Potassium hexafluoroacetylacetonate complex with 18-crown-6 ether as a volatile precursor of molecular and inorganic films: thermal and structural insights

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Supplementary Materials

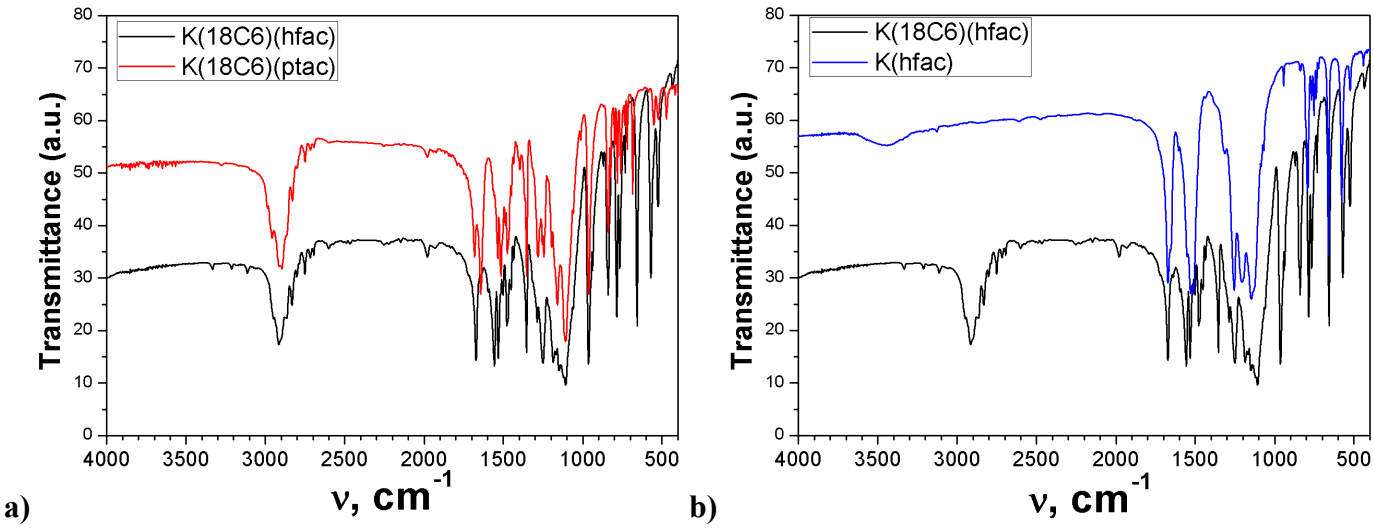


Fig. S1. IR spectra (in KBr) of heteroligand β-diketonate K(18C6)(L) complexes, L = hfac / ptac (a), and of K(18C6)(hfac) complex with the initial β-diketonate K(hfac) (b).

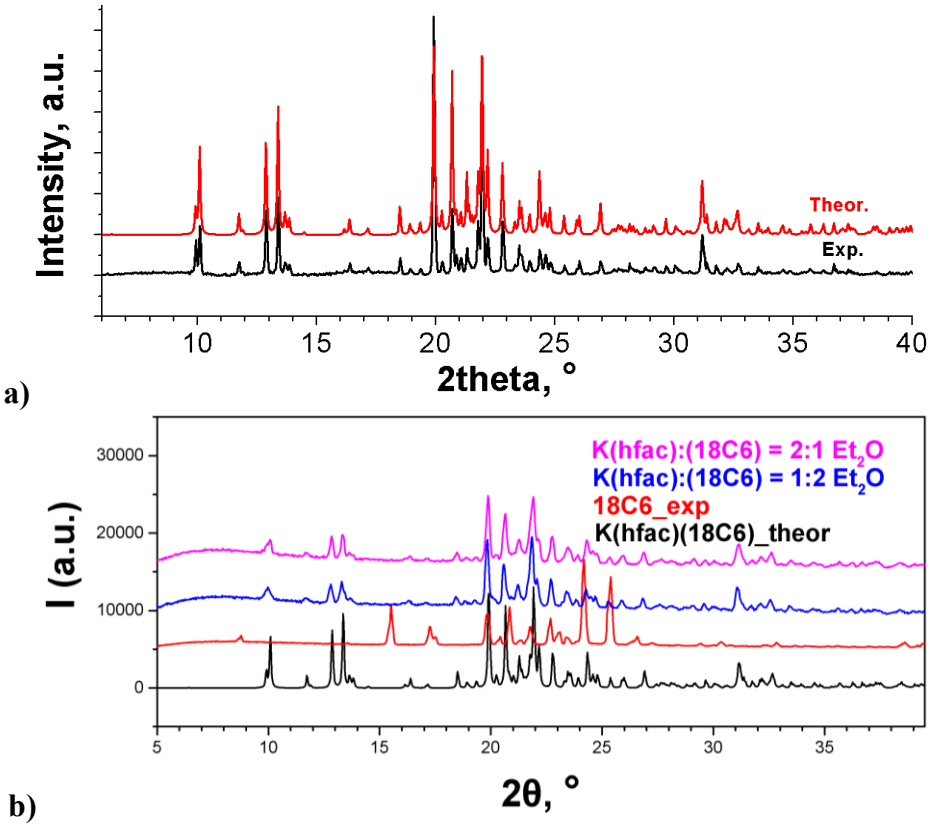


Fig. S2. X-ray diffraction patterns of K(18C6)(hfac) (a) and the products obtained with a non-stoichiometric ratio of reagents in Et_2O (b).

