Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Blue-shifted aggregation-induced enhancement of Sn(IV) fluoride complex: The role of fluorine of enhancing emission

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Experimental Section

Materials. Commercially available chemical reagents were used without further purification.

Synthesis of complex 1

A solution of 1.5 mmol(0.2227g) 8-hydroxyquinoline(q) in 4.00 mL acetonitrile was added to solution of 0.5 mmol(0.1933g) Sn(IV) bis acetylacetonate dichloride in 3.00 mL acetonitrile. Then a solution of 2.0 mmol(0.3242g) ammonium hexafluorophosphate (NH_4PF_6) in about 2.0 mL water was added to the solution. The reaction mixture formed crystals within minutes and was left at room temperature for 24 hours to ensure sufficient crystal growth. The resulting green block crystals were vacuum filtrated and washed with 3.0 mL of cold acetonitrile. Elemental analysis calculated (found) for $C_{18}H_{12}F_2N_2O_2Sn$ (molar mass 445.01): C 48.58(48.08), H 2.72(2.80), N 6.30(6.30).Yield: 0.1340g(60.22%)

Synthesis Sn(8-hydroxyqunioline)$_2$Cl$_2$

A solution of 1.0 mmol (0.1432 g) of 8-Hydroxyquinoline dissolved in 3.00 mL of acetonitrile was added to a 0.5 mmol (0.1930 g) of Sn (IV) bis acetylacetone dichloride in 3.00 mL acetonitrile. The mixture was left for 24 hours before yellow block crystal product was collected and washed with cold acetonitrile. Elemental analysis calculated (found) for $C_{18}H_{12}Cl_2N_2O_2Sn$ (molar mass 477.91): C 45.24(44.46), H 2.53(2.58) N 5.86(5.58) Yield: 0.2208 g (92.85%).

General Experiments

The UV-visible spectra and fluorescence emission were recorded on Agilent Technologies Cary 60 UV-Vis and Carry Eclipse Fluorescence Spectrometer, respectively. All the cyclic voltammetric measurements were carried out in BASi CV 27 system. Measurements were made in pure and dry acetonitrile using Glassy carbon as a working electrode and the redox potentials are referenced against Ag/AgCl electrode. Tetrabutylammonium hexafluorophosphate (TBAP) is used as supporting electrolyte. Moles of electroactive species to supporting electrolyte ratio was maintained at 1:100 ratio. Acetonitrile solvent potential window was checked between +2.0 V to -2.5V range before any measurement was carried out with complex and ligand.

Emission lifetime decay Sample was dissolved in 2-MeTHF to achieve an optical density (absorbance) between 0.1-0.2 at the wavelength of irradiation in a 10 x 10 mm cuvette. The sample was placed into an Edinburg FLS-980 equipped with a 405 nm nano-LED diode samples were measured with a repetition rate of 5,000,000 Hz (200 ns gate width) and irradiated until 1×10^4 Counts by monitoring at the sample emission maxima. Instrument response factor (IRF) was determined using a standard Sigma Aldrich Ludox® colloidal light scattering solution in water at 405 nm. Fitting analysis was performed using Edinburgh software, using mono-exponential decay kinetics while taking the IRF into consideration. Goodness-of-fit was determined by reducing the chi-squared function. A value of $0.99 \geq \chi^2 \geq 1.4$ was considered acceptable. The kinetic decays and fits were prepared using Igor® 7.1 software[1]

Single crystals X-ray diffraction data of complex 1 were collected with XtaLAB Mini (ROW) diffractometer. Data collection, cell refinement and data reduction were performed using CrysAlis PRO software. The structures were solved and refined using SHELXL software. All non-hydrogen atoms were located in difference Fourier maps and were refined anisotropically. Hydrogen atoms were placed geometrically and refined using riding model. Crystal data and structure details are in Table S1.

Table S1 Crystal data and structure refinement for compound **1**.

Compound	1
Formula	$C_{18}H_{12}F_2N_2O_2Sn$
Formula weight	444.99
Crystal color	yellow
Crystal system	Monoclinic
Space group	C2/c
a/Å	13.4420(11)
b/Å	9.4200(7)
c/Å	13.5862(9)
β/°	108.526(8)
V/$Å^3$	1631.2(2)
D_c/Mg m^{-3}	1.812
Z	4
μ(Cu-Ka)/mm^{-1}	1.602
T/K	293
Refln. collected (R_{int})	6917 (0.0426)
Unique refln.	1977
Parameters	114
R_1 (R_1 all data)	0.0295 (0.0384)
wR_2 (wR_2 all data)	0.0667 (0.0708)
Goodness of fit	1.001

