

## Supporting Information

### Self-discriminating and hierarchical assembly of racemic binaphthylbisbipyridines and silver ions: from metallocycles to gel nanofibers

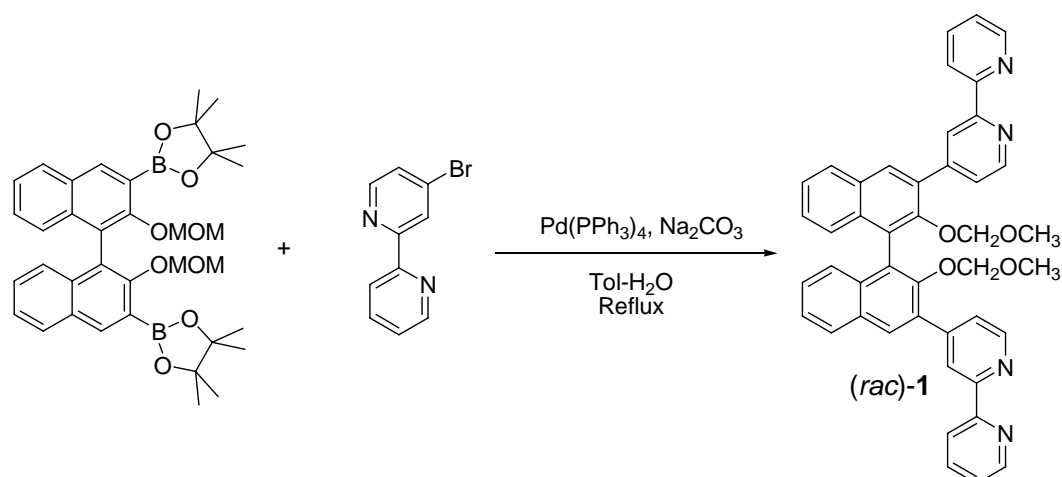
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#### 1. General Remarks

Melting points were measured with a hot-stage XT-4 microscope and were not corrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker AV600 or AV400 spectrometer at 298 K. Tetramethylsilane (TMS) was used as internal standard in  $^1\text{H}$  NMR experiments, and deuterated solvents as internal standard in  $^{13}\text{C}$  NMR experiments ( $\text{CDCl}_3$ ,  $\delta = 77.00$  ppm;  $\text{CD}_3\text{CN}$ ,  $\delta_{\text{CN}} = 117.70$  ppm). Mass spectra (ESI-MS) were recorded with a Thermo Finnigan LCQ instrument. Elemental analyses (C, H, N) were carried out with a VarioEL instrument. FTIR spectra were performed on a Bruker Vertex 70 infrared spectrometer at room temperature. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. Samples were prepared by wiping a small amount of gel samples onto carbon-coated copper grid followed by naturally evaporating the solvent. SEM pictures were taken using an XL 30 ESEM FEG field emission scanning electron microscope with 20 kV operating voltage. PXRD patterns were recorded by Bruker D8 advance X-ray diffractometer with  $\text{CuK}\alpha_1$  radiation source operated at 1.6 kW. X-ray crystallographic analysis was performed on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 2.0 kW (50 kV, 40 mA). The structures were solved by direct methods using the program SHELXL-97 and refined anisotropically by full matrix least squares on  $F^2$  values with SHELXL-97. Hydrogen atoms were located from the expected geometry and were refined only isotropically.

