Electronic Supplementary Material (ESI) for Soft Matter
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Exploring molecular recognition pathways in one- and two-component gels formed by dendritic lysine-based gelators

John G. Hardy*,[a] Andrew R. Hirst[a] and David K. Smith*,[a]

SUPPLEMENTARY INFORMATION

Contents

1. Thermal Stability Plots

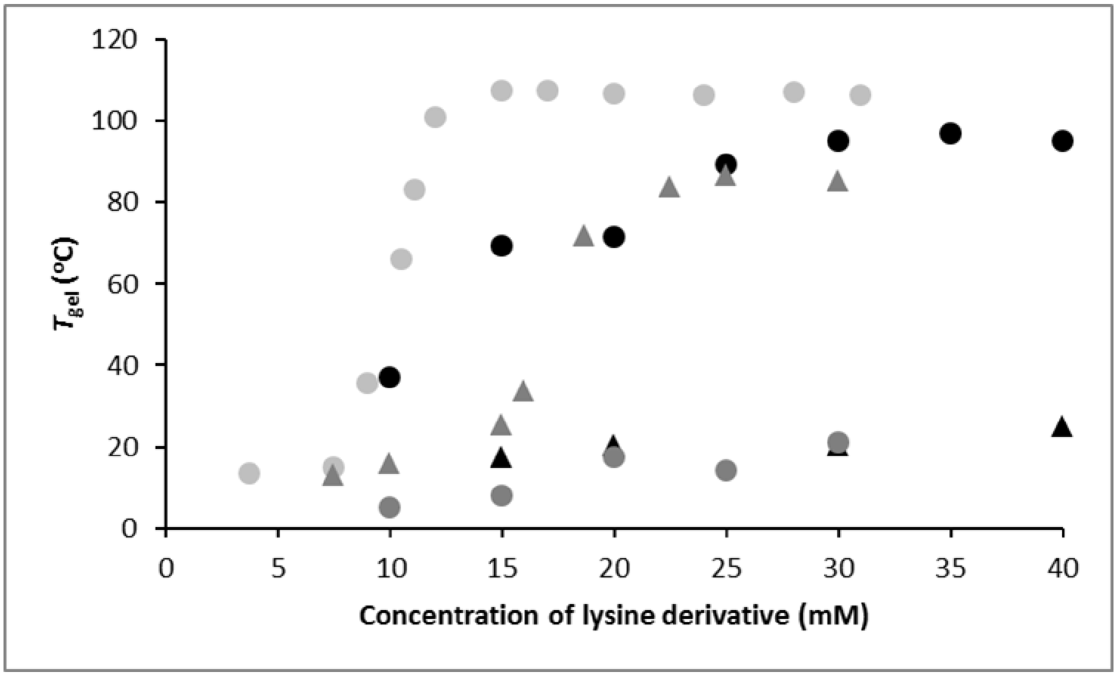

Figure S1. Effect of concentration of the lysine derivative on the T_{gel} value of the 1- and 2-component gels. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). For the 2-component systems, the components are present at a fixed molar ratio of 2:1 lysine derivative:diaminododecane.

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2. NMR Data

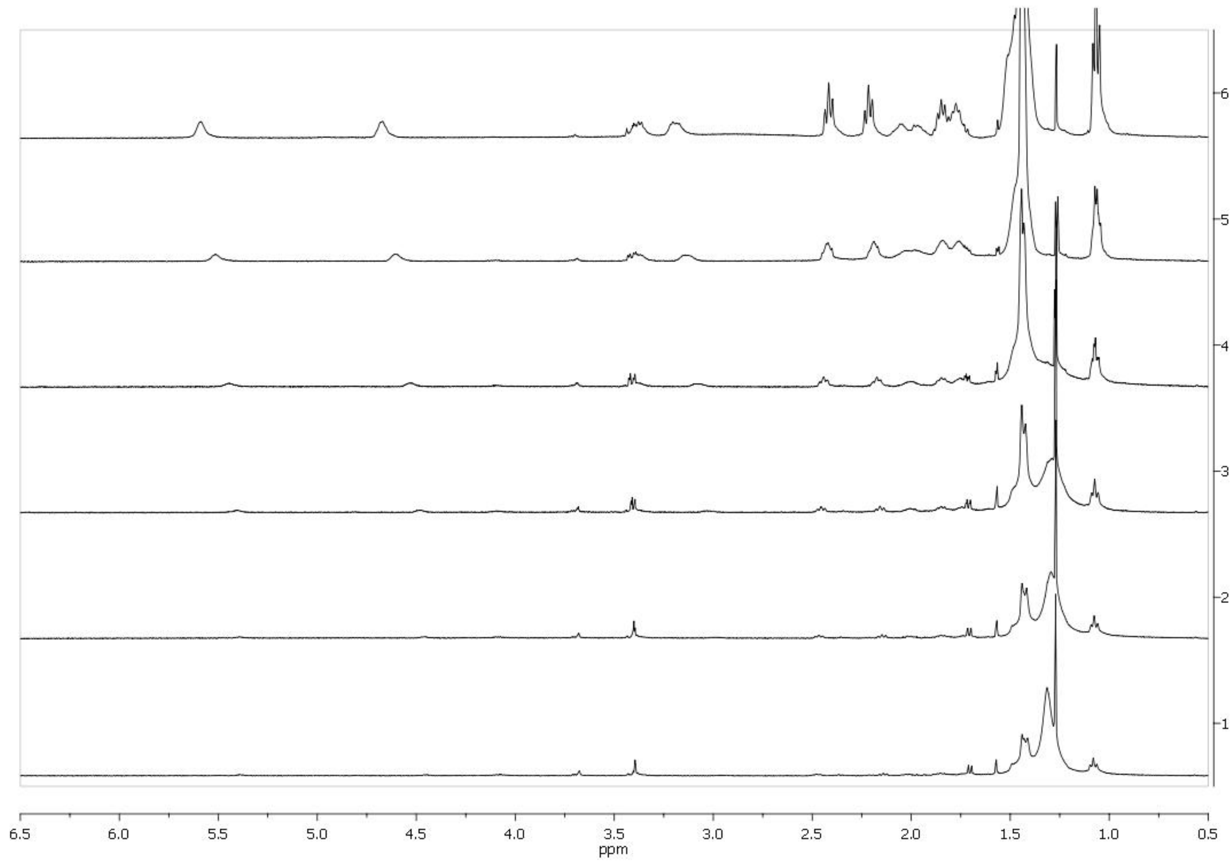

Figure S2. ^{1}H NMR spectra of **3A** (1 component system) in d_5-bromobenzene; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C, 5) 60^{o}C, 6) 70^{o}C. The lysine derivative is at a concentration of 15 mM.

