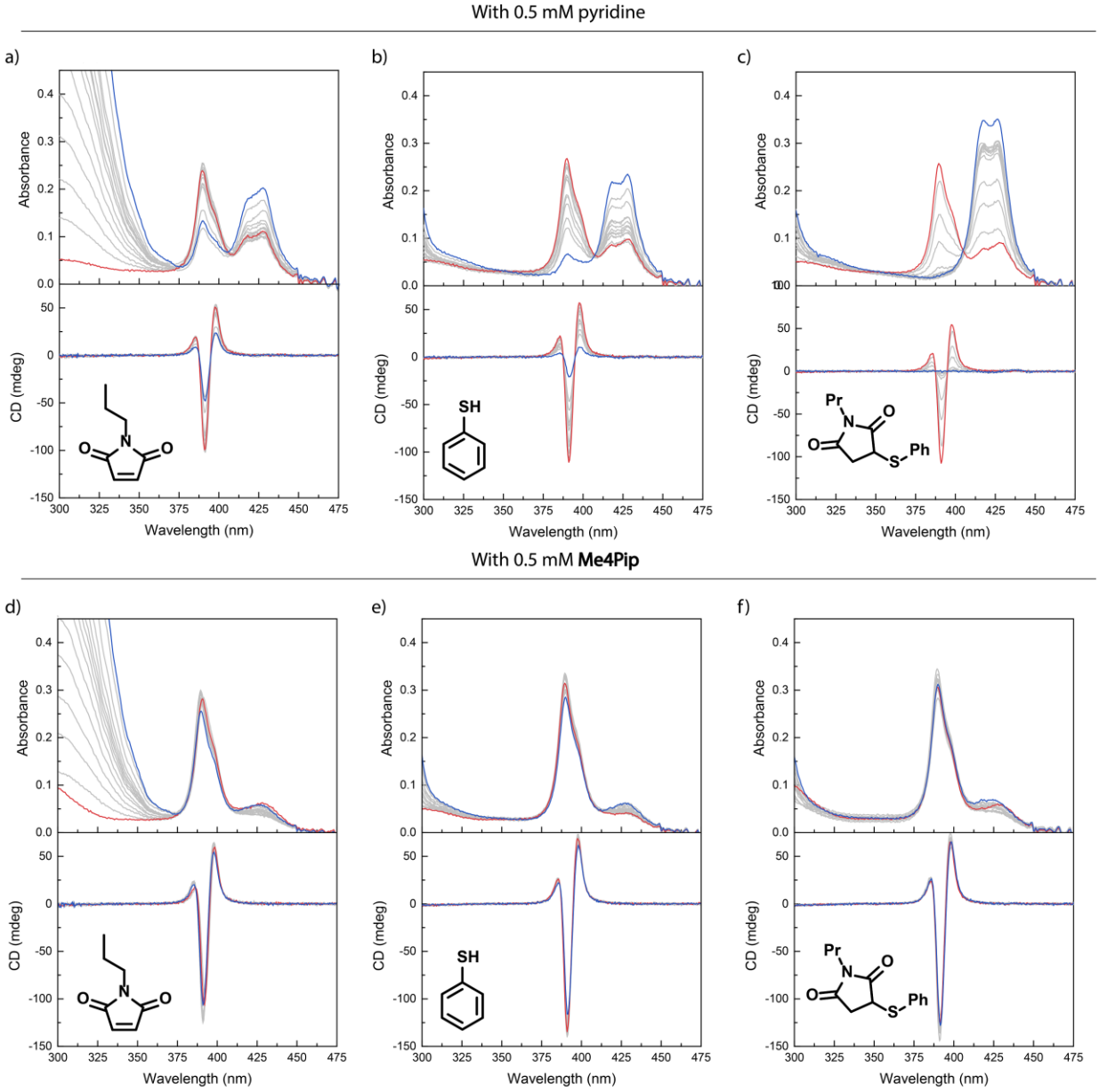

Figure S25 UV-Vis (top panels) and CD (bottom panels) spectra corresponding to the titrations of 10 µM **Zn-1** with **NPrMal** (a, d), **PhSH** (b, e) and **MA** (c, f) in dry MCH* and in the presence of 0.5 mM pyridine (top row, a-c) and **Me4Pip** (bottom row, d-f) From the spectra, the results given in Figure 6 in the main text and Figure S26 in the Supporting Information are obtained. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

