

Supporting Information

Encapsulated TADF Macrocycles for High-Efficiency Solution-Processed and Flexible Organic Light-Emitting Diodes

Xinxin Ban, ^{*ab} Qingpeng Cao, ^a Wenhao Zhang, ^a Wenzhong Bian, ^a Caixia Yang, ^a Jiayi Wang, ^a Youqiang Qian, ^a Hui Xu, ^a Chuanzhou Tao, ^{*a} Wei Jiang^{*b}

^a School of Environmental and Chemical Engineering, Jiangsu Key Laboratory of Function Control Technology for Advanced Materials, Jiangsu Ocean University, Lianyungang, Jiangsu, China

^b School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu, China

*Corresponding Authors Email: banxx@jou.edu.cn, taocz@jou.edu.cn, jiangw@seu.edu.cn.

Table of Contents:

1. General methods
2. Synthetic details
3. Tables and figures of physical properties
4. Tables and figures of EL devices
5. ¹H-NMR, ¹³C-NMR and MALDI-TOF spectra

1. General methods

Measurements and characterization: ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker AVANCE 400 spectrometer. MALDI-TOF mass spectra were recorded on an AXIMA CFR MS apparatus (COMPACT). Absorption spectra were measured by a UV-Vis spectrophotometer (UV-2450) in the range of 200–500 nm. Photoluminescence (PL) spectra were recorded using a HORIBA FLUOROMAX-4 spectrofluorometer containing a liquid N₂ attachment. The transient photoluminescence decay characteristics of film were measured with a Quantaaurus-Tau fluorescence lifetime measurement system (C11367-03, Hamamatsu Photonics Co. Japan). Differential scanning calorimetry (DSC) curves were obtained with a DSC 2910 Modulation Calorimeter at a heating rate of 10 °C min⁻¹ under a nitrogen flow. Thermal gravimetric analyzer was carried out on a Netzsch simultaneous thermal analyzer system (STA 409PC) under a nitrogen atmosphere at a heating rate of 20 °C min⁻¹. Cyclic voltammetry (CV) was measured on CHI600 electrochemical workstation in a solution of

tetra-n-butylammonium hexafluorophosphate (Bu4NPF6) (0.1 M) in dichloromethane at a scan rate of 100 mV s^{-1} , using a platinum wire as the counter electrode, a glass carbon disk as the working electrode and Ag as the reference electrode. The energy level of HOMO and LUMO were calculated according to the equation of [HOMO = $-(E_{\text{onset}} + 4.8) \text{ eV}$] and [LUMO = (HOMO + E_g) eV], where E_{onset} is the onset oxidation potentials, and E_g is the optical bandgap obtained from the absorption onset. Transient PL spectra were detected on an Edinburgh fluorescence spectrometer (FLS-980). The prompt (τ_p) and delayed (τ_d) lifetimes are obtained following a tri-exponential decay fitting by considering the smallest decay time as τ_p and the weight average of the other decay times as τ_d . The absolute PL quantum yield (PLQY) was measured on Horiba Instruments Inc. FL3C-111 fluorescence spectrometer combined with an integrating sphere under an excitation wavelength of 335 nm. All quantum chemical calculations were performed using the Gaussian 09 program package.

Device fabrication and testing: The glass substrate with ITO coating were rinsed in deionized water, sonicated in acetone, ethanol and isopropanol in sequence. Before device fabrication, the ITO substrate was treated in a UV-ozone oven for 20 minutes. Then PEDOT: PSS was spin-coated on the ITO substrate and dried at $150 \text{ }^\circ\text{C}$ for 10 minutes. Then put the substrate in a nitrogen glove box, $100 \text{ }\mu\text{L}$ of TADF solution was spin-coated onto the ITO/ PEDOT: PSS substrates at 2,000 rpm for 30 s. Finally, a 40 nm thick layer of TPBi, a 1 nm thick layer of Cs_2CO_3 , and a 100 nm thickness layer of Al were deposited using a thermal evaporation system under a vacuum of $<1.0 \times 10^{-4} \text{ Pa}$. TPBi, Cs_2CO_3 and Al were deposited at rates of $1\sim 2 \text{ A s}^{-1}$, 0.1 A s^{-1} , and 5 A s^{-1} , respectively. The effective emitting area of the devices was 4 mm^2 , determined by the overlap between the anode and cathode. EL spectra, device brightness and current density-voltage characteristics are recorded using a combination of Photo-Research PR-655 SpectraScan and Keithley 2400 Sourcemeter. The device is tested under atmospheric conditions without a protective package.

2. Synthetic details

All starting materials for the synthesis were purchased from commercial sources and used as received unless otherwise noted. Solvents (THF, DMF and toluene) were dried by sodium and distilled under argon atmosphere before usage.

(2S,3R,4R)-2,3,4,5,6-pentakis(4-methoxy-9H-carbazol-9-yl)benzotrile (5OCzBN): 4-methoxy-

9H-carbazole (M1, 1.00 g, 5.08 mmol) was dissolved in the anhydrous DMF (50 mL) solution containing sodium hydride (0.40 g, 16.7 mmol) under nitrogen atmosphere at room temperature. After stirring vigorously for 30 minutes, 2,3,4,5,6-pentafluorobenzonitrile (5F-CN, 0.16 g, 0.83 mmol) was added. The mixture was stirred at room temperature for 24 hours. After the reaction was complete, it was poured into ice water and 40 % NaCl solution (400 mL, 2:1 v/v) for 15 min to precipitate a yellow solid. The resulting solid was filtered, and the yellow solid was dried and purified by silica gel column chromatography (DCM: petroleum ether, 1:6 v/v) to obtain a yellow powder (0.73 g, 82.0% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 2H), 7.50 (d, *J* = 7.4 Hz, 3H), 7.15 – 6.77 (m, 13H), 6.68 (dd, *J* = 18.2, 8.7 Hz, 6H), 6.56 – 6.34 (m, 8H), 6.11 (dd, *J* = 19.8, 7.4 Hz, 3H), 3.82 (s, 6H), 3.58 (d, *J* = 20.2 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 154.92, 154.85, 154.11, 140.82, 139.50, 138.37, 137.19, 136.16, 136.05, 125.26, 125.15, 124.05, 123.32, 122.34, 122.20, 122.03, 121.96, 121.15, 120.06, 119.49, 116.02, 112.30, 111.91, 111.46, 109.14, 108.75, 102.96, 102.61, 102.34, 101.39, 101.05, 100.88, 76.31, 76.00, 75.68, 54.36, 54.10, 54.03.

(2s,4r)-2,4,6-tri(9H-carbazol-9-yl)-3,5-difluorobenzonitrile (3CzFBN): 9H-carbazole (Cz, 2.42 g, 14.5 mmol) was dissolved in the anhydrous THF (50 mL) solution containing sodium hydride (2.48 g, 0.104 mol) under nitrogen atmosphere at room temperature. After stirring vigorously for 30 minutes, 2,3,4,5,6-pentafluorobenzonitrile (5F-CN, 1.00 g, 5.2 mmol) was added. The mixture was stirred at room temperature for 24 hours. After the reaction was complete, it was poured into ice water and 40 % NaCl solution (400 mL, 2:1 v/v) for 15 min to precipitate a yellow solid. The resulting solid was filtered, and the yellow solid was dried and purified by silica gel column chromatography (DCM: petroleum ether, 1:8 v/v) to obtain a bright yellow powder (2.16 g, 65.9% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 7.7 Hz, 4H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.55 (dd, *J* = 11.3, 4.2 Hz, 4H), 7.52 - 7.44 (m, 2H), 7.37 (ddd, *J* = 11.3, 10.9, 4.1 Hz, 10H), 7.28 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 140.13, 139.30, 126.83, 126.82, 124.62, 124.50, 122.00, 121.85, 121.09, 120.84, 109.97, 109.38.

4,4'-((((9H-fluorene-9,9-diyl)bis(4,1-phenylene))bis(oxy))bis(hexane-6,1-diyl))bis(oxy))bis (9H-carbazole) (CzFu): Bisphenol Fluorene (2OH-Fu, 2.0 g, 5.7 mmol), K₂CO₃ (4.72 g, 34.2 mmol) and 4-((6-bromoheptyl)oxy)-9H-carbazole (Cz-Br, 3.05 g, 7.1 mmol) were dissolved in acetone (50 mL) under nitrogen condition. The reaction mixture was stirred at 65 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated by rotary evaporation. 4.11g white powder was obtained by

column chromatography (DCM: petroleum ether, 1:3 v/v) in a yield of 82.2%. ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 7.8 Hz, 2H), 8.00 (s, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.40 - 7.27 (m, 12H), 7.22 - 7.17 (m, 2H), 7.10 - 7.06 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.75 - 6.69 (m, 4H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.23 (t, *J* = 6.3 Hz, 4H), 3.91 (t, *J* = 6.4 Hz, 4H), 2.05 - 1.96 (m, 4H), 1.85 - 1.77 (m, 4H), 1.72 - 1.64 (m, 4H), 1.63 - 1.56 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 155.69, 155.19, 151.96, 138.67, 129.62, 129.13, 128.64, 127.23, 126.65, 124.84, 122.99, 119.60, 114.04, 109.86, 106.39, 103.25, 101.09, 77.26, 77.01, 76.76, 76.42, 67.77, 61.21, 53.41, 29.39, 29.25, 26.04, 25.89.

