Supporting Information

Rational Molecular Design of Highly Efficient Yellow-red Thermally Activated Delayed Fluorescent Emitters: A combined Effect of Auxiliary Fluorine and Rigidified Acceptor Unit

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Experimenal

General Information

4,5-Difluorobenzene-1,2-diamine and 9,9-dimethyl-9,10-dihydroacridine were purchased from P&H tech.4,4′-Dibromobenzil was acquired from Sigma Aldrich. Copper cyanide (CuCN) was purchased from Alfa Aesar. Sodium hydride (NaH) was purchased from Tokyo Chemical Industry (TCI) Ltd. *N,N* dimethyl formamide (DMF) and acetic acid were obtained from Duksan Sci. Co. All these chemicals were used without further purification. Column chromatography (Silica Gel 60, 230−400 mesh, Merck) and sublimation (10^{-3} Torr at 300 °C) purification processes were used to obtain pure products before applying for OLED devices.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform ($CDCl_3$) solution on an Avans 500 MHz spectrometer. Chemical shifts of the ^{1}H and ^{13}C NMR signals were quoted relative to tetramethylsilane ($\delta = 0.00$). All coupling constants are reported in Hertz. The ultraviolet−visible (UV−vis) spectra were obtained using a UV−vis spectrophotometer (JASCO, Easton, MD; V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, Waltham, MA; LS55). CV measurement was carried out in dichloromethane solution with scan rate at 100 mV/s. The glassy carbon, platinum wire and Ag/AgCl were used as working, counter and reference electrodes respectively. Internal standard was ferrocenium/ferrocene couple and supporting electrolyte was 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$). The mass spectra were recorded using aAdvion, Expresion LCMS spectrometer in APCI mode. Absolute photoluminescence quantum yields (PLQYs) of 1 wt % doped polystyrene film solid film were measured with a Hamamatsu

Quantaurus-QY C11347-11 spectrometer under a nitrogen atmosphere condition. The transient photoluminescence decay characteristics of solid film samples were recorded using a Quantaurus-Tau fluorescence lifetime measurement system (C11367-31, Hamamatsu Photonics).

Device Fabrication and Measurements

The device structure was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4′-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(N-carbazolyl)benzene (mCP, 10 nm)/ 2-phenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl) -1,3,5-triazine(PBICT):dopant (25 nm; 1, 3 and 5 wt%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 5 nm)/2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) (40 nm)/LiF(1.5 nm)/Al(200 nm).The dopants were FDQCNAc and FBPCNAc. All layers of the device structure were deposited by vacuum thermal evaporation under a high pressure of 3.0×10^{-7} Torr. The material was thermally evaporated and then encapsulated with a glass lid in a nitrogen-filled glove box to protect the device from moisture and oxygen. Electrical characterization of the devices was performed using a Keithley 2400 source meter and optical characterization was carried out using a CS 2000 spectroradiometer.

Synthesis of 2,3-bis(4-bromophenyl)-6,7-difluoroquinoxaline (1)

4,5-Difluorobenzene-1,2-diamine (2.5 g, 17.34 mmol) and 1,2-bis(4-bromophenyl)ethane-1,2-dione (6.38 g, 17.34 mmol) were dissolved in glacial acetic acid (80 mL) and the reaction mixture was refluxed for 12 h. Solid precipitated out after cooling to room temperature was filtered and dried well as a pure product (5.3 g, 64.24 %).MS (FAB) m/z 474 $[(M + H)^+]$.

Synthesis of 10-(2,3-bis(4-bromophenyl)-7-fluoroquinoxalin-6-yl)-9,9-dimethyl-9,10-dihydroacridine (2)

9,9-Dimethyl-9,10-dihydroacridine (0.79 g, 3.78 mmol) was dissolved in N,N dimethylformamide (30 mL) and cooled to 0^oC. Sodium hydride (0.22 g, 4.72 mmol, 55 wt %)

was added slowly in the reaction mixture and stirred for 1 hr at room temperature. Reaction mixture was again cooled to 0 ^{o}C. 2,3-Bis(4-bromophenyl)-6,7-difluoroquinoxaline (1.5 g, 3.15 mmol) was added slowly in the reaction mixture and was stirred at 70 ^{o}C for 8 h. After cooling to room temperature, water was added in the reaction mixture. The solid precipitated out was filtered and dried well. The crude product obtained was further purified by column chromatography (20 % DCM in hexane) to afford desired product as ayellow solid (1.3 g, 62.20 %). MS (FAB) m/z 664 [(M + H)$^{+}$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32-8.33 (d, *J* = 8 Hz, 1H), 8.06-8.08 (d, *J* = 9 Hz, 1H), 7.51-7.56 (m, 6H), 7.41-7.46 (m, 4H), 6.99-7.01 (m, 4H), 6.37-6.39 (m, 2H), 1.74 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 160.7, 153.5, 152.1, 142.1, 142.0, 140.0, 139.4, 137.3, 134.5, 133.0, 132.9, 132.1, 132.0, 131.6, 131.5, 130.9, 126.8, 125.6, 124.5, 124.3, 121.8, 115.6, 115.4, 113.6, 36.3, 30.9.

Synthesis of 3,6-dibromo-11,12-difluorodibenzo[a,c]phenazine (3)

Same procedure as described for the synthesis of intermediate 1 was followed to obtain 7.5 g (91.24 %) pure product. MS (FAB) m/z 472 [(M + H)$^{+}$].

Synthesis of 3,6-dibromo-11-(9,9-dimethylacridin-10(9H)-yl)-12-fluorodibenzo[a,c]phenazine (4)

The same procedure as described for the synthesis of intermediate 2 was followed to obtain 1.2 g (63.16 %) pure product. MS (FAB) m/z 662 [(M + H)$^{+}$]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17-9.15 (d, *J* = 8.5 Hz, 1H), 9.05-9.07 (d, *J* = 8.5 Hz, 1H), 8.45-8.47 (m, 3H), 8.14-8.16 (d, *J* = 9 Hz, 1H), 7.83-7.85 (d, *J* = 8.5 Hz, 1H), 7.78-7.80 (d, *J* = 8.5 Hz, 1H), 7.53-7.55 (m, 2H), 7.01-7.03 (m, 4H), 6.45-6.46 (m, 2H), 1.77 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 142.9, 142.6, 141.5, 140.4, 140.1, 134.7, 132.7, 132.4, 132.1, 130.9, 129.1, 129.0, 128.4, 128.1, 126.8, 126.4, 126.2, 126.1, 126.0, 125.6, 121.8, 115.3, 115.1, 113.7, 36.4, 31.1.

Synthesis of 4,4'-(6-(9,9-dimethylacridin-10(9H)-yl)-7-fluoroquinoxaline-2,3-diyl)dibenzonitrile (**FDQCNAc**)

10-(2,3-Bis(4-bromophenyl)-7-fluoroquinoxalin-6-yl)-9,9-dimethyl-9,10-dihydroacridine (0.9 g, 1.35 mmol) was dissolved in N,N dimethylformamide (50 mL). Copper cyanide (0.6 g, 6.76 mmol) was added and the reaction mixture was refluxed for 12 h. After cooling to room temperature, water was added in the reaction mixture. Solid precipitated out was filtered and dried well. The crude product was further purified with column chromatography (50 % DCM in hexane) to obtain pure product (0.38 g, 50.66 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37-8.39 (d, *J* = 7.5 Hz, 1H), 8.10-8.12 (d, *J* = 9.5 Hz, 1H), 7.64-7.73 (m, 8H), 7.52-7.54 (m, 2H), 6.99-7.03 (m, 4H), 6.36-6.38 (m, 2H), 1.74 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1, 161.1, 152.4, 151.0, 142.4, 139.9, 139.6, 134.8, 134.1, 133.9, 132.6, 131.1, 130.8, 126.8, 125.7, 122.0, 118.3, 115.8, 115.6, 113.8, 113.6, 36.4, 31.0. MS (FAB) m/z 558 [(M + H)$^+$]. HRMS: (M+H)$^+$, $C_{37}H_{24}FN_5$, calcd, 558.2094; found 558.2094.

Synthesis of 11-(9,9-dimethylacridin-10(9H)-yl)-12-fluorodibenzo[a,c]phenazine-3,6-dicarbonitrile (**FBPCNAc**)

Same procedure as described above for the synthesis of FDQCNAc was followed to obtain 0.32 g (47.76 %) pure product. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.56-9.58 (d, *J* = 8.5 Hz, 1H), 9.46-9.48 (d, *J* = 8.5 Hz, 1H), 8.85-8.87 (d, *J* = 9.5 Hz, 2H), 8.45 (s, 1H), 8.06-8.08 (d, *J* = 8.5 Hz, 1H), 7.99-8.01 (d, *J* = 8.5 Hz, 1H), 7.83 (s, 1H), 7.51-7.53 (m, 2H), 6.96-7.00 (m, 4H), 6.41-6.43 (m, 2H),1.76 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.7, 141.5, 140.1, 139.7, 139.3, 136.9, 134.3, 133.8, 131.3, 131.1, 130.8, 130.1, 127.8, 127.7, 127.5, 127.1, 126.5, 125.4, 121.3, 118.8, 118.7, 114.3, 113.8, 113.6, 108.9, 36.3, 14.4. MS (FAB) m/z 556 [(M + H)$^+$]. HRMS: (M+H)$^+$, $C_{37}H_{22}FN_5$, calcd, 556.1937; found 556.1937.

