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Supplementary data

High T_g Blue Emitting Materials for Electroluminescent Devices

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4. White solid. Yield: 92%. FAB MS: *m*/*e* 737 (M^+). ^{1}H NMR (acetone-d_6): δ 8.41 (s, 1 H, *H*-4 of carbazole), 7.90-7.87 (m, 3 H, *H*-4 and *H*-5 of spirobifluorene, *H*-2 of carbazole), 7.72-7.68 (m, 4 H, *H*-4' and *H*-5' of spirobifluorene, carbazole), 7.52 (d, *J* = 8.8 Hz, 1 H, carbazole), 7.38-7.35 (m, 3 H, *H*-6, *H*-3' and *H*-6' of spirobifluorene), 7.22 (d, *J* = 8.8 Hz, 1 H, spirobifluorene), 7.08-7.05 (m, 4 H), 6.88-6.86 (m, 3 H, ortho and para of C_6H_5), 6.79 (d, *J* = 1.7 Hz, 2 H, *H*-1' and *H*-8' of spirobifluorene), 6.59 (d, *J* = 7.6 Hz, 1 H, *H*-8 of spirobifluorene), 6.47 (d, *J* = 2.0 Hz, 1 H, *H*-1 of spirobifluorene), 4.49 (q, *J* = 7.2 Hz, 2 H, CH_2), 1.39 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.15 (s, 18 H, CH_3 of spirobifluorene). Anal. Calcd for $C_{54}H_{47}N_3$: C, 87.89; H, 6.42; N, 5.69. Found: C, 87.49; H, 6.31; N, 5.61.

9-Ethyl-6-(naphthalen-1-ylamino)-9*H*-carbazole-3-carbonitrile (5a). Compound **5a** was prepared by a similar procedure as described for compound **1** except that 6-bromo-9-ethyl-9*H*-carbazole-3-carbonitrile and naphthalen-1-amine were used instead of 2-bromo-(2',7'-di-*tert*-butyl)-9,9'-spirobifluorene and aniline, Compound **5a** was obtained as white solid in 50% yield. FAB MS: *m*/*e* 361 (M^+). ^{1}H NMR (acetone-d_6) δ: 8.50 (s, 1 H, *H*-4 of carbazole), 8.31(d, *J* = 8.6 Hz, 1 H, *H*-2 of carbazole), 8.06 (d, *J* = 2.0 Hz, 1 H, *H*-5 of carbazole), 7.88 (d, *J* = 7.6 Hz, 1 H, naphthalene), 7.74-7.69 (m, 2 H, naphthalene), 7.64 (d, *J* = 7.6 Hz, 1 H, *H*-8 of carbazole), 7.57 (s, 1 H, -NH), 7.52-7.43 (m, 4 H, *H*-1 and *H*-7 of carbazole, naphthalene), 7.34 (t, *J* = 7.9 Hz, 1 H, *H*-3 of naphthalene), 7.22 (d, *J* = 7.6 Hz, 1 H, *H*-2 of naphthalene), 4.54 (q, *J* = 7.2 Hz, 2 H, -CH_2-), 1.45 (t, *J* = 7.2 Hz, 3 H, -CH_3). Anal. Calcd. for $C_{25}H_{19}N_3$: C, 83.08; H, 5.30; N, 11.63, found: C, 82.68; H, 5.22; N, 11.49.

5. Milky white solid. Yield: 80%. FAB MS: *m*/*e* 787 (M^+). ^{1}H NMR (acetone-d_6): δ: 8.30 (s, 1 H, *H*-4 of carbazole), 7.91-7.89 (m, 3 H, *H*-2 of carbazole, *H*-4 and *H*-5 of spirobifluorene), 7.83 (d, *J* = 7.6 Hz, 1 H, naphthalene), 7.78 (d, *J* = 8.3 Hz, 1 H, naphthalene), 7.75 (d, *J* = 8.2 Hz, 1 H, naphthalene), 7.70-7.63 (m, 4 H, *H*-4' and *H*-5' of spirobifluorene, carbazole, naphthalene), 7.43-7.39 (m, 3 H, carbazole and naphthalene), 7.40-7.26 (m, 4 H, spirobifluorene and naphthalene), 7.19 (d, *J* = 7.4 Hz, 1 H, *H*-3 of spirobifluorene), 7.12 (dd, *J* = 8.7, 2.2 Hz, 1 H, *H*-7 of carbazole), 7.02 (t, *J* = 8.0 Hz, 1 H, *H*-7 of spirobifluorene), 6.82-6.79 (m, 3 H, *H*-1' and *H*-8' of spirobifluorene, naphthalene), 6.54 (d, *J* = 7.5 Hz, 1 H, *H*-8 of spirobifluorene), 6.47 (d, *J* = 2.0 Hz, 1 H, *H*-1 of spirobifluorene), 4.43 (q, *J* = 7.2 Hz, 2 H, CH_2), 1.35 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.19 (s, 18 H, CH_3 of spirobifluorene). Anal. Calcd for $C_{58}H_{49}N_3$: C, 88.40; H, 6.27; N, 5.33. Found: C, 88.68; H, 6.26; N, 5.36.

