Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Metal ion adaptive self-assembly of photoactive lanthanide-based supramolecular hosts

Xiao-Zhen Li,[a] Li-Peng Zhou,[a] Shao-Jun Hu,[a,b] Li-Xuan Cai,[a] Xiao-Qing Guo,[a,b] Zhuo Wang,[a,b] and Qing-Fu Sun*[a,b]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China.

[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China.

*Correspondence to: qfsun@fjirsm.ac.cn

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Supplementary Methods

1. General

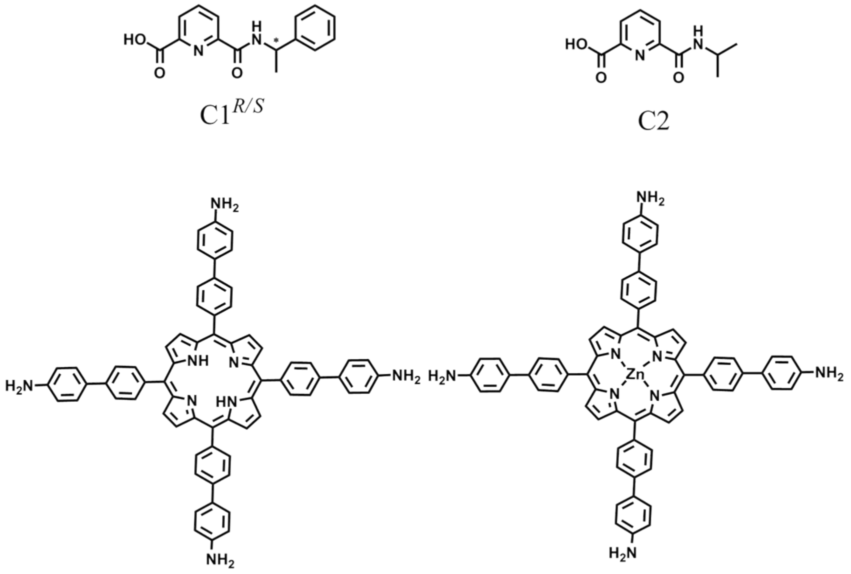
Unless otherwise stated, all chemicals and solvents were purchased from commercial companies and used without further purification. Deuterated solvents were purchased from Admas, J&K scientific and Sigma-Aldrich. 1D and 2D-NMR spectra were measured on a Bruker Biospin Avance III (400 MHz) spectrometer and JEOL ECZ600S (600 MHz) spectrometer. ^{1}H-NMR chemical shifts were determined with respect to residual signals of the deuterated solvents used. ESI-TOF-MS spectra were recorded on an Impact II UHR-TOF mass spectrometry from Bruker, with tuning mix as the internal standard. Data analysis was conducted with the Bruker Data Analysis software (Version 4.3) and simulations were performed with the Bruker Isotope Pattern software and Thermo Xcalibur Qual Browser software (Thermo Foundation 2.0). Some ESI-MS spectra were recorded on LC-QTOF-MS (G6520B). CD spectra were recorded on a MOS-450 circular dichroism spectrometer. Excitation and emission spectra were recorded on the FS5 and FLSP980 spectrofluorometer from Edinburg Photonics. Spectra were corrected for the experimental functions. Melting points were measured using a SGW Melting Point thermometer (X-4). Molecular-mechanical structure modeling was performed on Material Studio 6.0 by Accelrys Software, Inc.

Caution! Perchlorate salts are potentially explosive and should be handled carefully in small quantities.

2. Synthesis and characterization of La_6L_3 and Ln_8L_6 (Ln=Eu^{III}, Yb^{III})

Synthesis and characterization of ligands

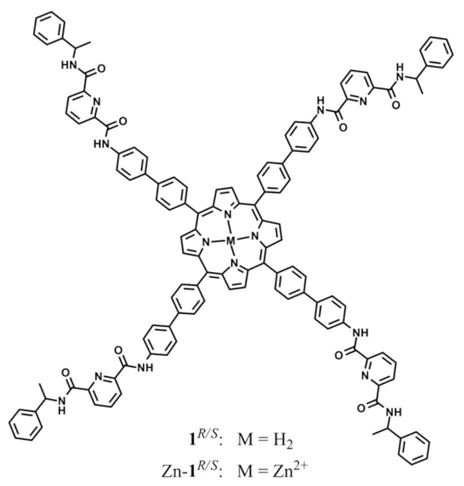
(R/S)-6-(1-phenylethylcarbamoyl) picolinic acid (**C1**$^{R/S}$) and 6-(isopropylcarbamoyl)picolinic acid (**C2**) were synthesized according to previous procedures.[1] **3** and **Zn-3** were synthesized according to reported literature.[2]



C1$^{R/S}$ C2

3 Zn-3

Scheme S1. Chemical structures of **C1**$^{R/S}$, **C2**, **3**, and **Zn-3.**



$\mathbf{1}^{R/S}$: M = H_2

Zn-$\mathbf{1}^{R/S}$: M = Zn^{2+}

Scheme S2. Chemical structures of ligands $\mathbf{1}^{R/S}$ and Zn-$\mathbf{1}^{R/S}$.

Synthesis of $\mathbf{1}^{R/S}$

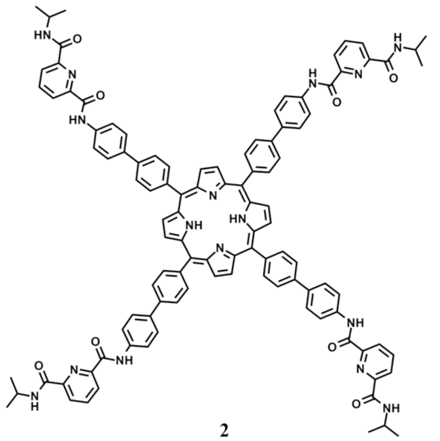
Chiral acid **C1**$^{R/S}$ (247.5 mg, 0.9191 mmol, 4.5 equiv.), Et_3N (186.0 mg, 1.838 mmol, 9 equiv.) and HATU (698.9 mg, 1.838 mmol, 9 equiv.) were dissolved in DMF (40 mL) and stirred at room temperature for 20 min. **3** (200.0 mg, 0.2042 mmol, 1 equiv., in 10 mL DMF) was then added to the reaction system. The resulting solution was stirred at 60°C for 20 h and monitored by TLC analysis. When the reaction was completed, the solvent was removed under reduced pressure and the resulting residue was washed with water. After dried under vacuum, the solid was purified by silica chromatography (CH_2Cl_2 : CH_3OH = 100:1 to 50:1) to give $\mathbf{1}^{R/S}$ as claret-colored powder (270.0 mg, 0.1358 mmol, 66.50% yield). m.p. > 250 ºC. ^{1}H NMR (400 MHz, d_6-DMSO, 298K) δ 11.06 (s, 1H), 9.68 (d, *J* = 8.3 Hz, 1H), 8.92 (s, 2H), 8.47 – 8.39 (m, 1H), 8.30 (ddd, *J* = 16.2, 10.7, 3.9 Hz, 4H), 8.11 (d, *J* = 6.7 Hz, 6H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 5.41 – 5.31 (m, 1H), 1.70 (d, *J* = 7.0 Hz, 3H), -2.81 (s, 0.5H). ESI-MS: calcd. for $C_{128}H_{98}N_{16}O_8$ $[M+2H]^{2+}$: 994.8965, found 994.9022.

Zn-1$^{R/S}$ was synthesized through the above procedure with the replacement of **3** with **Zn-3** (63.00% yield).

m.p. > 250 ºC.

Zn-1^{R}: ^{1}H NMR (400 MHz, d_6-DMSO, 298K) δ 11.06 (s, 1H), 9.68 (d, *J* = 8.3 Hz, 1H), 8.92 (s, 2H), 8.47 – 8.39 (m, 1H), 8.30 (ddd, *J* = 16.2, 10.7, 3.9 Hz, 4H), 8.11 (d, *J* = 6.7 Hz, 6H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 5.41 – 5.31 (m, 1H), 1.70 (d, *J* = 7.0 Hz, 3H). ESI-MS: calcd. for $C_{128}H_{96}N_{16}O_8Zn$ $[M+2H]^{2+}$: 1026.3532, found 1026.3543.

Zn-1^{S}: ^{1}H NMR (400 MHz, d_6-DMSO, 298K) δ 11.08 (s, 1H), 9.71 (d, J = 8.6 Hz, 1H), 8.93 (s, 2H), 8.42 (d, J = 6.8 Hz, 1H), 8.30 (m, 4H), 8.13 (m, 6H), 7.52 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 5.41 – 5.28 (m, 1H), 1.69 (d, J = 7.0 Hz, 3H).



2

Scheme S3. Chemical structures of ligands **2**.

2 was synthesized in similar procedures as above, starting from **C2** and **3**.

2: ^{1}H NMR (400 MHz, *d*$_6$-DMSO, 298K) δ 11.04 (s, 1H), 9.19 (d, *J* = 8.2 Hz, 1H), 8.94 (s, 2H), 8.41 (d, *J* = 7.0 Hz, 1H), 8.31 (m, 4H), 8.15 (m, 6H), 4.25 (q, *J* = 6.3 Hz, 1H), 1.36 (d, *J* = 6.6 Hz, 6H). ESI-MS: calcd for $C_{108}H_{90}N_{16}O_8$ $[M+2H]^{2+}$: 870.8652, found 870.8603. m.p. > 250 ºC.

Synthesis of La_6L_3

To a suspension of Zn-$\mathbf{1}^{R/S}$ (3.7 mg, 1.8 μmol) in 360 μL CD_3CN, a solution of $La(OTf)_3$ (2.1 mg, 3.6 μmol) in 240 μL CD_3OD was added and the reaction system was stirred at 45°C for 2 h. The turbid suspension turned clear quickly, giving a homogeneous purple solution as the final product La_6(Zn-$\mathbf{1}^{R/S}$)$_3$(OTf)$_{18}$. The self-assembled complex was characterized without further purification.

La_6($\mathbf{1}^{R/S}$)$_3$(OTf)$_{18}$ was synthesized in the same method as La_6(Zn-$\mathbf{1}^{R/S}$)$_3$(OTf)$_{18}$.

La_6(Zn-$\mathbf{1}^{R}$)$_3$(OTf)$_{18}$: ^{1}H NMR (400 MHz, CD_3CN/CD_3OD) δ 8.83-7.26 (broad, aromatic H), 5.59 (br, CH), 5.38 (br, CH), 1.81 (br, CH_3), 1.58 (br, CH_3). The severe line-broadening and over-lapping of the proton signals hindered the assignment of the ^{1}H NMR spectrum. ESI-TOF-MS for La_6(Zn-1^{R})$_3$(OTf)$_{18}$: the following signals are those at the highest intensities. m/z calcd. for $[La_6(Zn\text{-}1^{R})_3(OTf)_{12}]^{4+}$ 2268.7094, found 2268.4550; calcd. for $[La_6(Zn\text{-}1^{R})_3(OTf)_{13}]^{5+}$ 1785.1770, found 1785.1746; calcd. for $[La_6(Zn\text{-}1^{R})_3(OTf)_{12}]^{6+}$ 1462.8221, found 1462.6537; calcd. for $[La_6(Zn\text{-}1^{R})_3(OTf)_{11}]^{7+}$ 1232.5686, found 1232.5677; calcd. for $[La_6(Zn\text{-}1^{R})_3(OTf)_{10}]^{8+}$ 1059.8785, found 1059.8785.

La_6($\mathbf{1}^{R}$)$_3$(OTf)$_{18}$: ^{1}H NMR (400 MHz, CD_3CN/CD_3OD) δ 8.84-7.31 (br, aromatic H), 5.63 (br, CH), 5.44 (br, CH), 1.83 (br, CH_3), 1.61 (br, CH_3). It should also be noted that proton signals of the self-assembled complexes at around -3 ppm can not be detected because of the proton exchange between the active pyrrole-β H atoms and methanol-*d*$_4$. ESI-TOF-MS for La_6(1^{R})$_3$(OTf)$_{18}$: the following signals are those at the highest intensities. m/z calcd. for $[La_6(1^{R})_3(OTf)_{13}]^{5+}$ 1747.0298, found 1747.0311; calcd. for $[La_6(1^{R})_3(OTf)_{12}]^{6+}$ 1431.1997, found 1431.2020; calcd. for $[La_6(1^{R})_3(OTf)_{11}]^{7+}$ 1205.3206, found 1205.3230; calcd. for $[La_6(1^{R})_3(OTf)_{10}]^{8+}$ 1036.0365, found 1036.0397; calcd. for $[La_6(1^{R})_3(OTf)_{9}]^{9+}$ 904.3711, found 904.3752.

La$_6$(**1**^{S})$_3$(OTf)$_{18}$: ^{1}H NMR (400 MHz, CD$_3$CN/CD$_3$OD) δ 8.81-7.14 (br, aromatic H), 5.57 (br, CH), 5.38 (br, CH), 1.82 (br, CH$_3$), 1.59 (br, CH$_3$).

Synthesis of Ln$_8$(L)$_6$ (Ln^{III} = Pr^{III}, Nd^{III} and Eu^{III})

Eu$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$: To a suspension of Zn-**1**$^{R/S}$ (3.7 mg, 1.8 μmol) in 360 μL CD$_3$CN, a solution of Eu(OTf)$_3$ (1.56 mg, 2.6 μmol) in 240 μL CD$_3$OD was added and the reaction system was stirred at 45°C for 12 h. The turbid suspension turned clear gradually, giving a homogeneous purple solution as the final product. The self-assembled complex was characterized without further purification.

Ce$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$, Pr$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$, Nd$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$ and Eu$_8$(**1**$^{R/S}$)$_6$(OTf)$_{24}$ can be synthesized through the similar procedure as Eu$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$.

Eu$_8$(Zn-**1**$^{R/S}$)$_6$(OTf)$_{24}$ complexes can also be synthesized through the addition of Eu^{III} (4 equiv) to the prepared solution of La$_6$(Zn-**1**^{R})$_3$.

Eu$_8$(Zn-**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD$_3$CN/CD$_3$OD) δ 9.34 (s, 8H), 8.92 (s, 8H), 8.44 (d, *J* = 3.6 Hz, 8H), 8.25-7.91 (br, 56H), 7.23 (s, 8H), 7.02 (br, 48H), 6.56 (br, 16H), 5.87 (br, 8H), 1.91 (d, *J* = 1.6 Hz, 24H). The signals of amide proton (assigned as k) disappeared in the ^{1}H NMR spectrum possibly due to the proton exchange between amide proton and methanol-*d*$_4$. ESI-TOF-MS for Eu$_8$(Zn-1^R)$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{15}$]$^{9+}$ 1751.1987, found 1751.1948; calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$ 1561.1835, found 1561.1815; calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{13}$]$^{11+}$ 1405.6257, found 1405.6245; calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{12}$]$^{12+}$ 1276.0775, found 1276.0760; calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{11}$]$^{13+}$ 1166.5368, found 1166.5366; calcd. for [Eu$_8$(Zn-1^R)$_6$(OTf)$_{10}$]$^{14+}$ 1072.5018, found 1072.5017.

Eu$_8$(**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD$_3$CN/CD$_3$OD) δ 9.41 (br, 8H), 8.90 (br, 8H), 8.53 (br, 8H), 8.16-7.87 (br, 56H), 7.27-7.05 (br, 56H), 6.53 (br, 16H), 5.83 (br, 8H), 5.12 (br, 8H). ESI-TOF-MS for Eu$_8$(1^R)$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Eu$_8$(1^R)$_6$(OTf)$_{16}$]$^{8+}$ 1941.1586, found 1941.1565 calcd. for [Eu$_8$(1^S)$_6$(OTf)$_{15}$]$^{9+}$ 1709.0353, found 1709.1457; calcd. for [Eu$_8$(1^R)$_6$(OTf)$_{14}$]$^{10+}$ 1523.1364, found 1523.1367; calcd. for [Eu$_8$(1^R)$_6$(OTf)$_{13}$]$^{11+}$ 1371.1283, found 1371.3103; calcd. for [Eu$_8$(1^R)$_6$(OTf)$_{12}$]$^{12+}$ 1244.4549, found 1244.4559; calcd. for [Eu$_8$(1^R)$_6$(OTf)$_{11}$]$^{13+}$ 1137.2698, found 1137.3505.

Ce$_8$(Zn-**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD$_3$CN/CD$_3$OD) δ 13.84 (br), 12.77 (br), 9.10-6.04 (br), 2.02 (br), 1.36 (br), 1.27 (br), 0.86 (br). The self-assembly of Ce^{III} with **Zn-1$^{R/S}$** was conducted in a similar procedure as Eu$_8$(Zn-**1**^{R})$_6$(OTf)$_{24}$. A series of multi-charged species corresponding to [Ce$_8$(Zn-**1**^{R})$_6$(OTf)$_{24\text{-}n}$]$^{n+}$ complexes were obtained. ESI-MS for Ce$_8$(Zn-**1**^{R})$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Ce$_8$(Zn-1^R)$_6$-13H]$^{11+}$ 1219.7537, found 1219.7549; calcd. for [Ce$_8$(Zn-1^R)$_6$-14H]$^{10+}$ 1341.6281, found 1341.4290; calcd. for [Ce$_8$(Zn-1^R)$_6$-15H]$^{9+}$ 1490.5860, found 1490.3628; calcd. for [Ce$_8$(Zn-1^R)$_6$-16H]$^{8+}$ 1676.7833, found 1676.6614; calcd. for [Ce$_8$(Zn-1^R)$_6$-17H]$^{7+}$ 1916.1799, found 1916.6018. MS peaks corresponding to Ce$_6$(Zn-**1**^{R})$_3$(OTf)$_{18}$ were also observed in the MS spectra, but in a low intensity. We used Ce$_8$(Zn-**1**^{R})$_6$(OTf)$_{24}$ for the representation of the self-assembled complexes of Ce^{III} with **Zn-1^R**.

Pr_8(Zn-**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD_3CN/CD_3OD) δ 10.07 (br), 8.53 (br), 8.22 (br), 7.64 (br), 7.58 (br), 7.38 (br), 7.12 (br), 6.58 (br), 6.03 (br), 1.14 (br). ESI-MS for Pr_8(Zn-1^{R})$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Pr_8(Zn-1^{R})$_6$-13H]$^{11+}$ 1220.3002, found 1220.2111; calcd. for [Pr_8(Zn-1^{R})$_6$-14H]$^{10+}$ 1342.2295, found 1342.1325; calcd. for [Pr_8(Zn-1^{R})$_6$-15H]$^{9+}$ 1491.2543, found 1491.3677; calcd. for [Pr_8(Zn-1^{R})$_6$-16H]$^{8+}$ 1677.5351, found 1677.5398; calcd. for [Pr_8(Zn-1^{R})$_6$-17H]$^{7+}$ 1917.0391, found 1916.4652.

Nd_8(Zn-**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD_3CN/CD_3OD) δ 11.13 (s), 10.71 (s), 10.06 (s), 9.-6.54 (br), 5.02 (br), 2.62 (br), 2.24 (br), 1.67 (br). The severe overlapping and broadening of the ^{1}H NMR spectrum hindered the assignment and integration of the proton signals. ESI-MS for Nd_8(Zn-1^{R})$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Nd_8(Zn-1^{R})$_6$-13H]$^{11+}$ 1222.5753, found 1222.5794; calcd. for [Nd_8(Zn-1^{R})$_6$-14H]$^{10+}$ 1344.7321, found 1344.7371; calcd. for [Nd_8(Zn-1^{R})$_6$-15H]$^{9+}$ 1494.0349, found 1494.0379; calcd. for [Nd_8(Zn-1^{R})$_6$-16H]$^{8+}$ 1680.6633, found 1680.6672.

General protocols of transmetalation self-assembly of Yb_8L_6 (L = 1$^{R/S}$ or Zn-1$^{R/S}$)

$Yb(OTf)_3$ (2.4 μmol) was added to a solution of pre-prepared $Ln_8L_6(OTf)_{24}$ (Ln^{III} = Pr^{III}, Nd^{III} and Eu^{III}) (0.3 μmol) in CD_3CN/CD_3OD and the reaction system was stirred at 45ºC for 6 h. $Yb_8L_6(OTf)_{24}$ was formed as the final thermodynamically stable product. When $CHCl_3$ (1mL) was added to the solution of $Yb_8L_6(OTf)_{24}$ (CH_3CN/CH_3OH, 0.5mL), the self-assembled complexes were precipitated. The amaranth precipitation was centrifuged and dried for further characterization (yield, 78%).

$Yb(OTf)_3$ (2.4 μmol) was added to a solution of pre-prepared $La_6L_3(OTf)_{18}$ (0.4 μmol) in CD_3CN/CD_3OD and stirred at 45ºC for 1 h. $Yb_8L_6(OTf)_{24}$ complexes were formed as the final thermodynamically stable product. The product can be used for characterization without further purification. Also, amaranth precipitation appeared with the addition of $CHCl_3$ to the self-assembled solution and the precipitation was centrifuged and dried for further characterization (yield, 78%).

Except for the above mentioned one-step transmetalation reaction, $Yb_8L_6(OTf)_{24}$ can also be synthesized in a cascade metalion metathesis method, starting from $La_6L_3(OTf)_{18}$ to $Eu_8L_6(OTf)_{24}$ and to the final $Yb_8L_6(OTf)_{24}$.

Direct self-assembly of $Yb(OTf)_3$ with L in CD_3OD/CD_3CN (v/v=2:3) was not successful as the solution never turned clear and no signals was observed in the ^{1}H NMR spectrum upon prolonged reaction time (> 1 week), from which we speculated that dynamically trapped oligomers were formed in this case.

Reaction of L (3 equiv) with a mixture of La^{III} and Yb^{III} (2 equiv and 4 equiv, respectively) in CD_3OD/CD_3CN (v/v=2:3) also results in the formation of $Yb_8L_6(OTf)_{24}$ complexes, but needs a much longer reaction time (3 days) compared with the transmetalation self-assembly process.

Yb_8(**1**^{R})$_6$(OTf)$_{24}$: ^{1}H NMR (400 MHz, CD_3CN/CD_3OD) δ 10.67-8.85 (br, aromatic H), 7.35-6.50 (br, aromatic H), 3.00 (br, CH_3). The severe lien-broadening of the ^{1}H NMR spectrum caused by the paramagnetism of Yb^{III} ions hindered the accurate integration and assignment of the proton signals. ESI-TOF-MS for Yb_8(1^{R})$_6$(OTf)$_{24}$: the following signals are those at the highest intensities. m/z calcd. for [Yb_8(1^{R})$_6$-15H]$^{9+}$ 1477.5624, found

1477.5613; calcd. for $[Yb_8(1^{R})_6\text{-}14H]^{10+}$ 1330.0007, found 1330.2067; calcd. for $[Yb_8(1^{R})_6\text{-}13H]^{11+}$ 1209.0978, found 1209.0988; calcd. for $[Yb_8(1^{R})_6\text{-}12H]^{12+}$ 1108.5071, found 1108.5064 (Prepared through the transmetalation from $Eu_8(1^{R})_6(OTf)_{24}$).

$Yb_8(\mathbf{1}^{R})_6(OTf)_{24}$: ^1H NMR (400 MHz, CD_3CN/CD_3OD) δ 10.09-8.85 (br, aromatic H), 7.35-6.50 (br, aromatic H), 2.99 (br, CH_3). ESI-TOF-MS for $Yb_8(1^{R})_6(OTf)_{24}$: the following signals are those at the highest intensities. m/z calcd. for $[Yb_8(1^{R})_6\text{-}16H]^{8+}$ 1662.2570, found 1662.2605; $[Yb_8(1^{R})_6\text{-}15H]^{9+}$ 1477.5624, found 1477.5627; calcd. for $[Yb_8(1^{R})_6\text{-}14H]^{10+}$ 1330.0007, found 1329.8082; calcd. for $[Yb_8(1^{R})_6\text{-}13H]^{11+}$ 1209.0978, found 1209.0973 (Prepared through the transmetalation from $La_6(1^{R})_3(OTf)_{18}$).

$Yb_8(Zn\text{-}\mathbf{1}^{R})_6(OTf)_{24}$: ^1H NMR (400 MHz, CD_3CN) δ 10.59-8.83 (br, aromatic H), 7.30-6.51 (br, aromatic H), 2.95 (br, CH_3). The severe broadening of the ^1H NMR spectrum caused by the paramagnetism of Yb^{III} ions hindered the accurate integration and assignment of the proton signals. ESI-TOF-MS for $Yb_8(Zn\text{-}1^{R})_6(OTf)_{24}$: the following signals are those at the highest intensities. m/z calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_9\text{-}7H]^{8+}$ 1878.3955, found 1878.6445; calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_8\text{-}7H]^{9+}$ 1653.1346, found 1653.1319; calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_7\text{-}7H]^{10+}$ 1473.9259, found 1473.4284; calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_6\text{-}7H]^{11+}$ 1325.4824, found 1325.5763; calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_5\text{-}7H]^{12+}$ 1202.6128, found 1202.6150; calcd. for $[Yb_8(Zn\text{-}1^{R})_6(OTf)_5\text{-}6H]^{13+}$ 1110.1047, found 1110.1046.

Synthesis of $Eu_8(2)_6(ClO_4)_{24}$

To a suspension of **2** (3.1 mg, 1.8 μmol) in 360 μL CD_3CN, a solution of $Eu(ClO_4)_3\cdot 6H_2O$ (1.45 mg, 2.6 μmol) in 240 μL CD_3OD was added and the reaction system was stirred at 45°C for 12 h. The turbid suspension turned clear gradually, giving a homogeneous purple solution as the final product. The self-assembled complex was characterized without further purification.

$Eu_8(\mathbf{2})_6(ClO_4)_{24}$: ^1H NMR (400 MHz, CD_3CN) δ 9.46 (d, J = 4.0 Hz, 8H), 8.94 (d, J = 4.3 Hz, 8H), 8.58 (d, J = 6.8 Hz, 8H), 8.47 – 8.02 (br, 32H), 7.91 (br, 16H), 7.29 (br, 16H), 6.59 (br, 16H), 4.49 (br, 8H), 1.71 (br, 24H), 1.02 (br, 24H).

The ^{13}C NMR spectra of ligands **L** (**L** = $\mathbf{1}^{R/S}$ or $\mathbf{Zn\text{-}1}^{R/S}$), $La_6\mathbf{L}_3$ and $Ln_8\mathbf{L}_6$ (Ln = Eu^{III} and Yb^{III}) complexes were not successfully obtained due to their low solubility.

3. Host-guest chemistry

PAH molecules of naphthalene, anthracene, phenanthrene, perylene, 1,12-benzoperylene, coronene, tetraphenylethylene, rubrene and nonplanar (S/R)2,2'-dimethoxy-1,1'-binaphthyl were used as guests for the host-guest investigation.

Excess guest molecules were added to the solution of prepared $Ln_8(Zn\text{-}\mathbf{1}^{R})_6$ (Ln = Eu^{III} and Yb^{III}) in CD_3CN/CD_3OD. After stirring at 45°C for 2h, excess guest molecules were removed through centrifuge and the clear solution was characterized without further purification.

$^1H\text{-}^1H$ NOESY NMR spectra of the host-guest complexes were tested. But not all the cross-peaks between the signals of the encapsulated guests and the hosts can be observed due to the high molecule weight and the paramagnetism of the lanthanide ions.

It should be noted that, the preparation of $La_6(Zn\text{-}\mathbf{1}^R)_3$ and $Eu_8(Zn\text{-}\mathbf{1}^R)_6$ should be conducted in a mixture solution of CD_3CN/CD_3OD. Once formed, the $Eu_8(Zn\text{-}\mathbf{1}^R)_6$ complexes can be dissolved in CH_3CN (the solubility is not very good), but the $La_6(Zn\text{-}\mathbf{1}^R)_3$ complexes are only soluble in CD_3CN/CD_3OD (3/2, v/v). As the encapsulated signals of perylene tend to overlap with the signals of CD_3OD at ca. 3.28ppm, the host-guest complexes were dried under reduced pressure and redissolved in CD_3CN for NMR characterization.

4. Single crystal X-ray diffraction studies

Suitable single crystals of $Eu_8(\mathbf{2})_6$ were obtained by slow vapor diffusion of acetone into the acetonitrile solution of $Eu_8(\mathbf{2})_6(ClO_4)_{24}$. The X-ray diffraction data was collected at the BL17B macromolecular crystallography beamline in Shanghai Synchrotron Facility. The collected diffraction data were processed with the HKL3000 software program.[3] The structures were solved by direct methods and refined by full-matrix least-squares on *F2* with anisotropic displacement using the SHELX software package.[4] The crystals diffract weakly due to the large amounts of solvent molecules and anions. Details on crystal data collection and refinement are summarized in Table S1.

Crystal data for $Eu_8(\mathbf{2})_6$ (CCDC-1939386): Space group P4/n, a = 38.200(5) Å, b = 38.200(5) Å, c = 46.770(9) Å, α = 90°, β = 90°, γ = 90°, V = 68249(24) Å^3, Z = 2, T = 293(2) K. Anisotropic least-squares refinement for the cubic framework and isotropic refinement for the other fragments on 20682 independent merged reflections (Rint = 0.0937) converged at residual wR2 = 0.2962 for all data; residual R1 = 0.0857 for 13439 observed data [$I > 2\sigma(I)$], and goodness of fit (GOF) = 1.118.

Data availability

X-ray crystal structure of compounds $Eu_8(\mathbf{2})_6(ClO_4)_{24}$ reported in this paper has been deposited in the Cambridge Crystallographic Data Centre under accession numbers CCDC: 1939386. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif). All other data supporting the findings of this study are available in the article and its Supplementary Information files and from the corresponding authors on request.

5. NMR and ESI-TOF-MS spectra

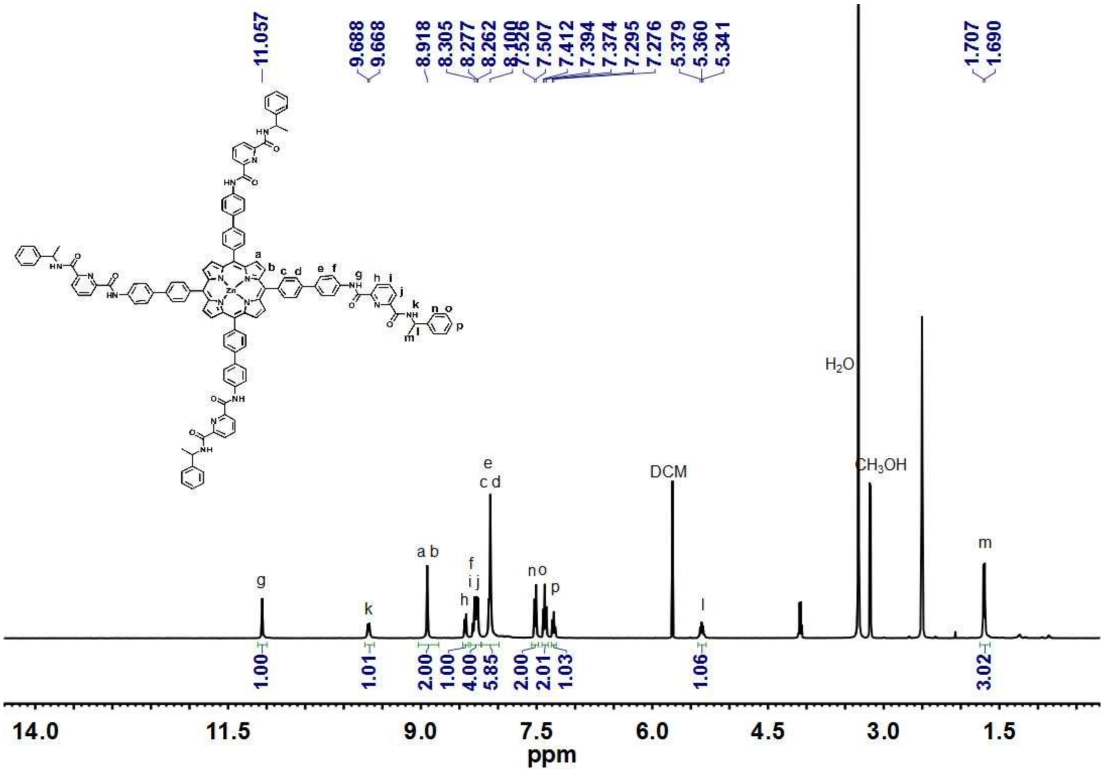


Figure S1. ^{1}H NMR spectrum of Zn-$\mathbf{1}^R$ (400 MHz, d_6-DMSO, 298K).

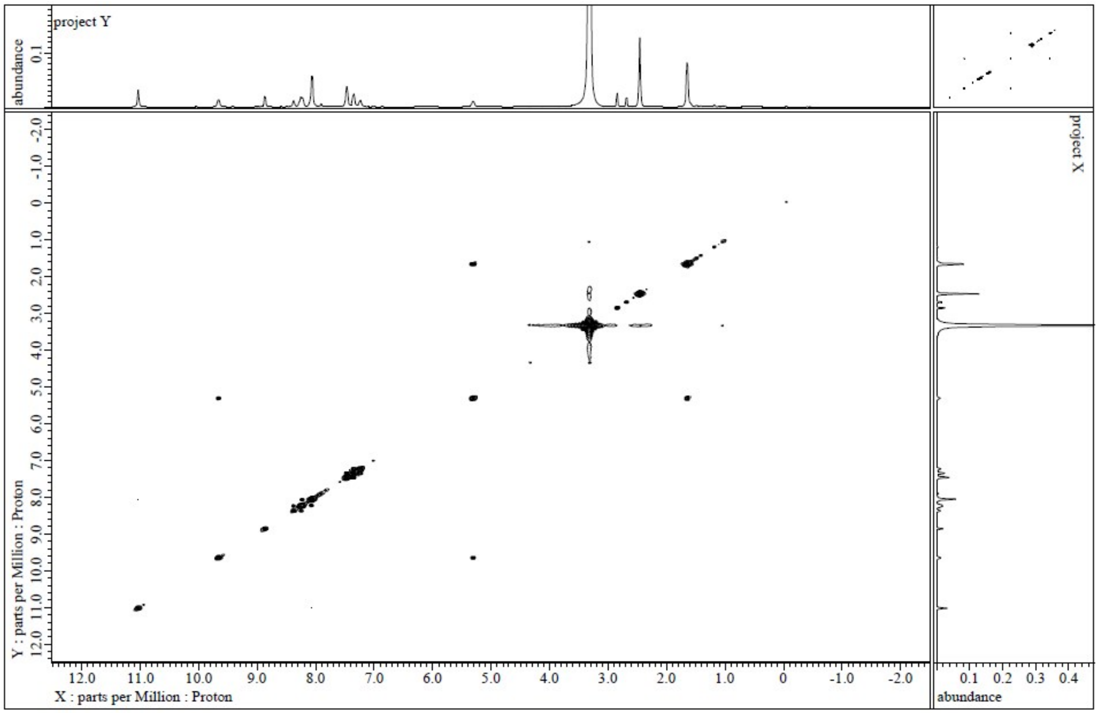


Figure S2. ^{1}H-^{1}H COSY NMR spectrum of Zn-$\mathbf{1}^R$ (600 MHz, d_6-DMSO, 298K).

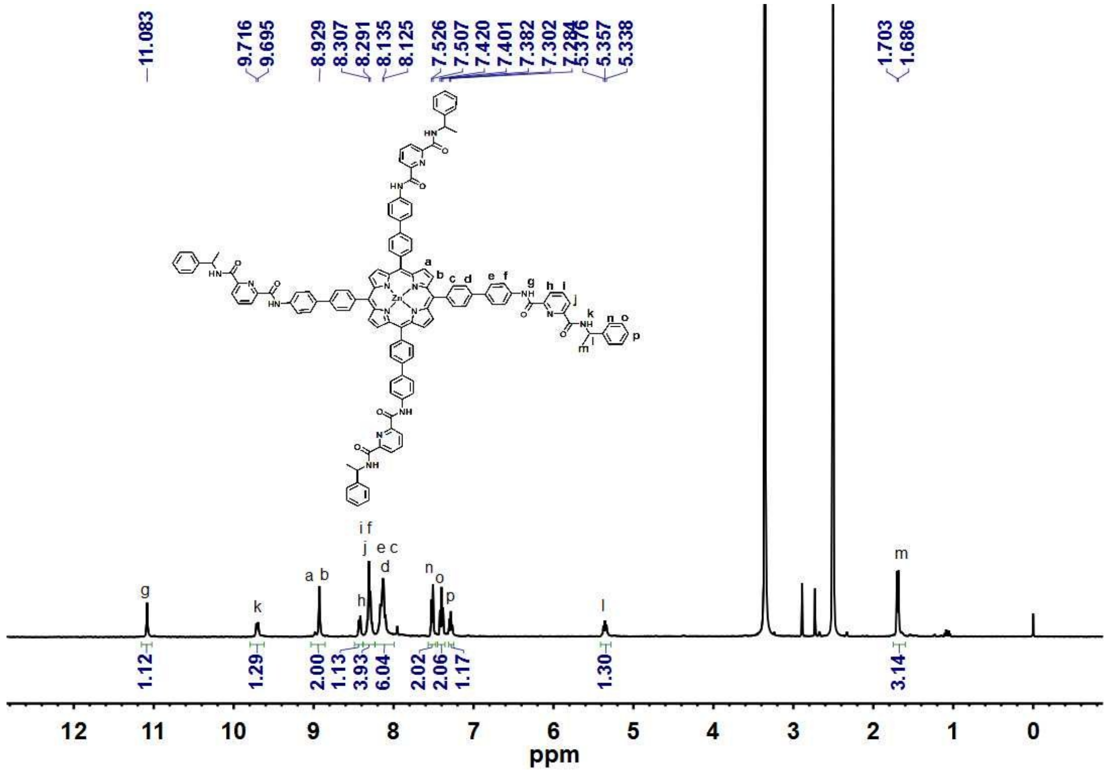


Figure S3. ^{1}H NMR spectrum of Zn-**1**^{S} (400 MHz, d_6-DMSO, 298K).

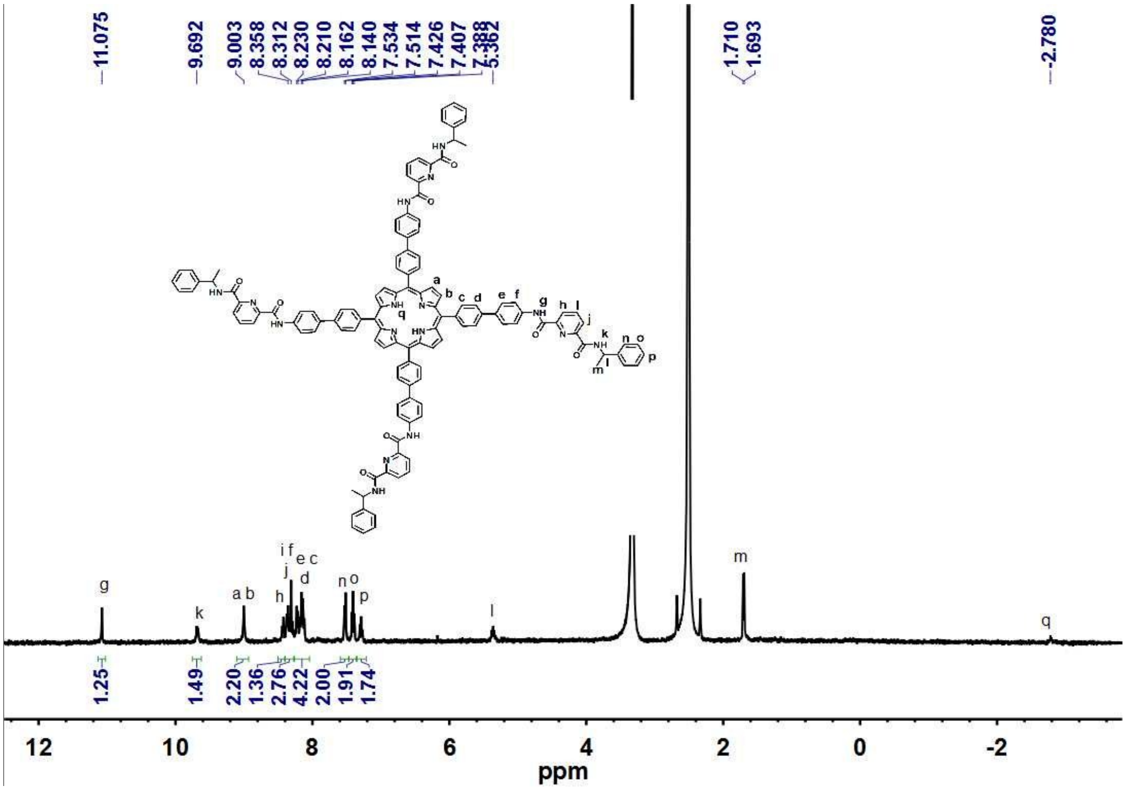


Figure S4. ^{1}H NMR spectrum of **1**^{R} (400 MHz, d_6-DMSO, 298K).

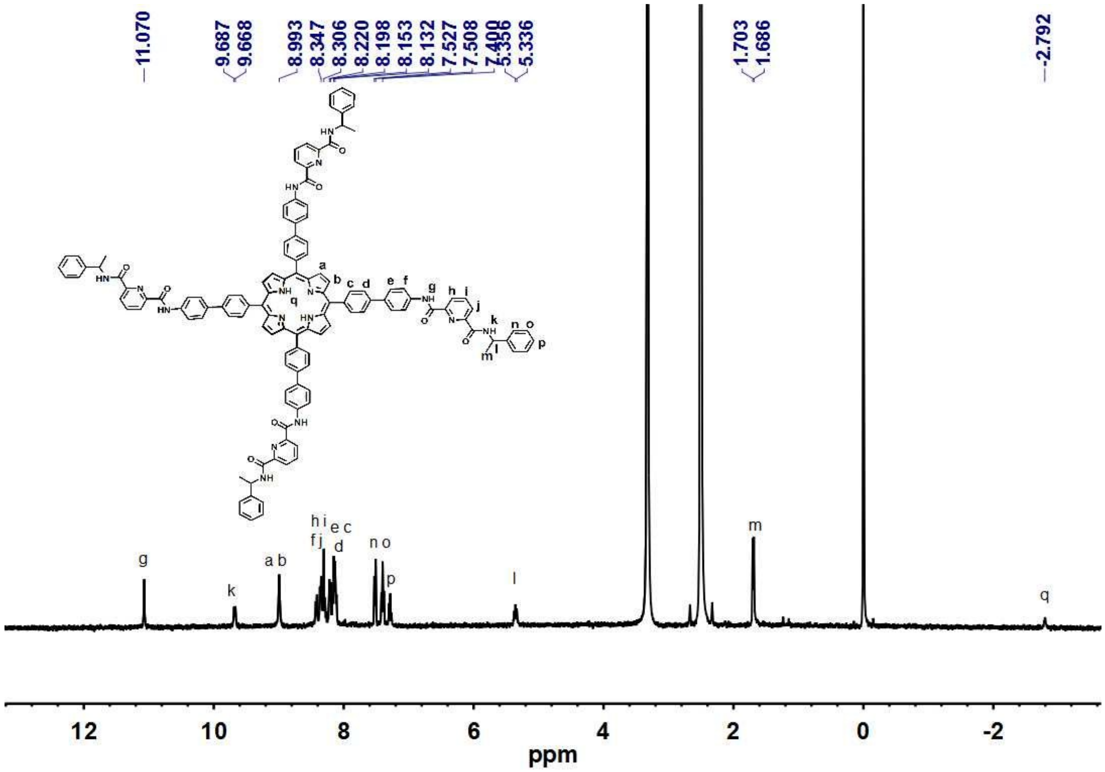


Figure S5. ^{1}H NMR spectrum of $\mathbf{1}^{S}$ (400 MHz, d_6-DMSO, 298K).

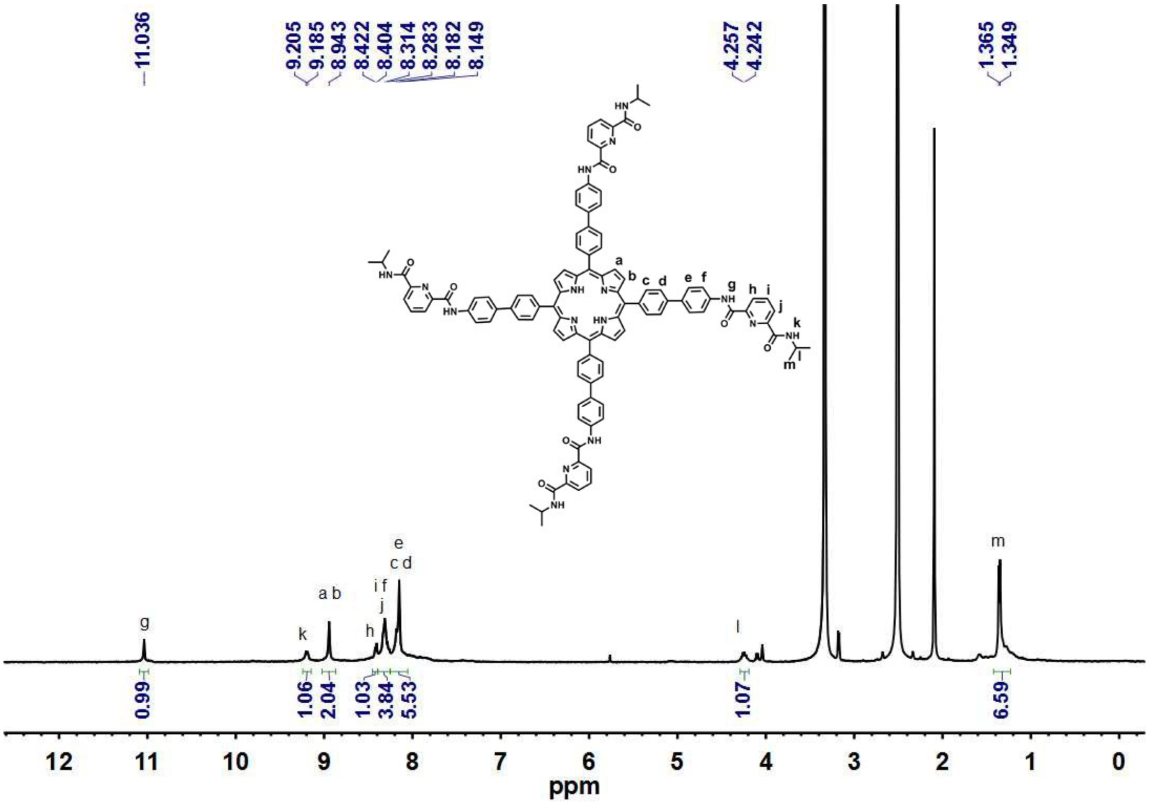


Figure S6. ^{1}H NMR spectrum of **2** (400 MHz, d_6-DMSO, 298K).

