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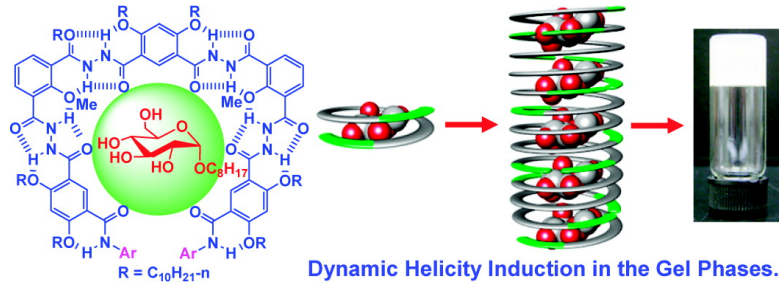
J. Am. Chem. Soc., **2008**, 130 (40), 13450-13459 • DOI: 10.1021/ja8043322 • Publication Date (Web): 13 September 2008



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Foldamer Organogels: A Circular Dichroism Study of Glucose-Mediated Dynamic Helicity Induction and Amplification

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Abstract: This paper reports a systematic study of the dynamic process for the self-assembly of chiral organogels from achiral hydrogen bonded hydrazide foldamers by induction of chiral glucose. Six foldamers incorporated with six decyl chains and two benzene, naphthalene, anthracene, or pyrene units at the ends are revealed to strongly gelate apolar and polar solvents, including alkanes, arenes, esters, alcohols, and 1,4-dioxane. The gels are characterized by UV−vis, fluorescent, XRD, SEM, and AFM methods, based on which a dislocated "tail-to-tail" stacking pattern is proposed. Addition of octylated glucose considerably enhances the capacity of the foldamers to gelate apolar solvents due to strong complexation. The complexation also causes unique dynamic helicity induction in the gels, which is studied systematically by circular dichroism. The results are treated with the Avrami theory according to a reported method (*J. Am. Chem. Soc.* **2005**, *127*, 4336), which suggests that the gelation involves a nucleation−elongation mechanism. In addition, the "Sergeants and Soldiers" effect in the gel phase is also revealed.

Introduction

Self-assembly provides new possibilities in both biology and materials sciences because it enables rapid formation of complicated, functionalized architectures.[1] One family of self-assembled architectures is organogels, which consist of an organic liquid and a low molecular mass organic gelator.[2−4] In an organogel, the liquid is immobilized by a continuous, three-dimensional, entangled network of fibers formed by a gelator through various noncovalent forces. On the other hand, chirality is a basic feature of nature that appears hierarchically at both molecular and supramolecular levels.[5] At the supramolecular level, chirality is strongly related to intermolecular interactions. Therefore, achiral molecules can be induced by chiral molecules to form various chiral architectures. Currently, this process can be readily realized in the solid and solution phases and membranes, as well as on surfaces or at interfaces.[6] In many cases, chirality amplification can be exhibited, giving rise to the so-called "Sergeants and Soldiers" effect.[7] In recent years, much effort has been devoted to developing chiral organogels from single chiral molecules, owing to their potentials as advanced materials and constrained media for chiral synthesis and separation.[8] Because gelation is a thermoreversible process of phase separation, systematic understanding of this dynamic process is of importance fundamentally and for practical applications. Pioneering studies by Feringa and Weiss and co-workers have focused on several chiral bisurea and cholesterol-derived gelators.[9,10] In this paper, we present a novel study of

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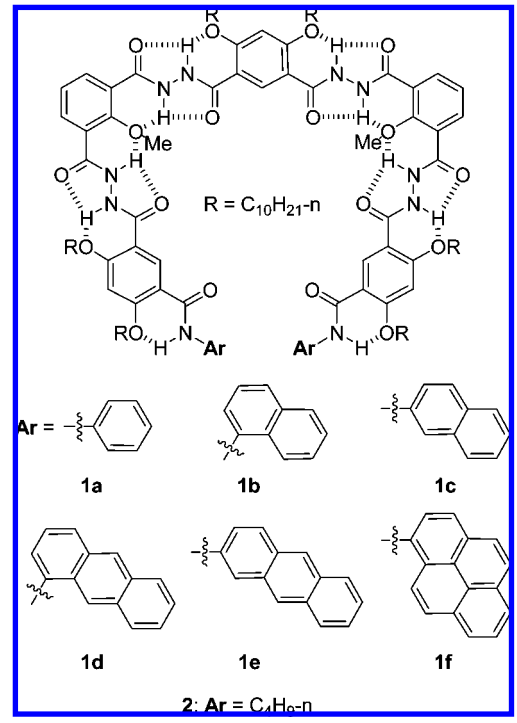
10.1021/ja8043322 CCC: $40.75

recognition-mediated dynamic helicity induction and amplification in the gel phase,[11] which is based on the complexation of achiral hydrazide foldamer gelators toward chiral glucoses.

Discotic molecules represent a class of structurally unique organic gelators consisting of a rigid aromatic core and aliphatic chains of suitable length.[12] They are also useful scaffolds for investigating discrete secondary interactions and chiral amplification in helical aggregates.[13] In recent years, a variety of hydrogen bonding-mediated aromatic amide, urea, and hydrazide-based foldamers have been developed,[14−19] some of which are found to complex chiral guests of matched sizes,[17−19] leading to interesting supramolecular helicity.[18,19] It was envisioned that suitably modified foldamers of this family might resemble discotic structures to gelate liquids, because they could fit well within the "rigid core/flexible tail" motif.[2a] We therefore have designed a new series of hydrazide-based foldamers **1a**−**f** for exploiting their tunable gelation properties. We herein report (i) their robust capacity to gelate both polar and apolar organic liquids,[20,21] which can be further enhanced through complexing with glucose, and (ii) a systematic circular dichroism investigation of their dynamic helicity transfer and amplification and "Sergeants and Soldiers" effect in the gel phase.

Results and Discussion

Design and Synthesis. For hydrazide-based foldamers, the backbone of a heptamer can fold to give rise to a helical conformation. Such a helix would facilitate a chiral differentiation upon complexing a chiral guest.[22] Therefore, compounds **1a**−**f** were synthesized, which consist of a heptameric framework and six *n*-decyl groups. The two arene units of varying size were incorporated at the ends to impose influence on intermolecular aggregation of the folded frameworks, owing to different stacking tendencies, whereas the long decyl chains were expected to induce phase separation and thus to facilitate gelation. Pentamer **2** was synthesized as a reference compound.



The synthetic routes for these oligomers are similar, and the route for **1f** is provided in Scheme 1 as an example. Compound **3**[23] was first reacted with *n*-decyl bromide to give **4**, which was then treated with excessive hydrazine to afford **5**. This intermediate was coupled with **6** to produce diester **7**, and its hydrolysis with lithium hydroxide yielded diacid **8**, which was then reacted with pentafluorophenol to give **9**. With intermediate **9** available, compound **4** was treated with potassium hydroxide to give **10**. This acid was then coupled with **11** to yield **12**, which was further reacted with hydrazine to generate **13**. Finally, compound **13** was coupled with **9** in hot DMF to afford **1f**. Details for the synthesis of **1a**−**e** and **2** are provided in the Supporting Information.

