Expanding New Chemistry of Aza-Boracyclophanes with Unique Dipolar Structures, AIE and Redox-Active Open-Shell Characteristics

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Table of Contents

1. General Experimental Section

Materials and Methods: 2-Bromo-1,3,5-triisopropylbenzene (TipBr) and $B(OMe)_3$ were distilled under vacuum. Dimethyl(2,4,6-triisopropylphenyl)-boronate [$TipB(OMe)_2$] were prepared according to the previously published procedures.[1] TBAF (1 M in THF) was purchased from Sigma-Aldrich. Other reagents were purchased from Adamas. Ether was distilled from Na prior to use. All reactions and manipulations involving reactive borane or *n*-BuLi species were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box.

400 MHz ^1H, 700 MHz ^1H, 101 MHz ^{13}C, 176 MHz ^{13}C, and 225 MHz ^{11}B NMR spectra were recorded the Bruker spectrometers. ^{11}B NMR spectra were acquired with boron-free quartz NMR tubes and the spectra were referenced externally to $BF_3{\cdot}Et_2O$ ($\delta = 0$).

High resolution mass spectral data were obtained *via* ESI on an Agilent (Q-TOF 6520) analyzer. MALDI-MS measurements were performed on a Bruker AutoFlex MAX in linear (+) mode. Benzo[α]pyrene (10 mg/mL) and DHB (10 mg/mL) used as the matrix were mixed with the samples (10 mg/mL in toluene) in a 10 : 1 ratio, and then spotted on the wells of a target plate.

UV-Visible absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer. The fluorescence data (including temperature-dependent emission spectra, lifetime) was measured on an Edinburgh Instruments FLS980 spectrophotometer. Other fluorescence spectra were recorded on a Lengguang Tech F97 Pro spectrophotometer. Fluorescent quantum efficiencies were determined using a Hamamatsu Quantaurus-QY spectrometer (C11347-11).

Electrochemical measurements were conducted on an AUTOLAB-CV-75W analyzer with a scan rate of 100 mV/s. The electrochemical cell was a standard three-compartment cell composed of a glass carbon working electrode, a Pt auxiliary electrode, and a Pt wire reference electrode. All tests were performed using $[Bu_4N][PF_6]$ (0.1 M) as the supporting electrolyte. The voltammograms were obtained

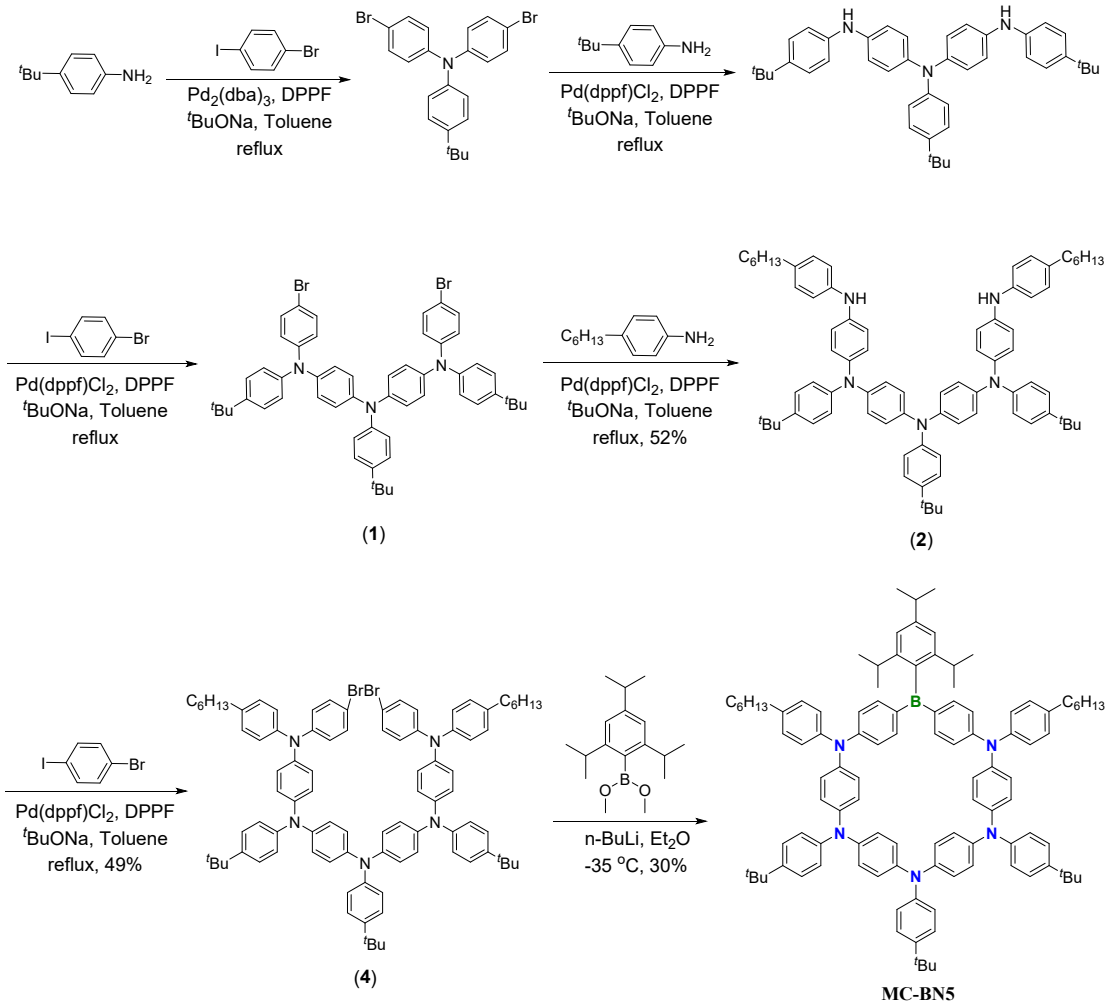
in anhydrous and nitrogen-saturated THF or CH_2Cl_2 solutions. The potentials are reported relative to the ferrocene/ferrocenium couple. The EPR measurement was performed on a JEOL JES FA200 X-band EPR spectrometer (9.05 GHz). Samples for EPR test were prepared under nitrogen atmosphere, the radical anion was obtained via oxidation of neutral compound with $AgSbF_6$ in CH_2Cl_2, and then the samples were sealed in capillary tube.

DFT calculations were performed with the Gaussian 09 program. Geometry optimizations and vertical excitations were calculated by means of hybrid density functional B3LYP with the basis set of 6-31G*. The input files and orbital representations were generated with Gaussview 5.0 (scaling radii of 75%, isovalue = 0.02). Excitation data were calculated using TD-DFT (B3LYP/6-311G*) and (TD-DFT) CAM-B3LYP/6-311G*. The resulting structures were confirmed to be stationary points through vibrational frequency analysis.

2. Synthetic Procedures

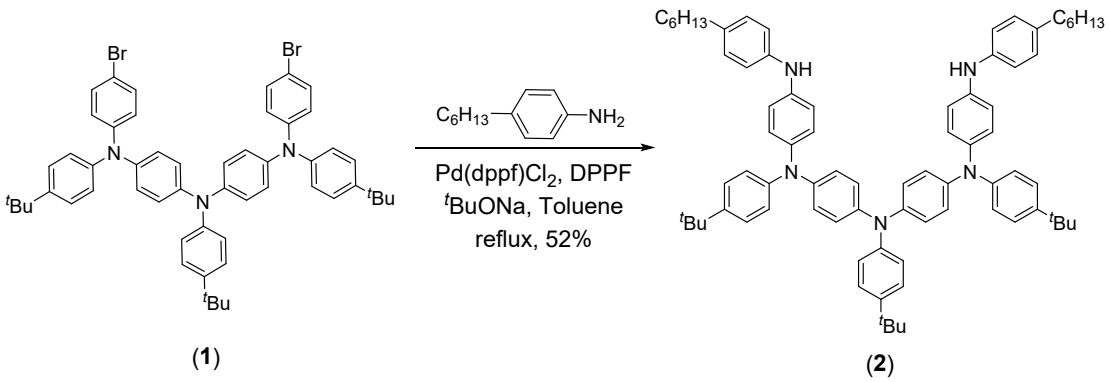
2.1 Synthesis

Synthesis of MC-BN5



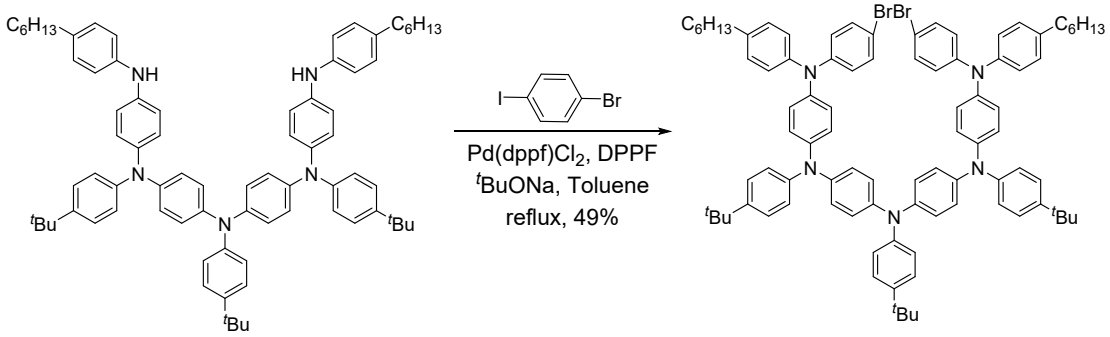
Compound **1** was prepared via a previously reported procedure.[2]

2.1.1 Synthesis of **2**



A mixture of **1** (1.0 g, 1.0 equiv), 4-hexylaniline (431.2 mg, 2.2 equiv), ^{t}BuONa (265.6 mg, 2.5equiv), Pd(dppf)Cl_2 (82 mg, 0.1 equiv) and DPPF (62 mg, 0.1 equiv) in toluene (20 mL) was refluxed at 120 °C overnight under N_2. After the mixture was cooled down, 100 mL of deionized water was added to the resulting solution and the mixture was extracted from ethyl acetate (EA). The organic phase was dried over Na_2SO_4 and was further purified by column chromatography on silica gel using EA/PE (1/25, v/v) as eluent to give **2** (626 mg, yield: 52%) as a brown solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.26–7.23 (m, 6H), 7.14 (s, 2H), 7.06–7.00 (m, 12H), 6.98–6.94 (m, 10H), 6.90–6.85 (m, 8H), 2.53 (t, *J* = 7.6 Hz, 4H), 1.59 (quint, *J* = 7.6 Hz, 4H), 1.36–1.28 (m, 39H), 0.89 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, acetone-d_6) δ 145.8, 144.5, 144.1, 143.3, 142.2, 141.7, 140.4, 140.1, 134.4, 129.0, 126.4, 125.94, 125.86, 124.9, 123.8, 122.6, 122.1, 118.0, 117.5, 35.0, 33.9, 33.8, 31.64, 31.61, 30.9, 22.4, 13.5 ppm. ESI-HRMS (m/z): calcd. for $C_{78}H_{91}N_5[M]^+$ 1097.7269, found 1097.7360.

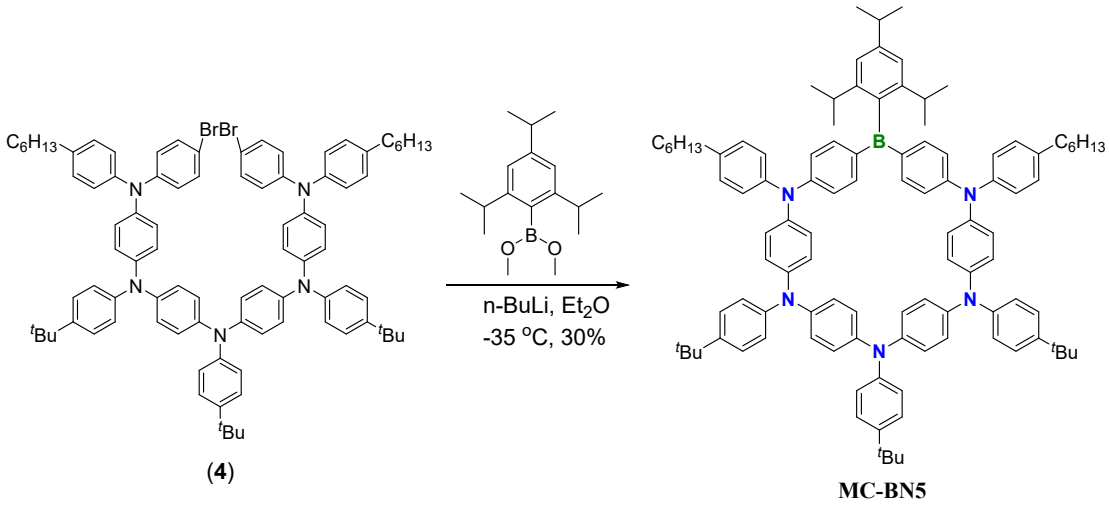
2.1.2 Synthesis of **4**



A mixture of **2** (1.24 g, 1.0 equiv), 1-bromo-4-iodobenzene (958.7 mg, 3.0 equiv), ^{t}BuONa (542.8 mg, 5.0 equiv), Pd(dppf)Cl_2 (83 mg, 0.1 equiv) and DPPF (63 mg, 0.1 equiv) in toluene (20 mL) was refluxed at 120 °C overnight under N_2. After the mixture was cooled down, 100 mL of deionized water was added to the resulting solution and the mixture was extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and was further purified by column chromatography on silica gel using CH_2Cl_2/PE (1/10, v/v) as eluent to give **4** (779 mg, yield: 49%) as a white solid. ^{1}H NMR (400 MHz, C_6D_6) δ 7.23–7.19 (m, 12H), 7.13–7.11 (m, 4H), 7.07–7.05 (m, 16H), 6.97 (d, *J* = 8.4 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 4H), 2.45 (t, *J* = 7.6 Hz, 4H), 1.53 (quint, *J* = 7.6 Hz, 4H), 1.26–1.22 (m, 39H), 0.87 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 147.4, 145.6, 145.5, 145.4, 145.3, 145.2, 143.9, 143.2, 142.8, 141.9, 137.9, 132.1, 129.4, 126.2, 125.6, 125.3, 124.9,

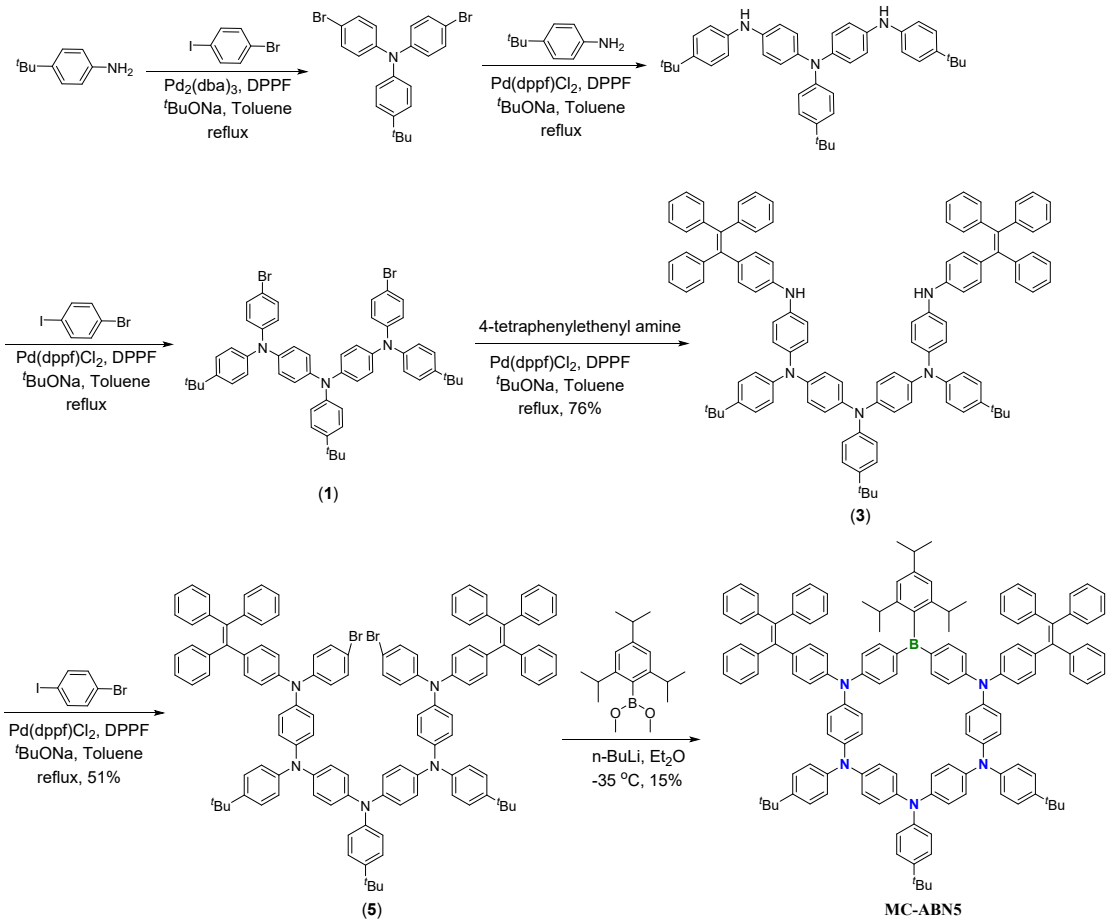
124.6, 124.4, 124.1, 123.9, 123.8, 113.9, 35.4, 34.0, 31.7, 31.6, 31.2, 29.1, 22.7, 14.0 ppm. MALDI-MS (pos.) (m/z): calcd. for $C_{90}H_{97}Br_2N_5$ $[M]^+$ 1407.6102, found 1407.6115.