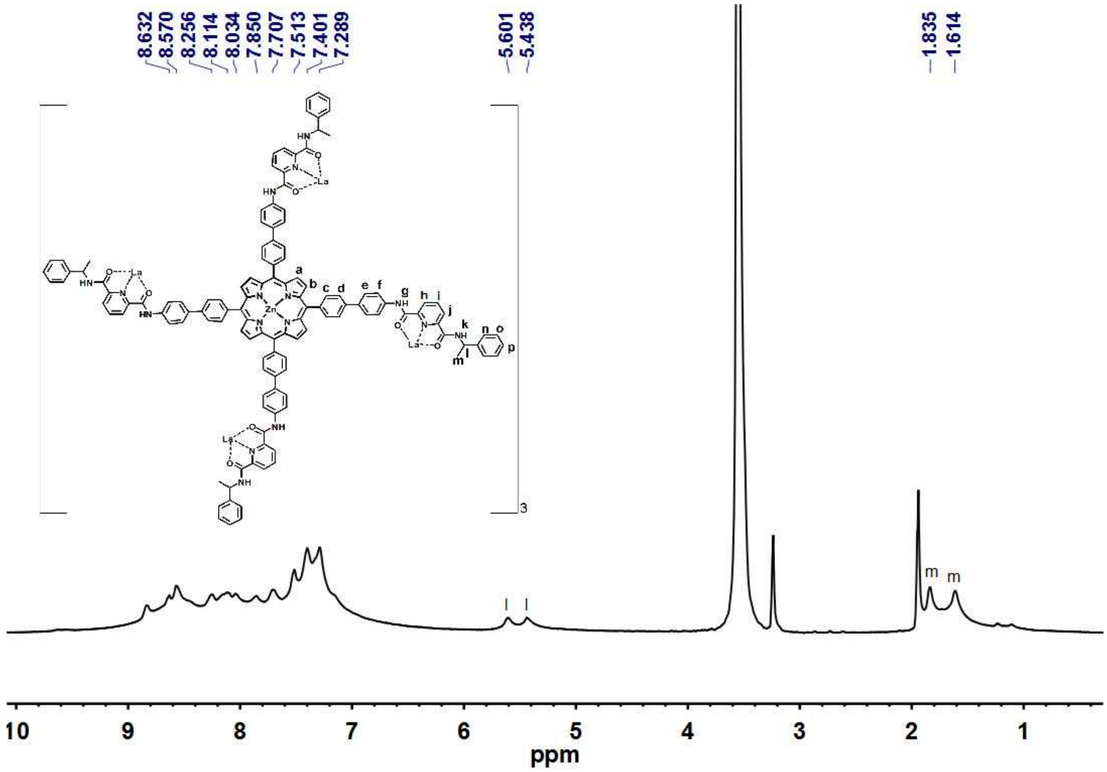


Figure S7. ^{1}H NMR spectrum of **La$_6$(Zn-1^R)$_3$(OTf)$_{18}$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

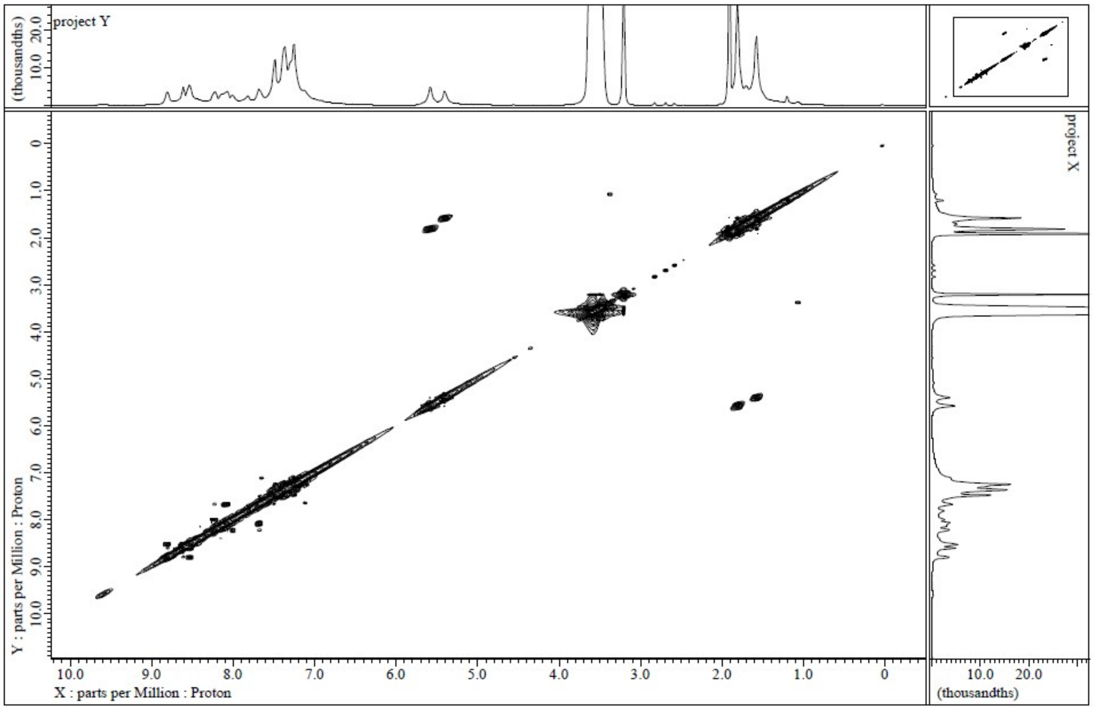
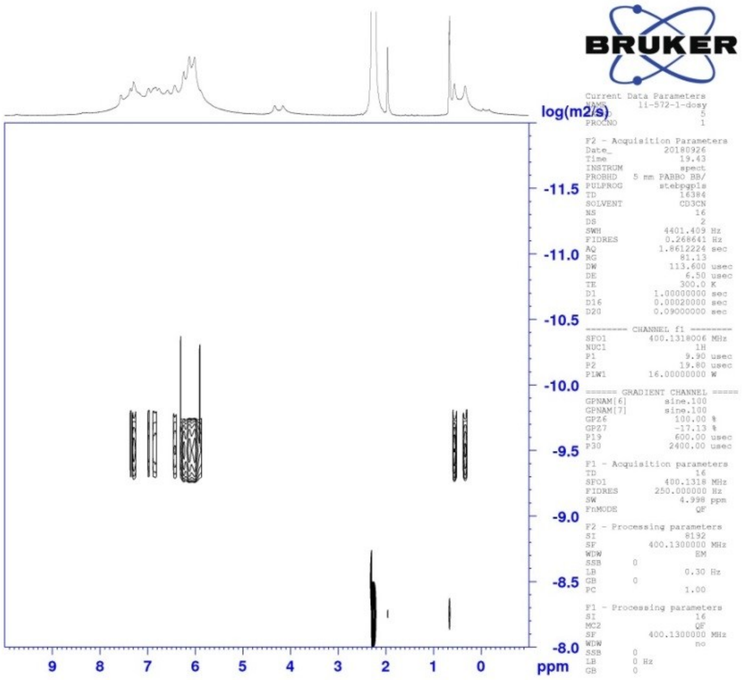


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of **La$_6$(Zn-1^R)$_3$(OTf)$_{18}$** (600 MHz, CD$_3$CN/CD$_3$OD, 298K).



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D20            0.09000000 sec

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P2                  19.80 usec
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P30               2400.00 usec

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FnMODE                 QF

F2 - Processing parameters
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WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00

F1 - Processing parameters
SI                     16
MC2                    QF
SF            400.1300000 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
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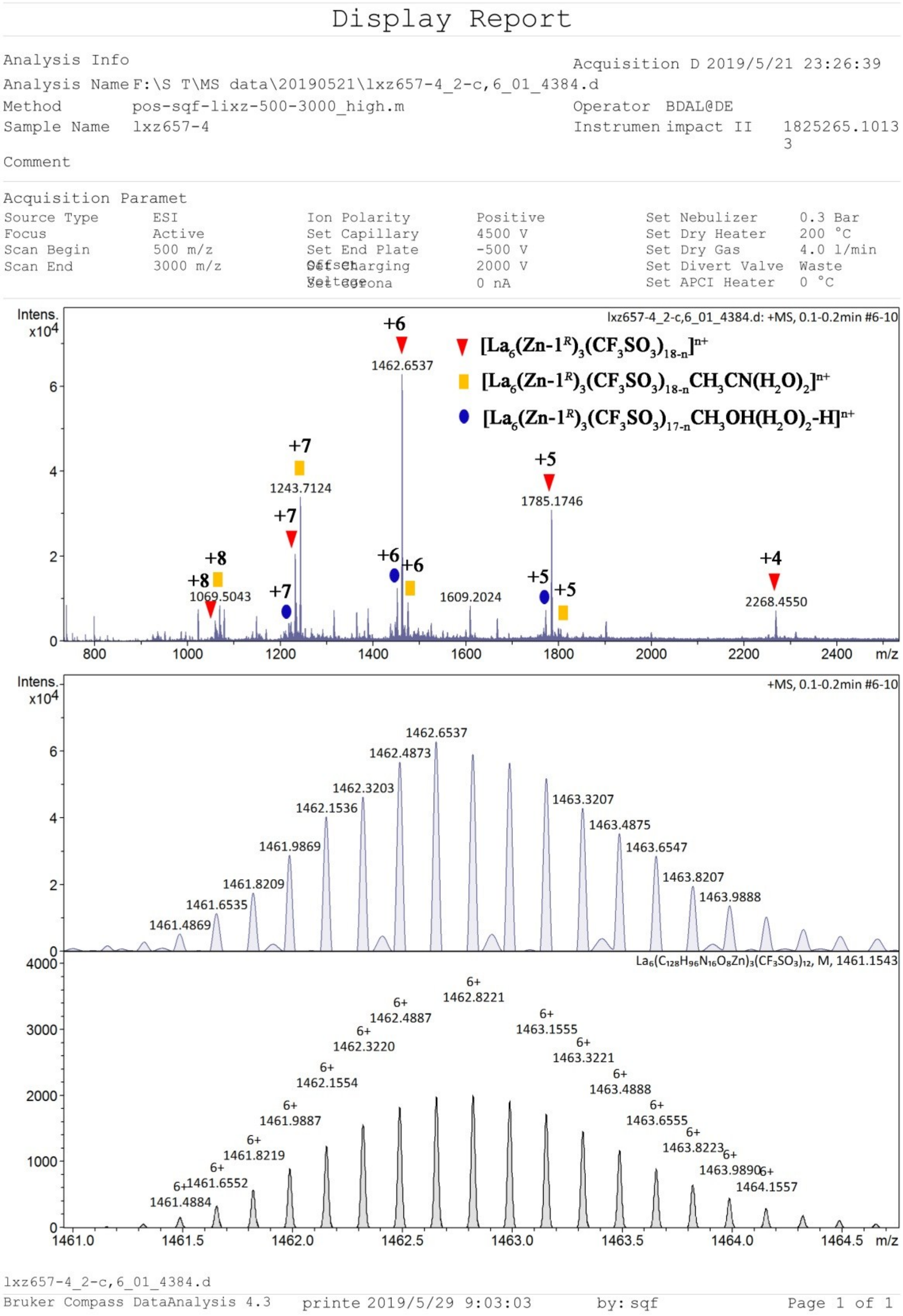
Figure S9. ^{1}H-DOSY NMR spectrum of **$La_6(Zn\text{-}1^R)_3(OTf)_{18}$** (log D = -9.498, r = 18.60Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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Sample Name   lxz657-4                            Instrumen impact II    1825265.1013
                                                                         3
Comment

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                              Voltage
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Bruker Compass DataAnalysis 4.3    printe 2019/5/29 9:03:03    by: sqf         Page 1 of 1
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Figure S10. ESI-TOF-MS spectra of **$La_6(Zn\text{-}1^R)_3(OTf)_{18}$** with insets showing the observed and simulated isotopic patterns of the +6 peaks.

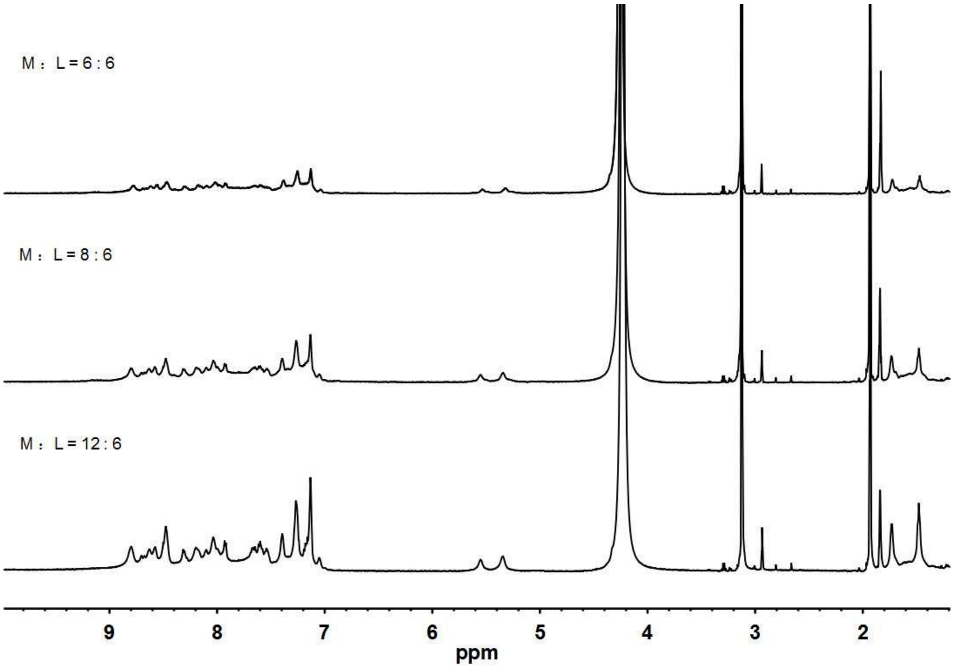


Figure S11. ^{1}H NMR spectra of the self-assembled complexes of Zn-$\mathbf{1}^{R}$ with La^{III} at different metal/ligand (M/L) ratios (600 MHz, CD_3CN/CD_3OD, 298K).

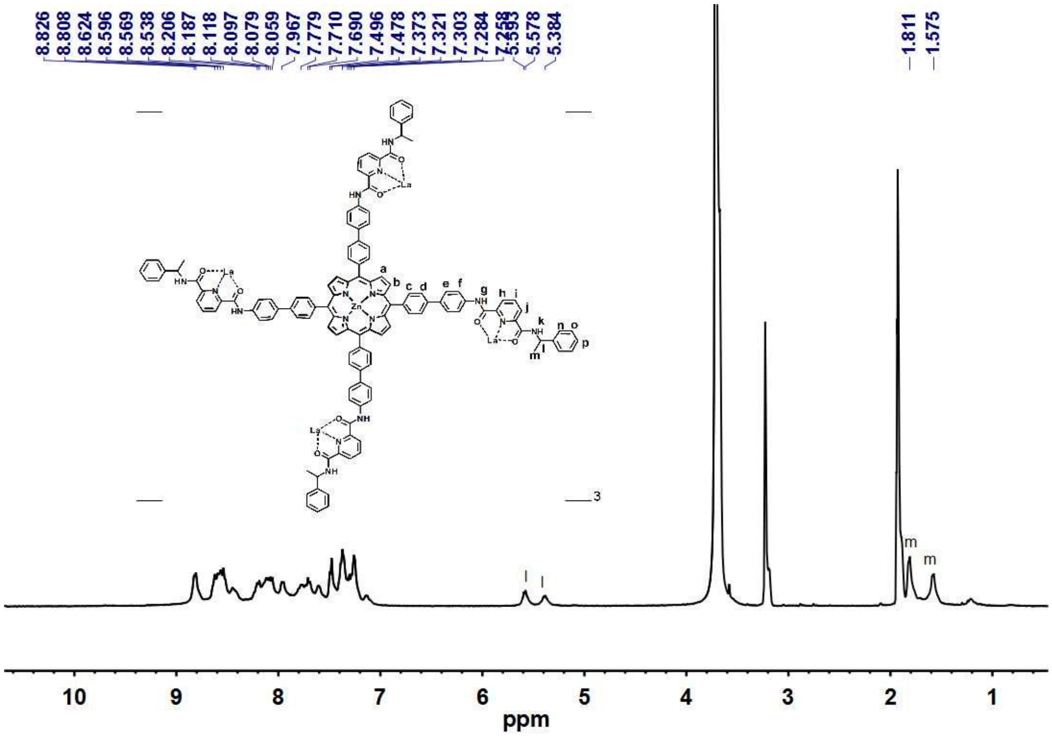


Figure S12. ^{1}H NMR spectrum of $\mathbf{La_6(Zn\text{-}1^{S})_3(OTf)_{18}}$ (400 MHz, CD_3CN/CD_3OD, 298K).

The integration ratio of the proton signals of l is not always the same. This may be ascribed to the perturbation of the coordination symmetry of La^{III} ions caused by the irregular coordination of solvent molecules or H_2O to the La^{III} ions.

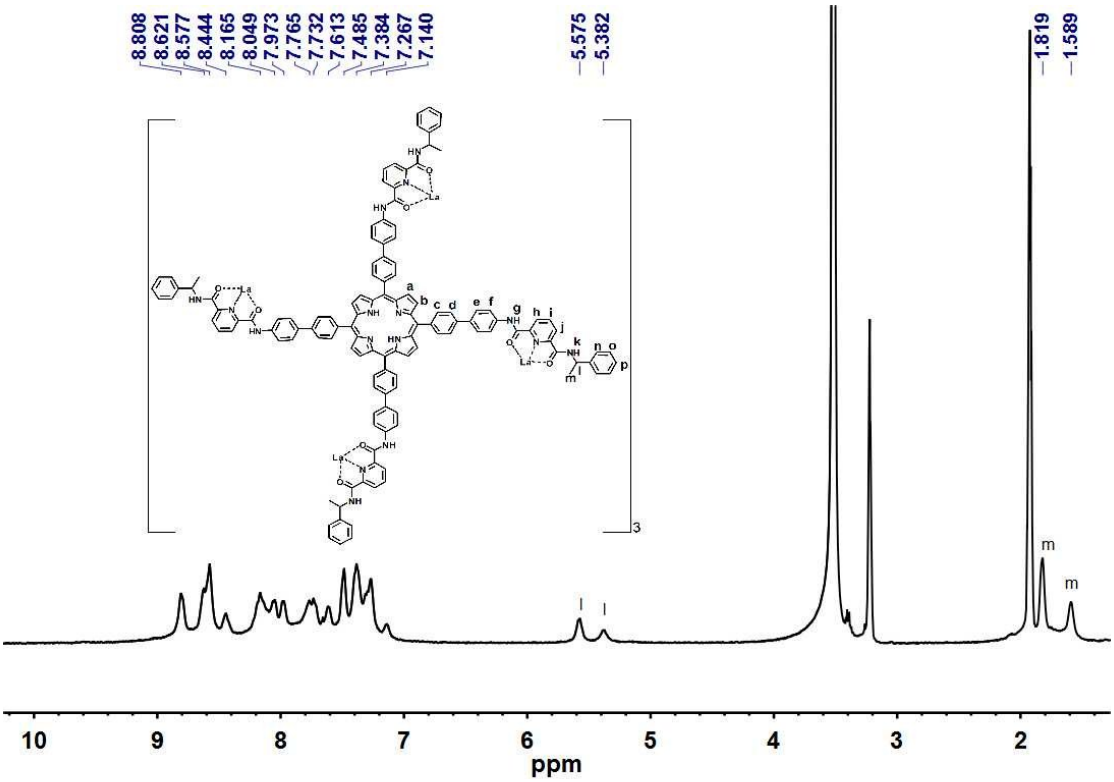
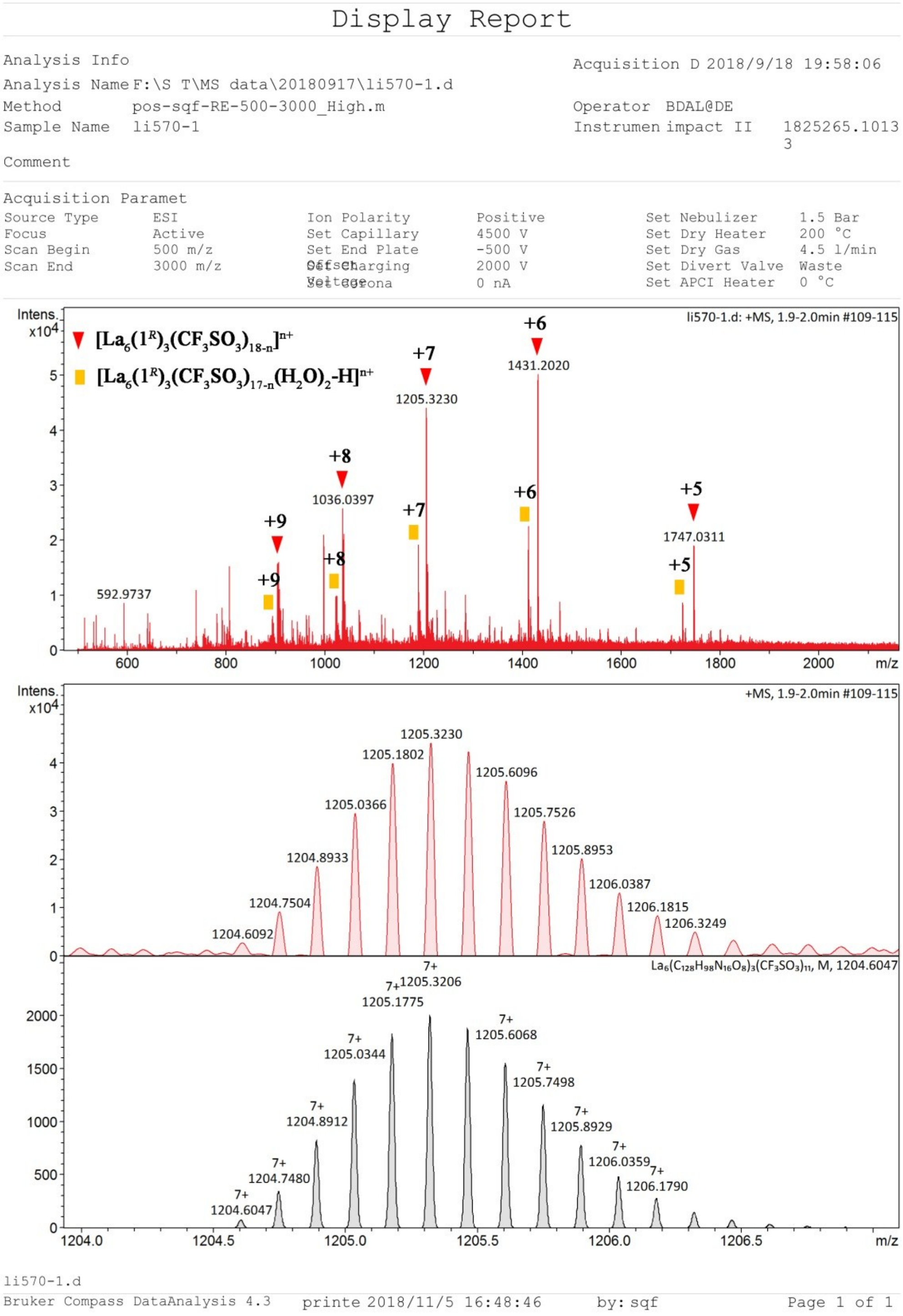


Figure S13. ^{1}H NMR spectrum of $\mathbf{La_6(1^{\mathit{R}})_3(OTf)_{18}}$ (400 MHz, CD_3CN/CD_3OD, 298K).



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Comment

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li570-1.d
Bruker Compass DataAnalysis 4.3    printe 2018/11/5 16:48:46      by: sqf            Page 1 of 1
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Figure S14. ESI-TOF-MS spectra of $\mathbf{La_6(1^{\mathit{R}})_3(OTf)_{18}}$ with insets showing the observed and simulated isotopic patterns of the +7 peaks.

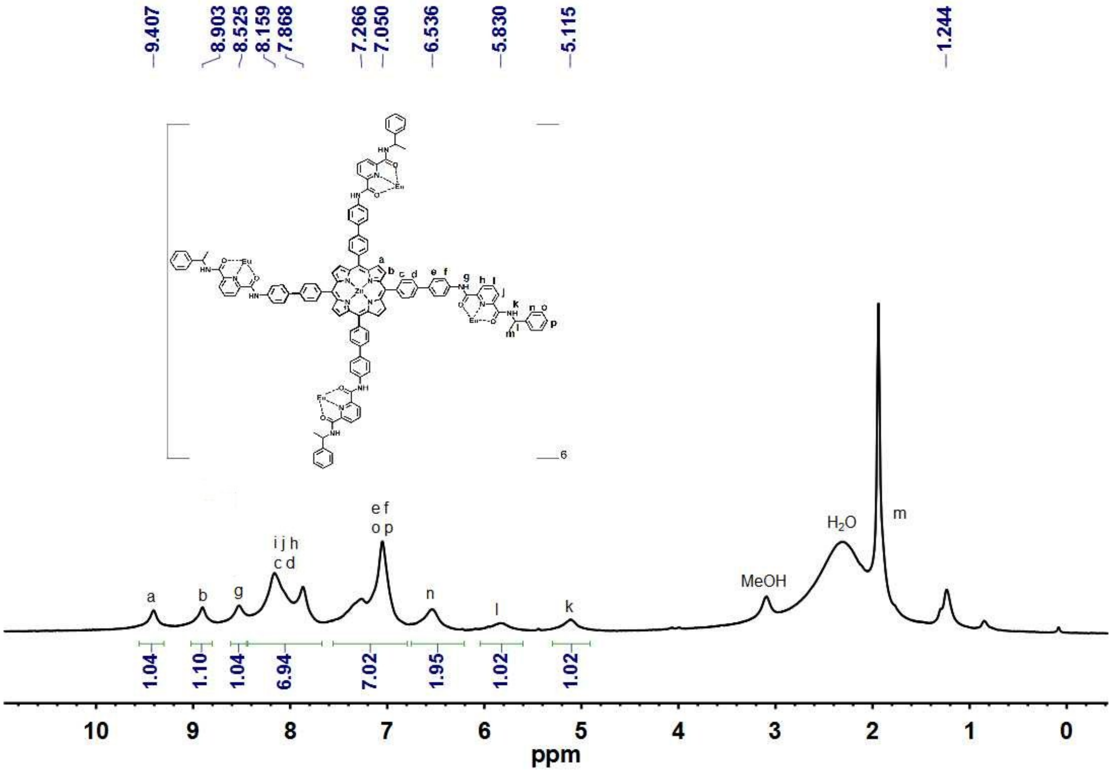
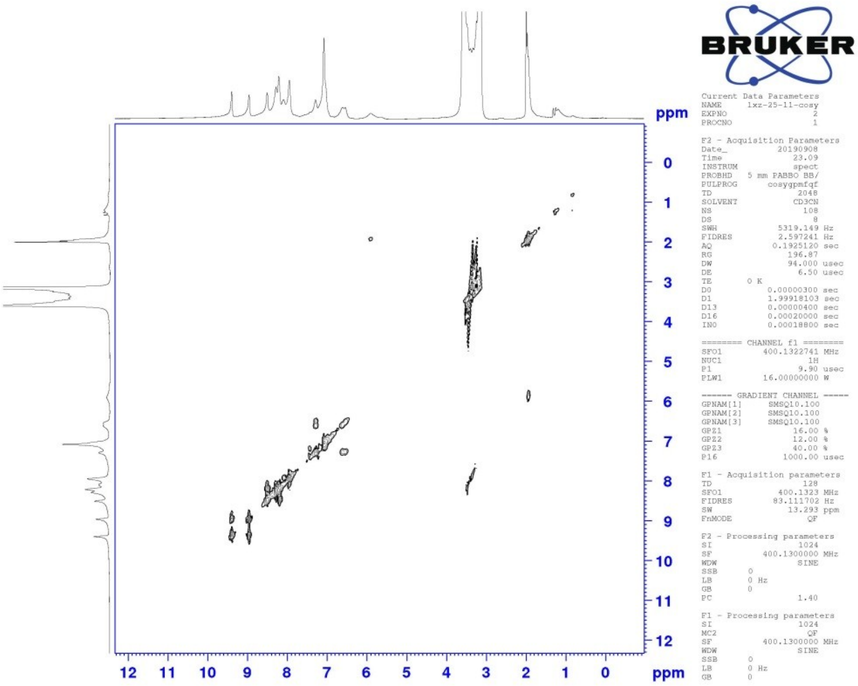


Figure S15. ^{1}H NMR spectrum of **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** (400 MHz, CD_3CN/CD_3OD, 298K).



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PROCNO                 1

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DS                     8
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P1                  9.90 usec
PLW1         16.00000000 W

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GPZ3               40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
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FnMODE                QF

F2 - Processing parameters
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PC                  1.40

F1 - Processing parameters
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GB          0
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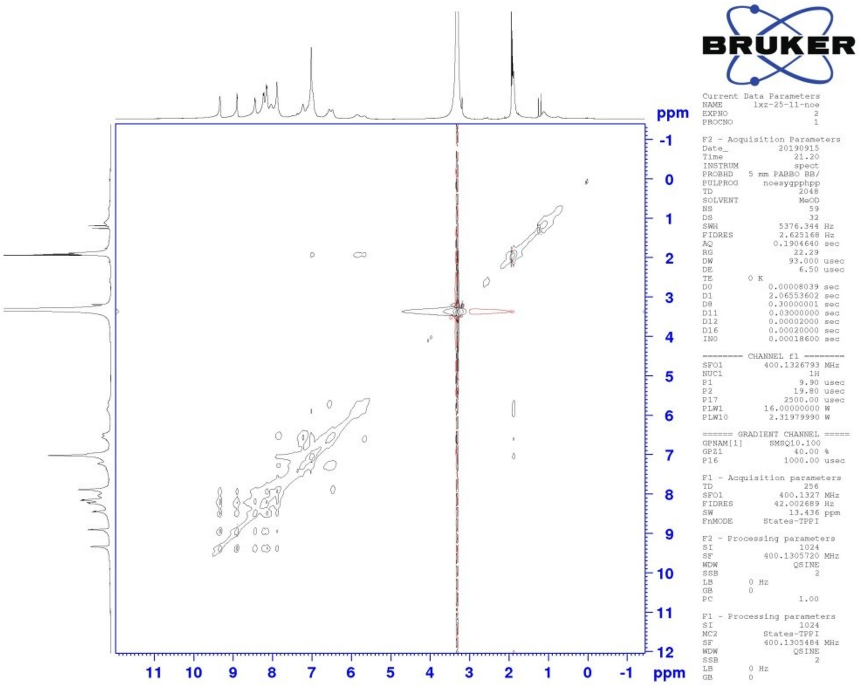
Figure S16. ^{1}H-^{1}H COSY NMR spectrum of **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** (400 MHz, CD_3CN/CD_3OD, 298K).



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TE           0 K
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D11            0.03000000 sec
D12            0.00002000 sec
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FnMODE        States-TPPI

F2 - Processing parameters
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WDW                 QSINE
SSB                     2
LB           0 Hz
GB           0
PC                   1.00

F1 - Processing parameters
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WDW                 QSINE
SSB                     2
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GB           0
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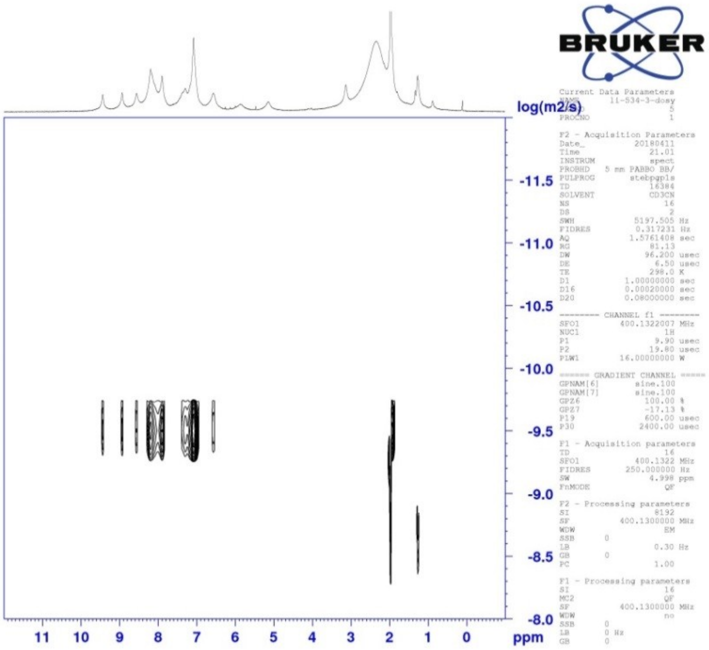
Figure S17. ^{1}H-^{1}H NOESY NMR spectrum of **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** (400 MHz, CD_3CN/CD_3OD, 298K).



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RG                  81.13
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TE                  298.0 K
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D20            0.08000000 sec

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PLW1          16.00000000 W

====== GRADIENT CHANNEL =====
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GPZ7               -17.13 %
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P30               2400.00 usec

F1 - Acquisition parameters
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FIDRES         250.000000 Hz
SW                  4.998 ppm
FnMODE                 QF

F2 - Processing parameters
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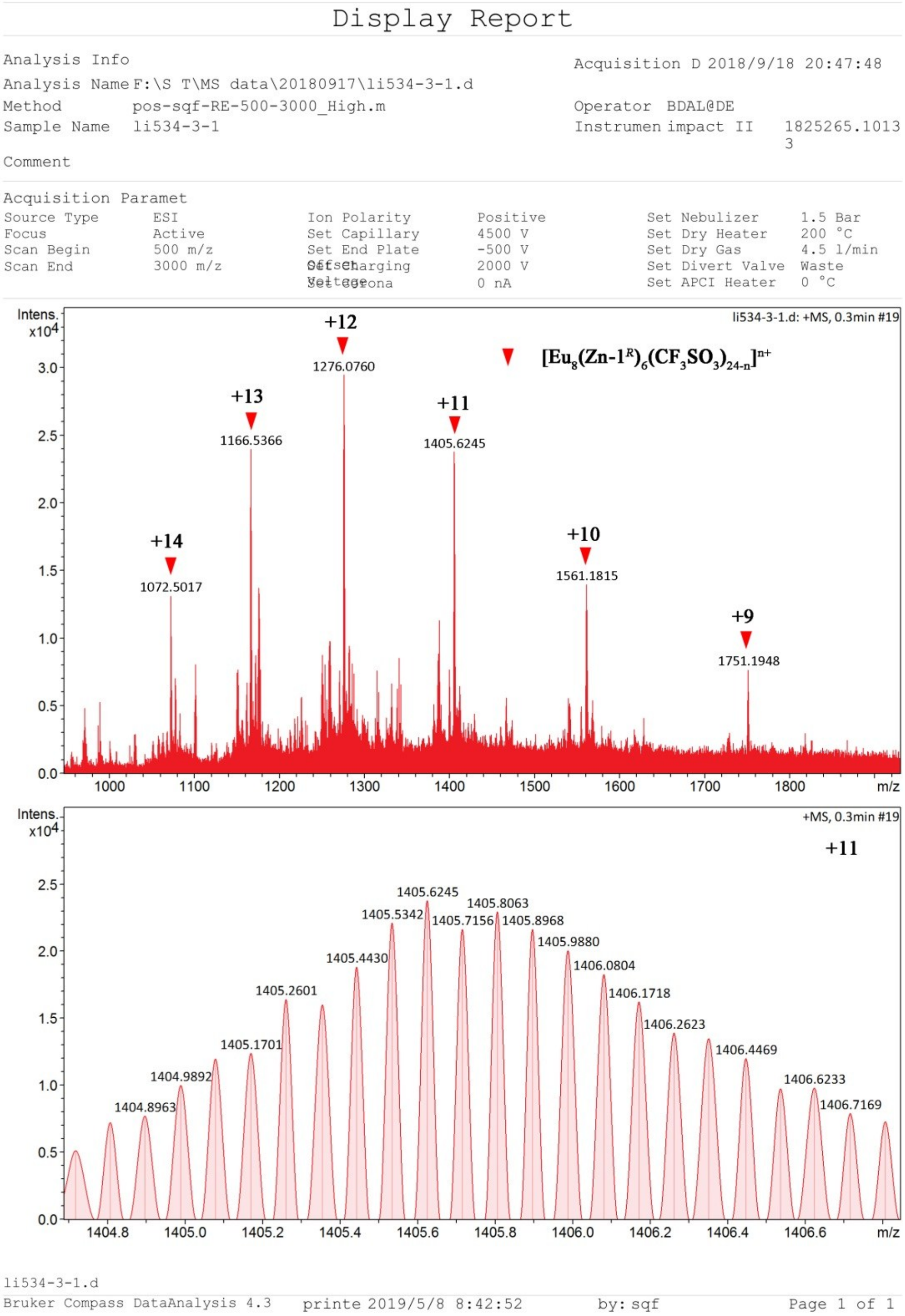
WDW                    EM
SSB          0
LB                   0.30 Hz
GB           0
PC                   1.00

F1 - Processing parameters
SI                     16
MC2                    QF
SF            400.1300000 MHz
WDW                    no
SSB          0
LB           0 Hz
GB           0
```

Figure S18. ^{1}H-DOSY NMR spectrum of **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** (log D=-9.510, r = 19.21Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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Comment

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li534-3-1.d
Bruker Compass DataAnalysis 4.3    printe 2019/5/8 8:42:52      by: sqf        Page 1 of 1
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Figure S19. ESI-TOF-MS spectra of **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +11 peaks.

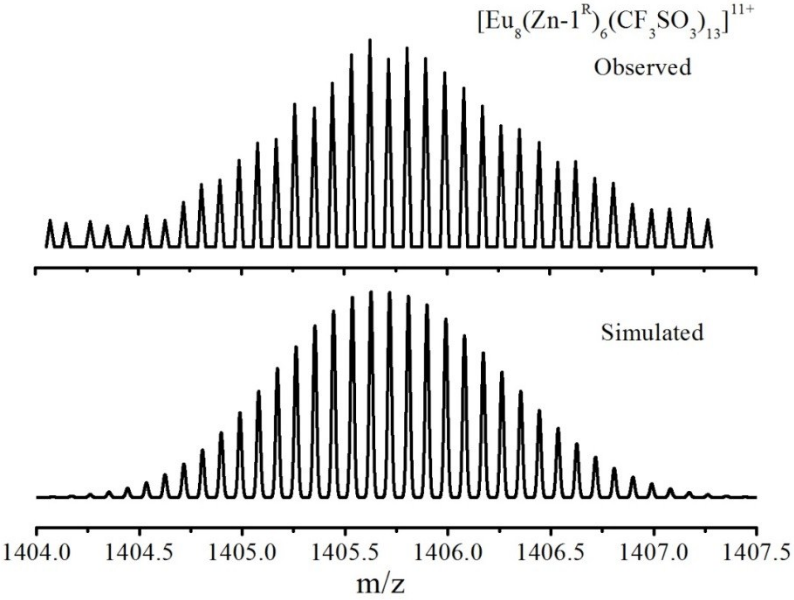


Figure S20. Comparison of the observed and simulated signals of [$\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6(OTf)_{13}}$]$^{11+}$.

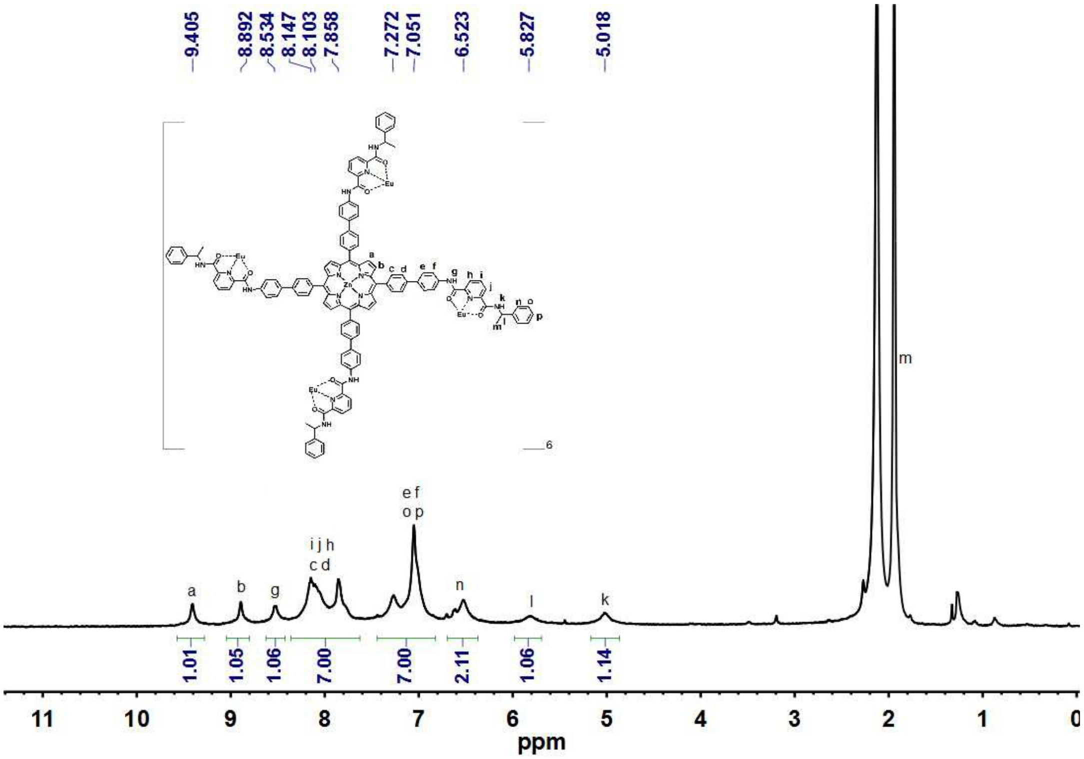


Figure S21. ^{1}H NMR spectra of $\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6(OTf)_{24}}$ self-assembled through transmetalation from $\mathbf{La_6(Zn\text{-}1^{\mathit{R}})_3(OTf)_{18}}$ (400 MHz, CD_3CN, 298K).

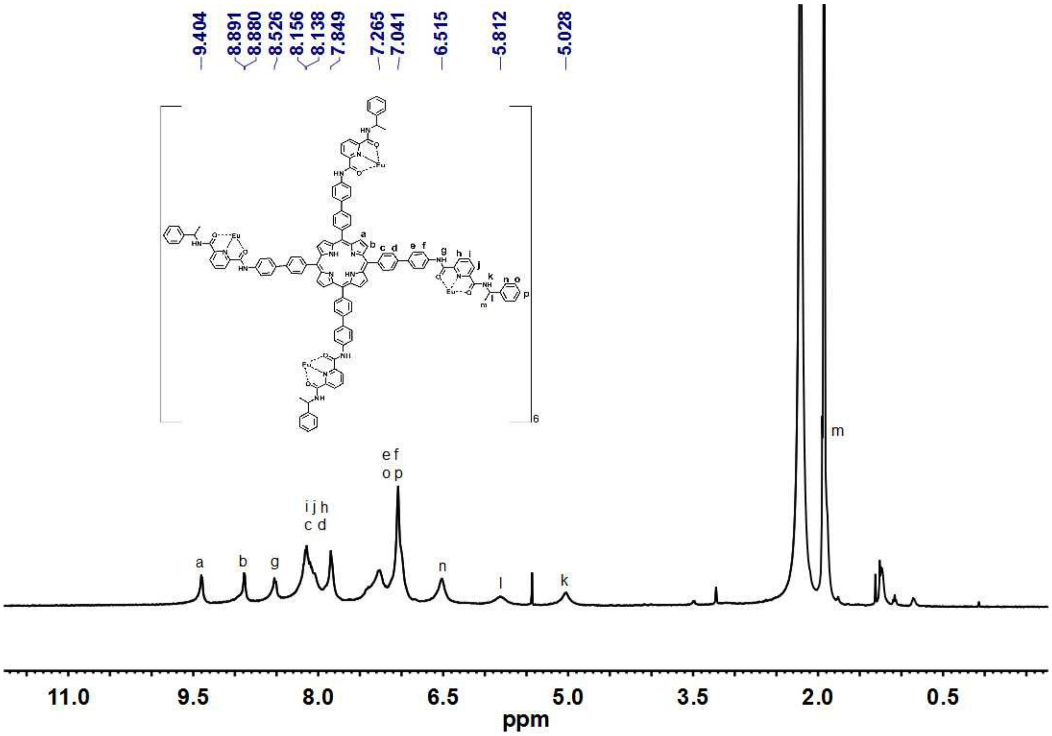
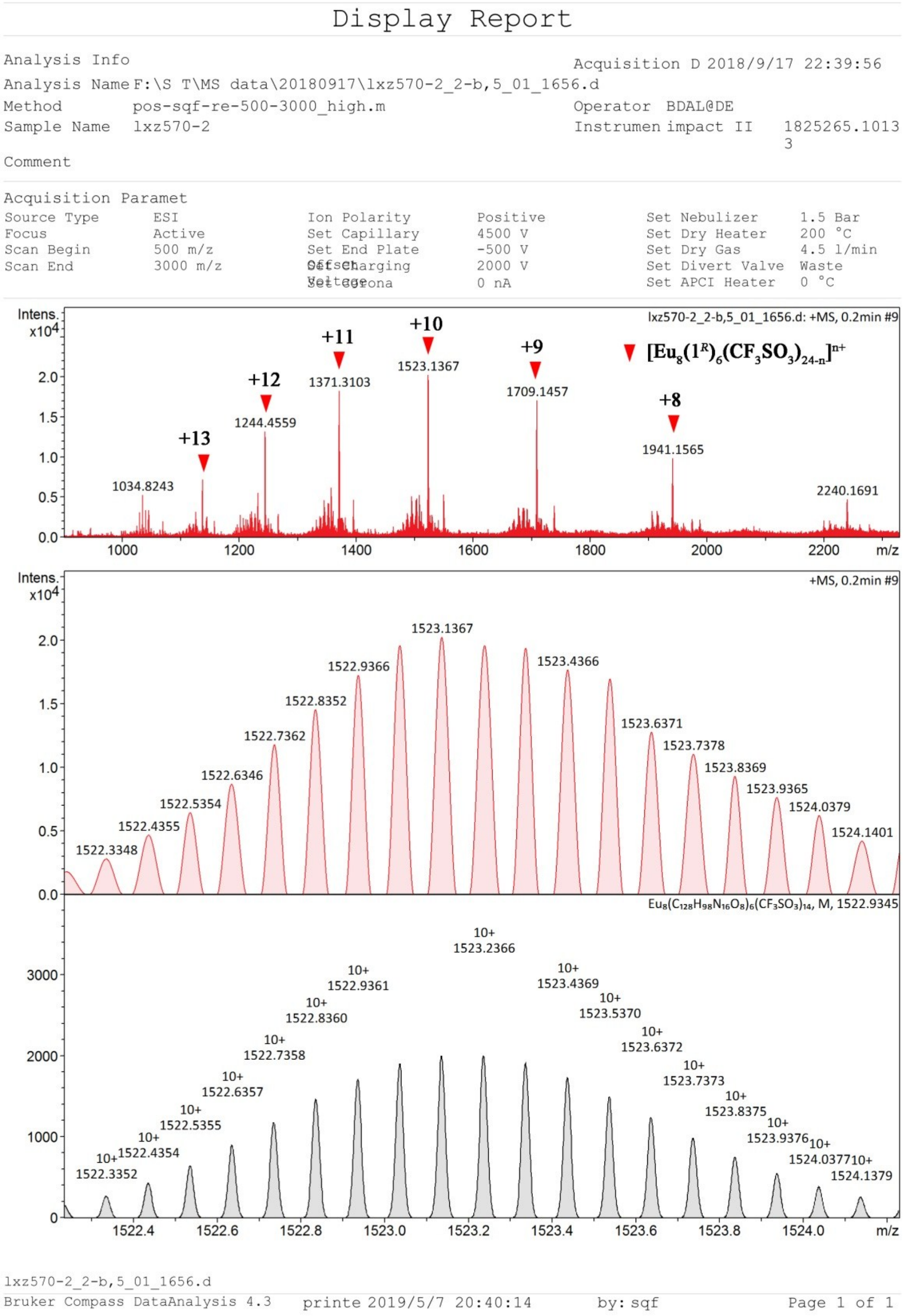


Figure S22. ^{1}H NMR spectra of $\mathbf{Eu_8(1^{\mathit{R}})_6(OTf)_{24}}$ (400 MHz, CD_3CN/CD_3OD, 298K).



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Comment

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Scan End        3000 m/z      Offset
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                              Voltage
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Bruker Compass DataAnalysis 4.3    printe 2019/5/7 20:40:14       by: sqf            Page 1 of 1
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Figure S23. ESI-TOF-MS spectra of $\mathbf{Eu_8(1^{\mathit{R}})_6(OTf)_{24}}$ with insets showing the observed and simulated isotopic patterns of the +10 peaks.

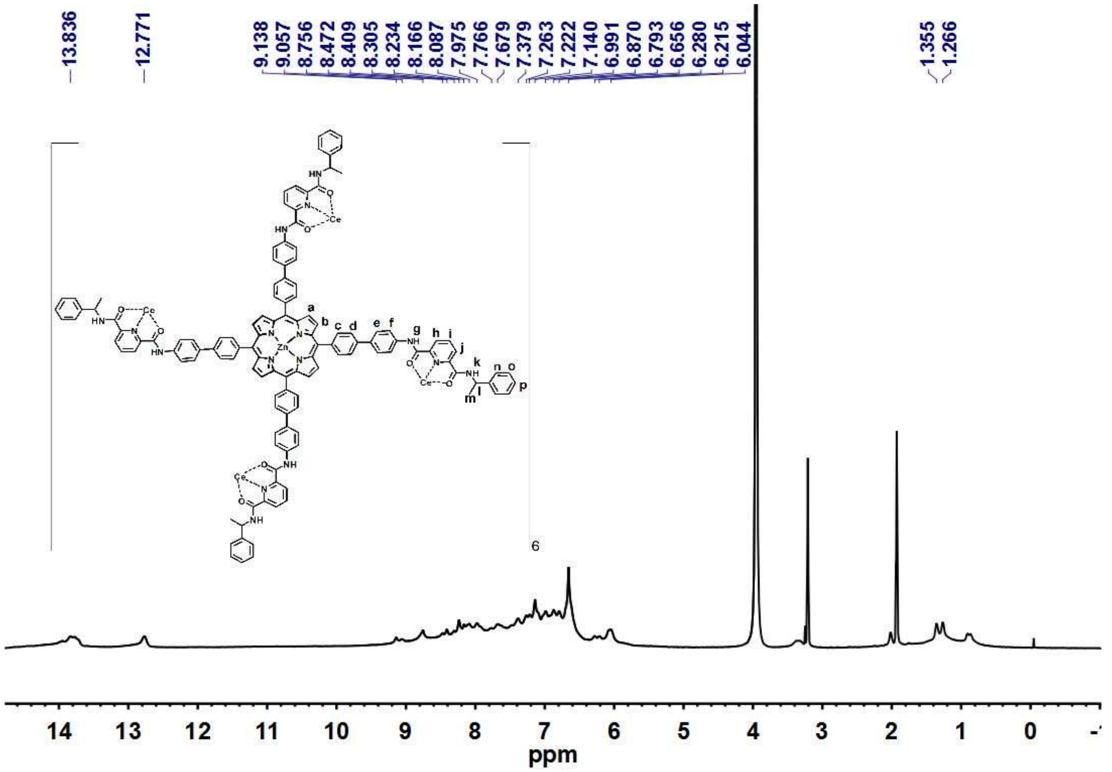
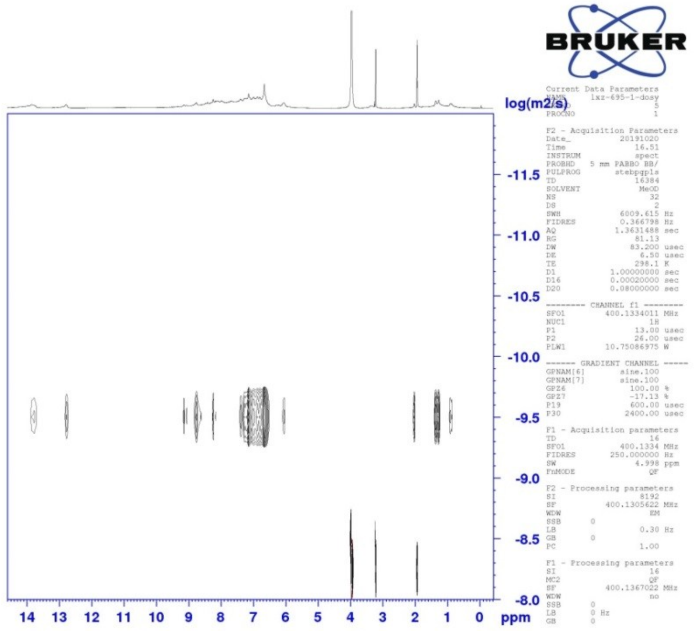


Figure S24. ^{1}H NMR spectrum of the self-assembled complexes of Ce^{III} with **Zn-1*^{R}*** (400 MHz, CD_3CN/CD_3OD, 298K).



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TD                   16384
SOLVENT               MeOD
NS                      32
DS                       2
SWH               6009.615 Hz
FIDRES            0.366798 Hz
AQ               1.3631488 sec
RG                   81.13
DW                  83.200 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.00000000 sec
D16             0.00020000 sec
D20             0.08000000 sec

======== CHANNEL f1 ========
SFO1           400.1334011 MHz
NUC1                    1H
P1                   13.00 usec
P2                   26.00 usec
PLW1           10.75086975 W

====== GRADIENT CHANNEL =====
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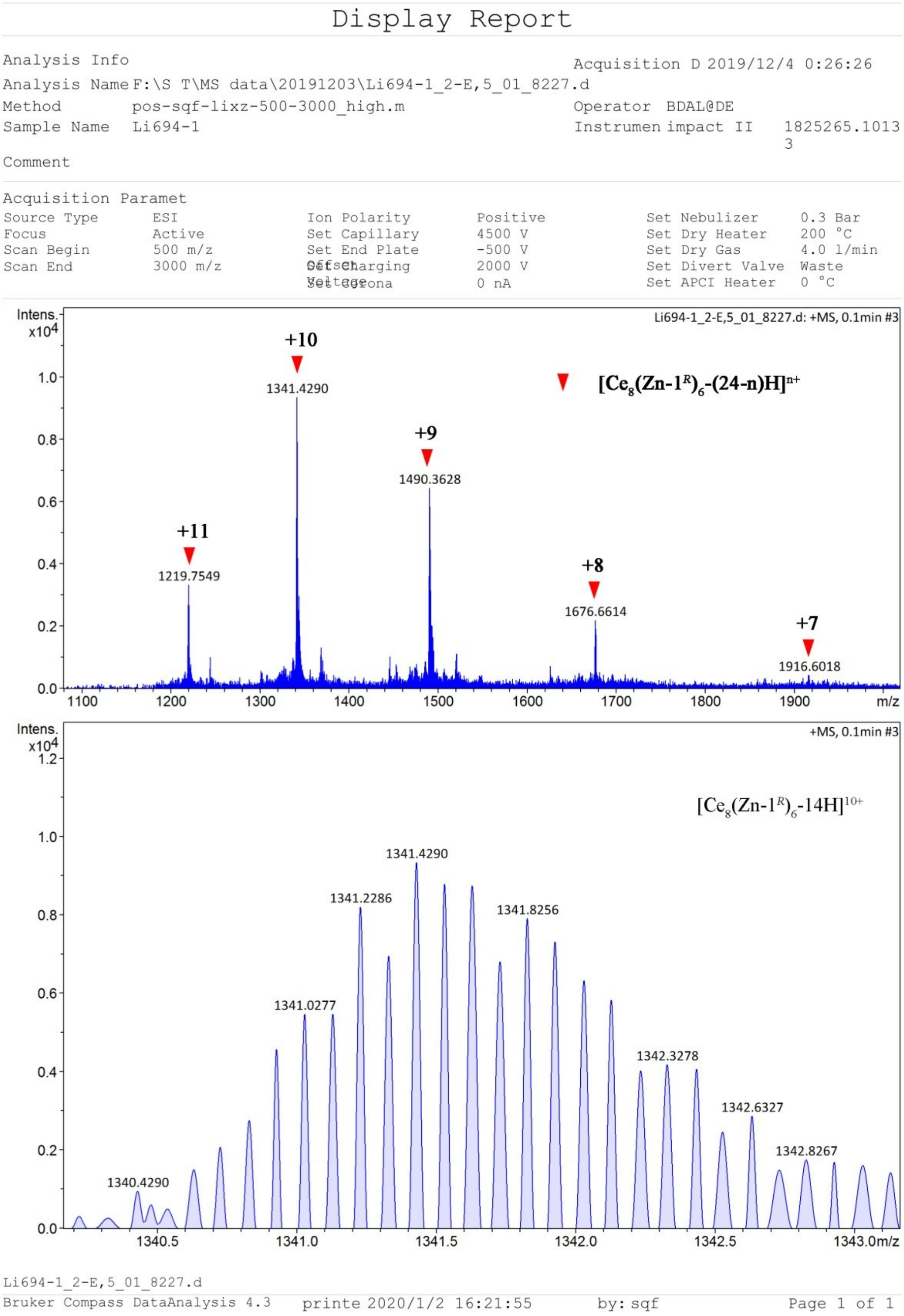
GPNAM[7]         sine.100
GPZ6                100.00 %
GPZ7                -17.13 %
P19                 600.00 usec
P30                2400.00 usec

F1 - Acquisition parameters
TD                      16
SFO1              400.1334 MHz
FIDRES          250.000000 Hz
SW                   4.998 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    8192
SF             400.1305622 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00

F1 - Processing parameters
SI                      16
MC2                     QF
SF             400.1367022 MHz
WDW                     no
SSB      0
LB       0 Hz
GB       0
```

Figure S25. ^{1}H-DOSY NMR spectrum of **$Ce_6(Zn\text{-}1^R)_3(OTf)_{24}$** (log D=-9.508, r = 19.12Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



Display Report

Analysis Info
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Method pos-sqf-lixz-500-3000_high.m
Operator BDAL@DE
Sample Name Li694-1
Instrumen impact II 1825265.10133
Comment

Acquisition Paramet

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	500 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

Li694-1_2-E,5_01_8227.d
Bruker Compass DataAnalysis 4.3 printe 2020/1/2 16:21:55 by: sqf Page 1 of 1

Figure S26. ESI-TOF-MS spectra of **$Ce_8(Zn-1^R)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +10 peaks.