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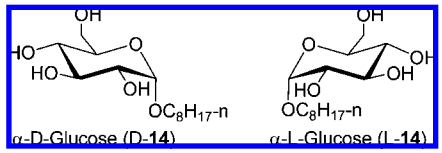
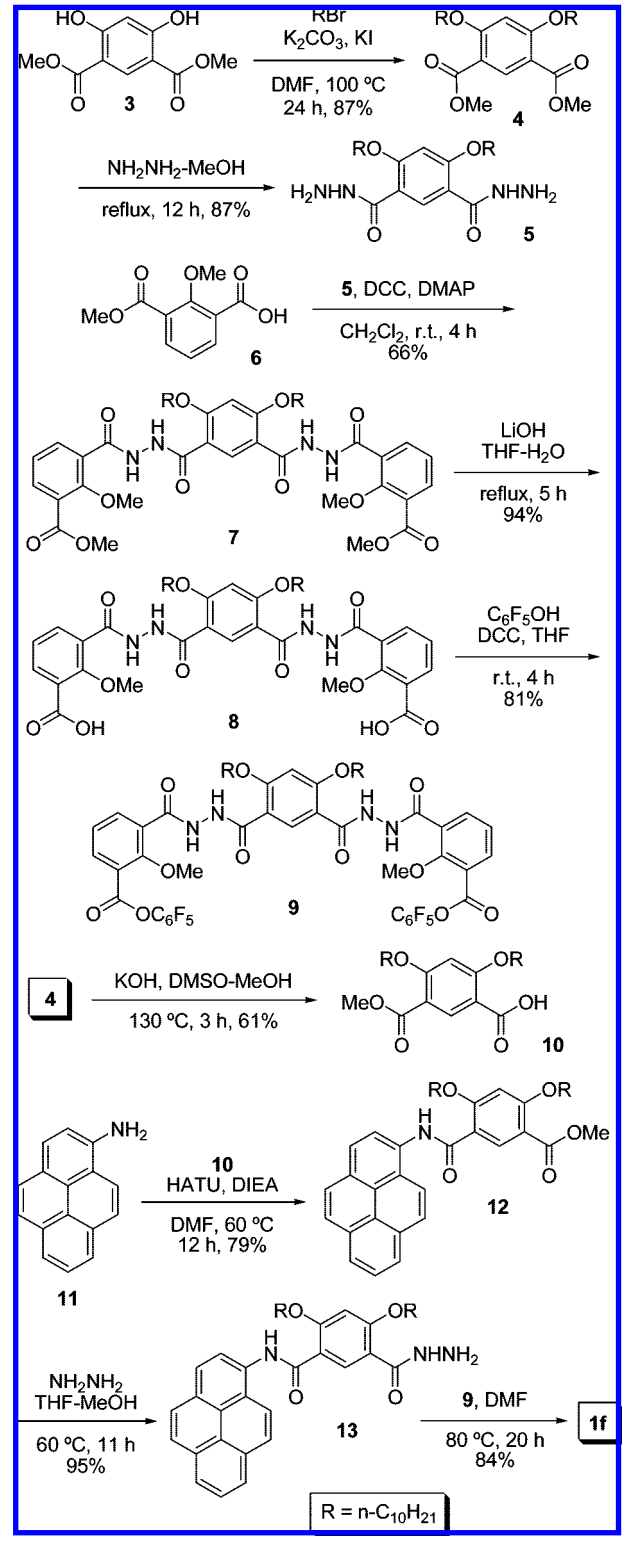
Molecular Modeling. Molecular mechanics calculations were performed to explore the possible conformations of methyl-substituted analogues of compounds **1a**−**f**. The results show that their low-energy conformations form a helical structure with more than one turn, in which the appended arene units do not stack with each other. In principle, the appended naphthalene, anthracene, or pyrene units of **1b**−**f** may adopt three different arrangements, that is, the "in-and-in", "in-and-out", and "out-and-out" arrangements. Molecular mechanics calculations of the "in-and-in" and "out-and-out" conformations indicate that the "in-and-in" arrangement is more stable, and the energy difference between the two conformers of **1d**−**f** is larger than the counterparts of **1b** or **1c.** Such an energetically favorable "in-and-in" conformation is expected to promote intermolecular dislocated "head-to-head" stacking (Figure 4, vide infra) because it allows for a larger stacking area, as demonstrated by **1e** in Figure 1. Details of the computational methods and results are provided in the Supporting Information.

Glucose Complexation in Chloroform. Previous studies have revealed that hydrazide-based foldamers complex alkylated saccharides in chloroform through multiple intermolecular hydrogen bonds.[19] By using the fluorescent titration method,[19] we evaluated the association constants of the complexes between **1a**−**f** and D- or L-glucose **14** in chloroform to be 1.6×10^4, 1.8×10^4, 1.6×10^4, 1.3×10^3, 7.7×10^3, and 9.6×10^3 M^{-1}, respectively. These values, except that of **1d**, are comparable to that of a heptamer whose appended benzene units are intramolecularly hydrogen bonded.[19a] Because **1a**−**f** possess the identical backbone, the difference of their capacity to bind **14** should be mainly affected by the appended arene units. The weaker binding capacity of **1d** relative to other foldamers may be attributed to its small cavity size and large energy of conversion from the "in-and-in" state to the "out-and-out" state, which should be more favorable for the binding. Although quantitative measurements could not be performed in hydrocarbon solvents due to gelation, the above result supports that, in these solvents of less polarity, similar complexes of even larger stability should be formed.



Gelation Behavior. The gelation capacity of **1a**−**f** and **2** was evaluated using the "inverse flow" method.[24] At room temperature, these compounds were soluble in chloroform and DMF but insoluble in lower alcohols and esters, such as methanol,

Scheme 1



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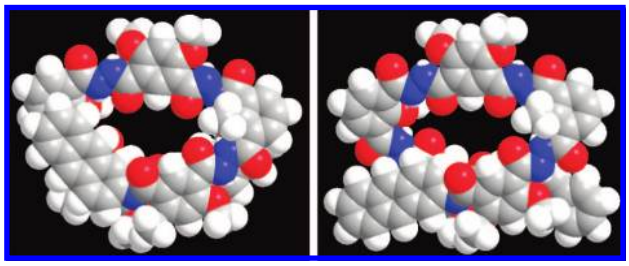

Figure 1. Minimized helical conformations of **1e** (left, the "in-and-in" arrangement; right, the "out-and-out" arrangement). The former is energetically more favorable because the anthracene units allow for a larger stacking area.