## 2. Synthetic procedure and characterization of compound (*rac*)-1



**Scheme S1** The synthetic route to compound (*rac*)-1.

To a degassed solution of 4-bromo-2,2'-bipyridine (0.57 g, 2.42 mmol) in toluene (45 mL) is added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.13 g, 0.11 mmol) under a nitrogen atmosphere. After the resulting mixture is stirred for 10 min at room temperature, (*rac*)-3,3'-bis(pinacolato)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (0.72 g, 1.15 mmol) and 1M Na<sub>2</sub>CO<sub>3</sub> (13.8 mL) are added sequentially into the mixture. Then the mixture is refluxed for 3 days under nitrogen. After removal of the solvent, the resulting residue is extracted with dichloromethane (50 mL × 3), washed with brine (40 mL) and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gives a residue, which is purified by flash silica gel column chromatography (dichloromethane/ethyl acetate, 2/1) to afford pure (*rac*)-1 in 79% yield as a white solid (0.62 g, 0.91 mmol). M.p. 190-192 °C; FTIR (KBr, cm<sup>-1</sup>): 1601, 1584, 1567, 1543, 1463, 1448, 1428, 1385, 1160, 1082, 1013, 992, 970, 931, 911, 848, 796, 747; <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600.1 MHz, 4.4 mM) δ (ppm): 8.865 (d, *J* = 1.2 Hz, 2H), 8.848 (d, *J* = 4.8 Hz, 2H), 8.773 (d, *J* = 4.2 Hz, 2H), 8.573 (d, *J* = 7.8 Hz, 2H), 8.276 (s, 2H), 8.126 (d, *J* = 7.8 Hz, 2H), 7.990 (td, *J* = 7.8 Hz, 1.8 Hz, 2H), 7.812 (dd, *J* = 5.4 Hz, 1.8 Hz, 2H), 7.580 (m, 2H), 7.483 (m, 2H), 7.446 (m, 2H), 7.309 (d, *J* = 9.0 Hz, 2H), 4.518 (d, *J* = 6.0 Hz, 2H), 4.457 (d, *J* = 6.0 Hz, 2H), 2.476 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.9 MHz) δ (ppm): 156.41, 155.99, 151.12, 149.24, 148.90, 148.13, 137.05, 134.18, 132.98, 131.08, 130.73, 128.23, 127.19, 126.51, 126.36, 125.63, 124.86, 123.88, 121.52, 121.35, 99.00, 56.13; MS (ESI) (*m/z*) Calcd. for C<sub>44</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>: 682.3, Found: 683.5 ([M+1]<sup>+</sup>); Anal. Calcd. for C<sub>44</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>: C, 77.40; H, 5.02; N, 8.21, Found: C, 77.36; H, 5.08; N, 8.22%.

### 3. Synthesis and characterization of complex $(rac)\text{-1}\cdot\text{AgPF}_6$

A solution of  $\text{AgPF}_6$  (0.1 mmol, 25.3 mg) and  $(rac)\text{-1}$  (0.1 mmol, 68.3 mg) in dry  $\text{CH}_3\text{CN}$  (20.0 mL) was stirred overnight in the dark, and the most part of solvents was removed under reduced pressure. The complex was precipitated with diethyl ether, filtered and dried (83.3 mg, 89%). Colorless rodlike single crystals were obtained by slow evaporation of a  $\text{CH}_3\text{CN}$  solution. FTIR ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 1604, 1572, 1543, 1479, 1433, 1158, 1081, 1016, 968, 920, 840, 793, 749, 558;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 600.1 MHz, 4.4 mM)  $\delta$  (ppm): 8.798 (m, 4H), 8.773 (s, 2H), 8.526 (d,  $J = 7.8$  Hz, 2H), 8.337 (s, 2H), 8.140 (d,  $J = 8.4$  Hz, 2H), 8.102 (m, 2H), 7.920 (m, 2H), 7.597 (m, 4H), 7.479 (m, 2H), 7.335 (d,  $J = 8.4$  Hz, 2H), 4.544 (d,  $J = 6.0$  Hz, 2H), 4.481 (d,  $J = 6.0$  Hz, 2H), 2.514 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 150.9 MHz, 12.6 mM)  $\delta$  (ppm): 153.51, 153.24, 150.55, 150.12, 149.79, 148.67, 138.24, 133.90, 132.14, 131.07, 130.56, 128.26, 127.21, 126.13, 125.71, 125.63, 125.29, 124.85, 122.26, 121.93, 98.70, 55.37; MS (ESI) ( $m/z$ ): 683.28 ( $[\text{1}+\text{H}]^+$ ), 789.17 ( $[\text{1}\cdot\text{Ag}]^+$  and  $[\text{1}_2\cdot\text{Ag}_2]^{2+}$ ).

