

Separation of Electrical and Optical Energy Gaps for Constructing Bipolar Organic Wide Bandgap Materials

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1. Experimental Section

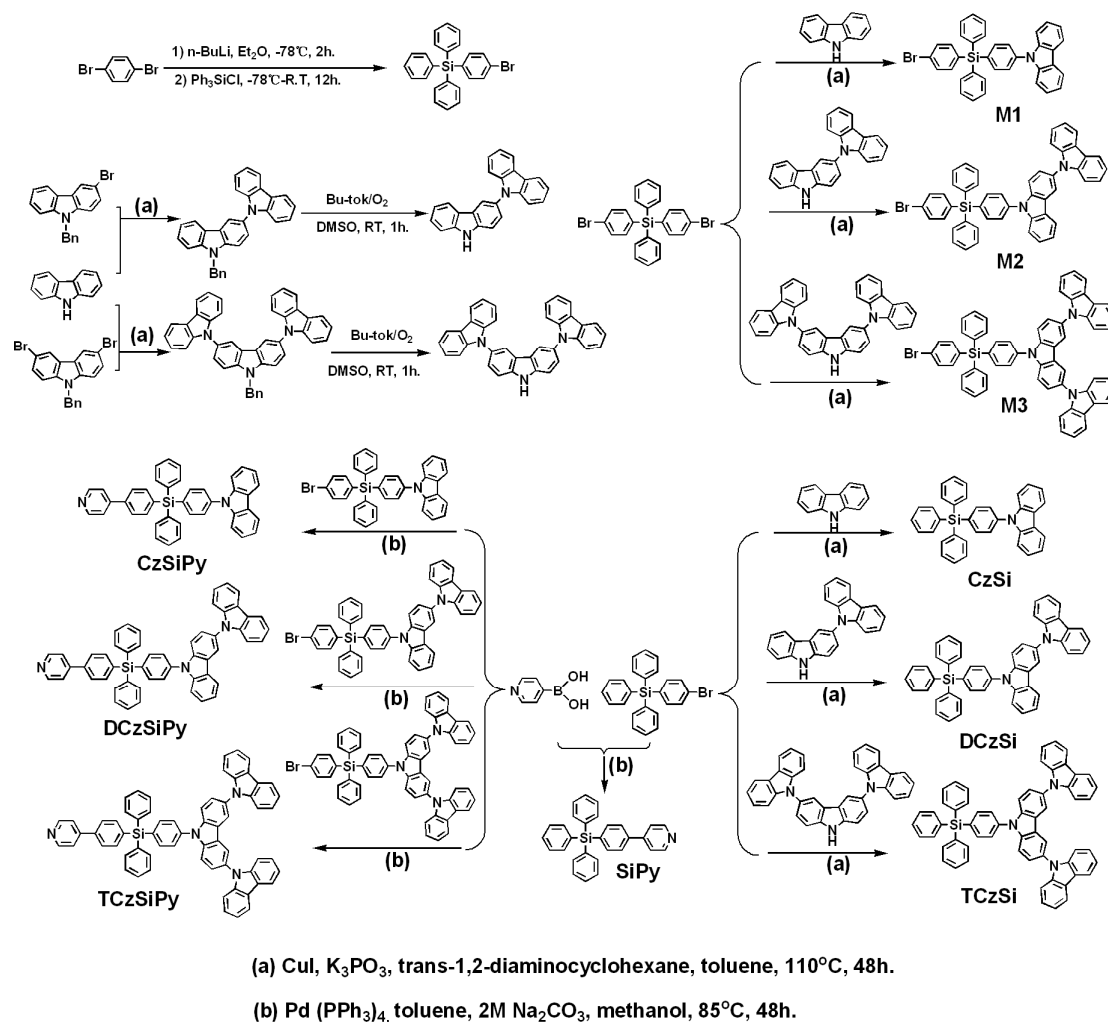
Synthesis: All the reagents and solvents were used as received or purified using standard procedure.

Characterization: ^1H and ^{13}C NMR spectra were measured on AVANCZ 500 spectrometers at 298 K using CDCl_3 as solvent and tetramethylsilane (TMS) as standard in all cases. Elemental analysis was performed by Flash EA 1112, CHNS-O elemental analysis instrument. Thermal gravimetric analysis (TGA) was undertaken on a Perkin-Elmer thermal analysis system at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and a nitrogen flow rate of $80\text{ mL}/\text{min}$. Differential scanning calorimetry (DSC) was performed on a NETZSCH (DSC-204) unit at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen. UV-visible absorption spectra were recorded on a UV-3100 spectrophotometer. Photoluminescent (PL) spectra were carried out with a RF-5301PC fluorometer. For the low-temperature phosphorescence spectra measurement, the sample solution (in dichloromethane) were mounted in a test tube, directly cooled in liquid nitrogen to 77 K , and then measured by the RF-5301PC fluorometer as soon as possible. The new peaks appeared in PL spectra at 77 K were assigned to phosphorescence emission as compared with their PL spectra at room temperature. The electrochemical properties of the compound were examined by cyclic voltammetry (CV) and performed by using a standard one-compartment, three-electrode electrochemical cell given by a BAS 100B/W electrochemical analyzer. The solvent was anhydrous acetonitrile, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) was the supporting electrolyte. The potentials were measured against an Ag/Ag^+ (0.1 M AgNO_3) reference electrode with ferrocene as the internal standard. EL spectra and Commission Internationale De L'Eclairage (CIE) coordination of these devices were measured by a PR650 spectrometer. The luminance-current density-voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.

