Bis(β-diketone)-based metallacycles with Haloalkane-induced Fluorescence Enhancement

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1. Materials and methods

The ligand 1, 4-bis-(3′-acetylacetonate)benzene (H_2L_1) and 4, 4′-bis-(3′-acetylacetonate)bibenzene (H_2L_2) were prepared by the literature method.[1] All other reagents were commercially available and used as received. The ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance Ⅲ HD 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets on Thermo Fisher Scientific FT-IR spectrometer (Thermo IS5). The photoluminescence (PL) excitation and emission spectra were performed on a Hitachi F-7000 spectrophotometer equipped with a 150W xenon lamp as the excitation source at room temperature. ESI-MS spectra were recorded on Agilent Q-TOF 6520 mass spectrometer.

2. Synthesis of 1-5

Synthesis of Metallarectangles **1-3**: A mixture of $[Ru_2(p\text{-cymene})_2Cl_4]$ (0.05 mmol) and one equivalent of N∩N ligand (0.05 mmol) in dichloromethane (4 mL) was stirred for 24 h, then added four equivalents of $AgPF_6$ (0.20 mmol) and one equivalent of H_2L_1 (0.05 mmol) the corresponding in this solution and kept stirring for 24 h, finally filtered to remove AgCl. The solvent was removed under vacuum and the residue was taken up in dichloromethane (2 mL) and diethyl ether was added to precipitate the product as yellow solids **1-3**.

1: Yield 65 mg, (88%). FT-IR spectrum (KBr, ν, cm^{-1}): ν = 3429 (s), 2975 (w), 1581 (s), 1415 (m), 1342 (m), 1286 (w), 1046(m), 842 (s), 732 (w), 622 (w), 566 (w) cm^{-1}. ^1H-NMR (400 MHz, DMSO-d_6): δ = 8.66 (d, $^3J_{H,H}$ = 4 Hz, 8 H, H_{bpy}), 8.21 (d, $^3J_{H,H}$ = 4 Hz, 8 H, H_{bpy}), 7.13 (s, 4 H, H_{Ar}), 6.26 (s, 4 H, H_{Ar}), 5.98 (d, $^3J_{H,H}$ = 8 Hz, 8 H, H_{cymene}), 5.74 (d, $^3J_{H,H}$ = 4 Hz, 8 H, H_{cymene}), 2.05 [s, 12H, $ArCH_3$], 1.65 (s, 24 H, L-CH_3), 1.33 [d, $^3J_{H,H}$ = 8 Hz, 24H, $CH(CH_3)_2$] ppm. ^{13}C-NMR (400 MHz, DMSO-d_6): δ = 186.62 (CO), 153.49 (CH_{bpy}), 144.93 (C_{bpy}), 138.88 (C_{L1}), 132.55 (C_{L1}), 131.99 (C_{L1}), 123.68 (CH_{bpy}), 113.77 (C_{L1}), 102.20 (C_{cymene}), 99.42 (C_{cymene}), 85.11 (CH_{cymene}), 81.72 (CH_{cymene}), 30.74 ($ArCH_3$), 27.91 (L-CH_3), 22.39 [$CH(CH_3)_2$], 17.24 [$CH(CH_3)_2$] ppm.

2: Yield 72 mg, (93%). FT-IR spectrum (KBr, ν, cm^{-1}): ν = 2982 (w), 1565 (s), 1431 (m), 1343 (m), 1285 (w), 1092(m), 1035(w), 975 (s), 841 (s), 724 (w), 547 (w), 487 (w) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.54 (d, $^{3}J_{H,\,H}$ = 4 Hz, 8 H, H_{bpb}), 8.14 (s, 8 H, H_{bpb}), 8.11 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{bpb}), 7.15 (s, 4 H, H_{Ar}), 6.30 (s, 4 H, H_{Ar}), 5.97 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 5.74 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 2.07 [s, 12H, $ArCH_3$], 1.69 (s, 24 H, L-CH_3), 1.33 [d, $^{3}J_{H,\,H}$ = 4 Hz, 24H, $CH(CH_3)_2$] ppm. ^{13}C-NMR (400 MHz, DMSO-d_6): δ = 186.70 (CO), 153.11 (CH_{bpb}), 148.46 (C_{bpb}), 138.73 (C_{L1}), 137.40 (C_{bpb}), 132.73 (C_{L1}), 132.05 (C_{L1}), 128.66 (CH_{bpb}), 123.63 (CH_{bpb}), 113.61 (C_{L1}), 102.17 (C_{cymene}), 99.14 (C_{cymene}), 84.69 (CH_{cymene}), 81.68 (CH_{cymene}), 30.74 ($ArCH_3$), 27.99 (L-CH_3), 22.66 [$CH(CH_3)_2$], 17.26 [$CH(CH_3)_2$] ppm.

3: Yield 62 mg, (85%). FT-IR spectrum (KBr, ν, cm^{-1}): ν =3655 (w), 2968 (w), 1565 (s), 1417 (m), 1343 (m), 1035(m), 841 (s), 636 (w), 561 (w), 459 (w) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.50 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{bpd}), 8.03 (d, $^{3}J_{H,\,H}$ = 4 Hz, 16 H, H_{bpd}), 7.94 (d, $^{3}J_{H,\,H}$ = 12 Hz, 8 H, H_{bpd}), 7.15 (s, 4 H, H_{Ar}), 6.07 (s, 4 H, H_{Ar}), 5.97 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 5.75 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 2.11 [s, 12H, $ArCH_3$], 1.68 (s, 24 H, L-CH_3), 1.34 [d, $^{3}J_{H,\,H}$ = 4 Hz, 24H, $CH(CH_3)_2$] ppm. ^{13}C-NMR (400 MHz, DMSO-d_6): δ = 186.39 (CO), 152.93 (CH_{bpd}), 149.20 (C_{bpd}), 141.29 (C_{bpd}), 138.79 (C_{L1}), 135.26 (C_{bpd}), 132.48 (C_{L1}), 131.46 (C_{L1}), 128.32 (CH_{bpd}), 126.63 (CH_{bpd}), 123.33 (CH_{bpd}), 113.96 (C_{L1}), 102.05 (C_{cymene}), 99.04 (C_{cymene}), 84.60 (CH_{cymene}), 82.09 (CH_{cymene}), 30.77 ($ArCH_3$), 27.96 (L-CH_3), 22.40 [$CH(CH_3)_2$], 17.56 [$CH(CH_3)_2$] ppm.

