Access tetracoordinate boron-doped polycyclic aromatic hydrocarbons with aggregation-induced emission under mild conditions

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1. Experimental section

1.1 General information

All reactions were carried out under an atmosphere of dry nitrogen. Dichloromethane was freshly distilled over calcium hydrogen and stored under nitrogen prior to use. All starting materials were purchased from Energy Chemical and Leyan and used without further purification. Proton nuclear magnetic resonance (\(^1\)H NMR) and carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectra were recorded on Bruker Avance 400 or 500 MHz spectrometers. All Photophysical property measurements were under nitrogen atmosphere. UV/vis and fluorescence measurements were performed on a Jasco V-770 UV/vis spectrophotometer and a F97 Pro fluorescence spectrophotometer, respectively. Quantum efficiencies were determined using an absolute PL quantum yield spectrometer C11347. Phosphorescence and phospholuminescence decay curves were recorded on an Edinburgh Instruments FLS980 spectrophotometer equipped with 365 nm picosecond pulsed LEDs and decay curves were analyzed using the Edinburgh Instruments F980 software. Bpin-carbazole\(^1\) and 7-Bpin-indole\(^2\) were synthesized according to the reported procedure.

1.2 Synthetic details

**Synthesis of Compound NBNN-1**

A mixture of 2-Methoxyethanol (48 ml) and water (8 ml) was stirred and degassed by nitrogen for 1 hour. 2,6-dibromopyridine (830 mg, 3.53 mmol), Bpin-carbazole (3.12 g, 7.70 mmol), Pd(PPh\(_3\))\(_4\) (200 mg, 0.173 mmol) and K\(_2\)CO\(_3\) (1.45 g, 10.51 mmol) were add to the mixed solvents. The reaction mixture was heated to 80 °C and stirred for 16 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH\(_2\)Cl\(_2\) for three times. The combined organic layers were dried
over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) afforded the product 1a as a white solid in 90% yield (2.01 g, 3.18 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.26 (s, 2H, -NH), 8.29 (s, 2H, carbazole), 8.16 (s, 2H, carbazole), 8.10 (s, 2H, carbazole), 8.03 (t, $J = 8.7$ Hz, 1H, Py), 7.98 (d, $J = 8.7$ Hz 2H, Py), 7.27 (d, $J = 8.9$ Hz, 2H, carbazole), 6.83 (d, $J = 8.9$ Hz, 2H, carbazole), 1.61 (s, 18H, tBu), 1.45 (s, 18H, tBu). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.68(Py), 142.47, 142.23, 138.48, 137.92, 136.61(Py), 125.30, 124.14, 122.82, 121.86, 120.85(Py), 119.06, 117.98, 116.12, 110.93, 35.05 (tBu), 34.84 (tBu), 32.35 (tBu), 32.17 (tBu). HRMS(ESI) (m/z): [M+H]$^+$ calcd for C$_{45}$H$_{52}$N$_3$: 634.4146; found: 634.4158.

**Method 1**

Boron tribromide (0.1 mL) was added to a solution of 1a (100 mg, 0.157 mmol) in CH$_2$Cl$_2$ (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Phenylmagnesium bromide (1 M in tetrahydrofuran, 4 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH$_2$Cl$_2$ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 30:1) afforded the product **NBNN-1** as an orange solid in 78% yield (88 mg, 0.122 mmol). The product was confirmed by X-ray diffraction analysis. $^1$H NMR (400 MHz, MHz, CD$_2$Cl$_2$) $\delta$ 8.39 (d, $J = 1.5$ Hz, 2H, carbazole), 8.35 (d, $J = 8.1$, 1H, Py), 8.23 – 8.18 (m, 2H, carbazole), 8.15 (d, $J = 1.6$ Hz, 1H, carbazole), 8.08 (t, $J = 8.1$ Hz, 1H, Py), 8.00 (d, $J = 8.1$, 1H, Py), 7.95 (d, $J = 1.6$ Hz, 1H, carbazole),
7.18 (ddd, J = 17.2, 8.7, 2.1 Hz, 2H, carbazole), 6.88 (d, J = 7.4 Hz, 2H, Ph), 6.86 – 6.80 (m, 1H, Ph), 6.73 (td, J = 7.4, 1.1 Hz, 2H, Ph), 6.17 (d, J = 7.3 Hz, 2H, carbazole), 1.59 (s, 9H, ‘Bu), 1.53 (s, 9H, ‘Bu), 1.44 (s, 18H, ‘Bu). 13C NMR (101 MHz, CD2Cl2) δ 152.6(Ph), 150.14(Py), 144.49, 144.05, 142.75, 142.62, 142.46, 142.14, 139.63, 139.01, 131.58(Py), 126.98(Ph), 126.62(Ph), 126.06, 125.50, 125.48, 124.84, 123.69, 123.12, 121.43, 121.22, 120.07(Py), 118.77, 118.17, 117.89, 117.07, 116.69, 116.43, 115.92, 112.23, 35.42 (‘Bu), 35.37 (‘Bu), 34.97 (‘Bu), 34.93 (‘Bu), 32.31 (‘Bu), 32.13 (‘Bu). HRMS(ESI) (m/z): [M+H]+ calcd for C51H55BN3: 720.4489; found: 720.4484.

**Method 2**

![Chemical structure](image)

Boron tribromide (0.1 mL) was added to a solution of 1a (100 mg, 0.157 mmol) in CH2Cl2 (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Phenyllithium (1 M in ethyl ether, 4 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH2Cl2 for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 30:1) afforded the product NBNN-1 as an orange solid in 57% yield (64 mg, 0.089 mmol)

**Synthesis of Compound NBNN-2**

![Chemical structure](image)
Boron tribromide (0.1 mL) was added to a solution of 1a (300 mg, 0.437 mmol) in CH2Cl2 (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Ethynylmagnesium bromide (0.5 M in tetrahydrofuran, 8 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH2Cl2 for three times. The combined organic layers were dried over magnesium sulfate and the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 30:1) afforded the product NBNN-2 as an orange solid in 58% yield (169 mg, 0.253 mmol).

1H NMR (500 MHz, CDCl3) δ 8.34 (s, 1H, carbazole), 8.31 (s, 1H, carbazole), 8.23 (d, J = 7.8 Hz, 1H, Py), 8.20 (s, 1H, carbazole), 8.15 (s, 1H, carbazole), 8.12 (d, J = 7.8 Hz, 1H, Py), 8.08 (m, 2H, Py, carbazole), 8.01 (s, 1H, carbazole), 7.57 (d, J = 8.5 Hz, 1H, carbazole), 7.45 (d, J = 8.5 Hz, 1H, carbazole), 7.11 (d, J = 8.8 Hz, 1H, carbazole), 6.81 (d, J = 8.8 Hz, 1H, carbazole), 1.89 (s, 1H, -C≡H), 1.58 (s, 9H, ‘Bu), 1.55 (s, 13H, ‘Bu, H2O), 1.51 (s, 9H, ‘Bu), 1.40 (s, 9H, ‘Bu). 13C NMR (126 MHz, CDCl3) δ 152.56(Py), 149.29(Py), 144.27, 142.90, 142.76, 142.62, 142.56, 142.31, 141.83, 139.29, 138.51(Py), 126.47, 125.90, 125.73, 124.59, 123.57, 123.45, 121.32, 120.89, 119.74(Py), 118.09, 117.68, 117.44, 116.49, 116.31, 116.26, 115.93, 111.67, 85.16 (-C≡H), 35.32 (‘Bu), 35.17 (‘Bu), 34.97 (‘Bu), 34.77 (‘Bu), 32.40 (‘Bu), 32.32 (‘Bu), 32.25 (‘Bu), 32.11 (‘Bu). HRMS(ESI) (m/z): [M+H]+ calcd for C47H51BN3: 668.4176; found: 668.4176.

Synthesis of Compound NBNN-3

Boron tribromide (0.1 mL) was added to a solution of 1a (100 mg, 0.157 mmol) in CH2Cl2 (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room
temperature for 2 hours. 2,4,6-trimethylphenylmagnesium bromide (1 M in tetrahydrofuran, 4 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH₂Cl₂ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 50:1) afforded the product **NBNN-3** as an orange solid in 69% yield (82 mg, 0.108 mmol). **1H NMR** (500 MHz, CDCl₃) δ 8.32 (s, 1H, carbazole), 8.19 (s, 1H, carbazole), 8.17 (s, 1H, carbazole), 8.05 (d, J = 7.9 Hz, 1H, Py), 8.01 (s, 1H, carbazole), 7.94 (s, 1H, carbazole), 7.88 (t, J = 7.9 Hz, 1H, Py), 7.84 (s, 1H, carbazole), 7.75 (d, J = 7.9 Hz, 1H, Py), 7.32 (d, J = 8.8 Hz, 1H, carbazole), 7.01 (d, J = 8.8 Hz, 1H, carbazole), 6.95 (d, J = 8.9 Hz, 1H, carbazole), 6.41 (s, 1H, Mes), 6.38 (s, 1H, Mes), 6.23 (d, J = 8.9 Hz, 1H, carbazole), 2.05 (s, 3H, -CH₃), 1.53 (s, 9H, tBu), 1.49 (s, 9H, tBu), 1.46 (s, 9H, tBu), 1.37 (s, 3H, -CH₃), 1.32 (s, 9H, tBu), 1.00 (s, 3H, -CH₃). **13C NMR** (126 MHz, CDCl₃) δ 153.81(Py), 151.08(Py), 143.70, 143.45, 143.17, 142.97, 142.18, 141.99, 141.85, 141.79, 141.56, 139.34, 137.93, 135.40(Py), 130.12, 129.79, 126.63, 125.54, 125.24, 124.51, 124.20, 124.02, 120.94, 120.14, 119.55(Py), 118.12, 117.87, 116.79, 116.36, 115.92, 113.95, 113.48, 112.96, 35.22 (tBu), 35.14 (tBu), 34.86 (tBu), 34.66 (tBu), 32.37 (tBu), 32.31 (tBu), 32.17 (tBu), 32.04 (tBu), 22.50 (-CH₃), 21.99 (-CH₃), 20.74 (-CH₃). **HRMS(ESI) (m/z):** [M+H]+ calcd for C₅₄H₆₁BN₃: 762.4959; found: 762.4951.