2.1.3 Synthesis of **MC-BN5**



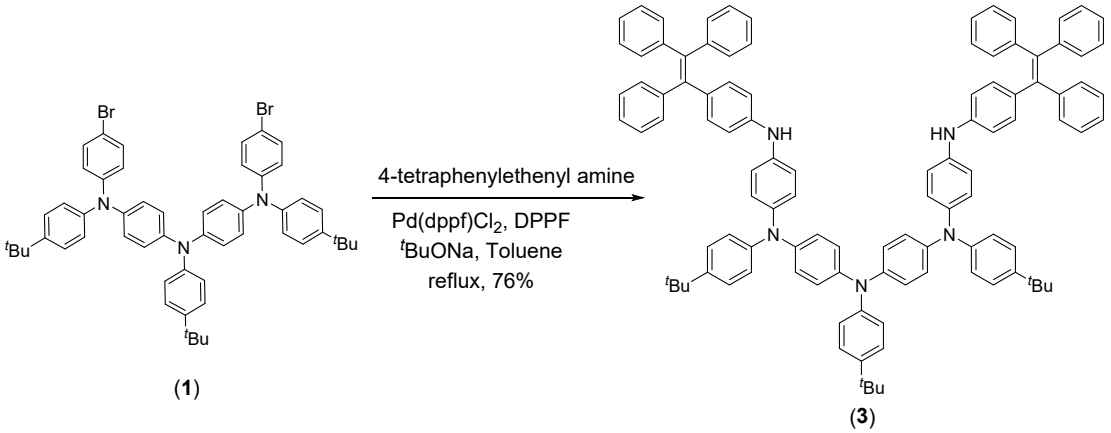
To a solution of **4** (300 mg,1.0 equiv) in anhydrous Et_2O (30 mL) was added *n*-BuLi (1.6 M solution in hexane, 0.3 mL, 2.2 equiv) dropwise at -35 °C. The mixture was stirred for 30 min and then allowed to warm up to 0 °C. $TipB(OMe)_2$ (88 mg, 1.5 equiv) was added via a syringe. The mixture was stirred at 0 °C for 30 min, then stirred at ambient temperature for 30 min and refluxed overnight under N_2. After the mixture was cooled down, the solid was removed by filtration through a fritted glass disk. The crude product was further purified by column chromatography on silica gel using toluene/hexane mixture (1/10, v/v) as the eluent. A solution of the purified product in EA was washed with EA and *n*-hexane to give a green solid. (94.0 mg, 30% yield). ^{1}H NMR (700 MHz, C_6D_6) δ 7.76 (d, J = 8.4 Hz, 4H), 7.27 (s, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.18–7.17 (m, 6H), 7.14–7.11 (m, 16H), 7.09 (d, J = 9.1 Hz, 4H), 7.01–6.98 (m, 12H), 2.97 (hept, J = 7.0 Hz, 1H), 2.91 (hept, J = 7.0 Hz, 2H), 2.47 (t, J = 7.7 Hz, 4H), 1.55 (quint, J = 7.0 Hz, 4H), 1.38 (d, J = 7.0 Hz, 6H), 1.27–1.19 (m, 51H), 0.87 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (176 MHz, C_6D_6) δ 151.6, 149.6, 148.5, 146.1, 146.0, 145.8, 145.1, 144.8, 144.6, 143.7, 143.1, 142.5, 142.2 (C-B), 139.8, 139.0, 136.1 (C-B), 129.8, 126.6, 126.4, 126.2, 126.1, 125.8, 124.9, 124.8, 123.1, 120.3, 119.0, 35.8, 35.7, 35.0, 34.3, 34.2, 32.1, 32.0, 31.6, 31.5, 29.4, 24.7, 23.0, 14.3 ppm. ^{11}B NMR (225 MHz, C_6D_6) δ = 31 ppm. MALDI-MS (pos.) m/z: calcd. for $C_{105}H_{120}BN_5$ $[M]^+$ 1462.9673, found 1462.9664.

Synthesis of MC-ABN5



Compound **1** was prepared via a previously reported procedure.[2]

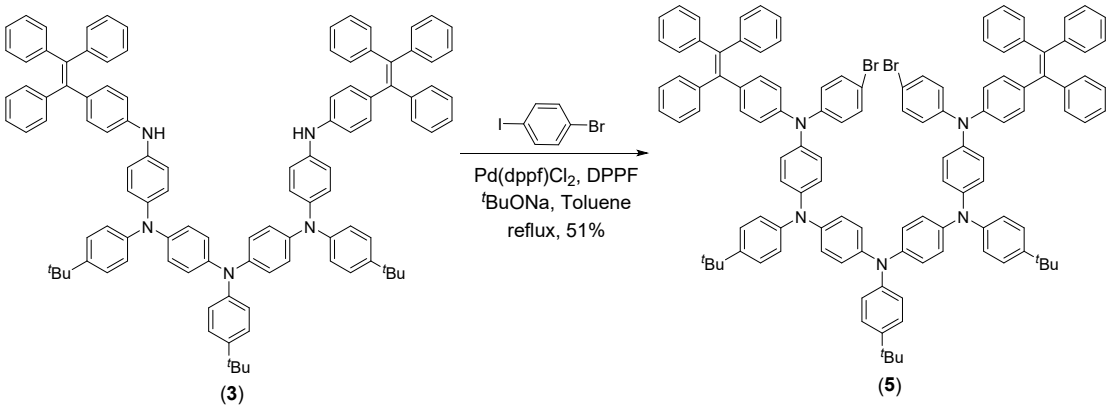
2.2.1 Synthesis of **3**



A mixture of **1** (473.5 mg, 1.0 equiv), 4-tetraphenylethenyl amine (364 mg, 2.0 equiv), ^{t}BuONa (151 mg, 3.0 equiv), $Pd(dppf)Cl_2$ (53 mg, 0.1 equiv) and DPPF (40 mg, 0.1 equiv) in toluene (10 mL) was refluxed at 120 °C overnight under N_2. After the mixture was cooled down, 100 mL of deionized water was added to the resulting solution and the mixture was extracted with CH_2Cl_2. The

organic phase was dried over Na_2SO_4 and was further purified by column chromatography on silica gel using EA/PE (1/10, v/v) as eluent to give **3** (572.6 mg, yield: 76%) as a green solid. ^{1}H NMR (700 MHz, C_6D_6) δ 7.25–1.24 (m, 10H), 7.19–7.16 (m, 14H), 7.11 (d, *J* = 9.1 Hz, 2H), 7.07–7.04 (m, 12H), 7.01–6.97 (m, 10H), 6.95–6.92 (m, 8H), 6.89 (t, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 4H), 6.57 (d, *J* = 7.7 Hz, 4H), 4.85 (s, 2H), 1.23 (s, 18H), 1.22 (s, 9H). ^{13}C NMR (176 MHz, C_6D_6) δ 145.9, 145.8, 144.8, 144.63, 144.55, 144.4, 143.2, 142.8, 142.5, 142.0, 141.1, 139.9, 137.6, 135.5, 132.6, 131.7, 131.61, 131.59, 126.5, 126.32, 126.25, 126.2, 126.1, 125.6, 125.0, 124.6, 123.4, 123.1, 120.0, 115.5, 33.9, 31.2, 31.2. ESI-HRMS (m/z): calcd. for $C_{106}H_{95}N_5$ $[M]^+$ 1438.7580, found 1438.7621.

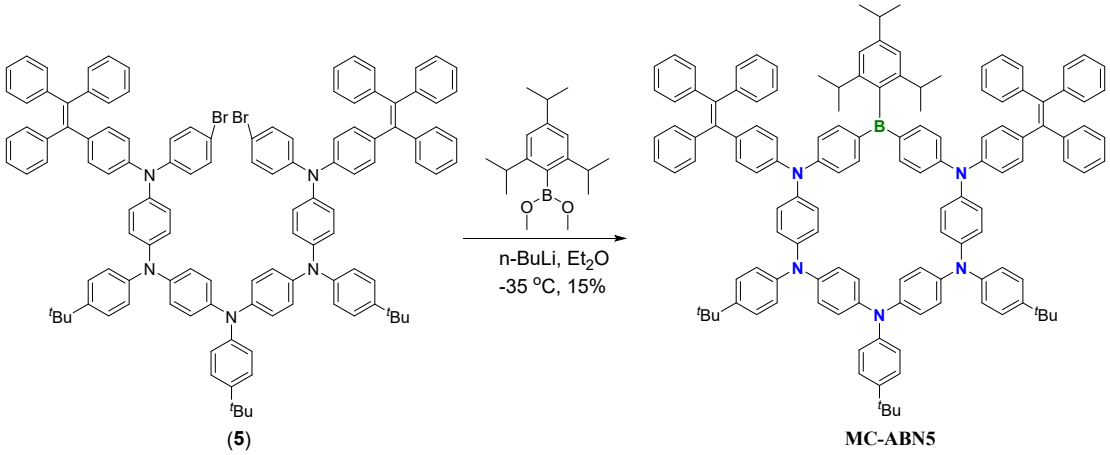
2.2.2 Synthesis of **5**



(**3**) (**5**)

A mixture of **3** (572.6 mg, 1.0 equiv), 1-bromo-4-iodobenzene (563 mg, 5.0 equiv), ^{t}BuONa (191.3 mg, 5.0 equiv), Pd(dppf)Cl_2 (29 mg, 0.1 equiv) and DPPF (22 mg, 0.1 equiv) in toluene (10 mL) was refluxed at 120 °C overnight under N_2. After the mixture was cooled down, 100 mL of deionized water was added to the resulting solution and the mixture was extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and was further purified by column chromatography on silica gel using CH_2Cl_2/PE (1/10, v/v) as eluent to give **5** (355 mg, yield: 51%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ 7.23–7.19 (m, 20H), 7.13–6.89 (m, 42H), 6.85 (d, *J* = 8.4 Hz, 4H), 6.79–6.76 (m, 8H), 1.22 (s, 27H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 146.8, 145.9, 145.5, 145.41, 145.35, 144.3, 143.9, 143.8, 143.3, 142.7, 141.2, 140.83, 140.79, 138.1, 132.5, 132.1, 131.5, 127.8, 127.6, 126.54, 126.48, 126.4, 126.3, 126.2, 126.1, 125.3, 125.1, 124.9, 124.2, 124.0, 123.8, 122.2, 114.7, 34.0, 31.2 ppm. MALDI-MS (pos.) m/z: calcd. for $C_{118}H_{101}Br_2N_5$ $[M]^+$ 1748.6441, found 1748.6464.

2.2.3 Synthesis of **MC-ABN5**



To a solution of **5** (167 mg, 1.0 equiv) in anhydrous Et_2O (25 mL) was added *n*-BuLi (1.6 M solution in hexane, 0.13 mL, 2.2 equiv) dropwise at -35 °C. The mixture was stirred for 30 min and then allowed to warm up to 0 °C. $TipB(OMe)_2$ (40 mg, 1.5 equiv) was added via a syringe. The mixture was stirred at 0 °C for 30 min, then stirred at ambient temperature for 30 min and refluxed overnight under N_2. After the mixture was cooled down, the solid was removed by filtration through a fritted glass disk. The crude product was further purified by column chromatography on silica gel using toluene/hexane mixture (1/10, v/v) as the eluent. A solution of the purified product in EA was washed with EA and *n*-hexane to give a green solid. (26.0 mg, 15% yield). ^{1}H NMR (700 MHz, C_6D_6) δ 7.73 (d, J = 8.4 Hz, 4H), 7.27 (s, 2H), 7.25–7.23 (m, 6H), 7.18 (d, J = 8.4 Hz, 4H), 7.13–7.09 (m, 22H), 7.03–6.88 (m, 38H), 2.96 (hept, J = 7.0 Hz, 1H), 2.87 (hept, J = 7.0 Hz, 2H), 1.36 (d, J = 7.0 Hz, 6H), 1.23–1.21 (m, 39H) ppm. ^{13}C NMR (176 MHz, C_6D_6) δ 150.9, 149.6, 148.7, 146.1, 146.0, 145.9, 145.34, 145.29, 144.9, 144.5, 144.2, 144.1, 143.8, 143.0, 142.1, 142.0 (C-B), 141.5, 141.2, 139.64, 139.56, 136.6 (C-B), 132.8, 131.86, 131.85, 131.8, 127.0, 126.9, 126.8, 126.7, 126.4, 126.3, 126.0, 125.1, 124.8, 124.5, 122.9, 120.4, 119.6, 35,8, 35.0, 34.34, 34.26, 31.6, 31.5, 24.7, 24.6 ppm. ^{11}B NMR (225 MHz, C_6D_6) δ = 56 ppm. MALDI-MS (pos.) m/z: calcd. for $C_{133}H_{124}BN_5$ $[M]^+$ 1802.9988, found 1802.9986.

3. Characterization by NMR and HRMS Spectroscopy

3.1 NMR Spectra of 2

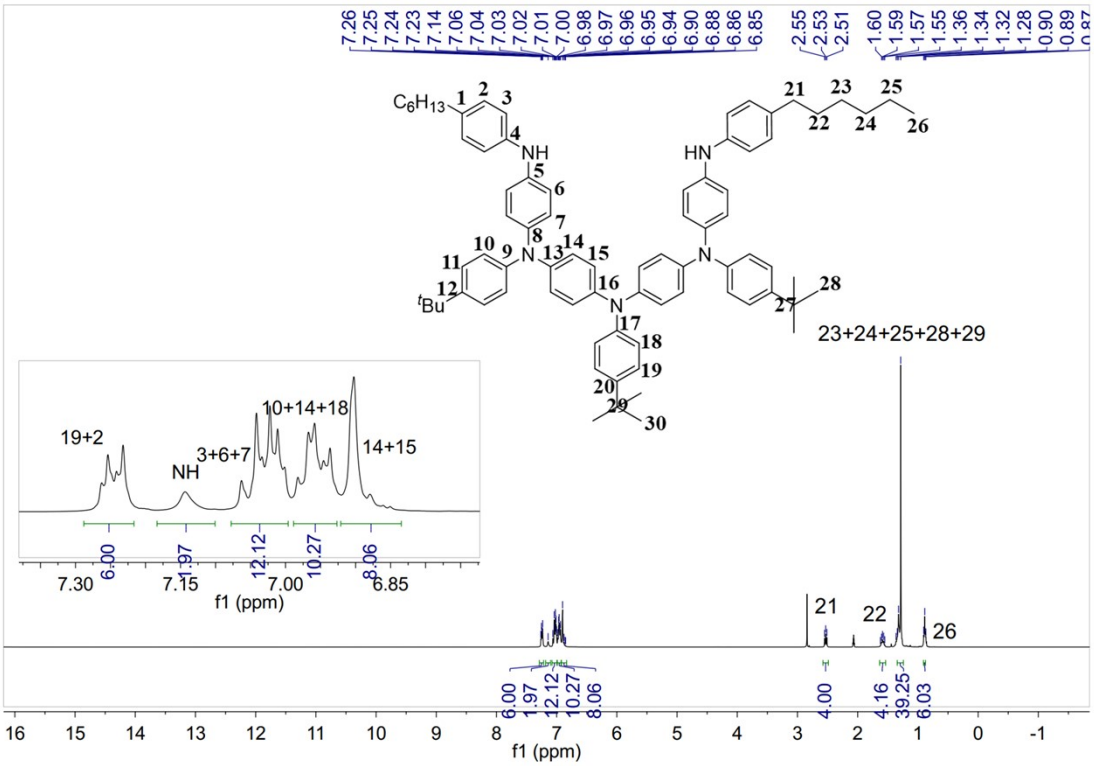
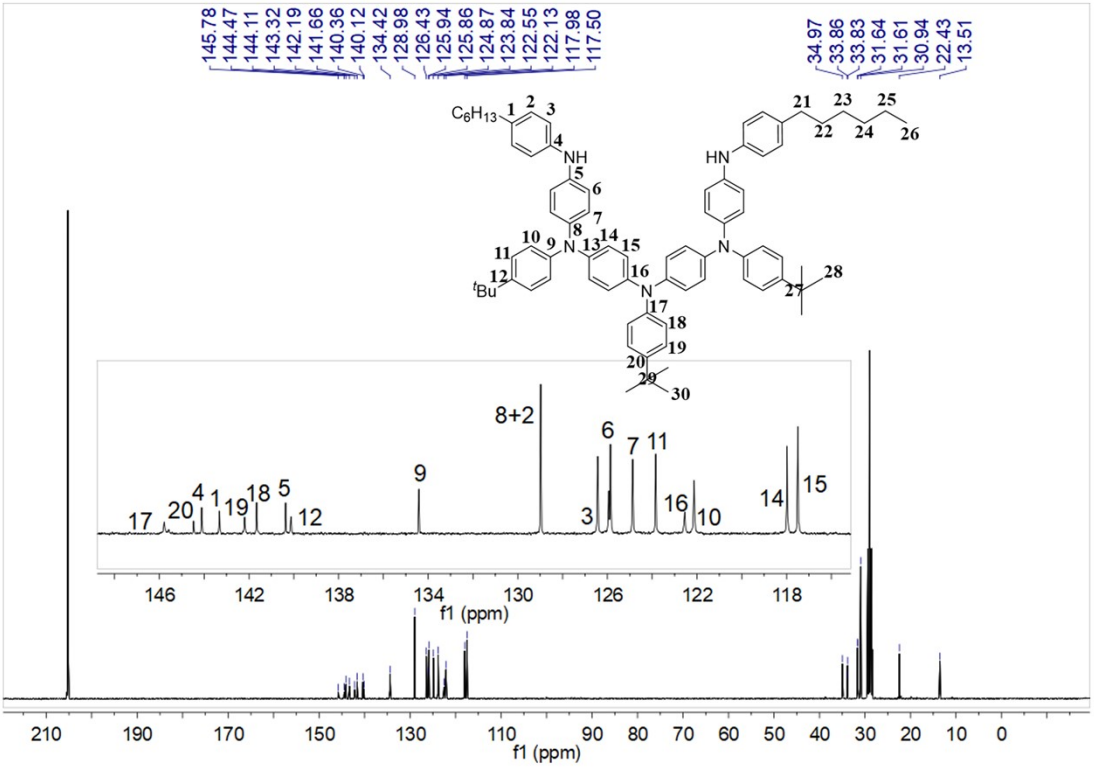


Figure S1. ^{1}H NMR (400 MHz, acetone-d_6) spectrum of **2**.



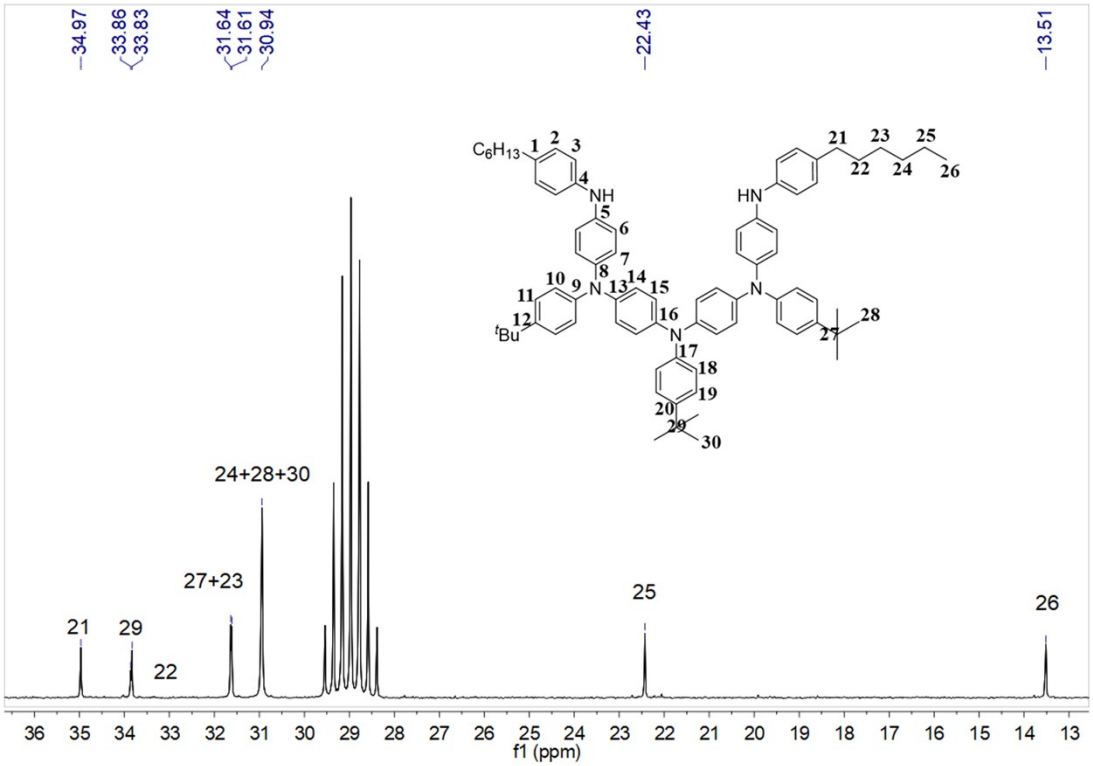


Figure S2. ^{13}C NMR (101 MHz, acetone-d_6) spectrum of **2**.

