Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

High efficiency above 20% in polymeric thermally activated delayed fluorescent organic light-emitting diodes by host embedded backbone structure

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General information

1-Bromo-4-methoxybenzene, magnesium, azobisisobutyronitrile (AIBN) 1-(chloromethyl)-4-vinylbenzene, boron tribromide (BBr_3), 9-vinyl-9H-carbazole (VCz) (from Sigma-Aldrich), cyanuric chloride, 1-bromo-4-chlorobenzene (from Alfa Aesar Co.) iodine (from TCI Co. Ltd.) tetrahydrofuran (THF), ethylacetate, dichloromethane, methanol, acetone, n-hexane, toluene, hydrochloric acid (HCl) (from Samchun pure chemical Co. Ltd.) tri-tert-butylphosphine, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), palladium(II) acetate ($Pd(OAc)_2$), X-phos (from P&H tech Co.) potassium carbonate (K_2CO_3), potassium acetate (CH_3COOK), magnesium sulfate ($MgSO_4$) anhydrous, N,N-dimethylformamide (DMF), 1,4-dioxane (from Duksan Sci. Co.) caesium carbonate (Cs_2CO_3), sodium hydroxide (NaOH) (from Daejung Chem. Co.) bis(pinacolato)diboron and 9,9-dimethyl-9,10-dihydroacridine (from INCO Co.) were used as received. Toluene and THF were distilled according to general purification. 1-(chloromethyl)-4-vinylbenzene was purified by column chromatography on silica gel using n-hexane (100%) before using it and also AIBN, VCz were recrystallized from methanol. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectrum were recorded using Avance-500 spectrometer. (Bruker, 500 MHz) The HOMO and LUMO were estimated using a cyclic voltammetry (Ivium Tech., Iviumstat) with conventional three electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and a non aqueous $Ag/AgNO_3$ acetonitrile reference electrode. Ferrocene and mCP internal standard were used to calibrate the peak potentials. The measurements were measured at room temperature in 1×10^{-4} M dichloromethane solution and the 0.1 M tetrabutyl ammonium perchlorate employed as supporting electrolyte and scan speed was 100mV/s. The mass spectrum was measured by Advion, Expresion^L

CMS spectrometer in APCI mode. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-AutoQ20 at a heating rate of 10 ^{o}C /min from 40 to 350 ^{o}C under nitrogen. Thermal data were collected using thermo gravimetric analyzer (TGA, Seiko Exstar 6000) performed under N_2 atmosphere at a heating rate of 10 °C/min. Molecular weight of the polymers were determined by gel permeation chromatography (GPC) on an Agilent 1100 S instrument using polystyrene as the standard and THF as the eluent.

Optical measurements.

The UV–vis spectrum were observed using UV–vis spectrophotometer (JASCO, V-730) and photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer (PerkinElmer, LS-55). The photophysical measurements were carried out using a toluene and THF solution. (10^{-5} M) The phosphorescence PL spectra were obtained at 77K with liquid nitrogen and setting delay time to get the value of triplet energy. Transient PL measurement was performed using a Hamamatsu Quantaurus-Tau system. (HAMAMATSU, C11367-31) Quantum yields were measured under nitrogen or oxygen atmosphere condition using a Quantaurus-QY absolute PL quantum yield spectrometer. (HAMAMATSU, C11347-11)

Synthesis

2,4-Dichloro-6-(4-methoxyphenyl)-1,3,5-triazine

2,4-Dichloro-6-(4-methoxyphenyl)-1,3,5-triazine was synthesized according to the literature methods.[1]

10-(4-Chlorophenyl)-9,9-dimethyl-9,10-dihydroacridine

A mixture of 9,9-dimethyl-9,10-dihydroacridine (6.55 g, 31.30 mmol), 1-bromo-4-chlorobenzene (7.20 g, 37.61mmol), caesium carbonate (30.63 g, 94.02 mmol), tri-tert-butylphosphine (50%) (1.90 g, 9.40 mmol) and $Pd(OAc)_2$ (0.10 g, 0.45 mmol) in toluene (210 ml) was added into a flask. The reaction mixture was stirred and refluxed for 24 h under a nitrogen atmosphere. After termination of the reaction, the reaction mixture was diluted with dichloromethane and washed with distilled water. The dichloromethane layer was dehydrated using anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using ethylacetate/n-hexane (1:99) eluent. The product was obtained as a white powder (6.20 g, yield 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.45 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.32 – 7.26 (m, 2H), 6.91 – 6.86 (m, 4H), 6.24 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.68 (s, 6H).

MS (APCI) m/z 321.0 [$(M+H)^+$].

9,9-Dimethyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydro acridine

A mixture of 10-(4-chlorophenyl)-9,9-dimethyl-9,10-dihydroacridine (6.0 g, 18.76 mmol), bis(pinacolato)diboron (9.53 g, 37.52 mmol), pottassium acetate (5.52 g, 56.28 mmol), X-phos (1.79 g, 3.75 mmol) and $Pd(OAc)_2$ (0.21 g, 0.94 mmol) in 1,4-dioxane (150 ml) was added into a flask. The reaction mixture was stirred and refluxed for 24 h under a nitrogen atmosphere. After termination of the reaction, the reaction mixture was diluted with dichloromethane and washed with distilled water. The dichloromethane layer was dehydrated using anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/n-hexane (20:80) eluent. The product was obtained as a white powder (3.50 g, yield 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.01 (m, 2H), 7.44 (dd, J = 7.5, 1.8 Hz, 2H), 7.38 – 7.31 (m, 2H), 6.99 – 6.86 (m, 4H), 6.25 (dd, J = 7.9, 1.5 Hz, 2H), 1.69 (s, 6H), 1.40 (s, 12H).

