# Supplementary Information for:

Competition and promotion of different mesophases in series of novel unsymmetrical discotic dimers via subtle modification of spacers and peripheral side chains

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# 1. Synthesis and characterization



### 2-(6'-Bromohexyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1a)

1.36g (49.98mmol) 1,6-dibromohexane and 0.5g (7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.3g (47%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.6 (14H, m,OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

#### 2-(7'-Bromoheptyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1b)

1.44g (49.98mmol) 1,7-dibromoheptane and 0.5g (7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.3g (46%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1254 (C-O-C);  $\delta_{H}$ (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.6 (16H, m,OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(8'-Bromooctyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1c)

1.52g (49.98mmol) 1,8-dibromooctane and 0.5g(7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.3g (45.5%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1256 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (18H, m,OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(9'-Bromononyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1d)

1.6g (49.98mmol) 1,9-dibromononane and 0.5g(7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent

CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.4g (60%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (20H, m,OCH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(10'-Bromodecyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1e)

1.67g (49.98mmol) 1,10-dibromodecane and 0.5g(7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography.(silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.4g (58.8%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1253 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (22H, m,OCH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

#### 2-(11'-Bromoundecyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1f)

1.75g (49.98mmol) 1,11-dibromoundecane and 0.5g (7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.35g (51%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (24H, m,OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

#### 2-(12'-Bromododecyloxy)-3,6,7,10,11-Pentabutoxytriphenylene (1g)

1.83g (49.98mmol) 1,12-dibromododecane and 0.5g (7.41mmol) **HAT4** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography.(silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1). Recrystallization from ethanol yields 0.4g (57%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1252 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Er), 1.7-1.5 (26H, m,OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).



2-(6'-Bromohexyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2a)

1.22g (49.98mmol) 1,6-dibromohexane and 0.5g(7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography.(silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.3g (48%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(7'-Bromoheptyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2b)

1.29g (49.98mmol) 1,7-dibromoheptane and 0.5g(7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography.(silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.28g (44%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (26H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(8'-Bromooctyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2c)

1.36g (49.98mmol) 1,8-dibromooctane and 0.5g(7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.3g (47%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (28H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(9'-Bromononyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2d)

1.43g (49.98mmol) 1,9-dibromononane and 0.5g (7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.3g (46%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1254 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (30H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

### 2-(10'-Bromodecyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2e)

1.5g (49.98mmol) 1,10-dibromodecane and 0.5g (7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.3g (45%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$ (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (32H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

#### 2-(11'-Bromoundecyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2f)

1.57g (49.98mmol) 1,11-dibromoundecane and 0.5g (7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.32g (47%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (34H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).

#### 2-(12'-Bromododecyloxy)-3,6,7,10,11-Pentapentyloxytriphenylene (2g)

1.64g (49.98mmol) 1,12-dibromododecane and 0.5g (7.41mmol) **HAT5** are dissolved in 12ml acetone and stirred for 15h after addition of 0.6g (43.31mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography. (silica gel eluent CH<sub>2</sub>Cl<sub>2</sub>/PE=1;1). Recrystallization from ethanol yields 0.35g (51%) pure product as a white soild. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); IR (KBr):  $v_{max}/cm^{-1}$  1255 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (6H, s, ArH), 4.4-4.2 (12H, t, OCH<sub>2</sub>), 3.5 (2H, t, CH<sub>2</sub>Br), 2.1-1.90 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>+CH<sub>2</sub>CH<sub>2</sub>Br), 1.7-1.5 (36H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 1.2-1.0 (15H, t, CH<sub>3</sub>).



# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-6-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-hexane (T<sub>3,4</sub>D<sub>6</sub>)

0.35g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1a** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.16g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:  $CH_2Cl_2:PE=1:1$ ) and subsequent recrystallization from acetone yields 0.24 (30.2%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 75.7; H 8.58.  $C_{77}H_{104}O_{12}$  requires: C, 75.8; H, 8.59%); IR (KBr):  $v_{max}/cm^{-1}$  1263 (C-O-C);  $\delta_H$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (14H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1220.7522

(C<sub>77</sub>H<sub>104</sub>O<sub>12</sub>), found m/z 1220.7518 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-7-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-heptane (T<sub>3,4</sub>D<sub>7</sub>)

