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# Fluorescence-Enhanced Organogels and Mesomorphic Superstructure Based on Hydrazine Derivatives

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New low-molecular-mass organic gelators (LMOGs) bearing hydrazine linkage and end-capped by phenyl, namely 1,4bis[(3,4-bisalkoxyphenyl)hydrozide]phenylene (BPH-n, n = 4, 6, 8, 10), were designed and synthesized. These organogelators have shown great ability to gel a variety of organic solvents to form stable organogels with the critical gelation concentration as low as  $8.7 \times 10^{-4}$  mol L<sup>-1</sup> (0.06 wt %). The formed gel has a high gel-sol transition temperature ( $T_{gel}$ ) at low gelation concentration. Aggregation-induced emission (AIE) has been observed after gelation though conventional chromophore units not incorporated in BPH-n. The fluorescence quantum yields of xerogel are 2 orders higher than that of dilute solution. In addition, the BPH-n (n = 6, 8, 10) exhibited thermotropic hexagonal column (Col<sub>h</sub>) mesophase, which are stable at room temperature as revealed by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) studies.

#### Introduction

Self-assembled systems, such as supramolecular gels<sup>1</sup> and liquid crystals (LCs),<sup>2</sup> are fascinating organized soft materials that can respond to external stimuli such as temperature, electrical pulses, light, and chemicals. In recent years, low-molecular-mass organic gelators (LMOGs) which could both gelate solvents and exhibit thermotropic mesomorphic behaviors received much attention from both theoretical and practical viewpoints. Generally speaking, there seems to be some inherent relationship between the LMOGs and LCs.<sup>3,4</sup> To achieve a gel/mesomorphic state, a balance is required between the tendency of the molecules to dissolve/melt and to aggregate. The shape of a molecule has an important effect on self-assembly. It is relatively rare to find rodlike compounds capable of both gelling solvents and exhibit-

ing thermotropic mesomorphic behaviors, whereas this is the usual case for some wedge-shaped or disklike molecules.<sup>4-13</sup>

Among the noncovalent interactions, hydrogen bonding was most commonly used to direct the self-assembling process because of their strength, directionality, reversibility, and selectivity. Peptide, amino acid, amide, and urea groups have been widely employed as building blocks to afford supramolecular gels and liquid crystals. In earlier reports, a star-shaped gelator containing amide tethers exhibited thermotropic cubic and columnar mesophases.<sup>4</sup> It was confirmed that the aggregation in the organogels and microsegregation in the mesophase could be tuned by inter- to intramolecular hydrogen bonds. Replacing the metallic luminophores by purely organic fluorophores,<sup>5</sup> these star-shaped molecules exhibited strong fluorescence in the gels and mesophases. Li et al. reported a series of bisurea-functionalized naphthalene derivatives to develop thermotropic liquid crystal and switchable fluorescent organogel systems, which are sensitive to temperature and chemical stimuli.<sup>6</sup> Furthermore, a new type of LMOGs, namely 5-cyano-2-(3, 4, 5-trialkoxybenzoylamino)tropones, exhibited hexagonal columnae order with identical lattice parameters in both their liquid crystal phase and gel states.<sup>7</sup> As noted by Mori, intermolecular hydrogen bonding between the tropone carbonyl group and NH of the amide part plays a crucial role. Analogously, amino acid based dendrons have been confirmed to give rise to gel, lyotropic, and thermotropic liquid crystal states with a hexagonal columnar arrangement.<sup>8</sup>

In contrast, little attention has been paid to LMOGs and LCs based on hydrazide derivatives. In our previous work, it was demonstrated that intermolecular hydrogen bonding was still interacting in the SmA phase and played important roles in stabilizing the mesophase<sup>9</sup> and organogels<sup>10</sup> of hydrazide derivatives. Furthermore, achiral wedge-shaped<sup>11</sup> and twin-tapered<sup>12,13</sup> compounds containing dihydrazide groups showed thermotropic mesophase and strong gelation ability in organic solvents. Both left- and right-handed helical ribbons with nonuniform helical pitch were observed after the formation of organogels.<sup>11,13</sup>

Many efforts have been devoted to the development of gels with optical absorption or fluorescence because of the inherent

