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Recrystallization and Shape Control of Crystals of the Organic Dye Acid Green 27 in a Mixed Solvent

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Abstract: Recrystallization of the unstructured dye acid green 27 (AG27) in a mixed solvent of alcohol (ethanol or methanol) and water was systematically studied. The results demonstrated that AG27 crystals with uniform sizes and controllable shapes can be produced by simply changing the volume ratio of ethanol (or methanol) and deionized water (DIW). Rodlike and shuttlelike AG27 crystals can be selectively synthesized. The XRD analyses revealed the periodic structures of the organic crystals. Furthermore, crystallization in another mixed solvent of *N*,*N*-dimethylformamide (DMF) and DIW results in the formation of longer fibers with high aspect ratio, which further validates the remarkable effects of mixed solvent on the shape of the AG27 crystals. This method of recrystallization in a mixed solvent is expected to facilitate the synthesis of other functional organic crystals with unusual shapes.

Keywords: acid green 27 • alcohols • crystal engineering • dyes/pigments • solvent effects

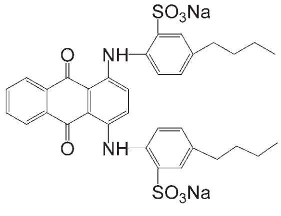
Introduction

Fabrication of functional materials with well-defined shapes, sizes, and dimensionalities by using a self-assembly approach has attracted a lot of attention.[1,2] In the past, many studies have focussed on inorganic functional nanomaterials, such as carbon, metallic, semiconductors, and other inorganic materials.[3,4]

In contrast, only few studies have been carried out on the fabrication of organic materials with special functions and properties. Recently, due to the unique properties of organic materials in the fields of electronics, optics, catalysis, energy storage, and biological systems,[5–11] controlled growth of organic compounds with unique shapes has aroused great interest. However, to a large degree, organic nanomaterials with potential applications in various fields depend on their shapes and sizes, thus, scientists have made great efforts to control organic assembled forms and their dimensionalities. Although organic particles,[12] tubes,[13] wires,[14] rods,[15] and other nanostructures have been synthesized, it remains a great challenge to explore new ways to fabricate organic functional materials with novel structures and properties.

Mixed solvents have been used as a reaction media to produce inorganic crystals with different shapes and morphologies.[16,17] Solvents have a great influence on controlling the morphologies and phases of the final structures. Until now, the fabrication of organic nanomaterials has involved directional, noncovalent interactions, such as hydrogen bonds,[18] van der Waals interactions,[19] and π–π stacking,[20] and ionic self-assembly (ISA),[21] that is, self-organization on the basis of electrostatic interactions.[22] Yao and co-workers fabricated low-dimensional dye aggregates[23] and novel mesostructures[24] by making use of the reprecipitation of dyes in a poor solvent from a good solvent, and nanotubes based on a templating method.[25] The application of such an idea for the morphosynthesis of inorganic materials to fabricate organic materials is interesting.

Herein, we present a facile method to prepare crystals of the organic dye acid green 27 (AG27) with well-defined



Acid Green 27 (AG27)

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shapes and uniform sizes. Uniform AG27 particles with controlled shapes can be recrystallized in an alcohol/water mixed solvent by using an unstructured AG27 precursor; the precursor dye dissolves in solvents at a higher temperature and precipitates as the temperature falls because the solution is supersaturated at the lower temperature. The results demonstrate that the shapes and sizes of dye crystals can be well controlled by varying the volume ratio of an organic solvent and water.

Results and Discussion

A series of crystallization experiments of AG27 in a mixed solvent of alcohol and pure deionized water (DIW) was carried out. The mean length of the crystals obtained was found to be strongly dependent on the volume ratio of alcohol and water. The main results are summarized in Table 1 and Figure 1.

Table 1. The mean length (L) of shuttlelike aggregates obtained by using different volume ratios of alcohol and DIW (V_{alcohol}:V_{DIW}) (total volume = 2 mL).

V_{alcohol}:V_{DIW}	L [µm]	V_{alcohol}:V_{DIW}	L [µm]
$V_{\text{EtOH}}/V_{\text{DIW}}$		$V_{\text{MeOH}}/V_{\text{DIW}}$	
1/1	80	1/1	>20[a]
1/2	75	1/2	<20[a]
1/3	50	1/3	25
1/8	40	1/8	8
1/30	15	1/30	5
pure DIW	4		

[a] Length of bending rods.