Table 1. Minimum Gelation Concentrations (wt %) of Hydrazide Foldamers in Different Solvents[a,b]

	1a	1b	1c	1d	1e	1f	2
decalin	0.57	0.56	0.54	0.27	PS	0.32	P
tetralin	2.01	0.23	0.98	0.24	2.11	0.11	0.06
	0.25[c]		0.26[c]		1.32[c]		
toluene	2.60	1.71	2.05	0.27	1.26	0.20	0.06
	0.30[c]		0.37[c]		0.62[c]		
p-xylene	1.48	0.36	1.38	0.17	2.15	0.17	0.07
	0.28[c]		0.24[c]		0.72[c]		
butyl acetate	0.67	0.59	0.26	0.24	0.45	0.34	P
isobutyl acetate	1.69	0.63	0.27	0.21	0.49	1.17	P
ethyl acrylate	0.49	0.59	0.62	0.27	1.08	1.19	P
n-butanol	0.74	0.07	0.21	0.31	0.32	P	P
	PS[c]		0.20[c]		P[c]		
n-octanol	0.10	0.06	0.08	0.06	0.36	0.06	P
1,4-dioxane	0.96	P	0.56	P	0.19	0.16	P
	0.98[c]		0.54[c]		0.18[c]		

[a] The incubation temperature is 25 °C. [b] The data are average values of two experiments. [c] In the presence of D-**14** (1 equiv). P = precipitation, PS = self-supporting precipitation.

ethanol, and ethyl acetate, or linear aliphatic hydrocarbons, such as *n*-hexane and *n*-decane, even with heating. However, the foldamers were found to gelate many solvents of varying polarity, including cyclic hydrocarbons, arenes, higher alcohols and esters, and 1,4-dioxane. The results are summarized in Table 1. Generally, introduction of the two arene units at the ends enhances the capacity of gelating polar solvents, even though **2** exhibits a surprisingly high capacity of immobilizing less polar tetralin, toluene, and *p*-xylene. Among the investigated systems, approximately 66% has a minimum gelation concentration of less than 1%. Notably, eight of them have a value of less than 0.1%, making them rank among the very limited "supergelators".[25] The possibility of shorter molecules, such as **7**, as gelators was also evaluated for all the solvents shown in Table 1. However, no gels were found to form even at the saturation concentration. This result indicates that the rigid framework of the longer foldamers, which should also possess increased stacking tendency,[20a,c] is crucial for gelating the solvents.

It was also revealed that addition of alkylated sugars considerably enhanced the capacity of the foldamers to gelate less polar solvents (Table 1), even though the sugars themselves could not gelate any solvent. For example, in the presence of D-**14** (1 equiv), the minimum gelation concentration of **1a** for toluene decreased from 2.60% to 0.30%. It is reasonable to propose that, in the gel phases of toluene or *p*-xylene, the foldamers strongly complexed D-**14**. Considering that D-**14** should also aggregate through intermolecular hydrogen bonding, this gelation enhancement by D-**14** may be attributed to the capacity of the glucose to promote the stacking of the foldamers by forming a hydrogen-bonded glucose chain in the hole of the column of the stacked foldamers (Figure 4, vide infra). Additional evidence for this mechanism comes from the observation that a similar enhancement effect did not occur for the gels of polar 1,4-dioxane and *n*-butanol, in which conplexation should not occur. Furthermore, the circular dichroism study of the two-component gels also supports this mechanism (vide infra).

UV−vis Spectroscopy. To ascertain how the foldamers self-assembled, UV−vis spectra of the gels (4 mM) in solvents of different polarity were recorded and compared with those of their corresponding dilute solutions (0.01 mM), in which the foldamers were assumed to exist in a single molecular state. It was found that the peaks assignable to the absorption of the appended arene units in the gel phases all red-shifted notably (2−7 nm). As examples, the spectra of **1a**, **1b**, and **1e** are provided in Figure 2. This result indicates that intermolecular stacking occurred in the gel phase[26] but does not provide useful information about the stacking pattern of the foldamers. Because the spectra were recorded at varying concentrations and the transparencies in solution and gel phases are different, they could not either be used to determine whether gelation caused hyperchromism or hypochromism.[20b]

Fluorescent Spectroscopy. Fluorescent spectra provided information on the stacking pattern of the foldamers. Although the spectra of **1b** and **1c** in chloroform exhibited an emission band at λ_{max} = ca. 420 nm, which may be attributed to the excimer band of the appended naphthalene units[27] or the emission of the benzene units of the backbones,[19a] the spectra of **1d−f** in chloroform did not exhibit the excimer band of the anthracene or pyrene units, which typically appears in the long-wavelength area of ca. 490 or 505 nm.[28] The results showed that the appended arene units of the foldamers did not stack intramolecularly, as indicated by the dynamic modeling (Figure 1). To detect whether intermolecular stacking occurred for the appended arene units, fluorescent spectra of the alkane gels of **1a−1f** were also recorded. Once again, the spectra of **1d−f** did not exhibit the excimer band of the anthracene or pyrene units in the expected area (Figure 3). This observation supports that in the gel phase the foldamers aggregated through the dislocated "head-to-head" stacking but not the "face-to-face" stacking of the appended arene units (Figure 4). A similar "head-to-head" stacking pattern has been revealed for the aggregation of a conjugated helicene.[29] The appended arenes should mainly adopt the "in-and-in" arrangement (Figure 1), because it could give rise to the maximum stacking area. Considering that "face-to-face" stacking of the appended arene units would prevent the other part of the frameworks from stacking intermolecularly

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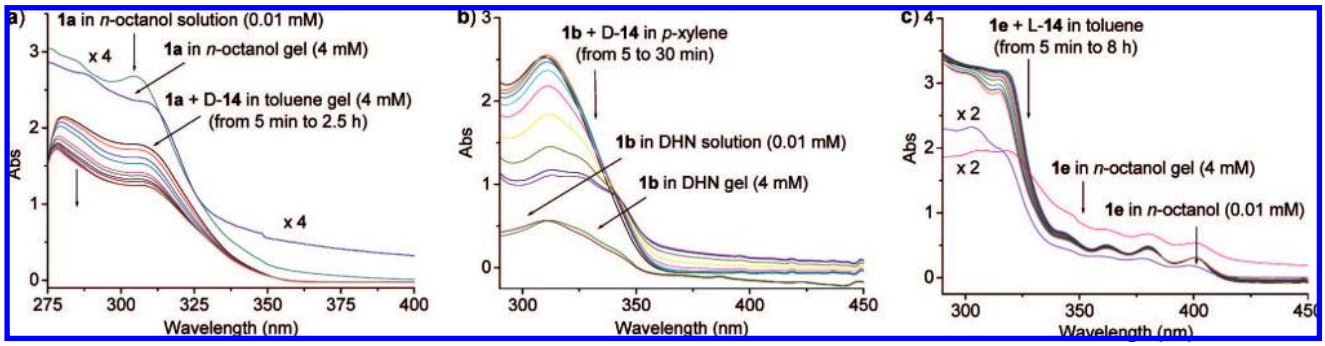

Figure 2. (Time-dependent) UV−vis spectra of compounds (a) **1a**, (b) **1b**, and (c) **1e** in sols and gels at 25 °C. The thickness of the sample cell was 1 cm for solution samples. The thickness of the gel samples was 0.1 mm.

