Engineering Tetraphenylethene-Based *Z* and *E* Stereoisomers: Structural Analysis and Sensing Application

Han-Jiang Yang, [a†] Yatuan Ma ,[a†] Xinpei Zhong,[a] Xin Yang,[a] You Xu,[a] Xiaoxue Zhang,[a] Zhixin Xiang,[a] Xiujuan Huang,[a] Wenji Wang,[a] Jinyi Wang,*[a] and Mao-Sen Yuan*[a]

[a] College of Chemistry & Pharmacy, Northwest A&F University, Yangling 712100, PR China

Correspondence

Jinyi Wang(jywang@nwsuaf.edu.cn), Mao-Sen Yuan(yuanms@nwsuaf.edu.cn)

1. Materials

(4-bromophenyl)(phenyl)methanone, fluorodimesitylborane, bis(pinacolato)diboron, 2-bromo-6-(bromomethyl)pyridine, bis(pyridin-2-ylmethyl)amine, $Pd(PPh_3)Cl_2$, $TiCl_4$ were purchased from Energy Chemical. Potassium carbonate, potassium acetate, zinc dust were all bought from Aladdin Reagent Company. All the above commercially available reagents were of in analytical grade and used without further purification. All solvents that required distilling were treated in a standard manner under protection of dry nitrogen prior to use. The ^1H and ^{13}C NMR spectra were obtained by the Bruker Avance spectrometer (500/400 MHz for ^1H and 126 MHz for ^{13}C). Mass analyses were operated by Bruker, model maxis, mode Ion Polarity, scanning mode Scan Mode, primary mass spectrometry MS voltage 4500v, nebulizer Nebulizer 0.3Bar, drying gas Dry Gas 4.0l/min, drying temperature Dry Temp 200℃. UV absorption spectra were recorded on N5000 UV-vis spectrophotometer (Yoke Instrument China). The

Shimadzu RF-5301PC fluorescence spectrometer was used to record photoluminescence (PL) spectra.

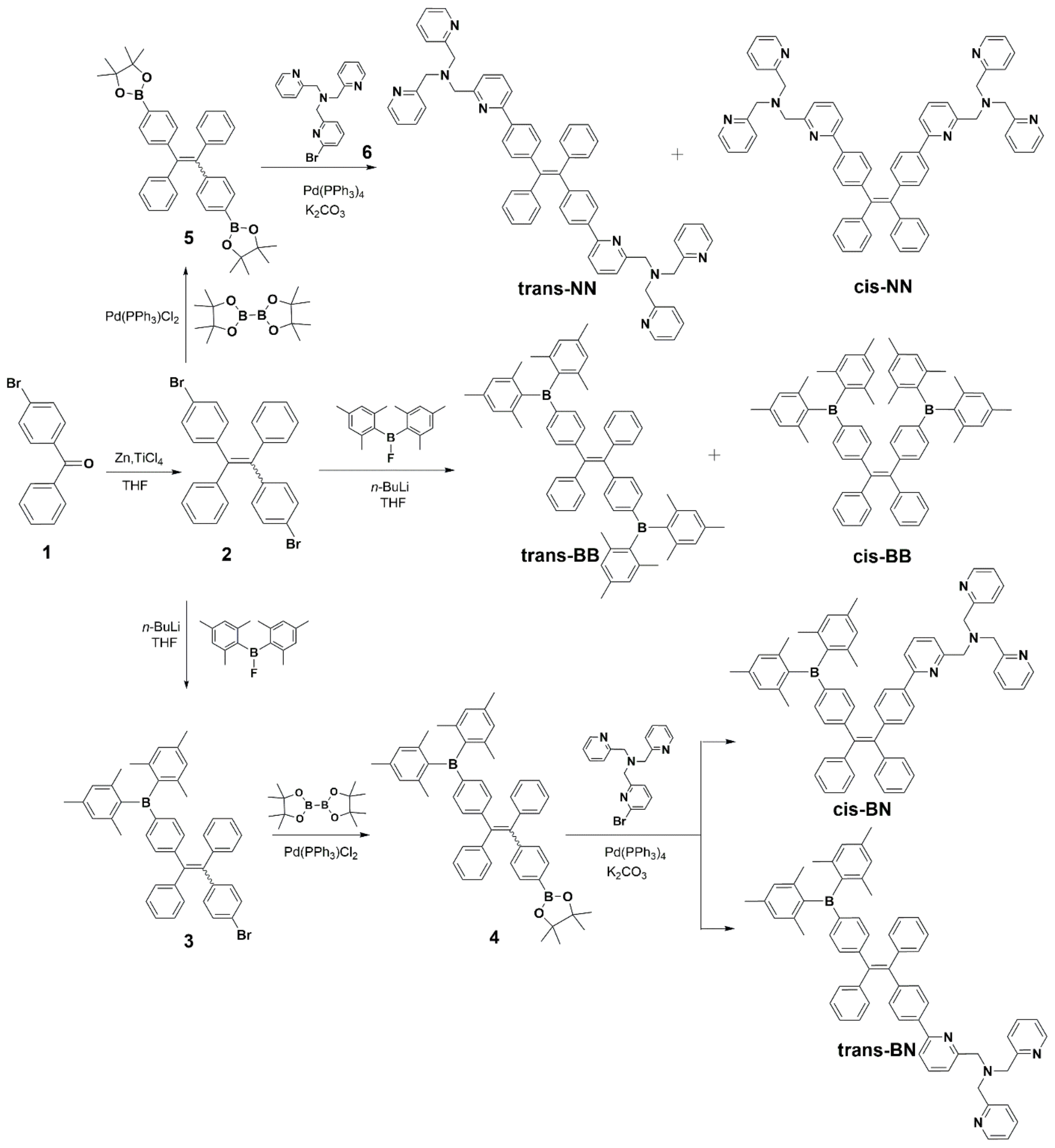
2. Supplementary Tables

Table S1. The Crystallographic Data of **trans-BB** and **cis-BB**.

Compound	**trans-BB**	**cis-BB**
Empirical formula	$C_{62}H_{62}B_2$	$C_{62}H_{62}B_2$
Temperature / K	180	180
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å	18.822(8)	11.6197(4)
b / Å	19.556(13)	15.3381(5)
c / Å	14.133(6)	28.4986(11)
α/°	90	90
β/°	107.537(12)	99.553(1)
γ/°	90	90
Volume / Å ^{3}	4960(4)	5008.7(3)
Z	4	4
ρcalc / g cm^{-3}	1.110	1.099
μ / mm^{-1}	0.062	0.061
R1 [a]/%	8.19	6.82
wR2 [b]/%	19.58	19.84
GOF	1.015	1.065

3. Synthesis

Scheme S1. The synthetic route of **trans/cis-BN**、**trans/cis-BB** and **trans/cis-NN**.



Synthesis of Compound 2: The hydrochloric acid activated zinc powder (2.60 g, 0.04 mol), $TiCl_4$ (10 mL, 10 mmol) and 4-Bromobenzophenone (2.61 g, 10 mmol) were stirred and refluxed in 90 mL of dry THF at 100°C for 20 h. The mixture was cooled to room temperature and quenched by adding 30 mL 30% K_2CO_3 solution. The solution was extracted 3 times with 50 mL of DCM, washed with saturated brine, and dried with anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=100:1, v/v) ,obtaining white solid powder compound 2. Yield: 2.451 g (90 %).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, J = 1.9 Hz, 2H), 7.23-7.17 (m, 2H), 7.15-7.08 (m, 6H), 6.98 (td, J = 7.0, 3.1 Hz, 4H), 6.92-6.84 (m, 4H).

Synthesis of Compound 3: Compound **2** (2.2g, 4.5 mmol) were stirred in 60 mL of dry THF at -78℃ for 5 min. Then, 2.4M n-butyl lithium (1.9 mL, 4.5 mmol) was slowly added and stirred for 30 min. Dried THF solution with fluoro-bis(2,4,6-trimethylphenyl)borane (1.2g, 4.5mmol) was added and the mixture reacted at room temperature for 12 h.The solution was extracted 3 times with 100 mL of DCM, washed with saturated brine, and dried with anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=50:1, v/v), obtaining light green solid powder compound **3**. Yield: 2.07 g (70 %).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31-7.27 (m, 2H), 7.24-7.11 (m, 8H), 7.11-7.02 (m, 8H), 6.84 (d, J = 8.2 Hz, 4H), 2.34 (d, J = 4.3 Hz, 6H), 2.02 (d, J = 4.7 Hz, 12H).

Synthesis of Compound 4: Combine compound **3** (1.32 g, 2 mmol), pinacol diborate (1.27 g, 5 mmol), potassium acetate (0.6 g, 6 mmol) and Pd(dppf)Cl_2 (0.1 g) with 50 mL of dry 1,4-Dioxane was stirred and refluxed at 120°C for 15 h. The mixture was cooled to room temperature, extracted with DCM, and washed with saturated brine. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=20:1), giving compound **4** as green solid powder. Yield: 1.05 g (74 %).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.15 (ddt, J = 8.7, 4.2, 1.9 Hz, 6H), 7.09-6.99 (m, 8H), 6.82 (d, J = 6.9 Hz, 4H), 2.33 (d, J = 3.6 Hz, 6H), 2.01 (s, 12H), 1.40 (d, J = 1.1 Hz, 12H).

Synthesis of Compound 5: Combine compound **2** (1.32 g, 2.0 mmol), pinacol diborate (2 g, 8 mmol), potassium acetate (0.8 g, 8 mmol) and Pd(dppf)Cl_2 (100 mg) with 60 mL of dry 1, 4-Dioxane was stirred and refluxed at 120°C for 15 h. The mixture was cooled to room temperature, extracted with DCM, and washed with saturated brine. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=20:1), giving compound **2** as light white solid powder. Yield: 0.982 g (61.3%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, J = 8.1, 2.3 Hz, 4H), 7.11-7.05 (m, 6H), 7.01 (ddd, J = 12.7, 7.7, 3.0 Hz, 8H), 1.32 (d, J = 5.6 Hz, 16H), 1.26 (s, 8H).