Fabrication of OLEDs: Devices consisting of ITO/PEDOT:PSS/LEL/TPBI/ LiF/Al were fabricated as follows: PEDOT:PSS was spin-coated onto the cleaned ITO-coated glass

substrate from its aqueous solution and then heated at 120 °C for 20 minutes to remove the residual water solvent. Then the organic layers, 0.5-nm-thick LiF, and 200-nm-thick Al were in sequence deposited by thermal evaporation at a pressure of 4.0×10^{-6} mbar.

2. Synthesis and Characterization



Scheme S1. Synthesis and molecular structures of the wide bandgap materials.

(4-Bromophenyl)triphenylsilane: 1,4-Dibromobenzene (2.36 g, 10 mmol) was dissolved in dry diethyl ether and cooled to -78 °C in ethanol bath. To the solution was added *n*-BuLi (2.5 M, 4.2 mL, 1.05 equiv) dropwise via a syringe. After stirred for 2 h, chlorotriphenylsilane (2.95 g, 10 mmol) was dissolved in dry diethyl ether and added dropwise in one portion. Then the reaction mixture was warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was poured into water and extracted with diethyl ether. The combined organic solution was wash with water and dried over anhydrous magnesium sulphate. The crude product was

purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid (3.36 g). Yield: 81 %. TPhSiBr: ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 7.55-7.53 (6H, d, $J = 7.02$ Hz, Ar-H), 7.51-7.50 (2H, d, $J = 8.55$ Hz, Ar-H), 7.45-7.41 (5H, m, Ar-H), 7.39-7.36 (6H, t, $J = 7.32$ Hz, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 138.36, 136.74, 134.04, 133.72, 131.52, 130.23, 128.41, 125.17.

9-Benzyl-3-(9-carbazolyl)-9H-carbazole: A mixture of (336.2)9-benzyl-3-bromo-9H-carbazole 0.67 g (2.0 mmol), (167.2)carbazole 0.67 g (4.0 mmol, 200 mol %), CuI 38 mg (10 mol %), trans-1,2-Diaminocyclohexane 46 mg (20 mol %), K_3PO_3 0.89 g (210 mol %) and 16 mL toluene was heated at 110°C for 26 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was extracted with dichloromethane and was wash with $\text{NH}_3\text{H}_2\text{O}$ and water. The organic phase was dried over anhydrous magnesium sulphate. After evaporation of the solvent, the residue was purified by column chromatography eluting with petroleum ether- dichloromethane mixtures to give a white solid (0.55 g). Yield: 65 %. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.31-8.30 (1H, d, $J = 1.53$ Hz, Ar-H), 8.24-8.23 (2H, d, $J = 7.63$ Hz, Ar-H), 8.13-8.12 (1H, d, $J = 7.94$ Hz, Ar-H), 7.59-7.51 (3H, m, Ar-H), 7.48-7.43 (5H, m, Ar-H), 7.37-7.30 (5H, m, Ar-H), 7.26-7.25(2H, m, Ar-H), 5.60 (2H, s, $-\text{CH}_2-$), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 142.42, 141.84, 140.24, 137.37, 129.77, 129.40, 128.17, 127.09, 126.98, 126.34, 125.91, 124.48, 123.59, 123.14, 121.16, 120.76, 120.20, 120.07, 110.37, 109.78, 47.31.

3-(9-Carbazolyl)-9H-carbazole: To a stirred of 9-benzyl-3-(9-carbazolyl)-9H-carbazole (2 mmol, 0.85 g) in 40 mL DMSO was added potassinm *tert*-butoxide (20 mmol, 20 mL, 1 M potassinm *tert*-butoxide in THF) at room temperature. The reaction mixture was stirred for 5 min and O_2 was bubbled through the reaction for 1 h. The reaction mixture was poured to 300 mL water and stirred overnight, the deposited crude product was filtrated and purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid (0.59 g). Yield: 89 %. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ

8.22-8.18(4H, m, Ar-H), 8.05-8.04 (1H, d, $J = 7.63$ Hz, Ar-H), 7.62-7.61 (1H, d, $J = 8.24$ Hz, Ar-H), 7.56-7.46 (3H, m, Ar-H), 7.43-7.37 (4H, m, Ar-H), 7.31-7.27 (3H, m, Ar-H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 141.90, 140.18, 138.59, 129.45, 126.59, 125.87, 125.47, 124.39, 123.09, 120.60, 120.29, 119.94, 119.59, 111.61, 110.94, 109.87.

9-Benzyl-3,6-di(9-carbazolyl)-9H-carbazole: Compound
9-benzyl-3,6-dibromo-9H-carbazole was reacted with carbazole by the same Ullmann reaction procedure as for the synthesis of 9-benzyl-3-(9-carbazolyl)-9H-carbazole, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 52 %. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.21 (2H, s, Ar-H), 8.14-8.12 (4H, d, $J = 7.94$ Hz, Ar-H), 7.62-7.55 (4H, m, Ar-H), 7.38-7.29 (11H, m, Ar-H), 7.26-7.24 (5H, m, Ar-H), 5.60 (2H, s, $-\text{CH}_2-$), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 142.27, 140.85, 137.01, 130.25, 129.52, 128.38, 127.01, 126.63, 126.33, 124.08, 123.59, 120.73, 120.50, 120.27, 120.13, 112.47, 110.81, 110.19, 47.60.

3,6-Di(9-carbazolyl)-9H-carbazole: 3,6-di(9-carbazolyl)-9H-carbazole was prepared by the same procedure as for 3-(9-carbazolyl)-9H-carbazole starting from 9-benzyl-3,6-di(9-carbazolyl)-9H-carbazole. Yield: 92 %. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.38 (1H, s, N-H), 8.18-8.14 (6H, t, $J = 7.94$ Hz, Ar-H), 7.67-7.65 (2H, d, $J = 8.55$ Hz, Ar-H), 7.60-7.58 (2H, d, $J = 8.24$ Hz, Ar-H), 7.40-7.35 (8H, m, Ar-H), 7.28-7.25 (4H, t, $J = 6.71$ Hz, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 142.23, 139.66, 130.40, 126.65, 126.29, 124.51, 123.55, 120.69, 120.23, 120.08, 112.43, 110.13.

