DOI: 10.1002/chem.200701273

Thixotropic Twin-Dendritic Organogelators

Virgil Percec,*[a] Mihai Peterca,[a, b] Michael E. Yurchenko,[a] Jonathan G. Rudick,[a] and Paul A. Heiney[b]

Abstract: Twin-dendritic organogelators have been prepared through selective functionalization of *N*-(3-aminopropyl)-1,3-propanediamine (APPDA) with self-assembling dendrons by using 1,1′-carbonyldiimidazole (CDI). Subsequent modification of the APPDA linker provided an additional degree of structural diversity by which to tailor the gelator self-assembly in bulk or in the gel state. These compounds are able to gel cyclohexane, toluene, *n*-butyl acetate, ethyl acetate, dichloromethane, and tetrahydrofuran. 3,4-Disubstituted apical branching units provided the most efficient organogelators and show a propensity to form thixotropic gels, wherein the gel recovers its elasticity after being subjected to shear. Structural and retrostructural analysis of the twin-dendritic organogelators reveals the bulk structural characteristics to be indicative of the subsequent gel properties. Diverse self-organized arrays were identified in bulk and all are able to form gels, thus indicating the role of quasiequivalence in mediating self-assembly in the gel state. Furthermore, we have found that porous columnar mesophases provide a strategy by which to prepare thixotropic gels. We demonstrate the importance of weak lateral hydrogen bonding within a column stratum versus hydrogen bonding along the length of the column for forming porous columnar mesophases and, by extension, thixotropic gels.

Keywords: dendrimers · gels · liquid crystals · self-assembly · supramolecular chemistry

Introduction

Molecular architectures capable of self-assembly in organic solvents with subsequent self-organization to entrain the bulk solvent are increasingly common in the pursuit of programmable organogelators.[1] Serendipity is the most frequent design principle.[1,2] Advancement beyond the gelation of organic liquids to the precision design of gel properties remains more elusive.[1,2] Thixotropic gels, wherein the gel recovers its elasticity after being subjected to shear, present a self-healing character in the self-assembled and self-organized structures. As such, these materials eliminate the need for heating and cooling to reconstitute thermotropic gels. This makes thixotropic gels more amenable to processing and manipulation.

Only a few recent organogel examples display thixotropic behavior.[3] Self-assembled fibrillar networks are critical to gelation phenomena,[3] while spherulitic networks facilitate reorganization after shearing.[3e] Such criteria may be generally true for the mesoscopic structural origins of thixotropic gels. We are investigating the relationship between bulk self-organization of low-molecular-weight organogelators and the properties of the resulting organogels. Design principles for and the syntheses of twin-dendritic gelators are elaborated herein. We report the propensity of porous cylindrical supramolecular dendrimers to form thixotropic organogels. The self-assembling twin-dendritic gelators provide a modular scaffold through which we can match the gelator to a broad range of solvent polarities. Relationships between the self-assembly and self-organization events at the nanoscale and the above-mentioned mesoscale structural features[3e] are the subjects of further investigation.

The design and convergent synthesis of the twin-dendritic organogelators are based upon our previously reported self-assembling dendrons[4–8] and twin-dendritic and Janus-dendritic benzamides.[9] Amphiphilic, self-assembling dendrons

[a] Prof. Dr. V. Percec, Dr. M. Peterca, Dr. M. E. Yurchenko, Dr. J. G. Rudick
Roy & Diana Vagelos Laboratories
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323 (USA)
Fax: (+1) 215-573-7888
E-mail: percec@sas.upenn.edu

[b] Dr. M. Peterca, Prof. Dr. P. A. Heiney
Department of Physics and Astronomy
University of Pennsylvania
Philadelphia, PA 19104-6396 (USA)

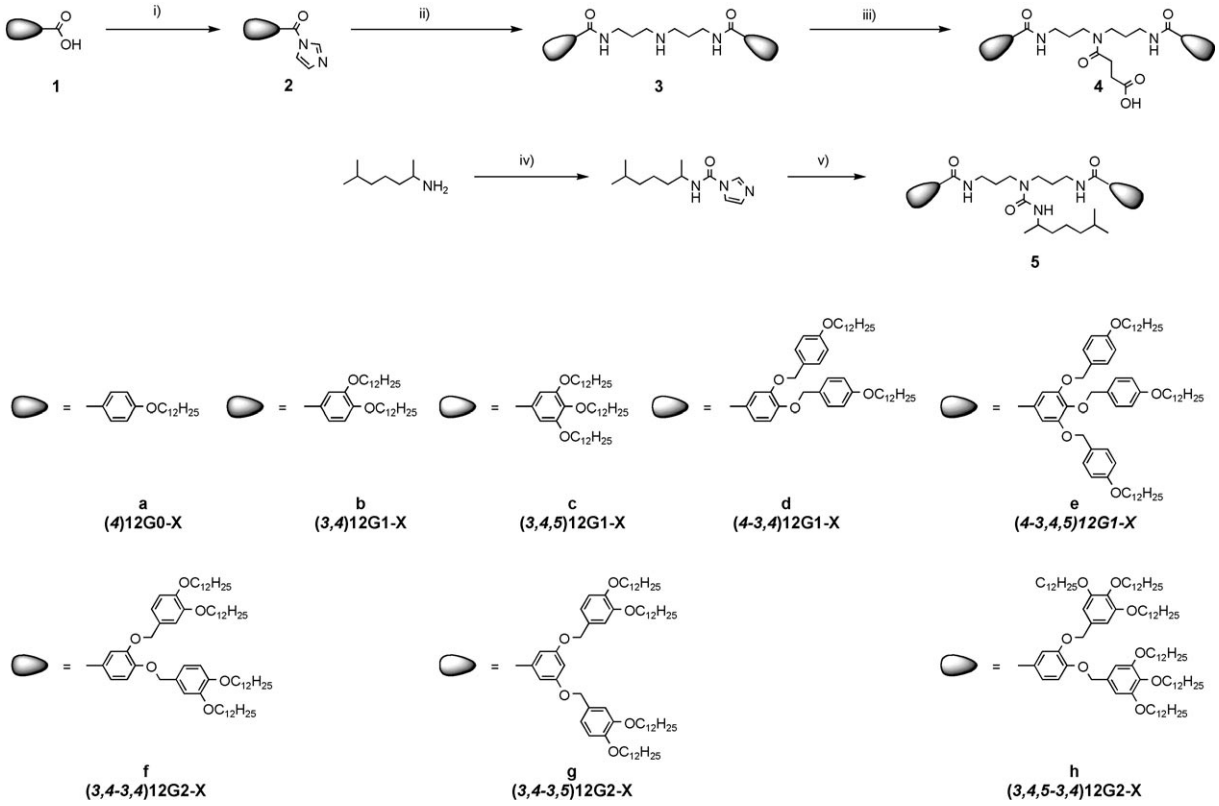
form either cylindrical[4,5] or spherical[6–8] supramolecular dendrimers in bulk and solution. The supramolecular dendrimers self-organize in periodic[4–8] and quasiperiodic[8] arrays. Symmetric twin-dendritic benzamides and dissymmetric Janus-dendritic benzamides undergo self-assembly to form periodic lattices and superlattices.[9] Structural and retrostructural analysis of self-organized arrays in bulk by using a combination of techniques, including thermal optical polarized microscopy (TOPM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and electron density mapping, allows us to elucidate the mechanisms by which self-assembly, self-organization, and subsequent functions arise.[4–9] In solution, structural and retrostructural analysis is achieved by using NMR, CD, and UV/Vis spectroscopies.[5]

Results and Discussion

Synthesis of the twin-dendritic organogelators: Twin-dendritic organogelators were designed by using *N*-(3-aminopropyl)-1,3-propanediamine (APPDA) and self-assembling monodendritic carboxylic acids. Selective condensation of the primary amines with the dendritic carboxylic acids was desired. Conditions were optimized for 4-dodecyloxybenzoic acid (**1a**) and APPDA. The use of 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) in *N*-methylmorpholine (NMM) as the carboxylate activating agent in a one-pot, two-step protocol[10] provided a complex mixture of mono-, di-, and triacylated products. When an excess of activated ester was used, the principle product was the triacylated species. By contrast, the use of 1,1′-carbonyldiimidazole (CDI)[11] led to products acylated only on the primary amines. This had previously been reported as only possible for aliphatic carboxylic acids.[11c,d] The selectivity we observe is likely due to the lower temperatures employed in our reactions. For both reactions, the activated acyl intermediate was isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy and by MALDI-TOF mass spectrometry, while the reaction products were monitored by TLC and ^{1}H NMR spectroscopy.

The synthetic strategy and corresponding library of twin-dendritic supramolecular building blocks is summarized in Scheme 1. Dendritic imidazoles **2a**–**h** were prepared from the corresponding dendritic carboxylic acids by using an excess of CDI. The dendritic imidazoles are readily purified by recrystallization from acetone and can be stored for days in the absence of moisture. Twin-dendritic APPDA derivatives **3a**–**h** were prepared in 75–93% yields by the reaction of the dendritic imidazoles with APPDA. Recrystallization was often sufficient to purify the twin-dendritic APPDA derivatives, although they are amenable to column chromatography if needed.

Polar and nonpolar derivatives of the twin-dendritic APPDA compounds were prepared by reactions with the secondary amine functionality. Succinimide derivatives **4a**, **4b**, and **4d**–**f** were prepared by the reaction of **3a**, **3b**, and



Scheme 1. Synthesis of twin-dendritic organogelators. i) 1,1-carbodiimidazole (CDI), CH_2Cl_2; ii) *N*-(3-aminopropyl)-1,3-propanediamine (APPDA), THF; iii) succinic anhydride, NEt_3, THF, 60°C; iv) CDI, THF; v) **3**, THF.

3d–f with succinic anhydride. The reactions proceeded with high yields and the resulting twin-dendritic carboxylic acids **4a**, **4b**, and **4d–f** were purified by recrystallization from acetone. Gelators containing chiral, branched alkyl moieties exhibit a high propensity to form thixotropic gels.[12] Mixed ureas were prepared by CDI coupling of racemic 2-amino-6-methylheptane and the twin-dendritic APPDA derivatives **3b**, **3d**, and **3f**. The resulting twin-dendritic ureas **5b**, **5d**, and **5f** were obtained in 87–89% yields. All new materials were found to be greater than 99% pure by a combination of ^{1}H NMR spectroscopy, HPLC, TLC, and MALDI-TOF mass spectrometry.