Synthesis of Compound 6: Combine 2-bromo-6-methylpyridine (3mL 26.37 mmol), NBS (4.8 g,27 mmol) and AIBN (0.5 g, 3 mmol) with 60 mL of dry CCl_4 was stirred and refluxed at 100°C for 15 h. The mixture was cooled to room temperature, extracted with DCM, and washed with saturated brine. The crude product was purified by silica gel column chromatography, giving compound 2-Bromo-6-(bromomethyl)pyridine as yellow solid powder. Yield: 4.63 g (70 %).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (t, J = 7.7 Hz, 1H), 7.46 (dd, J = 7.7, 2.9 Hz, 2H), 4.54 (s, 2H). Combine 10 mL aqueous solution containing di(2-picolyl)amine (0.54 mL, 3 mmol) and DCM solution containing compound 2-Bromo-6-(bromomethyl)pyridine (0.75g, 3 mmol) was stirred at 0 °C for 20 min. Then, adding NaOH (0.12g, 3 mmol), the mixture was stirred at room temperature for 12 h. The mixture was cooled to room temperature, extracted with DCM, and washed with saturated brine. The crude product was purified by silica gel column chromatography, giving compound **6** as light yellow solid powder. Yield: 0.886 g (80 %).^{1}H NMR (500 MHz, DMSO-*d*6) δ 8.52 (d, J = 4.9 Hz, 2H), 7.85-7.71 (m, 3H), 7.66 (d, J =

7.5 Hz, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 7.4, 4.8 Hz, 2H), 3.82 (s, 6H).

Synthesis of Compound trans/cis-BN: Compound **4** (0.75 g, 1 mmol), compound **6** (0.4 g, 1.1 mmol), potassium carbonate (0.28 g, 2 mmol) and $Pd[P(C_6H_5)_3]_4$ (50 mg) were combined in an anaerobic system with 20 mL of methylbenzene, 2 mL of water, and 2 mL of absolute ethanol. This was stirred and refluxed at 130 °C for 15 h. The mixture was cooled to room temperature, extracted with dichloromethane (DCM), washed with saturated NaCl solution, following dried with anhydrous $MgSO_4$. After that, the obtained isomers was separated and purified by column chromatography on silica gel (acetone : ethyl acetate = 1:50), giving the green solid powders compound **trans/cis-BN**. Yield: 0.521 g (60 %).**trans-BN**: ^{1}H NMR (400 MHz, Chloroform-d) δ 8.53 – 8.51 (m, 2H), 7.80 – 7.77 (m, 2H), 7.70 – 7.69 (m, 1H), 7.68 – 7.66 (m, 2H), 7.63 (d, J = 1.4 Hz, 2H), 7.53 (d, J = 3.4 Hz, 1H), 7.47 (d, J = 1.4 Hz, 1H), 7.26 (s, 1H), 7.24 (d, J = 1.7 Hz, 1H), 7.14 (p, J = 1.8 Hz, 4H), 7.10 (t, J = 2.1 Hz, 6H), 7.05 (d, J = 1.8 Hz, 2H), 7.02 (d, J = 2.4 Hz, 2H), 7.00 (d, J = 1.5 Hz, 2H), 6.78 (s, 4H), 3.95 (s, 6H), 2.28 (s, 6H), 1.97 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 159.59, 159.12, 149.09, 144.22, 143.48, 143.15, 141.83, 141.44, 141.39, 140.81, 138.49, 137.04, 136.45, 135.78, 132.17, 132.09, 131.99, 131.81, 131.51, 131.33, 130.94, 128.87, 128.59, 128.50, 128.13, 127.89, 127.72, 127.60, 126.73, 126.23, 122.98, 122.00, 121.15, 118.57, 65.60, 60.24, 60.22, 30.63, 29.74, 23.43, 21.25. HRMS m/z: $[M]^+$ Found 869.47491 (Fig. S12). **cis-BN**: ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.54 (dt, J = 4.9, 1.4 Hz, 2H), 7.72 (q, J = 3.5, 2.9 Hz, 2H), 7.70 (d, J = 3.0 Hz, 1H), 7.66 – 7.62 (m, 4H), 7.51 (d, J = 5.0 Hz, 1H), 7.49 (d, J = 4.9 Hz, 1H), 7.26 (s, 1H), 7.24 (d, J = 1.7 Hz, 1H), 7.17 – 7.12 (m, 4H), 7.12 – 7.08 (m, 6H), 7.07 (d, J = 1.8 Hz, 2H), 7.06 (d, J = 1.6 Hz, 2H), 7.04 (d, J = 2.4 Hz, 2H), 6.73 (s, 4H), 3.97 (s, 6H), 2.24 (s, 6H), 1.95 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 159.61, 159.17, 149.12, 147.71, 143.28, 141.82, 141.50, 141.41, 140.78, 138.45, 137.04, 136.45, 135.91, 131.86, 131.47, 131.33, 130.96, 128.14, 127.77, 127.75, 126.73, 126.65, 126.15, 123.01, 122.02, 121.16, 118.48, 60.34, 60.30, 23.47, 21.24. HRMS m/z: $[M]^+$ Found 869.47589 (Fig. S13).

Synthesis of Compound trans/cis-BB: Compound **2**（1.1g, 2.25 mmol） were stirred in 60 mL of dry THF at -78℃ for 5 min. Then, 2.4M n-butyl lithium (0.95 mL, 2.25 mmol) was slowly added and stirred for 30 min. Dried THF solution with fluoro-bis(2,4,6-trimethylphenyl)borane (1.2 g, 4.5 mmol) was added and the mixture reacted at room temperature for 12 h. The solution was extracted 3 times with 100 mL of DCM, washed with saturated brine, and dried with anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=50:1, v/v), obtaining green solid powder compound **trans/cis-BB**. Yield: 1.678 g (90 %). **trans-BB:**^{1}H NMR (400 MHz, Chloroform-d) δ 7.31-7.24 (m, 4H), 7.13-7.10 (m, 4H), 7.07-7.03 (m, 8H), 7.02 (d, J = 1.9 Hz, 2H), 6.81 (d, J = 3.6 Hz, 8H), 2.31 (dd, J = 5.1, 2.8 Hz, 12H), 1.99 (t, J = 4.7 Hz, 24H). HRMS m/z: $[M]^+$ Found 829.5129 (Fig. S16). **cis-BB**:^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 (s, 4H), 7.13 (d, J = 3.2 Hz, 8H), 7.06 (s, 4H), 7.04 (s, 2H), 6.81 (s, 8H), 2.31 (s, 12H), 1.99 (d, J = 5.6 Hz, 24H), HRMS m/z: $[M]^+$ Found 829.5129 (Fig. S17). **trans/cis-BB:**^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 147.56, 147.45, 144.39, 143.11, 141.99, 141.89, 140.86, 140.81, 138.55, 135.83, 135.60, 131.54, 131.41, 131.37, 131.08, 130.99, 130.21, 128.51, 128.41, 128.20, 127.80, 127.67, 126.81, 126.76, 55.72, 29.81, 23.50, 23.48, 21.33, 21.30.

Synthesis of Compound trans/cis-NN: Compound **5** (0.75 g, 1 mmol), compound **6** (0.4 g, 1.1 mmol), potassium carbonate (0.28 g, 2 mmol) and $Pd[P(C_6H_5)_3]_4$ (50 mg) were combined in an anaerobic system with 20 mL of methylbenzene, 2 mL of water, and 2 mL of absolute ethanol. This was stirred and refluxed at 130°C for 15 h. The mixture was cooled to room temperature, extracted with dichloromethane (DCM), washed with saturated NaCl solution, following dried with anhydrous $MgSO_4$. After that, the obtained isomers was separated and purified by column chromatography on silica gel (acetone: ethyl acetate = 1:1), giving the green solid powders compound **trans/cis-NN**. Yield: 0.545 g (60 %). **trans-NN**:^{1}H NMR (400 MHz, Chloroform-d) δ 8.53 (dt, J = 5.0, 1.5 Hz, 4H), 7.79 (dd, J = 8.6, 2.8 Hz, 4H), 7.53 (d, J = 7.7 Hz, 2H), 7.47 (d, J = 7.7 Hz, 2H), 7.14 (t, J = 1.8 Hz, 5H), 3.95 (s, 12H).^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 159.43, 158.97, 156.25, 149.02, 144.46, 143.63, 140.90, 137.40, 137.04, 136.46, 131.85, 131.48, 127.70, 126.59, 126.34, 122.98, 122.00, 121.13, 118.60, 60.18, 60.16. HRMS m/z: $[M]^+$ Found 909.43933 (Fig. S14). **cis-NN**:^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.51 (ddt, J = 11.2, 4.9, 1.4 Hz, 4H), 7.79 (dd, J = 8.3, 3.4 Hz, 4H), 7.70-7.63 (m, 4H), 7.62 (d, J = 1.6 Hz, 4H), 7.60 (s, 2H), 7.52 (t, J = 6.9 Hz, 2H), 7.44 (t, J = 8.2 Hz, 2H), 7.20-7.15 (m, 4H), 7.15-7.11 (m, 4H), 7.11 (s, 2H), 7.10 (d, J = 2.4 Hz, 4H), 7.07 (d, J = 6.9 Hz, 2H), 7.06-7.02 (m, 2H), 3.95 (d, J = 8.0 Hz, 12H).^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 159.54, 159.07, 156.28, 149.06, 144.53, 143.58, 140.90, 137.32, 137.04, 136.47, 131.83, 131.49, 127.86, 126.68, 126.21, 122.99, 122.00, 121.14, 118.57, 60.23. HRMS m/z: $[M]^+$ Found 909.43921 (Fig. S15).

Single crystal growth:

Weighed approximately 5 mg each of the **trans-BB** and **cis-BB** products and dissolved them in a good solvent for the products, such as dichloromethane, ethyl acetate, or tetrahydrofuran. The solutions were transferred into 5 mL glass vials, followed by the slow addition of a poor solvent-such as n-hexane, cyclohexane, methanol, or diethyl ether-until an obvious biphasic system was formed. The volume ratio of the good solvent to the poor solvent was 1:2. The vials were then placed in a quiet, dark environment to allow the solvents to evaporate and the crystals to grow.

Measurement of Fluorescence and UV–Vis Spectra:

Prepare a 5 mM stock solution of the probes in anhydrous THF (seal the container and store it in a refrigerator). Take 200 μL of the 5 mM probe solution and dilute it to 10 mL to obtain a 100 μM working solution. Then, mix 400 μL of the 100 μM probe solution with redistilled THF and the HPO_4^{2-} solution to a final volume of 4 mL, giving a final probe concentration of 10 μM. For fluorescence measurements, the excitation wavelength is set at 305 nm, and both excitation and emission slit widths are 5.0 nm.

Prepare a 5 mM stock solution of **trans-BN** in anhydrous THF. Various anions, including the Zn salts of Cl^-, CN^-, CO_3^{2-}, F^-, Br^-, I^-, NO_2^-, NO_3^-, OAC^-, SO_3^{2-}, SO_4^{2-}, HSO_3^-, HSO_4^-, S^{2-}, PO_4^{3-}, and $H_2PO_4^-$, as well as ATP and ADP, are prepared as 0.5 mM aqueous solutions. Dilute the 5 mM probe stock solution to 100 μM by adding 200 μL of the 5 mM probe to a 10 mL volumetric flask and filling to volume with redistilled THF. In a 5 mL glass vial, add 400 μL of the 100 μM probe solution, followed by 3.2 mL of redistilled THF and 400 μL of the 0.5 mM anion solution, yielding a final probe concentration of 10 μM. Record the absorption and emission spectra. The excitation wavelength is set to 310 nm, and the slit widths for both excitation and emission are set to 2.5 nm.

All the solvents used for absorption spectra and fluorescence measurements were HPLC grade. UV absorption spectra were recorded on N5000 UV-vis spectrophotometer (Yoke Instrument China). The Shimadzu RF-5301PC fluorescence spectrometer was used to record photoluminescence (PL) spectra. Lifetime decay curves were recorded on an Edinburgh FLS1000 fluorescence spectrometer equipped with an EPL-375 picosecond pulsed diode laser excitation source and a time-correlated single-photon-counting (TCSPC) card, and no IRF was used. Reconvolution fits of the decay profiles were performed with FLS1000 analysis software to obtain the lifetime values.

Powder X-ray diffraction:

Powder X-ray diffraction (XRD) patterns were recorded at room temperature with a Bruker AXS X-ray powder diffractometer using Cu Kα radiation. The data were recorded in the 2ϑ mode with a step size of 0.02626º.

Single-crystal X-ray diffraction:

The data collection was performed under nitrogen protection at 180K on a Bruker SMART APEX-II CCD area detector using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The data reduction and integration and global unit cell refinements were performed using the INTEGRATE program of the APEX2 software package. Semi-empirical absorption corrections were applied using the SCALE program for the area detector. The structures were solved by direct methods and refined using the full-matrix least-squares methods on F^2 using SHELX.