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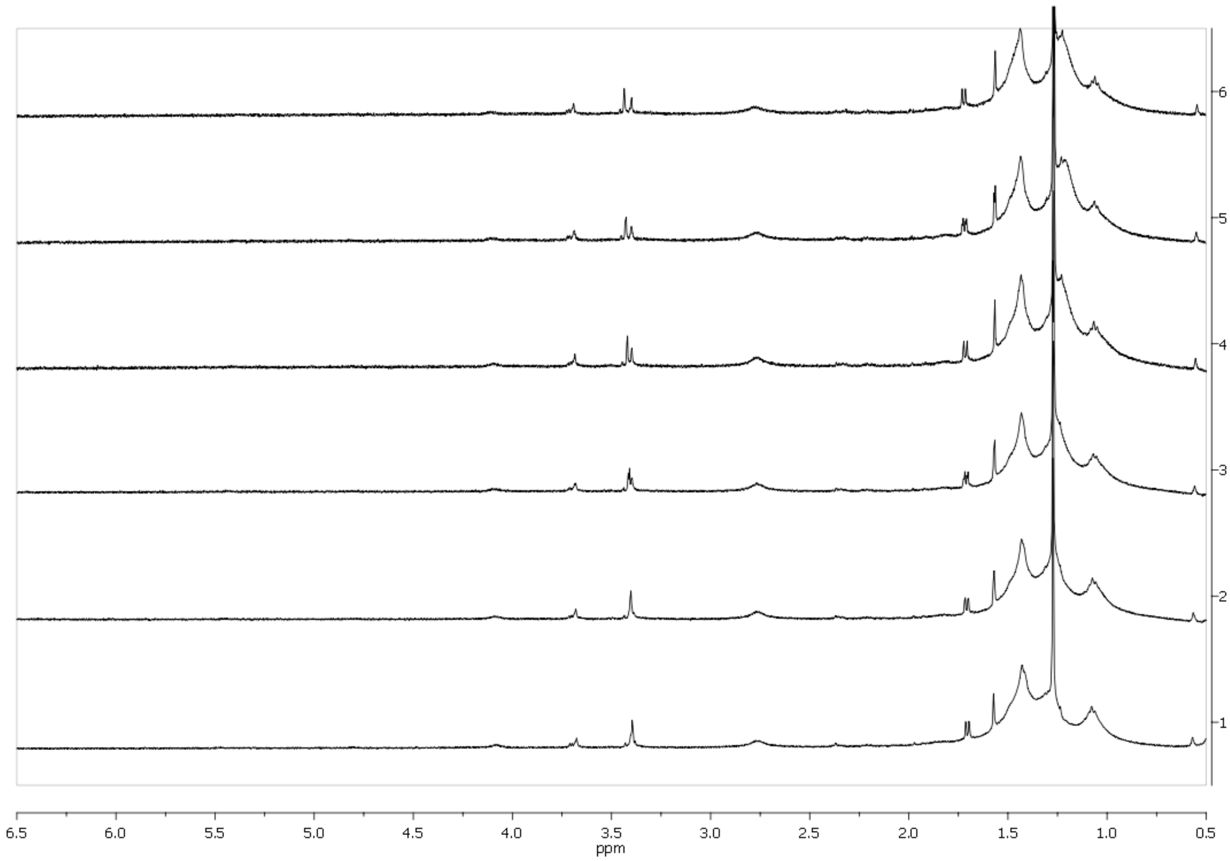

Figure S3. [1]H NMR spectra of **3A** (2 component system) in d_5-bromobenzene; 1) 20°C, 2) 30°C, 3) 40°C, 4) 50°C, 5) 60°C, 6) 70°C. The lysine derivative is at a concentration of 15 mM and diaminododecane is at a concentration of 7.5 mM.

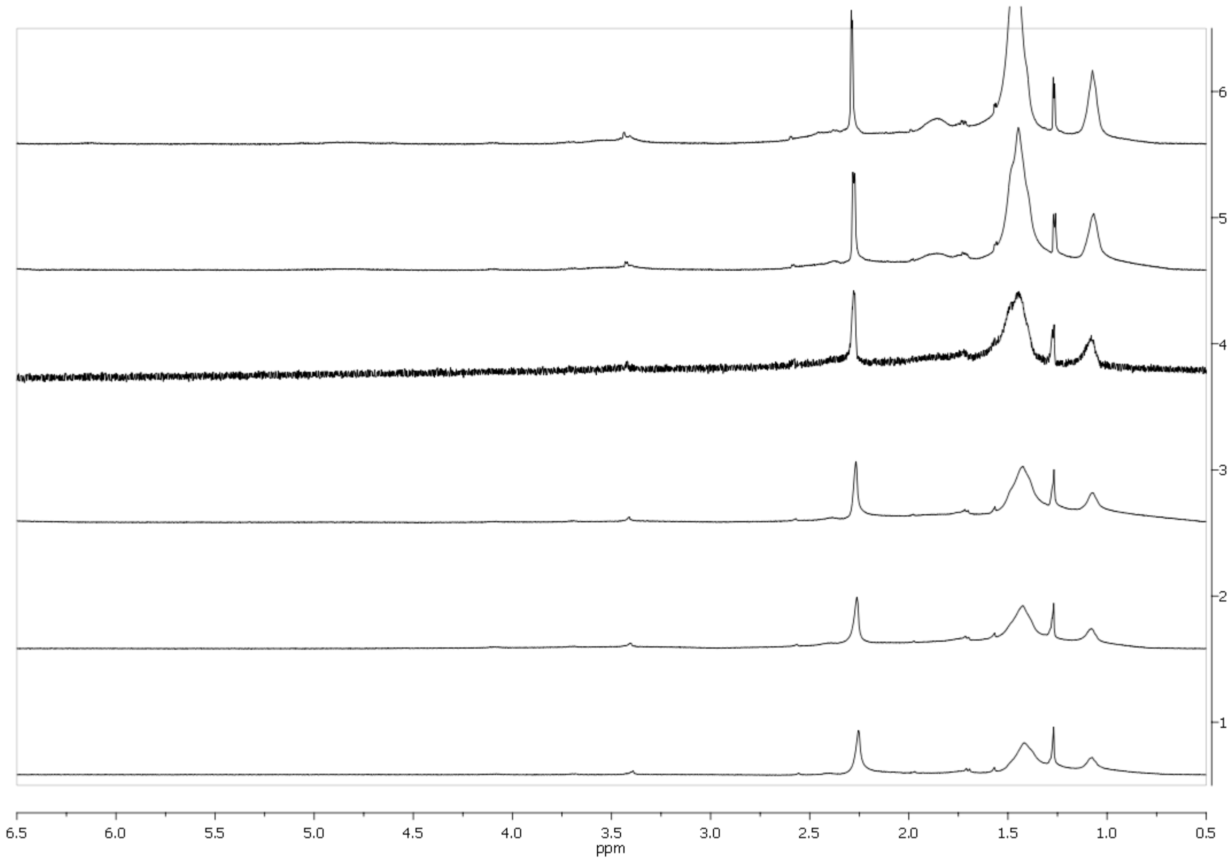

Figure S4. ^{1}H NMR spectra of **6A** (1 component system) in d_5-bromobenzene; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C, 5) 60^{o}C, 6) 70^{o}C. The lysine derivative is at a concentration of 15 mM.

