

## **Orderly Arranged NLO Materials on Exfoliated Layered Templates Based on Dendrons with Alternating Moieties in Periphery**

Ya-Yu Siao<sup>a</sup>, Shi-Min Shau<sup>a</sup>, Wei-Hsiang Tsai<sup>a</sup>, Yung-Chung Chen<sup>a</sup>, Tain-Hao Wu<sup>a</sup>,  
Jiang-Jen Lin<sup>b</sup>, Tzong-Ming Wu<sup>a</sup>, Rong-Ho Lee<sup>a\*</sup>, Ru-Jong Jeng<sup>b\*</sup>

<sup>a</sup>Departments of Chemical Engineering and Materials Science and Engineering,  
National Chung Hsing University, Taichung 402, Taiwan.

<sup>b</sup>Institute of Polymer Science and Engineering, National Taiwan University, Taipei  
10617, Taiwan.

\*To whom correspondence should be addressed.

Rong-Ho Lee—e-mail: rhl@nchu.edu.tw; tel.: +886-4-22854308; fax:  
+886-4-22854734.

Ru-Jong Jeng—e-mail: rujong@ntu.edu.tw; tel.: +886-2-33665884; fax:  
+886-2-33665237.

## Supporting Information

### Tables of Content

Synthesis of IPDA

Synthesis of building block IPDA based dendrons comprising peripheral DR1 chromophores

Synthesis of building block IDD based dendrons comprising alternating peripheral moieties of C18 and DR1

Synthesis of building block IPDA based dendrons comprising alternating peripheral moieties of C18 and DR1

Figure S1. TGA thermograms of the dendron-intercalated MMT/PI composites ((a) A-G(x)-DR1-M/PI; (b) D-G(x)-CD-M/PI; (c) A-G(x)-CD-M/PI).

Figure S2. TEM images of (a)A-G1-DR1-M-PI10; (b) A-G2-DR1-M-PI10; (c) A-G3-DR1-M-PI10; (d) A-G1-DR1-M-PI20; (e) A-G2-DR1-M-PI20;(f) A-G3-DR1-M-PI20.

Figure S3. TEM images of (a)A-G1-CD-M-PI10; (b) A-G2-CD-M-PI10; (c) A-G3-CD-M-PI10; (d) A-G1-CD-M-PI20; (e) A-G2-CD-M-PI20;(f) A-G3-CD-M-PI20.

The Optical Nonlinearity of the DR1 in Polyimide

## Synthesis of IPDA

A solution of triethylamine (6.99 g, 0.069 mol) in xylene (10 mL) was added to a solution of 1,4-phenylene diisocyanate (10 g, 0.062 mol) and isobutyryl chloride (6.65 g, 0.062 mol) using xylene as solvent (35 mL). The reaction mixture was refluxed for 7 h and then cooled to room temperature. The resulting solution was filtered to remove the quaternary salt and concentrated to about 50 mL. The product was then crystallized from cyclohexane, yielding the compound as white powder (25%). IR (KBr): 2250  $\text{cm}^{-1}$  (N=C=O), 1854  $\text{cm}^{-1}$ , 1735  $\text{cm}^{-1}$  (C=O stretching, -azetidine-2,4-dione).

It is important to note that it was difficult to obtain 100% pure IPDA product, due to the similar solubility of the product IPDA and byproduct bis(azetidine-2,4-dione). Conveniently, the IPDA sample comprising a small amount of byproduct bis(azetidine-2,4-dione) was used directly as the building block for dendron synthesis. The isocyanate group of IPDA selectively reacted with the hydroxyl group of stearyl alcohol or DR1 during reaction, while bis(azetidine-2,4-dione) remained intact. The byproduct bis(azetidine-2,4-dione) originally in the IPDA sample could be removed easily after this reaction stage.

## Synthesis of building block IPDA based dendrons comprising peripheral DR1 chromophores

### Synthesis of dendron A-G0.5-DR1

IPDA (3.70 g, 16 mmol) was added to a solution of DR1 (5.00 g, 16 mmol) in dry THF (50 ml). The mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G0.5-DR1 (9.07 g, yield = 47 %). IR (KBr): 1854, 1735 (C=O stretch, -azetidine-2,4-dione), 1516, 1335 cm<sup>-1</sup> (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 1.16 (t, 3H, -CH<sub>3</sub>), 1.38 (s, 6H, -CH<sub>3</sub>), 3.55 (q, 2H, -CH<sub>2</sub>N), 3.76 (t, 2H, -CH<sub>2</sub>N), 4.30 (t, 2H, -CH<sub>2</sub>OCO-), 6.93-7.05 (d, 2H, Ar-H), 7.45-7.60 (d, 4H, Ar-H), 7.81-7.98 (d, 4H, Ar-H), 8.35-8.48 (d, 2H, Ar-H), 9.85 (s, N-H). Anal. Calcd (%) for C<sub>28</sub>H<sub>28</sub>N<sub>6</sub>O<sub>6</sub> (544.56): C, 61.76; H, 5.18; N, 15.43. Found (%): C, 61.58; H, 5.20; N, 15.27. MS (FAB MS): *m/z* = 545 (M<sup>+</sup>)

### Synthesis of dendron A-G1-DR1

DETA (0.47 g, 4.55 mmol) was added to a solution of A-G0.5-DR1 (5.00 g, 9.17 mmol) in THF (25 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G1-DR1 (3.52 g, yield = 65 %). IR (KBr): 1658 (C=O stretch), 1518, 1337 cm<sup>-1</sup> (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 1.13-1.21 (t, 6H, -CH<sub>3</sub>), 1.35-1.42 (s, 12H, -CH<sub>3</sub>), 2.58-2.62 (m, 4H, -NH(CH<sub>2</sub>)), 3.13-3.20 (t, 4H, -N(CH<sub>2</sub>)), 3.55-3.62 (q, 4H, -CH<sub>2</sub>N), 3.73-3.80 (t, 4H, -CH<sub>2</sub>N), 4.21-4.36 (t, 4H, -CH<sub>2</sub>OCO), 6.85-7.00 (d, 2H, -ArH), 7.31-7.42 (d, 2H, -ArH), 7.44-7.55 (d, 2H, -ArH), 7.80-7.95 (d, 4H, -ArH), 8.30-8.40 (d, 2H, -ArH), 6.80-6.82(s, 1H, N-H), 7.58-7.62 (s, 2H, N-H), 9.32-9.40 (s, 2H, N-H), 9.58-9.62 (s,

2H, N-H). Anal. Calcd (%). for  $C_{60}H_{69}N_{15}O_{12}$  (1192.28): C, 60.44; H, 5.83; N, 17.62. Found: C, 60.75; H, 6.02; N, 17.58. MS (FAB MS):  $m/z = 1192$  ( $M^+$ ).

