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Self-assembly of linear-shaped bi-dihydrazine derivative through intermolecular quadruple hydrogen bonding

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ABSTRACT

A linear-shaped bi-1,3,4-oxadiazole derivative, oxalyl acid *N*′,*N*′-di(4-(2-ethylhexyloxy)benzoyl)-hydrazide (FH-Z8) was designed and synthesized. Quadruple hydrogen bonds between bi-dihydrazide units and π–π interactions cooperatively participated in forming supramolecules in chloroform at higher concentrations of FH-Z8. The association constants (K) in chloroform were 2.2×10^3 and 1.8×10^3 M^{-1} based on NH1 and NH2 in FH-Z8, respectively. FH-Z8 could gel dichloroethane efficiently with the critical gelation concentration (CGC) of 0.14 wt %, while spontaneously crystallized from the gel during storage.

1. Introduction

Hydrogen bonds play an important role in building superstructures in chemical and biological systems due to their specificity and directionality.[1] Since Meijer and co-workers first reported a series of 2-ureido-4(1*H*)-pyrimidone derivatives that can dimerize through intermolecular quadruple hydrogen bonds,[2] quadruple hydrogen-bonded systems have attracted much attention and have been used in the field of materials science to synthesize, for the first time, supramolecular polymers through the self-association of self-complementary monomers.[3] In the quadruple hydrogen-bonding motifs, the linear self-complementary H-bonding arrays offer distinct advantages in the self-assembly of supramolecular polymers.[4]

Low-molecular-weight organogels are the materials in which three-dimensional networks are formed due to the self-assembling of low-molecular-weight compounds (organogelators) through noncovalent interactions, and the networks can absorb a large amount of solvent therein.[5] Organogelators containing amide,[6] hydroxyl,[7] and urea[8] groups are the most studied gelators whose driving force for the formation of one-dimensional self-associated chains is hydrogen bonding. However, organogels based on quadruple hydrogen bonds were rather limited. Wan and co-workers reported a hydrazide quinolinone-based quadruple hydrogen-bonded building block, which can gel dichloromethane/hexane at concentrations higher than 2 wt %.[9] Li and co-workers reported a new class of highly stable hydrazide-based ADDA–DAAD heterodimers, which represented the first successful application of hydrazide derivatives in the self-assembly of hydrogen-mediated supramolecular systems with well-established structures.[10] Chen and co-workers reported a new family of molecular duplex strands from hydrazide-based oligomers with malonyl groups as linkers.[11] Recently, we reported the synthesis and self-assembly of twin-tapered dihydrazide derivatives, oxalyl acid *N*′,*N*′-di(3,4,5-trialkoxybenzoyl)-hydrazide (FH-Tn), which self-assembled in chloroform at concentrations higher than 255 μM or in bulk through intermolecular quadruple H-bonding.[12a] The association constants (K) in chloroform were 447.5 and 217.2 M^{-1} based on NH-1 and NH-2 in FH-T7, respectively. Furthermore, the achiral FH-Tns are effective gelators in ethanol.[12b] The gelling ability in ethanol, the morphologies, packing structures, and intermolecular H-bonding strength were significantly influenced by the length of the alkyl side chains. FH-T6 and FH-T7 showed strong gelation ability in ethanol with critical gelation concentrations of 0.25 and 0.30 wt %, respectively. Both left- and right-handed helical ribbons with non-uniform helical pitch were observed in FH-Tn (n=5, 6, 7) gels. Herein we report the synthesis and self-assembly of a linear-shaped bi-dihydrazine derivative, oxalyl acid *N*′,*N*′-di(4-(2-ethylhexyloxy)benzoyl)-hydrazide. Quadruple hydrogen bonds between bi-dihydrazide units and π–π interactions between neighbor phenyl rings cooperatively participated in forming supramolecules in chloroform at concentrations higher than 80 μM. The association constants (K) in chloroform were