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optoelectronic properties.<sup>4–6,14–18</sup> For example, Shinkai and coworkers reported a novel visible-light-harvesting organogel system utilizing the 1D alignment nature of perylene-containing cholesterol-based gelators.<sup>15a</sup> In a recent report, Ajayaghosh et al. demonstrated gelation-assisted trapping of fluorescent supramolecular architectures in a polymer film and its application in erasable thermal imaging.<sup>15b</sup> Fluorescent gelators possessed the AIE feature attracted extremely much attention since organogels are thermoreversible, and accordingly thermal fluorescence modulation can be realized.<sup>4–6,16</sup> As a result, these fluorescent organogels based on molecular assemblies can be applied as model systems for light-emitting diodes,<sup>15a</sup> fluorescence sensors,<sup>1a,17,21</sup> and other optoelectronic devices. A number of possible mechanistic pathways, including excimers/exciplex formation,<sup>16a,16e,19</sup> conformational planarization,<sup>16b,18</sup> J-aggregate formation,<sup>16c,16d,18</sup> restriction of intramolecular rotation (RIR),<sup>16d,16e,20</sup> and twisted intramolecular charge transfer (TICT),<sup>20</sup> were considered to be responsible for the AIE effect.

In this context as part of our continuing effort in hydrazide derivatives, a novel class of symmetric dumbbell-shaped molecules, namely 1,4-bis[(3,4-bisalkoxyphenyl)hydrozide]phenylene (BPH-n, n = 4, 6, 8, 10) (see Scheme 1), was designed. The compounds showed thermotropic columnar mesophase and excellent gelation ability in organic solvents. The formed gel has a high  $T_{gel}$  at low gelation concentration. Interestingly, enhanced fluorescence emission was observed after gelation, although the solution of BPH-n was almost nonfluorescent. It was attributed to the combination of the partial double-bond properties of C–N bonds in the hydrazide group, the restricted intramolecular rotational motions in aggregate state, and J-aggregation by hydrogenbonding interactions between the hydrazide groups.

### **Experimental Section**

**Characterization.** <sup>1</sup>H NMR spectra were recorded with a Mercury-300BB 300 MHz spectrometer, using tetramethylsilane

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 Table 1. Thermal Transitional Properties of BPH-n<sup>a</sup> Transitional Temperatures (°C) and the Enthalpies of Transition (kJ/mol, in Parentheses)

compound	first heating	first cooling		
BPH-4	Cr 253 (72.53) I	I 243 (65.04) Cr		
BPH-6	Cr 207 (55.64) Col <sub>h1</sub> 254 (5 51) I	I 247 (5.12) Col <sub>h1</sub> 185 (17.22)		
BPH-8	$Cr 193 (65.48) Col_{h1}$ 264 (6 69) I	I 257 (6.51) Col <sub>h1</sub> 176 (9.11)		
BPH-10	Cr 197 (49.03) Col <sub>h1</sub> 253 (4.96) I	$I 241 (4.98) \operatorname{Col}_{h1} 163 (7.53) Col_{h2}$		

<sup>*a*</sup> Cr, Col<sub>h</sub>, and I indicate crystalline state, hexagonal columnar phase, and isotropic liquid, respectively.



Figure 1. Pseudo-focal-conic fan-shaped textures of the hexagonal columnar phase of BPH-10 at 205 °C ( $400 \times$ ).

(TMS) as an internal standard. UV-vis absorption spectra were recorded on a Shimazu UV-160 spectrometer, and photoluminescence was measured on a Perkin-Elmer LS 55 spectrometer. Field emission scanning electron microscopy (FE-SEM) images were taken with a JSM-6700F apparatus. Samples for FE-SEM measurement were prepared by wiping a small amount of gel onto a silicon plate followed by evaporating the solvent at ambient temperature. Phase transitional properties were investigated with a Netzsch DSC 204. The rate of heating and cooling was 10 °C min<sup>-1</sup>; the weight of the sample was about 3 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. Texture observation was conducted on a Leica DMLP polarizing optical microscope equipped with a Leitz 350 microscope heating stage. X-ray diffraction was carried out with a Bruker Avance D8 X-ray diffractometer. FT-IR spectra were recorded with a Perkin-Elmer spectrometer (Spectrum One B); the sample was in the form of a pressed tablet with KBr. The gelator was mixed in a capped sealed test tube [3.5 cm (height)  $\times$  0.5 cm (radius)] with the appropriate amount of solvent, and the mixture was heated until the solid was dissolved. The sample vial was cooled to 4 °C and then turned upside down. When a clear or slightly opaque gel formed, the solvent therein was immobilized at this stage.

**Synthesis.** The synthesis of BPH-*n* is similar to that of FH-T*n*.<sup>12</sup> The detailed description of the synthesis and purification of the intermediate compounds can be found in our previous work.<sup>12,13,22</sup> The obtained dihydrazide derivatives were purified by repeated recrystallization from tetrahydrofuran for further <sup>1</sup>H NMR, FT-IR measurements, and elemental analysis; yield > 60%. (Because of the poor solubility, the <sup>1</sup>H NMR measurement of BPH-10 was not performed).

