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**Electronic Supplementary Information**

# Efficient Luminescence Control in Dithienylethene Functionalized Cyclen Macrocyclic Lanthanide Complexes

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※ These authors contributed equally to the work

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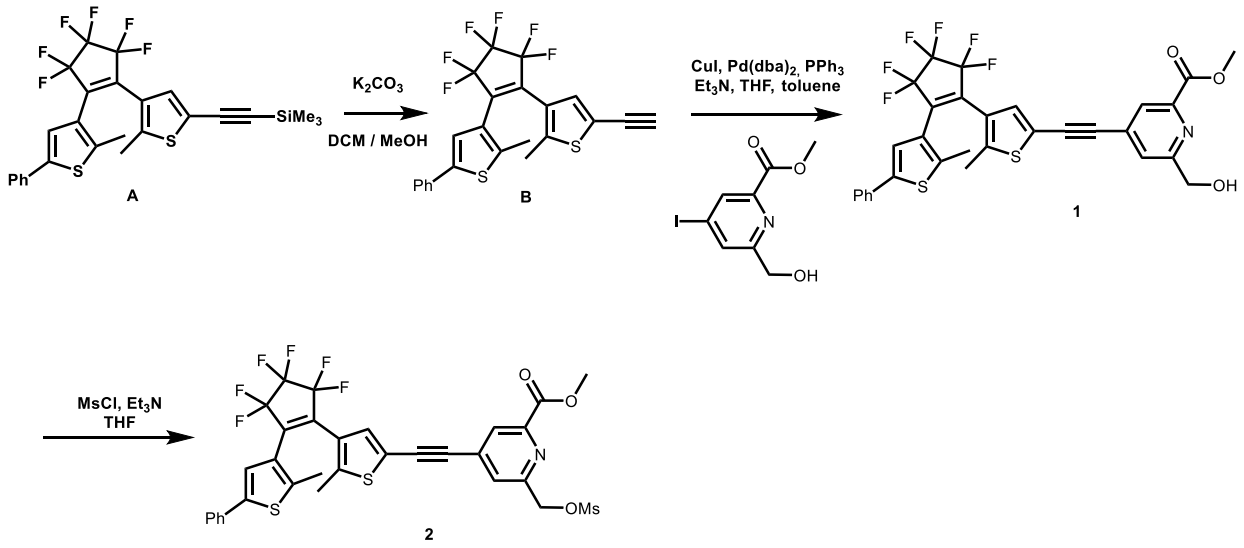
## 1. Synthetic procedures and characterizations

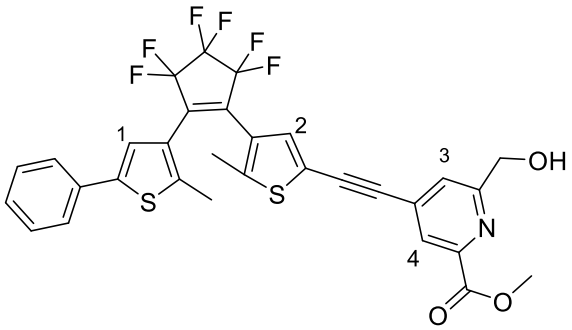
Reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were dried and distilled under argon using standard procedures. Solvents were taken from MB SPS-800 machine. Pre-coated TLC sheets ALUGRAM® Xtra SIL G/UV254 were used. UV-vis measurements were performed in $CH_2Cl_2$ at 20 °C using an "Analytik jena specord 205" spectrometer. $^1$H and $^{13}$C NMR spectra were recorded using Bruker Avance 500 (500MHz), Bruker Avance 400 (400 MHz), or Bruker AMX-3 300 (300 MHz) spectrometers or at the Centre Régional de Mesures Physiques de l'Ouest on a Bruker Avance III HD 500 (500 MHz). HRMS analyses were realized on a HRMS Q-Tof MaXis, sources ESI, APCI, APPI, nano-ESI (at the Institute of Organic and Analytic Chemistry – ICOA in Orléans). Note that for some paramagnetic lanthanide complexes, it was not possible to assign all of the signals precisely.




**Compound A.** n-BuLi (2.5 M in hexanes, 2.3 mmol) was slowly added to a solution of ((4-bromo-5-methylthiophen-2-yl)ethynyl)trimethylsilane[1] (0.530 g, 2.1 mmol) in THF (17 mL) at -78°C. The resulting mixture was stirred for 2 hours at -78°C and then cannula transferred to a second Schlenk tube containing 2-methyl-3-perfluorocyclopent-1-en-yl)-5-phenylthiophene[2] (0.85g, 2.3 mmol) dissolved in THF (17 mL) and also cooled to -78°C. The mixture was then stirred at low temperature for 2 hours and then slowly warmed up to room temperature overnight. After the addition of water (10 mL), the organic phase was separated and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic phases were dried over $MgSO_4$ and dried under

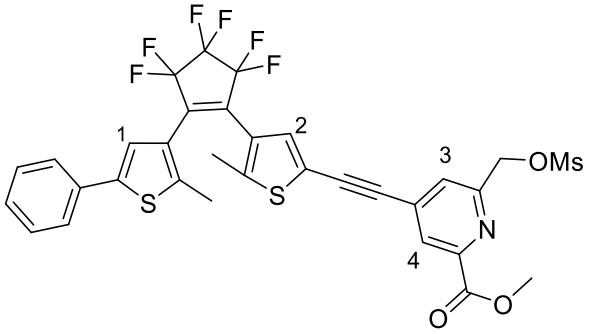
vacuum. Column chromatography (silica gel, petroleum ether, Rf = 0.2) afforded the compound as a yellowish solid (0. 85 g, 77 %). Its NMR spectra matched previously published data.[3]

**Compound B.** Potassium carbonate (0.340 g, 2.47 mmol) and compound **A** (0.450 g, 0.82 mmol) were dissolved in a 1:1 mixture of DCM and methanol (30 mL). After 12h of stirring at room temperature, the solvents were evaporated under vacuum and the residue was taken with ether and filtrated through a celite pad. Column chromatography (silica gel, pentane, Rf = 0.3) afforded the compound as a yellowish solid (0. 37 g, 96 %). $^1$H NMR (300 MHz, $CDCl_3$) : $\delta$ = 7.54 (d, J = 7.3 Hz, 2H, $H_{Ph}$), 7.39 (t, J = 7.8 Hz, 2H, $H_{Ph}$), 7.31 (t, J = 7.2 Hz, 1H, $H_2$), 7.24 (s, 1H), 7.22 (s, 1H), 3.34 (s, 1H, CH alkyne), 1.92 (s, 3H, $H_8$), 1.90 (s, 3H, $H_8$).




**Compound 1**. The alkyne **B** (1.40 g, 2.99 mmol) was dissolved in a 1:1:1 mixture of THF, toluene and trimethylamine (300 mL). After argon bubbling for 15 min, the mixture was cannula transferred into a second Schlenk tube containing methyl 6-(hydroxymethyl)-4-iodopicolinate (0.890 g, 3.03 mmol), CuI (0.230 g, 1.20 mmol), $Pd(dba)_2$ (0.690 g, 1.20 mmol) and $PPh_3$ (0.390 g, 2.40 mmol). The resulting mixture was stirred at 50 °C for 12 hours. The solvent was evaporated under vacuum. Column chromatography (silica gel, dichloromethane with 0 →3 % methanol) afforded the compound as a yellowish solid (1.650 g, 87 %). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.07 (s, 1H, $H_4$), 7.60 (s, 1H, $H_3$), 7.54 (d, *J* = 7.32 Hz, 2H, $H_{Ph}$), 7.39 (t, *J* = 7.76 Hz, 2H, $H_{Ph}$), 7.32 (s, 1H, $H_2$), 7.30 (t, *J* = 7.20 Hz, 1H, $H_{Ph}$), 7.25 (s, 1H, $H_1$), 4.86 (s, 2H, $H_5$), 4.00 (s, 3H, $H_7$), 1.98 (s, 3H, $H_8$), 1.96 (s, 3H, $H_8$). $^{13}$C NMR (126 MHz, $CDCl_3$) δ (ppm) = 165.0 ($CO_2$), 160.7 ($C_q$), 147.3 ($C_q$), 145.3 ($C_q$), 142.6 ($C_q$), 141.3 ($C_q$), 133.4 ($C_2$), 133.1 ($C_q$), 132.7 ($C_q$), 129.0 (Ph), 128.0 (Ph), 125.5 (Ph), 125.3 ($C_4$), 124.9 ($C_3$), 122.1($C_1$), 119.8 ($C_q$), 90.6 (≡C-py), 87.4 (≡C-thio), 64.5 ($CH_2OH$), 53.0 ($OCH_3$), 14.6 (Me), 14.5 (Me), 7 quaternary carbons from the

perfluorocyclopentene ring and the connected thiophene carbons are not observed because of $^{13}C$-$^{19}F$ coupling. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ (ppm) = -110.11 (m, 2F), -110.24 (m, 2F), -131.86 (quintet, *J* = 5.34 Hz, 2F). IR (ν $cm^{-1}$): 2166 (C≡C), 1728 (C=O), 1595 (C=N). HR-MS ESI ($CH_2Cl_2$/MeOH): *m/z* 634.0931 ($[M + H]^+$, Calcd 634.09291); 656.0763 ($[M + Na]^+$, Calcd 656.0759). **EA** C 58.83; H 3.65; S 10.19; N 2.20, **Calcd** for $C_{31}H_{21}F_6NO_3S_2$ C 58.76; H 3.34; S 10.12; N 2.21. UV-vis (DCM) $\lambda_{max}$ = 273 nm (ε = 28660 $mol^{-1}.L.cm^{-1}$).




**Compound 2.** To a solution of compound **1** (271 mg, 0.43 mmol) and $Et_3N$ (179 µL, 1.28 mmol, 3 eq) in THF (12.2 mL) at 0 °C was added dropwise mesyl chloride (43 µL, 0.56 mmol, 1.3 eq). The reaction was stirred at room temperature for 1h before addition of saturated $NaHCO_3$ (50 mL). The reaction mixture was extracted with $CH_2Cl_2$ (3 ×50 mL) and the combined organic phases were washed with $H_2O$ (2×50 mL), dried over $MgSO_4$ and solvents were evaporated to dryness to give compound **2** (295 mg, 0.41 mmol, 97%) as a green foam which was used in the next step without further purification. Rf ($CH_2Cl_2$/MeOH 100/1) = 0.88. $^1H$ NMR ((400 MHz, $CDCl_3$) *δ* 8.15 (s, 1H, $H_4$), 7.72 (s, 1H, $H_3$), 7.54 (d, *J* = 7.4 Hz, 2H, $H_{Ph}$), 7.43 – 7.36 (m, 3H, $H_{Ph}$), 7.32 (d, *J* = 7.2 Hz, 1H, $H_{Ph}$), 7.26 (s, 1H, $H_1$), 5.43 (s, 2H, $H_5$), 4.02 (s, 3H, $H_7$), 3.17 (s, 3H, $SCH_3$), 1.99 (s, 3H, $H_8$), 1.97 (s, 3H, $H_8$). $^{13}C$ NMR (125 MHz, $CDCl_3$) *δ* 164.7 (C=O), 154.9 ($C_q$), 148.0 ($C_q$), 145.6 ($C_q$), 142.7 ($C_q$), 141.3 ($C_q$), 133.7 ($C_2$), 133.5 ($C_q$), 133.1 ($C_q$), 129.0 (Ph), 128.1, 126.3, 126.0 (Ph+$C_3$+$C_4$), 125.6 (Ph), 125.4 (Cq), 122.1 ($C_1$), 119.6 ($C_q$), 90.3 (≡C-py), 88.4 (≡C-thio), 70.5 ($C_5$), 53.2 ($C_7$), 38.1 ($SCH_3$), 14.6 ($C_8$), signals of *C*$F_2$ and *C*-$CF_2$ are not observed)..

## 2. NMR spectra and HRMS of new compounds

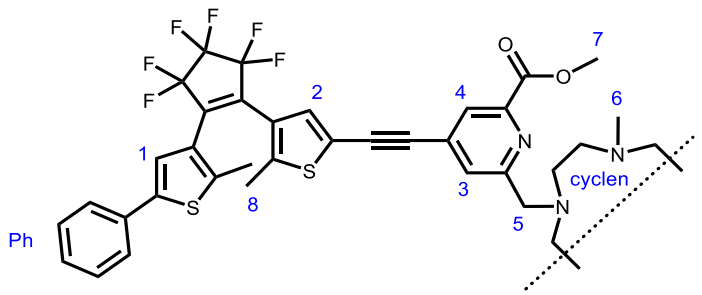



Chart S1. Numbering used for NMR assignment.

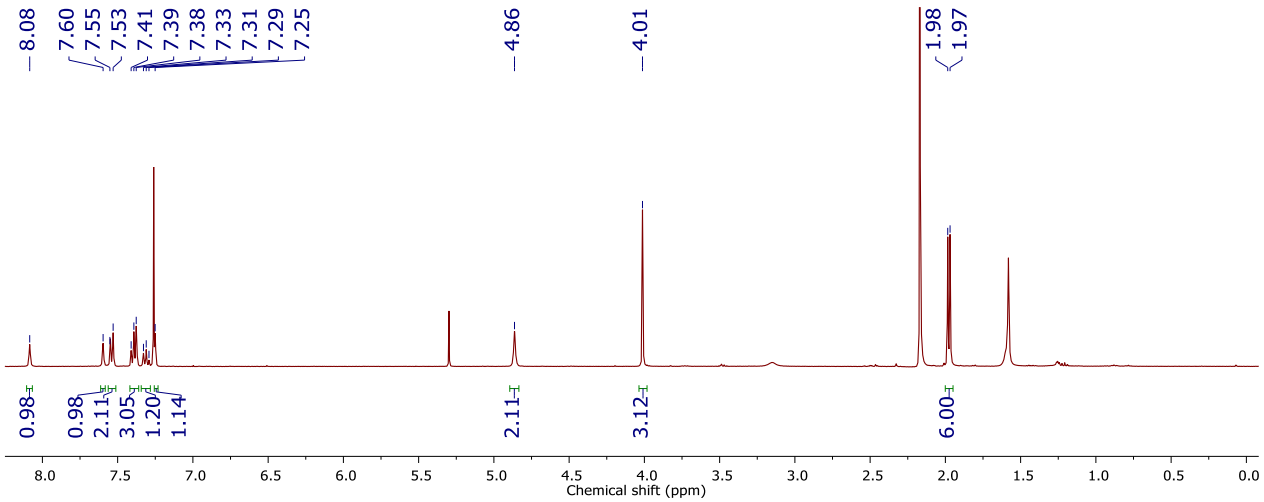



Figure S1: $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **1** in $CDCl_3$. $\delta$ (ppm) = 8.07 (s, 1H, $H_4$), 7.60 (s, 1H, $H_3$), 7.54 (d, $J$ = 7.32 Hz, 2H, $H_{Ph}$), 7.39 (t, $J$ = 7.76 Hz, 2H, $H_{Ph}$), 7.32 (s, 1H, $H_2$), 7.30 (t, $J$ = 7.20 Hz, 1H, $H_{Ph}$), 7.25 (s, 1H, $H_1$), 4.86 (s, 2H, $H_5$), 4.00 (s, 3H, $H_7$), 1.98 (s, 3H, $H_8$), 1.96 (s, 3H, $H_8$).