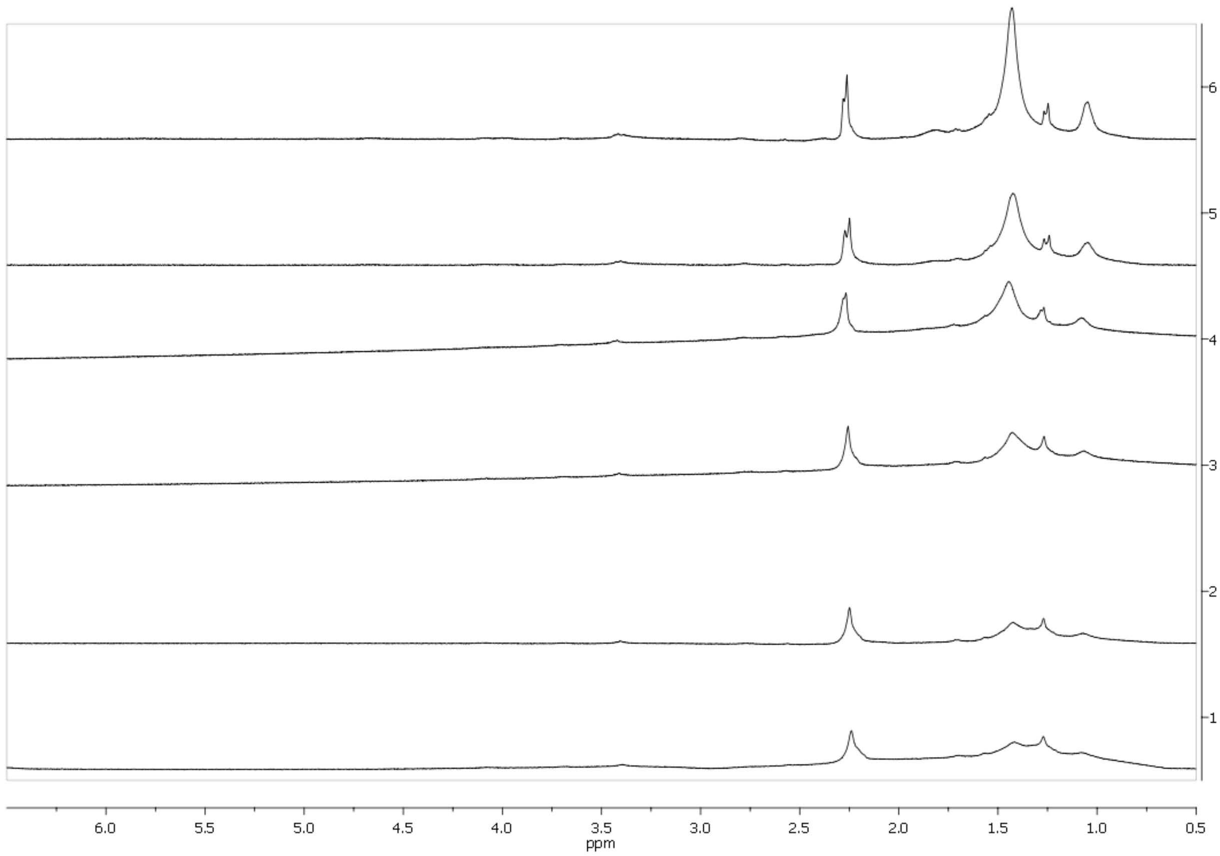

Figure S5. ^{1}H NMR spectra of **6A** (2 component system) in d_5-bromobenzene; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C, 5) 60^{o}C, 6) 70^{o}C. The lysine derivative is at a concentration of 15 mM and diaminododecane is at a concentration of 7.5 mM.

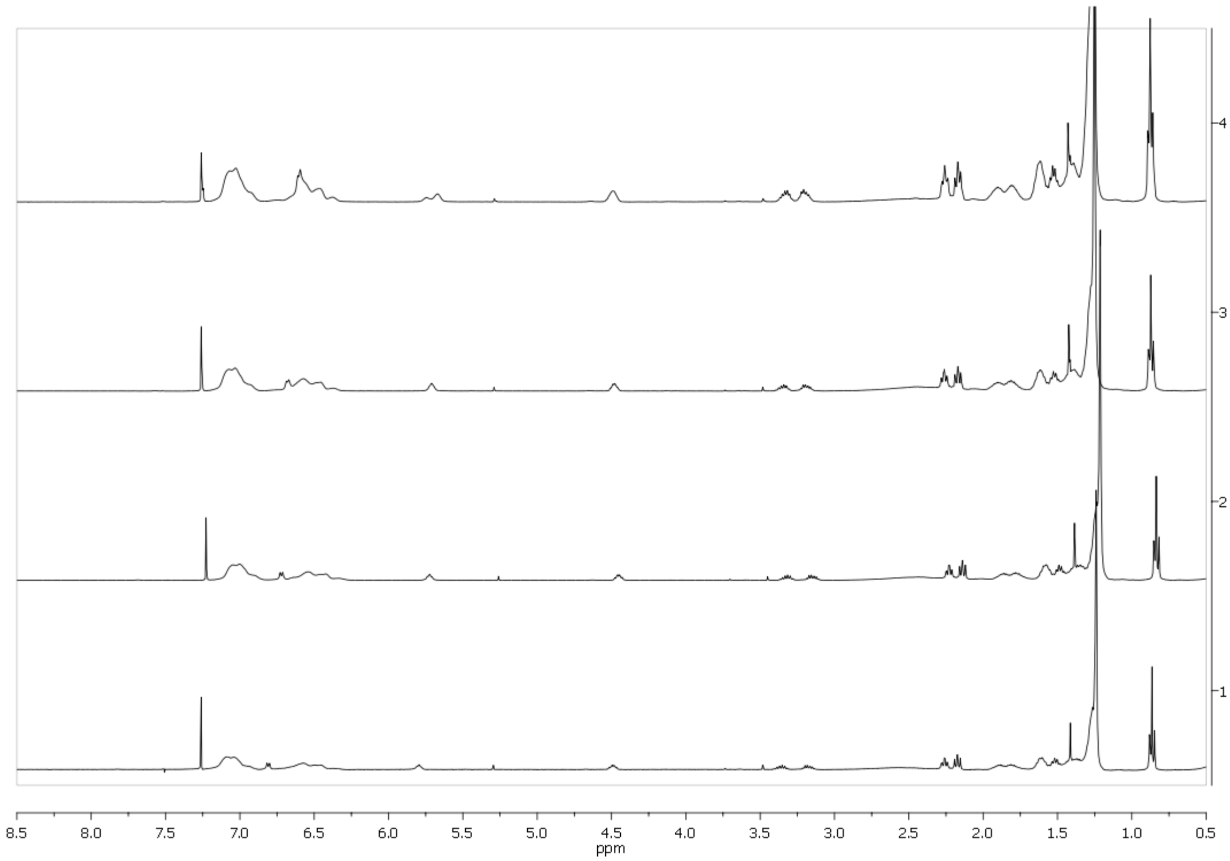

Figure S6. ^{1}H NMR spectra of **3A** (1 component system) in $CDCl_3$; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C. The lysine derivative is at a concentration of 15 mM.

