New Journal of Chemistry

ELECTRONIC SUPPLEMENTARY INFORMATION

Versatile functionalization of trifluoromethyl based deep blue thermally activated delayed fluorescence materials for organic light emitting diodes

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General information: All reactions were carried out in a dry atmosphere and with positive pressure of nitrogen. Most of the reagents and solvents were commercially available and used without further purification. ^{1}H, ^{13}C NMR were carried out using Bruker AVANCE 400 MHz NMR spectrometers in $CDCl_3$ solutions at 298 K. UV-Vis spectra was obtained on a UV-3100. Fluorescence and phosphorescence spectra at 298 K and 77 K were recorded on a Hitachi F-4600 spectrophotometer in chromatographically pure toluene. The thermogravimetric analysis and differential scanning calorimetry analysis were recorded on PerkinElmer Pyris 1. The elemental analysis was recorded by Heraeus CHN-O-Rapid. Transient photoluminescence decay lifetime was performed on Horiba FL-3. Cyclic-voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, employing a polished Pt plate as the working electrode, platinum thread as the counter electrode and $Ag/AgNO_3$ (0.1 M) in CH_3CN as the reference electrode, and tetra-n-butylammonium perchlorate (0.1 M) as the supporting electrolyte, Fc^{+}/Fc was used as the internal standard, with scan rate of 0.1 V/s. All final products were purified by sublimation before applied to device fabrication.

Cartesian coordinates:

DTF-PCZ (-1653.2783 a.u.)

Table S1: Cartesian coordinates for **DTF-PCZ**

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000757034	0.000628603	-0.000140137
2	6	-0.000572225	-0.000935321	-0.000493553
3	6	-0.009615546	0.011604343	0.008578248
4	6	0.001184895	0.000185828	-0.000060179
5	6	-0.000663169	-0.000689898	0.000066853
6	6	-0.001222991	0.001455998	0.001082244
7	6	0.008848523	-0.010680180	-0.007886245
8	6	0.000824648	-0.000520484	-0.001096332
9	6	0.000867060	0.000158564	-0.000840692
10	6	-0.000748436	0.000928818	0.000679173
11	6	0.000016472	-0.001250051	0.000061285
12	6	0.000678981	-0.001285023	-0.000246444
13	7	-0.001608398	0.001981273	0.001452230
14	6	0.005077735	0.000432456	-0.000115476
15	6	0.003173501	0.003352607	0.001983919
16	6	-0.004795219	-0.001398185	-0.000537308
17	6	-0.002211536	-0.003892603	-0.002449264
18	6	-0.002011317	-0.001168532	-0.000857885
19	6	-0.000082545	0.001582035	0.001102505
20	6	0.001800393	-0.000495785	-0.000328140
21	6	-0.001990771	-0.001283761	-0.001005350
22	6	0.002272440	0.000947737	0.000758377
23	6	-0.000151278	-0.001494908	-0.001144848
24	6	-0.001742031	0.000619730	0.000526128
25	6	0.002086451	0.001042130	0.000761625
26	6	-0.000191708	-0.002557422	-0.001658435
27	9	-0.000095407	-0.000353166	0.000533575
28	9	0.000394217	0.000595721	0.001272502
29	9	-0.000792269	0.001006208	-0.000286586
30	6	0.002878809	-0.000681825	-0.000768820
31	9	-0.000013012	0.000476133	-0.000444604
32	9	-0.001274295	0.000455210	-0.000454737
33	9	-0.000310226	0.000293502	0.001269816
34	1	-0.000264057	-0.000014503	0.000211164
35	1	0.000001263	0.000342142	0.000027144
36	1	0.000470209	-0.000566994	-0.000419654
37	1	0.000532911	-0.000152253	-0.000366292

38	1	-0.000027583	-0.000809955	0.000030163
39	1	0.000606167	0.000125677	-0.000544138
40	1	0.000110662	-0.000628634	-0.000206423
41	1	-0.000335348	0.000543003	0.000387508
42	1	-0.000650334	-0.000327117	-0.000142423
43	1	-0.000619856	0.000062054	0.000125531
44	1	-0.000399855	0.000470517	0.000388305
45	1	-0.000407399	0.000503476	0.000331363
46	1	0.000123139	0.000536589	0.000317303
47	1	0.000568422	0.000419760	0.000211894
48	1	-0.000477116	0.000436486	0.000335112

NTN-PCZ (-1348.3478 a.u.)

Table S2: Cartesian coordinates for **NTN-PCZ**

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	7	-0.000016581	0.000026199	-0.000010333
2	6	0.000032897	-0.000012302	0.000019670
3	6	-0.000008184	-0.000020837	-0.000005855
4	6	-0.000016805	0.000020000	-0.000024131
5	7	0.000010463	0.000006612	-0.000005260
6	6	0.000007701	-0.000033575	0.000041505
7	6	-0.000007793	0.000013823	0.000005868
8	6	0.000005372	0.000005113	0.000008039
9	6	0.000008799	-0.000004016	-0.000012003
10	6	-0.000016959	0.000016635	0.000012263
11	6	0.000008304	-0.000009035	0.000002185
12	6	-0.000000131	0.000002191	0.000003905
13	7	0.000022300	-0.000035087	-0.000020857
14	6	-0.000022224	0.000008857	0.000015129
15	6	0.000001006	-0.000006145	-0.000008298
16	6	0.000009388	-0.000006746	-0.000001464
17	6	-0.000006422	0.000026881	0.000007639
18	6	0.000001102	-0.000000938	-0.000002368
19	6	0.000000462	-0.000002608	-0.000004214
20	6	-0.000000587	0.000000159	-0.000000785
21	6	0.000000709	0.000004538	-0.000002861
22	6	-0.000002214	-0.000003133	0.000004703
23	6	-0.000001588	0.000001062	0.000000342
24	6	0.000002409	-0.000002177	0.000000011
25	6	0.000002301	-0.000001325	0.000002081

26	6	-0.000005300	0.000024576	-0.000019960
27	9	0.000001527	-0.000007447	-0.000004062
28	9	-0.000000512	-0.000003261	-0.000002221
29	9	0.000008034	-0.000008269	0.000010179
30	1	-0.000007322	0.000004693	-0.000009343
31	1	0.000003843	-0.000002649	0.000006952
32	1	-0.000001910	-0.000002632	-0.000002577
33	1	-0.000001156	-0.000000606	0.000002839
34	1	-0.000005032	0.000001477	-0.000003477
35	1	-0.000000364	-0.000001452	-0.000003565
36	1	0.000001048	0.000001440	-0.000001654
37	1	-0.000000541	0.000001277	-0.000001152
38	1	-0.000000319	0.000000409	-0.000001486
39	1	-0.000001739	-0.000001613	-0.000000467
40	1	0.000000632	0.000001089	-0.000000832
41	1	-0.000001119	-0.000000866	0.000001133
42	1	-0.000001445	-0.000000022	0.000002139
43	1	-0.000002048	-0.000000291	0.000002644

TN3T-PCZ (-1669.2877 a.u.)

Table S3: Cartesian coordinates for **TN3T-PCZ**

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000004642	0.000000306	0.000006976
2	6	0.000004039	-0.000005521	0.000001609
3	6	-0.000006208	0.000007921	0.000007057
4	6	0.000006332	0.000000042	-0.000003313
5	7	0.000005869	-0.000003914	0.000000764
6	6	0.000007926	0.000004314	0.000003552
7	6	0.000012915	0.000002881	-0.000012187
8	6	0.000006088	-0.000005713	-0.000005037
9	6	0.000000391	-0.000000909	0.000003892
10	6	-0.000010248	0.000020648	0.000002171
11	6	0.000000659	-0.000008403	-0.000003969
12	6	-0.000008055	0.000001483	0.000006226
13	7	0.000014309	-0.000019620	0.000000709
14	6	-0.000007169	0.000002009	-0.000001934
15	6	-0.000001885	-0.000001293	-0.000003333
16	6	0.000000102	-0.000000562	-0.000000468
17	6	-0.000003623	0.000005937	-0.000003131
18	6	0.000000927	0.000000443	-0.000003472