3.2 NMR Spectra of 4

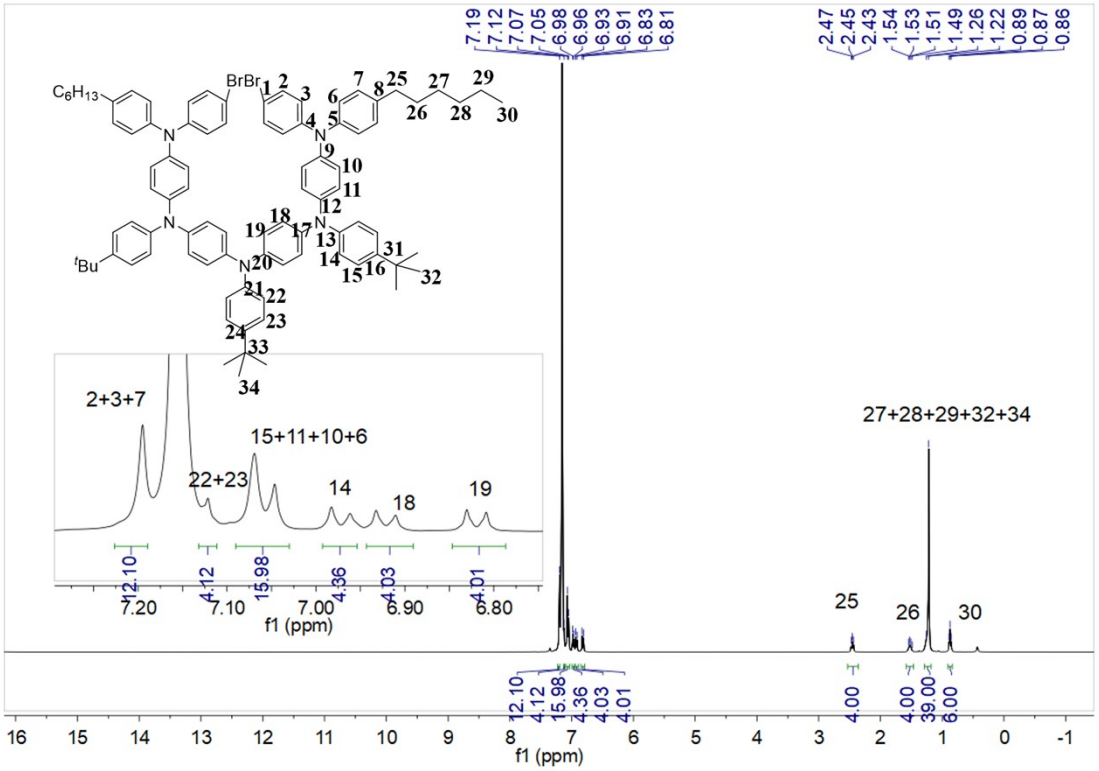


Figure S3. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **4**.

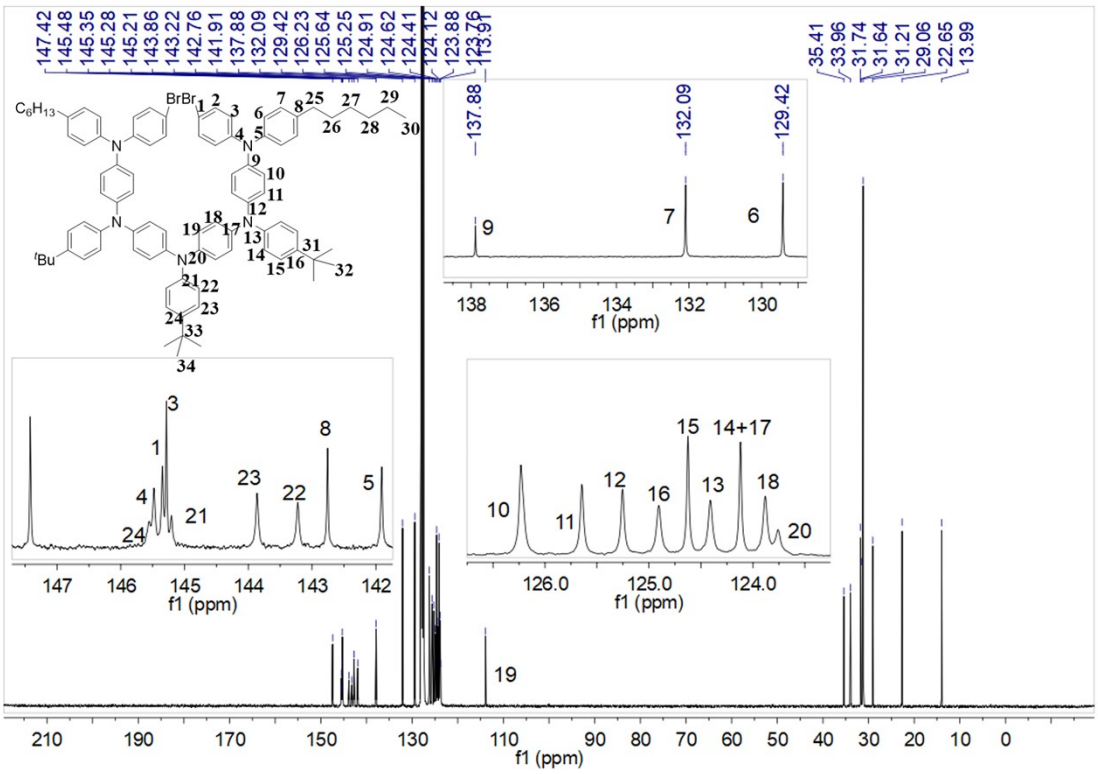


Figure S4. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **4**.

3.3 NMR Spectra of MC-BN5

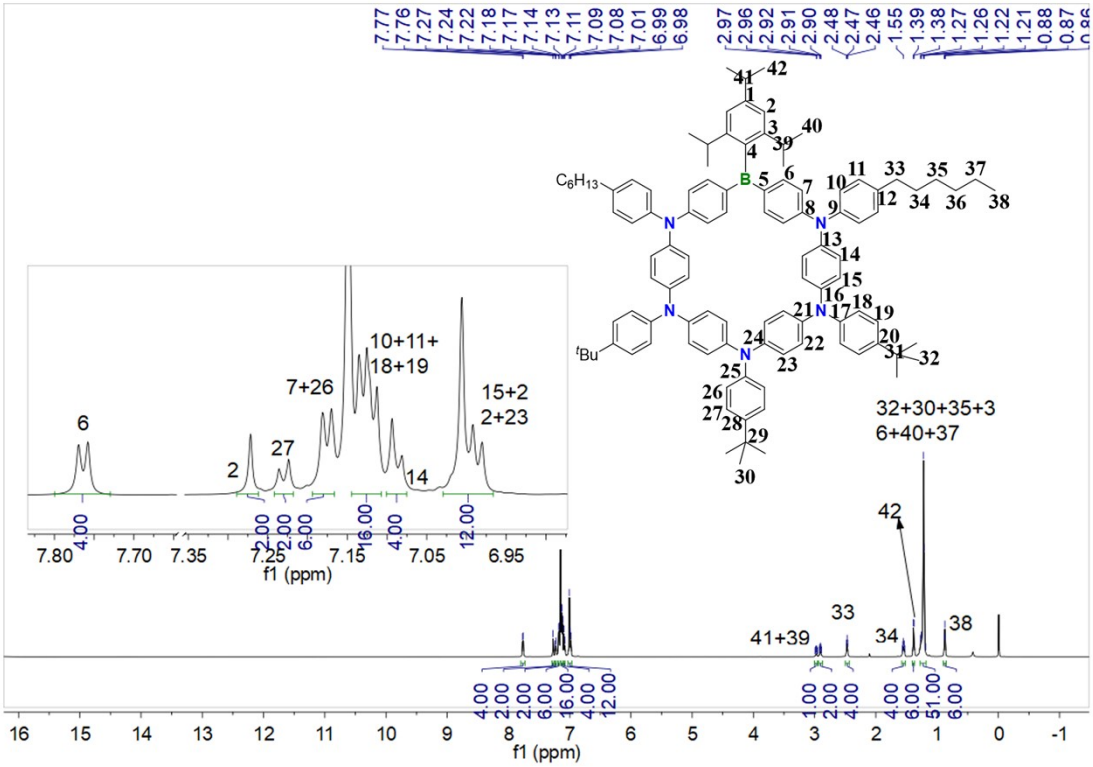


Figure S5. ^{1}H NMR (700 MHz, C_6D_6) spectrum of **MC-BN5**.

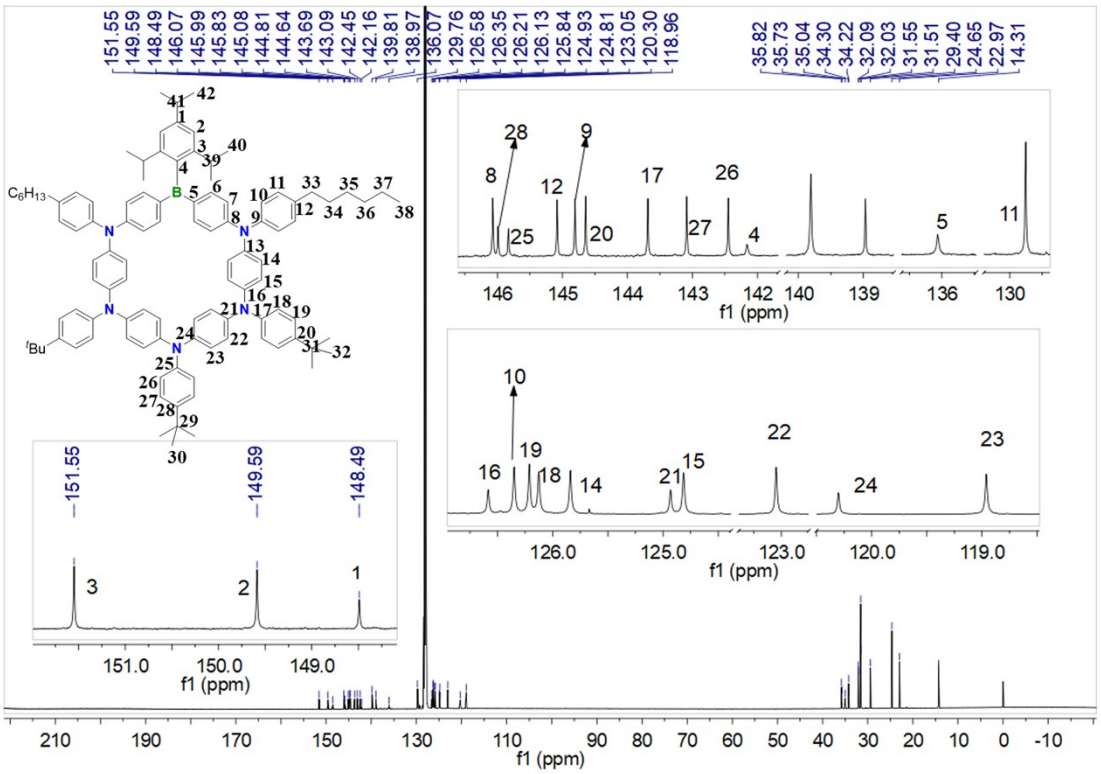


Figure S6. ^{13}C NMR (176 MHz, C_6D_6) spectrum of **MC-BN5**.

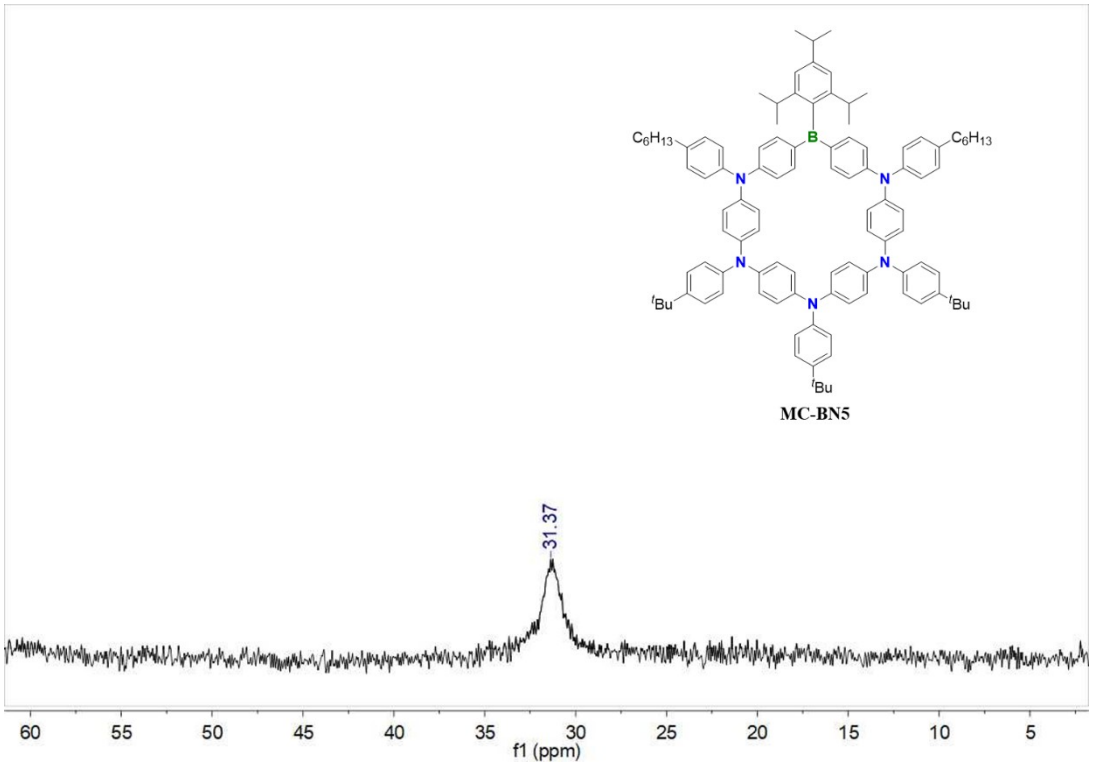


Figure S7. ^{11}B NMR (225 MHz, C_6D_6) spectrum of **MC-BN5**.

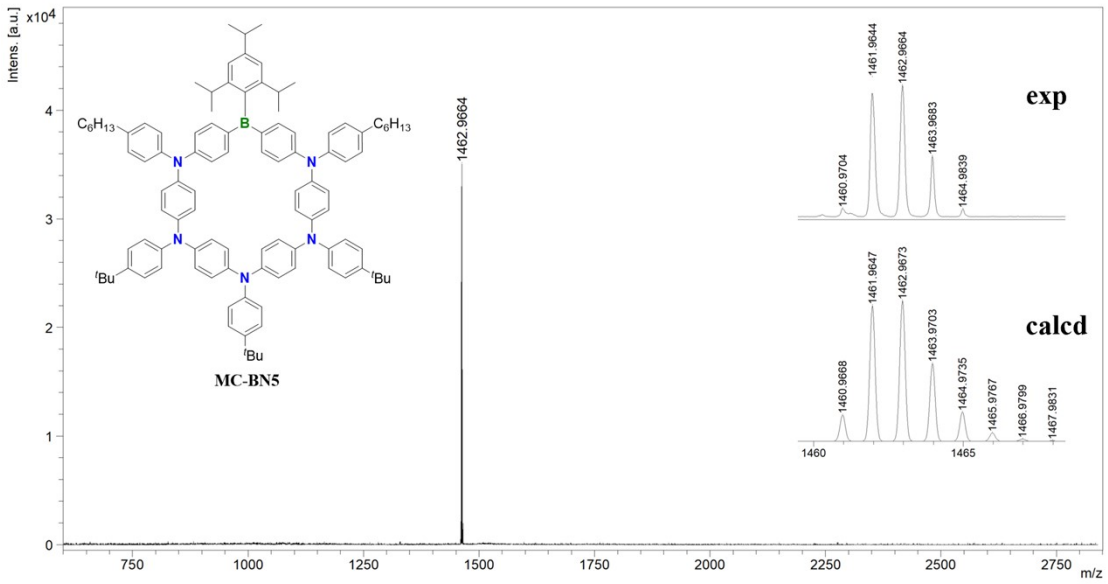


Figure S8. MALDI-TOF spectra (positive) of **MC-BN5**. Inset: experimental and simulated isotopic patterns.

3.4 NMR Spectra of 3

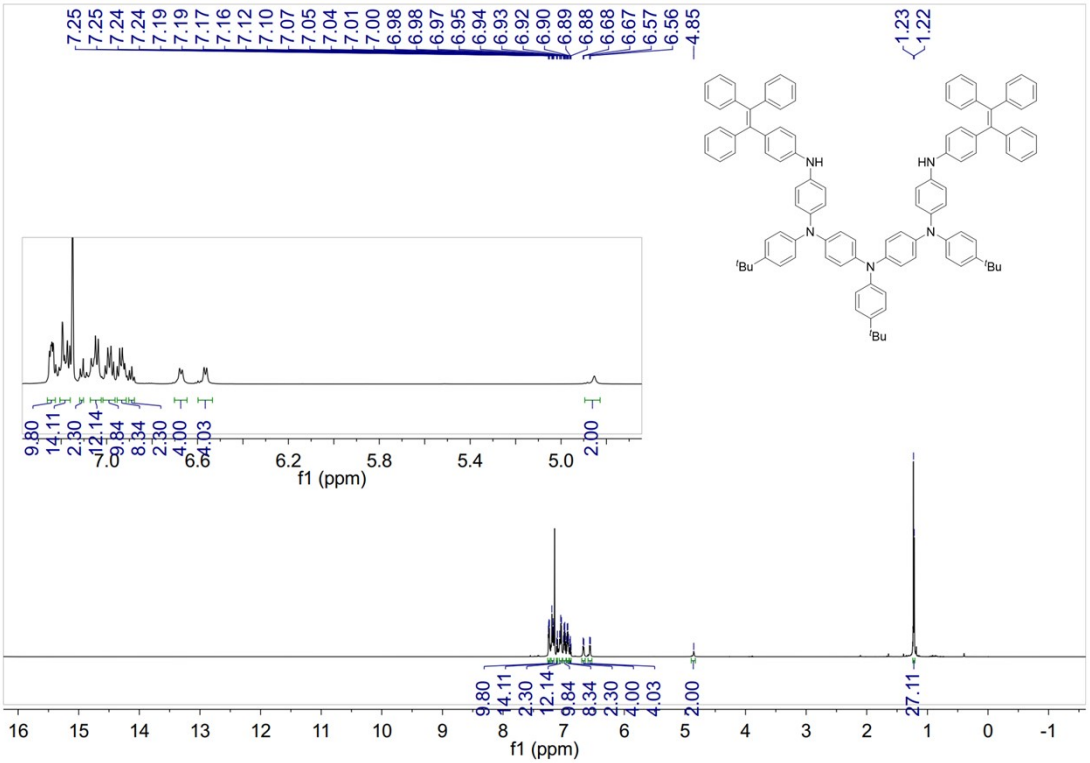


Figure S9. ^{1}H NMR (700 MHz, C_6D_6) spectrum of **3**.