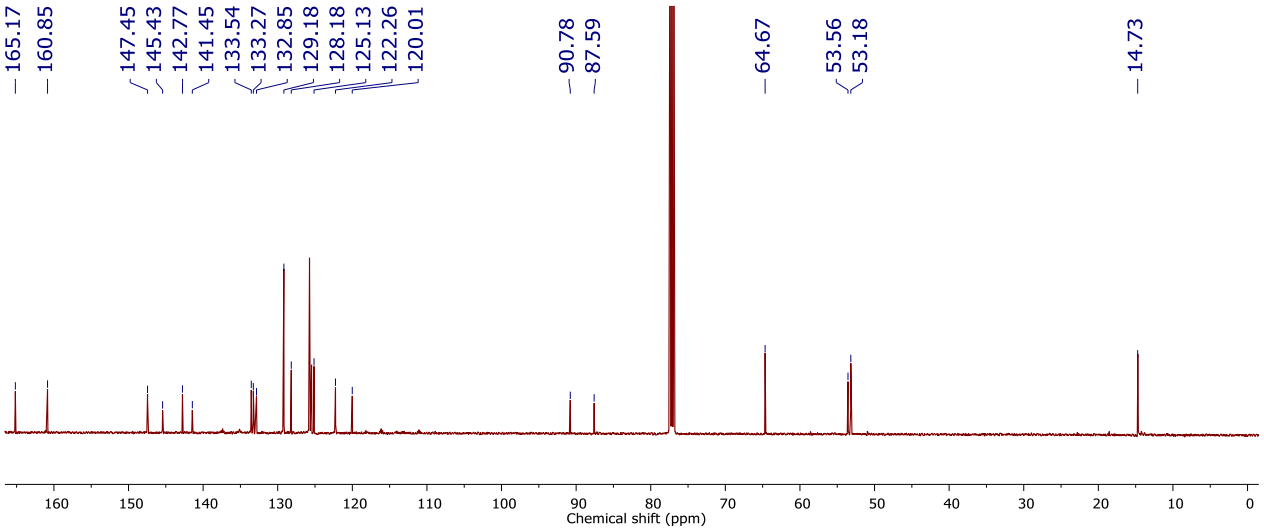



Figure S2: $^{13}$C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of compound **1** in $CDCl_3$. $\delta$ 165.0 ($CO_2$), 160.7 ($C_q$), 147.3 ($C_q$), 145.3 ($C_q$), 142.6 ($C_q$), 141.3 ($C_q$), 133.4 ($C_2$), 133.1 ($C_q$), 132.7 ($C_q$), 129.0 (Ph), 128.0 (Ph), 125.5 (Ph), 125.3 ($C_4$), 124.9 ($C_3$), 122.1($C_1$), 119.8 ($C_q$), 90.6 (≡C-py), 87.4 (≡C-thio), 64.5 ($C_5$), 53.0 ($C_7$), 14.6 ($C_8$), 14.5 ($C_8$), 7 quaternary carbons from the perfluorocyclopentene ring and the connected thiophene carbons are not observed because of $^{13}$C-$^{19}$F coupling.

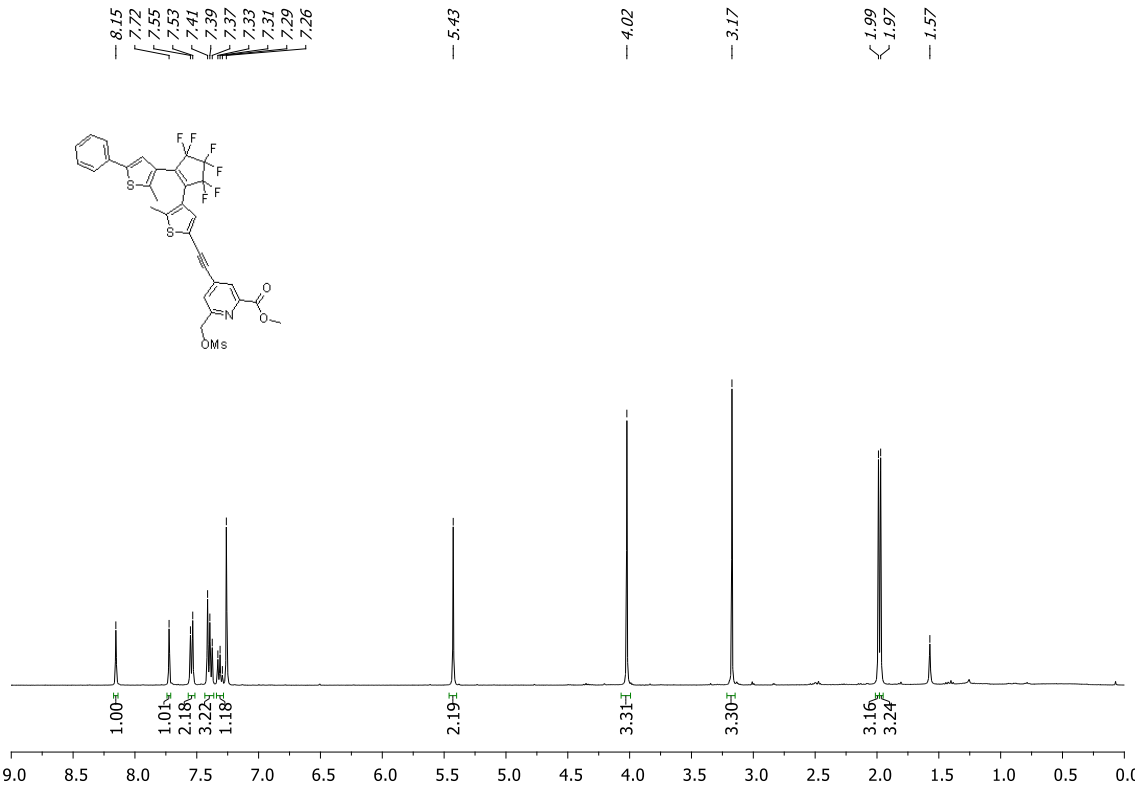



Figure S3: $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **2**. $\delta$ 8.15 (s, 1H, $H_4$), 7.72 (s, 1H, $H_3$), 7.54 (d, $J$ = 7.4 Hz, 2H, $H_{Ph}$), 7.43 – 7.36 (m, 3H, $H_{Ph}$), 7.32 (d, $J$ = 7.2 Hz, 1H, $H_{Ph}$), 7.26 (s, 1H, $H_1$), 5.43 (s, 2H, $H_5$), 4.02 (s, 3H, $H_7$), 3.17 (s, 3H, $SCH_3$), 1.99 (s, 3H, $H_8$), 1.97 (s, 3H, $H_8$).

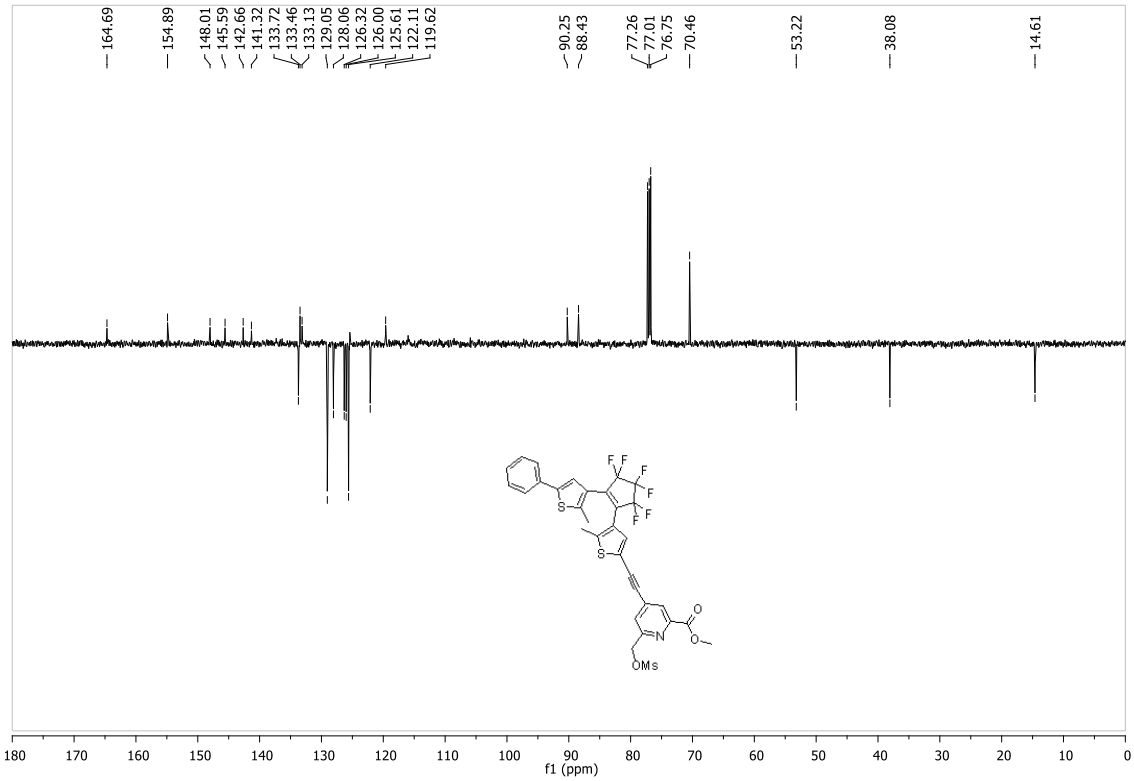



Figure S4: $^{13}$C NMR (125 MHz, $CDCl_3$, 298 K) of compound **2**. $\delta$ 164.7 (C=O), 154.9 ($C_q$), 148.0 ($C_q$), 145.6 ($C_q$), 142.7 ($C_q$), 141.3 ($C_q$), 133.7 ($C_2$), 133.5 ($C_q$), 133.1 ($C_q$), 129.0 (Ph), 128.1, 126.3, 126.0 (Ph+$C_3$+$C_4$), 125.6 (Ph), 125.4 ($C_q$), 122.1 ($C_1$), 119.6 ($C_q$), 90.3 (≡C-py), 88.4 (≡C-thio), 70.5 ($C_5$), 53.2 ($C_7$), 38.1 ($SCH_3$), 14.6 ($C_8$), signals of *C*$F_2$ and *C*-$CF_2$ are not observed)..

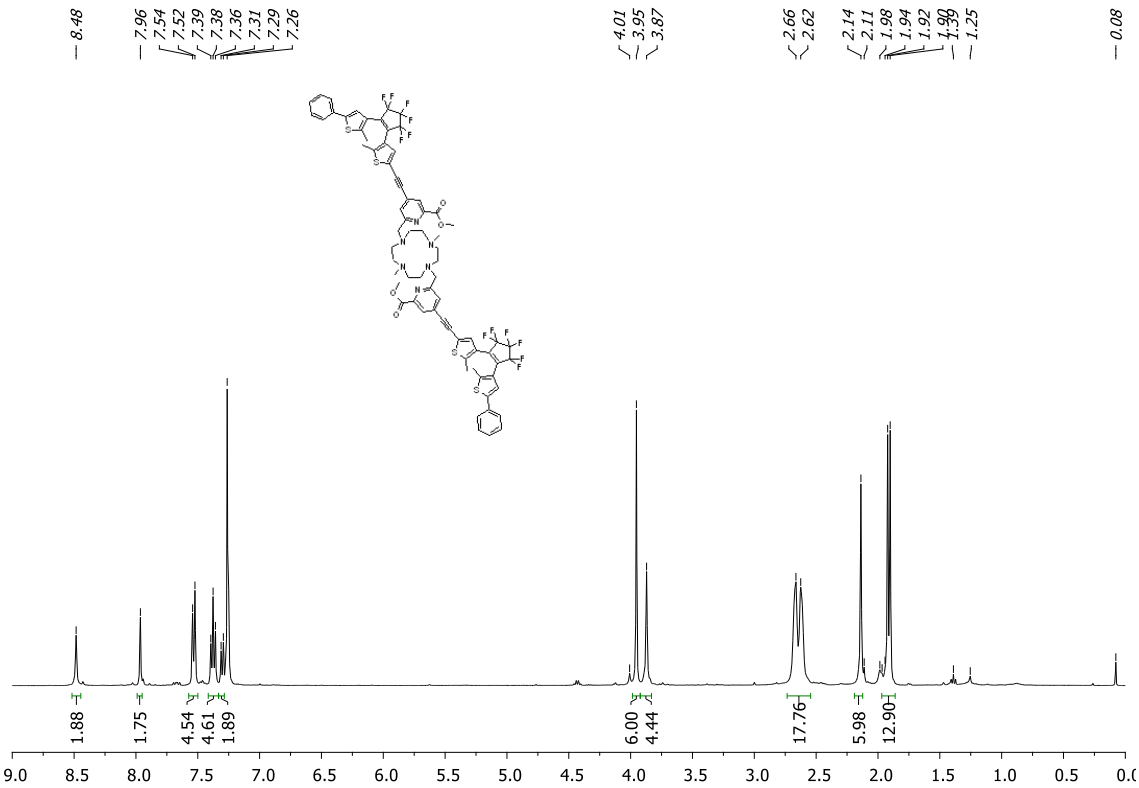



Figure S5: $^1$H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **3**. $\delta$ 8.48 (s, 2H, $H_4$), 7.96 (s, 2H, $H_3$), 7.53 (d, $J$ = 7.6 Hz, 5H, Ar), 7.38 (t, $J$ = 7.6 Hz, 5H, Ar), 7.30 (d, $J$ = 7.2 Hz, 2H), 7.26 (s, 2H, $H_1$), 3.95 (s, 6H, $H_7$), 3.87 (s, 4H, $H_5$), 2.66 (br s, 8H, $CH_2$ cyclen), 2.63 (brs, 8H, $CH_2$ cyclen), 2.13 (s, 6H, 2* $H_6$), 1.92 (s, 6H, $H_8$), 1.90 (s, 6H, 2* $H_8$)

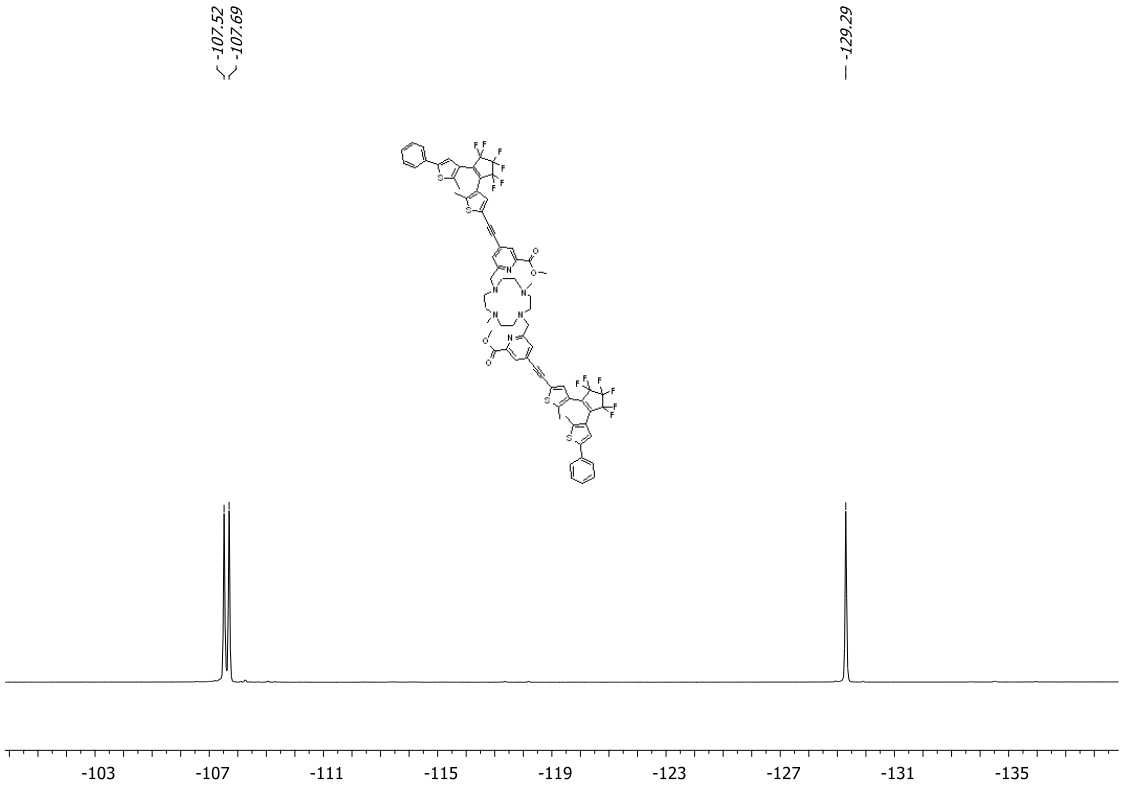



Figure S6: $^{19}$F NMR (282 MHz, $CDCl_3$, 298 K) spectrum of compound **3** in $CDCl_3$.