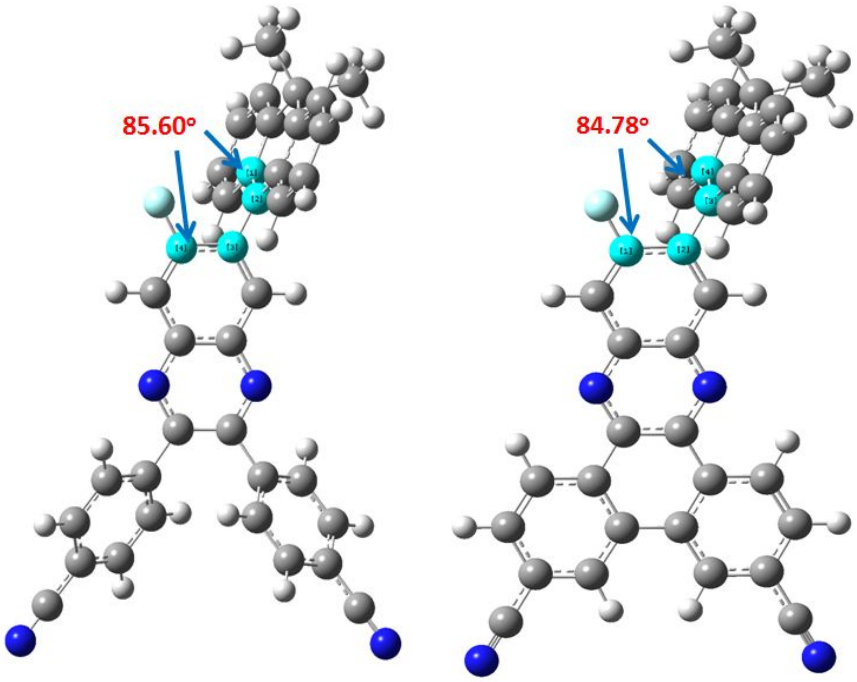


Figure. S1. DFT optimized structures of FDQCNAc and FBPCNAc with respective dihedral angles between donor and acceptor unit.

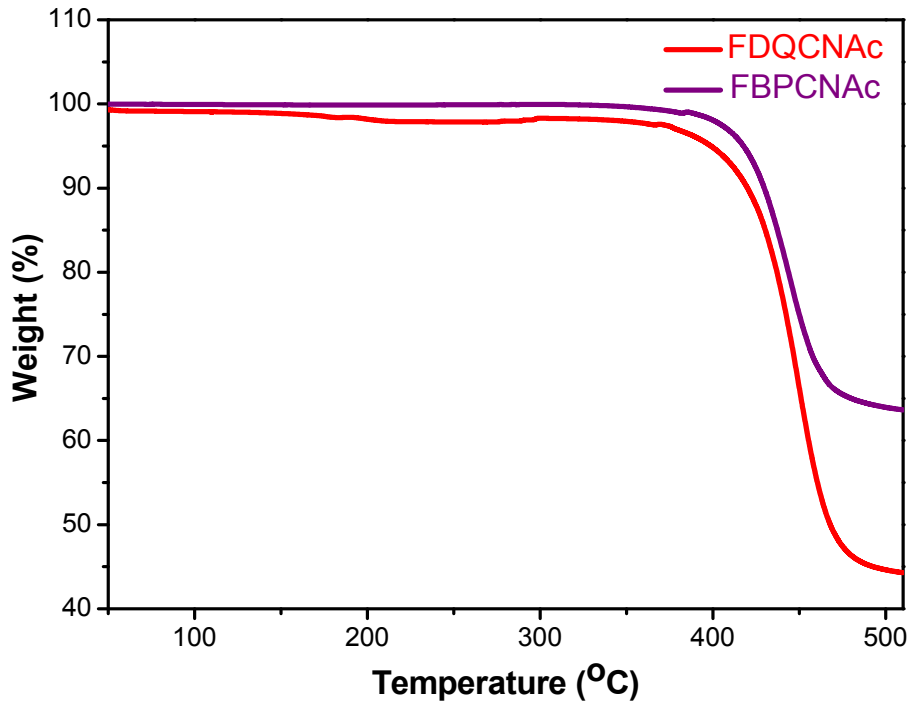


Figure S2. Thermogravimmetric analysis (TGA) curves of two emitters under nitrogen.

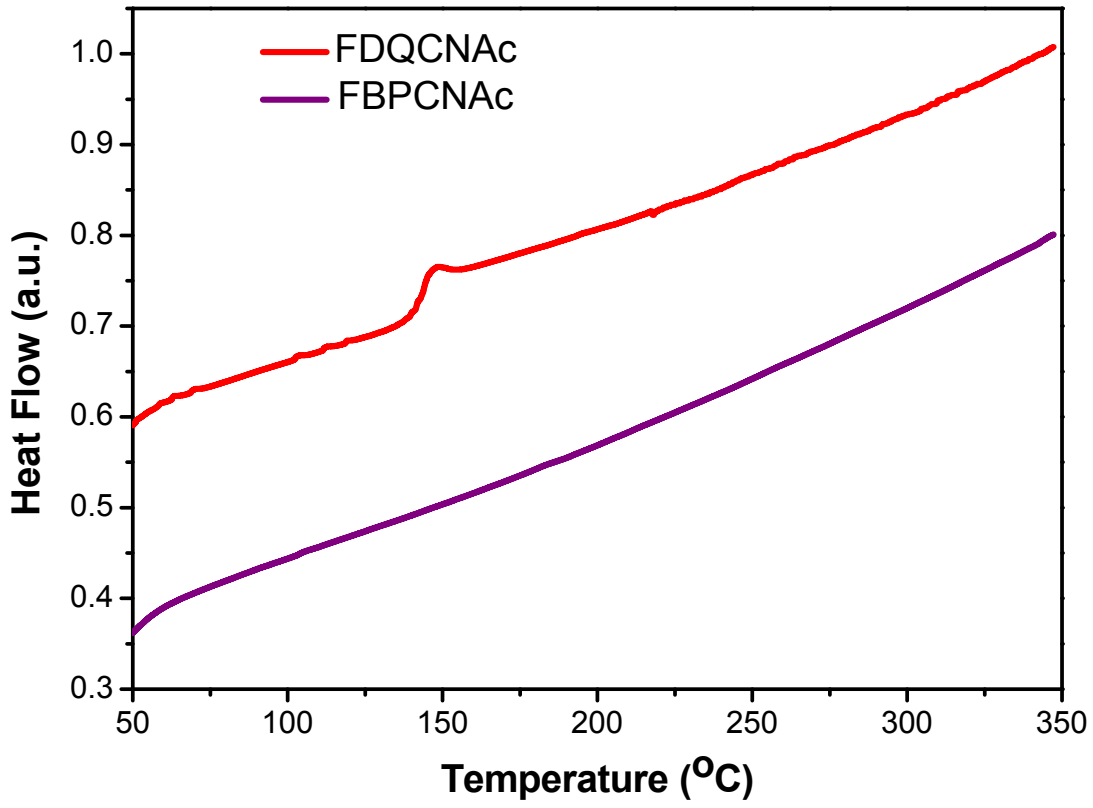


Figure S3. DSC thermograms of FDQCNAc and FBPCNAc TADF emitters.

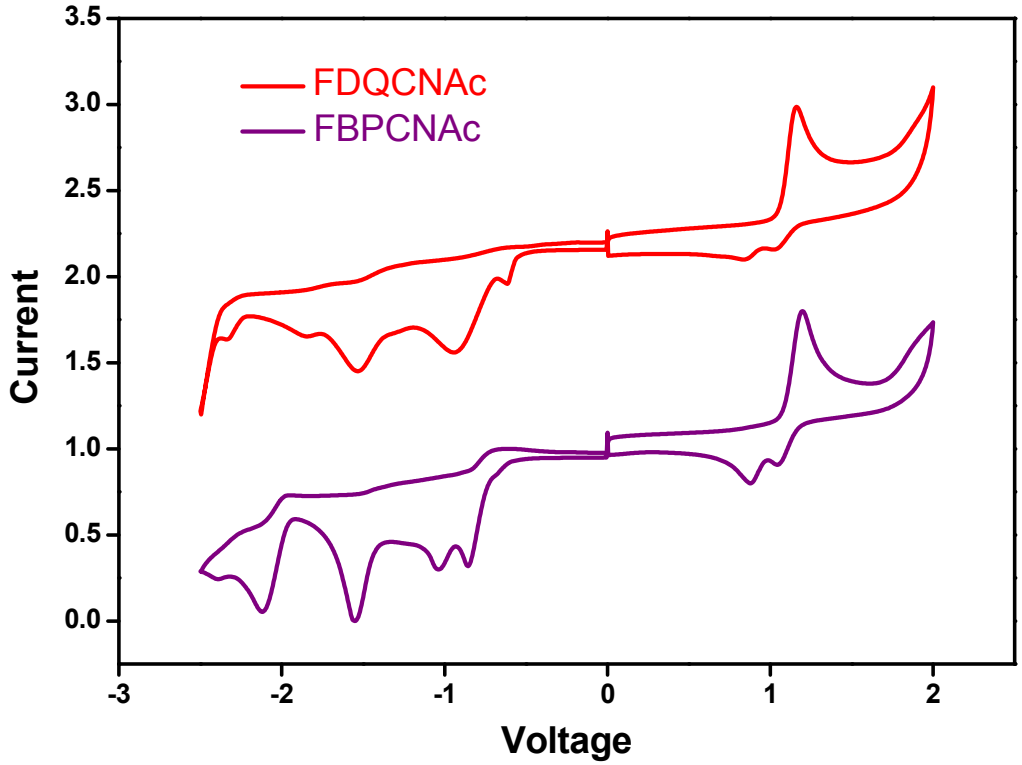


Figure S4. Cyclic voltammograms of TADF emitters FDQCNAc and FBPCNAc.