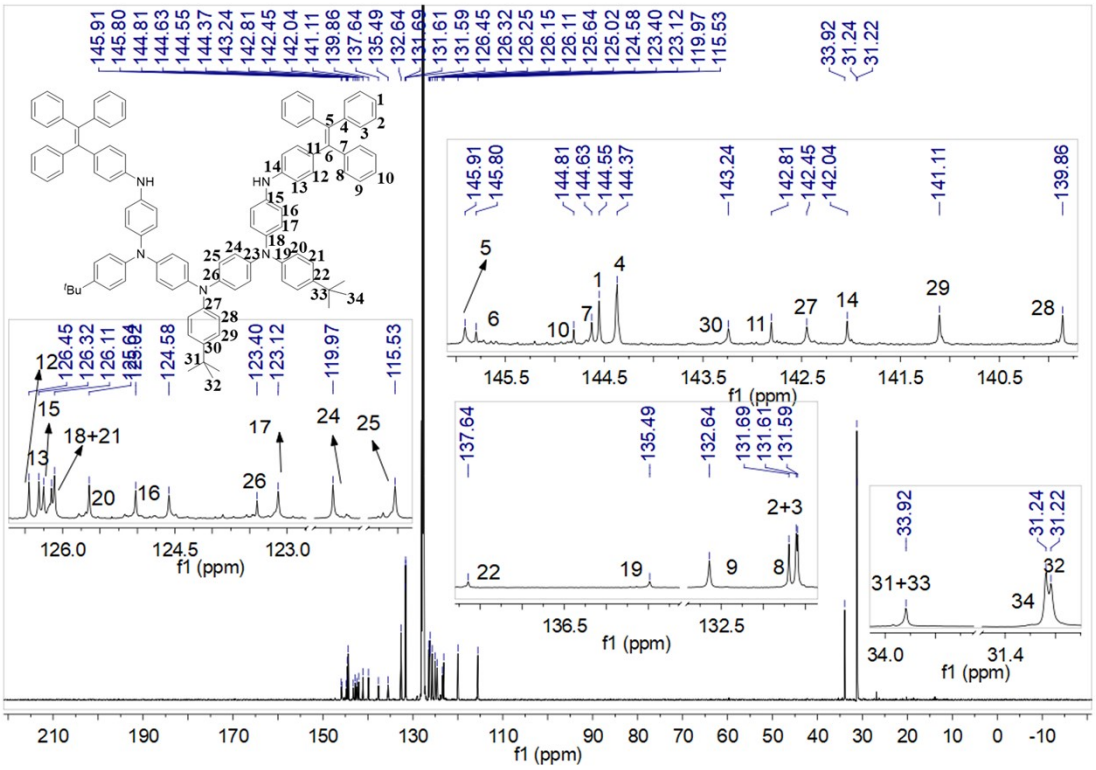


Figure S10. ^{13}C NMR (176 MHz, C_6D_6) spectrum of **3**.

3.5 NMR Spectra of 5

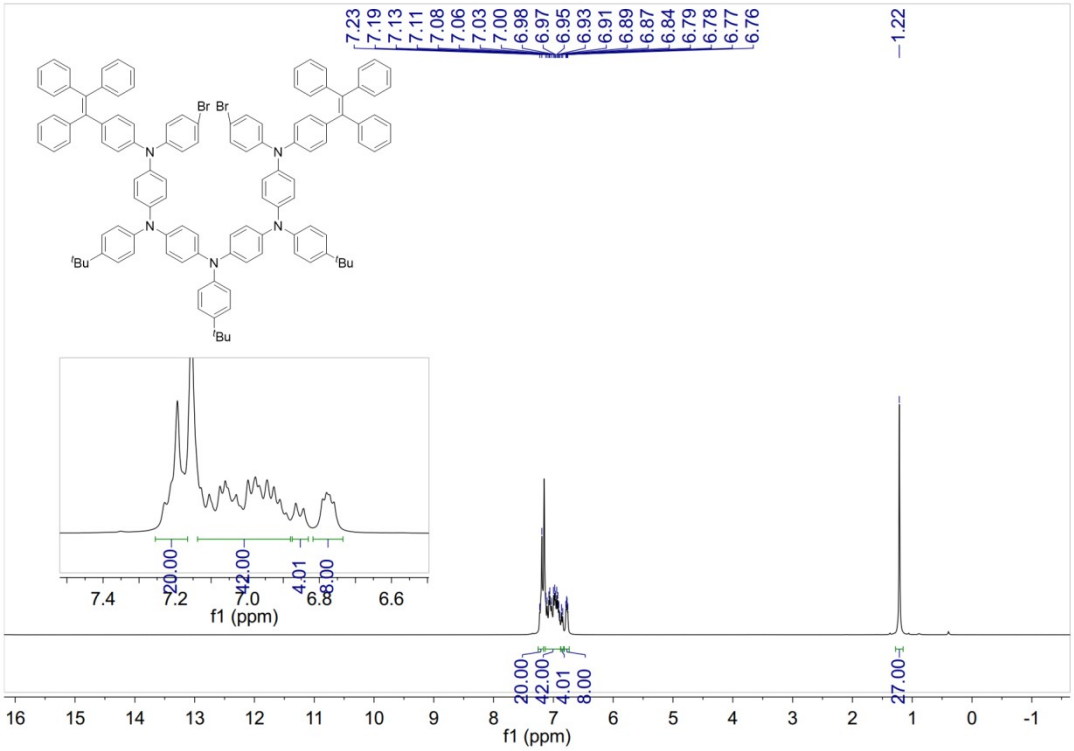


Figure S11. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **5**.

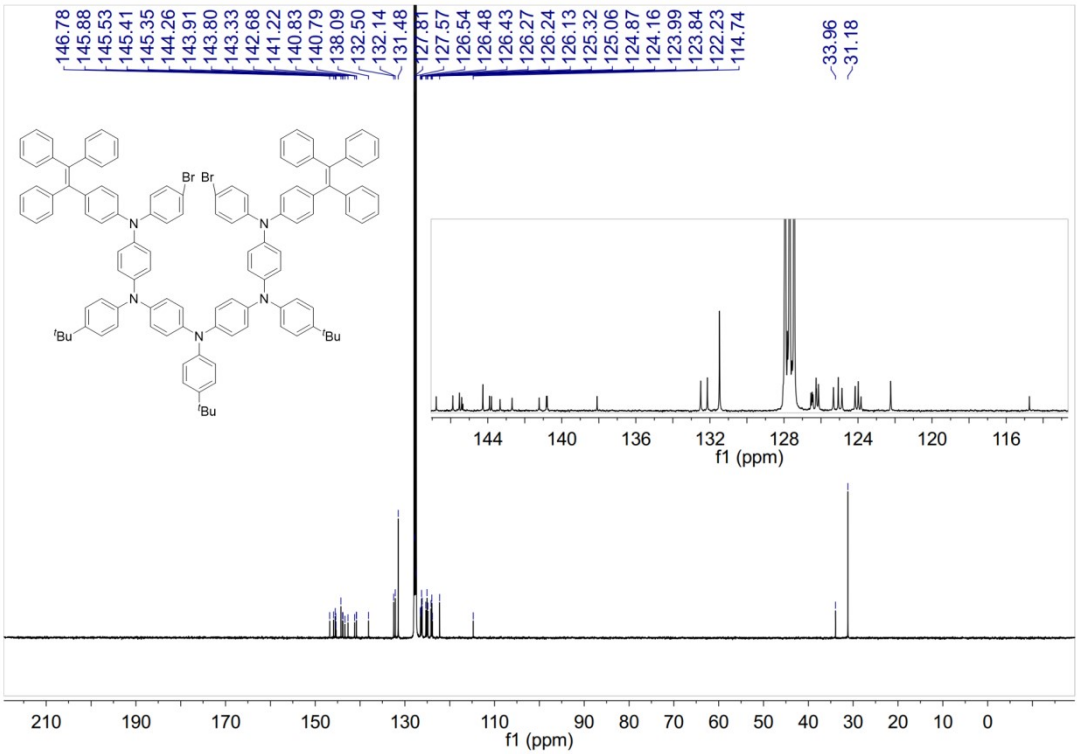


Figure S12. ^{13}C NMR (101 MHz, C_6D_6) spectrum of **5**.

3.6 NMR Spectra of MC-ABN5

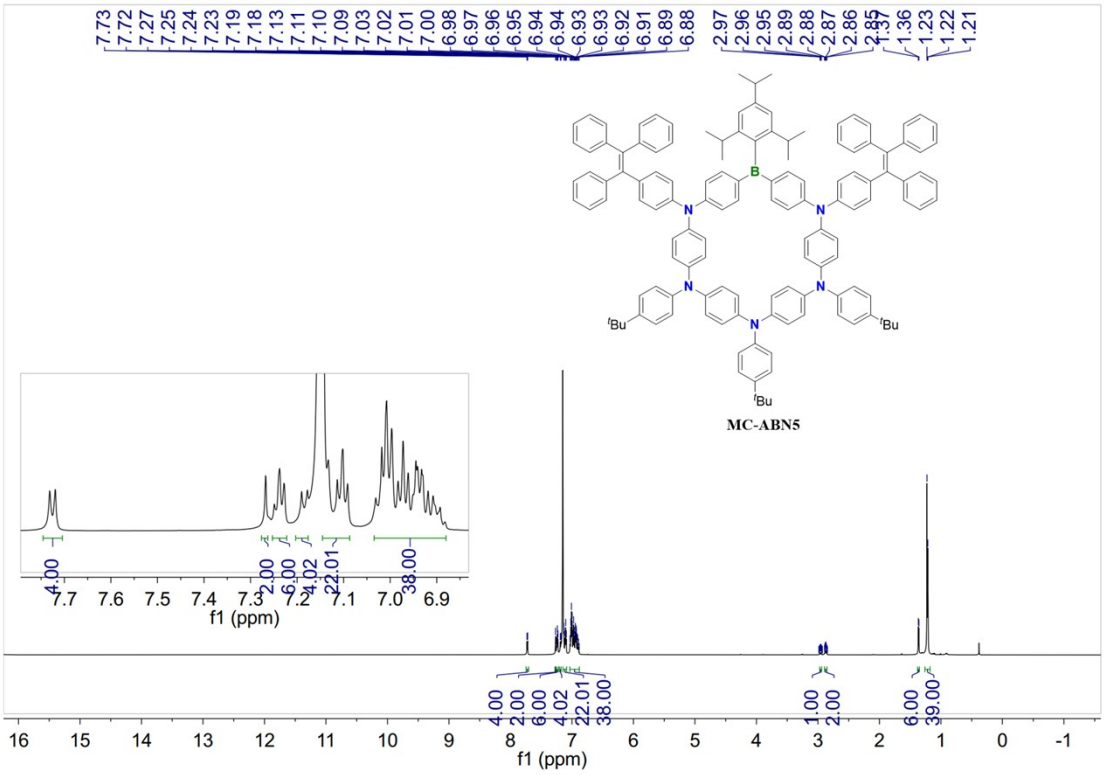


Figure S13. ^{1}H NMR (700 MHz, C_6D_6) spectrum of **MC-ABN5**.

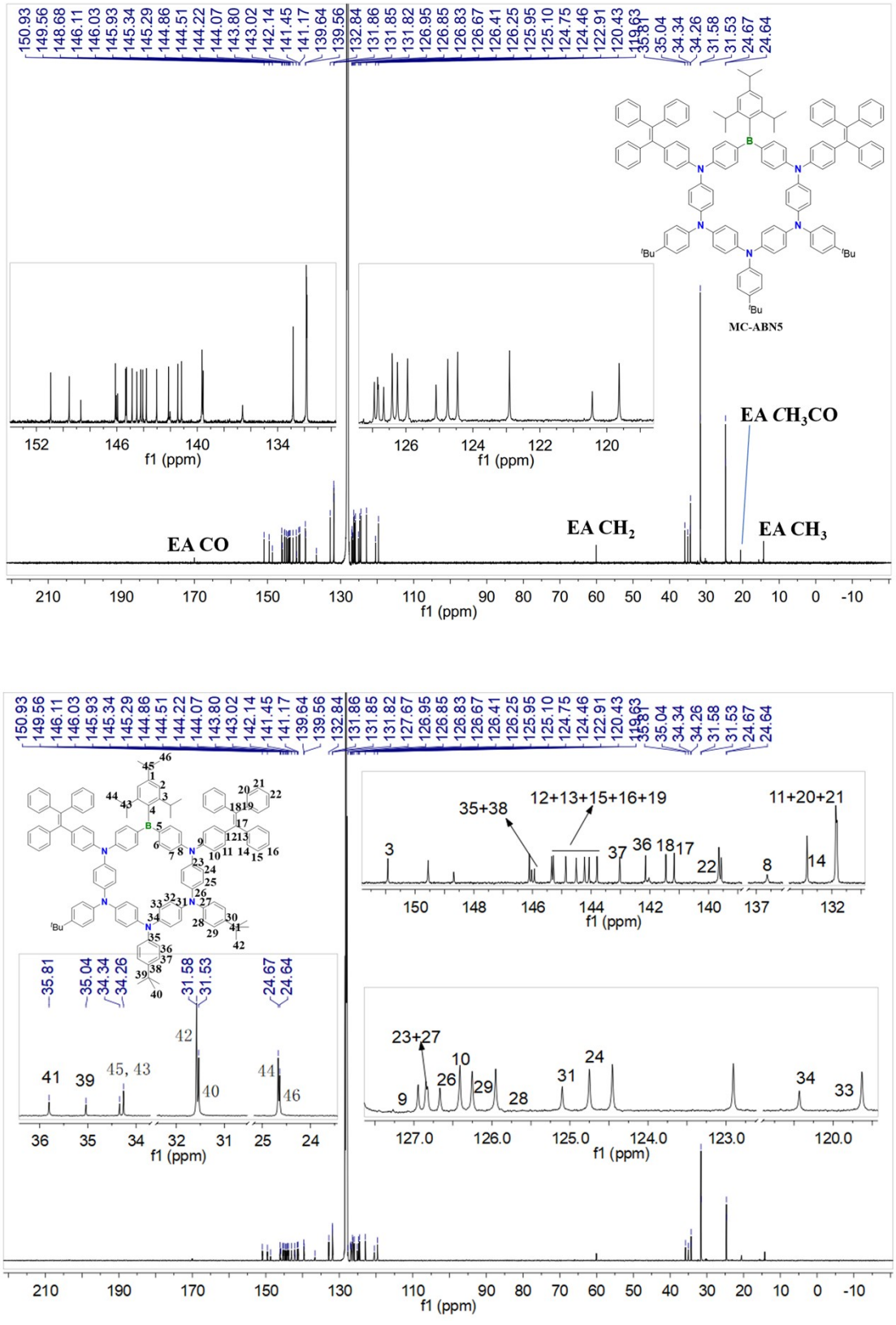


Figure S14. ^{13}C NMR (176 MHz, C_6D_6) spectrum of **MC-ABN5**.

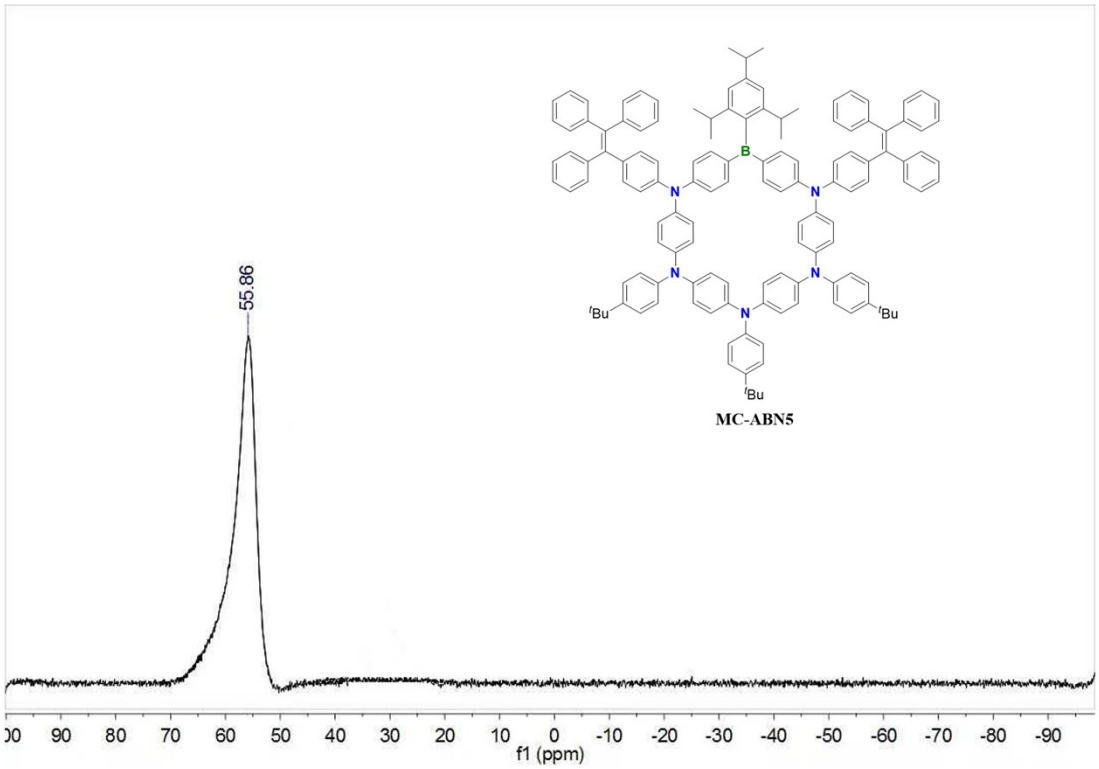


Figure S15. ^{11}B NMR (225 MHz, C_6D_6) spectrum of **MC-ABN5**.

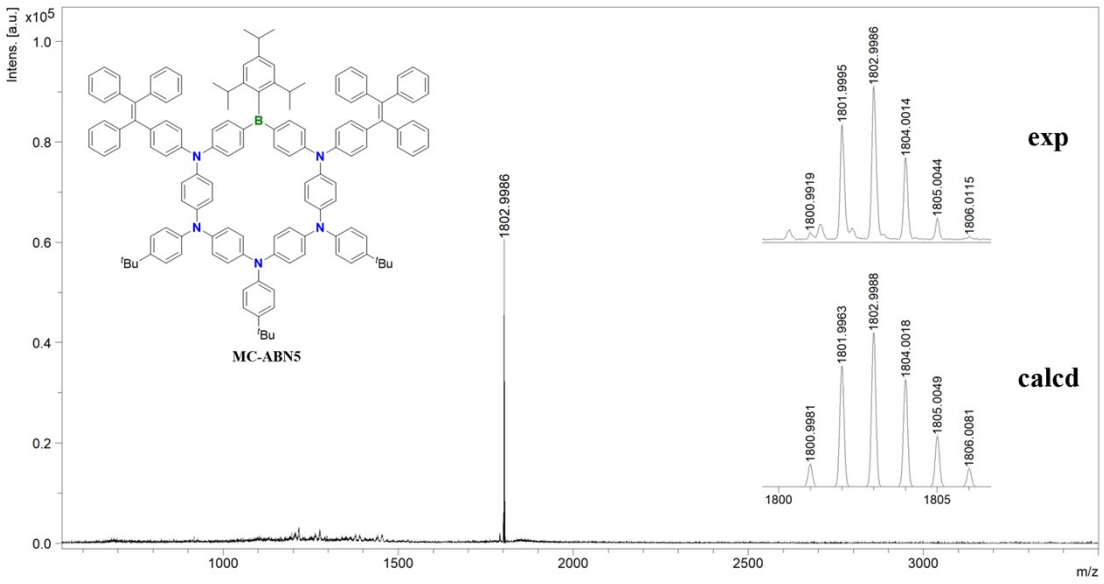


Figure S16. MALDI-TOF spectra (positive) of **MC-ABN5**. Inset: experimental and simulated isotopic patterns.