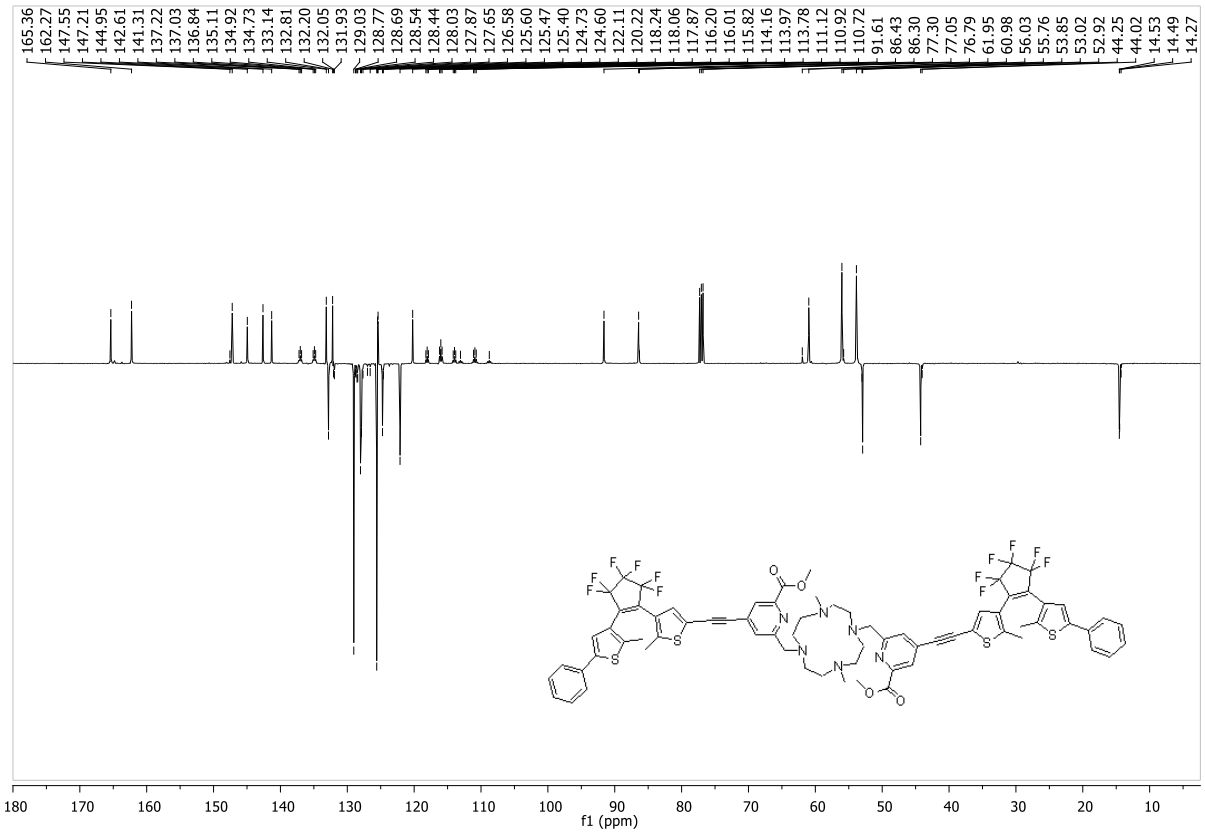



Figure S7: $^{13}$C NMR (125 MHz, $CDCl_3$, 298 K) spectrum **3**. $\delta$ 165.4 (C=O), 162.3, 147.2, 144.9, 142.6, 141.3 ($C_q$), 137.1 (t, $J$ = 23 Hz, $\underline{C_q}$-$CF_2$), 134.9 (t, $J$ = 23 Hz, $\underline{C_q}$-$CF_2$), 133.2 ($C_q$), 132.8 ($C_2$), 132.2 ($C_q$), 129.1 (Ph), 128.1, 127.9 (Ph+$C_3$), 125.6 (Ph), 125.5, 125.4 ($C_q$), 124.7 (Ph), 122.1 ($C_1$), 120.2 ($C_q$), 116.0 (tt, $^1J_{C\text{-}F}$ = 255 Hz, $^2J_{C\text{-}F}$ = 23 Hz, external $CF_2$), 110.9 (tquint, $^1J_{C\text{-}F}$ = 270 Hz, $^2J_{C\text{-}F}$ = 25 Hz, central $CF_2$), 91.7, 86.5 (alkyne), 61.0 ($C_5$), 56.1, 53.9 ($CH_2$ cyclen), 52.9 ($C_7$), 44.3 ($C_6$), 14.54, 14.49 ($C_8$).

**Acquisition Parameter**

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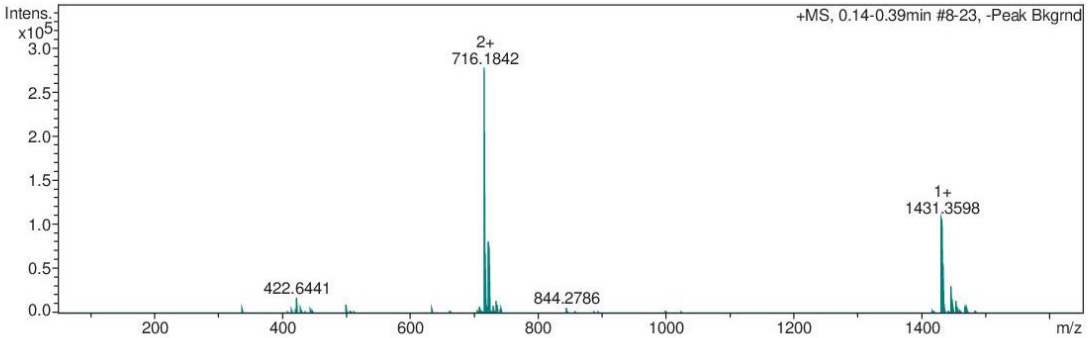


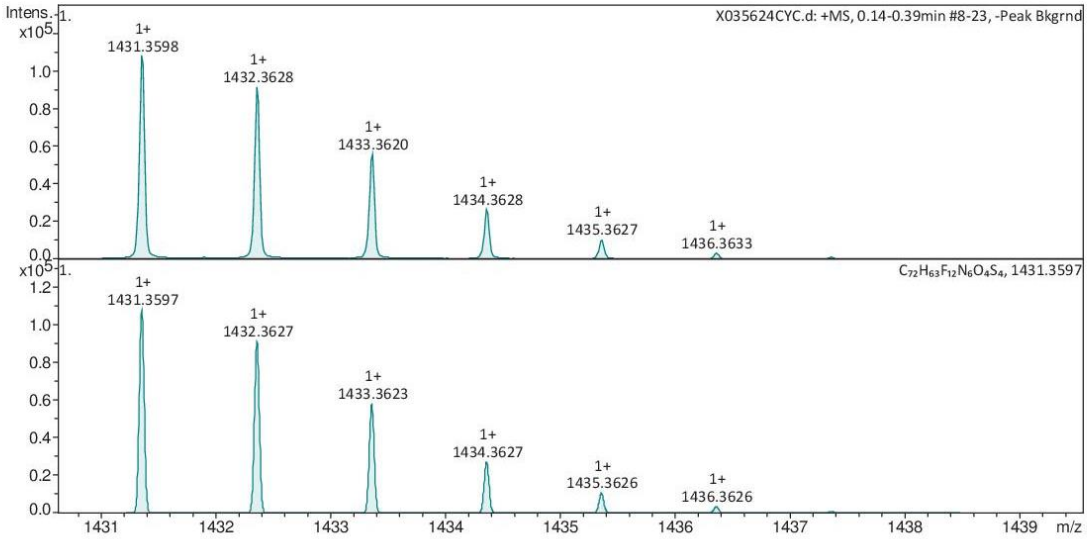


| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
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| | 2+ | 2 | C71H68F12N2O8S4 | 716.182796 | -1.9 | 10.4 | 34.0 | even |
| | 2+ | 3 | C73H60F12N10S4 | 716.184134 | -0.0 | 13.5 | 44.0 | even |
| | 2+ | 4 | C76H68F12O6S4 | 716.184808 | 0.9 | 18.9 | 38.0 | even |
| | 2+ | 5 | C77H64F12N4O2S4 | 716.185476 | 1.8 | 28.7 | 43.0 | even |
| 723.192005 | 2+ | 1 | C74H62F12N10S4 | 723.191959 | -0.1 | 8.3 | 44.0 | even |
| | 2+ | 2 | C77H70F12O6S4 | 723.192633 | 0.9 | 10.6 | 38.0 | even |
| | 2+ | 3 | C78H66F12N4O2S4 | 723.193301 | 1.8 | 12.2 | 43.0 | even |

| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| | 2+ | 4 | C73H66F12N6O4S4 | 723.191290 | -1.0 | 18.6 | 39.0 | even |
| | 2+ | 5 | C72H70F12N2O8S4 | 723.190621 | -1.9 | 29.3 | 34.0 | even |
| 1431.359806 | 1+ | 1 | C72H63F12N6O4S4 | 1431.359654 | -0.1 | 9.2 | 39.0 | even |
| | 1+ | 2 | C71H67F12N2O8S4 | 1431.358316 | -1.0 | 12.4 | 34.0 | even |
| | 1+ | 3 | C73H59F12N10S4 | 1431.360991 | 0.8 | 16.0 | 44.0 | even |
| | 1+ | 4 | C76H67F12O6S4 | 1431.362339 | 1.8 | 21.9 | 38.0 | even |
| 1445.375536 | 1+ | 1 | C73H65F12N6O4S4 | 1445.375304 | -0.2 | 13.4 | 39.0 | even |
| | 1+ | 2 | C72H69F12N2O8S4 | 1445.373966 | -1.1 | 16.2 | 34.0 | even |
| | 1+ | 3 | C74H61F12N10S4 | 1445.376641 | 0.8 | 18.5 | 44.0 | even |
| | 1+ | 4 | C77H69F12O6S4 | 1445.377989 | 1.7 | 24.9 | 38.0 | even |
| 1453.342014 | 1+ | 1 | C76H66F12NaO6S4 | 1453.344283 | 1.6 | 11.7 | 38.0 | even |
| | 1+ | 2 | C73H58F12N10NaS4 | 1453.342935 | 0.6 | 14.9 | 44.0 | even |
| | 1+ | 3 | C72H62F12N6NaO4S4 | 1453.341598 | -0.3 | 21.6 | 39.0 | even |
| | 1+ | 4 | C71H66F12N2NaO8S4 | 1453.340260 | -1.2 | 30.8 | 34.0 | even |

Figure S8: HRMS data of compound **3**

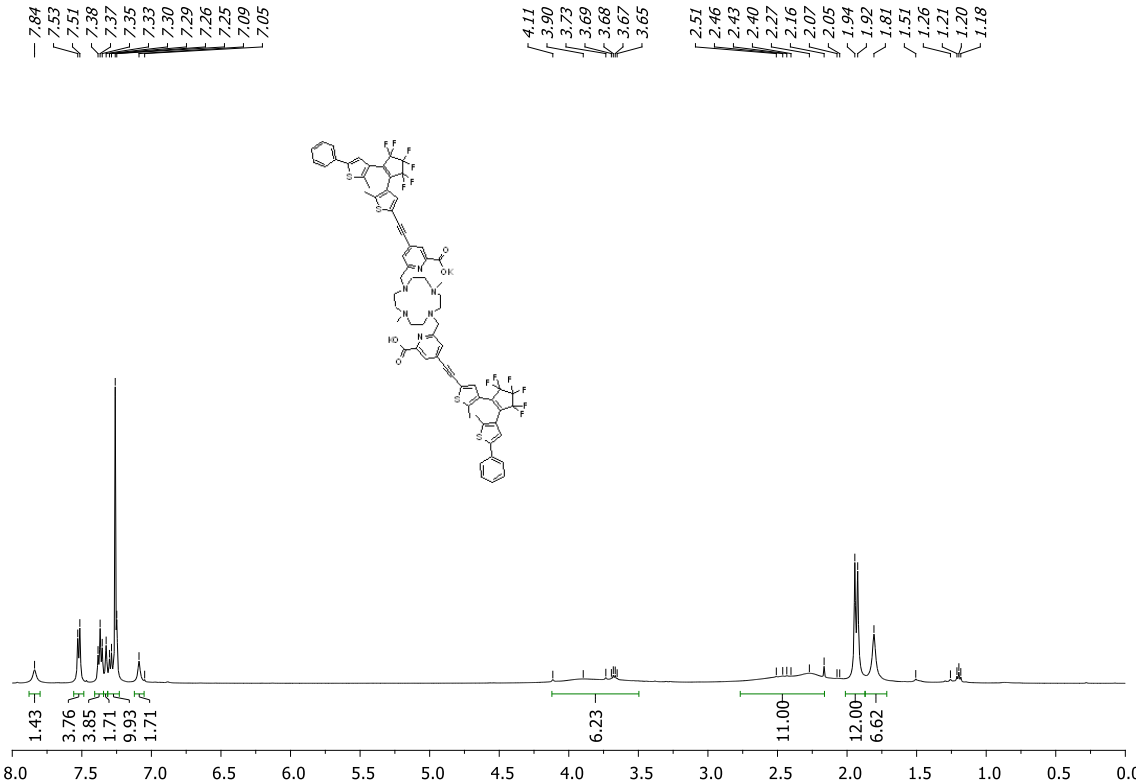


Figure S9: $^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **$L_{oo}$**. $\delta$ 7.84 (s, 2H, $H_4$), 7.52 (d, $J$ = 7.5 Hz, 4H, Ph), 7.37 (t, $J$ = 7.5 Hz, 4H, Ph), 7.33 (s, 2H, $H_2$), 7.31 – 7.23 (m, 4H, Ph, $H_3$), 7.09 (s, 2H, $H_1$), 4.12 - 2.16 ($CH_2$ of the cyclen), 1.94 (s, 6H, 2* $H_8$), 1.92 (s, 6H, 2* $H_8$), 1.81 (s, 6H, 2* $H_6$).

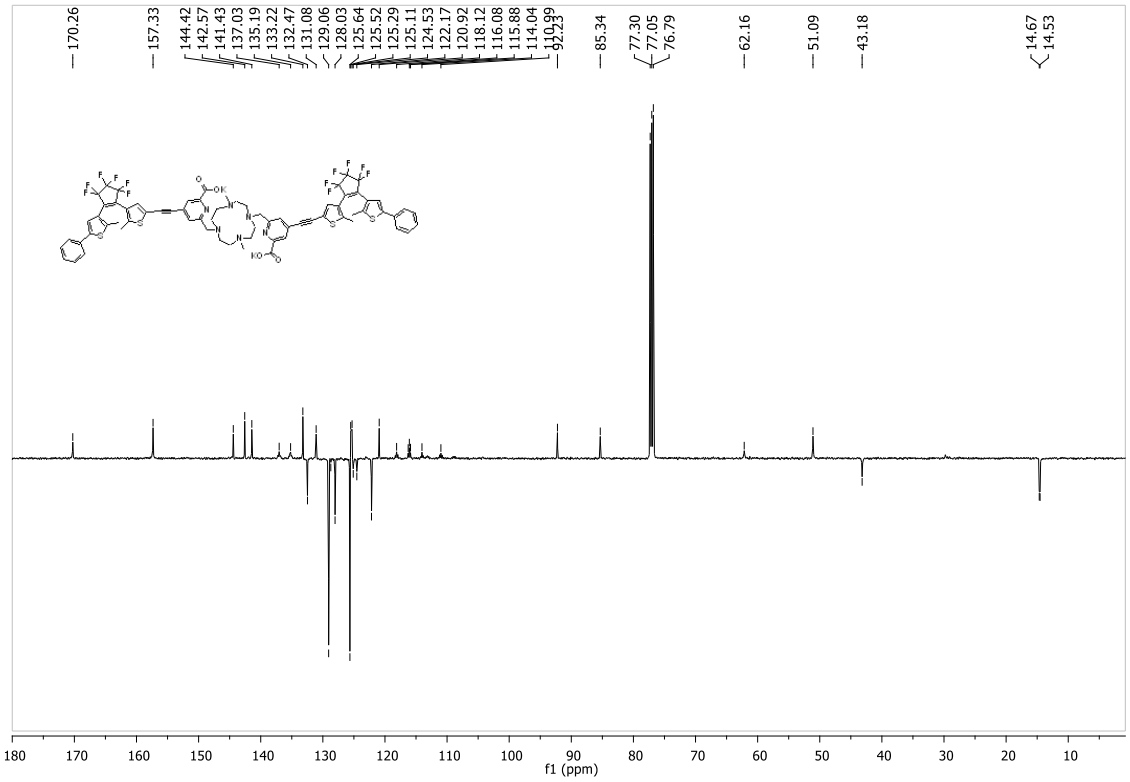


Figure S10: $^{13}$C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of compound **L$_{oo}$**. $\delta$ 170.3 (C=O), 157.3, 144.4, 142.6, 141.4 ($C_q$), 137.0 (t, $J$ = 23 Hz, $\underline{C_q}$-$CF_2$), 135.2 (t, $J$ = 23 Hz, $\underline{C_q}$-$CF_2$), 133.2 ($C_q$), 132.5 ($C_2$), 131.1 ($C_q$), 129.1 (Ph), 128.0 (Ph+$C_3$), 125.6 (Ph), 125.5, 125.3 ($C_q$), 124.5 ($C_4$), 122.2 ($C_1$), 120.9 ($C_q$), 116.0 (tt, $^1J_{C\text{-}F}$ = 255 Hz, $^2J_{C\text{-}F}$ = 25 Hz, external $CF_2$), 110.9 (tquint, $^1J_{C\text{-}F}$ = 270 Hz, $^2J_{C\text{-}F}$ = 25 Hz, central $CF_2$), 92.2, 85.3 (alkyne), 62.1 ($C_5$), 51.1 ($CH_2$ cyclen), 43.2 ($C_6$), 14.7 ($C_8$), 14.5 ($C_8$).