### 4. Comparison of FTIR spectra of ligand $(rac)\text{-1}$ with its silver complex $(rac)\text{-1}\cdot\text{AgPF}_6$

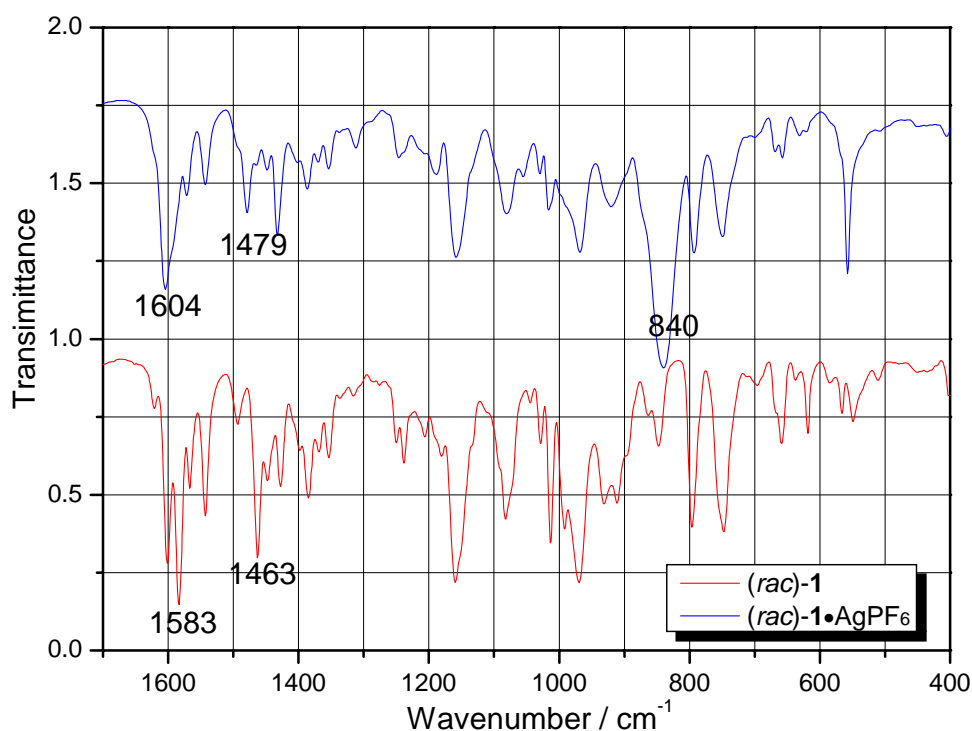
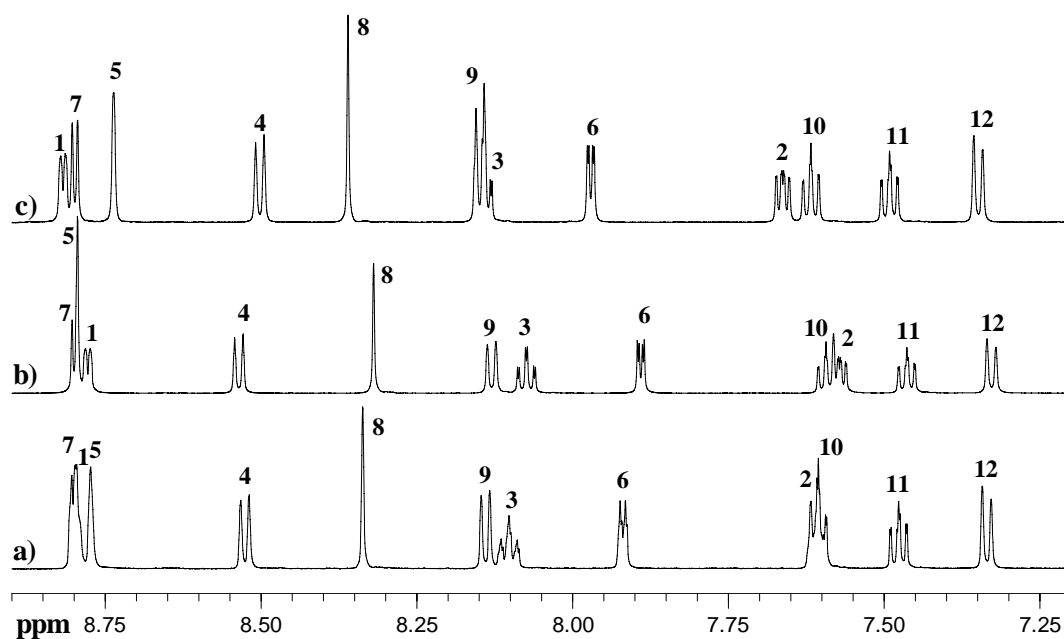


