Supporting Information

Multiple Resonance Thermally Activated Delayed Fluorescence Enhanced by Halogen Atoms

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1. Experimental Procedures

1.1. Quantum chemical calculations

Density functional theory (DFT) calculations were performed to predict optimized molecular structures, total enthalpies, and orbital distributions of frontier orbitals using Gaussian 09 software. B3LYP functionals and 6-31G(d) basis set were utilized for calculation of MR and Cl-MR. B3LYP functional and 6-31G(d) and LanL2DZ basis set were utilized for calculation of Br-MR. Time-dependent density functional theory (TD-DFT) calculations were performed to estimate singlet and triplet energies and spin-orbit coupling constants of excited states using Orca 5.0.1 software at B3LYP/G functional and def2-SVP basis set. Natural transition orbital calculations were performed to predict orbital distributions of excited states using Gaussian 09 software at B3LYP/6-31G(d) level.

1.2. Photophysical property analysis

UV-visible spectra were recorded on a Jasco V-730 spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Jasco FP-8300 spectrophotometer. Absolute quantum efficiencies were obtained with a PTI QuantaMaster 40 spectrofluorometer using a

3.2 in. integrating sphere at room temperature. Transient photoluminescence (PL) was measured through the time-correlated single-photon counting (TCSPC) techniques by using a PicoQuant, FluoTime 250 instrument. A 377 nm pulsed laser was used as an excitation source.

1.3. Electrochemical and thermal analysis

Cyclic voltammetry (CV) experiments were conducted in dichloromethane solution (1.00 mM) with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. A glassy carbon electrode was employed as the working electrode and referenced to an Ag reference electrode. All potential values were calibrated against the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with DSC Q10 and TGA Q50 of TA instruments in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

1.4. Device fabrication and measurements

The patterned indium-tin-oxide (ITO, 70 nm) substrates were washed with water and isopropyl alcohol, followed by 10 min UV-ozone treatment. Organic layers, LiF, and Al were thermally evaporated at a deposition rate of 1−2 Å s^{-1} for organic layers, 0.1 Å s^{-1} for LiF, and 3−5 Å s^{-1} for the Al electrode. OLED properties were measured using a Keithley source meter 2400 and a PR-650 spectrascan colorimeter.

1.5. Synthesis and characterization

Commercially available reagents and solvents were used without further purification unless otherwise noted. MR was synthesized by following previously reported references.[1] ^{1}H- and ^{13}C-spectra were recorded using a Varian/Oxford As-500 500 MHz in CDCl$_3$ and DMSO. ^{1}H-NMR chemical shifts were referenced to CHCl$_3$ (7.26 ppm) and DMSO (2.50 ppm). ^{13}C-NMR chemical shifts in CDCl$_3$ were reported relative to CHCl$_3$ (77.23 ppm). Elemental analysis (EA) data (Thermo Fisher Scientific, Flash2000) and high-resolution mass spectrometric (HRMS) data (JEOL, JMS-700) with fast atom bombardment (FAB) positive mode were received directly from the National Center for Inter-University Research Facilities (NCIRF).
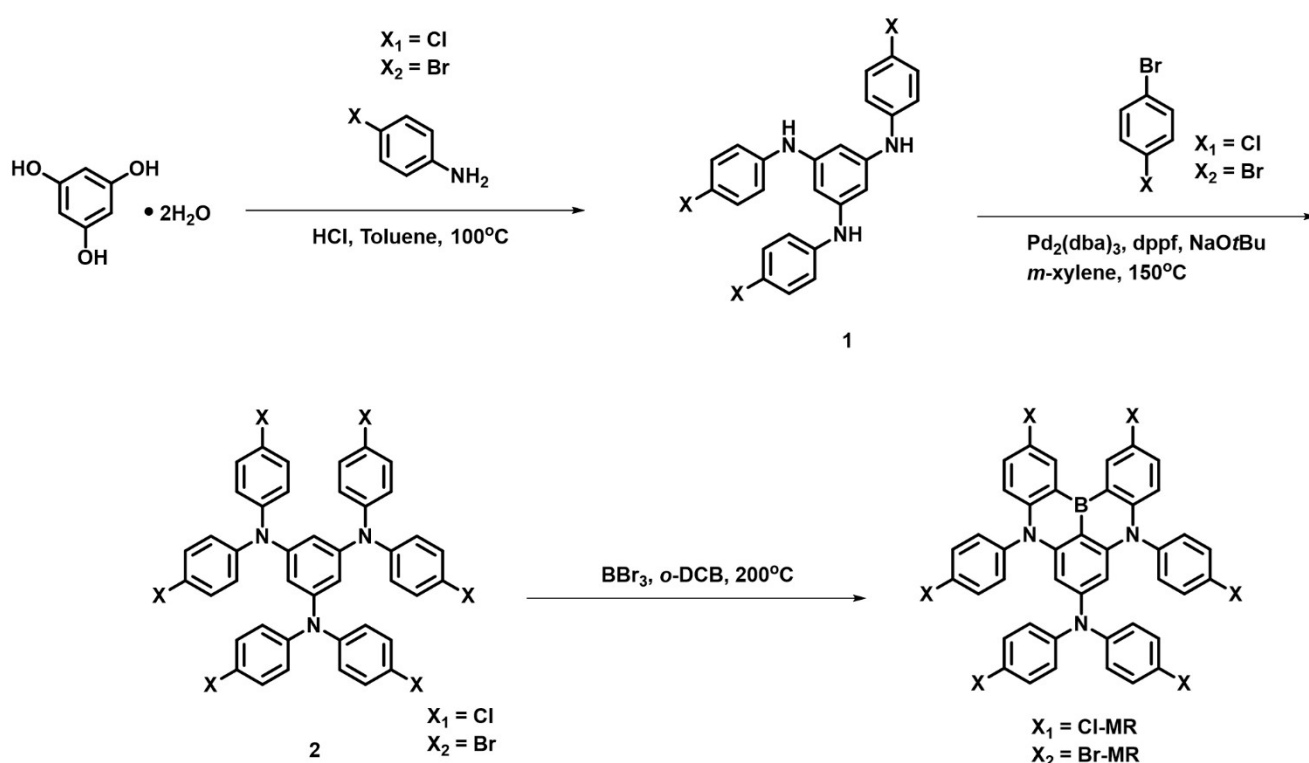
Scheme S1. Synthesis routes of Cl-MR and Br-MR

2. Synthesis

2.1. Synthesis of N1,N3,N5-tris(4-chlorophenyl)benzene-1,3,5-triamine (1-Cl)

A mixture of phloroglucinol dihydrate (3.0 g, 18.5 mmol), 4-chloroaniline (9.4 g, 74.0 mmol), and catalytic amount of HCl in toluene (14 mL) was degassed and refilled with nitrogen gas. Then, the reaction mixture was stirred at 100°C for 1 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The crude product was purified by recrystallization from single phase ethanol to afford 1-Cl (7.1 g, 84%) as a pale brown solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.21 (d, J = 8.7 Hz, 6H), 7.00 (d, J = 8.7 Hz, 6H), 6.26 (s, 3H), 5.60 (s, 3H).

