Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Rational Design of Host Materials for Phosphorescent Organic Light-Emitting Diodes by Modifying 1- Position of Carbazole

Sung Moo Kim[a], Sung Yong Byeon[b], Seok Ho Hwang[b], Jun Yeob Lee[a]*

[a]*School of Chemical Engineering, Sungkyunkwan University, Suwo, Gyeonggi-do, 446-740, Korea*

[b]*Department of Polymer Science and Engineering, Dankook University, Yongin-si, Gyeonggi-do, 448-701, Korea*

leej17@skku.edu

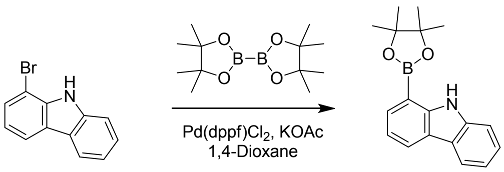
Experimental Section

General information

Sodium tert-butoxide (NaO(t-bu)), tri-tert-butylphosphine (P(t-bu)$_3$), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos), [1,1-bis-(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl$_2$), tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$), palladium(II)acetate (Pd(OAc)$_2$), bis(pinacolato)diboron and cesium carbonate (Cs_2CO_3) (P&H Tech Co.) were used without further purification. Potassium acetate (CH_3COOK), sodium hydroxide (NaOH), 1,4-dioxane, toluene, ethanol (EtOH), tetarhydrofuran (THF), dimethylformamide (DMF) (Duksan Sci. Co.) and sodium hydride (NaH) (Aldrich Chem. Co.) were also used as received.

Nuclear magnetic resonance (NMR) spectra were recorded on Varian (^{1}H NMR: 400 MH_Z), Avance-500 (^{13}C NMR: 500 MH_Z). Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2501PC and fluorescence spectra were recorded on Hitachi F-7000. Low temperature PL measurement of the synthesized materials were carried out at 77 K using a dilute solution of materials in tetrahydrofuran. Glass transition temperature (T_g) and melting point (T_m) of synthesized materials were determined using Mettler Toledo DSC 822 under nitrogen atmosphere at a heating rate of 10°C min^{-1}. The thermogravimetric analysis (TGA) measurement was performed on a TA instrument Q50 at a scanning rate of 10°C min^{-1} under nitrogen atmosphere. The mass spectra were recorded using a Waters Xevo TQ-S spectrometer in API mode and elemental analysis were recorded using a CE instrument Flash 2000. The HOMO energy levels were measured with a cyclic voltammetry (CV). CV measurement of organic materials was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Ag was used as the reference electrode and Pt was counter electrode. Ferrocene was used as the standard material for the cyclic voltammetry measurement. The purity of the host materials were measured using high performance liquid chromatograpy (HPLC) from YL instrument YL-9100.

Synthesis



1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole 1-Bromo-9H-carbazole (6.0 g, 24.4 mmol), bis(pinacolato)diboron (9.3 g, 36.6 mmol), CH_3COOK (4.8 g, 48.8 mmol) and Pd(dppf)Cl_2 (1.0 g, 1.22 mmol) were dissolved in 1,4-dioxane (120 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was celite filtered, diluted with ethyl acetate, and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as a white powder (4.8 g, Yield 67%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 10.30 (s, 1H), 8.24 (d, 1H, J= 7.6Hz), 8.09 (d, 1H, J= 8.0Hz), 7.71 (d, 1H, J=8.0Hz), 7.67 (d, 1H, J=7.6Hz), 7.37 (t, 1H, J=7.6H$_Z$), 7.15 (m, 2H), 1.37 (s, 12H). MS (API+) m/z: 294.1 [(M+H)$^+$]

9-Phenyl-9H,9'H-1,1'-bicarbazole (1) 1-Bromo-9-phenyl-9H-carbazole (3.2 g, 9.95 mmol), 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3.5 g, 11.9 mmol), NaOH (1.2 g, 29.9 mmol) and Pd(PPh$_3$)$_4$ (0.57 g, 0.50 mmol) were dissolved in THF (60 ml) and water (30 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as a white powder (2.7 g, Yield 67%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 10.44 (s, 1H), 8.37 (dd, 1H, J=6.4, 2.0Hz), 8.31 (d, 1H, J=7.6Hz), 7.92 (d, 1H, J=7.6Hz), 7.74 (d, 1H, J=7.6Hz), 7.42 (m, 2H), 7.34 (m, 2H), 7.28 (m, 2H), 7.07 (m, 2H), 7.00 (d, 1H, J=8.4Hz), 6.91 (t, 1H, J=7.6Hz), 6.80 (m, 3H), 6.69 (t, 1H), 6.25 (m, 1H). MS (API+) m/z: 409.9 [(M+H)$^+$]

9-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-1,1'-bicarbazole (1-PCz-1-TCz) 9-Phenyl-9H,9'H-1,1'-bicarbazole (1.7 g, 4.17 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (1.45 g, 5.42 mmol), NaO(t-bu) (0.8 g, 8.34 mmol), P(t-bu)$_3$ (50%) (0.34 g, 0.83 mmol) and Pd$_2$(dba)$_3$ (0.19 g, 0.21 mmol) were dissolved in toluene (30 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product.

The crude product was purified by column chromatography on silica gel using DCM/n-hexane. The product was obtained as a yellow powder (1.4 g, Yield 52%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 8.08 (d, 4H, J=7.6Hz), 8.05 (d, 1H, J=8.0Hz), 7.92 (d, 1H, J=7.6Hz), 7.90 (d, 1H, J=7.2Hz), 7.76 (d, 1H, J=8.0Hz), 7.63 (d, 1H, J=7.6Hz), 7.53 (m, 2H), 7.45 (m, 8H), 7.31 (m, 2H), 7.01 (m, 2H), 6.81 (m, 1H), 6.70 (m, 2H), 6.57 (t, 1H, J=7.6Hz), 6.37 (m, 2H). ^{13}C NMR (400 MH$_Z$, CDCl$_3$): δ 170.95, 163.62, 141.30, 140.15, 136.29, 136.13, 135.33, 135.12, 132.11, 128.70, 128.03, 127.89, 127.03, 126.69, 126.49, 126.12, 125.82, 125.66, 125.00, 124.58, 124.10, 122.58, 121.73, 120.57, 120.45, 119.83, 119.69, 119.02, 118.86, 118.62, 112.01, 111.89, 109.70. MS (API+) m/z: 640.8 [(M+H)$^+$]

9'-Phenyl-9H,9'H-1,2'-bicarbazole (2) 1-Bromo-9H-carbazole (3.0 g, 12.2 mmol), (9-phenyl-9H-carbazol-2-yl)boronic acid (4.2 g, 14.6 mmol), NaOH (1.5 g, 36.6 mmol) and Pd(PPh$_3$)$_4$ (0.70 g, 0.61 mmol) were dissolved in THF (80 ml) and water (40 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as a beige powder (3.3 g, Yield 66%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 11.13 (s, 1H), 8.43 (d, 1H, J=8.4Hz), 8.32 (d, 1H, J=7.2Hz), 8.11 (t, 1H, J=8.0Hz), 7.77 (d, 1H, J=8.4Hz), 7.76 (d, 1H, J=8.4Hz), 7.63 (m, 4H), 7.45 (m, 6H), 7.33 (m, 2H), 7.23 (t, 1H, J=7.6Hz), 7.14 (t, 1H, J=8.0Hz). MS (API+) m/z: 409.9 [(M+H)$^+$]

9-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-1,2'-bicarbazole (2-PCz-1-TCz) 9'-Phenyl-9H,9'H-1,2'-bicarbazole (0.8 g, 1.96 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (0.68 g, 2.54 mmol), NaO(t-bu) (0.38 g, 3.92 mmol), P(t-bu)$_3$ (50%) (0.16 g, 0.08 mmol) and Pd$_2$(dba)$_3$ (0.18 g, 0.20 mmol) were dissolved in toluene (20 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24 h. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using DCM/n-hexane. The product was obtained as yellow powder (0.7 g, Yield 56%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 8.38 (d, 1H, J=8.4Hz), 8.30 (m, 2H), 8.25 (d, 4H, J=7.6Hz), 7.94 (d, 1H, J=8.0Hz), 7.68 (d, 1H, J=8.4Hz), 7.63 (m, 3H), 7.56 (t, 2H), 7.47 (m, 5H), 7.39 (m, 3H), 7.29 (m, 2H), 7.19 (s, 1H), 7.15 (t, 1H, J=7.6Hz), 7.08 (m, 3H). ^{13}C NMR (500 MH$_Z$, $CDCl_3$): δ 171.93, 165.01, 141.31, 140.84, 139.18, 137.26, 137.00, 135.50, 132.67, 130.79, 129.80, 129.48, 129.28, 128.48, 127.79, 127.40, 127.19, 126.01, 125.68, 123.25, 123.22, 122.88, 122.13, 120.35, 120.27, 120.24, 119.80, 118.99, 113.60, 109.69, 107.85. MS (API+) m/z: 640.9 [$(M+H)^+$]