4-((6-(9H-carbazol-9-yl)hexyl)oxy)-9H-carbazole (Cz-Cz): 4-((6-bromohexyl)oxy)-9H-carbazole (Cz-Br, 3 g, 9.09 mmol), 9H-carbazol-4-ol (OH-Cz, 1.48 g, 8.08 mmol) and K₂CO₃ (3.78 g, 27.2 mmol) were dissolved in acetone (50 mL) under nitrogen condition. The reaction mixture was stirred at 65 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated by rotary evaporation. 3.11 g white powder was obtained by column chromatography (DCM: petroleum ether, 1:3 v/v) in a yield of 79.3%. ¹H NMR (300 MHz, CDCl₃, δ): 8.29 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.99 (s, 1H), 7.50-7.35 (m, 6H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.23-7.16 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.32 (t, *J* = 7.1 Hz, 2H), 4.19 (t, *J* = 6.3 Hz, 2H), 2.04-1.88 (m, 4H), 1.74-1.60 (m, 2H), 1.56-1.48 (m, 2H).

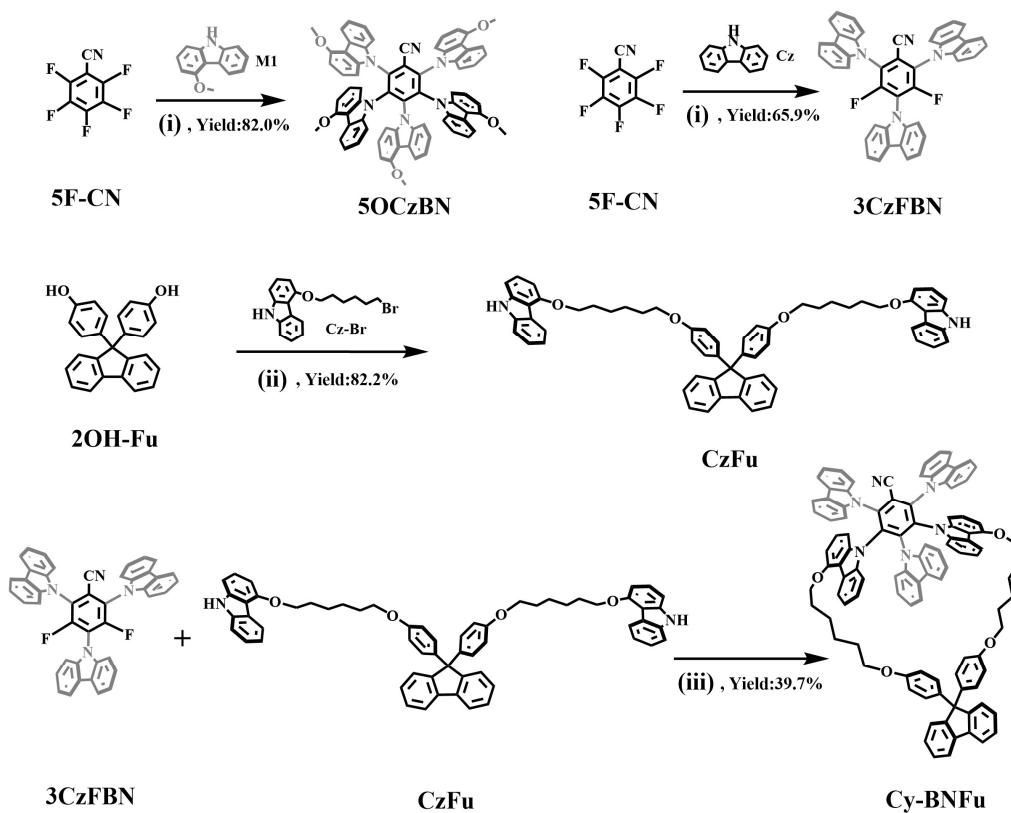
(2R,4R)-2,4,6-tris(4-((6-(9H-carbazol-9-yl)hexyl)oxy)-9H-carbazol-9-yl)-3,5 difluorobenzonitrile (Cz-3CzFBN): Cz-Cz (6.26 g, 14.5 mmol) was dissolved in the anhydrous THF (50 mL) solution containing sodium hydride (2.49 g, 0.104 mol) under nitrogen atmosphere at room temperature. After stirring vigorously for 30 minutes, 2,3,4,5,6-pentafluorobenzonitrile (5F-CN, 1.00 g, 5.2 mmol) was added. The mixture was stirred at room temperature for 24 hours. After the reaction was complete, it was poured into ice water and 40 % NaCl solution (400 mL, 2:1 v/v) for 15 min to precipitate a yellow solid. The resulting solid was filtered, and the yellow solid was dried and purified by silica gel column chromatography (DCM: petroleum ether, 1:10 v/v) to obtain a bright yellow powder (5.02 g, 67.7% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, *J* = 7.3 Hz, 2H), 8.31 (d, *J* = 7.5 Hz, 1H), 8.08 (d, *J* = 6.7 Hz, 6H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45 - 7.27 (m, 21H), 7.20 (dd, *J* = 8.7, 2.9 Hz, 7H), 6.94 (t, *J* = 13.1 Hz, 2H), 6.85 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 1H), 4.33 - 4.22 (m, 6H), 4.19 - 4.08 (m, 6H), 1.96 - 1.84 (m, 12H), 1.61 (tt, *J* = 14.9, 7.6 Hz, 6H), 1.53 - 1.46 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 156.00, 155.81, 141.56, 140.76, 140.51, 139.45, 138.64, 127.73, 125.81, 125.68, 124.08, 123.98, 123.78, 123.59, 122.91, 122.07, 121.93, 120.40, 118.81, 113.85, 113.75, 109.29, 108.72, 108.68,

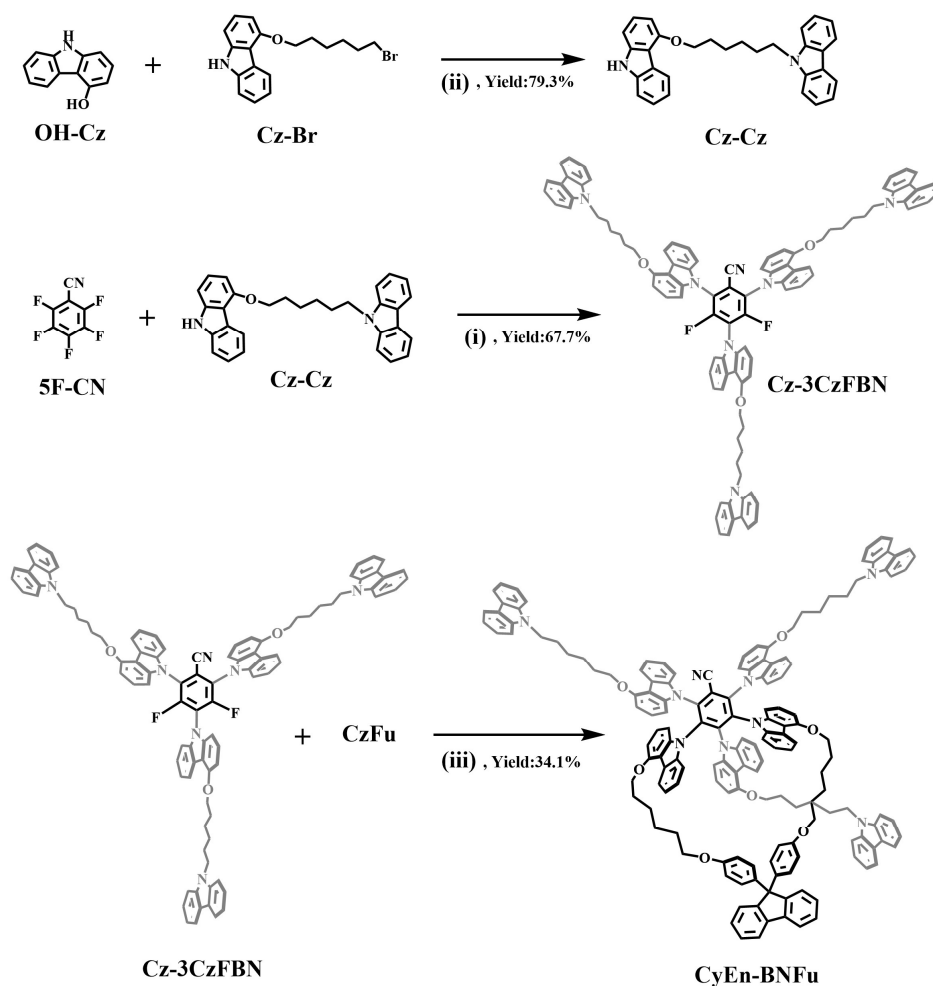
103.80, 103.66, 102.43, 101.89, 77.35, 77.10, 76.84, 68.06, 68.03, 42.99, 42.96, 29.33, 29.28, 29.04, 27.13, 27.11, 27.00, 26.19, 26.16. MS (MALDI-TOF) [m/z]: calcd for C₉₇H₈₁F₂N₇O₃, 1429.6; found, 1429.6. Anal. Calcd. for C₉₇H₈₁F₂N₇O₃: C, 81.43; H, 5.71; N, 6.85. Found: C, 81.44; H, 5.71; N, 6.83.