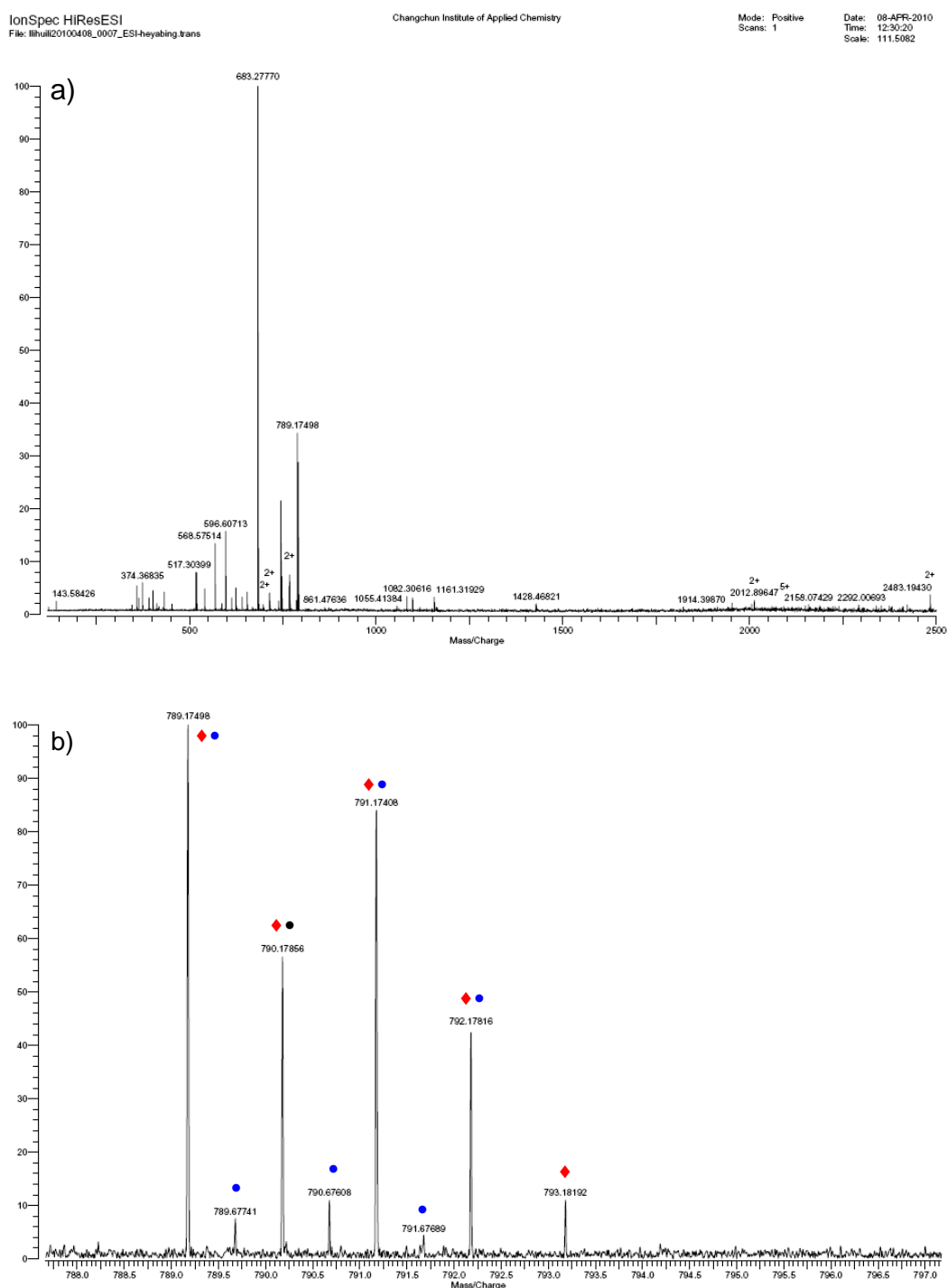
Fig. S1 Comparison of FTIR spectra of complex  $(rac)\text{-1}\cdot\text{AgPF}_6$  with ligand  $(rac)\text{-1}$ .