19	6	-0.000002366	0.000001456	-0.000004704
20	6	-0.000001587	-0.000000439	-0.000004184
21	6	-0.000001687	0.000001793	-0.000005007
22	6	-0.000002478	-0.000002553	0.000001852
23	6	-0.000001625	-0.000001465	0.000001687
24	6	-0.000001508	-0.000001214	0.000003678
25	6	-0.000001215	-0.000002793	0.000002533
26	6	-0.000023764	-0.000017290	-0.000002950
27	9	0.000012325	0.000010020	-0.000003427
28	9	0.000002524	0.000001239	0.000003472
29	9	0.000011089	0.000007875	0.000008221
30	6	-0.000009549	-0.000004514	0.000006851
31	9	0.000007781	0.000003206	0.000004684
32	9	0.000003564	0.000004186	-0.000004655
33	9	0.000010791	0.000003191	-0.000004122
34	1	-0.000000070	-0.000000113	0.000000259
35	1	-0.000001887	0.000000242	0.000001408
36	1	-0.000004984	0.000001336	0.000009139
37	1	0.000002037	-0.000000294	0.000000850
38	1	-0.000001692	-0.000000066	-0.000001740
39	1	-0.000000048	-0.000000639	-0.000002032
40	1	-0.000001157	0.000001337	-0.000003334
41	1	-0.000000946	0.000001406	-0.000005872
42	1	-0.000001760	0.000000786	-0.000005715
43	1	-0.000002168	-0.000000447	-0.000002854
44	1	-0.000002283	-0.000001041	-0.000000331
45	1	-0.000002332	-0.000002148	0.000002848
46	1	-0.000001695	-0.000002188	0.000004249
47	1	-0.000001037	-0.000000919	0.000003083

TN4T-PCZ (-1669.2948 a.u.)

Table S4: Cartesian coordinates for **TN4T-PCZ**

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000000936	-0.000004472	0.000000673
2	6	-0.000000469	0.000003054	0.000003855
3	6	0.000001544	-0.000000280	-0.000003027
4	6	0.000000925	-0.000000921	0.000000742
5	6	-0.000000657	-0.000001612	-0.000000840
6	7	-0.000001524	0.000002215	-0.000001973
7	6	-0.000001549	0.000002177	0.000002024

8	6	0.000000926	-0.000001895	-0.000001073
9	6	-0.000001011	0.000000657	0.000001567
10	6	0.000001901	0.000000372	-0.000006120
11	6	-0.000001551	0.000001035	-0.000000325
12	6	0.000000450	-0.000000861	-0.000001165
13	7	-0.000000364	-0.000000063	0.000011281
14	6	0.000001175	-0.000000208	-0.000002948
15	6	0.000000149	0.000001718	-0.000000775
16	6	-0.000001006	0.000000179	0.000000375
17	6	-0.000001379	-0.000002469	-0.000004573
18	6	0.000000214	0.000000541	0.000000717
19	6	0.000000290	0.000000503	-0.000000225
20	6	0.000000389	0.000000242	-0.000000073
21	6	-0.000000810	0.000000113	-0.000001101
22	6	0.000001048	0.000000008	0.000001055
23	6	-0.000000325	-0.000000127	0.000000058
24	6	-0.000000281	-0.000000608	0.000000074
25	6	0.000000138	-0.000000196	0.000002156
26	6	-0.000001766	-0.000001902	-0.000001985
27	9	-0.000000119	0.000001367	-0.000000338
28	9	0.000001743	0.000001017	0.000000312
29	9	0.000002142	0.000001643	0.000001278
30	6	-0.000001775	-0.000000195	0.000000582
31	9	0.000001619	0.000000472	0.000001178
32	9	0.000000200	-0.000000215	-0.000001669
33	9	-0.000001520	-0.000000044	0.000000342
34	1	0.000000438	-0.000000742	-0.000000866
35	1	-0.000000804	-0.000000835	0.000000182
36	1	0.000000702	-0.000000155	0.000001233
37	1	0.000000415	-0.000000454	-0.000000082
38	1	-0.000000089	0.000000233	0.000000080
39	1	-0.000000260	0.000000423	-0.000000508
40	1	-0.000000272	-0.000000005	-0.000000960
41	1	-0.000000046	0.000000302	-0.000000792
42	1	-0.000000215	0.000000377	-0.000000402
43	1	-0.000000007	0.000000202	0.000000162
44	1	-0.000000167	0.000000103	0.000000091
45	1	0.000000056	-0.000000199	0.000000624
46	1	0.000000228	-0.000000301	0.000000591
47	1	0.000000339	-0.000000198	0.000000587

Table S5 : Calculated photophysical properties of four compounds

Compound	α[a](°)	β[b] (°)	f[c]	HOMO[d](eV)	LUMO[e] (eV)
DTF-PCZ	35.74	51.70	0.2912	-5.58	-1.72
NTN-PCZ	33.11	51.48	0.2912	-5.63	-2.20
TN3T-PCZ	54.95	52.95	0.1984	-5.64	-2.29
TN4T-PCZ	30.85	50.83	0.2799	-5.62	-2.08

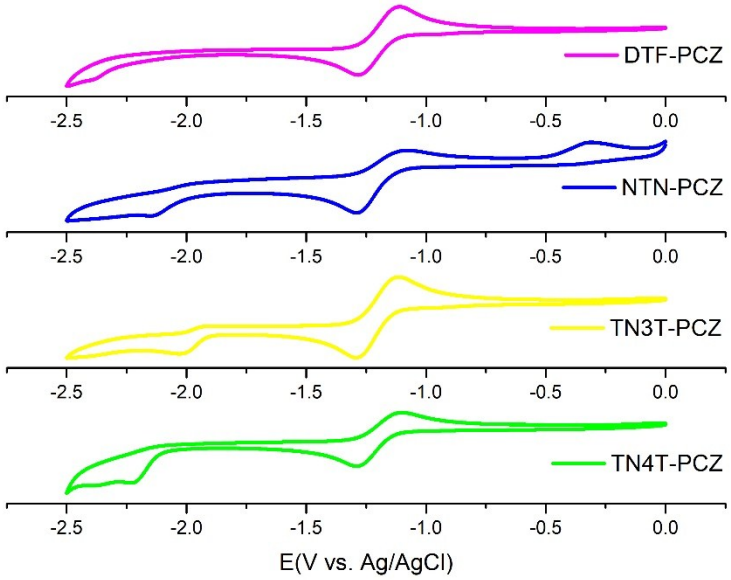

Fig. S1 Cyclic voltammetry of four compounds in negative voltage.

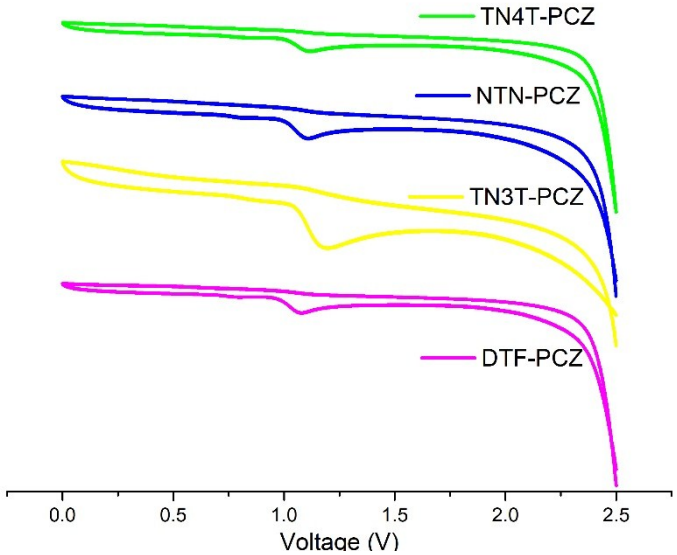

Fig. S2 Cyclic voltammetry of four compounds in positive voltage.