4. Electrochemical Data

Table S1. Summary of the electrochemical data of **MC-BN5**.

	$E_{red}^{CV,a}$ (V)	$E_{red}^{DPV,b}$ (V)	$E_{ox}^{CV,c}$ (V)	$E_{ox}^{DPV,d}$ (V)	$E_{HOMO/LUMO}^{e}$ (eV)	$E_{gap(elec)}^{f}$ (eV)
MC-BN5	–2.66	–2.66	–0.16, 0.08, 0.34, 0.65, 1.14	–0.16, 0.07, 0.33, 0.64, 1.12	–4.64/–2.14	2.50

Cyclic and differential pulse voltammetry (CV and DPV) curves (*vs* Fc/Fc^+), using *n*-Bu_4NPF_6 (0.1 M) as the electrolyte, ν = 100 mV/s. [a] Reduction potential from cyclic voltammetry (CV), [b] Peak potentials determined by the reduction peak positions from differential pulse voltammetry (DPV). [c] Oxidation potentials from CV. [d] Peak potentials determined by the oxidation peak positions from DPV. [e] The HOMO and LUMO energy levels are obtained by DPV, $E_{LUMO}/E_{HOMO} = -(4.8 + E^{l}_{red(DPV)}/E^{l}_{ox(DPV)})$. [f] The electrochemical energy gap, $E_{gap(elec)} = E_{LUMO} - E_{HOMO}$.

5. Photophysical Measurements

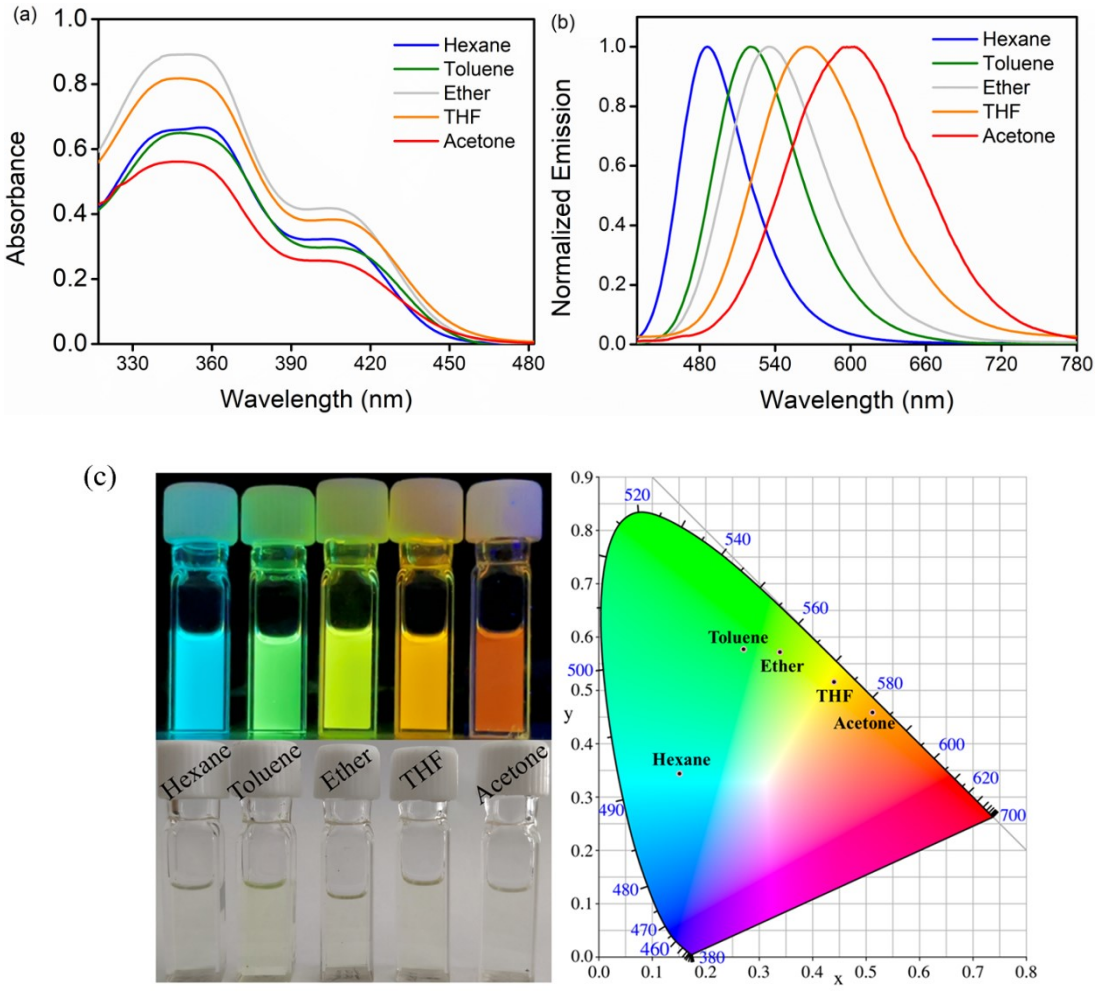


Figure S17. (a) UV/vis absorption and (b) emission spectra for **MC-BN5** in solvents of different polarity (c = 1.0 × 10^{-5} M). (c) Photographs showing the emission colors under the 365 nm UV lamp and CIE color coordinates.

Table S2. Photophysical data of **MC-BN5** in different solvents.

	λ_{abs}/nm	λ_{em}/nm	Φ_F/%	τ/ns
Hexane	356, 407	486	52	5
Toluene	349, 408	520	66	7
Ether	348, 407	535	60	10
THF	345, 408	565	36	8
CH_2Cl_2	347, 408	597	16	4
Acetone	346, 407	603	5	7

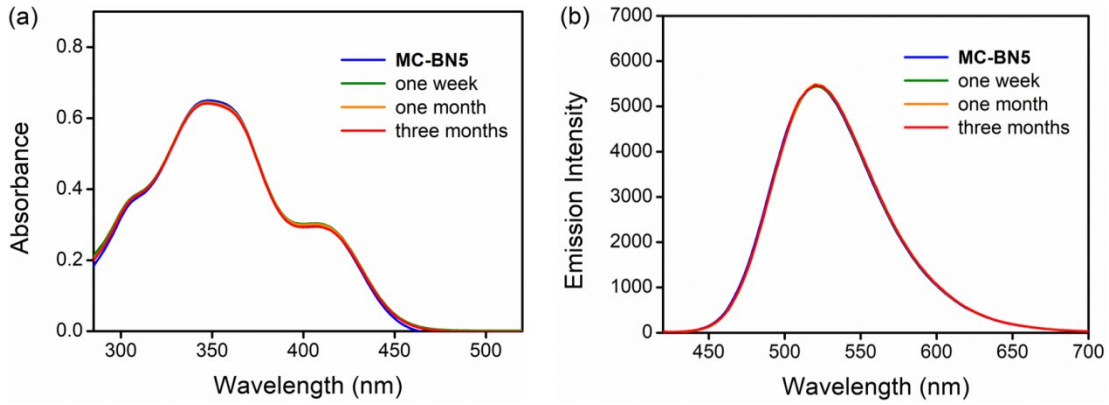


Figure S18. (a) UV-Vis absorption and (b) emission spectra of **MC-BN5** in toluene (c = 1.0 × 10^{-5} M, λ_{ex} = 408 nm) at ambient conditions under air over a time period of three months.

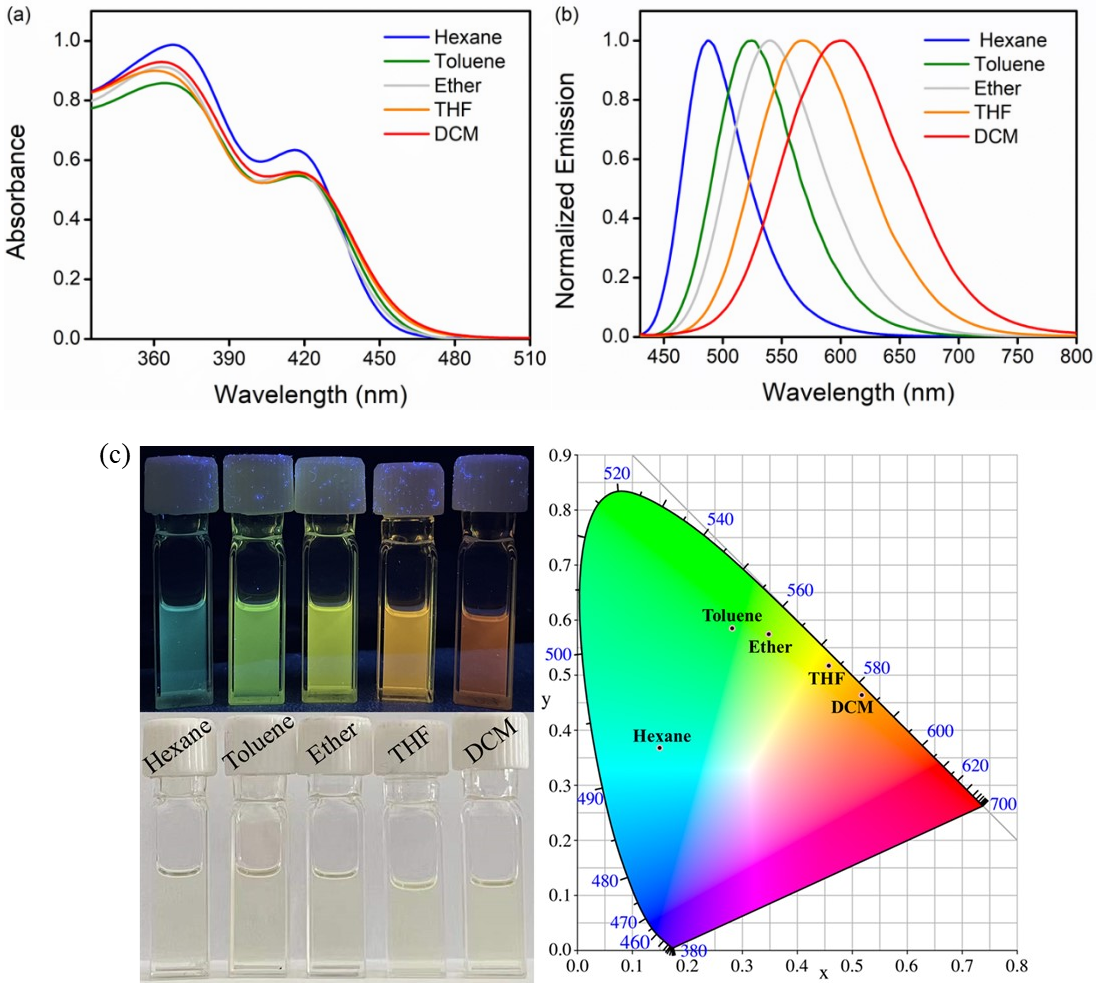


Figure S19. (a) UV-Vis absorption and (b) emission spectra for **MC-ABN5** in solvents of different polarity (c = 1.0 × 10^{-5} M). (c) Photographs showing the emission colors under the 365 nm UV lamp and CIE color coordinates.

Table S3. Photophysical data of **MC-ABN5** in different solvents.

	λ_{abs}/nm	λ_{em}/nm	Φ_F/%	τ/ns
Hexane	368, 416	488	6	2
Toluene	365, 418	525	18	3
Ether	364, 416	540	23	4
THF	362, 418	568	25	6
CH_2Cl_2	364, 417	600	10	3

Table S4. Photophysical properties of **MC-BN5** and **MC-ABN5** in different solvents.

$$\Delta\nu = \frac{2(\Delta\mu)^2}{hca^3}\Delta f + \text{constant}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

Entry	Solvent	ε[a]	n[b]	Δf[c]	**MC-BN5**		
					λ_{abs}[d](nm)	λ_{em}[e] (nm)	Δv[f]cm^{-1} (nm)
1	Hexane	1.88	1.372	0.001	356	486	7514 (130)
2	Toluene	2.37	1.496	0.0126	349	520	9423 (171)
3	Ether	4.34	1.353	0.1668	348	535	10044(187)
4	THF	7.58	1.404	0.2107	345	565	11286(220)
5	CH_2Cl_2	10.37	1.424	0.2276	347	597	12068(250)
6	Acetone	20.70	1.358	0.2846	346	603	12318(257)
Entry	Solvent	ε[a]	n[b]	Δf[c]	**MC-ABN5**		
					λ_{abs} (nm)	λ_{em} (nm)	Δv cm^{-1} (nm)
1	Hexane	1.88	1.372	0.001	368	488	6682 (120)
2	Toluene	2.37	1.496	0.0126	365	525	8350 (160)
3	Ether	4.34	1.353	0.1668	364	540	8954 (176)
4	THF	7.58	1.404	0.2107	362	568	10019(206)
5	CH_2Cl_2	10.37	1.424	0.2276	364	600	10806(236)
6	Acetone	20.70	1.358	0.2846	–	–	–

[a] ε = solvent dielectric constant

[b] n = index of refraction

[c] Δf = the orientation polarizability

[d] λ_{abs} = absorption maximum wavelength (nm)

[e] λ_{em} = emission maximum wavelength (nm)

[f] Δv = Stokes shifts (cm-1 or nm)

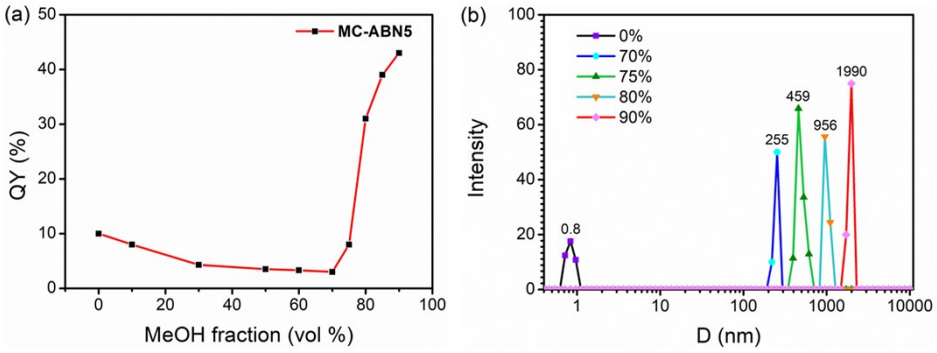
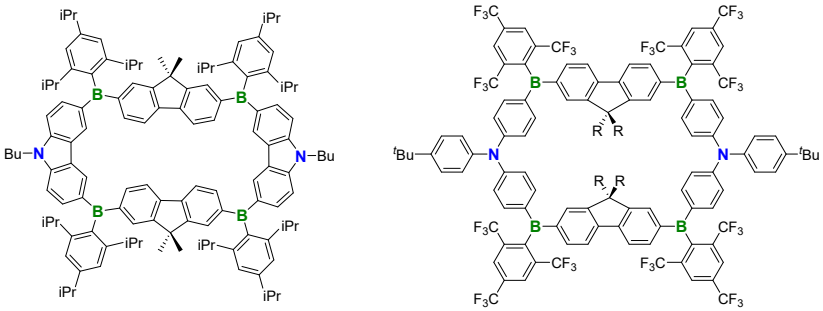


Figure S20. AIE behavior of **MC-ABN5**: (a) Change of the fluorescence quantum yields (QY) with increasing f_{MeOH}. (b) Selected DLS size distribution at different ratios of f_{MeOH}.

Table S5. Comparison of the photophysical, computational and electrochemical data for **MC-BN5**, **MC-ABN5** and related boracyclophanes.

	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	E_{HOMO}[b] (eV)	E_{LUOMO}[c] (eV)	$E_{gap(DFT)}$[d] (eV)	E_{TDDFT}[e] (eV)	$E_{gap(optical)}$[f] (eV)	$E^{ox1}{}_{1/2}$[g] (V)	$E^{red1}{}_{1/2}$[g] (V)	$E_{gap(elec)}$ (eV)
MC-BN5	408	520	-4.34	-1.32	3.02	2.73	2.70	–0.16	–2.66	2.50
MC-ABN5	418	525	–	–	–	–	2.63	–	–	–
M1[h]	348	–	–	–	–	–	–	–0.28	–	–
M2[i]	420	460	-5.01	-1.69	3.32	–	–	+0.46	–2.53	2.99
M3[j]	302	427	-7.02	-2.91	4.11	–	–	–	–1.56	–
M4[k]	416	612	-4.62	-2.02	2.60	2.30	2.51	+0.02	–2.10	1.93
MC-B6-Flu[l]	366	425	-5.69	-2.20	3.49	–	–	–	–2.10	–
MC-B4N2[m]	374	399	-5.41	-1.87	3.54	–	3.22	+0.95	-2.30	3.25
MC-B4N2-^{F}Mes[n]	406	483	-5.33	-2.29	3.04	–	3.05	+0.74	-2.02	2.76



MC-B4N2 **MC-B4N2-^{F}Mes**

[a] Recorded in toluene (c = 1.0 × 10^{-5} M). [b] E_{HOMO}: obtained by DFT calculation (B3LYP, 6-31G*). [c] E_{LUMO} obtained by DFT calculation (B3LYP, 6-31G*). [d] Energy gaps: $E_{gap} = E_{LUMO} – E_{HOMO}$ obtained by DFT calculation (B3LYP, 6-31G*). [e] Vertical excitation of the lowest transition ($S_o \rightarrow S_1$) calculated by TD-DFT (B3LYP, 6-311G*). [f] $E_{gap(optical)}$: experimental optical energy gap obtained from the onset of absorption spectra in toluene. [g] $E^{ox1}{}_{1/2}$ and $E^{red1}{}_{1/2}$: half-wave potential of oxidation and reduction in CH_2Cl_2 determined by cyclic voltammetry (*vs* Fc^+/Fc). [h] Ref S3a. [i] Ref S3b. [j] Ref S3c. [k] Ref S2c. [l] Ref S3d. [m] Ref S3e. [n] Ref S3f. Inset: structures of **MC-B4N2** and **MC-B4N2-^{F}Mes**.

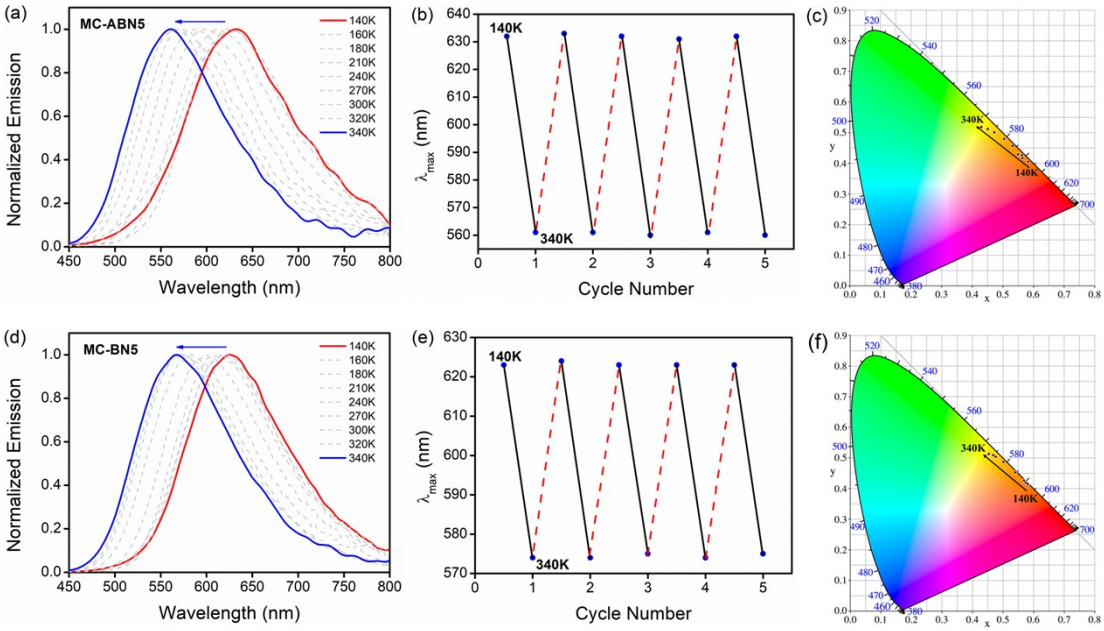


Figure S21. (a, d) Temperature-dependent emission spectra for **MC-ABN5** and **MC-BN5** in 2-methyltetrahydrofuran between 140 and 340 K under N_2 (c = 1.0 × 10^{-5} M, λ_{ex} = 418 nm for **MC-ABN5** and 408 nm for **MC-BN5**). (b, e) Reversible emission modulation with cycling T changes. (c, f) CIE color coordinates.

