Morphology and Wettability Tunable Two-Dimensional Superstructure Assembled by Hydrogen Bonds and Hydrophobic Interactions

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A novel tripodal gelator, functionalized by three urea and three azobenzene moieties grafted with three long alkyl chains, was designed and synthesized. The morphologies and surface properties of the xerogels prepared from this gelator strongly depend on the polarity of the gelling solvent. Cabbage-like topography and superhydrophobicity were observed in the xerogel formed from a low polar aromatic solvent such as xylene. The wettability of a xerogel could be turned from hydrophobicity to hydrophilicity by applying a sol—gel process with different solvents. Spectral and structural analysis of the xerogels revealed a basic bilayer arrangement of molecules with polarity changing on going from the inner hydrophilic regions toward the outer region (edge) of the layer. The cooperation and relative competition of hydrogen bonds, hydrophobic interactions, and azobenzene—azobenzene interactions are suggested to be the main contribution for the bilayer structure self-assembly. This two-dimensional self-assembly and the growth of nanostructures are remarkable in view of the usual fibrous aggregates given by organogels.

Introduction

Functional surfaces with controllable wettability have come to the forefront of research for their great interest in biological and industrial applications.¹ Many of the functionalities of living organisms prove to be governed not only by the chemical nature of their constituents but also by their micro- (or nano-) structure, as frequently observed in nature.^{1,2} Synthetic materials with tunable surface properties have been reported recently, including a polymer modified surface,³ ACNT,⁴ and specifically treated TiO₂ nanofilms.⁵ The most significant feature common to these materials is

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that they possess well-defined micro- and nanostructures on the surface. Their wettability can be tuned between superhydrophilicity and superhydrophobicity by modifying the surface chemistry or topographic structure by various stimuli including light irradiation,⁶ pH change,⁷ thermal treatment,^{3b,8} solvent,⁹ and so on. Several efforts have been made to construct micro- and nanostructures on various surfaces. One of the most common techniques employed consists of coating the surface with a polymer. However, polymer coating once spread generally displays untunable properties. According to our previous experience on low weight molecular (LWM) assembly,¹⁰ the challenging idea appeared that if the assembled LWM material itself could intrinsically contribute to the micro- or nanostructure on the surface, tunable surface properties could be more easily achieved.

The self-assembling of small functional molecules into supramolecular structures is a powerful approach toward the

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development of new materials and nanoscale devices.¹¹ As a novel class of self-assembled materials, LWM gels have received considerable attention in recent years because they can organize into regular nanoarchitectures through specific noncovalent interactions including hydrogen bonds, hydrophobic interactions, $\pi - \pi$ interactions, and Van der Waals forces.^{11,12} The intermolecular hydrogen bonds or $\pi - \pi$ interactions usually facilitate the growth of linear, elongated aggregates in the gels.^{13,14} Therefore, the microscale morphology of most of these gels consists of fibers or ribbons. Because the morphology of a gel is essentially the same over the whole system, the surface properties of related xerogels have rarely attracted much attention. A few examples of lamella-,15 vesicle-,16 and platelet-shaped17 gels have been reported, but the origin of the specific topography is not clear. Very recently, Smith et al found,¹⁸ in the case of a twocomponent dendritic system, that the morphology of the gels could be tuned by varying the ratio of the gelators, a method evidently not applicable to one-component systems. However, those "nonfibrous" examples which generally contain more than one interaction site suggest the fact that occurrence

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of several competitive or cooperative interactions in a single system could possibly allow controlling the topography of the self-assembled materials and perhaps tune the surface properties, thus providing new opportunities to LWM materials. In this report, we describe a novel microscopic gelation system that leads to materials whose morphologies and surface properties strongly depend on the solvents.

