Electronic Supplementary Information (ESI) for

Synthesis, supramolecular isomerism, and photoluminescence of scandium(III) complexes with a tetrafluoroterephthalate ligand

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Abstract

Here we present a new family of seven Sc(III) complexes with tetrafluoroterephthalate ligand ($tFBDC^{2-}$), having non-polymeric and polymeric 2D and 3D structures. These complexes are characterized by SC XRD, PXRD, FT-IR, elemental analysis, and TGA. Among these complexes, 3D coordination polymers $[Sc(H_2O)(tFBDC)_{1.5}]\cdot H_2O$ (**1**), $[Sc_2(H_2O)_2(tFBDC)_3]\cdot 2H_2O$ (**2**), and $[Sc(H_2O)(tFBDC)_{1.5}]\cdot 4H_2O$ (**3**) are supramolecular isomers. Complex **1** is obtained as a phase pure material, while **2** and **3** are found as admixtures. The reaction of $Sc(CF_3SO_3)_3$ with H_2tFBDC in the presence of NH_3 as a base produces layered coordination polymer $[Sc(H_2O)(OH)(tFBDC)]$ **(4).** Complexes $(NH_4)[Sc(H_2O)_4(tFBDC)_2]\cdot 5H_2O$ (**5**), $[K(H_2O)_2Sc(H_2O)_4(tFBDC)_2]\cdot 3H_2O$ (**6**) and $[Cs(H_2O)_4Sc(H_2O)_4(tFBDC)_2]\cdot 0.5H_2O$ (**7**) based on the same $[Sc(H_2O)_4(tFBDC)_2]^-$ anionic unit are obtained by precipitation with NH_3, KOH or CsOH. Coordination polymer **1** and **4** are stable in an aqueous solution in the range of pH 2–12. Solid complexes **1**, **4**–**7** show ligand-centred purple/blue photoluminescence, with **1** and **4** having high quantum yields of 28 and 34% at room temperature.

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Identification codes

H_2tFBDC tetrafluoroterephthalic acid

1 $[Sc(H_2O)(tFBDC)_{1.5}]\cdot H_2O$

2 $[Sc_2(H_2O)_2(tFBDC)_3]\cdot 2H_2O$

3 $[Sc(H_2O)(tFBDC)_{1.5}]\cdot 4H_2O$

4 $[Sc(H_2O)(OH)(tFBDC)]$

5 $(NH_4)[Sc(H_2O)_4(tFBDC)_2]\cdot 5H_2O$ (SC XRD)

5' $(NH_4)[Sc(H_2O)_4(tFBDC)_2]\cdot 4H_2O$ (isolated product, according to elemental CHNF analysis)

6 $[K(H_2O)_2Sc(H_2O)_4(tFBDC)_2]\cdot 3H_2O$

7 $[Cs(H_2O)_4Sc(H_2O)_4(tFBDC)_2]\cdot 0.5H_2O$

Characterization of complexes 1–7

$[Sc(H_2O)(tFBDC)_{1.5}]\cdot H_2O$ (1)

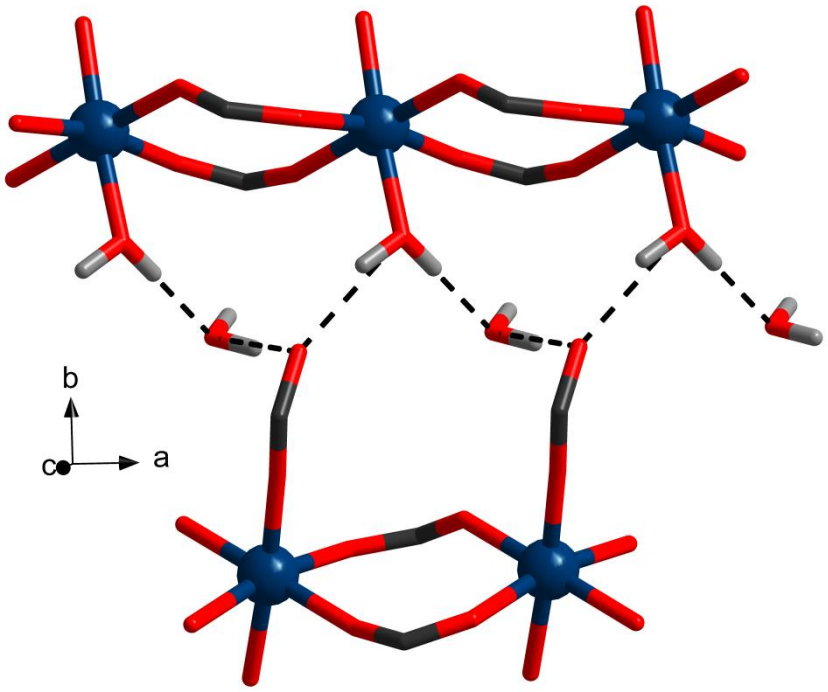

Fig. S1. Hydrogen bonding interactions between guest and coordinated water molecules and non-coordinated O atom of $tFBDC^{2-}$ in crystal packing of **1**.

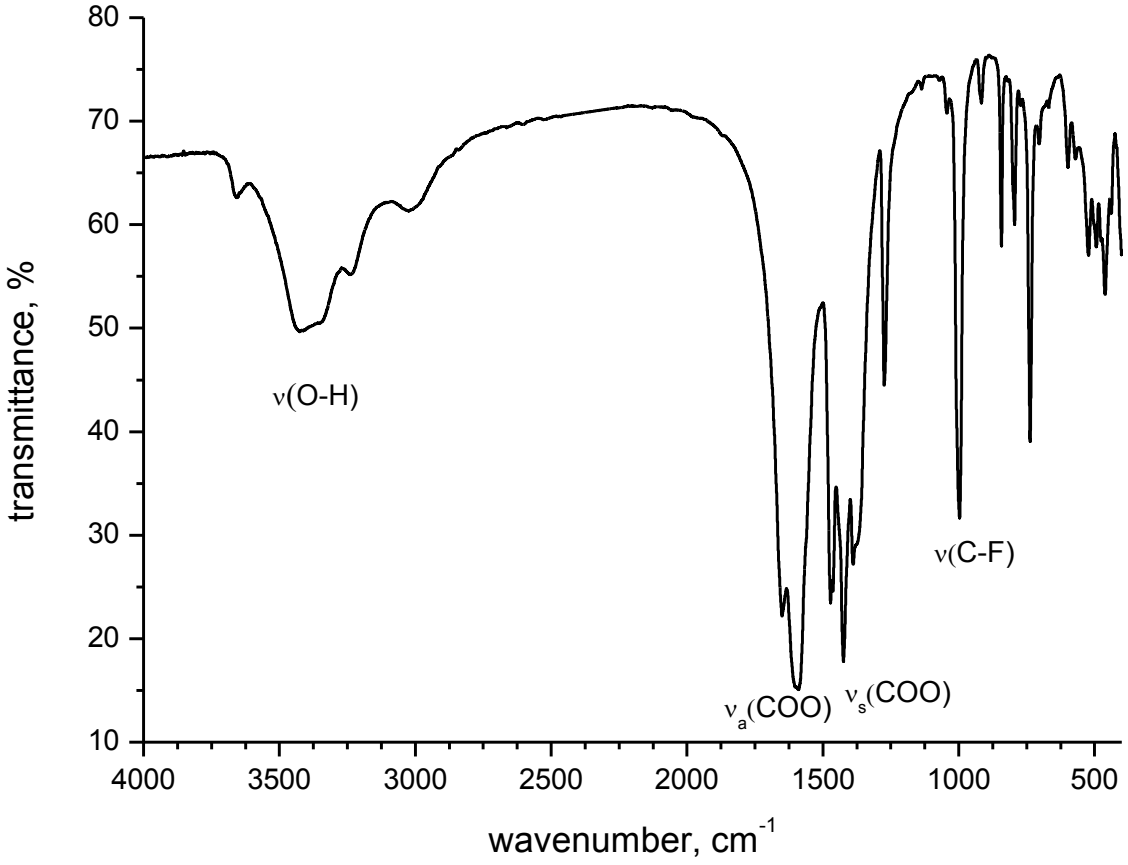

Fig. S2. The FT-IR spectrum of complex **1**.

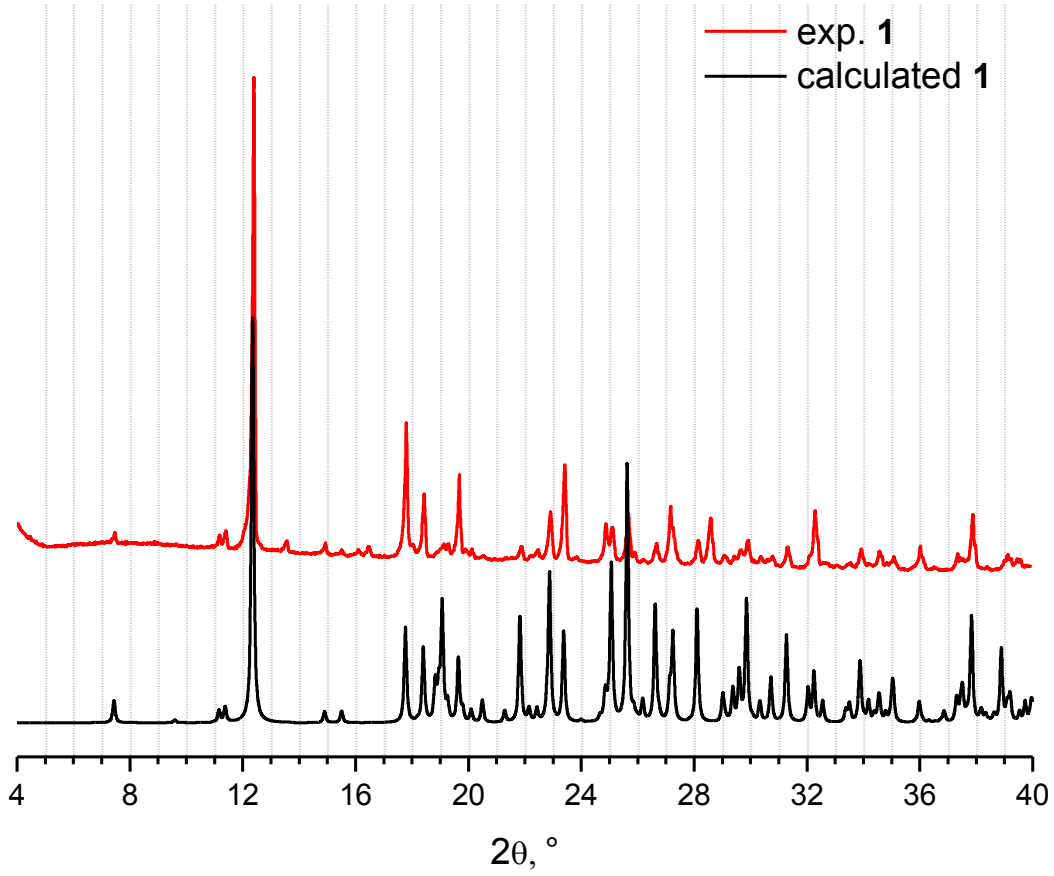

Fig. S3. Experimental (red line) and calculated (black line) PXRD patterns of complex **1**. Black curve is calculated for refined at room temperature unit cell parameters: a = 4.959 Å, b = 15.545 Å, c = 18.479 Å; β = 94,62°; V = 1420.0 Å^3.

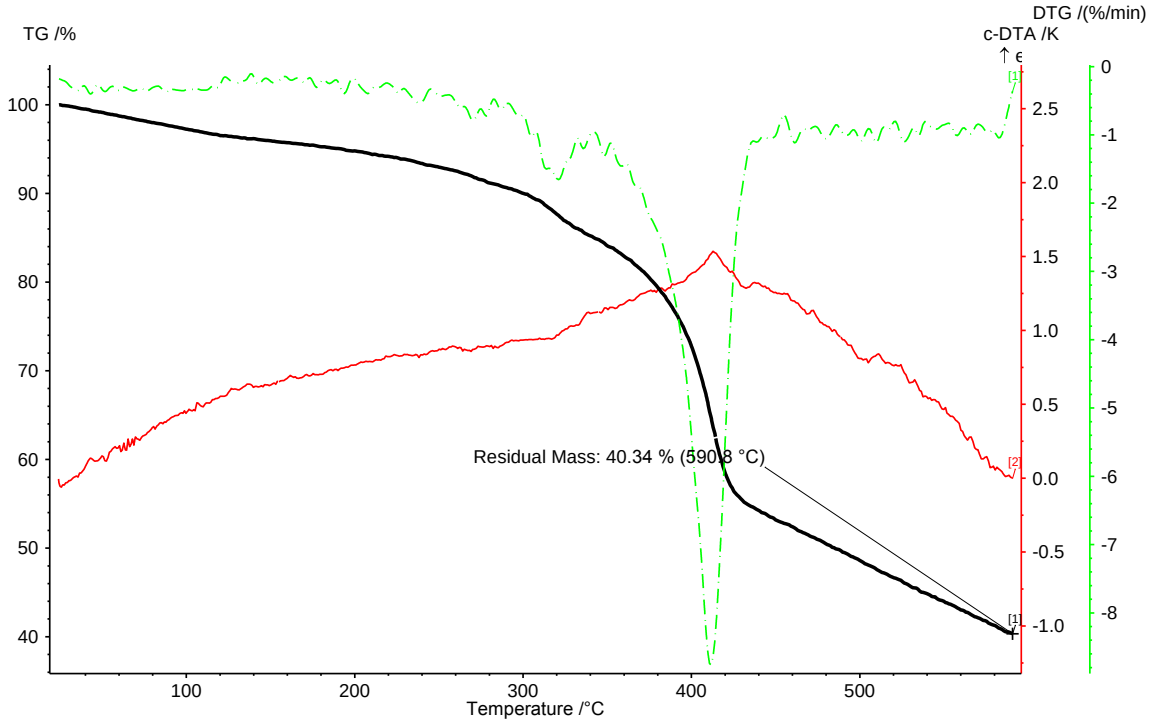

Fig. S4. TG curve of complex **1**.

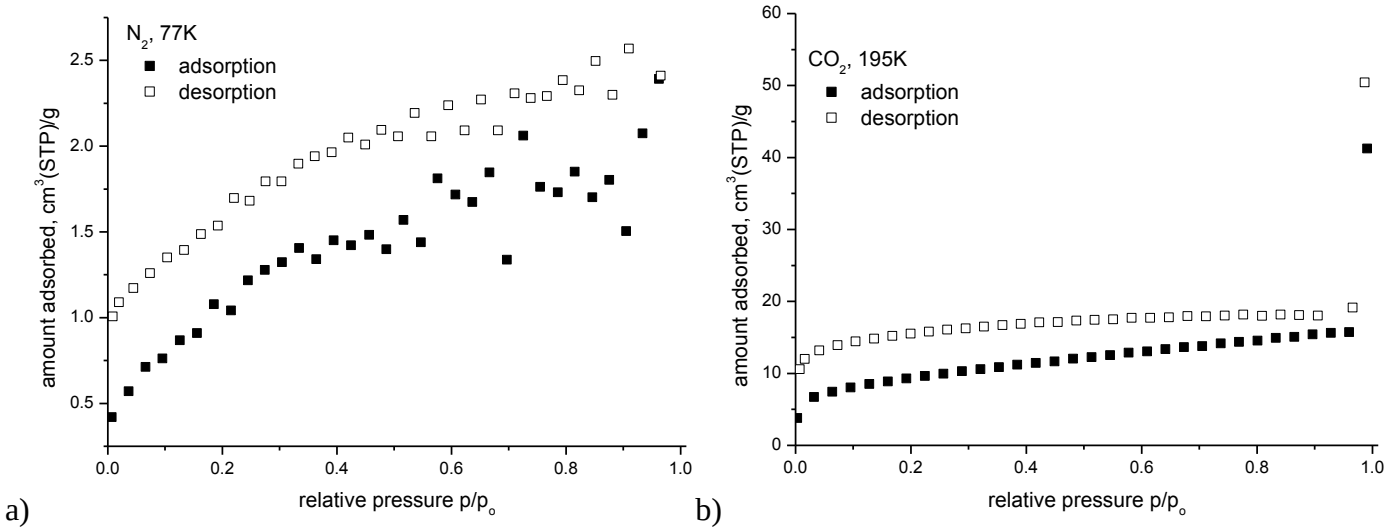

Fig. S5. The isotherms of adsorption of activated **1** (250 °C, 5 h, heating rate – 1°C/min): a) N_2, 77 K, b) CO_2, 195 K.

$[Sc_2(H_2O)_2(tFBDC)_3]\cdot 2H_2O$ (2)

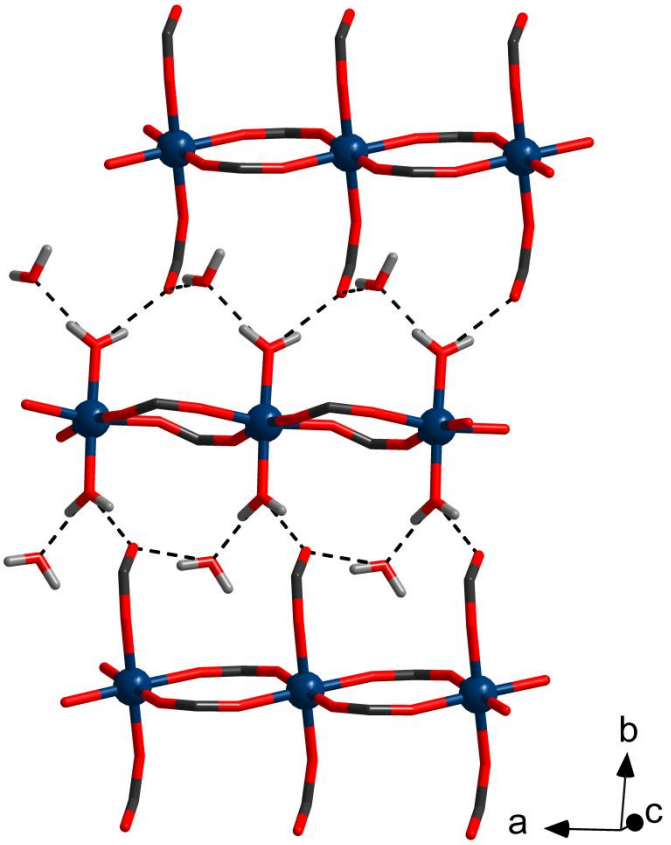

Fig. S6. Hydrogen bonding interactions between guest and coordinated water molecules and non-coordinated O atom of $tFBDC^{2-}$ in crystal packing of **2**.

