Supporting Information – A Luminescent Two Component Supramolecular Hydrogelator

# **Supporting Information**

## A Stimuli Responsive Two Component Supramolecular Hydrogelator with Aggregation-Induced Emission Properties

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## 1. General information

All solvents were distilled before use. Millipore water was obtained with a TKA MicroPure ultrapure water system. All other commercially available reagents were used as obtained unless otherwise specified. Reactions were monitored by TLC on silica gel plates (Macherey-Nagel POLYGRAM SIL G/UV254). Spots were visualized by UV light (254 nm and 366 nm). Reversed phase column chromatography was performed with an Armen Instrument Spot Flash Liquid Chromatography MPLC apparatus with RediSep C-18 Reversed Phase columns. Lyophilisation was done with a Christ Alpha 1-4 LD plus freeze dryer. The pH determination was performed with a pH-meter 766 Calimatic from Knick. The melting points were obtained with a Büchi Melting-Point B-540 apparatus with open end glass capillary tubes. The melting points are not corrected. The NMR spectra were measured with Bruker DMX 300, DRX 500 or AVHD 600 spectrometers. All measurements were recorded at room temperature using DMSO-d<sub>6</sub> as solvent. The chemical shifts are relative to the signals of DMSO-d<sub>6</sub> ( $\delta^{1}$ H = 2.50 ppm and  $\delta^{13}$ C = 39.5 ppm). The apparent coupling constants are given in Hertz (Hz). The description of the fine structure means: s = singlet, br. s = broad singlet, d = doublet, t = triplet, m = multiplet. The IR spectra were measured on a Varian 3100 FT-IR Excalibur Series.

## 2. Synthesis

The GCP binding motif **E** was synthesized starting from Boc-*L*-Dap(Boc)-OH **B** and the synthesis of the introduced GCP **E** is literature known.<sup>[1]</sup> The synthesis of the AIE building block **G** was previously reported by us.<sup>[2]</sup>





#### Boc-L-Dap(Boc)-propargylamine C



Boc-*L*-Dap(Boc)-OH **B** (2 g, 4.12 mmol) were dissolved in DCM (20 mL) followed by addition of HCTU (2.05 g, 4.94 mmol) and DIPEA (2.12 mL, 12.4 mmol). After 15 min propargylamine (0.91, 16 mmol) is added and stirred following overnight. The resulting mixture was washed with 0.5 N NaHSO<sub>4</sub> (3 x 30 mL)

and water (3 x 30 mL). The organic Layer was dried over MgSO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, Cy/EA = 1/1) to give **C** (989 mg, 2.90 mmol, 70.4 %) as a white solid. **Molecular Formular:** C<sub>16</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub>; **Molecular Mass:** 341.41 g/mol; <sup>1</sup>H NMR: (600 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 1.36 (m, 18H, Boc-CH<sub>3</sub>), 3.09 (m, 2H, β-CH<sub>2</sub> & alkyne-CH), 3.16 (m, 1H, β-CH<sub>2</sub>), 3.99 (m, 1 H, ,  $\alpha$ -CH ), 6.64 (d, 1H, <sup>3</sup>J(H, H) = 8.22 Hz,  $\alpha$ -NH), 6.70 (m, 1H,  $\beta$ -NH), 8.27 (m, 1H, NH); <sup>13</sup>C NMR: (75 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 28.1, 41.7, 54.6, 73.0, 77.9, 78.2, 80.9, 155.0, 155.7, 169.9 ; **HR-MS:** (pos. ESI, MeOH) m/z = 364.1872 ([M+Na]<sup>+</sup>, calc.: 364.1843), 705.3818 ([2M+Na]<sup>+</sup>, calc.: 705.3794).

#### L-Dap-propargylamine hydrochlorid salt D



Boc-*L*-Dap(Boc)-propargylamine **C** (935 mg, 2.74 mmol) was dissolved in MeOH (10 mL), followed by addition of conc. HCl (2 mL). The reaction was stirred for 30 min. Then the solvent was removed under reduced pressure. The resulting solid was taken up by a small amount of MeOH and precipitated in  $Et_2O$  (30 mL), drying under reduced pressure gave **D** (324 mg, 55.1%) as a white solid.