2.2. *Synthesis of N^1,N^1,N^3,N^3,N^5,N^5-hexakis(4-chlorophenyl)benzene-1,3,5-triamine (2-Cl)*

A mixture of 1-Cl (1.1 g, 1.87 mmol), 1-bromo-4-chlorobenzene (3.2 g, 16.8 mmol), tris(dibenzylideneacetone)dipalladium(0) (86 mg, 0.094 mmol), 1,1'-bis(diphenylphosphino)ferrocene (209 mg,   0.37 mmol), and NaO^{t}Bu (650 mg, 6.73 mmol) in *m*-xylene (37 mL) was degassed   and refilled with nitrogen gas. Then, the reaction mixture was stirred at 150°C for 24 h. The reaction mixture was cooled to room temperature and filtered with silica using dichloromethane. After the solvent was evaporated, the crude product was purified by column chromatography using dichloromethane and hexane (1:6) to afford 2-Cl (1.2 g, 82%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.15 (d, J = 8.7 Hz, 12H), 6.91 (d, J = 8.7 Hz, 13H), 6.26 (s, 3H).

2.3. *Synthesis of 2,12-dichloro-N,N,5,9-tetrakis(4-chlorophenyl)-5,9-dihydro-5,9-diaza-13b-boranaphtho[3,2,1-de]anthracen-7-amine (Cl-MR)*

A mixture of 2-Cl (1.1 g, 1.40 mmol) and *o*-DCB were degassed and refilled with nitrogen gas.   After the reaction mixture was cooled using ice water, boron tribromide (12.6 g, 50.4 mmol) was added to the mixture. Then, the reaction mixture was stirred at 200°C for

24 h. The reaction mixture was cooled to room temperature and degassed to remove HBr gas. After the mixture was poured into the ice water, organic phase was extracted with dichloromethane. The solvent was evaporated, and the crude product was purified by column chromatography (CHCl$_3$:Hex=1:6) and recrystallized from dichloromethane and ethanol to afford Cl-MR (640 mg, 56%) as a yellow solid ^{1}H NMR (500 MHz, DMSO) δ 8.58 (d, J = 2.5 Hz, 2H), 7.67 (d, J = 8.6 Hz, 4H), 7.53 (dd, J = 9.3, 2.4 Hz, 2H), 7.34 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 8.7 Hz, 4H), 6.97 (d, J = 8.8 Hz, 4H), 6.74 (d, J = 9.2 Hz, 2H), 5.35 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.00, 147.67, 145.63, 144.38, 139.96, 134.83, 133.38, 131.38, 131.27, 130.91, 129.70, 129.20, 126.76, 126.06, 118.35, 98.28, 77.25, 77.00, 76.75; HRMS (FAB+) m/z: [M]$^+$ calcd for C$_{42}$H$_{24}$BCl$_6$N$_3$: 791.0194; found: 791.0202. EA : calcd for C$_{42}$H$_{24}$BCl$_6$N$_3$ C 63.52, H 3.05, N 5.29; found C 63.54, H 3.04, N 5.39.

2.4. Synthesis of N^1,N^3,N^5-tris(4-bromophenyl)benzene-1,3,5-triamine (1-Br)

A mixture of phloroglucinol dihydrate (500 mg, 3.96 mmol), 4-bromoaniline (2.73 g, 15.86 mmol), and catalytic amount of HCl in toluene (3 mL) was degassed and refilled with nitrogen gas. The reaction mixture was stirred at 100°C for 1 h and then was cooled to room temperature. The crude product obtained after solvent removal was purified by recrystallization from single phase ethanol to afford 1-Br (1.21 g, 52%) as a dark brown solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, J = 8.7 Hz, 6H), 6.95 (d, J = 8.6 Hz, 6H), 6.28 (s, 3H), 5.61 (s, 3H).

2.5. Synthesis of N^1,N^1,N^3,N^3,N^5,N^5-hexakis(4-bromophenyl)benzene-1,3,5-triamine (2-Br)

A mixture of 1-Br (1.0 g, 1.7 mmol), 1,4-dibromobenzene (6 g, 25.5 mmol), tris(dibenzylideneacetone)dipalladium(0) (78 mg, 0.085 mmol), 1,1'-bis(diphenylphosphino)ferrocene (188 mg, 0.34 mmol), and NaO^{t}Bu (588 mg, 6.12 mmol) in *m*-xylene (17 mL) was degassed and refilled with nitrogen gas. Then, the reaction mixture was stirred at 150°C for 24 h and was cooled to room temperature and filtered with silica using dichloromethane. After the solvent was evaporated, the crude product was purified by column chromatography using dichloromethane and hexane (1:6) to afford 2-Br (1.1 g, 65%) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.28 (m, 12H), 6.88 – 6.84 (m, 12H), 6.28 (s, 3H).

2.6. *Synthesis of 2,12-dibromo-N,N,5,9-tetrakis(4-bromophenyl)-5,9-dihydro-5,9-diaza-13b-boranaphtho[3,2,1-de]anthracen-7-amine (Br-MR)*

A mixture of 2-Br (1.0 g, 0.94 mmol) and *o*-DCB were degassed and refilled with nitrogen gas. After the reaction mixture was cooled using ice water, boron tribromide (8.5 g, 33.8 mmol) was added to the mixture. Then, the reaction mixture was stirred at 200°C for 24 h. The reaction mixture was cooled to room temperature and degassed for removing HBr gas. After the mixture was poured into the ice water, organic phase was extracted with dichloromethane. After the solvent was evaporated, the crude product was purified by recrystallization from chloroform and ethanol to afford Br-MR (630 mg, 63%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 8.69 (d, *J* = 1.8 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 4H), 7.64 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 4H), 6.68 (d, *J* = 9.1 Hz, 2H), 5.38 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.00, 147.67, 145.63, 144.38, 139.96, 134.83, 133.38, 131.38, 131.27, 130.91, 129.70, 129.20, 126.76, 126.06, 118.35, 98.28, 77.25, 77.00, 76.75; HRMS (FAB+) *m/z*: [M]$^+$ calcd for

$C_{42}H_{24}BCl_6N_3$: 791.0194; found: 791.0202. EA : calcd for $C_{42}H_{24}BBr_6N_3$ C 47.55, H 2.28, N 3.96; found C 47.66, H 2.23, N 3.95.

3. Equations for the calculation of the rate constants[2, 3]

$$k_{PF} = 1/\tau_{PF} \tag{1}$$

$$k_{DF} = 1/\tau_{DF} \tag{2}$$

$$k_r^S = \Phi_{PF}/\tau_{PF} \tag{3}$$

$$\Phi = k_r^S/(k_r^S + k_{IC}) \rightarrow k_{IC} = k_r^S/\Phi - k_r^S \tag{4}$$

$$\Phi_{PF} = k_r^S/(k_r^S + k_{IC} + k_{ISC}) \rightarrow k_{ISC} = k_r^S/\Phi_{PF} - k_r^S - k_{IC} \tag{5}$$

By assuming (i) $k_{PF} \gg k_{DF}$, (ii) $k_r^S \gg k_{IC}, k_{RISC}$ and (iii) $k_{RISC} \gg k_r^T, k_{nr}^T, k_{CQ}, k_{PF}$ and $k_{PF}k_{DF}$ can be expresses as $k_r^S + k_{ISC}$ and $k_r^S * k_{RISC}$, where k_{PF} and k_{DF} are the rate constants for prompt and delayed fluorescence, respectively, $k_r^S, k_{IC},$ and k_{ISC} are the rate constants for radiative decay, internal conversion, and intersystem crossing from S_1, respectively, $k_r^T, k_{nr}^T, k_{RISC},$ and k_{CQ} are the rate constants of radiative decay, non-radiative decay, reverse intersystem crossing, and concentration quenching from T_1, respectively. Thus k_{RISC} can be simplified to (6).

