Electronic Supplementary Material (ESI) for Dalton Transactions.

Self-assembly of triangular metallomacrocycles using unsymmetrical bisterpyridine ligands: isomer differentiation *via* TWIM mass spectrometry

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Contents

Materials and Methods

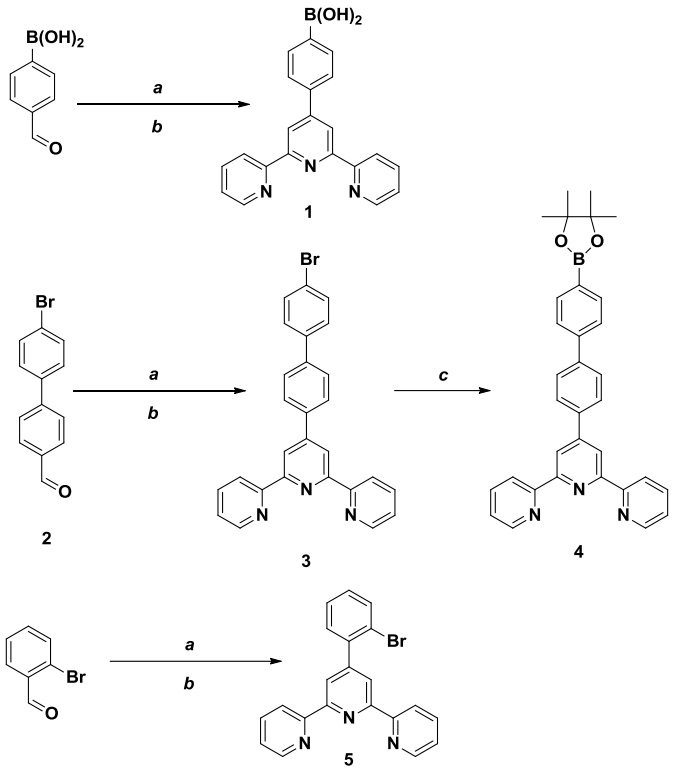
Materials and General Methods. Unless otherwise noted, reagents and solvents were used as received from Fisher Scientific and Sigma-Aldrich without further purification. $Zn(NTf_2)_2$ were synthesized according to the literature procedure.[1] Column chromatography was conducted using basic Al_2O_3 (50-200 μm) from Acros and silica gel (75-200 μm) from Fuji Silysia GS series. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Mercury NMR 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to the nondeuterated solvents as a reference.

X-ray Crystallography. Single crystal X-ray data were collected from Oxford Diffraction Gemini A CCD diffractometer using CrysAlisPro software (Agilent Technologies). Graphite monochromated Cu-K_α radiation (λ = 1.54178 Å) at 200(2) K was used to collect diffraction data. Empirical absorption correction using spherical harmonics from SCALE3 ABSPACK[2] was applied. The structure was solved and refined using SHELXS-97[3] and SHELXL-97[4] programs, respectively. In the crystal, three MeCN solvent molecules were not properly modeled. Therefore, the structure was refined by masking MeCN molecules with PLATON/SQUEEZE technique. The structure was deposited at the Cambridge Crystallographic Data Center with the deposition number of CCDC 1024226.

MALDI TOF Mass Spectrometry. Matrix-assisted laser desorption/ionization coupled with time-of-flight detector (MALDI TOF) mass spectrometry was conducted on a Bruker Autoflex Speed MALDI TOF/TOF Mass spectrometer with a Nd-YAG 355 nm laser. 1 μL of CHCA (α-cyano-4-hydroxycinnamic acid) matrix solution (10 mg/ml in a mixture of $MeCN/H_2O$/TFA = 50/49.9/0.1 wt%) was first deposited on a MALDI plate and air-dried. Aliquots of sample solution (1 mg/ml in $CHCl_3$) were then added onto the matrix spots for characterization. The spectra were acquired in reflection mode.

Ligand Synthesis

4'-(4-Boronophenyl)-2,2':6',2''-terpyridine (**1**)[5] and 4'-bromo-1,1'-biphenyl-4-carboxaldehyde (**2**)[6] were synthesized according to the literature procedures.



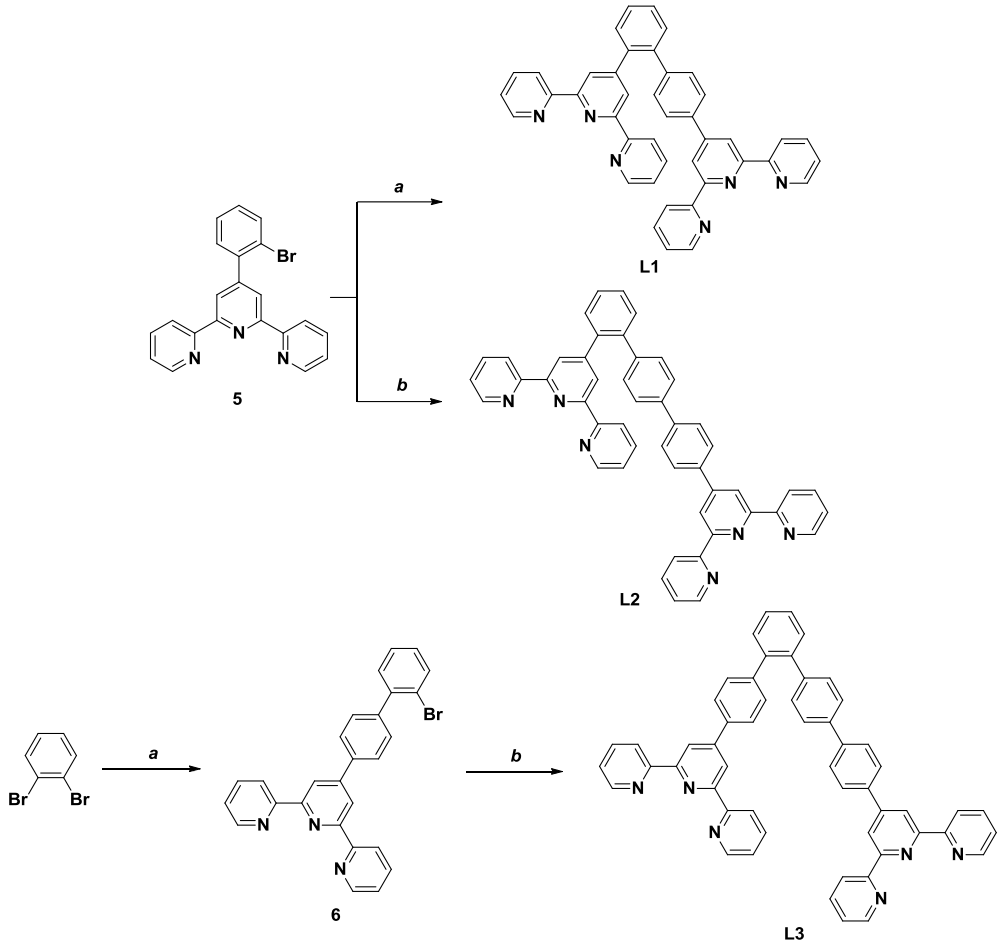
Scheme S1 Synthesis of terpyridine derivatives. *Reagents and conditions*: (a) 2-acetylpyridine, NaOH, EtOH, 25 °C; (b) NH_4OH, reflux; (c) bis(pinacolato)diboron, $PdCl_2$(dppf), KOAc, DMSO, 80 °C.

4'-[4'-Bromo-(1,1'-biphenyl)-4-yl]-2,2':6',2''-terpyridine (3). To an EtOH solution (147 mL) of 2-acetylpyridine (4.9 g, 40.6 mmol) and **2** (4.8 g, 18.5 mmol), NaOH (4.4 g, 110.7 mmol) was added. After being stirred at 25 °C for 10 h under N_2, NH_4OH (28 wt%, 70 ml) was added into the mixture, which was then refluxed for additional 20 h. After cooling to 25 °C, the precipitate was filtered and washed with EtOH/H_2O (1:1, v/v) to allow isolation of **3** as a white solid (4.8 g, 10.3 mmol) in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.74 (s, 2H), 8.72-8.70 (d, J = 4.0 Hz, 2H), 8.66-8.64 (d, J = 8.0 Hz, 2H), 7.94-7.92 (d, J = 8.4 Hz, 2H), 7.86-7.82 (dt, J = 7.6 Hz, 2H), 7.65-7.63 (d, J = 8.4 Hz, 2H), 7.55-7.46 (d, J = 8.8 Hz, 4H), and 7.34-7.30 (dd, J = 4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.34, 156.13, 149.63, 149.30, 140.65, 139.42, 137.78, 137.03, 132.12, 128.82, 127.97, 127.50, 124.03, 122.08, 121.54, and 118.78. ESI MS: calcd. for $C_{27}H_{18}BrN_3$ $[M + Na]^+$: m/z = 486.0576; found: 486.0577.

4'-[4'-Pinacolatoboron-(1,1'-biphenyl)-4-yl]-2,2':6',2''-terpyridine (4). Borylation of aryl bromides was referenced to the method described in the literature.[7] To a degassed two-neck flask containing bis(pinacolato)diboron (2.9 g, 11.3 mmol),

$PdCl_2$(dppf) (0.2 g, 0.3 mmol), and KOAc (3.0 g, 30.1 mmol), **3** (4.8 g, 10.3 mmol) and anhydrous DMSO (62 ml) were added and the mixture was stirred at 80 °C for 1 day under N_2. After cooling to 25 °C, the reaction mixture was extracted with toluene and the combined organic extract was washed with H_2O, dried over anhydrous $MgSO_4$, and then evaporated to dryness under reduced pressure to give **4** as a brownish solid (2.5 g, 4.9 mmol) in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.77 (s, 2H), 8.73-8.71 (d, J = 4.0 Hz, 2H), 8.67-8.65 (d, J = 8.0 Hz, 2H), 8.00-7.98 (d, J = 8.4 Hz, 2H), 7.91-7.85 (m, J = 8.0 Hz, 4H), 7.76-7.74 (d, J = 8.4 Hz, 2H), 7.68-7.66 (d, J = 8.4 Hz, 2H), 7.36-7.33 (dd, J = 4.8 Hz, 2H), and 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.48, 156.21, 149.93, 149.36, 143.25, 141.83, 137.81, 137.08, 135.57, 127.95, 127.90, 126.62, 124.04, 121.60, 118.92, 84.08, and 25.10. ESI MS: calcd. for $C_{33}H_{30}BN_3O_2$ $[M + Na]^+$: m/z = 534.2329; found: 534.2334.

4'-(2-Bromophenyl)-2,2':6',2''-terpyridine (5). To an EtOH solution (270 mL) of 2-acetylpyridine (14.5 g, 119.6 mmol) and 2-bromobenzaldehyde (10.0 g, 54.4 mmol), NaOH (13.0 g, 326.2 mmol) was added. After being stirred at 25 °C for 10 h under N_2, NH_4OH (28 wt%, 200 ml) was added into the mixture, which was then refluxed for additional 20 h. After cooling to 25 °C, the precipitate was filtered and washed with EtOH/H_2O (1:1, v/v) to allow isolation of **5** as a white solid (3.3 g, 8.5 mmol) in 15.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.70-8.66 (m, 4H), 8.53 (s, 2H), 7.90-7.85 (dt, J = 7.8 Hz, 2H), 7.70-7.68 (d, J = 8.0 Hz, 1H), 7.47-7.45 (d, J = 7.6 Hz,1H), 7.41-7.37 (dt, J = 7.4 Hz, 1H), 7.35-7.32 (m, J = 4.8 Hz, 2H), and 7.28-7.23 (dt, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.10, 155.36, 150.84, 149.23, 140.51, 136.91, 133.25, 131.01, 129.77, 127.57, 119.48, 123.92, 122.04, 121.75, and 121.42. ESI MS: calcd. for $C_{21}H_{14}BrN_3$ $[M + Na]^+$: m/z = 410.0263; found: 410.0267.



Scheme S2 Synthesis of bisterpyridine ligands. *Reagents and conditions*: (a) **1**, Na_2CO_3, $Pd(PPh_3)_4$, toluene/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux; (b) **4**, Na_2CO_3, $Pd(PPh_3)_4$, toluene/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux.

4'-[2'-Bromo-(1,1'-biphenyl)-4-yl]-2,2':6',2''-terpyridine (6). To a degassed two-neck flask containing 1,2-dibromobenzene (3.1 g, 13.4 mmol), **1** (0.7 g, 2.1 mmol), and Na_2CO_3 (6.8 g, 64.2 mmol), a mixed solvent (168 mL) of toluene/H_2O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (39.4 mg, 33.9 μmol) was added into the mixture, which was then refluxed for 1 day under N_2. After cooling to 25°C, the mixture was extracted with $CHCl_3$ and the combined organic extract was dried over anhydrous $MgSO_4$ and then evaporated to dryness under reduced pressure. The residue was subjected to flash column chromatography (basic Al_2O_3, $CHCl_3$) and then recrystallized from MeOH to give **6** as a white solid (0.5 g, 1.0 mmol) in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.78 (s, 2H), 8.71-8.70 (d, J = 4.8 Hz, 2H), 8.66-8.64 (d, J = 7.6 Hz, 2H), 7.96-7.94 (d, J = 8.0 Hz, 2H), 7.86-7.82 (dt, J = 7.6 Hz, 2H), 7.68-7.66 (dd, J = 7.2 Hz, 1H), 7.55-7.53 (d, J = 8.0 Hz, 2H), 7.36-7.35 (d, J = 4.0 Hz, 2H), 7.33-7.30 (dd, J = 6.0 Hz, 2H), and 7.22-7.18 (m, J = 4.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.15, 155.91, 149.73, 149.12, 141.93, 141.76, 137.68, 136.85, 133.25, 131.27, 130.04, 128.99, 127.52, 126.99, 123.90, 122.61, 121.40, and 118.90. ESI MS: calcd. for $C_{27}H_{18}BrN_3$ $[M + Na]^+$: *m/z* = 486.0576; found: 486.0567.

2,4'-Di(4'-terpyridinyl)biphenyl (L1). By a similar procedure to that for **6**, **L1** was obtained in 85.9 % yield (0.8 g, 1.3 mmol) from **5** (0.6 g, 1.5 mmol), **1** (0.7 g, 1.9 mmol), Na_2CO_3 (1.6 g, 15.5 mmol), and $Pd(PPh_3)_4$ (125.4 mg, 108.5 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.69-8.67 (d, *J* = 4.8 Hz, 2H), 8.65-8.63 (d, *J* = 4.8 Hz, 2H), 8.63 (s, 2H), 8.63-8.60 (d, *J* = 8 Hz, 2H), 8.56-8.54 (d, *J* = 8 Hz, 2H), 8.30 (s, 2H), 7.87-7.80 (m, 4H), 7.77-7.74 (d, *J* = 8.5 Hz, 2H), 7.62-7.60 (d, *J* = 6.6 Hz, 1H), 7.53-7.46 (m, 3H), 7.40-7.37 (d, *J* = 8.5 Hz, 2H), 7.34-7.31 (m, 2H), and 7.28-7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.22, 156.13, 155.79, 155.26, 151.64, 149.76, 149.16, 149.14, 149.09, 149.08, 141.72, 140.04, 138.53, 136.85, 136.76, 136.69, 130.65, 130.53, 128.66, 127.86, 127.09, 123.83, 123.73, 122.19, 121.39, 121.37, and 118.75. ESI MS: calcd. for $C_{42}H_{28}N_6$ $[M + H]^+$: *m/z* = 617.2448; found: 617.2441.

2,4''-Di(4'-terpyridinyl)-1,1':4',1''-terphenyl (L2). By a similar procedure to that for **6**, **L2** was obtained in 76.3 % yield (0.9 g, 1.2 mmol) from **5** (0.6 g, 1.6 mmol), **4** (0.8 g, 1.6 mmol), Na_2CO_3 (1.7 g, 16.4 mmol), and $Pd(PPh_3)_4$ (132.5 mg, 114.6 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73 (s, 2H), 8.72-8.70 (d, *J* = 4.8 Hz, 2H), 8.66-8.64 (d, *J* = 8 Hz, 2H), 8.61-8.59 (d, *J* = 4.8 Hz, 2H), 8.53-8.51 (d, *J* = 8 Hz, 2H), 8.29 (s, 2H), 7.92-7.90 (d, *J* = 8.5 Hz, 2H), 7.89-7.84 (dt, *J* = 8 Hz, 2H), 7.81-7.77 (dt, *J* = 7.6 Hz, 2H), 7.62-7.60 (d, *J* = 8.5 Hz, 3H), 7.54-7.44 (m, 5H), 7.36-7.32 (m, 4H), and 7.28-7.25 (dd, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.28, 156.19, 155.96, 155.24, 151.64, 149.74, 149.16, 141.47, 140.30, 140.27, 140.43, 138.76, 138.43, 137.15, 136.94, 136.79, 130.64, 130.51, 128.71, 127.78, 127.68, 127.50, 126.89, 123.93, 123.75, 122.32, 121.49, 121.33, and 118.72. ESI MS: calcd. for $C_{48}H_{32}N_6$ $[M + H]^+$: *m/z* = 693.2761; found: 693.2775.