Cy-BNFu: CzFu (5.00 g, 5.7 mmol) was dissolved in the anhydrous DMF (50 mL) solution containing sodium hydride (2.73 g, 0.114 mol) under nitrogen atmosphere at room temperature. After stirring vigorously for 30 minutes, 3CzFBN (3.6 g, 5.7 mmol) was added. The reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction solution was poured into ice water ice water and 40 % NaCl solution (400 mL, 2:1 v/v) for 15 min. The light yellow precipitate was collected by suction filtration and then the precipitation was purified by column chromatography (DCM: petroleum ether, 1:4 v/v) to give 3.33 g light-green flocculent powder in a yield of 39.7%. ¹H NMR (500 MHz, CDCl₃) δ 8.44 (d, *J* = 7.7 Hz, 2H), 8.32 – 8.27 (m, 8H), 8.16 (dd, *J* = 8.9, 5.4 Hz, 5H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.79 (m, 9H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 4H), 7.51 – 7.42 (m, 8H), 7.41 (t, *J* = 6.5 Hz, 2H), 7.35 (ddd, *J* = 15.7, 9.8, 4.8 Hz, 9H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.3 Hz, 4H), 2.17 – 2.12 (m, 4H), 1.85 (d, *J* = 6.7 Hz, 4H), 1.81 – 1.49 (m, 8H), 1.42 – 1.16 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 156.75, 153.53, 150.87, 139.50, 139.40, 138.91, 138.25, 137.95, 136.93, 136.00, 135.80, 128.10, 126.62, 126.22, 125.57, 124.99, 124.35, 124.08, 123.25, 123.02, 122.70, 122.23, 122.12, 121.19, 120.29, 120.06, 119.52, 119.19, 119.06, 118.34, 112.98, 112.10, 109.66, 109.29, 108.88, 108.71, 102.34, 101.77, 76.31, 76.00, 75.68, 69.62, 66.61, 63.13, 29.29, 28.68, 28.13, 28.02, 24.75, 13.43. MS (MALDI-TOF) [m/z]: calcd for C₁₀₄H₇₈N₆O₄, 1475.61; found, 1476.64.

CyEn-BNFu: CzFu (3.00 g, 0.3 mmol) was dissolved in the anhydrous DMF (50 mL) solution containing sodium hydride (1.62 g, 67.5 mmol) under nitrogen atmosphere at room temperature. After stirring vigorously for 30 minutes, Cz-3CzFBN (5 g, 3.50 mmol) was added. The reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction solution was poured into ice water ice water and 40 % NaCl solution (400 mL, 2:1 v/v) for 15 min. The light-yellow precipitate was collected by suction filtration and then the precipitation was purified by column chromatography (DCM: petroleum ether, 1:6 v/v) to give 2.62 g light-green flocculent powder in a yield of 34.1%. ¹H NMR (500 MHz, CDCl₃) δ 8.32 (d, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 5H), 8.10 – 7.98 (m, 3H), 7.77 (t, *J* = 8.1 Hz, 2H), 7.55 (s, 2H), 7.52 – 7.30 (m, 22H), 7.23 (dd, *J* = 15.7, 8.1 Hz, 11H), 7.12 (d, *J* = 8.7 Hz, 4H), 7.04 – 6.99 (m, 2H), 6.96 (d, *J* = 7.0 Hz, 3H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.77 – 6.70 (m, 4H), 6.67 (d, *J* =

7.9 Hz, 2H), 6.55 (dd, $J = 13.3, 5.9$ Hz, 4H), 6.35 (dd, $J = 27.2, 22.9$ Hz, 5H), 6.22 – 6.10 (m, 3H), 4.31 (t, $J = 6.7$ Hz, 4H), 4.29 – 4.15 (m, 4H), 4.13 – 4.00 (m, 4H), 3.97 – 3.86 (m, 4H), 3.85 – 3.64 (m, 4H), 2.05 – 1.98 (m, 2H), 1.97 – 1.89 (m, 4H), 1.88 – 1.82 (m, 4H), 1.74 – 1.57 (m, 12H), 1.52 – 1.45 (m, 6H), 1.41 – 1.25 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.75, 154.62, 150.88, 139.85, 139.37, 138.90, 137.61, 136.89, 128.09, 126.62, 126.22, 125.60, 125.02, 124.58, 123.79, 121.92, 121.76, 121.70, 119.31, 119.05, 118.53, 117.70, 112.99, 111.60, 108.85, 107.62, 107.58, 102.22, 99.98, 76.31, 75.99, 75.68, 66.90, 66.70, 66.66, 63.12, 41.90, 28.67, 28.33, 28.23, 28.19, 27.96, 26.04, 25.88, 25.10, 24.98, 24.84. MS (MALDI-TOF) [m/z]: calcd for $\text{C}_{151}\text{H}_{131}\text{N}_9\text{O}_7$, 2255.01; found, 2255.21.





Scheme S1. The synthesis of monomer (3CzFBN, CzFu, Cz-Cz and Cz-3CzFBN) and TADF compound (5OCzBN, Cy-BNFu and CyEn-BNFu): (i). NaH, DMF, RT; (ii). NaH, THF, RT; (iii). K₂CO₃, Acetone, 65 °C; (iv). Cs₂CO₃, DMSO, 160 °C.

3. Tables and figures of physical properties

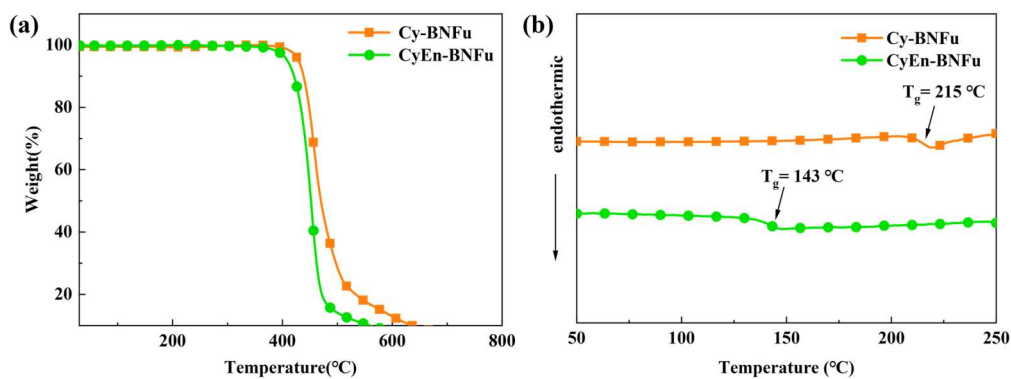


Figure S1. TGA (a) and DSC (b) curves of Cy-BNFu and CyEn-BNFu recorded at a heating rate of 10 °C min⁻¹.

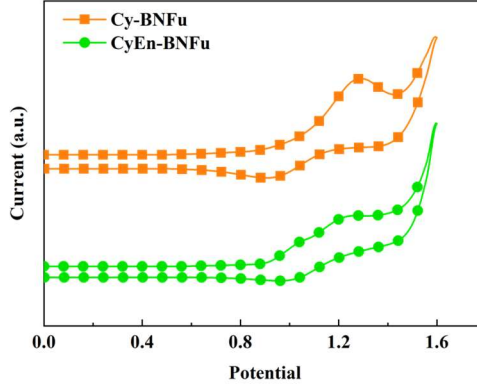


Figure S2. Cyclic voltammetry (CV) curves of Cy-BNFu (a) and CyEn-BNFu (b) measured at room temperature in CH₂Cl₂.

Table S1 Summary of photophysical parameters for Cy-BNFu and CyEn-BNFu films.

Compound	τ_p [ns]	τ_d [us]	$\Phi_p/\Phi_d/\Phi_{PL}$ [%]	k_p [10^7 s^{-1}]	k_d [10^5 s^{-1}]	k_r^S [10^5 s^{-1}]	k_{ISC} [10^7 s^{-1}]	k_{RISC} [10^6 s^{-1}]	k_{nr}^T [10^5 s^{-1}]
Cy-BNFu	33	1.59	13.5/51.5/65	3.03	6.29	4	2.62	2.77	2.54
CyEn-BNFu	35	2.68	10.2/71.8/82	2.86	3.73	2.9	2.56	2.92	0.74

Notes: The data is collected in doped films for Cy-BNFu and CyEn-BNFu under nitrogen atmosphere. τ_p and τ_d are prompt and delayed lifetimes; Φ_{PL} is the total PLQY; Φ_p and Φ_d are the PLQY of prompt and delayed components; k_p , k_d , k_r^S , k_{ISC} , k_{RISC} and k_{nr}^T are the rate constants of the prompt fluorescence, delayed fluorescence, singlet radiation, intersystem crossing from S₁ to T₁, reverse intersystem crossing from T₁ to S₁ and triplet non-radiation, respectively. All these parameters are obtained following the three-energy-level model by ignoring the non-radiative pathway of S₁ and the radiation of T₁.

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

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

$$k_r^S = k_p \cdot \Phi_p \quad (3);$$

$$k_{ISC} = k_p \cdot (1 - \Phi_p) \quad (4);$$

$$k_{RISC} = (k_p \cdot k_d / k_{ISC}) \cdot (\Phi_d / \Phi_p) \quad (5);$$

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

4. Tables and figures of EL devices

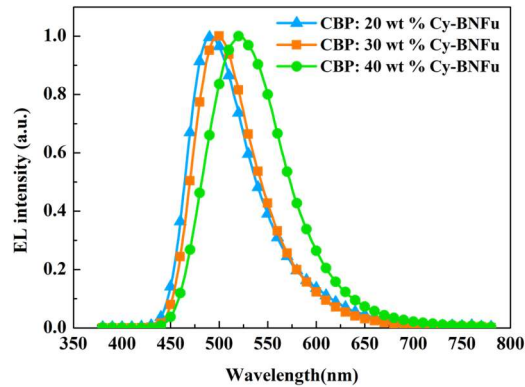


Figure S3. EL spectra for different doping ratios of Cy-BNFu.

