Electronic Supporting Information

Binding discrepancy of fluoride in quaternary ammonium and alkali salts by a tris(amide) receptor in solid and solution-states

*Sandeep Kumar Dey, Barun Datta and Gopal Das**

Department of Chemistry, Indian Institute of Technology Guwahati, Assam-781039, India

E-mail: gdas@iitg.ernet.in

Characterization of receptor L:

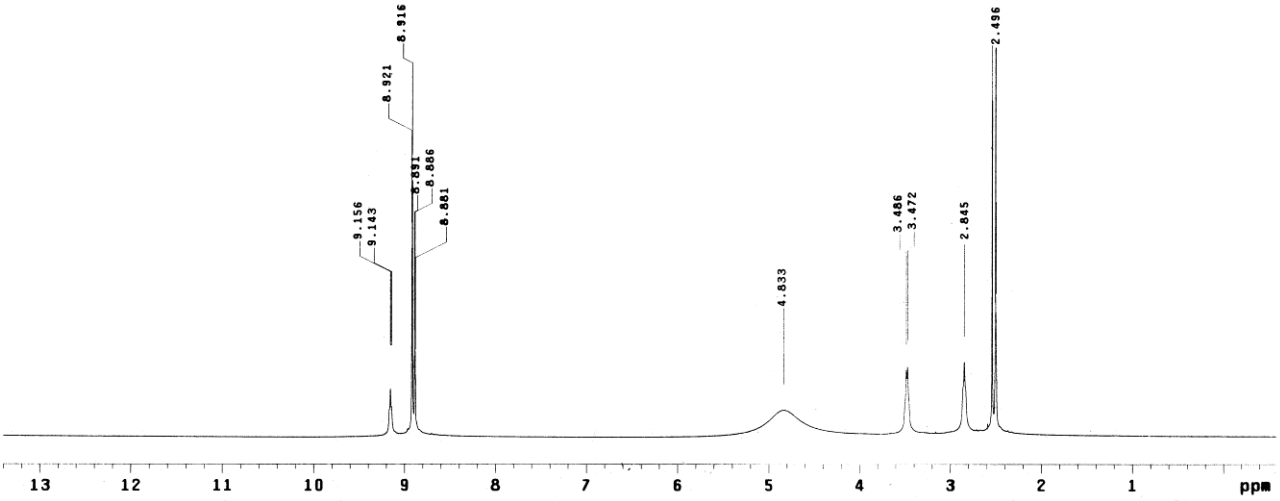

Figure S1. ^{1}H NMR spectrum of **L** in DMSO-d_6 at 298 K.

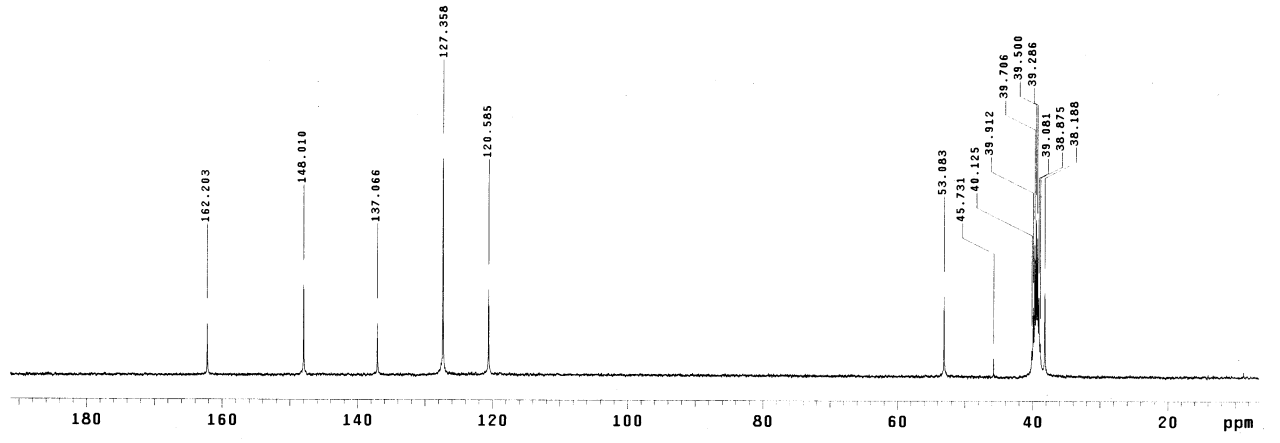

Figure S2. ^{13}C NMR spectrum of **L** in DMSO-d_6 at 298 K.