$$k_{RISC} = k_{PF}k_{DF}/(k_{PF} - k_{ISC}) \tag{6}$$

4. Supplementary figures
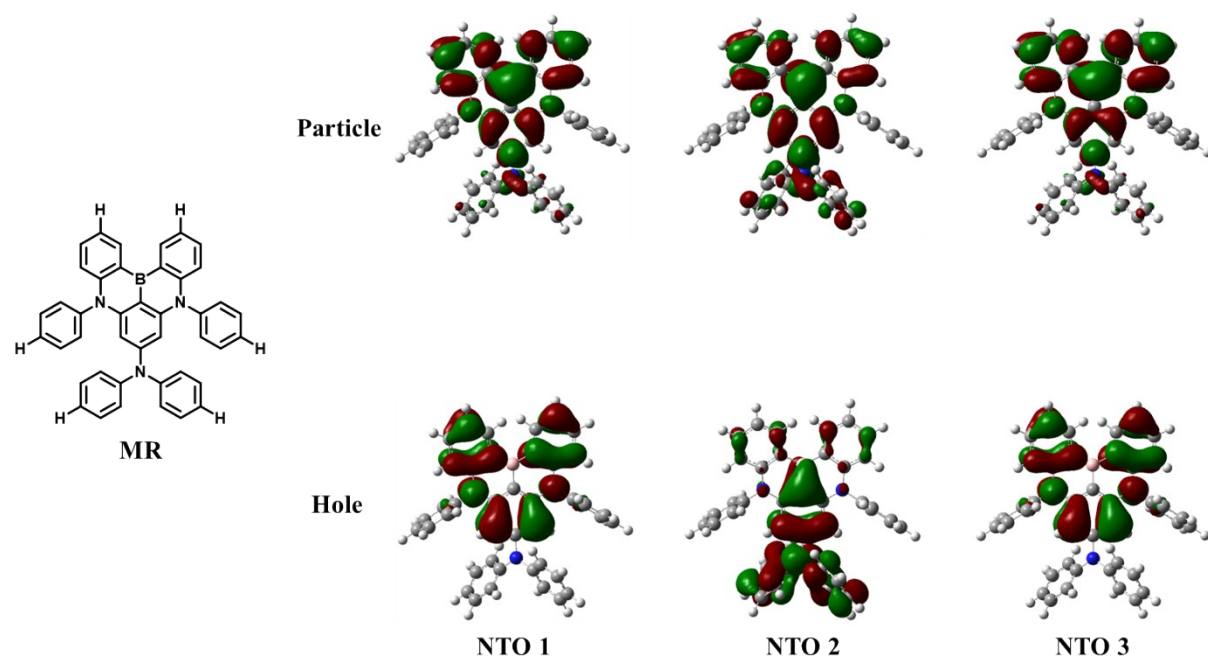
Figure S1. NTO distribution of MR.
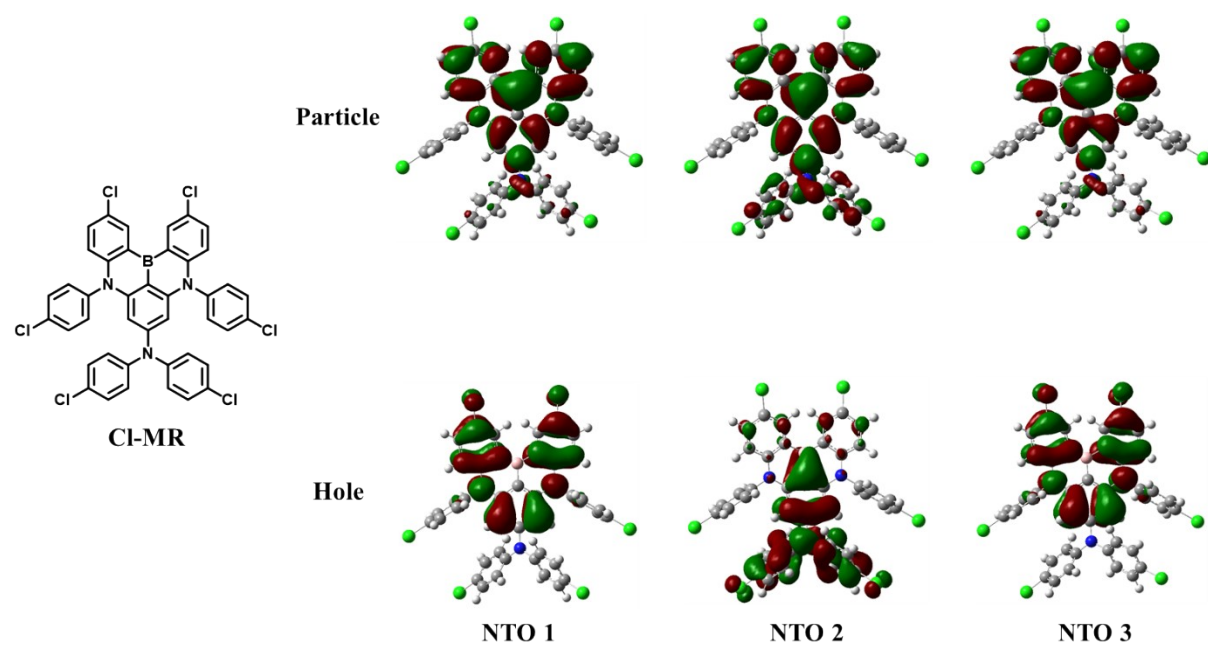
Figure S2. NTO distribution of Cl-MR.
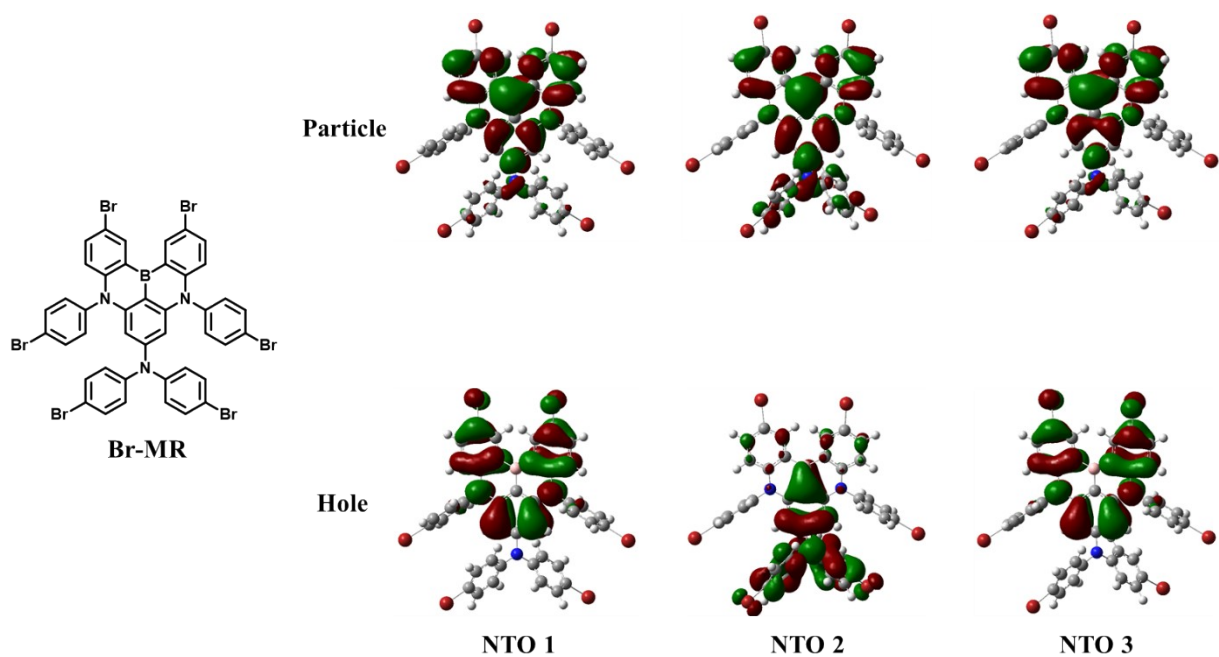
Figure S3. NTO distribution of Br-MR.
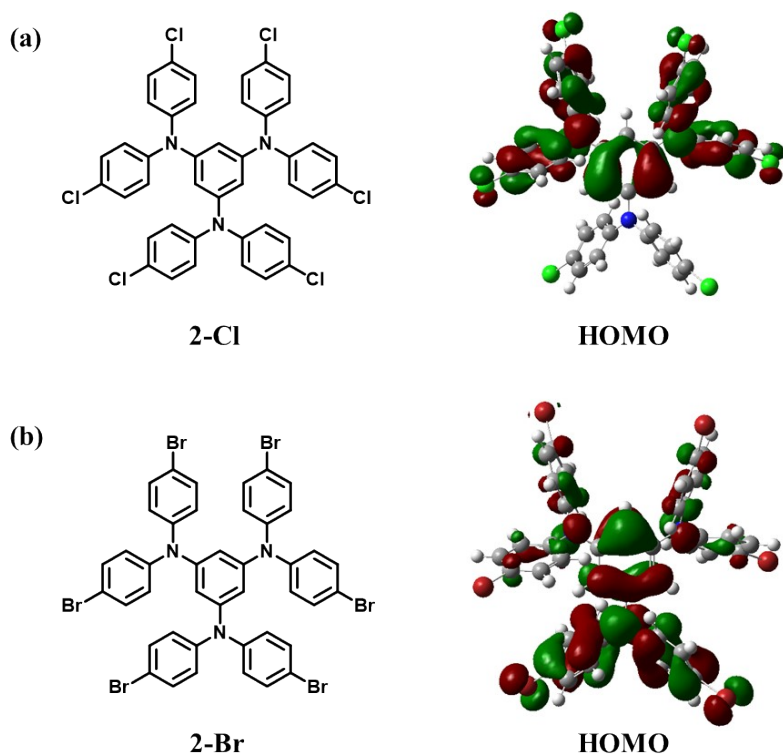
Figure S4. Molecular structures and orbital distributions of 2-Cl and 2-Br
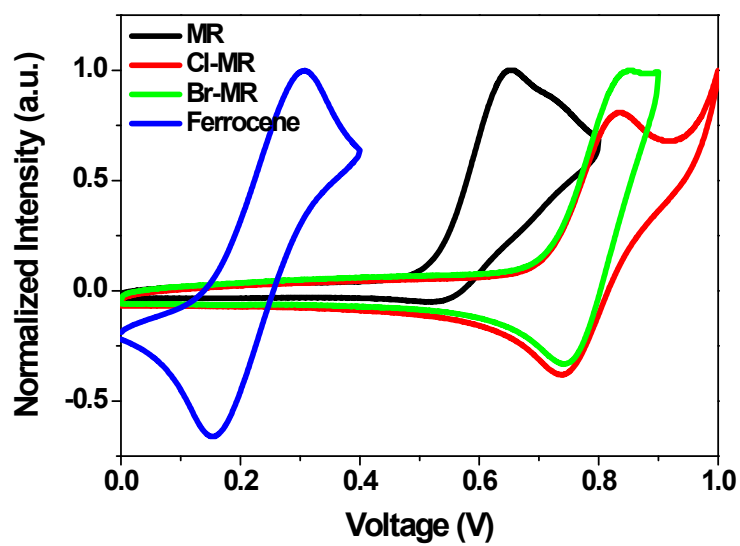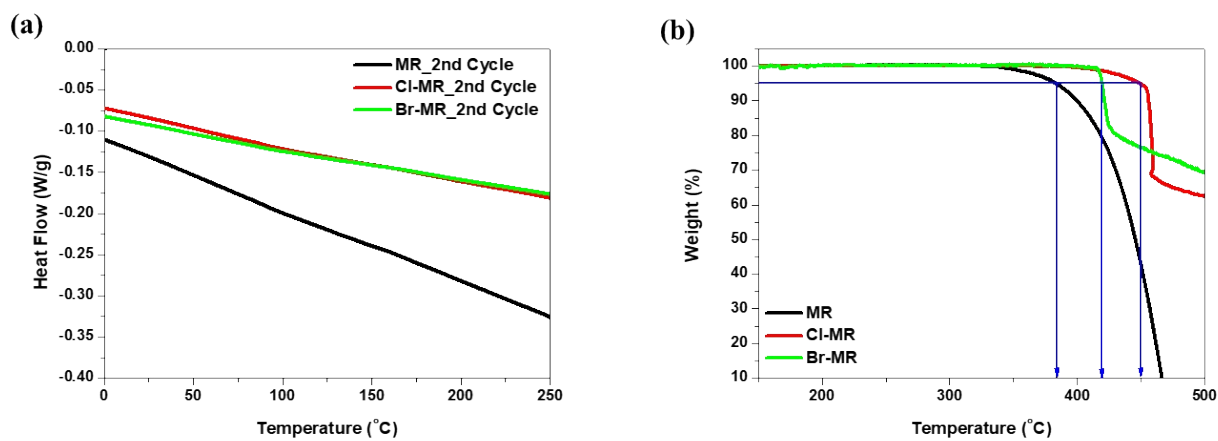
Figure S5. Cyclic voltammograms.

