Sumanene-Functionalised Bis(terpyridine)-Ruthenium(II) Complexes Showing Photoinduced Structural Change and Cation Sensing

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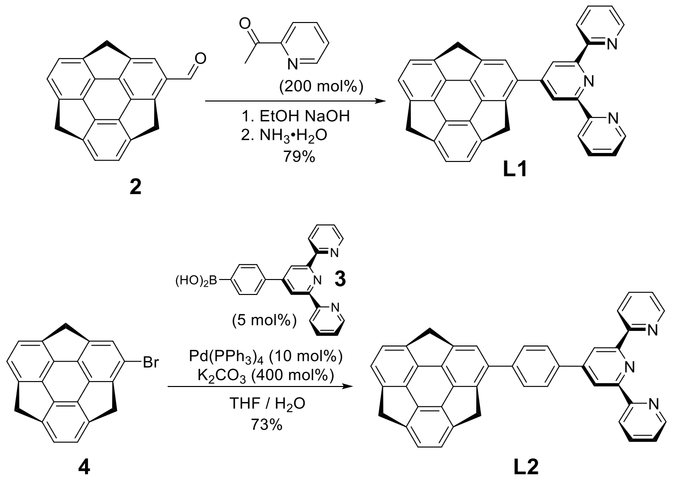
1) General Methods

All the chemical reagents and solvents were commercially purchased and purified according to the standard methods, if necessary. Air- and moisture-sensitive reactions were carried out using commercially available anhydrous solvents under inert atmosphere of nitrogen. Unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 NMR spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz). Chemical shift (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H ($CDCl_3$: ^{1}H(δ) = 7.26 ppm) and for ^{13}C ($CDCl_3$: ^{13}C(δ) = 77.0 ppm). High resolution mass spectra (HRMS) were measured using electron impact (EI) methods on JEOL JMS-777V spectrometer. Matrix-assisted laser desorption/ionization coupled to time-of-flight (MALDI-TOF) mass spectra were measured on Bruker Autoflex III spectrometer. The preparative TLC (PTLC) purification was conducted using Wako gel B-5F PTLC plates. Flash column chromatography was prepared using Kanto Silica gel 60N (neutral, spherical, 40-50 µm) and performed with a Yamazen preparative medium pressure liquid chromatography system. UV-vis spectra were recorded on a JASCO V-670 spectrophotometer. Steady-state emission spectra were recorded on a JASCO FP-6500DS spectrometer. Lifetime measurements were recorded on a HAMAMATSU C11347-01 spectrometer with an integrating sphere. Elemental analyses were measured on a J-Science Micro corder JM10 at the Analysis Center in Osaka University.

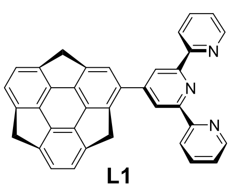
2) Synthesis

*a) Synthesis of ligand **L1** and **L2***



Scheme S1. Synthetic route to the ligand **L1** and **L2**.

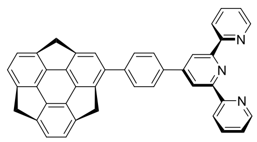
4'-(4,7-dihydro-1H-tricyclopenta[def,jkl,pqr]triphenylen-2-yl)-2,2':6',2''-terpyridine (L1)



To a solution of NaOH (100.0 mg, 2.40 mmol) in EtOH (10 mL), **2** (40.0 mg, 0.14 mmol)[S1] and 2-acetylpyridine (17.0 mg, 0.30 mmol) was added. After stirring at room temperature for 24 h, aqueous NH_3 (28%, 2 mL) was added. The resulting mixture was refluxed for 16 h. After cooling to room temperature, the solid was collected by suction filtration and was washed with MeOH to give the product **L1** as a pale-yellow solid (52.5 mg, 0.11 mmol, 79%).
L1: mp: 287 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.73 (s, 2H), 8.72 (d, 2H), 8.67 (d, J =

7.9 Hz, 2H), 7.87 (td, J = 7.7, 1.8 Hz, 2H), 7.73 (s, 1H), 7.34 (ddd, J = 7.6, 4.8, 1.2 Hz, 2H), 7.17–7.04 (m, 4H), 5.17 (d, J = 19.8 Hz, 1H), 4.80 (d, J = 19.5 Hz, 1H), 4.72 (d, J = 19.5 Hz, 1H), 3.59 (d, J = 19.5 Hz, 1H), 3.49 (d, J = 19.5 Hz, 1H), 3.44 (d, J = 19.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.60, 155.96, 150.18, 150.02, 149.90, 149.36, 149.12, 148.98, 148.81, 148.64, 148.58, 137.00, 123.95, 123.55, 123.89, 123.78, 123.30, 122.92, 121.49, 120.34, 51.51, 43.52, 41.97. HRMS (EI) *m/z* Calcd. for $C_{36}H_{21}N_3$ $[M]^+$: 495.1735. Found: 495.1787.

4'-(4-(4,7-dihydro-1H-tricyclopenta[def,jkl,pqr] triphenylen-2-yl)phenyl)-2,2':6',2''-terpyridine (L2)

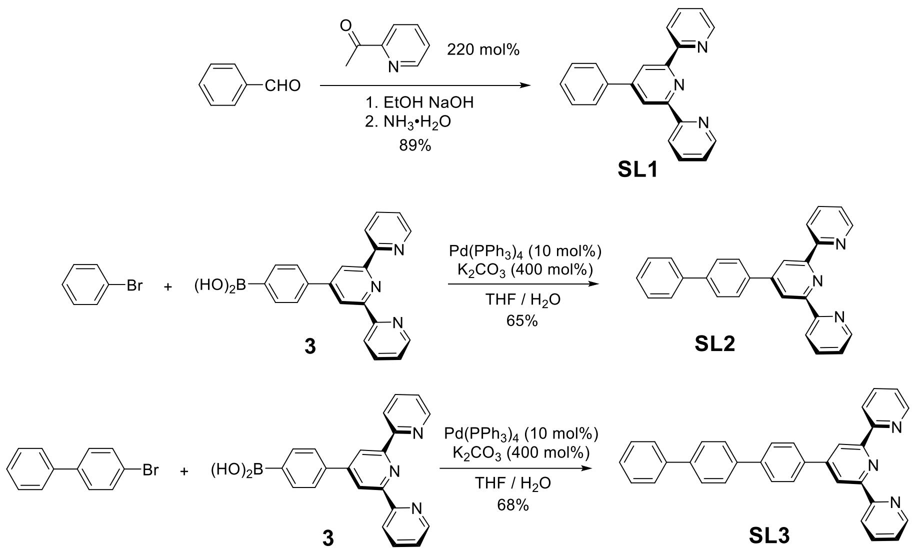


L2

An aqueous solution of K_2CO_3 (1.0 M, 0.16 mL, 0.16 mmol) was added to a THF solution (5 mL) of a mixture of **4** (13.7 mg, 0.040 mmol) **3** (17.6 mg, 0.050 mmol), and Pd $(PPh_3)_4$ (14.0 mg, 0.005 mmol) under N_2 at 25 °C. After stirring at 70 °C for 20 h, the reaction mixture was cooled to room temperature and was extracted with chloroform (3 × 10mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and then concentrated in vacuo. The crude product was then purified by column chromatography on neutral alumina gel with $CHCl_3$ to afford **L2** as a pale-yellow powder (16.7 mg, 0.029 mmol, 73%).

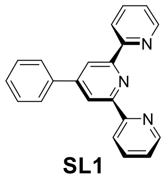
L2: mp: 252 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.79 (s, 2H), 8.74 (d, J = 4.4 Hz, 2H), 8.69 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 7.89 (t, J = 7.5 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.44 (s, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.16–7.05 (m, 4H), 4.96 (d, J = 19.8 Hz, 1H), 4.80 (d, J = 19.2 Hz, 1H), 4.72 (d, J = 19.7 Hz, 1H), 3.55 (d, J = 19.3 Hz, 1H), 3.43 (d, J = 17.0 Hz, 1H), 3.38 (d, J = 17.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.35, 156.07, 150.18, 149.88, 149.25, 149.15, 149.06, 148.88, 148.74, 148.52, 146.46, 141.61, 137.59, 137.27, 137.01, 132.25, 132.15, 129.12, 128.72, 128.55, 127.69, 123.96, 123.60, 123.51, 123.46, 123.28, 122.74, 121.48, 118.81, 42.67, 41.97, 41.86. HRMS (EI) *m/z* Calcd. for $C_{42}H_{25}N_3$ $[M]^+$: 571.2048. Found: 571.2050.

b) Synthesis of phenyl-terpy ligands ***SL1****,* ***SL2****, and* ***SL3****.*



Scheme S2. Synthetic route to the ligand **SL1**, **SL2**, and **SL3**.

4'-phenyl-2,2':6',2''-terpyridine (SL1)

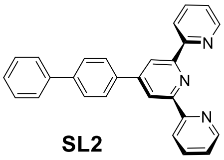


SL1

To a solution of NaOH (0.96 g, 24.00 mmol) in EtOH (20 mL), benzaldehyde (0.60 g, 4.40 mmol) and 2-acetylpyridine (1.06 g, 8.80 mmol) was added. After stirring at room temperature for 24 h, aqueous NH_3•H_2O (28%, 3 mL) was added. The resulting mixture was refluxed for 20 h and was cooled to room temperature. The solid so formed was collected by suction filtration and was washed with EtOH and $CHCl_3$ to give the product **SL1** as a white solid (1.21 g, 3.92 mmol, 89%).

SL1: mp: 189 °C (dec.); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 2H), 8.76 (d, *J* = 4.4 Hz, 2H), 8.71 (d, *J* = 8.0 Hz, 2H), 7.98–7.91 (m, 4H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.48–7.38 (m, 3H). HRMS (EI) m/z Calcd. for $C_{21}H_{15}N_3$ [M^+]: 309.1266. Found: 309.1215.

4'-([1,1'-biphenyl]-4-yl)-2,2':6',2''-terpyridine (SL2)

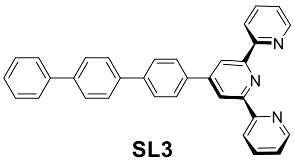


SL2

An aqueous solution of K_2CO_3 (1.0 M, 0.4 mL, 0.40 mmol) was added to a THF solution (10 mL) of a mixture of Bromobenzene (15.5 mg, 0.10 mmol), **3** (35.3 mg, 0.10 mmol), and Pd (PPh3)4 (30.0 mg, 0.01 mmol) under N_2 at 25 °C. After stirring at 70 °C for 24 h. After cooling to room temperature, the mixture was extracted with chloroform. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuo, the crude product was purified by column chromatography on neutral alumina gel with $CHCl_3$ to afford the product **SL2** as a pale-yellow powder (25.0 mg, 0.065 mmol, 65%).

SL2: mp: 206 °C (dec.); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 2H), 8.77 (d, *J* = 4.8 Hz, 2H), 8.72 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.93 (t, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.36 (m, 3H). HRMS (EI) m/z Calcd. for $C_{27}H_{19}N_3$ [M^+]: 385.1579. Found: 385.1587.

4'-([1,1':4',1''-terphenyl]-4-yl)-2,2':6',2''-terpyridine (SL3)

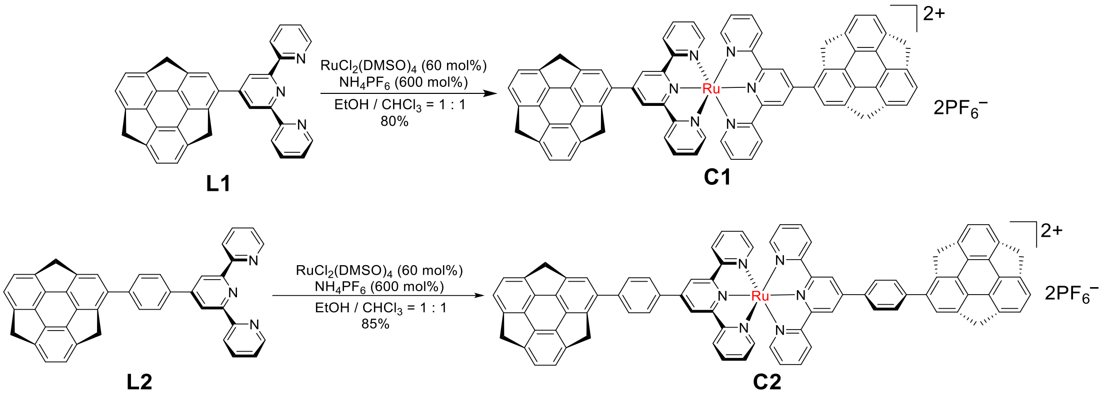


SL3

An aqueous solution of K_2CO_3 (1.0 M, 0.4 mL, 0.40 mmol) was added to a THF solution (10 mL) of a mixture of 4-bromobiphenyl (23.3 mg, 0.10 mmol), **3** (35.3 mg, 0.10 mmol), and Pd $(PPh_3)_4$ (30.0 mg, 0.01 mmol) under N_2 at 25 °C. After stirring at 70 °C for 24 h. After cooling to room temperature, the mixture was extracted with chloroform. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuo, the crude product was purified by column chromatography on neutral alumina gel with $CHCl_3$ to afford the product **SL3** as a pale-yellow powder (31.3 mg, 0.068 mmol, 68%).

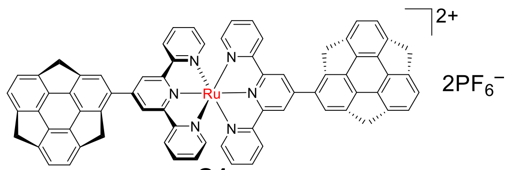
SL3: mp: 271 °C (dec.); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.89 (s, 2H), 8.79 (d, *J* = 4.9 Hz, 2H), 8.75 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.97 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 6.2 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H). HRMS (EI) m/z Calcd. for $C_{33}H_{23}N_3$ [M^+]: 416.1892. Found: 416.1823.

*c) Synthesis of [Ru(**L1**)$_2$](PF$_6$)$_2$ complex (**C1**) and [Ru(**L2**)$_2$](PF6)$_2$ complex (**C2**)*



Scheme S3. Synthetic route to **C1** and **C2**.

[Ru (L1)$_2$](PF$_6$)$_2$ (C1)

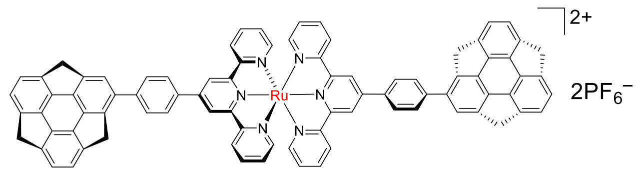


C1

L1 (20.0 mg, 0.04 mmol) was dissolved in EtOH/CHCl$_3$ (10 mL, v/v=1:1) and the mixture was degassed by N_2 bubbling (10 min). RuCl$_2$(DMSO)$_4$ (9.7mg, 0.02 mmol) was added and the suspension was heated to 80 °C for 24 hours. The deep red solution was allowed to cool and NH$_4$PF$_6$ (40.0 mg, 0.24 mmol) was added. A red solid immediately precipitated which was collected by filtration and subsequently washed with water (3×10 mL) and MeOH (3×10 mL, to aid drying). The solid material was washed down with acetonitrile. The solvent was removed in vacuo to yield the complex **C1** as red solid (22.1 mg, 0.016 mmol, 80%).

C1: mp: 371 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 8.96 (s, 4H), 8.60 (d, *J* = 9.1 Hz, 4H), 7.99 (s, 2H), 7.94 (td, *J* = 7.9, 1.5 Hz, 4H), 7.44 (d, *J* = 4.3 Hz, 4H), 7.34 – 7.22 (m, 8H), 7.19 (ddd, *J* = 7.1, 5.6, 1.3 Hz, 4H), 5.40 (d, *J* = 19.9 Hz, 2H), 4.96 (d, *J* = 19.9 Hz, 2H), 4.79 (d, *J* = 19.9 Hz, 2H), 3.83 (d, *J* = 15.4 Hz, 2H), 3.78 (d, *J* = 15.5 Hz, 2H), 3.59 (d, *J* = 20.0 Hz, 2H). MALDI-TOF MS (*m/z*): Calcd. for $[C_{72}H_{42}N_6Ru]^+$: 1092.25. Found: 1092.48. Anal. Calcd for $C_{72}H_{42}N_6RuF_{12}P_2$: C, 62.57; H, 3.06; N, 6.08. Found: C, 62.74; H, 3.01; N, 6.17.

[Ru (L2)$_2$](PF$_6$)$_2$ (C2)

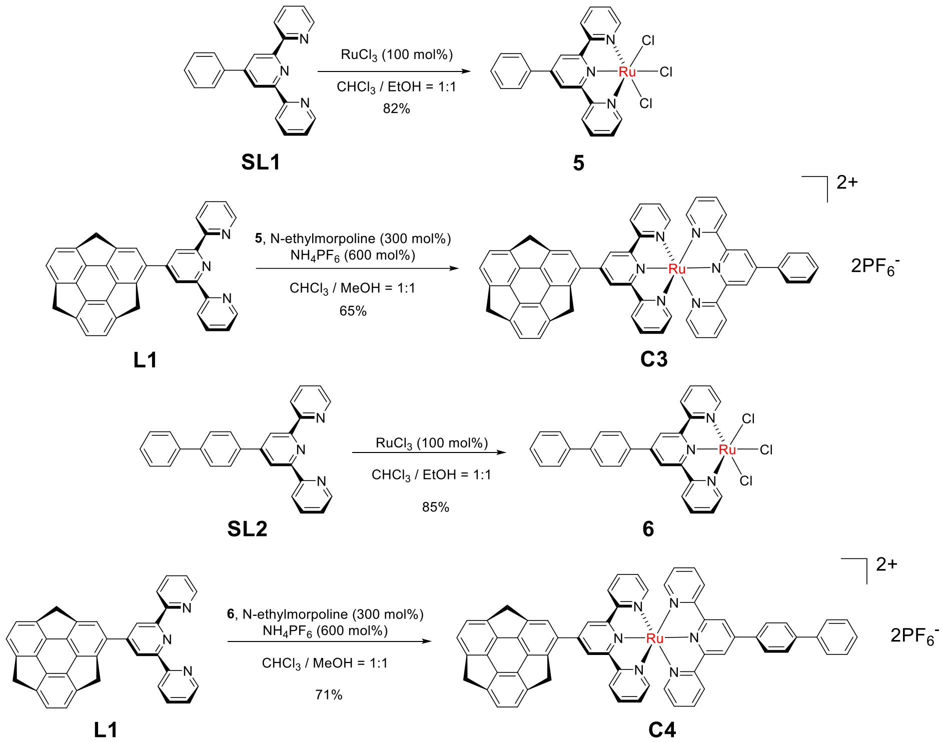


C2

L2 (15.0 mg, 0.026 mmol) was dissolved in EtOH/CHCl$_3$ (10 mL, v/v=1:1) and the mixture was degassed by N_2 bubbling (10 min). RuCl$_2$(DMSO)$_4$ (6.3 mg, 0.013 mmol) was added and the suspension was heated to 80 °C for 24 hours. The deep red solution was allowed to cool and NH$_4$PF$_6$ (25.4 mg, 0.16mmol) was added. A red solid immediately precipitated which was collected by filtration and subsequently washed with water (3×10 mL) and MeOH (3×10 mL, to aid drying). The solid material was washed down with acetonitrile. The solvent was removed in vacuo to yield the complex **C2** as red solid (16.8 mg, 0.011 mmol, 85%).

