Supporting information for the Communication “New symmetrically substituted 1,3,5-triazines as host compounds for channel-type inclusion formation”

General procedure for the cyclotrimerization of aromatic nitriles:
The neat benzonitrile and zinc chloride, in a molar ratio as specified in Table 01, were filled into an ampoule under inert gas and sealed under vacuum. The ampoule was heated in a furnace for the given time and broken after cooling to room temperature. The zinc chloride was removed from the reaction mixture by mixing with water and treatment in an ultrasonic bath for 1 h. The aqueous solution was removed by suction and the product purified by soxhlet extraction and subsequent recrystallization from chloroform.

Selected data for triazines:
2,4,6-Tris(4-fluorophenyl)-1,3,5-triazine. (1) Mp 303 °C. 1H-NMR (300 MHz, CDCl3) δ = 7.25 (m); 8.76 (m). 13C-NMR (75 MHz, CDCl3) δ = 115.76, 131.29, 132.19, 164.22/167.58, 170.70 (NCN). EI(+)-MS: m/z: found 363; calc. 363.33. v(KBr)/cm⁻¹: 3086, 3071, 1667, 1602, 1506, 1414, 1371, 1226, 1142, 859, 816, 581, 510.

2,4,6-Tris(4-chlorophenyl)-1,3,5-triazine. (2) Mp 343 °C. 1H-NMR (300 MHz, CDCl3) δ = 8.69 (6H, d, 3JHH = 8.6 Hz); 7.55 (6H, d, 3JHH = 8.7 Hz). 13C-NMR (75 MHz, CDCl3) δ = 129.03, 130.32, 134.40, 139.16, 170.97 (NCN). EI(+)-MS: m/z: found 412; calc. 412.68. v(KBr)/cm⁻¹: 3072, 1583, 1520, 1487, 1405, 1367, 1350, 1089, 1013, 804, 512, 479.

2,4,6-Tris(4-bromophenyl)-1,3,5-triazine. (3) Mp 360 °C. 1H-NMR (300 MHz, CDCl3) δ = 8.61 (6H, d, 3JHH = 8.6 Hz); 7.71 (6H, d, 3JHH = 8.7 Hz). 13C-NMR (75 MHz, CDCl3) δ = 127.84, 130.49, 132.03, 134.81, 171.13 (NCN). EI-MS: m/z: found 546; calc. 546.03. v(KBr)/cm⁻¹: 3069, 3039, 1579, 1514, 1486, 1401, 1370, 1355, 1067, 1010, 805, 495.

2,4,6-Tris(4-iodophenyl)-1,3,5-triazine. (4) Mp 378 °C. 1H-NMR (300 MHz, CDCl3) δ = 7.98 (6H, d, 3JHH = 8.5 Hz); 8.52 (6H, d, 3JHH = 8.7 Hz). 13C-NMR (75 MHz, CDCl3) δ = 101.41, 131.48, 136.66, 139.17, 172.50 (NCN). EI(+)-MS: m/z: found 688; calc. 687.03. v(KBr)/cm⁻¹: 3062, 3033, 1584, 1574, 1526, 1508, 1396, 1367, 1176, 1055, 1005, 803, 492.

2,4,6-Tris(4-bromo-3-fluorophenyl)-1,3,5-triazine. (5) Mp 278 °C. 1H-NMR (300 MHz, CDCl3) δ = 7.48 (m); 8.34 (t, 3JHF = 8.3 Hz). 13C-NMR (75 MHz, CDCl3) δ = 121.01, 123.26, 127.39, 127.90, 133.26, 160.41/163.94, 170.20 (NCN). EI(+)-MS: m/z: found 601; calc. 600.00. v(KBr)/cm⁻¹: 1618, 1601, 1578, 1522, 1358, 1225, 1215, 1072, 892, 808, 563.

2,4,6-Tris(4-bromo-3,5-difluorophenyl)-1,3,5-triazine. (6) Mp 366 °C. 1H-NMR (300 MHz, THF-d8) δ = 8.57 (d, 3JHF = 8.3 Hz). 19F-NMR (376.5 MHz, THF-d8) δ = -106.89 (m). 13C-NMR (75 MHz, THF-d8) δ = 104.45, 113.53, 138.68, 160.13/163.35, 171.38 (NCN). MALDI-TOF-MS: m/z: found 655; calc. 653.97. v(KBr)/cm⁻¹: 1637, 1526, 1474, 1379, 1193, 1032, 826, 730, 584.