**Molecular Formular:** C<sub>6</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>; **Molecular Mass:** 214.09 g/mol; **Mp:** 198.1 °C (decomposition); <sup>1</sup>H NMR: (300 MHz, DMSO-d<sub>6</sub>) δ [ppm] = 3.23 (t, 1H, <sup>3</sup>J(H,H) = 5.00 Hz, alkyne-CH), 3.27 (d. 2H, <sup>3</sup>J(H,H) = 5.00 Hz, CH<sub>2</sub>), 4.01 (m, 2H, β-CH<sub>2</sub>), 4.27 (t, 1H, <sup>3</sup>J(H,H) = 10.63 Hz, α-CH), 8.76 (br. s, 6H, R-NH<sub>3</sub><sup>+</sup>), 9.34 (t, 1H, <sup>3</sup>J(H,H) = 10.33 Hz, NH); <sup>13</sup>C NMR: (75 MHz, DMSO-d<sub>6</sub>) δ [ppm] = 28.7, 30.8, 50.0, 74.0, 79.7, 164.9; **HR-MS:** (pos. ESI, MeOH) m/z = 142.0975 ([M+H]<sup>+</sup>, calc.: 142.0993).

## Binding motif F



GCP **E** (1.79, 4.51 mmol), HCTU (1.92, 4.65 mmol) and DIPEA (1.54 mL, 9 mmol) were dissolved in dry DMF (2 mL). After 15 min **D** (300 mg, 1.50 mmol) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was precipitated in water (20mL) and dried under vacuo. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM/ACN/MeOH = 9/1/0.5) to give **F** 

(176 mg, 2.50 mmol, 18 %) as a white solid. **Molecular Formular:**  $C_{30}H_{39}N_{11}O_9$ ; **Molecular Mass:** 697.71 g/mol; **Mp:** 173.4 °C (decomposition); <sup>1</sup>**H NMR:** (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 1.44 (s, 18H, Boc-CH<sub>3</sub>), 3.06 (t, 1H, <sup>3</sup>J(H,H) = 4.69 Hz, alkyne-CH), 3.64 (m, 2H,  $\beta$ -CH<sub>2</sub>), 3.85 (m, 2H, alkyne-CH<sub>2</sub>), 4.60 (m, 1H,  $\alpha$ -CH), 6.79 (m, 4H, Py-CH), 8.52 (m, 5H, NH-Amid), 9.31 (s, 2H, NH-Gua), 10.82 (s, 2H, NH-Gua), 11.42 (s, 2H, Pyrrol-NH); <sup>13</sup>**C NMR:** (151 MHz, DMSO-d6)  $\delta$  [ppm] = 28.1, 40.6, 53.0, 73.0, 80.9, 112.1, 112.3, 112.6, 158.4, 159.5, 160.1, 169.5; HR-MS: (pos. ESI, MeOH) m/z = 698.3007 ([M+H]<sup>+</sup>, calc.: 698.3005), 720.2821 ([M+Na]<sup>+</sup>, calc.: 720.2824).

#### 4,5-bis((4-(2-azidoethoxy)phenyl)thio)phthalonitrile H



4,5-bis((4-hydroxyphenyl)thio)phthalonitrile<sup>[2]</sup> (800 mg, 2.13 mmol) and potassiumcarbonate (1.8 g, 13 mmol) were dissolved in dry DMF (20 mL), followed by the addition of the 2-azidoethyl 4-methylbenzenesulfonate (1.13 g, 4.69 mmol). The mixture was stirred at 50°C for 6 h. The reaction was diluted with 20 mL of distilled water and the crude mixture was filtrated. After washing with water and

