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Supporting Information

Combinatorial donor engineering for highly efficient blue thermally activated delayed fluorescence emitters with low efficiency roll-off

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Experimental

12*H*-benzofuro[3,2-*a*]carbazole was supplied from GOM tech. The ^{1}H and ^{13}C NMR spectra of synthesized compounds in deuterated $CDCl_3$ were identified using Unity Inova (Varian, 500 MHz) spectrometer. The molecular weight was measured by Advion, ExpresionL CMS spectrometer in APCI mode. The PL spectra of the compounds dissolved in 1.0×10^{-5} M tetrahydrofuran (THF) and toluene solution were obtained using a fluorescence spectrophotometer (PerkinElmer, LS-55). The triplet energy of compounds was measured by low temperature PL spectra at 77 K. The UV-vis absorptions spectra were observed using UV-vis spectrophotometer (JASCO, V-730) dissolved in 1.0 × 10-5 M THF solution. The CV measurements of the compounds were carried out by IVIUM STAT. The standard material was Ferrocene, working electrode was carbon electrode, reference electrode was Ag and counter electrode was Pt. PL quantum yield and transient PL decay data were recorded using

QuantaurusQY Absolute system (Hamamatsu, C11347-11) and Hamamatsu Quantaurus-Tau system (Hamamatsu, C11367-31).

Synthesis

6-Bromo-12H-benzofuro[3,2-a]carbazole

12H-benzofuro[3,2-a]carbazole (5 g, 19.43 mmol) and N-bromosuccinimide (4.50 g, 25.26mmol) were put into a two-neck round bottomed (RB) flask. The compound was stirred with magnetic bar with dimethyl formamide (DMF, 20 ml) solvent at room temperature. After 8 hours, the mixture was extracted with deionized water (DI water) and dichloromethane (MC) until organic material is completely separated from DI water. The crude organic material then was purified by column chromatography using an eluent of MC : hexane (1 : 4). The 6-bromo-12H-benzofuro[3,2-a]carbazole was obtained as a product. (5.22g, 80.0% yield)

^{1}H NMR (300 MHz, DMSO-d6) δ 12.17 (s, 1H), 8.71 – 8.51 (m, 2H), 8.23 (d, J = 7.7 Hz, 1H), 7.90 – 7.80 (m, 1H), 7.69 – 7.50 (m, 3H), 7.44 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H)

6-(9H-carbazol-9-yl)-12H-benzofuro[3,2-a]carbazole

6-Bromo-12H-benzofuro[3,2-a]carbazole (4.71 g, 14.00 mmol), 9H-carbazole (3.51 g, 21.00 mmol), sodium tert-butoxide (2.69 g, 28.00 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (0.67 g, 1.4 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.38 g, 0.42 mmol) were poured to a RB flask. The mixture undergoes reaction under a reflux condition for 6 hours with o-xylene (25 ml) solvent. Further work-up and purification processes were the same as those of 6-bromo-12H-benzofuro[3,2-a]carbazole. Finally, a new donor moiety of 6-(9H-carbazol-9-yl)-12H-benzofuro[3,2-a]carbazole was synthesized as a product. (1.6 g, 27.1% yield)

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.35 (s, 1H), 8.75 (d, J = 7.6 Hz, 1H), 8.58 (s, 1H), 8.27 (dd, J = 14.6, 7.7 Hz, 3H), 7.75 – 7.20 (m, 10H), 7.15 (d, J = 8.1 Hz, 2H)

6-(9H-carbazol-9-yl)-12-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-12H-benzofuro[3,2-a]carbazole (Trz-BFCzCz)

6-(9H-carbazol-9-yl)-12H-benzofuro[3,2-a]carbazole (0.3 g, 0.71 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (0.43g, 1.1 mmol), Tri-*tert*-butylphosphine in 50 wt% toluene solution (0.37 ml, 0.07 mmol), sodium tert-butoxide (0.14 g, 1.42 mmol), palladium(II) acetate (0.01 g, 0.04 mmol) were poured to two-neck RB flask. 1,4-Dioxane (5 ml) was poured to the RB flask and stirred with magnetic bar in reflux condition for 6 hours. Further work-up and purification processes were the same as those of 6-bromo-12H-benzofuro[3,2-a]carbazole. 6-(9H-carbazol-9-yl)-12-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-12H-benzofuro[3,2-a]carbazole was obtained as a product. (0.29 g, 62.6 % yield)

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.19 – 9.14 (m, 1H), 8.89 – 8.80 (m, 3H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 7.7 Hz, 1H), 8.16 – 8.11 (m, 1H), 7.79 – 7.74 (m, 1H), 7.73 – 7.67 (m, 2H), 7.56 – 7.52 (m, 1H), 7.49 – 7.40 (m, 3H), 7.37 – 7.33 (m, 1H), 7.31 – 7.27 (m, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 11.8, 4.5 Hz, 1H), 6.02 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 171.32, 170.29, 155.01, 151.51, 142.54, 141.79, 141.24, 136.00, 135.29, 134.84, 133.25, 130.61, 129.64, 129.58, 129.09, 128.83, 126.91, 126.30, 123.36, 123.21, 122.91, 122.71, 121.94, 121.39, 120.60, 120.56, 120.23, 120.01, 114.79, 111.69, 110.35, 110.02, 109.71.

HRMS (FAB+) m/z 729.2529 [(M+H)+]; Calcd. For C45H31N6, 729.2529.

9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-3,9'-bicarbazole (Trz-CzCz)

9H-3,9'-bicarbazole (0.5 g, 1.50 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (0.87 g, 2.25 mmol), Tri-*tert*-butylphosphine in 50 wt% toluene solution (1.22 ml, 0.23 mmol), Sodium tert-butoxide (0.29 g, 3.00 mmol), Palladium(II) acetate (0.02 g, 0.08 mmol) were poured to two neck RB flask. 5ml of 1,4-dioxane was poured to RB flask and stirred with magnetic bar in reflux condition for 6 hours. Further work-up and purification processes were same as 6-bromo-12H-benzofuro[3,2-a]carbazole purification.

9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-3,9'-bicarbazole was obtained as a product. (0.61 g, 71.3 % yield)

^{1}H NMR (500 MHz, DMSO) δ 9.09 (d, J = 8.5 Hz, 1H), 8.85 – 8.78 (m, 2H), 8.61 (d, J = 2.0 Hz, 1H), 8.41 (d, J = 7.9 Hz, 1H), 8.29 (d, J = 7.7 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.78 – 7.63 (m, 4H), 7.57 (t, J = 7.7 Hz, 1H), 7.46 (t, J = 7.1 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.31 (t, J = 7.4 Hz, 1H).