2,4,6-Tris(4-bromo-2,3,5,6-tetrafluorophenyl)-1,3,5-triazine. (7) Mp 183 °C. 19F-NMR (376.5 MHz, CDCl3) δ = -131.16 (d, 3JFF = 10.43 Hz, F3); -139.58 (d, 3JFF = 12.12 Hz, F2). 13C-NMR (75 MHz, CDCl3) δ = 104.41 (t, 3JCF = 22.3 Hz); 115.37 (t, 3JCF = 13.6 Hz); 143.66/147.15 (d, 1JCF = -167.4 Hz); 167.4 (t, 3JCF = -3.11 Hz, NCN). GC-MS: m/z: 762.1 [M]+, 683 [M-Br]+, 254 [BrC3F7CN]+. v(KBr)/cm⁻¹: 1641, 1527, 1497, 1411, 1355, 1154, 988, 838, 708.
2,4,6-Tris(4′-bromobiphenylyl)-1,3,5-triazine. (8) Mp decomps. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.56\; (d, \; ^3\)J\(_{HH} = 8.7\; Hz); \; 7.63\; (d, \; ^3\)J\(_{HH} = 8.6\; Hz); \; 7.76\; (d, \; ^3\)J\(_{HH} = 8.5\; Hz); \; 8.83\; (d, \; ^3\)J\(_{HH} = 8.3\; Hz). \(^1\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta = 122.42;\; 127.12;\; 128.83;\; 129.60;\; 132.09;\; 135.51;\; 139.26;\; 143.97;\; 171.31\) (NCN). MALDI-TOF-MS: \(m/z\) found 775.5; calc. 774.3.

2,4,6-Tris(4′-bromo-2′,3′,5′,6′-tetrafluorobiphenylyl)-1,3,5-triazine. (9) Mp 358 °C. \(^1\)H-NMR (300 MHz, THF-d\(_8\)) \(\delta = 7.80\; (d, \; ^3\)J\(_{HH} = 8.7\; Hz);\; 9.00\; (d, \; ^3\)J\(_{HH} = 8.7\; Hz). \(^1\)F-NMR (376.5 MHz, THF-d\(_8\)) \(\delta = -137.10\) (m), -144.84 (m). \(^1\)C-NMR (75 MHz, THF-d\(_8\)) \(\delta = 100.37,\; 120.99,\; 130.41,\; 131.71,\; 132.59,\; 138.26,\; 147.20/143.69\) (d, \(^1\)J\(_{CF} = -264.8\) Hz), 148.39/145.12 (d, \(^1\)J\(_{CF} = -245.3\) Hz), 172.66 (NCN). MALDI-TOF-MS: \(m/z\) found 991.6; calc. 990.2.

2,4,6-Tris(2′,3′,4′,5′,6′-pentafluorobiphenylyl)-1,3,5-triazine. (10) Mp decomposition. \(^1\)H-NMR (300 MHz, THF-d\(_8\)) \(\delta = 7.70\; (d, \; ^3\)J\(_{HH} = 8.5\; Hz);\; 8.91\; (d, \; ^3\)J\(_{HH} = 8.7\; Hz). \(^1\)F-NMR (376.5 MHz, THF-d\(_8\)) \(\delta = -144.30\) (m), -157.75 (7, \(^3\)J\(_{FF} = 19.9\) Hz), -164.53 (m). EI(+)-MS: \(m/z\) found 809; calc. 807.5.

Crystal-Structure Determination:
A crystal of 8 · (toluene)\(_{0.69}\) was mounted with Paratone-N\(^1\) in a MiTeGen loop and used for X-ray structure determination at 90 K. All measurements were made on a Bruker APEX II area-detector diffractometer\(^2\) using graphite monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 8056 reflections in the range 2.30° < \(\theta\) < 28.00°. A total of 1429 frames were collected using \(\omega\) and \(\phi\) scans, 240 seconds exposure time and a rotation angle of 0.5° per frame, and a crystal-detector distance of 59.5 mm.

Crystal data for 8 · (toluene)\(_{0.69}\):
- **Empirical formula**: C\(_{43.80}\)H\(_{29.49}\)Br\(_{3}\)N\(_3\)
- **Formula weight**: 837.54
- **Temperature**: 90(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Monoclinic
- **Space group**: I2/a
- **Unit cell dimensions**:
  - \(a = 39.8459(11)\) Å \(\alpha = 90°\)
  - \(b = 3.84340(10)\) Å \(\beta = 104.3980(10)°\)
  - \(c = 46.6728(18)\) Å \(\gamma = 90°\)
- **Volume**: 6923.2(4) Å\(^3\)
- **Z**: 8
- **Density (calculated)**: 1.607 Mg/m\(^3\)
- **Absorption coefficient**: 3.534 mm\(^-1\)
- **F(000)**: 3346
- **Crystal size**: 0.31 x 0.12 x 0.05 mm\(^3\)