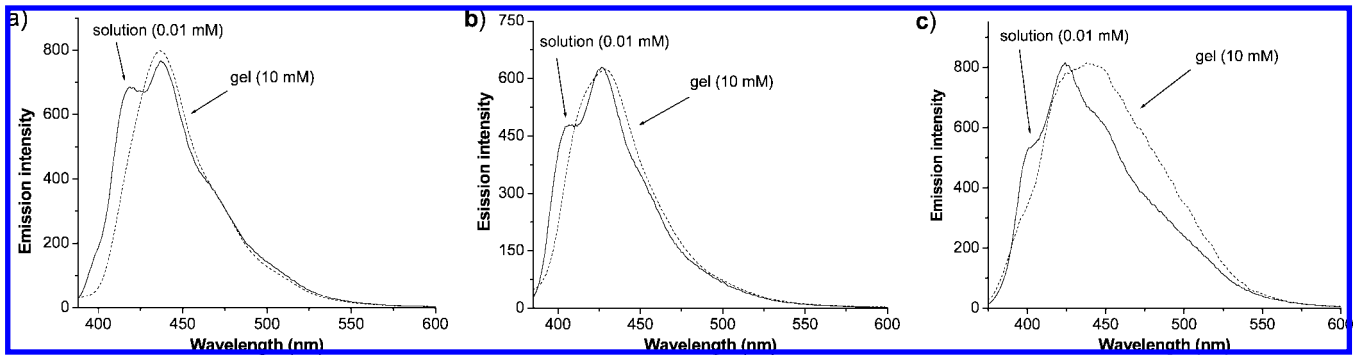

Figure 3. Fluorescent emission of the solution and gel of (a) **1d** in decalin (λ_{ex} = 360 nm), (b) **1e** in *n*-octanol (λ_{ex} = 360 nm) and (c) **1f** in decalin (λ_{ex} = 350 nm) at 25 °C. The thickness of the sample cell was 1 cm for solution samples. The gel samples were sandwiched between two quartz plates.

(Figure 4), this result is not surprising. Because the aggregation was a dynamic process, the less stable "in-and-out" or even "out-and-out" arrangement might also exist, even though it should be of a minor percentage. XRD diffraction study and SEM images (Figures 5 and 6, vide infra) also support such cylindrical column assemblies of the folded frameworks. It is expected that such cylindrical aggregates were driven by van der Waals forces of the long decyl chains to further assemble into bundle fibrils, which finally immobilized the solvents.[2a]

X-Ray Diffraction (XRD). XRD measurements were carried out for the gels of **1a**−**f** and **2**. The spectra of **1a**, **1d**, and **1f** in *n*-octanol are shown in Figure 5. The broad peak at 2θ = ca. 19.2° was generated by the solvents.[10b] All the samples gave rise to a sharp peak in the range of 2.36−2.59 nm. Molecular modeling suggested that the helical framework of the foldamers had a diameter of approximately 2.1 nm. Considering the contribution of the flexible side chains, this result supports that this ordered structure was generated through stacking of the folded frameworks (Figure 4). The spectra of the *n*-octanol gel of **1d** and the *p*-xylene gel of **2** also exhibited a peak at 0.36 (Figure 5b) and a peak at 0.35 nm (not shown), respectively, which reflect the average distance between the stacked foldamers[12d] and also further support the "head-to-head" stacking pattern (Figure 4). Similar shoulder peaks were not observed in the profiles of other investigated gels, which we consider might also exist but be buried in the strong peak of the solvents.

Morphology Study. SEM images were recorded for the gels of **1a**−**f** and **2** in all the solvents shown in Table 1. The images of the *n*-ocatanol gels showed fibrils of micrometers in length and hundreds of nanometers in width, supporting that the cylindrical column aggregates of the foldamers further assembled to form bundle structures (Figure 4). Representative results are provided in Figures 6. Similar fibrous structures could also be observed for the gels of other solvents including tetralin, toluene, and *p*-xylene. For the gels of polar solvents such as 1,4-dioxane and esters, fibers of wider and thicker cotton wadding were exhibited. The fibrous structures of the gels could also be evidenced by AFM, as shown by the images of **1d** and **1f** in Figure 6.

Induced Circular Dichroism. It has been found that in chloroform hydrazide foldamers are induced by chiral saccharides to produce supramolecular helicity, as evidenced by formation of induced circular dichroism (ICD).[19] Upon addition of D- or L-**14**, the solutions of foldamers **1a**−**f** in chloroform also exhibited ICD signals (see the Supporting Information), which well suggested that helicity induction might occur in the gel phases. To test this possibility, ICD spectra of the *p*-xylene and/or toluene gels of **1a**−**f** in the presence of D- or L-**14** were measured. These two solvents were chosen mainly because of their low polarity, which guaranteed strong complexation occurred between **1a**−**f** and **14**.

The ICD spectra of all the gels of **1a**−**f** and D- or L-**14** were recorded in a cell of 0.1 mm thickness (Figure 7). As expected, addition of D- or L-**14** (1 equiv) caused all the foldamers to produce ICDs of mirror symmetry. In contrast, their gels in polar solvents, including butyl acetate, isobutyl acetate, ethyl acrylate, *n*-butanol, *n*-octanol, and 1,4-dioxane, did not give rise to any detectable signals. For compound **2**, even excessive D- or L-**14** did not induce its toluene or *p*-xylene gels or chloroform solution to produce observable ICD, implying that the appended arene units in **1a**−**f** played a key role in amplifying the helicity differentiation of their frameworks.

Because the orientation of gelators might be affected by macroscopic anisotropy and observed CD spectra might hence