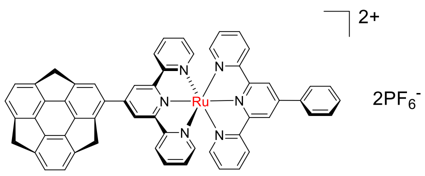
C2: mp: 335 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 9.09 (s, 4H), 8.69 (d, *J* = 7.8 Hz, 4H), 8.34 (d, *J* = 6.7 Hz, 4H), 8.05 (d, *J* = 7.1 Hz, 4H), 7.96 (t, *J* = 7.9 Hz, 4H), 7.66 (s, 2H), 7.46 (d, *J* = 5.6 Hz, 4H), 7.26 – 7.14 (m, 12H), 5.13 (d, *J* = 19.6 Hz, 2H), 4.85 (d, *J* = 19.6 Hz, 2H), 4.75 (d, *J* = 20.0 Hz, 2H), 3.69 (d, *J* = 19.7 Hz, 2H), 3.54 (d, *J* = 18.8 Hz, 2H), 3.50 (d, *J* = 18.4 Hz, 2H). MALDI-TOF MS (*m/z*): Calcd. for $[C_{84}H_{50}N_6Ru]^+$: 1244.31. Found: 1244.40. Anal. Calcd for $C_{84}H_{50}N_6RuF_{12}P_2$: C, 65.76; H, 3.28; N, 5.48. Found: C, 65.91; H,3.21; N, 5.57.

*d) Synthesis of [Ru(**L1**)(**SL1**)](PF$_6$)$_2$ (**C3**) and [Ru(**L1**)(**SL2**)](PF$_6$)$_2$ (**C4**) complexes*



Scheme S4. Synthetic route to **C3** and **C4**.

[Ru (L1) (SL1)](PF6)$_2$ (C3)



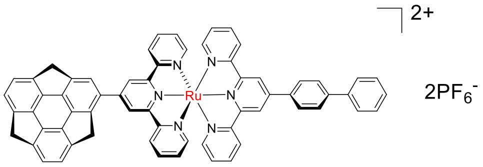
C3

To a solution of **SL1** (50.0 mg, 0.16 mmol) and $RuCl_3 \cdot 3H_2O$ (33.1 mg, 0.16 mmol) in $CHCl_3$ (5mL) and EtOH (5 mL). The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **5** (67.7 mg, 0.13 mmol, 82%).[S3] After evaporated to dryness under vacuum, it was applied to the synthesis of **C3** directly. To a flask containing a mixture of **5** (10.0 mg, 0.019 mmol) and **L1** (9.6 mg, 0.019 mmol), MeOH (4 mL), $CHCl_3$ (4 mL), and N-ethylmorpholine (6.5 mg, 0.057 mmol) were added. The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was counterion exchanged with NH_4PF_6 (18.5 mg, 0.114 mmol) to give **C3**, as a red precipitate (14.4 mg, 0.012 mmol, 65%).

C3: mp: 355 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 8.99 (s, 2H), 8.93 (s, 2H), 8.62

(d, J = 7.8 Hz, 2H), 8.58 (d, J = 8.1 Hz, 2H), 8.18 (d, J = 7.3 Hz, 2H), 7.96 (s, 1H), 7.94 – 7.88 (m, 4H), 7.74 (t, J = 7.6 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.42 (d, J = 4.1 Hz, 2H), 7.41 (d, J = 4.3 Hz, 2H), 7.29 – 7.12 (m, 8H), 5.37 (d, J = 20.1 Hz, 1H), 4.92 (d, J = 19.4 Hz, 1H), 4.76 (d, J = 20.1 Hz, 1H), 3.81 (d, J = 17.6 Hz, 1H), 3.76 (d, J = 17.1 Hz, 1H), 3.55 (d, J = 20.0 Hz, 1H). MALDI-TOF MS (m/z): Calcd. for $[C_{57}H_{36}N_6Ru]^+$: 906.20. Found: 906.06. Anal. Calcd for $C_{57}H_{36}N_6RuF_{12}P_2$: C, 57.25; H, 3.03; N, 7.03. Found: C, 57.41; H, 3.01; N, 7.09.

[Ru (L1) (SL2)] (PF6)$_2$ (C4)

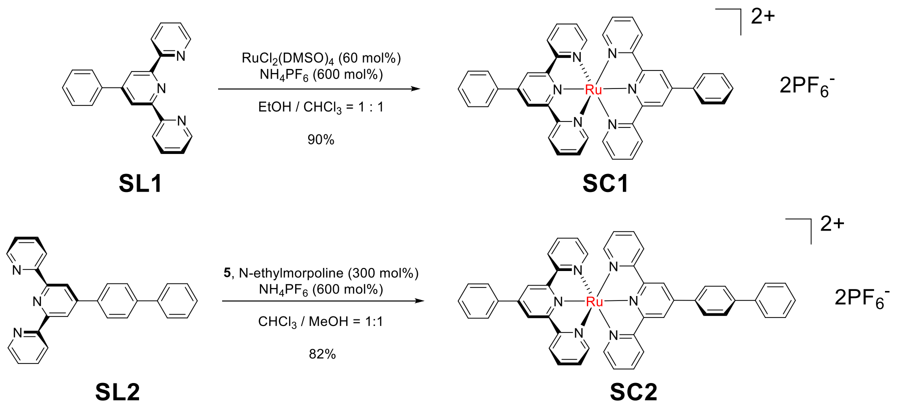


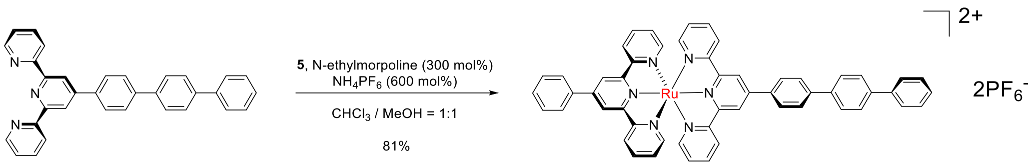
C4

To a solution of **SL2** (30.8 mg, 0.080 mmol) and $RuCl_3 \cdot 3H_2O$ (16.6 mg, 0.080 mmol) in $CHCl_3$ (5mL) and EtOH (5 mL). The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **6** (33.8 mg, 0.066 mmol, 82%).[S3] After dryness under vacuum, it was applied to the synthesis of **C4** directly. To a flask containing a mixture of **6** (11.2 mg, 0.019 mmol) and **L1** (9.6 mg, 0.019 mmol), MeOH (4 mL), $CHCl_3$ (4 mL), and N-ethylmorpholine (6.5 mg, 0.057 mmol) were added. The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was counterion exchanged with NH_4PF_6 (18.5 mg, 0.114 mmol) to give **C4**, as a red precipitate (17.8 mg, 0.014 mmol, 71%).

C4: mp: 296 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.05 (s, 2H), 8.94 (s, 2H), 8.65 (d, J = 7.7 Hz, 2H), 8.58 (d, J = 8.0 Hz, 2H), 8.30 (d, J = 7.9 Hz, 2H), 8.03 (d, J = 8.1 Hz, 2H), 7.97 – 7.90 (m, 4H), 7.83 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.47 (t, J = 7.0 Hz, 1H), 7.42 (d, J = 4.3 Hz, 4H), 7.31 – 7.21 (m, 4H), 7.14 - 7.18 (m, 4H), 5.37 (d, J = 20.2 Hz, 1H), 4.93 (d, J = 19.9 Hz, 1H), 4.77 (d, J = 20.5 Hz, 1H), 3.81 (d, J = 15.8 Hz, 1H), 3.75 (d, J = 15.8 Hz, 1H), 3.56 (d, J = 19.8 Hz, 1H). MALDI-TOF MS (m/z): Calcd. for $[C_{63}H_{40}N_6Ru]^+$: 982.23. Found: 982.22. Anal. Calcd for $C_{63}H_{40}N_6RuF_{12}P_6$: C, 59.49; H, 3.17; N, 6.61. Found: C, 59.55; H, 3.14; N, 6.68.

*e) Synthesis of [Ru(**SL1**)$_2$](PF$_6$)$_2$ complex (**SC1**), [Ru(**SL1**)(**SL2**)](PF$_6$)$_2$ complex (**SC2**) and [Ru(**SL1**)(**SL3**)](PF$_6$)$_2$ complex (**SC3**)*

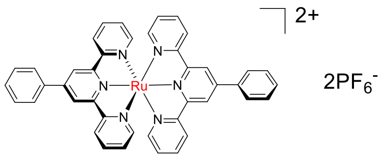




SL3 **SC3**

Scheme S5. Synthetic route to support complex **SL1**, **SL2** and **SC3**.

[Ru(SL1)$_2$](PF6)$_2$ (SC1)

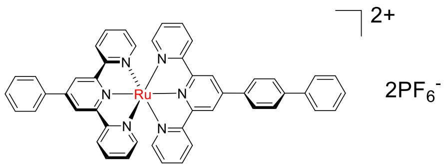


SC1

SL1 (8.0 mg, 0.026 mmol) was dissolved in EtOH/$CHCl_3$ (10 mL, v/v=1:1) and the mixture was degassed by N_2 bubbling (10 min). $RuCl_2(DMSO)_4$ (6.3 mg, 0.013 mmol) was added and the suspension was heated to 80 °C for 24 hours. The deep red solution was allowed to cool and NH_4PF_6 (25.4 mg, 0.16mmol) was added. A red solid immediately precipitated which was collected by filtration and subsequently washed with water (3×5 mL) and MeOH (3×5 mL, to aid drying). The solid material was washed down with acetonitrile. The solvent was removed in vacuo to yield the complex **SC2** as red solid (11.8 mg, 0.012 mmol, 90%).

SC1: mp: 216 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 9.02 (s, 4H), 8.66 (d, *J* = 8.1 Hz, 4H), 8.22 (d, *J* = 7.6 Hz, 4H), 7.95 (t, *J* = 7.9 Hz, 4H), 7.78 (t, *J* = 7.5 Hz, 5H), 7.70 (t, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 5.5 Hz, 4H), 7.19 (t, *J* = 6.7 Hz, 4H). MALDI-TOF MS (m/z): Calcd. for $[C_{42}H_{30}N_6Ru]^+$: 720.16. Found: 720.18.

[Ru(SL1)(SL2)](PF6)$_2$ (SC2)

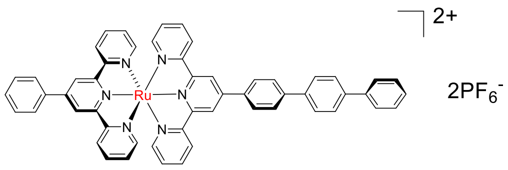


SC2

To a flask containing a mixture of **5** (10.0 mg, 0.019 mmol) and **SL2** (8.1 mg, 0.019 mmol), MeOH (4 mL), $CHCl_3$ (4 mL), and N-ethylmorpholine (6.5 mg, 0.057 mmol) were added. The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was counterion exchanged with NH_4PF_6 (18.5 mg, 0.114 mmol) to give **SC2**, as a red precipitate (16.9 mg, 0.015 mmol, 82%).

SC2: mp: 233 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 9.07 (s, 2H), 9.02 (s, 2H), 8.68 (d, *J* = 9.8 Hz, 2H), 8.65 (d, *J* = 9.2 Hz, 2H), 8.32 (d, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.96 (t, *J* = 8.0 Hz, 4H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.44 -7.46 (m, 4H), 7.19 (t, *J* = 8.0 Hz, 4H). MALDI-TOF MS (m/z): Calcd. for $[C_{48}H_{34}N_6Ru]^+$: 796.19. Found: 796.22.

[Ru(SL1) (SL3)](PF6)$_2$ (SC3)

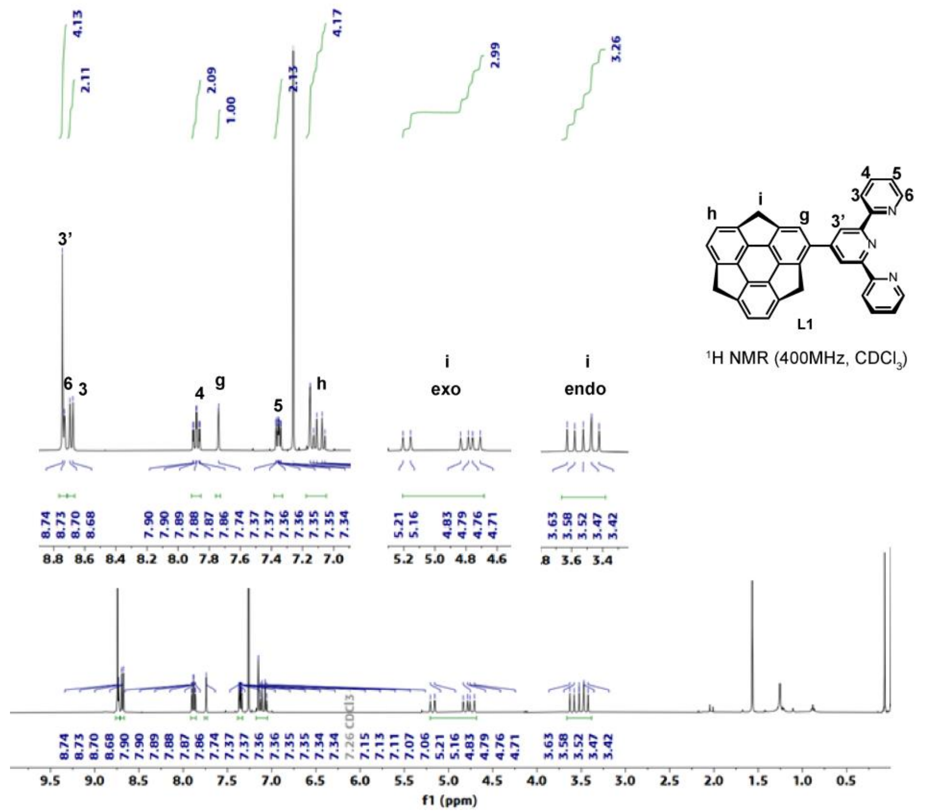


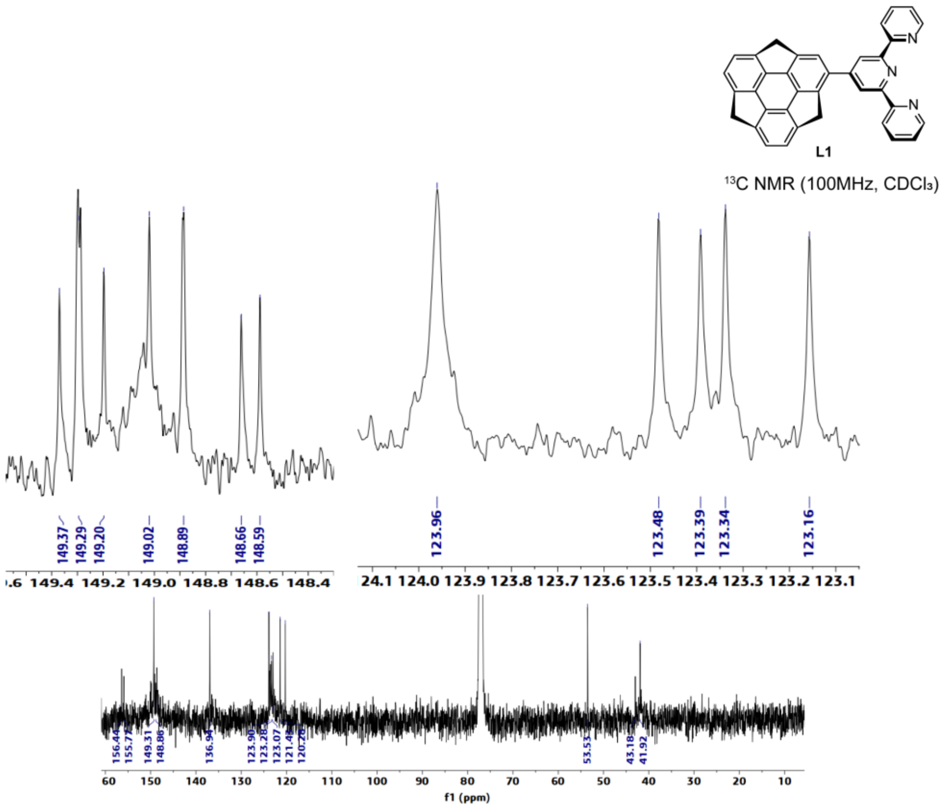
SC3

To a flask containing a mixture of **5** (10.0 mg, 0.019 mmol) and **SL3** (8.8 mg, 0.019 mmol), MeOH (4 mL), $CHCl_3$ (4 mL), and N-ethylmorpholine (6.5 mg, 0.057 mmol) were added. The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was counterion exchanged with NH_4PF_6 (18.5 mg, 0.114 mmol) to give **SC3**, as a red precipitate (17.9 mg, 0.015 mmol, 81%). **SC3**: mp: 302 °C (dec.); ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.09 (s, 2H), 9.03 (s, 2H), 8.69 (d, *J* = 8.0 Hz, 2H), 8.66 (d, *J* = 8.2 Hz, 2H), 8.35 (d, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 7.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.97 (t, *J* = 6.5 Hz, 4H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 4.9 Hz, 2H), 7.45 (d, *J* = 4.9 Hz, 2H), 7.44 (t, *J* = 4.8 Hz, 1H), 7.20 (t, *J* = 6.6 Hz, 4H). MALDI-TOF MS (m/z): Calcd. for $[C_{54}H_{38}N_6Ru]^+$: 872.22. Found: 872.48.

