Supplementary materials

Exploring the Luminescent and Thermometric Potentials of Samarium(III) Diketonate Complexes with Extended Fluoroalkyl Chains

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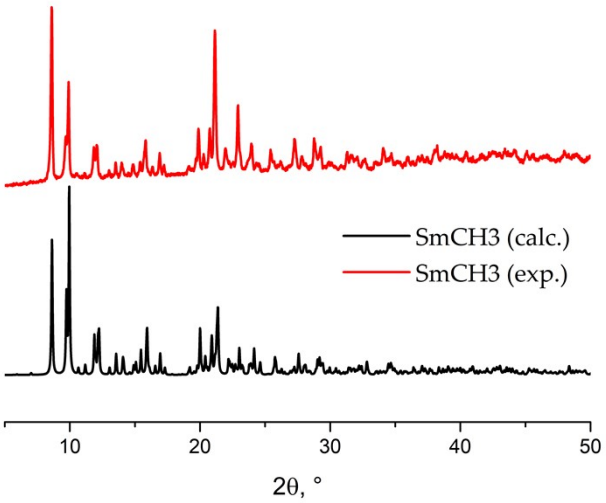
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SmCH3 (exp.)
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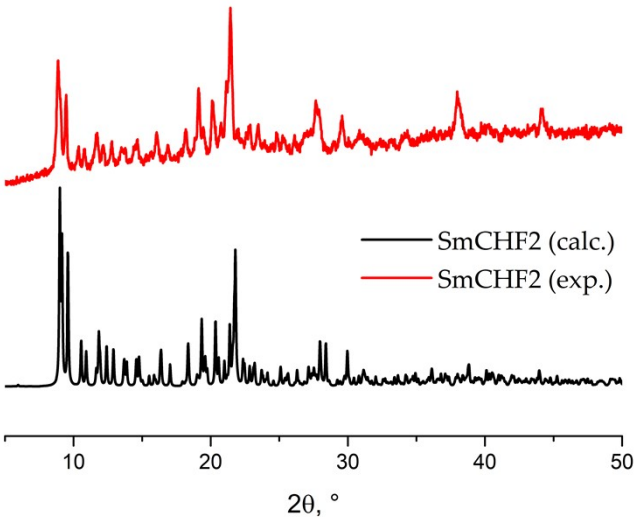
20
30
40
50
2θ, °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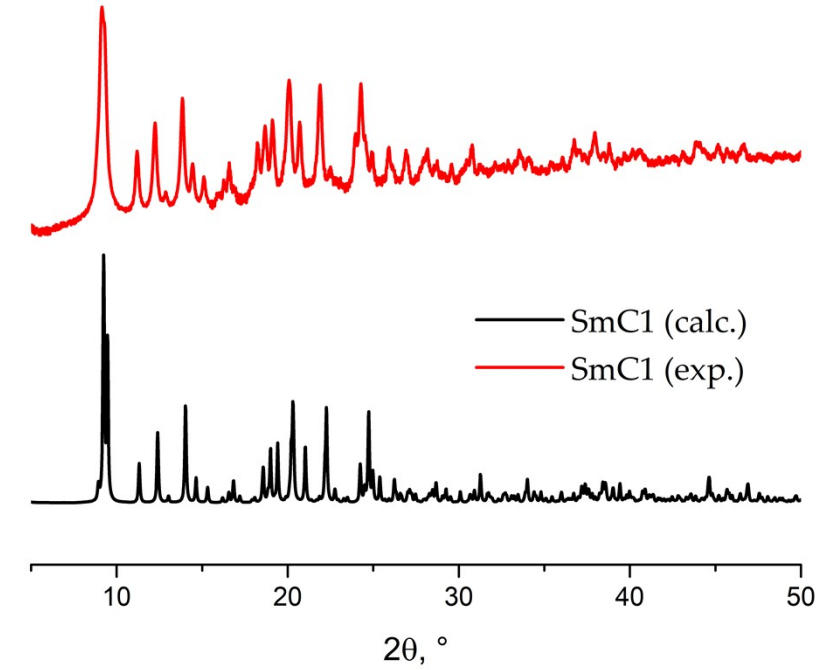
40
50
2θ, °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40
