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Supporting Information

Heads vs. tails: a double-sided study of the influence of substituents on glass-forming ability and stability of aminotriazine molecular glasses

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I. Spectral data for compounds 2b-q and 4a-q

2-Methylamino-4,6-bis[(2-methylphenyl)amino]-1,3,5-triazine (2b)

The mixture was refluxed for 3 days. Yield: 62 %; T_g 55 °C, T_c 128 °C, T_m 149 °C; FTIR (ATR/CH_2Cl_2) 3422, 3262, 3165, 3060, 2952, 1573, 1502, 1487, 1451, 1412, 1397, 1359, 1293, 1251, 1190, 1172, 1117, 1047, 1007, 989, 938, 859, 810, 748, 717 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.23 (br s, 1H), 8.10 (br s, 1H), 7.55 (d, ^3J = 7.0 Hz, 1H), 7.43 (d, ^3J = 7.0 Hz, 1H), 7.16 (d, ^3J = 7.0 Hz, 2H), 7.10 (d, ^3J = 7.6 Hz, 2H), 7.00 (t, ^3J = 7.0 Hz, 2H), 6.76 (br q, ^3J = 5.3 Hz, 1H), 2.73 (d, ^3J = 4.7 Hz, 3H), 2.23 (s, 3H), 2.20 (s, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.75 (s, 2H), 7.58 (d, ^3J = 7.8 Hz, 2H), 7.16 (d, ^3J = 7.3 Hz, 2H), 7.11 (t, ^3J = 7.1 Hz, 2H), 7.00 (t, ^3J = 7.6 Hz, 2H), 6.41 (br s, 1H), 2.77 (d, ^3J = 4.7 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 164.9, 137.6, 132.3, 131.8, 129.9, 125.9, 125.6, 124.1, 124.0, 27.1, 18.1 ppm; HRMS (ESI, MNa^+) calcd. for $C_{18}H_{20}NaN_6$ *m/e*: 343.1642, found: 343.1644.

2-Methylamino-4,6-bis[(3-methylphenyl)amino]-1,3,5-triazine (2c)

Yield: 77 %; T_g 60 °C; FTIR (ATR/CH_2Cl_2) 3411, 3277, 3183, 3050, 2950, 2920, 1580, 1558, 1511, 1487, 1426, 1400, 1361, 1294, 1256, 1243, 1178, 1167, 1092, 1036, 1000, 975, 924, 892, 866, 809, 777, 748, 691 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.07 (br s, 1H), 8.92 (br s, 1H), 7.60 (m, 4H), 7.13 (t, ^3J = 7.6 Hz, 2H), 6.93 (br s, 1H), 6.76 (d, ^3J = 7.6 Hz, 2H), 2.85 (d, ^3J = 4.7 Hz, 3H), 2.27 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.54 (s, 2H), 7.57 (m, 4H), 7.13 (t, ^3J = 7.3 Hz, 2H), 6.78 (d, ^3J = 7.8 Hz, 2H), 6.54 (br s, 1H), 2.89 (d, ^3J = 4.8 Hz, 3H), 2.29 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.2, 163.9, 140.2, 137.3, 128.1, 122.2, 120.4, 117.0, 27.3, 21.2 ppm; HRMS (ESI, MNa^+) calcd. for $C_{18}H_{20}NaN_6$ *m/e*: 343.1642, found: 343.1644.

2-Methylamino-4,6-bis[(4-methylphenyl)amino]-1,3,5-triazine (2d)

Yield: 82 %; T_g 67 °C, T_c 139 °C, T_m 169 °C; FTIR (ATR/CH_2Cl_2) 3415, 3280, 3199, 3109, 3026, 2945, 2921, 2868, 1575, 1496, 1419, 1403, 1361, 1312, 1292, 1241, 1181, 1168, 1148, 1122, 1076, 1040, 1019, 936, 809, 736, 706, 672 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.02 (br s, 1H), 8.88 (br s, 1H), 7.67 (br s, 4H), 7.05 (d, ^3J = 8.2 Hz, 4H), 6.89 (br s, 1H), 2.83 (d, ^3J = 4.7 Hz, 3H), 2.25 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.51 (s, 2H), 7.63 (d, ^3J = 8.6 Hz, 4H), 7.06 (d, ^3J = 8.1 Hz, 4H), 6.50 (br s, 1H), 2.87 (d, ^3J = 4.5 Hz, 3H), 2.27 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.0, 163.8, 137.8, 130.2, 128.6, 119.8, 27.3, 20.3 ppm; HRMS (ESI, MNa^+) calcd. for $C_{18}H_{20}NaN_6$ *m/e*: 343.1642, found: 343.1645.

2-Methylamino-4,6-bis[(2,3-dimethylphenyl)amino]-1,3,5-triazine (2e)

