

Supporting Information

Morphology Control in Metallosupramolecular Assemblies through Solvent-induced Steric Demand

Nils Bäumer,^a Kalathil K. Kartha,^a Jasnamol P. Palakkal^b and Gustavo Fernández^a

a) Organisch-Chemisches Institut, Westfälische Wilhelms Universität Münster, Corrensstraße 40, 48149 Münster (Germany)

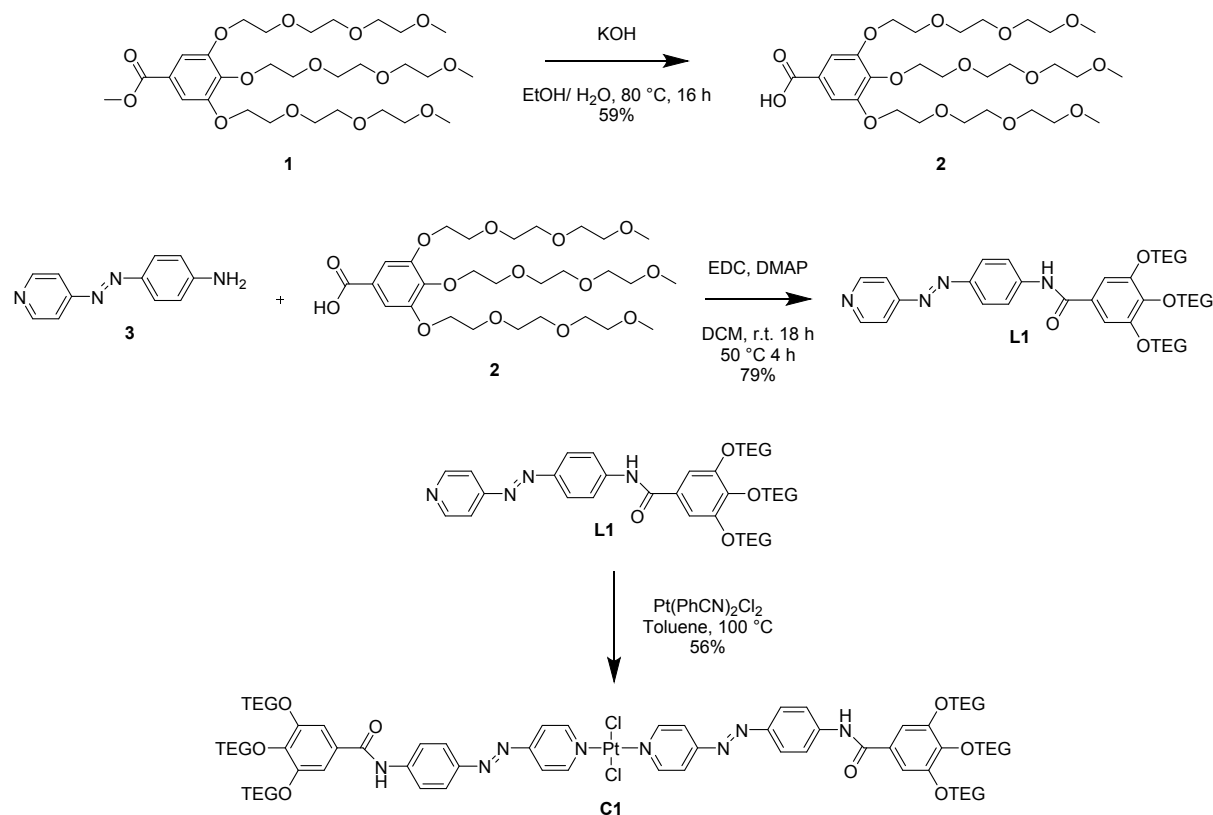
b) Technische Universität Darmstadt, Department of Materials and Earth Sciences, Alarich-Weiss-Straße 2. 64287 Darmstadt (Germany)

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Experimental

Compounds **1-3** have been synthesized according to previously reported procedures.¹



Scheme S1: Synthesis of L1 and C1.