Synthesis of Metalla-Rectangles **4** and **5**: these rectangles were synthesized in a procedure analogous to that of **1-3** except that H_2L_1 was took the place of H_2L_2 (0.05 mmol). The yellow solids were obtained.

4: Yield 69 mg, (90%). FT-IR spectrum (KBr, ν, cm^{-1}): ν = 3646 (s), 2969 (w), 2356 (w), 1609 (w), 1569 (s), 1415 (m), 1353 (m), 1306 (w), 1266 (m), 1112 (m), 1058 (s), 829 (s), 748 (s), 634 (w), 486 (m) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.71 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{bpy}), 8.16 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{bpy}), 6.90 (s, 8 H, H_{Ar}), 6.35 (d, $^{3}J_{H,\,H}$ = 4 Hz, 4 H, H_{Ar}), 6.04 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 5.82 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 5.36 (d, $^{3}J_{H,\,H}$ = 8 Hz, 4 H, H_{Ar}), 2.20 [s, 12H, $ArCH_3$], 1.60 (s, 24 H, L-CH_3), 1.38 [d, $^{3}J_{H,\,H}$ = 4 Hz, 24H, $CH(CH_3)_2$] ppm. ^{13}C-NMR (400 MHz, DMSO-d_6): δ = 186.58 (CO), 154.31 (CH_{bpy}), 145.88 (C_{bpy}), 137.63 (C_{L2}), 131.36 (C_{L2}), 130.70 (C_{L2}), 129.28 (C_{L2}), 127.36 (C_{L2}), 126.56 (C_{L2}), 126.31 (C_{L2}), 123.50 (CH_{bpy}), 114.02 (C_{L2}), 102.35 (C_{cymene}), 98.98 (C_{cymene}), 84.11 (CH_{cymene}), 82.19 (CH_{cymene}), 30.90 ($ArCH_3$), 27.75 (L-CH_3), 22.47 [$CH(CH_3)_2$], 17.33 [$CH(CH_3)_2$] ppm.

5: Yield 60 mg, (82%). FT-IR spectrum (KBr, ν, cm^{-1}): ν = 3643 (w), 2969 (w), 2363 (w), 1609 (s), 1576 (s), 1495 (w), 14210 (m), 1347 (m), 1307 (m), 1091 (m), 1044 (m), 1010 (m), 836 (s), 735 (w), 634 (w), 554 (m), 446 (w) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.54 (d, $^{3}J_{H,\,H}$ = 4 Hz, 8 H, H_{bpd}), 8.09 (d, $^{3}J_{H,\,H}$ = 8 Hz, 16 H, H_{bpd}), 8.03 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{bpd}), 7.69 (s, 4 H, H_{Ar}), 7.41 (s, 4 H, H_{Ar}), 7.25 (s, 4 H, H_{Ar}), 6.31 (s, 4 H, H_{Ar}), 6.00 (d, $^{3}J_{H,\,H}$ = 8 Hz, 8 H, H_{cymene}), 5.77 (d, $^{3}J_{H,\,H}$ = 4 Hz, 8 H, H_{cymene}), 2.14 [s, 12H, $ArCH_3$], 1.74 (s, 24 H, L-CH_3), 1.36 [d, $^{3}J_{H,\,H}$ = 4 Hz, 24H,

$CH(CH_3)_2$] ppm. ^{13}C-NMR (400 MHz, DMSO-d_6): δ = 186.51 (CO), 152.92 (CH_{bpd}), 149.30 (C_{bpd}), 141.21 C_{bpd}), 138.96 (C_{L2}), 138.34 (C_{bpd}), 135.03 (C_{L2}), 132.19 (C_{L2}), 128.36 (CH_{bpd}), 128.21 (CH_{bpd}), 127.33 (C_{L2}), 123.18 (CH_{bpd}), 113.69 (C_{L2}), 102.08 (C_{cymene}), 99.11 (C_{cymene}), 84.51 (CH_{cymene}), 82.04 (CH_{cymene}), 30.81 ($ArCH_3$), 28.14 (L-CH_3), 22.42 [$CH(CH_3)_2$], 17.26 [$CH(CH_3)_2$] ppm.

Metallarectangle with L_2 and L_b: Yield 63 mg (80%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.57 (d, $^3J_{H,\,H}$ = 4 Hz, 8 H, H_{bpb}), 8.19 (s, 8 H, H_{bpb}), 8.15 (d, $^3J_{H,\,H}$ = 8 Hz, 8 H, H_{bpb}), 7.71 (s, 4 H, H_{Ar}), 7.43 (s, 4 H, H_{Ar}), 7.25 (s, 4 H, H_{Ar}), 6.46 (s, 4 H, H_{Ar}), 5.99 (d, $^3J_{H,\,H}$ = 4 Hz, 8 H, H_{cymene}), 5.76 (d, $^3J_{H,\,H}$ = 4 Hz, 8 H, H_{cymene}), 2.10 [s, 12H, $ArCH_3$], 1.75 (s, 24 H, L-CH_3), 1.35 [d, $^3J_{H,\,H}$ = 4 Hz, 24H, $CH(CH_3)_2$] ppm.

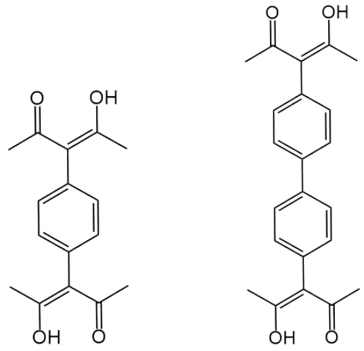


Figure S1. Structure of H_2L_1 and H_2L_2.