### Synthesis of dendron A-G1.5-DR1

IPDA (0.29 g, 1.25 mmol) was added to a solution of A-G1-DR1 (1.50 g, 1.3 mmol) in THF (25 mL) and then the mixture was stirred at 60 °C under  $N_2$  for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G1.5-DR1 (1.01 g, yield = 77 %). IR (KBr): 1855, 1735 ( $-C=O$  stretch, -azetidine-2,4-dione), 1517, 1334  $cm^{-1}$  ( $-NO_2$  stretch).  $^1H$ -NMR ( $\delta/ppm$ , 400 MHz, d-DMSO): 1.24-1.28 (t, 6H,  $-CH_3$ ), 1.45-1.50 (s, 12H,  $-CH_3$ ), 1.51-1.60 (s, 6H,  $-CH_3$ ), 3.45-3.46 (t, 4H,  $-CO-N-CH_2$ ), 3.51-3.53 (t, 4H,  $-NHCH_2$ ), 3.62-3.65 (t, 4H,  $-CH_2N$ ), 4.00-4.10 (t, 4H,  $-CH_2N$ ), 4.35-4.42 (t, 4H,  $-CH_2OCO$ ), 6.85-7.00 (d, 4H,  $-ArH$ ), 7.31-7.60 (m, 12H,  $-ArH$ ), 7.80-8.02 (m, 8H,  $-ArH$ ), 8.30-8.40 (d, 4H,  $-ArH$ ), 8.65-8.86 (s, 2H, N-H), 8.88-9.00 (s, 2H, N-H), 9.20-9.28 (s, 2H, N-H). Anal. Calcd (%). for  $C_{72}H_{79}N_{17}O_{15}$  (1422.50): C, 60.79; H, 5.60; N, 16.74. Found (%): C, 60.76; H, 5.70; N, 16.49. MS (FAB MS):  $m/z = 1422$  ( $M^+$ ).

### Synthesis of dendron A-G2-DR1

DETA (0.5 g, 0.362 mmol) was added to a solution of A-G1.5-DR1 (1.00 g, 0.725 mmol) in THF and then the mixture was stirred at 60 °C under  $N_2$  for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G2-DR1 (1.26 g, yield = 61 %). IR (KBr): 1654 ( $C=O$  stretch), 1515, 1334  $cm^{-1}$  ( $-NO_2$  stretch).  $^1H$  NMR ( $\delta/ppm$ , 400 MHz, d-DMSO): 1.15-1.22 (t, 12H,  $-CH_3$ ), 1.34-1.42 (s, 36H,  $-CH_3$ ), 3.20-3.42 (t, 12H,  $-NH(CH_2)$ ), 3.17-3.22 (t, 12H,  $-N(CH_2)$ ), 3.58-3.62 (q, 8H,  $-CH_2N$ ), 3.73-3.78 (t, 8H,  $-CH_2N$ ),

4.26-4.35 (t, 8H, -CH<sub>2</sub>OCO), 6.80-8.40 (d, 56H, -ArH), 8.45-8.52 (s, 4H, N-H), 9.25-9.30 (s, 4H, N-H), 9.30-9.33 (s, 4H, N-H), 9.59-9.62 (s, 2H, N-H). Anal. Calcd (%). for C<sub>148</sub>H<sub>171</sub>N<sub>37</sub>O<sub>30</sub> (2948.17): C, 60.29; H, 5.85; N, 17.58. Found (%): C, 60.55; H, 6.14; N, 17.34. MS (FAB MS):  $m/z$  = 2971 (M<sup>+</sup>Na<sup>+</sup>).

### Synthesis of dendron A-G2.5-DR1

IPDA (0.078 g, 0.339 mmol) was added to a solution of A-G2-DR1 (1g, 0.339 mmol) in THF and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G2.5-DR1 (0.377 g, yield = 35 %). IR (KBr): 1851, 1737 (–C=O stretch, -azetidine-2,4-dione), 1515, 1334 cm<sup>-1</sup> (–NO<sub>2</sub> stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 1.13-1.22 (t, 12H, -CH<sub>3</sub>), 1.22-1.28 (s, 6H, -CH<sub>3</sub>), 1.28-1.35 (s, 36H, -CH<sub>3</sub>), 3.21-3.23 (t, 12H, -N(CH<sub>2</sub>)), 3.24-3.40 (t, 12H, -NH (CH<sub>2</sub>)), 3.42-3.60 (q, 8H, -CH<sub>2</sub>N), 3.71-3.80 (t, 8H, -CH<sub>2</sub>N), 4.26-4.34 (t, 8H, -CH<sub>2</sub>OCO), 6.85-8.40 (m, 60H, -ArH), 8.41-8.44 (s, 4H, N-H), 9.13-9.20 (s, 4H, N-H), 9.30-9.36 (s, 4H, N-H), 9.59-9.65 (s, 2H, N-H). Anal. Calcd (%). for C<sub>160</sub>H<sub>181</sub>N<sub>39</sub>O<sub>33</sub> (3178.39): C, 60.46; H, 5.74; N, 17.19. Found (%): C, 60.22; H, 6.09; N, 17.08. MS (FAB MS):  $m/z$  = 3201 (M<sup>+</sup>Na<sup>+</sup>).

