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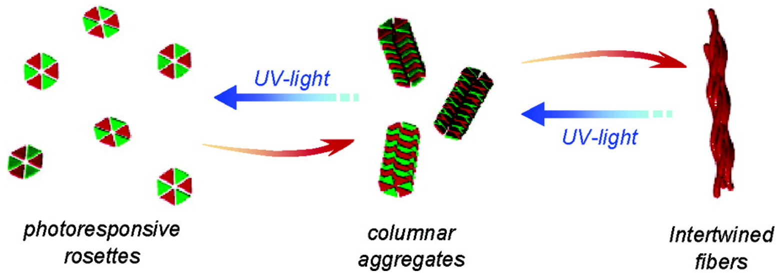

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Hierarchical Organization of Photoresponsive Hydrogen-Bonded Rosettes

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Abstract: Hydrogen-bonded disk-shaped aggregates (rosettes) composed of azobenzene-appended melamine and barbiturate or cyanurate are investigated in view of their hierarchical organization and photoresponsive behavior by ^{1}H NMR and UV/vis spectroscopies, dynamic light scattering, and gelation behavior in aliphatic solvents and liquid crystalline behavior in bulk state. In the bulk state the rosette possessing a sterically bulky tridodecyloxyphenyl substituent in the barbiturate component stacks in an offset arrangement to form a rectangular columnar mesophase, whereas in aliphatic solvents it does not hierarchically organize into higher-order columnar aggregates. This drawback is improved by exchanging the barbiturate component into a more sterically nondemanding *N*-dodecylcyanurate component. The resulting new rosette stacks in a face-to-face arrangement to form a hexagonal columnar mesophase in the bulk state and hierarchically organizes into elongated fibrous aggregates in cyclohexane, which eventually leads to the formation of organogel. Dynamic light scattering and UV−vis experiments upon UV-irradiation of the columnar aggregates in cyclohexane revealed that the dissociation and the reformation of columnar aggregates can be controlled by the trans−cis isomerization of the azobenzene moiety. Molecular modeling indicates that the rosette possessing *cis*-azobenzene side chains loses its planarity. Using this photoinduced morphological change of the rosette, photoresponsive organogel is created by the use of a disk-shaped supramolecule the first time.

Introduction

Supramolecular materials can be tailored from specifically designed small molecular components through self-assembly and self-organization that are programmed under the control of directional noncovalent interactions.[1] Principles underlying such specific molecular designs as prerequisite for directional noncovalent interactions have been widely established, and supramolecular materials are now regarded as promising smart materials requiring well-defined, regular nanoarchitectures.[2] At the same time, they encompass a unique property arising from dynamic nature of noncovalent interactions, i.e., response to various external inputs such as electric and magnetic field, redox potential, and light.

The particularly attractive self-assembled motif is a columnar superstructure built up from disk-shaped aggregates via aromatic $\pi-\pi$ stacking interactions.[3−5] They comprise potential applicability to the one-dimensional mass transporting[3a−c] and optoelectronic nanomaterials.[3d] Well-defined columnar aggregates laterally organize into larger columns via van der Waals interactions, which is often accompanied with the formation of elongated fibers[4] and only rarely encounters gelation of organic solvents employed.[5] The propensity of disk-shaped entities to organize into extended columnar aggregates strongly depends on the morphology of the disks including peripheral substituents.[6,7] If the morphology of disk-shaped entities can be transformed by means of external stimuli, the formation of columnar aggregates becomes regulatable at will. Establishment

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(1) Reinhoudt, D. N., Ed. *Supramolecular Materials and Technologies*. Wiley & Sons: Chichester, 1999.

(2) (a) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) Lawrence, D. S.; Jiang, T.; Levette, M. *Chem. Rev.* **1995**, *95*, 2229−2260.

(3) (a) Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994−995. (b) Beggin, U.; Zipp, G.; Mourran, A.; Walther, P.; Möller, M. *Adv. Mater.* **2000**, *12*, 513−516. (c) Lee, H.-K.; Lee, H.; Ko, Y. H.; Chang, Y. J.; Oh, N.-K.; Zin, W.-C.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2669−2671. (d) Percec, V.; et al. *Nature* **2002**, *419*, 384−387. (e) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302−1315. (f) Kleppinger, R.; Lillya, C. P.; Yang, C. *J. Am. Chem. Soc.* **1997**, *119*, 4097−4102. (g) Suárez, M.; Lehn, J.-M.; Zimmerman, S. C.; Skoulios, A.; Heinrich, B. *J. Am. Chem. Soc.* **1998**, *120*, 9526−9532. (h) Barberá, J.; Puig, L.; Romero, P.; Serrano, J. L.; Sierra, T. *J. Am. Chem. Soc.* **2005**, *127*, 458−464. (i) Kamikawa, Y.; Nishii, M.; Kato, T. *Chem.—Eur. J.* **2004**, *10*, 5942−5951. (j) Kanie, K.; Yasuda, T.; Nishii, M.; Ujiie, S.; Kato, T. *Chem. Lett.* **2001**, 480−481. (k) Yang, W.; Chai, X.; Tian, Y.; Chen, S.; Cao, Y.; Lu, R.; Jiang, Y.; Li, T. *Liq. Cryst.* **1997**, *22*, 579−583. (l) Gottarelli, G.; Mezzina, E.; Spada, G. P.; Carsughi, F.; Di Nicola, G.; Mariani, P.; Sabatucci, A.; Bonazzi, S. *Helv. Chim. Acta* **1996**, *79*, 220−234. (m) Giorgi, T.; Lena, S.; Mariani, P.; Cremonini, M. A.; Masiero, S.; Pieraccini, S.; Rabe, J. P.; Samori, P.; Spada, G. P.; Gottarelli, G. *J. Am. Chem. Soc.* **2003**, *125*, 14741−14749. (n) Palmans, A. R. A.; Vekemans, J. A. J. M.; Hikmet, R. A.; Fischer, H.; Meijer, E. W. *Adv. Mater.* **1998**, *10*, 873−876. (o) Yelamaggad, C. V.; Achalkumar, A. S.; Rao, D. S. S.; Prasad, S. K. *J. Am. Chem. Soc.* **2004**, *126*, 6506−6507. (p) Shu, W.; Valiyaveettil, S. *Chem. Commun.* **2002**, 1350−1351. (q) Palmans, A. R. A.; Vekemans, J. A. J. M.; Fischer, H.; Hikmet, R. A.; Meijer, E. W. *Chem.—Eur. J.* **1997**, *3*, 300−307. (r) Barbera, J.; Cavero, E.; Lehmann, M.; Serrano, J.-L.; Sierra, T.; Vazquez, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 4527−4533. (s) Barbera, J.; Puig, L.; Serrano, J. L.; Sierra, T. *Chem. Mater.* **2004**, *16*, 3308−3317. (t) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067−2077.