$[Sc(H_2O)(tFBDC)_{1.5}]\cdot 4H_2O$ (3)

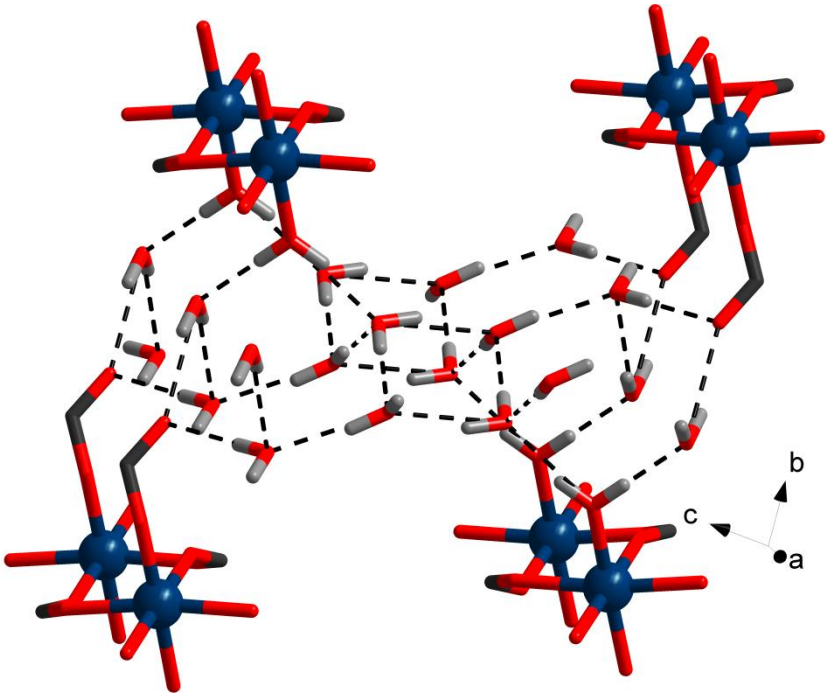

Fig. S7. Hydrogen bonding interactions between guest and coordinated water molecules and non-coordinated O atom of $tFBDC^{2-}$ in crystal packing of **3**.

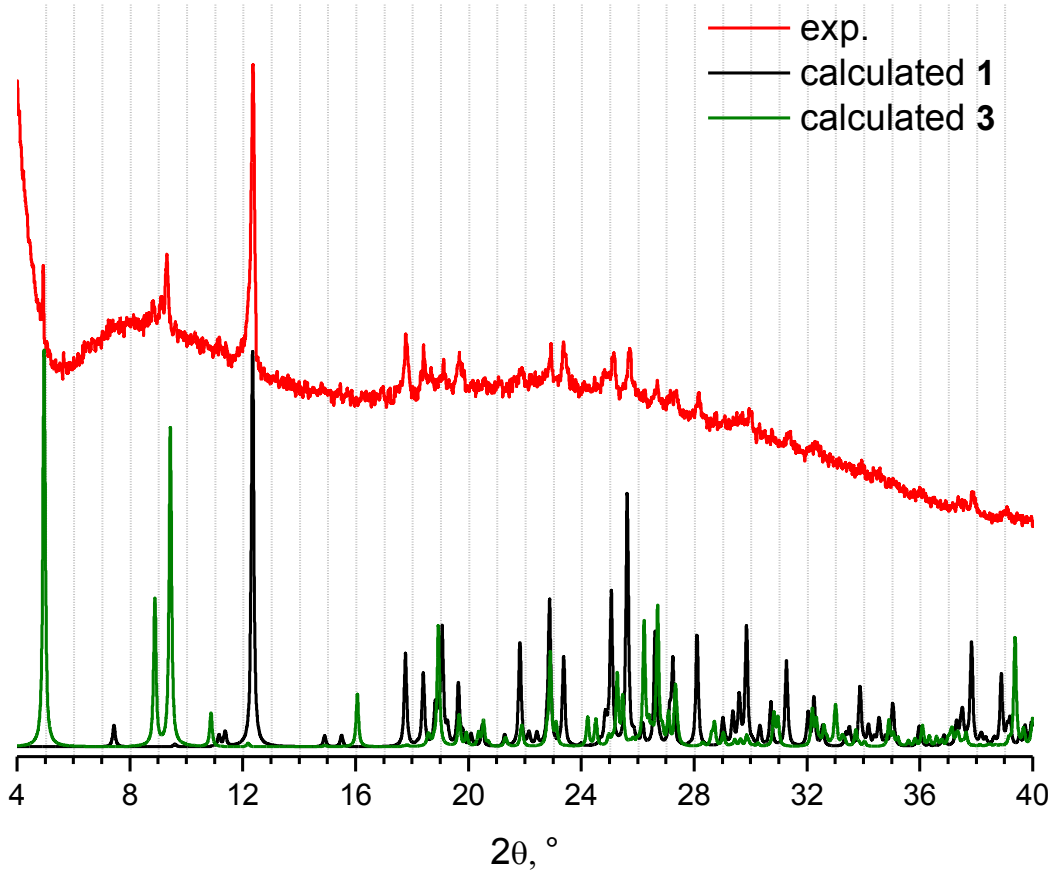

Fig. S8. Comparison of powder pattern (red line) of the solid after evaporation of aqueous solution $Sc(CF_3SO_3)_3$ + H_2tFBDC + LiOH with the calculated patterns of **1** (black line) and **3** (green line).

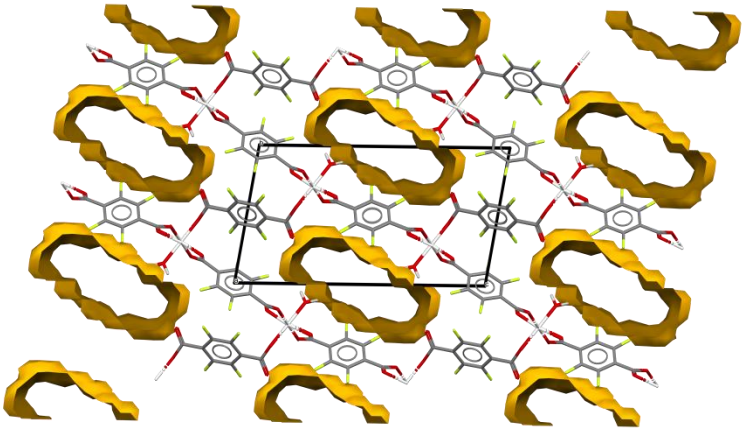

Fig. S9. Visualization of the solvent accessible volume in crystal structure of CP **3**. Empty CP **3** has a solvent accessible volume of 19.8% and an expected pore volume of 0.12 cm^3/g if all guest molecules are removed from the framework without any other changes.

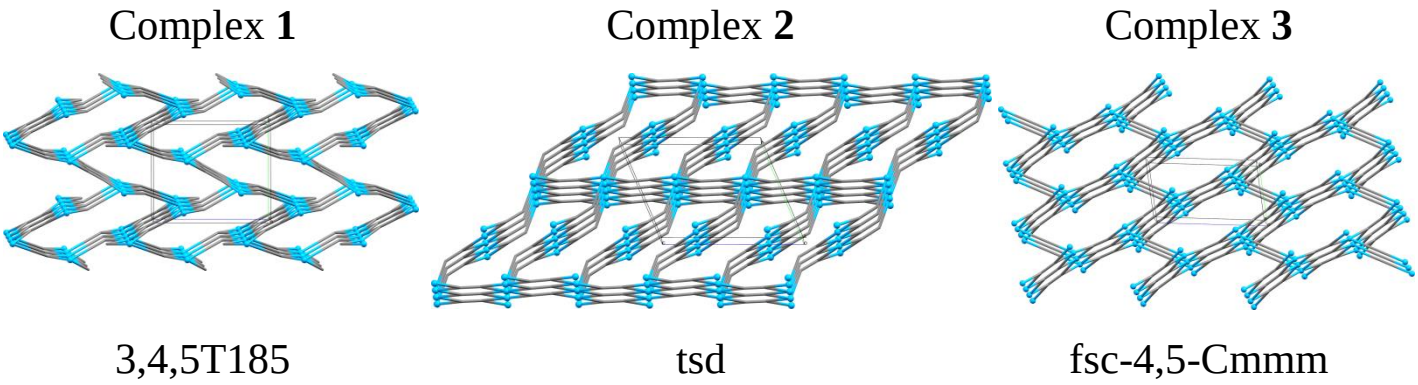

Fig. S10. Simplified nets of coordination polymers **1**, **2** and **3** and their topology names.

[Sc(H_2O)(OH)(tFBDC)] (4)

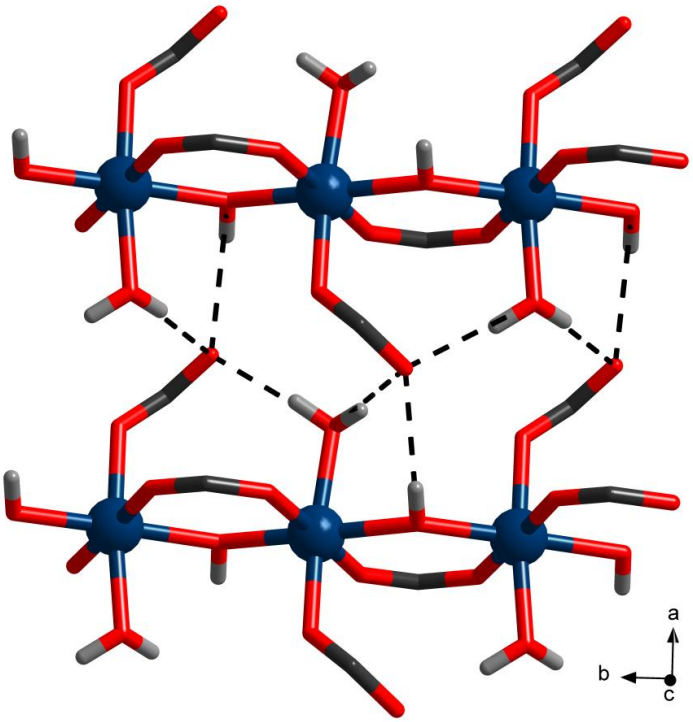

Fig. S11. Intra- and interlayer hydrogen bonding interactions between coordinated water molecules and non-coordinated O atom of $tFBDC^{2-}$ in crystal packing of **4**.

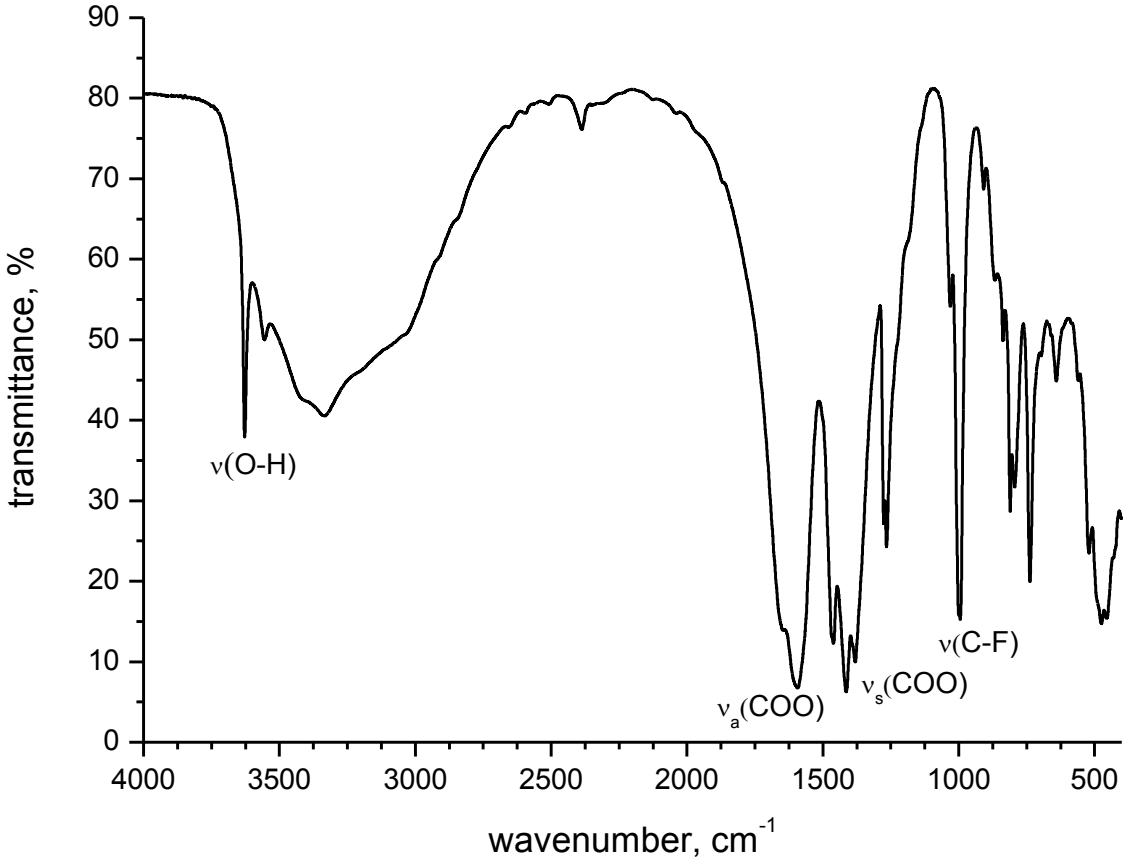

Fig. S12. The FT-IR spectrum of complex **4**.

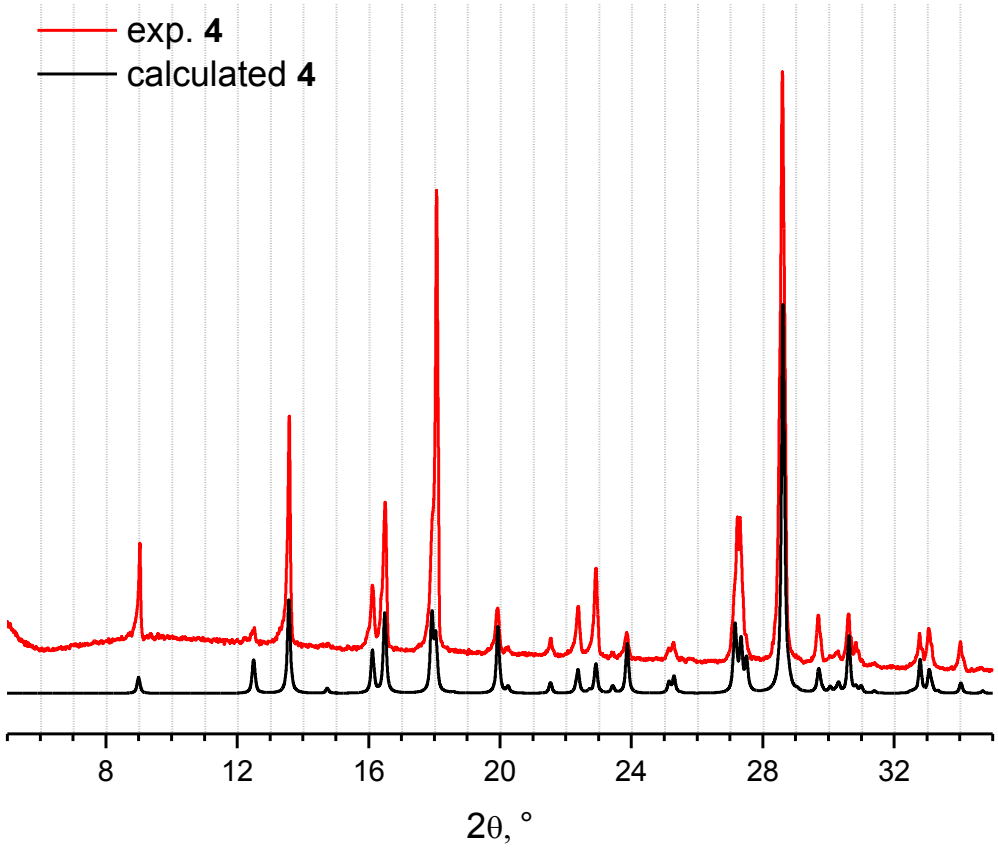

Fig. S13. Experimental (red line) and calculated (black line) PXRD patterns of complex **4**. Black curve is calculated for refined at room temperature unit cell parameters: a = 6.521 Å, b = 7.586 Å, c = 19.652 Å; β = 91.416°; V = 971.9 Å^3.

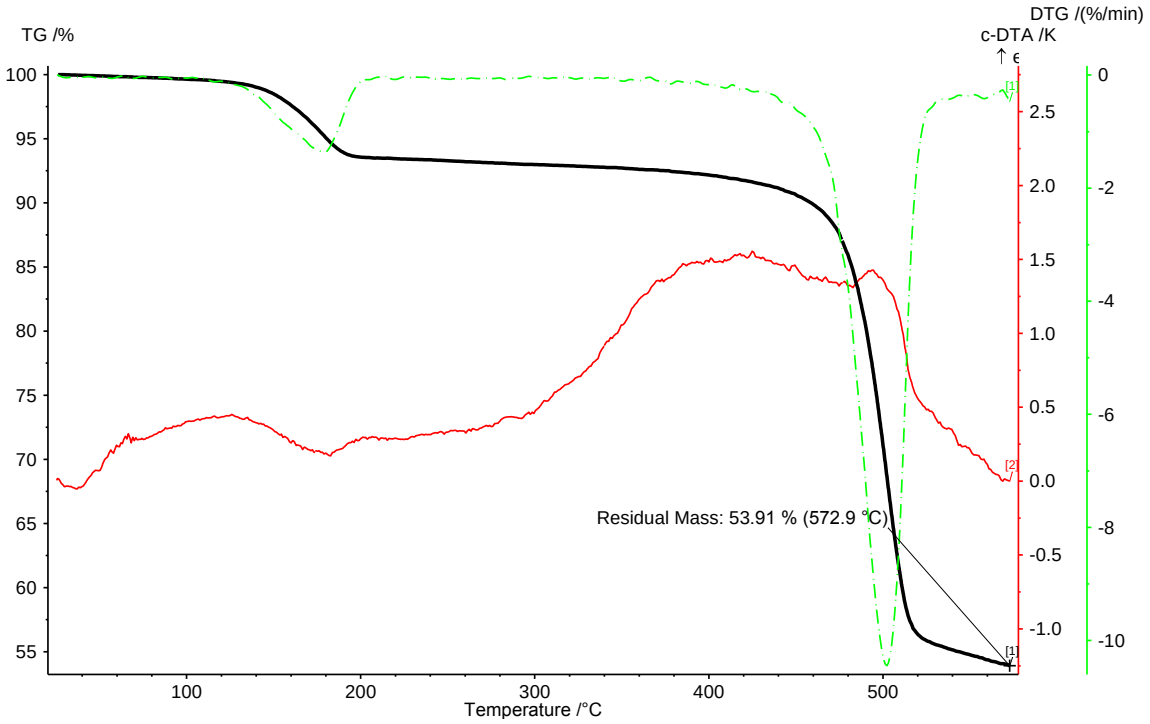

Fig. S14. TG curve of complex **4**.

