

Electronic Supporting Information

for

Responsive Aggregation-Induced Emissive Supramolecular Gels based on bis-Cyanostilbene Derivatives

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Contents	Page
1 Materials and methods, synthesis of 1-3	S2 - S4
2 ¹ H and ¹³ C-NMR spectra of 1-3	S5 - S7
3 Gelation experiment	S8
4 SEM and TEM images of gels of 1	S9
5 UV-Vis absorption and fluorescence spectra of 1-3 in THF/water mixtures	S10
6 Temperature-dependent ¹ H-NMR spectra	S11 - S12
7 Temperature dependent FT-IR spectra of the toluene gel 1	S13
8 ¹ H-NMR spectral changes of 1 upon photoirradiation in DMSO solution	S14
9 ¹ H-NMR spectra of the toluene gel 1 after irradiation	S15
10 ¹⁹ F-NMR spectrum of the toluene gel 1 after its exposure to TFA vapors	S16
11 Effect of TFA addition on 1	S17 - S18
12 Additional reference	S19

Materials and Methods

All reagents and solvents are obtained from commercial supplies and used directly without further purification unless otherwise stated. The solvents for spectroscopic studies are purified according to standard methods. Melting points were determined on a KER-3100-08s heating stage with a microscope and are uncorrected. ^1H and ^{13}C -NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts, in ppm, are referred to TMS as internal standard. UV-Vis absorption spectra were recorded on a Shimadzu 3600 UV-Vis-near-IR spectrophotometer. The solvents for spectroscopic studies were spectroscopic grade and used as received. The spectra were recorded in quartz glass cuvettes and the extinction coefficients were calculated according to Lambert-Beer's law. FT-IR spectra were recorded on gels with a closed IR cell equipped with dried CaF_2 windows on a Bruker Optics VERTEX 80v apparatus. For solid samples, the powder was simply deposited between two dried KBr pellets. Fluorescence spectroscopic studies were performed on a Shimadzu RF-5301PC spectrofluorophotometer. SEM pictures were taken using a JEOL JEM-6700F scanning electron microscope with 3 kV operating voltage. TEM was performed on a JEOL JEM-2100F transmission electron microscope. Samples were prepared by wiping a small amount of gel samples onto a carbon-coated copper grid followed by naturally evaporating the solvent. Elemental analysis was carried out using a Vario micro cube elemental analyzer.

***N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-octyloxyisophthalamide (1)**

5-(octyloxy)isophthalic acid¹ (0.2 g, 0.68 mmol) and dry triethylamine (0.19 mL, 1.36 mmol) were dissolved in dry CH_2Cl_2 (20 mL) under N_2 atmosphere and to it oxalyl chloride (0.16 mL, 1.51 mmol) was added dropwise. The reaction mixture was stirred for 30 minutes at room temperature and then was refluxed for 1 hr. After cooling the reaction mixture, solvent was removed under reduced pressure to yield a white solid which was dried thoroughly under vacuum and used in the next step without further purification.

2-Phenyl-3-(4-aminophenyl)acrylonitrile² (0.45 g, 2.05 mmol) and triethylamine (0.29 mL, 2.08 mmol) were dissolved in dry CH_2Cl_2 (30 mL). A solution of 5-(octyloxy)isophthaloyl chloride (0.23 g, 0.68 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise for 1 hr while the mixture was stirred vigorously under a nitrogen atmosphere. The reaction mixture was refluxed for 5 hrs. The solvent was evaporated in vacuo to yield a red oil. The residue was taken up in ethanol (50 mL) to precipitate the product. The precipitate was filtered and washed several

times with ethanol and water, respectively. The product was obtained as a yellow solid (0.39 g, yield 82%).

M.p.: 227 °C; FT-IR (KBr) ν/cm^{-1} = 3323, 3180, 3093, 3034, 2927, 2855, 2216, 1671, 1592, 1516; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ/ppm = 10.69 (s, 2H, NH-), 8.17 (s, 1H, ArH), 8.00 (d, J = 5.9, 10H, ArH), 7.77 (d, J = 7.9, 4H, ArH), 7.73 (s, 2H, CH-), 7.53 (t, J = 7.6, 4H, ArH), 7.45 (t, J = 7.3, 2H, ArH), 4.16 (t, J = 6.2, 2H, CH_2 -), 1.84-1.76 (m, 2H, CH_2 -), 1.52-1.44 (m, 2H, CH_2 -), 1.32 (dd, J = 23.6, 16.4, 8H, CH_2 -), 0.87 (t, J = 6.5, 3H, CH_3 -); $^{13}\text{C-NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ/ppm = 165.47, 159.14, 142.82, 141.66, 136.70, 134.50, 130.51, 129.65, 129.50, 126.11, 120.69, 119.93, 118.70, 117.31, 108.91, 68.56, 31.69, 29.13, 25.95, 22.50, 14.35; Anal. Calcd for $\text{C}_{46}\text{H}_{42}\text{N}_4\text{O}_3$: C, 79.06; H, 6.06; N, 8.02. Found: C, 79.04; H, 5.99; N, 7.98; MS: m/z = 698.01.

***N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-dodecyloxyisophthalamide (2)**

5-(dodecyloxy)isophthalic acid³ (0.2 g, 0.57 mmol) and DMF (0.01 mL, 0.13 mmol) were dissolved in dry CH_2Cl_2 (20 mL) under N_2 atmosphere and to it oxalyl chloride (0.11 mL, 1.28 mmol) was added dropwise. The reaction mixture was stirred for 30 minutes at room temperature and then was refluxed for 1 hr. After cooling the reaction mixture, solvent was removed under reduced pressure to yield a light green solid which was dried thoroughly under vacuum and used in the next step without further purification.

2-Phenyl-3-(4-aminophenyl)acrylonitrile² (0.38 g, 1.73 mmol) and triethylamine (0.25 mL, 1.79 mmol) were dissolved in dry CH_2Cl_2 (30 mL). A solution of 5-(dodecyloxy)isophthaloyl chloride (0.22 g, 0.57 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise for 1 hr while the mixture was stirred vigorously under a nitrogen atmosphere. The reaction mixture was refluxed for 5 hrs. The solvent was evaporated in vacuo to yield a red oil. The residue was taken up in ethanol (50 mL) to precipitate the product. The precipitate was filtered and washed several times with ethanol and water, respectively. The product was obtained as a yellow solid (0.32 g, yield 74%).

M.p.: 202 °C; FT-IR (KBr) ν/cm^{-1} = 3321, 3173, 3094, 3047, 2924, 2853, 2215, 1671, 1590, 1516; $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ/ppm = 10.68 (s, 2H, NH-), 8.17 (s, 1H, ArH), 8.00 (d, J = 4.7, 10H, ArH), 7.77 (d, J = 7.8, 4H, ArH), 7.73 (s, 2H, CH_2 -), 7.52 (t, J = 7.6, 4H, ArH), 7.45 (t, J = 7.3, 2H, ArH), 4.16 (t, J = 6.0, 2H, CH_2 -), 1.84-1.75 (m, 2H, CH_2 -), 1.51-1.42 (m,

2H, CH₂-), 1.30 (d, *J* = 59.2, 16H, CH₂-), 0.84 (t, *J* = 6.6, 3H, CH₃-); ¹³C-NMR (126 MHz, DMSO-*d*₆) δ/ppm = 165.42, 159.11, 142.75, 141.68, 136.65, 134.51, 130.49, 129.61, 129.46, 126.07, 120.64, 119.94, 118.68, 117.28, 108.85, 68.64, 31.79, 29.56, 29.26, 29.12, 26.00, 22.58, 14.39; Anal. Calcd for C₅₀H₅₀N₄O₃: C, 79.55; H, 6.68; N, 7.42. Found: C, 79.67; H, 6.65; N, 7.36; MS: *m/z* = 754.03.

***N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-butyloxyisophthalamide (3)**

5-(butyloxy)isophthalic acid⁴ (0.2 g, 0.84 mmol) and dry triethylamine (0.24 mL, 1.72 mmol) were dissolved in dry CH₂Cl₂ (20 mL) under N₂ atmosphere and to it oxalyl chloride (0.16 mL, 1.86 mmol) was added dropwise. The reaction mixture was stirred for 30 minutes at room temperature and then was refluxed for 1 hr. After cooling the reaction mixture, solvent was removed under reduced pressure to yield a white solid which was dried thoroughly under vacuum and used in the next step without further purification.