Gelation of organic solvents: Solutions of the twin-dendritic APPDA derivatives **3a–h**, succinimide derivatives **4a**, **4b**, and **4d–f**, and ureas **5b**, **5d**, and **5f** were prepared by heating in various organic solvents with a range of polarities. The formation of a stable gel upon cooling was identified visually. Similarly, the presence of thixotropic behavior was confirmed by the visual observation that the gel reforms upon standing after being shaken. The results are detailed in Table 1.

Most of the twin-dendritic compounds are able to form gels in at least one organic solvent. The more polar solvents, dichloromethane and THF, are the most difficult to gel. Similarly, we less frequently found thixotropic gels for the more polar solvents. Nonetheless, thixotropic gels of BuOAc and dichloromethane were obtained.

Evaluation of the gelation properties of the twin-dendritic APPDA derivatives revealed that 3,4 branching of the aryl amide moiety was necessary to ensure that gels would form and were likely to exhibit thixotropic behavior in the less polar solvents, CyH and PhMe. The incorporation of strong hydrogen bonding in the succinimide derivatives decreased the propensity for organogel formation, as indicated by the lower number of gels obtained. A higher minimum concentration for the formation of a gel was found for those succinimide derivatives than for the corresponding twin-dendritic APPDA compounds in the same organic solvents. By contrast, the chiral alkyl urea derivatives showed enhanced propensity and efficiency in the gelation of organic solvents. Finally, we noted that higher generation dendrons carrying an appropriate number of peripheral alkyl chains were able to gel the more polar solvents and impart thixotropic behavior in some cases.

Low-molecular-weight gelators of organic solvents function by self-assembly to form fibrillar networks.[3] Self-assembly of amphiphilic dendritic dipeptides in solution to form elongated supramolecules has been previously reported.[5] Other dendritic organogelators have been shown to self-assemble into bundles of wormlike aggregates.[13] We envision that the twin-dendritic organogelators reported herein self-assemble into elongated supramolecules similar to the self-assembling dendritic dipeptides previously reported by our group.[5] Subsequent self-organization of the elongated supramolecules promotes the formation of stable thermoreversible and thixotropic gels of organic solvents. This self-organization is likely manifested as the formation of fibrillar bundles in the gel state.

Structural and retrostructural analysis of the twin-dendritic gelators in bulk: Phase transitions of the twin-dendritic gelators were identified in bulk by using a combination of DSC and TOPM. Tentative phase assignments were made on the basis of the diagnostic textures observed by TOPM. The phase assignments were confirmed by XRD. Table 2 reports the phase sequences, transition temperatures, and corresponding enthalpy changes observed. Table 3 presents the structural and retrostructural analysis of the self-organized lattices, along with the XRD results.

Significantly greater structural diversity has been obtained from the present libraries of twin-dendritic gelators than from previously reported twin-dendritic and Janus-dendritic benzamides.[9] The greater flexibility of the spacer between the dendrons, as well as the structural variety of the dendrons in the library, facilitates diversity at the self-organized level through hierarchical self-assembly. Examples of thermoreversible shape change accompanied by dramatic differences in the transmission of polarized light are found for **3f**, **3g**, and **4e**. The columnar lattice is comprised of flat-taper dendrons, while the cubic phase is composed of dendrons adopting a conical shape. The columnar lattice is optically anisotropic and therefore bire-

Table 1. Gelation properties of twin-dendritic compounds in various organic solvents.[a]

Compound	CyH	PhMe	*n*BuOAc	EtOAc	CH_2Cl_2	THF
***(4)*12G0-APPDA (3a)**	10[b]	P	P	P	S	P
***(3,4)*12G1-APPDA (3b)**	13[c]	S	10[c]	5[c]	S	S
***(3,4,5)*12G1-APPDA (3c)**	S	S	P	P	S	S
***(4-3,4)*12G1-APPDA (3d)**	15, T	10, T	4[c]	P	30	40
***(4-3,4,5)*12G1-APPDA (3e)**	20, T	P	P	P	S	S
***(3,4-3,4)*12G2-APPDA (3f)**	S	20, T	6[c]	4[c]	80	40[d]
***(3,4-3,5)*12G2-APPDA (3g)**	P	S	P	P	S	S
***(3,4,5-3,4)*12G2-APPDA (3h)**	S	S	P	**10**[c]	S	S
***(4)*12G0-APPDA-Suc (4a)**	I	P	P	P	S	S
***(3,4)*12G1-APPDA-Suc (4b)**	10	10	P	10[c]	S	S
***(4-3,4)*12G1-APPDA-Suc (4d)**	40, T	30, T	5[c]	P	S	S
***(4-3,4,5)*12G1-APPDA-Suc (4e)**	S	S	P	P	S	S
***(3,4-3,4)*12G2-APPDA-Suc (4f)**	S	S	P	P	80, T	S
***(3,4)*12G1-APPDA-U (5b)**	S	–	S	S	S	S
***(4-3,4)*12G1-APPDA-U (5d)**	5, T	–	15[d], T	15[c]	S	S
***(3,4-3,4)*12G2-APPDA-U (5f)**	2.5, T	–	2.5[c], T	2.5[c]	S	S

[a] CyH: cyclohexane; P: precipitate forms upon cooling; S: solution persists even after cooling; T: thixotropic gel; I: compound is insoluble at all temperatures. Values indicate the minimum concentraion [mg mL^{-1}] of twin-dendritic compound required to gel the solvent. [b] Gel forms a precipitate upon standing. [c] Opaque gel is formed. [d] First a transparent gel is formed, which turns opaque after 2–3 h.

Table 2. Thermal transitions [°C] and corresponding enthalpy changes [kcal mol^{-1}] for the twin-dendritic compounds.[a]

Compound	First and second heating scans	First cooling scans
3a	*S* 115 (24.5) i *S* 113 (18.9) i	i 101 (19.0) *S*
3b	$\Phi_{r\text{-}c}$ 120 (28.4) i $\Phi_{r\text{-}c}$ 96 (2.0) *x* 98 (−1.0) *x* 106 (8.5) *i*	i 67 (11.8) $\Phi_{r\text{-}c}$
3c	k 52 (20.5) $\Phi_{r\text{-}s}$ 102 (12.3) i k 29 (1.8) $\Phi_{r\text{-}s}$ 102 (12.7) i	i 64 (9.4) $\Phi_{r\text{-}s}$ 19 (4.0) k
3d	Φ_h^{io} 175 (20.6) i Φ_h^{io} 175 (21.1) i	i 156 (0.3) Φ_h^{io} 149 (15.1) Φ_h^{io}
3e	$S_{(bilayer)}$ 99 (20.5) $\Phi_{r\text{-}c}$ 145 (13.0) i k 36 (7.4) $\Phi_{r\text{-}c}$ 144 (13.3) i	i 123 (12.3) $\Phi_{r\text{-}s}$
3f	Φ_h 105 (2.8) *x* 120 (7.5) *x* 137 (7.4) Cub 168 (0.9) i Φ_h 131 (32.2) Cub 168 (0.9) i	i 166 (0.8) Cub 84 (21.9) Φ_h
3g	Φ_h 95 (34.4) Tet Φ_h 84 (5.7) Tet	Tet 36 (2.9) Φ_h
3h	k 63 (11.1) Cub 130 (0.6) i Cub 129 (0.6) *i*	i 124 (0.5) Cub
4a	*S* 82 (1.6) $\Phi_{r\text{-}s}$ 113 (0.8) *x* 116 (0.9) *x* 123 (−7.6) *k* 131 (8.1) $\Phi_{r\text{-}s}$ 135 (1.0) *i* *g* 36 $\Phi_{r\text{-}s}$ 106 (0.3) $\Phi_{r\text{-}s}$ 116(0.8) $\Phi_{r\text{-}s}$ 130(1.0) *i*	*i* 128 (0.4) $\Phi_{r\text{-}s}$
4b	*k* 76 (4.5) Φ_h 101 (3.5) Φ_h 109 (2.0) Φ_h 140 (0.3) i Φ_h 140 (0.3) *i*	i 137 (0.3) Φ_h
4d	Φ_h^{io} 157 (12.0) Φ_h^{io} 206 (0.4) dec	
4e	Φ_h 94 (3.5) Tet 151 (0.3) *i*	*i* 145 (0.2) Tet
4f	*k* 59 (3.7) *k* 110 (19.4) Cub Cub	Cub
5b	*k* 57 (18.7) $\Phi_{r\text{-}c}$ 73 (−0.3) *x* 88 (18.2) *i* *k* 38 (−8.7) $\Phi_{r\text{-}c}$ 75 (−2.5) *x* 88 (15.5) *i*	*i*
5d	*k* 109 (10.9) *i* *k* 109 (9.6) *i*	*i* 106 (2.7) Φ_h 73 (5.1) *k*
5f	*k* 90 (22.7) Cub 127 (0.8) *i* Cub 128 (0.8) *i*	*i* 120 (0.7) Cub

[a] Values were determined by DSC (10 °C min^{-1}). Enthalpy changes [kcal mol^{-1}] are given in parentheses. Data from first heating and cooling scans are on the first line, and data from the second heating scans are on the second line. *S*: smectic phase; *i*: isotropic liquid phase; $\Phi_{r\text{-}c}$: *c2mm* centered rectangular columnar lattice; *x*: unidentified phase; *k*: crystalline phase; $\Phi_{r\text{-}s}$: *p2mm* simple rectangular columnar latice; Φ_h^{io}: hexagonal columnar lattice with internal order; $S_{(bilayer)}$: smectic bilayer phase; Φ_h: *p6mm* hexagonal columnar lattice; Cub: $Pm\bar{3}n$ cubic lattice; Tet: $P4_2/mnm$ tetragonal lattice; *g*: glass; dec: sample decomposes.

fringent under polarized light, while the cubic mesophase is optically isotropic. Very few examples of reversible shape change have been reported for self-assembling dendrons.[6e] The reversible shape change reveals new conformations available to the constituent self-assembling dendrons in **3f**, **3g**, and **4e** that have been elusive in previous libraries of self-assembling dendrons.[4–8]

Examination of the self-assembled structure as the core functionality changes provides further insight into the self-assembly process. Twin-dendritic compounds **3d**, **4d**, and **5d** contain ***(4-3,4)*12G1-X** self-assembling dendrons while **3f**, **4f**, and **5f** contain ***(3,4-3,4)*12G2-X** self-assembling dendrons (Scheme 1). As noted above, 3,4-substituted apical branching units provide highly efficient gelators for organic solvents. Furthermore, **3d**, **3f**, **4d**, **4f**, **5d**, and **5f** form thixotropic gels in at least one solvent. The incorporation of the carboxylic acid functionality in **4d** and **4f** decreases the propensity to form thixotropic gels. By contrast, the alkyl urea functionalized twin-dendritic gelators **5d** and **5f** form thixotropic gels at low concentrations in multiple solvents.