6. White solid. Yield 73%. FAB MS: *m*/*e* 1189 $(M+H)^+$. ^{1}H NMR (acetone-d_6): δ 7.92 (d, *J* = 8.3 Hz, 4 H, *H*-4 and *H*-5 of spirobifluorene), 7.74 (d, *J* = 8.0 Hz, 4 H, *H*-4' and *H*-5' of spirobifluorene), 7.41-7.33 (m, 10 H, *H*-6, *H*-3' and *H*-6' of spirobifluorene and C_6H_4), 7.17-7.07 (m, 8 H, *H*-3, *H*-7 of spirobifluorene and para-C_6H_5), 6.94-6.92 (m, 10 H, ortho and para of C_6H_5 and C_6H_4), 6.79-6.78 (m, 4 H, *H*-1' and *H*-8' of spirobifluorene), 6.63 (d, *J* = 8.3 Hz, 2 H, *H*-8 of spirobifluorene), 6.45 (d, *J* = 1.2 Hz, 2 H, *H*-1 of spirobifluorene), 1.19 (s, 36 H, CH_3). Anal. Calcd for $C_{90}H_{80}N_2$: C, 90.87; H, 6.78; N, 2.35. Found: C, 90.47; H, 6.80; N, 2.19.

7. White solid. Yield 80%. FAB MS: *m*/*e* 1463 $(M+H)^+$. ^{1}H NMR (acetone-d_6): δ 7.84 (d, *J* = 7.5 Hz, 2 H, *H*-5 of spirobifluoren-2-yl), 7.77 (d, *J* = 8.2 Hz, 2 H, *H*-4 of spirobifluoren-2-yl), 7.69 (d, *J* = 8.0 Hz, 4 H, *H*-4' and *H*-5' of spirobifluoren-2-yl), 7.65 (d, *J* = 8.2 Hz, 2 H, *H*-4 of spirobifluoren-2,7-yl), 7.54 (d, *J* = 8.0 Hz, 2 H, *H*-4' of spirobifluoren-2,7-yl), 7.38-7.32 (m, 6 H, *H*-6, *H*-3' and *H*-6' of spirobifluoren-2-yl), 7.29 (dd, *J* = 8.0, 1.8 Hz, 2 H, *H*-3' of spirobifluoren-2,7-yl), 7.05 (t, *J* = 7.4 Hz, 2 H, *H*-7 of spirobifluoren-2-yl), 6.91-6.83 (m, 8 H, *H*-3 of spirobifluoren-2-yl, *H*-3 of spirobifluoren-2,7-yl and meta-C_6H_5), 6.75 (d, *J* = 1.4 Hz, 2 H, *H*-1' of spirobifluoren-2,7-yl), 6.70-6.68 (m, 6 H, *H*-1' and *H*-8' of spirobifluoren-2-yl and para-C_6H_5), 6.64 (d, *J* = 7.6 Hz, 4 H, ortho-C_6H_5), 6.58 (d, *J* = 7.5 Hz, 2 H, *H*-4 of spirobifluoren-2,7-yl), 6.32 (d, *J* = 1.9 Hz, 2 H, *H*-1 of spirobifluoren-2-yl), 6.27 (d, *J* = 1.9 Hz, 2 H, *H*-1 of spirobifluoren-2,7-yl), 1.19 (s, 18 H, CH_3), 1.15 (s, 36 H, CH_3). Anal. Calcd for $C_{111}H_{102}N_2$: C, 91.06; H, 7.02; N, 1.91. Found: C, 90.66; H, 6.81; N, 1.70.