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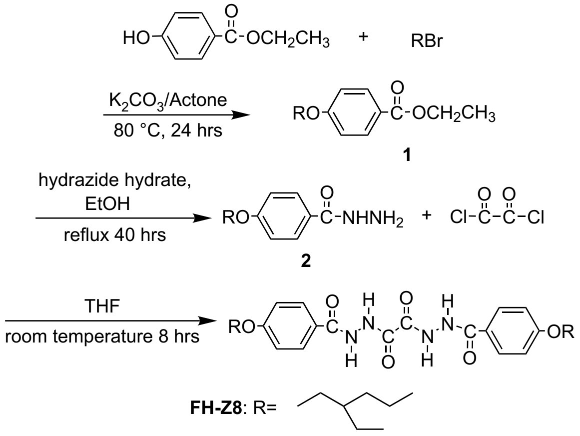
2.2×10^3 and 1.8×10^3 M^{-1} based on NH1 and NH2 in FH-Z8, respectively, which are larger than those of FH-T7. FH-Z8 could gel dichloroethane efficiently with the critical gelation concentrations (CGCs) of 0.14 wt %, and spontaneously crystallization from its gel was observed during storage.

2. Results

2.1. Synthesis

Ethyl *p*-hydroxybenzoate, oxalyl chloride, and 2-ethylhexyl bromide were used as-received. Tetrahydrofuran (THF) was refluxed over sodium under argon and distilled before use. 4-(2-Ethylhexyloxy)-benzoyl hydrazine **2** was prepared according to the literature.[13] A mixture of 6.6 g (40.0 mmol) of ethyl *p*-hydroxybenzoate, 15.0 g of potassium carbonate (dried under vacuum at 80 °C for 12 h prior to use), and 7.7 g (40 mmol) of 2-ethylhexyl bromide in 150 mL of acetone was stirred and refluxed for 24 h. After cooling the reaction mixture to room temperature, the solid particles were removed by filtration and successively washed with 100 mL of acetone and 100 mL of chloroform. After removal of the solvent from the combined filtrate, the crude liquid product **1** and excess of hydrazine hydrate in 150 mL of methanol were refluxed for 24 h. The reaction mixture was cooled to room temperature and the precipitate was filtered. The precipitate was washed with water then dried under vacuum. The product **2** was obtained as a white solid (8.5 g, 80%). FH-Z8 was prepared through the route reported in our previous work,[12,14] as shown in Scheme 1. Oxalyl chloride (1.4 g, 11 mmol) was regularly injected into the THF solution of 6.1 g (23 mmol) of 4-(2-ethylhexyloxy)-benzoyl hydrazine **2** with vigorous stirring at room temperature for 8 h, yielding the product of oxalyl acid *N′*,*N′*-di(4-(2-ethylhexyloxy)benzoyl)-hydrazide (FH-Z8), which was purified through washing with alcohol (4.8 g, 75%).



Scheme 1. Synthesis of FH-Z8.

2.2. Self-assembly behaviors in chloroform

To understand the self-assembly behaviors of the linear-shaped bi-dihydrazine derivative, ^1H NMR diluting experiments were carried out for FH-Z8 in $CDCl_3$. Figure 1 shows the partial ^1H NMR spectra (500 MHz, $CDCl_3$) of FH-Z8 at different concentrations. At 0.040 mM, peaks of NH1 (near to bi-carbonyl group, 9.92 ppm) and NH2 (near to alkoxy phenyl, 8.56 ppm) in FH-Z8 were sharp, and Ar-H1 (near to amide group, 7.81 ppm) and Ar-H2 (near to alkoxy, 6.97 ppm) exhibited double peaks, suggesting its monomeric feature. Increasing concentrations of FH-Z8 in $CDCl_3$ from 0.080 to 40 mM led remarkable broadening and downfield shift of both NH1 ($\Delta\delta$=0.92 ppm) and NH2 ($\Delta\delta$=1.23 ppm), concomitance with the broadening and upfield shift of both Ar-H1 ($\Delta\delta$=0.20 ppm) and Ar-H2 ($\Delta\delta$=0.34 ppm). The dependence of the chemical shifts of NH1, NH2, Ar-H1, and Ar-H2 in FH-Z8 on concentrations is shown in Figure 2. The chemical shifts of NH1 and NH2 increased, while those of Ar-H1 and Ar-H2 decreased almost linearly with the increase in concentration and then slowed down and appeared to level off at 8 mM. The above results demonstrated that quadruple hydrogen bonds between bi-dihydrazide units and π–π interactions between neighbor phenyl rings cooperatively

