

## Supplementary Information

### Spontaneous Resolution of Polyoxometalate-Based Chiral Hybrids Driven by Solvent and Common Ion

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#### Experimental Section

##### General methods and materials

All syntheses and manipulations were performed in the open air, all other chemicals, including solvents, were commercially available as reagent grade and used as received without further purification from Adamas-beta®.  $[\text{NH}_4]_3[\text{CrMo}_6\text{O}_{18}(\text{OH})_6]$  was synthesized according to literature methods<sup>1</sup>. IR spectra were measured using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile with UV2100s spectrophotometer. The mass spectra were obtained using an ion trap mass spectrometer (ThermoFisher LTQ). Negative mode was chosen for the experiments (capillary voltage 33 V). Sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300  $\mu\text{L min}^{-1}$ . Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). The liquid and solid state circular dichroic (CD) spectra were measured in Applied Photophysics Chirascan spectropolarimeter. <sup>13</sup>C NMR spectra were obtained on a JOEL JNM-ECA400 spectrometer and are reported in ppm.

##### X-ray Crystallographic Structural Determinations

Suitable single crystals were selected. Data collections were performed at 100, 101, 293, 100, 293, 103 and 104 K for 1a, 1b, 2a, 2b, 2c, 3b and 3c respectively, by using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, ver 2.30). Structures were solved by direct methods and refined against  $F^2$  by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. All calculations were carried out by the program package of SHELXTL ver 5.1<sup>2</sup> and Olex2 ver 1.2<sup>3</sup>. It should be note that solvent-masking procedure was conducted by SQUEEZE in PLATON program<sup>4</sup> for compound 2a during refinement calculation process.

##### TDDFT stimulated CD spectrum calculations

All of the calculations presented herein were carried out with the Gaussian09 program package.<sup>5</sup> The stationary point structure of compound 3 was fully optimized using the B3LYP method<sup>6</sup>, in combination with the LANL2DZ basis set for molybdate and Chromium atoms and the 6-31+G(d) basis set for main group elements. Configurations were optimized before TDDFT stimulated CD spectrum calculation. The calculation is completed on the “Explorer 100” cluster system of Tsinghua National Laboratory for Information Science and Technology.

##### Synthesis and Recrystallization process

The synthesis of  $[\text{TBA}]_3\{[\text{H}_2\text{NC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}$ , compound 1:

$(\text{NH}_4)_3[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]$  was according to literature methods<sup>7</sup>. Then it was precipitated from the aqueous by changing the equivalent amount of cation of TBA<sup>+</sup>.  $\text{C}_{52}\text{H}_{119}\text{N}_4\text{CrMo}_6\text{O}_{24}$   $M=1812.17$ , H 6.60 C 34.45 N 3.11 while calcd H 6.62 C 34.47 N 3.09. IR (KBr pellet, major absorbances,  $\text{cm}^{-1}$ ): 3343, 2960, 2874, 1632, 1480, 1384, 1050, 935, 913, 895, 794, 659. UV-Vis (MeCN, nm):  $\lambda_{\text{LMCT}} = 230$  ( $\epsilon_{\text{LMCT}}=4.66 \times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ),  $\lambda_{\text{d-d}}=533$  ( $\epsilon_{\text{d-d}}=5.66 \times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). ESI mass spectrometry (MeCN): calcd  $m/z=1569.70$   $\{(\text{TBA})_2[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^-$ , 1328.23  $\{[\text{H}^+](\text{TBA})[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^-$ , 663.61  $\{(\text{TBA})[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^{2-}$ , 1086.76  $\{[\text{H}^+]_2[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^-$ , 542.88  $\{[\text{H}^+][\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^{2-}$ , 361.59  $\{[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^{3-}$ ; found 1569.78, 1328.37, 1086.65, 663.48, 542.66, 361.46, respectively. <sup>13</sup>C NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ , ppm):  $\delta = 13.8$  ( $\text{C}_a$ ), 19.0 ( $\text{C}_b$ ), 23.5 ( $\text{C}_7$ ), 57.8 ( $\text{C}_8$ ), 61.6 ( $\text{C}_a$ ), 64.8 ( $\text{C}_b$ ).

The recrystallization of compound 1a:  $[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3]_2\{[\text{H}_3\text{NC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot 6\text{H}_2\text{O}$   
 $\text{C}_{12}\text{H}_{51}\text{N}_3\text{CrMo}_6\text{O}_{36}$   $M_r=1441.17$

3.468 g  $(\text{NH}_4)_3[\text{NH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]$  and 1.413 g aminomethane hydrochloride salt were redissolved in 15 mL MeCN. After recrystallization, compound 1a was obtained as pink crystalline products.

The recrystallization of compound **1b**:  $[\text{TBA}]_3\{[\text{H}_2\text{NC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot[\text{TBA}]\text{Br}\cdot 2\text{H}_2\text{O}$   
 $\text{C}_{68}\text{H}_{162}\text{BrCrMo}_6\text{N}_5\text{O}_{26}$   $M_r=2173.54$

3.624 g compound 1 were redissolved in the  $V\%$  ratio of 60/40 in DMF/MeCN mix solvent of 9 mL DMF and 6 mL MeCN. Additional 0.2 g of  $[\text{TBA}]\text{Br}$  is added into the recrystallization solution to accelerate recrystallization process. After recrystallization, compound 1b was obtained as pink crystalline products.

The synthesis of  $[\text{TBA}]_3\{[\text{H}_3\text{CC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}$ , compound **2**:

The synthesis process is similar to synthesis of compound **1** while used  $(\text{HOCH}_2)_3\text{CCH}_3$  instead of  $(\text{HOCH}_2)_3\text{CNH}_2$ .

$\text{C}_{53}\text{H}_{120}\text{N}_3\text{CrMo}_6\text{O}_{24}$   $M_r=1811.18$ , H 6.66 C 35.12 N 2.31 while calcd H 6.68 C 35.15 N 2.32. IR (KBr pellet, major absorbances,  $\text{cm}^{-1}$ ): 2961, 2874, 1480, 1384, 1050, 935, 914, 895, 794, 659. UV-Vis (MeCN, nm):  $\lambda_{\text{LMCT}} = 230$  ( $\epsilon_{\text{LMCT}}=4.64\times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ),  $\lambda_{\text{d-d}}=533$  ( $\epsilon_{\text{d-d}}=5.63\times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). ESI mass spectrometry (MeCN): calcd  $m/z = 1568.71$   $(\text{TBA})_2[\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^-$ , 1327.23  $[\text{H}^+(\text{TBA})[\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]]^-$ , 1085.76  $[\text{H}^+]_2[\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^-$ , 663.11  $(\text{TBA})[\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{2-}$ , 542.38  $[\text{H}^+][\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{2-}$ , 361.25  $[\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{3-}$ ; found 1568.66, 1327.12, 1085.88, 663.12, 542.27, 361.16, respectively.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ , ppm):  $\delta = 13.8$  ( $\text{C}_\alpha$ ), 19.0 ( $\text{C}_\beta$ ), 23.5 ( $\text{C}_\gamma$ ), 57.8 ( $\text{C}_\epsilon$ ), 14.9 ( $\text{C}_a$ ), 44.8 ( $\text{C}_b$ ), 67.1 ( $\text{C}_c$ ).