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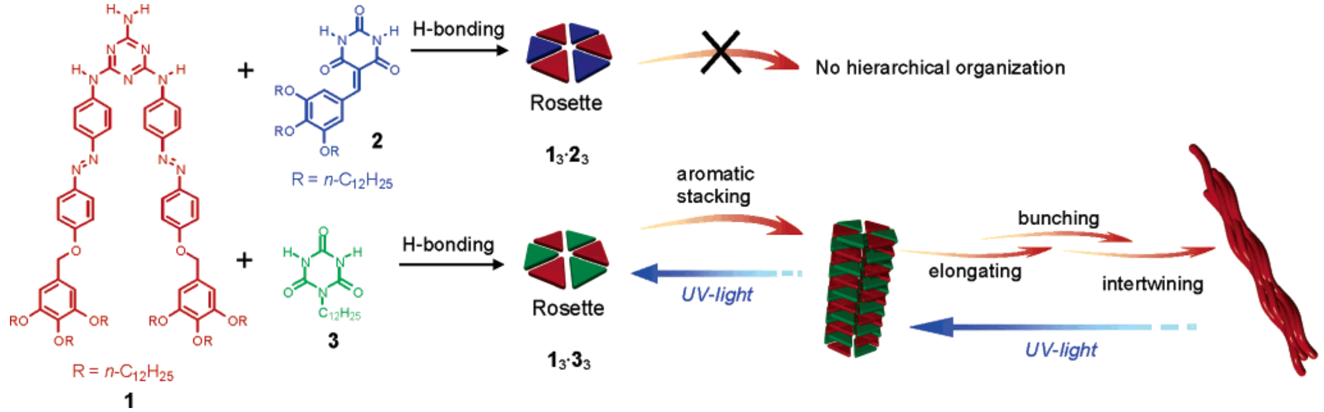
Scheme 1. Aggregation of Melamine-Azobenzene Conjugate **1** with Barbit[a]



[a] Rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ can hierarchically organize into intertwined fibers (red arrows). The fiber formation can be regulated by light (blue arrows)

of such a novel system may eventually lead to a smart soft material where the mass transporting capability is switchable at will.

One promising strategy to controlling molecular self-assembly by means of convenient external stimuli is the use of photoinduced morphological changes of photochromic modules introduced in the supramolecular building components.[8] Based on this approach, a diverse kind of photoresponsive self-assembly has been elaborated.[9] We previously reported an azobenzene-appended hydrogen-bonded rosette ($\mathbf{1}_3\cdot\mathbf{2}_3$ in Scheme 1),[10] the formation of which is triggerable by light illumination.[11] One may easily envisage that our photoresponsive rosette also acts as a supramolecular building block for photoresponsive columnar aggregates because it is composed of (i) a hydrogen-bonded macrocycle required for the formation of columnar aggregates, (ii) a photoresponsive mechanical switch required for the morphological change of the disk, and (iii) peripheral flexible aliphatic chains to stabilize columns. However, a preliminary dynamic light scattering experiment showed that rosette $\mathbf{1}_3\cdot\mathbf{2}_3$ exists as a supramolecularly dissolved state in the least polar solvents even at millimolar regime. This is indicative of an unfavorable morphology of the rosette for stacking. Molecular modeling revealed that the presence of tridodecyloxyphenyl (TDP) wedges in **2** sterically inhibits the aromatic stacking interaction of the hydrogen-bonded macrocycles.[11]

Here we report that the exchange of **2** with sterically nondemanding cyanurate **3** provides photoresponsive rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ that is capable of hierarchically organizing into higher-order fibrous aggregates.[12] A combination of the photoresponse with the hierarchical organization resulted in the creation of an unprecedented type of photoresponsive self-assembly (Scheme 1).