Synthesis of **2**

Compound **2** was synthesized following previously reported procedures.^{1b} Methyl 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (4.00 g, 6.42 mmol, 1 eq.) and KOH (0.84 mg, 15.00 mmol, 2.3 eq.) were dissolved in a mixture of EtOH and water (10:1, 33 ml) and stirred at 80 °C for 16 h. Concentrated HCl (4 mL) was added and the precipitate filtered off. The solvent was removed in vacuo and the remaining oil dissolved in water (20 mL) and extracted with DCM (3 x 10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL) and dried over MgSO₄. The crude product was purified by column chromatography (SiO₂, DCM/ MeOH (95:5)). The product was obtained as a colorless oil. yield: 2.30 g, 3.78 mmol, 59%

¹H NMR (300 MHz, CDCl₃, 298 K): δ = 7.36 (s, 2H); 4.27-4.17 (m, 6H); 3.90-3.83 (m, 4H); 3.83-3.77 (m, 2H); 3.77-3.69 (m, 6H); 3.69-3.58 (m, 12H); 3.59-3.50 (m, 6H); 3.38 (s, 9H) ppm.

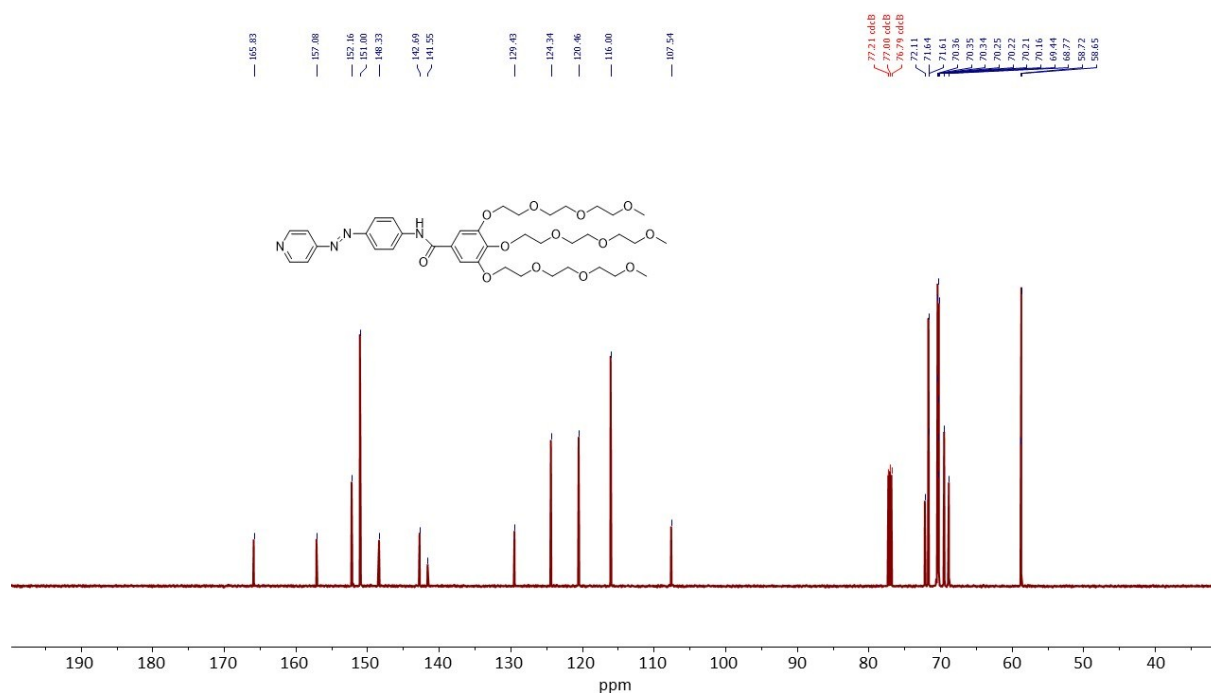
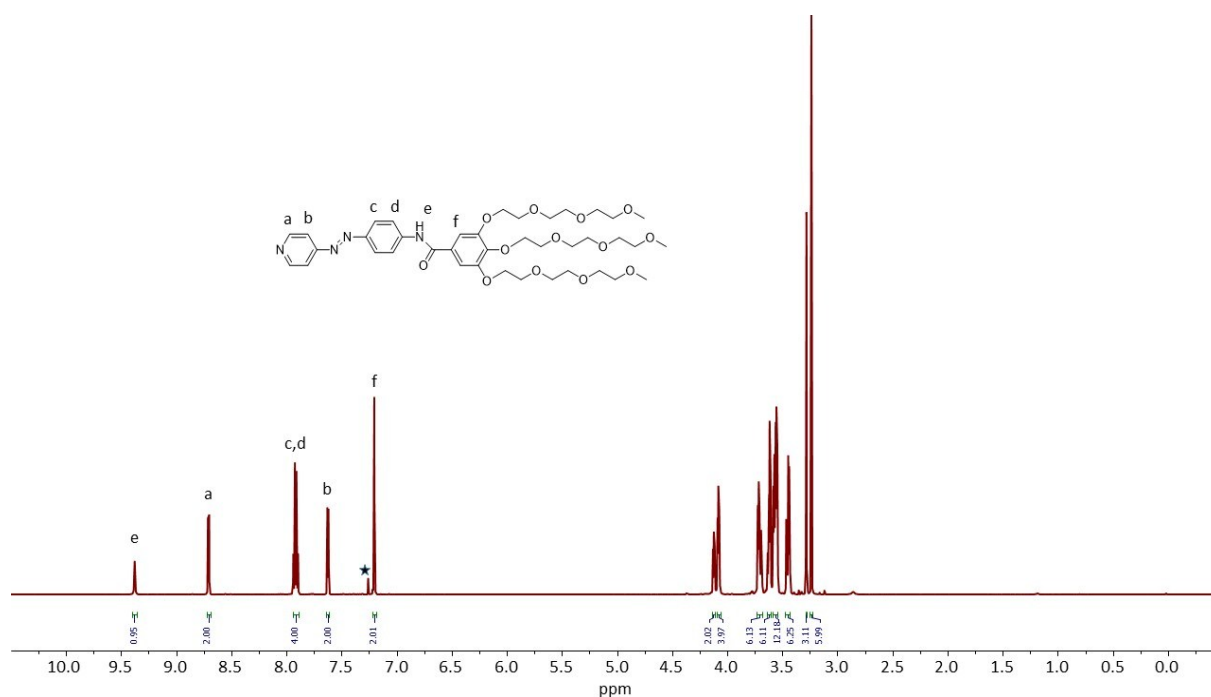
Synthesis of **L1**

