

Synthesis and luminescent properties of branched oligophenylenefluorenes

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2-Bromo-9,9-di-*n*-octylfluorene **1a**. Yield 66%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.67-7.70 (m, 1H), 7.57 (d, *J*=8 Hz, 1H), 7.45-7.49 (m, 2H), 7.33-7.37 (m, 3H), 1.90-2.00 (m, 4H), 1.19-1.26 (m, 4H), 1.03-1.18 (m, 16H), 0.84 (t, *J*=7.2 Hz, 6H), 0.57-0.65 (m, 4H). MS (EI) *m/z* 469⁺. Found (%): C, 74.8; H, 8.9; Br, 16.3. Calc. for C₂₉H₄₁Br (%): C, 74.2; H, 8.7; Br, 17.1.

9,9-Di-*n*-octylfluorene **1b**. Yield 64%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.72 (d, *J*=7.1 Hz, 2H), 7.30-7.38 (m, 6H), 1.96-2.00 (m, 4H), 1.19-1.26 (m, 4H), 1.03-1.18 (m, 16H), 0.84 (t, *J*=7.2 Hz, 6H), 0.60-0.67 (m, 4H). MS (EI) *m/z* 390⁺. Found (%): C, 89.5; H, 10.5. Calc. for C₂₉H₄₂ (%): C, 89.2; H, 10.8.

2-Acetyl-7-bromo-9,9-di-*n*-octylfluorene **2a**. Yield 74%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.95-7.99 (m, 2H), 7.74 (d, *J*=7.8 Hz, 1H), 7.63 (d, *J*=8.5 Hz, 1H), 7.50-7.53 (m, 2H), 2.68 (s, 3H), 1.93-2.06 (m, 4H), 1.18-1.25 (m, 4H), 1.00-1.17 (m, 16H), 0.83 (t, *J*=7.2 Hz, 6H), 0.51-0.62 (m, 4H). MS (EI) *m/z* 511⁺. Found (%): C, 73.0; H, 8.5; Br, 15.3. Calc. for C₃₁H₄₃BrO (%): C, 72.8; H, 8.4; Br, 15.6.

2-Acetyl-7-bromofluorene **2b**. Yield 59%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 8,16 (s, 1H), 8,03 (d, *J*=8,0 Hz, 1H), 7,83 (d, *J*=7,9 Hz, 1H), 7,75 (s, 1H), 7,72 (d, *J*=8,1 Hz, 1H), 7,56 (d, *J*=8,1 Hz, 1H), 3,97 (s, 2H), 2,68 (s, 3H). MS (EI) *m/z* 287⁺. Found (%): C, 63.0; H, 3.7; Br, 27.6. Calc. for C₁₅H₁₁BrO (%): C, 62.7; H, 3.8; Br, 27.9.

2-Acetyl-9,9-di-*n*-octylfluorene **2c**. Yield 67%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.97-7.99 (m, 2H), 7.76-7.80 (m, 2H), 7.37-7.40 (m, 3H), 2.69 (s, 3H), 1.97-2.07 (m, 4H), 1.17-1.24 (m, 4H), 1.00-1.16 (m, 16H), 0.83 (t, *J*=7.2 Hz, 6H), 0.55-0.62 (m, 4H). MS (EI) *m/z* 432⁺. Found (%): C, 86.0; H, 9.9. Calc. for C₃₁H₄₄O (%): C, 86.1; H, 10.2.

2-Acetylfluorene **2d**. Yield 79%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 8,18 (s, 1H), 8,03 (d, *J*=7,9 Hz, 1H), 7,86-7,88 (m, 2H), 7,62 (d, *J*=7,3 Hz, 1H), 7,45 (t, *J*=7,2 Hz, 1H), 7,41 (t, *J*=7,1 Hz, 1H), 3,99 (s, 2H), 2,69 (s, 3H). MS (EI) *m/z* 208⁺. Found (%): C, 86.8; H, 5.6. Calc. for C₁₅H₁₂O (%): C, 86.5; H, 5.8.

1,3,5-Tris(7-bromo-9,9-di-*n*-octylfluorenyl-2-yl)benzene **3a**. Yield 69%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.90 (s, 3H), 7.77 и 7.82 (dd, *J*=7.7 Hz, 6H), 7.69 (s, 3H), 7.63 (d, *J*=8.4 Hz, 3H), 7.50-7.53 (m, 6H), 1.98-2.09 (m, 12H), 1.06-1.25 (m, 60H), 0.80-0.85 (m, 18H), 0.67-0.74 (m, 12H). MS (MALDI) *m/z* 1479⁺. Found (%): C, 75.1; H, 8.9; Br, 16.0. Calc. for C₉₃H₁₂₃Br₃ (%): C, 75.4; H, 8.4; Br, 16.2.

1,3,5-Tris(7-bromofluorenyl-2-yl)benzene **3b**. Yield 31%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7,93 (s, 3H), 7,92 (s, 3H), 7,89 (d, *J*=7,9 Hz, 3H), 7,79 (d, *J*=8,0 Hz, 3H), 7,74 (s, 3H), 7,72 (d, *J*=8,1 Hz, 3H), 7,56 (d, *J*=7,9 Hz, 3H), 4,02 (s, 6H). MS (EI) *m/z* 807⁺. Found (%): C, 70.1; H, 3.0; Br, 29.9. Calc. for C₄₅H₂₇Br₃ (%): C, 66.9; H, 3.4; Br, 29.7.

1,3,5-Tris(9,9-di-*n*-octylfluorenyl-2-yl)benzene **3c**. Yield 62%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7.94 (s, 3H), 7.86 (d, *J*=7.9 Hz, 3H), 7.77-7.81 (m, 6H), 7.73 (s, 3H), 7.33-7.43 (m, 9H), 2.07 (t, *J*=8.1 Hz, 12H), 1.06-1.26 (m, 60H), 0.82 (t, *J*=7 Hz, 18H), 0.68-0.78 (m, 12H). MS (MALDI) *m/z* 1242⁺. Found (%): C, 89.6; H, 10.4. Calc. for C₉₃H₁₂₆ (%): C, 89.8; H, 10.2.

1,3,5-Tris(fluorenyl-2-yl)benzene **3d**. Yield 29%. ¹H NMR (600 MHz, CDCl₃) δ, ppm: 7,96 (s, 3H), 7,94 (s, 3H), 7,92 (d, *J*=7,9 Hz, 3H), 7,87 (d, *J*=7,5 Hz, 3H), 7,80 (d, *J*=7,6 Hz, 3H), 7,80 (d, *J*=7,6 Hz, 3H), 7,61 (d, *J*=Hz, 3H), 7,44 (t, *J*=7,4 Hz, 3H), 7,36 (t, *J*=7,2 Hz, 3H), 4,03 (s, 6H). MS (EI) *m/z* 570⁺. Found (%): C, 95.1; H, 4.9. Calc. for C₄₅H₃₀ (%): C, 94.7; H, 5.3.

Oligophenylenefluorenes **OPF-1**. Yield 32%. Found (%): C, 79.9; H, 4.4; Br, 12.1. Calc. for C₁₆₅H₁₁₈Br₄BO₂ (%): C, 80.4; H, 4.8; Br, 13.0.

Oligophenylenefluorenes **OPF-2**. Yield 45%. Found (%): C, 81.8; H, 8.9; Br, 7.0. Calc. for C₂₉₁H₃₈₅Br₄BO₂ (%): C, 82.4; H, 9.1; Br, 7.5.