Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information†

Rotational characterization of a S···F chalcogen bond in the complex of 2,2,4,4-tetrafluoro-1,3-dithietane and difluoromethane

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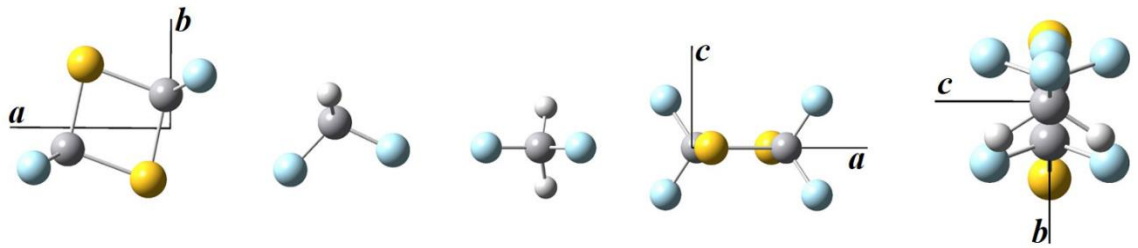

Fig. S1 The MP2/6-311++G(d,p) calculated equilibrium structures of the observed conformer of $C_2F_4S_2$-DFM dimer in the *ab*-, *ac*-, and *bc*-planes.

Table S1. *Ab initio* and DFT predictions for the structure of conformer I of $C_2F_4S_2$-DFM in the principal inertial axis system (MP2/6-311++G(d,p) and B3LYP-D3(BJ)/def2-TZVP).

	a / Å		***b*** / Å		***c*** / Å	
	MP2	B3LYP-D3(BJ)	MP2	B3LYP-D3(BJ)	MP2	B3LYP-D3(BJ)
C (1)	2.1671	2.1809	-0.4513	-0.4772	-0.0001	0.0000
F (2)	2.8813	2.8835	-0.8461	-0.8878	1.0751	1.0749
F (3)	2.8805	2.8836	-0.8460	-0.8878	-1.0758	-1.0748
S (4)	1.8041	1.8439	1.3303	1.3207	0.0001	0.0000
C (5)	0.1027	0.1137	0.7012	0.7425	0.0001	0.0000
F (6)	-0.6123	-0.5904	1.1098	1.1648	1.0745	1.0745
F (7)	-0.6121	-0.5904	1.1093	1.1648	-1.0749	-1.0745
S (8)	0.4620	0.4466	-1.0754	-1.0502	0.0005	0.0000
F (9)	-2.5353	-2.5946	-0.8544	-0.9249	0.0002	0.0000
C (10)	-3.4705	-3.4840	0.1446	0.1167	-0.0001	0.0000
H (11)	-3.3486	-3.3353	0.7264	0.6948	0.9123	0.9119
H (12)	-3.3484	-3.3353	0.7260	0.6948	-0.9128	-0.9119
F (13)	-4.7020	-4.7412	-0.4278	-0.3993	-0.0001	0.0000

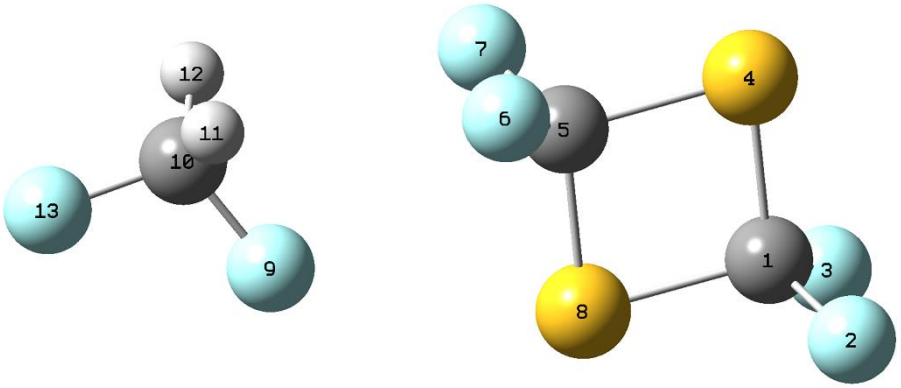

Table S2. *Ab initio* and DFT predictions for the structure of conformer II of $C_2F_4S_2$-DFM in the principal inertial axis system (MP2/6-311++G(d,p) and B3LYP-D3(BJ)/def2-TZVP).