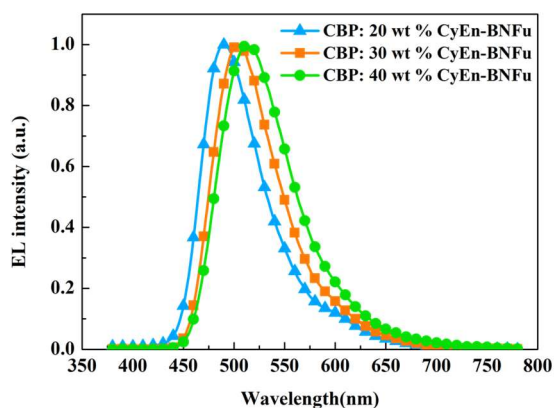


Figure S4. EL spectra for different doping ratios of CyEn-BNFu.

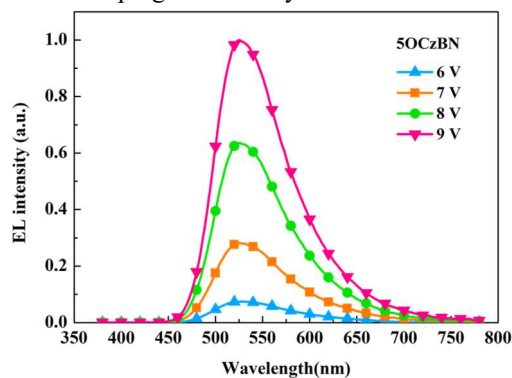


Figure S5. EL spectra of 50CzBN at different voltages.

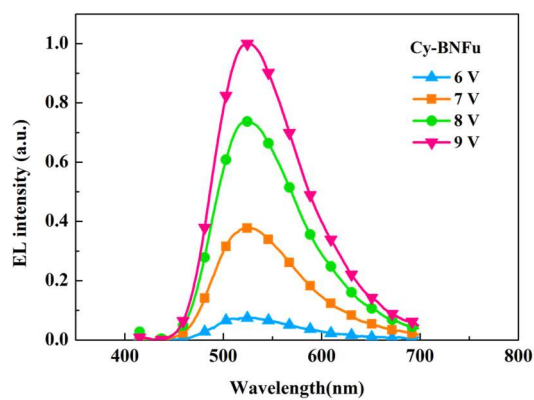


Figure S6. EL spectra of Cy-BNFu at different voltages.

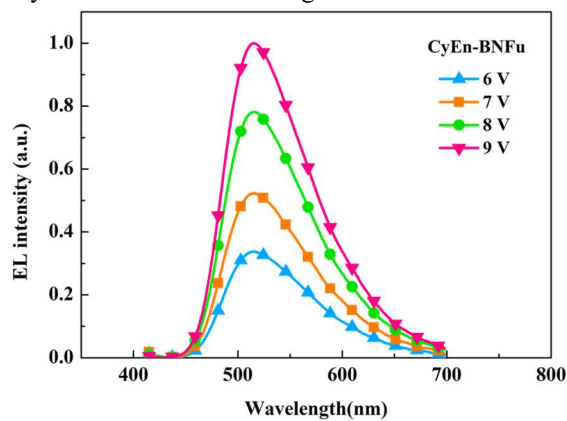


Figure S7. EL spectra of CyEn-BNFu at different voltages.

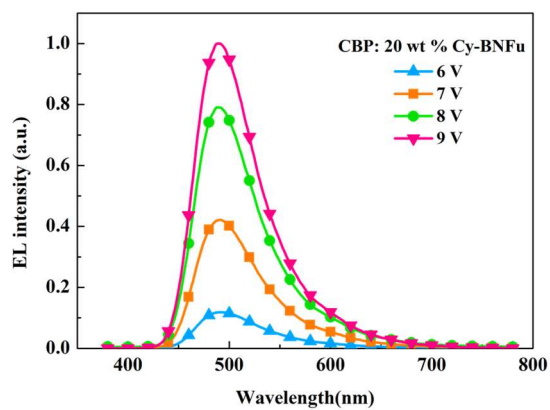


Figure S8. EL spectra for 20 wt % doping ratio concentration of Cy-BNFu in CBP at different voltages.

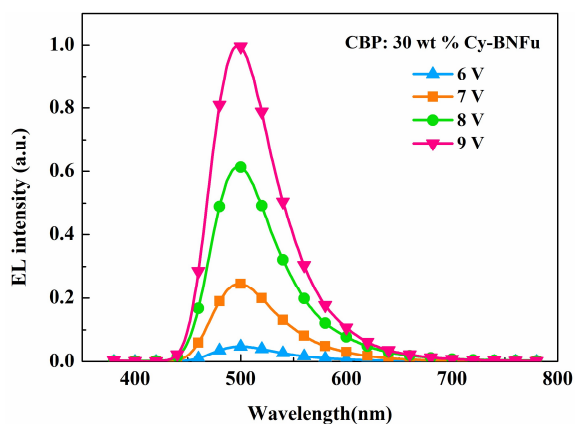


Figure S9. EL spectra for 30 wt % doping ratio concentration of Cy-BNFu in CBP at different voltages.

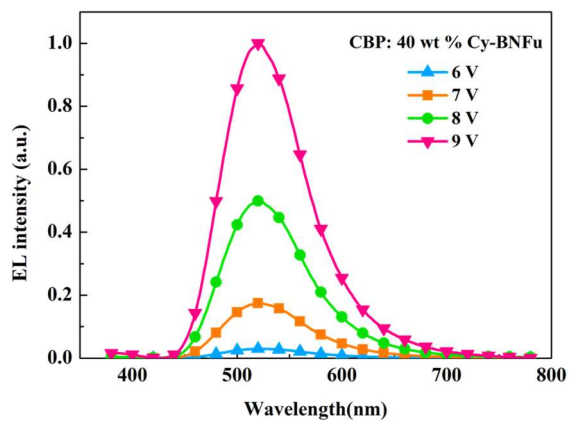


Figure S10. EL spectra for 40 wt % doping ratio concentration of Cy-BNFu in CBP at different voltages.

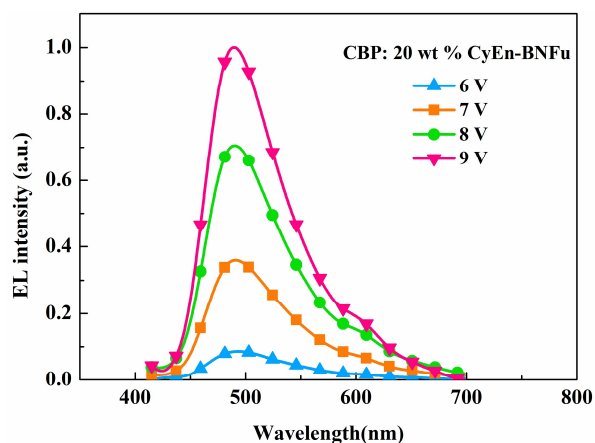


Figure S11. EL spectra for 20 wt % doping ratio concentration of CyEn-BNFu in CBP at different voltages.

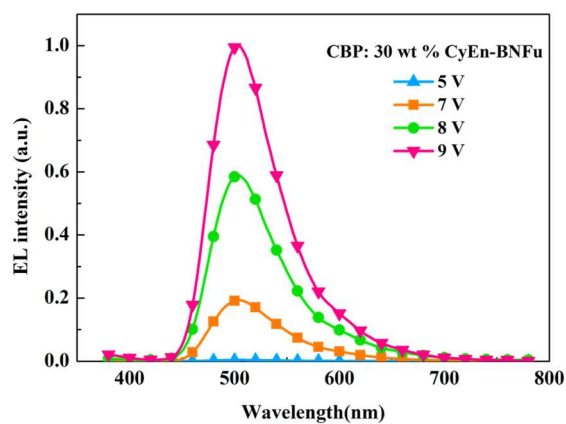


Figure S12. EL spectra for 30 wt % doping ratio concentration of CyEn-BNFu in CBP at different voltages.

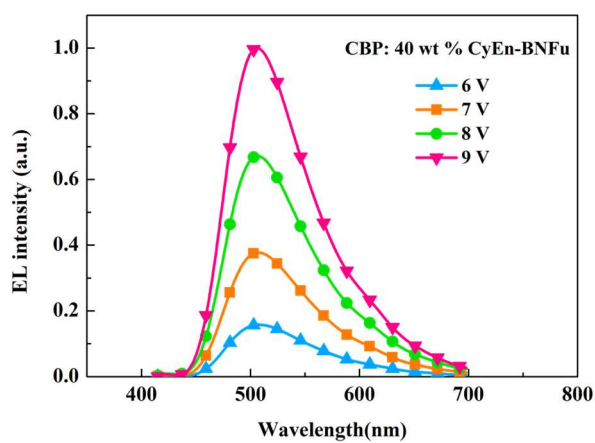


Figure S13. EL spectra for 40 wt % doping ratio concentration of CyEn-BNFu in CBP at different voltages.

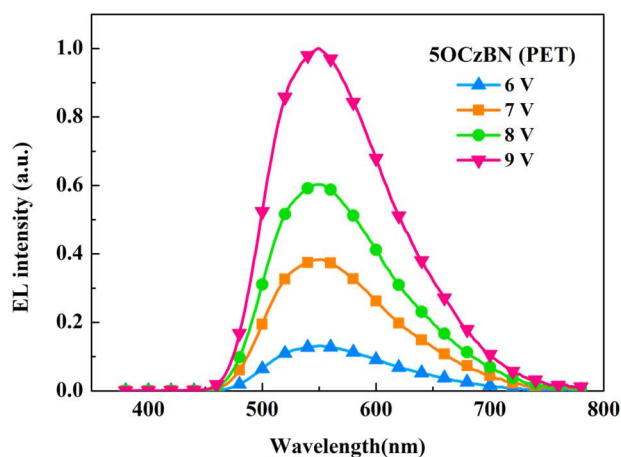


Figure S14. EL spectra for OLED (PET) of 5OCzBN at different voltages.