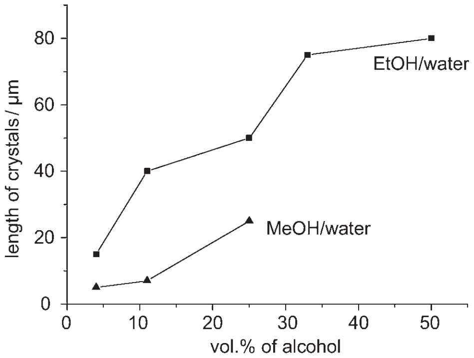

Figure 1. Dependence of length of the AG27 crystals on the compositions of a mixed solvent with different alcohol/water volume ratios.

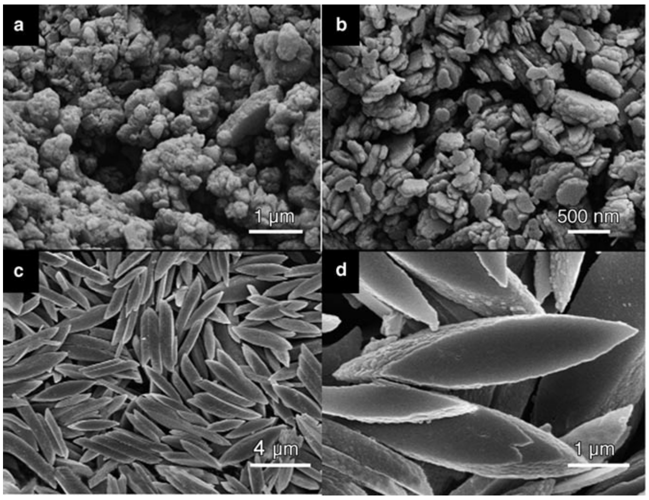

Figure 2. SEM images of the AG27 crystals: a) raw materials; b) flakelike aggregates formed by placing a drop of an aqueous solution with dissolved AG27 onto a glass substrate; c) and d) shuttlelike structures crystallized from pure deionized water.

Recrystallization of acid green 27 crystals in pure DIW: The SEM image in Figure 2a shows that the morphology of the original AG27 precursor is that of rather irregular aggregates. The agglomerates are composed of grains of different sizes. If a small quantity of AG27 precursor is dissolved in pure DIW without heating and then a drop of this solution is removed and placed onto the glass substrate directly for SEM observation, aggregates with a flakelike shape are observed, as shown in Figure 2b. Although these particles are not uniform, they have a more regular shape than the agglomerates of the original precursor shown in Figure 2a. It simply proves that this method has a clear effect on shape control of the AG27 crystals. SEM images (Figure 2c and d) show that well-defined, uniform shuttlelike AG27 particles can be produced by recrystallization in pure DIW. The mean size of the shuttlelike crystals is about 4 µm and the surfaces of these crystals are quite smooth. The formation process of self-assembled organic crystals involves different intermolecular interactions, such as hydrogen bonds, van der Waals interactions, and π–π stacking. Furthermore, these crystals are so stable that they can be sustained on the glass substrates for several months without changing their morphologies.

XRD analyses were performed on the original dye AG27 precursor and the AG27 shuttlelike crystals, respectively (Figure 3). The results indicate that the crystallinity of the raw AG27 precursor was poor and that it contained some noncrystalline phase substances, as indicated in Figure 3a. The poor crystallinity of the raw AG27 precursor could be related to the specific chemical reaction process for producing this compound. In contrast, the crystallinity can be much improved by recrystallization of the precursor AG27 in water, as shown in Figure 3b, in which the well-oriented diffraction peaks can be detected, suggesting that the well-packed dye molecules and the ordered arrangements of the AG27 crystals have formed. It is known that the structural properties and spatial configuration of the organic molecules have important effects on the final packing mode and the possible shape of the crystals. Here, we propose that AG27 molecules with highly conjugated phenyl rings may form a face-to-face arrangement along with the preferred oriented planes to give the largest orbital overlap and the lowest molecular energy. The formation of the shuttlelike crystals with the most stable structures completes this recrystallization process.