$(NH_4)[Sc(H_2O)_4(tFBDC)_2]\cdot 5H_2O$ (5)

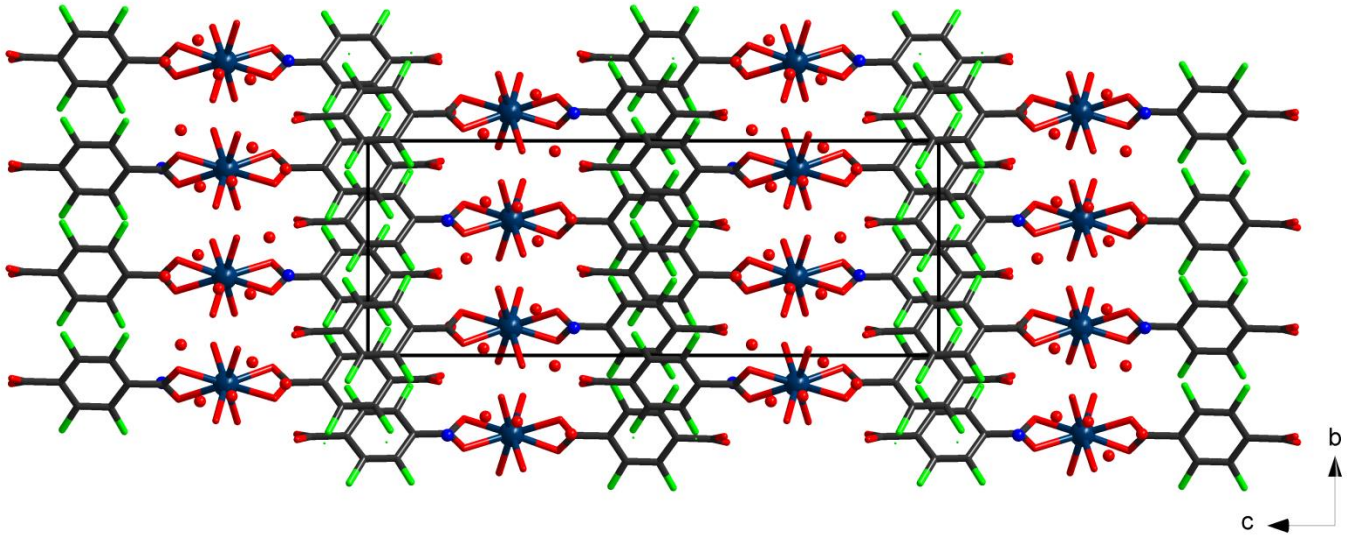

Fig. S15. Fragment of crystal packing of **5** (projection on *bc* plane). Oxygen and nitrogen atoms of lattice water and ammonium cations are shown as red and blue spheres. Hydrogen atoms are omitted for clarity.

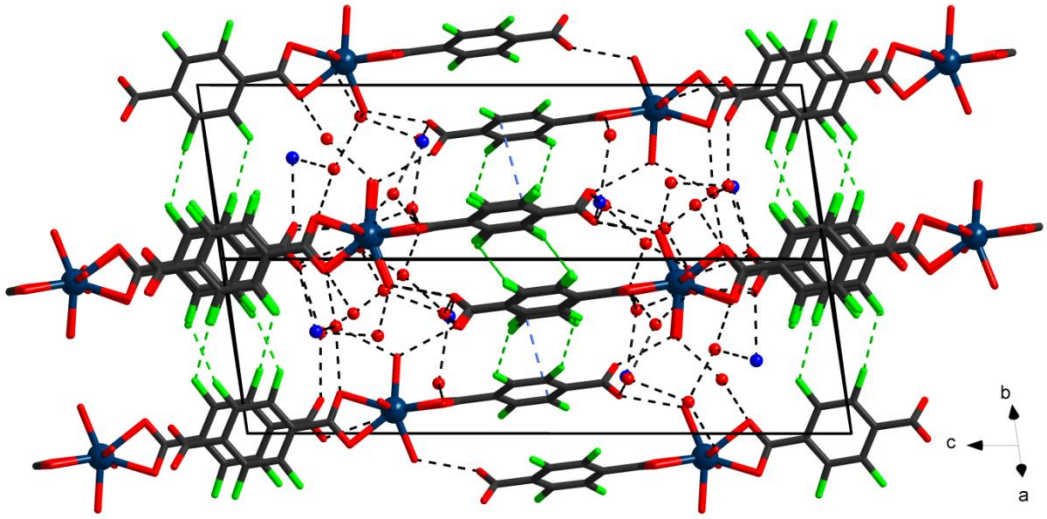

Fig. S16. Fragment of crystal packing of **5**. Hydrogen atoms are omitted for clarity. Oxygen and nitrogen atoms of lattice water and ammonium cations are shown as red and blue spheres. Hydrogen bonds are shown with black dashed lines. The shortest C…C distance between adjacent phenylene rings of 3.562 Å is shown with light blue dashed line. Bright green dashed line shows F…F contacts.

Table S1. The summary of Continuous Shape Measures calculations of Sc(III) coordination polyhedron in structures **5**, **6**, and **7**.

	OP	HPY	HBPY	CU	SAPR	TDD	JGBF	JETBPY	JBTPR	BTPR	JSD	TT	ETBPY
5	29.656	24.013	11.995	9.214	3.227	2.629	10.406	25.698	2.602	**2.150**	2.723	10.047	23.323
6	29.045	24.858	11.765	8.442	2.727	2.704	10.667	26.026	2.893	**2.574**	2.897	9.308	23.714
7	30.478	25.409	12.226	10.423	4.099	**2.444**	9.927	26.097	3.499	3.145	2.589	11.263	23.123

OP – octagon, HPY – heptagonal pyramid, HBPY – hexagonal bipyramid, CU – cube, SAPR – square antiprism, TDD – triangular dodecahedron, JGBF – Johnson gyrobifastigium J26, JETBPY – Johnson elongated triangular bipyramid J14, JBTPR – biaugmented trigonal prism J50, BTPR – biaugmented trigonal prism, JSD – snub diphenoid J84, TT – triakis tetrahedron, ETBPY – elongated trigonal bipyramid

Table S2. The summary of structural features of crystal structures **5**, **6**, and **7**.

	5	**6**	**7**
d(Sc–OCO), Å	2.2894(10), 2.2998(10), 2.2759(10), 2.6420(14)	2.2802(7), 2.2802(7), 2.2802(7), 2.2803(7)	2.289(7), 2.289(7), 2.281(7), 2.281(7)
d(Sc–OH_2), Å	2.1509(11), 2.1548(11), 2.1592(11), 2.1592(11)	2.1564(8), 2.1564(8), 2.1564(8), 2.1565(8)	2.175(9), 2.175(9), 2.177(10), 2.177(10)
Torsion angles between carboxylate group and phenylene group, °	22.5, 25.3 (bidentate); 51.6, 56.31 (free)	25.4; 51.4	19.5, 20.1, 22.1; 57.5, 59.8

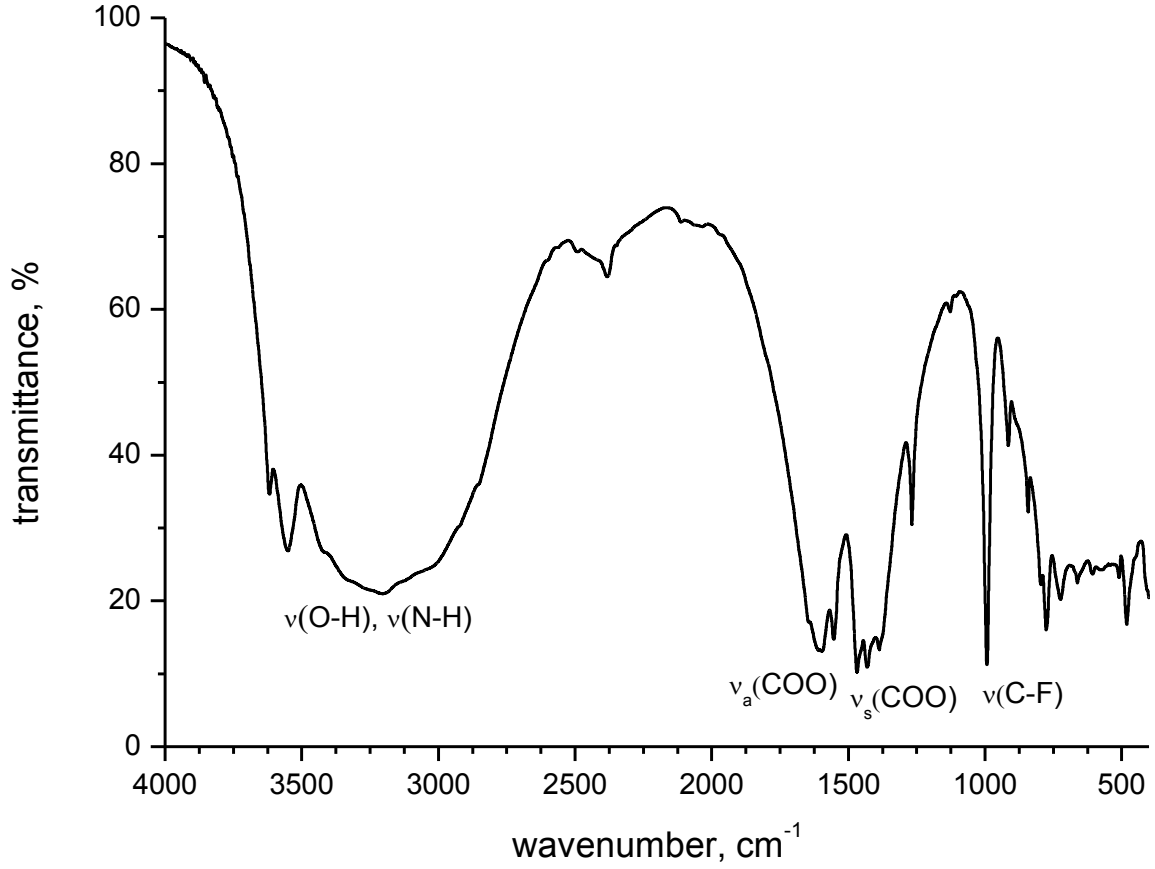

Fig. S17. The FT-IR spectrum of complex **5'**.

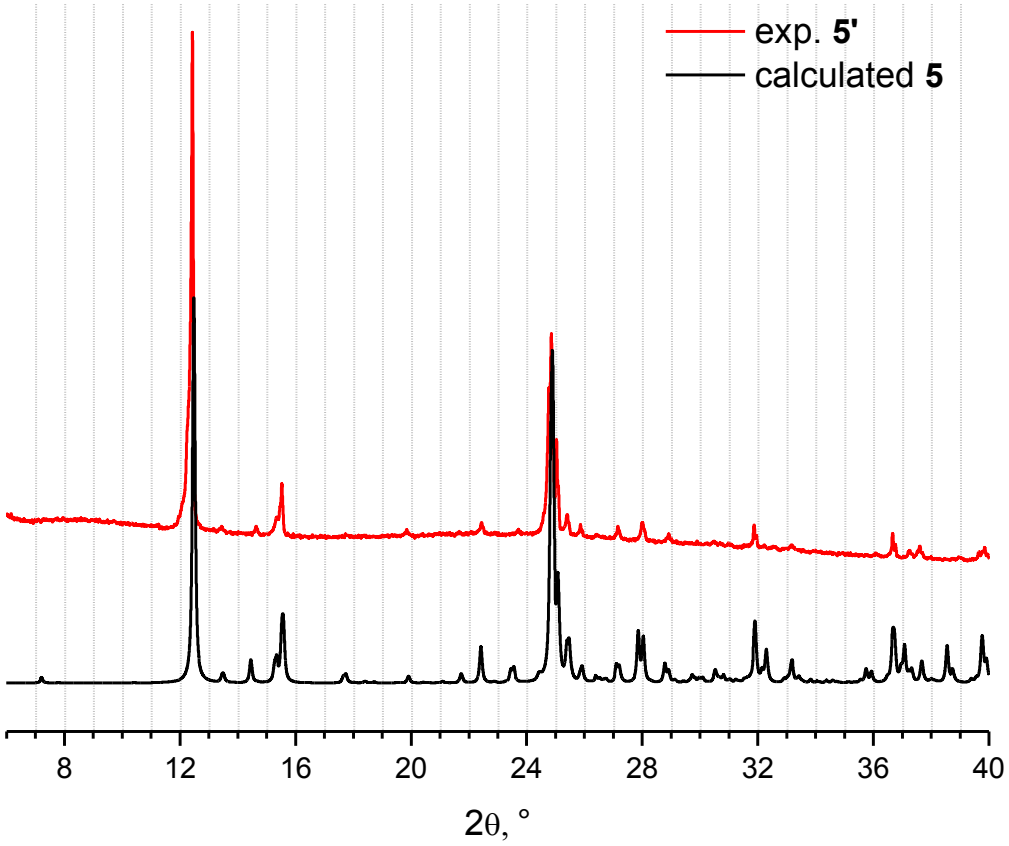

Fig. S18. Experimental (red line) and calculated (black line) PXRD patterns of complex **5'**. Black curve is calculated for refined at room temperature unit cell parameters: a = 11.704 Å, b = 9.064 Å, c = 25.143 Å; β = 91.416°; V = 2598.8 Å^3.

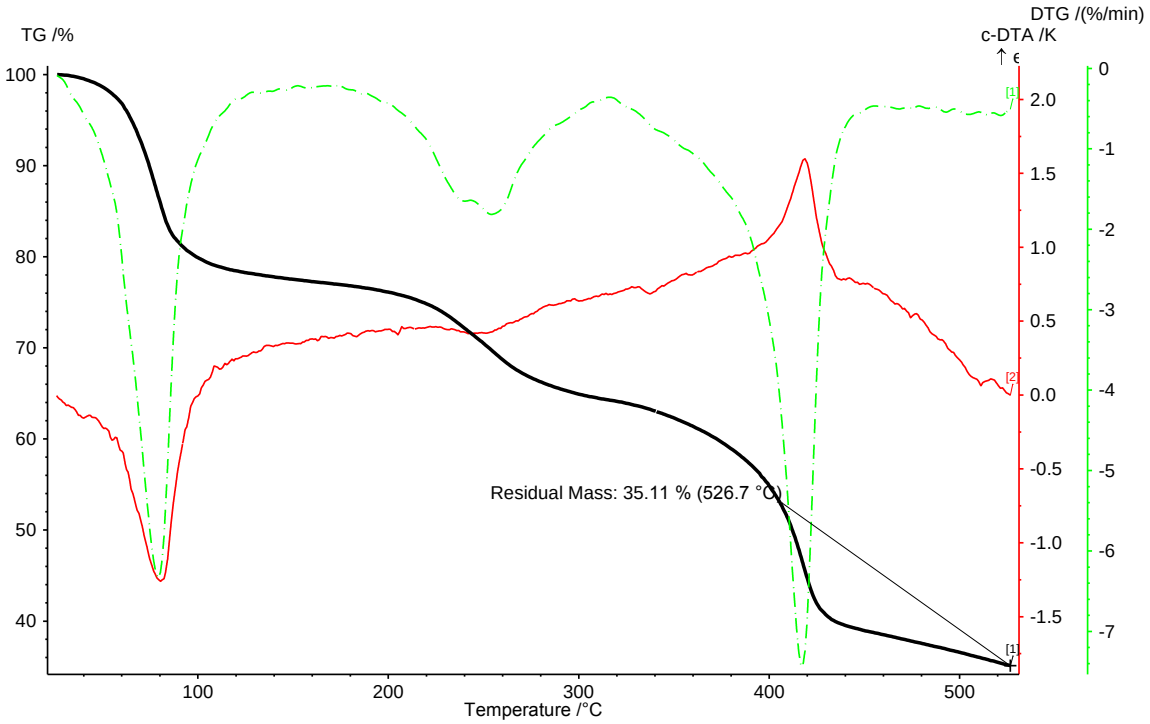

Fig. S19. TG curve of complex **5'**.

$[K(H_2O)_2Sc(H_2O)_4(tFBDC)_2]\cdot 3H_2O$ (6)

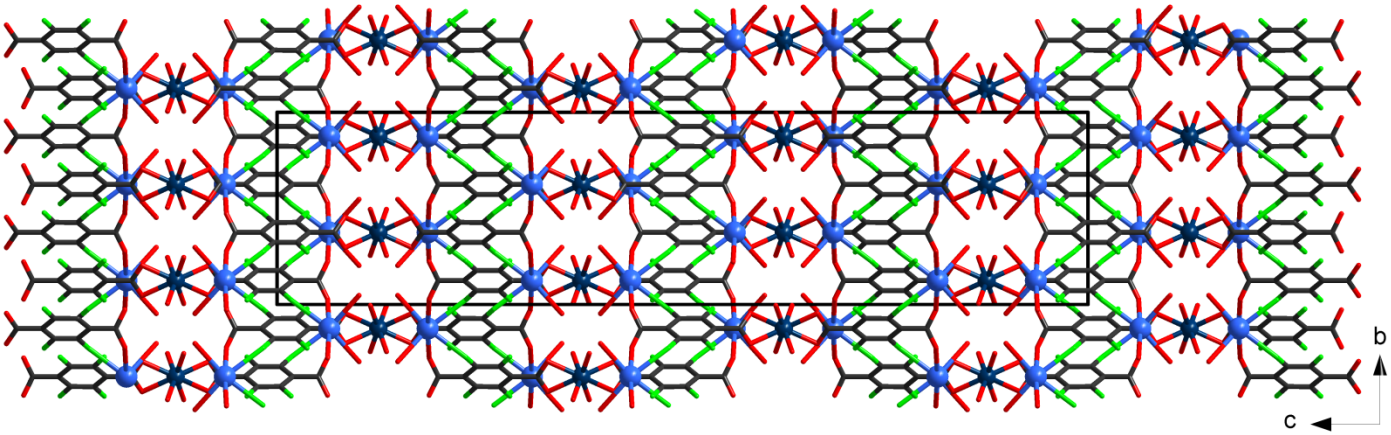

Fig. S20. Fragment of crystal packing of **6** (projection on *bc* plane). Potassium cations and lattice water molecules share almost the same position shown with light blue spheres with the occupancy of 0.5. Hydrogen atoms are omitted for clarity.