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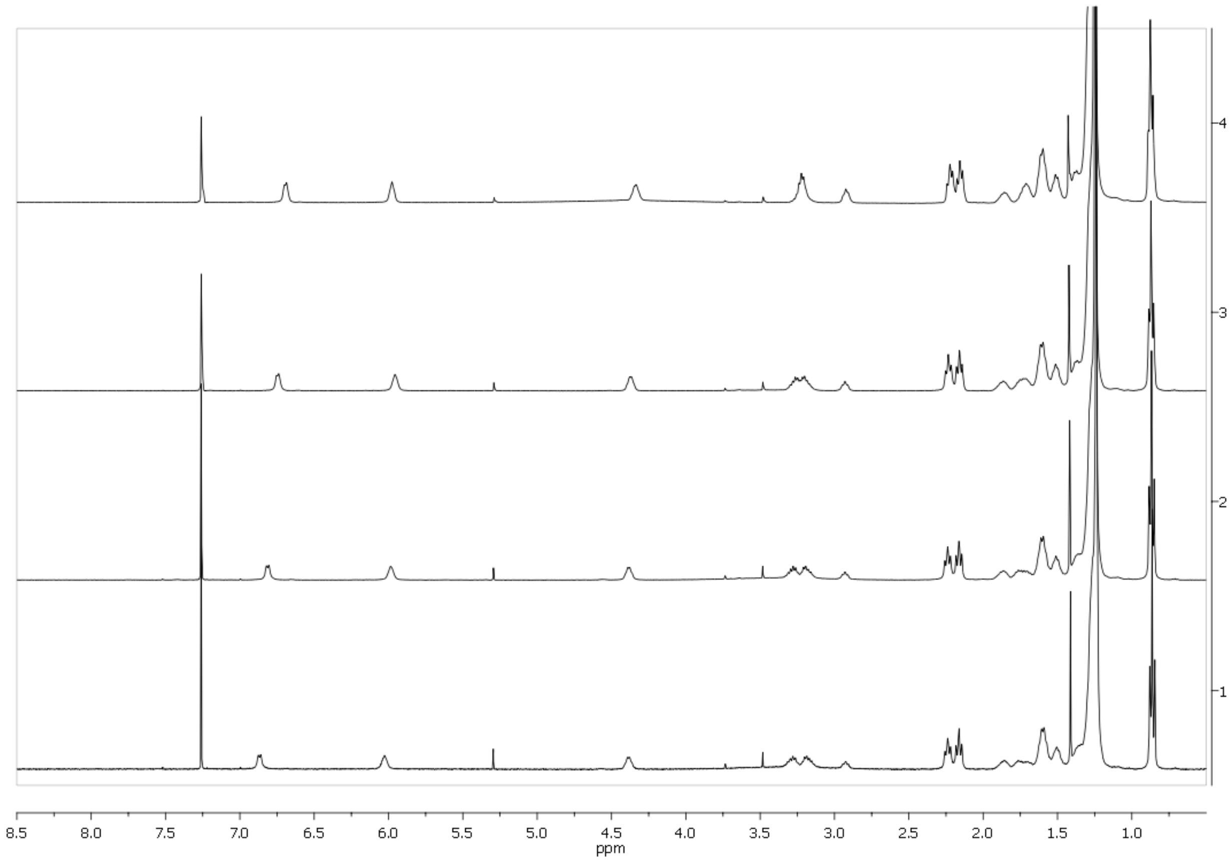

Figure S7. ^{1}H NMR spectra of **3A** (2 component system) in $CDCl_3$; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C. The lysine derivative is at a concentration of 15 mM and diaminododecane is at a concentration of 7.5 mM.

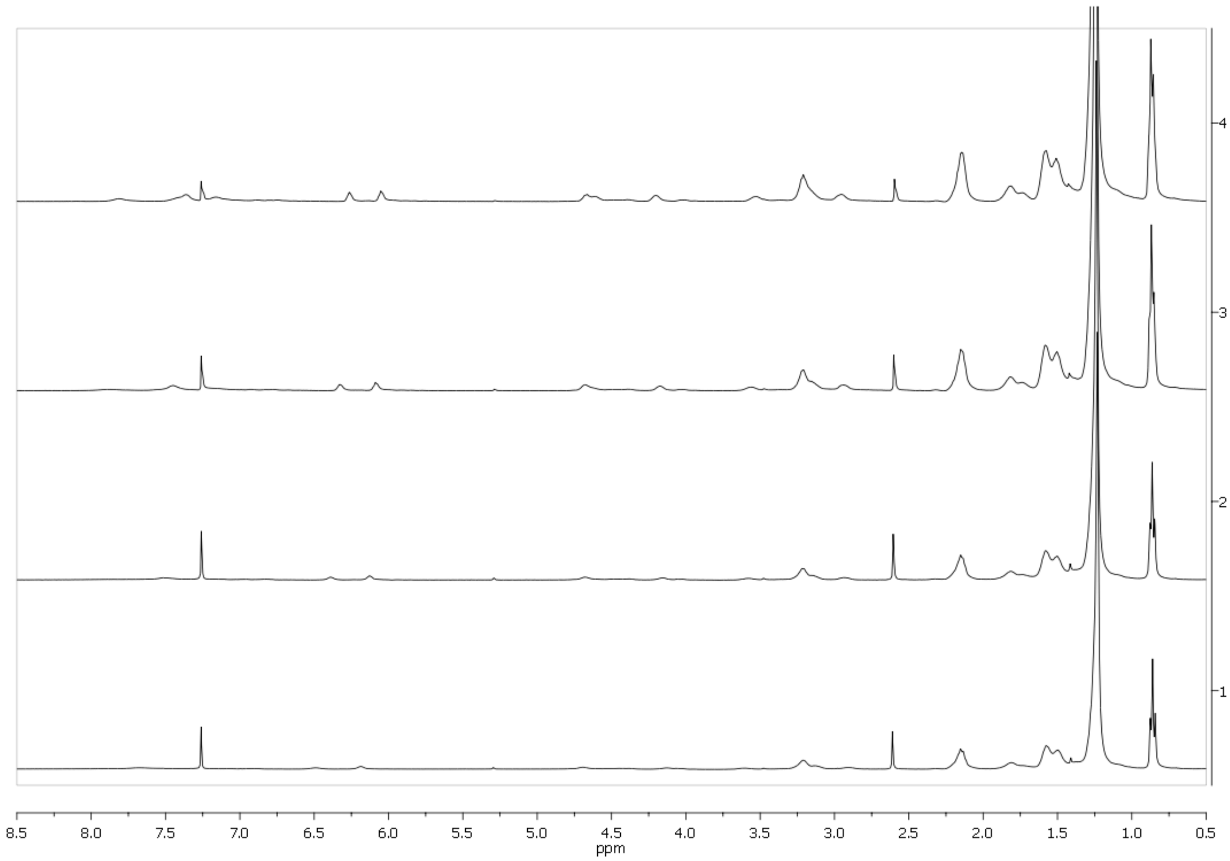

Figure S8. ^{1}H NMR spectra of **6A** (1 component system) in $CDCl_3$; 1) 20°C, 2) 30°C, 3) 40°C, 4) 50°C. The lysine derivative is at a concentration of 15 mM.

