Colorimetric and luminescent sensing of F⁻ anion through strong anion–π interaction inside π-acidic cavity of a pyridyl-triazine bridged trinuclear Re(I)-tricarbonyl diimine complex

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Supporting Information

## Contents

Experimental Section

Materials. All chemicals are commercially available unless mentioned elsewhere. All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used for synthesis were dried by standard procedures and stored under N_2. Solvents used in luminescent and electrochemical studies were spectroscopic and anhydrous grade, respectively. The compounds 2,4,6-tris(3-pyridyl)triazine (L)[1] and (dmbpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$)[2] were prepared according to published procedures. Tetrabutylammonium hexafluorophosphate (TBAH) used as supporting electrolyte was rigorously dried (*in vacuo* at 100 ^{o}C for 18 h) prior to use.

Synthesis of complex 1. A 100-mL flask was charged with (dmbpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (0.52 mmol) and bridging ligand L (0.17 mmol). To this mixture was added 30-mL THF and the resulting suspension was refluxed for 16 h under a nitrogen atmosphere. The solvent was removed under reduced pressure. Subsequently, 20-mL CH$_3$CN was added to redissolve the solid and filtered to remove any undissolved solid. Slow diffusion of diethyl ether into the filtrate CH$_3$CN solution of **1** afforded the analytical pure product in 76% yield. IR ($\upsilon_{C\equiv O}$, CH$_3$CN): 2035, 1934. ^{1}H NMR (300 MHz, DMSO-d_6): 9.23 (d, 6 H, J = 5.6 Hz), 9.19 (s, 3 H, H$_2$), 8.77 (m, 6 H), 8.60 (s, 6 H), 7.96 (d, 3 H, J = 7.3 Hz), 7.76 (d, 6 H, J = 5.4 Hz), 2.45 (s, 18 H). ^{13}C NMR (75 MHz, DMSO-d_6): 195.6, 192.1, 168.4, 155.9, 154.9, 153.9, 153.3, 151.1, 139.4, 132.9, 129.5, 127.8, 125.5, 21.0. ESI-MS: (m/z) = 1964.96 ([M-PF$_6$]$^+$, calculated m/z = 1965.16). Anal. Calcd. for C$_{63}$H$_{48}$F$_{18}$N$_{12}$O$_9$P$_3$Re$_3$: C, 35.85; H, 2.29; N, 7.96. Found: C, 35.61; H, 2.44; N, 7.91.

Equipment and Procedures. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a Brücker AC 300 or a Brücker AMX 400 spectrometer. Infrared spectra were measured on a Nicolet 20SXC Fourier transform infrared spectrophotometer. UV-Vis spectra were obtained using a Varian Cary 300 UV-Vis spectrophotometer. Emission spectra were recorded in deoxygenated CH$_3$CN solution at 293 K with a Fluorolog III fluorescence spectrophotometer. Luminescence quantum yields were calculated relative to Ru(bpy)$_3$Cl$_2$ in air-equilibrated water (Φ = 0.028). Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%. Luminescence lifetimes were determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument. Samples were degassed via freeze-thaw-pump cycle at least 5 times prior to measurements. Samples were excited at 337 nm from a nitrogen pulsed flashlamp with 1 ns FWHM

pulse duration transmitted through a Czerny-Turner design monochromator. Emission was detected at 90° via a second Czerny-Turner design monochromator onto a thermoelectrically cooled red-sensitive photomultiplier tube. The resulting photon counts were stored on a microprocessor-based multichannel analyzer. The instrument response function was profiled using a scatter solution and subsequently deconvoluted from the emission data to yield an undisturbed decay. Nonlinear least squares fitting of the decay curves were performed with the Levenburg-Marquardt algorithm and implemented by the Edinburgh Instruments F900 software.