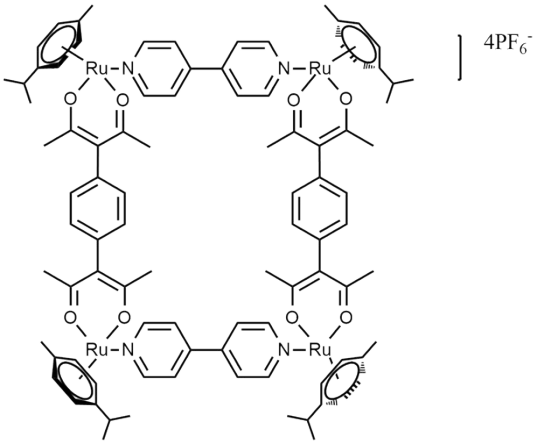


Figure S2. Structure of metallarectangle **1**.

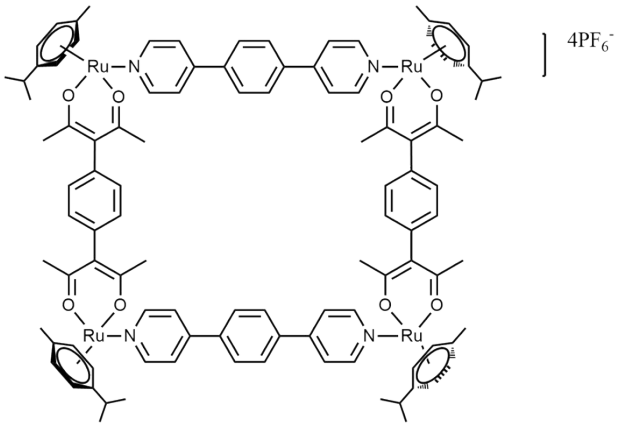


Figure S3. Structure of metallarectangle **2**.

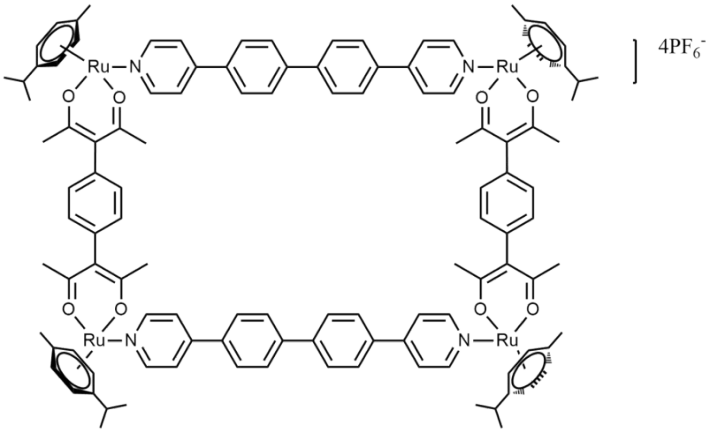


Figure S4. Structure of metallarectangle **3**.

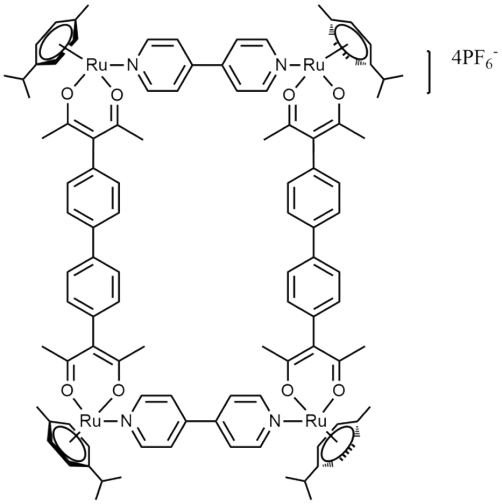


Figure S5. Structure of metallarectangle **4**.

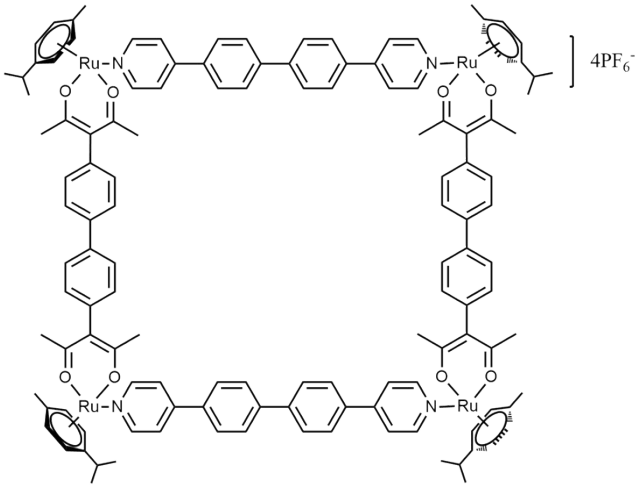


Figure S6. Structure of metallarectangle **5**.

3. Single-Crystal Structure Determination

X-ray Crystallography Details. Single crystals of metallarectangle **4** suitable for X-ray diffraction study were obtained at low temperature. X-ray intensity data of data of **4** was collected at 296 K on a Bruker APEXII DUO (APEX Ⅱ DUO) system. In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route.

4. X-Ray crystal structure parameters of metallarectangle 4

Table S1. Crystal data and structure refinement for metallarectangle **4**

Empirical formula	$C_{104}H_{112}N_4O_8Ru_4$
Formula weight	1950.25
Temperature	296(2)K
Wavelength	0.71073Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.0358(5) Å, α = 76.380(2)°
	b = 16.7175(8) Å, β = 79.745(2)°
	c = 19.5909(10) Å, γ = 78.049(2)°
Volume	3096.1(3) $Å^3$
Z	1
Density (calculated)	1.046 Mg/m^3
Absorption coefficient	0.522 mm^{-1}
F(000)	1004.0
Theta range for data collection	2.158 to 52.746
Index ranges	-12<=h<=12, -20<=k<=20, -24<=l<=24
Reflections collected	33650
Independent reflections	12639 [*R*(int) = 0.0371, *R*(sigma) = 0.0574]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12639 / 43 / 541
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R_1 = 0.0562, wR_2 = 0.1495
R indices (all data)	R_1 = 0.0818, wR_2 = 0.1603
Largest diff. peak and hole	1.52 and -1.04 $e.Å^{-3}$