4-(4'-terpyridinyl)-2''-[4-(4'-terpyridinyl)phenyl]-1,1':4',1''-terphenyl (L3). By a similar procedure to that for **6**, **L3** was obtained in 72.1 % yield (1.1 g, 1.4 mmol) from **6** (0.8 g, 1.9 mmol), **4** (1.1 g, 2.1 mmol), Na_2CO_3 (2.0 g, 19.0 mmol), and $Pd(PPh_3)_4$ (153.7 mg, 133.0 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.78 (s, 2H), 8.75 (s, 2H), 8.74-8.71 (dd, *J* = 6.9 Hz, 4H), 8.69-8.65 (dd, *J* = 6.7.0 Hz, 4H), 7.99-7.97 (d, *J* = 8.5 Hz, 2H), 7.91-7.86 (dt, *J* = 5.4 Hz, 4H), 7.84-7.82 (d, *J* = 8.4 Hz, 2H), 7.77-7.75 (d, *J* = 8.5 Hz, 2H), 7.59-7.57 (d, *J* = 8.3 Hz, 2H), 7.52-7.45 (m, 4H), 7.38-7.33 (dd, *J* = 3.4 Hz, 6H), and 7.30-7.28 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.32, 156.28, 155.96, 149.91, 149.58, 149.17, 142.43, 141.33, 140.81, 140.18, 139.96, 138.52, 137.19, 136.93, 136.60, 130.86, 130.80, 130.53, 130.46, 127.93, 127.75, 127.58, 127.1, 126.83, 123.91, 121.50, 121.44, 118.88, and 118.78. ESI MS: calcd. for $C_{54}H_{36}N_6$ $[M + Na]^+$: *m/z* = 791.2894; found: 791.2871.

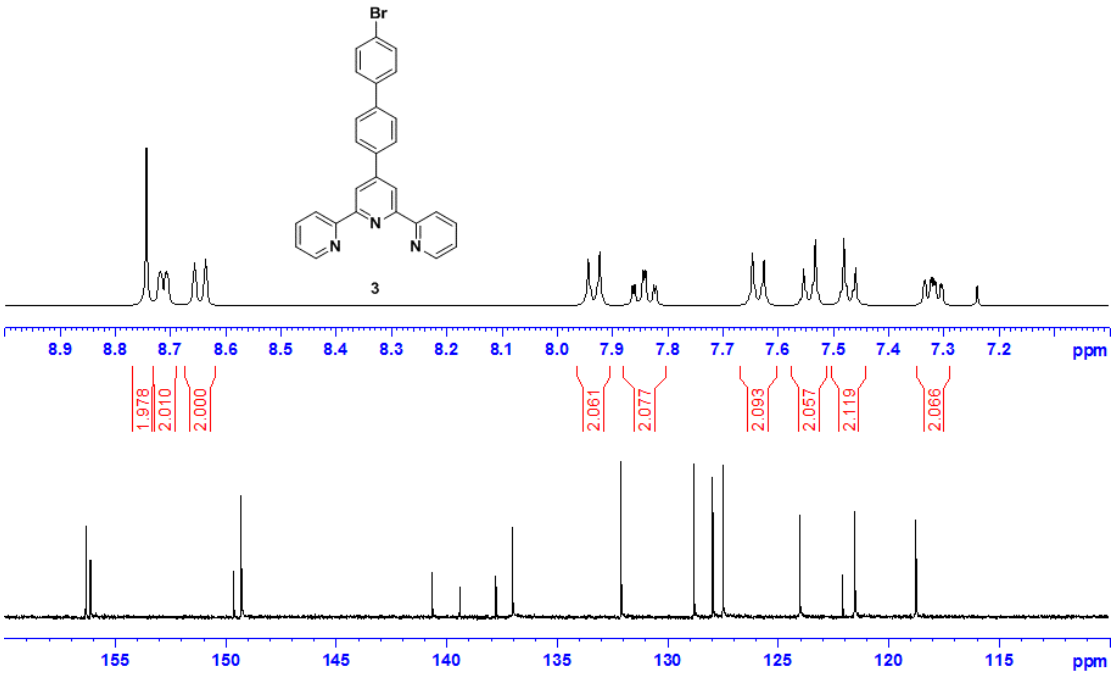


Fig. S1 ^{1}H and ^{13}C NMR spectra of **3**.

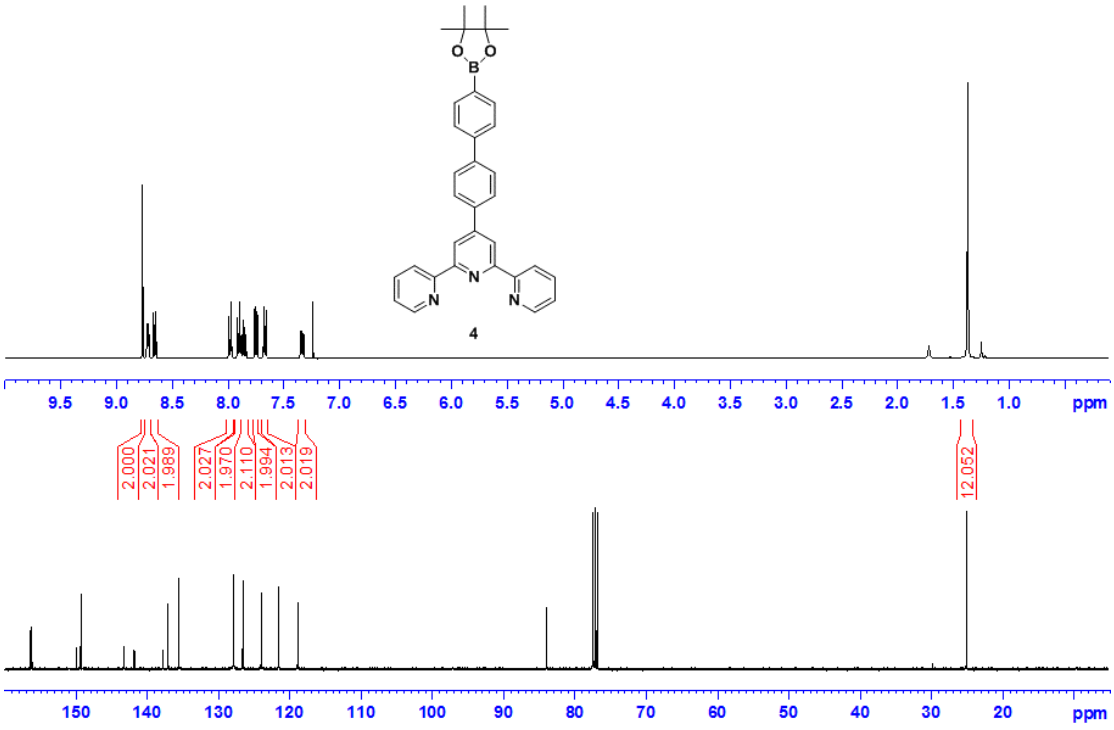


Fig. S2 ^{1}H and ^{13}C NMR spectra of **4**.

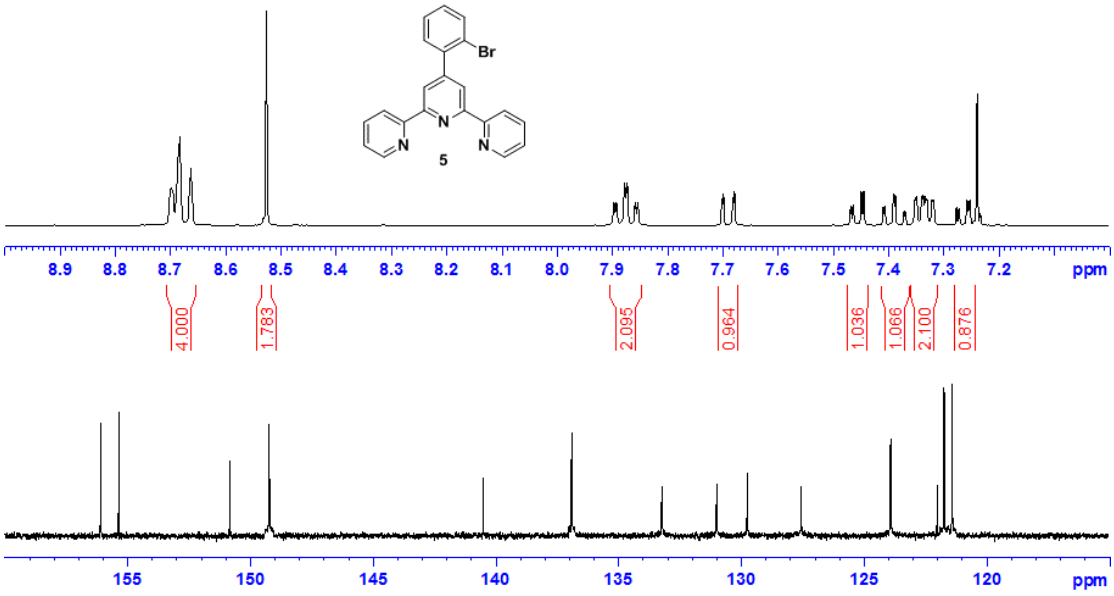


Fig. S3 ^{1}H and ^{13}C NMR spectra of **5**.

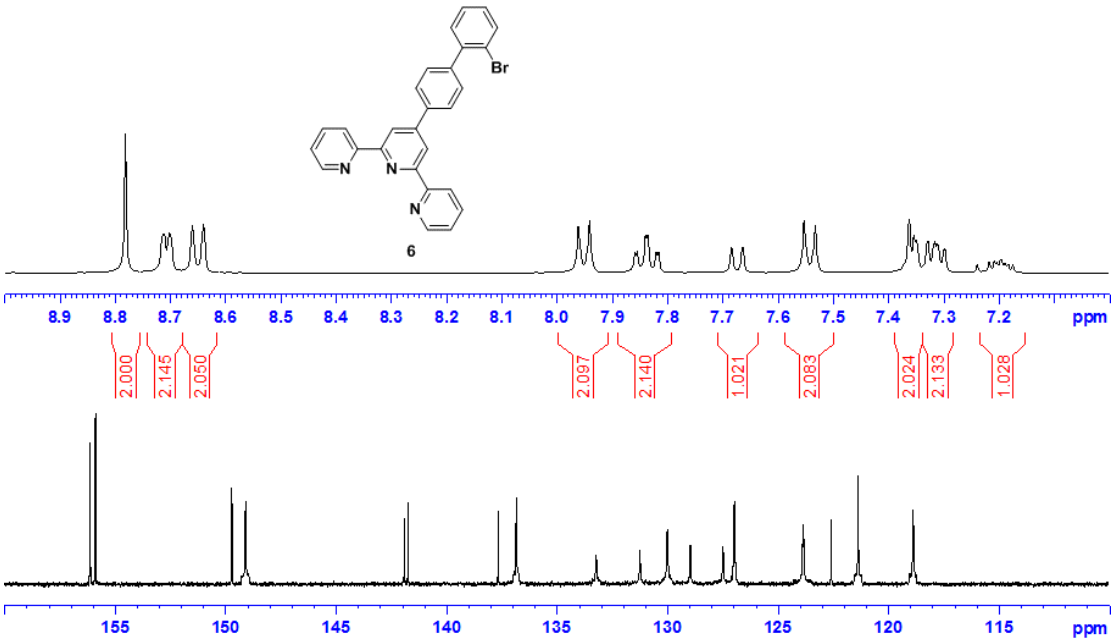


Fig. S4 ^{1}H and ^{13}C NMR spectra of **6**.

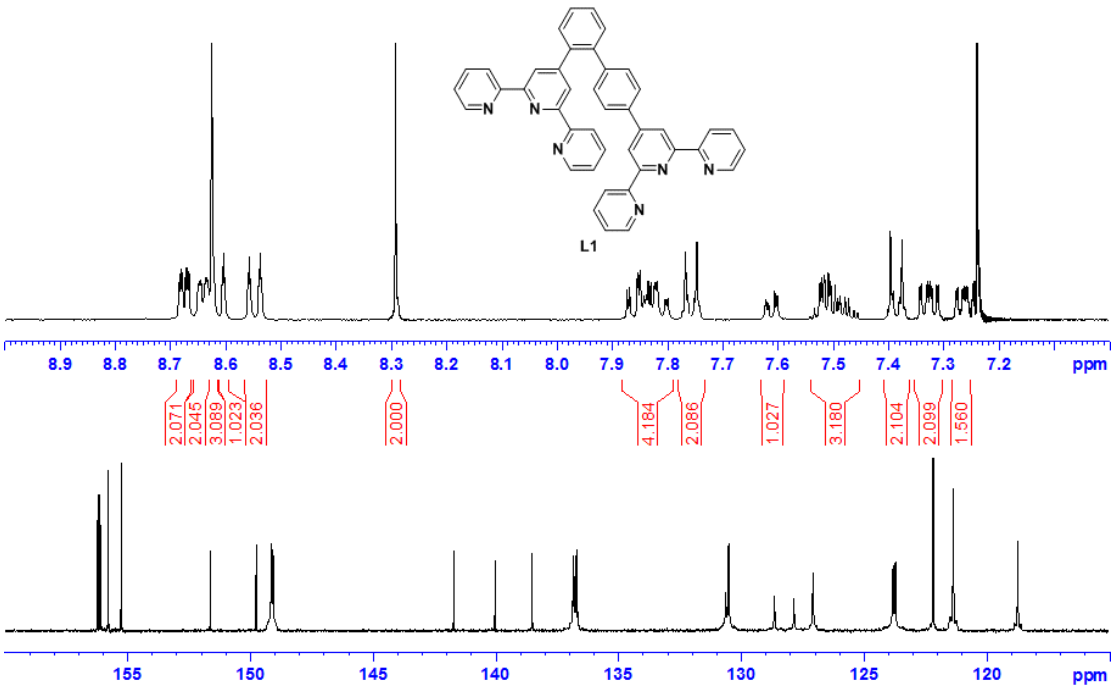


Fig. S5 ^{1}H and ^{13}C NMR spectra of **L1**.

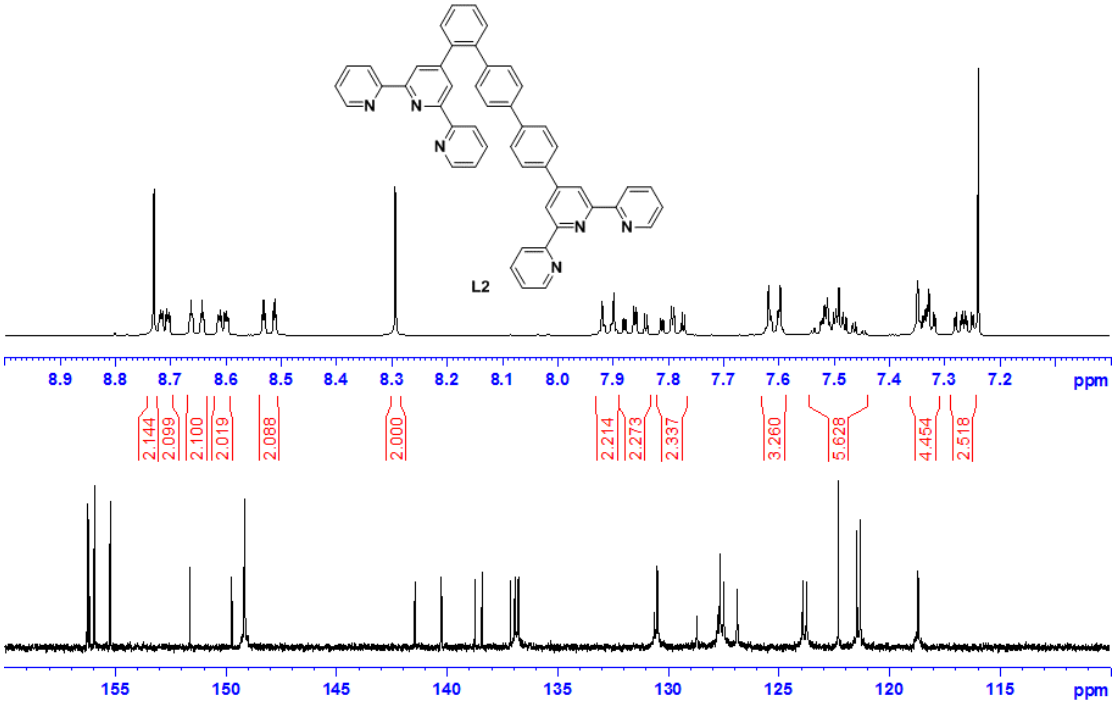


Fig. S6 ^{1}H and ^{13}C NMR spectra of **L2**.

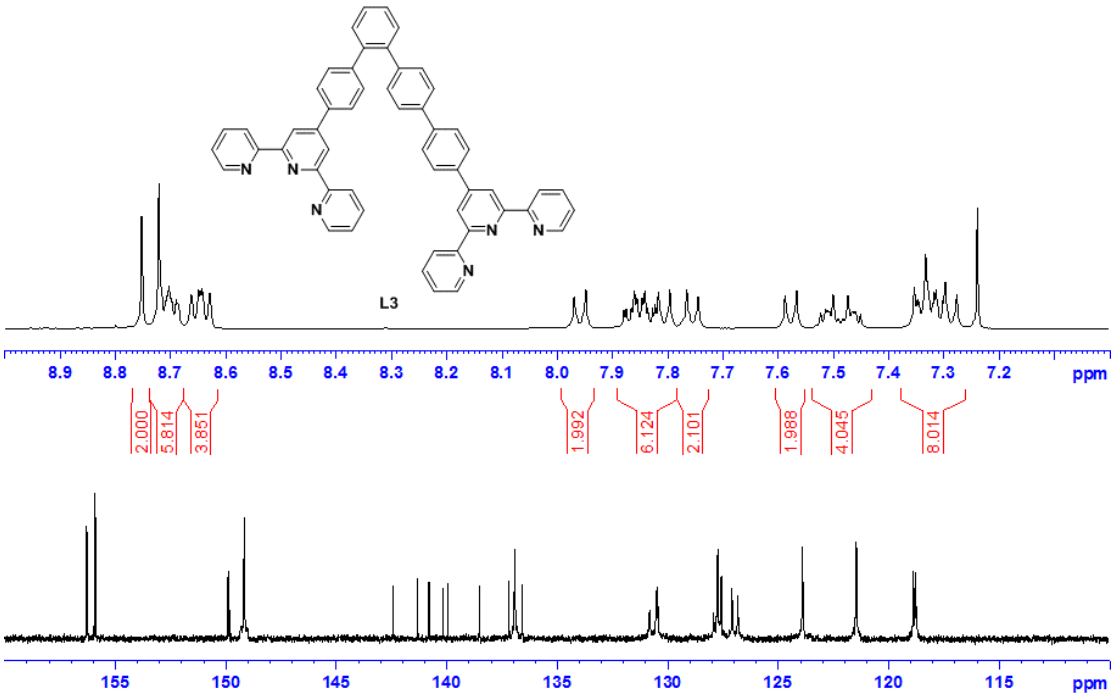


Fig. S7 ^{1}H and ^{13}C NMR spectra of **L3**.