Electrochemical measurements were recorded on a CHI potentiostat/galvanostat. The electrochemical cell consisted of a platinum working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ (0.01 M in CH_3CN solution) reference electrode. Cyclic voltammograms were obtained in deoxygenated CH_3CN with the electroactive material (1.0 x 10^{-3} M) and 0.1 M TBAH as supporting electrolyte. Ferrocene (Fc) was used as an internal standard for both potential calibration and reversibility criteria. All potentials for the complexes in the study are reported relative to Fc/Fc^{+}. The scan rate was 200 mV/s. All experiments were run under a nitrogen atmosphere.
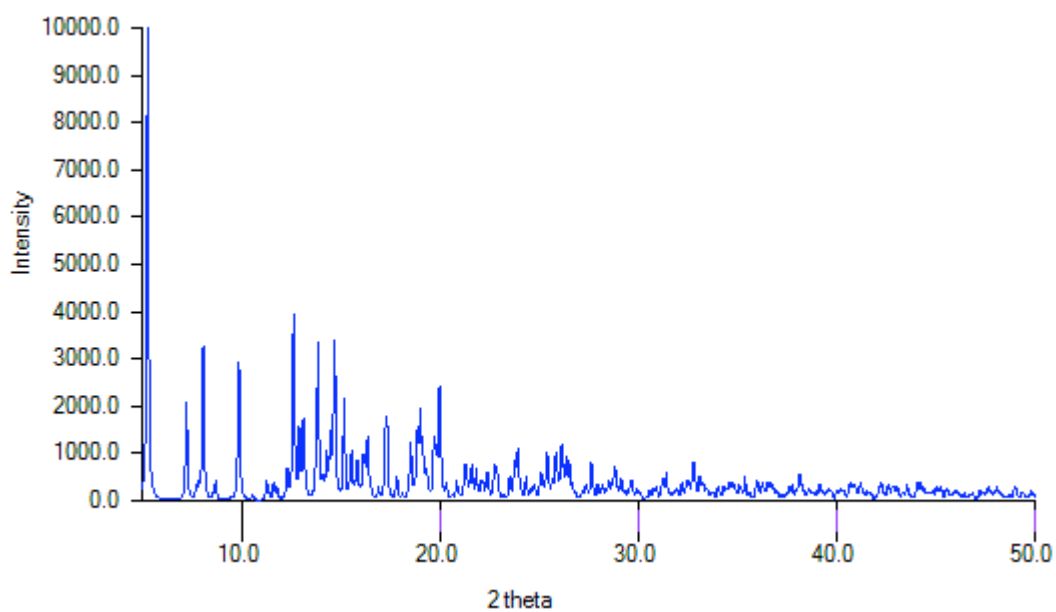
(a)
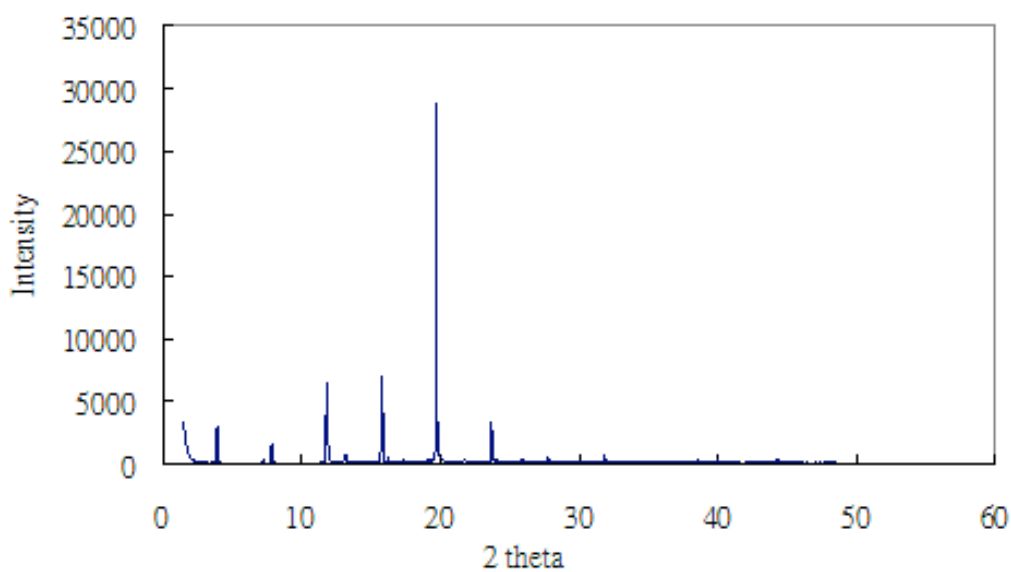
(b)

Fig. S1 X-ray powder pattern for complex **1**: the calculated powder pattern for the hkl reflections based on the single-crystal model (a) and that of experimentally observed powder pattern (b).

Single crystal X-ray diffraction: X-Ray diffraction data for **1** was collected on a Bruker APEX II CCD diffractometer having graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz polarisation effects[1] and a multiscan absorption correction[2]. The structures were solved by direct methods (SHELXS[3] or SIR–97[4]) and refined on F^2 using all data by full-matrix least squares procedures (SHELXL 97[5]). The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms and refined. All calculations were performed using the WinGX interface.[6] Detailed analyses of the extended structure were carried out using PLATON[7] and MERCURY[8] (Version 1.4.1). One solvent molecule (acetone) and one PF_6^- anion are disordered that lead to deviation in bond length (C67-C69, C68-C69 and P2-F9, P2-F11) and bond angle. This may be a probable reason that the second WGHT parameter could not be reduced further.