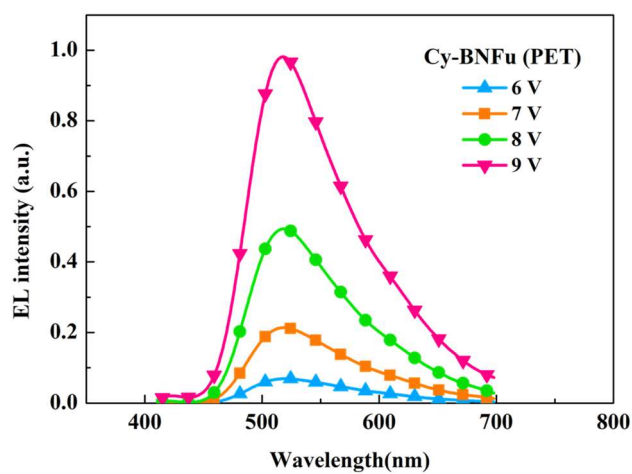


Figure S15. EL spectra for OLED (PET) of Cy-BNFu at different voltages.

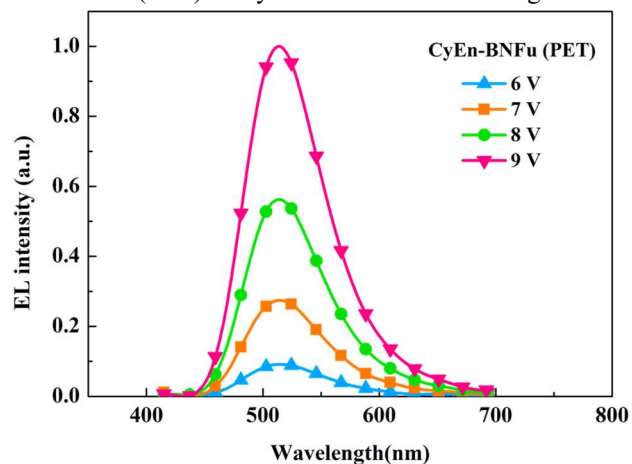


Figure S16. EL spectra for OLED (PET) of CyEn-BNFu at different voltages.

Table S2. EL Peak and FWHM of 5OCzBN, Cy-BNFu and CyEn-BNFu in pure film or doped in CBP.

Pure film		Doped in CBP (20 wt %)		Doped in CBP (30 wt %)		Doped in CBP (40 wt %)		Pure film (PET)	
EL	FWHM	EL	FWHM	EL	FWHM	EL	FWHM	EL	FWHM
Peak	[nm]	Peak	[nm]	Peak	[nm]	Peak	[nm]	Peak	[nm]
[nm]		[nm]		[nm]		[nm]		[nm]	

5OCzBN	531	104	—	—	—	—	—	546	123	
Cy-BNFu	523	100	490	73	498	71	520	91	522	97
CyEn-BNFu	515	96	489	68	503	74	512	82	519	88

Table S3. Device performance data of TADF-OLEDs (PET).

Emission layer	V_{on}^a [V]	CE_{max}^b [cd A ⁻¹]	PE_{max}^c [lm W ⁻¹]	EQE_{max}^d [%]	L_{max}^e [cd m ⁻²]	CIE [x, y] ^f
5OCzBN (PET)	6.4	18.6	7.8	5.2	1180	(0.40, 0.54)
Cy-BNFu (PET)	5.5	21.4	11.2	7.2	1907	(0.31, 0.57)
CyEn-BNFu (PET)	4.6	43.6	24.9	13.6	4607	(0.31, 0.57)

^{a)} V_{on} = turn-on voltage at 1 cd m⁻², ^{b)} CE_{max} = maximum current efficiency, ^{c)} PE_{max} = maximum power efficiency,

^{d)} EQE_{max} = maximum external quantum efficiency, ^{e)} L_{max} = maximum luminance, ^{f)} CIE = the Commission Internationale de L'Eclairage coordinates.

5. ¹H-NMR, ¹³C-NMR and MALDI-TOF spectra

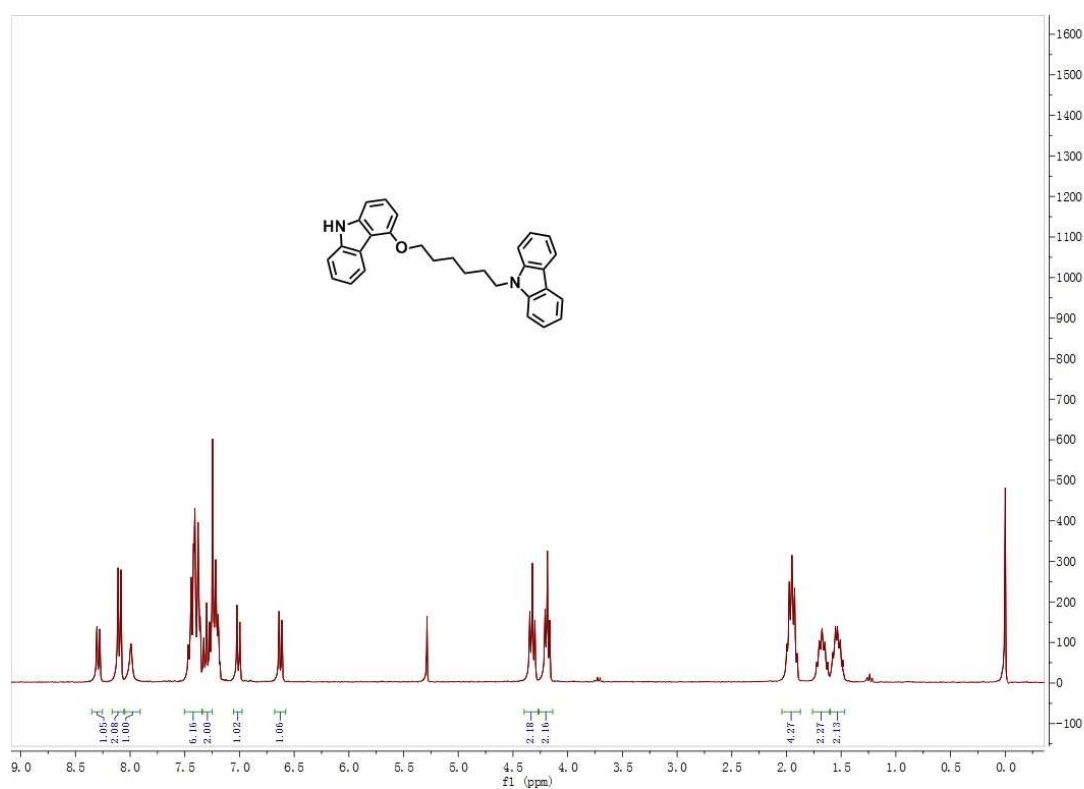


Figure S17. ¹H NMR spectra of Cz-Cz.

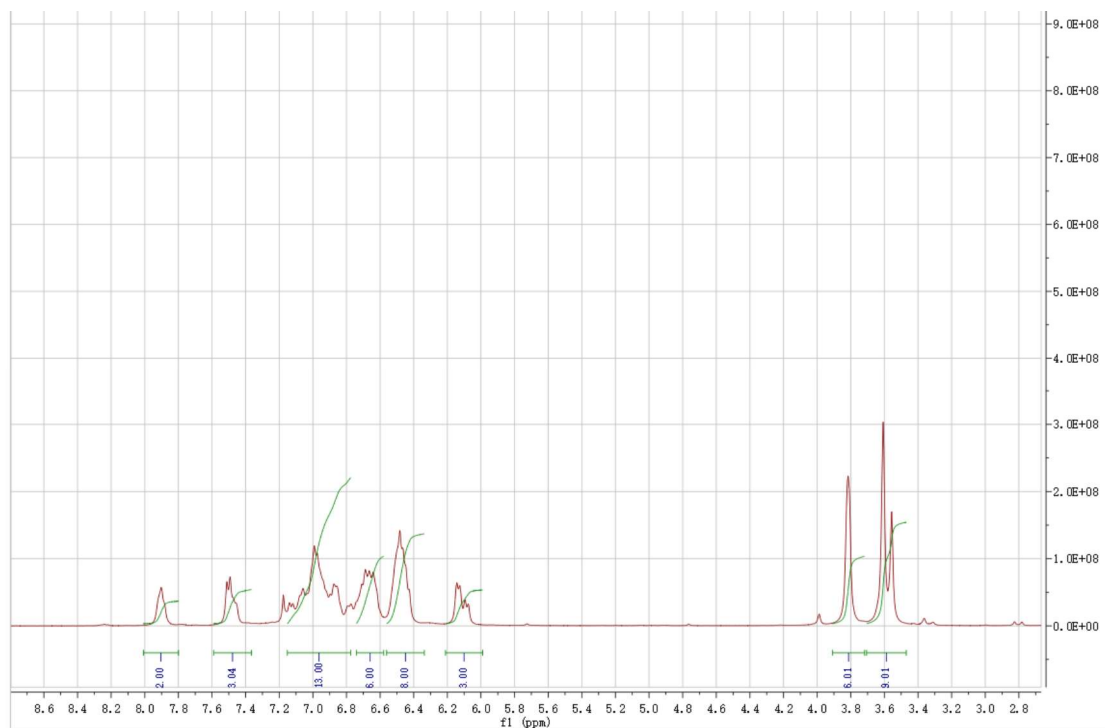


Figure S18. ^1H NMR spectra of 5OCzBN.