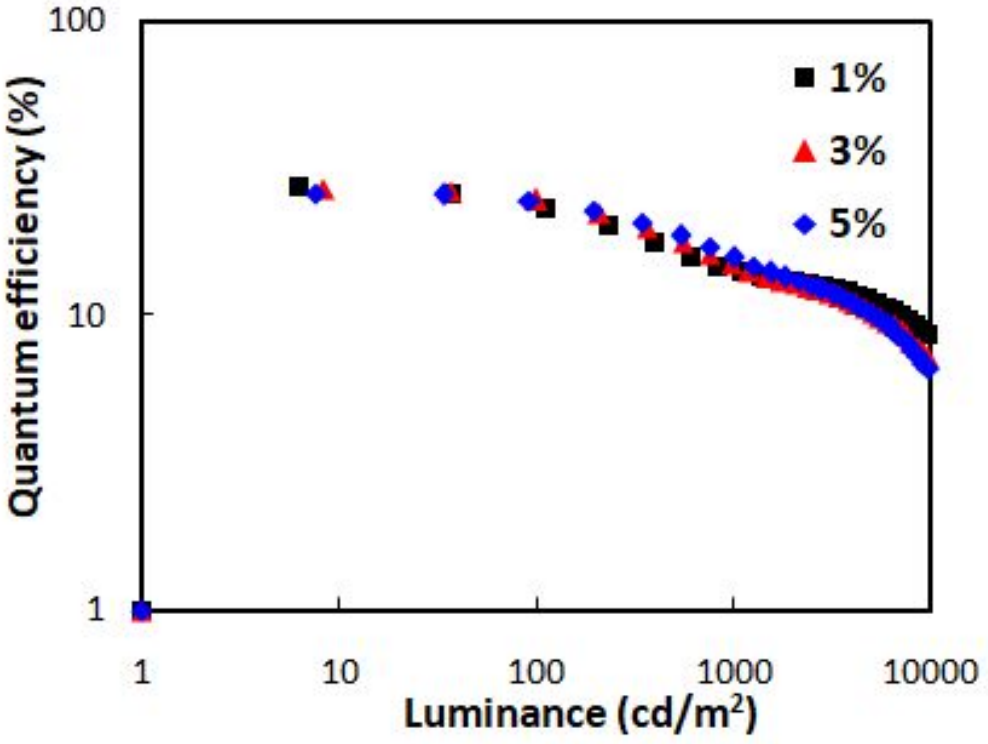


Figure S5. EQE−luminance curves of FDQCNAc doped OLED (1-5 %)

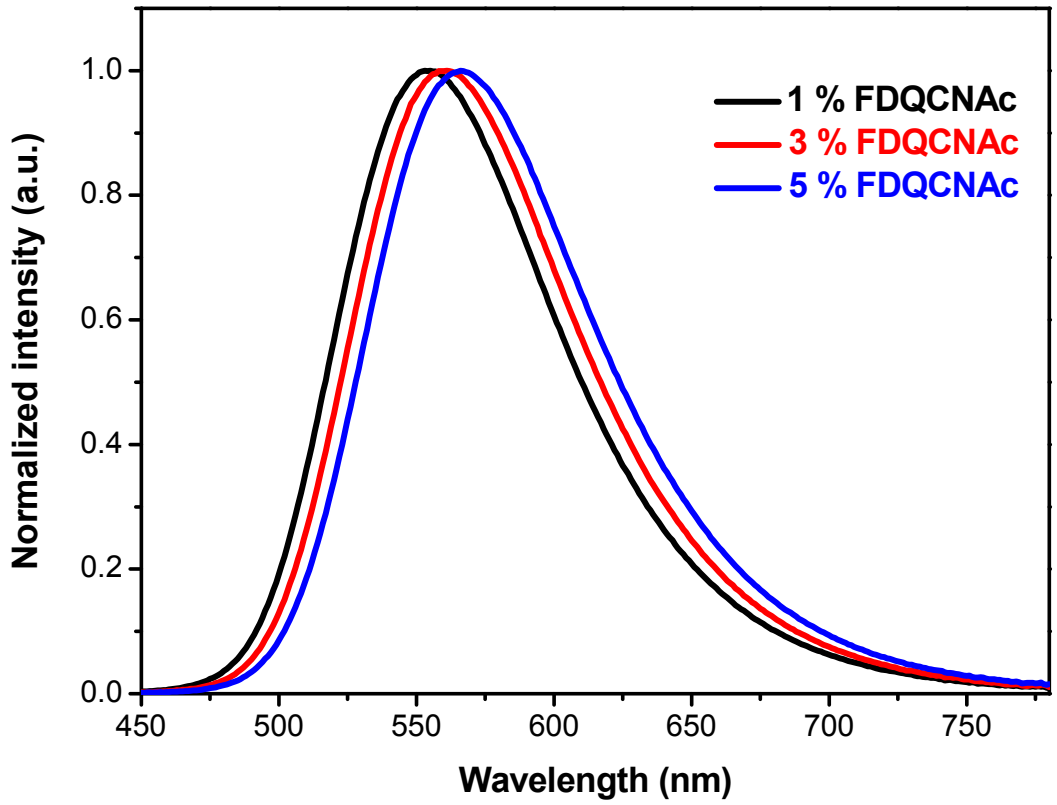


Figure S6. EL spectra of FDQCNAc at 1-5 % doping concentration

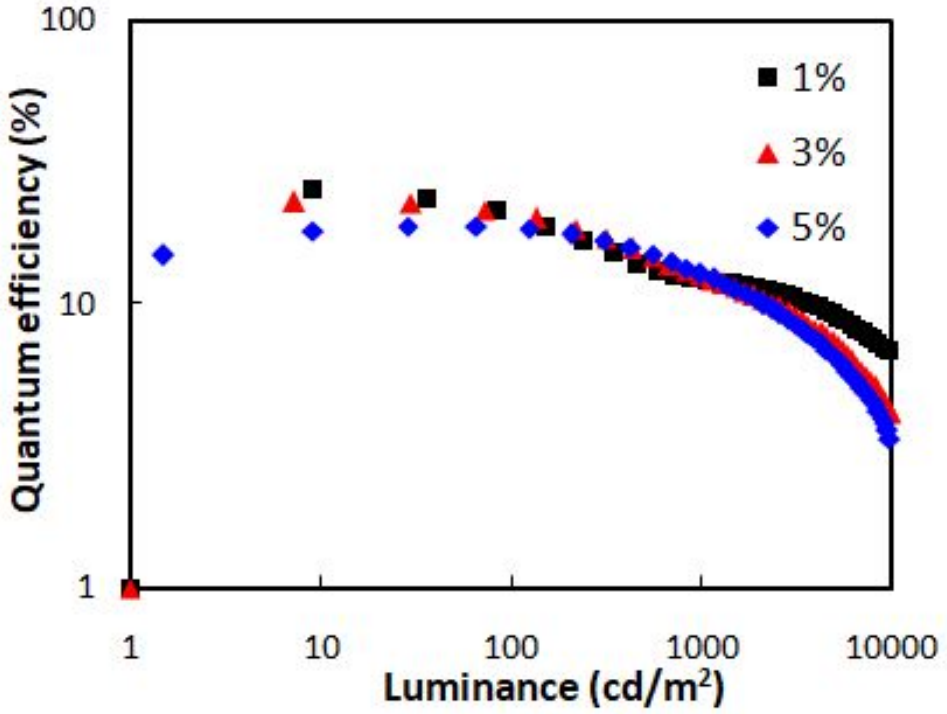


Figure S7. EQE−luminance curves of FBPCNAc doped OLED (1-5 %)

