Electronic Supplementary Information (ESI)

For

Aggregation Induced Emission Active Bis-heteroleptic Ruthenium(II) Complex for Luminescent Light-up Detection of Pyrophosphate Ion

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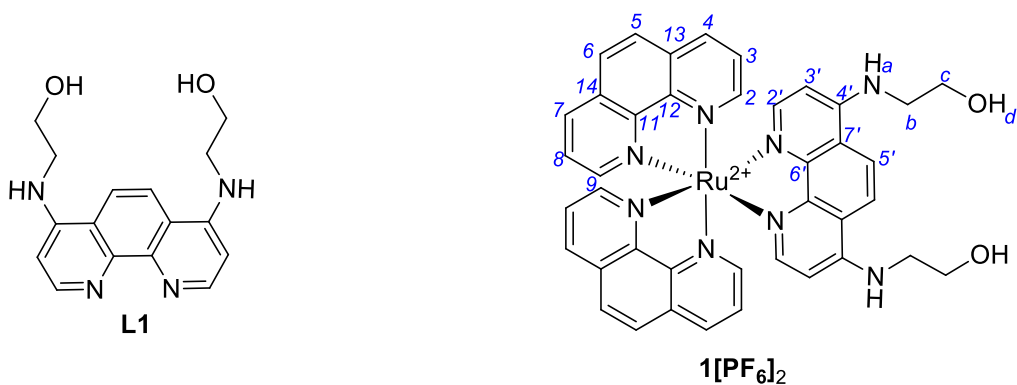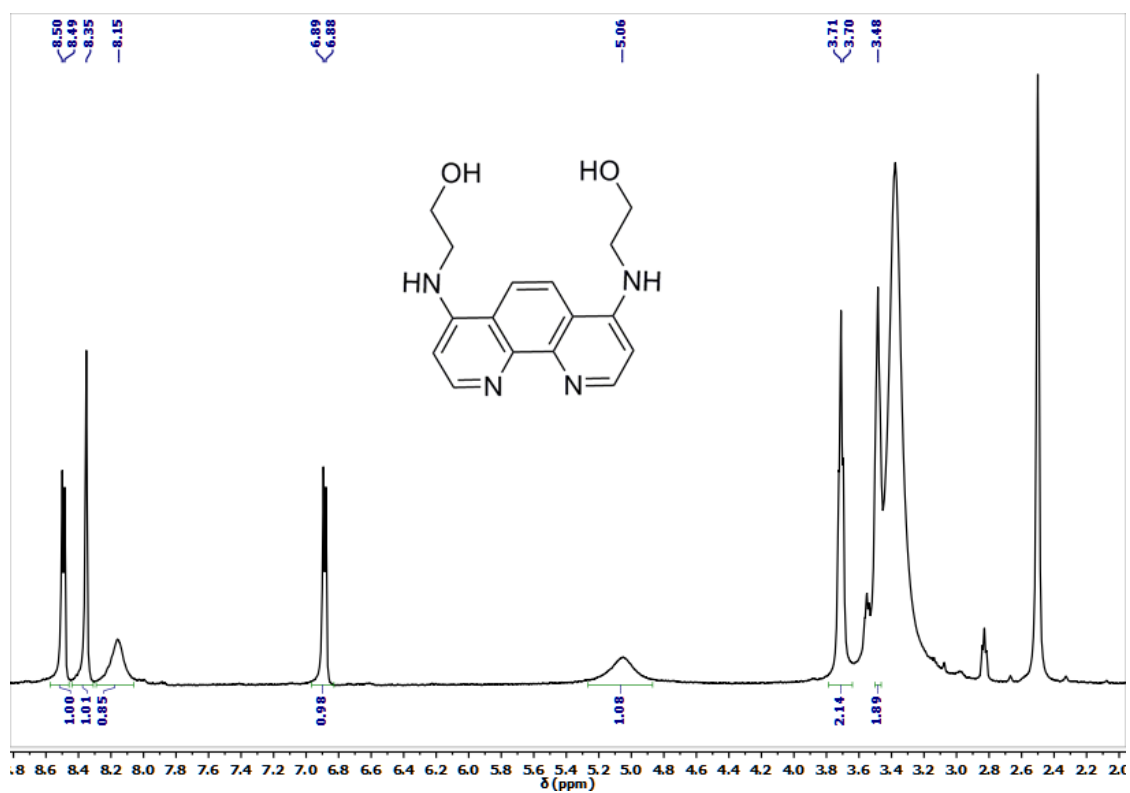
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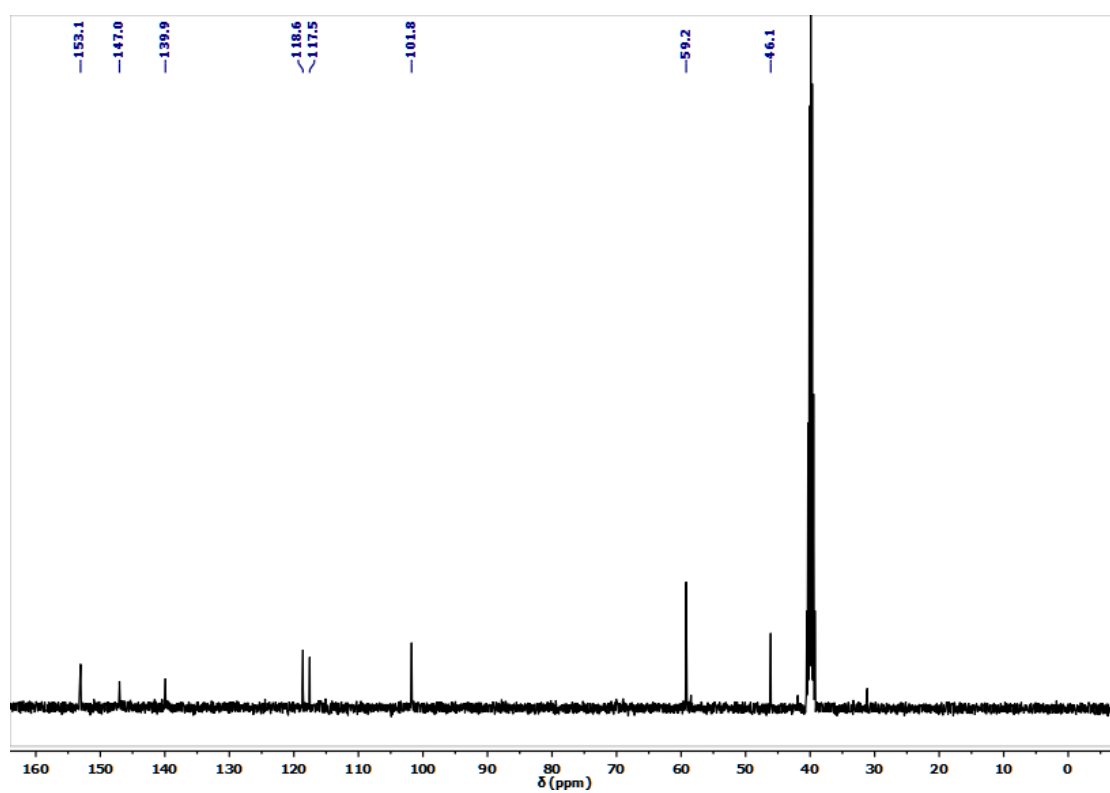
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Chart S1: Compound used in this study