5. ^{1}H NMR spectra of 1-5

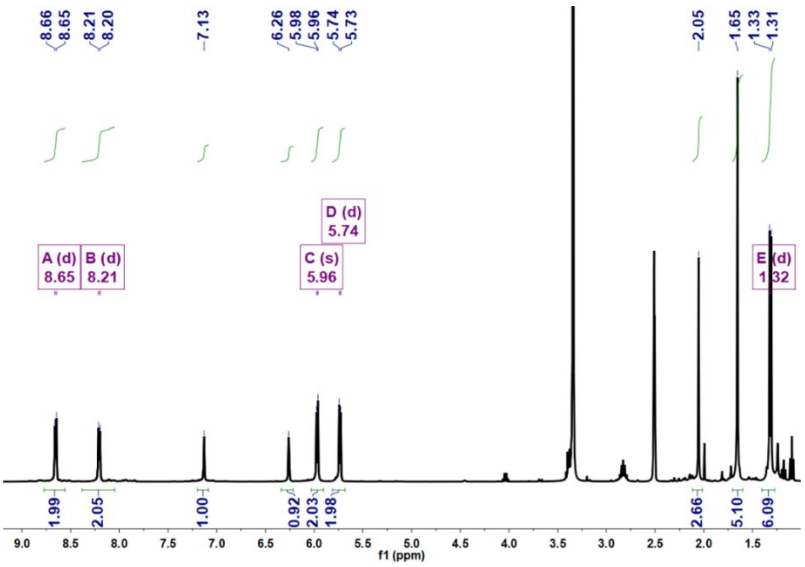


Figure S7. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle **1**.

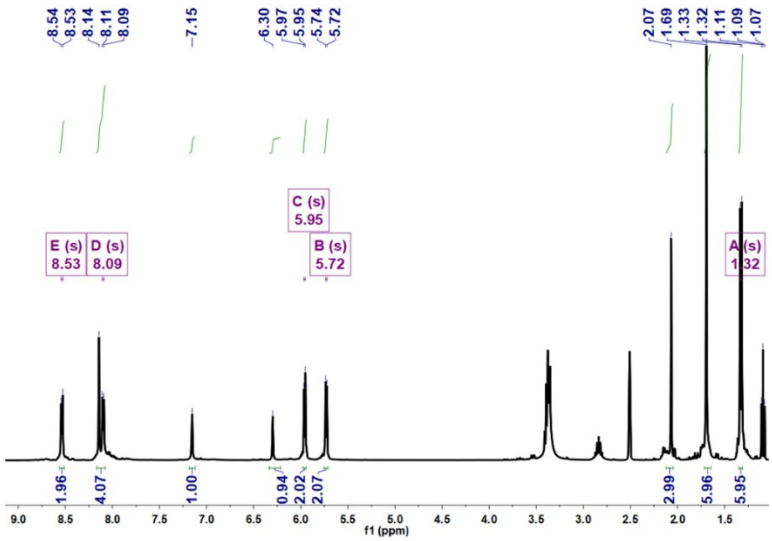


Figure S8. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle **2**.

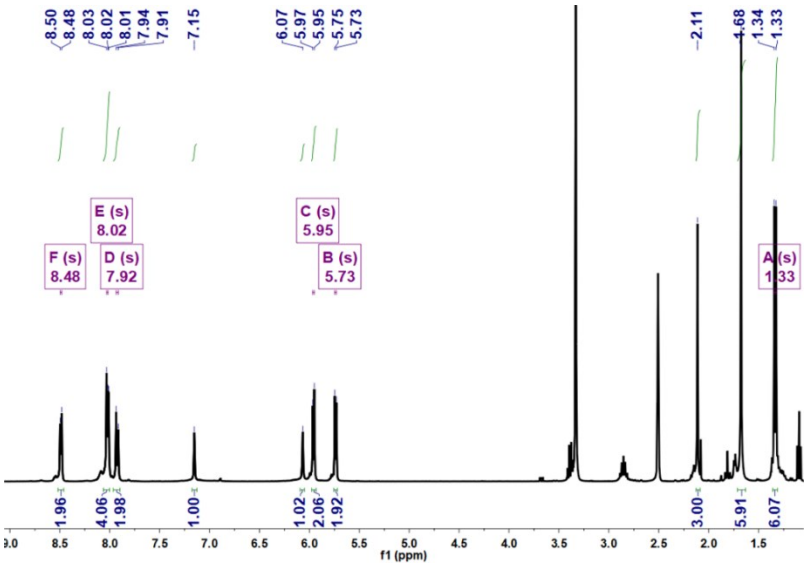


Figure S9. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle **3**.

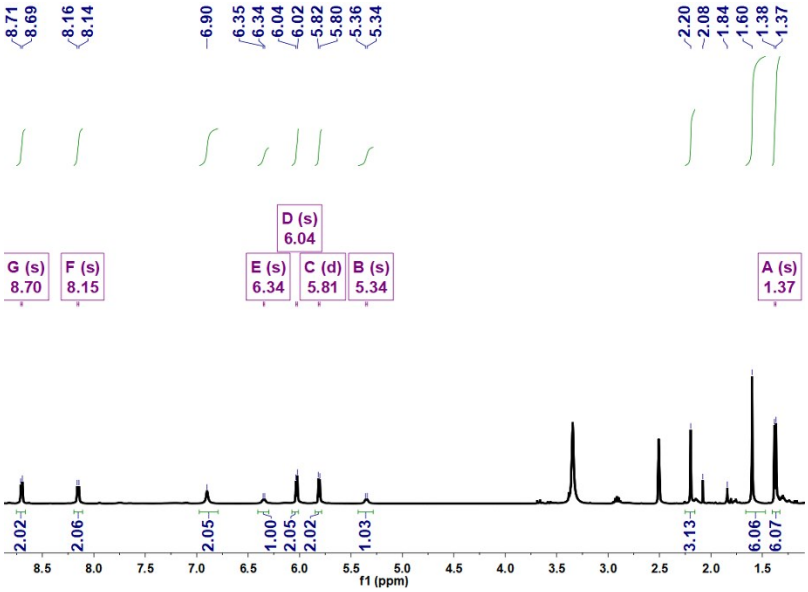
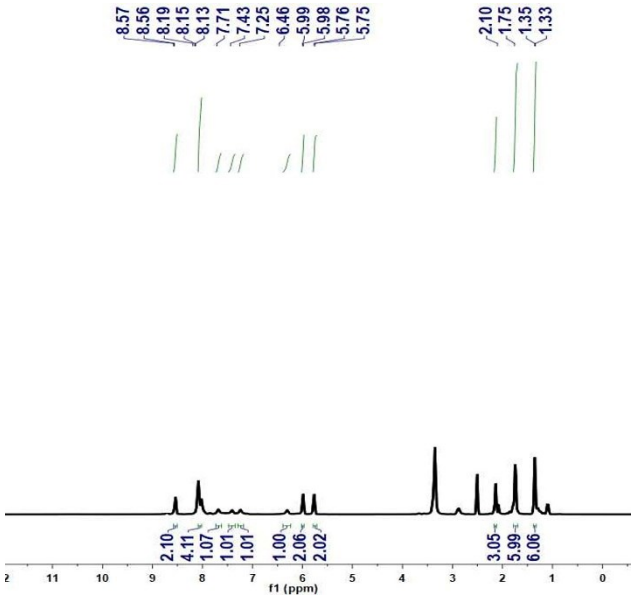