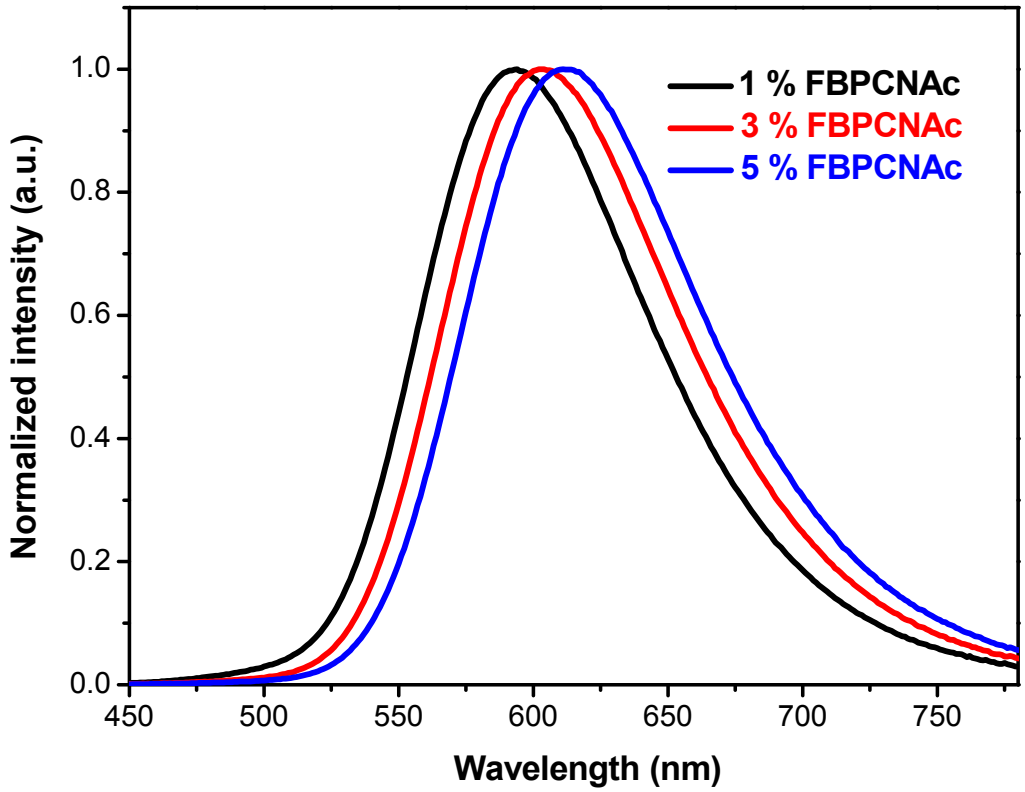


Figure S8. EL spectra of FBPCNAc at 1-5 % doping concentration

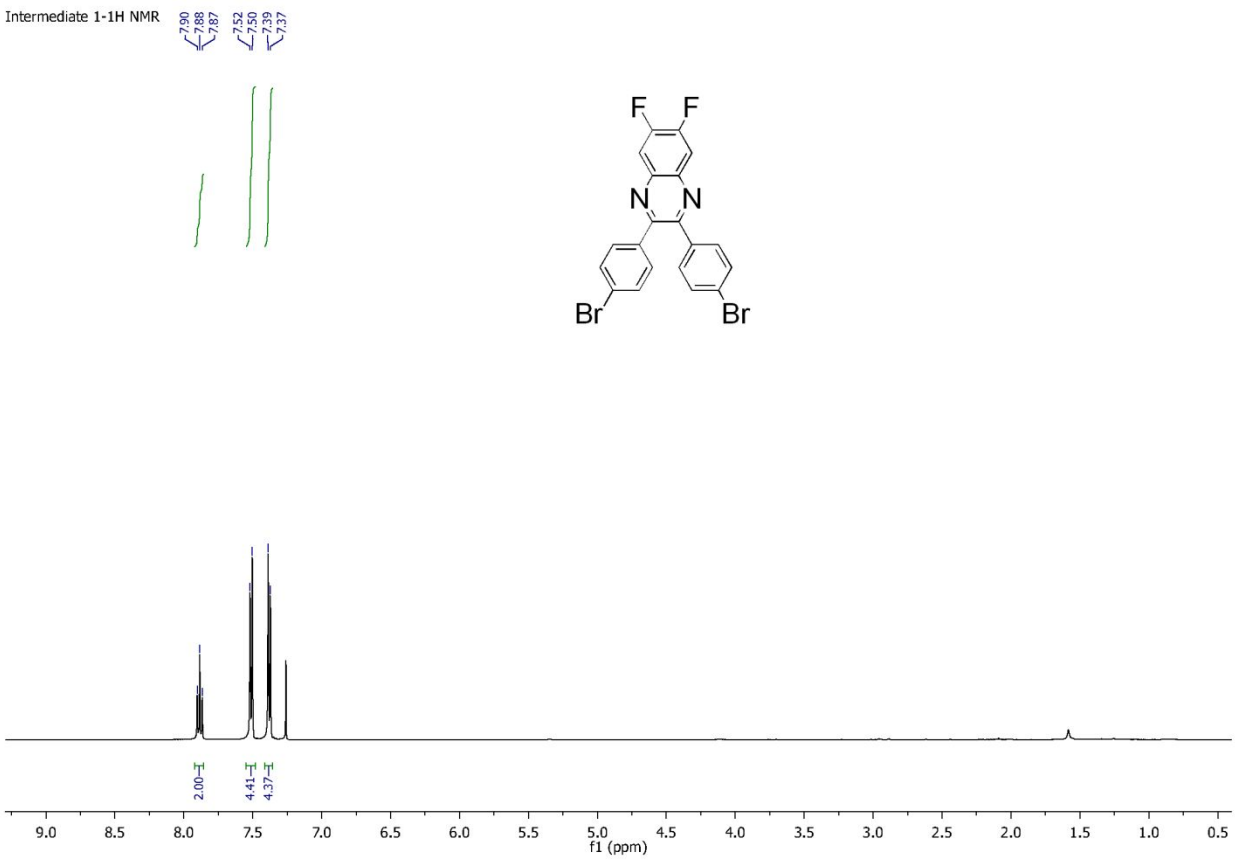


Figure S9. ^{1}H NMR spectrum of Intermediate 1

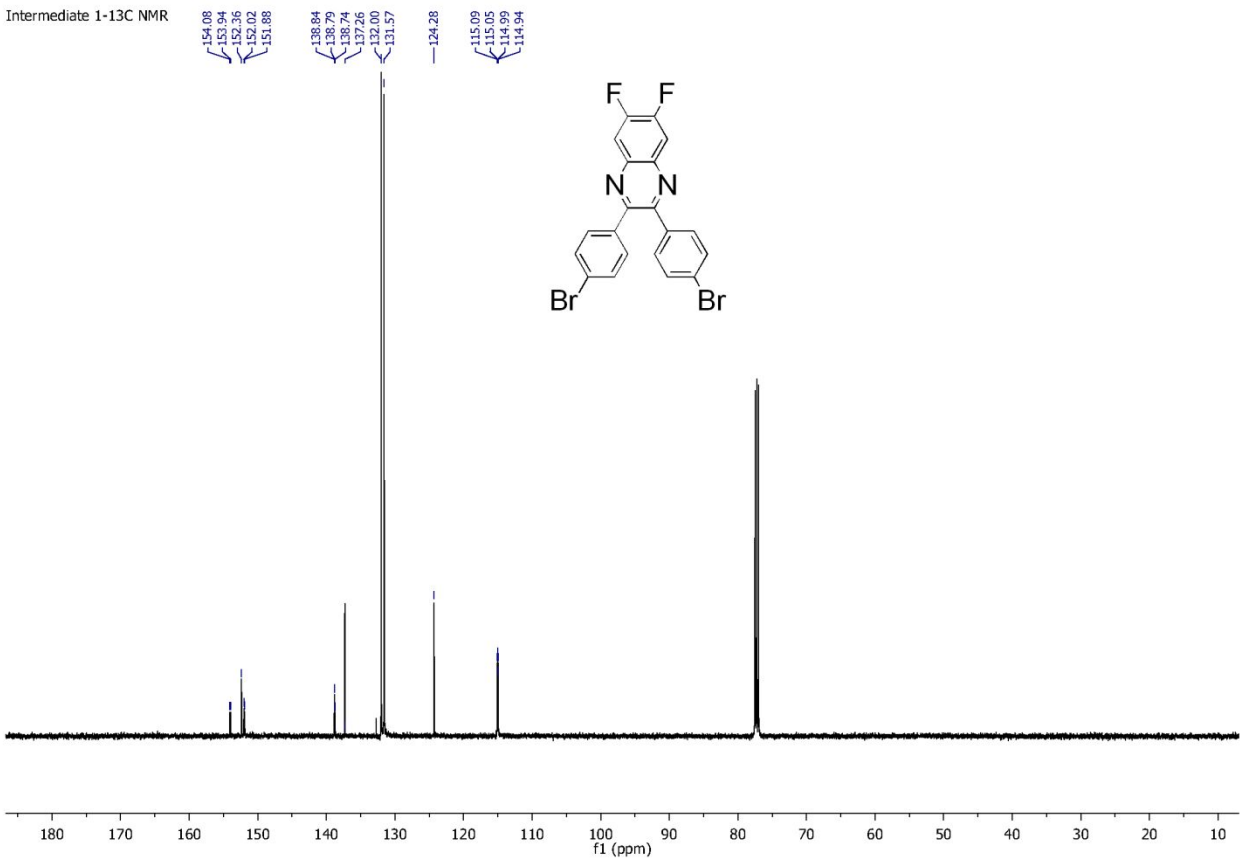