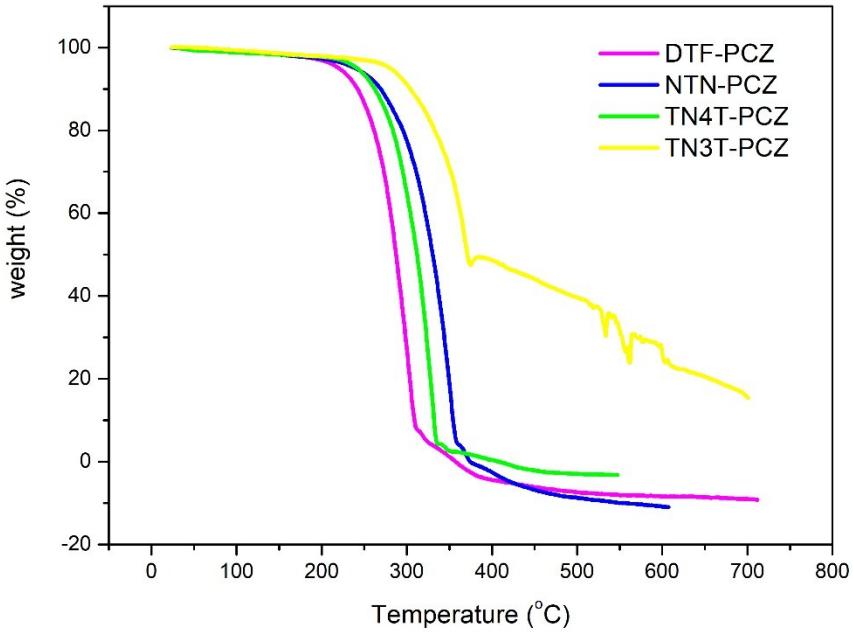

Fig. S3 TGA profiles of four compounds.

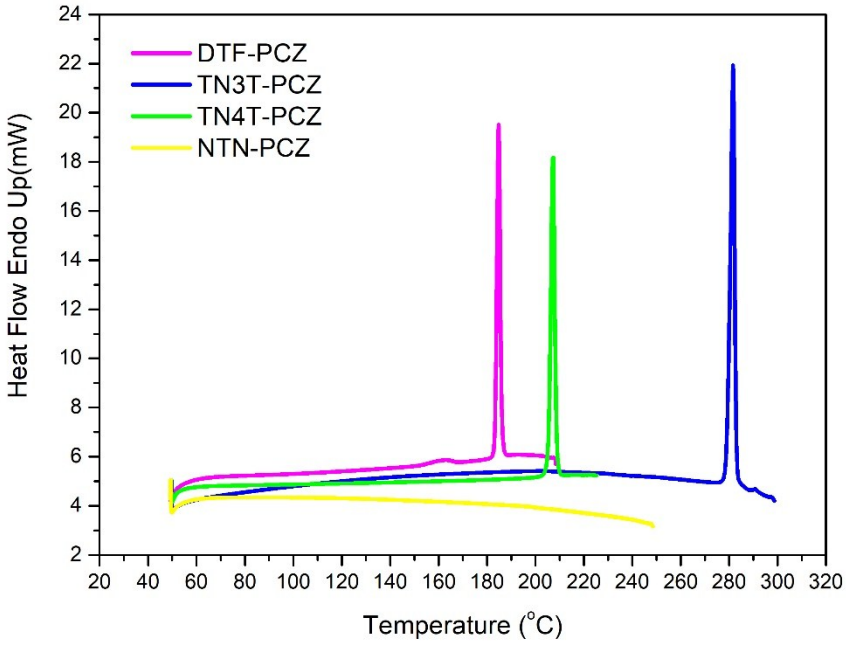

Fig. S4 DTA profiles of four compounds.

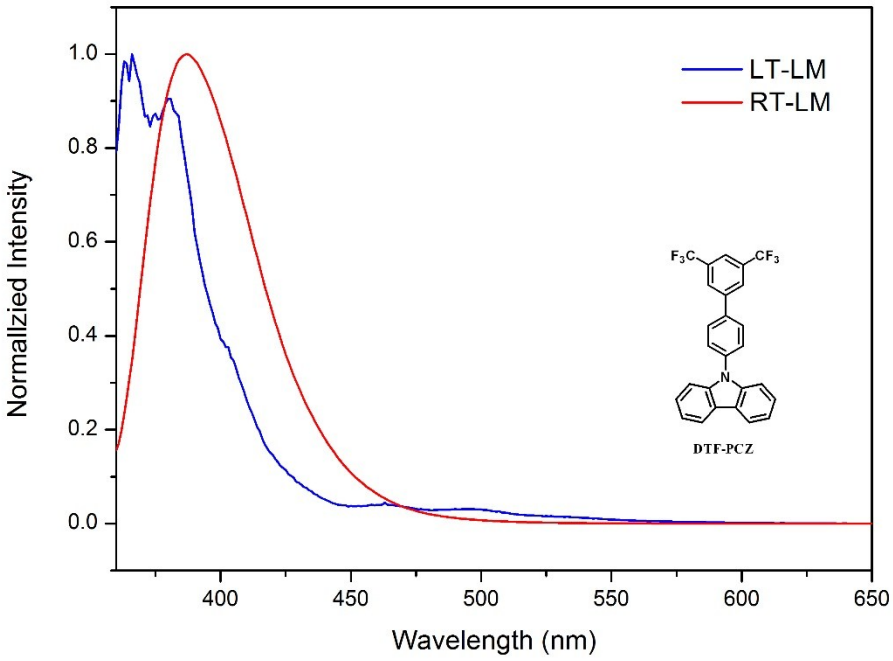

Fig. S5 Photoluminescence spectrum of **DTF-PCZ** at 300 K (red line) and 77 K (blue line) in toluene solution.

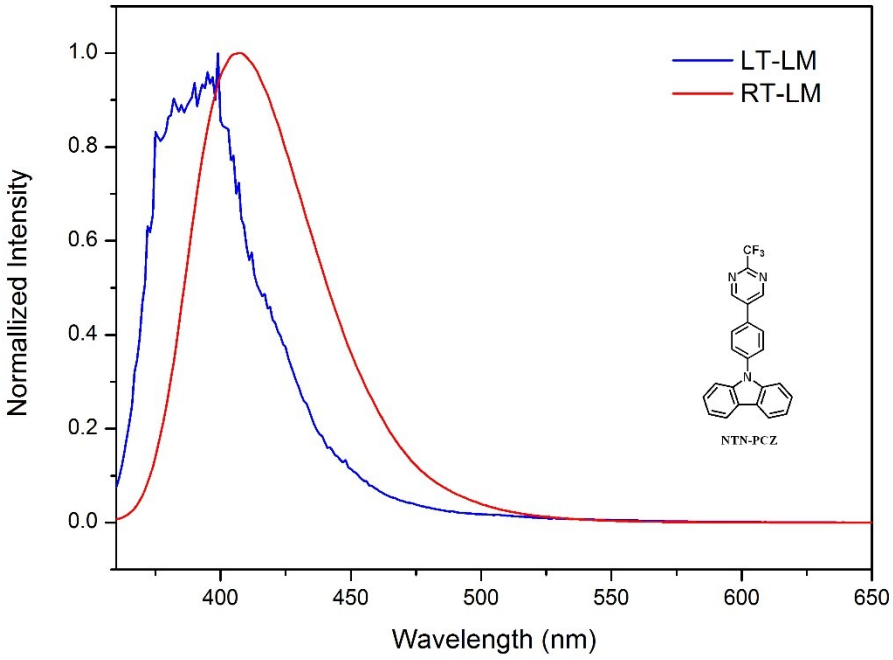

Fig. S6 Photoluminescence spectrum of **NTN-PCZ** at 300 K (red line) and 77 K (blue line) in toluene solution.

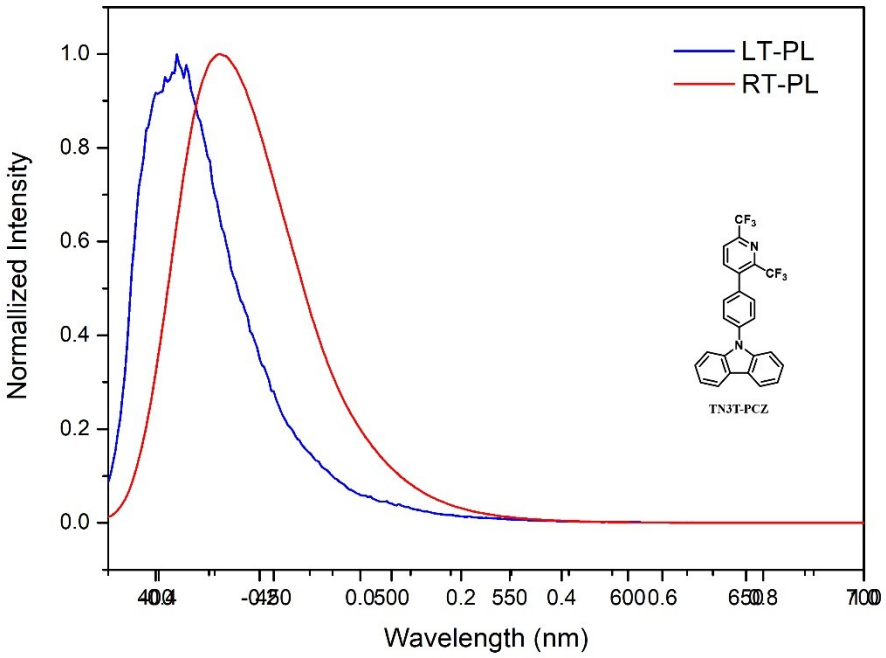

Fig. S7 Photoluminescence spectrum of **TN3T-PCZ** at 300 K (red line) and 77 K (blue line) in toluene solution.