### Synthesis of dendron A-G3-DR1

DETA (0.0083 g, 0.080 mmol) was added to a solution of A-G2.5-CD (0.5 g, 0.161 mmol) in THF and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid (0.27 g, yield = 33%). IR (KBr): 1652 (C=O stretch), 1514, 1336 cm<sup>-1</sup> (–NO<sub>2</sub> stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 1.17-1.25 (t, 24H, -CH<sub>3</sub>), 1.20-1.45 (84H, -CH<sub>3</sub>), 3.20-3.23 (t, 28H, NH(CH<sub>2</sub>)), 3.24-3.31 (t, 28H,

-N(CH<sub>2</sub>)), 3.48-3.62 (q, 16H, -CH<sub>2</sub>N), 3.74-3.83 (t, 16H, -CH<sub>2</sub>N), 4.25-4.35 (t, 16H, -CH<sub>2</sub>OCO), 6.89-8.41 (d, 120H, -ArH), 8.42-8.52 (s, N-H), 9.15-9.23 (s, N-H), 9.30-9.35 (s, N-H), 9.58-9.64 (s, N-H). Anal. Calcd (%). for C<sub>324</sub>H<sub>375</sub>N<sub>81</sub>O<sub>66</sub> (6459.95): C, 60.24; H, 5.85; N, 17.56. Found: C, 59.88; H, 5.95; N, 17.34. MS (MALDI-TOF): m/z = 6483 (M<sup>+</sup>Na<sup>+</sup>).

## Synthesis of building block IDD based dendrons comprising alternating peripheral moieties of C18 and DR1

### Synthesis of dendron D-G1-CD

DETA (1.046 g, 10.14 mmol) was added to a solution of D-G0.5-C18 (2.00 g, 3.38 mmol) in THF (25 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to ambient temperature, the solution was poured into a mixed solvent (EA: Hexane = 1: 9) to remove the excess DETA. The crude product was precipitated in the solution. The white solid of crude product was filtered and dried in a vacuum. Subsequently, the filter cake and D-G0.5-DR1 (2.145 g, 3.38 mmol) were added in THF. The reaction mixture was stirred at 60 °C under N<sub>2</sub> for 2 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron D-G1-CD (2.47 g, yield = 55 %). IR (KBr): 1650 (C=O stretch), 1515, 1340 cm<sup>-1</sup> (-NO<sub>2</sub> stretch), 3500-3300 (-NH stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 0.72-0.80 (t, 3H, -CH<sub>3</sub>), 1.13-1.18 (m, 30H, -CH<sub>2</sub>-), 1.20-1.24 (t, 3H, -CH<sub>3</sub>), 1.25-1.37 (s, 12H, -CH<sub>3</sub>), 2.42-2.58 (2H, -CH<sub>2</sub>-), 2.49-2.58 (t, 4H, NH(CH<sub>2</sub>)), 3.05-3.16 (t, 4H, -N(CH<sub>2</sub>)), 3.40-3.58 (q, 2H, -CH<sub>2</sub>N), 3.60-3.73 (m, 6H, -Ar-CH<sub>2</sub>-Ar, -CH<sub>2</sub>N), 3.92-3.98 (t, 2H, -OCH<sub>2</sub>-), 4.18-4.21 (t, 2H, -CH<sub>2</sub>OCO), 6.80-6.92 (d, 2H, -ArH), 6.95-7.06 (d, 8H, -ArH), 7.20-7.32 (d, 4H, -ArH), 7.38-7.42 (d, 4H, -ArH), 7.71-7.90 (d, 4H, -ArH), 8.21-8.32 (d, 2H, -ArH), 9.20-9.60 (7H, N-H). Anal. Calcd (%). for C<sub>76</sub>H<sub>101</sub>N<sub>11</sub>O<sub>10</sub> (1328.68): C, 68.70; H, 7.66; N, 11.60. Found (%): C, 68.94; H, 7.71; N, 11.45. MS (FAB MS): *m/z* = 1329 (M<sup>+</sup>).

### Synthesis of dendron D-G1.5-CD

IDD (0.36 g, 1.13 mmol) was added to a solution of D-G1-CD (1.50 g, 1.13 mmol) in dry THF (25 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness.



The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron D-G1.5-CD (1.43 g, yield = 77 %). IR (KBr) : 1855, 1743 (-C=O stretch, -azetidine-2,4-dione), 1516, 1336  $\text{cm}^{-1}$  (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR ( $\delta$ /ppm, 400 MHz, d-DMSO): 0.77-0.96 (t, 3H, -CH<sub>3</sub>), 1.11-1.25 (m, 33H, -(CH<sub>2</sub>)<sub>15</sub>-, -CH<sub>3</sub>), 1.35-1.42 (s, 18H, -CH<sub>3</sub>), 2.42-2.58 (t, 4H, NH(CH<sub>2</sub>)), 3.18-3.22 (t, 4H, -N(CH<sub>2</sub>)), 3.42-3.53 (q, 2H, -N(CH<sub>2</sub>)), 3.66-3.87 (m, 6H, -Ar-CH<sub>2</sub>-Ar, -CH<sub>2</sub>N), 4.01-4.11 (t, 2H, -OCH<sub>2</sub>), 4.25-4.38 (t, 2H, -CH<sub>2</sub>O), 6.80-7.2 (m, 10, -ArH), 7.20-7.58 (d, 8H, -ArH), 7.81-8.02 (d, 4H, -ArH), 8.28-8.42 (d, 2H, -ArH), 8.40-9.70 (7H, N-H). ANAL. Calcd. for C<sub>95</sub>H<sub>117</sub>N<sub>13</sub>O<sub>13</sub> (1649.02): C, 69.19; H, 7.15; N, 11.04. Found: C, 69.11; H, 7.51; N, 10.89. MS (FAB MS):  $m/z$  = 1649 (M<sup>+</sup>).