2-Phenyl-3-(4-aminophenyl)acrylonitrile² (0.55 g, 2.50 mmol) and triethylamine (0.35 mL, 2.51 mmol) were dissolved in dry CH₂Cl₂ (30 mL). A solution of 5-(butyloxy)isophthaloyl chloride (0.23 g, 0.84 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise for 1 hr while the mixture was stirred vigorously under a nitrogen atmosphere. The reaction mixture was refluxed for 5 hrs. The solvent was evaporated in vacuo to yield a red oil. The residue was taken up in ethanol (50 mL) to precipitate the product. The precipitate was filtered and washed several times with ethanol and water, respectively. The product was obtained as a yellow solid (0.44 g, yield 82%).

M.p.: 264 °C; FT-IR (KBr) ν/cm⁻¹ = 3324, 3175, 3094, 3035, 2956, 2873, 2218, 1672, 1592, 1519, 1450; ¹H-NMR (500 MHz, DMSO-*d*₆) δ/ppm = 10.69 (s, 2H, NH-), 8.18 (s, 1H, ArH), 8.00 (d, *J* = 5.2, 10H, ArH), 7.77 (d, *J* = 7.4, 4H, ArH), 7.74 (d, *J* = 1.2, 2H, CH-), 7.53 (t, *J* = 7.6, 4H, ArH), 7.45 (t, *J* = 7.3, 2H, ArH), 4.18 (t, *J* = 6.4, 2H, CH₂-), 1.82-1.76 (m, 2H, CH₂-), 1.56-1.47 (m, 2H, CH₂-), 0.98 (t, *J* = 7.4, 3H, CH₃-); ¹³C-NMR (126 MHz, DMSO-*d*₆) δ/ppm = 165.46, 159.14, 142.80, 141.67, 136.68, 134.51, 130.51, 129.63, 129.48, 126.10, 120.68, 119.95, 118.70, 117.30, 108.90, 68.37, 31.18, 19.23, 14.18; Anal. Calcd for C₄₂H₃₄N₄O₃: C, 78.48; H, 5.33; N, 8.72. Found: C, 78.45; H, 5.34; N, 8.76. MS: *m/z* = 641.98.

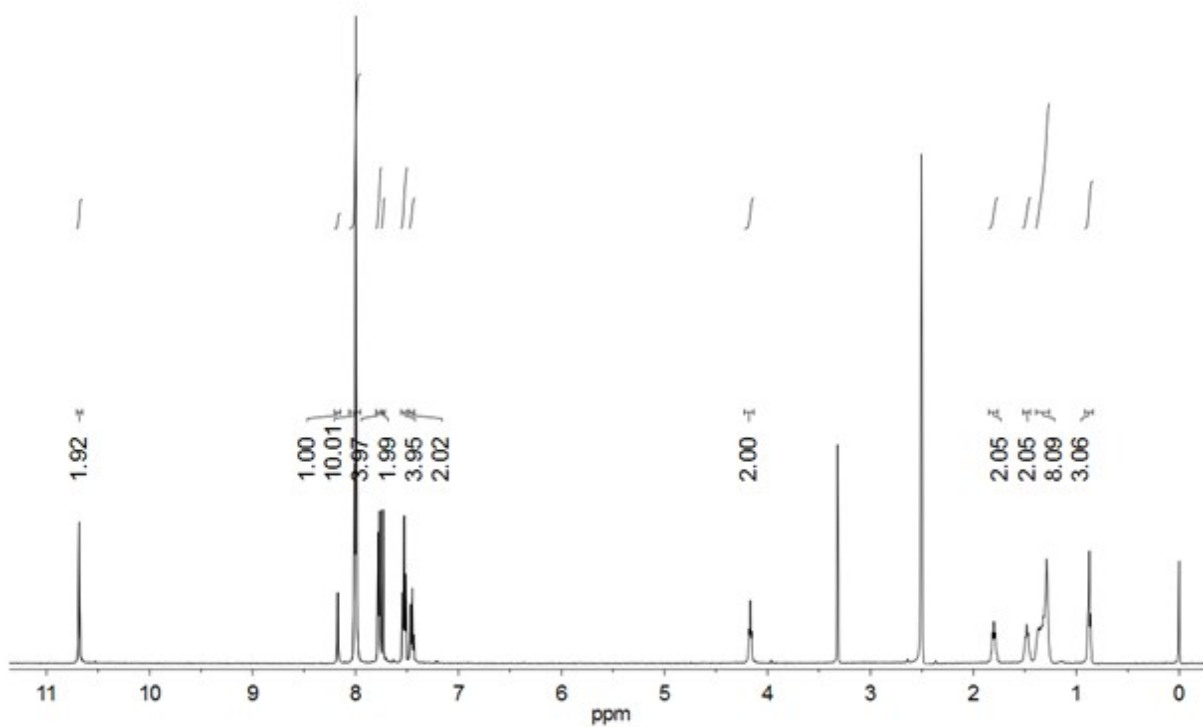


Fig. S1 ¹H-NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-octyloxyisophthalamide (**1**) in DMSO-*d*₆.

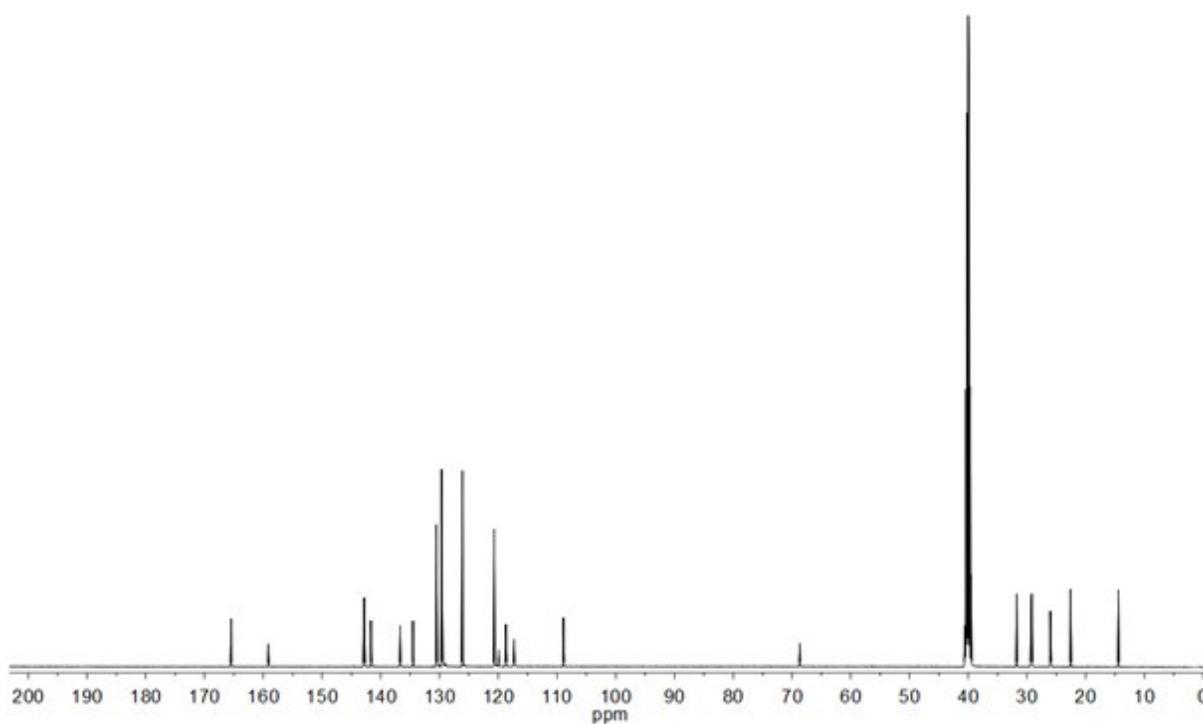


Fig. S2 ¹³C-NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-octyloxyisophthalamide (**1**) in DMSO-*d*₆.