Results and Discussion

Formation and Photoisomerization Property of Rosette $\mathbf{1}_3\cdot\mathbf{3}_3$. ^{1}H NMR spectrum of an equimolar mixture of **1** (100% *trans*-azobenzene) and **3** in $CDCl_3$ showed resonances of the hydrogen-bonded imide protons of **3** at δ 14.4 ppm and the amino protons of **1** at δ 9.80 ppm (Figure 1A), which are characteristic features for the formation of well-defined rosette assembly. Dynamic light scattering (DLS) measurements showed the presence of a single aggregate species with an average hydrodynamic diameter of 6.8 nm. This value is shorter than that of the molecular modeled structure of rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ with extended alkyl chains (ca. 7.8 nm). The shorter hydrodynamic

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(4) (a) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6360–6361. (b) Kimizuka, N.; Fujikawa, S.; Kuwahara, H.; Kunitake, T.; Marsh, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1995**, 2103–2104. (c) Yang, W.; Chai, X.; Tian, Y.; Chen, S.; Cao, Y.; Lu, R.; Jiang, Y.; Li, T. *Chem.—Eur. J.* **1999**, *5*, 1144–1149. (d) Klok, H.-A.; Jolliffe, K. A.; Schauer, C. L.; Prins, L. J.; Spatz, J. P.; Möller, M.; Timmerman, P.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1999**, *121*, 7154–7155. (e) Brunsveld, L.; Zhang, H.; Glasbeek, M.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 6175–6182. (f) Enomoto, M.; Kishimura, A.; Aida, T. *J. Am. Chem. Soc.* **2001**, *123*, 5608–5609. (g) Fenniri, H.; Deng, B.-L.; Ribbe, A. E. *J. Am. Chem. Soc.* **2002**, *124*, 11064–11072. (h) Jonkheijm, P.; Miura, A.; Zdanowska, M.; Hoeben, F. J. M.; De Feyter, S.; Schenning, A. P. H. J.; De Schryver, F. C.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 74–79.

(5) (a) Choi, I. S.; Li, X.; Simanek, E. E.; Akaba, R.; Whitesides, G. M. *Chem. Mater.* **1999**, *11*, 648–690. (b) van Gorp, J. J.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 14759–14769. (c) Kishimura, A.; Yamashita, T.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 179–183.

(6) (a) Pisula, W.; Kastler, M.; Wasserfallen, D.; Pakula, T.; Müllen, K. *J. Am. Chem. Soc.* **2004**, 125, 8074–8075. (b) Wu, J.; Fechtenkotter, A.; Gauss, J.; Watson, M. D.; Kastler, M.; Fechtenkotter, C.; Wagner, M.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 11311–11321. (c) Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Müllen, K. *J. Am. Chem. Soc.* **2005**, *127*, 4286–4296.

(7) Höger et al. demonstrated that columnar mesophase is not only stabilized by "peripheral" substituents but also by substituents pointing to the inside of the macrocycles: Höger, S.; Cheng, X. H.; Ramminger, A.-D.; Enkelmann, V.; Rapp, A.; Mondeshki, M.; Schnell, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 2–6.

(8) (a) Yagai, S.; Karatsu, T.; Kitamura, A. *Chem.—Eur. J.* **2005**, in press. (b) Hecht, S. *Small* **2005**, *1*, 26–29.

(9) Selected examples of photoresponsive self-assembly: (a) Vollmer, M. S.; Clark, T. D.; Steinem, C.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1598–1601. (b) Liang, X.; Asanuma, H.; Komiyama, M. *J. Am. Chem. Soc.* **2002**, *124*, 1877–1883. (c) Moriyama, M. Mizoshita, N.; Yokota, T.; Kishimoto, K.; Kato, T. *Adv. Mater.* **2003**, *15*, 1335–1338. (d) Yagai, S.; Karatsu, T.; Kitamura, A. *Chem. Commun.* **2003**, 1844–1845. (e) Rakotondradany, F.; Whitehead, M. A.; Lebuis, A.-M.; Sleiman, H. F. *Chem.—Eur. J.* **2003**, *9*, 4771–4780. (f) Molard, Y.; Bassani, D. M.; Desvergne, J.-P.; Horton, P. N.; Hursthouse, M. B.; Tucker, J. H. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 2–5. (g) Takeshita, M.; Hayashi, M.; Kadota, S.; Mohammed, K. H.; Yamato, T. *Chem. Commun.* **2005**, 761–763.

(10) Reviews for hydrogen-bonded rosette: (a) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37–44. (b) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229–2260. (c) Sherrington, D. C.; Taskinen, K. A. *Chem. Soc. Rev.* **2001**, *30*, 83–93. (d) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382–2426. (e) Timmerman, P.; Prins, L. J. *Eur. J. Org. Chem.* **2001**, 3191–3205.

(11) Yagai, S.; Nakajima, T.; Karatsu, T.; Kitamura, A. *J. Am. Chem. Soc.* **2004**, 126, 11500–11508.

(12) Kunitake, Kimizuka, and Würthner et al. intensively studied hierarchical organization of melamine-diimide hydrogen-bonded tapelike aggregates: (a) Kimizuka, N.; Kawasaki, T.; Kunitake, T. *J. Am. Chem. Soc.* **1993**, *115*, 5, 4387–4388. (b) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1998**, *120*, 4094–4104. (c) Kawasaki, T.; Tokuhiro, M.; Kimizuka, N.; Kunitake, T. *J. Am. Chem. Soc.* **2001**, *123*, 6792–6800. (d) Würthner, F.; Thalacker, C. Sautter, A. *Adv. Mater.* **1999**, *11*, 754–758. (e) Würthner, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem.—Eur. J.* **2000**, *6*, 3871–3886. (f) Thalacker, C.; Würthner, F. *Adv. Funct. Mater.* **2002**, *12*, 209–218. (g) Thalacker, C.; Miura, A.; De Feyter, S.; De Schryver, F. C.; Würthner, F. *Org. Biomol. Chem.* **2005**, *3*, 414–422.