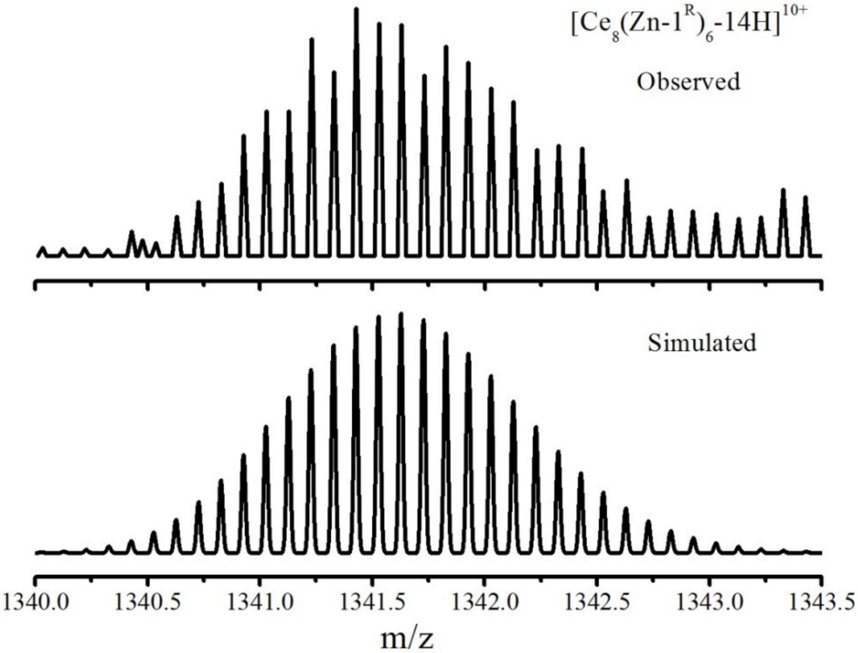


Figure S27. Comparison of the observed and simulated signals of $[\mathbf{Ce_8(Zn\text{-}1^{\mathit{R}})_6\text{-}14H}]^{10+}$.

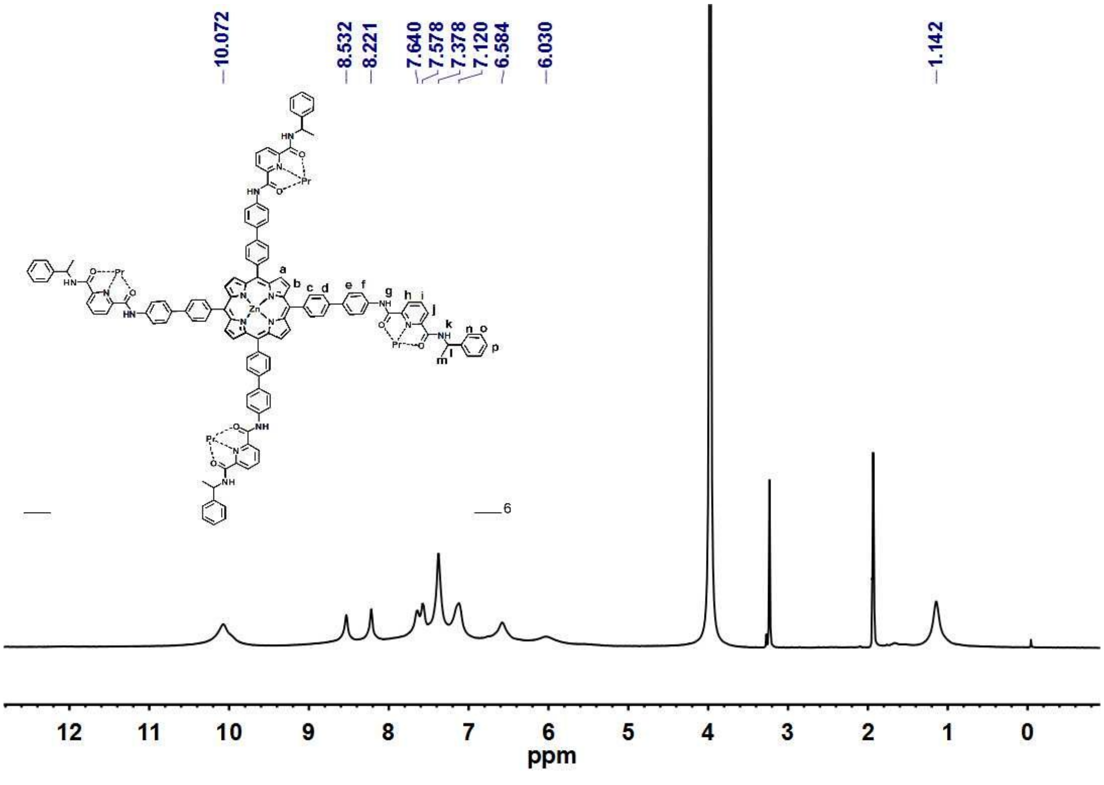
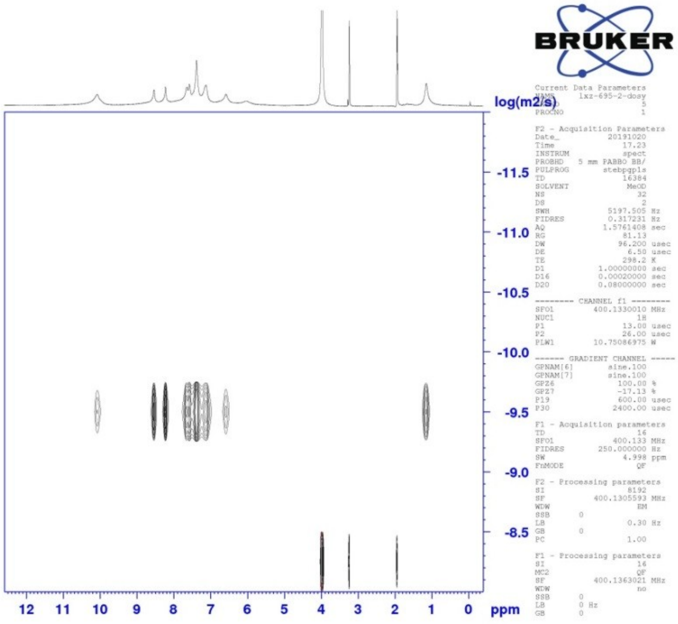


Figure S28. ^{1}H NMR spectrum of $\mathbf{Pr_8(Zn\text{-}1^{\mathit{R}})_6(OTf)_{24}}$ (400 MHz, CD_3CN/CD_3OD, 298K).



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                        5
PROCNO                  1

F2 - Acquisition Parameters
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Time                17.23
INSTRUM             spect
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PULPROG          stebpgp1s
TD                  16384
SOLVENT              MeOD
NS                     32
DS                      2
SWH             5197.505 Hz
FIDRES          0.317231 Hz
AQ             1.5761408 sec
RG                  81.13
DW                 96.200 usec
DE                   6.50 usec
TE                  298.2 K
D1           1.00000000 sec
D16          0.00020000 sec
D20          0.08000000 sec

======== CHANNEL f1 ========
SFO1         400.1330010 MHz
NUC1                   1H
P1                  13.00 usec
P2                  26.00 usec
PLW1         10.75086975 W

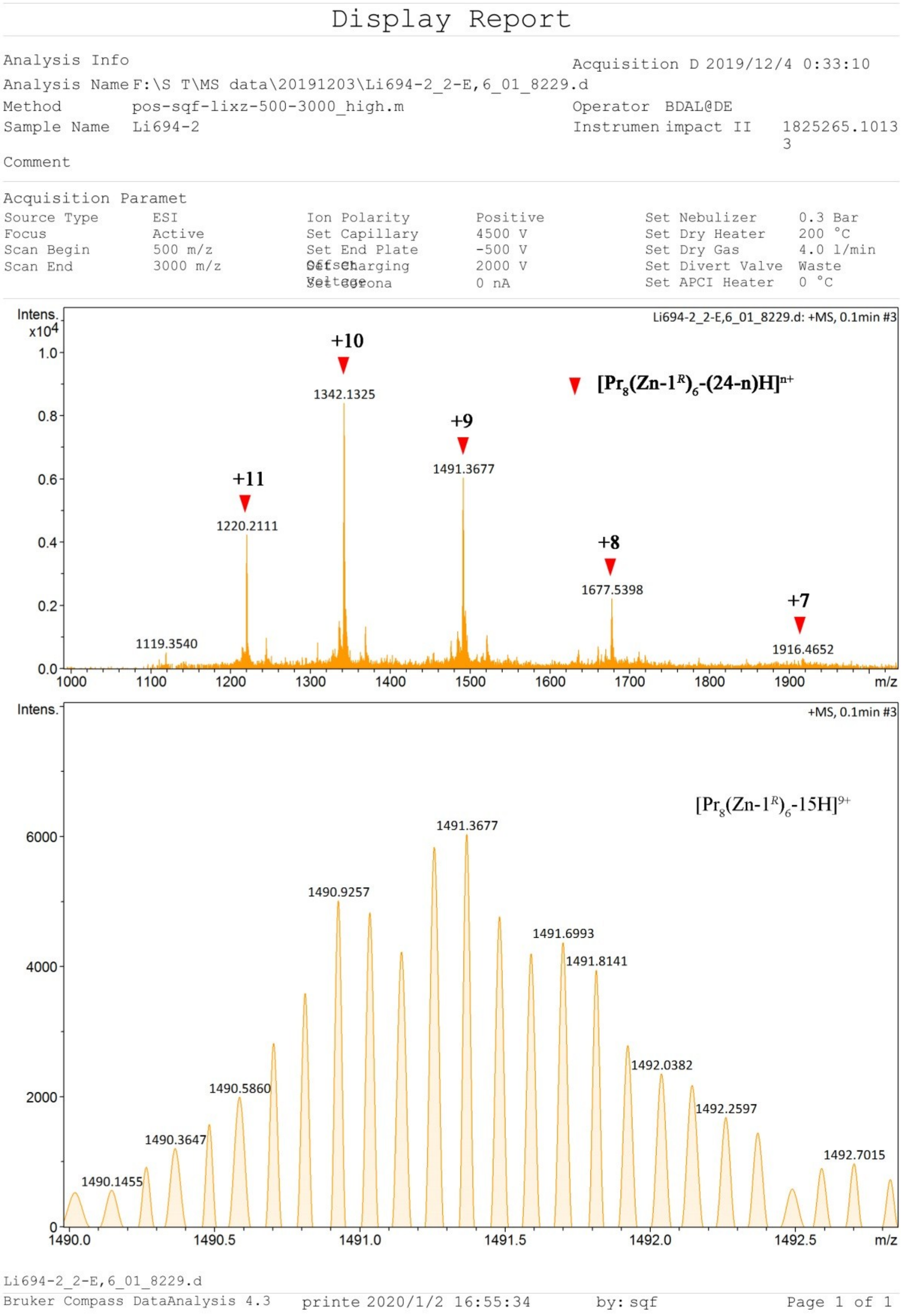
====== GRADIENT CHANNEL =====
GPNAM[6]         sine.100
GPNAM[7]         sine.100
GPZ6               100.00 %
GPZ7               -17.13 %
P19                600.00 usec
P30               2400.00 usec

F1 - Acquisition parameters
TD                     16
SFO1              400.133 MHz
FIDRES         250.000000 Hz
SW                  4.998 ppm
FnMODE                 QF

F2 - Processing parameters
SI                   8192
SF            400.1305593 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00

F1 - Processing parameters
SI                     16
MC2                    QF
SF            400.1363021 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
```

Figure S29. ^{1}H-DOSY NMR spectrum of **$Pr_8(Zn\text{-}1^R)_6(OTf)_{24}$** (log D=-9.499, r = 18.73Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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                           Display Report

Analysis Info                                           Acquisition D 2019/12/4 0:33:10
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Method        pos-sqf-lixz-500-3000_high.m              Operator  BDAL@DE
Sample Name   Li694-2                                   Instrumen impact II    1825265.1013
                                                                               3
Comment

Acquisition Paramet
Source Type      ESI          Ion Polarity       Positive        Set Nebulizer      0.3 Bar
Focus            Active       Set Capillary      4500 V          Set Dry Heater     200 °C
Scan Begin       500 m/z      Set End Plate      -500 V          Set Dry Gas        4.0 l/min
Scan End         3000 m/z     Offset             2000 V          Set Divert Valve   Waste
                              Set Charging
                              Voltage
                              Set Corona         0 nA            Set APCI Heater    0 °C
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Li694-2_2-E,6_01_8229.d
Bruker Compass DataAnalysis 4.3    printe 2020/1/2 16:55:34    by: sqf         Page 1 of 1
```

Figure S30. ESI-TOF-MS spectra of **$Pr_8(Zn\text{-}1^R)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +9 peaks.

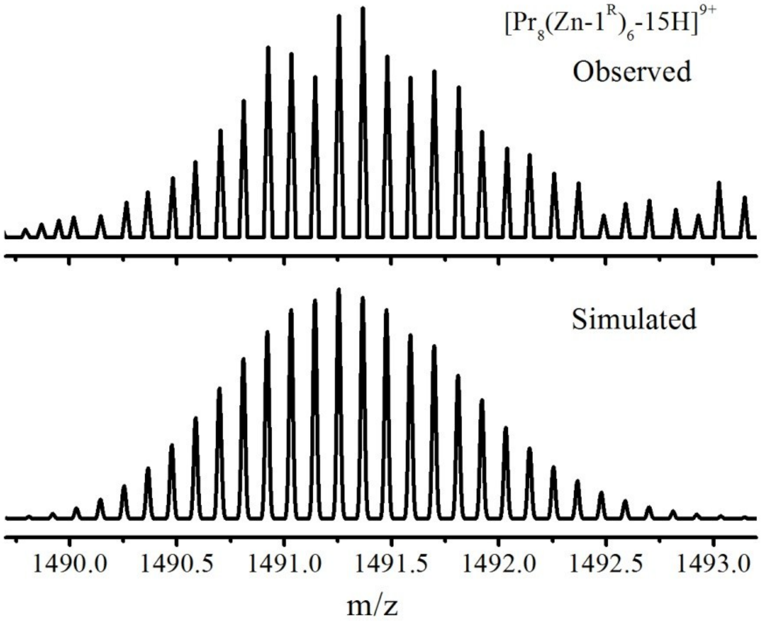


Figure S31. Comparison of the observed and simulated signals of [**Pr$_8$(Zn-1^R)$_6$-15H**]$^{9+}$.

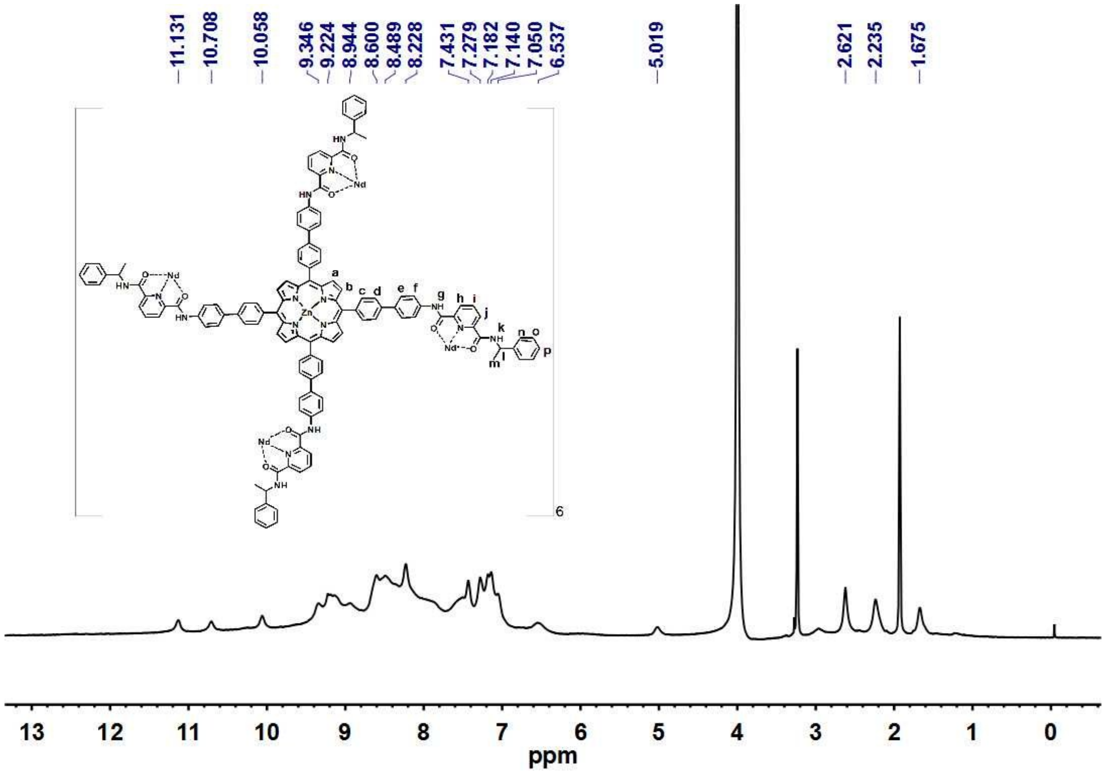
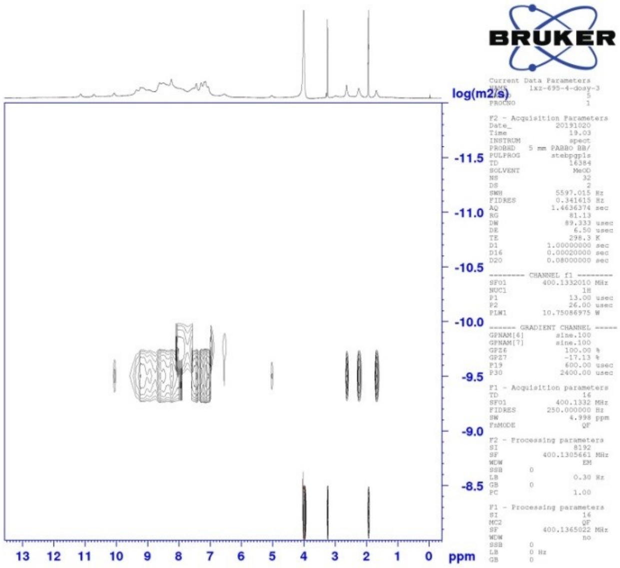


Figure S32. ^{1}H NMR spectrum of **Nd$_8$(Zn-1^R)$_6$(OTf)$_{24}$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).



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EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
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Time                  19.03
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG           stebpgp1s
TD                    16384
SOLVENT                MeOD
NS                       32
DS                        2
SWH                5597.015 Hz
FIDRES             0.341615 Hz
AQ                1.4636374 sec
RG                    81.13
DW                   89.333 usec
DE                     6.50 usec
TE                    298.3 K
D1               1.00000000 sec
D16              0.00020000 sec
D20              0.08000000 sec

======== CHANNEL f1 ========
SFO1            400.1332010 MHz
NUC1                     1H
P1                    13.00 usec
P2                    26.00 usec
PLW1            10.75086975 W

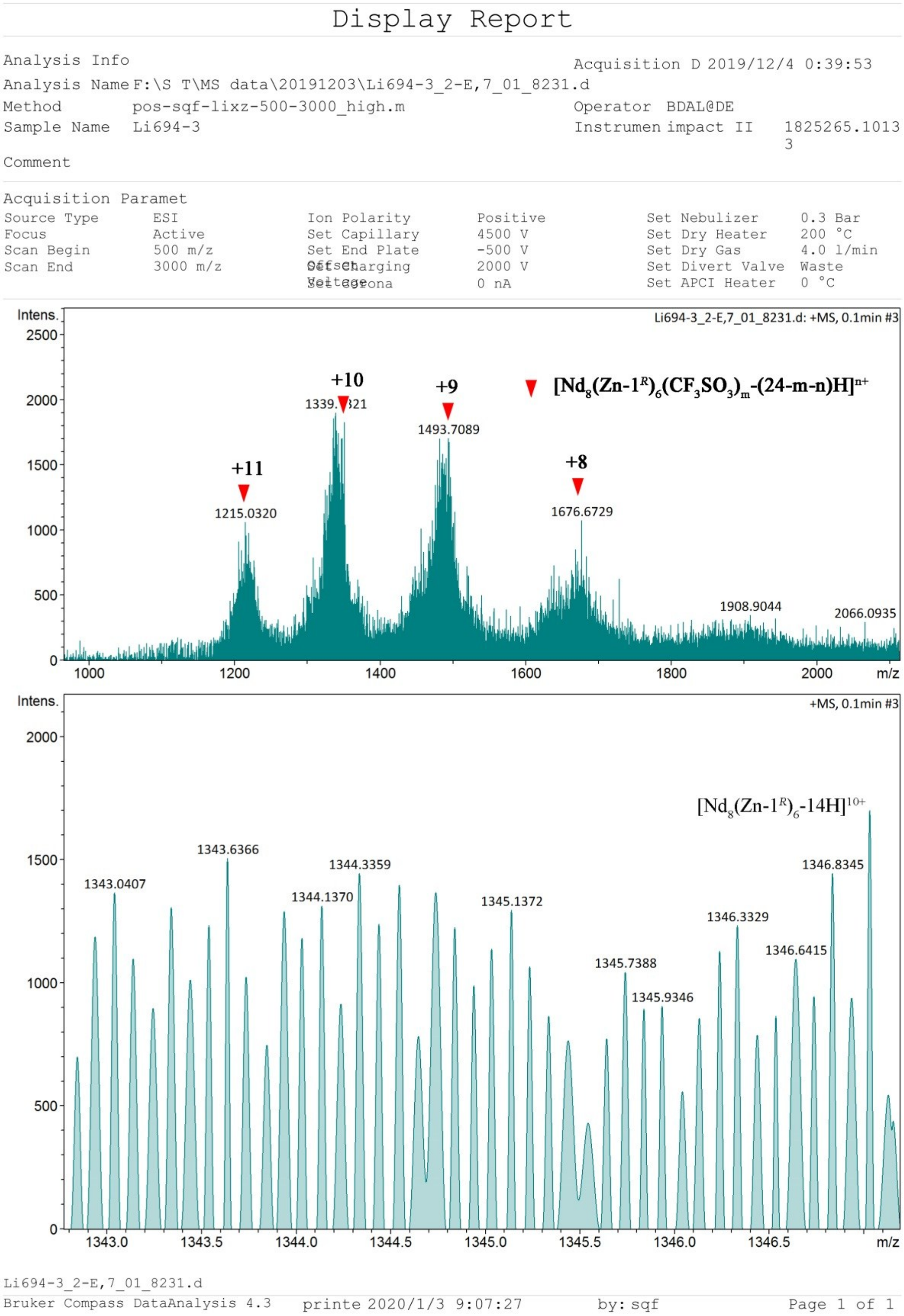
====== GRADIENT CHANNEL =====
GPNAM[6]           sine.100
GPNAM[7]           sine.100
GPZ6                 100.00 %
GPZ7                 -17.13 %
P19                  600.00 usec
P30                 2400.00 usec

F1 - Acquisition parameters
TD                       16
SFO1                400.1332 MHz
FIDRES           250.000000 Hz
SW                    4.998 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     8192
SF              400.1305661 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00

F1 - Processing parameters
SI                       16
MC2                      QF
SF              400.1365022 MHz
WDW                      no
SSB        0
LB         0 Hz
GB         0
```

Figure S33. ^{1}H-DOSY NMR spectrum of **$Nd_8(Zn\text{-}1^R)_6(OTf)_{24}$** (log D=-9.501, r = 18.80Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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                         Display Report

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Method        pos-sqf-lixz-500-3000_high.m       Operator  BDAL@DE
Sample Name   Li694-3                            Instrumen impact II    1825265.1013
                                                                        3
Comment

Acquisition Paramet
Source Type     ESI         Ion Polarity       Positive      Set Nebulizer     0.3 Bar
Focus           Active      Set Capillary      4500 V        Set Dry Heater    200 °C
Scan Begin      500 m/z     Set End Plate      -500 V        Set Dry Gas       4.0 l/min
                            Offset Voltage
Scan End        3000 m/z    Set Charging       2000 V        Set Divert Valve  Waste
                            Set Corona         0 nA          Set APCI Heater   0 °C
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Li694-3_2-E,7_01_8231.d
Bruker Compass DataAnalysis 4.3    printe 2020/1/3 9:07:27      by: sqf          Page 1 of 1
```

Figure S34. ESI-TOF-MS spectra of **$Nd_8(Zn\text{-}1^R)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +10 peaks.

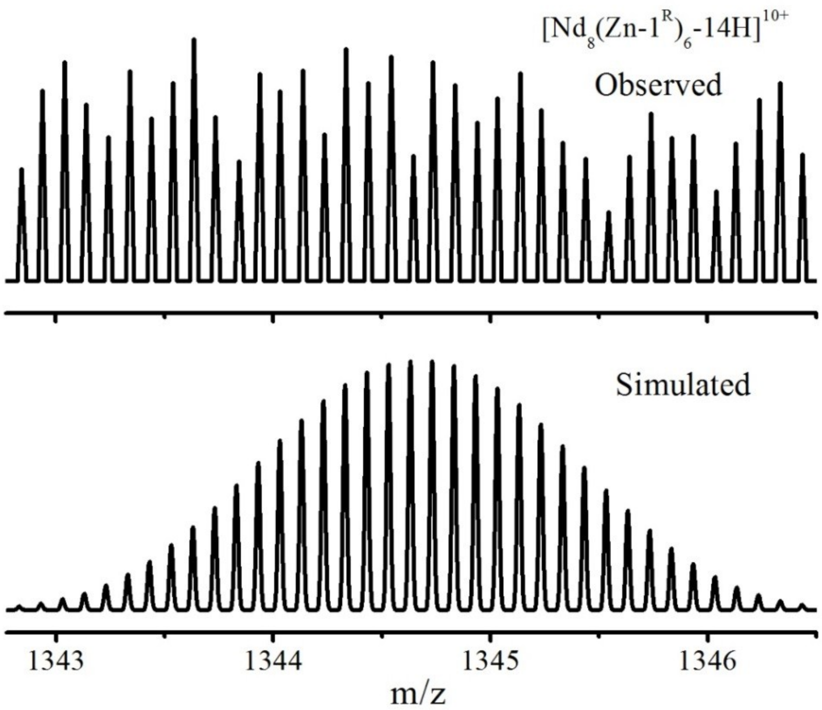


Figure S35. Comparison of the observed and simulated signals of [**Nd$_8$(Zn-1^R)$_6$-14H**]$^{10+}$.

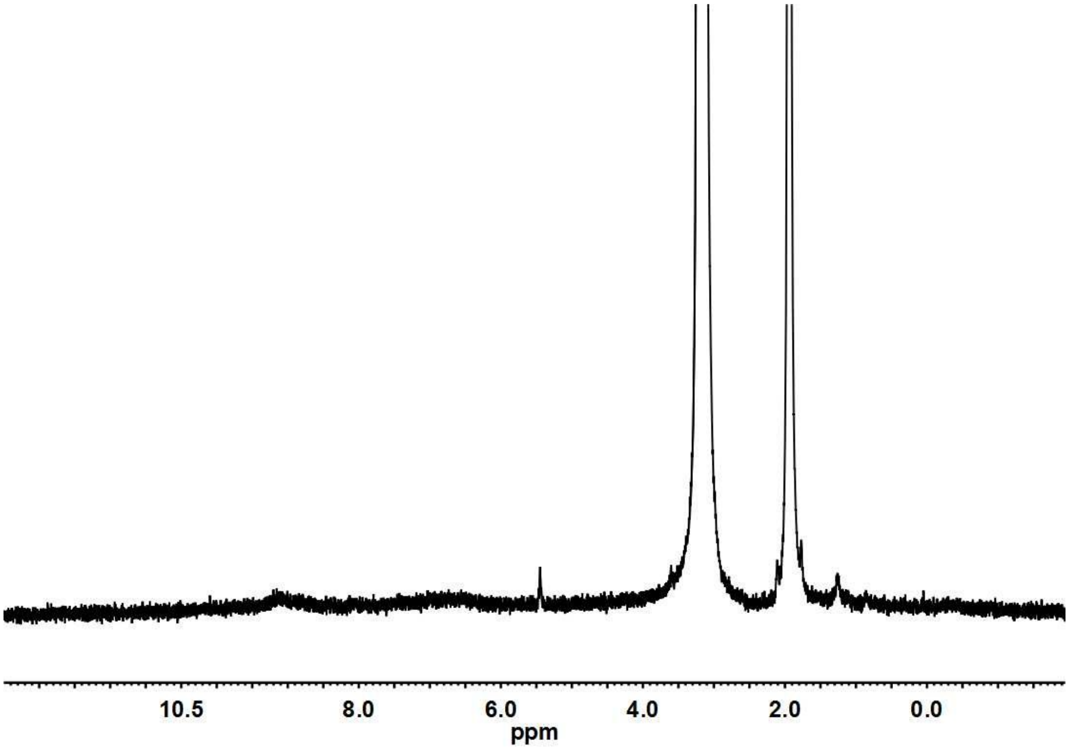


Figure S36. ^{1}H NMR spectrum of direct self-assembly of Zn-**1^R** with Yb(OTf)$_3$ (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

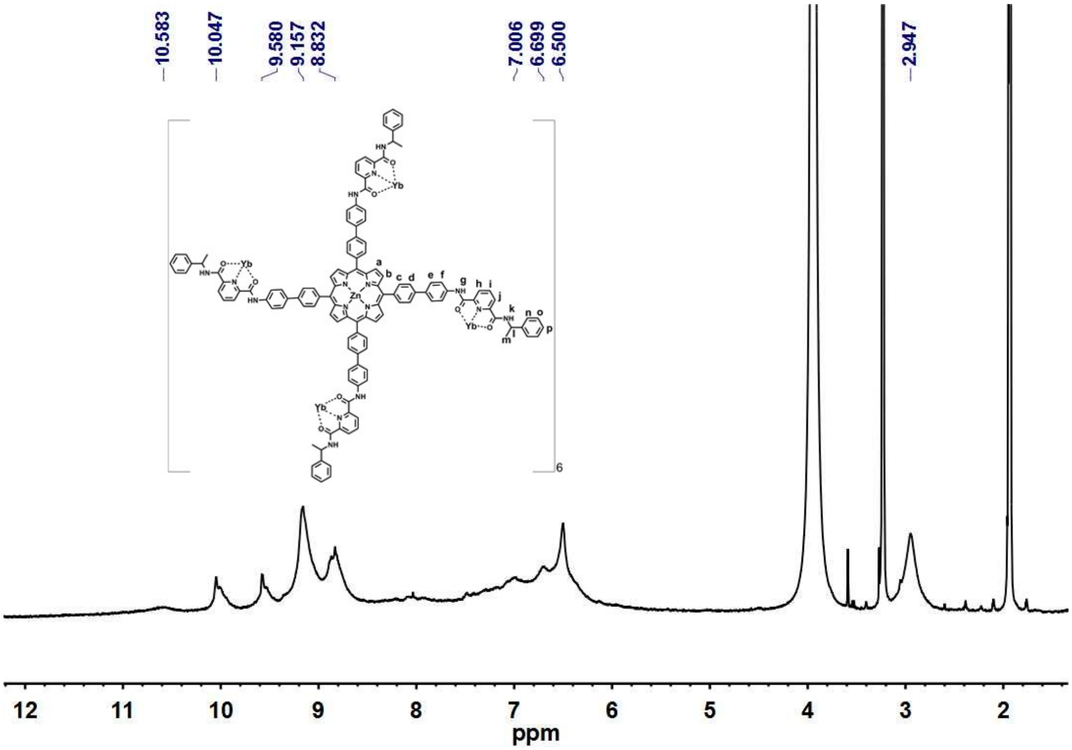


Figure S37. ^{1}H NMR spectrum of **$Yb_8(Zn\text{-}1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$La_6(Zn\text{-}1^R)_3(OTf)_{18}$** (400 MHz, CD_3CN, 298K).

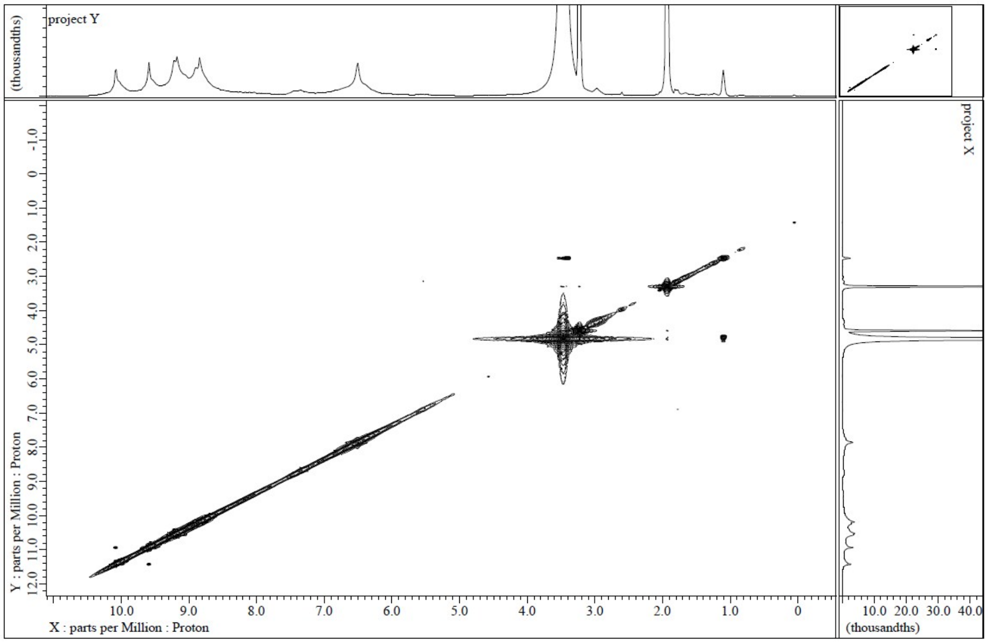
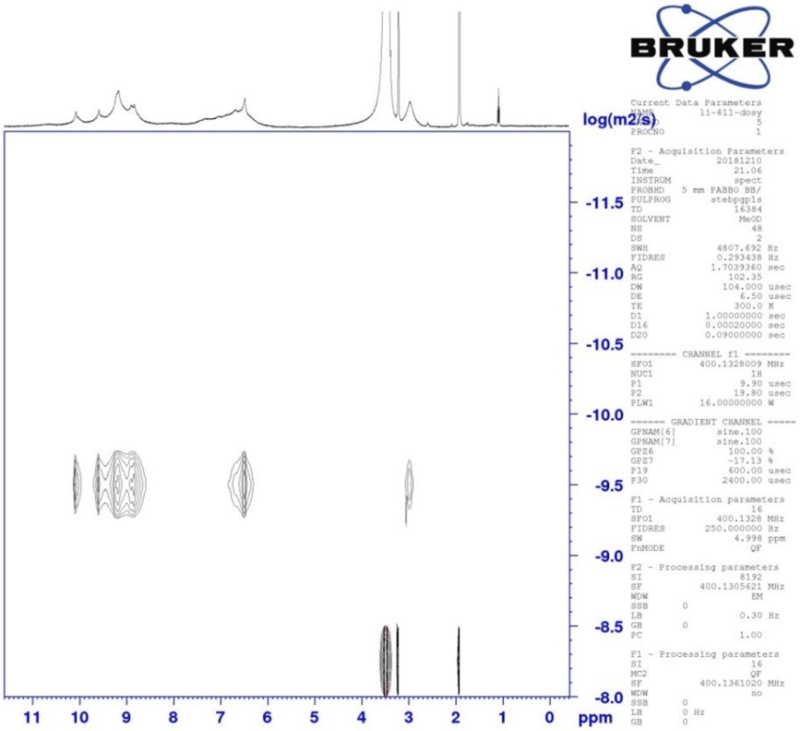


Figure S38. ^{1}H-^{1}H COSY NMR spectrum of **$Yb_8(Zn\text{-}1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$La_8(Zn\text{-}1^R)_6(OTf)_{24}$** (600 MHz, CD_3CN/CD_3OD, 298K).