MI: A mixture of (167.2) carbazole 0.33 g (2 mmol), (494.3)bis(4-bromophenyl)diphenylsilane 1.98 g (4.0 mmol, 200 mol %), CuI 38 mg (10 mol %), trans-1,2-Diaminocyclohexane 46 mg (20 mol %), K_3PO_3 0.89 g (210 mol %) and 16 mL toluene was heated at 110°C for 26 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was extracted with dichloromethane and was wash with $\text{NH}_3\text{H}_2\text{O}$ and water. The organic phase was dried over anhydrous magnesium sulphate. After

evaporation of the solvent, the residue was purified by column chromatography eluting with petroleum ether- dichloromethane mixtures to give a white solid (1.49 g). Yield: 45 %. CzSiBr: ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.14-8.12 (2H, d, $J = 7.94$ Hz, Ar-H), 7.78-7.76 (2H, d, $J = 8.24$ Hz, Ar-H), 7.63-7.56 (8H, m, Ar-H), 7.50-7.47 (6H, m, Ar-H), 7.5245-7.38 (6H, m, Ar-H), 7.30-7.27 (2H, t, $J = 7.02$ Hz, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 140.47, 139.15, 137.88, 137.74, 136.28, 133.22, 132.86, 131.21, 129.97, 128.10, 126.16, 125.90, 124.93, 123.48, 120.27, 120.07, 109.81.

M2: Compound 3-(9-carbazolyl)-9H-carbazole was reacted with bis(4-bromophenyl)diphenylsilane by the same Ullmann reaction procedure as for the synthesis of M2, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 45 %. DCzSiBr: ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.29-8.28 (1H, d, $J = 1.83$ Hz, Ar-H), 8.19-8.17 (2H, d, $J = 7.94$ Hz, Ar-H), 8.11-8.10 (1H, d, $J = 7.63$ Hz, Ar-H), 7.84-7.83 (2H, d, $J = 8.24$ Hz, Ar-H), 7.69-7.63 (7H, m, Ar-H), 7.59-7.57 (2H, d, $J = 8.24$ Hz, Ar-H), 7.56-7.38 (15H, m, Ar-H), 7.33-7.27 (3H, m, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 141.77, 141.19, 139.60, 138.83, 137.89, 136.27, 133.48, 133.11, 132.76, 131.24, 130.02, 128.12, 126.63, 126.20, 125.79, 125.45, 124.97, 124.50, 123.05, 120.53, 120.21, 119.55, 119.43, 110.90, 110.18, 109.72.

M3: Compound 3,6-di(9-carbazolyl)-9H-carbazole was reacted with bis(4-bromophenyl)diphenylsilane by the same Ullmann reaction procedure as for the synthesis of M2, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 45 %. TCzSiBr: ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.27-8.26 (2H, d, $J = 2.14$ Hz, Ar-H), 8.16-8.14 (4H, d, $J = 7.63$ Hz, Ar-H), 8.12-8.10 (1H, d, $J = 7.63$ Hz, Ar-H), 7.92-7.91 (2H, d, $J = 8.55$ Hz, Ar-H), 7.76-7.73 (4H, t, $J = 6.71$ Hz, Ar-H), 7.69-7.68 (6H, m, Ar-H), 7.62-7.61 (1H, d, $J = 1.83$ Hz, Ar-H), 7.60-7.59 (1H, d, $J = 2.14$ Hz, Ar-H), 7.51-7.44 (9H, m, Ar-H), 7.39-7.38 (8H, d, $J = 3.66$ Hz, Ar-H), 7.29-7.25 (4H, m, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 141.69, 140.35, 138.32, 138.16, 136.37, 134.78, 133.62, 130.44, 129.87, 128.05, 126.18, 125.84, 124.06, 123.10, 120.23,

119.64, 111.40, 109.62, 120.69, 120.02.

CzSiPy: Compound M2 was reacted with pyridin-4-yl-4-boronic acid by the same suzuki reaction procedure as for the synthesis of SiPy, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 78 %. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.69-8.68 (2H, d, J = 5.80 Hz, Ar-H), 8.15-8.13 (2H, d, J = 7.63 Hz, Ar-H), 7.83-7.82 (2H, d, J = 8.55 Hz, Ar-H), 7.80-7.78 (2H, d, J = 8.24 Hz, Ar-H), 7.71-7.70 (2H, d, J = 8.24 Hz, Ar-H), 7.68-7.66 (4H, m, Ar-H), 7.63-7.62 (2H, d, J = 8.24 Hz, Ar-H), 7.60-7.58 (2H, d, J = 5.80 Hz, Ar-H), 7.52-7.50 (4H, m, Ar-H), 7.47-7.44 (4H, m, Ar-H), 7.42-7.39 (2H, t, J = 7.32 Hz, Ar-H), 7.30-7.28 (2H, t, J = 7.32 Hz, Ar-H), ¹³C NMR (CDCl₃, 125 MHz, ppm): 149.42, 148.81, 140.46, 139.14, 138.90, 137.78, 137.16, 136.32, 135.67, 133.31, 132.94, 129.97, 128.10, 126.48, 126.16, 125.89, 123.47, 121.79, 120.28, 120.07, 109.79. Elemental Anal. Calcd. for C₄₁H₃₀N₂Si: C, 85.08%; H, 5.22%; N, 4.84%. Found: C, 84.96%; H, 5.04%, N, 4.71%. MALDI-TOF-MS(M): *m/z* 578.3 (100%).