### Synthesis of dendron D-G2-CD

DETA (0.031 g, 0.303 mmol) was added to a solution of D-G1.5-CD (1.00 g, 0.606 mmol) in THF (20 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron D-G2-CD (0.498 g, yield = 54 %). IR (KBr): 1654 (C=O stretch), 1515, 1338  $\text{cm}^{-1}$  (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR ( $\delta$ /ppm, 400 MHz, d-DMSO): 0.80-0.91 (t, 6H, -CH<sub>3</sub>), 1.19-1.40 (m, 42H, -CH<sub>3</sub>; 60H, -CH<sub>2</sub>-), 1.41-1.59 (q, 4H, -CH<sub>2</sub>-), 2.38-2.60 (t, 12H, -NH(CH<sub>2</sub>)), 3.18-3.20 (t, 12H, -N(CH<sub>2</sub>)), 3.42-3.53 (q, 4H, -N(CH<sub>2</sub>)), 3.60-3.81 (m, 16H, Ar-CH<sub>2</sub>-Ar, -NCH<sub>2</sub>-), 3.82-4.12 (t, 4H, -CH<sub>2</sub>O-), 4.21-4.38 (t, 4H, -CH<sub>2</sub>OCO-), 6.80-8.38 (m, 64H, -ArH), 8.40-9.82 (m, 19H, -NH). Anal. Calcd (%). for C<sub>194</sub>H<sub>247</sub>N<sub>29</sub>O<sub>26</sub> (3401.22): C, 68.51; H, 7.32; N, 11.94. Found (%): C, 68.25; H, 7.33; N, 11.85. MS (FAB MS):  $m/z$  = 3401 (M<sup>+</sup>).

### Synthesis of dendron D-G2.5-CD

IDD (0.1 g, 0.294 mmol) was added to a solution of D-G2-CD (1.00 g, 0.249 mmol) in dry THF (20 mL). The solution was stirred at 60 °C under N<sub>2</sub> for 6 h.

After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron D-G2.5-CD (0.77 g, yield = 71 %). IR (KBr): 1854, 1740 (-C=O, stretch, -azetidine-2,4-dione), 1516, 1320  $\text{cm}^{-1}$  (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR ( $\delta$ /ppm, 400 MHz, d-DMSO): 0.79-0.85 (t, 6H, -CH<sub>3</sub>), 1.16-1.40 (m, 48H, -CH<sub>3</sub>; 60H, -CH<sub>2</sub>-), 1.51-1.62 (m, 4H, -CH<sub>2</sub>-), 2.38-2.50 (t, 12H, -NH(CH<sub>2</sub>)), 3.18-3.20 (t, 12H, -N(CH<sub>2</sub>)), 3.25-3.40 (q, 4H, -NCH<sub>2</sub>-), 3.50-3.61 (m, 14H, Ar-CH<sub>2</sub>-Ar; 4H, -NCH<sub>2</sub>-), 3.63-3.81 (t, 4H, -CH<sub>2</sub>O-), 3.91-4.12 (t, 4H, -CH<sub>2</sub>OCO-), 6.86-8.42 (d, 72H, -ArH), 8.41-9.72 (s, 17H, N-H). Anal. Calcd (%). for C<sub>213</sub>H<sub>263</sub>N<sub>31</sub>O<sub>29</sub> (3721.56): C, 68.74; H, 7.12; N, 11.67. Found (%): C, 68.48; H, 7.16; N, 11.52. MS (FAB MS):  $m/z$  = 3721 (M<sup>+</sup>).

### Synthesis of dendron D-G3-CD

DETA (0.0069 g, 0.067 mmol) was added to a solution of D-G2.5-CD (0.5g, 0.134 mmol) in dry THF (20 mL). The solution was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron D-G3-CD (0.498 g, yield = 54 %). IR (KBr): 1656 (-C=O, stretch), 1515, 1337  $\text{cm}^{-1}$  (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR ( $\delta$ /ppm, 400 MHz, d-DMSO): 0.81-0.96 (t, 12H, -CH<sub>3</sub>), 1.07-1.35 (m, 96H, -CH<sub>3</sub>; 120H, -CH<sub>2</sub>-), 1.50-1.61 (m, 8H, -CH<sub>2</sub>-), 2.12-2.25 (t, 28H, -NH(CH<sub>2</sub>)), 3.15-3.23 (t, 28H, -N(CH<sub>2</sub>)), 3.40-3.60 (q, 8H, -NCH<sub>2</sub>-), 3.763 (br, 36H, Ar-CH<sub>2</sub>-Ar; -NCH<sub>2</sub>-), 3.91-4.12 (t, 8H, -CH<sub>2</sub>O-), 4.27-4.31 (t, 8H, -CH<sub>2</sub>OCO-), 6.64-8.40 (d, 72H, -ArH), 8.40-9.81 (s, 43H, N-H). Anal. Calcd (%). for C<sub>430</sub>H<sub>539</sub>N<sub>65</sub>O<sub>58</sub> (7546.28): C, 68.44; H, 7.20; N, 12.06. Found (%): C, 68.22; H, 7.26; N, 11.88. MS (MALDI-TOF):  $m/z$  = 7546.

## Synthesis of building block IPDA based dendrons comprising alternating peripheral moieties of C18 and DR1

### Synthesis of dendron A-G0.5-C18

Stearyl alcohol (5.00 g, 18.5 mmol) was added to a solution of IPDA (4.25 g, 18.50 mmol) in dry THF (40 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was precipitated from methanol to give A-G0.5-C18 (7.8 g, 85%) as a white powder. IR (KBr): 1853, 1733 (-C=O stretch, azetidine-2,4-dione), 3330 cm<sup>-1</sup> (NH). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 0.75-0.98 (t, 3H, -CH<sub>3</sub>), 1.01-1.37 (m, 30H, -CH<sub>2</sub>-), 1.38-1.44 (s, 6H, -CH<sub>3</sub>), 1.45-1.64 (m, 2H, -CH<sub>2</sub>-), 3.98-4.14 (t, 2H, -COO-CH<sub>2</sub>), 7.45-7.64 (d, 2H, Ar-H), 8.11-8.32 (d, 2H, Ar-H), 9.664 (1H, Ar-NHCOO). Anal. Calcd (%) for C<sub>30</sub>H<sub>48</sub>N<sub>2</sub>O<sub>4</sub> (500.7): C, 71.04; H, 9.66; N, 5.59. Found (%): C, 71.25; H, 9.48; N, 5.35. MS (FAB MS): *m/z* = 500 (M<sup>+</sup>).