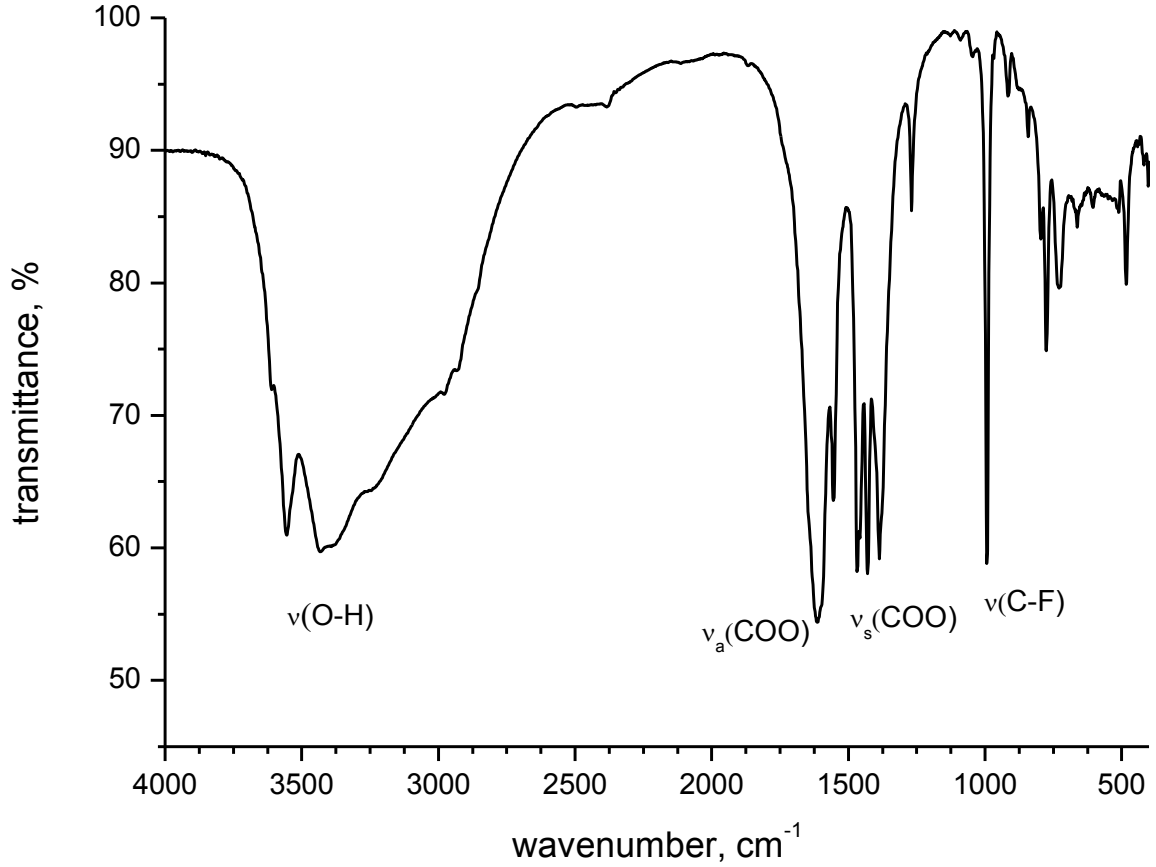

Fig. S21. The FT-IR spectrum of complex **6**.

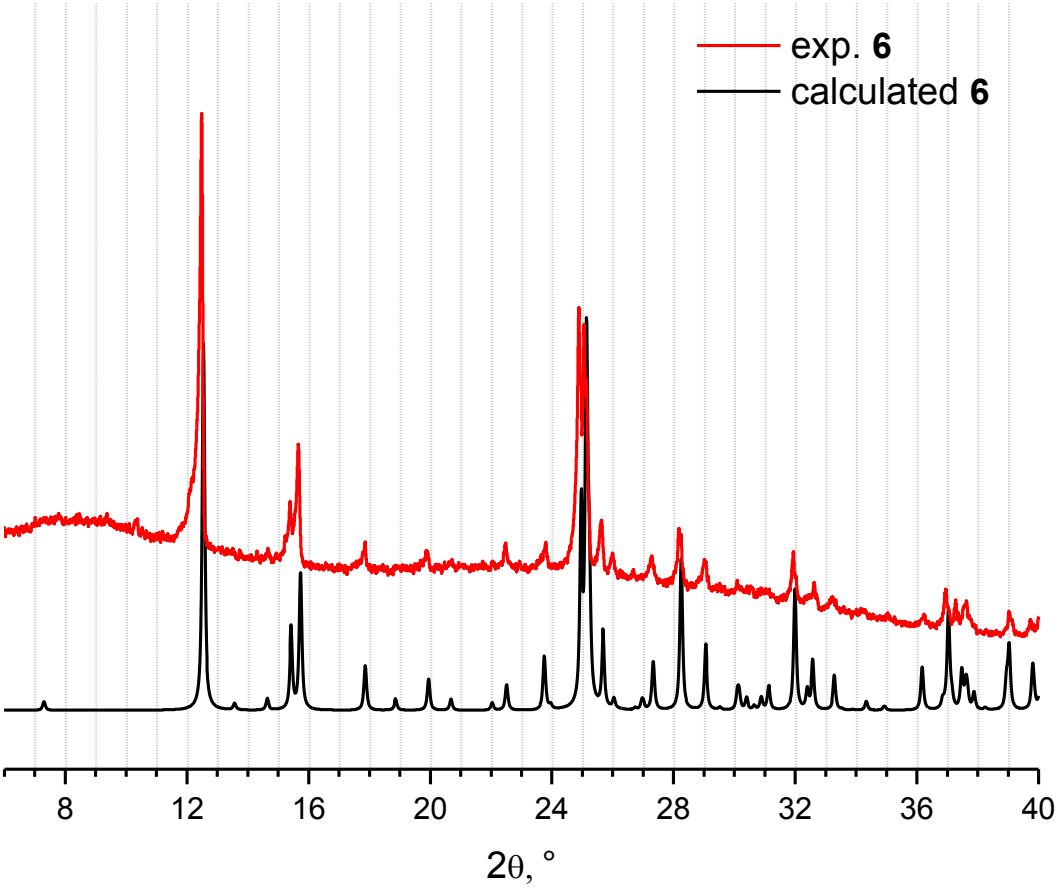

Fig. S22. Experimental (red line) and calculated (black line) PXRD patterns of complex **6**. Black curve is calculated for refined at room temperature unit cell parameters: a = 9.051 Å, b = 11.573 Å, c = 48.372 Å; β = 91.416°; V = 5066.8 Å^3.

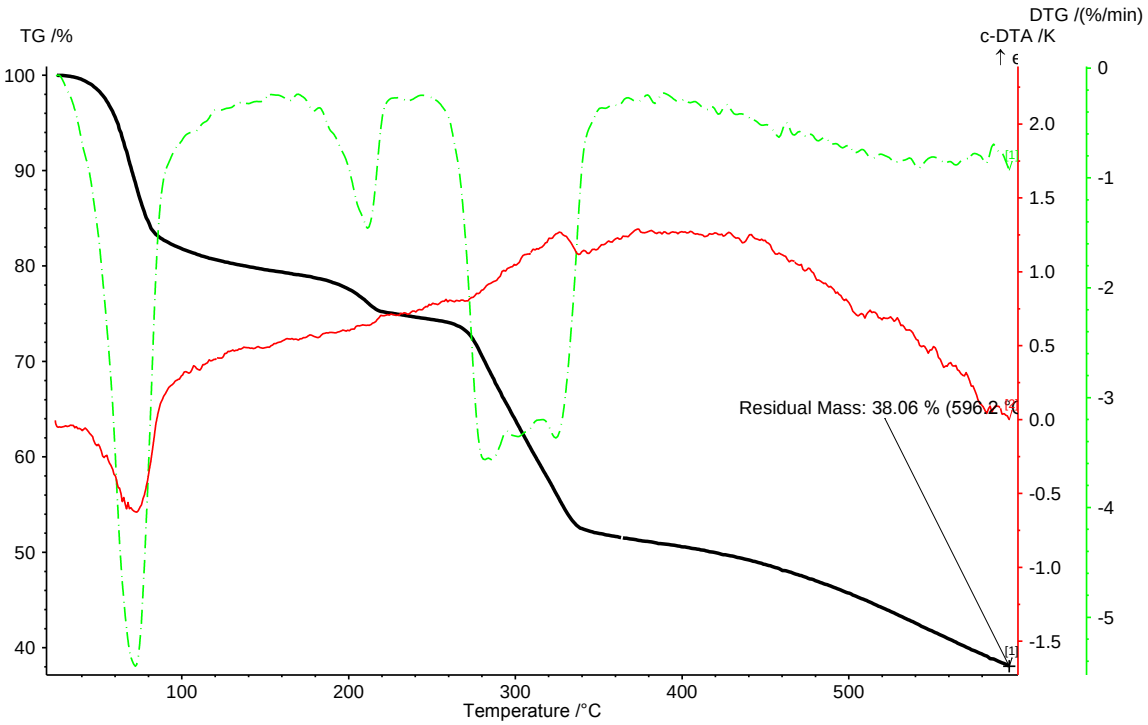

Fig. S23. TG curve of complex **6**.

$[Cs(H_2O)_4Sc(H_2O)_4(tFBDC)_2]\cdot 0.5H_2O$ (7)

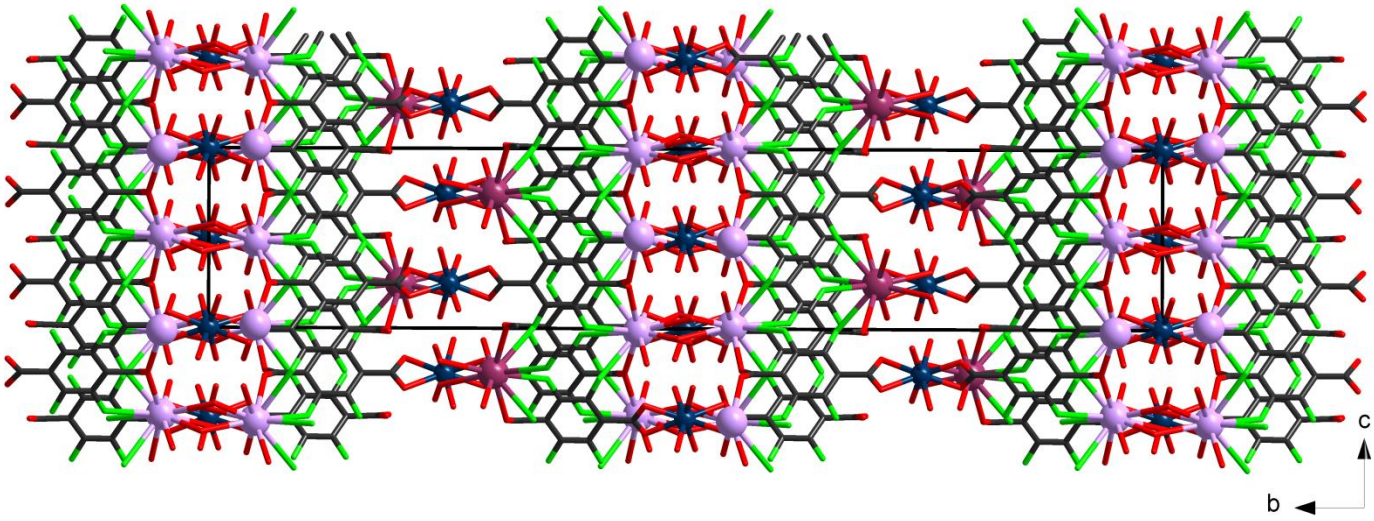

Fig. S24. Fragment of crystal packing of **7** (projection on *bc* plane). Two different positions of caesium cations with occupancies of 1.0 and 0.5 are shown as plum and lavender spheres, respectively. Oxygen atoms of lattice water molecules are shown as red spheres. Hydrogen atoms are omitted for clarity.

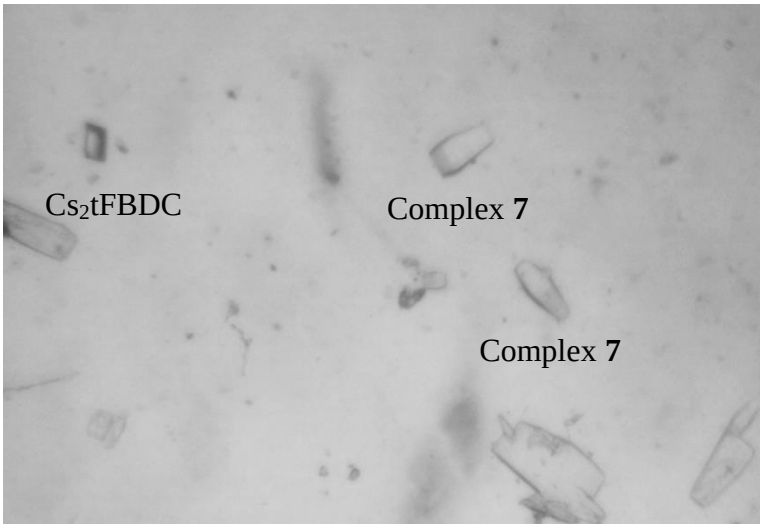

Fig. S25. Crystals of complex **7** and byproduct Cs_2tFBDC.

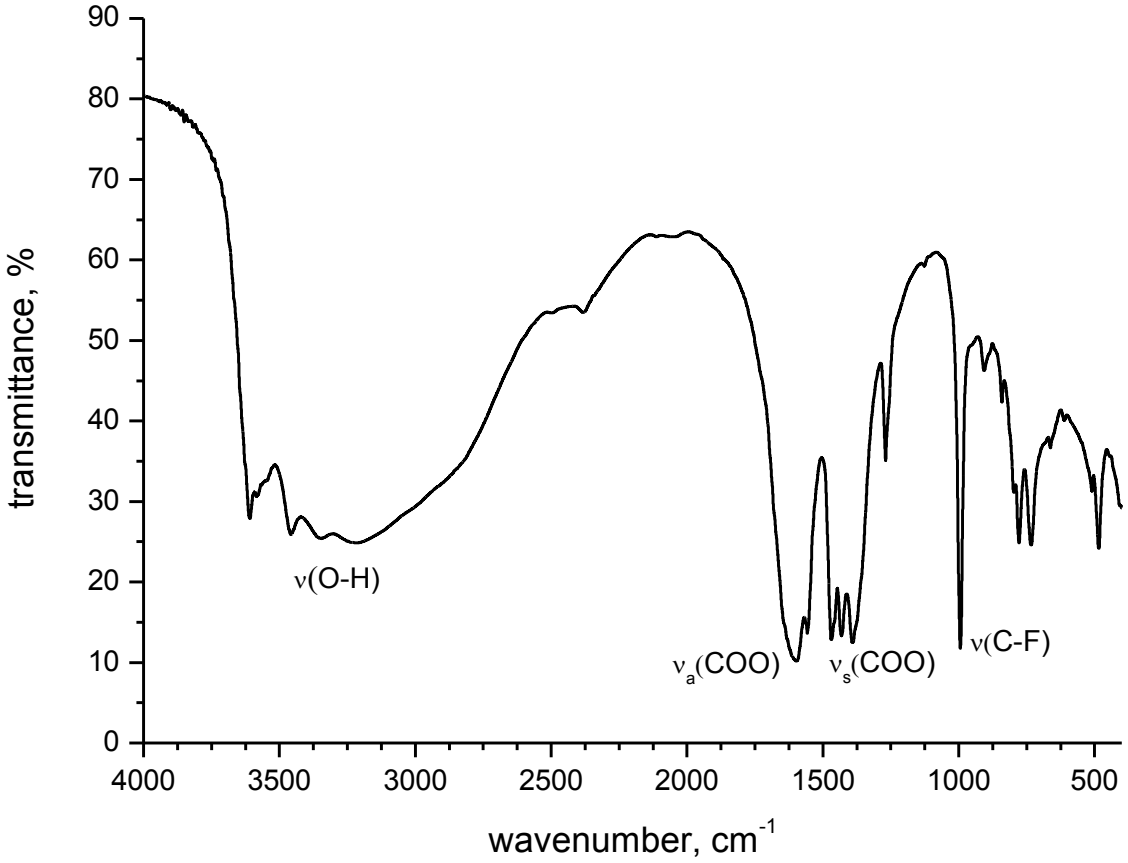

Fig. S26. The FT-IR spectrum of complex **7**.

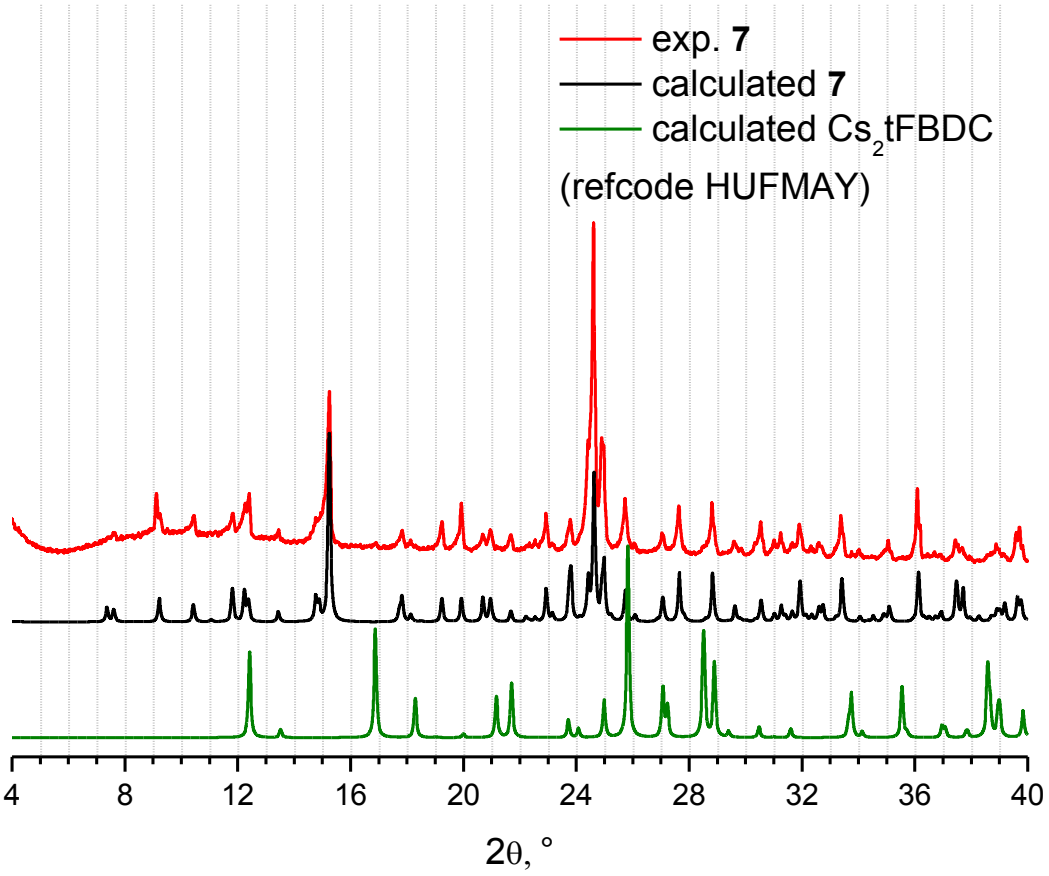

Fig. S27. Experimental (red line), calculated (black line) PXRD patterns of complex **7**, and calculated powder pattern of caesium tetrafluoroterephthalate (refcode HUFMAY). Refined unit cell parameters at room temperature of **7** are the following: a = 11.973 Å, b = 47.973 Å, c = 9.060 Å; V = 5204.1 Å^3. The absence of intensive peaks at 2θ = 17°, 28.5° and 35.5° confirm the phase purity of isolated CP **7**.