DCzSiPy: Compound M3 was reacted with pyridin-4-yl-4-boronic acid by the same suzuki reaction procedure as for the synthesis of SiPy, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 70 %. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 8.70-8.69 (2H, d, J = 5.19 Hz, Ar-H), 8.28-8.27 (1H, d, J = 1.83 Hz, Ar-H), 8.19-8.17 (2H, d, J = 7.94 Hz, Ar-H), 8.11-8.10 (1H, d, J = 7.63 Hz, Ar-H), 7.89-7.87 (2H, d, J = 8.24 Hz, Ar-H), 7.82-7.80 (2H, d, J = 7.94 Hz, Ar-H), 7.73-7.67 (9H, m, Ar-H), 7.64-7.62 (2H, d, J = 5.80 Hz, Ar-H), 7.57-7.46 (9H, m, Ar-H), 7.42-7.38 (4H, m, Ar-H), 7.33-7.27 (3H, m, Ar-H), ¹³C NMR (CDCl₃, 125 MHz, ppm): 149.39, 148.85, 141.76, 141.19, 139.60, 138.86, 138.71, 137.95, 137.21, 136.32, 135.87, 133.53, 133.17, 132.00, 130.06, 128.15, 126.62, 126.55, 126.22, 125.79, 125.45, 124.51, 123.05, 121.94, 120.56, 120.22, 119.56, 119.44, 110.89, 110.17, 109.70. Elemental Anal. Calcd. for C₅₃H₃₇N₃Si: C, 85.56%; H, 5.01%; N, 5.65%. Found: C, 85.42%; H, 5.23%, N, 5.48%. MALDI-TOF-MS(M): *m/z* 744.5 (100%).

TCzSiPy: Compound M4 was reacted with pyridin-4-yl-4-boronic acid by the same

suzuki reaction procedure as for the synthesis of SiPy, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 82 %. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.70-8.69 (2H, d, $J = 5.49$ Hz, Ar-H), 8.27-8.26 (2H, d, $J = 1.83$ Hz, Ar-H), 8.16-8.15 (4H, d, $J = 7.63$ Hz, Ar-H), 7.95-7.93 (2H, d, $J = 8.24$ Hz, Ar-H), 7.83-7.82 (2H, d, $J = 8.24$ Hz, Ar-H), 7.79-7.78 (2H, d, $J = 8.24$ Hz, Ar-H), 7.75-7.69 (8H, m, Ar-H), 7.64-7.63 (2H, d, $J = 5.80$ Hz, Ar-H), 7.62-7.62 (1H, d, $J = 1.83$ Hz, Ar-H), 7.60-7.60 (1H, d, $J = 2.14$ Hz, Ar-H), 7.54-7.47 (6H, m, Ar-H), 7.41-7.37 (8H, m, Ar-H), 7.30-7.25 (4H, m, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 149.59, 148.61, 141.65, 140.28, 138.66, 138.56, 138.12, 137.23, 136.32, 135.88, 134.14, 133.05, 130.51, 130.11, 128.19, 126.58, 126.28, 126.20, 125.83, 124.09, 123.10, 122.00, 120.24, 119.67, 111.34, 109.58. Elemental Anal. Calcd. for $\text{C}_{65}\text{H}_{44}\text{N}_4\text{Si}$: C, 85.87%; H, 4.88%; N, 6.16%. Found: C, 85.77%; H, 4.84%, N, 5.92%. MALDI-TOF-MS(M): m/z 909.8 (100%).

SiPy: In a 100 ml round flask, methanol (15 mL) and a Na_2CO_3 solution (2 M, 15 mL) were added to a solution of (415.4)(4-bromophenyl)triphenylsilane (415 mg, 1.0 mmol) and pyridin-4-yl-4-boronic acid (122.9)(147 mg, 1.2 mmol) in toluene (30 mL). $\text{Pd}(\text{PPh}_3)_4$ (47 mg, 0.04 mmol) was added and the resultant solution was degassed and stirred at 85°C for 2 d under nitrogen atmosphere. Water was added to quench the reaction, and the mixture was then extracted with dichloromethane, and organic solution was wash with water and dried over anhydrous magnesium sulphate. The crude product was purified by column chromatography eluting with ethyl acetate-dichloromethane mixtures to give a white solid (0.32 g). Yield: 78 %. (413.6)SiPy: ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.67-8.66 (2H, d, $J = 4.27$ Hz, Ar-H), 7.71-7.69 (2H, d, $J = 7.94$ Hz, Ar-H), 7.65-7.64 (2H, d, $J = 8.24$ Hz, Ar-H), 7.59-7.58 (6H, d, $J = 6.71$ Hz, Ar-H), 7.55-7.54 (2H, d, $J = 6.41$ Hz, Ar-H), 7.46-7.44 (3H, m, Ar-H), 7.41-7.38 (6H, t, $J = 7.02$ Hz, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 150.32, 148.94, 139.35, 137.59, 136.79, 136.33, 134.18, 130.21, 128.41, 126.79, 122.16.

CzSi: A mixture of (167.2)carbazole 0.33 g (2 mmol), (415.4)(4-bromophenyl)triphenylsilane 1.0 g (2.4 mmol, 120 mol %), CuI 38 mg

(10 mol %), trans-1,2-Diaminocyclohexane 46 mg (20 mol %), K_3PO_3 0.89 g (210 mol %) and 16 mL toluene was heated at 110°C for 26 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was extracted with dichloromethane and was wash with NH_3H_2O and water. The organic phase was dried over anhydrous magnesium sulphate. After evaporation of the solvent, the residue was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid (0.61 g). Yield: 61 %. 1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.16-8.14 (2H, d, $J = 7.94$ Hz, Ar-H), 7.82-7.81 (2H, d, $J = 8.24$ Hz, Ar-H), 7.67-7.65 (6H, m, Ar-H), 7.62-7.60 (2H, d, $J = 8.24$ Hz, Ar-H), 7.52-7.40 (13H, m, Ar-H), 7.31-7.28 (2H, t, $J = 7.63$ Hz, Ar-H), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 141.22, 139.43, 138.31, 136.86, 134.32, 134.01, 130.25, 128.46, 126.56, 126.36, 123.95, 120.73, 120.49, 110.34. Elemental Anal. Calcd. for $C_{37}H_{27}NSi$: C, 86.19%; H, 5.42%; N, 2.79%. Found: C, 86.03%; H, 5.35%, N, 2.74%. MALDI-TOF-MS(M): m/z 502.0 (100%).