	a / Å		***b*** / Å		***c*** / Å	
	MP2	B3LYP-D3(BJ)	MP2	B3LYP-D3(BJ)	MP2	B3LYP-D3(BJ)
C (1)	3.5742	3.6007	0.0534	0.0379	-0.2551	-0.3307
H (2)	4.4832	4.4033	0.2787	0.1639	-0.8123	-1.0584
H (3)	3.2920	3.1840	-0.9978	-0.9684	-0.2740	-0.3055
C (4)	-0.0144	-0.0514	-0.7234	-0.7495	-0.0945	-0.0819
C (5)	-2.0624	-2.1151	0.4465	0.4663	0.0871	0.0865
S (6)	-0.3918	-0.4019	1.0382	1.0377	-0.3039	-0.1834
S (7)	-1.6827	-1.7620	-1.3174	-1.3248	0.3056	0.1920
F (8)	-2.9568	-2.9544	0.6777	0.7859	-0.8982	-0.9198
F (9)	-2.5866	-2.6797	1.0165	0.9656	1.1933	1.2046
F (10)	0.5010	0.5096	-1.3033	-1.2585	-1.2018	-1.2009
F (11)	0.8834	0.7904	-0.9694	-1.0806	0.8864	0.9217
F (12)	2.5515	2.5970	0.7845	-0.9141	-0.7936	-0.6461
F (13)	3.7403	4.0702	0.4431	-0.3543	1.0344	0.9044

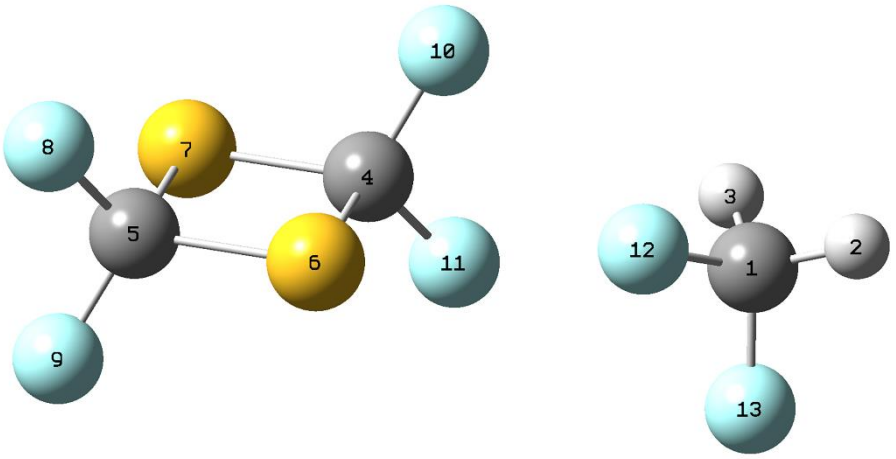

Table S3. Experimental transition frequencies of the observed parent species of $C_2F_4S_2$-DFM.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz
2	2	1	1	1	0	5597.2285	0.0014
2	2	0	1	1	1	5628.1781	0.0010
3	2	2	2	1	1	6315.4595	0.0009
3	2	1	2	1	2	6409.3254	0.0045
3	3	1	2	2	0	9104.2718	0.0005
3	3	0	2	2	1	9104.7832	-0.0001
4	2	3	3	1	2	7018.3892	-0.0001
4	2	2	3	1	3	7208.6414	0.0077
4	3	2	3	2	1	9851.9061	-0.0016
4	3	1	3	2	2	9854.4766	-0.0005
4	4	1	3	3	0	12596.4721	0.0012
4	4	0	3	3	1	12596.4721	-0.0041
5	3	3	5	2	4	6862.9230	0.0012
5	3	2	5	2	3	6845.3867	-0.0009
5	4	2	5	3	3	9600.1949	-0.0022
5	4	1	5	3	2	9600.0507	0.0008
5	2	4	4	1	3	7706.0713	-0.0001
5	2	3	4	1	4	8028.1470	0.0010
5	3	3	4	2	2	10597.5866	-0.0015
5	3	2	4	2	3	10605.3244	-0.0021
5	4	2	4	3	1	13345.2173	-0.0004
5	4	1	4	3	2	13345.2588	0.0038
5	5	1	4	4	0	16088.2933	-0.0008
5	5	0	4	4	1	16088.2933	-0.0009
6	3	4	6	2	5	6867.8280	0.0007
6	3	3	6	2	4	6833.0102	0.0005
6	4	3	6	3	4	9599.2576	0.0003
6	4	2	6	3	3	9598.8177	0.0007
6	1	6	5	0	5	5554.4052	0.0014
6	2	5	5	1	4	8378.6178	0.0021
6	2	4	5	1	5	8870.3719	0.0020
6	3	4	5	2	3	11339.9125	-0.0014
6	3	3	5	2	4	11358.0360	-0.0020
6	4	3	5	3	2	14093.7837	0.0001
6	4	2	5	3	3	14093.9309	-0.0023
6	5	2	5	4	1	16837.0672	0.0007
6	5	1	5	4	2	16837.0672	0.0003
6	6	1	5	5	0	19579.9666	0.0015
6	6	0	5	5	1	19579.9666	0.0015
7	3	5	7	2	6	6875.6328	-0.0010
7	3	4	7	2	5	6813.5623	0.0008