Description of Crystal Structure [L.Re₃(dmbpy)₃(CO)₉](PF₆)₃•2(acetone) (1):

(dmbpy = 4,4'-dimethyl-2,2'-bipyridine)
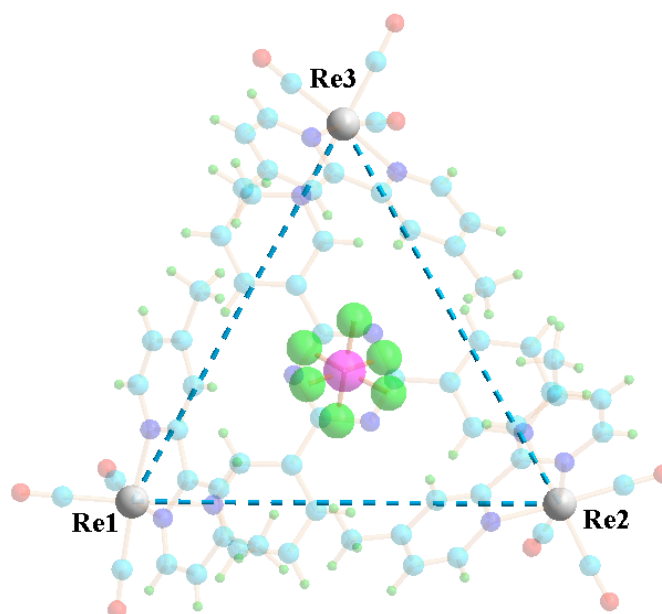
Fig. S2 Crystal structure of **1** showing encapsulation of PF_6^- anion inside cavity of metallacavitand formed by isohedrally arranged Re- metal ion.

(a)