## 5. $^1\text{H}$ NMR spectra of complexes of (*rac*)-**1** and $\text{AgPF}_6$ with different metal / ligand ratios

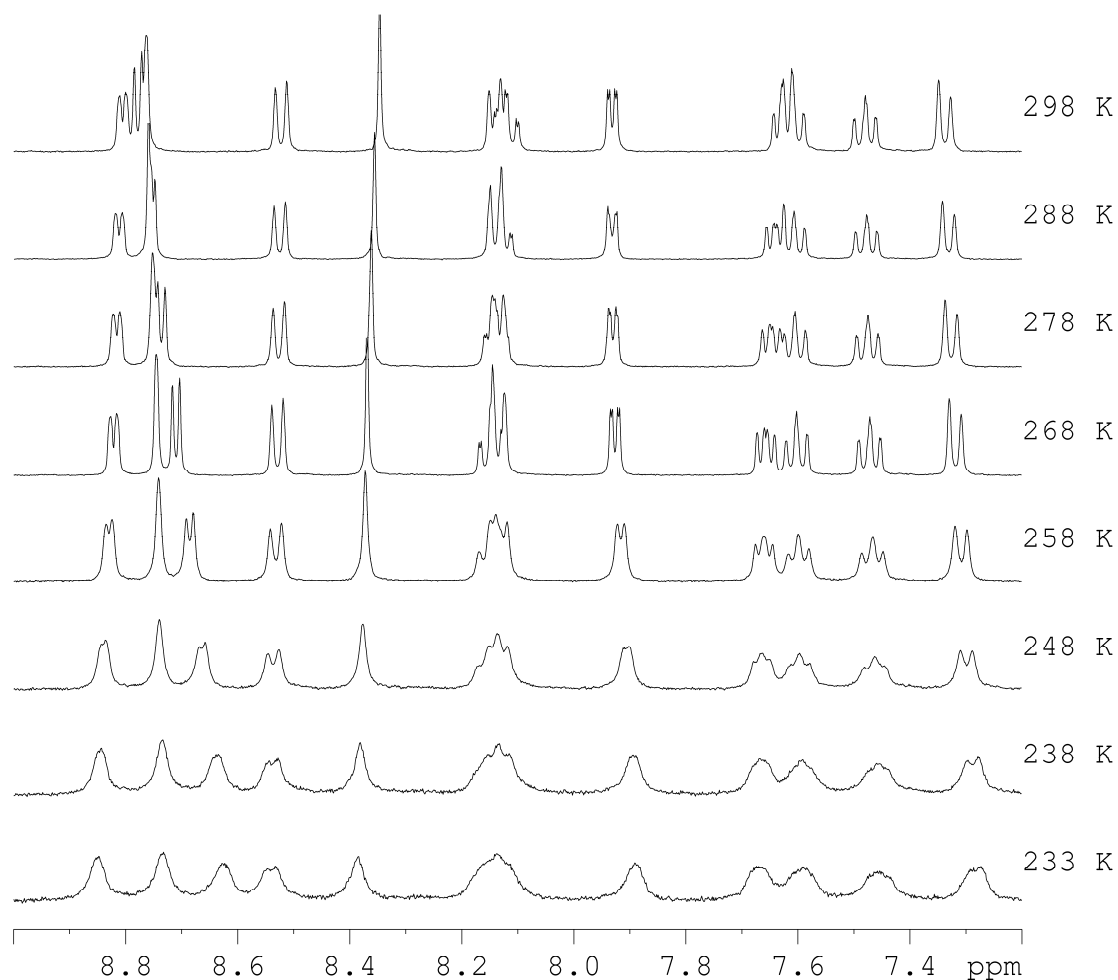


**Fig. S2**  $^1\text{H}$  NMR spectra ( $\text{CD}_3\text{CN}$ , 600.1 MHz, 298 K) of complexes of (*rac*)-**1** and  $\text{AgPF}_6$  with different M/L ratios. a)  $\text{AgPF}_6/(\textit{rac})\text{-1} = 1/1$ ,  $[(\textit{rac})\text{-1}] = 4.4$  mM; b)  $\text{AgPF}_6/(\textit{rac})\text{-1} = 1/2$ ,  $[(\textit{rac})\text{-1}] = 8.8$  mM; c)  $\text{AgPF}_6/(\textit{rac})\text{-1} = 2/1$ ,  $[(\textit{rac})\text{-1}] = 4.4$  mM.