Results and Discussion

Molecular Design and Gelation Properties. The strategy of our research is to build up a single system containing hydrogen bonding and hydrophobic and azobenzeneazobenzene interactions. These interactions play on their mutual balance to modulate the packing arrangement of the molecules and eventually obtain a particular superstructure and functional surface. For this purpose, we designed and synthesized the tripodal tris-urea derivative 1a, which contains triethylamine, three azobenzene moieties, and three hydrophobic alkyl chains (Scheme 1). Tris-urea-based gelators have been previously reported by van Esch et al.¹⁹ 1a displays several original points. First, it possesses a hydrophilic amino core with urea groups and hydrophobic alkyl chains as adjustable tails, an overall geometry that should render the morphology sensitive to the polarity of the gelling solvent and perhaps even controllable. Furthermore, the numerous interactions in this compound should offer, at least to some extent, the possibility of controlling the morphology of the gel. Actually we found that 1a has the ability for gelating a wide variety of organic solvents, such as 1-butanol (n-BuOH), 1-methyl-2-pyrrolidone (NMP), chloroform, xylene, and *n*-hexane, in a critical gelation concentration range of 10-30 mg/mL (Table 1 and Figure 1). The related shortchain compound 1b cannot gel any of the above solvents, while it even can crystallize from the mixed solvent of dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF; 1:4, v/v). The most dramatic feature is that the xerogels formed

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Table 1. Gelation Properties of 1a^a

			-		
solvents	state	CGC	solvents	state	CGC
ethanol	PG		benzene	S(R)	
acetone	Ι		dichloromethane	S(R)	
ethyl acetate	PG		toluene	S(R)	
NMP	G	25 mg/mL	THF	S(R)	
chloroform	G	30 mg/mL	cyclohexane	S(R)	
xylene	G	20 mg/mL	1,4-dioxane	S(R)	
hexane	G	15 mg/mL	1,2-dichloroethane	S(R)	
1-butanol	G	10 mg/mL	bromobenzene	S(R)	

^{*a*} CGC: critical gelation concentration, the minimum concentration necessary for gelation of solvents. PG: partial gel. I: insoluble. S: solution when heated. R: recrystallization. G: gel.



Figure 1. Pictures of the sol-gel transition of 1-butanol (20 mg/mL).

by **1a** display morphologies and surface properties that strongly depend on the nature of the gelling solvent.

Morphologies of the Xerogels. To obtain visual images of the assembled 1a from various organic solvents, the morphology of the xerogels obtained from 1a were investigated by scanning and transmission electron microscopy (SEM and TEM). The NMP and xylene xerogels were obtained from the corresponding initial gel with a concentration of 30 mg/mL; the n-BuOH xerogel was obtained from the gel of 20 mg/mL. Micrographs of the xerogels are strongly dependent on the gelling solvent. The xerogel from *n*-BuOH shows regular flakes of about 100-200 nm in size, connected by thin ribbons (Figure 2a,b). There is no appreciable difference in the SEM images over the concentration range of 1a in the gels from 10 to 30 mg/mL. TEM images of the xerogel show that the flakes actually consist of a mosaic assembly of "nested" tiny thin platelets (Figure 3a). The ribbons connecting the flakes displayed by the SEM images are wrinkles formed by thin platelets (Figure 3b), and their widths range from 10 to 50 nm.

Figure 2c,d shows the SEM images of the NMP xerogel. The molecules of 1a aggregate to form flowerlike architectures about 1000 nm in diameter. The thickness of the flower petals is about 7-10 nm. The flowers are connected by spacious silklike soft ribbons. TEM images of NMP xerogel (Figure 3c) also show thin platelets tiled up to form flowerlike architectures. Furthermore, randomly distributed nanodots and grains were found in TEM images by careful analysis of the images; these dots were residues of H₄PWO₃ used as the staining agent as evidenced by energy-dispersive X-ray (EDX) analysis of the constituting elements. The grains display a very homogeneous dimension of about 1.6 nm, which proved to be the cell parameter b of the structure model discussed below. In contrast, the gel formed in xylene provides homogeneous cabbagelike spherical structures with a diameter of 1000-1500 nm (Figure 2e). These sphericalshaped balls are composed of hierarchical structures of



Figure 2. SEM images of the xerogels from *n*-BuOH (a and b), NMP (c and d), and xylene (e and f).



Figure 3. TEM images of the xerogels from *n*-BuOH (a, b) and NMP (c, d).

closely stacked thin films with the thickness about 8-9 nm (Figure 2f).