(b)
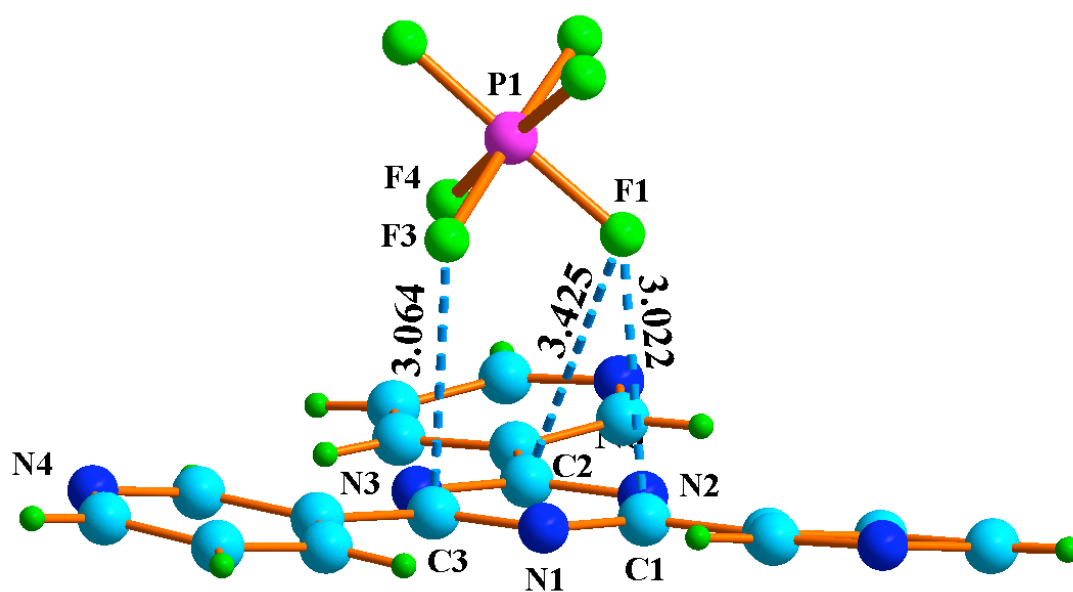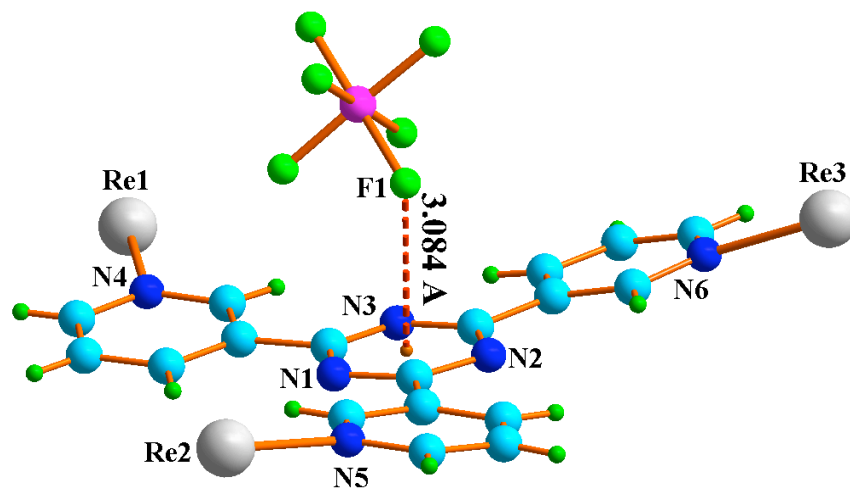
Fig. S3 Crystal structure of **1** showing strong anion-π interaction between fluorine atom of PF_6^- anion and centroid of triazine of ligand (a) and (b) the shortest distance between fluorine atom of PF_6^- anion and C-atom of triazine center is 3.022 Å.
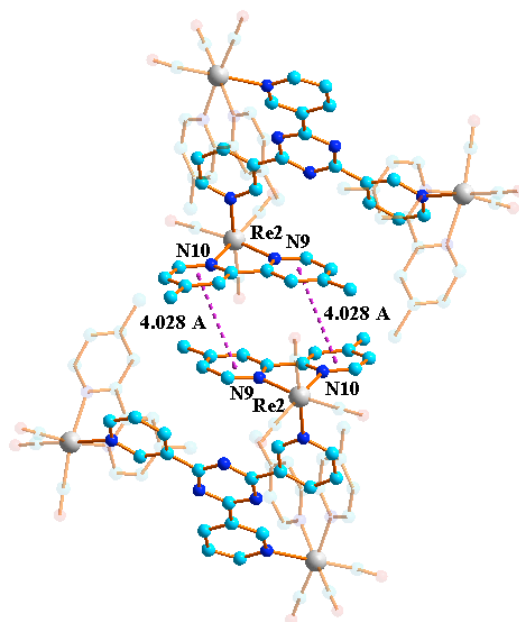
Fig. S4 Crystal packing showing π-π interaction between two dmbpy moieties of two neighboring Re-complexes. All H-atoms has been removed for clarity.
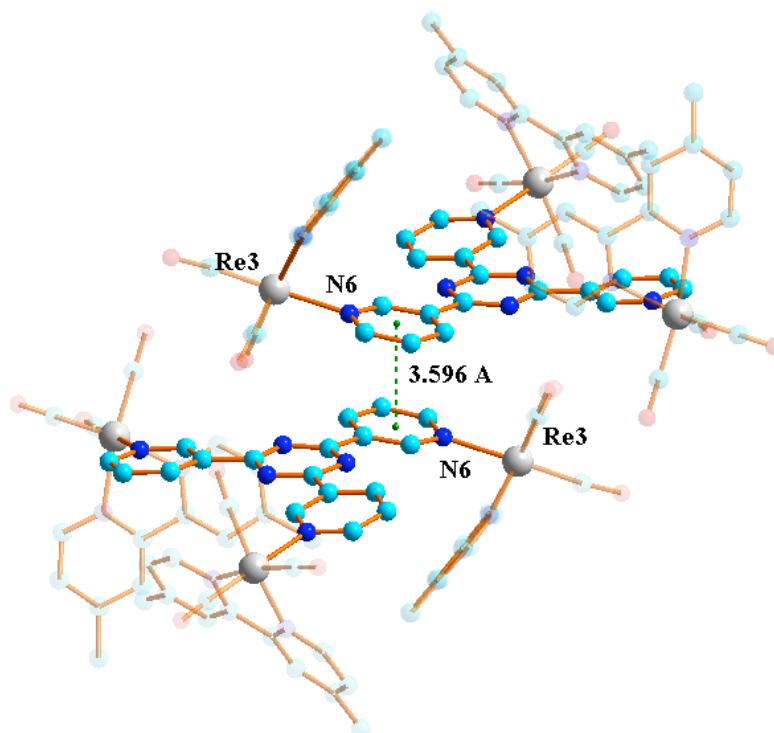
Fig. S5 Crystal packing showing π-π interaction between one arm (3-pyridyl) each of two neighboring Re-complexes. All H-atoms has been removed for clarity.
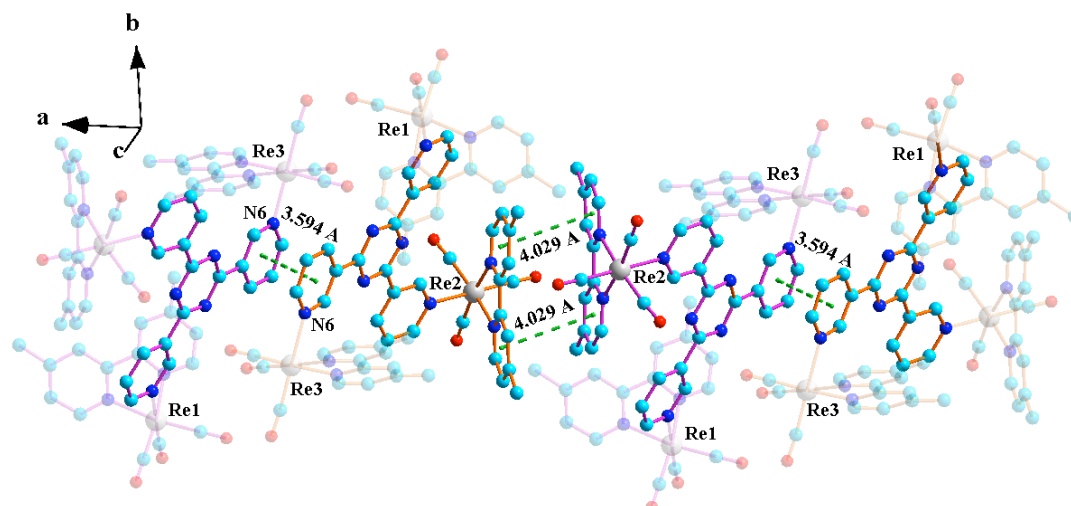
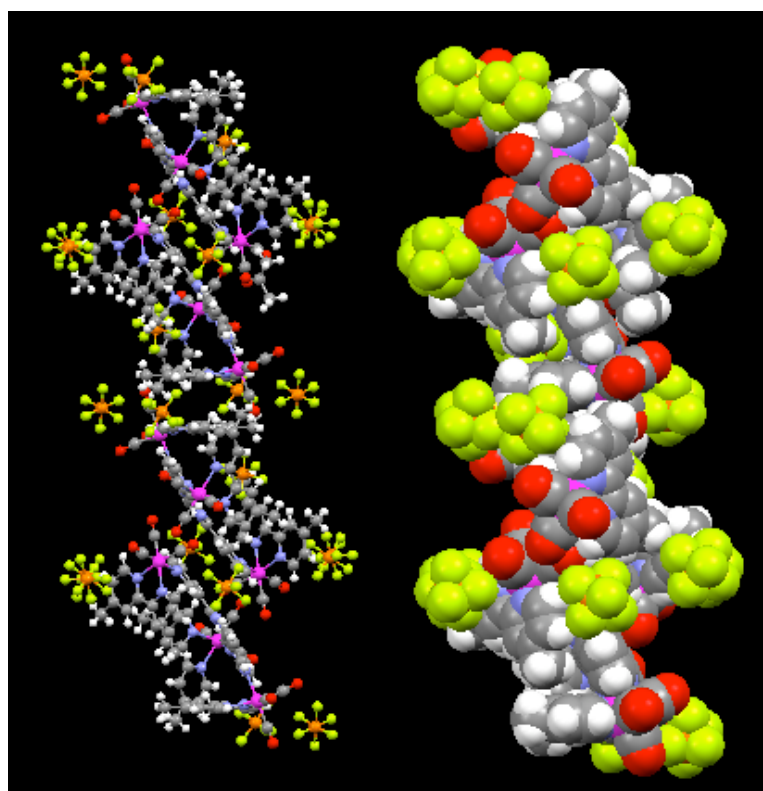**Fig. S6** Helical arrangement of complex **1** via two different types of π-π stacking along *a*-axis (one, π-π interaction between two dmbpy moieties and second, π-π interaction between one arm (3-pyridyl) each of two neighboring Re-complexes). All H-atoms has been removed for clarity.

