

## Supporting Information

### **Controllable Multicolor Switching of the Oligopeptide-based Mechanochromic Molecules: From Gel Phase to Solid Powder**

**Zhiyong Ma, Zhijian Wang, Zejun Xu, Xinru Jia,\* and Yen Wei**

*Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

*Department of Chemistry, Tsinghua University, Beijing 100084, China*

Mr. Z. Y. Ma and Z. J. Wang, Dr. Z. J. Xu, Prof. X. R. Jia

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Tel: +86-10-62752102 , Fax: +86-010-62751708

E-mail: [xrjia@pku.edu.cn](mailto:xrjia@pku.edu.cn)

Prof. Y. Wei

Department of Chemistry, Tsinghua University, Beijing, China.

## 1. Materials and General Methods

All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

<sup>1</sup>H NMR was recorded on the 400 MHz (Bruker ARX400) and <sup>13</sup>C NMR spectra were recorded on the Bruker 125 MHz spectrometer at room temperature with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. UV-vis spectra were acquired on the Hitachi U-4100 UV-vis spectrophotometer. Steady fluorescence spectra were performed on the Hitachi F-7000 fluorescence spectrophotometer. Fluorescence lifetime were acquired on the Lifespec-Red Picosecond Lifetime Spectrometer ( $\lambda_{\text{ex}}=372$  nm). 1D small angle X-ray scattering (SAXS) experiments were performed with a SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system. Circular Dichroism measurement was conducted on the J-810 Circular Dichroism Spectrometer (JASCO Corporation, Japan). Certain amounts of PHE-2 and PHE-5 powder were dissolved in ethyl acetate and CD measurements were performed at different temperatures. Differential scanning calorimetry (DSC) measurement was carried out by using TA instruments Q100 DSC. Fourier Infrared spectra were obtained on a Bruker Tensor 27 spectrometer.

## 2. Synthesis of the molecules of PHE-2 and PHE-5

### Compound 1

**RhB-NH<sub>2</sub>** (2.21 g, 4.6 mmol) and **Boc-PHE-PHE-OH** (2.25 g, 5.5 mmol) were dissolved in CHCl<sub>3</sub> (50 mL). After stirring at -15 °C (ice-salt bath) for 15 min, a CHCl<sub>3</sub> solution containing dicyclohexylcarbodiimide (DCC, 1.12 g, 5.5 mmol) and DMAP (0.10 g, 0.8 mmol) was added dropwise. The solution was kept stirring for 48 h, then the solvent was evaporated. The residue was purified by column chromatography (ethyl acetate/petroleum ether =1/1, v/v) to afford **compound 1** (white solid, yield 85%).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 7.87~7.85 (m, 1H, Ar-H), 7.45~7.43 (m, 2H, Ar-H), 7.24~7.23 (m, 1H, Ar-H), 7.21~7.15 (m, 6H, Ar-H), 7.07~7.05 (m, 4H, Ar-H), 6.53~6.51 (d, 1H, NH-), 6.37~6.32 (m, 4H, Ar-H), 6.27~6.24 (m, 2H, Ar-H), 5.05~5.03 (m, 1H, ArCH<sub>2</sub>CH-), 4.55~4.50 (m, 1H, ArCH<sub>2</sub>CH-), 3.34~3.32 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-), 3.21~3.19 (m, 1H, ArCH<sub>2</sub>-), 3.16~3.01 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 2.99~2.93 (m, 2H, ArCH<sub>2</sub>-), 2.83~2.78 (m, 1H, ArCH<sub>2</sub>-), 1.37 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C-), 1.18~1.15 (t, 12H, CH<sub>3</sub>CH<sub>2</sub>-).

<sup>13</sup>C NMR: (125 MHz, CDCl<sub>3</sub>) δ/ppm: 170.79, 169.83, 169.71, 153.73, 153.31, 153.24, 148.93, 136.91, 136.68, 132.76, 130.36, 129.43, 129.34, 128.57, 128.52, 128.49, 128.40, 128.11, 126.79, 126.71, 123.84, 122.96, 108.23, 104.70, 97.74, 80.01, 65.60, 55.81, 54.46, 44.37, 40.72, 39.55, 38.21, 28.27, 12.62.

ESI-MS Calcd. For C<sub>53</sub>H<sub>62</sub>N<sub>6</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 879.48036. Found: 879.47786.

### Compound 2

**Compound 1** (1.01 g, 1.15 mmol) was dissolved in dichloromethane, with trifluoroacetic acid (TFA, 1.6 mL, 21 mmol) added dropwise. The solution was stirred for 12 h, then the solvent and TFA were removed by evaporation. The residue was dissolved in dichloromethane, and then triethylamine (1.4 mL, 10 mmol) was added to dissociate the amino for 10 min. Then **Boc-PHE-OH** (0.39 g, 1.5 mmol) was dissolved into the mixture. After stirring at -15 °C (ice-salt bath) for 15 min, a CHCl<sub>3</sub> solution