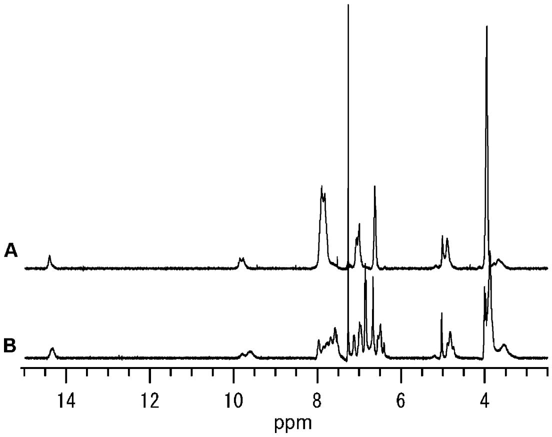

Figure 1. ^{1}H NMR spectra of a 1:1 mixture of **1** and **3** (5 mM, 25 °C) in $CDCl_3$ before (A) and after irradiation with UV-light for 1 h (B).

diameter in the DLS result is very likely due to the flexibility of the external alkyl chains.

When the supramolecularly dissolved rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ in $CDCl_3$ (5 mM) was irradiated at around 350 nm for 1 h (λ_{max} of the absorption band of the azobenzene moiety), the ^{1}H NMR spectrum drastically changed especially in the aromatic region, indicating the trans→cis isomerization of the azobenzene moieties (Figure 1B). UV/vis absorption measurements revealed that the cis content changed from 0% to 60% (photostationary state). This is in sharp contrast to rosette $\mathbf{1}_3\cdot\mathbf{2}_3$ where the cis content was only 24% at the photostationary state upon the irradiation of UV-light. Therefore, the photoresponse of the rosette to UV-light is roughly 2.5-fold enhanced by exchanging **2** with **3** lacking bulky TDP wedges.

Hierarchical Organization of Rosettes in Nonpolar Solvents and in Bulk State. An equimolar mixture of **1** and **2** is highly soluble in nonpolar organic solvents such as cyclohexane, but neither gelation nor increase in viscosity was observed when the solution was concentrated to 100 mM.[13] This observation guided us to assume that rosette $\mathbf{1}_3\cdot\mathbf{2}_3$ cannot associate into well-defined columnar aggregates. This assumption was confirmed by the DLS experiment which revealed only the presence of concentration-independent ($c = 0.5-20$ mM) small particles with the hydrodynamic diameter 7.8 nm corresponding to the supramolecularly dissolved rosette $\mathbf{1}_3\cdot\mathbf{2}_3$.

In sharp contrast, DLS measurements of an equimolar mixture of **1** and **3** dissolved in cyclohexane showed the presence of higher-order aggregates. The average hydrodynamic diameter of the aggregates was 52 nm for 1 mM solution at 20 °C. The higher-order aggregates were very sensitive to temperature: the average hydrodynamic diameter attained to 95 nm at 10 °C, whereas it showed the minimum value of 6.9 nm at 40 °C.[14] These results demonstrate that higher-order aggregates are constructed from hydrogen-bonded rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ via weak aromatic stacking and solvophobic interactions between the rosettes.[15] The average hydrodynamic diameter of 52 nm indicates that over 125 rosettes stack to form columnarnanostructures assuming a rosette–rosette distance of ca. 0.41 nm.[4c]

As a consequence of the formation of higher-order columnar aggregates, a freshly prepared concentrated cyclohexane solution of rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ ($c = 10$ mM or 63 mg/mL) gradually became viscous at room temperature, and eventually a transparent organogel was obtained over 24 h (Figure 2A).[16] The macroscopic gelation indicates the formation of elongated fibrous assemblies, which was further confirmed by FE-SEM observation of the dried gel. Surprisingly, intertwined cylindrical fibers with a uniform diameter of ca. 500 nm overwhelm the whole area of the specimen surface (Figure 2C). Based on a lattice parameter of ca. 6 nm in the hexagonal columnar mesophase of $\mathbf{1}_3\cdot\mathbf{3}_3$ (vide infra), the diameter 500 nm corresponds to that of approximately 7500 rosette columns constituting a single fiber. Such a hierarchical organization of small building blocks into well-defined nanoscale superstructures is quite intriguing in view of the bottom-up approach as well as its analogy to organized biomolecules. The slow gelation process (within 24 h) is consistent with the slow generation of fibrous aggregates from the structurally related rosette by Li et al.[4c] Since such a slow hierarchical organization was not observed in the DLS condition at submillimolar concentration regime, it must be attributed to the process involving further elongation of rosette columns and their association into cylindrical fibers via weak van der Waals interactions of aliphatic chains (Scheme 1).

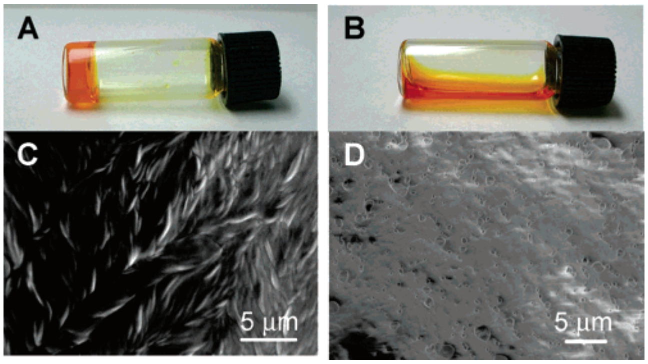

Figure 2. Photographs of a cyclohexane gel (10 mM) of $\mathbf{1}_3\cdot\mathbf{3}_3$ before (A) and after UV-irradiation for 1 h (B) and the corresponding FE-SEM images after air-drying (C from A and D from B).