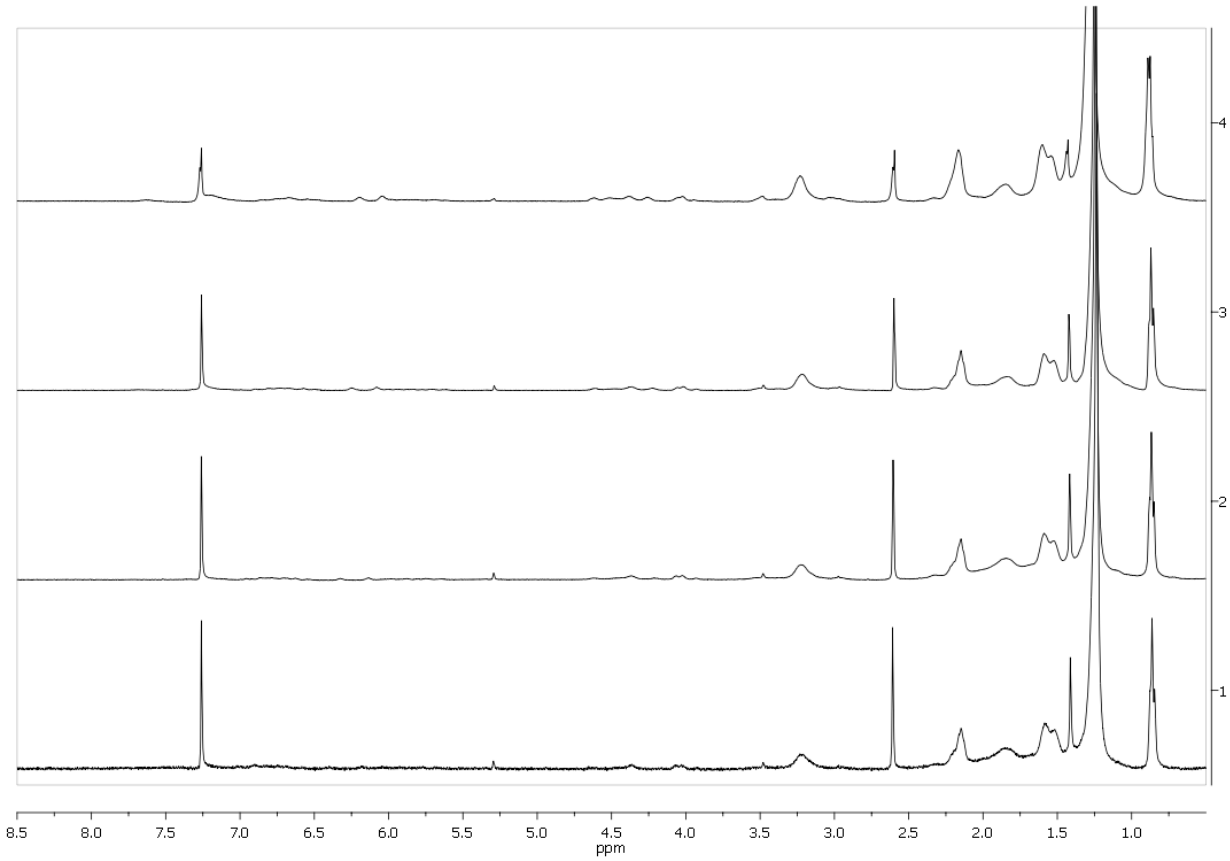

Figure S9. ^{1}H NMR spectra of **6A** (2 component system) in $CDCl_3$; 1) 20^{o}C, 2) 30^{o}C, 3) 40^{o}C, 4) 50^{o}C. The lysine derivative is at a concentration of 15 mM and diaminododecane is at a concentration of 7.5 mM.

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3. Solvent Parameters for Solvents Investigated in Gelation

Table S1: Dielectric constant (ε), normalized Reichardt E_T values and Kamlet-Taft parameters for the selection of solvents investigated in this paper.

Solvent	**ε**	E_T^N	**α**	**β**	π^*
Ethylbenzene	2.300		0.00		
Mesitylene	2.270	0.068	0.00		0.45
Toluene	2.380	0.099	0.00	0.11	0.49
Cyclohexane	2.100	0.006	0.00	0.00	0.00
Benzene	2.270	0.111	0.00	0.10	0.55
1,2,3,4-tetrahydronapthalene	2.660	0.093			
1-bromonapthalene	4.830				
Trichloroethylene	3.270	0.160	0.00	0.00	0.48
Bromobenzene	5.400	0.182	0.00	0.06	0.77
1,2-dichlorobenzene	9.930	0.225	0.00		0.77
1,2-dichloroethane	10.370	0.327	0.00	0.00	0.73
Tetrahydrofuran	7.580	0.207	0.00	0.55	0.55
Chloroform	4.800	0.259	0.44	0.00	0.69
1,1,2,2-tetrachloroethane	8.200	0.269		0.00	0.88
Dichloromethane	8.930	0.309	0.30	0.00	0.73
Pyridine	12.900	0.302	0.00	0.64	0.87

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Table S2: Hildebrand solvent parameters for the selection of solvents investigated in this paper.

Solvent	δ_O	δ_d	δ_p	δ_h	δ_a
Ethylbenzene	8.70	8.70	0.30	0.70	0.76
Mesitylene	8.80	8.80	0.00	0.30	0.30
Toluene	8.90	8.80	0.70	1.00	1.22
Cyclohexane	8.20	8.20	0.00	0.10	0.10
Benzene	9.10	9.00	0.00	1.00	1.00
1,2,3,4-tetrahydronapthalene	9.80	9.60	1.00	1.40	1.72
1-bromonapthalene	10.20	9.90	1.50	2.00	2.50
Trichloroethylene	9.30	8.80	1.50	2.60	3.00
Bromobenzene	10.60	10.00	2.70	2.00	3.36
1,2-dichlorobenzene	10.00	9.40	3.10	1.60	3.49
1,2-dichloroethane	10.20	9.30	3.60	2.00	4.10
Tetrahydrofuran	9.50	8.20	2.80	3.90	4.80
Chloroform	9.30	8.70	1.50	2.80	3.18
1,1,2,2-tetrachloroethane	10.60	9.20	2.50	4.60	5.24
Dichloromethane	9.90	8.90	3.10	3.00	4.31
Pyridine	10.70	9.30	4.30	2.90	5.19