1,4-Bis[(3,4-bisbutyloxyphenyl)hydrozide] phenylene (BPH-4). <sup>1</sup>H NMR (300 MHz, DMSO) (ppm, from TMS): 10.61 (s, 2H);

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Figure 2. X-ray diffraction patterns of BPH-6 (a), -8 (b), and -10 (c).

10.41 (s, 2H); 8.04 (s, 4H); 7.57–7.53 (m, 4H); 7.08 (d, 2H, J = 8.4 Hz); 4.07–4.01 (m, 8H); 1.77–1.68 (m, 8H); 1.53–1.40 (m, 8H); 0.97–0.93 (m, 12H). FT-IR (KBr, pellet, cm<sup>-1</sup>): 3192, 3020, 2972, 1659, 1601, 1573, 1509, 1459, 1393, 1340, 1273, 1223, 1146, 1124, 1067, 997, 867, 717, 642, 507. Elemental analysis: calculated for C<sub>38</sub>H<sub>50</sub>N<sub>4</sub>O<sub>8</sub> (%): C, 66.07; H, 7.30; N, 8.11. Found: C, 66.23; H, 7.44; N, 8.02.

1,4-Bis[(3,4-bishexyloxyphenyl)hydrozide]phenylene (BPH-6). <sup>1</sup>H NMR (300 MHz, DMSO) (ppm, from TMS): 10.61 (s, 2H); 10.41 (s, 2H); 8.04 (s, 4H); 7.56–7.52 (m, 4H); 7.07 (d, 2H, J = 8.7Hz); 4.06–4.0 (m, 8H); 1.78–1.69 (m, 8H); 1.47–1.43 (m, 8H); 1.35–1.30 (m, 16H); 0.91–0.86 (m, 12H). FT-IR (KBr, pellet, cm<sup>-1</sup>): 3192, 3020, 2954, 2929, 2872, 2858, 1659, 1602, 1573, 1509, 1459, 1393, 1339, 1271, 1222, 1147, 1124, 1070, 1001, 867, 716, 640, 507. Elemental analysis: calculated for C<sub>46</sub>H<sub>66</sub>N<sub>4</sub>O<sub>8</sub> (%): C, 68.80; H, 8.28; N, 6.98. Found: C, 68.89; H, 8.44; N, 6.77.



**Figure 3.** Chemical shifts of NH-1 and NH-2 of BPH-6 ( $1.78 \times 10^{-3}$  mol L<sup>-1</sup>) in 20% DMSO- $d_6$ /CDCl<sub>3</sub> vs temperature (500 MHz; NH-1: near to alkoxyphenyl; NH-2: near to central phenyl).



Figure 4. Temperature-dependent FT-IR spectra of BPH-10 during first heating run in the range of  $3500-1200 \text{ cm}^{-1}$ .



**Figure 5.** Plot of v(N-H) wavenumbers and hydrogen bond length of N-H...O=C of BPH-10 vs temperature.

*1,4-Bis*[(*3,4-bisoctyloxyphenyl*)*hydrozide*]*phenylene* (*BPH-8*). <sup>1</sup>H NMR (300 MHz, DMSO) (ppm, from TMS): 10.61 (s, 2H); 10.41 (s, 2H); 8.04 (s, 4H); 7.56–7.52 (m, 4H); 7.07 (d, 2H, *J* = 8.4 Hz); 4.05–3.99 (m, 8H); 1.78–1.69 (m, 8H); 1.47–1.43 (m, 8H);

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Table 2. Gelation Properties of BPH-n (n = 4, 6, 8, 10)<sup>a,b</sup>

compound	ethanol	THF	chloroform	DCE	benzene	toluene	DMF	DMSO	
BPH-4 BPH-6	$5.80 \times 10^{-3}$ $2.24 \times 10^{-3}$	$6.52 \times 10^{-3}$ $1.12 \times 10^{-2}$	$7.58 \times 10^{-3}$ $1.86 \times 10^{-3}$	$1.35 \times 10^{-2}$ $1.09 \times 10^{-3}$	$P \\ 8.75 \times 10^{-3}$	$P = 6.48 \times 10^{-3}$	S S	S S	
BPH-8 BPH-10	$\frac{1.64 \times 10^{-3}}{1.36 \times 10^{-3}}$	$\begin{array}{c} 7.87 \times 10^{-3} \\ 4.38 \times 10^{-3} \end{array}$	$\begin{array}{c} 1.31 \times 10^{-3} \\ 8.73 \times 10^{-4} \end{array}$	$1.02 \times 10^{-3}$ P	$\begin{array}{c} 5.76 \times 10^{-3} \\ 3.42 \times 10^{-3} \end{array}$	$\begin{array}{c} 3.79 \times 10^{-3} \\ 1.69 \times 10^{-3} \end{array}$	$\begin{array}{c} 8.26 \times 10^{-3} \\ 5.52 \times 10^{-3} \end{array}$	S P	
							L		