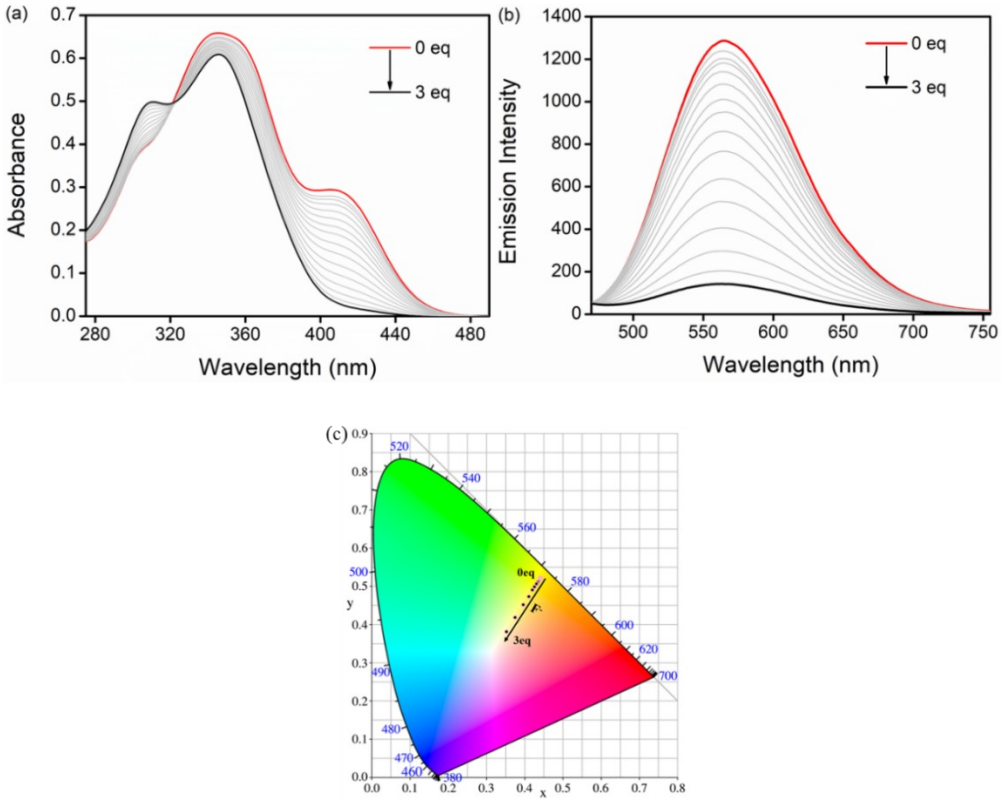


Figure S22. (a) UV-Vis absorption and (b) emission spectra for **MC-BN5** (c = 1.0 × 10^{-5} M, in THF) as addition of TBAF and (c) CIE diagram showing the emission color changes in response to addition of F^-.

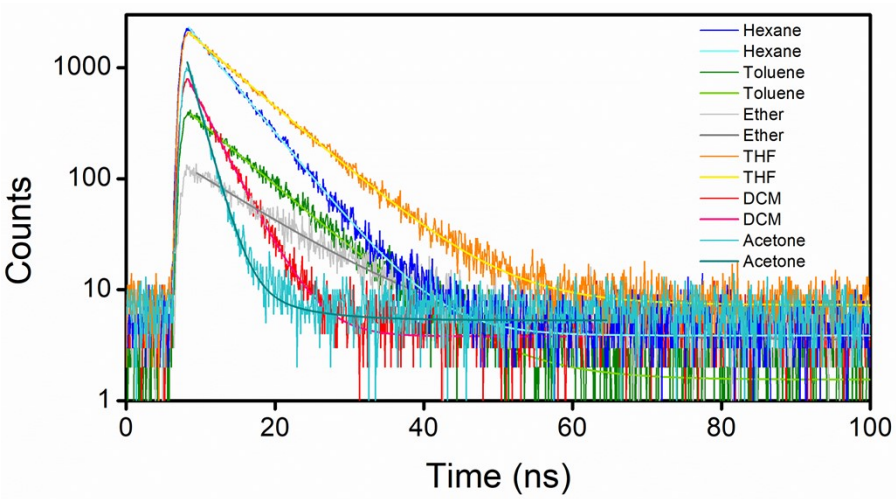


Figure S23. PL decay-fitting curves of **MC-BN5** in solvents of different polarity (c = 1.0 × 10^{-5} M).

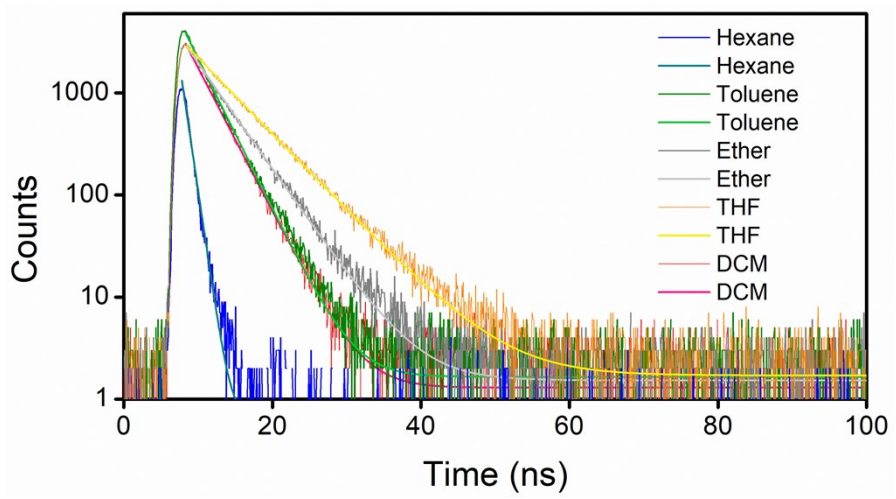


Figure S24. PL decay-fitting curves of **MC-ABN5** in solvents of different polarity (c = 1.0 × 10^{-5} M).

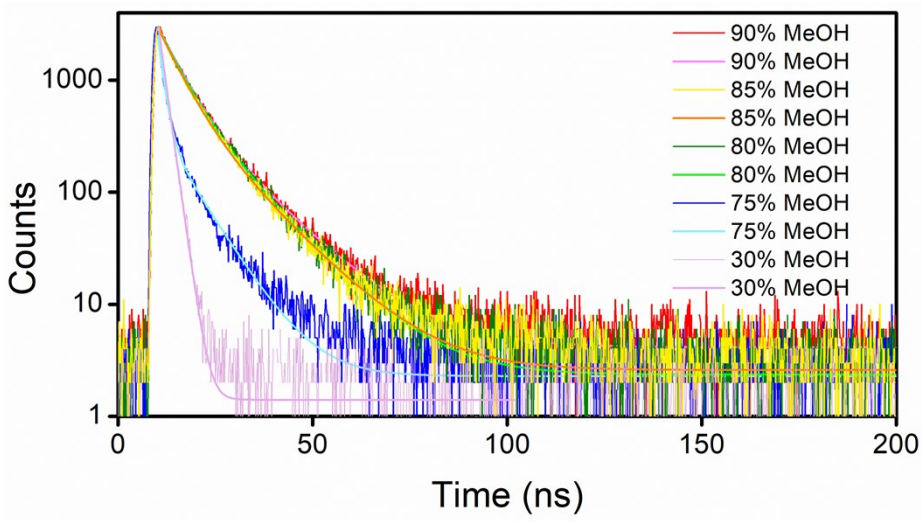


Figure S25. PL decay-fitting curves of **MC-ABN5** (c = 1.0 × 10^{-5} M) in CH_2Cl_2 with different f_{MeOH}.

Table S6. Summary of emission photophysical properties of **MC-ABN5** (c = 1.0 × 10^{-5} M) in CH_2Cl_2 with different f_{MeOH}.

	λ_{em} [nm]	Φ_F (%)	τ [ns]			Rel %	x^2
			τ_1	τ_2	τ_{ave}		
90% MeOH	532	43	5.49	13.54	9.04	55.92/44.08	1.183
85% MeOH	533	39	5.13	12.61	8.50	55.03/44.97	1.202
80% MeOH	538	31	5.08	12.06	8.50	50.87/49.13	1.244
75% MeOH	539	8	1.40	7.79	4.35	53.89/46.11	1.295
30% MeOH	600	4	1.72	-	1.72	100	1.001

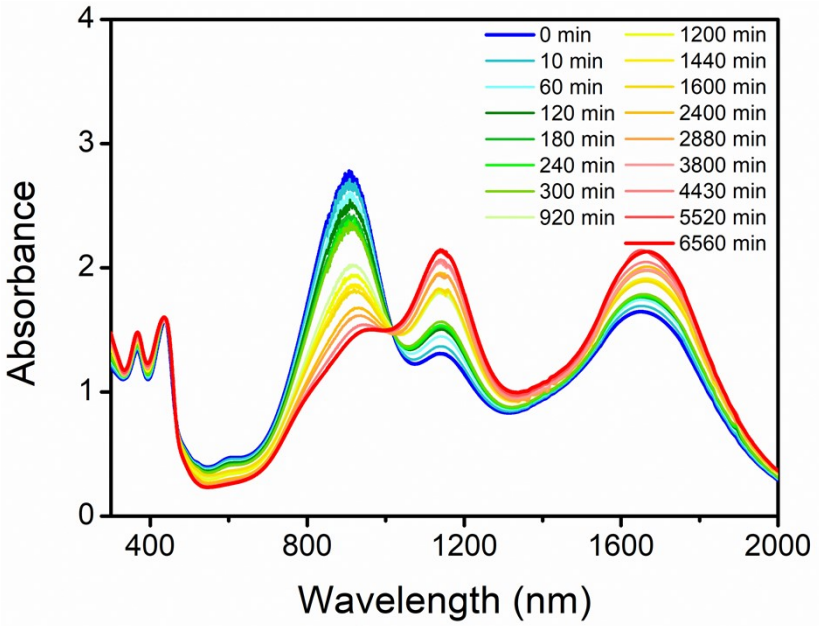


Figure S26. Time dependent spectra of fully oxidized **MC-BN5** (c = 5.0 × 10^{-5} M) monitored by UV-Vis-NIR absorption spectra in dry CH_2Cl_2 under air.

6. DFT and TD-DFT Computations

DFT and TD-DFT calculations were performed using the Gaussian 09 suite of programs.[4] Geometry optimizations and vertical excitations of all compounds were obtained at the (DFT) B3LYP/6-31G*, (TD-DFT) B3LYP/6-311G* and (TD-DFT) CAM-B3LYP/6-311G* and level of theory,[5,6] and the resulting structures were confirmed to be stationary points through vibrational frequency analysis.

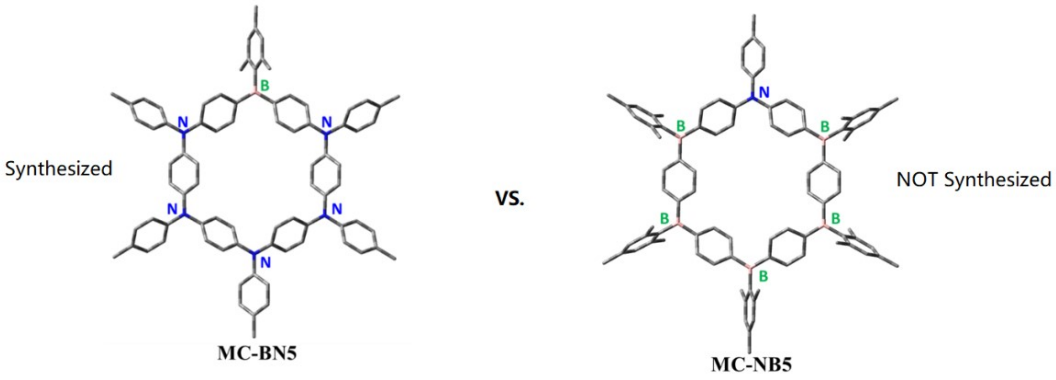


Figure S27. DFT-optimized structures of the simplified **MC-BN5** and **MC-NB5** (B3LYP/6-31G*). Hydrogen atoms are omitted. The *iso*-propyl, *t*-butyl and *n*-hexyl groups are simplified as Me groups.

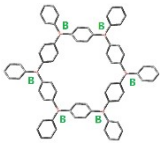
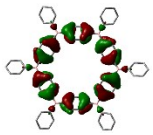
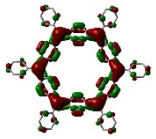
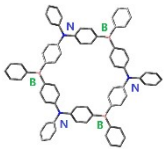
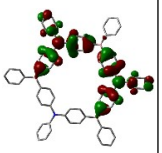
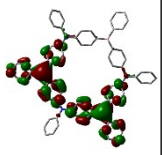
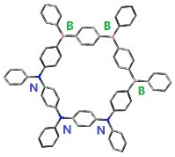
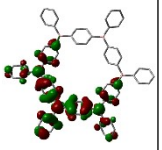
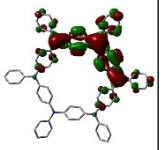
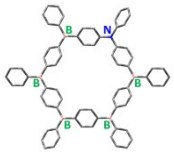
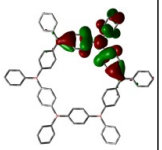
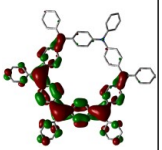
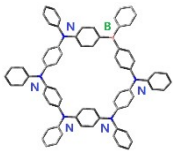
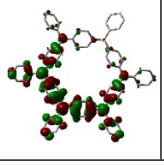
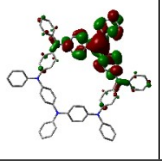
	DFT Structure	HOMO	LUMO	$E_{gap(DFT)}$ (eV)	Dipole Moment μ_g (D)
MC-B6 (D_{3d})				4.07	0.00
MC-*alt*-B3N3 (D_3)				3.32	0.00
MC-*b*-B3N3 (C_2)				2.60	3.17
MC-NB5 (C_2)				2.96	1.63
MC-BN5 (C_2)				**2.94**	**1.77**

Figure S28. Computational comparison of the model systems without any substituents on aryl

groups (B3LYP/6-31G*).

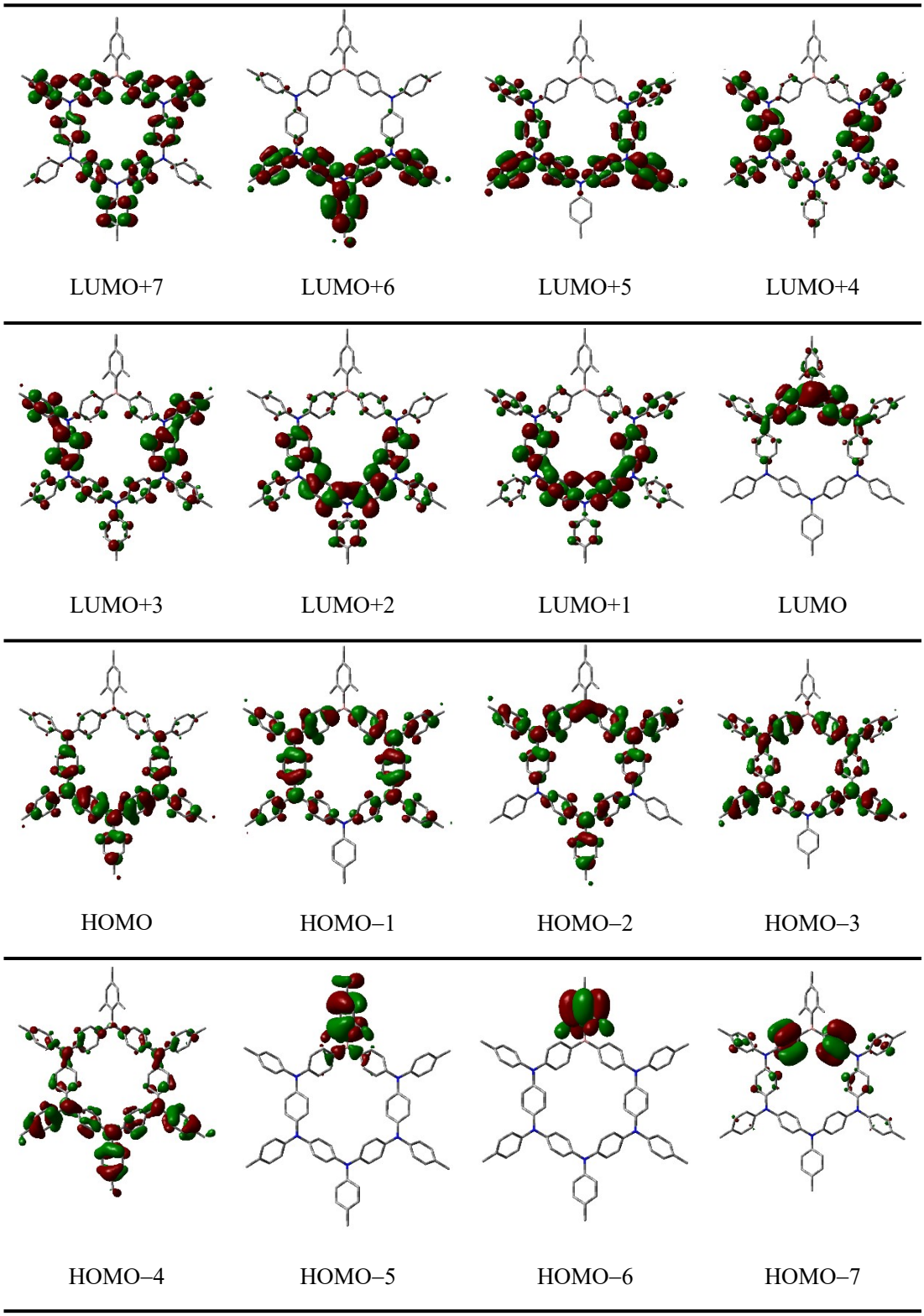


Figure S29. Molecular orbitals contributing to the TD-DFT calculated transitions of **MC-BN5** (iso = 0.02, B3LYP/6-31G*). The *iso*-propyl, *t*-butyl and *n*-hexyl groups are simplified as Me groups.

Table S7. Summary of DFT and TD-DFT calculations for simplified **MC-BN5** and **MC-NB5**.