9'-Phenyl-9H,9'H-1,3'-bicarbazole (3) 1-Bromo-9H-carbazole (2.0 g, 8.13 mmol), (9-phenyl-9H-carbazol-3-yl)boronic acid (2.8 g, 9.75 mmol), NaOH (1.0 g, 24.4 mmol) and $Pd(PPh_3)_4$ (0.47 g, 0.41 mmol) were dissolved in THF (40 ml) and water (20 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as a beige powder (2.2 g, Yield 66%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 11.10 (s, 1H), 8.54 (s, 1H), 8.33 (d, 1H, J=7.2Hz), 8.12 (t, 2H, J=9.4Hz), 7.70 (m, 5H), 7.42 (m, 9H), 7.15 (t, 1H, J=7.6Hz). MS (API+) m/z: 409.7 [$(M+H)^+$]

9-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-1,3'-bicarbazole (3-PCz-1-TCz) The Sodium hydride (0.14 g, 5.88 mmol) added to a stirred solution of 9'-phenyl-9H,9'H-1,3'-bicarbazole (1.6 g, 3.92 mmol) in dry DMF (30 mL) under a nitrogen atmosphere at room temperature. After stirring for 30 min, 2-chloro-4,6-diphenyl-1,3,5-triazine (1.36 g, 5.10 mmol) was added. The reaction mixture was stirred at room temperature for overnight. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using DCM/n-hexane. The product was obtained as a yellow powder (0.8 g, Yield 32%).

^{1}H NMR (400 MH$_Z$, CDCl$_3$): δ 8.38 (d, 1H, J=8.4Hz), 8.29 (m, 3H), 8.19 (dd, 1H, J=7.6, 0.8Hz), 8.16 (dd, 1H, J=8.0, 1.2Hz), 8.05 (d, 1H, J=2.0Hz), 7.70 (dd, 1H, J=6.4, 1.2Hz), 7.64 (d, 1H, J=7.6Hz), 7.57 (t, 1H, J=7.6Hz), 7.53 (m, 1H), 7.45 (m, 3H), 7.38 (m, 7H), 7.23 (m, 4H), 7.19 (m, 2H), 6.94 (m, 1H), 6.76 (d, 1H, J=8.0Hz). ^{13}C NMR (500 MH$_Z$, CDCl$_3$): δ 171.68, 164.98, 141.00, 140.64, 139.29, 137.78, 137.48, 135.15, 132.78, 132.53, 130.37, 129.87, 128.83, 128.75, 128.24, 127.46, 127.23, 127.11, 126.85, 125.80, 125.76, 125.30, 123.89, 123.09, 123.05, 122.63, 120.75, 120.37, 119.60, 118.79. 113.01, 109.33, 109.24. MS (API+) m/z: 640.8 [(M+H)$^+$]

9'-Phenyl-9H,9'H-1,4'-bicarbazole (4) 4-Chloro-9-phenyl-9H-carbazole (4.5 g, 16.2 mmol), 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (4.8 g, 16.2 mmol), Cs_2CO_3 (10.5 g, 32.4 mmol), X-phos (0.77 g, 1.62 mmol) and $Pd(OAc)_2$ (0.18 g, 8.18 mmol) were dissolved in toluene (80 ml), ethanol (30 ml) and water (30 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 2 h. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as a beige powder (4.1 g, Yield 62%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 10.67 (s, 1H), 8.27 (d, 1H, J=7.6Hz), 8.18 (d, 1H, J=7.2Hz), 7.72 (t, 2H, J=7.8Hz), 7.65 (d, 2H, J=7.2H), 7.57 (t, 2H, J=7.8Hz), 7.45 (d, 2H, J=8.4Hz), 7.29 (m, 6H), 7.15 (t, 1H), 6.77 (t, 1H, J=7.6Hz), 6.69 (d, 1H, J=7.6Hz). MS (API+) m/z: 408.9 [(M+H)$^+$]

9-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9H,9'H-1,4'-bicarbazole (4-PCz-1-TCz) 9'-phenyl-9H,9'H-1,4'-bicarbazole (2.0 g, 4.91 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (1.7 g, 6.38 mmol), NaO(t-bu) (1.42 g, 14.7 mmol), P(t-bu)$_3$ (50%) (0.20 g, 0.49 mmol) and $Pd_2(dba)_3$ (0.23 g, 0.25 mmol) were dissolved in toluene (30 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using DCM/n-hexane. The product was obtained as yellow powder (1.6 g, Yield 81%).

^1H NMR (400 MH_Z, $CDCl_3$): δ 8.29 (d, 1H, J=7.6Hz), 8.23 (d, 2H, J=8.4Hz), 8.20 (m, 3H), 7.95 (d, 1H, J=7.6Hz), 7.89 (d, 1H, J=8.0Hz), 7.62 (m, 2H) 7.45 (m, 10H), 7.20 (m, 6H), 6.92 (m, 1H), 6.80 (m, 2H). ^{13}C NMR (500 MH_Z, $CDCl_3$): δ 171.77, 164.94, 141.71, 141.48, 140.64, 137.49, 137.09, 135.70, 135.07, 132.52, 129.82, 129.69, 128.98, 128.32, 127.64, 127.60, 127.35, 127.15, 125.72, 125.59, 125.42, 123.71, 123.11, 122.57, 120.35, 120.27, 119.73, 112.96, 109.68, 108.28. MS (API+) m/z: 640.8 $[(M+H)^+]$

Device fabrication and measurements

Devices were constructed on a 120 nm thick indium tin oxide (ITO) coated substrate which was cleaned using acetone and hot isopropanol. The cleaned ITO substrate was dried in convection oven and then was coated with a 60 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole injection layer by spin coating process. The PEDOT:PSS film was baked in ambient air and under nitrogen at 150 ^oC for 10 min to remove residual solvent. Small molecule hole transport material, 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) was deposited by vacuum thermal evaporation process at a thickness of 20 nm and a 10 nm thick mCP exciton blocking layer was also formed by thermal evaporation. Emitting layer was deposited by co-doping of synthesized hosts and tris[2-phenylpyridinato-N,C^2] iridium(III) ($Ir(ppy)_3$) at a thickness of 25 nm. Doping concentration of $Ir(ppy)_3$ was 3%, which was controlled by managing the evaporation rate of the host and $Ir(ppy)_3$. After the emitting layer deposition, diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) was evaporated as an exciton blocking layer at a thickness of 5 nm and

2,2′,2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI) was deposited as an electron transport layer at a thickness of 30 nm. LiF (1 nm)/Al (200 nm) double layer was formed on the TPBI layer by thermal evaporation. In the optimization of the 2-PCz-1-TCz devices, a double layer hole transport structure of 4,4′,4″-tris(N-carbazolyl)triphenylamine/mCP instead of mCP was selected as the hole transport layer and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene was used as the electron transport material. The green devices were encapsulated inside a glove box and all device performances were measured outside the glove box. Electrical and light-emitting performances were characterized using CS 2000 spectroradiometer and Keithley 2400 source measurement unit.

