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A transparent photo-responsive organogel based on a glycoluril supergelator

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Supporting Information

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Materials and General Methods

All reactions were carried out under an atmosphere of argon unless otherwise indicated. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Analytical thin-layer chromatography (TLC) was performed on Silicycle 60 F254 glass-baked plates. Column chromatography was performed using Silicycle R10030B 60 Å 230-400 mesh silica gel. ^{1}H NMR (300 K) and ^{13}C NMR (300 K) spectra were recorded at 600 MHz and 150 MHz respectively, using a Bruker DRX-600 spectrometer equipped with a 5 mm QNP probe. Chemical shifts of ^{1}H NMR and ^{13}C NMR are given in ppm by using $CHCl_3$ or DMSO as references (7.26 ppm, 2.50 ppm respectively for ^{1}H spectrum, and 77.16 ppm, 39.52 ppm respectively for 13C spectrum). Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). MALDI-TOF spectra and high-resolution mass spectra (HRMS) were recorded on an Applied Biosystems Voyager STR (2) apparatus and an Agilent ESI-TOF mass spectrometer respectively. UV measurements were performed with a 1mm cuvette on a Varian Cary 50 Bio UV-VIS Spectrophotometer. Irradiation (365 nm) was conducted with a Blak-Ray Long Wave Ultraviolet Lamp, Model B-100 AP). Irradiation (450nm) was conducted with a Luxeon LXML-PR01-0500 LED. During irradiation the samples were kept in a nontransparent box which was kept at 20 °C by a constant flow of pressurized air. Cavitand **19** was prepared according to literature procedures.[1]

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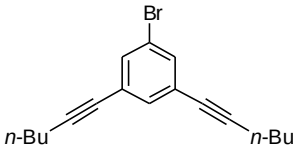
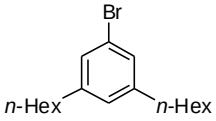
Synthethic procedures

1-Bromo-3,5-di(hex-1-ynyl)benzene (21)



1,3,5-Tribromobenzene (**7**) (10 g, 60.9 mmol), $Pd(PPh_3)_4$ (1.40 g, 1.22 mmol), CuI (464 mg, 2.44 mmol), and 1-hexyne (**6**) (15.4 mL, 11 g, 134.0 mmol) were added to diisopropylamine (250 mL) and the mixture was heated to 65 ºC for 12 h under N_2 atmosphere. After that time, the reaction mixture was allowed to cool to ambient temperature. The solvent was removed *in vacuo*. A saturated aqueous solution of NH_4Cl (500 mL) and EtOAc (250 mL) were added, and the phases were separated. The aqueous phase was extracted with EtOAc (2x 250 mL), the organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude material was purified by column chromatography (SiO_2, hexane) to afford 11 g (57%) of **21** as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42 (d, *J*=1.4, 2H), 7.32 (t, *J*=1.4, 1H), 2.39 (t, *J*=7.1, 4H), 1.63 – 1.53 (m, 4H), 1.50 – 1.42 (m, 4H), 0.94 (t, *J*=7.2, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 133.29, 133.17, 125.89, 121.54, 92.32, 78.69, 77.46, 30.60, 21.96, 19.02, 13.58; HRMS(ESI-TOF) calcd. for $C_{18}H_{22}Br$ $[MH]^+$: 317.0887, found: 317.0899.

1-Bromo-3,5-di(hexyl)benzene (9)



Bromobenzene **21** (11 g, 34.67 mmol), was dissolved in a mixture of THF (40 mL) and MeOH (40 mL). To this solution Pd on coal (1.8 g, 10%) was added. The mixture was stirred for 2 h under H_2 pressure (50 bar) at 20 ºC. The solvent was removed *in vacuo* and the crude material was

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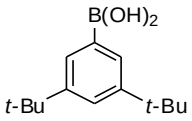
pre-purified by column chromatography (SiO_2, hexane).to obtain 10 g of a mixture of 3,5-dihexylbromobenzene and debrominated product (ca. 1:1) was directly used for the next step.

Boronic acid 22



Was synthesized according to literature[2], but the chromatography was omitted and the crude material directly used for the next step (yield: quant.).

Bromobenzene 10

To a mixture of 1,3,5-tribromobenzene (**5**) (4.67 g, 14.8 mmol), $Pd(PPh_3)_4$ (855 mg, 0.74 mmol) and boronic acid **22** (7.39 g, 31.6 mmol) in dry toluene (60 mL) was 1M aqueous Na_2CO_3 solution (49 mL). The mixture was degassed by applying three vacuum/N_2-cycles and afterwards refluxed for 21 h. The mixture was diluted with water and extracted with ethyl acetate (4x), dried over sodium sulfate, filtered and the solvent was removed under vacuum. Purification by column chromatography (800 mL silica gel) using hexane as an eluent yielded compound **10** (3.77 g, 48%). ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.69-7.67 (m, 1H), 7.67 (d, *J* = 1.5 Hz, 2H), 7.49 (t, *J* = 1.7 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 4H), 1.39 (s, 36H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=151.6, 145.1, 139.7, 129.1, 125.8, 123.0, 122.3, 122.0, 35.2, 31.7. HRMS(ESI-TOF) calcd. for C34H46Br [M+H]: 533.2777, found: 533.2789.

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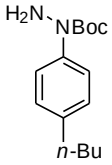
General procedure for the preparation of the hydrazinecarboxylates

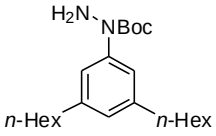
To a 0.4 M solution of bromobenzene (1.0 eq.) in anhydrous toluene was added $Pd(OAc)_2$ (0.03 – 0.10 eq.), 2-di-t-butylphosphino-2′,4′,6′-triisopropylbiphenyl (**12**) (0.03 – 0.10 eq.), K_2CO_3 (1.0 eq.) and t-butyl carbazate (**11**) (2.0 eq.) and the suspension stirred at 80 ºC for 20 h. The reaction mixture was allowed to cool to ambient temperature, diluted with aqueous NH_4Cl solution and extracted with ethyl acetate (3x). The combined organic fractions were dried over sodium sulfate, filtered and the solvent was removed under vacuum. The crude material was purified by silica gel column chromatography.

***n*-Butyl 1-(4-butylphenyl)hydrazinecarboxylate 13**



According to the general procedure n-Butylbromobenzene (**8**) (7.06 mL, 8.53 g, 40.00 mmol) was reacted with $Pd(OAc)_2$ (269 mg, 1.20 mmol), 2-di-t-butylphosphino-2′,4′,6′-triisopropylbiphenyl (**12**) (510 mg, 1.20 mmol), K_2CO_3 (5.53 g, 40 mmol) and t-butyl carbazate (**11**) (10.58 g, 80.00 mmol). Purification by chromatography (hexane/EtOAc = 95/5) afforded 2.26 g (21%) of **13** as pale yellow resin. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (d, J=8.2, 2H), 7.11 (d, J=8.3, 2H), 4.43 (s, 2H), 2.58 (t, J=6.0, 2H), 1.58 (dt, J=6.6, 13.2, 2H), 1.50 (s, 9H), 1.39 – 1.27 (m, 2H), 0.92 (dd, J=7.0, 7.7, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 140.70, 139.37, 128.79, 128.10, 123.40, 81.52, 35.00, 33.56, 28.30, 22.28, 13.90; ESI-TOF: m/z: 287.1735 ($[MNa]^+$, $C_{15}H_{24}N_2NaO_2^+$, calc. 287.173).

***tert*-Butyl 1-(3,5-dihexylphenyl)hydrazinecarboxylate 14**



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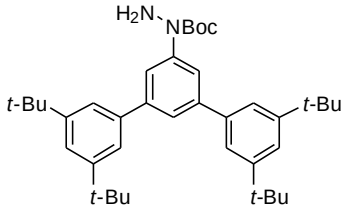
9.5 g of the 10 g mixture of 3,5-dihexylbromobenzene and debrominated product obtained were dissolved in toluene (300 mL). $Pd(OAc)_2$ (983 mg, 4.38 mmol), 2-(di-*tert*-butylphosphino)-2',4',6'-*iso*-propylbiphenyl (1.86 g, 4.38 mmol), K_2CO_3 (6.05 g, 43.8 mmol), and *tert*-butyl carbazate (4.25 g, 32.12 mmol) were added and the mixture was heated to 80 ºC for 21 h. After cooling to 20 ºC, EtOAc (200 mL) and a saturated aqueous solution of NH_4Cl (500 mL) were added and the phases were separated. The aqueous phase was extracted with EtOAc (3x 200 mL), the organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude material was purified by column chromatography (SiO_2, hexane/EtOAc = 95/5) to afford 2.13 g (17% based on **7**) of **14** as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.09 (s, 2H), 6.78 (s, 1H), 2.60 – 2.53 (t, *J*=7.9, 4H), 1.66 – 1.59 (m, 4H), 1.52 (s, 9H), 1.40 – 1.29 (m, 10H), 0.91 (t, *J*=6.9, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.37, 142.77, 125.14, 120.92, 81.46, 35.99, 31.72, 31.42, 29.06, 28.35, 22.58, 14.07. HRMS(ESI-TOF) calcd. for $C_{23}H_{41}N_2O_2Na$ $[MNa]^+$: 399.2982, found: 399.2954.