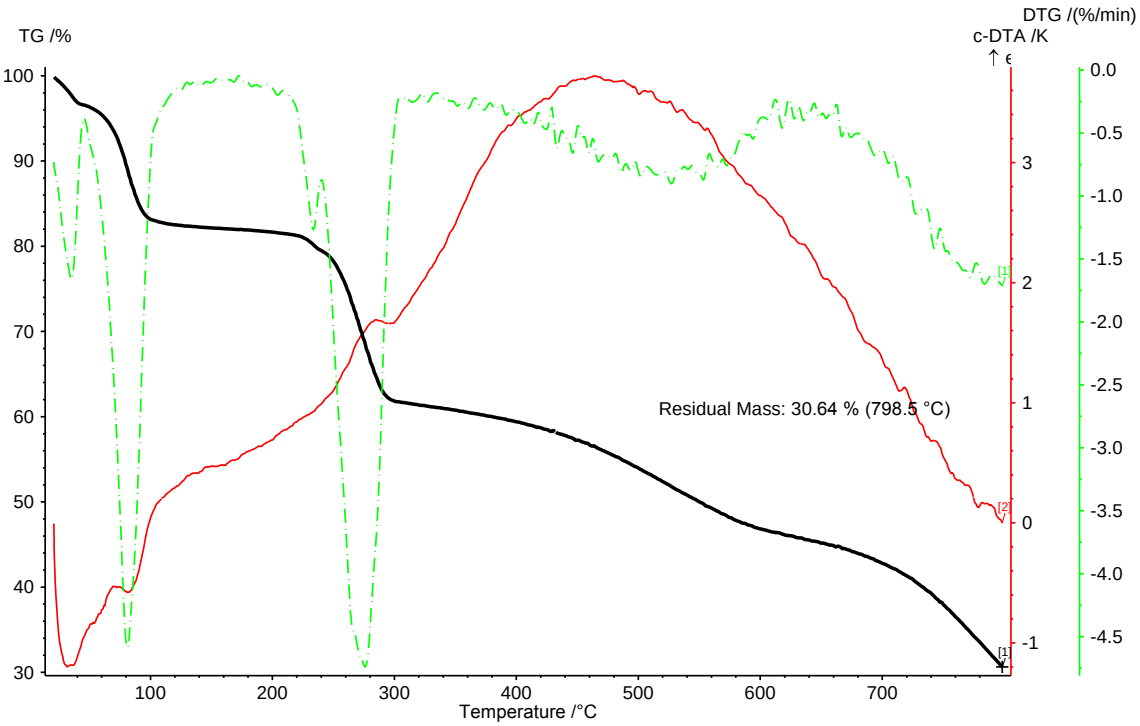

Fig. S28. TG curve of complex **7**.

Table S3. The parameters of F…F contacts in crystal structures **1**–**5**.

Complex	d(F…F), Å	θ_1, °	θ_2, °	Type
1	2.834	84.05	136.97	II
2	2.935	90.63	135.86	II
	2.889	126.68	126.68	I
3	2.869	82.11	141.77	II
4	2.847	144.35	162.67	quasi I/II
	2.880	143.46	161.49	quasi I/II
5	2.866 – 2.920	*ca.* 130	*ca.* 160	quasi I/II

The study of photoluminescence properties of solid H_2tFBDC and complexes 1, 4–7

H_2tFBDC

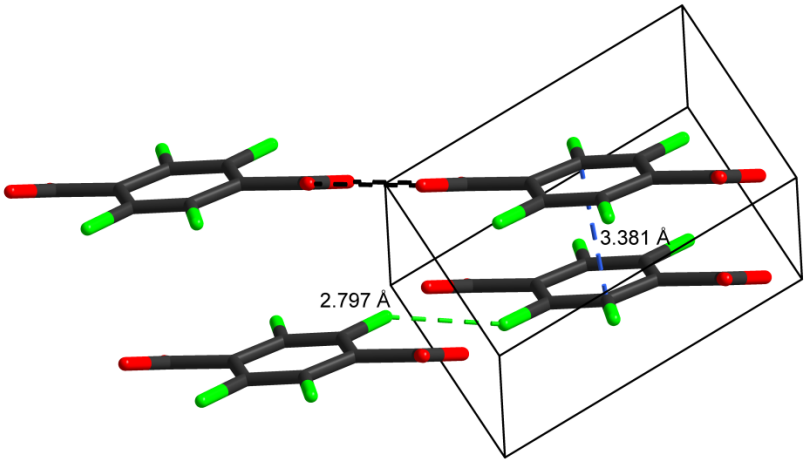

Fig. S29. The fragment of crystal packing of H_2tFBDC (refcode BITCEM13), showing hydrogen bonds between carboxylic groups (black dashed lines), C…C contact with the distance of 3.381 Å (light blue dashed line), and F…F contact (bright green dashed line) with the distance of 2.797 Å.

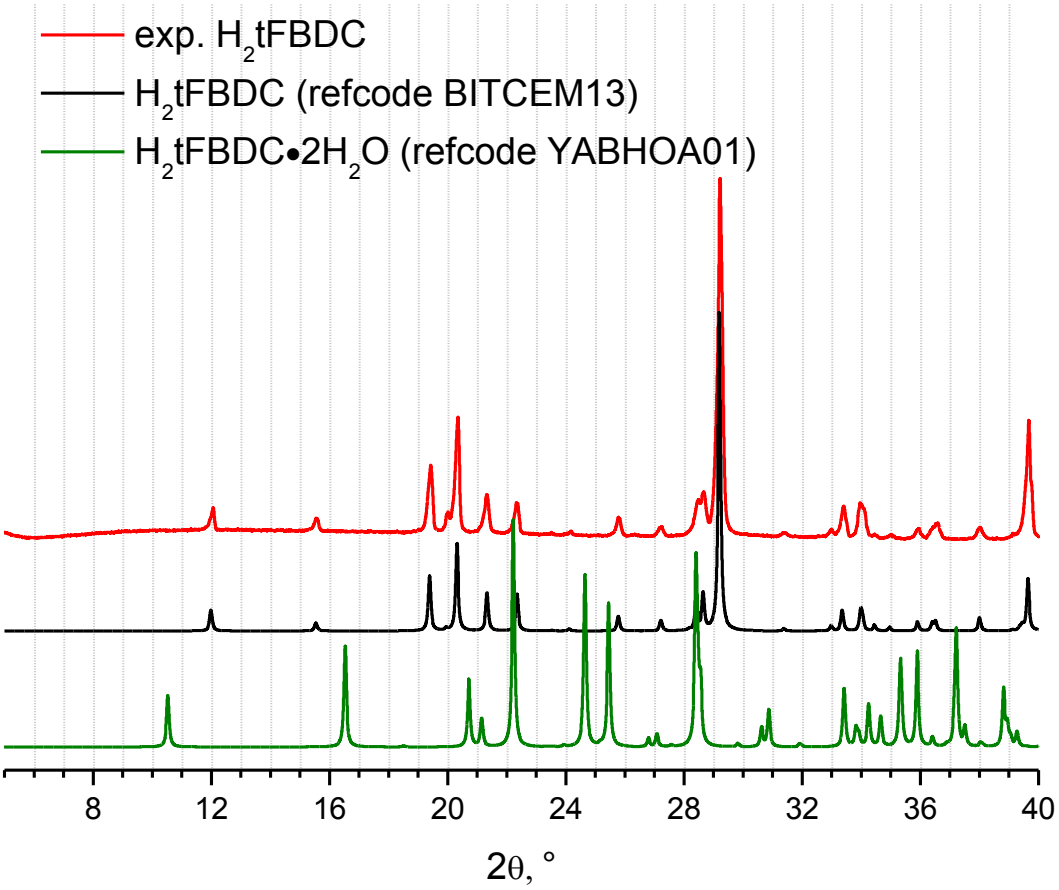

Fig. S30. The comparison of powder pattern of commercial H_2tFBDC (red curve) with calculated powder patterns of H_2tFBDC (black curve, refcode BITCEM13) and H_2tFBDC·2H_2O (green curve, refcode YABHOA01).

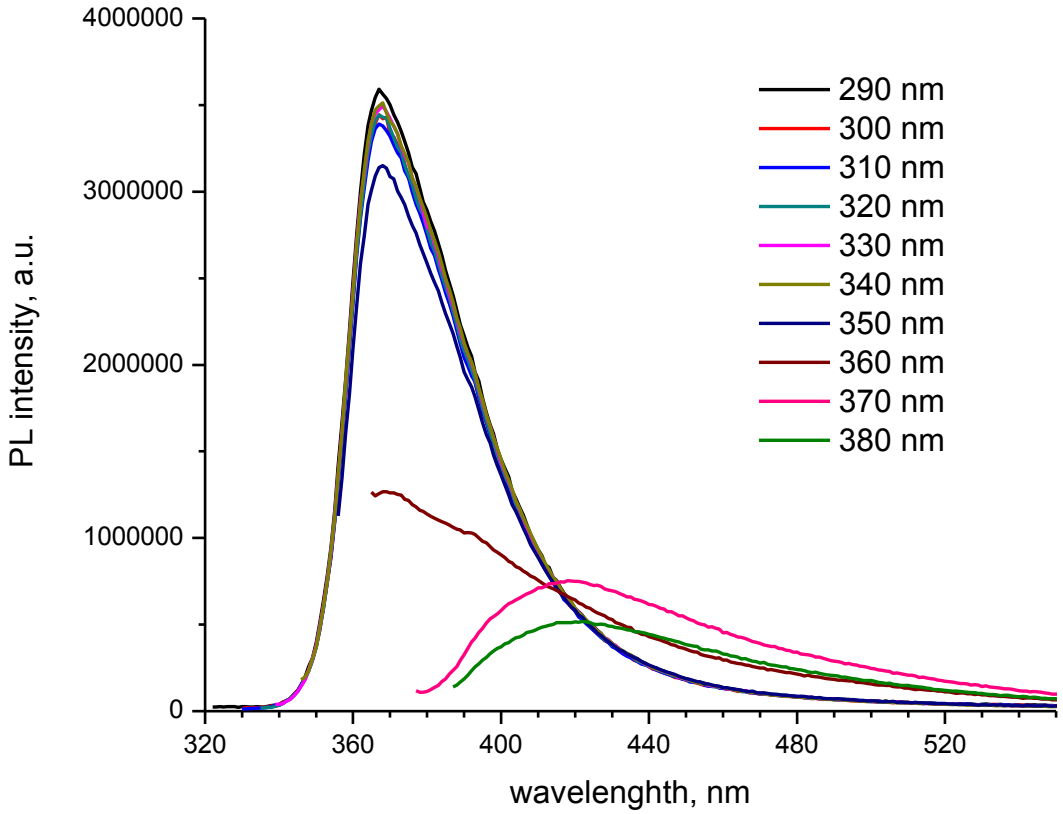

Fig. S31. The emission spectra of H_2tFBDC at room temperature.

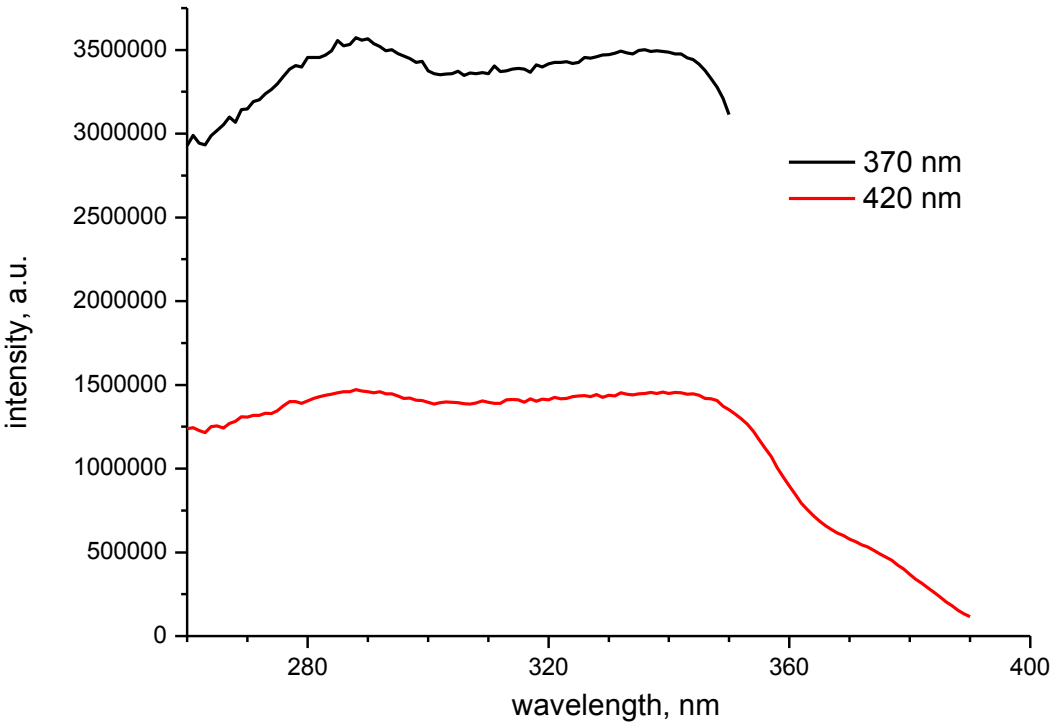

Fig. S32. The excitation spectra of H_2tFBDC.

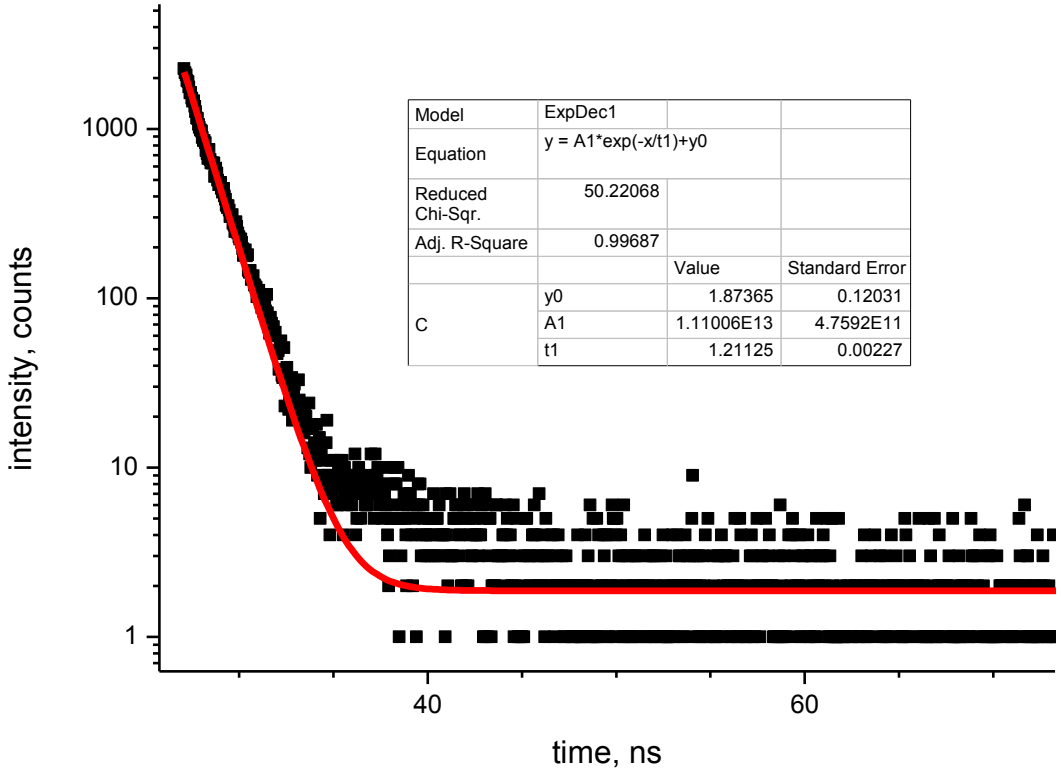

Fig. S33. The fitting of luminescence decay kinetics of H_2tFBDC, λ_{em}=370 nm, λ_{ex}=300 nm, t=1.2 ns

