Electronic Supplementary Information (ESI)

For

Cationic Organoiridium(III) Complex Based AIEgen for Selective Light up Detection of rRNA and Nucleolar Staining

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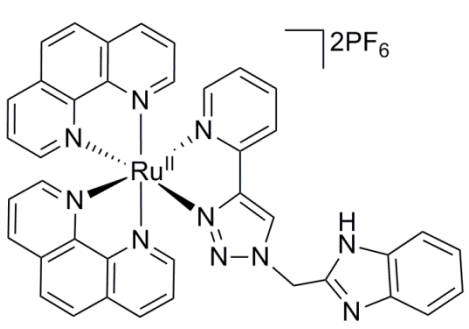
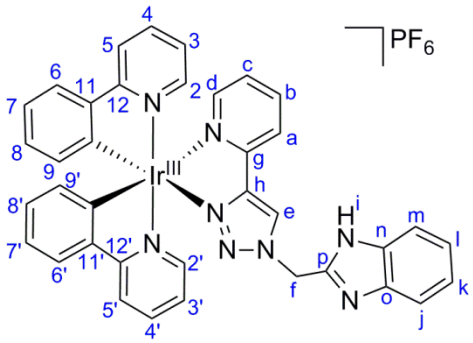
Chart S1. List of Compounds used in this study



1[PF_6]$_2$



2[PF_6]

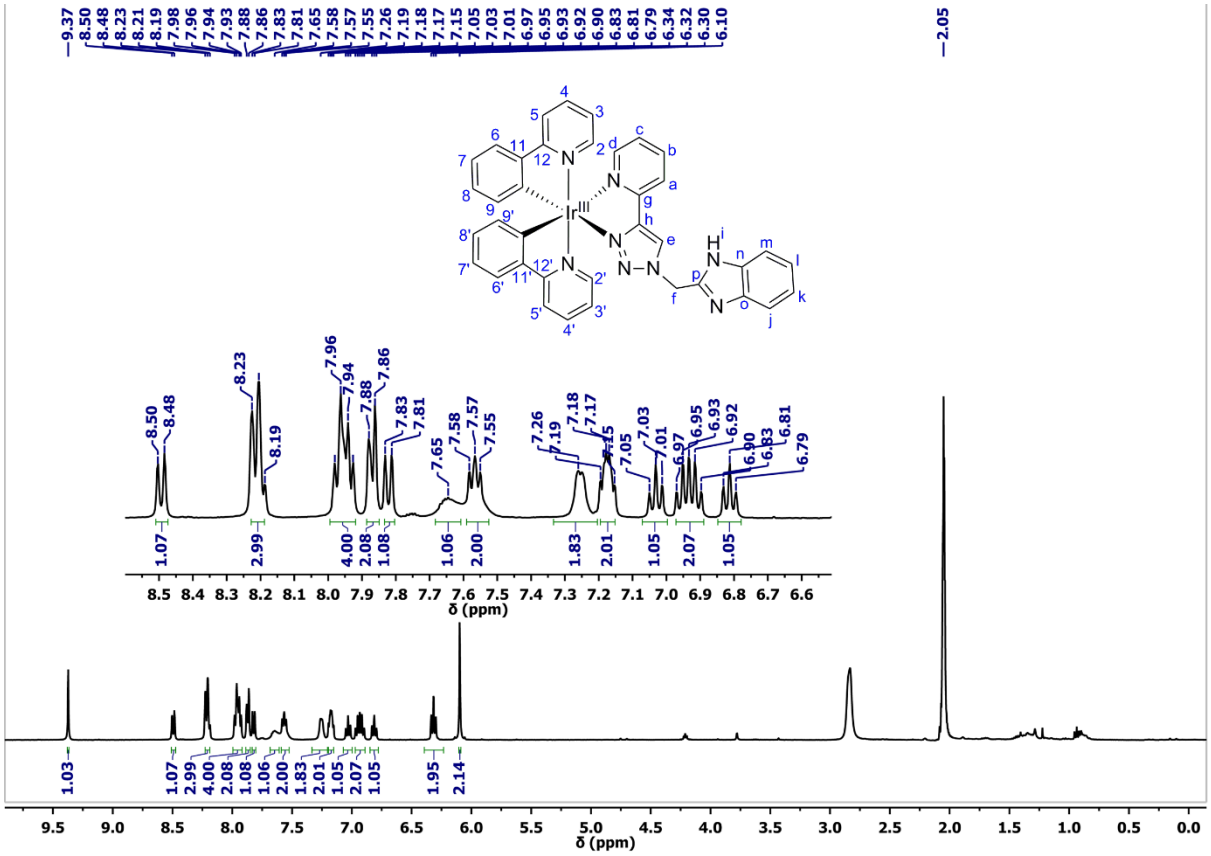


Figure S1. ^{1}H NMR of **2[PF$_6$]** in acetone–*d*$_6$.

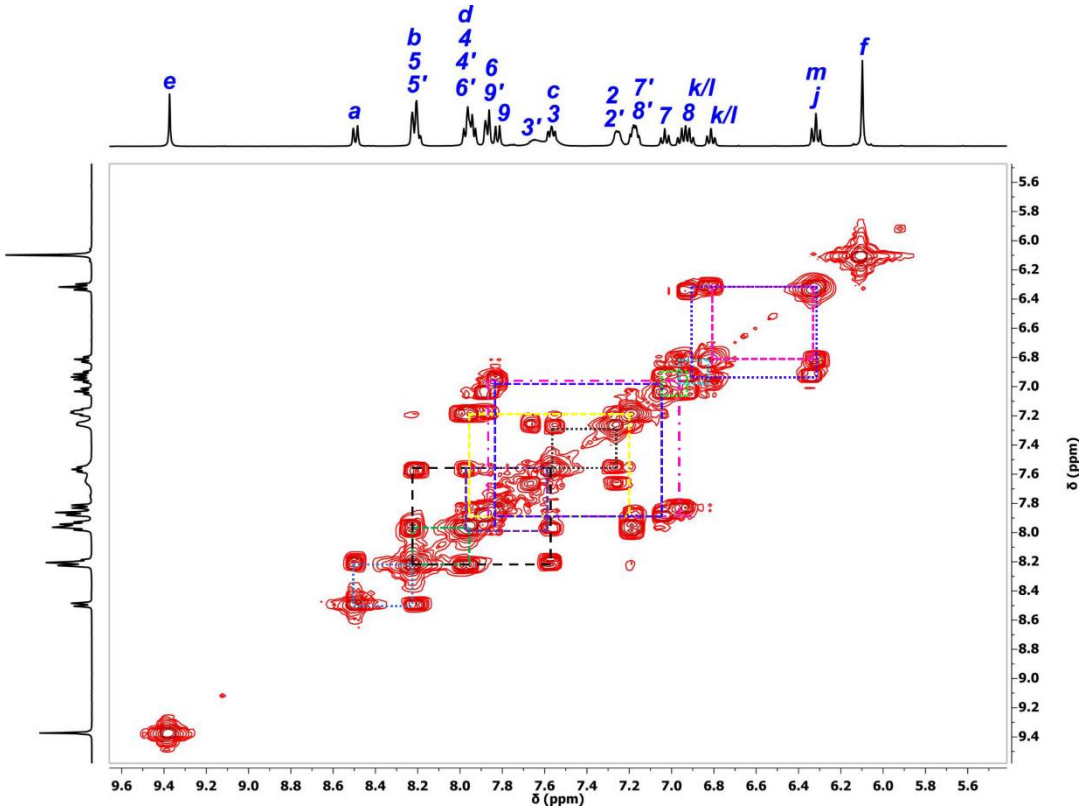


Figure S2. ^{1}H-^{1}H COSY NMR spectrum of **2[PF$_6$]** in acetone–*d*$_6$.