Figure S1. ^{1}H NMR spectrum of **L1** in DMSO-d_6.

Figure S2. ^{13}C NMR spectrum of **L1** in DMSO-d_6.
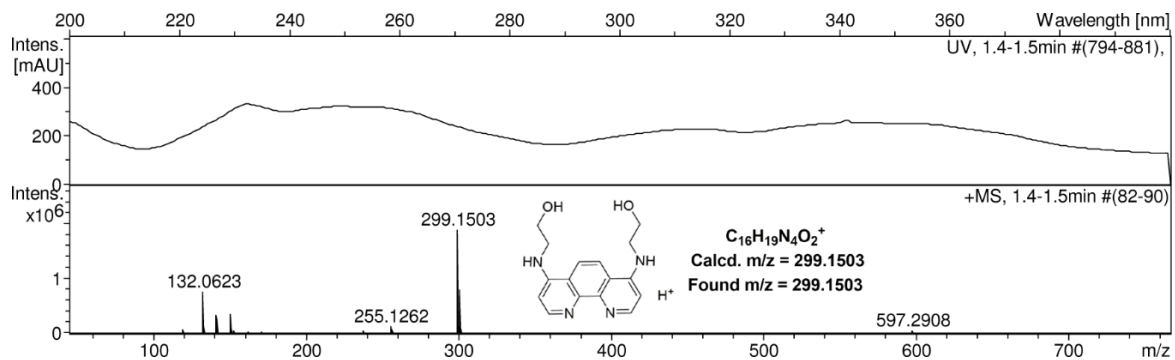
Figure S3. ESI-MS spectrum of **L1** in CH$_3$OH