**Synthesis of Compound NBNN-4**

Boron tribromide (0.1 mL) was added to a solution of **1a** (100 mg, 0.157 mmol) in CH₂Cl₂ (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was quenched with N,N-
diisopropylethylamine (0.34 ml, 1.96 mmol) and then the mixture was washed with brine and CH₂Cl₂ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 10:1) afforded the product **NBNN-4** as a yellow solid in 48% yield (50 mg, 0.076 mmol). ¹H NMR (500 MHz, DMSO-d₆) δ 8.70 (d, J = 8.0 Hz, 1H, Py), 8.67 (d, J = 8.0 Hz, 1H, Py), 8.50 (s, 1H, carbazole), 8.43 (s, 1H, carbazole), 8.41 (s, 1H, carbazole), 8.36 (s, 1H, carbazole), 8.35 – 8.31 (m, 1H, Py), 8.30 (s, 1H, carbazole), 8.24 (s, 1H, carbazole), 7.45 (d, J = 8.6 Hz, 1H, carbazole), 7.33 (d, J = 8.6 Hz, 1H, carbazole), 7.06 (d, J = 8.7 Hz, 1H, carbazole), 6.72 (d, J = 8.7 Hz, 1H, carbazole), 4.53 (s, 1H, -OH), 1.57 (s, 9H, 'Bu), 1.54 (s, 9H, 'Bu), 1.48 (s, 9H, 'Bu), 1.37 (s, 9H, 'Bu). ¹³C NMR (126 MHz, CDCl₃) δ 151.60(Py), 149.19(Py), 143.30, 143.00, 142.65, 142.58, 142.21, 141.96, 138.57, 138.52, 126.47, 125.62, 124.65, 123.70, 123.48, 120.98, 120.80, 119.83(Py), 118.20, 117.91, 116.93, 116.41, 116.38, 115.80, 115.38, 112.14, 35.29 ('Bu), 35.20 ('Bu), 34.99 ('Bu), 34.78 ('Bu), 32.42 ('Bu), 32.36 ('Bu), 32.24 ('Bu), 32.13 ('Bu). HRMS(ESI) (m/z): [M-OH]⁺ calcd for C₄₅H₄₉BN₃: 642.4020; found: 642.4022.

**Synthesis of Compound NBNN-5**

![Synthesis of Compound NBNN-5](image)

A mixture of 1,2-dimethoxyethane (DME, 24 ml) and water (4 ml) was stirred and degassed by nitrogen for 1 hour. 2,6-dibromopyridine (592 mg, 2.52 mmol), 7-Bpin-indole (1.34 g, 5.51 mmol), Pd(PPh₃)₄ (144 mg, 0.124 mmol) and K₂CO₃ (1.03 g, 7.45 mmol) were added to the mixed solvents. The reaction mixture was heated to 80 °C and stirring for 16 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH₂Cl₂ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by silica gel column
chromatography (petroleum ether/ethyl acetate = 50:1) afforded the product **1b** as a white solid in 46% yield (355 mg, 1.15 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.36 (s, 2H, -NH), 7.96 (t, $J = 7.8$ Hz, 1H, Py), 7.93 – 7.71 (m, 6H, indole, Py), 7.31 (t, $J = 7.5$ Hz, 2H, indole), 7.22 (m, 2H, indole), 6.67 (d, $J = 9.7$ Hz, 2H, indole). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.35 (Py), 138.17, 133.99(Py), 129.59, 125.07, 122.44, 120.65(Py), 119.95, 119.35, 102.62. HRMS(ESI) (m/z): [M+H]$^+$ calcd for C$_{21}$H$_{16}$N$_3$: 310.1344; found: 310.1356.

**1b**

Boron tribromide (0.1 mL) was added to a solution of **1b** (150 mg, 0.485 mmol) in CH$_2$Cl$_2$ (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Phenylmagnesium bromide (1 M in tetrahydrofuran, 4 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH$_2$Cl$_2$ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 50:1) afforded the product **NBNN-5** as a yellow-green solid in 46% yield (88 mg, 0.223 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.0$ Hz, 2H, indole), 7.88 (t, $J = 7.8$ Hz, 1H, Py), 7.83 (m, 4H, indole), 7.68 (d, $J = 7.8$ Hz, 2H, Py), 7.18 (t, $J = 7.6$ Hz, 2H, indole), 6.89 (t, $J = 7.3$ Hz, 1H, Ph), 6.79 (m, 4H, Ph), 6.15 (d, $J = 7.5$ Hz, 2H, indole). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.23(Py), 139.95, 137.01, 130.51(Py), 129.67, 128.83(Ph), 127.37(Ph), 127.27(Ph), 125.24, 119.70, 118.85(Py), 117.83, 115.05, 104.21. HRMS(ESI) (m/z): [M+H]$^+$ calcd for C$_{27}$H$_{19}$N$_3$: 396.1672; found: 396.1682.

**Synthesis of Compound NBNN-6**
Boron tribromide (0.1 mL) was added to a solution of 1a (300 mg, 0.437 mmol) in CH₂Cl₂ (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Isopropylmagnesium chloride (2 M in tetrahydrofuran, 2 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH₂Cl₂ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 20:1). Although we saw yellow product spots on both silica plate and alumina plate, we did not get the stable product NBNN-6 by column chromatography.

**Synthesis of Compound NBNN-7**

Boron tribromide (0.1 mL) was added to a solution of 1a (100 mg, 0.157 mmol) in CH₂Cl₂ (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Methyl lithium diethyl ether (1.6 M in diethyl ether, 2.5 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH₂Cl₂ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 20:1). Although we saw yellow product spots on both silica plate and alumina plate, we did not get the stable product NBNN-7 by column chromatography.
ether/ethyl acetate = 25:1). Although we saw orange product spots on both silica plate and alumina plate, we did not get the stable product NBNN-7 by column chromatography.

**Synthesis of Compound NBNN-8**

Boron tribromide (0.1 mL) was added to a solution of 1a (300 mg, 0.437 mmol) in CH$_2$Cl$_2$ (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours. Vinylmagnesium bromide (2 M in tetrahydrofuran, 2 ml, 4.0 mmol) was dripped into the reaction mixture and the reaction mixture was stirred for 1.5 hours. The reaction mixture was quenched with water and then the mixture was washed with brine and CH$_2$Cl$_2$ for three times. The combined organic layers were dried over magnesium sulfate and then the solvents were evaporated under reduced pressure. We saw lighter orange product spots on both silica plate and alumina plate, but we did not get the stable product NBNN-8 by column chromatography.

**Synthesis of Compound NBNN-1f**

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (56.8 mg, 0.250 mmol) was added to a solution of compound NBNN-1 (72 mg, 0.10 mmol) in CH$_2$Cl$_2$ (20 mL), after stirring for 5 min at room temperature, triflic acid (1.10 mL) was added under nitrogen atmosphere at 0 °C. Then the mixture was stirred for 15 min at the same temperature. After quenching with triethylamine, the reaction mixture was concentrated under
reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 20:1) afforded the product NBNN-1f as a red solid in 78% yield (56 mg, 0.078 mmol), which was confirmed by X-ray diffraction analysis. 

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.45 (s, 2H, carbazole), 8.21 (s, 2H, carbazole), 8.06 (s, 2H, carbazole), 7.97 (d, $J = 7.3$ Hz, 2H, Py), 7.94 - 7.87 (m, 1H, Py), 7.84 (s, 2H, carbazole), 6.80 (t, $J = 7.3$ Hz, 1H, Ph), 6.71 (t, $J = 7.6$ Hz, 2H, Ph), 6.49 (d, $J = 6.7$ Hz, 2H, Ph), 1.58 (s, 18H, tBu), 1.52 (s, 18H, tBu). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.49 (Py), 142.41, 141.91, 140.84, 140.30, 139.56(Py), 129.31, 127.24(Ph), 126.94(Ph), 126.41, 125.08, 121.97, 121.79, 121.05(Py), 118.54, 118.44, 116.59, 113.91, 35.19 (tBu), 35.10 (tBu), 32.33 (tBu), 32.27 (tBu). HRMS(ESI) (m/z): [M+H]$^+$ calcd for C$_{51}$H$_{53}$BN$_3$: 718.4333; found: 718.4381.

**Synthesis of Compound NBNN-2f**

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (28.4 mg, 0.125 mmol) was added to a solution of compound NBNN-2 (33 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL), after stirring for 5 min at room temperature, triflic acid (0.55 mL) was added under nitrogen atmosphere at 0 °C. Then the mixture was stirred for 15 min at the same temperature. After quenching with triethylamine, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 20:1) afforded the product NBNN-2f as a red solid in 58% yield (19 mg, 0.029 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.45 (s, 2H, carbazole), 8.20 (s, 2H, carbazole), 8.06 (s, 2H, carbazole), 7.92 (m, 3H, Py), 7.85 (s, 2H, carbazole), 1.86 (s, 1H, -C≡H), 1.59 (s, 18H, tBu), 1.53 (s, 18H, tBu). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.79(Py), 142.96, 142.39, 140.64, 140.47, 139.23(Py), 127.00, 125.55, 122.13, 121.95, 121.30(Py), 118.81, 118.65, 116.83, 113.42, 86.93, 35.25 (tBu), 32.27 (tBu), 35.19 (tBu), 35.10 (tBu), 32.33 (tBu), 32.27 (tBu).
35.15 (tBu), 32.34 (tBu), 32.27 (tBu). HRMS(ESI) (m/z): [M+H]$^+$ calcd for C$_{47}$H$_{49}$BN$_3$: 666.4020; found: 666.4019.

**Synthesis of Compound NBNN-4f**

![Chemical structure](image)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (28.4 mg, 0.125 mmol) was added to a solution of compound NBNN-4 (33 mg, 0.05 mmol) in CH$_2$Cl$_2$ (10 mL), after stirring for 5 min at room temperature, triflic acid (0.55 mL) was added under nitrogen atmosphere at 0 °C. Then the mixture was stirred for 15 min at the same temperature. After quenching with triethylamine, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by alumina column chromatography (petroleum ether/ethyl acetate = 4:1) afforded the mixed product NBNN-4f as a red solid. We found that the stability of product NBNN-4f was not good, so we did not get clean NMR spectrum (Figure S3.15 and Figure S3.16), but we got a HRMS spectrum. HRMS(ESI) (m/z): [M-OH]$^+$ calcd for C$_{45}$H$_{47}$BN$_3$: 640.3863; found: 640.3872.
2. Electrochemical Properties

Electrochemical measurements were through a three-electrode system with a glassy carbon working electrode, a Pt wire reference electrode and a Pt wire counter electrode. **NBNN-1, NBNN-3, NBNN-4, NBNN-1f, NBNN-2f**, and 1a were measured in CH₃CN (0.1 mol/L "Bu₄NBF₄ vs Fe/Fe⁺) at a scan rate of 100 mV/s. The solubility of **NBNN-2** in CH₃CN is not good, so it was measured in CH₂Cl₂ (0.1 mol/L "Bu₄NBF₄ vs Fe/Fe⁺) at a scan rate of 100 mV/s. No obvious peak can be found of **NBNN-5** and 1b in either CH₃CN or CH₂Cl₂.