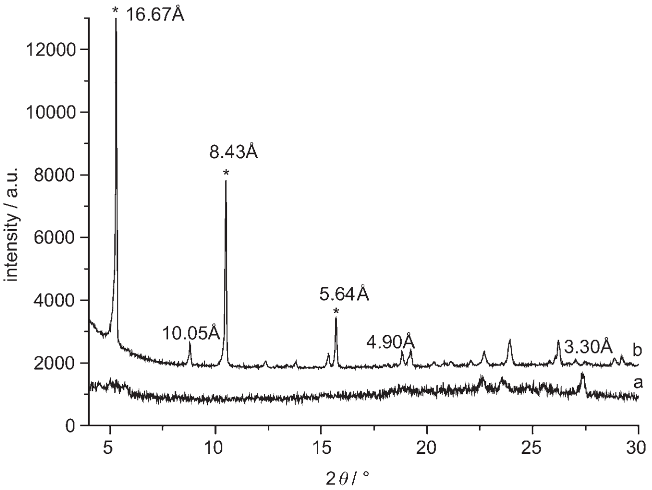

Figure 3. XRD patterns of a) the original AG27 precursor; b) shuttlelike nanostructures of AG27 in pure water. * denotes the periodic lamellar structure of the recrystallized product.

Furthermore, a set of the diffraction peaks can be readily assigned to a periodic and lamellar structure, as shown in Figure 3b. The first three peaks with strong diffraction intensities and *d* spacings of 16.67, 8.43, and 5.64 Å, respectively, were assigned as the first-, second-, and third-order diffraction peaks of a certain (*hkl*) crystal plane of the three-dimensional crystals (Figure 3b), which are typical features for a periodic lamellar structure. The remainder of the peaks of relatively low intensity could be assigned as another set of periodic diffraction peaks, such as the *d* spacings of 10.05, 4.90, and 3.30 Å.

The IR spectrum in Figure 4b shows that vibration bands of -OH-, -CH_3, -CH_2-, -SO_3, and –C=C- appeared for the dye AG27 crystals that were recrystallized from water. These bands are similar to the characteristic bands for the original AG27 precursor (Figure 4a), suggesting the invariable molecular component of the shuttlelike crystals.

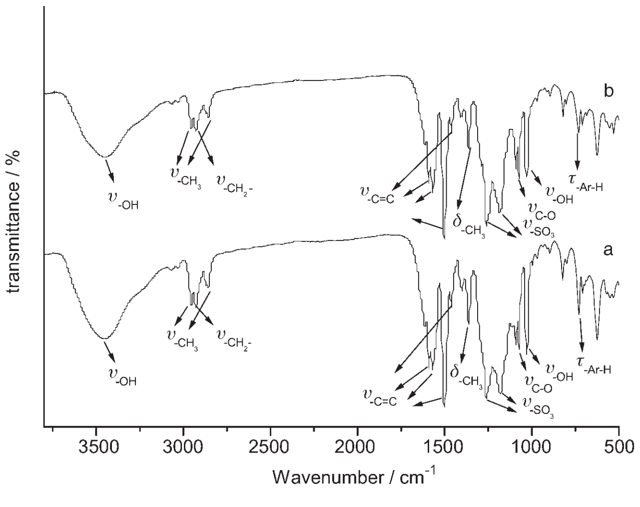

Figure 4. FTIR spectra of a) the AG27 precursor and b) the AG27 crystals prepared in the pure-water system.

Shape control of acid green 27 in a mixed solution of ethanol and DIW: The structural characteristics of AG27 crystals formed in a mixed solvent of ethanol and DIW are revealed by the XRD patterns shown in Figure 5. All of the products are clearly crystalline with diffraction patterns similar to those produced in pure water (Figure 3b). There are three diffraction peaks with *d* values of 16.92, 8.49, and 5.67 Å, corresponding to the first-, second-, and third-order diffraction peaks, respectively, with a ratio of 1:2:3. This implies the existence of a periodic lamellar structure in the structures.

