

## Supporting Information

# Luminescent Micro and Nanogel Formation from AB<sub>3</sub> Type Poly(aryl ether) Dendron Derivatives *without* Conventional Multi-Interactive Gelation Motifs

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## 1. Synthetic procedure and characterization of dendrons

### 1.1 Synthesis of [(AB)<sub>3</sub> G<sub>1</sub>-Cl]

To a solution of (AB)<sub>3</sub>G<sub>1</sub>-CH<sub>2</sub>OH (5g, 0.0117moles) in dichloromethane (40 mL) was added a catalytic amount of DMF (3mL) followed by SOCl<sub>2</sub> (1.6mL, 0.014moles) with stirring. The reaction mixture was stirred at room temperature for 2 hours. The solvent and excess SOCl<sub>2</sub> were distilled out under reduced pressure. The resulting yellow solid was dissolved in diethyl ether and washed with water and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and washed with methanol to get pure product. The yield

(AB)<sub>3</sub>G<sub>1</sub>-Cl was 4.4g (84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.20 (s, CH<sub>2</sub>Cl, 2H), 4.91 (s, ArCH<sub>2</sub>O, 2H), 5.01 (s, ArCH<sub>2</sub>O, 4H), 6.52 (s, ArH, 2H), 7.12-7.34 (m, PhH, 15H). MS: *m/z* Calcd for C<sub>28</sub>H<sub>25</sub>O<sub>5</sub>:444, found: 445 [M+H]<sup>+</sup>, 467 [M+Na]<sup>+</sup>.

## 1.2. Synthesis of poly(aryl ether) (AB)<sub>3</sub> G<sub>2</sub> dendrons

### 1.2.1. Synthesis of (AB)<sub>3</sub>G<sub>2</sub>-COOCH<sub>3</sub>(VI)

Methyl-3, 4, 5- trihydroxy benzoate (0.61g, 0.0034moles) and K<sub>2</sub>CO<sub>3</sub> (3.31g, 0.0204moles) in 35 mL dry acetone were taken in a 100 mL round bottom flask. (AB)<sub>3</sub>G<sub>1</sub>-Cl (4.5g,0.010moles) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (0.365g, 0.001 moles).The solution was heated to reflux with stirring for 24 hours. After completion of reaction the reaction mixture was cooled to room temperature and filtered. The filtered salts were further washed twice with dichloromethane. The solvent was then removed under reduced pressure using a rotary evaporator to afford an oil that turned into a solid upon standing. The solid was recrystallized from hexane: toluene (70:30). The yield (AB)<sub>3</sub> G<sub>2</sub>-COOCH<sub>3</sub> was 4.2g (89.3%) Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ :3.82 (s, COOCH<sub>3</sub>, 3H), 4.75-4.93 (s, ArCH<sub>2</sub>O, 24H), 6.66 (s, ArH, 2H) 6.68 (s, ArH, 4H), 7.10-7.29 (m, ArH & PhH, 47H). <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ: 52.31,71.03, 71.25,71.49, 75.10, 75.21, 107.03, 107.65, 109.71, 125.44, 127.45, 127.49, 127.67, 127.77, 127.88, 128.10, 128.16, 128.40,128.49, 132.29, 133.06, 136.99, 137.03, 137.92, 138.30, 142.43, 152.51, 152.83, 153.11, 166.51. MS: *m/z* Calcd for C<sub>92</sub>H<sub>80</sub>O<sub>14</sub>: 1408, Found : 1426 [M+NH<sub>4</sub>]<sup>+</sup>.

### 1.2.2. Synthesis of (AB)<sub>3</sub>G<sub>2</sub>-COOH(V)

A solution of KOH (5mL, 10N) was added to the compound **2** (5g, 0.0035 moles) in 60 mL ethanol. The mixture was refluxed for 3 hours and then acidified with concentrated HCl. After refluxing the acidified reaction mixture for 15 minute the precipitate was filtered and washed

with water for several times to get the product **(AB)<sub>3</sub>G<sub>2</sub>-COOH** with a yield of 4.3g(89.5%)

Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ :4.89-5.06 (s, ArCH<sub>2</sub>O, 24H), 6.80 (s, ArH, 6H), 7.23-7.47 (m, ArH& PhH, 47H), <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ : 71.06, 71.27, 71.52, 75.13, 75.23, 107.09, 107.67, 110.22, 127.49, 127.72, 127.81, 27.91, 128.14, 128.19, 128.44, 128.52, 132.25, 137.00, 137.92, 138.31, 143.02, 152.53, 152.86, 153.13, 170.23. MS : m/z Calcd for C<sub>91</sub>H<sub>78</sub>O<sub>14</sub>: 1394, found: 1414 [M+NH<sub>4</sub>]<sup>+</sup>.