Figure S10. ^{13}C NMR spectrum of Intermediate 1

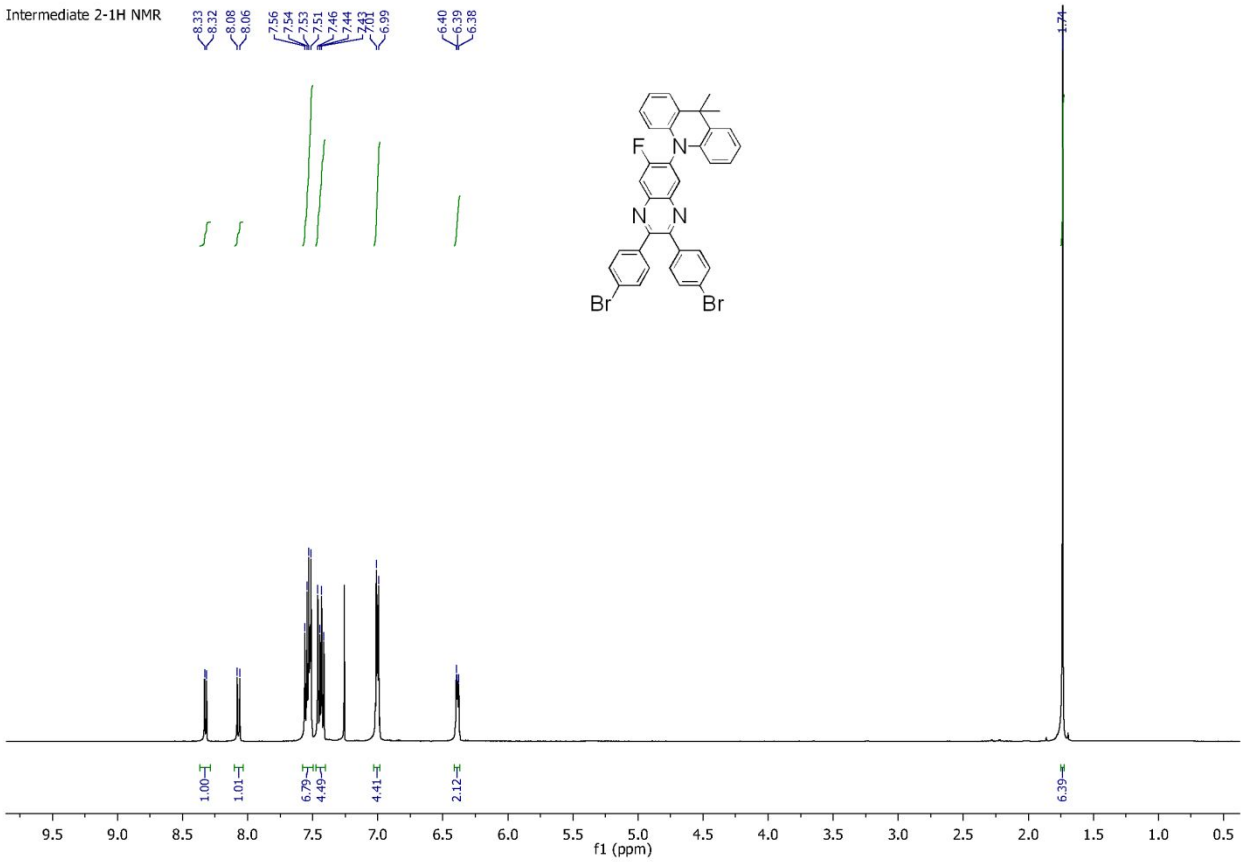


Figure S11. ^{1}H NMR spectrum of Intermediate 2

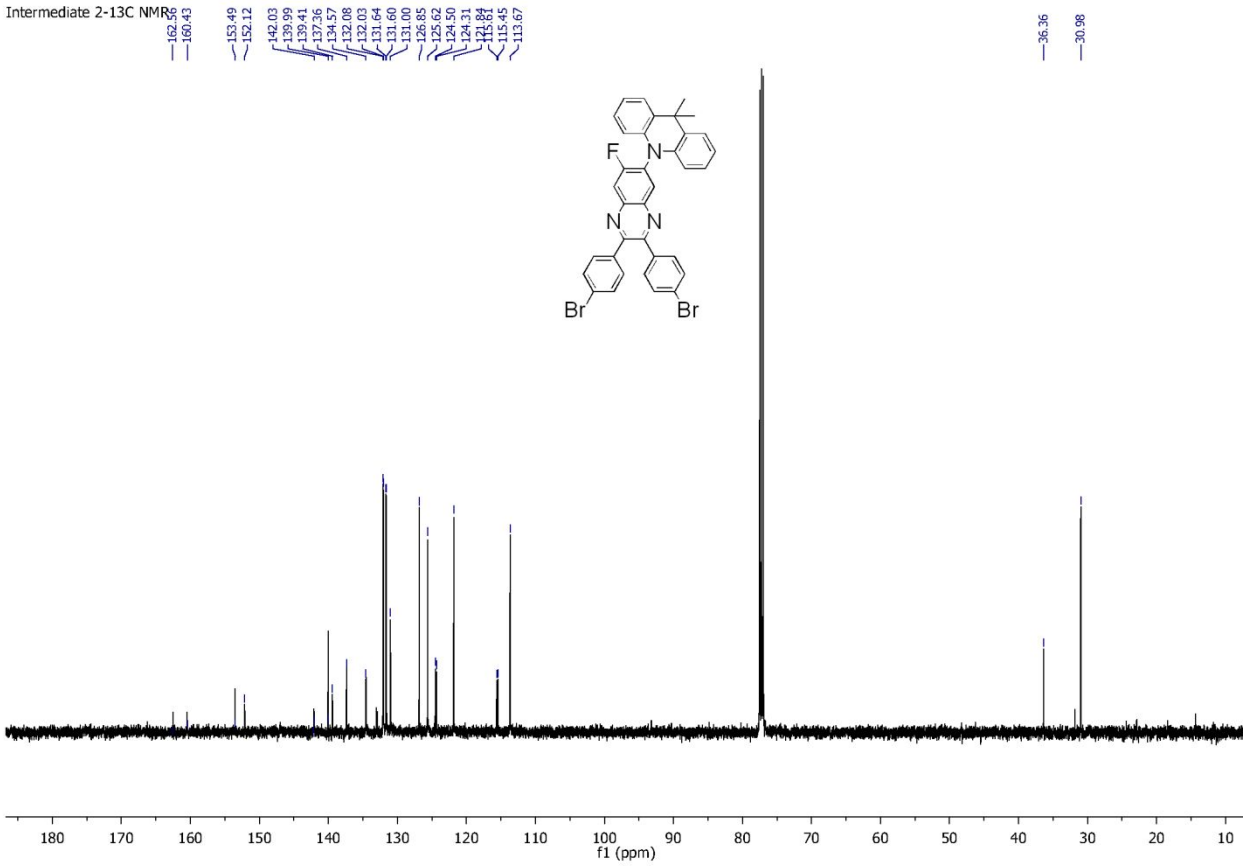


Figure S12.^{13}C NMR spectrum of Intermediate 2

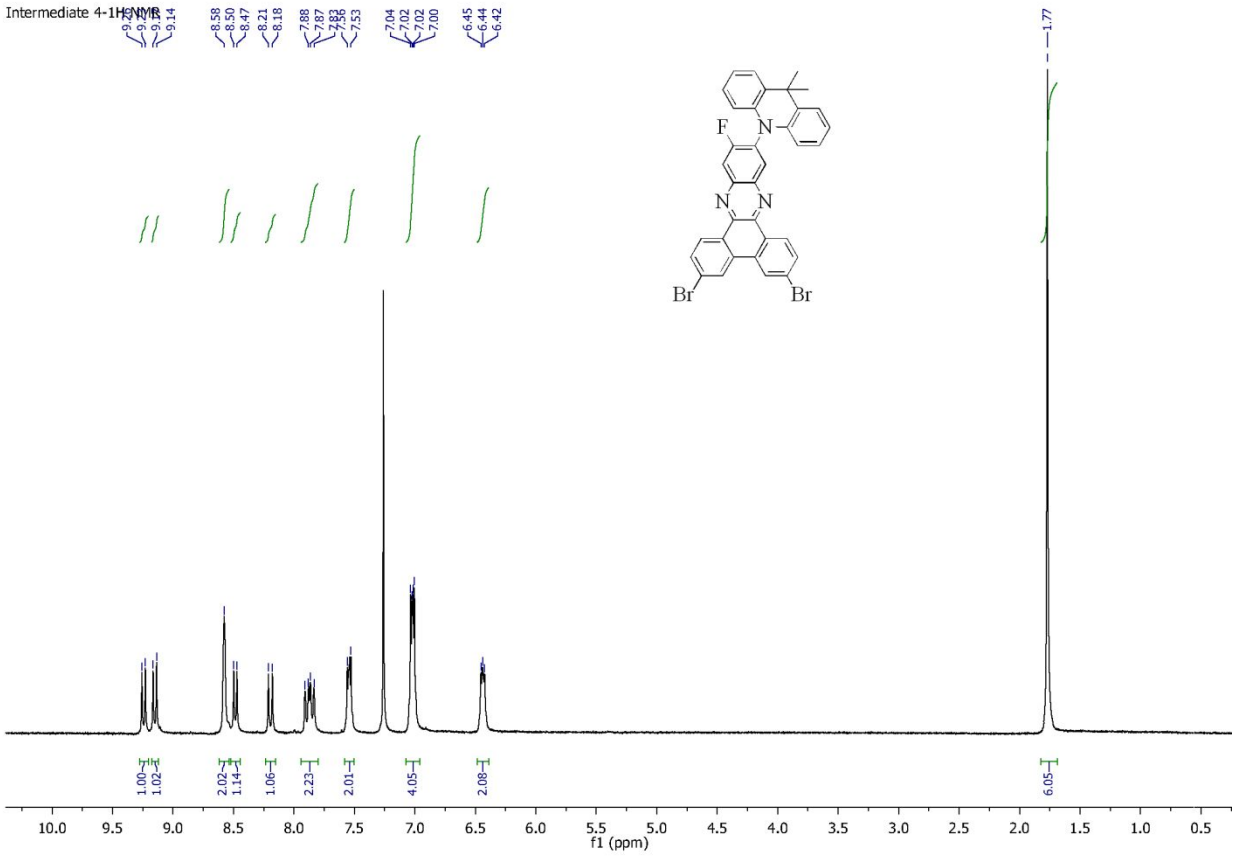