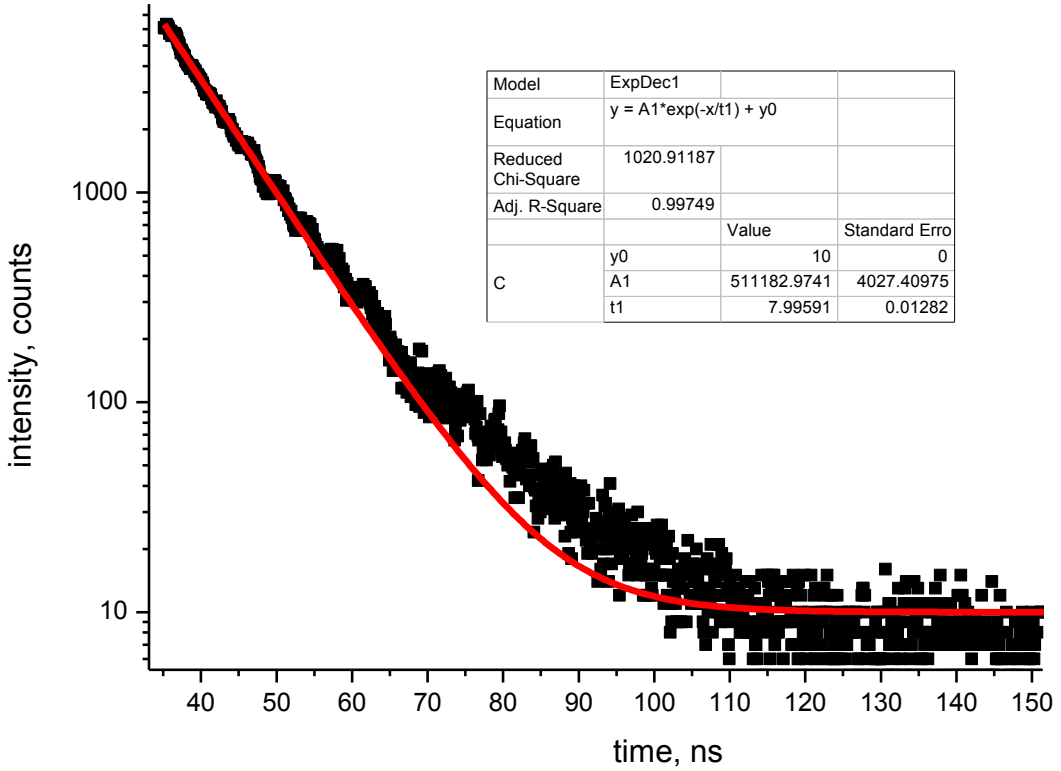

Fig. S34. The fitting of luminescence decay kinetics of H_2tFBDC, λ_{em}=420 nm, λ_{ex}=350 nm, t=8 ns

Complex 1

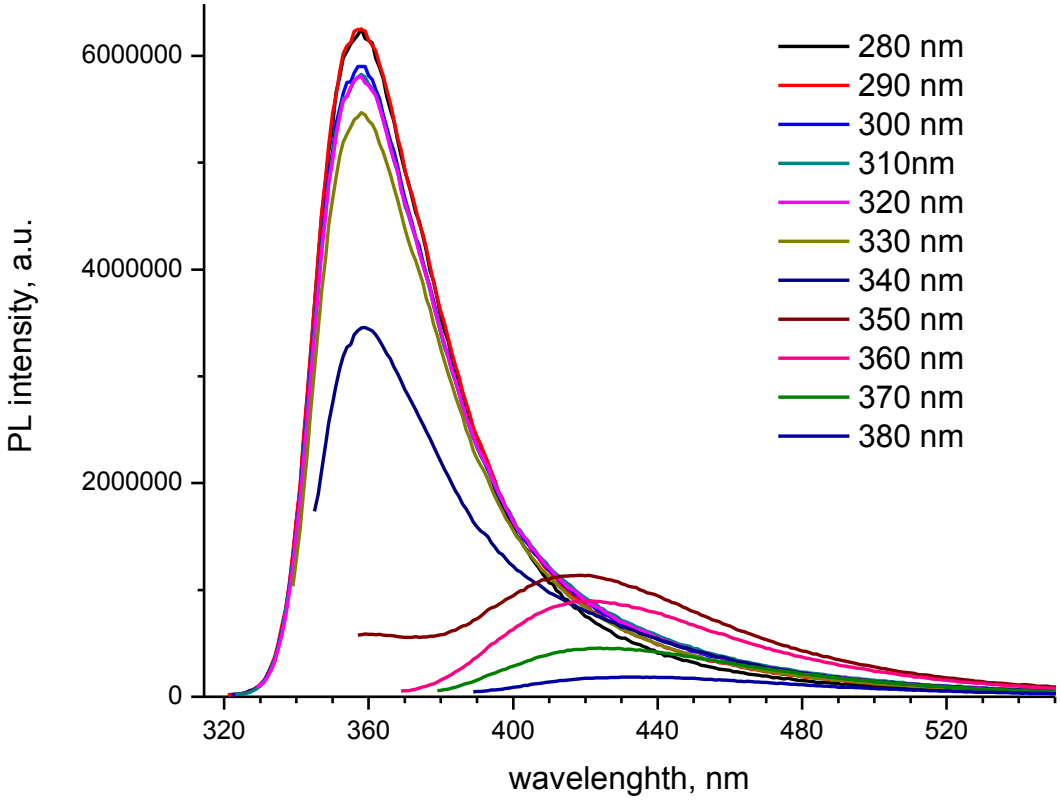

Fig. S35. The emission spectra of **1** at room temperature.

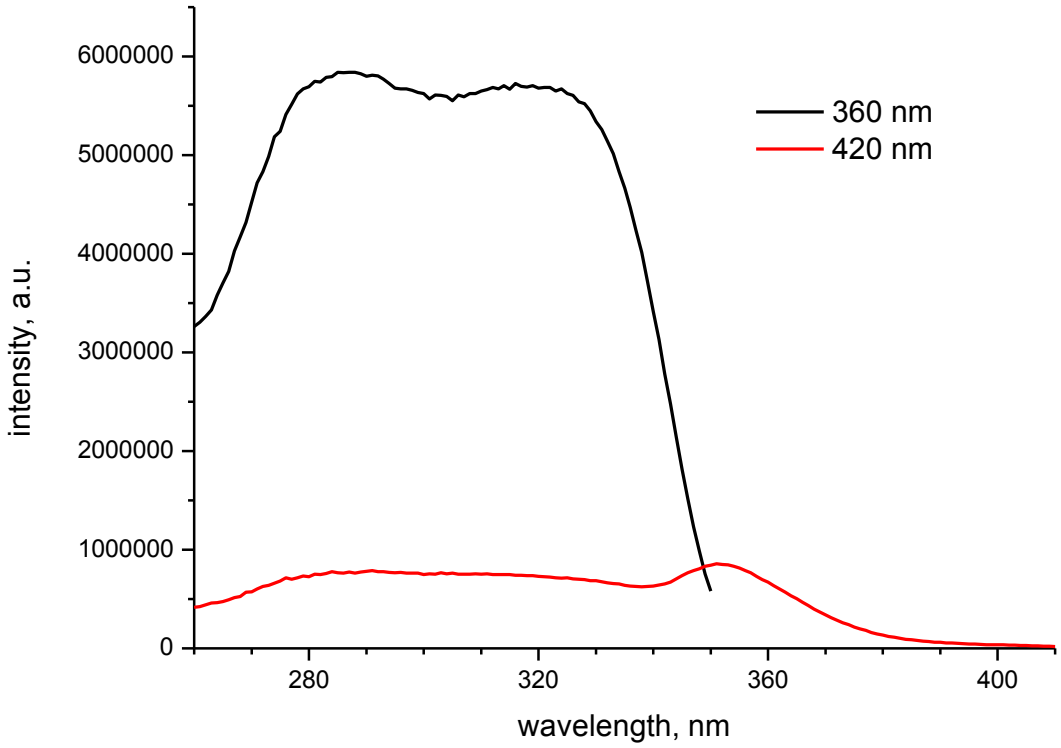

Fig. S36. The excitation spectra of **1**.

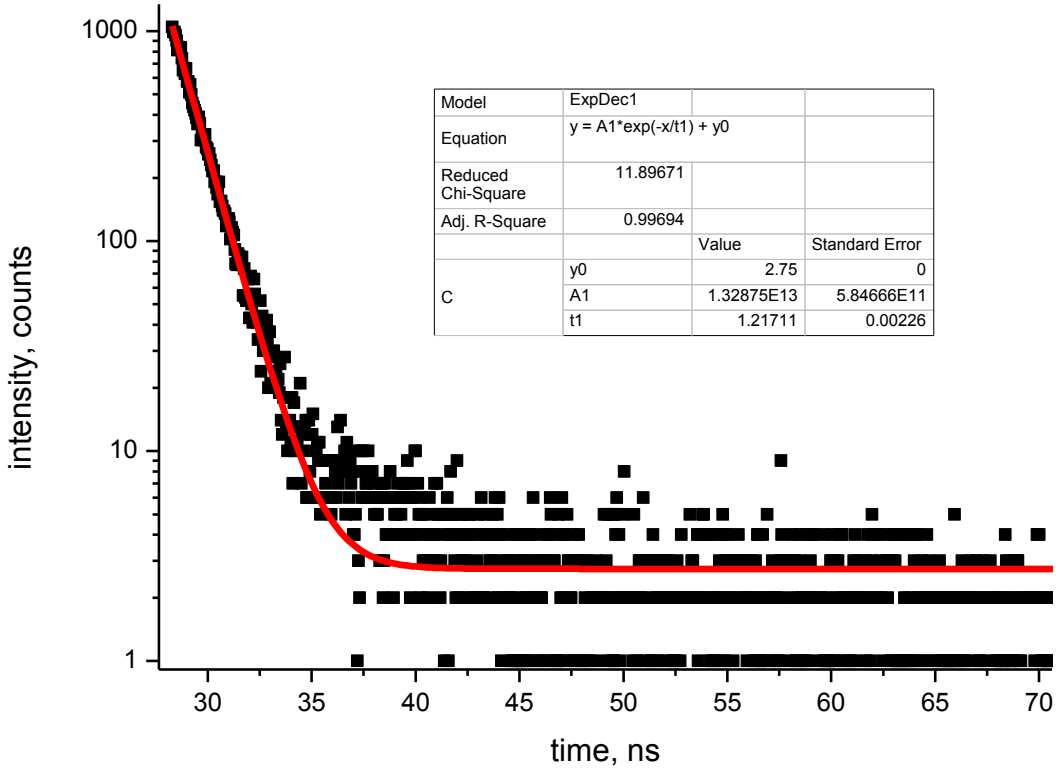

Fig. S37. The fitting of luminescence decay kinetics of complex **1**, λ_{em}=360 nm, λ_{ex}=300 nm, t=1.2 ns

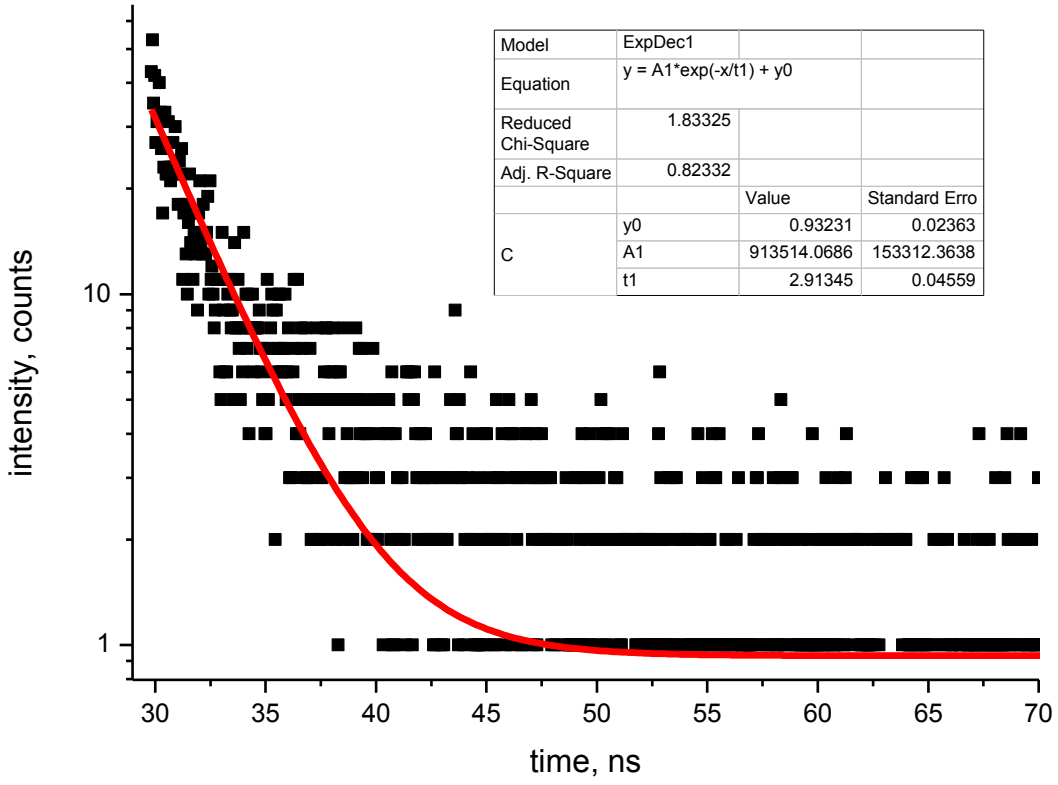

Fig. S38. The fitting of luminescence decay kinetics of complex **1**, λ_{em}=420 nm, λ_{ex}=350 nm, t=2.9 ns

Complex 4

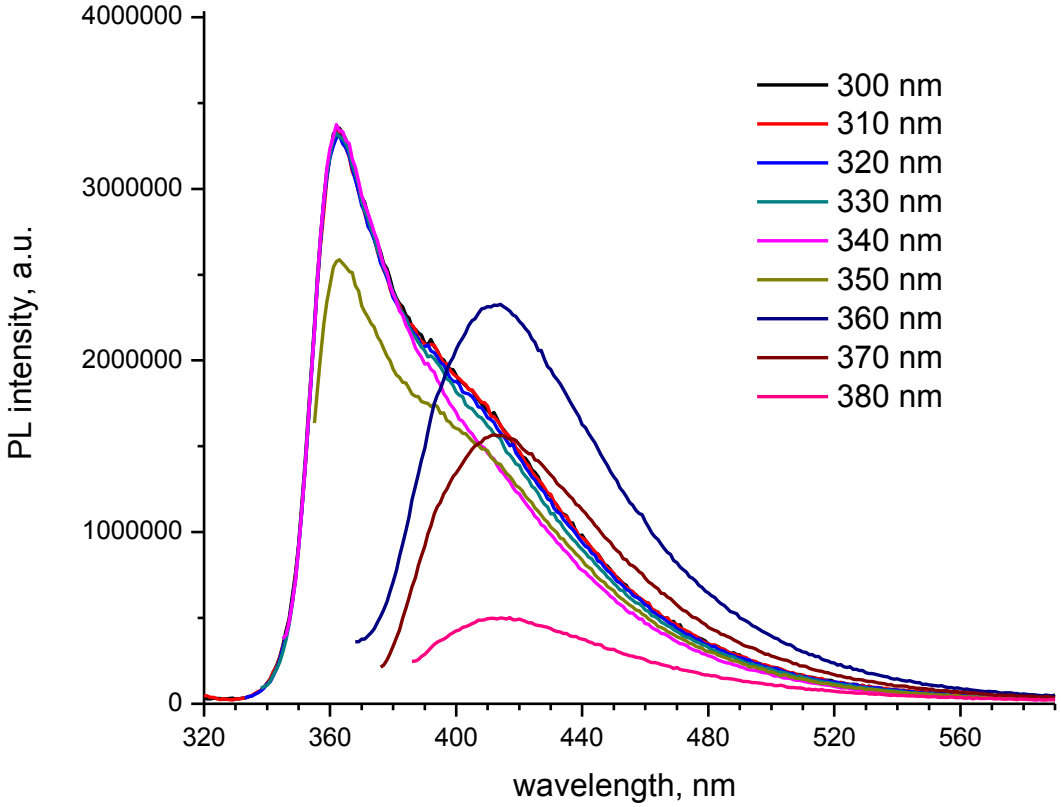

Fig. S39. The emission spectra of **4** at room temperature.

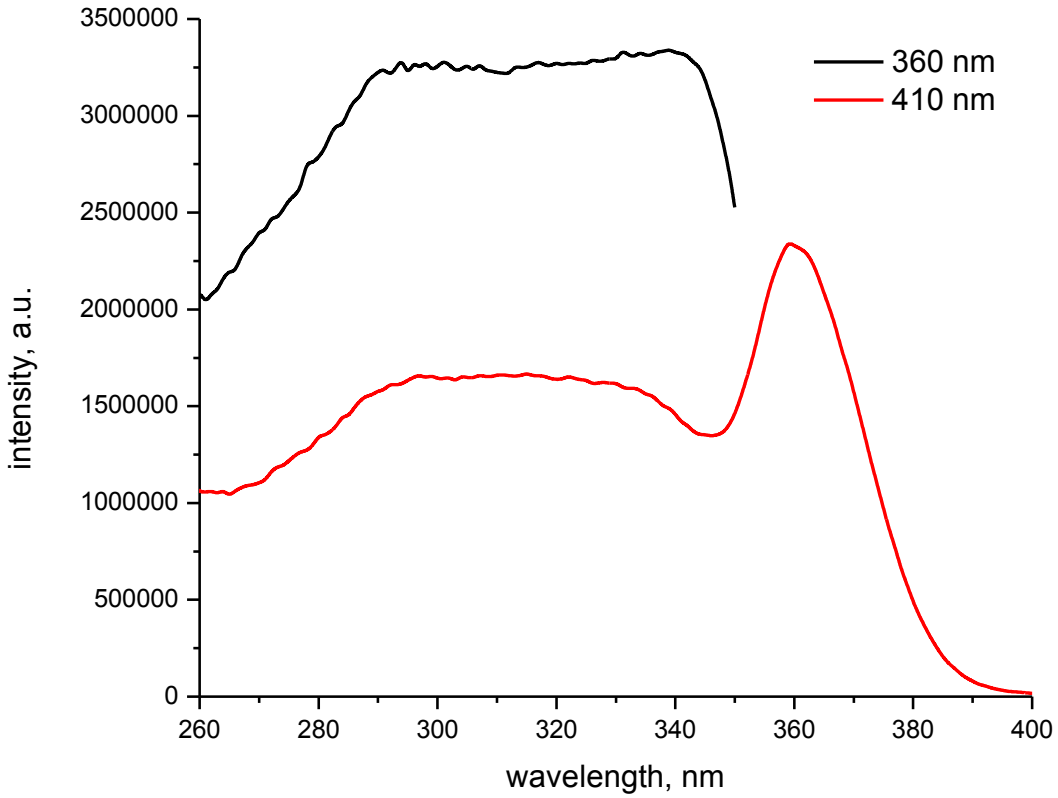

Fig. S40. The excitation spectra of **4**.