Compound **3** (397 mg, 2.01 mmol, 1 eq.) and **2** (1.83 g, 3.02 mmol, 1.5 eq.) were dissolved in dried DCM (20 mL) under an argon atmosphere. DMAP (171 mg, 1.4 mmol, 0.7 eq.) and EDC·HCl (1.27 g, 6.6 mmol, 3.3 eq.) were added. The reaction mixture was stirred at room temperature for 18 h and subsequently at 50 °C for 4 h. The reaction mixture was washed with water (3 x 10 mL) and brine (10 mL) and dried over MgSO₄. The solvent was evaporated and purified by column chromatography (SiO₂, DCM/ MeOH (95:5)). The product was obtained as a red oil. yield: 1.25 g, 1.58 mmol, 79%

^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 9.37 (s, 1H); 8.70 (d, J = 6.2 Hz, 2H); 7.94-7.87 (m, 4H); 7.61 (d, J = 6.2 Hz, 2H); 7.19 (s, 2H); 4.13-4.10 (m, 2H); 4.09-4.05 (m, 4H); 3.72-3.67 (m, 6H); 3.63-3.59 (m, 6H); 3.58-3.53 (m, 12H); 3.46-3.42 (m, 6H); 3.27 (s, 3H); 3.23 (s, 6H) ppm.

^{13}C NMR (600 MHz, CDCl_3 , 298 K): δ = 165.83, 157.08, 152.16, 151.00, 148.33, 142.69, 141.55, 129.43, 124.34, 120.46, 116.00, 107.54, 72.11, 71.64, 71.61, 70.36, 70.35, 70.34, 70.25, 70.22, 70.21, 70.16, 69.44, 68.77, 58.72, 58.65 ppm.

HRMS (ESI) m/z : Calculated 811.3736 $[\text{M}+\text{Na}]^+$; Found 811.3752.



Synthesis of **C**₁

Compound **L**₁ (100 mg, 0.125 mmol, 2 eq.) and Pt(PhCN)₂Cl₂ (29.9 mg, 0.063 mmol, 1 eq.) were dissolved in dry toluene under argon atmosphere and stirred at 100 °C for 5 days. The solvent was removed under reduced pressure and the crude product was purified using column chromatography (SiO₂, DCM/ Acetone 1:1). The product was obtained as a red solid. yield: 65 mg, 0.035 mmol, 56%.

¹H NMR (600 MHz, CDCl₃, 298 K): δ = 9.12 (s, 2H); 8.86 (d, *J* = 6.7 Hz, 4H); 7.95-7.90 (m, 8H); 7.58 (d, *J* = 6.7 Hz, 4 Hz), 7.32 (s, 4H); 4.24-4.20 (m, 12 H); 3.84-3.80 (m, 8 H); 3.76-3.72 (m, 4 H); 3.71-3.60 (m, 36 H); 3.54-3.50 (m, 12H); 3.36 (s, 6 H); 3.33 (s, 12 H) ppm.