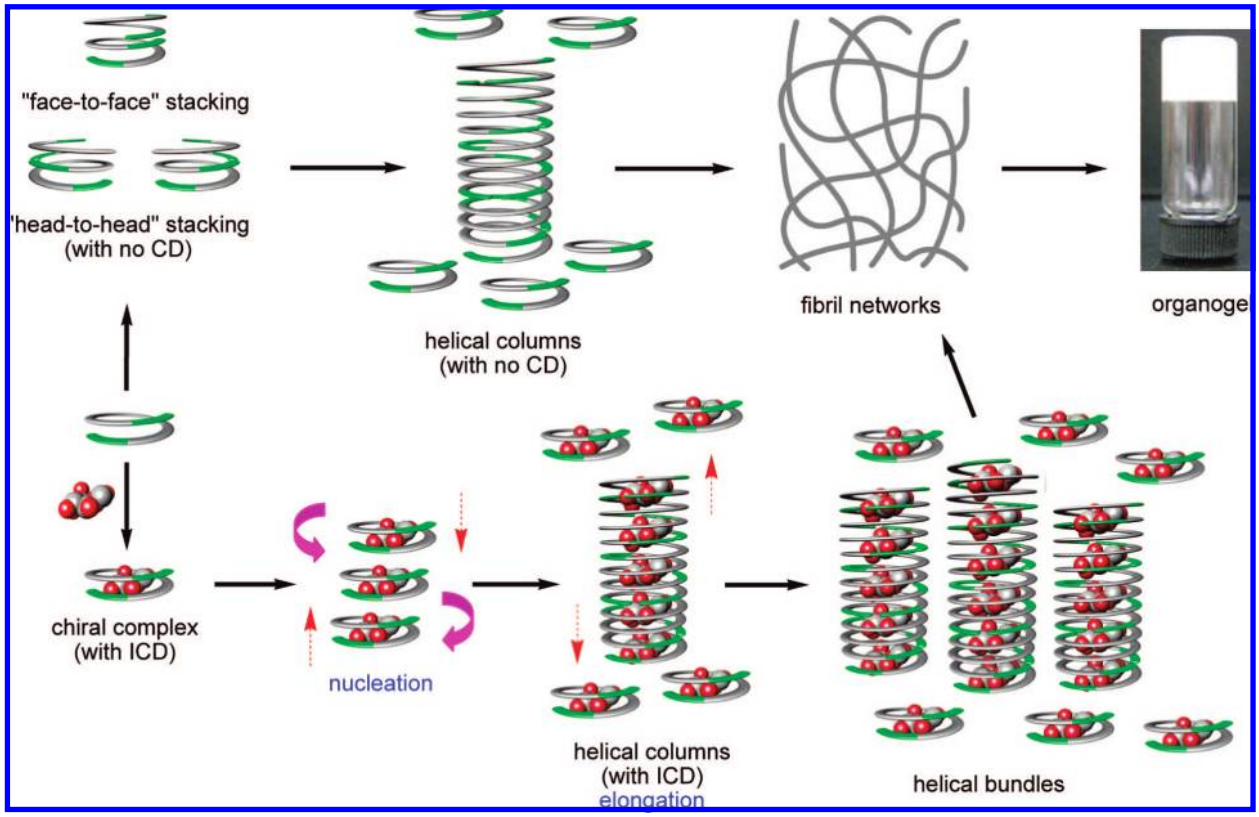

Figure 4. Schematic representation of the self-assembly of foldamer gels and glucose-initiated helicity induction. It is assumed that the stacked columns of the foldamers were driven by van der Waals forces of the decyl chains of the foldamers to aggregate into bundle fibrils, which gelated the solvent molecules. The decyl chains are not shown in the model for clarity. In the two-component system, there should also be free foldamer and glucose molecules, which are not presented for clarity.

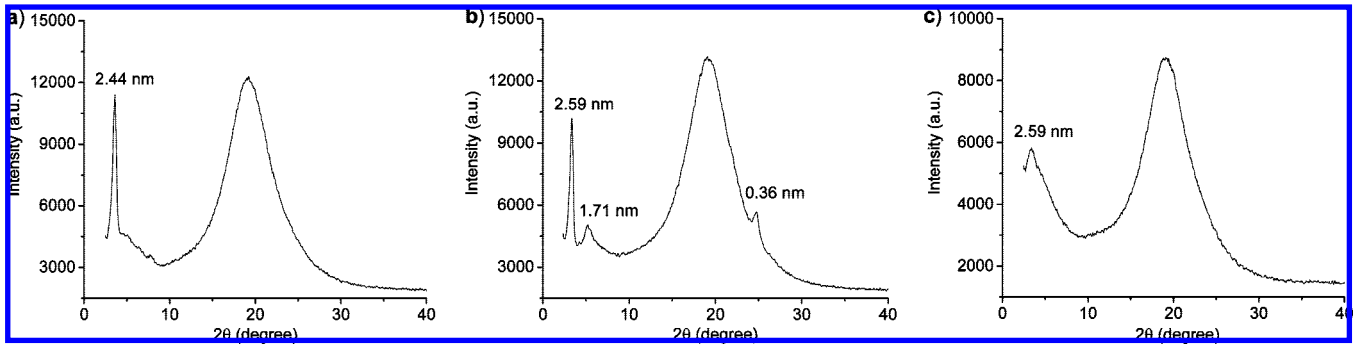

Figure 5. XRD spectra of the *n*-octanol gels of (a) **1a**, (b) **1d**, and (c) **1f** (0.1 g/mL) at 25 °C. The samples were prepared by drop casting of the gels on a silica plate and then measured immediately.

include components arising from linear dichroism (LD),[30] we also recorded the LD spectra under the same measurement conditions. The spectra, together with the related UV−vis spectra, are shown in Figure 7. It can be found that the optical densities of the gels of **1a**, **1c**, and **1e** were very weak (<0.001). Their contribution to the CD spectra can be neglected.[30b] The optical densities of the LD spectra of **1b**, **1d**, and **1f** were considerably stronger. Thus, their contributions to the CDs were not negligible. Control experiments showed that the gels of **1a**−**f** themselves were all LD-silent. Therefore, these LDs should be produced though the induction of the glucose. Because the LDs could not be easily subtracted from the CDs, we may more reasonably regard the observed CDs of **1b**, **1d** and **1f** as "apparent" ones, which implies including the contribution of the LDs.

The toluene gel of **1a** and D-**14** featured a strong positive band (λ_{max} = 322 nm) and a weak negative band (λ_{max} = 357 nm). A small shoulder peak was also exhibited at λ = ca. 300 nm. A similar shoulder peak was also observed in the spectra of the *p*-xylene gel of **1c**. These results suggest that the ICDs were generated by superimposition of signals of discrete aromatic units. Conformers **1b** and **1c** were induced by chiral **14** to form a strong positive CD band at λ_{max} = 322 and 324 nm, respectively. However, only **1b** exhibited a strong negative band above 350 nm, indicating that the geometry of the naphthalene units remarkably affected their helical conforma-

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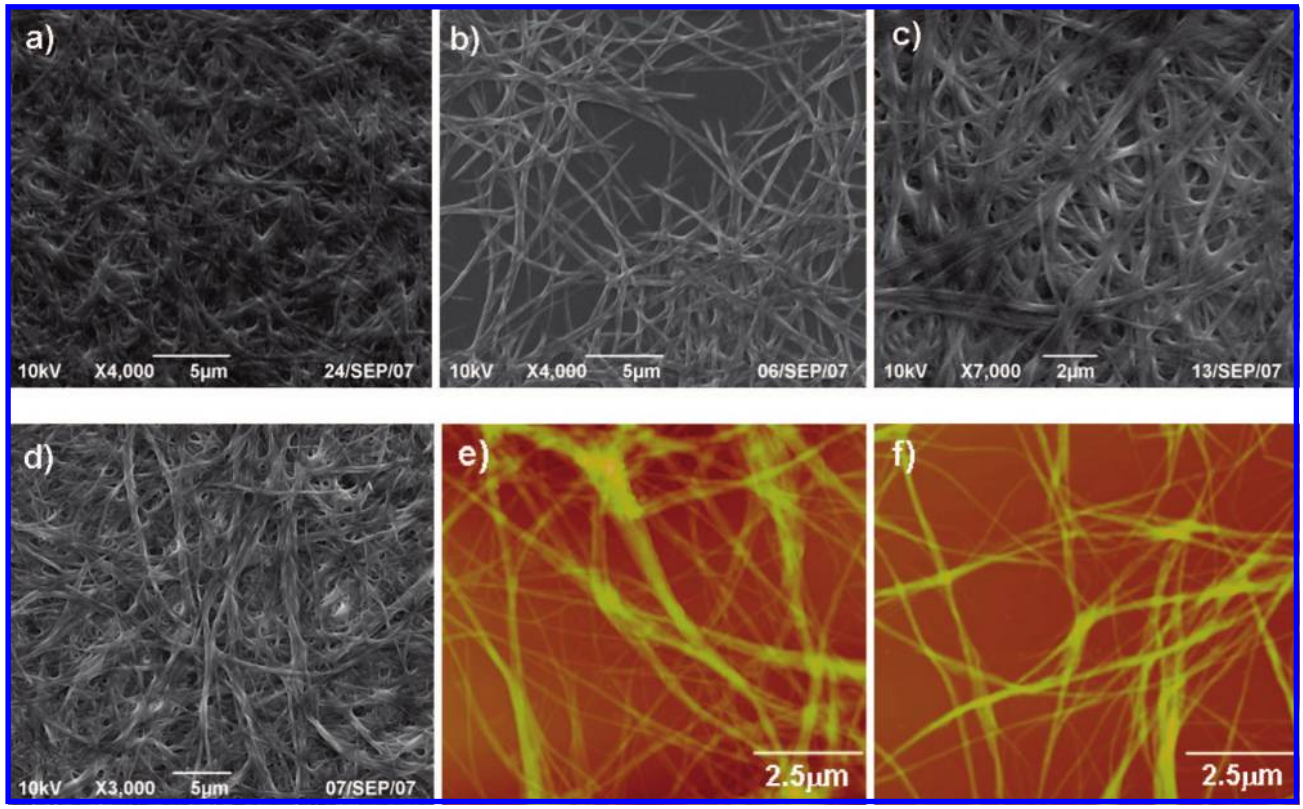

