Organic Materials

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Supporting Information

Supramolecular Chirogenesis Engineered by Pt(II) ··Pt(II) Metal-Metal Interactions

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1. Materials and methods

Reagents. Methyl 4-iodobenzoate, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane, (1*R*,2*R*)-(-)-1,2-diaminocyclohexane, copper(I) iodide (CuI) were reagent grade and used as received. Compounds chloroplatinum(II) terpyridine ([Pt(tpy)Cl](BF$_4$)),[S1] **2**,[S2] **3**,[S3] and **6**[S4] were synthesized according to the previously reported procedures. Other reagents and solvents were employed as purchased.

Experimental apparatus. ^{1}H NMR spectra was collected on a Bruker Ascend^{TM} 400 MHz spectrometer with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Bruker Ascend^{TM} 400 MHz spectrometer at 100 MHz. Time-of-flight mass spectra (TOF-MS) were obtained on matrix-assisted laser desorption ionization-time of flight (autoflex speed TOF/TOF, Bruker). UV–Vis spectra were recorded on a UV-1800 Shimadzu spectrometer. Fluorescent spectra were recorded on a Fluoromax-4 spectrofluorometer (Horiba Scientific). Circular dichroism (CD) measurements were performed on a Jasco J-1500 circular dichroism spectrometer, equipped with a PFD-425S/15 Peltier-type temperature controller. Dynamic light scattering (DLS) experiments were conducted on a Malvern Zeta-sizer Nano ZS Instrument. Transmission electron microscope (TEM) images were acquired on a Hitachi HT7700 electron microscope (acceleration voltage: 100 kV).

Computational details. The optimized structures were optimized by using G09 D.01software packages.[S5] The Pt atoms were described by the Lanl2dz core potential. Considering that the computation of complex (*SS*)-**1** or (*RR*)-**1** is time-consuming, the basis sets for the non-metallic elements were decreased to 3-21G.

General methods for the determination of binding constants. Non-covalent binding constants (K_a) of tweezer/guest complexes were determined *via* UV–Vis and Emission titration experiments. Taking the UV–Vis titration measurements as the example: treating the collected absorbance data (A) *vs* concentration of the titrating species (C_A) with a non-linear least-squares curve-fitting equation affords the binding constants. For 1 : 1 host/guest complexation, the binding constant is calculated according to the following equation:

$$A = A_0 + \frac{A_{\lim} - A_0}{2C_0}\left[C_0 + C_A + 1/K_S - \left[\left(C_0 + C_A + 1/K_S\right)^2 - 4C_0C_A\right]^{1/2}\right] \quad \textbf{(Equation S1)}$$

In particular, A_0 and A are the absorbance intensity of the titrated sample at the MMLCT band with and without presence of the titrating species, respectively. [C_0] is the total concentration of the titrated sample, while [C_A] is the concentration of the titrating species. $A_{\lim}$ is the limiting value of absorbance in the presence of excess donor and K_S is the binding constant.

The above one is the local fitting analysis method. In addition, a global fitting analysis is also adopted *via* the Matlab-based global analysis program (*fittingprogram*) written by P.

Thordarson *et al.* (*Supramol. Chem.* **2012**, *24*, 585; *Chem. Soc. Rev.* **2011**, *40*, 1305). It is documented that the global fitting analysis provides more accurate K_a values than those obtained via the traditional local fitting analysis method.[S6]

*2. Spectroscopy of (SS)-**1***

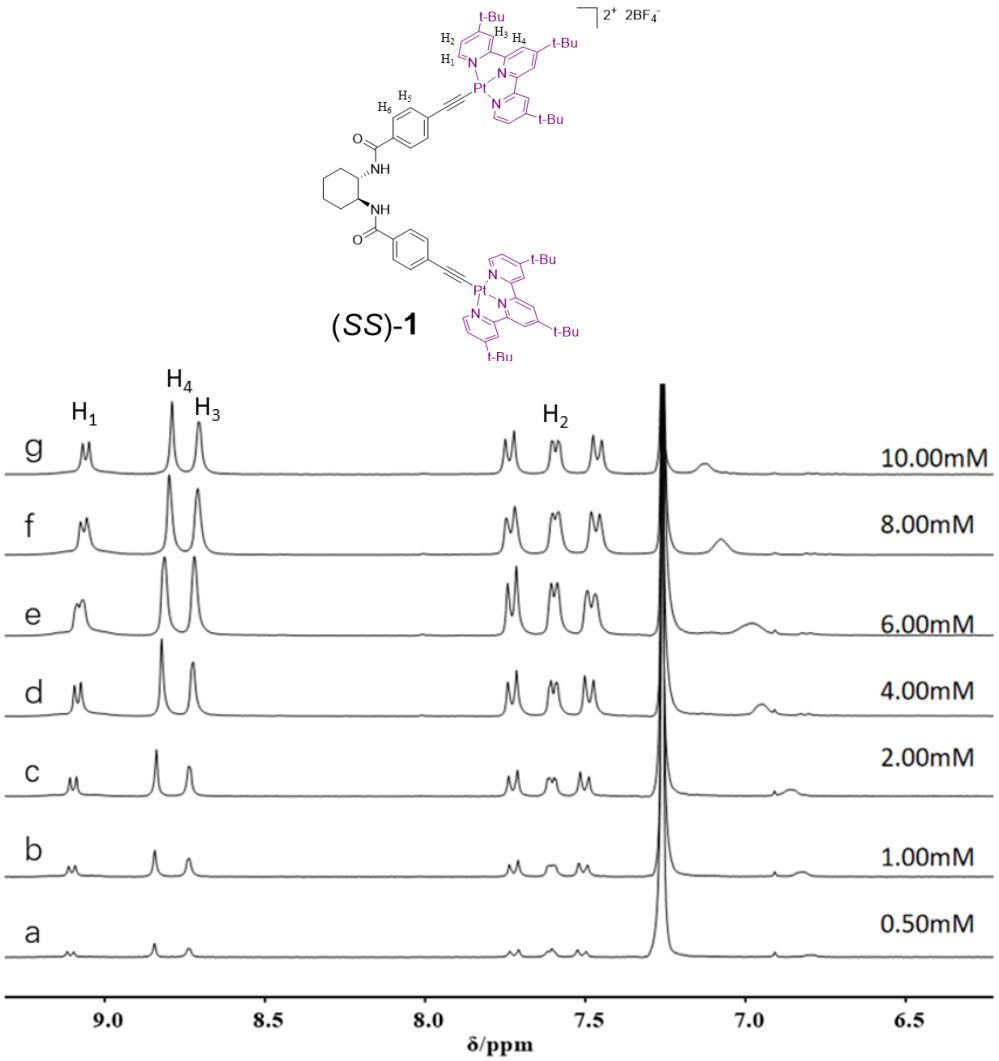


Figure S1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K) of compound (*SS*)-**1** with different concentration: a) 0.50 mM, b) 1.00 mM, c) 2.00 mM, d) 4.00 mM, e) 6.00 mM, f) 8.00 mM, g) 10.0 mM. As can be seen, the aromatic resonances on (*SS*)-**1** exhibited very slight changes upon varying the concentration of (*SS*)-**1** from 0.50 to 10.0 mM (δ for H_1: from 9.11 to 9.06 ppm), denoting weak self-association tendency of (*SS*)-**1**.

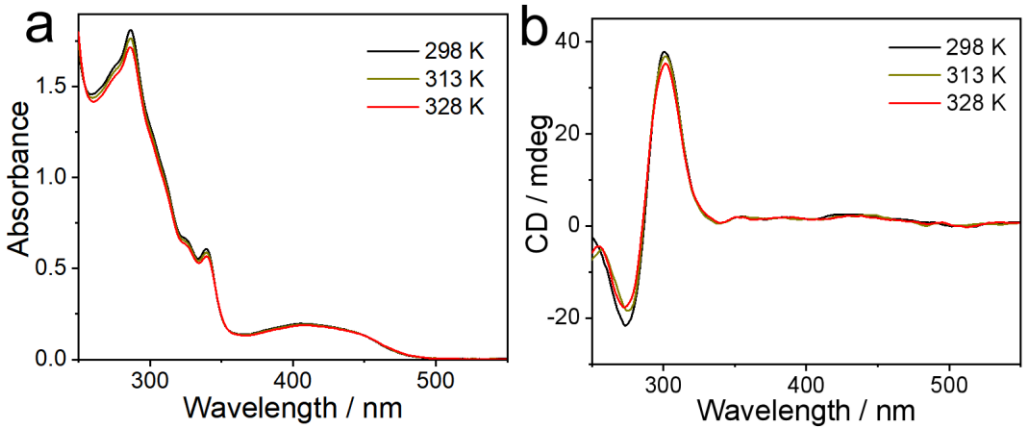


Figure S2. (a) UV–Vis absorption and (b) CD spectra (0.02 mM in $CHCl_3$) of (*SS*)-**1** upon varying the temperature. The Cotton effects in (*SS*)-**1** are ascribed to intrinsic molecular chirality, as validated by the maintenance of CD signals upon elevating the temperature.