4. Effect of Solvent on Thermal Stability

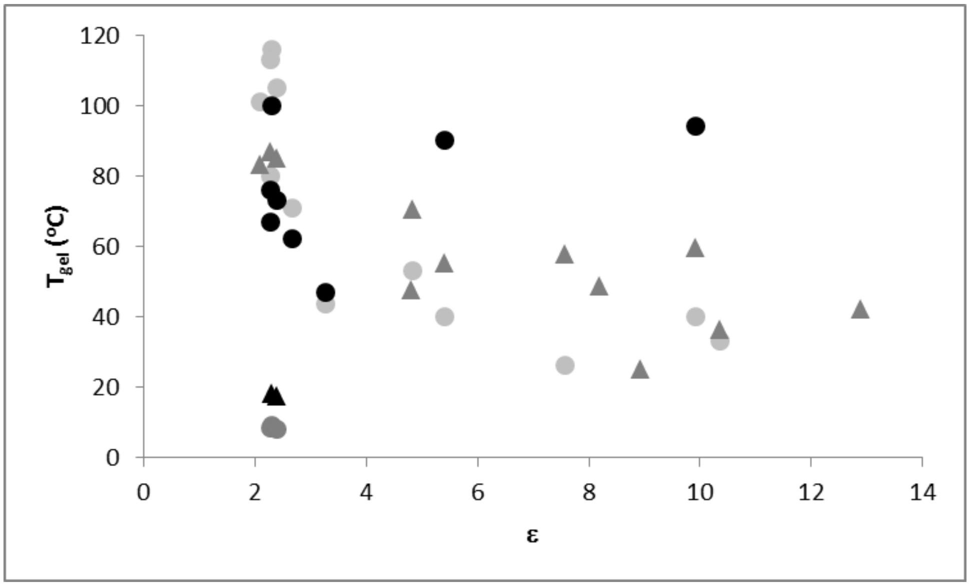

Figure S10. Effect of the dielectric constant (ε) on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

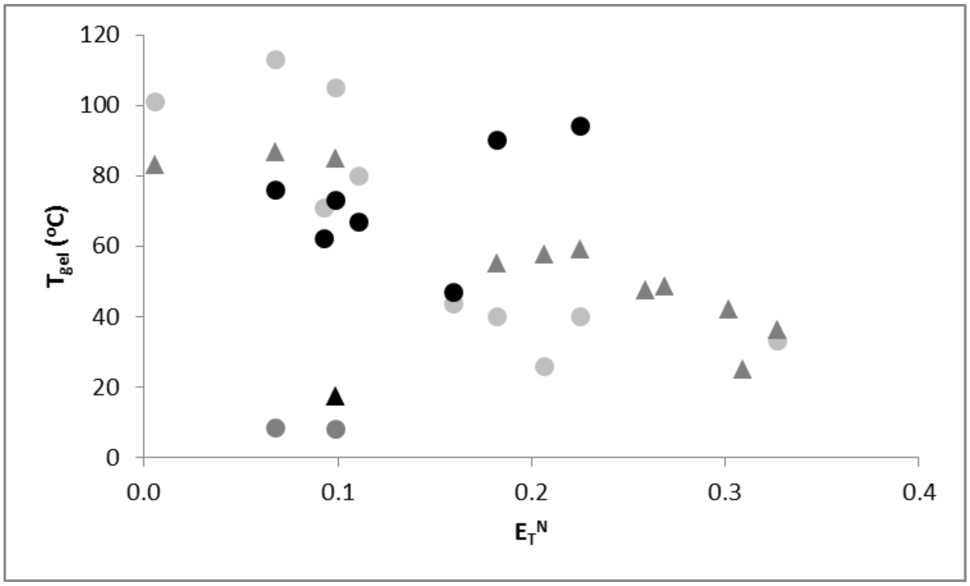

Figure S11. Effect of the normalized E_T value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

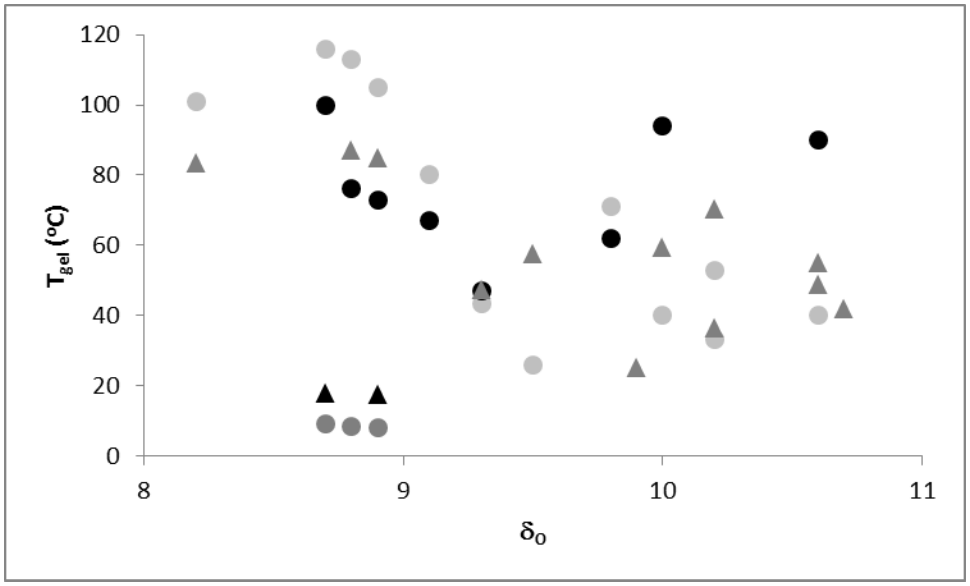

Figure S12. Effect of Hildebrand's total solubility parameter (δ_0) value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

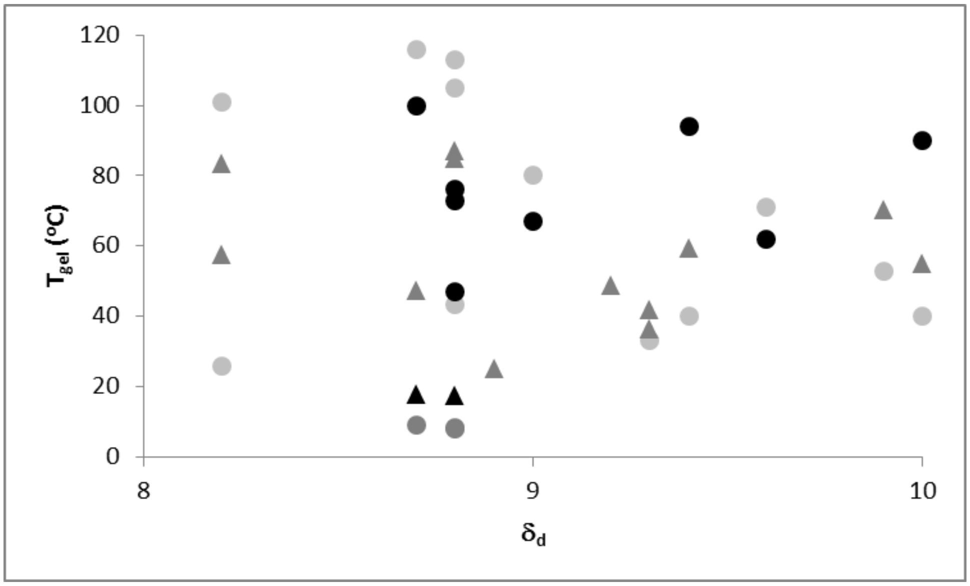

Figure S13. Effect of Hildebrand's dispersion solubility parameter (δ_d) value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