Figure 6. SEM images of the dried gels of (a) **1a**, (b) **1c**, (c) **1d**, and (d) **1f** obtained from *n*-octanol and AFM images of the dried gels of (e) **1d** and (f) **1f** from toluene (0.1 mM).

tions. The LD of **1b** in the area was positive. Therefore, its exact role for the formation of this negative band is not clear yet. For anthracene-bearing conformers **1d** and **1e**, in addition to a strong band below 350 nm, several weak bands were also exhibited in the region of longer wavelength, which should be produced by the anthracene units with a negligible LD component (Figure 7d and e). The gels of **1f** exhibited two strong CDs which were severalfold stronger than those of other foldamers. Notably, the strength of the bands at above 350 nm, produced by the pyrene units, was comparable to that of the band of the shorter wavelength. This result should reflect the increased capacity of its pyrene units in helicity induction relative to that of its smaller counterparts in **1a**−**e**. It also indicates that the helicity differentiation was not linearly related to the stability of their single complex. Because **1a**−**f** contain different aromatic units, the signals of the ICD spectra could not be used to assign their P or M helicity.[31,32]

The temperature-dependent CD spectra of the *p*-xylene gels of the mixtures were also recorded, and those of **1a**−**c** and D-**14** are shown in Figure 8. For all the investigated systems, the intensity of the main signals remained unchanged within a range of lower temperature but began to decrease after a turning point and vanished at high enough temperature (Figure 8, insets). This result can be easily explained by considering gradual deaggregation of both helical stacking architectures and chiral molecular complexes. Interestingly, the negative signal of **1b** first underwent an enhancement before turning weaker, which further supports that the signals were formed by a combination of those of discrete aromatic units that were nonlinearly temperature-dependent.

Most reported organogels form very quickly once their solution phases are cooled to below gelation temperature. Recently, Weiss et al. found that the transformation of two chiral cholesteryl *N*-(2-naphthyl) carbamates in *n*-alkanes from sols to gels occurred on a time scale of minutes to hours, allowing for a CD investigation of the gelation kinetics.[10] By using a similar method, we have followed the transformation of our two-component systems from sols to gels. It was found that the ICD intensities of the toluene or *p*-xylene gels of **1d** and **1f** in the presence of D- or L-**14** reached a maximum in less than one minute and then became stable for days. This result implied that their appended arenes were well orientated for intermolecular stacking. In contrast, those of other foldamers needed much longer time (from 0.5 to 10 h) to reach equilibrium (Figure 7). Furthermore, the ICDs were weak at the early stage, implying existence of an induction or incubation period. The processes could be repeated. However, the ICDs recorded for the gel phases were different in shape from those of the solutions of the same samples in chloroform, indicating that the ICDs of the gels were produced by the helical assemblies of chiral complexes (Figure 4). The remarkable time-dependent enhancement of the ICDs of the systems of **1a**, **1c**, and **1e** should be attributed to stacking-resulted elongation of the cylindrical column architectures, which was further driven by van der Waals forces of the decyl chains to lead to the formation of the gels, as shown in Figure 4. The stacking process was expected to have several outcomes. First, induced helicity of the single folded molecule was transferred to supramolecular helicity of cylindrical column architectures. Second, it gave rise to a tube-

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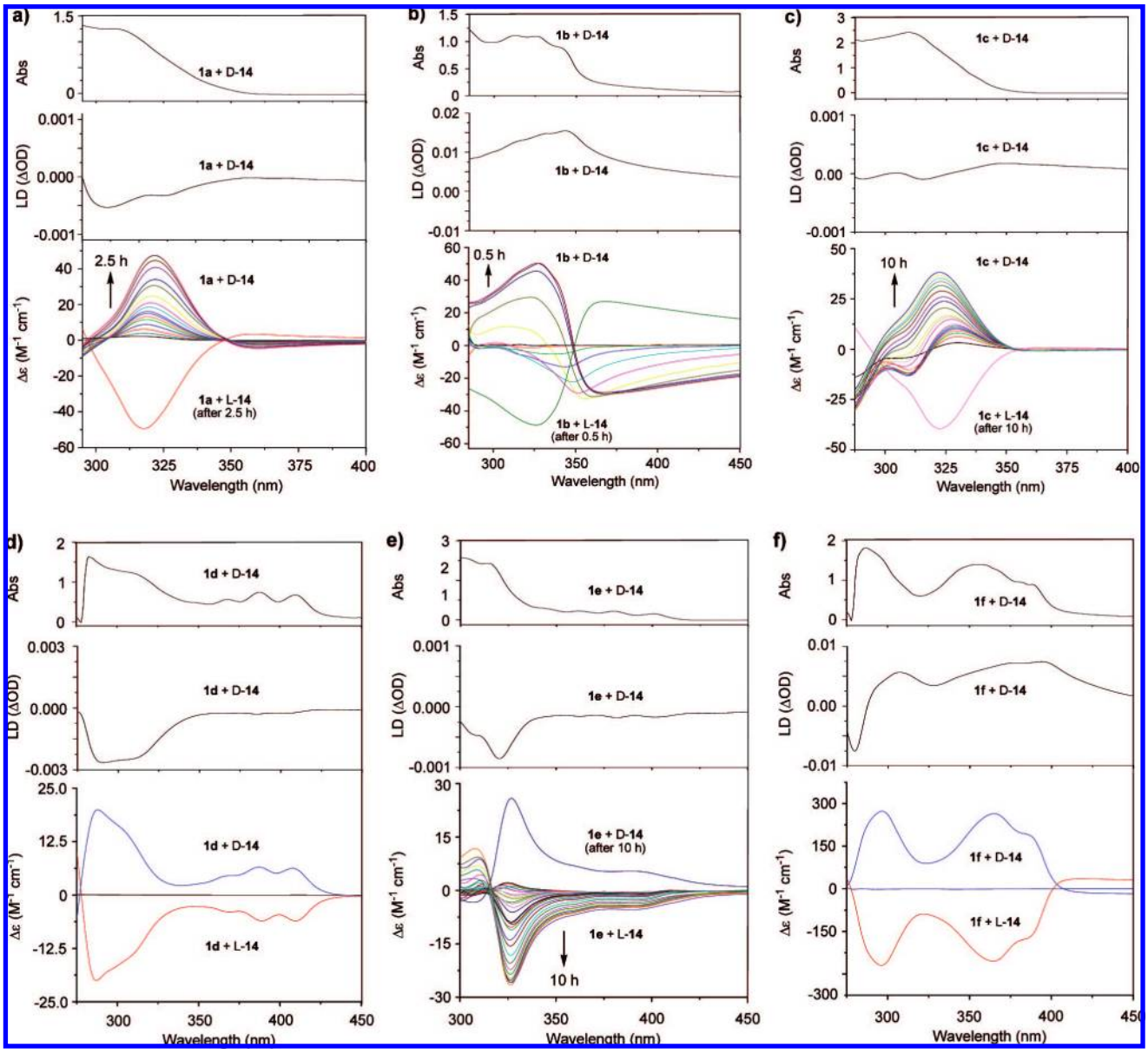