*3. Non-covalent complexation between (SS)-**1** and **2***

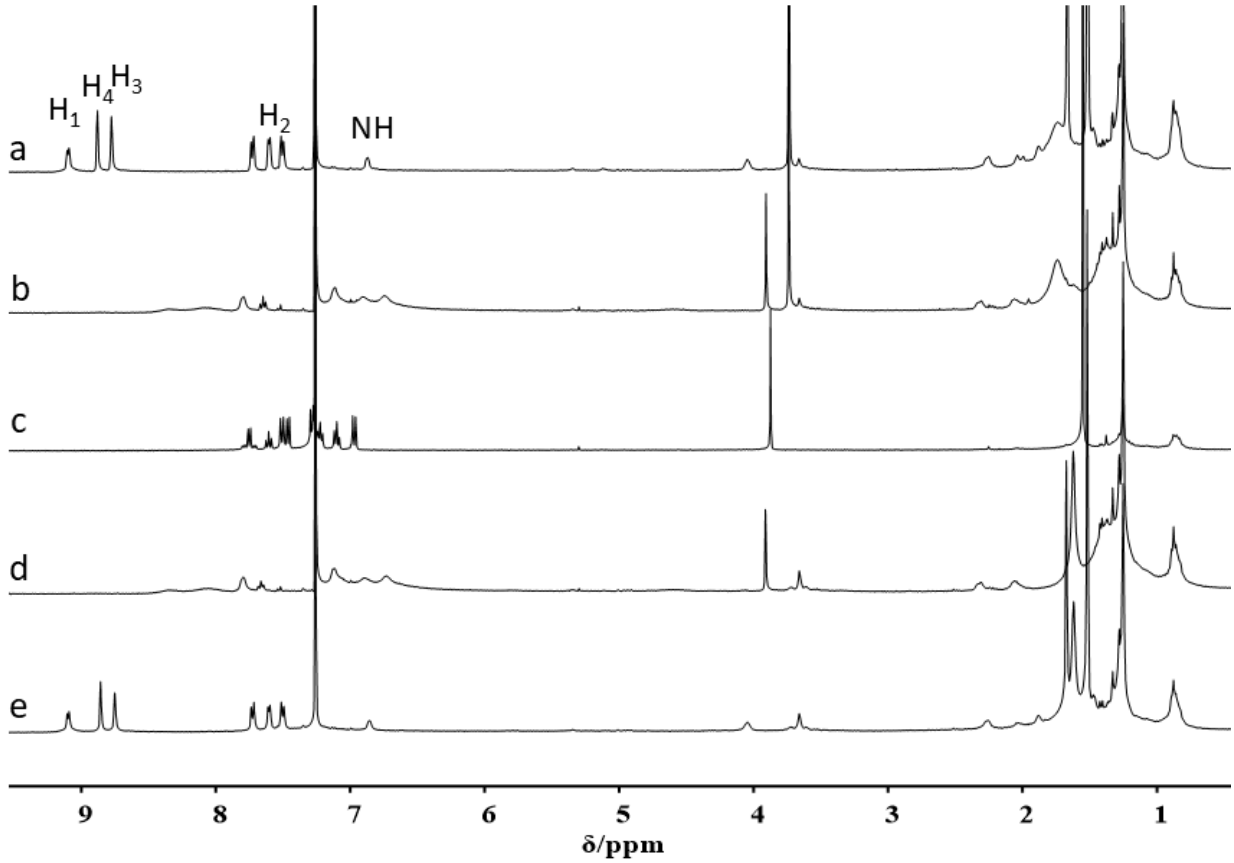


Figure S3. Partial ^{1}H NMR spectra (400 MHz, 2.00 mM in $CDCl_3$ for each compound, 293 K) of a) (*SS*)-**1**; b) complex (*SS*)-**1**/**2**; c) **2**; d) complex (*RR*)-**1**/**2**; e) (*RR*)-**1**. Upon mixing (*SS*)-**1** [or (*RR*)-**1**] and the neutral Pt(II) guest **2** together in $CDCl_3$, the aromatic ^{1}H NMR resonances became broadened and ill-defined, suggesting non-covalent complexation between (*SS*)-**1** [or (*RR*)-**1**] and **2**.

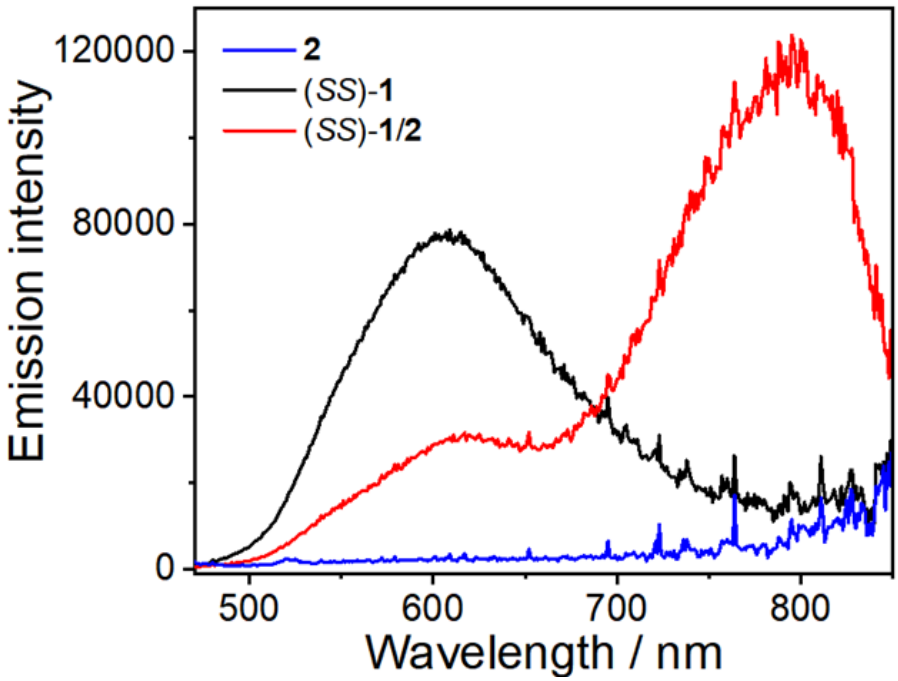


Figure S4. a) Emission spectra (0.10 mM for each compound in $CHCl_3$) of **2** (blue line), (*SS*)-**1** (black line) and complex (*SS*)-**1**/**2** (red line).

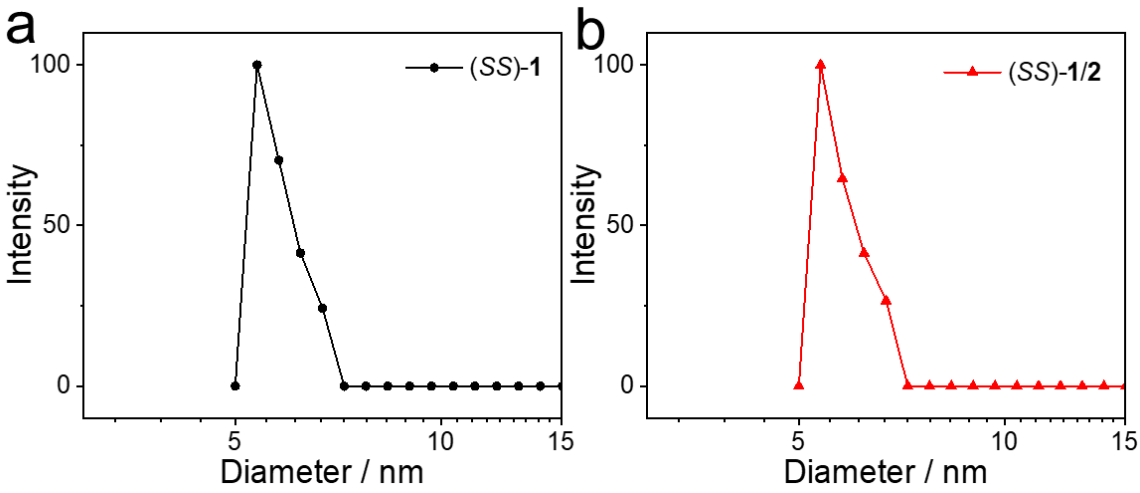
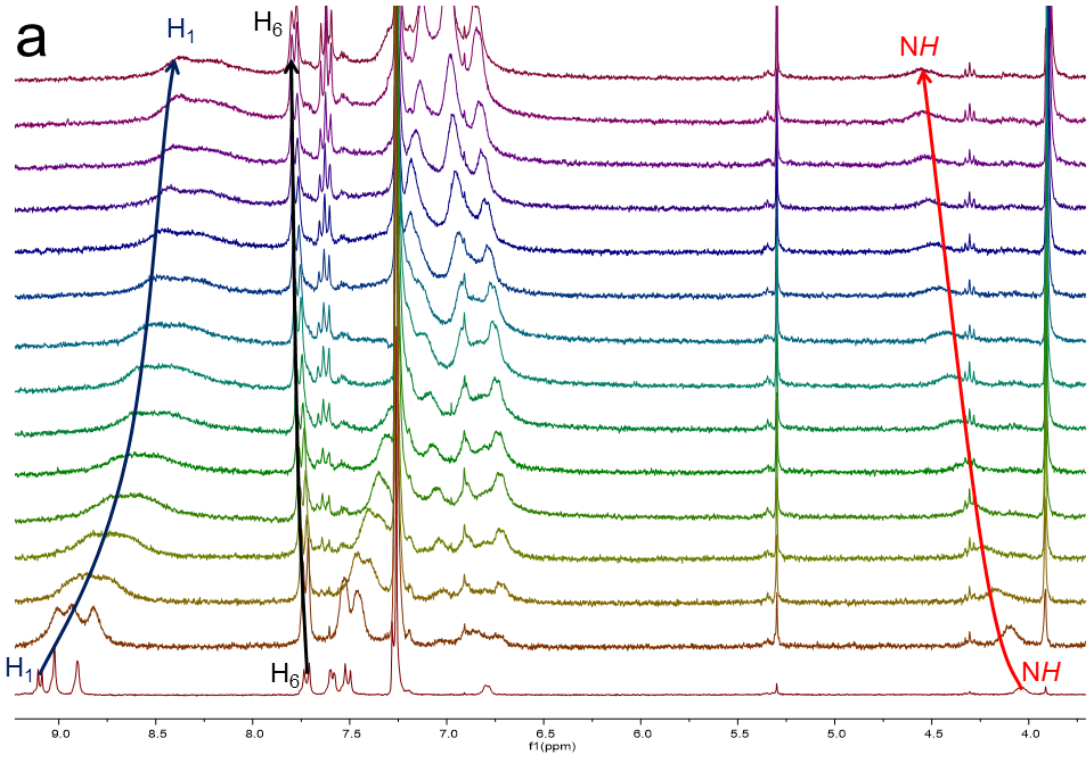


Figure S5. (a) DLS measurement of (*SS*)-**1** (0.05 Mm, $CHCl_3$) at 298 K. (b) DLS measurement of (*SS*)-**1**/**2** (0.05 mM for each compound in $CHCl_3$) at 298 K. Depending on DLS experiments, no large-sized aggregates formed for the mixture of (*SS*)-**1** and **2** in chloroform (hydrodynamic diameter: < 6 nm). The result suggests the formation of discrete supramolecular entity rather than long-range-ordered nanostructures.



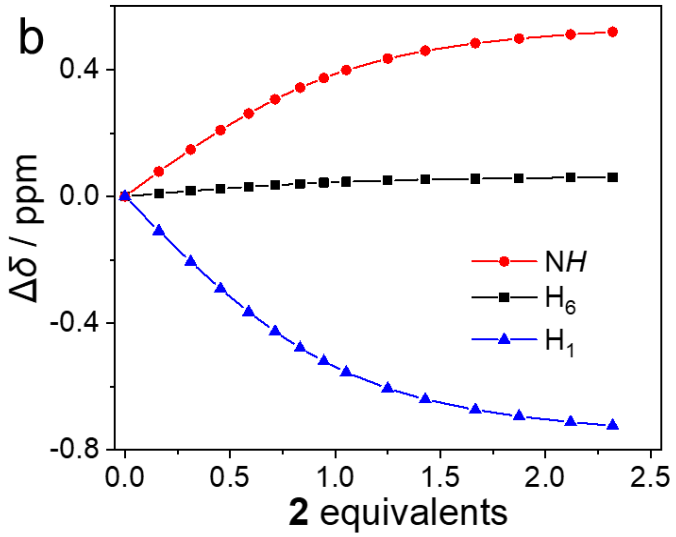


Figure S6. (a) Partial ^{1}H NMR spectra changes upon gradual addition of **2** into (*SS*)-**1** (0.50 mM in $CDCl_3$, 293 K). (b) Chemical shifts (δ) changes of protons H_6, H_1, N*H*, together with the non-linear fitting curves. The association constant of (*SS*)-**1**/**2** is determined to be 1.20×10^4 M^{-1} (±14%), by fitting the collected δ dates of protons H_6, H_1 and N*H* with the global analysis method.