0.34g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1b** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.14g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.25g (31.6%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 75.8; H 8.66. C<sub>78</sub>H<sub>106</sub>O<sub>12</sub> requires: C, 75.9; H, 8.65%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (16H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1234.7679 (C<sub>78</sub>H<sub>106</sub>O<sub>12</sub>), found m/z 1234.7679 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-8-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-octane (T<sub>3,4</sub>D<sub>8</sub>)

0.33g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1c** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.12g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.25 (31.8%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 75.96; H 8.72. C<sub>79</sub>H<sub>108</sub>O<sub>12</sub> requires: C, 75.98; H, 8.71%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (18H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1248.7834 (C<sub>79</sub>H<sub>108</sub>O<sub>12</sub>), found m/z 1248.7835 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-9-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-nonane (T<sub>3,4</sub>D<sub>9</sub>)

0.327g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1d** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.1g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.25g (32%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 75.9; H 8.76. C<sub>80</sub>H<sub>110</sub>O<sub>12</sub> requires: C, 76.1; H, 8.78%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (20H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1262.7990 (C<sub>80</sub>H<sub>110</sub>O<sub>12</sub>), found m/z 1262.7992 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-10-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-decane (T<sub>3,4</sub>D<sub>10</sub>)

0.32g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1e** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.08g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:  $CH_2Cl_2:PE=1:1$ ) and subsequent recrystallization from acetone yields 0.26 (34%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.1; H 8.84. C<sub>81</sub>H<sub>112</sub>O<sub>12</sub> requires: C, 76.2; H, 8.84%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_H$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (22H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1276.8145

 $(C_{81}H_{112}O_{12})$ , found m/z 1276.8148 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-11-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-undecane (T<sub>3,4</sub>D<sub>11</sub>)

0.316g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1f** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.07g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.26 (33.7%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.1; H 8.87. C<sub>82</sub>H<sub>114</sub>O<sub>12</sub> requires: C, 76.3; H, 8.9%); IR (KBr):  $\nu_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1290.8304 (C<sub>82</sub>H<sub>114</sub>O<sub>12</sub>), found m/z 1290.8305 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-12-(3,6,7,10,11-pentabutoxytriphenylen-2-yloxy)-dodecane (T<sub>3,4</sub>D<sub>12</sub>)

0.31g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **1g** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.05g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:  $CH_2Cl_2:PE=1:1$ ) and subsequent recrystallization from acetone yields 0.25 (32.6%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.3; H 8.94. C<sub>83</sub>H<sub>116</sub>O<sub>12</sub> requires: C, 76.4; H, 8.96%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_H$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (26H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1304.8461 (C<sub>83</sub>H<sub>116</sub>O<sub>12</sub>), found m/z 1304.8461 (M)<sup>+</sup>



# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-6-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-hexane (T<sub>4,5</sub>D<sub>6</sub>)

0.358g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2a** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.07g (28.94mmol) potassium carbonate

and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.31g (38%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.75; H 9.17.  $C_{87}H_{124}O_{12}$  requires: C, 76.78; H, 9.18%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (34H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1360.9088 (C<sub>87</sub>H<sub>124</sub>O<sub>12</sub>), found m/z 1360.9087 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-7-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-heptane (T<sub>4,5</sub>D<sub>7</sub>)

0.35g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2b** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.05g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.36g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.84; H 9.22 C<sub>88</sub>H<sub>126</sub>O<sub>12</sub> requires: C, 76.87; H, 9.24%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (36H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1374.9247 (C<sub>88</sub>H<sub>126</sub>O<sub>12</sub>), found m/z 1374.9244 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-8-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-octane (T<sub>4,5</sub>D<sub>8</sub>)

0.35g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2c** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.03g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.36g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.94; H 9.27. C<sub>89</sub>H<sub>128</sub>O<sub>12</sub> requires: C, 76.96; H, 9.29%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (38H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1388.9403 (C<sub>89</sub>H<sub>128</sub>O<sub>12</sub>), found m/z 1388.9400 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-9-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-nonane (T<sub>4,5</sub>D<sub>9</sub>)