Figure S13.[1]H NMR spectrum of Intermediate 4

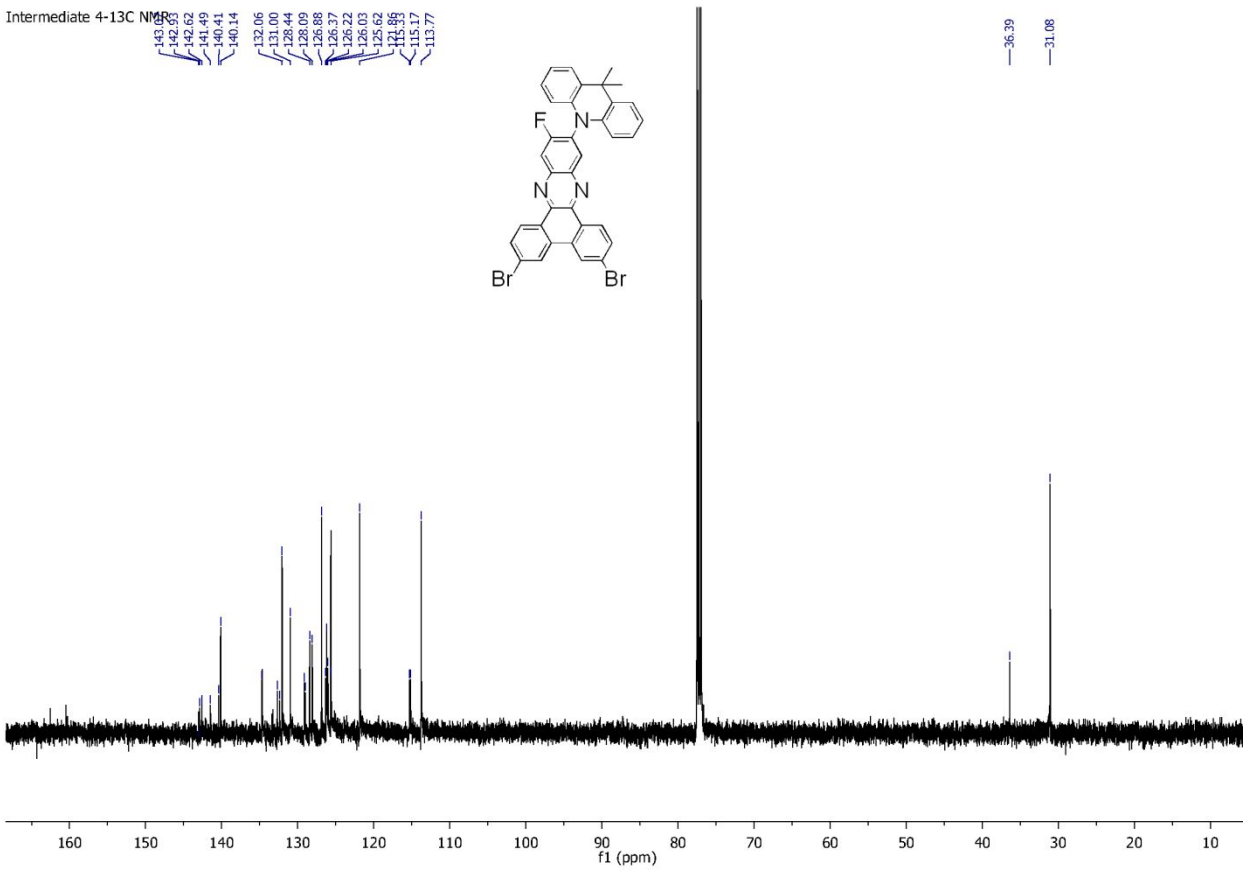


Figure S14.^{13}C NMR spectrum of Intermediate 4

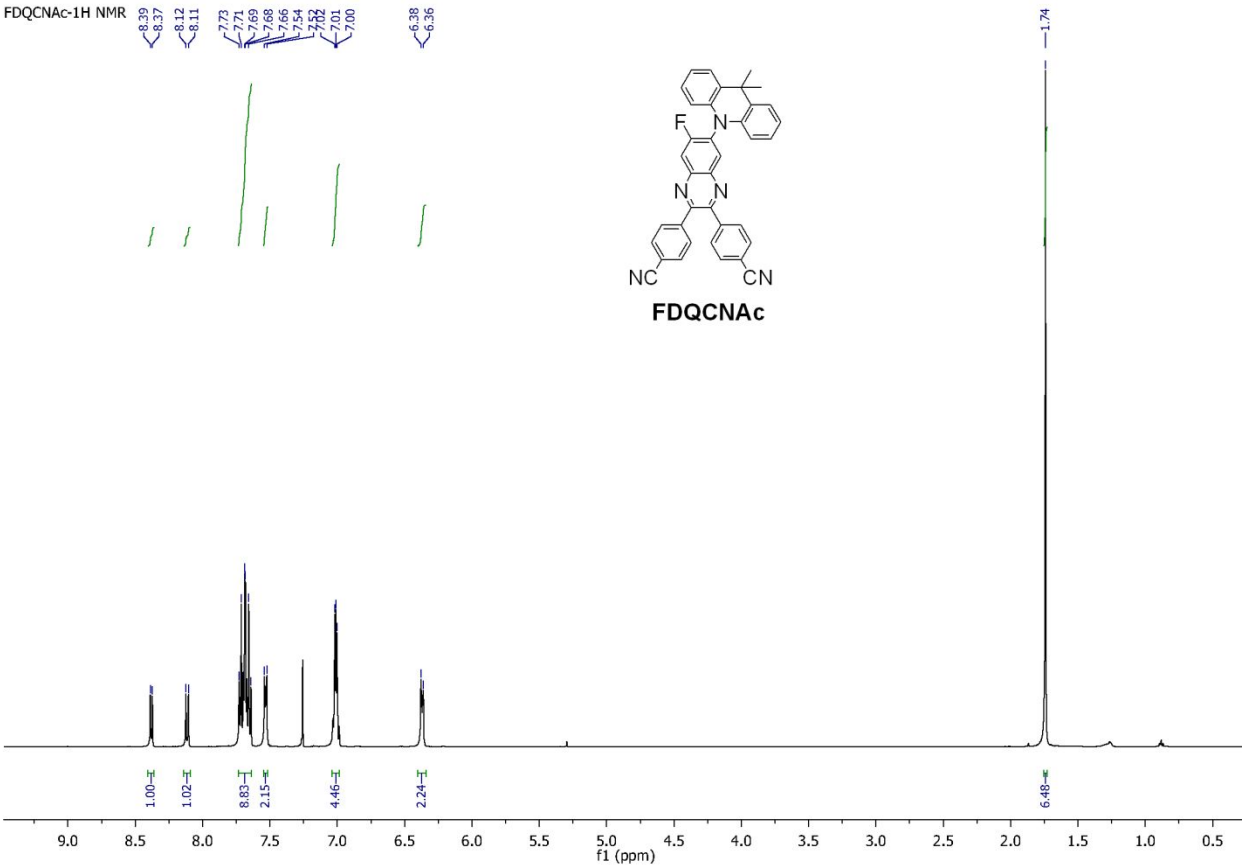


Figure S15.[1]H NMR spectrum of FDQCNAc

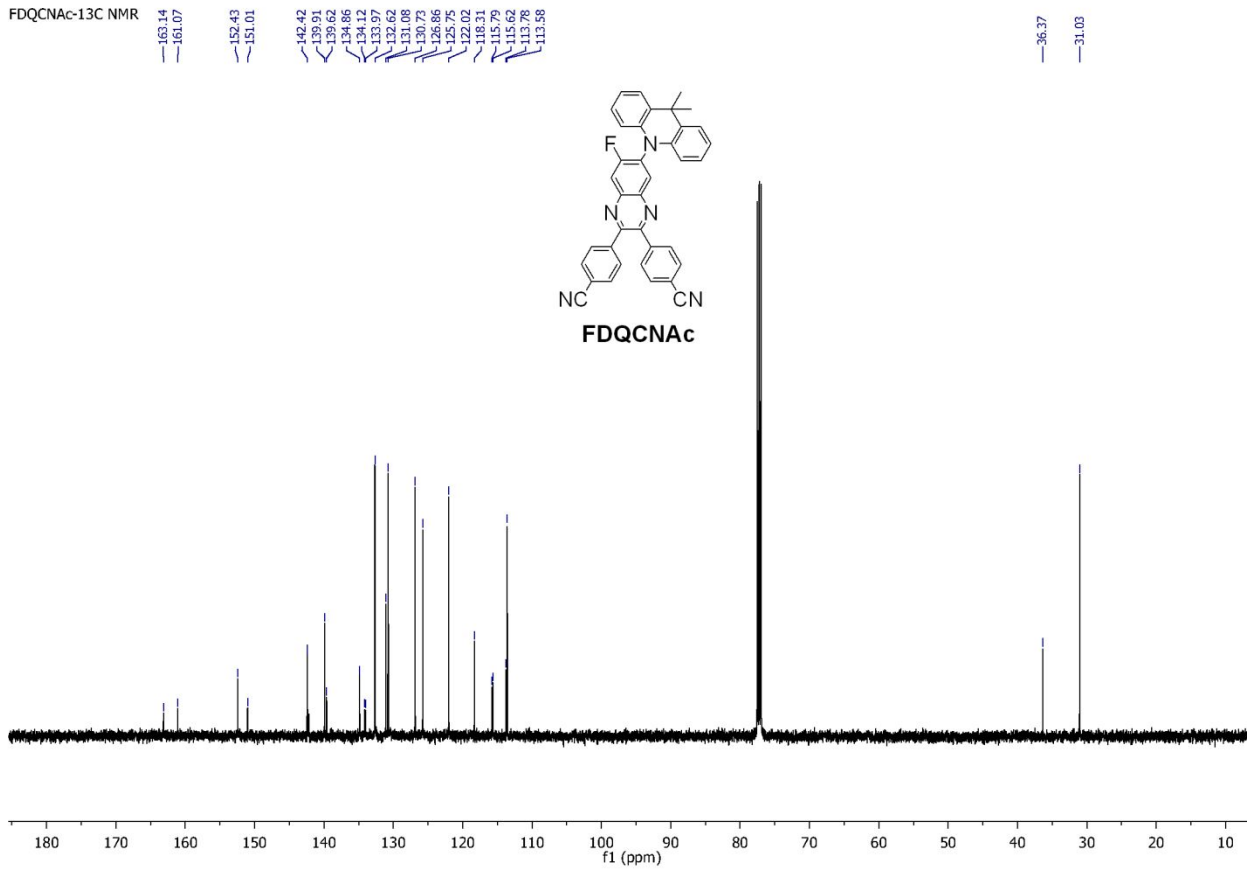