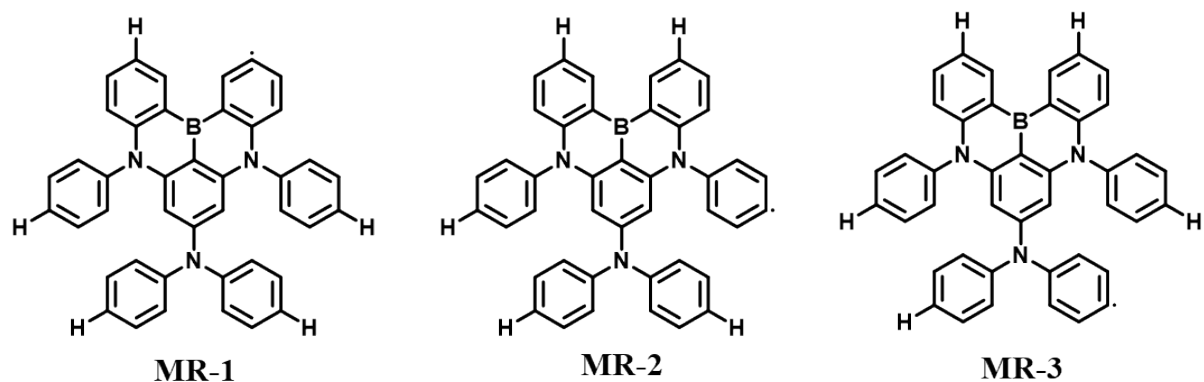**Figure S6.** (a) DSC thermograms, (b) TGA thermograms.

Figure S7. Homolytically cleavaged MR structures.