MS (APCI) m/z 412.4 [$(M+H)^+$].

10,10'-((6-(4-Methoxyphenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine)

A mixture of 9,9-dimethyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridin (2.47 g, 6.02 mmol), 2,4-dichloro-6-(4-methoxyphenyl)-1,3,5-triazine (0.65 g, 2.54mmol), K_2CO_3 (2.10 g, 15.23 mmol) and $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol) in THF (30 ml) and water (10ml) was added into a flask. The reaction mixture was stirred and refluxed for 24 h under a nitrogen atmosphere. The reaction mixture was filtered and residual materials on the filter was washed with hexane, methanol, distilled water and acetone. The product was obtained as a green powder (1.00 g, yield 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 – 9.00 (m, 4H), 8.85 – 8.78 (m, 2H), 7.62 – 7.54 (m, 4H), 7.49 (dd, *J* = 7.5, 1.7 Hz, 4H), 7.15 – 7.08 (m, 2H), 6.94 – 7.02 (m, 8H), 6.39 (dd, *J* = 8.0, 1.3 Hz, 4H), 3.95 (s, 3H), 1.73 (s, 12H).

MS (APCI) m/z 754.2[(M+H)$^+$].

(4-(4,6-Bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-1,3,5-triazin-2-yl)phenol)

10,10'-((6-(4-Methoxyphenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (1.0 g, 1.33 mmol) was dissolved in dehydrated dichloromethane (35ml) at -78 ^{o}C using acetone and dry ice. BBr_3 (2.33 g, 9.28 mmol) was added and the mixture was stirred for 12 h. The reaction product was neutralized by dropwise addition with a 2 M aqueous NaOH solution. The reaction product was extracted with ethyl acetate and distilled water solution. The ethyl acetate layer was dehydrated using anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/n-hexane (60:40) eluent. The product was obtained as green powder (0.60 g, yield 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 – 8.95 (m, 4H), 8.85 – 8.71 (m, 2H), 7.68 – 7.54 (m, 4H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 4H), 7.07 – 7.02 (m, 2H), 7.02 – 6.93 (m, 8H), 6.39 (dd, *J* = 8.0, 1.4 Hz, 4H), 5.34 (s, 1H), 1.73 (s, 12H).

MS (APCI) m/z 740.6[(M+H)$^+$].

10,10'-((6-(4-((4-Vinylbenzyl)oxy)phenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine)

A mixture of (4-(4,6-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-1,3,5-triazin-2-yl)phenol)

(0.6 g, 0.81 mmol), K_2CO_3 (0.34 g, 2.43 mmol), 1-(chloromethyl)-4-vinylbenzene (0.19 g, 1.22 mmol) in DMF (35 ml) was added into a flask. The reaction mixture was stirred at 80 °C for 12 h under a nitrogen atmosphere. After termination of the reaction, the reaction mixture was diluted with dichloromethane and washed with distilled water. The dichloromethane layer was dehydrated using anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/n-hexane (10:90) eluent. The product was obtained as a green powder (0.4 g, yield 58%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 – 8.99 (m, 4H), 8.84 – 8.76 (m, 2H), 7.61 – 7.54 (m, 4H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 4H), 7.45 (d, *J* = 2.1 Hz, 4H), 7.20 – 7.15 (m, 2H), 7.01 – 6.94 (m, 8H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.39 (dd, *J* = 8.0, 1.4 Hz, 4H), 5.78 (dd, *J* = 17.6, 0.6 Hz, 1H), 5.27 (dd, *J* = 10.9, 0.5 Hz, 1H), 5.20 (s, 2H), 1.73 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.73, 171.24, 162.96, 145.57, 140.81, 137.80, 136.56, 136.29, 136.07, 131.78, 131.73, 131.26, 130.47, 128.85, 127.99, 126.73, 126.65, 125.57, 121.07, 115.22, 114.52, 114.40, 70.17, 36.26, 31.51.

MS (APCI) m/z 856.6[$(M+H)^+$].

VTD3

A mixture of 10,10'-((6-(4-((4-vinylbenzyl)oxy)phenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (0.04g, 0.05mmol), 9-vinyl-9H-carbazole (0.89g, 4.61mmol), AIBN (7mg, 0.043mmol), toluene (10 ml), and THF (10ml) was added into a flask. The reaction mixture was stirred at 70 °C for 120 h under a nitrogen atmosphere. The reaction mixture was poured into large excess amount of acetone. After cooling to -10 °C, the precipitated material was obtained by centrifugation at 8000 rpm for 10 min using a centrifuge. After drying, it was dissolved again in 20 ml of THF. Then, it was reprecipitated in the same manner as above and centrifuged to obtain a final product. (0.35g, Yield 38%)

GPC: Mn = 10260 g/mol, Mw = 16910 g/mol, PDI = 1.65

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.10−8.68 (br, aromatic VTD), 8.13−5.67 (br, aromatic VTD, aromatic VCz), 5.43−4.40 (br, aromatic VTD, aromatic VCz), 3.78−2.21 (br, $C\underline{H}$ of VTD, $C\underline{H}$ of VCz), 2.15−0.76 (br, $C\underline{H}_3$ $C\underline{H}_2$ $C\underline{H}$ of VTD, $C\underline{H}_2$ of VCz).