	E_{HOMO}[a] (eV)	E_{LUMO}[a] (eV)	$E_{gap(DFT)}$[b] (eV)	E_{TDDFT}[c] (eV)	$E_{gap(optical)}$[d] (eV)	E_{TDDFT}/CAM[e] (eV)
MC-BN5	–4.34	–1.32	3.02	2.73	2.70	3.49
MC-NB5	–5.26	–2.33	2.93	2.63	–	3.46

[a] Obtained by DFT calculation (B3LYP, 6-31G*). [b] HOMO–LUMO energy gap: $E_{gap}= E_{LUMO} - E_{HOMO}$ (B3LYP, 6-31G*). [c] Vertical excitation of the lowest energy transition ($S_0 \rightarrow S_1$) calculated by TD-DFT (B3LYP, 6-311G*). [d] Obtained from the onset of absorption spectra in CH_2Cl_2. [e] Vertical excitation of the lowest energy transition ($S_0 \rightarrow S_1$) calculated by TD-DFT (CAM-B3LYP, 6-311G*).

Table S8. Summary of the TD-DFT calculations (B3LYP, 6-311G*) for the simplified **MC-BN5**.

Compound	Transition	λ, nm (eV)	Oscillator Strength, f	Orbital Contributions
MC-BN5	$S_0 \rightarrow S_1$	455 (2.73)	0.1600	HOMO→LUMO (99%)
	$S_0 \rightarrow S_2$	443 (2.80)	0.3471	HOMO–1→LUMO (91%)
	$S_0 \rightarrow S_3$	381 (3.26)	0.4569	HOMO→LUMO+1 (86%)
	$S_0 \rightarrow S_4$	375 (3.30)	0.3305	HOMO→LUMO+2 (90%)
	$S_0 \rightarrow S_5$	364 (3.41)	0.3974	HOMO–2→LUMO (43%) HOMO→LUMO+3 (33%)

Table S9. Summary of the TD-DFT calculations (CAM-B3LYP, 6-311G*) for the simplified **MC-BN5**.

Compound	Transition	λ, nm (eV)	Oscillator Strength, f	Orbital Contributions
MC-BN5	$S_0 \rightarrow S_1$	356 (3.49)	0.3593	HOMO–3→LUMO (10%) HOMO–1→LUMO (60%) HOMO→LUMO+1 (12%)
	$S_0 \rightarrow S_2$	321(3.86)	1.1897	HOMO–2→LUMO (20%) HOMO→LUMO (46%)
	$S_0 \rightarrow S_3$	318 (3.90)	1.6555	HOMO→LUMO+1 (51%)
	$S_0 \rightarrow S_4$	310 (3.99)	0.1287	HOMO→LUMO+2 (61%)
	$S_0 \rightarrow S_5$	301 (4.12)	0.0866	HOMO–1→LUMO+2 (14%) HOMO→LUMO+3 (26%)

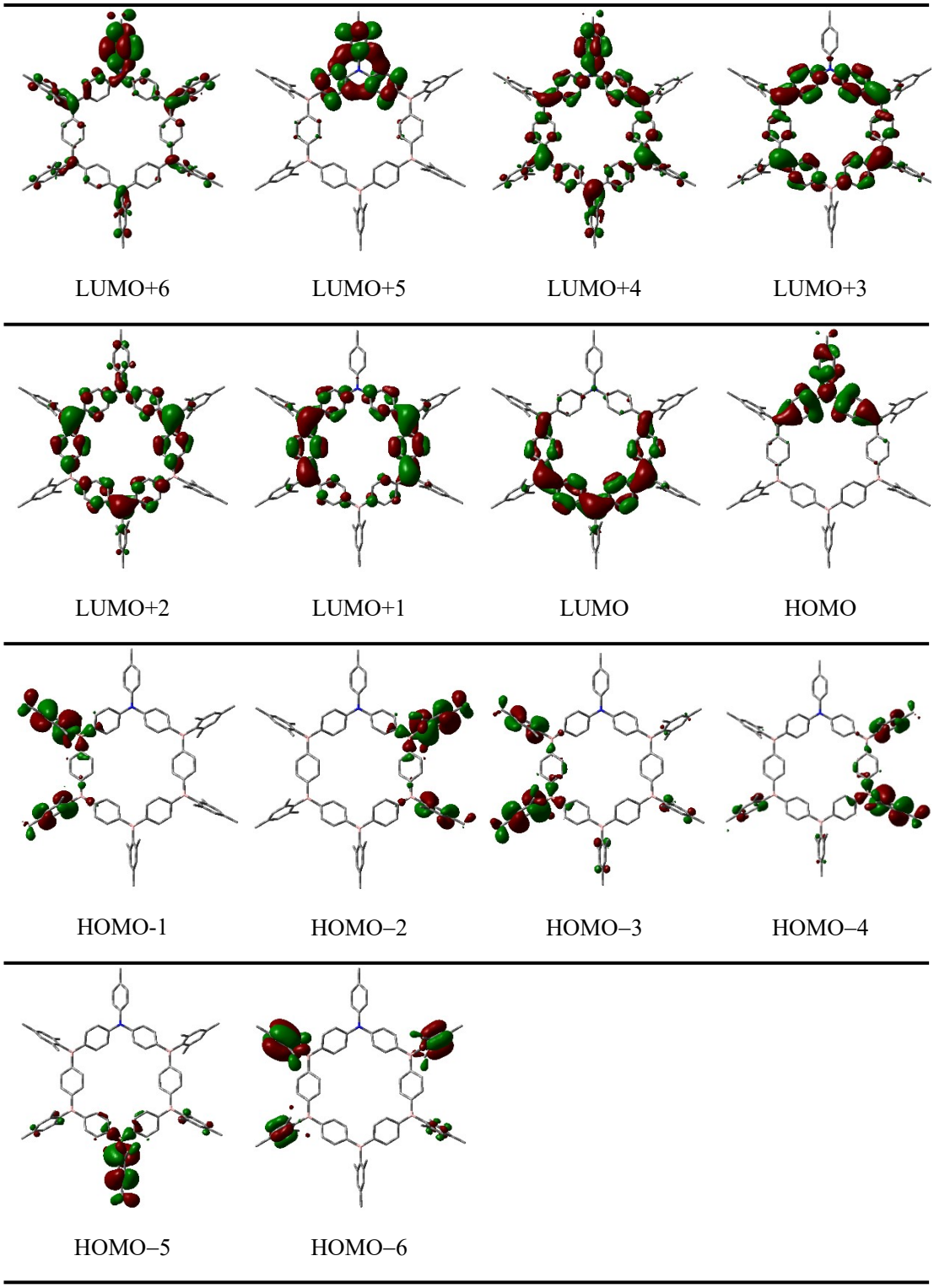


Figure S30. Molecular orbitals contributing to the TD-DFT calculated transitions of simplified **MC-NB5** (iso = 0.02, B3LYP/6-31G*). The substituents on aryl groups are simplified as Me groups.

Table S10. Summary of the TD-DFT calculations (B3LYP, 6-311G*) for the simplified **MC-NB5**.

Compound	Transition	λ, nm (eV)	Oscillator Strength, f	Orbital Contributions
MC-NB5	$S_0 \rightarrow S_1$	471 (2.63)	0.1094	HOMO→LUMO (99%)
	$S_0 \rightarrow S_2$	460 (2.70)	0.3297	HOMO→LUMO+1 (96%)
	$S_0 \rightarrow S_3$	407 (3.05)	0.0030	HOMO–3→LUMO (54%) HOMO–1→LUMO (17%)
	$S_0 \rightarrow S_4$	406 (3.05)	0.0163	HOMO–4→LUMO (57%) HOMO–2→LUMO (13%)
	$S_0 \rightarrow S_5$	403 (3.08)	0.0446	HOMO–5→LUMO (88%)

Table S11. Summary of the TD-DFT calculations (CAM-B3LYP, 6-311G*) for the simplified **MC-NB5**.

Compound	Transition	λ, nm (eV)	Oscillator Strength, f	Orbital Contributions
MC-NB5	$S_0 \rightarrow S_1$	358 (3.46)	0.5051	HOMO→LUMO+1 (66%) HOMO→LUMO+3 (17%)
	$S_0 \rightarrow S_2$	320(3.87)	0.7833	HOMO→LUMO (37%)
	$S_0 \rightarrow S_3$	319 (3.89)	0.0611	HOMO–4→LUMO (15%) HOMO–3→LUMO (24%) HOMO–3→LUMO+1 (18%)
	$S_0 \rightarrow S_4$	319 (3.89)	0.0693	HOMO–4→LUMO (25%)
	$S_0 \rightarrow S_5$	317 (3.92)	0.0088	HOMO–5→LUMO (48%) HOMO–5→LUMO+2 (10%)

Table S12. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of simplified **MC-BN5**.

Atom	X	Y	Z	Atom	X	Y	Z
C	4.836226	3.535218	-0.807055	C	3.778471	-6.169715	-0.059843
C	3.688790	3.723770	-0.020510	C	4.912610	-6.267171	-0.881409
C	3.233963	2.648164	0.758811	C	3.393883	-7.297241	0.682993
C	3.907237	1.430616	0.759694	C	5.638464	-7.454038	-0.944175
C	5.061058	1.244961	-0.019311	H	5.219963	-5.410379	-1.472568
C	5.509279	2.318570	-0.807197	C	4.119285	-8.482479	0.594542
H	5.196066	4.348851	-1.429116	H	2.521011	-7.241024	1.325773
H	2.354918	2.775866	1.382899	C	5.260316	-8.586942	-0.211894
H	3.548019	0.619159	1.384705	H	6.511762	-7.503419	-1.591350
H	6.389089	2.191979	-1.429926	H	3.796316	-9.342083	1.178168
C	5.067284	-1.223582	0.011321	C	1.591683	5.006725	-0.046304
C	5.521800	-2.292197	0.802250	C	0.866608	5.867188	0.794050

C	3.913601	-1.417507	-0.765730	C	0.877811	4.173016	-0.922885
C	4.854636	-3.512083	0.807252	C	-0.524176	5.881836	0.769061
H	6.401832	-2.159122	1.423354	H	1.399651	6.514281	1.483359
C	3.246206	-2.638271	-0.759875	C	-0.512254	4.192161	-0.950349
H	3.549814	-0.609879	-1.393088	H	1.421736	3.515507	-1.593780
C	3.707068	-3.708928	0.022807	C	-1.236017	5.039190	-0.097085
H	5.219108	-4.321713	1.431804	H	-1.068205	6.539076	1.440348
H	2.367119	-2.772355	-1.382538	H	-1.046647	3.547193	-1.640847
C	7.189662	0.016387	-0.010682	C	3.749169	6.184500	0.076102
C	7.907105	0.886209	0.824751	C	3.366188	7.311516	-0.668603
C	7.907382	-0.852409	-0.846202	C	4.881660	6.282345	0.899583
C	9.299492	0.889345	0.810708	C	4.089757	8.497532	-0.577524
H	7.367009	1.556574	1.486161	H	2.501258	7.250997	-1.321673
C	9.300242	-0.850802	-0.835954	C	5.605692	7.470322	0.965280
H	7.368022	-1.531933	-1.498798	H	5.194653	5.422488	1.483279
C	10.026855	0.022870	-0.016431	C	5.224452	8.605021	0.237527
H	9.832038	1.571032	1.470707	H	3.772831	9.354645	-1.168139
H	9.833023	-1.536892	-1.491053	H	6.481735	7.517676	1.608831
C	-3.379707	3.832943	-0.059935	C	-3.337313	6.300916	-0.129487
C	-4.666685	3.720876	-0.624198	C	-4.397856	6.566717	0.748741
C	-2.823526	2.694337	0.555412	C	-2.931509	7.307123	-1.017806
C	-5.355737	2.515876	-0.569817	C	-5.040248	7.802473	0.721993
H	-5.118265	4.583051	-1.103524	H	-4.714447	5.802414	1.451587
C	-3.509522	1.488307	0.555350	C	-3.571085	8.544145	-1.020768
H	-1.850700	2.763847	1.029881	H	-2.108746	7.115531	-1.699701
C	-4.797663	1.344612	-0.009032	C	-4.642310	8.816336	-0.159410
H	-6.352906	2.468191	-1.000870	H	-5.859347	7.986856	1.413718
H	-3.046007	0.633261	1.039400	H	-3.236371	9.310498	-1.716608
C	1.615366	-5.000234	0.050358	B	-5.568681	-0.012541	-0.000892
C	0.896198	-4.169180	0.925031	N	5.766221	0.012536	-0.006424
C	0.895856	-5.863563	-0.791714	N	3.010352	4.973779	-0.009693
C	-0.493842	-4.193908	0.949335	N	-2.662134	5.045398	-0.108286
H	1.435998	-3.509442	1.597087	N	3.034210	-4.961821	0.017600
C	-0.494927	-5.883930	-0.769901	N	-2.638176	-5.056768	0.103105
H	1.433232	-6.508634	-1.479582	C	-7.157479	0.653500	2.459170
C	-1.212168	-5.044159	0.094649	H	-6.528007	-0.175089	2.809391
H	-1.032432	-3.551080	1.638556	C	-7.160924	-0.696358	-2.455267
H	-1.034736	-6.543516	-1.442284	H	-6.534540	0.133501	-2.807996
C	-4.791024	-1.365935	0.006513	C	-11.511005	-0.008659	-0.000106
C	-3.502075	-1.503066	-0.557675	H	-11.920913	-0.786366	-0.654505
C	-5.343594	-2.540256	0.566390	C	-5.358406	10.146034	-0.197555
C	-2.810259	-2.705786	-0.558364	H	-6.164779	10.145770	-0.943602
H	-3.042551	-0.645510	-1.041082	H	-5.813041	10.384196	0.770047

C	-4.648881	-3.742036	0.619829	H	-4.676465	10.962284	-0.459923
H	-6.341021	-2.497669	0.997369	C	5.991526	9.902095	0.345884
C	-3.361275	-3.847509	0.055804	H	5.939301	10.477620	-0.584903
H	-1.836948	-2.770342	-1.032564	H	5.590733	10.541807	1.144213
H	-5.096493	-4.606760	1.098287	H	7.048409	9.725547	0.573390
C	-7.153699	-0.016331	0.000700	C	11.537127	0.049086	-0.041919
C	-7.878368	0.306496	1.171858	H	11.914235	0.779793	-0.770570
C	-7.880598	-0.348214	-1.167642	H	11.950247	0.325218	0.934505
C	-9.277570	0.285864	1.159643	H	11.950994	-0.926498	-0.318779
C	-9.278997	-0.343352	-1.149184	C	6.066800	-9.863182	-0.268231
C	-9.999820	-0.029596	0.006467	H	6.578925	-9.971721	-1.230555
H	-9.816713	0.524415	2.075354	H	6.838446	-9.886862	0.513560
H	-9.819586	-0.595529	-2.060561	H	5.433526	-10.745215	-0.122816
C	-3.307952	-6.315242	0.122017	C	-5.313534	-10.168539	0.183553
C	-4.365860	-6.584623	-0.758272	H	-6.120926	-10.172246	0.928485
C	-2.899603	-7.320479	1.010263	H	-5.765862	-10.407602	-0.784905
C	-5.003294	-7.822986	-0.733618	H	-4.628654	-10.982273	0.446088
H	-4.684321	-5.821018	-1.461031	H	-11.918498	-0.163344	1.004825
C	-3.534163	-8.560086	1.011125	H	-11.897233	0.953823	-0.362883
H	-2.078874	-7.126085	1.693817	H	-7.871286	-0.934443	-3.253888
C	-4.602776	-8.835920	0.147684	H	-6.497698	-1.559339	-2.324918
H	-5.820452	-8.010130	-1.426891	H	-7.867170	0.888044	3.259430
H	-3.197588	-9.325626	1.706962	H	-6.497137	1.518762	2.329338

Table S13. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of the model **MC-BN5** (without substituents).

Atom	X	Y	Z	Atom	X	Y	Z
C	0.779799	3.522143	4.659712	C	0.666467	-1.00706	-9.51962
C	-0.02103	3.703368	3.520971	H	1.170232	-1.80332	-7.59208
C	-0.80518	2.625456	3.08069	C	0	0	-10.2212
C	-0.79578	1.41122	3.759741	H	-1.19148	1.790986	-10.0601
C	-0.00171	1.232724	4.904032	H	1.191483	-1.79099	-10.0601
C	0.78986	2.30877	5.338518	H	0	0	-11.3086
H	1.405766	4.337991	5.007425	C	-0.11895	-6.28101	-3.50486
H	-1.43947	2.748503	2.20835	C	0.719166	-6.5392	-4.60109
H	-1.42313	0.596479	3.412173	C	-0.9899	-7.28766	-3.06003
H	1.423829	2.186486	6.210924	C	0.674261	-7.77539	-5.24306
C	0.00171	-1.23272	4.904032	H	1.401092	-5.76742	-4.94381
C	-0.78986	-2.30877	5.338518	C	-1.01572	-8.52676	-3.69741
C	0.795777	-1.41122	3.759741	H	-1.6418	-7.0913	-2.21459
C	-0.7798	-3.52214	4.659712	C	-0.18879	-8.77759	-4.79431
H	-1.42383	-2.18649	6.210924	H	1.329663	-7.95936	-6.09035

C	0.805175	-2.62546	3.08069	H	-1.69654	-9.2953	-3.3408
H	1.423127	-0.59648	3.412173	H	-0.21591	-9.74228	-5.29295
C	0.02103	-3.70337	3.520971	C	0.109138	-6.16395	3.566155
H	-1.40577	-4.33799	5.007425	C	0.919948	-6.26519	4.709084
H	1.439467	-2.7485	2.20835	C	-0.6332	-7.28575	3.160304
C	0	0	7.032282	C	0.977325	-7.45752	5.427867
C	-0.8232	0.886298	7.745957	H	1.502305	-5.40658	5.027531
C	0.823196	-0.8863	7.745957	C	-0.5549	-8.4787	3.875898
C	-0.81325	0.888565	9.139411	H	-1.26931	-7.21482	2.283818
H	-1.46743	1.569532	7.201612	C	0.245871	-8.57355	5.016065
C	0.813253	-0.88857	9.139411	H	1.611065	-7.51631	6.309079
H	1.467431	-1.56953	7.201612	H	-1.13716	-9.3352	3.545812
C	0	0	9.846172	H	0.298881	-9.50313	5.575466
H	-1.45768	1.5812	9.674665	C	-0.00543	4.971818	1.414499
H	1.457683	-1.5812	9.674665	C	-0.84064	5.835856	0.687774
H	0	0	10.9324	C	0.861862	4.127107	0.702696
C	0.04793	3.815501	-3.56843	C	-0.812	5.850961	-0.70264
C	0.694786	3.704596	-4.81425	H	-1.526	6.488403	1.219239
C	-0.62354	2.685677	-3.06428	C	0.891533	4.144889	-0.68761
C	0.653549	2.511139	-5.52454	H	1.526147	3.463778	1.247603
H	1.231488	4.55771	-5.21616	C	0.051643	5.003851	-1.41274
C	-0.61595	1.490183	-3.77071	H	-1.4758	6.514633	-1.24801
H	-1.14802	2.753851	-2.11694	H	1.577653	3.493913	-1.22036
C	0.013611	1.352213	-5.02891	C	-0.10914	6.163945	3.566155
H	1.163552	2.464275	-6.48313	C	0.633198	7.285753	3.160304
H	-1.14138	0.638254	-3.34774	C	-0.91995	6.265186	4.709084
C	0.005434	-4.97182	1.414499	C	0.554902	8.478702	3.875898
C	-0.86186	-4.12711	0.702696	H	1.269311	7.214819	2.283818
C	0.840638	-5.83586	0.687774	C	-0.97733	7.457521	5.427867
C	-0.89153	-4.14489	-0.68761	H	-1.50231	5.406577	5.027531
H	-1.52615	-3.46378	1.247603	C	-0.24587	8.573549	5.016065
C	0.812003	-5.85096	-0.70264	H	1.137157	9.335204	3.545812
H	1.526001	-6.4884	1.219239	H	-1.61107	7.516312	6.309079
C	-0.05164	-5.00385	-1.41274	H	-0.29888	9.503129	5.575466
H	-1.57765	-3.49391	-1.22036	C	0.118954	6.281013	-3.50486
H	1.475795	-6.51463	-1.24801	C	-0.71917	6.539199	-4.60109
C	-0.01361	-1.35221	-5.02891	C	0.989897	7.287657	-3.06003
C	0.615945	-1.49018	-3.77071	C	-0.67426	7.775391	-5.24306
C	-0.65355	-2.51114	-5.52454	H	-1.40109	5.767415	-4.94381
C	0.623544	-2.68568	-3.06428	C	1.015721	8.52676	-3.69741
H	1.14138	-0.63825	-3.34774	H	1.641799	7.091301	-2.21459
C	-0.69479	-3.7046	-4.81425	C	0.188789	8.77759	-4.79431
H	-1.16355	-2.46428	-6.48313	H	-1.32966	7.959355	-6.09035

C	-0.04793	-3.8155	-3.56843	H	1.696538	9.295303	-3.3408
H	1.148021	-2.75385	-2.11694	H	0.215914	9.742283	-5.29295
H	-1.23149	-4.55771	-5.21616	B	0	0	-5.813
C	0	0	-7.38549	N	0	0	5.610133
C	-0.6532	1.009808	-8.12514	N	-0.03857	4.94872	2.834065
C	0.653196	-1.00981	-8.12514	N	0.07724	5.023184	-2.83767
C	-0.66647	1.007058	-9.51962	N	0.038569	-4.94872	2.834065
H	-1.17023	1.803324	-7.59208	N	-0.07724	-5.02318	-2.83767

Table S14. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of simplified **MC-NB5**.

