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Supporting information

Selective decoration of dibenzofuran with multi-donors and a triazine acceptor for triplet to singlet up-conversion

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Experimental

General information

Cyanuric chloride and n-butyllithium were supplied from Sigma Aldrich Co.. 9H-carbazole-3-carbonitrile and tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) were purchased from P&H Tech Co.. Potassium carbonate from Daejung Chemicals & Metals Co. LTD. and tetrahydrofuran (THF), methylene chloride (MC), acetone, toluene, methanol from Samchun Pure Chemical Co. were used without purification. THF was dehydrated with calcium hydride and sodium.

Synthesis

2-Bromo-3,4,5,6-tetrafluoro-2'-methoxy-1,1'-biphenyl

9H-carbazole-3-carbonitrile (0.50 g, 2.60 mmol) was dissolved in distilled THF (20 ml) and cooled down to 0 °C under a N_2 gas. After 30 min, n-butyllithium (0.18 g, 2.86 mmol) was added dropwisely and stirred for 30 min. The reagent was dropped into the cyanuric chloride (0.47 g, 2.60 mmol) dissolved in THF (20 ml). After stirring for 10 min, the reaction solution was quenched with distilled water and extracted with MC. The organic solvent was removed under a vacuum condition and the crude product was washed with acetone. A white powder was obtained as a product (0.51 g, yield 58.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.504 (td, 1H, J=7.8, 1.8 Hz), 7.189 (dd, 1H, J=7.5, 1.8 Hz), 7.132-7.051 (m, 2H), 3.822 (s, 3H). LC/MS (m/z): found, 334.99 ($[M + H]^+$); Calcd. for $C_{13}H_7BrF_4O$, 333.96.

2'-Bromo-3',4',5',6'-tetrafluoro-[1,1'-biphenyl]-2-ol

9H-carbazole-3-carbonitrile (0.50 g, 2.60 mmol) was dissolved in distilled THF (20 ml) and cooled down to 0 °C under a N_2 gas. After 30 min, n-butyllithium (0.18 g, 2.86 mmol) was added dropwisely and stirred for 30 min. The reagent was dropped into the cyanuric chloride (0.47 g, 2.60 mmol) dissolved in THF (20 ml). After stirring for 10 min, the reaction solution was quenched with distilled water and extracted with MC. The organic solvent was removed under a vacuum condition and the crude product was washed with acetone. An ivory powder was obtained as a product (0.51 g, yield 58.0%).

LC/MS (m/z): found, 321.16 ($[M + H]^+$); Calcd. for $C_{12}H_5BrF_4O$, 319.95.

1-Bromo-2,3,4-trifluorodibenzo[b,d]furan

9H-carbazole-3-carbonitrile (0.50 g, 2.60 mmol) was dissolved in distilled THF (20 ml) and cooled down to 0 °C under a N_2 gas. After 30 min, n-butyllithium (0.18 g, 2.86 mmol) was added dropwisely and stirred for 30 min. The reagent was dropped into the cyanuric chloride

(0.47 g, 2.60 mmol) dissolved in THF (20 ml). After stirring for 10 min, the reaction solution was quenched with distilled water and extracted with MC. The organic solvent was removed under a vacuum condition and the crude product was washed with acetone. The product was obtained as a white powder (0.51 g, yield 58.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.428 (dd, 1H, J=8.4, 0.6 Hz), 7.642-7.532 (m, 2H), 7.443 (td, 1H, J=7.5, 1.2 Hz). LC/MS (m/z): found, 300.06 ($[M + H]^+$); Calcd. for $C_{12}H_4BrF_3O$, 299.94.