VTD6

A mixture of (10,10'-((6-(4-((4-vinylbenzyl)oxy)phenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (0.08g, 0.09mmol), 9-vinyl-9H-carbazole (0.58g, 3.00mmol), AIBN (7mg, 0.043mmol), toluene (10ml) and THF (10ml) was added into a flask. The reaction mixture was stirred at 70 ^{o}C for 120 h under a nitrogen atmosphere. The reaction mixture was poured into large excess amount of acetone. After cooling to -10 ^{o}C, the precipitated material was obtained by centrifugation at 8000 rpm for 10 min using a centrifuge. After drying, it was dissolved again in 20 ml of THF. Then, it was reprecipitated in the same manner as above and centrifuged to obtain a final product. (0.25g, Yield 38%)

GPC: Mn = 6790g/mol, Mw = 10120g/mol, PDI = 1.49

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.10−8.64 (br, aromatic VTD), 8.30−5.69 (br, aromatic VTD, aromatic VCz), 5.49−4.46 (br, aromatic VTD, aromatic VCz), 3.90−2.22 (br, $C\underline{H}$ of VTD, $C\underline{H}$ of VCz), 2.15−0.75 (br, $C\underline{H}_3$ $C\underline{H}_2$ $C\underline{H}$ of VTD, $C\underline{H}_2$ of VCz).

VTD38

A mixture of 10,10'-((6-(4-((4-vinylbenzyl)oxy)phenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (0.3g, 0.35mmol), 9-vinyl-9H-carbazole (0.6g, 3.11mmol), AIBN (7mg, 0.043mmol), toluene (10 ml), and THF (10ml) was added into a flask. The reaction mixture was stirred at 70 °C for 120 h under a nitrogen atmosphere. The reaction mixture was poured into large excess amount of acetone. After cooling to -10 °C, the precipitated material was obtained by centrifugation at 8000 rpm for 10 min using a centrifuge. After drying, it was dissolved again in 20 ml of THF. Then, it was reprecipitated in the same manner as above and centrifuged to obtain a final product. (0.25g, Yield 28%)

GPC: Mn = 8400 g/mol, Mw = 11720 g/mol, PDI = 1.39

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.10−8.57 (br, aromatic VTD), 8.13−6.25 (br, aromatic VTD, aromatic VCz), 5.31−4.52 (br, aromatic VTD, aromatic VCz), 3.87−2.15 (br, $C\underline{H}$ of VTD, $C\underline{H}$ of VCz), 1.79−0.76 (br, $C\underline{H}_3$ $C\underline{H}_2$ $C\underline{H}$ of VTD, $C\underline{H}_2$ of VCz).