**Table S2.1** Electrochemical Data.

|       | E\text{HOMO} (eV)\(^a\) | E\text{LUMO} (eV)\(^b\) | E\text{red} (eV) | E\text{ox} (eV) |
|-------|--------------------------|--------------------------|-----------------|----------------|
| NBNN-1| -5.10                    | -2.79                    | -2.02           | 0.30           |
| NBNN-1f| -4.93                    | -3.01                    | -1.93           | 0.13           |
| NBNN-2| -5.06                    | -2.62                    | -2.16           | 0.26           |
| NBNN-2f| -4.99                    | -2.96                    | -1.96           | 0.19           |
| NBNN-3| -5.07                    | -2.74                    | -2.09           | 0.27           |
| NBNN-4| -5.08                    | -2.70                    | -2.06           | 0.28           |
| 1a    | -5.06                    | -2.69                    | N/A             | 0.22           |

\(^a\) Calculated from the first oxidation peak using E\text{HOMO} = -E\text{ox} - 4.80 eV.

\(^b\) Estimated according to E\text{LUMO} = E\text{HOMO} + \text{the UV/vis absorption edge.}

**Figure S2.1** Cyclic voltammetry curve of **NBNN-1**
Figure S2.2 Cyclic voltammetry curve of NBNN-1f

Figure S2.3 Cyclic voltammetry curve of NBNN-2

Figure S2.4 Cyclic voltammetry curve of NBNN-2f
Figure S2.5 Cyclic voltammetry curve of NBNN-3

Figure S2.6 Cyclic voltammetry curve of NBNN-4

Figure S2.7 Cyclic voltammetry curve of NBNN-5
Figure S2.8 Cyclic voltammetry curve of 1a

Figure S2.9 Cyclic voltammetry curve of 1b
3. NMR Data

$^1$H and $^{13}$C NMR spectra of NbNN-1 in CD$_2$Cl$_2$

**Figure S3.1** $^1$H NMR spectrum of NbNN-1 (400 MHz, CD$_2$Cl$_2$)

**Figure S3.2** $^{13}$C NMR spectrum of NbNN-1 (101 MHz, CD$_2$Cl$_2$)
1H and 13C NMR spectra of NBNN-2 in CDCl₃

Figure S3.3 1H NMR spectrum of NBNN-2 (500 MHz, CDCl₃)

Figure S3.4 13C NMR spectrum of NBNN-2 (126 MHz, CDCl₃)
$^1$H and $^{13}$C NMR spectra of NBNN-3 in CDCl$_3$

**Figure S3.5** $^1$H NMR spectrum of NBNN-3 (500 MHz, CDCl$_3$)

**Figure S3.6** $^{13}$C NMR spectrum of NBNN-3 (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of NBNN-4

Figure S3.7 $^1$H NMR spectrum of NBNN-4 (500 MHz, DMSO-d$_6$)

Figure S3.8 $^{13}$C NMR spectrum of NBNN-4 (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of NBNN-5 in CDCl$_3$

Figure S3.9 $^1$H NMR spectrum of NBNN-5 (500 MHz, CDCl$_3$)

Figure S3.10 $^{13}$C NMR spectrum of NBNN-5 (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of NBNN-1f in CDCl$_3$

**Figure S3.11** $^1$H NMR spectrum of NBNN-1f (500 MHz, CDCl$_3$)

**Figure S3.12** $^{13}$C NMR spectrum of NBNN-1f (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of NBNN-2f in CDCl$_3$

**Figure S3.13** $^1$H NMR spectrum of NBNN-2f (500 MHz, CDCl$_3$)

**Figure S3.14** $^{13}$C NMR spectrum of NBNN-2f (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of NBNN-4f in CDCl$_3$ (the stability of NBNN-4f was not good, so we did not get clean NMR spectra)

Figure S3.15 $^1$H NMR spectrum of NBNN-4f (500 MHz, CDCl$_3$)

Figure S3.16 $^{13}$C NMR spectrum of NBNN-4f (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of 1a in CDCl$_3$

Figure S3.17 $^1$H NMR spectrum of 1a (500 MHz, CDCl$_3$)

Figure S3.18 $^{13}$C NMR spectrum of 1a (126 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of 1b in CDCl$_3$

Figure S3.19 $^1$H NMR spectrum of 1b (500 MHz, CDCl$_3$)

Figure S3.20 $^{13}$C NMR spectrum of 1b (126 MHz, CDCl$_3$)
4. Computational Results

All calculations were performed using the Gaussian 16 suite of programs. Initial input coordinates were taken from the corresponding crystal structure data if applicable, while all others were generated in GausView 6.0. DFT and TD-DFT calculations were performed using the B3LYP/6-311g(d,p) level of theory based on optimized structures.

Table S4.1 HOMO and LUMO energy levels.

| Compounds | LUMO/eV | HOMO/eV |
|-----------|---------|---------|
| NBNN-1    | -2.24   | -5.31   |
| NBNN-2    | -2.26   | -5.33   |
| NBNN-3    | -2.23   | -5.29   |
| NBNN-4    | -2.15   | -5.27   |
| NBNN-5    | -2.36   | -5.55   |
| NBNN-1f   | -2.33   | -4.98   |
| NBNN-2f   | -2.34   | -4.99   |

Table S4.2 NICS(1) values (in ppm) of NBNN-PAHs were calculated at B3LTP/6-311+g(d,p) level using optimized structures.

|       | NBNN-1 | NBNN-2 | NBNN-3 | NBNN-4 | NBNN-5 | NBNN-1f | NBNN-2f |
|-------|--------|--------|--------|--------|--------|---------|---------|
| 1     | 2      | 1      | 2      | 1      | 2      | 1       | 2       |
| 2     | 9.7    | 4.9    | 10.4   | 4.9    | 7.3    | 2.5     | 9.7     |
| 1     | 2      | 1      | 2      | 1      | 2      | 1       | 2       |
| 2     | 2.5    | 9.7    | 5.4    | 7.7    | 5.8    | 12.8    | 11.8    |
| 3     | 12.8   | 11.8   | 14.6   | 12.6   | 12.0   | 15.7    |         |
### Table S4.3 TD-DFT calculated electronic transitions for NBNN-1 along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|----------------------------|---------------------|
| NBNN-1   | T1         | HOMO → LUMO (88%)        | 576 nm, 2.15 eV            | 0                   |
|          |            | H-1 → L+1 (6%)           |                            | 0                   |
|          | T2         | H-1 → LUMO (58%)         | 576 nm, 2.21 eV            | 0                   |
|          |            | HOMO → L+1 (33%)         |                            | 0                   |
|          | T3         | H-1 → LUMO (37%)         | 500 nm, 2.48 eV            | 0                   |
|          |            | HOMO → L+1 (43%)         |                            | 0                   |
|          | S1         | HOMO → LUMO (98%)        | 497 nm, 2.49 eV            | 0.1508              |
|          | S2         | H-1 → LUMO (98%)         | 478 nm, 2.60 eV            | 0.0437              |
|          | S3         | H-1 → L+1 (97%)          | 432 nm, 2.87 eV            | 0.0168              |

![Energy Diagrams](image1.png)  

**NBNN-1**

| Compound | Energy Level |
|----------|--------------|
|          | L+1 -1.90 eV |
|          | LUMO -2.24 eV|
|          | HOMO -5.31 eV|
|          | H-1 -5.36 eV |
**Table S4.4** TD-DFT calculated electronic transitions for **NBNN-2** along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|----------------------------|-------------------|
| NBNN-2   | T1         | HOMO → LUMO (88%)        | 578 nm, 2.15 eV            | 0                 |
|          |            | H-1 → L+1 (5%)           |                            |                   |
|          | T2         | H-1 → LUMO (53%)         | 551 nm, 2.25 eV            | 0                 |
|          |            | HOMO → L+1 (37%)         |                            |                   |
|          | T3         | H-1 → LUMO (40%)         | 495 nm, 2.50 eV            | 0                 |
|          |            | HOMO → L+1 (37%)         |                            |                   |
|          | S1         | HOMO → LUMO (98%)        | 500 nm, 2.49 eV            | 0.1530            |
|          | S2         | H-1 → LUMO (97%)         | 468 nm, 2.65 eV            | 0.0473            |
|          | S3         | H-1 → L+1 (75%)          | 423 nm, 2.93 eV            | 0.0269            |
|          |            | HOMO → L+1 (21%)         |                            |                   |

**Images:**
- L+1: -1.91 eV
- LUMO: -2.26 eV
- HOMO: -5.33 eV
- H-1: -5.43 eV
Table S4.5 TD-DFT calculated electronic transitions for NBNN-3 along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|----------------------------|-------------------|
| NBNN-3   | T1         | HOMO → LUMO (89%)         | 583 nm, 2.13 eV            | 0                 |
|          |            | H-1 → L+1 (4%)           |                            |                   |
|          | T2         | H-1 → LUMO (46%)         | 550 nm, 2.25 eV            | 0                 |
|          |            | HOMO → L+1 (43%)         |                            |                   |
|          | T3         | H-1 → LUMO (47%), HOMO → L+1 (33%), H-2 → LUMO (5%) | 496 nm, 2.50 eV | 0                 |
|          | S1         | HOMO → LUMO (98%)        | 502 nm, 2.47 eV            | 0.1419            |
|          | S2         | H-1 → LUMO (97%)         | 465 nm, 2.67 eV            | 0.0416            |
|          | S3         | HOMO → L+1 (86%)         | 421 nm, 2.95 eV            | 0.0679            |
|          |            | H-1 → L+1 (5%)           |                            |                   |

L+1 -1.87 eV  LUMO -2.23 eV
HOMO -5.29 eV  H -1 -5.43 eV
Table S4.6 TD-DFT calculated electronic transitions for NBNN-4 along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|-----------------------------|-------------------|
| NBNN-4   | T1         | HOMO → LUMO (87%)         | 563 nm, 2.20 eV             | 0                 |
|          | T2         | H-1 → LUMO (27%), HOMO → L+1 (54%), H-4 → L+1 (4%), H-1 → L+1 (4%) | 537 nm, 2.32 eV | 0                 |
|          | T3         | H-2 → LUMO (16%), H-2 → L+1 (11%), H-1 → LUMO (48%), HOMO → L+1 (10%) | 480 nm, 2.58 eV | 0                 |
|          | S1         | HOMO → LUMO (97%)         | 484 nm, 2.56 eV             | 0.1680            |
|          | S2         | H-1 → LUMO (84%), HOMO → L+1 (13%) | 439 nm, 2.82 eV | 0.0379            |
|          | S3         | H-1 → LUMO (12%), HOMO → L+1 (77%), H-1 → L+1 (5%) | 420 nm, 2.95 eV | 0.0934            |