Characterization of TBAF complex, 1d:

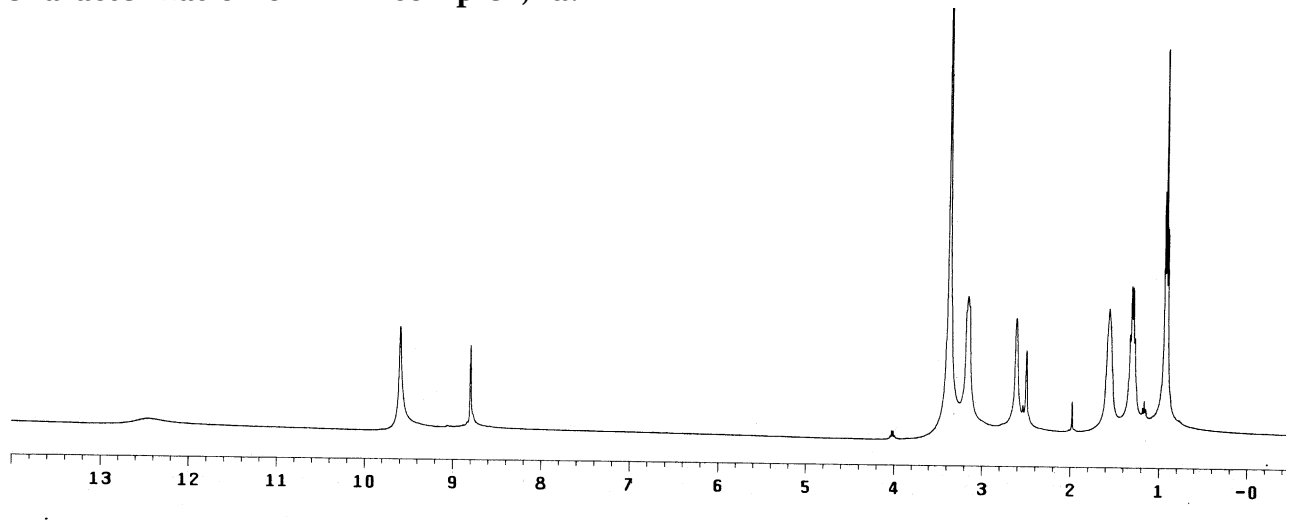

Figure S3. ^{1}H NMR spectrum of TBAF complex, **1d** in DMSO-d_6 at 298 K.

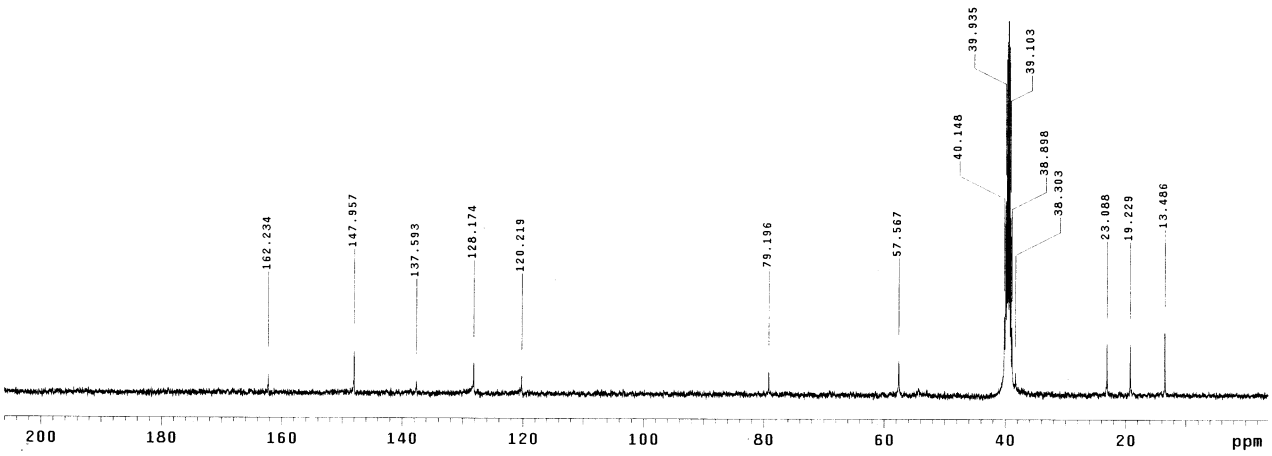

Figure S4. ^{13}C NMR spectrum of TBAF complex, **1d** in DMSO-d_6 at 298 K.