## 6. Mass spectrum of complex (S)-1•AgPF<sub>6</sub>



## 7. Variable temperature $^1\text{H}$ NMR spectra of complex $(rac)\text{-1}\cdot\text{AgPF}_6$ in $\text{CD}_3\text{CN}$



**Fig. S4** VT- $^1\text{H}$ NMR spectra of complex  $(rac)\text{-1}\cdot\text{AgPF}_6$  (400 MHz,  $\text{CD}_3\text{CN}$ ,  $c = 9.0$  mM). Lowering the temperature led to broader signals, resulting from a slower exchange process or the formation of the aggregated species.

## 8. Gel tests

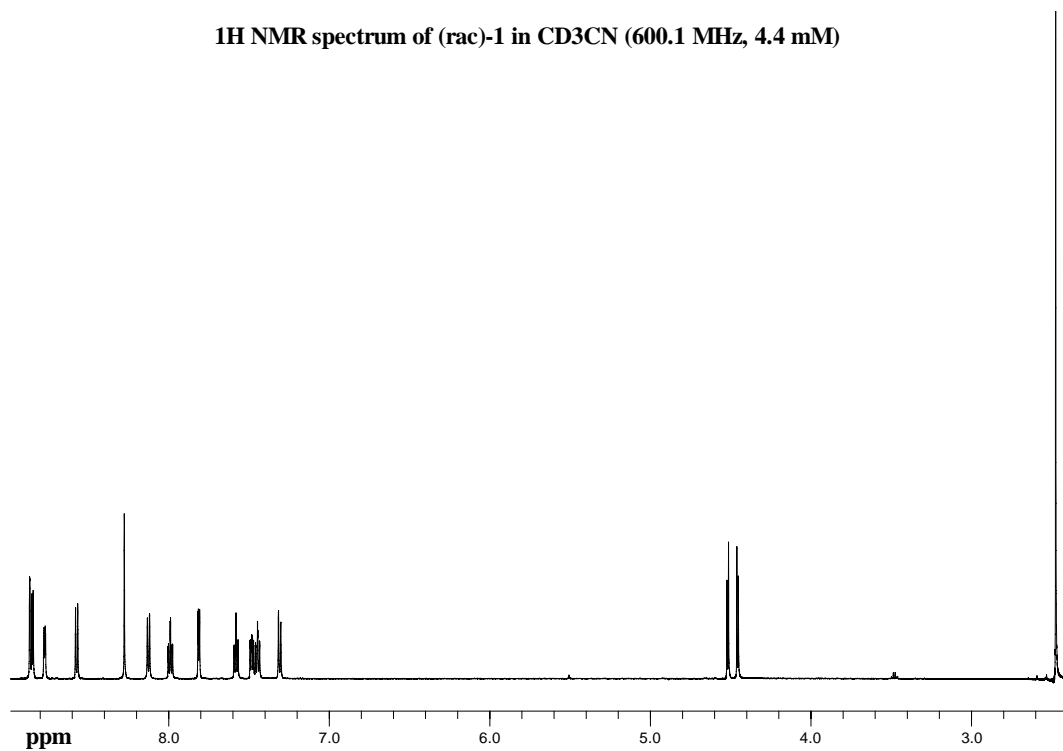
A mixture of complex  $(rac)\text{-1}\cdot\text{AgPF}_6$  and the tested solvent (1.0 mL) were charged with a glass test tube (35 mm  $\times$  15 mm), which was capped and sonicated for a few minutes using sonoreactor (0.26  $\text{Wcm}^{-1}$ , 40 kHz), and heated in an oil bath ( $T = 80$   $^\circ\text{C}$ ) until it turned into a clear solution (if soluble). After the solution was allowed to stand at room temperature ( $25 \pm 5$   $^\circ\text{C}$ ) for 5 h, the state of the mixture was evaluated by the “stable to inversion of test tube” method. The complex  $(rac)\text{-1}\cdot\text{AgPF}_6$  can successfully gelate  $\text{CH}_3\text{CN}$  after screening common solvents. The minimum gel concentration (MGC) of complex  $(rac)\text{-1}\cdot\text{AgPF}_6$  in  $\text{CH}_3\text{CN}$  is  $9.4 \times 10^{-2}$  M at room temperature.