4,4,5,5-Tetramethyl-2-(2,3,4-trifluorodibenzo[b,d]furan-1-yl)-1,3,2-dioxaborolane

9H-carbazole-3-carbonitrile (0.50 g, 2.60 mmol) was dissolved in distilled THF (20 ml) and cooled down to 0 °C under a N_2 gas. After 30 min, n-butyllithium (0.18 g, 2.86 mmol) was added dropwisely and stirred for 30 min. The reagent was dropped into the cyanuric chloride (0.47 g, 2.60 mmol) dissolved in THF (20 ml). After stirring for 10 min, the reaction solution was quenched with distilled water and extracted with MC. The organic solvent was removed under a vacuum condition and the crude product was washed with acetone. A yellowish white powder was obtained as a product (0.51 g, yield 58.0%).

LC/MS (m/z): found, 340.25 ($[M + H]^+$); Calcd. for $C_{18}H_{16}BF_3O_3$, 348.11.

2,4-Diphenyl-6-(2,3,4-trifluorodibenzo[b,d]furan-1-yl)-1,3,5-triazine

9H-carbazole-3-carbonitrile (0.50 g, 2.60 mmol) was dissolved in distilled THF (20 ml) and cooled down to 0 °C under a N_2 gas. After 30 min, n-butyllithium (0.18 g, 2.86 mmol) was added dropwisely and stirred for 30 min. The reagent was dropped into the cyanuric chloride (0.47 g, 2.60 mmol) dissolved in THF (20 ml). After stirring for 10 min, the reaction solution was quenched with distilled water and extracted with MC. The organic solvent was removed under a vacuum condition and the crude product was washed with acetone. A white powder was obtained as a product (0.51 g, yield 58.0%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.745 (d, 1H, J=7.8 Hz), 8.644-8.612 (m, 4H), 7.676-7.522 (m, 9H). LC/MS (m/z): found, 453.49 ($[M + H]^+$); Calcd. for $C_{27}H_{14}F_3N_3O$, 453.11.

9,9',9''-(1-(4,6-Diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan-2,3,4-triyl)tris(9H-carbazole) (3CzDBFTrz)

9-(4,6-Dichloro-1,3,5-triazin-2-yl)-9H-carbazole-3-carbonitrile (0.50 g, 1.47 mmol) and triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1.50 g, 3.23 mmol) were dissolved in THF (20 ml). 2M potassium carbonate aqueous solution (10 ml) and $Pd(PPh_3)_4$ (0.085 g, 0.07 mmol) were added in the solution and refluxed overnight. The mixture was extracted with MC and purified by column chromatography, recrystallization with toluene/methanol and vacuum train sublimation. The product was obtained as a white powder (0.59 g, yield 42.8%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.966 (d, 4H, J=7.5 Hz), 7.878 (d, 1H, J=7.5 Hz), 7.810 (d, 2H, J=7.5 Hz), 7.567 (d, 1H, J=8.0 Hz), 7.529 (dd, 1H, J=7.5, 1.5 Hz), 7.505-7.445 (m, 4H), 7.370 (d, 2H, J=7.5 Hz), 7.332-7.301 (m, 6H), 7.221 (td, 1H, J=7.5, 1.0 Hz), 7.144 (d, 2H, J=8.0 Hz), 7.103-7.059 (m, 4H), 7.008 (td, 2H, J=7.0, 1.5 Hz), 6.958 (td, 2H, J=7.75, 1.0 Hz), 6.879 (t, 2H, J=7.5 Hz), 6.760 (t, 2H, J=7.25 Hz), 6.670 (td, 2H, J=7.75, 1.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.75, 171.56, 157.84, 153.07, 141.15, 139.59, 139.28, 135.14, 133.30, 132.92, 132.86, 132.00, 129.40, 129.08, 128.73, 125.45, 125.13, 125.03, 124.61, 124.18, 124.04, 123.95, 123.68, 123.58, 123.49, 122.95, 120.50, 120.08, 120.05, 119.95, 119.89, 119.49, 112.64, 110.83, 110.62, 110.47. HRMS (FAB+) m/z 895.3185 [(M+H)+]; Calcd. For $C_{63}H_{38}N_6O$, 895.3190.