DCzSi: Compound 3,6-di(9-carbazolyl)-9H-carbazole was reacted with (4-bromophenyl)triphenylsilane by the same Ullmann reaction procedure as for the synthesis of M2, and the product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 58%. 1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.29-8.28 (1H, d, $J = 1.83$ Hz, Ar-H), 8.19-8.18 (2H, d, $J = 7.94$ Hz, Ar-H), 8.12-8.10 (1H, d, $J = 7.63$ Hz, Ar-H), 7.88-7.86 (2H, d, $J = 8.24$ Hz, Ar-H), 7.69-7.66 (9H, m, Ar-H), 7.57-7.54 (2H, m, Ar-H), 7.51-7.43 (10H, m, Ar-H), 7.41-7.39 (4H, m, Ar-H), 7.34-7.28 (3H, m, Ar-H), ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 142.29, 141.74, 140.16, 139.11, 138.47, 136.86, 134.64, 134.21, 130.46, 130.30, 128.49, 127.10, 126.60, 126.28, 125.93, 124.96, 123.54, 121.00, 120.69, 120.02, 119.91, 111.44, 110.72, 110.23. Elemental Anal. Calcd. for $C_{48}H_{34}N_2Si$: C, 86.45%; H, 5.14%; N, 4.20%. Found: C, 86.71%; H, 5.04%, N, 4.16%. MALDI-TOF-MS(M): m/z 667.3 (100%).

TCzSi: Compound 3,6-di(9-carbazolyl)-9H-carbazole was reacted with (4-bromophenyl)triphenylsilane by the same Ullmann reaction procedure as for the synthesis of M2, and the product was purified by column chromatography eluting

with petroleum ether-dichloromethane mixtures to give a white solid. Yield: 52%.

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 8.27-8.26 (2H, d, $J = 2.14$ Hz, Ar-H), 8.16-8.14 (4H, d, $J = 7.63$ Hz, Ar-H), 8.12-8.10 (1H, d, $J = 7.63$ Hz, Ar-H), 7.92-7.91 (2H, d, $J = 8.55$ Hz, Ar-H), 7.76-7.73 (4H, t, $J = 6.71$ Hz, Ar-H), 7.69-7.68 (6H, m, Ar-H), 7.62-7.61 (1H, d, $J = 1.83$ Hz, Ar-H), 7.60-7.59 (1H, d, $J = 2.14$ Hz, Ar-H), 7.51-7.44 (9H, m, Ar-H), 7.39-7.38 (8H, d, $J = 3.66$ Hz, Ar-H), 7.29-7.25 (4H, m, Ar-H), ^{13}C NMR (CDCl_3 , 125 MHz, ppm): 141.69, 140.35, 138.32, 138.16, 136.37, 134.78, 133.62, 130.44, 129.87, 128.05, 126.18, 125.84, 124.06, 123.10, 120.23, 119.64, 111.40, 109.62, 120.69, 120.02. Elemental Anal. Calcd. for $\text{C}_{60}\text{H}_{41}\text{N}_3\text{Si}$: C, 86.61%; H, 4.97%; N, 5.05%. Found: C, 86.84%; H, 4.86%, N, 5.01%. MALDI-TOF-MS(M): m/z 832.7 (100%).

3. Electrochemical Properties

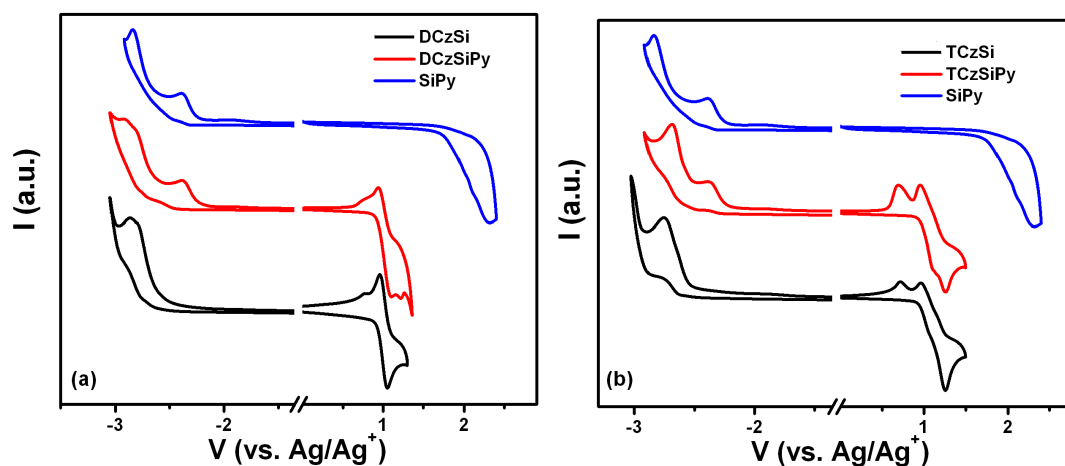


Figure S1. Cyclic voltammogram of the wide bandgap materials.