L+1 -1.85 eV
LUMO -2.15 eV
### Table S4.7 TD-DFT calculated electronic transitions for NBNN-5 along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound  | Spin State | Transition Configuration                                                                 | Excitation Energy (nm, eV) | Oscillator Strength |
|-----------|------------|------------------------------------------------------------------------------------------|----------------------------|-------------------|
| NBNN-5    | T1         | HOMO → LUMO (86%), H-1 → L+1 (8%)                                                          | 576 nm, 2.15 eV            | 0                 |
|           | T2         | H-1 → LUMO (45%), HOMO → L+1 (46%)                                                        | 550 nm, 2.25 eV            | 0                 |
|           | T3         | H-1 → LUMO (47%), HOMO → L+1 (39%), H-3 → L+1 (5%)                                         | 463 nm, 2.68 eV            | 0                 |
|           | S1         | HOMO → LUMO (98%)                                                                         | 467 nm, 2.67 eV            | 0.1762            |
|           | S2         | H-1 → LUMO (96%)                                                                          | 438 nm, 2.84 eV            | 0.0111            |
|           | S3         | H-3 → LUMO (18%), H-2 → LUMO (44%), H-1 → L+1 (10%), HOMO → L+1 (26%)                     | 396 nm, 3.13 eV            | 0.0213            |
Table S4.8 TD-DFT calculated electronic transitions for NBNN-1f along with their corresponding excitation energies and oscillator strengths (iso = 0.020).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|-----------------------------|--------------------|
| NBNN-1f  | T1         | HOMO → LUMO (94%)         | 654 nm, 1.89 eV             | 0                  |
|          | T2         | H-1 → LUMO (15%) HOMO → L+1 (74%) | 584 nm, 2.12 eV             | 0                  |
|          | T3         | H-3 → L+1 (10%), H-2 → LUMO (31%) HOMO → L+2 (37%), H-2 → L+2 (9%) | 516 nm, 2.40 eV | 0                  |
|   | HOMO → LUMO (%) | Energy (nm, eV) | Intensity (a.u.) |
|---|----------------|-----------------|-----------------|
| S1 | 607 nm, 2.04 eV | 0.0280          |
| S2 | 494 nm, 2.51 eV | 0.0454          |
| S3 | 461 nm, 2.69 eV | 0.0413          |

LUMO -2.33 eV

HOMO -4.98 eV

H-1 -5.57 eV

H-2 -5.72 eV
Table S4.9 TD-DFT calculated electronic transitions for NBNN-2f along with their corresponding excitation energies and oscillator strengths (iso = 0.02).

| Compound | Spin State | Transition Configuration | Excitation Energy (nm, eV) | Oscillator Strength |
|----------|------------|--------------------------|----------------------------|--------------------|
| NBNN-2f  | T1         | HOMO → LUMO (94%)        | 652 nm, 1.90 eV            | 0                  |
|          | T2         | H-1 → LUMO (10%), HOMO → L+1 (78%), H-4 → L+1 (5%) | 575 nm, 2.16 eV            | 0                  |
|          | T3         | H-3 → L+1 (10%), H-2 → LUMO (36%), HOMO → L+2 (33%), H-2 → L+2 (9%) | 515 nm, 2.41 eV            | 0                  |
|          | S1         | HOMO → LUMO (99%)        | 605 nm, 2.05 eV            | 0.0292             |
|          | S2         | HOMO → L+1 (98%)         | 488 nm, 2.54 eV            | 0.0482             |
|          | S3         | H-1 → LUMO (96%)         | 440 nm, 2.81 eV            | 0.0497             |
|       |       |
|-------|-------|
| LUMO  | -2.34 eV |
| HOMO  | -4.99 eV |
| H-1   | -5.68 eV |
| H-2   | -5.71 eV |
| H-3   | -5.93 eV |
| H-4   | -6.34 eV |
DFT calculated UV/vis spectra

Figure S4.1 DFT calculated UV/vis spectra of NBNN-1

Figure S4.2 DFT calculated UV/vis spectra of NBNN-2
**Figure S4.3** DFT calculated UV/vis spectra of NBNN-3

**Figure S4.4** DFT calculated UV/vis spectra of NBNN-4
Figure S4.5 DFT calculated UV/vis spectra of NBNN-5

Figure S4.6 DFT calculated UV/vis spectra of NBNN-1f
Figure S4.7 DFT calculated UV/vis spectra of NBNN-2f