¹³C NMR (600 MHz, CDCl₃, 298 K): δ = 165.66, 157.47, 154.60, 152.38, 148.37, 143.74, 141.80, 129.51, 125.19, 120.29, 117.71, 107.94, 72.26, 71.83, 71.81, 70.53, 70.53, 70.52, 70.40, 70.39, 70.38, 70.35, 69.64, 69.04, 58.96, 58.92 ppm.

HRMS (ESI) *m/z*: Calculated 944.32514 [M+2Na]²⁺; Found 944.32693.

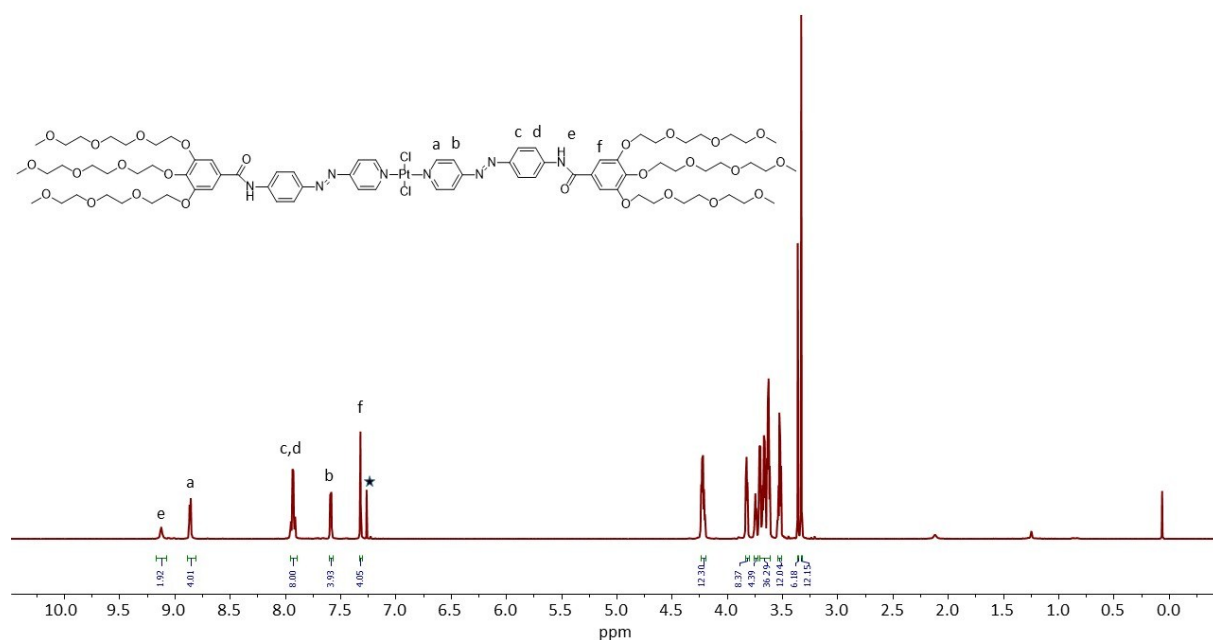


Figure S3: ¹H NMR spectrum of **C**₁ (400 MHz, CDCl₃, 298 K). The star denotes the CDCl₃ signal.