The formation of the columnar aggregates in $\mathbf{1}_3\cdot\mathbf{3}_3$ is in clear contrast to the case of rosette $\mathbf{1}_3\cdot\mathbf{2}_3$. This marked difference unambiguously shows the presence of the effective aromatic stacking interactions between rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ featuring the sterically less crowding periphery, which was further supported from its liquid crystalline behavior in the bulk state.

The solid obtained after the air-drying of the homogeneous cyclohexane solution of rosette $\mathbf{1}_3\cdot\mathbf{2}_3$ gave no specific X-ray diffraction peaks (data not shown), consistent with the absence of the highly ordered superstructure in solution. Differential scanning calorimetry (DSC) upon heating and subsequent cooling showed the presence of two thermotropic mesophases

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(13) No specific superstructure was observed in the FE-SEM measurements of the dried samples.

(14) Decomposition of the rosette into the individual components could not be observed at the temperature near the boiling point of cyclohexane.

(15) The ^{1}H NMR spectrum of an equimolar mixture of **1** and **3** in cyclohexane-d_{12} ($c = 1$ mM) at 20 °C was also highly broadened and exhibited no proton resonance in the aromatic region (see Figure S2 in Supporting Information). Upon increasing temperature, the broadened resonances appeared in the aromatic region of the NMR spectrum, which became well-resolved by further elevating the temperature. A spectral resolution leveled off at 40 °C, where the characteristic resonances of the H-bonded protons at low magnetic region (the imide protons of **3** at δ 14.6 and the secondary amino protons of **1** at δ 9.70) were observed.

(16) Melamine-cyanurate organogels: (a) Hanabusa, K.; Miki, T.; Taguchi, Y.; Koyama, T.; Shirai, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1382. (b) Jeong, S. W.; Murata, K.; Shinkai, S. *Supramol. Sci.* **1996**, *3*, 83−86. (c) Yagai, S.; Higashi, M.; Karatsu, T.; Kitamura, A. *Chem. Mater.* **2004**, *16*, 3582−3585. (d) Plater, M. J.; Sinclair, J. P.; Aiken, S.; Gelbrich, T.; Hursthouseb, M. B. *Tetrahedron* **2004**, *60*, 6385−6394.

Table 1. Phase Transition Behavior of the Aggregates **1** + **2** and **1** + **3**[a]

aggregate	phase transition
1 + 2	$\mathbf{K} \xrightleftharpoons[117\ (4.2)]{129\ (5.6)} \mathbf{Col_r} \xrightleftharpoons[176\ (3.3)]{189\ (7.7)} \mathbf{Col_r} \xrightarrow{215} \mathbf{decomp.}$
1 + 3	$\mathbf{K} \xrightleftharpoons[111\ (2.1)]{124\ (4.2)} \mathbf{X} \xrightleftharpoons[125\ (1.7)]{130\ (3.3)} \mathbf{Col_h} \xrightarrow{230} \mathbf{decomp.}$

[a] The transition temperatures (°C) and corresponding enthalpies (in parentheses, kJ/mol) were determined by DSC (°C/min) and are shown above and below the arrows. K = crystalline phase; X = unidentified mesophase; $\mathrm{Col_r}$ = rectangular columnar mesophase; $\mathrm{Col_h}$ = hexagonal columnar mesophase; decomp.; decomposition of compounds with clearing.

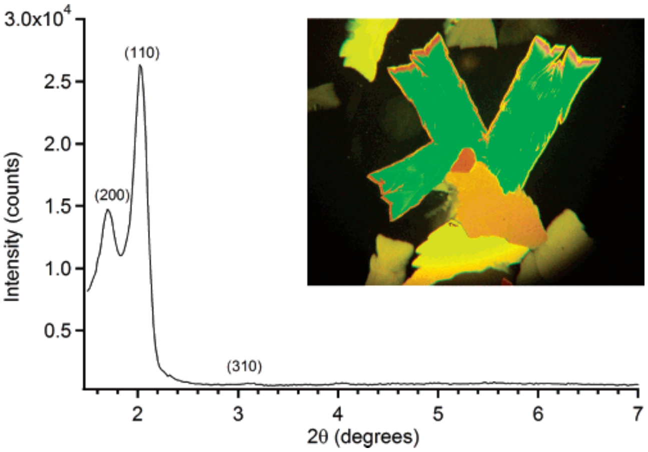

Figure 3. XRD pattern of a 1:1 molar mixture of **1** and **2** at 170 °C prepared via air-drying of the homogeneous cyclohexane solutions of the complexes. Inset: a mosaic texture observed by optical polarized microscopy.

in temperatures from ca. 120 to 200 °C (Table 1). Above 215 °C, decomposition of the compounds was observed. In the mesophase, a clear mosaic texture was observed by optical polarized microscopy (inset in Figure 3). X-ray diffraction (XRD) measurements at 170 °C showed the *d*-spacing of 52.1 (200), 43.7 (110), 28.3 (310), indicating the formation of a rectangular columnar ($\mathrm{Col_r}$) mesophase with the lattice parameters a = 98.6 Å and b = 49.3 Å (Figure 3). The formation of the $\mathrm{Col_r}$ phase from circular rosette architectures (diameter ca. 80 Å) strongly suggests the offset stacking motif of the rosette disks; thereby the disks tilt to the long axis of a column.[17,18] As a result, the cross-section of the column is ellipsoidal, which favors rectangular packing rather than hexagonal packing.[19] Such an offset stacking motif is considered to be not stable enough to persist in the presence of solvent molecules.