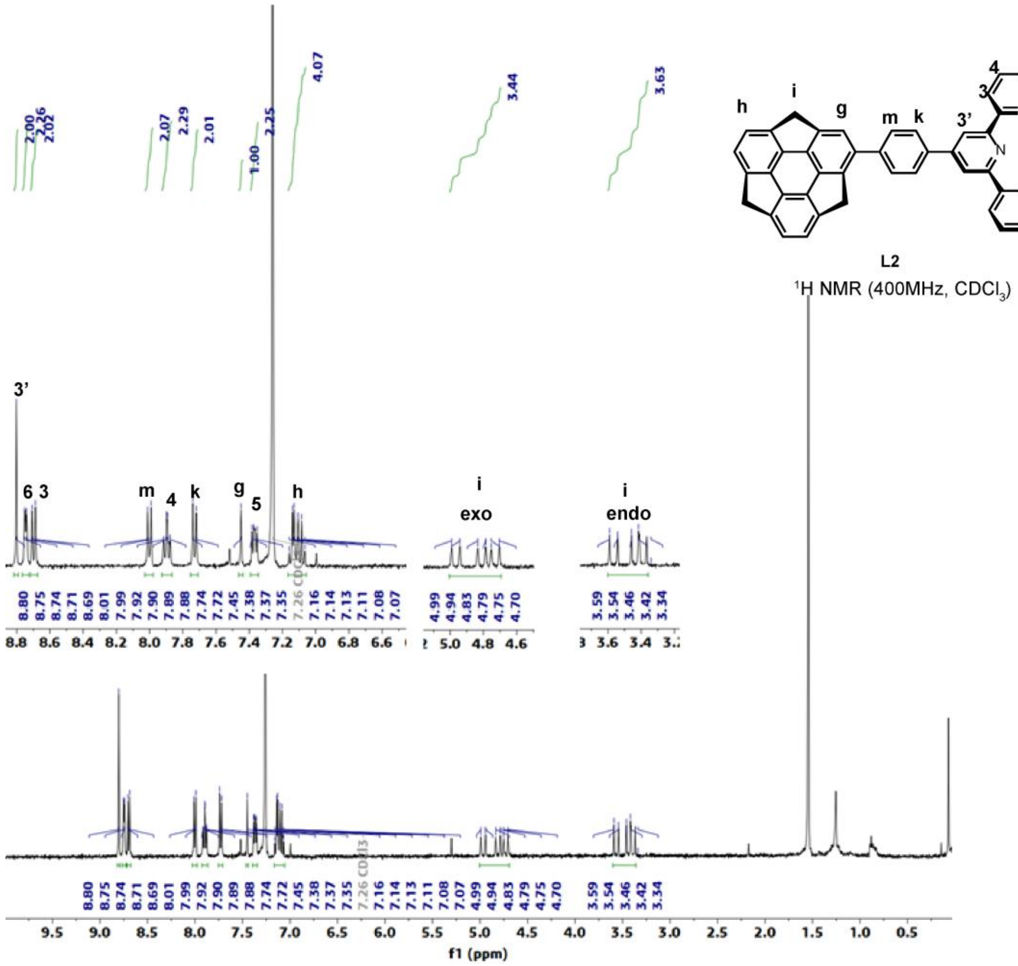
NMR Charts

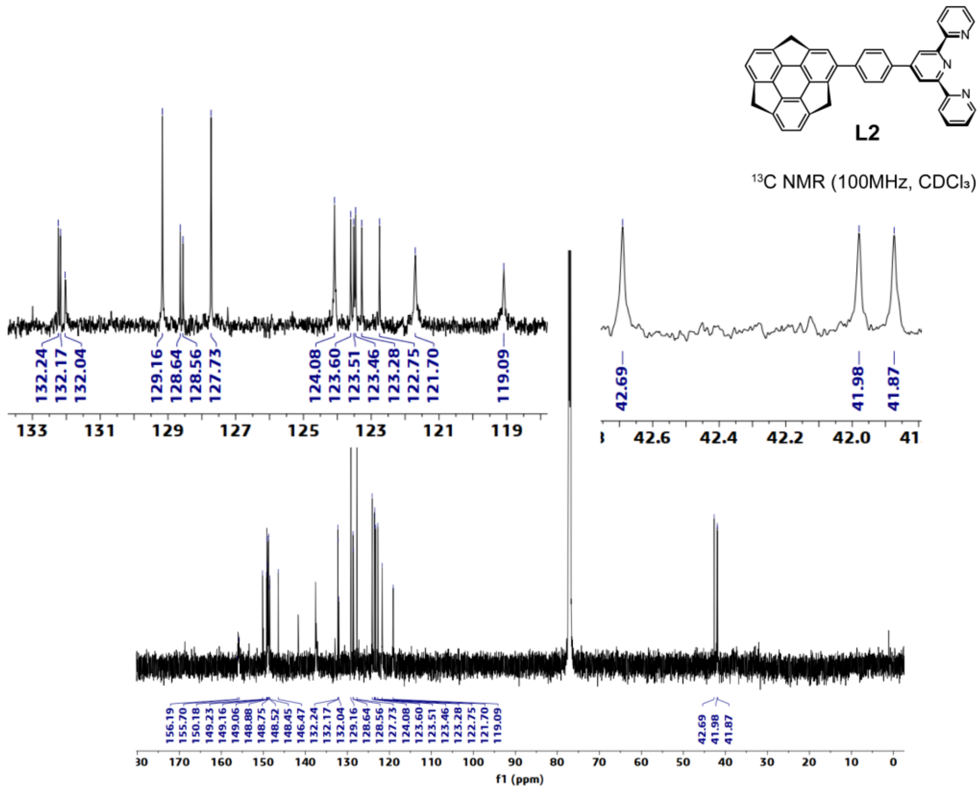
^{1}H NMR and ^{13}C NMR charts of **L1**



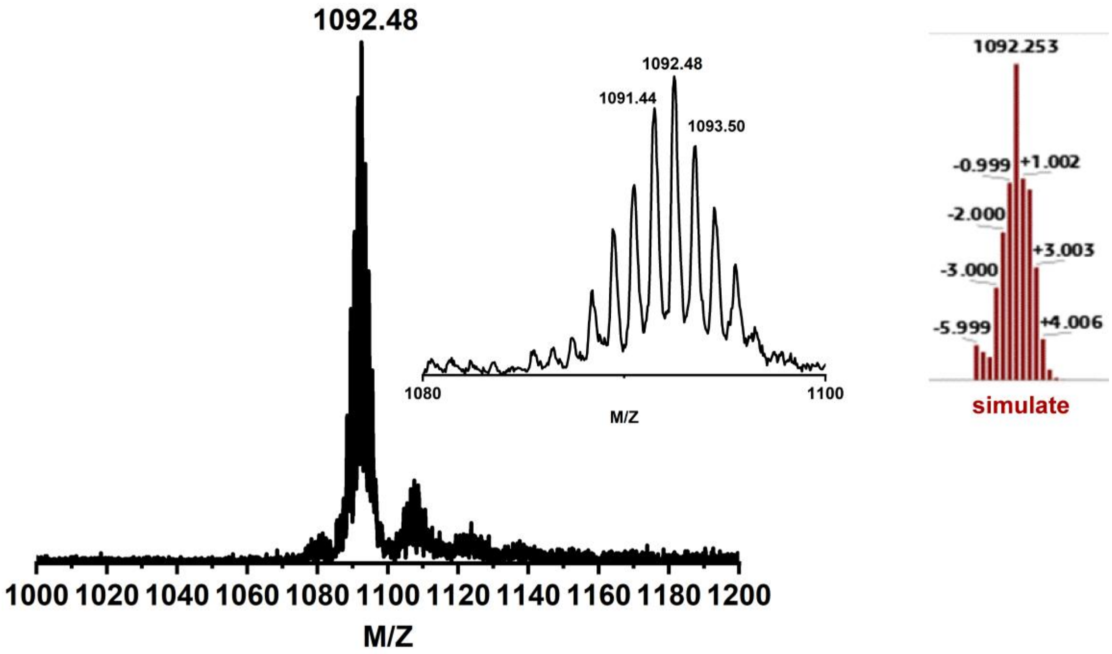


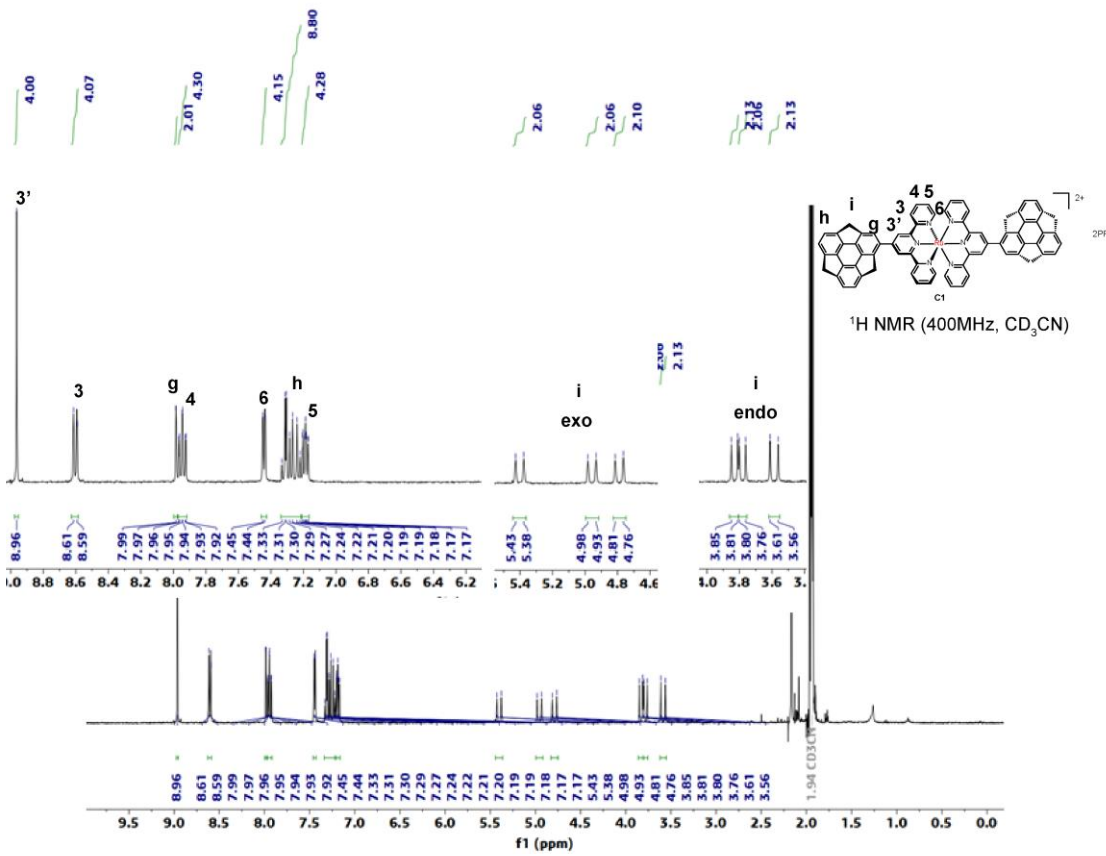
^{1}H NMR and ^{13}C NMR charts of **L2**

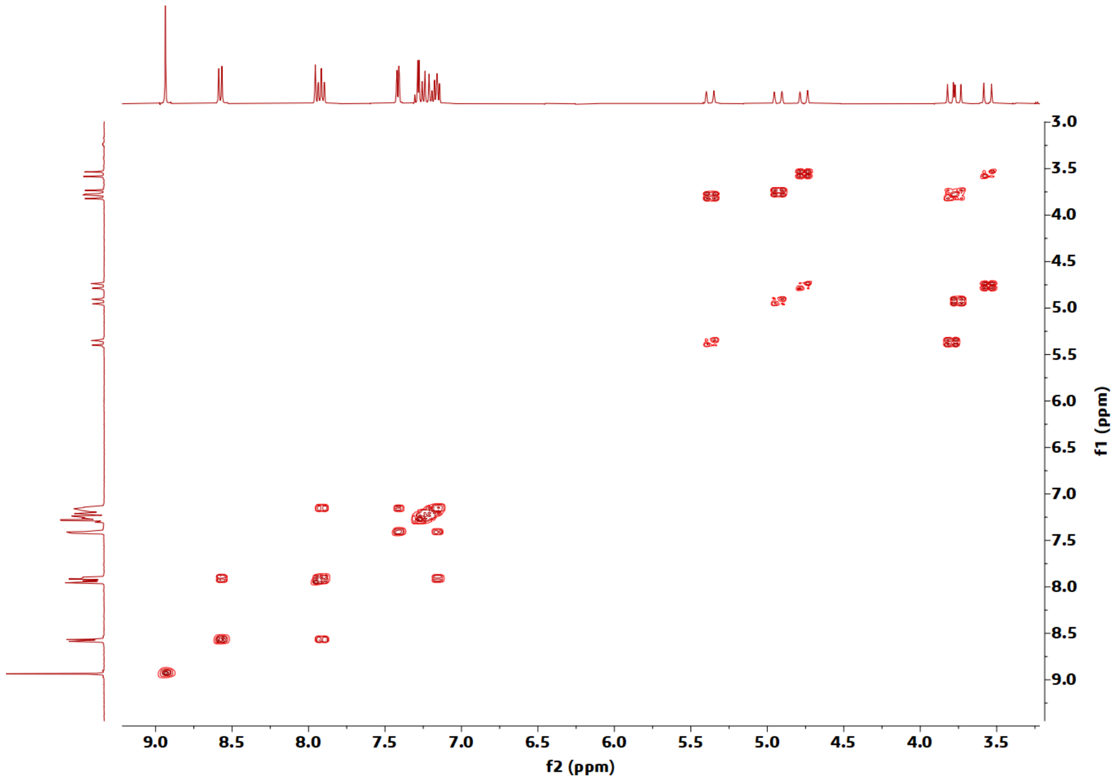




MALDI-TOF MS, ^{1}H NMR and COSY NMR charts of **C1**







3.0
3.5
4.0
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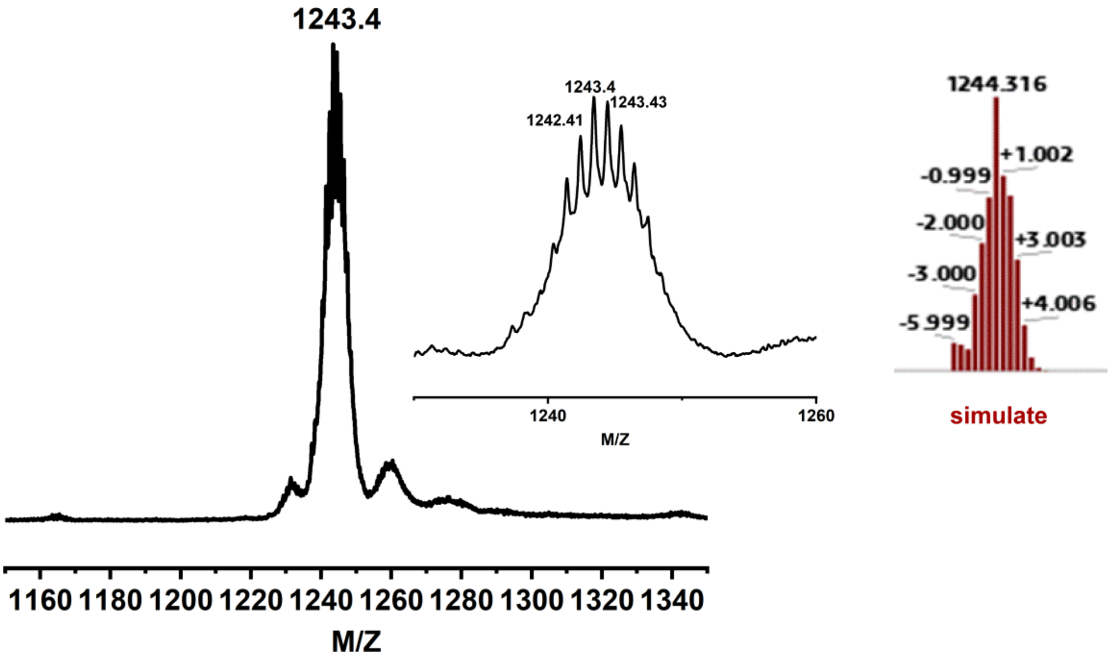
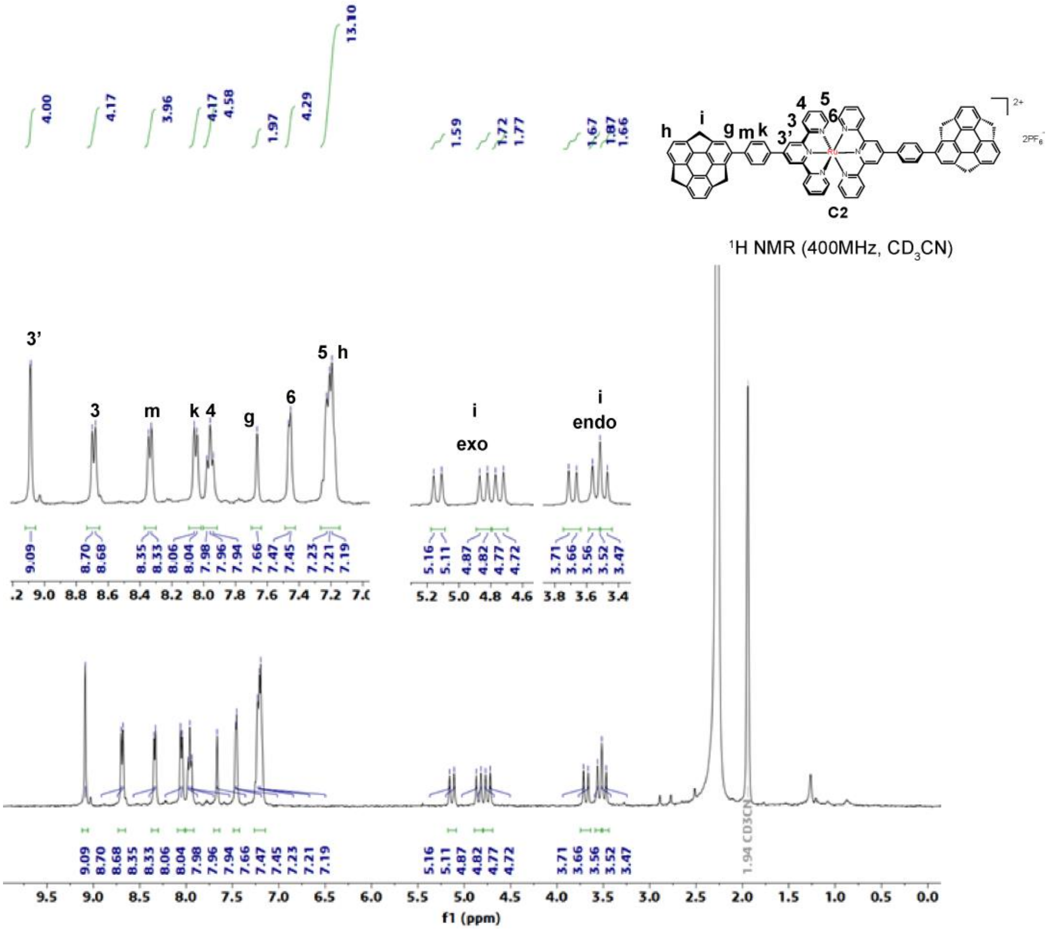
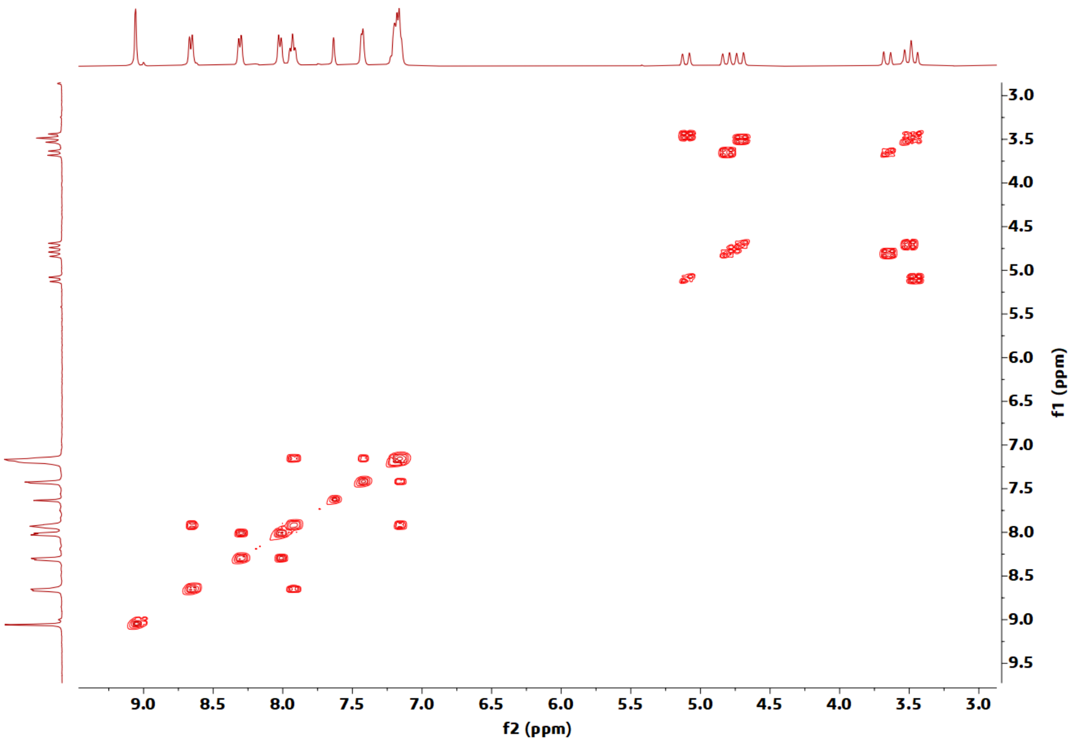
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
f2 (ppm)