Results titration Zn-1 with PhSH and MA

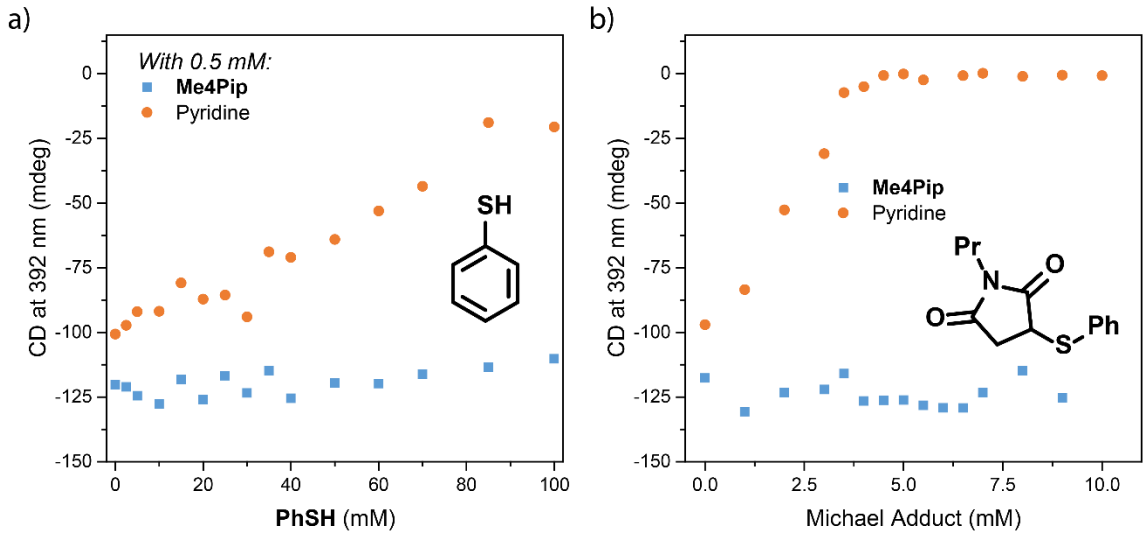

Figure S26 Titrations of 10 µM solutions of **Zn-1** with **PhSH** (a) and **MA** (b) in dry MCH* ([H_2O] below detection limit of Karl-Fisher titrator) in the presence of 0.5 mM **MePip**.

Results titration H_2-1 with MA and PhSH

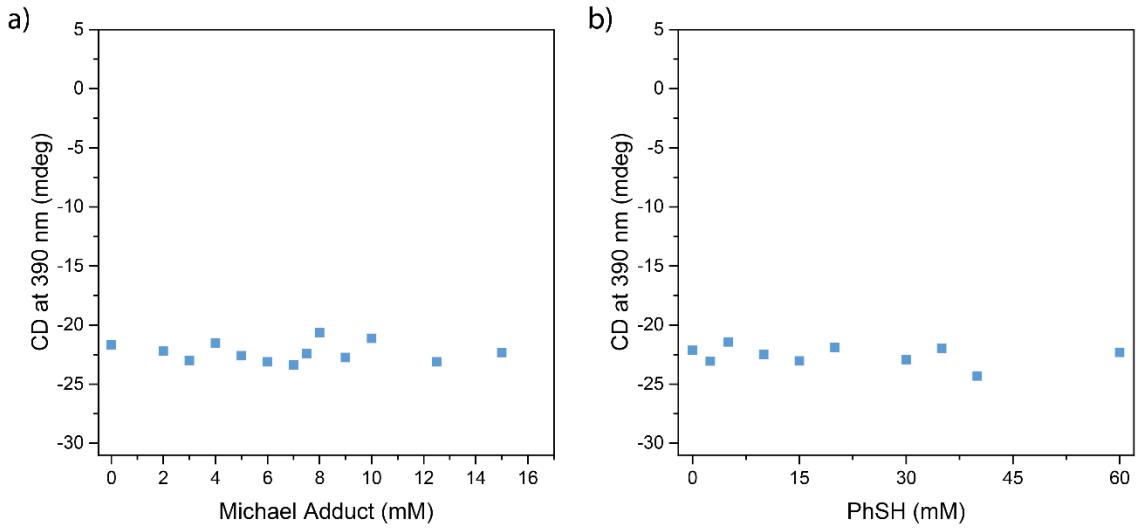

Figure S27 Titrations of 10 µM solutions of **H_2-1** with **PhSH** (a) and **MA** (b) in dry MCH* ([H_2O] below detection limit of Karl-Fisher titrator) in the presence of 0.5 mM **MePip**.