**Theta range for data collection**: 1.55 to 28.57°.

**Index ranges**: -53 ≤ \(h\) ≤ 51, -5 ≤ \(k\) ≤ 4, -62 ≤ \(l\) ≤ 58

**Reflections collected**: 31239
Independent reflections 8626 [R(int) = 0.0407]
Completeness to theta = 27.00° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9281 and 0.7137
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 8626 / 57 / 474
Goodness-of-fit on F^2 1.028
Final R indices [I>2sigma(I)] R1 = 0.0581, wR2 = 0.1421
R indices (all data) R1 = 0.0881, wR2 = 0.1567
Largest diff. peak and hole 1.130 and -2.058 e.Å^-3

A crystal of 8·(p-xylene)_{0.72} was mounted with Paratone-N on a glass needle and used for X-ray structure determination at -100 °C. All measurements were made on a Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated MoKα radiation (λ = 0.71073 Å). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 23023 reflections in the range 1.50° < θ < 28.17°. A total of 2236 frames were collected using ω scans, 80 seconds exposure time and a rotation angle of 0.5° per frame, and a crystal-detector distance of 65.0 mm.

Crystal data for 8·(p-xylene)_{0.72}
Empirical formula C_{44.77}H_{31.21}Br_{3}N_{3}
Formula weight 850.85
Temperature 173(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group I2/a
Unit cell dimensions a = 39.9115(7) Å  a = 90°
b = 3.86753(7) Å  β = 103.6149(15)°
c = 46.7250(7) Å  γ = 90°
Volume 7009.7(2) Å^3
Z 8
Density (calculated) 1.612 Mg/m^3
Absorption coefficient 3.491 mm^-1
F(000) 3406.3
Crystal size 0.46 x 0.23 x 0.07 mm^3
Theta range for data collection 1.53 to 28.23°.
Index ranges -50 ≤ h ≤ 50, -5 ≤ k ≤ 4, -60 ≤ l ≤ 60
Reflections collected 54702
Independent reflections 7995 [R(int) = 0.0320]
Completeness to theta = 26.00° 100.0 %
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 7995 / 12 / 454
Goodness-of-fit on F^2 1.042
Final R indices [I>2sigma(I)] R1 = 0.0809, wR2 = 0.2554
A crystal of 8 · (mesitylene)$_2$·0 was mounted with Paratone in a MiTeGen loop and used for X-ray structure determination at -50 °C. All measurements were made on a Oxford Diffraction SuperNova area-detector diffractometer$^3$ using mirror optics monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 17273 reflections in the range 1.51° < θ < 28.25°. A total of 5958 frames were collected using ω scans, 80 seconds exposure time and a rotation angle of 0.5° per frame, and a crystal-detector distance of 65.0 mm.

**Crystal data for 8 · (mesitylene)$_2$·0**

- **Empirical formula**: C$_{57}$H$_{48}$Br$_3$N$_3$
- **Formula weight**: 1014.71
- **Temperature**: 223(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Triclinic
- **Space group**: $P\overline{1}$
- **Unit cell dimensions**:
  - $a = 3.86154(9)$ Å
  - $b = 22.1115(7)$ Å
  - $c = 27.1691(7)$ Å
  - $\alpha = 67.429(3)^\circ$
  - $\beta = 88.114(2)^\circ$
  - $\gamma = 87.127(2)^\circ$
- **Volume**: 2139.20(10) Å$^3$
- **Density (calculated)**: 1.575 Mg/m$^3$
- **Absorption coefficient**: 2.874 mm$^{-1}$
- **F(000)**: 1032
- **Crystal size**: 0.446 x 0.1475 x 0.0172 mm$^3$
- **Theta range for data collection**: 1.51 to 28.31°.
- **Index ranges**:
  - $-4 \leq h \leq 5$,
  - $-27 \leq k \leq 28$,
  - $-35 \leq l \leq 35$
- **Reflections collected**: 99271
- **Independent reflections**: 9845 [R(int) = 0.0955]
- **Completeness to theta = 26°**: 99.9 %
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 1 and 0.52964
- **Refinement method**: Full-matrix least-squares on $F^2$
- **Data / restraints / parameters**: 9845 / 0 / 406
- **Goodness-of-fit on $F^2$**: 1.118
- **Final R indices [I>2sigma(I)]**: $R_1 = 0.1229$, $wR_2 = 0.3324$
- **R indices (all data)**:
  - $R_1 = 0.1685$, $wR_2 = 0.3607$
- **Largest diff. peak and hole**: 1.012 and -1.385 e Å$^{-3}$

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1 Hampton Research, Catalog Number HR2-643; H. Hope, Acta Cryst, 1988, B44, 22.