containing dicyclohexylcarbodiimide (DCC, 0.39 g, 1.9 mmol), DMAP (0.08 g, 0.7 mmol) and HOBt (0.03 g, 0.2 mmol) was added dropwise. The solution was kept stirring for 48 h before evaporation of the solvent. The residue was purified by column chromatography (ethyl acetate/petroleum ether =2/1, v/v) to afford **compound 2** (white solid, yield 90%).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 7.88~7.86 (m, 1H, Ar-H), 7.45~7.41 (m, 2H, Ar-H), 7.22~7.09 (m, 10H, Ar-H), 7.12~7.07 (m, 6H, Ar-H), 6.88~6.86 (b, 1H, NH), 6.59~6.57 (b, 1H, NH), 6.39~6.34 (m, 4H, Ar-H), 6.28~6.24 (m, 2H, Ar-H), 5.09~5.07 (m, H, ArCH<sub>2</sub>CH-), 4.63~4.61 (m, H, ArCH<sub>2</sub>CH-), 4.45~4.43 (m, H, ArCH<sub>2</sub>CH-), 3.36~3.30 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-), 3.19~3.14 (m, 2H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 3.08~3.05 (m, 2H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 3.01~2.92 (m, 5H, ArCH<sub>2</sub>-), 2.85~2.83 (m, H, ArCH<sub>2</sub>-), 1.38 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C-), 1.18~1.14 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>-).

ESI-MS Calcd. For C<sub>62</sub>H<sub>71</sub>N<sub>7</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 1026.54877. Found: 1026.54954.

### Compound 3

**Compound 2** (1.11 g, 1.08 mmol) was dissolved in dichloromethane, and trifluoroacetic acid (TFA, 1.6 mL, 21 mmol) was added dropwise. The solution was kept stirring for 12 h, then the solvent and TFA were removed by evaporation. The residue was dissolved in dichloromethane, and then triethylamine (1.2 mL, 8.6 mmol) was added to dissociate the amino for 30 min. Then **Boc-PHE-PHE-OH** (0.58 g, 1.4 mmol) was dissolved into the mixture. After stirring at -15 °C (ice-salt bath) for 15 min, a CHCl<sub>3</sub> solution containing dicyclohexylcarbodiimide (DCC, 0.32 g, 1.6 mmol), DMAP (0.05 g, 0.4 mmol) and HOBt (0.05 g, 0.4 mmol) was added dropwise. The solution was kept stirring for 72 h before evaporation of the solvent. The residue was purified by column chromatography using ethyl acetate as the eluent to afford **compound 3** (white solid, yield 60%).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 7.86~7.82 (m, 1H, Ar-H), 7.45~7.42 (m, 2H, Ar-H), 7.24~7.03 (m, 24H, Ar-H), 6.95~6.93 (m, 2H, Ar-H), 6.41~6.35 (m, 4H, Ar-H), 6.28~6.24 (m, 2H, Ar-H), 4.70~4.60 (m, 3H, ArCH<sub>2</sub>CH-), 4.50~4.48 (m, H, ArCH<sub>2</sub>CH-), 4.33~4.29 (m, H, ArCH<sub>2</sub>CH-),

3.33~3.30 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-), 3.14~3.16 (m, 2H, ArCH<sub>2</sub>-), 3.06~2.99 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 2.96~2.80 (m, 8H, ArCH<sub>2</sub>-), 1.34~1.29 (d, 9H, (CH<sub>3</sub>)<sub>3</sub>C-), 1.17~1.14 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>-).

ESI-MS Calcd. For C<sub>80</sub>H<sub>89</sub>N<sub>9</sub>O<sub>9</sub> [M+H]<sup>+</sup>:1320.68560. Found: 1320.68137.

## PHE-2

**Compound 1** (0.61 g, 0.69 mmol) was dissolved in dichloromethane and trifluoroacetic acid (TFA, 1.1 mL, 14 mmol) was added dropwise. The solution was kept stirring for 12 h, then the solvent and TFA were removed by evaporation. The residue was dissolved in dichloromethane, and then triethylamine (0.5 mL, 3.6 mmol) was added to dissociate the amino for 30 min. Then 1-pyrenecarboxylic acid (0.35 g, 1.4 mmol) was dissolved into the mixture. After stirring at -15 °C (ice-salt bath) for 15 min, a CHCl<sub>3</sub> solution containing dicyclohexylcarbodiimide (DCC, 0.31 g, 1.5 mmol) and HOBT (0.07 g, 0.5 mmol) was added dropwise. The solution was kept stirring for 96 h before evaporation of the solvent. The residue was purified by column chromatography (ethyl acetate/petroleum ether =2/1, v/v) to afford **PHE-2** (white solid, yield 55%).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.27~8.24 (m, H, Pyrene-H), 8.19~8.17 (m, 2H, Pyrene-H), 8.09~7.98 (m, 5H, Pyrene-H), 7.87~7.84 (m, 1H, Ar-H), 7.71~7.69 (d, 1H, Pyrene-H), 7.47~7.43 (d, 1H, -NH-), 7.41~7.35 (m, 3H, Ar-H), 7.33~7.28 (m, 4H, Ar-H), 7.18~7.10 (m, 4H, Ar-H), 7.04~7.02 (d, 2H, Ar-H), 6.91~6.88 (m, 2H, -NH-), 6.39~6.36 (m, 3H, Ar-H), 6.33~6.31 (d, H, Ar-H), 6.27~6.20 (m, 2H, Ar-H), 5.20~5.18 (m, 1H, ArCH<sub>2</sub>CH-), 4.70~4.68 (m, 1H, ArCH<sub>2</sub>CH-), 3.48~3.42 (m, 1H, ArCH<sub>2</sub>-), 3.35~3.30 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-), 3.22~3.15 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 3.11~3.06 (m, 1H, ArCH<sub>2</sub>-), 2.98~2.90 (b, 1H, ArCH<sub>2</sub>-), 2.89~2.84 (b, 1H, ArCH<sub>2</sub>-), 1.17~1.13 (t, 12H, CH<sub>3</sub>CH<sub>2</sub>-).