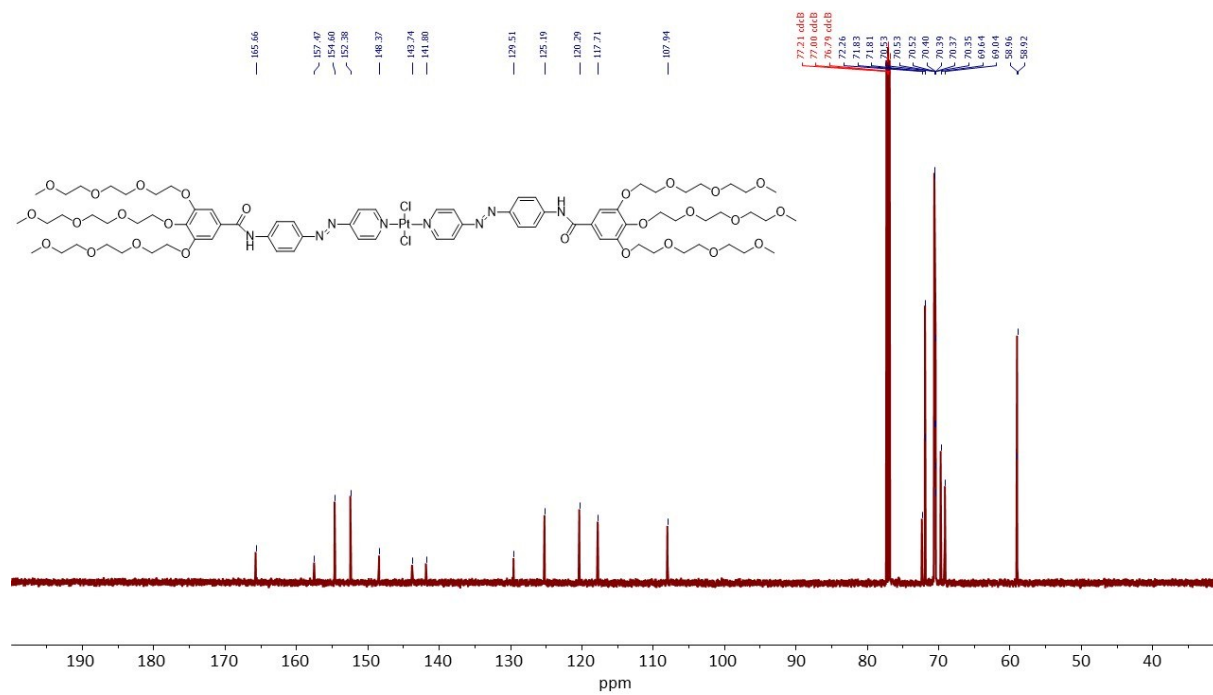


Figure S4: ^{13}C NMR spectrum of C_1 (100.6 MHz, $CDCl_3$, 298 K).

Materials and methods

General Procedures: All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere.

NMR measurements: ^1H and ^{13}C NMR spectra were recorded on a *Bruker Avance 400* (^1H : 400 MHz; ^{13}C : 100.6 MHz) and a *Bruker AV300* (^1H : 300 MHz; ^{13}C : 100.6 MHz). Additional 1D ^1H as well as 2D H,H-COSY and 2D H,H ROESY spectra were recorded on an *Agilent DD2 500* (^1H : 500 MHz) and an *Agilent DD2 600* (^1H : 600 MHz) at a standard temperature of 298 K in deuterated solvents. Deviating temperature is explicitly mentioned when used. The recorded spectra were referenced to the remaining resonance signals of the deuterated solvents. The coupling constant J of the measured spin multiplets is given in Hertz (Hz) and the chemical shifts are given in reference to the chemical shift of trimethylsilane (0 ppm). The abbreviations used to analyze the recorded spectra are: s (singlet), d (doublet), m (multiplet).

Mass spectroscopy: ESI - accurate mass spectra were recorded on an *Orbitrap LTQ XL* manufactured by *Thermo Fisher Scientific*. The signals are described by their mass/charge ratio (m/z) in u.

UV-Vis spectroscopy: All UV-Vis spectra were recorded on a *V-770* and a *V-750* by the company *JASCO* with a spectral bandwidth of 1.0 nm and a scan rate of 1000 nm min^{-1} . Glass cuvettes with an optical length of 1 cm were used. All measurements have been conducted in solvents from commercial sources with spectroscopic grade.

Atomic force microscopy: The AFM images have been recorded on a *Multimode[®]8 SPM Systems* manufactured by *Bruker AXS*. The used cantilevers were *AC200TS* by *Oxford Instruments* with an average spring constant of 9 N m^{-1} , an average frequency of 150 kHz, an average length of 200 μM , an average width of 40 μM and an average tip radius of 7 nm.

Irradiation Methods: Irradiation-based experiments were performed using a LED *LED Engin LZ1-10UV00-0000* by *Mouser electronics* at 365 nm.