The recrystallization of compound **2a**:  $[\text{TBA}]_3\{[\text{H}_3\text{CC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot 4\text{H}_2\text{O}$   
 $\text{C}_{53}\text{H}_{126}\text{N}_3\text{CrMo}_6\text{O}_{27}$ ,  $M_r=1865.20$

3.622 g compound 2 were redissolved in the  $V\%$  ratio of 60/40 in DMF/MeCN mix solvent of 9 mL DMF and 6 mL MeCN. After recrystallization, compound 2a was obtained as pink crystalline products.

The recrystallization of compound **2b**:  $[\text{TBA}]_3\{[\text{H}_3\text{CC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot 1\text{H}_2\text{O}$   
 $\text{C}_{53}\text{H}_{142}\text{N}_3\text{CrMo}_6\text{O}_{35}$   $M_r=2009.16$

3.622 g compound 2 were redissolved in the  $V\%$  ratio of 80/20 in DMF/MeCN mix solvent of 12 mL DMF and 3 mL MeCN. After recrystallization, compound 2b was obtained as pink crystalline products.

The recrystallization of compound **2c**:  $[\text{TBA}]_3\{[\text{H}_3\text{CC}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot [\text{TBA}]\text{Br}$   
 $\text{C}_{69}\text{H}_{156}\text{N}_4\text{CrMo}_6\text{O}_{24}\text{Br}$ ,  $M_r=2133.52$

3.622 g compound 2 were redissolved in the  $V\%$  ratio of 80/20 in DMF/MeCN mix solvent of 12 mL DMF and 3 mL MeCN. Additional 0.2 g of  $[\text{TBA}]\text{Br}$  is added into the recrystallization solution to accelerate recrystallization process. After recrystallization, compound 2c was obtained as pink crystalline products.

The synthesis of  $[\text{TBA}]_3\{[\text{H}_5\text{C}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}$ , compound **3**:

The synthesis process is similar to synthesis of compound **1** while used  $(\text{HOCH}_2)_3\text{CC}_2\text{H}_5$  instead of  $(\text{HOCH}_2)_3\text{CNH}_2$ .

$\text{C}_{54}\text{H}_{122}\text{N}_3\text{CrMo}_6\text{O}_{24}$   $M_r=1825.20$ , H 6.72 C 35.52 N 2.31 while calcd H 6.74 C 35.54 N 2.30. IR (KBr pellet, major absorbances,  $\text{cm}^{-1}$ ): 3459, 3189, 2962, 2874, 1650, 1469, 1384, 1117, 1055, 943, 911, 674, 566. UV-Vis (MeCN, nm):  $\lambda_{\text{LMCT}} = 230$  ( $\epsilon_{\text{LMCT}}=4.74\times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ),  $\lambda_{\text{d-d}}=530$  ( $\epsilon_{\text{d-d}}=5.70\times 10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). ESI mass spectrometry (MeCN): calcd  $m/z = 1582.53$   $(\text{TBA})_2[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^-$ , 1341.06  $[\text{H}^+(\text{TBA})[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]]^-$ , 1099.59  $[\text{H}^+]_2[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^-$ , 670.03  $(\text{TBA})[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{2-}$ , 549.29  $[\text{H}^+][\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{2-}$ , 365.86  $[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\text{CrMo}_6\text{O}_{18}(\text{OH})_3]^{3-}$ ; found 1582.83, 1341.03, 1099.69, 670.23, 549.49, 365.76, respectively.  $^{13}\text{C}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ , ppm):  $\delta = 13.8$  ( $\text{C}_\alpha$ ), 19.0 ( $\text{C}_\beta$ ), 23.5 ( $\text{C}_\gamma$ ), 57.8 ( $\text{C}_\epsilon$ ), 7.9 ( $\text{C}_a$ ), 22.3 ( $\text{C}_b$ ), 43.8 ( $\text{C}_c$ ), 64.8 ( $\text{C}_d$ ).

The recrystallization of compound **3b**:  $[\text{TBA}]_3\{[\text{H}_5\text{C}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot [\text{TBA}]\text{Br}\cdot \text{NH}_4\text{Br}$   
 $\text{C}_{70}\text{H}_{162}\text{N}_5\text{CrMo}_6\text{O}_{24}\text{Br}_2$   $M_r=2245.43$

3.65g compound 3 were redissolved in the  $V\%$  ratio of 60/40 in DMF/MeCN mix solvent of 9 mL DMF and 6 mL MeCN. Additional 0.2 g of  $[\text{TBA}]\text{Br}$  and 0.1 g  $\text{NH}_4\text{Br}$  is added into the recrystallization solution to accelerate recrystallization process. After recrystallization, compound 3b was obtained as pink crystalline products.

The recrystallization of compound **3c**:  $[\text{TBA}]_3\{[\text{H}_5\text{C}_2\text{C}(\text{CH}_2\text{O})_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}\cdot [\text{TBA}]\text{Br}\cdot \text{NH}_2$   
 $\text{C}_{70}\text{H}_{158}\text{N}_4\text{CrMo}_6\text{O}_{24}\text{Br}$ ,  $M_r=2147.55$

3.65g compound 3 were redissolved in the  $V\%$  ratio of 30/70 in DMF/MeCN mix solvent of 4.5 mL DMF and 10.5 mL MeCN. Additional 0.2 g of  $[\text{TBA}]\text{Br}$  and 0.1 g  $\text{NH}_4\text{Br}$  is added into the recrystallization solution to accelerate recrystallization process. After recrystallization, compound **3c** was obtained as pink crystalline products.

### Reversible spontaneous resolution cycle process

7.244 g compound 2 were redissolved in DMF/MeCN mix solvent of 12 mL DMF and 3 mL MeCN with the  $V\%$  ratio of 80/20. After recrystallization, single crystals which have the same cell parameters as compound 2b were obtained as pink crystalline products. And then the whole solution including compound 2b was redissolved by adding another 5 mL extra MeCN forming the DMF/MeCN mix solvent with the  $V\%$  ratio of 60/40. After recrystallization, single crystals which have the same cell parameters as compound 2a were obtained as pink crystalline products. After that, the whole solution including compound 2a was added to another 20 mL extra DMF forming the  $V\%$  ratio of 80/20 DMF/MeCN mix solvent back. After recrystallization, single crystals which has the same cell parameters as compound 2b were obtained as pink crystalline products again.

