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Supporting Information

Pyrimidine-5-carbonitrile acceptor for high efficiency and long lifetime thermally activated delayed fluorescence organic light-emitting diodes

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Key words: pyrimidine-5-carbonitrile, acceptor, efficiency, organic light-emitting diodes, thermally activated delayed fluorescence

Experimental

General information

Ethyl alcohol, n-hexane, chloroform, and toluene were purchased from Samchun Pure Chemical Co. 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole and 9-phenyl-9H,9'H-3,3'-bicarbazole were supplied by LG Chem. Ltd. 4-Bromobenzaldehyde, benzaldehyde, piperdine, sodium-t-butoxide and pyridine were products of Sigma Aldrich Co. Benzoylacetonitrile, benzamidine, and 4-chlorobenzimidamide were products of J&H Chemical Co., Ltd. Magnesium sulfate ($MgSO_4$) was supplied by Duksan Sci. Co. Tris(dibenzylidenacetone)dipalladium(0) and tris-tert-butylphosphinewere were purchased from P&H Tech Co. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured by NMR spectrometry (Bruker, Avance-500). The mass spectra instrument was Advion, Expression^{L} CMS spectrometer in APCI mode. The HOMO and LUMO were obtained by cyclic voltammetry (Ivium Tech., Iviumstat). The UV-vis spectra were measured by UV-vis spectrophotometry (JASCO, V-730). The PL spectra were measured by fluorescence spectrophotometry (PerkinElmer, LS-55). The PL quantum yield was measured by Quantaurus-QY Absolute PL quantum yield spectrometry (HAMAMATSU, C11347-11). The transient PL decay was obtained by Quantaurus-Tau Fluorescence lifetime spectrometry (HAMAMATSU, C11367-31).

Synthesis

(E)-2-benzoyl-3-phenylacrylonitrile

Benzoylacetonitrile (20 g, 0.15 mol) and benzaldehyde (17.5 g, 0.17 mol) were dissolved in ethyl alcohol in a 500 ml 2-neck round-bottomed flask. Piperidine (0.66 g, 0.008 mol) was slowly dropped into the flask using a syringe under nitrogen atmosphere. The mixture was stirred and refluxed for 12 h, and cooled to room temperature (RT). The mixture was filtered,

and the crude product was re-crystallized with ethyl alcohol. The final product was obtained as a yellowish powder (24 g, Yield 63 %). ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 8.06 (s, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.64 (t, J = 7.25 Hz, 1H), 7.58 (t, J = 7.25 Hz, 1H), (7.54–7.52) (m, 4H). MS (APCI) m/z Found : 234.09 [$(M + H)^+$]. Calculated For $C_{16}H_{11}NO$: 233.26

2-(4-Chlorophenyl)-4,6-diphenylpyrimidine-5-carbonitrile

(E)-2-benzoyl-3-phenylacrylonitrile (20 g, 0.08 mol), 4-chlorobenzimidamide (15 g, 0.09 mol), and pyridine (0.34 g, 0.004 mol) were dissolved in a 500 ml 2-neck round-bottomed flask filled with ethyl alcohol. The mixture was stirred, and refluxed for 12 h. The mixture was filtered with hot ethyl alcohol several times. The final product was obtained as a white power (5.3 g, Yield 18 %). ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 8.62 (d, J = 9.0 Hz, 2H), 8.15 (d, J = 7.5 Hz, 4H), (7.63–7.59) (m, 6H), 7.51 (d, J = 8.5 Hz, 2H). MS (APCI) m/z Found : 368.04 [$(M + H)^+$]. Calculated For $C_{23}H_{14}ClN_3$: 367.83

4,6-Diphenyl-2-(4-(5-phenylindolo[3,2-a]carbazol-12(5H)-yl)phenyl)pyrimidine-5-carbonitrile (2PyCNICz)