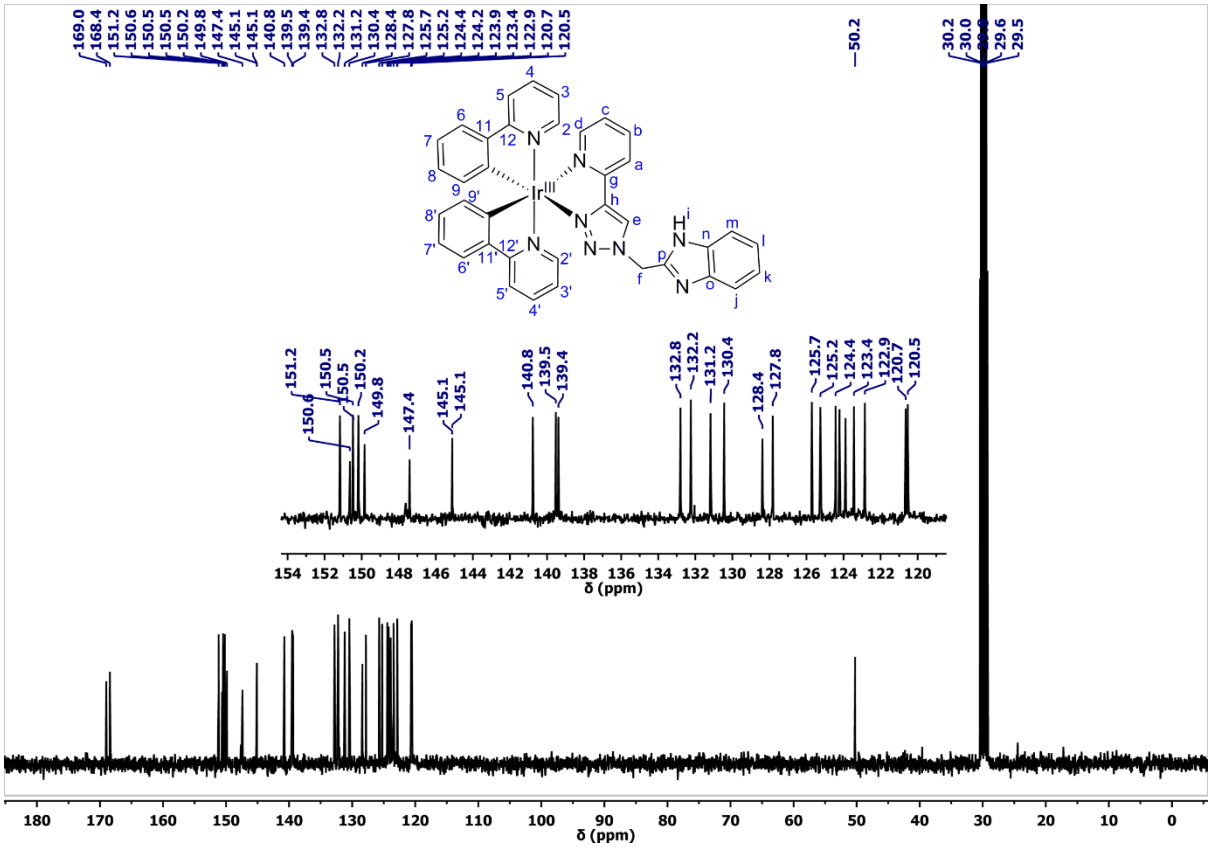


Figure S3. ^{13}C NMR spectrum of **2[PF$_6$]** in acetone–d_6.

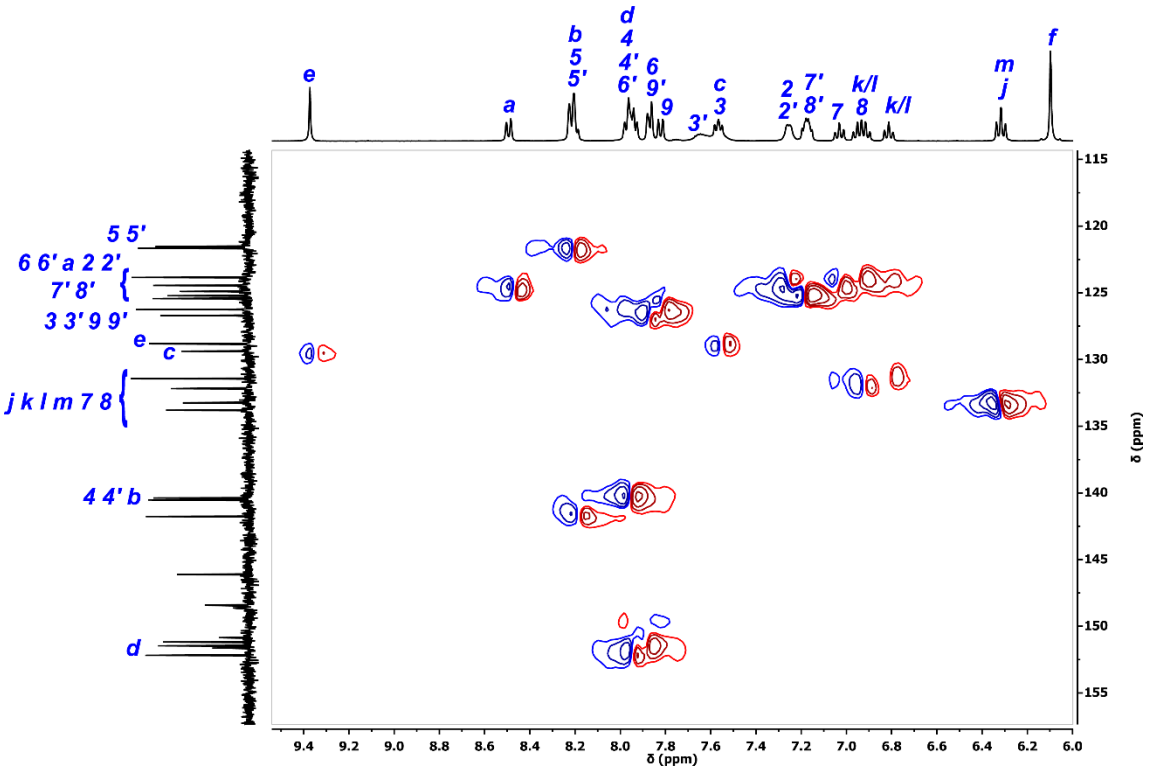


Figure S4. ^{1}H-^{13}C HSQC spectrum of **2[PF$_6$]** in acetone–d_6.

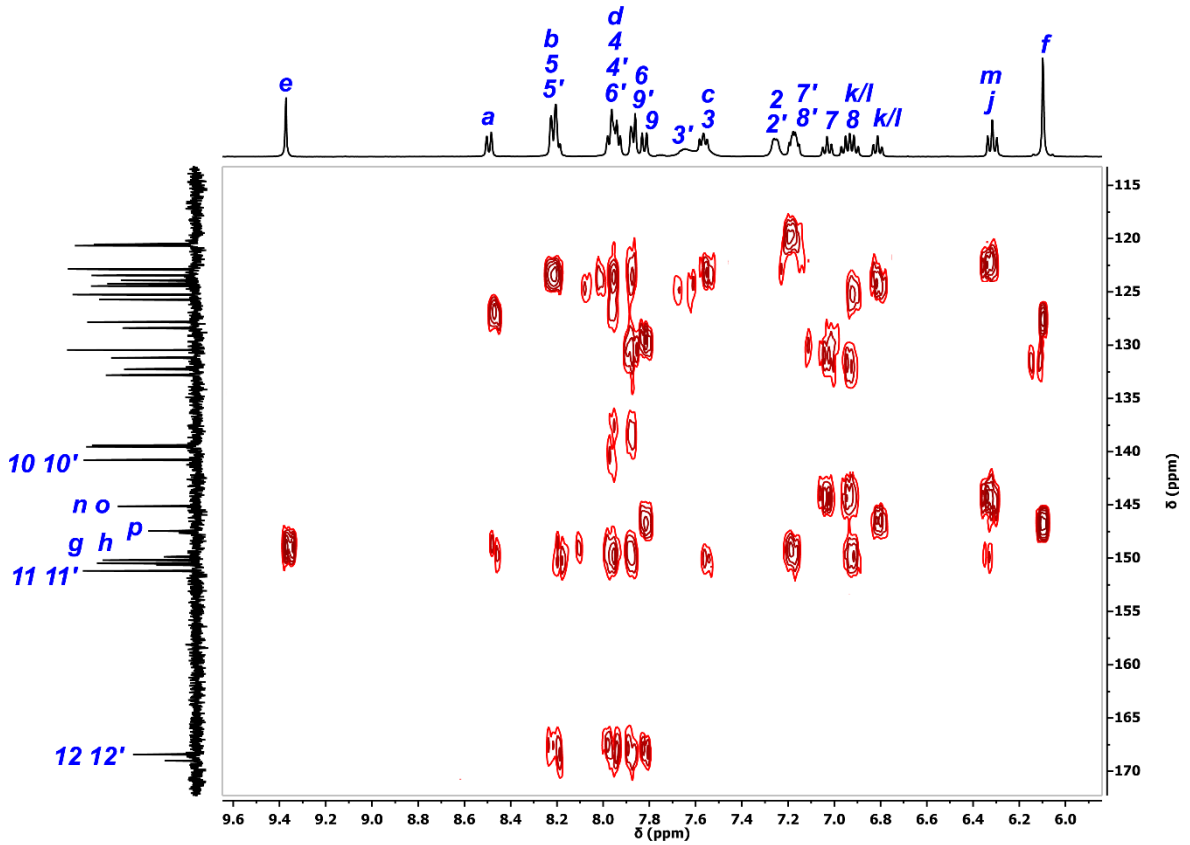


Figure S5. ^{1}H-^{13}C HMBC spectrum of **2[PF$_6$]** in acetone–*d*$_6$.