List of figures

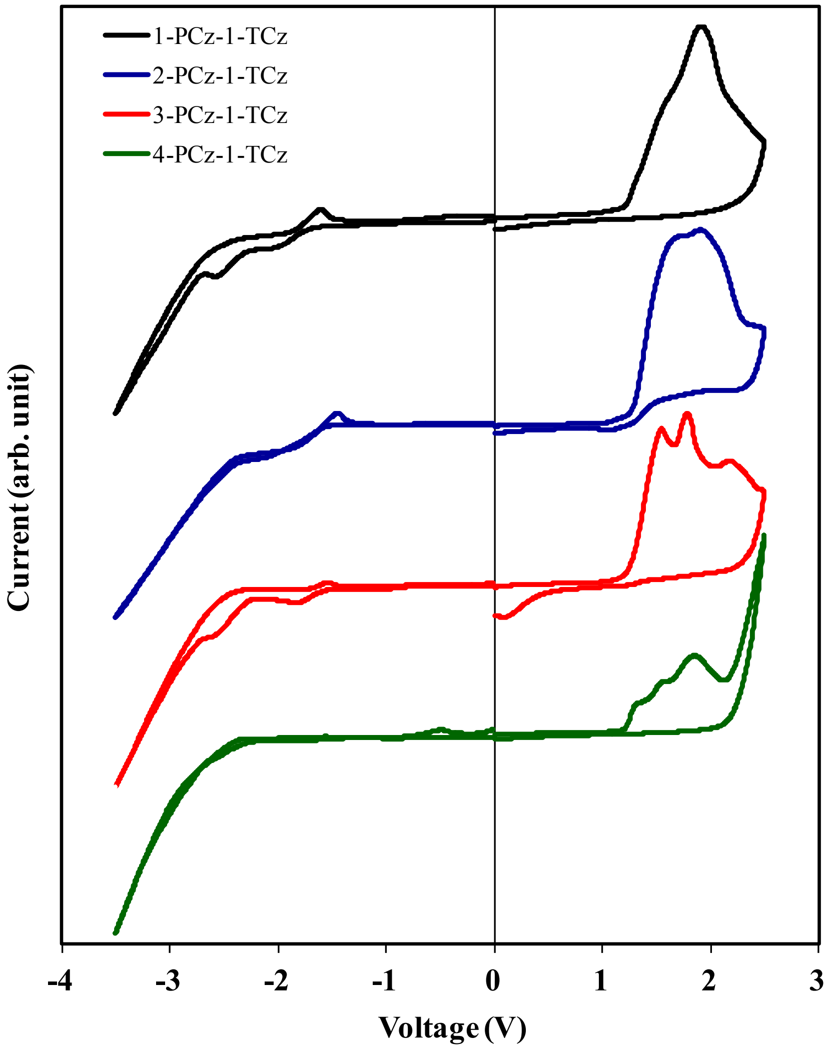

1-PCz-1-TCz
2-PCz-1-TCz
3-PCz-1-TCz
4-PCz-1-TCz
Current (arb. unit)
-4
-3
-2
-1
0
1
2
3
Voltage (V)

Figure S1

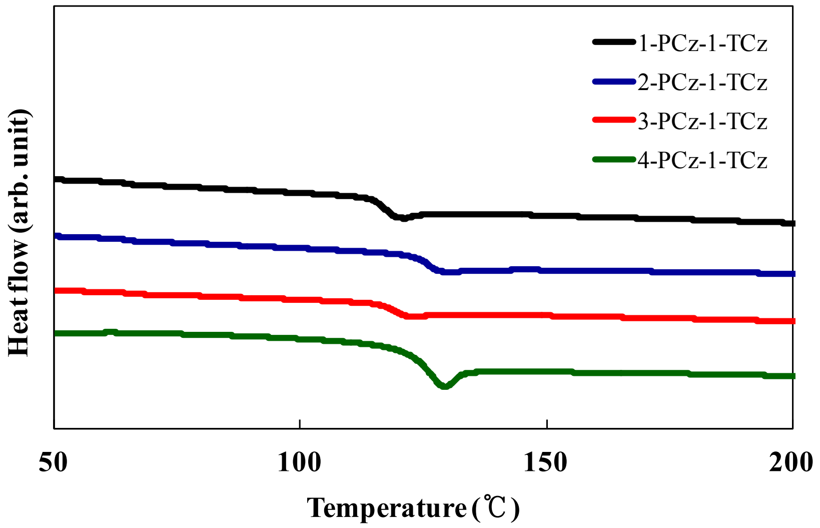

1-PCz-1-TCz
2-PCz-1-TCz
3-PCz-1-TCz
4-PCz-1-TCz
Heat flow (arb. unit)
50
100
150
200
Temperature (℃)

Figure S2

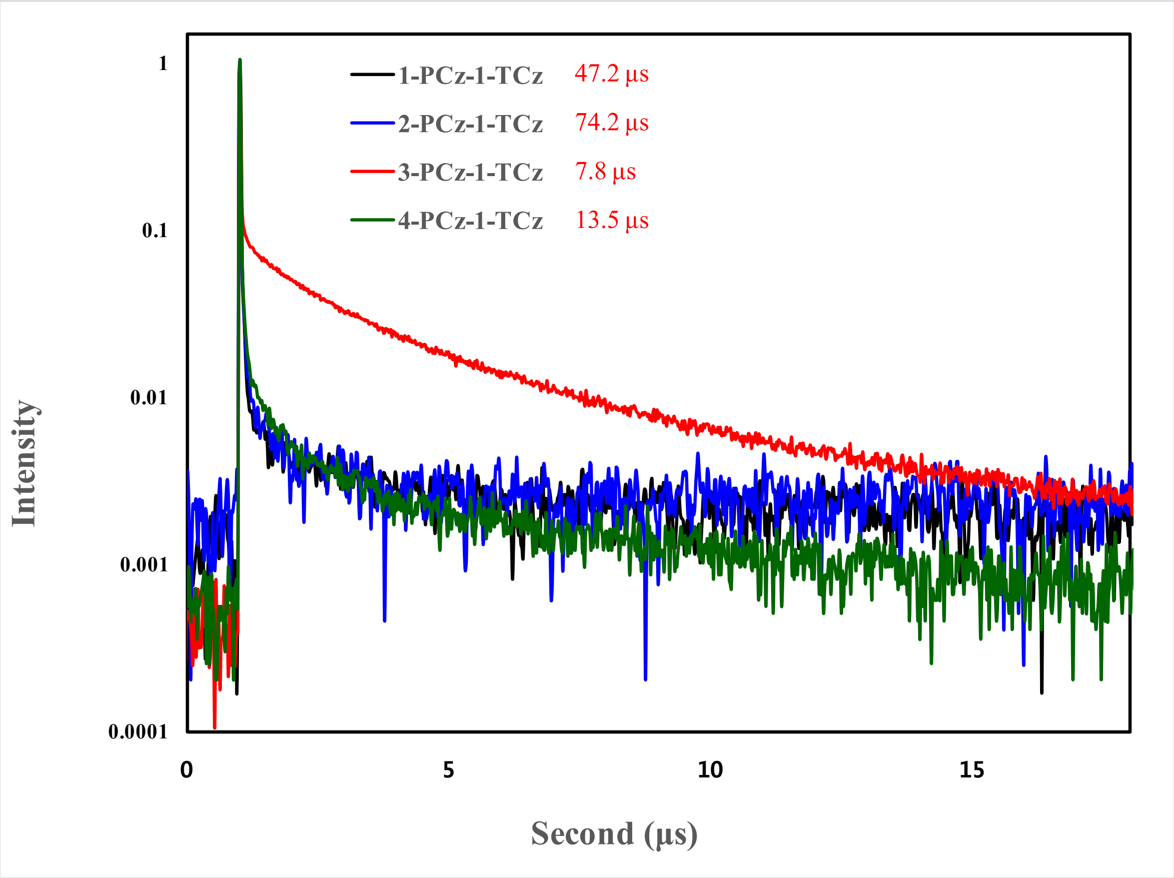

1-PCz-1-TCz 47.2 µs
2-PCz-1-TCz 74.2 µs
3-PCz-1-TCz 7.8 µs
4-PCz-1-TCz 13.5 µs
Intensity
1
0.1
0.01
0.001
0.0001
0
5
10
15
Second (µs)

