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Bis amide-aromatic-ureas—highly effective hydro- and organogelator systems

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ABSTRACT

A series of hydro- and organo-supergelators have been synthesised via coupling of simple bis aromatic-ureas via alkyl amide linkages. These bis amide-aromatic-ureas exhibited reduced critical gelator concentrations, improved gelator stability, mechanical and dye removal properties for potential use in water purification, in comparison to related bis aromatic-ureas. Systematic structure studies via variation of the bis amide-aromatic-urea linker length as well as functionalization of the terminal aromatic moieties have enabled control over the gel properties.

1. Introduction

Low Molecular Weight Gelators (LMWG) are systems that will self-assemble via non-covalent interactions (i.e., hydrogen bonding, aromatic π–π stacking and van der Waals forces of attraction) under the required stimuli[1,2] to form supramolecular networks that entrap large volumes of solvent.[3,4] As a result of their highly effective self-assembly, LMWGs are able to gel solvents in very low percentage weights when compared to their polymeric counterparts[5,6] (indeed gels formed at weight % values <1 are referred to as *supergelators*[7]). LMWGs have found application in drug delivery,[8] tissue engineering,[9] catalysis,[10,11] electronics[12] and water purification.[13,14]

The recent interest in aromatic urea-based gelator systems has arisen in the light of the effectiveness of the association of urea moieties, permitting aggregation of fibrils and entrapment of solvents to afford stable gels.[3,4,13–15] Linking aromatic units directly to ureas facilitates an increase in thickness, strengthening fibrils formed, on account of π–π stacking perpendicular to the axis of fibril growth.[4,13–17]

Notable independent studies conducted by the groups of Weiss,[18] van Esch,[19] Miravet and Escuder,[20] respectively, have demonstrated the positive effects of linking recognised structural units that are responsible for gel assembly.[18a] There have been further successes in exploring the effects of creating bolaamphiphilic gelators[21,22] from the corresponding mono amphiphilic hydrogelators and multicomponent linked gelator systems,[23] which exhibit increased gelating efficiency. Furthermore, detailed studies of the linker unit length between the established gelator units[24] have enabled the properties of the gels thus formed to be tailored.[25]

Herein we report the effects of coupling bis aromatic-urea based pH tuneable hydrogelator units (**1**) that have dye uptake capabilities, via alkyl amide linkages (Fig. 1).[13] Several structural modifications of this gelator motif have been carried out to assess the optimal group interactions[14] and have also led to the creation of

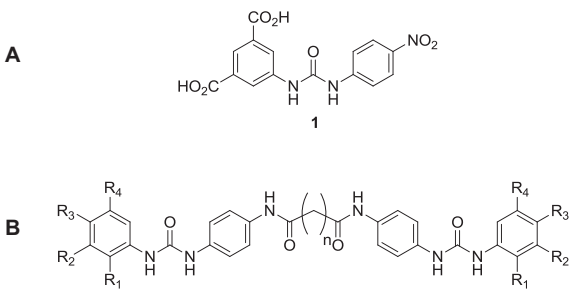

Fig. 1. A) Hydrogelator 5-(3-(4-nitrophenyl)ureido)isophthalic acid (**1**); B) Generalised structure of the novel linked bis amide-aromatic-ureas (R_{1-4}=CO_2H/CO_2Et/H/NO_2).

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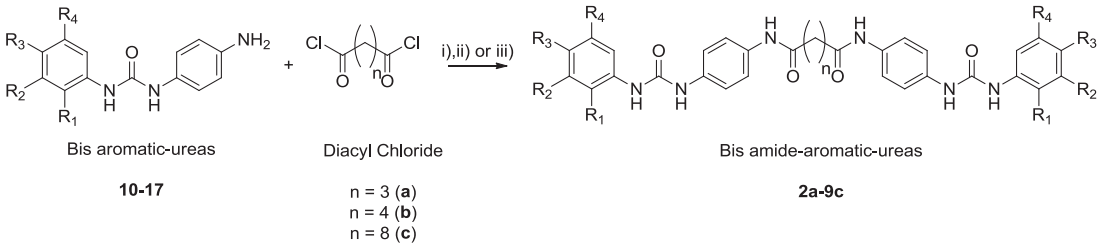
organogels.[15] In designing these new linked gelators, the aromatic and urea moieties of **1** were retained as terminal units whilst bridging alkyl chains were used to couple the bis aromatic-ureas together via amide residues. The functionality on the terminal aromatic unit group was also varied within this study.

2. Results and discussion

2.1. Synthesis

The bis amide-aromatic-ureas **2a**–**9c** were generated from the corresponding bis aromatic-urea precursors, which featured an aniline moiety **10**–**17** (Scheme 1, Table 1). The aniline functionalised bis aromatic-ureas **10**–**17** were linked together using commercially available diacyl chlorides with increasing alkyl chain lengths (glutaryl, adipoyl and sebacoyl) in a variety of solvents (Scheme 1). Acid functionalised bis amide-aromatic-ureas **2a**–**3c** were recovered via precipitation into acid media (pH<4) whereas the ester, nitro and unfunctionalised bis amide-aromatic-ureas **4a**–**9c** precipitated from the reaction medium.



Scheme 1. Generic synthesis of bis amide-aromatic-ureas **2a**–**9c** from bis aromatic-ureas **10**–**17** with (i) DMF, (ii) NMP or (iii) THF, each with Et_3N at room temperature, 24 h, with the respective diacyl chloride.

Table 1
Structural conformations of bis amide-aromatic-ureas **2a**–**9c** (where i–iii are synthetic routes reported in Scheme 1) and corresponding bis aromatic-urea precursor **10**–**17**

Bis amide-aromatic-urea	Bis aromatic-urea	R_1	R_2	R_3	R_4
2a–**c**[i]	**10**	H	CO_2H	H	CO_2H
3a–**c**[ii]	**11**	H	H	CO_2H	H
4a–**c**[iii]	**12**	H	CO_2Et	H	CO_2Et
5a–**c**[iii]	**13**	H	H	CO_2Et	H
6a–**c**[iii]	**14**	H	H	H	H
7a–**c**[iii]	**15**	NO_2	H	H	H
8a–**c**[iii]	**16**	H	NO_2	H	H
9a–**c**[iii]	**17**	H	H	NO_2	H

Bis aromatic-ureas **10**–**13** were synthesised via procedures based upon previous reports.[14,26] The bis aromatic-ureas **14** and **15**–**17** were synthesised according to a variation upon a procedure described by Rodriguez et al.[27] and Denny et al.,[28] respectively. Addition of a solution of an isocyanate dropwise to a solution of 1,4-phenyldiamine afforded the bis aromatic-ureas. A ratio of 2:1 (diamine:isocyanate), in conjunction with reduced temperature (<10 °C), was used to minimize the bis-substitution of the diamine.

Successful synthesis of each bis amide-aromatic-urea **2a**–**9c** was confirmed via a range of analytical techniques (see Supplementary data for analytical data). For example, the synthesis of the amide links in **4c** was confirmed by a combination of ^{1}H NMR and IR spectroscopic analysis, revealing a key amide proton resonance at 8.64 ppm and the characteristic amide carbonyl stretch at 1654 cm^{-1}, respectively. Further verification was provided by ^{13}C NMR spectroscopic analysis with the key carbonyl amide resonance evident at 170.8 ppm.

2.2. Gelation studies

The tetra-acid bis amide-aromatic-ureas **2a**–**c** were found to be supergelators,[7] readily soluble in basic solutions (pH>12) yet upon acidification (pH<4) they formed translucent gels (Fig. 2) at wt % values<1. Interestingly, it was found that only bis amide-aromatic-urea **2a** formed stable gels upon direct pH switching achieved via addition of $HCl_{(aq)}$. Stable hydrogel systems of **2b** and **2c** were accessed via the established glucono-δ-lactone protocol[29] to produce rapid (ca.<1 h) formation of homogeneous gel. In contrast, the *para*-di-acid bis amide-aromatic-ureas **3a**–**c** (Table 1) failed to gel under analogous conditions.

This preliminary study revealed that stable hydrogels in the case of **2a**–**c** were afforded at higher wt % values in comparison to the bis aromatic-urea **1** (Table 2).[13] The trend of decreasing CGC with increasing linker chain length indicated a surfactant like driving force in the self-assembly process for these gels, analogous to reported hydrogelators studies,[4,21–25] (the anti-parallel/parallel stacking effects of linked urea based gelators, evident in other studies,[24] have been discounted in these systems as **2a**–**c** feature both odd and even numbers of methylene units yet self-assemble effectively). The hydrogels **2a**–**c** exhibited a thermal stability (T_{gel})>100 °C and a vial inversion stability of >1 week. Interestingly, the bis amide-aromatic-urea **2c** was able to thermogelate in both neutral and basic water, however, under these conditions the CGC value required was in excess of 38 mM.

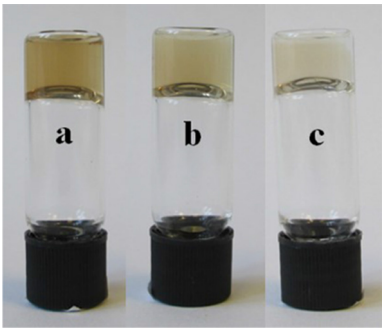


Fig. 2. Hydrogelators (a) **2a**, (b) **2b**, (c) **2c**, at their respective critical gelator concentration (CGC) after pH switching.