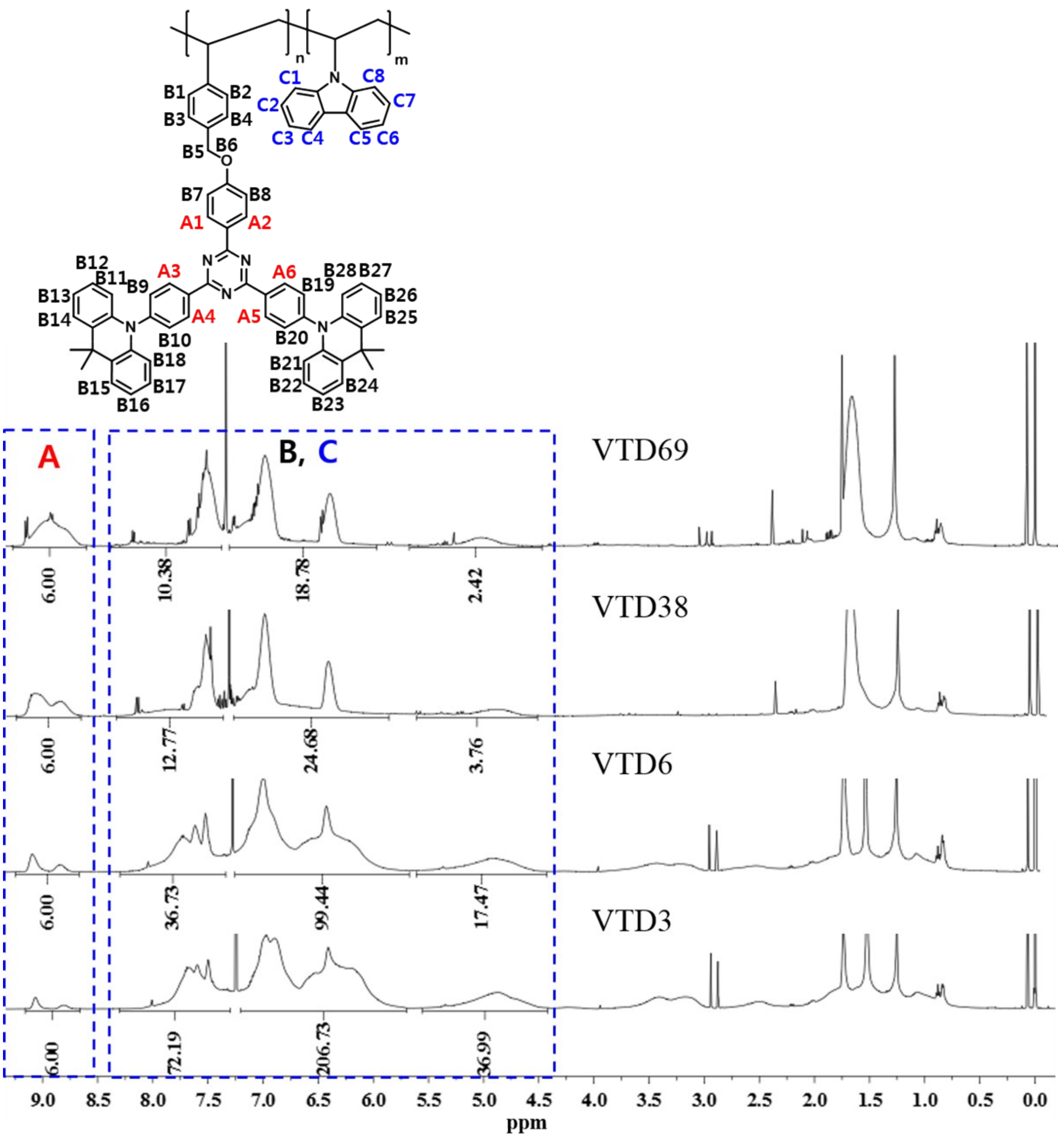
VTD69

A mixture of (10,10'-((6-(4-((4-vinylbenzyl)oxy)phenyl)-1,3,5-triazine-2,4-diyl)bis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (0.6g, 0.70mmol), 9-vinyl-9H-carbazole (0.32g, 1.66mmol), AIBN (7mg, 0.043mmol), toluene (10ml) and THF (10ml) was added into a flask. The reaction mixture was stirred at 70 °C for 120 h under a nitrogen atmosphere. The reaction mixture was poured into large excess amount of acetone. After cooling to -10 °C, the precipitated material was obtained by centrifugation at 8000 rpm for 10 min using a centrifuge. After drying, it was dissolved again in 20 ml of THF. Then, it was reprecipitated in the same manner as above and centrifuged to obtain a final product. (0.20g, Yield 22%)

GPC: Mn = 7510g/mol, Mw = 10220g/mol, PDI = 1.36

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.07−8.52 (br, aromatic VTD), 8.14−6.19 (br, aromatic VTD, aromatic VCz), 5.25−4.58 (br, aromatic VTD, aromatic VCz), 3.93−2.17 (br, CH of VTD, CH of VCz), 1.77−0.77 (br, $C\underline{H}_3$ $C\underline{H}_2$ $C\underline{H}$ of VTD, $C\underline{H}_2$ of VCz).

Composition ratio calculation of the VTD polymer using ^1H NMR spectra in $CDCl_3$



	Integration of fixed A proton #[a]	Integration of B,C proton #[b]			Total B,C proton # (A)	Fixed B proton #[c] (B)	(A)-(B) : Carbazole proton # (C)	Fixed C proton #[d] (D)	(C)/(D) :Carbazole mole # (E)	mol% of VTD[e]
VTD3	**6**	**72.19**	**206.73**	**36.99**	**315.91**	**28**	**287.91**	**8**	**35.99**	**3**
VTD6	**6**	**36.73**	**99.44**	**17.47**	**153.64**	**28**	**125.64**	**8**	**15.71**	**6**
VTD38	**6**	**12.77**	**24.69**	**3.76**	**41.22**	**28**	**13.23**	**8**	**1.65**	**38**
VTD69	**6**	**10.38**	**18.78**	**2.42**	**31.58**	**28**	**3.58**	**8**	**0.45**	**69**

(a) 1mole of VTD proton number in NMR spectrum (A1−A6) (b) Mixed VTD, VCz peaks in NMR spectrum (B1−B28, C1−C8) (c) 1mole of VTD proton number (B1−B28) (d) 1mole of VCz proton number (C1−C8) (e) VTD mol% in the VTD polymer = 1/(1+E)∗100%

