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**Electronic Supplementary Information**

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

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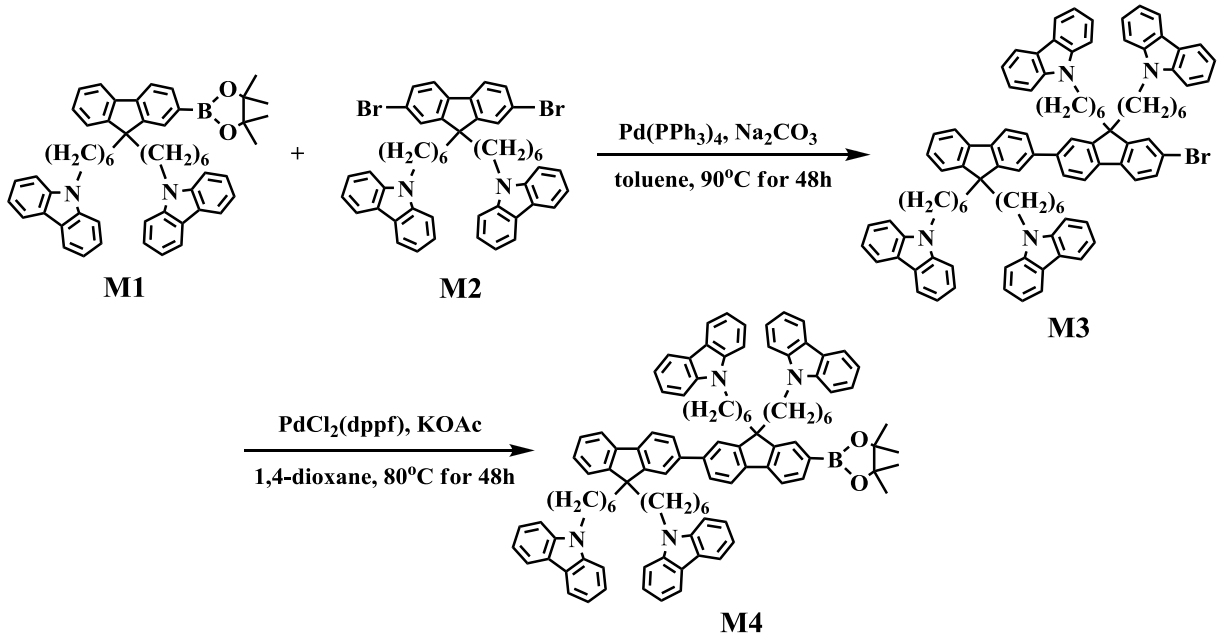
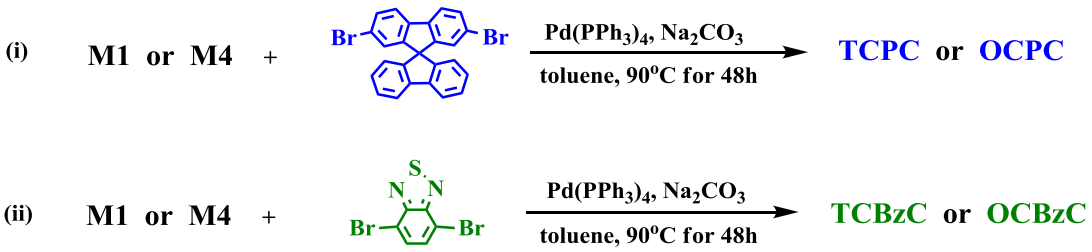
## Contents

## 1. Synthesis and characterization of OCPC, TCPC, DCPC, OCBzC and TCBzC.[s1]




**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,9'H-[2,2'-bifluorene] -9,9,9',9'-tetrayl) tetrakis (hexane-6,1-diyl) ) tetrakis(9Hcarbazole) (**M3**), was prepared from the Suzuki coupling reaction of **M1** and **M2** in a biphasic system (toluene/aqueous $Na_2CO_3$) using $Pd(PPh_3)_4$ as catalyst.[s2] 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'-tetrakis(6-(9H-fluoren-9-yl)hexyl)-9H,9'H-[2,2'-bifluoren]-7-yl)-1,3, 2-ioxaborolane (**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℃ 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. [s2]

**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; $CH_2$), 1.88–1.84 (m, 8H; $CH_2$), 1.64–1.58 (m, 8H; $CH_2$), 1.12–1.02 (m, 16H; $CH_2$), 0.57–0.52 ppm (m, 8H; $CH_2$). MS (MALDI-TOF) mass (m/z): 1642 [$M^+$]. elemental analysis calcd (%) for $C_{123}H_{108}N_4$: C, 89.96; H, 6.63; N, 3.41. Found: C, 89.73; H, 6.92; N, 3.36.