9,9',9''-(1-(4,6-Diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan-2,3,4-triyl)tris(3,6-dimethyl-9H-carbazole) (3mCzDBFTrz)

9-(4,6-Dichloro-1,3,5-triazin-2-yl)-9H-carbazole-3-carbonitrile (0.50 g, 1.47 mmol) and triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1.50 g, 3.23 mmol) were dissolved in THF (20 ml). 2M potassium carbonate aqueous solution (10 ml) and $Pd(PPh_3)_4$ (0.085 g, 0.07 mmol) were added in the solution and refluxed overnight. The mixture was extracted with MC and purified by column chromatography, recrystallization with toluene/methanol and vacuum train sublimation. The product was obtained as a white powder (0.59 g, yield 42.8%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.947 (dd, 4H, J=8.5, 1.0 Hz), 7.785 (d, 1H, J=8.0 Hz), 7.577 (s, 2H), 7.508-7.443 (m, 4H), 7.323 (t, 4H, J=8.0 Hz), 7.178-7.135 (m, 7H), 7.045 (d, 2H, J=8.5 Hz), 6.924 (d, 2H, J=8.5 Hz), 6.815 (dd, 2H, J=8.5, 1.0 Hz), 6.754 (dd, 2H, J=8.5, 1.5 Hz), 6.511 (dd, 2H, J=8.5, 1.5 Hz), 2.392 (s, 6H), 2.240 (s, 6H), 2.185 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.68, 171.59, 157.71, 152.99, 140.19, 138.38, 138.19, 135.33, 134.03, 132.70, 132.59, 132.50, 129.37, 129.13, 129.02, 128.71, 128.63, 128.58, 126.55, 126.22, 125.81, 124.44, 124.08, 123.95, 123.81, 123.70, 123.68, 123.02, 119.98, 119.95, 119.47, 112.55, 110.48, 110.33, 110.29. HRMS (FAB+) m/z 979.4124 [(M+H)+]; Calcd. For $C_{69}H_{51}N_6O$, 979.4125.

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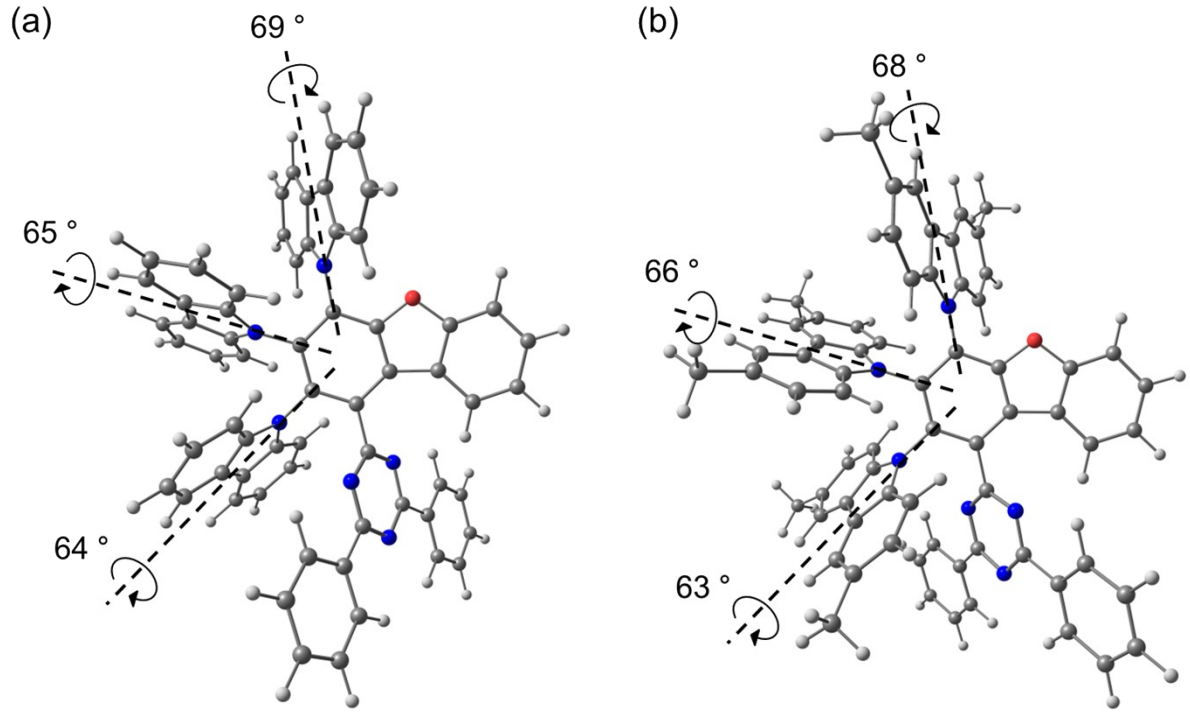