^{13}C NMR (176 MHz, DMSO) δ 167.15, 166.14, 137.12, 136.54, 136.46, 134.86, 131.39, 130.70, 127.97, 126.07, 125.64, 124.30, 124.00, 122.16, 122.08, 121.15, 120.97, 120.09, 118.60, 118.44, 116.11, 115.98, 115.56, 114.93, 114.86, 106.29, 105.55, 105.06.

HRMS (FAB+) m/z 639.2429 [(M+H)+]; Calcd. For C45H31N6, 639.2429.

12-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-12H-benzofuro[3,2-a]carbazole (Trz-BFCz)

12H-benzofuro[3,2-a]carbazole (0.5 g, 1.94 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.13 g, 2.91 mmol), Tri-*tert*-butylphosphine in 50 wt% toluene solution (1.54ml, 0.29 mmol), Sodium tert-butoxide (0.37 g, 3.88 mmol), Palladium(II) acetate (0.02 g, 0.10 mmol) were poured to two neck RB flask. 5ml of 1,4-dioxane was poured to RB flask and stirred with magnetic bar in reflux condition for 6 hours. Further work-up and purification processes were same as 6-bromo-12H-benzofuro[3,2-a]carbazole purification.

12-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-12H-benzofuro[3,2-a]carbazole was obtained as a product. (0.65 g, 68.3 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 – 9.05 (m, 1H), 8.82 (dd, *J* = 5.2, 3.2 Hz, 3H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 7.81 (dd, *J* = 6.1, 4.4 Hz, 1H), 7.66 – 7.52 (m, 6H), 7.45 – 7.35 (m, 2H), 7.28 – 7.23 (m, 1H), 7.16 (dd, *J* = 10.8, 6.0 Hz, 1H), 6.88 (td, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.12, 170.95, 156.83, 155.96, 143.41, 142.02, 136.52, 136.26, 136.04, 132.95, 130.78, 129.30, 129.26, 128.95, 128.44, 126.07, 125.51, 125.45, 124.37, 123.68, 122.80, 122.63, 121.18, 119.88, 119.75, 119.66, 111.30, 110.39, 109.21, 105.36.

HRMS (FAB+) m/z 564.1949 [(M+H)+]; Calcd. For C45H31N6, 564.1949.

Table S1. Calculated Rate constants of Trz-CzCz, Trz-BFCz and Trz-BFCzCz.

	τ_p[c] [ns]	k_p [x10^7 s^{-1}]	τ_d[c] [μs]	k_d [x10^3 s^{-1}]	PLQY[a] / [b] [%]	k_{ISC} [x10^7 s^{-1}]	k_{RISC} [x10^4 s^{-1}]	k_r [x10^7 s^{-1}]	k_{nr} [x10^3]
Trz-CzCz	14.2	7.04	106.28	9.41	33[a]/ 89[b]	2.80	2.48	2.24	1.52
Trz-BFCz	12.9	7.75	36.71	27.2	27[a] / 61[b]	5.64	4.65	2.11	14.6
Trz-BFCzCz	27.1	3.69	37.48	26.7	28[a] / 75[b]	2.68	6.37	1.01	9.20

[a] PLQY measured in 20 wt% doped DPEPO film under air. [b] PLQY measured in 20 wt% doped DPEPO film under nitrogen. [c] Fluorescence decay lifetimes are measured in 20 wt% doped DPEPO film.

Table S2. Summary of blue TADF OLEDs performances

	ΔE_{ST} [eV]	k_{RISC} [x10^5 s^{-1}]	CIE (x, y)	EQE[a] / [b] [%]	roll-off [%]	Ref.
Trz-BFCzCz	0.13	0.637	(0.18, 0.32)	23.3 / 13.1	43.8	This work
BisCz-Trz	0.06	-	(0.15, 0.20)	12.2 / 8.9	27.0	[1]
TrisCz-Trz	0.03	-	(0.15, 0.23)	11.3 / 9.2	18.6	[1]
DMAC2PTO	0.03	4.21	(0.155,0.107)	13.4 / -	-	[2]
TDBA-TPDICz	0.41	1.15	(0.14, 0.14)	16.9 / 3.5	79.3	[3]
MeMOC	0.25	16.8	(0.22, 0.42)	12.4 / 4.2	66.1	[4]
4CzCNPhPy	0.04	-	(0.15, 0.20)	13.7 / -	-	[5]
2SPAc-MPM	0.19	-	(0.17,0.29)	24.3 / 9.1	62.4	[6]
2SPAc-PPM	0.16	-	(0.18,0.32)	31.4 / 10.8	65.5	[6]
TrzBFCz	0.27	-	(0.15, 0.10)	18.0 / 8.0	55.6	[7]
TrzCNBFCz	0.13	-	(0.17, 0.31)	26.6 / 16.8	36.8	[7]
BTPAc	0.33	0.006	(0.18, 0.32)	19.0 / 1.3	93.2	[8]
BTPCNAc	0.15	4.89	(0.18, 0.41)	27.6 / 14.4	47.8	[8]
1PCTrz	0.16	0.397	(0.171 0.302)	26.7 / 11.7	56.2	[9]
2PCTrz	0.11	0.727	(0.182 0.348)	28.5 / 19.4	31.9	[9]
CzBM-2	0.01	-	(0.18, 0.24)	12.5 / -	-	[10]
CzPBM-3	0.15	-	(0.18, 0.19)	13.3 / -	-	[10]