### IR spectrum test

The IR spectra obtained in the crystal solid state were analyzed in detail. IR spectra of these compounds are very similar from each other and in agreement with the typical Anderson-type structures. The characteristic peaks at 935, 913 and 895  $\text{cm}^{-1}$

in compound **1** and **2** while 943, and 911  $\text{cm}^{-1}$  in compound **3** are assigned to the vibrations of terminal Mo=O units. And the peaks at 659, 794  $\text{cm}^{-1}$  and 674  $\text{cm}^{-1}$  in compound **1**, **2** and **3** separately are belonged to the vibrations of the Mo-O-Mo groups. It is consistent with the spectroscopic description for the skeleton structure of the parent Anderson cluster. The characteristic peaks at 1050  $\text{cm}^{-1}$  in compound **1** and **2** while 1055  $\text{cm}^{-1}$  in compound **3** are assigned to the vibration peak of the C-O bonds which demonstrates the grafting of triol onto the surface of POMs. (Fig. S5 in ESI†)

#### NMR spectrum test

Because the central  $\text{Cr}^{\text{III}}$  ion in Anderson structure is paramagnetic, it would disturb peaks splitting in the  $^1\text{H}$  NMR spectra and hinder the structural analysis of compound **1-3**. As a compromise,  $^{13}\text{C}$  NMR spectra were conducted instead since the spin-spin coupling between carbon atoms can be decoupled. (Fig. S6 in ESI†)

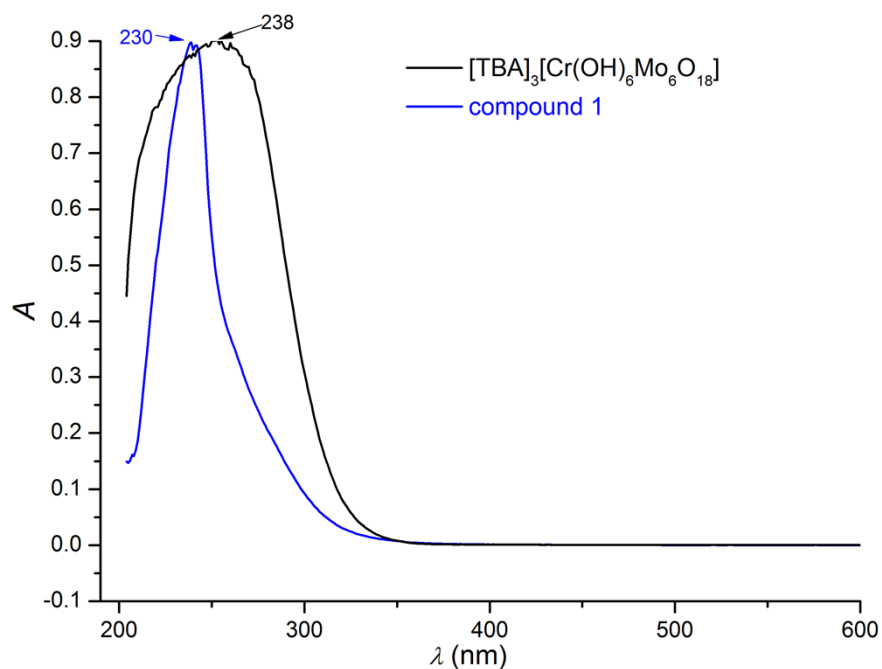


Fig. S1 UV/Vis LMCT spectra of  $[\text{TBA}]_3[\text{CrMo}_6\text{O}_{18}(\text{OH})_6]$  and compound **1**

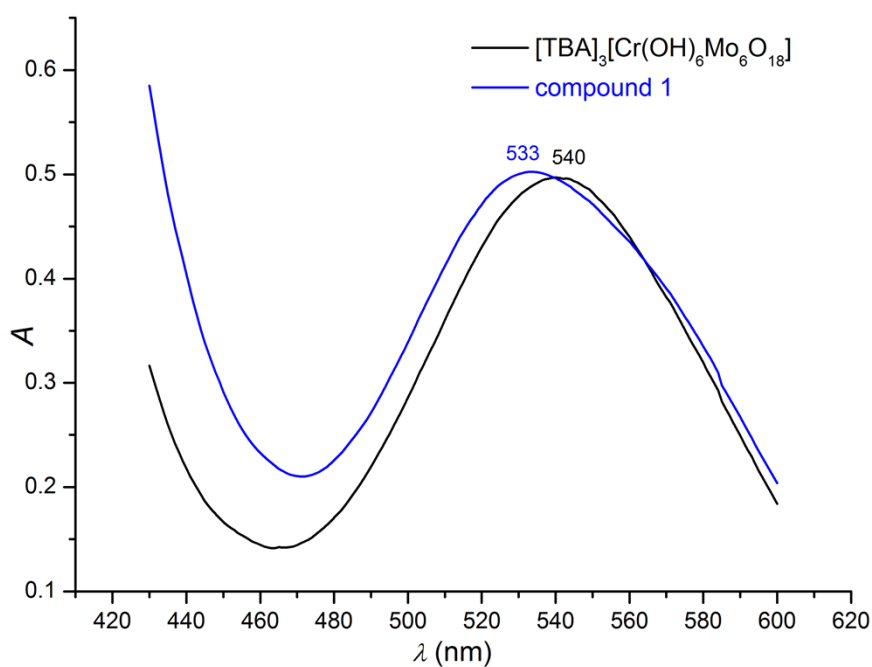


Fig. S2 UV/Vis d-d transition spectra of  $[\text{TBA}]_3[\text{CrMo}_6\text{O}_{18}(\text{OH})_6]$  and compound **1**