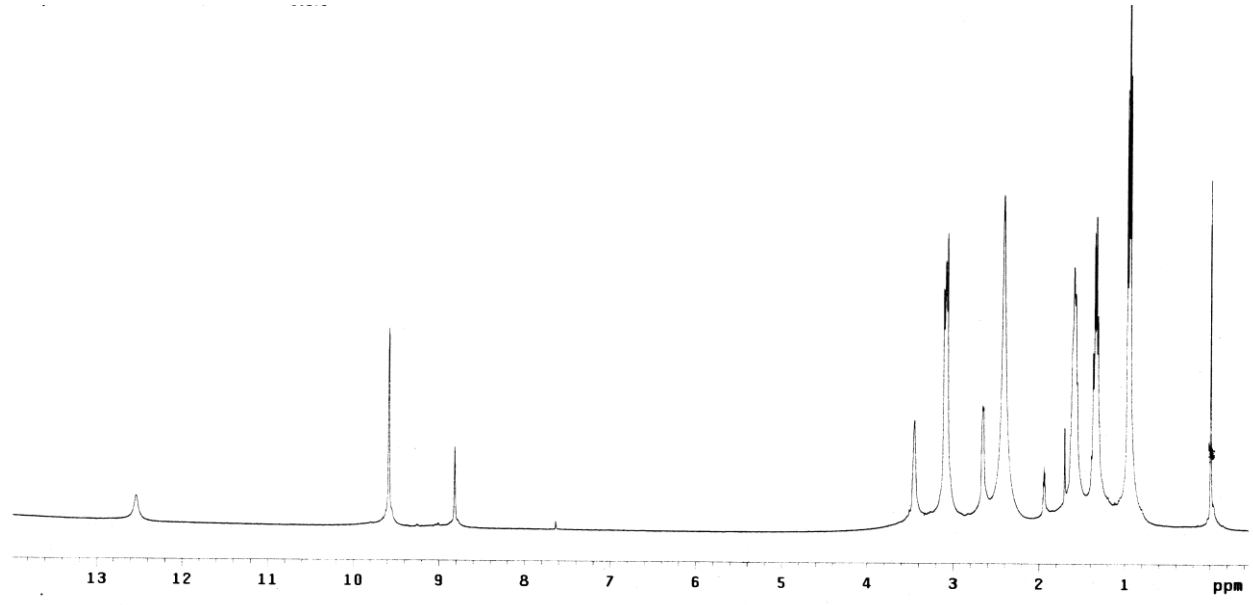

Figure S5. ^{1}H NMR spectrum of TBAF complex, **1d** in CD_3CN at 298 K.

Characterization of KF complex, 2:

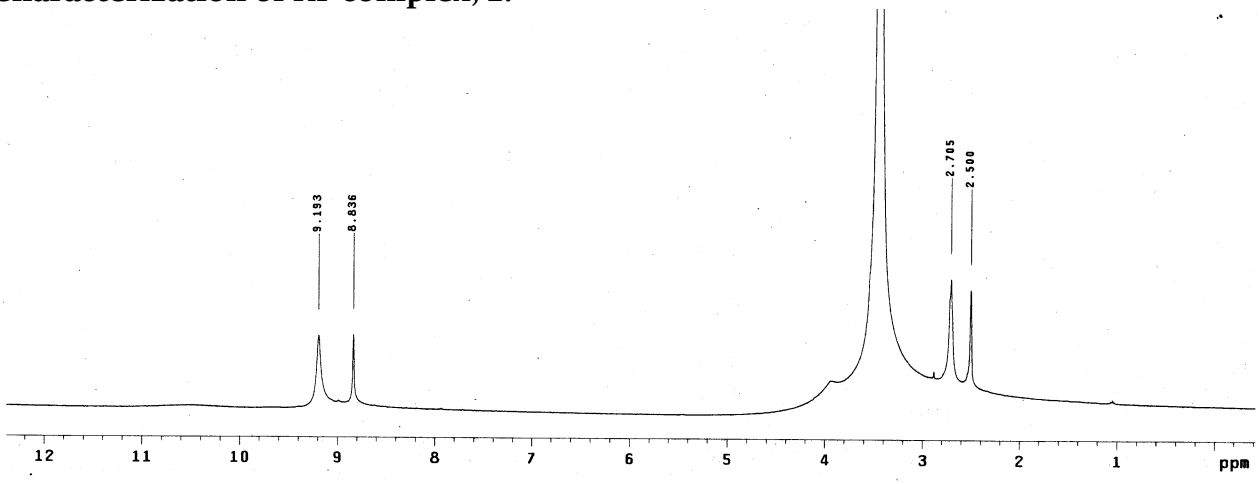

Figure S6. ^{1}H NMR spectrum of KF complex, **2** in DMSO-d_6 at 298 K.