Table 2
Gelation studies for **1**[13] and **2a**–**c**, G=gel each accessed via the glucono-δ-lactone protocol.[29]

Gelator	Obs	CGC [mM]	wt % gel
1	G	0.9	0.03
2a	G	7.4	0.54
2b	G	4.1	0.30
2c	G	1.8	0.14

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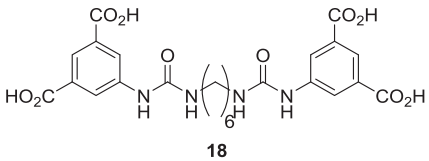
The importance of the aromatic ring adjacent to both the amide and urea moieties in hydrogels of **2a**–**c** was assessed via synthesis of the tetra-acid **18** (Fig. 3). Disappointingly, attempts to generate stable hydrogels of **18** via pH switching resulted only in precipitation. It is feasible that this amide linked aromatic unit limits self-assembly of the urea groups via internal hydrogen bonding (as observed in related bis aromatic-urea systems[4,13–15]) and thus in the case of **18** precipitation occurs (hydrophobic effects were discounted as bis-amide-aromatic-ureas featuring both shorter, **2a**, and longer, **2c**, alkyl chains successfully gelated, Table 2).



18

Fig. 3. The tetra-acid **18**.

The tetra-ester, **4a**–**c**, and unfunctionalised bis amide-aromatic-ureas (**6a**–**c**) proved to be highly effective organo-supergelators[7] within functionalized aromatic solvents, affording translucent gels (Fig. 4) at wt % values <1 (Table 3). In each case, the gels exhibit a vial inversion stability >1 week. In contrast, the *para*-di-ester, **5a**–**c**, and *para*, *ortho* and *meta*-nitro, **7a**–**9c**, bis amide-aromatic-ureas failed to gel in any of the solvents reported in Table 3.

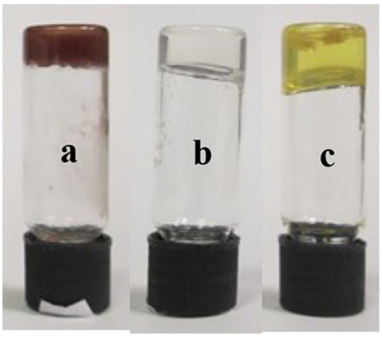


Fig. 4. Organogelator systems of (a) **12** in 1,2 DCB, (b) **4a** in 1,2 DCB and (c) **6a** in nitrobenzene all at their CGC values (see Table 3).

Table 3
Gelation studies for thermogelators bis amide-aromatic-ureas **4a**–**c**, **6a**–**c** and bis aromatic-urea **12** where: G=Gel, GP=gelatinous precipitate, S=sol, P=precipitate, 1,2 DCB=1,2 dichlorobenzene, 1,2,4 TCB=1,2,4 trichlorobenzene

Gelator	1,2 DCB			1,2,4 TCB			Nitrobenzene		
	Obs	CGC [mM]	wt %	Obs	CGC [mM]	wt %	Obs	CGC [mM]	wt %
4a	G	2.2	0.14	G	4.1	0.23	P	—	—
4b	G	2.3	0.15	G	4.0	0.23	P	—	—
4c	G	4.2	0.29	G	4.4	0.27	P	—	—
6a	P	—	—	S	—	—	G	5.81	0.27
6b	P	—	—	GP	—	—	G	5.31	0.25
6c	P	—	—	P	—	—	G	7.73	0.40
12	G	64.6	1.85	G	75.4	1.92	GP	—	—

The di-ester bis aromatic-urea **12** was also found to be able to effectively gelate in organic solvents (Table 3), however, linking of the molecules with alkyl chains to afford **4a**–**c** increased the gelation efficiency (Fig. 4). This was attributed to the increased propensity of the gelators to assemble into fibrils as observed with other aliphatic systems.[20b,21,22]

In contrast, the trend of increasing efficiency of the gelators **4a**–**c** and **6a**–**c** as the chain length decreased was attributed to solubility changes rather than an increased ability to self-assemble.[17] Although the CGC values increase as the length of the alkyl chain was extended it became progressively more difficult to dissolve the gelator, with temperatures $>T_{gel}$ required in all of the solvents in linked systems reported in Table 3.

The tetra-ester, **4a**–**c**, and *meta*-nitro, **8a**–**c**, bis amide-aromatic-ureas formed stable opaque gels at wt % values <1 in combinations of water and polar aprotic solvents (20% v/v) (Table 4). The decrease in CGC values as the linker chain length increased indicated a surfactant like effect, with irregular sized vesicles forming upon addition of the second solvent (see Fig. 5). The vesicles were found to degrade as the water in the bulk medium evaporated under the analysis conditions used in the optical or scanning electron (ESEM) microscopic studies, but they re-formed rapidly following addition of water post-analysis (see Supplementary data), observations that are analogous to other organic/aqueous LMWG systems that have been reported.[30,31] This property was also observed upon addition of other miscible polar solvents (i.e., methanol, ethanol and acetonitrile). In each case, the resultant gels exhibited a vial inversion stability of greater than 1 week.

Table 4
Gelation studies for bis amide-aromatic-ureas **4a**–**9c** and bis aromatic-urea **12** where; G=Gel, GP=gelatinous precipitate, S=solution, P=precipitate, DMSO=dimethyl sulfoxide, NMP=*N*-methyl-2-pyrrolidone, DMF=dimethylformamide, gelation stimulated via addition of water in 4:1 ratio with respect to the organic solvent

Gelator	DMSO			NMP			DMF		
	Obs	CGC [mM]	wt %	Obs	CGC [mM]	wt %	Obs	CGC [mM]	wt %
4a	G	11.9	0.93	G	33.4	2.74	GP	—	—
4b	G	10.8	0.85	G	26.0	2.17	G	48.1	4.28
4c	G	4.6	0.39	G	16.5	1.47	G	35.3	3.35
8a	G	17.2	1.02	GP	—	—	G	13.4	0.90
8b	G	10.1	0.61	G	15.0	0.96	G	12.2	0.83
8c	G	5.1	0.33	G	7.32	0.51	G	6.5	0.48
12	GP	—	—	GP	—	—	S	—	—

It was found that derivatives of **8a**–**c** whereby the nitro end group was located in the *ortho* (**7a**–**c**) or *para* position (**9a**–**c**) with respect to the urea functionality, failed to gel in any of the solvents via thermal or solvent triggering effects (indeed, these compounds formed precipitates in all of the gel studies). Analogous results were obtained in gelation tests for derivatives of **4a**–**c** in which the ester groups are situated in the *para* position (**5a**–**c**). From this simple gelation assay, it is clear that a key structural motif for effective gelation (both in aqueous and organic media) is the location of hydrogen bond acceptor groups *meta* to the urea moiety. It is thus proposed that interactions between these hydrogen bond acceptor moieties and the effective hydrogen bond acceptor/donor capability of the bis aromatic-urea moiety[4] facilitate self-assembly, and hence gelation, when located in the *meta* position. Conversely, when the hydrogen bond acceptor moieties are situated in the *ortho* or *para* position on the aromatic rings, precipitation results. However, in the case of the unfunctionalised bis amide-aromatic-ureas **6a**–**c**, which feature phenyl end groups, specific solvents with hydrogen bond acceptor moieties are required to effect gelation.

The presence of hydrogen bond interactions in these assemblies was confirmed by solid state infrared spectroscopic analysis of compounds **2a**–**c**, **4a**–**c** and **8a**–**c** (see Supplementary data). The decreased frequencies of the N–H and C=O amide and urea absorptions when compared to those found in non-hydrogen bonded moieties are as a result of ordering induced through hydrogen

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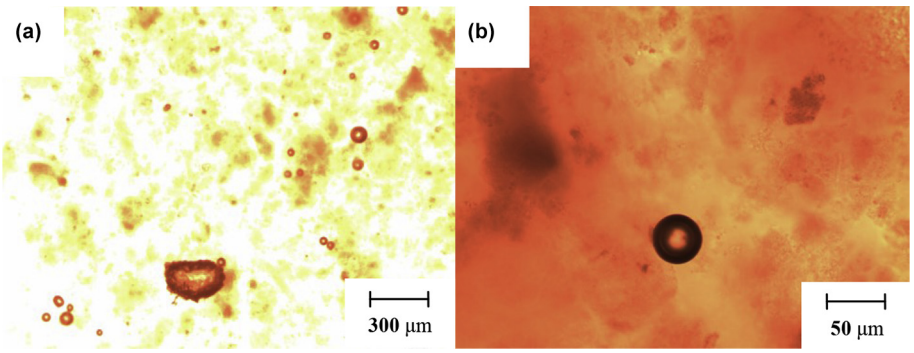

Fig. 5. Optical micrographs of the gel of **4c** in water/DMSO (20% v/v) at its CGC, revealing micelle formation; (a) scale bar 300 μm, (b) scale bar 50 μm.

bonding.[32,33] The result is consistent with structural analysis of **1**[13] and its analogues.[14]

2.3. Solvent parameter analysis

The use of solubility parameters such as Hildebrand, Hasen, Kamlet–Taft and Flory–Huggins have been employed effectively in the analysis of the assembly mechanisms operating in gel networks.[34] Kamlet–Taft solvent parameters[34a,35] (see Supplementary data) have, in this study, also allowed further investigation of the interactions within the organogels thus formed. It is apparent from gelation studies on **4a**–**c**, **6a**–**c** and **8a**–**c** that solvents with low hydrogen bonding donating parameters (α) are desirable for gelation (Table 2). This trend is consistent with observations from previous studies[14]—the urea moiety is an efficient source of hydrogen bond donation and thus solvents interfering with this intermolecular interaction serve to disrupt the gel network.[4,15,34c,36,37]