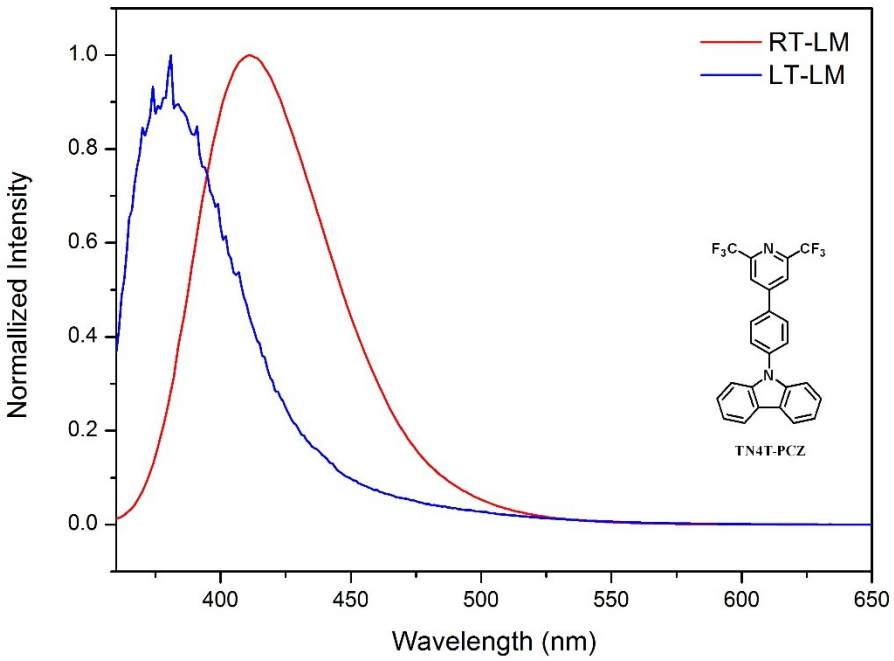

Fig. S8 Photoluminescence spectrum of **TN4T-PCZ** at 300 K (red line) and 77 K (blue line) in toluene solution.

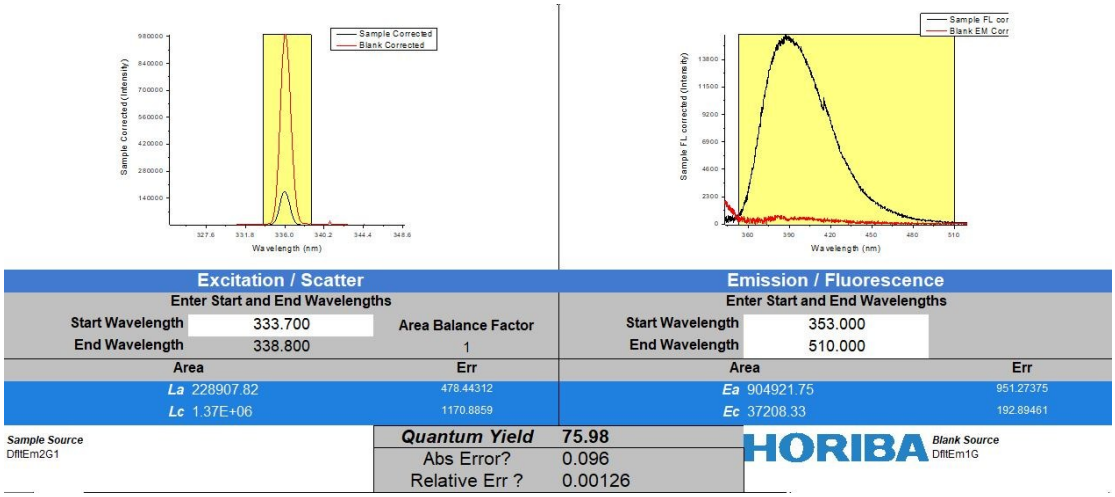

Fig. S9 Absolute quantum yield of **DTF-PCZ** in toluene solution.

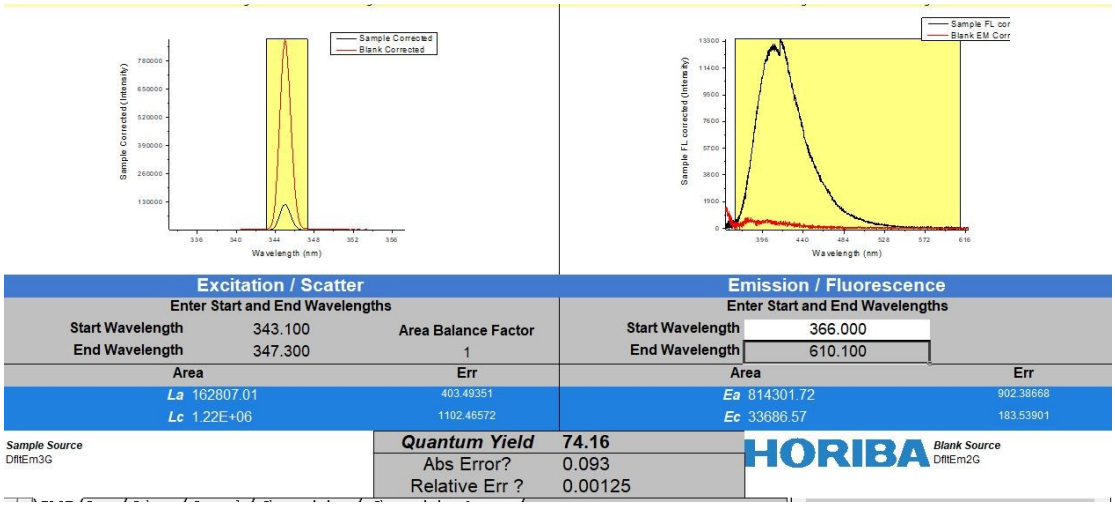

Fig. S10 Absolute quantum yield of **NTN-PCZ** in toluene solution.

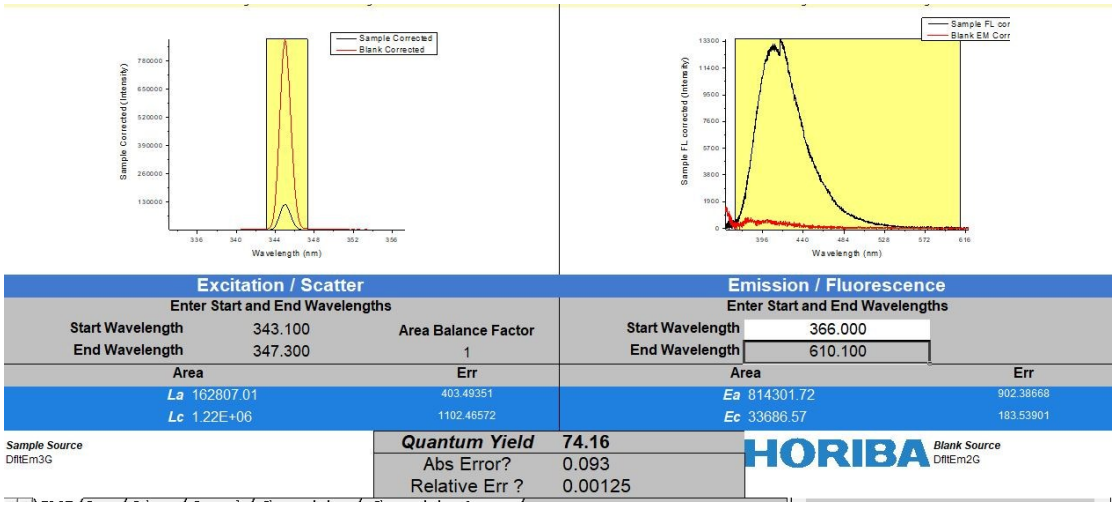

Fig. S11 Absolute quantum yield of **TN3T-PCZ** in toluene solution.