Figure 7. UV−vis, LD, and (time-dependent) CD spectra of (a) **1a** in toluene, (b) **1b** in *p*-xylene, (c) **1c** in *p*-xylene, (d) **1d** in *p*-xylene, (e) **1e** in toluene, and (f) **1f** in *p*-xylene in the presence of D- or L-**14** ([**1**] = [**14**] = 4 mM) at 25 °C. The UV−vis and LD spectra were recorded after the intensity became unchanged. The thickness of the sample cell for the optical path is 0.1 mm.

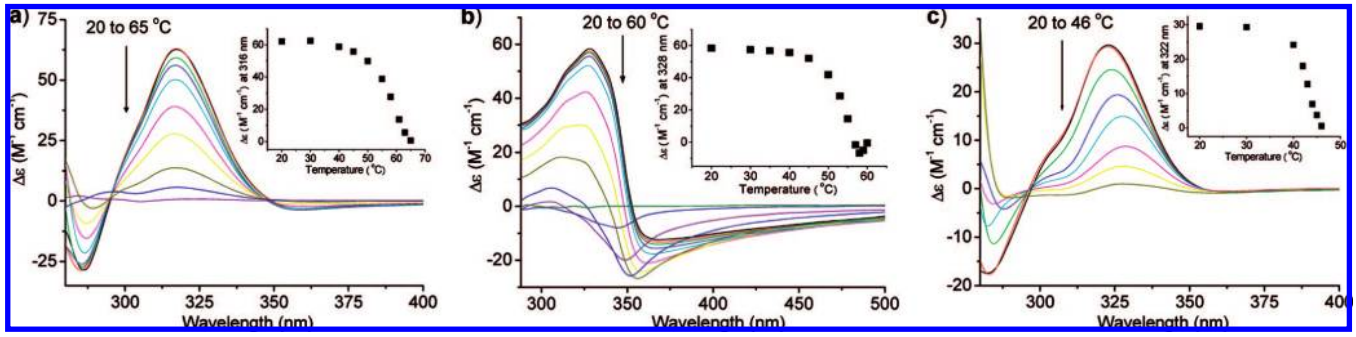

Figure 8. Temperature-dependent ICD spectra of the *p*-xylene gels of (a) **1a**, (b) **1b**, and (c) **1c** and D-**14** (1:1, 4 mM) (inset: plots of the CD intensity at the defined wavelength against temperature). The thickness of the sample cell for the optical path is 0.1 mm.

styled structure, which as a whole forced complexed glucose molecules to form a chiral hydrogen-bonded glucose chain. It is expected that the foldamer column and the chiral glucose chain in it would stabilize each other because the density of the hydrogen bonding sites of both aggregates were increased in the compact structure. Third, the stacking also decreased the

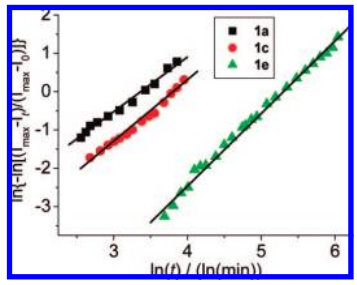

Figure 9. ICD intensities of the gels of **1a** (toluene), **1c** (*p*-xylene), and **1e** (toluene) and L- or D-**14** (1:1, 4 mM), which were obtained from the spectra in Figure 7, plotted against time according to eq 1. The time period covered is from 20 to 600 min. Each spectrum required 40 s to record.

conformational flexibility of the backbones of the foldamers, especially the appended arene units, facilitating amplification of the helicity of the single complexes. The fact that the sol−gel transformation of **1d** and **1f** took a very short time might suggest that they possessed even larger stacking capacity and hence did not have the induction period. In accordance with the ICD spectra, UV−vis spectra of the investigated systems also exhibited a similar time-dependent decrease (Figure 2), which may be ascribed to enhancement of intermolecular stacking but may also result from a transparency decrease. The gelation of **1a**−**f** in the absence of **14** should also undergo a similar two-stage mechanism, even although the process is CD-silent and cannot be investigated by the CD method.

The dynamic ICD data of **1a**, **1c**, and **1e** (Figure 7), which covered a time scale of hours and could be repeated with acceptable precision, were also treated with the Avrami equation (eq 1)[33] according to the method established by Weiss and co-workers for chiral cholesterol-based organogels,[10] where I_0, I_t, and I_{max} are the CD intensities at times = 0, t, and ∞, respectively, K is a temperature-dependent parameter that is like a rate constant, n is the Avrami exponent reflecting the type of growth leading to phase separation, and t is time. For the cholesterol-based single molecular systems, the chirality of the gels is generated exclusively by the gelators themselves. For the present two-component systems, while gelation is mainly driven by stacking of the foldamers, the helicity is generated through chirality transfer from the complexed glucoses to the stacked foldamers. Therefore, the n values were extracted on the assumption that the helicity transfer is a statistical outcome of the whole system. The n values of **1a**, **1c**, and **1e** were derived to be 1.44 (322 nm), 1.57 (325 nm), and 1.87 (326 nm), respectively (Figure 9).[34,35] The result suggests that gelation of the two-component systems underwent a nucleation−elongation mechanism (Figure 4),[10b,36] which involves two distinct phases of self-assembly.[37] The first was the slow nucleation phase. At this stage, cylindrical column assemblies were not formed yet, and the helicity was mainly expressed by the single complex species, as reflected by the small and slow change of the ICD intensity. Once stable nuclei were formed, the system entered the second elongation phase. Further addition of helical complexes onto the ends of the cylindrical assemblies became favorable, leading to quick enhancement of the helicity. The cylindrical structures further aggregated into long fibril networks, immobilizing the solvents.