Figure S3

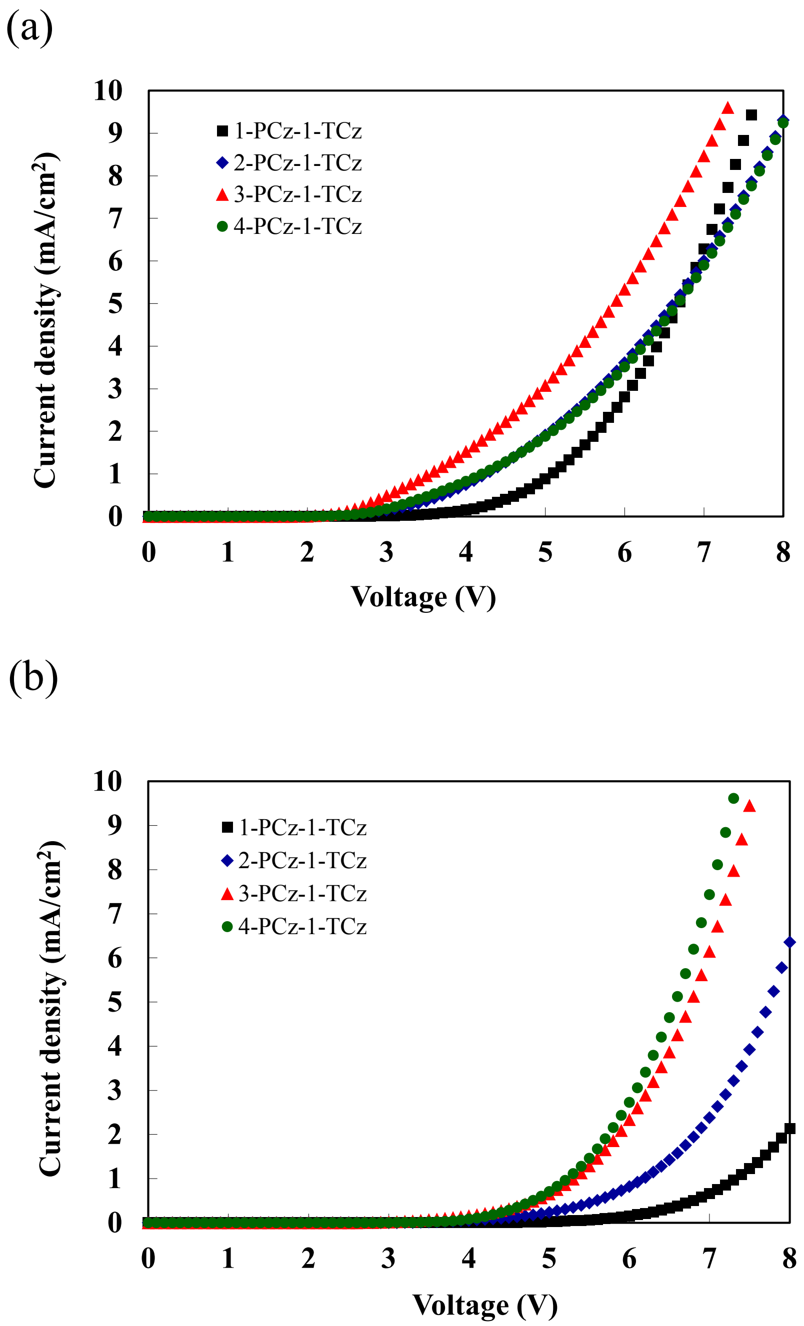

(a)
Current density (mA/cm^2)
Voltage (V)
0
1
2
3
4
5
6
7
8
9
10
■ 1-PCz-1-TCz
◆ 2-PCz-1-TCz
▲ 3-PCz-1-TCz
● 4-PCz-1-TCz
(b)
Current density (mA/cm^2)
Voltage (V)
■ 1-PCz-1-TCz
◆ 2-PCz-1-TCz
▲ 3-PCz-1-TCz
● 4-PCz-1-TCz

Figure S4

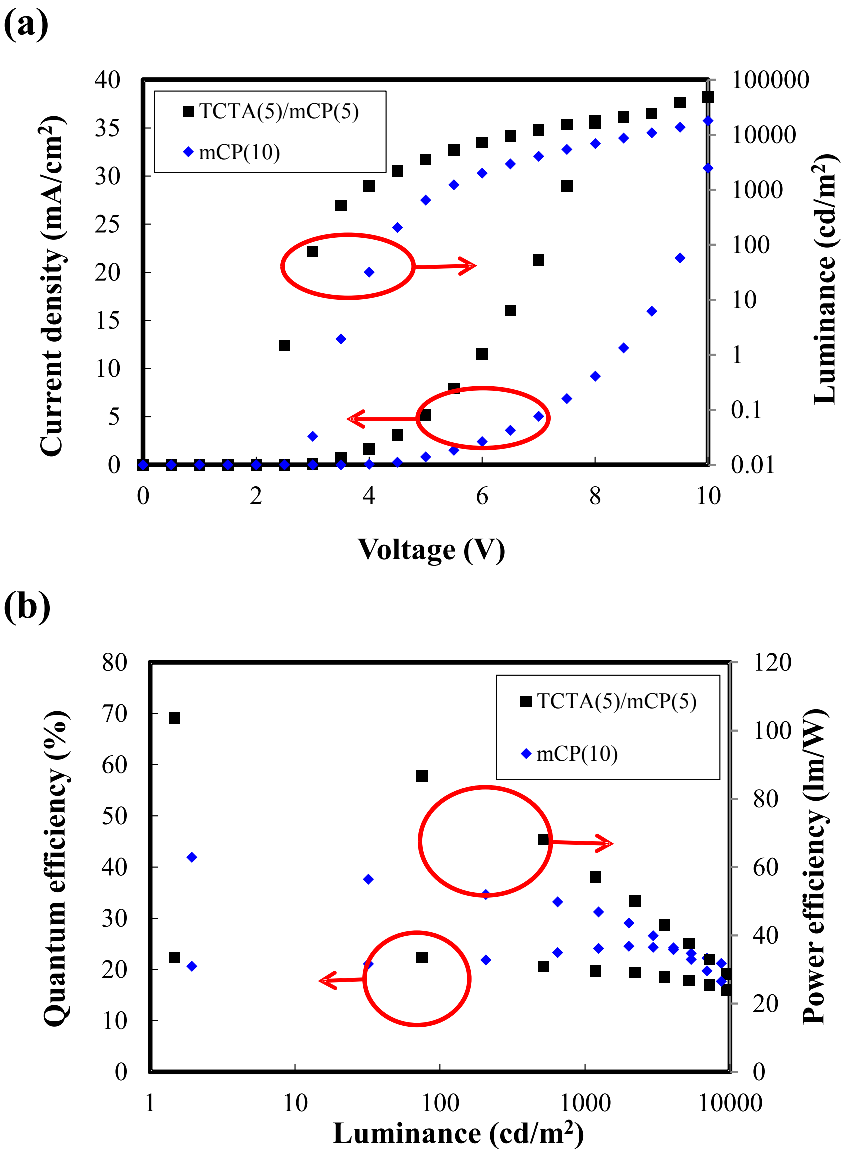
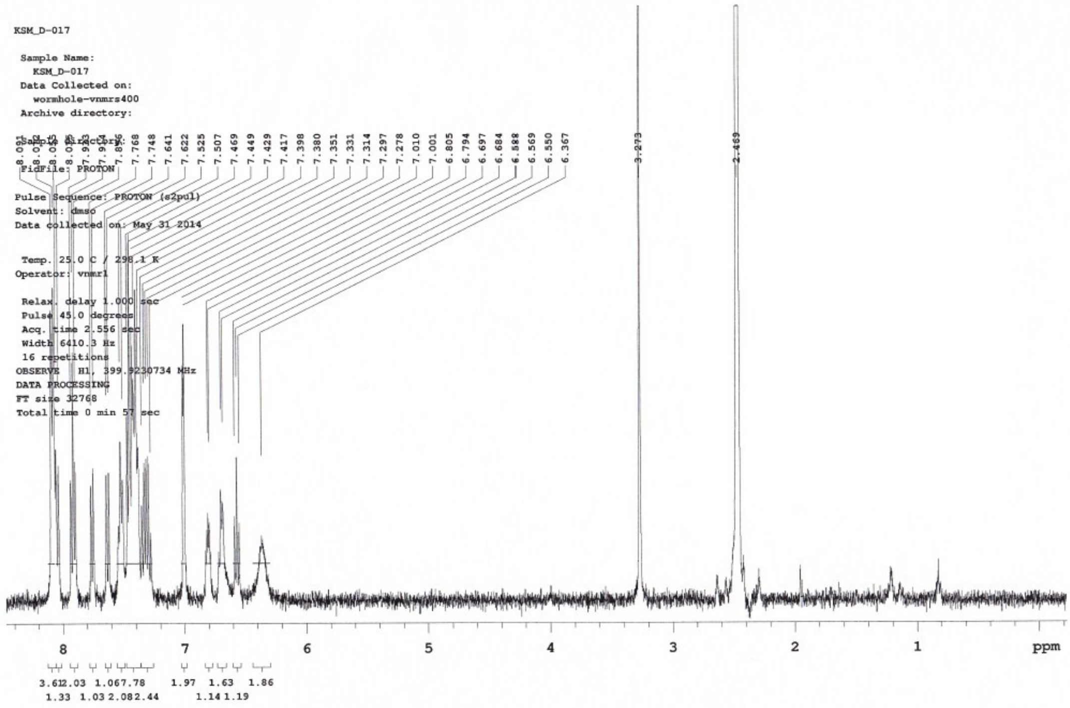
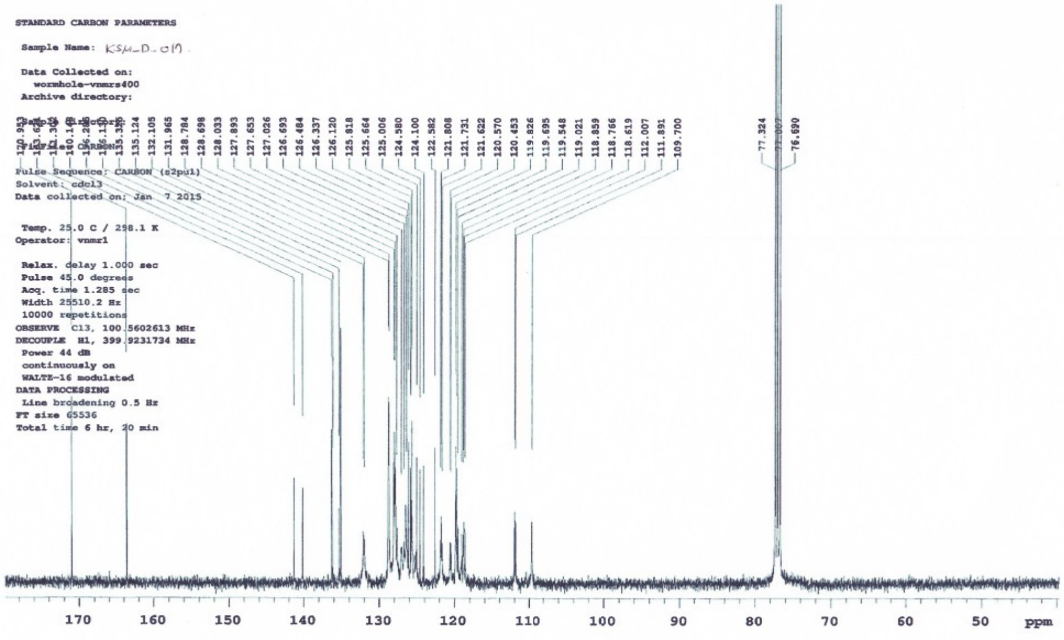