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PROCNO                1

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PULPROG        stebpgp1s
TD                16384
SOLVENT            MeOD
NS                   48
DS                    2
SWH            4807.692 Hz
FIDRES         0.293438 Hz
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RG               102.35
DW              104.000 usec
DE                 6.50 usec
TE                300.0 K
D1           1.00000000 sec
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D20          0.09000000 sec

======== CHANNEL f1 ========
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NUC1                 1H
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P2                19.80 usec
PLW1        16.00000000 W

====== GRADIENT CHANNEL =====
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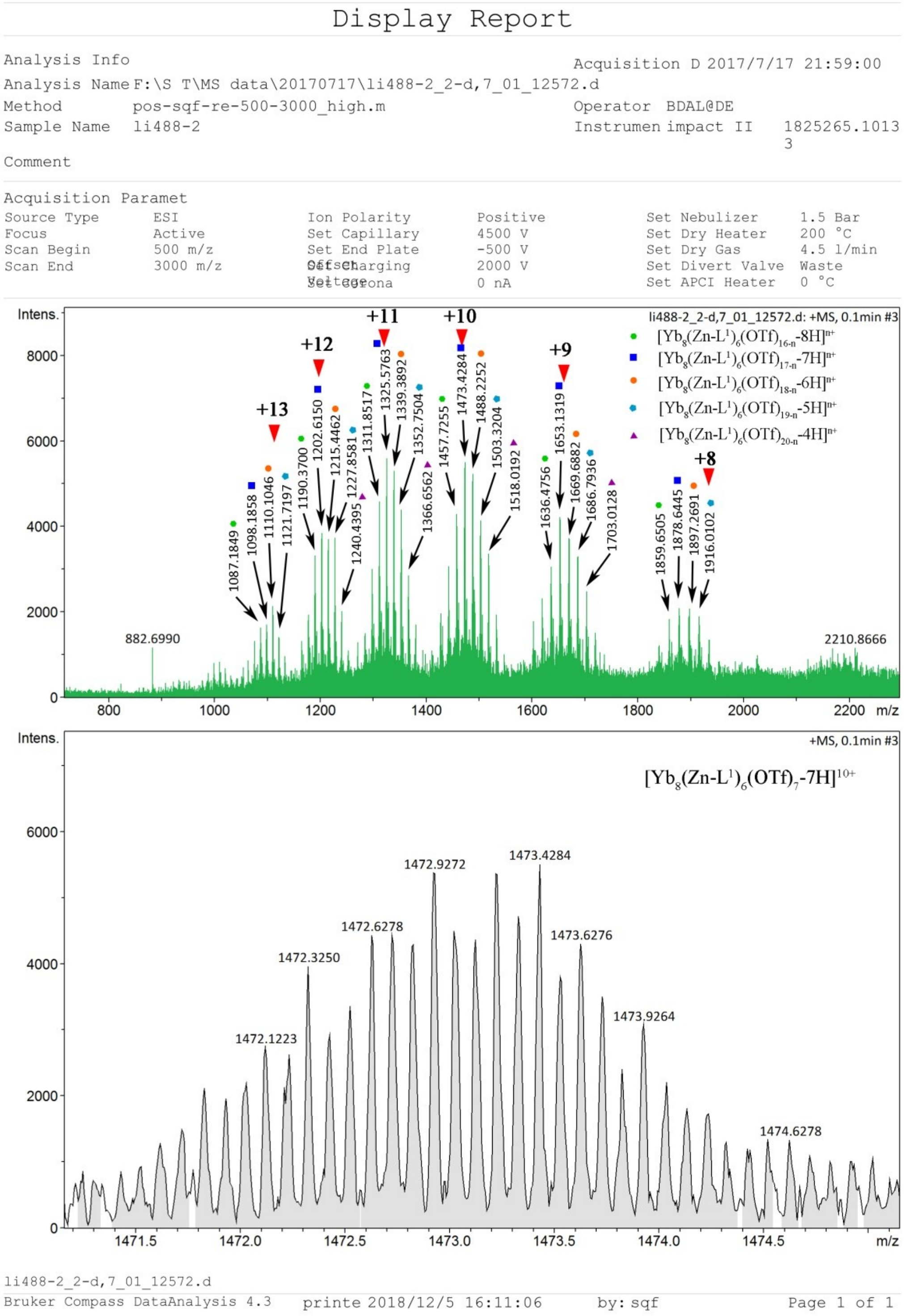
GPNAM[7]       sine.100
GPZ6             100.00 %
GPZ7             -17.13 %
P19              600.00 usec
P30             2400.00 usec

F1 - Acquisition parameters
TD                   16
SFO1           400.1328 MHz
FIDRES       250.000000 Hz
SW                4.998 ppm
FnMODE               QF

F2 - Processing parameters
SI                 8192
SF          400.1305621 MHz
WDW                  EM
SSB        0
LB                 0.30 Hz
GB         0
PC                 1.00

F1 - Processing parameters
SI                   16
MC2                  QF
SF          400.1361020 MHz
WDW                  no
SSB        0
LB         0 Hz
GB         0
```

Figure S39. ^{1}H-DOSY NMR spectrum of **$Yb_8(Zn\text{-}1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$La_8(Zn\text{-}1^R)_6(OTf)_{24}$** (log D=-9.502, r = 18.80Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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Display Report

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Method        pos-sqf-re-500-3000_high.m           Operator  BDAL@DE
Sample Name   li488-2                              Instrumen impact II   1825265.1013
                                                                         3
Comment

Acquisition Paramet
Source Type   ESI        Ion Polarity          Positive   Set Nebulizer      1.5 Bar
Focus         Active     Set Capillary         4500 V     Set Dry Heater     200 °C
Scan Begin    500 m/z    Set End Plate Offset  -500 V     Set Dry Gas        4.5 l/min
Scan End      3000 m/z   Set Charging Voltage  2000 V     Set Divert Valve   Waste
                         Set Corona            0 nA       Set APCI Heater    0 °C
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li488-2_2-d,7_01_12572.d
Bruker Compass DataAnalysis 4.3   printe 2018/12/5 16:11:06   by: sqf   Page 1 of 1
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Figure S40. ESI-TOF-MS spectra of **$Yb_8(Zn\text{-}1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$La_6(Zn\text{-}1^R)_3(OTf)_{18}$**, with insets showing the observed isotopic patterns of the +10 peaks.

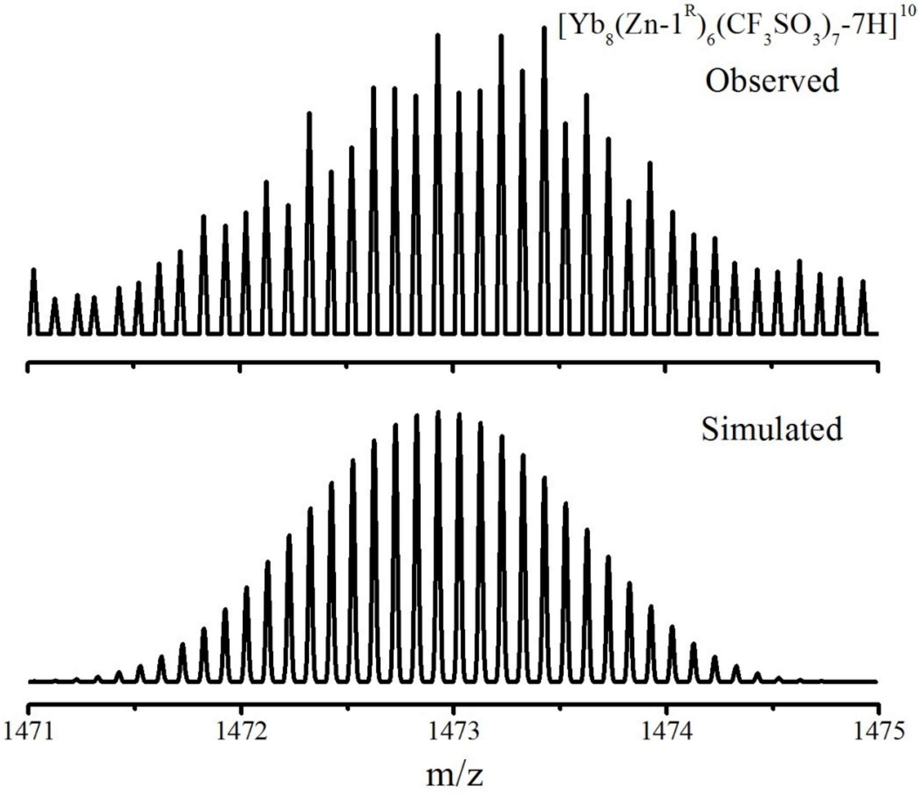


Figure S41. Comparison of the observed and simulated signals of [**Yb$_8$(Zn-1^{R})$_6$(OTf)$_7$-7H]$^{10+}$**.

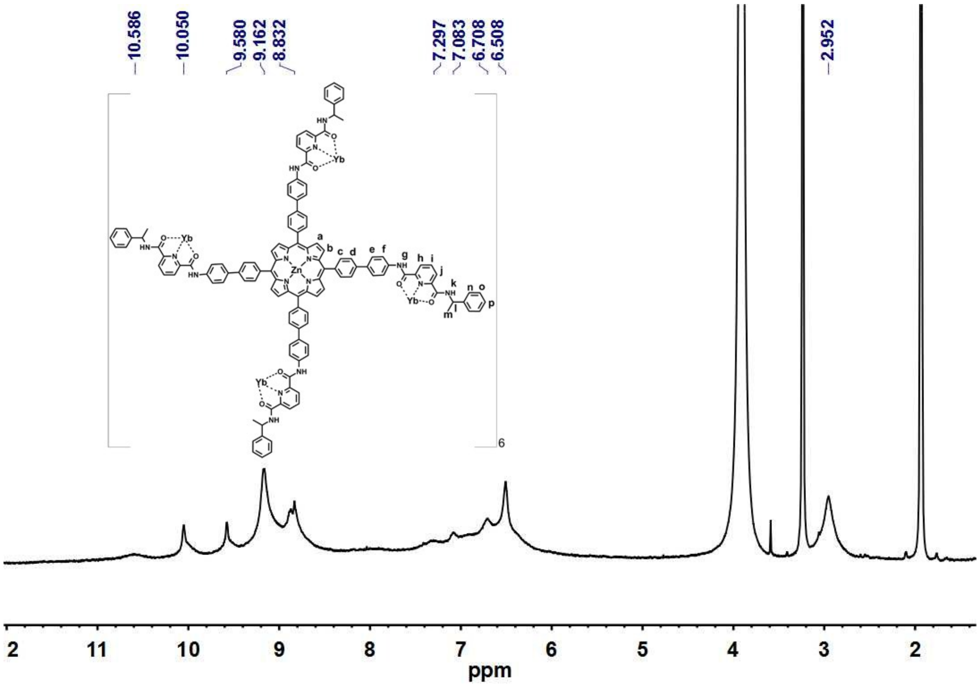
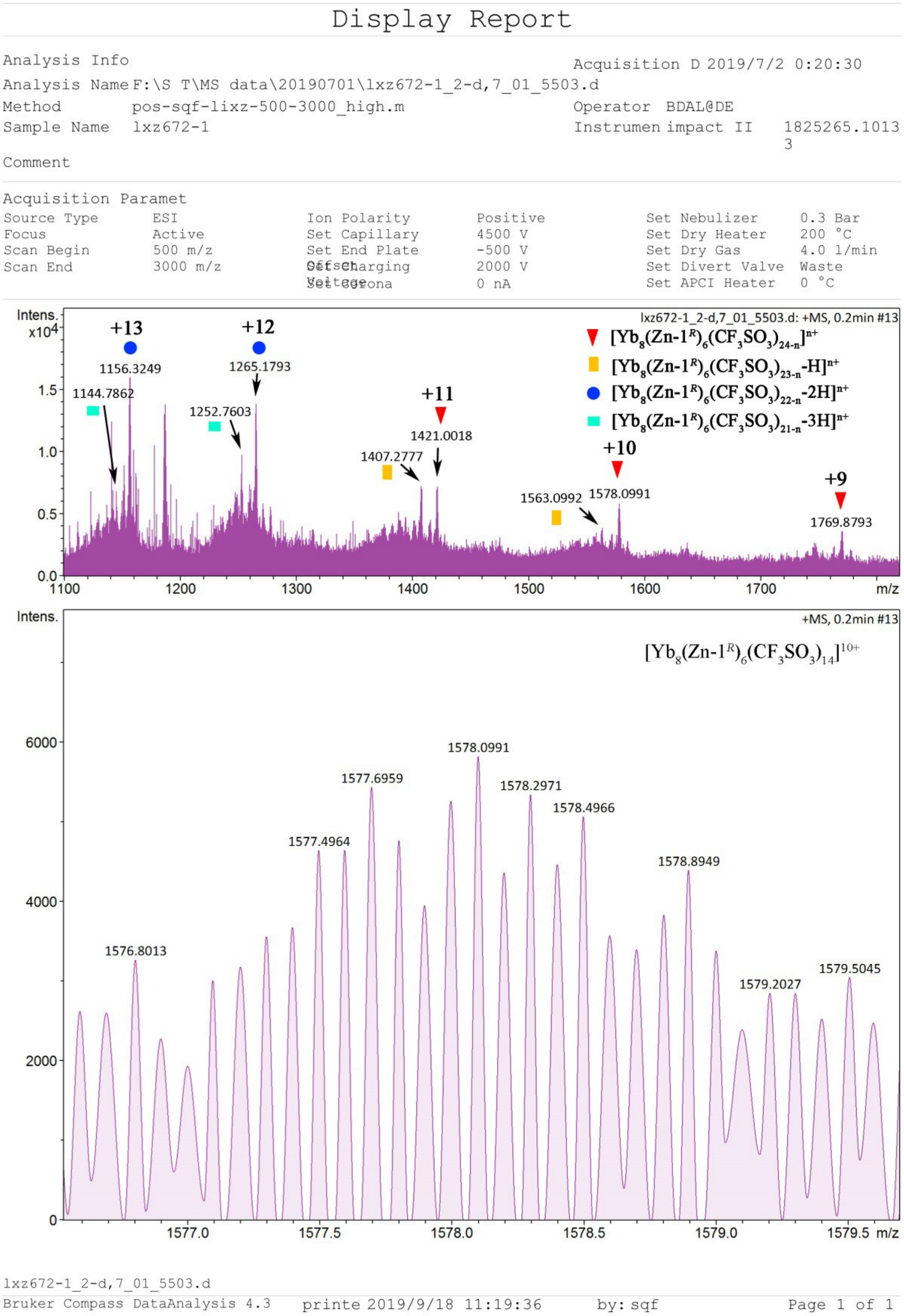


Figure S42. ^{1}H NMR spectra of **Yb$_8$(Zn-1^{R})$_6$(OTf)$_{24}$** self-assembled through transmetalation from **Eu$_8$(Zn-1^{R})$_6$(OTf)$_{24}$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).



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                              Display Report

Analysis Info                                      Acquisition D 2019/7/2 0:20:30
Analysis Name F:\S T\MS data\20190701\lxz672-1_2-d,7_01_5503.d
Method        pos-sqf-lixz-500-3000_high.m         Operator  BDAL@DE
Sample Name   lxz672-1                             Instrumen impact II    1825265.1013
                                                                          3
Comment

Acquisition Paramet
Source Type      ESI          Ion Polarity       Positive      Set Nebulizer      0.3 Bar
Focus            Active       Set Capillary      4500 V        Set Dry Heater     200 °C
Scan Begin       500 m/z      Set End Plate      -500 V        Set Dry Gas        4.0 l/min
                              Offset
Scan End         3000 m/z     Set Charging       2000 V        Set Divert Valve   Waste
                              Voltage
                              Set Corona         0 nA          Set APCI Heater    0 °C

lxz672-1_2-d,7_01_5503.d
Bruker Compass DataAnalysis 4.3   printe 2019/9/18 11:19:36    by: sqf        Page 1 of 1
```

Figure S43. ESI-TOF-MS spectra of **$Yb_8(Zn\text{-}1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$Eu_8(Zn\text{-}1^R)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +10 peaks.

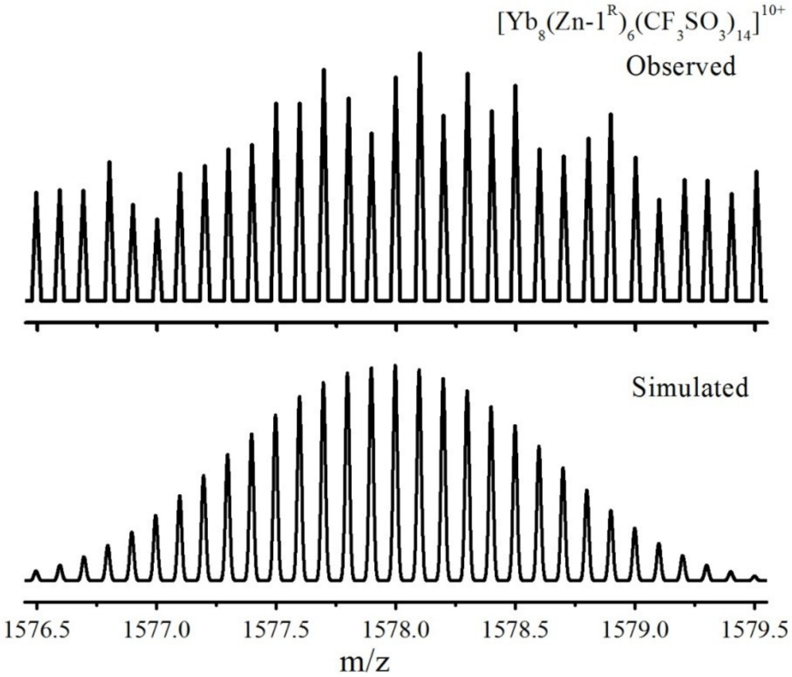


Figure S44. Comparison of the observed and simulated signals of $[\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6(OTf)_{14}}]^{10+}$.

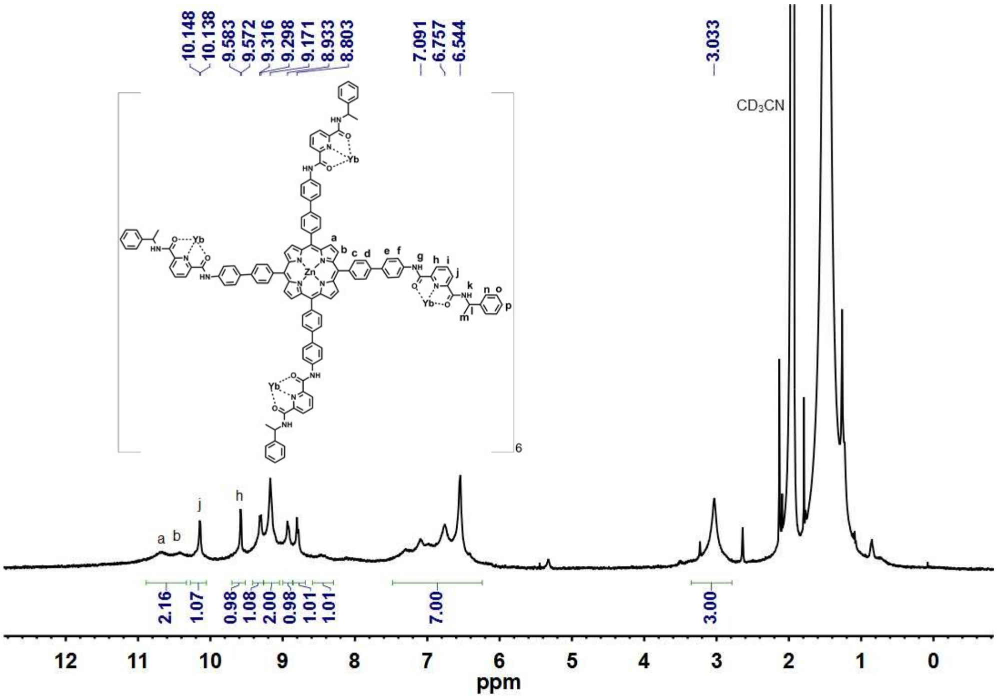
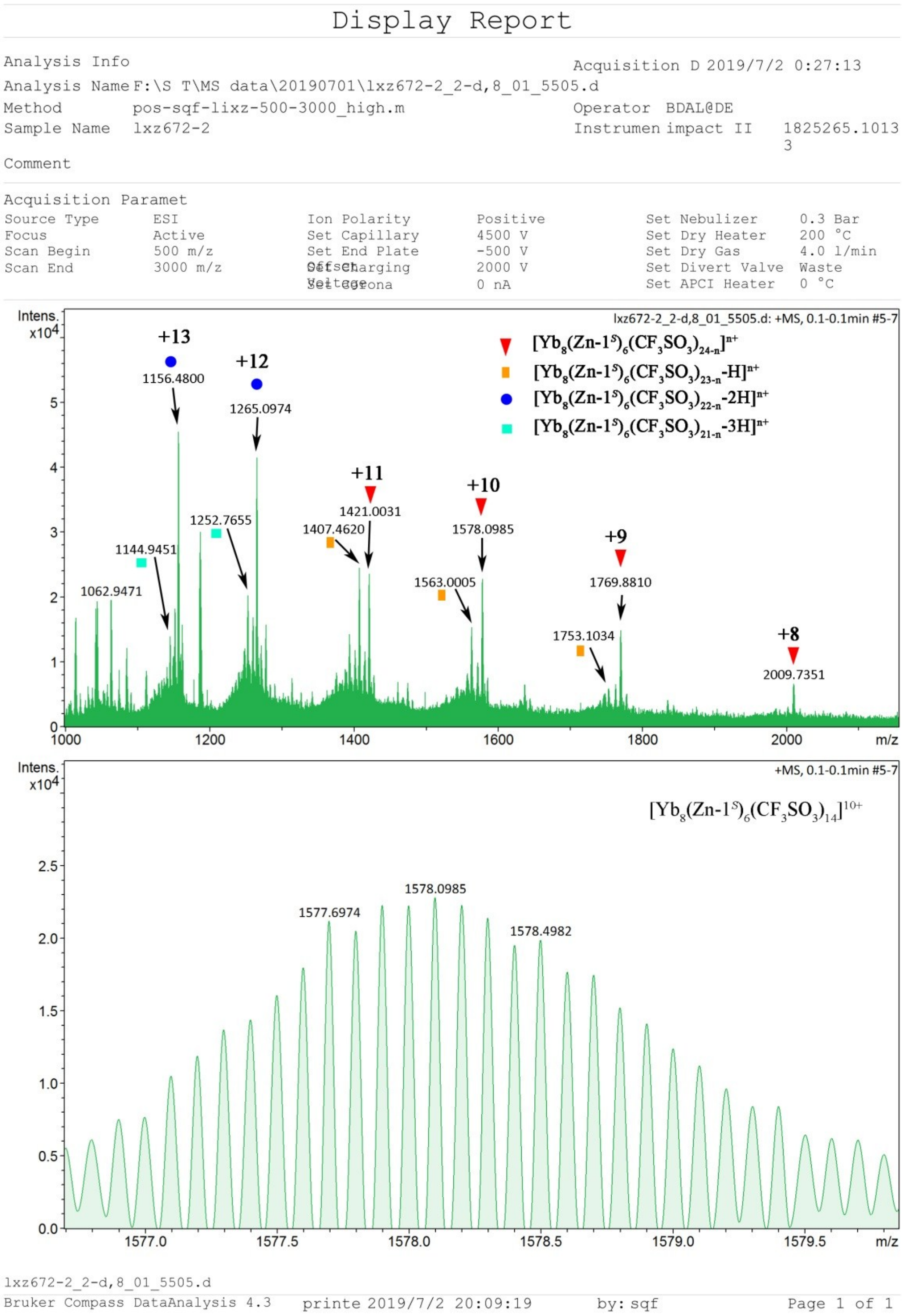


Figure S45. ^{1}H NMR spectrum of $\mathbf{Yb_8(Zn\text{-}1^{\mathit{S}})_6(OTf)_{24}}$ self-assembled through transmetalation from $\mathbf{Eu_8(Zn\text{-}1^{\mathit{S}})_6(OTf)_{24}}$ (400 MHz, CD_3CN, 298K).



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                         Display Report

Analysis Info                                     Acquisition D 2019/7/2 0:27:13
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Method        pos-sqf-lixz-500-3000_high.m        Operator  BDAL@DE
Sample Name   lxz672-2                            Instrumen impact II   1825265.1013
                                                                        3
Comment

Acquisition Paramet
Source Type    ESI        Ion Polarity          Positive     Set Nebulizer     0.3 Bar
Focus          Active     Set Capillary         4500 V       Set Dry Heater    200 °C
Scan Begin     500 m/z    Set End Plate Offset  -500 V       Set Dry Gas       4.0 l/min
Scan End       3000 m/z   Set Charging Voltage  2000 V       Set Divert Valve  Waste
                          Set Corona            0 nA         Set APCI Heater   0 °C
```

```
lxz672-2_2-d,8_01_5505.d
Bruker Compass DataAnalysis 4.3    printe 2019/7/2 20:09:19    by: sqf    Page 1 of 1
```

Figure S46. ESI-TOF-MS spectra of **$Yb_8(Zn\text{-}1^S)_6(OTf)_{24}$** self-assembled through transmetalation from **$Eu_8(Zn\text{-}1^S)_6(OTf)_{24}$** with insets showing the observed isotopic patterns of the +10 peaks.

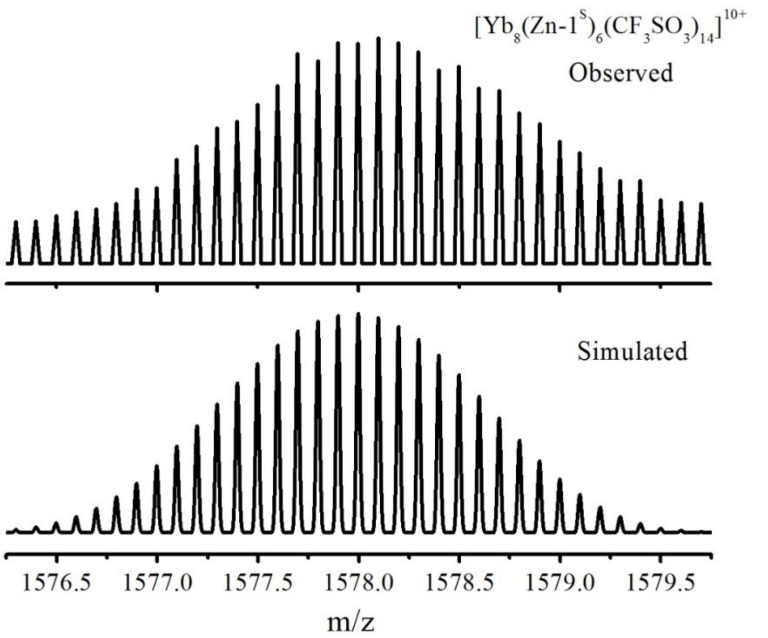


Figure S47. Comparison of the observed and simulated signals of $[\mathbf{Yb_8(Zn\text{-}1^{\mathit{S}})_6(OTf)_{14}}]^{10+}$.

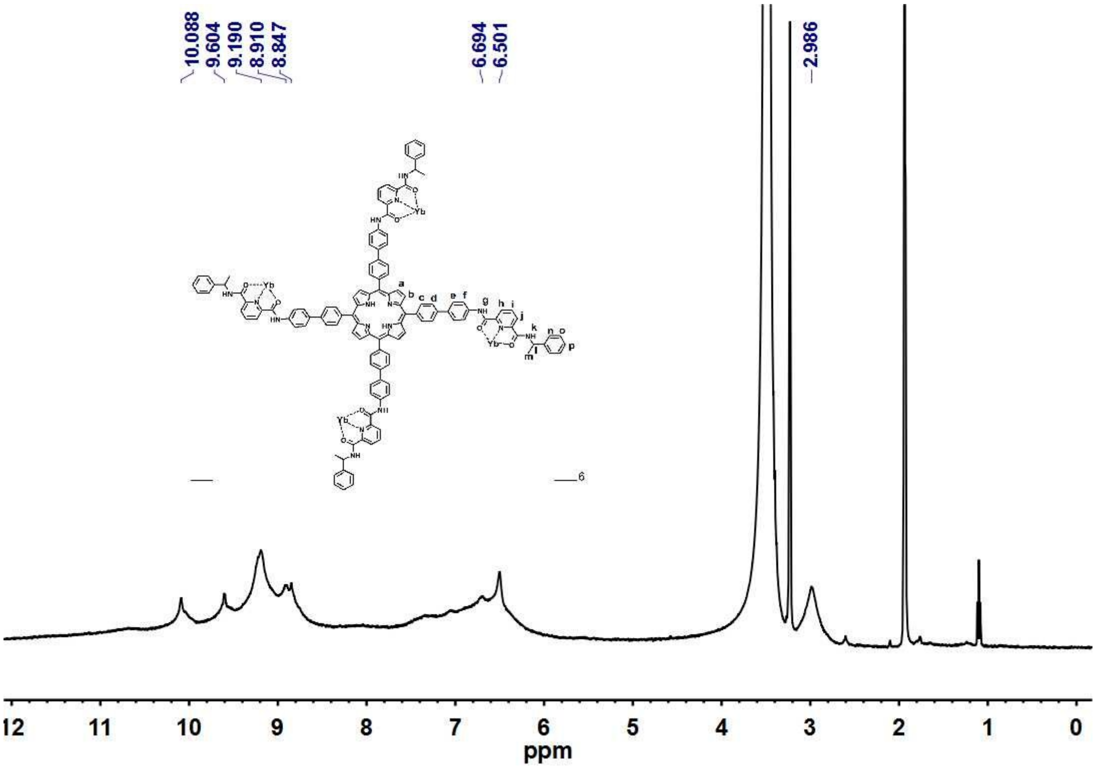
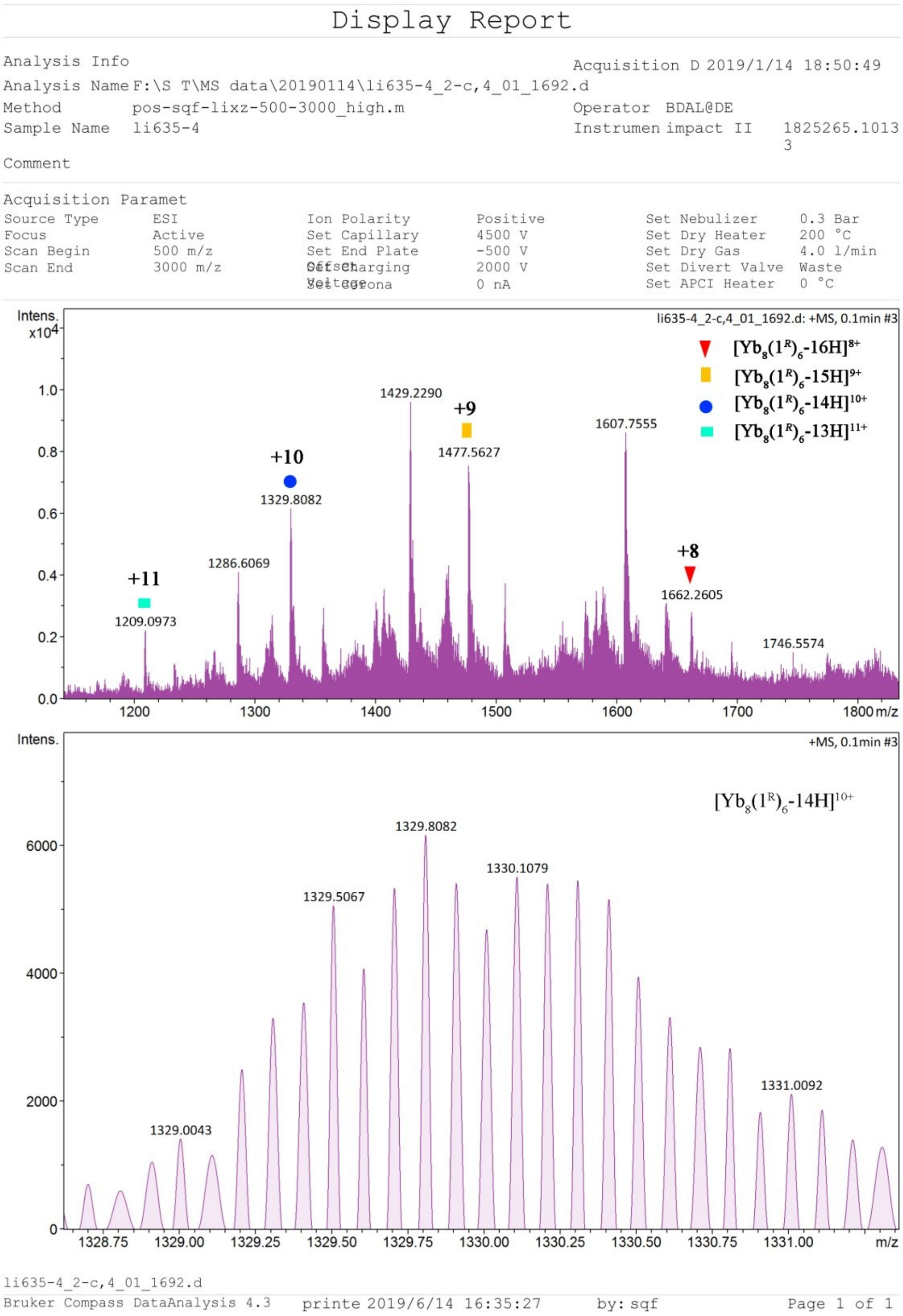


Figure S48. ^{1}H NMR spectra of $\mathbf{Yb_8(1^{\mathit{R}})_6(OTf)_{24}}$ self-assembled through transmetalation from $\mathbf{La_6(1^{\mathit{R}})_3(OTf)_{18}}$ (400 MHz, CD$_3$CN/CD$_3$OD, 298K).



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                           Display Report

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Method        pos-sqf-lixz-500-3000_high.m          Operator  BDAL@DE
Sample Name   li635-4                               Instrumen impact II    1825265.1013
                                                                           3
Comment

Acquisition Paramet
Source Type    ESI        Ion Polarity       Positive      Set Nebulizer     0.3 Bar
Focus          Active     Set Capillary      4500 V        Set Dry Heater    200 °C
Scan Begin     500 m/z    Set End Plate      -500 V        Set Dry Gas       4.0 l/min
Scan End       3000 m/z   Offset
                          Set Charging       2000 V        Set Divert Valve  Waste
                          Voltage
                          Set Corona         0 nA          Set APCI Heater   0 °C
```

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li635-4_2-c,4_01_1692.d
Bruker Compass DataAnalysis 4.3   printe 2019/6/14 16:35:27   by: sqf          Page 1 of 1
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Figure S49. ESI-TOF-MS spectra of **$Yb_8(1^R)_6(OTf)_{24}$** self-assembled through transmetalation from **$La_6(1^R)_3(OTf)_{18}$**, with insets showing the observed and simulated isotopic patterns of the +10 peaks.

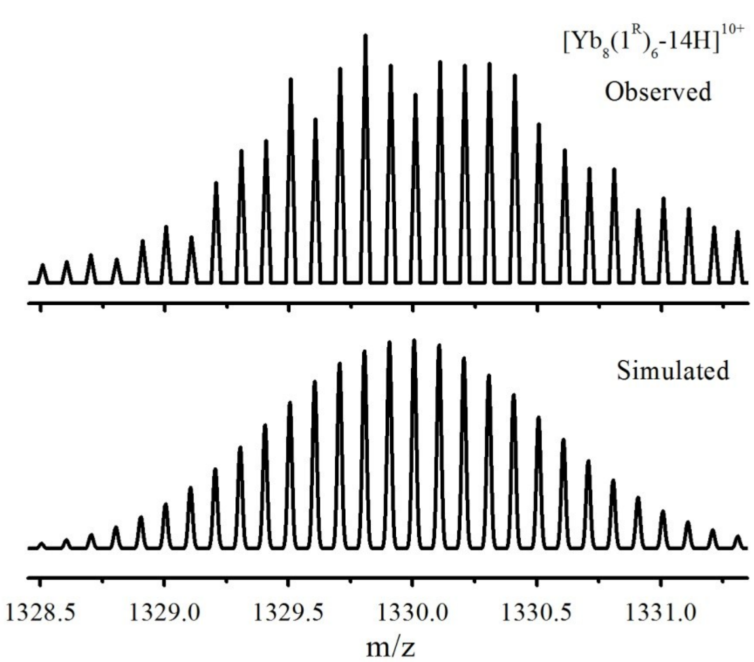


Figure S50. Comparison of the observed and simulated signals of [$\mathbf{Yb_8(1^{\mathit{R}})_6\text{-}14H}$]$^{10+}$.

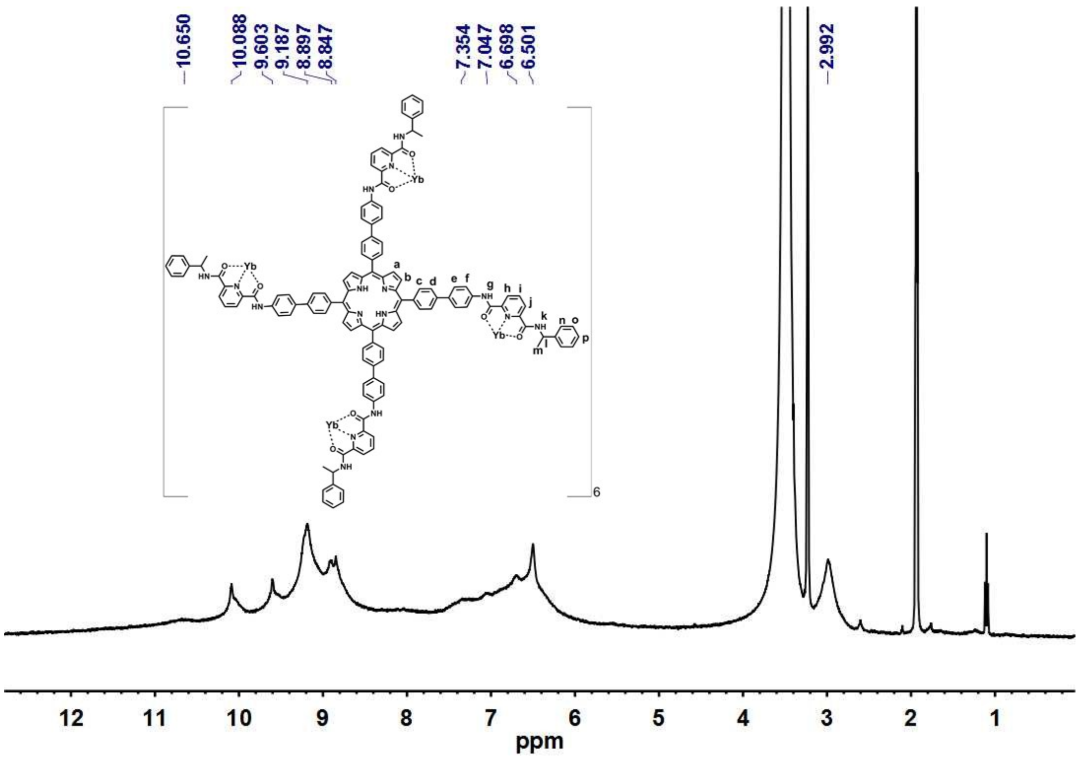
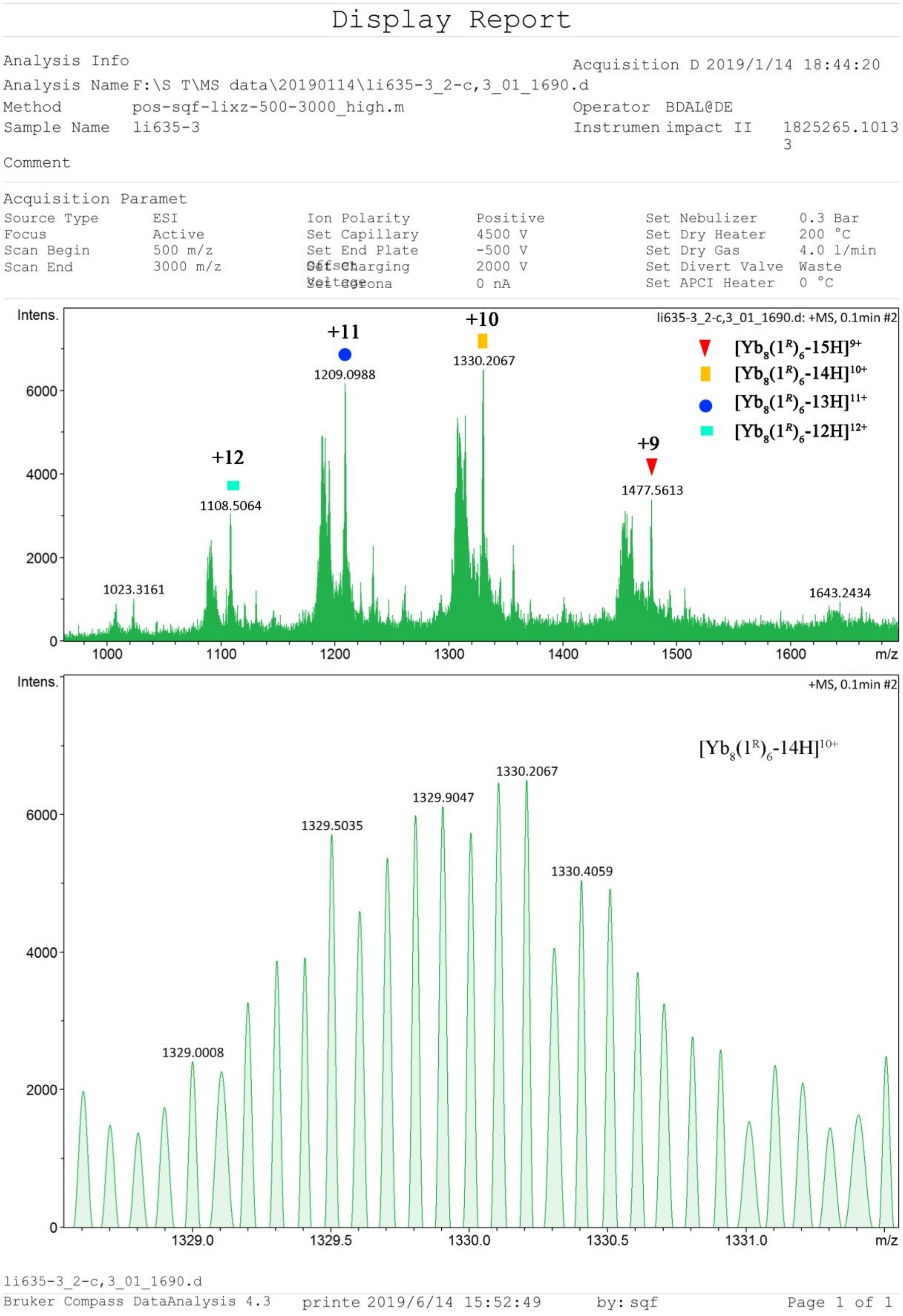


Figure S51. ^{1}H NMR spectrum of $\mathbf{Yb_8(1^{\mathit{R}})_6(OTf)_{24}}$ self-assembled through transmetalation from $\mathbf{Eu_8(1^{\mathit{R}})_6(OTf)_{24}}$ (400 MHz, CD_3CN/CD_3OD, 298K).



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Comment

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Bruker Compass DataAnalysis 4.3    printe 2019/6/14 15:52:49    by: sqf        Page 1 of 1
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Figure S52. ESI-TOF-MS spectra of $\mathbf{Yb_8(1^{\mathit{R}})_6(OTf)_{24}}$ self-assembled through transmetalation from $\mathbf{Eu_8(1^{\mathit{R}})_6(OTf)_{24}}$, with insets showing the observed isotopic patterns of the +10 peaks.

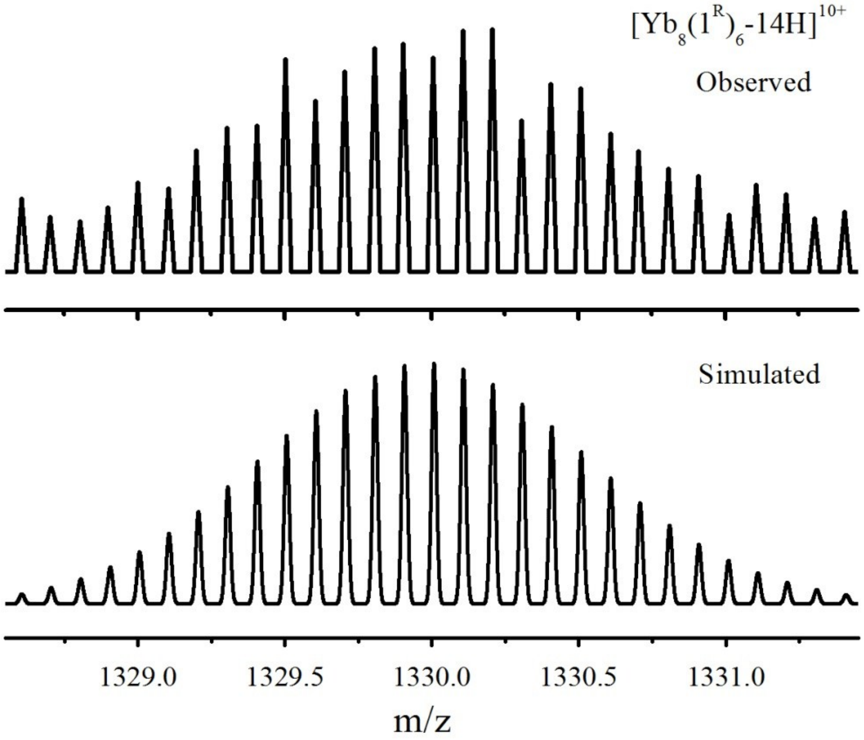


Figure S53. Comparison of the observed and simulated signals of [$\mathbf{Yb_8(1^{\mathit{R}})_6\text{-}14H]^{10+}}$.

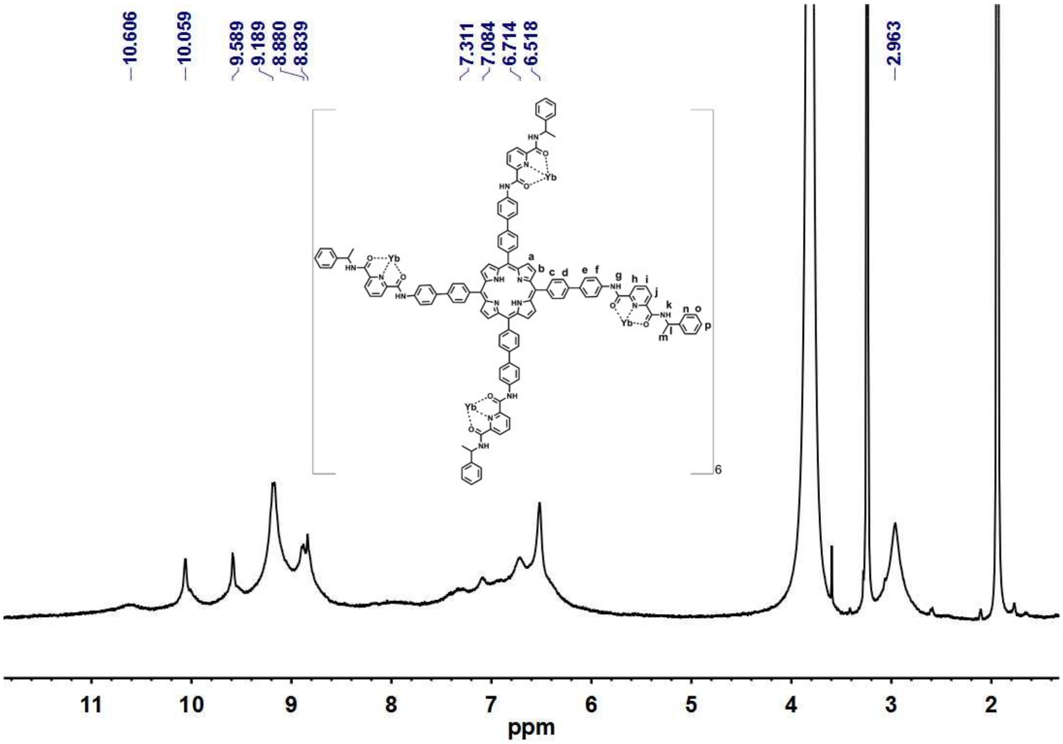


Figure S54. ^{1}H NMR spectrum of $\mathbf{Yb_8(1^{\mathit{R}})_6(OTf)_{24}}$ self-assembled through cascade transmetalation reaction from $\mathbf{La_6(1^{\mathit{R}})_3(OTf)_{18}}$ (400 MHz, CD_3CN/CD_3OD, 298K).

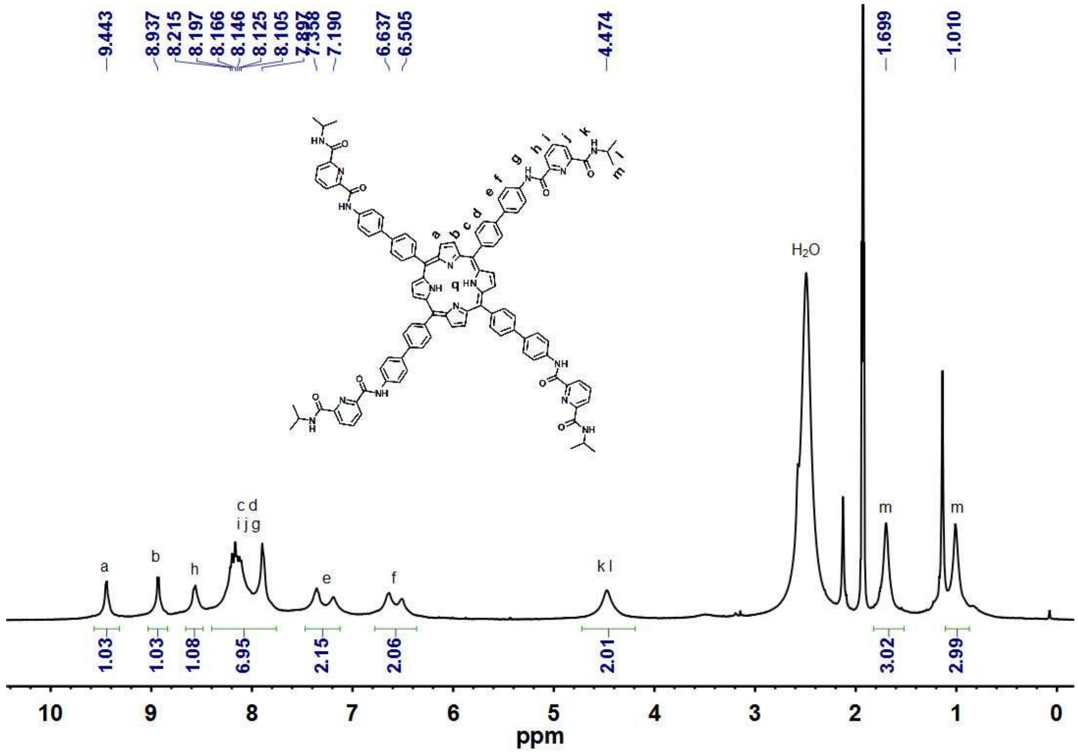


Figure S55. ^{1}H NMR spectrum of **$Eu_8(2)_6(ClO_4)_{24}$** (400 MHz, CD_3CN, 298K).

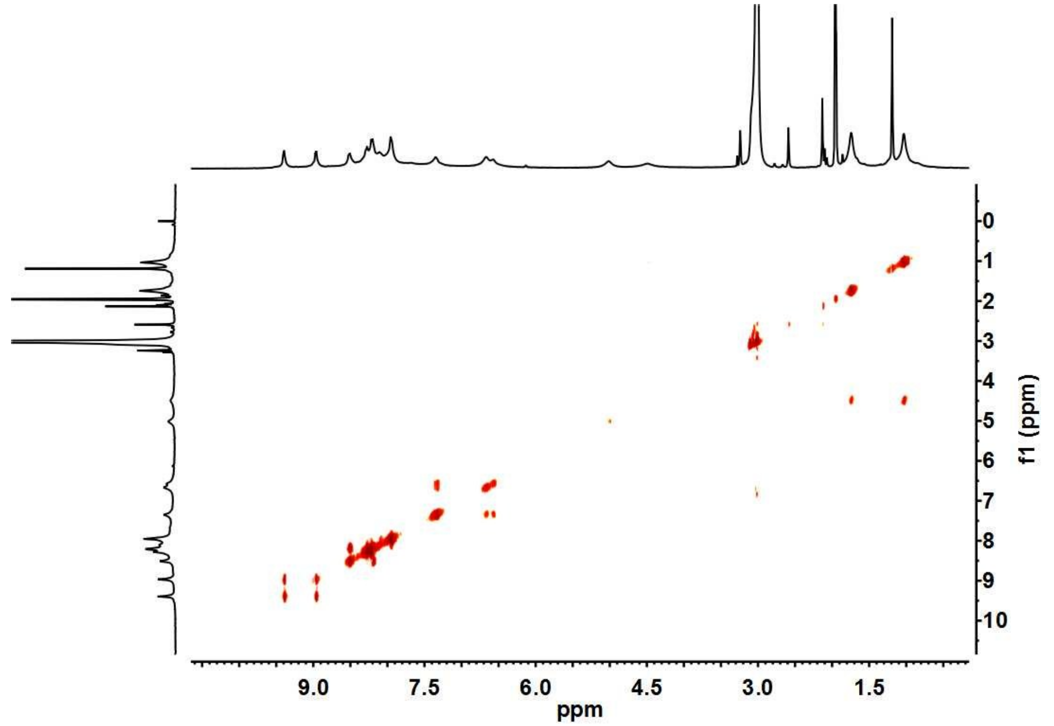


Figure S56. ^{1}H-^{1}H COSY NMR spectrum of **$Eu_8(2)_6(ClO_4)_{24}$** (400 MHz, CD_3CN/CD_3OD, 298K).

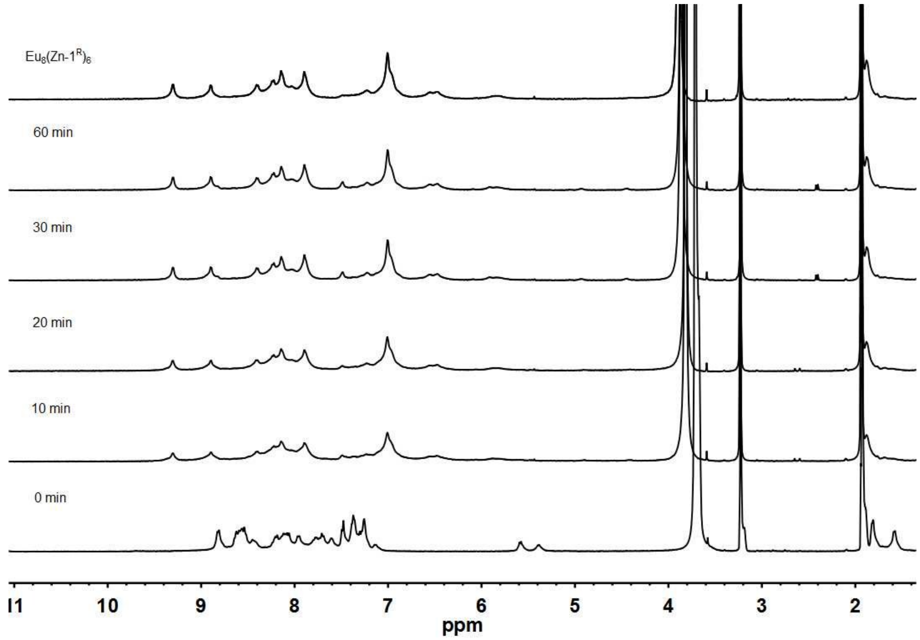


Figure S57. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Eu^{III} toward **La$_6$(Zn-1$^{\boldsymbol{R}}$)$_3$** systems (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

According to the ^{1}H NMR spectra, the La^{III} ions in **La$_6$(Zn-1$^{\boldsymbol{R}}$)$_3$** were substituted by Eu^{III} ions, leading to the formation of **Eu$_8$(Zn-1$^{\boldsymbol{R}}$)$_6$** complexes.