$$\ln\{\ln[(I_{max}-I_t)/(I_{max}-I_0)]\} = \ln K + n \ln t \qquad (1)$$

One of the unique behaviors of chiral supramolecular assemblies is the so-called "Sergeant and Soldiers" effect—chiral amplification occurring through the induction of chiral components for similar achiral components to follow their helicity.[38] Such a nonlinear effect has also been revealed between chiral folded *m*-phenylene ethynylene oligomers and their achiral counterparts in solution.[39] To test whether a similar effect existed in the gel phases,[40,41] ICDs of the *p*-xylene gels of the foldamers in the presence of varying amounts of D-**14** were recorded. Deviations from linearity were observed for all the investigated systems, but the patterns were different (Figure 10a−e). The

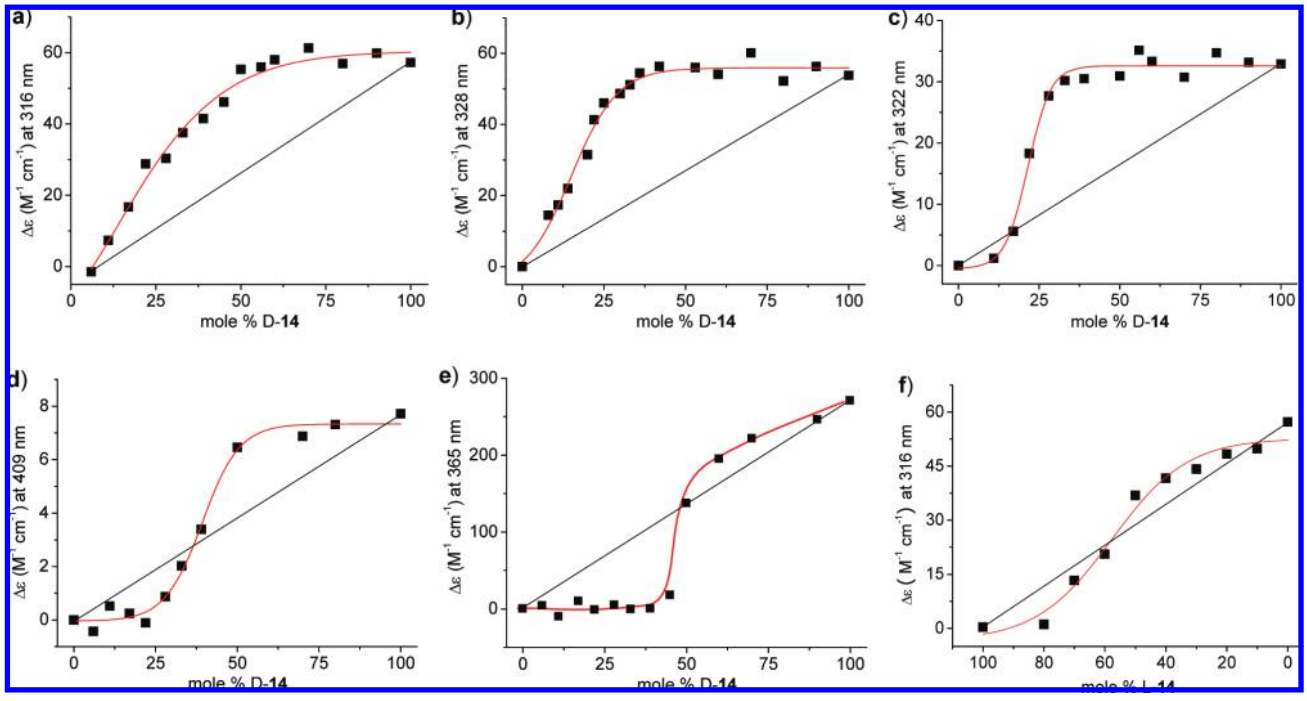

Figure 10. "Sergeants-and-Soldiers" measurements of the *p*-xylene gels of (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, and (e) **1f** in the presence of D-**14** (0 to 1 equiv), and (f) **1a** + D-**14** (1:1, in toluene) in the presence of L-**14** (0 to 1 equiv) at 25 °C ([**1a**−**f**] = 4 mM). The thickness of the sample cell for the optical path is 0.1 mm.

plots of the ICD intensity of **1a**−**c** against mole percent of D-**14** showed positive nonlinearity. Thus, addition of approximately 50, 35, and 30% of D-**14** induced them to produce signals comparable in strength to that induced by 1 equiv of D-**14**. This phenomenon is similar to the common "Sergeant and Soldiers" effect in the context of helicity amplification, except that the new "Sergeant" and "Soldiers" are completely different in shape. The plots of **1d** and **1f** exhibited interesting sigmoidal curves—the intensity changed from negative to positive nonlinearity with the increase of the amount of D-**14**. That is, the "Sergeants and Soldiers" effect occurred only after a considerable amount of D-**14** was added. A possible explanation for this observation is that the large appended anthracene or pyrene units of **1d** and **1f** have even larger stacking capacity. As a result, more glucose molecules are needed to "trigger" the helicity differentiation. This result is also consistent with the formation of the hydrogen-bonded glucose chain in the cylindrical assemblies, because it is reasonable to propose that the more the amount of the glucose was, the easier the chain would be formed. It can also be found that, for the foldamer series from **1a** to **1f**, the tendency of producing positive nonlinearity is gradually decreased. Once again, this can be ascribed to the increasing stacking capacity of the appended arene units. The CD spectra of the toluene gels of **1a** and D-**14** (1:1) with varying amounts of L-**14** were also measured, which also revealed a sigmoidal curve and a weak "Sergeants and Soldiers" effect (Figure 10f).

Conclusions

We have described the self-assembly of a new family of foldamer gelators that can immobilize a broad range of organic solvents. Intramolecular hydrogen bonding stabilizes the rigid helical conformations of the foldamers, whereas large arene units at the ends of the backbones facilitate intermolecular dislocated "tail-to-tail" stacking. As a result, cylindrical column aggregates are formed, which are held together by van der Waals forces of long aliphatic side chains to give rise to fibrous networks, leading to a new class of organogels with minimal gelation concentrations as low as 0.06% in weight.

One unique feature of the new foldamer gelators is their capacity to complex chiral glucoses. As a result, helicity induction can occur in both sols and gels. A systematic circular dichroism investigation has shown that this helicity induction in the gel phases is dynamic and, in several cases, helicity amplification occurs during the sol−gel transfer. The fact that addition of glucoses notably raises the gelation capacity of the foldamers shows that, through doping or mixing, we may endow organogels with new tunable or required properties.

Acknowledgment. We thank the National Science Foundation of China (Nos. 20732007, 20621062, 20425208, 20572126, 20672137), the National Basic Research Program (2007CB808000), and the Chinese Academy of Sciences (KJCX2-YW-H13) for financial support.

Supporting Information Available: Experimental procedures and characterizations, ^{1}H NMR of **1a**−**f** and **2**, and additional UV−vis, fluorescent, CD, and XRD spectra and SEM and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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