MALDI-TOF MS, ^{1}H NMR and COSY NMR charts of **C2**







3.0
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7.0
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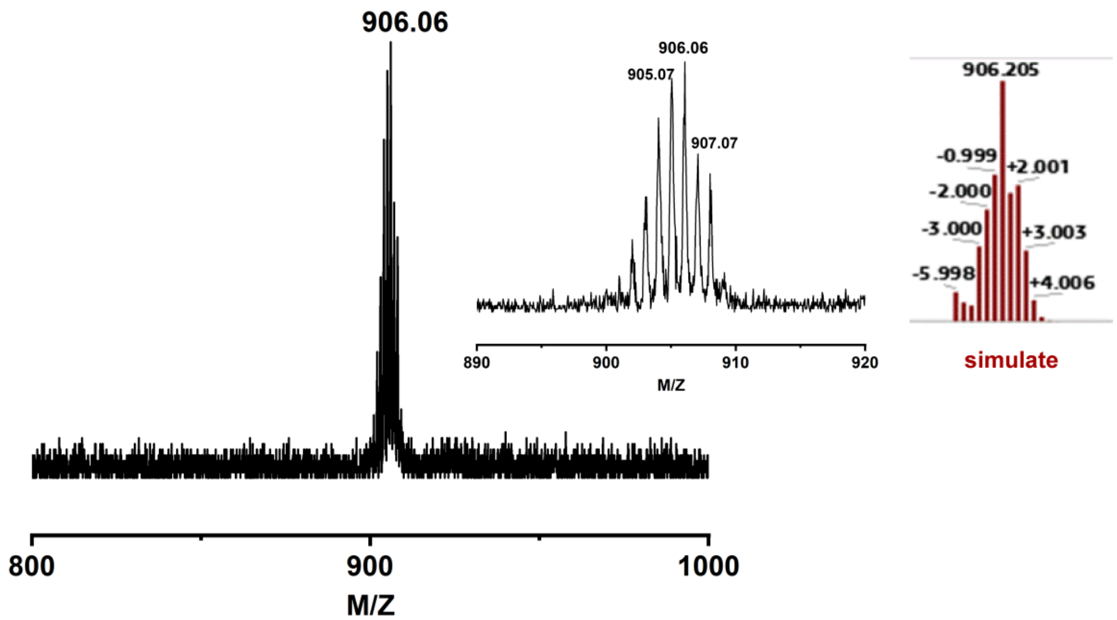
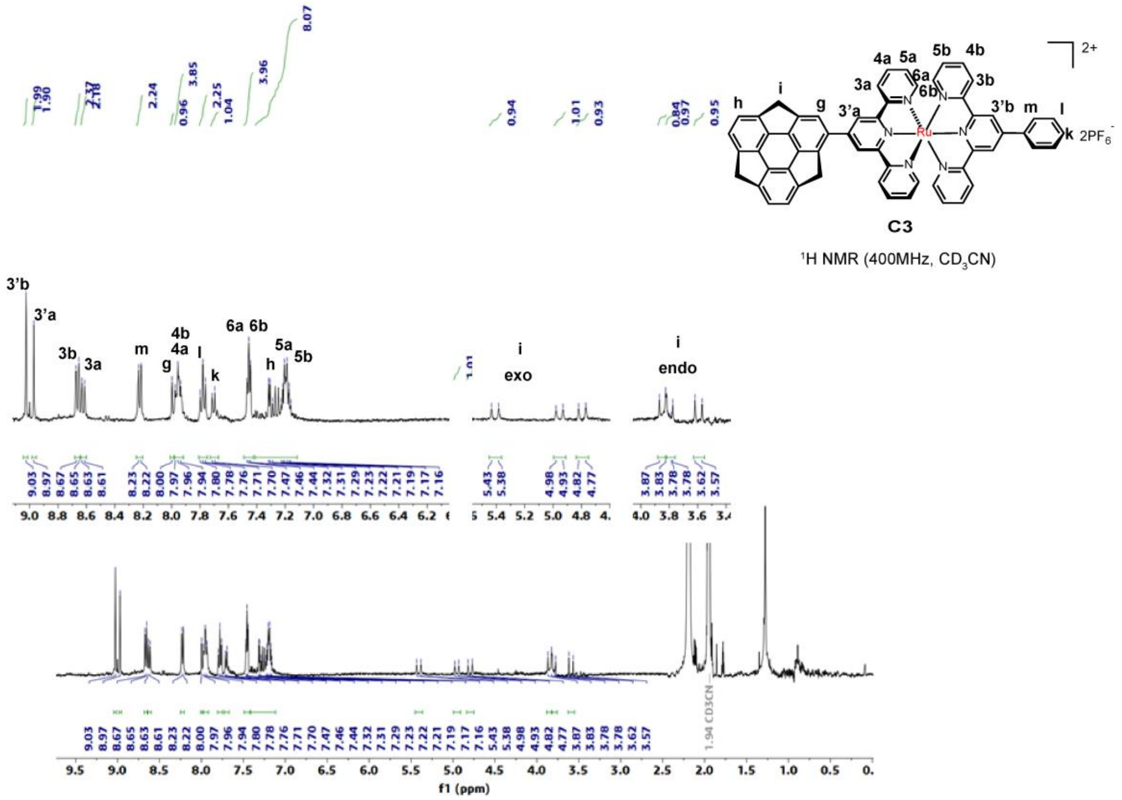
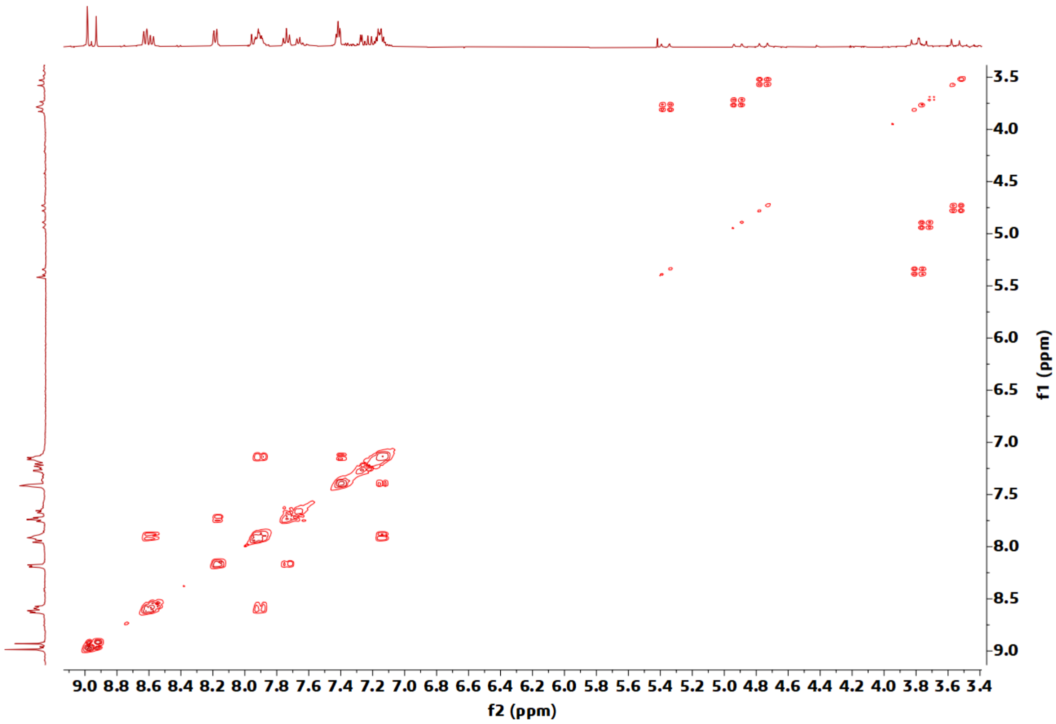
8.0
8.5
9.0
9.5
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
f2 (ppm)

MALDI-TOF MS, ^{1}H NMR and COSY NMR charts of **C3**

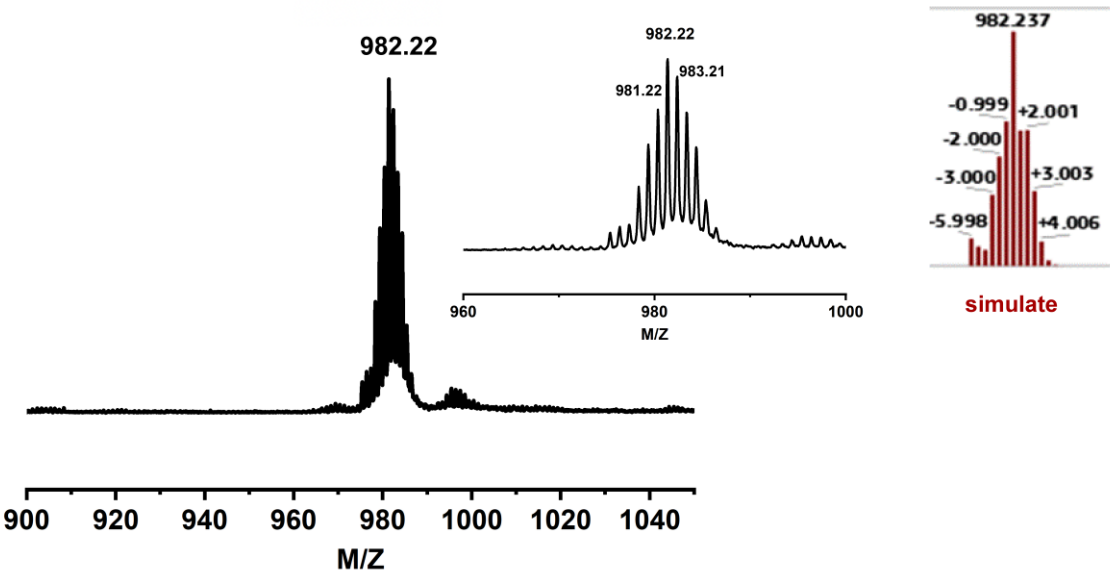


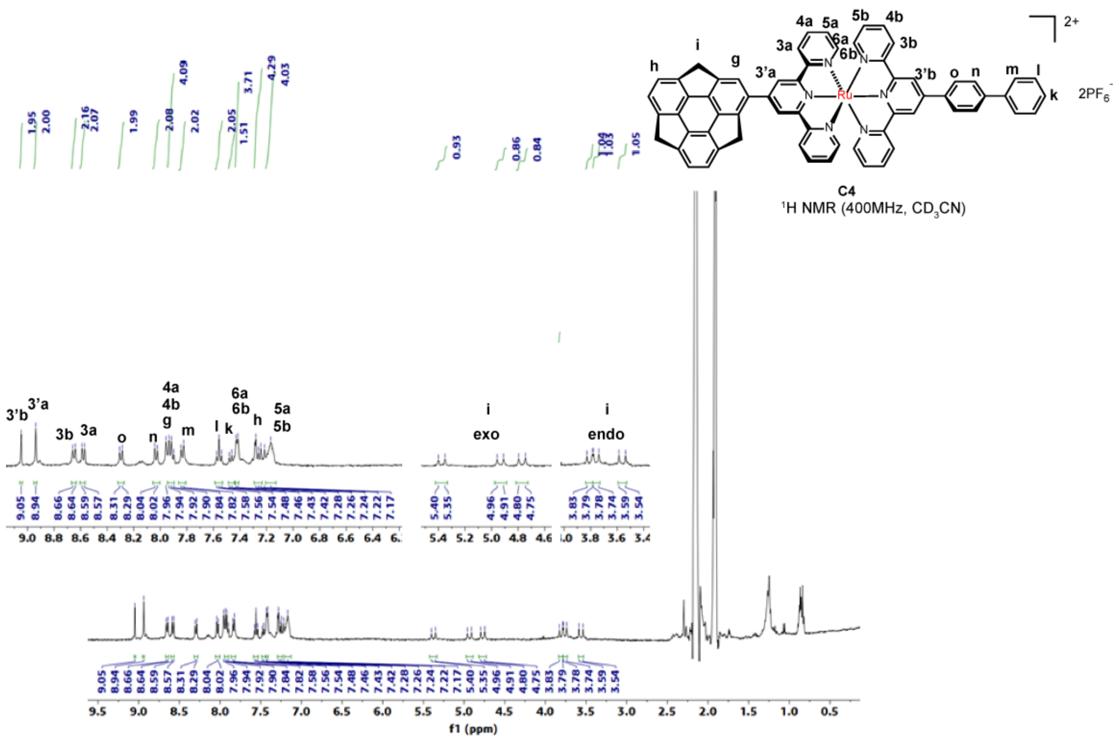


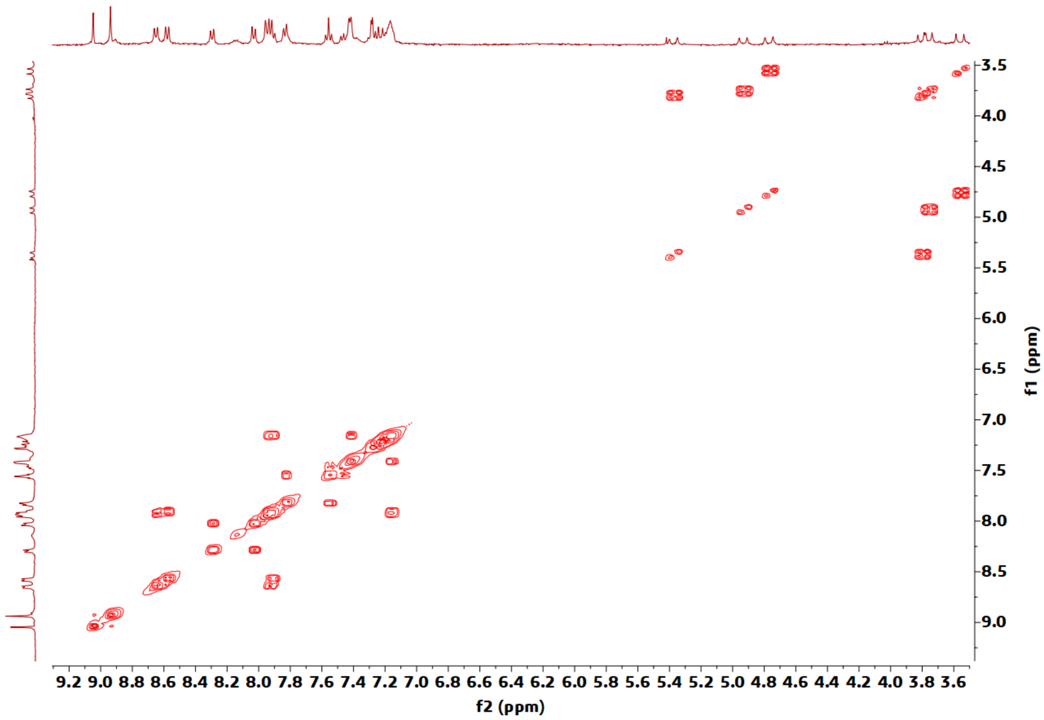


f2 (ppm)
f1 (ppm)
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0

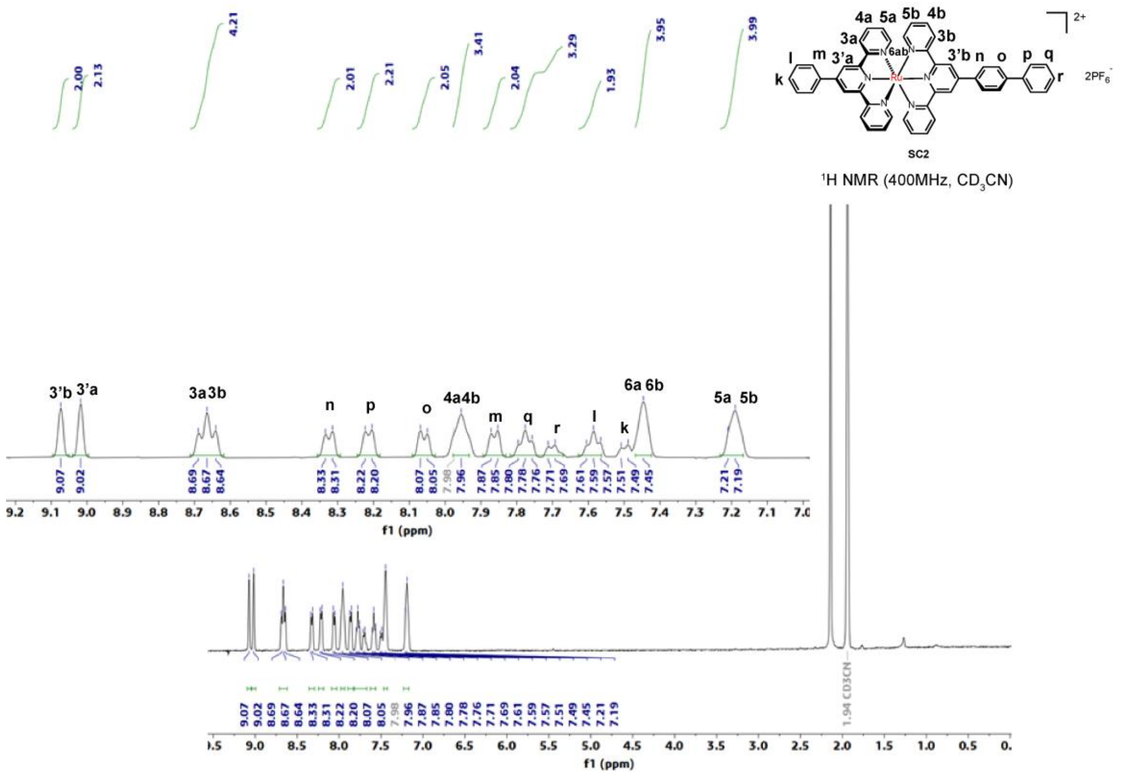
MALDI-TOF MS, ^{1}H NMR and COSY NMR charts of **C4**