Cartesian coordinates of DFT calculated structure

NBNN-1

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N    | 1.23171800 | -0.09406800 | -0.28880400 |
| N    | -1.30201600 | -0.39469100 | 0.28502000 |
| N    | 0.29543100  | -2.39561600 | -0.01453400 |
| C    | 0.45668200  | -0.84459300 | 2.13567600 |
| C    | -4.10961500 | 5.35228300  | 0.98971400  |
| H    | -3.11179900 | 5.56695800  | 1.37883900  |
| H    | -4.75136800 | 6.20691700  | 1.22667400  |
| H    | -4.03393600 | 5.27461100  | -0.09840900 |
| C    | 2.69569000  | -2.02087100 | 0.13249300  |
| C    | -1.98363800 | 0.75893600  | 0.69452800  |
| C    | 1.45393500  | 1.21010000  | -0.75869000 |
| C    | -0.75459300 | -3.17038000 | -0.44041600 |
|   |          |          |          |
|---|----------|----------|----------|
| C | 2.84786900 | 1.43906400 | -0.90724800 |
| C | -3.32921700 | 0.70491200 | 0.25633500  |
| C | 2.46265500  | -0.68319900 | -0.19741100 |
| C | -2.22440100 | -1.20253900 | -0.31884900 |
| C | 3.32233600  | 2.66713800  | -1.37923500 |
| H | 4.39049100  | 2.81112100  | -1.47966100 |
| C | 1.56184900  | -2.93634600 | 0.06396200  |
| C | 4.04160100  | -2.41459500 | 0.26492200  |
| H | 4.25609200  | -3.43243100 | 0.55625400  |
| C | 2.43200400  | 3.68196900  | -1.72425100 |
| C | -0.58030300 | -4.54927400 | -0.59526900 |
| H | -1.42591600 | -5.16156500 | -0.86820500 |
| C | 5.10752300  | -1.54034000 | 0.02808500  |
| C | -3.77474200 | 2.86703300  | 1.25413900  |
| C | 1.05132900  | 3.41674000  | -1.58927800 |
| H | 0.33571400  | 4.18176200  | -1.86777500 |
| C | -4.20862800 | 1.75849500  | 0.53105700  |
| H | -5.23072100 | 1.69218600  | 0.18105700  |
| C | 4.82301100  | -0.22635600 | -0.39912900 |
| H | 5.63572700  | 0.45442600  | -0.62605700 |
| C | -0.32654000 | -1.64398000 | 2.98489400  |
| H | -1.11174800 | -2.26521300 | 2.56272100  |
| C | -2.03846100 | -2.52974400 | -0.70599300 |
| C | 1.43928600  | -0.04971600 | 2.74249700  |
| H | 2.06764800  | 0.58845400  | 2.13051400  |
| C | 3.51064300  | 0.20958300  | -0.52078900 |
| C | 0.54957000  | 2.20972600  | -1.12128900 |
| H | -0.51736600 | 2.05733000  | -1.05311200 |
| C | -3.49201800 | -0.57271700 | -0.40250000 |
|   |   |   |   |
|---|---|---|---|
| C | 1.74239100 | -4.31230600 | -0.08831800 |
| H | 2.73793400 | -4.72486900 | -0.02279400 |
| C | -1.53373800 | 1.85760800 | 1.43002300 |
| H | -0.51762100 | 1.91317500 | 1.79532000 |
| C | -3.13765100 | -3.18085600 | -1.29888800 |
| H | -3.01059600 | -4.19429700 | -1.64834900 |
| C | -4.38327200 | -2.56635100 | -1.46644300 |
| C | 6.57808600 | -1.97092600 | 0.19910000 |
| C | 2.89247000 | 5.05318300 | -2.25189700 |
| C | -2.43152500 | 2.88138500 | 1.69517000 |
| H | -2.07332900 | 3.72632600 | 2.27176500 |
| C | 0.66049900 | -5.12394700 | -0.38077700 |
| H | 0.79149000 | -6.19502500 | -0.48327000 |
| C | -4.55185200 | -1.25431000 | -0.98576600 |
| H | -5.51948900 | -0.77079700 | -1.05881300 |
| C | -5.57220200 | -3.28259700 | -2.13737300 |
| C | -4.69464000 | 4.05418000 | 1.59355100 |
| C | 1.63444500 | -0.05055100 | 4.12377300 |
| H | 2.40186000 | 0.57998200 | 4.56073800 |
| C | 0.84952800 | -0.86012500 | 4.94016500 |
| H | 1.00031700 | -0.86561200 | 6.01433200 |
| C | -0.13577200 | -1.66036300 | 4.36396800 |
| H | -0.75820400 | -2.29114500 | 4.99020300 |
| C | 2.32016000 | 5.28314400 | -3.67014100 |
| H | 2.67067500 | 4.51089600 | -4.36031500 |
| H | 2.63797200 | 6.25665900 | -4.05710000 |
| H | 1.22806600 | 5.26321400 | -3.67509400 |
| C | 2.38356500 | 6.16833600 | -1.30889700 |
| H | 1.29352400 | 6.17385600 | -1.23887600 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 2.69996800| 7.15091100| -1.67345300|
| H       | 2.78171700| 6.03503800| -0.29926200|
| C       | 4.42598500| 5.16269600| -2.33408500|
| H       | 4.89519700| 5.03676800| -1.35439800|
| H       | 4.70427100| 6.15164600| -2.70847600|
| H       | 4.85037300| 4.42075900| -3.01612200|
| C       | -6.74940000| -3.38267000| -1.13928400|
| H       | -6.46010900| -3.95188500| -0.25167800|
| H       | -7.60226200| -3.88654600| -1.60477900|
| H       | -7.08699400| -2.39815500| -0.80779600|
| C       | -6.02209800| -2.47880300| -3.37968000|
| H       | -6.33157200| -1.46492600| -3.11590200|
| H       | -6.87035700| -2.97029100| -3.86648500|
| H       | -5.20994000| -2.40012800| -4.10744200|
| C       | -5.21897200| -4.70886700| -2.59768400|
| H       | -4.40827100| -4.71124200| -3.33165600|
| H       | -6.09138800| -5.16720500| -3.07084200|
| H       | -4.92832600| -5.34775500| -1.75885700|
| C       | 6.71515800 | -3.43361800| 0.66008900 |
| H       | 6.22979500 | -3.60395400| 1.62501100 |
| H       | 7.77325200 | -3.68287100| 0.77579300 |
| H       | 6.29239900 | -4.13184500| -0.06796900 |
| C       | 7.32429800 | -1.82431400| -1.14752900|
| H       | 6.86798800 | -2.45406600| -1.91617600|
| H       | 8.37106600 | -2.12456200| -1.03774600|
| H       | 7.31162100 | -0.79417900| -1.51057100|
| C       | -6.11750200| 3.86924800 | 1.03529700 |
| H       | -6.73073300| 4.73560800 | 1.29792300 |
| H       | -6.60471500| 2.98274900 | 1.45057000 |
| Atom | X     | Y     | Z      |
|------|-------|-------|--------|
| N    | 1.28038800 | -0.20162600 | -0.05566200 |
| N    | -1.26309400 | -0.41886200 | 0.51468200  |
| N    | 0.29211300  | -2.46490100 | 0.31570700  |
| C    | -3.94835600 | 5.40351800  | 1.00880400  |
| H    | -2.93912800 | 5.61633100  | 1.36837900  |
| H    | -4.56939100 | 6.28024700  | 1.21868400  |
| H    | -3.89596400 | 5.27512700  | -0.07587300 |
| C    | 2.69571800  | -2.12418700 | 0.51254400  |
| C    | -1.91479700 | 0.76472200  | 0.88261000  |
| C    | 1.54287200  | 1.09139900  | -0.53669500 |
| C    | -0.77333600 | -3.23691100 | -0.07716300 |
| C    | 2.94447400  | 1.30355400  | -0.61089100 |
| C    | -3.26896000 | 0.71386400  | 0.47321600  |
| C    | 2.49937600  | -0.79682500 | 0.12659200  |
| C    | -2.21022800 | -1.24127300 | -0.02720600 |
| C    | 3.45695600  | 2.51412200  | -1.08714000 |
|   |          |          |          |
|---|----------|----------|----------|
| C | 4.53037700 | 2.64655000 | -1.13075400 |
| C | 1.54831300 | -3.02226400 | 0.43493100 |
| C | 4.02743200 | -2.53190400 | 0.72330800 |
| H | 4.21217200 | -3.54261000 | 1.05707300 |
| C | 2.59730600 | 3.52796700 | -1.50633200 |
| C | -0.61642200 | -4.62146900 | -0.19028700 |
| H | -1.46928000 | -5.23076600 | -0.44651500 |
| C | 5.11508300 | -1.67729900 | 0.51618300 |
| C | -3.65390900 | 2.92637000 | 1.38030600 |
| C | 1.20879900 | 3.27876000 | -1.44317800 |
| H | 0.51782500 | 4.04294000 | -1.78006700 |
| C | -4.12301800 | 1.79563400 | 0.71618500 |
| H | -5.15315100 | 1.73368800 | 0.38990100 |
| C | 4.87028700 | -0.37050600 | 0.04373300 |
| H | 5.70253500 | 0.29543000 | -0.15428300 |
| C | -2.05122800 | -2.58806100 | -0.35228600 |
| C | 3.57197700 | 0.07735600 | -0.15760800 |
| C | 0.66993900 | 2.08763500 | -0.97497100 |
| H | -0.40070800 | 1.94448200 | -0.96354400 |
| C | -3.46699200 | -0.59207000 | -0.11925200 |
| C | 1.70797100 | -4.40439200 | 0.32404800 |
| H | 2.69624300 | -4.82996900 | 0.41294900 |
| C | -1.42887900 | 1.88356900 | 1.56115000 |
| H | -0.40463100 | 1.93126300 | 1.90500900 |
| C | -3.17272400 | -3.24765700 | -0.89234500 |
| H | -3.07126000 | -4.27978200 | -1.19156800 |
| C | -4.41056100 | -2.61998700 | -1.06689500 |
| C | 6.56950000 | -2.12101200 | 0.77154200 |
| C | 3.10078600 | 4.88181700 | -2.03964500 |
| C   | -2.30258100  | 2.93529200  | 1.79635300 |
|-----|--------------|--------------|------------|
| H   | -1.91862000  | 3.79825900  | 2.32793500 |
| C   | 0.61589300   | -5.20674700 | 0.04378000 |
| H   | 0.73171400   | -6.28193500 | -0.02988500|
| C   | -4.54845100  | -1.28266000 | -0.64937400|
| H   | -5.50928700  | -0.78689300 | -0.72906400|
| C   | -5.62443900  | -3.34782800 | -1.67799800|
| C   | -4.54497200  | 4.14572200  | 1.68252300 |
| C   | 2.61157200   | 5.08263900  | -3.49292300|
| H   | 2.99289400   | 4.29123900  | -4.14396500|
| H   | 2.96007800   | 6.04394000  | -3.88400300|
| H   | 1.52134200   | 5.07173100  | -3.55913200|
| C   | 2.55117500   | 6.02382900  | -1.15332100|
| H   | 1.45902900   | 6.04113900  | -1.14559400|
| H   | 2.89816200   | 6.99447300  | -1.52202300|
| H   | 2.89001800   | 5.91076600  | -0.11986800|
| C   | 4.63755500   | 4.97580500  | -2.03758500|
| H   | 5.04955700   | 4.86960200  | -1.03024700|
| H   | 4.94644400   | 5.95288200  | -2.41909200|
| H   | 5.09217700   | 4.21382500  | -2.67669600|
| C   | -6.78269700  | -3.37744000 | -0.65354200|
| H   | -6.48492800  | -3.90646600 | 0.25582000 |
| H   | -7.65285200  | -3.88907300 | -1.07663600|
| H   | -7.09741400  | -2.37189800 | -0.36551400|
| C   | -6.08581400  | -2.59911900 | -2.95018200|
| H   | -6.37361700  | -1.56818300 | -2.73186500|
| H   | -6.95141800  | -3.09959200 | -3.39548800|
| H   | -5.28716100  | -2.57079100 | -3.69637500|
| C   | -5.30434000  | -4.80124300 | -2.07301300|
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -4.50879100 | -4.85449500 | -2.82152700 |
| H    | -6.19368400 | -5.26692800 | -2.50572000 |
| H    | -5.00771100 | -5.40271700 | -1.20900900 |
| C    | 6.66377800  | -3.57200600 | 1.27807800  |
| H    | 6.13043500  | -3.70928600 | 2.22276500  |
| H    | 7.71148000  | -3.83151300 | 1.45149900  |
| H    | 6.26644800  | -4.28478300 | 0.54980600  |
| C    | 7.38232900  | -2.02113400 | -0.54034500 |
| H    | 6.95582100  | -2.66675300 | -1.31294300 |
| H    | 8.41852700  | -2.33039000 | -0.37123000 |
| H    | 7.40066200  | -1.00151000 | -0.93166500 |
| C    | -5.98193000 | 3.96318600  | 1.16073700  |
| H    | -6.57350300 | 4.85250100  | 1.39472100  |
| H    | -6.47723600 | 3.10637000  | 1.62575600  |
| H    | -6.00620000 | 3.82697400  | 0.07598900  |
| C    | 7.20697900  | -1.20206400 | 1.83991800  |
| H    | 7.21619400  | -0.15677300 | 1.52287900  |
| H    | 8.24219000  | -1.50113600 | 2.03218400  |
| H    | 6.65455100  | -1.25925400 | 2.78161900  |
| C    | -4.61651300 | 4.37017600  | 3.21102900  |
| H    | -3.62928100 | 4.55292600  | 3.64117700  |
| H    | -5.04173300 | 3.49649000  | 3.71236900  |
| H    | -5.24607700 | 5.23580000  | 3.44069400  |
| B    | 0.16092900  | -0.88327400 | 0.77807700  |
| C    | 0.48411800  | -0.82283400 | 2.32984400  |
| C    | 0.68862900  | -0.76501000 | 3.51856100  |
| H    | 0.86976700  | -0.70841900 | 4.56466200  |