Table S1. Experimental values on the basis of ^{1}H NMR titration experiment of (*SS*)-**1**/**2** in $CDCl_3$ at 293 K.

Host / M	Guest / M	Chemical shifts (δ) of **2** / ppm		
(*SS*)-**1**	**2**	$\delta(H_6)$	δ(N*H*)	$\delta(H_1)$
0.00050	0	7.736	4.035	9.097
	0.00008	7.745	4.113	8.988
	0.00016	7.753	4.183	8.891
	0.00023	7.76	4.244	8.806
	0.00029	7.766	4.297	8.732
	0.00036	7.772	4.341	8.67
	0.00042	7.776	4.378	8.619
	0.00047	7.779	4.409	8.577
	0.00053	7.782	4.434	8.542
	0.00063	7.787	4.47	8.491
	0.00071	7.789	4.495	8.457
	0.00083	7.792	4.518	8.424
	0.00094	7.794	4.533	8.403
	0.00106	7.795	4.546	8.385
	0.00116	7.796	4.554	8.374

Table S2. Calculated association constants (K_a) for complexes (*SS*)-**1**/**2** *via* ^{1}H NMR and Emission titrations.

	^{1}H NMR	Emission
K_a (M^{-1}) of (*SS*)-**1**/**2**	1.20×10^4 (± 14%)	1.35×10^4 (± 6%)

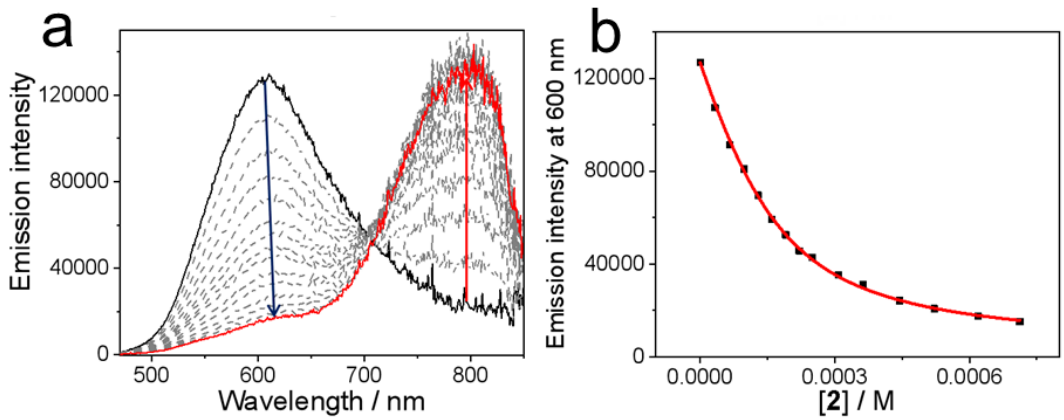


Figure S7. (a) Partial emission changes upon gradual addition of **2** into (*RR*)-**1** (0.20 mM in $CHCl_3$). (b) Intensity changes of emission intensity at 600 nm and non-linear curve fitting (red line). The arrows in (a) indicate the spectral change upon increasing the amount of **2**.

*4. Supramolecular Chirogenesis for Complexes (SS)-**1/2** and (RR)-**1/2***

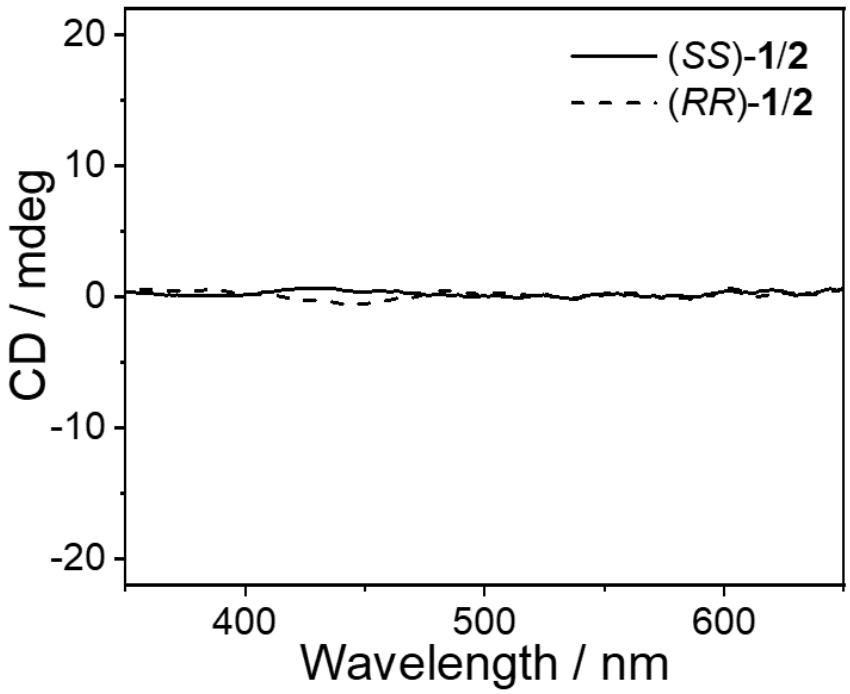


Figure S8. CD spectra (0.10 mM for each compound in $CHCl_3$) of (*SS*)-**1**/**2** (solid line) and (*RR*)-**1**/**2** (dash line) at 298 K.

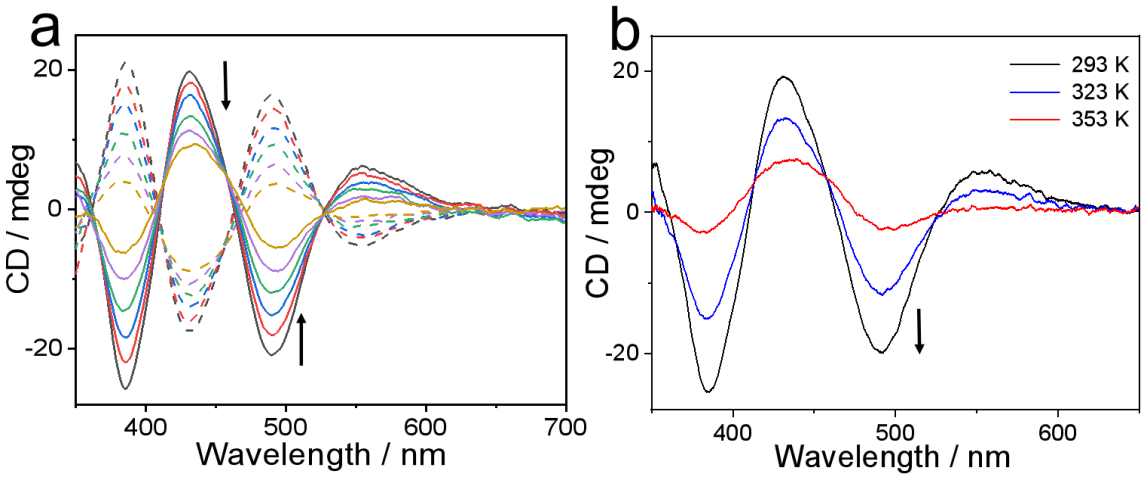


Figure S9. Partial CD spectra (1.00 mM for each compound in 1,2-dichloroethane) of (*SS*)-**1**/**2** (solid line) and (*RR*)-**1**/**2** (dash line) upon (a) elevating (from 293 K to 353 K) and (b) lowering (from 353 K to 293 K) the temperature. The arrows in (a) and (b) indicate the spectral change upon changing the temperature. It is evident that supramolecular chirogenesis is temperature-dependent in organic media.

*5. Supramolecular Chirogenesis for Complexes (SS)-**1/3** and (RR)-**1/3***

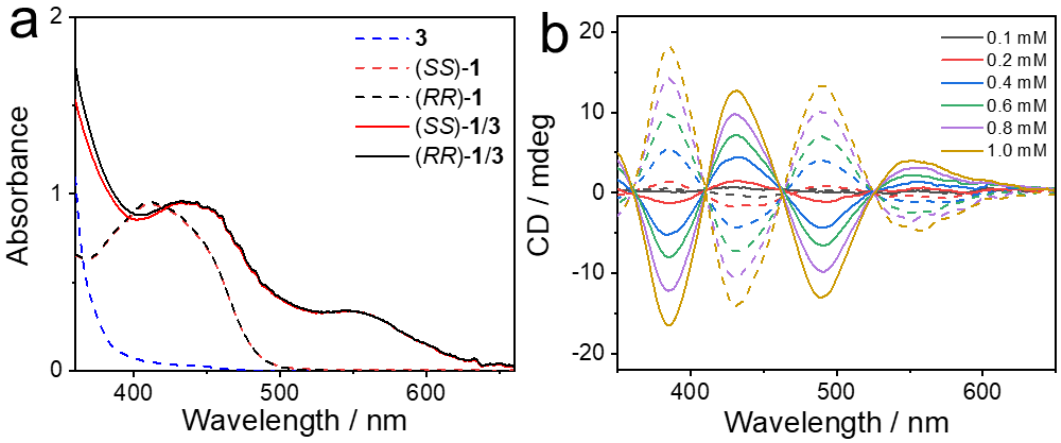


Figure S10. a) Partial UV–Vis spectra (0.20 mM in 1,2-dichloroethane) of **3**, (*SS*)-**1**, (*RR*)-**1**, (*SS*)-**1**/**3** and (*RR*)-**1**/**3**. b) Partial CD spectra of (*SS*)-**1**/**3** (solid line) and (*RR*)-**1**/**3** (dash line) in 1,2-dichloroethane with different concentrations.

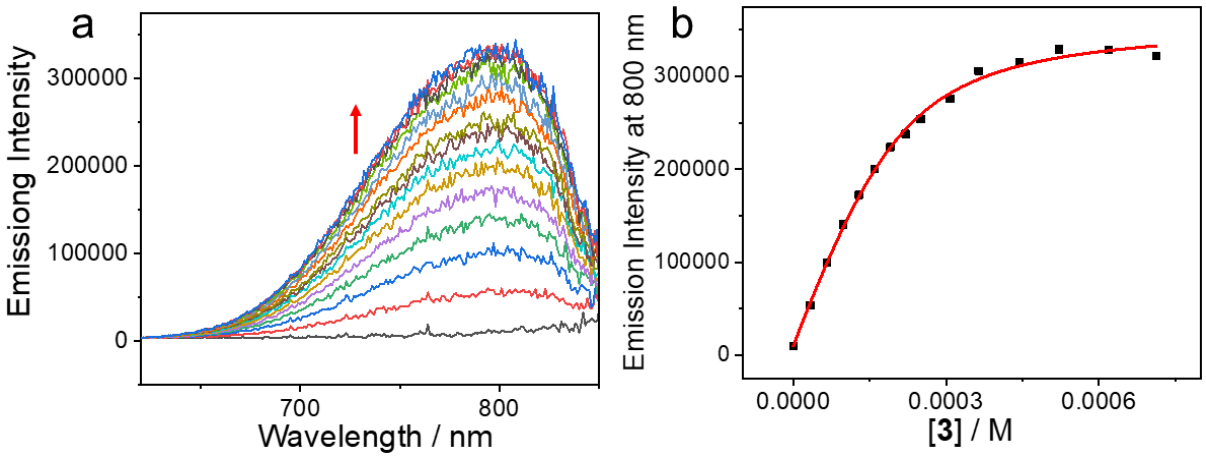


Figure S11. (a)Partial emission changes upon gradual addition of **3** into (*SS*)-**1** (0.20 mM in $CHCl_3$). (b) Intensity changes of emission intensity at 800 nm and non-linear curve fitting (red line). The arrows in (a) indicate the spectral change upon increasing the amount of **3**.