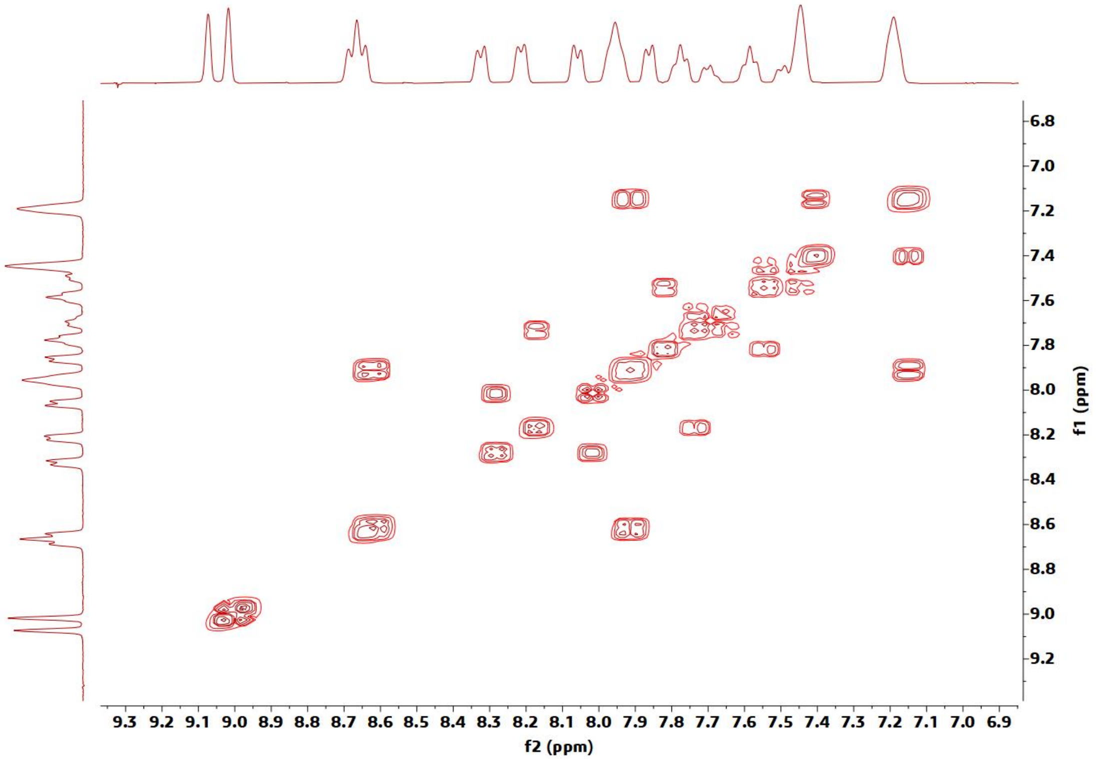




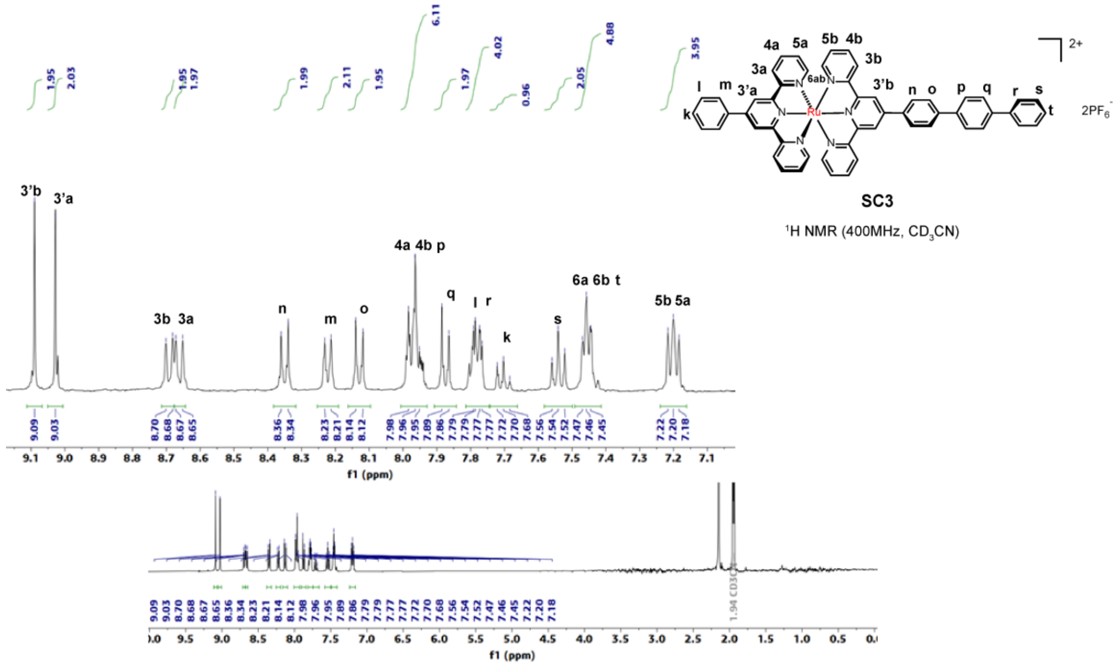

f1 (ppm)
f2 (ppm)

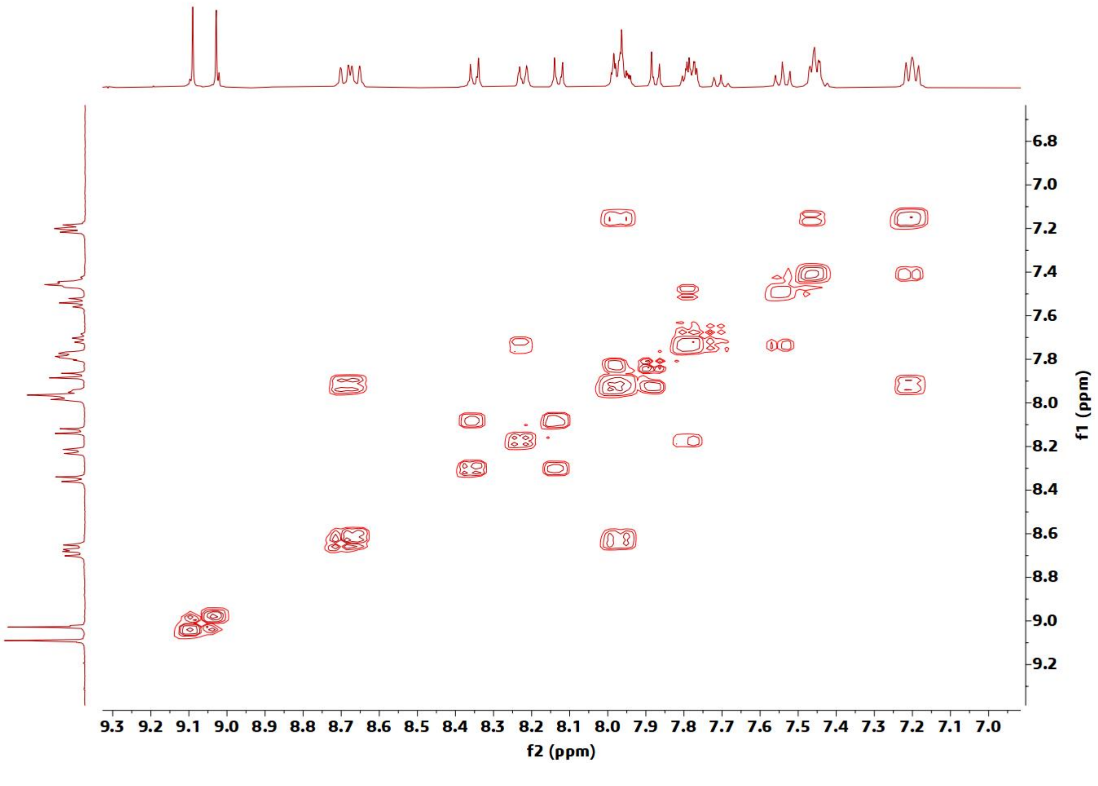
^{1}H NMR and COSY NMR charts of **SC2**





[1]H NMR and COSY NMR charts of **SC3**





3) Evaluation of Quantum Yield

A relative value of quantum yield was obtained by following relationship with using the corrected spectra data JASCO Spectra Manager™.

$$\Phi_u = \Phi_{st} \cdot \left(\frac{F_u}{F_{st}}\right) \cdot \left(\frac{A_{st}}{A_u}\right) \cdot \left(\frac{D_u}{D_{st}}\right) \cdot \left(\frac{I_{ex,st}}{I_{ex,u}}\right) \cdot \left(\frac{{n_u}^2}{{n_{st}}^2}\right)$$

Here, is the fluorescence quantum yield for the standard sample; F_u and F_{st} are the integrated values for the emission spectra of the unknown and standard samples; A_{st} and A_u are the absorbance at the excitation wavelength of the standard and unknown samples; $I_{ex,st}$ and $I_{ex,u}$ are the intensities of the excitation light at the excitation wavelengths for the standard and unknown samples; and n_u and n_{st} are the average refractive indexes for the emission spectra measurement range for the standard and unknown samples.

In this measurement, quinine sulfate in 0.5 M H_2SO_4 was used as the standard (λ_{ex} = 310 nm, Φ = 0.55).[S4] Sample concentrations were low enough (less than 10% absorption across the spectrum) and the same sample solutions were used in both absorption and emission spectra measurements. Also, $I_{ex,st}/I_{ex,u}$ was corrected automatically in the software and considered to be 1.0. Therefore the above equation becomes:

$$\Phi_u = \Phi_{st} \cdot \left(\frac{F_u}{F_{st}}\right) \cdot \left(\frac{A_{st}}{A_u}\right) \cdot \left(\frac{{n_u}^2}{{n_{st}}^2}\right)$$

The obtained parameters for the calculation of Φ_u are shown below table.

Table S1. The parameter used to calculate quantum yields using quinine sulfate as a standard.

	F_u	A_u	n_u	F_{st}	A_{st}	n_{st}
C1	1472	0.08	1.34[S5] (CH$_3$CN)	63255	0.05	1.33[S5] (water)
C2	5933	0.06				
C3	9085	0.05				
C4	11592	0.06				

4) Stern-Volmer plots

The effectiveness of **C1-C4** for Li^+ trapping were evaluated from emission titration data using the following Stern-Volmer equation,

$$\frac{I_0}{I} = 1 + K_{SV} \cdot [Q]$$

where I_0 and I are emission intensity of complexes in the absence and presence of Li^+ and [Q] is the concentration of Li^+. K_{sv} is the Stern-Volmer constant of the complex of the present system which is represented by the equation,

$$K_{sv} = \tau_0 \cdot k_q$$

where τ_0 is the life time of the complex without Li^+ and k_q is the rate of the emission quenching process. The plots for **C1-C4** are available in page S34.

5) Supporting Figures

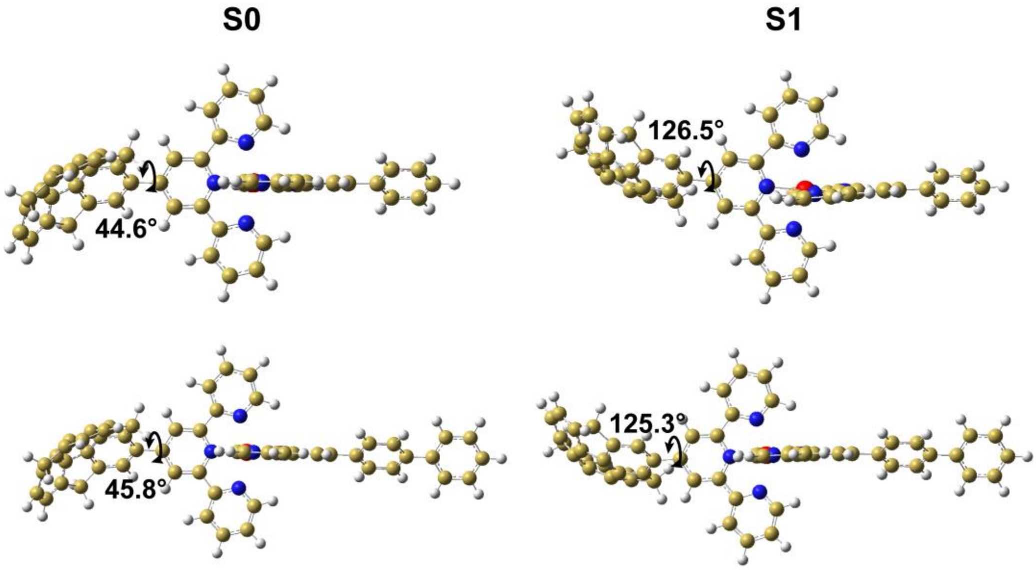


Figure S1. Optimized structure of **C3** and **C4** in both S0 and S1 states.

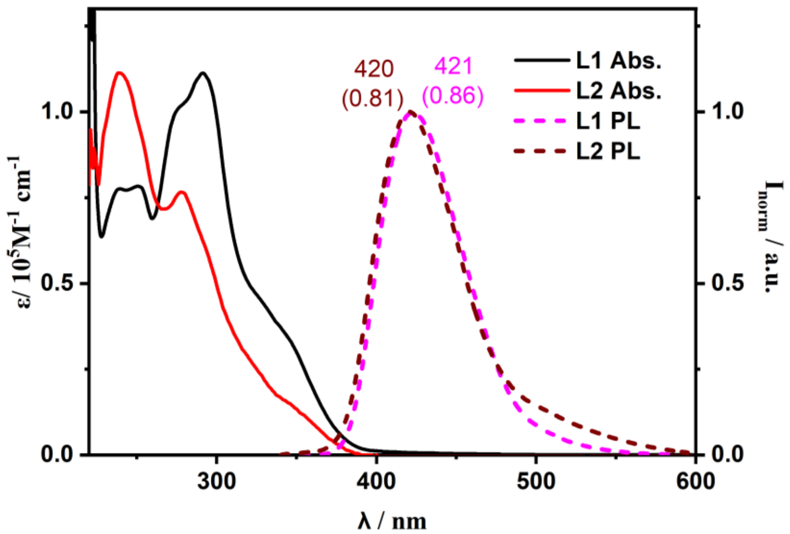


Figure S2. Absorption (ε, solid lines) and fluorescence spectra (dashed lines) of **L1** and **L2** in CH_3CN (1.0×10^{-6} M) at 298 K. The values on the PL spectra and in parentheses show the emission maximum (nm) and photoluminescence quantum yield (PLQY) determined with the Quinine sulfate standard. The excitation wavelength λ_{ex} for PL measurements was 300 nm.

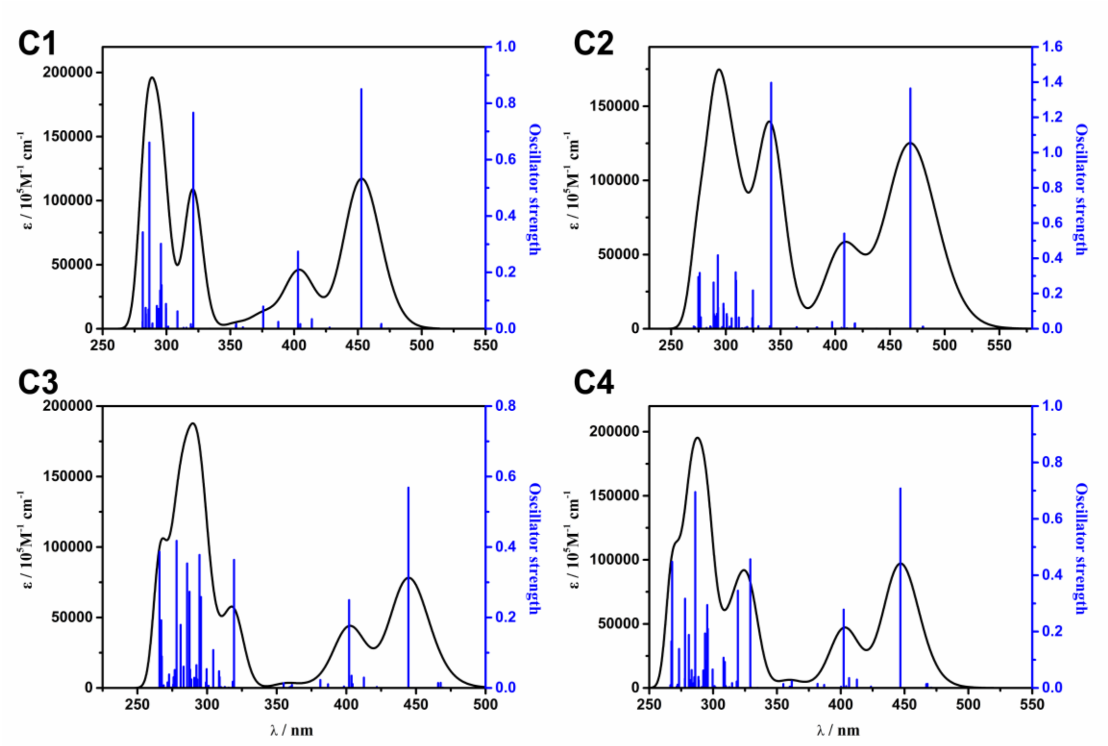


Figure S3. Simulated absorption spectra of **C1–C4** in acetonitrile.

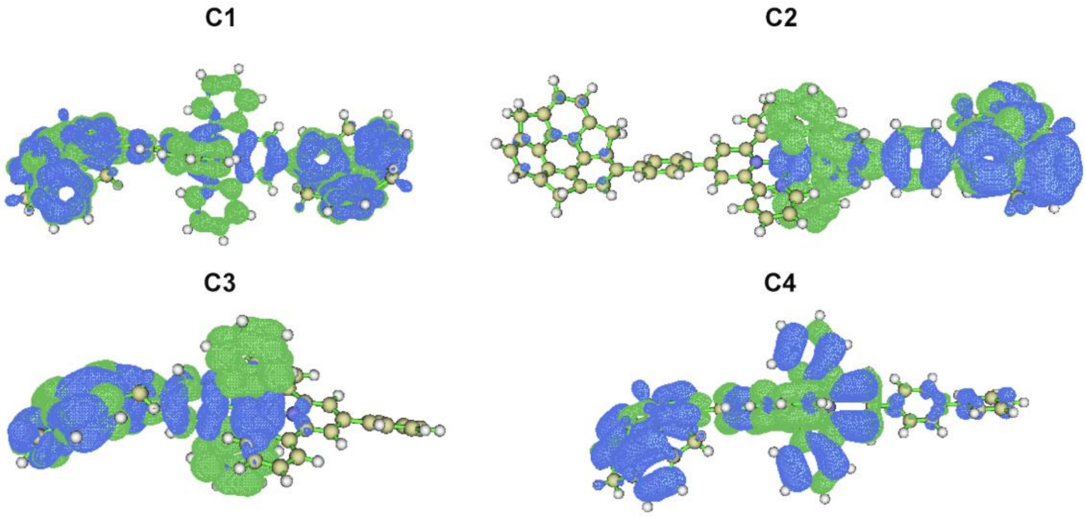


Figure S4. The distribution of hole (blue) and electron (green) of **C1-C4** at absorption around 280 nm.

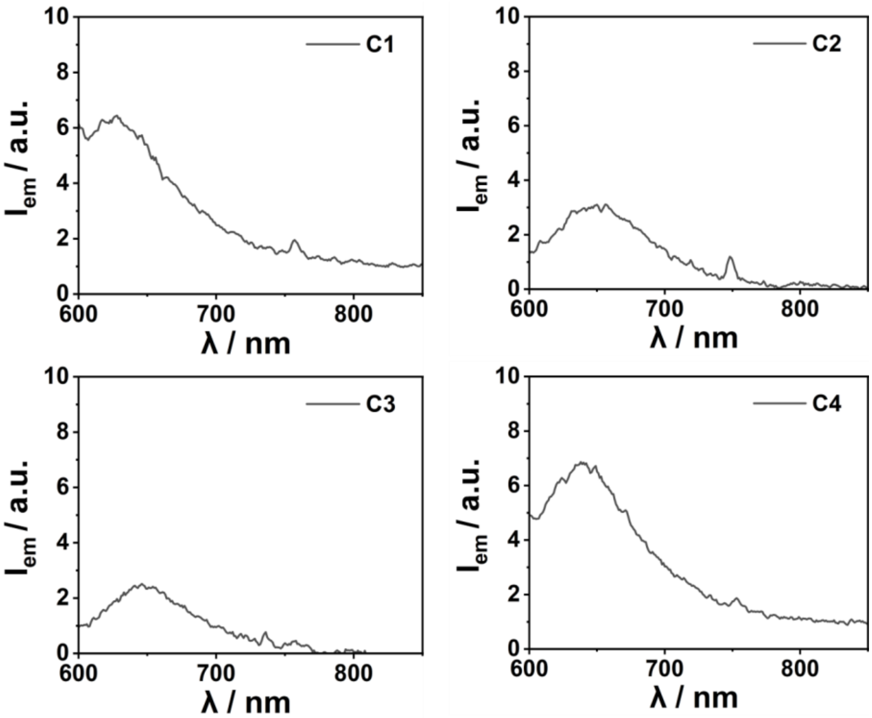


Figure S5. Emission spectra of **C1-C4** in CH_3CN (1.0×10^{-4} M) at 298 K. Excitation wavelength was 510 nm for all the spectra.

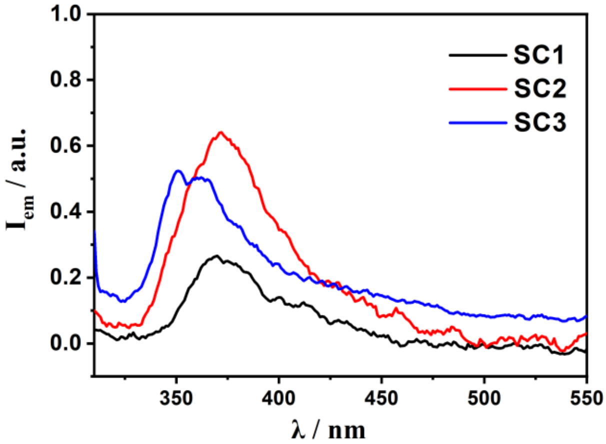


Figure S6. Photoluminescence spectra (λ_{ex} = 300 nm) of **SC1-SC3** in CH_3CN ($c = 10^{-5}$ M) at room temperature.