Table S1. Selected distances in the structures of potassium 18-crown-6 ether complexes (L^- anions are designated as follows: hfac = $CF_3C(O)CHC(O)CF_3$; ptac = $CF_3C(O)CHC(O)C(CH_3)_3$; acet = $CH_3C(O)CHC(O)OC_2H_5$; acetate = $CH_3C(O)O$, picrate = O-C_6H_2-2,4,6-$(NO_2)_3$, triflate = OSO_2CF_3).

Complex	K–O(D_{at}*)$_L$, Å	K–O_{18C6}, Å	K…(186C)**, Å	Ref***
K(18C6)(hfac)	2.689(2)–2.780(2)	2.801(2)–2.948(2)	0.71	[36], this work
K(18C6)(ptac)	2.648(3)–2.688(3)	2.802(1)–3.032(1)	0.92	[38]
K(18C6)(acet)	2.650(3)–2.732(3)	2.828(3)–3.016(3)	0.91	[37]
K(18C6)(acetate)·solv****	2.699(3)–3.030(3)	2.786(1)–3.034(1)	0.80	[43]
K(18C6)(picrate)	2.742(3)–2.845(3)	2.862(4)–2.989(4)	0.93	[44]
K(18C6)(triflate)	2.903(2)–2.969(2)	2.765(4)–2.853(4)	0.44	
K(18C6)(PF_6)	3.125(8)–3.218(2)	2.791(2)–2.825(5)	0	[46]
K(18C6)(SCN)	2.955(5)–3.136(5)	2.768(1)–2.836(1)	0	

* Any else donor atoms in L-anion

** distance from the cation to the midplane of the crown ether

*** Reference corresponds to the main text of the article

**** solv. is H_2O or $CH_3C(O)OH$ molecule

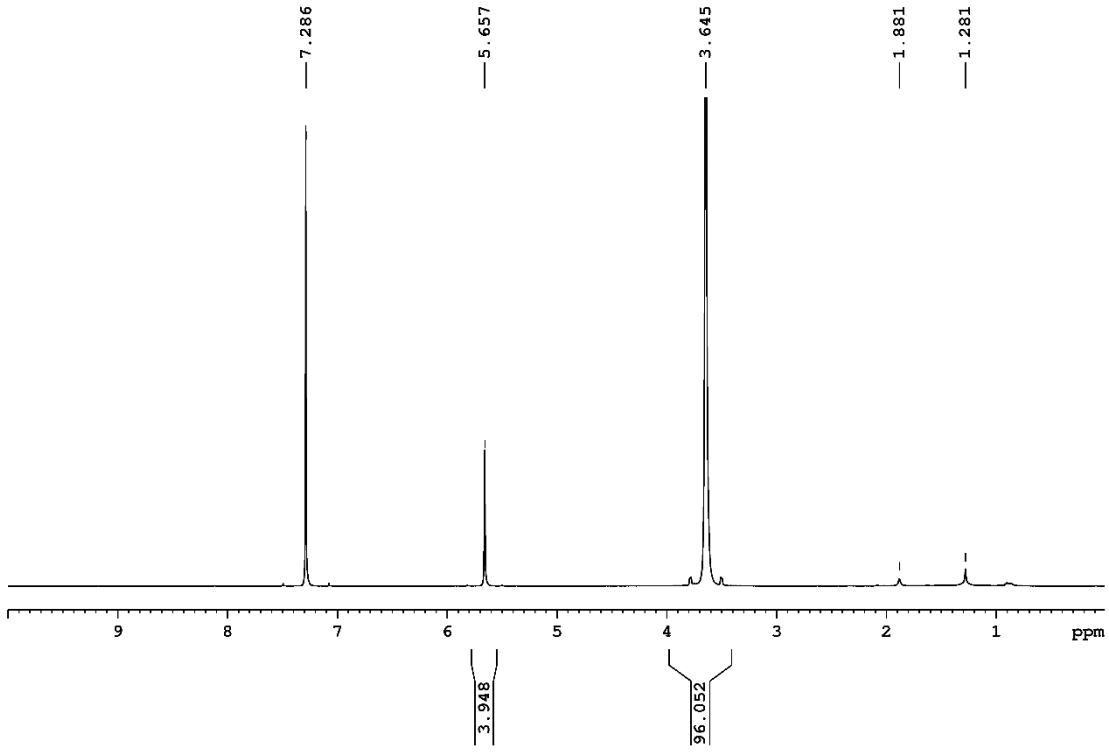


Fig. S3. ^{1}H NMR spectrum of complex K(18C6)(hfac) in $CDCl_3$.
The signal at 7.28 ppm is related to residual solvent protons,
the signals at 1.28 and 1.88 ppm are related to water and impurities from the solvent.