Figure S1. Dihedral angle of carbazoles of (a) 3CzDBFTrz and (b) 3mCzDBFTrz

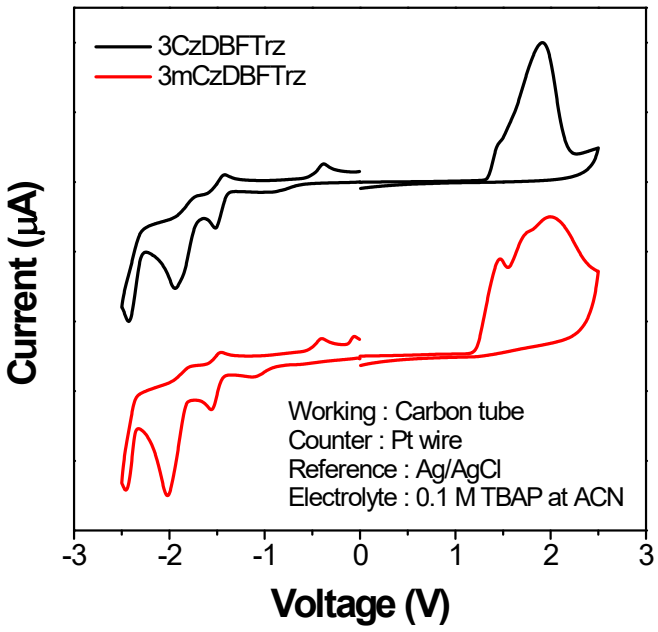


Figure S2. Cyclic voltammetry curves of 3CzDBFTrz and 3mCzDBFTrz

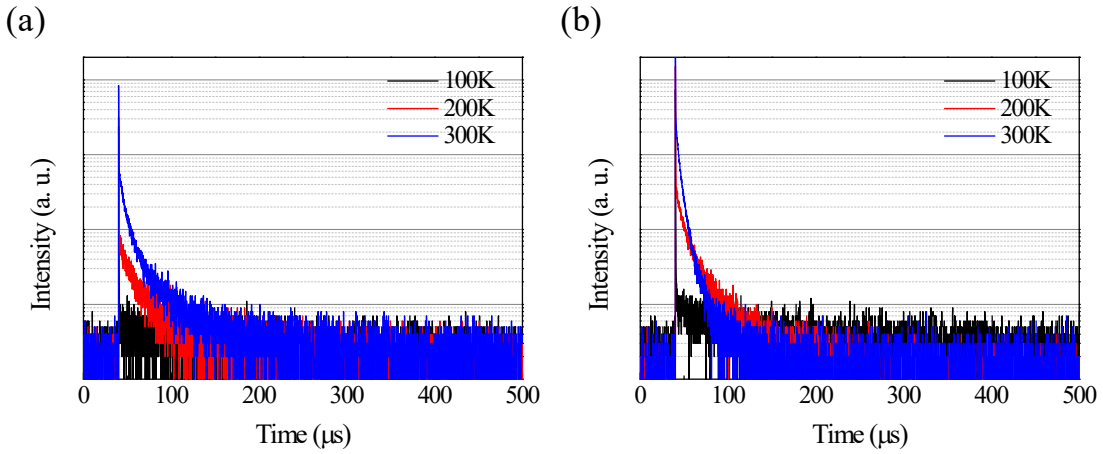


Figure S3. Temperature dependence delayed emission of (a) 3CzDBFTrz and (b) 3mCzDBFTrz