### Synthesis of dendron A-G1-CD

DETA (1.23 g, 11.98 mmol) was added to a solution of A-G0.5-C18 (2.00 g, 4.00 mmol) in THF (20 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to ambient temperature, the solution was poured into the mixed solvent (EA: Hexane = 1: 9) to remove the excess DETA. The crude product was precipitated in the solution. The white solid of crude product was filtered and dried in a vacuum. Next, the filter cake and as-prepared A-G0.5-DR1 (2.18 g, 4.00 mmol) were added in THF at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G1-CD (2.98 g, yield = 65 %). IR (KBr): 1646 (-C=O stretch), 1518, 1337 (-NO<sub>2</sub> stretch), 3295 cm<sup>-1</sup> (-NH stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 0.79-0.89 (t, 3H, -CH<sub>3</sub>), 1.15-1.28 (m, 33H, -CH<sub>2</sub>-, -NCH<sub>2</sub>(CH<sub>3</sub>)), 1.36-1.41 (s, 12H,

-COC(CH<sub>3</sub>)<sub>2</sub>), 1.43-1.62 (t, 2H, -OC(CH<sub>2</sub>)), 2.58-2.62 (t, 4H, -NH(CH<sub>2</sub>)), 3.02-3.23 (t, 4H, -CH<sub>2</sub>NH), 3.30-3.41 (t, 2H, -N(CH<sub>2</sub>-), 3.70-3.81 (m, 2H, -N(CH<sub>2</sub>-), 4.01-4.26 (t, 2H, -COO(CH<sub>2</sub>)), 6.923-7.02 (d, 2H, -ArH), 7.23-8.01 (m, 12H, -ArH), 8.33-8.41 (d, 2H, -ArH), 9.20-9.80 (s, 7H, N-H). Anal. Calcd (%). for C<sub>62</sub>H<sub>89</sub>N<sub>11</sub>O<sub>10</sub> (1148.44): C, 64.84; H, 7.81; N, 13.42. Found (%): C, 64.55; H, 8.02, N, 13.22. MS (FAB MS):  $m/z$  = 1148 (M<sup>+</sup>).

### Synthesis of dendron A-G1.5-CD

IPDA (0.3 g, 1.30 mmol) was added to a solution of A-G1-CD (1.50 g, 1.3 mmol) in dry THF (20 mL). The solution was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G1.5-CD (1.37 g, Yield = 77 %). IR (KBr): 1854, 1741 (-C=O stretch, -azetidine-2,4-dione), 1514, 1335 cm<sup>-1</sup> (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR (δ/ppm, 400 MHz, d-DMSO): 1.01-1.18 (t, 3H, -CH<sub>3</sub>), 1.20-1.52 (m, 33H, -CH<sub>2</sub>-, -NC(CH<sub>3</sub>)), 1.35-1.78 (m, 18H, -CH<sub>3</sub>), 1.79-1.89 (m, 2H, -OC(CH<sub>2</sub>)), 2.61-2.78 (t, 4H, -CH<sub>2</sub>N), 3.42-3.52 (t, 4H, -N(CH<sub>2</sub>-), 3.73-3.82 (q, 2H, -NCH<sub>2</sub>-), 3.91-4.02 (t, 2H, -N-CH<sub>2</sub>-), 4.21-4.32 (t, 2H, -COO(CH<sub>2</sub>-), 4.40-4.58 (t, 2H, -COO(CH<sub>2</sub>-), 7.10-7.25 (d, 2H, -ArH), 7.50-8.30 (m, 16H, -ArH), 8.52-8.61 (d, 2H, -ArH), 8.61-9.95 (s, 7H, N-H). Anal. Calcd (%). for C<sub>74</sub>H<sub>99</sub>N<sub>13</sub>O<sub>13</sub> (1378.66): C, 64.47; H, 7.24; N, 13.21. Found: C, 64.16; H, 7.28; N, 13.08. MS (FAB MS):  $m/z$  = 1378 (M<sup>+</sup>).

### Synthesis of dendron A-G2-CD

DETA (0.5 g, 0.362 mmol) was added to a solution of A-G1.5-CD (1.00g, 0.725 mmol) in THF (20 mL) and then the mixture was stirred at 60 °C under N<sub>2</sub> for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to

give a red solid of dendron A-G2-CD (1.26 g, yield = 61 %). IR (KBr): 1655 (C=O stretch), 1517, 1337  $\text{cm}^{-1}$  ( $\text{NO}_2$  stretch).  $^1\text{H}$  NMR ( $\delta/\text{ppm}$ , 400 MHz, d-DMSO): 0.82-0.91 (t, 6H,  $-\text{CH}_3$ ), 1.12-1.35 (m, 66H,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ), 1.35-1.41 (s, 36H,  $-\text{NH-COC}(\text{CH}_3)_2$ ), 1.45-1.361 (m, 4H,  $-\text{COO-C}(\text{CH}_2)-$ ), 2.58-2.62 (t, 12H,  $-\text{CH}_2\text{NH}$ ), 3.12-3.20 (t, 12H,  $-\text{CH}_2\text{N}$ ), 3.54-3.62 (q, 4H,  $-\text{N}(\text{CH}_2)$ ), 3.73-3.80 (t, 4H,  $-\text{N}(\text{CH}_2)$ ), 4.01-4.09 (t, 4H,  $-\text{COO}(\text{CH}_2)-$ ), 4.26-4.32 (t, 4H,  $-\text{COO}(\text{CH}_2)-$ ), 6.91-7.01 (d, 4H,  $-\text{ArH}$ ), 7.31-7.98 (m, 36H,  $-\text{ArH}$ ), 8.31-8.38 (d, 4H,  $-\text{ArH}$ ), 8.41-9.68 (s, 19H, N-H). Anal. Calcd (%). for  $\text{C}_{152}\text{H}_{211}\text{N}_{29}\text{O}_{26}$  (2860.48): C, 63.82; H, 7.43; N, 14.2. Found: C, 63.77; H, 7.54; N, 14.21. MS (FAB MS):  $m/z = 2860$  ( $\text{M}^+$ ).