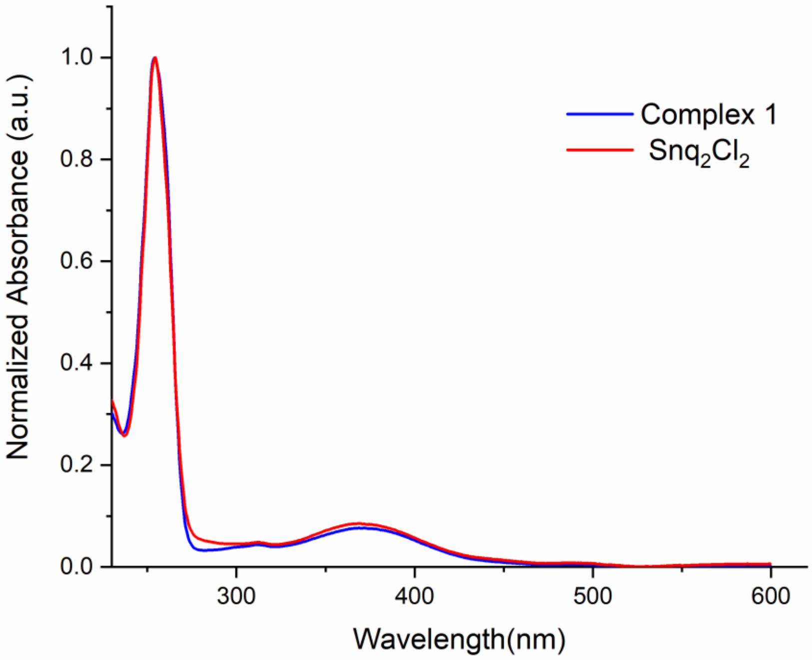

Figure S1 Absorption spectra of complex **1** and Snq_2Cl_2 in DMSO solution

Table S1 Selected bond length (Å) and angle (°) of complex **1** and Snq_2Cl_2 (X= Cl or F)

	Snq_2Cl_2	**1**
Sn-X distance (Å)	2.3893(9)	1.944(2)
X-Sn-X angle(°)	93.22(5)	94.2(1)
Sn-O distance(Å)	2.042(3)	2.031(2)
Sn-N distance(Å)	2.211(3)	2.205(2)