Atom	X	Y	Z	Atom	X	Y	Z
C	3.691055	-4.97712	-0.28277	H	7.052422	1.409183	0.890901
C	3.760131	-3.67537	0.260644	H	3.18397	1.296869	-0.98478
C	2.563261	-3.14235	0.786443	C	6.483717	-3.64676	0.338721
C	1.362899	-3.84239	0.721696	C	7.316837	-3.77983	-0.79738
C	1.282526	-5.12226	0.130528	C	6.905729	-4.22881	1.557519
C	2.48937	-5.67894	-0.34627	C	8.524092	-4.47935	-0.6997
H	4.599273	-5.43721	-0.66484	C	8.128398	-4.90441	1.62289
H	2.577602	-2.16177	1.25426	C	8.954535	-5.04292	0.504353
H	0.466435	-3.39179	1.138655	H	9.145626	-4.58465	-1.58762
H	2.475377	-6.67726	-0.77714	H	8.441169	-5.33813	2.571484
C	-1.41871	-5.08705	-0.14748	C	6.477461	3.898359	-0.30086
C	-2.63846	-5.60887	0.335861	C	7.069283	4.608019	0.770134
C	-1.46682	-3.80821	-0.7444	C	7.147042	3.87851	-1.54802
C	-3.82103	-4.87524	0.273451	C	8.291782	5.263381	0.583781
H	-2.6499	-6.60513	0.771522	C	8.358229	4.558942	-1.70292
C	-2.64807	-3.07613	-0.80754	C	8.9509	5.258493	-0.64748
H	-0.56013	-3.38361	-1.16652	H	8.73912	5.793515	1.423176
C	-3.85691	-3.57428	-0.27491	H	8.854785	4.537991	-2.67196
H	-4.73972	-5.30925	0.660917	C	0.17851	11.86138	-0.00465
H	-2.63758	-2.09733	-1.27921	H	-0.78608	12.28706	-0.30199
C	-0.09987	-7.47289	-8.6E-05	C	10.25058	6.004402	-0.84255
C	0.180808	-8.19508	1.184832	H	10.08122	6.99165	-1.29361
C	-0.40687	-8.19984	-1.17597	H	10.76707	6.166328	0.109529
C	0.14063	-9.59311	1.177243	H	10.93022	5.459763	-1.50772
C	-0.41677	-9.59781	-1.15064	C	10.28246	-5.75756	0.599996
C	-0.14767	-10.3165	0.017296	H	10.55334	-6.23005	-0.35048
H	0.342096	-10.131	2.102263	H	11.09259	-5.06196	0.858345
H	-0.64553	-10.1399	-2.06692	H	10.26509	-6.53454	1.372019
C	3.768972	3.935447	-0.02873	C	-0.14423	-11.8274	0.018461
C	3.640063	5.207431	-0.63161	H	0.841831	-12.2245	-0.25885
C	2.61811	3.443311	0.629522	H	-0.38796	-12.2285	1.008131

C	2.440751	5.908738	-0.643	H	-0.86764	-12.231	-0.69856
H	4.502183	5.640665	-1.13231	C	-10.4023	-5.5406	-0.57617
C	1.425322	4.15131	0.671801	H	-10.8636	-5.43664	-1.56442
H	2.670273	2.490389	1.148488	H	-10.2712	-6.61568	-0.39214
C	1.305195	5.385252	0.004076	H	-11.1128	-5.1689	0.17015
H	2.372345	6.862673	-1.15522	C	-10.0886	6.268886	0.862216
H	0.575767	3.751447	1.214919	H	-9.89223	7.251635	1.31216
C	-5.13309	-1.16849	-0.14968	H	-10.6051	6.443632	-0.0876
C	-4.04019	-0.48743	0.429518	H	-10.7788	5.74176	1.5306
C	-6.20319	-0.37028	-0.6135	H	0.436588	12.26445	0.98013
C	-4.00101	0.901652	0.503527	H	0.928761	12.23263	-0.71572
H	-3.21282	-1.05955	0.839415	B	-5.02123	3.270984	0.1044
C	-6.16827	1.019093	-0.52989	B	-5.18468	-2.73352	-0.26061
H	-7.07653	-0.85795	-1.03979	B	-0.07852	-5.89442	-0.00694
C	-5.05667	1.699988	0.013164	B	5.110433	-2.87109	0.250359
H	-3.14243	1.381444	0.965487	B	5.105337	3.135972	-0.10814
H	-7.01769	1.596582	-0.88713	C	-6.29422	4.821281	-2.12984
C	-1.16335	5.419263	-0.01049	H	-5.26701	5.200363	-2.07861
C	-1.31861	4.192862	-0.68481	H	-6.24106	3.818567	-2.57439
C	-2.28247	5.969725	0.642669	H	-6.85331	5.457034	-2.82401
C	-2.52985	3.516946	-0.64259	C	-6.46679	3.301273	2.732732
H	-0.4816	3.773442	-1.23268	H	-6.38213	2.229428	2.517724
C	-3.50026	5.300893	0.631336	H	-5.46054	3.653559	2.99491
H	-2.18696	6.918617	1.159934	H	-7.09628	3.415785	3.621049
C	-3.66493	4.036036	0.02231	C	-6.98196	-3.00963	2.131441
H	-2.60917	2.568526	-1.16635	H	-6.03233	-3.43953	2.476206
H	-4.34888	5.754176	1.137347	H	-6.83759	-1.9243	2.074357
C	0.100334	7.524255	0.001182	H	-7.73074	-3.20727	2.905198
C	0.833492	8.221906	0.968675	C	-6.17929	-3.93356	-2.81694
C	-0.61705	8.247136	-0.96071	H	-5.97029	-2.8891	-3.08298
C	0.853282	9.615217	0.962738	H	-5.20977	-4.43057	-2.69207
C	-0.60261	9.639628	-0.94488	H	-6.6835	-4.39487	-3.67219
C	0.136927	10.35142	0.010038	C	-0.70578	-7.4857	-2.47901
H	1.426787	10.14006	1.723298	H	-1.57978	-6.83047	-2.38887
H	-1.16921	10.18353	-1.69734	H	0.133531	-6.85546	-2.80102
C	-6.37258	4.067747	0.30444	H	-0.90493	-8.20082	-3.28357
C	-6.94846	4.796006	-0.76279	C	0.497507	-7.4759	2.481021
C	-7.03925	4.061319	1.553262	H	1.399617	-6.85999	2.389991
C	-8.15323	5.481903	-0.57143	H	-0.31659	-6.80583	2.786702
C	-8.23202	4.772447	1.713355	H	0.659111	-8.18752	3.297009
C	-8.80911	5.490277	0.661587	C	6.055266	-4.11519	2.806683
H	-8.58894	6.025829	-1.40812	H	5.871902	-3.06805	3.081008
H	-8.72654	4.761294	2.683583	H	5.074018	-4.58511	2.669865

C	-6.5779	-3.47347	-0.34274	H	6.540768	-4.59737	3.661235
C	-7.02268	-4.03725	-1.56208	C	6.907721	-3.1948	-2.13447
C	-7.40917	-3.58673	0.796645	H	5.948947	-3.60165	-2.48192
C	-8.26357	-4.67883	-1.62396	H	6.789884	-2.10616	-2.07937
C	-8.63565	-4.25269	0.702349	H	7.653979	-3.41163	-2.9055
C	-9.08428	-4.80562	-0.49983	C	6.55805	3.137344	-2.73139
H	-8.59631	-5.09249	-2.57472	H	6.444763	2.067398	-2.5201
H	-9.25906	-4.33737	1.591118	H	5.562108	3.51675	-2.99503
C	5.101354	-1.30523	0.138448	H	7.192682	3.238083	-3.61772
C	6.189014	-0.53558	0.609544	C	6.413405	4.644731	2.136116
C	4.030142	-0.59542	-0.44672	H	5.393076	5.041694	2.083588
C	6.190587	0.854333	0.527611	H	6.342209	3.642955	2.580343
H	7.046607	-1.04626	1.0408	H	6.982563	5.270381	2.83129
C	4.027224	0.794301	-0.5188	N	0.080462	6.092952	-0.00274
H	3.190784	-1.14564	-0.86214	H	-1.18843	7.71314	-1.7139
C	5.100147	1.564416	-0.02077	H	1.384324	7.668909	1.723428

Table S15. Coordinates (Å) for the optimized structure (B3LYP, 6-31G*) of the model system **MC-NB5** (without substituents).

Atom	X	Y	Z	Atom	X	Y	Z
C	3.730143	0.508151	-5.03361	C	-0.79744	0.905126	9.38525
C	3.836123	-0.14967	-3.78891	H	-1.40368	1.625249	7.443163
C	2.664502	-0.76477	-3.29645	C	0	0	10.089
C	1.464469	-0.72145	-4.00105	H	1.416842	-1.6186	9.922118
C	1.356928	-0.05943	-5.24385	H	-1.41684	1.618603	9.922118
C	2.529368	0.553135	-5.73753	H	0	0	11.17528
H	4.605726	1.000329	-5.44914	C	-6.45436	-0.25844	3.808337
H	2.700214	-1.28764	-2.34415	C	-6.62434	0.288578	5.09932
H	0.588565	-1.2121	-3.58447	C	-7.5625	-0.93242	3.249268
H	2.492443	1.080975	-6.68693	C	-7.83075	0.178023	5.789653
C	-1.35693	0.059425	-5.24385	H	-5.79806	0.823036	5.560281
C	-2.52937	-0.55314	-5.73753	C	-8.76332	-1.07107	3.943693
C	-1.46447	0.721452	-4.00105	H	-7.4724	-1.36443	2.256254
C	-3.73014	-0.50815	-5.03361	C	-8.90198	-0.50986	5.215236
H	-2.49244	-1.08098	-6.68693	H	-7.93586	0.623639	6.775751
C	-2.6645	0.764766	-3.29645	H	-9.59311	-1.60983	3.493
H	-0.58857	1.212096	-3.58447	H	-9.84087	-0.60629	5.754958
C	-3.83612	0.149667	-3.78891	C	-6.55053	0.25371	-3.75811
H	-4.60573	-1.00033	-5.44914	C	-6.66119	0.938691	-4.98851
H	-2.70021	1.287636	-2.34415	C	-7.72208	-0.3569	-3.25842
C	0	0	-7.60021	C	-7.87294	1.026348	-5.67218
C	0.993207	-0.68043	-8.3389	H	-5.78141	1.420396	-5.4066

C	-0.99321	0.680434	-8.3389	C	-8.93104	-0.29822	-3.95024
C	0.988482	-0.69488	-9.73289	H	-7.67661	-0.89826	-2.31746
H	1.773306	-1.2177	-7.80651	C	-9.01065	0.401364	-5.15648
C	-0.98848	0.69488	-9.73289	H	-7.9305	1.575071	-6.60889
H	-1.77331	1.217703	-7.80651	H	-9.81208	-0.7921	-3.54812
C	0	0	-10.4336	H	-9.95471	0.458278	-5.69274
H	1.756924	-1.2415	-10.2738	C	5.164392	-0.11259	-1.41904
H	-1.75692	1.2415	-10.2738	C	6.151253	-0.74377	-0.62974
H	0	0	-11.5208	C	4.153135	0.587033	-0.72481
C	3.73923	0.085924	3.785447	C	6.132755	-0.67212	0.76081
C	3.54537	0.753085	5.016483	H	6.943371	-1.30414	-1.11952
C	2.61948	-0.61303	3.278585	C	4.13119	0.652852	0.665829
C	2.326488	0.74821	5.683114	H	3.375435	1.09341	-1.29035
H	4.366753	1.319882	5.445894	C	5.121522	0.027877	1.453704
C	1.405722	-0.66571	3.951714	H	6.914562	-1.17211	1.327134
H	2.714282	-1.15594	2.342221	H	3.335859	1.207953	1.156813
C	1.234672	0.029827	5.162761	C	6.550526	-0.25371	-3.75811
H	2.209672	1.302194	6.608822	C	7.722084	0.356902	-3.25842
H	0.582596	-1.24408	3.545269	C	6.661188	-0.93869	-4.98851
C	-5.16439	0.112589	-1.41904	C	8.931043	0.298223	-3.95024
C	-4.15314	-0.58703	-0.72481	H	7.676612	0.898257	-2.31746
C	-6.15125	0.743772	-0.62974	C	7.872942	-1.02635	-5.67218
C	-4.13119	-0.65285	0.665829	H	5.781411	-1.4204	-5.4066
H	-3.37544	-1.09341	-1.29035	C	9.010647	-0.40136	-5.15648
C	-6.13276	0.672115	0.76081	H	9.812083	0.792098	-3.54812
H	-6.94337	1.304139	-1.11952	H	7.930495	-1.57507	-6.60889
C	-5.12152	-0.02788	1.453704	H	9.954714	-0.45828	-5.69274
H	-3.33586	-1.20795	1.156813	C	6.454363	0.258442	3.808337
H	-6.91456	1.172108	1.327134	C	6.624338	-0.28858	5.09932
C	-1.23467	-0.02983	5.162761	C	7.562495	0.932424	3.249268
C	-1.40572	0.665709	3.951714	C	7.830749	-0.17802	5.789653
C	-2.32649	-0.74821	5.683114	H	5.798059	-0.82304	5.560281
C	-2.61948	0.613032	3.278585	C	8.763324	1.071067	3.943693
H	-0.5826	1.244082	3.545269	H	7.472402	1.364427	2.256254
C	-3.54537	-0.75309	5.016483	C	8.901976	0.509855	5.215236
H	-2.20967	-1.30219	6.608822	H	7.935859	-0.62364	6.775751
C	-3.73923	-0.08592	3.785447	H	9.593114	1.609829	3.493
H	-2.71428	1.155939	2.342221	H	9.840867	0.606294	5.754958
H	-4.36675	-1.31988	5.445894	B	-5.10187	-0.1214	3.024092
C	0	0	7.283886	B	-5.18753	0.176212	-2.98716
C	0.793834	-0.91381	7.991268	B	0	0	-6.03248
C	-0.79383	0.913813	7.991268	B	5.187527	-0.17621	-2.98716
C	0.797444	-0.90513	9.38525	B	5.101869	0.121399	3.024092

H	1.403682	-1.62525	7.443163	N	0	0	5.854418

References

[1] (a) A. Pelter, K. Smith, D. Buss, Z. Jin, *Heteroatom Chemistry*, 1992, **3**, 275–277; (b) K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.*, 1993, **115**, 11353–11357.

[2] (a) S. I. Hauck, K. V. Lakshmi, J. F. Hartwig, *Org. Lett.*, 1999, **1**, 2057–2060; (b) R. A. Singer, J. P. Sadighi, S. L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 213–214; (c) P. Li, D. Shimoyama, N. Zhang, Y. Jia, G. Hu, C. Li, X. Yin, N. Wang, F. Jäkle and P. Chen, *Angew. Chem., Int. Ed.*, **2022**, 61, e2022006.

[3] (a) A. Ito, Y. Yokoyama, R. Aihara, K. Fukui, S. Eguchi, K. Shizu, T. Sato, K. Tanaka, *Angew. Chem., Int. Ed.*, 2010, **49**, 8205-8208. (b) P. Chen, R. A. Lalancette, F. Jäkle, *Angew. Chem., Int. Ed.*, 2012, **51**, 7994-7998. (c) N. Baser-Kirazli, R. A. Lalancette, F. Jäkle, *Angew. Chem., Int. Ed.*, 2020, **59**, 8689-8697. (d) P. Chen, F. Jäkle, *J. Am. Chem. Soc.*, 2011, **133**, 20142-20145. (e) P. Chen, X. Yin, N. Baser-Kirazli, F. Jäkle, *Angew. Chem., Int. Ed.*, 2015, **54**, 10768-10772. (f) N. Baser-Kirazli, R. A. Lalancette, F. Jäkle, *Organometallics* 2021, **40**, 520-528.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. H. Petersson, M. Nakatsuji, X. Caricato, H. P. F. Li, A. Hratchian, J. Izmaylov, G. Bloino, J. L. Zheng, M. Sonnenberg, M. Hada, K. Ehara, R. Toyota, J. Fukuda, M. Hasegawa, T. Ishida, Y. Nakajima, O. Honda, H. Kitao, T. Nakai, J. A. Vreven, J. E. Montgomery Jr., F. Peralta, M. Ogliaro, J. J. Bearpark, E. Heyd, K. N. Brothers, V. N. Kudin, T. Staroverov, R. Keith, J. Kobayashi, K. Normand, A. Raghavachari, J. C. Rendell, S. S. Burant, J. Iyengar, M. Tomasi, N. Cossi, J. M. Rega, M. Millam, J. E. Klene, J. B. Knox, V. Cross, C. Bakken, J. Adamo, R. Jaramillo, R. E. Gomperts, O. Stratmann, A. J. Yazyev, R. Austin, C. Cammi, J. W. Pomelli, R. L. Ochterski, K. Martin, V. G. Morokuma, G. A. Zakrzewski, P. Voth, J. J. Salvador, S. Dannenberg, A. D. Dapprich, O. Daniels, J. B. Farkas, J. V. Foresman, J. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Revision C. 01, 2010.

[5] (a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

[6] (a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724–728; (b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.