Theoretical calculation

To gain deeper insight into the luminescence mechanisms of **trans/cis-BB**, the orbital energy levels of **trans/cis-BB** were calculated using the Gaussian 09 program at the B3LYP-

D3 Time-Dependent Density Functional Theory (TD-DFT). The geometries of **trans/cis-BB** used for electronic structure calculations were directly from their respective determined X-ray single crystal structures.

Table 1: Table of individual lifetime components (τ_1, τ_2, etc.) of **trans/cis-NN/BB/BN** and their corresponding relative contributions.

	trans-NN(ns)	**cis-NN**(ns)	**trans-BB**(ns)	**cis-BB**(ns)	**trans-BN**(ns)	**cis-BN**(ns)
τ_1(rel%)	0.7697(27.15)	0.9243(26.09)	2.7367(52.68)	1.8730(42.93)	1.7310(27.13)	0.9402(16.16)
τ_2(rel%)	2.4090(66.46)	2.8218(68.86)	7.7748(47.32)	3.8905(57.07)	4.4156(72.87)	2.9006(76.21)
τ_3(rel%)	7.7474(6.38)	10.0080(5.05)				8.7580(7.63)
τ_{ave}	2.30	2.69	5.12	3.02	3.69	3.03

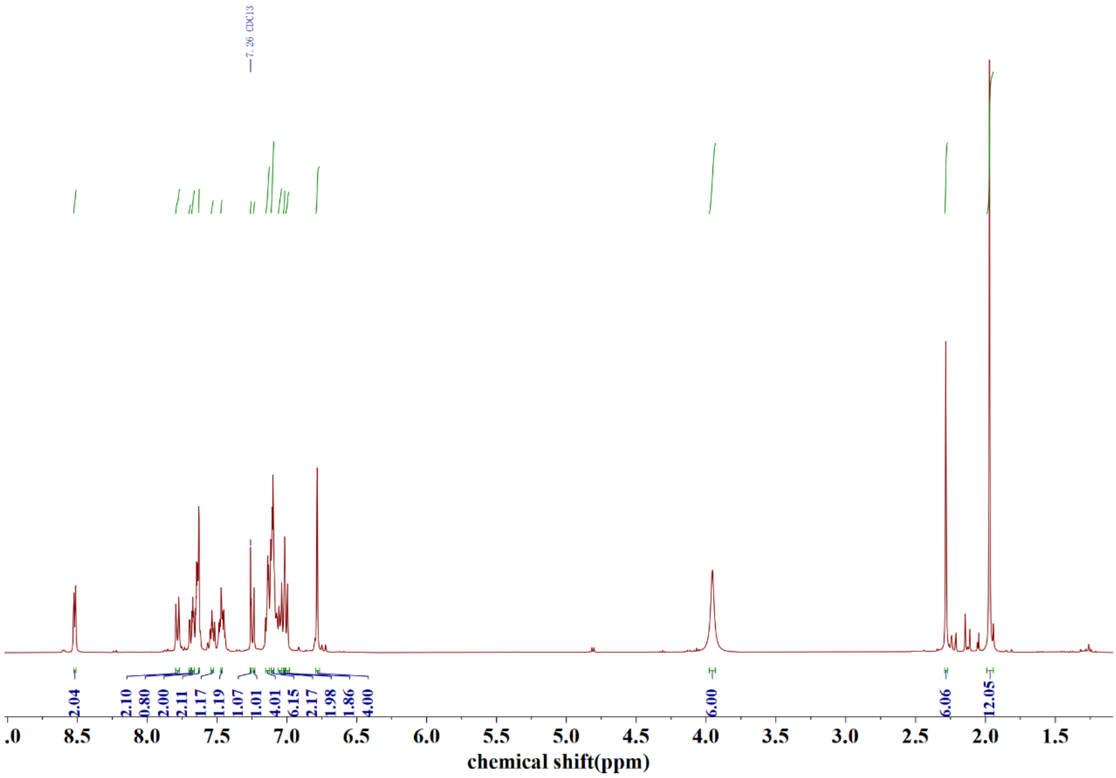


Fig. S1. ^{1}H NMR spectrum of **trans-BN.**

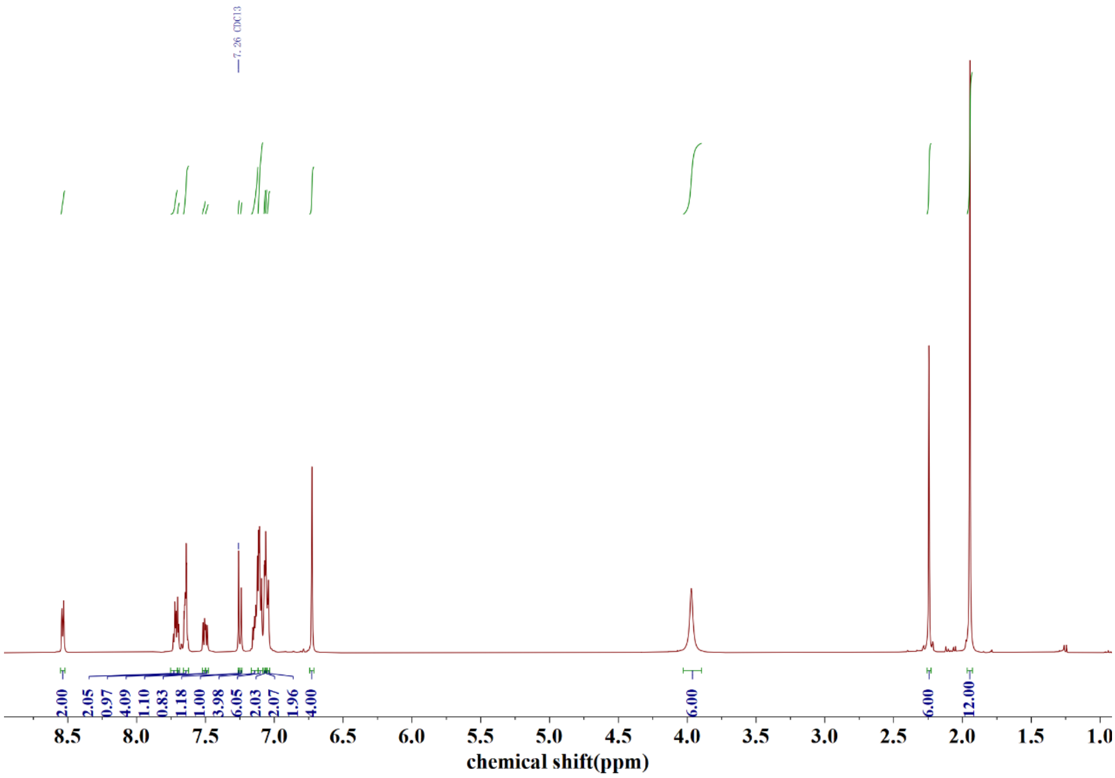


Fig. S2. [1]H NMR spectrum of **cis-BN.**

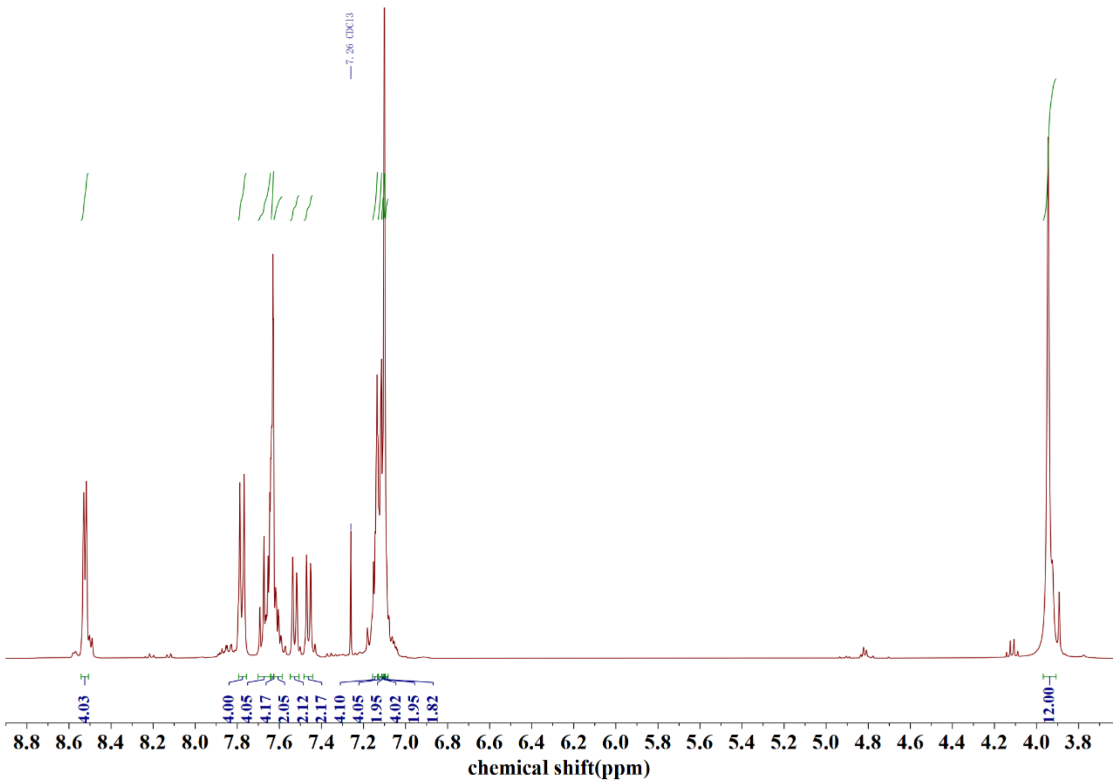


Fig. S3. [1]H NMR spectrum of **trans-NN**.

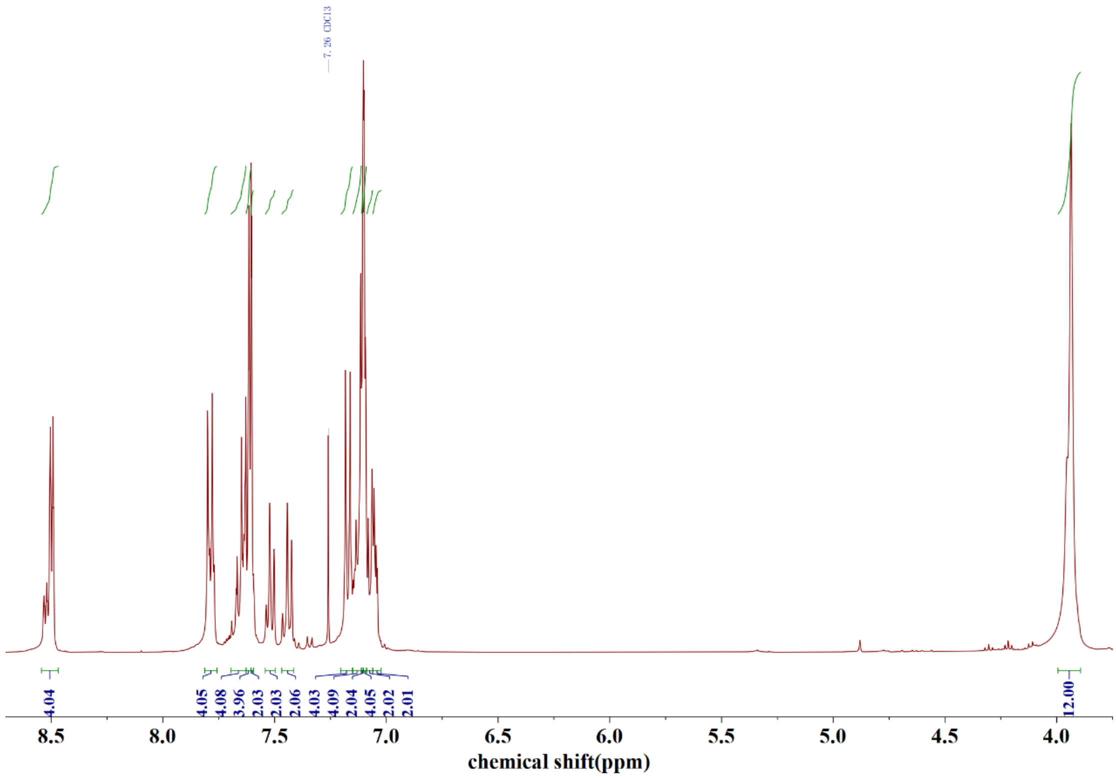


Fig. S4. ^{1}H NMR spectrum of **cis-NN**.