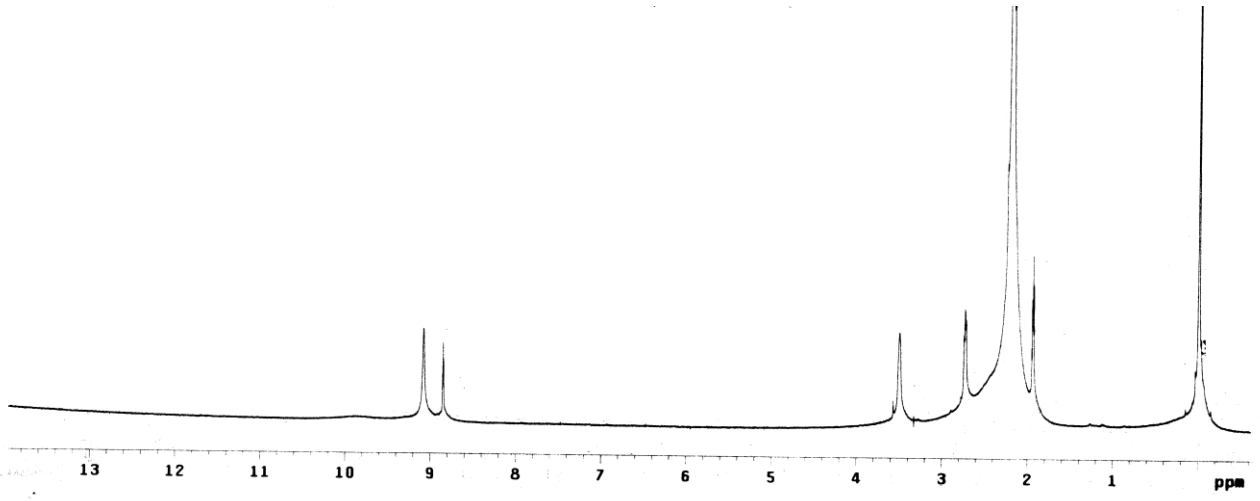

Figure S7. ^{1}H NMR spectrum of KF complex, **2** in CD_3CN at 298 K.

Additional Crystallographic data:

Table S1. Crystallographic parameters and refinement details of **L**-DMSO, **L**-DMF and complexes **1d** and **2**.

Parameters	**L**-DMSO	**L**-DMF	Complex **1d**	Complex **2**
Formula	$C_{29}H_{30}N_{10}O_{16}S$	$C_{30}H_{31}N_{11}O_{16}$	$C_{46}H_{60}FN_{11}O_{16}$	$C_{27}H_{24}FKN_{10}O_{17}$
Fw	806.70	801.66	1042.05	1858.21
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*-1	P_21/c	*P*-1	*P*-1
a/Å	11.2942(3)	17.2139(6)	10.1372(3)	11.2710(12)
b/Å	12.4744(4)	11.1890(3)	16.4160(5)	12.4543(13)
c/Å	12.8671(4)	25.1968(7)	17.3515(8)	12.8718(14)
α/°	84.723(2)	90.00	109.413(2)	84.825(6)
β/°	79.650(3)	131.890(2)	97.059(2)	79.744(6)
γ/°	88.404(2)	90.00	106.906(1)	88.329(6)
V/Å^3	1775.65(9)	3612.8(2)	2527.35(17)	1770.6(3)
Z	2	4	2	2
D_c/g cm^{-3}	1.509	1.474	1.369	1.536
μ Mo K_α/mm^{-1}	0.180	0.122	0.107	0.246
T/K	298(2)	298(2)	180(2)	298(2)
θ max.	28.29	28.390	28.270	27.140
Total no. of reflections	13679	49295	26140	26731
Independent reflections	8734	8991	9814	7784
Observed reflections	7605	4777	7233	6870
Parameters refined	520	516	683	505
R_1, $I > 2\sigma(I)$	0.0508	0.0580	0.0645	0.0838
wR_2 (all data)	0.1510	0.2115	0.2429	0.2728
GOF (F^2)	0.911	1.023	1.005	1.035

Table S2. Hydrogen bond interactions involved in the crystal structures of **L**-DMSO.

L-DMSO	D-H···A	*d*(H···A)	*d*(D···A)	<(D-H···A)
Intraligand interactions	N8-H···O6	1.94(3)	2.891(3)	167(3)
	C27-H···O6	2.46(2)	3.185(3)	134(2)
	C1g···C2g		3.756	
Interactions with lattice DMSO	N5-H···O16	1.98(3)	2.834(3)	157(2)
	C14-H···O16	2.34(2)	3.239(3)	161(2)
	O16···C2g		3.532	
Interligand interactions	N2-H···O11	1.98(3)	2.856(3)	134(2)
	C1-H···O11	2.70(2)	3.427(3)	132(1)
	C20-H···O2	2.65(2)	3.127(4)	110(2)
	C19-H···O13	2.64(2)	3.309(3)	125(2)
	C19-H···O15	2.66(2)	3.530(4)	148(2)
	O8···C24		3.169(3)	
	O5···C12		3.023(3)	
	O12···N3		2.987(3)	
	O12···O3		3.007(3)	

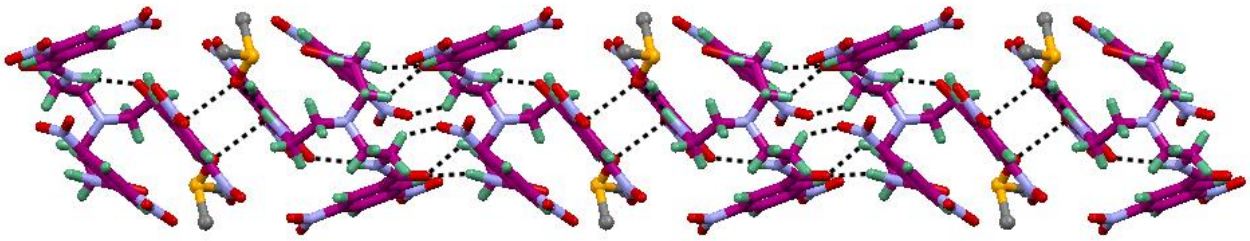

Figure S8. Solvent bridged 1D chain in **L**-DMSO diagonally along a*c*-axis.