**NBNN-3**

Atom | X | Y | Z |
-----|---|---|---|
...
|   |           |          |          |          |
|---|-----------|----------|----------|----------|
| N | 1.15958600| 0.09878400| -0.31248700|
| N | -1.28990000| -0.49593600| 0.30748000|
| N | 0.49611700| -2.26254100| -0.26129600|
| C | 0.57788800| -0.97431100| 2.11796600|
| C | -4.61556200| 4.82501600| 1.74173900|
| H | -3.67218900| 5.03358600| 2.25131500|
| H | -5.34252100| 5.57749000| 2.06373100|
| H | -4.44932400| 4.94968200| 0.66815300|
| C | 2.84310500| -1.67450000| -0.11166600|
| C | -2.09557900| 0.51313400| 0.85214400|
| C | 1.18140600| 1.40442200| -0.82379900|
| C | -0.45188800| -3.02518800| -0.89303700|
| C | 2.51623700| 1.77473700| -1.13949400|
| C | -3.39281000| 0.45312600| 0.28547400|
| C | 2.44310700| -0.35930800| -0.36906900|
| C | -2.08873900| -1.22608700| -0.53119400|
| C | 2.79863300| 3.04028100| -1.66191400|
| H | 3.82565400| 3.29405500| -1.89116800|
| C | 1.80591000| -2.69255300| -0.23033600|
| C | 4.22971800| -1.92615400| -0.11881100|
| H | 4.57515900| -2.92277200| 0.11589400|
| C | 1.77203900| 3.95561800| -1.88860000|
| C | -0.15310900| -4.34196200| -1.25496800|
| H | -0.92478100| -4.96069700| -1.68680200|
| C | 5.16744800| -0.94185200| -0.44726900|
| C | -4.09639500| 2.36167100| 1.60181800|
| C | 0.45507400| 3.55549200| -1.57372700|
| H | -0.36322900| 4.24462200| -1.74817100|
| C | -4.37646000| 1.37620700| 0.65836400|
|  |     |     |      |      |
|---|-----|-----|------|------|
| C | 1.18874700 | -1.39993000 | 4.90261300 |
| C | 0.35534300 | -2.26351100 | 4.20135300 |
| H | -0.07979700 | -3.11348600 | 4.72004000 |
| C | 1.24801900 | 5.51723100 | -3.79845000 |
| H | 1.58320400 | 4.77767500 | -4.53077100 |
| H | 1.41199300 | 6.51403600 | -4.22032300 |
| H | 0.17227500 | 5.38623200 | -3.66158000 |
| C | 1.52652200 | 6.42891100 | -1.46297100 |
| H | 0.45964100 | 6.32604900 | -1.25252700 |
| H | 1.69271700 | 7.43448700 | -1.86251900 |
| H | 2.06275900 | 6.34634600 | -0.51364000 |
| C | 3.51035000 | 5.62353900 | -2.74732100 |
| H | 4.11254800 | 5.55762200 | -1.83692600 |
| H | 3.63606100 | 6.63091800 | -3.15353200 |
| H | 3.91634700 | 4.91995600 | -3.47936900 |
| C | -6.33801200 | -3.50671400 | -2.16020700 |
| H | -6.07216500 | -4.21567900 | -1.37138900 |
| H | -7.10667200 | -3.96763800 | -2.78840000 |
| H | -6.78178000 | -2.62973100 | -1.68365200 |
| C | -5.51593200 | -2.14031500 | -4.11552900 |
| H | -5.92900000 | -1.21964700 | -3.69708200 |
| H | -6.27916700 | -2.58450000 | -4.76224400 |
| H | -4.65866900 | -1.86800900 | -4.73711600 |
| C | -4.59280900 | -4.42045100 | -3.69229100 |
| H | -3.73005400 | -4.22653800 | -4.33566800 |
| H | -5.38427500 | -4.83661000 | -4.32114300 |
| H | -4.31580600 | -5.18799600 | -2.96400300 |
| C | 7.02220500 | -2.64724000 | 0.01957500 |
| H | 6.65123700 | -2.85631000 | 1.02667700 |
|   |   |   |   |
|---|---|---|---|
| H | 8.10717000 | -2.78039900 | 0.03390900 |
| H | 6.61031500 | -3.39608700 | -0.66295400 |
| C | 7.26986400 | -1.00774100 | -1.84610800 |
| H | 6.80557300 | -1.69141100 | -2.56211300 |
| H | 8.34796800 | -1.19636700 | -1.84430000 |
| H | 7.11276100 | 0.01070600 | -2.20835400 |
| C | -6.49012000 | 3.22419500 | 1.34529200 |
| H | -7.19256800 | 3.98478100 | 1.69691800 |
| H | -6.93218400 | 2.24596400 | 1.55354300 |
| H | -6.39835800 | 3.33599200 | 0.26136100 |
| C | 7.36883600 | -0.23464000 | 0.55389000 |
| H | 7.20729600 | 0.80706700 | 0.26735900 |
| H | 8.44896600 | -0.41007000 | 0.57795900 |
| H | 6.97929900 | -0.36581000 | 1.56697900 |
| C | -5.37337300 | 3.27001800 | 3.57799400 |
| H | -4.45563400 | 3.43152400 | 4.14780400 |
| H | -5.74896500 | 2.27385400 | 3.82711000 |
| H | -6.10957300 | 4.00672800 | 3.91512500 |
| B | 0.19456300 | -0.81085400 | 0.51410200 |
| C | -0.92513800 | -3.09027200 | 2.27627000 |
| H | -1.69130700 | -2.64070500 | 1.64686900 |
| H | -0.41086200 | -3.85384100 | 1.68612400 |
| H | -1.43954500 | -3.61103200 | 3.08637400 |
| C | 1.96253400 | 1.22833800 | 2.31354300 |
| H | 2.86000900 | 1.05351100 | 1.71644400 |
| H | 1.26868900 | 1.79048700 | 1.69073100 |
| H | 2.25335800 | 1.87727600 | 3.14235800 |
| C | 1.54945300 | -1.64915400 | 6.34645700 |
| H | 0.72452200 | -2.11832100 | 6.88896000 |
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| N    | -1.29132100 | -0.19630300 | -0.01677800 |
| N    | 1.26243700  | -0.42745100 | -0.59324200 |
| N    | -0.30762800 | -2.46549000 | -0.40749400 |
| C    | 3.97370700  | 5.38522100  | -1.03144200 |
| H    | 2.97158400  | 5.60166100  | -1.40825500 |
| H    | 4.60087300  | 6.26041600  | -1.22890400 |
| H    | 3.90190100  | 5.25521400  | 0.05189000  |
| C    | -2.70856100 | -2.12090300 | -0.59541000 |
| C    | 1.92567600  | 0.75556400  | -0.94355700 |
| C    | -1.55578200 | 1.09306400  | 0.46860300  |
| C    | 0.75299000  | -3.25055500 | -0.03146000 |
| C    | -2.95693200 | 1.30061300  | 0.55068800  |
| C    | 3.27248100  | 0.69722000  | -0.51179400 |
| C    | -2.50856300 | -0.79485300 | -0.20467100 |
| C    | 2.19668200  | -1.25607400 | -0.03488700 |
| C    | -3.47027000 | 2.50795000  | 1.03406400  |
| H    | -4.54380000 | 2.63754700  | 1.08348300  |
| C    | -1.56100600 | -3.01996000 | -0.55230800 |
| C    | -4.04190800 | -2.52695900 | -0.79829600 |
| H    | -4.22954900 | -3.53593600 | -1.13547500 |
| C    | -2.61116700 | 3.52296000  | 1.45202200  |
| C    | 0.60494900  | -4.63920800 | 0.02322000  |
| H    | 1.45864600  | -5.25536900 | 0.26087400  |
| C    | -5.12953000 | -1.67559300 | -0.57806900 |
| C    | 3.67871900  | 2.91015800  | -1.41174200 |
C    -1.22226000  3.27906800  1.37872700
H    -0.53170900  4.04489600  1.71285800
C     4.13376100  1.77655700 -0.74125700
H     5.15843600  1.71171500 -0.39878400
C    -4.88167100 -0.37166800 -0.10119600
H    -5.71227400  0.29315900  0.10756000
C     2.02567100  2.60366400  0.28165400
C    -3.58198800  0.07526200  0.09259900
C    -0.68299300  2.09107800  0.90276900
H     0.38818600  1.95161300  0.88272900
C     3.45417900 -0.61211700  0.08091800
C    -1.71692900 -4.40788100 -0.49946200
H    -2.70248000 -4.83426600 -0.61260900
C     1.45383300  1.87439900 -1.63271300
H     0.43461200  1.91842500 -1.99315300
C     3.13343300 -3.26812600  0.84186100
H     3.02004300 -4.30018200  1.13781400
C     4.37063200 -2.64519900  1.04270800
C    -6.58538900 -2.12029600 -0.82306800
C    -3.11581400  4.87332200  1.99324000
C     2.33465600  2.92394900 -1.85144900
H     1.96289700  3.78898100 -2.38825900
C    -0.62509200 -5.21807500 -0.24435000
H    -0.73855700 -6.29570900 -0.21568900
C     4.52304400 -1.30834700  0.63040200
H     5.48368000 -0.81622900  0.73192500
C     5.56806100 -3.37883400  1.67918400
C     4.57859400  4.12687600 -1.69674300
C    -2.61760500  5.07114800  3.44387400
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 1.34120800 | 1.72954200 | 0.45179400 |
| C    | 1.38118300 | 2.93160100 | 1.16352400 |
| C    | 0.20934900 | 3.53568400 | 1.58079400 |
| C    | -1.00382200 | 2.97351000 | 1.22582500 |
| C    | -1.04054800 | 1.77172400 | 0.51758600 |
| N    | 0.13400200 | 1.11800900 | 0.20783500 |
| H    | 0.24075000 | 4.45944500 | 2.14677000 |
| H    | 2.33631800 | 3.38172600 | 1.38552500 |
| H    | -1.93021900 | 3.47239700 | 1.46613800 |
| C    | -2.29963700 | 1.25154000 | -0.01683900 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       |-2.24020400 | 0.23483600 | -0.97570200|
| C       |-3.56634200 | 1.81145400 | 0.20635800 |
| C       |-3.34202400 | -0.18167100| -1.76656900|
| C       |-4.68048900 | 1.38984700 | -0.52985500|
| H       |-3.70419300 | 2.58813900 | 0.94769700 |
| C       |-4.58273000 | 0.41906200 | -1.52701000|
| C       |-2.82068800 | -1.20111600| -2.63140000|
| C       |-1.49452600 | -1.35258300| -2.30975700|
| H       |-5.64187000 | 1.84683400 | -0.32604300|
| H       |-5.46062600 | 0.13316900 | -2.09603200|
| H       |-3.35358100 | -1.74800400| -3.39341900|
| H       |-0.77114700 | -2.02397800| -2.74271800|
| C       | 2.56606400  | 1.11835100 | -0.06414500|
| C       | 2.48676200  | -0.11483600| -0.71929400|
| C       | 3.84217500  | 1.69515200 | 0.01575400 |
| C       | 3.61310700  | -0.79804700| -1.25390900|
| C       | 4.96313600  | 1.05494200 | -0.52700500|
| H       | 3.98438600  | 2.65666600 | 0.49135700 |
| C       | 4.86652200  | -0.18425900| -1.15651400|
| C       | 3.10636200  | -2.04215700| -1.75003000|
| C       | 1.75915800  | -2.04867900| -1.49168100|
| H       | 5.92944000  | 1.53902000 | -0.44686100|
| H       | 5.75353100  | -0.66552500| -1.55371600|
| H       | 3.66520200  | -2.83419500| -2.22310800|
| H       | 1.04219900  | -2.83298600| -1.67442200|
| N       | 1.36559800  | -0.86628000| -0.88583800|
| N       | -1.12643300 | -0.47730200| -1.29945700|
| B       | 0.01922900  | -0.47838700| -0.27143200|
| C       | 0.38818800  | -2.21694100| 3.23153800 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.79810400 | -2.94012300 | 3.35028900 |
| C    | -1.73750100 | -2.88355100 | 2.32506700 |
| C    | -1.49481600 | -2.10337500 | 1.19410100 |
| C    | -0.31184400 | -1.36412400 | 1.04913700 |
| C    | 0.62303200  | -1.44698400 | 2.09604200 |
| H    | 1.13131500  | -2.25887900 | 4.02110200 |
| H    | -0.98458700 | -3.54418400 | 4.23175100 |
| H    | -2.66201300 | -3.44606100 | 2.40383100 |
| H    | -2.24376000 | -2.07835500 | 0.41031300 |
| H    | 1.56272000  | -0.90707600 | 2.02262000 |