drying in vacuo H (975 mg, 1.89 mmol, 89%) was obtained as a yellow solid. Molecular Formular:  $C_{24}H_{18}N_8O_2S_2$ ; Molecular Mass: 514.58 g/mol; <sup>1</sup>H NMR: (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 7.58 (d,<sup>3</sup>J = 8.8 Hz, 4H), 7.17 (d, <sup>3</sup>J = 8.8 Hz, 4H), 7.11 (s, 2H), 4.31 – 4.23 (t, <sup>3</sup>J = 5.0 Hz, 4H), 3.73 – 3.67 (t, <sup>3</sup>J = 5.0 Hz, 4H); <sup>13</sup>C-NMR (75 MHz, DMSO-d<sub>6</sub>): 159.86, 143.67, 136.98, 129.46, 118.46, 116.75, 115.57, 111.11, 67.09, 49.50; IR: v (cm<sup>-1</sup>) = 3074, 2937, 2528, 2231, 2112, 1593, 1562, 1492, 1452, 1412, 1394, 1348, 1284, 1242, 1176, 1109, 1092, 1059, 1001, 924, 891, 833, 804, 737, 675, 658; HR-MS: (pos. ESI, MeOH) m/z = 537.0895 ([M+Na]<sup>+</sup>, calc.: 537.0886).

#### Protected compound I



Scaffold **H** (57 mg, 0.11 mmol) and **F** (155 mg, 0.22 mmol) were dissolved in degased THF (2 mL). Then a solution of CuSO<sub>4</sub> (19.4 mg, 0.07 mmol) and Na-*L*-Ascorbate (30.8 mg, 0.15 mmol) solved in H<sub>2</sub>O (0.5 mL) was added. The reaction was stirred under argon atmosphere at room temperature for 48 hours. Then the solvent was removed under reduced pressure and the resulting solid was taken up with a small amount of THF and precipitated in MeOH (20 mL). The precipitate was dried under vacuo and was purified by column chromatography (SiO<sub>2</sub>, DCM/ACN/MeOH/NH<sub>3</sub> = 10/1/1/0.1) to give I (86.3 mg, 0.05 mmol, 41%) as yellow solid. **Molecular Formular**:  $C_{84}H_{96}N_{30}O_{20}S_2$ ; **Molecular Mass**: 1909.98 g/mol; <sup>1</sup>**H NMR**: (600 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 1.44 (s, 36H, Boc-CH<sub>3</sub>), 3.56 (m, 2H, β-CH<sub>2</sub>), 4.62 (q, 2H, <sup>3</sup>J(H, H) = 5.94 Hz,  $\alpha$ -CH), 4.73 (t, 4H, CH<sub>2</sub>), 6.78 (m, 8H, Pyrrol-CH), 7.01 (s, 2H, Ar-CH), 7.08 (d, 4H, <sup>3</sup>J(H, H) = 8.88 Hz, Ar-CH), 7.50 (d, 4 H, <sup>3</sup>J(H, H) = 8.76 Hz, Ar-CH), 7.91 (s, 2 H, Triazol-CH), 8.45-8.70 (m, 10 H, NH), 9.34 (s, 4H, Gua-NH), 10.60-11.50 (br. s, 8H, Gua-amide-NH & Py-NH); <sup>13</sup>**C NMR**: (151 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 27.7, 34.5, 40.7, 48.8, 53.3, 66.4, 111.0, 112.2, 112.6, 115.6, 116.7, 118.4, 123.3, 129.2, 131.6, 137.0, 143.5, 145.1, 158.4, 159.6, 160.2, 169.8; **HR-MS**: (pos. ESI, MeOH) m/z = 955.8535 [M+2H]<sup>2+</sup>, calc.: 955.8515).