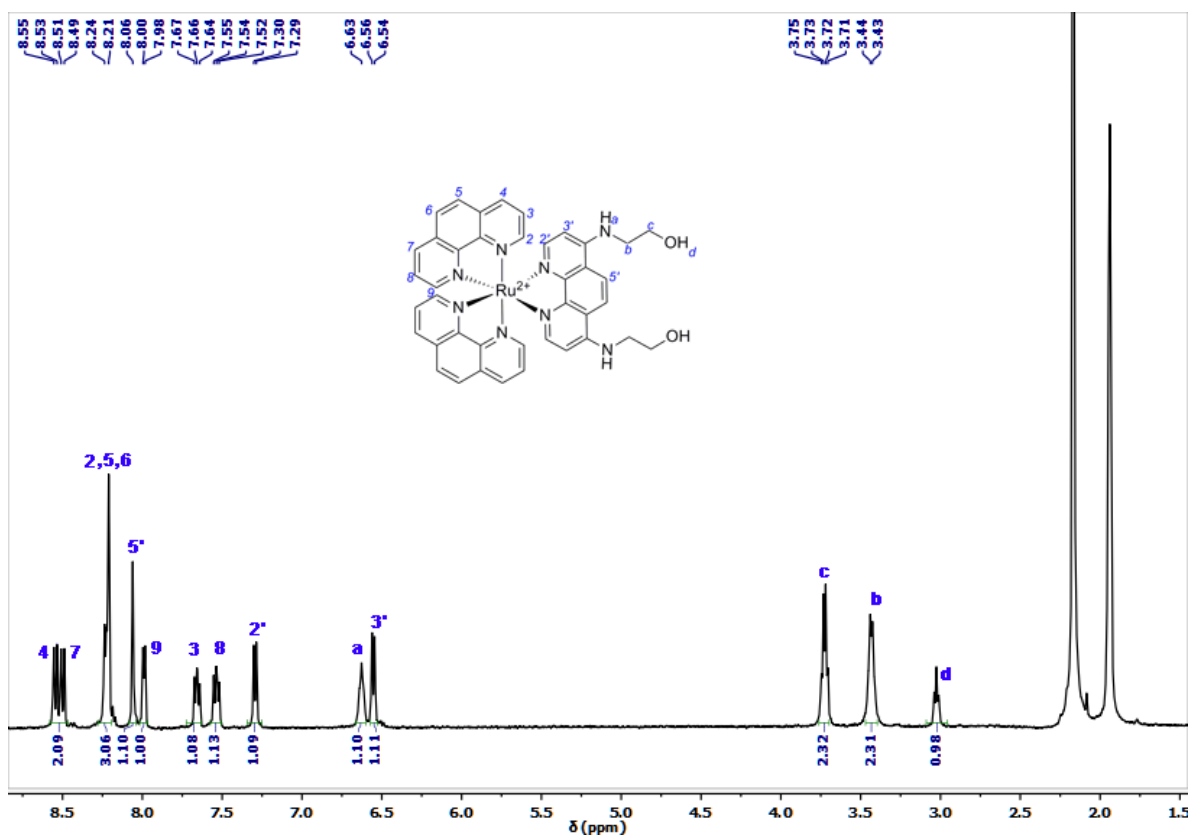
Figure S4. ^{1}H NMR spectrum of **1[PF$_6$]$_2$** in CD$_3$CN.
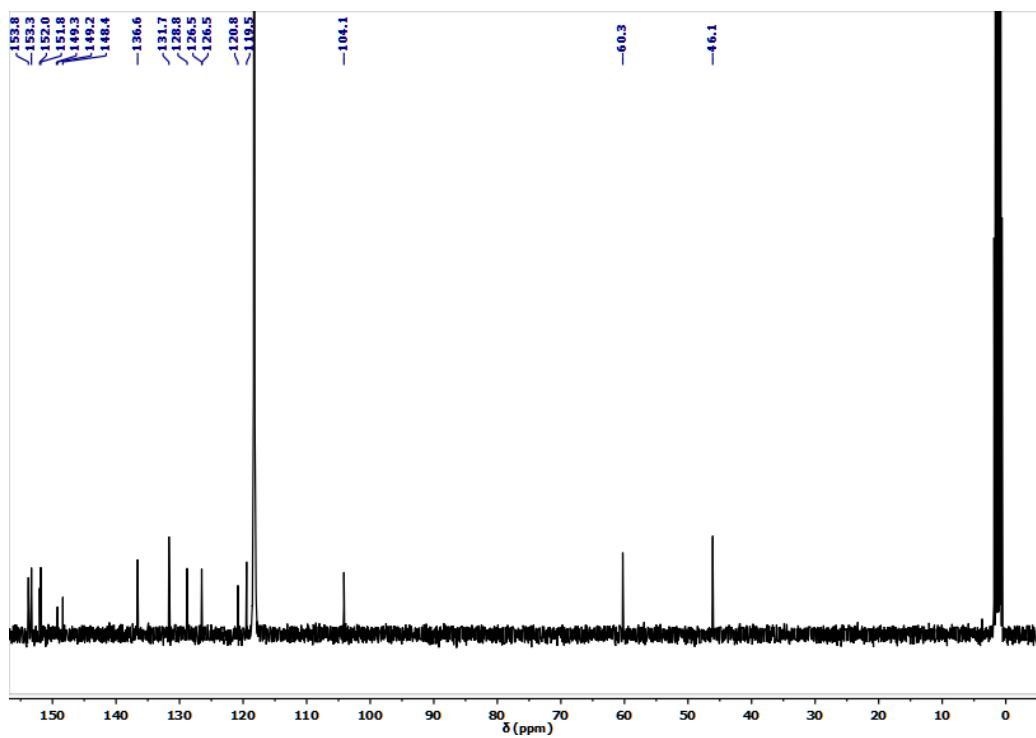
Figure S5. ^{13}C NMR spectrum of **1[PF$_6$]$_2$** in CD$_3$CN.
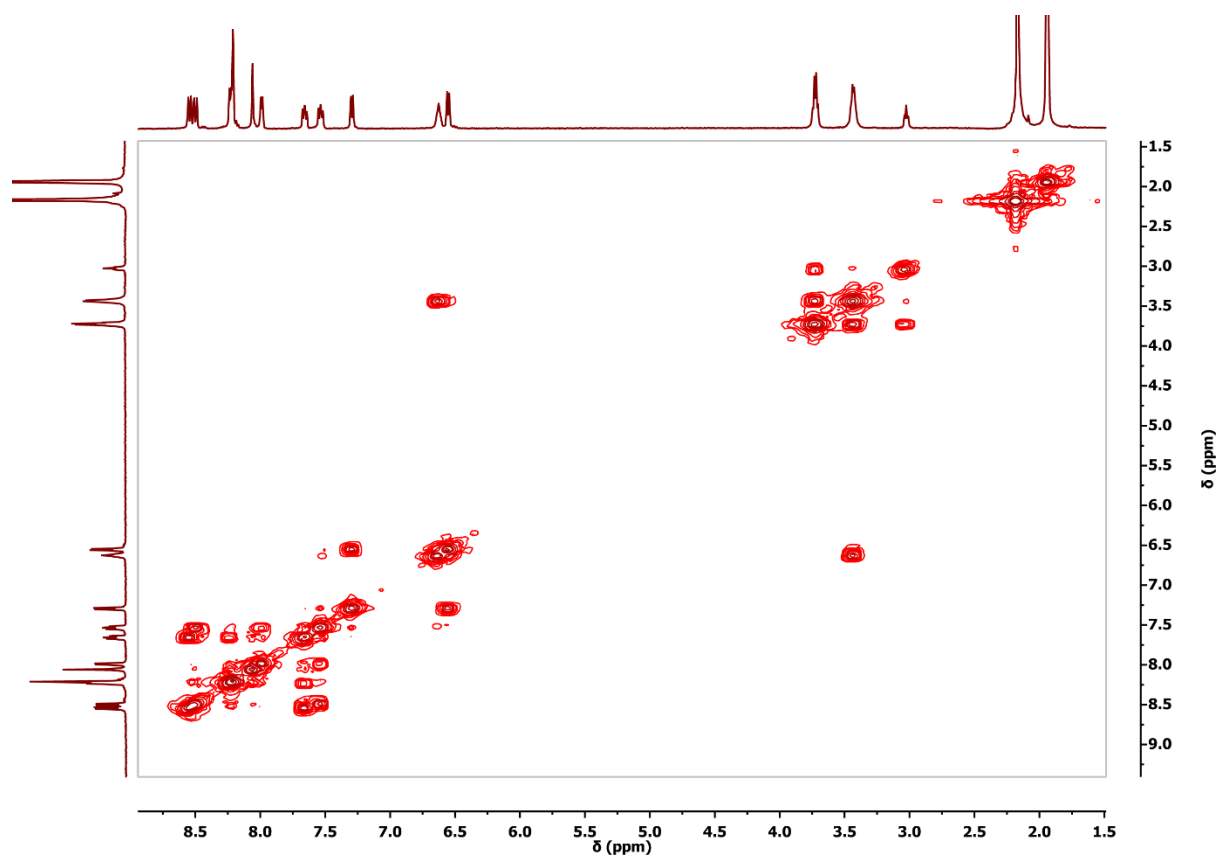
