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%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 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). $^{13}$C (CDCl$_3$, 400 MHz, ppm) $\delta$ 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%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.497 (s, 1H), 7.247 (d, 4H), 7.165(s, 1H), 7.251(d, 2H), 2.444 (s, 3H), 2.277 (s, 3H), 1.687 (m, 1H), 1.379(m, 8H), 0.973(m, 6H). $^{13}$C (CDCl$_3$, 400 MHz, ppm) $\delta$ 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%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 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). $^{13}$C (CDCl$_3$, 400 MHz, ppm) $\delta$ 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%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 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). $^{13}$C (CDCl$_3$, 400 MHz, ppm) $\delta$ 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%). $^1$H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 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). $^{13}$C (CDCl$_3$, 400 MHz, ppm) $\delta$ 158.076, 143.468, 135.039, 134.314, 132.767, 131.720, 130.405, 128.819, 126.963, 125.519,
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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%). \(^1\)H NMR (CDCl$_3$, 400 MHz, ppm) \(\delta\) 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). \(^1\)C (CDCl$_3$, 400 MHz, ppm) \(\delta\) 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%). \(^1\)H NMR (CDCl$_3$, 400 MHz, ppm) \(\delta\) 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). \(^1\)C (CDCl$_3$, 400 MHz, ppm) \(\delta\) 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.