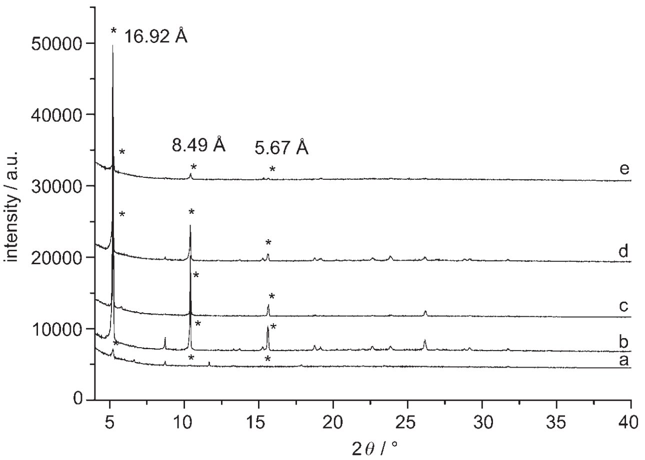

Figure 5. XRD patterns of the AG27 crystals crystallized in solutions with different volume ratios of ethanol/DIW: a) V_{EtOH}:V_{DIW}=1:1; b) V_{EtOH}:V_{DIW}=1:2; c) V_{EtOH}:V_{DIW}=1:3; d) V_{EtOH}:V_{DIW}=1:8; e) V_{EtOH}:V_{DIW}=1:30.

The morphology and size of the AG27 crystals can be changed dramatically by altering the volume ratio of ethanol and water (V_{EtOH}:V_{DIW}). The particles become slimmer as V_{EtOH}:V_{DIW} increases from 1:3 to 1:2 and to 1:1. Figure 6a

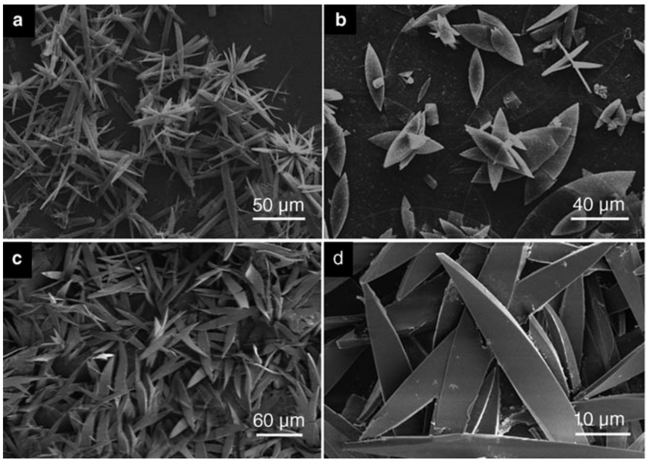

Figure 6. SEM images of the AG27 crystals produced in a mixed solvent with different volume ratios of ethanol/DIW: a) V_{EtOH}:V_{DIW}=1:1; b) V_{EtOH}:V_{DIW}=1:3; c) and d) V_{EtOH}:V_{DIW}=1:2.

presents almost rodlike crystals with a mean length of 80 μm that were prepared in a mixed solution of V_{EtOH}:V_{DIW} = 1:1. Notably, as V_{EtOH}:V_{DIW} is decreased to 1:3, the length of the crystals becomes shorter and the width increases (Figure 6b). The shuttlelike crystals with an average length of about 75 μm and smooth surface were produced, and each crystal has two sharp tips if V_{EtOH}:V_{DIW} = 1:2 (Figure 6c,d). Decreasing V_{EtOH}:V_{DIW} further results in the formation of oval-shaped particles with shorter length and greater width, as shown in Figure 7. As V_{EtOH}:V_{DIW} is reduced from 1:8 to 1:30, the length of the crystals decreases from 40 to 15 μm (see also Table 1 and Figure 1).

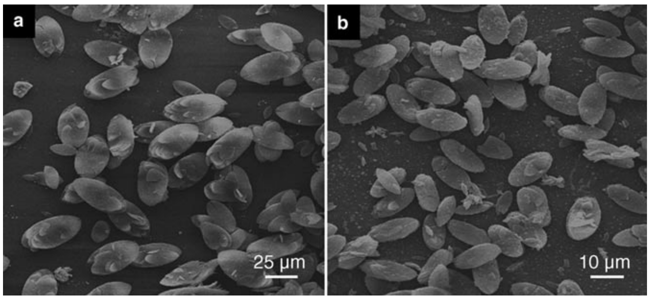

Figure 7. SEM images of the AG27 crystals produced in a mixed solvent with different volume ratios of ethanol/DIW: a) V_{EtOH}:V_{DIW} = 1:8; b) V_{EtOH}:V_{DIW} = 1:30.