50
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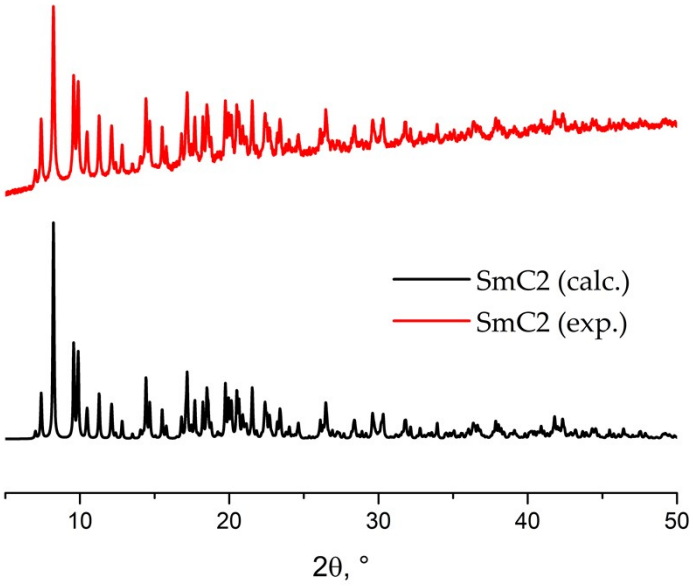
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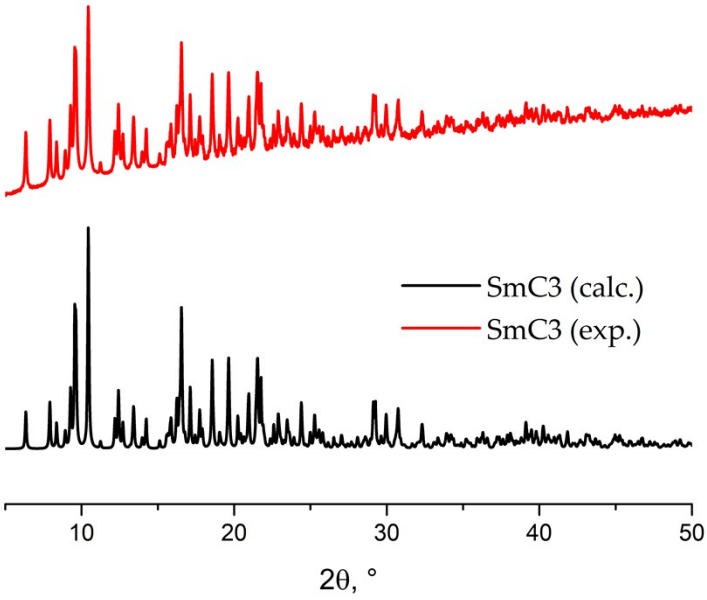
2θ, °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SmC3 (exp.)
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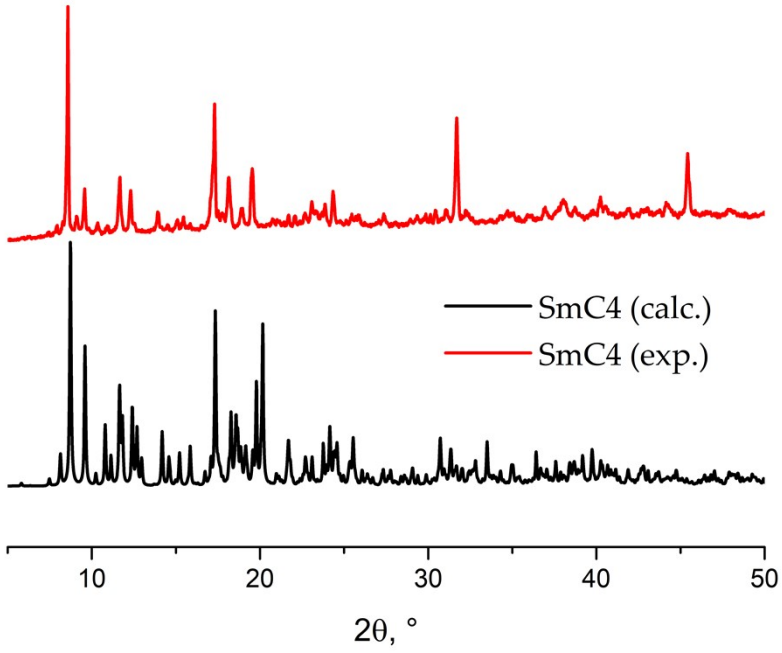
2θ, °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SmC4 (exp.)
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20
30
40
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2θ, °