Additional spectroscopic investigations

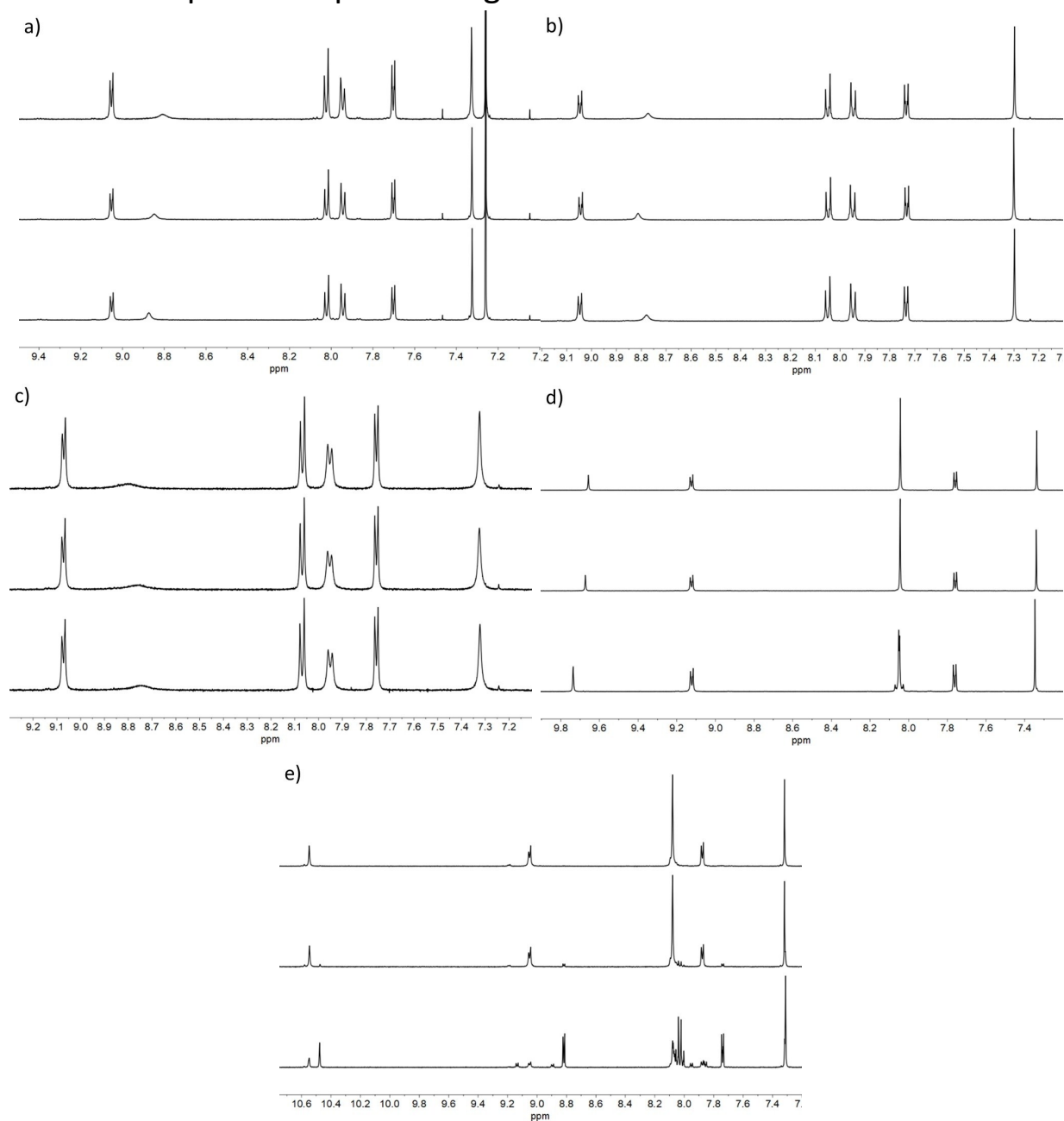


Figure S5: Time-dependent ¹H NMR at 298 K ($c = 1 \times 10^{-3}$ M) immediately after dissolving (top), after one week (middle) and after 1 h of heating in chloroform (a), dichloromethane (b), tetrachloroethane (c) tetrahydrofurane (d) and DMSO (e) at 323 K (a), 303 K (b), 373 K (c), 333 K (d) and 373 K (e) respectively.