Shape control of acid green 27 in a mixed solution of methanol and DIW: Figure 8 shows the XRD patterns of a series of samples produced in a methanol/DIW solution. The well-developed diffraction peaks indicate good crystallinity. The first three peaks of strong intensity denoted with asterisks can be assigned as those found in the samples crystallized from the ethanol/DIW solution (Figure 5).

The effects of the methanol/DIW system on the morphology and sizes of the AG27 crystals in solution were also systematically investigated. The results indicate that the length/width ratio of the dye crystals deceases in response to decreasing the content of methanol in a series of mixed methanol/DIW solutions. Interestingly, uniformly bent rod-shaped crystals can be obtained (Figure 9a,b) if V_{MeOH}:V_{DIW} is 1:1. The heads of these rods are not flat, but are in a form of lamellar structures, as revealed by the magnified SEM image (Figure 9b). Upon decreasing the volume ratio of methanol and water to 1:2, a mixture of rods and shuttlelike crystals was obtained (Figure 9c). The magnified SEM image (marked area in Figure 9c) showed that the rods become bent relative to those shown in Figure 9b. By decreasing V_{MeOH}:V_{DIW} further to 1:3, only shuttlelike crystals were produced (Figure 9d). The results suggest that the rods are not stable as the methanol content in the methanol/DIW system decreases and that they finally transform into shuttlelike crystals.

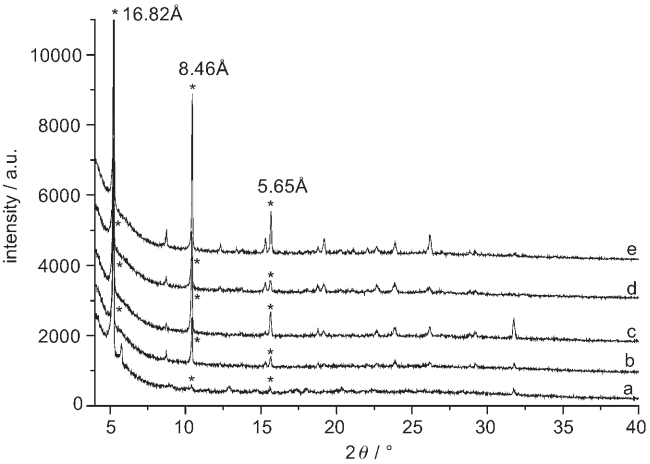

Figure 8. XRD patterns of the AG27 crystals produced in a mixed solvent with different volume ratios of methanol/DIW: a) V_{MeOH}:V_{DIW} = 1:1; b) V_{MeOH}:V_{DIW} = 1:2; c) V_{MeOH}:V_{DIW} = 1:3; d) V_{MeOH}:V_{DIW} = 1:8; e) V_{MeOH}:V_{DIW} = 1:30.

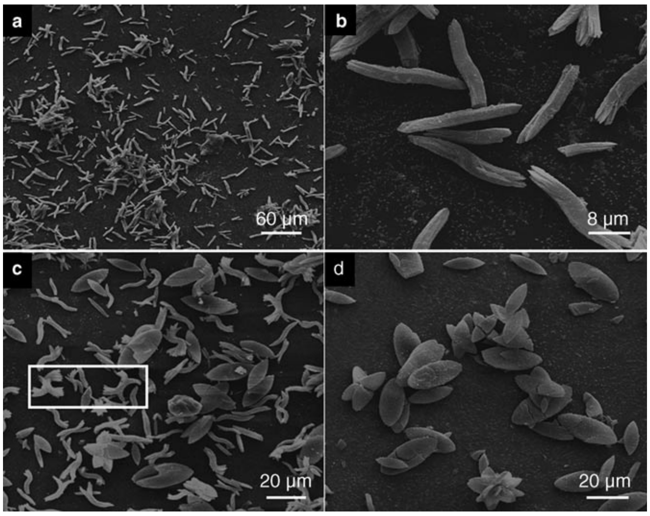

Figure 9. SEM images showing morphologies of AG27 produced in a mixed solvent with different volume ratios of methanol/DIW: a) and b) V_{MeOH}:V_{DIW} = 1:1; c) V_{MeOH}:V_{DIW} = 1:2; d) V_{MeOH}:V_{DIW} = 1:3.