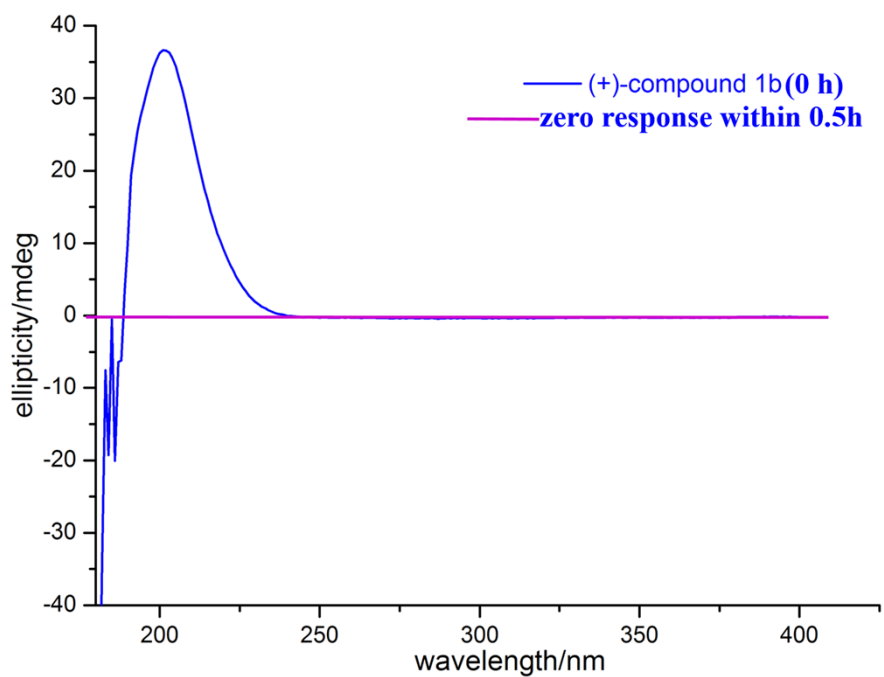


Fig. S3 the initial Liquid state CD spectra of enantiopure crystal grain of compound **1** (0 h) and lifetime (zero response within 0.5h)

Fig. S4. Solid state CD spectra of enantiopure crystal grains of compounds **1-3**

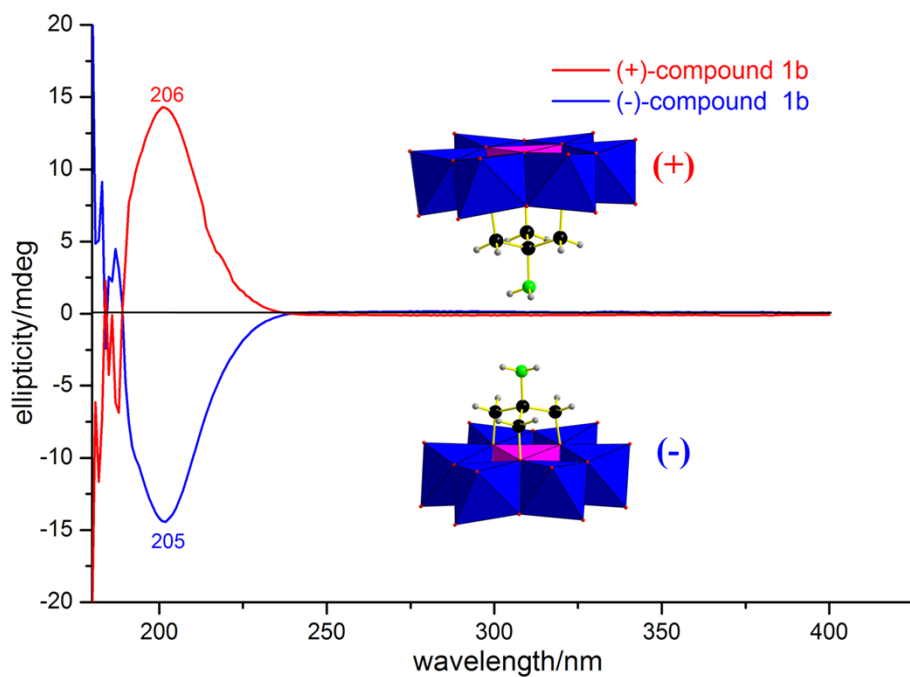
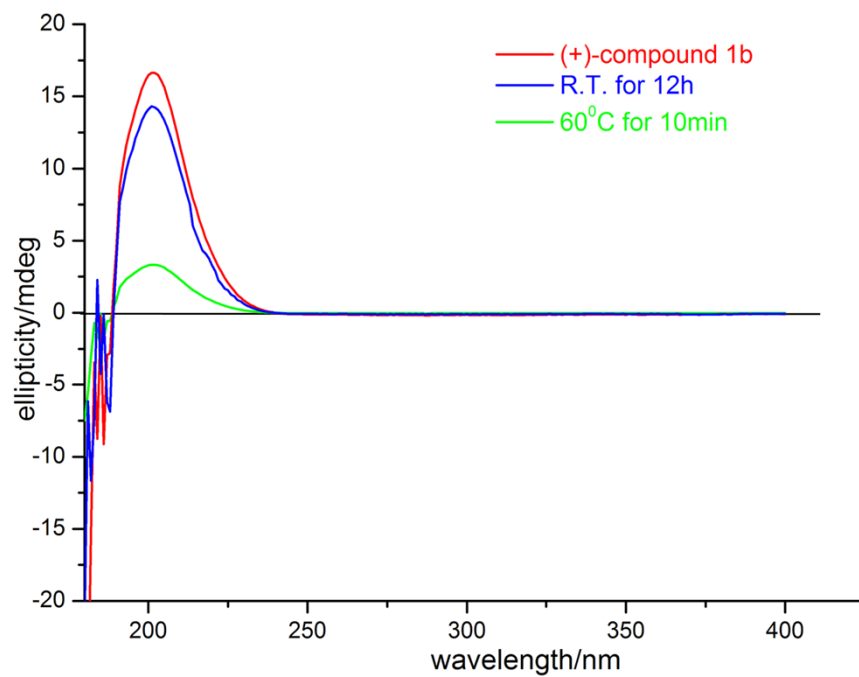
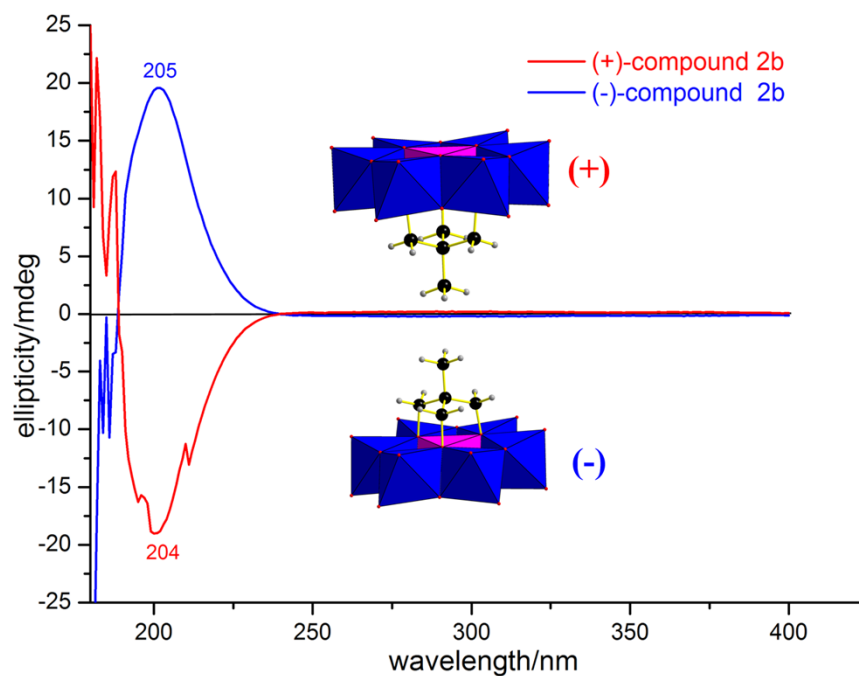


Fig. S4a Solid state CD spectra of enantiopure crystal grain of compound **1b**.