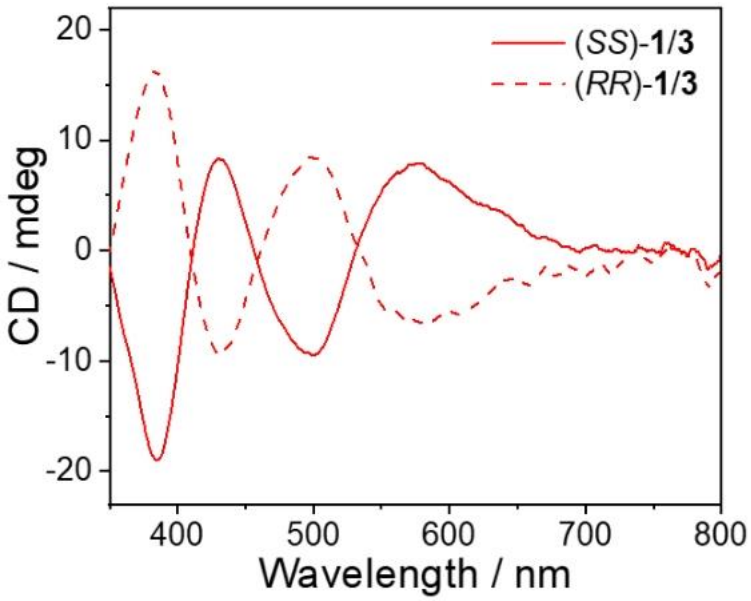


Figure S12. CD spectra (1.00 mM for each compound in water) of (*SS*)-**1**/**3** and (*RR*)-**1**/**3**.

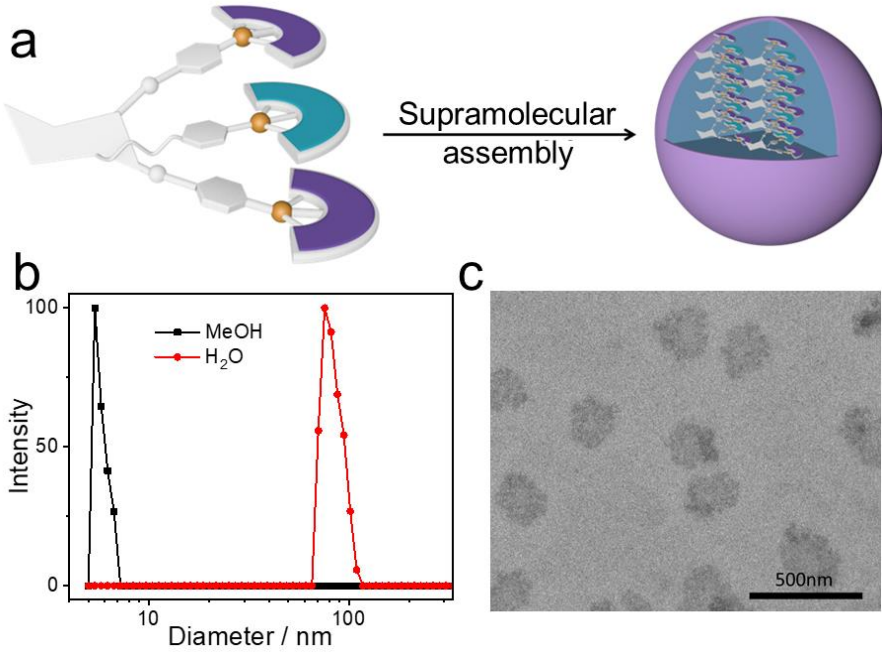


Figure S13. (a) Schematic representation for supramolecular assembly of (*SS*)-**1**/**3** in water. (b) DLS measurements (0.10 mM) of (*SS*)-**1**/**3** in MeOH and H_2O at 298 K. (c) TEM image of (*SS*)-**1**/**3** recorded by drop-casting of the H_2O solution at 0.05 mM on a copper grid.

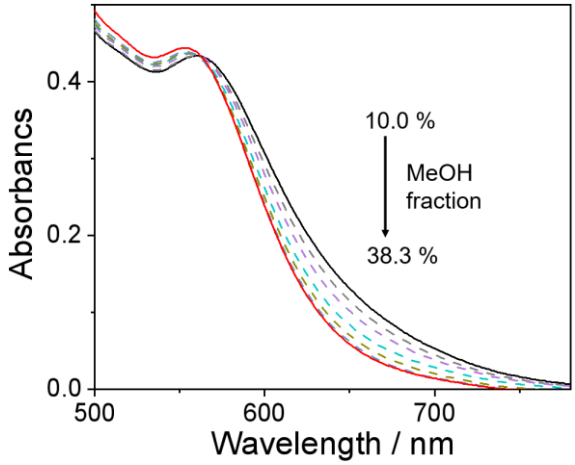


Figure S14. Solvent-dependent absorption curves of (*SS*)-**1**/**3** in the mixture of MeOH/H_2O at 298 K.

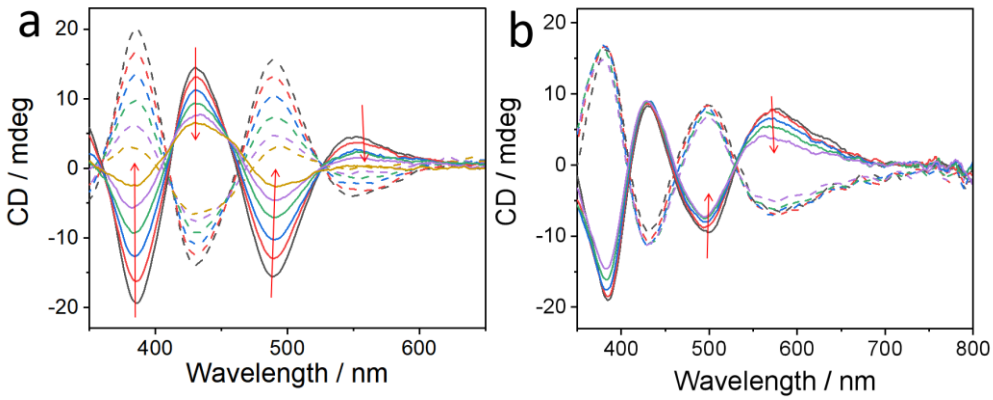
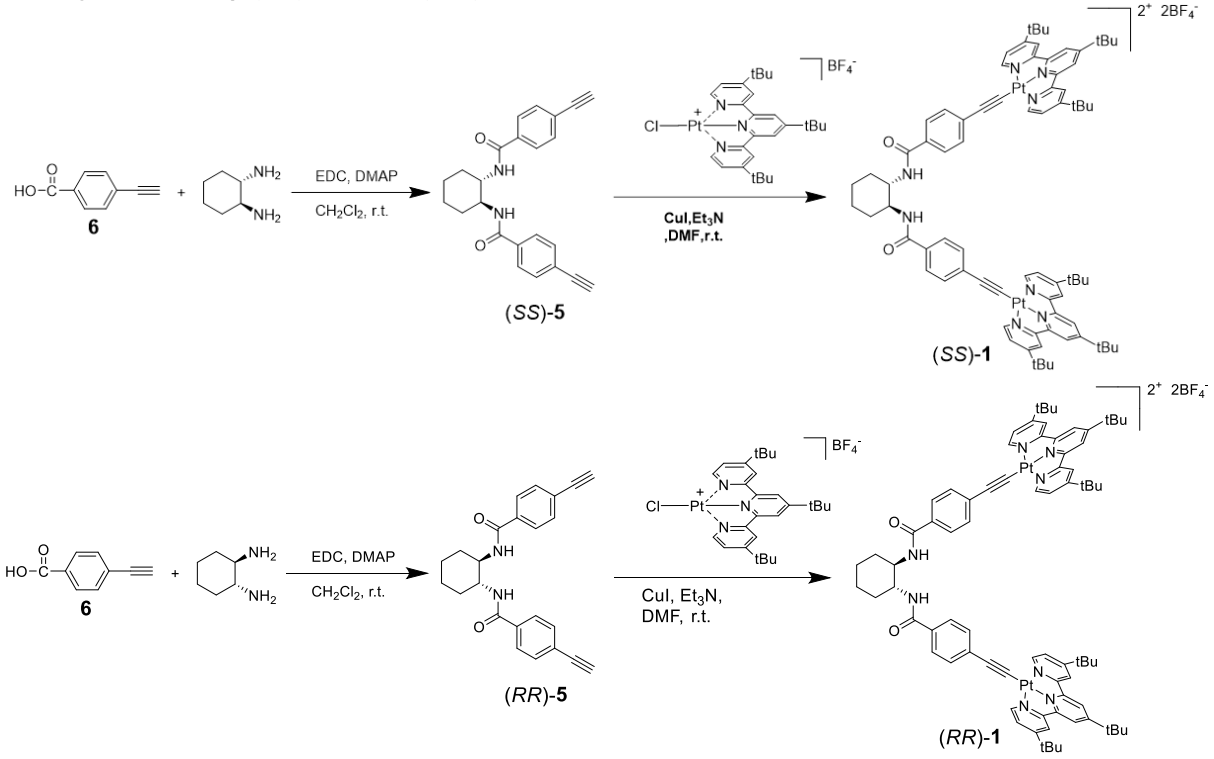


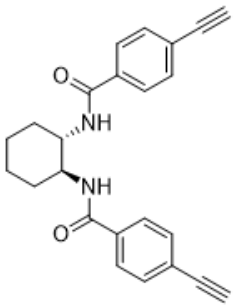
Figure S15. CD spectra (1.00 mM) of (*SS*)-**1**/**3** (solid line) and (*RR*)-**1**/**3** (dash line) in (a) 1,2-dichloroethane and (b) H_2O at different temperature. The arrows represent the trend of CD intensity changes of (*SS*)-**1**/**3** and (*RR*)-**1**/**3** upon heating.

*6. Synthesis of (SS)-**1** and (RR)-**1***



Scheme S1. Synthetic routes to compounds (*SS*)-**1** and (*RR*)-**1**.