The twin-dendritic gelators containing ***(4-3,4)*12G1-X** self-assembling dendrons self-organize into a hexagonal columnar (Φ_h) lattice. Gelators **3d** and **4d** possess internal order within the columnar lattice (Φ_h^{io}). The internal order is likely due to facile hydrogen bonding which creates a seam within the columnar object, as has been found for porous columnar structures formed by dendritic dipeptides.[5] By contrast, **5d** lacks internal order in the Φ_h phase. If the unsymmetric urea functionality forms any hydrogen bonds, they appear unable to form a well-defined arrangement within the columnar object. The decreased thermodynamic stability of **5d** relative to that of **3d** and **4d** is further indicated by the fact that **5d** forms only a monotropic mesophase.

Twin-dendritic gelators containing ***(3,4-3,4)*12G2-X** self-assembling dendrons reveal a different criterion for efficacy in the gel state. ***(3,4-3,4)*12G2-X** dendrons prefer to adopt a conical shape, which self-assembles into spheres. Spherical assemblies are not expected to gel organic solvents.[1,3] The phase behavior of **3f**, which exhibits both Φ_h and $Pm\bar{3}n$ phases, reflects quasiequivalence[14] of the self-assembling dendron. It is capable of adopting both flat-taper and conical shapes. Additionally, we can refer to the observed isotropization temperatures, which reinforce the stability trend observed for **3d**, **4d**, and **5d**. Gelator **5f** exhibits the smallest range of temperatures over which the mesophase exists. The least efficient of these gelators, **4f**, has the most ubiquitous mesophase.

Table 3. Structural and retrostructural analysis of the twin-dendritic libraries.

Compound	T [°C]	Phase	a[a,b,d] a, b[c,f] a, c[e] [Å]	d_{10}, d_{20}, d_{30}, d_{40}[a] d_{10}, d_{11}, d_{20}, d_{21}, d_{30}[b] d_{20}, d_{11}, d_{02}, d_{22}, d_{13}, d_{40}, d_{31}, d_{42}, d_{24}[c] d_{110}, d_{200}, d_{210}, d_{211}, d_{220}, d_{310}, d_{321}, d_{400}[d] d_{002}, d_{410}, d_{330}, d_{202}, d_{212}, d_{411}, d_{312}[e] d_{10}, d_{11}, d_{02}, d_{12}, d_{20}, d_{21}, d_{40}[f] [Å]	μ[g]
3a	25	S	39.5	39.5, 19.8[a]	
3b	110	$\Phi_{r\text{-}c}$	84.8, 36.5	42.5, 33.6, –, –, –, 21.2, 22.4[c]	
3c	100	$\Phi_{r\text{-}s}$	44.4, 73.9	44.5, 38.3, 37.0, 28.5, 22.2, 21.1[f]	
3d	25	Φ_h^{io}	43.4	37.6, 21.7, 18.8[b]	2.0
	150	Φ_h^{io}	43.3	37.5, 21.5, 18.7[b]	
3e	65	$S_{(bilayer)}$	69.4	69.3, 34.6, 23.0, 17.3[a]	
	95	$\Phi_{r\text{-}c}$	77.9, 73.9	39.0, –, 37.3, 27.0, 23.7, 19.5[c]	
3f	40	Φ_h	52.2	45.4, 26.1, 22.6, 17.1, 15.1[b]	
	145	$Pm\bar{3}n$	93.9	66.4, 47.0, 41.9, 38.3, 33.2, 29.6, 25.1, 23.4[d]	
3g	35	Φ_h	49.2	42.7, 24.6, 21.3[b]	
	65	$P4_2/mnm$	164.9, 87.3	43.7, 40.0, –, –, 37.6, –, 33.5[e]	
3h	120	$Pm\bar{3}n$	80.9	57.2, 40.5, 36.2, 33.0, 28.6, 25.6, 21.6, 20.2[d]	
4a	20	$\Phi_{r\text{-}s}$	98.5, 41.5	–, 38.2, –, –, 49.4, 24.6[f]	
4b	90	Φ_h	45.2	39.2, 22.6, 19.6[b]	
4d	25	Φ_h^{io}	57.2	49.5, 28.6, 24.7[b]	3.0
	140	Φ_h^{io}	55.5	48.1, 27.7, 24.0[b]	
4e	25	Φ_h	47.6	41.3, 23.8, 20.6[b]	
	140	$P4_2/mnm$	168.8, 88.9	44.5, 40.9, 39.8, 39.3, 38.3, 37.2, 34.2[e]	
4f	100	$Pm\bar{3}n$	112.9	–, 56.5, 50.3, 45.9[d]	
5b	85	$\Phi_{r\text{-}c}$	129.2, 69.8	65.2, 61.5, –, 30.7, –, 32.4[c]	
5d	100	Φ_h	61.2	52.9, 30.6, 26.5, 20.0[b]	
5f	20	$Pm\bar{3}n$	113.1	–, 56.6, 50.5, 46.2, –, –, 30.3[d]	
	110	$Pm\bar{3}n$	102.9	–, 51.4, 45.9, 42.1, –, –, 27.4, 25.7[d]	

[a] Lattice parameter $a=0.25(d_{10}+2d_{20}+3d_{30}+4d_{40})$ and d-spacings in the ratio d_{10}:d_{20}:d_{30}:d_{40} = 1:2:3:4 for the smectic phases. [b] Lattice parameter $a=0.5(d_{10}+3^{0.5}d_{11}+2d_{20}+7^{0.5}d_{21})3^{-0.5}$ and d-spacings in the ratio d_{10}:d_{11}:d_{20}:$d_{21}=1:3^{0.5}:2:7^{0.5}$ for columnar hexagonal phases. [c] Lattice parameters a and b and d-spacings for centered rectangular columnar phases. In general, $a=d_{10}$ and $b=d_{01}$. The ratio of the d-spacings can be calculated from the general equation $d_{hk}=((ha^{-1})^2+(kb^{-1})^2)^{-0.5}$. [d] Lattice parameter a and d-spacing for the $Pm\bar{3}n$ cubic phases. [e] Lattice parameters $a=b$,c and d-spacings for the $P4_2/mnm$ tetragonal phases. The ratio of the d-spacings can be calculated from the general equation $d_{hkl}=((h^2+k^2)a^{-2}+(l^2c^{-2}))^{-0.5}$. [f] Lattice parameters a and b and d-spacings for the simple rectangular columnar phases. In general $a=d_{10}$ and $b=d_{01}$. The ratio of the d-spacings can be calculated from the general equation $d_{hk}=((ha^{-1})^2+(kb^{-1})^2)^{-0.5}$. [g] Number of dendrons per column stratum $=(3^{0.5}N_A\rho)(2M)^{-1}$, in which Avogadro's number $N_A=6.0220455\times10^{23}$, ρ is the density of the twin-dendron (assumed to be 1 g cm^{-3}), and M is the molecular weight of the compound. [h] Smectic phase observed only in the as-prepared first heating.

As **5d** exhibits only a monotropic mesophase, we were limited to further structural interrogation of **3d** and **4d**. Figure 1 presents plots of the XRD intensity from the Φ_h^{io} lattice, relative electron-density plots, and reconstructed electron-density maps for the two twin-dendritic gelators. The q_{11} and q_{20} reflections of the Φ_h^{io} lattice (Figure 1a) are more prominent for **3d** than for **4d**. We have previously demonstrated this feature to be indicative of porous columnar structures.[5] The relative electron-density profile and reconstructed electron-density map (Figure 1b and c) confirm that the self-organized lattice of **3d** is comprised of porous columns. We infer that hydrogen bonding between the carboxylic acid functionalities of **4d** within the column interacts laterally with adjacent twin-dendritic gelators within a column stratum. Such interactions occur at the core of the column and prevent a hollow structure from forming (Figure 1d). On the other hand, hydrogen bonding between the secondary amines must occur along the length of the column to create a seam that supports the pore through the column. In both **3d** and **4d**, the hydrogen bonding of the amides can occur laterally in the column.

Figure 2 presents the wide-angle XRD patterns and plots of their relative intensities. Stacking features and features indicating helical order within the columns of **3d** and **4d** are noted in the figure. Both patterns can be indexed to a 2_1-helical packing. Nonetheless, significantly more order is found in the columns of **3d** than those of **4d**. Figure 3 illustrates models constructed to fit the XRD results for **3d** and **4d**. The models support the structural interactions inferred above. Here we can appreciate the role of the lateral amide hydrogen bonds (that is, those within a column stratum). A reduction in the number of lateral contacts in bulk correlates with a higher propensity to form gels with thixotropic behavior. We can reason that the alkyl urea groups (for example, in **5d**) strain the lateral hydrogen bonding within the column strata while providing some mechanism for strong association along the length of the column (for example, hydrogen bonding or van der Waals interactions).

Conclusion

We have demonstrated a novel design for dendritic organogelators. The unique hierarchical assembly of the twin-dendritic organogelators promotes the formation of thixotropic gels. We have subjected these gelators to structural and retrostructural analysis in bulk to correlate with their ability to gel organic solvents. A diverse set of self-assembled structural motifs and resulting self-organized arrays were obtained from libraries of twin-dendritic gelators. While extended fibrillar structures are implicated in gel formation, gels were obtained from compounds that self-assemble into lamellar, columnar, and spherical objects. We attribute this to quasie-quivalence[14] of the self-assembling dendrons.