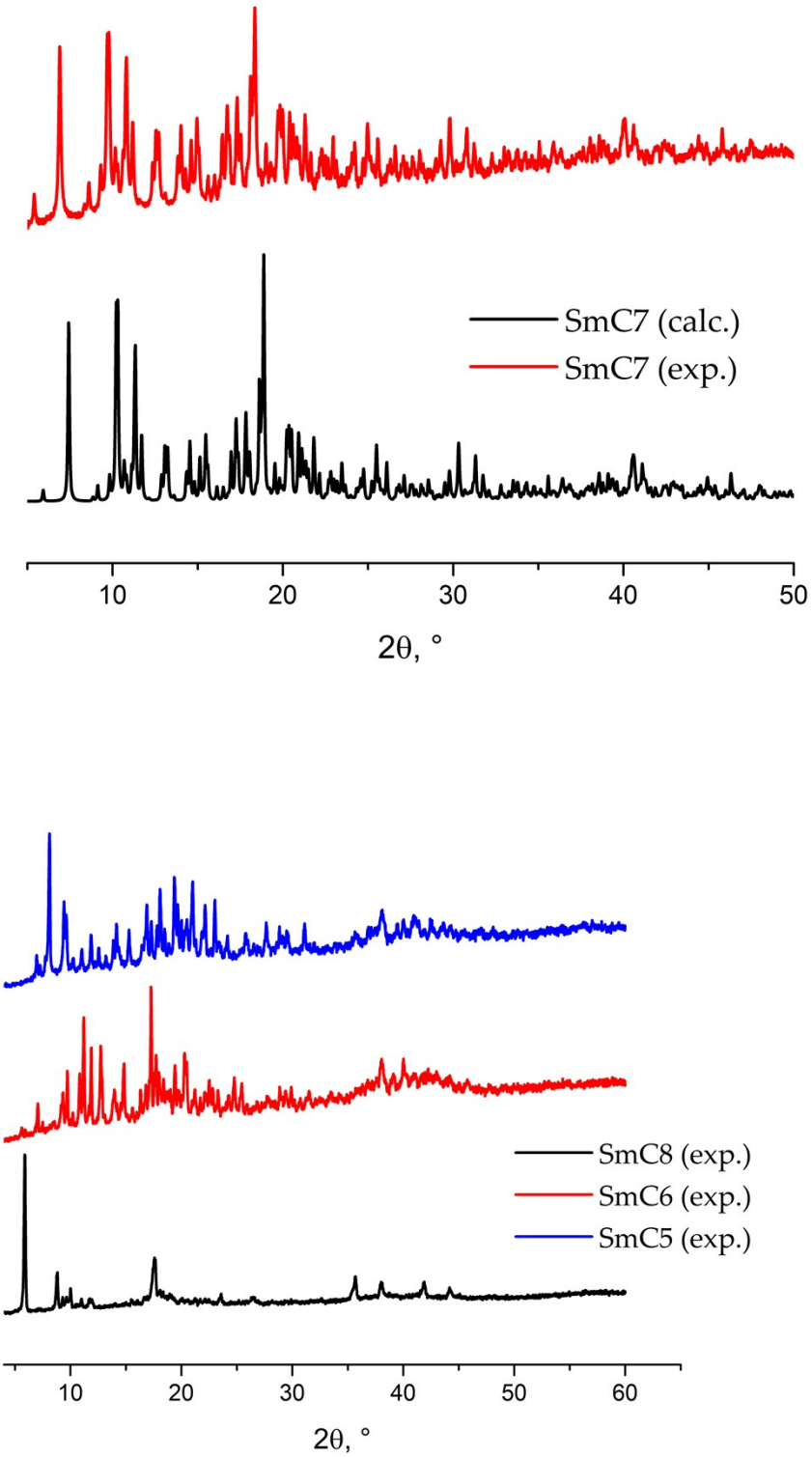

Figure S1. PXRD patterns of SmCH3, SmCHF2 and SmC1-SmC8 and simulated from single crystal data for SmCH3, SmCHF2, SmC1-SmC4, SmC7.