(a)
TCTA(5)/mCP(5)
mCP(10)
Current density (mA/cm²)
40
35
30
25
20
15
10
5
0
Luminance (cd/m²)
100000
10000
1000
100
10
1
0.1
0.01
0
2
4
6
8
10
Voltage (V)
(b)
TCTA(5)/mCP(5)
mCP(10)
Quantum efficiency (%)
80
70
60
50
40
30
20
10
0
Power efficiency (lm/W)
120
100
80
60
40
20
0
1
10
100
1000
10000
Luminance (cd/m²)

Figure S5

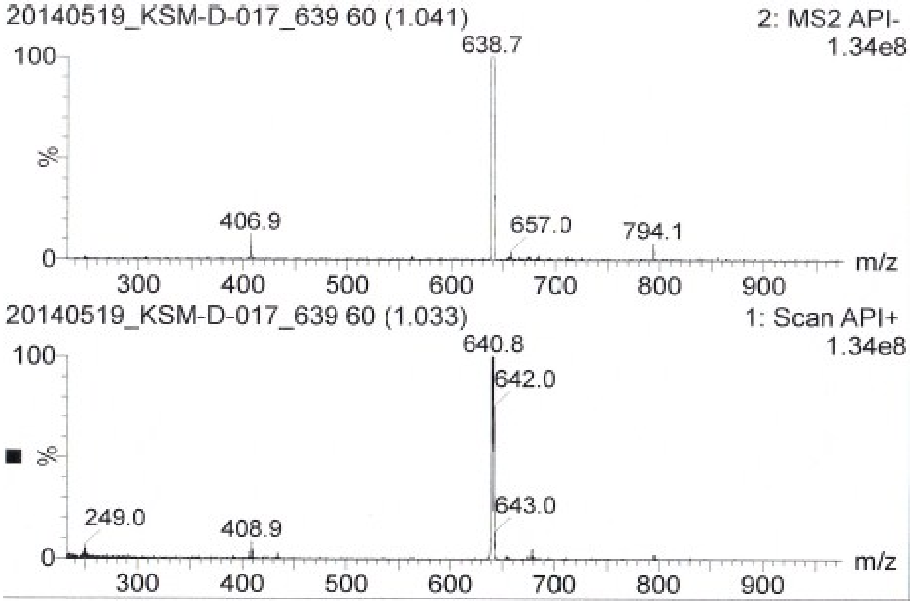
1H-NMR of 1-PCz-1-TCz



13C-NMR of 1-PCz-1-TCz



Mass of 1-PCz-1-TCz



HPLC spectra of 1-PCz-1-TCz

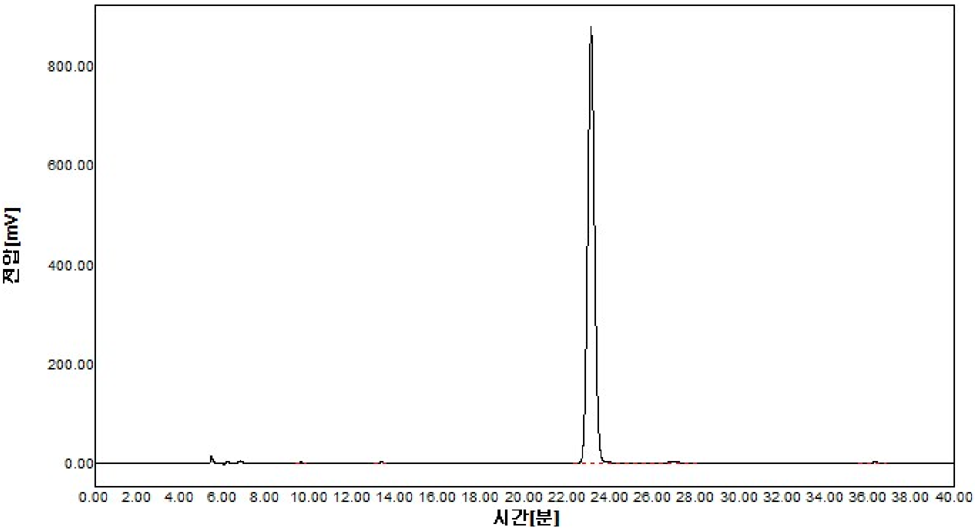
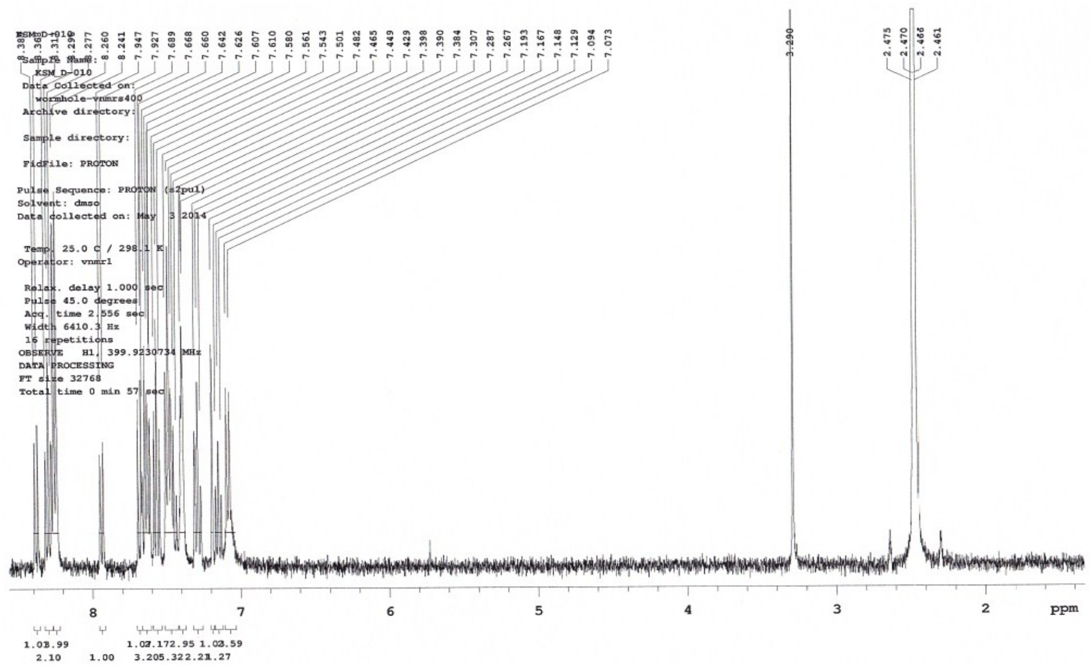
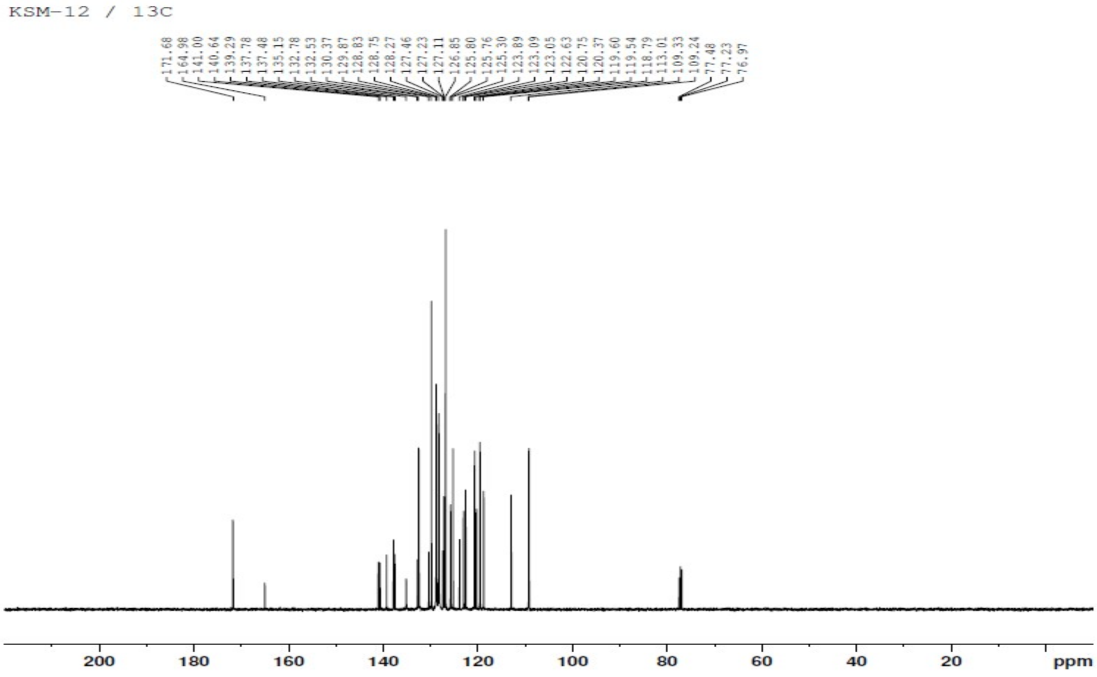