UV-Vis and CD spectra titrations H_2-1 with NPrMal, PhSH and MA

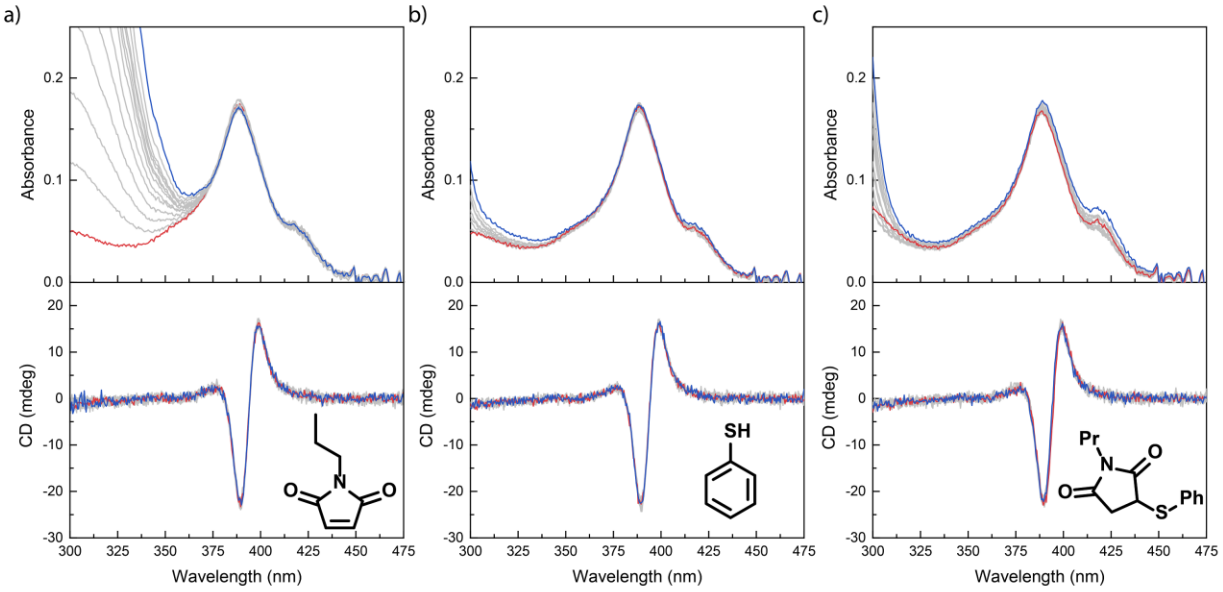

Figure S28 UV-Vis (top panel) and CD (bottom panels) spectra corresponding to the titrations of 10 µM solutions of **H_2-1** with **NPrMal** (a), **PhSH** (b) and **MA** (c) in dry MCH* ([H_2O] below detection limit of Karl-Fisher titrator) in the presence of 0.5 mM **MePip.** The spectra are used to obtain the data depicted in Figure 5b in the main text and Figure S27 in the Supplementary Information. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

UV-Vis spectra of H_2-1 in MCH* and $CHCl_3$

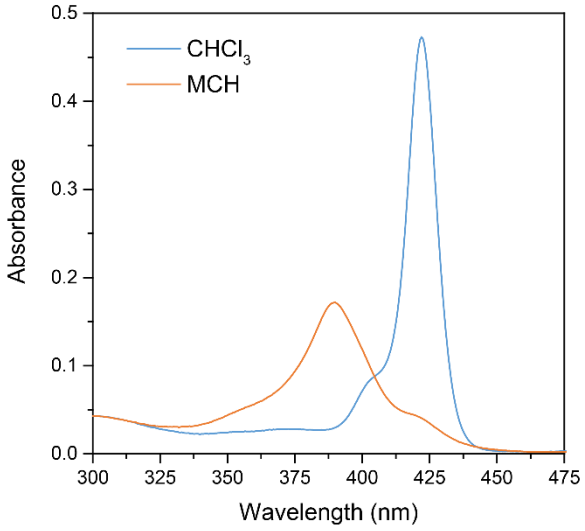

Figure S29 UV-Vis spectra of 10 µM solutions of **H_2-1** in ambient MCH* and $CHCl_3$.

UV-Vis and CD spectra titrations Zn-1 with *N*-*t*-butylmaleimide and 4-*t*-butylthiophenol