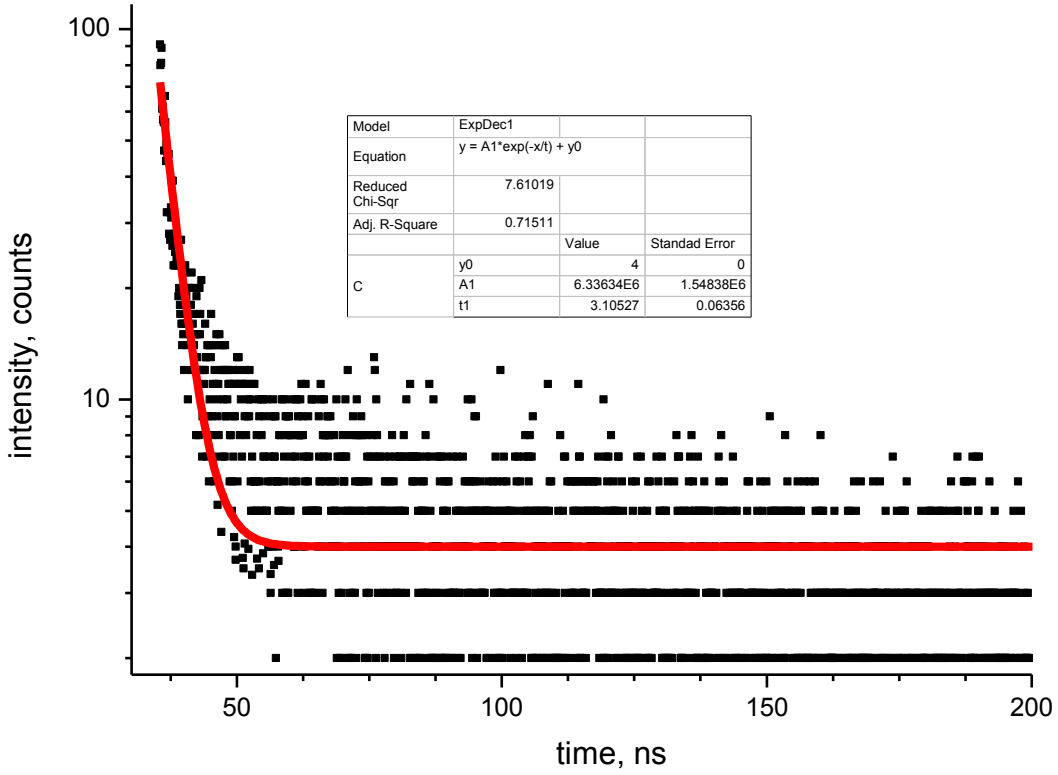

Fig. S41. The fitting of luminescence decay kinetics of complex **4**, λ_{em}=360 nm, λ_{ex}=300 nm, t=3.1ns

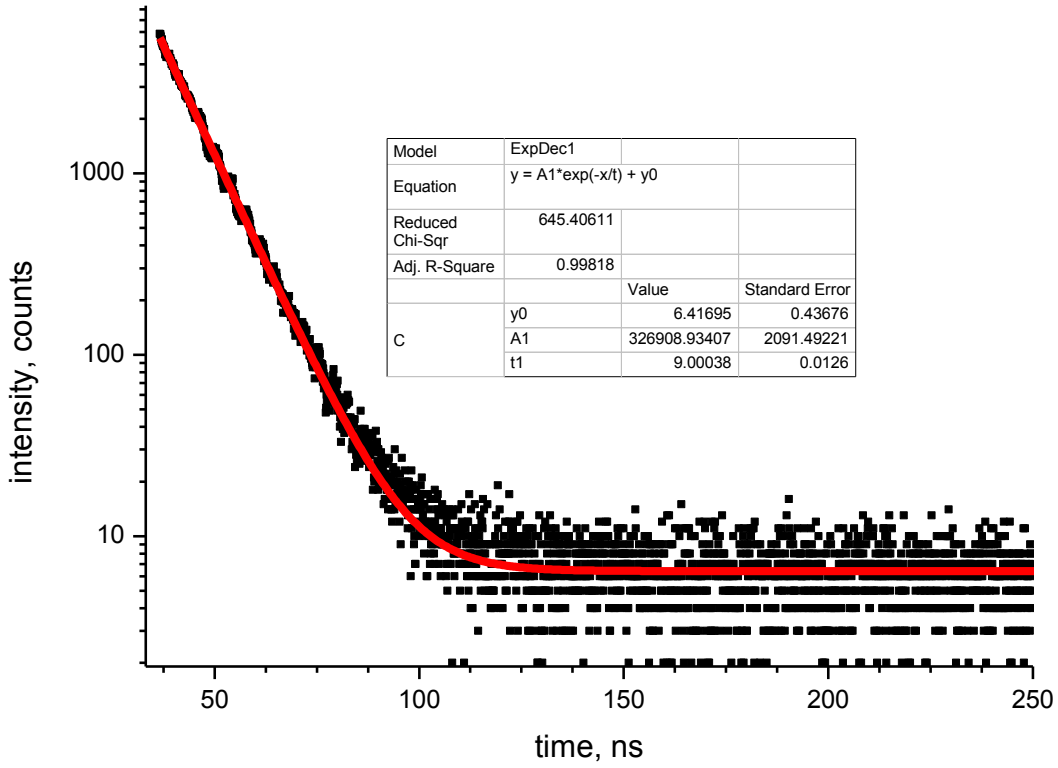

Fig. S42. The fitting of luminescence decay kinetics of complex **4**, λ_{em}=410 nm, λ_{ex}=350 nm, t=9ns

Complex 5'

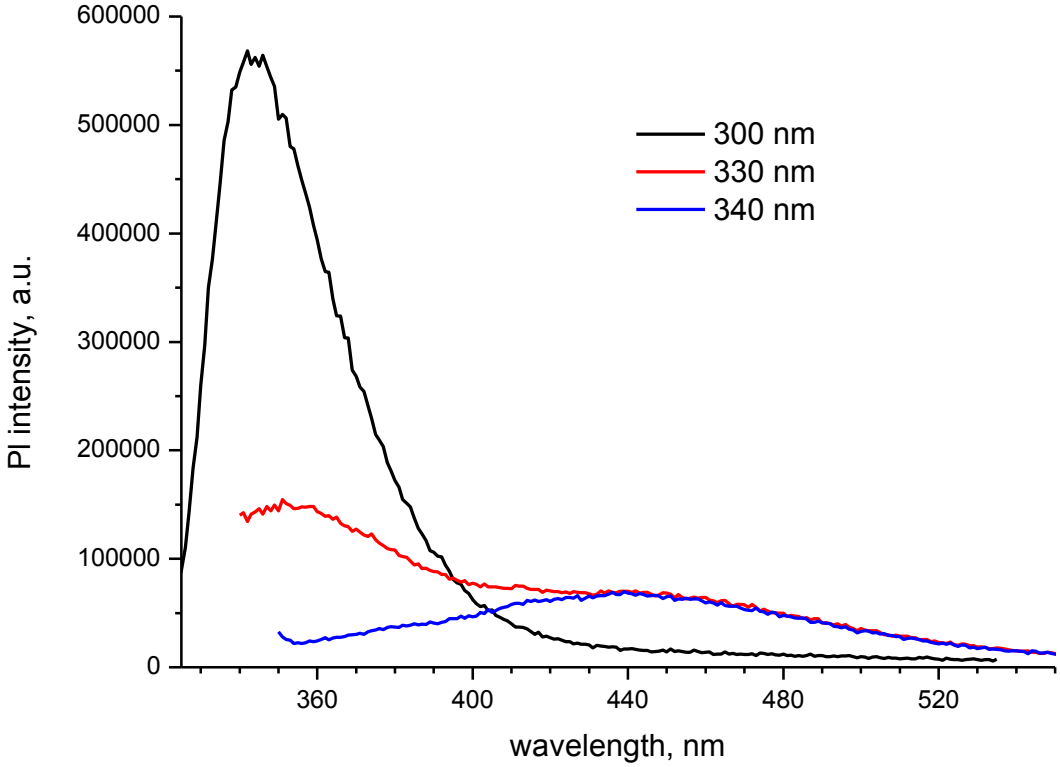

Fig. S43. The emission spectra of **5'** at room temperature.

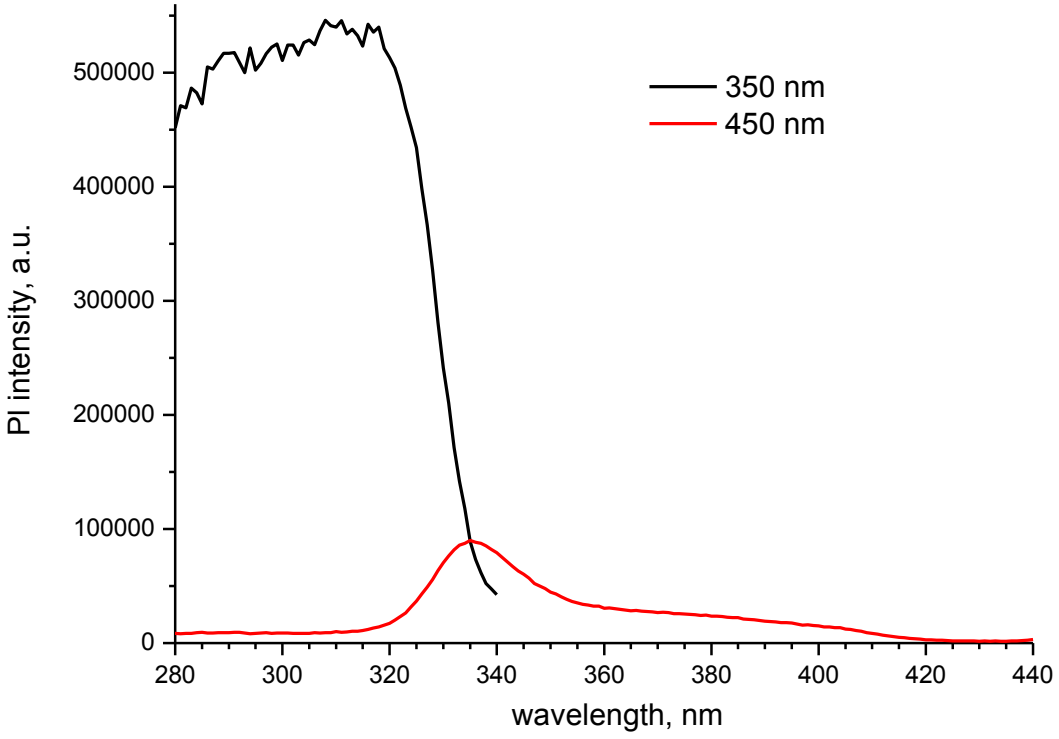

Fig. S44. The excitation spectra of **5'**.

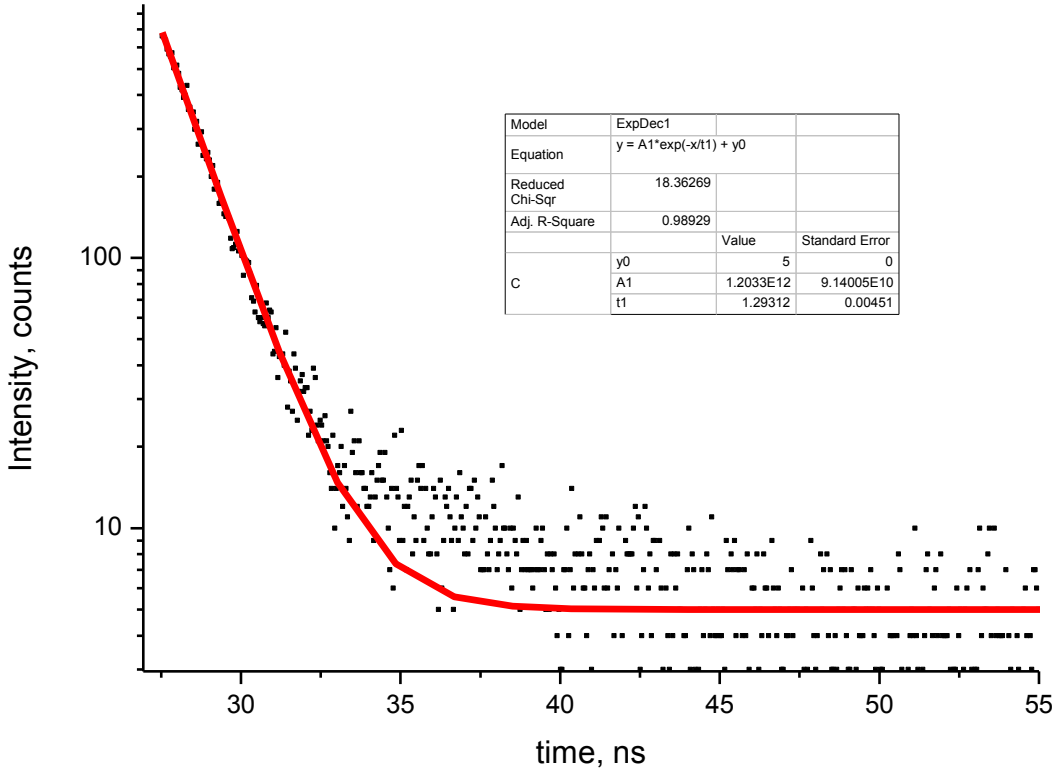

Fig. S45. The fitting of luminescence decay kinetics of complex **5'**, λ_{em}= 350 nm, λ_{ex} = 300 nm, t = 1.3 ns

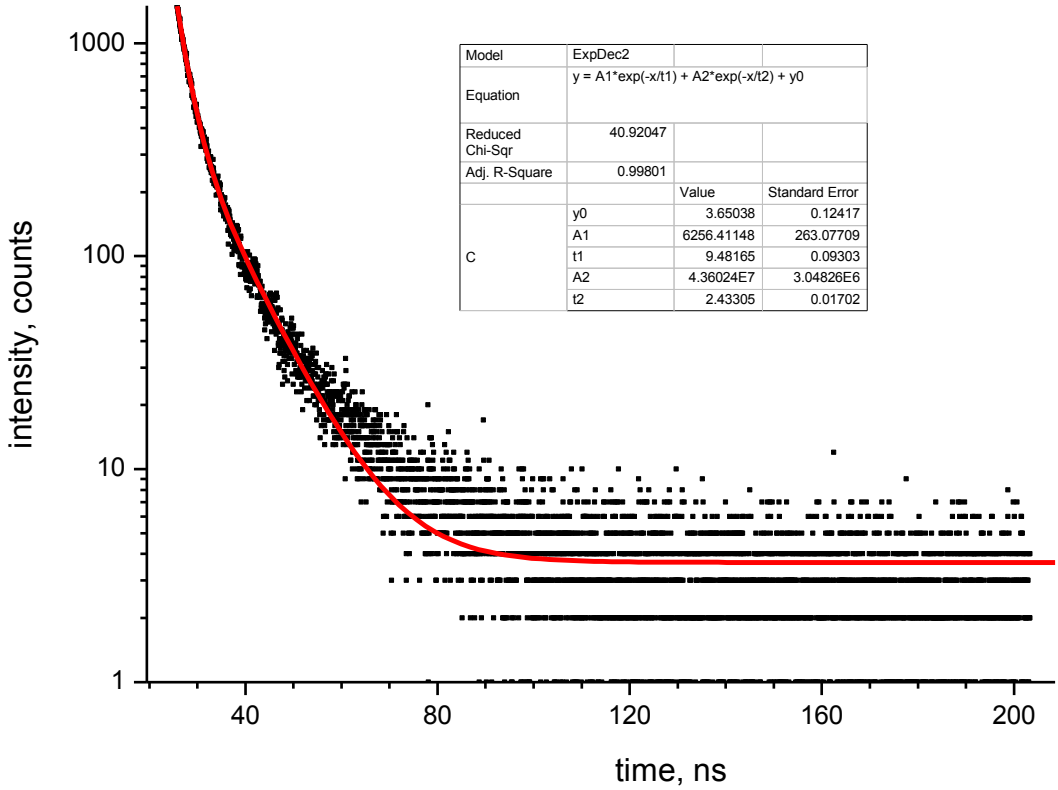

Fig. S46. The fitting of luminescence decay kinetics of complex **5'**, λ_{em} = 450 nm, λ_{ex} = 350 nm, t_1 = 9.5 ns, t_2 = 2.4 ns

Complex 6

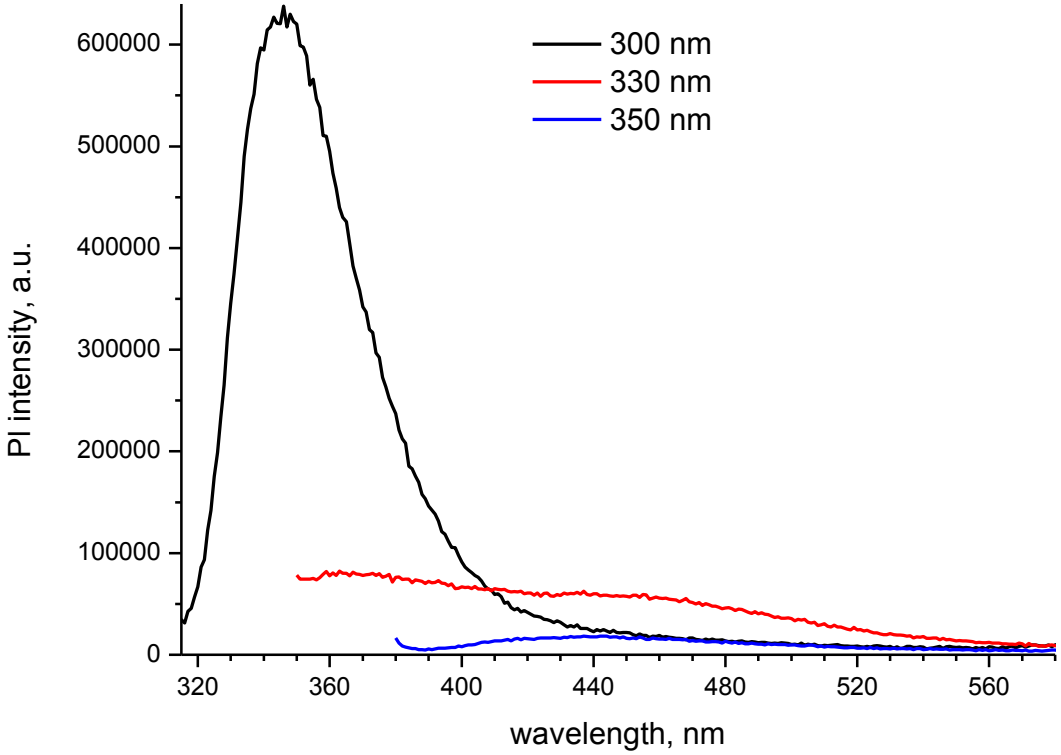

Fig. S47. The emission spectra of **6**.