[a] : EQE at maximum luminance [b] : EQE at 1000 cd/m^2

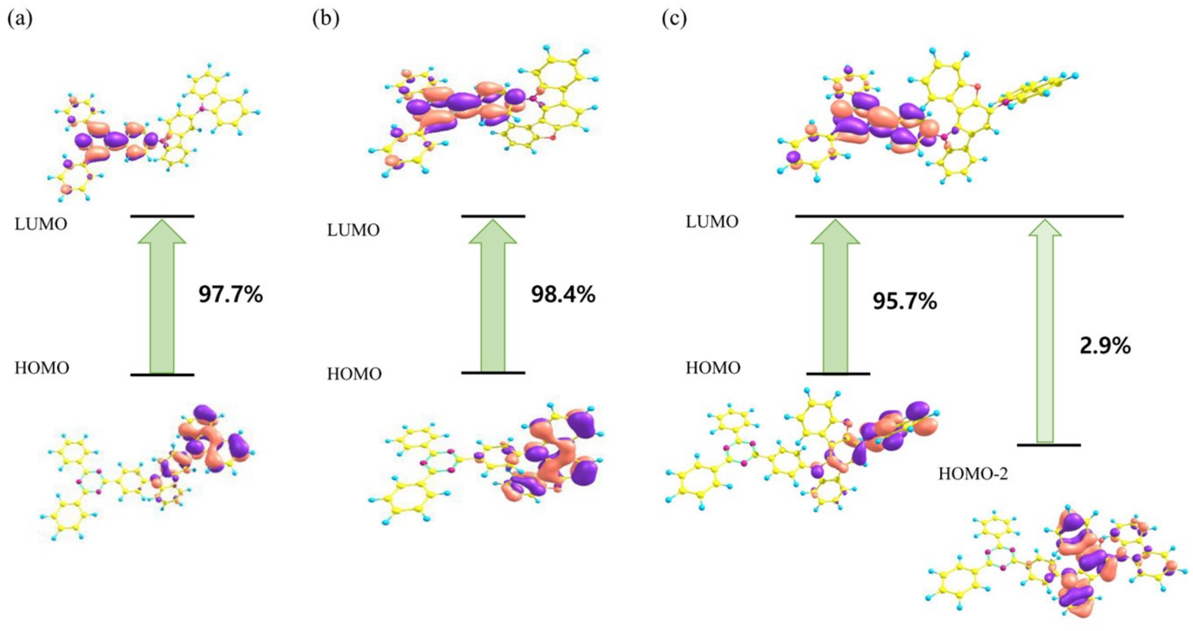
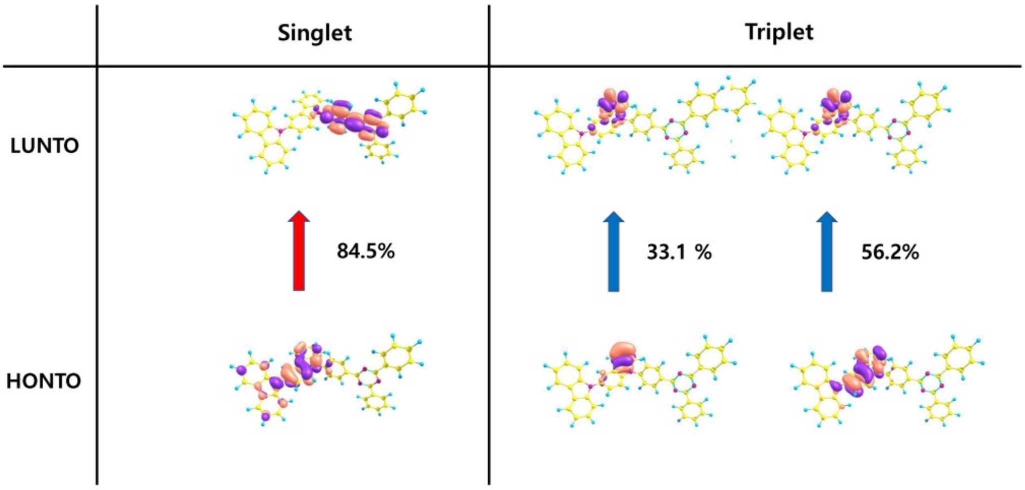


Figure S1. Vertical transition probabilities in S1 state for (a) Trz-CzCz, (b) Trz-BFCz and (c) Trz-BFCzCz.

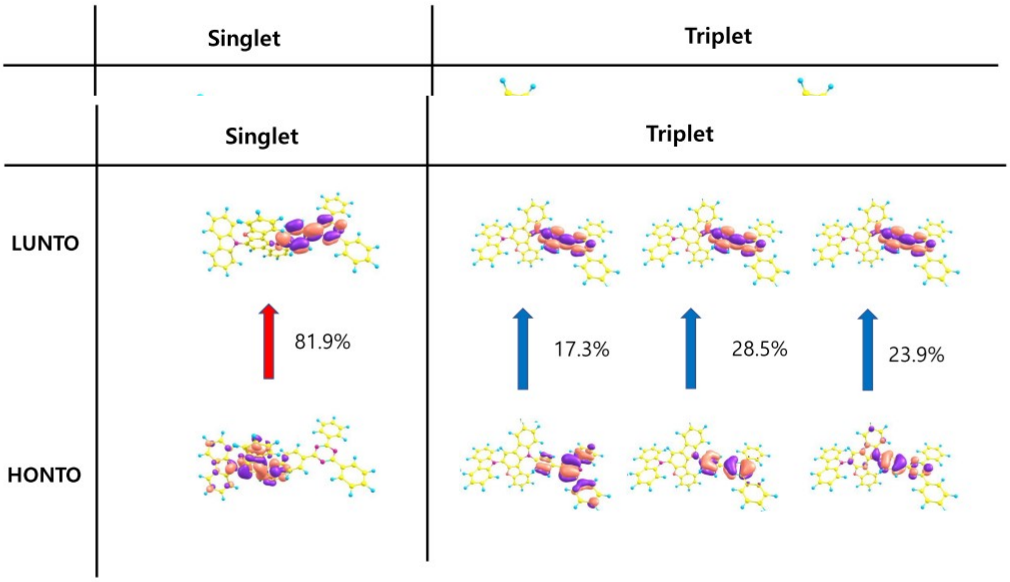


(a)

(b)

(c)

Figure S2. Natural transition orbital analysis of (a) Trz-CzCz, (b) Trz-BFCz and (c) Trz-BFCzCz.