On the basis of the above results, we can see that the morphology of the xerogels strongly depends on the nature of the gelling solvents. This feature most likely results from a strongly anisotropic growth, a process related to highly directional intermolecular interactions that in turn may be due to the partial or full extension of the long alkyl chains of **1a** or to the formation of directional molecular aggregates.

Spectral Analysis of the Gel and Xerogel States. Electronic UV-vis absorption spectra of the gels were studied to obtain information about the aggregated state of



Figure 4. Absorption spectra of 1a in solution, gel, and xerogel from xylene (a) and *n*-BuOH (b) at room temperature. Concentration: the solutions, 1×10^{-5} M; xylene gel, 30 mg/mL; *n*-BuOH gel, 20 mg/mL. UV irradiation: 365 nm for 20 min.

azobenzene on the molecular scale.11d,20 The concentration of **1a** in both xylene and *n*-BuOH is 1×10^{-5} M (Figure 4), and the absorption band centered at 351 nm can be assigned to $\pi - \pi^*$ transitions of the azobenzene moiety.²⁰ This band appears to split into two bands both in the gel and in the xerogel obtained from the corresponding solvents, one blueshifted and the other red-shifted. These "bands" do not exhibit obvious change when going from gel to xerogel state, but their positions slightly depend on the gelling solvent. Gelation with xylene and n-BuOH give a component blueshifted to 302 and 305 nm, respectively. These strong blue shifts of the $\pi - \pi^*$ absorption band suggest the formation of H-aggregates (Scheibe) by the molecules of 1a in the gel and xerogel states.²⁰ A red-shifted component at about 360 nm also accompanies gelation in both solvents. Interestingly, the intensity of this band is reduced by UV light irradiation, which indicates that the azobenzene species contributing to this absorption are not strongly aggregated. The red-shifted component is more intense in a gel with nonpolar xylene (Figure 4a) than in a gel or xerogel with polar n-BuOH solvent. In xylene xerogel it only appears as a shoulder (Figure 4b). It suggested that the formation of aggregates in both gels and xerogels in turn implies that 1a is arranged in an extended linear conformation in the gels and that this conformation is retained in the related xerogels.

Figure 5 compares the IR spectra of the gel, xerogels, and the powder of **1a**. In the powder, the NH and CO stretching modes of urea groups are located at 3281 and 1638 cm⁻¹; the NH bending vibration is located at 1547 cm⁻¹. These peaks become broad and move to slightly higher wavenumbers of 3320, 1648, and 1542 cm⁻¹ in the xylene gel and 3327, 1642, and 1545 cm⁻¹ in the related xerogel. These shifts suggest that the hydrogen bonds in the gels are somewhat more disordered than that in the solid state.^{14,21,22} The CH₂ stretching vibrations at 2916 cm⁻¹ (ν_{anti}) and 2849 cm⁻¹ (ν_{sym}) in both the xerogels and the powder indicate that the alkyl chains are closely packed to form quasicrystalline domains.²³ These peaks are observed at 2922 and



Figure 5. FT-IR spectra of the powder (1), *n*-BuOH xerogel (2), xylene xerogel (3), and xylene gel (30 mg/mL; 4) of **1a**.

2854 cm⁻¹ as broader bonds in the xylene gel. The IR spectrum of the native gel from *n*-BuOH is poorly resolved because of the dominant signal of the solvent. It is worth pointing out that there is no appreciable difference between IR spectra given by the xerogels from different gelling solvents. On the basis of the UV–vis and IR data, it is reasonable to suggest that the aggregates of the molecules in the gel and xerogel states do not significantly depend on the nature of the gelling solvent. The supermolecular structure of the gel may result from the combined effects of hydrogen bonds, aggregation of azobenzene moieties, and hydrophobic interactions.

Molecular Structure of the Xerogel. Information about the structure at the molecular level of the *n*-BuOH, NMP, and xylene xerogels was obtained by small-angle X-ray scattering (SAXS; Figure 6). The SAXS patterns of the xerogels prepared with the three solvents show similar series of reflections. In each series, the various spacings observed form a suite of fractions (d/1:d/2:d/3:d/4), a feature that strongly suggests a lamellar structure.^{13,24,25} The gelling solvent influences the value of the basal spacing d_{001} to a small but significant extent. The d_{001} values are 7.49, 7.88,

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Figure 6. (a) SAXS patterns of xerogels of 1a from *n*-BuOH (solid line), NMP (dotted line), and xylene (dotted-dashed line); (b) WAXS pattern of xylene xerogel.