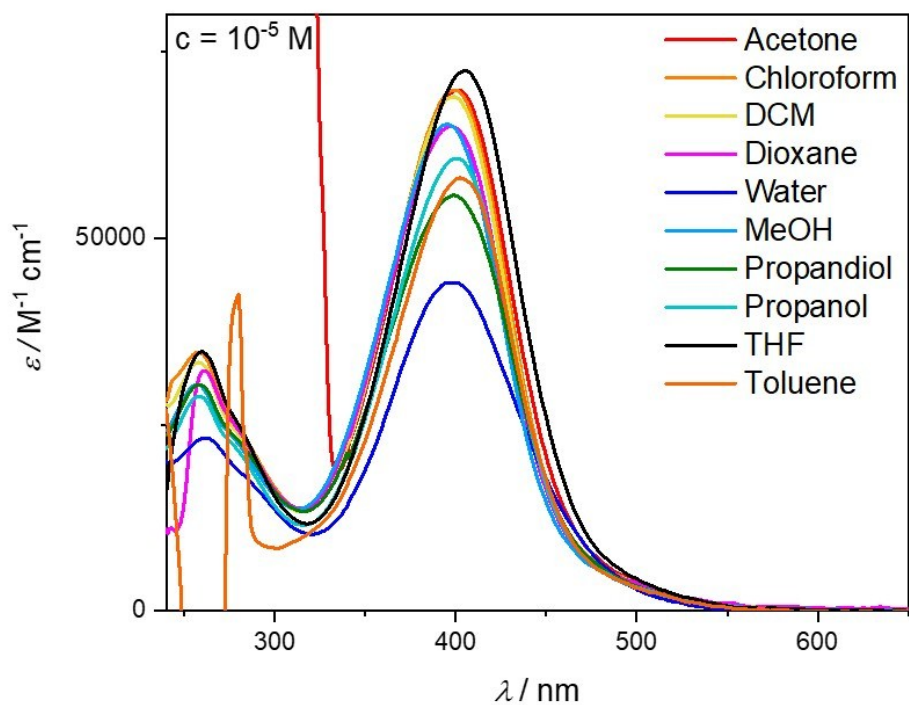


Figure S6: Solvent-dependent UV/Vis absorption spectra of C_1 at 298 K ($c = 1 \times 10^{-5} \text{ M}$, $l = 1 \text{ cm}$).