**Acquisition Parameter**

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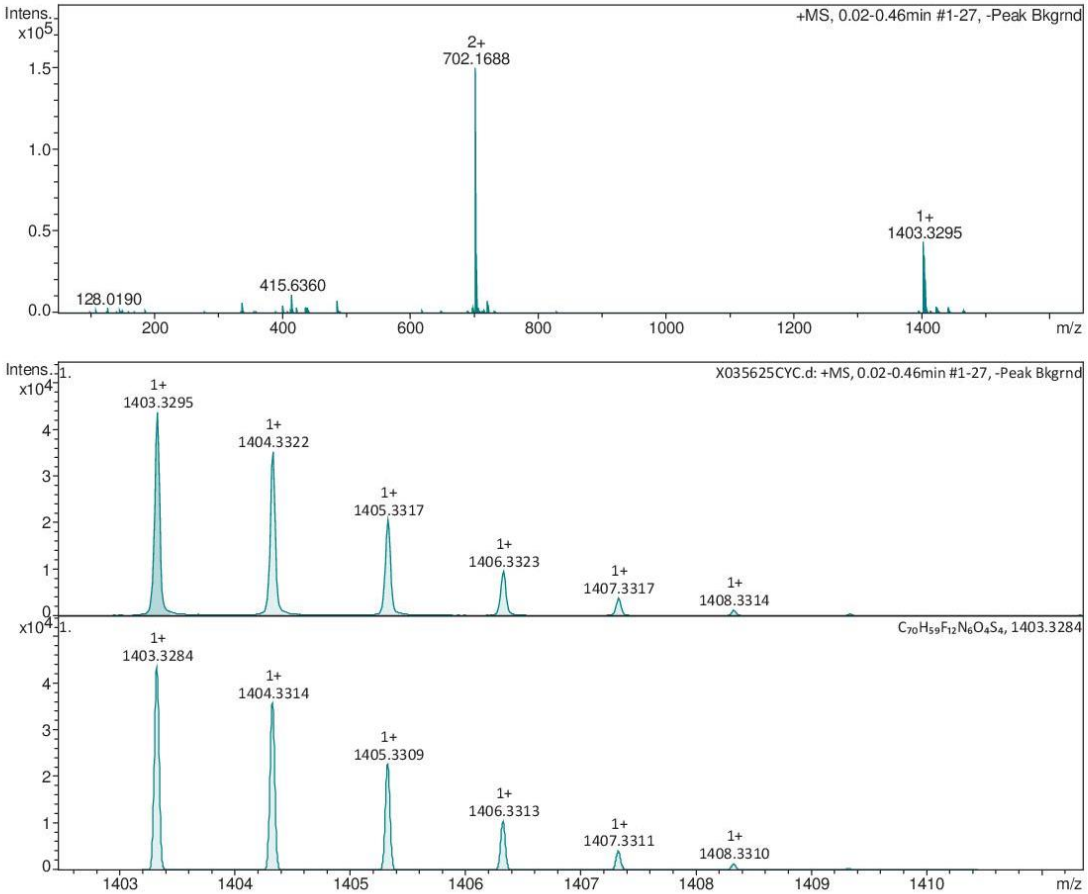
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.6 Bar |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan End | 2500 m/z | Set Collision Cell RF | 1800.0 Vpp | Set Dry Gas | 7.0 l/min |




| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| 702.168776 | 2+ | 1 | C71H56F12N10S4 | 702.168484 | -0.4 | 8.0 | 44.0 | even |
| | 2+ | 2 | C74H64F12O6S4 | 702.169158 | 0.5 | 13.9 | 38.0 | even |
| | 2+ | 3 | C70H60F12N6O4S4 | 702.167815 | -1.4 | 14.4 | 39.0 | even |
| | 2+ | 4 | C75H60F12N4O2S4 | 702.169826 | 1.5 | 18.7 | 43.0 | even |
| 1403.329545 | 1+ | 1 | C69H63F12N2O8S4 | 1403.327016 | -1.8 | 15.9 | 34.0 | even |
| | 1+ | 2 | C70H59F12N6O4S4 | 1403.328353 | -0.8 | 20.9 | 39.0 | even |
| | 1+ | 3 | C71H55F12N10S4 | 1403.329691 | 0.1 | 29.3 | 44.0 | even |
| | 1+ | 4 | C74H63F12O6S4 | 1403.331039 | 1.1 | 34.7 | 38.0 | even |

Figure S11: HRMS data of $\mathbf{L_{oo}}$.

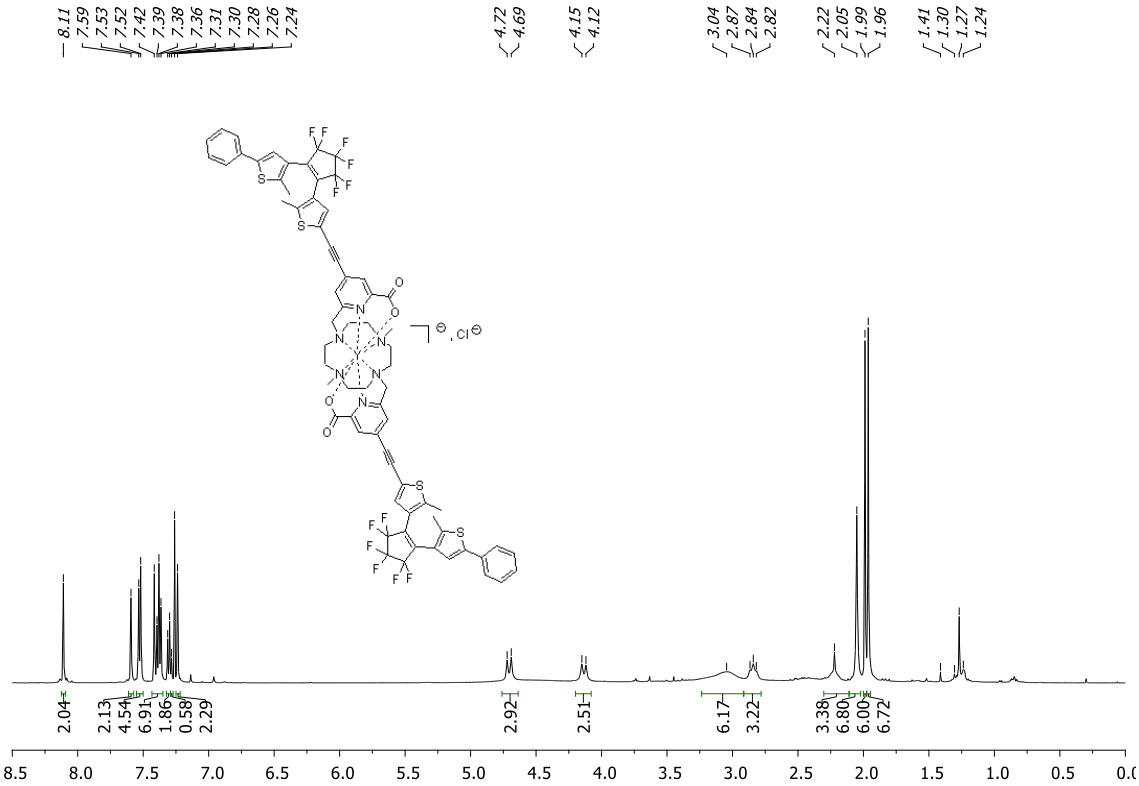


Figure S12: $^{1}$H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **[YL$_{oo}$]Cl**.

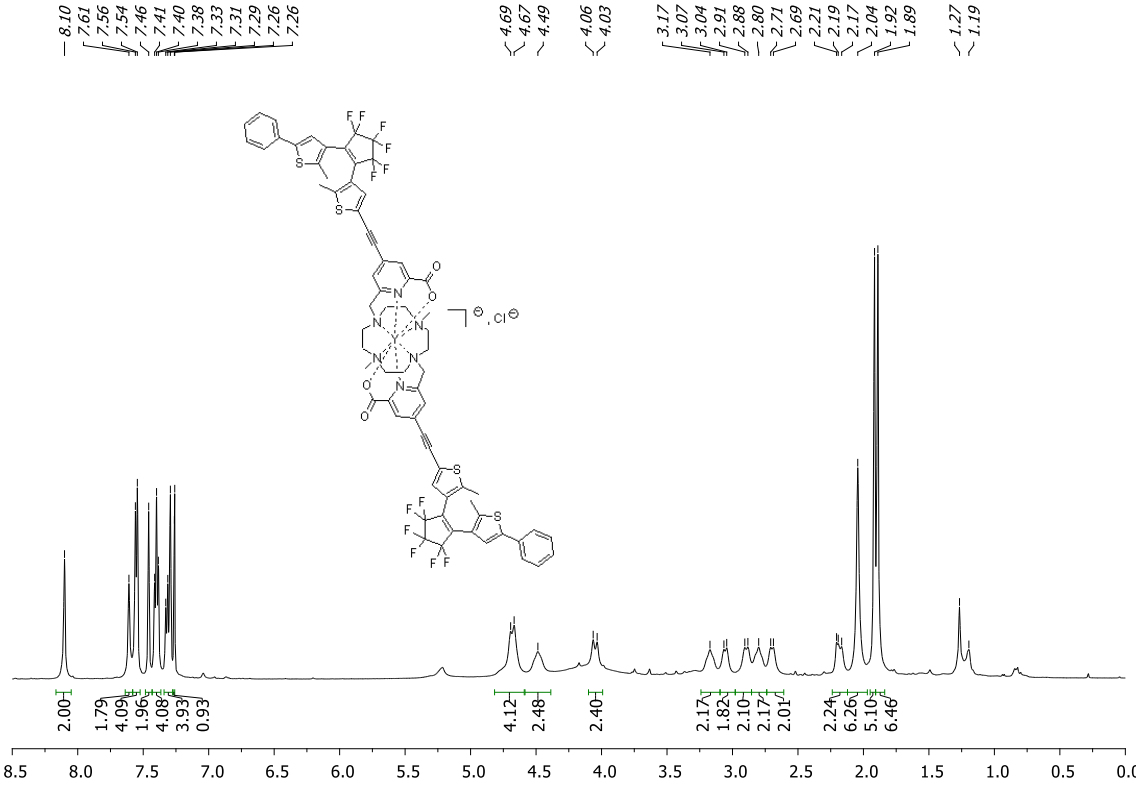


Figure S13: $^{1}$H NMR (500 MHz, $CDCl_3$, 253 K) spectrum of compound **[YL$_{oo}$]Cl**. $\delta$ 8.10 (s, 2H), 7.61 (s, 2H), 7.55 (d, $J$ = 7.5 Hz, 4H), 7.46 (s, 2H), 7.40 (t, $J$ = 7.2 Hz, 4H), 7.32 (d, $J$ = 7.7 Hz, 2H), 7.29 (s, 2H), 4.68 (d, $J$ = 13.3 Hz, 4H), 4.49 (br s, 2H), 4.05 (d, $J$ = 15.2 Hz, 2H), 3.17 (br s, 2H), 3.05 (d, $J$ = 10.7 Hz, 2H), 2.89 (d, $J$ = 11.8 Hz, 2H), 2.80 (s, 2H), 2.70 (d, $J$ = 10.5 Hz, 2H), 2.24 – 2.12 (m, 2H), 2.04 (s, 6H, $H_6$), 1.92 (s, 6H, $H_8$), 1.89 (s, 6H, $H_8$).

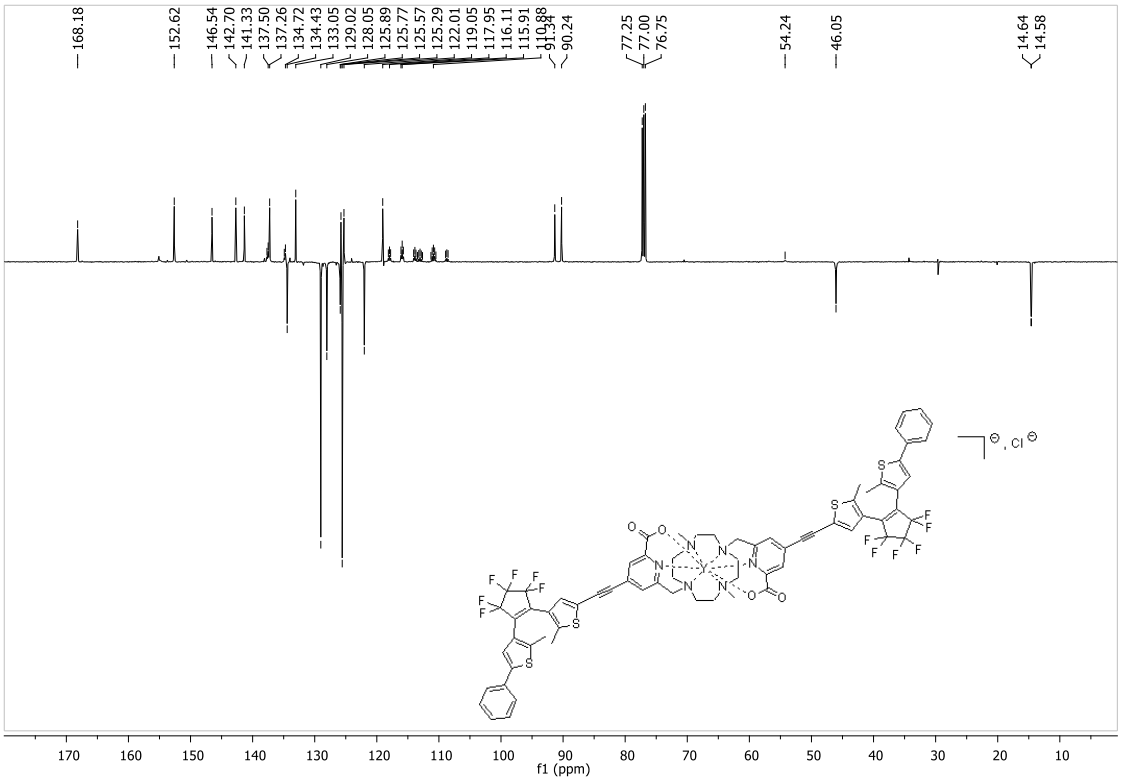



Figure S14: $^{13}$C NMR (125 MHz, $CDCl_3$, 298 K, J-mod) spectrum of compound **[YL$_{oo}$]Cl**. $\delta$ 168.2 (C=O), 152.6, 146.5, 142.7, 141.3 ($C_q$), 137.6 (m, $\underline{C_q}$-$CF_2$), 137.3 (Cq), 134.8 (m, $\underline{C_q}$-$CF_2$), 134.4 ($C_2$), 133.1 ($C_q$), 129.0, 128.1 , 125.9 (Ph + $C_3$+$C_4$), 125.8 ($C_q$), 125.6 (Ph), 125.3 ($C_q$), 122.0 ($C_1$), 119.1 ($C_q$), 115.9 (tt, $^{1}J_{C\text{-}F}$ = 255 Hz, $^{2}J_{C\text{-}F}$ = 25 Hz, external $CF_2$), 110.9 (tquint, $^{1}J_{C\text{-}F}$ = 270 Hz, $^{2}J_{C\text{-}F}$ = 25 Hz, central $CF_2$), 91.3, 90.2 (Cq alkyne), 54.2 ($CH_2$ cyclen), 46.1 ($C_6$), 14.64 ($C_8$), 14.58 ($C_8$).