**Fig. S4b** Solid state CD spectra of enantiopure crystal grain of original (+)-compound **1b**(red one),keeping in room temperature for 12h(blue second) and heating to 60 °C for 10min(green third )



**Fig. S4c** Solid state CD spectra of enantiopure crystal grain of compound **2b**.

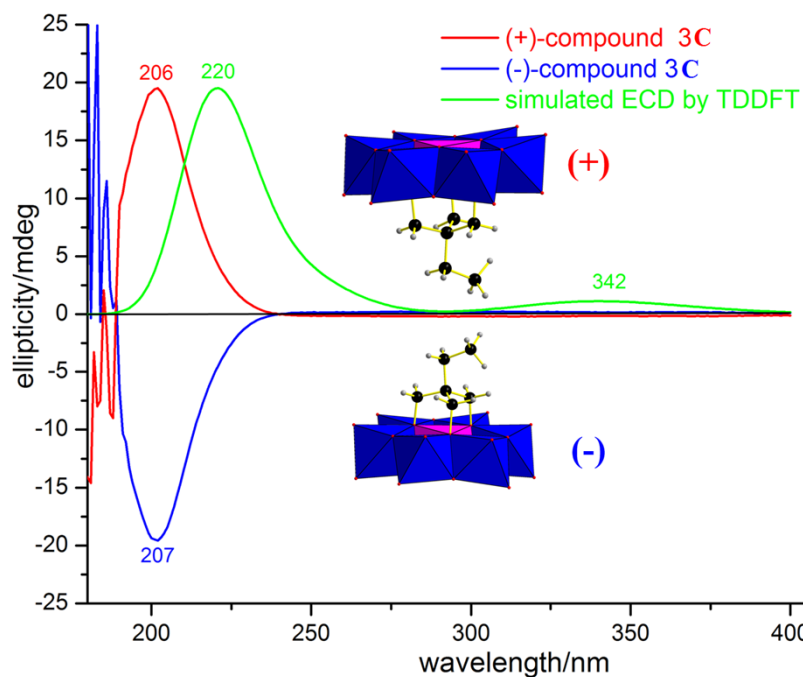


Fig. S4d Solid state CD spectra of enantiopure crystal grain of compound 3c and the simulated ECD spectrum generated by TDDFT.