*6.1. Synthesis of (SS)-**5***



Compound **6** (736 mg, 5.04 mmol), (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (250 mg, 2.19 mmol), EDC•HCl (841 mg, 4.38 mmol) and DMAP (134 mg, 1.10 mmol) in 60 mL CH_2Cl_2 were stirred at room temperature for 24 hours. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was extracted with H_2O/CH_2Cl_2. The combined organic extracts were removed with a rotary evaporator, and the residue was purified by flash column chromatography (CH_2Cl_2/CH_3OH, 100 : 1 *v*/*v* as the eluent; R_f = 0.45) to provide compound (*SS*)-**5** as a white solid (0.67 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 – 7.62 (m, 4H), 7.53 – 7.41 (m, 4H), 6.84 – 6.73 (m, 2H), 3.99 (s, 2H), 3.17 (d, J = 2.9 Hz, 2H), 2.22 (s, 2H), 1.43 (d, J = 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$: CH_3OD = 3 : 1) δ: 167.1, 133.1, 131.2, 126.1, 124.4, 81.8, 78.6, 53.2, 31.1, 23.8.

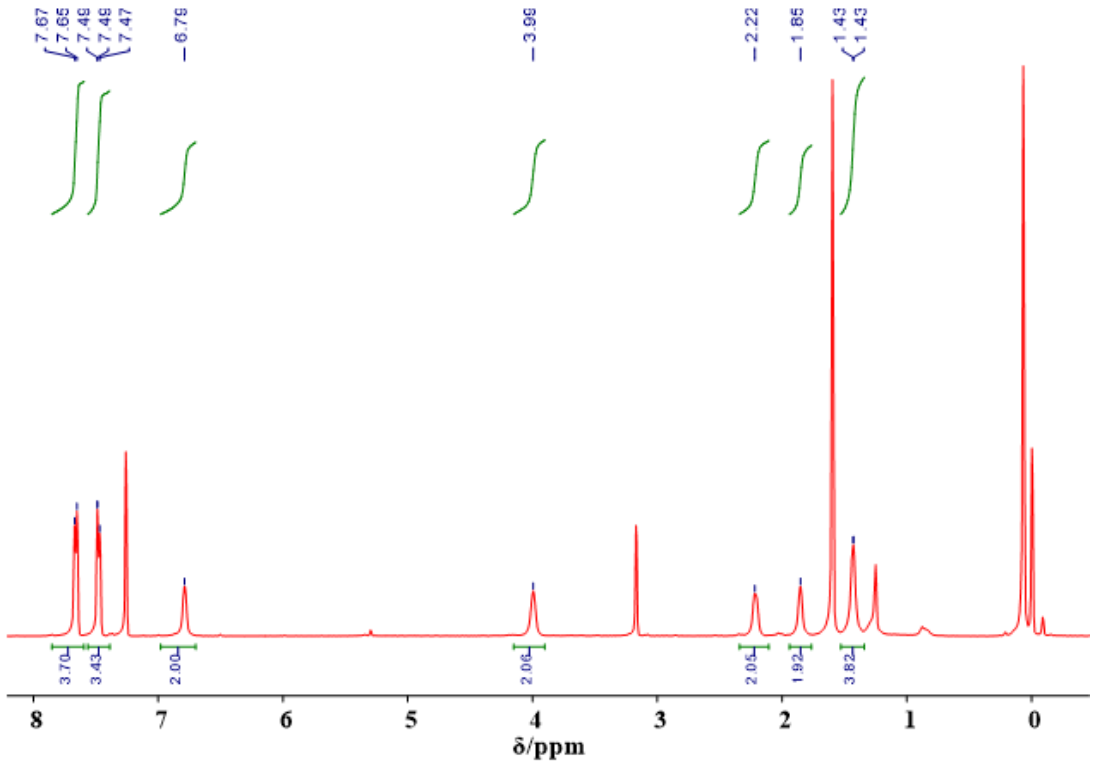


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of (*SS*)-**5**.

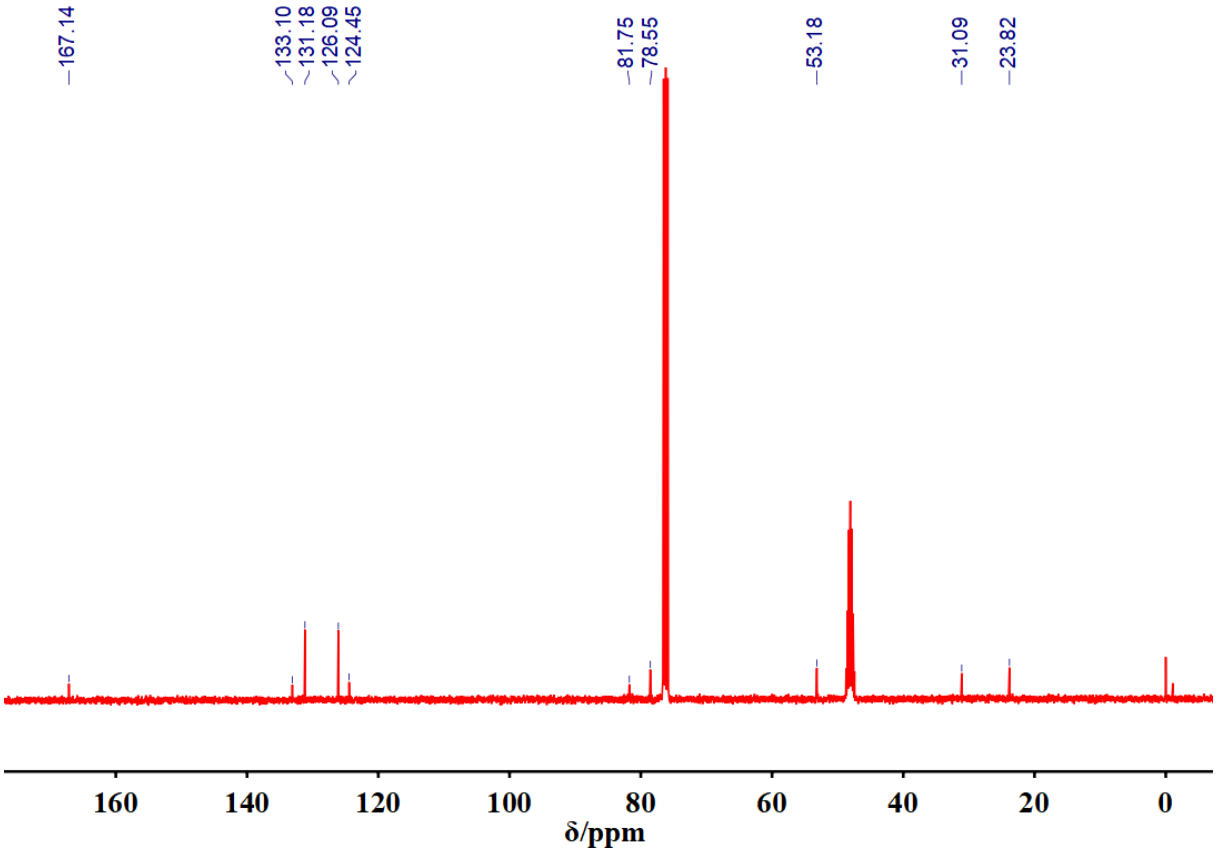
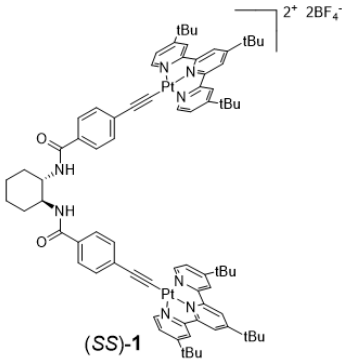


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$: CH_3OD = 3 : 1, 293 K) of (*SS*)-**5**.

*6.2. Synthesis of (SS)-**1***



Compound (*SS*)-**5** (30.0 mg, 0.08 mmol), [Pt(tpy)Cl](BF$_4$) (128 mg, 0.18 mmol), CuI (20.0 mg, 0.10 mmol) and TEA (3 mL) in DMF were stirred under nitrogen atmosphere at room temperature for 48 hours. The mixture was evaporated under reduced pressure, and the residue was extracted with H$_2$O/CH$_2$Cl$_2$. The combined organic extracts were removed with a rotary evaporator, and the residue was purified by flash column chromatography (CH$_2$Cl$_2$/CH$_3$OH, 50:1 *v*/*v* as the eluent; R_f = 0.3) to afford (*SS*)-**1** as a yellow solid (120 mg, 86%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.09 (d, J = 6.0 Hz, 4H), 8.86 (s, 4H), 8.75 (d, J = 2.1 Hz, 4H), 7.76 – 7.69 (m, 4H), 7.60 (dd, J = 6.1, 2.1 Hz, 4H), 7.53 – 7.46 (m, 4H), 6.91 (s, 2H), 4.05 (s, 2H), 2.26 (d, J = 9.6 Hz, 2H), 1.88 (s, 2H), 1.66 (s, 18H), 1.51 (s, 36H). ^{13}C NMR (100 MHz, CDCl$_3$: CH$_3$OD = 3 : 1) δ:167.4, 166.3, 157.6, 152.8, 152.6, 130.9, 130.8, 130.1, 127.8, 126.0, 124.5, 122.6, 121.0, 51.7, 36.7, 35.6, 30.5, 29.8, 29.3, 28.7. HRMS: *m*/*z*: [M – 2BF$_4$]$^{2+}$, experimental, 780.3229; calculated, 780.3241, error 1.5 ppm.

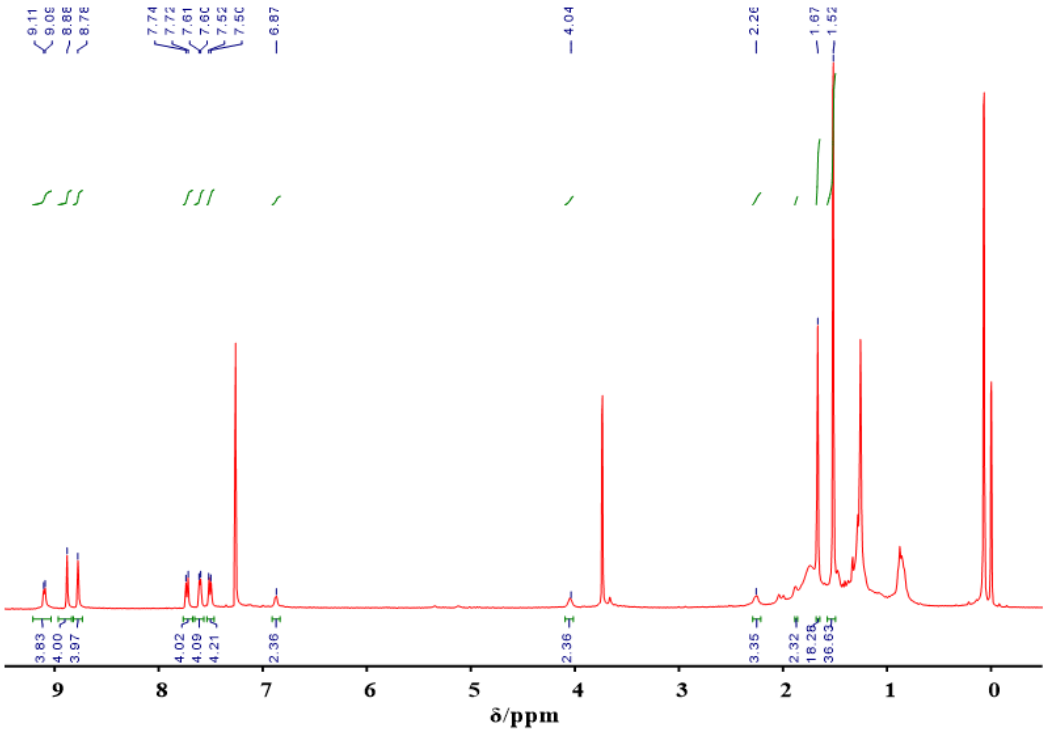


Figure S18. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 293K) of (*SS*)-**1**.