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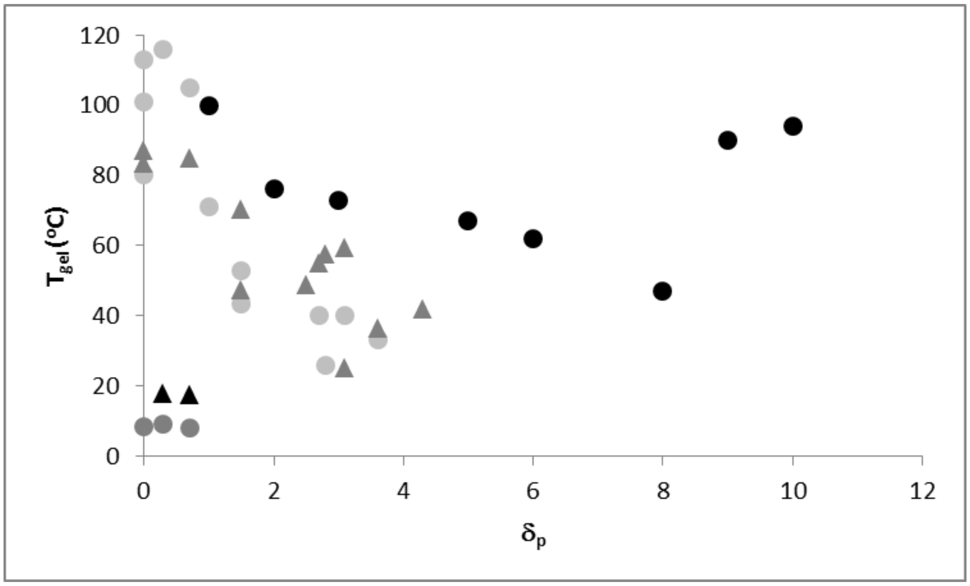

Figure S14. Effect of Hildebrand's polar solubility parameter (δ_p) value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

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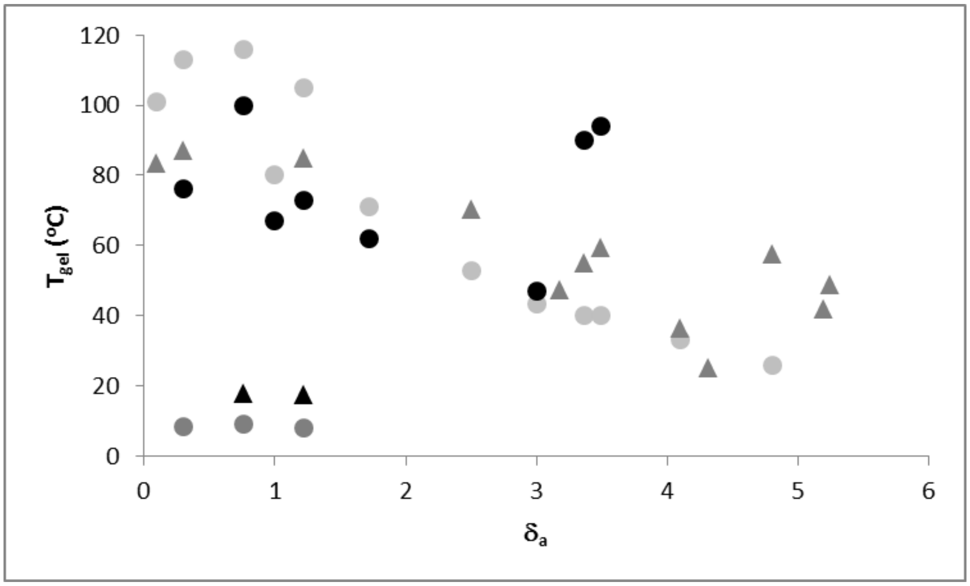

Figure S15. Effect of Hildebrand's combined polar solubility parameter (δ_a) value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

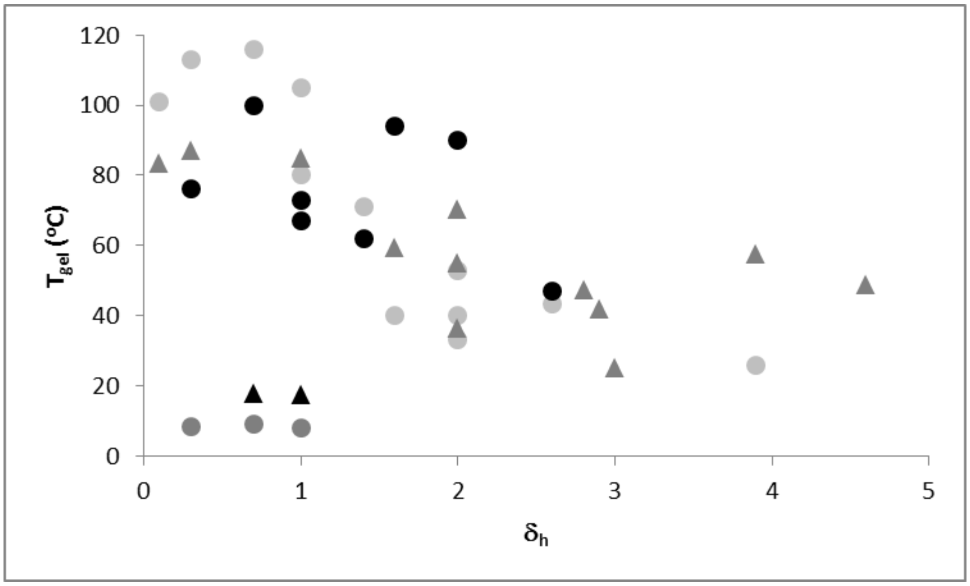

Figure S16. Effect of Hildebrand's hydrogen bonding solubility parameter (δ_h) value on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

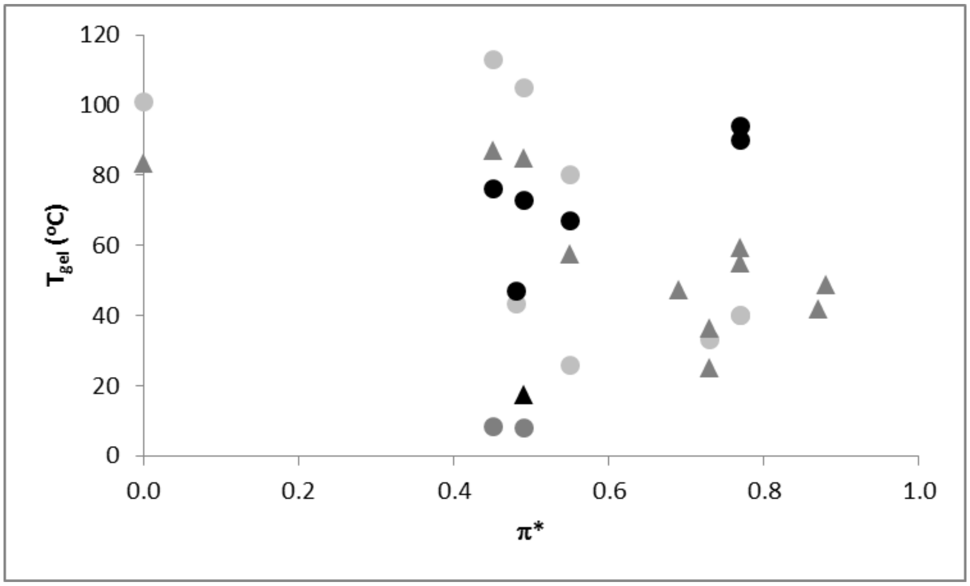

Figure S17. Effect of the Kamlet-Taft parameter, π* (a generalized polarity parameter), on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