Figure S6

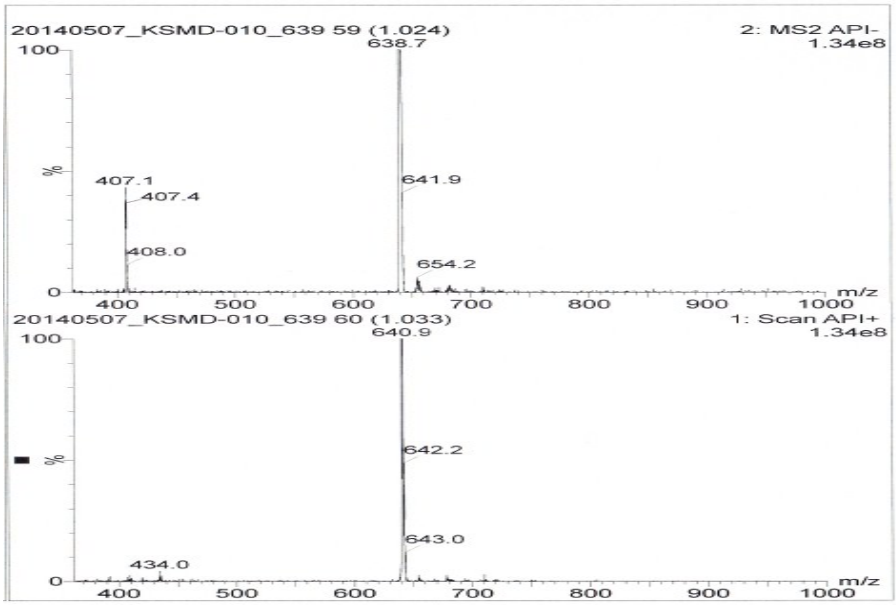
1H-NMR of 2-PCz-1-TCz



13C-NMR of 2-PCz-1-TCz



Mass of 2-PCz-1-TCz



HPLC spectra of 2-PCz-1-TCz

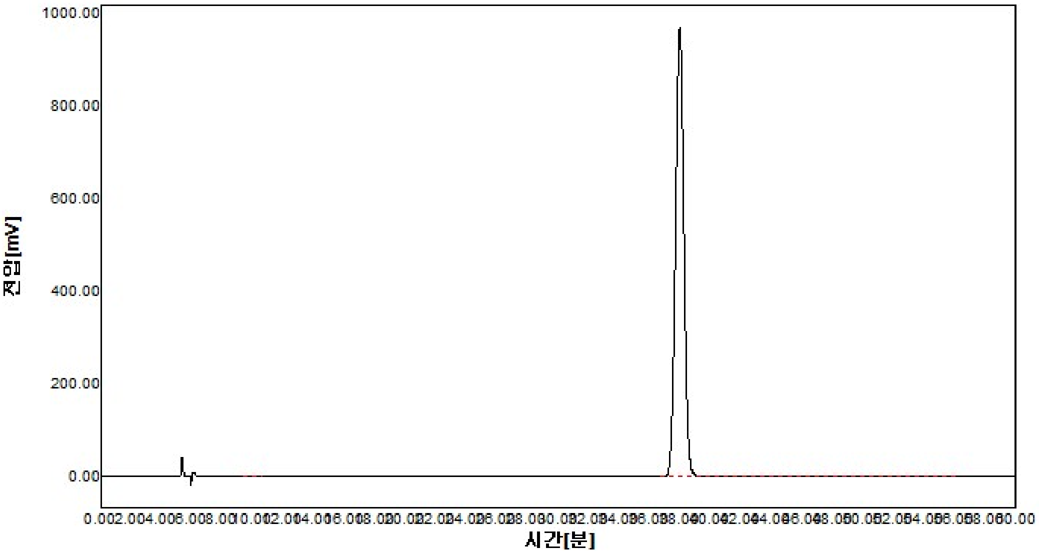
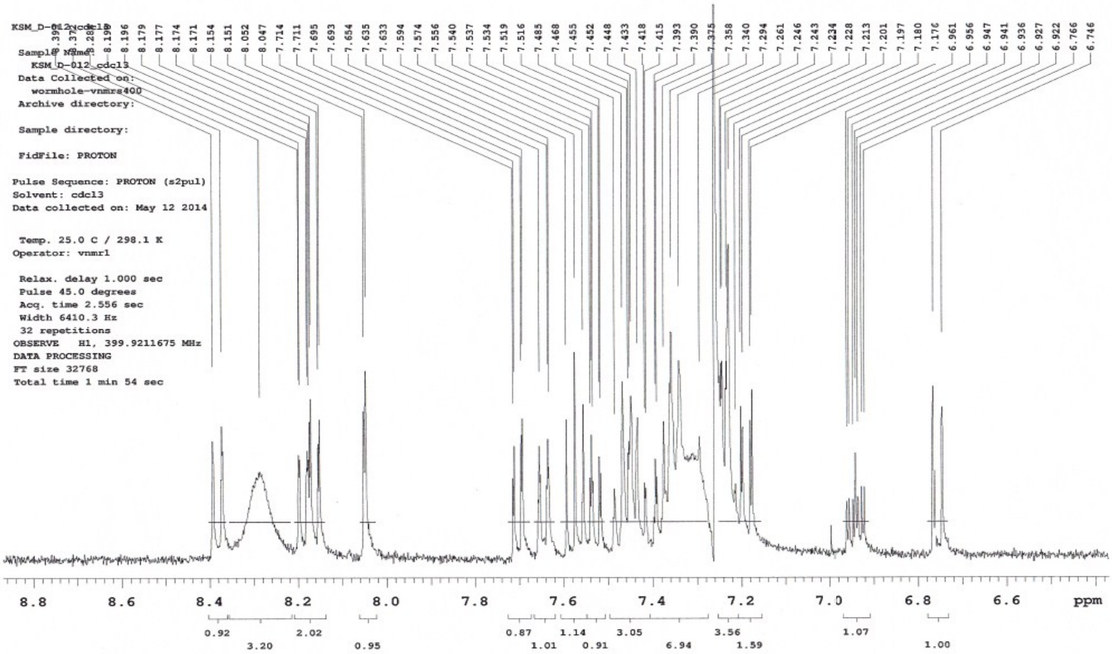
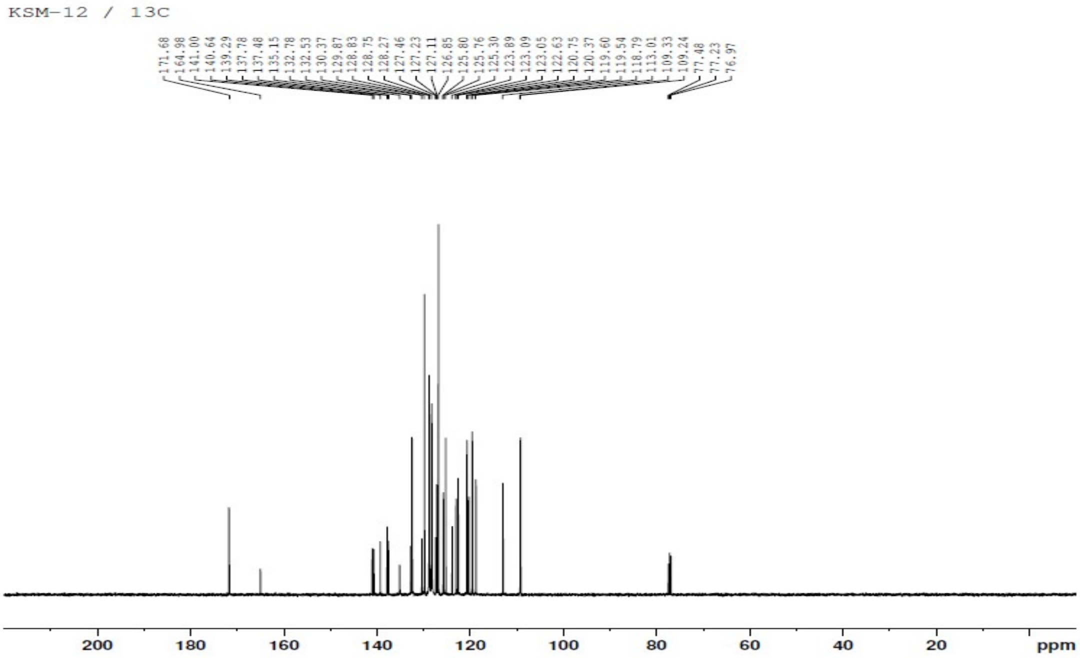