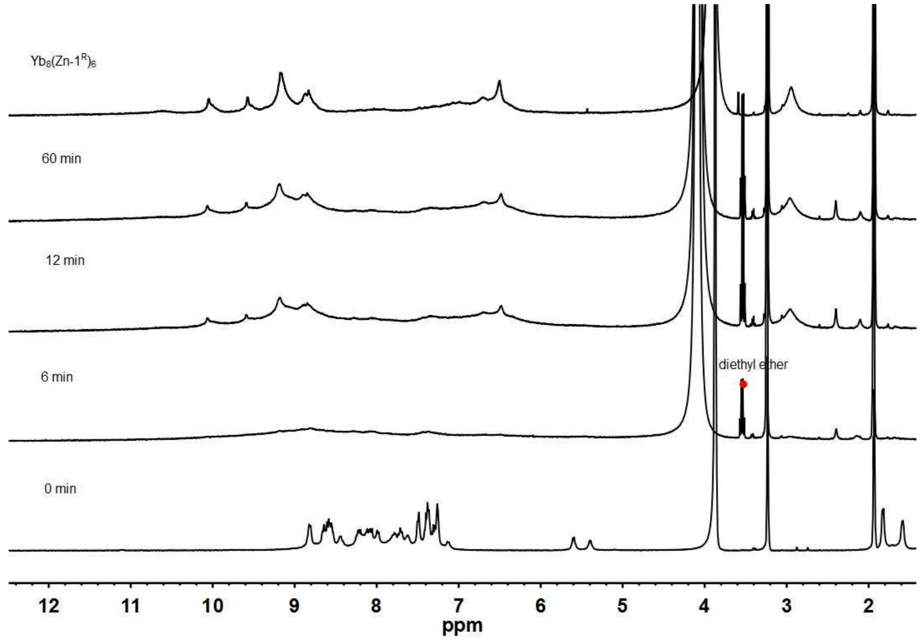


Figure S58. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Yb^{III} toward **La$_6$(Zn-1$^{\boldsymbol{R}}$)$_3$** systems (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

According to the ^{1}H NMR spectra, the La^{III} ions in **La$_6$(Zn-1$^{\boldsymbol{R}}$)$_3$** were substituted by Yb^{III} ions, leading to the formation of **Yb$_8$(Zn-1$^{\boldsymbol{R}}$)$_6$** complexes.

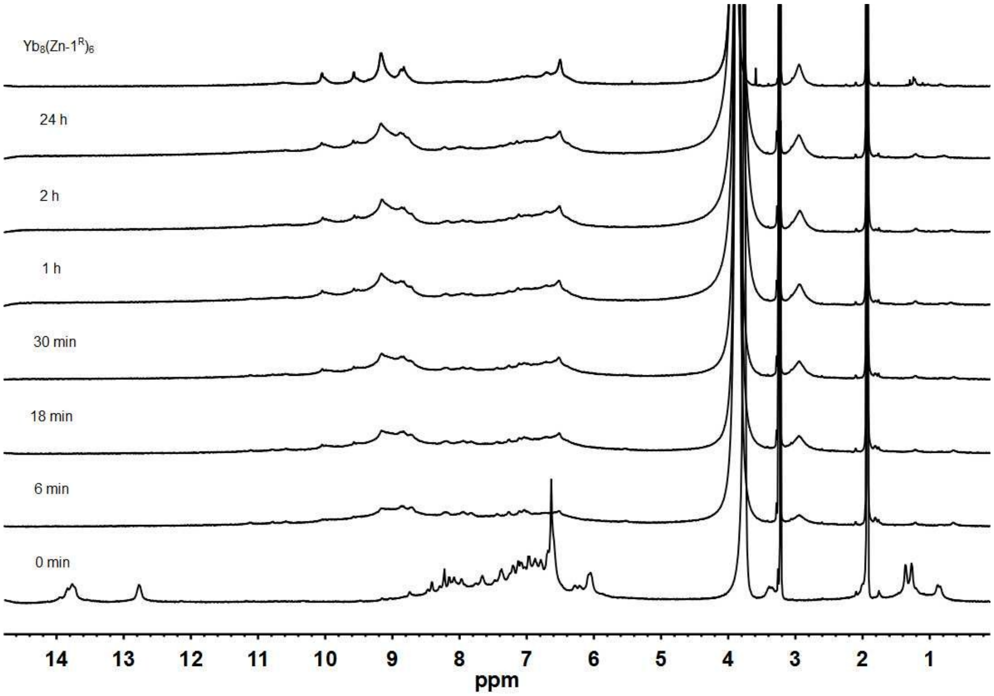


Figure S59. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Yb^{III} toward **Ce$_8$(Zn-1^R)$_6$** systems (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

According to the ^{1}H NMR spectra, the Ce^{III} ions in **Ce$_8$(Zn-1^R)$_6$** were substituted by Yb^{III} ions, leading to the formation of **Yb$_8$(Zn-1^R)$_6$** complexes.

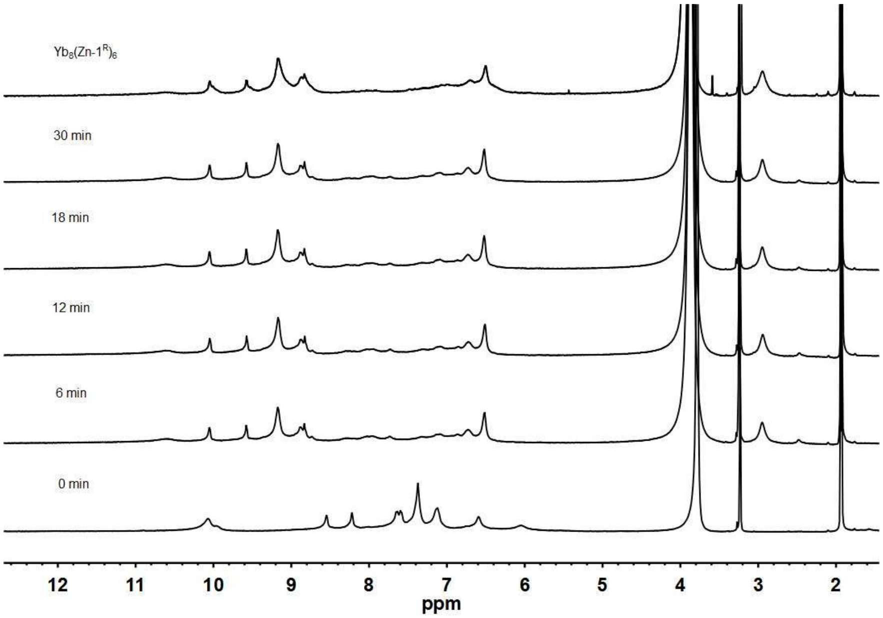


Figure S60. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Yb^{III} toward **Pr$_8$(Zn-1^R)$_6$** systems (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

According to the ^{1}H NMR spectra, the Pr^{III} ions in **Pr$_8$(Zn-1^R)$_6$** were substituted by Yb^{III} ions, leading to the formation of **Yb$_8$(Zn-1^R)$_6$** complexes.

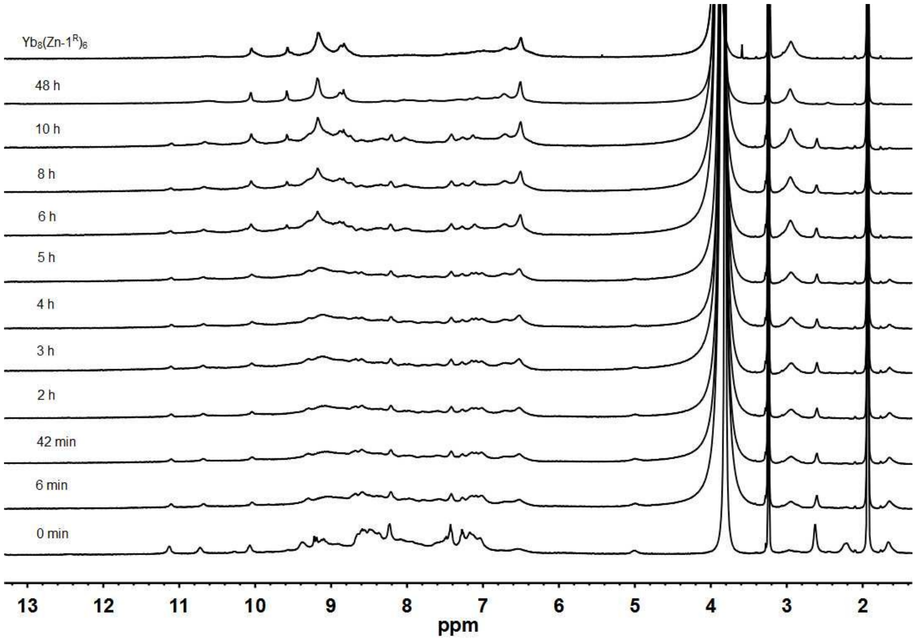


Figure S61. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Yb^{III} toward **$Nd_8(Zn\text{-}1^R)_6$** systems (400 MHz, CD_3CN/CD_3OD, 298K).

According to the ^{1}H NMR spectra, the Nd^{III} ions in **$Nd_8(Zn\text{-}1^R)_6$** were substituted by Yb^{III} ions, leading to the formation of **$Yb_8(Zn\text{-}1^R)_6$** complexes.

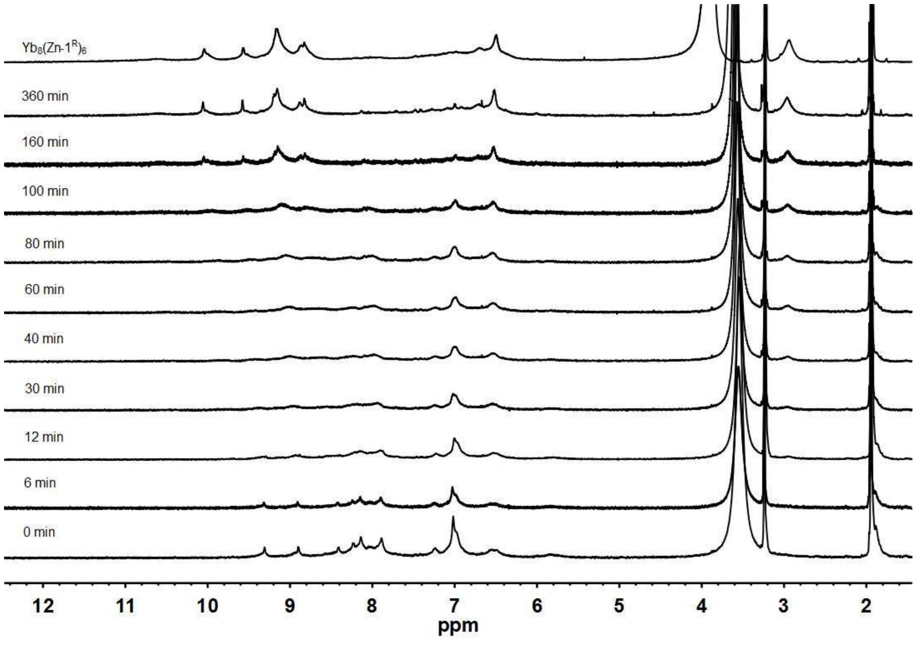


Figure S62. ^{1}H NMR spectra of post-synthetic metal-ion metathesis experiments with the addition of Yb^{III} toward **$Eu_8(1^R)_6$** systems at 37 ºC (600 MHz, CD_3CN/CD_3OD, 298K).

According to the ^{1}H NMR spectra, the Eu^{III} ions in **$Eu_8(Zn\text{-}1^R)_6$** were substituted by Yb^{III} ions, leading to the formation of **$Yb_8(Zn\text{-}1^R)_6$** complexes.

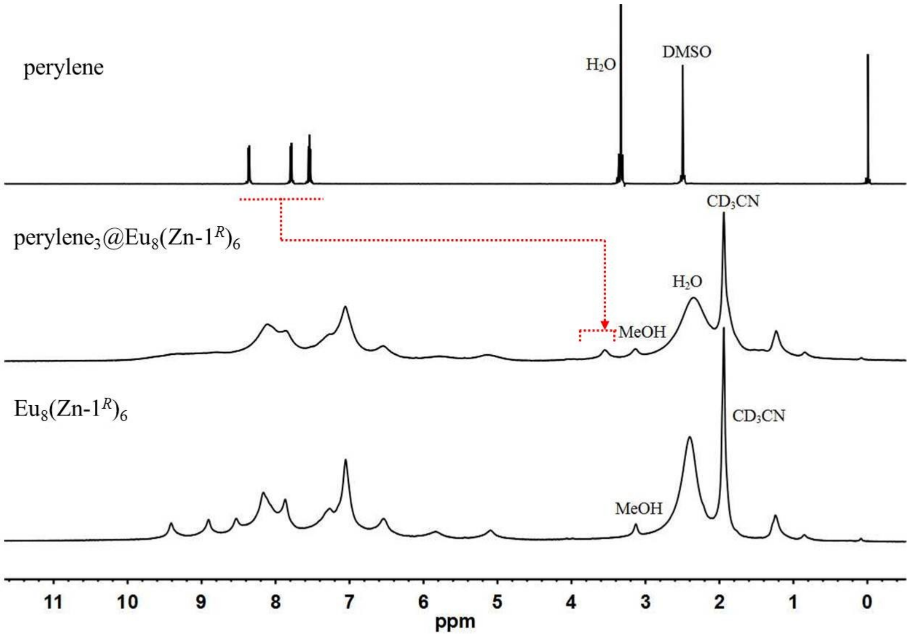


Figure S63. ^{1}H NMR spectra of perylene, perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** and **Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

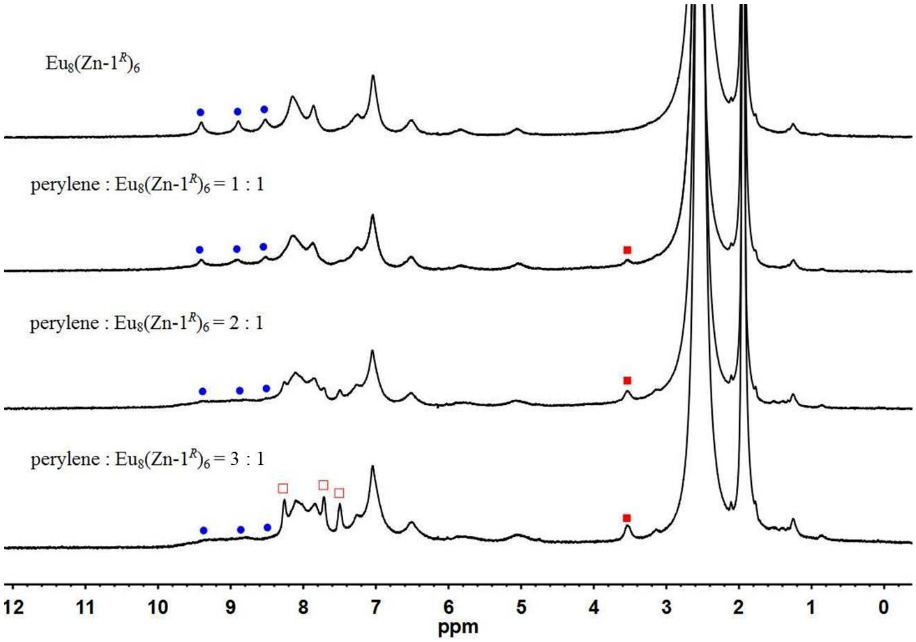
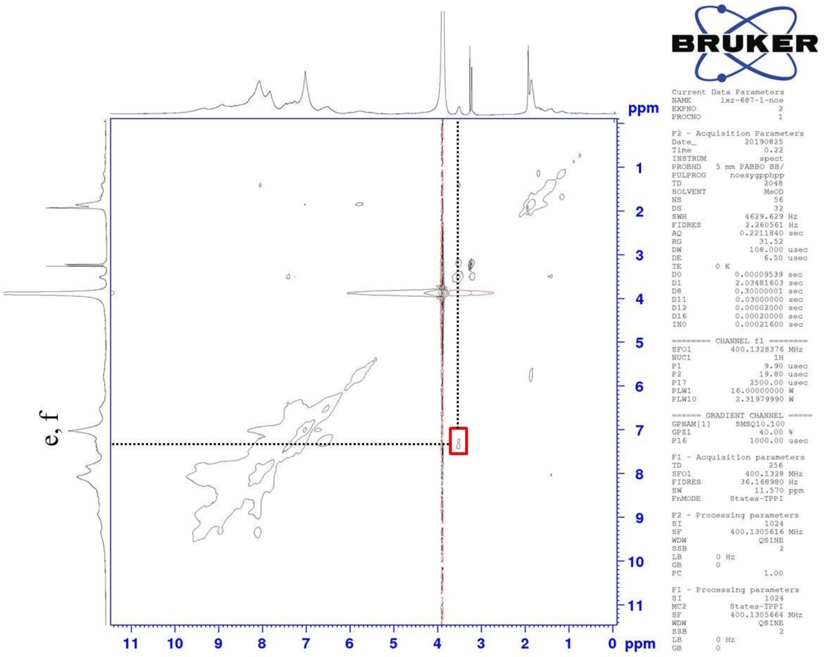


Figure S64. ^{1}H NMR spectra of **Eu$_8$(Zn-1^R)$_6$** with different equivalents of perylene (400 MHz, CD$_3$CN, 298K) (● denotes the signals of **Eu$_8$(Zn-1^R)$_6$** that undergo sever broadening during the host-guest complexation process, ■ denotes the signals of the encapsulated guests, □ denotes the signals of free guests).



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F1 - Processing parameters
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GB          0
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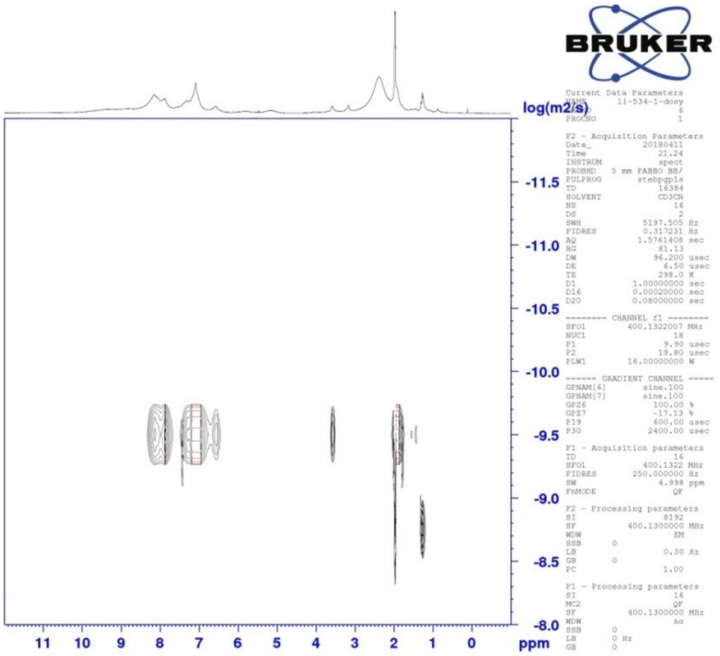
Figure S65. ^{1}H-^{1}H NOESY NMR spectrum of perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

^{1}H-^{1}H NOESY NMR spectra of the host-guest complexes were tested. But not all the cross-peaks between the signals of the encapsulated guests and the hosts can be observed due to the high molecule weight and the paramagnetism of the lanthanide ions.



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GPZ7               -17.13 %
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FnMODE                 QF

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F1 - Processing parameters
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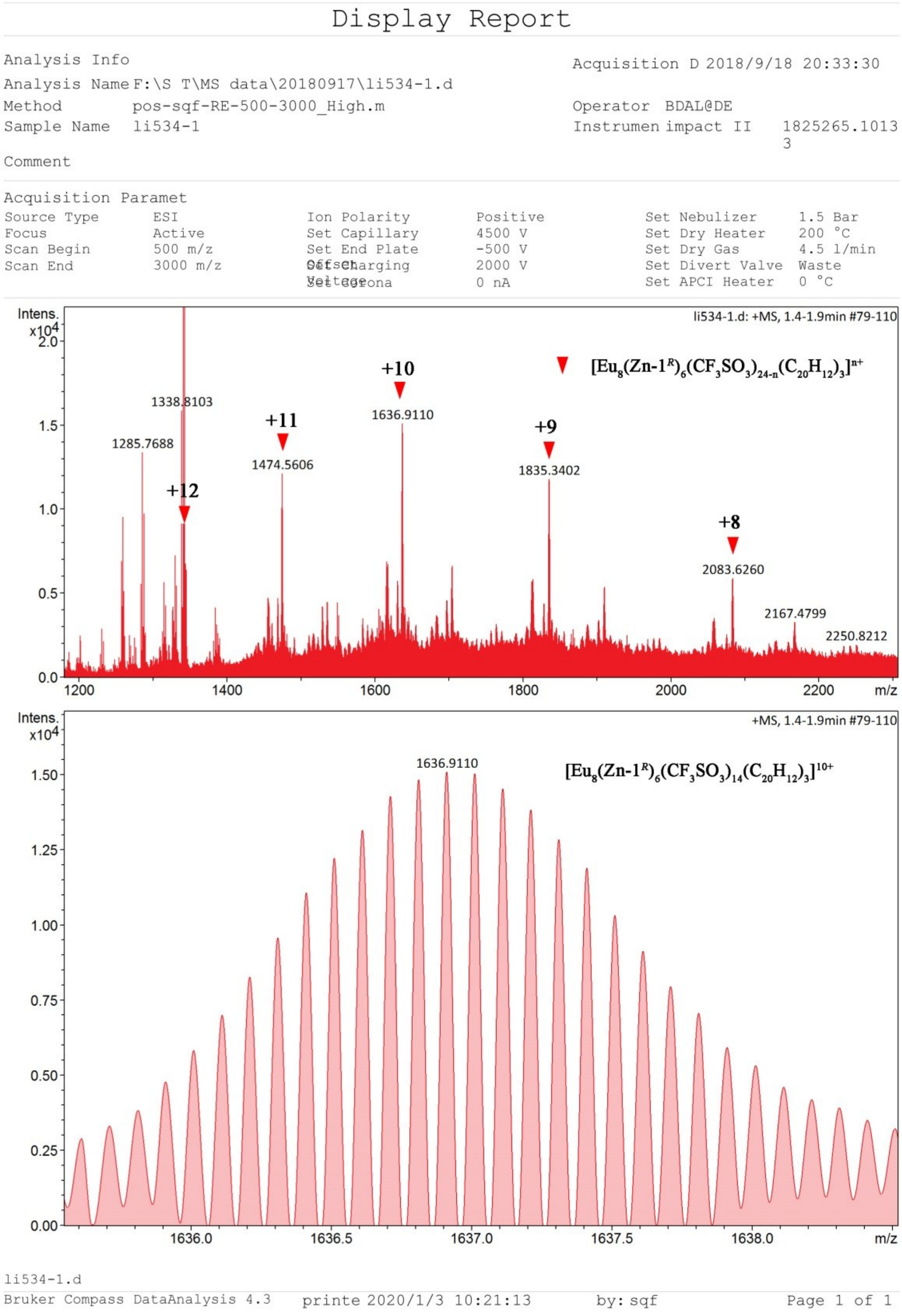
Figure S66. ^{1}H-DOSY NMR spectrum of perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (log D=-9.505, r = 18.92Å, 400 MHz, CD$_3$CN/CD$_3$OD, 298 K).



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li534-1.d
Bruker Compass DataAnalysis 4.3    printe 2020/1/3 10:21:13     by: sqf          Page 1 of 1
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Figure S67. ESI-TOF-MS spectra of perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** with insets showing the observed isotopic patterns of the +10 peaks.

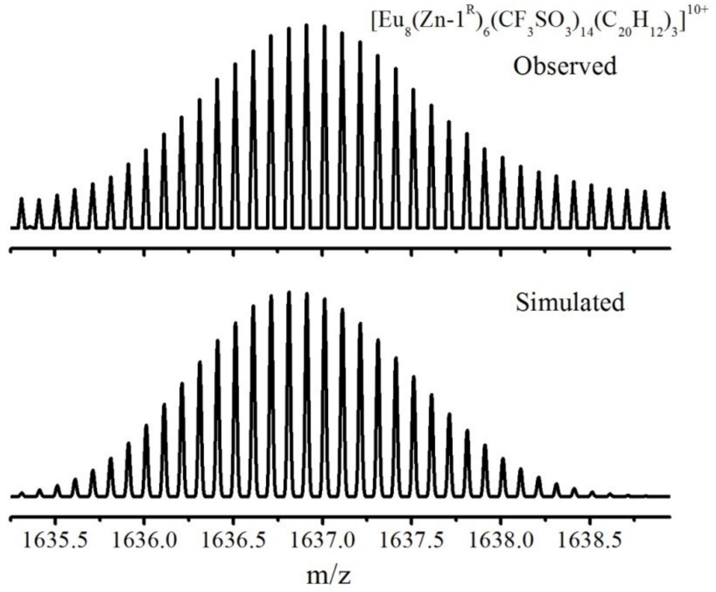

Figure S68. Comparison of the observed and simulated signals of **[**perylene$_3$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$**.

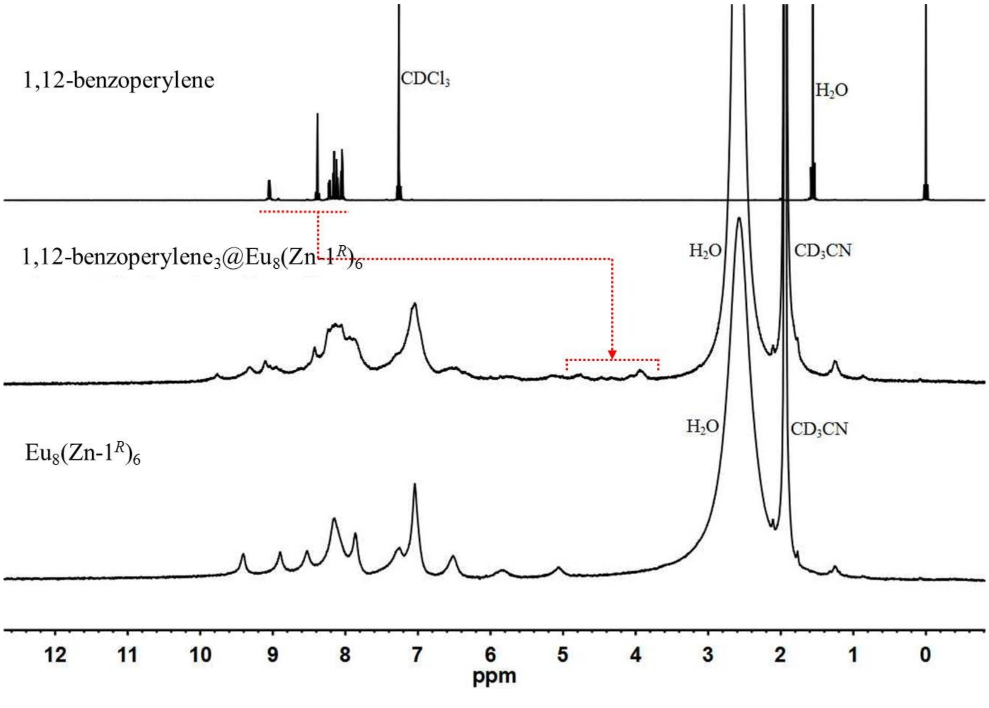

Figure S69. ^{1}H NMR spectra of 1,12-benzoperylene, 1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$** and **Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD_3CN, 298K).

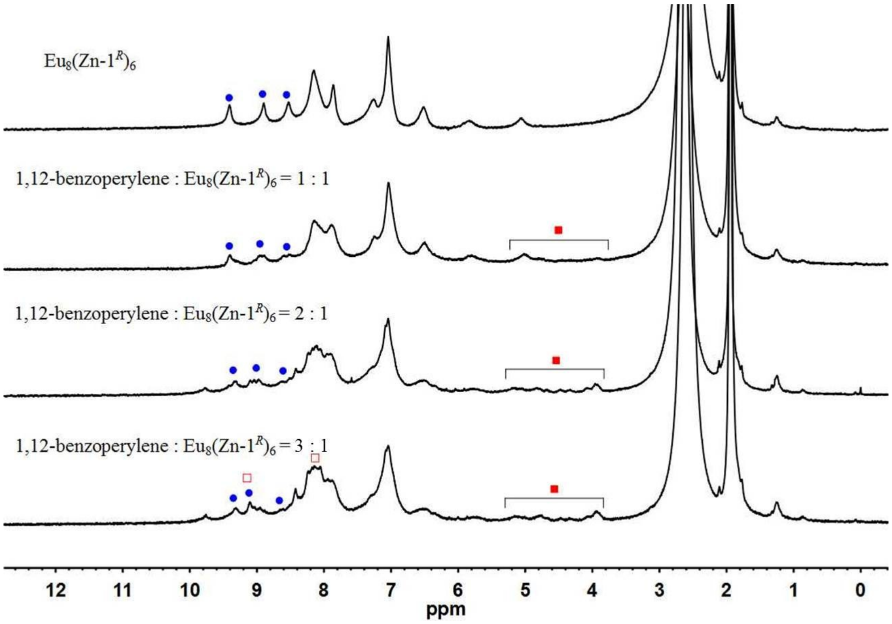

Figure S70. ^{1}H NMR spectra of **Eu$_8$(Zn-1^R)$_6$** with different equivalents of 1,12-benzoperylene (400 MHz, CD$_3$CN, 298K) (● denotes the signals of **Eu$_8$(Zn-1^R)$_6$** that undergo sever broadening during the host-guest complexation process, ■ denotes the signals of the encapsulated guests, □ denotes the signals of free guests).

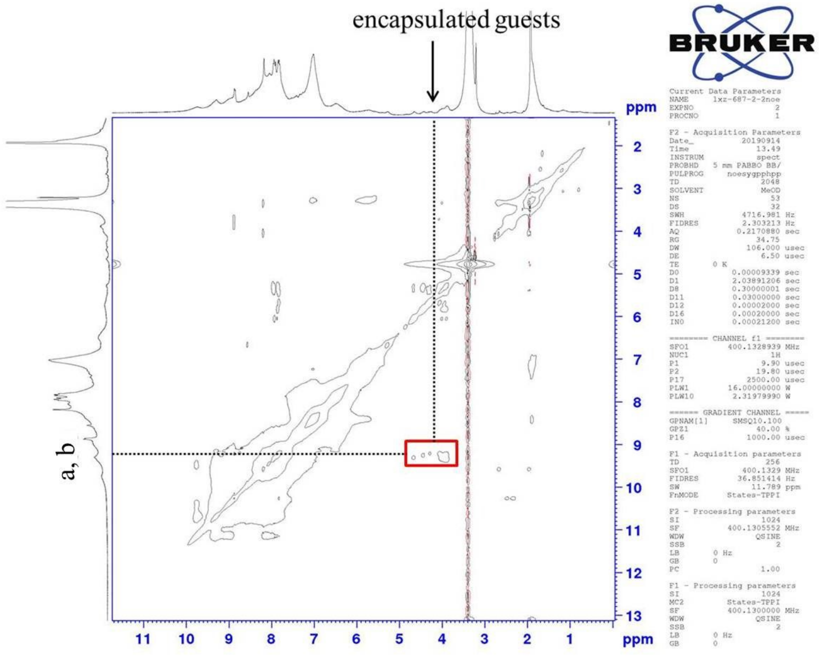

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Figure S71. ^{1}H-^{1}H NOESY NMR spectrum of 1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).

^{1}H-^{1}H NOESY NMR spectra of the host-guest complexes were tested. But not all the cross-peaks between the signals of the encapsulated guests and the hosts can be observed due to the high molecule weight and the paramagnetism of the lanthanide ions.

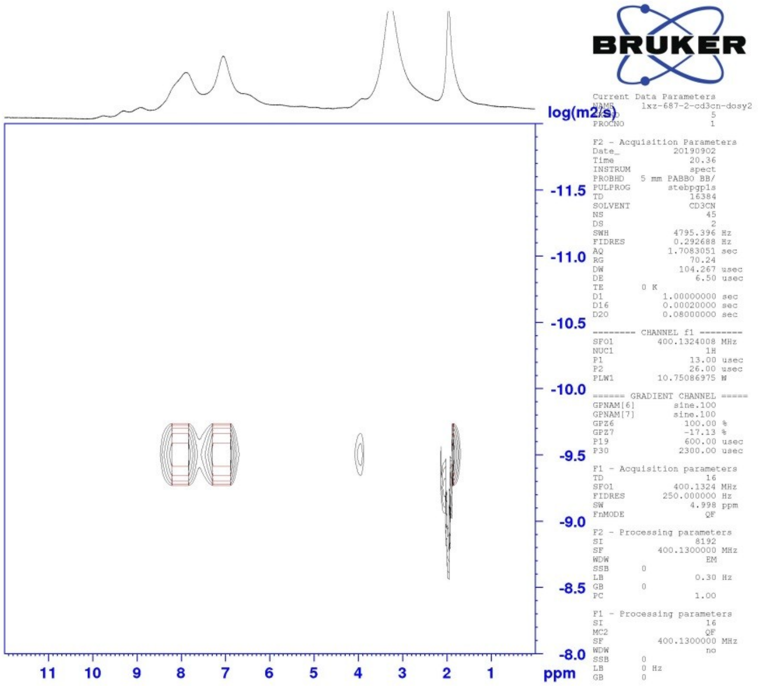
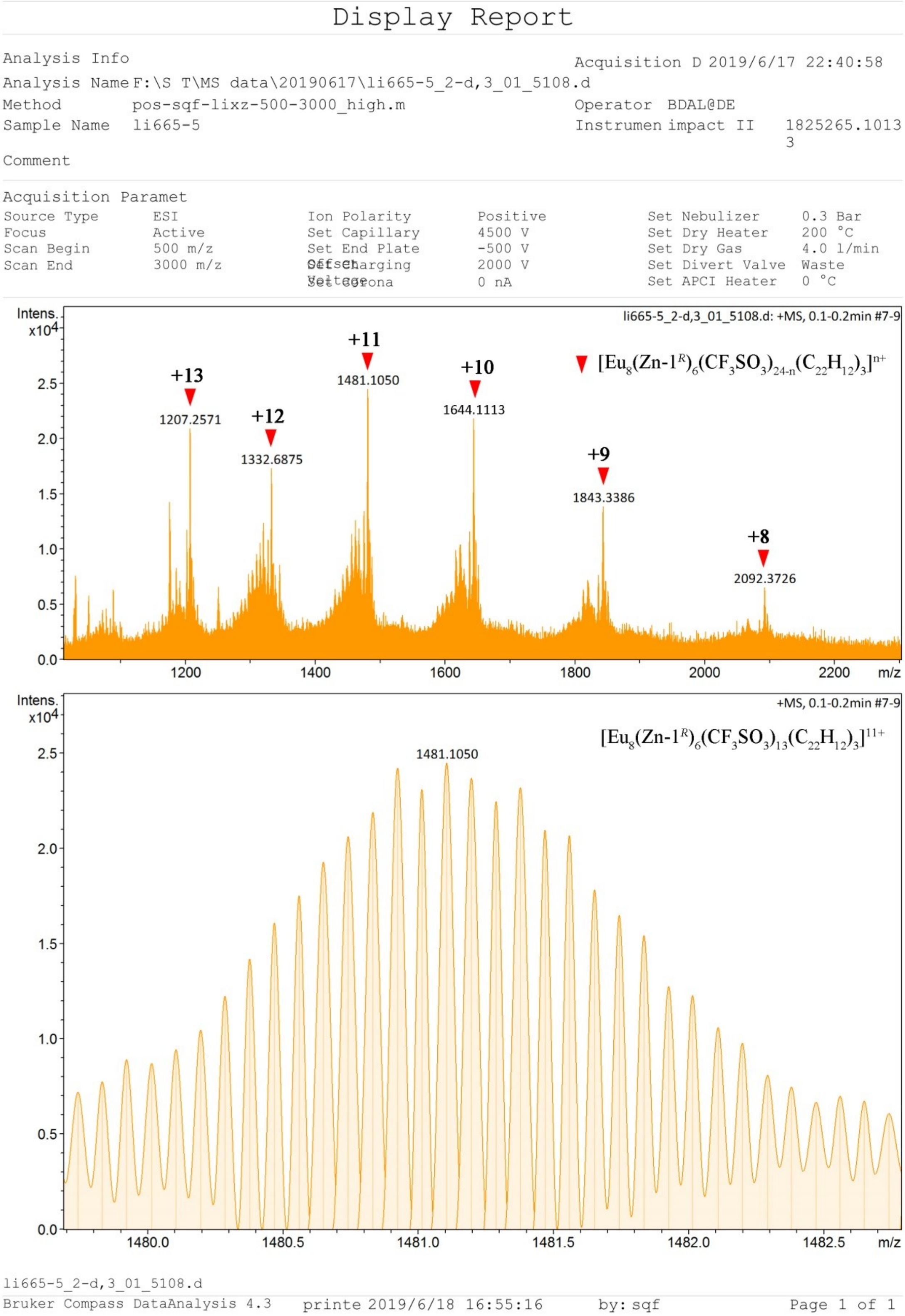


Figure S72. ^{1}H-DOSY NMR spectrum of 1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (log D=-9.523, r = 19.72Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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Comment

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Bruker Compass DataAnalysis 4.3   printe 2019/6/18 16:55:16     by: sqf            Page 1 of 1
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Figure S73. ESI-TOF-MS spectra of 1,12-benzoperylene$_3$@$\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ with insets showing the observed isotopic patterns of the +11 peaks.

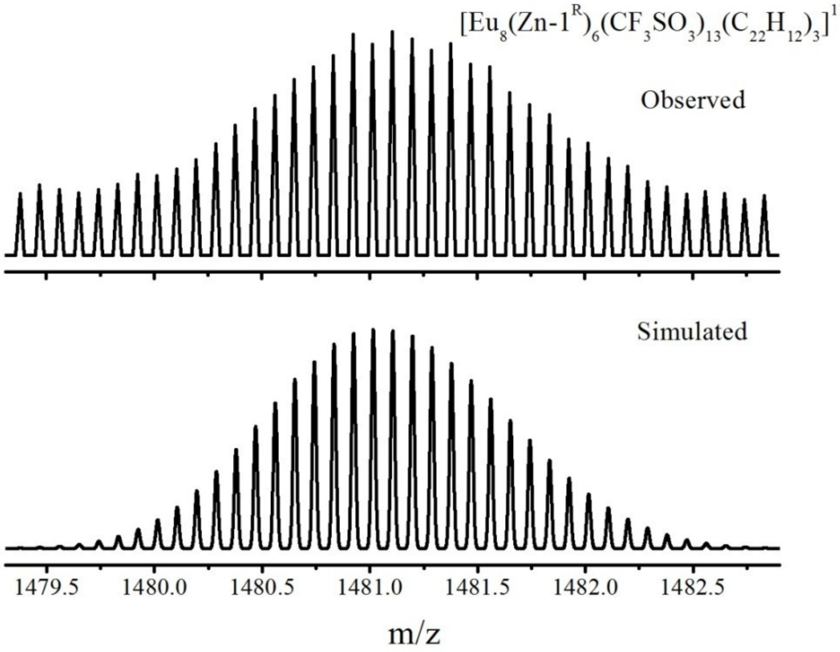


Figure S74. Comparison of the observed and simulated signals of **[**1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{13}$]$^{11+}$**.

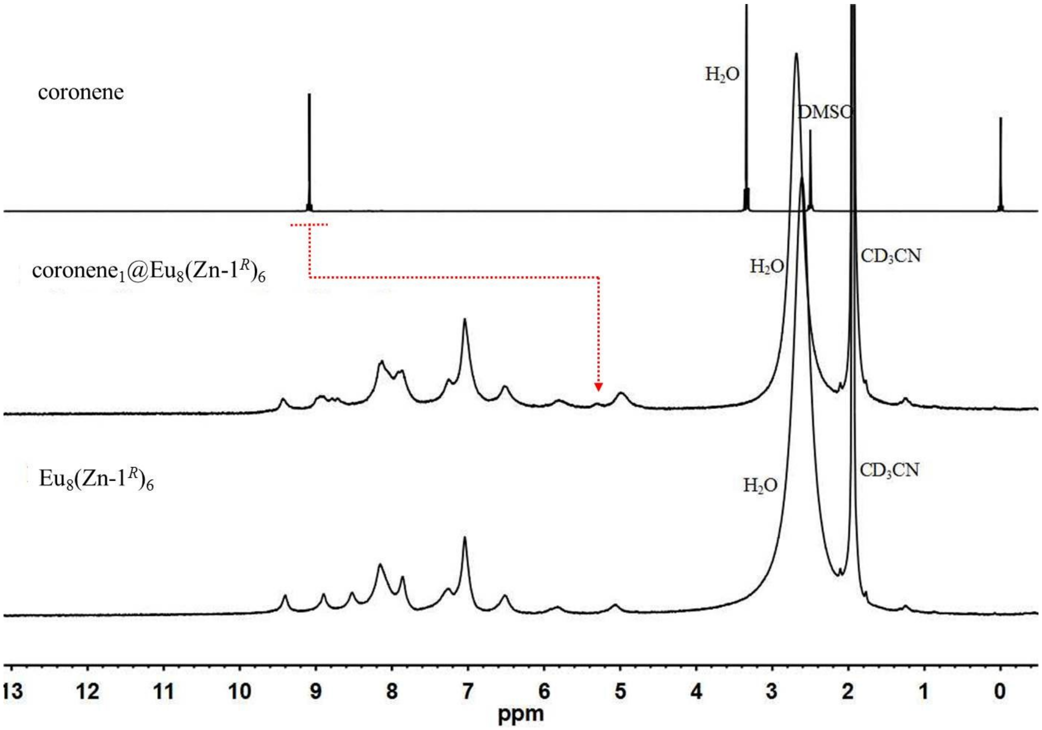


Figure S75. ^{1}H NMR spectra of coronene, coronene$_1$@**Eu$_8$(Zn-1^R)$_6$** and **Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD_3CN, 298K).

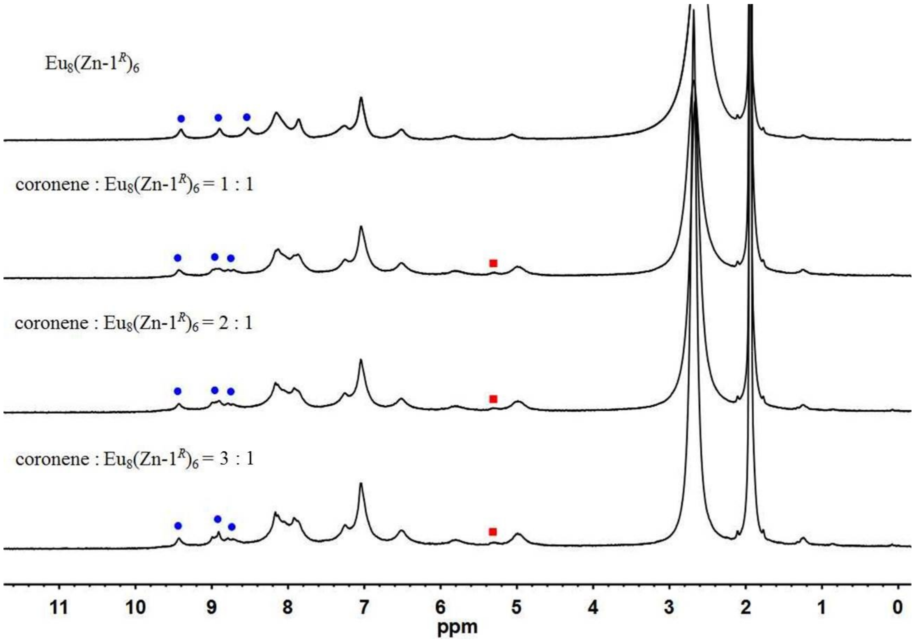
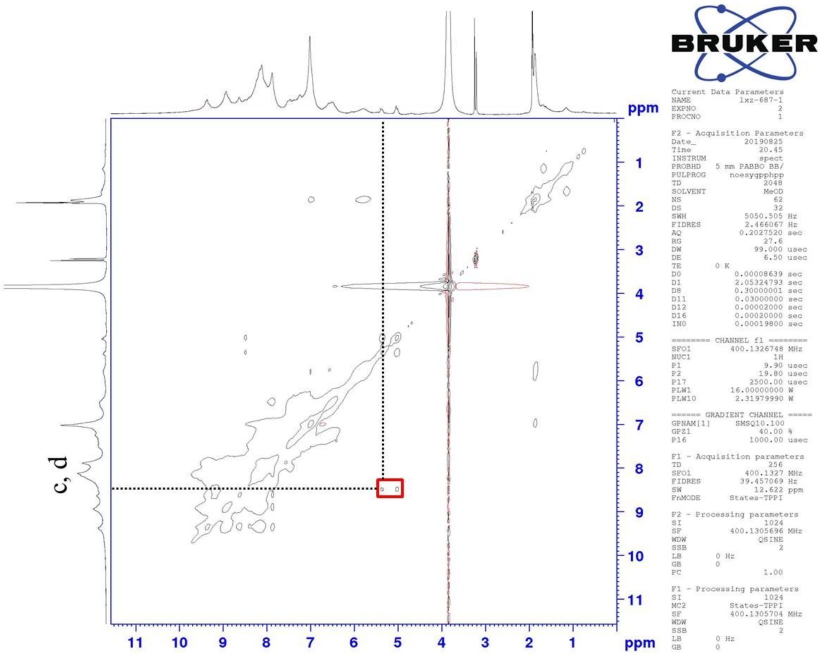


Figure S76. ^{1}H NMR spectra of **$Eu_8(Zn\text{-}1^R)_6$** with different equivalents of coronene (400 MHz, CD_3CN, 298K) (● denotes the signals of **$Eu_8(Zn\text{-}1^R)_6$** that undergo sever broadening during the host-guest complexation process, ■ denotes the signals of the encapsulated guests).



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D0             0.00008639 sec
D1             2.05324793 sec
D8             0.30000001 sec
D11            0.03000000 sec
D12            0.00002000 sec
D16            0.00020000 sec
IN0            0.00019800 sec

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SFO1         400.1326748 MHz
NUC1                   1H
P1                   9.90 usec
P2                  19.80 usec
P17               2500.00 usec
PLW1          16.00000000 W
PLW10          2.31979990 W

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FnMODE        States-TPPI

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LB           0 Hz
GB           0
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F1 - Processing parameters
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WDW                 QSINE
SSB                     2
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GB           0
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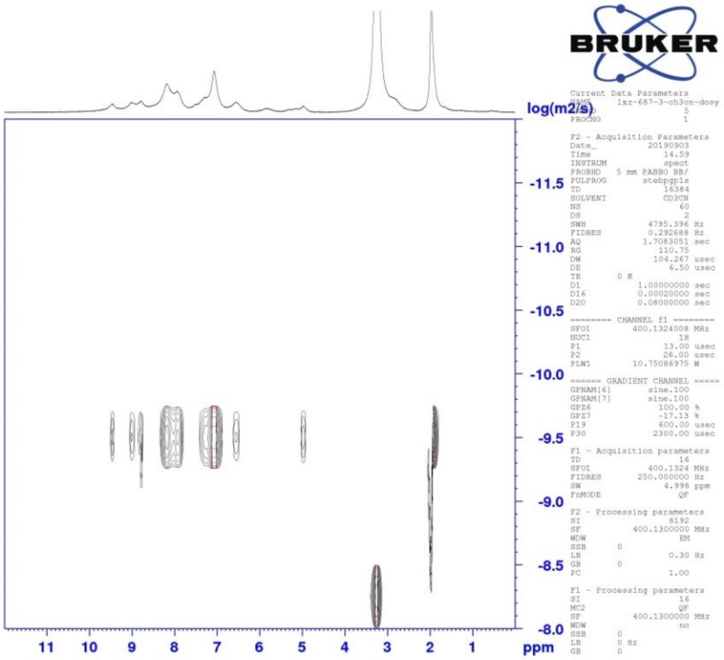
Figure S77. ^{1}H-^{1}H NOESY NMR spectrum of coronene$_1$@**$Eu_8(Zn\text{-}1^R)_6$** (400 MHz, CD_3CN/CD_3OD, 298K).

^{1}H-^{1}H NOESY NMR spectra of the host-guest complexes were tested. But not all the cross-peaks between the signals of the encapsulated guests and the hosts can be observed due to the high molecule weight and the paramagnetism of the lanthanide ions.