Table S1. Calculated enthalpies of MR structures

	MR [eV]	MR-1 [eV]	MR-2 [eV]	MR-3 [eV]	H· [eV]
Enthalpy	49172.7714	49154.3996	49154.3996	49154.3914	13.5489
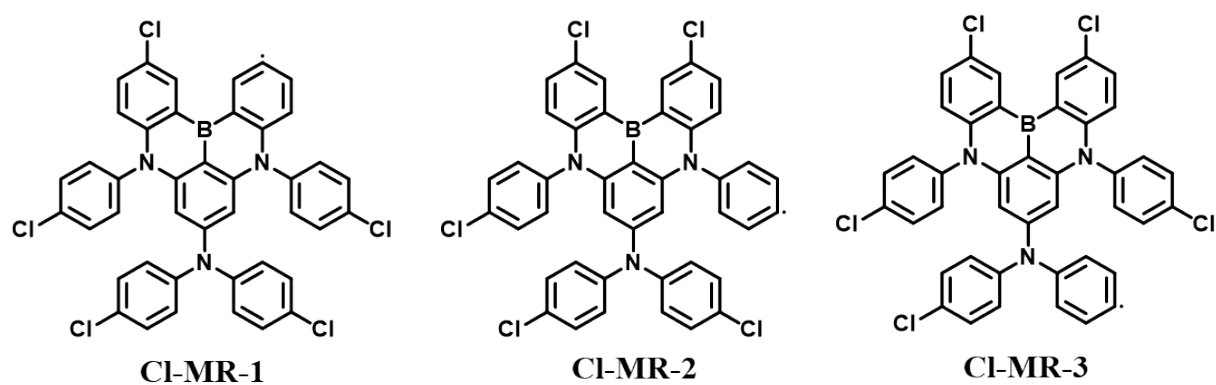
Figure S8. Homolytically cleavaged Cl-MR structures.

Table S2. Calculated enthalpies of Cl-MR structures

	Cl-MR [eV]	Cl-MR-1 [eV]	Cl-MR-2 [eV]	Cl-MR-3 [eV]	Cl· [eV]
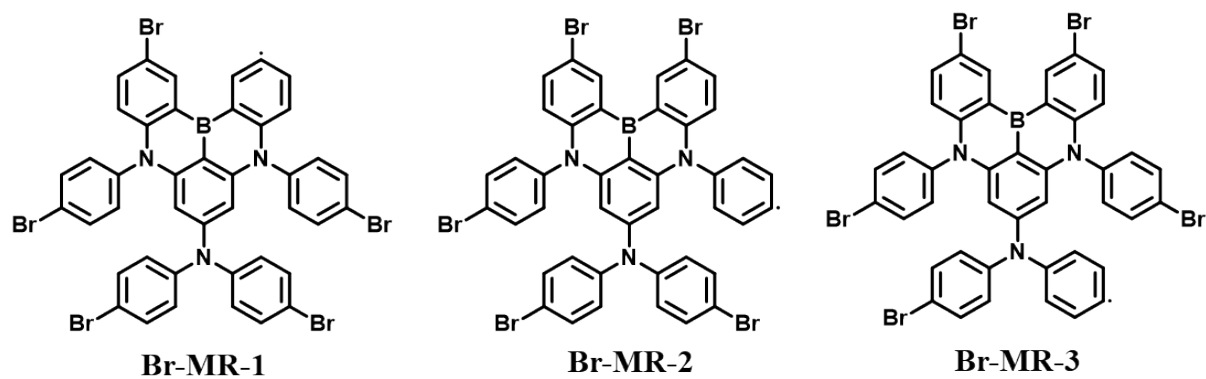
Figure S9. Homolytically cleavaged Br-MR structures.