4. Photophysical Properties

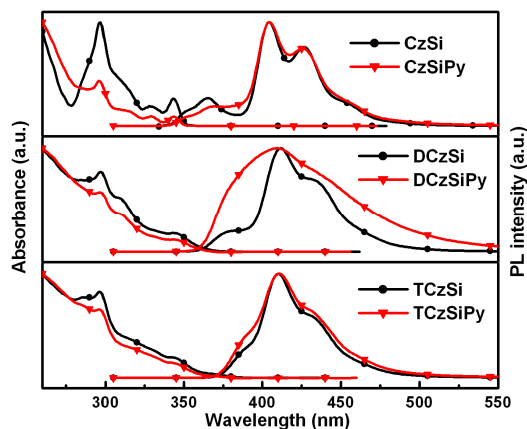


Figure S2. UV spectra and PL spectra of the wide bandgap materials in solid thin film.

Table S1. Photophysical data of the wide bandgap materials.

compd	solution ^a		film		E_g (eV)	E_T (eV)
	UV(nm) (ϵ , $10^4 \text{ cm}^{-1} \text{ M}^{-1}$)	PL(nm)	UV(nm)	PL(nm)		
CzSi	294 (2.43),342 (0.50)	348,363	297,329,343	365,404,427	3.62	2.99
CzSiPy	293 (2.66),340 (0.52)	348,363	297,329,343	368,404,427	3.62	3.08
DCzSi	294 (3.82),342 (0.84)	377	297,310,346	379,412,433	3.58	2.99
DCzSiPy	294 (3.92),342 (0.81)	377	297,310,346	409	3.58	2.99
TCzSi	293 (2.77),342(0.63)	385(402)	296,346	410,433	3.58	2.90
TCzSiPy	293 (2.94),342(0.68)	385(402)	296,346	410,433	3.58	2.86

[a] 10^{-5} M in dichloromethane solution

5. Theoretical Calculations

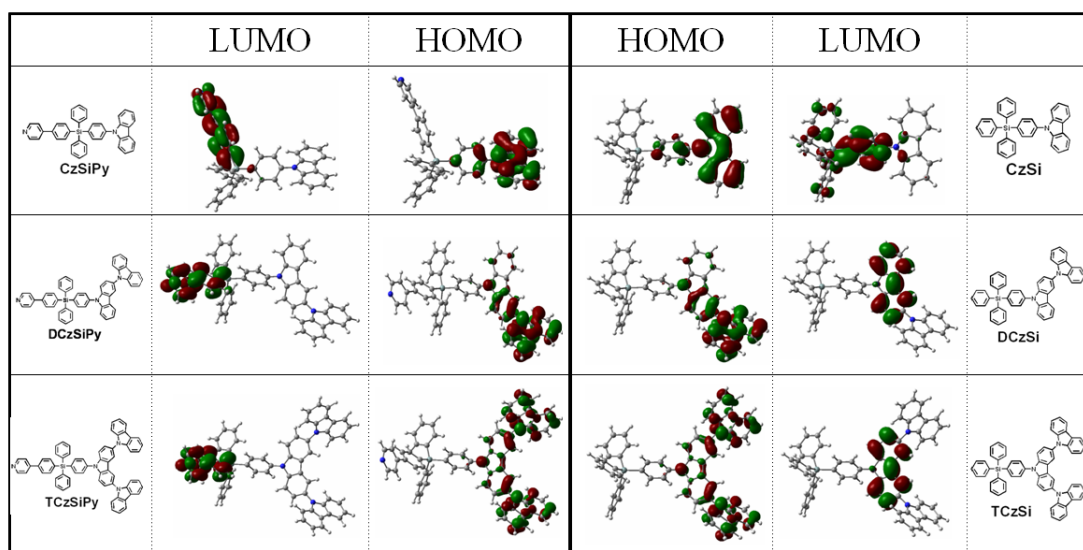


Figure S3. B3LYP/6-31G calculated HOMO and LUMO density maps of the wide bandgap materials.

Table S2. The HOMO and LUMO levels calculated by B3LYP/6-31G.

compd	LUMO _{cal} (eV)	HOMO _{cal} (eV)
CzSi	-0.76	-5.32
CzSiPy	-1.39	-5.38
DCzSi	-0.94	-5.11
DCzSiPy	-1.45	-5.15
TCzSi	-1.18	-5.15
TCzSiPy	-1.48	-5.18

6. Triplet energy levels

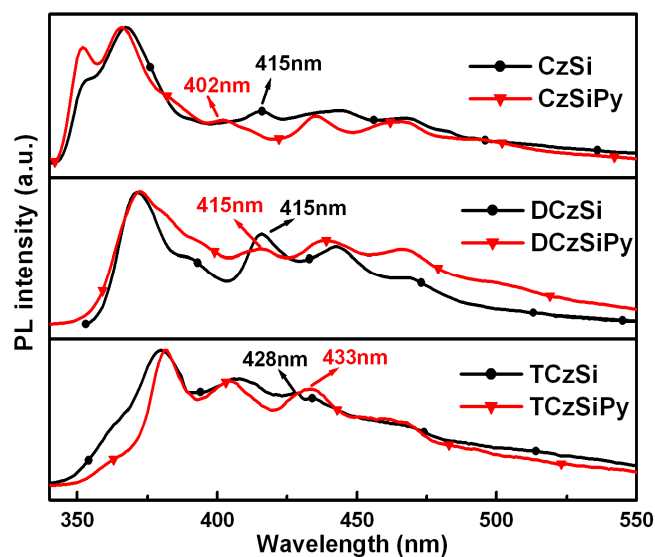


Figure S4. Phosphorescence spectra of the wide bandgap materials at 77 K in dichloromethane.