0.34g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2d** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.01g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.36g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 76.8; H 9.3. C<sub>90</sub>H<sub>130</sub>O<sub>12</sub> requires: C, 77.1; H, 9.34%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (40H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1402.9562 (C<sub>90</sub>H<sub>130</sub>O<sub>12</sub>), found m/z 1402.9557 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-10-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-decane (T<sub>4,5</sub>D<sub>10</sub>)

0.34g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2e** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.998g (28.94mmol) potassium carbonate

and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.36g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 77.05; H 9.32. C<sub>91</sub>H<sub>132</sub>O<sub>12</sub> requires: C, 77.14; H, 9.39%); IR (KBr):  $\nu_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (42H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1416.9713 (C<sub>91</sub>H<sub>132</sub>O<sub>12</sub>), found m/z 1416.9713 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-11-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-undecane (T<sub>4,5</sub>D<sub>11</sub>)

0.33g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2f** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.98g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.35g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 77.13; H 9.35. C<sub>92</sub>H<sub>134</sub>O<sub>12</sub> requires: C, 77.22; H, 9.44%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (44H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1430.9877 (C<sub>92</sub>H<sub>134</sub>O<sub>12</sub>), found m/z 1430.9870 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentabutoxytriphenylene-2-yloxy)-12-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-dodecane (T<sub>4,5</sub>D<sub>12</sub>)

0.33g (2.22mmol) **HAT4** and 0.5g (2.24mmol) **2g** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.97g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.35g (45%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (found: C 77.1; H 9.43. C<sub>93</sub>H<sub>136</sub>O<sub>12</sub> requires: C, 77.3; H, 9.49%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (46H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+ OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>O+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1445.0021 (C<sub>93</sub>H<sub>136</sub>O<sub>12</sub>), found m/z 1445.0027 (M)<sup>+</sup>



# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-6-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-hexane (T<sub>3,5</sub>D<sub>6</sub>)

0.32g (2.22mmol) HAT3 and 0.5g (2.24mmol) 2a are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.07g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.25g (32%) of the dimer as a white solid. TLC Rf: 0.6 (dichloromethane-light petroleum 1:1); Found: C, 76.17; H, 8.94. C<sub>82</sub>H<sub>114</sub>O<sub>12</sub> requires: C, 76.24; H, 8.90%); IR (KBr): ν<sub>max</sub>/cm<sup>-1</sup> 1263 (C-O-C); δ<sub>H</sub> (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, OCH<sub>2</sub>), 2.1-1.90 (24H, m. OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 t. (24H, m. OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1290.8307 (C<sub>82</sub>H<sub>114</sub>O<sub>12</sub>), found m/z 1290.8305 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-7-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-heptane (T<sub>3,5</sub>D<sub>7</sub>)

0.31g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **2b** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.05g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.3g (39%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.26; H, 9.02. C<sub>83</sub>H<sub>116</sub>O<sub>12</sub> requires: C, 76.34; H, 8.95%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (26H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1304.8462 (C<sub>83</sub>H<sub>116</sub>O<sub>12</sub>), found m/z 1304.8461 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-8-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-octane (T<sub>3,5</sub>D<sub>8</sub>)

0.31g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **2c** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.03g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.3g (39%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.38; H, 8.95. C<sub>84</sub>H<sub>118</sub>O<sub>12</sub> requires: C, 76.44; H, 9.01%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (28H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1318.8608 (C<sub>84</sub>H<sub>118</sub>O<sub>12</sub>), found m/z 1318.8618 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-9-(3,6,7,10,11-pentapentyloxytriphenylen-2-yloxy)-nonane (T<sub>3,5</sub>D<sub>9</sub>)

0.3g (2.22mmol) HAT3 and 0.5g (2.24mmol) 2d are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 1.01g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.3g (40%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.57; H, 9.0. C<sub>85</sub>H<sub>120</sub>O<sub>12</sub> requires: C, 76.54; H, 9.07%); IR (KBr): v<sub>max</sub>/cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{\rm H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t. OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (30H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1332.8750 (C<sub>85</sub>H<sub>120</sub>O<sub>12</sub>), found m/z 1332.8774 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-10-(3,6,7,10,11-