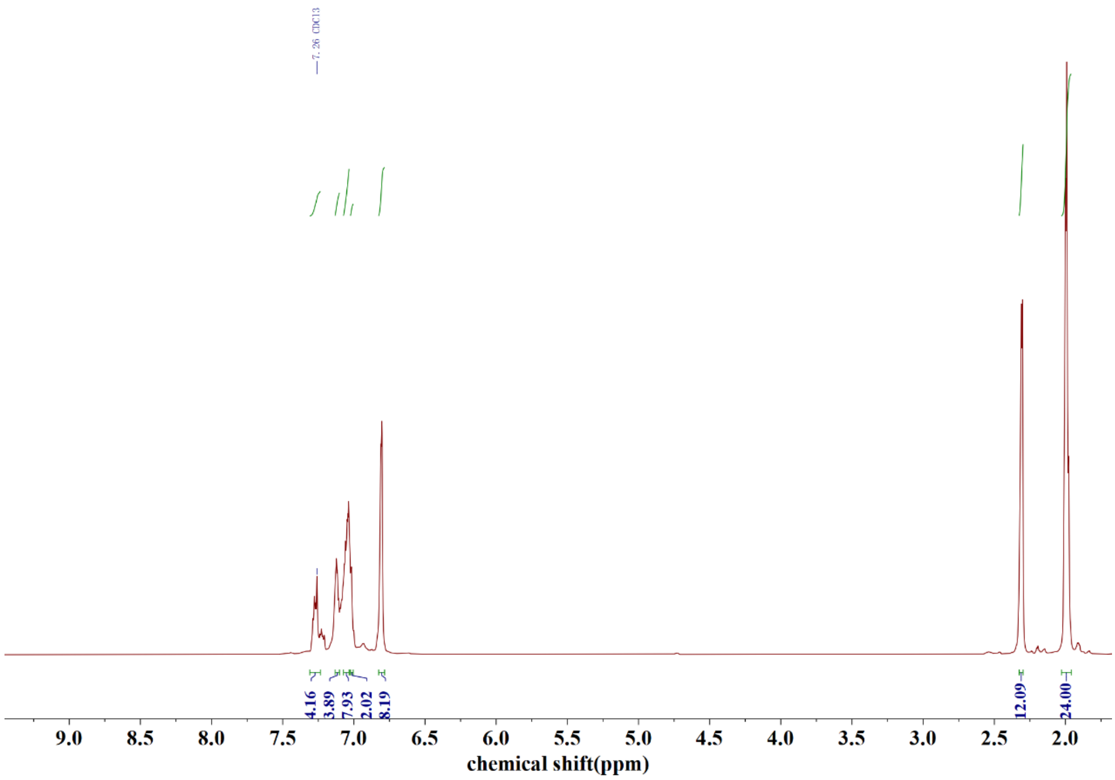


Fig. S5. ^{1}H NMR spectrum of **trans-BB**.

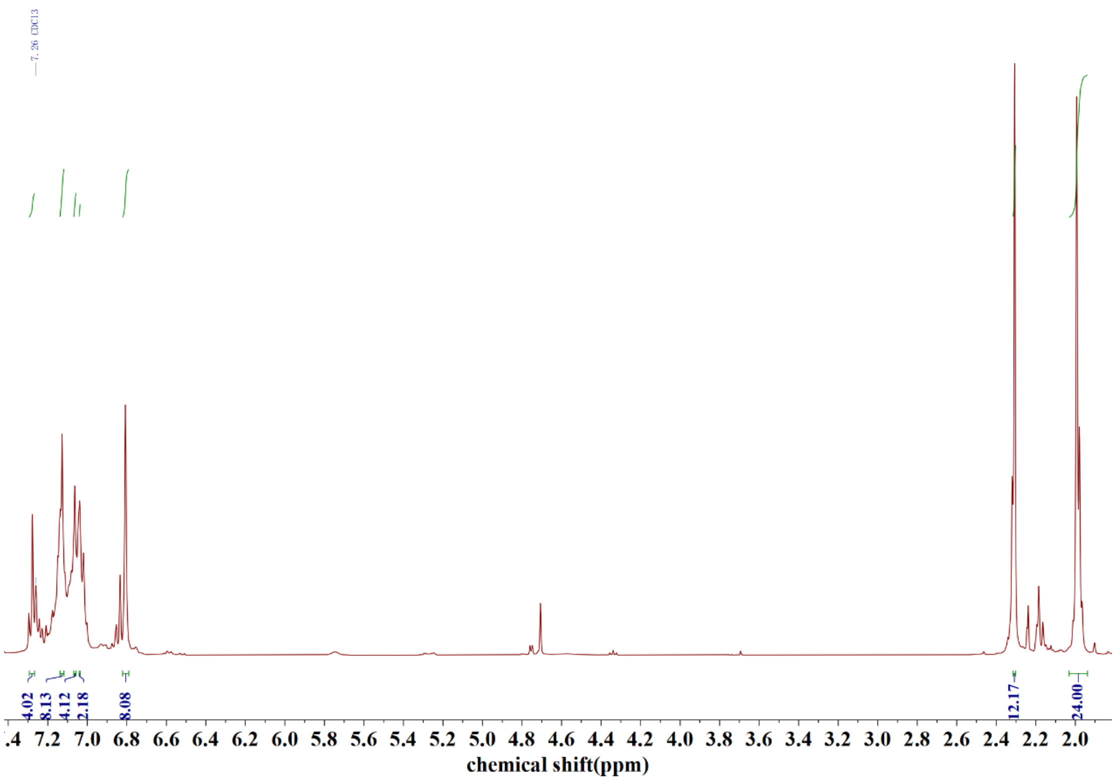


Fig. S6. ^{1}H NMR spectrum of **cis-BB**.

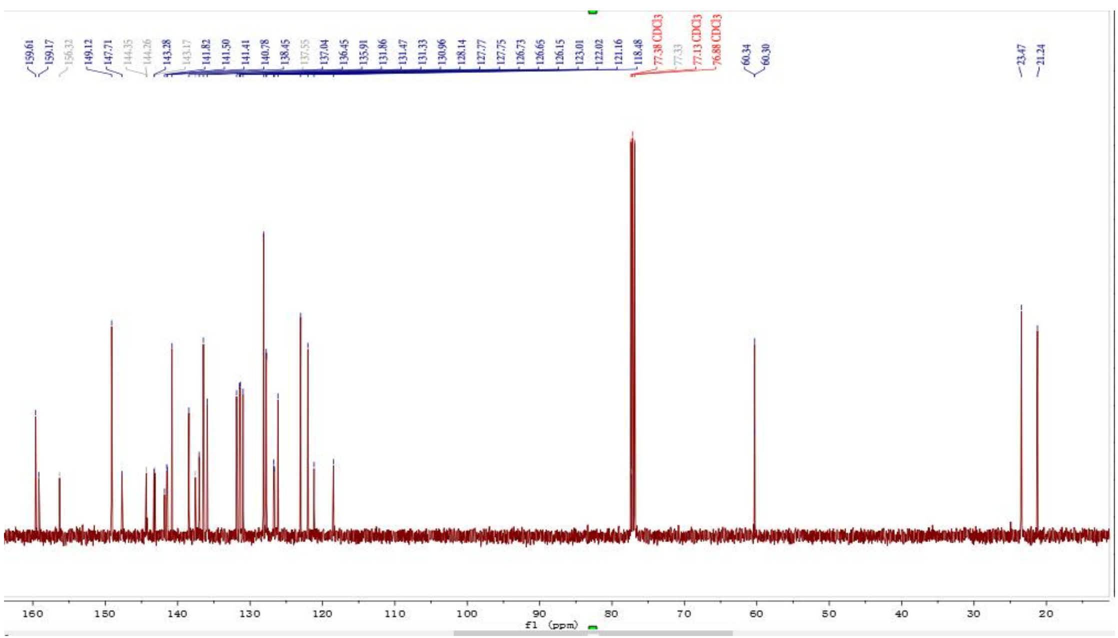


Fig. S7. ^{13}C NMR spectrum of **trans-BN**.

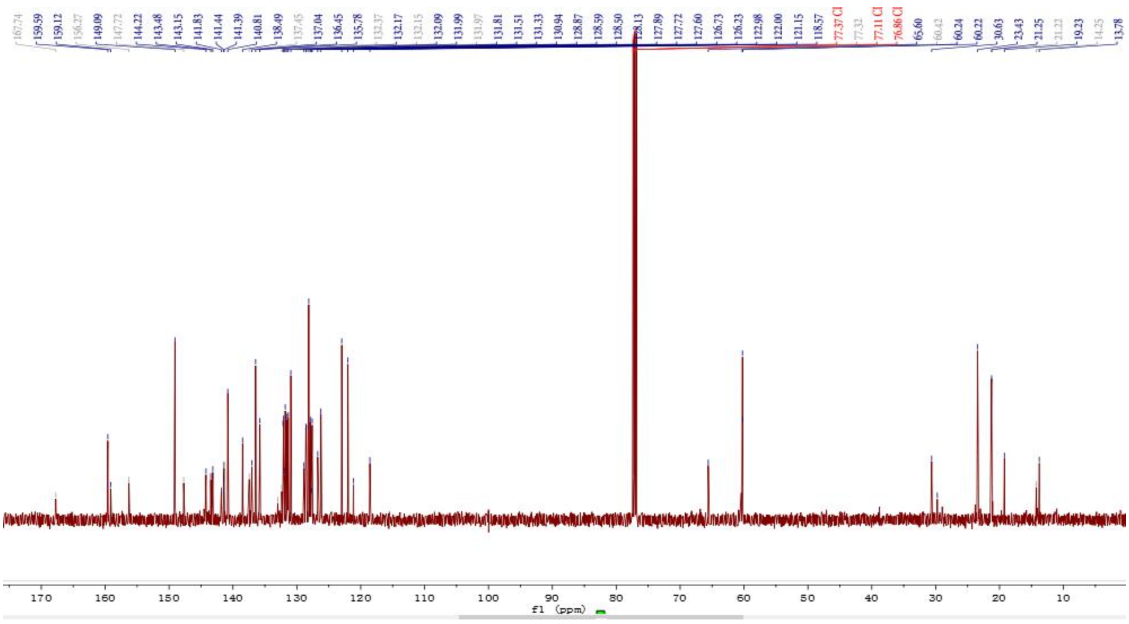


Fig. S8. ^{13}C NMR spectrum of **cis-BN**.