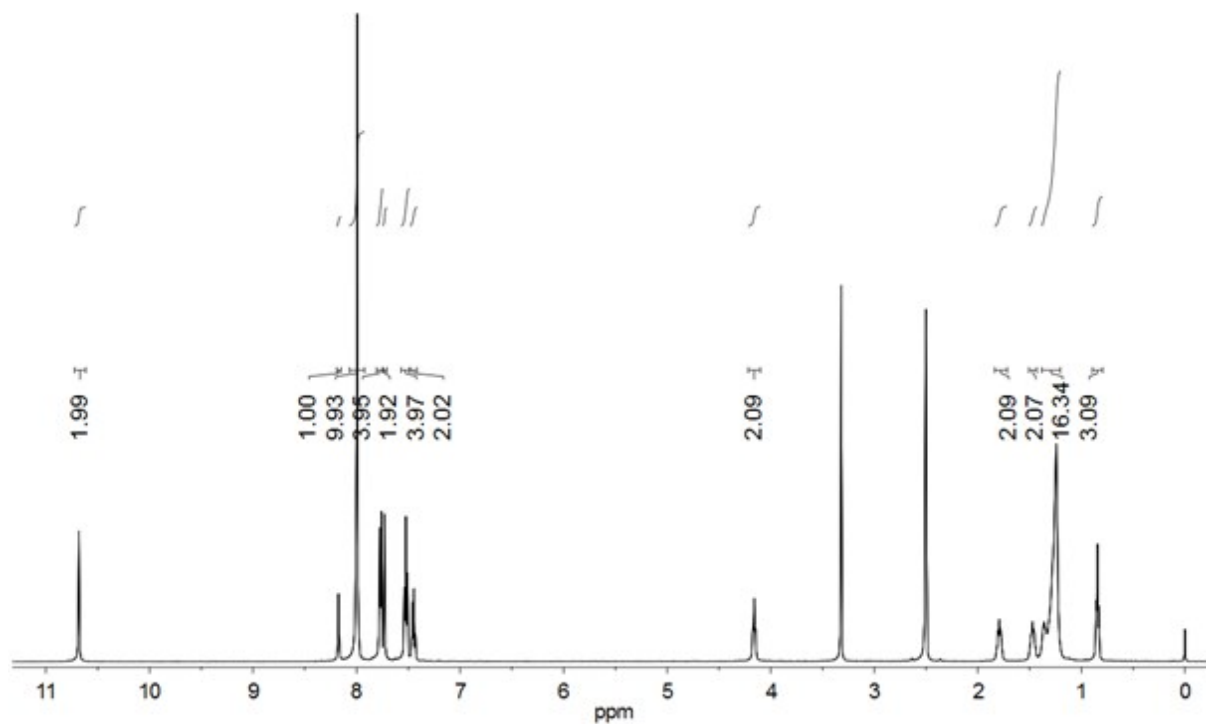


Fig. S3 ^1H -NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-dodecyloxyisophthalamide (**2**) in $\text{DMSO-}d_6$.

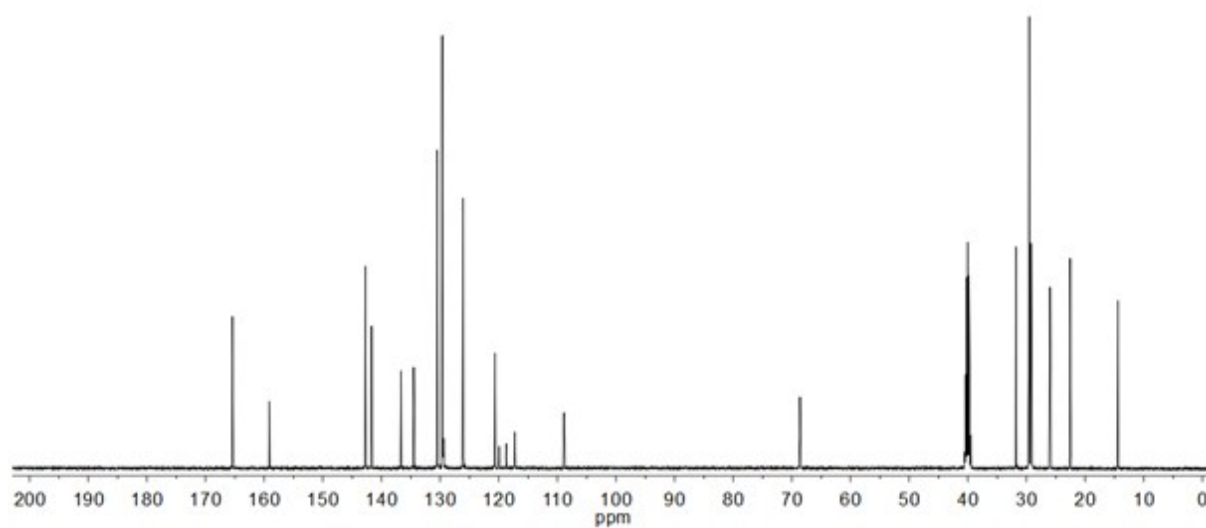


Fig. S4 ^{13}C -NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-dodecyloxyisophthalamide (**2**) in $\text{DMSO-}d_6$.

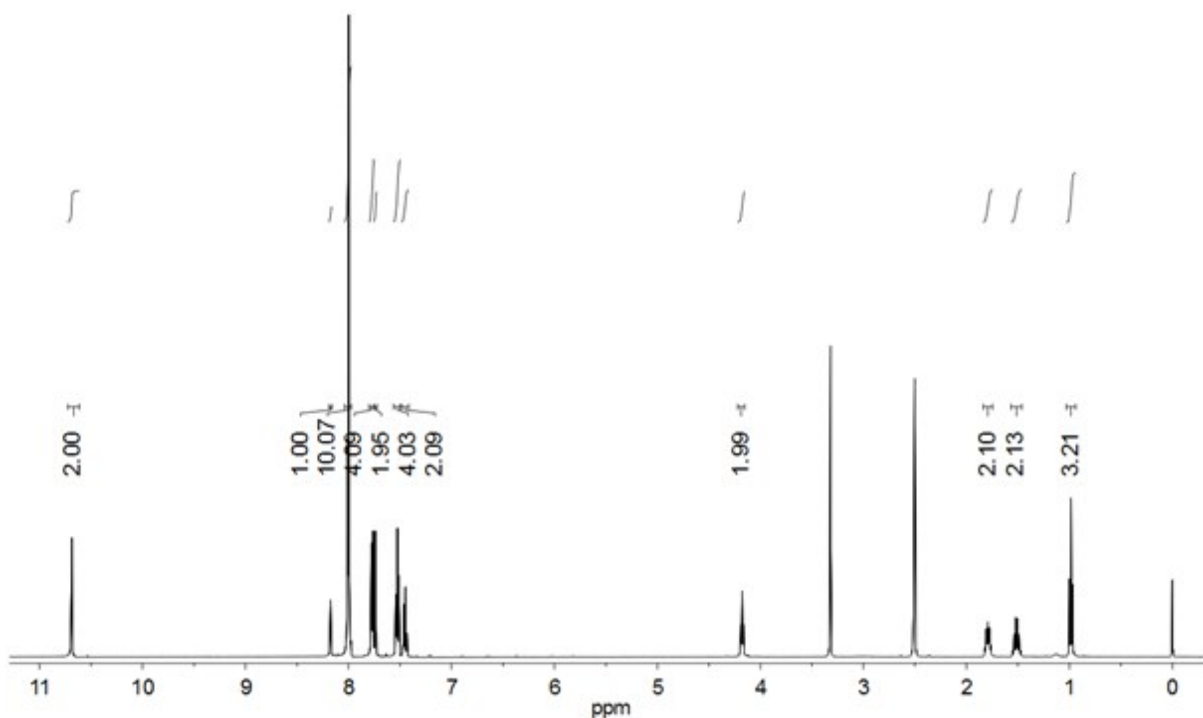


Fig. S5 ^1H -NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-butyloxyisophthalamide (**3**) in $\text{DMSO-}d_6$.