# pentapentyloxytriphenylen-2-yloxy)-decane (T<sub>3,5</sub>D<sub>10</sub>)

0.3g (2.22mmol) HAT3 and 0.5g (2.24mmol) 2e are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.998g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.26g (35%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.52; H, 9.09. C86H122O12 requires: C, 76.63; H, 9.12%); IR (KBr): ν<sub>max</sub>/cm<sup>-1</sup> 1263 (C-O-C); δ<sub>H</sub> (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, OCH<sub>2</sub>), 2.1-1.90 (24H, m. OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 t. (32H, m. OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1346.8938 (C<sub>86</sub>H<sub>122</sub>O<sub>12</sub>), found m/z 1346.8931 (M)<sup>+</sup>

# 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-11-(3,6,7,10,11-

## pentapentyloxytriphenylen-2-yloxy)-undecane (T<sub>3,5</sub>D<sub>11</sub>)

0.29g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **2f** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.98g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent:  $CH_2Cl_2:PE=1:1$ ) and subsequent recrystallization from acetone yields 0.26g (35%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.55; H, 9.15.  $C_{87}H_{124}O_{12}$  requires: C, 76.73; H, 9.18%); IR (KBr):  $v_{max}/cm^{-1}$  1263 (C-O-C);  $\delta_H$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (34H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1360.9083 ( $C_{87}H_{124}O_{12}$ ), found m/z 1360.9087 (M)<sup>+</sup>

### 1-(3,6,7,10,11-pentapropoxytriphenylene-2-yloxy)-12-(3,6,7,10,11-

### pentapentyloxytriphenylen-2-yloxy)-dodecane (T<sub>3,5</sub>D<sub>12</sub>)

0.29g (2.22mmol) **HAT3** and 0.5g (2.24mmol) **2g** are dissolved in 15ml acetone under nitrogen. The mixture is refluxed for twenty hours after addition of 0.97g (28.94mmol) potassium carbonate and potassium iodide (50mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>:PE=1:1) and subsequent recrystallization from acetone yields 0.26g (35%) of the dimer as a white solid. TLC R<sub>f</sub>: 0.6 (dichloromethane-light petroleum 1:1); (Found: C, 76.54; H, 9.10. C<sub>88</sub>H<sub>126</sub>O<sub>12</sub> requires: C, 76.82; H, 9.23%); IR (KBr):  $v_{max}$ /cm<sup>-1</sup> 1263 (C-O-C);  $\delta_{H}$  (300MHZ, CDCl<sub>3</sub>) 8-7.8 (12H, s, ArH), 4.4-4.2 (24H, t, OCH<sub>2</sub>), 2.1-1.90 (24H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.7-1.35 (36H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>+OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.2-1.0 (30H, t, CH<sub>3</sub>), HRMS (ESI): calc.m/z 1374.9247 (C<sub>88</sub>H<sub>126</sub>O<sub>12</sub>), found m/z 1374.9244 (M)<sup>+</sup>

# 2 <sup>1</sup>H-NMR and HRMS spectra

















Fig.S15 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>6</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
346	C <sub>77</sub> H <sub>104</sub> O <sub>12</sub>	[M]+	1220.7518	1220.7522	-0.3277



Fig.S16 HRMS spectra of T<sub>3,4</sub>D<sub>6</sub>



Fig.S17 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>7</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
347	C <sub>78</sub> H <sub>106</sub> O <sub>12</sub>	[M]+	1234.7679	1234.7679	0.0000



Fig.S18 HRMS spectra of T<sub>3,4</sub>D<sub>7</sub>



Fig.S19 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>8</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
348	C <sub>79</sub> H <sub>108</sub> O <sub>12</sub>	[M]+	1248.7835	1248.7834	0.0801



Fig.S20 HRMS spectra of T<sub>3,4</sub>D<sub>8</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
349	C <sub>80</sub> H <sub>110</sub> O <sub>12</sub>	[M]+	1262.7992	1262.7990	0.1584



Fig.S22 HRMS spectra of T<sub>3,4</sub>D<sub>9</sub>



Fig.S23 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>10</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3410	C <sub>81</sub> H <sub>112</sub> O <sub>12</sub>	[M]+	1276.8148	1276.8145	0.2350



Fig.S24 HRMS spectra of T<sub>3,4</sub>D<sub>10</sub>



Fig.S25 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>11</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3411	C <sub>82</sub> H <sub>114</sub> O <sub>12</sub>	[M]+	1290.8305	1290.8304	0.0775