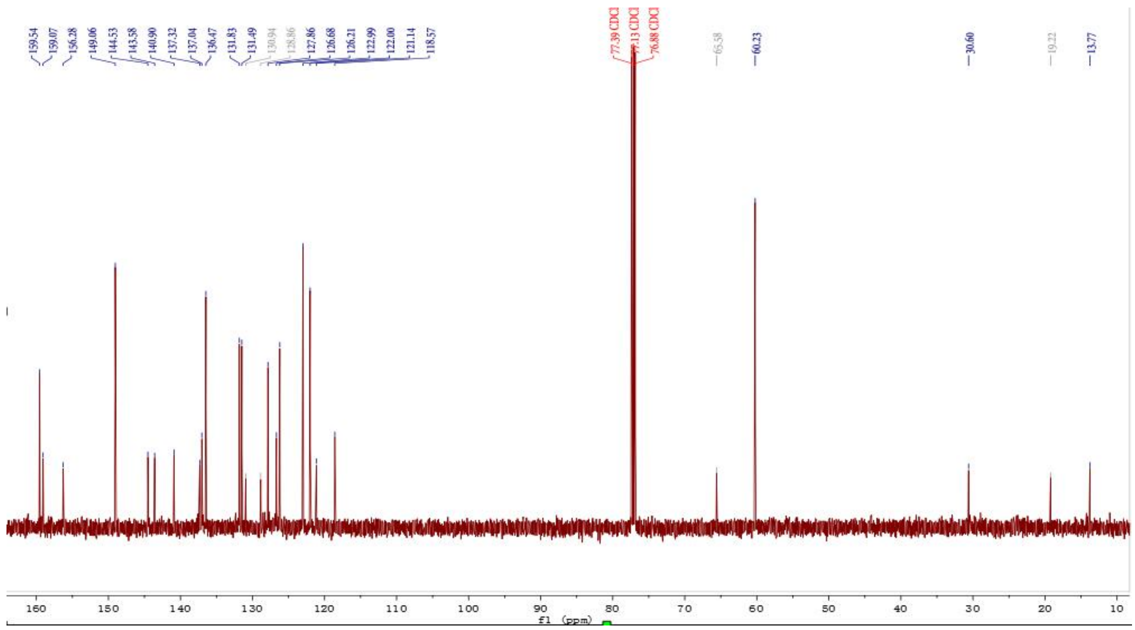


Fig. S9. ^{13}C NMR spectrum of **trans-NN**.

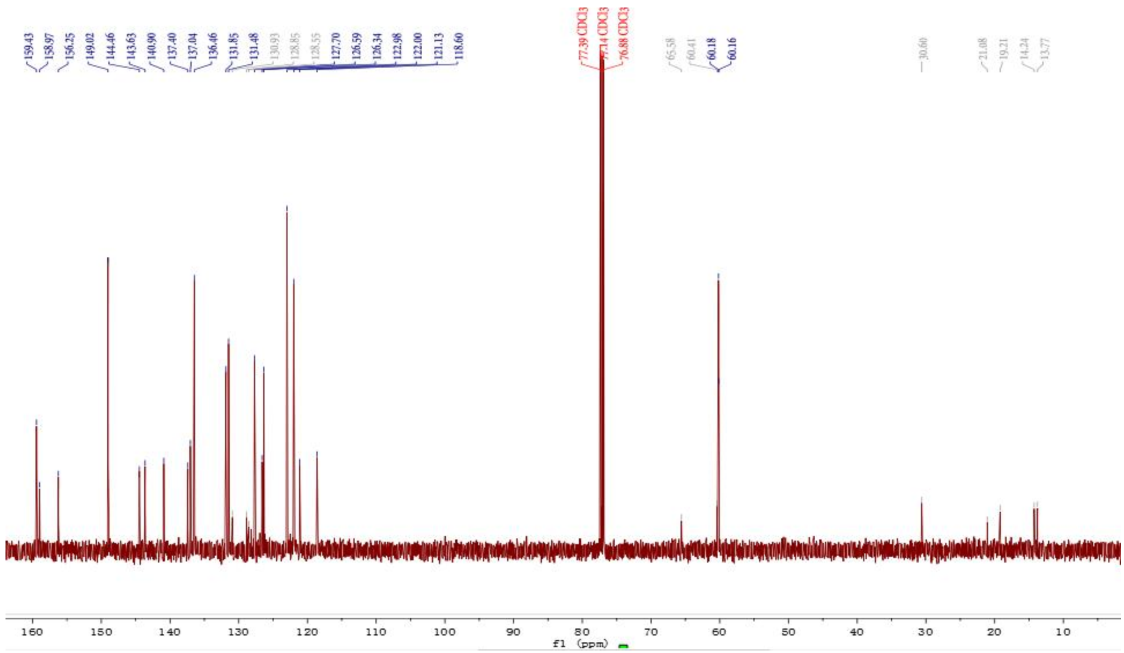


Fig. S10. ^{13}C NMR spectrum of **cis-NN**.

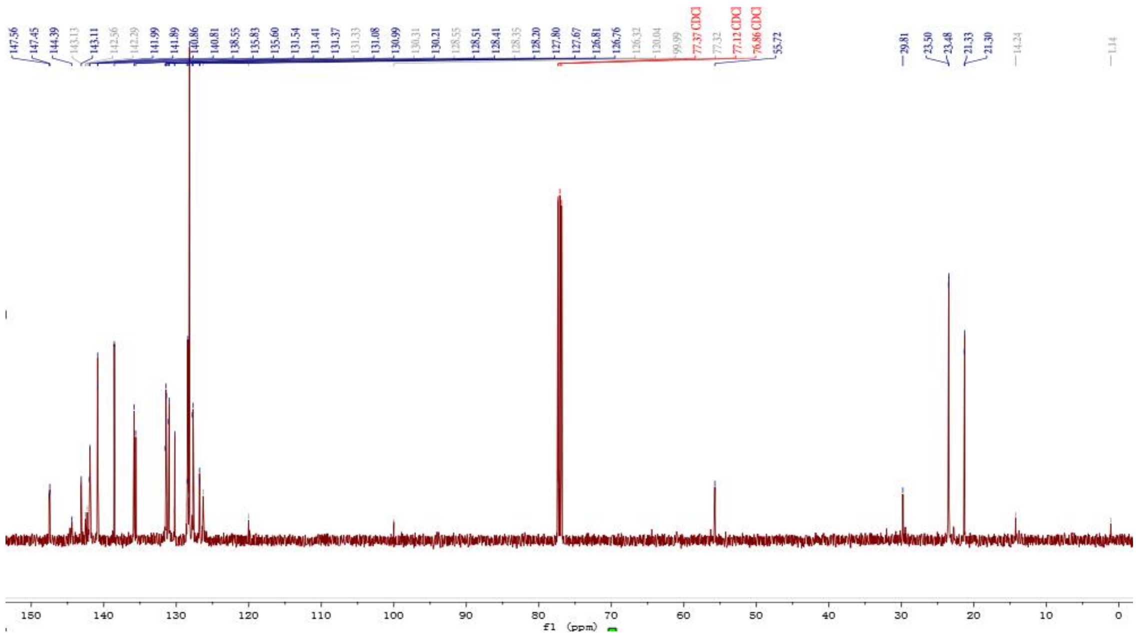


Fig. S11. ^{13}C NMR spectrum of **trans/cis-BB**.

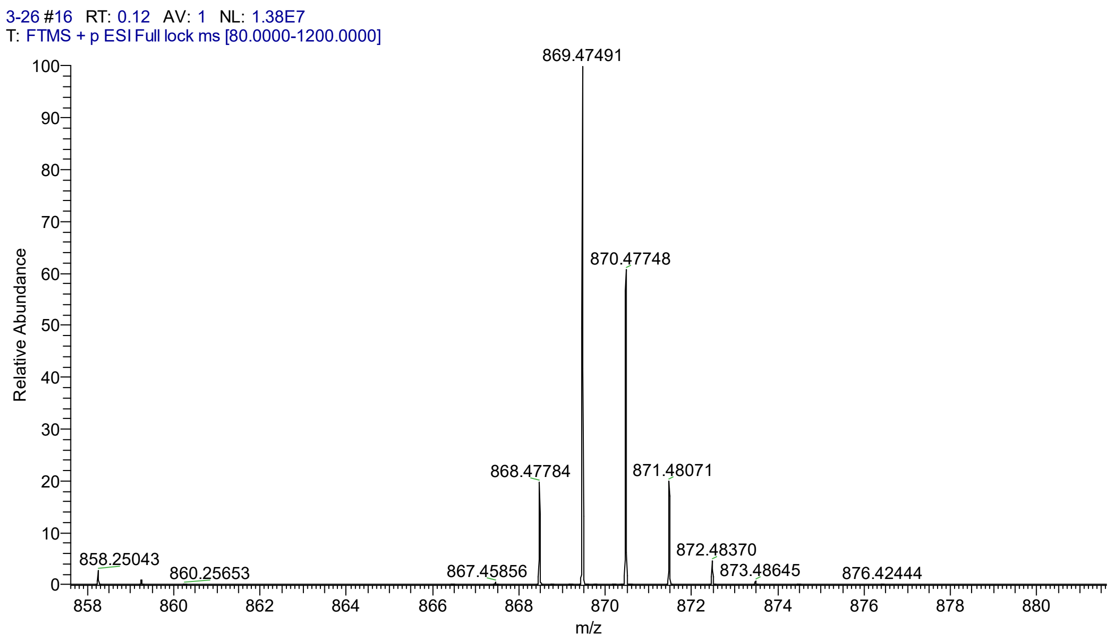


Fig. S12. MS of **trans-BN**.

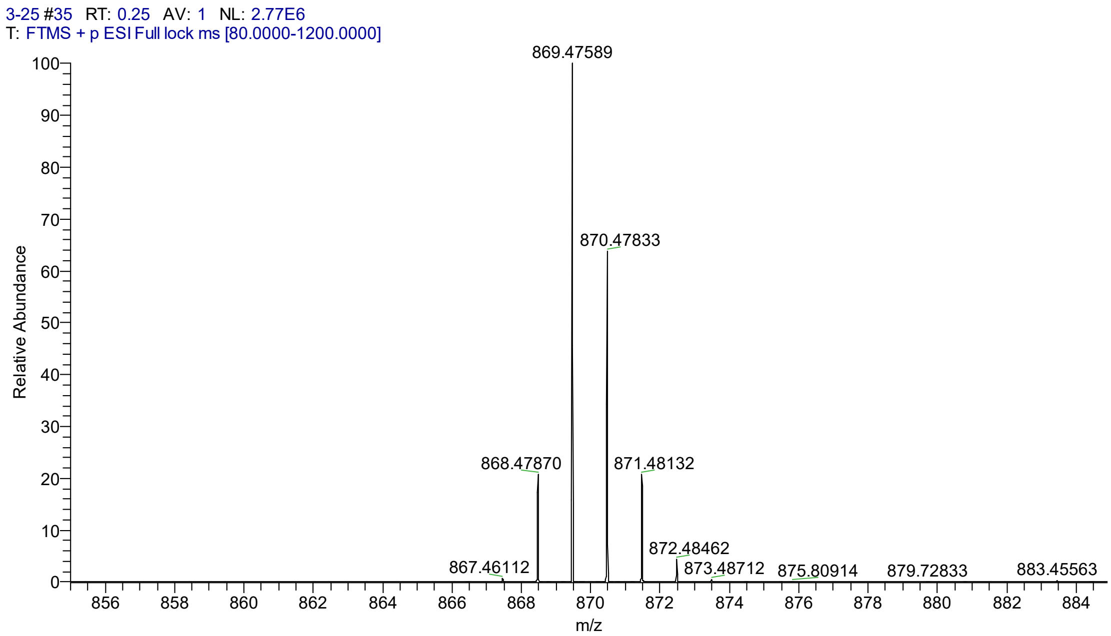


Fig. S13. MS of **cis-BN**.