Figure S10. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle **4**.



^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle synthesized from L_2 and L_b.

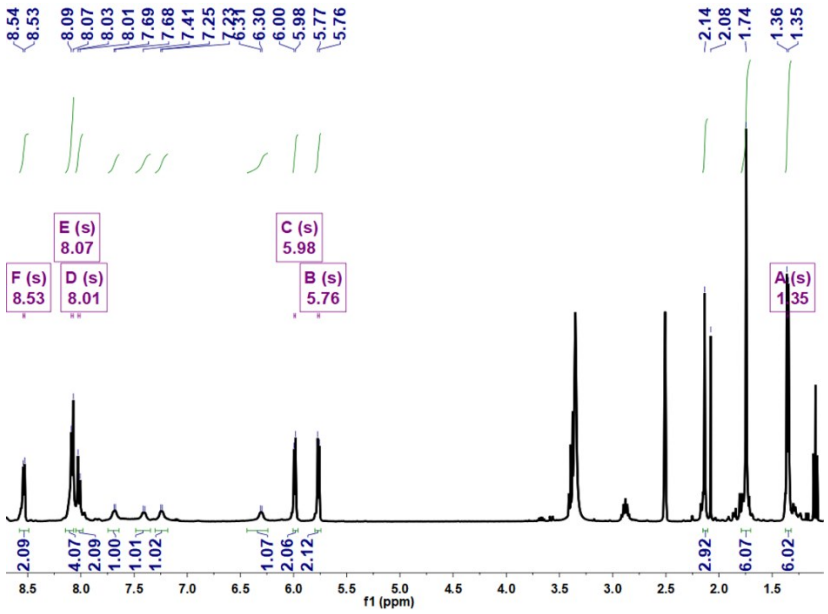


Figure S11. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of metallarectangle **5**.

6. ESI-MS spectra of 1-5

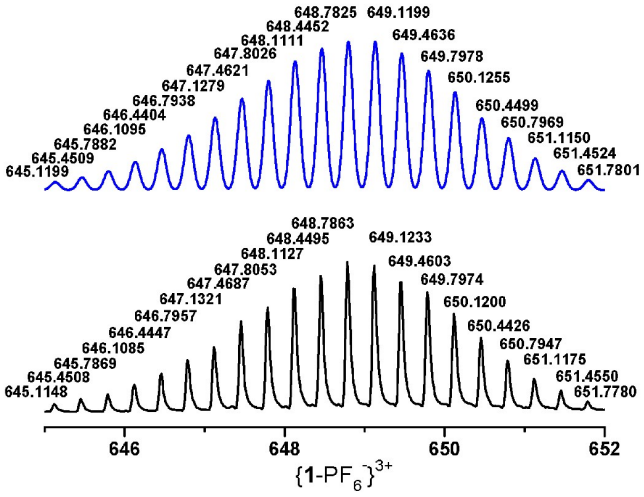


Figure S12. Experimental below, black) and calculated (above, blue) ESI-MS spectra (3+) of metallarectangle **1**.

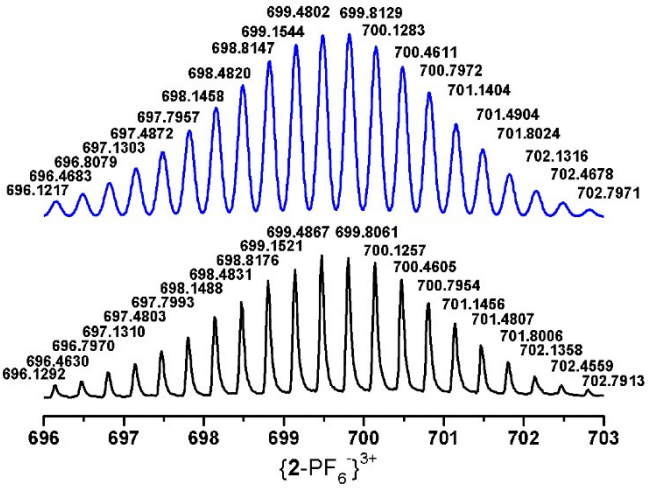


Figure S13. Experimental below, black) and calculated (above, blue) ESI-MS spectra (3+) of metallarectangle **2**.

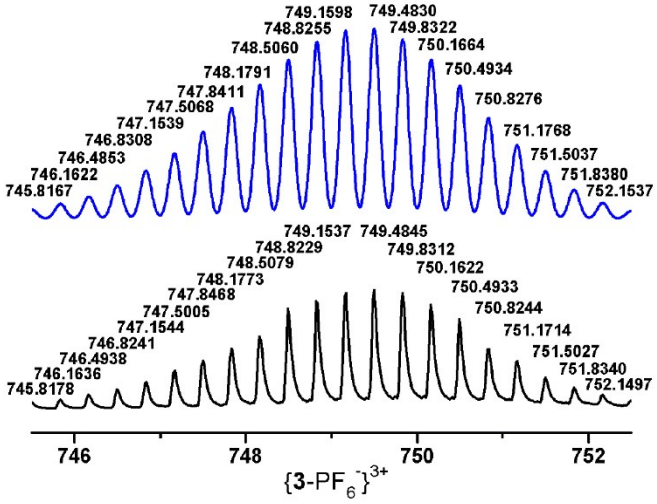


Figure S14. Experimental below, black) and calculated (above, blue) ESI-MS spectra (3+) of metallarectangle **3**.