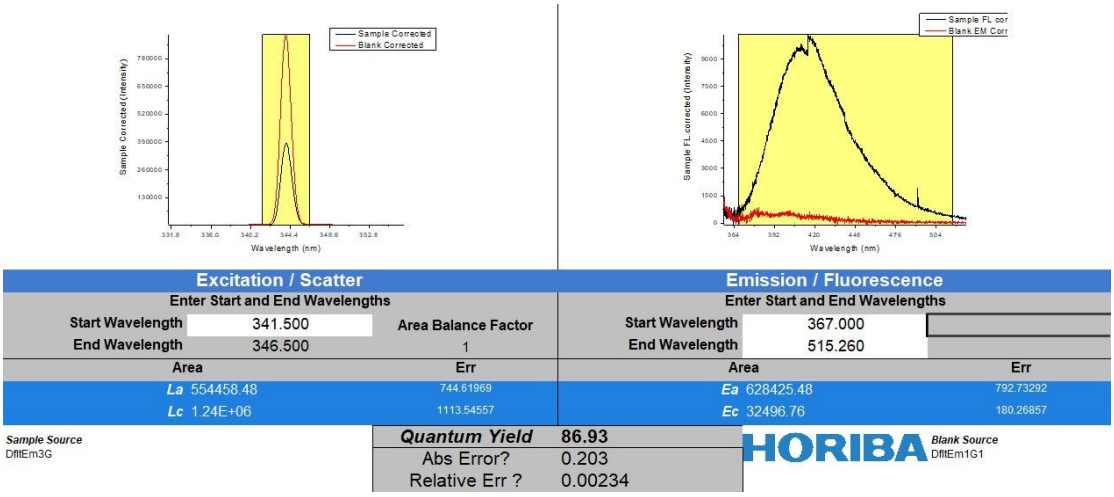

Fig. S12 Absolute quantum yield of **TN4T-PCZ** in toluene solution.

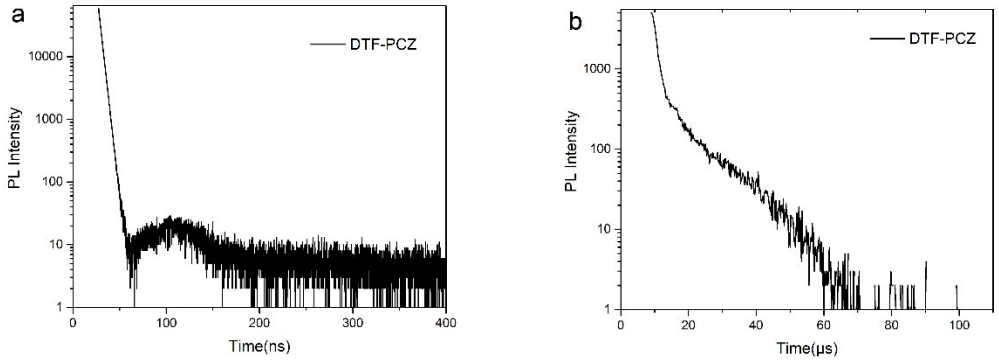

Fig. S13 Photoluminescence decay in nanosecond and microsecond scale of **DTF-PCZ** in degassed toluene.

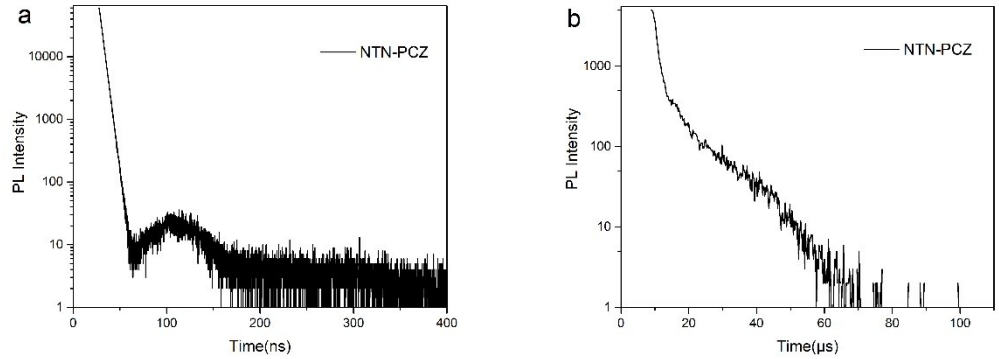

Fig. S14 Photoluminescence decay in nanosecond and microsecond scale of **NTN-PCZ** in degassed toluene.

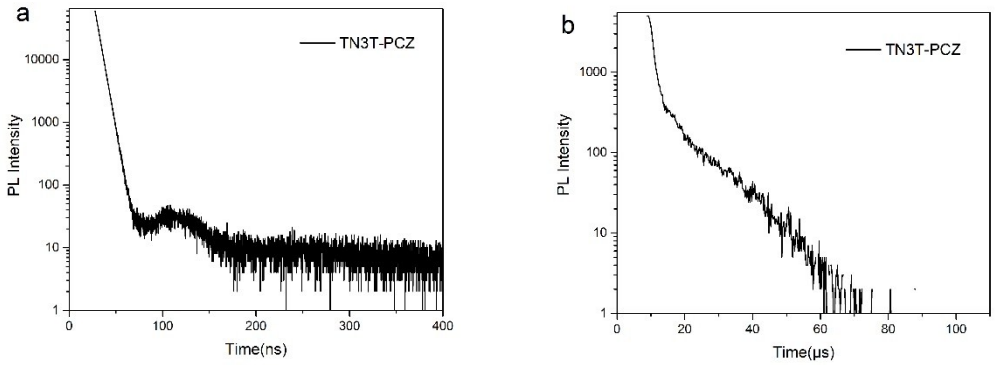

Fig. S15 Photoluminescence decay in nanosecond and microsecond scale of **TN3T-PCZ** in degassed toluene.

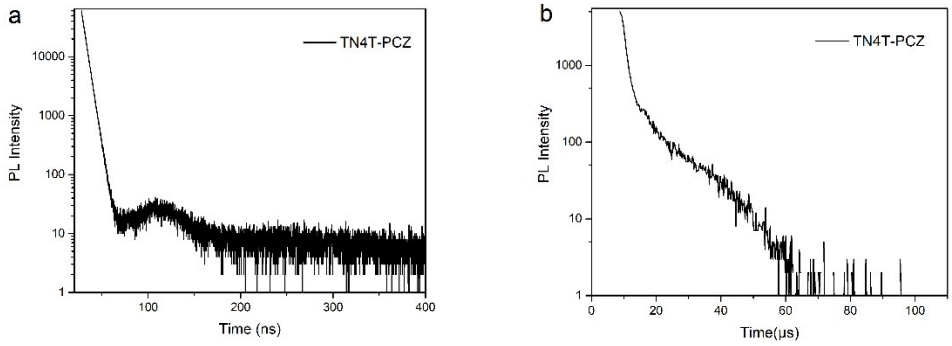

Fig. S16 Photoluminescence decay in nanosecond and microsecond scale of **TN4T-PCZ** in degassed toluene.