Figure 10 shows an SEM image of the dye crystals formed in a mixed solution with lower methanol content. The shapes of the crystals resemble closely those obtained in

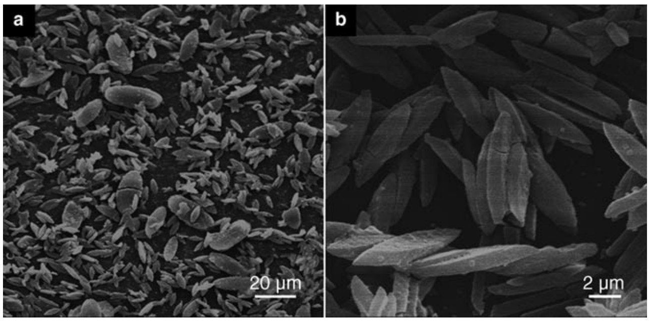

Figure 10. SEM images of AG27 crystals produced in a mixed solvent with different volume ratios of methanol/DIW: a) V_{MeOH}:V_{DIW} = 1:8; b) V_{MeOH}:V_{DIW} = 1:30.

pure DIW. This is because methanol is more similar than ethanol to water. However, the crystals shown in Figure 10 are larger than those obtained in water. Furthermore, the lower the methanol content of the mixed solvent, the smaller the crystals, which can be seen by comparing the crystals in Figure 10a with the ones in Figure 10b.

Shape control of acid green 27 in a DMF/DIW mixed solution: To shed light on the effects of mixed solvents on controlling the growth and shape of organic AG27 crystals, *N*,*N*-dimethylformamide (DMF) was used to replace ethanol and methanol. The results demonstrate that the morphologies of the AG27 aggregates obtained in the DMF/DIW solution were dramatically different from those crystallized in the alcohol/DIW systems. The size of the AG27 microfibers ranged from tens to hundreds of micrometers, as shown in Figure 11. The length of the shortest AG27 wire is about 80 μm and the longest is up to 350 μm in length. The mean diameter of the fibers is about 2 μm. This proves that the solvent mixture plays a crucial role in controlling the growth and shape of acid green 27 crystals.

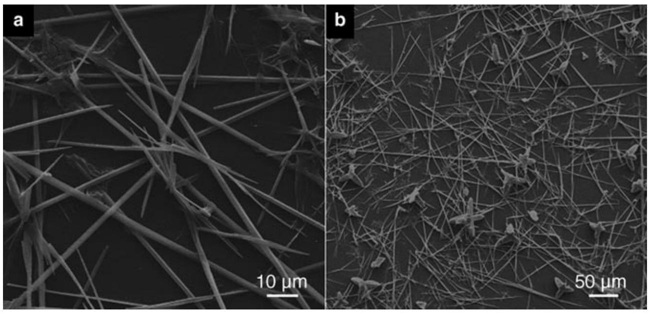

Figure 11. SEM image of AG27 crystals produced in a mixed solvent of DMF and DIW with a volume ratio of V_{DMF}:V_{DIW}=1:1.

Thermodynamic and kinetic analysis in a mixed-solution system: Of course, thermodynamic and kinetic processes also play a key role in controlling crystal growth, shapes, and sizes. Thermodynamic studies reveal the possibility of a reaction, and kinetic studies are concerned with reaction velocity. The theory of precipitation–dissolution balance is considered here. We prepared dye solutions in the supersaturated state at room temperature. The solutions were heated to a high temperature and then allowed to cool to room temperature, which induced precipitation of crystals. The supersaturated solution can be represented by the following equation:[17]

$$\ln S = \ln c + z_+ z_- e^2 / 4\pi\varepsilon_0 \varepsilon k T(r_+ + r_-) \tag{1}$$

in which S represents the degree of supersaturation, c is the solute concentration, T is the Kelvin temperature, and k is Boltzmann's constant. ε_0 is the permittivity in a vacuum and ε is the dielectric constant in a given solution. The symbols r_+ and r_- stand for the radii of ions charged z_+ and z_-, respectively, and e is the elementary charge ($e = 1.602 \times 10^{-19}$ C).