<sup>*a*</sup> Values denote the minimum gel concentration (mol  $L^{-1}$ ) necessary for organogelation. I: insoluble, S: soluble, P: precipitation. <sup>*b*</sup> THF, DCE, DMF, and DMSO indicate tetrahydrofuran, 1,2-dichloroethane, dimethylformamide, and dimethyl sulfoxide.



**Figure 6.** Concentration-dependent melting temperature of BPH-8 gels in 1,2-dichloroethane, chloroform, and tetrahydrofuran.

1.30–1.27 (m, 32H); 0.88–0.84 (m, 12H). FT-IR (KBr, pellet, cm<sup>-1</sup>): 3187, 3020, 2954, 2924, 2872, 2851, 1660, 1601, 1572, 1510, 1459, 1393, 1339, 1271, 1224, 1147, 1124, 1067, 997, 867, 716, 641, 509. Elemental analysis: calculated for  $C_{54}H_{82}N_4O_8$  (%): C, 70.86; H, 9.03; N, 6.12. Found: C, 70.67; H, 9.08; N, 6.23.

1,4-Bis[(3,4-bisdodecyloxyphenyl)hydrozide]phenylene (BPH-10). FT-IR (KBr, pellet, cm<sup>-1</sup>): 3182, 3022, 2954, 2922, 2872, 2850, 1659, 1602, 1572, 1510, 1460, 1394, 1341, 1273, 1224, 1147, 1124, 1071, 997, 867, 718, 643, 504. Elemental analysis: calculated for  $C_{62}H_{98}N_4O_8$  (%): C, 72.48; H, 9.61; N, 5.45. Found: C, 72.53; H, 9.36; N, 5.68.

### **Results and Discussion**

Mesophase Properties of the Compounds. The phase behavior of BPH-n was studied by POM, DSC, and XRD. The phase transition temperatures and the associated enthalpic changes for BPH-n (n = 4, 6, 8, 10) in first heating and cooling are summarized in Table 1. It can be seen that the phase behaviors were strongly affected by the length of the flexible terminal chains. BPH-4 is nonmesomorphic. However, BPH-6 showed two transitions at 207  $^{\circ}\mathrm{C}$  (55.64 kJ/mol) and 254  $^{\circ}\mathrm{C}$  (5.51 kJ/mol) corresponding to Cr-Colh1 and Colh1-I transitions during heating, while two exothermic peaks at 247 °C (5.12 kJ/mol) and 185 °C (17.22 kJ/mol) corresponding to I-Colh1 and  $Col_{h1}-Col_{h2}$  transitions upon cooling from its isotropic phase. Similar phase behaviors were observed for the higher homologues of BPH-n (n = 8, 10) (Table 1 and Figure S1). It should be mentioned that no crystallization was observed for the higher homologues of BPH-n (n = 6, 8, 10) even when they were cooled to 20 °C at cooling rate of 10 °C/min. Figure 1 shows the optical texture of BPH-10 in its Col<sub>h1</sub> phase on the cooling run (10 °C/min). The typically pseudo focal-conic texture with linear birefringent defects and the black areas, which are homeotropic domains with the columns aligned perpendicular to the glass substrates, suggesting the characteristic of hexagonal columnar phase of BPH-10.