Hydrazinecarboxylate 15:



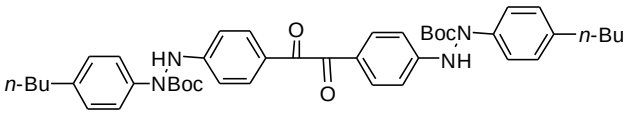
According to the general procedure bromobenzene **10** (3.75 g, 7.03 mmol) was reacted with $Pd(OAc)_2$ (79 mg, 0.35 mmol), 2-di-t-butylphosphino-2',4',6'-triisopropylbiphenyl (**12**) (149 mg, 0.35 mmol), K_2CO_3 (972 mg, 7.03 mmol) and t-butyl carbazate (**11**) (1.86 g, 14.1 mmol). Purification by chromatography (toluene/EtOAc = 1/0 → 20/1) afforded 1.10 g (27%) of **15**. ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.65 (d, *J* = 1.5 Hz, 2H), 7.54 (t, *J* = 1.6 Hz, 1H), 7.48 (t, *J* = 1.8 Hz, 2H), 7.46 (d, *J* = 1.8 Hz, 4H), 4.57 (bs, 2H), 1.59 (s, 9H), 1.40 (s, 36H). ^{13}C NMR (150 MHz, $CDCl_3$)

δ=151.2, 143.6, 143.1, 140.8, 123.5, 122.0, 121.6, 121.6, 100.0, 81.9, 35.0, 31.6, 28.5. HRMS(ESI-TOF) calcd. for C39H56N2O2Na [M+Na]: 607.4234, found: 607.4243.

General procedure for the preparation of benzil hydrazines

To a 0.08 M solution of the hydrazine (2.0 eq.) in anhydrous toluene was added 4,4'-dibromobenzil (1.0 eq.), $Pd(OAc)_2$ (0.08 eq.), tri-tert-butylphosphonium tetrafluoroborate (0.08 eq) and Cs_2CO_3 (2.5 eq.). After stirring at rt for 1 h, the mixture was heated to 110 ºC for 12 h. The reaction mixture was allowed to cool to ambient temperature, diluted with aqueous NH_4Cl solution and extracted with ethyl acetate (3x). The combined organic fractions were dried over sodium sulfate, filtered and the solvent was removed under vacuum. The crude material was purified by silica gel column chromatography.

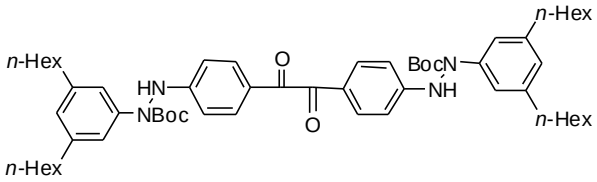
Benzil hydrazine 16



According to the general procedure hydrazine **13** (2.16 g, 8.17 mmol) was reacted with 4,4'-dibromobenzil (1.5 g, 4.08 mmol), $Pd(OAc)_2$ (73 mg, 0.33 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (95 mg, 0.33 mmol), and Cs_2CO_3 (3.32 g, 10.2 mmol). Purification by chromatography (hexane/EtOAc = 95/5) afforded 1.50 g (50%) of **16**.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, J=7.7, 4H), 7.38 (d, J=8.0, 4H), 7.12 (d, J=8.0, 4H), 6.83 (d, J=7.7, 4H), 6.73 (s, 2H, NH), 2.57 (t, J=7.7, 4H), 1.62 – 1.54 (m, 4H), 1.40 (s, 18H), 1.38 – 1.30 (m, 4H), 0.91 (td, J=1.1, 7.3, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 193.43, 153.59, 153.56, 140.02, 139.58, 132.28, 128.58, 126.12, 121.81, 112.04, 82.80, 34.97, 33.52, 28.07, 22.28, 13.90; ESI-TOF: m/z: 735.4108 ($[MH]^+$, $C_{44}H_{55}N_4O_6^+$, calc. 735.4116).

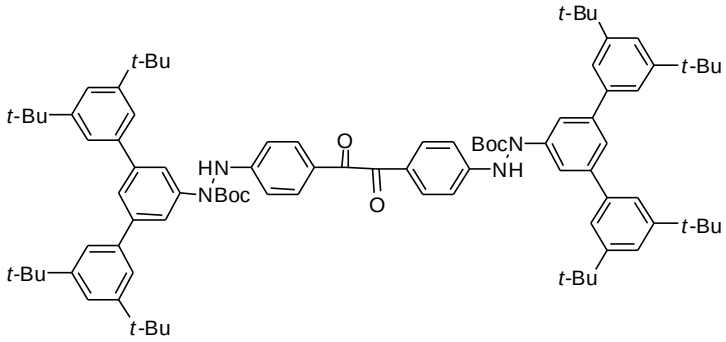
Benzil hydrazine 17



According to the general procedure hydrazine **14** (2.13 g, 5.66 mmol) was reacted with 4,4'-dibromobenzil (1.04 g, 2.82 mmol), $Pd(OAc)_2$ (50 mg, 0.22 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (65 mg, 0.22 mmol), and Cs_2CO_3 (2.30 g, 7.05 mmol). Purification by chromatography (hexane/EtOAc = 9/1 to 8/2) to afford 2.08 g (77%) of **17**.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 – 7.87 (d, *J*=8.9, 4H), 7.11 (s, 4H), 6.84 (d, *J*=8.9, 4H), 6.80 (s, 2H), 2.55 (t, *J*=7.9, 8H), 1.58 (dt, *J*=15.5, 7.6, 8H), 1.41 (s, 18H), 1.34 – 1.24 (m, 32H), 0.87 (t, *J*=7.0, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 193.40, 153.69, 143.37, 143.35, 141.75, 132.23, 125.98, 125.56, 119.31, 112.04, 82.66, 35.95, 31.62, 31.37, 28.97, 28.06, 22.53, 14.01. ESI-TOF: m/z: 959.6618 ($[MH]^+$, $C_{60}H_{87}N_4O_6^+$, calc. 959.6620).

Benzil hydrazine 18



According to the general procedure hydrazine **15** (380 mg, 0.65 mmol) was reacted with 4,4'-dibromobenzil (120 mg, 0.325 mmol), $Pd(OAc)_2$ (5.8 mg, 0.026 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (7.5 mg, 0.026 mmol), and Cs_2CO_3 (265 mg, 0.81 mmol).

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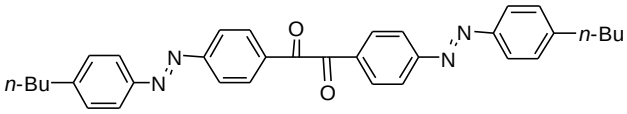
Purification by chromatography (hexane/EtOAc = 5/1) to afford 276 mg (62%) of **18**. ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.88 (d, *J* = 8.8 Hz, 4H), 7.65 (d, *J* = 1.5 Hz, 4H), 7.53 (t, *J* = 1.5 Hz, 2H), 7.46 (t, *J* = 1.7 Hz, 4H), 7.39 (d, *J* = 1.8 Hz, 8H), 6.91 (d, *J* = 8.9 Hz, 4H), 6.83 (s, 2H), 1.49 (s, 18H), 1.36 (s, 72H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=193.5, 153.8, 153.7, 151.4, 143.9, 142.7, 140.7, 132.4, 126.5, 124.2, 122.1, 121.9, 120.1, 112.5, 83.3, 35.1, 31.7, 28.4. HRMS(ESI-TOF) calcd. for C92H119N4O6 [M+H]: 1375.9124, found: 1375.9100.

General procedure for the preparation of the azobenzene benzils

To a 0.048 M solution of the benzil (1.0 eq.) in CH_2Cl_2 was added pyridine (2.4 eq.) and dropwise a 0.11 M solution of NBS (2.4 eq.) in CH_2Cl_2. After stirring at rt for 1 h, the solvent was removed under vacuum. The crude material was purified by silica gel column chromatography.