As can be seen from above equation, only the ε value varies greatly with the nature of the solution. Thus, we can simplify the equation as:

$$\ln S = A + B/\varepsilon \tag{2}$$

in which:,

$$A = \ln c \tag{3}$$

$$B = z_+ z_- e^2 / 4\pi\varepsilon_0 k T(r_+ + r_-) \tag{4}$$

The values of A and B can be regarded as constant in the alkyl alcohol and water solvents. Therefore, the supersaturation degree (S) is inversely proportional to the dielectric constant (ε) of the solution, that is, the greater the value of ε, the smaller the supersaturation degree S. A solution with a large S value can provide a greater quantity of precipitated solutes for crystal growth. Furthermore, the formation of organic crystals involves molecular interactions. π–π stacking interactions have an important effect on the precipitation and formation of the AG27 crystals with highly conjugated phenyl rings. However, a solution with a low dielectric constant ε has improved π–π stacking of AG27 molecules and, thus, forms large crystals.

According to the literature,[26] ε increases in the order: ethanol < methanol < water. Moreover, the ε value decreases as the alcohol content in the alcohol/DIM solvent increases. Our experimental results are highly consistent with the above theories. For the same alcohol system, increasing the alcohol content in the mixed solvent will decrease the dielectric constant ε and increase the supersaturation degree S. Thus, the crystals grown will be larger in the solution with a high volume percentage of alcohol (see Table 1 and Figure 1). For the different alcohol systems, the ε value of methanol is larger than that of ethanol, and the S value of the former is smaller than that of the latter for a fixed volume percentage of alcohol in a mixed solvent. Therefore, the crystals in the methanol/water solvent are smaller than those in the ethanol/water system. Because water has the largest ε value and the smallest S value among these solvents, the crystals obtained in pure water are the smallest, as the tendency for homogeneous nucleation to occur in this case is high.

Conclusion

AG27 crystals of different shapes and sizes with periodic lamellar structures were synthesized by a recrystallization method in an alcohol/water mixed solvent. The shapes and sizes of the dye crystals can be well controlled by changing the volume ratios of alcohol and water in the mixed solvents. The lower the alcohol content, the smaller the crystals. A dramatic change in shape of the AG27 particles crystallized in the mixed-solvent system DMF/DIW was observed, and AG27 microfibers can be obtained. The thermodynamics and kinetics of crystal growth in this mixed-solvent system were analyzed by studying the effects of methanol and ethanol on the changing morphologies and sizes of the final crystals. The approach reported here could aid in the design and fabrication of other organic crystals with unique shapes and novel functionalities.

Experimental Section

Materials: The model dye compound used here, acid green 27 (AG27), was purchased from Sigma–Aldrich and was used without further purification. Methanol, ethanol, and *N*,*N*-dimethylformamide (DMF) were of analytical grade and were used as received without further purification. Pure water was doubly distilled deionic water (DIW). All glass bottles and small pieces of glass substrates were cleaned, sonicated in ethanol and acetone, and rinsed three times with distilled water.

Preparation procedures: Control of the morphologies of the AG27 assembles in a mixed solvent was achieved by using the following facile recrystallization method. In a typical synthesis, AG27 (18 mM, 0.0254 g) was added to solvents (total volume: 2 mL) in a glass bottle with a volume of 15 mL under vigorous magnetic stirring at RT. The AG27 solution was then heated to 80 °C and stirred for 10 min. Finally, the bottle was allowed to cool naturally to ambient temperature without stirring, and three pieces of glass substrate were put into the solution. While maintaining the total volume (2 mL), different structures and sizes of the AG27 crystals could be obtained by changing the volume ratio of alcohol to water. After 24 h, the samples were collected by removing the small pieces of glass substrates, which were then dried in air for further characterization.

Characterization: The morphologies of the AG27 crystals were observed by SEM using a BYBY-1010A microscope and by field emission scanning electron microscopy by using a JEOL JSM-6700F (15 kV) microscope. The cover slips were sputtered with gold directly to improve the sample conductivity. The X-ray diffraction measurement was performed by using an X-ray powder diffractometer (Philips X'Pert Pro Super) with $Cu_{K\alpha}$ radiation ($\lambda = 1.541874$ Å). FTIR spectra were measured by using a Bruker Vector-22 FTIR spectrometer from 4000 to 400 cm^{-1} at RT.

Acknowledgements

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