A direct comparison of the hydrogen bonding accepting parameters (β) of 1,2-dichlorobenzene and nitrobenzene provided insights into the networks formed in gels of tetra-ester, **4a**–**c**, and non-functionalised, **6a**–**c**, bis amide-aromatic-ureas. It is proposed that the successful gelation of 1,2-dichlorobenzene by **4a**–**c** arises as a result of the low β value of the solvent and the hydrogen bond accepting ability of the terminal ester groups, allowing the intermolecular interaction of hydrogen bond withdrawing and donating groups and ultimately self-assembly of the gelator. Absence of the hydrogen bond accepting ester moieties, i.e., bis amide-aromatic-ureas **6a**–**c**, thus favours gelation of solvents with larger β values (as achieved in nitrobenzene) that are able to interact with the gelators hydrogen bond donating moieties. This conclusion was reinforced since **4a**–**c** failed to gel in nitrobenzene and **6a**–**c** also do not gel in 1,2-dichlorobenzene. However, use of the Kamlet Taft parameters did not successfully predict suitable gelating solvents for **4a**–**c** and **6a**–**c** therefore revealing the limitation of this approach.[34c]

The tetra-ester, **4a**–**c**, and *meta*-nitro **8a**–**c** bis amide-aromatic-ureas only dissolved in solvents with high hydrogen bonding accepting parameters (β>0.45). Gelation was then achieved after increasing the α value (via addition of water) in order to cause precipitation of the gelator (Table 4). However, stable gels of *para*-ester. **5a**–**c**, *ortho*-nitro **7a**–**c** and *para*-nitro **9a**–**c** could not be realised via this approach, again highlighting the necessity of the interaction between the *meta* withdrawing group on terminal aromatic moiety and the urea moieties in successful gelators.

2.4. Rheological studies

All of the gels reported revealed similar rheological profiles with a storage modulus (G') that was an order of magnitude greater than the loss modulus (G'') (Fig. 6) (indicating successful gelation rather than the presence of highly viscous fluids).[34a] The storage modulus was also independent of shear rates above certain thresholds and thus these gels behave as Bingham type fluids.[38,39] Rheological studies on the gels were performed at a concentration of 20 mM using both cone (1°) and plate geometries at 1% strain (see Supplementary data) to allow comparison with previous studies.[13–15]

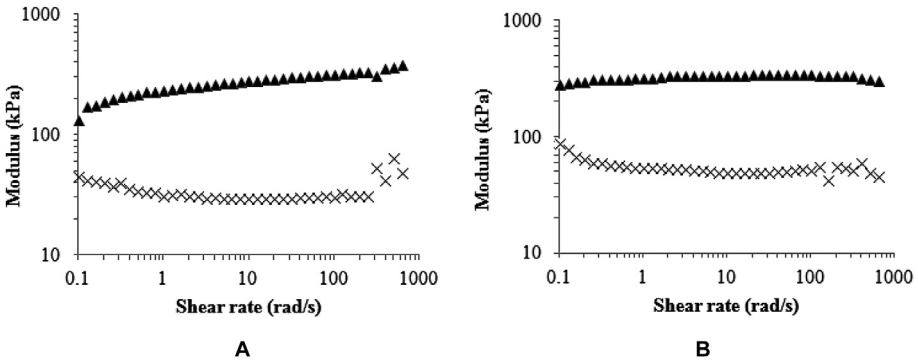

Fig. 6. Rheological data (1° cone geometry) for (A) hydrogelator **2c** (20 mM), (B) organogelator **4a** in 1,2 DCB (20 mM), G': ▲ and G'': ×.

Table 5 demonstrates the correlation of increasing chain length against increasing storage modulus (G') in hydrogelator systems of tetra-acid bis amide-aromatic-ureas **2a**–**c**. The gel **2c** exhibited higher G' values when compared to the bis aromatic-urea **1**, forming more physically robust gels at equal concentrations, thus demonstrating the ability to improve this characteristic of the gel

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Table 5
Maximum storage and loss moduli (kPa) for hydrogelators **1**[14] and **2a**–**c** each at 20 mM (1° cone geometry)

Gelator	G'	G''
1	294	31.5
2a	3.3	0.4
2b	281	41.8
2c	327	44.5

system. The maximum storage modulus value for **2c** also reveals an improvement in comparison to the parent hydrogelator **1**[14] and related bis urea hydrogelator systems,[25] though not as substantial an increase as observed for a structurally related chiral linked urea gelator.[20d] It is proposed that the sudden decrease in G' between bis amide-aromatic-ureas **2a** and **2b** occurs as a result of the latter's decreased ability to cross-link gel fibrils.[19,39–42]

The mechanical studies of thermally stimulated organogels of tetra-ester, **4a**–**c**, and *meta*-nitro, **6a**–**c**, bis amide-aromatic-ureas demonstrate an inverse correlation than that observed for hydrogelators **2a**–**c** (i.e., a decrease in G' as the linker chain length increases) (Table 6). In stark contrast, the gels **4a**–**c** generated in 1,2 DCB exhibited a reversal of this trend indicating a different gelator–solvent interaction/aggregation mechanism.[38–42] Gels **4a** and **4b** in 1,2 DCB, **4b** and **4c** in 1,2,4 TCB and **6c** in nitrobenzene exhibit higher G' values, at identical concentrations to the organogelator analogues of the parental gelator **1**.[15] The bis aromatic-urea **12** was not used as it could not form stable gels at concentrations ca. 20 mM and thus could not be directly compared within this study.

Table 6
Maximum storage and loss moduli (kPa) for thermally stimulated organogelators **4a**–**c** and **6a**–**c** (20 mM) and solvent variation stimulated organogelators **4a**–**c** and **8a**–**c** (20 mM) (gelation initiated via addition of water) (1° cone geometry)

Gelator	1,2 DCB		1,2,4 TCB		Nitrobenzene		DMSO	
	G'	G''	G'	G''	G'	G''	G'	G''
4a	348.5	88.8	61.3	12.9	—	—	188.6	43.0
4b	299.0	79.8	167.0	38.3	—	—	290.1	54.6
4c	103.1	14.9	173.8	24.3	—	—	2032.0	234.5
6a	—	—	—	—	80.9	8.2	—	—
6b	—	—	—	—	88.9	18.3	—	—
6c	—	—	—	—	398.1	36.7	—	—
8a	—	—	—	—	—	—	148.3	17.3
8b	—	—	—	—	—	—	1694.2	250.4
8c	—	—	—	—	—	—	2595.0	477.0

The mechanical properties of gels of tetra-ester, **4a**–**c**, and *meta*-nitro **8a**–**c** bis amide-aromatic-ureas formed in DMSO (via addition of water to the organic solution) were also compared at concentrations of 20 mM (Table 6). The G' reduction as the linker length decreased was attributed to a decrease in surfactant like interactions, an increase in solubility, and hence a weakening of the gel.[19,21,40] The organogelators **4c** and **8c** exhibited vastly increased G' values when compared to the thermogelator counterparts. The possibility of evaporation of the water component on the rheometer plate to afford more viscous gels or even inhomogenous samples, as well as movement of the gels under the cone, was decreased by repeating the two sweeps using a flat plate and oil around the outside of the sample. The data obtained via this method was in agreement with that reported in Table 6 (see Supplementary data). The larger G' values observed for gels of **8a**–**c**, when compared to **4a**–**c**, were assigned to the larger hydrogen bond acceptor tendencies of the nitro groups, in comparison to the ester, resulting in increased self-assembly efficiency of the systems.[13–15,38–42]

2.5. Dye absorption studies

Tetra-acid bis amide-aromatic-ureas **2a**–**c** exhibited dye absorption capabilities relevant to contamination extraction techniques based on molecular gelators[43–48] and linked gelators.[49] Removal of a model containing methylene blue from aqueous media was monitored via UV/vis spectroscopic analysis, employing the absorption maxima at 667 nm of the dye to calculate the degree of extraction (Fig. 7).

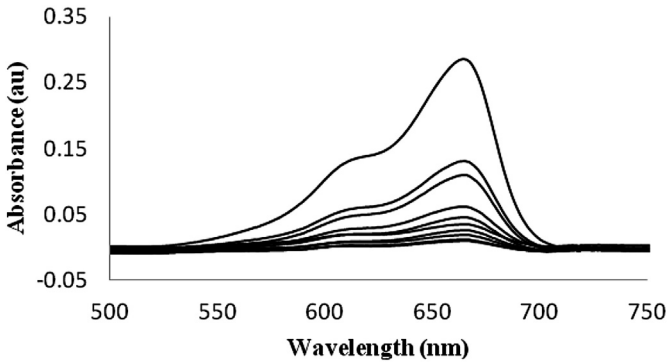

Fig. 7. UV/vis absorption spectra of stirred solution of aqueous methylene blue (250 mL, 0.25 mg L^{-1}) up to 48 h after addition of 1 mL of hydrogelator **2a** (1 mL, 10 mM).