**TCBzC**: $^1$H NMR (500 MHz, $CDCl_3$, 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; $CH_2$), 2.05–1.93 (m, 8H; $CH_2$), 1.71–1.65 (m, 8H; $CH_2$), 1.19–1.10 (m, 16H; $CH_2$), 0.80–0.68 ppm (m, 8H; $CH_2$); $^{13}$C NMR (125 MHz, $CDCl_3$, 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), 127.44 (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 ($CH_2$), 40.64 ($CH_2$), 30.13 ($CH_2$), 29.14 ($CH_2$), 27.21 ($CH_2$), 24.10 ppm ($CH_2$); MS (MALDI-TOF) mass (m/z): 1462 [$M^+$]; elemental analysis calcd (%) for $C_{104}H_{96}N_6S$: C, 85.44; H, 6.62; N, 5.75; found: C, 85.28; H, 6.95; N, 5.56.

**OCPC:** $^1$H NMR (500 MHz, $CDCl_3$, 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; $CH_2$), 1.97 (m, 16H; $CH_2$), 1.59 (m, 16H; $CH_2$), 1.05 (m, 32H; $CH_2$), 0.63 ppm (m, 16H; $CH_2$); $^{13}$C NMR (125 MHz, $CDCl_3$, 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), 140.27 (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 ($CH_2$), 40.68 ($CH_2$), 30.05 ($CH_2$), 29.08 ($CH_2$), 27.18 ($CH_2$), 24.03 ppm ($CH_2$); MS (MALDI-TOF) mass (m/z): 2966 [$M^+$+H]; Anal. Calcd (%) for $C_{221}H_{200}N_8$: C, 89.43; H, 6.79; N, 3.78; found: C, 89.32; H, 6.67; N, 3.89.

**OCBzC**: 1H NMR (500 MHz, $CDCl_3$, 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; $CH_2$), 1.99 (m, 16H; $CH_2$), 1.63 (m, 16H; $CH_2$), 1.11 (m, 32H; $CH_2$), 0.71 ppm (m, 16H; $CH_2$); $^{13}$C NMR (125 MHz, $CDCl_3$, 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 ($CH_2$), 40.75 ($CH_2$), 30.14 ($CH_2$), 29.14 ($CH_2$), 27.22 ($CH_2$), 24.27 ($CH_2$), 24.06 ppm ($CH_2$); MS (MALDI-TOF) mass (m/z): 2837 [$M^+$]; Anal. Calcd (%) for $C_{202}H_{188}N_{10}S$: 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**: $^1$H NMR (500 MHz, $CDCl_3$, 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; $CH_2$), 1.89–7.85 (m, 4H; $CH_2$), 1.70–1.63 (m, 4H; $CH_2$), 1.17–1.03 (m, 8H; $CH_2$), 0.60–0.53 ppm (m, 4H; $CH_2$).

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

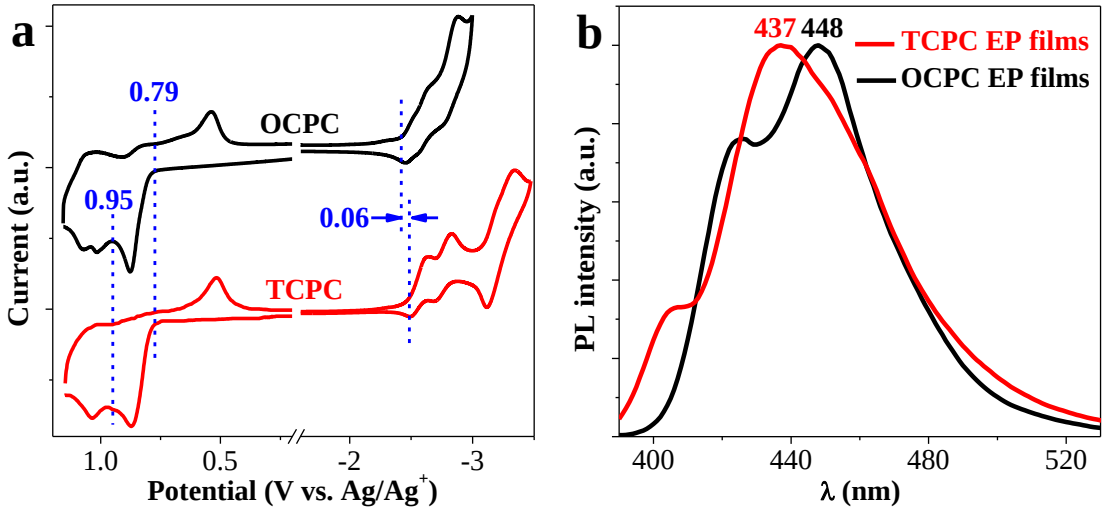



**Fig. S1.** a) CV curve of OCPC and TCPC for the first cycle; b) PL spectra of OCPC and TCPC EP films prepared at the scan rang -0.80 ~ 0.85 V and the scan rate 50 mV $s^{-1}$ for 10 cycles, using $Bu_4NPF_6$ (0.1 mol $L^{-1}$) as supporting electrolyte in $CH_3CN/CH_2Cl_2$ (V/V = 2/3) solution.