Figure S6. ^{1}H-^{1}H COSY NMR spectrum of **1[PF$_6$]$_2$** in CD$_3$CN.
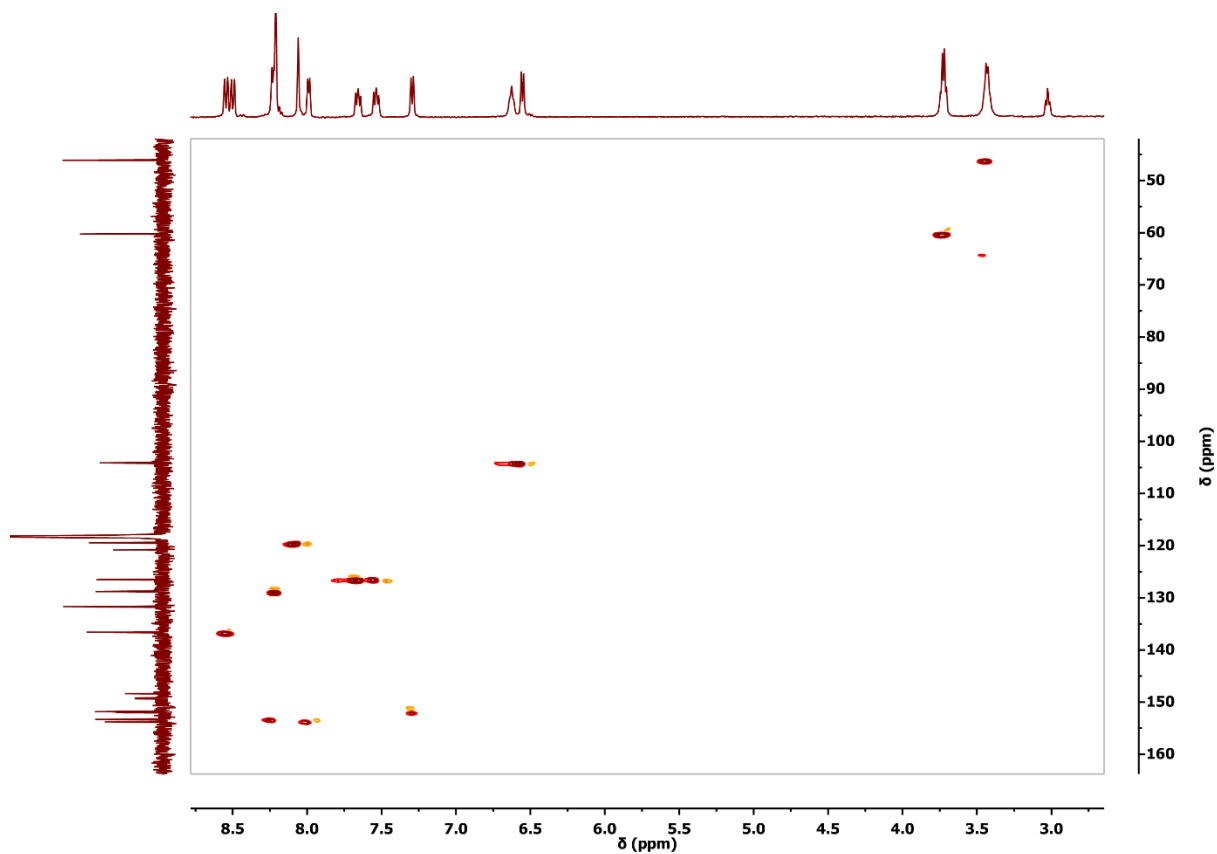
Figure S7. ^{1}H-^{13}C HSQC NMR spectrum of **1[PF$_6$]$_2$** in CD$_3$CN.