Figure S16.^{13}C NMR spectrum of FDQCNAc

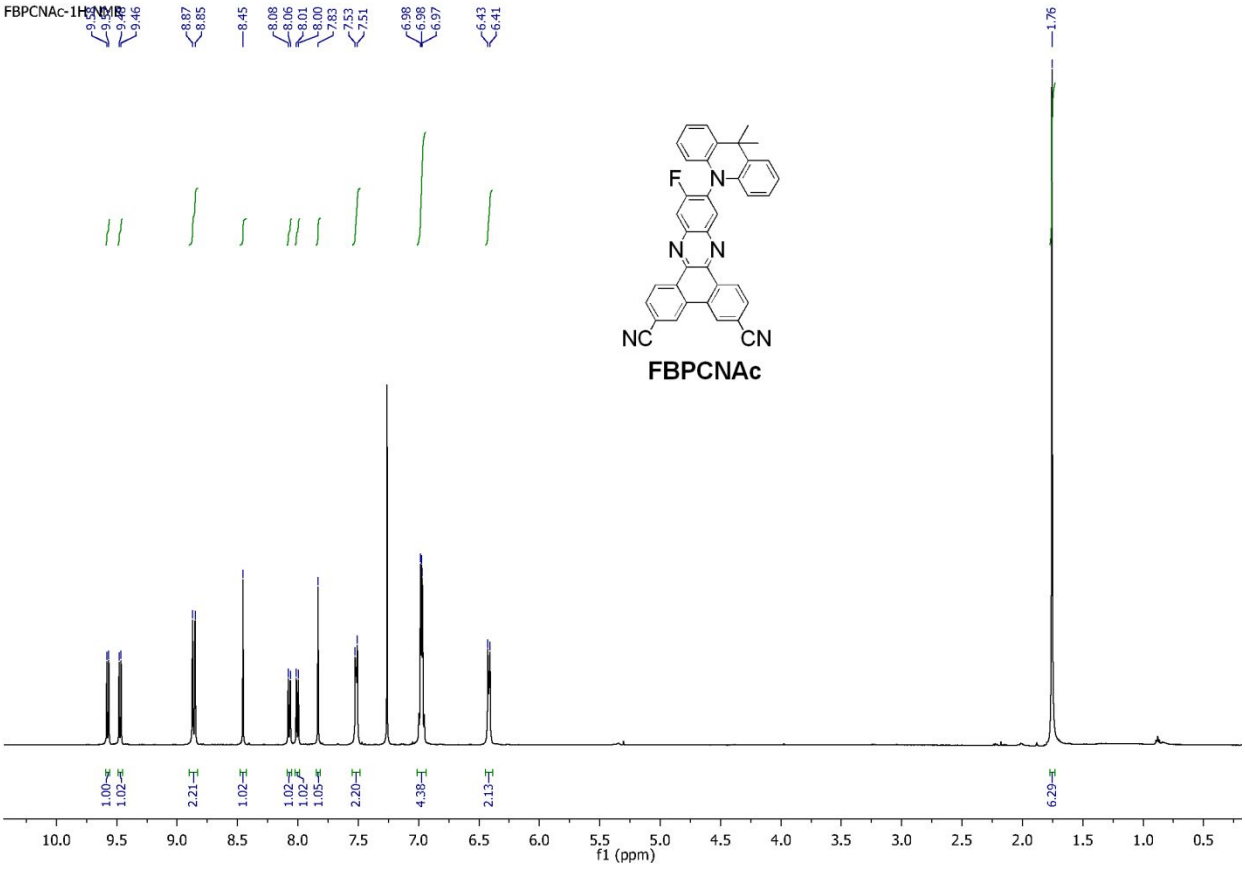


Figure S17.[1]H NMR spectrum of FBPCNAc

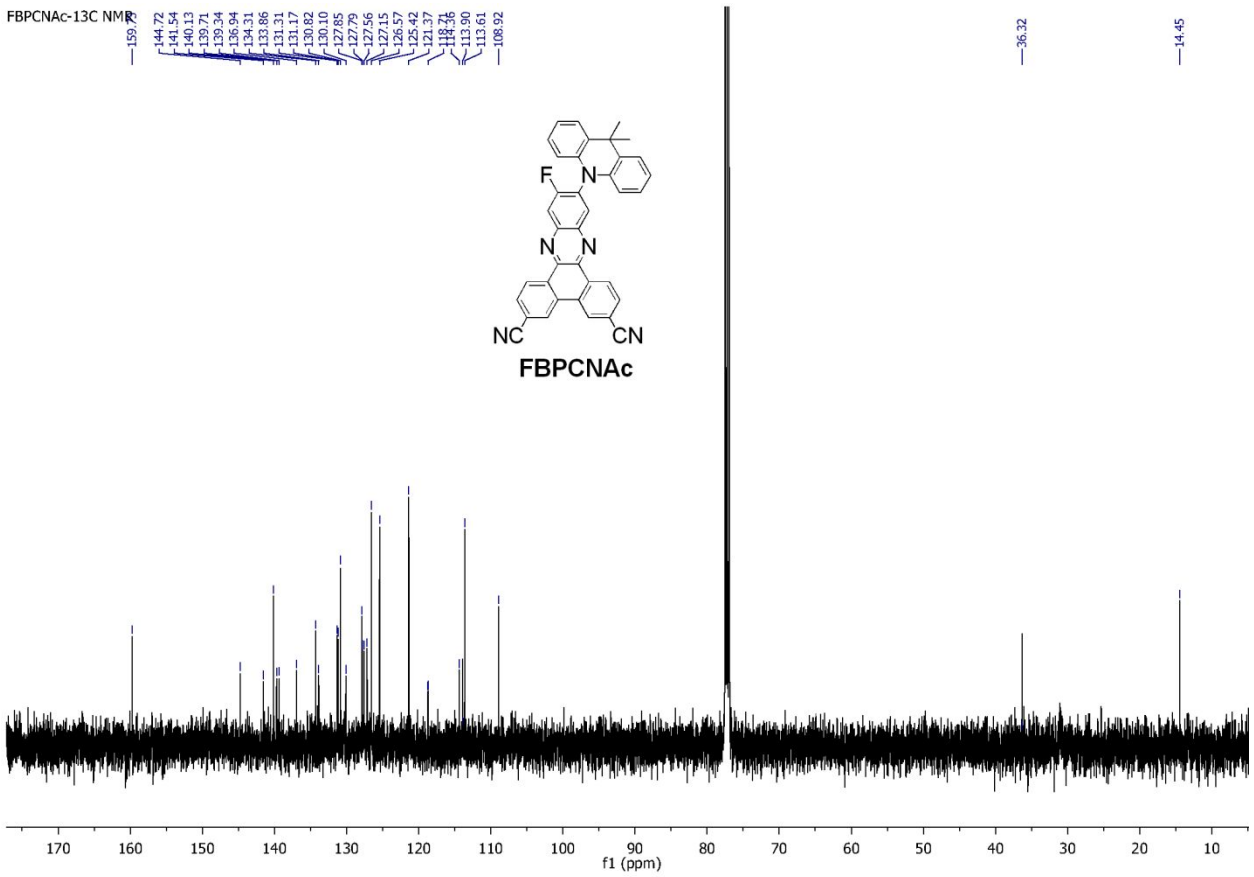
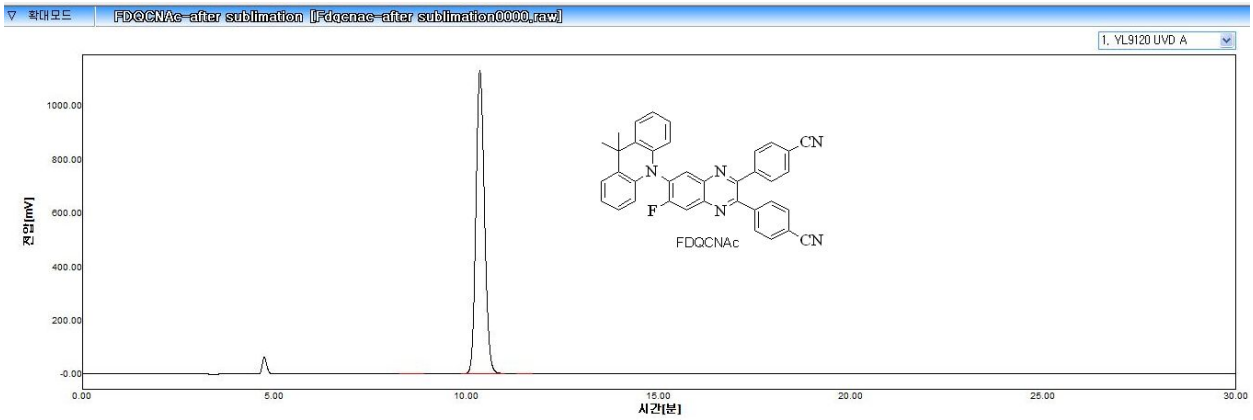
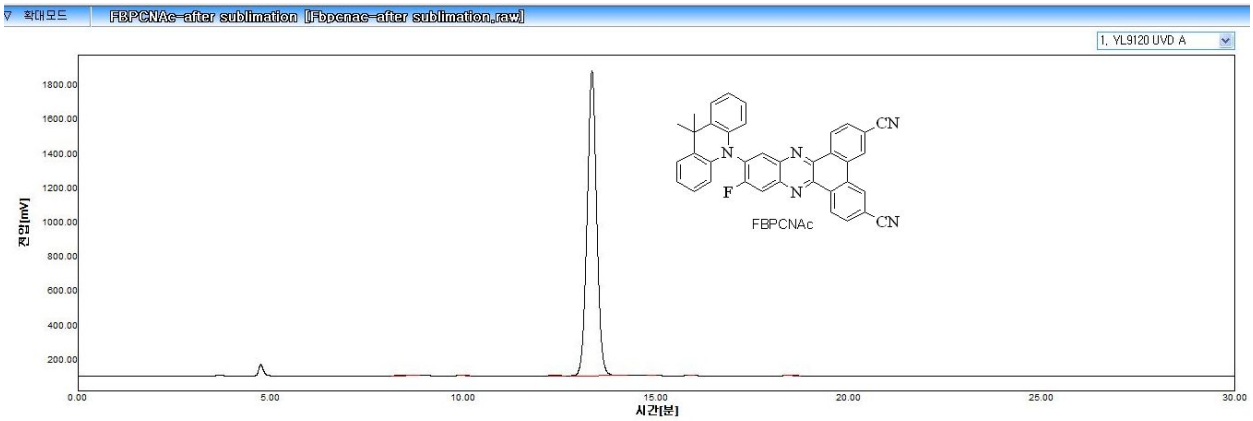