### Synthesis of dendron A-G2.5-CD

IPDA (0.5 g, 0.349 mmol) was added to a solution of A-G2-CD (1g, 0.349 mmol) in dry THF (20 mL). The solution was stirred at 60  $^\circ\text{C}$  under  $\text{N}_2$  for 6 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G2.5-CD (0.57 g, yield = 57 %). IR (KBr): 1854, 1740 (C=O stretch,  $-\text{azetidine-2,4-dione}$ ), 1515, 1335  $\text{cm}^{-1}$  ( $\text{NO}_2$  stretch).  $^1\text{H}$  NMR ( $\delta/\text{ppm}$ , 400 MHz, d-DMSO): 0.79-0.85 (t, 6H,  $-\text{CH}_3$ ), 1.15-1.28 (m, 66H,  $-\text{CH}_2-$ ), 1.30-1.41 (br, 42H,  $-\text{NHCOC}(\text{CH}_3)_2$ ), 1.45-1.60 (m, 4H,  $-\text{OC}(\text{CH}_2)$ ), 2.45-2.56 (t, 12H,  $-\text{CH}_2\text{N}$ ), 3.19-3.25 (t, 4H,  $-\text{N}(\text{CH}_2)-$ ), 3.45-3.61 (q, 4H,  $-\text{N}(\text{CH}_2)-$ ), 3.72-3.80 (t, 4H,  $-\text{N}(\text{CH}_2)-$ ), 3.91-4.09 (t, 4H,  $-\text{CH}_2\text{OCO}-$ ), 4.21-4.29 (t, 4H,  $-\text{COO}(\text{CH}_2)-$ ), 6.89-7.00 (d, 2H,  $-\text{ArH}$ ), 7.25-8.00 (d, 40H,  $-\text{ArH}$ ), 8.31-8.38 (d, 2H,  $-\text{ArH}$ ), 8.40-9.68 (s, 19H, N-H). Anal. Calcd (%). for  $\text{C}_{164}\text{H}_{221}\text{N}_{31}\text{O}_{29}$  (3090.7): C, 63.73; H, 7.21; N, 14.05. Found (%): C, 63.15; H, 7.70; N, 14.15. MS (FAB MS):  $m/z = 3091$  ( $\text{M}^+$ ).

### Synthesis of dendron A-G3-CD

DETA (0.0083 g, 0.080 mmol) was added to a solution of A-G2.5-CD (0.5 g, 0.161 mmol) in THF (20 mL) and then the mixture was stirred at 60  $^\circ\text{C}$  under  $\text{N}_2$  for 6

h. The reaction mixture was evaporated to dryness. The crude product was purified by silica gel chromatography (EA/hexane as eluent) to give a red solid of dendron A-G3-CD (0.24 g, yield =24 %). IR (KBr): 1655 (-C=O stretch), 1517, 1338  $\text{cm}^{-1}$  (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR ( $\delta$ /ppm, 400 MHz, d-DMSO): 0.79-0.88 (t, 12H, -CH<sub>3</sub>), 1.15-1.32 (br, 132H, -CH<sub>2</sub>-, -NC-CH<sub>3</sub>), 1.38-1.42 (s, 84H, -NCOC(CH<sub>3</sub>)<sub>2</sub>), 1.52-1.61 (m, 8H, -COOC(CH<sub>2</sub>)-), 2.42-2.58 (t, 28H, -NCH<sub>2</sub>-), 3.20-3.31 (t, 28H, -NCH<sub>2</sub>-), 3.55-3.60 (t, 8H, -N(CH<sub>2</sub>)-), 3.55-3.60 (t, 8H, -N(CH<sub>2</sub>)-), 3.72-3.78 (t, 8H, -N(CH<sub>2</sub>)-), 3.92-4.16 (t, 8H, -COO(CH<sub>2</sub>)-), 4.41-4.30 (m, 8H, -COO(CH<sub>2</sub>)-), 6.88-8.41 (m, 88H, -ArH), 8.42-9.58 (s, 43H, N-H). Anal. Calcd (%). for C<sub>332</sub>H<sub>455</sub>N<sub>65</sub>O<sub>58</sub> (6284.57): C, 63.45; H, 7.30; N, 14.49. Found (%): C, 62.83; H, 7.25; N, 14.22. MS (MALDI-TOF):  $m/z$  = 6285 (M<sup>+</sup>).

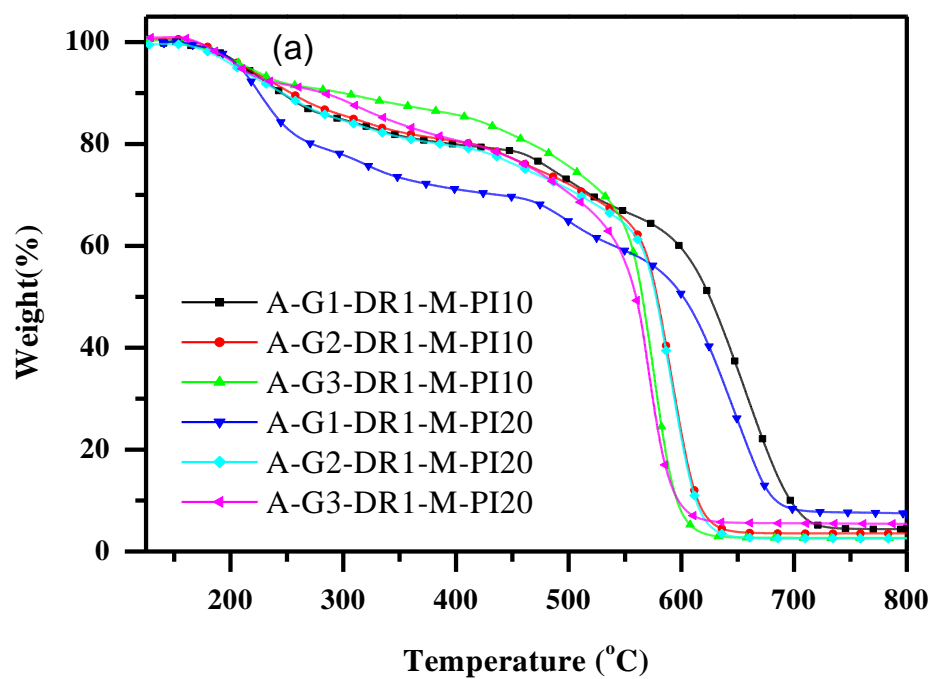


Figure S1. TGA thermograms of the dendron-intercalated MMT/PI composites ((a) A-G(X)-DR1-M/PI; (b) D-G(X)-CD-M/PI; (c) A-G(X)-CD-M/PI).