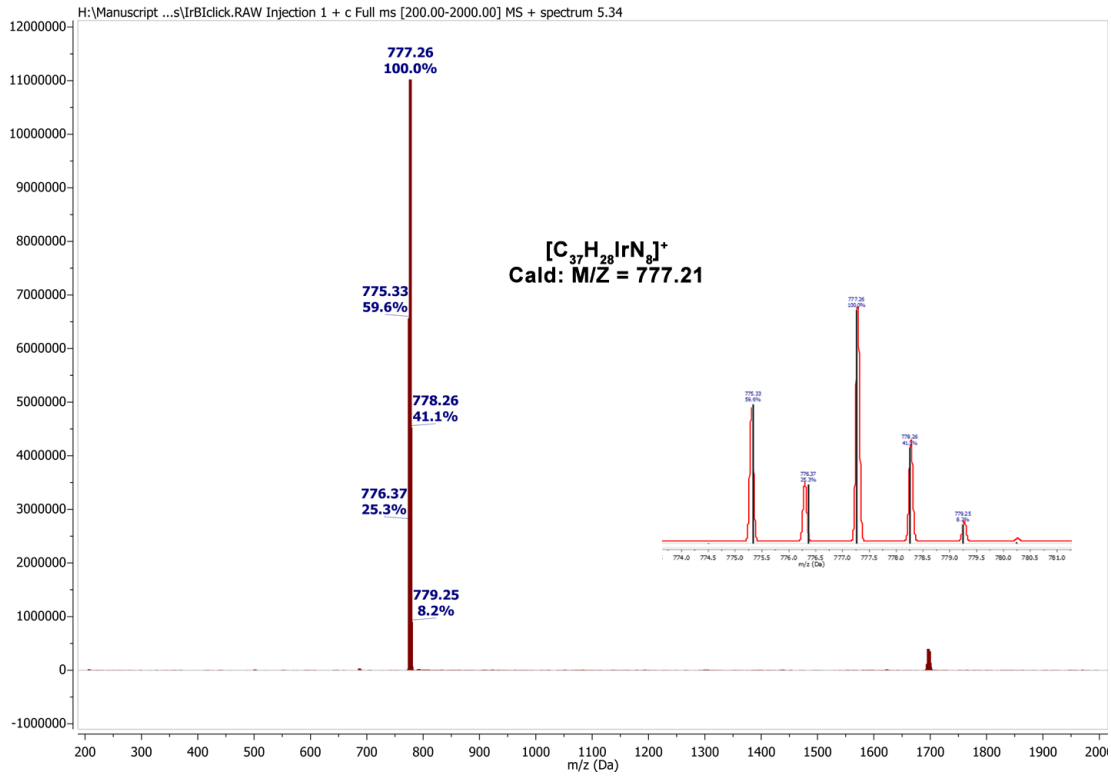
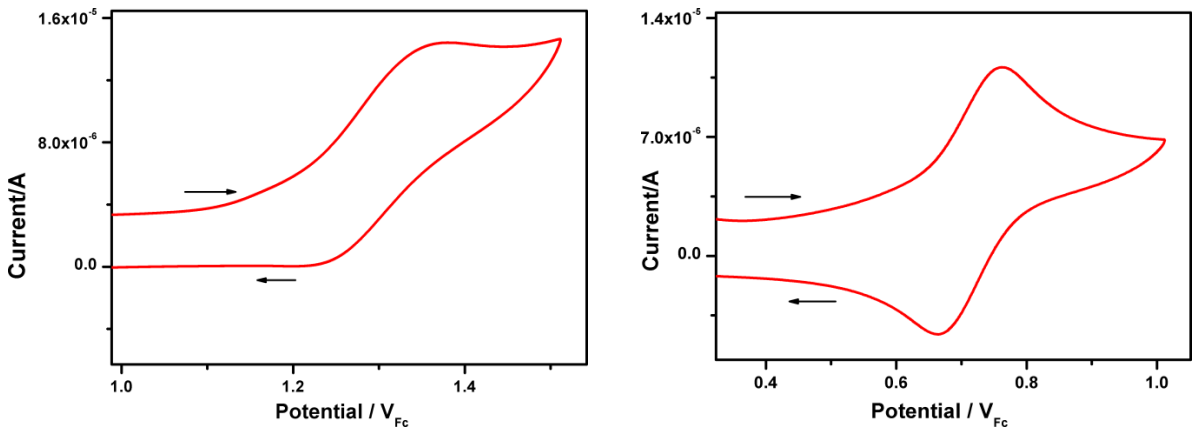


Figure S6. ESI-MS spectrum of **2[PF$_6$]** in CH_3CN and isotopic distribution pattern. Colour code: black corresponds to experimentally obtained and red corresponds to theoretically calculated.



(a) (b)

Figure S7. Cyclic voltammetric (CV) analysis of (a) **2[PF_6]** (1.0 mM) and (b) [$Ir(ppy)_3$] in dry and degassed acetonitrile solution versus the Fc/Fc^+ couple.

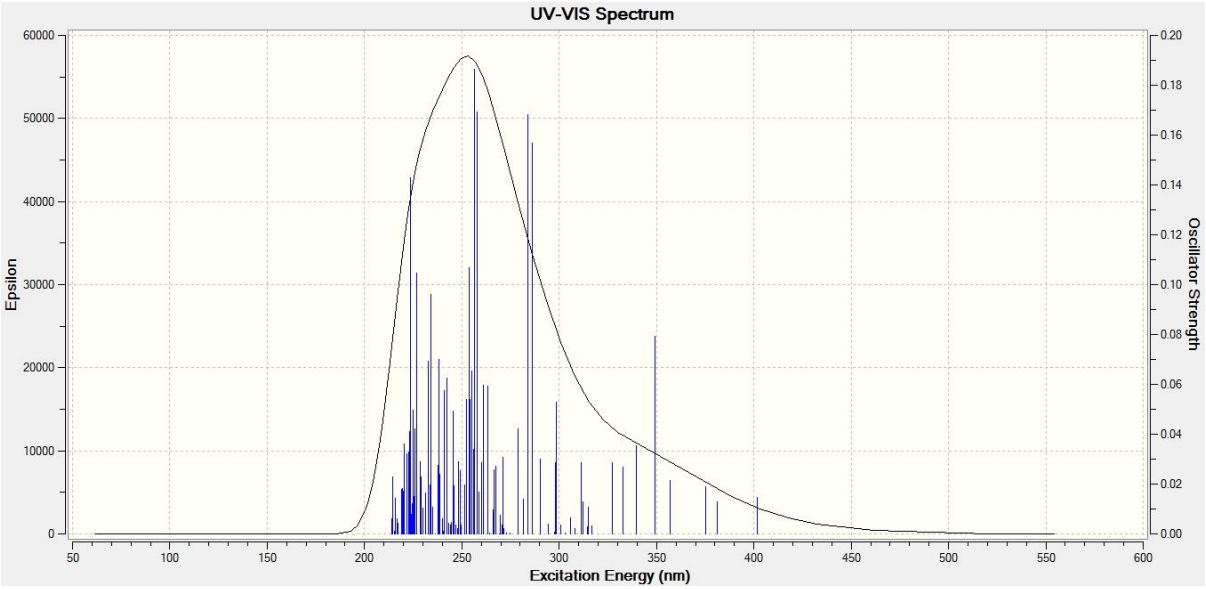


Figure S8. Theoretical UV-vis spectrum of **2**.

Chart S2. Solubility Chart

Solvents	Solubility	
	1[PF_6]$_2$	**2[PF_6]**
Hexane	×	×
Dichloromethane	✓	✓
Chloroform	×	✓
MeOH	✓	✓
Acetone	✓	✓
Acetonitrile	✓	✓
THF	✓	✓
DMSO	✓	✓
Water*	×	×

**It is notable that the compound is insoluble in water at high concentration of the probe but at 10 μM concentration both the compounds have better solubility even in 99% water (CH$_3$CN or DMSO as a co solvent).*

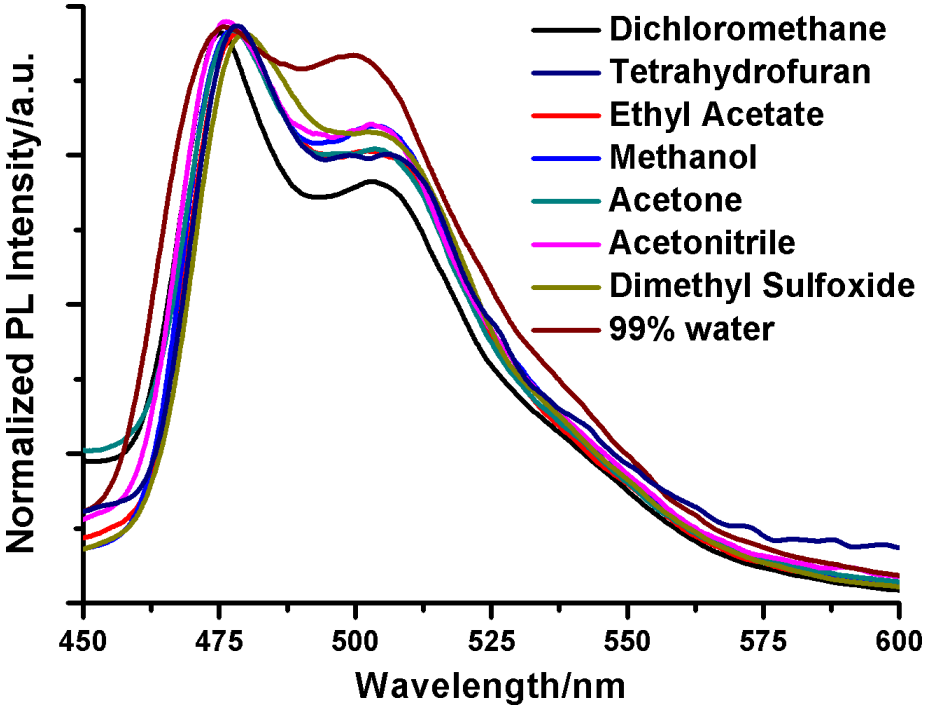


Figure S9. PL spectra of **2[PF_6]** in different solvents.