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RG                   110.75
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DE                     6.50 usec
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FIDRES          250.000000 Hz
SW                    4.998 ppm
FnMODE                   QF

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WDW                      EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00

F1 - Processing parameters
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MC2                      QF
SF              400.1300000 MHz
WDW                      no
SSB         0
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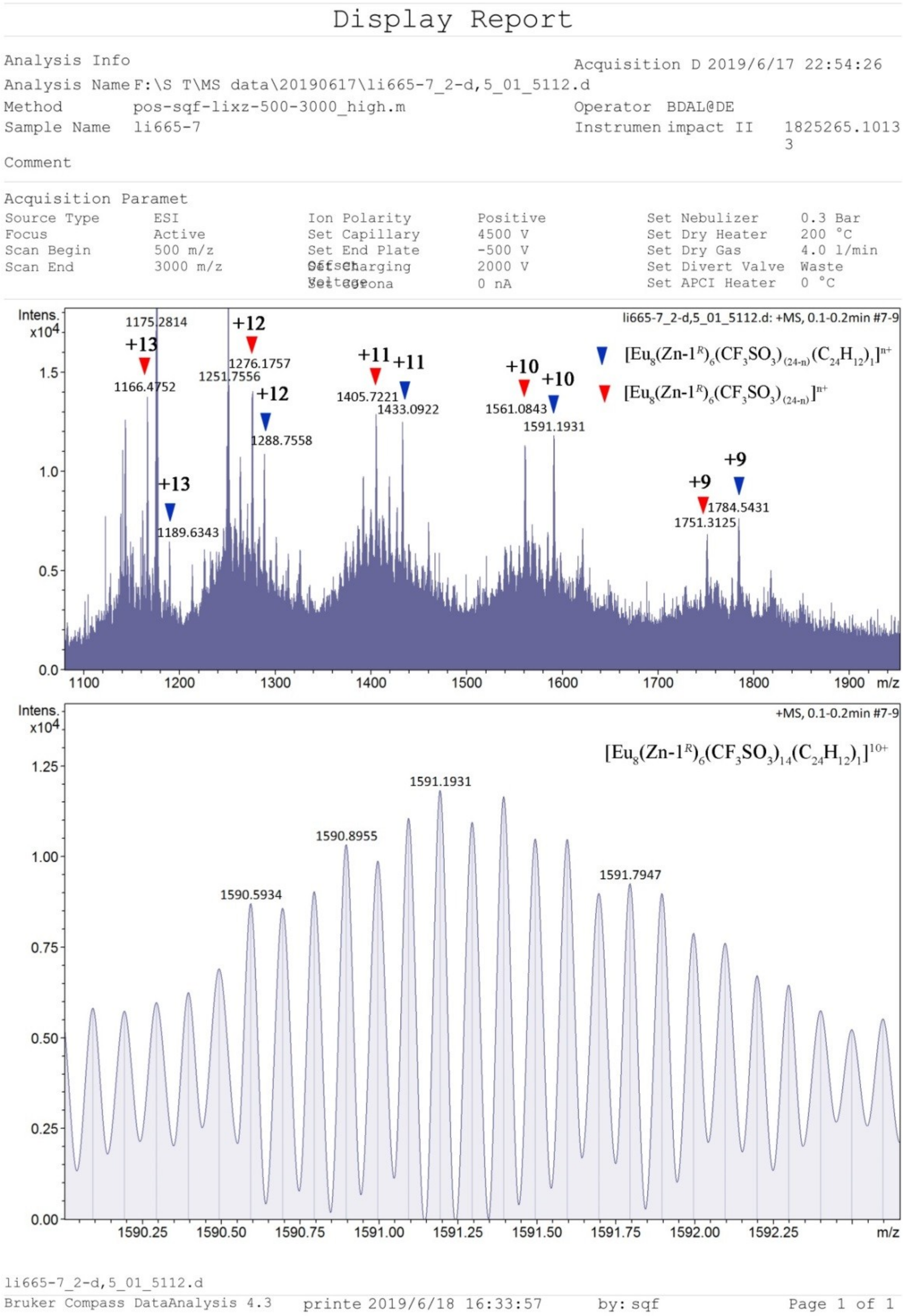
GB          0
```

Figure S78. ^{1}H-DOSY NMR spectrum of coronene$_1$@$\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ (log D=-9.512, r = 19.20Å, 400 MHz, CD_3CN/CD_3OD, 298 K).



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Sample Name li665-7
Comment

Acquisition D 2019/6/17 22:54:26
Operator BDAL@DE
Instrumen impact II 1825265.10133

Acquisition Paramet

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li665-7_2-d,5_01_5112.d
Bruker Compass DataAnalysis 4.3 printe 2019/6/18 16:33:57 by: sqf Page 1 of 1

Figure S79. ESI-TOF-MS spectra of coronene$_1$@$\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ with insets showing the observed isotopic patterns of the +10 peaks.

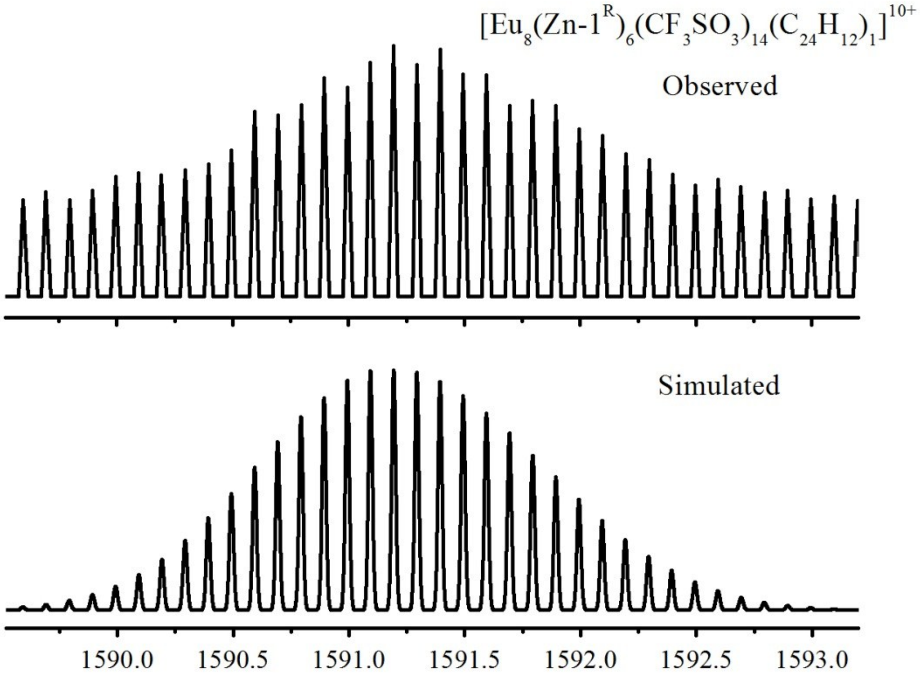


Figure S80. Comparison of the observed and simulated signals of **[**coronene$_1$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$**

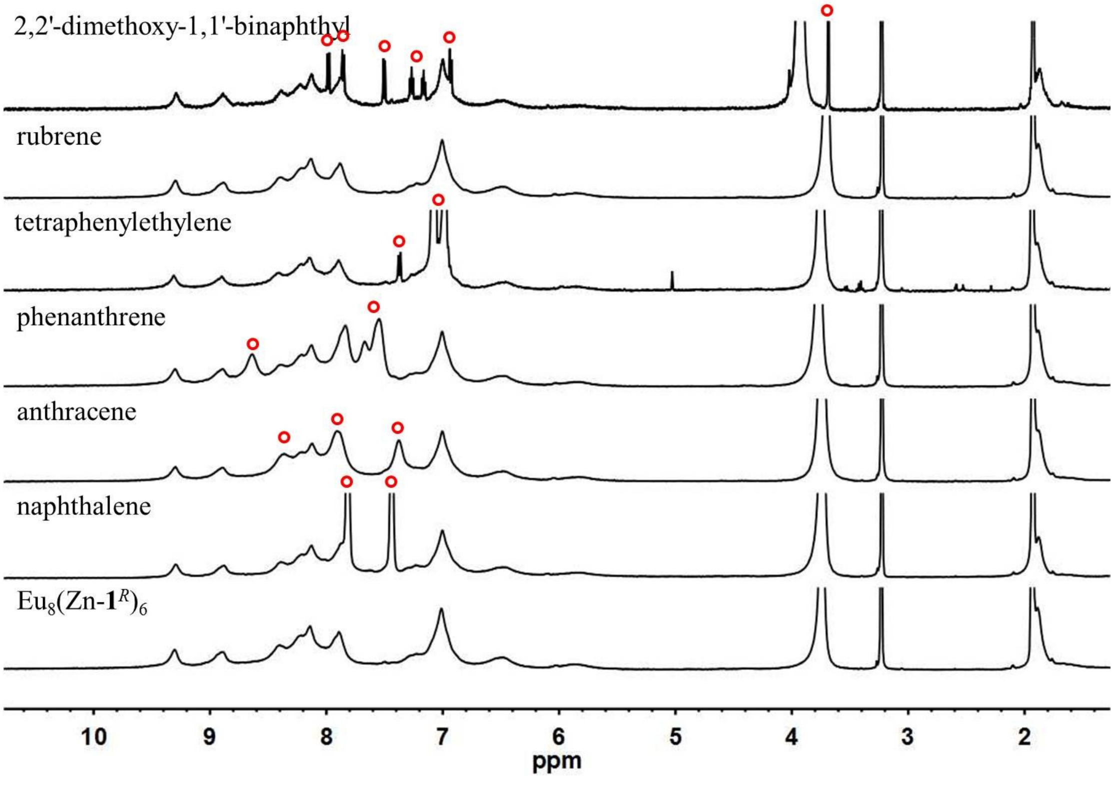


Figure S81. ^{1}H NMR spectra of **Eu$_8$(Zn-1^R)$_6$** (bottom) and **Eu$_8$(Zn-1^R)$_6$** with different guest molecules (400 MHz, CD$_3$CN, 298K, the empty circles denote signals of free guests).

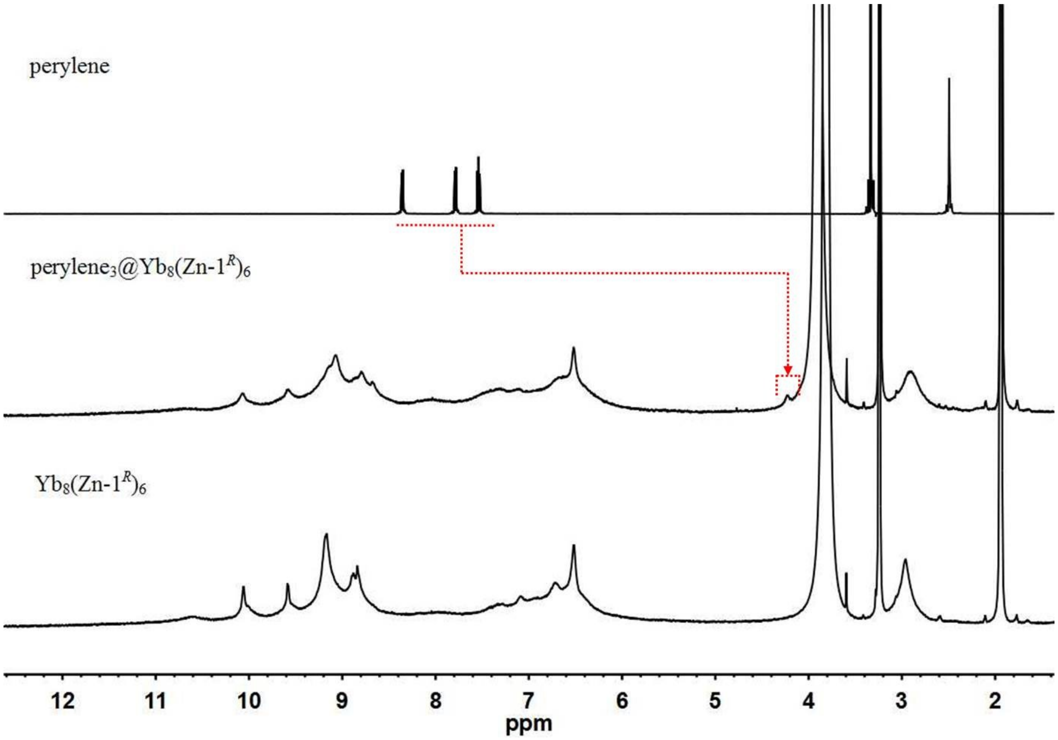
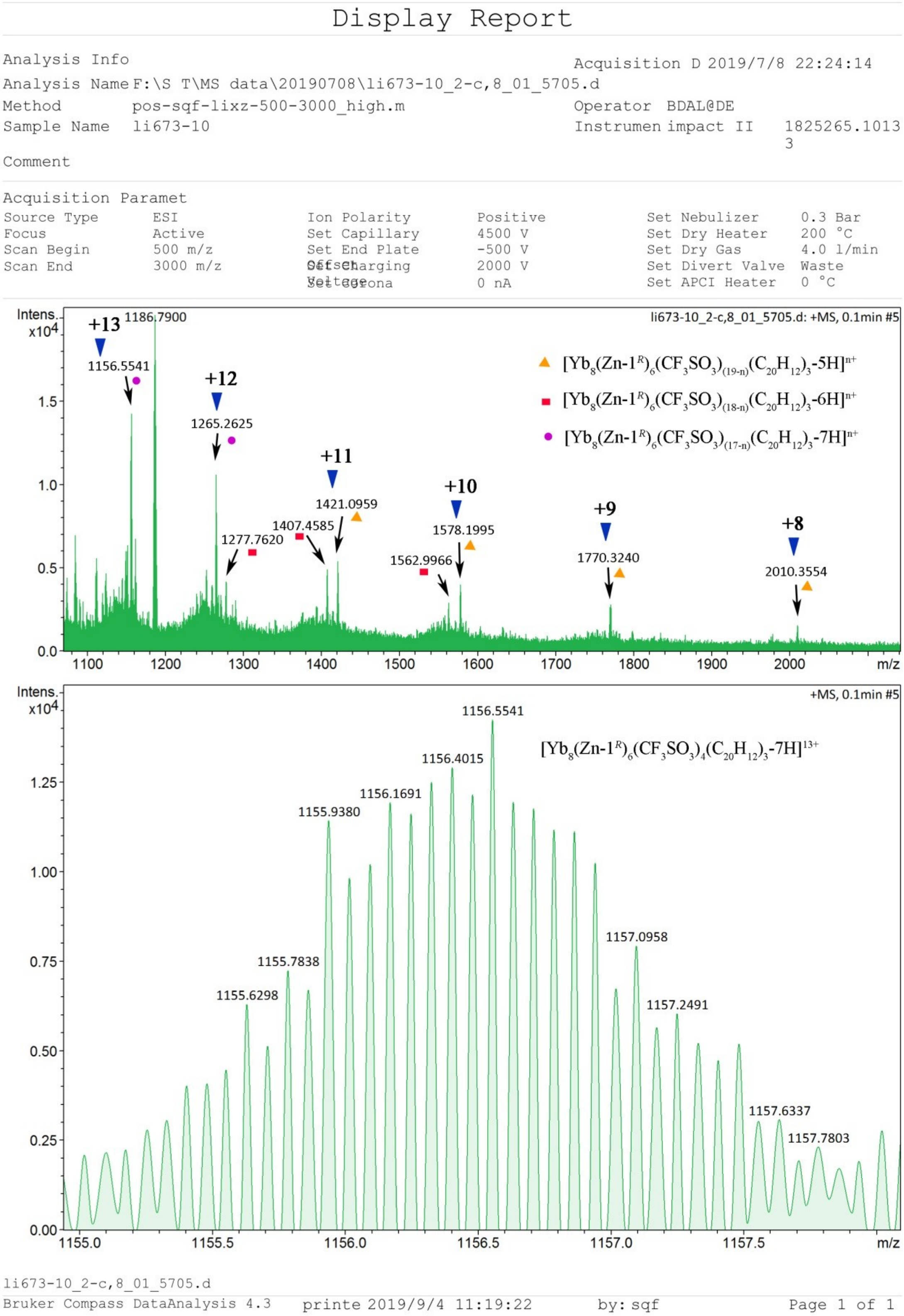


Figure S82. ^{1}H NMR spectra of perylene, perylene$_3$@**Yb$_8$(Zn-1^R)$_6$** and **Yb$_8$(Zn-1^R)$_6$** (400 MHz, CD_3CN/CD_3OD, 298K).



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Operator BDAL@DE

Sample Name li673-10

Instrumen impact II 1825265.10133

Comment

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li673-10_2-c,8_01_5705.d

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Figure S83. ESI-TOF-MS spectra of perylene$_3$@$\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6}$ with insets showing the observed isotopic patterns of the +13 peaks.

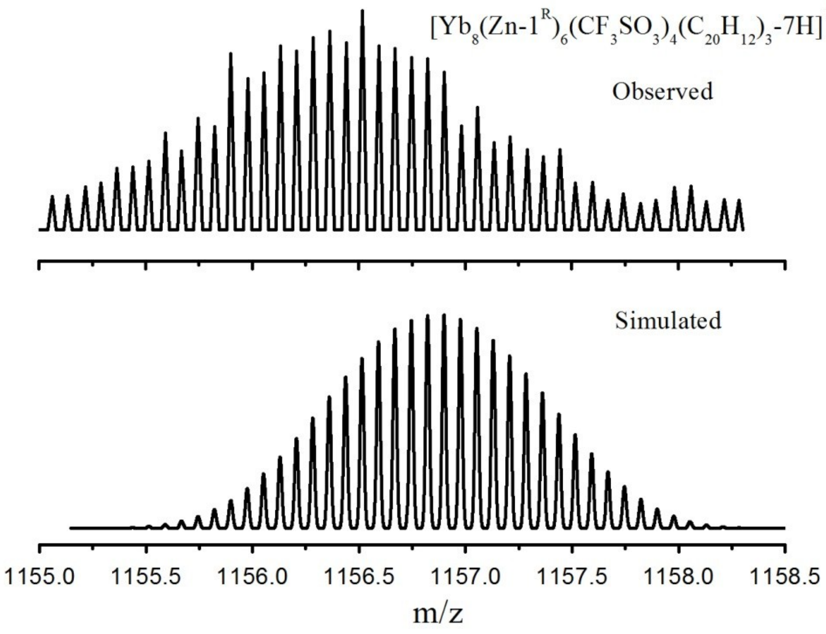


Figure S84. Comparison of the observed and simulated signals of [perylene$_3$@$\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6(OTf)_4\text{-}7H]^{13+}}$. The molecular weight of perylene$_3$@$\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6}$ complex is too large to simulate using Bruker Data Analysis software (Version 4.3) and Bruker Isotope Pattern software. So the simulations were performed with the Thermo Xcalibur Qual Browser software (Thermo Foundation 2.0).

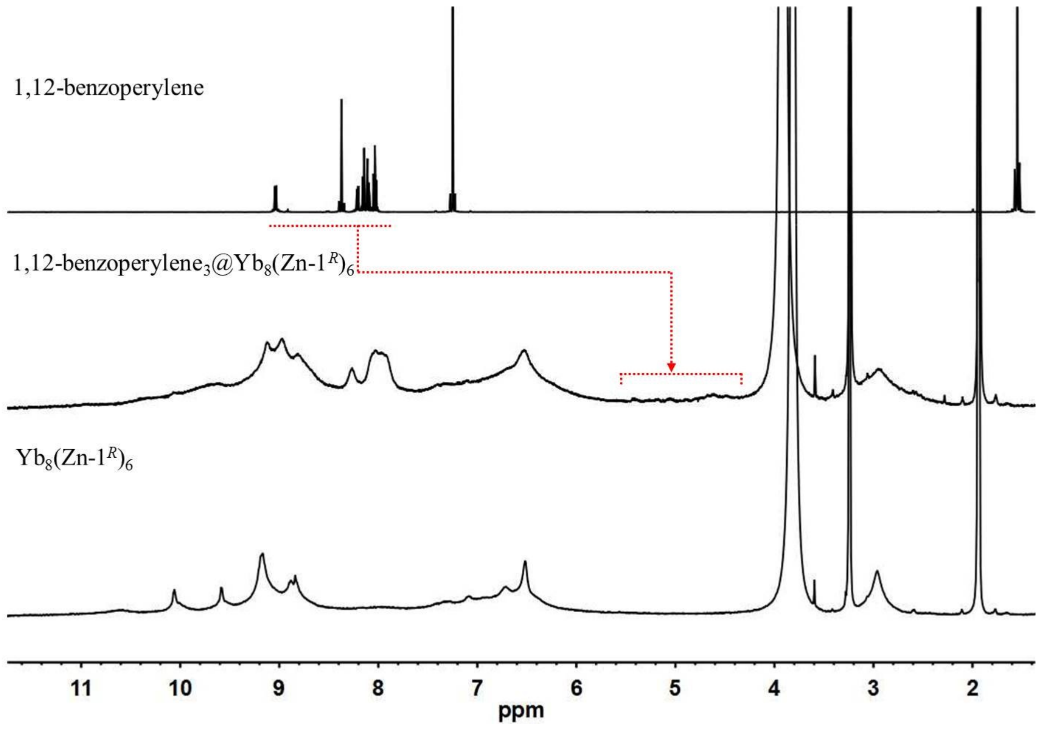
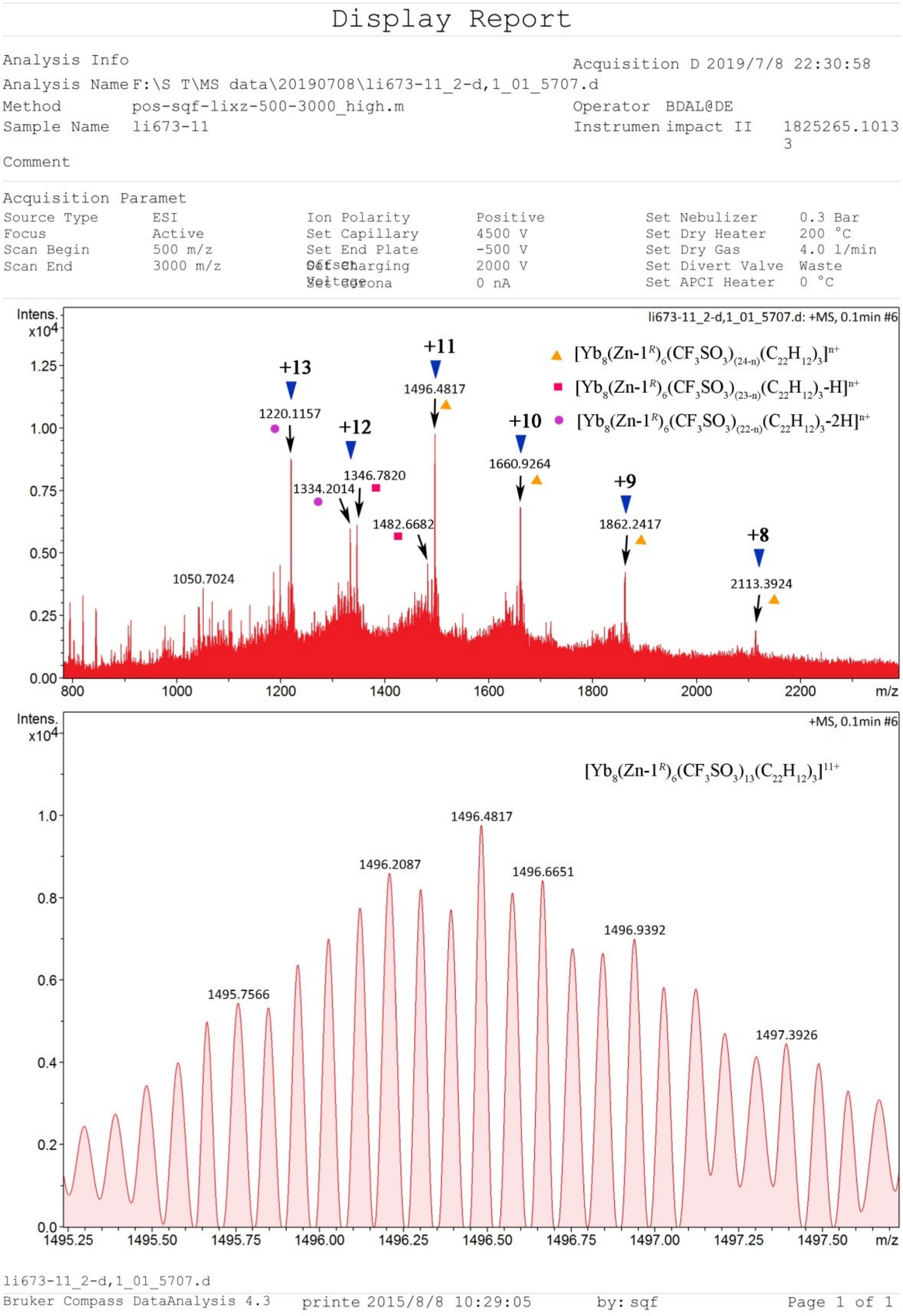


Figure S85. ^{1}H NMR spectra of 1,12-benzoperylene, 1,12-benzoperylene$_3$@$\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6}$ and $\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6}$ (400 MHz, CD_3CN/CD_3OD, 298K).



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Comment

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li673-11_2-d,1_01_5707.d
Bruker Compass DataAnalysis 4.3    printe 2015/8/8 10:29:05    by: sqf    Page 1 of 1
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Figure S86. ESI-TOF-MS spectra of 1,12-benzoperylene$_3$@**Yb$_8$(Zn-1^R)$_6$** with insets showing the observed isotopic patterns of the +11 peaks.

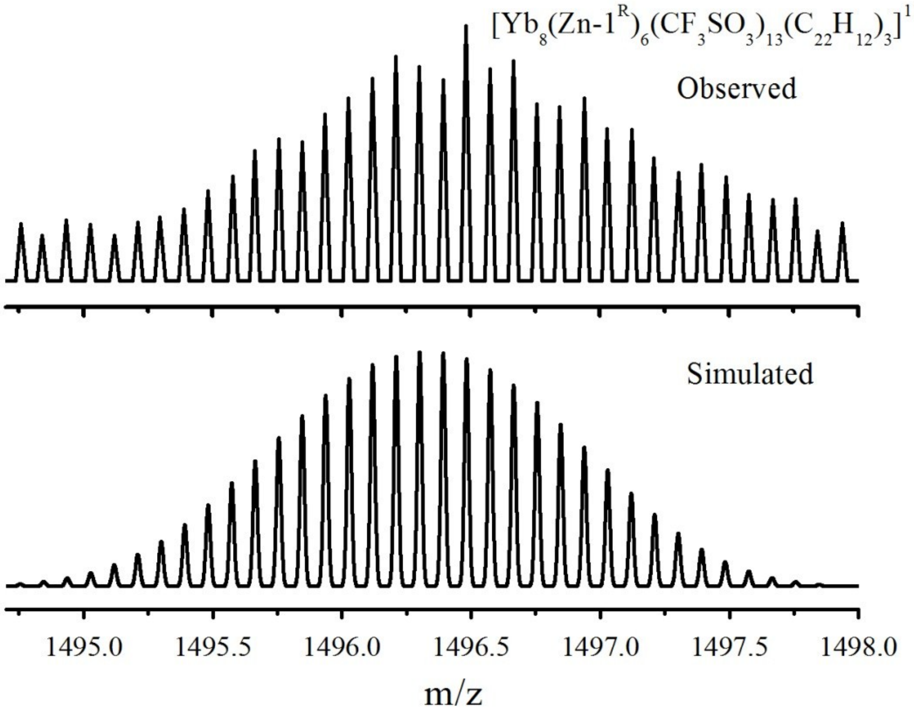


Figure S87. Comparison of the observed and simulated signals of **[**1,12-benzoperylene$_3$@**Yb$_8$(Zn-1^R)$_6$(OTf)$_{13}$]$^{11+}$**.

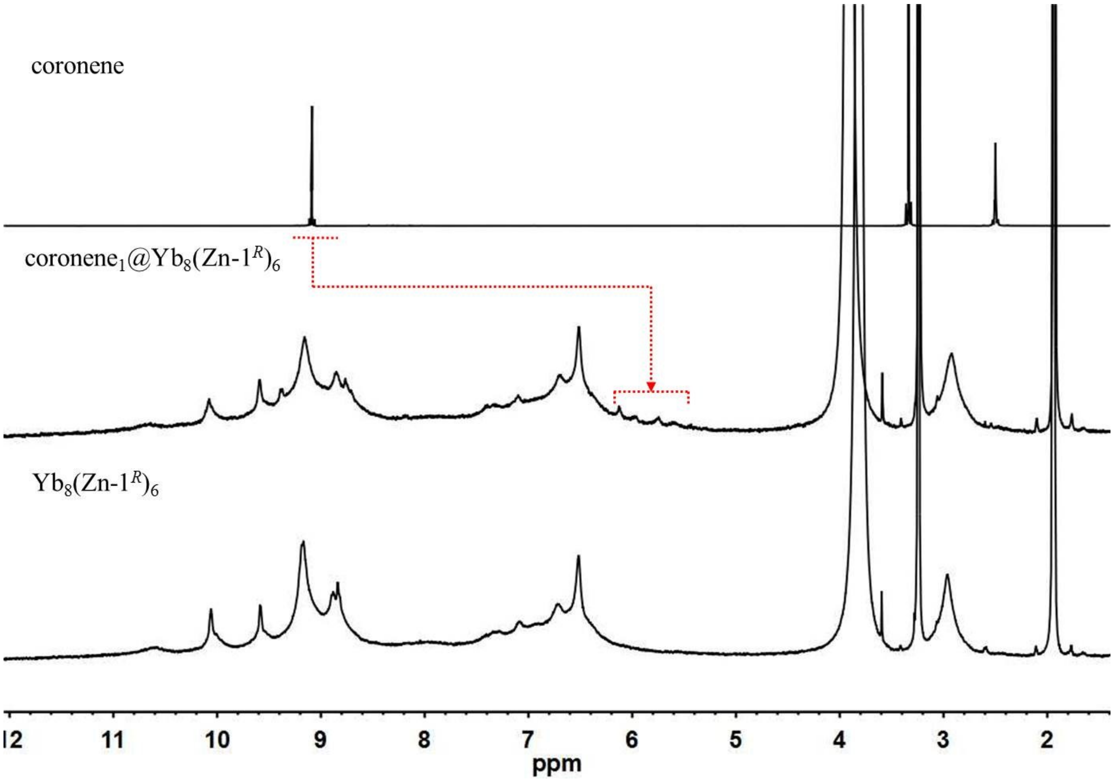
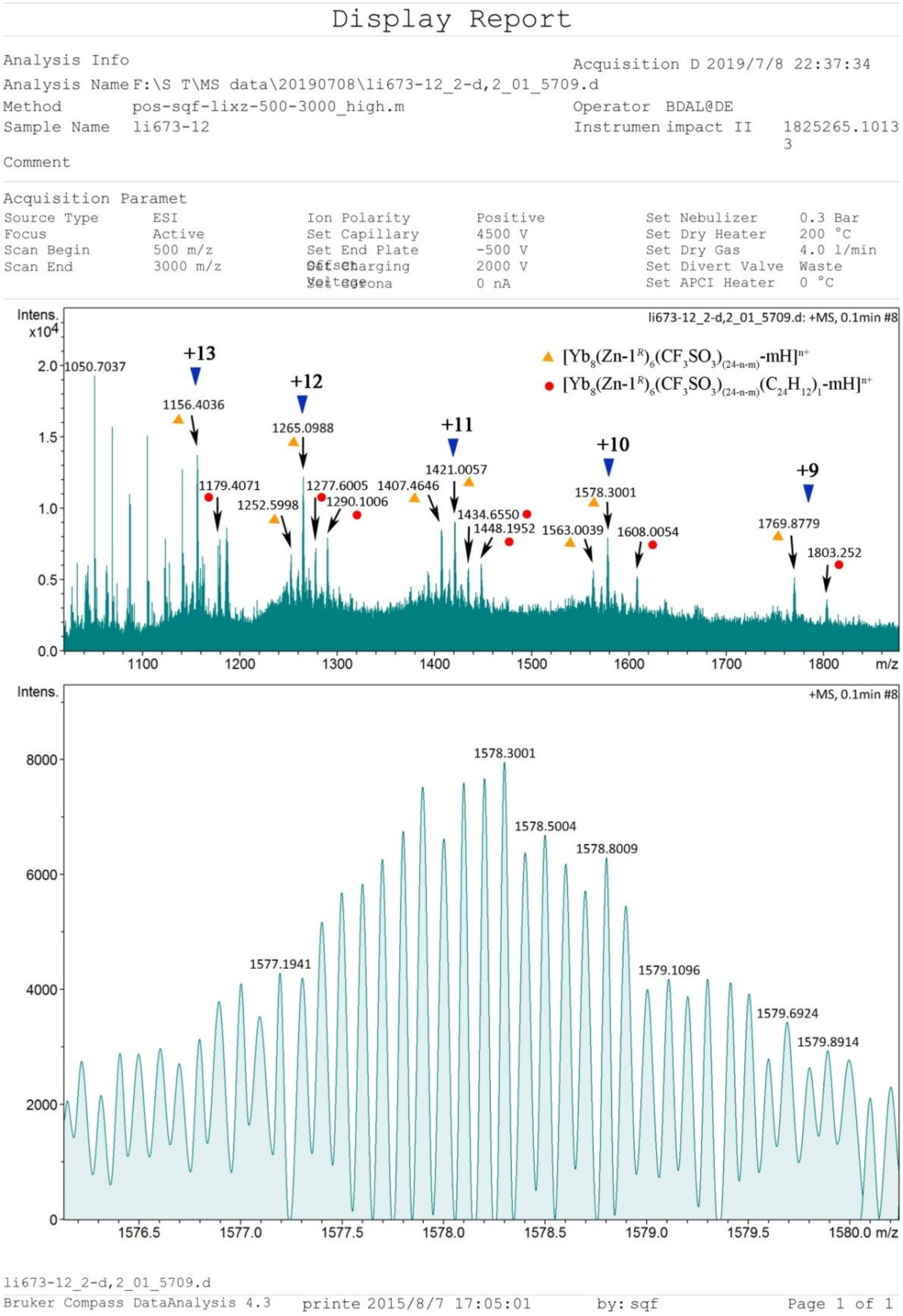


Figure S88. ^{1}H NMR spectra of coronene, coronene$_1$@**Yb$_8$(Zn-1^R)$_6$** and **Yb$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K).



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Comment

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li673-12_2-d,2_01_5709.d
Bruker Compass DataAnalysis 4.3    printe 2015/8/7 17:05:01      by: sqf          Page 1 of 1
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Figure S89. ESI-TOF-MS spectra of **$Yb_8(Zn\text{-}1^R)_6$** and coronene$_1$@**$Yb_8(Zn\text{-}1^R)_6$** with insets showing the observed isotopic patterns of the +10 peaks.

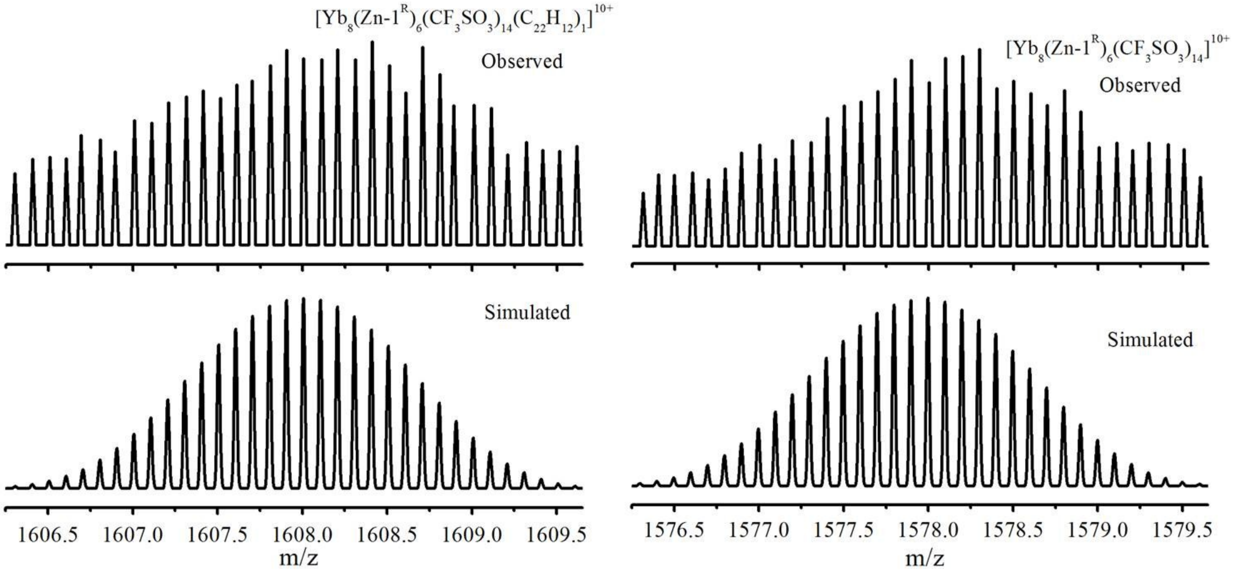


Figure S90. Comparison of the observed and simulated signals of [Coronene$_1$@**Yb$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$** and **[Yb$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$**.

Valence	Molecular formula	Observed	Simulated
+9	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{15}$	1769.8779	1769.8811
+9	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{15}(C_{24}H_{12})_1$	1803.2252	1803.2250
+10	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{14}$	1578.3001	1577.9978
+10	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{13}$-H	1563.0039	1563.0018
+10	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{14}(C_{24}H_{12})_1$	1608.0054	1608.0072
+11	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{13}$	1421.0057	1421.0023
+11	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{12}$-H	1407.4646	1407.2786
+11	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{13}(C_{24}H_{12})_1$	1448.1952	1448.1926
+11	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{12}(C_{24}H_{12})_1$-H	1434.6550	1434.6509
+12	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{10}$-2H	1265.0988	1265.0961
+12	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_9$-3H	1252.5998	1252.5994
+12	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_{10}(C_{24}H_{12})_1$-2H	1290.1006	1290.1039
+12	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_9(C_{24}H_{12})_1$-3H	1277.6005	1277.6073
+13	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_9$-2H	1156.4036	1156.3231
+13	$Yb_8(C_{128}H_{96}N_{16}O_8Zn)_6(CF_3SO_3)_9(C_{24}H_{12})_1$-2H	1179.4071	1179.4073

Figure S91. Comparison of the observed and simulated signals in the ESI-TOF-MS spectra of coronene$_1$@**Yb$_8$(Zn-1^R)$_6$**.

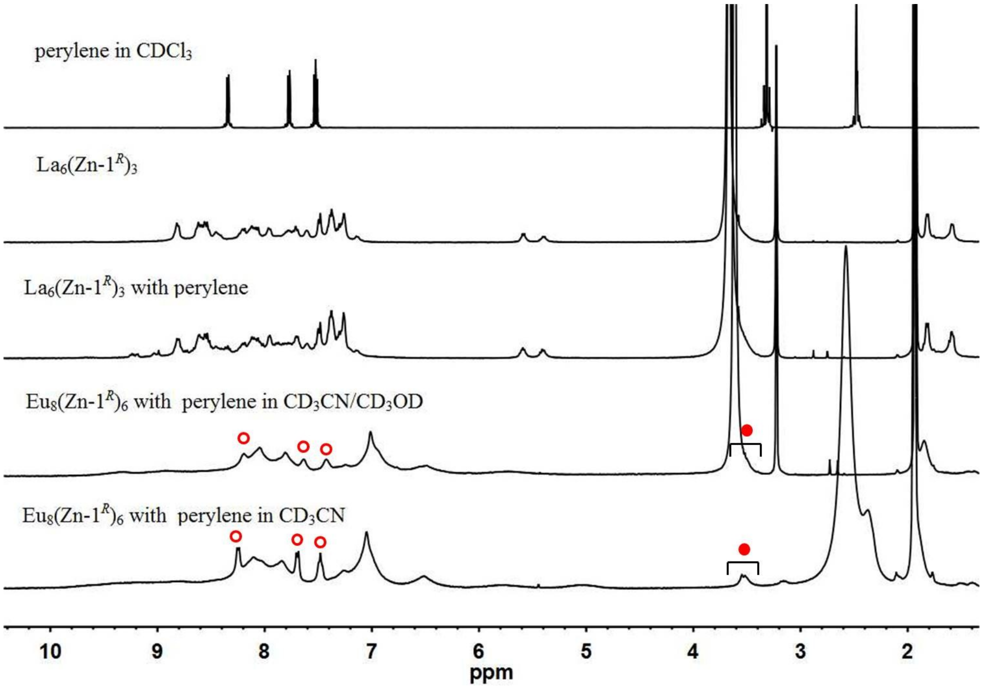
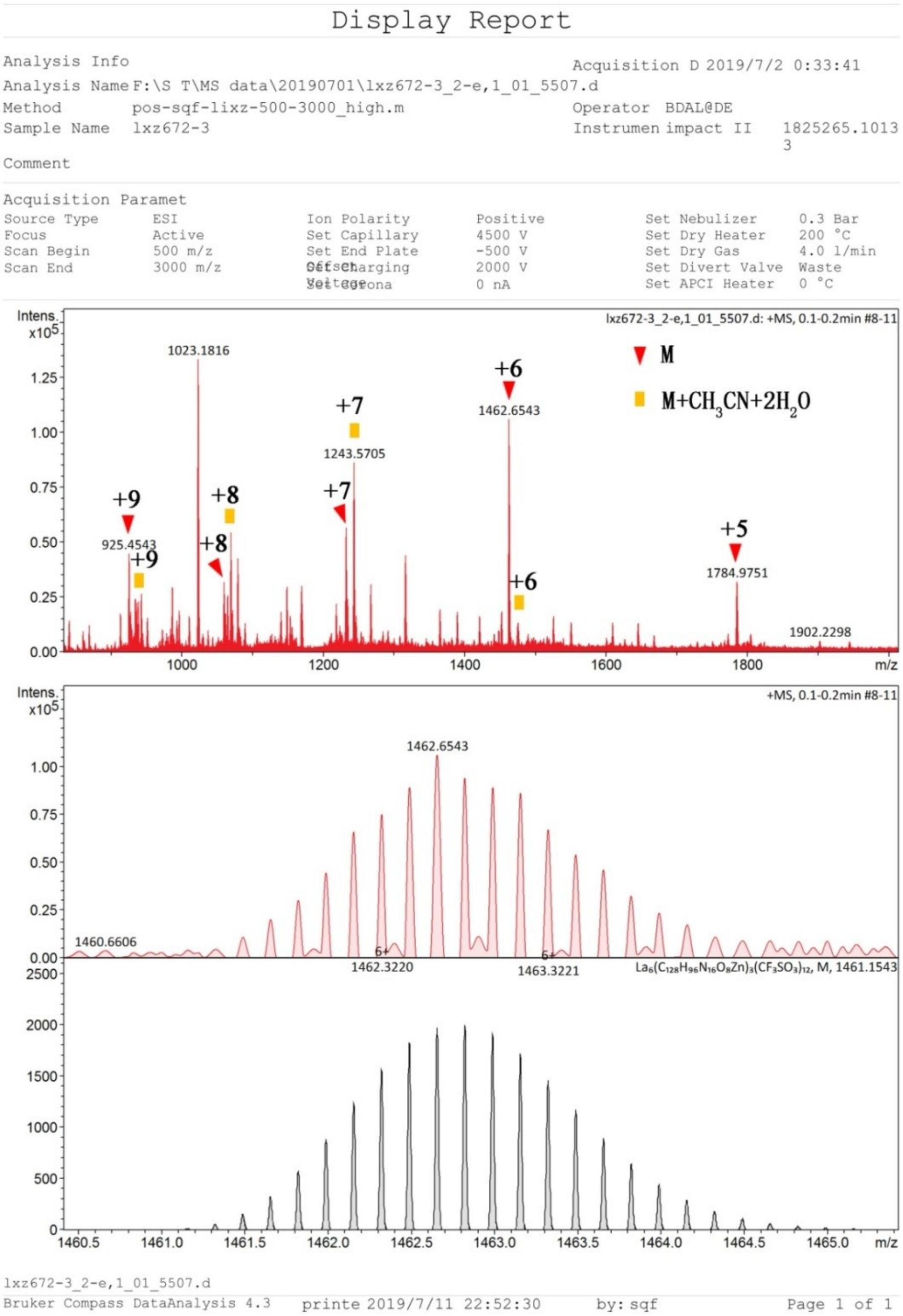


Figure S92. ^{1}H NMR spectra of of the Eu^{III} ion induced structural transformation and guest encapsulation, from top to bottom: perylene (CDCl$_3$), **La$_6$(Zn-1^R)$_3$**, **La$_6$(Zn-1^R)$_3$** with perylene and perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K, the solid and empty circle denote encapsulated and free guests).

The preparation of **La$_6$(Zn-1^R)$_3$**, **Eu$_8$(Zn-1^R)$_6$** and the host-guest complexation of **Eu$_8$(Zn-1^R)$_6$** with perylene were conducted in a mixture solution of CD$_3$CN/CD$_3$OD (2/1, v/v). Considering the overlap between the signals of encapsulated perylene and CD$_3$OD, the host-guest complexes were dried under reduced pressure and redissolved in CD$_3$CN for ^{1}H NMR characterization. The host-guest complexation of **Eu$_8$(Zn-1^R)$_6$** with perylene molecules was further confirmed through ESI-TOF-MS analysis.