Fig. S7 Crystal packing showing helical arrangement of complex **1** via π-π stacking (a) ball-stick model (left) and (b) space-fill model (right). Each conical cavity occupying one PF_6^- anion and rest two PF_6^- anions (per molecule) are involved in helical arrangement of complex **1**. Solvent molecules have been removed for clarity.
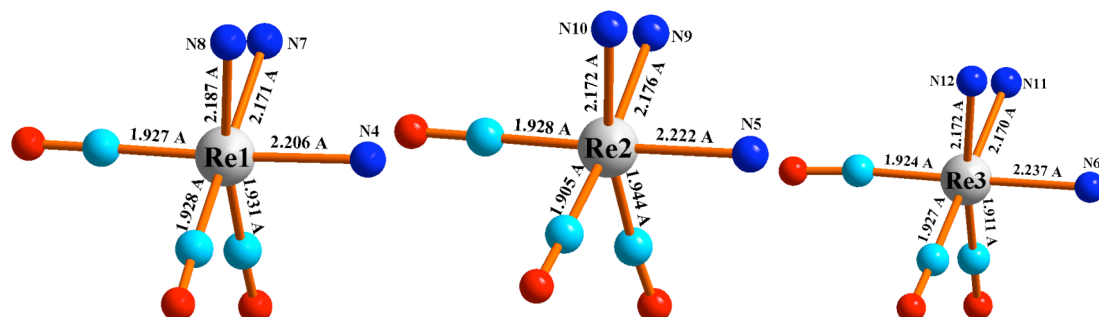
Fig. S8 The coordination environment around each octahedrally arranged Re-metal ion in complex **1**, showing dmbpy moiety binds at equatorial position.