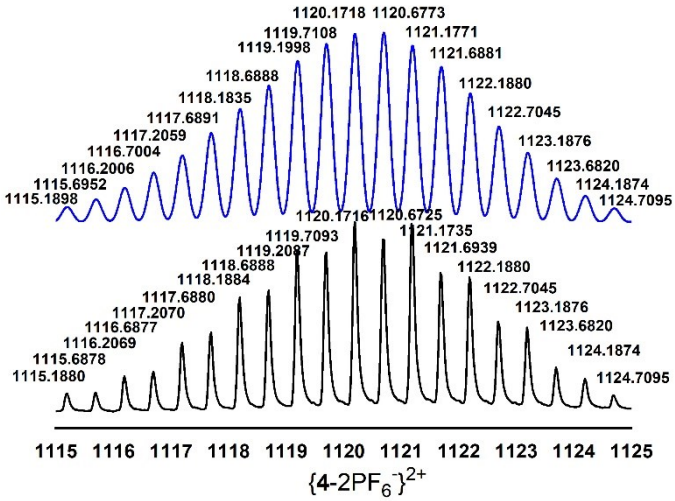


Figure S15. Experimental below, black) and calculated (above, blue) ESI-MS spectra (2+) of metallarectangle **4**.

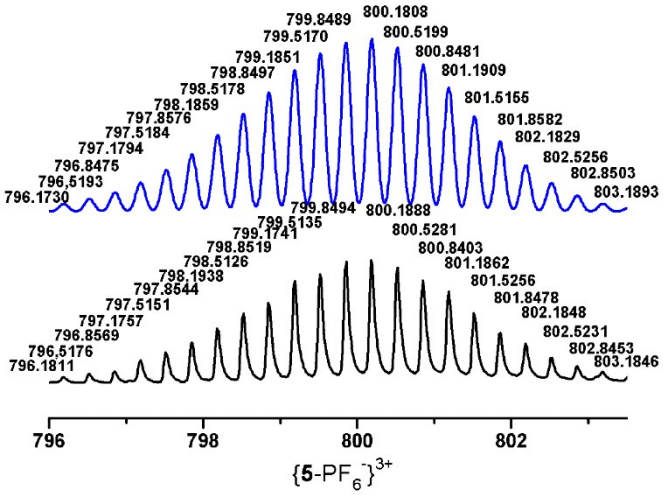


Figure S16. Experimental below, black) and calculated (above, blue) ESI-MS spectra (3+) of metallarectangle **5**.

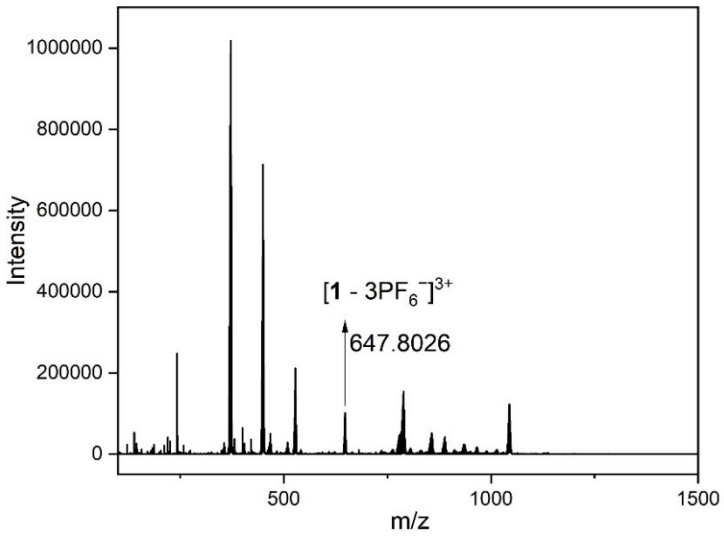


Figure S17. The ESI-MS spectra of metallarectangle **1**.

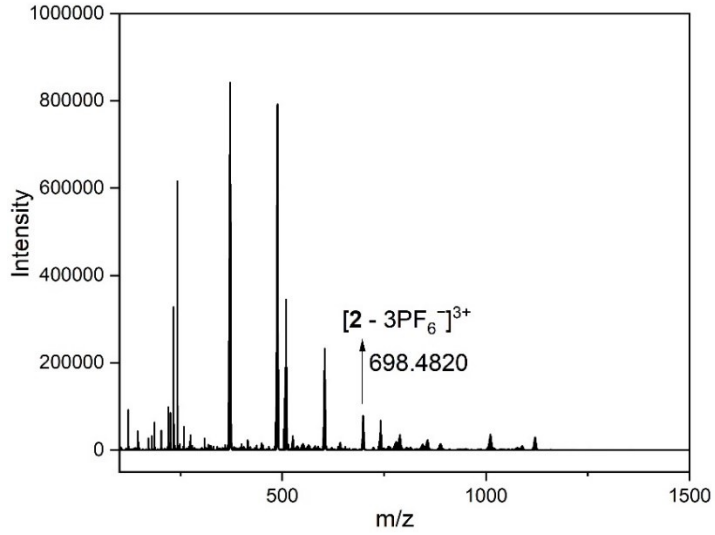


Figure S18. The ESI-MS spectra of metallarectangle **2**.

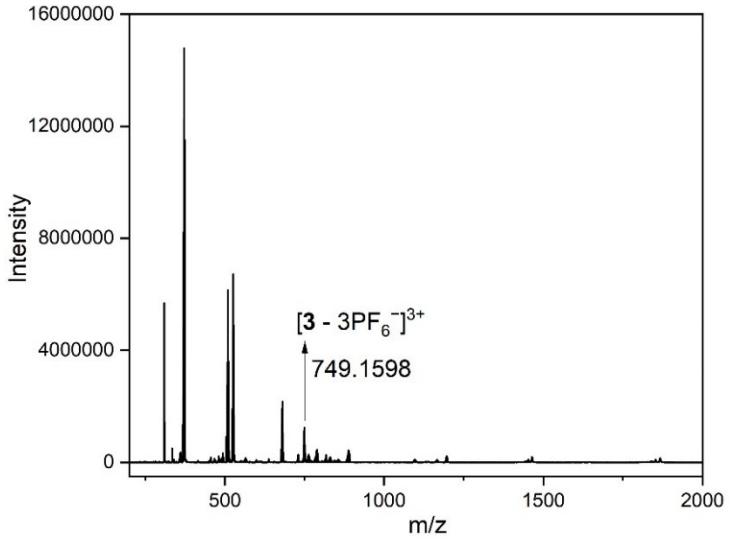


Figure S19. The ESI-MS spectra of metallarectangle **3**.