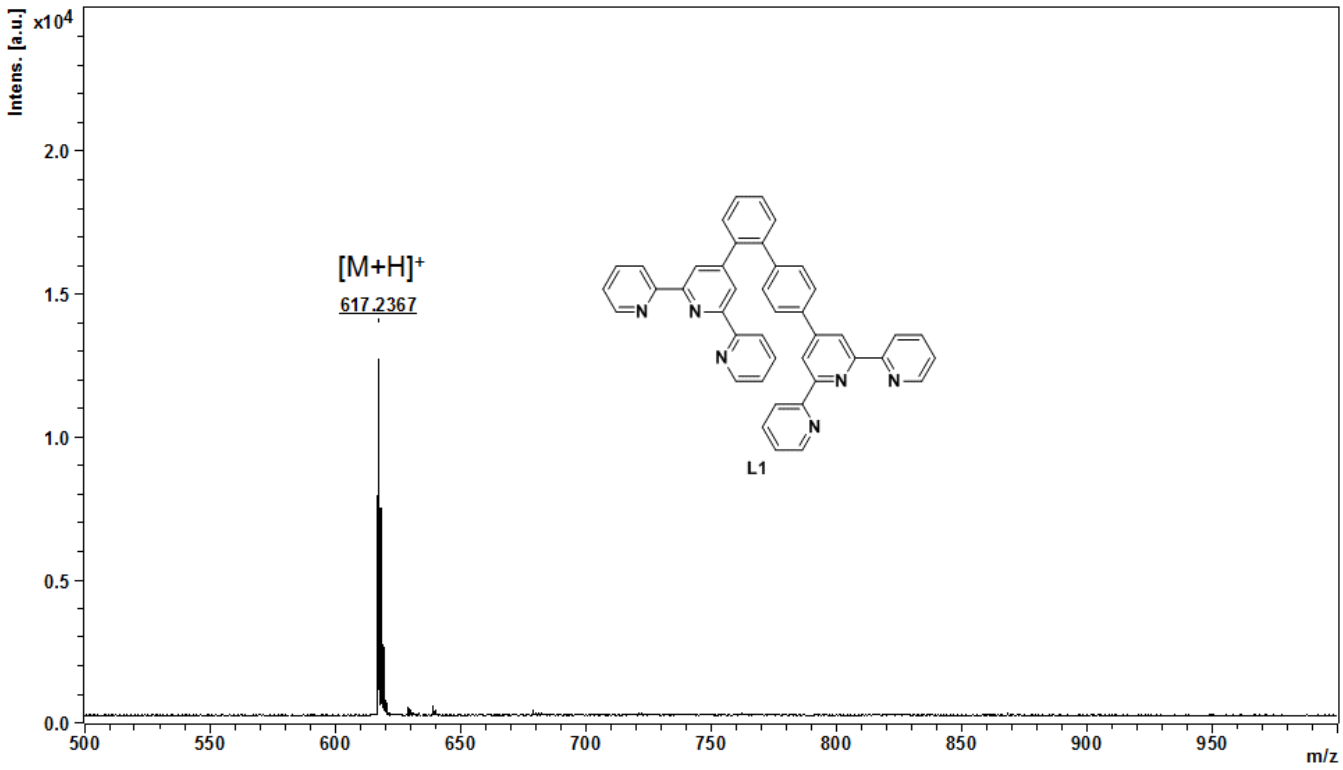


Fig. S8 MALDI TOF MS spectrum of **L1**.

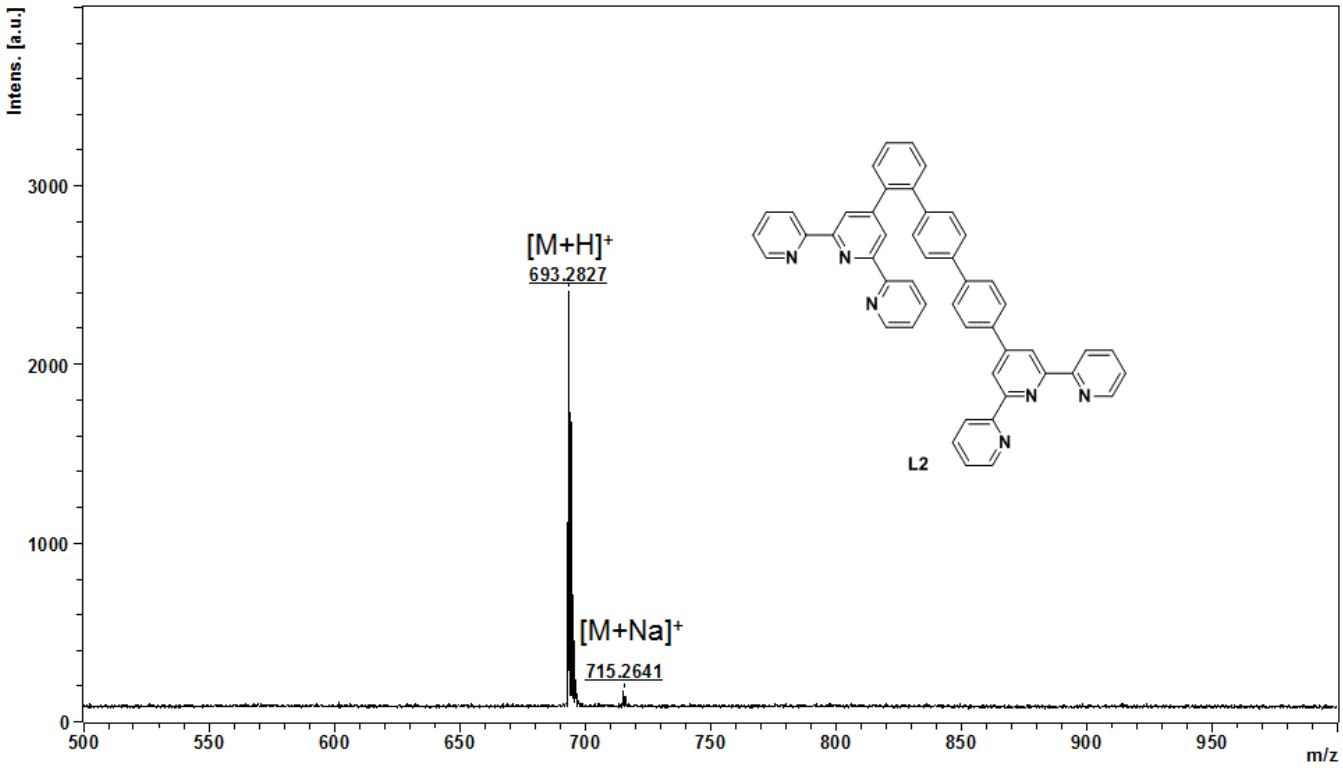


Fig. S9 MALDI TOF MS spectrum of **L2**.

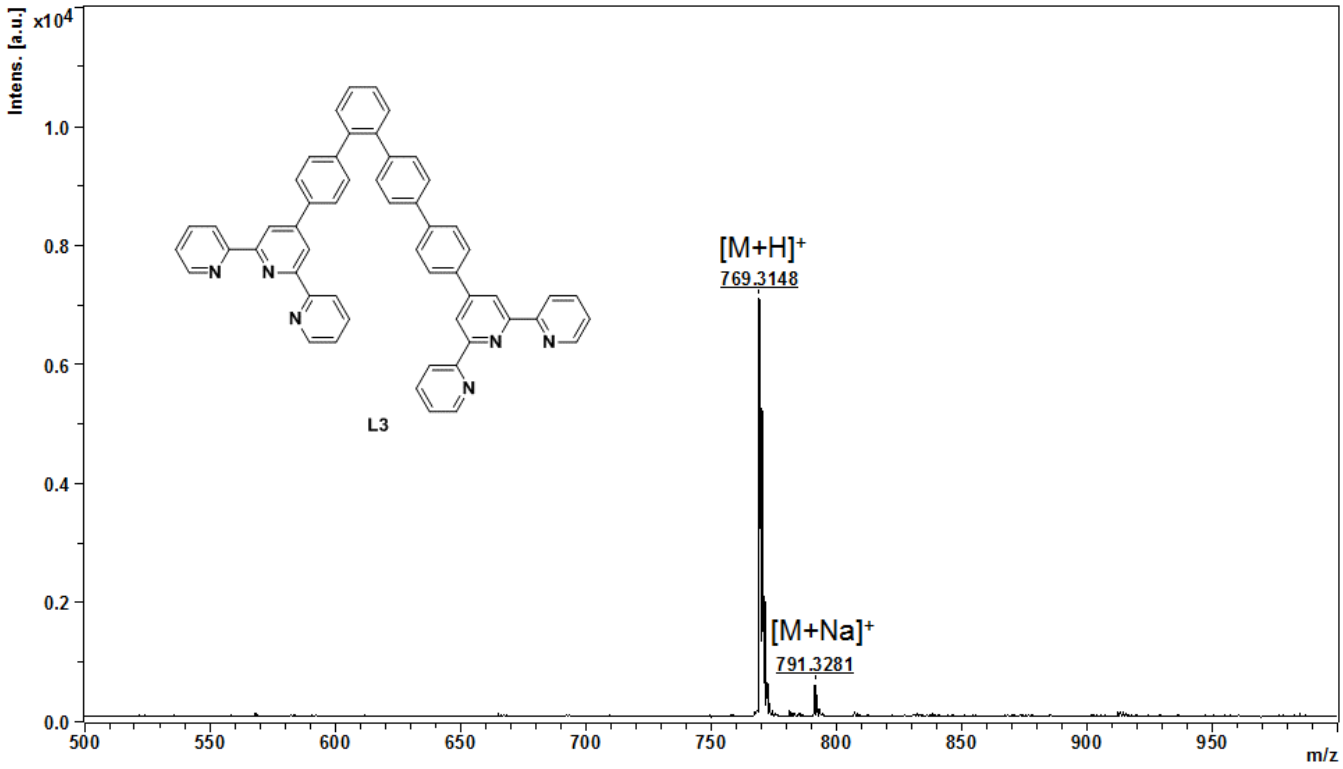
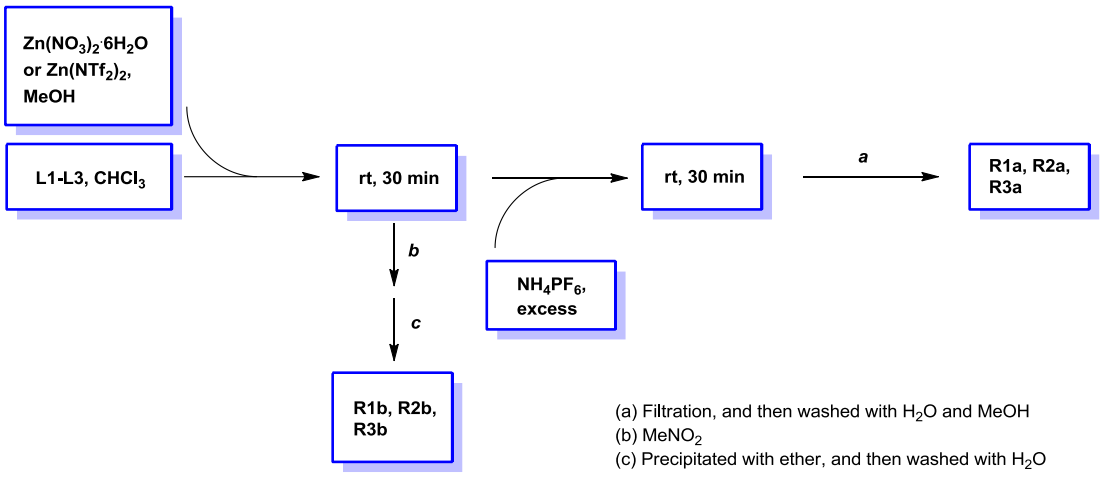


Fig. S10 MALDI TOF MS spectrum of **L3**.

Complexation

Table S1 Six complexation reactions from different combinations of anions and ligands.

Anion / Ligand	PF_6^-	NTf_2^-
L1	R1a	R1b
L2	R2a	R2b
L3	R3a	R3b



Scheme S3 Complexation flowchart of Zn^{II} complexes.

Characterization of complexes using NMR

A mixture of Z1a and Z1a'. Yield: 56.1 mg, 91.4% as a mixture. ^{1}H NMR (400 MHz, CD_3CN) of **Z1a**: δ (ppm) 8.77 (s, 6H), 8.60 (s, 6H), 8.48-8.46 (d, J = 8.1 Hz, 6H), 8.33-8.31 (d, J = 8.2 Hz, 6H), 8.21-8.19 (d, J = 8.4 Hz, 6H), 8.12-8.08 (dt, J = 7.8 Hz, 6H), 8.05-8.00 (dt, J = 7.8 Hz, 6H), 8.00-7.98 (m, 3H), 7.87-7.78 (m, 21H), 7.70-7.68 (d, J = 5.1 Hz, 6H), 7.56-7.52 (dd, J = 5.2 Hz, 6H), and 7.26-7.23 (dd, J = 5.1 Hz, 6H). 3',5'-tpy*H* of **Z1a'**: δ (ppm) 8.96 (s, 1H), 8.65 (s, 1H), 8.52 (s, 1H), 8.40 (s, 1H), 8.35 (s, 1H), and 8.30 (s, 1H). ESI MS (*m/z*): 827.1281 $[M\text{-}3PF_6]^{3+}$ (calcd. *m/z* = 827.1304), 584.1057 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 584.1068), 438.2896 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 438.2925), and 341.0808 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 341.0831).

A mixture of Z1b and Z1b'. Yield: 67.0 mg, 95.1% as a mixture. ^{1}H NMR (400 MHz, CD_3CN) of **Z1b**: δ (ppm) 8.77 (s, 6H), 8.61 (s, 6H), 8.49-8.47 (d, J = 8.1 Hz, 6H), 8.34-8.32 (d, J = 8.1 Hz, 6H), 8.22-8.20 (d, J = 8.4 Hz, 6H), 8.13-8.09 (dt, J = 7.8 Hz, 6H), 8.04-8.02 (dt, J = 7.8 Hz, 6H), 8.00-7.98 (m, 3H), 7.87-7.78 (m, 21H), 7.70-7.68 (d, J = 4.4 Hz, 6H), 7.58-7.55 (dd, J = 5.1 Hz, 6H), and 7.26-7.23 (dd, J = 5.2 Hz, 6H). 3',5'-tpy*H* of **Z1b'**: δ (ppm) 8.98 (s, 1H), 8.68 (s, 1H), 8.55 (s, 1H), 8.41 (s, 1H). ESI MS (*m/z*): 962.1032 $[M\text{-}3NTf_2]^{3+}$ (calcd. *m/z* = 962.0834), 651.3428 $[M\text{-}4NTf_2]^{4+}$ (calcd. *m/z* = 651.3336), 465.0878 $[M\text{-}5NTf_2]^{5+}$ (calcd. *m/z* = 465.0834), and 340.9193 $[M\text{-}6NTf_2]^{6+}$ (calcd. *m/z* = 340.9166).

Z2a. Yield: 83.5 mg, 95.3%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.90 (s, 6H), 8.69-8.67 (d, J = 8.1 Hz, 6H), 8.52 (s, 6H), 8.28-8.26 (d, J = 8.1 Hz, 6H), 8.19-8.13 (m, 12H), 8.07-8.03 (dt, J = 7.7 Hz, 6H), 8.01-7.98 (d, J = 5.5 Hz, 3H), 7.85-7.75 (m, 33H), 7.61-7.59 (d, J = 8.4 Hz, 6H), 7.48-7.45 (dd, J = 5.1 Hz, 6H), and 7.34-7.31 (dd, J = 5.1 Hz, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 181.10, 158.73, 157.05, 150.98, 150.17, 149.34, 149.23, 148.96, 143.92, 142.63, 142.52, 142.12, 141.35, 140.26, 137.45, 136.72, 132.68, 132.21, 132.14, 131.51, 130.19, 130.05, 129.22, 128.80, 128.48, 126.24, 124.67, 124.05, and 122.84. ESI MS (*m/z*): 903.1733 $[M\text{-}3PF_6]^{3+}$ (calcd. *m/z* = 903.1620), 641.1351 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 641.1304), 483.9145 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 483.9115), and 379.0996 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 379.0989).

Z2b. Yield: 67.0 mg, 90.4%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.91 (s, 6H), 8.69-8.67 (d, J = 8.1 Hz, 6H), 8.54 (s, 6H), 8.30-8.28 (d, J = 8.1 Hz, 6H), 8.20-8.13 (m, 12H), 8.08-8.04 (dt, J = 7.8 Hz, 6H), 8.02-8.00 (d, J = 5.3 Hz, 3H), 7.85-7.76 (m, 33H), 7.62-7.60 (d, J = 8.3 Hz, 6H), 7.49-7.45 (dd, J = 5.1 Hz, 6H), and 7.35-7.33 (dd, J = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 181.13, 158.76, 157.09, 151.00, 150.18, 149.31, 149.20, 148.97, 143.97, 142.63, 142.53, 142.12, 141.36, 140.30, 137.44, 136.70, 132.70, 132.21, 131.51, 130.19, 129.23, 128.81, 128.51, 126.28, 124.68,

124.07, 122.87, 122.81, and 119.63. ESI MS (*m/z*): 1038.1305 $[M\text{-}3NTf_2]^{3+}$ (calcd. *m/z* = 1038.1150), 708.6121 $[M\text{-}4NTf_2]^{4+}$ (calcd. *m/z* = 708.6069), 510.9054 $[M\text{-}5NTf_2]^{5+}$ (calcd. *m/z* = 510.9021), and 378.9378 $[M\text{-}6NTf_2]^{6+}$ (calcd. *m/z* = 378.9324).