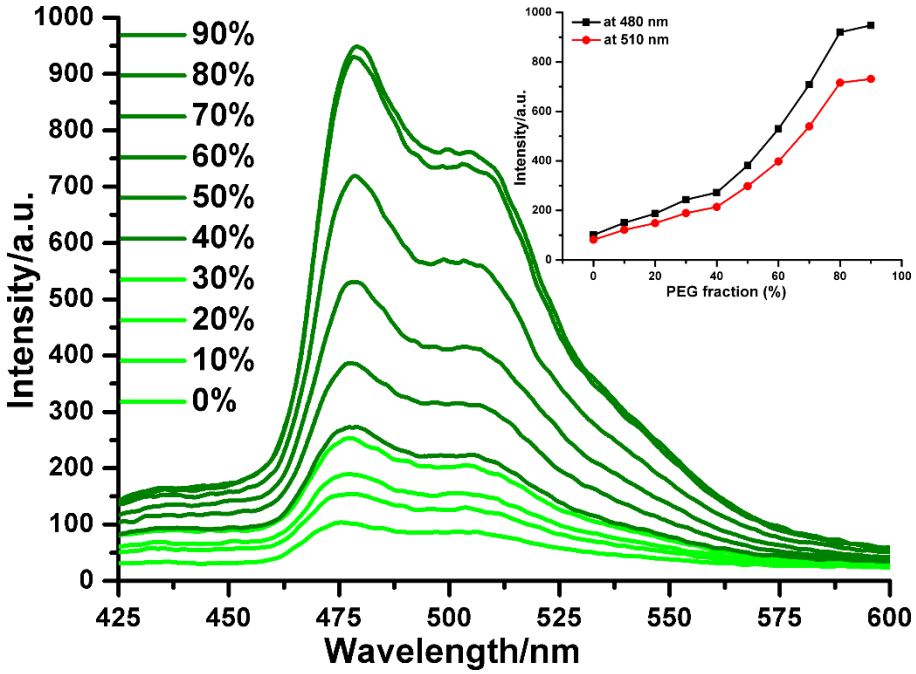


Figure S10. PL spectra of **2[PF_6]** (10 μM) in CH_3CN–PEG mixture, (inset) Plot of PL intensity vs. different fraction of PEG in CH_3CN. (λ_{ex} = 384 nm; λ_{em} = 480 and 510).

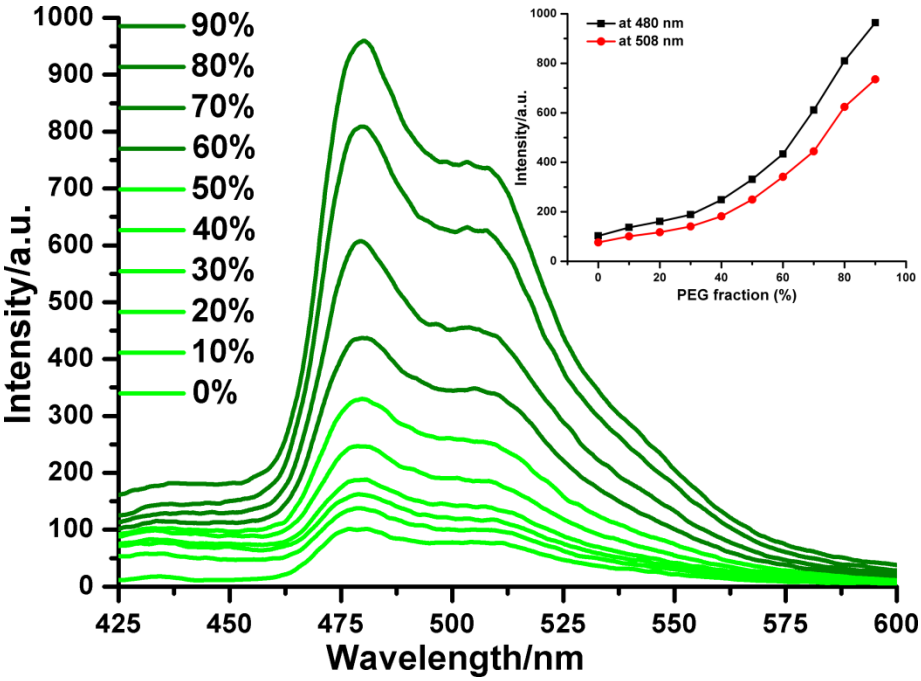


Figure S11. PL spectra of **2[PF_6]** (10 μM) in THF–PEG mixture, (*inset*) Plot of PL intensity vs. different fraction of PEG in THF. (λ_{ex} = 384 nm; λ_{em} = 480 and 508).

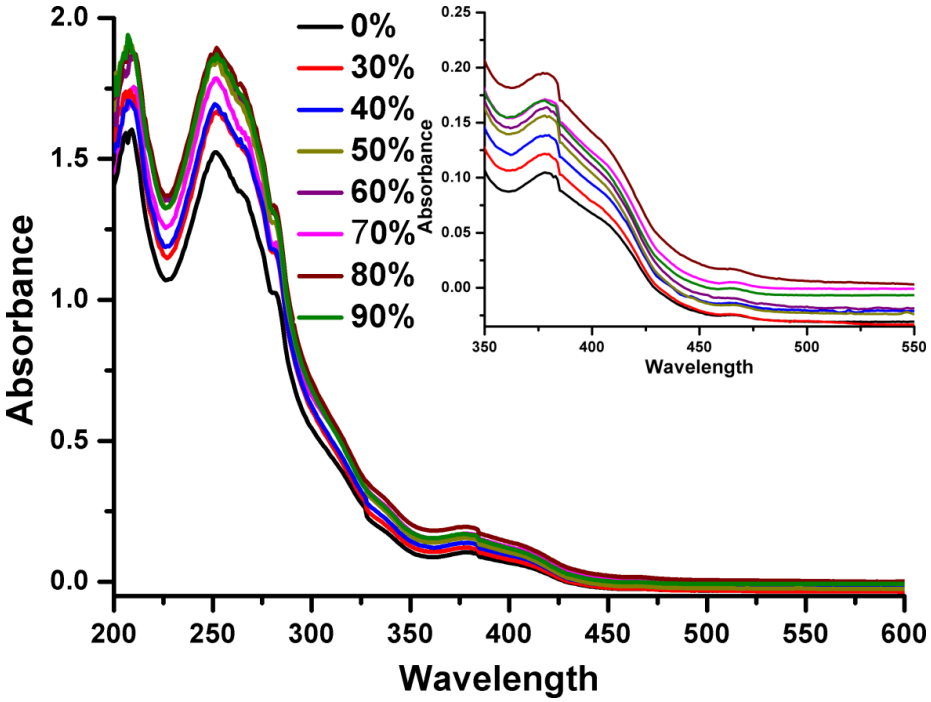


Figure S12. Absorption spectra of **2[PF_6]** in CH_3CN/H_2O mixtures with different H_2O fraction (0-90%).