The solid obtained after air-drying of the homogeneous cyclohexane gel of rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ is birefringent and showed a single X-ray diffraction peak corresponding to a *d*-spacing of 48.1 Å (Supporting Information), indicating that highly ordered superstructures had been already constructed in solution. DSC measurement showed the presence of two thermotropic mesophases above 124 °C that persist until the decomposition of compounds at around 230 °C (Table 1). In the mesophase a coffee-beans texture was observed (inset in Figure 4). The XRD measurement at 200 °C showed a *d*-spacing of 50.9 (100), 29.4 (110), 25.4 (200), and 19.2 Å (210), which can be indexed as a hexagonal columnar ($\mathrm{Col_h}$) mesophase with the lattice parameter a = 58.8 Å (Figure 4B). The calculated lattice parameter is shorter than the hydrodynamic diameter of rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ measured by DLS. The smaller lattice parameter in comparison with the average hydrodynamic diameter of the rosette measured by DLS (6.8 nm) might be due to the interdigitation of the exterior alkyl chains between the columns. The formation of the $\mathrm{Col_h}$ phase indicates that the peripheral substituents in rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ do not preclude face-to-face (nonoffset) aromatic stacking interaction between the hydrogen-bonded macrocycles, which is fully consistent with the formation of the columnar aggregates that can persist in solution.

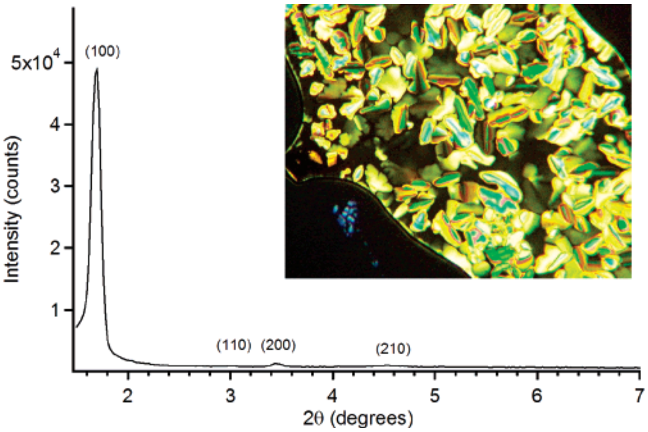

Figure 4. XRD pattern of a 1:1 molar mixture of **1** and **3** at 200 °C, prepared by air-drying of the homogeneous cyclohexane solutions of the complexes. Inset: coffee-beans texture observed by optical polarized microscopy.

Photocontrol of the Hierarchical Organization of Rosette $\mathbf{1}_3\cdot\mathbf{3}_3$. The improved photoresponse as well as the formation of higher-order columnar aggregates in rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ motivated us to control the hierarchical organization by means of external light input. Figure 5 shows the UV−vis spectral changes of cyclohexane solution of the rosette (c = 0.5 mM) upon irradiation at around 350 nm. UV-irradiation resulted in the decrease in the $\pi-\pi^*$ absorption band of the *trans*-azobenzene moieties which peaked at 354 nm with concomitant increase of the $\pi-\pi^*$ and $\mathrm{n}-\pi^*$ bands of the cis isomer at around 290 and 460 nm, respectively. A photostationary state was attained within 40 min at which the cis content was ca. 45%. When the irradiated solution was then exposed to visible light at around 450 nm, another photostationary state was achieved within 5 min where the cis content decreased to ca. 10%. The original state (0% cis content) was recovered when the UV-irradiated solution was kept in the dark for 12 h. Thus, the trans−cis isomerization of the azobenzene moieties in rosette $\mathbf{1}_3\cdot\mathbf{3}_3$ is fully reversible and could be repeated many times without decomposition of the components.

To investigate the effect of photoisomerization on the hierarchical organization of the rosette, UV-irradiation was followed by the DLS measurements. Figure 6A shows the changes of the hydrodynamic diameter distribution of a cyclo-

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(17) Würthner et al. reported the formation of the $\mathrm{Col_r}$ mesophase from the structurally related supramolecular components: Würthner, F.; Yao, S.; Heise, B.; Tschierske, C. *Chem. Commun.* **2001**, 2260−2261. In this study, formation of the linear tapelike assembly was deduced from the small lattice parameter.

(18) (a) Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem.*−*Eur. J.* **2001**, *7*, 2245−2253. (b) Jin, S.; Ma, Y.; Zimmerman, S. C.; Cheng, S. Z. D. *Chem. Mater.* **2004**, *16*, 2975−2977.

(19) Mair et al. reported the formation of $\mathrm{Col_r}$ mesophase from a benzene-1,3,5-tricarboxamide derivative which is not derived from the offset stacking of the aromatic moiety: Lightfoot, M. P.; Mair, F. S.; Pritchard, R. G.; Warren, J. E. *Chem. Commun.* **1999**, 1945−1946.