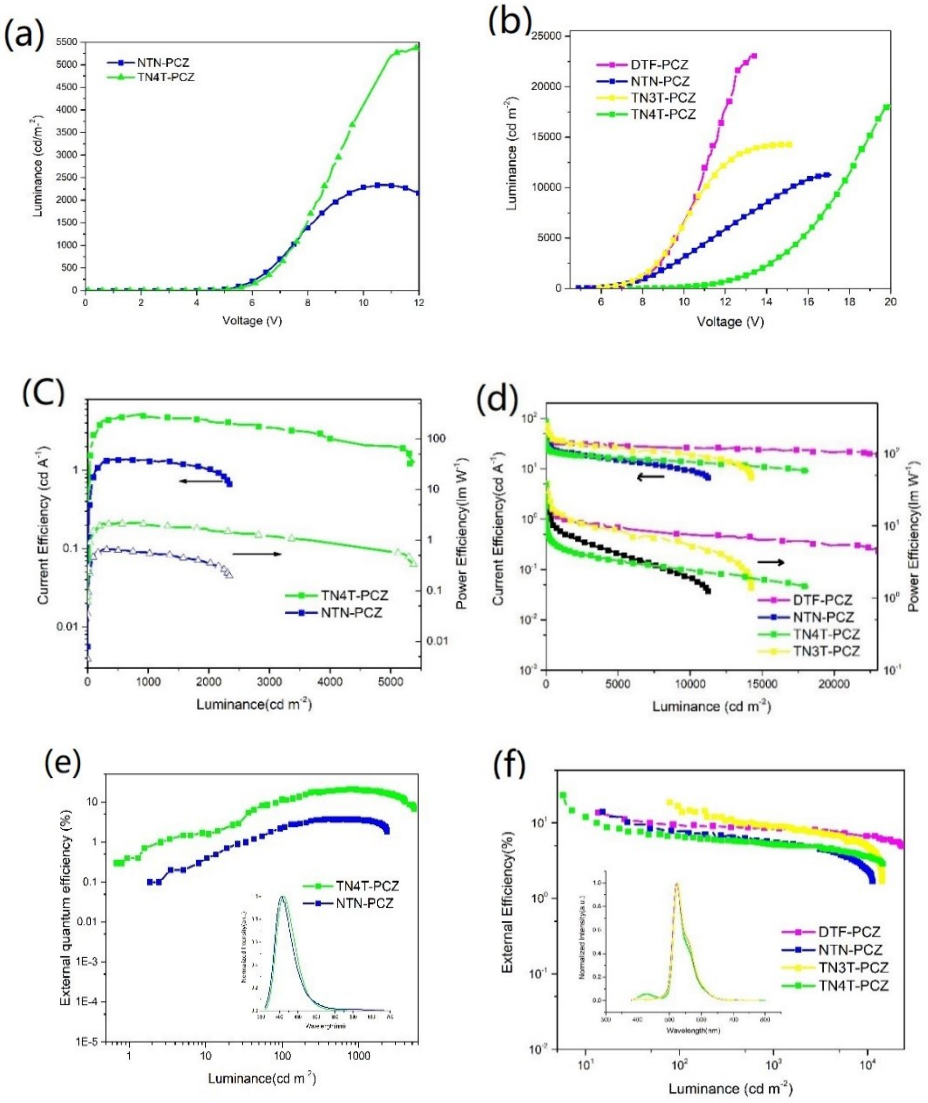

Fig. S17 (a) Luminance-voltage curve for type 1 devices; (b) Luminance-voltage curve for type 2 devices; (c) Current efficiency-luminance curve for type 1 devices; (d) Current efficiency-luminance curve for type 2 devices; (e) External quantum efficiency curve-luminance curve for type 1 devices; (f) External quantum efficiency-luminance curve for type 2 devices.