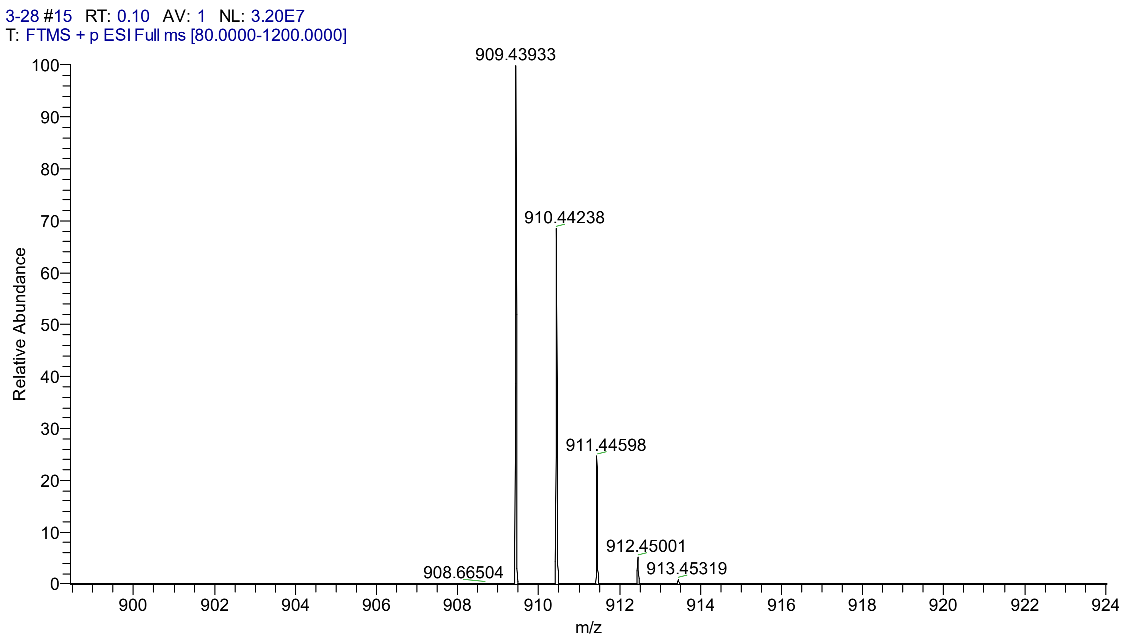


Fig. S14. MS of **trans-NN**.

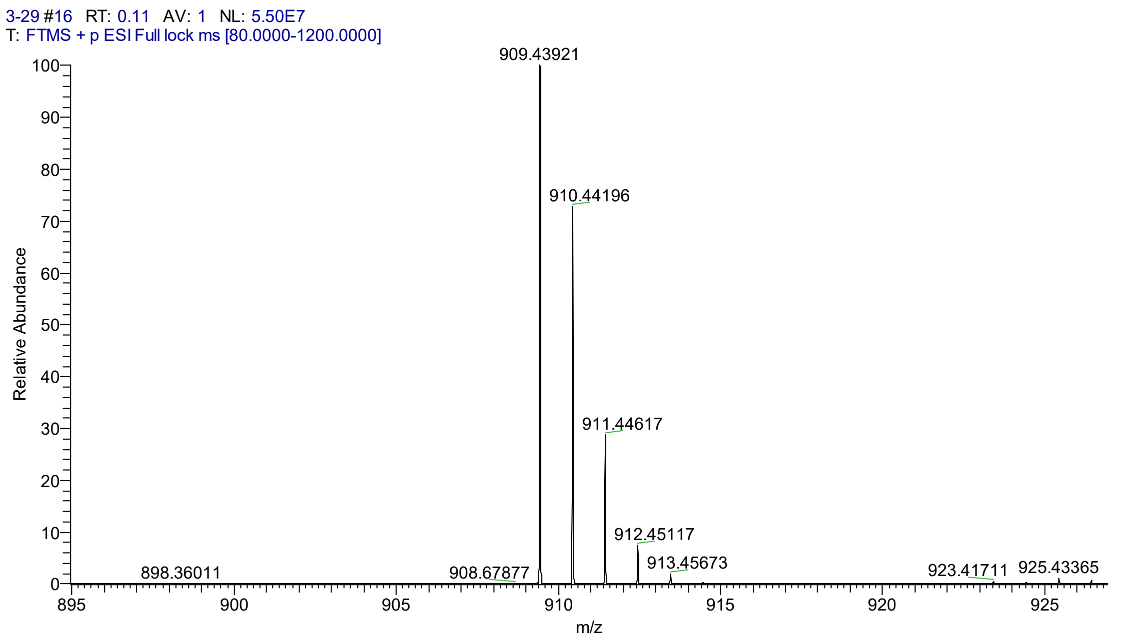


Fig. S15. MS of **cis-NN**.

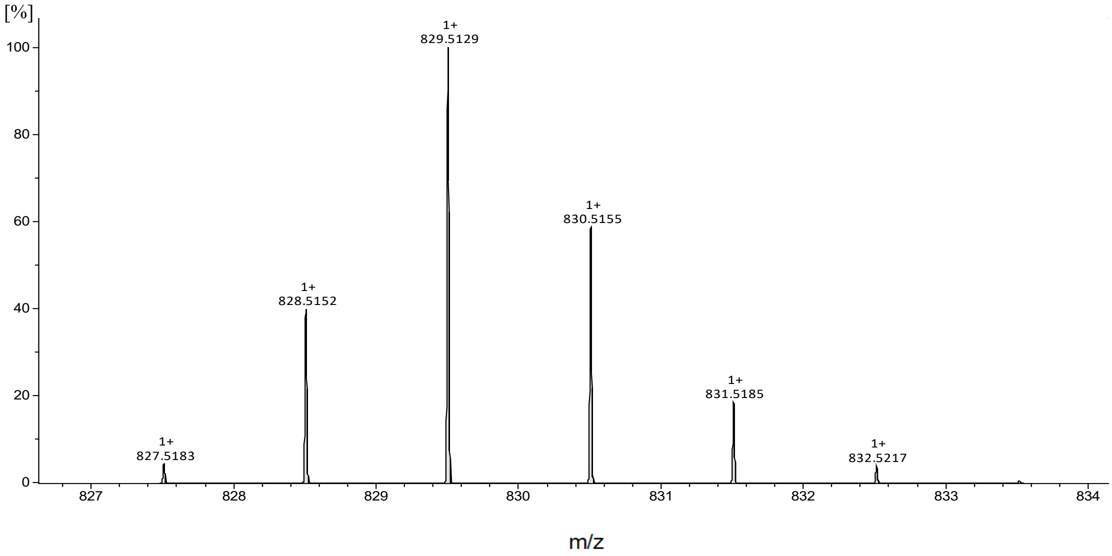


Fig. S16. MS of **trans-BB**.

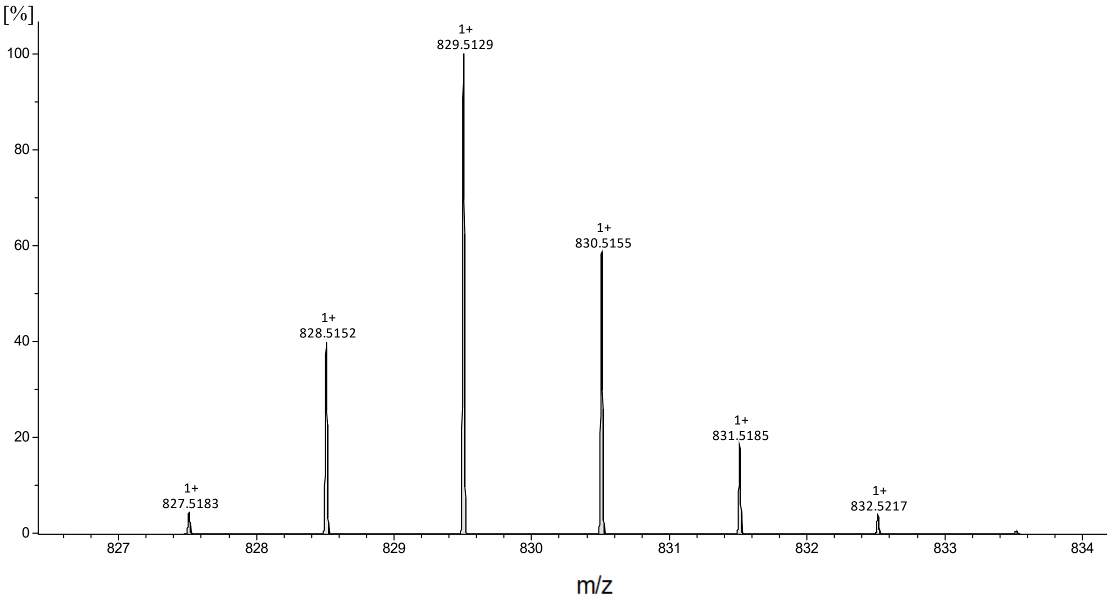


Fig. S17. MS of **cis-BB**.

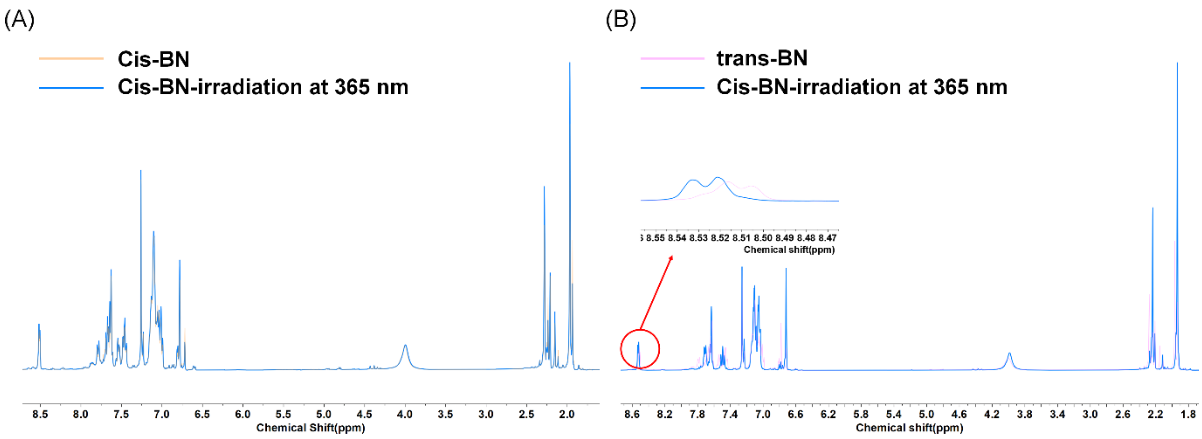


Fig. S18. (A) ^{1}H NMR spectra comparison between non-irradiated **cis-BN** (orange curve) and **cis-BN** after 30 min of 365 nm light irradiation (blue curve); (B) ^{1}H NMR spectra comparison between pure **trans-BN** (pink curve) and **cis-BN** after 30 min of 365 nm light irradiation (blue curve).