Table S2. The data of the SC-XRD analysis for complex K(18C6)(hfac).

Crystal size 0.10x0.18x0.25 mm, Empirical formula $C_{17}H_{25}F_6O_8K$, Space group $P\bar{1}$, Formula weight 510.46 g·mol^{-1}, Z = 2.

Temperature, K	**100(2)**	**150(2)**	**200(2)**	**250(2)**	**300(2)**	**350(2)**	**400(2)**
a, Å	8.9821(2)	9.0192(2)	9.0632(2)	9.1149(2)	9.1747(6)	9.2375(14)	9.3076(18)
b, Å	9.1052(2)	9.1351(2)	9.1682(2)	9.1958(2)	9.2292(6)	9.2626(15)	9.3266(17)
c, Å	14.3797(4)	14.3968(3)	14.4165(2)	14.4430(4)	14.4693(8)	14.497(3)	14.526(3)
α, °	71.8680(10)	72.0000(10)	72.1590(10)	72.3010(10)	72.488(2)	72.649(5)	72.886(6)
β, °	89.2540(10)	89.2420(10)	89.2480(10)	89.2650(10)	89.290(2)	89.234(8)	89.331(9)
γ, °	86.2250(10)	86.1830(10)	86.1000(10)	85.9900(10)	85.813(2)	85.603(5)	85.325(6)
V, Å^3	1115.17(5)	1125.58(4)	1137.63(4)	1150.43(5)	1165.23(13)	1180.4(3)	1201.1(4)
Density (calculated), g cm^{-3}	1.658	1.643	1.626	1.607	1.587	1.567	1.540
Absorption coefficient, mm^{-1}	2.310	2.289	2.264	2.239	2.211	2.182	2.145
Data collection range by 2θ, °	1.490-30.548	1.487-29.174	1.484-28.326	2.240-27.507	2.320-27.504	2.644-26.461	2.191-26.389
Index ranges	$12 \le h \le 12$	$-12 \le h \le 12$	$-12 \le h \le 12$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-11 \le h \le 11$
	$-13 \le k \le 12$	$-12 \le k \le 12$	$-12 \le k \le 11$	$-11 \le k \le 11$	$-11 \le k \le 11$	$-11 \le k \le 11$	$-11 \le k \le 11$
	$-20 \le l \le 20$	$-19 \le l \le 19$	$-19 \le l \le 19$	$-18 \le l \le 18$	$-18 \le l \le 18$	$-18 \le l \le 18$	$-18 \le l \le 18$
Number of measured reflexes	15853	15117	14503	13909	14047	12315	13079
Number of independent reflexes	6621	6046	5636	5240	5306	4792	4888
Rint	0.0241	0.0245	0.0231	0.0242	0.0237	0.0530	0.0503
Completeness of data collection (θ = 25.25°)	99.6 %	99.6 %	99.6 %	99.4 %	99.4 %	98.7 %	99.4 %
Max / min transmission	0.540 и 0.746	0.540 и 0.746	0.539 и 0.746	0.539 и 0.746	0.533 и 0.746	0.427 и 0.745	0.417 и 0.745
Data / restraints / parameters	6621 / 0 / 317	6046 / 0 / 317	5636 / 0 / 317	5240 / 0 / 317	5306 / 12 / 317	4792 / 0 / 317	4888 / 12 / 317
GOOF	1.051	1.057	1.058	1.064	1.052	1.003	1.041
R-factors [I>2 σ(I)]	$R_1 = 0.0251$	$R_1 = 0.0257$	$R_1 = 0.0249$	$R_1 = 0.0265$	$R_1 = 0.0287$	$R_1 = 0.0509$	$R_1 = 0.0492$
R-factors (all data)	$R_1 = 0.0296$	$R_1 = 0.0305$	$R_1 = 0.0292$	$R_1 = 0.0318$	$R_1 = 0.0360$	$R_1 = 0.0664$	$R_1 = 0.0638$
Residual electron density (ρ_{max}/ρ_{min})., e Å^{-3}	0.529 / -0.471	0.402 / -0.436	0.283 / -0.342	0.304/-0.305	0.322 / -0.358	0.720 / -0.716	0.582 / -0.443
CCDC number	2524276	2524277	2524278	2524279	2524280	2524281	2524282

Table S3. Selected bond lengths and angles for K(18C6)(hfac) at different temperatures.

Chevrons show average values.