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

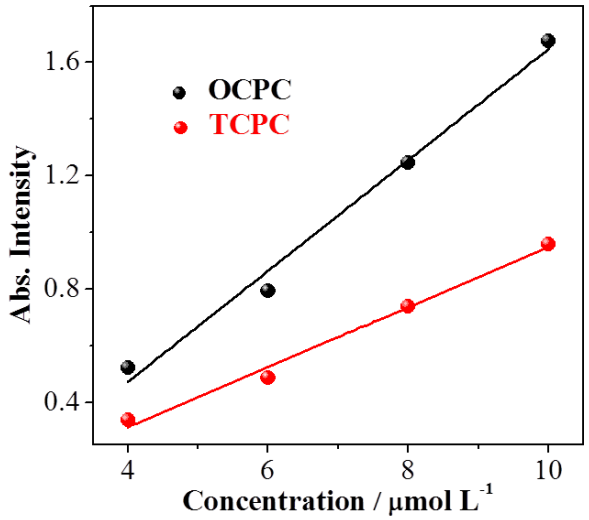



**Fig. S2.** Absorption intensities of **OCPC** and **TCPC** backbones with different concentration in $CH_2Cl_2$. According to the Lambert-Beer's law, the mean calculated molar absorption coefficients of **OCPC** and **TCPC** backbone are $1.44 \times 10^5$ L $mol^{-1}$

$cm^{-1}$ and $8.72 \times 10^4$ L $mol^{-1}$ $cm^{-1}$, respectively.