7	4	4	7	3	5	9597.8681	0.0003
7	4	3	7	3	4	9596.7693	-0.0010
7	1	7	6	0	6	6207.7711	-0.0006
7	2	6	6	1	5	9036.2044	0.0015
7	2	5	6	1	6	9738.2332	0.0018
7	3	5	6	2	4	12077.1390	-0.0020
7	3	4	6	2	5	12113.5039	-0.0021
7	4	4	6	3	3	14841.9982	-0.0009
7	4	3	6	3	4	14842.4494	0.0004
7	5	3	6	4	2	17585.7627	0.0009
7	5	2	6	4	3	17585.7627	-0.0012
8	4	5	8	3	6	9595.9608	-0.0004
8	4	4	8	3	5	9593.5519	-0.0039
8	1	8	7	0	7	6853.0989	0.0036
8	2	7	7	1	6	9679.1001	0.0023
8	2	6	7	1	7	10634.9626	-0.0028
8	3	6	7	2	5	12807.2232	-0.0005
8	3	5	7	2	6	12872.8291	0.0002
8	4	5	7	3	4	15589.6236	0.0002
8	4	4	7	3	5	15590.7502	-0.0007
8	5	4	7	4	3	18334.3193	-0.0033
8	5	3	7	4	4	18334.3341	0.0039
9	0	9	8	1	8	5774.5909	-0.0051
9	1	9	8	0	8	7492.7310	-0.0016
9	2	8	8	1	7	10307.6657	-0.0008
9	2	7	8	1	8	11563.9717	-0.0019
9	3	7	8	2	6	13527.8900	-0.0007
9	3	6	8	2	7	13637.3273	0.0006
9	4	6	8	3	5	16336.3250	-0.0019
9	4	5	8	3	6	16338.8122	-0.0011
9	5	5	8	4	4	19082.6805	0.0034
9	5	4	8	4	5	19082.6979	-0.0020
10	0	10	9	1	9	6595.1853	-0.0006
10	1	10	9	0	9	8129.1794	0.0007
10	2	9	9	1	8	10922.3964	-0.0009
10	2	8	9	1	9	12528.6503	0.0034
10	3	8	9	2	7	14236.7570	-0.0004
10	3	7	9	2	8	14408.5607	-0.0007
10	4	7	9	3	6	17081.6739	0.0028
10	4	6	9	3	7	17086.6542	-0.0002
11	0	11	10	1	10	7412.3740	-0.0023
11	1	11	10	0	10	8764.9258	0.0009
11	2	10	10	1	9	11523.9223	-0.0015
11	2	9	10	1	10	13532.1725	0.0001