2-(4-Chlorophenyl)-4,6-diphenylpyrimidine-5-carbonitrile (1.0 g, 0.0027 mol), 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole (1.08 g, 0.0033 mol), sodium-t-butoxide (0.52 g, 0.0054 mol), and tris(dibenzylidenacetone)dipalladium(0) (0.07 g, 0.00008 mol) dissolved in anhydrous toluene were stirred in a 100 mL 2-neck round flask. Tris-tert-butylphosphine (0.08 g, 0.00041 mol) was dropped into the mixture slowly under nitrogen atmosphere. The mixture was refluxed and stirred for 18 h, and quenched by distilled water at RT. The crude solution was extracted with chloroform and distilled water, using a separatory funnel. The organic layer was dried over $MgSO_4$, and concentrated using a rotary evaporator. The product was purified by

column chromatography, using a mixed eluent of n-hexane:chloroform (1:1). The final product was re-crystallized with toluene, and sublimed. The final product was obtained as a bright yellow powder (1.1 g, Yield 56 %). ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 9.00 (d, J = 8.5 Hz, 2H), 8.23 (d, J = 7.0 Hz, 4H), 8.18 (t, J = 8.0 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), (7.67–7.59) (m, 10H), 7.54 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), (7.41–7.35) (m, 3H), 7.31 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.0 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.31 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ 170.20, 164.06, 144.13, 141.98, 141.76, 140.78, 137.89, 136.59, 136.21, 135.93, 131.92, 131.10, 130.17, 129.71, 129.04, 128.28, 128.24, 125.12, 124.65, 123.79, 121.41, 121.08, 119.71, 119.29, 118.65, 118.09, 117.67, 110.36, 109.55, 108.21, 104.36, 101.14, 77.47, 77.22, 76.96. MS (HR-FAB) m/z Found 663.2427 [$(M + H)^+$]. Calculated For $C_{47}H_{29}N_5$: 663.7667

4,6-Diphenyl-2-(4-(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phenyl)pyrimidine-5-carbonitrile (2PyCNBCz)

2PyCNBCz was synthesized according to the synthetic method of 2PyCNICz, using 9-phenyl-9H,9'H-3,3'-bicarbazole instead of 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole. The crude product was purified by column chromatography, using a n-hexane:chloroform (1:2) mixed eluent. The final product was recrystallized with toluene, and then sublimed. Final product was obtained as a yellow power (1.2 g, Yield 60 %). ^{1}H NMR (500 MH_Z, $CDCl_3$): δ8.95 (d, J = 8.5 Hz, 2H), 8.47 (s, 2H), 8.26 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 7.0 Hz, 4H), (7.85–7.78) (m, 4H), (7.65–7.63) (m, 11H), 7.59 (d, J = 8.0 Hz, 1H), (7.53–7.44) (m, 5H), (7.38–7.31) (m, 2H). ^{13}C NMR (125 MH_Z, $CDCl_3$): δ 170.17, 164.14, 141.69, 141.57, 141.00, 140.30, 139.65, 137.95, 136.27, 135.13, 135.05, 134.32, 131.91, 131.26, 130.13, 129.70, 129.05, 127.68, 127.29, 126.50, 126.23, 125.99, 124.64, 124.24, 124.20, 123.74, 120.78, 120.63, 120.22, 119.21, 119.11, 117.68, 110.39, 110.26, 110.13, 100.98, 77.48, 77.22, 76.97, 29.91. MS (HR-FAB)

m/z Found 739.2736 [(M + H)$^+$]. Calculated For $C_{53}H_{33}N_5$: 739.8626

(E)-2-(4-bromobenzoyl)-3-phenylacrylonitrile

(E)-2-(4-bromobenzoyl)-3-phenylacrylonitrile was synthesized according to the same synthetic method as for (E)-2-benzoyl-3-phenylacrylonitrile, using 4-bromobenzaldehyde instead of benzaldehyde. The mixture was recrystallized with ethyl alcohol. The final product was obtained as an orange powder (21 g, Yield 45 %). ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ 8.00 (s, H), 7.90 (d, J = 8.5 Hz, 4H), (7.68–7.63) (m, 3H), 7.53 (t, J = 7.75 Hz, 2H). MS (APCI) m/z Found 312.01 [(M + H)$^+$]. Calculated For $C_{16}H_{10}BrNO$: 312.16