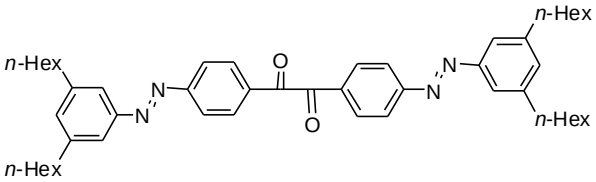
Azobenzene benzil 23



According to the general procedure benzil **16** (1.50 g, 2.04 mmol) was reacted with pyridine (0.4 mL, 388 mg, 4.90 mmol) and NBS (872 mg, 4.90 mmol). Purification by chromatography (hexane/EtOAc = 95/5 to CH_2Cl_2/MeOH = 95/5) afforded 1.00 g (90%) of **23** as orange solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.16 (d, J=8.4, 4H), 8.01 (d, J=8.4, 4H), 7.89 (d, J=8.3, 4H), 7.35 (d, J=8.2, 4H), 2.71 (t, J=6.0, 4H), 1.70 – 1.62 (m, 4H), 1.55 (s, 18H), 1.44 – 1.35 (m, 4H), 0.95 (t, J=7.4, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 193.50, 156.23, 150.73, 148.00, 133.35, 131.11, 129.27, 123.40, 123.17, 35.68, 33.35, 22.33, 13.92; ESI-TOF: m/z: 531.2731 ($[MH]^+$, $C_{34}H_{35}N_4O_2^+$, calc. 531.2754).

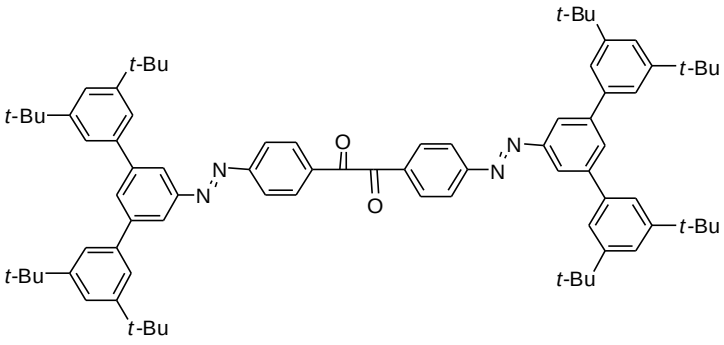
Azobenzene benzil 24



According to the general procedure benzil **17** (1.8 g, 1.88 mmol) was reacted with pyridine (0.36 mL, 356 mg, 4.5 mmol) and NBS (802 mg, 4.5 mmol). Purification by chromatography (hexane/CH_2Cl_2 = 7/3 to 1/1 to CH_2Cl_2 to CH_2Cl_2/MeOH = 95/5) afforded 1.21 g (85%) of **24** as orange solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.17 (d, *J*=8.8, 4H), 8.01 (d, *J*=8.8, 4H), 7.61 (d, *J*=1.4, 4H), 7.18 (s, 2H), 2.69 (t, *J*=7.9, 8H), 1.71 – 1.64 (m, 8H), 1.42 – 1.28 (m, 26H), 0.89 (t, *J*=7.1, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 193.48, 156.25, 152.87, 144.08, 133.83, 132.72, 131.11, 123.17, 120.72, 35.79, 31.69, 31.34, 28.98, 22.58, 14.08; ESI-TOF: m/z: 755.5263 ($[MH]^+$, $C_{50}H_{67}N_4O_2^+$, calc. 755.5258).

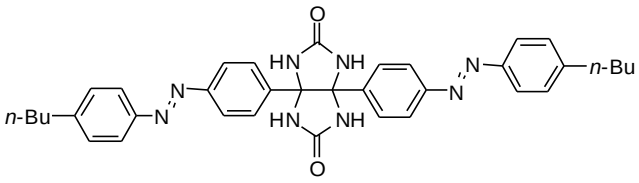
Azobenzene benzil 25



According to the general procedure benzil **18** (226 mg, 0.164 mmol) was reacted with pyridine (32 uL, 0.39 mmol) and NBS (70 mg, 0.39 mmol). Purification by chromatography (hexane/EtOAc = 30:1) afforded 77 mg (40%) of **25** as orange solid. ^{1}H NMR (600 MHz, $CDCl_3$)

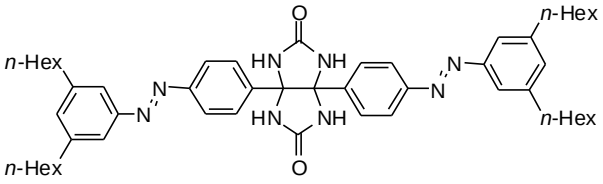
δ=8.22 – 8.19 (m, 4H), 8.14 (d, *J* = 1.7 Hz, 4H), 8.11 – 8.09 (m, 4H), 7.96 (t, *J* = 1.7 Hz, 2H), 7.54 (d, *J* = 1.8 Hz, 8H), 7.53 (t, *J* = 1.7 Hz, 4H), 1.42 (s, 72H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=193.6, 156.4, 153.5, 151.7, 144.4, 140.1, 134.3, 131.3, 130.6, 123.6, 122.3, 122.1, 121.1, 35.2, 31.7. HRMS(ESI-TOF) calcd. for C82H99N4O2 [M+H]: 1171.7762, found: 1171.7760.

Azobenzene glycoluril 4



Compound **23** (448 mg, 0.84 mmol), urea (243 mg, 4.05 mmol), and TFA (0.37 mL, 556 mg, 4.96 mmol) were suspended in benzene (20 mL) and the mixture was stirred for 4 days under reflux and azeotropic removal of water using a *Dean Stark* apparatus. The formed orange precipitate was filtered, thoroughly washed with CH_2Cl_2 to remove remaining starting material, washed with EtOH, and crystallized 2x from EtOH. Thus, 180 mg (35%) of pure **4** was obtained as orange solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.98 (s, 4H), 7.71 (d, J=8.1, 4H), 7.60 (d, J=8.4, 4H), 7.38 – 7.29 (m, 8H), 2.63 (t, J=7.6, 4H), 1.62 – 1.51 (m, 4H), 1.29 (dd, J=7.5, 14.7, 4H), 0.88 (t, J=7.4, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ = 160.49, 151.25, 150.05, 146.68, 141.33, 129.24, 128.31, 122.59, 121.53, 81.62, 34.62, 32.79, 21.70, 13.73; MALDI-TOF: m/z: 615.3 ($[MH]^+$, $C_{36}H_{39}N_8O_2^+$, calc. 615.32).

Glycoluril 3



Benzil **24** (500 mg, 0.66 mmol) was dissolved in benzene (23 mL) and urea (190 mg, 3.17 mmol), and TFA (0.21 mL, 382 mg, 3.89 mmol) were added. The mixture was stirred for 4 days under reflux and azeotropic removal of water using a *Dean Stark* apparatus. After 5 days urea (100

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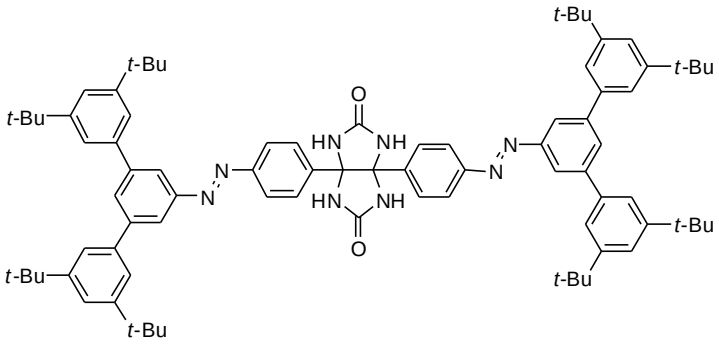
mg, 1.66 mmol), and TFA (0.21 mL, 382 mg, 3.89 mmol) were added again and the solution was stirred under reflux for another 12 h. The solvent was removed *in vacuo*. The residual orange wax was filtered, thoroughly washed with H_2O to remove remaining urea, and washed with ice cold Et_2O to remove residual starting material. Thus, 315 mg (57%) of pure **3** was obtained as orange waxy solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.99 (s, 4H), 7.59 (d, *J*=8.5, 4H), 7.40 (s, 4H), 7.34 (d, *J*=8.5, 4H), 7.14 (s, 2H), 2.57 (t, *J*=7.5, 8H), 1.52 (t, *J*=6.5, 8H), 1.28 – 1.17 (m, 26H), 0.81 (t, *J*=6.6, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.47, 151.92, 151.23, 143.38, 141.36, 128.24, 121.47, 119.80, 81.62, 34.79, 30.98, 30.64, 28.13, 21.93, 13.80.
MALDI-TOF: m/z: 839.6 ($[MH]^+$, $C_{52}H_{71}N_8O_2^+$, calc. 839.57).