11	3	9	10	2	8	14931.4703	0.0001
11	3	8	10	2	9	15188.3573	0.0003
11	4	8	10	3	7	17825.0829	-0.0020
11	4	7	10	3	8	17834.3571	0.0011
12	0	12	11	1	11	8224.1447	-0.0006
12	1	12	11	0	11	9402.3030	0.0015
12	3	10	11	2	9	15609.8614	-0.0048
12	3	9	11	2	10	15978.8227	0.0037
12	4	9	11	3	8	18565.8408	0.0008
12	4	8	11	3	9	18582.0861	0.0014
13	0	13	12	1	12	9028.9272	0.0000
13	1	13	12	0	12	10043.3295	0.0012
7	0	7	6	0	6	5212.7956	-0.0017
7	1	7	6	1	6	5127.8438	-0.0039
7	1	6	6	1	5	5340.2744	-0.0009
8	0	8	7	0	7	5947.9481	0.0021
8	1	8	7	1	7	5858.1223	0.0013
8	1	7	7	1	6	6100.3249	-0.0001
9	0	9	8	0	8	6679.7441	-0.0012
9	1	9	8	1	8	6587.5853	0.0020
9	1	8	8	1	7	6859.1248	-0.0009
10	0	10	9	0	9	7408.1737	0.0005
10	1	10	9	1	9	7316.1918	0.0004
10	1	9	9	1	8	7616.4532	0.0003
11	0	11	10	0	10	8133.3824	0.0006
11	1	11	10	1	10	8043.9193	-0.0002
11	1	10	10	1	9	8372.0619	0.0019
12	0	12	11	0	11	8855.6901	0.0017
12	1	12	11	1	11	8770.7572	-0.0012
12	1	11	11	1	10	9125.6765	-0.0021

Table S4. Measured transition frequencies of the three observed ^{13}C isotopic species of $C_2F_4S_2$-DFM.

J'	K_a'	K_c'	J''	K_a''	K_c''	^{13}C-C1		^{13}C-C5		^{13}C-C10	
						ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz
4	4	1	3	3	0	12585.9847	-0.0002	12574.1450	0.0020	12591.9739	-0.0013
4	4	0	3	3	1	12585.9902	0.0001	12574.1503	0.0019	12591.9792	-0.0010
5	4	2	4	3	1	13332.1151	-0.0042	13322.7542	-0.0009	13334.0614	-0.0042
5	4	1	4	3	2	13332.1592	0.0032	13322.7966	0.0036	13334.1022	0.0014
5	5	1	4	4	0	16075.1840	-0.0015	16059.6043	-0.0020	16083.4657	0.0006
5	5	0	4	4	1	16075.1840	-0.0015	16059.6043	-0.0020	16083.4657	0.0006
6	4	3	5	3	2	14078.0714	-0.0034	14071.1842	0.0002	14075.9804	-0.0020
6	4	2	5	3	3	14078.2244	0.0023	14071.3327	-0.0036	14076.1228	-0.0007
6	5	2	5	4	1	16821.3485	0.0035	16808.2450	0.0005	16825.5777	-0.0015
6	5	1	5	4	2	16821.3485	0.0031	16808.2450	0.0000	16825.5777	-0.0019
7	4	4	6	3	3	14823.6857	0.0021	14819.2608	0.0028	14817.5658	0.0023
7	4	3	6	3	4	14824.1262	-0.0007	14819.7140	-0.0021	14817.9932	0.0055
7	5	3	6	4	2	17567.4285	0.0004	17556.8046	-0.0003	17567.6229	0.0042
7	5	2	6	4	3	17567.4285	-0.0016	17556.8046	-0.0025	17567.6229	0.0023
8	3	6	7	2	5	12786.6987	-0.0001	12790.1175	-0.0007	12771.3143	-0.0020
8	3	5	7	2	6	12851.6557	-0.0016	12856.4745	-0.0007	12834.4356	-0.0014
9	3	7	8	2	6	13505.0219	-0.0006	13510.3397	0.0001	13486.3597	0.0000
9	3	6	8	2	7	13613.3818	-0.0007	13621.0272	0.0012	13591.6611	-0.0008
10	3	8	9	2	7	14211.6531	0.0006	14218.6400	0.0005	14190.0113	0.0002
10	3	7	9	2	8	14381.7758	0.0014	14392.3961	0.0000	14355.3536	0.0001

Table S5. Measured transition frequencies of the two observed ^{34}S isotopic species of $C_2F_4S_2$-DFM.