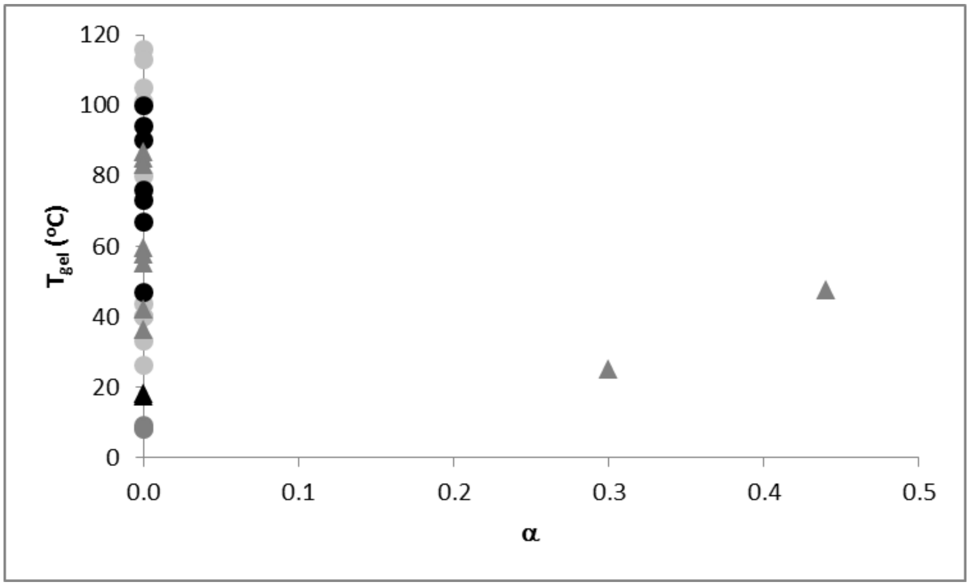

Figure S18. Effect of the Kamlet-Taft parameter, α (ability to donate hydrogen bonds), on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

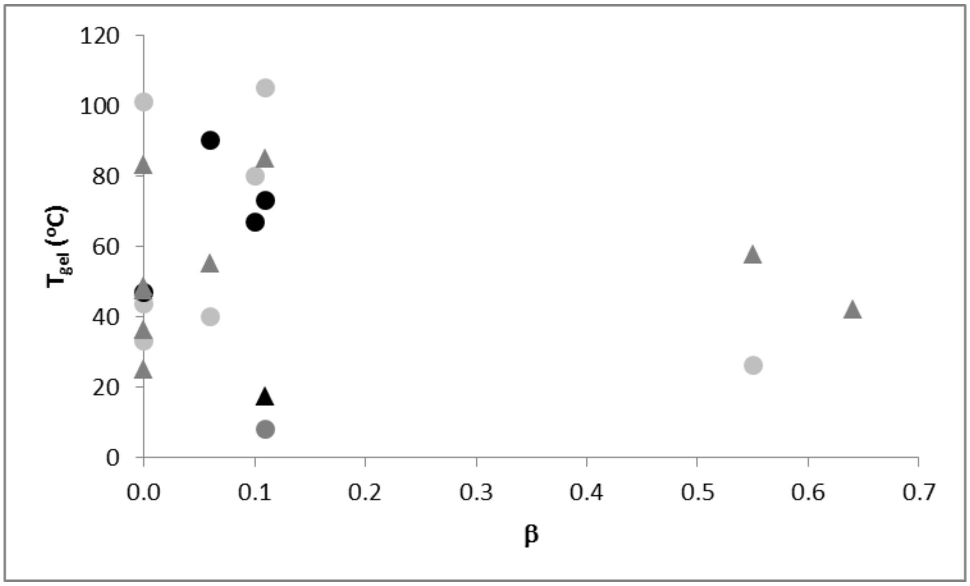

Figure S19. Effect of the Kamlet-Taft parameter, β (ability to accept hydrogen bonds), on the T_{gel} value of the 1- and 2-component lysine-based supramolecular polymers. Black triangles **3A** (1 component system), black circles **3A** (2 component system), light grey circles **5A** (2 component system), dark grey triangles **6A** (1 component system), dark grey circles **6A** (2 component system). The lysine derivatives are at a concentration of 15 mM, and in the case of the 2-component systems diaminododecane is at a concentration of 7.5 mM.

5. Effect of Stoichiometry on Thermal Stability

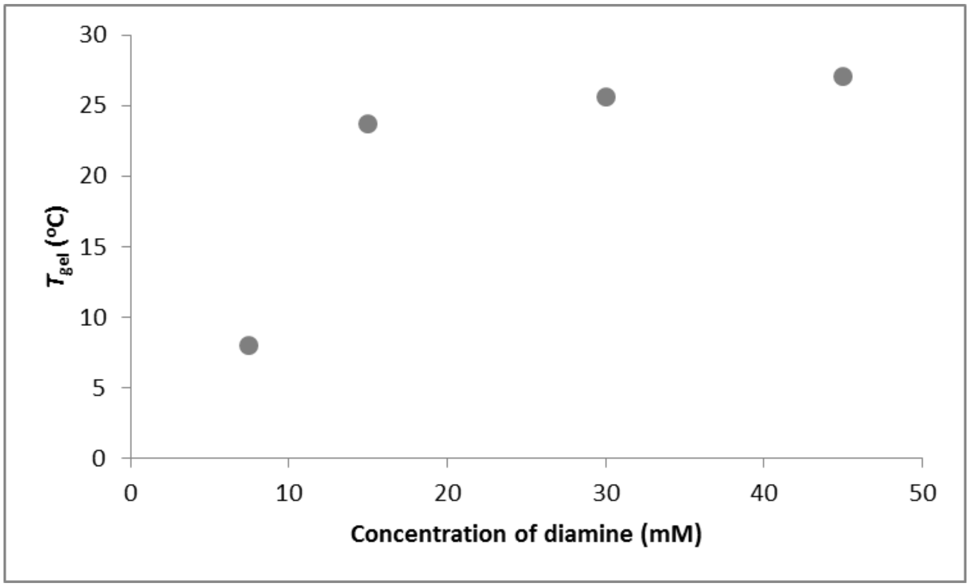

Figure S20. Effect of the stoichiometry of the lysine derivative **6A** and diaminododecane on the T_{gel} value, The concentration of the lysine derivative is fixed at 15 mM.