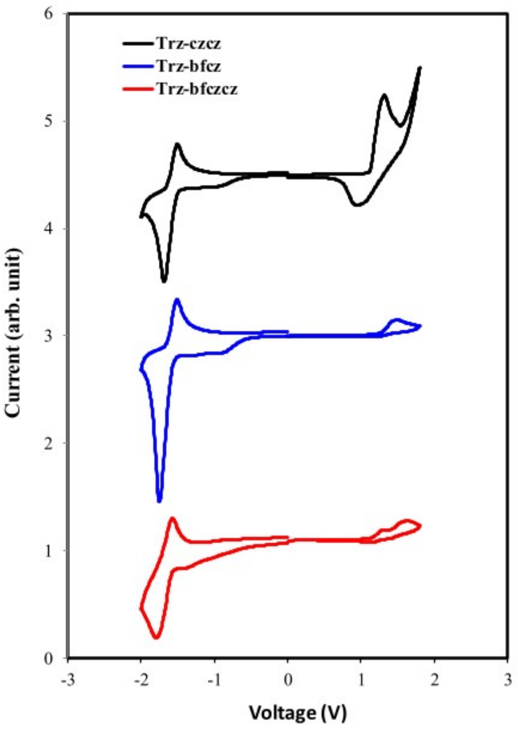


Figure S3. CV data of Trz-CzCz, Trz-BFCz and Trz-BFCzCz

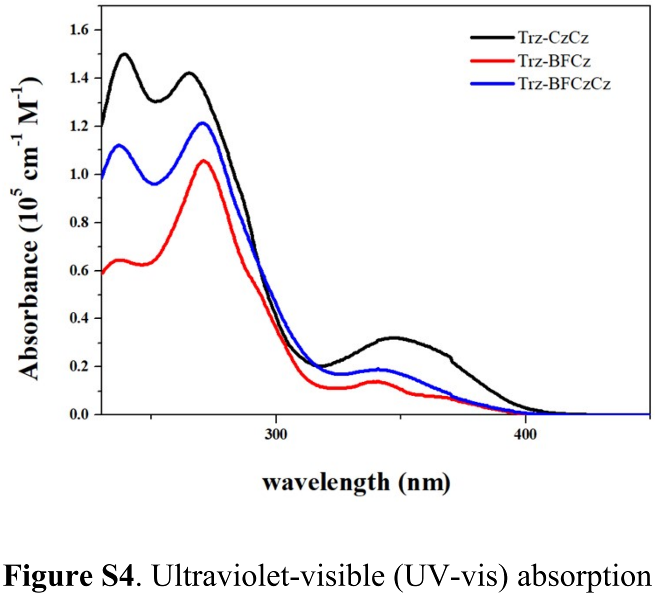


Figure S4. Ultraviolet-visible (UV-vis) absorption data of the emitters recorded using a dilute tetrahydrofuran solution (concentration of 1 × 10^{-5} M).

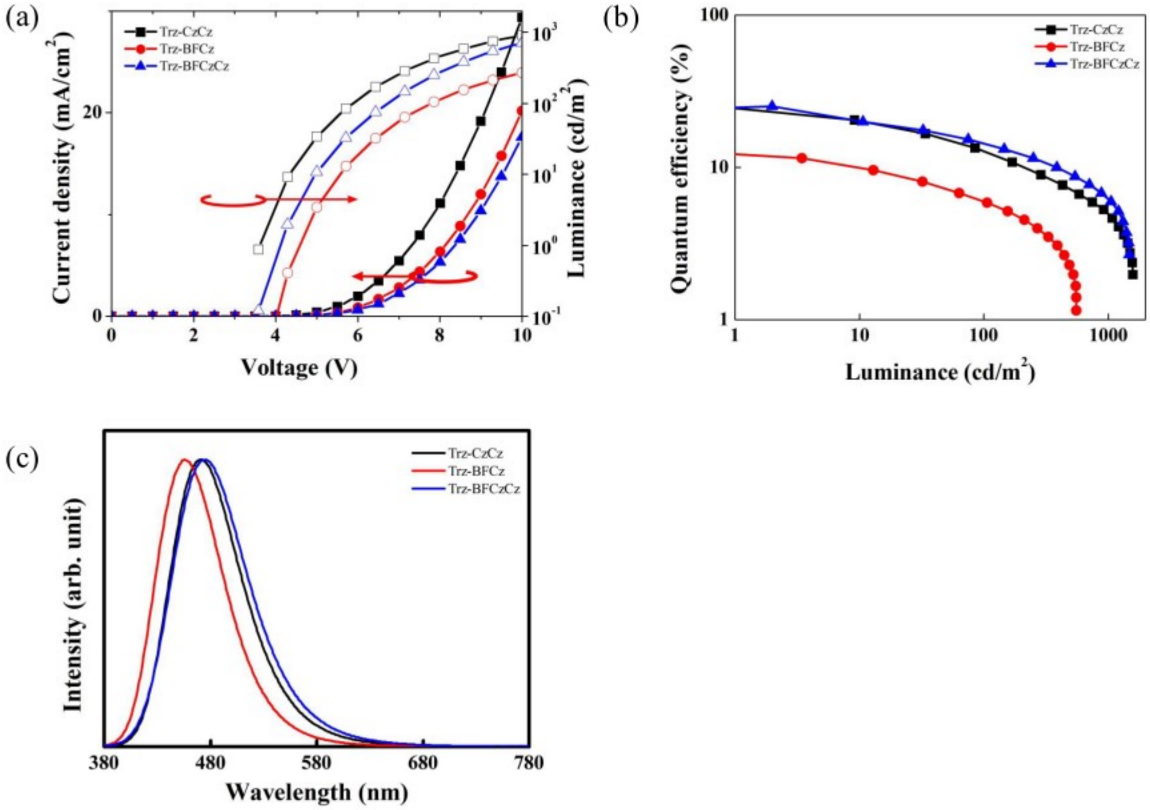


Figure S5. Device performances describing (a) relations between current density (J), voltage (V), and luminance (L) (b) EQE-Luminance relations and (c) wavelength at 10% doping concentration.