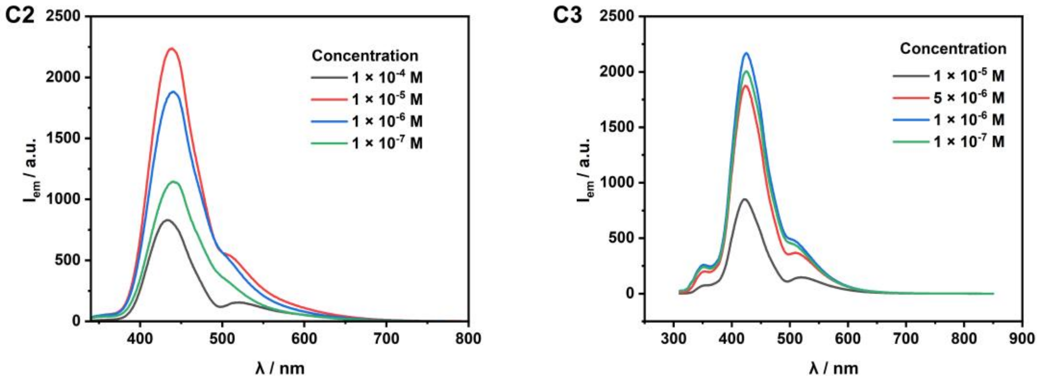


Figure S7. Photoluminescence spectra of **C2** and **C3** with different concentrations in CH_3CN at room temperature ($\lambda_{ex.}$ = 300 nm).

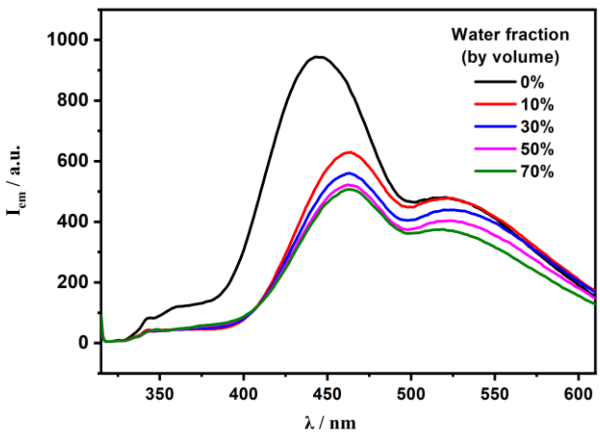


Figure S8. Photoluminescence spectra (λ_{ex} = 300 nm) of **C4** in a water/CH_3CN mixture (1.0 × 10^{-5} M, water fraction 0–70%).

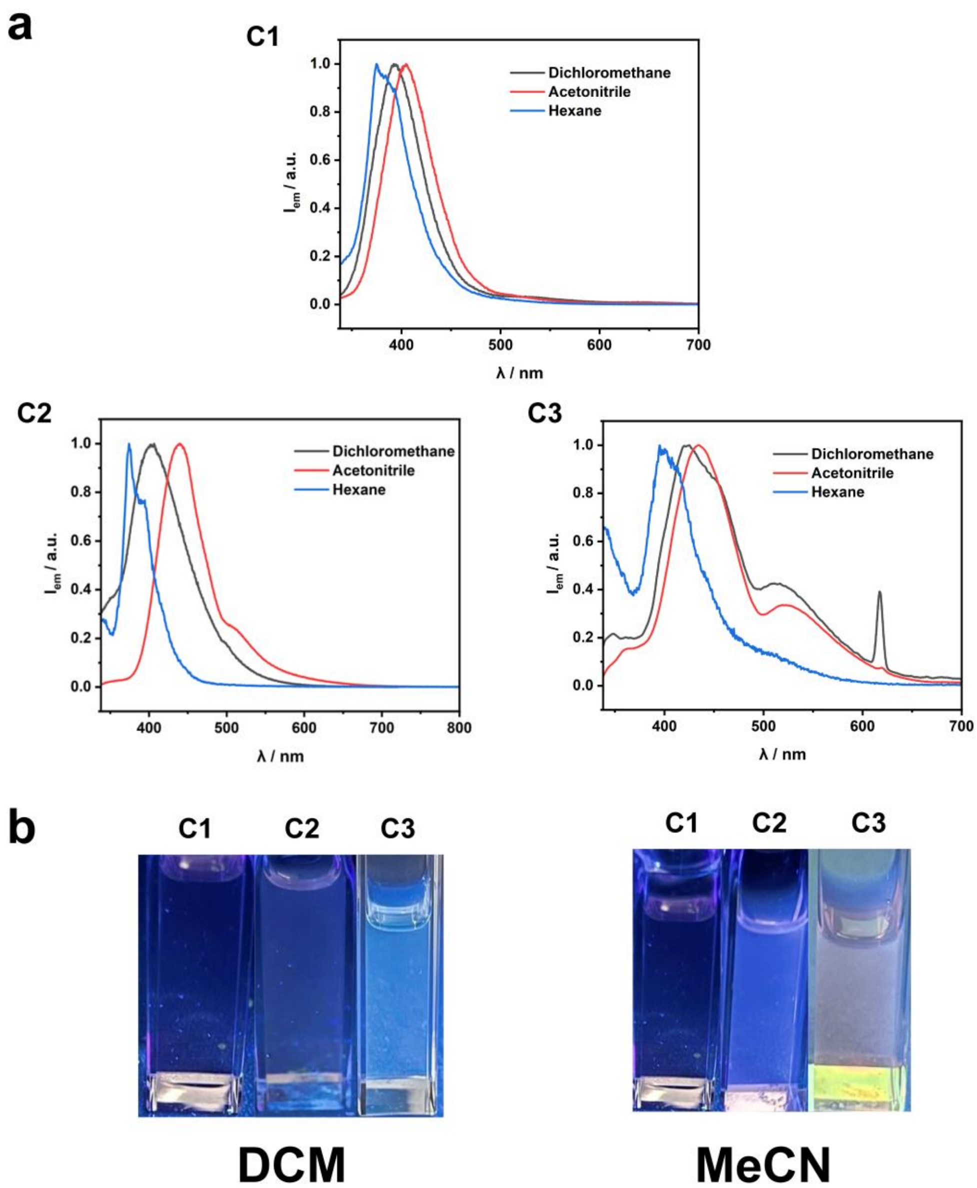


Figure S9. a) Normalized photoluminescence spectra (λ_{ex} = 300 nm) of **C1** to **C3** ($c = 10^{-6}$ M), in different solvents. b) Photographs of **C1**-**C3** in DCM and CH_3CN on excitation at 365 nm with an ultraviolet lamp at 298 K ($c = 10^{-5}$ M). Low solubility of the complexes to hexane prohibited the clear emergence of the dual emission.

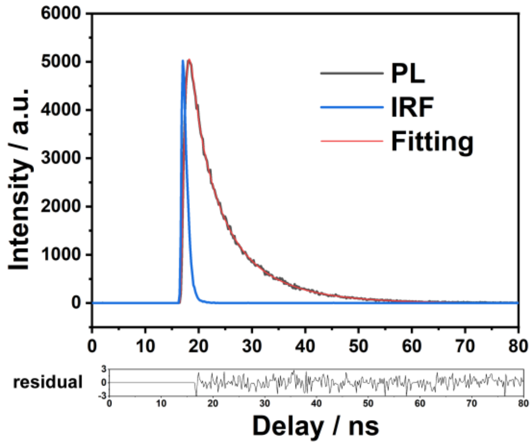


Figure S10. Time-resolved fluorescence emission λ_{em} = 400 nm for **C1** (10^{-4} M) in MeCN at 300 K under nitrogen. (λ_{ex} = 280 nm).

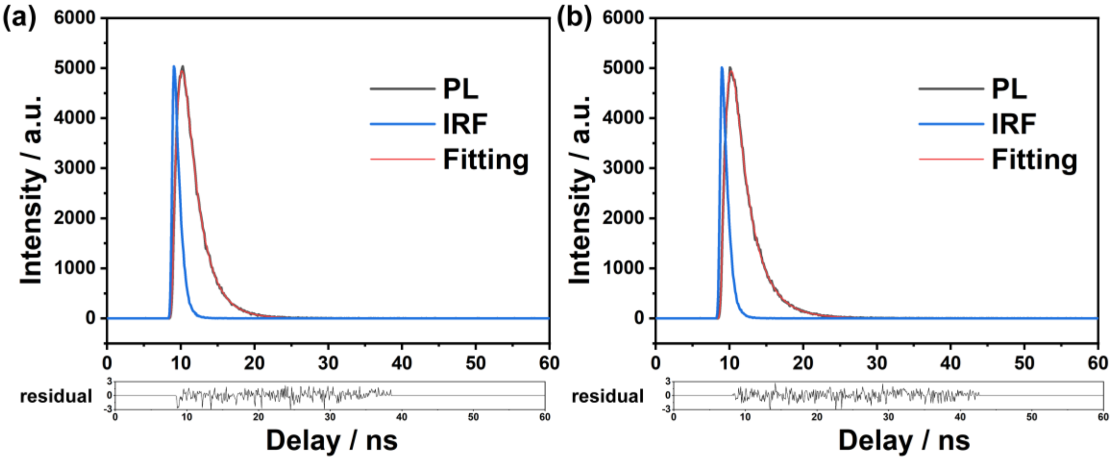


Figure S11. Time-resolved fluorescence emission (a) λ_{em} = 430 nm and (b) λ_{em} = 515 nm for **C2** (10^{-4} M) in MeCN at 300 K under nitrogen. (λ_{ex} = 280 nm).

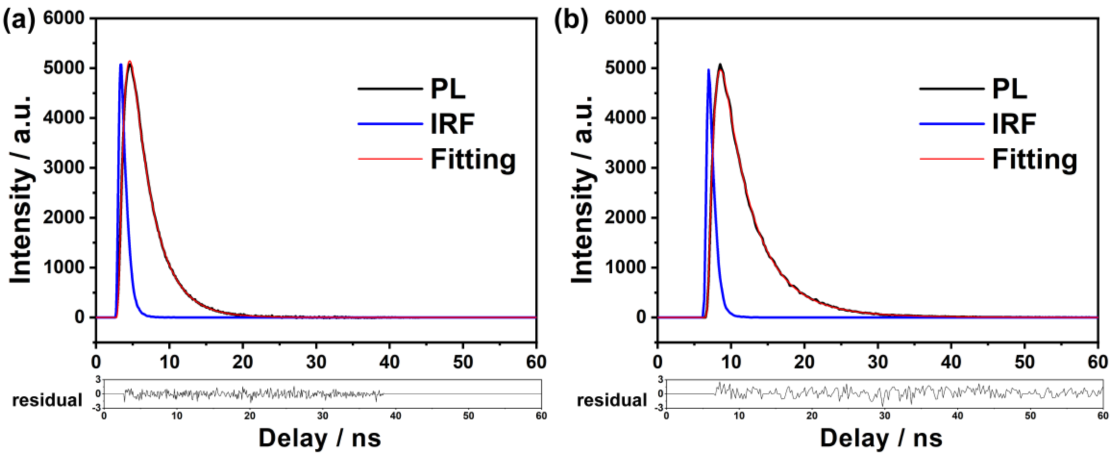


Figure S12. Time-resolved fluorescence emission (a) λ_{em} = 424 nm and (b) λ_{em} = 511 nm for **C3** (10^{-4} M) in MeCN at 300 K under nitrogen. (λ_{ex} = 280 nm).

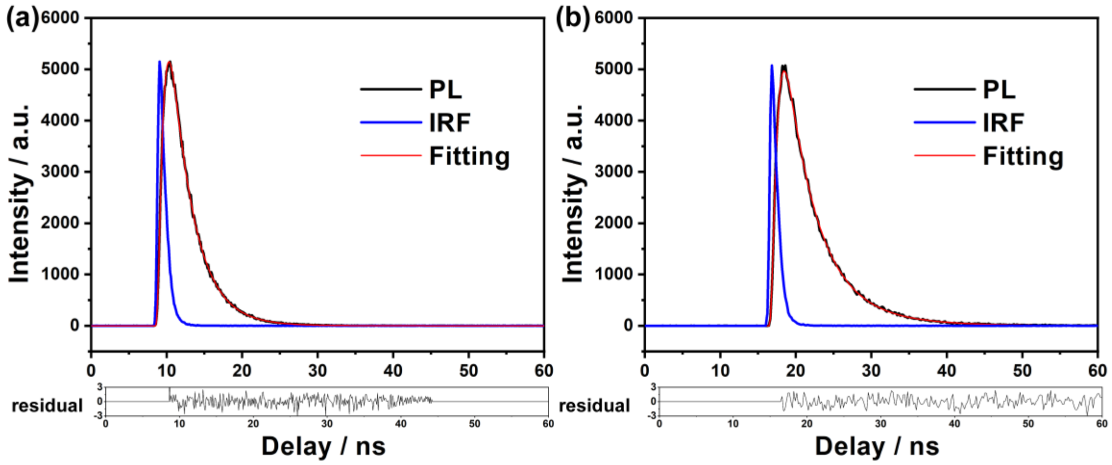


Figure S13. Time-resolved fluorescence emission (a) λ_{em} = 434 nm and (b) λ_{em} = 534 nm for **C4** (10^{-4} M) in MeCN at 300 K under nitrogen. (λ_{ex} = 280 nm).

The fittings for the emissions of **C2** (at 430 nm), **C3** (at 424 nm) and **C4** (at 434 nm) were done by using second order equation (1), and fittings for **C1** (at 400 nm), **C2** (at 515 nm), **C3** (at 511 nm) and **C4** (at 534 nm) were by using third order equation (2).

$$F_{it} = B + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

$$F_{it} = B + A'_1 e^{-t/\tau_1} + A'_2 e^{-t/\tau_2} + A'_3 e^{-t/\tau_3} \quad (2)$$

Table S2. Lifetime of **C1** to **C4** at different emission maxima.

complex	λ_{em} [nm]	τ [ns]	A_1	A_2	A'_1	A'_2	A'_3
C1	400	7.3	–	–	566.894	448.254	429.909
C2	430 515	3.8 3.2	673.468	29.1798	−928.279	517.818	201.204
C3	424 511	3.1 6.8	200.634	513.121	−1434.45	889.63	135.61
C4	434 534	3.2 7.5	84.238	476.555	−1505.83	1038.29	147.223

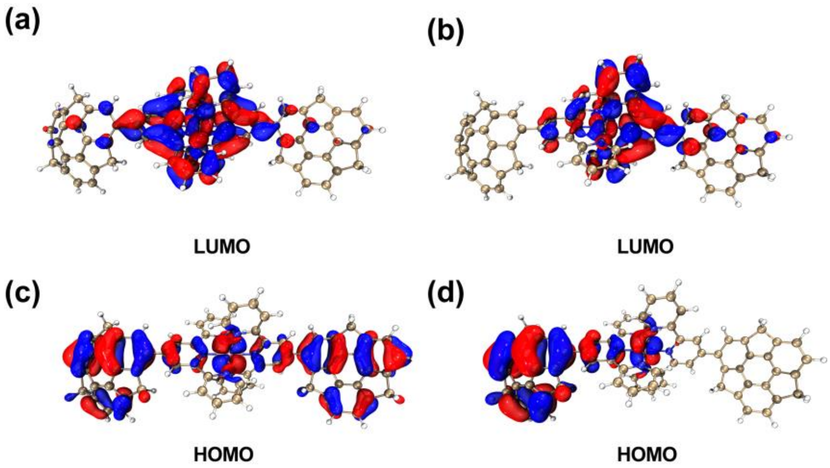


Figure S14. Molecular orbitals of **C1**. (a) LUMO of S_0 geometry. (b) LUMO of S_1 geometry. (c) HOMO of S_0 geometry. (d) HOMO of S_1 geometry.

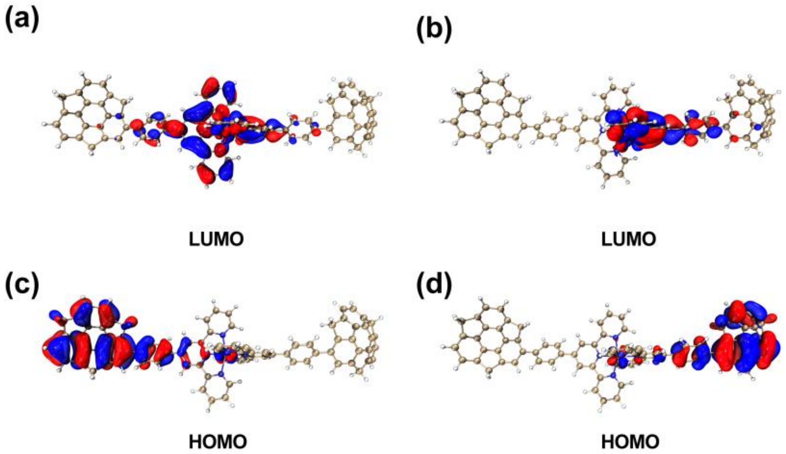


Figure S15. Molecular orbitals of **C2**. (a) LUMO of S_0 geometry. (b) LUMO of S_1 geometry. (c) HOMO of S_0 geometry. (d) HOMO of S_1 geometry.

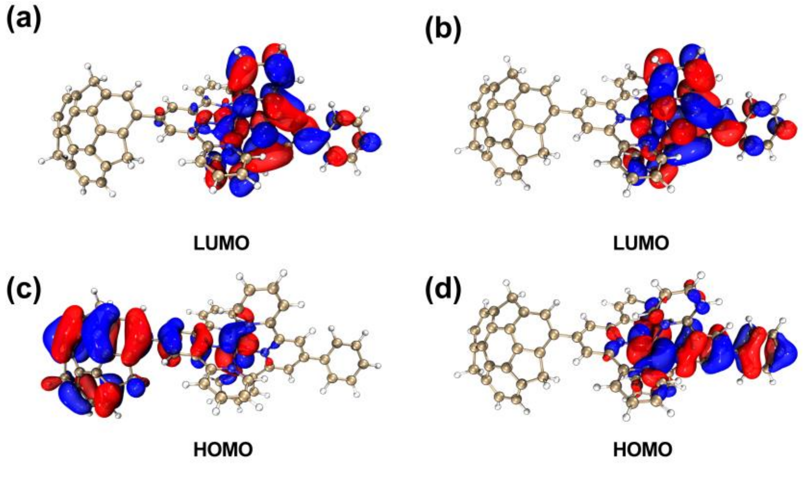


Figure S16. Molecular orbitals of **C3**. (a) LUMO of S_0 geometry. (b) LUMO of S_1 geometry. (c) HOMO of S_0 geometry. (d) HOMO of S_1 geometry.

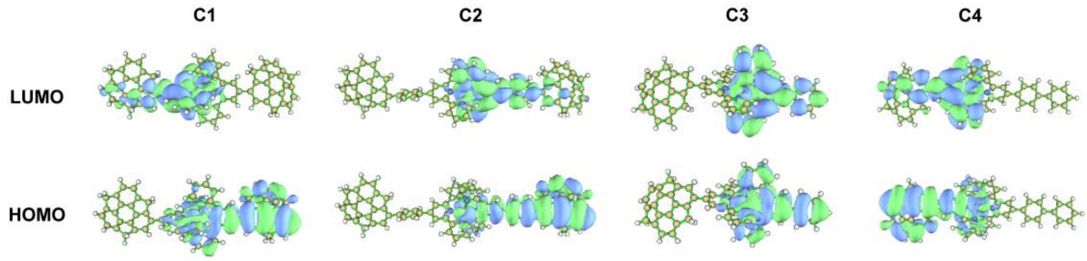


Figure S17. Schematic drawings of the selective frontier molecular orbitals for **C1** to **C4** in T_1 state.