4-(4-Bromophenyl)-2,6-diphenylpyrimidine-5-carbonitrile

(E)-2-(4-bromobenzoyl)-3-phenylacrylonitrile (20 g, 0.064 mol) and benzamidine (15 g, 0.096 mol) dissolved in pyridine were stirred and refluxed in a 500 ml 2-neck round-bottomed flask for 18 h. The mixture was filtered with hot ethyl alcohol several times. The final product was obtained as a yellowish white powder (7.1 g, Yield 27 %). ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ 8.66 (d, J = 7.0 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), (7.62–7.55) (m, 6H). MS (APCI) m/z Found 411.94 [(M + H)$^+$]. Calculated For $C_{23}H_{14}BrN_3$: 412.28

2,4-Diphenyl-6-(4-(5-phenylindolo[3,2-a]carbazol-12(5H)-yl)phenyl)pyrimidine-5-carbonitrile (4PyCNICz)

4PyCNICz was synthesized according to the synthetic method of 2PyCNICz, using 4-(4-bromophenyl)-2,6-diphenylpyrimidine-5-carbonitrile (0.5g, 0.0012 mol) instead of 2-(4-chlorophenyl)-4,6-diphenylpyrimidine-5-carbonitrile. The crude product was purified by column chromatography, using a n-hexane:chloroform (1:2) mixed eluent. The final product

was recrystallized with toluene, and then sublimed. Final product was obtained as a yellow power (0.6 g, Yield 75 %). ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ 8.75 (d, J = 8.0 Hz, 2H), 8.45 (d, J = 8.0 Hz, 2H), (8.26–8.24) (m, 2H), (8.20–8.17) (m, 2H), 7.90 (d, J = 8.5 Hz, 2H), (7.67–7.64) (m, 5H), (7.62–7.58) (m, 5H), 7.52 (t, J = 8.25 Hz, 2H), 7.42 (t, J = 8.0 Hz, 1H), (7.39–7.35) (m, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.75 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ 170.12, 169.31, 165.10, 143.46, 141.98, 141.72, 140.76, 137.93, 136.68, 136.40, 136.27, 136.10, 132.63, 131.94, 131.33, 130.16, 129.73, 129.66, 129.29, 129.06, 129.04, 128.31, 128.22, 125.08, 124.80, 124.69, 123.75, 121.38, 121.11, 120.09, 119.28, 118.62, 118.03, 117.54, 110.42, 109.53, 108.18, 104.38, 101.13, 77.48, 77.22, 76.97, 29.92. MS (HR-FAB) m/z Found 663.2423 [$(M + H)^+$]. Calculated For $C_{47}H_{29}N_5$: 663.7667

2,4-Diphenyl-6-(4-(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phenyl)pyrimidine-5-carbonitrile (4PyCNBCz)

4PyCNBCz was synthesized according to the synthetic method of 4PyCNICz, using 9-phenyl-9H,9'H-3,3'-bicarbazole instead of 5-phenyl-5,12-dihydroindolo[3,2-a]carbazole. The crude product was purified by column chromatography, using a n-hexane:chloroform (1:2) mixed eluent. The final product was recrystallized with toluene, and then sublimed. Final product was obtained as a yellow power (0.5 g, Yield 57 %). ^{1}H NMR (500 MH$_Z$, $CDCl_3$): δ 8.75 (d, J = 8.0 Hz, 2H), 8.50 (d, J = 8.5 Hz, 4H), 8.26 (d, J = 7.5 Hz, 2H), (8.23–8.21) (m, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), (7.67–7.59) (m, 11H), (7.54–7.44) (m, 5H), 7.40 (t, J = 7.0 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H). ^{13}C NMR (125 MH$_Z$, $CDCl_3$): δ 170.28, 168.83, 165.05, 141.57, 141.27, 141.00, 140.30, 139.65, 137.96, 136.39, 136.29, 135.22, 134.76, 134.34, 132.65, 131.93, 131.49, 130.13, 129.73, 129.63, 129.05, 127.68, 127.29, 126.94, 126.57, 126.29, 126.02, 124.67, 124.25, 124.20,