The mixture was refluxed for 3 days. Yield: 76 %; T_g 70 °C; FTIR (ATR/CH_2Cl_2) 3419, 3255, 3163, 3064, 3028, 2944, 2919, 1575, 1501, 1457, 1410, 1398, 1359, 1276, 1189, 1152, 1111, 1095, 1074, 1044, 1018, 992, 895, 811, 767, 738, 708 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.30 (br s, 1H), 8.15 (br s, 1H), 7.24 (br d, ^3J = 5.3 Hz, 1H), 7.12 (br d, ^3J = 5.9 Hz, 1H), 6.99 (t, ^3J = 7.6 Hz, 2H), 6.92 (d, ^3J = 7.6 Hz, 2H), 6.67 (q, ^3J = 4.7 Hz, 1H), 2.70 (d, ^3J = 4.7 Hz, 3H), 2.22 (s, 6H), 2.06 (s, 3H), 2.03 (s, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.79 (s, 2H), 7.28 (d, ^3J = 7.8 Hz, 2H), 6.98 (t, ^3J = 7.8 Hz, 2H), 6.93 (d, ^3J = 7.1 Hz, 2H), 6,33 (br s, 1H), 2.74 (d, ^3J = 4.8 Hz, 3H), 2.25 (s, 6H), 2.10 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.4, 165.2, 137.5, 136.3, 132.0, 131.4, 126.0, 125.9, 124.7, 124.5, 124.1, 27.1, 20.2, 14.3 ppm; HRMS (ESI, MNa^+) calcd. for $C_{20}H_{24}NaN_6$ *m/e*: 371.1955, found: 371.1947.

2-Methylamino-4,6-bis[(2,4-dimethylphenyl)amino]-1,3,5-triazine (2f)

The mixture was refluxed for 3 days. Yield: 78 %; T_g 54 °C, T_m 170 °C; FTIR (ATR/CH_2Cl_2) 3417, 3262, 3168, 3012, 2945, 2921, 2860, 1573, 1490, 1448, 1399, 1377, 1359, 1294, 1266, 1219, 1173, 1157, 1126, 1035, 1013, 933, 872, 811, 736, 703 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.09 (br s, 1H), 7.96 (br s, 1H), 7.34 (d, ^3J = 6.4 Hz, 1H), 7.21 (d, ^3J = 7.6 Hz, 1H), 6.94 (s, 2H), 6.88 (d, ^3J = 7.0 Hz, 2H), 6.66 (br q, ^3J = 4.7 Hz, 1H), 2.67 (d, ^3J = 4.1 Hz, 3H), 2.22 (s, 6H), 2.16 (s, 3H), 2.13 (s, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.64 (s, 2H), 7.40 (d, ^3J = 8.1 Hz, 2H), 6.98 (s, 2H), 6.91 (d, ^3J = 8.1 Hz, 2H), 6.33 (br s, 1H), 2.75 (d, ^3J = 4.5 Hz, 3H), 2.26 (s, 6H), 2.20 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.3, 165.0, 135.0, 133.2, 132.9, 132.6, 131.9, 130.4, 126.1, 125.7, 27.1, 20.4, 18.0 ppm; HRMS (ESI, MNa^+) calcd. for $C_{20}H_{24}NaN_6$ *m/e*: 371.1955, found: 371.1952.

2-Methylamino-4,6-bis[(2,5-dimethylphenyl)amino]-1,3,5-triazine (2g)

The mixture was refluxed for 3 days. Yield: 61 %; T_g 66 °C; FTIR (ATR/CH_2Cl_2) 3416, 3261, 3162, 3022, 2949, 2921, 2863, 1591, 1570, 1515, 1481, 1456, 1410, 1358, 1291, 1263, 1247, 1210, 1167, 1148, 1128, 1036, 997, 940, 877, 808, 736 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.15 (br s, 1H), 8.01 (br s, 1H), 7.35 (s, 1H), 7.22 (s, 1H), 7.03 (d, ^3J = 7.6 Hz, 2H), 6.81 (d, ^3J = 7.6 Hz, 2H), 6.75 (br q, ^3J = 4.7 Hz, 1H), 2.73 (d, ^3J = 4.7 Hz, 3H), 2.20 (s, 6H), 2.18 (s, 3H), 2.15 (s, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.68 (s, 2H), 7.38 (s, 2H), 7.03 (d, ^3J = 7.8 Hz, 2H), 6.81 (d, ^3J = 7.6 Hz, 2H), 6.41 (br s, 1H), 2.77 (d, ^3J = 4.8 Hz, 3H), 2.22 (s, 6H), 2.18 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.3, 164.8, 137.4, 134.6, 129.7, 129.1, 128.6, 126.3, 125.9, 124.8, 124.6, 27.0, 20.5, 17.5 ppm; HRMS (ESI, MH^+) calcd. for $C_{20}H_{25}N_6$ *m/e*: 349.2141, found: 349.2149.

2-Methylamino-4,6-bis[(2,6-dimethylphenyl)amino]-1,3,5-triazine (2h)

Dioxane was used as the solvent instead of THF, and the mixture was refluxed for 3 days. Yield: 81 %; T_g 89 °C; FTIR (ATR/CH_2Cl_2) 3419, 3393, 3254, 3176, 3041, 3022, 2954, 2920, 2855, 1596, 1571, 1557, 1495, 1477, 1439, 1409, 1396, 1373, 1358, 1265, 1219, 1165, 1146, 1098, 1076, 1035, 989, 921, 875, 849, 811, 767, 736, 702, 690 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.67 (s, 2H), 7.01 (s, 6H), 6.18 (br s, 1H), 2.64 (d, ^3J = 4.5 Hz, 3H), 2.17 (s, 12H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.5, 165.2, 136.7, 136.0, 127.4, 125.6, 27.0, 18.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{20}H_{24}NaN_6$ *m/e*: 371.1955, found: 371.1957.