Figure S7

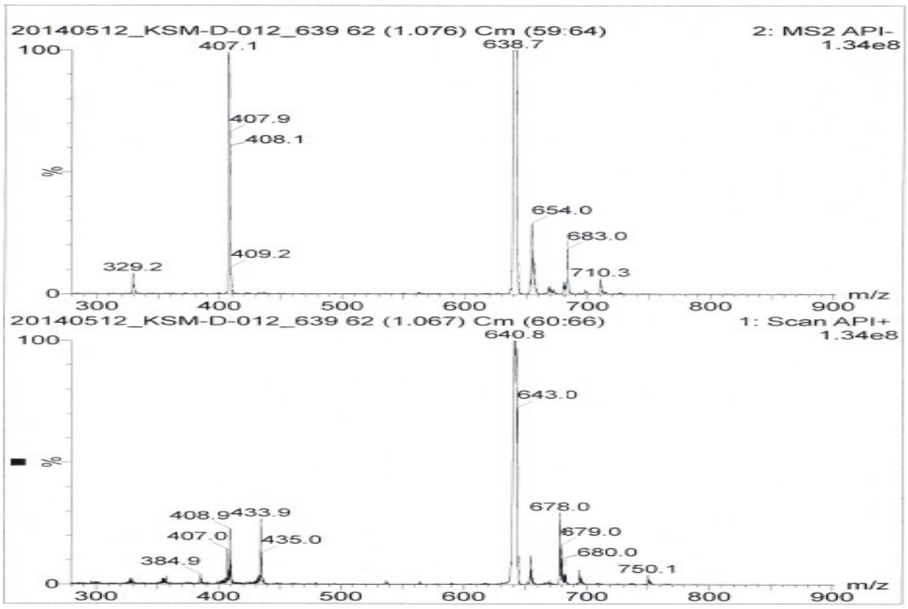
1H-NMR of 3-PCz-1-TCz



13C-NMR of 3-PCz-1-TCz



Mass of 3-PCz-1-TCz



HPLC spectra of 3-PCz-1-TCz

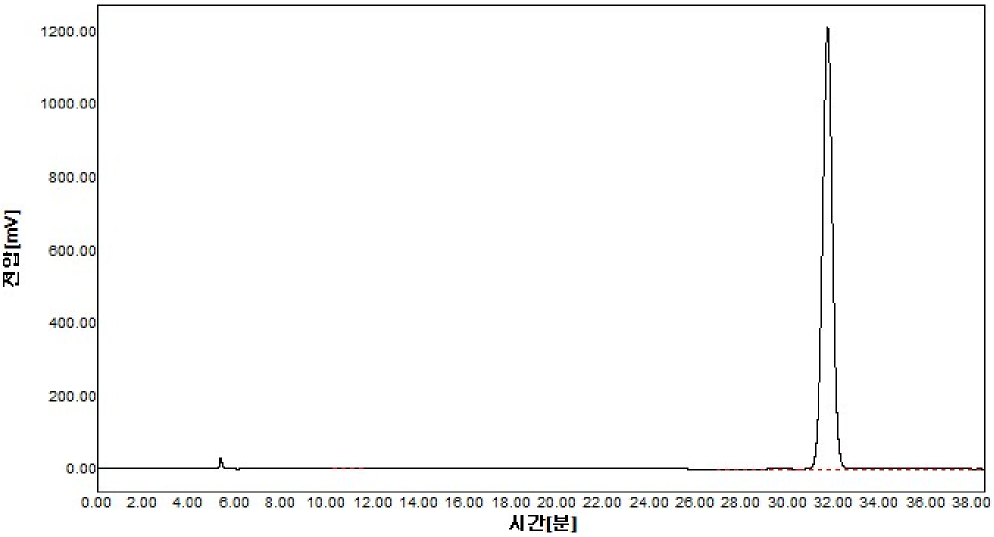
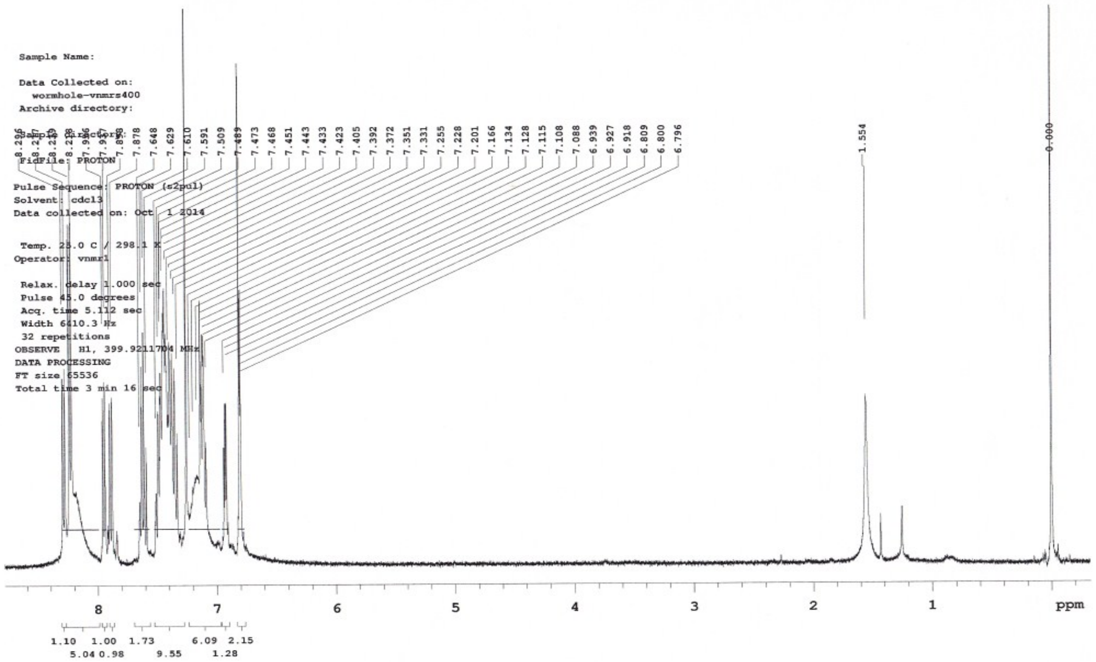