***T* (K)** / **Parameters**	**100(2)**	**150(2)**	**200(2)**	**250(2)**	**300(2)**	**350(2)**	**400(2)**
The nearest environment of the cation							
d(K–O_{hfac}), Å	2.6881(8)-2.7708(8) <2.73>	2.6894(9)-2.7802(8) <2.73>	2.6926(9)-2.7913(9) <2.74>	2.6959(10)-2.8035(10) <2.75>	2.6991(11)-2.8149(11) <2.76>	2.7025(13)-2.8283(13) <2.76>	2.7087(16)-2.8407(16) <2.78>
d(K–O_{18C6}), Å	2.7992(8)-2.9530(8) <2.89>	2.8011(8)-2.9476(9) <2.89>	2.8053(9)-2.9424(10) <2.89>	2.8085(10)-2.9397(11) <2.89>	2.8133(11)-2.9366(12) <2.89>	2.8162(13)-2.9343(14) <2.89>	2.8207(16)-2.9310(17) <2.89>
d(K...F), Å	3.000(4)-3.020(2)	3.026(5)-3.073(3)	3.060(5)-3.127(4)	3.090(6)-3.192(6)	3.056(4)	3.098(4)	3.165(5)
d(K...(18C6)), Å	0.699	0.705	0.713	0.722	0.731	0.742	0.757
∠O11–K1–O12,°	65.09(2)	64.87(2)	64.61(3)	64.32(3)	64.02(3)	63.75(4)	63.45(5)
∠K1–O12–C11,°	133.81(7)-135.50(7)	133.67(7)-135.70(7)	133.57(8)-135.89(8)	133.41(9)-136.09(9)	133.36(10)-136.39(10)	133.09(11)-136.51(12)	132.93(13)-136.62(14)
The bending angle of the chelate metallocycle along {O...O} line,°	12.64	12.85	13.14	13.38	13.64	14.03	14.52
The tilt of the anion to (18C6),°	65.47	65.42	65.37	65.42	65.49	65.58	65.70
β-Diketonate anion							
d(C–O), Å	1.2355(12)-1.2363(12) <1.24>	2x1.2337(13) <1.23>	1.2317(14)-1.2320(14) <1.23>	1.2272(16)-1.2309(16) <1.23>	1.2234(17)-1.2290(17) <1.23>	1.2200(19)-1.2277(19) <1.22>	1.215(2)-1.229(2) <1.22>
d(C–Cγ), Å	1.4060(14)-1.4070(14) <1.41>	1.4039(15)-1.4043(15) <1.40>	1.4017(16)-1.4022(16) <1.4>	1.3986(18)-1.3994(17) <1.40>	1.396(2)-1.3983(19) <1.40>	1.394(2)-1.397(2) <1.40>	1.389(3)-1.397(3) <1.39>
d(C–C), Å	1.5441(14)-1.5480(14) <1.55>	1.5420(15)-1.5460(15) <1.54>	1.5395(17)-1.5438(17) <1.54>	1.5381(18)-1.5416(19) <1.54>	1.535(2)-1.538(2) <1.54>	1.533(2)-1.540(2) <1.54>	1.527(3)-1.535(3) <1.53>
∠C11–C4B–C13,°	122.13(9)	122.28(10)	122.54(10)	122.66(11)	122.92(13)	122.95(15)	123.11(17)
Crown ether							
C_{18C6}—C_{18C6}, Å	1.4975(16)-1.5015(15) <1.50>	1.490(2)-1.4953(17) <1.49>	1.488(2)-1.492(2) <1.49>	1.484(3)-1.490(2) <1.49>	1.480(3)-1.486(3) <1.48>	1.477(4)-1.481(4) <1.48>	1.458(4)-1.476(4) <1.47>
C_{18C6}—O_{18C6}, Å	1.4195(13)-1.4266(13) <1.42>	1.4186(16)-1.4260(15) <1.42>	1.4168(18)-1.4248(17) <1.42>	1.414(2)-1.423(2) <1.42>	1.410(2)-1.424(2) <1.42>	1.407(3)-1.425(3) <1.42>	1.401(3)-1.427(3) <1.41>

Table S4. Relative changes in unit cell parameters and equations for them in the temperature range of 100–400 K.

Cell parameters	$\Delta x_{400K}/x_{100K}$ (%)	Equation x(*T*)
a	4.0	$1.65\cdot10^{-6}T^2 + 3.17\cdot10^{-4}T + C$
b	2.1	$6.48\cdot10^{-4}T + C$
c	0.6	$5.89\cdot10^{-7}T^2 - 6.20\cdot10^{-6}T + C$
α	1.8	$4.79\cdot10^{-6}T^{-6} + 1.78\cdot10^{-3}T + C$
β	0.05	$1.81\cdot10^{-4}T + C$, (T = 100-350 K)
γ	-0.01	$-1.25\cdot10^{-6}T^{-6} + 3.38\cdot10^{-3}T + C$
V	7.44	$2.80\cdot10^{-4}T^2 + 0.13T + C$

Table S5. Hirschfeld surface parameters and shortest intermolecular distances for K(18C6)(hfac).