Enthalpy	124211.5962	111686.7381	111686.7792	111686.7470	12520.8871

Table S3. Calculated enthalpies of Br-MR structures

	Br-MR [eV]	Br-MR-1 [eV]	Br-MR-2 [eV]	Br-MR-3 [eV]	Br· [eV]
Enthalpy	51223.5700	50862.4611	50863.2612	50863.2227	357.2336
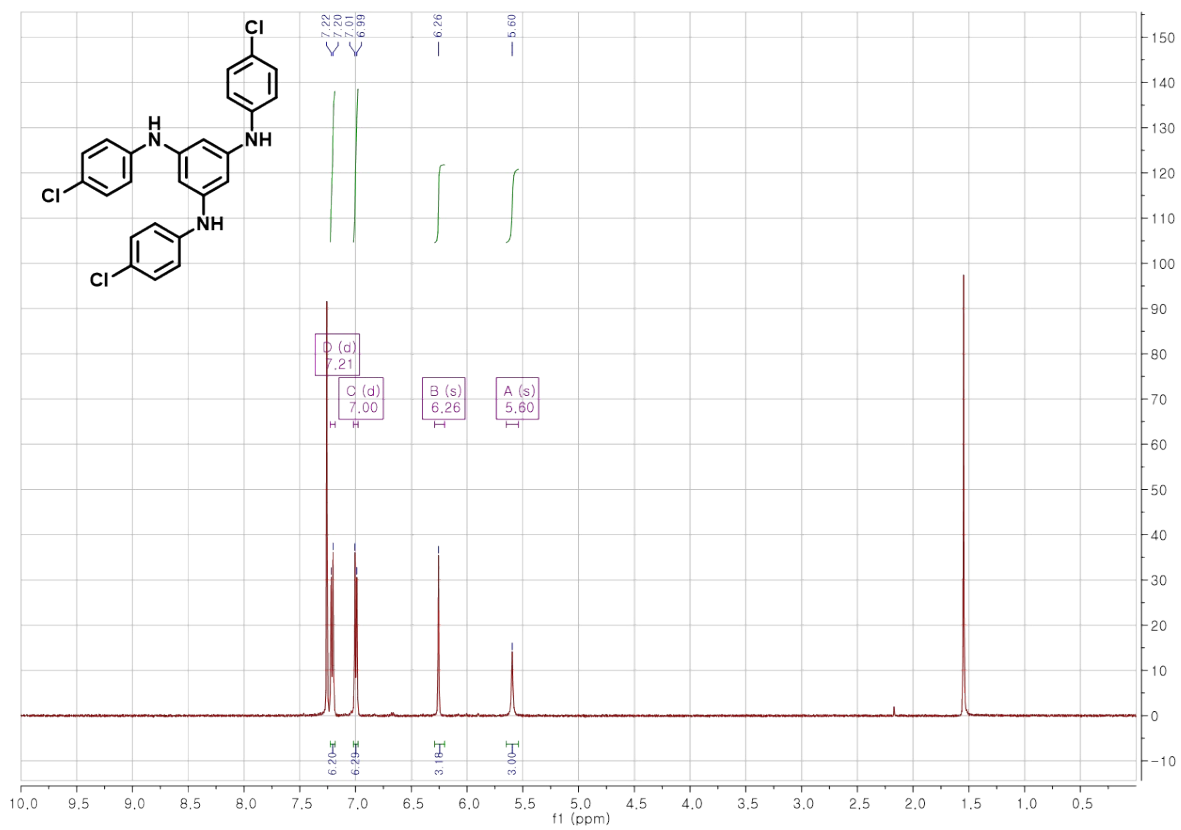
Figure S10. ^{1}H-NMR spectra of 1-Cl
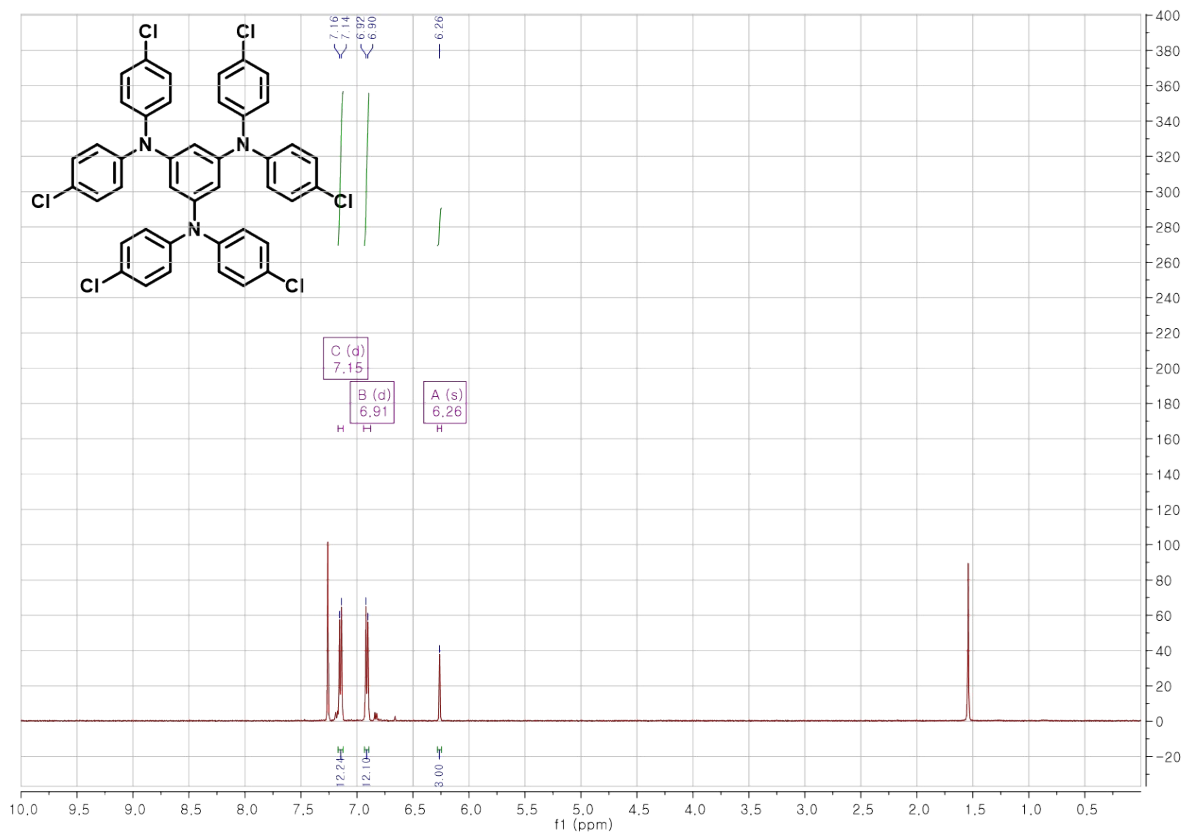