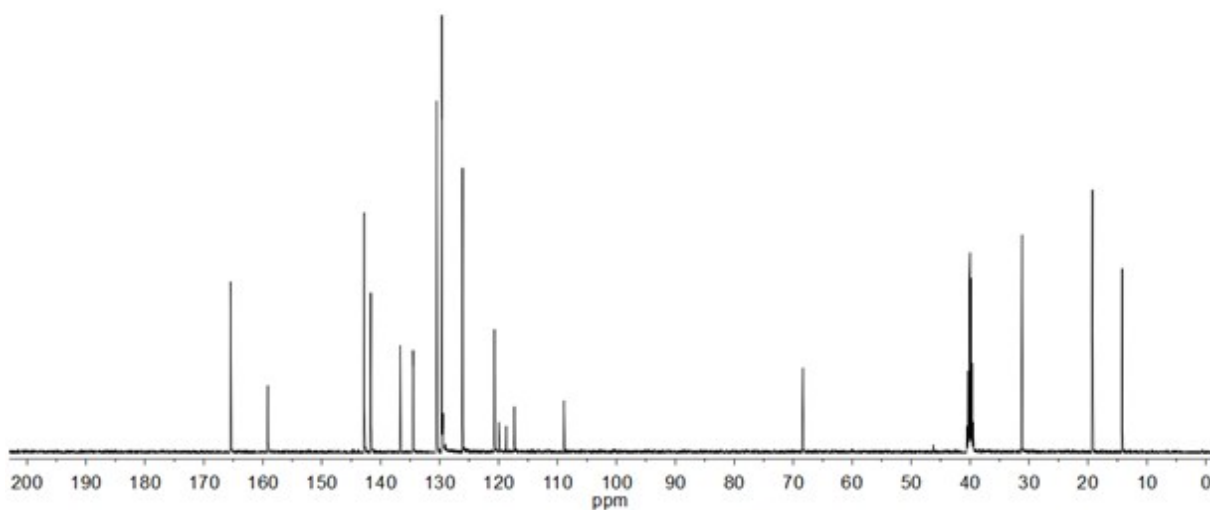


Fig. S6 ^{13}C -NMR spectrum of *N,N'*-bis(4-(2-cyano-2-phenylvinyl)phenyl)-5-butyloxyisophthalamide (**3**) in $\text{DMSO-}d_6$.

Gelation experiment

In a typical gelation test, a weighed amount of the gelator was mixed with a measured volume of the selected solvent in a test tube, which was capped and heated in an oil bath until the compound dissolved. After the solution was allowed to stand at room temperature, the sample was sonicated for *ca.* 60 seconds. Finally the test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G), insoluble material (I), or solution (S) was determined.

Gel–sol photoswitching experiments

A toluene gel of *Z,Z*- **1** (4.1 mM) were made in a 1 mm quartz cuvette. Then the cuvette was placed upside down at a distance of 5 cm from the 365 nm hand-held UV lamp (1.2 mW/cm²) under atmospheric conditions and irradiated. The resulting solution was then heated to reobtain the gel upon cooling to room temperature.

Table S1 Gelation properties and *cgc* of **1-3** in various organic solvents at 25°C.^[a]

Solvent	1 (<i>cgc</i>) ^a	2 (<i>cgc</i>)	3 (<i>cgc</i>)
Methanol	I	I	I
Acetonitrile	I	I	I
Acetone	I	I	I
Dichloromethane	I	I	I
Chloroform	I	I	I
1,2-Dichloroethane	I	I	I
Ethyl acetate	I	I	I
DMSO	S	S	S
DMF	S	S	S
THF	S	S	S
1,4-Dioxane	S	S	S
Benzene	G (4.2)	G (5.9)	I
Toluene	G (3.3)	G (6.3)	I
<i>o</i> -Xylene	G (3.5)	G (3.5)	I
<i>m</i> -Xylene	G (2.9)	G (3.6)	I
<i>p</i> -Xylene	G (2.9)	G (3.9)	I
Bromobenzene	G (8.3)	G (10.0)	G (5.0)
Chlorobenzene	G (7.7)	G (7.1)	I

^[a] The values in parentheses are *cgc* (mg mL⁻¹). G: gel; S: solution; I: insoluble.

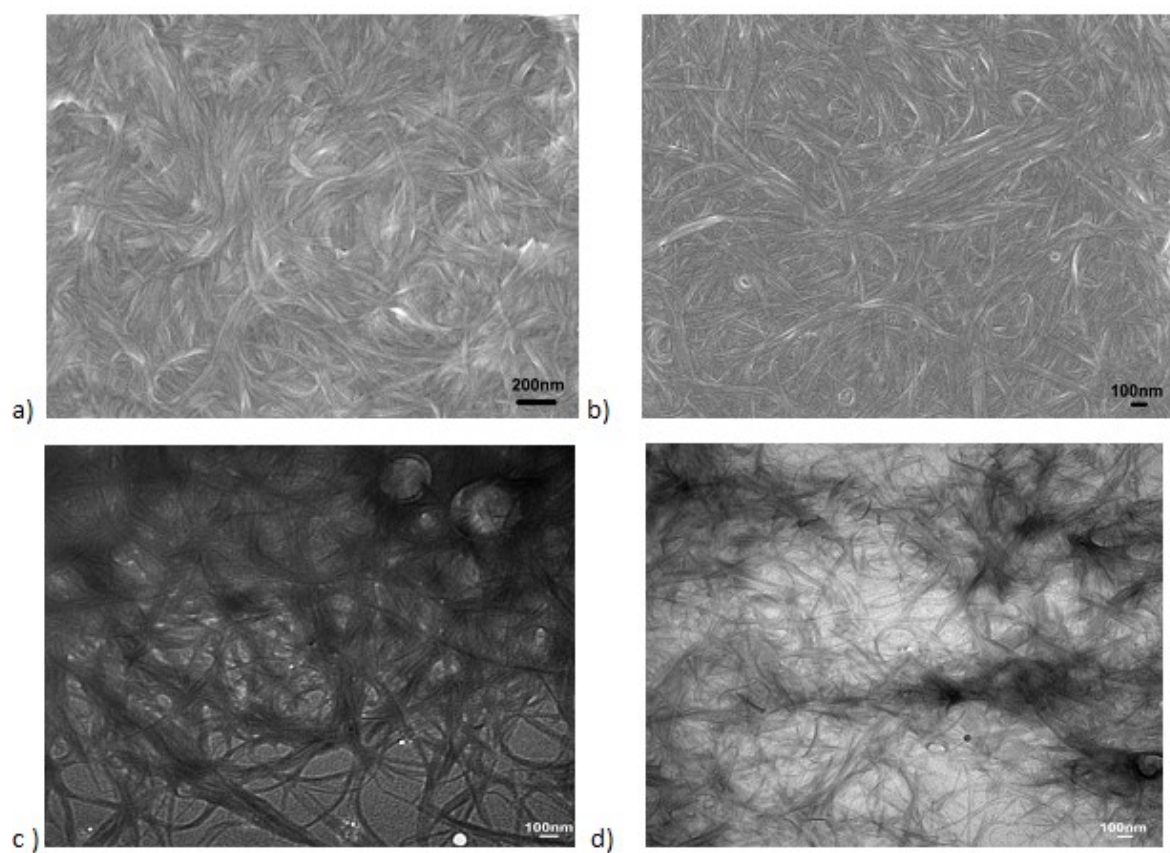
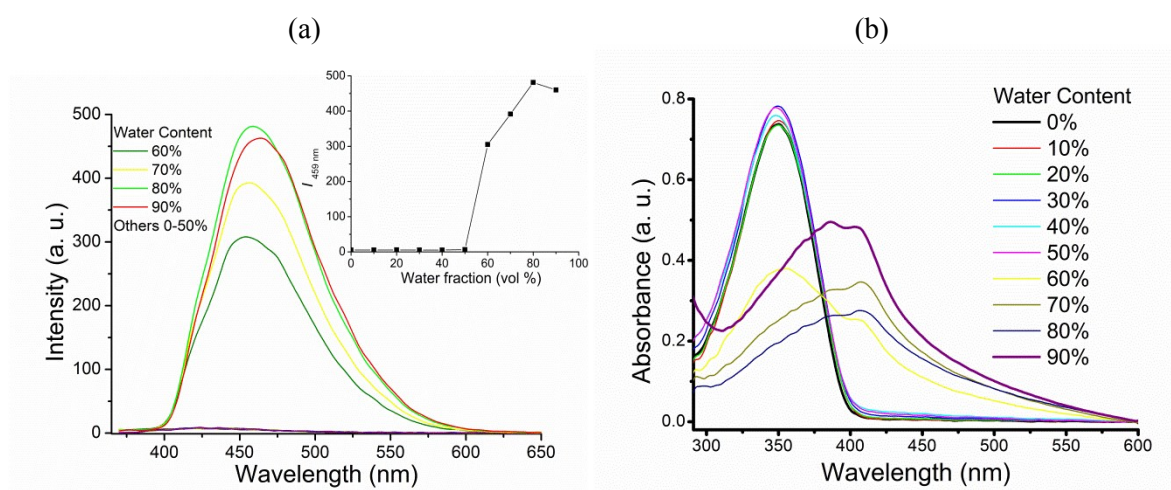


Fig. S7 SEM images of gels of **1** in a) toluene and b) bromobenzene; TEM images of gels of **1** in c) *o*-xylene and d) chlorobenzene.