T, K	G	Ω	V_H, Å^3	S_H, Å^2	Intermolecular distances, Å		
					K...F	H(28A)...H(30A)	H(26B)...C(4B)
100	0.729	0.013	541.93	441.00	3.000	2.239	2.715
150	0.731	0.012	547.07	442.48	3.026	2.250	2.730
200	0.733	0.012	552.83	444.15	3.060	2.661	2.744
250	0.736	0.012	559.21	445.99	3.090	2.294	2.768
300	0.739	0.012	566.04	447.73	3.056	2.329	2.796
350	0.742	0.011	573.83	449.83	3.098	2.355	2.822
400	0.746	0.011	582.65	452.19	3.165	2.386	2.846

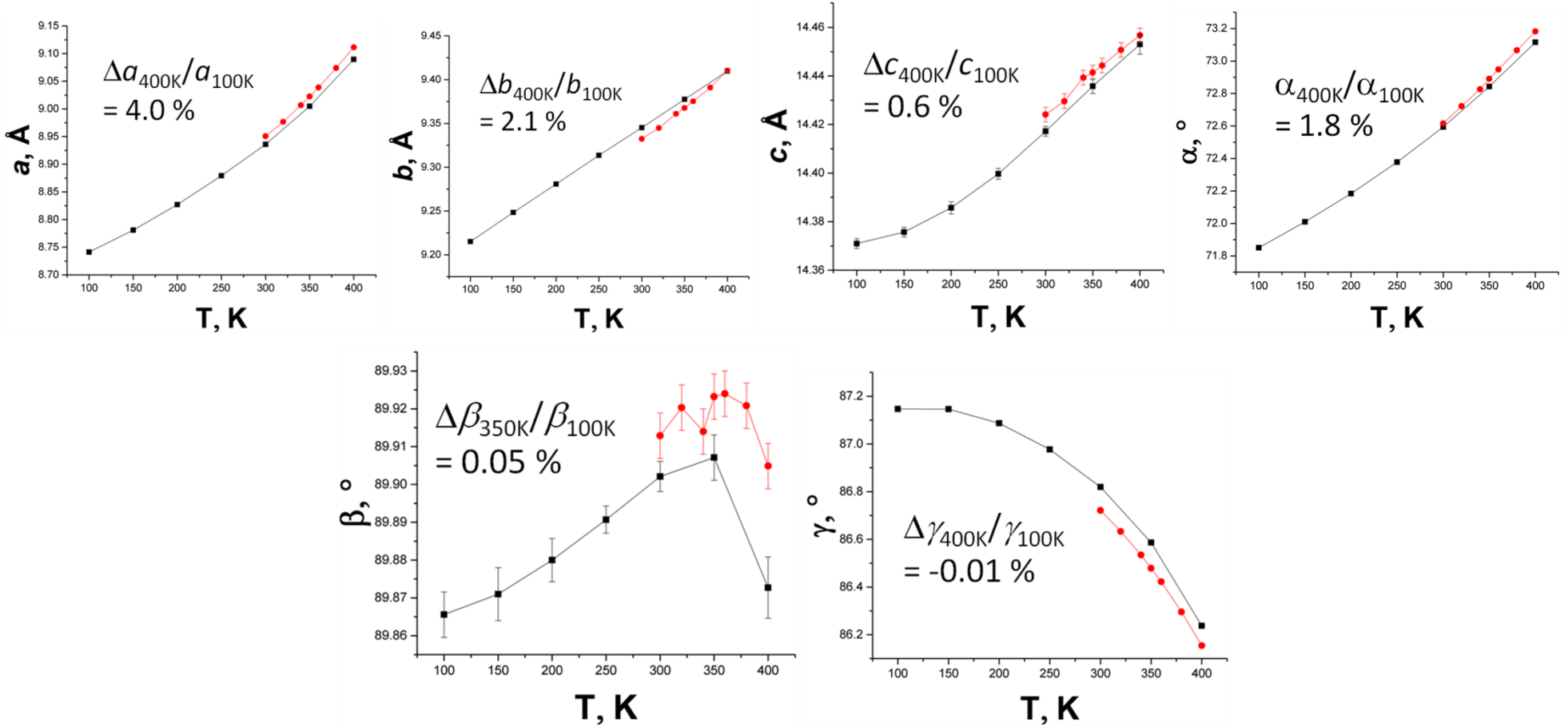


Fig. S4. Change in unit cell parameters and angles as functions of temperature for K(18C6)(hfac).

Red and black dots represent different crystals.