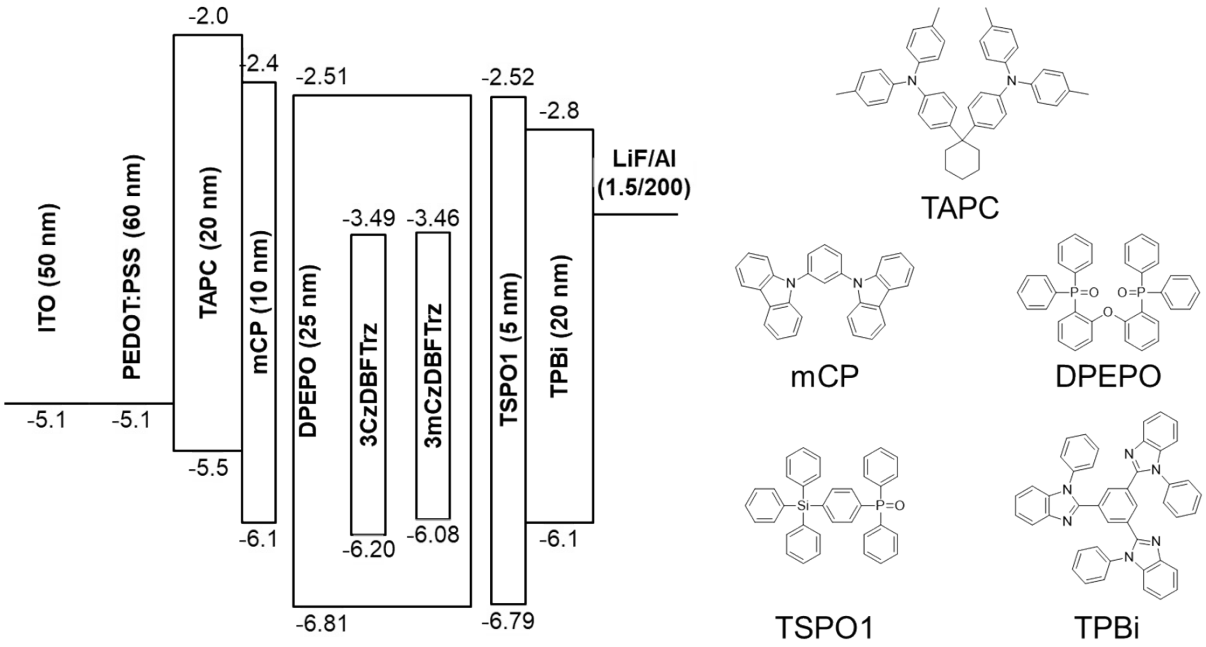
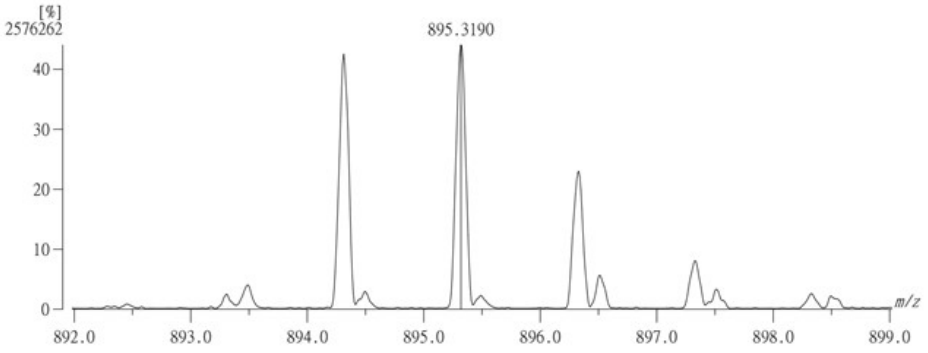


Figure S4. Energy level diagram of the device and chemical structure.