Variable temperature X-ray diffraction was performed on these tetracatenar dihydrazide derivatives to get further information on molecular arrangements in their mesophases. Figure 2a shows the XRD patterns of BPH-6 in its Col<sub>h1</sub> (at 220 °C), Col<sub>h2</sub> (at 25 °C), and Colh2 phase hold for 5 months. The characteristic patterns of Col<sub>h1</sub> phase at 220 °C during first cooling run consists of two sharp peaks (28.1, 14.0 A) in the low-angle region and a diffuse broad halo with maximum at about 4.5 Å, which is characteristic of the liquidlike arrangement of the aliphatic. The peaks in the small-angle region were assigned to (100) and (200) reflection, thus the two-dimensional hexagonal arrangement of the columns with a lattice parameter of a = 33.5 Å. At room temperature, some additional diffraction peaks at both low-angle (29.5 Å) and wide-angle regions (17.0, 14.7, 8.9, and 4.9 Å) were observed in the XRD patterns, which was assigned to  $Col_{h2}$  phase. The *d* values are slightly larger than that in its Colh1 phase, which revealed that the packing modes of the aggregates in both cases are the same. Interestingly, the columnar order of the Col<sub>h2</sub> phase could be retained even after being held at room temperature for more than 5 months (Figure 2a). Likewise, X-ray diffraction measurements of BPH-n (n = 8, 10) was performed (Figure 2b,c). Similar phase structures were also observed for BPH-n (n = 8, 10), and the XRD results of BPH-n (n = 6, 8, 10) in the columnar phases are listed in Table S1.

Tetracatenar columnar mesophases was considered a slice of column contain more than one molecules. According to these information mentioned above, the average number of molecules  $(\mu)$  in a column slice can be calculated through the equation  $\mu = (3^{1/2}N_Aa^2h\rho)/2M$  for the hexagonal phase, where  $N_A$  is Avogadro's number,  $a_r$ ,  $b_r$ , and a are lattice parameters, h is the intracolumnar periodicity,  $\rho$  is the density (assumed to be 1 g cm<sup>-3</sup>), and M is the molecular weight of the compound.<sup>27</sup> For these materials, it can be estimated that approximately three molecules (3.0–3.3, as calculated) are included in a unit cell on average (Table S1).

Intermolecular Hydrogen Bonding in BPH-n. <sup>1</sup>H NMR spectroscopic study can give more information about the selfassembly process. Unfortunately, the <sup>1</sup>H NMR diluting experiments were not performed for BPH-n in CDCl<sub>3</sub> because of its poor solubility at room temperature and strong gelation tendency at low concentration. Temperature-dependent <sup>1</sup>H NMR spectroscopic experiments were performed to explore the hydrogenbonding motif. Generally, internally hydrogen-bonded amides are expected to show a much smaller shift with temperature  $(< 3.0 \times 10^{-3} \text{ ppm K}^{-1})$  compared to those directed externally and accessible for hydrogen bonding to a polar solvent (>4.0  $\times$  $10^{-3}$  ppm K<sup>-1</sup>).<sup>36</sup> As shown in Figure 3, both NH-1 (near to alkoxyphenyl) and NH-2 (near to central phenyl) of BPH-6 showed large shifts ( $5.45 \times 10^{-3}$  and  $5.43 \times 10^{-3}$  ppm K<sup>-1</sup>, respectively) with temperature in 20% DMSO-d<sub>6</sub>/CDCl<sub>3</sub>, suggesting the primary involvement of N-H protons in intermolecular hydrogen bonding.

Intermolecular hydrogen bonding in BPH-*n* was further confirmed by temperature-dependent FT-IR spectroscopy. Table S2



Figure 7. SEM images of xerogel from (a) BPH-4 in 1,2-dichloroethane (0.9 wt %), (b) BPH-6 in 1,2-dichloroethane (0.15 wt %), (c) BPH-8 in 1,2-dichloroethane (0.15 wt %), (d) BPH-8 in chloroform (0.15 wt %), (e) BPH-8 in benzene (0.7 wt %), (f) BPH-8 in dimethylformamide (0.9 wt %), (g) BPH-8 in tetrahydrofuran (0.9 wt %), and (h) BPH-8 in toluene (0.6 wt %). The original larger SEM images are in the Supporting Information.

presents the assignments of infrared frequencies for BPH-10 at 25 °C.9,12 At room temperature, BPH-10 exhibits characteristic bands of N-H stretching vibrations of hydrazide group at 3182  $cm^{-1}$  and amide I bands at 1659 (weak) and 1602  $cm^{-1}$  (strong), indicating that the majority of the N-Hs of the hydrazide group are associated with the C=O groups via N-H...O=C hydrogen bonding in the crystalline phase.<sup>9,12,24</sup> Moreover, these conclusions were further supported by the fact that the N-H stretching vibration band and amide I bond became weaker and shifted to higher frequencies upon heating. Figure 4 shows the FT-IR spectra of BPH-10 at different temperatures during first heating run. The blue shift of C=O stretching vibration was companied by an increase in intensity at around 1689 and 1663  $\text{cm}^{-1}$ , while the absorption at  $1602 \text{ cm}^{-1}$  diffused and decreased, and a sharp decrease of the absorption intensity at columnar-isotropic transition. The v(N-H) became weaker and broader and shifted to higher frequencies as well as the hydrogen-bonding length<sup>28</sup> of N-H...O=C increasing upon heating, as shown in Figure 5. The