Glycoluril 2



To a mixture of azo-benzil **25** (89 mg, 0.076 mmol) and urea (68 mg, 1.14 mmol) in dry benzene (3 mL) was added TFA (0.16 mL) and the suspension heated to reflux with azeotropic removal of water using a *Dean Stark* apparatus. After 24 and 48 h additional urea (68 mg, 1.14 mmol) and TFA (0.16 mL) were added. 9 h after the last addition, the solvents were removed under vacuum. The residue was dissolved in Et_2O and washed with water (3x), dried over sodium sulfate, filtered, silica gel was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (20 mL silica gel) using ethyl acetate/MeOH 100:0 → 99:1 as an eluent yielded compound **2** (75 mg, 79%) as an orange crystalline solid. ^{1}H NMR (600 MHz, $CDCl_3$ + d-MeOD) δ=8.00 (s, 4H), 7.85 (s, 2H), 7.76 (d, *J* = 8.2

Hz, 4H), 7.53 – 7.44 (m, 16H), 1.36 (s, 72H). ^{13}C NMR (150 MHz, $CDCl_3$) δ=^{13}C NMR (151 MHz, $CDCl_3$+ d-MeOD) δ 161.8, 153.1, 152.5, 151.4, 144.0, 140.1, 139.5, 129.8, 128.1, 122.8, 122.0, 121.9, 120.7, 82.8, 35.1, 31.6. HRMS(ESI-TOF) calcd. for C84H103N8O2 [M+H]: 1255.8198, found: 1255.8233.

Gelation experiments with compound 2

1.5 mg of compound **2** was suspended in the solvent and heated in a closed glass vial either till a clear solution was obtained or to the boiling temperature of the mixture by the use of a heatgun. The sample was allowed to return to 20 °C in the dark. There were four kind of results: 1) Gel formation at 20 °C (G); 2) a solution at 20 °C (S); 3) precipitation at 20 °C, although a clear solution was observed in the heated sample (P); 4) mainly insoluble at 20 °C and in the heated state (I). For results see Table 1 in the article.

TEM images

Carbon coated, 400 mesh, copper grids (Electron Microscopy Sciences, Hatfield PA) were attached to the edge of a small strip of double sided adhesive tape on a clean, glass, microscope slide and 1 µl of a hot toluene solution (0.1 % (w/v); 0.79 mM) of **2** was applied. The entire glass slide was then placed under vacuum (3 mbar) overnight. Grids were then individually removed and placed on droplets of 1% aqueous uranyl acetate (Ted Pella, Redding CA) for 2 minutes. Excess stain was wicked off and the grids allowed to dry. Grids were examined on a Philips CM100 electron microscope (FEI, Hillsbrough OR) at 80kV and images collected using a Megaview III ccd camera (Olympus Soft Imaging Solutions, Lakewood CO).

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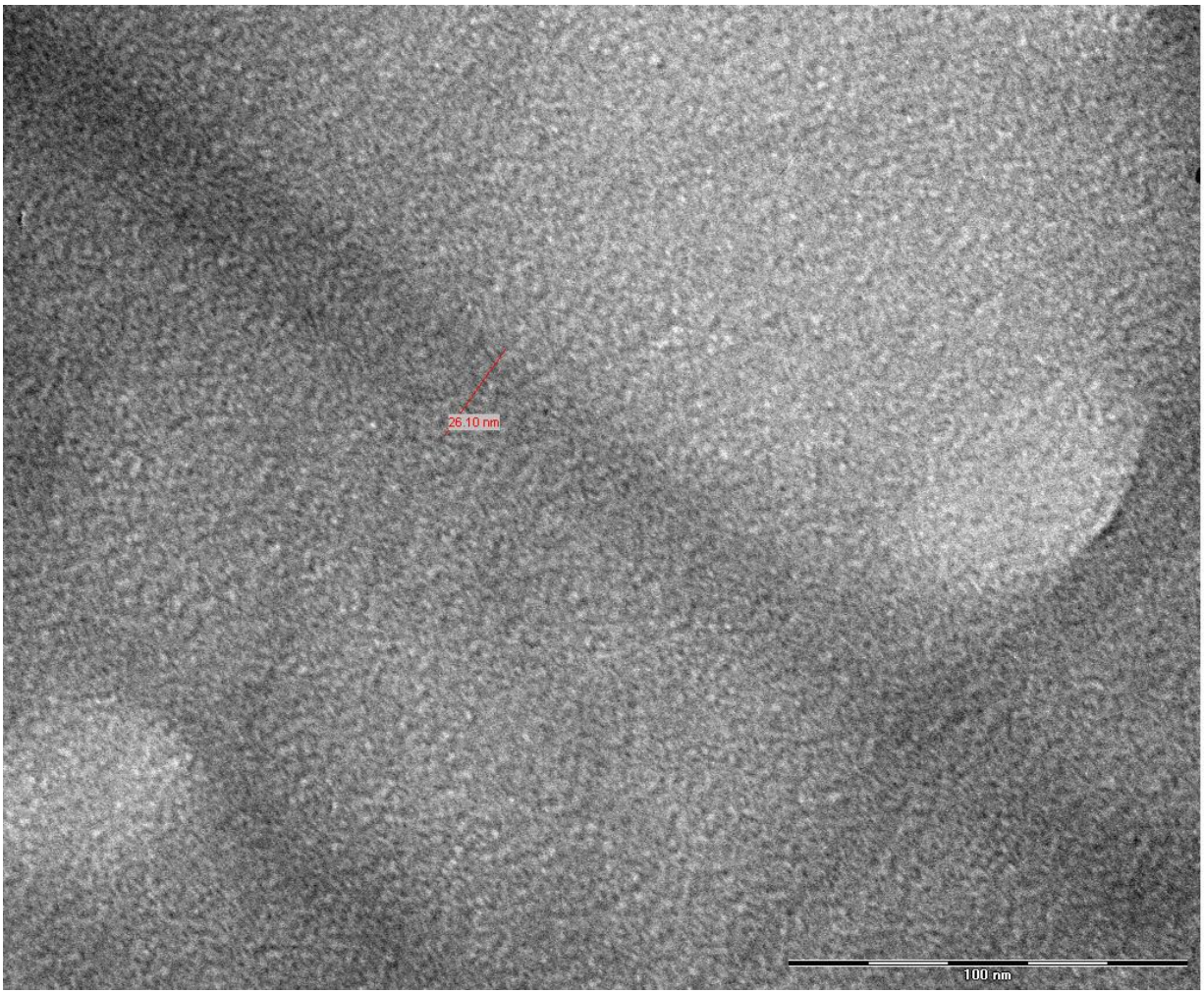

SIFigure 1. **Additional TEM-image** of xerogel obtained from organogel in toluene at 0.1 % (w/v) **2** after evaporation of the solvent under vacuum. magnification of 245,000.

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Discussion of the determination of *cis*/*trans*-ratios in the samples

Although a series of UV-VIS experiments were performed we were not able to obtain quantitative data about the stereomeric forms of the azobenzene moieties in the gel state and after irradiation with 365 nm. We obtained comparable UV-data to the azobenzene-containing gel described by Koumura and Tamaoki:[3] A decrease in the π-π*-absorption region (ca. 330 nm) and the n- π*absorption region (ca. 440 nm) was observed after radiation with 365 nm as shown in **SIFigure 2**. However, this is not the UV-VIS spectroscopical behavior that is expected for the transition from *trans*- to the *cis*-conformation of azobenzenes where a decrease of the π-π*-absorbtion region is accompanied by a significant *increase* of the n- π*absorption region. When measuring a diluted sample (0.002 % m/V) of azobenzene glycoluril **2** in a $CHCl_3$/MeOH (4 : 1) mixture this expected behavior is indeed observed: starting with strong absorption at 330 nm and low absorption at 440 nm, the first band decreases while the second increases with continued irradiation (365 nm) as shown in the **SIFigure 3**. Thus, the spectral changes associated with the transition from gel to sol state are overriding the spectral changes associated with the *trans*- to *cis*-conformational changes and the spectra recorded cannot be used for the assignment of stereomeric forms.

There is another difficulty that hampers monitoring the stereomeric forms of our azobenzene glycoluril **2** with UV-VIS methods: As both absorptions of the *trans*- as well as the *cis*-isomer overlap almost completely, each observed transition is a composite of the *trans*- and *cis*-forms. In order to assign spectral changes to percentage of isomeric forms one needs to know the spectral intensities of the pure *trans*- as well as the pure *cis*-form. This is impossible for compound **2**, as we cannot generate 100% of the *cis*-isomer.