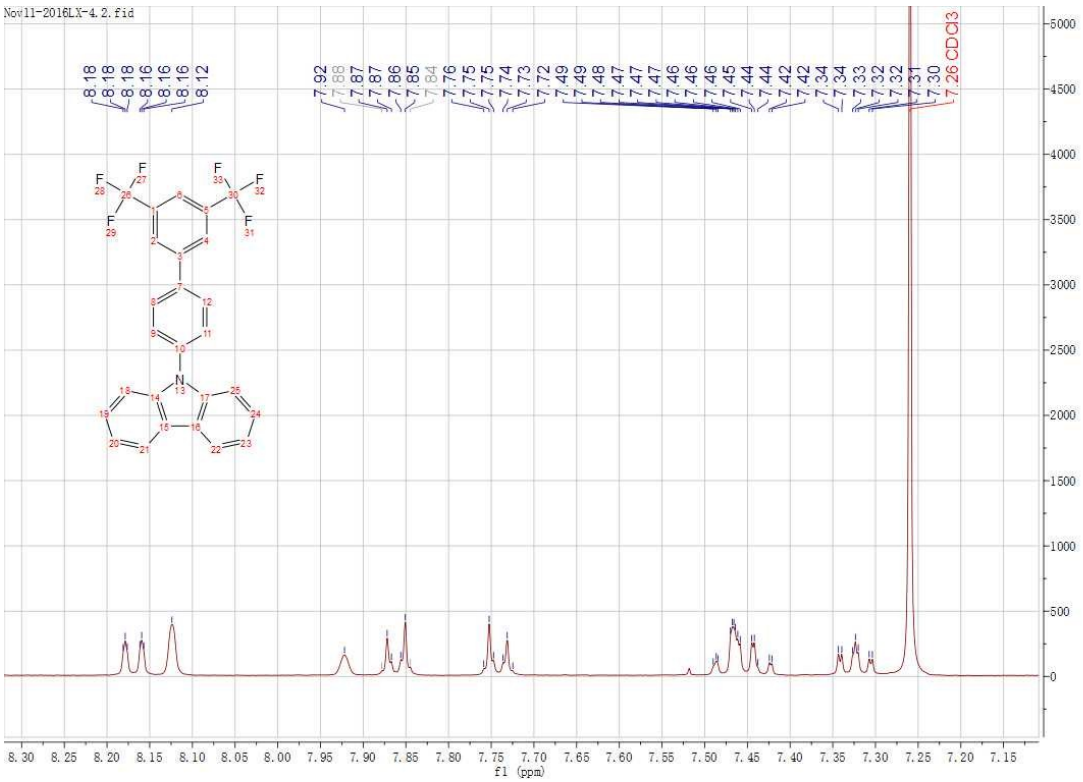

Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **DTF-PCZ**

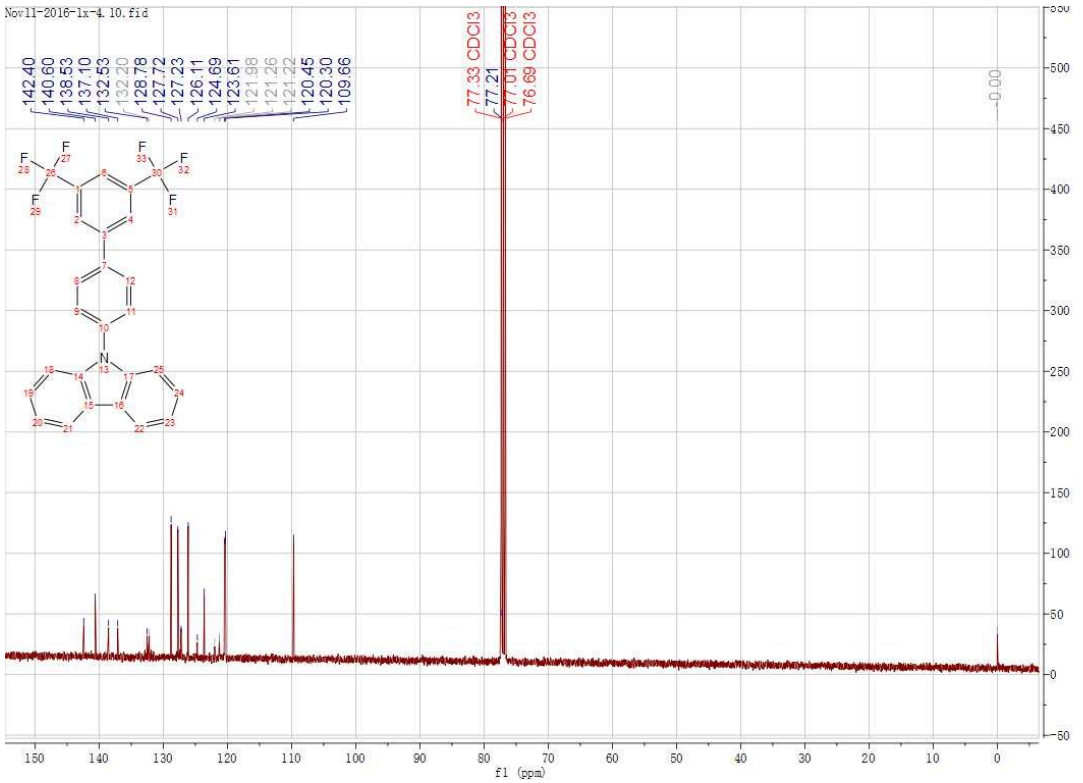

Figure S19: ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **DTF-PCZ**

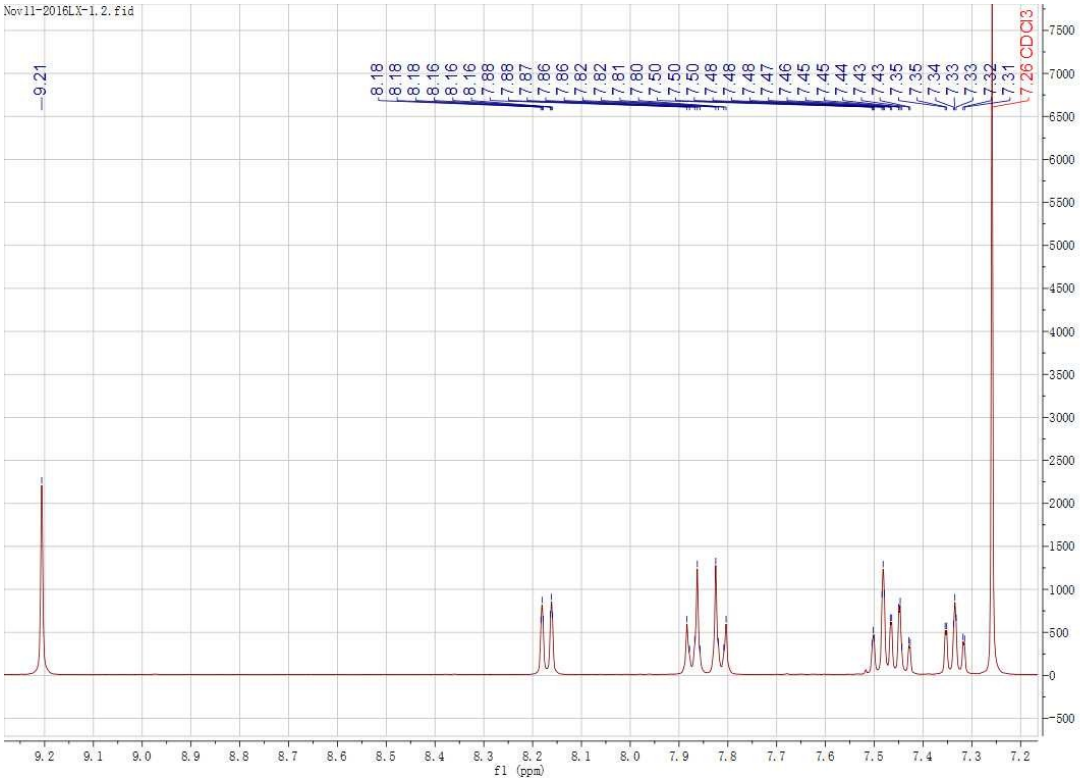

Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **NTN-PCZ**

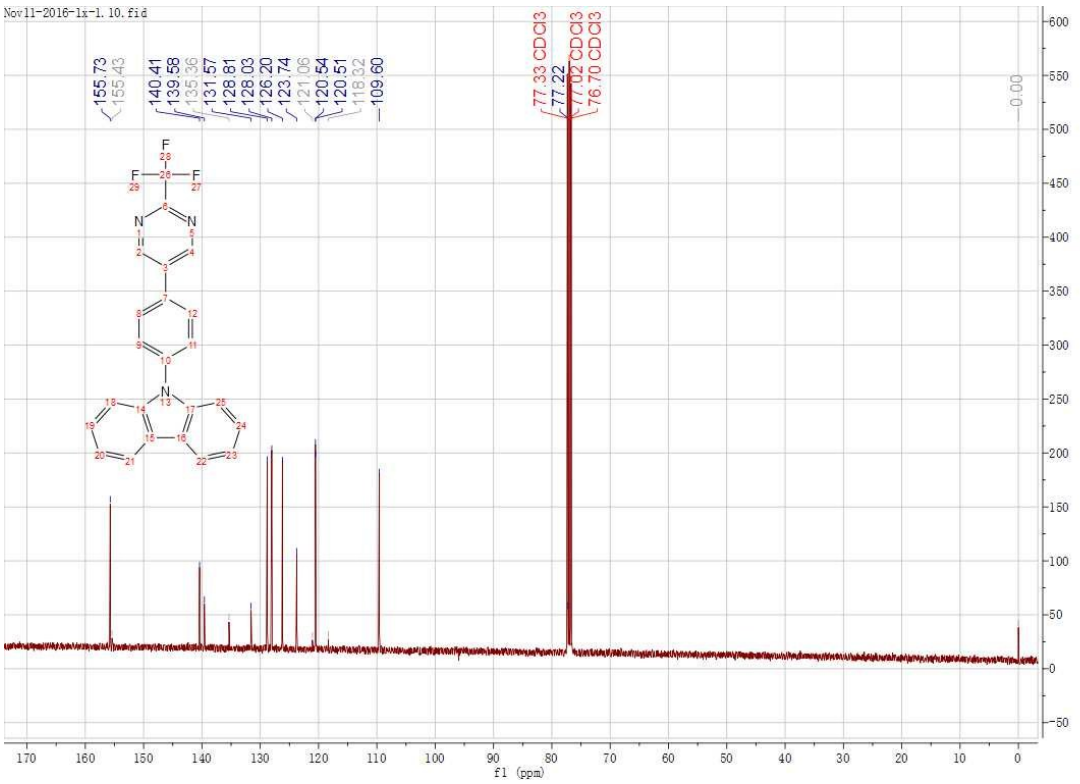

Figure S21: ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **NTN-PCZ**