The formation of cylindrical objects in bulk and solution is attributed to lateral hydrogen bonding within the column strata. Dendrons with 3,4-disubstituted apical branching

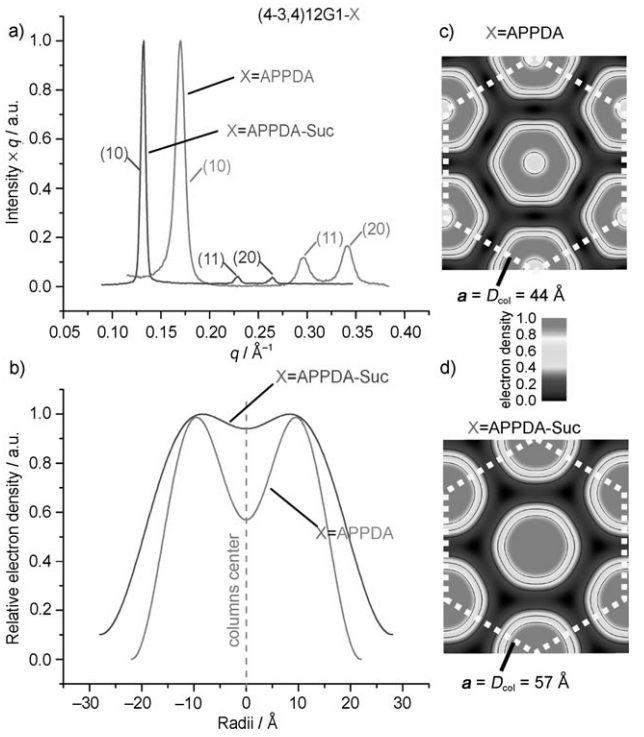


Figure 1. Comparison of **3d** (X = APPDA) and **4d** (X = APPDA-Suc): a) XRD plots of the columnar hexagonal phase; b) relative electron-density profiles indicating a lower electron-density region at the center of the self-assembled supramolecular columns with X = APPDA; reconstructed electron-density maps for c) **3d** (X = APPDA) and d) **4d** (X = APPDA-Suc) suggesting a different packing at the apex region of the two dendrons.

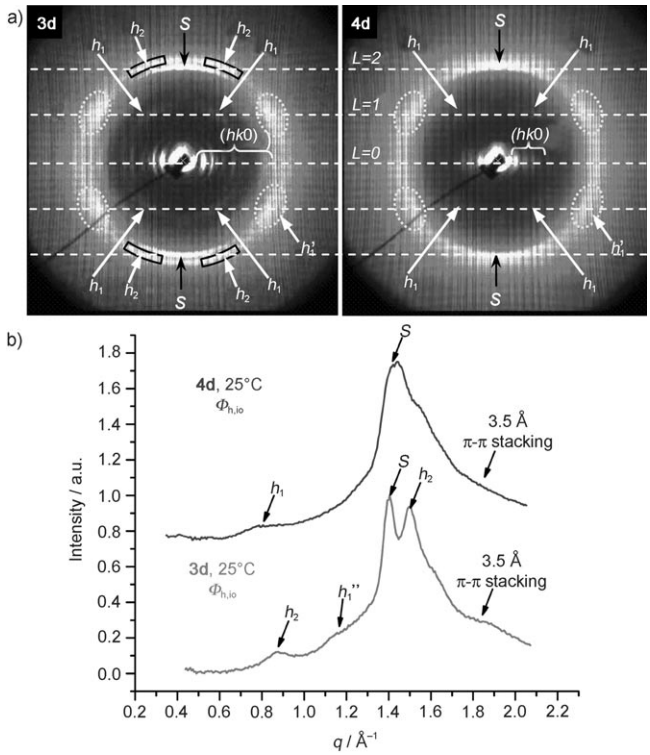


Figure 2. a) Wide-angle XRD results from oriented fiber patterns collected at 25 °C and indexed to a 2_1-helical packing; b) the corresponding meridional q plots. s: 4.4 Å stacking feature (also the maxima of the second helical layer line); h_1, h_1', and h_1'': various maxima observed on the first helical layer line; h_2: helical features observed for **3d**; L: helical layer line order (position indicated by the dotted horizontal lines).

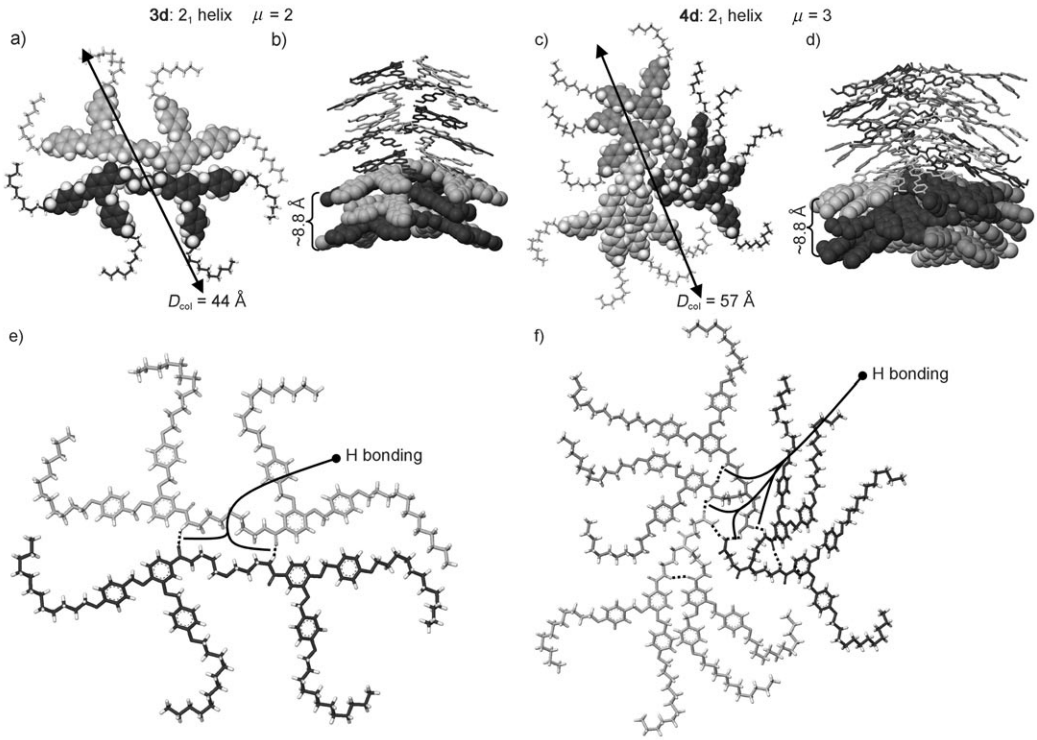


Figure 3. a) Top (a, e) and side (b) views of the molecular model constructed for **3d**. Top (c,f) and side (d) views of the molecular model constructed for **4d**. The models both show the lateral hydrogen bonds with a column stratum and the helical arrangement of the dendrons.

units exhibit the greatest propensity to form gels and to impart thixotropic behavior to the gel. Thixotropic gels appear to result from twin-dendritic gelators that have comparatively weak lateral interactions in bulk. One strategy to prepare thixotropic gels is to employ gelators that form porous columnar mesophases in bulk. The seam of hydrogen bonds that reinforce the pore wall in bulk appears to play a critical role in the emergence of gel properties. These design principles expand upon those of earlier dendritic organogelators[13] and compliment the growing understanding of thixotropic organogels.[3]

Experimental Section

Materials: 1,1′-Carbonyldiimidazole (CDI; Acros, 97%) was used as received. Its purity was assessed by a melting-point measurement and ^{1}H NMR spectroscopy. Succinic anhydride (Aldrich, 99+%) was used as received. *N*-(3-aminopropyl)-1,3-propanediamine (APPDA) was also purchased from Aldrich (99+%) and used as received. THF was refluxed over sodium ketyl until the solution turned purple and was then distilled before use. CH_2Cl_2 was freshly distilled from CaH_2. 2-Amino-6-methylheptane (Acros, 99%) was used as received. *N*-methylmorpholine (NMM; Aldrich, 99%) was used without purification. 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) was prepared according to the procedure reported previously.[10c]

Techniques: All ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 (500 MHz) machine at 20°C with $CDCl_3$ as the solvent (with tetramethylsilane (TMS) as an internal standard). DSC was performed on a Differential Scanning Calorimeter 2920 (TA Instruments) at rates of 5°C min^{-1}. A polarized optical microscope (Olympus BX-60) equipped with a Mettler FP 82 hot stage was used to investigate the bulk properties of the synthesized compounds. All MALDI-TOF spectra were recorded on a Voyager-DE mass spectrometer (Perceptive Biosystems) with dihydroxybenzoic acid (Aldrich, 97%; recrystallized from water before use) as a matrix. The purity of products was determined by a combination of techniques including TLC on silica gel plates (Kodak) with fluorescent indicator and HPLC on a Perkin–Elmer Series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven, Nelson Analytical 900 Series integrator data station, and two Perkin–Elmer PL gel columns. Melting points were measured by using a Unimelt capillary melting-point apparatus (Arthur H. Thomas Company, Philadelphia, USA). XRD measurements were performed by using $CuK_{\alpha 1}$ radiation (l= 1.54178 Å) from a Bruker–Nonius FR-591 rotating anode X-ray source equipped with a 0.2×0.2 mm^2 filament operated at 3.4 kW. The Cu radiation beam was collimated and focused by a single bent mirror and sagitally focused through a Si(111) monochromator, thereby generating a 0.3×0.4 mm^2 spot on a Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. Samples were held in quartz capillaries (0.7–1.0 mm in diameter) mounted in a temperature-controlled oven (temperature precision: ±0.1°C; temperature range: −120 to 270°C). The distance between the sample and the detector was 12.0 cm for wide-angle diffraction experiments and 54.0 cm for intermediate-angle diffraction experiments. Aligned samples for fiber XRD experiments were prepared by using a custom-made extrusion device. Thus, powdered sample (≈10 mg) was heated inside the extrusion device above the melting temperature. The fiber was extruded in the mesophase and cooled to 23°C. Typically, the aligned samples have a thickness of ≈0.3–0.7 mm and a length of ≈3–7 mm. All XRD measurements were done with the aligned sample axis perpendicular to the beam direction. The XRD peak position and intensity analysis was performed with Datasqueeze Software (version 2.01) that allows background elimination and Gaussian, Lorentzian, Lorentzian-squared, or Voigt peak-shape fitting.

Synthesis of 4-(4,6-dimethoxy-1,3,5-triazine-2-yl)-4-methyl-morpholinium chloride (DMT-NMM$^+$Cl$^-$): CDMT (1.58 g, 9 mmol) was dissolved in THF (30 mL). NMM (0.9 mL , 9 mmol) was added dropwise to the solution, thereby generating a thick white slurry. The reaction mixture was stirred for 30 min at 23°C, after which the white solid was filtered off and washed with THF several times to provide a colorless solid (97% yield). M.p. 116–117°C (literature value:[10c 116–117°C).]