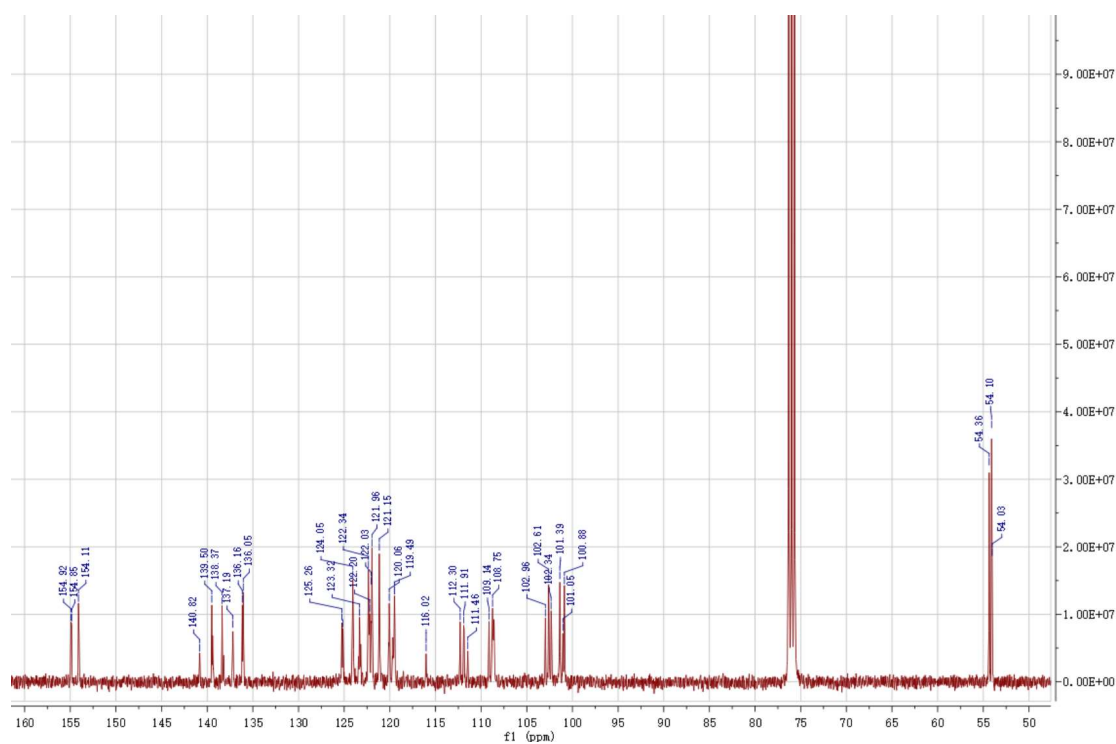


Figure S19. ^{13}C NMR spectra of 5OCzBN.

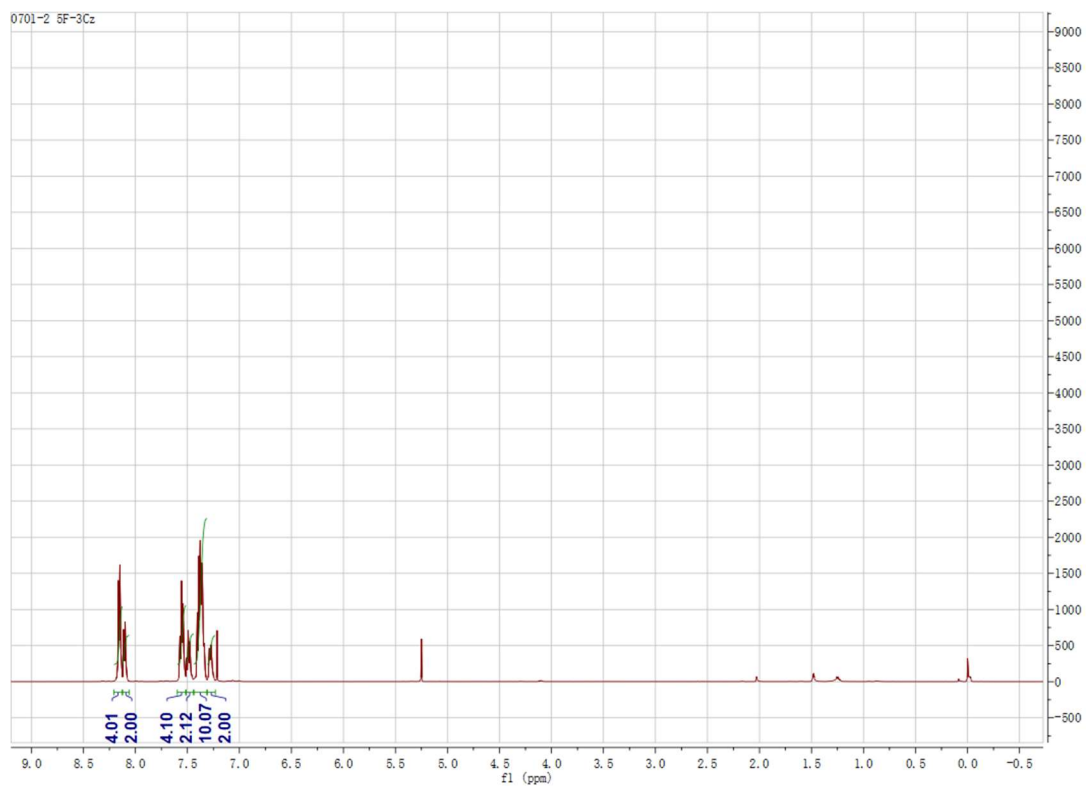


Figure S20. ^1H NMR spectra of 3CzFBN

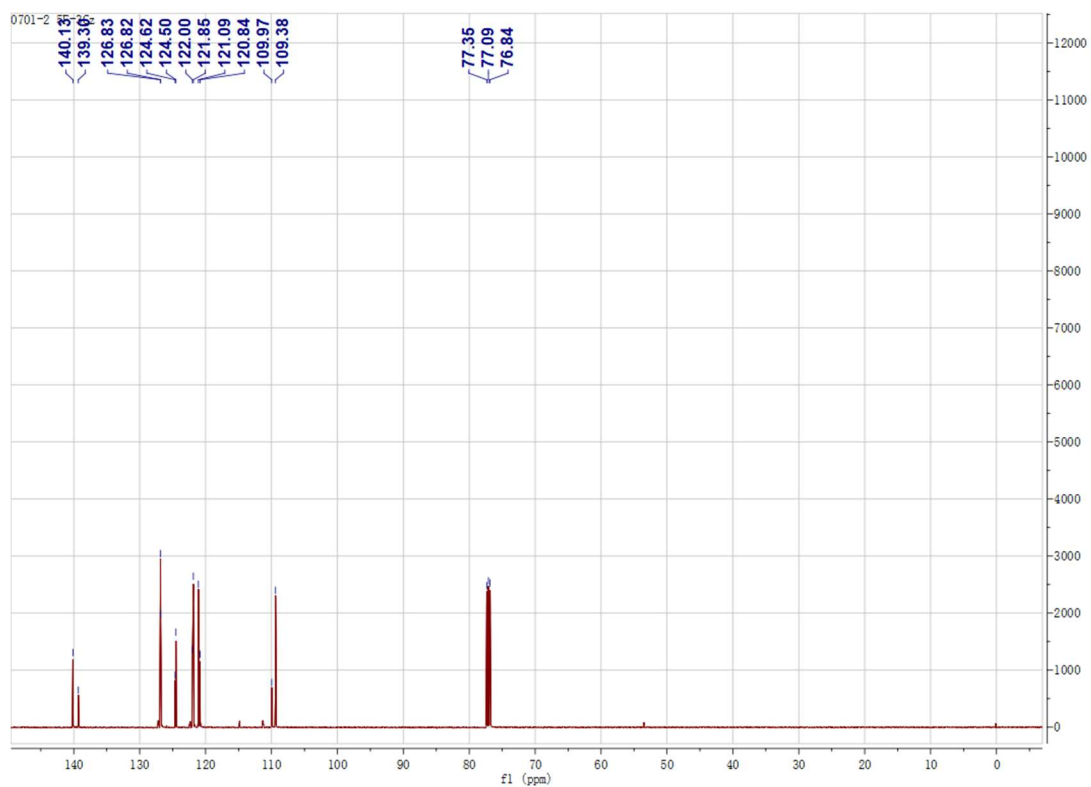


Figure S21. ^{13}C spectra of 3CzFBN.