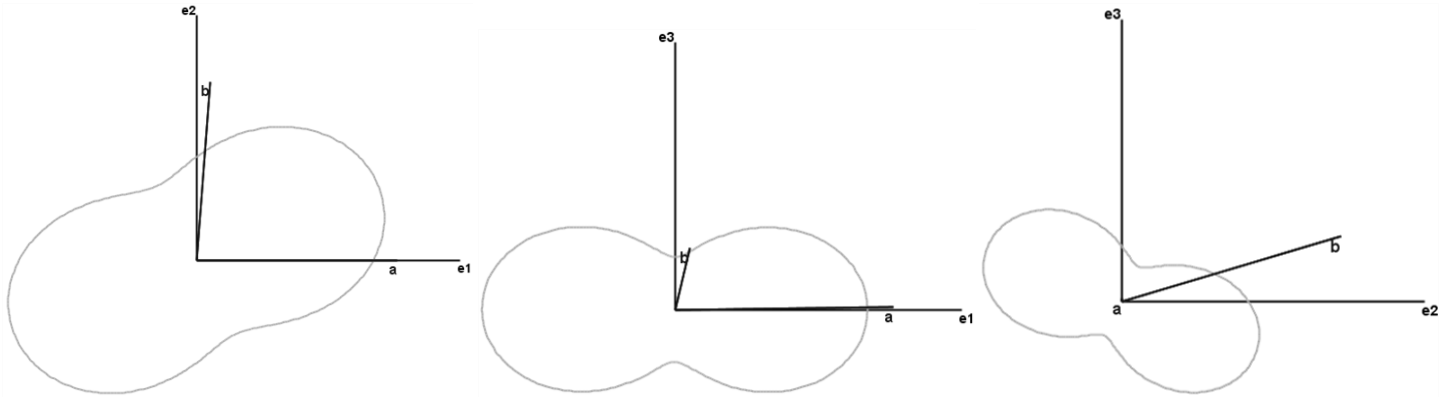


Fig. S5. Thermal expansivity projections for K(18C6)(hfac) at 100 K.

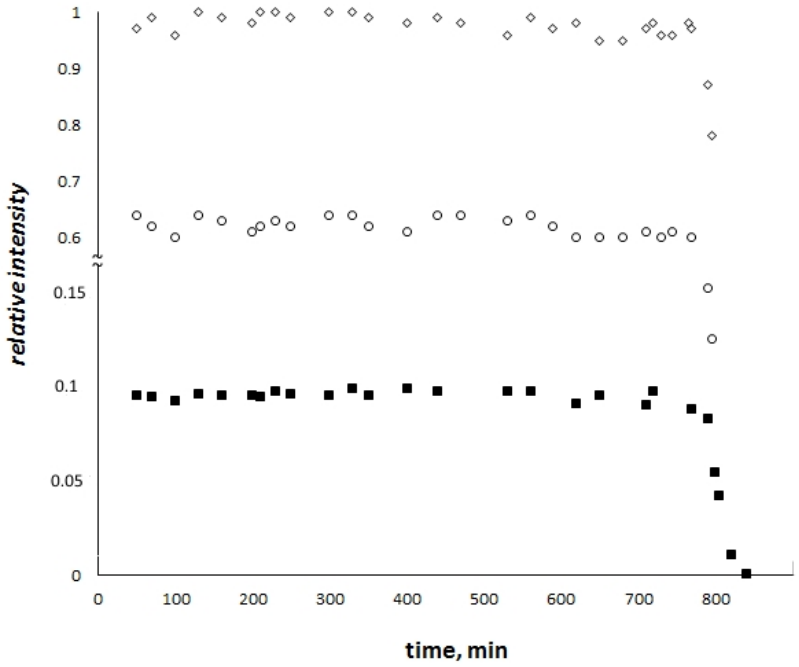


Fig. S6. Isotherm of complete sublimation of a weighted portion of K(18C6)(hfac) complex (T = 393K).
Ion currents $(CH_2CH_2O)_2^+$, K^+, and $K(18C6)^+$ are designated by ▪, ◊, and ○, respectively.

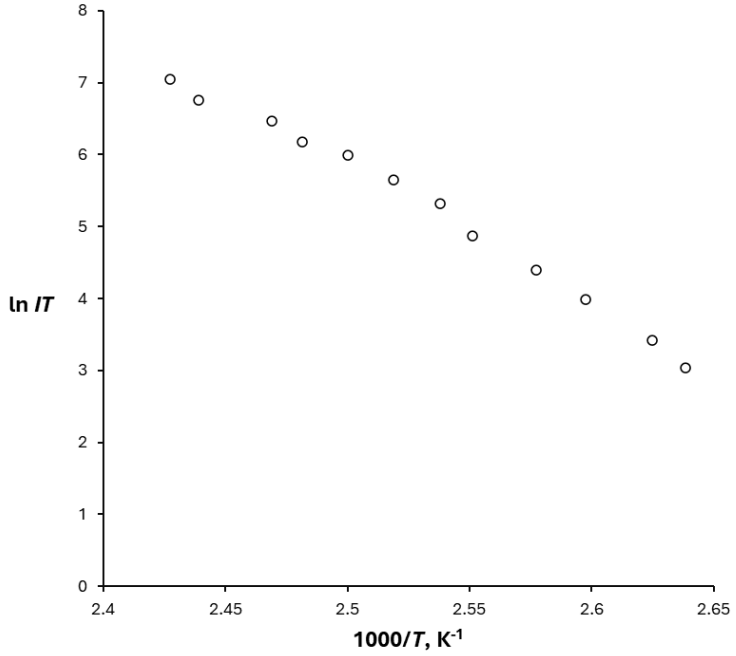


Fig. S7. Temperature dependence of the intensities of K^+ ion currents.
I is the ion current intensity, and T is the temperature.

Table S6. Sublimation enthalpy values of K(18C6)(hfac) complex in the temperature range of 379-421 K calculated using different ion currents (kJ/mol).

No.	$(CH_2CH_2O)_2^+$	$K(18C6)^+$	K^+
1	162.26 ± 2.50	160.76 ± 2.76	151.70 ± 5.60
2	159.02 ± 3.48	152.51 ± 1.49	159.93 ± 4.62
3	163.33 ± 6.69	151.80 ± 2.05	156.48 ± 5.27
4	162.30 ± 6.23	165.05 ± 9.63	162.44 ± 6.91
Average	161.73 ± 2.98	157.5 ± 10.3	157.64 ± 7.41

Table S7. Experimental and calculated vapor pressures over the solid K(18C6)(hfac) complex with relative deviations.