2-Methylamino-4,6-bis[(3,4-dimethylphenyl)amino]-1,3,5-triazine (2i)

Yield: 82 %; T_g 71 °C; FTIR (ATR/CH_2Cl_2) 3400, 3277, 3185, 3021, 2967, 2940, 2920, 2862, 1572, 1497, 1450, 1412, 1359, 1305, 1253, 1211, 1163, 1122, 1078, 1021, 998, 872, 810, 706, 661 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.99 (br s, 1H), 8.85 (br s, 1H), 7.57 (br s, 1H), 7.50 (d, ^3J = 7.0 Hz, 3H), 7.00 (d, ^3J = 8.2 Hz, 2H), 6.93 (br s, 1H), 2.84 (d, ^3J = 4.7 Hz, 3H), 2.18 (s, 6H), 2.16 (s, 6H) ppm; ^1H NMR (600 MHz, DMSO-d_6, 363 K) δ 8.45 (s, 2H), 7.49 (s, 2H), 7.44 (d, ^3J = 8.2 Hz, 2H), 7.00 (d, ^3J = 8.2 Hz, 2H), 6.53 (br s, 1H), 2.87 (s, 3H), 2.20 (s, 6H), 2.19 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.4, 163.6, 163.2, 137.7, 135.6, 129.2, 129.1, 121.2, 117.5, 27.2, 19.5, 18.5 ppm; HRMS (ESI, MH^+) calcd. for $C_{20}H_{25}N_6$ *m/e*: 349.2141, found: 349.2141.

2-Methylamino-4,6-bis[(2,4,6-trimethylphenyl)amino]-1,3,5-triazine (2j)

Dioxane was used as the solvent instead of THF, and the mixture was refluxed for 3 days. Yield: 82 %;

T_g 83 °C, T_c 180 °C, T_{dec} 249 °C; FTIR (ATR/CH_2Cl_2) 2415, 3381, 3250, 3185, 3163, 3004, 2953, 2919, 2857, 2731, 1569, 1558, 1492, 1436, 1411, 1396, 1374, 1360, 1309, 1264, 1229, 1174, 1155, 1140, 1077, 1035, 1012, 974, 937, 851, 811, 775, 736, 701, 679, 647 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 7.53 (s, 2H), 6.83 (s, 4H), 6.14 (br s, 1H), 2.65 (d, ^3J = 4.5 Hz, 3H), 2.24 (s, 6H), 2.14 (s, 12H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 165.4, 135.7, 134.5, 134.1, 128.0, 27.1, 20.4, 18.4 ppm; HRMS (ESI, MNa^+) calcd. for $C_{22}H_{28}NaN_6$ *m/e*: 399.2268, found: 399.2270.

2-Methylamino-4,6-bis[(3,5-difluorophenyl)amino]-1,3,5-triazine (2k)

The mixture was refluxed for 3 days. Yield: 65 %; T_g 54 °C, T_c 84°C, T_m 182, 191 °C; FTIR (ATR/CH_2Cl_2) 3460, 3428, 3290, 3223, 3123, 2954, 1625, 1594, 1559, 1516, 1478, 1436, 1412, 1364, 1304, 1255, 1216, 1186, 1170, 1153, 1115, 1082, 1034, 997, 983, 966, 837, 808, 747, 668 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.66 (br s, 1H), 9.54 (br s, 1H), 7.61 (br m, 4H), 7.40 (br s, 1H), 6.74 (br m, 2H), 2.85 (d, ^3J = 4.7 Hz, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.25 (s, 2H), 7.56 (d, $^3J_{H\text{-}F}$ = 8.3 Hz, 4H), 7.02 (br s, 1H), 6.64 (t, $^3J_{H\text{-}F}$ = 9.3 Hz, 2H), 2.90 (d, ^3J = 4.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.8, 163.9, 163.5, [164.0, 163.8, 160.9, 160.6 (dd, $^1J_{C\text{-}F}$ = 241 Hz, $^2J_{C\text{-}F}$ = 15 Hz)], [143.1, 142.9, 142.7 (t, $^2J_{C\text{-}F}$ = 14 Hz)], [102.3, 102.2, 101.9, 101.8 (dd, $^2J_{C\text{-}F}$ = 29 Hz, $^3J_{C\text{-}F}$ = 7 Hz)], [96.7, 96.6, 96.3, 96.2, 96.0, 95.9 (dt, $^2J_{C\text{-}F}$ = 27 Hz, $^3J_{C\text{-}F}$ = 8 Hz)], 27.3 ppm; HRMS (ESI, MNa^+) calcd. for $C_{16}H_{12}F_4NaN_6$ *m/e*: 387.0952, found: 387.0956.

2-Methylamino-4,6-bis[(3,5-dichlorophenyl)amino]-1,3,5-triazine (2l)

Yield: 87 %; T_g 83 °C, T_c 135, 195 °C, T_m 190, 212 °C; FTIR (ATR/CH_2Cl_2) 3242, 3415, 3396, 3275, 3178, 3113, 2958, 1606, 1570, 1519, 1500, 1413, 1358, 1303, 1267, 1253, 1226, 1170, 1150, 1114,

1082, 1015, 993, 924, 841, 807, 738, 691, 668 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.61 (br s, 1H), 9.46 (br s, 1H), 7.91 (br d, 4H), 7.38 (br s, 1H), 7.10 (t, ^{4}J = 1.7 Hz, 2H), 2.86 (d, ^{3}J = 4.7 Hz, 3H) ppm; ^{1}H NMR (600 MHz, DMSO-d_6, 363 K) δ 9.17 (s, 2H), 7.88 (s, 4H), 7.06 (t, ^{4}J = 1.7 Hz, 2H), 7.01 (br s, 1H), 2.90 (d, ^{3}J = 4.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.7, 163.8, 163.4, 142.6, 133.7, 120.5, 117.4, 27.2 ppm; HRMS (ESI, MH^+) calcd. for $C_{16}H_{13}Cl_4N_6$ *m/e*: 430.9922, found: 430.9932.