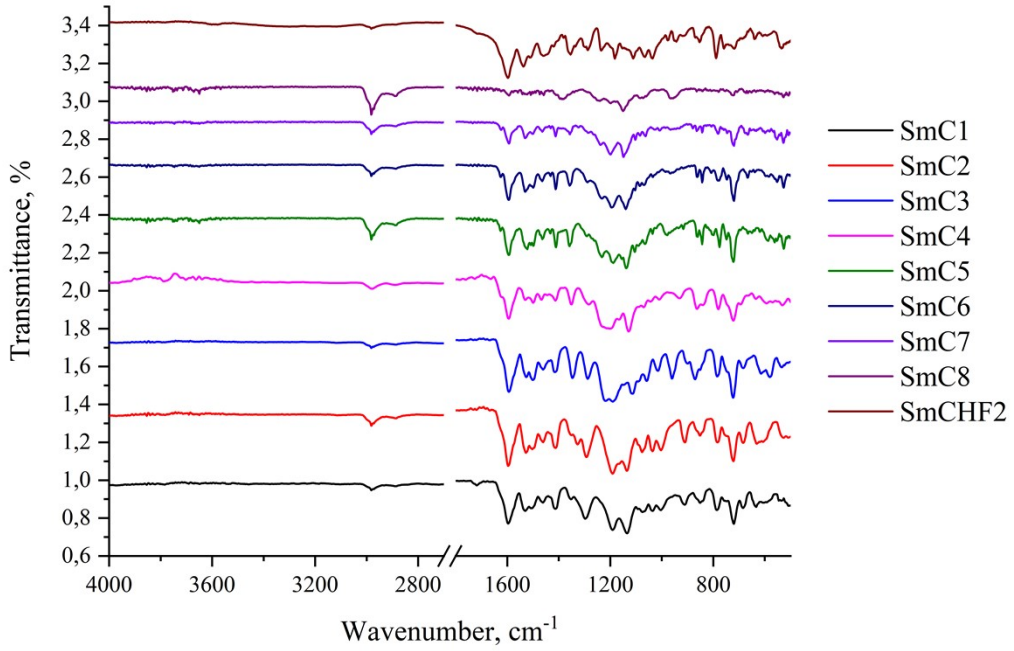

Figure S2. FTIR-spectra of the complexes SmCHF2 and SmC1-SmC8.

Table S1. Selected crystal data and parameters for structure refinement of **SmC_3**, **SmC_4** and **SmC_7.**

Complex/Parameters	**SmC_3**	**SmC_4**	**SmC_7**
Empirical formula	$C_{42}H_{20}F_{21}N_2O_6S_3Sm$	$C_{45}H_{20}F_{27}N_2O_6S_3Sm$	$C_{54}H_{20}F_{45}N_2O_6S_3Sm$
Formula weight	1294.13	1444.16	1894.25
T (K)	100	296	100
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	P-1	*Pbca*
a (Å)	11.9132(3)	11.5607(7)	20.520(3)
b (Å)	18.4956(4)	14.8128(9)	18.988(3)
c (Å)	21.5050(5)	15.9771(9)	32.676(4)
α (°)	90	100.744(2)	90
β (°)	100.7170(10)	101.341(2)	90
γ (°)	90	103.867(2)	90
V(Å^3)	4655.80(19)	2524.8(3)	12732(3)
Z	4	2	8
D_{calc} (g·cm^{-3})	1.846	1.900	1.976
μ (mm^{-1})	1.530	1.438	1.205
θ range (°)	2.06-27.10	2.36-25.00	1.92-24.71
F(000)	2532	1410	7368
Number of parameters	862	739	1064

Reflections collected	45016	30780	40177
Unique reflections	10268	8881	10589
Reflections with $I > 2\sigma(I)$	7854	7070	8143
R_{int}	0.0496	0.0736	0.1022
GooF	1.031	1.082	1.135
$R_1(I > 2\sigma(I))$	0.0541	0.0622	0.1238
$wR_2\,(I > 2\sigma(I))$	0.1296	0.1039	0.2609

Table S2. Selected bond lengths, the shortest interatomic distances (Å) and angles (°) in **SmC_3**, **SmC_4** and **SmC_7.**

Complex/Parameters	**SmC_3**	**SmC_4**	**SmC_7**
Sm–O, Å	2.327(13)– 2.390(4)	2.360(5)–2.418(4)	2.349(9)–2.391(9)
Sm–N, Å	2.599(6), 2.613(5)	2.593(6), 2.602(5)	2.578(10), 2.582(10)
C–O, Å	1.251(7)–1.269(8)	1.256(9)–1.275(9)	1.249(15)–1.287(16)
C–C(diketon), Å	1.346(13)–1.471(13)	1.371(9)–1.422(8)	1.380(18)–1.41(2)
Sm…Sm, Å	9.948(3)	9.321(1)	10.413(2)
O–Sm–O(chelate), deg.	70.5(2)–72.9(3)	70.62(16)–70.91(15)	70.0(3)–70.8(3)
N–Sm–N, deg.	63.0(2)	63.3(2)	62.8(3)

Table S3. Selected Continuous Shape Measures (CShM) values for the potential coordination polyhedra of Sm in the structure of **SmC_3**, **SmC_4** and **SmC_7**

Complex/Geometry	**SmC_3**	**SmC_4**	**SmC_7**
O_h, cube	9.997	10.595	8.845
D_{4d}, square antiprism	2.167	1.314	1.922
D_{2d}, triangular dodecahedron	0.819	1.485	0.624
C_{2v}, biaugmented trigonal prism	2.499	2.932	2.896
C_{2v}, biaugmented trigonal prism	1.938	2.293	2.182
D_{2d}, snub diphenoid	3.260	4.257	3.500
T_d, triakis tetrahedron	10.658	11.427	9.604

Table S4. Selected parameters for the C-H···A interactions in **SmC_3**, **SmC_4** and **SmC_7**.