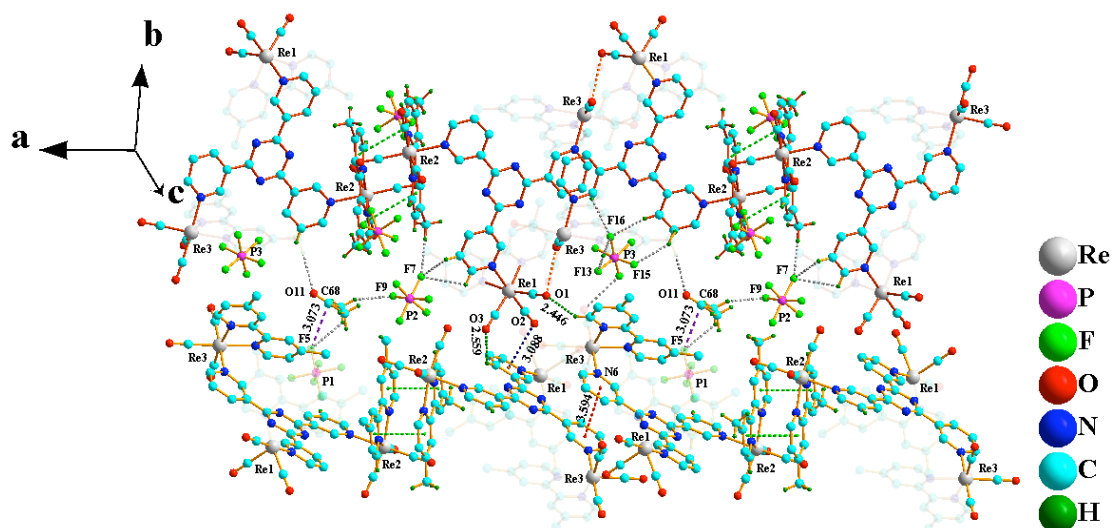**Fig. S9** Crystal packing diagram showing various interactions between two 1D-chain in *ab*-plane. Each discrete structure having three PF_6^- anions to balance the charge of three Re-metal ion, one PF_6^- anion (P1) is encapsulated within cavity (has been shown by light color) and rest two PF_6^- anions (P2 & P3) connecting two 1D-chain together (their interactions have been shown by gray colored dotted lines) to form two-dimensional sheet. All H-atoms (except those, playing role in intermolecular interactions) have been removed for clarity.

Table S1. Crystal Lattices and Refinement Data for the crystal of complex **1**

	1
Empirical formula	$C_{69}H_{60}F_{18}N_{12}O_{11}P_3Re_3$
Formula weight	2226.83
Temperature (K)	150.0(1)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a, Å	22.8100(5)
b, Å	25.0562(5)
c, Å	14.1649(3)
α (˚)	90
β (˚)	99.4580(10)
γ (˚)	90
V, Å^3	7985.6(3)
Z	4
ρ_{calc} Mg/m3	1.852
μ, mm^{-1}	4.702
F (000)	4312
T (min.)	0.125
T (max.)	0.205
Data/parameter	13979/1045
Reflection(Unique)	52621
GOOF	1.041
R $_{Final}$ R1 =	0.0424
I >2σ(I) wR2 =	0.1109
R $_{all}$ R1 =	0.0590
(all data) wR2 =	0.1230

Table S2. Selected bond distances (Å) and angles (°) in crystal structure of complex **1**