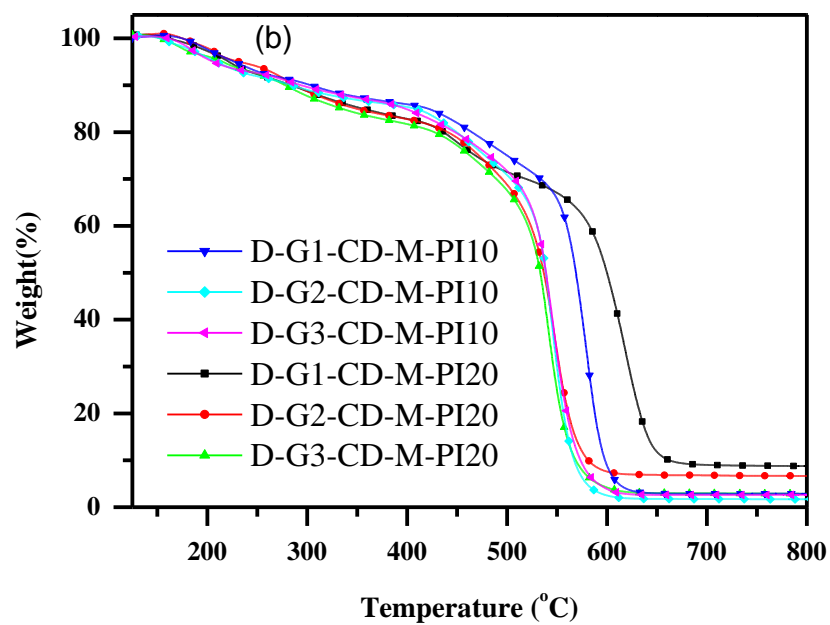


Figure S1. TGA thermograms of the dendron-intercalated MMT/PI composites ((a) A-G(X)-DR1-M/PI; (b) D-G(X)-CD-M/PI; (c) A-G(X)-CD-M/PI).



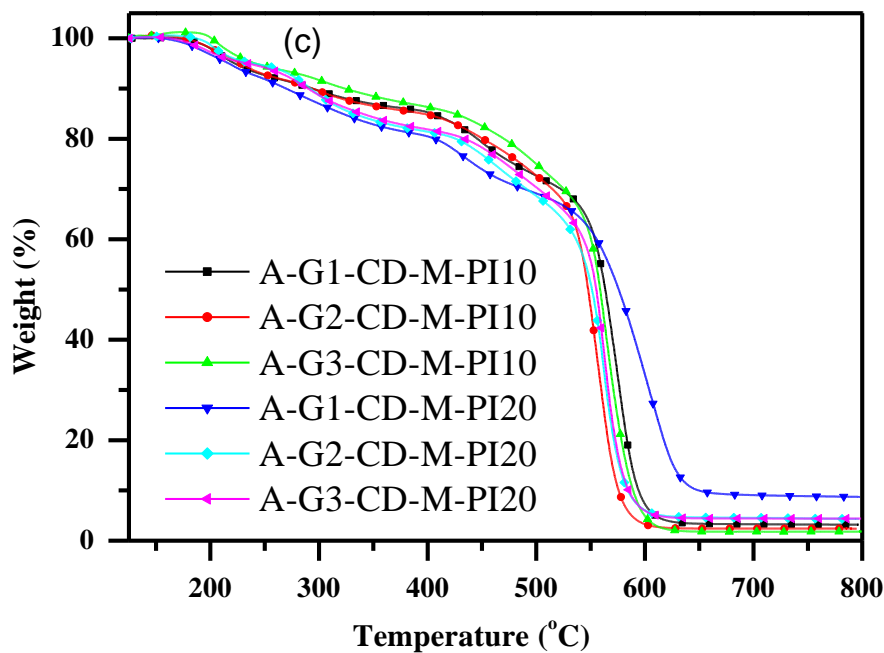


Figure S1. TGA thermograms of the dendron-intercalated MMT/PI composites ((a) A-G(X)-DR1-M/PI; (b) D-G(X)-CD-M/PI; (c) A-G(X)-CD-M/PI).