Table S3. The transition information of the complexes **C1-C4** in S_1 and T_1 states

Complex	$S_1 \rightarrow S_0$ (nm/oscillator strength)	$T_1 \rightarrow S_0$ (nm)
C1	519.88/0.0179	686.34
C2	528.45/0.0141	750.78
C3	548.85/0.0153	784.21
C4	549.60/0.0175	741.63

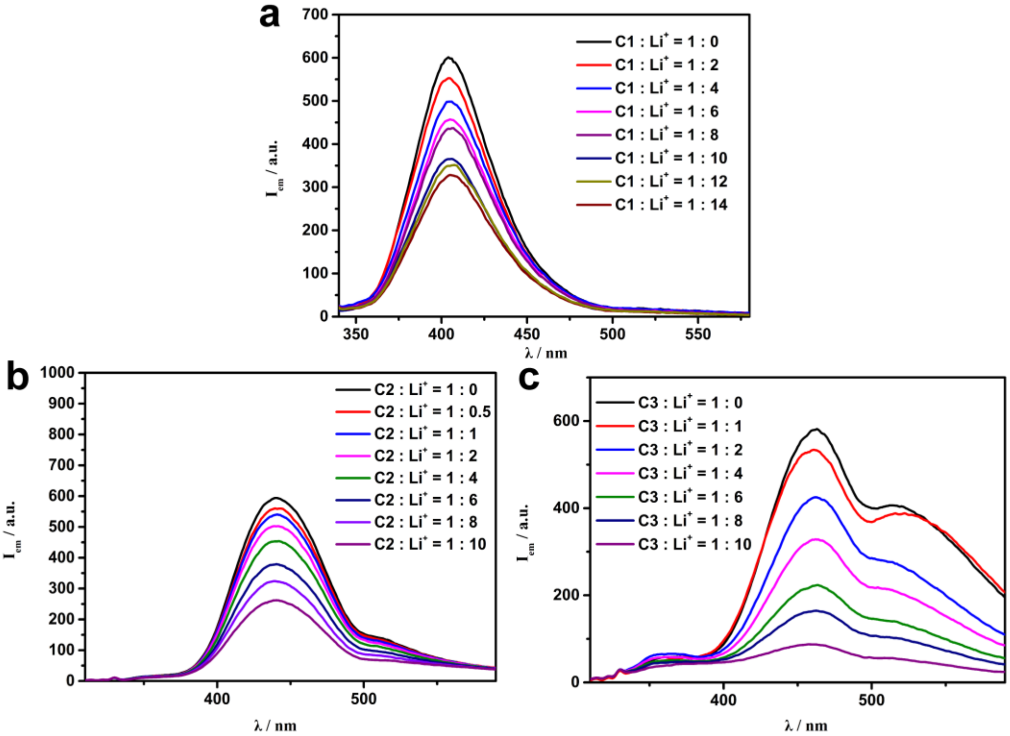


Figure S18. Lithium cation ($LiPF_6$) binding studies with a) **C1**, b) **C2** and c) **C3** using the photoluminescence spectra titration method (solvent: CH_3CN:water=1:1; concentration: 10^{-5} M; λ_{ex} = 300 nm).

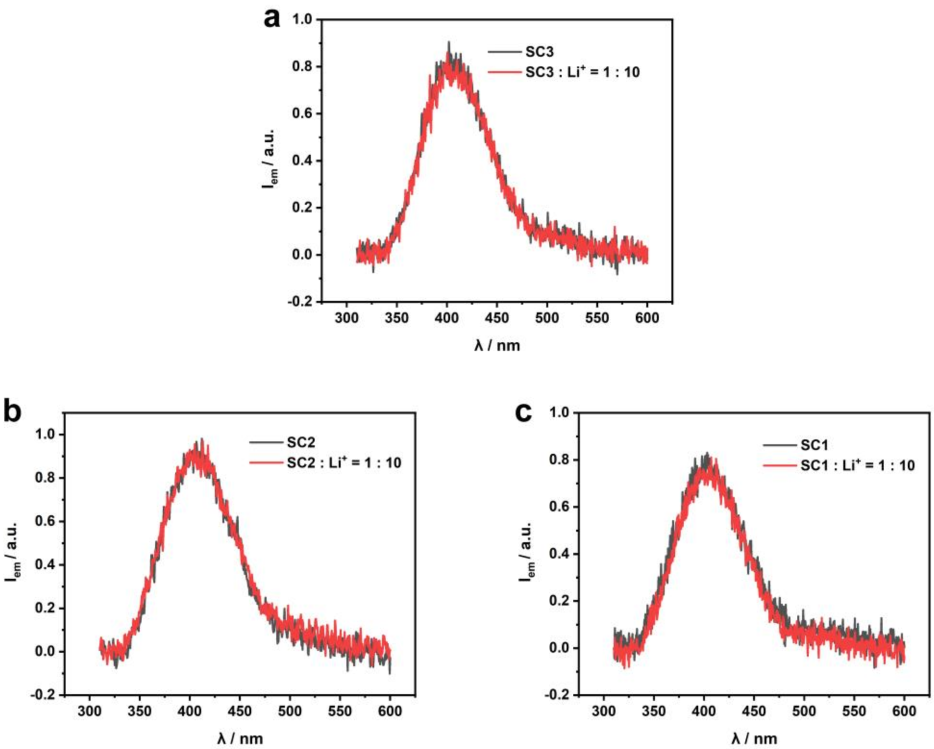


Figure S19. Lithium cation ($LiPF_6$) binding studies with a) **SC1**, b) **SC3**, and c) **SC3** using the photoluminescence spectra titration method (solvent: CH_3CN:water=1:1; concentration: 10^{-4} M; λ_{ex} = 300 nm).

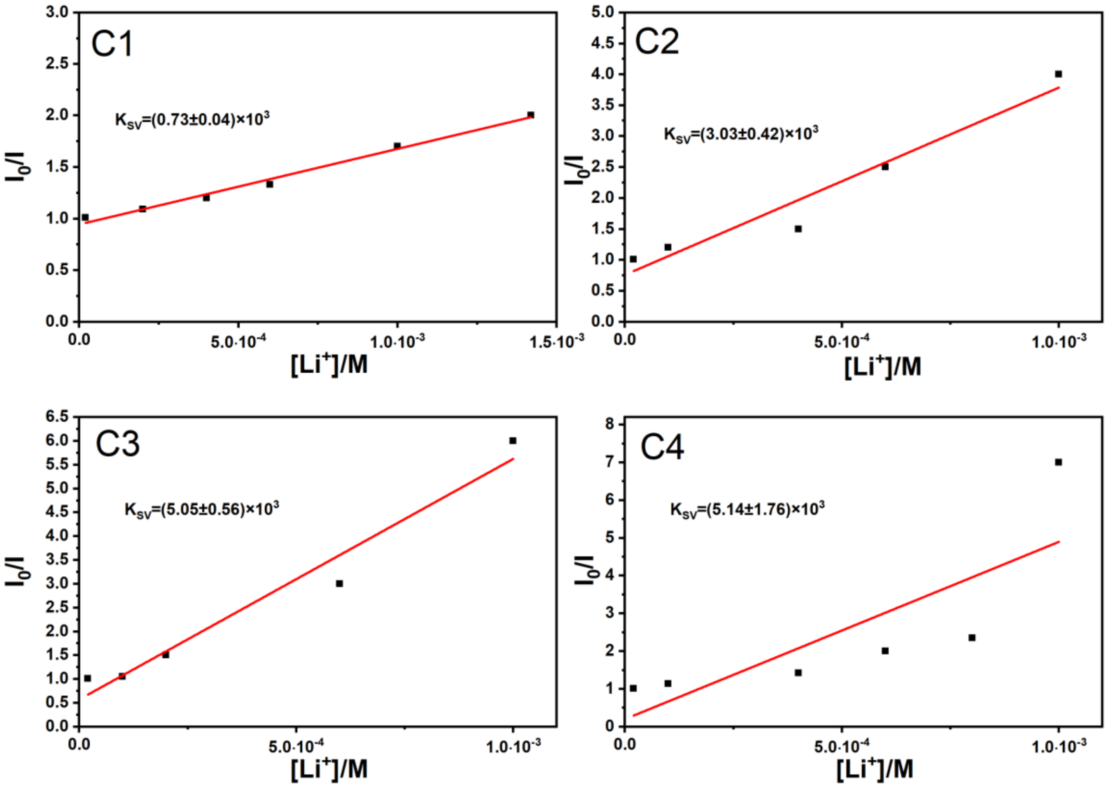


Figure S20. Stern-Volmer plots for the emission quenching of **C1-C4** by the addition of Li^+.

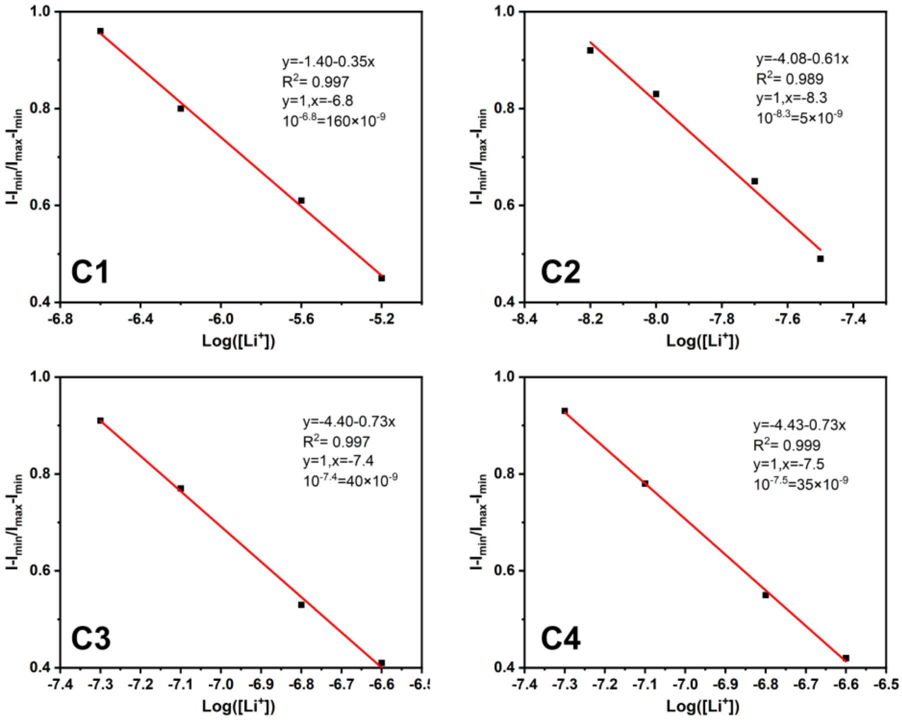


Figure S21. Plot of $(I–I_{min})/(I_{max}–I_{min})$ vs Log ([Li^+]) for the calculation of detection limit of **C1-C4**.

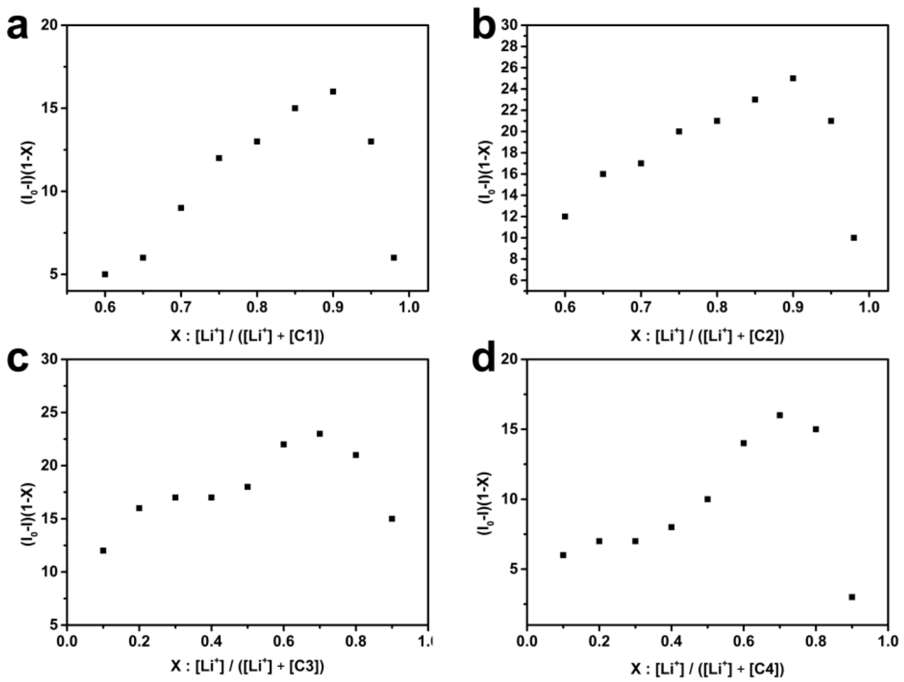


Figure S22. The Job's plot related to the interactions of the a) **C1**, b) **C2**, c) **C3** and d) **C4** with Li^+. All the data is based on the florescence spectra titration results. *x* stands for the molar fraction of Li^+, I_0 stands for the emission intensity of **C1-C4** without Li^+ added, and *I* stands for the emission intensity of **C1-C4** with the given amount of Li^+ added.

6) Computational Experiments

All the theoretical calculations were conducted by Gaussian09.[S6] The ground state structure optimizations were performed at the PBE0 functional and 6-311G(d) basis set for C, H, N, and O and SDD basis set for Ru. Simulation of UV-vis spectra, and excited state (S_1 and T_1) optimizations were performed by TD-DFT (time-dependent density functional theory) using the optimized coordinates at the PBE0 functional and 6-311G(d) basis set for C, H, N, and O and SDD basis set for Ru. Multiwfn 3.8 was used to analyze the wave functions.[S7]

Optimized cartesian coordinates of **C1**

C	8.91043	0.64005	-1.04443	C	-10.5094	-2.86646	-0.32605
C	10.24502	0.57568	-0.54083	C	-9.36383	2.69199	-0.03804
C	10.82763	-0.65297	-0.29071	C	-11.7556	-2.35027	-1.06608
C	10.09463	-1.85454	-0.54043	C	-6.46401	-2.0846	0.96014
C	8.80485	-1.78984	-1.03387	C	-4.69155	0.61126	0.63112
C	10.50937	-2.86645	0.32605	C	-3.87431	-0.24059	1.38371
C	9.59197	-3.88962	0.56354	C	-2.50556	-0.24761	1.1704
C	8.26372	-3.82261	0.0562	N	-1.96311	0.57203	0.25271
C	7.83331	-2.73085	-0.69683	C	-2.71271	1.40926	-0.48788
C	10.52922	1.70558	0.22746	C	-4.08785	1.4422	-0.3213
C	11.53823	1.56456	1.17931	C	-1.50738	-1.07446	1.86383
C	12.13901	0.29949	1.43589	C	-1.91485	2.21457	-1.42591
C	11.74042	-0.84539	0.74621	C	-1.82347	-2.0061	2.84295
C	6.81698	-0.59581	-1.14272	C	-0.80883	-2.73912	3.44033
C	6.14907	0.60439	-0.84315	C	0.50278	-2.52309	3.04223
C	6.89832	1.7989	-0.58812	C	0.75627	-1.58156	2.05843
C	8.28674	1.81402	-0.62127	N	-0.21608	-0.87167	1.47825
C	11.75562	-2.35026	1.06608	N	-0.57024	1.99555	-1.37996
C	9.36383	2.69199	0.03804	C	0.23189	2.68508	-2.19677
C	6.46402	-2.08461	-0.96015	C	-0.25074	3.62079	-3.09655
C	-8.80485	-1.78984	1.03387	C	-1.61759	3.85211	-3.15198
C	-10.0946	-1.85454	0.54043	C	-2.45649	3.14095	-2.30666
C	-10.8276	-0.65297	0.29071	Ru	0	0.56308	0
C	-10.245	0.57568	0.54083	C	4.69155	0.61125	-0.63112
C	-8.91043	0.64005	1.04444	C	3.8743	-0.24058	-1.38373
C	-8.19999	-0.5191	1.2937	C	2.50555	-0.24759	-1.17042
C	-8.28674	1.81403	0.62128	N	1.96311	0.57203	-0.25271
C	-6.89832	1.79891	0.58813	C	2.71272	1.40923	0.4879
C	-6.14907	0.6044	0.84315	C	4.08785	1.44218	0.32132
C	-6.81698	-0.59581	1.14272	C	1.50737	-1.07441	-1.86388
C	-11.7404	-0.84539	-0.74621	C	1.91485	2.21452	1.42596
C	-12.139	0.29948	-1.43589	C	1.82346	-2.00602	-2.84302
C	-11.5382	1.56456	-1.17932	C	0.80881	-2.73903	-3.44043
C	-10.5292	1.70558	-0.22746	C	-0.5028	-2.523	-3.04232
C	-7.8333	-2.73085	0.69683	C	-0.75629	-1.5815	-2.0585
C	-8.26371	-3.82261	-0.0562	N	0.21607	-0.87163	-1.47829
C	-9.59196	-3.88962	-0.56353	N	0.57024	1.99551	1.38

C	-0.23188	2.68501	2.19683	H	-11.6929	-2.53571	-2.1413
C	0.25075	3.62069	3.09664	H	-5.7728	-2.2345	0.1261
C	1.6176	3.85201	3.15207	H	-5.97894	-2.50666	1.8486
C	2.4565	3.14087	2.30673	H	-4.31043	-0.87361	2.1456
H	9.82526	-4.69431	1.25544	H	-4.6925	2.09198	-0.94053
H	7.559	-4.57912	0.3904	H	-2.85561	-2.1565	3.13561
H	11.79368	2.3859	1.84321	H	-1.04278	-3.469	4.20707
H	12.81788	0.22911	2.28145	H	1.32718	-3.07178	3.48168
H	6.35134	2.67775	-0.26054	H	1.76351	-1.37881	1.71461
H	12.67377	-2.83661	0.71451	H	1.29088	2.47023	-2.1177
H	11.69291	-2.5357	2.1413	H	0.44223	4.15236	-3.73771
H	9.02186	3.10442	0.99039	H	-2.03021	4.57737	-3.84427
H	9.64342	3.54298	-0.59482	H	-3.52604	3.30791	-2.33317
H	5.97895	-2.50667	-1.84861	H	4.31041	-0.87358	-2.14564
H	5.7728	-2.23451	-0.12611	H	4.6925	2.09193	0.94056
H	-6.35134	2.67776	0.26055	H	2.85559	-2.15642	-3.13569
H	-12.8179	0.2291	-2.28146	H	1.04276	-3.46888	-4.20719
H	-11.7937	2.38589	-1.84321	H	-1.3272	-3.07167	-3.48179
H	-7.55899	-4.57912	-0.3904	H	-1.76352	-1.37875	-1.71467
H	-9.82525	-4.69432	-1.25543	H	-1.29087	2.47017	2.11776
H	-9.02186	3.10442	-0.99039	H	-0.44222	4.15226	3.73781
H	-9.64343	3.54298	0.59482	H	2.03022	4.57725	3.84439
H	-12.6738	-2.83662	-0.71451	H	3.52605	3.30782	2.33325