Sample preparation for AIE measurement

Stock THF solutions of the cyanostilbene derivatives **1-3** with a concentration of 1×10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 1×10^{-5} M solutions with different water fractions (0-90 vol%). Emission spectra of the resulting solutions or suspensions were then recorded immediately.



F

fig. S8 (a) Emission and (b) UV-Vis absorption spectra of **2** in THF/water mixtures with different water volume fractions. Inset shows the changes at the emission maximum intensity of **2** ($[2] = 1 \times 10^{-5}$ M) as a function of water fraction.

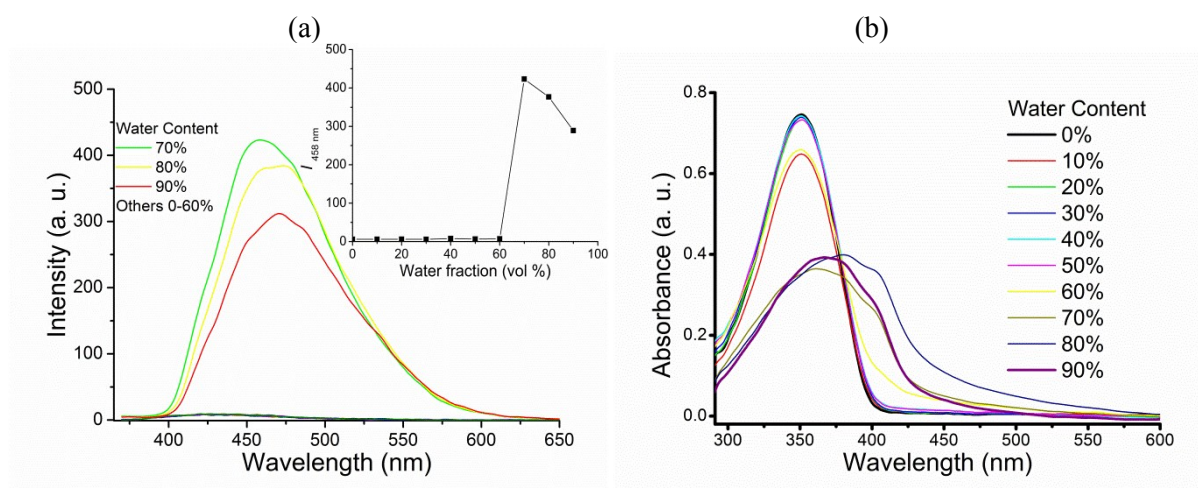


Fig. S9 (a) Emission and (b) UV-Vis absorption spectra of **3** in THF/water mixtures with different water volume fractions. Inset shows the changes at the emission maximum intensity of **3** ($[3] = 1 \times 10^{-5}$ M) as a function of water fraction.

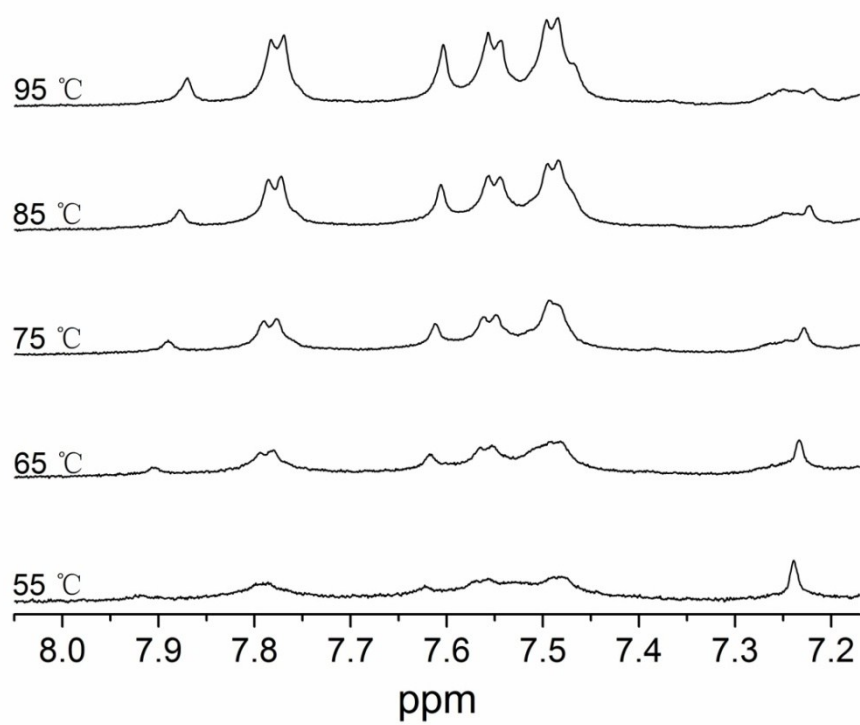
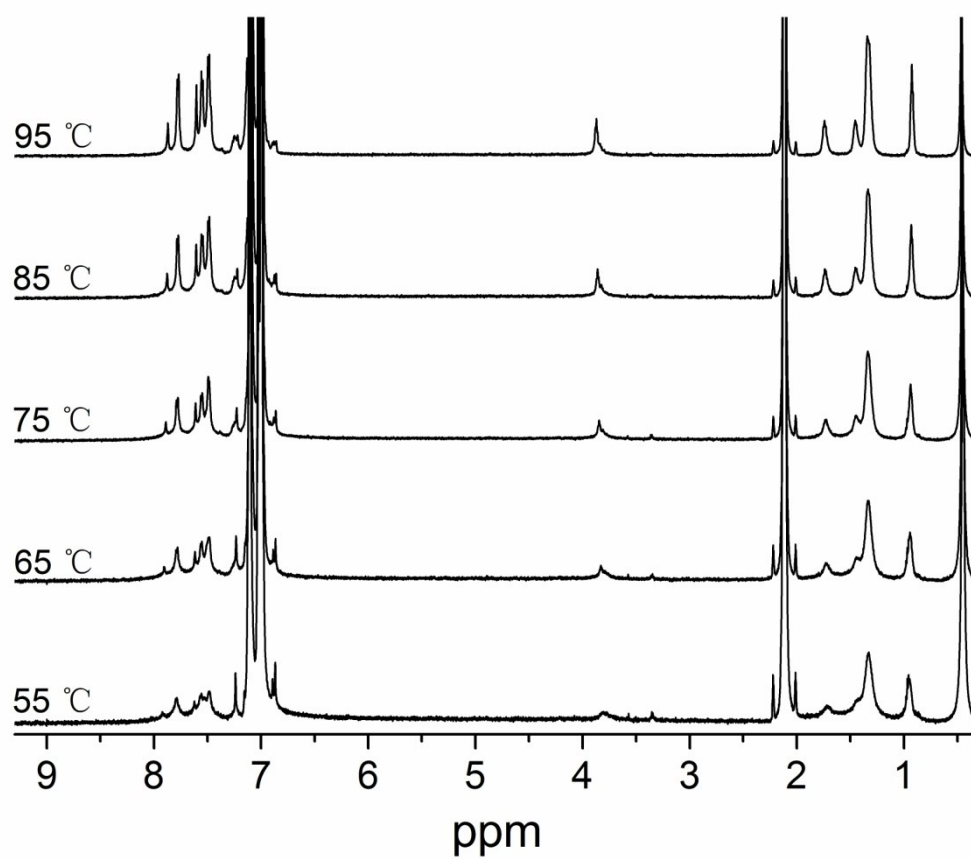


Fig. S10 Temperature-dependent ^1H -NMR spectra of the toluene- d_8 gel **1** (1 mL, $c_{\text{tol}} = 4.3$ mM).