A mixture of Z3a and Z3a'. Yield: 69.0 mg, 98.4% as a mixture. ^{1}H NMR (400 MHz, CD_3CN) of **Z3a**: δ (ppm) 8.99-8.96 (m, 12H), 8.71-8.68 (m, 12H**)**, 8.30-8.25 (m, 6H), 8.16-8.11 (m, 18H), 8.07-8.03 (m, 6H), 7.83-7.77 (m, 18H), 7.68-7.57 (m,18H), 7.52-7.42 (m, 6H), and 7.39-7.35 (m, 12H). 3',5'-tpy*H* of **Z3a'**: δ (ppm) 8.99 (s, 2H), 8.97 (s, 2H), 8.96 (s, 1H), 8.96 (s, 1H). ESI MS (*m/z*): 978.8776 $[M\text{-}3PF_6]^{3+}$ (calcd. *m/z* = 978.8604), 697.9171 $[M\text{-}4PF_6]^{4+}$ (calcd. *m/z* = 697.9043), 529.3398 $[M\text{-}5PF_6]^{5+}$ (calcd. *m/z* = 529.3306), and 417.1233 $[M\text{-}6PF_6]^{6+}$ (calcd. *m/z* = 417.1147).

A mixture of Z3b and Z3b'. Yield: 96.0 mg, 94.6% as a mixture. ^{1}H NMR (400 MHz, CD_3CN) of **Z3b**: 8.99-8.96 (m, 12H), 8.71-8.68 (m, 12H**)**, 8.29-8.25 (m, 6H), 8.16-8.12 (m, 18H), 8.06-8.04 (m, 6H), 7.82-7.77 (m, 18H), 7.68-7.57 (m,18H), 7.52-7.42 (m, 6H), and 7.39-7.36 (m, 12H). 3',5'-tpy*H* of **Z3b'**: δ (ppm) 8.99 (s, 2H), 8.97 (s, 2H), 8.97 (s, 1H), 8.96 (s, 1H). ESI MS (*m/z*): 1114.1704 $[M\text{-}3NTf_2]^{3+}$ (calcd. *m/z* = 1114.1465), 765.6414 $[M\text{-}4NTf_2]^{4+}$ (calcd. *m/z* = 765.6306), 556.5302 $[M\text{-}5NTf_2]^{5+}$ (calcd. *m/z* = 556.5211), and 417.1233 $[M\text{-}6NTf_2]^{6+}$ (calcd. *m/z* = 417.1147).

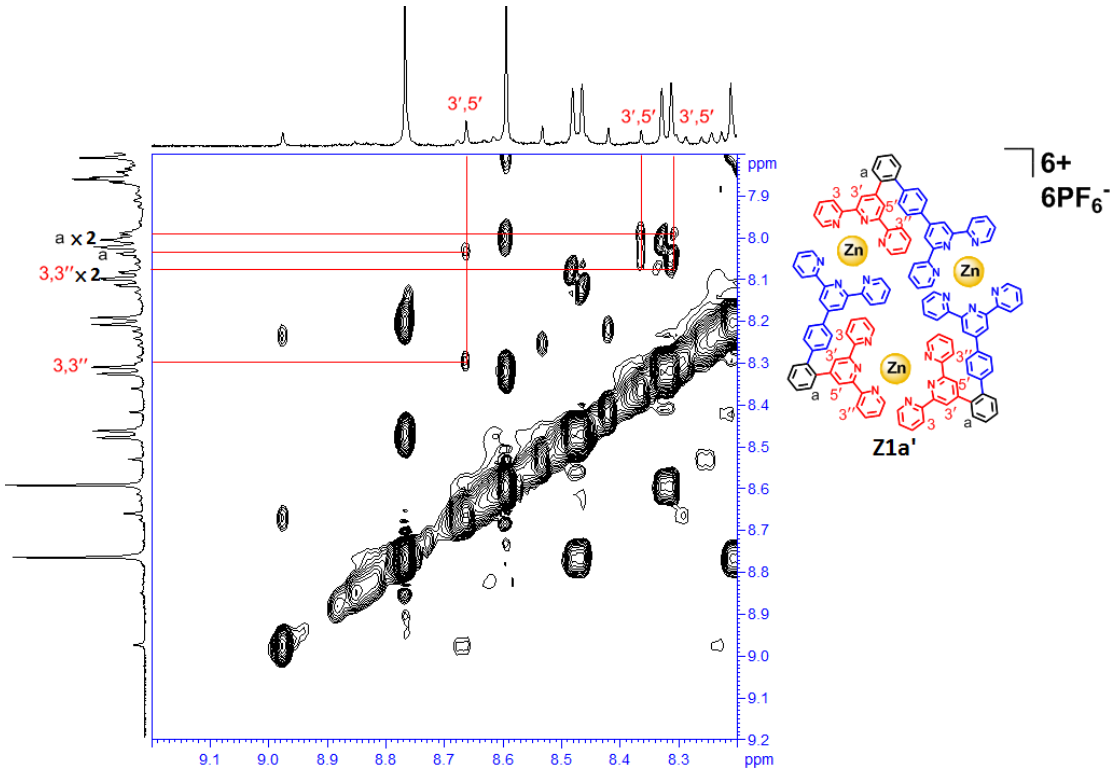


Fig. S11 2D ^{1}H ROESY spectrum of **R1a**, showing red 3',5'-tpy*H*s coupled with 3',3"-tpy*H*s and the adjacent phenyl protons of **Z1a'**. ([**L1**] = 1.2 x 10^{-3} M, CD_3CN).

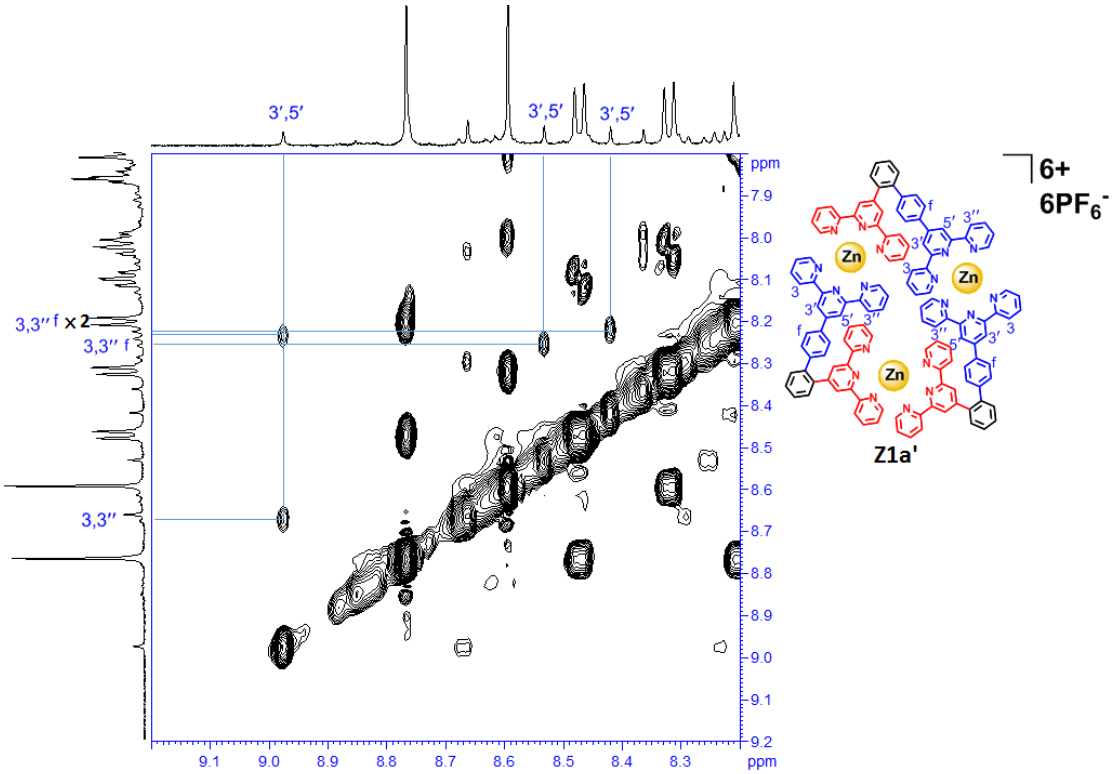


Fig. S12 2D ^{1}H ROESY spectrum of **R1a**, showing blue 3',5'-tpy*H*s coupled with 3',3"-tpy*H*s and adjacent phenyl protons of **Z1a'**. ([**L1**] = 1.2 x 10^{-3} M, CD_3CN).

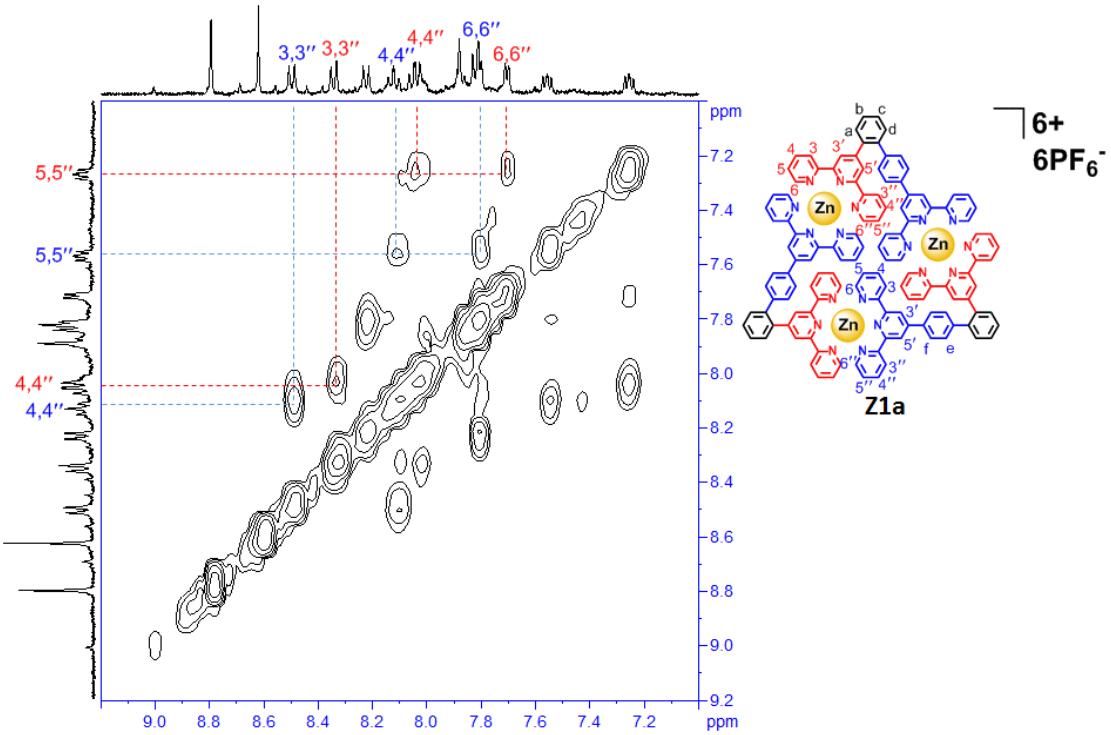


Fig. S13 2D ^{1}H COSY spectrum of **R1a**, showing 3',3"-, 4',4"-, 5',5"- and 6',6"-tpy*H*s' coupling correlations of **Z1a**. ([**L1**] = 1.2 × 10^{-3} M, CD_3CN).

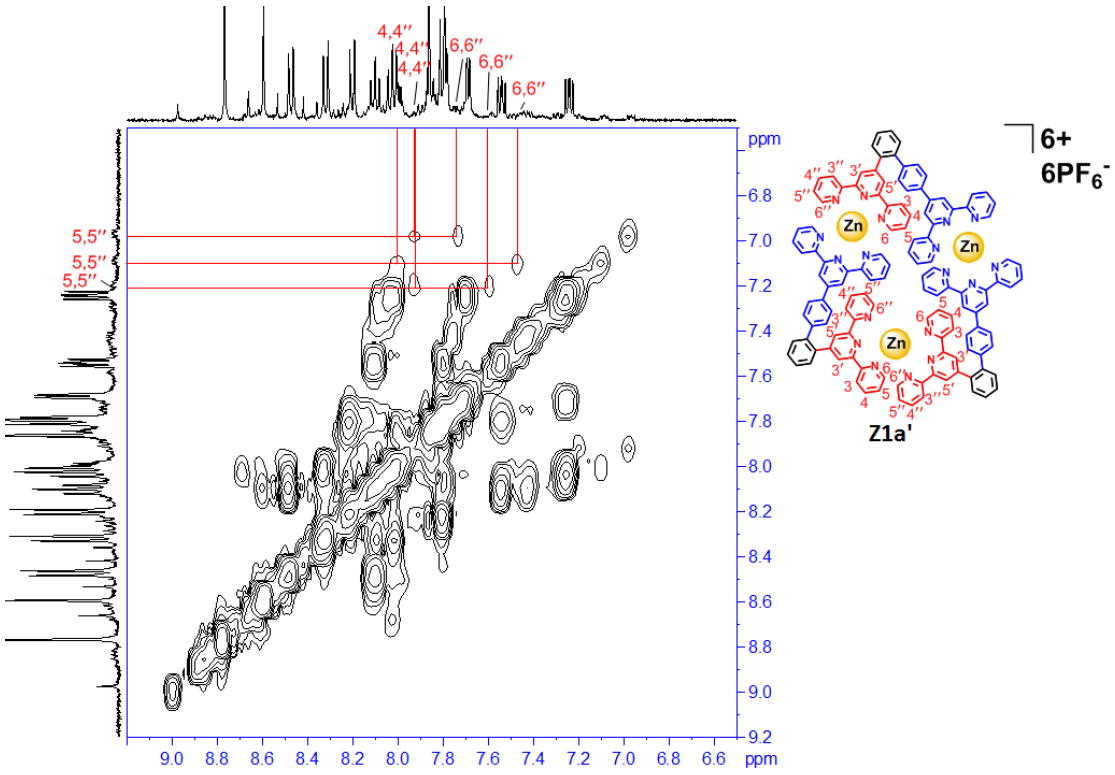


Fig. S14 2D ^{1}H COSY spectrum of **R1a**, showing red 5',5"-tpy*H*s coupled with 4',4"- and 6',6"-tpy*H*s of **Z1a'**. ([**L1**] = 1.2 × 10^{-3} M, CD_3CN).

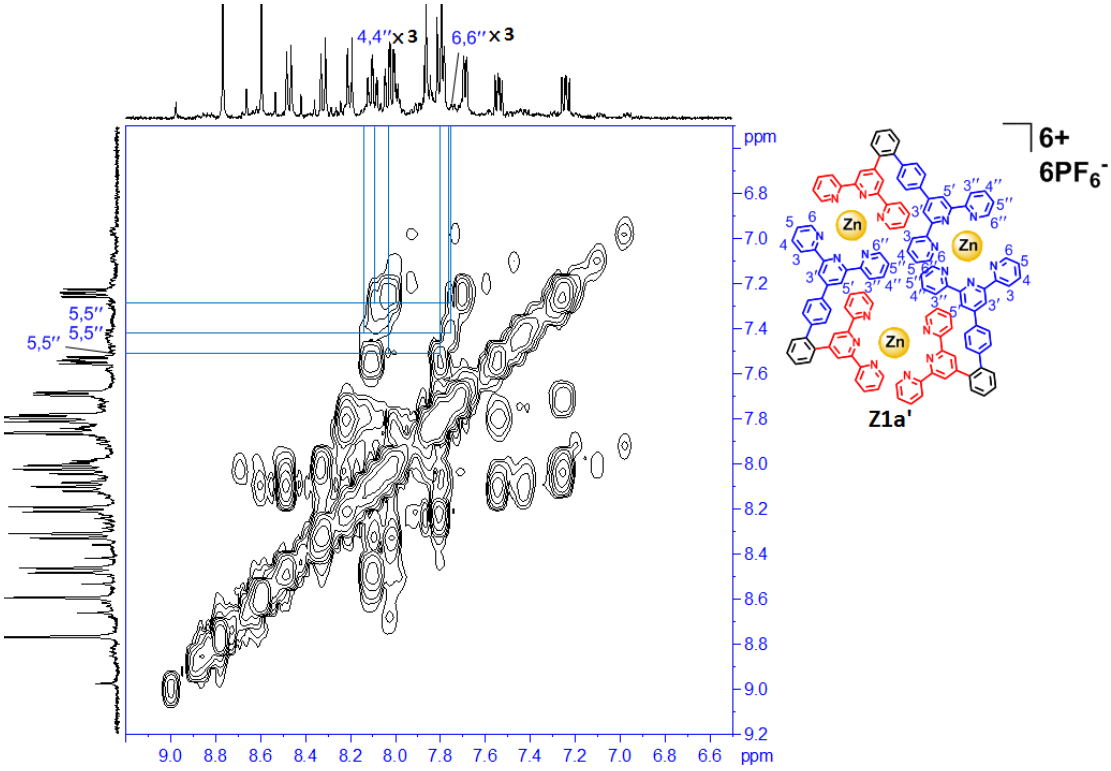


Fig. S15 2D ^{1}H COSY spectrum of **R1a**, showing blue 5',5''-tpy*H*s coupled with 4',4''- and 6',6''-tpy*H*s of **Z1a'**. ([**L1**] = 1.2 x 10^{-3} M, CD_3CN).