**Figure 8.** XRD patterns of BPH-8: (a) xerogel from chloroform (0.5 wt %) and (b) crystals.

wavenumbers of v(N-H) of BPH-10 are at around 3185, 3233, and 3309 cm<sup>-1</sup> in the crystalline state, Col<sub>h</sub> phase, and isotropic phase, respectively. The calculated hydrogen-bonding length of N-H<sup>...</sup>O=C was 1.97 Å at 25 °C, which is in the range of moderate hydrogen bonds.<sup>28</sup> It increased slowly with temperature within the crystalline and columnar phase, while jumped to 2.26 Å, which indicated a weak hydrogen bonding in the isotropic state.

Gelation Properties. The presence of two hydrazide tethers on the amphiphilic molecules and the formation of columnar aggregates in the mesomorphic state prompted us to probe their gelation ability. Their gelation potential was examined for eight different organic solvents, and the minimum gel concentrations are summarized in Table 2. It can be found that the length of the terminal alkoxy chains greatly affected the gelation ability. Compounds BPH-6, -8, and -10 bearing the longer terminal chains can gelate 6-7 kinds of solvents among the 8 solvents tested herein. The gelation ability is superior in some solvents with minimum gelation concentrations as low as  $8.7 \times 10^{-4}$  mol L<sup>-1</sup> (0.06 wt %), and therefore, compounds BPH-6, -8, and -10 can be considered as supergelators. In contrast, the compound BPH-4 with shorter terminal chains formed the organogels in three kinds of organic solvents, and the required minimum gel concentration is much higher. The only exception is tetrahydrofuran, where BPH-4, -6, -8, and -10 formed organogels with the minimum gelation concentration of  $6.52 \times 10^{-3}$ ,  $1.12 \times 10^{-2}$ ,  $7.87 \times 10^{-3}$ , and  $4.38 \times 10^{-3}$  mol L<sup>-1</sup>, respectively. The reason is not conclusive but likely to be the poor solubility of BPH-4 in THF. Moreover, the sol-gel transition is fully thermoreversible even after several cycles of heating and cooling. The organogels are remarkably stable which can be stored for months showing no sign of decomposition.

Figure 6 shows the gel-sol transition temperature ( $T_{gel}$ ) of BPH-8 gels in tetrahydrofuran, 1,2-dichloroethane, and chloroform as a function of concentration.  $T_{gel}$  values were determined by the "falling drop" method.<sup>23</sup> The  $T_{gel}$  of BPH-8 in DCE increases from 60 °C ( $1.42 \times 10^{-3} \text{ mol L}^{-1}$ ) to 108 °C ( $2.73 \times 10^{-2} \text{ mol L}^{-1}$ ), which are higher than the boiling point of 1,2dichloroethane (83.5 °C). The  $T_{gel}$  of BPH-8 in THF and chloro-

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**Figure 9.** Photographs showing progressive gelation of  $0.1 \text{ wt } \% (1.63 \times 10^{-3} \text{ mol } \text{L}^{-1})$  BPH-8 in chloroform under ultraviolet light (365 nm) illumination at different time periods (left: xerogel of BPH-8 from chloroform; middle: gel of BPH-8 in chloroform; right: the sol-gel transition of BPH-8 in chloroform).

form have similar behaviors, and among them, the  $T_{gel}$  values appear in the order of 1,2-dichloroethane > chloroform > tetrahydrofuran.

In order to investigate the aggregation morphology of the organogels, the xerogels of BPH-n were prepared and subjected to scanning electron microscope (SEM). As shown in Figure 7a-c, xerogel of BPH-4 from 1,2-dichloroethane consists of flexible ribbons with the width of  $0.5-2 \mu m$ , while BPH-6 and BPH-8 xerogel showed 3D cross-linking network, in which bundles of straight wirelike fibers with the width of  $0.2-1 \,\mu\text{m}$  are observed. The more entangled and dense fiber morphology is observed for BPH-6 and -8 compared to that of BPH-4 in 1,2-dichloroethane, indicating that the interactions between individual fibers are stronger in BPH-6 and -8 than BPH-4. Thus, the gelation efficiency and stability are qualitatively in agreement with the observed morphology. The SEM images of BPH-8 in different solvents are shown in Figure 7c-h. All SEM images show interconnected networks of fibers with the width of  $0.2-3 \,\mu m$ and tens to hundreds of micrometers in length. The formation of fibers in the gels indicates that the self-assembly is driven by strong directional intermolecular interactions.