|				
Re1 --- C56	1.927(8)		C55 ---Re1 ---N8	170.5(3)
Re1 --- C57	1.928(9)		C56 ---Re1 ---C57	90.4(3)
Re1 --- C55	1.931(9)		C56 ---Re1 ---C55	89.0(4)
Re1 --- N7	2.170(6)		C57 ---Re1 ---C55	87.3(4)
Re1 --- N8	2.186(6)		C56 ---Re1 ---N7	92.9(3)
Re1 --- N4	2.206(6)		C57 ---Re1 ---N7	172.4(3)
Re2 --- C60	1.906(8)		C55 ---Re1 ---N7	99.6(3)
Re2 --- C59	1.927(9)		C56 ---Re1 ---N8	98.6(3)
Re2 --- C58	1.943(10)		C57 ---Re1 ---N8	98.4(3)
Re2 --- N10	2.173(7)		N7 ----Re1 ---N8	74.4(2)
Re2 --- N9	2.176(6)		C56 ---Re1 ---N4	177.5(3)
Re2 --- N5	2.222(6)		C57 ---Re1 ---N4	91.9(3)
Re3 --- C61	1.912(9)		C55 ---Re1 ---N4	92.2(3)
Re3 --- C62	1.925(8)		N7 ----Re1 ----N4	84.7(2)
Re3 --- C63	1.928(8)		N8 ----Re1 ----N4	80.0(2)
Re3 --- N11	2.171(6)		C60 ---Re2 ---C59	87.9(4)
Re3 --- N12	2.172(7)		C60 ---Re2 ---C58	89.1(4)
Re3 --- N6	2.236(6)		C59 ---Re2 ---C58	91.0(4)
			C60---Re2 ---N10	97.5(3)
			C59---Re2 ---N10	99.0(3)
			C58 ---Re2 ---N10	168.2(3)
			C60 ---Re2 ---N9	171.9(3)
			C59 ---Re2 ---N9	90.9(3)
			C58 ---Re2 ---N9	99.0(3)
			N10 ---Re2 ---N9	74.8(3)
			C60 ---Re2 ---N5	93.5(3)
			C59 ---Re2 ---N5	178.3(3)
			C58 ---Re2 ---N5	90.0(3)
			N10 ---Re2 ---N5	79.9(3)
			N9 ----Re2 ---N5	87.5(2)
			C61---Re3---C62	87.3(4)
			C61---Re3---C63	87.1(3)
			C62 ---Re3---C63	85.3(3)
			C61 ---Re3---N11	97.9(3)
			C62 ---Re3---N11	96.5(3)
			C63 ---Re3---N11	174.8(3)
			C61 ---Re3---N12	171.3(3)
			C62 ---Re3---N12	97.5(3)
			C63 ---Re3---N12	100.5(3)
			N11 ---Re3---N12	74.4(3)
			C61 ---Re3---N6	95.7(3)
			C62 ---Re3---N6	176.6(3)
			C63 ---Re3---N6	93.3(3)
			N11 ---Re3---N6	84.6(2)
			N12 ---Re3---N6	79.7(2)
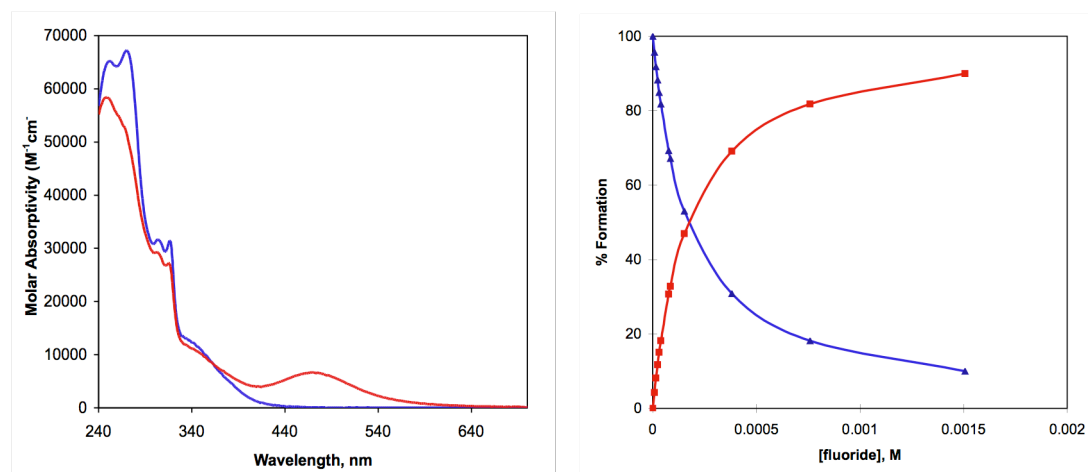
Fig. S10 Left: fitted spectra of complex **1** (blue curve) and 1•F⁻ adduct (red curve) in CH₃CN solution. Right: % formation vs. F⁻ concentration; blue curve, complex **1** and red curve, 1•F⁻ adduct.
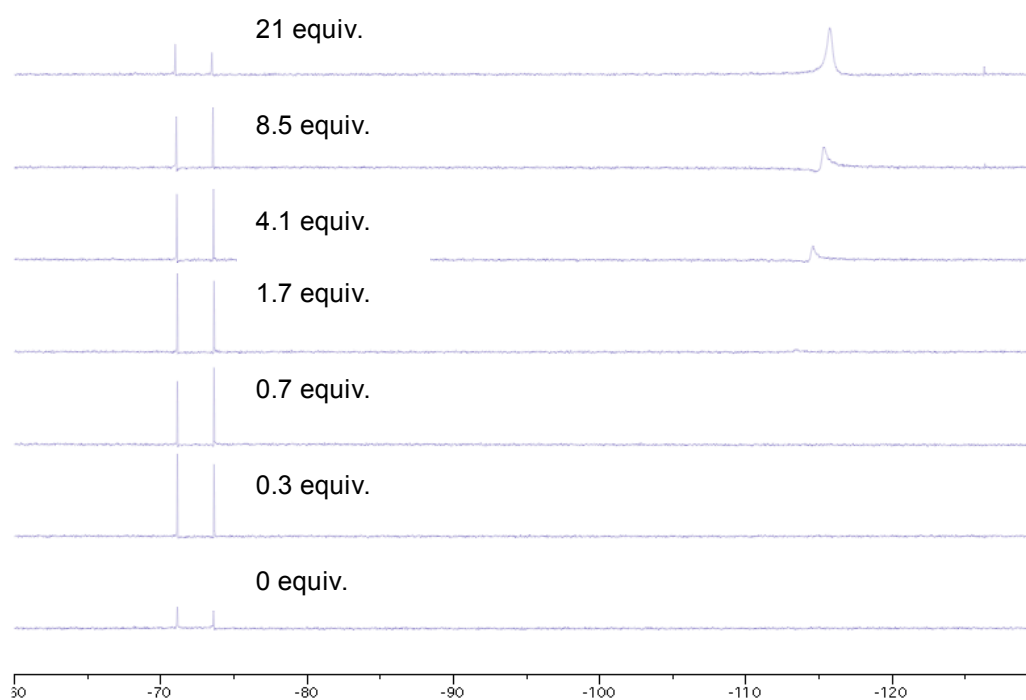
Fig. S11 Plots of ^{19}F NMR spectra of complex **1** on addition of F⁻ in CD₃CN. The doublet appeared at -72.1 ppm is the signal from PF_6^-, whereas the peak appeared at -117 ppm belongs to free TBAF.