2-Methylamino-4,6-bis[(3,5-dibromophenyl)amino]-1,3,5-triazine (2m)

Yield: 79 %; T_g 94 °C; FTIR (ATR/CH_2Cl_2) 3402, 3275, 3174, 3093, 2956, 2857, 1605, 1559, 1519, 1496, 1407, 1359, 1297, 1256, 1226, 1170, 1150, 1103, 1081, 1012, 988, 904, 840, 808, 749, 741, 688, 667 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.57 (br s, 1H), 9.41 (br s, 1H), 8.11 (br s, 2H), 8.03 (br s, 2H), 7.40 (br s, 1H), 7.36 (s, 2H), 2.85 (d, ^{3}J = 4.1 Hz, 3H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.15 (s, 2H), 8.06 (s, 4H), 7.32 (t, ^{4}J = 1.8 Hz, 2H), 7.02 (br s, 1H), 2.90 (d, ^{3}J = 4.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.7, 163.8, 163.4, 143.0, 125.8, 122.0, 120.8, 120.6, 27.2 ppm; HRMS (ESI, MH^+) calcd. for $C_{16}H_{13}Br_4N_6$ *m/e*: 608.7890, found: 608.7891.

2-Methylamino-4,6-bis[(3,5-diiodophenyl)amino]-1,3,5-triazine (2n)

Yield: 74 %; T_g 128 °C; FTIR (ATR/CH_2Cl_2) 3398, 3266, 3172, 3078, 2947, 2902, 1604, 1548, 1513, 1490, 1414, 1401, 1355, 1291, 1262, 1223, 1169, 1149, 1108, 1077, 1009, 990, 882, 840, 807, 764, 750, 709, 684, 668, 651 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.41 (br s, 1H), 9.26 (br s, 1H), 8.28 (br s, 2H), 8.15 (br s, 2H), 7.61 (s, 2H), 7.35 (br s, 1H), 2.85 (d, ^{3}J = 4.1 Hz, 3H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.99 (br s, 2H), 8.21 (s, 4H), 7.63 (t, ^{4}J = 1.3 Hz, 2H), 6.96 (br s, 1H),

2.90 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.7, 163.7, 163.4, 142.7, 137.0, 136.7, 127.1, 126.8, 95.5, 27.2 ppm; HRMS (ESI, MH$^+$) calcd. for $C_{16}H_{13}I_4N_6$ *m/e*: 796.7375, found: 796.7395.

2-Methylamino-4,6-bis[(3,5-dimethoxyphenyl)amino]-1,3,5-triazine (2o)

Yield: 64 %; T_g 65 °C; FTIR (ATR/CH_2Cl_2) 3380, 3286, 3132, 2999, 2956, 2939, 2907, 2838, 1591, 1556, 1513, 1480, 1451, 1421, 1355, 1262, 1248, 1202, 1175, 1151, 1087, 1063, 1021, 992, 974, 928, 833, 809, 735, 702, 682, 647 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.01 (br s, 1H), 8.86 (br s, 1H), 7.09 (br d, 4H), 7.02 (br s, 1H), 6.11 (s, 2H), 3.71 (s, 12H), 2.85 (d, ^3J = 4.7 Hz, 3H) ppm; ^{1}H NMR (600 MHz, DMSO-d_6, 363 K) δ 8.54 (s, 2H), 7.06 (d, ^4J = 1.8 Hz, 4H), 6.64 (br s, 1H), 6.13 (t, ^4J = 2.1 Hz, 2H), 3.73 (s, 12H), 2.89 (d, ^3J = 4.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 164.0, 163.7, 160.1, 141.9, 98.2, 98.0, 93.8, 93.6, 54.8, 27.2 ppm; HRMS (ESI, MH$^+$) calcd. for $C_{20}H_{25}N_6O_4$ *m/e*: 413.1932, found: 413.1937.

2-Methylamino-4,6-bis[(3,4,5-trimethoxyphenyl)amino]-1,3,5-triazine (2p)

Yield: 69 %; T_g 94 °C; FTIR (ATR/CH_2Cl_2) 3549, 3344, 3293, 3214, 3132, 2995, 2939, 2838, 1586, 1499, 1450, 1416, 1292, 1231, 1203, 1185, 1127, 1048, 1005, 972, 925, 832, 810, 786, 735 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.96 (br s, 1H), 8.81 (br s, 1H), 7.18 (br d, 4H), 7.02 (br s, 1H), 3.73 (s, 12H), 3.61 (s, 6H), 2.86 (d, ^3J = 4.7 Hz, 3H) ppm; ^{1}H NMR (600 MHz, DMSO-d_6, 363 K) δ x ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 163.9, 163.6, 152.4, 136.2, 132.2, 98.0, 97.5, 60.0, 55.5, 27.3 ppm; HRMS (ESI, MH$^+$) calcd. for $C_{22}H_{29}N_6O_6$ *m/e*: 473.2143, found: 473.2149.