Figure S11. ^{1}H-NMR spectra of 2-Cl
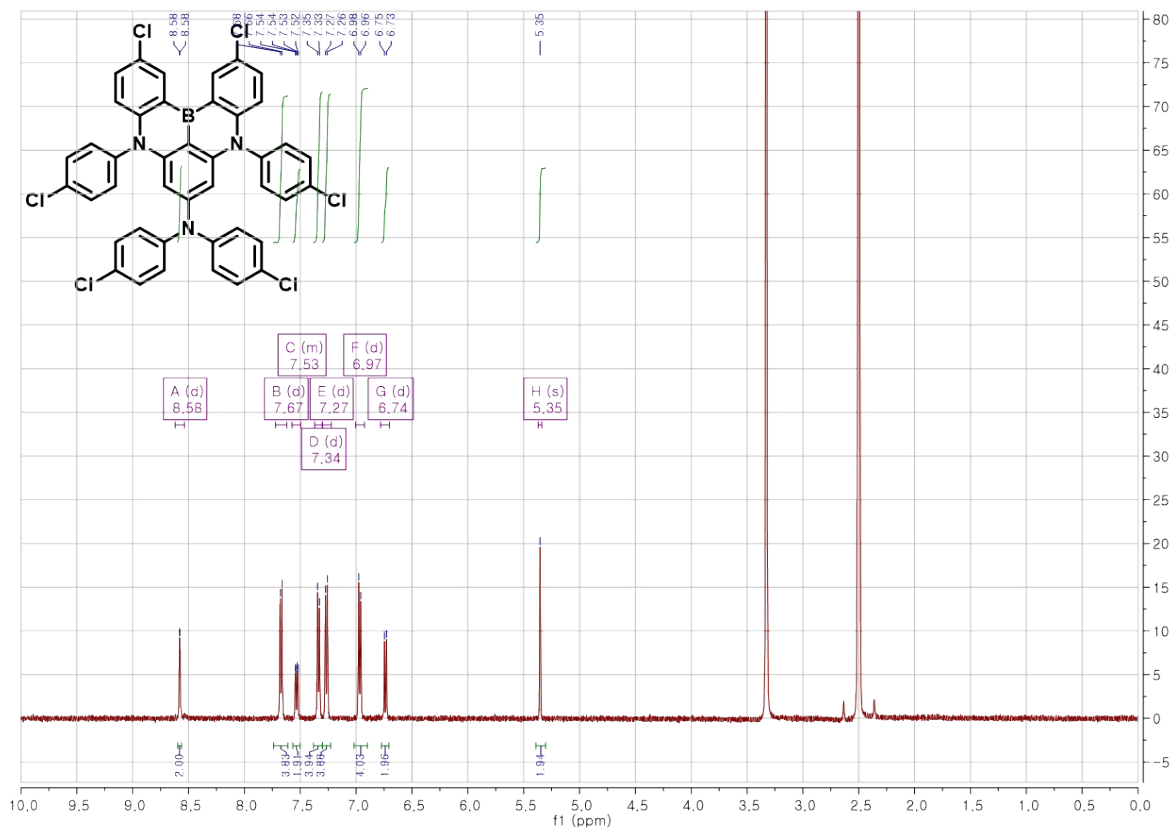
Figure S12. ^{1}H-NMR spectra of Cl-MR
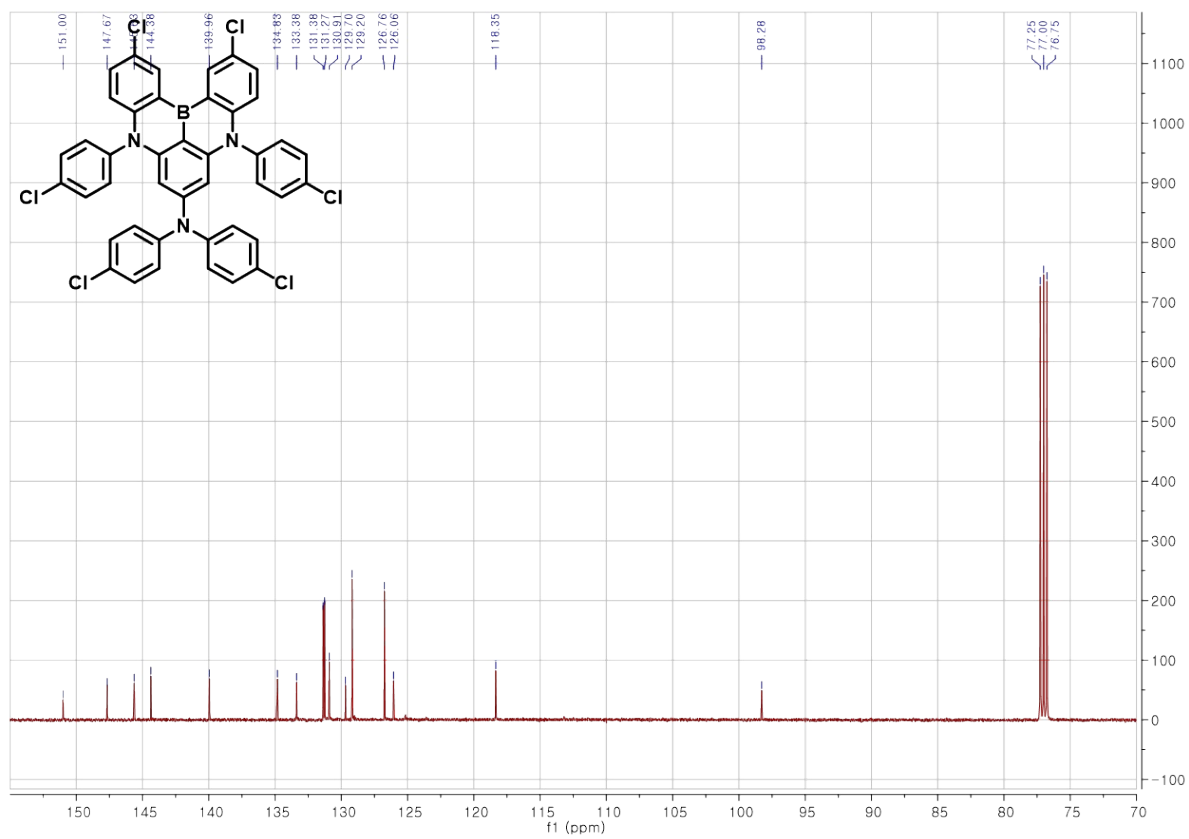
Figure S13. ^{13}C-NMR spectra of Cl-MR
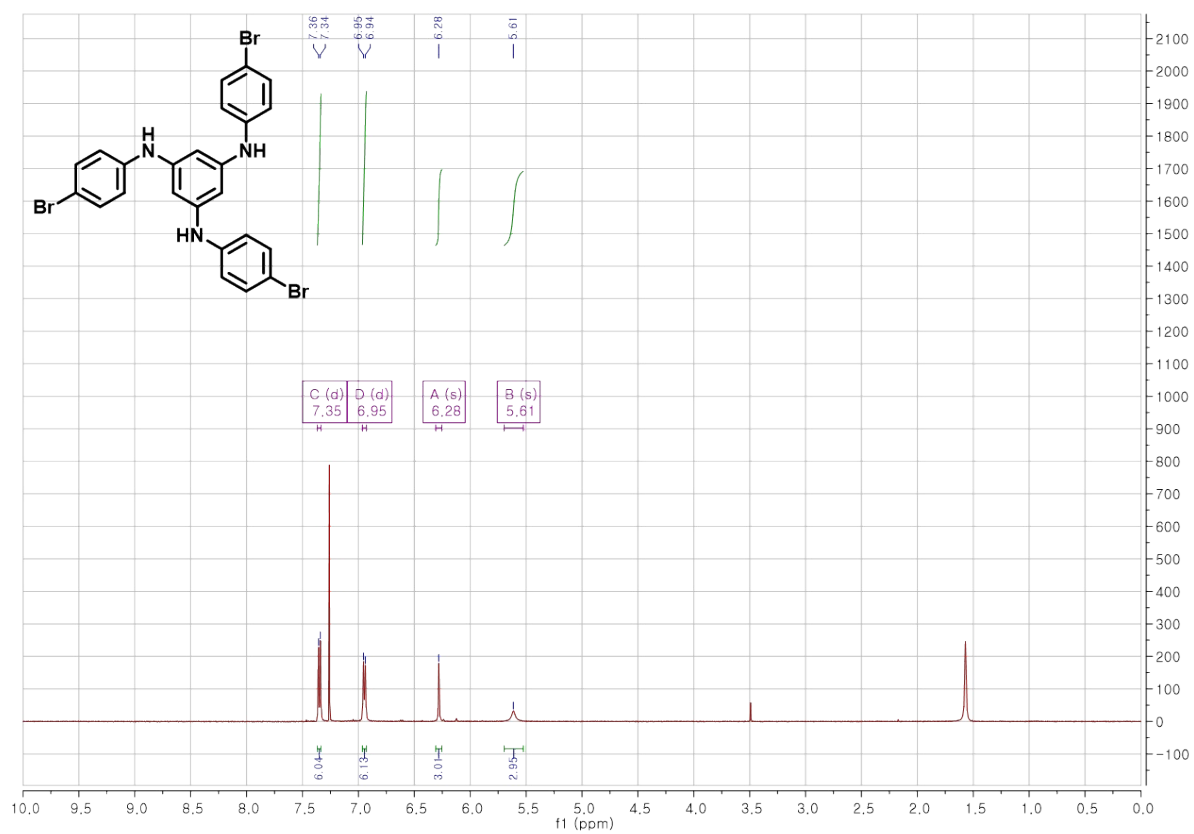
Figure S14. ^{1}H-NMR spectra of 1-Br
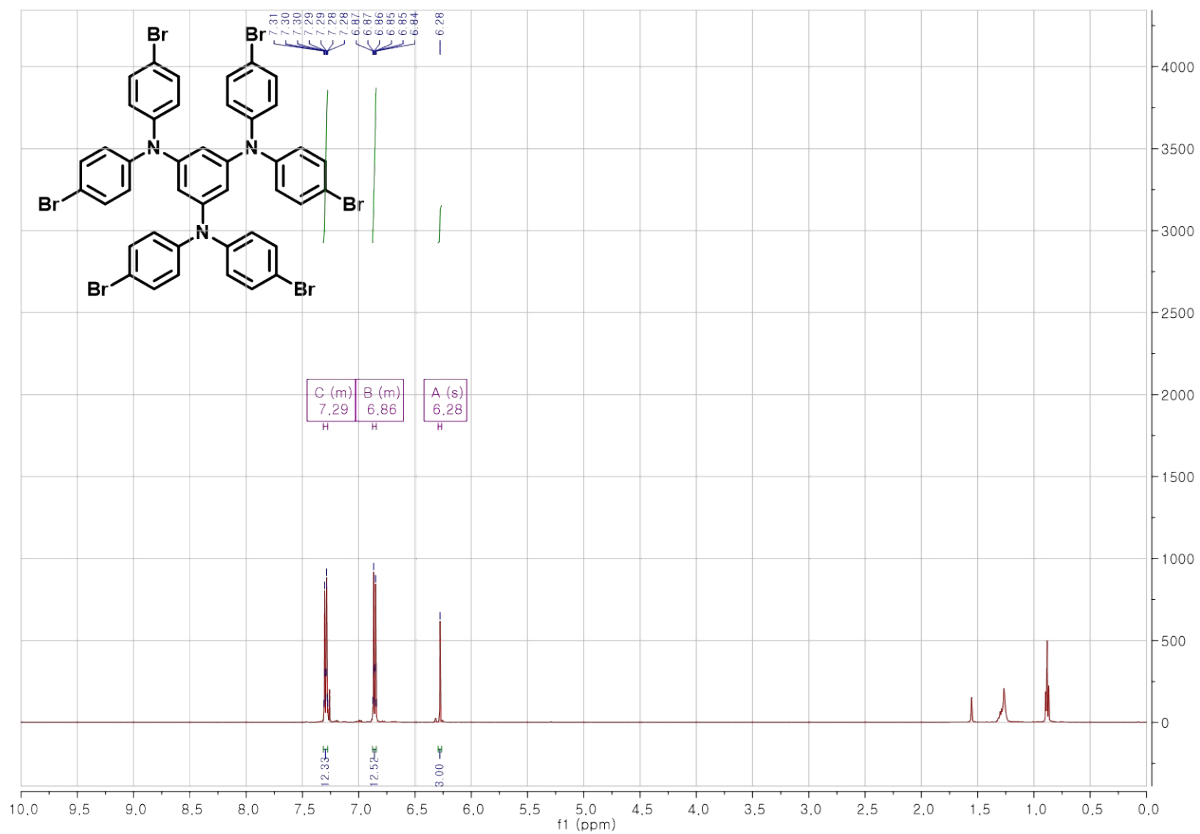
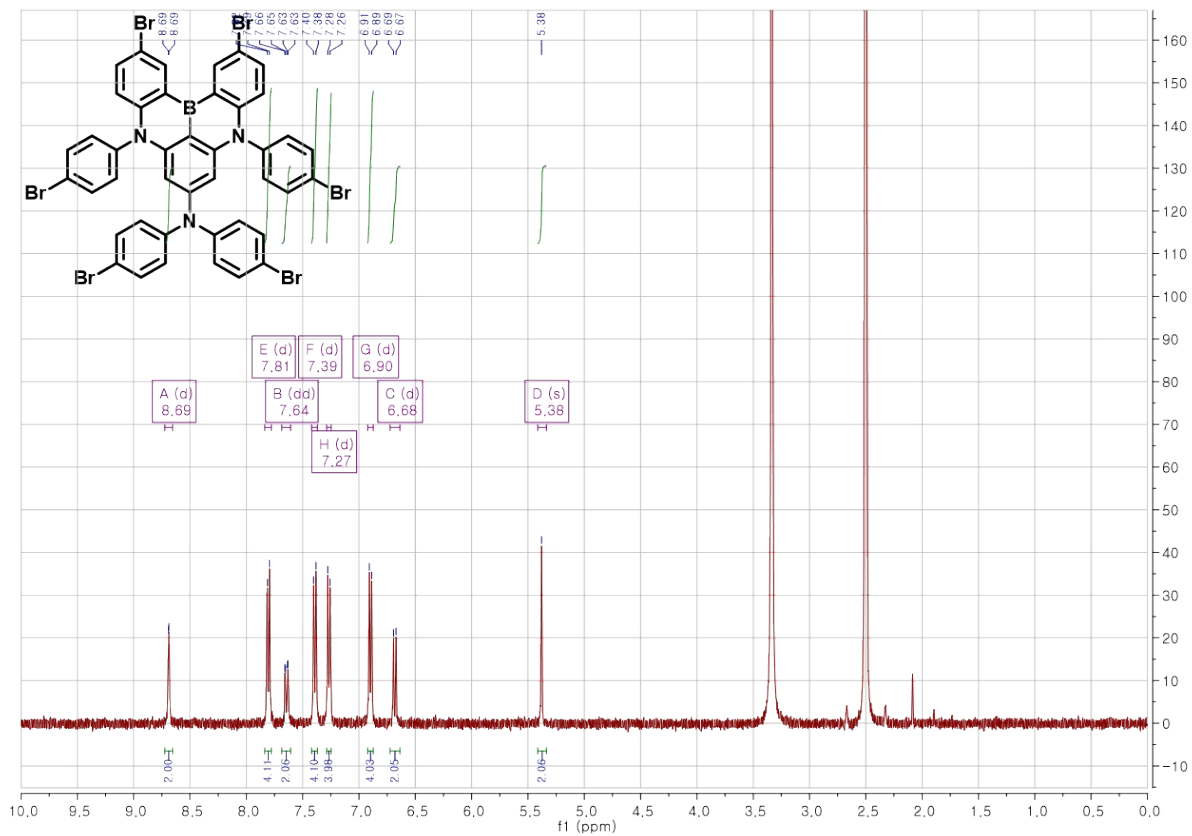**Figure S15.** ^{1}H-NMR spectra of 2-Br