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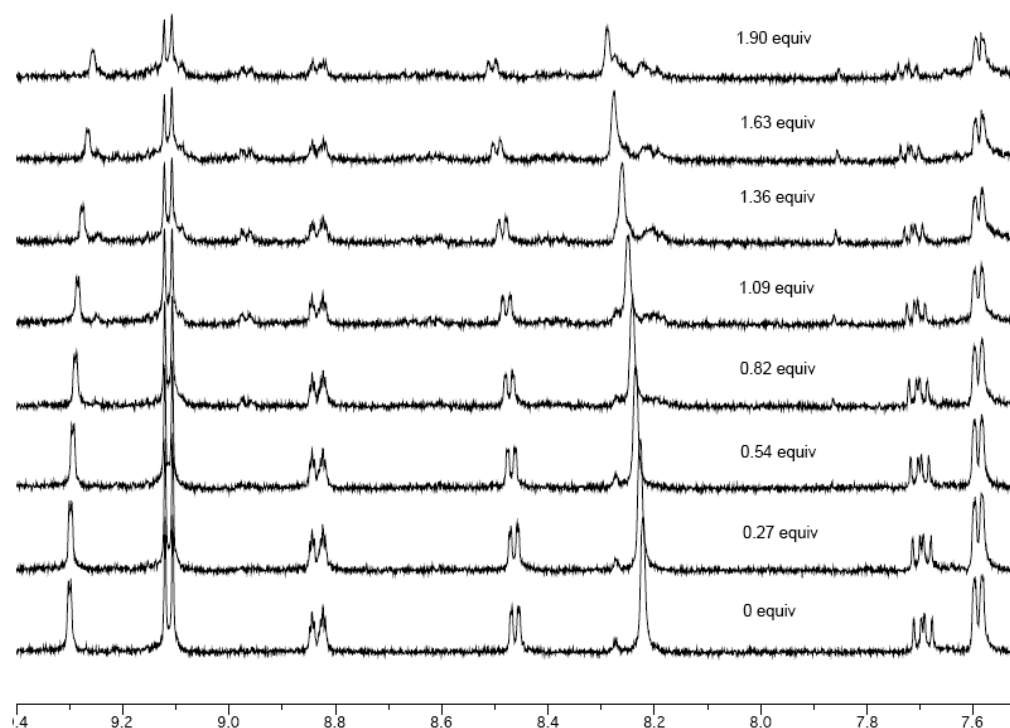
Fig. S12 Plots of ^{1}H NMR spectra of complex **1** on addition of F$^-$ in CD$_3$CN.

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