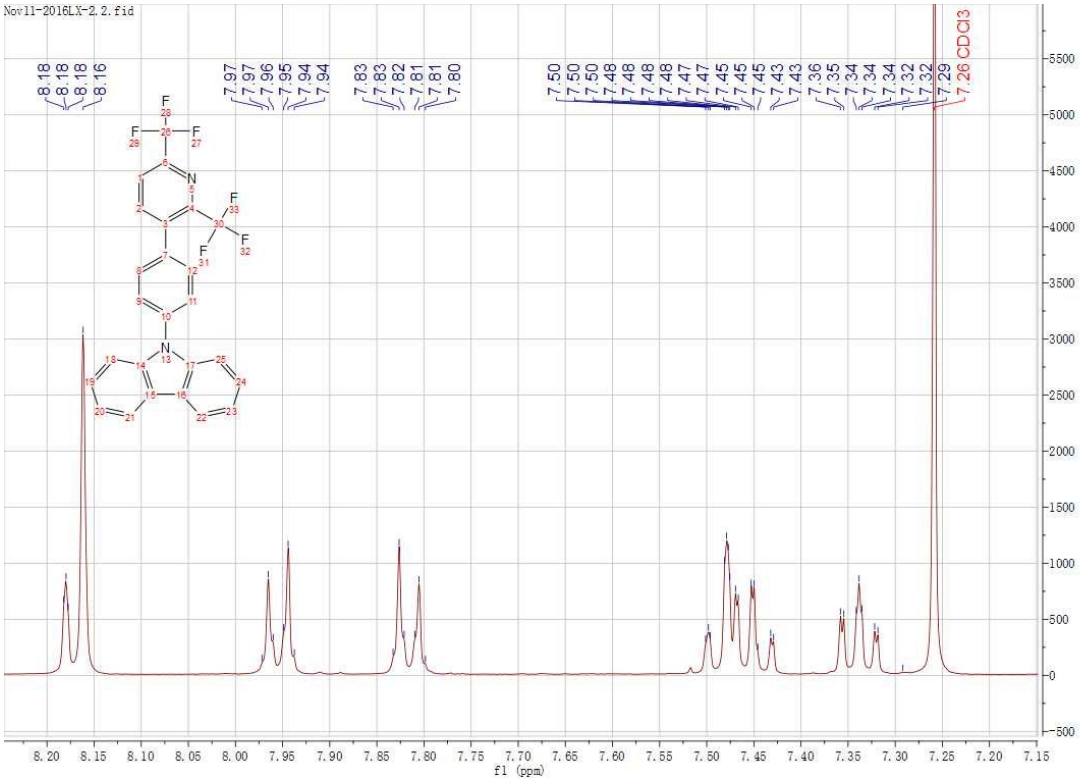

Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **TN3T-PCZ**

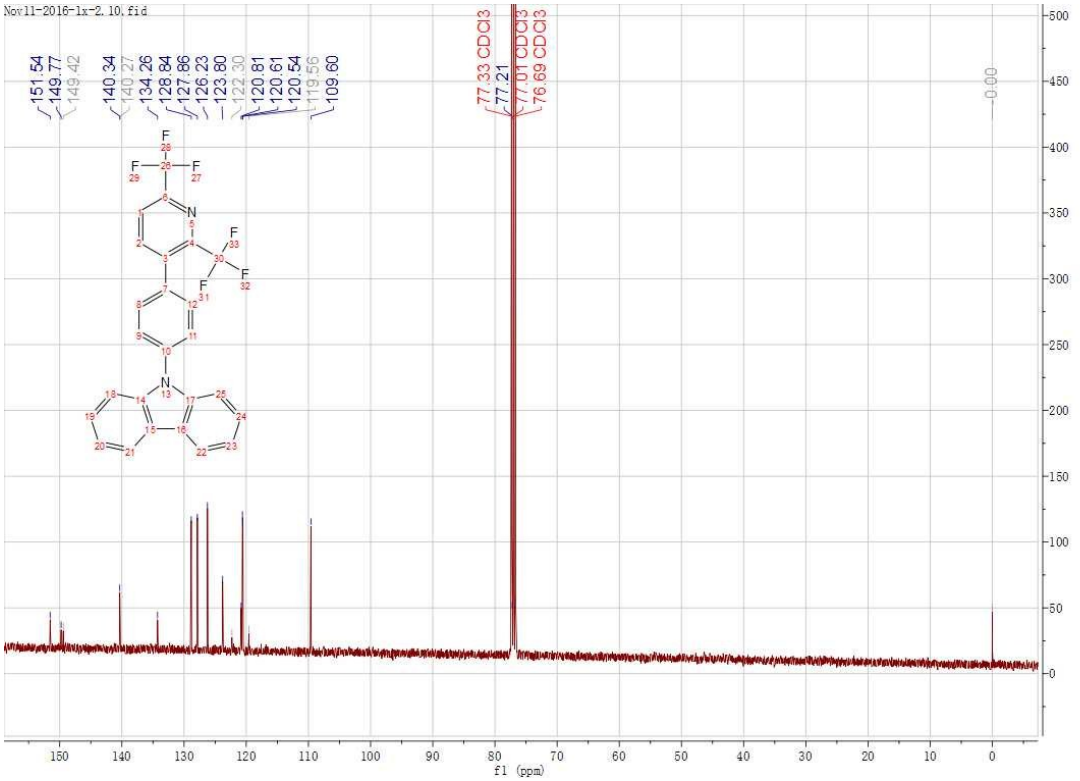

Figure S23: ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **TN3T-PCZ**

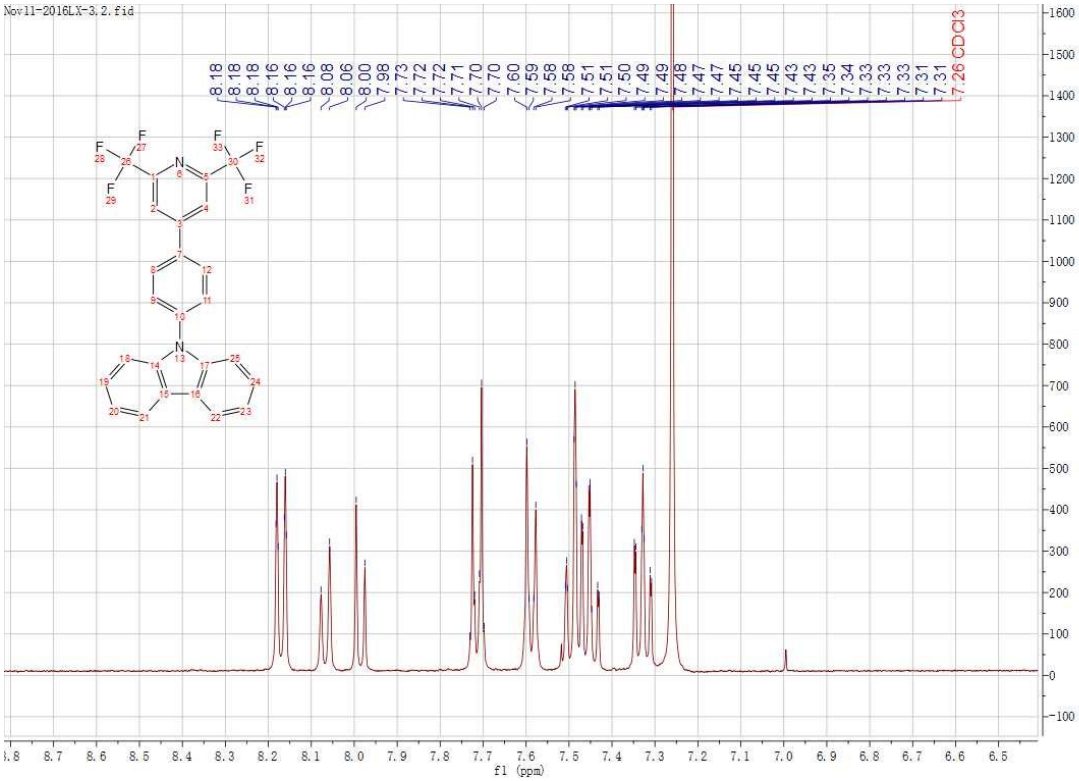

Figure S24: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **TN4T-PCZ**

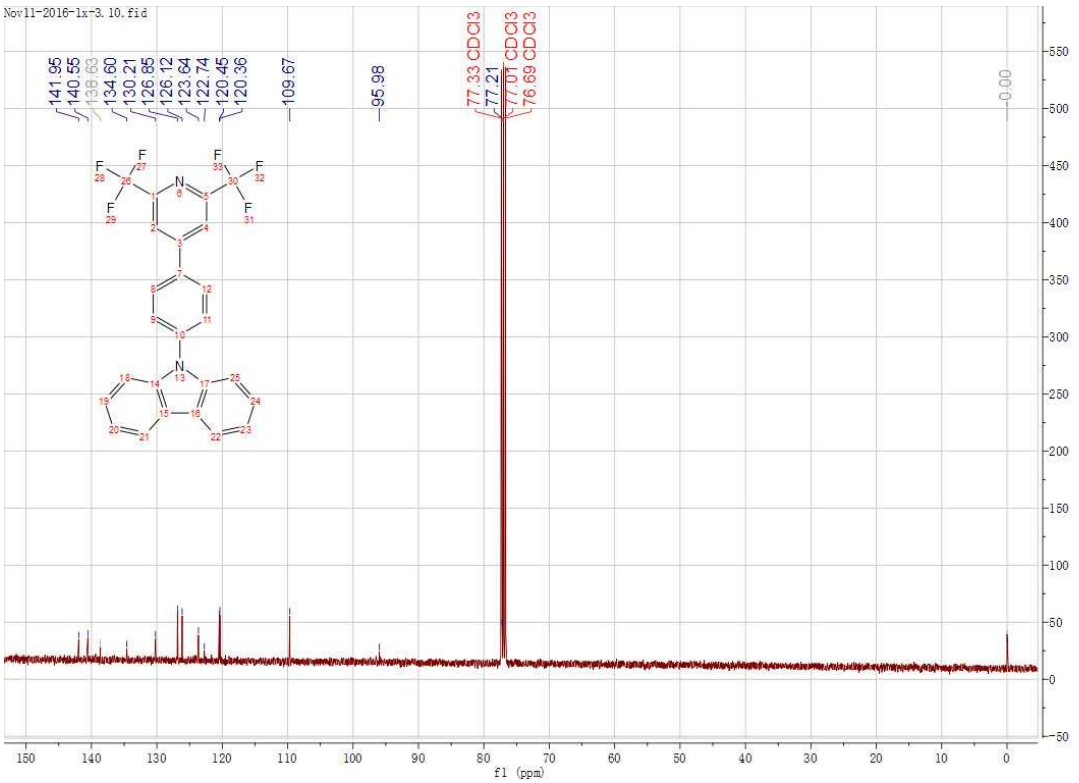

Figure S25: ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **TN4T-PCZ**