Synthesis of the 4,6-dimethoxy-1,3,5-triazine (DMT) ester of carboxylic acid 1a: DMT-NMM$^+$Cl$^-$ (8.28 g, 30 mmol) was dissolved in anhydrous THF (30 mL) that had been previously chilled in an ice-bath. A solution of acid **1a** (3 g, 10 mmol) and NMM (2 mL, 20 mmol) in anhydrous THF (5 mL) were added dropwise to this mixture. After 2 h, the reaction was diluted with dichloromethane (50 mL) and poured into cold water (10°C; 50 mL). The reaction was then partitioned between the organic and aqueous phases. The water layer was washed three times with small amounts of CH_2Cl_2. All of the organic extracts were combined and washed with 1 N HCl (50 mL), sat. $NaHCO_3$ (50 mL), water (50 mL), brine (50 mL), and water (50 mL) again. All aqueous solutions were previously chilled in a refrigerator (10°C). The organic phase was dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum at room temperature. The resulting colorless solid was purified by flash chromatography on a silica-gel column, with CH_2Cl_2 employed as the eluting solvent. ^{1}H NMR ($CDCl_3$, TMS): δ=8.10 (d, 2H), 6.93 (d, 2H), 4.14–4.00 (overlapped peaks, m, 8H), 1.81 (m, 2H), 1.43 (m, 2H), 1.22 (m, 18H), 0.88 ppm (t, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ=174.57, 171.47, 164.69, 162.57, 133.37, 120.36, 114.53, 68.81, 56.22, 32.30, 30.03, 30.02, 29.96, 29.93, 29.73, 29.44, 26.35, 23.07, 14.49 ppm; MALDI-TOF MS: m/z: 484.97 [M+K$^+$], 469.04 [M+Na$^+$].

Acylation of *N*-(3-aminopropyl)-1,3-propanediamine (APPDA) by the DMT ester of 1a: An excess of the DMT ester of acid **1a** (2.32 g, 4.8 mmol) was added to a solution of APPDA (0.17 mL, 1.18 mmol) in THF (25 mL). The solution was stirred at 23°C under an argon atmosphere for 2 h. A precipitate formed upon completion of the reaction. The reaction mixture was taken into methanol and filtered. The resulting solid was recrystallized from acetone to afford the triacylated product as a colorless solid (1.11 g, 95% yield). The resulting compound was found to have very low solubility in all solvents that were tried; therefore, a satisfactory ^{13}C NMR spectrum could not be obtained. ^{1}H NMR ($CDCl_3$, TMS): δ=7.86 (m, 2H), 7.67 (m, 1H), 7.52 (m, 2H), 7.32 (d, 2H), 6.88–6.83 (overlapped peaks, m, 6H), 5.91 (m, 1H), 3.98 (t, 4H), 3.83 (t, 2H), 3.66 (m, 2H), 3.45 (m, 4H), 3.31 (m, 2H), 1.88 (m, 4H), 1.76 (m, 6H), 1.44 (m, 6H), 1.27 (m, 48H), 0.88 ppm (t, 9H); MALDI-TOF MS: m/z: 1035.98 [M+K$^+$], 1018.95 [M+Na$^+$], 997.03 [M+2H$^+$].

Typical procedure of imidazolide synthesis: Synthesis of 4-(dodecan-1-yloxy)benzoyl imidazole (2a): CDI (1.459 g, 9.0 mmol) was placed into a round-bottomed flask under argon. Acid **1a** (0.918 g, 3 mmol) was dissolved in anhydrous dichloromethane (50 mL) and added to the flask by syringe. The reaction was stirred at room temperature for 1 h while argon was bubbled through. The progress of the reaction was monitored by TLC, MALDI mass spectrometry, and ^{1}H NMR spectroscopy. Upon completion of the reaction, the reaction mixture was cooled in a refrigerator, washed 4–5 times with cold water (5°C), and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the product was recrystallized from acetone to afford a colorless powder (1.003 g, 95% yield). M.p. 67–69°C; ^{1}H NMR ($CDCl_3$, TMS): δ=8.02 (s, 1H), 7.73 (d, 2H), 7.47 (s, 1H), 7.09 (s, 1H), 6.95 (d, 2H), 3.98 (t, 2H), 1.73 (m, 2H), 1.40 (m, 2H), 1.19 (m, 16H), 0.81 ppm (t, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ=165.86, 164.12, 138.54, 132.78, 131.03, 123.98, 118.64, 115.14, 68.95, 32.31, 30.05, 30.03, 29.98, 29.95, 29.73, 29.43, 26.36, 23.08, 14.51 ppm.

3,4-Bis(dodecan-1-yloxy)benzoyl imidazole (2b): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded **2b** as a colorless solid (88% yield). M.p. 72–74°C; ^{1}H NMR ($CDCl_3$, TMS): δ=8.09 (s, 1H), 7.54 (s, 1H), 7.36 (d, 1H), 7.34 (s, 1H), 7.15 (s, 1H), 6.94 (d, 1H), 4.09 (t, 2H), 4.04 (t, 2H), 1.85 (m, 4H), 1.48 (m, 4H), 1.36–1.27 (overlapped peaks, m, 32H), 0.88 ppm (t, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ=165.94, 154.55, 149.63, 138.63, 130.99, 124.83, 124.04, 118.72, 115.13, 112.35, 69.90, 69.64, 32.32,

30.08, 30.05, 30.00, 29.77, 29.75, 29.53, 29.41, 26.39, 26.36, 23.08, 14.49 ppm; MALDI-TOF MS: m/z: 580.44 [M+K^+], 564.23 [M+Na^+], 541.82 [M+H^+].

3,4,5-Tris(dodecan-1-yloxy)benzoyl imidazole (2c): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded the corresponding imidazolide as a colorless powder (92% yield). M.p. 61–62°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 8.10 (s, 1H), 7,46 (s, 1H), 7.16 (s, 1H), 6.98 (s, 2H), 4.07 (t, 2H), 3.99 (t, 4H), 1.80 (overlapped peaks, m, 6H), 1.46 (m, 6H), 1.26 (m, 48H), 0.88 ppm (t, 9H); ^{13}C NMR ($CDCl_3$, TMS): δ = 166.16, 153.66, 143.63, 138.67, 131.16, 126.47, 118.66, 109.10, 74.14, 69.92, 32.33, 32.32, 30.76, 30.14, 30.12, 30.09, 30.05, 30.01, 29.95, 29.76, 29.67, 26.45, 23.08, 14.49 ppm; MALDI-TOF MS: m/z: 764.22 [M+K^+], 748.61 [M+Na^+], 726.44 [M+H^+].

3,4-Bis[(4′-dodecan-1-yloxy)benzyloxy]benzoyl imidazole (2d): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded the corresponding imidazolide as a colorless powder (90% yield). M.p. 93–95°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 7.96 (s, 1H), 7.27 (overlapped peaks, m, 7H), 7.05 (s, 1H), 6.94 (d, 1H), 6.82 (overlapped peaks, m, 4H), 5.11 (s, 2H), 5.05 (s, 2H), 3.88 (t, 4H), 1.70 (m, 4H), 1.37 (m, 4H), 1.19 (m, 32H), 0.81 ppm (t, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 165.76, 159.63, 154.39, 149.07, 138.54, 130.97, 129.51, 129.33, 128.49, 128.23, 125.24, 124.39, 118.71, 116.87, 115.07, 115.04, 113.84, 71.64, 71.30, 68.50, 32.32, 30.07, 30.04, 30.01, 29.99, 29.82, 29.75, 29.68, 26.47, 23.09, 14.52 ppm; MALDI-TOF MS: m/z: 792.27 [M+K^+], 776.25 [M+Na^+], 754.22 [M+H^+].

3,4,5-Tris[(4′-dodecan-1-yloxy)benzyloxy]benzoyl imidazole (2e): A synthetic procedure analogous to the synthesis of **2a** was used. In this case, an excess of CDI (3.0 equiv) was necessary to convert all of the acid into imidazolide. Aqueous workup afforded the corresponding imidazolide as a colorless powder (90% yield). M.p. 78–79°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 8.00 (s, 1H), 7.28 (overlapped peaks, d, 7H), 7.10 (s, 1H), 7.03 (s, 2H), 6.81 (d, 4H), 6.76 (d, 2H), 5.08 (s, 2H), 5.05 (s, 4H), 3.92 (m, 6H), 1.78 (m, 6H), 1.45 (m, 6H), 1.26 (m, 48H), 0.87 ppm (t, 9H); ^{13}C NMR ($CDCl_3$, TMS): δ = 165.892, 159.65, 159.59, 153.23, 143.80, 138.51, 131.10, 130.70, 129.64, 129.52, 128.38, 126.55, 118.70, 115.04, 114.62, 110.61, 75.30, 71.72, 68.52, 68.44, 32.34, 30.09, 30.06, 30.03, 30.01, 29.87, 29.77, 29.73, 29.70, 26.49, 23.11, 14.53 ppm; MALDI-TOF MS: m/z: 1087.93 [M+K^+], 1066.84 [M+Na^+], 1044.83 [M+H^+].

3,4-Bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoyl imidazole (2f): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded **2f** as a colorless solid (91% yield). M.p. 95–97°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 8.04 (s, 1H), 7.40 (overlapped peaks, m, 3H), 7.12 (s, 1H), 6.98 (d, 1H), 6.96 (d, 2H), 6.93–6.90 (overlapped peaks, m, 2H), 6.84 (overlapped peaks, m, 2H), 5.16 (s, 2H), 5.11 (s, 2H), 3.96 (overlapped peaks, m, 8H), 1.81 (m, 8H), 1.45 (m, 8H), 1.26 (m, 64H), 0.87 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 165.74, 154.308, 149.80, 149.79, 149.66, 149.58, 149.07, 138.53, 131.00, 129.18, 128.94, 125.23, 124.44, 120.63, 120.46, 118.71, 116.65, 114.09, 113.76, 113.69, 113.60, 71.77, 71.49, 69.74, 69.76, 32.34, 30.14, 30.12, 30.08, 30.06, 29.91, 29.87, 29.78, 29.74, 26.51, 26.48, 23.10, 14.52 ppm; MALDI-TOF MS: m/z: 1161.7 [M+K^+], 1145.2 [M+Na^+], 1123.4 [M+2H^+].

3,5-Bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzoyl imidazole (2g): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded **2g** as a colorless solid (82% yield). M.p. 72–73°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 8.08 (s, 1H), 7.45 (s, 1H), 7.13 (s, 1H), 6.97–6.86 (overlapped peaks, m, 9H), 4.97 (s, 4H), 3.99 (m, 8H), 1.81 (m, 8H), 1.45 (m, 8H), 1.26 (m, 64H), 0.87 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 160.52, 149.86, 149.80, 138.60, 133,89, 131.30, 128.80, 120.99, 118.45, 114.20, 114.03, 109.11, 107.82, 71.05, 69.78, 32.34, 30.11, 30.07, 30.05, 29.86, 29.84, 29.77, 29.74, 29.70, 26.47, 26.46, 23.10, 14.51 ppm; MALDI-TOF MS: m/z: 1126.47 [M+5H^+].