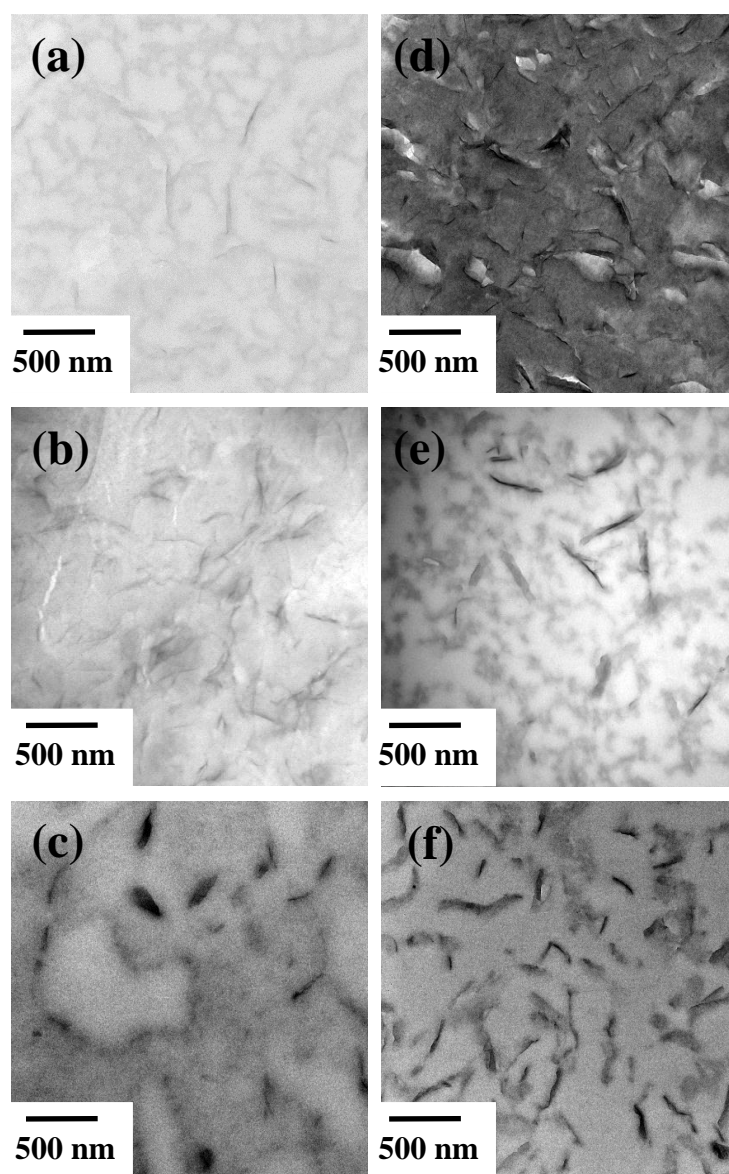


Figure S2. TEM images of (a)A-G1-DR1-M-PI10; (b) A-G2-DR1-M-PI10; (c) A-G3-DR1-M-PI10; (d) A-G1-DR1-M-PI20; (e) A-G2-DR1-M-PI20;(f) A-G3-DR1-M-PI20.

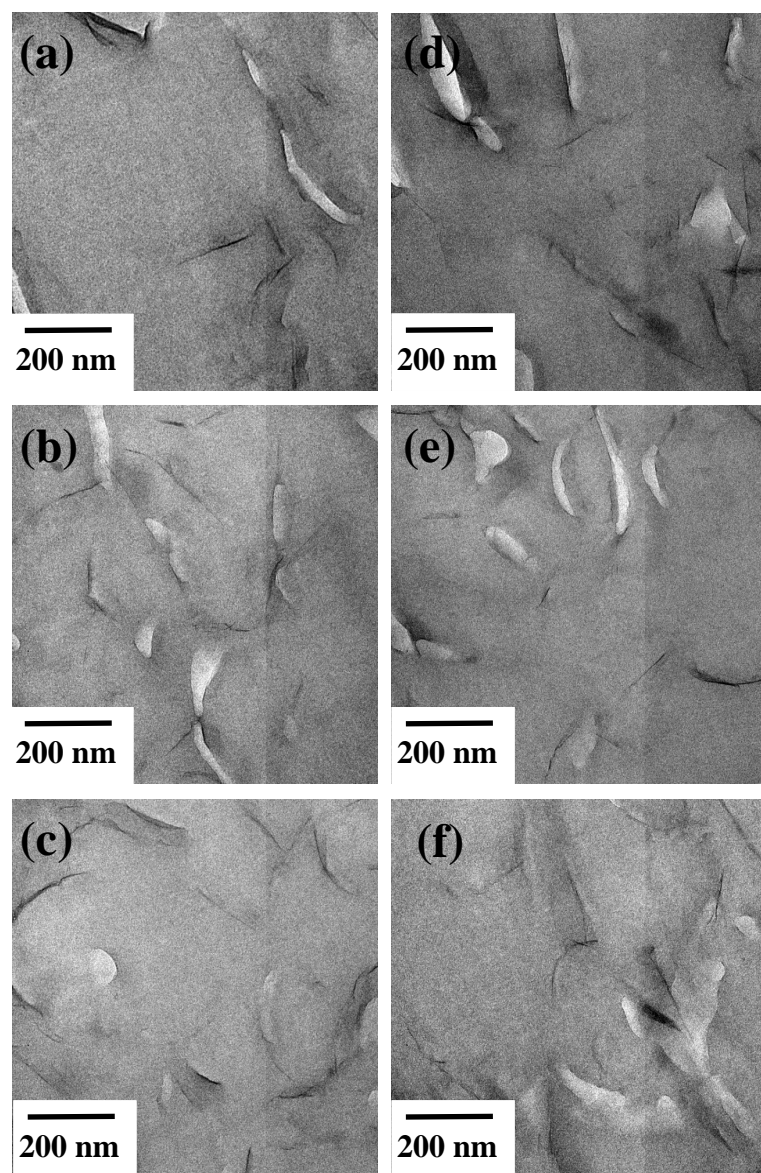


Figure S3. TEM images of (a)A-G1-CD-M-PI10; (b) A-G2-CD-M-PI10; (c) A-G3-CD-M-PI10; (d) A-G1-CD-M-PI20; (e) A-G2-CD-M-PI20;(f) A-G3-CD-M-PI20.

### **The Optical Nonlinearity of the DR1 in Polyimide**

DR1 was doped into the polyimide sample to form a guest–host system (10.5 wt%). The guest–host polymer solution (DMAc) was stirred at room temperature for 2 h and filtered through a 1.0  $\mu\text{m}$  microsyringe filter. High-quality polymer films were obtained by spin-coating the solution onto indium tin oxide (ITO) coated glass substrates. The spin-coated films were further dried in vacuum at 60  $^{\circ}\text{C}$  overnight to remove the residual solvent. The poling process for the second-order NLO polymer films was carried out using an *in situ* contact poling technique. The poling voltage was maintained at 100 V and the temperature was kept close to the  $T_g$  (193  $^{\circ}\text{C}$ ). Upon saturation of the EO signal intensity, the sample was then cooled down to room temperature in the presence of the poling field at which point the poling field was terminated. EO coefficients of the poled samples were measured at 830 nm wavelength using the simple reflection technique. The  $r_{33}$  value of this guest-host system was 12.5 pm/V.