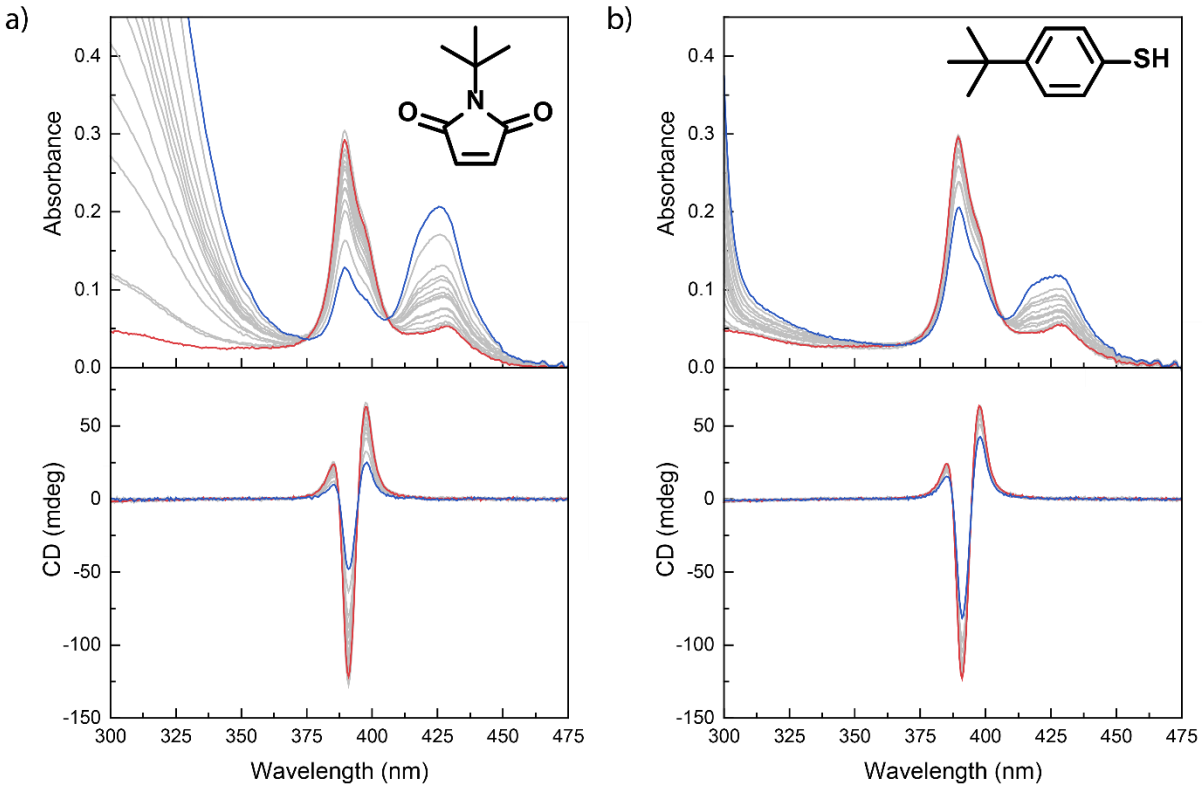

Figure S30 UV-Vis (top panel) and CD (bottom panels) spectra corresponding to the titrations of 10 µM solutions of **Zn-1** with **tBuMal** (a) and **tBuPhSH** (b) in dry MCH* ([H_2O] below detection limit of Karl-Fisher titrator) in the presence of 0.5 mM **MePip**. The spectra are used to obtain the data depicted in Figure 6 in the main text. The red spectra indicate the spectra without additive, while the blue spectra indicate the spectra collected at maximum additive concentration.

Results titration Zn-1 with bulky substrates

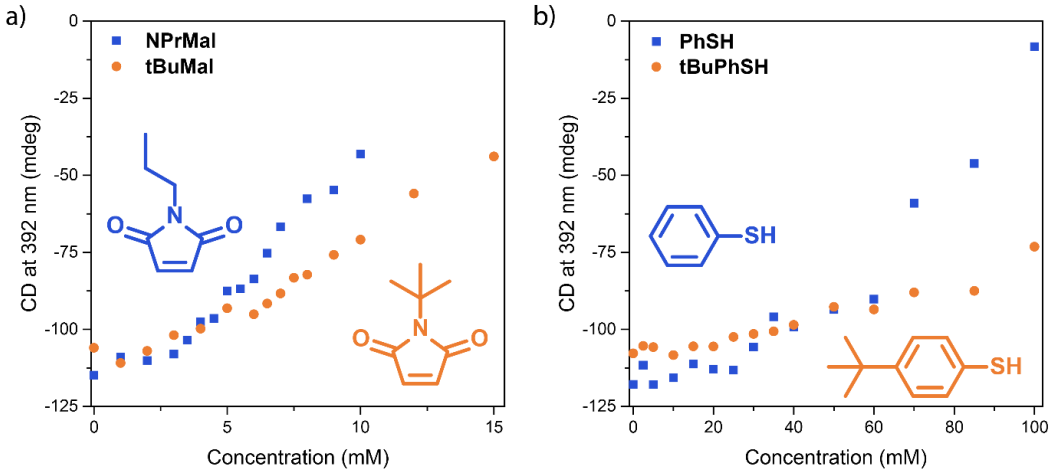

Figure S31 Titrations of 10 µM **Zn-1** in the presence of 0.5 mM **MePip** with **NPrMal** and the bulkier **tBuMal** (a) and **PhSH** and **tBuPhSH**. The titrations were performed in dry MCH* with [H2O] below the detection limit of the Karl-Fisher titrator. The data for **NPrMal** and **PhSH** is taken from Figure 4 in the main text.