### 1.2.3. Synthesis of **(AB)<sub>3</sub>G<sub>2</sub>-CH<sub>2</sub>OH(VII)**

Lithium aluminum hydride (0.114 g, 0.0213 moles) was suspended into 10 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. **(AB)<sub>3</sub>G<sub>2</sub>-COOCH<sub>3</sub>** (4 g, 0.0028 moles) was dissolved in 15 mL of freshly distilled THF and added dropwise to the lithium aluminum hydride solution. The reaction mixture was refluxed with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added very slowly drop wise to the vigorously stirred THF solution until the gray color of the lithium aluminum hydride disappeared and a white solid was formed which is filtered and washed with THF. Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the alcohol **(AB)<sub>3</sub>G<sub>2</sub>-CH<sub>2</sub>OH** with 90% yield (7.6g). Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.60 (s,CH<sub>2</sub>OH,2H),4.93-5.07 (s, ArCH<sub>2</sub>O, 24H), 6.69-6.89 (s,ArH,8H), 7.32-7.42(m, PhH, 45H). <sup>13</sup>C NMR(100MHz, CDCl<sub>3</sub>) δ : 65.20, 71.03, 71.20, 71.40, 75.24, 106.82, 107.61, 127.49, 127.55, 127.68, 127.79, 127.89, 128.19, 128.41, 128.45, 128.52, 132.83, 137.03, 137.09, 138.12, 152.90, 153.07. MS : m/z Calcdfor C<sub>91</sub>H<sub>80</sub>O<sub>13</sub>:1380, found: 1398 (M+NH<sub>4</sub>)<sup>+</sup>.

### 1.3. Synthesis of poly(aryl ether) (AB)<sub>2</sub> G<sub>1</sub> dendrons

#### 1.3.1. Synthesis of (AB)<sub>2</sub>G<sub>1</sub>-COOCH<sub>3</sub>(X)

Methyl-3, 5-dihydroxybenzoate (8g, 0.0476 moles) and potassium carbonate (13.2 g, 0.0952 moles) in 130 ml of 1-4 dioxane were taken in a 250ml round bottom flask. Benzyl chloride (10.95ml, 0.0952 moles) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (1.5 g, 0.0047 moles). The solution was heated to reflux with stirring for 24 hours. The solvent was then removed under reduced pressure using a rotary evaporator to afford an oil that turned into a solid upon standing. The solid was crystallized from methanol. (AB)<sub>2</sub>G<sub>1</sub>-COOCH<sub>3</sub> yield was 15 g (90.9%). Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 3.80 (s, COOCH<sub>3</sub>, 3H), 4.97 (s, ArCH<sub>2</sub>O, 4H), 6.71 (s, ArH, 1H), 7.23-7.34 (m, ArH & PhH, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 52.29, 70.34, 107.32, 108.46, 127.60, 128.15, 128.50, 128.67, 132.12, 136.54, 159.86, 166.80, MS : m/z Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>: 348, found: 349 [M+H]<sup>+</sup>.

#### 1.3.2. Synthesis of (AB)<sub>2</sub> G<sub>1</sub>-CH<sub>2</sub>-OH (XI)

Lithium aluminum hydride (1.54 g, 0.0405 moles) was suspended into 50 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. (AB)<sub>2</sub>G<sub>1</sub>-COOCH<sub>3</sub> (13.1 g, 0.0376 moles) was dissolved in 60 ml of freshly distilled THF and added drop wise to the lithium aluminum hydride solution. The reaction mixture was heated to reflux with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added very slowly drop wise to the vigorously stirred THF solution until the gray color of the lithium aluminum hydride disappeared and a white solid was formed which is filtered and washed with THF, Excess solvent was removed under reduced pressure and the crude product

was recrystallized from 95% methanol/water mixture to get the alcohol  $(AB)_2G_1-CH_2-OH$  with yield 10.9 g (90.6%). Spectral characterization:  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  :4.54 (s,  $CH_2OH$ , 2H), 4.95 (s,  $ArCH_2O$ , 4H), 6.47-6.54 (s,  $ArH$ , 3H), 7.17-7.34 (m,  $PhH$ , 10H).  $^{13}C$ NMR (100MHz,  $CDCl_3$ )  $\delta$  : 65.34, 70.13, 101.39, 105.82, 127.54, 128.03, 128.62, 136.89, 143.47, 160.22, MS: m/z Calcd for  $C_{21}H_{20}O_3$ : 320, found: 321  $[M+H]^+$ .