Fig. S5 The IR spectrum of compounds 1-3

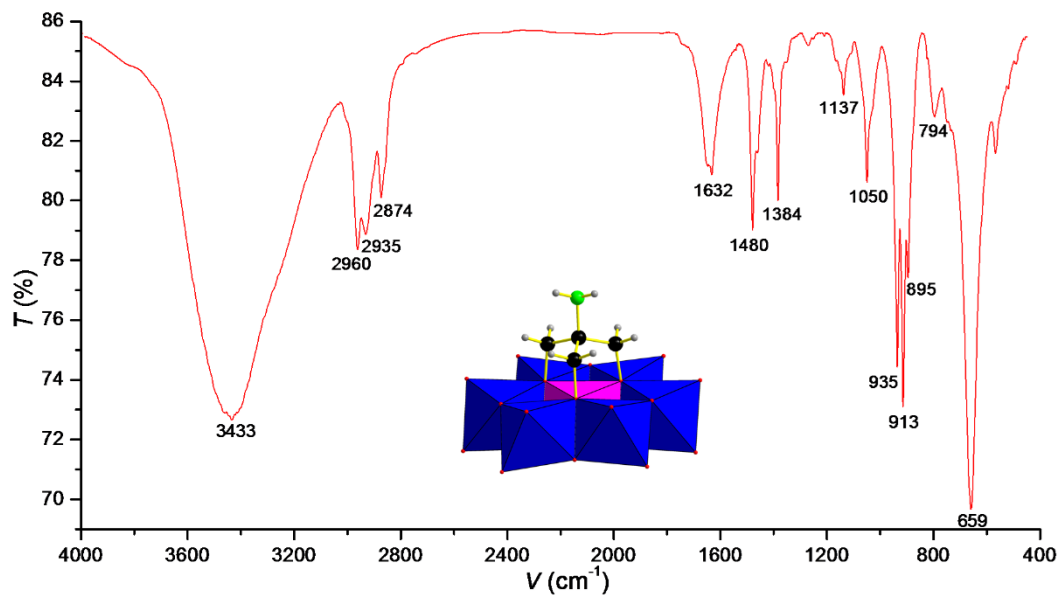


Fig. S5a the IR spectrum of compound 1

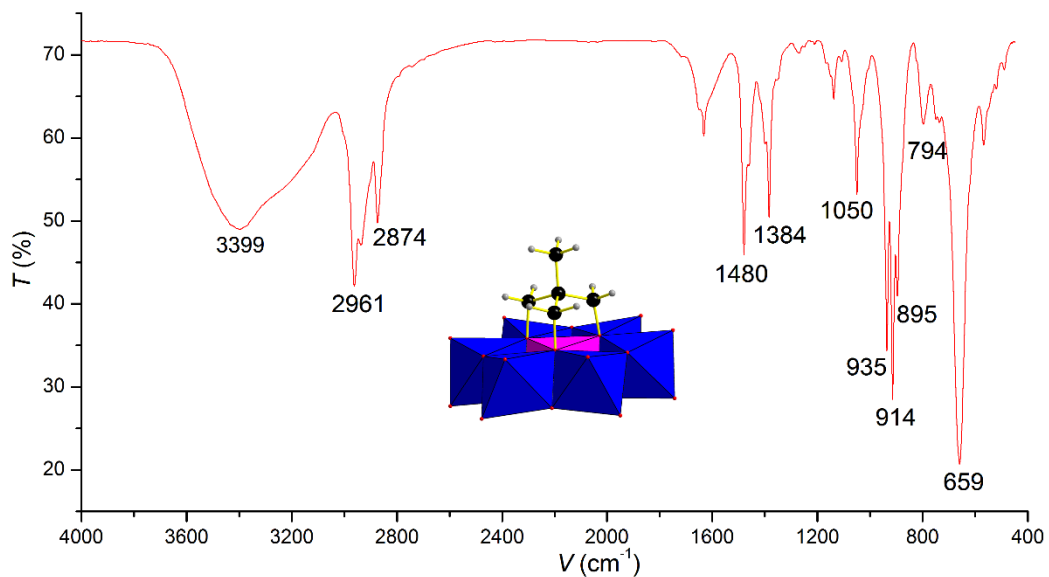


Fig. S5b the IR spectrum of compound 2

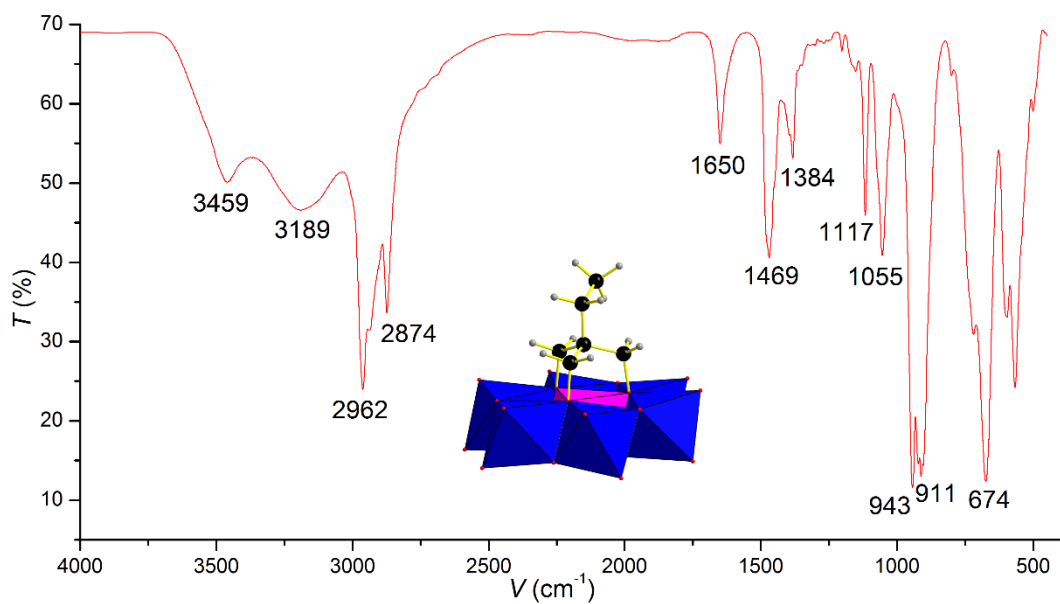


Fig. S5c the IR spectrum of compound 3

Fig. S6. The <sup>13</sup>C NMR spectrum and chemical shifts of compounds 1-3.

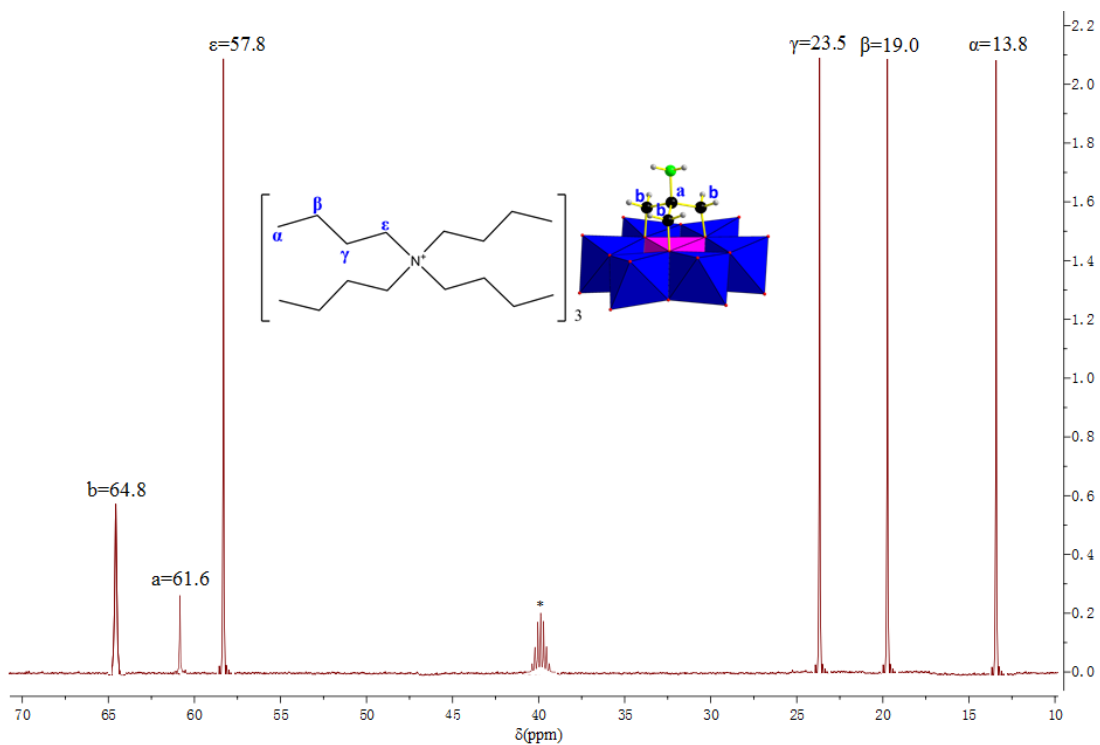


Fig. S6a the  $^{13}\text{C}$  NMR spectrum and chemical shifts of compound **1**