Influence of various amounts of water on the depolymerization by NPrMal and PhSH

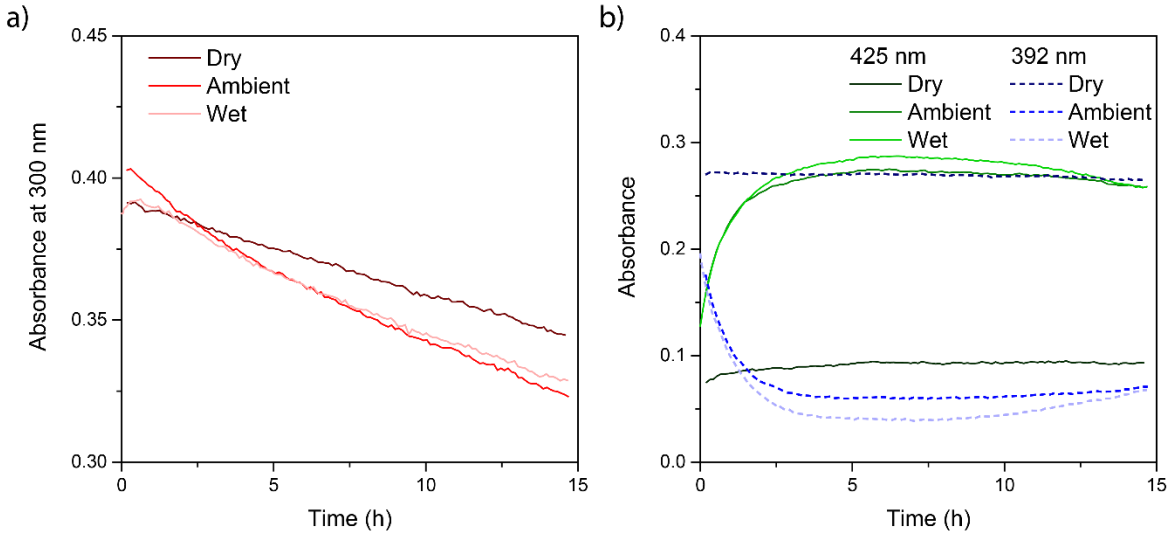

Figure S32 Comparison of the reaction kinetics in MCH* of the Michael reaction between **NPrMal** (4 mM) and **PhSH** (4 mM) which is catalyzed by **MePip** (0.5 mM) (a) and the stability of supramolecular polymers of **Zn-1** (10 µM)**,** indicated by the absorbance of the polymer at 392 nm (dashed blue lines) and the non-polymerized state (solid green lines) (b). In the dry experiment, the concentration of water was below the detection limit of the Karl Fisher titrator, in the ambient experiment, [H_2O] = 12.5 ppm and in the wet experiment, [H_2O] = 56.3 ppm.

Kinetic profiles of Michael reactions of other substrates

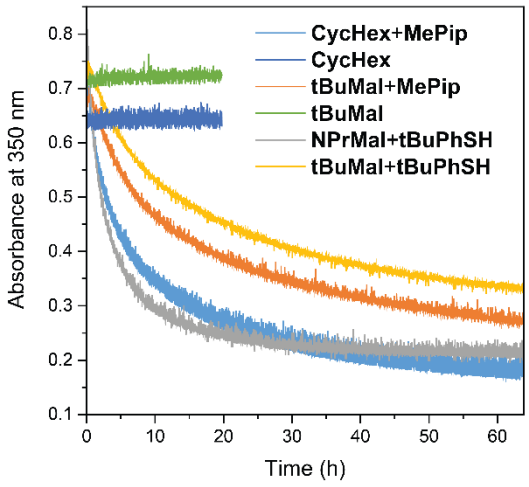

Figure S33 Absorbance at 350 nm of the reaction mixture of 30 mM **CycHex** and 30 mM **PhSH** with and without 0.5 mM **MePip** (green and dark blue), 10 mM **tBuMal** and 10 mM **PhSH** with and without 0.5 mM **MePip** and 10 mM NPrMal (orange and green) and 10 mM **NPrMal** with 10 mM **tBuPhSH** and 0.5 mM **MePip** (grey) and 10 mM **tBuMal** with 10 mM **tBuPhSH** and 0.5 mM **MePip** (yellow). The reactions were performed in ambient MCH* with [H_2O] = 35.0 ppm and the negative controls were performed in ambient MCH* with [H_2O] = 21.4 ppm.