3,4-Bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzoyl imidazole (2h): A synthetic procedure analogous to the synthesis of **2a** was used. Aqueous workup and recrystallization from acetone afforded **2h** as a waxy colorless solid (83% yield). M.p. 64–66°C; ^{1}H NMR ($CDCl_3$, TMS): δ = 8.07 (s, 1H), 7.40 (overlapped peaks, m, 3H), 7.13 (s, 1H), 7.02 (d, 1H), 6.62 (d, 4H), 5.15 (s, 2H), 5.09 (s, 2H), 3.92 (overlapped peaks, m, 12H), 1.75 (m, 12H), 1.45 (m, 12H), 1.26 (m, 96H), 0.87 ppm (t, 18H); ^{13}C NMR ($CDCl_3$, TMS): δ = 165.68, 154.22, 153.85, 153.81, 149.11, 138.62, 138.51, 131.58, 131.39, 131.05, 125.30, 124.61, 118.76, 116.55, 113.80, 106.23, 106.15, 73.85, 72.07, 71.82, 69.63, 69.56, 32.34, 30.80, 30.18, 30.14, 30.09, 30.06, 29.90, 29.85, 29.81, 29.79, 26.57, 23.10, 14.52 ppm; MALDI-TOF MS: m/z: 1531.5 [M+K^+], 1516.2 [M+Na^+], 1492.4 [M+2H^+].

Typical procedure for coupling of imidazolides with APPDA: Synthesis of *N,N*-bis(3-(4-(dodecan-1-yloxy)benzamido)propyl)amine (3a): APPDA (0.7 mL, 5 mmol) was placed into a round-bottomed flask under argon. **2a** (3.52 g, 10 mmol) dissolved in anhydrous THF was added to the flask gradually over a period of 20 min. The reaction was kept under argon and the mixture was stirred in an ice-bath at 0°C for 4 h. Upon completion of the reaction, the mixture was poured into methanol; this resulted in a white precipitate, which was filtered off, washed repeatedly with water, recrystallized from acetone and/or ethyl acetate, and dried under vacuum to provide a colorless solid (3.31 g, 93% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.74 (d, 4H), 7.19 (t, 2H), 6.89 (d, 4H), 3.98 (t, 4H), 3.59 (q, 4H), 2.74 (t, 4H), 1.70 (m, 9H), 1.43 (m, 4H), 1.19 (m, 32H), 0.81 ppm (t, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.63, 162.08, 129.07, 127.13, 114.57, 68.58, 48.23, 39.09, 32.32, 30.07, 30.04, 30.01, 29.98, 29.81, 29.75, 29.58, 26.42, 23.09, 14.51 ppm; MS (ESI): m/z: 708.32 [M+H^+].

***N,N*-Bis(3-(3,4-bis(dodecan-1-yloxy)benzamido)propyl)amine (3b)**: A synthetic procedure analogous to the synthesis of **3a** was used. Upon completion of the reaction, the mixture was poured into methanol and filtered. The product was recrystallized from acetone to yield a colorless powder (89% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.43 (s, 2H), 7.25–7.24 (overlapped peaks, m, 4H), 6.82 (d, 4H), 4.01 (t, 8H), 3.56 (q, 4H), 2.77 (t, 4H), 1.82 (m, 12H), 1.48 (m, 8H), 1.35 (m, 64H), 0.91 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.72, 152.33, 149.35, 127.59, 119.97, 113.52, 112.77, 69.86, 69.55, 48.20, 39.14, 32.33, 30.11, 30.06, 30.05, 29.85, 29.77, 29.70, 29.62, 29.57,26.43, 23.08, 14.49 ppm; MALDI-TOF MS: m/z: 1118.51 [M+2H^++K^+], 1102.23 [M+2H^++Na^+], 1078.94 [M+2H^+].

***N,N*-Bis(3-(3,4,5-tris(dodecan-1-yloxy)benzamido)propyl)amine (3c)**: A synthetic procedure analogous to the synthesis of **3a** was used. After 4 h of stirring under argon, the reaction mixture was poured into methanol and filtered. The solid was recrystallized twice from acetone to afford a pure colorless solid (89% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.13 (t, 2H), 6.97 (s, 4H), 3.95 (t, 12H), 3.52 (q, 4H), 2.73 (t, 4H), 1.77–1.71 (overlapped peaks, m, 16H), 1.43 (m, 12H), 1.26 (m, 96H), 0.88 ppm (t, 18H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.87, 153.46, 141.70, 129.98, 106.41, 73.90, 69.88, 48.09, 39.18, 32.33, 30.76, 30.16, 30.12, 30.10, 30.07, 30.02, 29.85, 29.79, 29.77, 29.63, 26.52, 23.09, 14.49 ppm; MALDI-TOF MS: m/z: 1485.74 [M+K^+], 1470.23 [M+Na^+], 1446.67 [M+H^+].

***N,N*-Bis(3-(3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzamido)propyl)-amine (3d)**: When an analogous procedure to that described above was used in dichloromethane or THF, the reaction mixture resulted in a gel. The gel/precipitate was filtered to afford fibrous colorless waxy solid (85% yield). The product obtained by this method is usually pure; however, additional recrystallization from a dichloromethane/EtOAc mixture was sometimes used. ^{1}H NMR ($CDCl_3$, TMS): δ = 7.47 (d, 2H), 7.28 (overlapped peaks, m, 12H), 6.82 (overlapped peaks, m, 8H), 5.10 (s, 4H), 5.01 (s, 4H), 3.90 (t, 8H), 3.50 (q, 4H), 2.75 (t, 4H), 1.75 (m, 13H), 1.41 (m, 8H), 1.26 (m, 64H), 0.87 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.45, 167.12, 159.34, 152.23, 149.18, 129.62, 129.54, 129.34, 129.24, 129.15, 128.98, 128.82, 127.68, 127.45, 120.88, 114.84, 114.84, 114.62, 114.21, 71.54, 71.23, 68.49, 48.15, 39.34, 32.31, 30.10, 30.07, 29.83, 29.73, 29.71, 29.43, 28.24, 27.75, 26.48, 23.08, 14.52 ppm; MALDI-TOF MS: m/z: 1543.54 [M+3H^++K^+], 1522.71 [M+Na^+], 1501.52 [M^+].

***N,N*-Bis(3-(3,4,5-tris[(4′-dodecan-1-yloxy)benzyloxy]benzamido)propyl)-amine (3e)**: A synthetic procedure analogous to the synthesis of **3a** was used. The reaction was left to stir under argon for 2 h. The reaction mixture was then poured into methanol and the precipitate was filtered off. Recrystallization from BuOAc (or alternatively column chromatography on silica gel, with first a dichloromethane/EtOAC mixture and then a $CHCl_3$/MeOH mixture employed as the eluting solvent, with subsequent evaporation of the solvent) afforded a colorless solid (1.04 g, 81% yield).

^{1}H NMR ($CDCl_3$, TMS): δ = 7.27 (d, 8H), 7.20 (d, 4H), 6.84 (d, 8H), 6.70 (d, 4H), 4.92 (s, 4H), 4.89 (s, 8H), 3.89 (m, 12H), 3.50 (q, 4H), 2.74 (t, 4H), 1.84 (m, 17H), 1.44 (m, 12H), 1.26 (m, 96H), 0.83 ppm (t, 18H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.66, 159.44, 159.36, 153.24, 141.90, 130.59, 130.31, 129.93, 129.71, 129.02, 114.82, 114.50, 107.76, 75.17, 71.79, 68.47, 68.38, 48.20, 39.24, 32.34, 30.10, 30.06, 30.03, 29.89, 29.77, 29.74, 29.57, 26.50, 23.10, 14.52 ppm; MALDI-TOF MS: *m*/*z*: 2123.92 [M+3H$^+$+K$^+$], 2107.79 [M+3H$^+$+Na$^+$], 2085.60 [M+3H$^+$].

***N,N*-Bis(3-(3,4-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzamido)propyl)amine (3f)**: A synthetic procedure analogous to the synthesis of **3a** was used. Upon completion, the reaction mixture was poured into methanol and filtered. The resulting product was recrystallized from acetone several times. A colorless solid was obtained (92% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.50 (s, 2H), 7.22 (m, 2H), 6.95 (d, 4H), 6.87 (overlapped peaks, m, 6H), 6.79 (d, 4H), 5.01 (s, 8H), 3.94 (t, 8H), 3.88 (t, 8H), 3.49 (q, 4H), 2.72 (t, 4H), 1.76 (m, 20H), 1.44 (m, 16H), 1.26 (m, 128H), 0.87 ppm (t, 24H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.42, 152.16, 149.75, 149.71, 149.44, 149.42, 149.21, 129.36, 129.95, 129.72, 128.27, 120.72, 120.61, 120.49, 114.86, 114.22, 114.14, 113.96, 113.73, 71.91, 71.48, 69.79, 69.66, 69.65, 48.30, 39.27, 32.35, 30.11, 30.09, 29.95, 29.81, 29.58, 26.55, 26.51, 23.10, 14.50 ppm; MALDI-TOF MS: *m*/*z*: 2275.51 [M+K$^+$], 2260.23 [M+Na$^+$], 2237.94 [M^+].

***N,N*-Bis(3-(3,5-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzamido)propyl)amine (3g)**: A synthetic procedure analogous to the synthesis of **3a** was used. Upon completion, the reaction mixture was poured into methanol and filtered. The resulting product was purified by column chromatography as described for **3c**. A colorless solid was obtained (78% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.48 (s, 2H), 7.02–6.81 (overlapped peaks, m, 7H), 6.66 (s, 2H), 4.87 (s, 8H), 3.95 (t, 16H), 3.46 (q, 4H), 2.76 (t, 4H), 1.81 (m, 16H), 1.45 (m, 16H), 1.26 (m, 128H), 0.87 ppm (t, 24H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.72, 160.42, 149.75, 149.64, 137.16, 129.36, 125.92, 121.08, 114.96, 106.48, 105.31, 70.81, 69.77, 48.15, 39.17, 32.35, 30.73, 30.13, 30.08, 29.90, 29.89, 29.79, 29.75, 26.51, 26.48, 23.11, 14.52 ppm; MALDI-TOF MS: *m*/*z*: 2277.35 [M+K$^+$], 2261.79 [M+Na$^+$], 2241.56 [M+3H$^+$].