Figure 7. Expected molecular packing model and cell parameters in 1a.

and 8.33 nm for n-BuOH, NMP, and xylene xerogels, respectively. The variation of the basal spacing thus parallels the change of polarity of the solvents. This may reflect a different capability of solvent penetration between the layers.²⁶ The weak polar aromatic solvent such as xylene swells the layer structure more efficiently than *n*-BuOH, and, therefore, the xerogel (even dried) gives a larger d value. The SAXS pattern of the native gels, from both *n*-BuOH and NMP, did not show any sharp diffraction peak, only a broad band around 8.5 nm. For the purpose of a deeper understanding of the detailed structure of the xerogel, the single-crystal structure of the related compound 1b was investigated, with the goal of obtaining a model of the molecular packing in the xerogel of 1a.²⁵ 1b gives a monoclinic unit cell (P2(1)/c) with the unit cell parameters a = 9.574(2) Å, b = 14.254(2) Å, c = 34.638(6) Å, $\beta =$ 95.818(3)°, and Z = 4.00. The molecules are arranged in the same way as in the previously reported tris-urea derivatives.¹⁹ The three urea branches extend along a common direction, with strong intramolecular hydrogen bonds between the urea and the central nitrogen atom of triamine. Weak intra- and intermolecular hydrogen bonds are also observed between urea groups in the [010] direction. In contrast, molecules along the [101] direction are arranged in an antiparallel way by azobenzene–azobenzene interactions. The cooperation of these two kinds of noncovalent interactions may be the driving force for **1b** to achieve a two-dimensional packing instead of a one-dimensional chain structure as already observed.¹⁹ (For the molecular packing of **1b**, see Figure S1 of Supporting Information.)

Comparing the structural data of 1b with the X-ray scattering patterns of 1a, it is clear that both of them have lamellar structures with large d spacings. According to the molecular length of 1a which reaches about 3.6 nm when the three branches extend along the same direction (from CPK molecular modeling) and considering the hydrophobic interaction along alkyl chains, the long axis (c axis) observed in the xerogels must be related to a pair of two head-to-tail molecules. The wide-angle X-ray scattering (WAXS) spectrum of the xylene xerogel provides values for the other two parameters of about 1.68 and 2.02 nm (Figure 6b). The first one (1.68 nm) is suspected to be determined by the hydrogen bonds between the urea groups, which was also observed as the smallest dimension in the TEM images. The weak peak at 2.02 nm suggests an insufficient packing of the long alkyl chain (a axis). Because of the unique length of the c axis, it is obvious that the molecules grow along the a and bdirections giving a two-dimensional architecture (Figure 7). The thickness of the film is expected to correspond to the length of the c parameter in the cell (d_{001} value), a value

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Figure 8. Photographs of the water droplet on glass slices spin-coated with xerogel of 1a from *n*-BuOH (a), NMP (b), and xylene (c). Reversible wettability transition between *n*-BuOH and xylene gel by the sol-gel process (d).



Figure 9. XPS spectra in the C 1s, N 1s, and O 1s regions of the *n*-BuOH (solid line) and xylene xerogels (dotted line), respectively.

consistent with the thickness of the flower petals (Figure 2d) and closely stacked thin film (Figure 2f) in SEM images. Taking into account the structure and parameters of the compound, it can be deduced that the film has a bilayer structure. The bilayer slab consists of two single layers, each of them comprising double antiparallel species packing along the b direction. The long hydrophobic chains are interdigitated to hold the bilayer structure, whereas the triamine core of each molecule located on the outside of the layer forms the hydrophilic environment of the surface. It seems that even though the polarity of the gelling solvent does not strongly influence the molecular level structure of the gel (proved by spectra and diffraction analysis); it greatly contributes to the configuration of the hierarchical nanostructure of the corresponding xerogel. The hydrophilic surface of the layer suppresses the formation of a multilayer structure in a polar solvent such as n-BuOH, while in a nonpolar solvent like xylene, the films tend to pile up to form cabbage shaped balls.