### 9. Crystal data and structure refinement for (*rac*)-1 and (*rac*)-1•AgPF<sub>6</sub>

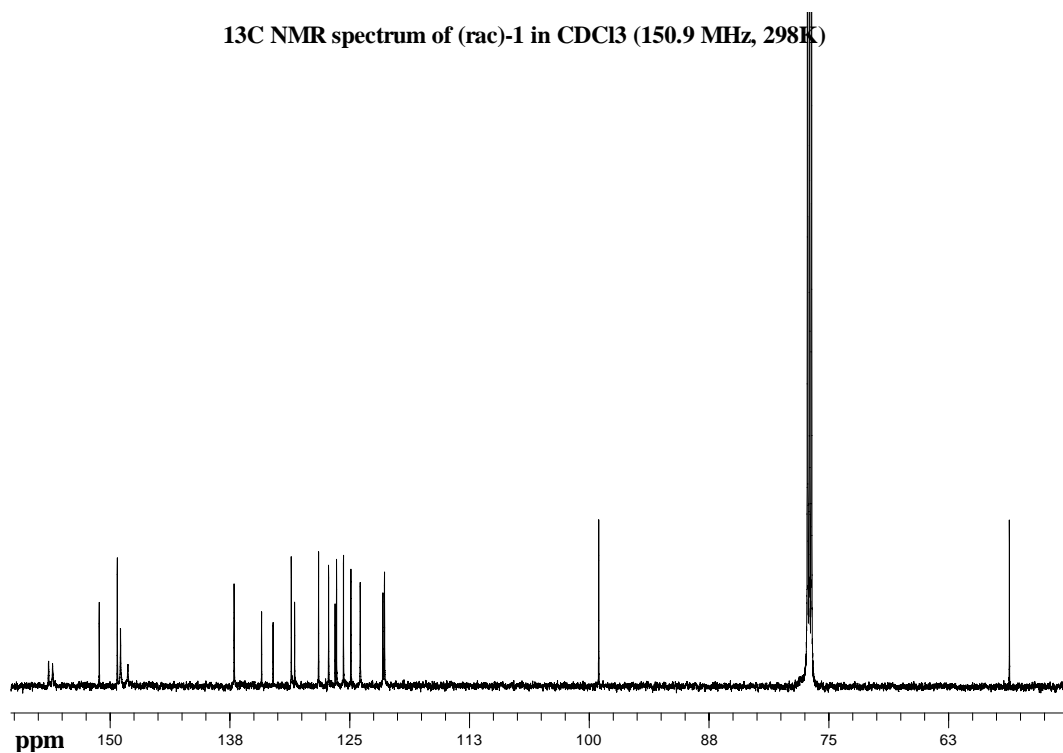
Compounds	( <i>rac</i> )-1	( <i>rac</i> )-1•AgPF <sub>6</sub>
Empirical formula	C <sub>44</sub> H <sub>34</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>88</sub> H <sub>68</sub> N <sub>8</sub> O <sub>8</sub> Ag <sub>2</sub> P <sub>2</sub> F <sub>12</sub>
Formula weight	682.75	1871.18
Temperature (K)	185(2)	185(2)
Crystal system, Space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 21.4815(13) Å <i>b</i> = 12.1504(7) Å <i>c</i> = 13.4906(8) Å $\alpha$ = 90° $\beta$ = 99.2200(10)° $\gamma$ = 90°	<i>a</i> = 8.6460(8) Å <i>b</i> = 13.9854(13) Å <i>c</i> = 18.4584(17) Å $\alpha$ = 89.7640(10)° $\beta$ = 84.3230(10)° $\gamma$ = 74.2640(10)°
Volume (Å <sup>3</sup> )	3475.7(4)	2137.2(3)
Z, Calculated density (Mg/m <sup>3</sup> )	4, 1.305	1, 1.454
Absorption coefficient (mm <sup>-1</sup> )	0.085	0.582
<i>F</i> (000)	1432	948
Crystal size (mm)	0.30 x 0.25 x 0.21	0.38 x 0.22 x 0.14
$\theta$ range for data collection (°)	0.96 to 26.10	1.11 to 25.09
Limiting indices	-20 ≤ <i>h</i> ≤ 26, -15 ≤ <i>k</i> ≤ 12, -16 ≤ <i>l</i> ≤ 16	-9 ≤ <i>h</i> ≤ 10, -16 ≤ <i>k</i> ≤ 16, -21 ≤ <i>l</i> ≤ 22
Reflections collected / unique	19104/6900 [ <i>R</i> <sub>int</sub> = 0.0571]	16807/7519 [ <i>R</i> <sub>int</sub> = 0.0343]
Completeness to $\theta$	26.10, 99.7%	25.09, 98.8%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.978 and 0.970	0.9230 and 0.8093
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	6900/0/469	7519/14/570
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.993	0.964
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0458, <i>wR</i> <sub>2</sub> = 0.0928	<i>R</i> <sub>1</sub> = 0.0693, <i>wR</i> <sub>2</sub> = 0.2194
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0987, <i>wR</i> <sub>2</sub> = 0.1201	<i>R</i> <sub>1</sub> = 0.0882, <i>wR</i> <sub>2</sub> = 0.2372
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.205 and -0.216	2.061 and -1.038
CCDC	787118	774705