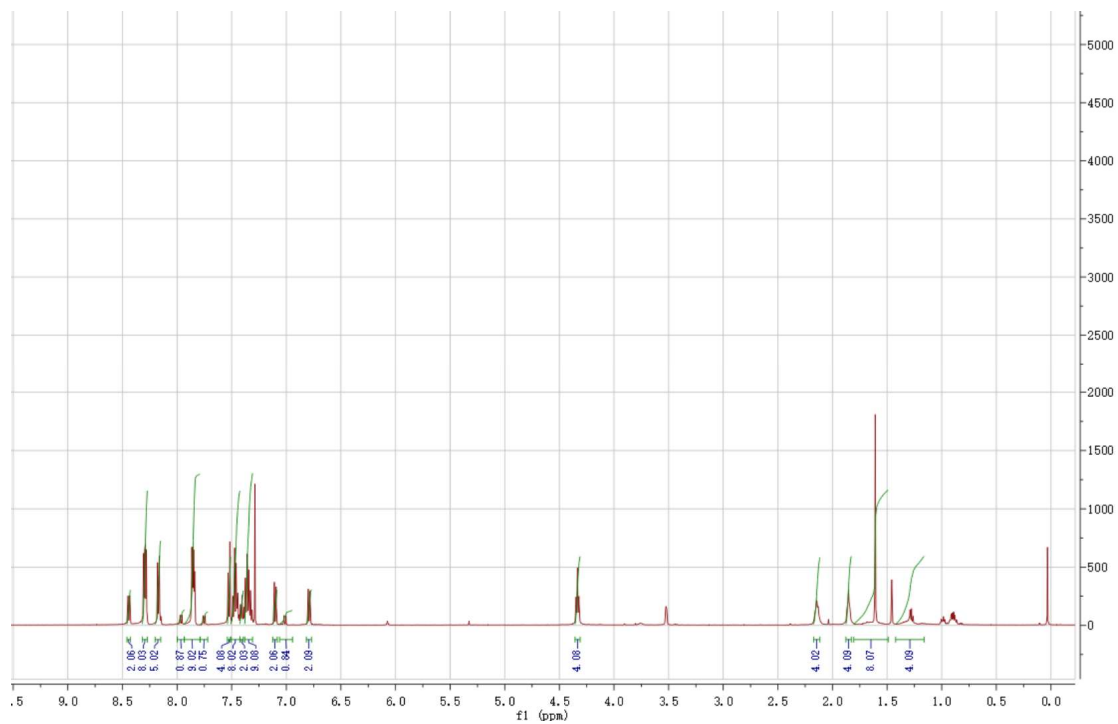


Figure S22. ^1H spectra of Cy-BNFu.

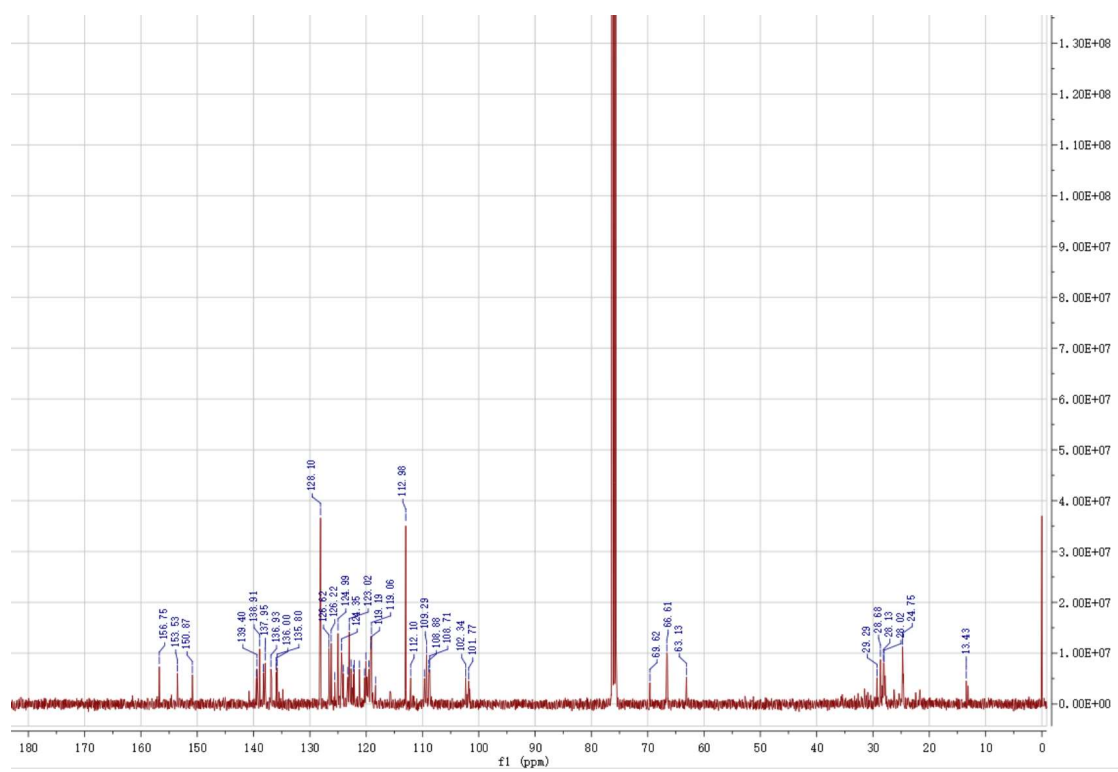


Figure S23. ^{13}C spectra of Cy-BNFu.

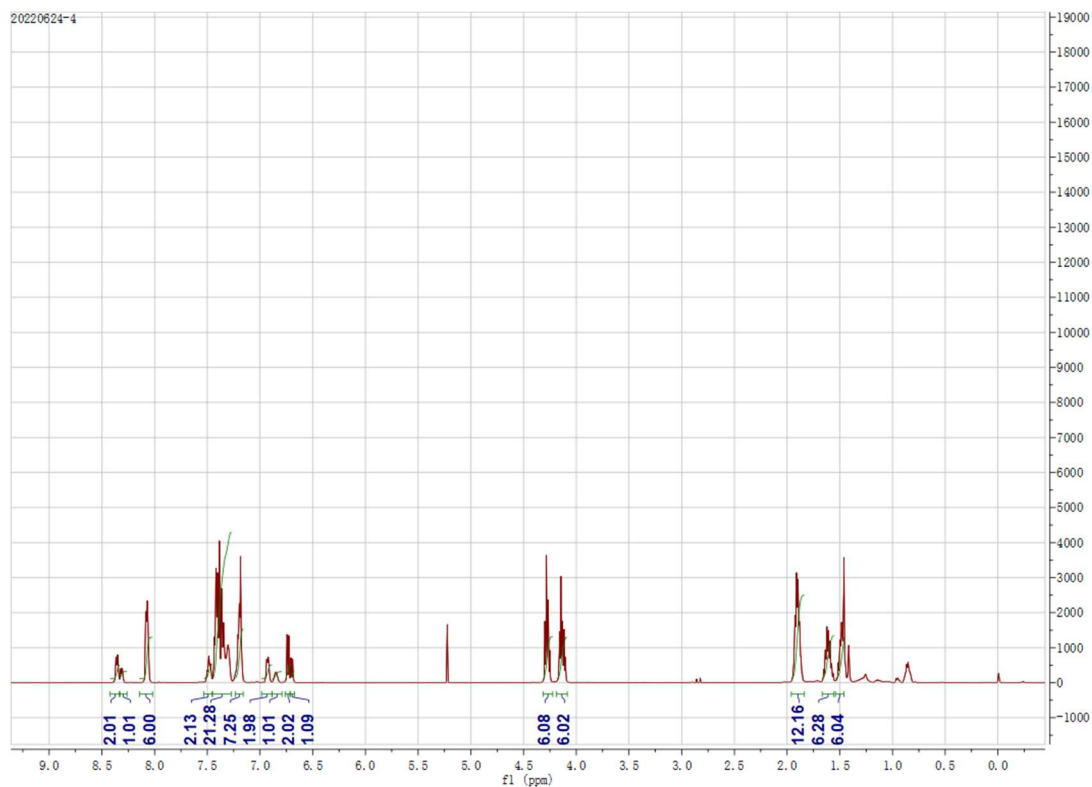


Figure S24. ^1H spectra of Cz-3CzFBN.

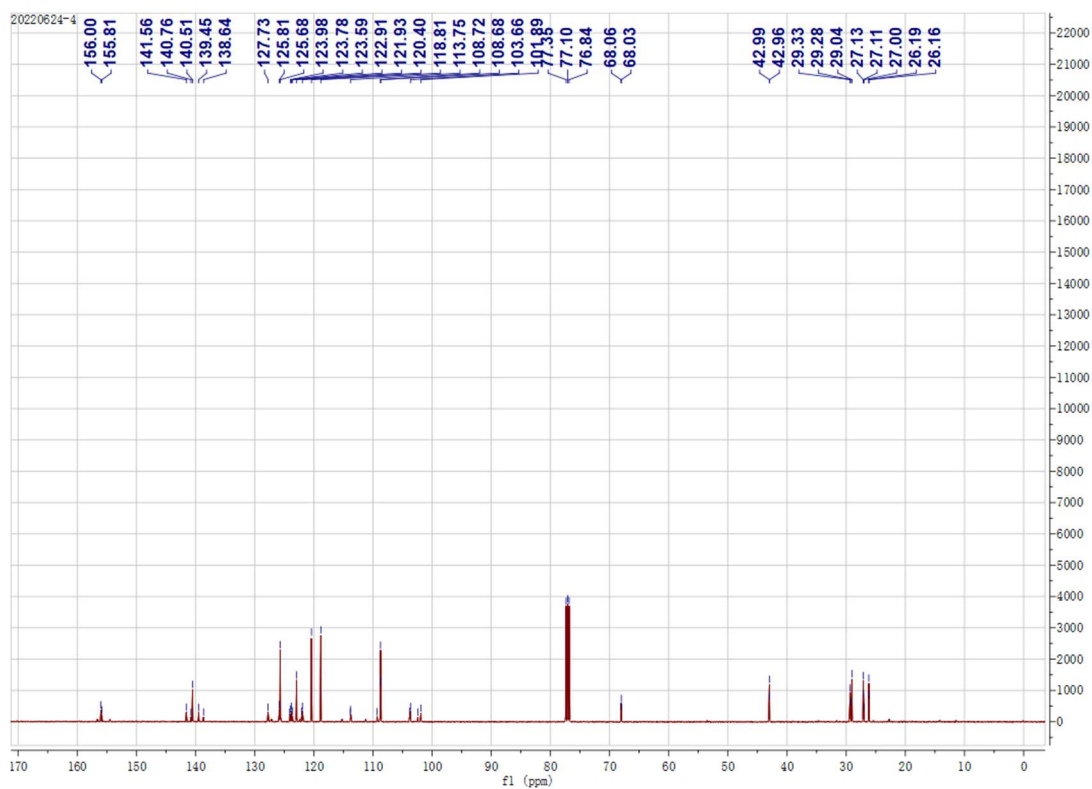


Figure S25. ^{13}C spectra of Cz-3CzFBN.