(a)

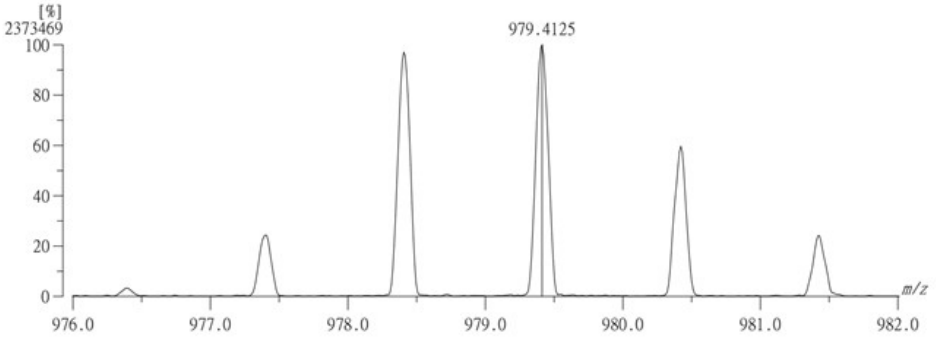
[Mass Spectrum]
Data : FAB-D560 Date : 03-Jun-2022 17:20
RT : 1.98 min Scan# : (47,69)+(60,79)
Elements : C 100/0, H 100/0, N 10/0, O 5/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : 30.0 – 60.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	895.3190	44.03	-5.5 / -4.9	51.0	C70 H41 N
2			+8.6 / +7.7	51.5	C69 H39 N2
3			+2.0 / +1.8	48.0	C61 H37 N9
4			+0.5 / +0.5	47.5	C63 H39 N6 O
5			-1.0 / -0.9	47.0	C65 H41 N3 O2
6			-7.5 / -6.7	43.5	C57 H39 N10 O2
7			-2.5 / -2.2	46.5	C67 H43 O3
8			-9.0 / -8.1	43.0	C59 H41 N7 O3
9			+5.0 / +4.5	43.5	C58 H39 N8 O3
10			+3.5 / +3.1	43.0	C60 H41 N5 O4
11			+2.0 / +1.8	42.5	C62 H43 N2 O5
12			-4.5 / -4.1	39.0	C54 H41 N9 O5
13			+9.5 / +8.5	39.5	C53 H39 N10 O5

(b)