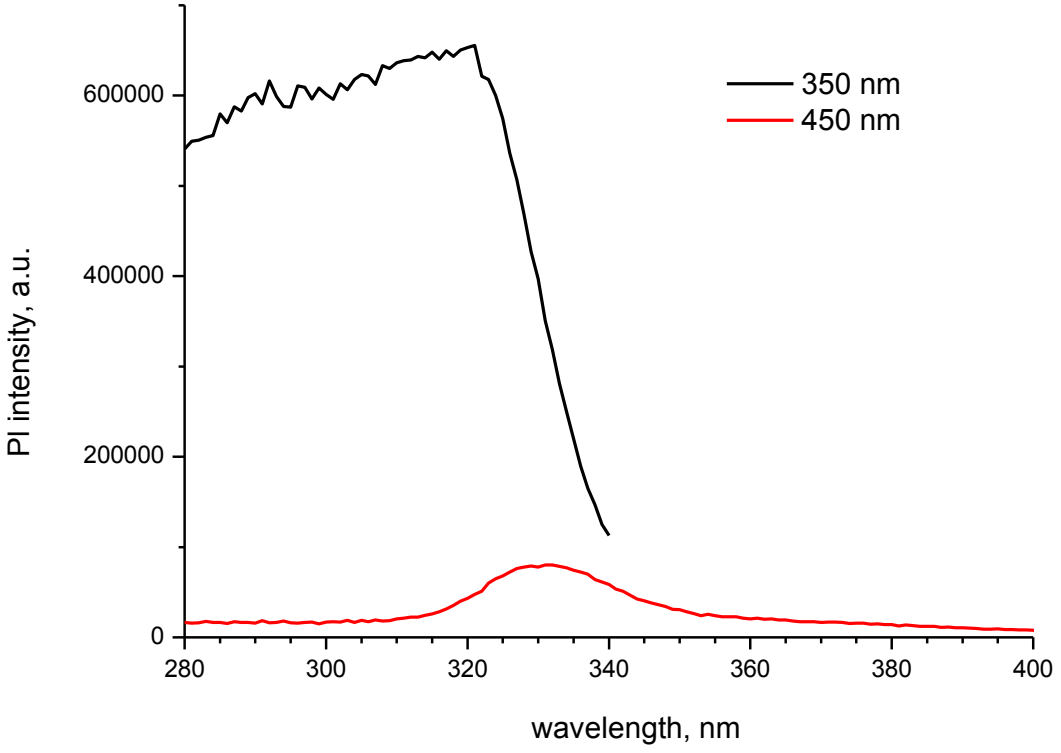

Fig. S48. The excitation spectra of **6**.

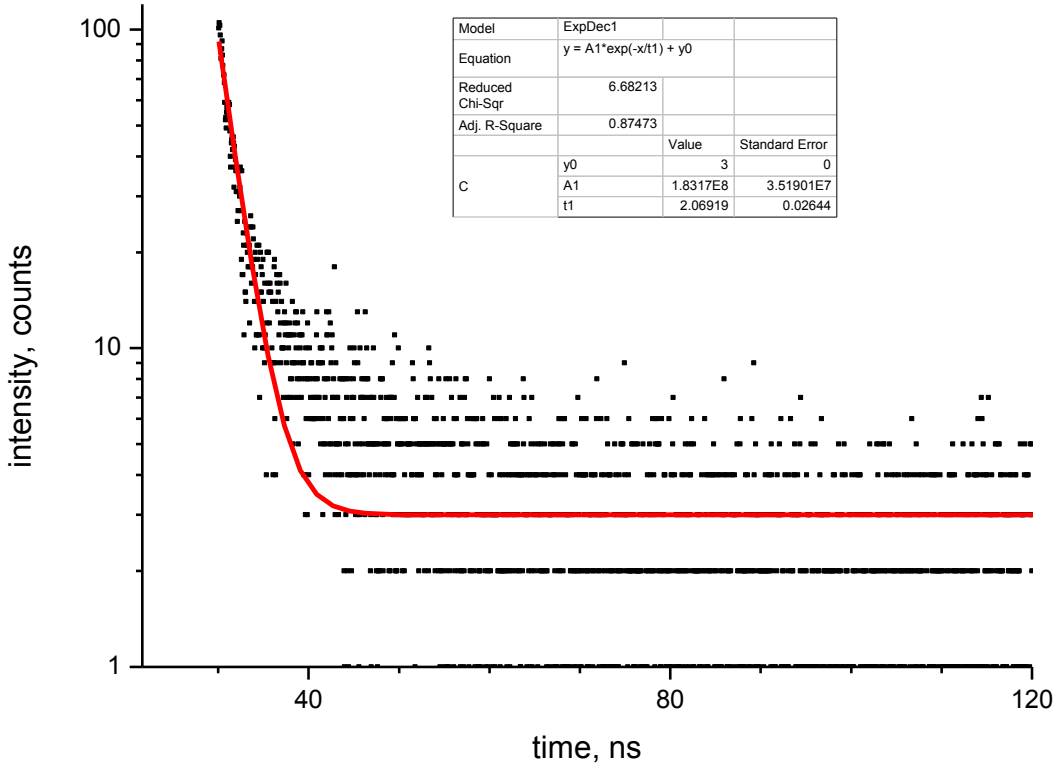

Fig. S49. The fitting of luminescence decay kinetics of complex **6**, λ_{em} = 350 nm, λ_{ex} = 300 nm, t = 2.1 ns

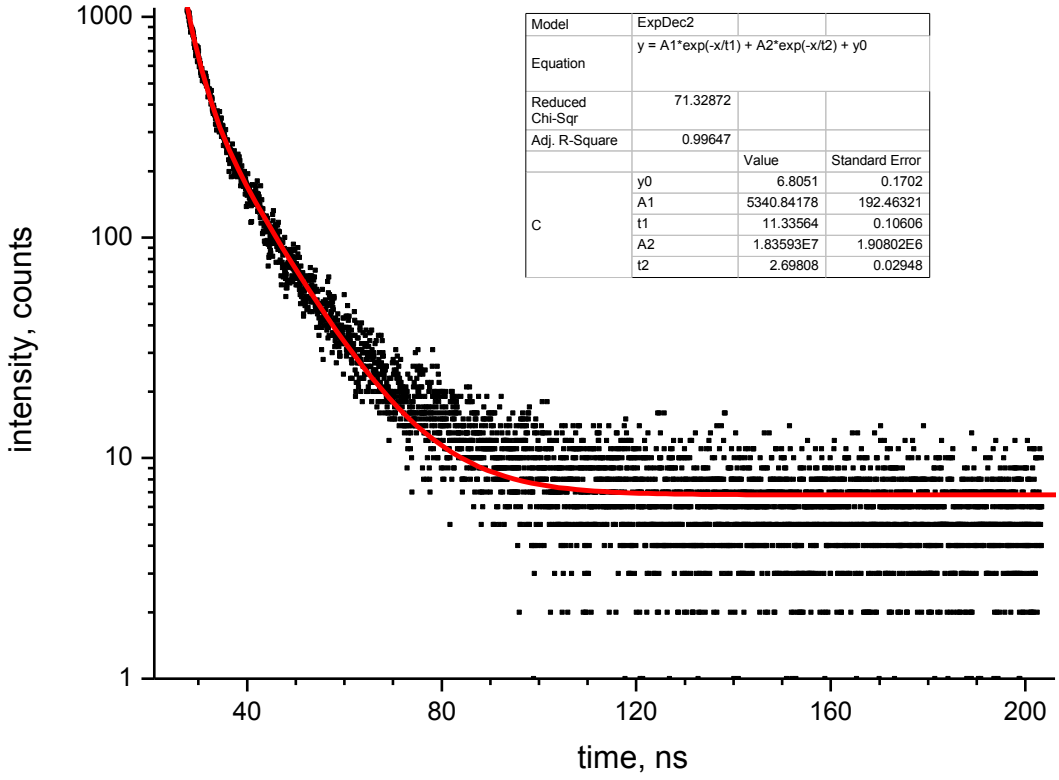

Fig. S50. The fitting of luminescence decay kinetics of complex **6**, λ_{em} = 450 nm, λ_{ex} = 350 nm, t_1 = 11.3 ns, t_2 = 2.7 ns

Complex 7

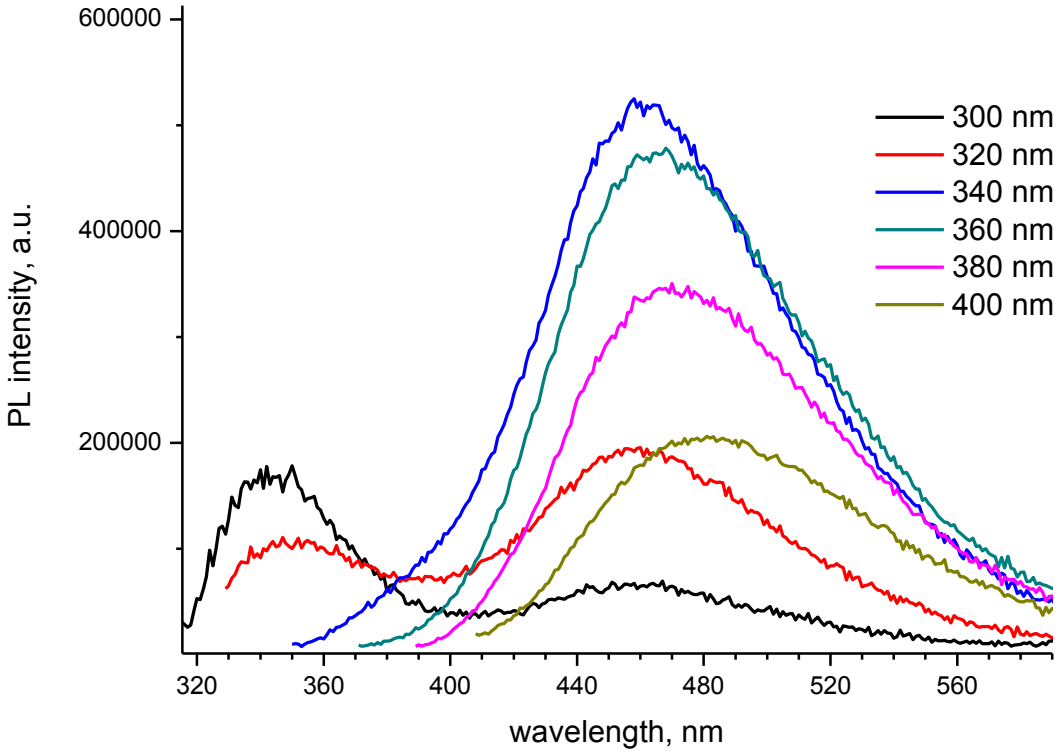

Fig. S51. The emission spectra of **7**.

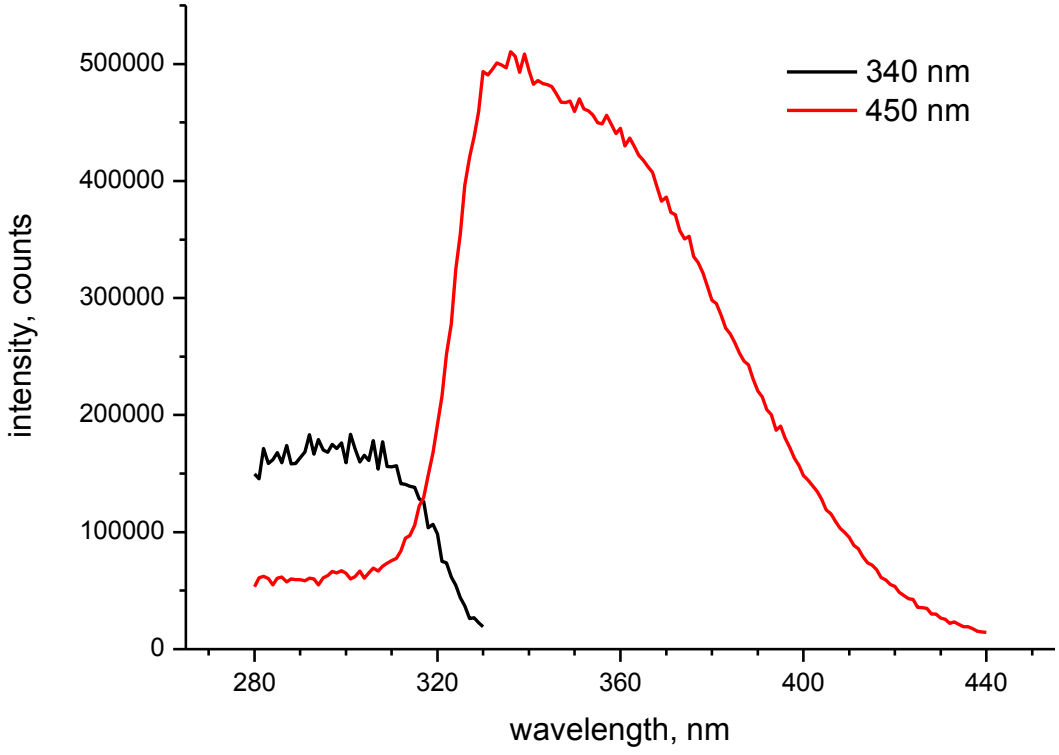

Fig. S52. The excitation spectra of **7**.

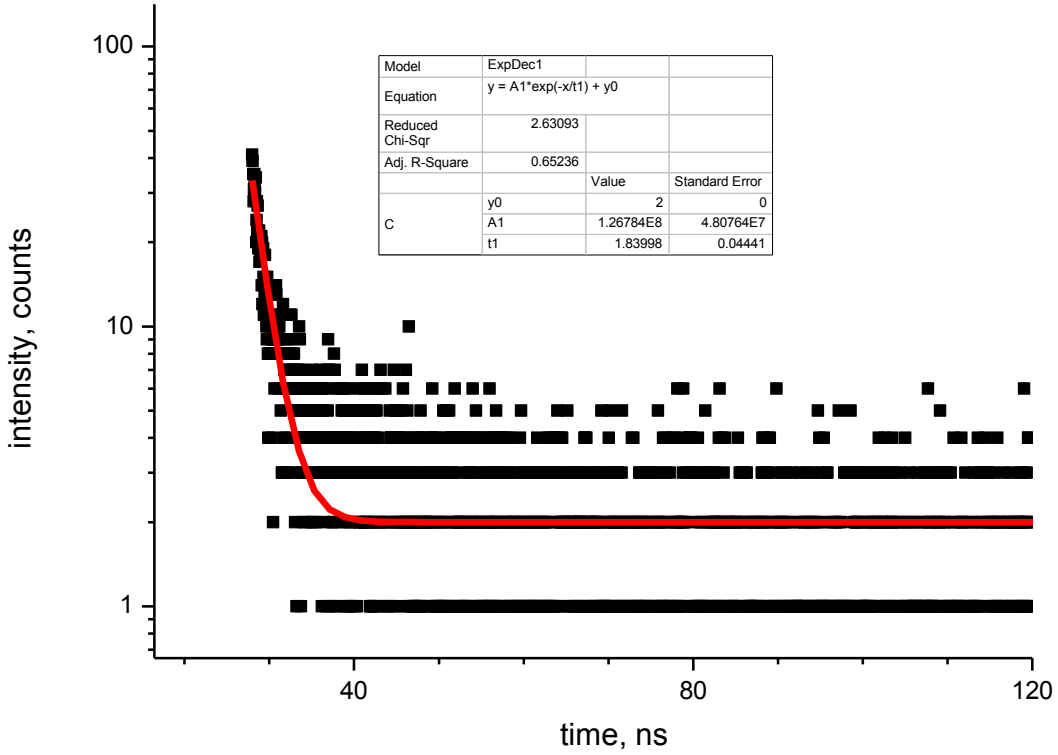

Fig. S53. The fitting of luminescence decay kinetics of complex **7**, λ_{em} = 340 nm, λ_{ex} = 300 nm, t = 1.8 ns

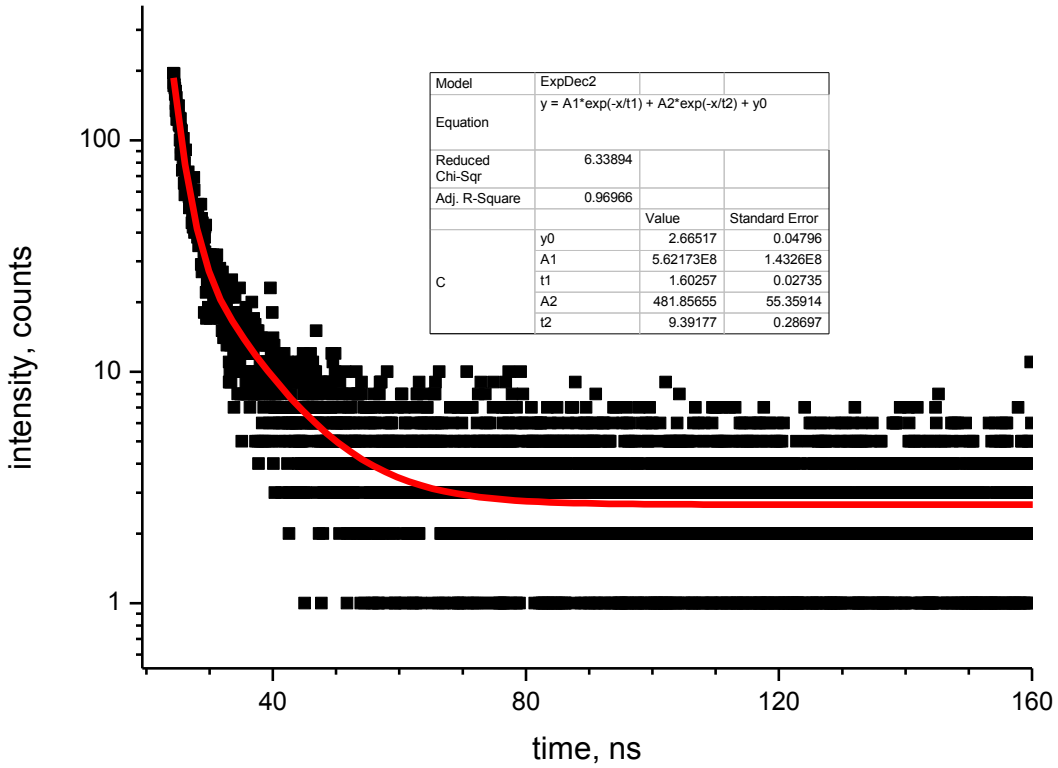

Fig. S54. The fitting of luminescence decay kinetics of complex **7**, λ_{em} = 450 nm, λ_{ex} = 350 nm, t_1 = 1.6 ns, t_2 = 9.4 ns