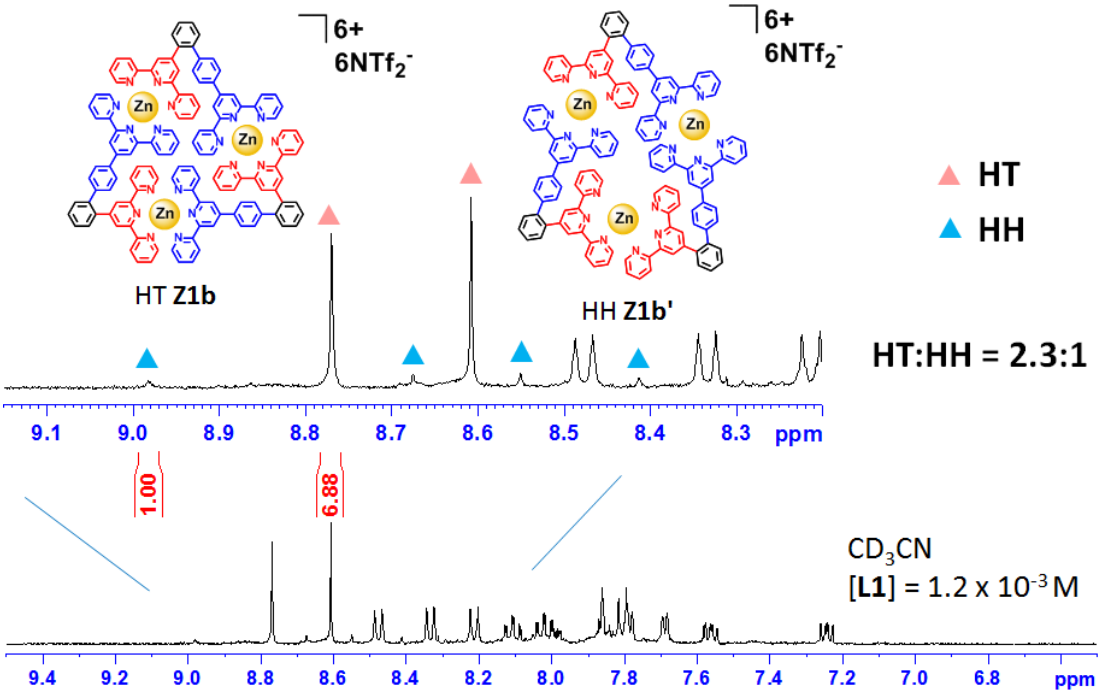


Fig. S16 Integration of 3',5'-tpy*H*s signals in the ^{1}H NMR spectrum of **R1b**. ([**L1**] = 1.2 x 10^{-3} M, CD_3CN).

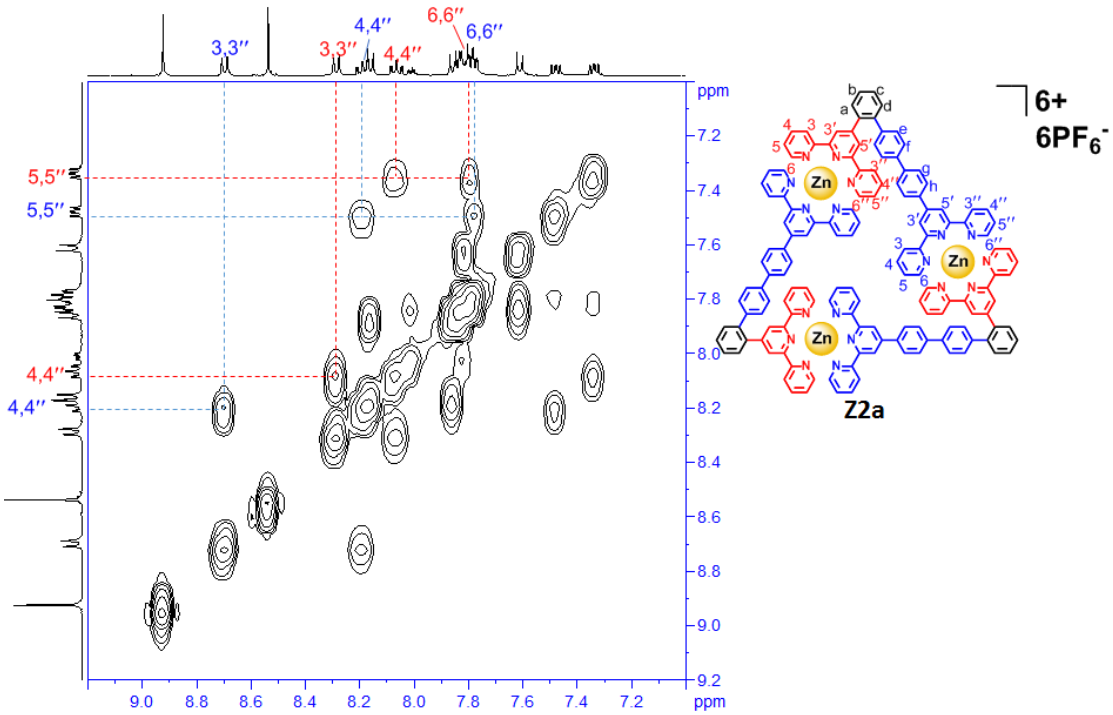


Fig. S17 2D ^{1}H COSY spectrum of **Z2a**.

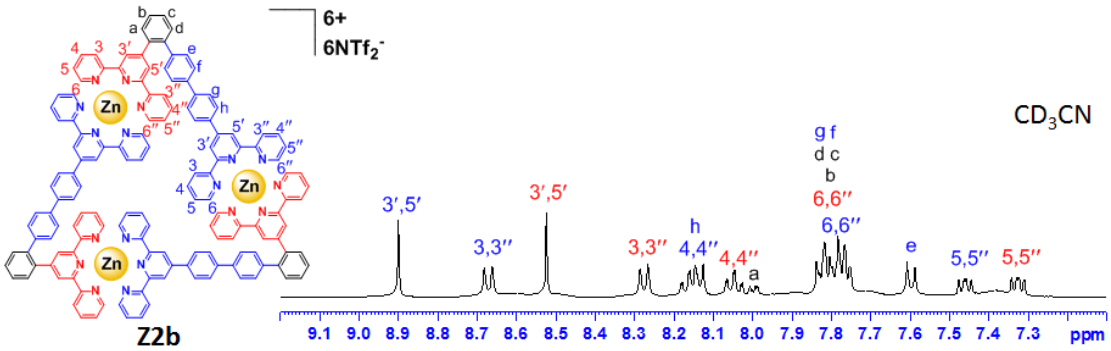


Fig. S18 ^{1}H NMR spectrum of **Z2b**.

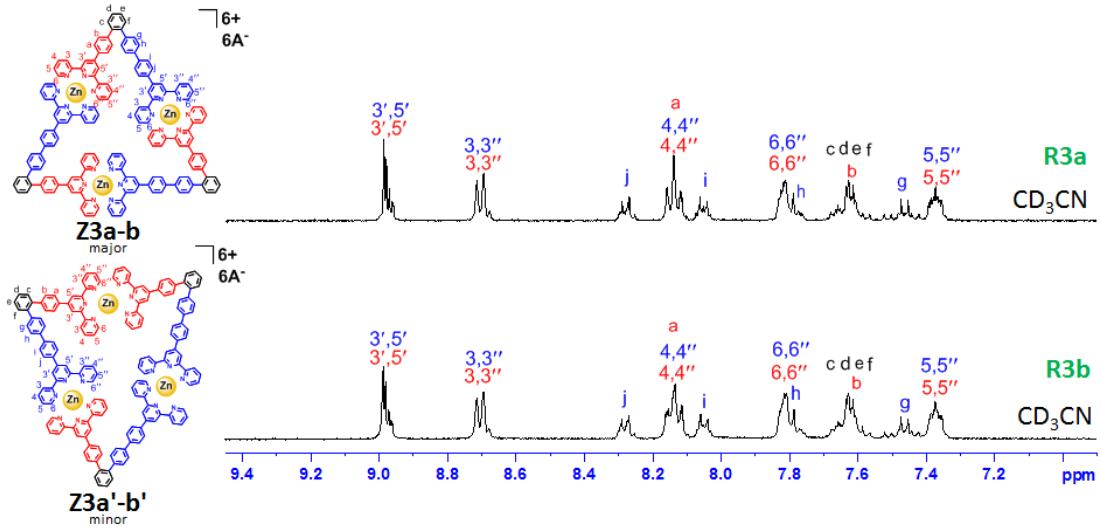


Fig. S19 ^{1}H NMR spectra of **R3a-b**.

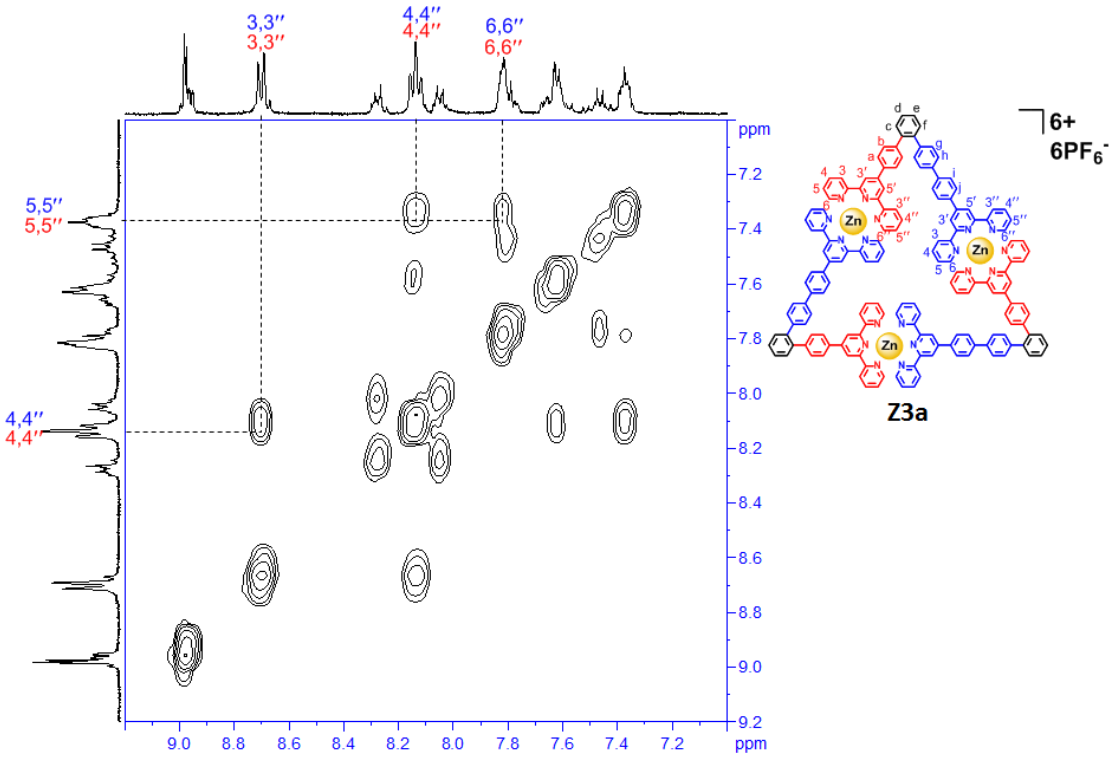
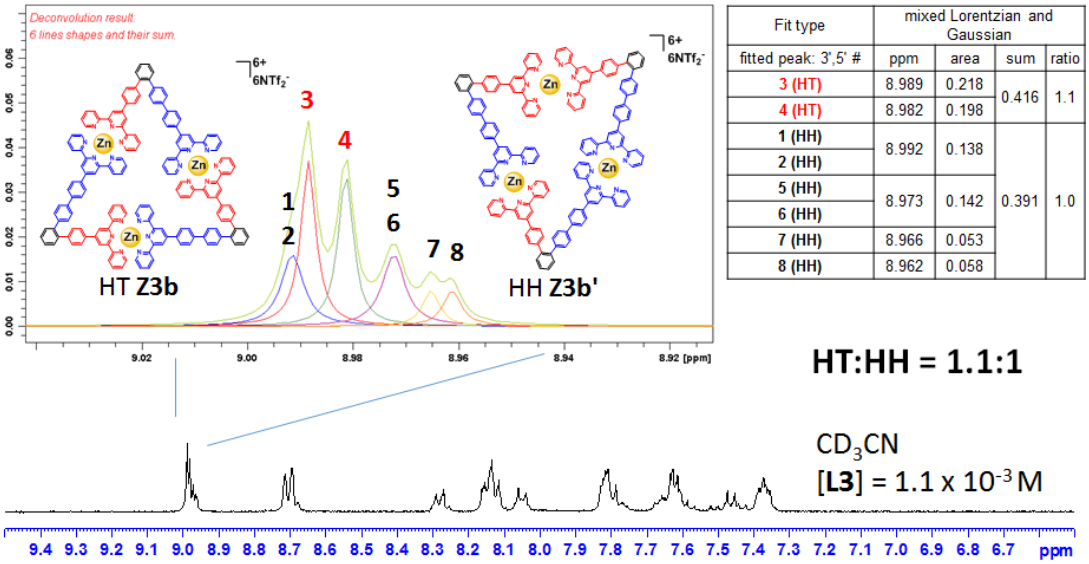


Fig. S20 2D ^{1}H COSY spectrum of **R3a**.



Fit type	mixed Lorentzian and Gaussian			
fitted peak: 3',5' #	ppm	area	sum	ratio
3 (HT)	8.989	0.218	0.416	1.1
4 (HT)	8.982	0.198		
1 (HH)	8.992	0.138	0.391	1.0
2 (HH)				
5 (HH)	8.973	0.142		
6 (HH)				
7 (HH)	8.966	0.053		
8 (HH)	8.962	0.058		

Fig. S21 Deconvolution of 3',5'-tpy*H*s signals in ^{1}H NMR spectrum of **R3b**. ([**L3**] = 1.1 x 10^{-3} M, CD_3CN).

2D DOSY NMR

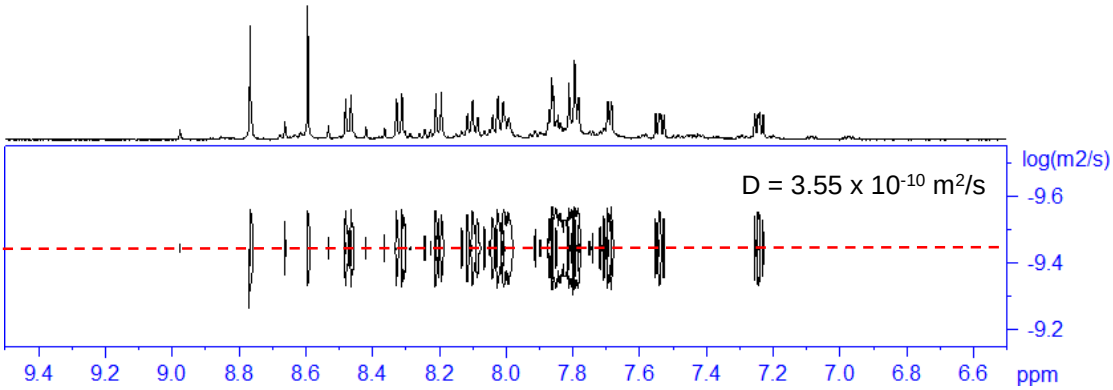


Fig. S22 DOSY NMR spectrum of **R1a** ([**L1**] = 1.20 × 10^{-3} M, CD_3CN).

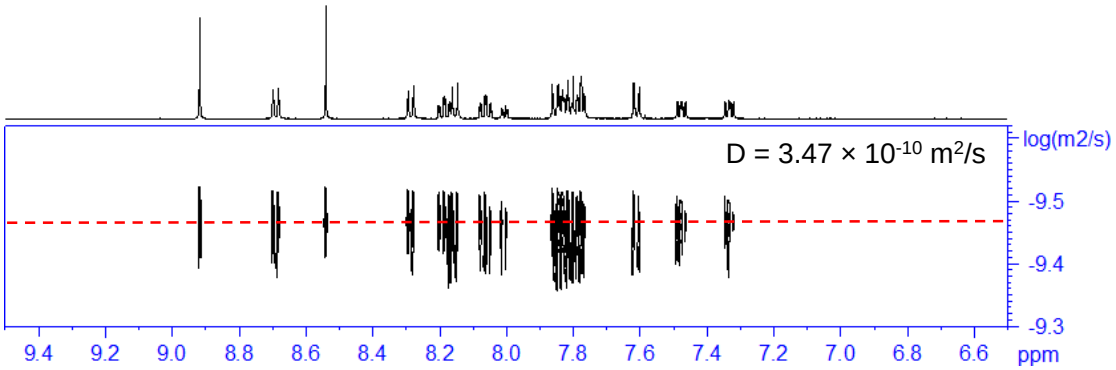


Fig. S23 DOSY NMR spectrum of **Z2a** ([**L2**] = 1.20 × 10^{-3} M, CD_3CN).

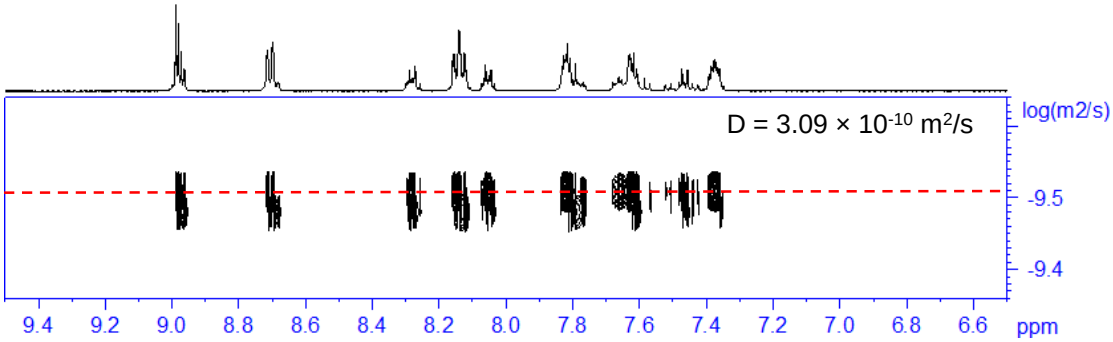


Fig. S24 DOSY NMR spectrum of **R3a** ([**L3**] = 1.20 × 10^{-3} M, CD_3CN).