Gelling Solvent Dependence of Surface Composition and Wettabilities. The wettabilities of *n*-BuOH, NMP, and xylene xerogels were characterized by the measurement of the water contact angle (CA) on their surface. The organogels were spin-coated on glass slices, which were pretreated with silicon oil/THF (1:10) solution, and dried in a vacuum for 12 h at room temperature. Thermogravimetric analysis (TGA) of the xylene, *n*-BuOH, and NMP xerogels shows the absence of any weight losses up to 250 °C (Figure S2 of Supporting Information), which indicates that no free solvent remains in these xerogels. The shapes of a water droplet sitting on xerogel films obtained from different gelling solvents are shown in Figure 8. The CAs on surfaces coated with *n*-BuOH, NMP, and xylene xerogel are $80.3 \pm 0.9^\circ$, $110.1 \pm 1.5^\circ$, and $146.0 \pm 0.6^\circ$, respectively. Therefore, the

surface wettability crucially depends on the gelling solvents. The chemical compositions of the top surface of *n*-BuOH and xylene xerogels were investigated by X-ray photoelectron spectroscopy (XPS). The intensity of the C 1s and N 1s peaks of the *n*-BuOH xerogel are weaker than that of xylene xerogels, whereas the intensity of O 1s peaks of n-BuOH xerogel is much stronger (Figure 9). The XPS measurement demonstrated a decreased C/O ratio for the xerogel from *n*-BuOH compared with that from xylene, which means that many more C=O groups are exposed on the surface of the n-BuOH xerogel and cause the hydrophilic surface. It is reverse in the case of xylene xerogels. Both results of XPS and the wetting experiment are consistent with our concept of the bilayer aggregate structure of 1a, with a triamine trisurea core of each molecule located on the surface of the layer forming a hydrophilic environment and the long hydrophobic chains located at the edge of the layer. The xerogel formed from a polar solvent like *n*-BuOH is covered by a large area of flat surface and, therefore, gives a comparatively small CA ($<90^{\circ}$). In a gel from the nonpolar solvent of xylene, the films stack in such a way as to create a hydrophobic external surface all around the cabbage balls, because only the nonpolar edges of the layers are located there. Thus, the film exhibits a large CA approaching superhydrophobicity $(\sim 150^\circ)$. The enhancement of the roughness of the surface is also an important factor for the hydrophobicity according to the Wenzel's equation.²⁷ SEM images suggest a much rougher, more corrugated surface of the xylene xerogel than that of the *n*-BuOH xerogel. In the case of a rough surface, air trapped in the cracks of the ball also prevents the contact of the water droplet with the surface of the layer.^{3a} The fraction of the air/water interface is calculated to be as high as 0.85 according to modified Cassie's equation,²⁸ which indicates that achievement of high hydrophobic xerogel film is mainly a result of the specific surface topographic structure.

The wettability could not be switched by simple immersion of a given xerogel film in a different solvent and drying again. Changing the wettability requires reabsorption of a new solvent. For example, after the *n*-BuOH xerogel was dipped in xylene and heated above 80 °C, the xerogel converted to a sol, and the sol turned to the xylene gel and subsequent xerogel after cooling to room temperature and drying. Thus the surface wettability of the xerogel can be easily modified from hydrophilic to hydrophobic by changing the gelling solvent from polar to nonpolar. The reversible switching was repeated several times from the *n*-BuOH xerogel to the xylene one, and good reversibility of the surface wettability was observed (Figure 8d).

Conclusions

In conclusion, the novel tripodal gelator 1a, functionalized by three urea and azobenzene moieties and tailed with three long alkyl chains, is capable of forming anisotropic bilayers which are hydrophilic along the plane but hydrophobic near the rim. The wettability of the surface, therefore, strongly depends on the morphology of the xerogel which is in turn controlled by the intermediate gelling solvent. The cooperation of hydrogen bonds, hydrophobic interactions, and azobenzene-azobenzene aggregation ability seems to be the key point of the bilayer self-assembly. This two-dimensional self-assembly and the growth of nanostructures are remarkable compared with the usual fibrous aggregates of most organogels. The unique and tunable surface properties such as superhydrophobicity distinguish the organogels as a novel class of functional materials. To the best of our knowledge, this is the first example that the wettability properties of the surface of a low molecular assembly are tuned by solvents, which opens a new method for the application of these organic molecules and also provides a strategy for the development of nanostructural advanced materials.