**NBNN-Hf**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.00025800 | -5.17724600 | -1.03813100 |
| C    | -1.19249300 | -4.51898800 | -0.79500300 |
| C    | -1.19082400 | -3.16684200 | -0.44192900 |
| C    | 1.19567200  | -3.13126900 | -0.59661000 |
| C    | 1.19285300  | -4.48018600 | -0.96033900 |
| H    | -0.00268100 | -6.22529000 | -1.31478400 |
| H    | -2.13374300 | -5.03590300 | -0.90282100 |
| H    | 2.12761400  | -4.96665100 | -1.19383500 |
| C    | 2.44145700  | -2.36152300 | -0.53359900 |
| C    | 3.73151900  | -2.90014600 | -0.65028400 |
| C    | 2.36241800  | -0.97100000 | -0.42830500 |
| C    | 4.88975400  | -2.10228300 | -0.67399500 |
| H    | 3.84929900  | -3.97389100 | -0.71486000 |
| C    | 3.49133500  | -0.13036900 | -0.45911300 |
| C    | 4.75407000  | -0.70742800 | -0.58505400 |
| C    | 2.96353400  | 1.21143800  | -0.31615900 |
| C    | 1.54695000  | 1.08843600  | -0.23099600 |
|   | X      | Y      | Z      |
|---|--------|--------|--------|
| H | 5.63013400 | -0.07283400 | -0.60331900 |
| C | 3.58415400 | 2.45722000  | -0.24101100 |
| C | 0.71349200 | 2.22764300  | -0.13806200 |
| C | 2.80487700 | 3.59556500  | -0.05640800 |
| H | 4.66214500 | 2.51867000  | -0.30965700 |
| C | 1.40717100 | 3.44260600  | -0.01189500 |
| H | 0.82724900 | 4.34222300  | 0.12817300  |
| C | -2.44217700 | -2.42133700 | -0.28411800 |
| C | -3.72678600 | -2.98440500 | -0.32184900 |
| C | -2.38601000 | -1.02493800 | -0.24737900 |
| C | -4.89840100 | -2.20728500 | -0.36147600 |
| H | -3.82833400 | -4.06170500 | -0.32097100 |
| C | -3.52695500 | -0.20518400 | -0.34084300 |
| C | -4.78271600 | -0.80805100 | -0.39471500 |
| C | -3.01464300 | 1.14944600  | -0.35130800 |
| C | -1.59568200 | 1.05617200  | -0.24174600 |
| H | -5.66846600 | -0.18958600 | -0.45431700 |
| C | -3.65121800 | 2.38501600  | -0.45738600 |
| C | -0.78093700 | 2.21479700  | -0.22731000 |
| C | -2.88608400 | 3.54682100  | -0.46489900 |
| H | -4.72920700 | 2.42051700  | -0.54290700 |
| C | -1.48893300 | 3.42087000  | -0.35782000 |
| H | -0.91842400 | 4.33579300  | -0.40468000 |
| N | 1.21070300  | -0.26201400 | -0.28703500 |
| N | -1.24688300 | -0.29010700 | -0.17363500 |
| C | 3.41174200  | 5.00492600  | 0.08909900  |
| C | 2.89228800  | 5.92033100  | -1.04391700 |
| C | 3.01048900  | 5.60440000  | 1.45696500  |
| C | 4.94967300  | 4.98459500  | 0.01336700  |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | 3.16592500 | 5.51970100 | -2.02376500|
| H       | 1.80499100 | 6.02250000 | -1.01848700|
| H       | 3.32253200 | 6.92278300 | -0.95265300|
| H       | 3.37366400 | 4.97890700 |  2.27680100|
| H       | 3.43818000 | 6.60516000 |  1.57514000|
| H       | 1.92657100 | 5.69164300 |  1.56129100|
| H       | 5.33624900 | 6.00122400 |  0.12530200|
| H       | 5.38719700 | 4.37557300 |  0.80908900|
| H       | 5.30431000 | 4.60129400 | -0.94738500|
| C       | 6.26622500 | -2.78864200 | -0.79545100|
| C       | 6.48216800 | -3.73823300 |  0.40600500|
| C       | 6.33061000 | -3.60191300 | -2.10935100|
| C       | 7.42520600 | -1.77463600 | -0.81064400|
| H       | 6.44577700 | -3.18661200 |  1.34913100|
| H       | 5.72088700 | -4.52088700 |  0.44929200|
| H       | 7.45825600 | -4.22827600 |  0.33448900|
| H       | 6.18489000 | -2.95235500 | -2.97662500|
| H       | 7.30502600 | -4.09031700 | -2.20886400|
| H       | 5.56506600 | -4.38083200 | -2.14450300|
| H       | 8.37583200 | -2.30744000 | -0.89784300|
| H       | 7.35437400 | -1.08736700 | -1.65806400|
| H       | 7.46204100 | -1.18452500 |  0.10897600|
| C       | -6.26654900 | -2.92027000 | -0.38160700|
| C       | -6.36486200 | -3.83192300 | -1.62705600|
| C       | -6.42234400 | -3.77856300 |  0.89540400|
| C       | -7.44207200 | -1.92656800 | -0.42998000|
| H       | -6.26036000 | -3.24851800 | -2.54579900|
| H       | -5.58940400 | -4.60174200 | -1.63119900|
| H       | -7.33444300 | -4.33897800 | -1.65347100|
|   | x-coordinates  | y-coordinates  | z-coordinates  |
|---|----------------|----------------|----------------|
| H | -6.36263200    | -3.15611700    | 1.79208400     |
| H | -7.39114400    | -4.28792900    | 0.89709800     |
| H | -5.64527500    | -4.54304800    | 0.97005300     |
| H | -8.38630600    | -2.47748300    | -0.43703400    |
| H | -7.45266700    | -1.26612400    | 0.44122900     |
| H | -7.41607600    | -1.30756700    | -1.33093800    |
| C | -3.50571900    | 4.95146500     | -0.60118900    |
| C | -3.13276300    | 5.80878800     | 0.63061000     |
| C | -2.97301700    | 5.63530700     | -1.88184100    |
| C | -5.04196800    | 4.90074200     | -0.69445100    |
| H | -3.50407100    | 5.34945400     | 1.55073700     |
| H | -2.05160200    | 5.92770300     | 0.73154400     |
| H | -3.57110900    | 6.80837200     | 0.54715700     |
| H | -3.23143500    | 5.05204900     | -2.76978600    |
| H | -3.40822700    | 6.63388200     | -1.99066200    |
| H | -1.88648700    | 5.74659200     | -1.86251300    |
| H | -5.43817400    | 5.91592500     | -0.78336900    |
| H | -5.37771800    | 4.33831200     | -1.56996700    |
| H | -5.48805400    | 4.44918700     | 0.19595500     |
| N | 0.00545400     | -2.49708500    | -0.32122900    |
| B | 0.01145700     | -0.97630500    | 0.31997100     |
| C | 0.07339800     | -1.11626500    | 1.94332200     |
| C | -0.49063100    | -0.11931300    | 2.75788500     |
| C | 0.71477600     | -2.17678800    | 2.60484900     |
| C | -0.41204000    | -0.17025400    | 4.14793700     |
| H | -1.00818300    | 0.71745500     | 2.30239100     |
| C | 0.79785100     | -2.23893400    | 3.99498900     |
| H | 1.16281200     | -2.98347900    | 2.03486300     |
| C | 0.23491000     | -1.23240800    | 4.77463100     |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.04431000 | -5.30801900 | -0.51468200 |
| C    | -1.23292600 | -4.61994000 | -0.34701600 |
| C    | -1.22022800 | -3.24907700 | -0.07710700 |
| C    | 1.17215500  | -3.25644600 | -0.16727400 |
| C    | 1.15764700  | -4.62523900 | -0.44334600 |
| H    | -0.05538900 | -6.37123500 | -0.72529000 |
| H    | -2.17853700 | -5.13089900 | -0.44474400 |
| H    | 2.09052600  | -5.13954700 | -0.61715000 |
| C    | 2.42539900  | -2.49780900 | -0.12780900 |
| C    | 3.71073600  | -3.05811300 | -0.17391000 |
| C    | 2.36456800  | -1.10249000 | -0.12362900 |
| C    | 4.87968200  | -2.27759800 | -0.22467200 |
| H    | 3.81534700  | -4.13498700 | -0.15743800 |
| C    | 3.50406400  | -0.27897300 | -0.17474600 |
| C    | 4.76157400  | -0.87827600 | -0.23168200 |
| C    | 2.99225400  | 1.07598100  | -0.10922900 |
| C    | 1.57376000  | 0.97819800  | -0.03554800 |
| H    | 5.64675800  | -0.25713100 | -0.26571800 |
| C    | 3.63104500  | 2.31458000  | -0.08121200 |
| C    | 0.75505600  | 2.12957500  | 0.03289600  |
| C    | 2.86682300  | 3.46993300  | 0.05103500  |
| H    | 4.71027600  | 2.35761200  | -0.14361200 |
| C    | 1.46734500  | 3.33802900  | 0.10698700  |
| H    | 0.90257400  | 4.25105600  | 0.21671200  |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -2.46281300| -2.48042500| 0.03067100 |
| C       | -3.75485900| -3.02770500| 0.01503600 |
| C       | -2.38923300| -1.08499300| 0.02804900 |
| C       | -4.91662700| -2.23658800| -0.03071000|
| H       | -3.87033800| -4.10320000| 0.04230200 |
| C       | -3.52056700| -0.25168000| -0.05520600|
| C       | -4.78418000| -0.83929500| -0.08405100|
| C       | -2.99217000| 1.09740100 | -0.08344300|
| C       | -1.57382500| 0.98919300 | 0.00194600 |
| H       | -5.66299200| -0.21059300| -0.13856700|
| C       | -3.61596500| 2.33925500 | -0.18935100|
| C       | -0.74297300| 2.13507600 | -0.01560900|
| C       | -2.83649100| 3.49110100 | -0.21804700|
| H       | -4.69473100| 2.38754400 | -0.25636000|
| C       | -1.43922900| 3.34880000 | -0.13817800|
| H       | -0.86080400| 4.25766200 | -0.19925700|
| N       | 1.21988500 | -0.37004400| -0.05257600|
| N       | -1.24072500| -0.36120500| 0.06751200 |
| C       | 3.49242700 | 4.87624200 | 0.13447200 |
| C       | 2.98012900 | 5.74848600 | -1.03526000|
| C       | 3.10458100 | 5.53918000 | 1.47665000 |
| C       | 5.02963300 | 4.83268000 | 0.05406500 |
| H       | 3.24569400 | 5.30294500 | -1.99778500|
| H       | 1.89422700 | 5.86467300 | -1.01131100|
| H       | 3.42273900 | 6.74859900 | -0.98825700|
| H       | 3.46289400 | 4.94469100 | 2.32133800 |
| H       | 3.54591000 | 6.53828200 | 1.55024200 |
| H       | 2.02240600 | 5.64529300 | 1.58116500 |
| H       | 5.42957300 | 5.84825900 | 0.11854200 |
|   |         |         |         |         |
|---|---------|---------|---------|---------|
| H | 5.46299100 | 4.25474000 | 0.87487500 |
| H | 5.37507900 | 4.40172900 | -0.88968200 |
| C | 6.24912600 | -2.98741000 | -0.26487000 |
| C | 6.42329800 | -3.85495500 | 1.00352000 |
| C | 6.33298300 | -3.88948100 | -1.51830500 |
| C | 7.42201500 | -1.99101400 | -0.32095700 |
| H | 6.37217700 | -3.23955600 | 1.90560200 |
| H | 5.65049500 | -4.62341300 | 1.08168300 |
| H | 7.39397300 | -4.36052700 | 0.98960900 |
| H | 6.21729300 | -3.29906300 | -2.43119200 |
| H | 7.30232900 | -4.39597900 | -1.56020900 |
| H | 5.55726400 | -4.65903900 | -1.51901000 |
| H | 8.36690800 | -2.54008000 | -0.35020800 |
| H | 7.37947900 | -1.36144200 | -1.21388900 |
| H | 7.44650100 | -1.34088600 | 0.55770300 |
| C | -6.29373300 | -2.93258500 | -0.02934100 |
| C | -6.41225100 | -3.86158500 | -1.26010600 |
| C | -6.45119600 | -3.76957600 | 1.26155900 |
| C | -7.45723000 | -1.92515100 | -0.08434700 |
| H | -6.30796100 | -3.29323600 | -2.18824400 |
| H | -5.64559400 | -4.64017700 | -1.25847200 |
| H | -7.38784200 | -4.35757300 | -1.27167700 |
| H | -6.37655600 | -3.13453800 | 2.14826200 |
| H | -7.42664000 | -4.26582100 | 1.27807700 |
| H | -5.68402100 | -4.54343100 | 1.34201100 |
| H | -8.40820500 | -2.46436200 | -0.07765900 |
| H | -7.45416900 | -1.25234000 | 0.77743600 |
| H | -7.42932700 | -1.31927200 | -0.99409900 |
| C | -3.44131100 | 4.90276000 | -0.34894800 |