7. Electroluminescence devices

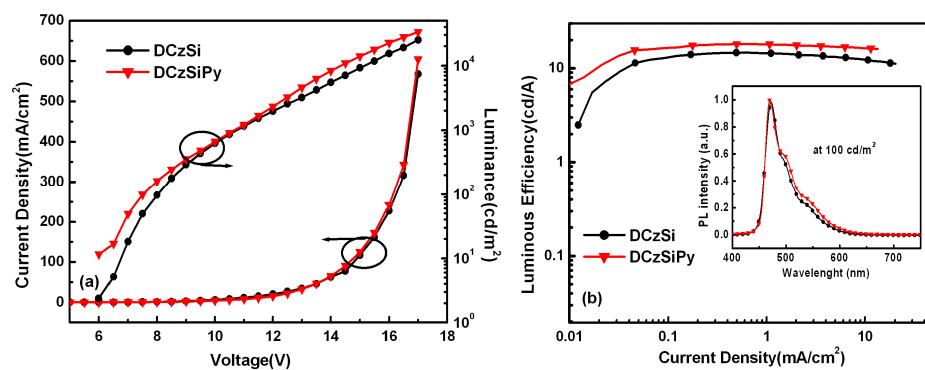


Figure S5. The J - V - L characteristics (a) and curves of luminous efficiency versus current density (b) of blue device based on DCzSi and DCzSiPy. Insert: Normalized EL spectra at 100 cd m⁻² of the devices.

Table S3. Summary of device performance.

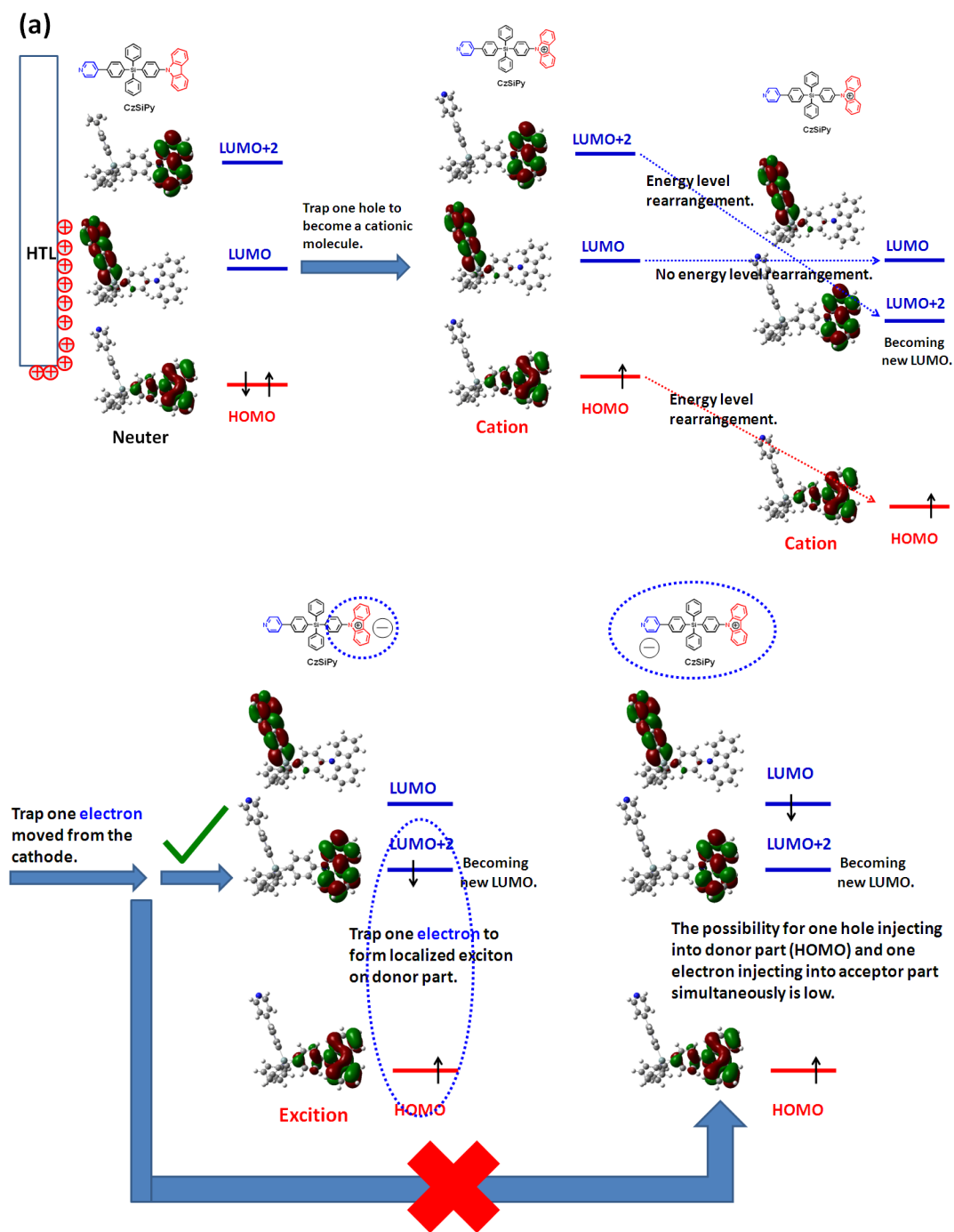
Host	Dopant	V_{on}^a [V]	L_{max}^b [cd m ⁻²]	$\eta_{\text{c,max}}^c$ [cd A ⁻¹]	$\eta_{\text{p,max}}^d$ [lm W ⁻¹]	CIE ^e
CzSi	FIrpic	4.4	21000	10.7	4.1	0.12, 0.23
DCzSi	FIrpic	3.6	25000	14.7	6.6	0.15, 0.29
TCzSi	FIrpic	3.6	20000	10.3	4.5	0.14, 0.25
CzSiPy	FIrpic	4.2	16000	6.4	2.5	0.15, 0.25
DCzSiPy	FIrpic	3.4	33000	18.1	9.0	0.17, 0.31
TCzSiPy	FIrpic	3.4	28000	14.0	6.5	0.15, 0.28

[a] Turn-on voltage; [b] Maximum luminance; [c] Maximum current efficiency; [d] Maximum power efficiency; [e] Commission Internationale de l'Éclairage coordinates.