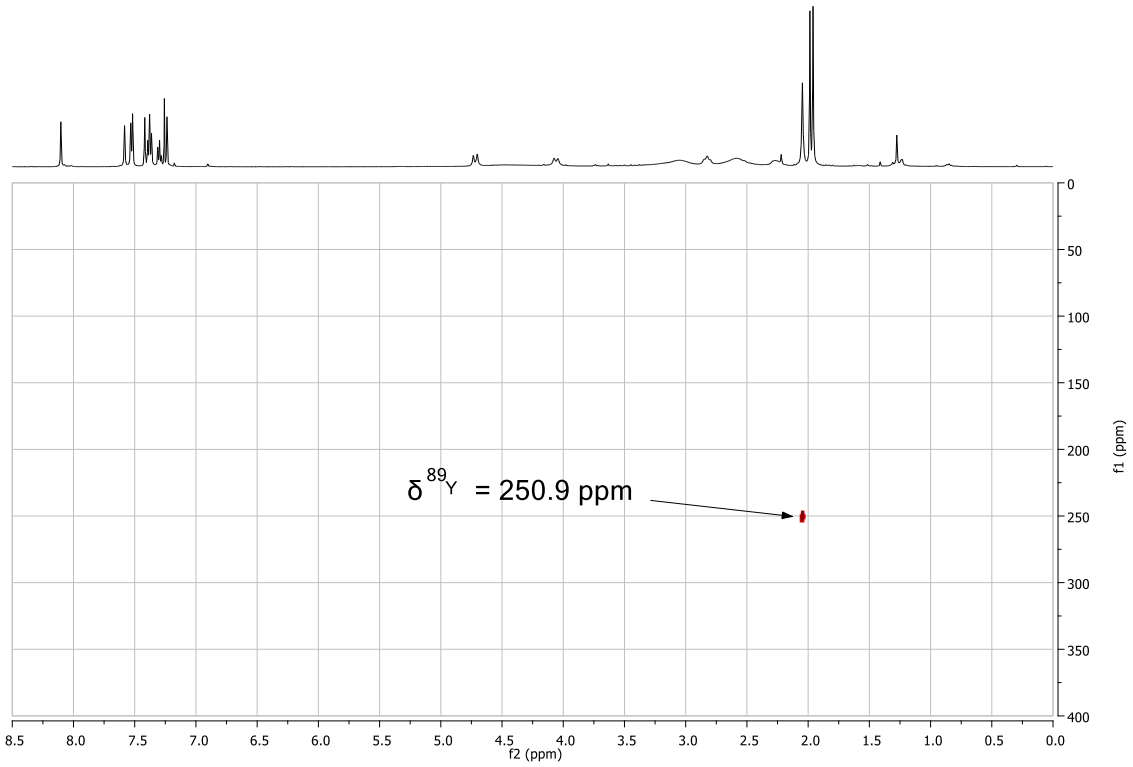



Figure S15: HMBC $^{1}H/^{89}Y$ ($CDCl_3$, 298 K) spectrum of compound **[YL$_{oo}$]Cl**.

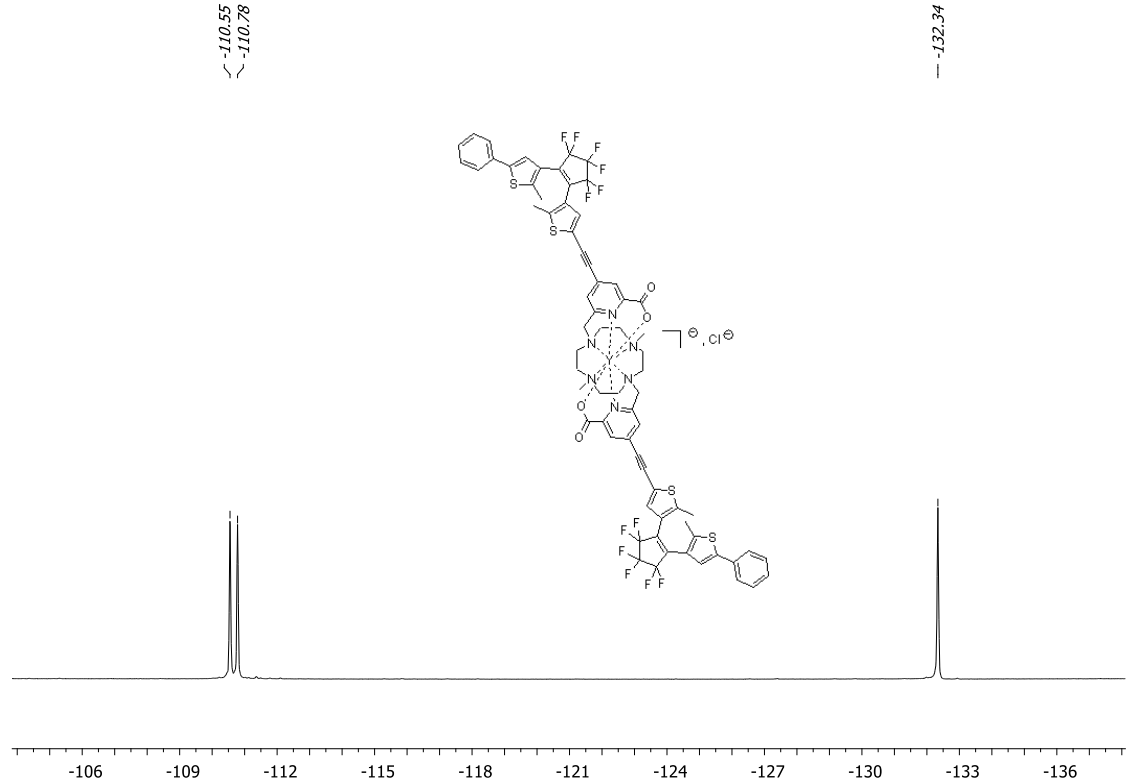
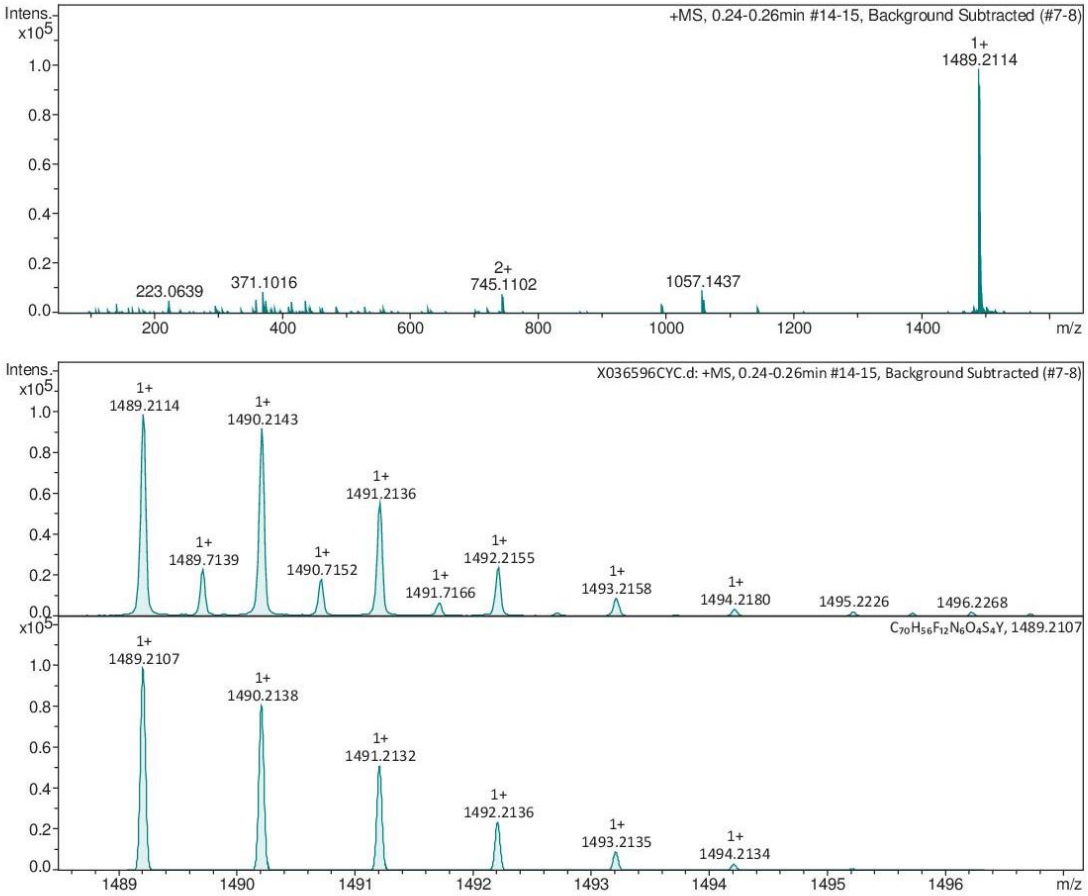



Figure S16: $^{19}F$ NMR (376 MHz, $CDCl_3$, 298 K) spectrum of compound **[YL$_{oo}$]Cl**.

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.6 Bar |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan End | 2500 m/z | Set Collision Cell RF | 1800.0 Vpp | Set Dry Gas | 7.0 l/min |




| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| 745.110227 | 2+ | 1 | C70H57F12N6O4S4Y | 745.109002 | -1.6 | 24.3 | 41.0 | even |
| | 2+ | 2 | C74H61F12O6S4Y | 745.110344 | 0.2 | 30.1 | 40.0 | even |
| | 2+ | 3 | C75H57F12N4O2S4Y | 745.111013 | 1.1 | 35.5 | 45.0 | even |
| 1489.211384 | 1+ | 1 | C74H60F12O6S4Y | 1489.213412 | 1.4 | 38.5 | 40.0 | even |
| | 1+ | 2 | C70H56F12N6O4S4Y | 1489.210727 | -0.4 | 49.5 | 41.0 | even |

Figure S17: HRMS data of **[YL$_{oo}$]Cl.**

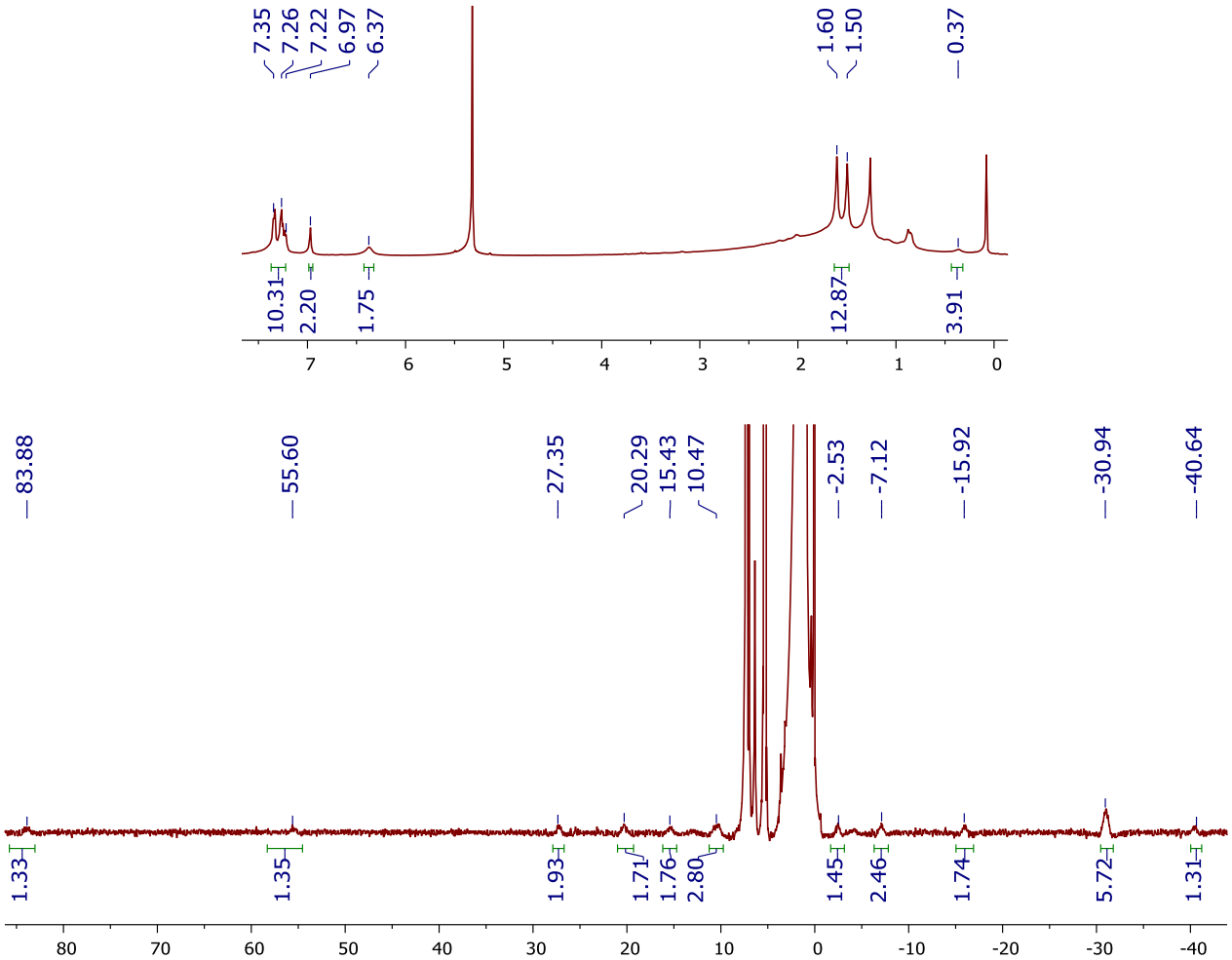



Figure S18: $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 298 K) spectrum of compound **[YbL$_{oo}$]Cl**. $\delta$ 83.88 (2H, $H_3/H_4$), 55.60 (2H, $H_3/H_4$), 27.35 (2H, $H_{cyclen}$), 20.29 (2H, $H_{cyclen}$), 15.43 (2H, $H_{cyclen}$), 10.47 (2H, $H_{cyclen}$), 7.35-7.22 (10H, $H_{ph}$), 6.97 (2H, $H_2$), 6.37 (2H, $H_1$), 1.60-1.50 (12H, 2*$H_8$), -2.53 (2H, $H_{cyclen}$), -7.12 (2H, $H_{cyclen}$), -15.92 (2H, $H_{cyclen}$), -30.94 (6H, $H_6$), -40.64 (2H, $H_{cyclen}$).