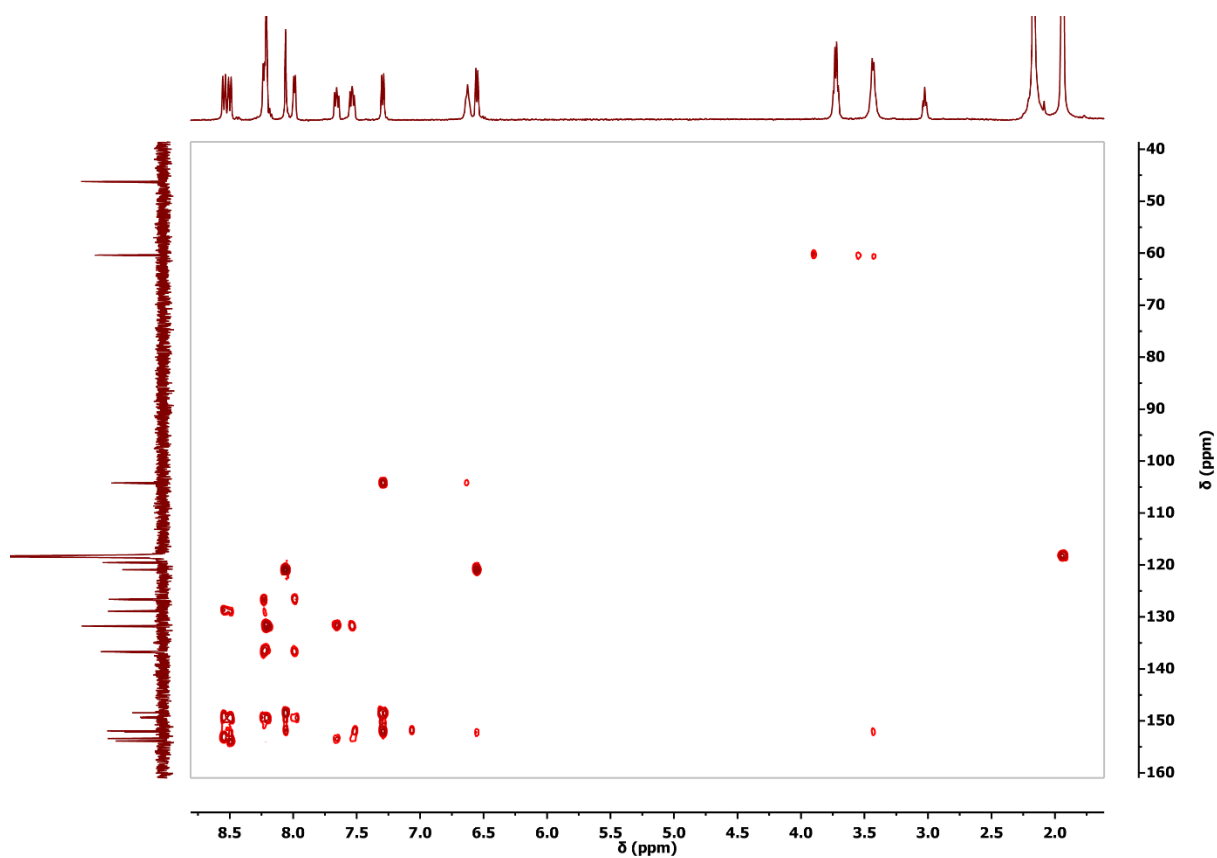
Figure S8. Partial ^{1}H-^{13}C HMBC NMR spectrum of **1[PF$_6$]$_2$** in CD$_3$CN.
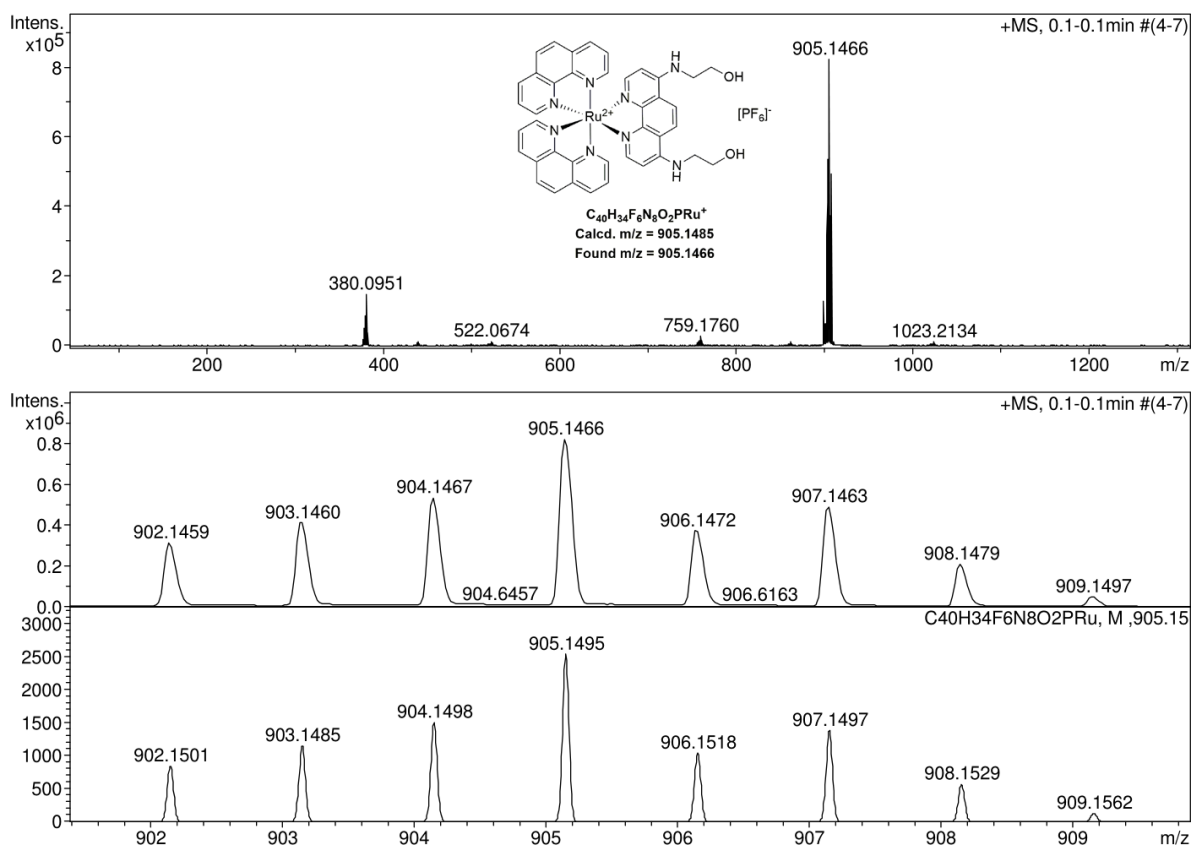
Figure S9. ESI-MS spectrum of **1[PF₆]₂** in CH₃CN.