<sup>13</sup>C NMR: (125 MHz, CDCl<sub>3</sub>) δ/ppm: 170.71, 170.06, 169.86, 169.77, 153.73, 153.32, 153.27, 148.96, 137.03, 136.78, 132.73, 132.67, 131.13, 130.68, 130.19, 129.56, 129.36, 128.76, 128.70, 128.46, 128.07, 127.11, 127.01, 126.72, 126.27, 125.76, 125.73, 124.88, 124.67, 124.44, 124.36, 124.25, 123.83, 122.85, 108.27, 104.67, 97.78, 65.73, 55.28, 54.64, 44.36, 40.96, 39.73, 38.23, 37.87, 12.62.

HR-MS Calcd. For  $C_{65}H_{62}N_6O_5$   $[M+H]^+$ : 1007.48545. Found: 1007.48454.

## PHE-5

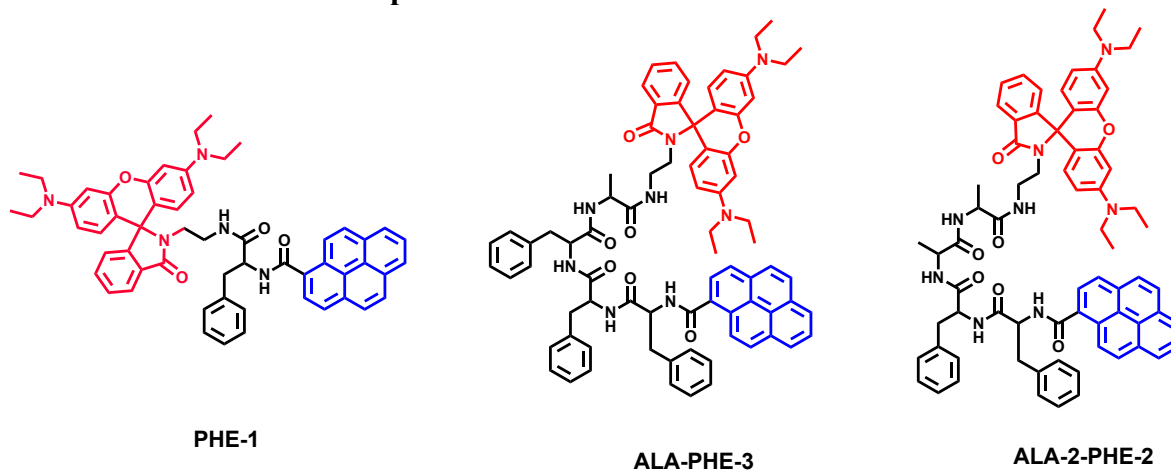
**Compound 3** (0.82 g, 0.62 mmol) was dissolved in dichloromethane and trifluoroacetic acid (TFA, 1.2 mL, 15 mmol) was added dropwise. The solution was kept stirring for 12 h, then the solvent and TFA were removed by evaporation. The residue was dissolved in dichloromethane, and then triethylamine (0.85 mL, 6.1 mmol) was added to dissociate the amino for 30 min. Then 1-pyrenecarboxylic acid (0.20 g, 0.81 mmol) was dissolved into the mixture. After stirring at  $-15\text{ }^\circ\text{C}$  (ice-salt bath) for 15 min, a  $CHCl_3$  solution containing dicyclohexylcarbodiimide (DCC, 0.20 g, 1.5 mmol), DMAP (0.05 g, 0.4 mmol) and HOBt (0.03 g, 0.2 mmol) was added dropwise. The solution was kept stirring for 96 h before evaporation of the solvent. The residue was purified by column chromatography using ethyl acetate as the eluent to afford **PHE-5** (white solid, yield 35%).

$^1\text{H}$  NMR: (400 MHz,  $CDCl_3$ )  $\delta$ /ppm: 8.37~8.34 (m, H, Pyrene-H), 8.20~8.12 (m, 3H, Pyrene-H), 8.03~7.95 (m, 5H, Pyrene-H), 7.85~7.81 (m, 1H, Ar-H), 7.73~7.69 (m, 1H, Ar-H), 7.54~7.51 (m, 2H, Ar-H), 7.41~7.45 (m, 2H, Ar-H), 7.25~7.18 (m, 6H, Ar-H), 7.13~7.04 (m, 8H, Ar-H), 6.99~6.95 (m, 4H, Ar-H), 6.82~6.77 (m, 3H, -NH-), 6.67~6.61 (d, 3H, -NH-), 6.41~6.31 (m, 4H, Ar-H), 6.26~6.24 (m, 2H, Ar-H), 4.97~4.94 (m, 1H,  $ArCH_2CH-$ ), 4.61~4.54 (m, 4H,  $ArCH_2CH-$ ), 3.33~3.27 (m, 8H,  $CH_3CH_2-$ ), 3.19~3.17 (m, H,  $ArCH_2-$ ), 3.11~3.02 (m, 4H,  $-NCH_2CH_2NH-$ ), 3.01~2.98 (m, H,  $ArCH_2-$ ), 2.89~2.77 (m, 4H,  $ArCH_2-$ ), 2.68~2.65 (m, 2H,  $ArCH_2-$ ), 2.55~2.51 (m, 2H,  $ArCH_2-$ ), 1.15~1.11 (m, 12H,  $CH_3CH_2-$ ).

