Electronic Supplementary Information

Cross-linked, Luminescent Films via Electropolymerization of Multifunctional Precursors for High-efficient Electroluminescence

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1. Synthesis and characterization of OCPC, TCPC, DCPC, OCBzC and TCBzC.\textsuperscript{41}

\begin{equation}
\text{M1} + \text{Br-} \xrightarrow{\text{Pd(PPh}_3)_4, \text{Na}_2 \text{CO}_3, \text{toluene, 90°C for 48h}} \text{M3}
\end{equation}

\begin{equation}
\text{M3} \xrightarrow{\text{PdCl}_2(dppf), \text{KOA}c, 1,4\text{-dioxane, 80°C for 48h}} \text{M4}
\end{equation}

(i) $\text{M1 or M4} + \text{Br-} \xrightarrow{\text{Pd(PPh}_3)_4, \text{Na}_2 \text{CO}_3, \text{toluene, 90°C for 48h}} \text{TCPC or OCPC}$

(ii) $\text{M1 or M4} + \text{Br-} \xrightarrow{\text{Pd(PPh}_3)_4, \text{Na}_2 \text{CO}_3, \text{toluene, 90°C for 48h}} \text{TCBzC or OCBzC}$

Scheme S1. Synthetic routes of OCPC, TCPC, OCBzC and TCBzC molecules.

Scheme S1 illustrates the synthetic procedures for OCPC, TCPC, OCBzC and TCBzC. The monomer, 9,9',9'',9'''-(7-bromo-9H,9H-[2,2'-bifluorene]-9,9,9',9''-tetral) tetraakis(hexane-6,1-diyl) tetraakis(9H-carbazole) (M3), was prepared from the Suzuki coupling reaction of M1 and M2 in a biphasic system (toluene/aqueous Na$_2$CO$_3$) using Pd(PPh$_3$)$_4$ as catalyst.\textsuperscript{42} To prevent from generating excess byproduct, less ratio amount of M1 (M2 was 1.5 times by mol more than M1) was put into. The key intermediate, 4,4,5,5-tetramethyl-2-(9,9,9',9''-tetraakis(6-(9H-fluoren-9-yl)hexyl)-9H,9H-[2,2'-bifluorene]-7-yl)-1,3,2-oxaborolane (M4), was synthesized from M3, and the reaction was carried out between M3 and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) catalyzed by PdCl$_2$(dppf) in the presence of KOAc and 1,4-dioxane at 80°C for 48h. The boronic ester was purified by chromatography using silica support in the yield of 63%. Finally, T-series and O-series were synthesized via Suzuki coupling reaction similarly to M3. 1H and 13C, MS, and elemental analysis were employed to confirm the chemical structures of the final compounds. FCz was synthesized following a general method reported by Ma and characterized by NMR.\textsuperscript{42}

TCPC: $^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS): $\delta$=8.07–8.05 (d, $J$=8.06, 8H; Ar-H), 7.94–7.92 (d, $J$=7.93, 2H; Ar-H),
7.80–7.79 (d, J = 7.79, 2H; Ar-H), 7.67–7.65 (d, J = 7.66, 2H; Ar-H), 7.63–7.61 (d, J = 7.62, 2H; Ar-H), 7.58–7.57 (d, J = 7.57, 2H; Ar-H), 7.40–7.29 (m, 16H; Ar-H), 7.26–7.24 (m, 8H; Ar-H), 7.22–7.17 (m, 12H; Ar-H), 7.08–7.07 (t, J = 7.07, 2H; Ar-H), 6.99 (s, 2H; Ar-H), 6.85–6.83 (d, J = 6.84, 2H; Ar-H), 4.10–4.09 (t, J = 4.09, 8H; CH₂), 1.88–1.84 (m, 8H; CH₂), 1.64–1.58 (m, 8H; CH₂), 1.12–1.02 (m, 16H; CH₂), 0.57–0.52 ppm (m, 8H; CH₂). MS (MALDI-TOF) mass (m/z): 1642 [M⁺]. Elemental analysis calcd (%) for C₁₂₂H₁₉₈N₁₀S: C, 89.96; H, 6.63; N, 3.41. Found: C, 89.73; H, 6.92; N, 3.36.