123.76, 120.86, 120.77, 120.66, 120.22, 119.21, 119.13, 117.81, 110.42, 110.27, 110.11, 100.65, 77.48, 77.22, 76.97, 29.92. MS (HR-FAB) m/z Found 739.2737 [$(M + H)^+$]. Calculated For $C_{53}H_{33}N_5$: 739.8626

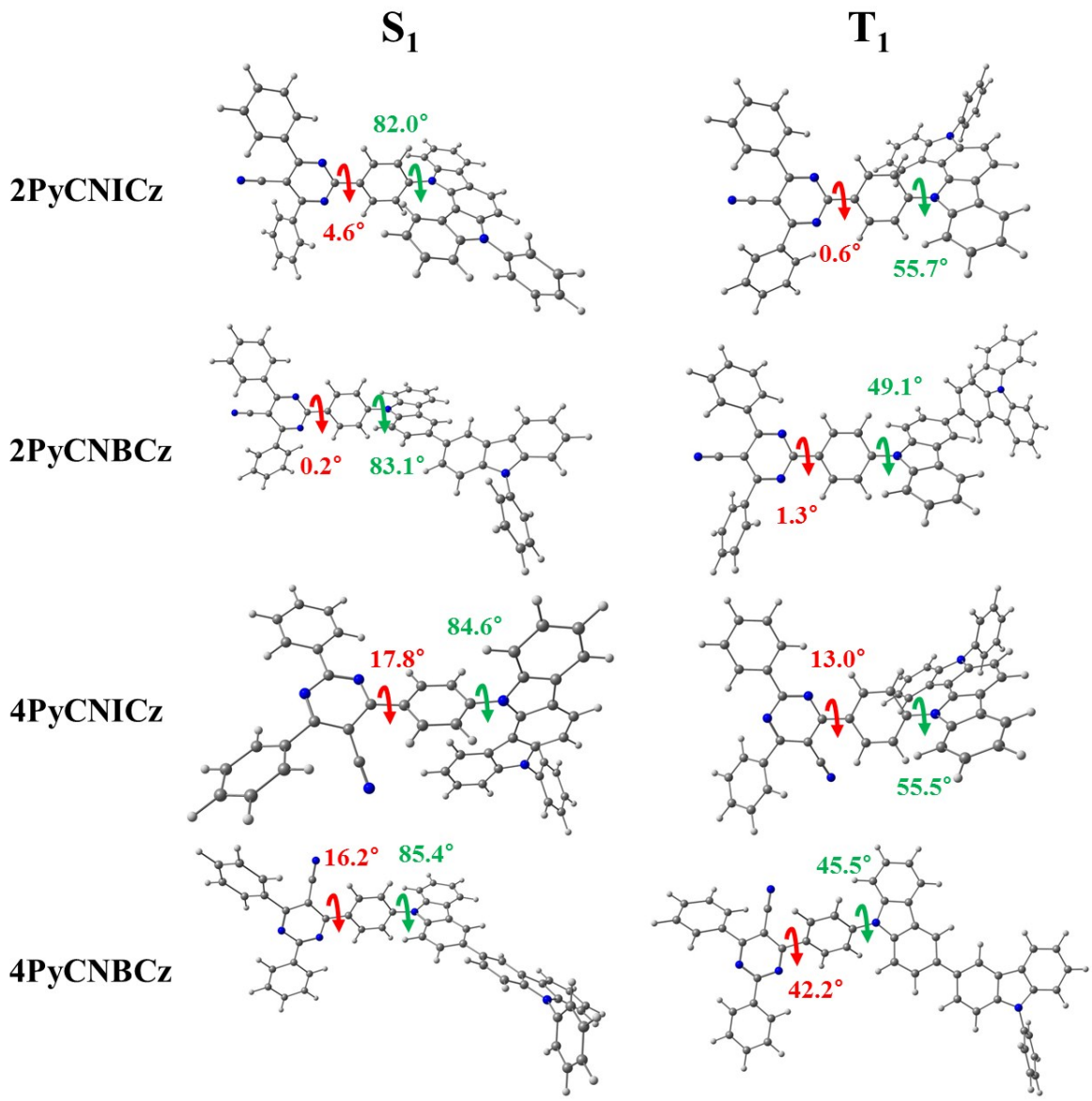