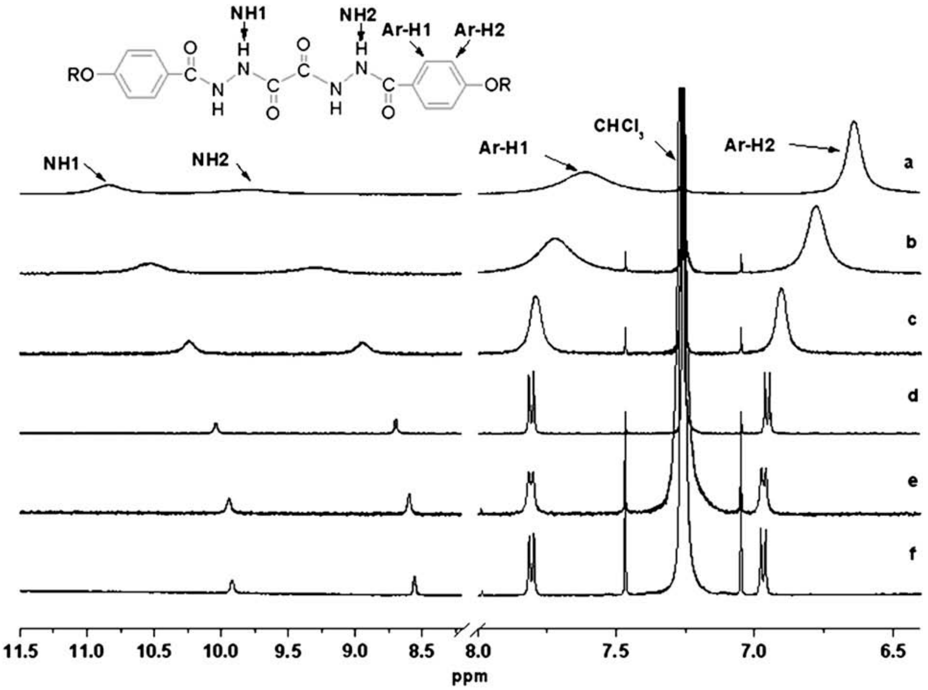


Figure 1. Partial proton NMR spectra (500 MHz, $CDCl_3$, 25 °C) of FH-Z8 at different concentrations: (a) 40, (b) 3.60, (c) 1.27, (d) 0.400, (e) 0.08, (f) 0.04 mM.

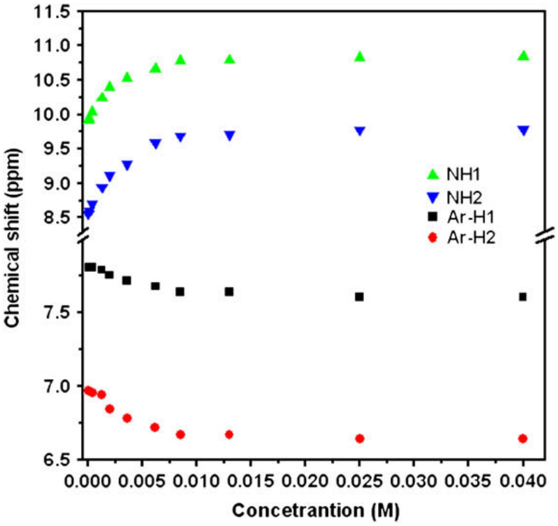


Figure 2. Concentration dependence of the chemical shifts of NH1, NH2, Ar-H1, and Ar-H2 protons in the ^{1}H NMR spectra of FH-Z8 in $CDCl_3$.

participated in forming supramolecules at concentrations higher than 80 μM.

The association constants for FH-Z8 were estimated using the simplest (isodesmic) model (i.e., K_n=K, for $n\geq2$) from Eq. 1:

$$KC_T = (P - P_\alpha)\left(P_\xi - P_\alpha\right)\Big/\left(P_\xi - P\right)^2 \qquad (1)$$

where P_α and P_ξ are the chemical shifts for monomers and molecules within a stack, P is the observed chemical shift, K is the association constant and C_T is total molar concentration of the compounds.[15] For FH-Z8, P_α was assigned to 9.92 and 8.56 ppm based on NH1 and NH2, respectively. The data from the diluting experiment fitted well with the calculated curves, giving association constants (K) of 2.2×10^3 and 1.8×10^3 M^{-1} based on NH1 and NH2, respectively.