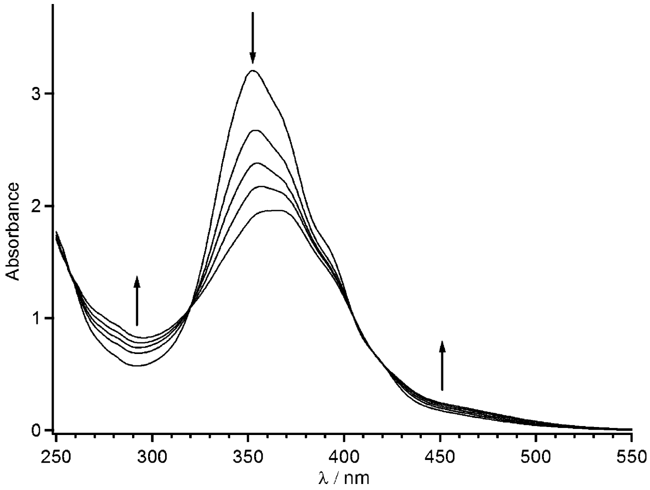

Figure 5. UV−vis spectral change of a 1:1 molar mixture of **1** and **3** (0.5 mM in 0.1 mm quartz cuvette) in cyclohexane upon irradiation with UV-light at 20 °C. Arrows indicate the changes upon irradiation. Each spectrum corresponds to a total irradiation period of 0, 10, 20, 30, and 40 min.

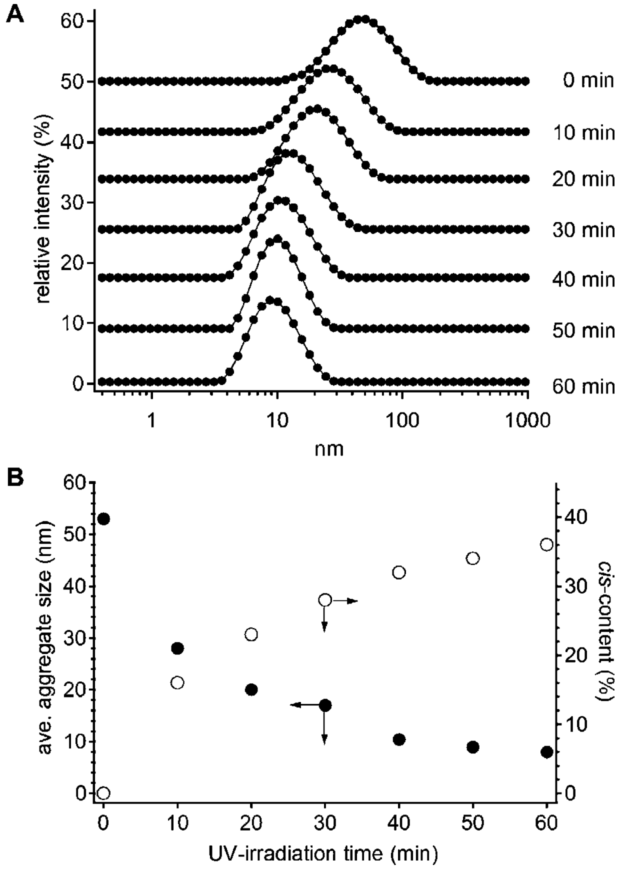

Figure 6. DLS-monitored UV-irradiation experiment for an equimolar mixture of **1** and **3** in cyclohexane ($c = 1$ mM) at 20 °C. (A) Change of hydrodynamic diameter distribution with irradiation time; (B) change of the average hydrodynamic diameters (left axis, closed circles) and the *cis*-contents of the azobenzene moiety (right axis, open circles) versus irradiation time.

hexane solution of rosette $\mathbf{1}_3{\cdot}\mathbf{3}_3$ ($c = 1$ mM) upon UV-irradiation. Clearly, UV-irradiation diminishes the hydrodynamic diameters and narrows the size distribution of the particles in the solution, indicating the photoinduced dissociation of the columnar aggregates. In Figure 6B the average hydrodynamic diameter and corresponding cis content of the azobenzene moiety are plotted against UV-irradiation time. Interestingly, the decrement of the aggregate size is not synchronous to the increase of the cis content: even at the cis content of only 16% (10 min), the aggregate size decrements to 28 nm, which is nearly 50% of the original size. This observation indicates that the isomerization of one of the six azobenzene moieties ($^1/_6$ = 17%) in a rosette drastically destabilizes the stacking interaction between the rosettes. The final aggregate size at a photostationary state (60 min, cis content = ca. 36%) reached 8 nm, which is close to that of the single rosette.

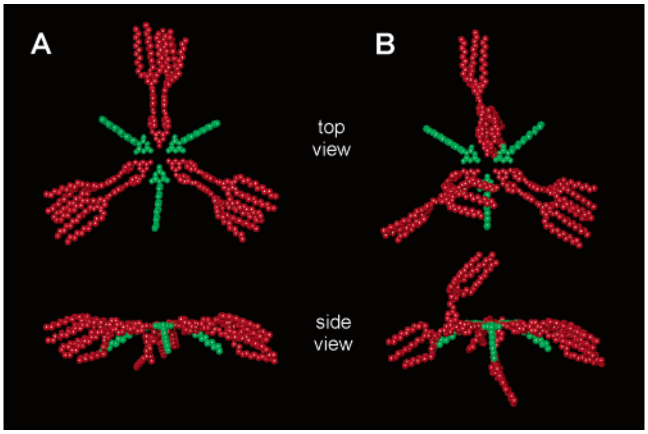

Figure 7. Molecular models of a energy-minimized (MM+) rosette $\mathbf{1}_3{\cdot}\mathbf{3}_3$ with (A) six *trans*-azobenzene side chains and (B) four *trans*- and two *cis*-azobenzene side chains (one upper side and one lower side of the rosette plane), based on the cis content in the photostationary state upon UV-irradiation. Molecules **1** and **3** are shown as red and green, respectively. Hydrogen atoms are omitted for clarity.