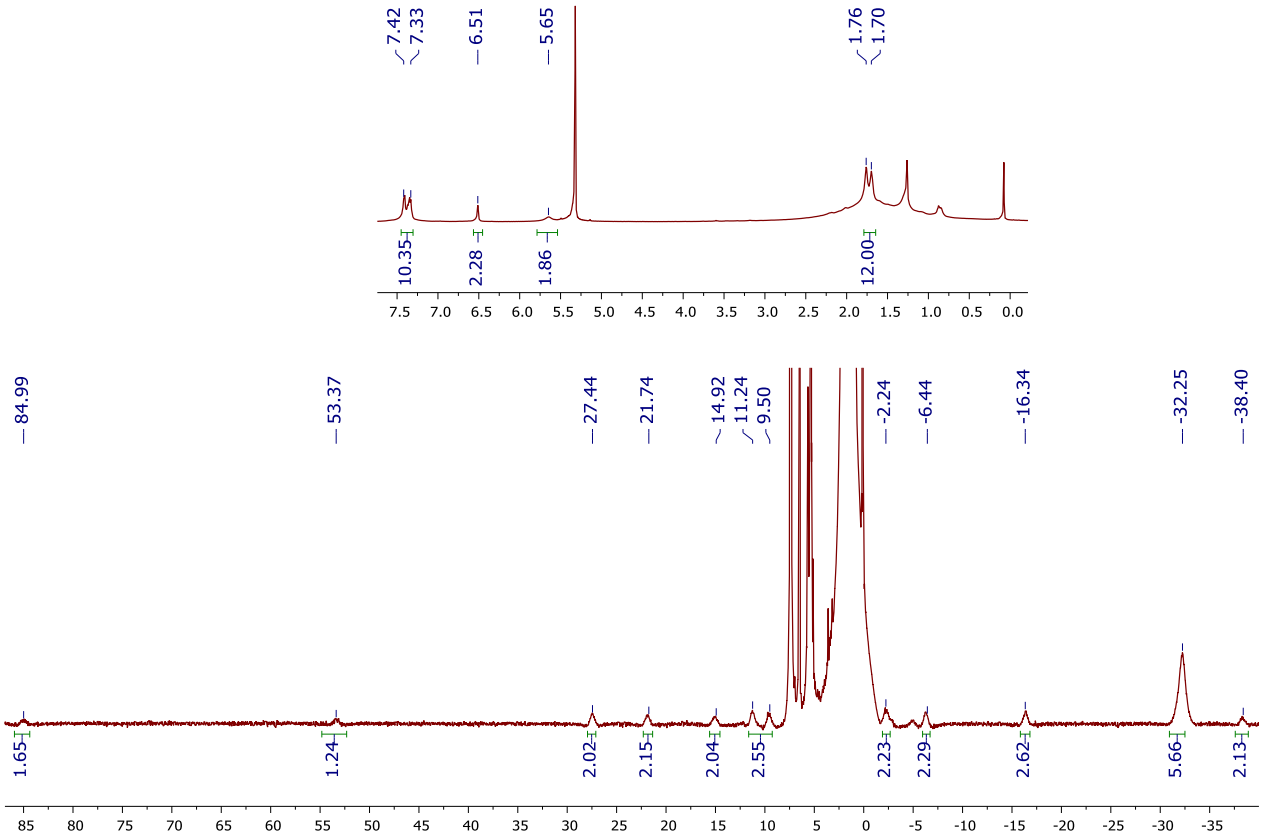
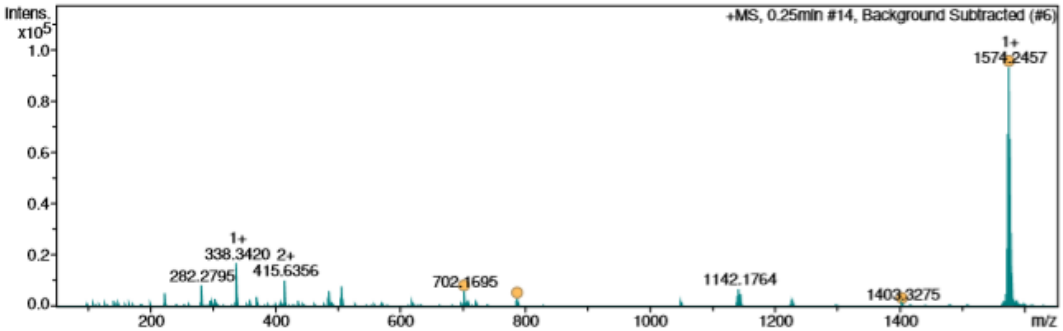
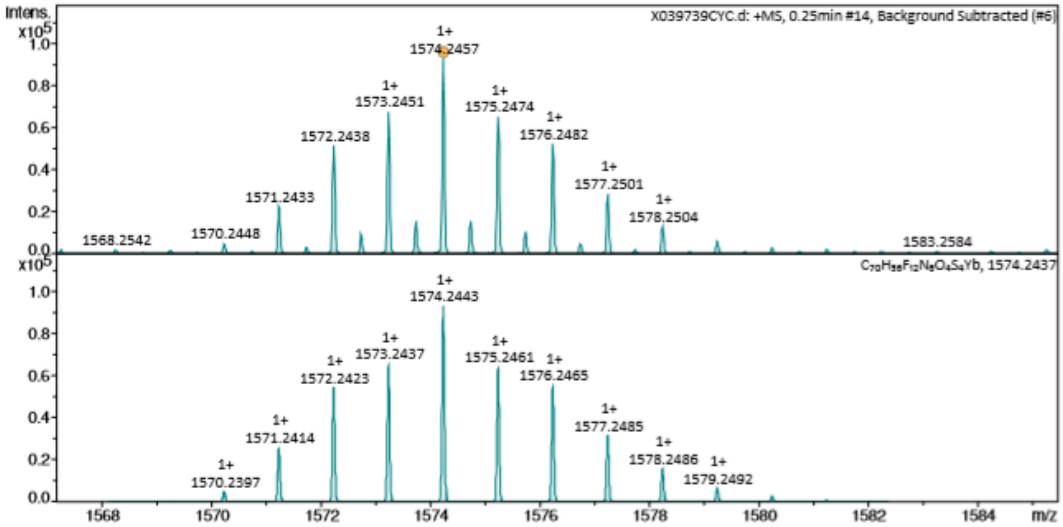



Figure S19: $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 298K) spectrum of compound **[YbL$_{cc}$]Cl.** $\delta$ 84.99 (2H, $H_3/H_4$), 53.37 (2H, $H_3/H_4$), 27.44 (2H, $H_{cyclen}$), 21.74 (2H, $H_{cyclen}$), 14.92 (2H, $H_{cyclen}$), 11.24-9.50 (2H, $H_{cyclen}$), 7.42-7.33 (10H, $H_{ph}$), 6.51 (2H, $H_2$), 5.65 (2H, $H_1$), 1.76-1.70 (12H, 2*$H_8$), -2.24 (2H, $H_{cyclen}$), -6.44 (2H, $H_{cyclen}$), -16.34(2H, $H_{cyclen}$), -32.25 (6H, $H_6$), -38.40 (2H, $H_{cyclen}$).

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.6 Bar |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan End | 2500 m/z | Set Collision Cell RF | 1800.0 Vpp | Set Dry Gas | 7.0 l/min |




| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| 702.169463 | 2+ | 1 | C75H60F12N4O2S4 | 702.169826 | 0.5 | 45.2 | 43.0 | even |
| | 2+ | 2 | C74H64F12O6S4 | 702.169158 | -0.4 | 50.6 | 38.0 | even |
| | 2+ | 3 | C70H60F12N6O4S4 | 702.167815 | -2.3 | 57.5 | 39.0 | even |
| 787.627740 | 2+ | 1 | C80H57F12N2S4Yb | 787.629531 | 2.8 | 50.2 | 48.5 | odd |
| | 2+ | 2 | C75H57F12N4O2S4Yb | 787.627520 | 0.1 | 50.5 | 44.5 | odd |
| | 2+ | 3 | C74H61F12O6S4Yb | 787.626851 | -0.7 | 51.3 | 39.5 | odd |
| | 2+ | 4 | C70H57F12N6O4S4Yb | 787.625508 | -2.5 | 52.5 | 40.5 | odd |
| | 2+ | 5 | C67H65F12O11S4Yb | 787.629788 | 3.0 | 56.0 | 30.5 | odd |

| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| | 2+ | 6 | C63H61F12N6O9S4Yb | 787.628445 | 1.2 | 58.7 | 31.5 | odd |
| | 2+ | 7 | C62H65F12N2O13S4Yb | 787.627776 | 0.3 | 60.9 | 26.5 | odd |
| 1403.327543 | 1+ | 1 | C69H63F12N2O8S4 | 1403.327016 | -0.4 | 110.8 | 34.0 | even |
| | 1+ | 2 | C70H59F12N6O4S4 | 1403.328353 | 0.6 | 115.0 | 39.0 | even |
| | 1+ | 3 | C81H59F12OS4 | 1403.325166 | -1.7 | 156.0 | 47.0 | even |
| 1574.245651 | 1+ | 1 | C70H56F12N6O4S4Yb | 1574.243740 | -0.9 | 23.1 | 40.5 | odd |
| | 1+ | 2 | C69H60F12N2O8S4Yb | 1574.242403 | -1.7 | 23.9 | 35.5 | odd |
| | 1+ | 3 | C74H60F12O6S4Yb | 1574.246426 | 0.9 | 24.9 | 39.5 | odd |
| | 1+ | 4 | C75H56F12N4O2S4Yb | 1574.247763 | 1.8 | 25.4 | 44.5 | odd |
| | 1+ | 5 | C62H64F12N2O13S4Yb | 1574.248276 | 2.0 | 29.6 | 26.5 | odd |
| | 1+ | 6 | C58H60F12N8O11S4Yb | 1574.245591 | 0.2 | 33.1 | 27.5 | odd |
| | 1+ | 7 | C57H64F12N4O15S4Yb | 1574.244254 | -0.7 | 36.3 | 22.5 | odd |
| | 1+ | 8 | C56H68F12O19S4Yb | 1574.242916 | -1.5 | 39.6 | 17.5 | odd |

Figure S20: HRMS data of **[YbL$_{oo}$]Cl**

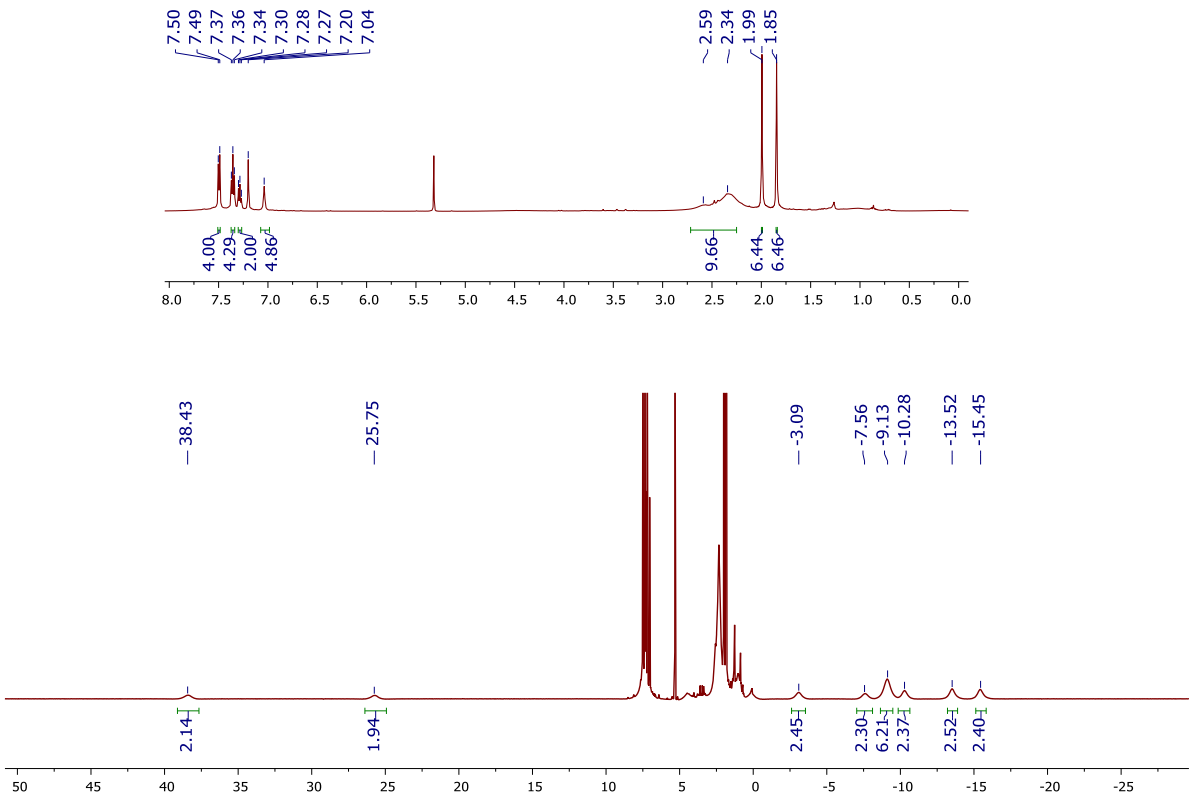



Figure S21: $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 298K) spectrum of compound **[EuL$_{oo}$]Cl.** $\delta$ 38.43(2H, $H_3/H_4$), 25.75(2H, $H_3/H_4$), 7.49 (d, 4H, $H_{ph}$), 7.36 (t, 4H, $H_{ph}$), 7.28 (t, 4H, $H_{ph}$), 7.20 (2H, $H_2$), 7.04 (2H, $H_1$), 2.59-2.34 (10H, $H_5$ + 6$H_{cyclen}$) 1.99 (6H, 2*$H_8$), 1.85 (6H, 2*$H_8$), -3.09 (2H, $H_{cyclen}$), -7.56 (2H, $H_{cyclen}$), -9.13 (6H, $H_6$), -10.28 (2H, $H_{cyclen}$), -13.52 (2H, $H_{cyclen}$), -15.45 (2H, $H_{cyclen}$).

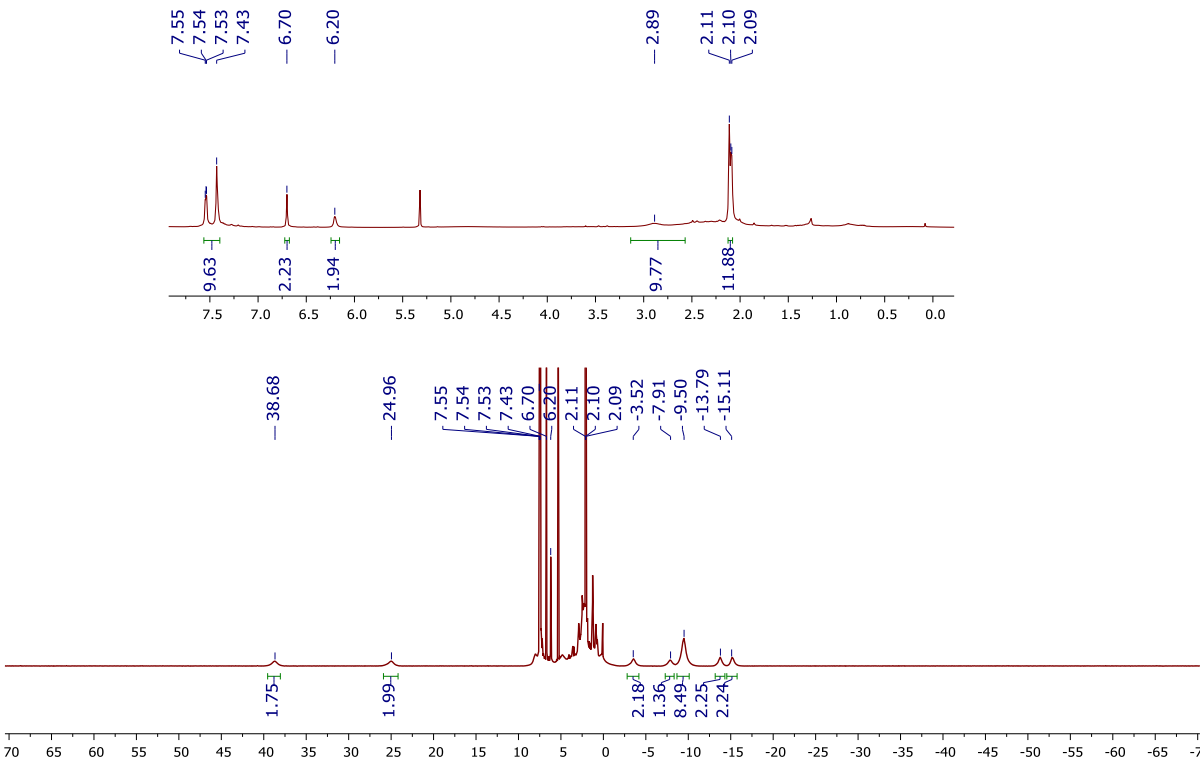
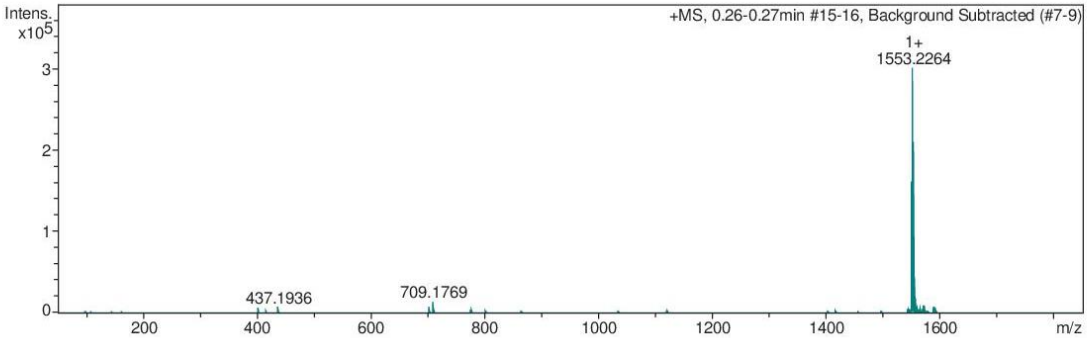
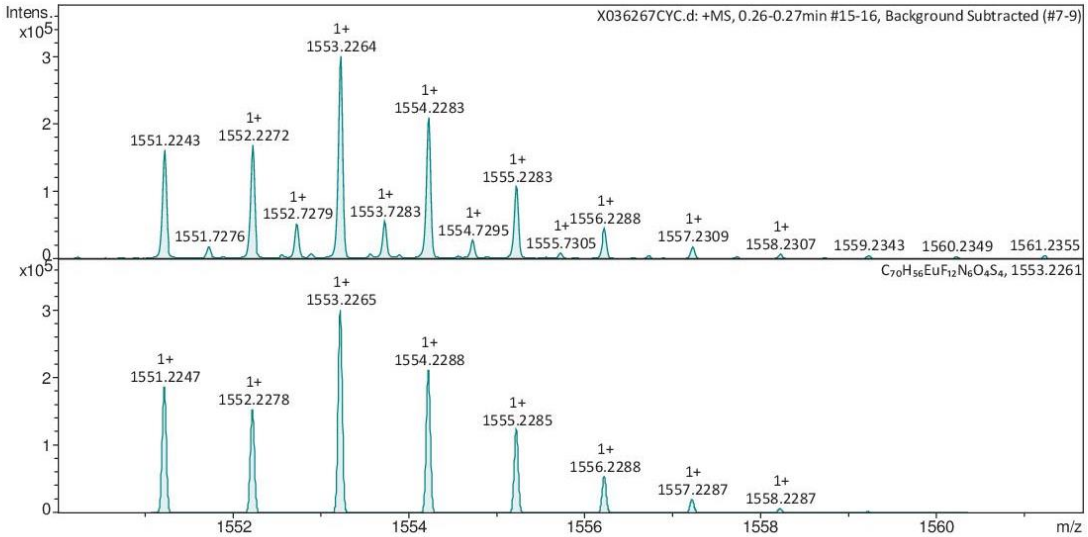



Figure S22: : $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 298K) spectrum of compound **[EuL$_{cc}$]Cl.** $\delta$ 38.68 (2H, $H_3/H_4$), 24.96 (2H, $H_3/H_4$), 7.55-7.43 (10H, $H_{ph}$), 6.70 (2H, $H_2$), 6.20 (2H, $H_1$), 2.89 (10H, $H_5$ + 6$H_{cyclen}$), 2.11-2.09 (12H, 2*$H_8$), -3.52 (2H, $H_{cyclen}$), -7.91 (2H, $H_{cyclen}$), -9.50 (8H, 2*$H_6$ and 2$H_{cyclen}$), -13.79 (2H, $H_{cyclen}$), -15.11 (2H, $H_{cyclen}$).