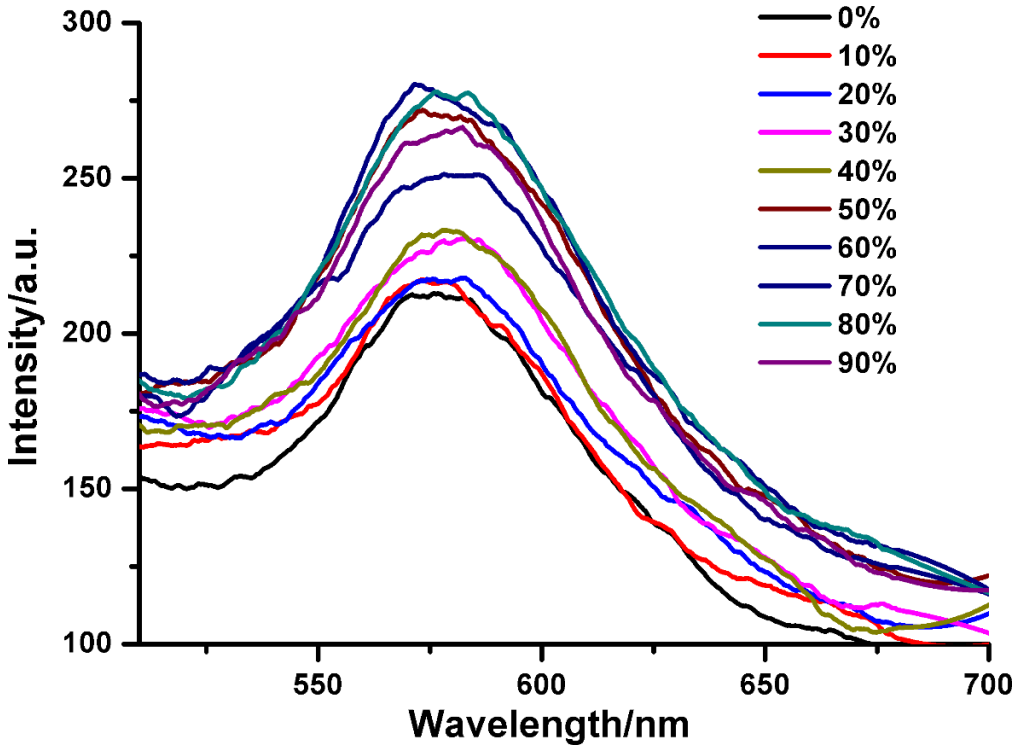


Figure S13. PL spectra of **1[PF_6]$_2$** (10 μM) in $CH_3CN–H_2O$ mixture (λ_{ex} = 459 nm; λ_{em} = 577 nm).

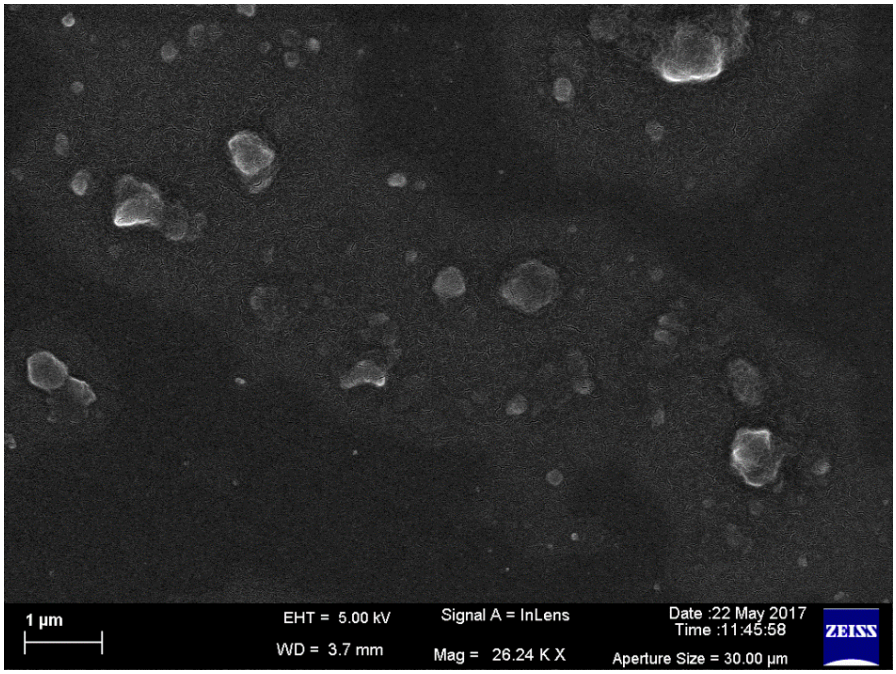


Figure S14. SEM image of **2[PF_6]** (10 µM) in CH_3CN.

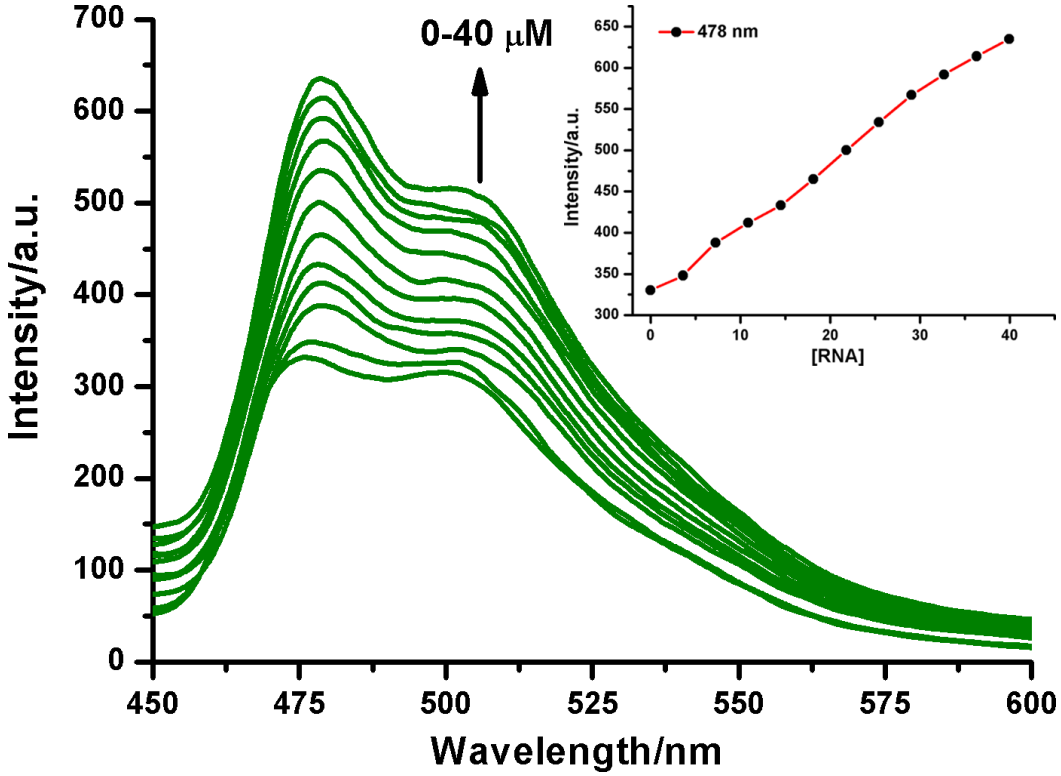


Figure S15. PL titration of **2[PF_6]** with rRNA (0-4 fold) in CH_3CN/PBS buffer (1:99; v/v, pH 7.4). (*Inset*) Plot of emission intensity as a function of [RNA].

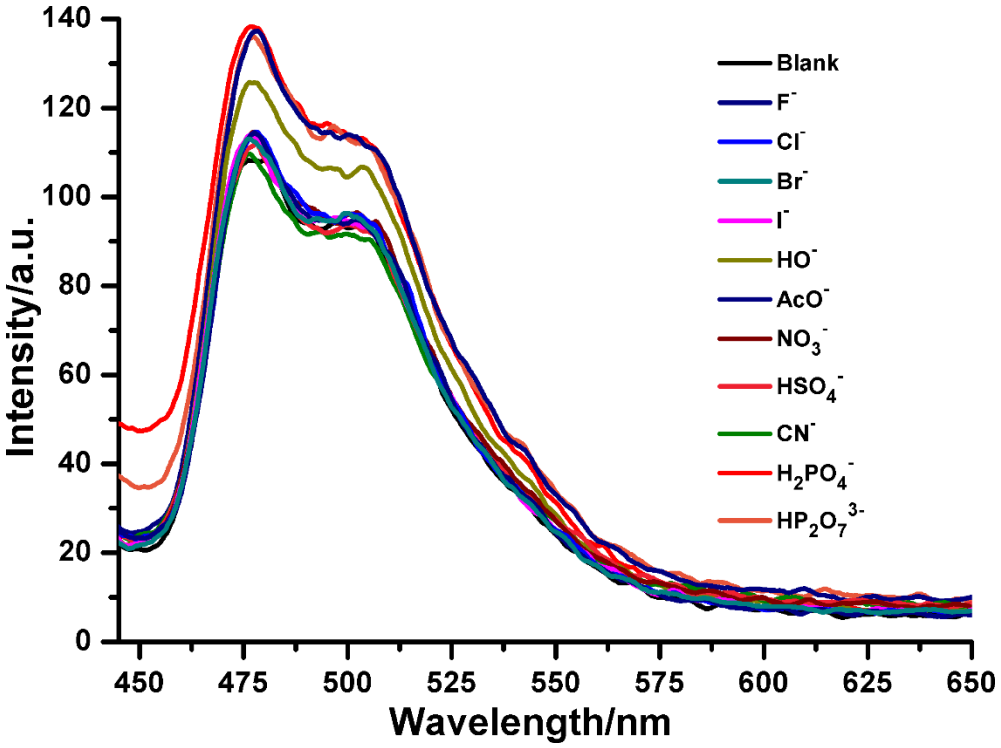


Figure S16. Emission spectra of **2[PF_6]** in the presence of several anions in CH_3CN.