Figure S1. Optimized structures at singlet and triplet excited state

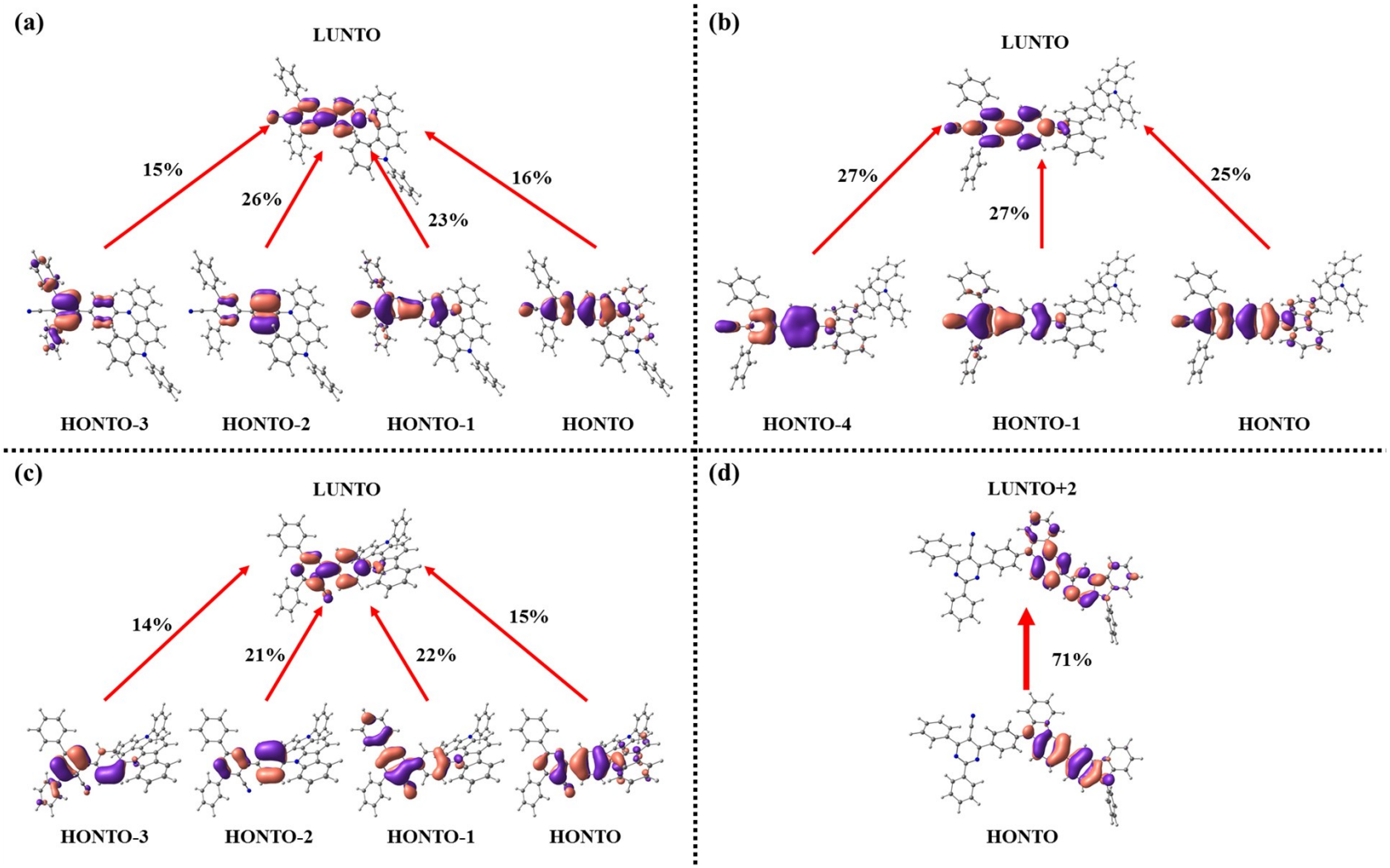

Figure S2. NTO calculation of (a) 2PyCNICz, (b) 2PyCNBCz, (c) 4PyCNICz and (d) 4PyCNBCz in triplet excited state