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Instrumen impact II 1825265.10133
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lxz672-3_2-e,1_01_5507.d
Bruker Compass DataAnalysis 4.3 printe 2019/7/11 22:52:30 by: sqf Page 1 of 1

Figure S93. ESI-TOF-MS spectra of **La$_6$(Zn-1^R)$_3$(OTf)$_{18}$** in the existence of perylene with insets showing the observed and simulated isotopic patterns of the +6 peaks.

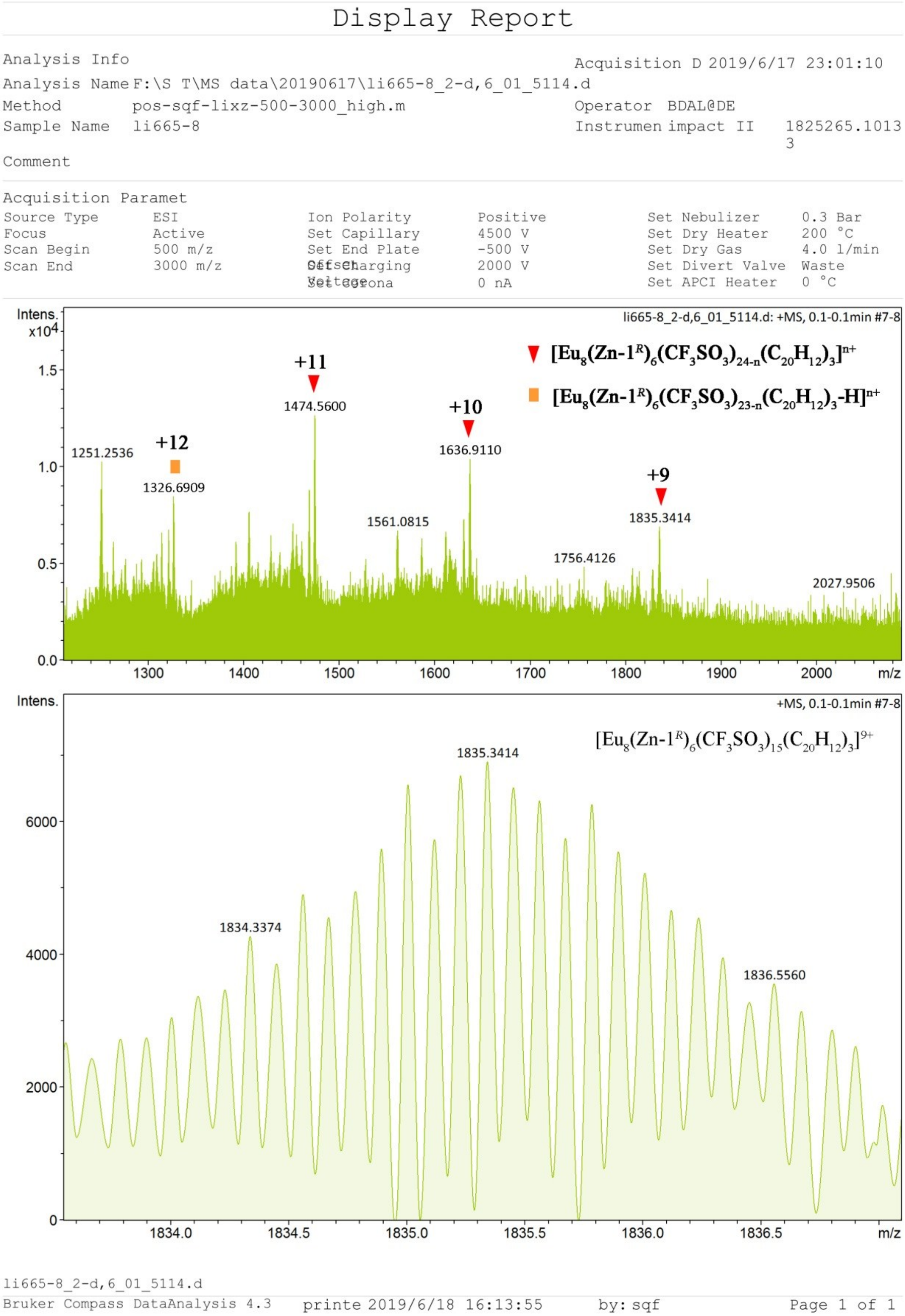

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Figure S94. ESI-TOF-MS spectra of perylene$_3$@**Eu$_8$(Zn-1^R)$_6$** with insets showing the observed isotopic patterns of the +10 peaks.

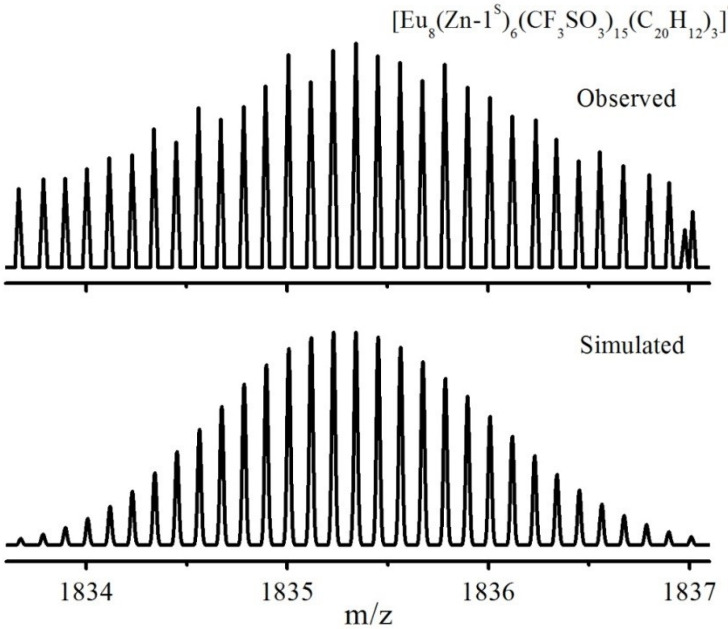

Figure S95. Comparison of the observed and simulated signals of **[**perylene$_3$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{15}$]$^{9+}$**.

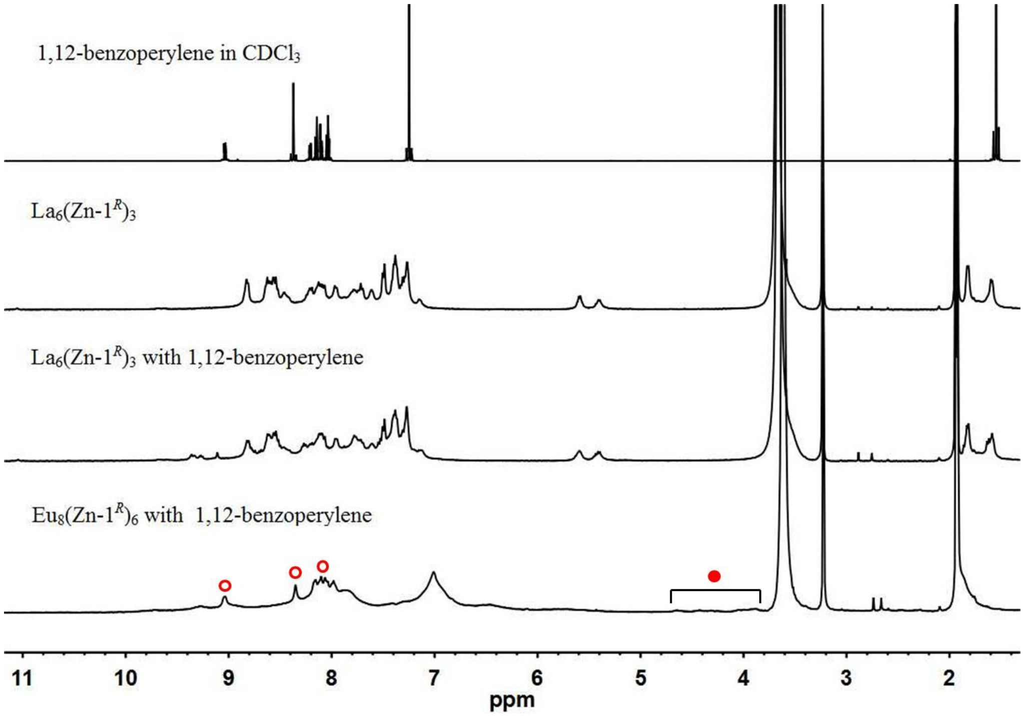

Figure S96. ^{1}H NMR spectra of of the Eu^{III} ion induced structural transformation and guest encapsulation, from top to bottom: 1,12-benzoperylene (CDCl$_3$), **La$_6$(Zn-1^R)$_3$**, **La$_6$(Zn-1^R)$_3$** with 1,12-benzoperylene and 1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD$_3$CN/CD$_3$OD, 298K, the solid and empty circle denote encapsulated and free guests).

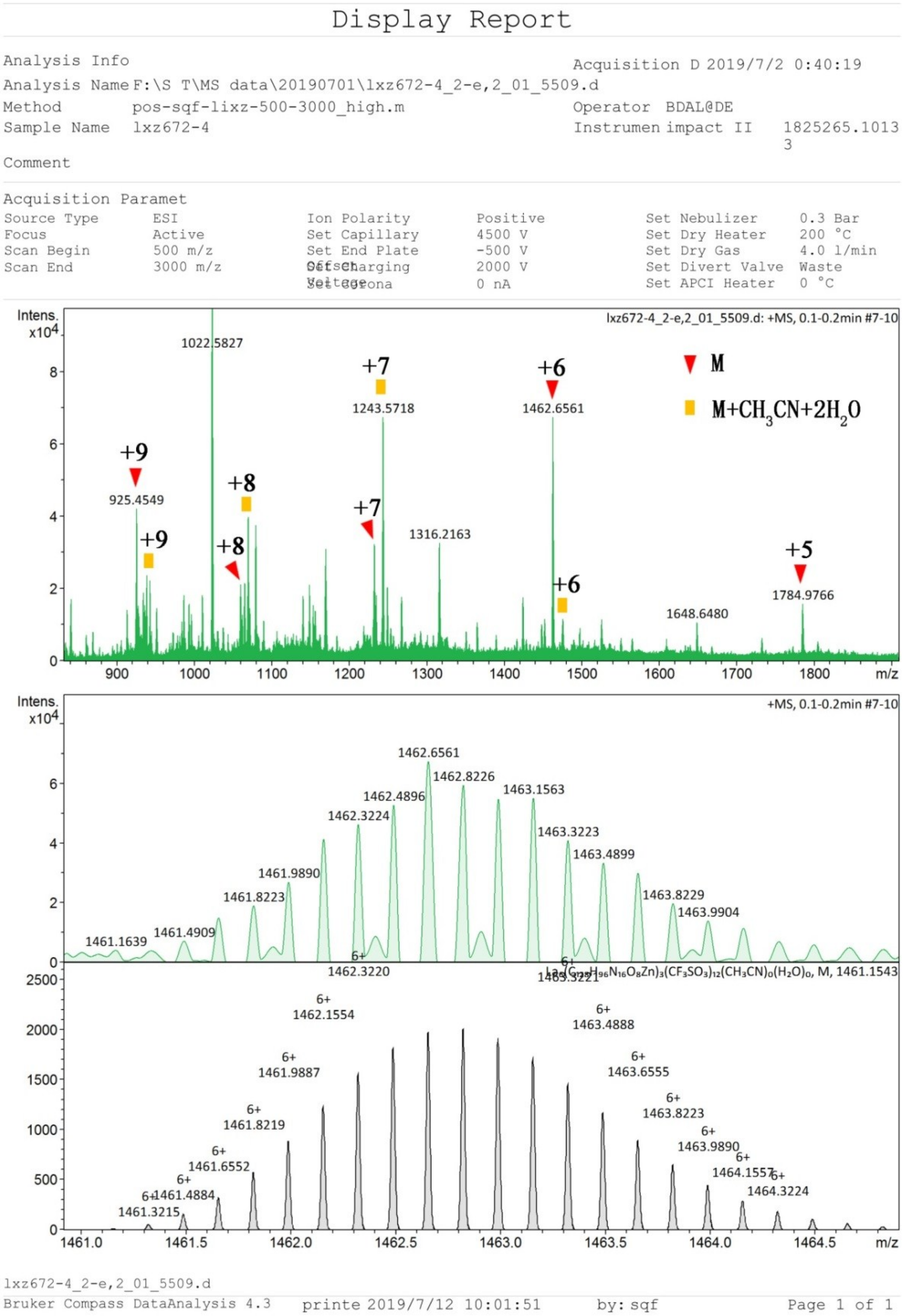

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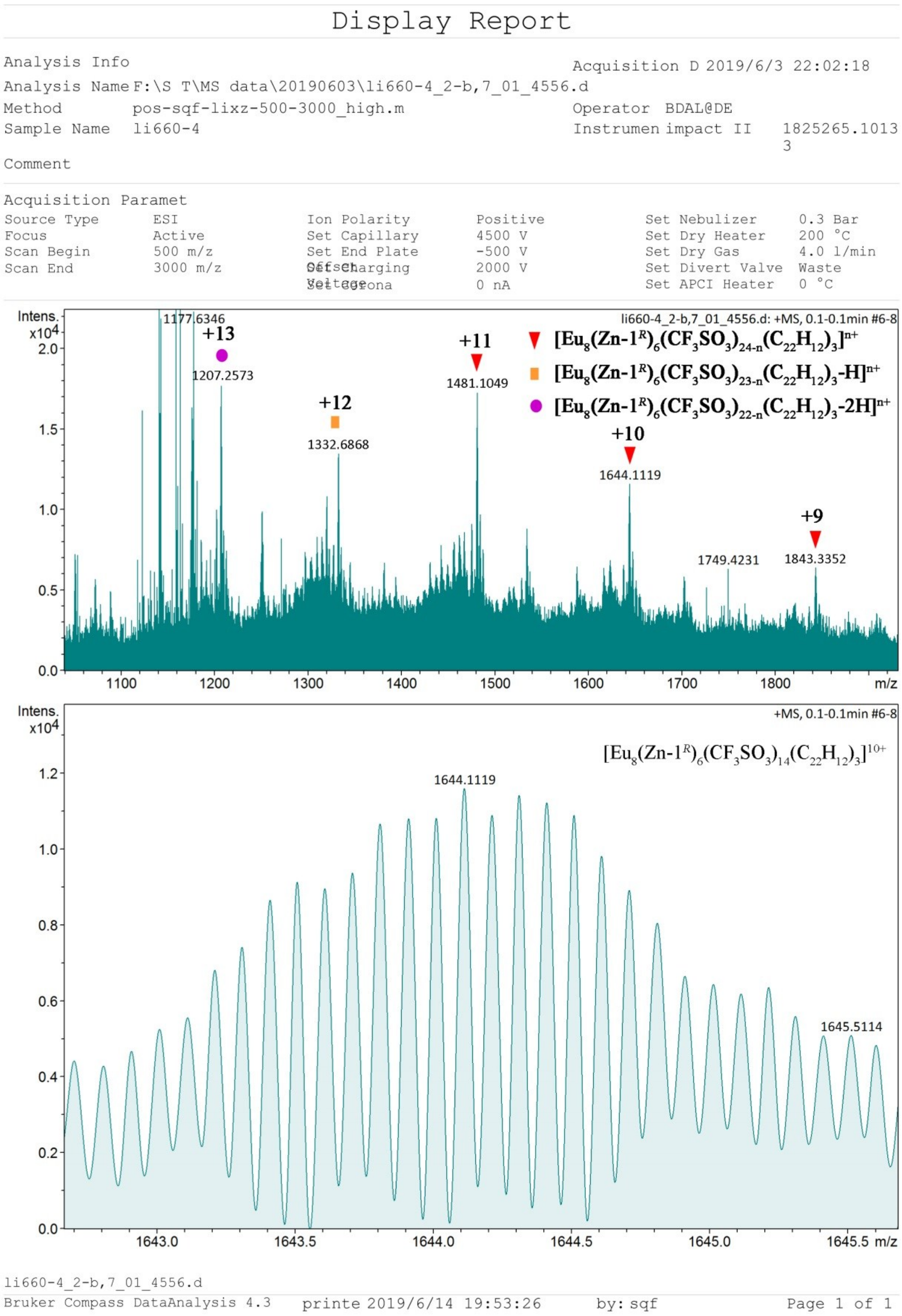
Figure S97. ESI-TOF-MS spectra of $\mathbf{La_6(Zn\text{-}1^{\mathit{R}})_3(OTf)_{18}}$ in the existence of 1,12-benzoperylene with insets showing the observed and simulated isotopic patterns of the +6 peaks.



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li660-4_2-b,7_01_4556.d

Bruker Compass DataAnalysis 4.3 printe 2019/6/14 19:53:26 by: sqf Page 1 of 1

Figure S98. ESI-TOF-MS spectra of 1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$** with insets showing the observed isotopic patterns of the +10 peaks.

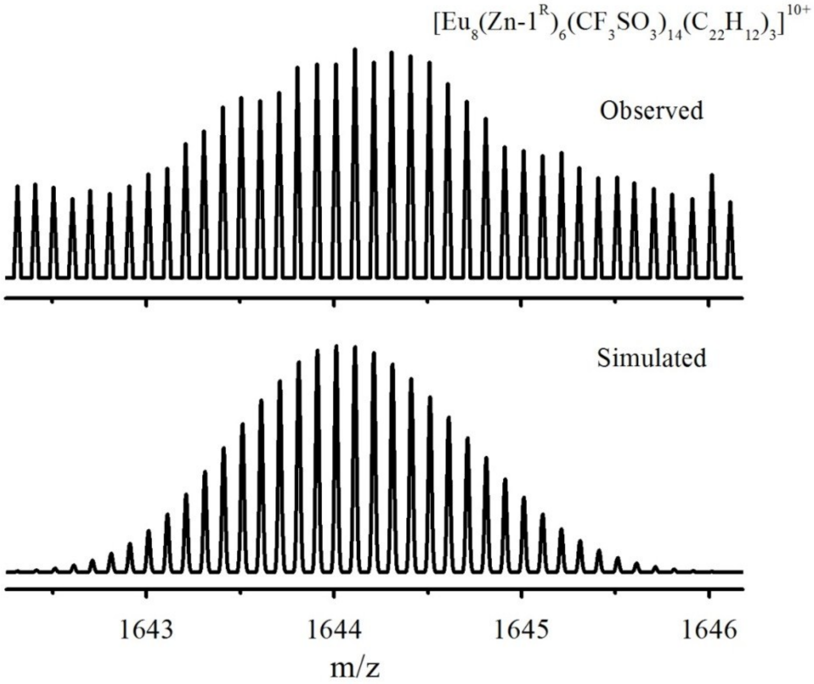


Figure S99. Comparison of the observed and simulated signals of **[**1,12-benzoperylene$_3$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{14}$]$^{10+}$**.

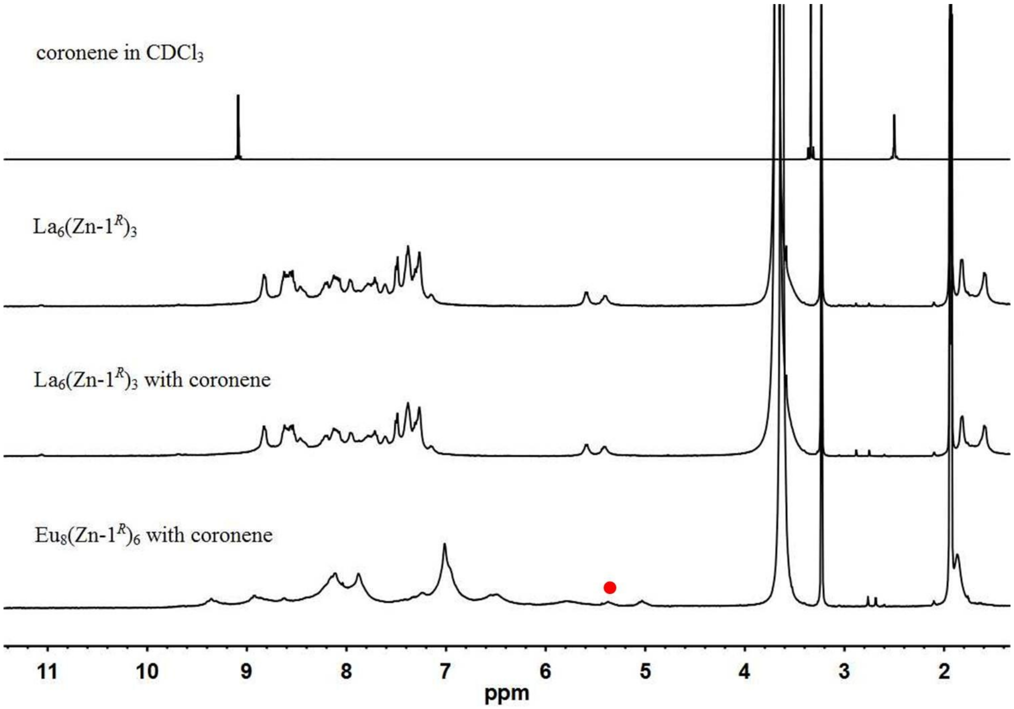
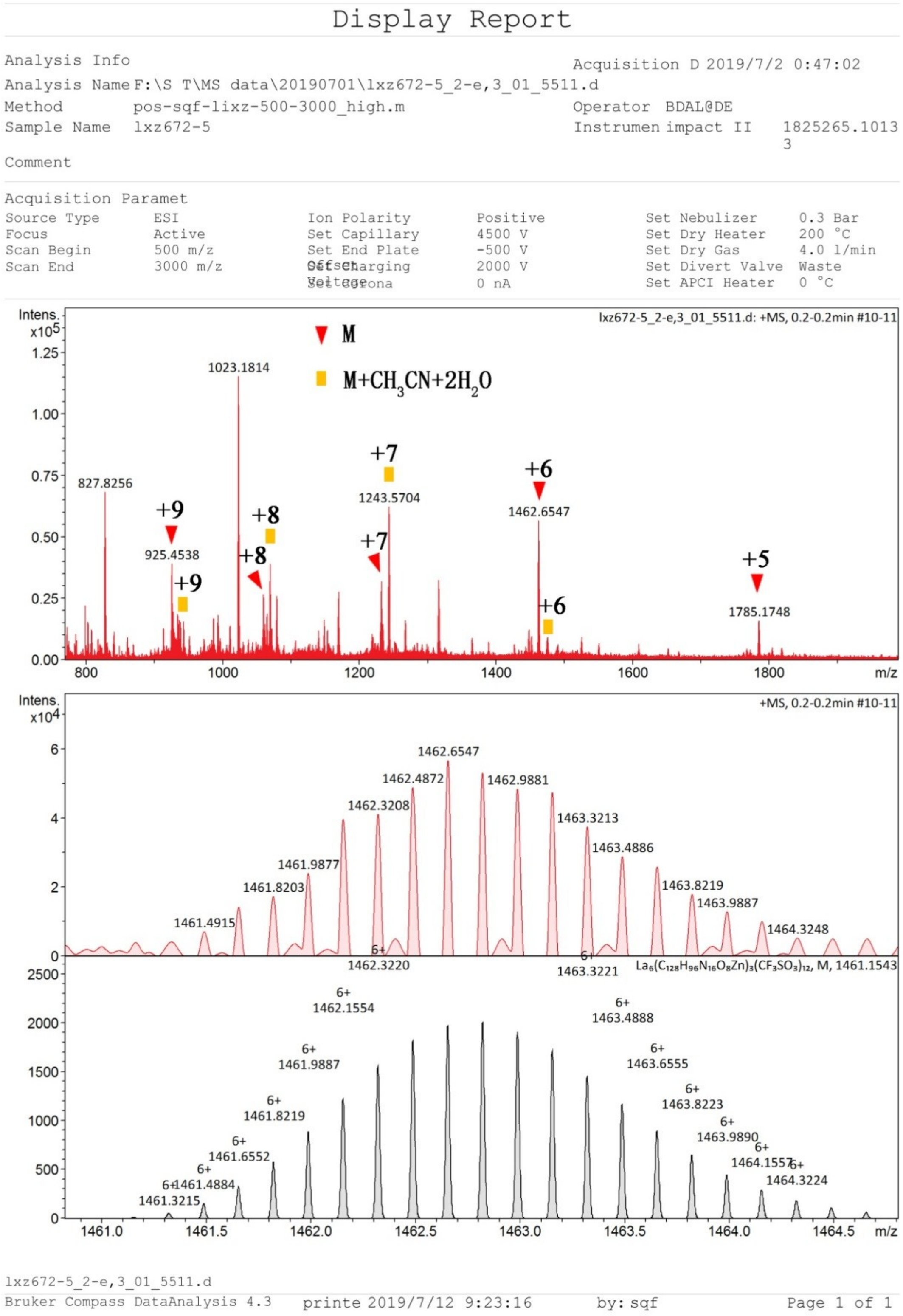


Figure S100. ^{1}H NMR spectra of of the Eu^{III} ion induced structural transformation and guest encapsulation, from top to bottom: coronene ($CDCl_3$), **La$_6$(Zn-1^R)$_3$**, **La$_6$(Zn-1^R)$_3$** with coronene and coronene$_1$@**Eu$_8$(Zn-1^R)$_6$** (400 MHz, CD_3CN/CD_3OD, 298K, the solid circle denotes encapsulated guests).



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Method        pos-sqf-lixz-500-3000_high.m        Operator  BDAL@DE
Sample Name   lxz672-5                            Instrumen impact II   1825265.1013
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Comment

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                          Offset
Scan End       3000 m/z   Set Charging     2000 V       Set Divert Valve  Waste
                          Voltage
                          Set Corona       0 nA         Set APCI Heater   0 °C
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lxz672-5_2-e,3_01_5511.d
Bruker Compass DataAnalysis 4.3   printe 2019/7/12 9:23:16   by: sqf   Page 1 of 1
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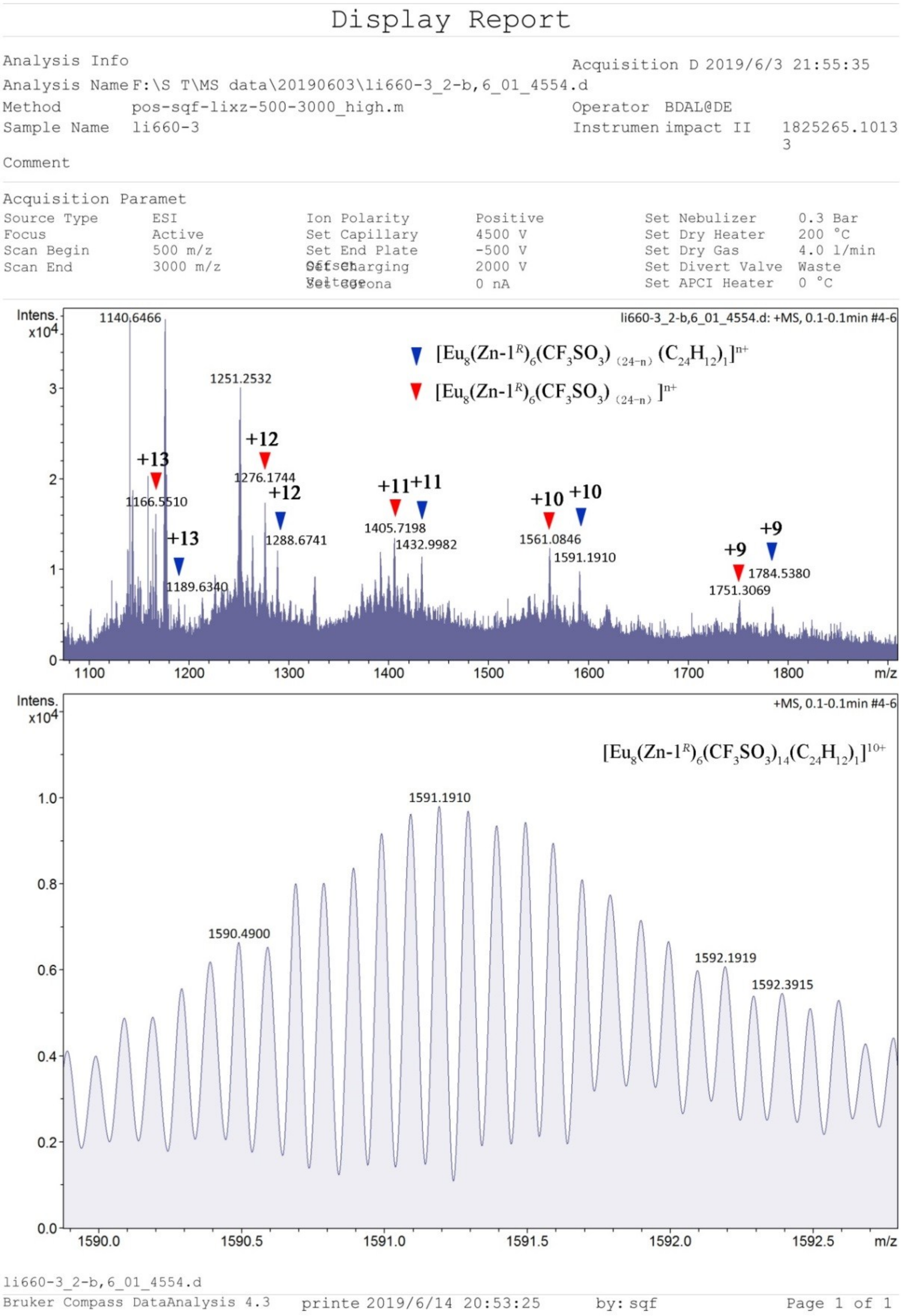
Figure S101. ESI-TOF-MS spectra of **La$_6$(Zn-1^R)$_3$(OTf)$_{18}$** in the existence of coronene with insets showing the observed and simulated isotopic patterns of the +6 peaks.



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Operator BDAL@DE

Sample Name li660-3

Instrumen impact II 1825265.10133

Comment

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Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C

li660-3_2-b,6_01_4554.d

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Figure S102. ESI-TOF-MS spectra of coronene$_1$@$\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ with insets showing the observed isotopic patterns of the +10 peaks.

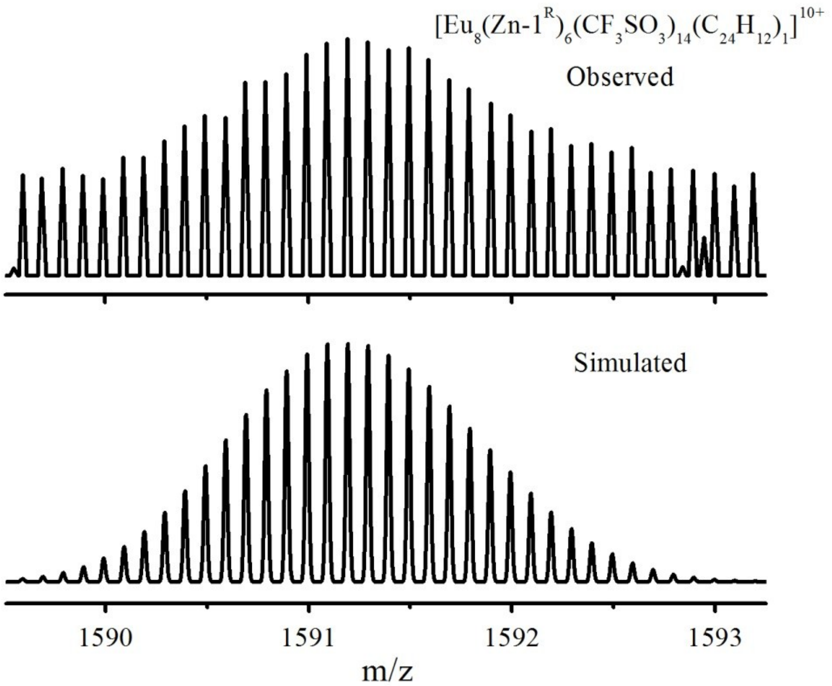

Figure S103. Comparison of the observed and simulated signals of [coronene$_1$@**Eu$_8$(Zn-1^R)$_6$(OTf)$_{14}$**]$^{10+}$.

6. UV-Vis, CD and FL spectra

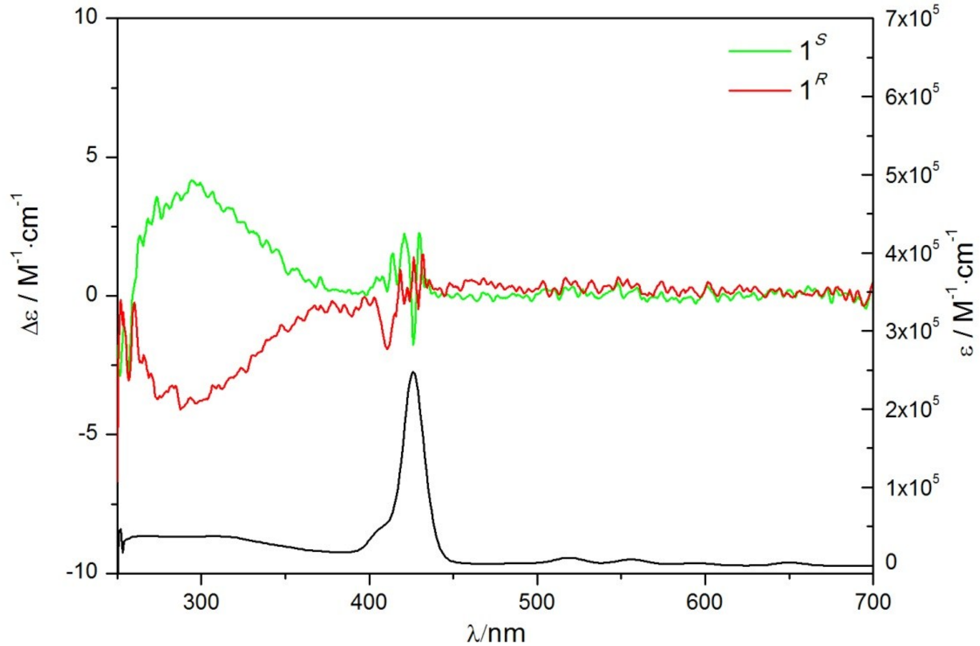

Figure S104. UV-vis ([**1^R**] =2.5×10^{-6} M) and CD ([**1^R**] =5.0×10^{-5} M) spectra of **1^R** in DMSO.

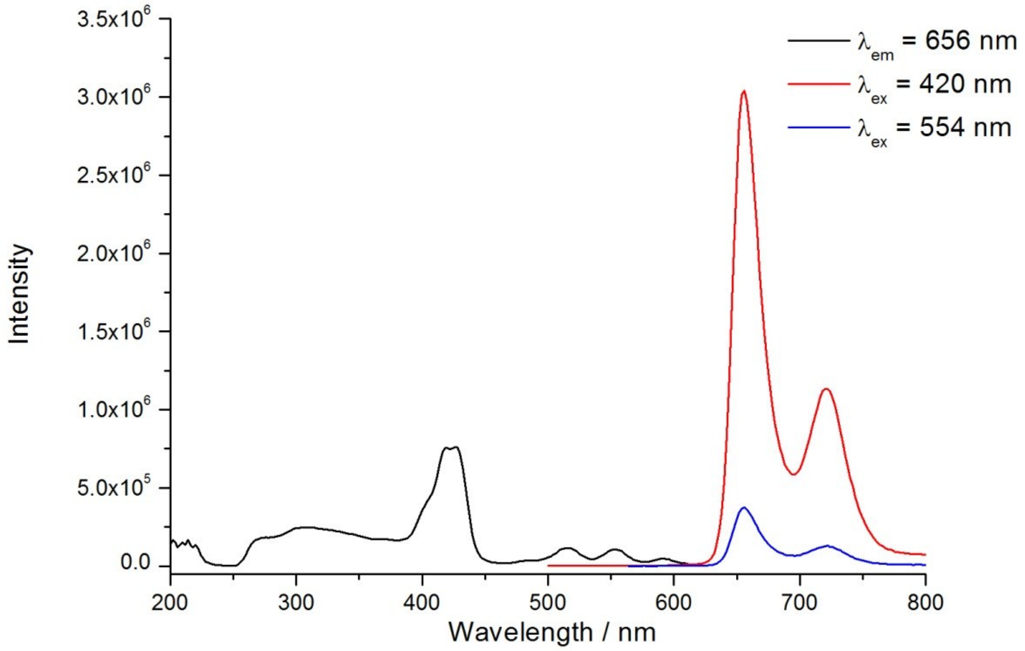

Figure S105. Excitation (black, λ_{em} = 656 nm) and emission (red, λ_{ex} = 420 nm, blue, λ_{ex} = 554 nm) spectra of $\mathbf{1}^{R}$ in DMSO (slits = 2 nm, [$\mathbf{1}^{R}$] = 5.0×10^{-6} M).

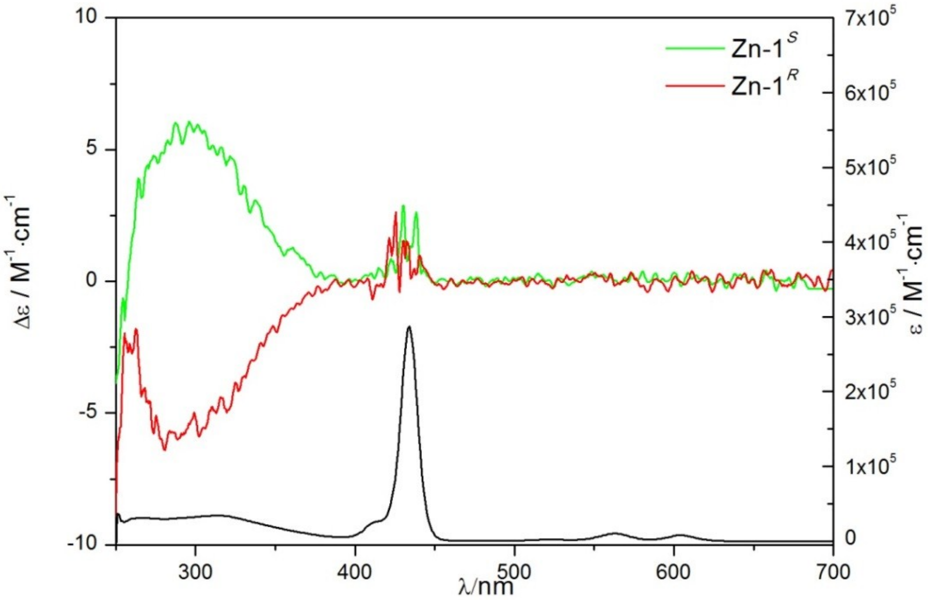

Figure S106. UV-vis ([**Zn-1**^{R}] =2.5×10^{-6} M) and CD ([**Zn-1**^{R}] =5.0×10^{-5} M) spectra of **Zn-1**^{R} in DMSO.

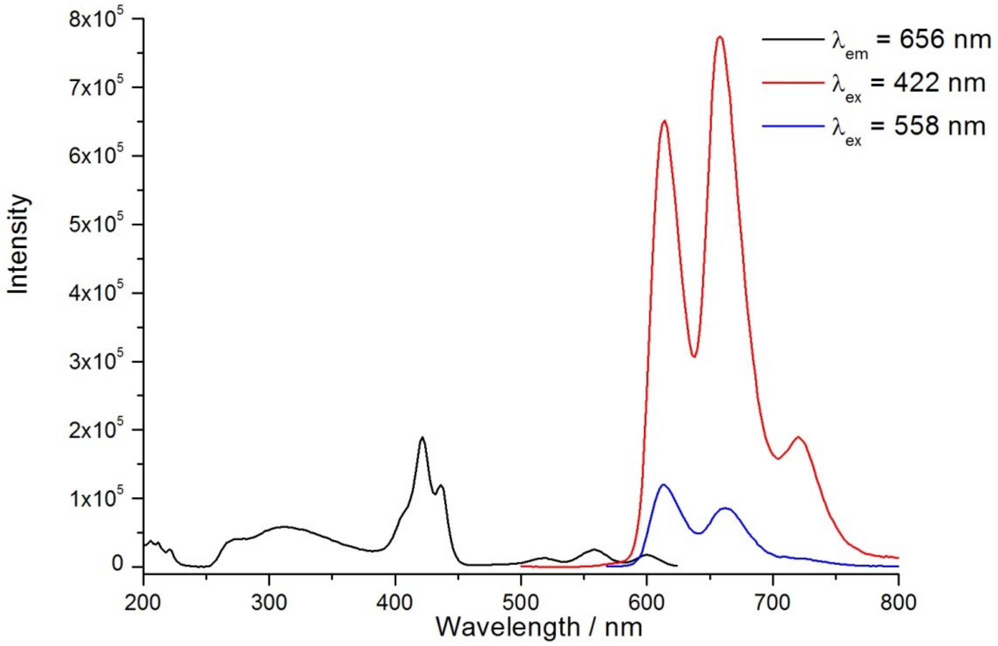

Figure S107. Excitation (black, λ_{em} = 656 nm) and emission (red, λ_{ex} = 422 nm, blue, λ_{ex} = 558 nm) spectra of **Zn-1*R*** in DMSO (slits = 2 nm, [**Zn-1*R***] = 5.0×10^{-6} M).

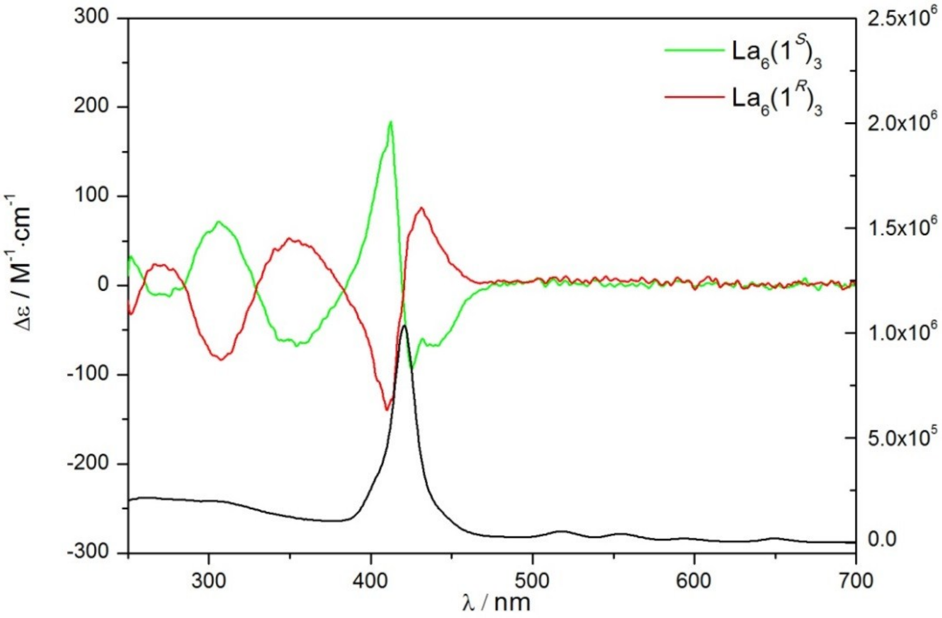

Figure S108. UV-vis ([**1*R***] =2.5×10^{-6} M) and CD ([**1*R***] =1.0×10^{-5} M) spectra of **La$_6$(1*R*)$_3$** in CH_3CN.

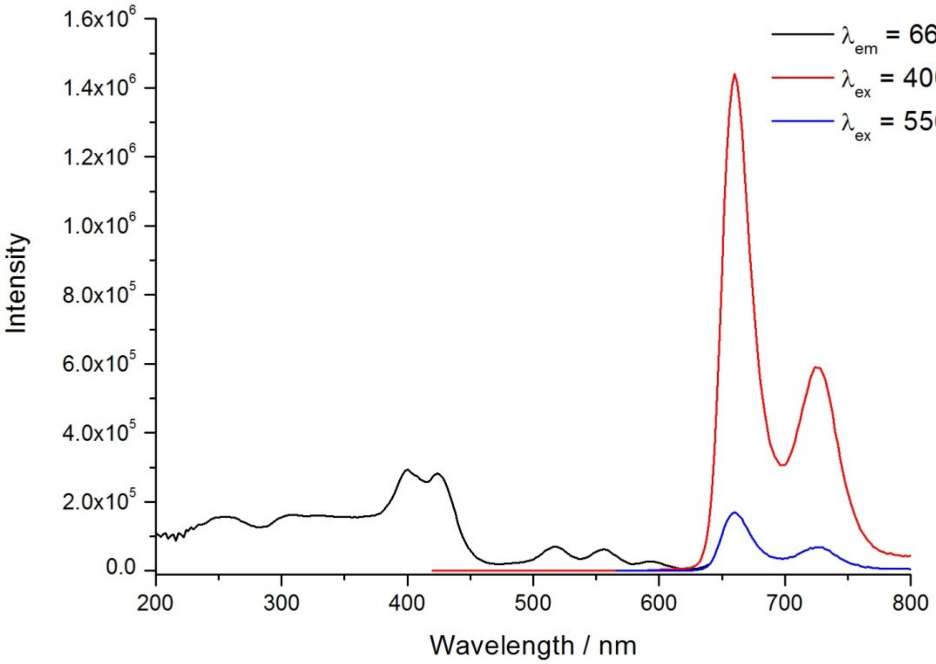

Figure S109. Excitation (black, λ_{em} = 660 nm) and emission (red, λ_{ex} = 400 nm, blue, λ_{ex} = 556 nm) spectra of **$La_6(1^R)_3$** in CH_3CN (slits = 2 nm, [$\mathbf{1}^R$] = 5.0×10^{-6} M).

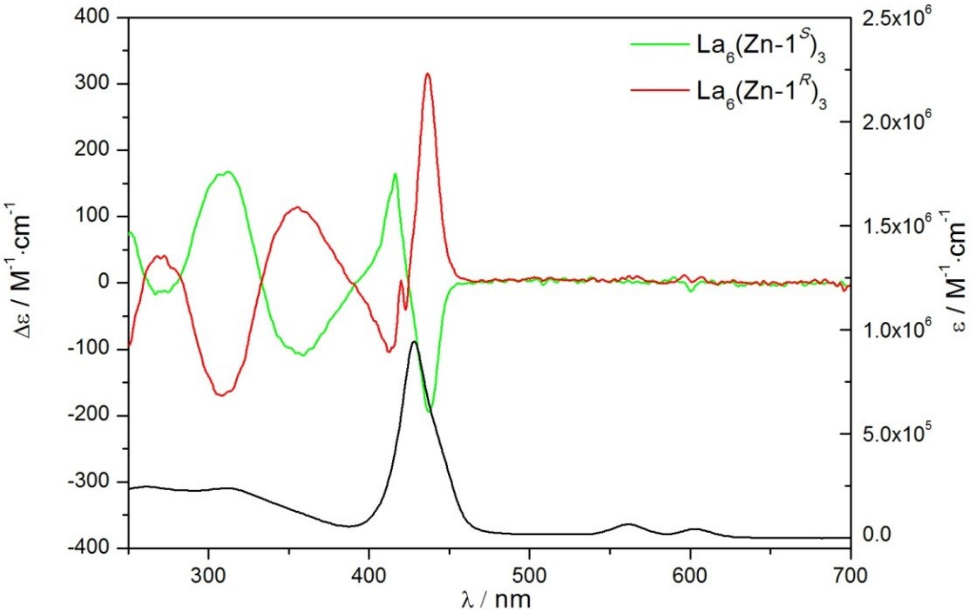

Figure S110. UV-vis ([**Zn-1^R**] =2.5×10^{-6} M) and CD ([**Zn-1^R**] =1.0×10^{-5} M) spectra of **$La_6(Zn\text{-}1^R)_3$** in CH_3CN.

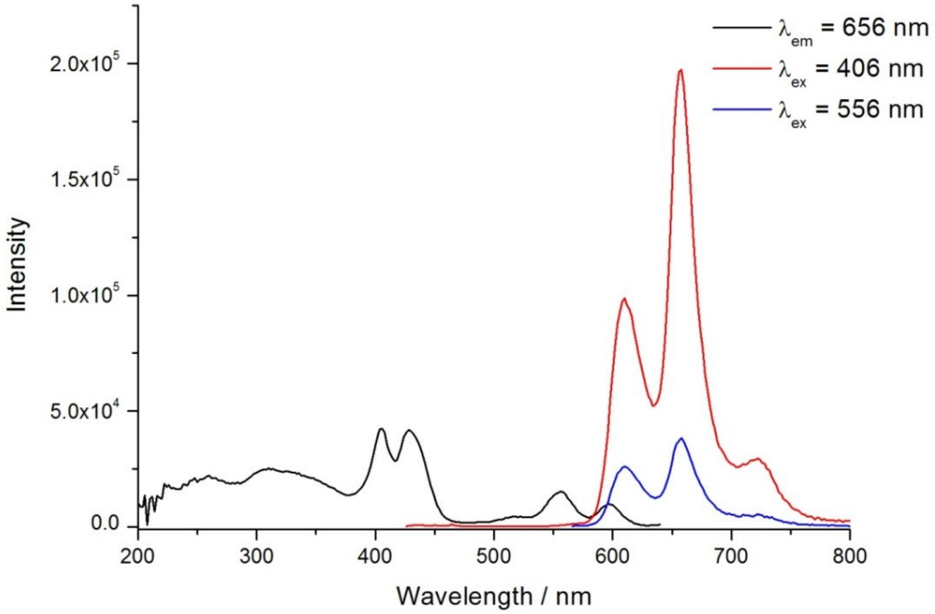

Figure S111. Excitation (black, λ_{em} = 656 nm) and emission (red, λ_{ex} = 406 nm, blue, λ_{ex} = 556 nm) spectra of **La$_6$(Zn-1^R)$_3$** in CH_3CN (slits = 2 nm, [**Zn-1^R**] = 5.0×10^{-6} M).

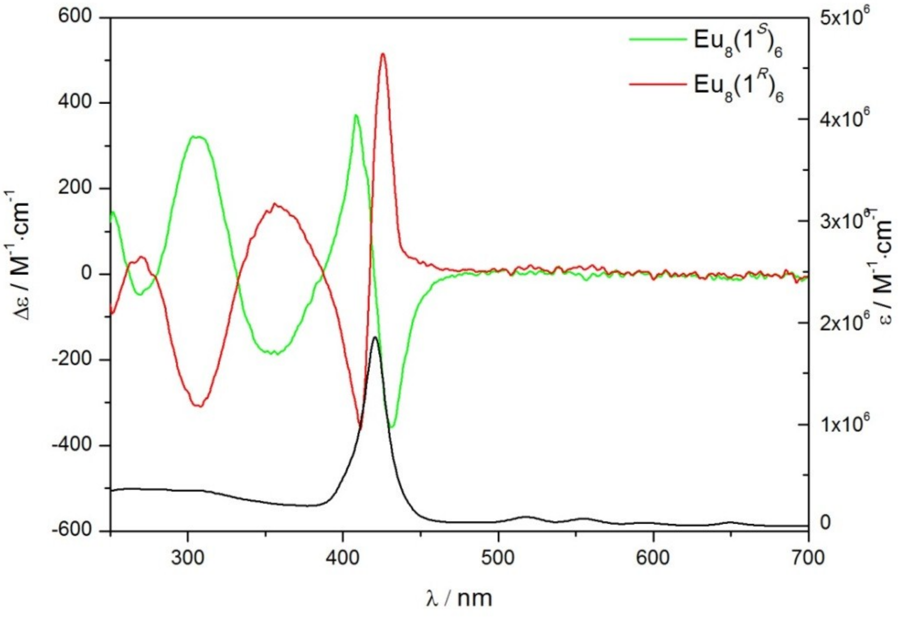

Figure S112. UV-vis ([**1^R**] =2.5×10^{-6} M) and CD ([**1^R**] =1.0×10^{-5} M) spectra of **Eu$_8$(1^R)$_6$** in CH_3CN.

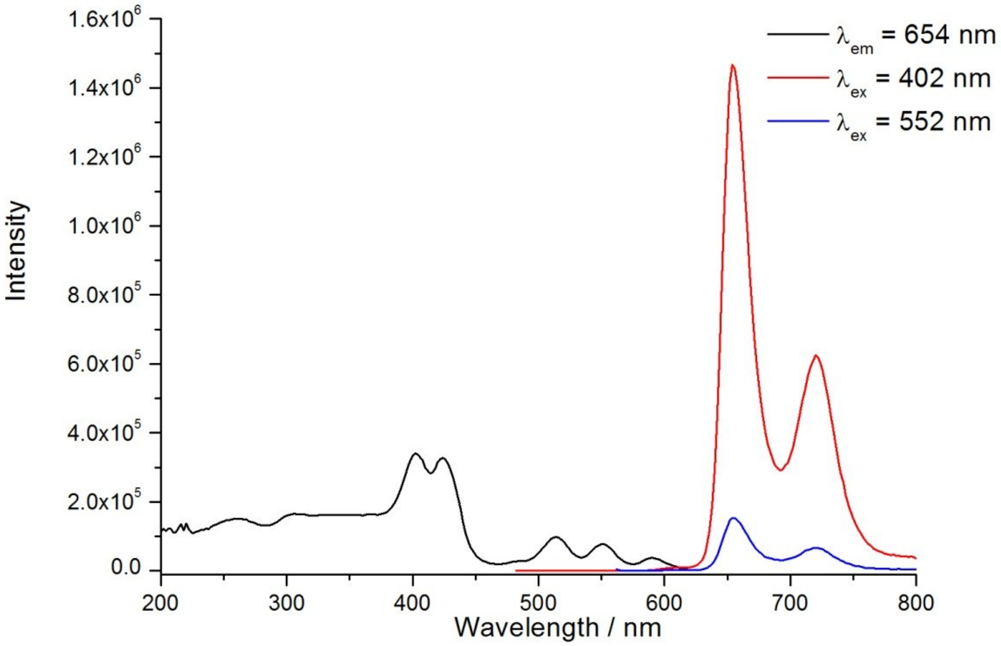

Figure S113. Excitation (black, λ_{em} = 654 nm) and emission (red, λ_{ex} = 402 nm, blue, λ_{ex} = 552 nm) spectra of $\mathbf{Eu_8(1^{\mathit{R}})_6}$ in CH_3CN (slits = 2 nm, [$\mathbf{1^{\mathit{R}}}$] = 5.0×10^{-6} M).

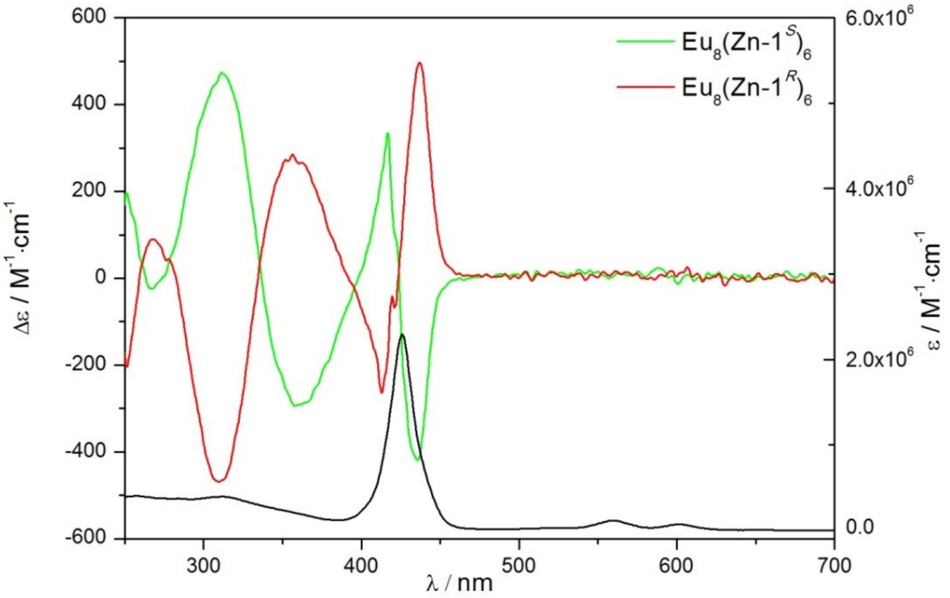

Figure S114. UV-vis ([$\mathbf{Zn\text{-}1^{\mathit{R}}}$] =$2.5\times10^{-6}$ M) and CD ([$\mathbf{Zn\text{-}1^{\mathit{R}}}$] =$1.0\times10^{-5}$ M) spectra of $\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ in CH_3CN.

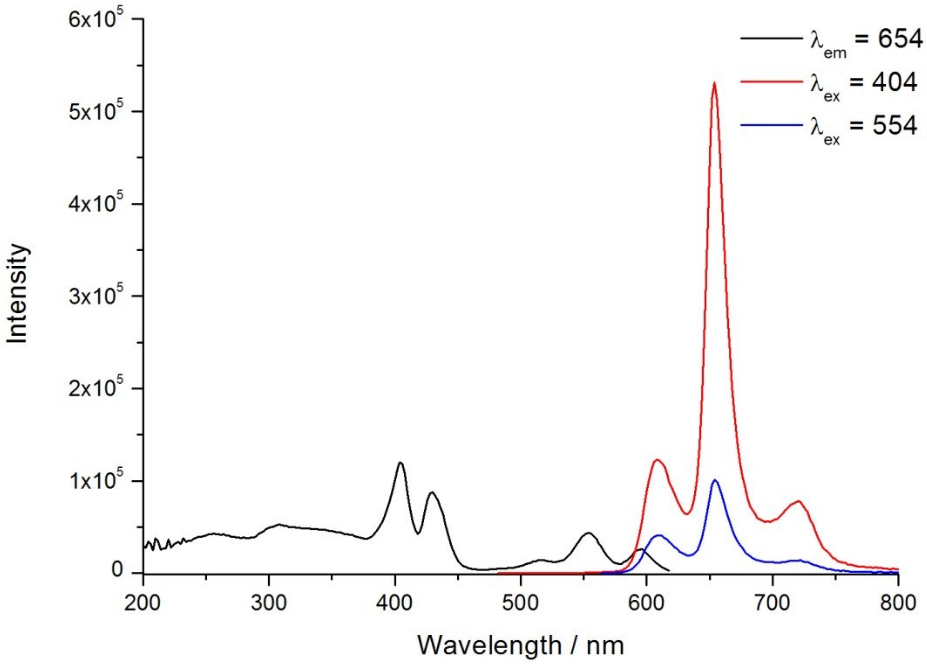

Figure S115. Excitation (black, λ_{em} = 654 nm) and emission (red, λ_{ex} = 404 nm, blue, λ_{ex} = 554 nm) spectra of **$Eu_8(Zn\text{-}1^R)_6$** in CH_3CN (slits = 2 nm, [**$Zn\text{-}1^R$**] = 5.0×10^{-6} M).

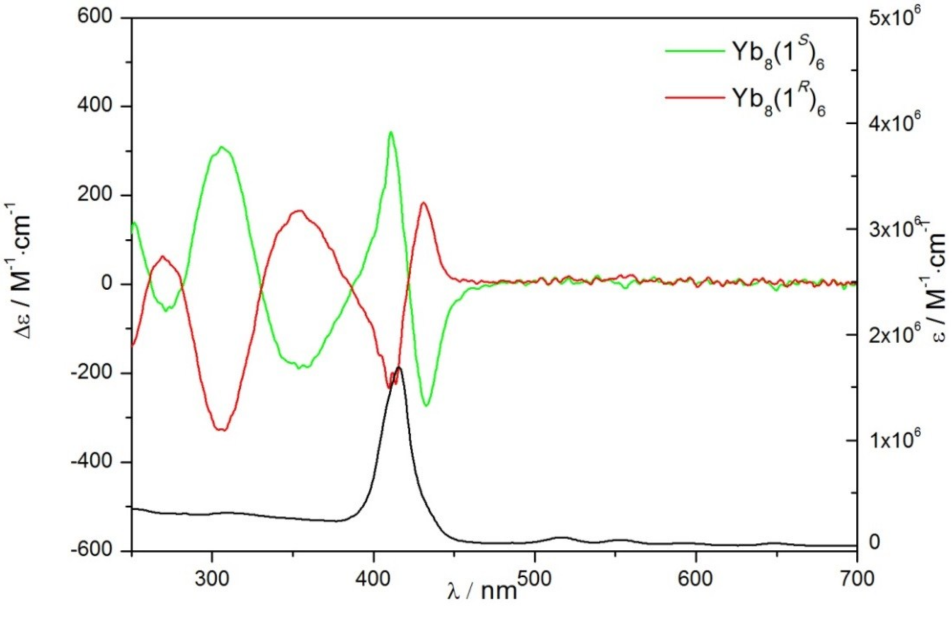

Figure S116. UV-vis ([**1^R**] =2.5×10^{-6} M) and CD ([**1^R**] =1.0×10^{-5} M) spectra of **$Yb_8(1^R)_6$** in CH_3CN.

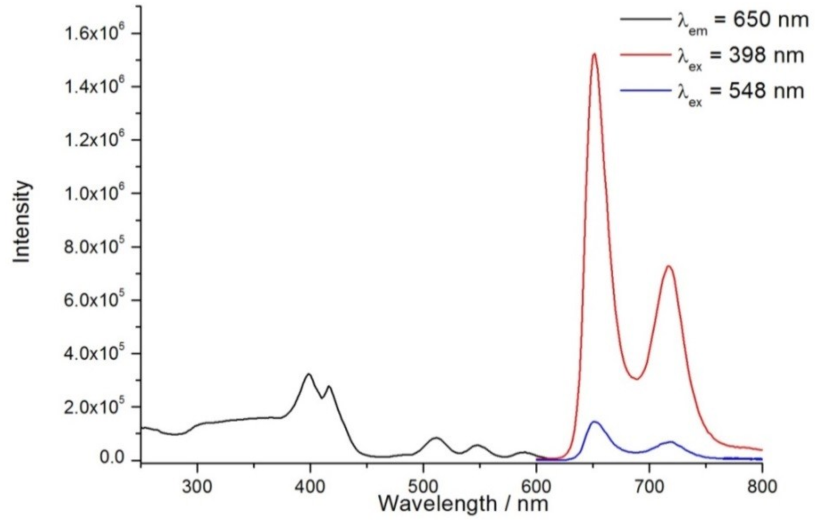

Figure S117. Excitation (black, λ_{em} = 650 nm) and emission (red, λ_{ex} = 398 nm, blue, λ_{ex} = 548 nm) spectra of **$Yb_8(1^R)_6$** in CH_3CN (slits = 2 nm, [1^R] = 5.0×10^{-6} M).

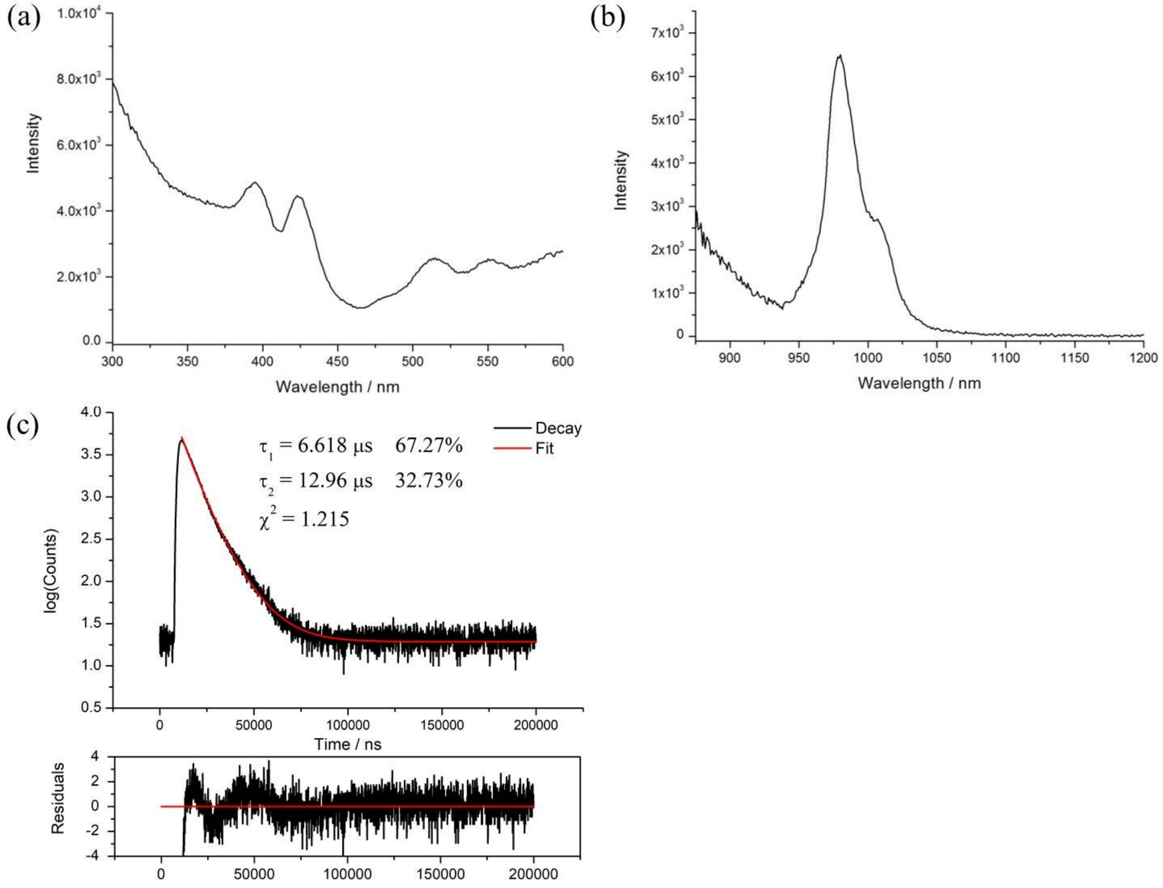