X-ray Crystallography

The single crystal X-ray data of **1[PF₆]₂** was collected at 293 K on a Bruker APEX II CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The data integration and reduction were processed with SAINT[1] software. A multi-scan absorption correction (SADABS)[2] was applied to the collected reflections. The structure was solved by direct methods using the programs SHELXT[3] and refined by full-matrix least-squares calculations (F^2) using the SHELXL-2018/3 software[4] within the WinGX[5] environment. All non-H atoms except six atoms (O1, O2, C10, C18, C32, and C33) were refined anisotropically against F^2 for all reflections. Due to the very weak crystal dataset, O1, O2, C10, C18, C32, and C33 have high ADP; therefore, they were refined isotropically. All hydrogen atoms were placed at their calculated positions and refined isotropically. Crystal data collection and refinement details of selected bond lengths and angles for **1[PF₆]₂** are given in Table S1 and S2, respectively. The .cif file was deposited with the Cambridge Crystallographic Data Centre, and the following code was allocated: *CCDC No 2215176.*
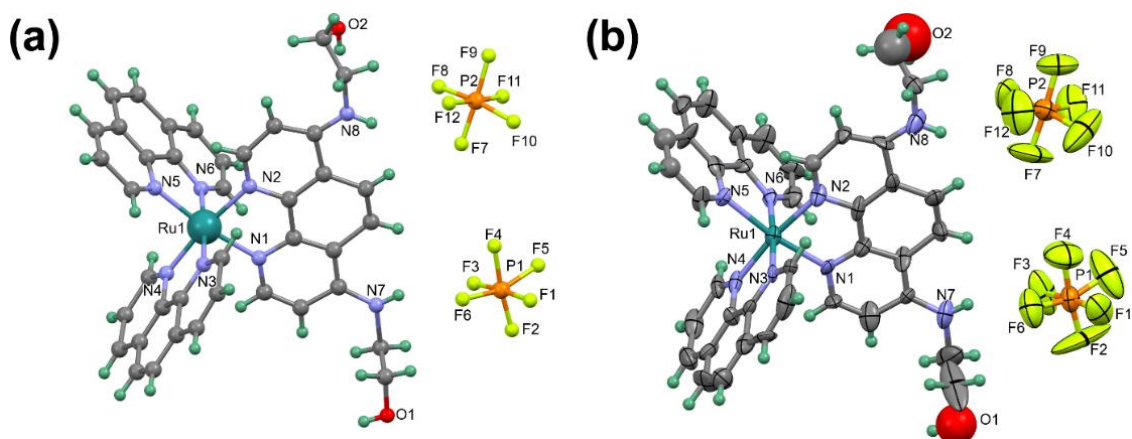
Figure S10. (a) Ball and stick representation of compound **1[PF₆]₂** (b) ORTEP of compound **1[PF₆]₂** with 30% thermal ellipsoid probability. Only non-carbon and non-hydrogens are labelled.
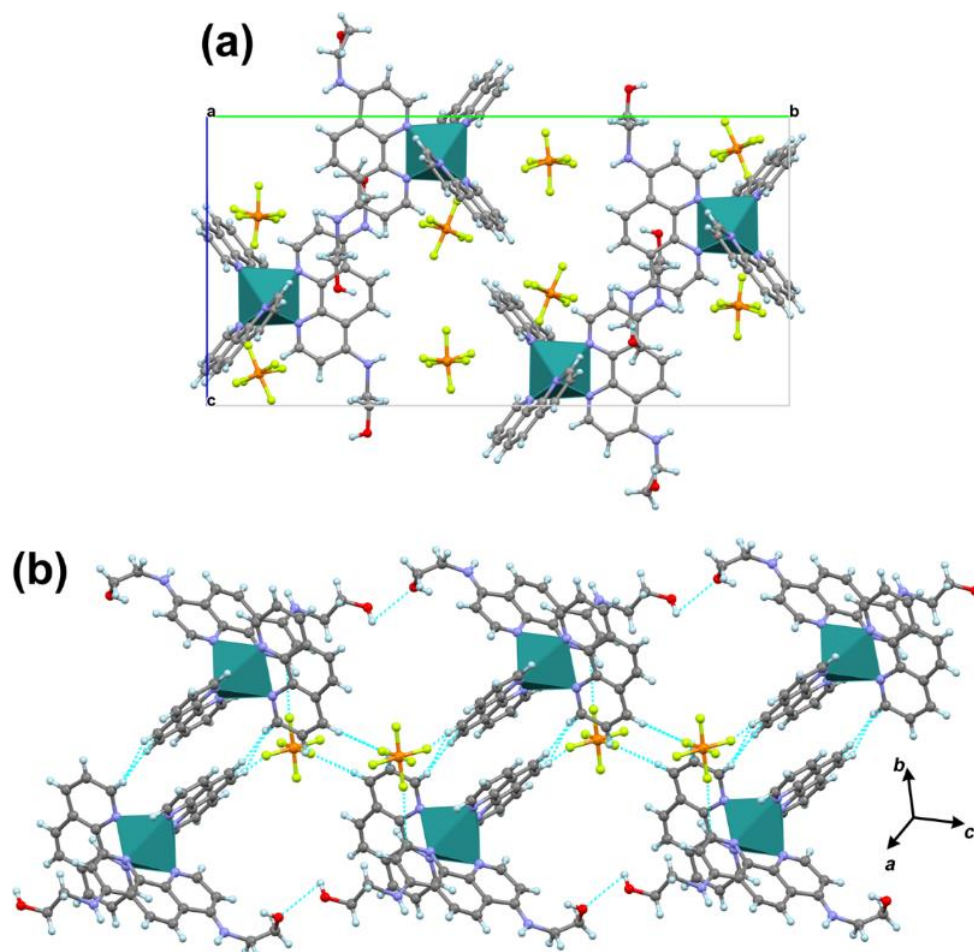
Figure S11. View of the (a) unit cell packing diagram along crystallographic *a*-axis and (b) 2-dimensional (2D) network formed through the weak supramolecular interaction.