TCBzC: ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ = 8.04–8.03 (d, J = 7.6 Hz, 8H; Ar-H), 7.98–7.96 (d, J = 7.9 Hz, 2H; Ar-H), 7.91 (s, 2H; Ar-H), 7.86–7.84 (d, J = 7.9 Hz, 2H; Ar-H), 7.77–7.74 (m, 4H; Ar-H), 7.38–7.35 (m, 10H; Ar-H), 7.32–7.29 (m, 4H; Ar-H), 7.27–7.25 (d, J = 7.6 Hz, 8H; Ar-H), 7.17–7.14 (t, J = 7.6 Hz, 8H; Ar-H), 4.15–4.12 (t, J = 7.3 Hz, 8H; CH₂), 2.05–1.93 (m, 8H; CH₂), 1.71–1.65 (m, 8H; CH₂), 1.19–1.10 (m, 16H; CH₂), 0.80–0.68 ppm (m, 8H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ = 154.66 (C), 151.34 (C), 151.11 (C), 141.73 (C), 141.07 (C), 140.74 (C), 136.65 (C), 133.78 (C), 128.66 (CH), 128.27 (CH), 127.81 (CH), 125.91 (CH), 124.23 (CH), 123.26 (CH), 123.14 (C), 120.68 (CH), 120.47 (CH), 120.23 (CH), 119.04 (CH), 109.00 (CH), 55.49 (C), 43.28 (CH₂), 40.64 (CH₂), 30.14 (CH₂), 29.14 (CH₂), 27.21 (CH₂), 24.10 ppm (CH₂); MS (MALDI-TOF) mass (m/z): 1462 [M⁺]; elemental analysis calcd (%) for C₁₀₈H₈₈N₈S: C, 85.44; H, 6.62; N, 5.75; found: C, 85.28; H, 6.95; N, 5.56.

OCPC: ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ = 8.03 (m, 16H; Ar-H), 7.95 (d, J = 7.9 Hz, 2H; Ar-H), 7.68 (m, 20H; Ar-H), 7.33 (m, 24H; Ar-H), 7.17 (m, 36H; Ar-H), 7.07 (t, J = 7.6 Hz, 2H; Ar-H), 7.01 (s, 2H; Ar-H), 6.85 (d, J = 7.6 Hz, 2H; Ar-H), 4.16 (m, 16H; CH₂), 1.97 (m, 16H; CH₂), 1.59 (m, 16H; CH₂), 1.05 (m, 32H; CH₂), 0.63 ppm (m, 16H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ = 151.79 (C), 151.63 (C), 150.94 (C), 150.31 (C), 149.17 (C), 142.27 (C), 141.77 (C), 141.10 (C), 140.73 (C), 140.43 (C), 128.38 (CH), 128.27 (CH), 127.64 (CH), 127.57 (CH), 127.36 (CH), 126.75 (CH), 126.62 (CH), 125.92 (CH), 124.76 (CH), 123.15 (C), 122.80 (CH), 121.50 (CH), 120.68 (CH), 120.51 (CH), 120.35 (CH), 120.25 (CH), 119.05 (CH), 108.99 (CH), 69.29 (C), 55.57 (C), 55.41 (C), 43.21 (CH₂), 40.68 (CH₂), 30.05 (CH₂), 29.08 (CH₂), 27.18 (CH₂), 24.03 ppm (CH₂); MS (MALDI-TOF) mass (m/z): 2966 [M⁺⁺H⁺]; Anal. Calcd (%) for C₂₅₁H₂₃₀N₆O₆S: C, 89.43; H, 6.79; N, 3.78; found: C, 89.32; H, 6.67; N, 3.89.