## Tetracationic compound (A)



I (81.3 mg, 0.04 mmol) was dissolved in MeOH (5 mL) followed by addition of TFA (1 mL). The reaction mixture was stirred for 4 h then the solvent was removed under reduced pressure. The crude product was purified by MPLC on C18 reversed-phase silica gel (gradient 10% → 100% methanol/water in 60 min, 0.1% TFA) to give **A** (81.1 mg, 0.05 mmol, 79%) as yellow solid. **Molecular Formula:** C<sub>64</sub>H<sub>64</sub>N<sub>30</sub>O<sub>12</sub>S<sub>2</sub>; **Molecular Mass:** 1509.52 g/mol; <sup>1</sup>H NMR: (600 MHz, DMSO-d<sub>6</sub>) δ [ppm] = 3.57 (m, 2H, β-CH<sub>2</sub>), 3.69 (m, 6H, β-CH<sub>2</sub>), 4.34 (d, 4H, <sup>3</sup>J(H, H) = 5.64 Hz, CH<sub>2</sub>), 4.45 (t, 4H, <sup>3</sup>J(H, H) = 9.53 Hz, Linker-CH<sub>2</sub>), 4.66 (q, 4H, <sup>3</sup>J(H, H) = 5.82 Hz, Linker-CH<sub>2</sub>), 4.75 (t, 4H, <sup>3</sup>J(H, H) = 9.90 Hz, Linker-CH<sub>2</sub>), 6.85 (m, 4H, Pyrrol-CH), 7.03 (m, 10H, Ar-CH), 7.51 (d, 4H, <sup>3</sup>J(H, H) = 8.76 Hz, Ar-CH), 7.97 (s, 2H, Triazol-CH), 8.31 (br. s, 14H, Gua-NH), 8.57 (m, 2H, amide-NH), 8.69 (m, 4H, amide-NH), 11.20 (s, 4H, Pyrrol-NH), 12.40-12.54 (m, 4H, Gua-NH); <sup>13</sup>C NMR: (151 MHz, DMSO-d<sub>6</sub>) δ [ppm] = 18.6, 27.0, 27.7, 34.5, 40.7, 48.9, 53.0, 56.0, 66.5, 111.1, 112.9, 113.4, 115.1, 115.3, 115.6, 116.8, 118.4, 123.4, 125.5, 125.6, 129.2, 132.4, 137.0, 143.5, 144.9, 155.0, 158.3, 158.6, 158.8, 159.0, 159.5, 159.7, 169.5; HR-MS: (pos. ESI, MeOH) m/z = 387.1204 ([M+4H]<sup>4+</sup>, calc.: 387.1263).



#### 3. NMR experiments

**Fig. S1:** <sup>1</sup>H-NMR of compound **A** shows peak splitting of aromatic signals by increasing the water value. a) compound **A** (c = 5 mM, DMSO-d<sub>6</sub>), addition of D<sub>2</sub>O leads to b) compound **A** (c = 3.75 mM, 25% D<sub>2</sub>O), c) compound **A** (c = 3 mM, 40% D<sub>2</sub>O), d) compound **A** (c = 2.5 mM, 50% D<sub>2</sub>O).



**Fig. S2:** NOESY of compound **A** (c = 2.5 mM) in DMSO-d<sub>6</sub>/D<sub>2</sub>O (50/50).

## 4. Dynamic Light Scattering (DLS)

Dynamic light scattering was performed on a Malvern Zetasizer Nano ZS the incooperated HeNe laser works at a wavelength of 633 nm and uses a detector at an angle of 173° (non-invasive back scatter technology). Measurements were recorded with 3 min equilibration time in UV cuvettes at 20 °C.



**Fig. S3:** DLS measurements of compound **A** (50  $\mu$ M) and compound **A** (25  $\mu$ M) + malonic acid (50  $\mu$ M) after 4 days.



Fig. S4: DLS measurement of compound A (25  $\mu M)$  + malonic acid (50  $\mu M)$  and after addition of 5 eq. TEA.



Fig. S5: DLS measurement of compound A (25  $\mu M)$  + malonic acid (50  $\mu M)$  and after addition of 5 eq. TFA.



Fig. S6: DLS measurement of compound A (25  $\mu$ M) + malonic acid (50  $\mu$ M) after different time.

## 5. Atomic Force Microscopy (AFM)

Atomic force microscopy images were performed in tapping mode using NanoDrive Controller with an Innova Scanning Probe Microscope (Veeco) and N-type silicon cantilever (Olympus AC 16TS). Samples were prepared by drop-coating the solution on a freshly cleaned mica surface (Plano) and waited for 2 h. The AFM data were analyzed using Gwyddion-2.42 software.