2.3. Gelling behavior

We found FH-Z8 could gel dichloroethane with high efficiency with the critical gelation concentrations (CGCs) of 0.14 wt %. Figure 3 shows the melting temperatures (T_ms) of FH-Z8 gel in dichloroethane as a function of concentration. T_ms were determined by the 'falling drop' method.[16] The T_m increased from 13 °C for the gel at 0.14 wt % to 42 °C at 1.8 wt %. The sol–gel transition can be repeated many times through a heating–cooling process. However, if the gel was allowed to stand more than 12 h at room temperature, it crystallizes spontaneously. The procedure for gel formation and gel–crystal transition is outlined in Figure 4. Crystallization from the gel was completed at 50 h.

In order to investigate the aggregation morphology of the organogel, the xerogel FH-Z8 from dichloroethane was prepared and subjected to the scanning electron microscope (SEM) observation. To avoid crystallization during storage, the FH-Z8 xerogel from dichloroethane was obtained once the gel formed and then immediately evaporating the solvent in vacuum. As shown in Figure 4a, the FE-SEM image of FH-Z8 xerogel revealed a network structure composed of intertwined fibers with the diameters of 200–400 nm. The formation of elongated fiber-like aggregates indicates that the self-assembly of FH-Z8 is driven by strong directional intermolecular interactions. The FE-SEM images of crystals developed from the gel in dichloroethane were board-like, as shown in Figure 5b.

Figure 6 shows the X-ray diffraction patterns of FH-Z8 xerogel, the corresponding crystal developed from the gel, and the FH-Z8 film casted from chloroform. The XRD pattern of FH-Z8 xerogel from dichloroethane showed one strong peak (20.7 Å), one relatively weak peak (14.9 Å), and several broad weak peaks in low-angle range, and two diffuse broad peaks with a maximum at about 4.4 and 4.6 Å, suggesting the coexistence ordered and disordered feature. The broad peak at 4.4 Å is characteristic of the liquid-like arrangement of the aliphatic chains, while that at 4.6 Å might be attributed to the repeat distance of bi-dihydrazide units in stacking, illustrated in Figure 8(a). The XRD pattern of the FH-Z8 film is almost the same as that of the xerogel, suggesting their similar molecular arrangement in both cases. In contrast, the XRD patterns of FH-Z8 crystals developed from dichloroethane gel showed three sharp strong diffractions with the ratio of 1:1/2:1/3 in low-angle range, indicating its well defined layer structure, and several sharp diffractions in high-angle range, suggesting its crystalline feature.

The FTIR spectra of the FH-Z8 film casted from chloroform and the xerogel in dichloroethane were similar, which showed the N–H stretching vibrations at 3245 cm^{-1} (the absence of free N–H, a relatively sharp peak with the frequency higher than 3400 cm^{-1}) and amide I vibration bands at 1693 and 1632 cm^{-1}, indicating that the N–H groups are associated with C═O groups via N–H···O═C hydrogen bonding.[17] The N–H stretching vibrations of the FH-Z8 crystal located at 3383, 3314, and 3272 cm^{-1} and amide I at 1700, 1683, 1658, and 1631 cm^{-1}, revealing that weaker H-bonding strength compared to that in its gel or casted film. The $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ in FH-Z8 in the casted film and the xerogel appeared at 2859 and 2930 cm^{-1}, indicating disordered alkyl chains, which was

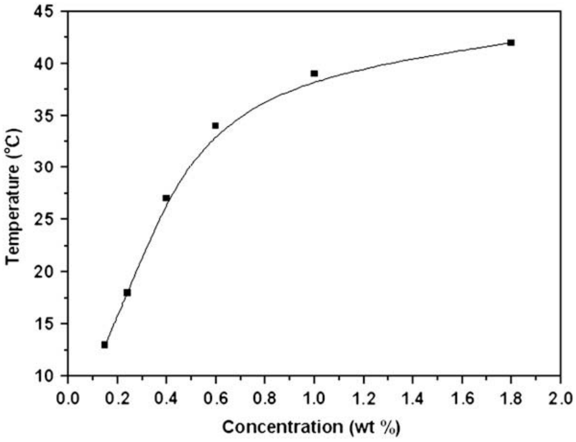


Figure 3. Concentration-dependent melting temperature of FH-Z8 gels in dichloroethane.