$^{13}\text{C}$  NMR: (125 MHz,  $CDCl_3$ )  $\delta$ /ppm: 172.38, 171.79, 170.89, 170.81, 170.32, 169.75, 153.77, 153.30, 153.23, 148.98, 137.20, 136.91, 136.53, 136.49, 136.30, 132.84, 132.71, 132.41, 132.35, 131.08, 130.89, 130.62, 130.18, 129.92, 129.23, 129.18, 129.02, 128.84, 128.51, 128.47, 128.25, 128.02, 127.14, 127.06, 126.72, 126.57, 126.39, 126.33, 125.94, 125.90, 124.77, 124.56, 124.36, 124.28, 124.16, 123.83, 123.00, 108.36, 108.19, 104.69, 104.61, 97.87, 65.55, 55.90, 55.68, 55.02, 54.82, 54.70, 44.34, 39.40, 38.35, 37.79, 36.97, 36.84, 36.71, 36.62, 36.54, 12.59.

HR-MS Calcd. For  $C_{92}H_{90}N_9O_8$   $[M+H]^+$ : 1448.69069. Found: 1448.68831.

### 3. The molecules with different spacers



**Scheme S1.** Molecular structures of three model compounds.

The compounds of PHE-1, ALA-PHE-3 and ALA-2-PHE-2 were synthesized with the similar synthetic procedures to the molecules of PHE-2 and PHE-5.

#### PHE-1

$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 8.38~8.36 (m, H, Pyrene-H), 8.19~8.15 (m, 2H, Pyrene-H), 8.13~8.07 (m, 3H, Pyrene-H), 8.01~7.98 (m, 2H, Pyrene-H), 7.98~7.95 (m, 1H, Ar-H), 7.62~7.59 (d, 1H, Pyrene-H), 7.41~7.37 (m, H, Ar-H), 7.34~7.26 (m, 4H, Ar-H), 7.22~7.18 (m, 2H, Ar-H), 7.04~7.01 (m, H, Ar-H), 6.97~6.94 (m, H, -NH-), 6.41~6.36 (m, 3H, Ar-H), 6.34~6.30 (d, 2H, Ar-H), 6.25~6.21 (m, H, Ar-H), 5.12~5.10 (m, 1H,  $\text{ArCH}_2\text{CH-}$ ), 3.43~3.38 (m, 2H,  $-\text{NCH}_2\text{CH}_2\text{NH-}$ ), 3.35~3.26 (m, 8H,  $\text{CH}_3\text{CH}_2-$ ), 3.22~3.18 (m, 2H,  $-\text{NCH}_2\text{CH}_2\text{NH-}$ ), 3.15~3.09 (b, 1H,  $\text{ArCH}_2-$ ), 2.93~2.88 (b, 1H,  $\text{ArCH}_2-$ ), 1.17~1.13 (t, 12H,  $\text{CH}_3\text{CH}_2-$ ).

$^{13}\text{C}$  NMR: (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 170.64, 169.83, 169.40, 153.62, 153.33, 149.02, 137.00, 132.71, 132.60, 131.14, 130.71, 130.54, 130.28, 129.54, 128.76, 128.59, 128.54, 128.04, 127.16, 126.88, 126.21, 125.68, 125.66, 124.89, 124.73, 124.61, 124.41, 124.30, 123.77, 122.84, 108.36, 104.80, 97.85, 65.57, 54.98, 44.39, 40.78, 39.71, 38.88, 12.61.

HR-MS Calcd. For  $\text{C}_{65}\text{H}_{62}\text{N}_6\text{O}_5$   $[\text{M}+\text{H}]^+$ : 860.41703. Found: 860.41635.

### ALA-PHE-3

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.16~8.06 (m, 3H, Pyrene-H), 8.14~8.08 (m, 2H, Pyrene-H), 8.02~7.96 (m, 2H, Pyrene-H), 7.95~7.85 (m, 3H, Ar-H), 7.75~7.68 (m, 2H, Pyrene-H), 7.53~7.49 (b, 2H, -NH-), 7.44~7.36 (m, 3H, Ar-H), 7.24~7.10 (m, 13H, Ar-H), 6.78~6.75 (b, 1H, -NH-), 6.40~6.35 (m, 3H, Ar-H), 6.24~6.19 (m, 2H, Ar-H), 6.03~6.00 (m, H, Ar-H), 5.25~5.21 (m, 1H, ArCH<sub>2</sub>CH-), 4.93~4.90 (m, H, ArCH<sub>2</sub>CH-), 4.78~4.75 (m, 1H, ArCH<sub>2</sub>CH-), 4.36~4.34 (m, 1H, CH<sub>3</sub>CH-), 3.30~3.20 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-, 4H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 3.02~2.72 (m, 6H, ArCH<sub>2</sub>-), 1.26~1.23 (d, 3H, CH<sub>3</sub>CH-), 1.12~1.01 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>-).

<sup>13</sup>C NMR: (125 MHz, CDCl<sub>3</sub>) δ/ppm: 172.13, 171.90, 170.98, 170.43, 170.14, 153.86, 153.33, 153.21, 153.17, 149.01, 148.91, 137.26, 136.81, 136.19, 133.06, 132.96, 132.60, 131.05, 130.92, 130.54, 130.09, 129.84, 129.40, 129.30, 128.83, 128.74, 128.64, 128.57, 128.46, 128.39, 128.27, 127.04, 126.70, 126.58, 126.27, 126.22, 125.80, 125.70, 124.92, 124.71, 124.52, 124.32, 124.23, 124.12, 124.04, 124.00, 122.82, 108.38, 108.16, 104.36, 104.31, 97.84, 65.58, 55.63, 54.84, 54.72, 54.11, 44.33, 40.22, 40.04, 38.31, 37.89, 37.39, 19.18, 12.59.