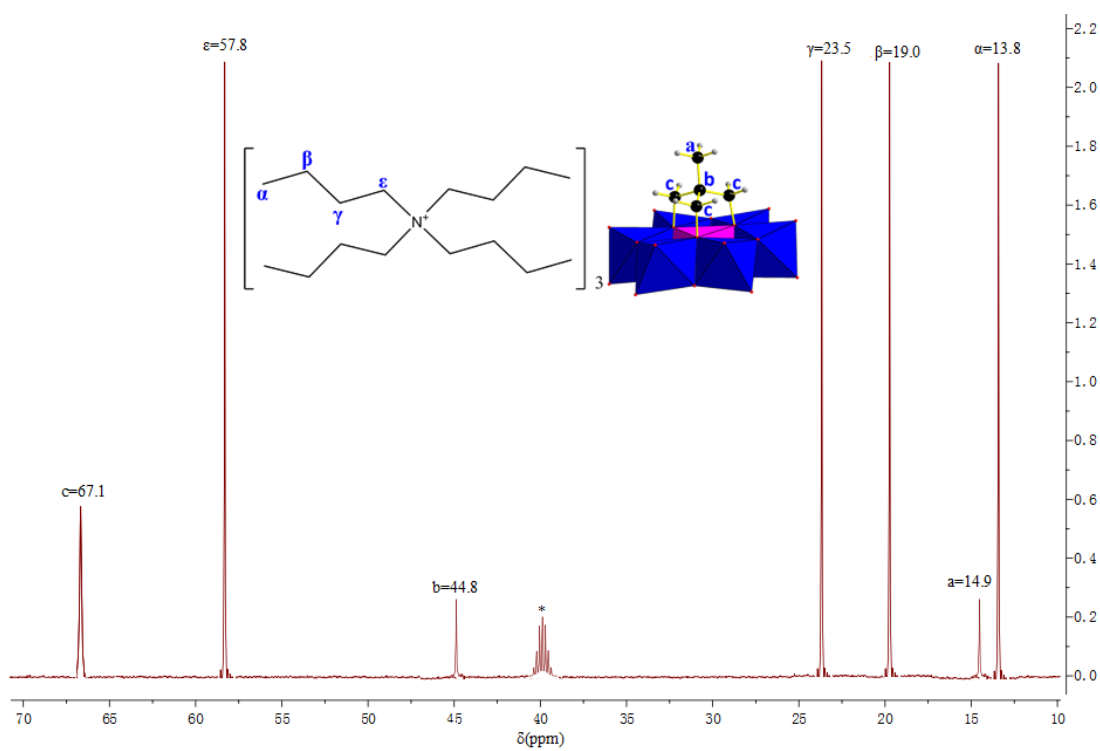


Fig. S6b the  $^{13}\text{C}$  NMR spectrum and chemical shifts of compound **2**