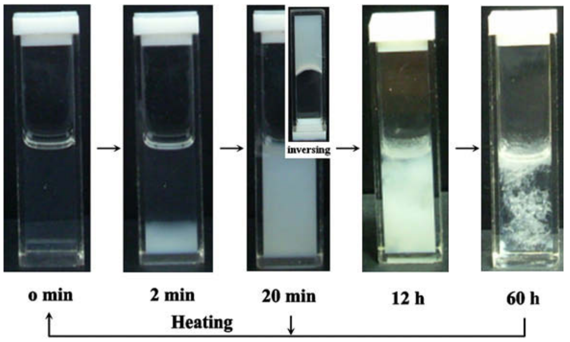


Figure 4. Photograghs showing progressive gellation and crystallization of FH-Z8 in dichloroethane with 0.5 wt % FH-Z8 at different time periods.

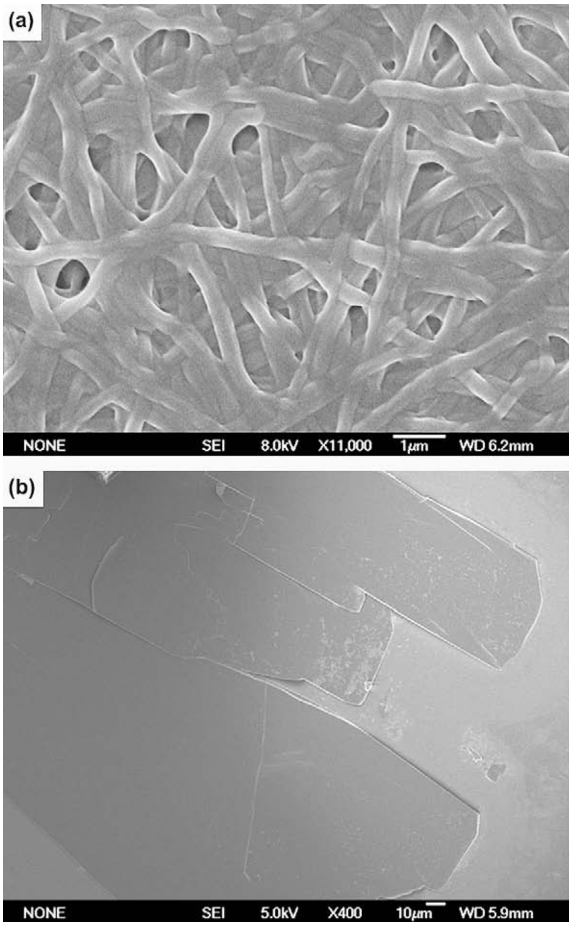


Figure 5. SEM images of FH-Z8: (a) xerogel in dichloroethane (0.5 wt %), (b) crystals developed from dichloroethane gel.

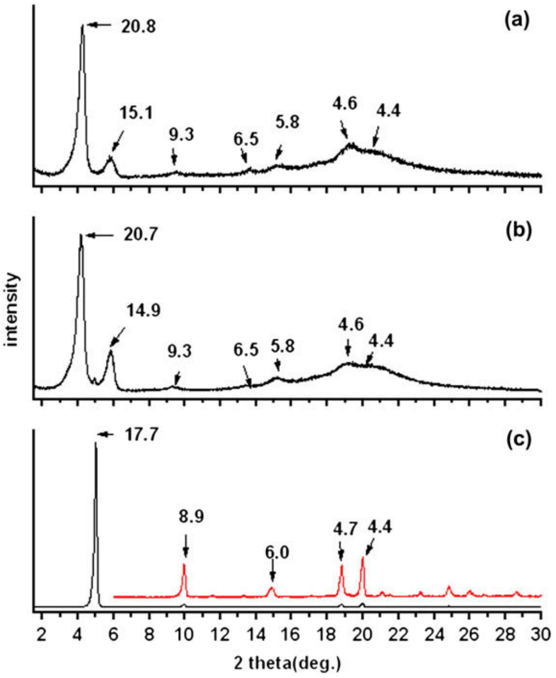


Figure 6. XRD patterns of FH-Z8: (a) film casted from chloroform, (b) xerogel from dichloroethane (0.5 wt %), and (c) crystals developed from dichloroethane gel.