Interestingly none of the hydrogelators demonstrated dye removal capabilities at gelator concentration >20 mM, in contrast to the parental bis aromatic urea and analogues.[14,15] It is proposed that this is as a result of transformations in the mode of self-assembly of the gelator at higher concentrations (see microscopic images in Supplementary data),[3,40,50] hence not affording an extended aromatic face, or permeability within the gel structure, necessary for intercalation of the aromatic dye molecules.[13,14,44,49] It is also noted that gels of both **4a**–**c** and **8a**–**c** in DMSO, NMP and DMF failed to remove methylene blue from solution.

To overcome this trend the gelators were used at a concentration of 10 mM, (removing methylene blue from 1 mg/250 mL aqueous solutions). The gelators did not show any visual increase in dye removal capabilities when compared to systems of **1**, verified by weight dye uptake calculations from UV/vis spectroscopic analysis (Table 7). However, as a result of the decreased concentration used and the increased molecular weight of the linked gelators they have a more effective mol mol^{-1} uptake of the dye than the initial gelator **1** (as would be expected, doubling the amount of aromatic moieties per molecule, hence increasing sites available for gel intercalation).[13,14]

Table 7
Maximum absorption of methylene blue dye from water from hydrogelators **1**[14] (20 mM) and **2a**–**c** (10 mM)

Gelator	Weight dye uptake [mg g^{-1}]	Dye uptake per molecule of gelator [mol mol^{-1}]
1	1020	1.1
2a	128	2.9
2b	56	1.3
2c	117	2.9

Unfortunately direct correlation was not observed between the chain length of the alkyl linker unit and dye uptake. For example, in the case of hydrogelator **2b**, UV/vis spectroscopic analysis revealed a decreased dye uptake in comparison to the other systems (see Supplementary data).

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Further spectroscopic studies were undertaken on the most efficient dye extractor, bis amide-aromatic-urea hydrogelator **2a**, in order to elucidate the mode of interaction between the host and guest. NMR spectroscopic studies revealed downfield shifts in the urea protons resonances with increasing dye concentration suggesting hydrogen bonding as a contributing factor to dye absorption (see Supplementary data). To ascertain the impact of π–π stacking on dye intercalation, a hydrogel of **2a** (10 mM, 1 mL) was prepared in D_2O and a solution of spermine (1 mL, 0.25 mg L^{-1}) was deposited on the gel. After a period of 48 h analysis of the gel and sol separately showed that absorption of the aliphatic tetracation spermine from the solution had not occurred thus supporting the hypothesis that intercalation is responsible for dye removal rather than electrostatic interactions. The hydrogelator also failed to remove methylene orange from solution, as monitored by UV–vis spectroscopy, yet was able to partially remove methylene green from solution (see Supplementary data), indicating selection for positively charged aromatic based molecule adsorption as demonstrated in dye removal studies involving **1**.[13]

3. Conclusions

It has been demonstrated that a range of both hydro- and organo-supergelators can be synthesised via linking a known gelator motif. The process of linking creates a significant improvement on the initial gelling properties. Control over the linked gelators CGC and mechanical properties has been demonstrated via variations of the alkyl linker lengths. It is proposed that functionalization of the links could also result in greater manipulation of the gelator properties, especially dye absorption.

It has also been demonstrated that by varying the number and position of groups capable of hydrogen bonding on the terminal aromatic ring, the gelators properties can also be altered. Furthermore it has been shown that the increase of aromatic moieties via linking known hydrogelators can facilitate increased efficiency of dye removal from aqueous media.

4. Experimental

4.1. General

All of the chemicals and solvents were purchased from Sigma Aldrich and used as purchased. THF was distilled from sodium and benzophenone under inert conditions prior to use. All other solvents were used as supplied. NMR spectra were obtained using Bruker Nanobay 400 and Bruker DPX 400 (operating at 400 MHz and 100 MHz for ^{1}H NMR and ^{13}C NMR, respectively). All samples were prepared in DMSO-d_6 and dissolution was achieved with slight heating and sonication (5–10 min). Mass spectra were generated from Thermo-Fisher Scientific Orbitrap XL LCMS (operating in electrospray mode)—samples were prepared in either 0.1 M $NaOH_{(aq)}$ or DMSO (for direct injection) (1 mg mL^{-1}). A Perkin Elmer 100 FT-IR (diamond ATR sampling attachment) was employed for IR spectroscopic analysis. All the samples in the characterisation were in powder form. UV spectra were recorded using a Varian Cary 300 Bio or a PerkinElmer Lambda 25 UV/Vis Spectrometer. Samples were analysed in quartz curettes with a 5.0 mm path length and were baseline corrected with respect to a blank cell with the appropriate solvent. Thermogravimetric Analysis employed TA Instruments TGA Q50 attached to TGA heat exchanger, platinum crucible and an aluminium TA-Tzero pan (ramp rate 15 °C/min to 500 °C). Differential scanning calorimetry analysis employed TA DSC Q2000 with TA Refrigerated Cooling System 90 (aluminium TA-Tzero pans and lids) (ramp rate 15 °C/min). Rheological analysis employed TA Instruments AR 2000 rheometer operating in the cone and plate geometry (20 mm steel cone with 1° gradient) (25 °C). Dye uptake measurements were carried out via extraction of 2 mL sample from dye/gelator mixtures, filtering through sterile syringe filters (0.2 μm, 33 mm).

Thermal stimulated organogel systems of **4a**–**c** and **6a**–**c** were achieved via sonication of the gelator in the desired solvent and subsequent heating. Solvent stimulated organogel systems of **4a**–**b** and **8a**–**c** were achieved via dissolution of the gelator in the desired solvent (0.8 mL) and addition of polar solvent (0.2 mL). pH stimulated hydrogelator systems of **2a**–**c** were achieved via dissolution of the gelator in $NaOH_{(aq)}$ (0.5 mL, 0.1 M) followed by addition of glucono-δ-lactone (0.5 mL, 0.2 M). The systems were then left for 2 h to acidify and gel. Critical Gelation Concentration (CGC) determination was carried out in a 2 mL screw top glass vial, minimum gelator mass was determined to nearest 1 mg, then varied every 0.2 mg to obtain increased accuracy of CGC.

Generic procedure for synthesis of bis amide-aromatic-ureas **2a**–**c** and **3a**–**c** was achieved via dissolution of **10** (0.20 g, 0.6 mmol) and **11** (0.16 g, 0.6 mmol), respectively, in anhydrous DMF (30 mL) or NMP (30 mL) respectively, with triethlyamine (0.25 mL, 1.8 mmol), followed by addition of respective diacyl chloride (glutaryl chloride 38.3 μL, 0.3 mmol/adipoyl chloride 43.6 μL, 0.3 mmol/sebacoyl chloride 64.1 μL, 0.3 mmol) then stirred for 24 h under inert conditions. Precipitating into acid solutions (pH<4) afforded:

*4.1.1. 5,5′-(((((Glutaroylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl)) bis(azanediyl))diisophthalic acid (**2a**).* Brown powder, (0.17 g, 79%). Mp 229 °C (dec); IR (ATR)/cm^{-1} 3299, 2962, 2567, 1692, 1657, 1559, 1516, 1403, 1299, 1259, 1225, 758, 665; ^{1}H NMR (DMSO-d_6)=9.84 (s, 2H), 9.19 (s, 2H), 8.77 (s, 2H), 8.26 (s, 4H), 8.09 (s, 2H), 7.53 (m, 4H), 7.41 (m, 4H), 2.37 (t, 4H, *J*=7.2 Hz), 1.92 (t, 2H, *J*=5.2 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 166.7, 152.5, 140.6, 134.6, 134.0, 131.8, 123.1, 122.5, 119.6, 119.0, 35.5, 21.0 ppm; MS (ESI) *m*/*z* [M+H$^+$] calculated for $C_{35}H_{31}N_6O_{12}$ 727.1994, found 727.2000.

*4.1.2. 5,5′-(((((Adipoylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl)) bis(azanediyl))diisophthalic acid (**2b**).* Brown powder, (0.20 g, 91%). Mp 209 °C (dec); IR (ATR)/cm^{-1} 3286, 3087, 2959, 2923, 2856, 1710, 1691, 1604, 1557, 1514, 1199, 754, 666; ^{1}H NMR (DMSO-d_6)=9.80 (s, 2H), 9.08 (s, 2H), 8.65 (s, 2H), 8.26 (s, 4H), 8.06 (s 2H), 7.50 (m, 4H), 7.39 (m, 4H), 2.31 (s, 4H), 1.62 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=170.7, 166.6, 152.5, 140.6, 134.5, 134.0, 131.7, 123.4, 122.5, 119.6, 119.0, 36.2, 25.0 ppm; MS (ESI) *m*/*z* [M+H$^+$] calculated for $C_{36}H_{33}N_6O_{12}$ 741.2151, found 741.2156.

*4.1.3. 5,5′-(((((Decanedioylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl)) bis(carbonyl))bis(azanediyl))diisophthalic acid (**2c**).* Dark brown powder, (0.20 g, 84%). Mp 197 °C (dec); IR (ATR)/cm^{-1} 3287, 3051, 2926, 2851, 2578, 1690, 1655, 1551, 1514, 1401, 1201, 1109, 1061, 756, 663; ^{1}H NMR (DMSO-d_6)=9.79 (s, 2H), 9.09 (s, 2H), 8.67 (s, 2H), 8.28 (s, 4H), 8.08 (s, 2H), 7.51 (m, 4H), 7.39 (m, 4H), 2.28 (t, 4H, *J*=7.2 Hz), 1.59 (s, 4H), 1.31 (s, 8H) ppm; ^{13}C NMR (DMSO-d_6)= 170.8, 166.7, 152.5, 140.6, 134.5, 134.1, 131.8, 123.1, 122.5, 119.6, 118.9, 36.3, 28.7, 28.7, 25.2 ppm; MS (ESI) *m*/*z* [M+H$^+$] calculated for $C_{40}H_{41}N_6O_{12}$ 797.2777, found 797.2783.