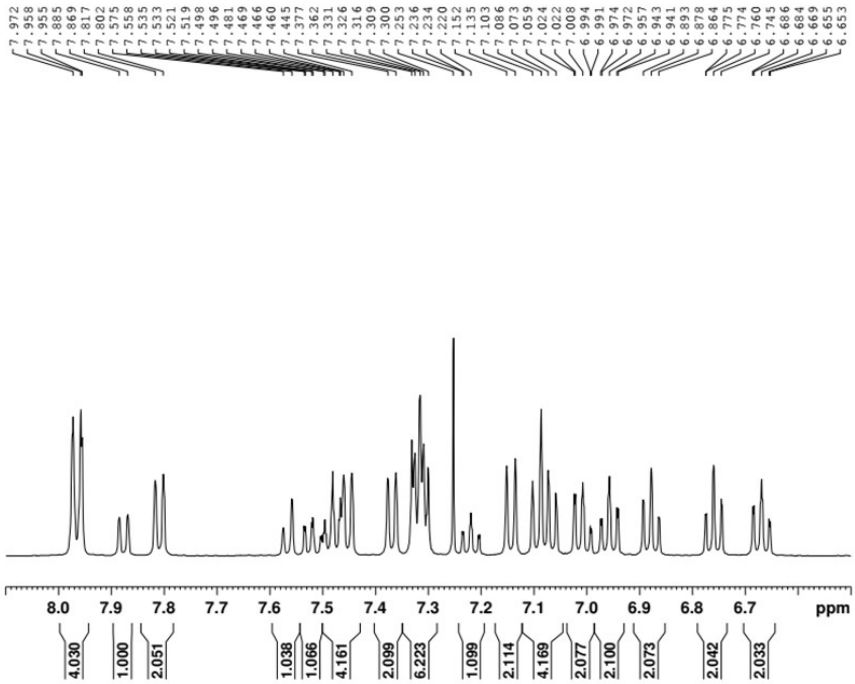
[Mass Spectrum]
Data : FAB-D561 Date : 03-Jun-2022 17:33
RT : 0.62 min Scan# : (15,25)
Elements : C 100/0, H 100/0, N 10/0, O 5/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : 20.0 – 60.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	979.4125	100.00	-5.4 / -5.3	51.0	C76 H53 N
2			+7.4 / +7.3	51.5	C75 H51 N2
3			+1.4 / +1.4	48.0	C67 H49 N9
4			+0.1 / +0.1	47.5	C69 H51 N6 O
5			-1.3 / -1.3	47.0	C71 H53 N3 O2
6			-7.3 / -7.1	43.5	C63 H51 N10 O2
7			-2.7 / -2.6	46.5	C73 H55 O3
8			-8.7 / -8.5	43.0	C65 H53 N7 O3
9			+4.2 / +4.1	43.5	C64 H51 N8 O3
10			+2.8 / +2.7	43.0	C66 H53 N5 O4
11			+1.4 / +1.4	42.5	C68 H55 N2 O5
12			-4.6 / -4.5	39.0	C60 H53 N9 O5
13			+8.3 / +8.1	39.5	C59 H51 N10 O5