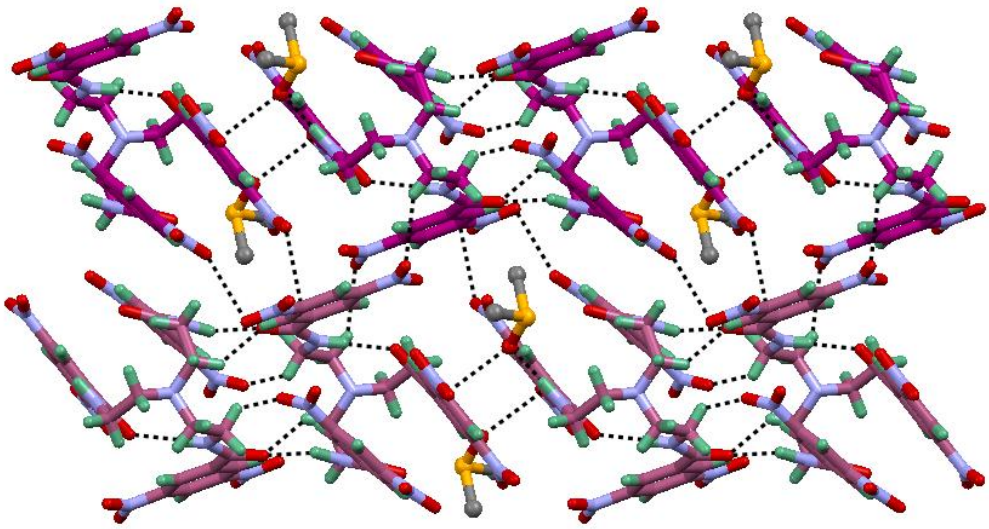

Figure S9. Crystal packing of **L**-DMSO as viewed down the *a*-axis showing the H-bonding and electron donor-acceptor interactions between two adjacent solvent-bridged 1D chains of receptor molecules.