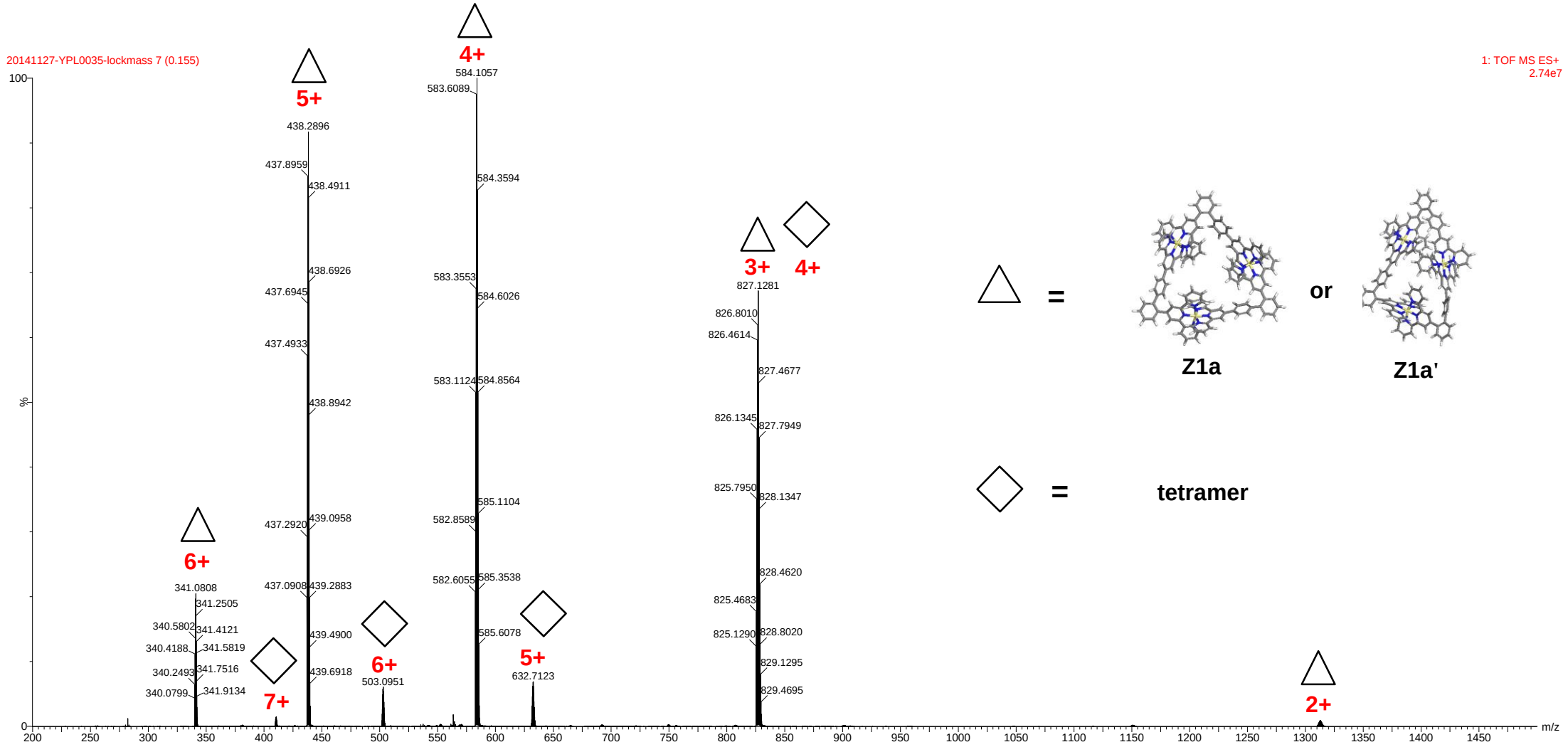


Fig. S25 ESI MS spectrum of **R1a**.

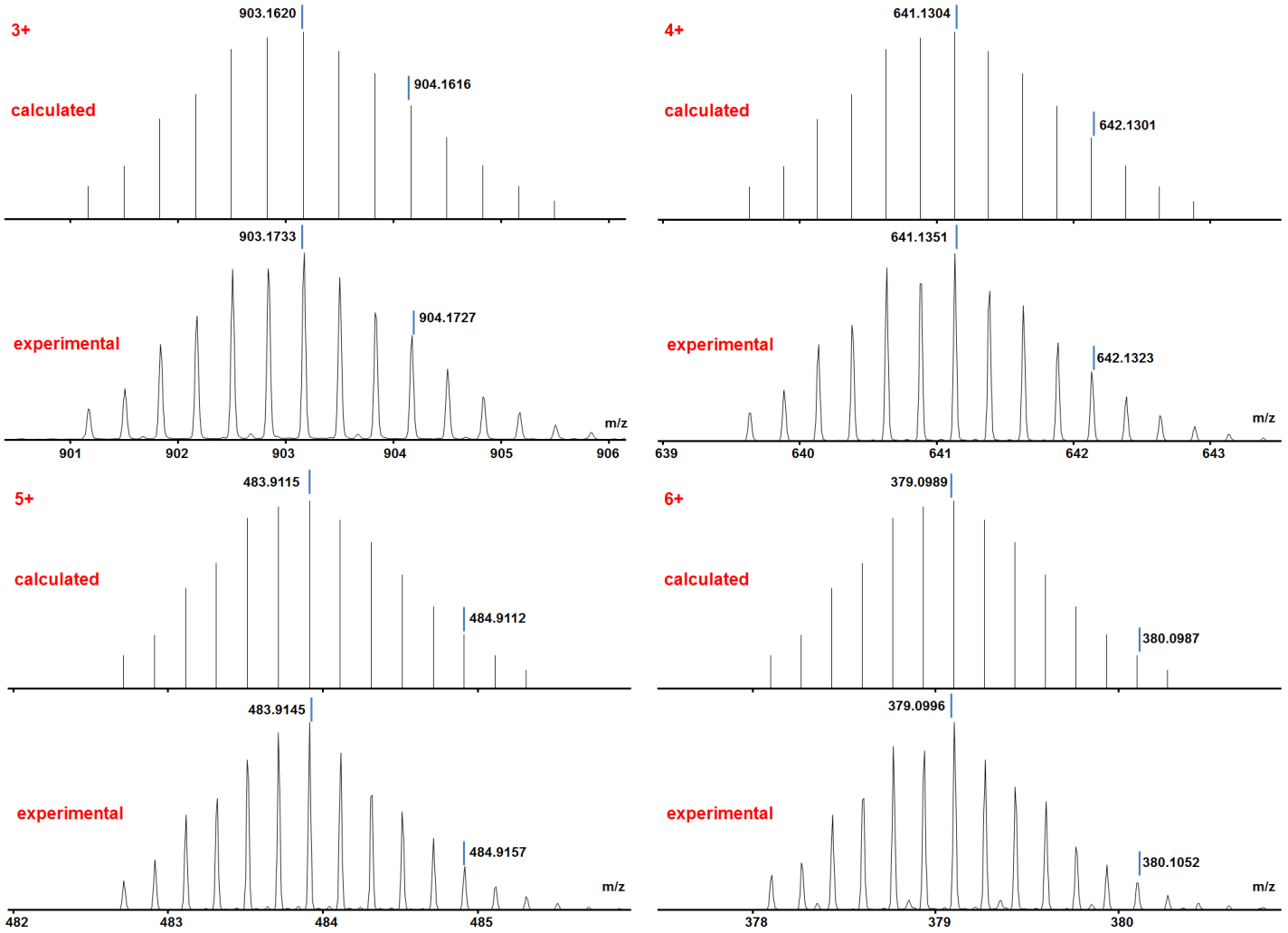


Fig. S26 Calculated and experimental isotope patterns of **Z2a**.

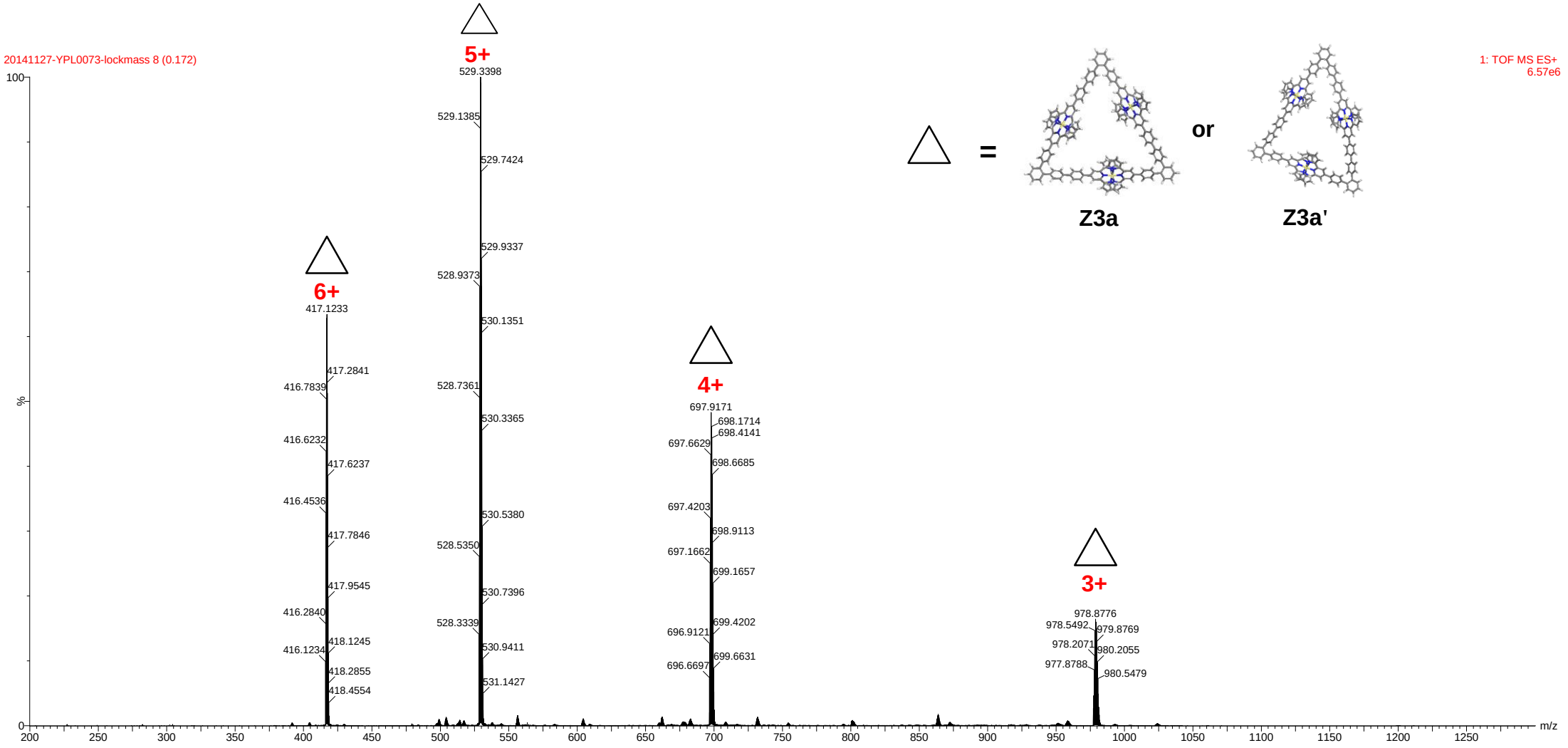


Fig. S27 ESI MS spectrum of **R3a**.

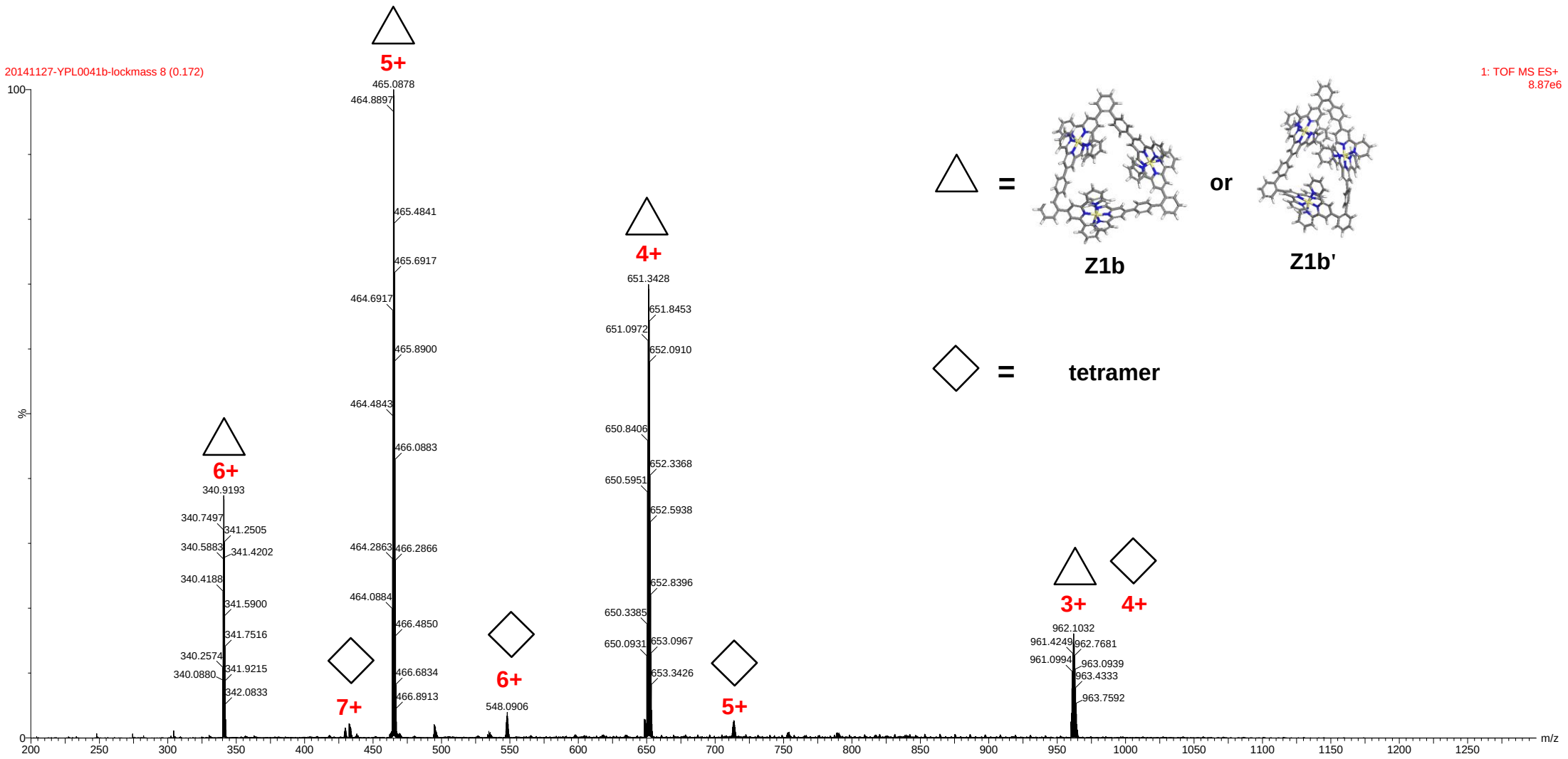


Fig. S28 ESI MS spectrum of **R1b**.

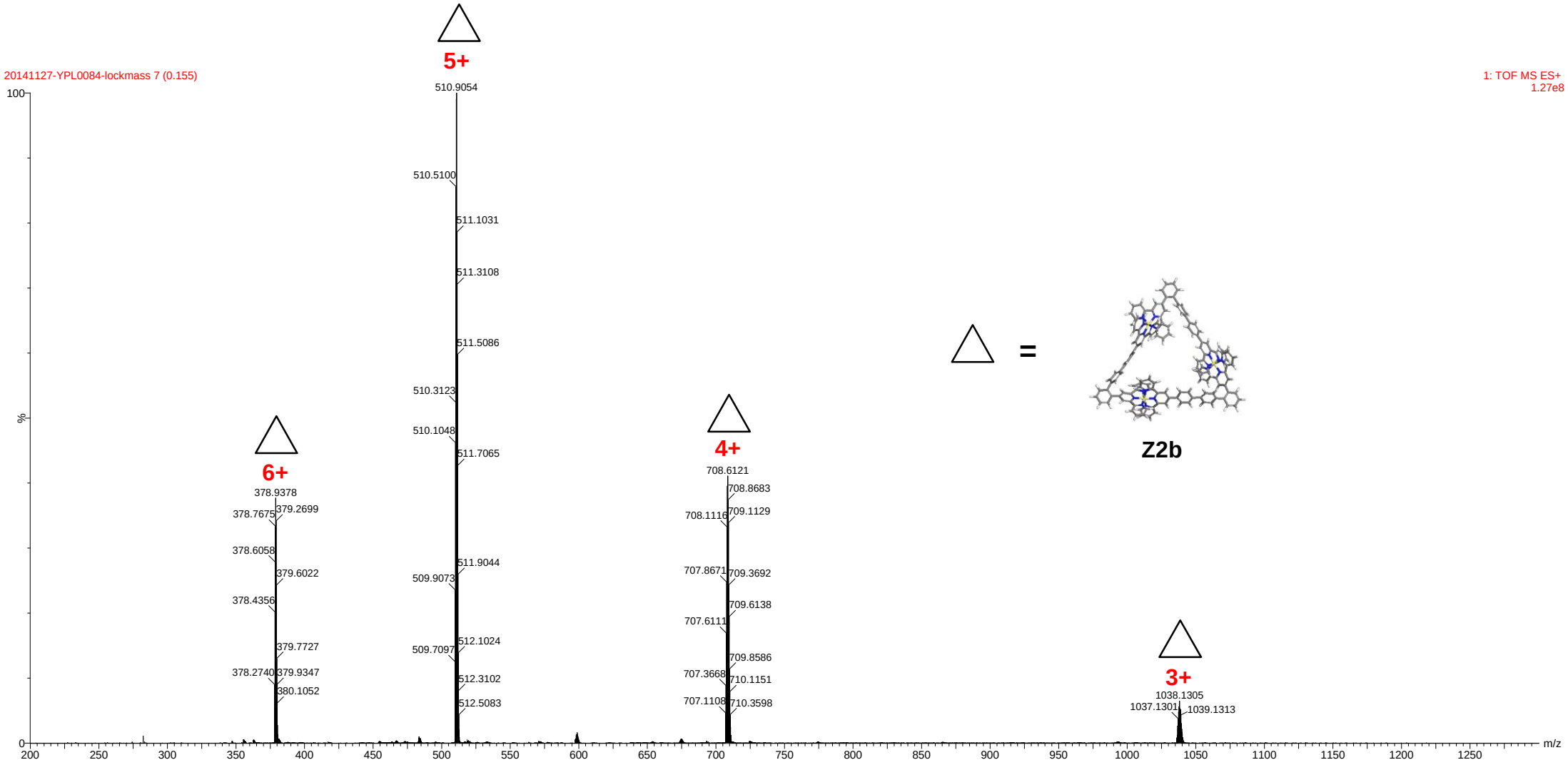


Fig. S29 ESI MS spectrum of **Z2b**.