T, K	1000/T, K^{-1}	p_{exp}, Pa	lg(p_{exp})	p_{calc}, Pa	100*(p_{calc}-p_{exp})/p_{exp}
379	2.64	0.002	-2.68	0.002	-12.8
381	2.62	0.003	-2.55	0.003	-9.52
385	2.60	0.005	-2.30	0.005	-4.00
388	2.58	0.008	-2.12	0.008	-0.78
392	2.55	0.012	-1.91	0.013	-3.10
394	2.54	0.019	-1.72	0.016	15.5
397	2.52	0.027	-1.58	0.023	12.8
400	2.50	0.037	-1.43	0.033	10.7
401	2.49	0.045	-1.35	0.037	16.5
403	2.48	0.045	-1.35	0.047	-5.19
404	2.48	0.054	-1.27	0.053	1.04
404	2.48	0.066	-1.18	0.053	19.1
405	2.47	0.060	-1.22	0.059	0.91
407	2.46	0.068	-1.17	0.074	-10.4
410	2.44	0.095	-1.02	0.105	-11.0
413	2.42	0.119	-0.93	0.148	-24.5
414	2.42	0.155	-0.81	0.165	-6.25
415	2.41	0.169	-0.77	0.185	-8.97
416	2.40	0.179	-0.75	0.206	-14.8
416	2.40	0.185	-0.73	0.206	-11.3
417	2.40	0.282	-0.55	0.229	18.6
417	2.40	0.209	-0.68	0.229	-10.1
417	2.40	0.269	-0.57	0.229	14.5
418	2.39	0.271	-0.57	0.256	5.52

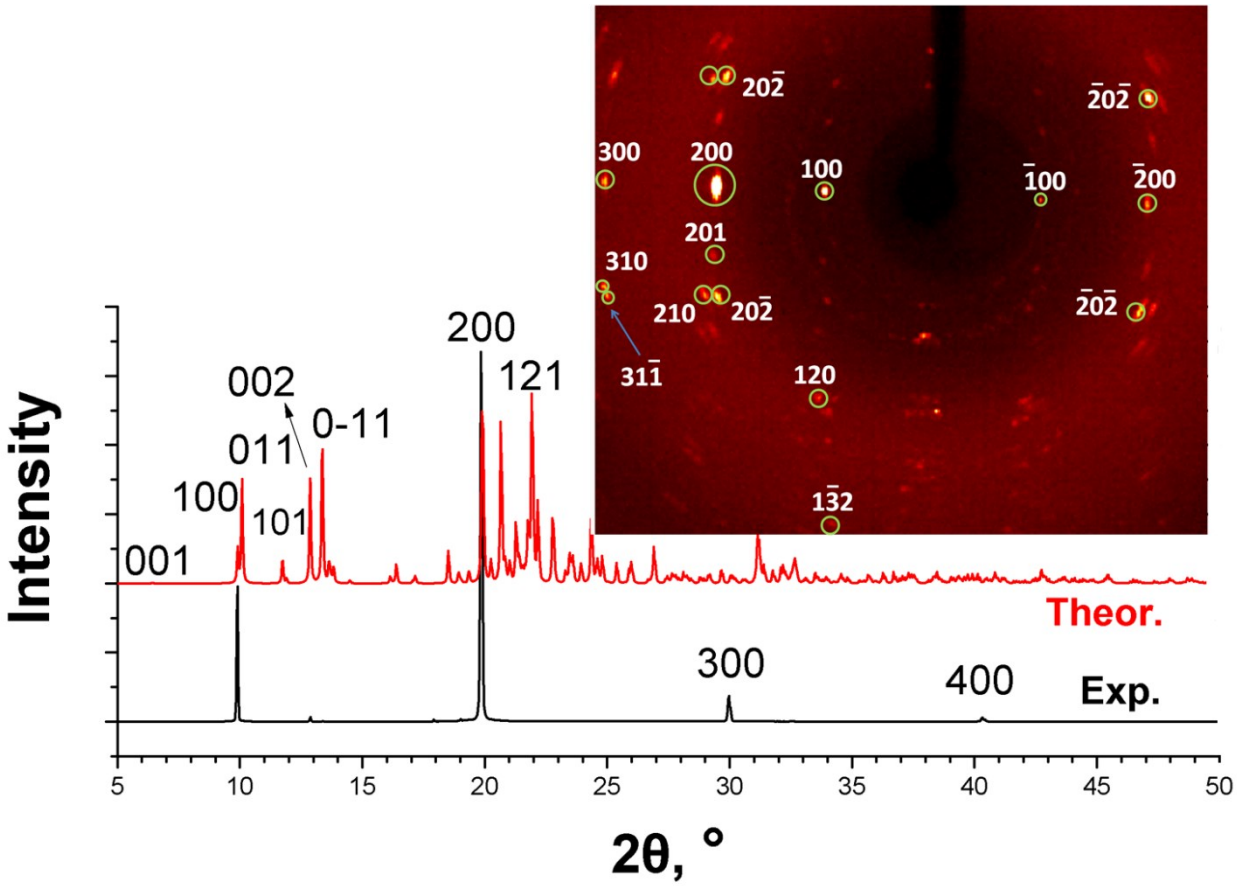


Fig. S8. The 2D-GIXRD pattern of the K(18C6)(hfac) molecular film obtained by PVD (**Exp.**) in comparison the XRD pattern of K(18C6)(hfac) complex calculated from SC-XRD data (**Theor.**).