***N,N*-Bis(3-(3,4-Bis(3′,4′,5′-tris(dodecan-1-yloxy)benzyloxy)benzamido)propyl)amine (3h)**: A synthetic procedure analogous to the synthesis of **3a** was used. Upon completion, the reaction mixture was poured into methanol and filtered. The resulting product was purified by column chromatography as described for **3c**. A colorless solid was obtained (75% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.53 (s, 2H), 7.31 (d, 4H), 6.88 (d, 1H), 6.59 (d, 8H), 5.02 (s, 8H), 3.92–3.86 (overlapped peaks, m, 24H), 3.49 (q, 4H), 2.76 (t, 4H), 1.74 (m, 28H), 1.45 (m, 24H), 1.26 (m, 192H), 0.87 ppm (t, 36H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.68, 153.72, 153.66, 152.19, 138.35, 132.27, 132.07, 128.09, 120.80, 114.82, 114.31, 106.39, 106.12, 73.82, 72.17, 71.80, 69.54, 47.66, 38.68, 32.35, 30.83, 30.19, 30.16, 30.11, 29.94, 29.91, 29.80, 28.99, 26.60, 23.10, 14.49 ppm; MALDI-TOF MS: *m*/*z*: 3008.8 [M+K$^+$], 2992.3 [M+Na$^+$], 2971.0 [M^+].

Typical procedure for coupling of amido amines with succinic anhydride: Synthesis of *N,N*-bis(3-(3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzamido)propyl)amino-4-oxo-butanoic acid (4d): Amido amine **3d** (1.502 g, 1 mmol) was mixed with succinic anhydride (0.110 g, 1.1 mmol). The mixture was dissolved in hot anhydrous THF and refluxed overnight under argon. The mixture was then poured into water; this resulted in a white precipitate, which was filtered, washed with water, and recrystallized from acetone. This procedure provided a colorless solid product (1.329 g, 83% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.57 (d, 2H), 7.32 (overlapped peaks, m, 12H), 6.80 (overlapped peaks, m, 8H), 4.99 (m, 8H), 3.87 (t, 8H), 3.38 (m, 4H), 3.28 (m, 4H), 2.60 (m, 2H), 2.53 (m, 4H), 1.84 (m, 2H), 1.65 (m, 10H), 1.43 (m, 8H), 1.26 (m, 64H), 0.87 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 177.58, 173.25, 167.80, 167.23, 159.37, 152.31, 152.07, 149.24, 149.12, 129.66, 129.58, 129.38, 129.23, 129.13, 128.96, 128.86, 127.67, 127.48, 120.86, 114.86, 114.81, 114.60, 114.0, 71.56, 71.28, 68.47, 46.17, 43.00, 37.99, 36.10, 32.33, 30.09, 30.05, 29.86, 29.76, 29.73, 29.43, 28.24, 27.78, 26.48, 23.09, 14.52 ppm; MALDI-TOF MS: *m*/*z*: 1643.20 [M+3H$^+$+K$^+$], 1627.27 [M+3H$^+$+Na$^+$], 1604.99 [M+3H$^+$].

***N,N*-Bis(3-(4-(dodecan-1-yloxy)benzamido)propyl)amino-4-oxo-butanoic acid (4a)**: A synthetic procedure analogous to the synthesis of **4d** was used, to afford a colorless powder (92% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.78 (overlapped peaks, d, 4H), 7.55 (t, 1H), 6.95 (t, 1H), 6.86 (dd, 4H), 3.96 (t, 4H), 3.47 (m, 4H), 3.38 (t, 2H), 3.31 (q, 4H), 2.67–2.58 (m, 4H), 1.96 (m, 2H), 1.78–1.75 (two overlapped peaks, m, 6H), 1.43 (m, 4H), 1.26 (m, 32H), 0.87 ppm (t, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 176.75, 173.27, 168.03, 167.50, 162.29, 162.17, 129.26, 126.65, 126.49, 114.62, 68.62, 46.22, 43.17, 37.87, 36.19, 32.32, 30.07, 30.04, 30.02, 29.99, 29.82, 29.75, 29.59, 28.13, 27.88, 26.42, 23.09, 14.51 ppm; MS (ESI): *m*/*z*: 808.43 [M+H$^+$].

***N,N*-Bis(3-(3,4-bis(dodecan-1-yloxy)benzamido)propyl)amino-4-oxo-butanoic acid (4b)**: A synthetic procedure analogous to the synthesis of **4d** was used, to afford a colorless powder in 93% yield. ^{1}H NMR ($CDCl_3$, TMS): δ = 8.06 (t, 1H), 7.46 (d, 2H), 7.38 (m, 2H), 7.28 (t, 1H), 6.81 (overlapped peaks, m, 2H), 3.99 (overlapped peaks, m, 8H), 3.45 (m, 4H), 3.32 (m, 2H), 3.29 (m, 2H), 2.60 (m, 2H), 2.57 (m, 2H), 1.95 (m, 2H), 1.81 (m, 8H), 1.69 (m, 2H), 1.43 (m, 8H), 1.26 (m, 64H), 0.87 ppm (t, 12H); ^{13}C NMR ($CDCl_3$, TMS): δ = 173.19, 168.03, 167.48, 152.40, 152.19, 149.28, 149.17, 126.99, 126.82, 120.39, 120.25, 113.15, 112.82, 112.73, 112.55, 69.70, 69.50, 46.22, 43.06, 37.94, 35.99, 32.35, 30.09. 29.88, 29.80, 29.67, 29.58, 28.15, 27.80, 26.45, 23.12, 14.54 ppm; MALDI-TOF MS: *m*/*z*: 1203.43 [M+3H$^+$+Na$^+$], 1180.13 [M+3H$^+$].

***N,N*-Bis(3-(3,4,5-tris[(4′-dodecan-1-yloxy)benzyloxy]benzamido)propyl)-amino-4-oxo-butanoic acid (4e)**: A synthetic procedure analogous to the synthesis of **4d** was used and resulted in a white solid as the final product (87% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.28 (d, 8H), 7.20 (d, 4H), 6.82 (d, 8H), 6.70 (d, 4H), 4.92 (s, 4H), 4.89 (s, 8H), 3.87 (m, 12H), 3.45 (m, 4H), 3.32 (m, 84H), 2.57 (m, 2H), 2.53 (m, 2H), 1.92 (m, 2H), 1.76 (m, 12H), 1.72 (m, 2H), 1.43 (m, 12H), 1.26 (m, 96H), 0.87 ppm (t, 18H); ^{13}C NMR ($CDCl_3$, TMS): δ = 177.58, 173.25, 167.77, 167.18, 159.43, 159.36, 159.32, 153.29, 153.24, 141.77, 141.41, 130.55, 130.09, 129.98, 129.75, 129.66, 129.51, 129.18, 129.03, 114.82, 114.78, 114.49, 107.48, 106.81, 75.17, 71.50, 71.20, 68.48, 68.45, 68.39, 46.44 ppm; MALDI-TOF MS: *m*/*z*: 2224.43 [M+3H$^+$+Na$^+$].

***N,N*-Bis(3-(3,4-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzamido)propyl)-amino-4-oxo-butanoic acid (4f)**: A synthetic procedure analogous to the synthesis of **4d** was used, to afford a colorless powder (91% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.60–7.59 (overlapped peaks, m, 3H), 7.41 (m, 1H), 7.00–6.79 (overlapped peaks, m, 16H), 5.05 (s, 4H), 5.04 (s, 4H), 3.94 (t, 8H), 3.88 (t, 8H), 3.48 (m, 2H), 3.45 (m, 2H), 3.38 (m, 2H), 3.32 (m, 2H), 2.67 (m, 2H), 2.63 (m, 2H), 1.94 (m, 2H), 1.76 (m, 18H), 1.43 (m, 16H), 1.26 (m, 128H), 0.88 ppm (t, 24H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.70, 167.21, 152.32, 152.11, 149.71, 149.45, 149.40, 149.34, 149.25, 149.15, 129.92, 129.62, 127.77, 127.49, 120.75, 120.65, 120.52, 114.50, 114.10, 113.91, 113.74, 71.53, 71.42, 69.77, 69.63, 46.12, 43.10, 37.98, 36.29, 32.35, 30.11, 29.98, 29.95, 29.84, 29.80, 29.50, 27.87, 26.58, 26.53, 23.09, 14.49 ppm; MALDI-TOF MS: *m*/*z*: 2375.40 [M+K$^+$], 2359.54 [M+Na$^+$]

Typical procedure for the synthesis of ureas: Synthesis of 1,1-bis(3-(3,4-bis[(4′-dodecan-1-yloxy)benzyloxy]benzamido)propyl)-3-(6-methylheptan-2-yl)urea (5d): CDI (0.13 g, 0.79 mmol) was dissolved in anhydrous THF (25 mL). 2-Amino-6-methylheptane (0.13 mL, 0.79 mmol) was added to that mixture dropwise. The reaction was left to stir for 1 h at 23 °C. Upon completion of this step (as monitored by TLC), compound **3d** (0.79 g, 0.53 mmol) was added to the mixture; the mixture was then refluxed for 6 h. The solvent was evaporated and the resulting solid was recrystallized twice from acetone to afford a colorless solid (87% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.58 (s, 2H), 7.36–7.30 (overlapped peaks, m, 12H), 6.90 (d, 2H), 6.85 (d, 8H), 5.09 (s, 4H), 5.08 (s, 4H), 4.80 (d, 1H), 3.94 (t, 8H), 3.89 (m, 1H), 3.41 (m, 4H), 3.34 (m, 4H), 1.77 (m, 12H), 1.43 (m, 10H), 1.29–1.26 (overlapped peaks, m, 67H), 1.10 (m, 5H), 0.87 (t, 12H), 0.79 ppm (d, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.43, 159.40, 158.60, 152.16, 149.30, 129.61, 129.31, 129.25, 129.02, 127.84, 120.66, 114.92, 114.87, 114.50, 71.51, 71.37, 68.48, 47.13, 44.35, 39.23, 38.07, 37.12, 32.32, 30.07, 30.01, 29.83, 29.75, 29.72, 28.92, 28.27, 26.48, 24.43, 23.09, 22.94, 22.00, 14.50 ppm; MALDI-TOF MS: *m*/*z*: 1697.10 [M+H$^+$+K$^+$], 1680.53 [M+H$^+$+Na$^+$], 1657.78 [M+H$^+$].