8. The possible recombination of holes and electrons on wide bandgap materials in EL devices

In such D-A insulated linking molecular system, the possibility for the state of one electron injecting into acceptor part and one hole injecting into donor part simultaneously is low and such state has little effect on the EL device, based on following considerations: 1. When the donor part (carbazole) of the molecule traps one hole to form a cation, the positive charge is localized on the donor part (carbazole) of the molecule because of the insulative silane. Then when an electron was injected into the molecule, it will be trapped by the cation because of the static interactions. In addition, the energy levels of cationic donor part (carbazole) will be rearranged when the donor part (carbazole) of the molecule traps one hole to form a cation. The cationic donor part will have a higher EA than that of neutral acceptor part because of localized positive charge on it. This makes the localized higher energy levels (LUMO+n, on donor part) fall below the previous LUMO level (on acceptor part), and replace it to become the new LUMO level. Therefore, it would preferentially trap the electrons moved from the cathode to form a localized exciton on donor part (**Figure 1a**). 2. When the acceptor part of the molecule traps one electron to form an anion, the negative charge is localized on the acceptor part because of the insulative

silane. Then when a hole was injected into the molecule, it will be trapped by the anion because of the static interactions. Moreover, similar with cationic molecule, the cationic acceptor part will have a lower IP than that of neuter donor part because of localized negative charge on it. Therefore, it would preferentially trap the holes moved from the anode to form a localized exciton on acceptor part (**Figure 1b**).



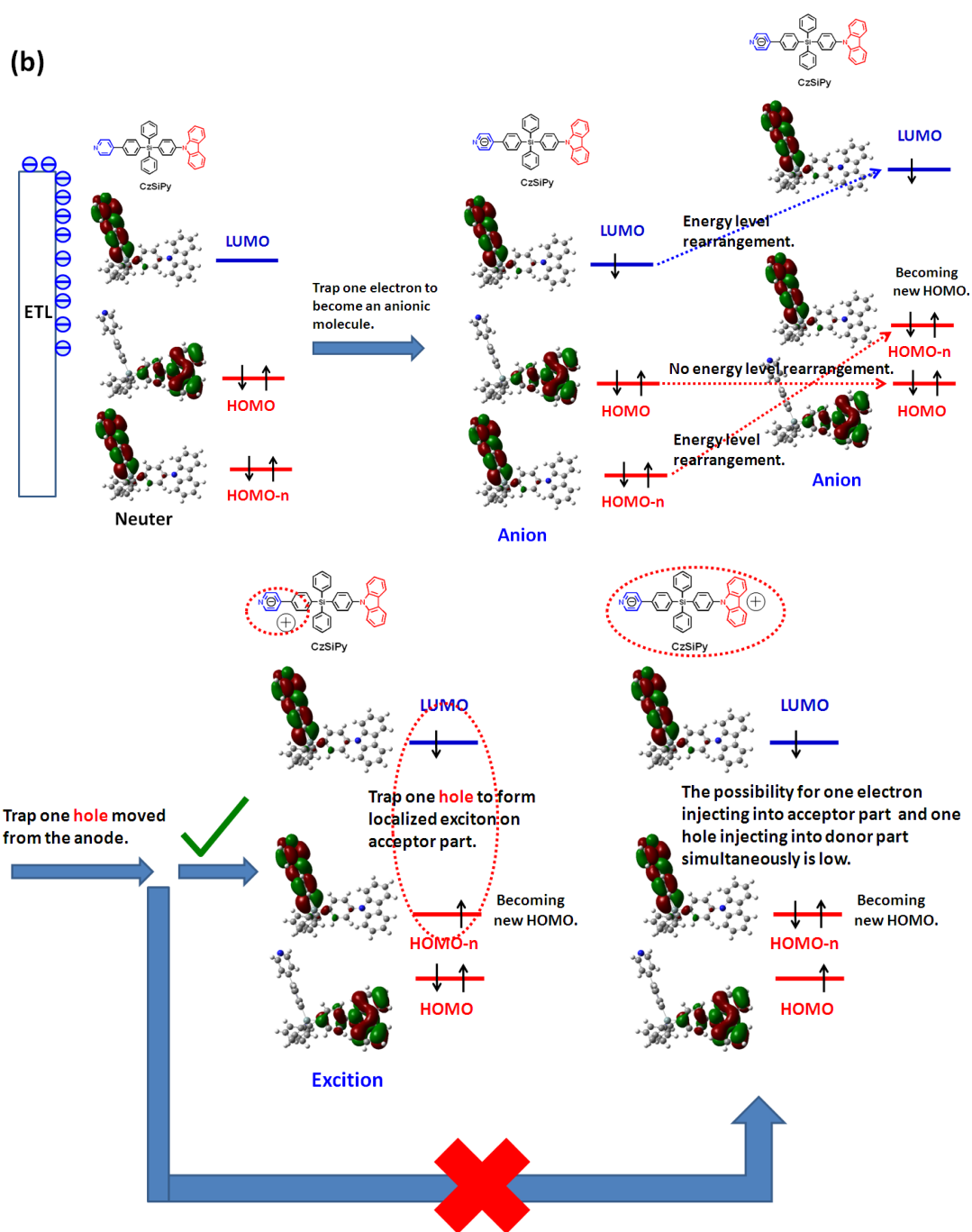


Figure S6. a) The recombination of holes and electrons on donor part of the bipolar wide bandgap materials in EL device. b) The recombination of holes and electrons on acceptor part of the bipolar wide bandgap materials in EL device.