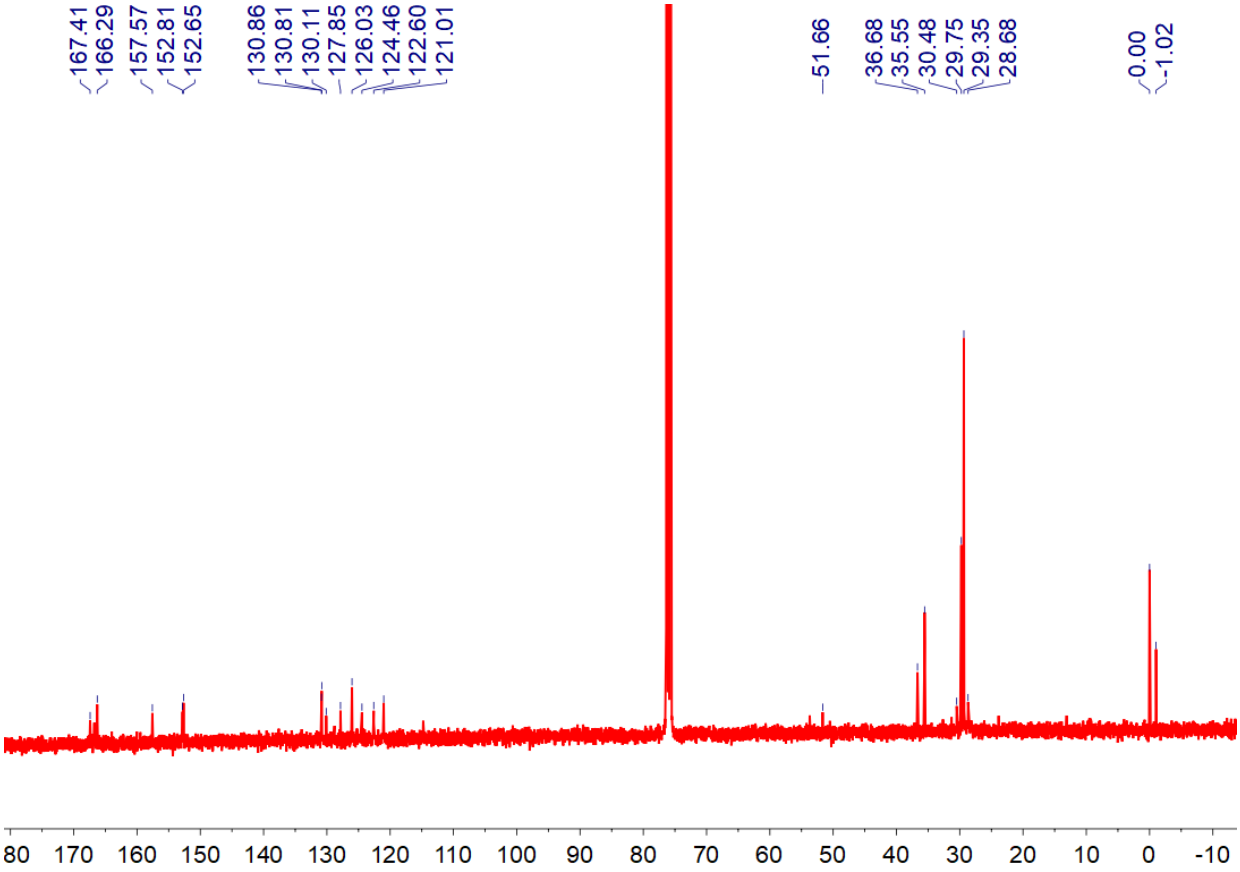


Figure S19. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of (*SS*)-**1**.

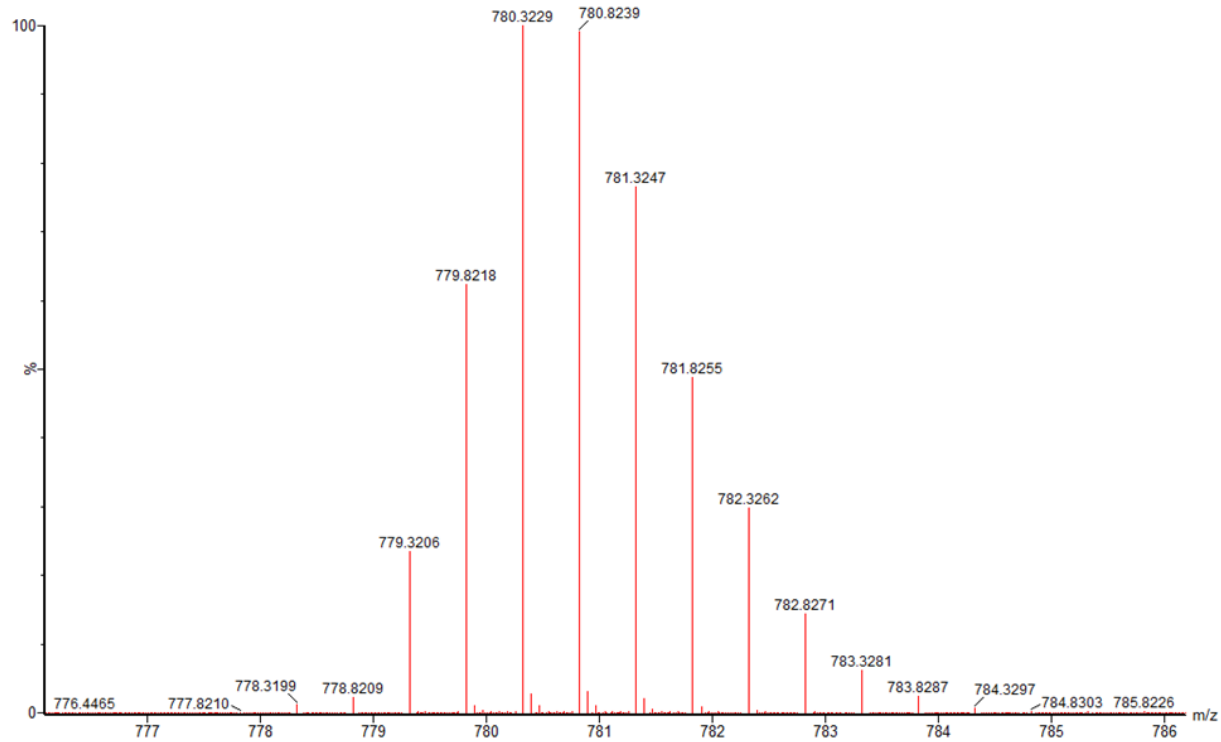


Figure S20. HRMS of (*SS*)-**1**.

6.3. Synthesis of (RR)-5

A similar procedure to that of (*SS*)-**5** was adopted, by employing (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (250 mg, 2.19 mmol) instead of (1*S*,2*S*)-(+)-1,2-diaminocyclohexane. Compound (*RR*)-5 was obtained as a white solid (0.65 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 8.1 Hz, 4H), 7.49 (d, J = 8.0 Hz, 4H), 6.80 – 6.72 (m, 2H), 4.00 (d, J = 8.1 Hz, 2H), 2.22 (d, J = 8.5 Hz, 2H), 1.43 (d, J = 7.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$:CH_3OD=3:1) δ: 168.2, 134.0, 132.1, 127.1, 125.5, 82.6, 79.6, 54.0, 31.9, 24.8.

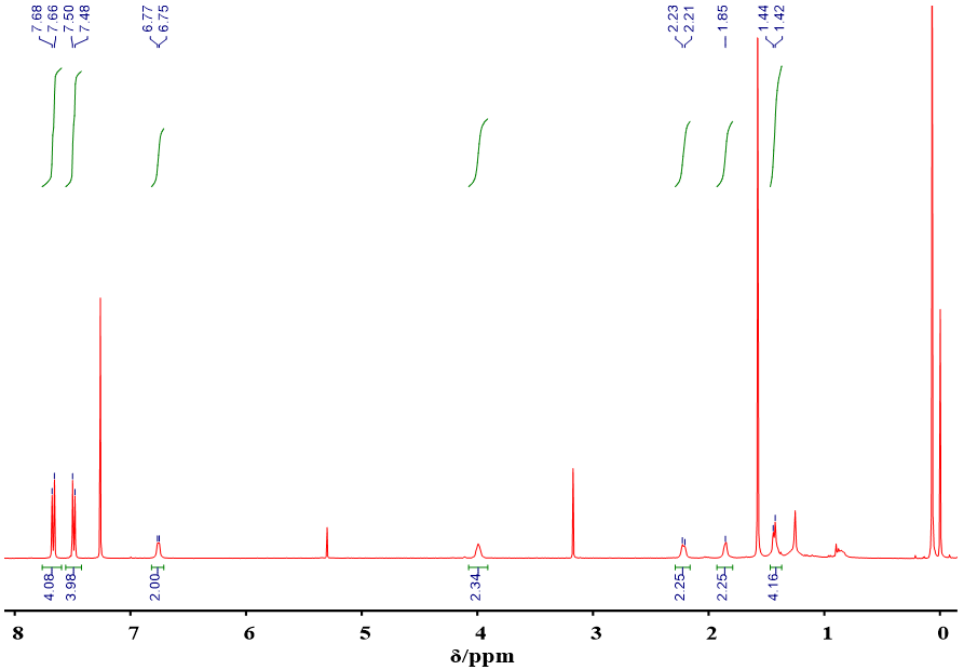


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293K) of (*RR*)-**5**.

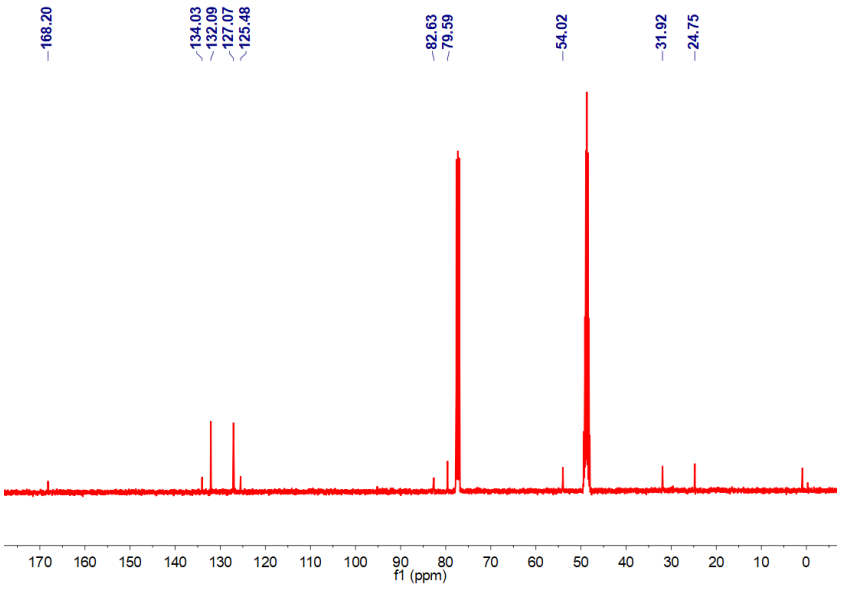


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$: CH_3OD = 3:1, 293K) of (*RR*)-**5**.