HR-MS Calcd. For C<sub>83</sub>H<sub>80</sub>N<sub>8</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 1225.59097. Found: 1225.58910.

### ALA-2-PHE-2

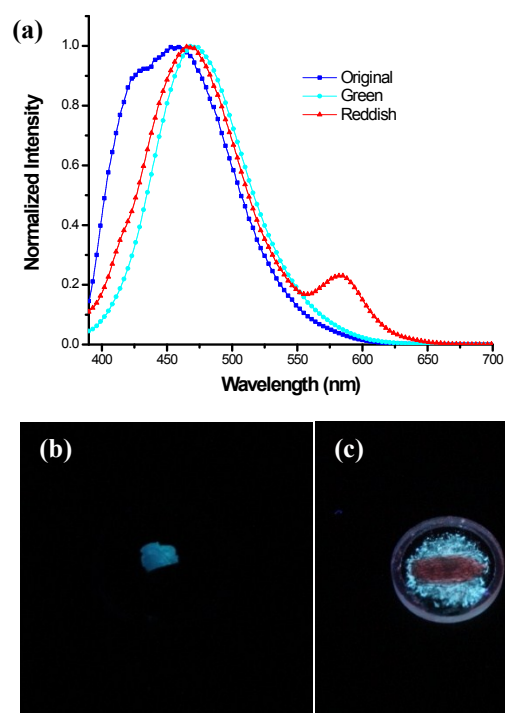
<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.21~8.19 (m, H, Pyrene-H), 8.16~8.14 (m, 2H, Pyrene-H), 8.03~7.96 (m, 4H, Pyrene-H), 7.90~7.87 (m, 1H, Ar-H) 7.85~7.83 (m, 2H, Ar-H), 7.74~7.70 (m, 2H, Pyrene-H), 7.55~7.51 (m, 3H, -NH-), 7.35~7.30 (m, 5H, Ar-H), 7.24~7.20 (m, 4H, Ar-H), 7.13~7.10 (m, 2H, Ar-H), 7.02~7.00 (m, H, -NH-), 6.35~6.32 (m, 3H, Ar-H), 6.21~6.16 (m, 2H, Ar-H), 5.98~5.96 (m, H, Ar-H), 5.27~5.25 (m, 1H, ArCH<sub>2</sub>CH-), 4.94~4.92 (m, 1H, ArCH<sub>2</sub>CH-), 4.66~4.64 (m, 1H, CH<sub>3</sub>CH-), 4.36~4.34 (m, 1H, CH<sub>3</sub>CH-), 3.27~3.21 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>-), 3.12~3.07 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>NH-), 2.98~2.80 (m, 4H, ArCH<sub>2</sub>-), 1.26~1.23 (d, 6H, CH<sub>3</sub>CH-), 1.17~1.12 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>-).



$^{13}\text{C}$  NMR: (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 171.86, 171.68, 171.58, 171.39, 170.47, 169.77, 169.46, 167.72, 153.87, 153.19, 148.88, 136.97, 136.60, 136.56, 136.42, 132.67, 132.40, 132.34, 131.02, 130.91, 130.59, 130.23, 130.14, 129.53, 128.85, 128.64, 128.50, 128.04, 127.05, 126.87, 126.17, 125.61, 124.99, 124.55, 124.48, 124.23, 124.09, 124.01, 123.79, 122.75, 108.21, 104.75, 104.66, 97.79, 65.57, 55.21, 54.92, 54.82, 44.28, 39.87, 39.72, 39.13, 38.57, 19.20, 19.17, 12.57.

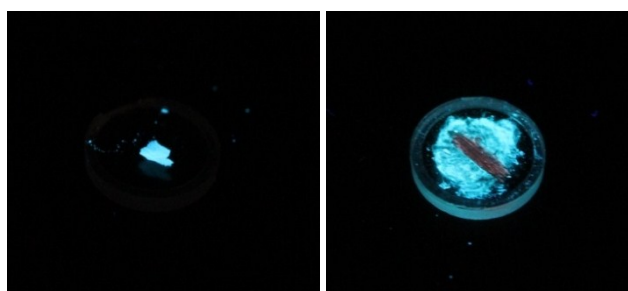
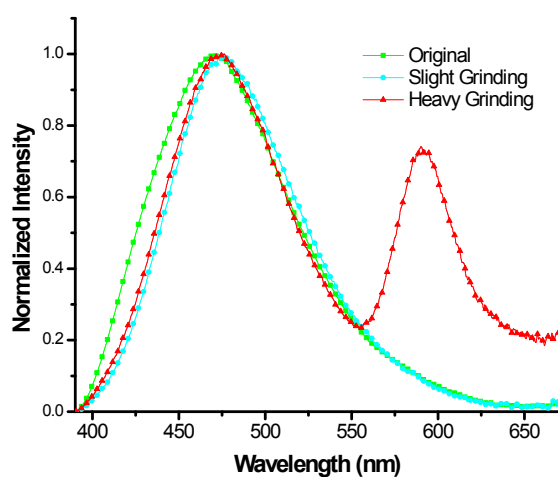
HR-MS Calcd. For  $\text{C}_{83}\text{H}_{80}\text{N}_8\text{O}_7$   $[\text{M}+\text{H}]^+$ : 1149.55967. Found: 1149.56126.