### 1.3.3. Synthesis of $(AB)_2G_1-COOH(IX)$

A solution of KOH (5mL, 10N) was added to the  $(AB)_2G_1-COOCH_3$  (5g, 0.0144 moles) in 95 mL ethanol. The mixture was refluxed for three hours and then acidified with concentrated HCl. After refluxing for the acidified reaction mixture for 15 minute the precipitate was filtered and washed with water for several times to get the product  $(AB)_2G_1-COOH$  with an yield of 4.3g(89.7%), Spectral characterization:  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 5.13(s,  $ArCH_2O$ , 4H), 6.90 (s,  $ArH$ , 1H), 7.30-7.49 (m,  $ArH$  &  $PhH$ , 12H).  $^{13}C$  NMR(100 MHz,  $CDCl_3$ )  $\delta$ : 70.38, 108.25, 108.96, 127.60, 128.18, 128.68, 131.09, 136.41, 159.89, MS : m/z Calcd for  $C_{21}H_{19}O_4$ : 334, found: 335  $[M+H]^+$ .

### 1.3.4. Synthesis of $(AB)_2G_1-CH_2Cl$

To a solution of  $(AB)_2G_1-CH_2-OH$  (7g, 0.0218 moles)in dichloromethane (40mL) was added a catalytic amount of DMF (3mL) followed by  $SOCl_2$  (1.95mL, 0.026 moles) with stirring. It was stirred at room temperature for 2hours. The solvent and excess  $SOCl_2$  were distilled out under reduced pressure. The resulting yellow solid was dissolved in diethyl ether and washed with water and the organic layer was dried over  $Na_2SO_4$ . The solvent was removed under reduced pressure and washed with methanol to get pure product. the  $(AB)_2G_1-CH_2Cl$  yield was obtained 6.5g (88.3%). Spectral characterization:  $^1H$  NMR (400 MHz,  $CDCl_3$ ) $\delta$ : 4.93 (s,

ArCH<sub>2</sub>O, 4H), 6.43-6.52 (s, ArH, 3H), 7.15-7.30 (m, ArH&PhH,10H) MS : m/z Calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>Cl: 338, found : 339 [M+H]<sup>+</sup>.

## 1.4. Synthesis of poly(aryl ether) (AB)<sub>2</sub> G<sub>2</sub> dendrons

### 1.4.1. Synthesis of (AB)<sub>2</sub>-G<sub>2</sub>-COOCH<sub>3</sub>(XIV)

Methyl-3, 5-dihydroxy benzoate (1.9g, 0.0118 moles) and K<sub>2</sub>CO<sub>3</sub> (3.9g, 0.0283 moles) in 35 mL dry acetone were taken in a 250 mL round bottom flask. (AB)<sub>2</sub>G<sub>1</sub>-CH<sub>2</sub>Cl (8g, 0.0236 moles) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (0.358g, 0.001 moles). The solution was heated to reflux for 24 hours. After completion of reaction the reaction mixture was cooled to room temperature and filtered. The filtered salts were further washed twice with dichloromethane. The solvent was then removed under reduced pressure to afford an oil that turned into a solid upon standing. The solid was recrystallized from hexane : toluene(70:30) with an yield of 7.9g(89.4%). Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : 3.96 (s, COOCH<sub>3</sub>, 3H), 5.06-5.09 (s, ArCH<sub>2</sub>O,12H), 6.63-6.82 (s, ArH, 7H), 7.30-7.47(m, ArH & PhH, 22H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 52.39, 70.27, 101.85, 106.54, 07.33, 108.54, 127.67, 128.14, 128.72, 132.21, 136.90, 139.02, 159.83, 160.33, 166.85. MS : m/z Calcd for C<sub>50</sub>H<sub>44</sub>O<sub>8</sub>:772, found:790 [M+NH<sub>4</sub>]<sup>+</sup>.