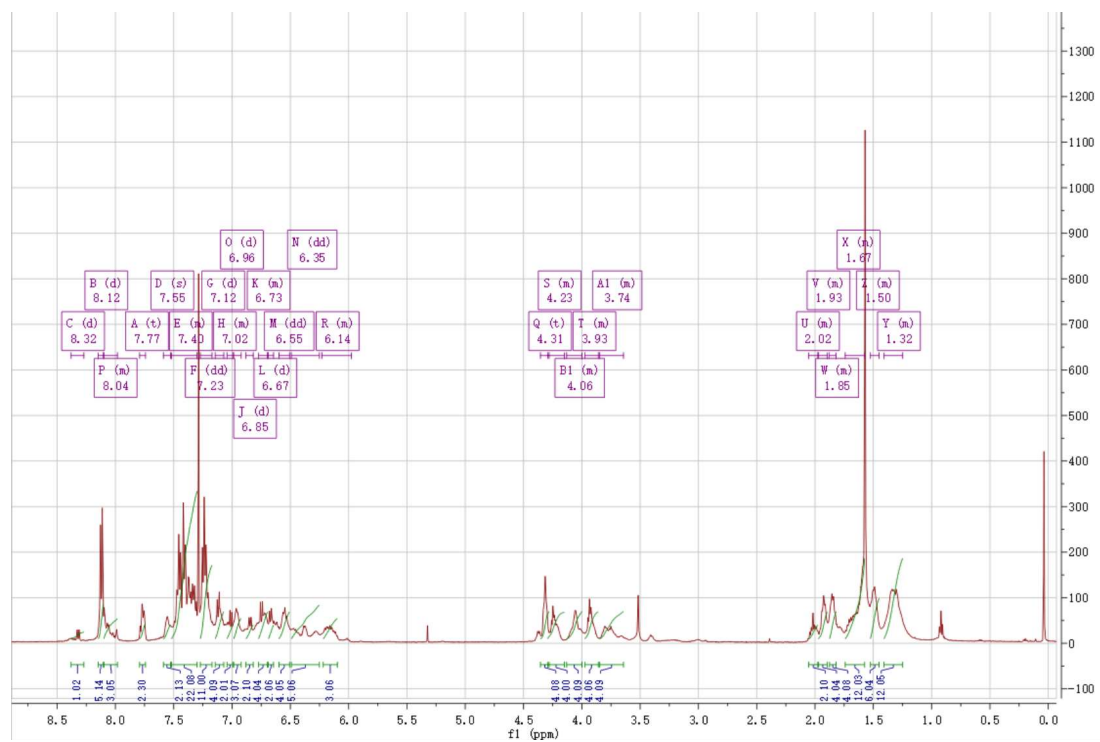


Figure S26. ^1H spectra of CyEn-BNFu.

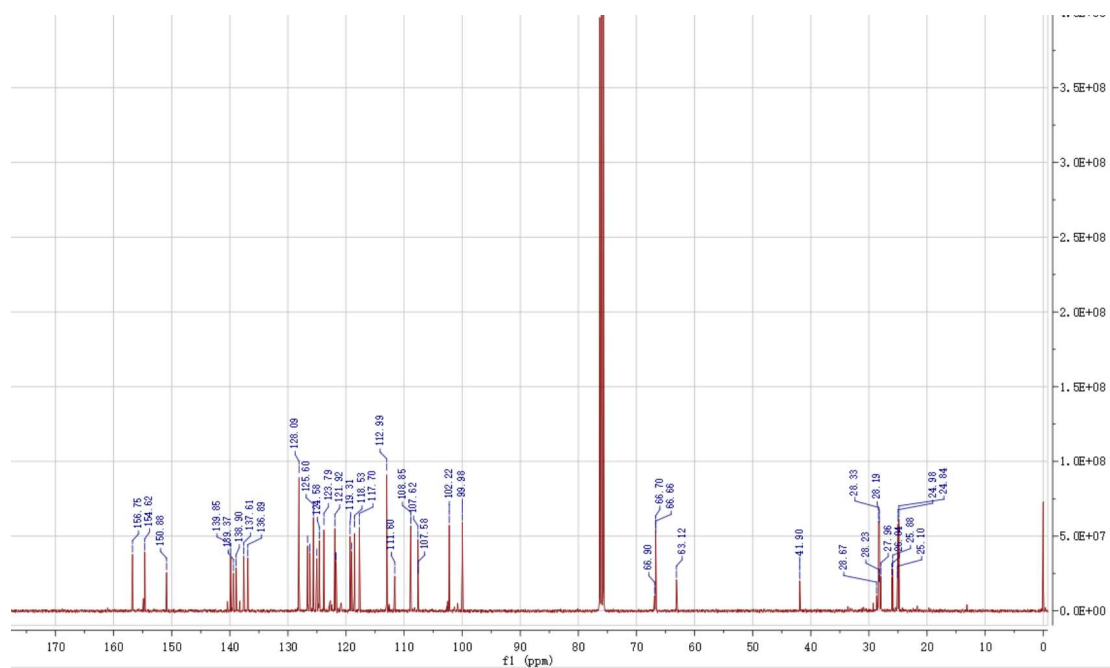


Figure S27. ^{13}C spectra of CyEn-BNFu.

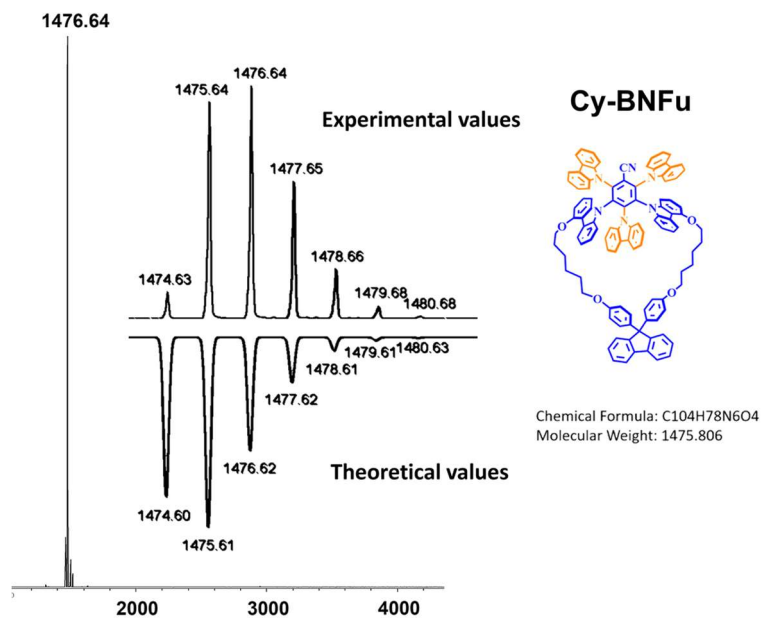


Figure S28. MALDI-TOF spectra of Cy-BNFu.

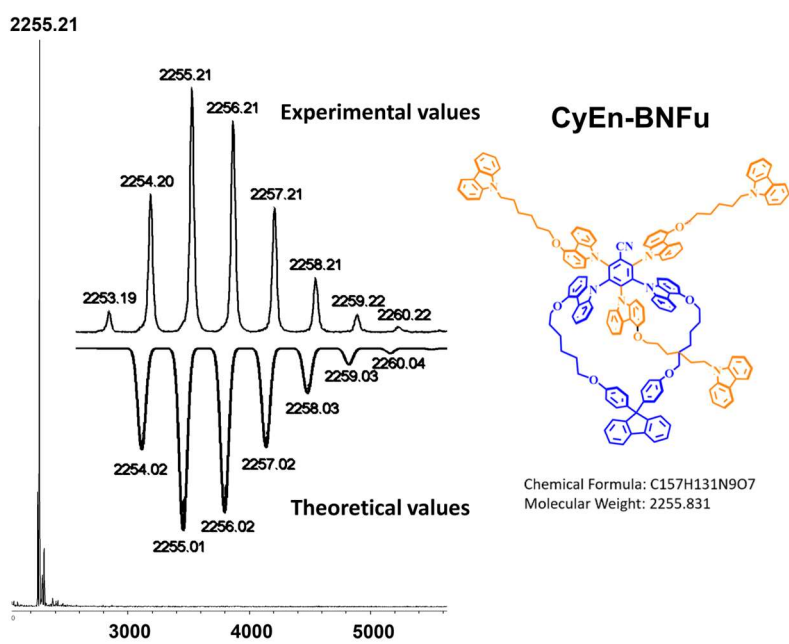


Figure S29. MALDI-TOF spectra of CyEn-BNFu.