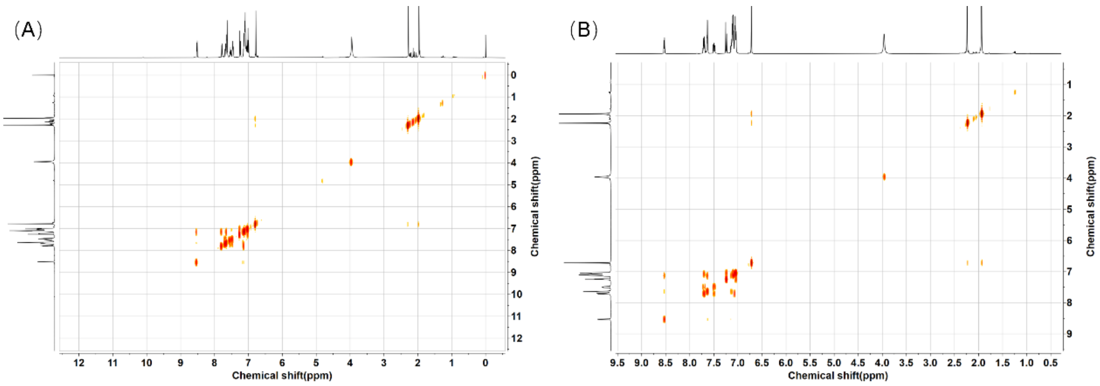


Fig. S19. COSY spectrum of **trans-BN**(A) and **cis-BN**(B).

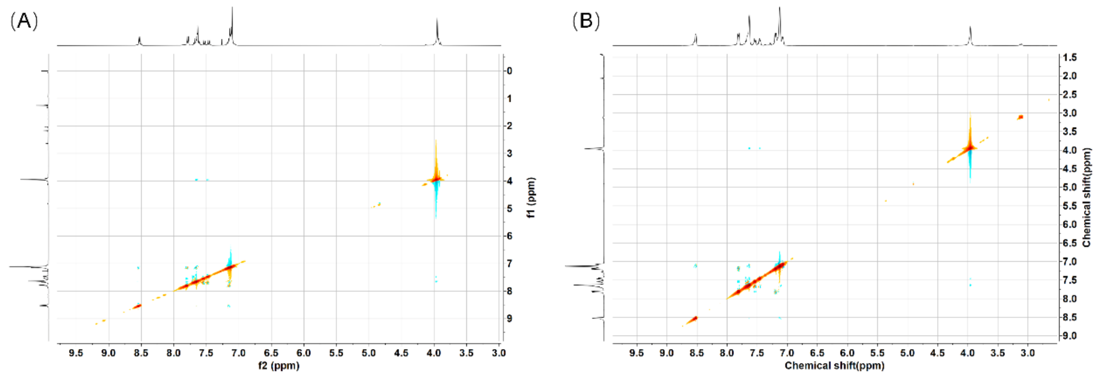


Fig. S20. NOESY spectrum of **trans-NN**(A) and **cis-NN**(B).

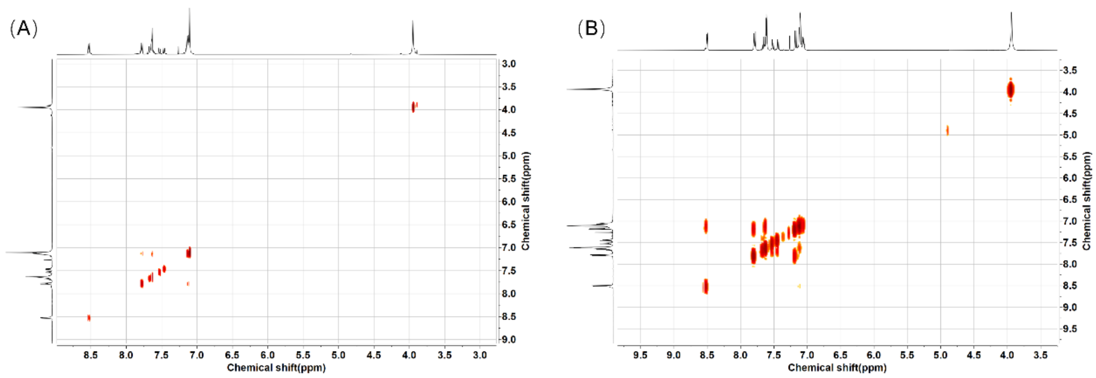


Fig. S21. COSY spectrum of **trans-NN**(A) and **cis-NN**(B).

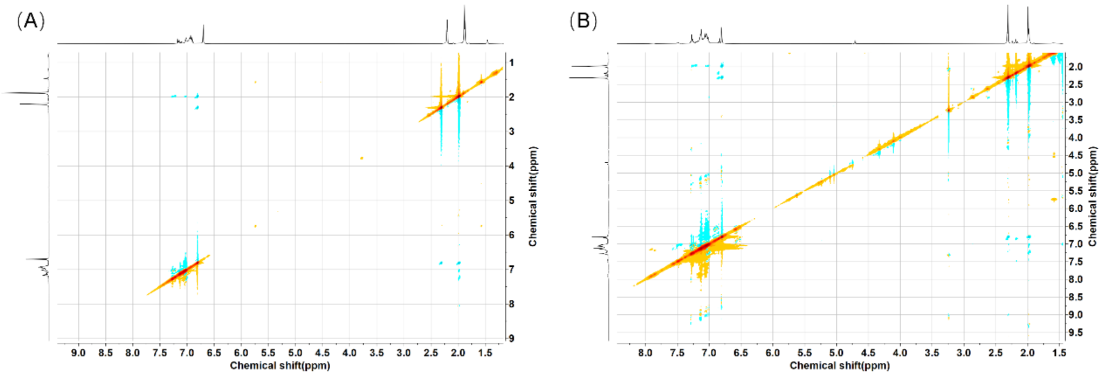


Fig. S22. NOESY spectrum of **trans-BB**(A) and **cis-BB**(B).

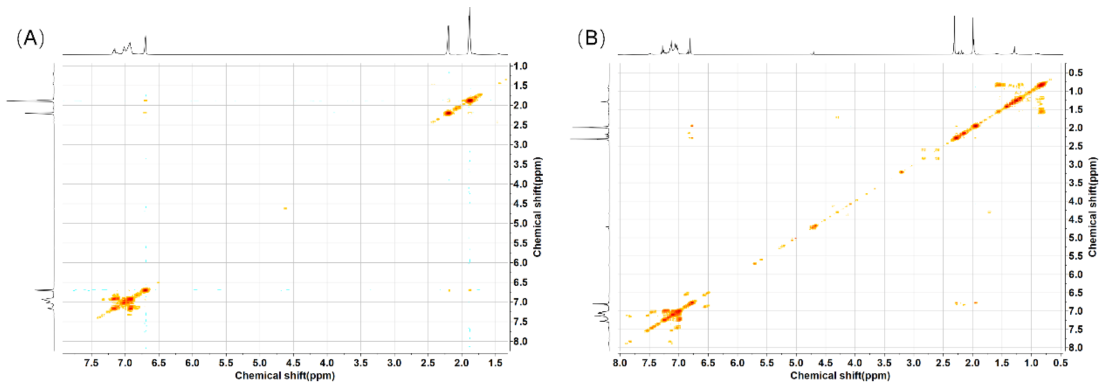


Fig. S23. COSY spectrum of **trans-BB**(A) and **cis-BB**(B).

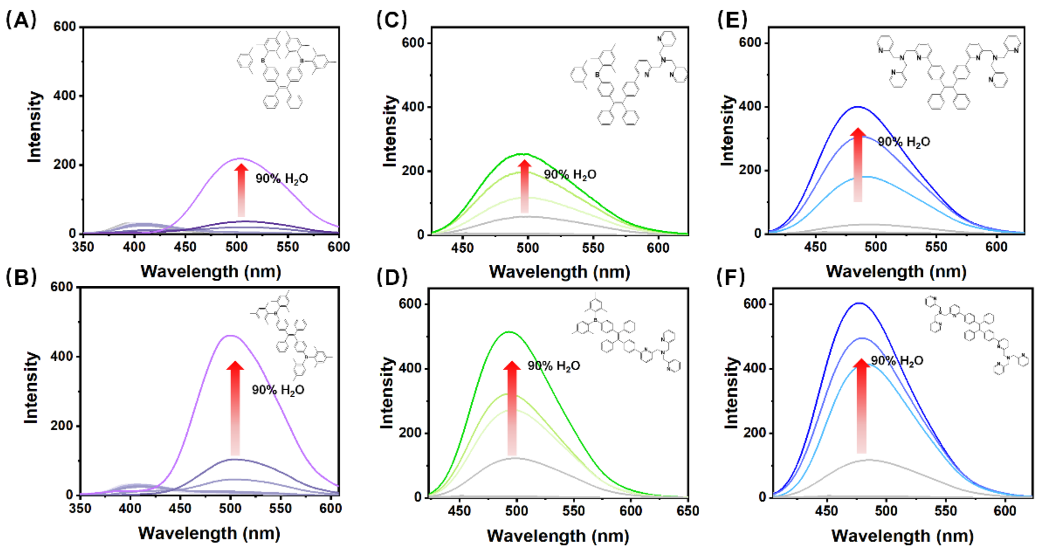


Fig. S24. As the water content in tetrahydrofuran increases gradually from 10% to 90%, the fluorescence spectra of the three isomers.

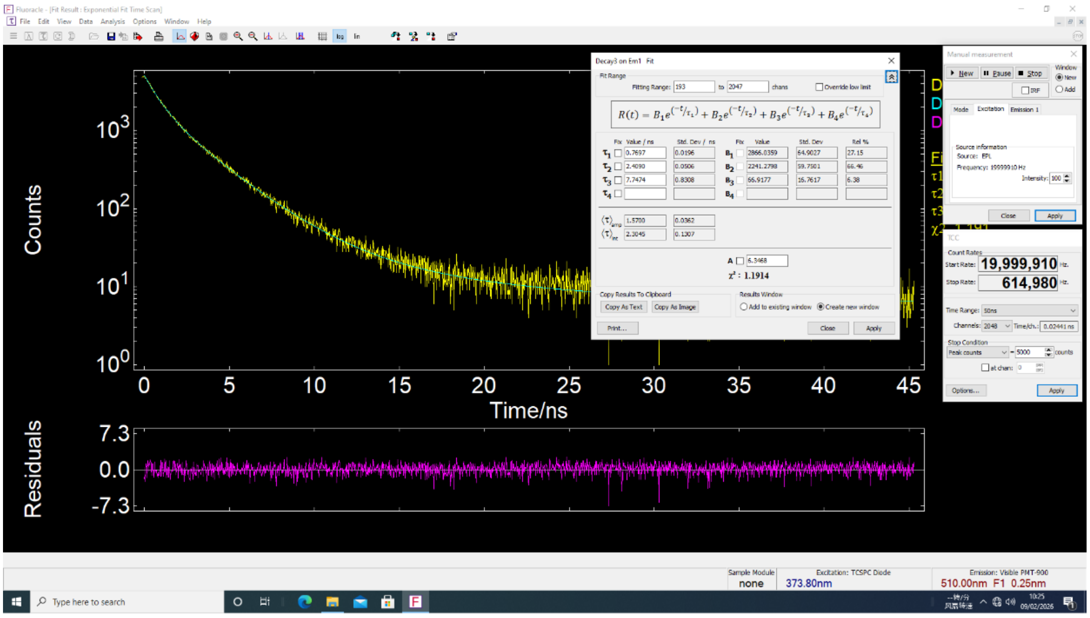


Fig. S25. Fluorescence lifetime fitting curve of **trans-NN**.