Figure 8 shows the X-ray diffraction patterns of BPH-8 crystal and xerogel from chloroform. The XRD pattern of BPH-8 crystal showed one sharp peak (30.6 Å) in low-angle range, several broad weak peaks (20.5, 15.5, 9.2, 8.0 6.7, and 5.1 Å) in wide-angle regions, and two diffuse broad peaks with a maximum at about 4.2 and 4.5 Å, suggesting the coexistence ordered and disordered feature. The broad peak at 4.5 Å is characteristic of the liquidlike arrangement of the aliphatic chains,<sup>32</sup> while that at 4.2 Å might be attributed to the repeat distance of hydrazide

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**Figure 10.** Absorption (a) and emission (b) spectra of BPH-8 in chloroform at  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. Emission spectra of BPH-8 gel in chloroform at 0.1 wt % (c) and xerogel from chloroform (d). Excitation wavelength ( $\lambda_{ex}$ ) = 320 nm.

units in stacking.<sup>31</sup> A similar arrangement can also be observed for the BPH-8 xerogel from chloroform, indicating a similar supramolecular arrangement in both cases. At room temperature, BPH-8 exhibits characteristic bands of N–H stretching vibrations of hydrazide group (Figure S2) at 3187 cm<sup>-1</sup> (the absence of free N–H, a relatively sharp peak with the frequency higher than 3400 cm<sup>-1</sup>) and amide I bands at 1660 (weak) and 1601 cm<sup>-1</sup> (strong), indicating that the N–H groups are associated with C=O groups via N–H<sup>···</sup>O=C hydrogen bonding in crystal and xerogel states.<sup>9,12,24</sup>

Aggregation-Induced Emission. Interestingly, although the dilute solution of BPH-*n* was almost nonfluorescent, a strongly enhanced fluorescence emission was induced by the gelation process. The gel–sol transition of the systems, as well as the fluorescent emission, is reversibly controlled by a change of the temperature. Herein, we typically discuss the fluorescent properties of BPH-8 gel (chloroform, 0.1 wt %) in detail. Figure 9 shows progressive gelation-induced-fluorescence enhancement under ultraviolet light (365 nm) illumination at different time periods, e.g. from 2 to 10 min. BPH-8 was completely dissolved in chloroform when heated to its boiling point. The fluid solution was almost nonfluorescent under the illumination of UV light. Upon cooling to room temperature, immobile gels formed within 10 min, showing macroscopical fluorescence emission in contrast to its isotropic solution.

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Table 3. Photophysical Properties of BPH-*n* Dilute Solution (Chloroform,  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) and Xerogels at Room Temperature

compound		fluorescence				
	absorption $\lambda_{abs} (nm)^a$	$\lambda_{\rm em}  ({\rm nm})^a$	quantum yield <sup>a</sup>	$\lambda_{\rm em} \left( {\rm nm} \right)^b$	quantum yield <sup>b</sup>	
BPH-4	304	372, 392	$0.13 \times 10^{-2}$	438	$22 \times 10^{-2}$	
BPH-6	305	371, 392	$0.17 \times 10^{-2}$	439	$19 \times 10^{-2}$	
BPH-8	304	373, 394	$0.16 \times 10^{-2}$	439	$18 \times 10^{-2}$	
BPH-10	306	373, 393	$0.16 \times 10^{-2}$	438	$21 \times 10^{-2}$	

<sup>*a*</sup> In chloroform solution. <sup>*b*</sup> Xerogels from chloroform. The quantum yields of xerogels were obtained in a calibrated integrating sphere.<sup>29a</sup> The quantum yields of solution were determined by using quinine sulfate in 0.1 M sulfuric acid as a reference.<sup>29b</sup>