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.6 Bar |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan End | 2500 m/z | Set Collision Cell RF | 1800.0 Vpp | Set Dry Gas | 7.0 l/min |




| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| 702.169437 | 2+ | 1 | C70H60F12N6O4S4 | 702.167815 | -2.3 | 18.2 | 39.0 | even |
| | 2+ | 2 | C71H56F12N10S4 | 702.168484 | -1.4 | 23.6 | 44.0 | even |
| | 2+ | 3 | C64H60F12N10O5S4 | 702.171420 | 2.8 | 26.0 | 35.0 | even |
| | 2+ | 4 | C74H64F12O6S4 | 702.169158 | -0.4 | 28.5 | 38.0 | even |
| | 2+ | 5 | C75H60F12N4O2S4 | 702.169826 | 0.6 | 36.7 | 43.0 | even |
| 777.117772 | 2+ | 1 | C71H53EuF12N10S4 | 777.117361 | -0.3 | 76.8 | 45.5 | odd |
| | 2+ | 2 | C70H57EuF12N6O4S4 | 777.116693 | -1.2 | 77.9 | 40.5 | odd |
| | 2+ | 3 | C60H53EuF12N16O3S4 | 777.118955 | 1.6 | 79.9 | 37.5 | odd |

| Meas. m/z | z | # | Ion Formula | m/z | err [ppm] | mSigma | rdb | e⁻ Conf |
|---|---|---|---|---|---|---|---|---|
| | 2+ | 4 | C75H57EuF12N4O2S4 | 777.118704 | 1.5 | 80.0 | 44.5 | odd |
| | 2+ | 5 | C74H61EuF12O6S4 | 777.118035 | 0.7 | 80.3 | 39.5 | odd |
| | 2+ | 6 | C59H57EuF12N12O7S4 | 777.118287 | 0.7 | 84.1 | 32.5 | odd |
| 1553.226407 | 1+ | 1 | C71H52EuF12N10S4 | 1553.227446 | 0.9 | 40.3 | 45.5 | odd |
| | 1+ | 2 | C70H56EuF12N6O4S4 | 1553.226109 | 0.0 | 41.2 | 40.5 | odd |
| | 1+ | 3 | C66H52EuF12N12O2S4 | 1553.223423 | -1.8 | 42.2 | 41.5 | odd |
| | 1+ | 4 | C74H60EuF12O6S4 | 1553.228794 | 1.9 | 42.3 | 39.5 | odd |
| | 1+ | 5 | C69H60EuF12N2O8S4 | 1553.224771 | -0.8 | 43.3 | 35.5 | odd |
| | 1+ | 6 | C59H56EuF12N12O7S4 | 1553.229297 | 1.9 | 55.5 | 32.5 | odd |
| | 1+ | 7 | C56H48EuF12N22OS4 | 1553.227949 | 1.0 | 55.9 | 38.5 | odd |
| | 1+ | 8 | C55H52EuF12N18O5S4 | 1553.226611 | 0.1 | 61.7 | 33.5 | odd |

Figure S23: HRMS data of **[EuL$_{oo}$]Cl.**

## 3. Study of photoisomerization by electronic absorption spectroscopy.

UV-vis irradiations were performed in UV cells or NMR tubes with a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters "330FS 10-25" and "650FS 20-25". Typical irradiation times were of one hour for isomerizations in UV cells.

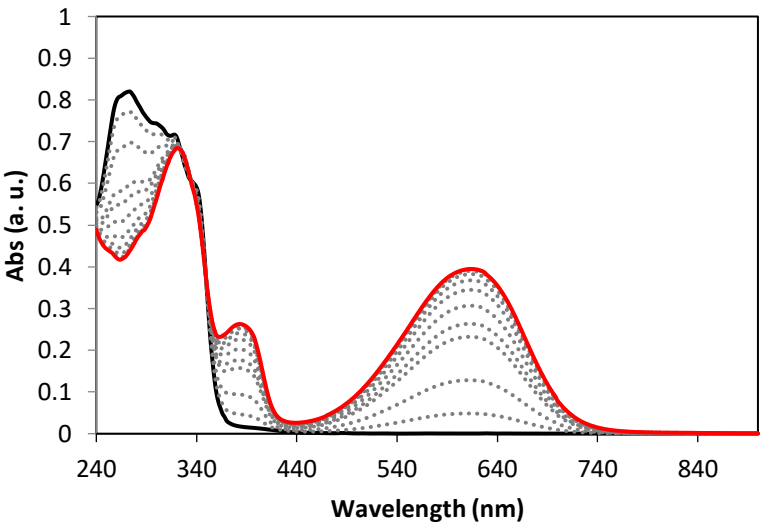



Figure S24: Change in absorbance during the course of $\mathbf{3_{oo}}$ (black) isomerization to $\mathbf{3_{cc}}$ (red) upon 330 nm excitation in dichloromethane.

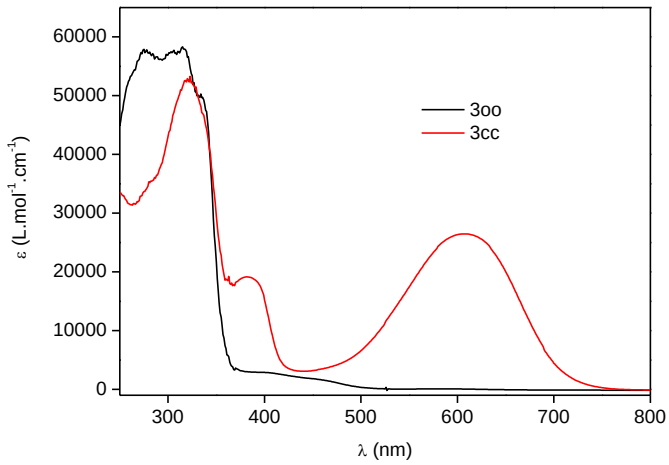



Figure 25: Electronic absorption spectra measured during the course of $\mathbf{3_{oo}}$ (black) isomerization to $\mathbf{3_{cc}}$ (red) upon 330 nm excitation in dichloromethane ($0.95 \times 10^{-5}$ M).

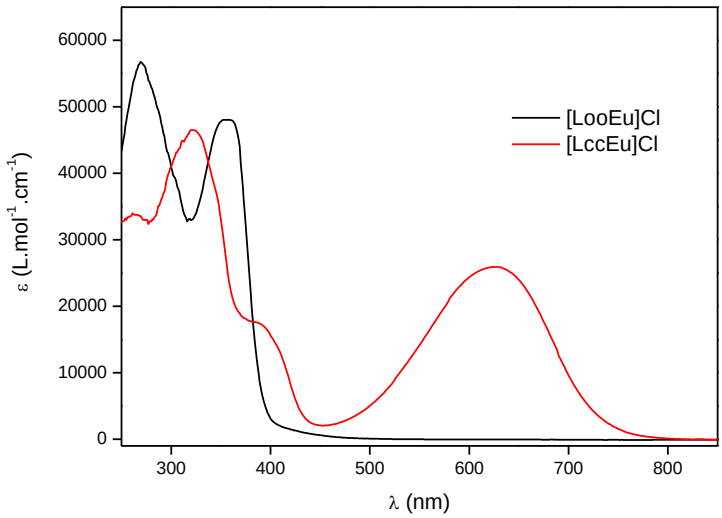



Figure S26: Electronic absorption spectra measured during the course of **[$L_{oo}$Eu]Cl** (black) isomerization to **[$L_{cc}$Eu]Cl** (red) upon 330 nm excitation in dichloromethane (0.85 x $10^{-5}$M).

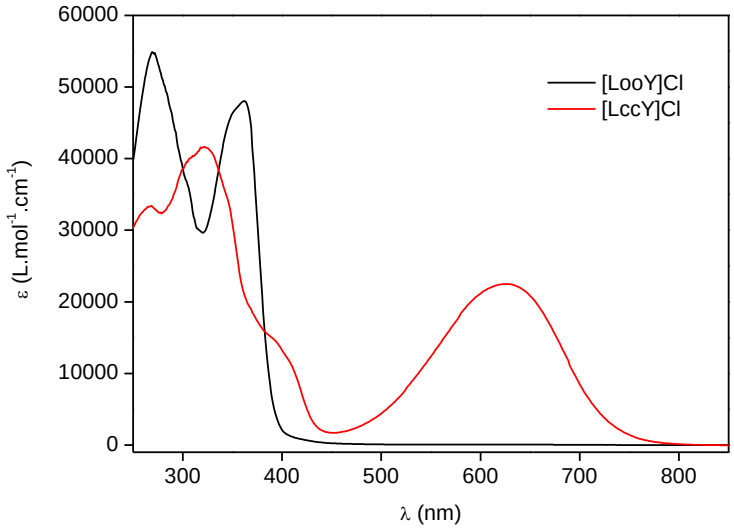



Figure S27: Electronic absorption spectra measured during the course of **[$L_{oo}$Y]Cl** (black) isomerization to **[$L_{cc}$Y]Cl** (red) upon 330 nm excitation in dichloromethane (1.3 x $10^{-5}$M).

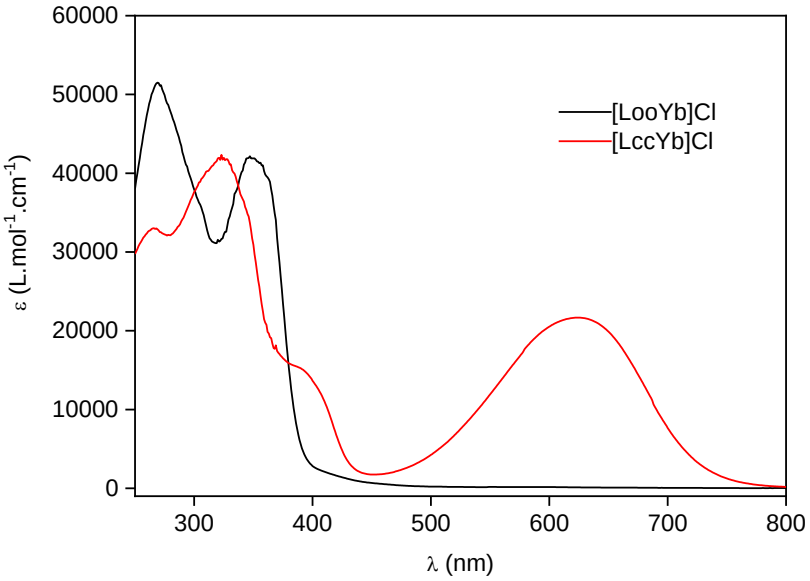



Figure S28: Electronic absorption spectra measured during the course of **[L$_{oo}$Yb]Cl** (black) isomerization to **[L$_{oo}$Yb]Cl** (red) upon 330 nm excitation in dichloromethane (0.95 x $10^{-5}$M).

## 3. Study of photoisomerization by 1H NMR spectroscopy.

Typical irradiation times were of 12-24 h for isomerizations in NMR tubes. Conversions were calculated based on the integration of the thiophene methyl groups of the respective isomers.

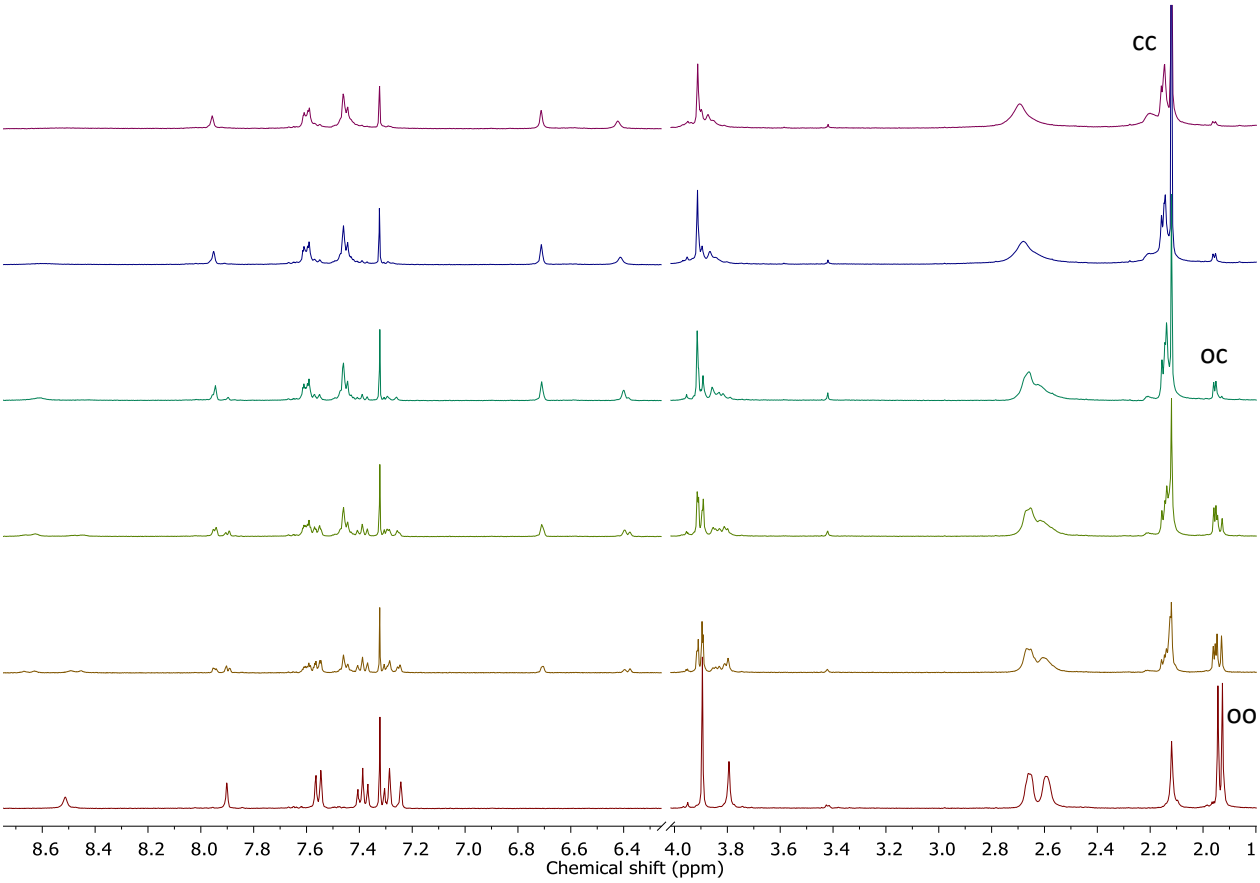



Figure S29: $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 278 K) spectra measured during the course of $\mathbf{3_{oo}}$ (down) isomerization to a PSS containing $\mathbf{3_{cc}}$ (94 %) and $\mathbf{3_{oc}}$ (6 %) (top) upon 330 nm excitation in $CD_2Cl_2$.