J'	K_a'	K_c'	J''	K_a''	K_c''	^{34}S-S4		^{34}S-S8	
						ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/MHz
4	4	1	3	3	0	12453.8676	0.0003	12505.4442	0.0011
4	4	0	3	3	1	12453.8676	-0.0054	12505.4442	-0.0046
5	4	2	4	3	1	13198.0696	-0.0078	13253.4689	-0.0064
5	4	1	4	3	2	13198.1138	-0.0040	13253.5144	-0.0010
5	5	1	4	4	0	15905.6000	0.0052	15971.3628	0.0014
5	5	0	4	4	1	15905.6000	0.0051	15971.3628	0.0014
6	4	3	5	3	2	13942.0982	0.0015	14001.3232	0.0049
6	4	2	5	3	3	13942.2494	-0.0093	14001.4701	-0.0088
6	5	2	5	4	1	16649.8383	0.0050	16719.4261	0.0039
6	5	1	5	4	2	16649.8383	0.0046	16719.4261	0.0034
7	4	4	6	3	3	14685.7416	-0.0038	14748.7929	-0.0006
7	4	3	6	3	4	14686.2272	-0.0056	14749.2744	-0.0021
7	5	3	6	4	2	17393.9972	0.0059	17467.4091	0.0056
7	5	2	6	4	3	17393.9972	0.0036	17467.4091	0.0033
8	3	6	7	2	5	12679.9820	-0.0083	12736.6916	0.0028
8	3	5	7	2	6	12748.9029	-0.0058	12805.2799	-0.0018
8	4	5	7	3	4	15428.7634	-0.0040	15495.6471	0.0008
8	4	4	7	3	5	15429.9879	-0.0011	15496.8576	0.0006
8	5	4	7	4	3	18138.0096	0.0011	18215.2527	0.0073
8	5	3	7	4	4	18138.0278	0.0108	18215.2527	-0.0011
9	3	7	8	2	6	13394.7539	-0.0015	13455.4114	0.0010
9	3	6	8	2	7	13509.6960	-0.0035	13569.8150	0.0007
9	4	6	8	3	5	16170.8096	-0.0019	16241.5280	-0.0002
9	4	5	8	3	6	16173.5056	0.0002	16244.1967	-0.0014
10	3	8	9	2	7	14097.1910	-0.0008	14161.8536	0.0007
10	3	7	9	2	8	14277.5915	-0.0014	14341.4137	0.0004
10	4	7	9	3	6	16911.4108	0.0017	16985.9740	0.0000
10	4	6	9	3	7	16916.8118	0.0032	16991.3260	0.0008
11	3	9	10	2	8	14784.8865	0.0036	14853.6033	-0.0004
11	3	8	10	2	9	15054.5224	0.0051	15121.9980	0.0015
11	4	8	10	3	7	17649.9541	0.0048	17728.3754	-0.0018
11	4	7	10	3	8	17659.9979	0.0034	17738.3299	-0.0026

Table S6. Experimental (r_s and r_0) and theoretical (r_e) coordinates of the three C and two S atoms for the observed conformer of $C_2F_4S_2$-DFM.

Atom		*a*/Å	*b*/Å
C1	r_s	±2.1513(7)[a]	±0.468(3)
	r_e	2.1670	-0.451
	r_0	2.1681	-0.469
C5	r_s	±0.085(18)	±0.727(2)
	r_e	0.103	0.701
	r_0	0.070	0.726
C10	r_s	±3.4732(4)	±0.167(9)
	r_e	-3.4705	0.145
	r_0	-3.4683	0.125
S4	r_s	±1.8354(8)	±1.309(1)
	r_e	1.8041	1.330
	r_0	1.8526	1.322
S8	r_s	±0.389(4)	±1.046(1)
	r_e	0.462	-1.075
	r_0	0.447	-1.047

[a] Costain's errors expressed in parentheses in units of the last digit.