The absorption spectrum of BPH-8 in dilute solution (chloroform,  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) exhibited a maximum at 304 nm (Figure 10a). As shown in Figure 10b, BPH-8 in the dilute solution (chloroform,  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) exhibited a weakly split structural emission band (373 and 394 nm) which was attributed to the characteristic monomer emission. The structureless broad emission centered at 439 nm was observed in the gel state (0.1 wt % in chloroform), with an impressive increase in the photoluminescence intensity compared with that in the solution (Figure 10c). As shown in Figure 10d, the xerogel developing from chloroform (0.1 wt %) exhibited blue fluorescence emission ( $\lambda_{\rm em} \approx 439$  nm) with the fluorescence quantum yield  $\Phi_{\rm F}$  about 18.0%, which is 113-fold higher than that ( $\Phi_{\rm F} \approx 0.16\%$ ) of the chloroform dilute solution ( $1.0 \times 10^{-5}$  mol L<sup>-1</sup>). Herein, the decrease of the fluorescent intensity in a high concentration by the inner filter effect<sup>33</sup> was neglected. The remarkable fluorescence enhancement from gels was unambiguously assigned to the phenomenon of aggregation-induced emission (AIE).<sup> $\overline{4}-6,16,20$ </sup> The absorption and fluorescence data along with fluorescence quantum yields of BPH-n (n = 4, 6, 8, 10) are summarized in Table 3. All compounds studied here exhibit weak fluorescence in chloroform dilute solution with quantum vields lower than 0.17%, whereas 2 orders higher in quantum yields were observed for xerogels compared to the corresponding solution quantum vields.

To obtain insights into a correlation relationship between the emission and the aggregation mode along with the sol-gel transition, temperature-dependent fluorescence spectra of BPH-8 with a high concentration in the 1,2-dichloroethane (1.2 mg  $mL^{-1}$ ) were measured from 80 to 25 °C. Its solution was almost nonfluorescent under the illumination of UV light, whereas its gel was highly fluorescent. As shown in Figure 11, the emission spectrum obtained from the gel of 1,2-dichloroethane at 25 °C displayed a strong peak at 439 nm. Upon heating, the emission spectrum obtained from the partial gel at 45 °C shown an additional emission band at 415 nm. Above 75 °C, the gels turned into fluid solution. A hypsochromic shift of the emission bands was observed from 439 nm in gel state (at 25 °C) to 402 and 423 nm in solution (at 80 °C) with the evident decreases of the fluorescence intensity. These results are in line with the formation of molecular J-aggregations.<sup>6,16c,16d,34</sup> This interesting property would provide an opportunity to modulate the fluorescent emission by conveniently controlling the aggregation degree.<sup>35</sup>

Isolated BPH-*n* molecules in the dilute chloroform solution are considered to be significantly twisted because the two aromatic



**Figure 11.** PL spectra of BPH-8 in 1,2-dichloroethane solution (at 80 °C), partial gel (from 45 to 75 °C), and gel state (below 40 °C) at the same concentration  $(1.2 \text{ mg mL}^{-1})$  excited at 320 nm.

rings were joined by the flexible linking group (-CO-NH-), which generally suppresses the radiative decay channel.<sup>21,25</sup> Through density functional theory (DFT) geometry optimization,<sup>30</sup> we found that the bond length of C-N in the hydrazide group is 1.35 Å, which is much shorter than the theoretical value of the C–N single bond (1.47 Å), while almost the same as that of C=N (1.34 Å). This indicates that the C-N bonds in the hydrazide group possess partial double bond properties and can be effectively conjugated with the aromatic rings, which must be the origin of the light emission. The distorted geometry makes the backbone deviate from a conjugated plane, which means that free intramolecular torsional motion in the solution can lead to fast nonradiative relaxation and reduce the PL quantum yield in the solution.<sup>19,20</sup> In the aggregate state, however, the free torsional motion is obviously restricted by supramolecular interactions resulting in the closure of the nonradiative decay channel and enhanced fluorescence emission.<sup>19,20,26</sup> Consequently, aggregation-induced emission phenomenon in the gelation process was attributed to the synergistic effect of the restricted intramolecular rotational motions and J-aggregate formation.

## Conclusion

We have prepared a new series of hydrazine-based derivatives BPH-n (n = 4, 6, 8, 10). BPH-n (n = 6, 8, 10) with longer terminal chains displayed Col<sub>h</sub> mesophase, in which the microsegregation effect and intermolecular hydrogen bonding between hydrazide groups played a crucial role in the formation of the columnar phase. The derivatives are capable of gelling a variety of organic solvents to form stable organogels via cooperative intermolecular hydrogen-bonding forces between hydrazine groups, with minimum gelation concentration as low as  $8.7 \times 10^{-4}$  mol L<sup>-1</sup> (0.06 wt %). BPH-n showed gelation-induced enhanced fluorescence

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emission, and it was attributed to the restricted intramolecular rotational motions and J-aggregate formation.

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**Supporting Information Available:** DSC curves of BPH-*n* (n = 6, 8, 10) (Figure S1); FT-IR spectra of BPH-8 (Figure S2); WAXD results for BPH-*n* (Table S1); assignments of infrared frequencies for BPH-10 (Table S2); original larger SEM images of Figure 7a-h. This material is available free of charge via the Internet at http://pubs.acs.org.