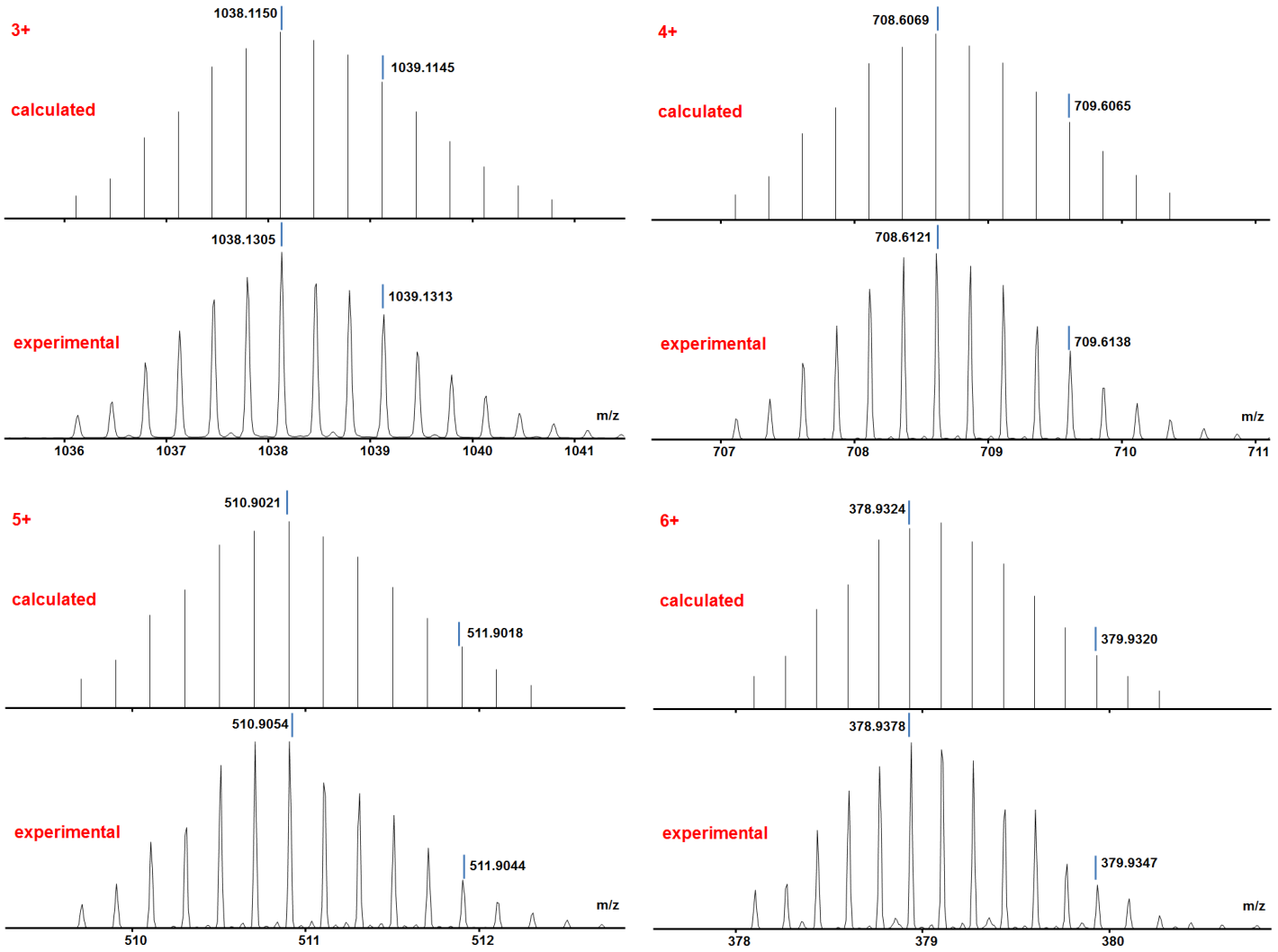


Fig. S30 Calculated and experimental isotope patterns of **Z2b**.

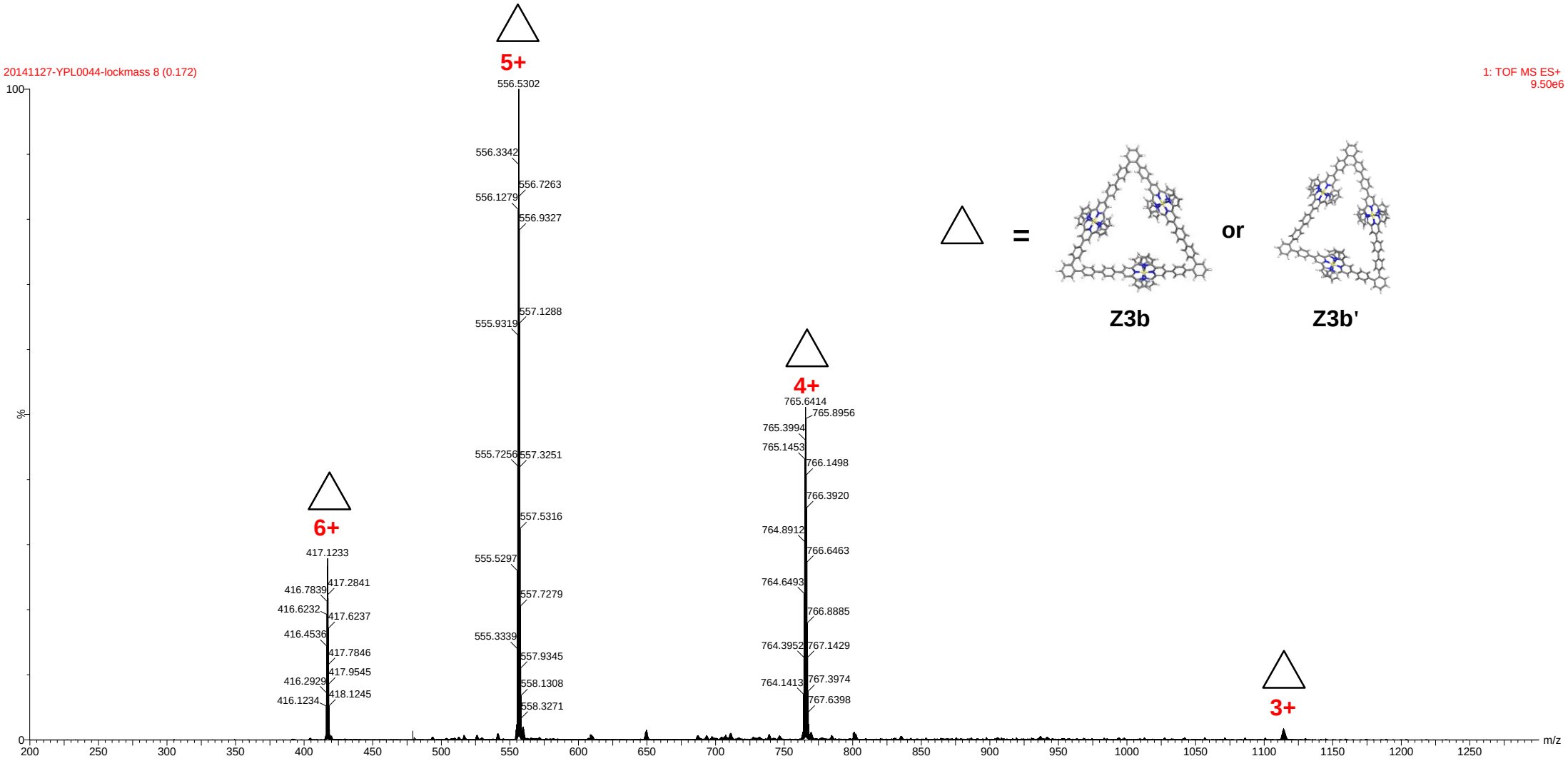


Fig. S31 ESI MS spectrum of **R3b**.

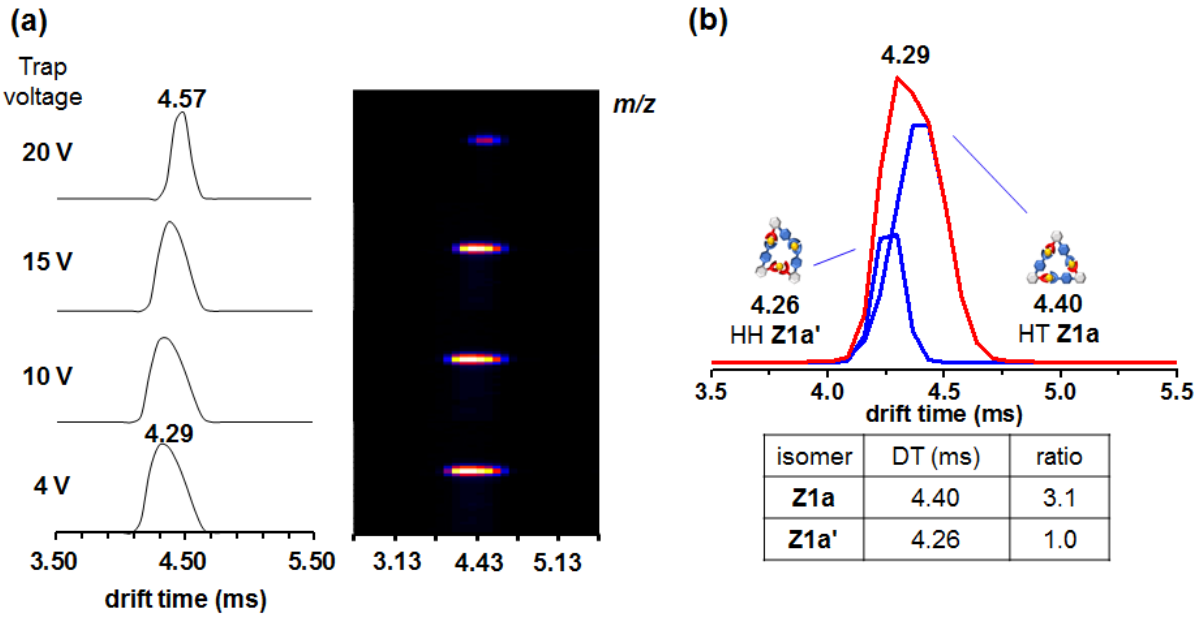
Tandem Mass Experiments

Table S2 Center-of-mass collision energies (E_{cm}) of Zn^{II} complexes.

Selected ion $[M-5A]^{5+}$	Counterion PF_6^-	Counterion NTf_2^-
Complex	Z1a	Z1b
E_{cm} (eV)	1.79	1.86
Complex	Z2a[a]	Z2b[a]
E_{cm} (eV)	3.17	3.42
Complex	Z3a	Z3b
E_{cm} (eV)	1.49	1.84

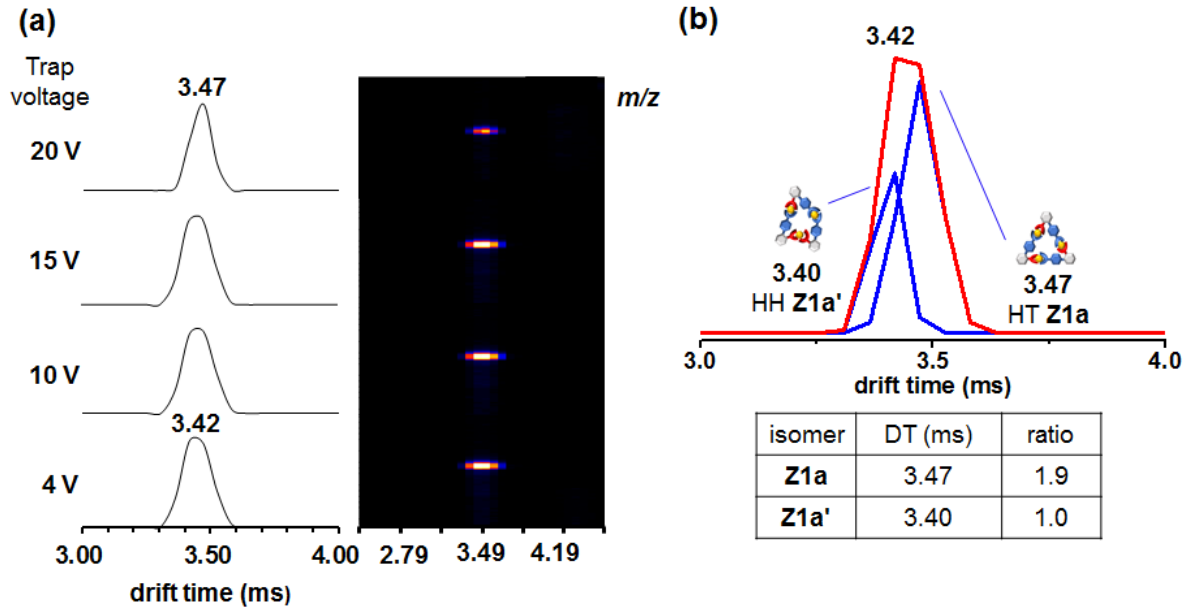
[a] The E_{cm} needed to completely fragment $[M-6A+F]^{5+}$ ions.

Characterization of Complex using ESI TWIM MS



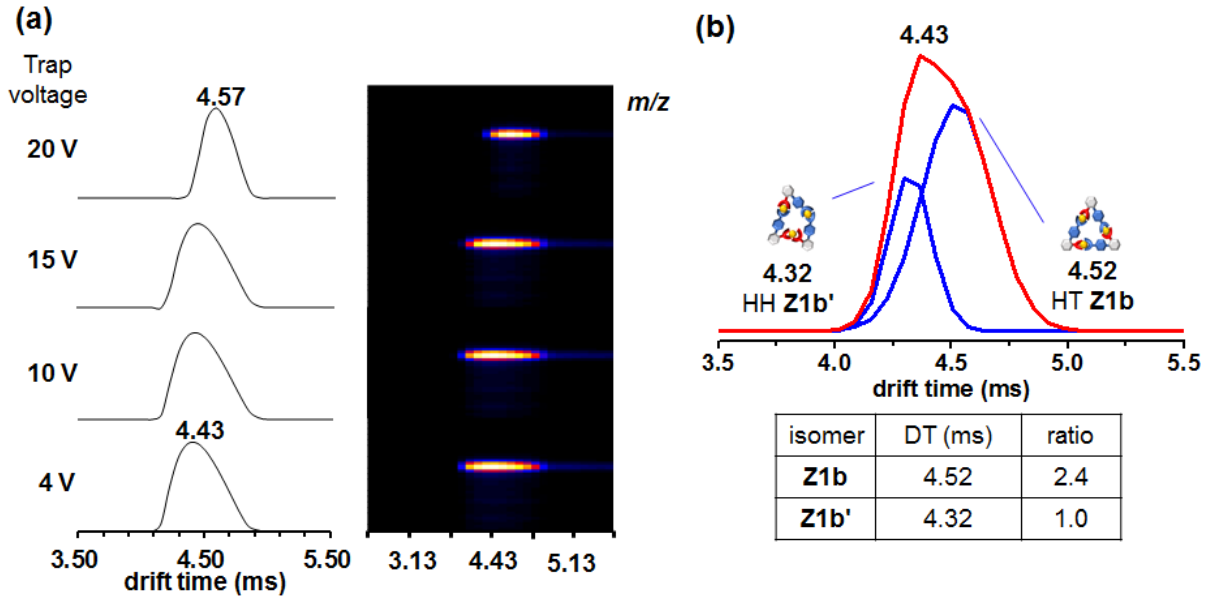
isomer	DT (ms)	ratio
Z1a	4.40	3.1
Z1a'	4.26	1.0

Fig. S32 (a) MS^2 TWIM MS spectra of **R1a** $[M\text{-}4PF_6]^{4+}$ ions and (b) the drift time deconvolution at 4 V.