*4.1.4. 4,4′-(((((Glutaroylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl)) bis(azanediyl))dibenzoic acid (**3a**).* Cream powder, (0.11 g, 59%). Mp 213 °C (dec); IR (ATR)/cm^{-1}; 3278, 2962, 2541, 1645, 1595, 1553, 1509, 1401, 1303, 1226, 1169, 1107, 1052, 837, 760; ^{1}H NMR (DMSO-d_6)=9.84 (s, 2H), 9.19 (s, 2H), 8.89 (s, 2H), 7.86 (m, 4H), 7.55 (m, 8H), 7.40 (m, 4H), 2.35 (m, 4H), 1.91 (t, 2H, *J*=6.8 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 167.0, 152.2, 144.1, 134.5, 134.0, 130.5, 123.4, 119.7, 118.8, 117.1, 35.5, 21.0 ppm; MS

(ESI) *m/z* [M+H$^+$] calculated for $C_{33}H_{31}N_6O_8$ 639.2198, found 639.2196.

*4.1.5. 4,4′-(((((Adipoylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl)) bis(azanediyl))dibenzoic acid (**3b**).* Cream powder, (0.15 g, at 80% purity, estimated from ^{1}H NMR). Mp 222 °C (dec); IR (ATR)/cm^{-1}; 3272, 2939, 2864, 2679, 2550, 1679, 1646, 1594, 1556, 1510, 1403, 1294, 1172, 1109, 1041, 907, 841, 760; ^{1}H NMR (DMSO-d_6)=9.81 (s, 2H), 9.12 (s, 2H), 8.80 (s, 2H), 7.86 (m, 4H), 7.54 (m, 8H), 7.38 (m, 4H), 2.28 (m, 5H), 1.57 (m, 5H) ppm; ^{13}C NMR (DMSO-d_6)=174.3, 170.6, 167.0, 152.4, 144.3, 134.7, 130.5, 123.2, 119.8, 119.7, 118.5, 116.8, 36.0, 33.4, 24.7, 24.1 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{34}H_{33}N_6O_8$ 652.2355, found 653.2358.

*4.1.6. 4,4′-(((((Decanedioylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl)) bis(azanediyl))dibenzoic acid (**3c**).* Brown powder, (0.16 g, 75%). Mp 217 °C (dec); IR (ATR)/cm^{-1} 3285, 2927, 2851, 1802, 1692, 1648, 1594, 1562, 1511, 1404, 1305, 1171, 1043, 839, 742; MS (ESI) *m/z*; ^{1}H NMR (DMSO-d_6)=9.78 (s, 2H), 9.05 (s, 2H), 8.73 (s, 2H), 7.86 (m, 4H), 7.53 (m, 8H), 7.37 (m, 4H), 2.27 (t, 4H, *J*=7.2 Hz), 1.59 (s, 4H), 1.29 (s, 8H) ppm; ^{13}C NMR (DMSO-d_6)=170.8, 167.0, 152.2, 144.4, 134.4, 134.1, 130.5, 123.4, 119.6, 118.8, 117.1, 36.3, 28.7 (d), 25.2 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{38}H_{41}N_6O_8$ 708.2980, found 708.2980.

Generic procedure for synthesis of bis amide-aromatic-ureas **4a**–**c**, **5a**–**c**, **6a**–**c**, **7a**–**c**, **8a**–**c** and **9a**–**c** were achieved via dissolution of bis aromatic-ureas **12** (0.15 g, 0.4 mmol), **13** (0.12 g, 0.4 mmol), **14** (0.10 g, 0.4 mmol), **15**–**17** (0.15 g, 0.5 mmol), respectively, in anhydrous THF (40 mL) and triethlyamine (69.7 μL, 0.5 mmol), followed by addition of respective diacyl chloride (glutaryl chloride 25.5 μL, 0.2 mmol/adipoyl chloride 29.3 μL, 0.2 mmol/sebacoyl chloride 42.7 μL, 0.2 mmol) then stirred for 24 h under inert conditions. The products were isolated as precipitates.

*4.1.7. Tetraethyl 5,5′-(((((glutaroylbis(azanediyl))bis(4,1-phenylene)) bis(azanediyl)) bis(carbonyl))bis(azanediyl))diisophthalate (**4a**).* Cream powder, (0.15 g, 91%). Mp 228 °C (dec); IR (ATR)/cm^{-1} 3708, 3676, 3354, 3267, 2982, 2939, 2923, 1724, 1660, 1650, 1562, 1228, 1058, 1033, 1018, 753; ^{1}H NMR (DMSO-d_6)=9.86 (s, 2H), 9.21 (s, 2H), 8.65 (s, 2H), 8.33 (s, 4H), 8.08 (s, 2H), 7.55 (m, 4H), 7.40 (m, 4H), 4.37 (q, 8H, *J*=6.8 Hz), 2.37 (t, 4H, *J*=6.8 Hz), 1.92 (t, 2H, *J*=6.8 Hz), 1.35 (q, 12H, *J*=6.8 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 164.9, 152.5, 140.9, 134.4, 134.1, 130.9, 122.5, 122.4, 119.6, 119.1, 61.2, 35.5, 21.0, 14.1 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{43}H_{47}N_6O_{12}$ 839.3246, found 839.3248.

*4.1.8. Tetraethyl 5,5′-(((((adipoylbis(azanediyl))bis(4,1-phenylene)) bis(azanediyl)) bis(carbonyl))bis(azanediyl))diisophthalate (**4b**).* Cream powder, (0.16 g, 88%). Mp 214 °C (dec); IR (ATR)/cm^{-1} 3708, 3675, 3352, 3288, 2982, 2946, 2923, 1719, 1656, 1655, 1554,1515, 1227, 1214, 1057, 1033, 1018, 752; ^{1}H NMR (DMSO-d_6)=9.83 (s, 2H), 9.21 (s, 2H), 8.64 (s, 2H), 8.33 (s, 4H), 8.08 (s, 2H), 7.53 (m, 4H), 7.40 (m, 4H), 4.39 (q, 8H, *J*=6.8 Hz), 2.33 (s, 4H), 2.10 (s, 4H), 1.35 (t, 12H, *J*=8.4 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.7, 164.9, 152.4, 140.9, 134.4, 134.1, 130.9, 122.5, 122.4, 119.6, 119.1, 61.1, 36.2, 25.0, 14.1 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{44}H_{49}N_6O_{12}$ 853.3403, found 853.3412.

*4.1.9. Tetraethyl 5,5′-(((((decanedioylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl)) bis(carbonyl))bis(azanediyl))diisophthalate (**4c**).* Brown powder, (0.17 g, 93%). Mp 204 °C (dec); IR (ATR)/cm^{-1} 3708, 3681, 3351, 3286, 2982, 2938, 2923, 1719, 1654, 1652, 1554, 1515, 1228, 1057, 1033, 1017, 752; ^{1}H NMR (DMSO-d_6)=9.77 (s, 2H), 9.22 (s, 2H), 8.64 (s, 2H), 8.32 (m, 4H), 8.08 (s, 2H), 7.52 (m, 4H), 7.39 (d, 4H) 4.36 (q, 8H, *J*=6.8 Hz), 2.28 (t, 4H, *J*=7.2 Hz), 1.60 (s, 4H) 1.35 (t, 12H, *J*=7.2 Hz), 1.31 (s, 8H) ppm; ^{13}C NMR (DMSO-d_6)=170.8, 164.9, 152.5, 140.9, 134.3, 134.2, 130.9, 122.5, 122.4, 119.6, 119.1, 61.2, 36.3, 28.7, 28.7, 25.2, 14.1 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{48}H_{57}N_6O_{12}$ 909.4029, found 909.4036.

*4.1.10. Diethyl 4,4′-(((((glutaroylbis(azanediyl))bis(4,1-phenylene)) bis(azanediyl)) bis(carbonyl))bis(azanediyl))dibenzoate (**5a**).* White powder, (0.11 g, 80%). Mp 231 °C (dec); IR (ATR)/cm^{-1} 3285, 3049, 2982, 2942, 2904, 1712, 1650, 1596, 1557, 1511, 1402, 1367, 1304, 1274, 1227, 1169, 1102, 1017, 835, 761; ^{1}H NMR (DMSO-d_6)=9.85 (s, 2H), 9.06 (s, 2H), 8.71 (s, 2H), 7.88 (m, 4H), 7.57 (m, 4H), 7.53 (m, 4H), 7.39 (m, 4H), 4.29 (q, 4H, *J*=8.0 Hz), 2.37 (m, 4H), 1.90 (m, 2H), 1.32 (t, 6H, *J*=8.0 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 165.4, 152.2, 144.4, 130.3, 122.5, 119.7, 118.8, 117.2, 60.2, 35.5, 21.0, 14.2 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{37}H_{39}N_6O_8$ 695.2824, found 695.2827.