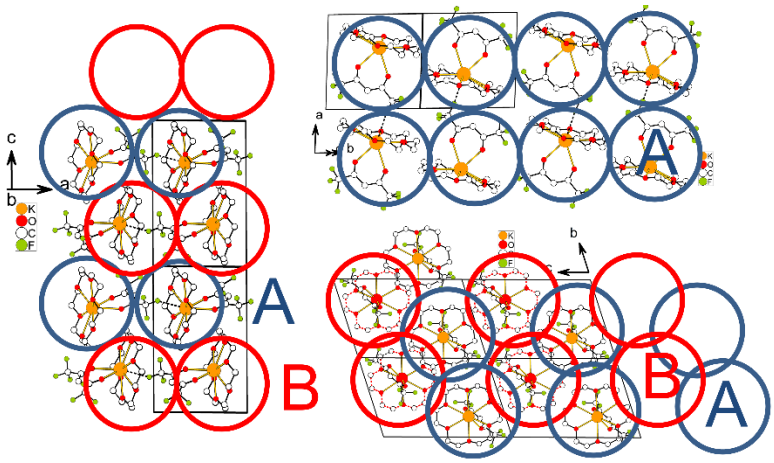
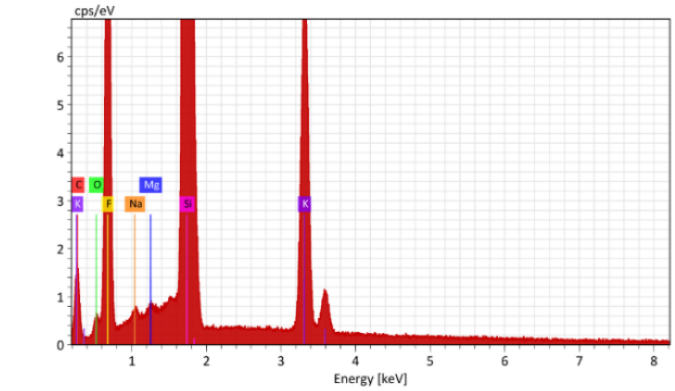


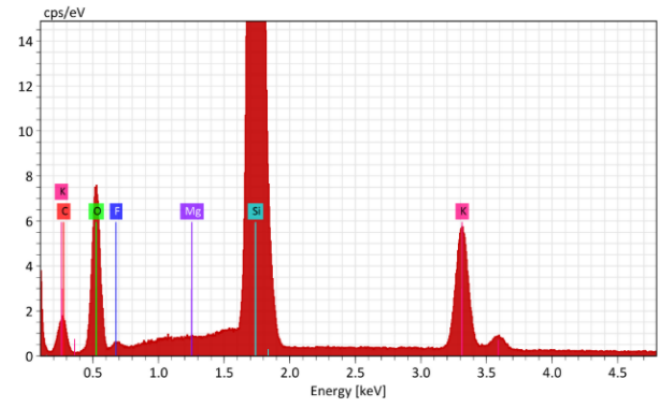
Fig. S9. Schematic representation of three projections of the crystal packing of K(18C6)(hfac) molecules in the form of layers of different symmetries (AAAA-type and ABAB-type).



764

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	3328	3.32	6.17	11.10	0.59	17.69
Oxygen	8	764	0.79	1.48	1.99	0.22	27.61
Fluorine	9	59684	32.68	60.69	68.98	3.83	11.71
Sodium	11	1988	0.48	0.88	0.83	0.06	12.43
Magnesium	12	1200	0.16	0.31	0.27	0.04	21.96
Silicon	14	468593	0.00	0.00	0.00	0.00	0.00
Potassium	19	66184	16.40	30.47	16.83	0.53	3.24
		Sum	**53.84**	**100.00**	**100.00**		

a)



N 770

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	3696	8.37	7.37	13.78	1.41	16.88
Oxygen	8	38112	25.52	22.44	31.53	3.10	12.15
Fluorine	9	1815	0.96	0.85	1.00	0.21	21.98
Magnesium	12	189	0.02	0.02	0.02	0.00	10.81
Silicon	14	651686	69.67	61.28	49.04	2.92	4.18
Potassium	19	49200	9.14	8.04	4.62	0.31	3.37
		Sum	**113.69**	**100.00**	**100.00**		

b)

Fig. S10. EDS spectra of the films obtained from K(18C6)(hfac) by MOCVD at 500°C (773 K) with reagent gas O_2 (a) and with reagent gas O_2 + H_2O (b).