Experiment Section

General Methods. All starting materials were obtained from commercial supplies and used as received. Moisture sensitive reactions were performed under an atmosphere of dry argon. ¹H NMR and ¹³C NMR spectra were recorded on a Mercuryplus, at 400 and 100 MHz, respectively. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass was recorded on an AXIMA-CFRPLVS mass spectrometer (Shimadzu). Element analysis was carried out on a VARIOEL3 apparatus (ELEMENTAR).

Synthesis. 4-(4-Hydroxyphenylazo)benzoic Acid (2). Yellow solid 2 was synthesized according to a previous report²⁹ (95% yield). ¹H NMR (DMSO- d_6 , 25 °C) δ 8.08–8.10 (d, J = 8.4 Hz, 2H), 7.81–7.85 (t, J = 8.8 Hz, 4H), 6.95–6.97 (d, J = 8.8 Hz, 2H); ^{13}C NMR (DMSO- $d_6,$ 25 °C) δ 167.00, 159.64, 150.70, 135.92, 130.66, 127.33, 121.46.

4-(4-Hydroxyphenylazo)benzoic Acid Ethyl Ester (3). To a solution of **2** (2.42 g, 10 mmol) in 50 mL of ethanol was added a catalytic amount of concentrated sulfuric acid. After the reaction mixture was refluxed and stirred for 6 h, 50 mL of water was poured into the mixture, and the reaction mixture was neutralized with 1 M NaOH solution. **3** was then obtained by filtration and purified by column chromatography on silica gel with chloroform as the eluent, yield 2.38 g (88%). ¹H NMR (CDCl₃, 25 °C) δ 8.17–8.19 (d, *J* = 8.4 Hz, ArH, 2H), 7.89–7.92 (dd, ArH, 4H), 6.97–6.99 (d, *J* = 8.8 Hz, ArH, 2H), 6.28 (s, –OH, 1H), 4.40–4.46 (q, *J* = 7.2 Hz, –OCH₂CH₃, 2H), 1.42–1.45 (t, *J* = 7.2 Hz, –OCH₂CH₃, 3H); ¹³C NMR (CDCl₃, 25 °C) δ 166.81, 159.53, 155.55, 147.24, 131.59, 130.82, 125.67, 122.59, 116.18, 61.67, 14.53.

4-(4-Alkoxyphenlazo)benzoic Acid Ethyl Ester (4a and 4b). To 50 mL of dry acetone solution containing 3 (2.16 g, 8 mmol) and 2.5-fold of the corresponding alkyl bromide (20 mmol) was added 2.78 g (20 mmol) of anhydrous potassium carbonate. The reaction mixture was refluxed and stirred for 8 h and then poured into excess water and filtered. The crude product was obtained by filtration and purified by column chromatography on silica gel with chloroform/petrol ether (1:2, v/v) as the eluent, yield 90% (4a) and 92% (4b) of corresponding product. 4a: ¹H NMR (CDCl₃, 25 °C) δ 8.16–8.18 (d, J = 8.4 Hz, ArH, 2H), 7.89–7.95 (q, J = 6.4 Hz, ArH, 4H), 7.00–7.02 (d, J = 7.2 Hz, ArH, 2H), 4.38–4.44 (q, J = 7.2 Hz, $-COOCH_2CH_3-$, 2H), 4.03-4.06 (t, J = 6.4 Hz, -OCH₂CH₂-, 2H), 1.80-1.84 (m, -CH₂-, 2H), 1.40-1.44 (t, J = 7.2 Hz, $-OCH_2CH_3$, 3H), 1.26 (s, $-CH_2-$, 26H), 0.87-0.89 (t, J = 7.2 Hz, $-CH_3$, 3H); ¹³C NMR (CDCl₃, 25 °C) δ 166.37, 162.55, 155.5, 147.06, 131.68, 130.75, 125.42, 122.54, 114.99, 68.64, 61.38, 32.18, 29.86, 26.25, 22.95, 14.58. 4b: ¹H NMR (CDCl₃, 25 °C) δ 8.16–8.18 (d, J = 8.4 Hz, ArH, 2H), 7.89–7.95 (q, J = 6.0 Hz, ArH, 4H), 7.00 (d, J = 8.8 Hz, ArH, 2H), 4.38-4.43 (q, J = 7.2 Hz, $-COOCH_2CH_3$, 2H), 4.09–4.14 (q, J = 6.8Hz, -OCH2CH3, 2H), 1.40-1.47 (m, -COOCH2CH3 and -OCH₂CH₃, 6H); ¹³C NMR (CDCl₃, 25 °C) δ 162.31, 155.53, 147.09, 131.70, 130.75, 125.42, 122.53, 114.97, 116.3, 64.11, 61.40, 14.97, 14.58.