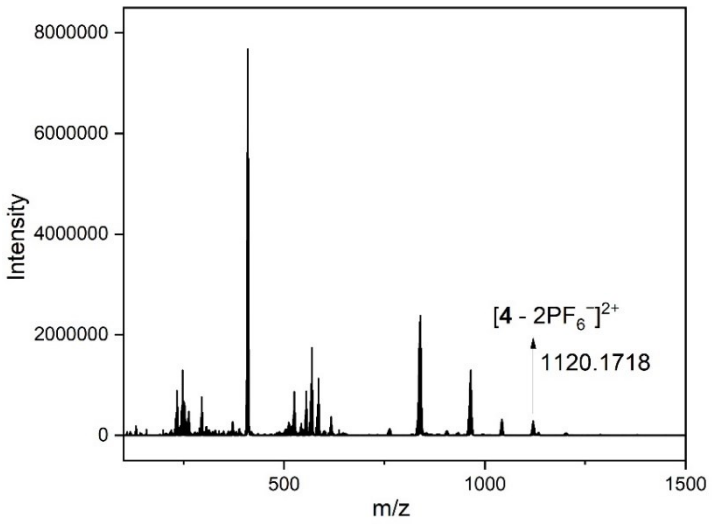


Figure S20. The ESI-MS spectra of metallarectangle **4**.

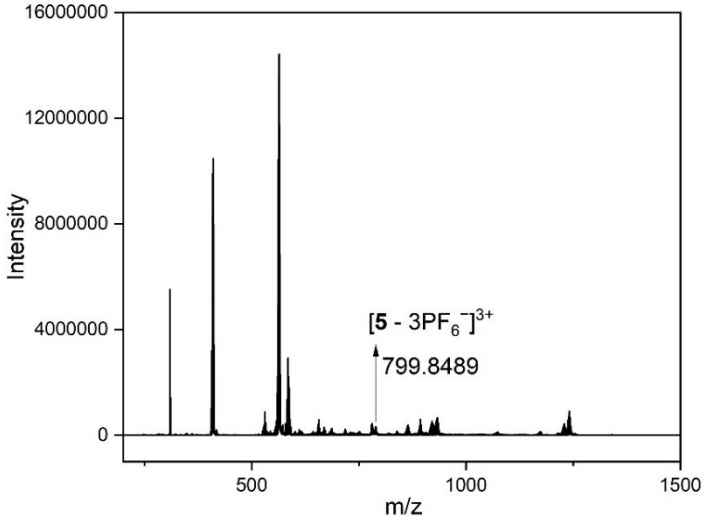


Figure S21. The ESI-MS spectra of metallarectangle **5**.

7. IR spectra of 1-5

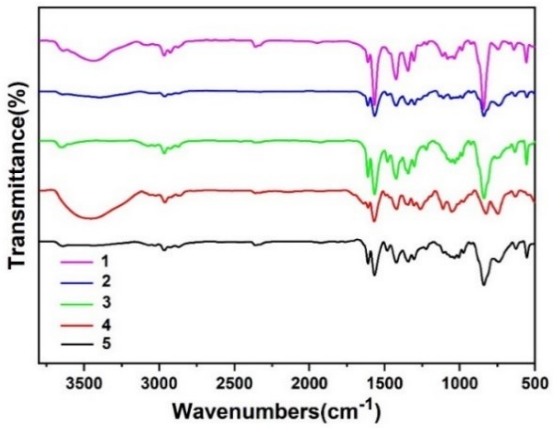


Figure S22. IR spectra of metallarectangle **1-5**.

8. Absorption spectra

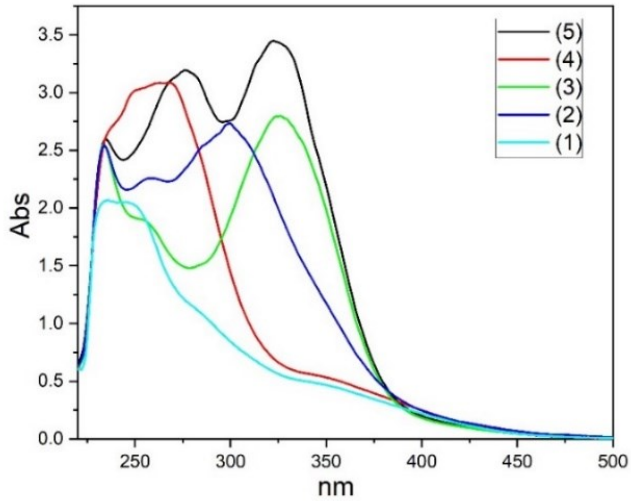


Figure S23. Absorption spectra of metallarectangle **1-5** in CH_2Cl_2 (c = 2.0 × 10^{-5} M).

9. The photoluminescence (PL) emission spectra

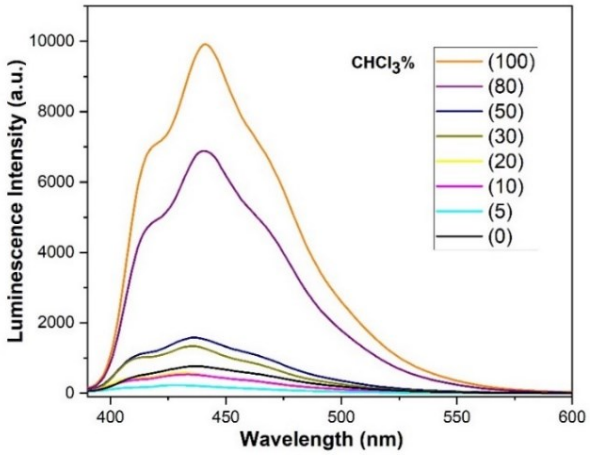


Figure S24. Emission spectra of metallarectangle **1** versus $CHCl_3$ fraction in $CHCl_3$/acetone mixtures (c = 2.0 × 10^{-5} M, λex = 375 nm).