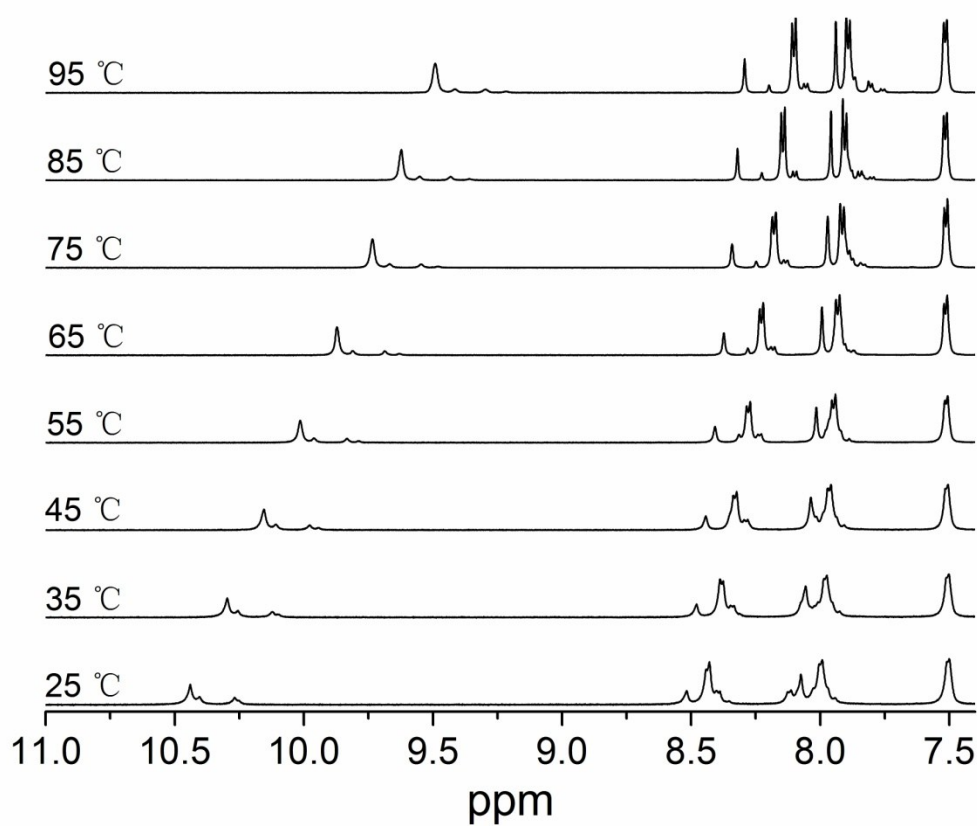
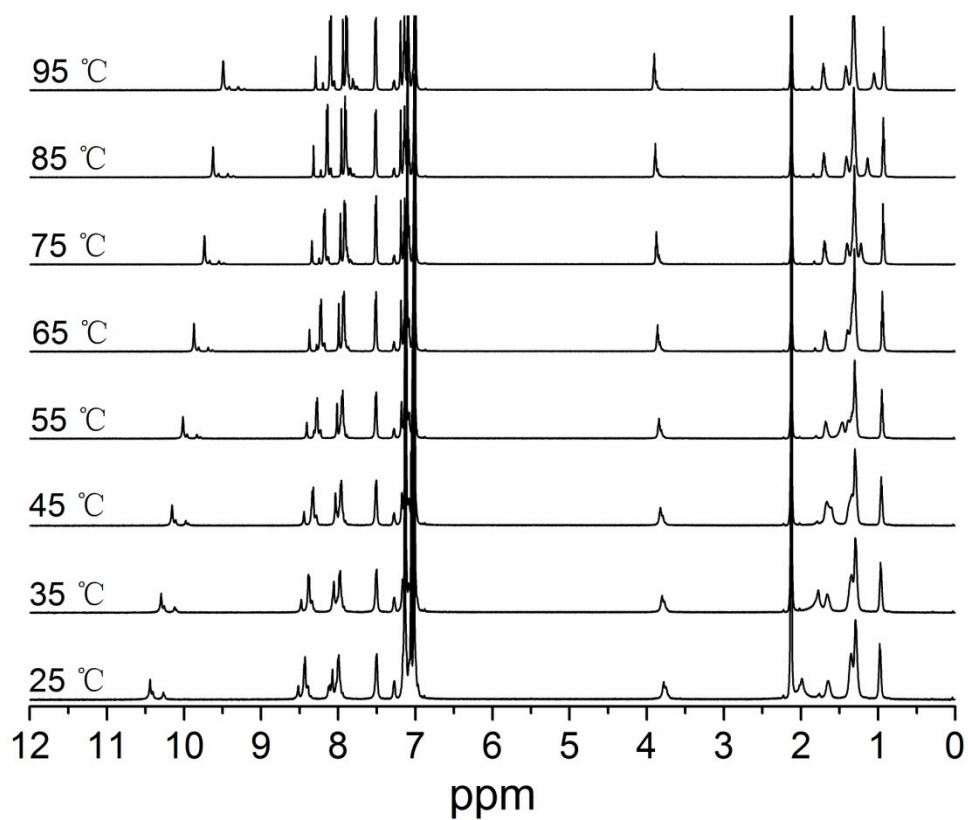


Fig. S11 Temperature-dependent ^1H NMR spectra of the toluene- d_8 gel **1** (1 mL, $c_{tol} = 4.3$ mM) containing 5 μL DMSO- d_6 .

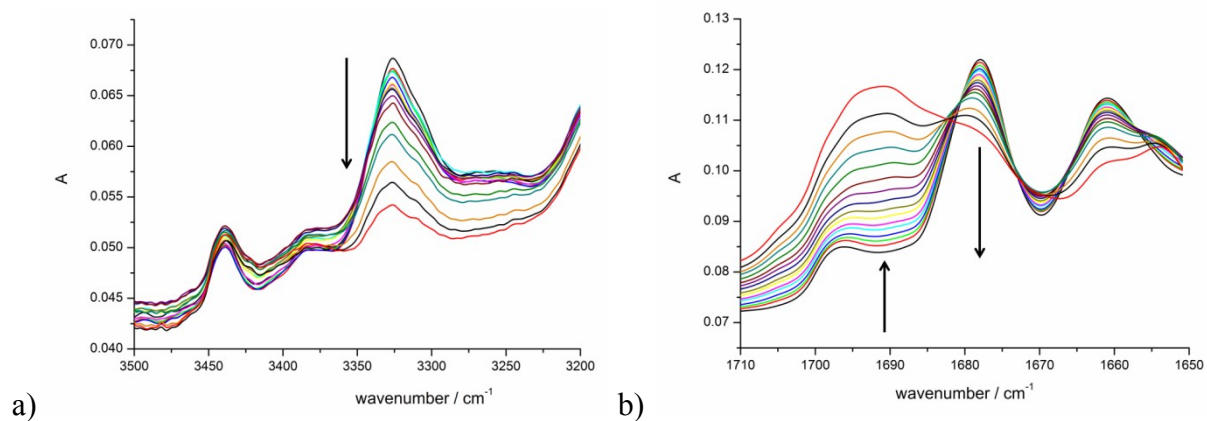


Fig. S12 Temperature dependent FT-IR spectra of the toluene gel **1**: a) NH regions, b) carbonyl regions (from 25 to 100 °C).