8. Milky white solid. Yield 70%. FAB MS: *m/e* 1477 $(M+H)^+$. ^1H NMR (acetone-d_6): δ 7.94-7.92 (m, 4 H, *H*-4 and *H*-5 of spirobifluorene), 7.76 (d, *J* = 8.1 Hz, 4 H, *H*-4' and *H*-5' of spirobifluorene), 7.61-7.57 (m, 4 H, anthracene), 7.48 (dd, *J* = 9.2, 1.9 Hz, 2 H, *H*-3 and *H*-7 of anthracene), 7.40-7.32 (m, 6 H, *H*-6, *H*-3' and *H*-6' of spirobifluorene), 7.22-7.15 (m, 14 H, *H*-7 of spirobifluoene, C_6H_4, ortho and meta of C_6H_5), 7.09-7.05 (m, 6 H, *H*-3 of spirobifluorene and C_6H_4), 6.95 (t, *J* = 7.1 Hz, 2 H, para-C_6H_5), 6.80 (d, *J* = 1.6 Hz, 4 H, *H*-1' and *H*-8' of spirobifluorene), 6.64 (d, *J* = 7.5 Hz, 2 H, *H*-8 of spirobifluorene), 6.61 (d, *J* = 2.0 Hz, 2 H, *H*-1 of spirobifluorene), 1.26 (s, 18 H, C*H*$_3$), 1.12 (s, 36 H, C*H*$_3$). Anal. Calcd for $C_{112}H_{104}N_2$: C, 91.01; H, 7.09; N, 1.90. Found: C, 90.81; H, 7.19; N, 1.67.

10. White solid. Yield: 95%. FAB MS: *m/e* 758 (M^+). ^1H NMR ($CDCl_3$): δ 8.15 (d , *J* = 8.1 Hz, 2 H, *H*-4 of spirobifluorene), 8.05-8.08 (m, 4 H, *H*-3' and *H*-4' of spirobifluorene), 7.65-7.61 (m, 4 H, carbazole), 7.38 (dd, *J* = 8.1, 1.6 Hz, 2 H, *H*-3 of spirobifluorene), 7.29-7.19 (m, 12 H, carbazole), 6.98 (d , *J* = 1.7 , 2 H, *H*-1' of spirobifluorene), 6.94 (d, *J* = 1.6 Hz, 2 H , *H*-1 of spirobifluorene), 1.20 (s , 18 H , C*H*$_3$). Anal. Calcd for $C_{57}H_{46}N_2$: C, 90.20; H, 6.11; N, 3.69. Found: C, 90.46; H, 6.22; N, 3.20.

11. Pale green solid. Yield: 65%. FAB MS: *m/e* 862 (M^+). ^1H NMR (acetone-d_6): δ 7.79 (d, *J* = 8.7 Hz, 2 H, $C_{10}H_7$), 7.75 (t , *J* = 7.3 Hz, 4 H, $C_{10}H_7$), 7.64 (d, *J* = 8.3 Hz, 2 H, *H*-4 of spirobifluorene), 7.59 (d, *J* = 8.0 Hz, 2 H, *H*-4' of spirobifluorene), 7.41 (t, *J* = 7.2 Hz, 4 H, $C_{10}H_7$), 7.33 (dd, *J* = 8.3, 1.8 Hz, 2 H, *H*-3' of spirobifluorene), 7.24 (t, *J* = 7.1 Hz, 2 H, $C_{10}H_7$), 7.16 (d, *J* = 7.4 Hz, 2 H, *H*-3 of spirobifluorene), 6.99 (t, *J* = 7.4 Hz, 4 H, meta-C_6H_5), 6.86 (d, *J* = 1.8 Hz, 2 H, *H*-1' of spirobifluorene), 6.85-6.75 (m, 4 H, para-C_6H_5 and $C_{10}H_7$), 6.71 (d, *J* = 7.8 Hz, 4 H, ortho-C_6H_5), 6.49 (d, *J* = 2.1 Hz, 2 H, *H*-1 of spirobifluorene), 1.2 (s, 18 H, C*H*$_3$). Anal. Calcd for $C_{65}H_{54}N_2$: C, 90.45; H, 6.31; N, 3.25. Found: C, 90.20; H, 6.55; N, 3.13.

12. Yellow green solid. Yield: 41%. FAB MS: *m/e* 812 (M^+). ^1H NMR (acetone-d_6): δ 8.01 (d, *J* = 8.2 Hz, 2 H, *H*-4 of spirobifluorene), 7.68 (d , *J* = 8.0 Hz, 2 H, *H*-4' of spirobifluorene), 7.39-7.36 (m , 6 H, *H*-3' of spirobifluorene and C_6H_4), 7.25 (t, *J* = 6.6 Hz, 4 H, meta-C_6H_5), 7.20 (dd, *J* = 8.2, 2.0 Hz, 2 H, *H*-3 of spirobifluorene), 7.09 (t, *J* = 8.0 Hz, 2 H, para-C_6H_5), 7.04 (d, *J* = 7.0 Hz, 4 H, ortho- C_6H_5), 6.86 (d , *J* = 1.3 Hz, 2 H, *H*-1 of spirobifluorene), 6.84 (d , *J* = 8.9 Hz, 4 H, C_6H_4), 6.47 (d, *J* = 1.6 Hz, 2 H, *H*-1' of

spirobifluorene), 1.20 (s , 18 H, CH_3). Anal. Calcd for $C_{59}H_{48}N_4$: C, 87.16; H, 5.95; N, 6.89. Found: C, 86.88; H, 5.90; N, 6.89.