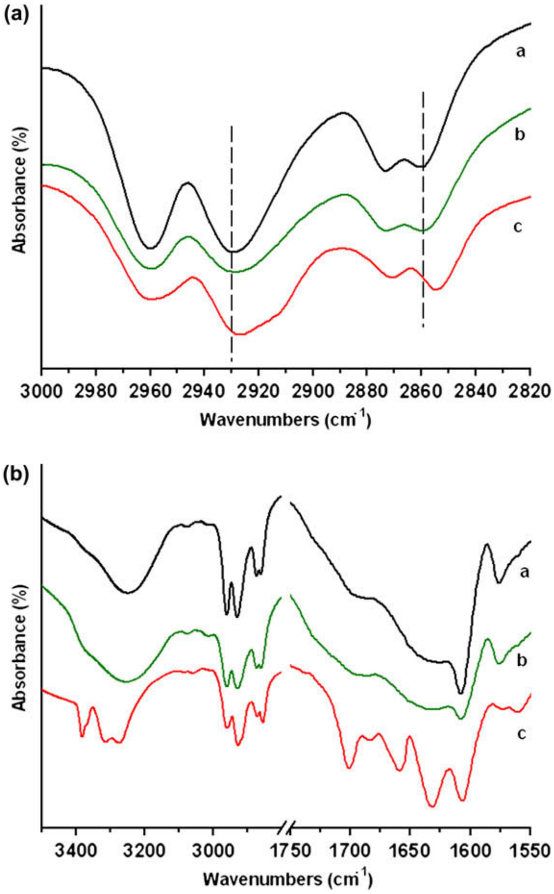


Figure 7. FTIR spectra of FH-Z8: (a) film casted from chloroform, (b) xerogel from dichloroethane (0.5 wt %), and (c) crystals developed from dichloroethane gel.

consistent with the XRD results.[18] Both $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ in the FH-Z8 crystal were detected at 2854 and 2926 cm^{-1}, respectively, indicating increased population of the trans conformation of alkyl chains in the FH-Z8 crystal (Fig. 7).

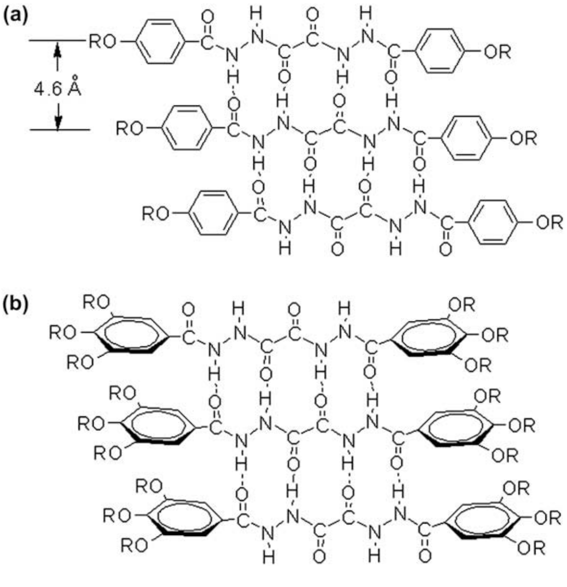


Figure 8. Schematic representation of FH-Z8 and FH-Tn self-assembling to supramolecules (the dashed line illustrates the hydrogen bonding).