Figure S18.^{13}C NMR spectrum of FBPCNAc



#	피크이름	RT[분]	면적[mV*sec]	면적비[%]	높이[mV]	높이비[%]	농도	농도비[%]	형태	폭[초]	반치폭[초]	이론단수	분리도	Tailing Factor	사용자 정의1	사용자 정의2
1		8,4533	32,8070	0,19	1,6715	0,15	0,000000	0,00	FF	28,65	19,24	5013,3	0,0000	1,5796	0,000000	0,000000
2		10,3400	17441,3156	99,71	1130,8501	99,73	0,000000	0,00	FF	24,50	14,29	10256,4	4,2591	1,1330	0,000000	0,000000
3		11,4333	18,2630	0,10	1,3455	0,12	0,000000	0,00	FF	22,12	13,61	15389,7	2,8141	1,4714	0,000000	0,000000
합계			17492,3844		1133,8671		0,000000									

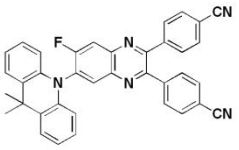
Figure S19. HPLC report of FDQCNAc after sublimation.



#	피크이름	RT[분]	면적[mV*sec]	면적비[%]	높이[mV]	높이비[%]	농도	농도비[%]	형태	폭[초]	반치폭[초]	이론단수	분리도	Tailing Factor	사용자 정의1	사용자 정의2
1		8,4667	43,5521	0,14	2,0465	0,11	0,000000	0,00	FF	35,21	20,66	3330,1	0,0000	1,1939	0,000000	0,000000
2		9,9733	5,4695	0,02	0,4700	0,03	0,000000	0,00	FF	17,85	11,90	17988,5	3,4075	1,3926	0,000000	0,000000
3		12,3667	11,0261	0,04	0,7660	0,04	0,000000	0,00	FF	23,59	14,27	15823,3	6,9303	1,2767	0,000000	0,000000
4		13,3267	30480,4875	99,77	1778,8087	99,77	0,000000	0,00	FF	27,57	15,65	13454,9	2,2514	1,0209	0,000000	0,000000
5		14,8400	1,7839	0,01	0,2012	0,01	0,000000	0,00	FF	11,64	9,38	93559,6	4,6306	1,4403	0,000000	0,000000
6		15,8933	0,8382	0,00	0,1162	0,01	0,000000	0,00	FF	10,29	7,60	137446,6	5,7631	1,2054	0,000000	0,000000
7		18,4600	8,0642	0,03	0,5106	0,03	0,000000	0,00	FF	23,83	16,01	34553,7	9,0263	1,3194	0,000000	0,000000
합계			30551,2219		1782,9191		0,000000									

Figure S20. HPLC report of FBPCNAc after sublimation.

Data : FAB735 Date : 30-Jan-2020 21:25
Instrument : MStation
Sample : KSS-38
Note : m-NBA
Inlet : Direct Ion Mode : FAB+
RT : 0.39 min Scan# : (14,20)
Elements : C 100/0, H 100/0, F 2/0, N 10/0
Mass Tolerance : 1000ppm, 5mmu if m/z < 5, 10mmu if m/z > 10
Unsaturation (U.S.) : 20.0 - 35.0

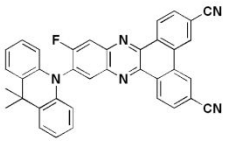


Chemical Formula: $C_{37}H_{24}FN_5$
Exact Mass: 557.2016

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	558.2093	16.75	-11.8 / -6.6	27.0	C41 H28 F2
2			+10.7 / +6.0	27.5	C40 H26 F2 N
3			-0.5 / -0.3	31.0	C42 H26 N2
4			-0.2 / -0.1	27.5	C37 H25 F N5
5			+0.2 / +0.1	24.0	C32 H24 F2 N8
6			-11.0 / -6.2	27.5	C34 H24 N9
7			+11.5 / +6.4	28.0	C33 H22 N10

Figure S21. HRMS report of FDQCNAc.

Data : FAB836 Date : 26-Feb-2020 14:26
Instrument : MStation
Sample : KSS-24-1
Note : m-NBA
Inlet : Direct Ion Mode : FAB+
RT : 1.62 min Scan# : (55,239)
Elements : C 100/0, H 100/0, F 2/0, N 10/0
Mass Tolerance : 1000ppm, 5mmu if m/z < 5, 20mmu if m/z > 20
Unsaturation (U.S.) : 15.0 - 40.0



Chemical Formula: $C_{37}H_{22}FN_5$
Exact Mass: 555.1859

	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	556.1937	50.01	-11.8 / -6.6	28.0	C41 H26 F2
2			-23.1 / -12.8	31.5	C43 H26 N
3			+10.8 / +6.0	28.5	C40 H24 F2 N
4			-0.4 / -0.2	32.0	C42 H24 N2
5			+33.4 / +18.6	29.0	C39 H22 F2 N2
6			+22.2 / +12.3	32.5	C41 H22 N3
7			-22.7 / -12.6	28.0	C38 H25 F N4
8			-0.1 / -0.0	28.5	C37 H23 F N5
9			+22.5 / +12.5	29.0	C36 H21 F N6
10			-22.3 / -12.4	24.5	C33 H24 F2 N7
11			-33.6 / -18.7	28.0	C35 H24 N8
12			+0.3 / +0.2	25.0	C32 H22 F2 N8
13			-11.0 / -6.1	28.5	C34 H22 N9
14			+22.9 / +12.7	25.5	C31 H20 F2 N9
15			+11.6 / +6.5	29.0	C33 H20 N10

Figure S22. HRMS report of FBPCNAc.

Equations for the calculation of rate constants

$$\tau_p = 1/k_p \quad (1)$$

$$\tau_d = 1/k_d \quad (2)$$

$$k_{ISC} = (1-\Phi_F) \times k_p \quad (3)$$

$$k_{RISC} = (k_p k_d / k_{ISC}) \times (\Phi_{TADF}/\Phi_F) \quad (4)$$

$$k_r^S = k_p \Phi_F \quad (5)$$

$$k_{nr}^T = k_d - k_{RISC} \Phi_F \quad (6)$$

$$\Phi_F = \Phi_{O_2} \quad (7)$$

$$\Phi_{TADF} = \Phi_{N_2\text{-}O_2} \quad (8)$$