Time-dependent UV-Vis and CD spectra of Zn-1 in the Michael reaction mixture of PhSH and CycHex

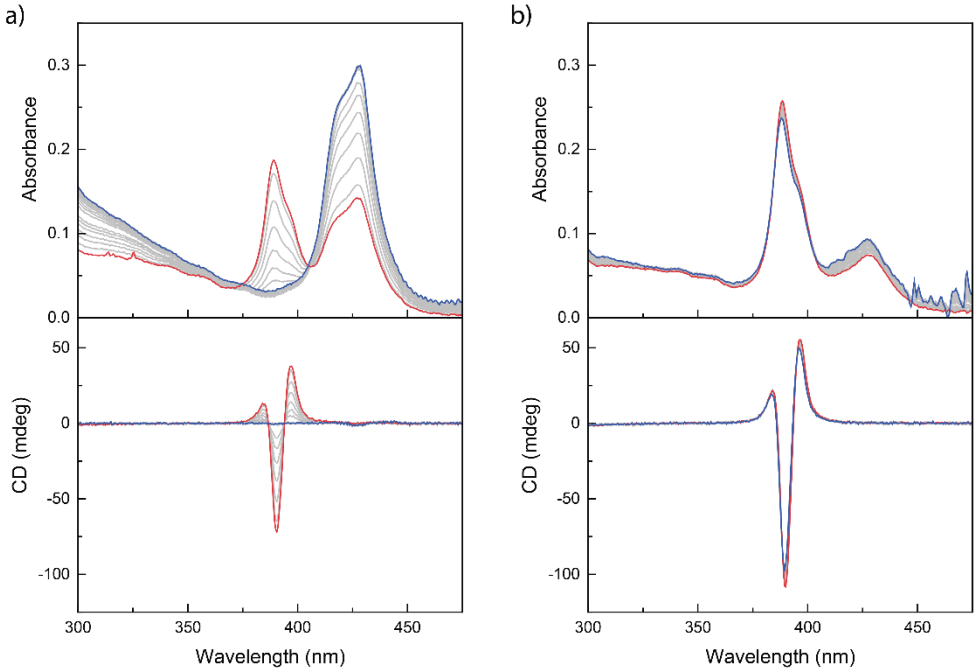

Figure S34 a) Selection of UV-Vis spectra of a solution of 10 µM **Zn-1** with 0.5 mM **MePip** and 10 mM **CycHex** and **PhSH** in ambient (a) and dry (b) MCH* between 0 (red spectrum) and 21 hours (blue spectrum) of the measurement. In the ambient sample, [H_2O] = 30.0 ppm and in the dry sample [H_2O] = 11.4 ppm.

Time dependency absorbance of spectra of Zn-1 in the Michael reaction mixture of PhSH and CycHex

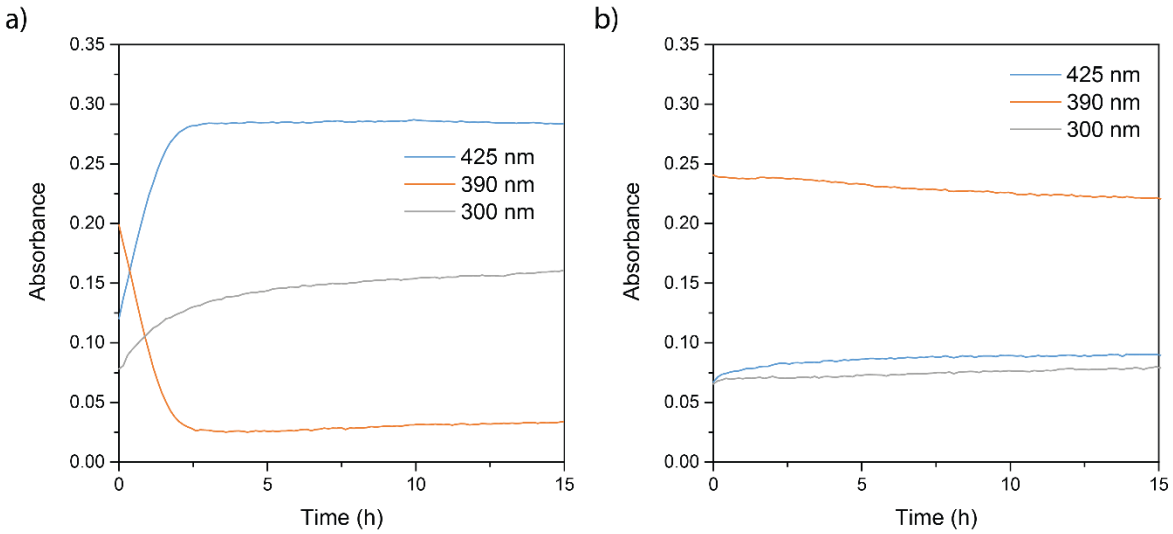

Figure S35 Time dependency of the absorbance at 300 nm, 390 nm, and 425 nm of a solution of 10 µM **Zn-1** with 0.5 mM **MePip** and 10 mM **CycHex** and **PhSH** in ambient (a) and dry (b) MCH*. In the ambient sample, [H_2O] = 30.0 ppm and in the dry sample [H_2O] = 11.4 ppm.