Table S1 Crystal data and structure refinement for **1[PF₆]₂**

Empirical formula	$C_{40}H_{34}F_{12}N_8O_2P_2Ru$
Formula weight	1049.76
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 12.766(4)$ Å $\alpha = 89.982(8)°$.
	$b = 29.689(8)$ Å $\beta = 101.429(8)°$.
	$c = 15.064(4)$ Å $\gamma = 90.015(9)°$.
Volume	5596(3) Å³
Z	4
Density (calculated)	1.246 Mg/m³
Absorption coefficient	0.413 mm⁻¹
F(000)	2112
Crystal size	0.180 x 0.110 x 0.090 mm³
Theta range for data collection	1.914 to 28.591°.
Index ranges	-16<=h<=17, -39<=k<=39, -20<=l<=20
Reflections collected	138492
Independent reflections	14102 [R(int) = 0.6848]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.946 and 0.929
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14102 / 8 / 558
Goodness-of-fit on F^2	1.200
Final R indices [*I>2sigma(I)*]	*R*1 = 0.2246, *wR*2 = 0.4580
R indices (all data)	*R*1 = 0.4986, *wR*2 = 0.5491
Largest diff. peak and hole	2.099 and -0.821 e.Å⁻³

Table S2. Selected bond lengths [Å] and angles [°] for **1[PF$_6$]$_2$**.

Bond lengths(Å)			
N(1)-Ru(1)	2.099(12)	N(2)-Ru(1)	2.096(12)
N(3)-Ru(1)	2.006(13)	N(4)-Ru(1)	2.025(14)
N(5)-Ru(1)	2.084(11)	N(6)-Ru(1)	2.089(13)
Bond Angles(°)			
N(3)-Ru(1)-N(4)	79.5(6)	N(3)-Ru(1)-N(6)	176.4(5)
N(4)-Ru(1)-N(6)	97.9(6)	N(3)-Ru(1)-N(5)	98.7(5)
N(4)-Ru(1)-N(5)	93.7(5)	N(6)-Ru(1)-N(5)	78.9(5)
N(3)-Ru(1)-N(1)	87.6(4)	N(4)-Ru(1)-N(1)	93.4(5)
N(6)-Ru(1)-N(1)	95.1(5)	N(5)-Ru(1)-N(1)	171.3(5)
N(3)-Ru(1)-N(2)	94.5(5)	N(4)-Ru(1)-N(2)	171.5(5)
N(6)-Ru(1)-N(2)	88.3(5)	N(5)-Ru(1)-N(2)	93.2(5)
N(1)-Ru(1)-N(2)	80.3(5)		
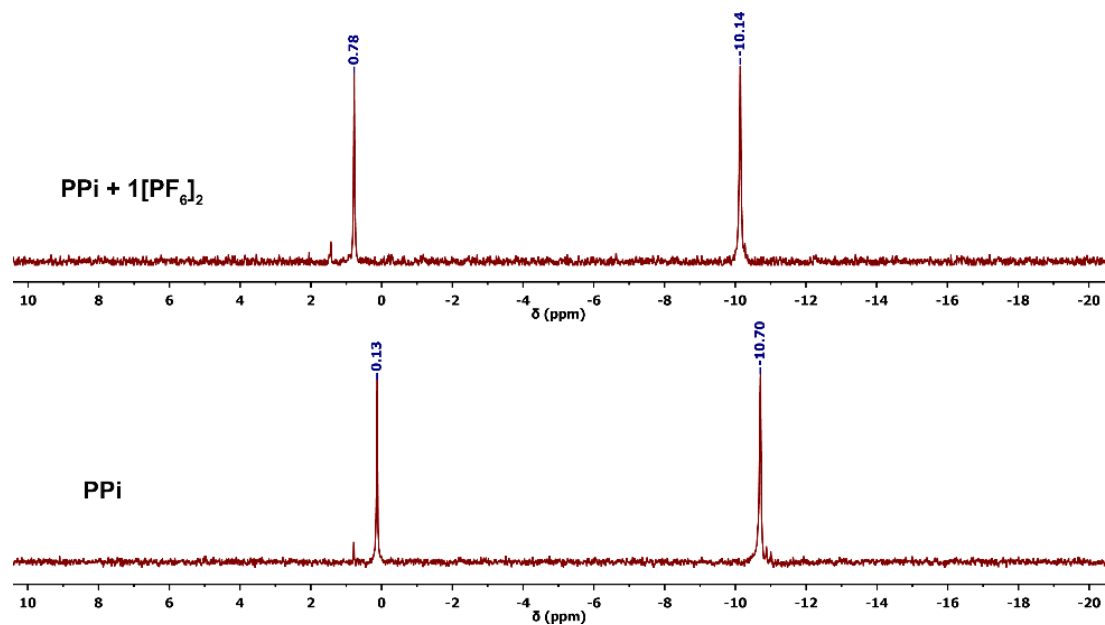
Figure S12. ^{31}P NMR spectra of H$_2$P$_2$O$_7{}^{2-}$ and with **1[PF$_6$]$_2$** (1.0 equiv.) in CD$_3$CN.