## 4. The measurement of $D_0$ of OCPC, TCPC and DCPC.

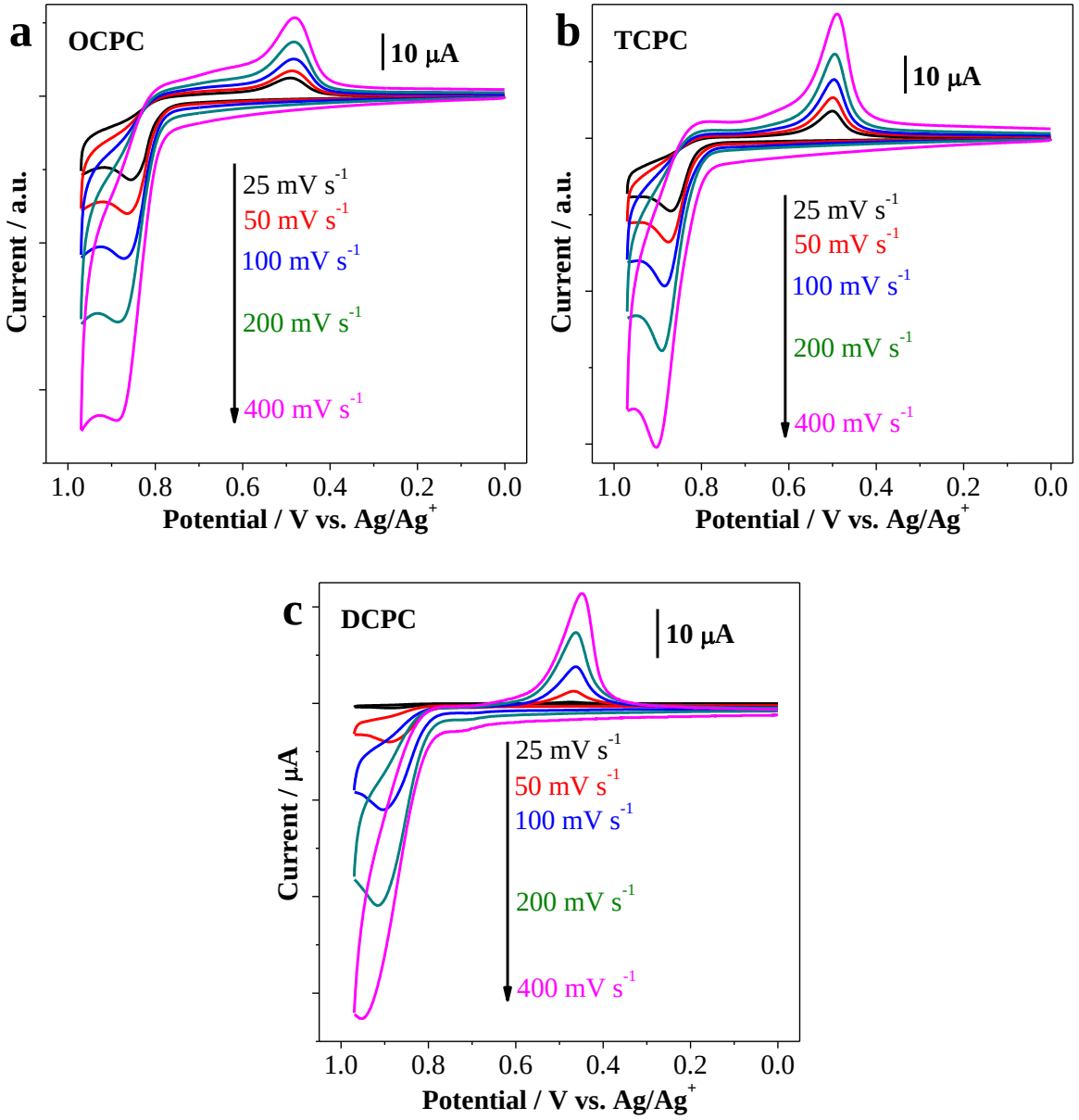



**Fig. S3.** CV curves of a) OCPC, b) TCPC, c) DCPC for the first cycle. The potential ranges from 0 to 0.97 V, and the scan rates are 25 mV $s^{-1}$, 50 mV $s^{-1}$, 100 mV $s^{-1}$, 200 mV $s^{-1}$ and 400 mV $s^{-1}$, respectively.

## 5. Electrochemical properties of OCBzC and TCBzC.

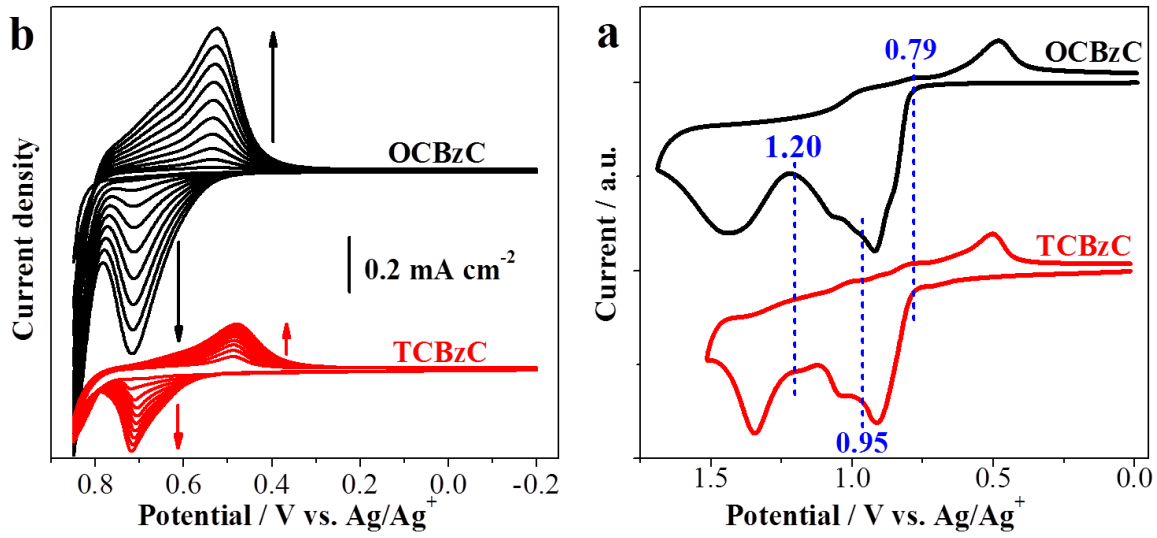



**Fig. S4**. a) CV of **OCBzC** and **TCBzC** for the first cycle. b) CV curves for the polymerization of **OCBzC** (0.17 mmol $L^{-1}$) and **TCBzC** (0.34 mmol $L^{-1}$) at the scan rate 50 mV $s^{-1}$ and the scan rang -0.20 V ~ 0.85 V for 10 cycles using $Bu_4NPF_6$ (0.1 mol $L^{-1}$) as supporting 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

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S2. S. Tang, M. Liu, P. Lu, H. Xia, M. Li, Z. Xie, F. Shen, C. Gu, H. Wang, B. Yang, Y. Ma*, *Adv. Funct. Mater.*, 2007, **17**, 2869-2877.