2-Methylamino-4,6-bis[(3,5-di-*tert*-butylphenyl)amino]-1,3,5-triazine (2q)

Yield: 60 %; T_g 129 °C, T_c 173 °C, T_m 234 °C; FTIR (ATR/CH_2Cl_2) 3467, 3270, 3216, 3138, 2963, 2905, 2868, 1706, 1666, 1601, 1558, 1523, 1476, 1429, 1395, 1362, 1307, 1275, 1248, 1223, 1204, 1170, 1132, 1087, 1025, 982, 946, 900, 867, 810, 792, 764, 750, 707 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.45 (br s, 2H), 7.34 (br d, 4H), 7.12 (s, 2H), 5.66 (br s, 1H), 2.91 (d, ^3J = 4.7 Hz, 3H), 1.31 (s, 36 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 163.7, 162.9, 151.2, 137.9, 137.4, 118.0, 117.4, 116.0, 115.1, 34.9, 31.4, 27.8 ppm; HRMS (ESI, MH^+) calcd. for $C_{32}H_{49}N_6$ *m/e*: 517.4013, found: 517.4017.

2-Ethyl-4,6-bis(phenylamino)-1,3,5-triazine (4a)

Yield: 76 %; T_g 27 °C, T_c 52 °C, T_m 162 °C; FTIR (ATR/CH_2Cl_2) 3251, 3160, 3084, 3032, 2981, 2944, 2879, 1624, 1599, 1574, 1549, 1515, 1495, 1458, 1443, 1429, 1389, 1309, 1291, 1283, 1243, 1212, 1172, 1158, 1121, 1103, 1077, 1038, 988, 944, 904, 867, 827, 772, 754, 710, 690 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.71 (s, 2H), 7.77 (d, ^3J = 5.9 Hz, 4H), 7.30 (t, 3J = 7.6 Hz, 4H), 7.01 (t, ^3J = 7.6 Hz, 2H), 2.57 (q, ^3J = 7.6 Hz, 2H), 1.26 (t, ^3J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.8, 163.9, 139.4, 128.3, 122.3, 120.3, 31.3, 11.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{17}H_{17}NaN_5$ *m/e*: 314.1376, found: 314.1381.

2-Ethyl-4,6-bis[(2-methylphenyl)amino]-1,3,5-triazine (4b)

Yield: 76 %; T_m 169 °C; FTIR (ATR/CH_2Cl_2) 3411, 3225, 3119, 3064, 3027, 2974, 2937, 2878, 1612, 1596, 1565, 1504, 1455, 1426, 1348, 1291, 1247, 1212, 1191, 1158, 1115, 1098, 1048, 1036, 986, 940, 824, 751, 719, 679 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.84 (s, 2H), 7.40 (d, ^3J = 7.6 Hz, 2H), 7.16 (d, ^3J = 7.0 Hz, 2H), 7.11 (t, ^3J = 7.6 Hz, 2H), 7.03 (t, ^3J = 7.6 Hz, 2H), 2.44 (q, ^3J = 7.6 Hz,

2H), 2.19 (s, 6H), 1.17 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.8, 164.8, 136.9, 132.4, 130.0, 126.0, 125.6, 124.7, 31.2, 18.0, 11.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{19}H_{21}NaN_5$ *m/e*: 342.1689, found: 342.1698.

2-Ethyl-4,6-bis[(3-methylphenyl)amino]-1,3,5-triazine (4c)

Yield: 91 %; T_g 19 °C, T_c 94 °C, T_m 112 °C; FTIR (ATR/CH_2Cl_2) 3387, 3269, 3168, 3115, 3048, 2973, 2938, 2877, 1599, 1577, 1550, 1513, 1488, 1462, 1423, 1347, 1302, 1284, 1254, 1206, 1170, 1118, 1091, 1043, 984, 939, 892, 867, 823, 777, 689 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.64 (s, 2H), 7.55 (s, 4H), 7.17 (t, ^{3}J = 7.6 Hz, 2H), 6.83 (d, ^{3}J = 7.6 Hz, 2H), 2.55 (q, ^{3}J = 7.0 Hz, 2H), 2.26 (s, 6H), 1.25 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.7. 163.9. 139.3. 137.5. 128.2. 123.1. 120.8. 117.5. 31.2. 21.2. 11.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{19}H_{21}NaN_5$ *m/e*: 342.1689, found: 342.1695.

2-Ethyl-4,6-bis[(4-methylphenyl)amino]-1,3,5-triazine (4d)

Yield: 86 %; T_g 35 °C, T_c 61,109 °C, T_m 152 °C; FTIR (ATR/CH_2Cl_2) 3391, 3265, 3189, 3101, 3028, 2974, 2938, 2922, 2875, 1613, 1569, 1499, 1464, 1434, 1409, 1352, 1312, 1291, 1239, 1205, 1189, 1104, 1040, 1020, 985, 936, 817, 748 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.59 (s, 2H), 7.64 (br s, 4H), 7.09 (d, ^{3}J = 8.2 Hz, 4H), 2.54 (q, ^{3}J = 7.6 Hz, 2H), 2.26 (s, 6H), 1.24 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 163.8, 136.9, 131.2, 128.7, 120.3, 31.3, 20.4, 11.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{19}H_{21}NaN_5$ *m/e*: 342.1689, found: 342.1697.

2-Ethyl-4,6-bis[(2,3-dimethylphenyl)amino]-1,3,5-triazine (4e)

Yield: 82 %; T_g 46 °C, T_c 73 °C, T_m 169 °C; FTIR (ATR/CH_2Cl_2) 3378, 3229, 3120, 3070, 2973, 2940, 2920, 1609, 1566, 1550, 1509, 1465, 1423, 1382, 1347, 1273, 1214, 1190, 1165, 1128, 1100, 1067, 1018, 987, 825, 783, 745, 707 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.87 (s, 2H), 7.10 (d, ^3J = 7.0 Hz, 2H), 6.94 (m, 4H), 2.40 (q, ^3J = 7.0 Hz, 2H), 2.17 (s, 6H), 1.97 (s, 6H), 1.14 (t, ^3J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 165.0, 136.7, 136.5, 131.9, 126.4, 124.8, 31.2, 20.1, 14.3, 11.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5$ *m/e*: 370.2002, found: 370.2008.