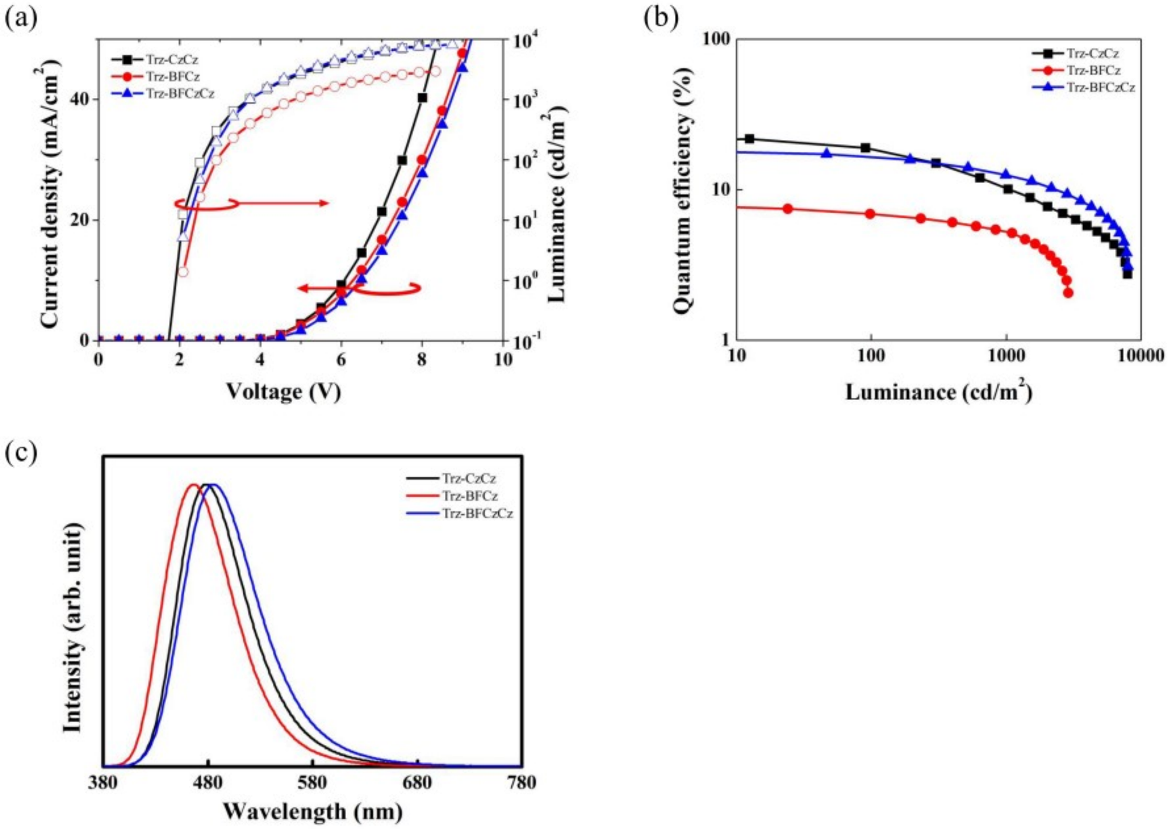


Figure S6. Device performances describing (a) relations between current density (J), voltage (V), and luminance (L) (b) EQE-Luminance relations and (c) wavelength at 30% doping concentration.

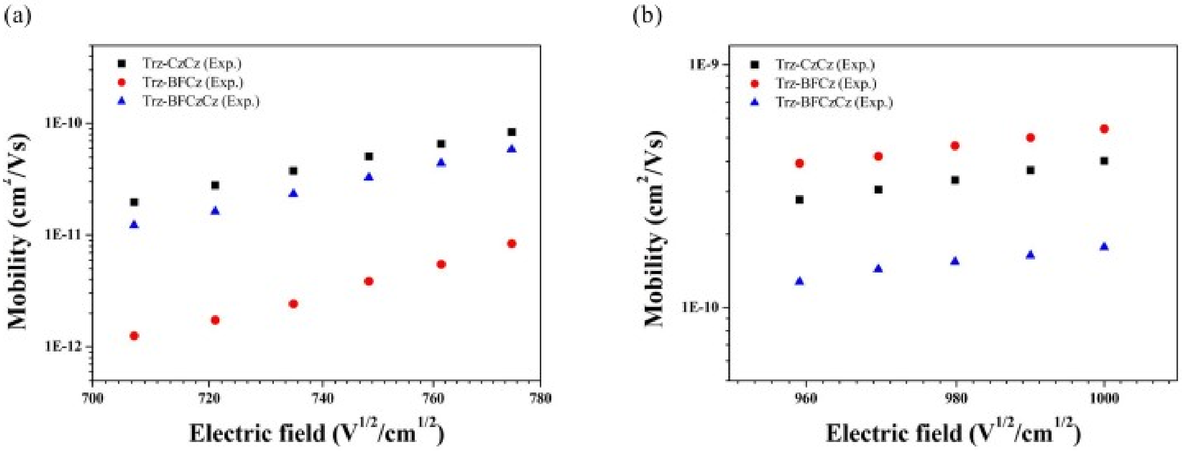
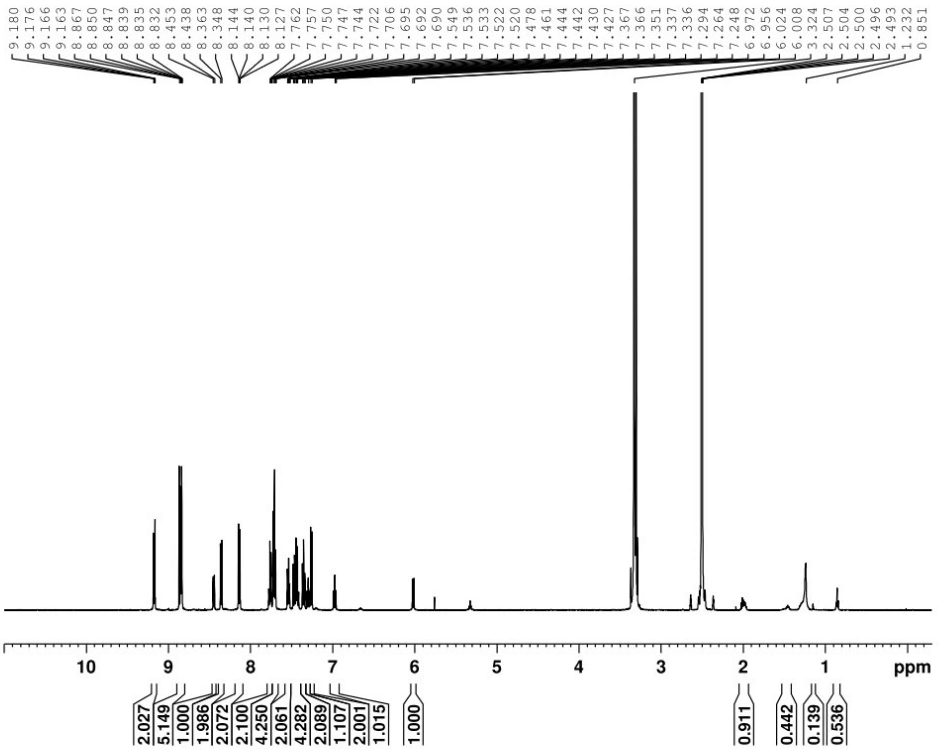