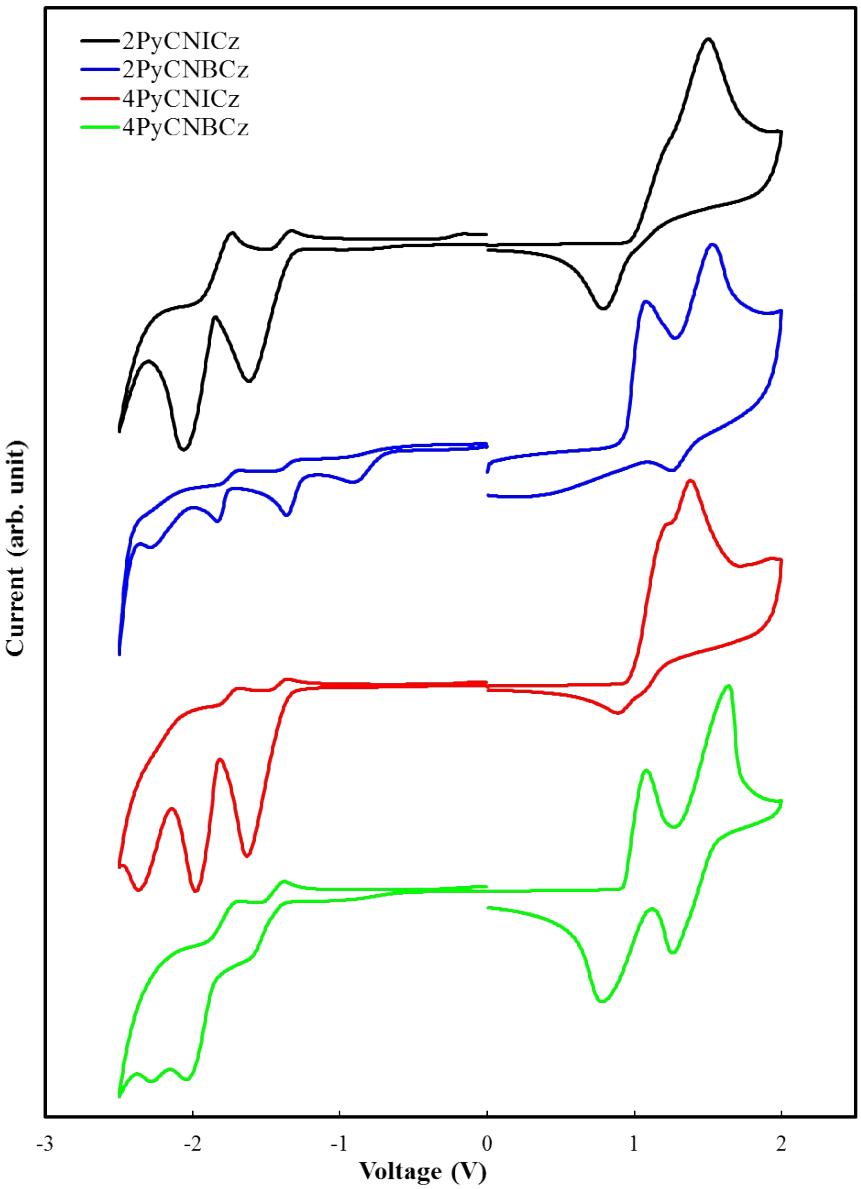

Figure S3. The cyclic voltammetry data of four TADF emitters.