*4.1.11. Diethyl 4,4′-(((((adipoylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl)) bis(carbonyl))bis(azanediyl))dibenzoate (**5b**).* White powder, (0.11 g, 79%). Mp 211 °C (dec); IR (ATR)/cm^{-1} 3263, 2945, 2870, 1712, 1647, 1552, 1511, 1401, 1273, 1212, 1169, 1075, 834, 760; ^{1}H NMR (DMSO-d_6)=9.85 (s, 2H), 9.06 (s, 2H) 8.71 (s, 2H), 7.87 (m, 4H), 7.57 (m, 4H), 7.51 (m, 4H), 7.37 (m, 4H), 4.28 (q, 4H, *J*=8.0 Hz), 2.32 (m, 4H), 1.63 (m, 4H), 1.31 (t, 6H, *J*=8.0 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.8, 165.5, 152.2, 144.4, 134.4, 134.0, 130.3, 122.6, 119.7, 118.9, 117.2, 60.3, 36.2, 24.9, 14.2 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{38}H_{41}N_6O_8$ 709.2980, found 709.2980.

*4.1.12. Diethyl 4,4′-(((((decanedioylbis(azanediyl))bis(4,1-phenylene))bis(azanediyl)) bis(carbonyl))bis(azanediyl))dibenzoate (**5c**).* White powder (0.09 g, 63%). Mp 216 °C (dec); IR (ATR)/cm^{-1} 3285, 2928, 2850, 1714, 1650, 1597, 1562, 1514, 1403, 1306, 1278, 1230, 1172, 1107, 1019, 838, 761; ^{1}H NMR (DMSO-d_6)=9.76 (s, 2H), 9.06 (s, 2H), 8.70 (s, 2H) 7.86 (m, 4H), 7.55 (m, 4H), 7.50 (m, 4H), 7.36 (m, 4H), 4.27 (q, 4H, *J*=8.0 Hz), 2.26 (m, 4H), 1.57 (m, 4H) 1.30 (m, 14H) ppm; ^{13}C NMR (DMSO-d_6)=170.8, 165.4, 152.2, 144.4, 130.3, 122.5, 119.6, 118.8, 117.1, 60.2, 36.3, 28.7, 14.2 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{42}H_{49}N_6O_8$ 765.3606, found 765.3607.

*4.1.13. N^1,N^5-Bis(4-(3-phenylureido)phenyl)glutaramide (**6a**).* White powder, (0.09 g, 82%). Mp 201 °C (dec); IR (ATR)/cm^{-1} 3310, 3284, 3040, 2959, 1659, 1637, 1557, 1538, 1445, 1403, 1298, 1227, 1169, 739, 692, 637, 619; ^{1}H NMR (DMSO-d_6)=9.82 (s, 2H), 8.61 (s, 2H), 8.56 (s, 2H), 7.52 (m, 4H), 7.45 (m, 4H), 7.37 (m, 4H), 7.28 (m, 4H), 6.97 (m, 4H), 2.36 (t, 4H, *J*=7.2 Hz), 1.91 (quin, 2H, *J*=7.2 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 152.5, 139.8, 134.9, 133.7, 128.7, 121.7, 119.7, 118.6, 118.1, 35.5, 21.1 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{31}H_{31}N_6O_4$ 551.2401, found 551.2413.

*4.1.14. N^1,N^6-Bis(4-(3-phenylureido)phenyl)adipamide (**6b**).* White powder, (0.11 g, 98%). Mp 249 °C (dec); IR (ATR)/cm^{-1} 3308, 3260, 3149, 3040, 2940, 2875, 1644, 1557, 1512, 1403, 1299, 1228, 842, 726, 690, 642; ^{1}H NMR (DMSO-d_6)=9.79 (s, 2H), 8.60 (s, 2H), 8.56 (s, 2H), 7.51 (m, 4H), 7.50 (m, 4H), 7.37 (m, 4H), 7.28 (m, 4H), 6.97 (m, 4H), 2.32 (s, 4H), 1.64 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=170.6, 152.5, 139.8, 134.9, 133.7, 128.7, 121.7, 119.7, 118.6, 118.1, 36.2, 25.0 ppm; MS (ESI) *m/z* [M+H$^+$] calculated for $C_{32}H_{33}N_6O_4$ 565.2558, found 565.2565.

*4.1.15. N^1,N^{10}-Bis(4-(3-phenylureido)phenyl)decanediamide (**6c**).* White powder, (0.12 g, 90%). Mp 254 °C (dec); IR (ATR)/cm^{-1} 3308, 3287, 3043, 2927, 2850, 1624, 1562, 1514, 1404, 1230, 741, 691, 638, 625; ^{1}H NMR (DMSO-d_6)=9.75 (s, 2H), 8.75 (s, 2H), 8.70 (s, 2H), 7.49 (m, 4H), 7.45 (m, 4H), 7.37 (m, 4H), 7.28 (m, 4H), 6.96 (m, 4H), 2.28 (t, 4H, *J*=7.2 Hz), 1.60 (s, 4H), 1.32 (s, 8H) ppm; ^{13}C NMR

(DMSO-d_6)=170.8, 152.7, 140.0, 135.1, 133.6, 128.7, 121.5, 119.7, 118.5, 118.1, 36.3, 28.7, 28.7, 25.2 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{36}H_{41}N_6O_4$ 621.3184, found 621.3198.

*4.1.16. N^1,N^5-Bis(4-(3-(2-nitrophenyl)ureido)phenyl)glutaramide (**7a**).* Yellow powder, (0.10 g, 85%), Mp 203 °C (dec); IR (ATR)/cm^{-1} 3275, 3140, 3051, 3036, 2935, 2362, 2322, 1660, 1609, 1586, 1559, 1541, 1496, 1461, 1435, 1403, 1336, 1282, 1221, 1145, 844, 779, 783, 739; ^{1}H NMR (DMSO-d_6)=9.88 (s, 2H), 9.79 (s, 2H), 9.59 (s, 2H), 8.32 (m, 2H), 8.10 (m, 2H), 7.70 (m, 2H), 7.56 (m, 4H), 7.42 (m, 4H), 7.19 (m, 4H), 2.38 (t, 4H, J=7.2 Hz), 1.92 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 151.8, 137.5, 135.0, 134.9, 134.3, 125.4, 122.6, 122.1, 119.7, 119.0, 35.5, 21.0 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{31}H_{29}N_8O_8$ 641.2103, found 641.2101.

*4.1.17. N^1,N^6-Bis(4-(3-(2-nitrophenyl)ureido)phenyl)adipamide (**7b**).* Yellow powder, (0.12 g, 93%), Mp 220 °C (dec); IR (ATR)/cm^{-1} 3262, 3146, 3041, 2923, 2364, 2336, 1651, 1584, 1558, 1543, 1499, 1456, 1434, 1401, 1337, 1283, 1253, 1213, 1147, 842, 782, 736; ^{1}H NMR (DMSO-d_6)=9.84 (s, 2H), 9.78 (s, 2H), 9.59 (s, 2H), 8.32 (m, 2H), 8.10 (m, 2H), 7.71 (m, 2H), 7.55 (m, 4H), 7.42 (m, 4H), 7.19 (m, 2H), 2.33 (s, 4H), 1.65 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=170.7, 151.8, 137.5, 135.1, 135.0, 134.3, 125.4, 122.4, 122.2, 119.7, 119.0, 36.2, 25.0 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{32}H_{31}N_8O_8$ 655.2259, found 655.2256.

*4.1.18. N^1,N^{10}-Bis(4-(3-(2-nitrophenyl)ureido)phenyl)decanediamide (**7c**).* Yellow powder, (0.09 g, 73%), Mp 229 °C (dec); IR (ATR)/cm^{-1} 3267, 2913, 2845, 2602, 2496, 2361, 2337, 1654, 1589, 1584, 1554, 1543, 1498, 1456, 1435, 1402, 1337, 1283, 1222, 838, 791, 735; ^{1}H NMR (DMSO-d_6)=9.83 (m, 4H), 9.61 (s, 2H), 8.30 (m, 2H), 8.10 (m, 2H), 7.70 (m, 2H), 7.54 (m, 4H), 7.40 (m, 4H), 7.21 (m, 2H), 2.29 (t, 4H, J=7.2 Hz), 1.60 (m, 4H), 1.30 (m, 8H) ppm; ^{13}C NMR (DMSO-d_6)=170.9, 151.8, 137.7, 134.9, 134.3, 125.4, 122.6, 122.1, 119.6, 119.0, 36.3, 28.7, 25.2 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{36}H_{39}N_8O_8$ 711.2885, found 711.2885.

*4.1.19. N^1,N^5-Bis(4-(3-(3-nitrophenyl)ureido)phenyl)glutaramide (**8a**).* Yellow powder, (0.09 g, 74%). Mp 240 °C (dec); IR (ATR)/cm^{-1} 3367, 3276, 3096, 2985, 1737, 1653, 1556, 1513, 1404, 1345, 1301, 1228, 1044, 802, 733, 681, 606; ^{1}H NMR (DMSO-d_6)=9.86 (s, 2H), 9.20 (s, 2H), 8.78 (s, 2H), 8.58 (s, 2H), 7.83 (m, 2H), 7.73 (m, 2H), 7.53 (m, 6H), 7.41 (m, 4H), 2.37 (t, 4H, J=6.8 Hz), 1.59 (t, 2H, J=7.2 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 152.4, 148.1, 141.2, 134.3, 134.2, 133.9, 130.0, 124.2, 119.6, 119.4, 119.0, 116.1, 112.0, 35.5, 21.0 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{31}H_{29}N_8O_8$ 641.2103, found 641.2103.