Optimized cartesian coordinates of **C2**

C	-13.35167	-0.68131	-0.90521	C	6.95572	0.40232	1.28868
C	-14.69788	-0.68291	-0.42871	C	8.33888	0.3668	1.38006
C	-15.34383	0.52157	-0.18975	C	13.37572	1.74341	0.8866
C	-14.66582	1.75856	-0.4331	C	14.67415	1.74821	0.40036
C	-13.36399	1.75715	-0.9102	C	15.34674	0.51303	0.13394
C	-15.15611	2.7671	0.40273	C	14.69893	-0.69296	0.35971
C	-14.29905	3.85208	0.62521	C	13.35623	-0.69458	0.84601
C	-12.95473	3.8501	0.13449	C	12.7014	0.49906	1.11748
C	-12.44972	2.76196	-0.58774	C	12.67412	-1.84379	0.42984
C	-14.95874	-1.83742	0.31822	C	11.28317	-1.76544	0.42789
C	-16.01074	-1.74905	1.23682	C	10.58157	-0.53255	0.71114
C	-16.67832	-0.50593	1.48164	C	11.31839	0.64348	1.00182
C	-16.30429	0.6679	0.81498	C	16.30048	0.67149	-0.87534
C	-11.30913	0.65291	-1.02577	C	16.66608	-0.49343	-1.56203
C	-10.5778	-0.52893	-0.74608	C	15.99656	-1.73814	-1.33079
C	-11.28481	-1.76378	-0.48622	C	14.95096	-1.83711	-0.40595
C	-12.67582	-1.83845	-0.50055	C	12.4622	2.75551	0.58578
C	-16.40702	2.18859	1.123	C	12.96533	3.85295	-0.12359
C	-13.73746	-2.78181	0.1337	C	14.30617	3.85838	-0.62374
C	-11.03346	2.17879	-0.8477	C	15.16155	2.7677	-0.42373
C	9.11345	-0.50078	0.57977	C	13.72824	-2.78065	-0.22629
C	8.41476	-1.32266	-0.33185	C	16.40572	2.19635	-1.16126
C	7.03244	-1.28331	-0.43212	C	11.04619	2.17289	0.8479
C	6.26382	-0.42428	0.38037	C	4.7987	-0.39983	0.29039

C	3.99753	-0.06876	1.40679
C	2.61056	-0.05979	1.30472
N	2.00844	-0.37441	0.13063
C	2.7347	-0.69831	-0.9681
C	4.12453	-0.71359	-0.9117
C	1.64831	0.2533	2.38468
C	1.89521	-1.00277	-2.14847
C	2.02776	0.60851	3.68111
C	1.05524	0.88824	4.63827
C	-0.28898	0.8072	4.27689
C	-0.6092	0.44889	2.97116
N	0.32196	0.17631	2.0383
N	0.53884	-0.92875	-1.94753
C	-0.28505	-1.1952	-2.97789
C	0.17536	-1.54273	-4.24413
C	1.55087	-1.6194	-4.45822
C	2.41334	-1.34681	-3.39899
Ru	-0.00094	-0.3798	0.0237
C	-4.7993	-0.41825	-0.26752
C	-4.05209	0.74962	-0.54221
C	-2.66415	0.73949	-0.44933
N	-2.01058	-0.39183	-0.08512
C	-2.68461	-1.53515	0.19397
C	-4.07221	-1.57122	0.10639
C	-1.75357	1.87762	-0.70589
C	-1.79404	-2.65931	0.55896
C	-2.19106	3.14964	-1.08177
C	-1.26498	4.16567	-1.30572
C	0.0921	3.88717	-1.14876
C	0.4711	2.60223	-0.77287
N	-0.41481	1.61307	-0.55301
N	-0.45027	-2.37736	0.55655
C	0.41767	-3.35419	0.87937
C	0.01506	-4.64254	1.21714
C	-1.34738	-4.93827	1.22264
C	-2.2551	-3.93533	0.89061
C	-6.26318	-0.43756	-0.37266
C	-6.94483	0.41402	-1.26572
C	-8.32627	0.37557	-1.37967
C	-9.11122	-0.50277	-0.60101
C	-8.42338	-1.34112	0.30442
C	-7.04151	-1.31568	0.41018
H	-14.59175	4.6684	1.28119
H	-12.30575	4.66488	0.44704
H	-16.26775	-2.5901	1.87613
H	-17.40167	-0.47911	2.29307
H	-10.69382	-2.62974	-0.20056
H	-16.3823	2.38688	2.20005
H	-17.341	2.62473	0.74266
H	-13.96898	-3.63473	-0.51914
H	-13.39444	-3.19688	1.08765
H	-10.57098	2.62581	-1.73906
H	-10.35122	2.36779	-0.01107
H	8.96802	-1.9896	-0.98434
H	6.54231	-1.95619	-1.13065
H	6.40997	1.10381	1.91397
H	8.83827	1.00463	2.10127
H	10.68785	-2.6262	0.13576
H	17.38368	-0.45671	-2.37816
H	16.2465	-2.57034	-1.98431
H	12.31662	4.67431	-0.41894
H	14.59672	4.68376	-1.26927
H	13.9621	-3.64397	0.41187
H	13.37684	-3.18039	-1.18373
H	17.34361	2.62388	-0.78076
H	16.37433	2.41101	-2.235
H	10.35804	2.3763	0.01954
H	10.59212	2.60874	1.74901
H	4.47435	0.14653	2.35499
H	4.70204	-0.94224	-1.79891
H	3.0784	0.66615	3.94141
H	1.34401	1.16431	5.64732
H	-1.08102	1.01616	4.9878
H	-1.64064	0.37254	2.64501
H	-1.34592	-1.12345	-2.76499
H	-0.53464	-1.74695	-5.03822
H	1.94791	-1.88653	-5.43228
H	3.4861	-1.4002	-3.54487
H	-4.57337	1.66289	-0.80121
H	-4.60505	-2.49544	0.29265
H	-3.25076	3.34561	-1.19821
H	-1.59917	5.15611	-1.5975
H	0.84954	4.64594	-1.31285
H	1.51477	2.33961	-0.63956
H	1.46652	-3.07948	0.86157
H	0.75891	-5.39067	1.46887
H	-1.6997	-5.93177	1.48074
H	-3.31874	-4.14403	0.88952
H	-6.38633	1.07421	-1.92395
H	-8.81432	1.00626	-2.11479
H	-8.98667	-1.99575	0.96069
H	-6.56486	-1.95042	1.15246

Optimized cartesian coordinates of **C3**

C	-6.81043	1.08566	0.81905	C	-1.89707	1.37971	-0.40283
C	-8.12217	1.088	0.25403	C	0.4052	-1.06734	2.14559
C	-8.7842	-0.10816	0.04704	C	0.35556	1.82403	-1.52084
C	-8.15729	-1.34257	0.40322	C	-0.00714	-1.84437	3.21965
C	-6.89035	-1.34209	0.95655	C	0.93005	-2.58012	3.92986
C	-8.60738	-2.37282	-0.42303	C	2.26272	-2.52171	3.54857
C	-7.76054	-3.47303	-0.55441	C	2.61375	-1.73142	2.46677
C	-6.45559	-3.47202	0.01402	N	1.71662	-1.02081	1.77658
C	-5.97848	-2.37054	0.72343	N	1.67128	1.48278	-1.42334
C	-8.28459	2.18535	-0.59303	C	2.54306	1.99044	-2.29997
C	-9.25836	2.06017	-1.5831	C	2.16032	2.8556	-3.31162
C	-9.94114	0.82887	-1.79486	C	0.8231	3.21026	-3.41924
C	-9.66066	-0.29727	-1.02129	C	-0.08749	2.688	-2.51266
C	-4.82503	-0.29258	1.09541	H	-8.02248	-4.29951	-1.20943
C	-4.05483	0.83232	0.75541	H	-5.79567	-4.29709	-0.23979
C	-4.69616	2.05986	0.38913	H	-9.42029	2.85513	-2.30592
C	-6.0798	2.18044	0.35581	H	-10.58506	0.75605	-2.66711
C	-9.77513	-1.81363	-1.25394	H	-4.06879	2.87029	0.02964
C	-7.05605	3.09213	-0.40648	H	-10.74301	-2.2091	-0.92239
C	-4.57712	-1.81094	1.01531	H	-9.67637	-2.06865	-2.3121
C	10.97358	-0.8563	-0.87969	H	-6.64217	3.41696	-1.36419
C	10.13898	-1.96913	-0.84936	H	-7.2964	3.9999	0.16017
C	10.4289	0.41754	-0.7512	H	-4.16267	-2.21308	1.94749
C	9.05919	0.57849	-0.59033	H	-3.86457	-2.05889	0.2237
C	8.21112	-0.53397	-0.56136	H	8.64349	1.5782	-0.51213
C	8.76825	-1.81061	-0.69444	H	6.2249	-2.00576	-1.68696
C	6.75563	-0.3632	-0.39409	H	6.91613	1.32626	0.9364
C	5.85735	-1.22019	-1.0387	H	4.64047	-3.21267	-2.56698
C	4.49415	-1.04013	-0.86589	H	2.69943	-4.44652	-3.49727
N	4.03982	-0.04472	-0.08347	H	0.38428	-3.70557	-2.87129
C	4.87192	0.80098	0.55051	H	0.12781	-1.76198	-1.34549
C	6.2436	0.66003	0.41093	H	1.00308	2.49207	1.95715
C	3.41421	-1.83629	-1.46785	H	2.02532	4.29846	3.32288
C	4.16302	1.81045	1.35143	H	4.52815	4.47929	3.39765
C	3.63006	-2.9143	-2.31552	H	5.88219	2.85101	2.10759
C	2.54366	-3.60317	-2.83399	H	-2.38786	-0.62007	2.28931
C	1.26204	-3.19712	-2.49061	H	-2.42651	2.001	-1.11387
C	1.10903	-2.11452	-1.64039	H	-1.05255	-1.87622	3.50002
N	2.15101	-1.44507	-1.13779	H	0.61969	-3.18999	4.77088
N	2.80307	1.72544	1.32026	H	3.02933	-3.07805	4.07457
C	2.07874	2.60576	2.01767	H	3.64093	-1.65593	2.13092
C	2.65802	3.6093	2.7764	H	3.57511	1.6853	-2.1752
C	4.0416	3.70541	2.81466	H	2.90633	3.23898	-3.99748
C	4.80043	2.79538	2.09368	H	0.48929	3.88545	-4.19908
Ru	2.08589	0.18586	0.13531	H	-1.13675	2.95025	-2.57452
C	-2.59424	0.71025	0.60997	H	12.04467	-0.98148	-1.00343
C	-1.87349	-0.11249	1.48355	H	10.55681	-2.96671	-0.94115
C	-0.50321	-0.24945	1.32795	H	11.0722	1.29126	-0.78208
N	0.13051	0.41229	0.3432	H	8.12989	-2.68774	-0.65356
C	-0.52644	1.21415	-0.51486	C	14.30324	-0.55447	-0.52274

C	12.18074	-1.54649	0.048	C	2.56594	-1.50053	-1.62707
C	11.5089	-0.39033	-0.37326	C	2.90644	1.72909	1.74534
C	12.26248	0.6822	-0.87059	C	2.90779	-2.43228	-2.60341
C	13.64731	0.5986	-0.94745	C	1.90812	-3.09236	-3.30703
C	-8.09864	-1.46892	0.79806	C	0.57958	-2.8044	-3.01551
C	-9.39549	-1.40671	0.32282	C	0.3008	-1.86627	-2.03149
C	-10.00376	-0.14361	0.0589	N	1.25799	-1.22367	-1.34816
C	-9.29626	1.02628	0.27472	N	1.55528	1.59931	1.59461
C	-7.95419	0.95791	0.74061	C	0.74444	2.33874	2.36395
C	-7.36188	-0.26385	1.01528	C	1.21795	3.23481	3.31229
C	-7.22198	2.06648	0.30873	C	2.59185	3.37365	3.4732
C	-5.84126	1.91717	0.29657	C	3.44065	2.61183	2.67977
C	-5.2079	0.65467	0.5823	C	7.21488	-0.13904	-0.15428
C	-5.99428	-0.48159	0.88496	C	7.85198	-1.34911	-0.46923
C	-10.96247	-0.25874	-0.94565	C	9.23294	-1.42909	-0.53426
C	-11.26927	0.91828	-1.63382	C	10.03918	-0.30454	-0.29635
C	-10.53915	2.12353	-1.41377	C	9.39721	0.90443	0.01596
C	-9.48797	2.17337	-0.49693	C	8.01663	0.9864	0.09011
C	-7.24131	-2.51992	0.4856	H	14.07292	-2.52281	0.31879
C	-7.80218	-3.5863	-0.2201	H	15.38549	-0.61808	-0.58079
C	-9.14034	-3.52282	-0.70714	H	11.61778	-2.37601	0.46687
C	-9.93648	-2.39381	-0.50074	H	11.75874	1.57422	-1.23256
C	-8.22648	3.04639	-0.33307	H	14.2161	1.43247	-1.34734
C	-11.14467	-1.76504	-1.22554	H	-5.20603	2.74868	0.00127
C	-5.80528	-2.01237	0.73289	H	-11.9898	0.91377	-2.44772
C	-3.75433	0.54681	0.44422	H	-10.74806	2.96294	-2.0717
C	-3.03041	-0.37673	1.22405	H	-7.19851	-4.43778	-0.52394
C	-1.65098	-0.46776	1.10768	H	-9.47628	-4.32984	-1.35312
N	-0.98562	0.3318	0.24856	H	-7.86632	3.42818	-1.29346
C	-1.63581	1.22778	-0.52353	H	-8.40962	3.91798	0.3093
C	-3.01564	1.3494	-0.44866	H	-12.09937	-2.14285	-0.83633
C	-0.75652	-1.36363	1.86443	H	-11.13175	-1.98297	-2.29799
C	-0.72602	1.99779	-1.3928	H	-5.1357	-2.25424	-0.10008
C	-1.20474	-2.28633	2.8057	H	-5.37448	-2.47227	1.63372
C	-0.28981	-3.08951	3.47477	H	-3.56471	-0.98689	1.94237
C	1.06288	-2.95137	3.18506	H	-3.53656	2.04668	-1.09371
C	1.44952	-2.01532	2.23623	H	-2.26468	-2.3758	3.01473
N	0.57447	-1.23586	1.58553	H	-0.62941	-3.81094	4.21084
N	0.60114	1.70356	-1.25962	H	1.81357	-3.55564	3.6823
C	1.48982	2.36579	-2.0136	H	2.49385	-1.8733	1.97875
C	1.12127	3.34089	-2.92957	H	2.53018	2.09462	-1.86817
C	-0.22734	3.64632	-3.0734	H	1.88233	3.84548	-3.51446
C	-1.15606	2.96664	-2.29544	H	-0.55322	4.40245	-3.78026
Ru	0.99899	0.21094	0.14299	H	-2.21297	3.18802	-2.39059
C	5.75209	-0.05439	-0.08403	H	5.39986	-1.50097	-1.64208
C	4.93681	-0.84346	-0.9156	H	5.71193	1.41614	1.49109
C	3.55451	-0.75154	-0.82942	H	3.95056	-2.64078	-2.81427
N	2.98282	0.10023	0.04732	H	2.16446	-3.81955	-4.07058
C	3.72585	0.87944	0.86105	H	-0.23425	-3.29441	-3.5385
C	5.11207	0.81707	0.81573	H	-0.71993	-1.60846	-1.7697

H	-0.31923	2.19678	2.20397
H	0.51668	3.80784	3.90881
H	2.99875	4.06379	4.20509
H	4.51549	2.70273	2.78786
H	7.26461	-2.24834	-0.63542
H	9.70047	-2.37431	-0.79178
H	9.99527	1.78719	0.21963
H	7.5572	1.94658	0.30965

Optimized cartesian coordinates of **C4**

C	13.46051	-1.72159	-0.06937
C	14.1893	-0.77358	-0.78076
C	12.07954	-1.61122	0.031709
C	11.39967	-0.54847	-0.57507
C	12.14434	0.399257	-1.28702
C	13.52509	0.286745	-1.38953
C	-7.99149	-1.47748	0.8244
C	-9.23943	-1.52146	0.230997
C	-9.88907	-0.31025	-0.16214
C	-9.2676	0.906872	0.048563
C	-7.97496	0.94931	0.654573
C	-7.34661	-0.21868	1.043658
C	-7.261	2.058373	0.199476
C	-5.87637	1.977914	0.278453
C	-5.21271	0.773623	0.681048
C	-5.96172	-0.36793	1.013112
C	-10.7253	-0.53839	-1.2548
C	-11.0126	0.569064	-2.05249
C	-10.3714	1.821935	-1.83692
C	-9.43346	1.98773	-0.81875
C	-7.04413	-2.48255	0.63508
C	-7.46709	-3.60656	-0.07335
C	-8.75251	-3.65239	-0.68293
C	-9.63365	-2.57505	-0.59438
C	-8.23778	2.931831	-0.60587
C	-10.7896	-2.06039	-1.4696
C	-5.66906	-1.8796	0.963512
C	-3.74552	0.691428	0.580516
C	-3.02782	-0.10276	1.482822
C	-1.65026	-0.20213	1.368734
N	-1.00679	0.469877	0.39738
C	-1.66028	1.245513	-0.48694
C	-3.03797	1.37144	-0.41807
C	-0.74345	-0.98774	2.219472
C	-0.76567	1.873843	-1.47009
C	-1.16521	-1.76969	3.286153
C	-0.22892	-2.47343	4.029269
C	1.112429	-2.37864	3.687767
C	1.472985	-1.58481	2.611693
N	0.57673	-0.90521	1.889988
N	0.555372	1.570047	-1.33079
C	1.438943	2.096271	-2.18422
C	1.063249	2.944619	-3.21265
C	-0.27924	3.262444	-3.36195
C	-1.20202	2.720413	-2.47956
Ru	0.960255	0.300016	0.251387
C	5.661527	-0.08666	-0.12503
C	4.814967	-0.98142	-0.78891
C	3.441701	-0.84895	-0.65972
N	2.927316	0.135223	0.099332
C	3.708458	1.01393	0.753179
C	5.087786	0.923227	0.655756
C	2.410681	-1.6892	-1.28659
C	2.939004	2.000638	1.52568
C	2.694147	-2.76751	-2.11324
C	1.652017	-3.50423	-2.65606
C	0.345829	-3.14405	-2.35722
C	0.125054	-2.05782	-1.52654
N	1.124007	-1.34199	-1.00103
N	1.584642	1.871821	1.44506
C	0.806947	2.731221	2.110383
C	1.325309	3.754561	2.886409
C	2.702775	3.892935	2.978066
C	3.516603	3.00555	2.28956
C	7.124921	-0.20456	-0.24476
C	7.737369	-1.45691	-0.35946
C	9.114564	-1.56616	-0.46341
C	9.931673	-0.42995	-0.46483
C	9.314979	0.821718	-0.35664
C	7.938585	0.93322	-0.24469
H	13.96991	-2.54838	0.416144
H	15.26846	-0.86059	-0.86024
H	11.5255	-2.34596	0.607725
H	11.63674	1.21998	-1.78428
H	14.08358	1.027644	-1.95343
H	-5.26123	2.802299	-0.07033
H	-11.626	0.466333	-2.94352
H	-10.5325	2.602346	-2.57562
H	-6.77651	-4.41584	-0.29426
H	-8.96997	-4.49467	-1.3341
H	-7.80263	3.256436	-1.55418
H	-8.5219	3.839278	-0.0593
H	-11.756	-2.47906	-1.16334
H	-10.6498	-2.32627	-2.52044
H	-4.92454	-2.11866	0.199105
H	-5.27451	-2.25647	1.914766

H	-3.55113	-0.61879	2.27726	H	3.722973	-3.02802	-2.32908
H	-3.56335	1.969519	-1.15154	H	1.860974	-4.34881	-3.30297
H	-2.21719	-1.82906	3.536193	H	-0.49971	-3.6907	-2.75738
H	-0.54679	-3.0868	4.864921	H	-0.87811	-1.74124	-1.26721
H	1.878548	-2.90912	4.24052	H	-0.26144	2.583093	2.009461
H	2.507137	-1.48086	2.305949	H	0.651106	4.425375	3.4054
H	2.474728	1.820298	-2.02669	H	3.142539	4.68216	3.577424
H	1.818769	3.34422	-3.87856	H	4.594497	3.094231	2.346014
H	-0.60774	3.924293	-4.15538	H	7.135818	-2.36032	-0.34897
H	-2.25577	2.953798	-2.57335	H	9.560071	-2.55109	-0.55909
H	5.23037	-1.75915	-1.41759	H	9.920558	1.722219	-0.34316
H	5.719582	1.61657	1.196802	H	7.492264	1.92012	-0.17326

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