1,1-Bis(3-(3,4-bis(dodecan-1-yloxy)benzamido)propyl)-3-(6-methylheptan-2-yl)urea (5b): A synthetic procedure analogous to the synthesis of

5d was used. A colorless solid was obtained (89% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.65 (s, 2H), 7.64 (m, 2H), 7.42 (d, 2H), 6.84 (d, 2H), 4.91 (d, 1H), 4.04 (t, 4H), 4.01 (t, 2H), 3.85 (m, 1H), 3.41–3.34 (overlapped peaks, m, 8H), 1.79 (m, 12H), 1.45 (m, 10H), 1.31–1.26 (overlapped peaks, m, 67H), 1.11 (m, 5H), 0.88 (t, 12H), 0.81 ppm (d, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.74, 158.59, 152.31, 149.33, 127.20, 120.22, 113.16, 112.84, 69.68, 69.56, 47.12, 44.35, 39.23, 38.04, 37.13, 32.32, 31.28, 30.09, 30.04, 29.85, 29.81, 29.75, 29.67, 29.56, 28.87, 26.45, 26.40, 24.45, 23.07, 22.92, 21.95, 14.48 ppm; MALDI-TOF MS: *m*/*z*: 1271.50 [M+H$^+$+K$^+$], 1256.83 [M+H$^+$+Na$^+$], 1232.78 [M+H$^+$].

1,1-Bis(3-(3,4-bis(3′,4′-bis(dodecan-1-yloxy)benzyloxy)benzamido)propyl)-3-(6-methylheptan-2-yl)urea (5f): A synthetic procedure analogous to the synthesis of **5d** was used. A colorless solid was obtained (87% yield). ^{1}H NMR ($CDCl_3$, TMS): δ = 7.60 (s, 2H), 7.37 (d, 2H), 7.27 (m, 2H), 7.00–6.81 (overlapped peaks, m, 14H), 5.09 (s, 4H), 5.07 (s, 4H), 4.83 (d, 1H), 3.96 (t, 8H), 3.91 (t, 8H), 3.44–3.34 (overlapped peaks, m, 8H), 1.77 (m, 20H), 1.44 (m, 18H), 1.32–1.26 (overlapped peaks, m, 131H), 1.11 (d, 5H), 0.88 (t, 24H), 0.79 ppm (d, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 167.40, 158.62, 152.15, 149.78, 149.74, 149.42, 149.40, 149.29, 130.02, 129.81, 127.91, 120.70, 120.64, 120.39, 114.37, 114.20, 113.95, 113.66, 71.64, 71.55, 69.81, 69.64, 47.14, 44.31, 39.24, 38.08, 37.10, 32.34, 30.09, 29.92, 29.89, 29.79, 28.93, 28.27, 26.53, 26.49, 24.43, 23.09, 22.98, 22.95, 22.02, 14.50 ppm; MALDI-TOF MS: *m*/*z*: 2433.90 [M+H$^+$+K$^+$], 2418.02 [M+H$^+$+Na$^+$], 2394.78 [M+H$^+$].

Typical procedure for gelation experiments: A carefully measured amount of solid (4–60 mg) was put into an NMR tube with a tight-fit twist cap and organic solvent (0.5 or 1 mL) was added. The mixture was carefully heated in an oil bath. Upon dissolution, the solution was slowly cooled to 23 °C. If the tube was inverted and the liquid did not flow, it was considered to be a gel. The tube was left for observation for 2 days at 23 °C.

Acknowledgement

Financial support by the National Science Foundation (grant nos.: DMR-05-48559 and DMR-05-20020), DuPont–Marshall Laboratories, and the P. Roy Vagelos Chair at the University of Pennsylvania are gratefully acknowledged.

[1] a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159; b) J. H. van Esch, B. L. Feringa, *Angew. Chem.* **2000**, *112*, 2351–2354; *Angew. Chem. Int. Ed.* **2000**, *39*, 2263–2266; c) D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237–1247; d) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489–497; e) K. Sada, M. Takeuchi, N. Fujita, M. Numata, S. Shinkai, *Chem. Soc. Rev.* **2007**, *36*, 415–435.

[2] a) M. de Loos, J. van Esch, R. M. Kellogg, B. L. Feringa, *Angew. Chem.* **2001**, *113*, 633–636; *Angew. Chem. Int. Ed.* **2001**, *40*, 613–616; b) L. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217; c) J. J. van Gorp, J. A. J. M. Vekemans, E. W. Meijer, *J. Am. Chem. Soc.* **2002**, *124*, 14759–14769.

[3] a) J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg, B. L. Feringa, *Chem. Eur. J.* **1999**, *5*, 937–950; b) M. de Loos, A. G. J. Ligtenbarg, J. van Esch, H. Kooijman, A. L. Spek, R. Hage, R. M. Kellogg, B. L. Feringa, *Eur. J. Org. Chem.* **2000**, 3675–3678; c) M. Lescanne, P. Grondin, A. d'Aléo, F. Fages, J.-L. Pozzo, O. M. Monval, P. Reinheimer, A. Colin, *Langmuir* **2004**, *20*, 3032–3041; d) X. Huang, P. Terech, S. R. Raghavan, R. G. Weiss, *J. Am. Chem. Soc.* **2005**, *127*, 4336–4344; e) X. Huang, S. R. Raghavan, P. Terech, R. G. Weiss, *J. Am. Chem. Soc.* **2006**, *128*, 15341–15352.

[4] a) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *Angew. Chem.* **2000**, *112*, 1661–1666; *Angew. Chem. Int. Ed.* **2000**, *39*, 1597–1602; b) V. Percec, C. M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2004**, *126*, 6078–6094; c) V. Percec, M. N. Holerca, S. Nummelin, J. J. Morrison, M. Glodde, J. Smidrkal, M. Peterca, B. M. Rosen, S. Uchida, V. S. K. Balagurusamy, M. J. Sienkowska, P. A. Heiney, *Chem. Eur. J.* **2006**, *12*, 6216–6241; d) V. Percec, M. Peterca, M. J. Sienkowska, M. A. Ilies, E. Aqad, J. Smidrkal, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 3324–3334.

[5] a) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov, S. A. Vinogradov, *Nature* **2004**, *430*, 764–768; b) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, J. S. Ladislaw, B. M. Rosen, U. Edlund, P. A. Heiney, *Angew. Chem.* **2005**, *117*, 6674–6679; *Angew. Chem. Int. Ed.* **2005**, *44*, 6516–6521; c) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, Y. Miura, U. Edlund, P. A. Heiney, *Aust. J. Chem.* **2005**, *58*, 472–482; d) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, M. J. Sienkowska, P. A. Heiney, *J. Am. Chem. Soc.* **2005**, *127*, 17902–17909; e) M. Peterca, V. Percec, A. E. Dulcey, S. Nummelin, S. Korey, M. Ilies, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 6713–6720; f) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, M. J. Sienkowska, P. A. Heiney, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 2518–2523.

[6] a) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449–452; b) V. S. K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, *J. Am. Chem. Soc.* **1997**, *119*, 1539–1555; c) V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070; d) V. Percec, W.-D. Cho, G. Ungar, *J. Am. Chem. Soc.* **2000**, *122*, 10273–10281; e) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2001**, *123*, 1302–1315; f) V. Percec, M. N. Holerca, S. Uchida, W.-D. Cho, G. Ungar, Y. Lee, D. J. P. Yeardley, *Chem. Eur. J.* **2002**, *8*, 1106–1117.

[7] G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, *Science* **2003**, *299*, 1208–1211.

[8] X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey, J. K. Hobbs, *Nature* **2004**, *428*, 157–160.

[9] a) G. Ungar, D. Abramic, V. Percec, J. A. Heck, *Liq. Cryst.* **1996**, *21*, 73–86; b) V. Percec, C.-H. Anh, T. K. Bera, G. Ungar, D. J. P. Yeardley, *Chem. Eur. J.* **1999**, *5*, 1070–1083; c) V. Percec, T. K. Bera, M. Glodde, Q. Fu, V. S. K. Balagurusamy, P. A. Heiney, *Chem. Eur. J.* **2003**, *9*, 921–935; d) V. Percec, M. R. Imam, T. K. Bera, V. S. K. Balagurusamy, M. Peterca, P. A. Heiney, *Angew. Chem.* **2005**, *117*, 4817–4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4739–4745.

[10] a) Z. J. Kaminski, *Tetrahedron Lett.* **1985**, *26*, 2901–2904; b) M. Kunishima, C. Kawachi, J. Morita, K. Terao, F. Iwasaki, S. Tani, *Tetrahedron* **1999**, *55*, 13159–13170; c) M. Kunishima, C. Kawachi, F. Iwasaki, K. Terao, S. Tani, *Tetrahedron Lett.* **1999**, *40*, 5327–5330; d) Z. J. Kaminski, *Biopolymers* **2000**, *55*, 140–164; e) C. E. Garrett, X. Jiang, K. Prasad, O. Repic, *Tetrahedron Lett.* **2002**, *43*, 4161–4165.

[11] a) H. A. Staab, *Angew. Chem.* **1962**, *74*, 407–423; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 1351–1367; b) S. P. Rannard, N. J. Davis, *Org. Lett.* **1999**, *1*, 933–936; c) S. P. Rannard, N. J. Davis, *Org. Lett.* **2000**, *2*, 2117–2120; d) S. Rannard, N. Davis, H. McFarland, *Polym. Int.* **2000**, *49*, 1002–1006.

[12] a) K. Hanabusa, K. Okui, K. Karaki, T. Koyama, H. Shirai, *J. Chem Soc. Chem. Commun.* **1992**, 1371–1373; b) K. Hanabusa, J. Tange, Y. Taguchi, T. Koyama, H. Shirai, *J. Chem Soc. Chem. Commun.* **1993**, 390–392.

[13] a) W.-D. Jang, D.-L. Jiang, T. Aida, *J. Am. Chem. Soc.* **2000**, *122*, 3232–3233; b) C. Kim, K. T. Kim, Y. Chang, *J. Am. Chem. Soc.* **2001**, *123*, 5586–5587; c) W.-D. Jang, T. Aida, *Macromolecules* **2003**, *36*, 8461–8469; d) A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts, A. C. Wright, *J. Am. Chem. Soc.* **2003**, *125*, 9010–9011.

[14] V. Percec, C.-H. Anh, G. Ungar, D. J. P. Yeardley, M. Möller, S. S. Sheiko, *Nature* **1998**, *391*, 161–164.

Received: August 16, 2007
Published online: November 19, 2007