### 1.4.2. Synthesis of (AB)<sub>2</sub> G<sub>2</sub>-CH<sub>2</sub>-OH(XV)

Lithium aluminum hydride (0.265g, 0.0069 moles) was suspended into 15 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. (AB)<sub>2</sub>-G<sub>2</sub>-COOCH<sub>3</sub> (5 g, 0.0065 moles) was dissolved in 20 mL of freshly distilled THF and added drop wise to the lithium aluminum hydride solution. The reaction mixture was heated to reflux with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added drop wise and very slowly to the vigorously stirred THF solution until the gray color of

the lithium aluminum hydride disappeared and a white solid was formed which is filtered and washed with THF, Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the alcohol **(AB)<sub>2</sub>G<sub>2</sub>-CH<sub>2</sub>-OH** with yield 4.4 g (91.6%) Spectral characterization- **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ:** 4.47(s, CH<sub>2</sub>OH, 2H), 4.84-4.90(s, ArCH<sub>2</sub>O, 12H), 6.46-6.57(s, ArH, 9H), 7.18-7.30(m, PhH, 20H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ:** 65.28, 70.00, 70.18, 101.40, 101.65, 105.81, 106.45, 127.41, 127.64, 127.83, 128.08, 128.52, 128.66, 138.86, 139.39, 143.58, 160.58, 160.24 MS: m/z Calcd for C<sub>49</sub>H<sub>44</sub>O<sub>7</sub>:744, found: 762 [M+NH<sub>4</sub>]<sup>+</sup>.

### 1.4.3. Synthesis of **(AB)<sub>2</sub>G<sub>2</sub>-COOH(XIII)**

A solution of KOH (5mL, 10N) was added to the compound (5g, 0.0065 moles) in 70mL ethanol. The mixture was refluxed for three hours and then acidified with concentrated HCl. After refluxing for the acidified reaction mixture for 15 minute the precipitate was filtered and washed with water for several times to get the product **(AB)<sub>2</sub>G<sub>2</sub>-COOH** with an yield of 4.5g(91.4%) spectral characterization: **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ:** 5.07-5.09(s, ArCH<sub>2</sub>O, 12H), 6.65-6.88 (s, ArH, 7H), 7.30-7.49 (m, ArH &PhH ,22H). **<sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ:** 69.44, 69.82, 70.20, 72.92, 76.39, 101.47, 101.85, 106.11, 106.49, 108.66, 126.84, 127.22, 127.60, 127.69, 127.88, 128.06, 128.26, 128.64, 128.83, 129.42, 130.31, 130.78, 131.36, 136.44, 136.84, 159.43, 159.89, 160.27, 162.98. MS: m/z Calcd for C<sub>49</sub>H<sub>42</sub>O<sub>8</sub>: 758, found: 759 [M+H]<sup>+</sup>, 776 [M+NH<sub>4</sub>]<sup>+</sup>.

## 2. Synthesis of anthracene cored dendrons

### 2.1. Synthesis of An-G<sub>1</sub>(AB)<sub>2</sub>(XII)

We follow the same procedure described in **An-G<sub>1</sub>-(AB)<sub>3</sub>** for synthesizing **An-G<sub>1</sub>(AB)<sub>2</sub>** with the appropriate starting material. Spectral characterization: **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

$\delta$ :4.70(s,ArCH<sub>2</sub>O,2H), 5.04-5.09 (S, ArCH<sub>2</sub>O, 4H), 5.54 (s, AnCH<sub>2</sub>O, 2H) 6.63-6.71 (s, ArH, 3H), 7.30-8.52 (m, AnH & PhH, 19H). <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>)  $\delta$ : 64.06, 70.09, 72.30, 101.75, 106.80, 124.48, 125.00, 126.19, 127.58, 128.00, 128.50, 128.60, 129.06, 131.13, 131.51, 136.94, 141.01, 160.13. MS: m/z Calcd for C<sub>36</sub>H<sub>30</sub>O<sub>3</sub>: 510, found: 511 [M+H]<sup>+</sup>.

## 2.2. Synthesis of An-G<sub>2</sub>(AB)<sub>2</sub>(XVI)

We follow the same procedure described above for synthesizing An-G<sub>2</sub>(AB)<sub>2</sub> with the appropriate starting material. Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.55(s, ArCH<sub>2</sub>O, 2H), 4.83-4.94 (s, ArCH<sub>2</sub>O, 12H), 5.40 (s, AnCH<sub>2</sub>O, 2H) 6.47-6.55(s, ArH, 3H), 7.22-8.36 (m, AnH&PhH, 19H). <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>)  $\delta$ :64.06, 69.97, 70.16, 72.27, 101.62, 101.77, 106.45, 106.84, 124.46, 125.01, 126.21, 127.59, 128.03, 128.51, 128.62, 129.05, 131.12, 131.50, 136.84, 139.37, 141.01, 160.02, 160.21. MS : m/z Calcd for C<sub>64</sub>H<sub>54</sub>O<sub>7</sub>:935 ,found: 954 [M+NH<sub>4</sub>]<sup>+</sup>.