#### 4. Mechanochromic property of ALA-PHE-3



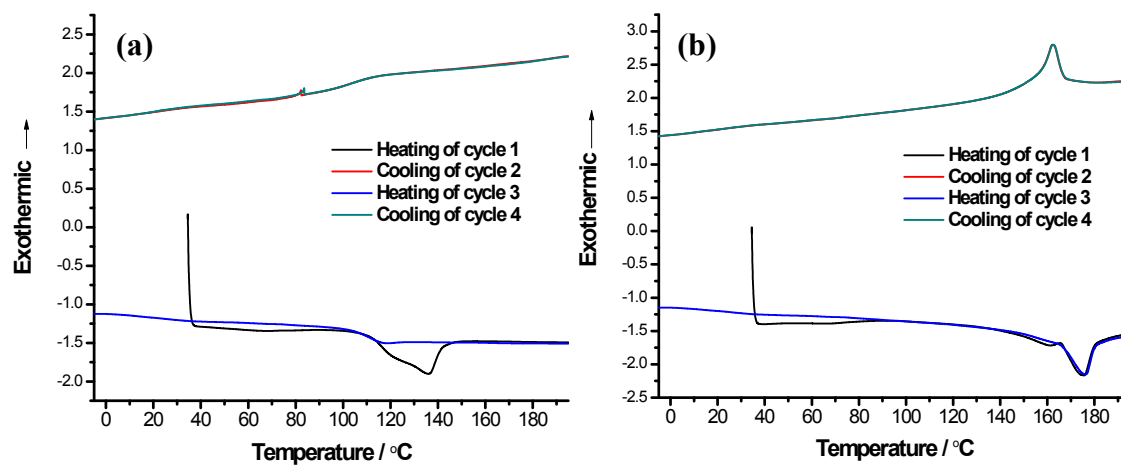
**Figure S1.** (a) Fluorescent spectra of ALA-PHE-3 sample in different states (original powder, green powder after slightly grinding, reddish powder after heavily grinding); Optical images of (b) original powder and (c) ground sample under 365 nm UV light.

## 5. Mechanochromic property of ALA-2-PHE-2



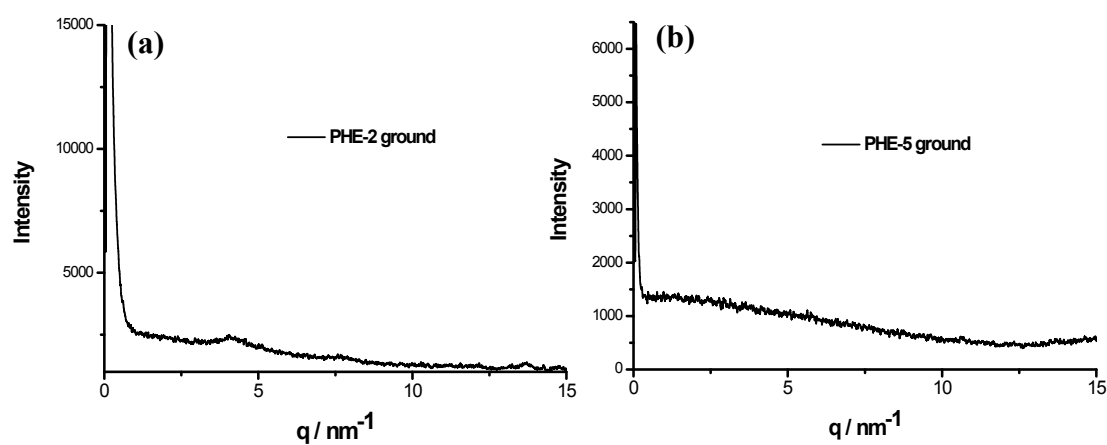
**Figure S2.** (a) Fluorescent spectra of ALA-2-PHE-2 samples in different states (original powder, green powder after slightly grinding, reddish powder after heavily grinding); Optical images of (b) original powder and (c) ground sample under 365 nm UV light.

## 6. DSC profiles of PHE-2 and PHE-5 xerogels



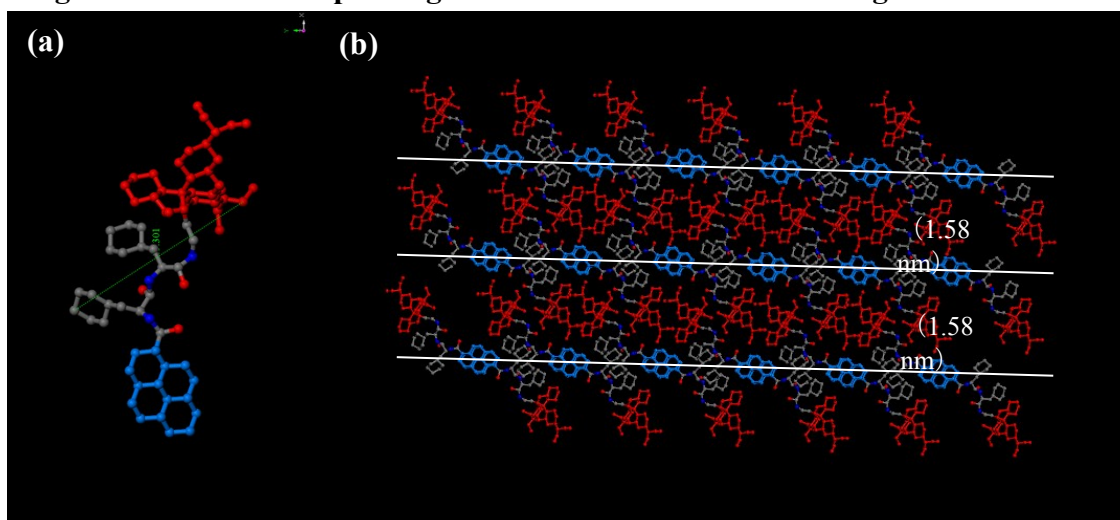
**Figure S3.** DSC profiles of (a) PHE-2 xerogel and (b) PHE-5 xerogel (heating or cooling rate:  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ).