We therefore turned to ^{1}H NMR as tool to investigate the *trans/cis* ratios of the gel and sol samples: Since the ^{1}H NMR of the gel and sol-samples in D_{12}-mesitylene (0.1 % m/V) were featureless we decided to add 40% (V/V) of D_8-THF to deaggregate the sample AFTER the sample was irradiated (**SIFigure 4**). This technique allowed the quantification of the stereomeric

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form of the azobenzene in the gel state (**SIFigure 5**), in the state where the self-supporting capability was lost (**SIFigure 6**), and the photostationary state at 365 nm irradiation (**SIFigure 8**) as well. We believe that the quantification of the *trans/cis* ratios by this method has the additional advantage that all three possible isomers (*trans/trans*, *trans/cis* and *cis/cis*) can be differentiated.

Interestingly attempts to convert samples after the phase transition (11% *cis/cis*-, 37% *trans/cis*- and 52% *trans/trans*-GU **2)** back to the *trans/trans*- isomeric gel by the use of irradiation with 450 nm – even after extended irradiation (8 h) – failed: 11% *cis/cis*- and 89% *trans/trans*-GU **2** were detected (**SIFigure 7**). Although the *cis/cis*-isomer resisted isomerisation by irradiation (450 nm), heating any sample (160 °C, 1min) and then allowing it to cool it to cool to 20 ºC in the dark, readily regenerated the (all *trans/trans*) gel-state.

The respective ratios under different illumination conditions are given in **SITable 1**.

SITable 1. The isomer distribution of a D12-mesitylene sample of 2 (0.1 % m/V) at different stages of the irradiation process. 40% (V/V) of d8-THF were added before NMR measurements.

Sample	Irradiation	State	Ratio[a] trans/trans	trans/cis	cis/cis
1	-	Gel	> 95	-	-
2	365 nm (7min)	Transition to Sol	52	37	11
3	365 nm (7min) then 450 nm (8 h)	Sol	89	-	11
4	365 nm (8 h)	Sol Photostationary	51	30	19
5	365 nm (8 h) then 160 °C (1 min)	Gel	> 95	-	-

[a] Ratios were determined by integration of corresponding peaks in the 1H-NMR spectra: signal at 7.95 ppm (2 H) for the *trans/trans*-compound; signals at 8.22 ppm (4H), 8.02 ppm (2 H) and 7.18 ppm (4 H) for the *trans/cis*-compound; signal at 6.45 ppm (2 H) for the *cis/cis*-compound.

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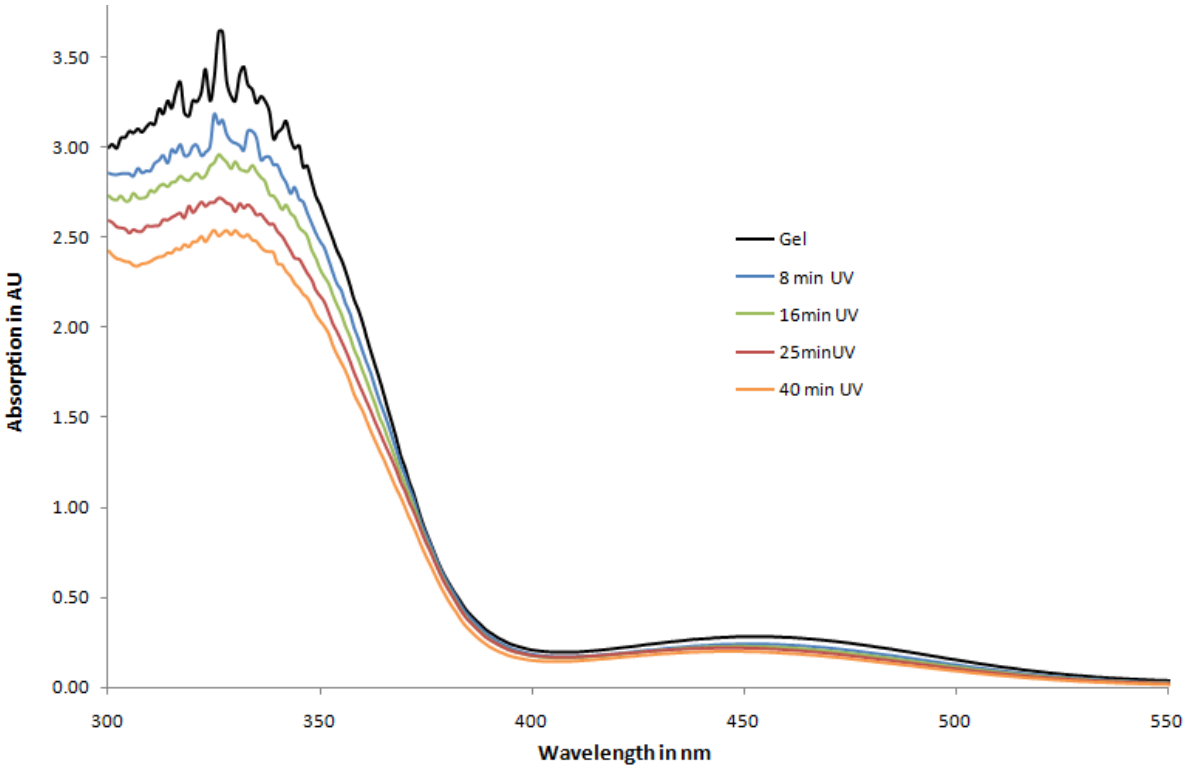
UV-VIS measurements



SIFigure 2. UV-VIS spectra of a sample of 2 at 0.1 % (m/V) in mesitylene in the gel state (black), after the phase transition to sol (blue) and the photo stationary state (orange) (Irradiation with 365 nm)