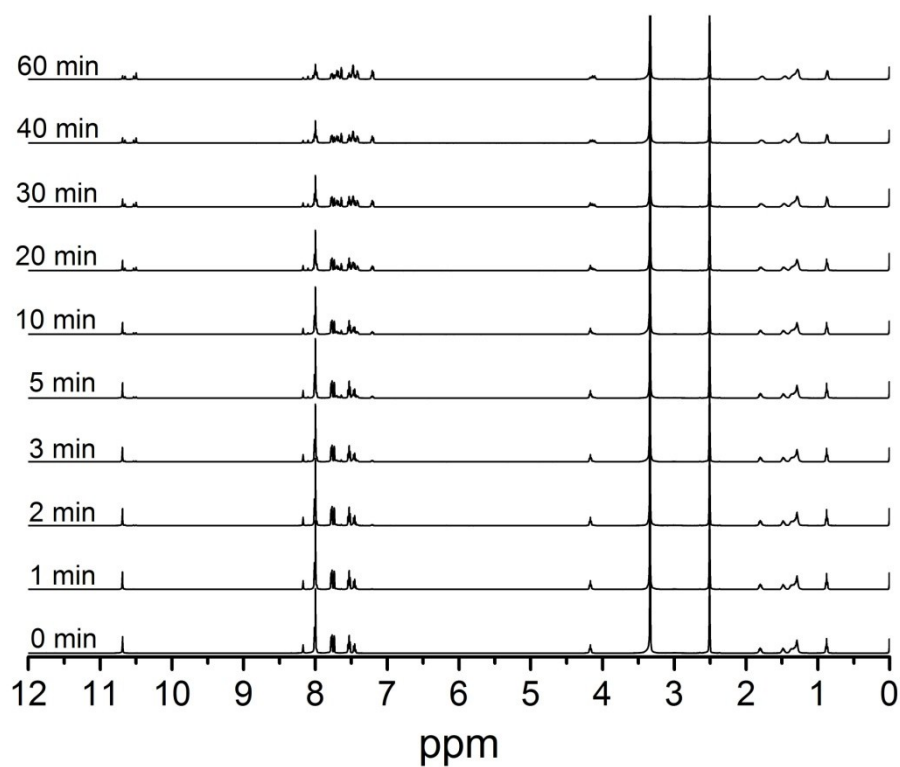


Fig. S13 ¹H-NMR spectral changes of **1** upon photoirradiation (7 mM in DMSO-*d*₆ at 298 K). A DMSO-*d*₆ solution of **1** in a NMR tube was irradiated with 365 nm light. ¹H-NMR spectra were recorded at different time intervals up to reaching a photostationary state (after ca. 60 minutes). *Z,Z*, *Z,E* and *E,E* isomer distribution was estimated by integral analysis of amidic signals (in the 10.5-10.8 ppm region).

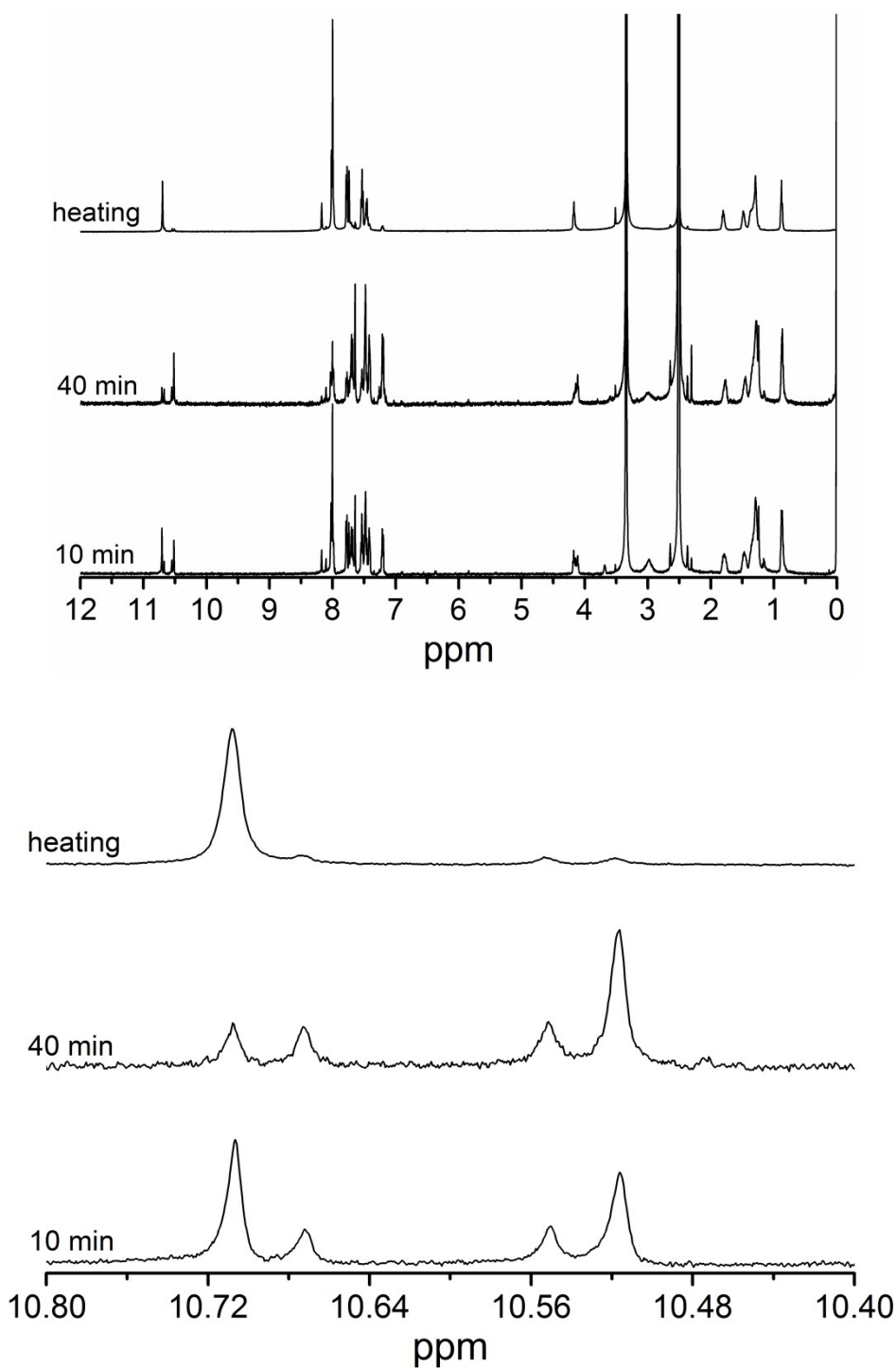


Fig. S14 $^1\text{H-NMR}$ spectra of the toluene gel **1** (4.1 mM) irradiated with 365 nm UV light for 10 and 40 minutes, respectively. As the irradiation time increases, it was found that the Z,Z form decreases whereas the E,E form increases. As indicated by integral analysis of the above $^1\text{H-NMR}$ spectra, a $Z,Z : Z,E : E,E$ ratio of ca. 41 : 25 : 34 was found after 10 min of irradiation at 365 nm, while a prolonged (40 minutes) irradiation gave a 14 : 32 : 54 ratio of the three isomers. Then, the sample vessel is heated and maintained at $t = 105\text{ }^\circ\text{C}$ for 60 minutes and cooled, whereupon, the gel was formed. The spectrum shows that the gelator **1** has been converted back almost completely to the Z,Z isomer. Note: solvent was removed from the gel samples at r.t. under high vacuum and the solid residue obtained was dissolved in $\text{DMSO-}d_6$.