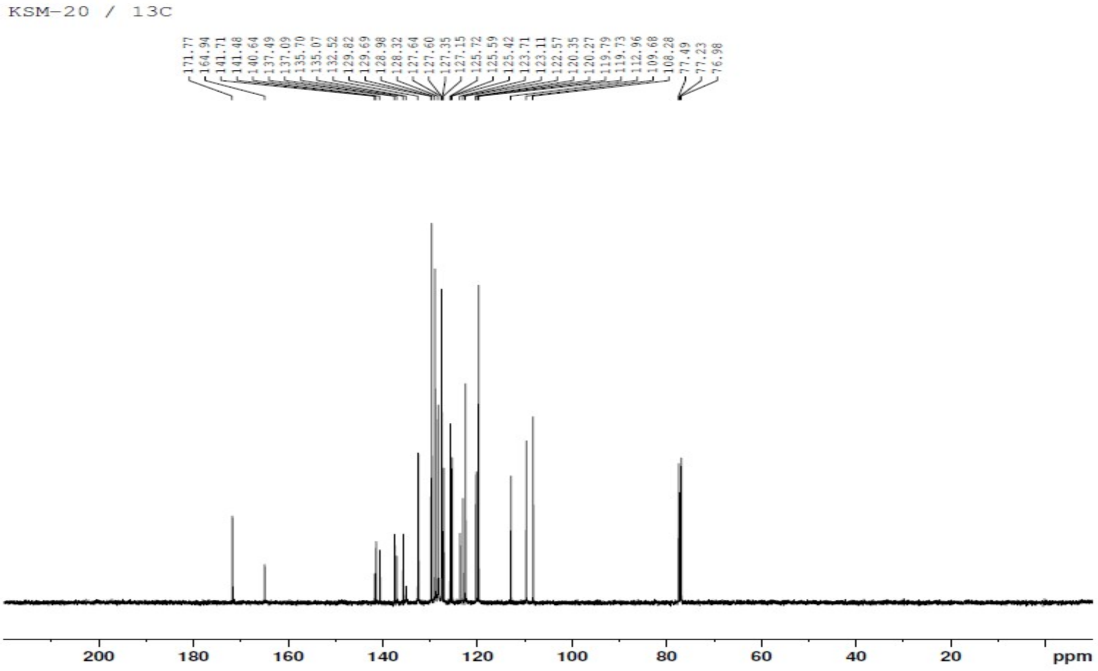


Figure S8

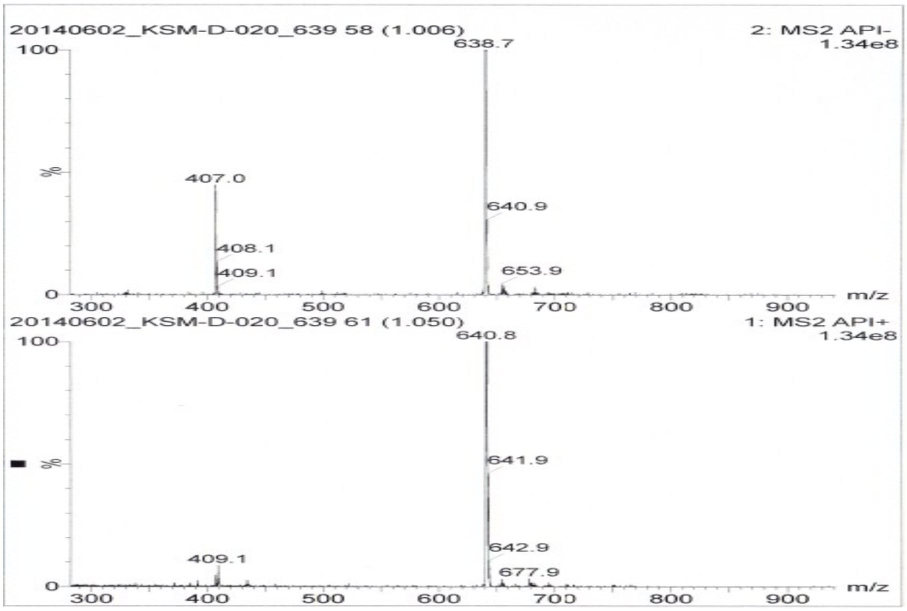
1H-NMR of 4-PCz-1-TCz



13C-NMR of 4-PCz-1-TCz



Mass of 4-PCz-1-TCz



HPLC spectra of 4-PCz-1-TCz

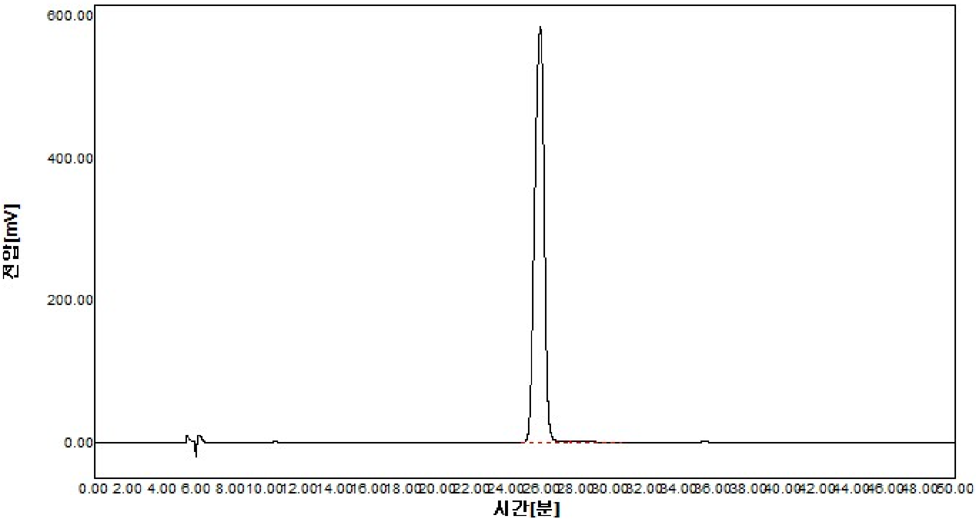


Figure S9