Table S3 Selected theoretical bond lengths [Å] and angles [°] for complex **1[PF$_6$]$_2$** obtained from ground state optimized geometry.

Bond lengths(Å)			
N(32)-Ru(51)	2.120	N(39)-Ru(51)	2.120
N(11)-Ru(51)	2.119	N(4)-Ru(51)	2.126
N(25)-Ru(51)	2.126	N(18)-Ru(51)	2.119

Bond Angles(°)			
N(32)-Ru(51)-N(39)	77.65	N(25)-Ru(51)-N(18)	78.54
N(4)-Ru(51)-N(11)	78.54	N(39)-Ru(51)-N(18)	95.92
N(4)-Ru(51)-N(18)	96.92	N(32)-Ru(51)-N(18)	88.98
N(4)-Ru(51)-N(25)	88.96	N(4)-Ru(51)-N(39)	96.92
N(25)-Ru(51)-N(11)	96.92	N(39)-Ru(51)-N(11)	88.98
N(18)-Ru(51)-N(11)	172.72	N(39)-Ru(51)-N(25)	172.4
N(32)-Ru(51)-N(4)	172.4		

Table S4. The x,y,z cartesian coordinates of complex **1,** obtained from DFT optimization at B3LYP/6-31G (d, p) // LANL2DZ level.

	x	y	z		x	y	z
C	4.35282	3.47608	-0.24455	C	-4.37904	5.03714	0.65587
C	4.07275	2.92444	0.99171	C	-4.3352	5.4963	2.1186
C	3.08265	1.93308	1.09897	O	-4.26657	6.90509	2.0661
N	2.38636	1.48857	0.04921	N	-4.31093	-3.58586	-0.49623
C	2.66007	2.02391	-1.18055	C	-4.37959	-5.03667	-0.65589
C	3.6382	3.02876	-1.37835	C	-4.33576	-5.49584	-2.11861
C	1.90736	1.52908	-2.29453	O	-4.26727	-6.90471	-2.06606
C	2.137	2.05047	-3.59096	Ru	0.86905	-0.00004	0.0
C	3.13241	3.07139	-3.76346	H	5.11242	4.24478	-0.35312
C	3.85285	3.53886	-2.70372	H	4.60316	3.24329	1.88251
N	0.98488	0.54957	-2.04308	H	2.84241	1.48763	2.05792
C	0.26963	0.07809	-3.06787	H	3.30263	3.46566	-4.76085
C	0.43158	0.54126	-4.38471	H	4.60433	4.30959	-2.84671
C	1.3644	1.52606	-4.6513	H	-0.45299	-0.69461	-2.83117
C	1.36422	-1.5262	4.6513	H	-0.17886	0.11756	-5.17488
C	0.43152	-0.5413	4.38471	H	1.50895	1.89905	-5.66109
C	0.26962	-0.07811	3.06787	H	1.50873	-1.8992	5.66109
N	0.98482	-0.54967	2.04308	H	-0.17889	-0.11754	5.17488
C	1.90719	-1.52928	2.29453	H	-0.45292	0.69466	2.83117
C	2.13678	-2.05069	3.59097	H	4.60386	-4.31008	2.84672
C	2.65985	-2.02419	1.18055	H	3.30225	-3.46601	4.76085
C	3.63788	-3.02914	1.37835	H	2.84226	-1.48792	-2.05792
C	3.85247	-3.53926	2.70373	H	4.60282	-3.24377	-1.88251
C	3.13208	-3.07172	3.76347	H	5.11196	-4.24532	0.35313
N	2.38621	-1.48881	-0.04921	H	-1.77825	-4.4824	-0.72167
C	3.08245	-1.9334	-1.09897	H	0.21689	-3.08742	-0.51655
C	4.07245	-2.92487	-0.9917	H	-5.4066	1.17691	0.17535
C	4.35245	-3.47653	0.24456	H	-5.40672	-1.17635	-0.17537
C	-3.18051	-2.84791	-0.42656	H	0.21721	3.0874	0.51656
C	-1.90075	-3.42213	-0.54226	H	-1.77778	4.48259	0.72166
C	-0.76422	-2.63316	-0.42953	H	-5.19407	3.10683	0.41739
N	-0.78339	-1.31058	-0.22037	H	-3.56081	5.51044	0.10494
C	-2.01198	-0.71051	-0.11289	H	-5.30773	5.38376	0.19539
C	-3.23203	-1.41693	-0.21531	H	-5.23278	5.13641	2.64431
C	-2.01191	0.71072	0.11288	H	-3.45888	5.05562	2.62328
C	-3.23189	1.41727	0.2153	H	-4.43988	7.26827	2.94757
C	-4.44672	0.6769	0.10051	H	-5.19439	-3.10626	-0.4174
C	-4.44679	-0.67644	-0.10052	H	-3.56143	-5.51007	-0.10493
N	-0.78325	1.31066	0.22037	H	-5.30834	-5.38317	-0.19544
C	-0.76395	2.63324	0.42952	H	-5.23329	-5.1359	-2.64435
C	-1.90039	3.42233	0.54225	H	-3.45938	-5.05529	-2.62329
C	-3.18021	2.84825	0.42655	H	-4.44053	-7.26787	-2.94755
N	-4.31055	3.58632	0.4962				

References

1. SAINT Plus, version 7.03; Bruker AXS, Inc.: Madison, WI, **2004**.

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3. Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3–8.

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