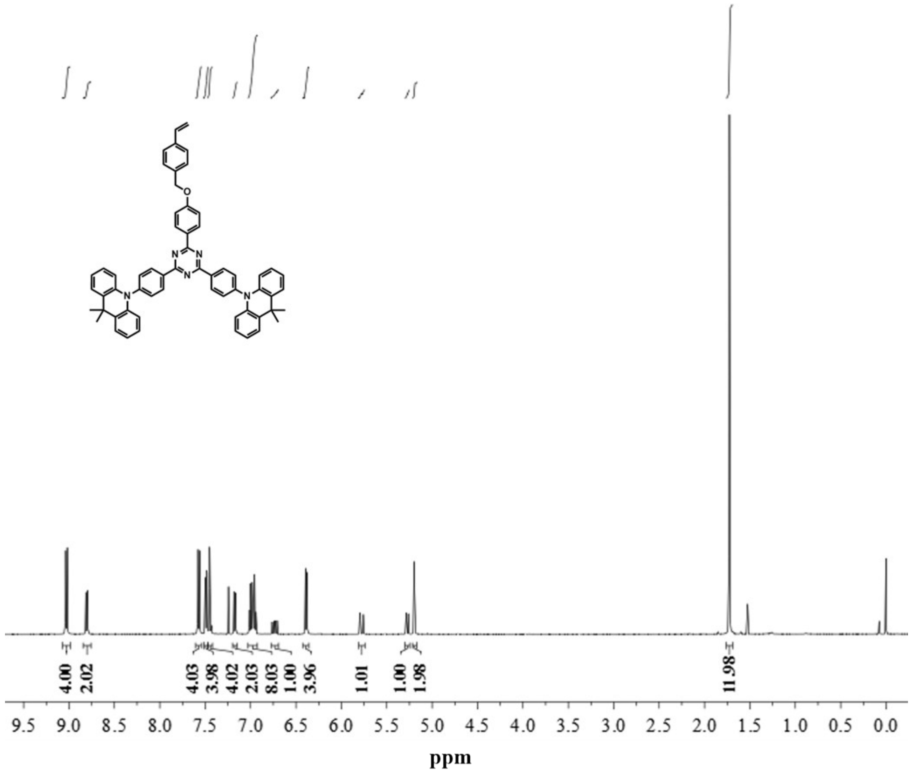


Figure S1. ^{1}H NMR spectrum of the VTD monomer in $CDCl_3$

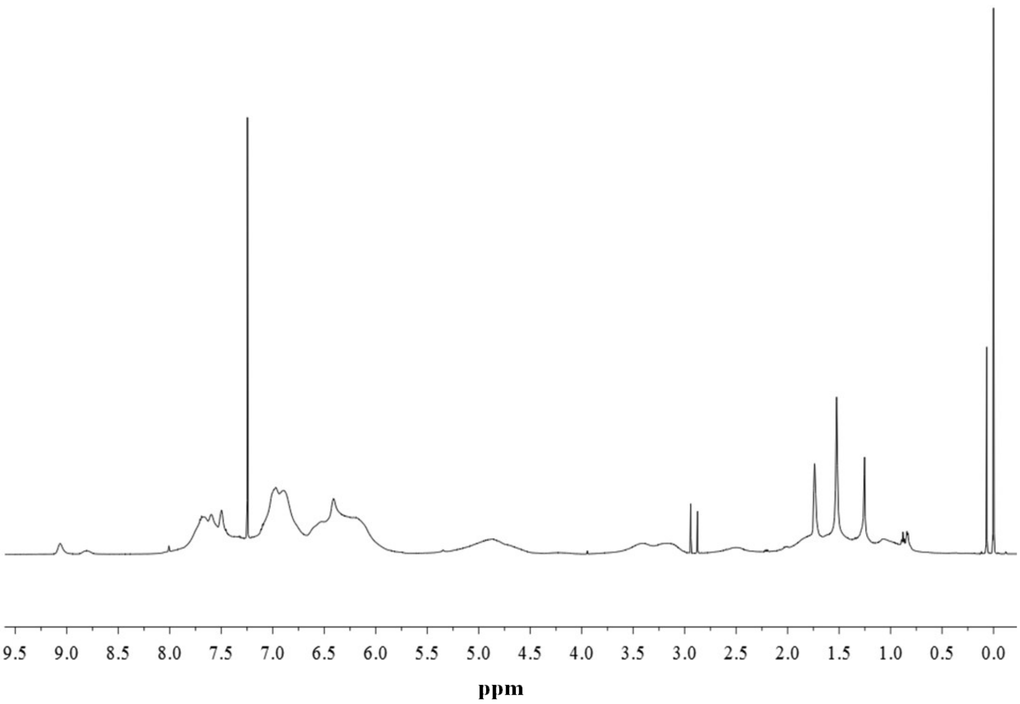


Figure S2. ^{1}H NMR spectrum of the VTD3 polymer in $CDCl_3$

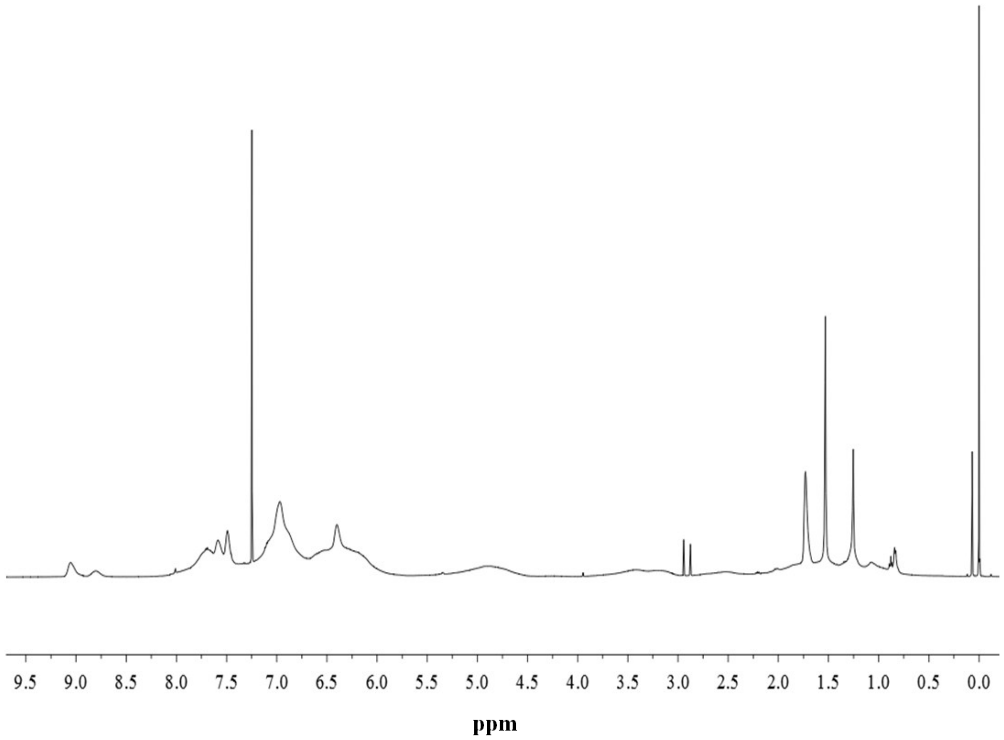


Figure S3. ^{1}H NMR spectrum of the VTD6 polymer in $CDCl_3$