Interaction	D–H, Å	H···A, Å	D···A, Å	D–H–A, deg.
SmC_3				
C22–H22···S3’	0.95	2.38	2.729(10)	110
C25–H25···F16 (-1+x,y,z)	0.95	2.46	3.22(2)	136
C25–H25···F1A (1/2-x,-1/2+y,3/2-z)	0.95	2.51	3.280(15)	139
C26–H26···F2 (1/2-x,-1/2+y,3/2-z)	0.95	2.37	3.187(16)	136
C32–H32···F4 (1-x,1-y,1-z)	0.95	2.53	3.100(11)	135
C36–H36…O6	0.95	2.38	3.050(10)	127
C42–H42···F3 (3/2-x,1/2+y,3/2-z)	0.95	2.31	3.212(13)	159
SmC_4				
C16–H16···O5 (1-x,2-y,1-z)	0.95	2.60	3.330(9)	136

C34–H34···O6	0.95	2.57	3.155(10)	121
C44–H44···F9 (-x,1-y,-z)	0.95	2.52	3.428(10)	167
SmC_7				
C20–H20···F19' (1-x,1-y,1-z)	0.95	2.51	3.26(3)	135
C34–H34···O1 (3/2-x,1/2+y,z)	0.95	2.52	3.331(17)	144

Table S5. Selected parameters for the S···F and C-F···F-C intermolecular interactions in **SmC_3**, **SmC_4** and **SmC_7**.

X···Y	**Symmetry**	***d*, Å**
SmC_3		
S3···F9B	-1+x, y, z	2.886(16)
F1A···F9A	3/2-x, 1/2+y, 3/2-z	2.963(19)
F1A···F9	-1/2+x, 1/2-y, 1/2+z	3.026(15)
F2A···F4A	-1/2+x, 1/2-y, 1/2+z	2.803(12)
F3B···F4	-1/2+x, 1/2-y, 1/2+z	2.952(11)
F5···F6	2-x, 1-y, 1-z	3.087(17)
F6···F6	2-x, 1-y, 1-z	2.965(15)
F9···F9A	2-x, -y, 1-z	2.95(3)
F1···H37	-1+x, y, z	2.77
SmC_4		
S2···F5	1-x, 2-y, 1-z	3.402(5)
F1···F11A	1-x, 1-y, -z	3.075(7)
F3A···F6A	x, -1+y, z	3.117(7)
F3A···F8A	x, -1+y, z	3.120(7)
F4···F11	-x, 1-y, -z	3.066(7)
F4A···F12	-x, 1-y, -z	2.904(7)
F4B···F10	-x, 1-y, -z	3.089(7)
F4B···F11	-x, 1-y, -z	3.109(7)
F5···F12A	1-x, 2-y, -z	3.029(7)
F5A···F12A	1-x, 2-y, -z	3.090(6)
F6···F12B	1-x, 2-y, -z	3.074(7)
F8···F8	-x, 2-y, -z	2.996(9)
F8A···F10A	-1+x, y, z	3.003(7)
F8B···F10A	-1+x, y, z	2.981(8)
F12···F12	1-x, 2-y, -z	3.016(6)
SmC_7		
S1···F21A	x, 1/2-y, 1/2+z	3.139(18)
S3'···F7A	x, 1/2-y, 1/2+z	3.236(14)
F1A···F7C	1-x, -y, 1-z	2.799(16)
F3A···F13A	x, 1/2-y, -1/2+z	2.689(17)
F3B···F10B	1-x, -1/2+y, 3/2-z	2.644(12)
F3B···F7C	1-x, -y, 1-z	3.009(16)
F4···F7B	3/2-x, 1/2+y, z	2.86(3)

F4A···F17B	3/2-x, -1/2+y, z	2.914(18)
F5···F14B	1/2+x, y, 3/2-z	2.57(3)
F5···F7B	3/2-x, 1/2+y, z	3.02(3)
F5A···F5A	1-x, -y, 1-z	2.788(14)
F5B···F10B	1-x, -1/2+y, 3/2-z	3.113(14)
F5B···F12B	1-x, -1/2+y, 3/2-z	2.743(14)
F6A···F14C	1/2+x, y, 3/2-z	2.94(2)
F9B···F21A	x, 1/2-y, 1/2+z	2.81(2)
F10A···F15A	-1/2+x, y, 3/2-z	2.925(13)
F11A···F21A	x, 1/2-y, 1/2+z	3.00(2)
F13B···F17A	1-x, -1/2+y, 3/2-z	3.09(3)
F14B···F21B	-1/2+x, y, 3/2-z	2.82(3)
F14C···F17A	1-x, -1/2+y, 3/2-z	2.91(3)