Time-dependent UV-Vis and CD spectra of Zn-1 in control experiments of the Michael reaction between PhSH and CycHex

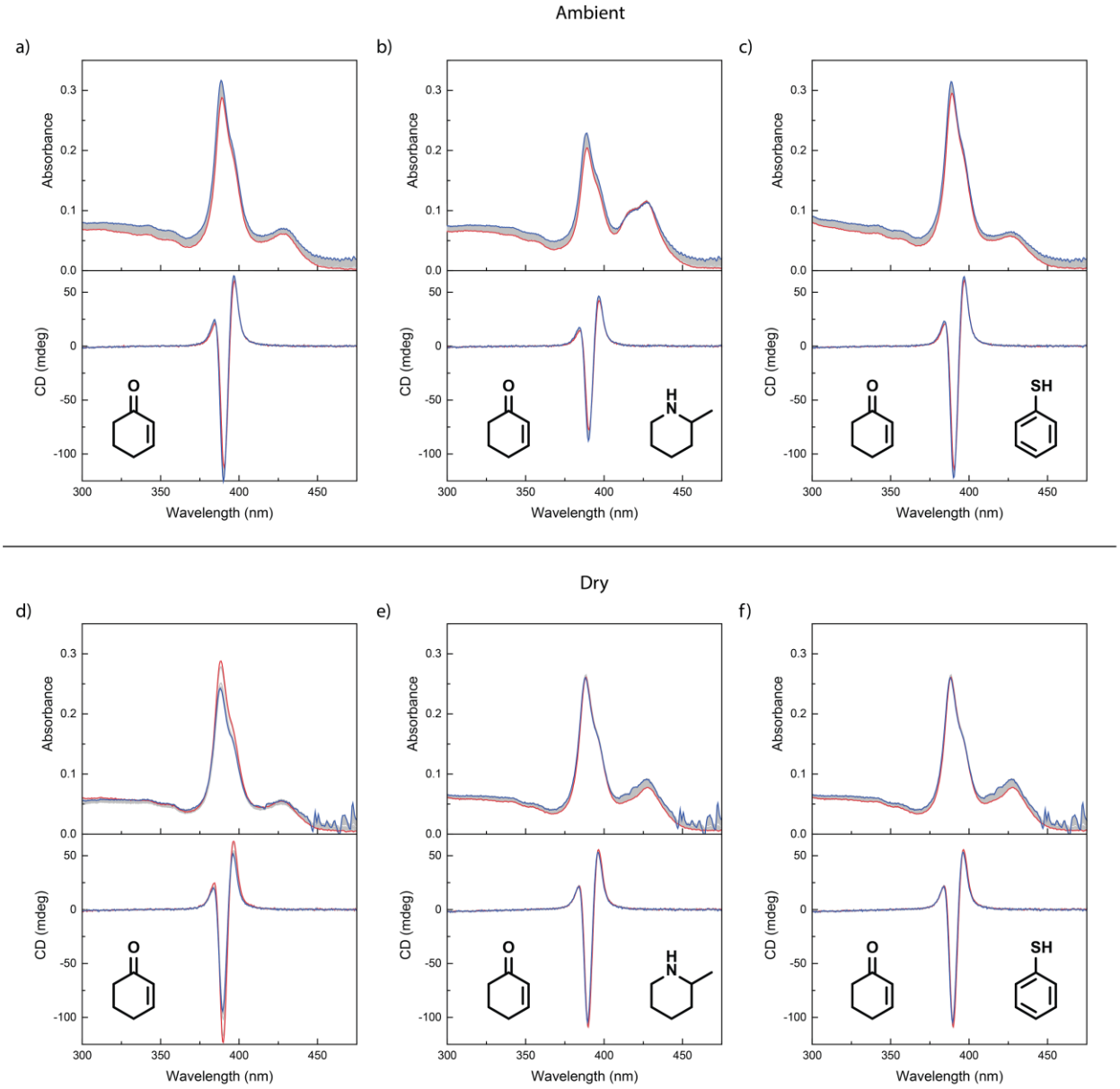

Figure S36 Selection of UV-Vis spectra (top panels) and simultaneously collected CD spectra (bottom panels) of samples of 10 µM **Zn-1** with 10 mM **CycHex** (a, d), 10 mM **CycHex** with 0.5 mM **MePip** (b, e) and 10 mM **NPrMal** with 10 mM **PhSH** (c, f) in ambient MCH* (a-c) ([H_2O] = 30.0 ppm) and dry MCH* (d-f) ([H_2O] = 11.4 ppm). The spectra were collected between 0 hours (red spectrum) and 21 hours (blue spectrum) after sample preparation.