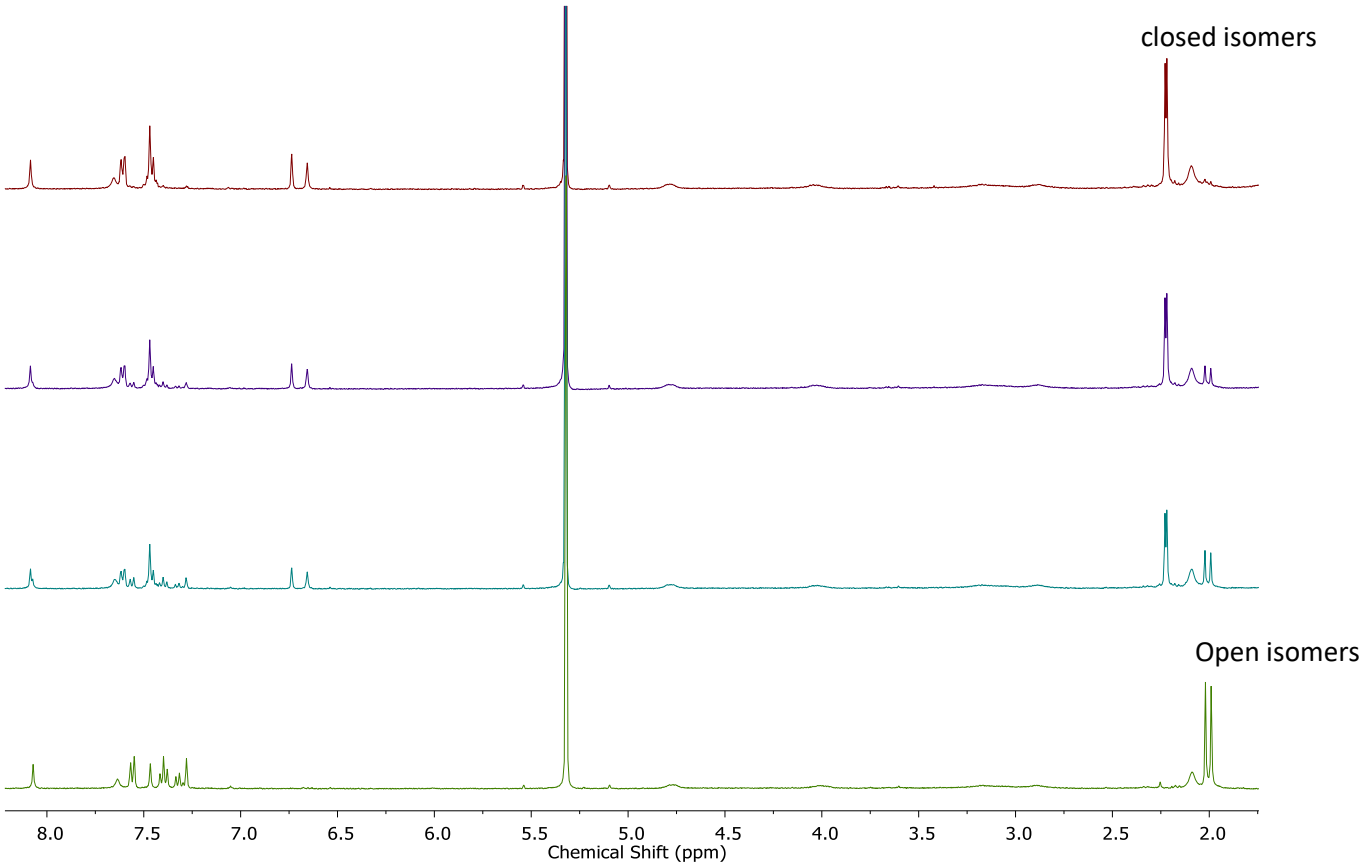



Figure S30: $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 278 K) spectra measured during the course of **[L$_{oo}$Y]Cl** (down) isomerization to a PSS containing **[L$_{cc}$Y]Cl** and **[L$_{oc}$Y]Cl** with 97 % of closed DTE overall (top) upon 364nm excitation in $CD_2Cl_2$.

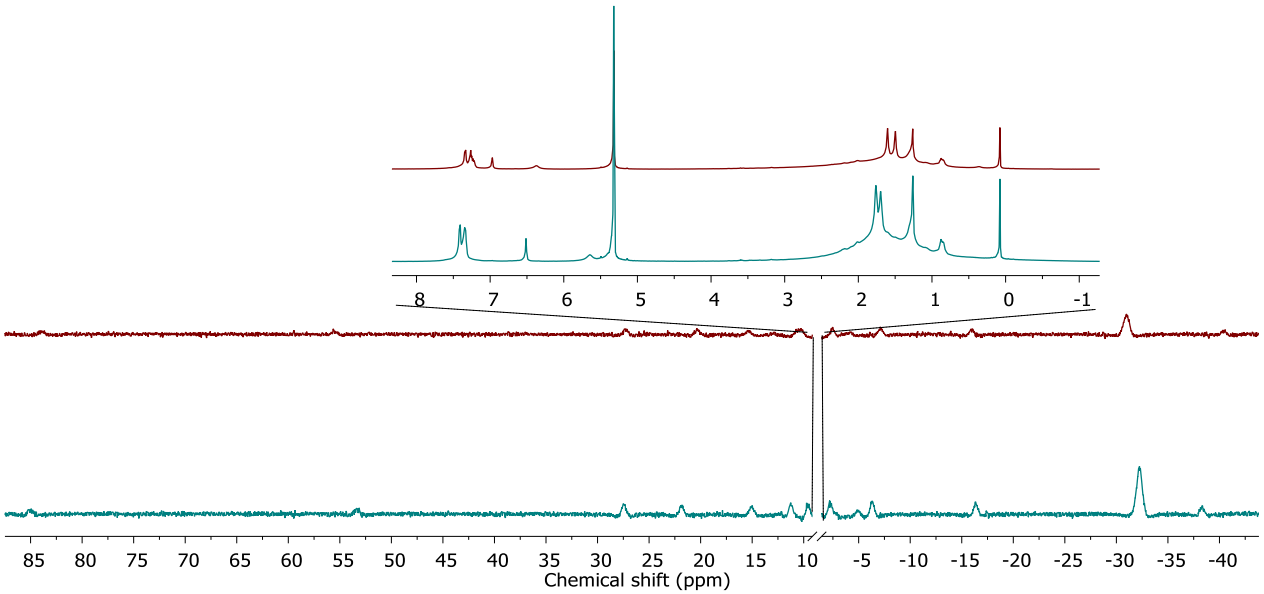



Figure S31: $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 278 K) spectra measured during the course of **[$L_{oo}$Yb]Cl** (down) isomerization to a PSS containing **[$L_{cc}$Yb]Cl** and **[$L_{oc}$Yb]Cl** with 94 % of closed DTE overall (top) upon 364 nm excitation in $CD_2Cl_2$.

## 4. Emission spectroscopy.

The luminescence measurement were performed using Horiba-Jobin Yvon Fluorolog-3® spectrofluorimeters. The steady-state luminescence was excited by a 450 W xenon CW lamp and detected at an angle of 90° with either a Hamamatsu R928 photomultiplier tube for the visible range (single grating emission monochromator with dispersions of 2.1 nm/mm (1200 grooves per mm)) or a liquid nitrogen cooled Symphony® II CCD detector for the near infrared range (single grating with a dispersion of 4.9 nm/mm (600 grooves/mm)). Time gated measurement is obtained tanks to a pulsed excitation using a FL-1040 UP Xenon Lamp with a 50 µs delay before integration of the emission signal. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detectors and gratings). Phosphorescence lifetime was obtained by an exponential least-squares fitting using Origin®. The sample were dissolved in a 4 : 1 ethanol : methanol mixture and placed either in 1 cm squared cuvettes measurements at RT or 4 mm width quartz tubes inserted in a quartz dewar filled with liquid nitrogen for 77K measurements.

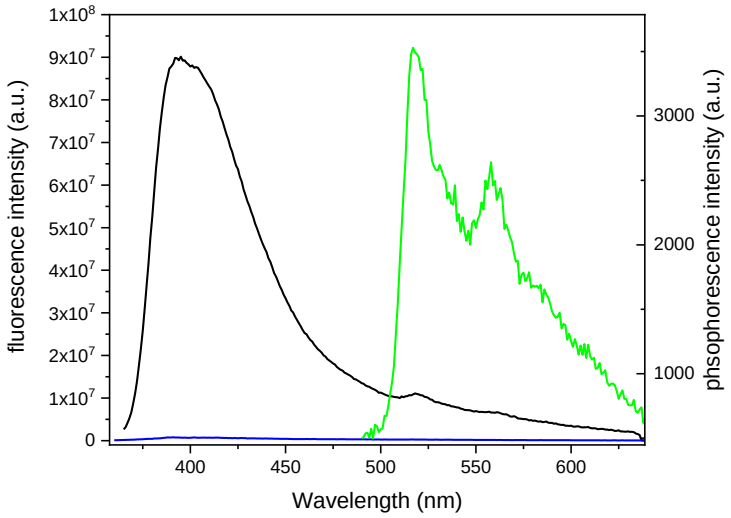



Figure S32: Emission spectrum ($\lambda_{ex}$ = 350 nm) of **[$L_{oo}$Y]Cl** in ethanol : methanol (4:1) organic glass at 77K (black curve) and of **[$L_{cc}$Y]Cl** at PSS (blue curve). The green spectrum is obtained for **[$L_{oo}$Y]Cl** after a 1ms delay.

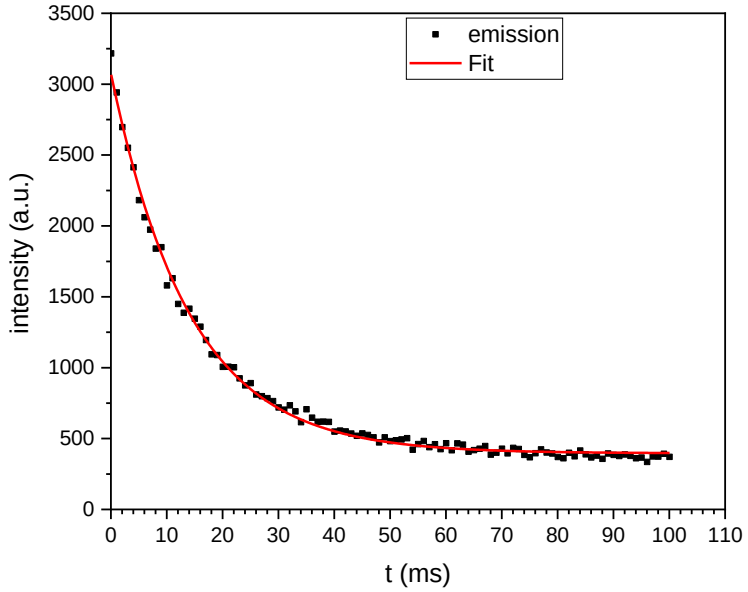



Figure S33: Phosphorescence decay (black dots) of **[$L_{oo}$Y]Cl** in ethanol : methanol (4:1) organic glass at 77K ($\lambda_{ex}$ = 350 nm and $\lambda_{ex}$ = 350 nm) and best mono-exponential fit with a lifetime of 14 ms (red curve).

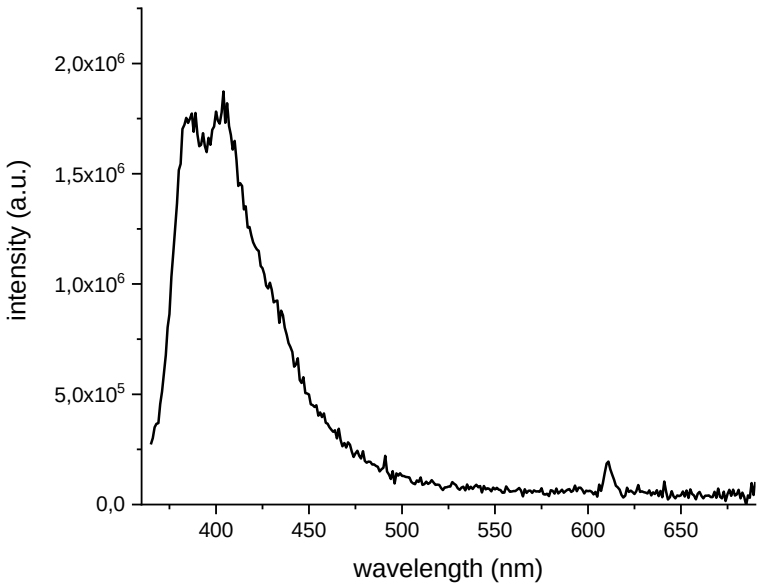



Figure S34: Emission spectrum ($\lambda_{ex}$ = 350 nm) of **[$L_{oo}$Eu]Cl** at room temperature.

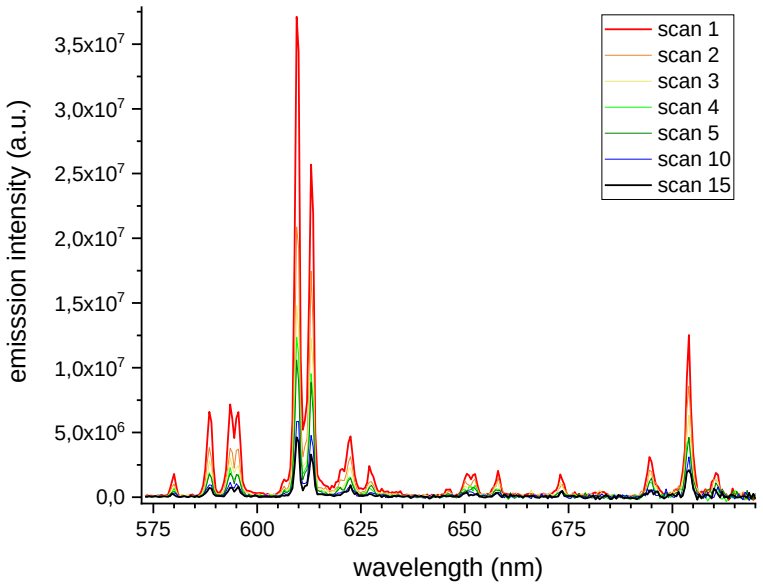



Figure S35: Successive emission spectra ($\lambda_{ex}$ = 350 nm) of **[$L_{oo}$Eu]Cl** in ethanol : methanol (4:1) organic glass at 77K showing the quenching of emission due to closing to **[$L_{cc}$Eu]Cl**. The inset monitor the intensity maximum with time.

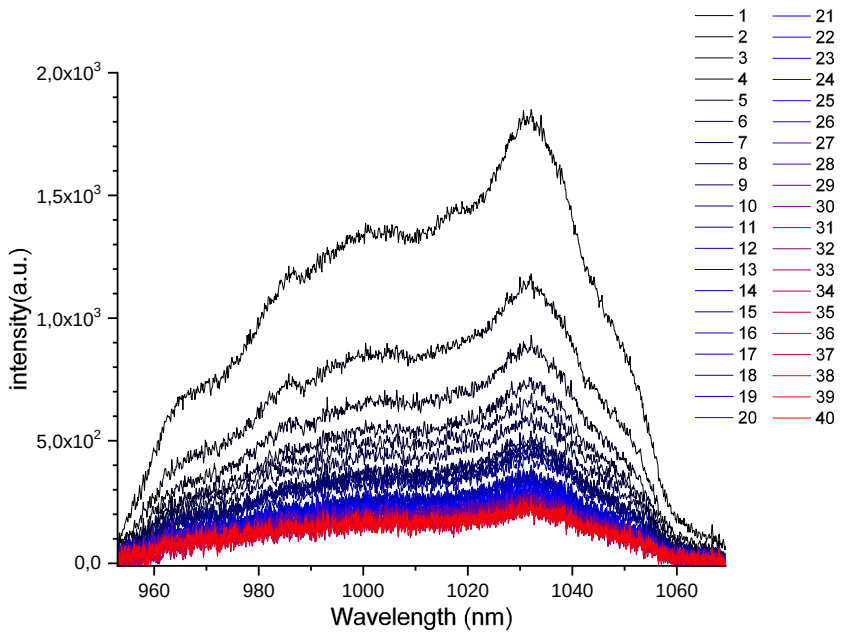



Figure S36: Successive emission spectra ($\lambda_{ex}$ = 350 nm) of **[$L_{oo}$Yb]Cl** in ethanol : methanol (4:1) organic glass at 77K showing the quenching of emission due to closing to **[$L_{cc}$Y]Cl**. Successive CCD camera snapshot with a 0.5 s integration time (low resolution due to the 30 nm slit apertures for the emission monochromator).

## 5. References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3 Roberts, M. N.; Nagle, J. K.; Finden, J. G.; Branda, N. R.; Wolf, M. O., Linker-dependent metal-sensitized photoswitching of dithienylethenes. *Inorg. Chem.* **2009,** *48* (1), 19-21.