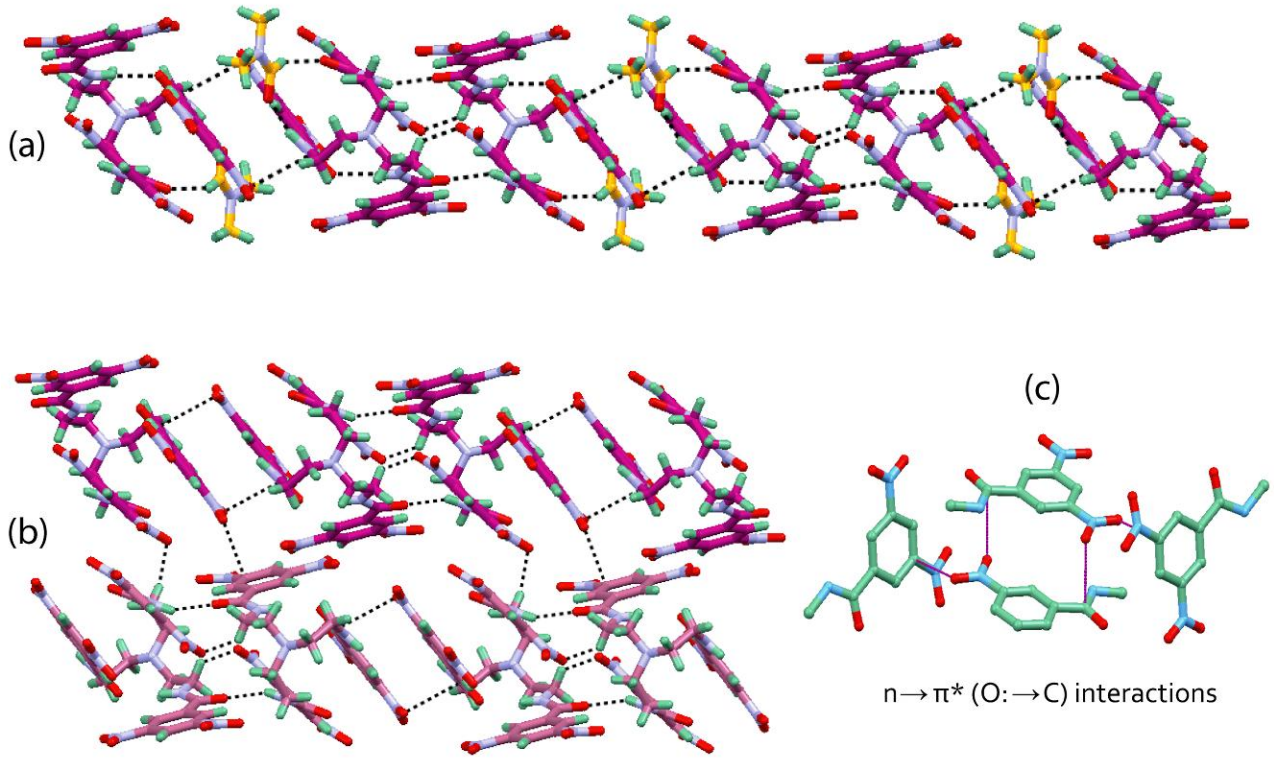

Figure S10. (a) Solvent bridged 1D chain of **L**-DMF along *c*-axis. (b) Crystal packing of **L**-DMF as viewed down the *b*-axis showing the intermolecular H-bonding and electron donor-acceptor interactions between two adjacent 1D chains of receptor molecules (Lattice DMF molecules are omitted for clarity). (c) Magnified view of the n→π* (O:→C) electron donor-acceptor interactions between the adjacent receptor molecules in **L**-DMF.

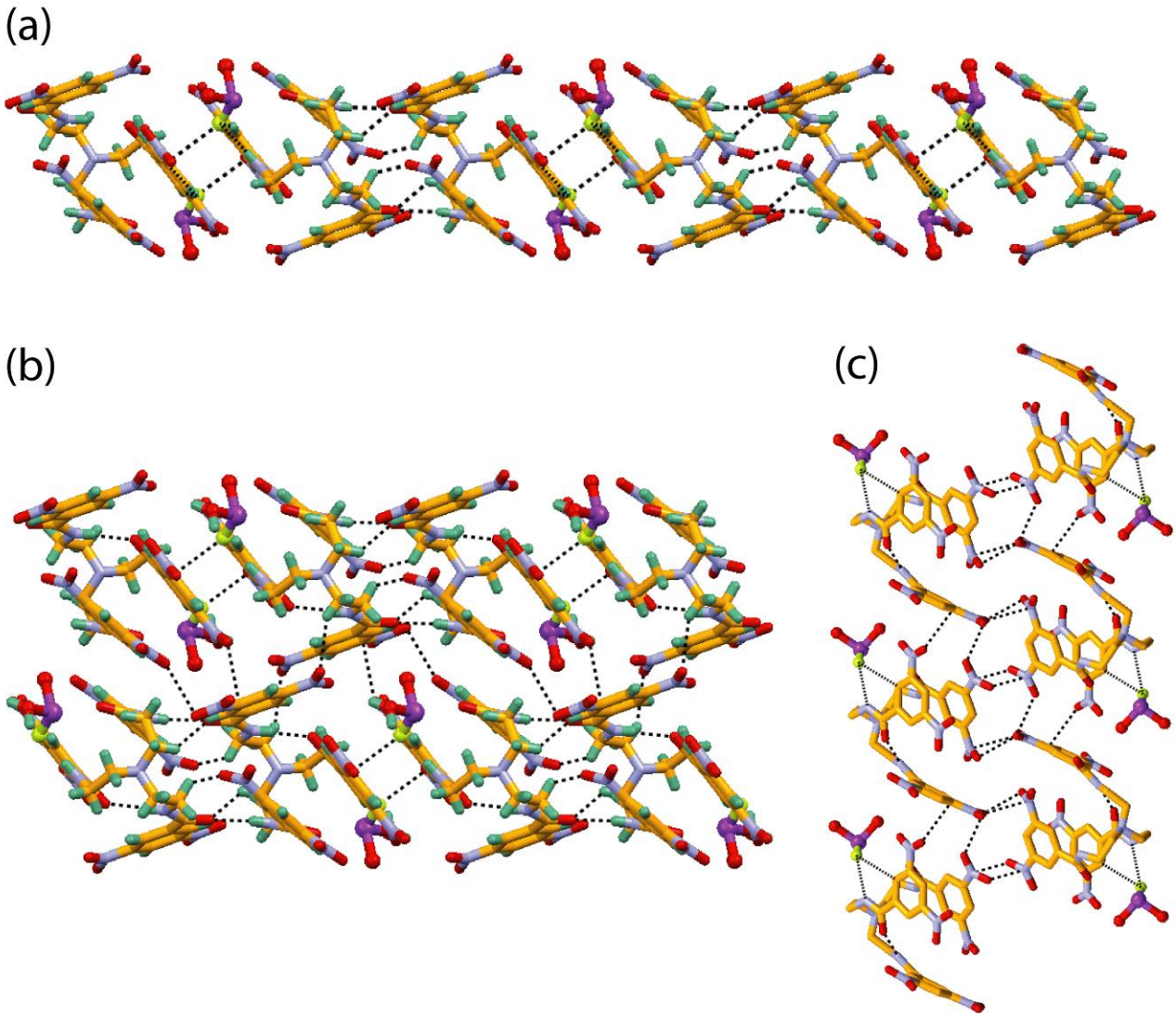

Figure S11. (a) H-bonded $KF(H_2O)_2$ bridged 1D chain of **L** in **2** diagonally along *ac*-axis. (b) Crystal packing of **2** as viewed down the *a*-axis showing the H-bonding and electron donor-acceptor interactions between two adjacent 1D chains of receptor molecules. (c) View of the n→π* (O:→N/C) electron donor-acceptor interactions between the adjacent 1D chains.