## 2.3. Synthesis of An-G<sub>2</sub>(AB)<sub>3</sub>(VIII)

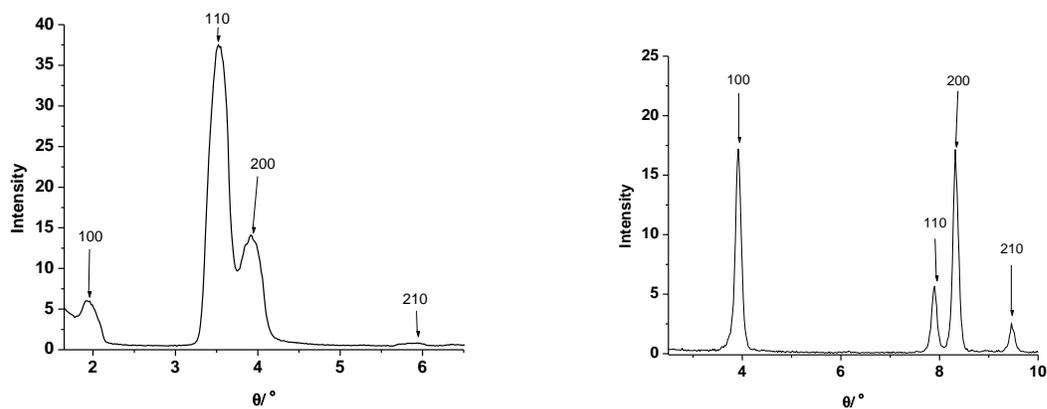
We follow the same procedure described above for synthesizing An-G<sub>2</sub>(AB)<sub>3</sub> with the appropriate starting material. Spectral characterization: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.50 (s, ArCH<sub>2</sub>O, 2H), 4.76-4.94 (s, ArCH<sub>2</sub>O, 24H), 5.42 (s, AnCH<sub>2</sub>O, 2H) 6.64-6.66 (s, ArH, 8H), 7.16-8.26 (m, AnH & PhH,54H). <sup>13</sup>C NMR (100MHz,CDCl<sub>3</sub>)  $\delta$ :57.43, 65.23, 71.03, 71.20, 75.13, 75.21, 106.84, 106.92, 107.64, 123.96, 125.13, 126.48, 127.46, 127.52, 127.65, 125.76, 127.86, 128.10, 128.16, 128.39, 128.42, 128.49, 129.18, 132.79, 137.02, 137.09, 152.85, 152.91, 153.06.

### 3. SEM images of gel formed by the poly(aryl ether) dendrons and photograph of gel

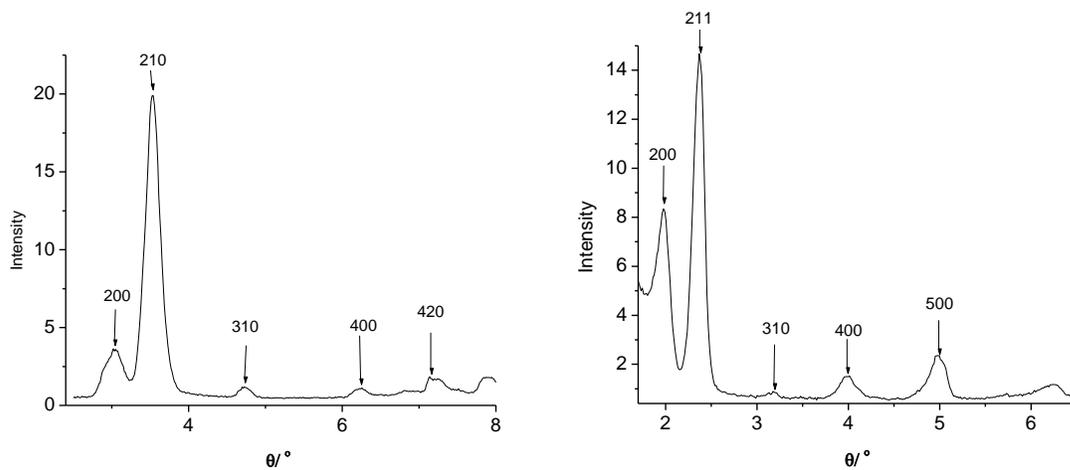


**Fig. S1** SEM image of compound **VI** on silicon wafer (left), Photographs of **V** in dichloromethane: hexane mixture (1:3 % v/v), below and above the critical gel concentration (a and b respectively)(right).

### 4. Powder X-Ray Diffraction patterns



**Fig. S2** Powder XRD pattern of **III** (left) and **I** (right)



**Fig. S3.** Powder XRD pattern of **II** (left) and **VI** (right)