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C  -3.03373800  5.76046400  0.87156000
C  -2.92556000  5.57442500 -1.64291300
C  -4.97961600  4.87076500 -0.41196400
H  -3.39202800  5.30925800  1.80075800
H  -1.94944400  5.86653400  0.95072800
H  -3.46158200  6.76494800  0.79233100
H  -3.20828200  4.99045500 -2.52296400
H  -3.35073700  6.57773100 -1.74785300
H  -1.83759600  5.67264800 -1.64531000
H  -5.36487700  5.89043000 -0.49778500
H  -5.33947800  4.30878200 -1.27816100
H  -5.41358100  4.42868600  0.48909500
N  -0.01648500 -2.59068700  0.02712700
B   0.01275600 -1.03552200  0.56727000
C   0.08799500 -1.11544900  2.14728800
C   0.14500500 -1.16883800  3.35251200
H   0.19516700 -1.20351200  4.41396800
5. Photophysical Properties

Figure S5.1 Fluorescence spectra in PMMA(10 wt%) film

Figure S5.2 Phosphorescence spectra in PMMA(10 wt%) film at 77K
Figure S5.3 Fluorescence spectra of NBNN-1f in THF (10^{-5} M) with different H_2O fractions (vol%).

Figure S5.4 Fluorescence spectra of NBNN-2f in THF (10^{-5} M) with different H_2O fractions (vol%).
Figure S5.5 Phosphorescence decay curve of NBNN-1 in PMMA(10 wt%) film at 77K

Figure S5.6 Phosphorescence decay curve of NBNN-1f in PMMA(10 wt%) film at 77K
Figure S5.7 Phosphorescence decay curve of NBNN-2 in PMMA(10 wt%) film at 77K.

Figure S5.8 Phosphorescence decay curve of NBNN-2f in PMMA(10 wt%) film at 77K.
Figure S5.9 Phosphorescence decay curve of NBNN-3 in PMMA (10 wt%) film at 77K

Figure S5.10 Phosphorescence decay curve of NBNN-4 in PMMA (10 wt%) film at 77K
Figure S5.11 Phosphorescence decay curve of NBNN-5 in PMMA (10 wt%) film at 77K

Figure S5.12 Transient fluorescence decay curve of NBNN-1 in THF (10^{-5} M)
Figure S5.13 Transient fluorescence decay curve of NBNN-2 in THF ($10^{-5}$ M)

Figure S5.14 Transient fluorescence decay curve of NBNN-3 in THF ($10^{-5}$ M)
Figure S5.15 Transient fluorescence decay curves of NBNN-1f in THF (10^{-5} M) with different H_2O fractions (vol%).

Figure S5.16 UV/vis and emission spectra of 1a and 1b in THF (10^{-5} M).

Table S5.1 Photophysical data of NBNN-1f and NBNN-2f

|       | H_2O(%) | 10     | 30     | 50     | 70     | 90     |
|-------|---------|--------|--------|--------|--------|--------|
| NBNN-1f | λ_{em} (nm) | 657    | 659    | 656    | 641    | 638    |
|        | Φ_d (%)   | 0.6    | 0.7    | 0.5    | 1.2    | 2.0    |
|        | τ_{PF}(ns) | 1.28   | 1.19   | 1.29   | 1.87   | 1.88   |
| NBNN-2f | λ_{em} (nm) | 653    | 658    | 657    | 622    | 618    |
|        | Φ_d (%)   | 0.8    | 0.8    | 0.8    | 1.9    | 1.9    |
6. X-ray Crystallographic Analysis

Crystals of \textbf{NBNN-1} and \textbf{NBNN-1f} were grown by mixed solution of CH\textsubscript{2}Cl\textsubscript{2} and petroleum ether. The crystal data were collected on a Bruker SMART APEX-II diffractometer at 296.15 K. Crystal of \textbf{NBNN-3} was grown by mixed solution of ethyl acetate and petroleum ether. The crystal data were collected on a Bruker SMART APEX-II diffractometer at 180.00 K. The crystal data of \textbf{NBNN-1}, \textbf{NBNN-1f} and \textbf{NBNN-3} have been deposited at the Cambridge Crystallographic Data Center (CCDC). No. 2128933 (\textbf{NBNN-1}), 2128995 (\textbf{NBNN-1f}), and 2129008 (\textbf{NBNN-3}).
Table 6.1 Crystal data and structure refinement for NBNN-1.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | nbnn-1                                     |
| Empirical formula               | C51 H54 B N3                               |
| Formula weight                  | 719.78                                     |
| Temperature                     | 296.15 K                                   |
| Crystal system                  | monoclinic                                 |
| Space group                     | C2/c                                       |
| Unit cell dimensions            |                                           |
| a                               | 15.582(3) Å                               |
| α                               | 90°                                        |
| b                               | 33.295(6) Å                               |
| β                               | 90.452(3)°                                |
| c                               | 18.241(3) Å                               |
| γ                               | 90°                                        |
| Volume                          | 9463(3) Å³                                 |
| Z                               | 8                                          |
| ρcalc                           | 1.010 g/cm³                                |
| μ                               | 0.058 mm⁻¹                                 |
| F(000)                          | 3088.0                                     |
| Crystal size                    | 0.21 × 0.19 × 0.18 mm³                     |
| Radiation                       | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection   | 3.312° to 49.998°                          |
| Index ranges                    | -18 ≤ h ≤ 14, -37 ≤ k ≤ 39, -21 ≤ l ≤ 21 |
| Reflections collected           | 23691                                      |
| Independent reflections         | 8337 [ R_int = 0.1065, R_sigma = 0.1328 ]  |
| Data/restraints/parameters      | 8337/138/571                               |
| Goodness-of-fit on F²           | 0.906                                      |
| Final R indexes [ I >= 2σ (I) ] | R₁ = 0.0897, wR₂ = 0.2024                  |
| Final R indexes [ all data ]    | R₁ = 0.1804, wR₂ = 0.2425                  |
| Largest diff. peak and hole     | 0.56 and -0.60 eÅ⁻³                        |
### Table 6.2 Crystal data and structure refinement for NBNN-1f.

| Property                        | Value                        |
|--------------------------------|------------------------------|
| Identification code            | NBNN-1f                      |
| Empirical formula              | C56 H62 B N3                 |
| Formula weight                 | 787.89                       |
| Temperature                    | 296.15 K                     |
| Crystal system                 | triclinic                    |
| Space group                    | P-1                          |
| Unit cell dimensions           |                              |
| a                              | 11.0795(12) Å                |
| α                              | 83.621(2)°                   |
| b                              | 14.2380(16) Å                |
| β                              | 78.486(2)°                   |
| c                              | 15.3074(17) Å                |
| γ                              | 77.897(2)°                   |
| Volume                         | 2307.5(4) Å³                 |
| Z                              | 2                            |
| ρcalc                          | 1.134 g/cm³                  |
| μ                              | 0.065 mm⁻¹                   |
| F(000)                         | 848.0                        |
| Crystal size                   | 0.20 × 0.19 × 0.18 mm³       |
| Radiation                      | MoKα (λ = 0.71073)           |
| 2Θ range for data collection  | 2.722° to 55.32°             |
| Index ranges                   | -14 ≤ h ≤ 14, -14 ≤ k ≤ 18, -12 ≤ l ≤ 19 |
| Reflections collected          | 13990                        |
| Independent reflections        | 10109 [ R_int = 0.0257, R_sigma = 0.0686 ] |
| Data/restraints/parameters     | 10109/52/554                 |
| Goodness-of-fit on F²          | 1.020                        |
| Final R indexes [ I >= 2σ (I) ]| R₁ = 0.0949, wR₂ = 0.2608    |
| Final R indexes [ all data ]   | R₁ = 0.1631, wR₂ = 0.3179    |
| Largest diff. peak and hole    | 0.98 and -0.60 eÅ⁻³          |
| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Identification code            | nbnn-3                                     |
| Empirical formula              | C60 H72 B N3                               |
| Formula weight                 | 846.01                                     |
| Temperature                    | 180.00 K                                   |
| Crystal system                 | monoclinic                                 |
| Space group                    | I2/a                                       |
| Unit cell dimensions           |                                            |
| a = 21.747(2) Å                | α = 90°                                    |
| b = 19.582(2) Å                | β = 90.748(7)°                             |
| c = 23.834(3) Å                | γ = 90°                                    |
| Volume                         | 10148.8(16) Å³                            |
| Z                              | 8                                          |
| \( \rho_{\text{calc}} \)      | 1.107 g/cm³                                |
| \( \mu \)                      | 0.063 mm\(^{-1}\)                         |
| \( F(000) \)                   | 3664.0.0                                   |
| Crystal size                   | 0.28 × 0.20 × 0.14 mm\(^3\)               |
| Radiation                      | MoKα (\( \lambda = 0.71073 \))            |
| 2Θ range for data collection   | 4.4° to 55.272°                            |
| Index ranges                   | -28 ≤ h ≤ 24, -25 ≤ k ≤ 24, -30 ≤ l ≤ 31  |
| Reflections collected          | 57572                                      |
| Independent reflections        | 11749 [ \( R_{\text{int}} = 0.1938, R_{\text{sigma}} = 0.1567 \) ] |
| Data/restraints/parameters     | 11749/42/592                               |
| Goodness-of-fit on F\(^2\)     | 0.986                                      |
| Final R indexes [ 1 >= 2σ (I) ]| \( R_1 = 0.1053, wR_2 = 0.2829 \)          |
| Final R indexes [ all data ]   | \( R_1 = 0.2383, wR_2 = 0.3589 \)          |
| Largest diff. peak and hole    | 1.04 and -0.50 eÅ\(^{-3}\)                |
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