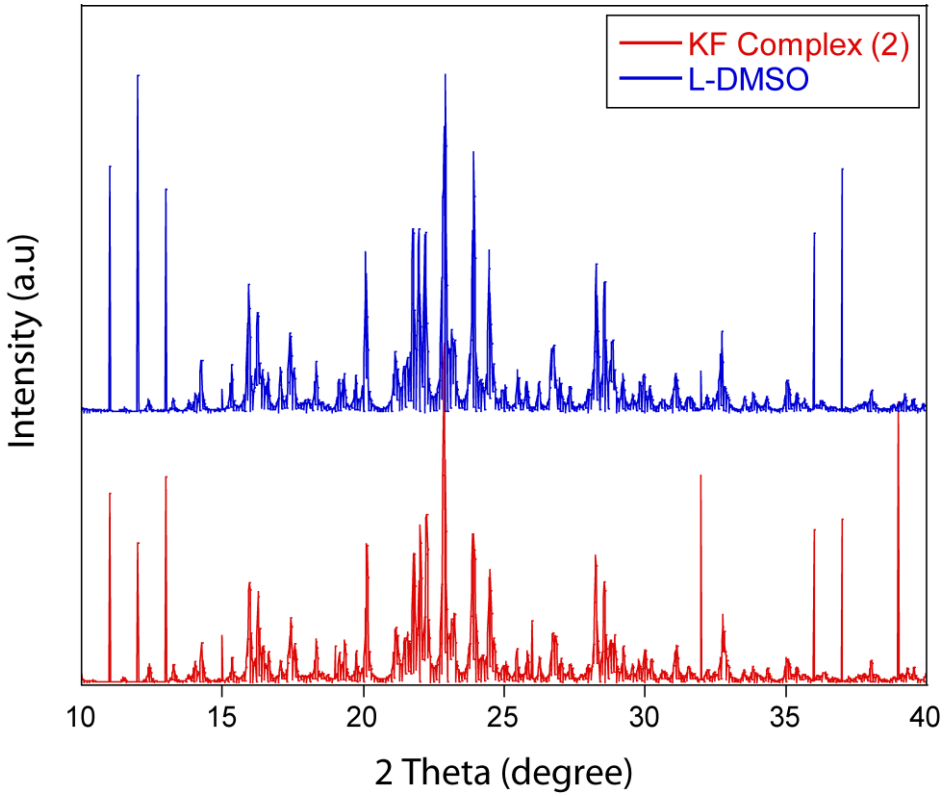

Figure S12. Simulated PXRD patterns of isostructural **L**-DMSO and KF complex (**2**).