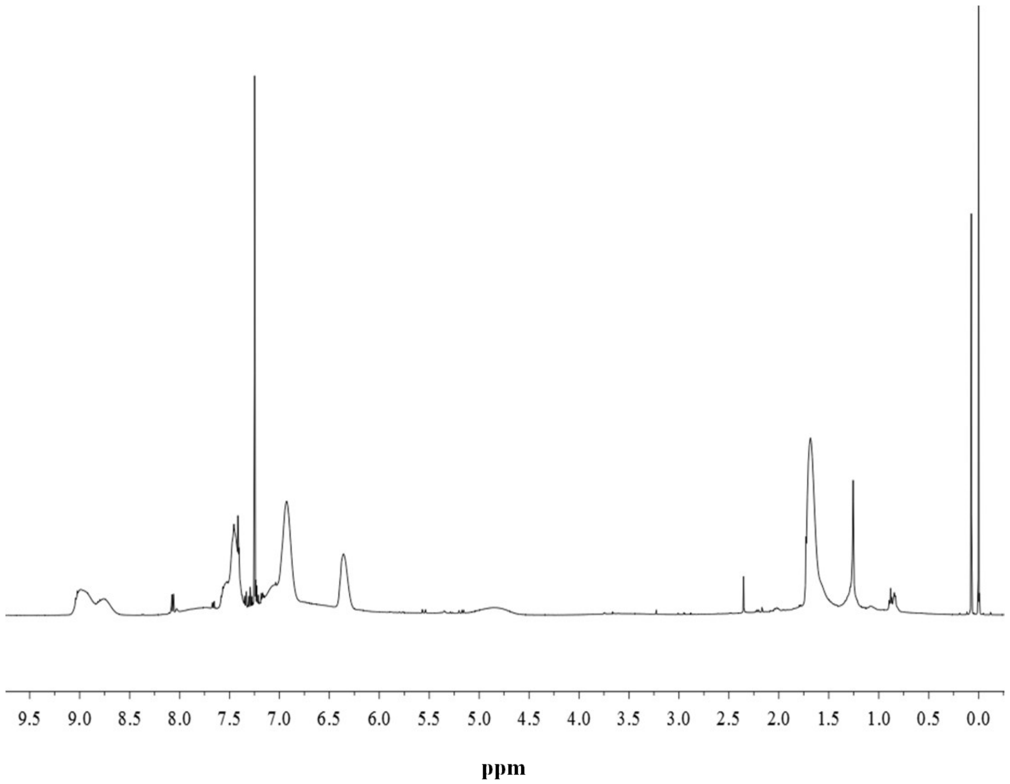


Figure S4. ^1H NMR spectrum of the VTD38 polymer in $CDCl_3$

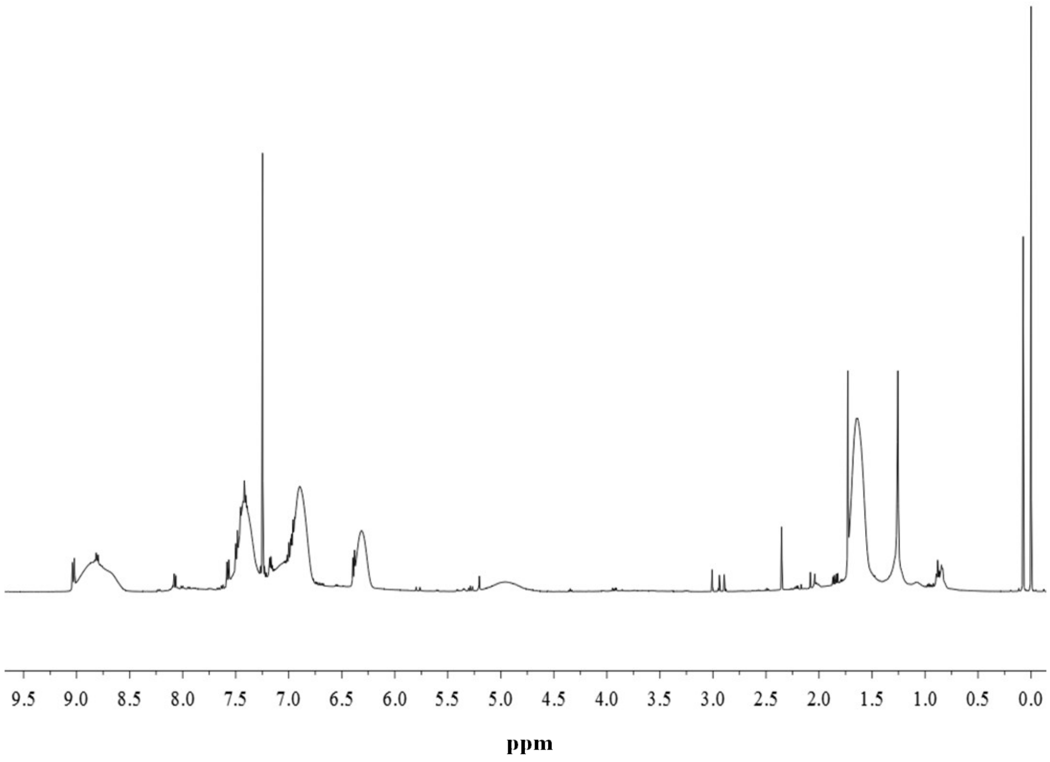


Figure S5. ^{1}H NMR spectrum of the VTD69 polymer in CDCl3

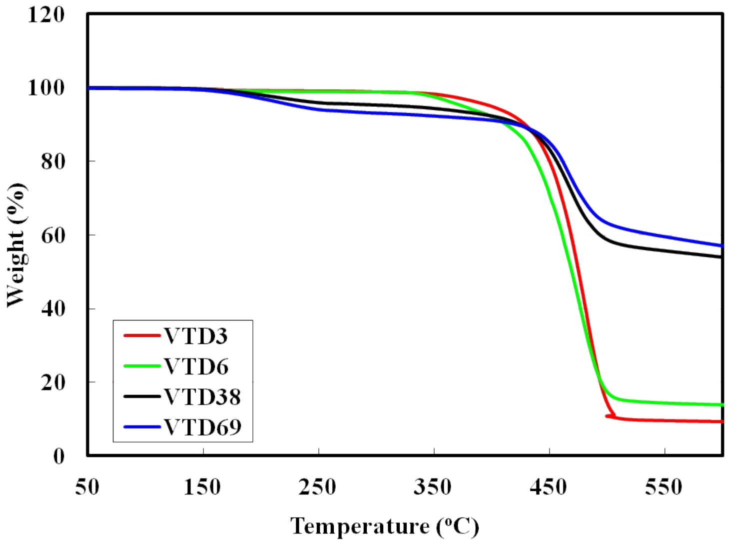