4-(4-Alkoxyphenlazo)benzoic Acid (**5a** and **5b**). A total of 20 mL of 0.5 M NaOH solution was added to 30 mL of an ethanol solution of **4a** or **4b** (6 mmol). The reaction mixture was refluxed overnight and then neutralized with 1 M hydrochloric acid. After the ethanol was evaporated, over 90% yield of crude product **5a** or **5b** was obtained by filtering and used without further purification.

4-(4-Alkoxyphenlazo)benzoyl Azide (6a and 6b). A total of 2 mL of SOCl₂ (excess) was dropped into 10 mL of THF solution of 5a or 5b (5 mmol). The reaction mixture was refluxed and stirred for 3 h, and then the solvent and excess SOCl₂ were evaporated under reduced pressure to yield 4-(4-alkoxyphenlazo)benzoyl chloride, which was dissolved in 10 mL of THF and dropped into 50 mL of an aqueous solution of NaN3 (3.25 g, 50 mmol) in an ice bath. The reaction mixture was stirred overnight, the precipitate was filtered, and 6a or 6b was obtained as a yellowish solid. The crude product was purified by column chromatography on silica gel with chloroform/petrol ether (3:1, v/v) as the eluent, giving 75% yield of **6a** or **6b**, respectively. **6a**: ¹H NMR (CDCl₃, 25 °C) δ 8.15-8.17 (d, J = 8.4 Hz, ArH, 2H), 7.90–7.95 (q, J = 5.6 Hz, ArH, 4H), 7.00–7.03 (d, J = 9.2 Hz, ArH, 2H), 4.04–4.07 (t, J = 6.4Hz, -OCH2CH2-, 2H), 1.79-1.84 (m, -OCH2CH2-, 2H), 1.44-1.51 (m, -CH₂CH₃, 2H), 1.26 (s, -CH₂-, 22H), 0.86-0.89 (t, J = 7.2 Hz, $-CH_3$, 3H); ¹³C NMR (CDCl₃, 25 °C) δ 172.19. 162.81, 156.48, 147.07, 131.65, 130.78, 125.60, 122.82, 115.06, 68.70, 32.17, 29.84, 26.24, 22.94, 14.37. **6b**: ¹H NMR (CDCl₃, 25 °C) δ

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8.12–8.14 (d, J = 8.4 Hz, ArH, 2H), 7.88–7.94 (q, J = 8.4 Hz, ArH, 4H), 7.00 (d, J = 8.8 Hz, ArH, 2H), 4.09–4.14 (q, J = 7.2 Hz, $-OCH_2CH_3$, 2H), 1.44–1.48 (t, J = 7.2 Hz, $-OCH_2CH_3$, 3H); ¹³C NMR (CDCl₃, 25 °C) δ 172.15, 162.57, 155.43, 147.08, 131.63, 130.75, 125.61, 122.81, 115.02, 64.15, 14.96.