6.4. Synthesis of (*RR*)-***1***

A similar procedure to that of (*SS*)-**1** was adopted, by employing (*RR*)-**5** (250 mg, 2.19 mmol) instead of (*SS*)-**5**. Compound (*RR*)-**1** was obtained as a yellow solid (117 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (d, J = 6.0 Hz, 4H), 8.68 (s, 4H), 8.59 (s, 4H), 7.73 (d, *J* = 7.9 Hz, 4H), 7.62 (d, *J* = 6.0 Hz, 4H), 7.49 (d, *J* = 8.0 Hz, 4H), 6.96 – 6.88 (m, 2H), 4.06 (s, 2H), 2.24 (s, 2H), 1.88 (s, 2H), 1.66 (s, 18H), 1.51 (s, 36H), 1.47 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 152.7, 130.8, 126.0, 124.2, 121.4, 53.9, 36.8, 35.6, 29.8, 29.3, 28.3, 28.3. HRMS: *m*/*z*: $[M - 2BF_4]^{2+}$, experimental 780.3226; calculated, 780.3241, error 1.9 ppm.

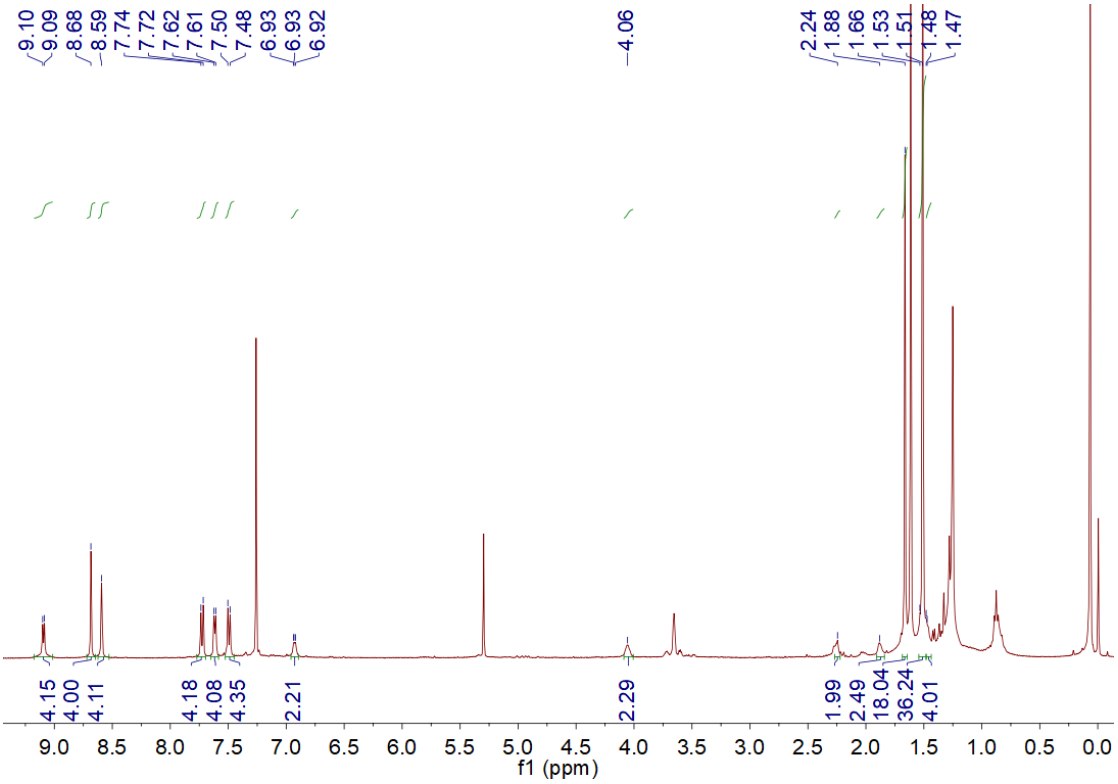


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$,293 K) of (*RR*)-**1**.

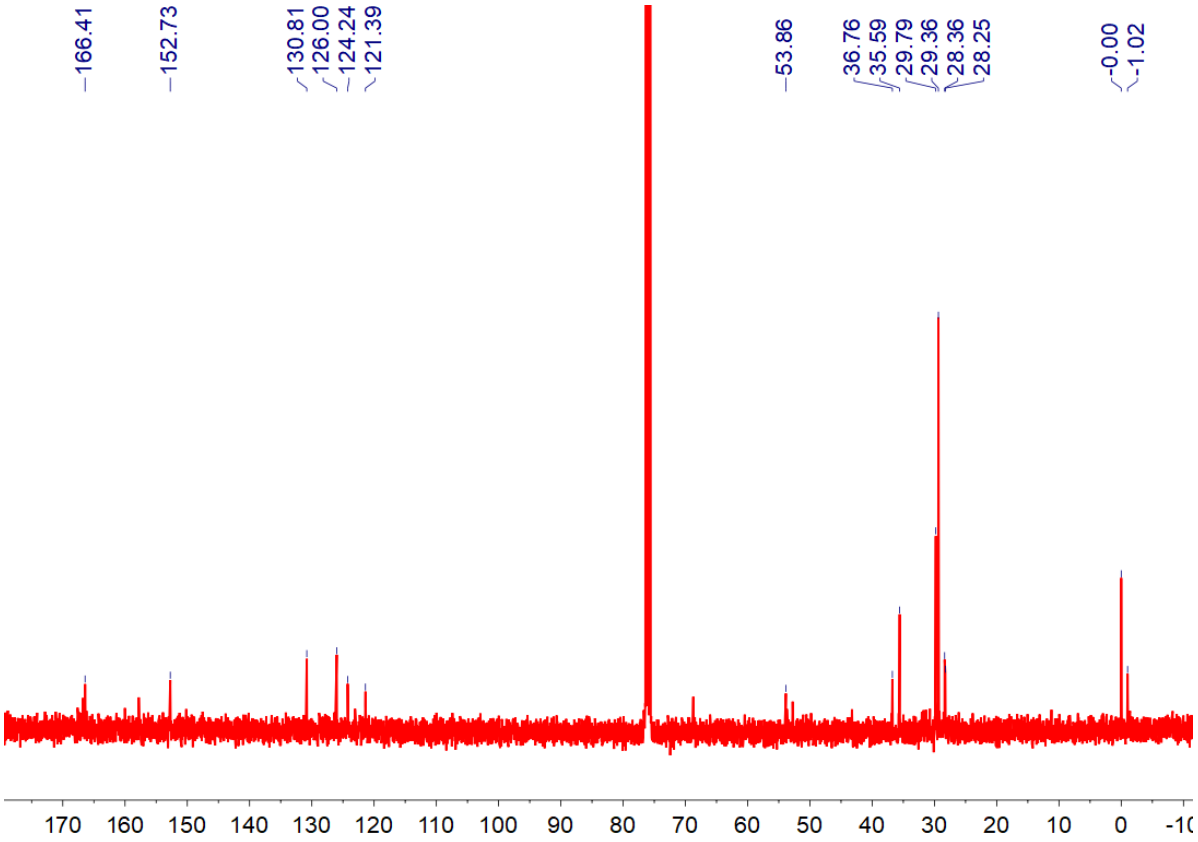


Figure S24. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of (*RR*)-**1**.

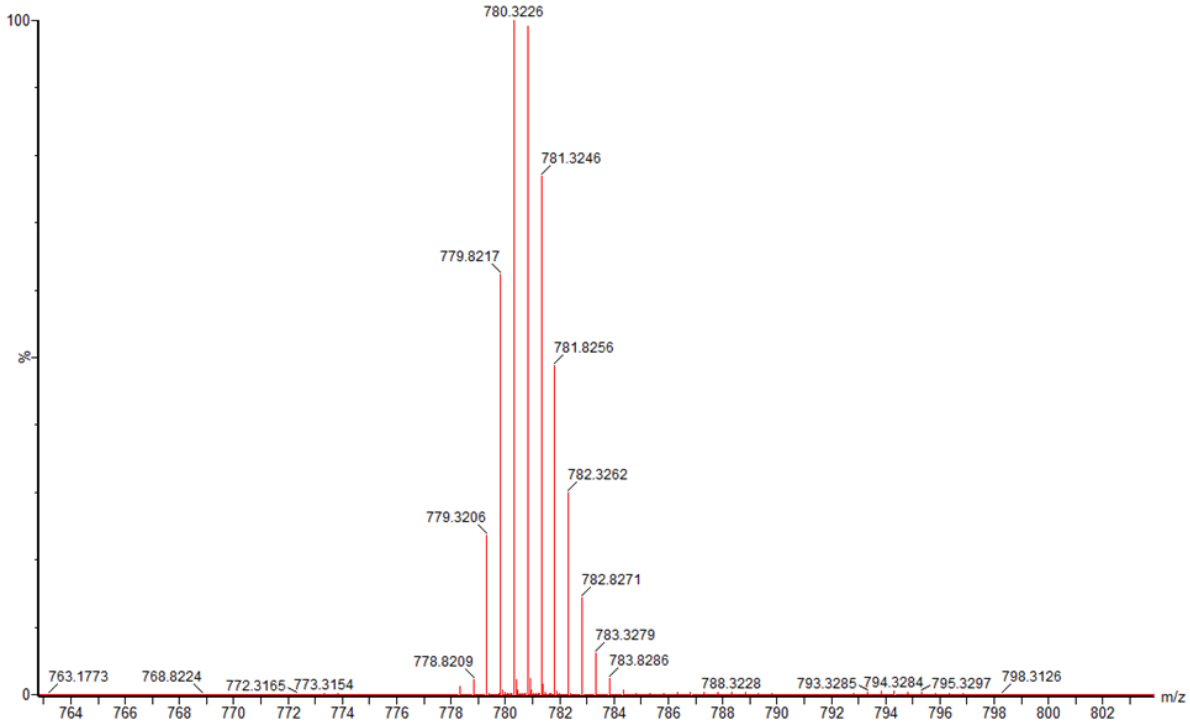


Figure S25. HRMS of (*RR*)-**1**.