## 7. SAXS patterns of ground PHE-2 and PHE-5 samples



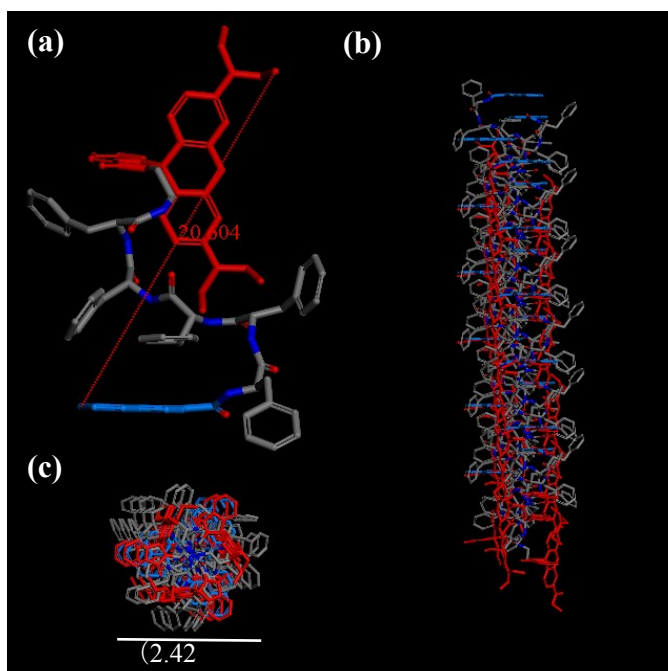
**Figure S4.** SAXS patterns of ground xerogel samples: (a) PHE-2 and (b) PHE-5.

## 8. Diagrammatic lamellar packing of PHE-2 molecules in the xerogel state



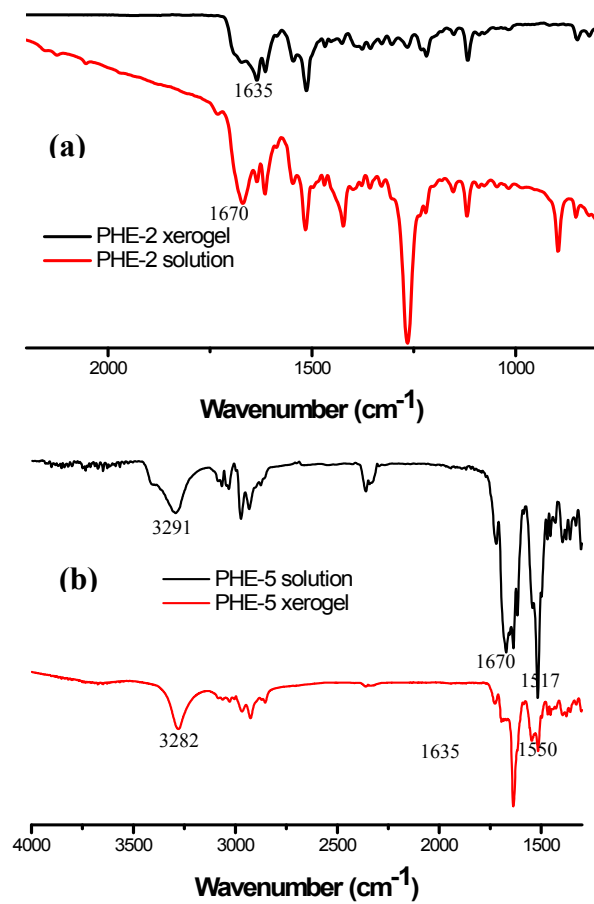
**Figure S5.** (a) The optimized geometry of PHE-2 in the gas phase calculated by using Forcite in Material Studio 5.0; (b) diagrammatic lamellar packing of PHE-2 molecules in the xerogel state.

## 9. Diagrammatic helical-like packing of PHE-5 molecules in the xerogel state



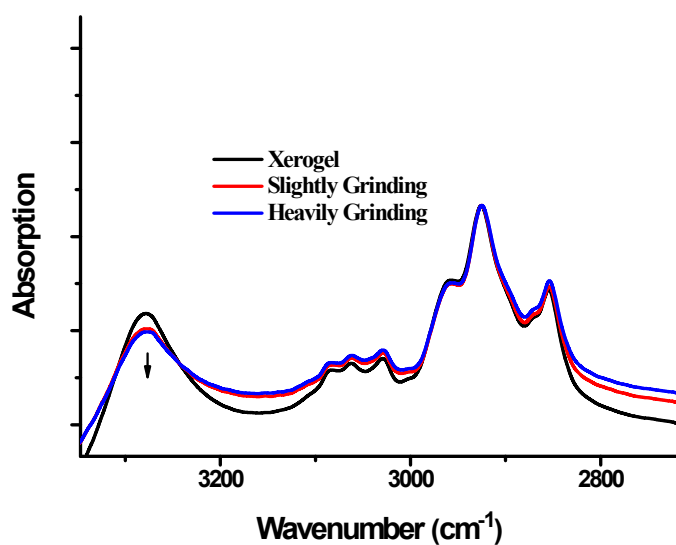
**Figure S6.** (a) The optimized geometry of PHE-5 in the gas phase calculated by using Forcite in Material Studio 5.0; (b) diagrammatic columnar packing of the PHE-5 molecules in the xerogel state by side view and (c) top view.