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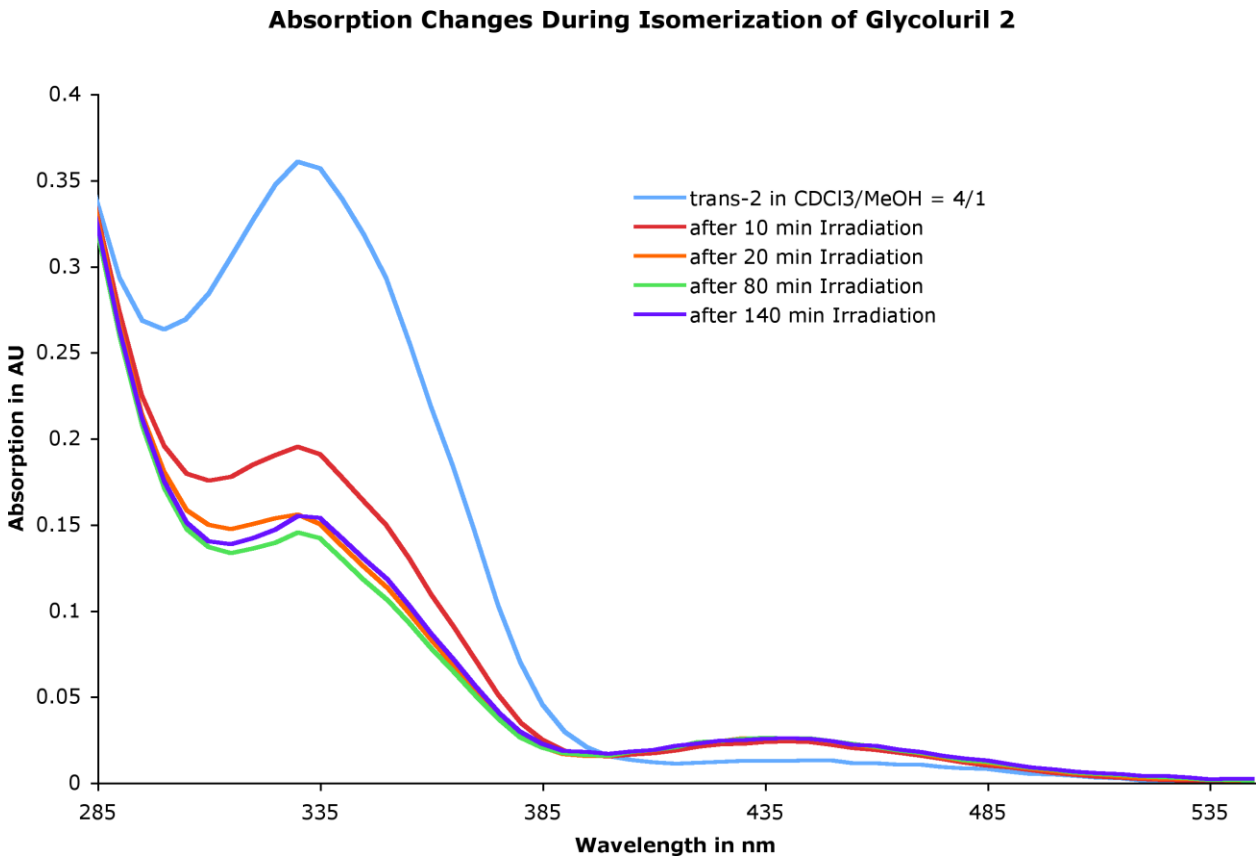
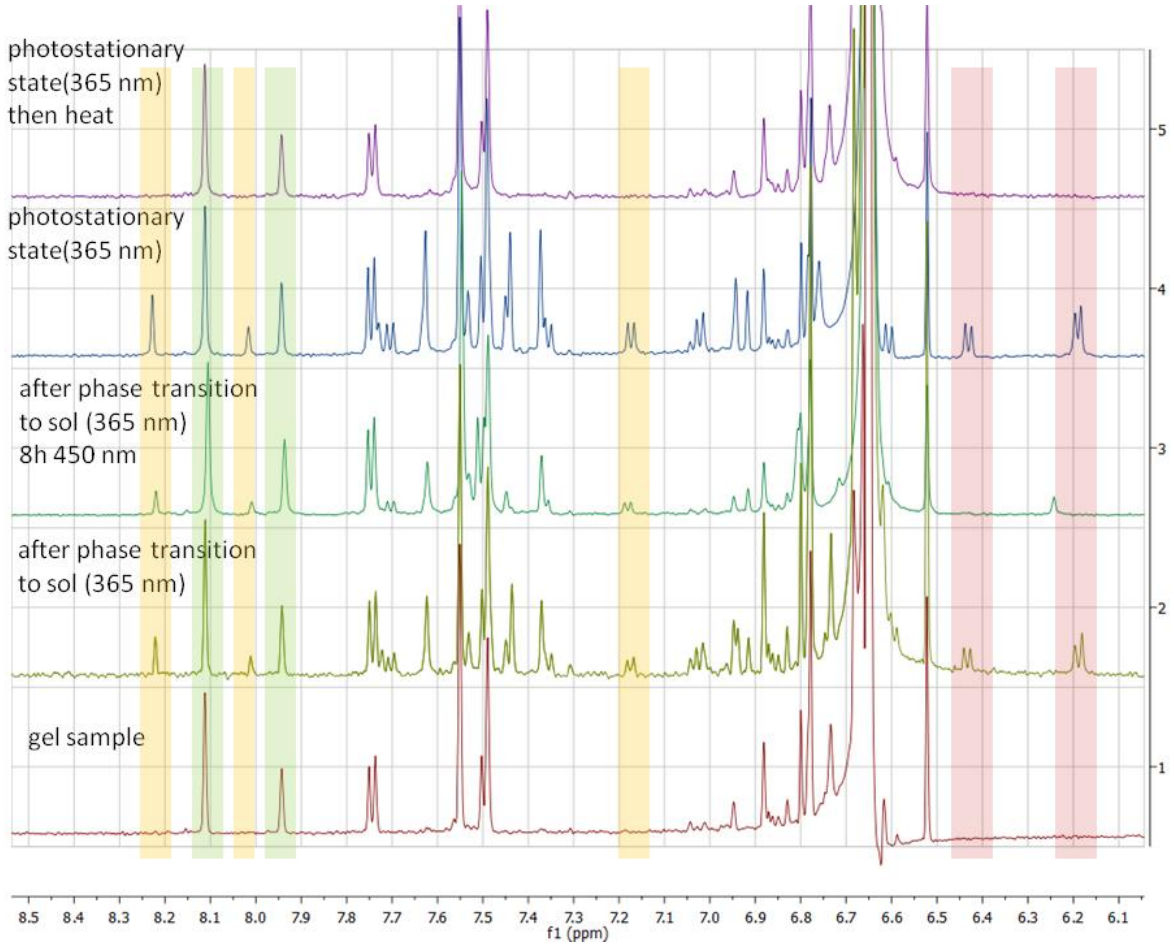


SIFigure 3. UV-VIS spectra of a sample of 2 at 0.002 % (m/V) in chloroform/methanol 4:1 before and after irradiation (365 nm).

NMR measurements of cis/trans-ratios



SIFigure 4. Overview of the ^{1}H-NMR spectra (D12-mesitylene sample of **2** (0.1 % m/V). 40% (V/V) of D8-THF were added just before NMR measurement.) for samples 1 – 5 (cf. **SITable 1**). Indicative peaks of the *trans/trans*-isomer of **2** are highlighted in green. Indicative peaks of the *trans/cis*-isomer of **2** are highlighted in yellow. Indicative peaks of the *cis/cis*-isomer of **2** are highlighted in red.

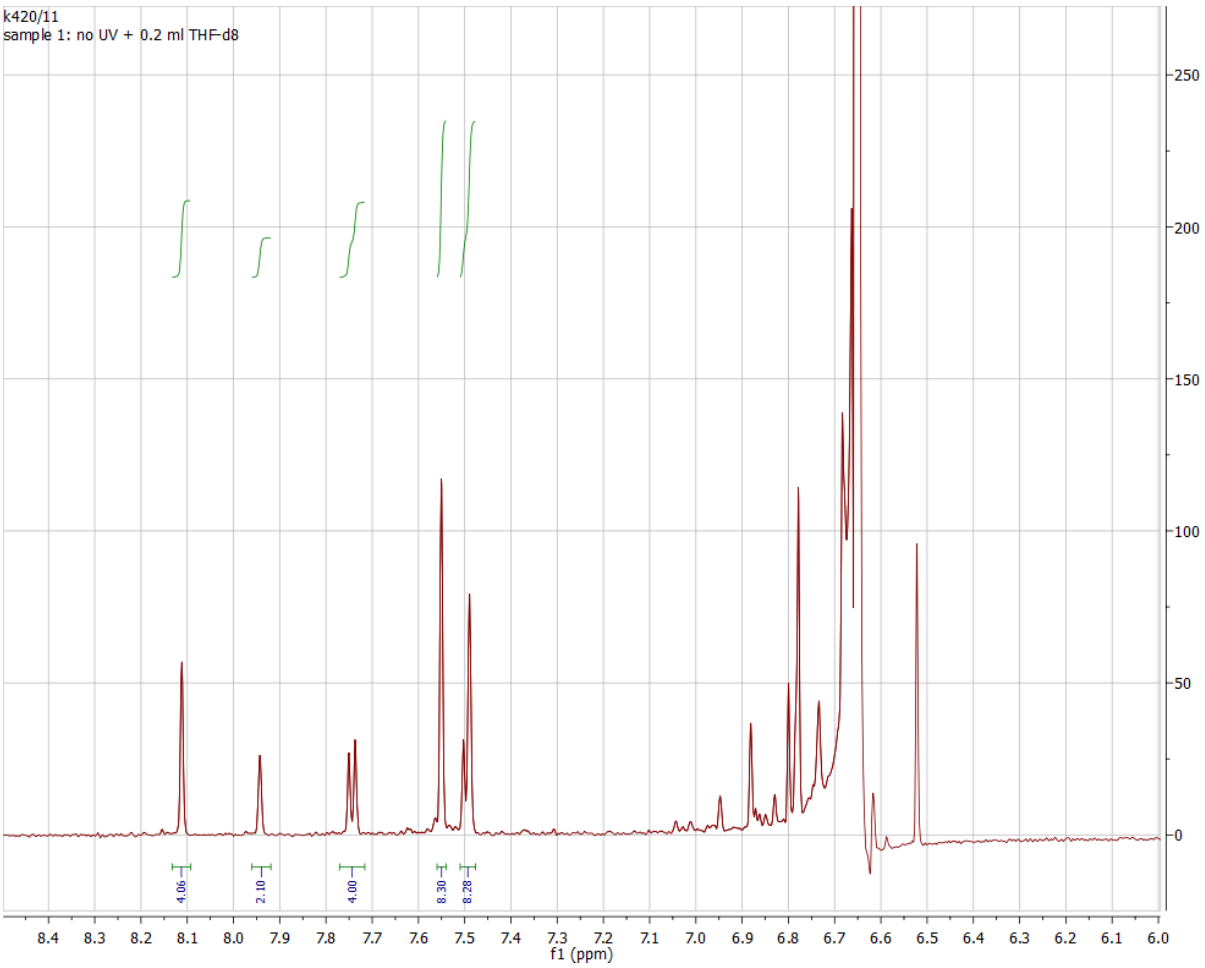


Figure 5. Integrated ^{1}H-NMR spectrum of a D12-mesitylene gel sample of **2** (0.1 % m/V). 40% (V/V) of D8-THF were added before NMR measurement.