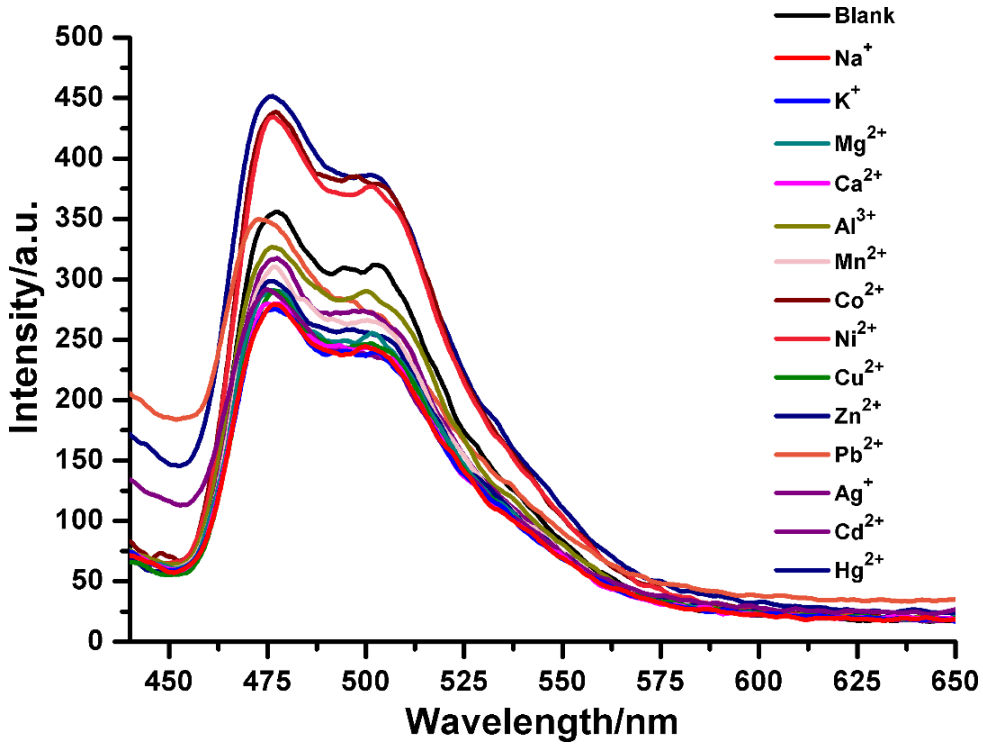


Figure S17. Emission spectra of **2[PF_6]** with several cations in 50% aqueous carbonate buffer (pH 9.2)

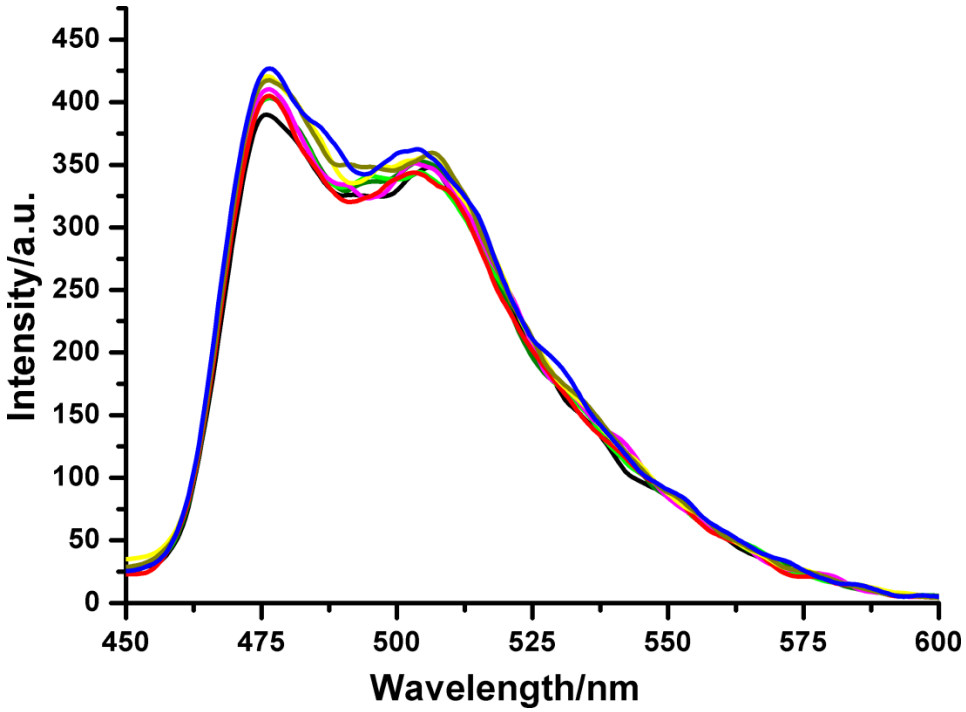


Figure S18. PL titration of **2[PF_6]** with gradual addition of DNase and RNase free aqueous buffer (0-4 fold).

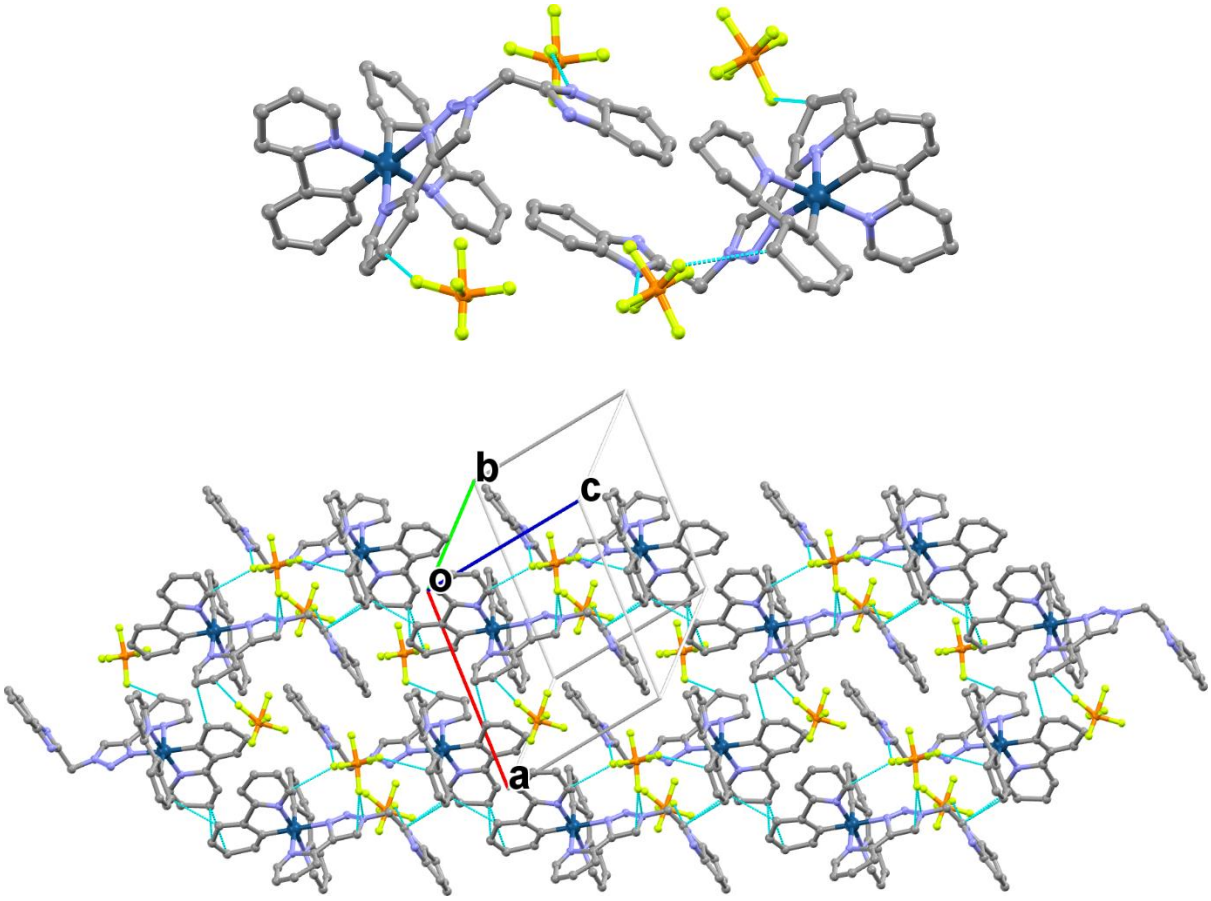


Figure S19. Ball stick packing representation of partially solved crystal structure of **2[PF_6]**.

Table S1. Selected bond lengths and angles in the optimized structure.