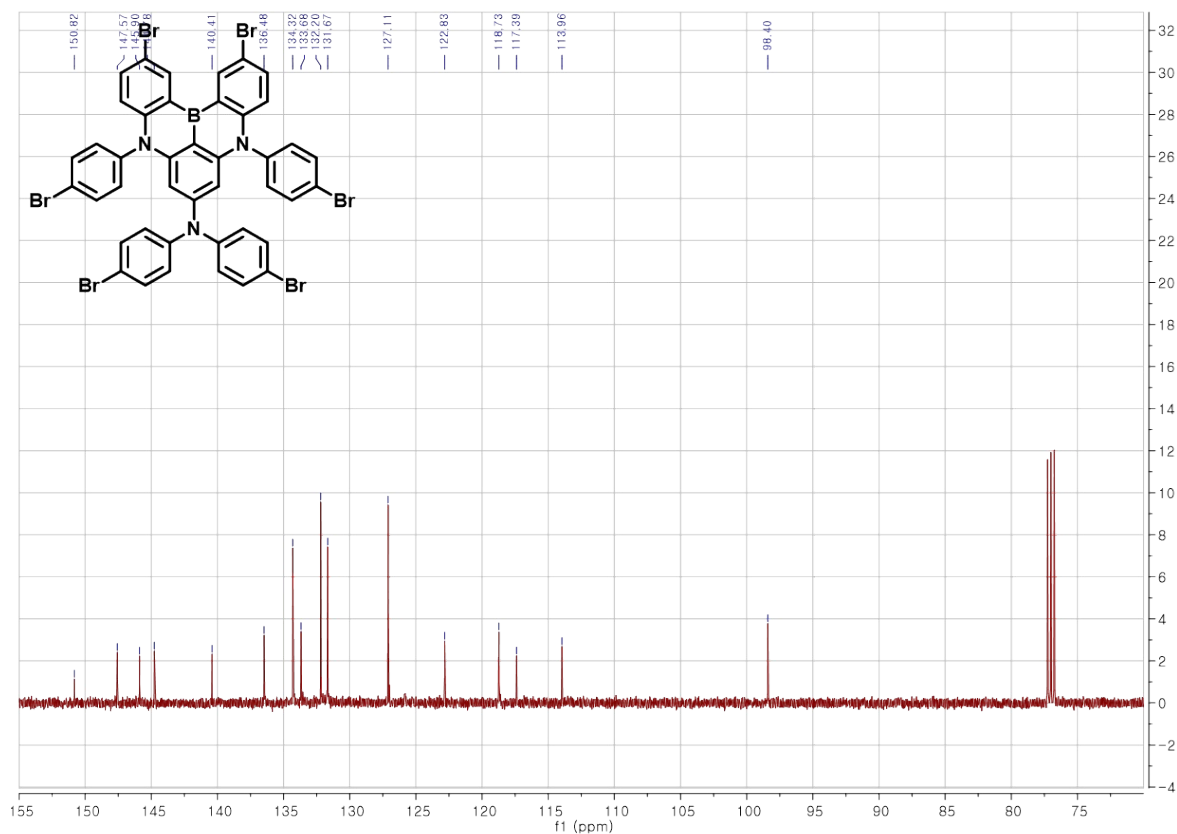**Figure S16.** [superscript 1]H-NMR spectra of Br-MR

Figure S17. ^{13}C-NMR spectra of Br-MR

3. References

1.   Y. Wang, Y. Duan, R. Guo, S. Ye, K. Di, W. Zhang, S. Zhuang and L. Wang, *Org. Electron.*, 2021, **97**, 106275.

2.   J. Lee, N. Aizawa, M. Numata, C. Adachi and T. Yasuda, *Adv. Mat.*, 2017, **29**, 1604856.

3.   S. Oda, B. Kawakami, R. Kawasumi, R. Okita and T. Hatakeyama, *Org. Lett.*, 2019, **21**, 9311-9314.