Fig.S26 HRMS spectra of T<sub>3,4</sub>D<sub>11</sub>



Fig.S27 <sup>1</sup>HNMR spectra of T<sub>3,4</sub>D<sub>12</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3412	C <sub>83</sub> H <sub>116</sub> O <sub>12</sub>	[M]+	1304.8461	1304.8461	0.0000



Fig.S28 HRMS spectra of T<sub>3,4</sub>D<sub>12</sub>



Fig.S29 <sup>1</sup>HNMR spectra of T<sub>4,5</sub>D<sub>6</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
456	C <sub>87</sub> H <sub>124</sub> O <sub>12</sub>	[M]+	1360.9087	1360.9088	-0.0735



Fig.S30 HRMS spectra of T<sub>4,5</sub>D<sub>6</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
457	C <sub>88</sub> H <sub>126</sub> O <sub>12</sub>	[M]+	1374.9244	1374.9247	-0.2182







Fig.S33 <sup>1</sup>HNMR spectra of T<sub>4,5</sub>D<sub>8</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
458	C <sub>89</sub> H <sub>128</sub> O <sub>12</sub>	[M]+	1388.9400	1388.9403	-0.2160



Fig.S34 HRMS spectra of T<sub>4,5</sub>D<sub>8</sub>



Fig.S35 <sup>1</sup>HNMR spectra of T<sub>4,5</sub>D<sub>9</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
459	C <sub>90</sub> H <sub>130</sub> O <sub>12</sub>	[M]+	1402.9557	1402.9562	-0.3564



Fig.S36 HRMS spectra of T<sub>4,5</sub>D<sub>9</sub>



Fig.S37 <sup>1</sup>HNMR spectra of T<sub>4,5</sub>D<sub>10</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
4510	C <sub>91</sub> H <sub>132</sub> O <sub>12</sub>	[M]+	1416.9713	1416.9713	0.0000







Fig. S39 <sup>1</sup>HNMR spectra of T<sub>4,5</sub>D<sub>11</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
4511	C <sub>92</sub> H <sub>134</sub> O <sub>12</sub>	[M]+	1430.9870	1430.9877	-0.4892



Fig.S40 HRMS spectra of T<sub>4,5</sub>D<sub>11</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
4512	C <sub>93</sub> H <sub>136</sub> O <sub>12</sub>	[M]+	1445.0027	1445.0021	0.4152



Fig.S42 HRMS spectra of T<sub>4,5</sub>D<sub>12</sub>



Fig.S43 <sup>1</sup>HNMR spectra of T<sub>3,5</sub>D<sub>6</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
356	C <sub>82</sub> H <sub>114</sub> O <sub>12</sub>	[M]+	1290.8305	1290.8307	-0.1549



Fig.S44 HRMS spectra of T<sub>3,5</sub>D<sub>6</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
357	C <sub>83</sub> H <sub>116</sub> O <sub>12</sub>	[M]+	1304.8461	1304.8462	-0.0766



Fig.S46 HRMS spectra of T<sub>3,5</sub>D<sub>7</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
358	C <sub>84</sub> H <sub>118</sub> O <sub>12</sub>	[M]+	1318.8618	1318.8608	0.7582



Fig.S48 HRMS spectra of T<sub>3,5</sub>D<sub>8</sub>



Fig.S49 <sup>1</sup>HNMR spectra of T<sub>3,5</sub>D<sub>9</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
359	C <sub>85</sub> H <sub>120</sub> O <sub>12</sub>	[M]+	1332.8774	1332.8750	1.8006



Fig.S50 HRMS spectra of T<sub>3,5</sub>D<sub>9</sub>





Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3510	C <sub>86</sub> H <sub>122</sub> O <sub>12</sub>	[M]+	1346.8931	1346.8938	-0.5197



Fig.S52 HRMS spectra of T<sub>3,5</sub>D<sub>10</sub>



Fig.S53 <sup>1</sup>HNMR spectra of T<sub>3,5</sub>D<sub>11</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3511	C <sub>87</sub> H <sub>124</sub> O <sub>12</sub>	[M]+	1360.9087	1360.9083	0.2939