2-Ethyl-4,6-bis[(2,4-dimethylphenyl)amino]-1,3,5-triazine (4f)

Yield: 94 %; T_g 39 °C, T_c 59, 88, 114 °C, T_m 121, 158 °C; FTIR (ATR/CH_2Cl_2) 3435, 3229, 3129, 3059, 3018, 2973, 2938, 2922, 1604, 1570, 1504, 1464, 1452, 1428, 1376, 1289, 1266, 1222, 1157, 1126, 1099, 1058, 986, 871, 824, 734, 719, 678 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.67 (s, 2H), 7.21 (d, ^3J = 8.2 Hz, 2H), 6.96 (s, 2H), 6.89 (d, ^3J = 8.2 Hz, 2H), 2.38 (q, ^3J = 7.6 Hz, 2H), 2.22 (s, 6H), 2.12 (s, 6H), 1.12 (t, ^3J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 164.9, 134.2, 133.7, 132.5, 130.5, 126.1, 126.0, 31.2, 20.4, 17.9, 11.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5$ *m/e*: 370.2002, found: 370.2008.

2-Ethyl-4,6-bis[(2,5-dimethylphenyl)amino]-1,3,5-triazine (4g)

Yield: 93 %; T_g 32 °C, T_c 121 °C, T_m 136 °C; FTIR (ATR/CH_2Cl_2) 3437, 3372, 3231, 3133, 3047, 3022, 2973, 2937, 2923, 1596, 1566, 1516, 1485, 1464, 1416, 1376, 1349, 1291, 1262, 1214, 1163, 1132, 1096, 1040, 985, 949, 878, 824, 805, 721 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.73 (s, 2H), 7.16 (s, 2H), 7.02 (d, ^3J = 7.6 Hz, 2H), 6.82 (d, ^3J = 7.0 Hz, 2H), 2.43 (q, ^3J = 7.6 Hz, 2H), 2.15 (s, 6H),

2.12 (s, 6H), 1.16 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 164.8, 136.6, 134.6, 129.8, 129.2, 126.2, 125.4, 31.2, 20.5, 17.6, 11.5 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5$ *m/e*: 370.2002, found: 370.2013.

2-Ethyl-4,6-bis[(2,6-dimethylphenyl)amino]-1,3,5-triazine (4h)

Dioxane was used as the solvent instead of THF, and the mixture was refluxed for 3 days. Yield: 72 %; T_{dec} 240 °C; FTIR (ATR/CH_2Cl_2) 3386, 3211, 3046, 2977, 2938, 2923, 1613, 1597, 1525, 1467, 1421, 1375, 1299, 1268, 1223, 1163, 1121, 1094, 1068, 1036, 985, 919, 884, 844, 825, 7665, 704, 664 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.25 (s, 2H), 7.02 (s, 6H), 2.35 (q, ^{3}J = 7.6 Hz, 2H), 2.13 (s, 12H), 1.09 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 165.2, 165.0, 135.8, 135.6, 127.7, 127.4, 126.1, 125.8, 31.1, 18.4, 18.2, 11.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5$ *m/e*: 370.2002, found: 370.2008.

2-Ethyl-4,6-bis[(3,4-dimethylphenyl)amino]-1,3,5-triazine (4i)

Yield: 88 %; T_g 31 °C, T_c 74, 126 °C, T_m 135, 144 °C; FTIR (ATR/CH_2Cl_2) 3385, 3268, 3170, 3105, 3023, 2970, 2938, 2921, 2879, 1606, 1568, 1552, 1497, 1439, 1408, 1344, 1304, 1252, 1210, 1169, 1124, 1107, 1046, 1021, 1000, 985, 960, 873, 823, 758, 733, 708 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.53 (s, 2H), 7.51 (br s, 4H), 7.04 (d, ^{3}J = 8.2 Hz, 2H), 2.54 (q, ^{3}J = 7.6 Hz, 2H), 2.17 (s, 12H), 1.25 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.04 (s, 2H), 7.48 (s, 2H), 7.44 (d, ^{3}J = 8.1 Hz, 2H), 7.03 (d, ^{3}J = 8.3 Hz, 2H), 2.55 (q, ^{3}J = 7.6 Hz, 2H), 1.26 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.5, 163.9, 137.1, 135.9, 130.0, 129.3, 121.6, 117.9, 31.3, 19.6, 18.7, 11.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5$ *m/e*: 370.2002, found: 370.1998.

2-Ethyl-4,6-bis[(2,4,6-trimethylphenyl)amino]-1,3,5-triazine (4j)

Dioxane was used as the solvent instead of THF, and the mixture was refluxed for 3 days. Yield: 84 %; T_g 60 °C, T_{dec} 240 °C; FTIR (ATR/CH_2Cl_2) 3373, 3350, 3216, 3055, 3007, 2974, 2945, 2921, 1614, 1568, 1520, 1487, 1467, 1421, 1375, 1311, 1279, 1234, 1218, 1157, 1114, 1062, 1034, 1012, 986, 937, 846, 826, 738, 672 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.13 (s, 2H), 6.84 (s, 4H), 2.34 (q, ^3J = 7.6 Hz, 2H), 2.24 (s, 6H), 2.10 (s, 12H), 1.09 (t, ^3J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.4, 165.3, 165.1, 135.4, 135.2, 135.0, 134.6, 133.2, 128.3, 128.0, 31.1, 20.4, 18.2, 18.1, 11.6 ppm; HRMS (ESI, MNa^+) calcd. for $C_{23}H_{29}NaN_5$ *m/e*: 398.2315, found: 398.2320.