Table S7. The r_0 structure of conformer I of $C_2F_4S_2$-DFM in the principal inertial axis system.

	a / Å	***b*** / Å	***c*** / Å
F(1)	-4.6940	-0.4595	0.0000
C(2)	-3.4683	0.1251	0.0000
H(3)	-3.3520	0.7078	0.9125
H(4)	-3.3520	0.7078	-0.9125
F(5)	-2.5232	-0.8646	0.0000
S(6)	0.4471	-1.0473	0.0000
C(7)	2.1681	-0.4688	0.0000
F(8)	2.8716	-0.8836	1.0747
F(9)	2.8716	-0.8836	-1.0747
S(10)	1.8526	1.3219	0.0000
C(11)	0.0702	0.7256	0.0000
F(12)	-0.6317	1.1566	1.0744
F(13)	-0.6317	1.1566	-1.0744

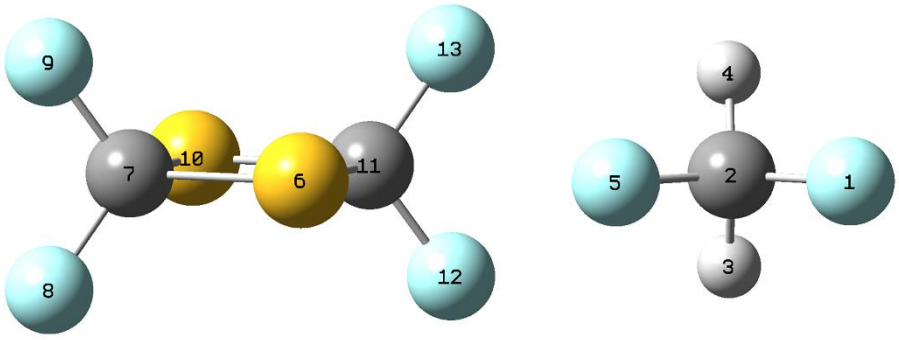

Table S8. Stabilization energy contributions (≥ 0.21 kJ mol^{-1}) for conformer I of the $C_2F_4S_2$-DFM complex.

Donor NBO	Acceptor NBO	E(2) (kJ mol^{-1})
From DFM to $C_2F_4S_2$		
BD (1) F9 – C10	RY*(2) C5	0.33
BD (1) F9 – C10	RY*(3) C5	0.21
BD (1)C10 – H11	RY*(1) F6	0.38
BD (1)C10 – H11	RY*(2) F6	0.29
BD (1)C10 – H12	RY*(1) F7	0.38
BD (1)C10 – H12	RY*(2) F6	0.29
LP (1) F9	BD*(1) C1 – S8	1.42
LP (1) F9	BD*(1) S4 – C5	0.33
LP (1) F9	BD*(1) C5– S8	0.29
LP (3) F9	BD*(1) C1 – S8	1.51
LP (3) F9	BD*(1) S4 – C5	1.42
LP (3) F9	BD*(1) C5 – F6	0.50
LP (3) F9	BD*(1) C5 – F7	0.50
From $C_2F_4S_2$ to DFM		
BD (1) S4 – C5	RY*(1) C10	0.38
LP (2) F6	RY*(1) H11	0.29
LP (2) F7	RY*(1) H12	0.29

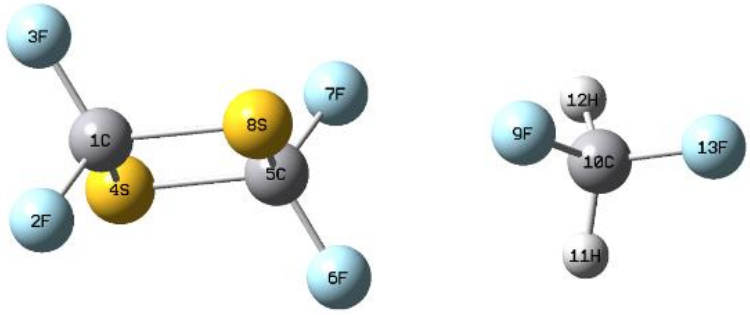

Table S9. NPA charge distributions for conformer I of $C_2F_4S_2$-DFM complex, and isolated $C_2F_4S_2$ and DFM molecules. Bold values highlight the charges of the sulfur and fluorine atoms involved in the charge transfer.

	$C_2F_4S_2$-DFM-I	$C_2F_4S_2$	DFM
C	0.432	0.435	
F	-0.342	-0.341	
F	-0.342	-0.341	
S	0.248	0.247	
C	0.426	0.435	
F	-0.350	-0.341	
F	-0.350	-0.341	
S	**0.274**	**0.247**	
F	**-0.369**		**-0.356**
C	0.462		0.463
H	0.132		0.125
H	0.132		0.125
F	-0.353		-0.356