Bond lengths (Å)			
N(17)-Ir(71)	2.08370	N(61)-Ir(71)	2.20668
C(72)-Ir(71)	2.01863	N(73)-Ir(71)	2.08102
N(60)-Ir(71)	2.26676	C(74)-Ir(71)	2.01809
Bond angles (º)			
N(17)-Ir(71)-C(72)	80.15564	N(61)-Ir(71)-N(73)	96.59987
N(60)-Ir(71)-N(61)	74.23891	N(61)-Ir(71)-C(72)	98.99612
N(73)-Ir(71)-C(74)	80.14838	C(72)-Ir(71)-N(73)	95.22523
N(17)-Ir(71)-N(60)	96.57373	C(72)-Ir(71)-C(74)	90.39341
N(17)-Ir(71)-N(61)	88.56240	N(17)-Ir(71)-N(73)	173.58341
N(17)-Ir(71)-C(74)	95.35121	N(60)-Ir(71)-C(72)	172.64396
N(60)-Ir(71)-N(73)	88.51983	N(61)-Ir(71)-C(74)	170.33257
N(60)-Ir(71)-C(74)	96.49361		

Table S2. The x,y,z Cartesian coordinates of the complex **2** calculated using Gaussian09 at B3LYP/6-31G(d,p) level and LANL2DZ for iridium.

2							
C	2.30990900	1.92082500	-2.26060200	C	-0.14586400	-4.11148400	2.41063700
H	2.65655700	1.05153100	-2.81000800	H	-0.51615100	-5.00881200	2.89580300
C	2.42972900	3.17958200	-2.85271000	C	-0.96906300	-3.38777300	1.55238700
H	2.86376500	3.26689400	-3.84523300	H	-1.98616800	-3.70826800	1.35434300
C	2.00257400	4.32916300	-2.17963100	C	-0.46647300	-2.23621300	0.94021300
H	2.10028000	5.30566400	-2.64314900	C	-1.24413100	-1.41061500	0.01930500
C	-0.17203900	3.42197900	3.14756900	C	-2.54674700	-1.45537700	-0.44193500
H	-0.51825500	4.20240100	3.81796800	H	-3.40191500	-2.08596000	-0.24989800
C	-0.21621000	2.07932600	3.53667800	C	-3.78025300	0.02536100	-2.10903800
H	-0.59158600	1.77885600	4.50808000	H	-3.82742700	-0.64144600	-2.97654400
C	0.24188700	1.12147100	2.64608500	H	-3.53980600	1.02917100	-2.46242600
H	0.23889900	0.06809700	2.89748700	C	-5.07780100	-0.01501400	-1.35676900
C	1.45695800	4.21147600	-0.90755500	C	-6.76194300	-0.69175000	-0.21375400
C	1.33495800	2.94644700	-0.30694600	C	-7.69174900	-1.42549000	0.53595400
C	0.32493700	3.74794100	1.89456600	H	-7.50088300	-2.46374900	0.78611100
C	0.77893500	2.74158200	1.02683600	C	-8.85572500	-0.78005100	0.93341500
N	0.72530400	1.43390500	1.42695300	H	-9.59706200	-1.32189000	1.51207500
C	3.85726500	0.76689200	1.81847200	C	-9.10251800	0.56889600	0.59872100
H	3.21009500	1.40983200	2.40678600	H	-10.02592300	1.03472400	0.92799000
C	5.19803600	0.64245200	2.19033000	C	-8.19463400	1.31558400	-0.14457300
H	5.56779800	1.18377800	3.05707600	H	-8.39010300	2.35177100	-0.40157400
C	6.07023100	-0.16659900	1.45457300	C	-7.02618000	0.65956500	-0.53980400
H	7.11164500	-0.25874600	1.74581300	N	0.80243800	-1.80434900	1.16324000
C	3.70286900	-2.79118100	-3.18083600	N	-0.64572300	-0.32764200	-0.57251300
H	4.24180900	-3.42161800	-3.88103100	N	-1.48573300	0.28939700	-1.35827200
C	2.33994000	-2.53465600	-3.35823300	N	-2.64110100	-0.39178500	-1.27657400
H	1.78589600	-2.94901300	-4.19258200	N	-5.53877600	-1.08058500	-0.74659600
C	1.69726500	-1.72207200	-2.43715700	N	-5.91969900	1.06764700	-1.27015300

H	0.64651500	-1.47749700	-2.53125400	H	-5.77037200	1.98114400	-1.67191800
C	5.59363000	-0.84917200	0.34159100	H	5.42194500	-2.40235000	-1.95382100
C	4.24547200	-0.72637100	-0.03640900	H	6.27494200	-1.47382100	-0.22877800
C	4.36386800	-2.22325400	-2.10109800	H	1.12942800	5.10635100	-0.38636300
C	3.67066100	-1.40379400	-1.19728600	H	0.37228600	4.78302600	1.57902000
C	1.59169500	-2.51111300	1.99054200	Ir	1.44017000	0.05643200	0.03663500
H	2.59403200	-2.12039800	2.13039200	C	1.75602500	1.77039600	-0.98191700
C	1.15781800	-3.66697300	2.63383600	N	2.33444400	-1.17504800	-1.38281600
H	1.83207800	-4.20163900	3.29340900	C	3.34442000	0.08599800	0.70428000

Table S3. The x,y,z Cartesian coordinates of the complex **2** dimer calculated using Gaussian09 at WB97XD/6-31G(d,p) level and LANL2DZ for iridium.

2-Dimer							
Ir	6.89130100	0.01704200	-0.01103500	C	-6.16838700	-1.89761400	2.42552400
C	9.27177900	-3.18451900	-1.71991200	N	-3.92568800	2.91219800	1.06593400
N	0.66706300	-1.17811000	-2.59798000	C	-5.41811900	-0.40446200	-2.66864000
C	6.92769300	1.12566600	-1.68014800	C	-7.13881700	3.89758000	-1.85285000
C	10.75521400	-1.65506000	-0.62150900	C	-5.05123600	-2.37997100	0.35350700
C	3.89581900	3.62926300	1.11817300	C	-9.44968800	-1.20885600	0.33932100
C	8.47714400	2.23642900	1.40115900	C	-9.33991000	-0.25456400	1.44493900
C	8.22305800	-2.37704700	-1.32754200	C	-8.27621900	3.86150700	-2.65108200
C	5.32414100	2.44277900	-0.42035200	C	-9.49506000	-2.98558400	-1.78682900
N	5.54636600	1.49296400	0.52697200	C	-8.34625700	-2.24220800	-1.52977700
C	9.66123400	2.77943900	1.89183700	C	0.27526800	1.85875700	0.52788500
C	-0.39079400	-1.60047000	-0.70521300	C	2.21917200	0.57341300	0.12569600
C	4.85835400	-2.17806500	0.42883500	C	-9.02730600	2.69278600	-2.70365200
C	4.14683500	2.65223200	2.07783900	N	-8.15576800	0.40929000	1.50133700
N	4.52961200	-1.47232700	-1.61851600	C	-4.36996500	-3.44147500	0.95956000
N	0.70981300	-2.44121500	-0.75042800	C	-10.31907700	-0.00719700	2.41073600
C	10.87791800	2.12726200	1.69592200	C	-5.49129400	-2.95343800	3.02714000
C	2.60380900	-2.76288200	-2.29354600	C	2.07558700	-0.02710600	1.39188200
C	6.05321000	2.23449500	-1.67114600	C	-4.66162100	3.58882000	0.15399300
C	7.30411400	-1.19361100	2.90397800	C	-5.63177400	2.69456200	-0.23722000
C	3.79795100	-2.89676100	-0.07323200	C	1.03850500	0.31280200	2.24103200
C	10.90424000	0.92868000	0.99925900	C	-8.29654700	-1.33399300	-0.46746100
C	-2.32880400	-0.47908600	0.10575200	C	-4.58981000	-3.72902500	2.29718900
C	7.06186300	-2.01514500	3.99687600	N	-0.79070700	2.72849700	0.41440400
C	4.97584600	1.60174000	1.73765500	C	-4.85045400	-1.98767200	-1.03945500
C	5.27367800	-3.02255700	2.75871800	C	1.32521100	1.52748200	-0.32946300
C	6.02826900	-2.94232300	3.92311100	C	0.12221200	1.27081400	1.79618300
C	-2.37219400	0.29876800	-1.06600200	N	-7.51666000	1.62461500	-1.19166600
C	5.92949300	3.07134700	-2.78631000	N	-5.53357200	-0.87560900	-1.41521400
C	9.65870800	-0.87220200	-0.24961700	N	-5.40596100	1.54340600	0.45933000
C	4.48393000	3.52119800	-0.12971600	C	-5.96194500	-1.58246600	1.07923100
C	9.71526700	0.38246300	0.50386900	C	-2.77202500	3.37688600	1.84593300
C	6.68004200	2.82206800	-3.92434300	C	-10.62766600	-2.84333800	-0.98671100
C	1.30417700	-2.14728500	-1.87169200	C	-8.85443500	1.56706800	3.46989600
C	7.55896400	1.73837600	-3.94295100	C	-4.62089400	-1.00971600	-3.61808600
N	5.25657200	-1.32091700	-0.55423700	C	-3.91561100	-2.15703700	-3.25352100
C	-1.43622800	0.15113300	-2.07770500	H	9.07947700	-4.07845100	-2.30019400
N	3.64950100	-2.43099500	-1.33121800	H	0.97584700	-0.78585400	-3.47237200
C	-1.35264800	-1.44113600	0.29481500	H	11.75446100	-1.34615900	-0.34159200
N	6.57575400	-1.26264100	1.78214500	H	3.25188800	4.47148700	1.34762700
C	5.57686000	-2.16911300	1.70410300	H	7.19864200	-2.60387500	-1.59628700
N	8.40584700	-1.25620100	-0.60918700	H	9.63777400	3.72320100	2.42838800