**Fig. S7:** AFM height images (10  $\mu$ m x 10  $\mu$ m) and height profiles of **A** (25  $\mu$ M) at different solvents a) particles at DMSO b) formation of fibrillar network at DMSO/H<sub>2</sub>O (1/1) c) completely formed fibrillar network at H<sub>2</sub>O.



**Fig. S8:** AFM height images (10  $\mu$ m x 10  $\mu$ m) and height profiles of **A** (1 eq) + malonic acid (2 eq) at different concentrations in H<sub>2</sub>O a) **A** (10  $\mu$ M) + malonic acid (20  $\mu$ M) b) **A** (12.5  $\mu$ M) + malonic acid (25  $\mu$ M) c) (25  $\mu$ M) + malonic acid (50  $\mu$ M).



**Fig. S9:** AFM height images (10  $\mu$ m x 10  $\mu$ m) and height profiles of **A** (25  $\mu$ M) + malonic acid (50  $\mu$ M) after addition of acid/base a) after addition of 5 eq. TFA b) after addition of 5 eq. TEA.

## 6. Transmission electron microscope (TEM)

Transmission electron microscope images were prepared by dropping the sample solution on a 400-mesh formvar copper grid coated with carbon. About 2 min after deposition the grid was tapped with filter paper to remove remaining solvent from the surface. Negative staining was performed by addition of a drop of an ethanol solution of uranyl onto the copper grid. After 1 min, the liquid on the surface of the grid was removed by tapping it with a filter paper.

## 7. Gelation Procedure

In a glass vial, a weighed amount of **A** was solved in DMSO (1  $\mu$ L), than H<sub>2</sub>O (99  $\mu$ L) was added to give a 10 mM stock solution of **A** (1% DMSO). The resulting stock solution (1  $\mu$ L) was mixed with a 10 mM solution of malonic acid (2  $\mu$ L), diluted with H<sub>2</sub>O (97  $\mu$ L) and heated up to 70 °C. Storing the sample at room temperature leads to the gel formation after 7-8 days. The gel state was evaluated by the "stable to inversion of a test tube" method.





**Fig. S10:** Oscillatory tests of the hydrogel **A** (100  $\mu$ M) + malonic acid (200  $\mu$ M), frequency sweep at a constant strain ( $\gamma$  = 0.1 %).



**Fig. S11:** Oscillatory tests of the hydrogel **A** (100  $\mu$ M) + malonic acid (200  $\mu$ M), strain sweep at a constant frequency (*f* = 2 Hz).

## 9. NMR Spectra



**Fig. S12:** <sup>1</sup>H-NMR spectrum of **C** (600 MHz, DMSO- $d_6$ ).



**Fig. S13:** <sup>1</sup>H-NMR spectrum of **D** (300 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S14:** <sup>1</sup>H-NMR spectrum of **F** (300 MHz, DMSO- $d_6$ ).



**Fig. S15:** <sup>1</sup>H-NMR spectrum of **H** (300 MHz, DMSO- $d_6$ ).



**Fig. S16:** <sup>1</sup>H-NMR spectrum of I (600 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S17:** <sup>1</sup>H-NMR spectrum of **A** (600 MHz, DMSO- $d_6$ ).



**Fig. S18:** <sup>13</sup>C-NMR spectrum of **C** (75 MHz, DMSO- $d_6$ ).



**Fig. S19:** <sup>13</sup>C-NMR spectrum of **H** (75 MHz, DMSO- $d_6$ ).



**Fig. S20:** <sup>13</sup>C-NMR spectrum of **D** (75 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S21:** <sup>13</sup>C-NMR spectrum of **F** (151 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S22:** <sup>13</sup>C-NMR spectrum of I (151 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S23:** <sup>13</sup>C-NMR spectrum of **A** (151 MHz, DMSO-*d*<sub>6</sub>).

## 10. Mass Spectra



**Fig. S24:** HR-ESI mass spectrum of **C** (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to **C**.



**Fig. S25:** HR-ESI mass spectrum of **H** (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to **H**.



**Fig. S26:** HR-ESI mass spectrum of **D** (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to **D**.

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**Fig. S27:** HR-ESI mass spectrum of **F** (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to **F**.