Fig.S54 HRMS spectra of T<sub>3,5</sub>D<sub>11</sub>



Fig.S55 <sup>1</sup>HNMR spectra of T<sub>3,5</sub>D<sub>12</sub>

Sample No.	Formula (M)	Ion Formula	Measured	Calc m/z	Diff (ppm)
			m/z		
3512	C <sub>88</sub> H <sub>126</sub> O <sub>12</sub>	[M]+	1374.9244	1374.9247	-0.2182



Fig.S56 HRMS spectra of T<sub>3,5</sub>D<sub>12</sub>

# Mesomorphism

# 1. POM and DSC

Mesomorphism of T<sub>3,4</sub>D<sub>6</sub>



Fig.S57 DSC trace of compound  $T_{3,4}D_6$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>.

## Mesomorphism of T<sub>3,4</sub>D<sub>7</sub>



Fig.S58 DSC trace of compound  $T_{3,4}D_7$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>.





**Fig.S59** Mosaic texture observed by POM with of compound  $T_{3,4}D_8$  sandwiched between clean glass slides on cooling from isotropic phase at 30°C(left); DSC trace of compound  $T_{3,4}D_8$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>3,4</sub>D<sub>9</sub>



**Fig.S60** Mosaic texture observed by POM with of compound  $T_{3,4}D_9$  sandwiched between clean glass slides on cooling from isotropic phase at 30°C(left); DSC trace of compound  $T_{3,4}D_9$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>3,4</sub>D<sub>10</sub>



**Fig.S61** Mosaic texture observed by POM with of compound  $T_{3,4}D_{10}$  sandwiched between clean glass slides on cooling from isotropic phase at 146°C(left); DSC trace of compound  $T_{3,4}D_{10}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

Mesomorphism of T<sub>3,4</sub>D<sub>11</sub>



**Fig.S62** Fan-shaped texture observed by POM with of compound  $T_{3,4}D_{11}$  sandwiched between clean glass slides on cooling from isotropic phase at 25°C(left); DSC trace of compound  $T_{3,4}D_{11}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of $T_{3,4}D_{12}$



**Fig.S63** Fan-shaped texture observed by POM with of compound  $T_{3,4}D_{12}$  sandwiched between clean glass slides on cooling from isotropic phase at 30°C(left); DSC trace of compound  $T_{3,4}D_{12}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>4,5</sub>D<sub>6</sub>



**Fig.S64** Fan-shaped texture observed by POM of compound  $T_{4,5}D_6$  sandwiched between clean glass slides on cooling from isotropic phase at 100°C(left); DSC trace of compound  $T_{4,5}D_6$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).





**Fig.S65** Fan-shaped texture observed by POM of compound  $T_{4,5}D_7$  sandwiched between clean glass slides on cooling from isotropic phase at 90°C(left); DSC trace of compound  $T_{4,5}D_7$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

#### Mesomorphism of T<sub>4,5</sub>D<sub>8</sub>



**Fig.S66** Fan-shaped texture observed by POM of compound  $T_{4,5}D_8$  sandwiched between clean glass slides on cooling from isotropic phase at 30°C(left); DSC trace of compound  $T_{4,5}D_8$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

#### Mesomorphism of T<sub>4,5</sub>D<sub>9</sub>



**Fig.S67** Fan-shaped texture observed by POM of compound  $T_{4,5}D_9$  sandwiched between clean glass slides on cooling from isotropic phase at 110°C(left); DSC trace of compound  $T_{4,5}D_9$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>4,5</sub>D<sub>10</sub>



**Fig.S68** Fan-shaped texture observed by POM of compound  $T_{4,5}D_{10}$  sandwiched between clean glass slides on cooling from isotropic phase at 25°C(left); DSC trace of compound  $T_{4,5}D_{10}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

# Mesomorphism of T<sub>4,5</sub>D<sub>11</sub>



Fig.S69 DSC trace of compound  $T_{4,5}D_{11}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>. Mesomorphism of  $T_{4,5}D_{12}$ 



**Fig.S70** Fan-shaped texture observed by POM of compound  $T_{4,5}D_{12}$  sandwiched between clean glass slides on cooling from isotropic phase at 30°C(left); DSC trace of compound  $T_{4,5}D_{12}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>3,5</sub>D<sub>6</sub>