C	8.47198300	1.02472100	0.70219300
C	-0.44113100	-0.80196100	-1.86396800
C	10.56506700	-2.81268200	-1.35501300
C	7.68157200	0.90451800	-2.83658200
Ir	-6.79855000	-0.09507400	0.02473500
C	-10.08029900	0.90456400	3.42357000
C	-10.60384900	-1.95504700	0.07796100
C	-4.03249000	-2.64277600	-1.96569500
C	-7.92208400	1.28865300	2.49042400
C	-1.52334400	2.60134800	1.56952000
C	-8.61386100	1.59604600	-1.95928100
N	-4.38837300	1.67922600	1.25242600
C	-6.78900000	2.76132900	-1.13258000
N	-1.01037700	1.76082100	2.42215200
H	4.31710700	4.28360700	-0.88046500
H	6.59253600	3.47138400	-4.78872900
H	8.15634600	1.54735600	-4.82944900
H	-1.47702700	0.74570700	-2.98469000
H	-1.32271800	-2.04370400	1.19523800
H	11.41569600	-3.41885800	-1.64749200
H	8.38054000	0.07471600	-2.87886900
H	-10.83752100	1.09409100	4.17664500
H	-11.48892100	-1.85065500	0.69787900
H	-3.49187400	-3.53092800	-1.66514400
H	-6.94564800	1.75695300	2.48607300
H	-9.15816700	0.65714900	-1.96514500
H	-6.86580400	-1.31571100	3.02006200
H	-6.00280200	0.47821500	-2.89888300
H	-6.53776200	4.79738800	-1.78445400
H	-8.57296500	4.73611500	-3.21942400
H	-9.50756900	-3.68675600	-2.61580900
H	-7.48078300	-2.38097700	-2.17025700
H	3.70337100	2.69372400	3.06447400
H	11.79745200	2.55467300	2.08022700
H	2.51278600	-3.84989800	-2.33804600
H	2.94660200	-2.39676800	-3.26198000
H	8.09361600	-0.44895800	2.90505000
H	3.13308300	-3.63611700	0.34327200
H	11.85534200	0.42796300	0.84631000
H	-3.08022800	-0.32631000	0.87052200
H	7.67583900	-1.92470600	4.88477800
H	5.20925800	0.81432000	2.44382600
H	4.46742200	-3.74153400	2.66638600
H	5.81333900	-3.59888700	4.75901500
H	-3.17299400	1.02297300	-1.18717700
H	5.25323300	3.92129500	-2.77414100
H	3.05853600	0.29730100	-0.50375400
H	-9.92338000	2.62482700	-3.30862700
H	-3.66485100	-4.04477000	0.39572100
H	-11.26103600	-0.53914600	2.36805100
H	-5.66867300	-3.17769900	4.07465400
H	2.80199500	-0.76828100	1.70667000
H	-4.45807100	4.61345100	-0.11345100
H	0.91747400	-0.14692600	3.21536400
H	-4.06992800	-4.55509700	2.77028600
H	-1.04676400	3.24783100	-0.40829600
H	1.44172100	1.98949100	-1.30381900
H	-3.00583000	3.25447800	2.90360100
H	-2.65261500	4.44072500	1.62718800
H	-11.52092500	-3.42319700	-1.19112400
H	-8.62201500	2.28013200	4.25108900
H	-4.56371100	-0.59806200	-4.61828800
H	-3.28470000	-2.66778000	-3.97300700
H	7.54807500	2.77371500	1.56539000

Molecular Docking Study

To check the interaction between **2[PF_6]** and ribosomal RNA, in silico docking study was executed using Autodock Tools. The docking study was operated by energy minimised structure of **2[PF_6]** and rRNA (PDB code: 1C2X). The lowest energy-ranked results of nine **2[PF_6]** were listed in Table S4. The docked conformations with minimum binding energy were chosen for further analysis (see Fig. S20). For docking study, a grid size 70Å × 126Å × 52 Å with a grid coordinates 28.006 × 81.763 × 24.496 were taken around the active site. It is clearly observed that **2[PF_6]** interact with cytosine-70, cytosine-71, guanine-13, adenine-66 nucleosides by weak supramolecular interactions such as, N-H$\cdots\pi$ and π-π interactions between benzimidazole ring of **2[PF_6]** and purine, pyrimidine bases of the nucleosides.

Table S4. Docking summary of rRNA with **2[PF_6]** by Autodock program generating different conformations applying Lamarckian GA.

Rank	Binding Energy (kcal/mol)
1	-11.3
2	-11.0
3	-10.6
4	-10.0
5	-9.9
6	-9.6
7	-9.5
8	-9.3
9	-9.2

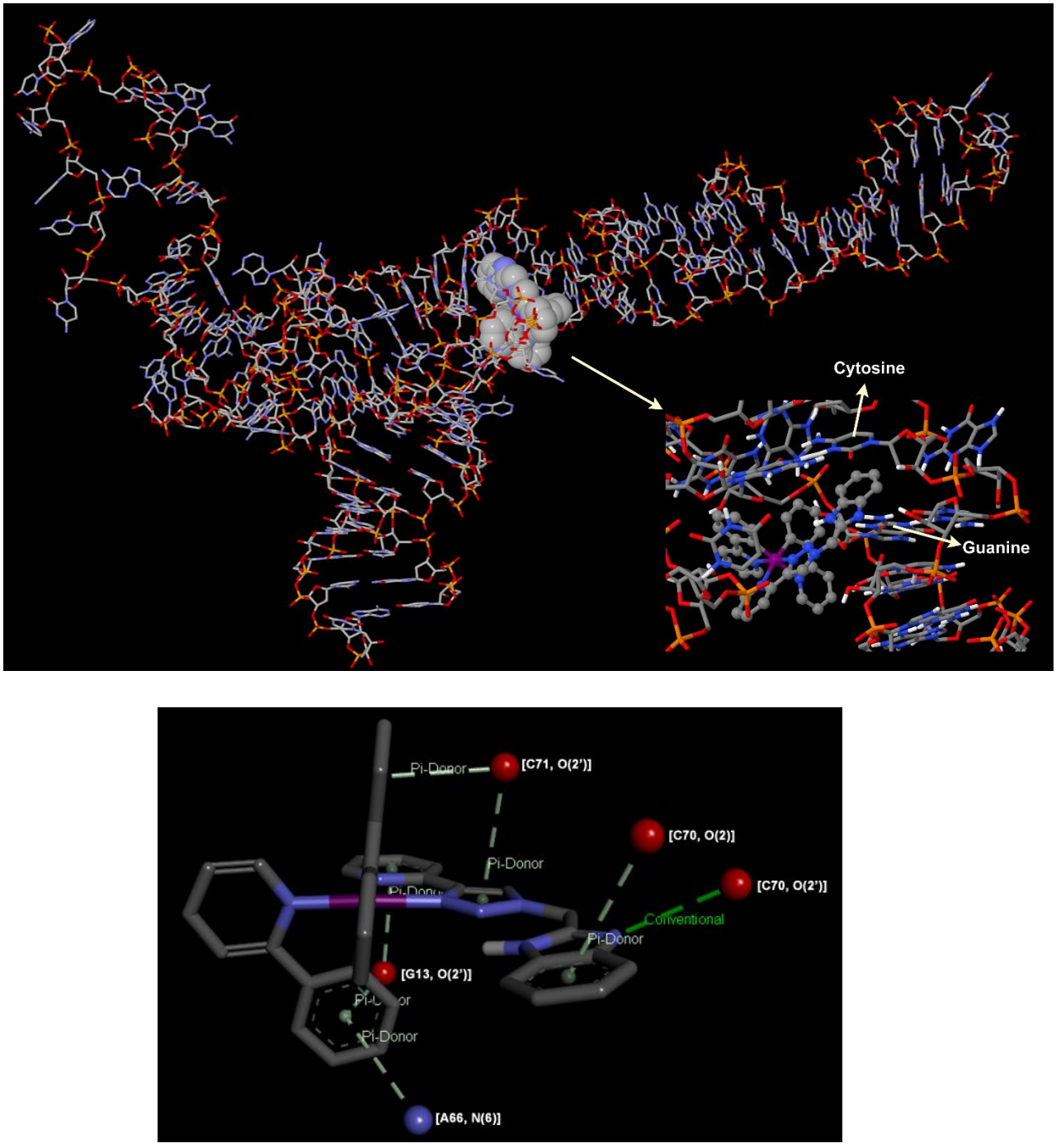


Figure S20. View of the interactions of **2[PF_6]** with nearby pyrimidine and purine bases of rRNA in docked structure.