Figure S7. Mobility, Electric field plots of (a) HOD and (b) EOD of TADF molecules.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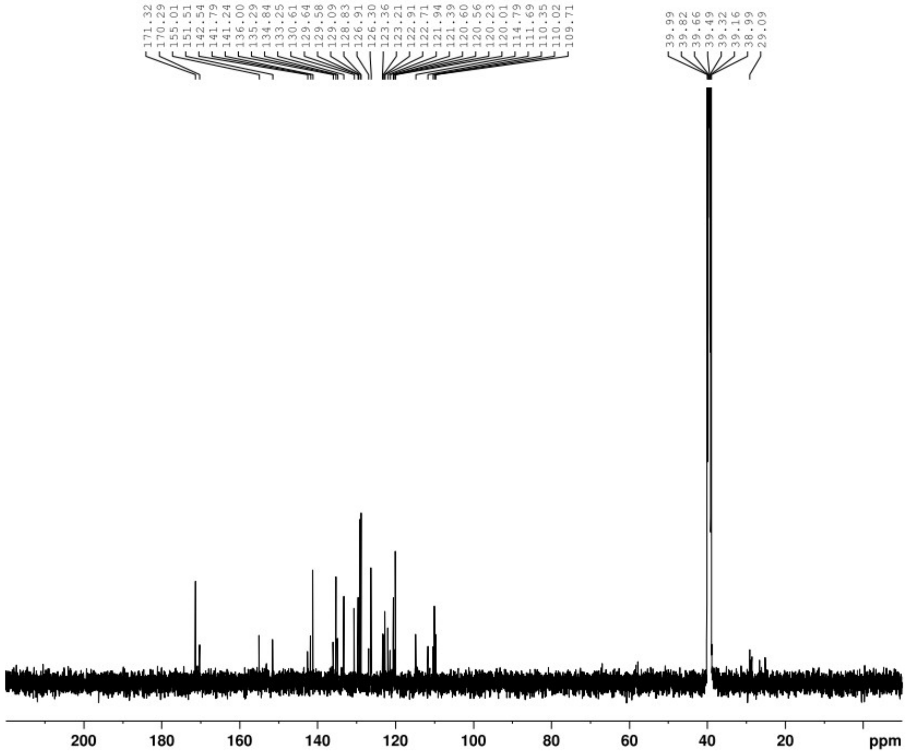
(a)

(b)

(c)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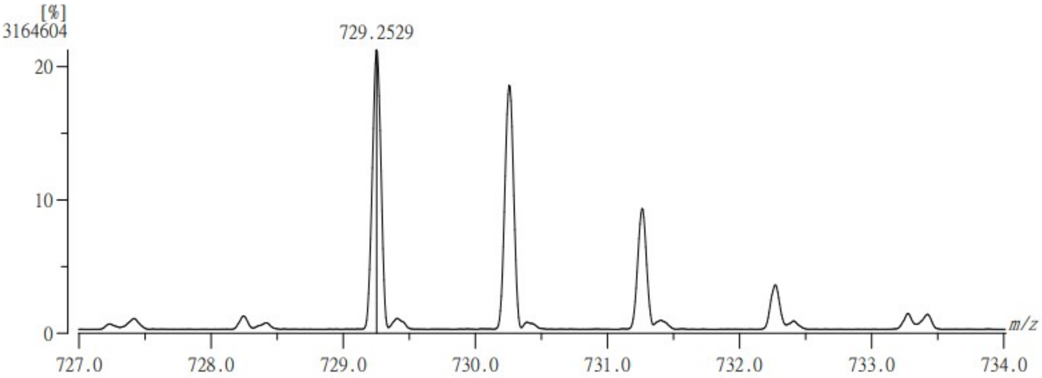