## 10. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of (*rac*)-1 and (*rac*)-1•AgPF<sub>6</sub>

$^1\text{H}$  NMR spectrum of (*rac*)-1 in CD<sub>3</sub>CN (600.1 MHz, 4.4 mM)

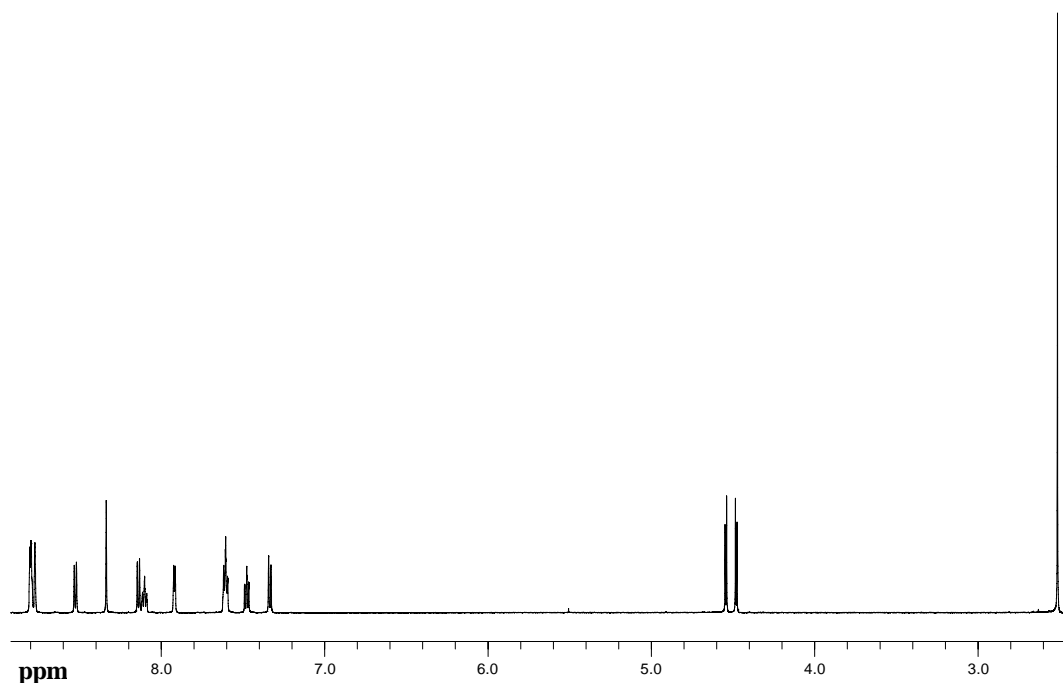


$^{13}\text{C}$  NMR spectrum of (*rac*)-1 in CDCl<sub>3</sub> (150.9 MHz, 298K)





**<sup>1</sup>H NMR spectrum of (rac)-1AgPF<sub>6</sub> in CD<sub>3</sub>CN (600.1 MHz, 4.4 mM)**



**<sup>13</sup>C NMR spectrum of (rac)-1AgPF<sub>6</sub> in CD<sub>3</sub>CN (150.9 MHz, 12.6 mM)**