Tris-[4-(4-Alkoxyphenlazo)phenylureidoethyl]amine (1a and 1b). A total of 0.15 g (1 mmol) of tris-(2-aminoethyl)amine was dropped into 10 mL of a toluene solution of 6a or 6b (3.1 mmol) under an atmosphere of dry argon. The reaction mixture was stirred overnight at 80 °C and concentrated to 5 mL. The resulted precipitate was then filtered and washed with toluene to obtain an over 70% yield of 1a or 1b as a yellowish powder. 1a: mp 165–167 °C, ¹H NMR (CDCl₃, 65 °C) & 8.38 (s, NH, 3H), 7.23-7.73 (m, ArH, 18H), 6.77-6.94 (m, ArH, 6H), 6.57 (s, NH, 3H), 3.89-4.04 (t, -OCH₂-, 6H), 3.28-3.71 (NCH₂CH₂-, 6H), 2.51-2.76 (m, NCH₂-, 6H), 1.79-1.84 (m, -OCH₂CH₂-. 6H), 1.48-1.51 (m, -CH₂-, 6H), 1.30 (s, -CH₂-, 72H), 0.89 (t, -CH₃, 9H); ¹³C NMR (CDCl₃, 65 °C) δ 167.91, 162.11, 154.60, 147.35, 134.81, 128.02, 125.14, 124.55, 123.81, 122.53, 119.20, 114.76, 68.58, 53.78, 38.02, 31.94, 29.50, 26.15, 22.64, 13.96. Anal. Calcd (%) for C₉₃H₁₄₁N₁₃O₆: C, 72.66; H, 9.2; N, 11.85. Found: C, 72.51; H, 9.21; N, 11.66. MALDI-TOF-MS: 1536.8 [M + H]⁺. 1b: mp 241-243 °C, ¹H NMR (DMSO-*d*₆, 25 °C) δ 7.62–7.86 (m, ArH, 18H), 6.95-6.97 (d, ArH, 6H), 4.09-4.14 (q, -OCH₂CH₃, 6H), 3.41-3.47 (t, -NCH₂CH₂, 6H), 2.70-2.76 (t, -NCH₂, 6H), 1.35-1.39 (t, -OCH₂CH₃, 9H). Anal. Calcd for C₅₁H₅₇N₁₃O₆: C, 64.61; H, 6.06; N, 19.21. Found: C, 64.75; H, 5.96; N, 18.95. MALDI-TOF-MS: 948.2 $[M + H]^+$.

Techniques. UV-visible spectra were recorded on an UV-vis 2550 spectroscope (Shimadzu). Fourier transform infrared (FT-IR) spectra were performed using an IRPRESTIGE-21 spectroscope (Shimadzu) with KBr pellets. TGA curves were recorded on a DTG-60H (Shimadzu) with a heating rate of 10 °C/min.

SEM images of the xerogels were obtained using a SSX-550 (Shimadzu) with an accelerating voltage of 15 kV. Samples were prepared by spinning the gels on glass slices and coating with Au. TEM was recorded on a JEOL JEM-2011 apparatus, operating at 200 KV and fitted with an EDX analysis accessory. The sample was prepared by putting the gel on a carbon-coated copper grid and by staining with phosphotungstic acid (2.0 wt % aqueous solution).

XPS spectra were recorded with a Perkin-Elmer PHI 5000C ESCA system with Mg K α radiation ($h\nu = 1253.6$ eV) at a power of 250 W. The pass energy was set as 93.9 eV and the binding energies (BEs) were calibrated by using contaminant carbon at a BE of 284.6 eV. The base pressure of the analyzer chamber was about 5 \times 10⁻⁸ Pa.

The SAXS diagram was obtained on a NanoSTAR U SAXS System (Bruker), using a Cu K α radiation source ($\lambda = 0.1542$ nm). The SAXS data were corrected for absorption and background scattering. The structure data of **1b** were collected on a Bruker SMART charge-couple device diffractometer, with a σ scan and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. The full-matrix least-squares refinement used was Shelxl 97³⁰ based on F^2 . Because of the disorder of the alkyl chain in the structure, the atoms were only refined isotropically with position occupancy.

CA measurements were performed using the sessile drop method (Dataphysics, OCA 20). The water droplets were introduced using a microsyringe, and images were captured to measure the angle of the liquid—solid interface; each sample was recorded at five different points.

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Supporting Information Available: Diagram of molecular packing of **1b** along the *a* and *b* axes and TGA spectra of the xerogels. This material is available free of charge via the Internet at http://pubs.acs.org.

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