Exposure of the UV-irradiated solution to visible light (450 nm) for 10 min decreased the cis content up to ca. 10% (photostationary state), and the aggregate size immediately recovered up to 30 nm. When the UV-irradiated solution was kept in the dark for 12 h, the average hydrodynamic diameter again showed 50 nm with the total loss of the *cis*-azobenzene moiety.

The mechanistic aspect in the present photoresponsive self-assembly can be easily understood by visualizing photoinduced morphological changes of rosettes $\mathbf{1}_3{\cdot}\mathbf{3}_3$ using molecular modeling calculation. Figure 7 compares the energy-minimized structures of the rosette possessing six *trans*-azobenzene moieties assuming a non-UV-irradiated structure (A) and the rosette possessing four trans- and two *cis*-azobenzene moieties assuming a UV-irradiated structure (B). Compared with the planar shape of the former, in the latter the bulky TDP wedges attached to the *cis*-azobenzene moieties project toward the stacking direction of the rosette. Obviously, such a structural defect is expected to hinder the rosette in stacking toward elongated columnar aggregates.

Finally, we investigated the applicability of our rosette to a photoresponsive gel system.[20] When cyclohexane gel (10 mM) of rosette $\mathbf{1}_3{\cdot}\mathbf{3}_3$ in glass vial was irradiated at around 350 nm for 1 h at 20 °C, the gel turned into a complete fluid with the increase of cis content to ca. 34% (Figure 2B). Using a 0.1 mm cuvette, the irradiation period required for gel-to-sol transition could be shortened to 15 min by diminishing inner filter effect. When the gel was irradiated at the wavelength regions not overlapping with the absorption band of the *trans*-azobenzene moiety, no transition to sol was observed. The photogenerated sol phase was not gelated when cooled to the temperature near the melting point of cyclohexane (6.5 °C), indicating that the isomerized rosette no longer has the ability to form large fibrous aggregates responsible for gelation. The solid film prepared from the photogenerated sol phase showed neither birefringence in optical polarized microscopic observation nor fibrous superstructures in FE-SEM observation (Figure 2D). Taken together with the aforementioned DLS experiments, it can be concluded that trans→cis isomerization of the azobenzene side chains breaks the planarity of the rosette disk (Figure 7), thereby the macroscopic fibers are dissolved into the discrete rosette species.

The photogenerated sol phase recovered the original gel state when it was kept in the dark at rt for 48 h. The long recovery time is convincing by taking thermal cis→trans isomerization (12 h) as well as the slow gelation process of the rosette into account. As expected, visible-light irradiation (450 nm) gave rise to a trans-dominant photostationary state (90%) immediately, promoting the recovery of the gel state (ca. 30 h). A sequence of procedures involving photoinduced gel-to-sol transition and subsequent thermal recovery of the gel could be repeated at least 20 times.

Conclusion

In summary, a novel hydrogen-bonded rosette possessing photoswitchable side chains at the periphery was shown to stack into extended columnar aggregates. The formation of columnar aggregates and further hierarchically organized fibrous assembly could be controlled by photoswitching the peripheral substituents. Though several photoresponsive self-assemblies[8,9] and organogels[20] have been already reported, this is the first example for photoresponsive disk-shaped self-assembly of which the stacking propensity can be regulatable by light input. The significance of the present study is emphasized by the fruitful applicability of columnar assemblies in materials science. This smart system can be extended to the functional supramolecular nanomaterials where the mass transporting property[3a−c] and discotic liquid crystallinity[21] can be controlled by the external light stimulus.

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Supporting Information Available: Complete ref 3d, Experimental Section, temperature-dependent ^{1}H NMR spectra of $\mathbf{1}_3\cdot\mathbf{3}_3$ in cyclohexane-d_{12}, XRD pattern of a dried gel of $\mathbf{1}_3\cdot\mathbf{3}_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Photoresponsive organogels: (a) Murata, K.; Aoki, M.; Nishi, T.; Ikeda, A.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1715−1718. (b) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664−6676. (c) Ahmed, S. A.; Sallenave, X.; Fages, F.; Mieden-Gundert, G.; Müller, W. M.; Müller, U.; Vögtle, F.; Pozzo, J.-L. *Langmuir* **2002**, *18*, 7096−7101. (d) Frkanec, L.; Jokić, M.; Makarevi, J.; Wolsperger, K.; Žinić, M. *J. Am. Chem. Soc.* **2002**, *124*, 9716−9717. (e) Koumura, N.; Kudo, M.; Tamaoki, N. *Langmuir* **2004**, *20*, 9897−9900. (f) Eastoe, J.; Sánchez-Dominguez, M.; Wyatt, P.; Heenan, R. K. *Chem. Commun.* **2004**, 2608−2609. (g) de Jong, J. J. D.; Lucas, L. N.; Kellog, R. M.; van Esch, J. H.; Feringa, B. L. *Science* **2004**, *304*, 278−281. (h) de Jong, J. J. D.; Hania, P. R.; Pugžlys, A.; Lucas, L. N.; de Loos, M.; Kellog, R. M.; Feringa, B. L.; Duppen, K.; van Esch, J. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2−5.

(21) Shimizu, Y.; Kurobe, A.; Monobe, H.; Terasawa, N.; Kiyohara, K.; Uchida, K. *Chem. Commun.* **2003**, 1676−1677.