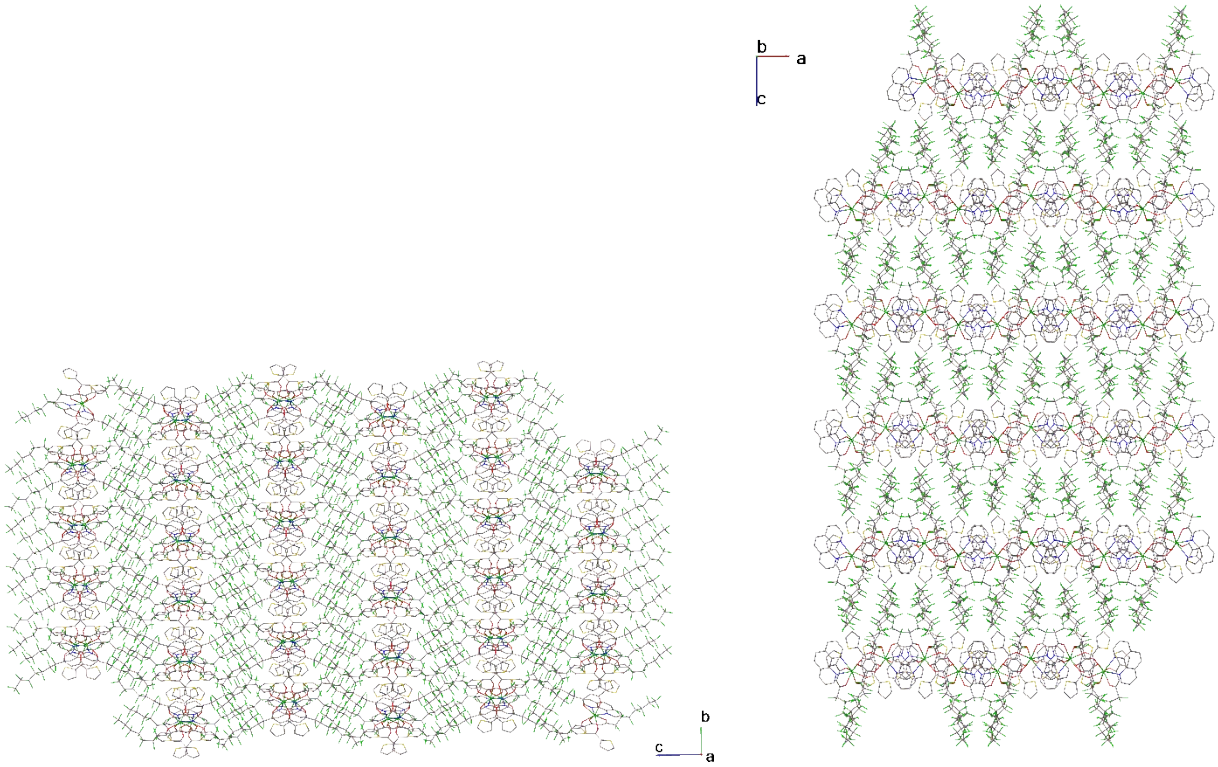

Figure S3. Crystal packing of SmC7 along a) (100) plane; b) (010) plane.

Table S6. Observed maxima of Stark components for f-f transitions of the Sm^{3+} ion in ***$SmCH_3$, $SmCHF_2$, SmC-SmC_8*** *complexes.*

Transition, $^4G_{5/2}$->	**$SmCH_3$**	**$SmCHF_2$**	**SmC1**	**SmC_2**	**SmC_3**	**SmC_4**	**SmC_5**	**SmC_6**	**SmC_7**	**SmC_8**
	Energy, cm^{-1}									
$^6H_{5/2}$	17699 17660 17582 17558 17495	17689 17570 17391	17698 17571 17413	17696 17583 17470	17691 17574 17416	17676 17613 17473	17676 17589 17489	17682 17562 17442	17691 17589 17457	17691 17666 17581 17472