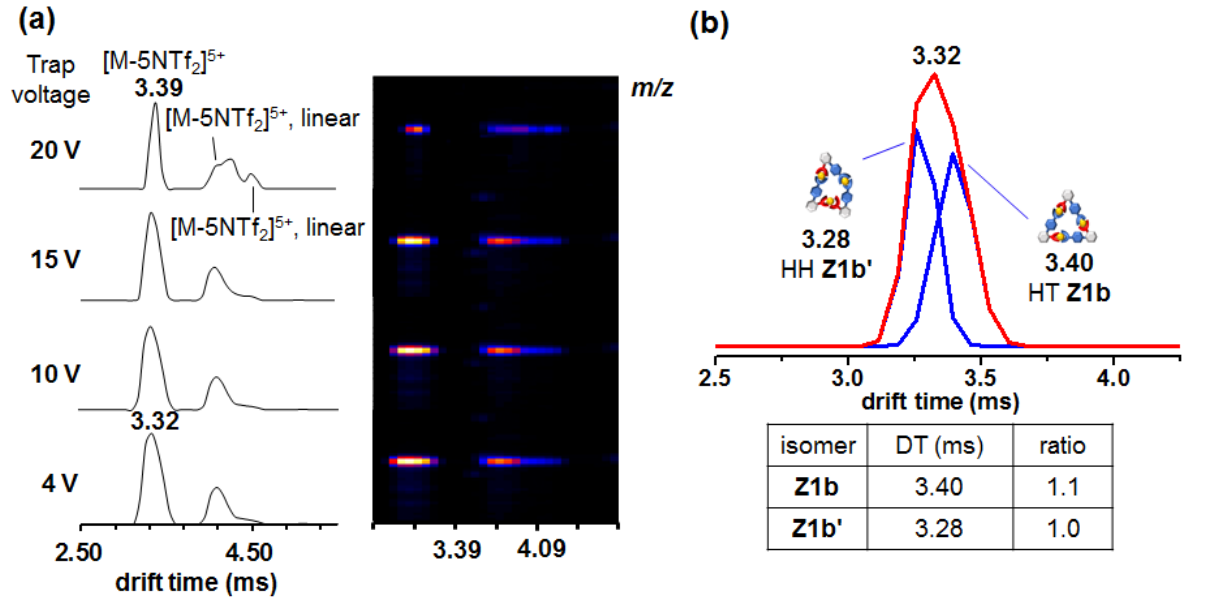
isomer	DT (ms)	ratio
Z1a	3.47	1.9
Z1a'	3.40	1.0

Fig. S33 (a) MS^2 TWIM MS spectra of **R1a** $[M\text{-}5PF_6]^{5+}$ ions and (b) the drift time deconvolution at 4 V.



isomer	DT (ms)	ratio
Z1b	4.52	2.4
Z1b'	4.32	1.0

Fig. S34 (a) MS^2 TWIM MS spectra of **R1b** $[M\text{-}4NTf_2]^{4+}$ ions and (b) the drift time deconvolution at 4V.



isomer	DT (ms)	ratio
Z1b	3.40	1.1
Z1b'	3.28	1.0

Fig. S35 (a) MS^2 TWIM MS spectra of **R1b** $[M\text{-}5NTf_2]^{5+}$ ions and (b) the drift time deconvolution at 4 V.

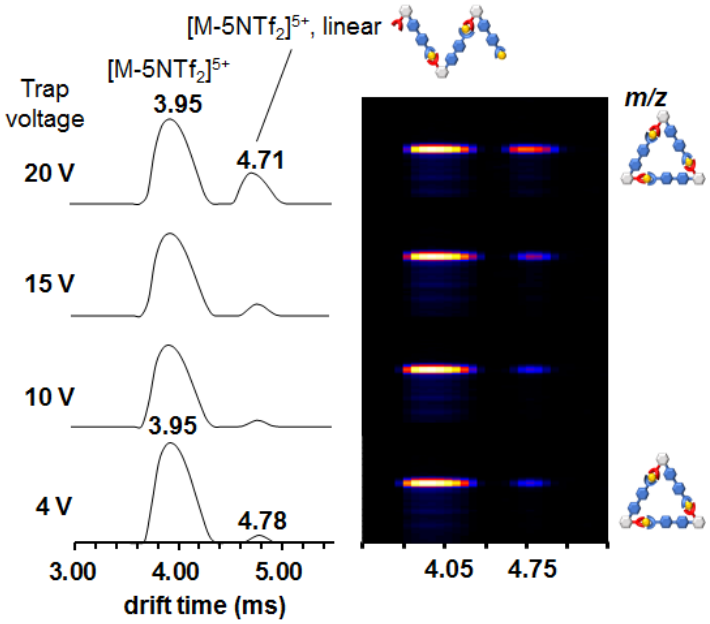
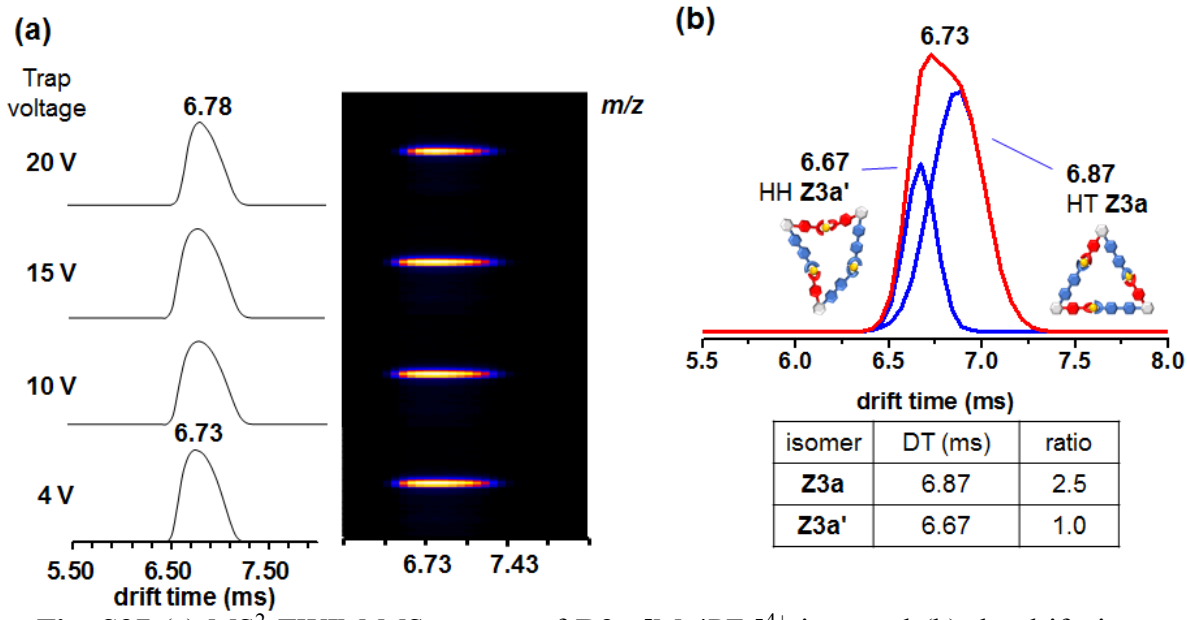
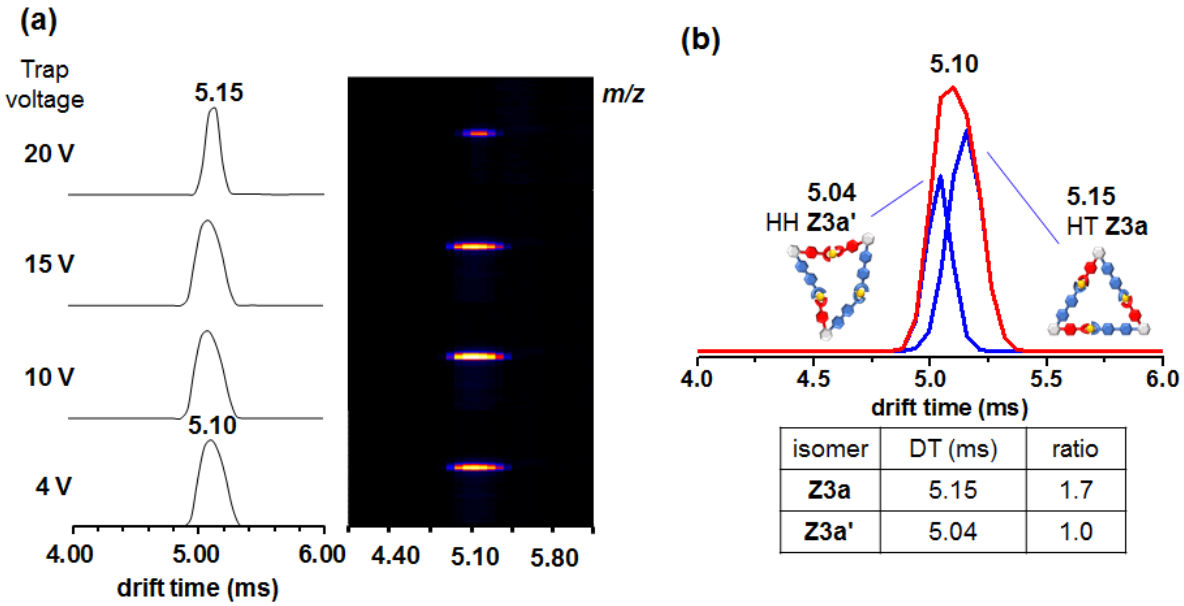


Fig. S36 MS^2 TWIM MS experiment of **Z2b** $[M\text{-}5NTf_2]^{5+}$ ions. Similar to the phenomenon in the literature,[8] linear isomers were observed.



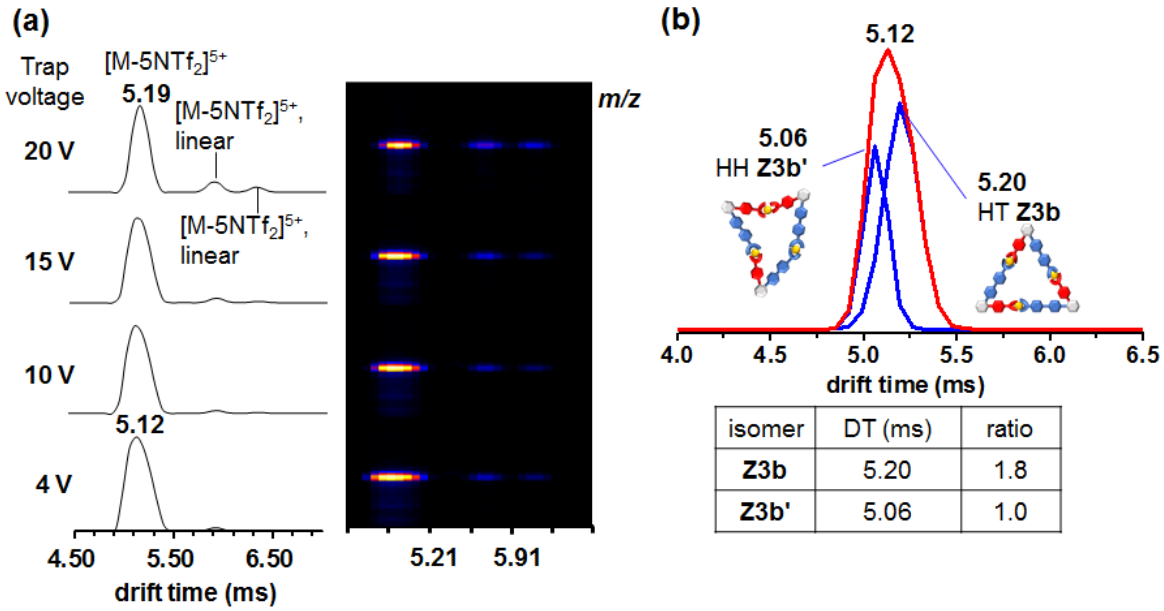
isomer	DT (ms)	ratio
Z3a	6.87	2.5
Z3a'	6.67	1.0

Fig. S37 (a) MS^2 TWIM MS spectra of **R3a** $[M\text{-}4PF_6]^{4+}$ ions and (b) the drift time deconvolution at 4 V.



isomer	DT (ms)	ratio
Z3a	5.15	1.7
Z3a'	5.04	1.0

Fig. S38 (a) MS^2 TWIM MS spectra of **R3a** $[M\text{-}5PF_6]^{5+}$ ions and (b) the drift time deconvolution at 4V.



isomer	DT (ms)	ratio
Z3b	5.20	1.8
Z3b'	5.06	1.0

Fig. S39 (a) MS^2 TWIM MS spectra of **R3b** $[M\text{-}5NTf_2]^{5+}$ ions and (b) the drift time deconvolution at 4 V.

CCS experiment, Molecular Modelling and Crystal Data

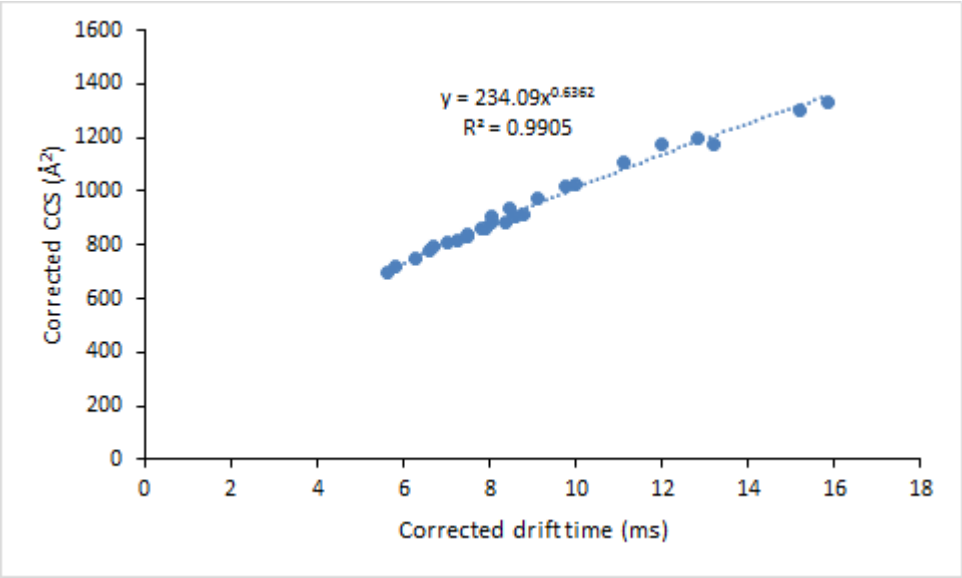


Fig. S40 CCS calibration curve

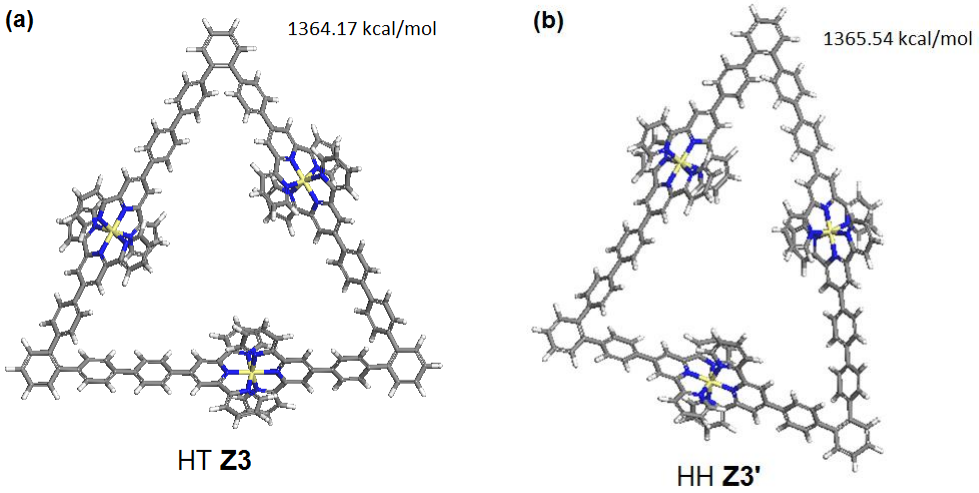


Fig. S41 Energy-minimized structures of (a) HT **Z3** and (b) HH **Z3'** along with their calculated total potential energies using universal force field in Forcite module of Materials Studio program.

Table S3 (a) Experimental and (b) theoretical average CCS (standard deviation) results (in Å²).

(a)

Experimental					
charge state / structure	6+	5+	4+	3+	avg. (stdv.)
HT **Z1a**	386.4	384.3	391.3	405.1	391.8 (9.4)
HH **Z1a'**	378.3	377.2	385.9	399.7	385.3 (10.4)
HT **Z1b**	379.6	381.7	398.4	417.8	394.4 (17.7)
HH **Z1b'**	375.9	373.8	389.8	407.8	386.8 (15.7)
Z2a	425.5	445.2	448.7	464.7	446.0 (16.1)
Z2b	433.3	438.3	448.3	478.7	449.6 (20.3)
HT **Z3a**	531.1	539.9	540.9	NA	537.3 (5.4)
HH **Z3a'**	523.1	530.3	528.9	NA	527.4 (3.8)
HT **Z3b**	530.8	544.0	553.6	575.9	551.1 (19.0)
HH **Z3b'**	519.6	532.2	542.0	565.4	539.8 (19.4)

(b)

Theoretical		
Method	**MOBCAL**	
CCS type / Structure	**PA**	**TM**
HT **Z1**	378.4 (0.6)	424.3 (6.7)
HH **Z1'**	371.3 (1.7)	417.9 (8.0)
Z2	455.6 (1.1)	505.9 (8.5)
Z2 crystal	450.1	516.6
HT **Z3**	536.3 (2.1)	579.9 (11.7)
HH **Z3'**	531.5 (2.6)	576.9 (12.9)

Table S4 Crystal data and structure refinement for **Z2a**.

Identification code	ic16714_sq	
Empirical formula	C156 H120 F36 N18 O3 P6 Zn3	
Formula weight	3360.62	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Trigonal	
Space group	P-3	
Unit cell dimensions	a = 32.7382(5) Å	α= 90°.
	b = 32.7382(5) Å	β= 90°.
	c = 9.1893(4) Å	γ = 120°.
Volume	8529.5(5) $Å^3$	
Z	2	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	1.834 mm^{-1}	
F(000)	3420	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	9.587 to 67.981°.	
Index ranges	-39<=h<=34, -28<=k<=36, -8<=l<=11	
Reflections collected	22133	
Independent reflections	10236 [R(int) = 0.0721]	
Completeness to theta = 67.679°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.90111	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10236 / 284 / 760	
Goodness-of-fit on F^2	1.175	
Final R indices [I>2sigma(I)]	R1 = 0.0947, wR2 = 0.2265	
R indices (all data)	R1 = 0.2105, wR2 = 0.2862	
Extinction coefficient	0	
Largest diff. peak and hole	0.619 and -0.535 $e.Å^{-3}$	

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