*7. Standard orientation and frequency calculation of complex (SS)-**1***

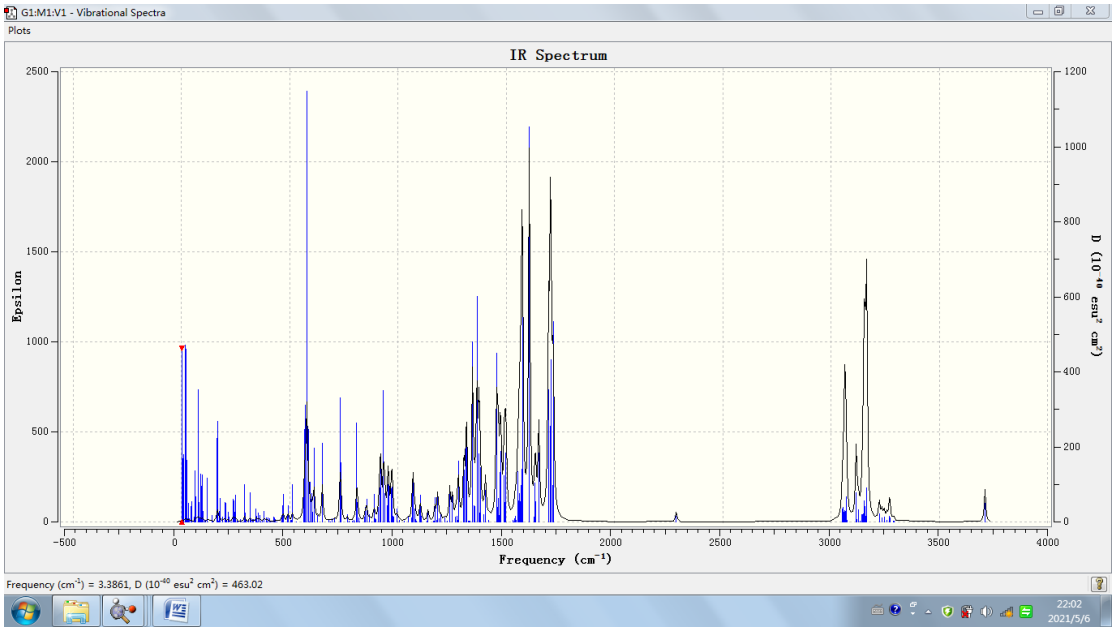


Figure S26. Frequency analysis of complex (*SS*)-**1**. The lowest frequency of (*SS*)-**1** was determined to be 3.3861 cm^{-1}, which unambiguously has no imaginary frequencies for the optimized structure.

```
Stoichiometry    C78H90N8O2Pt2(2+)
 Framework group  C1[X(C78H90N8O2Pt2)]
 Deg. of freedom   534
 Full point group                 C1      NOp   1
 Largest Abelian subgroup         C1      NOp   1
 Largest concise Abelian subgroup C1      NOp   1
                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
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      3          6           0       -0.574009    6.843695   -0.539523
      4          6           0        0.553750    6.847415    0.518159
      5          6           0        1.418777    8.111368    0.354780
      6          6           0        0.566367    9.382326    0.487255
      7          1           0       -1.928597    8.084715    0.600358
      8          1           0       -2.231373    8.087829   -1.141953
      9          1           0       -0.182987    9.433715   -1.541229
     10          1           0       -1.220875   10.264006   -0.381852
     11          1           0        0.073345    6.861508    1.500284
     12          1           0        2.208657    8.098025    1.114438
     13          1           0        1.906236    8.084734   -0.627888
     14          1           0        0.157960    9.442435    1.506023
     15          1           0        1.194449   10.268143    0.342118
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141	6	0	14.114758	-3.927492	0.569707
142	6	0	12.688108	1.994990	-4.134410
143	6	0	7.877201	-6.186779	4.281040
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149	6	0	13.969185	2.464988	-3.402716
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173	1	0	13.740166	1.263631	-5.889817
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179	6	0	6.236066	1.297503	0.066328
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---

*8. Standard orientation and frequency calculation of complex (SS)-**1/2***

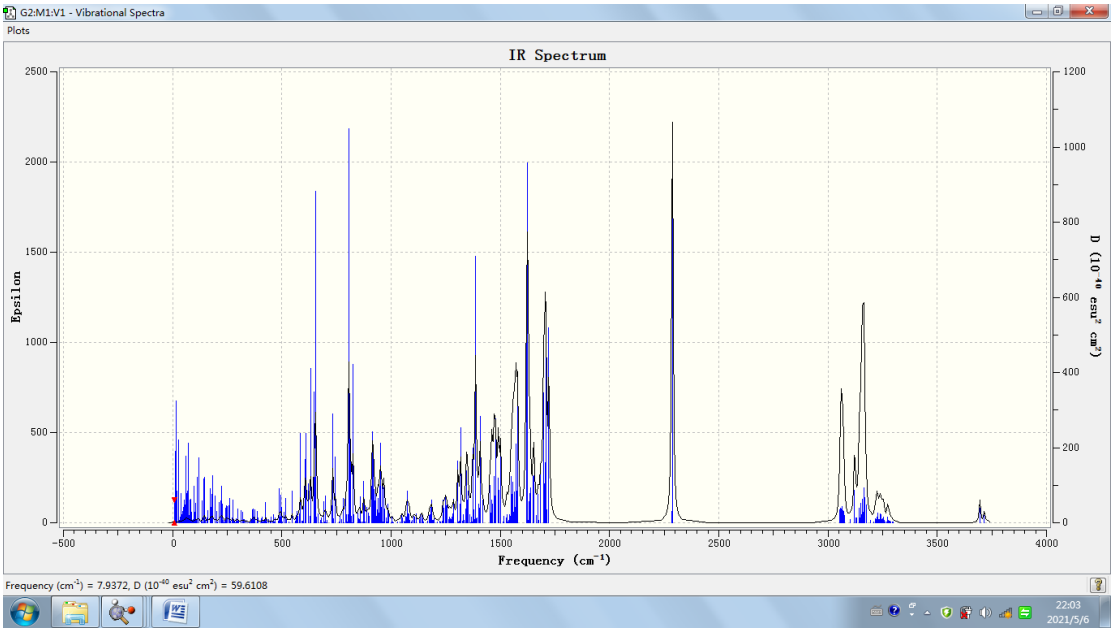

Figure S27. Frequency analysis of complex (*SS*)-**1/2**. The lowest frequency of (*SS*)-**1/2** were determined to be 7.9372 cm^{-1}, which unambiguously has no imaginary frequencies for the optimized structure.

```
Stoichiometry    C102H106N10O2Pt3(2+)
 Framework group  C1[X(C102H106N10O2Pt3)]
 Deg. of freedom   663
 Full point group                 C1      NOp   1
 Largest Abelian subgroup         C1      NOp   1
 Largest concise Abelian subgroup C1      NOp   1
                       Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
```

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3	6	0	10.263324	1.578656	0.495719
4	6	0	10.185692	1.039346	-0.950614
5	6	0	11.390661	1.572565	-1.741416
6	6	0	12.696107	1.079689	-1.090997
7	1	0	11.446229	-0.091514	1.197777
8	1	0	11.562631	1.353856	2.208290
9	1	0	12.875584	2.542581	0.494306
10	1	0	13.666217	1.009691	0.851927
11	1	0	10.260004	-0.052238	-0.890858
12	1	0	11.327961	1.226117	-2.779058
13	1	0	11.353032	2.669226	-1.760649
14	1	0	12.753238	-0.013448	-1.192724
15	1	0	13.558222	1.492791	-1.625040
16	1	0	10.364364	2.665961	0.431797
17	7	0	9.028672	1.370880	1.253453
18	7	0	8.890521	1.287767	-1.585170
19	1	0	8.658872	2.193184	1.704101
20	6	0	8.270350	0.253539	1.275961
21	8	0	8.614765	-0.847571	0.776040
22	1	0	8.540308	0.533070	-2.151244
23	6	0	8.076723	2.352956	-1.375703
24	8	0	8.445709	3.408265	-0.808610
25	6	0	6.920960	0.402675	1.906250
26	6	0	6.100087	1.503532	1.631044
27	6	0	6.434292	-0.640568	2.701470
28	6	0	4.785703	1.530733	2.092664
29	1	0	6.464073	2.315237	1.008744
30	6	0	5.136515	-0.600149	3.190582
31	1	0	7.078295	-1.487529	2.909604
32	6	0	4.278450	0.467767	2.858353
33	1	0	4.135454	2.357610	1.831086
34	1	0	4.759243	-1.407376	3.808656
35	6	0	6.646221	2.175234	-1.784833
36	6	0	6.049143	0.912841	-1.891286
37	6	0	5.857075	3.319506	-1.947450
38	6	0	4.695107	0.799519	-2.178182
39	1	0	6.618728	0.009671	-1.695703
40	6	0	4.497968	3.209140	-2.216611
41	1	0	6.327783	4.289802	-1.839034
42	6	0	3.894316	1.943587	-2.333038
43	1	0	4.239147	-0.179779	-2.260951
44	1	0	3.892023	4.099477	-2.339935
45	6	0	2.887478	0.365895	3.173263
46	6	0	1.701363	0.100117	3.327923
47	6	0	2.492931	1.796773	-2.571418
48	6	0	1.294778	1.612084	-2.748518

49	78	0	-0.127306	-0.639405	3.308935
50	7	0	0.394815	-2.529692	2.750199
51	7	0	-1.929761	-1.464251	3.184795
52	7	0	-1.272023	0.960470	3.829143
53	6	0	1.639459	-2.984730	2.542367
54	6	0	-0.681660	-3.358658	2.541558
55	6	0	-2.009055	-2.748388	2.795414
56	6	0	-2.998641	-0.685684	3.437924
57	6	0	-2.623313	0.701159	3.809296
58	6	0	-0.831152	2.182222	4.158918
59	6	0	1.877691	-4.282814	2.107584
60	1	0	2.437528	-2.275605	2.717296
61	6	0	-0.483956	-4.657795	2.107210
62	6	0	-3.262747	-3.338715	2.675442
63	6	0	-4.266580	-1.241505	3.336710
64	6	0	-3.528063	1.698151	4.126623
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66	1	0	0.240318	2.322651	4.133192
67	6	0	0.812060	-5.155586	1.875074
68	1	0	2.902052	-4.585674	1.945049
69	1	0	-1.345081	-5.288695	1.928393
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73	6	0	-3.089906	2.985314	4.490647
74	1	0	-4.587475	1.475781	4.100487
75	1	0	-1.296277	4.166705	4.760913
76	6	0	1.008032	-6.582633	1.356344
77	6	0	-5.814512	-3.224981	2.964112
78	6	0	-4.110716	4.063729	4.869174
79	6	0	0.293840	-7.581861	2.295825
80	6	0	0.395601	-6.663653	-0.061988
81	6	0	2.497624	-6.962569	1.270342
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83	6	0	-6.313456	-3.272204	4.430651
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86	6	0	-4.935947	3.565793	6.080747
87	6	0	-3.429590	5.391698	5.246673
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94	1	0	2.587312	-7.990598	0.907351
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96	1	0	2.984279	-6.914724	2.250213
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218	1	0	6.312249	-2.033860	0.197062
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222	7	0	1.819781	-1.408592	-0.305473
223	1	0	-2.715786	-5.308357	-3.849433

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