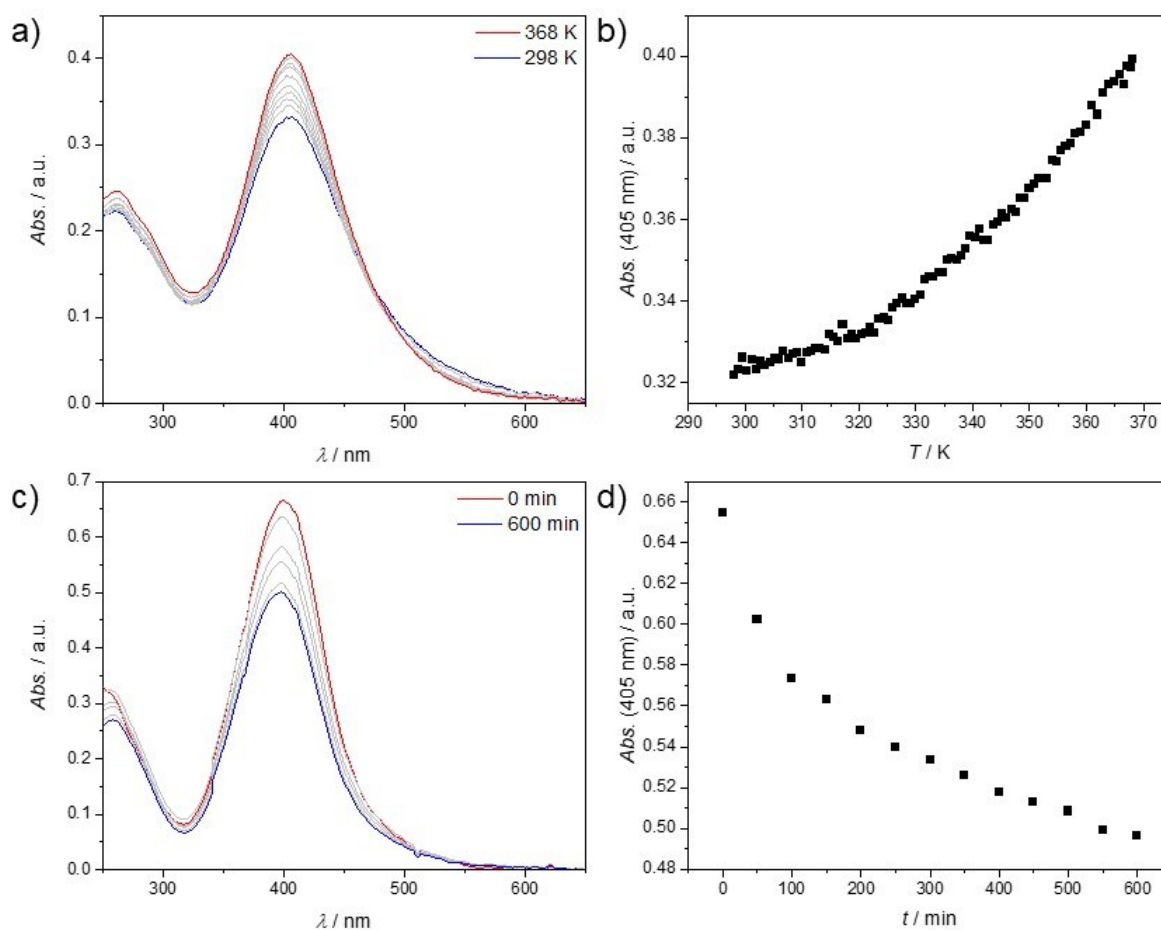


Figure S7: a) Temperature-dependent UV/Vis spectroscopy of **C1** in chloroform/MCH 15:85 at $c = 1 \times 10^{-5}$ M obtained by cooling from 368 K to 298 K. b) plot of absorbance at 405 nm against the temperature extracted from (a). The solution was kept at 298 K for 12 hours before starting the solvent-dependent investigation. Changes in the absorption spectra could not be monitored during this time (see main text and Fig. 2). c) Time-dependent UV/Vis spectroscopy of **C1** in THF/water 6:94 at $c = 1 \times 10^{-5}$ M at 298 K. The sample was heated to 323 K to break possible clusters formed during sample preparation and rapidly cooled to 298 K. Precipitation occurs if the sample is heated to high temperatures. d) Plot of absorbance at 405 nm vs. time extracted from (c). The solvent-dependent measurement was started 2 hours after the time-dependent measurement was completed.

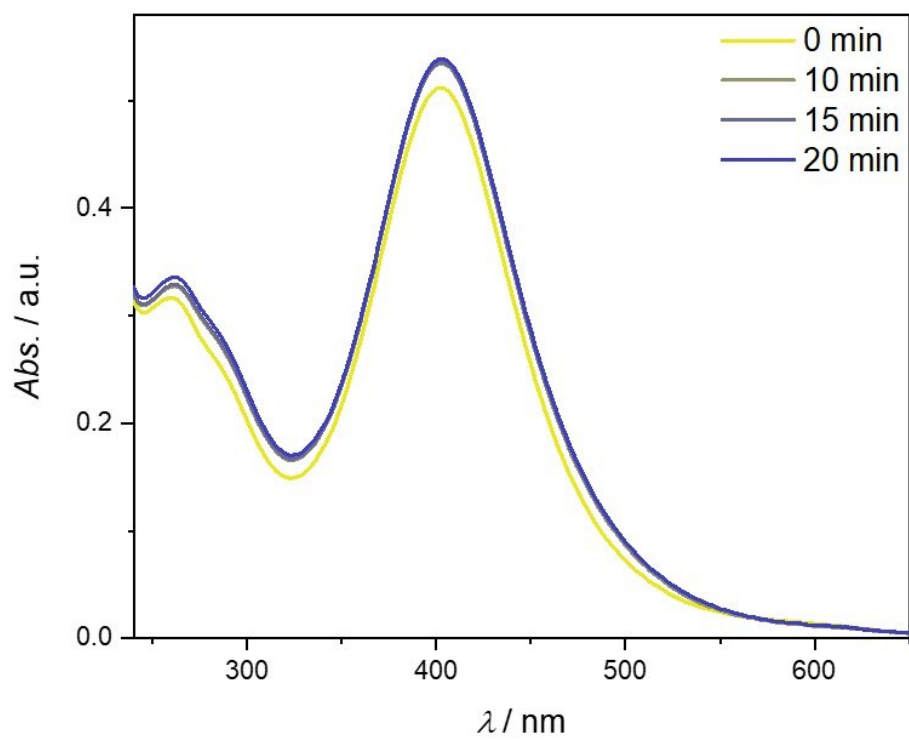


Figure S8: Time-dependent UV/Vis absorption spectra of C_1 in THF/water (5:95) at 298 K ($c = 1 \times 10^{-5}$ M, $l = 1$ cm) during irradiation using a LED ($\lambda = 365$ nm).

References

- 1 a) K. K. Kartha, N. K. Allampally, A. T. Politi, D. D. Prabhu, H. Ouchi, R. Q. Albuquerque, S. Yagai and G. Fernández, *Chem. Sci.* 2019, **10**, 752–760; b) M. R. Molla and S. Ghosh, *Chem. Eur. J.* 2012, **18**, 9860–9869;