3. Discussion

Based on the results above, a packing model of FH-Z8 in chloroform at high concentration and the gel in dichloroethane was proposed in Figure 8(a). Considering that FH-Z8 molecules are linear shaped, self-assembly of the FH-Z8 molecules through quadruple hydrogen bonding would cause the approach of the neighboring molecules and induce π–π interactions between phenyl rings, which were confirmed by the ^{1}H NMR diluting experiment. The broad weak diffraction at 4.6 Å in the XRD patterns of FH-Z8 film and the xerogel was attributed to the repeat distance of bi-dihydrazide units of the stacks. The association constants (K) of FH-Z8 in chloroform were 2.2×10^3 and 1.8×10^3 M^{-1} based on NH1 and NH2, which are bigger than those of FH-T7, which are measured to be 447.5 and 217.2 M^{-1} based on NH-1 and NH-2, respectively. The relative small association constants in FH-T7 was attributed to the energy required for the out-of-plane rotation of the phenyl rings for stacking and no π–π interactions between neighboring phenyl rings cooperating in forming supramolecules of the twin-tapered FH-T7. In the present case, through decreasing the number of terminal alkyl chains to reduce the packing hindrance, linear-shaped FH-Z8 with branched terminal chains was designed and demonstrated to self-assemble through both hydrogen bonding and π–π interactions and to give relatively large association constant.

We noticed that the layer spacing from XRD of FH-Z8 in crystals developed from its gel (17.7 Å) was much smaller than the length of full extended molecular length of FH-Z8 (35.4 Å). It can be deduced that FH-Z8 molecules might be large angle tilted in layers or might not be in linear conformation and thus cause less rigid intermolecular H-bonding sites between bi-dihydrazide units, which is consistent with weaker intermolecular H-bonds as measured by the FTIR spectroscopy. The exact packing of FH-Z8 in the crystal needs to be examined further.

4. Conclusion

A linear-shaped bi-1,3,4-oxadiazole derivative (FH-Z8) with branched terminal alkyl chains was designed and synthesized. Quadruple hydrogen bonds between bi-dihydrazide units and π–π interactions cooperatively participated in forming supramolecules in chloroform at higher concentrations of FH-Z8. The association constants (K) in chloroform were 2.2×10^3 and 1.8×10^3 M^{-1} based on NH1 and NH2 in FH-Z8, respectively, which are relatively larger than those of the twin-tapered FH-T7 reported in our previous publication. FH-Z8 could gel dichloroethane with the critical gelation concentrations (CGCs) of 0.14 wt %, and spontaneously crystallization from its gel upon storage at room temperature. It is believed that the linear-shaped building block containing bi-dihydrazide units might find wide applications in the development of new self-assemblies, material science, and construction of various nanostructures.

5. Experimental section

5.1. Characterization

^{1}H NMR spectra were recorded with Bruker Avance 500 MHz spectrometer. FTIR spectra were recorded with a Perkin–Elmer spectrometer (Spectrum One B). The samples were pressed tablets with KBr. Mass spectra were obtained by MALDI-TOF mass spectrometry. SEM observations were taken with a JSM-6700F apparatus. X-ray diffraction (XRD) was carried out with a Bruker Avance D8 X-ray diffractometer.

Oxalyl acid N',N'-di(4-(2-ethylhexyloxy)benzoyl)-hydrazide. ^{1}H NMR: (500 MHz, $CDCl_3$), (ppm, from TMS): 10.0 (s, 2H); 8.7 (s, 2H); 7.81 (d, 4H, J=8.8 Hz); 6.95 (d, 4H, J=8.8 Hz); 3.91–3.89 (m, 4H); 1.77–1.73 (m, 2H); 1.51–1.39 (m, 8H); 1.34–1.31 (m, 8H); 0.95–0.90 (m, 12H).

FTIR (KBr disc, cm^{-1}): 3383, 3314, 3272, 2959, 2927, 2870, 2854, 1700, 1683, 1658, 1631, 1606, 1573, 1559, 1490, 1464, 1441, 1417, 1390, 1314, 1292, 1259, 1244, 1177, 1119, 1080, 1029, 1014, 967, 920, 840, 816, 779, 762, 752, 726, 694, 674, 654, 645, 632.

Anal. Calcd for $C_{32}H_{46}N_4O_6$: C, 65.96; H, 7.96; N, 9.61. Found C, 65.75; H, 8.12; N, 9.70.

MALDI-TOF MS: m/z: calcd for: 582.3, found: 582.6.

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Supplementary data

It includes gelation properties of FH-Z8 in different solvents. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.013.

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