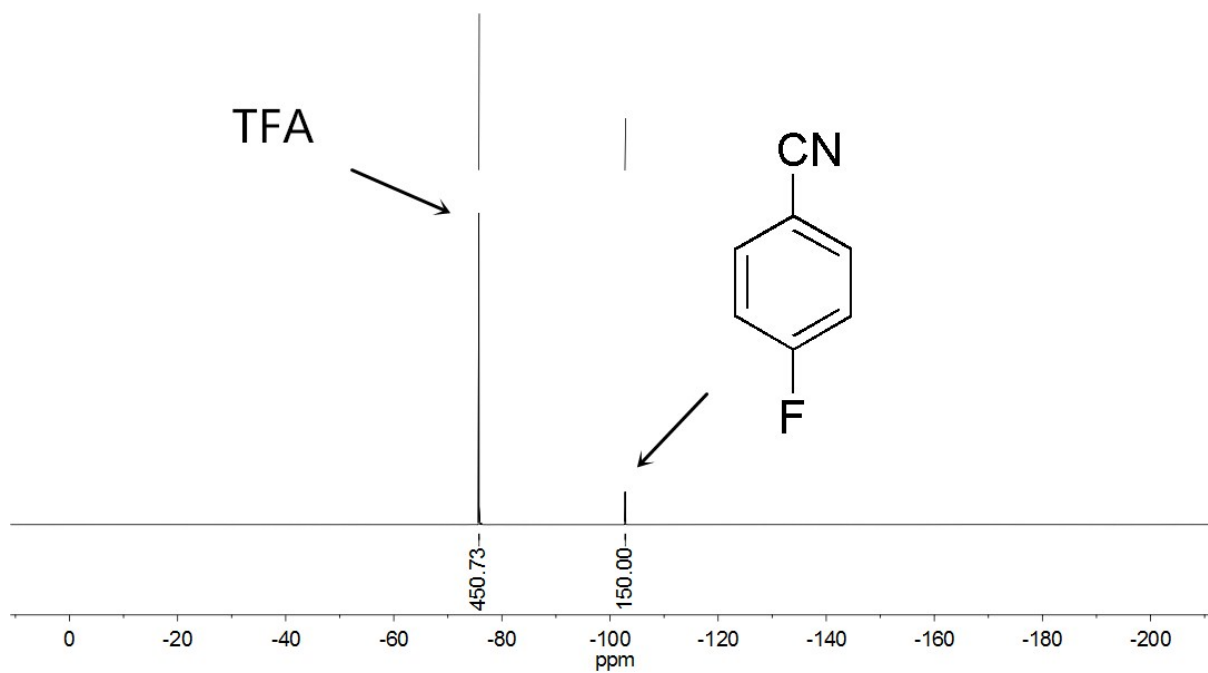


Fig. S15 The concentration of TFA within the toluene gel **1** after its exposure to TFA vapors was estimated by ^{19}F -NMR spectroscopy. Integral analysis was applied to a sample of the gel in the presence of an internal standard of known concentration (1-fluoro-4-cyano benzene).

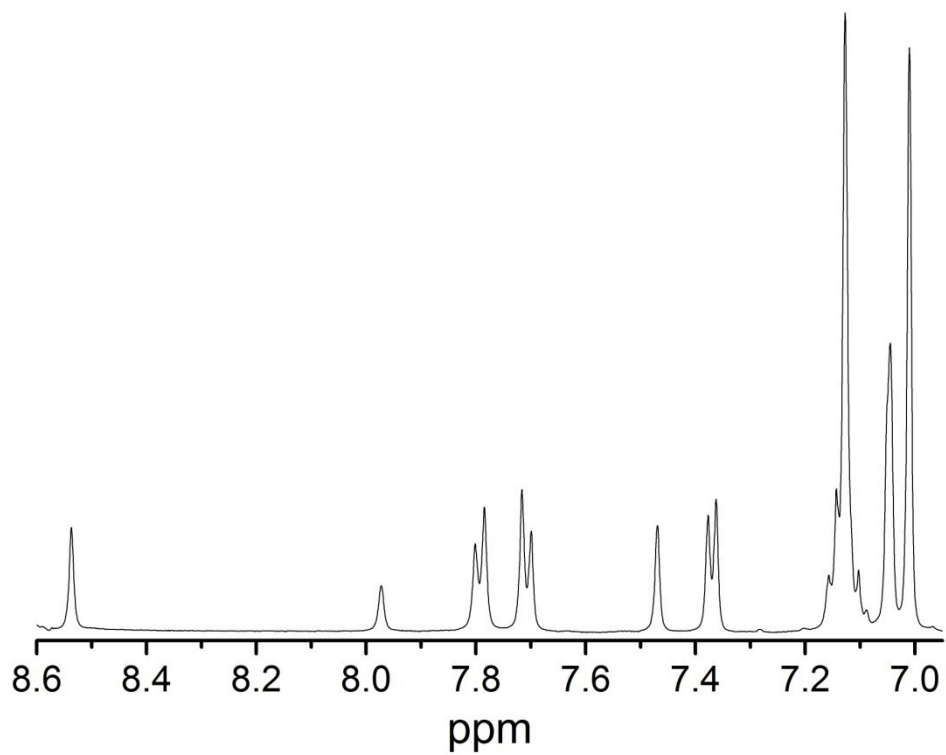


Fig. S16 Effect of TFA addition on **1**. Partial $^1\text{H-NMR}$ spectrum of the sample after the gel to sol transformation of the toluene- d_8 gel **1** obtained by exposing to TFA vapors.

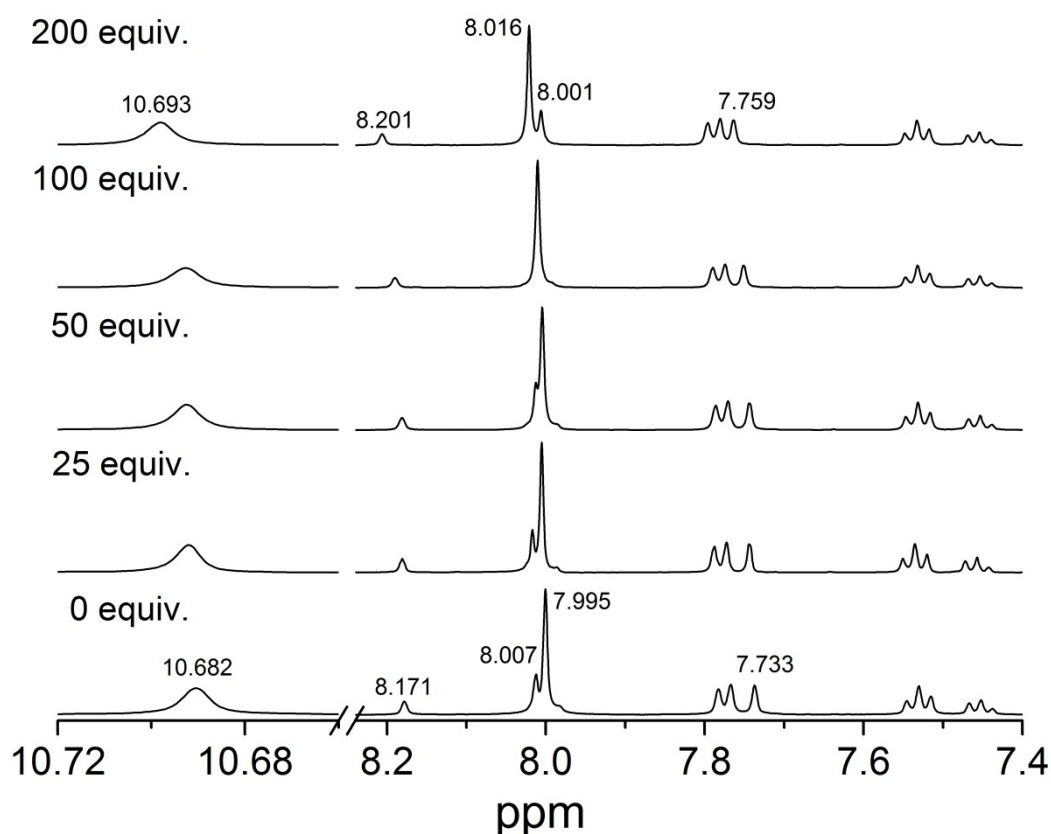


Fig. S17 Effect of TFA addition on **1**. Partial ^1H -NMR spectra of **1** in $\text{DMSO-}d_6$ ($c = 4.3$ mM), showing the shifting of the aromatic protons upon addition of incremental quantities of TFA (from 25 to 200 equiv.).

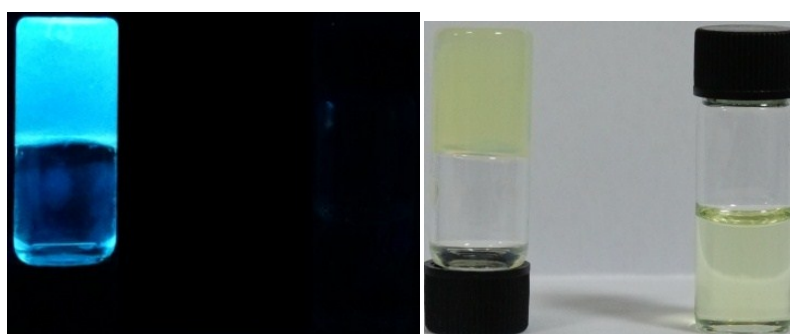


Fig. S18 The photographs show that aggregated **1** in toluene gel (left vessels, 5.7 mM) is strongly fluorescent, while isolated **1** in DMSO solution (right vessels, 5.7 mM) is non fluorescent: fluorescence enhancement in the gel state is associated with an aggregation-induced enhanced emission (AIEE) behaviour. The gelator molecules are non-fluorescent in the monomer state in solution but becomes highly fluorescent upon self-assembly into supramolecular aggregates due to the synergistic effect of intramolecular planarization and restricted excimer formation.

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