Figure S118. Excitation (a), emission spectra (b) and emission decay curve (c) of **$Yb_8[1^R]_6$** (λ_{em} = 980 nm, λ_{ex} = 395 nm, slits = 10 nm, [1^R] = 7.5×10^{-6} M, in CH_3CN).

The emission at 980nm corresponds to the $^5F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{III} ions.

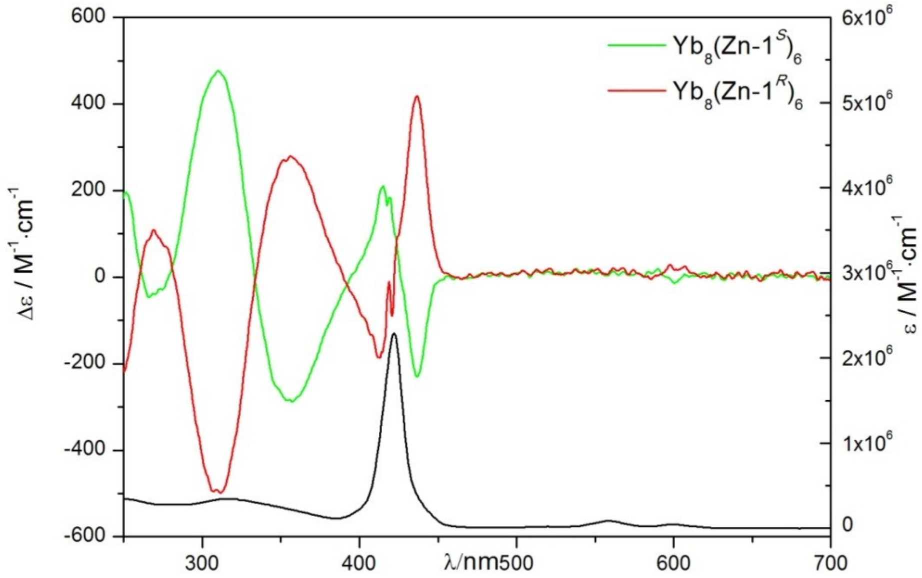

Figure S119. UV-vis ([**Zn-1**$^{\boldsymbol{R}}$] =2.5×10^{-6} M) and CD ([**Zn-1**$^{\boldsymbol{R}}$] =1.0×10^{-5} M) spectra of **Yb$_8$(Zn-1^{R})$_6$** in CH$_3$CN.

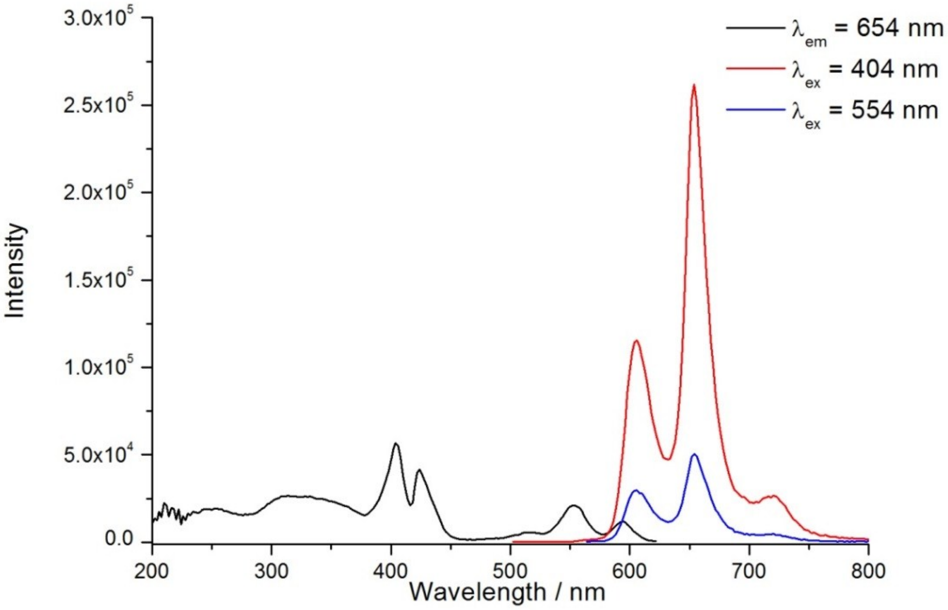

Figure S120. Excitation (black, λ_{em} = 654 nm) and emission (red, λ_{ex} = 404 nm, blue, λ_{ex} = 554 nm) spectra of **Yb$_8$(Zn-1^{R})$_6$** in CH$_3$CN (slits = 2 nm, [**Zn-1**$^{\boldsymbol{R}}$] = 5.0×10^{-6} M).

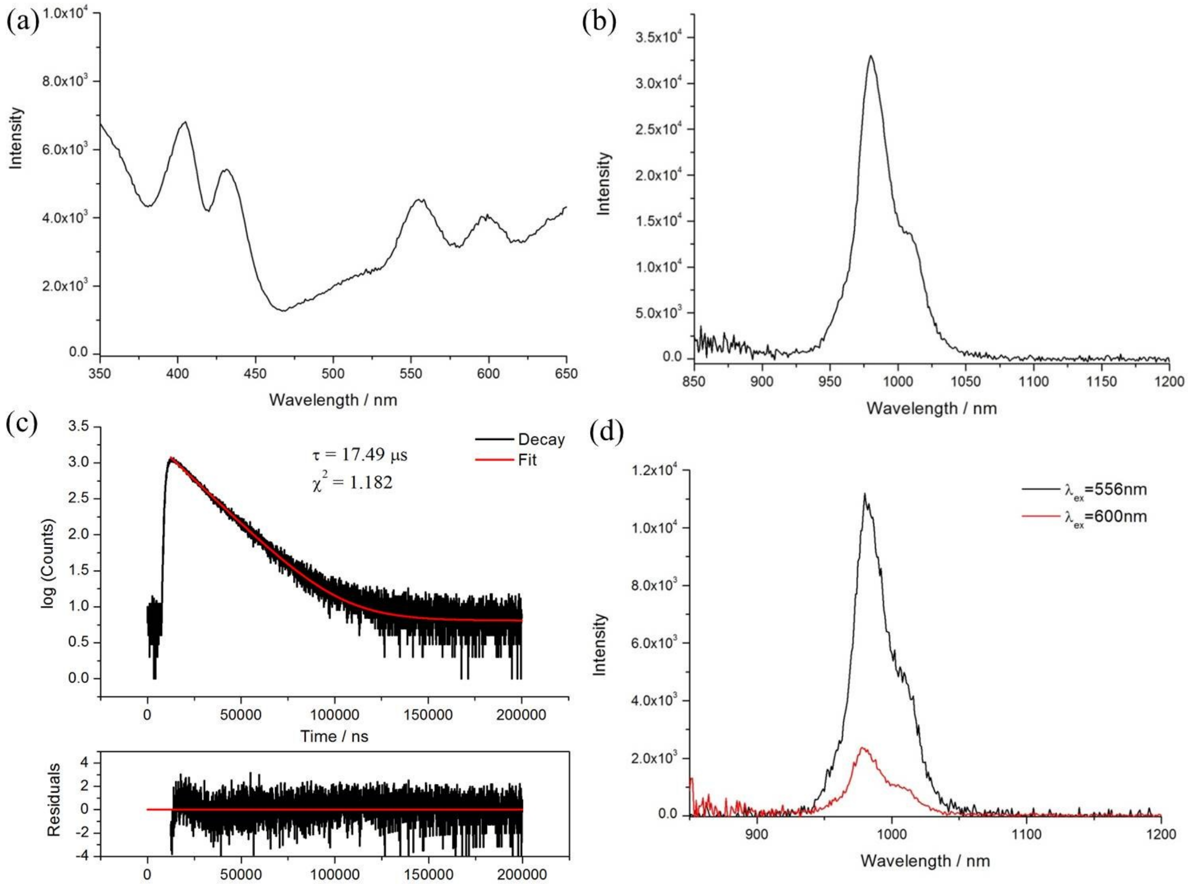

Figure S121. Excitation (a), emission (b, d) spectra and emission decay curve of **Yb$_8$[Zn-1^{R}]$_6$** (λ_{em} = 980 nm, (λ_{ex} = 405 nm, slits = 10 nm, [**Zn-1^{R}**] = 1.0×10^{-5} M, in CH$_3$CN).

The emission at 980nm corresponds to the $^5F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{III} ions.

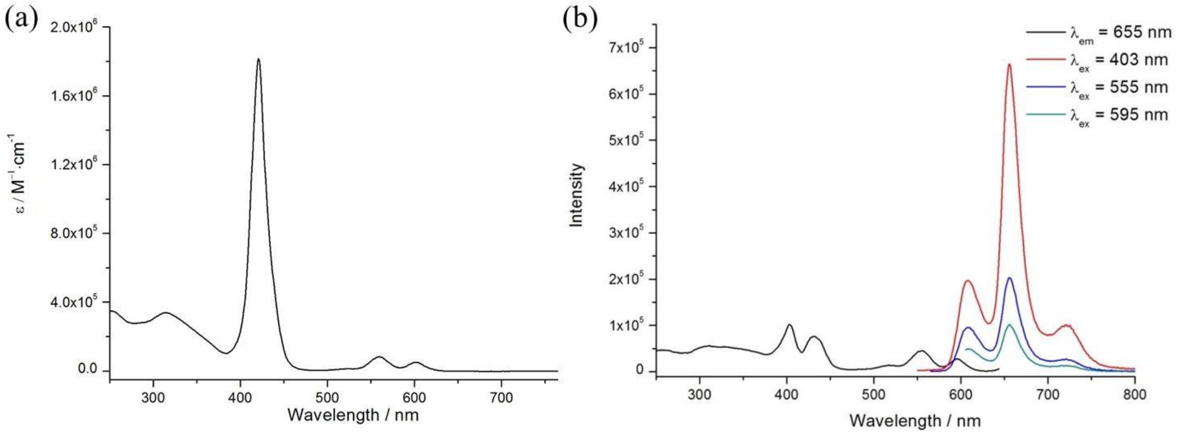

Figure S122. UV-vis spectrum (a, [**Zn-1^{R}**] =2.5×10^{-6} M), excitation (black, λ_{em} = 655 nm) and emission (b, red, λ_{ex} = 403 nm, blue, λ_{ex} = 555 nm, cyan, λ_{ex} = 595 nm, slits = 2.5 nm, [**Zn-1^{R}**] = 5.0×10^{-6} M) spectra of **Ce$_8$[Zn-1^{R}]$_6$** in CH$_3$CN.

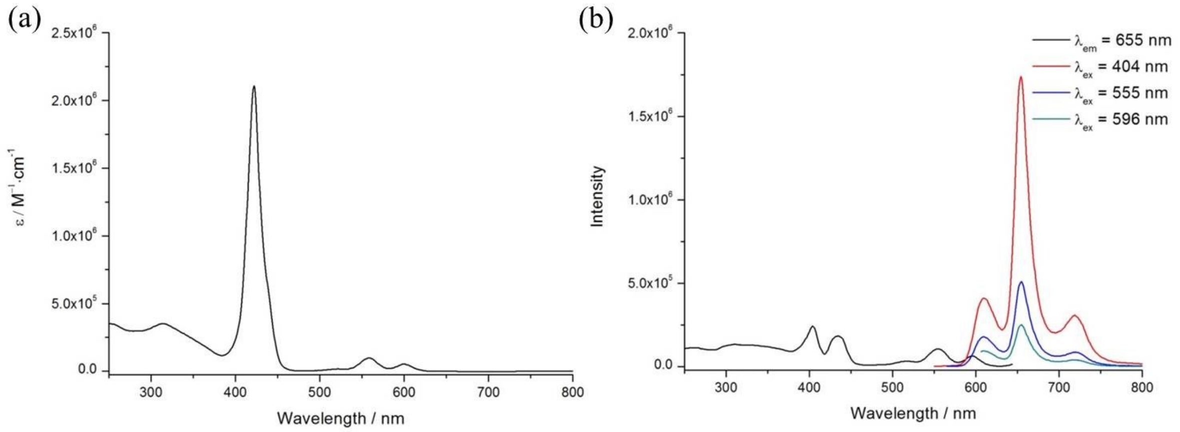

Figure S123. UV-vis spectrum (a, [**Zn-1^{R}**] =2.5×10^{-6} M), excitation (black, λ_{em} = 655 nm) and emission (b, red, λ_{ex} = 404 nm, blue, λ_{ex} = 555 nm, cyan, λ_{ex} = 595 nm, slits = 2.5 nm, [**Zn-1^{R}**] = 5.0×10^{-6} M) spectra of **Pr$_8$[Zn-1^{R}]$_6$** in CH$_3$CN.

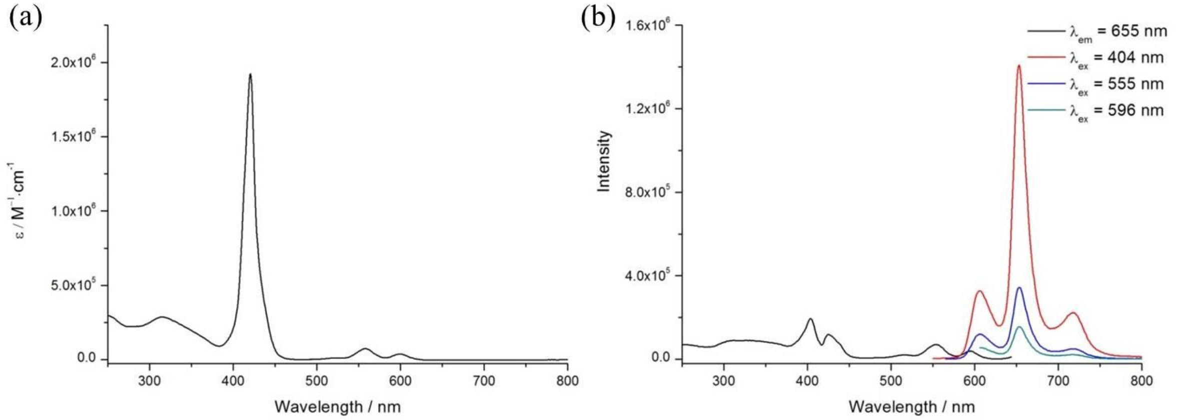

Figure S124. UV-vis spectrum (a, [**Zn-1^{R}**] =2.5×10^{-6} M), excitation (black, λ_{em} = 655 nm) and emission (b, red, λ_{ex} = 404 nm, blue, λ_{ex} = 555 nm, cyan, λ_{ex} = 596 nm, slits = 2.5 nm, [**Zn-1^{R}**] = 5.0×10^{-6} M) spectra of **Nd$_8$[Zn-1^{R}]$_6$** in CH$_3$CN.

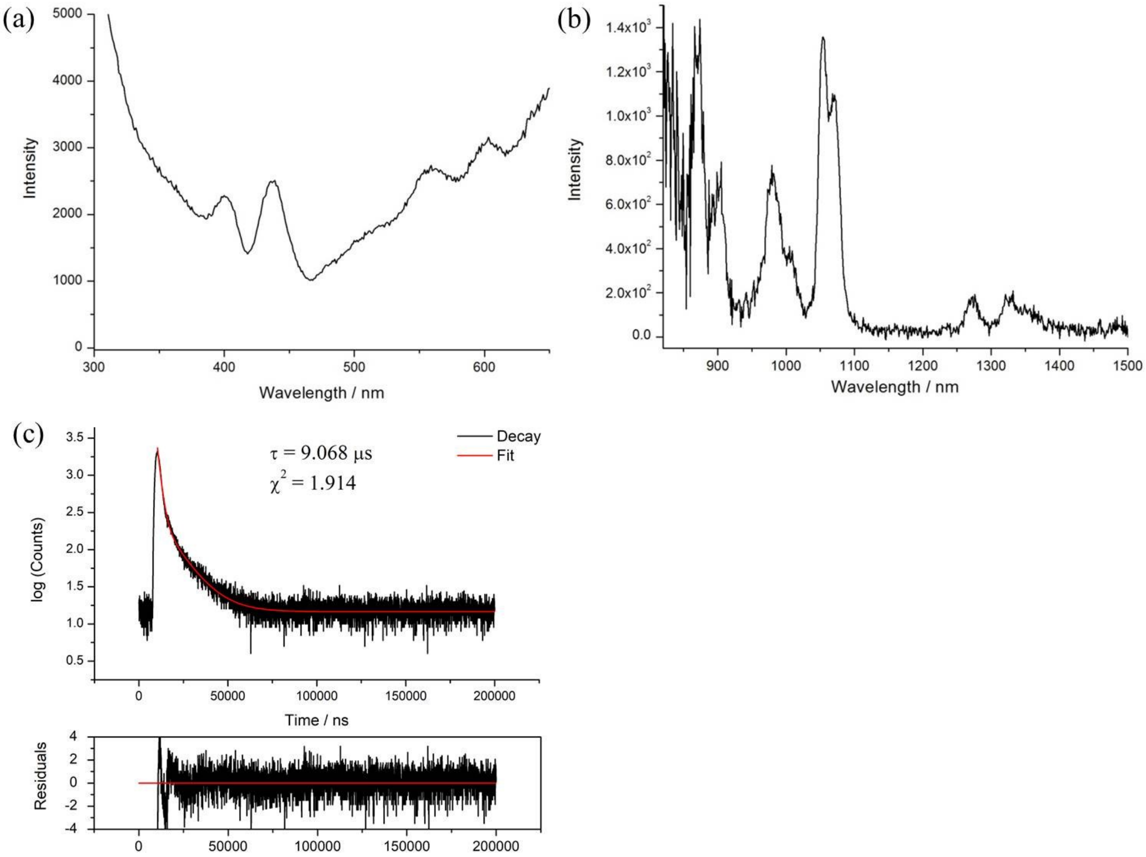

Figure S125. Excitation (a), emission (b) spectra and emission decay curve of **Nd$_8$[Zn-1^{R}]$_6$** (λ_{em} = 1054 nm, λ_{ex} = 402 nm, slits = 10 nm, [**Zn-1^{R}**] = 1.0×10^{-5} M, in CH$_3$CN).

The NIR emission in the range of 890 nm – 1350 nm corresponds to the $^4F_{3/2}\rightarrow{}^4I_J$ (J = 9/2, 11/2, 13/2) transitions of Nd^{III} ions.

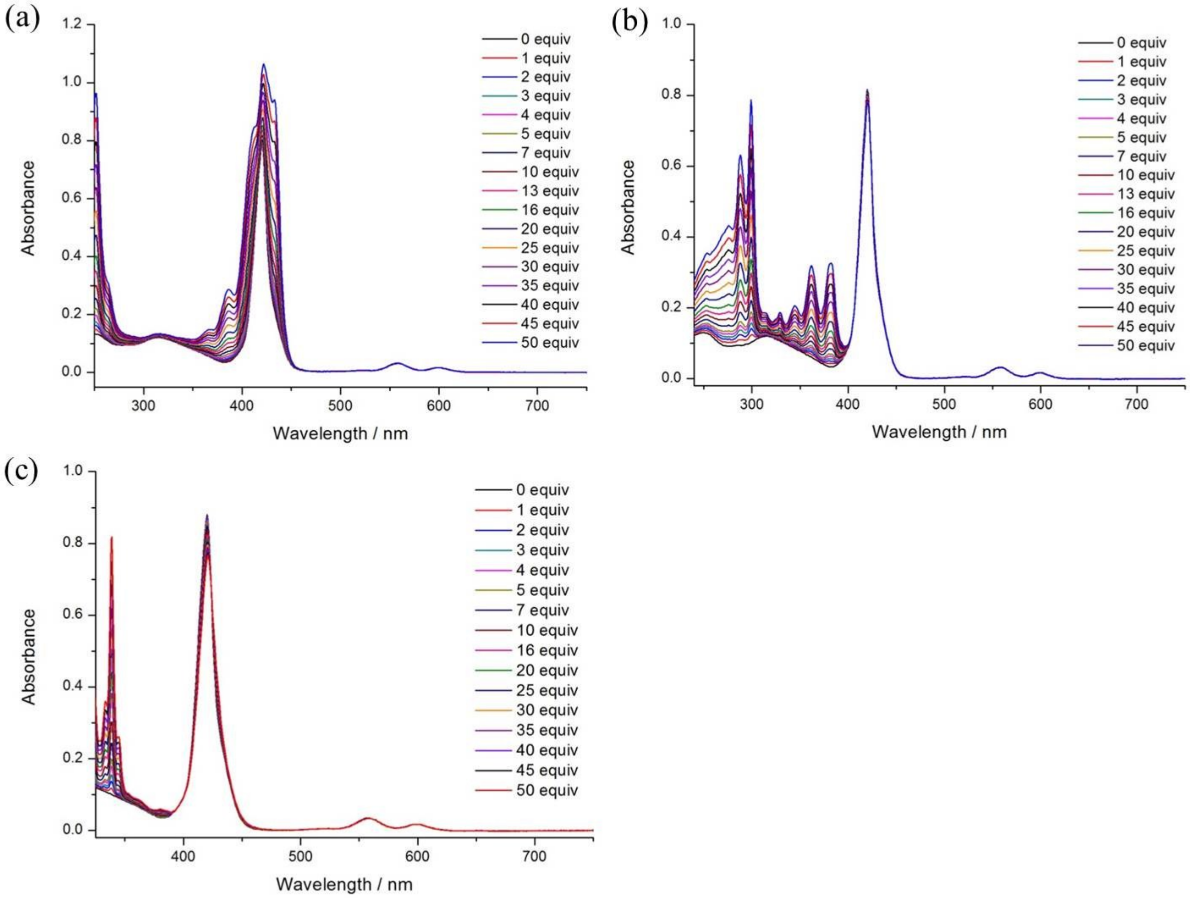

Figure S126. Absorption spectra of $\mathbf{Eu_8(Zn\text{-}1^{\mathit{R}})_6}$ with the addition of different equivalents of perylene (a), 1,12-benzoperylene (b) and coronene (c) molecules ([$\mathbf{Zn\text{-}1^{\mathit{R}}}$]=2.5×10^{-6} M, in CH_3CN).

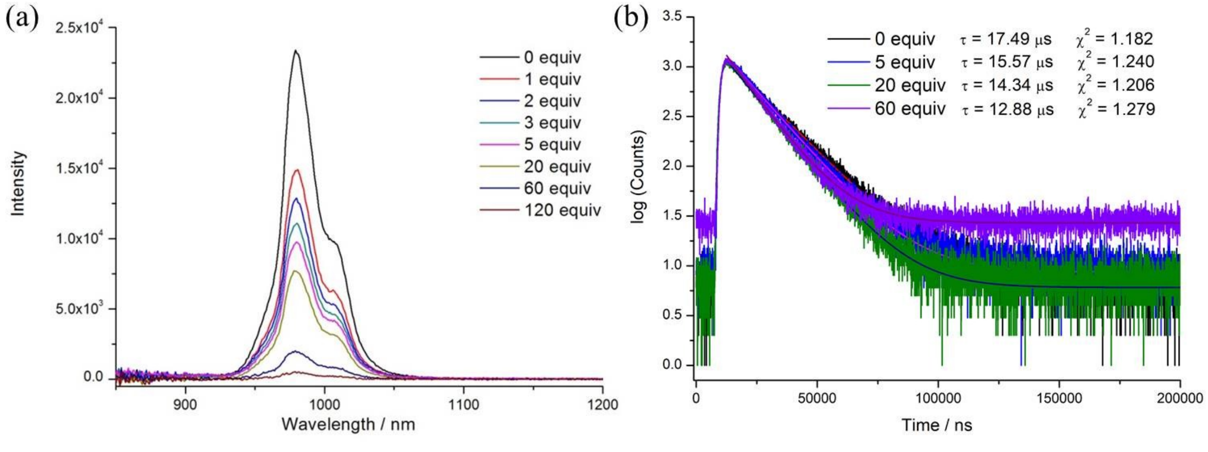

Figure S127. NIR emission spectra (a) and excited-state lifetime analysis (b) of $\mathbf{Yb_8(Zn\text{-}1^{\mathit{R}})_6}$ ([$\mathbf{Zn\text{-}1^{\mathit{R}}}$]=1.0×10^{-5} M) with different equivalents of perylene molecules (λ_{ex}= 405 nm, in CH_3CN).

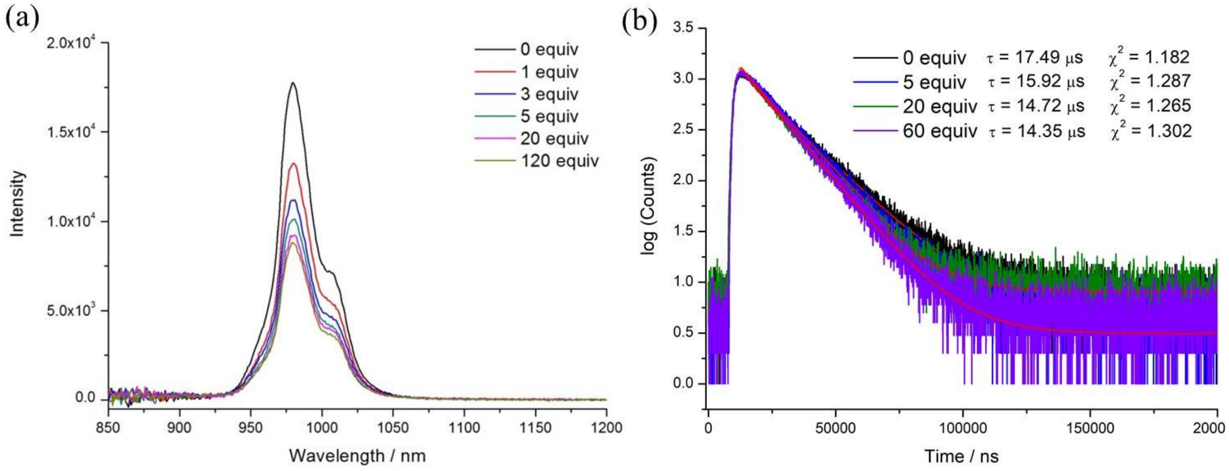

Figure S128. NIR emission spectra (a) and excited-state lifetime analysis (b) of **Yb$_8$(Zn-1^R)$_6$** ([**Zn-1^R**]=1.0×10^{-5} M) with different equivalents of 1,12-benzoperylene molecules (λ_{ex}= 405 nm, in CH_3CN).

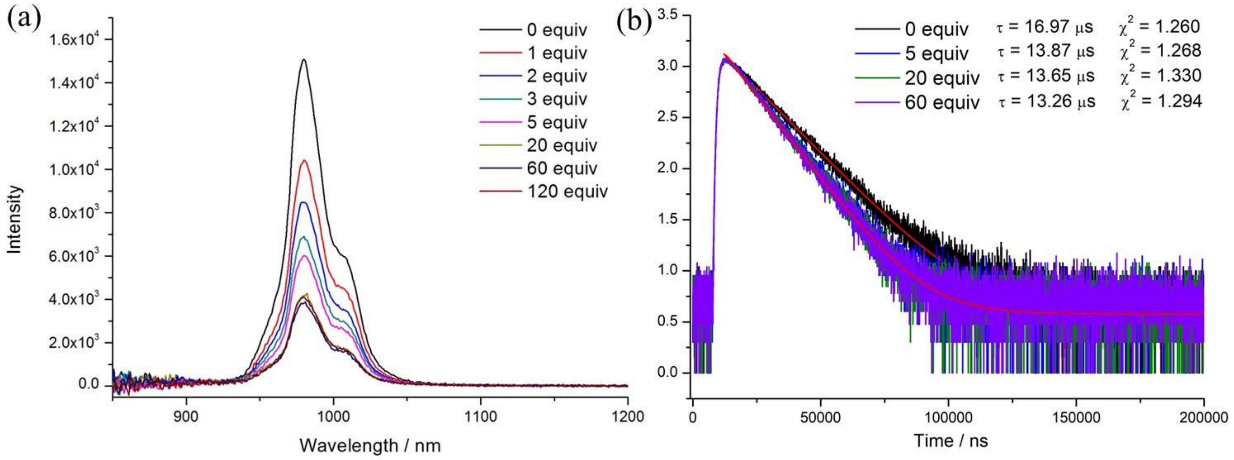

Figure S129. NIR emission spectra (a) and excited-state lifetime analysis (b) of **Yb$_8$(Zn-1^R)$_6$** ([**Zn-1^R**]=1.0×10^{-5} M) with different equivalents of coronene molecules (λ_{ex}= 405 nm, in CH_3CN).

7. Crystal data and structures

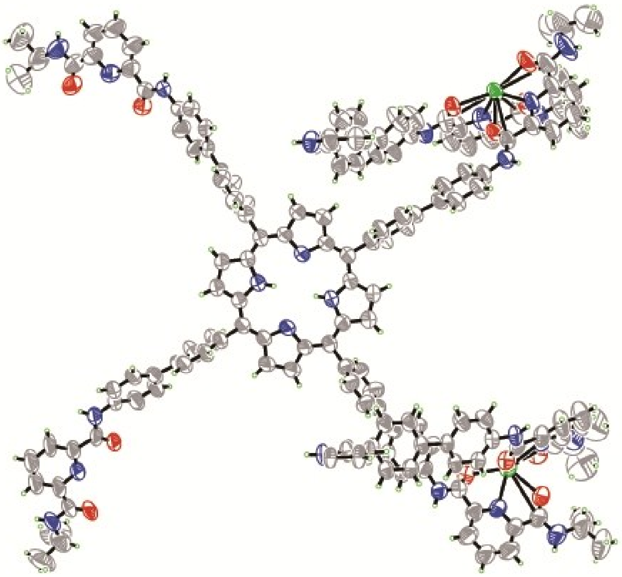

Figure S130. Ortep-drawing for the asymmetric unit in the crystal structure of $\mathbf{Eu_8(2)_6}$ at 30 % ellipsoids level.

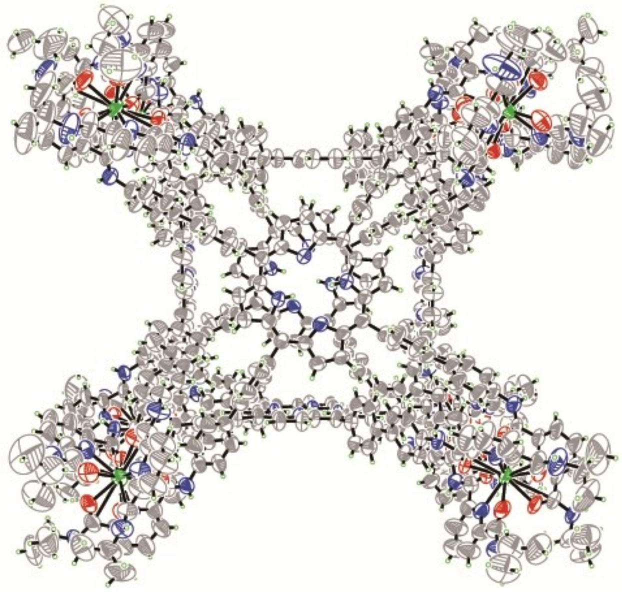

Figure S131. Ortep drawing of the crystal structure of $\mathbf{Eu_8(2)_6}$ (ClO_4^- salt) at 30% probability level.

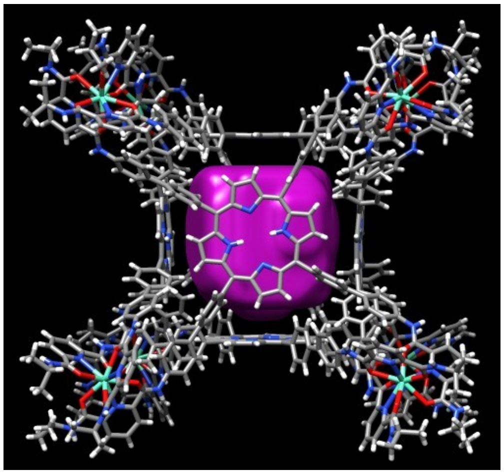

Figure S132. Cavity Volume of $Eu_8(\mathbf{2})_6(ClO_4)_{24}$ calculated by using 3V webserver.[5] Coordination of crystal structure of $Eu_8(\mathbf{2})_6(ClO_4)_{24}$ (CCDC 1939386), the outer probe radius 8.0 Å and the inner probe radius of 1.25 Å were used. The framework of $Eu_8(\mathbf{2})_6(ClO_4)_{24}$ are represented as stick and the cavity is shown as purple surface. The cavity volume was estimated as 1291 Å^3 and graphics were generated with UCSF Chimera.[6]

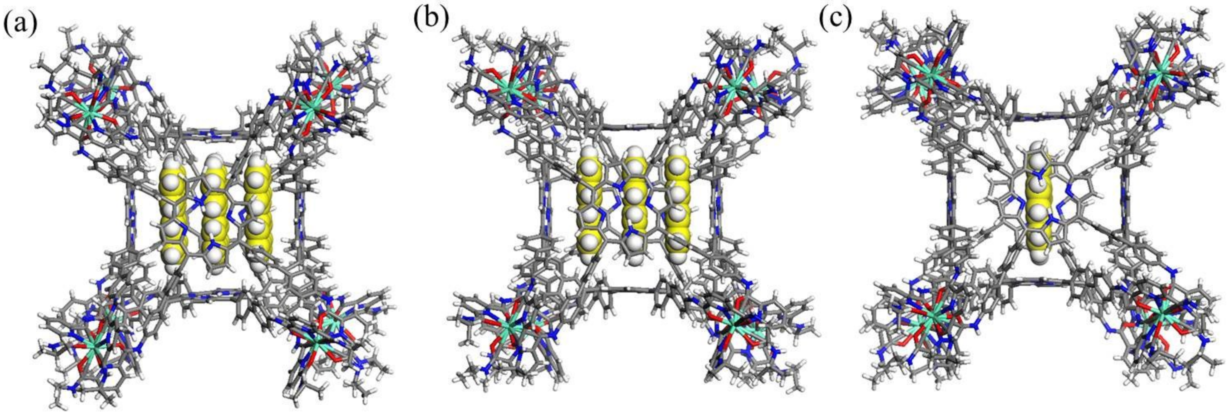

Figure S133. Simulated structures of perylene$_3$@$\mathbf{Eu_8(2)_6}$ (a), 1,12-benzoperylene$_3$@$\mathbf{Eu_8(2)_6}$ (b) and coronene$_1$@$\mathbf{Eu_8(2)_6}$ (c).

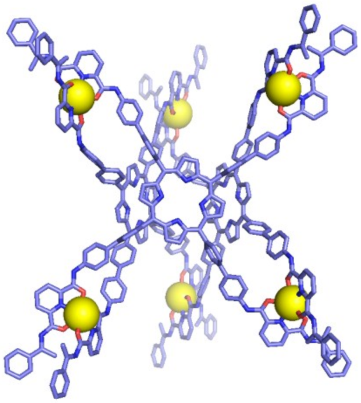

Figure S134. Energy-minimized structure of $\mathbf{La_6(1^{\mathit{R}})_3}$. For clarity, only the cubic cage framework is shown.

A triangular prism and triple-decker structures are assumed for Ln$_6$**L**$_3$ complexes. The latter structure can be excluded since it needs two Ln^{III} ions sandwiched by adjacent ligands which is impossible in Ln$_6$**(Zn-1$^{R/S}$)**$_3$ complexes. In the triangular prism, six Ln^{III} ions sit on the vertices and three ligands span the quadrilateral planes. The Ln^{III} atoms are six-coordinated with two pcam chelating moieties from two different ligands, with residual coordination sites available for solvent molecules and/or counter-ions. The ligands endure less distortion on the triangular prism compared with the strong twisting conformation observed on the crystal structure of the cubic cage. Thus when the coordination bonds of lanthanide ions, i.e. La^{III}, are not strong enough to compensate the torsional stress in constructing a cube, triangular prisms are formed as thermodynamic stable products. Based on the mechanical coupling effect in the self-assembly process of high-nuclearity lanthanide-organic polyhedral, the La centres are predicted to adopt the same *Λ* or Δ configurations.[1]

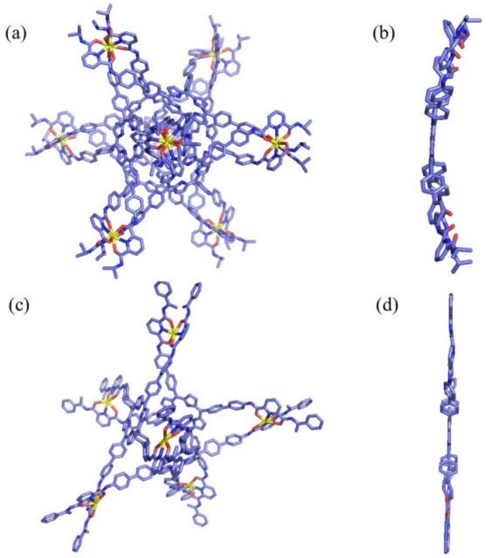

Figure S135. Aerial view of the structure of **Eu$_8$(2)$_6$** (a), **La$_6$(1^R)$_3$** (c) and side view of the structure of the ligands in **Eu$_8$(2)$_6$** (b), **La$_6$(1^R)$_3$** (d). For clarity, only the framework is shown.

Table S1. Crystal data and structure refinement for **Eu$_8$(2)$_6$** (ClO$_4^-$ salt).

Identification code	p4n_sq	
Empirical formula	C648 H540 Cl0 Eu8 N96 O48	
Formula weight	11655.41	
Temperature	293(2) K	
Wavelength	0.65253 Å	
Crystal system	Tetragonal	
Space group	P4/n	
Unit cell dimensions	a = 38.200(5) Å	□ = 90°.

	b = 38.200(5) Å	□ = 90°.
	c = 46.770(9) Å	□ = 90°.
Volume	68249(24) Å^3	
Z,	2	
Calculated density	0.567 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	11976	
Crystal size	0.35 x 0.3 x 0.2 mm^3	
Theta range for data collection	0.435 to 17.225°.	
Limiting indices	-31<=h<=31, -31<=k<=31, -38<=l<=38	
Reflections collected	158163	
Independent reflections	20682 [R(int) = 0.0937]	
Completeness to theta = 17.225	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20682 / 1975 / 1531	
Goodness-of-fit on F^2	1.118	
Final R indices [I>2sigma(I)]	R1 = 0.0857, wR2 = 0.2564	
R indices (all data)	R1 = 0.1177, wR2 = 0.2962	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.057 and -0.366 e. Å^{-3}	

8. Supplementary References

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