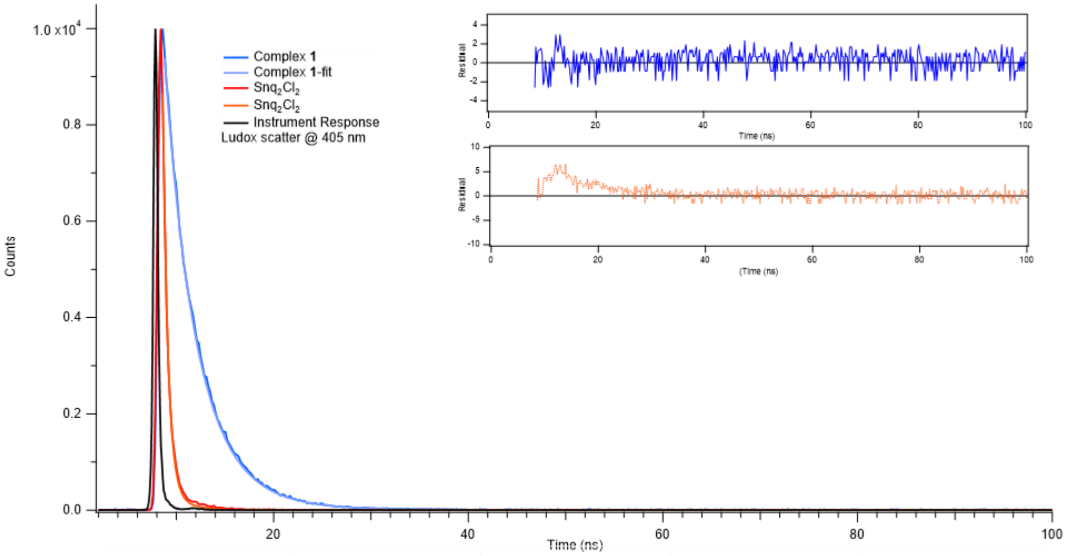

Fig.S2 Lifetime measurement of complex **1** and Snq_2Cl_2

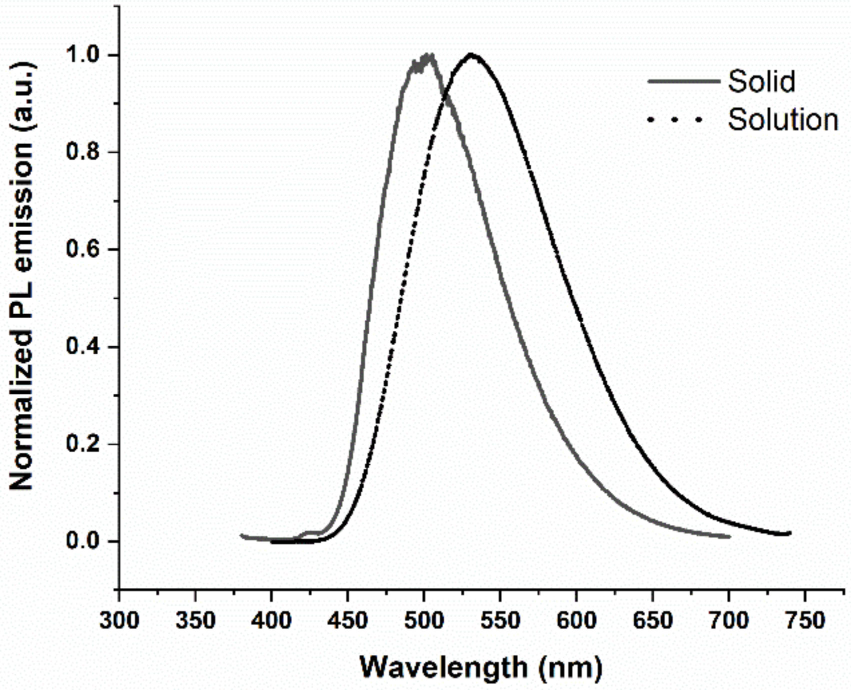

Figure S3 Phosphorescence spectra of **1** in acetonitrile solution and microcrystalline solid state (λ_{ex}=370 nm).

Both complexes show one irreversible reduction peak (E_{red}) assigned to Sn(IV)-Sn(III) reduction followed by a quasi-reversible redox couple ($E_{1/2}$) assigned to coordinated ligand (8-hydroxyquinoline) and an irreversible oxidation peak (E_{ox}) (ligand based) at room temperature. However, complex Snq_2F_2 **1**, showed systemic shift in the reduction potentials (~ 60-65 mV more negative) compared to Snq_2Cl_2 complex which is an indicative of a strong bonding interaction between Sn(IV) - F compared to the corresponding Snq_2Cl_2 complex. Similar trend is also notice in their ligand based oxidation potentials (E_{ox} = 1.71V vs 1.64V) of the two complexes which could be attributable to the enhancement of bonding interaction between the 8-hydroxyquinoline to Sn(IV) ion when F^- ion is bonded to the same metal center as an ancillary ligand. The origin of an unknown reduction peak (~ 1.44 V) for Snq_2F_2 complex is still not clear. The CV of ligand (8-hydroxy quinolone) under identical condition showed one irreversible reduction (E_{red}) at -2.0 V and one irreversible oxidation (E_{ox}) peak at +1.2 V however, when it is coordinated to Sn (IV) metal center, the irreversible reduction process changed to a quasi-reversible ($E_{1/2}$ ~ -1.7 V) in nature. The results are tabulated in Table S3.

Table S3 Electrochemical data of complex **1** and Snq_2Cl_2 in acetonitrile solution (CV data of ligand, 8-hydroxyquinoline, is presented for comparison.

compounds	*$E^1{}_{red}$ (V)	*$E^2{}_{red}$ (V) ($E_{1/2}$)	E_{ox} (V)
Snq_2F_2 ,**1**	-1.33	-1.78 (-1.7)	+1.71
Snq_2Cl_2	-1.26	-1.72 (-1.75)	+1.64
8-hydroxyquinoline	-2.0	-	+ 1.2

*****E^1 and E^2 correspond to 1st and 2nd reduction potentials.

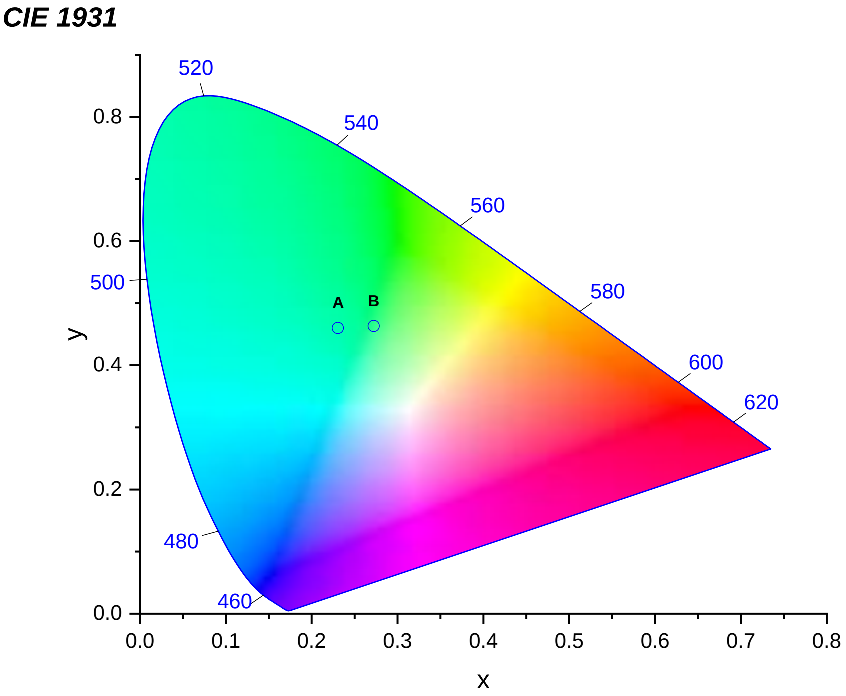

Figure S4 CIE coordinates calculated using the Origin software. A(solid): (0.2306, 0.46003); B(solution): (0.2722, 0.46325).

Reference

1. B. C. Pemberton, E. Kumarasamy, S. Jockusch, D. K. Srivastava and J. Sivaguru, *Can. J. Chem.* *2011,**89**,310-316*