*4.1.20. N^1,N^6-Bis(4-(3-(3-nitrophenyl)ureido)phenyl)adipamide (**8b**).* Yellow powder, (0.11 g, 84%). Mp 199 °C (dec); IR (ATR)/cm^{-1} 3259, 2937, 2871, 1648, 1554, 1513, 1403, 1347, 1298, 1238, 1178, 1013, 842, 797, 732, 679; ^{1}H NMR (DMSO-d_6)=9.84 (s, 2H), 9.19 (s, 2H), 8.76 (s, 2H), 7.82 (m, 2H), 7.70 (m, 2H), 7.56 (m, 6H), 7.41 (m, 4H), 2.33 (s, 4H), 1.64 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=170.7, 152.6, 148.1, 141.4, 130.0, 124.2, 119.7, 119.6, 119.3, 119.0, 116.0, 112.0, 36.2, 25.0, 24.9 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{32}H_{31}N_8O_8$ 655.2259, found 655.2258.

*4.1.21. N^1,N^{10}-Bis(4-(3-(3-nitrophenyl)ureido)phenyl)decanediamide (**8c**).* Brown powder, (0.12 g, 90%). Mp 211 °C (dec); IR (ATR)/cm^{-1} 3367, 3286, 2924, 2925, 2850, 1654, 1554, 1514, 1403, 1345, 1303, 1230, 843, 804, 734, 681; ^{1}H NMR (DMSO-d_6)=9.82 (s, 2H), 9.52 (s, 2H), 9.01 (s, 2H), 8.57 (s, 2H), 7.81 (m, 2H), 7.72 (m, 2H), 7.58 (m, 2H), 7.51 (m, 4H), 7.39 (m, 4H), 2.28 (t, 4H, J=7.2 Hz), 1.59 (s, 4H), 1.31 (s, 8H) ppm; ^{13}C NMR (DMSO-d_6)=170.9, 152.5, 148.1, 141.2, 134.4, 134.1, 133.9, 130.0, 124.0, 119.7, 119.4, 119.2, 118.9, 116.0, 111.8, 36.3, 28.7, 28.7, 25.2 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{36}H_{39}N_8O_8$ 711.2885, found 711.2886.

*4.1.22. N^1,N^5-Bis(4-(3-(4-nitrophenyl)ureido)phenyl)glutaramide (**9a**).* Yellow powder, (0.11 g, 78%). Mp 213 °C (dec); IR (ATR)/cm^{-1}; 3368, 3271, 3153, 2930, 2851, 1654, 1550, 1503, 1401, 1326, 1303, 1215, 1176, 1111, 854, 834, 747; ^{1}H NMR (DMSO-d_6)=9.84 (s, 2H), 9.39 (s, 2H), 8.83 (s, 2H), 8.17 (m, 4H), 7.67 (m, 4H), 7.53 (m, 4H), 7.38 (m, 4H), 2.35 (t, 4H, J=7.3 Hz), 1.88 (quin, 2H, J=6.9 Hz) ppm; ^{13}C NMR (DMSO-d_6)=170.4, 151.9, 146.5, 140.9, 134.4, 134.1, 125.1, 119.7, 119.1, 117.3, 35.5, 30.7 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{31}H_{29}N_8O_8$ 641.2103, found 641.2110.

*4.1.23. N^1,N^6-Bis(4-(3-(4-nitrophenyl)ureido)phenyl)adipamide (**9b**).* Yellow powder, (0.11 g, 82%). Mp 234 °C (dec); IR (ATR)/cm^{-1}; 3367, 3270, 2929,2850, 1654, 1549, 1495, 1401, 1325, 1300, 1214, 1178, 1110, 834, 747; ^{1}H NMR (DMSO-d_6)=9.81 (s, 2H), 9.38 (s, 2H), 8.82 (s, 2H), 8.17 (m, 4H), 7.67 (m, 4H), 7.52 (m, 4H), 7.37 (m, 4H), 2.31 (s, 4H), 1.62 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=170.7, 151.9, 146.5, 140.9, 134.3, 134.1, 125.1, 119.7, 119.1, 117.3, 36.2, 25.0 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{32}H_{31}N_8O_8$ 655.2259, found 655.2272.

*4.1.24. N^1,N^{10}-Bis(4-(3-(4-nitrophenyl)ureido)phenyl)decanediamide (**9c**).* Yellow powder, (0.12 g, 91%). Mp 226 °C (dec); IR (ATR)/cm^{-1} 3370, 3280, 2930, 2919, 2850, 1654, 1550, 1503, 1493, 1401, 1326, 1303, 1227,1215, 1176, 1111, 853, 834,747; ^{1}H NMR (DMSO-d_6)=9.80 (s, 2H), 9.40 (s, 2H), 8.83 (s, 2H), 8.20 (m, 4H), 7.70 (m, 4H), 7.54 (m, 4H), 7.40 (m, 4H), 2.28 (s, 4H) 1.60 (s, 4H), 1.32 (s, 8H) ppm; ^{13}C NMR (DMSO-d_6)=170.9, 151.9, 146.5, 140.9, 134.4, 134.0, 125.1, 119.7, 119.1, 117.3, 36.3, 28.7, 28.7, 25.14 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{36}H_{39}N_8O_8$ 711.2885, found 711.2886.

*4.1.25. 1-(4-Aminophenyl)-3-phenylurea (**14**).* Phenylisocyanate (273 μL, 2.5 mmol) in anhydrous THF (25 mL) was added dropwise to a solution of 1,4-phenyldiamine (0.30 g, 2.8 mmol) in anhydrous THF (25 mL, 5 °C). The product was then recovered in vacuo as a white powder, (0.54 g, 95%). Mp 155 °C (dec); IR (ATR)/cm^{-1} 3452, 3364, 3291, 3036, 2940, 1621, 1593, 1551, 1509, 1303, 1228, 835, 799, 738, 691, 667; ^{1}H NMR (DMSO-d_6)=8.53 (s, 1H), 8.19 (s, 1H), 7.43 (m, 2H), 7.27 (m, 2H), 7.08 (m, 2H), 6.94 (m, 1H), 6.52 (m, 2H), 4.79 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6)=152.9, 144.0, 140.2, 128.7, 128.5, 121.3, 120.7, 117.9, 114.1 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{13}H_{14}N_3O$ 228.1131, found 228.1131.

Bis aromatic-ureas **15**–**17** were synthesised by addition of the respective 2/3/4-nitrophenlyisocyanate (0.45 g, 2.7 mmol) in anhydrous THF (25 mL) in a dropwise fashion to a solution of 1,4-phenyldiamine (0.30 g, 2.8 mmol) in anhydrous THF (25 mL, 5 °C). The product was then recovered in vacuo.

*4.1.26. 1-(4-Aminophenyl)-3-(2-nitrophenyl)urea (**15**).* Yellow powder, (0.65 g, 89%), Mp 184 °C (dec); IR (ATR)/cm^{-1} 3325, 3288, 3045, 2841, 2539, 2325, 1715, 1661, 1582, 1549, 1499, 1420, 1335, 1280, 1257, 1118, 1090, 1038, 861, 789, 733; ^{1}H NMR (DMSO-d_6)=10.11 (s, 1H), 9.93 (s, 2H), 9.68 (s 1H), 8.22 (m, 1H) 8.10 (m, 1H), 7.72 (m, 1H), 7.58 (m, 2H), 7.27 (m, 3H) ppm; ^{13}C NMR (DMSO-d_6)=151.9, 138.5, 138.2, 134.8, 134.4, 125.4, 123.2, 122.8, 122.5, 119.4 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{13}H_{13}N_4O_3$ 273.0982, found 273.0984.

*4.1.27. 1-(4-Aminophenyl)-3-(3-nitrophenyl)urea (**16**).* Yellow solid, (0.69 g, 94%), Mp 198 °C (dec); IR (ATR)/cm^{-1} 3403, 3338, 3299, 1669, 1606, 1553, 1522, 1511, 1435, 1347, 1311, 1279, 1236, 884, 842, 804, 738, 681; ^{1}H NMR (DMSO-d_6)=9.07 (s, 1H), 8.57 (s, 1H), 8.31 (s, 1H), 7.78 (m, 1H), 7.67 (m, 1H), 7.56 (m, 1H), 7.09 (m, 2H), 6.53 (m, 2H), 4.83 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6)=152.7, 148.1, 144.5, 141.5, 129.9, 127.8, 124.0, 121.2, 119.4, 115.7, 114.0, 111.8 ppm; MS

(ESI) m/z [M+H$^+$] calculated for $C_{13}H_{13}N_4O_3$ 273.0982, found 273.0982.

*4.1.28. 1-(4-Aminophenyl)-3-(4-nitrophenyl)urea (**17**).* Yellow solid, (0.65 g, 88%), Mp 161 °C (dec); IR (ATR)/cm^{-1} 3402, 3319, 3071, 1700, 1597, 1539, 1501, 1488, 1338, 1234, 1204, 1112, 853, 853, 749; ^{1}H NMR (DMSO-d_6)=9.29 (s, 1H), 8.42 (s, 1H), 8.18 (m, 2H), 7.67 (m, 2H), 7.11 (m, 2H), 6.54 (m, 2H), 4.87 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6)=152.1, 146.9, 144.7, 140.6, 127.6, 125.1, 121.1, 117.1, 114.0 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{13}H_{13}N_4O_3$ 273.0982, found 273.0982.