	17387 17315									
$^6H_{7/2}$	16633 16520 16445 16376 16347 16280	16636 16532 16500 16346 16160 16102	16641 16548 16478 16359	16649 16547 16404	16654 16533 16454 16360	16656 16557 16502 16419	16633 16550 16493 16433	16625 16535 16480 16381	16638 16552 16393 16294	16633 16556 16496 16423 16390
$^6H_{9/2}$	15430 15407 15361 15334 15296 15255 15233 15172 15132 15067	15421 15354 15279 15145	15431 15365 15272 15169	15650 15436 15373 15309 15209	15433 15377 15276 15162	15445 15386 15317 15272 15242 15209	15427 15370 15322 15281 15244	15420 15351 15302 15263 15190	15434 15370 15290 15194	15496 15425 15371 15319 15276 15205
$^6H_{11/2}$	14110 14069 13996 13897	14369 14237 14114 14054 14011 13964 13817	14120 14060 13992 13825	14124 14004	14125 14072 14012 13950 13822	14124 14075 14045 13987 13915	14099 14032 13987	14103 14053 13975 13870	14111 14003 13876	14107 13998 13900

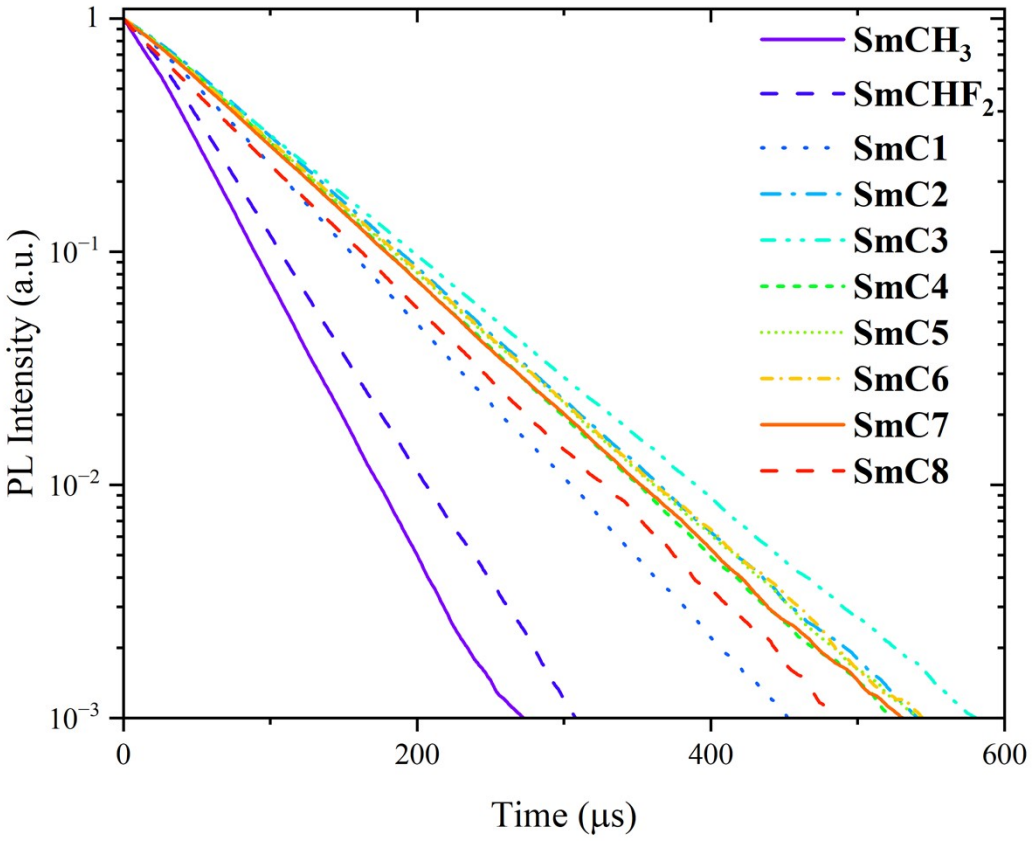

Figure S4. Photoluminescence decay curves for complexes registered at 648 nm wavelength with excitation at 375 nm. Experiments performed at 300 K.

Table S7. CIE coordinates for samarium complexes.

Complex	(X,Y)	
	300 K	77 K
$SmCH_3$	0.64, 0.36	0.65, 0.34
$SmCHF_2$	0.64, 0.36	0.65, 0.34
SmC1	0.64, 0.36	0.65, 0.35
SmC_2	0.63, 0.36	0.65, 0.35
SmC_3	0.64, 0.36	0.66, 0.34
SmC_4	0.65, 0.36	0.66, 0.34
SmC_5	0.63, 0.37	0.65, 0.35
SmC_6	0.64, 0.37	0.65, 0.35
SmC_7	0.64, 0.36	0.65, 0.35
SmC_8	0.64, 0.36	0.63, 0.37