Figure S5. HRMS data of (a) 3CzDBFTrz and (b) 3mCzDBFTrz

1H



13C

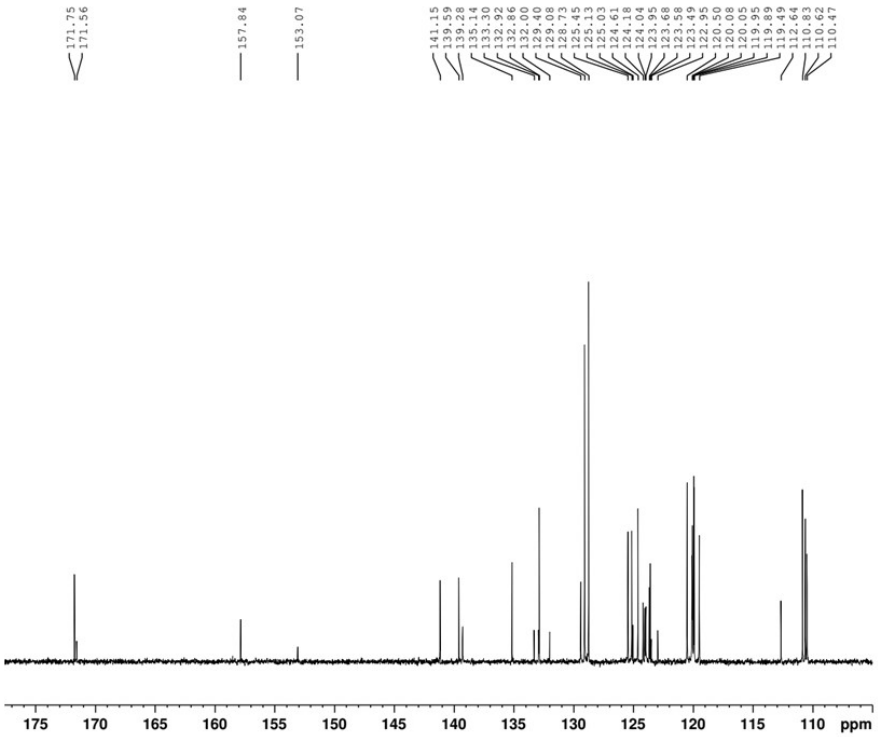


Figure S6. 1H and 13C NMR data of 3CzDBFTrz

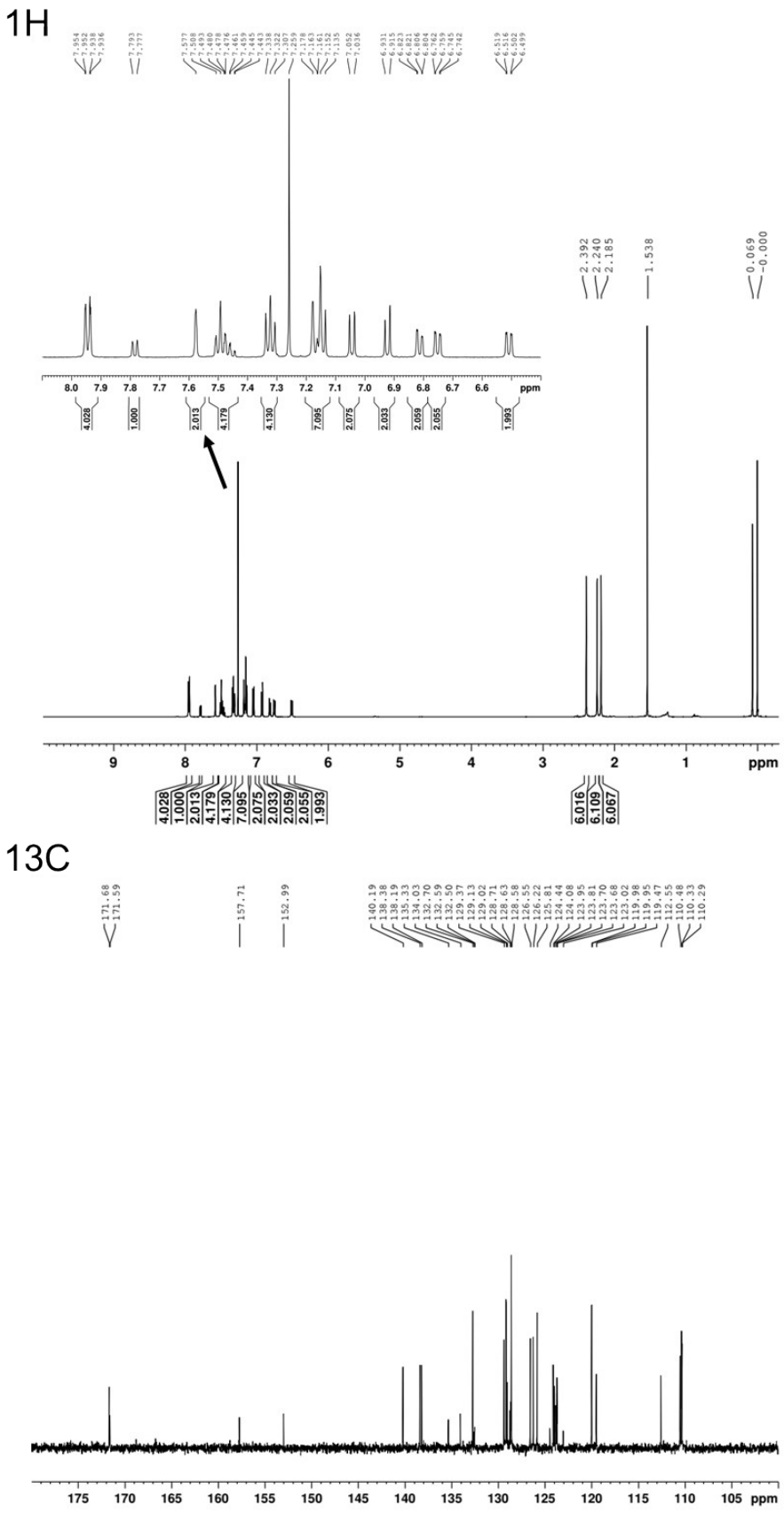


Figure S7. 1H and 13C NMR data of 3mCzDBFTrz