Figure S6. The TGA measurement of the VTD3, VTD6, VTD38 and VTD69.

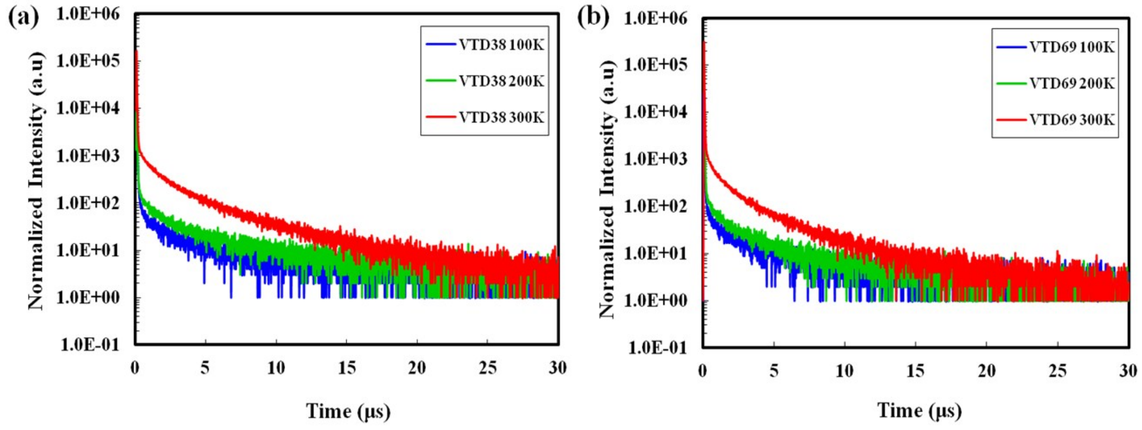


Figure S7. Temperature dependence transient PL data of the (a) VTD38 and (b) VTD69 polymer.

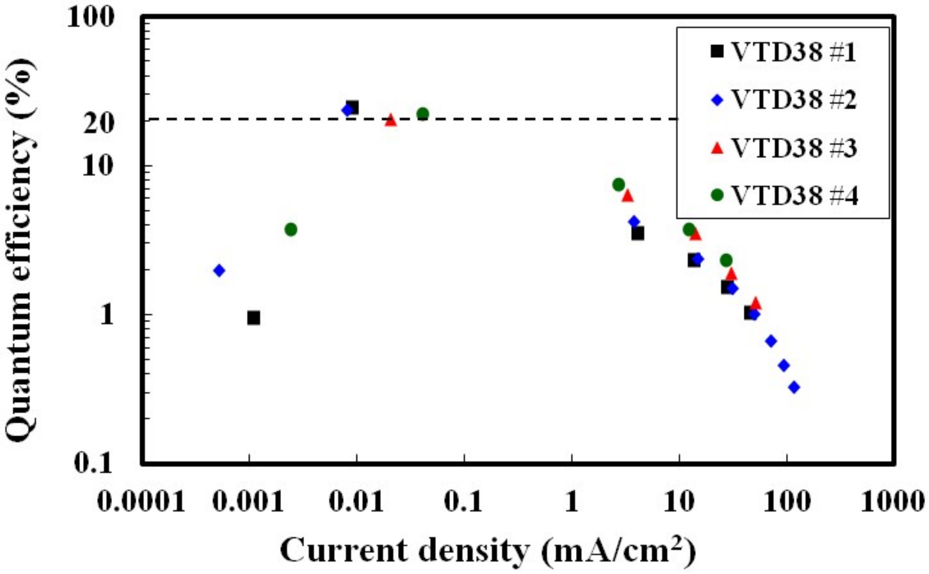


Figure S8. Reproducibility test of EQE against current density of the VTD38 polymer.