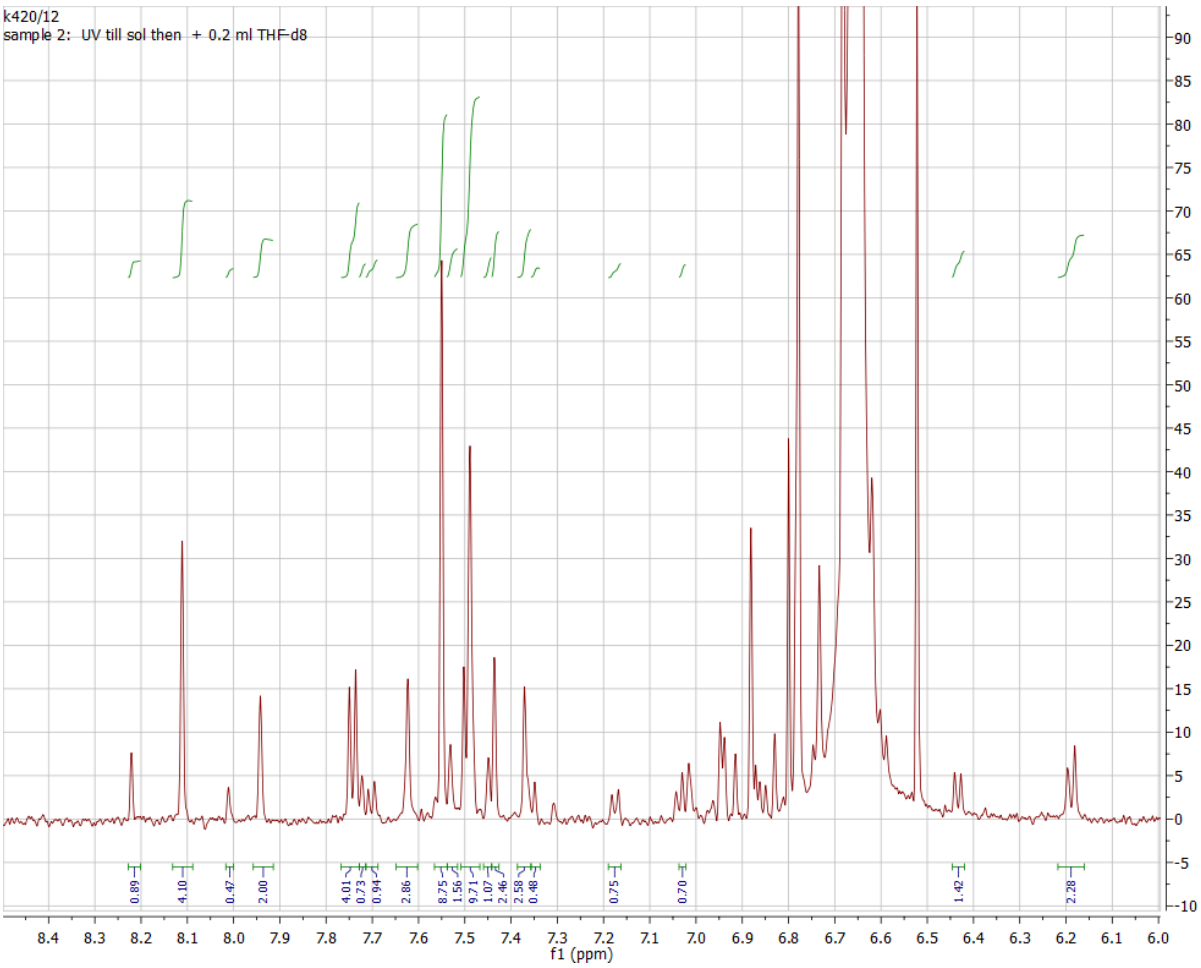


Figure 6. Integrated ^{1}H-NMR spectrum of a D12-mesitylene sample of **2** (0.1 % m/V) right after the gel/sol transition by irradiation with 365 nm. 40% (V/V) of D8-THF were added before NMR measurement.

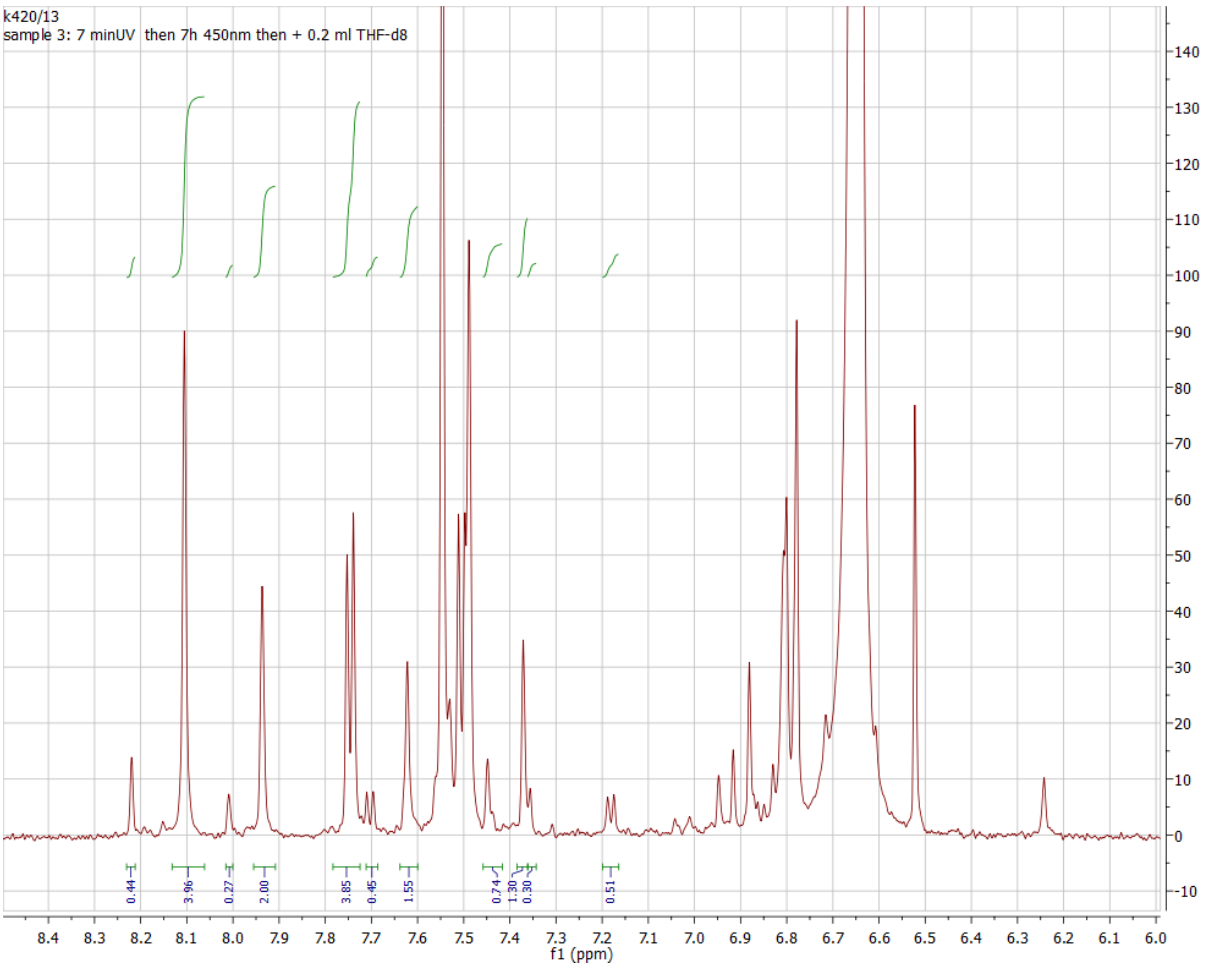


Figure 7. Integrated ^{1}H-NMR spectrum of a D12-mesitylene sample of **2** (0.1 % m/V) after the gel/sol transition by irradiation with 365 nm followed by irradiation with 450 nm (8 h). 40% (V/V) of D8-THF were added before NMR measurement.