**Fig.S71** Fan-shaped texture observed by POM of compound  $T_{3,5}D_6$  sandwiched between clean glass slides on cooling from isotropic phase at 40°C(left); DSC trace of compound  $T_{3,5}D_6$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

## Mesomorphism of T<sub>3,5</sub>D<sub>7</sub>



Fig.S72 DSC trace of compound  $T_{3,5}D_7$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>. Mesomorphism of  $T_{3,5}D_8$ 



**Fig.S73** Fan-shaped texture observed by POM of compound  $T_{3,5}D_8$  sandwiched between clean glass slides on cooling from isotropic phase at 40°C(left); DSC trace of compound  $T_{3,5}D_8$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

Mesomorphism of T<sub>3,5</sub>D<sub>9</sub>



**Fig.S74** Dendritic texture observed by POM of compound  $T_{3,5}D_9$  sandwiched between clean glass slides on cooling from isotropic phase at 128°C(left); DSC trace of compound  $T_{3,5}D_9$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

Mesomorphism of T<sub>3,5</sub>D<sub>10</sub>



**Fig.S75** Dendritic texture observed by POM of compound  $T_{3,5}D_{10}$  sandwiched between clean glass slides on cooling from isotropic phase at 122°C(left); DSC trace of compound  $T_{3,5}D_{10}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>3,5</sub>D<sub>11</sub>



**Fig.S76** Dendritic texture observed by POM of compound  $T_{3,5}D_{11}$  sandwiched between clean glass slides on cooling from isotropic phase at 35°C(left); DSC trace of compound  $T_{3,5}D_{11}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

### Mesomorphism of T<sub>3,5</sub>D<sub>12</sub>



**Fig.S77** Dendritic texture observed by POM of compound  $T_{3,5}D_{12}$  sandwiched between clean glass slides on cooling from isotropic phase at 36°C(left); DSC trace of compound  $T_{3,5}D_{12}$  run at 10°Cmin<sup>-1</sup> under N<sup>2</sup>(right).

# 2. 1D WAXD



**Fig.S78** (a) 1D WAXD of  $T_{3,4}D_{11}$  at 130°C and 40°C during the first cooling runs; (b) 1D WAXD of  $T_{3,4}D_6$  at 130°C and 40°C during the first cooling runs.



**Fig.S79** (a) 1D WAXD of  $T_{3,4}D_7$  at 90°C (red line) and  $T_{3,4}D_8$  at 95°C (black line) during the first heating runs; (b) 1D WAXD of  $T_{3,4}D_9$  at 95°C (red line) and  $T_{3,4}D_{10}$  at 90°C (black line) during the first heating runs.



**Fig.S80** (a) 1D WAXD of  $T_{4,5}D_6$  at 90°C (red line) and  $T_{4,5}D_7$  at 100°C (black line) during the first heating runs; (b) 1D WAXD of  $T_{4,5}D_{11}$  at 90°C (red line) and  $T_{4,5}D_{12}$  at 80°C (black line) during the first heating runs.



**Fig.S81** (a) 1D WAXD of  $T_{4,5}D_8$  at 105°C and 115°C during the first heating runs; (b) 1D WAXD of  $T_{4,5}D_{10}$  at 90°C and 120°C during the first heating runs.



Fig.S82 1D WAXD of  $T_{3,5}D_m$  (m=6-12) at 90°C during the first heating runs.

# 3. 2D WAXD



**Fig.S83** 2D WAXD of T<sub>3,5</sub>D<sub>6</sub> at 25°C



Fig.S84 2D WAXD of  $T_{3,5}D_7$  at 25°C (polydomain)



Fig.S85 2D WAXD of  $T_{3,5}D_8$  at 25°C



Fig.S86 2D WAXD of  $T_{3,5}D_9$  at 25°C



Fig.S87 2D WAXD of  $T_{3,5}D_{10}$  at  $25^\circ C$ 



Fig.S88 2D WAXD of  $T_{3,5}D_{11}$  at  $25^\circ C$ 



Fig.S89 2D WAXD of  $T_{3,5}D_{12}$  at 25°C



**Fig.S90** 2D WAXD of T<sub>3,4</sub>D<sub>7</sub> at 25°C