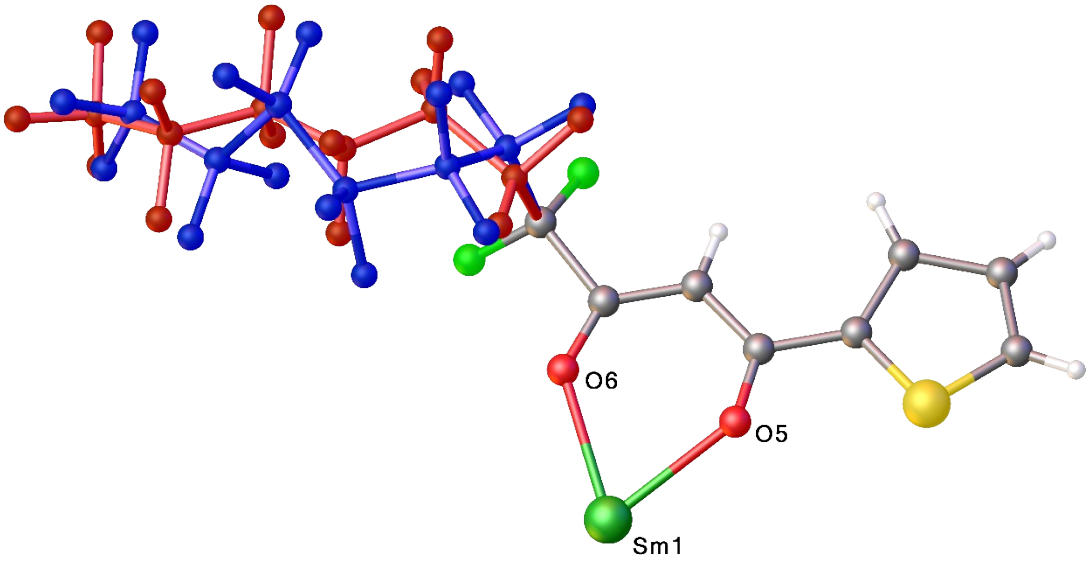

Figure S5. View of the "bending" positional disorder of perfluorinated alkyl chain in the crystal structure of SmC7. Red- and blue-colored atoms represent the occupied sites of carbon and fluorine atoms, fractions are 50% each. All thermal ellipsoids of atomic displacement are omitted for clarity.

Table S8. Comparison of photoluminescence decay times of the investigated complexes with reported in literature in recent years.

Complex	τ_{obs}, μs
$SmCH_3$	38±0.02
$SmCHF_2$	46±0.05
SmC1	68±0.06
SmC_2	83±0.03
SmC_3	85±0.06
SmC_4	79±0.03
SmC_5	80±0.07
SmC_6	80±0.08
SmC_7	78±0.06
SmC_8	69±0.08
$Sm(hfaa)_3(impy)_2$	36[1]
$Sm(hfaa)_3(pz)_2$	39[2]
$Sm(hfaa)_3(TPPO)_2$	97[3]
$Sm(hfpd)_3(prehen)$	53[4]
$Sm(hfpd)_3(TOPO)_2$	26[4]
Sm(L3)bipy	45.3[5]
Sm(L3)phen	41.1[5]

[1] Z. Ahmed, W. Ahmed Dar, and K. Iftikhar, ‘Synthesis and luminescence study of a highly volatile Sm(III) complex’, *Inorganica Chim. Acta*, vol. 392, pp. 446–453, Sep. 2012, doi: 10.1016/j.ica.2012.05.025.

[2] Z. Ahmed, W. Ahmed Dar, and K. Iftikhar, ‘Synthesis and luminescence study of a highly volatile Sm(III) complex’, *Inorganica Chim. Acta*, vol. 392, pp. 446–453, Sep. 2012, doi: 10.1016/j.ica.2012.05.025.

[3] H. Kawai, C. Zhao, S. Tsuruoka, T. Yoshida, Y. Hasegawa, and T. Kawai, ‘Emission properties of Sm(III) complexes having remarkably deep-red emission band’, *J. Alloys Compd.*, vol. 488, no. 2, pp. 612–614, Dec. 2009, doi: 10.1016/j.jallcom.2008.09.091.

[4] S. Malik *et al.*, ‘Exploring the role of neutral ligands in modulating the photoluminescence of samarium complexes with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione’, *Luminescence*, vol. 39, no. 7, Jul. 2024, doi: 10.1002/bio.4810.

[5] V. S. Sizov *et al.*, ‘Effect of ancillary ligands on visible and NIR luminescence of Sm3+ β-diketonate complexes’, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, vol. 225, p. 117503, Jan. 2020, doi: 10.1016/j.saa.2019.117503.