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 2                         +9.9 /  +7.2     43.0  C57 H31 N
 3                         +1.9 /  +1.4     39.5  C49 H29 N8
 4                         +0.1 /  +0.0     39.0  C51 H31 N5 O
 5                         -1.8 /  -1.3     38.5  C53 H33 N2 O2
 6                         -9.8 /  -7.2     35.0  C45 H31 N9 O2
 7                         +7.4 /  +5.4     35.5  C44 H29 N10 O2
 8                         +5.6 /  +4.1     35.0  C46 H31 N7 O3
 9                         +3.7 /  +2.7     34.5  C48 H33 N4 O4
10                         +1.9 /  +1.4     34.0  C50 H35 N O5
11                         -6.2 /  -4.5     30.5  C42 H33 N8 O5
12                         -8.0 /  -5.8     30.0  C44 H35 N5 O6
13                         +9.2 /  +6.7     30.5  C43 H33 N6 O6
14                         -9.8 /  -7.2     29.5  C46 H37 N2 O7
15                         +7.4 /  +5.4     30.0  C45 H35 N3 O7
16                         -0.6 /  -0.5     26.5  C37 H33 N10 O7
17                         +5.6 /  +4.1     29.5  C47 H37 O8
18                         -2.5 /  -1.8     26.0  C39 H35 N7 O8
19                         -4.3 /  -3.2     25.5  C41 H37 N4 O9
20                         -6.2 /  -4.5     25.0  C43 H39 N O10
21                         +3.0 /  +2.2     22.0  C34 H35 N9 O10
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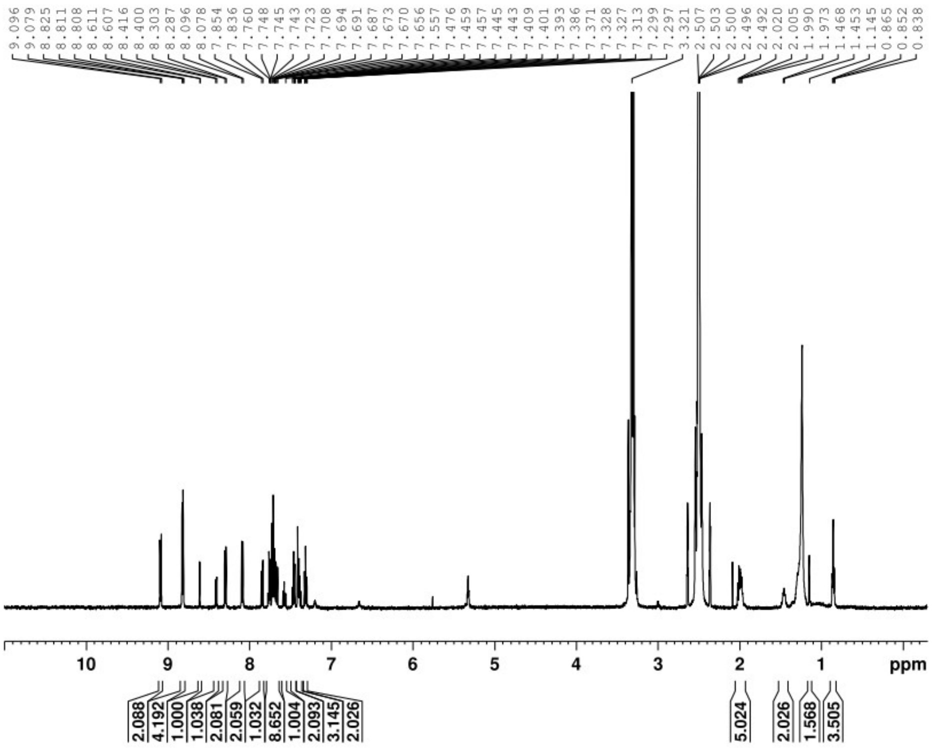
Figure S8. (a) ^{1}H NMR spectrum of Trz- BFCzCz (500 MHz, DMSO), (b) ^{13}C NMR spectrum of Trz-BFCzCz (176 MHz, DMSO), (c) HRMS spectrum of Trz-BFCzCz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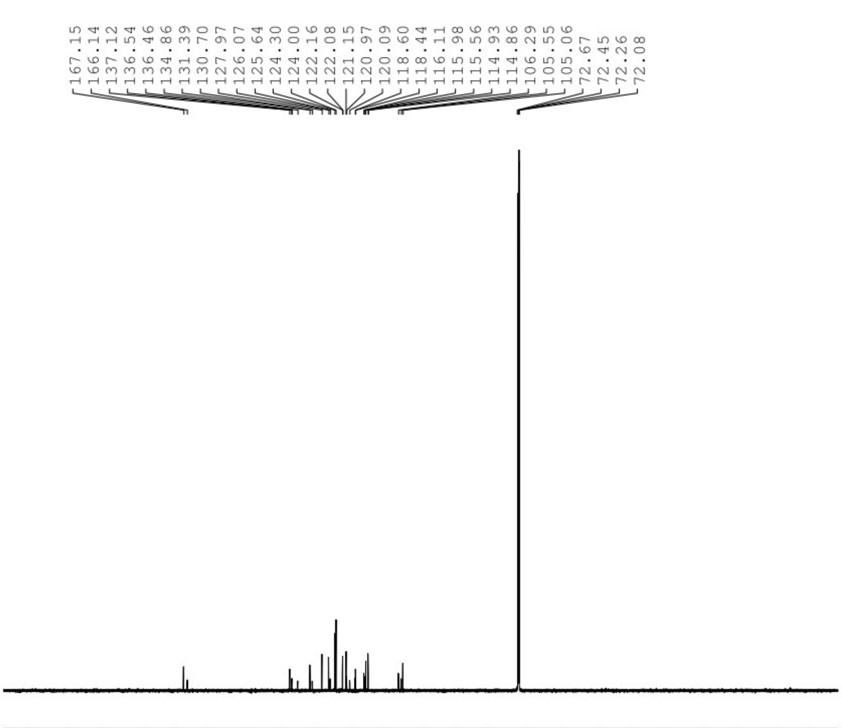
(a)

(b)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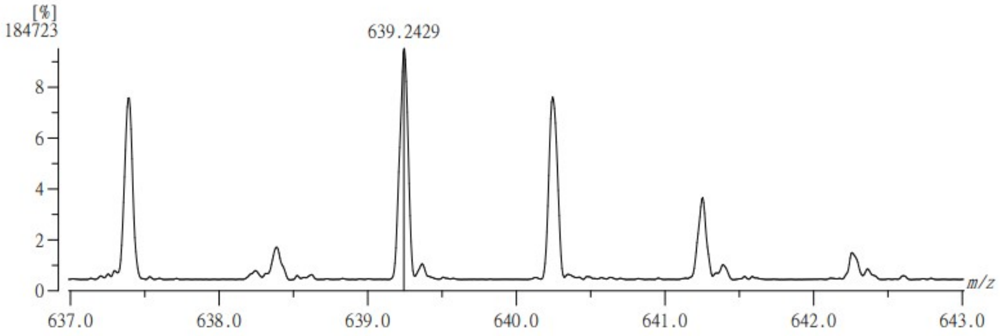