14. Yellow solid. Yield: 87%. FAB MS: *m/e* 1011 $(M+H)^+$. ^{1}H NMR ($CDCl_3$): δ 8.12-7.95 (m, 14 H, pyrene), 7.77 (d , *J* = 8.0 Hz, 2 H, *H*-4 of spirobifluorene), 7.67 (d , *J* = 8.3 Hz, 2 H, *H*-4' of spirobifluorene), 7.51 (d, *J* = 7.9 Hz, 2 H, *H*-3 of spirobifluorene), 7.45 (d , *J* = 8.2 Hz, 2 H, *H*-3' of spirobifluorene) 7.27 (d, *J* = 7.8 Hz, 2 H, pyrene), 6.93 (t , *J* = 7.8 Hz, 4 H, meta-C_6H_5), 6.87 (d , *J* = 1.5 Hz, 2 H, *H*-1' of spirobifluorene), 6.78-6.71 (m ,10 H, *H*-1 of spirobifluorene, pyrene, C_6H_5), 1.20 (s, 18 H, CH_3). Anal. Calcd for $C_{77}H_{58}N_2$: C, 91.45; H, 5.78; N, 2.77. Found: C, 91.48; H, 5.84; N, 2.47.

15. Pale yellow solid. Yield: 53%. FAB MS: *m/e* 1047 $(M+H)^+$. ^{1}H NMR (acetone-d_6): δ 8.40 (s , 2 H, *H*-5 of carbazole), 7.88 (d , *J* = 2.0 Hz, 2 H, *H*-4 of carbazole), 7.81 (d, *J* = 8.3 Hz, 2 H, *H*-7 of carbazole), 7.68-7.74 (m, 4 H, carbazole), 7.55-7.50 (m, 4 H, spirobifluorene), 7.29 (dd, *J* = 8.0, 1.8 Hz, 2 H, *H*-3' of spirobifluorene), 7.19 (dd , *J* = 8.7, 2.1 Hz, 2 H, *H*-3 of spirobifluorene), 7.09-7.02 (m , 6 H, meta-C_6H_5, carbazole), 6.90 (d , *J* = 1.6 Hz, 2 H, *H*-1' of spirobifluorene), 6.90-6.81 (m , 6 H, ortho and para of C_6H_5), 6.43 (d, *J* = 2.0 Hz, 2 H, *H*-1 of spirobifluorene), 4.39 (q , *J* = 6.4 Hz, 4 H, CH_2CH$_3$), 1.41 (t , *J* = 7.2 Hz , 6 H, CH$_2$CH_3), 1.20 (s , 18 H, CH_3). Anal. Calcd for $C_{75}H_{62}N_6$: C, 86.01; H, 5.97; N, 8.02. Found: C, 85.55; H, 5.95; N, 7.91.

16. Pale yellow solid. Yield: 31%. FAB MS: *m/e* 1163 $(M+H)^+$. ^{1}H NMR ($CDCl_3$): δ 7.98 (d, *J* = 8.5 Hz, 4 H, C_6H_4), 7.75 (d , *J* = 8.8 Hz, 4 H, C_6H_4), 7.73 (d, *J* = 8.1 Hz, 2 H, *H*-4 of spirobifluorene), 7.54 (d , *J* = 8.0 Hz, 2 H, *H*-4' of spirobifluorene), 7.51 (d , *J* = 8.5 Hz, 4 H, C_6H_4), 7.30 (dd , *J* = 8.0, 1.9 Hz, 2 H, *H*-3' of spirobifluorene), 7.16 (t , *J* = 7.8 Hz, 4 H, meta-C_6H_5), 7.08 (dd, *J* = 8.2, 2.0 Hz, 2 H, *H*-3 of spirobifluorene), 7.01-6.97 (m , 6 H, ortho and para of C_6H_5), 6.92 (d , *J* = 8.8 Hz, 4 H, C_6H_4), 6.80 (d , *J* = 1.6 Hz, 2 H, *H*-1' of spirobifluorene), 6.57 (d , *J* = 2.0 Hz, 2 H, *H*-1 of spirobifluorene), 1.34 (s, 18 H, CH_3), 1.12 (s ,18 H, CH_3). Anal. Calcd for $C_{81}H_{74}N_6O_2$: C, 83.62; H, 6.41; N, 7.22. Found: C, 84.09; H, 6.06; N, 7.16.