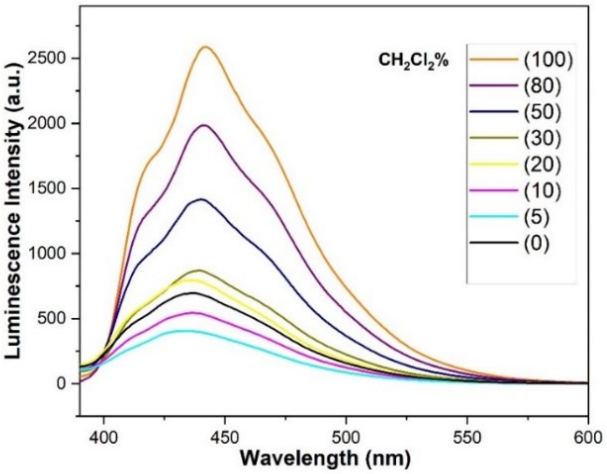


Figure S25. Emission spectra of metallarectangle **1** versus CH_2Cl_2 fraction in CH_2Cl_2/acetone mixtures (c = 2.0 × 10^{-5} M, λex = 375 nm).

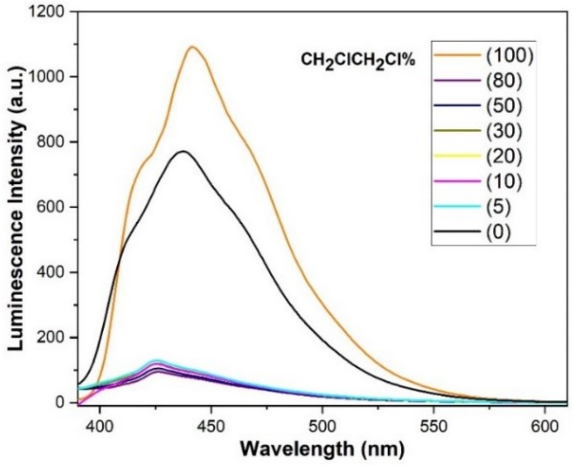


Figure S26. Emission spectra of metallarectangle **1** versus CH_2ClCH_2Cl fraction in CH_2ClCH_2Cl/acetone mixtures (c = 2.0 × 10^{-5} M, λex = 375 nm).

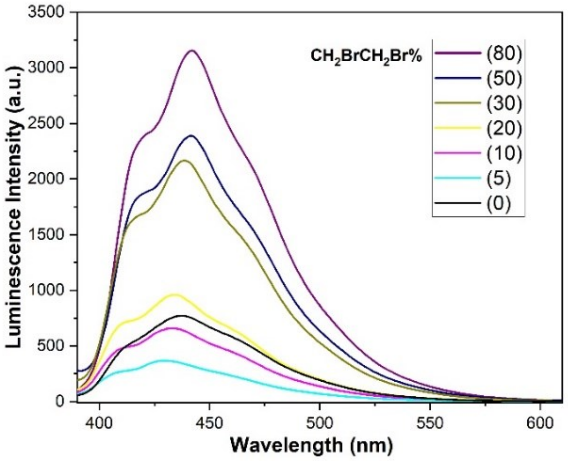


Figure S27. Emission spectra of metallarectangle **1** versus CH_2BrCH_2Br fraction in CH_2BrCH_2Br/acetone mixtures (c = 2.0 × 10^{-5} M, λex = 375 nm).

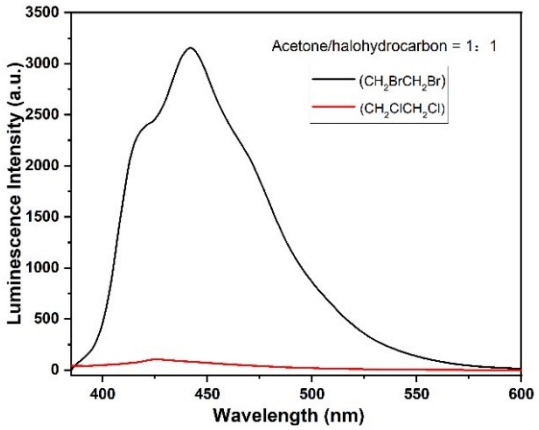


Figure S28. Emission spectra of metallarectangle **1** in acetone/haloalkane = 1:1 mixed solution (c = 2.0 × 10^{-5} M, λex = 375 nm).

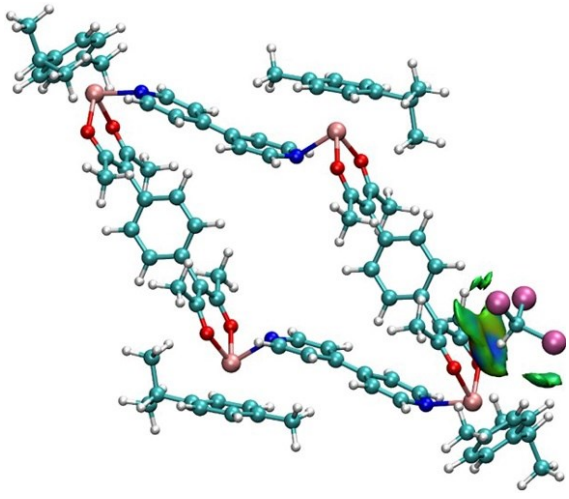


Figure S29. Independent Gradient Method (IGM) analysis the interaction of complex **1** and $CHCl_3$. Color code: pink-Ru; mauve-chlorine; blue-nitrogen; red-oxygen; cyan-carbon; white-hydrogen.

To evaluate the noncovalent interactions between metallarectangles and haloalkane molecules, the Independent Gradient Method (IGM)[2] is performed by Multiwfn program.[3] The strong attractive/repulsive interaction and VDW (Van der Waals) interaction are shown in blue/red and green, respectively.

10. References

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