2-Ethyl-4,6-bis[(3,5-difluorophenyl)amino]-1,3,5-triazine (4k)

Yield: 86 %; T_g 25 °C, T_c 69 °C, T_m 153 °C; FTIR (ATR/CH_2Cl_2) 3423, 3275, 3218, 3121, 2981, 2943, 1611, 1586, 1552, 1516, 1475, 1436, 1350, 1307, 1256, 1214, 111, 1117, 1057, 994, 983, 972, 935, 837, 823, 751, 668, 643 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 10.17 (s, 2H), 7.54 (s, 4H), 6.79 (t, ^3J = 8.8 Hz, 2H), 2.61 (q, ^3J = 7.6 Hz, 2H), 1.25 (t, ^3J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.4, 163.7, [164.1, 163.9, 160.9, 160.7 (dd, $^1J_{C\text{-}F}$ = 242 Hz, $^2J_{C\text{-}F}$ = 15 Hz)], [142.2, 142.0, 141.8 (t, $^2J_{C\text{-}F}$ = 14 Hz)], [102.8, 102.5 (d, $^2J_{C\text{-}F}$ = 27 Hz)], [97.5, 97.2, 96.9 (t, $^2J_{C\text{-}F}$ = 27 Hz)], 31.2, 11.2 ppm; HRMS (ESI, MH^+) calcd. for $C_{17}H_{14}F_4N_5$ *m/e*: 364.1180, found: 364.1190.

2-Ethyl-4,6-bis[(3,5-dichlorophenyl)amino]-1,3,5-triazine (4l)

Yield: 83 %; T_g 52 °C, T_c 109 °C, T_m 169 °C; FTIR (ATR/CH_2Cl_2) 3404, 3269, 3152, 3111, 2979, 2940, 1592, 1568, 1545, 1502, 1445, 1413, 1343, 1306, 1263, 1228, 1203, 1116, 1053, 989, 965, 948, 918,

841, 823, 806, 737, 691, 667 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 10.14 (s, 2H), 7.85 (s, 4H), 7.18 (s, 2H), 2.63 (q, ^{3}J = 7.6 Hz, 2H), 1.26 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.4, 163.6, 141.8, 133.9, 121.5, 118.0, 31.2, 11.1 ppm; HRMS (ESI, MH^+) calcd. for $C_{17}H_{14}Cl_4N_5$ *m/e*: 429.9970, found: 429.9971.

2-Ethyl-4,6-bis[(3,5-dibromophenyl)amino]-1,3,5-triazine (4m)

Yield: 83 %; T_g 66 °C, T_c 135-140 °C, T_m 191 °C; FTIR (ATR/CH_2Cl_2) 3396, 3374, 3267, 3147, 3110, 2977, 2937, 1587, 1555, 1497, 1463, 1437, 1407, 1372, 1345, 1303, 1262, 1230, 1202, 1100, 1050, 1020, 987, 957, 898, 840, 822, 750, 738, 686, 665 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 10.08 (s, 2H), 8.02 (s, 4H), 7.39 (s, 2H), 2.63 (q, ^{3}J = 7.6 Hz, 2H), 1.26 (t, ^{3}J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.3, 163.6, 142.1, 126.7, 122.2, 121.2, 31.1, 11.0 ppm; HRMS (ESI, MH^+) calcd. for $C_{17}H_{14}Br_4N_5$ *m/e*: 607.7937, found: 607.7950.

2-Ethyl-4,6-bis[(3,5-diiodophenyl)amino]-1,3,5-triazine (4n)

Yield: 80 %; T_g 96 °C, T_c 166 °C, T_m 196 °C; FTIR (ATR/CH_2Cl_2) 3391, 3263, 3154, 3125, 3082, 2973, 2934, 1593, 1574, 1544, 1492, 1462, 1402, 1344, 1298, 1263, 1231, 1202, 1117, 1095, 1048, 990, 951, 881, 840, 821, 738, 708, 685, 666 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.91 (br s, 2H), 8.18 (s, 4H), 7.68 (s, 2H), 2.62 (q, ^{3}J = 7.0 Hz, 2H), 1.27 (t, ^{3}J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.2, 163.5, 141.8, 137.8, 127.4, 95.6, 31.1, 10.9 ppm; HRMS (ESI, MH^+) calcd. for $C_{17}H_{14}I_4N_5$ *m/e*: 795.7422, found: 795.7431.

2-Ethyl-4,6-bis[(3,5-dimethoxyphenyl)amino]-1,3,5-triazine (4o)

Yield: 93 %; T_g 35 °C, T_c 108 °C, T_m 126 °C; FTIR (ATR/CH_2Cl_2) 3335, 3283, 3234, 3124, 2995, 2961, 2938, 2909, 2838, 1607, 1581, 1550, 1514, 1479, 1453, 1421, 1345, 1295, 1248, 1204, 1169, 1153, 1111, 1067, 990, 930, 823, 736, 681 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.62 (s, 2H), 7.06 (s, 4H), 6.18 (s, 2H), 3.69 (s, 12H), 2.58 (q, ^3J = 7.0 Hz, 2H), 1.26 (t, ^3J = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.8, 163.9, 160.3, 141.0, 98.6, 94.4, 54.9, 31.2, 11.4 ppm; HRMS (ESI, MNa^+) calcd. for $C_{21}H_{25}NaN_5O_4$ *m/e*: 434.1799, found: 434.1802.

