

Nano-hybrid luminescent dot: synthesis, characterization and optical properties

1 Monomer synthesis

1-Bromo-4-[2-ethylhexyloxy]-p-xylene (1a)^[17]. A colorless liquid was prepared according to the literature by reaction between 2-Ethylhexyl bromide with 2,5-dimethyl-phenol with NaOH in acetone (yield 90%), followed by brominating at 0-10°C in CHCl₃ (yield 98%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.231 (s, 1H), 6.663 (s, 1H), 3.803 (d, 2H), 2.332 (s, 3H), 2.146 (s, 3H), 1.730 (m, 1H), 1.545(m, 8H), 0.923(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 157.903, 136.865, 135.683, 134.076, 127.650, 115.658, 115.369, 113.815. MS (EI, *m/z*): 313.2. Calculate (%) C, 61.34, H, 7.99; Found (%) C, 61.29, H, 8.02.

4-Bromo-4'-[2-ethylhexyloxy]-2',5'-dimethyl-biphenyl (2a). A Grignard reagent of 4-[2-ethylhexyloxy]p-xylene-1-magnesium bromide (31.95mmol) prepared from the reaction of 10g (31.95mmol) of 1-bromo-4-[2-ethylhexyloxy]p-xylene (**1a**) with 0.92g (38.34mmol) of Mg in 80ml of dry THF, was added dropwise into a solution of 1,4-dibromo-benzene (6.28g, 26.62mmol) in 40ml of dry THF containing Pd(PPh₃)₄ (0.6mmol) as catalyst over a period of 1 hour. After refluxing for 24 hours, the reaction mixture was quenched with saturated NH₄Cl aqueous solution and extracted with ether. The extract was washed with water two times and with brine once and then dried over anhydrous MgSO₄. After removal of solvent, the dark-brown liquid of mixture was subjected to purification by column chromatography on silica gel using hexane as eluant. A 8.45g (yield 68%) of colorless liquid was obtained. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.556 (d, 2H), 7.224 (d, 2H), 7.021(s, 1H), 6.761(s, 1H), 3.936(d, 2H), 2.283 (s, 3H), 2.263 (s, 3H), 1.822 (m, 1H), 1.547(m, 8H), 1.004(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 158.252, 142.273, 134.798, 133.986, 133.611, 133.326, 132.435, 131.695, 125.669, 121.962, 121.845, 121.733, 114.823, 113.283. MS (EI, *m/z*): 389.1. Calculate (%) C, 67.87, H, 7.46; Found (%) C, 67.80, H, 7.49.

4-Bromo-4''-[2-ethylhexyloxy]-2'',5''-dimethyl-triphenyl (3a). A white crystalline was obtained following a similar method of obtaining **2a** using 4,4'-Dibromobiphenyl to replace 1,4-dibromo-benzene (yield 51%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.615 (d, 4H), 7.545 (d, 2H), 7.421(d, 2H), 7.083(s, 1H), 6.770(s, 1H), 3.932(d, 2H), 2.233 (s, 3H), 2.262 (s, 3H), 1.811 (m, 1H), 1.553(m, 8H), 0.991(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 157.971, 142.731, 141.210, 139.150, 134.022, 132.527, 132.347, 132.108, 130.706, 130.532, 129.137, 128.582, 126.986, 125.512, 122.719, 114.752, 113.202. MS (EI, *m/z*): 466.3. Calculate (%) C, 72.26, H, 7.10; Found (%) C, 72.24, H, 7.13.

4-Bromo-2,5-dimethyl-4'-[2-ethylhexyl]-biphenyl (4a). A colorless liquid was synthesized following a similar method of obtaining **2a** using 2,5-Dibromo-p-xylene and 1-bromo-4-Ethylhexyl-benzene (yield 62%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.497 (s, 1H), 7.247 (d, 4H), 7.165(s, 1H), 2.651(d, 2H), 2.444 (s, 3H), 2.277 (s, 3H), 1.687 (m, 1H), 1.379(m, 8H), 0.973(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 142.512, 142.007, 139.467, 136.202, 135.847, 134.243, 132.689, 131.102, 130.867, 129.540, 129.294, 124.589. MS (EI, *m/z*): 372.1. Calculate (%) C, 70.78, H, 7.78; Found (%) C, 70.89, H, 7.82.