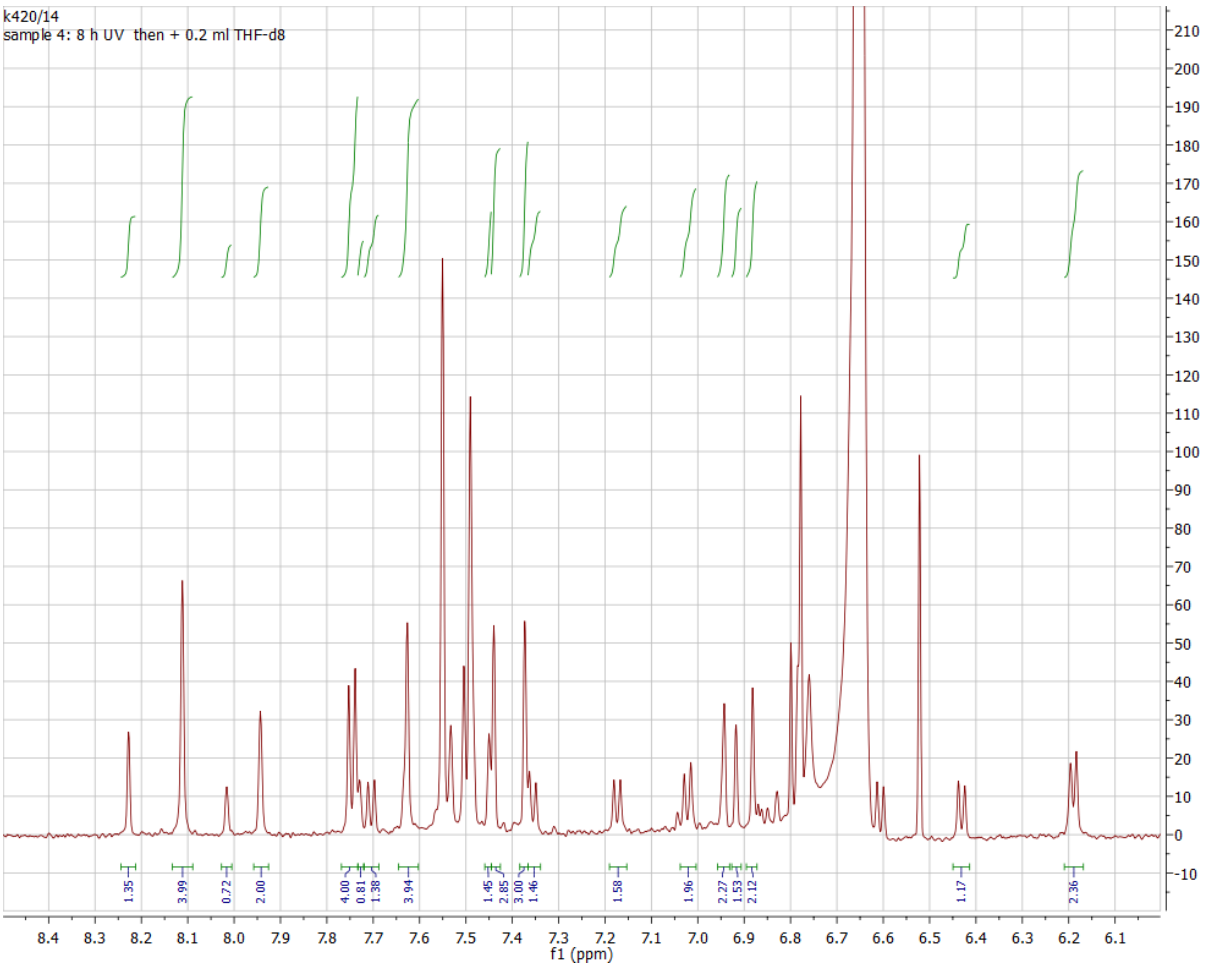
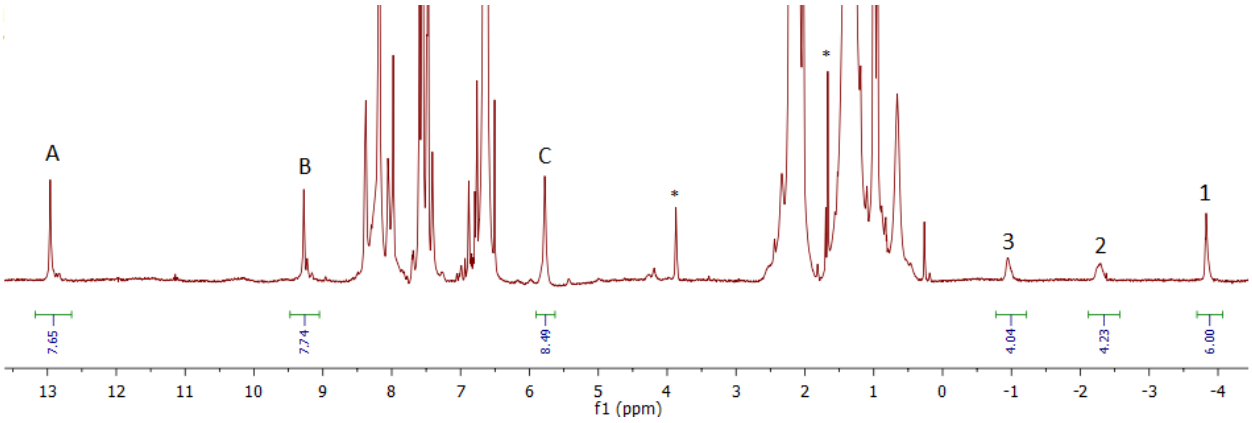


Figure 8. Integrated ^{1}H-NMR spectrum of a D12-mesitylene sample of **2** (0.1 % m/V) at the photo stationary state after irradiation with 365 nm (8 h). 40% (V/V) of D8-THF were added before NMR measurement.

NMR spectrum of assembly 20



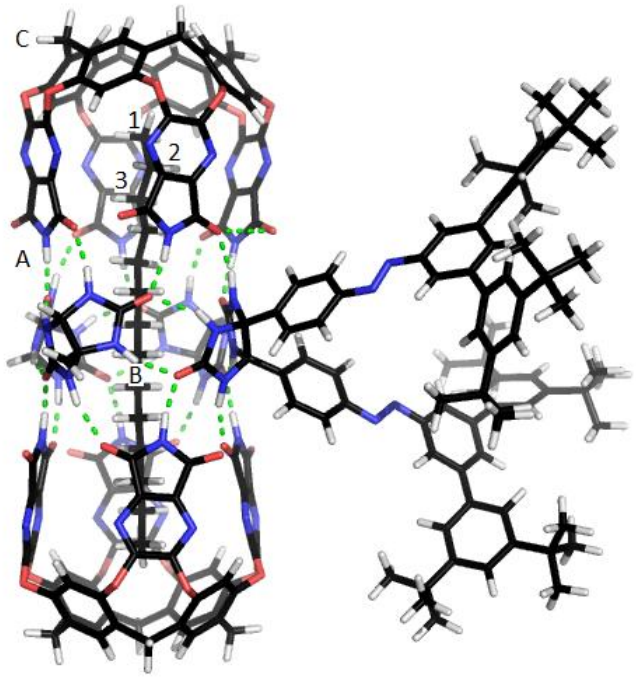


Figure 9. Integrated ^{1}H-NMR spectrum of a D12-mesitylene sample of **2** (0.1 % m/V) after addition of cavitand **19** and tetradecane. The extended assembly **20** is formed with 4 glycoluril units of **2** incorporated and tetradecane serving as the guest. Indicative signals are assigned to the extended capsular structure shown below. For clarity, only one azobenzene glycoluril **2** is shown completely. Traces of ethyl acetate are labeled with an asterix.

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Determination of minimum required concentrations of cavitand 19 to inhibit gel formation

To a mesitylene-gel sample of **2** (2 mg/ 0.50 mL, 0.4 % w/v, 0.0016 mmol) incremental amounts (50 µL) of a solution of **2** (2 mg/ 0.50 mL, 0.4 % w/v, 0.0016 mmol), cavitand **19** (2.7 mg, 0.0016 mmol), guest n-tetradecane (0.2 µL, 0.0008 mmol) in 500 µL of mesitylene were added. The sample was heated by the use of a heat gun until a homogenous solution was obtained. The sample was allowed to cool to 20 °C in the dark. After the addition of 300 µL, the gel sample lost its ability to support its own weight. At this point the sample (800 µL) contained a total of 0.00256 mmol of **2**, 0.00096 mmol of **19**, and 0.00048 mmol n-tetradecane. The formation of the extended capsule **20** (0.00048 mmol), which contains 2 eq. of **19**, and 4 eq. of **2,** and 1 eq. of n-tetradecane, leaves 0.00064 mmol or 0.8 mg of **2** in 0.8 mL of solution. This corresponds to a concentration of 0.1 % (w/v).

Addition of TBAF to a gel sample

A gel sample was prepared by dissolving 2.0 mg of **2** (0.0016 mmol) in 0.50 mL of hot mesitylene and allowing it to cool to 20 °C. To this gel sample 15 µl (0.00016 mmol) of a hot TBAF solution (3.0 mg $TBAF{\cdot}H_2O$ in 1.0 ml mesitylene) was added, the mixture heated by the use of a heat gun to obtain a homogenous solution. After allowing the sample to cool to 20 °C, its ability to support its own weight was tested by turning the sample upside down. After the addition of a total of 75 µl TBAF solution (0.00080 mmol) the gel lost its ability to support its own weight.

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References

1. T. Heinz, D. M. Rudkevich and J. Rebek, *Nature*, 1998, **394**, 764-766.

2. N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chemistry – A European Journal*, 2007, **13**, 4433-4451.

3. N. Koumura, M. Kudo and N. Tamaoki, *Langmuir*, 2004, **20**, 9897-9900.