**Fig. S28:** HR-ESI mass spectrum of I (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to I.



**Fig. S29:** HR-ESI mass spectrum of **A** (positive ion mode, MeOH) and predicted mass spectrum of peaks which belongs to **A**.

## 11. X-Ray Crystallography

The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoKa radiation, I = 0.71073 Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)<sup>[3]</sup> and refined anisotropically by full-matrix least-squares on F2 (SHELXL-2017)<sup>[4]</sup>,<sup>[5]</sup>. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups.

**CCDC-1916292** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

| D–H…A          | Symmetry operation | Н…А      | < DH…A | H…plane  | <<br>H/Cnt/plane[parallel<br>shift] |
|----------------|--------------------|----------|--------|----------|-------------------------------------|
| within layers  |                    |          |        |          |                                     |
| C2–H2…N6       | 1+x, -1+y, +z      | 2.56     | 146.6  |          |                                     |
| C5–H5…N2       | -1-x, 1-y, 1-z     | 2.66     | 125.7  |          |                                     |
| C15–H15b…N8    | 1+x, -1+y, +z      | 2.75     | 142.5  |          |                                     |
| C16-           | 1+x, -1+y, +z      | 2.62     | 167.8  | 2.598(3) | 82.6[0.34]                          |
| H16a…Cnt3      |                    |          |        |          |                                     |
| C23–H23a…N1    | -1-x, 1-y, 1-z     | 2.74     | 114.9  |          |                                     |
| S2…N3          | 1-x, 1-y, 2-z      | 3.306(3) |        |          |                                     |
| S2…N4          | 1-x, 1-y, 2-z      | 3.301(3) |        |          |                                     |
| N3…N4          | 2-x, -y, 2-z       | 3.105(3) |        |          |                                     |
| Cnt2…Cnt2a     | 1-x, 1-y, 2-z      | 3.91     |        | 3.54     | 64.8[1.67]b                         |
| between layers |                    |          |        |          |                                     |
| C10-H10…N2     | -x, 1-y, 1-z       | 2.64     |        | 122.9    |                                     |
| C13-H13…N5     | 1-x, -y, 2-z       | 2.69     | 155.1  |          |                                     |
| C18-H18…N1     | -x, 1-y, 1-z       | 2.62     |        | 164.5    |                                     |
| C23–H23a…N5    | -x, 1-y, 2-z       | 2.71     | 133.2  |          |                                     |
| C11-H11…Cnt1   | 1+x, +y, +z        | 3.01     | 165.5  | 2.893(3) | 73.9[0.83]                          |
| N8…C4          | +x, 1+y, +z        | 3.173(4) |        |          |                                     |
| N8…C8          | +x, 1+y, +z        | 3.051(4) |        |          |                                     |

a interplanar angle equals 0° because of symmetry.

b shifted towards S atom.

Cnt1: Centroid of C1 to C6

Cnt2: Centroid of C9 to C14

Cnt3: Centroid of C17 to C22



Fig. S30: Molecular packing of (1) showing parallel layer to (11  $\overline{2}$ )



**Fig. S31:** Magnified TEM images of compound (A) without MA (image A) and with 2 equivalents of MA (image B) including measurements of the fibre thicknesses.



+ 2 eq MA under UV-light

+ 2 eq MA + 2 eq MA

+ 2 eq MA

+ 2 eq MA

Fig. S32: Determination of the critical gelation concentration by the inverted vial methods using different concentrations of (A) in the presence of 2 eq. of MA.



Fig. S33: FT-IR measurements of (A), MA and the complex consisting of (A) and 2 eq. MA.

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9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.1 f1 (ppm)

**Fig. S34:** <sup>1</sup>H-NMR titration of compound **A** (2.5 mM) with malonic acid in  $H_2O/D_2O$  (9/1) and 2% DMSO-d<sub>6</sub>, a) compound **A**, b) compound **A** + 0.33 eq. MA, c) compound **A** + 0.66 eq. MA, d) compound **A** + 1 eq. MA, e) compound **A** + 2 eq. MA.

## 12. References

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