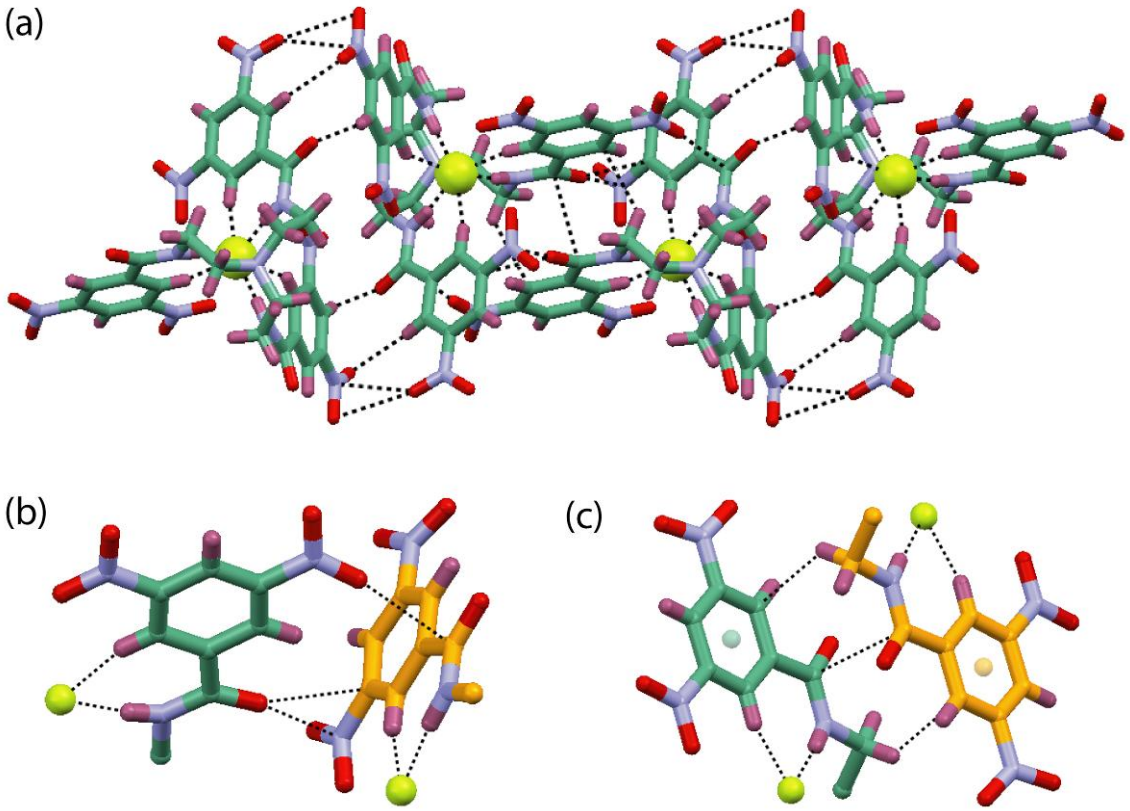

Figure S13. (a) H-bonding and electron donor-acceptor interactions (n→π*/n→π*(k) and π→π*) between two F^- encapsulated receptor dimers. (b) Magnified view of the n→π* (O:→N/C) interactions. (c) Magnified view of the aliphatic C-H•••π and π→π* (C:→C) interactions.

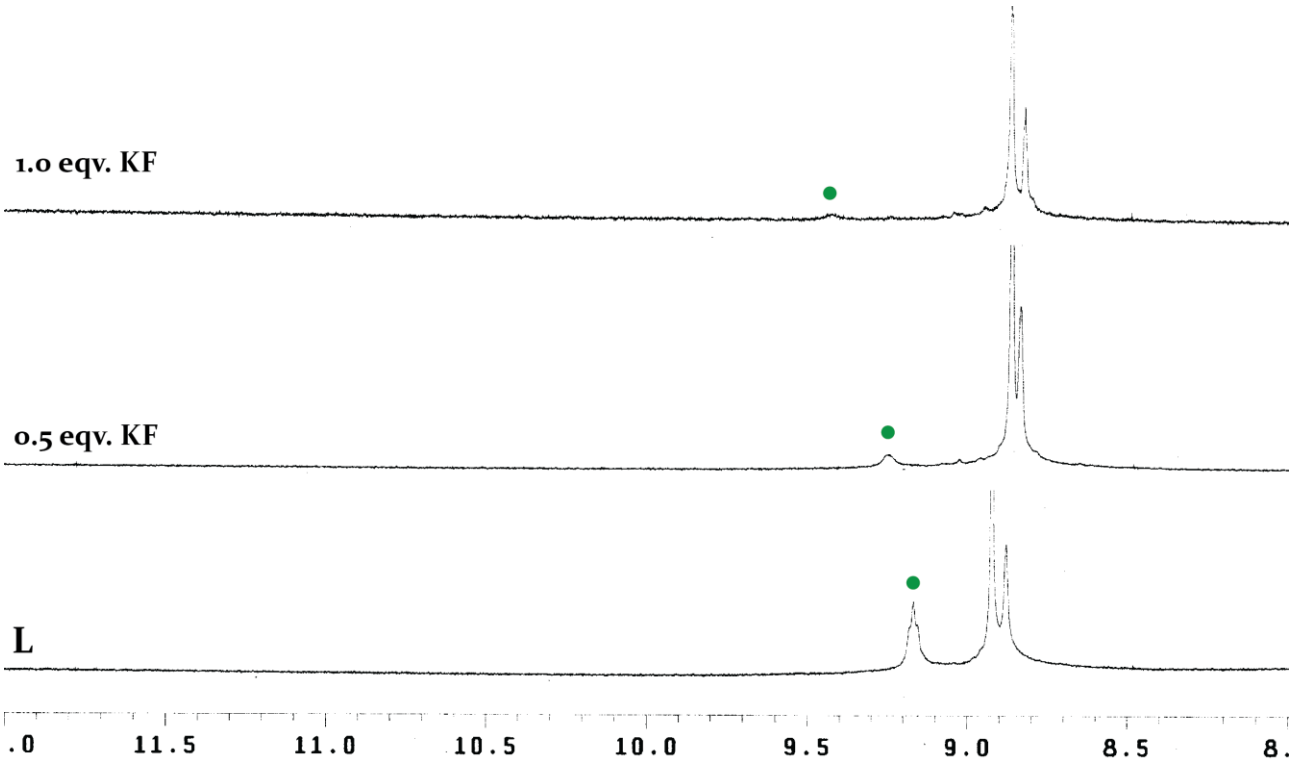

Figure S14. ^{1}H NMR titration of **L** with KF in DMSO-d_6 at 298 K, showing the downfield shift of amide –NH protons up to 1 equiv. of KF beyond which precipation occurs.