Time dependency of absorbance of specra of Zn-1 in control experiments of the Michael reaction between PhSH and CycHex

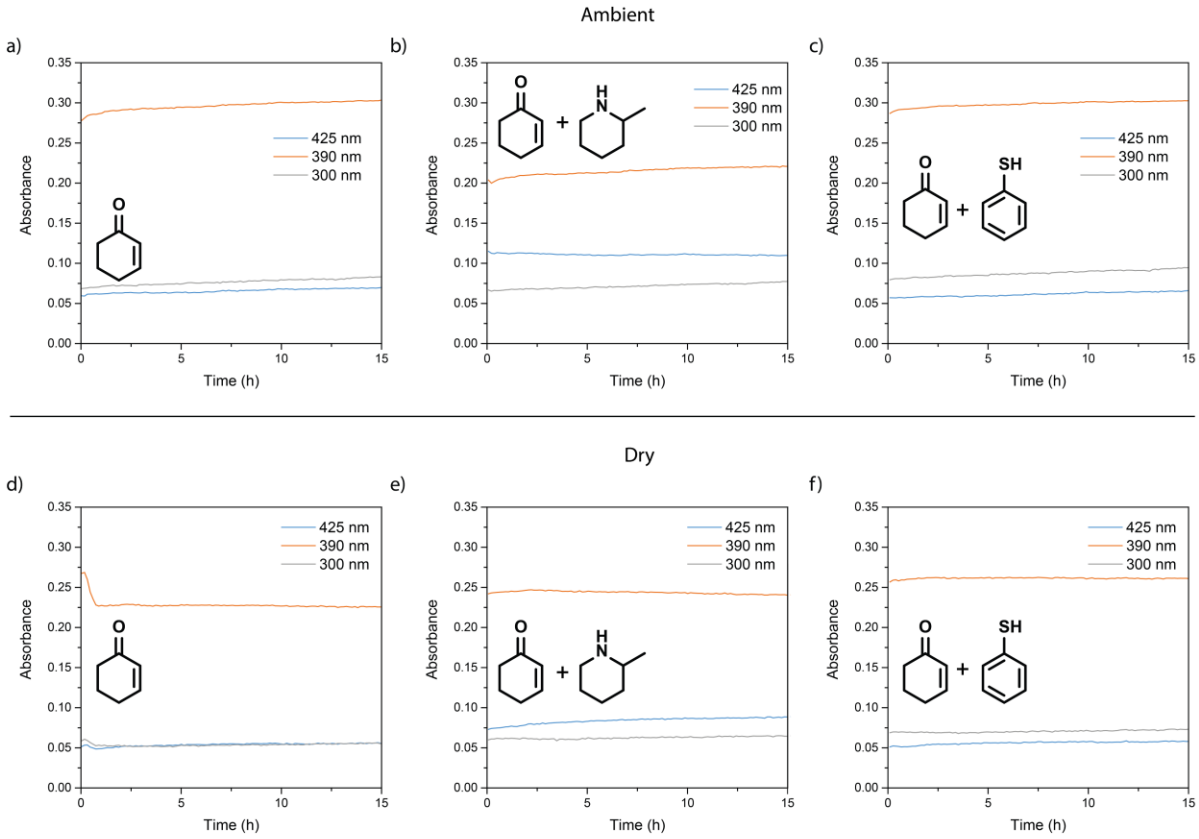

Figure 37 Time dependency of the absorbance at 300 nm, 390 nm, and 425 nm of a solution of 10 μM **Zn-1** with 0.5 mM **MePip** and 10 mM **CycHex** (a, d), 10 mM **CycHex** with 0.5 mM **MePip** (b, e) and 10 mM **CycHex** and 10 mM **PhSH** (10 mM) in ambient (a-c) and dry (d-f) MCH*. In the ambient sample, [H_2O] = 30.0 ppm and in the dry sample [H_2O] = 11.4 ppm.

Supplementary references

1. Helmich, F., Lee, C. C., Nieuwenhuizen, M. M. L., Gielen, J. C., Christianen, P. C. M., Larsen, A., Fytas, G., Leclère, P. E. L. G., Schenning, A. P. H. J., Meijer, E. W. *Angew. Chem., Int. Ed.*, 2010, **49**, 3939–3942.

2. Thordarson, P. *Chem. Soc. Rev.*, 2011, **6**, 1305–1323.

3. Malkov, A. V., Stončius, S., MacDougall, K. N., Mariani, A., McGeoch, G. D., Kočovský, P. *Tetrahedron*, 2006, **62**, 264–284.