OCBzC: ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ = 8.04 (d, J = 7.6 Hz, 8H; Ar-H), 8.00 (d, J = 7.6 Hz, 10H; Ar-H), 7.94 (s, 2H; Ar-H), 7.79 (d, J = 7.9 Hz, 2H; Ar-H), 7.82 (d, J = 7.9 Hz, 2H; Ar-H), 7.74 (m, 6H; Ar-H), 7.64 (m, 6H; Ar-H), 7.59 (s, 2H; Ar-H), 7.34 (m, 18H; Ar-H), 7.25 (d, J = 7.9 Hz, 12H; Ar-H), 7.20 (d, J = 8.2 Hz, 8H; Ar-H), 7.17 (t, J = 7.9 Hz, 8H; Ar-H), 7.12 (t, J = 7.3 Hz, 8H; Ar-H), 4.09 (m, 16H; CH₂), 1.99 (m, 16H; CH₂), 1.63 (m, 16H; CH₂), 1.11 (m, 32H; CH₂), 0.71 ppm (m, 16H; CH₂); ¹³C NMR (125 MHz, CDCl₃, 25°C, TMS): δ = 154.67 (C), 152.25 (C), 151.64 (C), 151.36 (C), 150.96 (C), 141.40 (C), 141.15 (C), 140.91 (C), 140.74 (C), 140.36 (C), 136.69 (C), 133.77 (C), 128.80 (CH), 128.29 (CH), 127.61 (CH), 127.40 (CH), 126.83 (CH), 126.66 (CH), 126.51 (CH), 126.39 (CH), 125.93 (CH), 124.36 (CH), 123.26 (CH), 123.14 (C), 121.63 (CH), 121.56 (CH), 120.70 (CH), 120.51 (CH), 120.30 (CH), 119.07 (CH), 108.99 (CH), 55.69 (C), 55.46 (C), 43.23 (CH₂), 40.75 (CH₂), 30.14 (CH₂), 29.14 (CH₂), 27.22 (CH₂), 24.27 (CH₂), 24.06 ppm (CH₂); MS (MALDI-TOF) mass (m/z): 2837 [M⁺⁺]; Anal. Calcd (%) for C₂₃₂H₁₈₀N₁₀: C, 87.03; H, 6.80; N, 5.02; S, 1.15; found: C, 86.95; H, 6.60; N, 4.94; S, 1.23.

DCPC: ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ = 8.08–8.07 (d, J = 8.07, 4H; Ar-H), 7.68–7.66 (d, J = 7.67, 2H; Ar-H),
7.44–7.42 (t, J=7.42, 4H; Ar-H), 7.31–7.28 (m, 6H; Ar-H), 7.24–7.19 (m, 8H; Ar-H), 4.16–4.15 (t, J=4.15, 4H; CH₂), 1.89–7.85 (m, 4H; CH₂), 1.70–1.63 (m, 4H; CH₂), 1.17–1.03 (m, 8H; CH₂), 0.60–0.53 ppm (m, 4H; CH₂).

2. 2. Electrochemical property and PL spectra of OCPC and TCPC.

![Graph](image)

Fig. S1. a) CV curve of OCPC and TCPC for the first cycle; b) PL spectra of OCPC and TCPC EP films prepared at the scan range -0.80 ~ 0.85 V and the scan rate 50 mV s⁻¹ for 10 cycles, using Bu₄NPF₆ (0.1 mol L⁻¹) as supporting electrolyte in CH₃CN/CH₂Cl₂ (V/V = 2/3) solution.

3. Determination of molar absorption coefficient of OCPC and TCPC backbone.

![Graph](image)

Fig. S2. Absorption intensities of OCPC and TCPC backbones with different concentration in CH₂Cl₂. According to the Lambert-Beer’s law, the mean calculated molar absorption coefficients of OCPC and TCPC backbone are 1.44 × 10⁵ L mol⁻¹
cm⁻¹ and 8.72 × 10⁴ L mol⁻¹ cm⁻³, respectively.

4. The measurement of D₀ of OCPC, TCPC and DCPC.

Fig. S3. CV curves of a) OCPC, b) TCPC, c) DCPC for the first cycle. The potential ranges from 0 to 0.97 V, and the scan rates are 25 mV s⁻¹, 50 mV s⁻¹, 100 mV s⁻¹, 200 mV s⁻¹ and 400 mV s⁻¹, respectively.
5. Electrochemical properties of OCBzC and TCBzC.

Fig. S4. a) CV of OCBzC and TCBzC for the first cycle. b) CV curves for the polymerization of OCBzC (0.17 mmol L$^{-1}$) and TCBzC (0.34 mmol L$^{-1}$) at the scan rate 50 mV s$^{-1}$ and the scan range -0.20 V ~ 0.85 V for 10 cycles using Bu$_4$NPF$_6$ (0.1 mol L$^{-1}$) as supporting electrolyte. The oxidation of carbazole, fluorene and 2, 1, 3-benzothiadiazole (BTz) unit occur at 0.79 V, 0.95 V and 1.20 V, implying the emission center (backbone) will not be affected in the EP process at the potential below 0.95 V. Similar to the comparison of OCPC and TCPC, the film growth rate of OCBzC is enhanced by ca. 2 times compared with TCBzC.

References