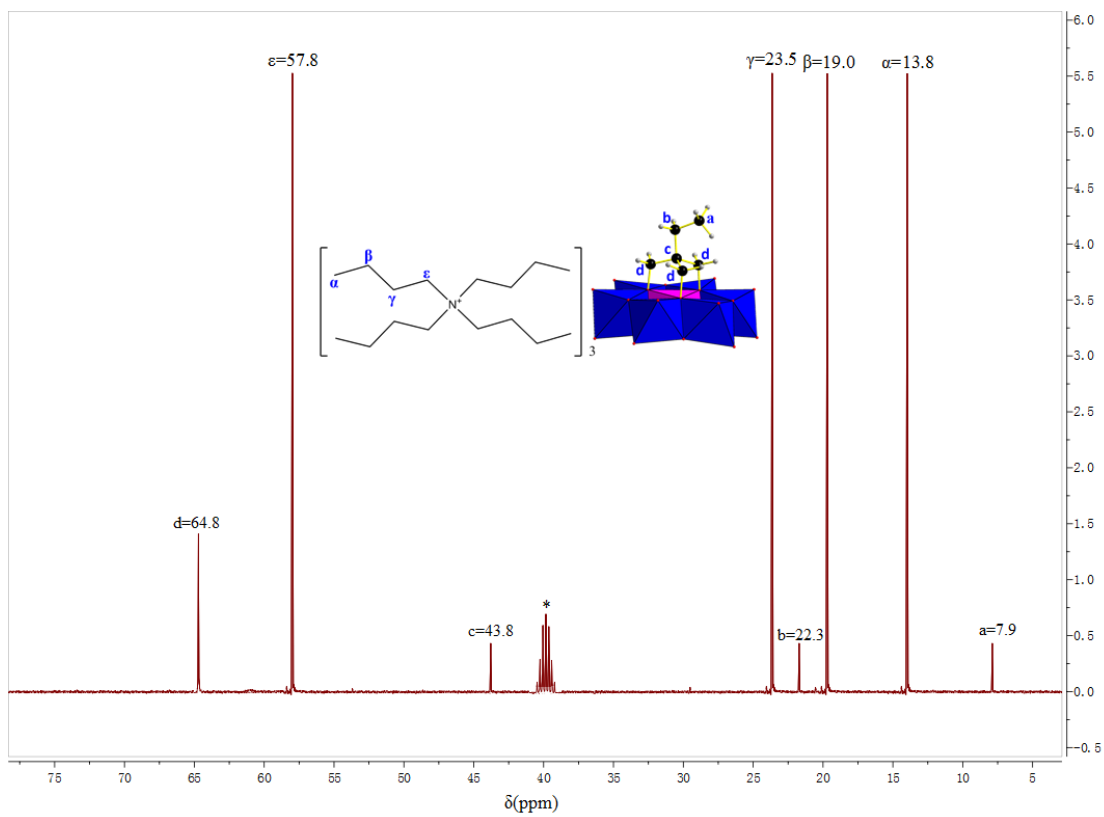


Fig. S6c the <sup>13</sup>C NMR spectrum and chemical shifts of compound **3**

Fig. S7 ESI mass spectrometry of compounds **1-3**

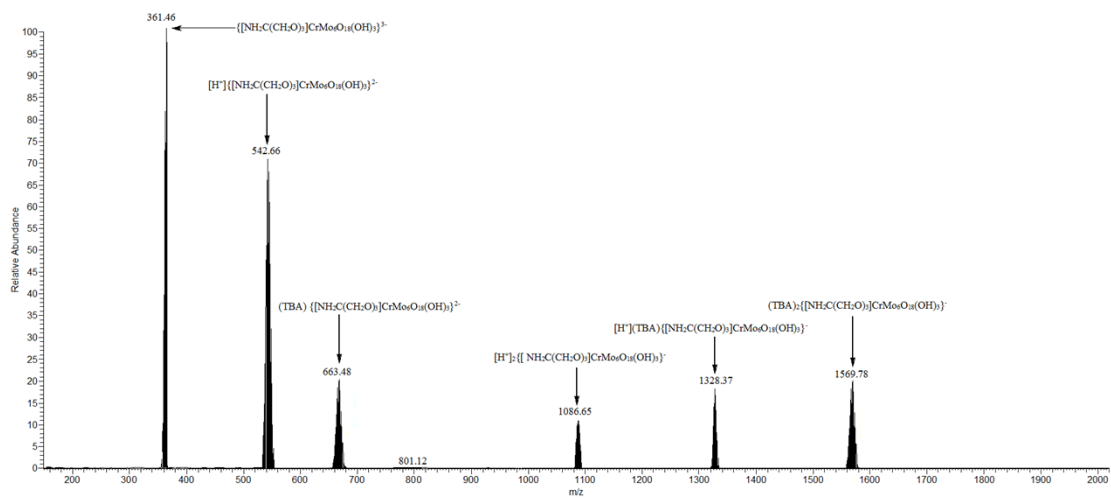


Fig. S7a ESI mass spectrometry of compound **1**

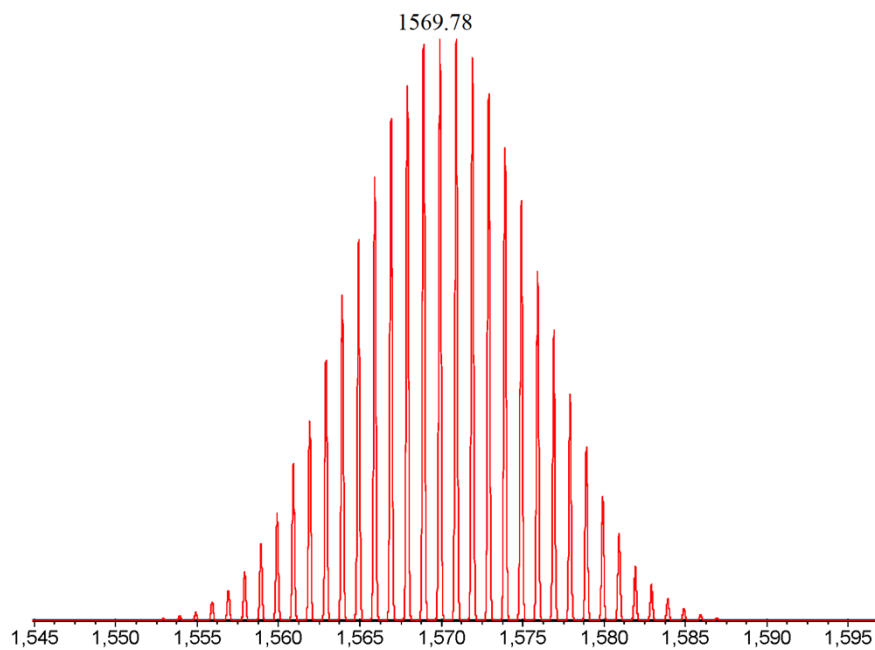


Fig. S7a1 ESI mass spectrometry of compound 1 (Partial peak in original size)

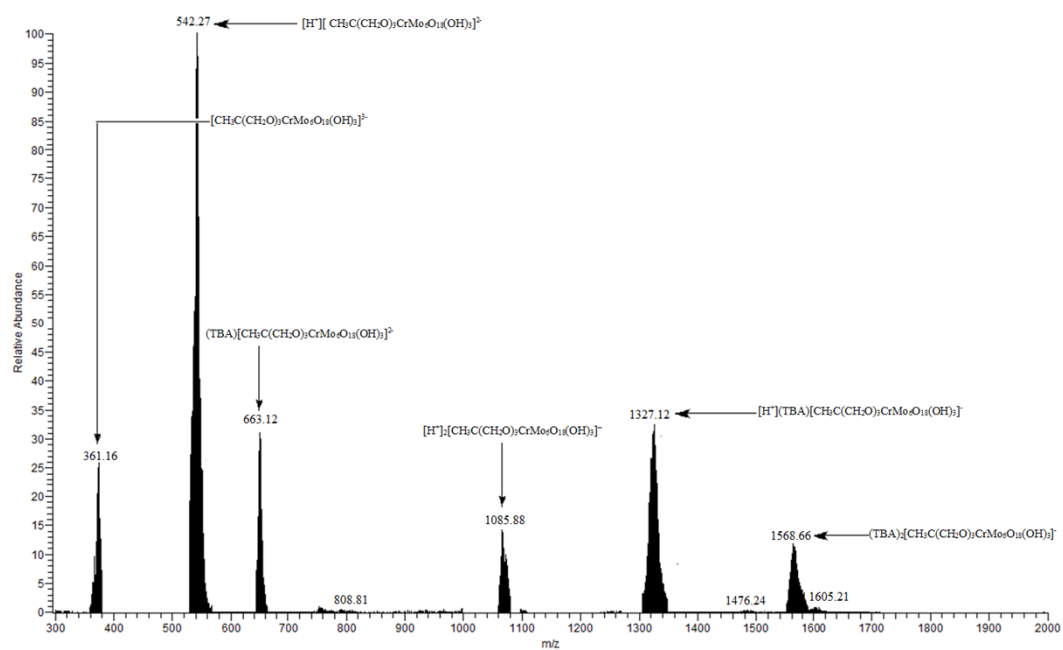


Fig. S7b ESI mass spectrometry of compound 2

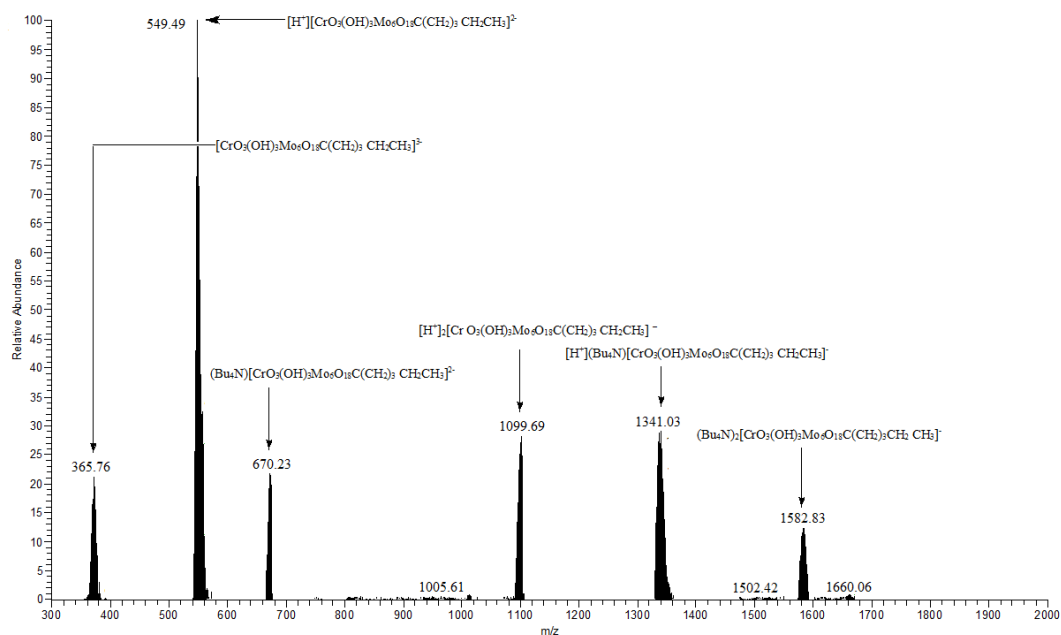


Fig. S7c ESI mass spectrometry of compound 3

## Reference

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