4-Bromo-2,5-dimethyl-4'-[2-ethylhexyloxy]-biphenyl (5a). A colorless liquid was obtained following a similar method of obtaining **2a** using 2,5-Dibromo-p-xylene and 1-bromo-4-Ethylhexyloxy-benzene (yield 59%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.556 (d, 2H), 7.223 (d, 2H), 7.020(s, 1H), 6.760(s, 1H), 3.936(d, 2H), 2.281 (s, 3H), 2.263 (s, 3H), 1.823 (m, 1H), 1.581(m, 8H), 1.004(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 159.922, 142.230, 136.210, 135.870, 134.317, 132.749, 132.219, 132.011, 130.582, 124.460, 116.327, 114.752. MS (EI, *m/z*): 388.1. Calculate (%) C, 67.87, H, 7.46; Found (%) C, 67.89, H, 7.45.

4-Bromo-2,5-dimethoxy-4'-[2-ethylhexyloxy]-biphenyl (6a). A colorless liquid was obtained following a similar method of obtaining **2a** using 1,4-dibromo-2,5-dimethoxy-benzene and 1-bromo-4-Ethylhexyloxy-benzene (yield 58%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.463 (d, 2H), 7.178 (s, 1H), 7.020(s, 1H), 6.986(d, 2H), 6.904(s, 1H), 3.902(s, 5H), 3.782(s, 3H), 1.816 (m, 1H), 1.463(m, 8H), 0.923(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 160.117, 152.154, 151.584, 132.564, 132.454, 131.828, 131.073, 130.950, 119.054, 117.443, 116.843, 116.322, 115.273, 114.739, 111.136. MS (EI, *m/z*): 420.2. Calculate (%) C, 62.71, H, 6.89; Found (%) C, 62.78, H, 6.90.

2 Organic chain synthesis (for comparison with hybrid dots)

4-[2-ethylhexyloxy]-2,5-dimethyl-biphenyl (1c). A colorless liquid was obtained following a similar method of obtaining **2a** using Bromobenzene and **1a** (yield 72%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.484 (m, 2H), 7.412 (m, 3H), 7.135(s, 1H), 6.834(s, 1H), 3.995(d, 2H), 2.369 (s, 3H), 2.338 (s, 3H), 1.863 (m, 1H), 1.598(m, 8H), 1.063(m, 6H). ¹³C (CDCl₃, 400 MHz, ppm) δ 158.076, 143.468, 135.039, 134.314, 132.767, 131.720, 130.405, 128.819, 126.963, 125.519,

114.797, 113.262. MS (EI, m/z): 310.1. Calculate (%) C, 85.16, H, 9.68; Found (%) C, 85.17, H, 9.68.

4-[2-ethylhexyloxy]-2,5-dimethyl-triphenyl (2c). A color-less liquid was obtained following a similar method of obtaining **2a** using Bromobenzene and **2a** (yield 67%). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.804 (m, 4H), 7.575 (m, 4H), 7.505(t, 1H), 7.266(s, 1H), 6.936(s, 1H), 4.092(d, 2H), 2.502 (s, 3H), 2.442 (s, 3H), 1.945 (m, 1H), 1.720(m, 8H), 1.159(m, 6H). ^{13}C (CDCl_3 , 400 MHz, ppm) δ 158.148, 142.442, 140.552, 135.010, 134.536, 134.307, 132.765, 132.122, 131.044, 130.542, 129.406, 129.291, 128.958, 127.722, 127.383, 125.616, 114.88, 113.358. MS (EI, m/z): 386.2. Calculate (%) C, 87.05, H, 8.81; Found (%) C, 86.98, H, 8.79.

4-[2-ethylhexyloxy]-2,5-dimethyl-p-quaterphenyl (3c). A white crystalline was obtained following a similar method of obtaining **2a** using Bromobenzene and **3a** (yield 62%). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.788 (m, 8H), 7.511 (m, 2H), 7.460(m, 3H), 7.130(s, 1H), 6.798(s, 1H), 3.956(d, 2H), 2.233(s, 3H), 2.291(s, 3H), 1.835(m, 1H), 1.577(m, 8H), 1.015(m, 6H). ^{13}C (CDCl_3 , 400 MHz, ppm) δ 157.914, 142.411, 142.068, 141.246, 139.874, 134.919, 134.326, 134.156, 132.566, 132.029, 130.972, 130.487, 129.610, 129.484, 129.301, 129.149, 128.708, 128.123, 127.910, 127.568, 127.144, 125.517, 114.761, 113.226. MS (EI, m/z): 462.2. Calculate (%) C, 88.31, H, 8.22; Found (%) C, 88.34, H, 8.24.