*4.1.29. 5,5′-(((Hexane-1,6-diylbis(azanediyl))bis(carbonyl))bis(azanediyl))diisophthalic acid (**18**).* 5-Aminoisophthalic acid (0.15 g, 0.8 mmol) was added to a solution of 1,6-Diisocyanatohexane (64.6 μL, 0.4 mmol) in anhydrous DMF (50 mL) and stirred under inert conditions for 24 h. The solvent was removed in vacuo to afford **18** as a white powder (0.14 g, 64%). Mp 189 °C (dec); IR (ATR)/cm^{-1} 3306, 2935, 2853, 1695, 1645, 1600, 1558, 1513, 1403, 1297, 1207, 1105, 1059, 757, 647; ^{1}H NMR (DMSO-d_6)=8.97 (s, 2H), 8.23 (s, 4H), 8.02 (s, 2H), 6.35 (s, 2H), 3.11 (s, 4H), 1.47 (s, 4H), 1.33 (s, 4H) ppm; ^{13}C NMR (DMSO-d_6)=166.9, 155.0, 141.2, 132.0, 122.4, 121.9, 30.0, 29.7, 26.1 ppm; MS (ESI) m/z [M+H$^+$] calculated for $C_{24}H_{27}N_4O_{10}$ 531.1722, found 531.1719.

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Supplementary data

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References and notes

1. Yang, X.; Zhang, G.; Zhang, D. *J. Mater. Chem.* **2012**, *22*, 38–50.
2. Segarra-Maset, M. D.; Nebot, V. J.; Miravet, J. F.; Escuder, B. *Chem. Soc. Rev.* **2013**, *42*, 7086–7098.
3. Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133–3159.
4. Steed, J. W. *Chem. Commun.* **2011**, 1379–1383.
5. Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039–1046.
6. Lyon, R. P.; Atkins, W. M. *J. Am. Chem. Soc.* **2001**, *123*, 4408–4413.
7. Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinka, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664–6676.
8. Vintiloiu, A.; Leroux, J. C. *J. Controlled Release* **2008**, *125*, 179–192.
9. Skilling, K. J.; Citossi, F.; Bradshaw, T. D.; Ashford, M.; Kellam, B.; Marlow, M. *Soft Matter* **2014**, *10*, 237–256.
10. Días Días, D.; Kühbeck, D.; Koopmans, R. J. *Chem. Soc. Rev.* **2011**, *40*, 427–448.
11. Escuder, B.; Rodriguez-Llansola, F.; Miravet, J. F. *New J. Chem.* **2010**, *34*, 1044–1054.
12. Puigmartí-Luis, J.; Amabilino, D. B. In *Functional Molecular Gels*; Escuder, B., Miravet, J. F., Eds.; Royal Society of Chemistry: Cambridge, UK, 2014; pp 195–254.
13. Rodríguez-Llansola, F.; Escuder, B.; Miravet, J. F.; Hermida-Merino, D.; Hamley, I. W.; Cardin, C. J.; Hayes, W. *Chem. Commun.* **2010**, 7960–7962.
14. Wood, D. M.; Greenland, B. W.; Acton, A. L.; Rodríguez-Llansola, F.; Murray, C. A.; Cardin, C. J.; Miravet, J. F.; Escuder, B.; Hamley, I. W.; Hayes, W. *Chem.—Eur. J.* **2012**, *18*, 2692–2699.
15. Bajaj, N.; Hart, L. R.; Greenland, B. W.; Hayes, W. *Macromol. Symp.* **2013**, *329*, 118–124.
16. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
17. Chen, J.; Kampf, J. W.; McNeil, A. J. *Langmuir* **2010**, *26*, 13076–13080.
18. (a) George, M.; Tan, G.; John, V. T.; Weiss, R. G. *Chem.—Eur. J.* **2005**, *11*, 3243–3254; (b) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237–1247.
19. van Esch, J. H.; De Feyter, S.; Kellogg, R. M.; De Schryver, F.; Feringa, B. L. *Chem.—Eur. J.* **1997**, *3*, 1238–1243.
20. (a) Miravet, J. F.; Escuder, B. *Org. Lett.* **2005**, *7*, 4791–4794; (b) Escuder, B.; LLusar, M.; Miravet, J. F. *J. Org. Chem.* **2006**, *71*, 7747–7752; (c) Hirst, A. R.; Coates, I. A.; Boucheteau, T. R.; Miravet, J. F.; Escuder, B.; Castelletto, V.; Hamley, I. W.; Smith, D. K. *J. Am. Chem. Soc.* **2008**, *130*, 9113–9121; (d) Rodríguez-Llansola, F.; Hermida-Merino, D.; Nieto-Ortega, B.; Ramírez, F. J.; Navarrete, J. T.; Casado, J.; Hamley, I. W.; Escuder, B.; Hayes, W.; Miravet, J. F. *Chem.—Eur. J.* **2012**, *46*, 14725–14731.
21. van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263–2266.
22. Jung, J. H.; Shinkai, S.; Shimizu, T. *Chem.—Eur. J.* **2002**, *8*, 2684–2690.
23. Nakazawa, I.; Masuda, M.; Okada, Y.; Hanada, T.; Yase, K.; Asai, M.; Shimizu, T. *Langmuir* **1999**, *15*, 4757–4764.
24. Buerkle, L. E.; Rowan, S. J. *Chem. Soc. Rev.* **2012**, *41*, 6089–6102.
25. Lloyd, G. O.; Piepenbrock, M. M.; Foster, J. A.; Clarke, N.; Steed, J. W. *Soft Matter* **2012**, *8*, 204–216.
26. San-José, N.; Gómez-Valdemoro, A.; García, F. C.; De La Peña, J. L.; Serna, F.; García, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5398–5407.
27. Rodriguez, F.; Rozas, I.; Brun, R.; Kaiser, M.; Nguyen, B.; Wilson, W. D.; Garcia, R. N.; Dardonville, C. *J. Med. Chem.* **2008**, *51*, 909–923.
28. Denny, W. A.; Atwell, G. J.; Baguley, B. C.; Cain, B. F. *J. Med. Chem.* **1979**, *22*, 134–150.
29. Weng, W.; Beck, J. B.; Jamieson, A. M.; Rowan, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 11663–11672.
30. Yan, N.; Xu, Z.; Diehn, K. K.; Raghavan, S. R.; Fang, Y.; Weiss, R. G. *J. Am. Chem. Soc.* **2013**, *135*, 8989–8999.
31. Laouini, A.; Jaafar-Maalej, C.; Limayem-Blouza, I.; Sfar, S.; Charcosset, C.; Fessi, H. *J. Colloid Sci. Biotechnol.* **2012**, *1*, 147–168.
32. (a) Teo, L. S.; Chen, C. Y.; Kuo, J. F. *Macromolecules* **1997**, *30*, 1793–1799; (b) Yilgör, E.; Burgaz, E.; Yurtsever, E.; Yilgör, Í. *Polymer* **2000**, *41*, 849–857.
33. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, NY, 1997.
34. (a) Hirst, A. R.; Smith, D. K. *Langmuir* **2004**, *20*, 10851–10857; (b) Barton, A. F. M. *Chem. Rev.* **1975**, *75*, 731–753; (c) Edwards, W.; Lagadec, C. A.; Smith, D. K. *Soft Matter* **2011**, *7*, 110–117.
35. Adams, D. J.; Butler, M. F.; Frith, W. J.; Kirkland, M.; Mullen, L.; Sanderson, P. *Soft Matter* **2009**, *5*, 1856–1862.
36. Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887.
37. Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Carr, P. W.; Doherty, R. F.; Taft, R. W. *J. Phys. Chem.* **1987**, *91*, 1996–2004.
38. Macocosko, C. W. *Rheology Principles, Measurements and Applications*; Wiley VCH: New York, NY, 1993.
39. Terech, P.; Pasquier, D.; Bordas, V.; Rossat, C. *Langmuir* **2000**, *16*, 4485–4494.
40. Breedveld, V.; Nowak, A. P.; Sato, J.; Deming, T. J.; Pine, D. J. *Macromolecules* **2004**, *37*, 3943–3953.
41. Raghavan, S. R. *Langmuir* **2009**, *25*, 8382–8385.
42. Cai, X.; Liu, K.; Yan, J.; Zhang, H.; Hou, X.; Liu, Z.; Fang, Y. *Soft Matter* **2012**, *8*, 3756–3761.
43. Hule, R. A.; Nagarkar, R. P.; Hammouda, B.; Schneider, J. P.; Pochan, D. J. *Macromolecules* **2009**, *42*, 7137–7145.
44. Wang, J.; Wang, H.; Song, Z.; Kong, D.; Chen, X.; Yang, B. Z. *Colloids Surf., B* **2010**, *80*, 155–160.
45. Adhikari, B.; Palui, G.; Banerjee, A. *Soft Matter* **2009**, *5*, 3452–3460.
46. Dutta, S.; Das, D.; Dasgupta, A.; Das, P. K. *Chem.—Eur. J.* **2010**, *16*, 1493–1505.
47. Sukul, P. K.; Malik, S. *RSC Adv.* **2013**, *3*, 1902–1915.
48. Kar, T.; Debnath, S.; Das, D.; Shome, A.; Das, P. K. *Langmuir* **2009**, *25*, 8639–8648.
49. Ray, S.; Das, A. K.; Banerjee, A. *Chem. Mater.* **2007**, *19*, 1633–1639.
50. Raghavan, S. R.; Douglas, J. F. *Soft Matter* **2012**, *8*, 8539–8546.