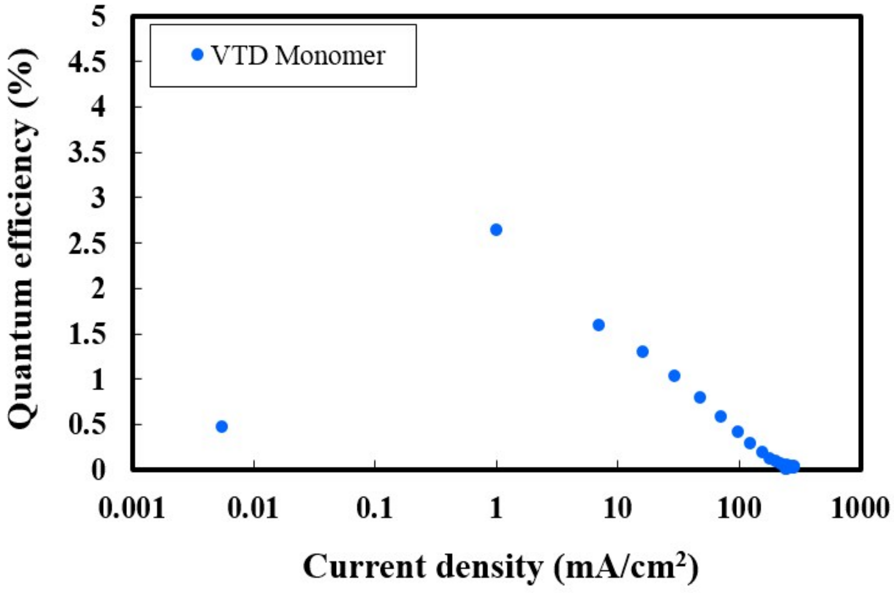


Figure S9. EQE against current density of the VTD monomer.

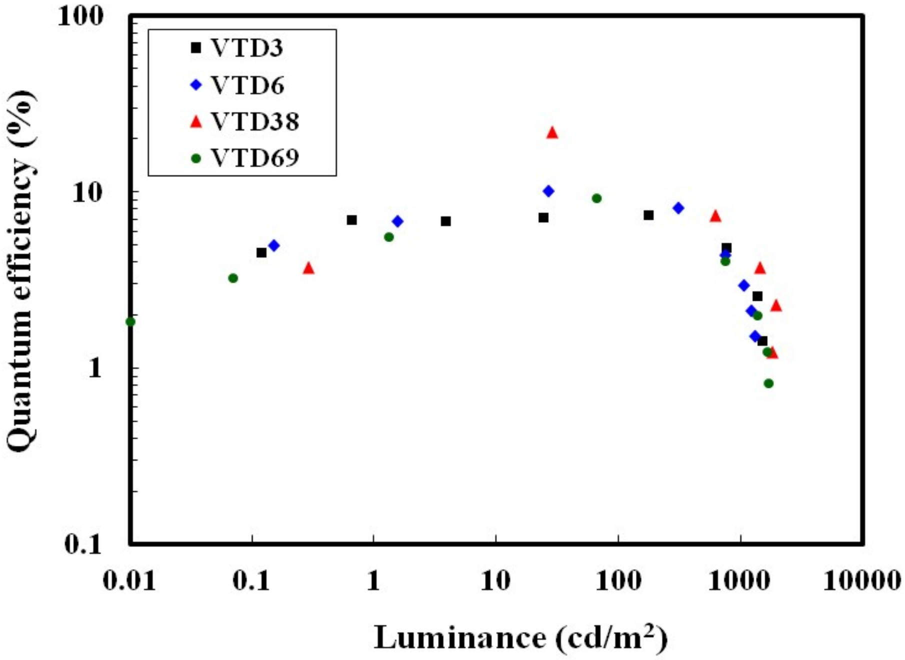


Figure S10. EQE against luminanance of the VTD polymer.

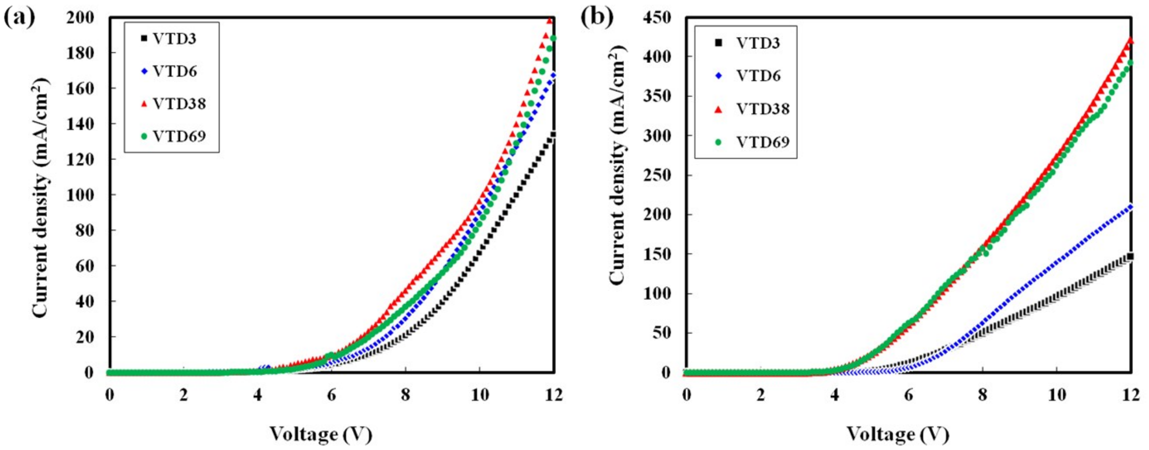


Figure S11. Current density-voltage curves of the single carrier devices of the VTD polymer (a) Hole only device (b) Electron only device

References

[1] Zhong, H.; Xu, E.; Zeng, D.; Du, J.; Sun, J.; Ren, S.; Jiang, B.; Fang, Q. New Optoelectronic Materials Based on Bitriazines: Synthesis and Properties. *Org.lett.* **2008**, *10*, 709−712.