2-Ethyl-4,6-bis[(3,4,5-trimethoxyphenyl)amino]-1,3,5-triazine (4p)

Yield: 73 %; T_g 63 °C, T_c 117 °C, T_m 186 °C; FTIR (ATR/CH_2Cl_2) 3329, 3128, 2964, 2938, 2839, 1604, 1576, 1498, 1451, 1415, 1349, 1233, 1197, 1128, 1059, 1036, 1006, 924, 824, 785, 737 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.57 (br s, 2H), 7.10 (br d, 4H), 3.75 (br s, 6H), 3.62 (s, 12H), 2.57 (br s, 2H), 1.26 (t, ^3J = 7.0 Hz, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.10 (s, 2H), 7.11 (s, 4H), 3.73 (s, 12H), 3.68 (s, 6H), 2.59 (q, ^3J = 7.6 Hz, 2H), 1.28 (t, ^3J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 163.7, 152.5, 135.3, 132.9, 98.4, 60.0, 55.6, 31.2, 11.3 ppm; HRMS (ESI, MNa^+) calcd. for $C_{23}H_{29}NaN_5O_6$ *m/e*: 494.2010, found: 494.2008.

2-Ethyl-4,6-bis[(3,5-di-*tert*-butylphenyl)amino]-1,3,5-triazine (4q)

Yield: 78 %; T_m 215 °C; FTIR (ATR/CH_2Cl_2) 3429, 3256, 3082, 2963, 2905, 2868, 1587, 1553, 1521, 1510, 1437, 1422, 1363, 1307, 1247, 1204, 1134, 1054, 1026, 986, 943, 900, 868, 824, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.40 (s, 4H), 7.30 (br s, 2H), 7.17 (s, 2H), 2.68 (q, ^3J = 7.6 Hz, 2H), 1.36 (t, ^3J = 7.6 Hz, 3H), 1.32 (s, 36H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 164.0, 151.3, 137.2,

118.1, 115.7, 34.9, 31.4, 11.3 ppm; HRMS (ESI, MH^+) calcd. for $C_{33}H_{49}NaN_5$ *m/e*: 538.3880, found: 538.3884.

II. Additional thermal analyses for compounds 1-5

Table S1: T_g comparison between compounds bearing NHMe and Et headgroups.

2 x R	NHMe headgroup		Et headgroup		Tg Comparison	
	Compound	T_g °C	Compound	T_g °C	Difference °C	Difference %
3,5-$Me_2C_6H_3$	1a	94	1b	41	53	14
Ph	2a	56	4a	27	29	9
3-MeC_6H_4	2c	60	4c	19	41	12
4-MeC_6H_4	2d	67	4d	35	32	9
2,3-$Me_2C_6H_3$	2e	70	4e	46	24	7
2,4-$Me_2C_6H_3$	2f	54	4f	39	15	5
2,5-$Me_2C_6H_3$	2g	66	4g	32	34	10
3,4-$Me_2C_6H_3$	2i	71	4i	34	37	11
2,4,6-$Me_3C_6H_2$	2j	83	4j	60	23	6
3,5-$F_2C_6H_3$	2k	54	4k	25	29	9
3,5-$Cl_2C_6H_3$	2l	83	4l	52	31	9
3,5-$Br_2C_6H_3$	2m	94	4m	66	28	8
3,5-$I_2C_6H_3$	2n	128	4n	96	32	8
3,5-$(OMe)_2C_6H_3$	2o	65	4o	35	30	9
3,4,5-$(OMe)_3C_6H_2$	2p	94	4p	63	31	8

Table S2: T_g comparison between compounds bearing one (unsymmetrical and two (symmetrical) ancillary groups R.

R	Unsymmetrical[1] 1 x R		Symmetrical 2 x R		T_g Comparison	
	Compound	T_g °C	Compound	T_g °C	Difference °C	Difference %
Ph	3	73	2a	56	17	4.9
2-MeC_6H_4	4	61	2b	55	6	1.8
3-MeC_6H_4	5	64	2c	60	4	1.2
4-MeC_6H_4	6	70	2d	67	3	0.9
2,4-$Me_2C_6H_3$	7	63	2f	54	9	2.7
2,5-$Me_2C_6H_3$	8	71	2g	66	5	1.5
2,6-$Me_2C_6H_3$	9	84	2h	89	-5	-1.4
3,4-$Me_2C_6H_3$	10	72	2i	71	1	0.3
2,4,6-$Me_3C_6H_2$	11	79	2j	83	-4	-1.1
3,5-$Cl_2C_6H_3$	18	84	2l	83	1	0.3
3,5-$(OMe)_2C_6H_3$	27	68	2o	65	3	0.9
3,4,5-$(OMe)_3C_6H_2$	28	82	2p	94	-12	-3.4
Cy	42	74	3c	58	16	4.6

1. Eren, R. N.; Plante, A.; Meunier, A.; Laventure, A.; Huang, Y. S.; Briard, J. G.; Creber, K. J.; Pellerin, C.; Soldera, A.; Lebel, O., One ring to rule them all: effect of aryl substitution on glass-forming ability in mexylaminotriazine molecular glasses. *Tetrahedron* **2012,** *68* (49), 10130-10144.