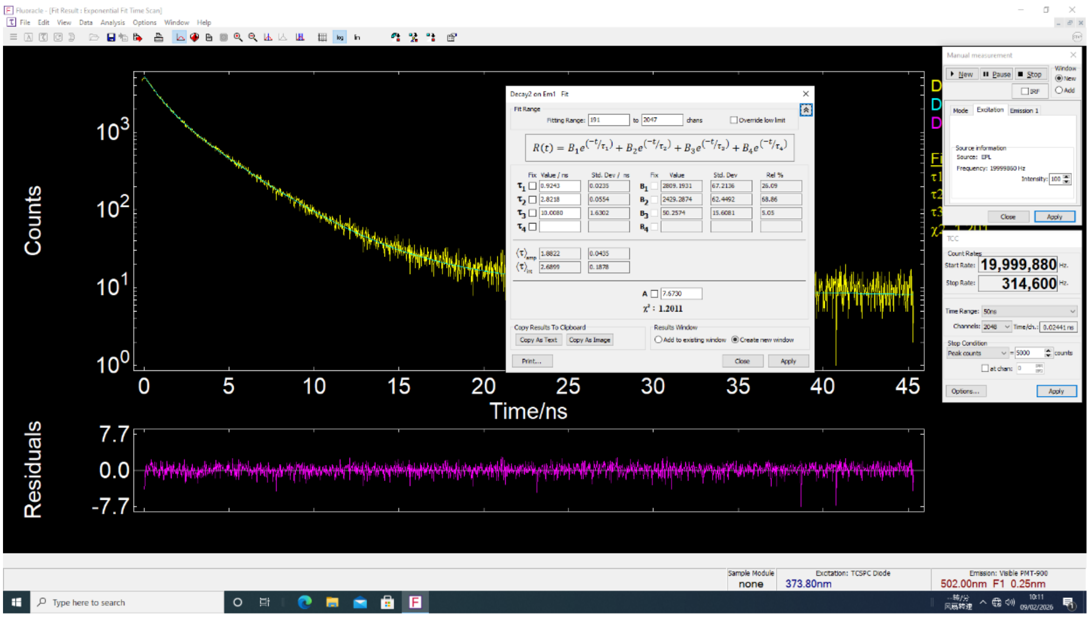


Fig. S26. Fluorescence lifetime fitting curve of **cis-NN**.

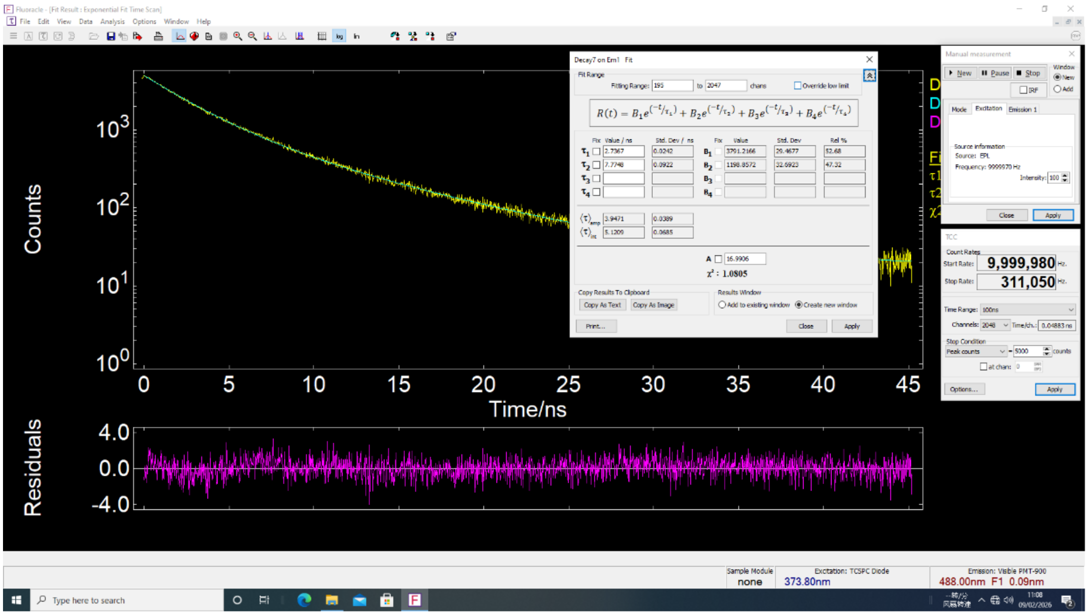


Fig. S27. Fluorescence lifetime fitting curve of **trans-BB**.

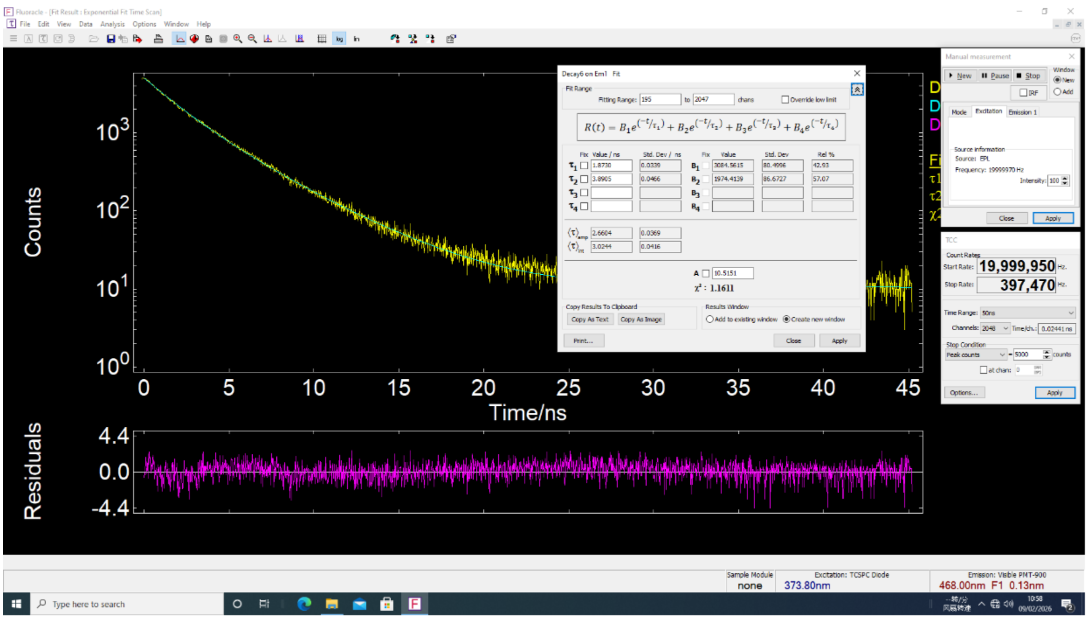


Fig. S28. Fluorescence lifetime fitting curve of **cis-BB**.

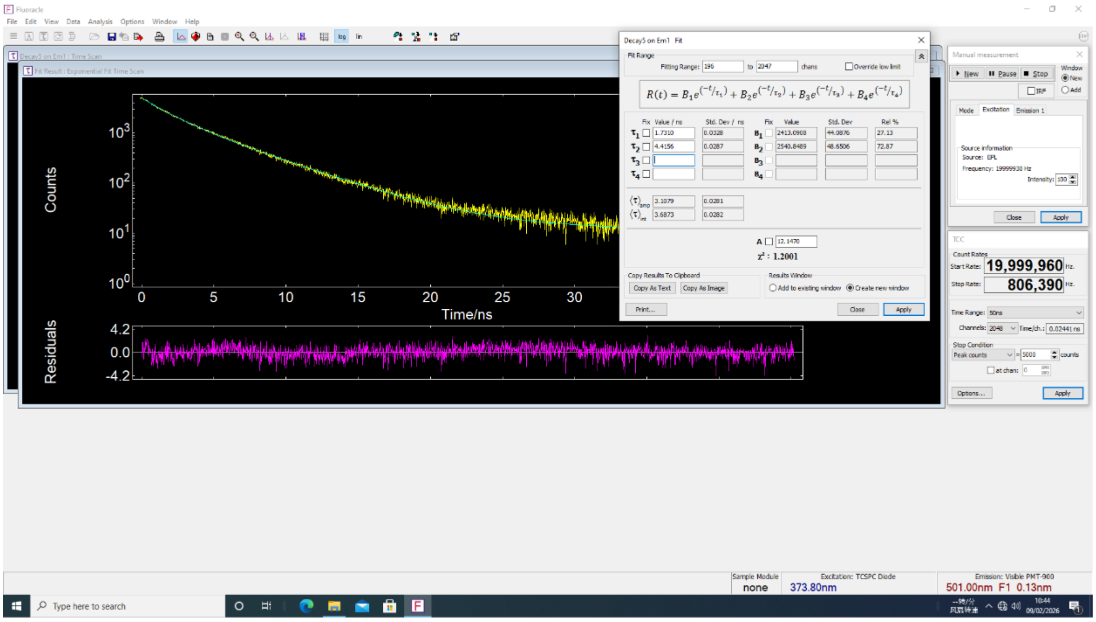


Fig. S29. Fluorescence lifetime fitting curve of **trans-BN**.

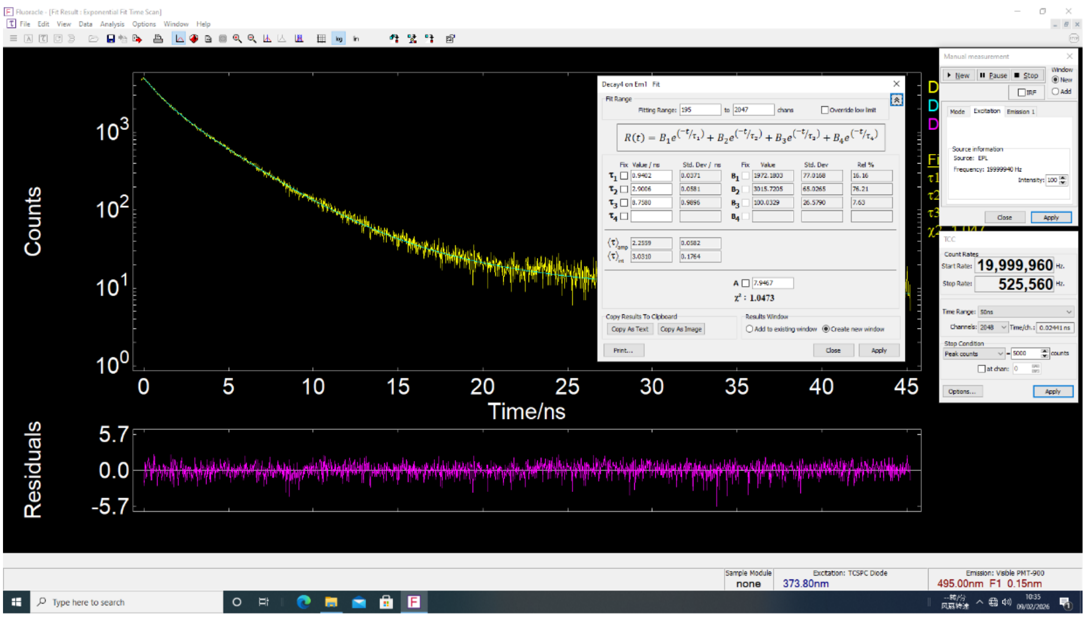


Fig. S30. Fluorescence lifetime fitting curve of **cis-BN**.