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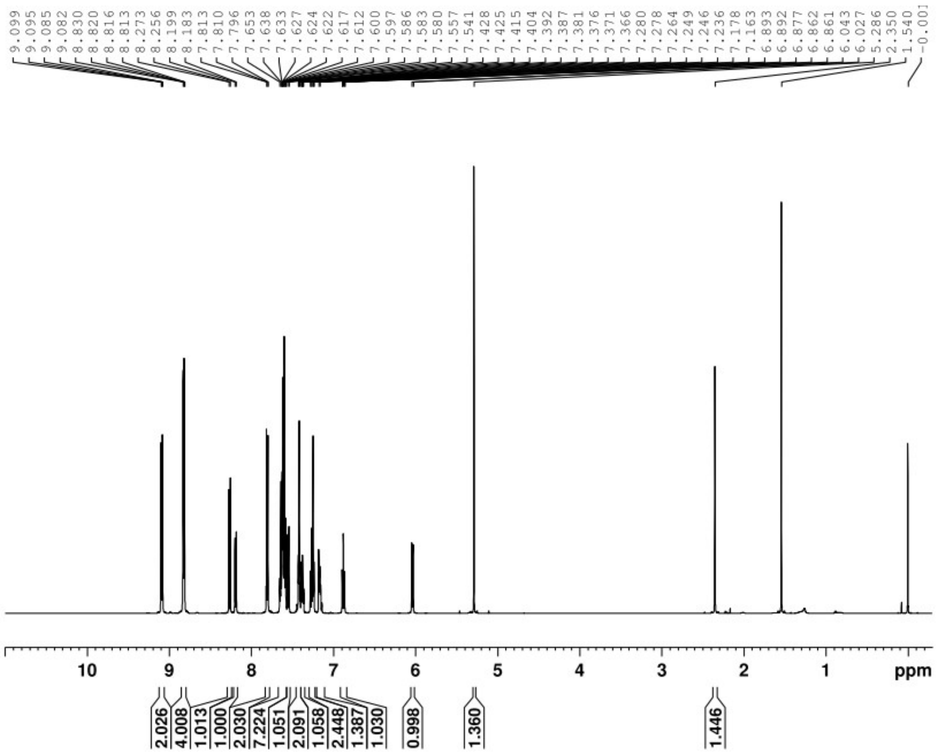
```

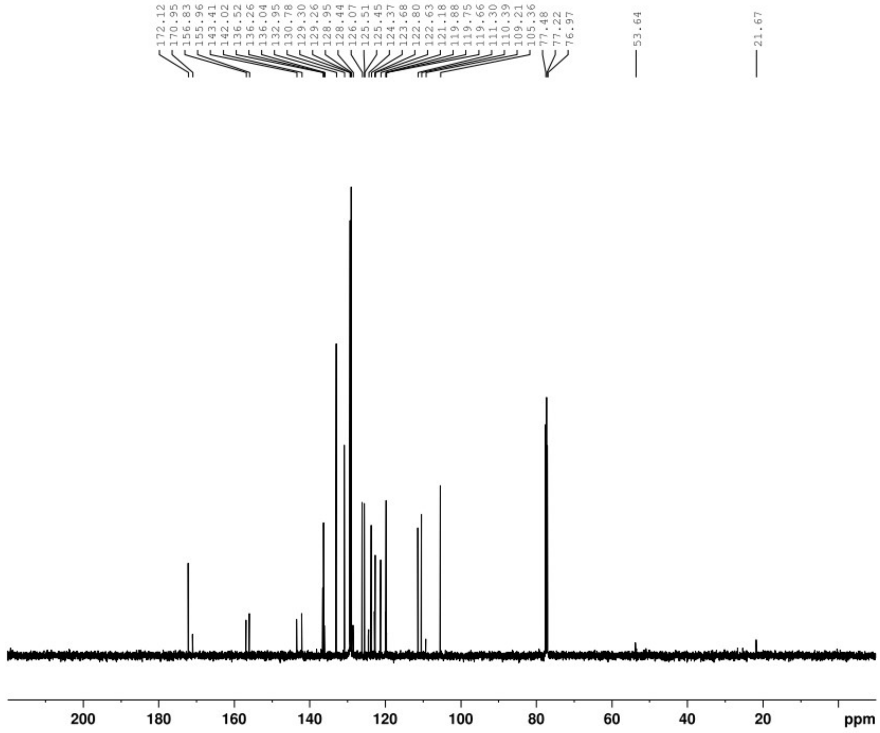
(c)

Figure S9. (a) ^{1}H NMR spectrum of Trz- CzCz (500 MHz, DMSO), (b) ^{13}C NMR spectrum of Trz-CzCz (176 MHz, DMSO), (c) HRMS spectrum of Trz-CzCz

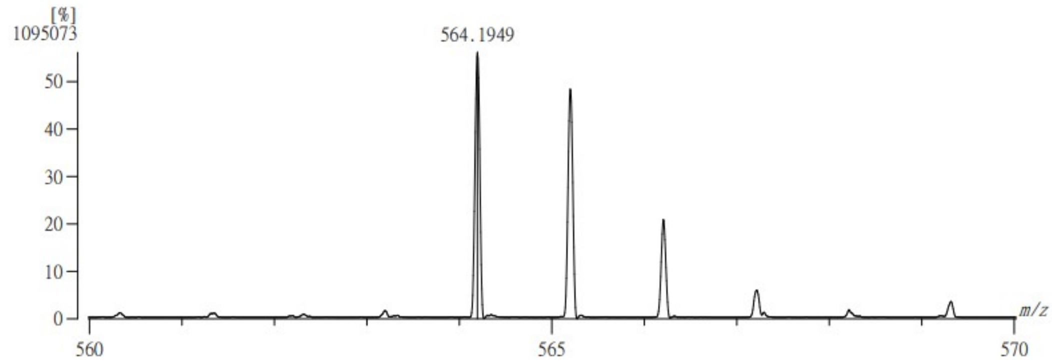

9.099
9.095
9.085
9.082
8.830
8.820
8.816
8.813
8.273
8.256
8.199
8.183
7.813
7.810
7.796
7.653
7.638
7.633
7.627
7.624
7.622
7.617
7.612
7.600
7.597
7.586
7.583
7.580
7.557
7.541
7.428
7.425
7.415
7.404
7.392
7.387
7.381
7.376
7.371
7.366
7.280
7.278
7.264
7.249
7.246
7.236
7.178
7.163
6.893
6.892
6.877
6.862
6.861
6.043
6.027
5.286
2.350
1.540
-0.001
10
9
8
7
6
5
4
3
2
1
ppm
2.026
4.008
1.013
1.000
2.030
7.224
1.051
2.091
1.058
2.448
1.387
1.030
0.998
1.360
1.446

(a)

(b)



(c)



```
 Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
 1   564.1949   56.17      +2.2 /  +1.2    30.5  C37 H22 N7
 2                         -0.2 /  -0.1    30.0  C39 H24 N4 O
 3                         -2.6 /  -1.5    29.5  C41 H26 N O2
 4                         +9.3 /  +5.3    26.5  C32 H22 N9 O2
 5                         +6.9 /  +3.9    26.0  C34 H24 N6 O3
 6                         +4.6 /  +2.6    25.5  C36 H26 N3 O4
 7                         -5.8 /  -3.3    22.0  C28 H24 N10 O4
 8                         +2.2 /  +1.2    25.0  C38 H28 O5
 9                         -8.2 /  -4.6    21.5  C30 H26 N7 O5
10                         +9.3 /  +5.2    21.0  C33 H28 N2 O7
11                         -1.1 /  -0.6    17.5  C25 H26 N9 O7
12                         -3.5 /  -2.0    17.0  C27 H28 N6 O8
13                         -5.9 /  -3.3    16.5  C29 H30 N3 O9
14                         -8.2 /  -4.6    16.0  C31 H32 O10
15                         +3.7 /  +2.1    13.0  C22 H28 N8 O10
```

Figure S10. (a) ^{1}H NMR spectrum of Trz- BFCz (500 MHz, CDCl3), (b) ^{13}C NMR spectrum of Trz-BFCz (126 MHz, $CDCl_3$), (c) HRMS spectrum of Trz-BFCz

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