## 10. FTIR spectra of PHE-2 and PHE-5 in different states



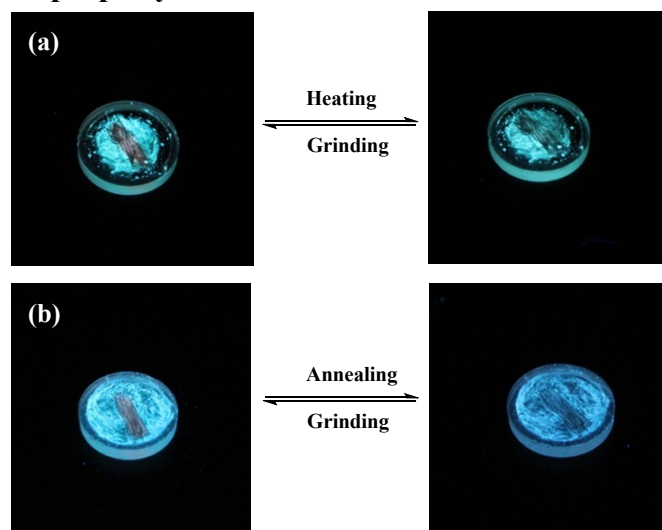
**Figure S7.** (a) FTIR spectra of PHE-2 and (b) PHE-5 in dichloromethane solution and in the xerogel state.

## 11. FTIR spectra of PHE-5 in different states



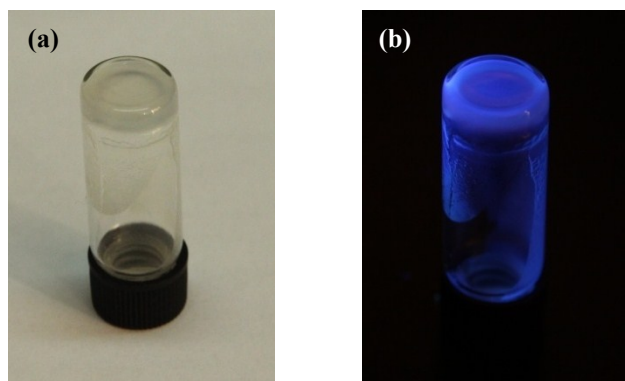
**Figure S8.** FTIR spectra of the PHE-5 sample with different colors (The absorption is normalized to the C-H stretching at 2926 cm<sup>-1</sup>).

## 12. Reversible color switch property of PHE-2 and PHE-5



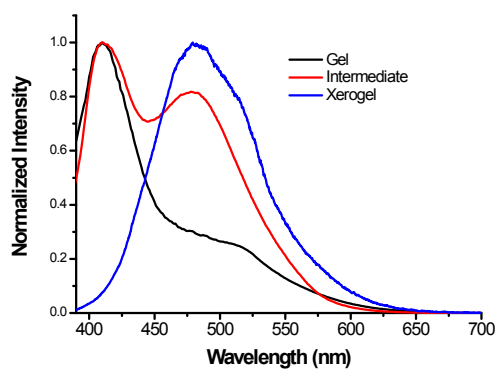
**Figure S9.** Optical images of ground samples before and after annealing (or heating): (a) PHE-2 and (b) PHE-5.

### 13. Reversible gelation property of PHE-5



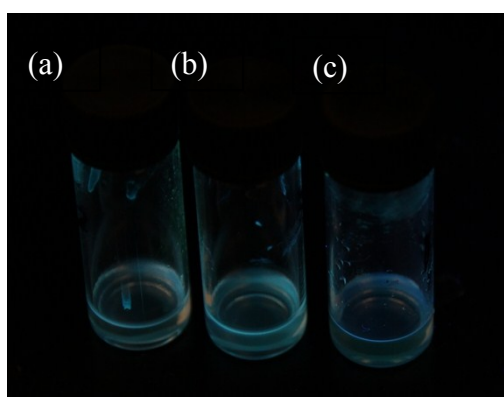
**Figure S10.** Optical images of recovered gels by PHE-5 under (a) room light and (b) 365 nm UV light.

### 14. Fluorescent spectra of PHE-2 indifferent states



**Figure S11.** The fluorescent spectra of PHE-2 gel (black line), xerogel (blue line) and the intermediate during the solvent evaporation (red line).

### 15. PHE-2 solutions in different solvent



**Figure S12.** The emissions of PHE-2 solutions in (a) dichloromethane, (b) ethyl acetate and (c) dimethyl formamide (Concentration: 29.1, 19.4, 21.8 mg/mL).



## Reference

- [1] S. Kang, S. Kim, Y.-K. Yang, S. Bae and J. Tae, *Tetrahedron Letters*, 2009, **50**, 2010-2012.