Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information for

"Sensing properties, energy transfer mechanism and tuneable particle size processing of luminescent two-dimensional rare earth coordination networks"

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Contents

Section S1. Powder X-Ray Diffraction Refinements

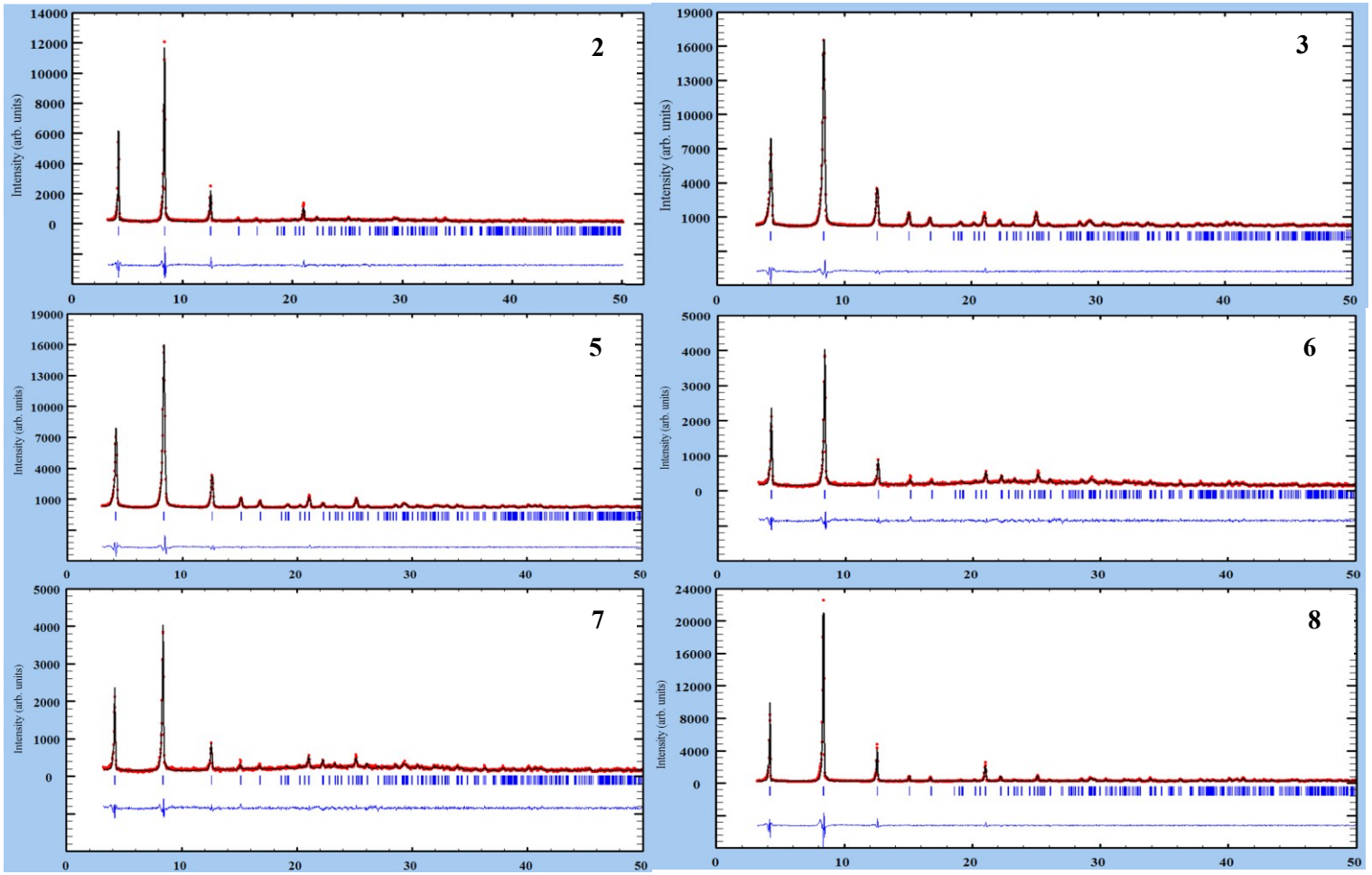

Figure S1. Rietveld refinements for compounds 2-8.

Table S1: Rietveld refinement values for compounds 2-8.

Compound	2	3	5	6	7	8
Crystal system	Monoclinic					
Space group	$P2_1/c$					
Unit cell dimensions						
***a*/Å**	21.151(4)	21.132(3)	21.132(3)	21.150(6)	21.114(4)	21.146(2)
***b*/Å**	6.104(2)	6.1136(8)	6.1063(8)	6.108(1)	6.096(1)	6.1137(9)
***c*/Å**	7.640(2)	7.639(1)	7.631(1)	7.643(1)	7.613(1)	7.646(1)
β	92.35(3)	92.35(1)	92.31(1)	92.38(2)	92.26(2)	92.34(1)
Rwp	13.1	10.4	10.4	10.5	17.2	13.4
Rp	10	7.58	7.45	8.27	12.3	9.57
χ^2	5.11	4.51	4.19	2.72	13.4	7.79
Vol.	985.5(4)	986.1(2)	983.9(3)	986.4(4)	979.1(3)	987.7(2)

Section 2. SEM-EDS

Table S2: Estimated composition based on the semi-quantitative analysis of the EDS spectra obtained for compounds 3-9.

Compounds	mmol		
	Y	Eu	Tb
3	0.9563	0.0437	-
4	0.9102	0.0898	-
5	0.9562	-	0.0438
6	0.9352	-	0.0648
7	0.9510	0.0248	0.0242
8	0.8835	0.0699	0.0466
9	0.8620	0.0440	0.0940

Section S3. Thermal Analysis

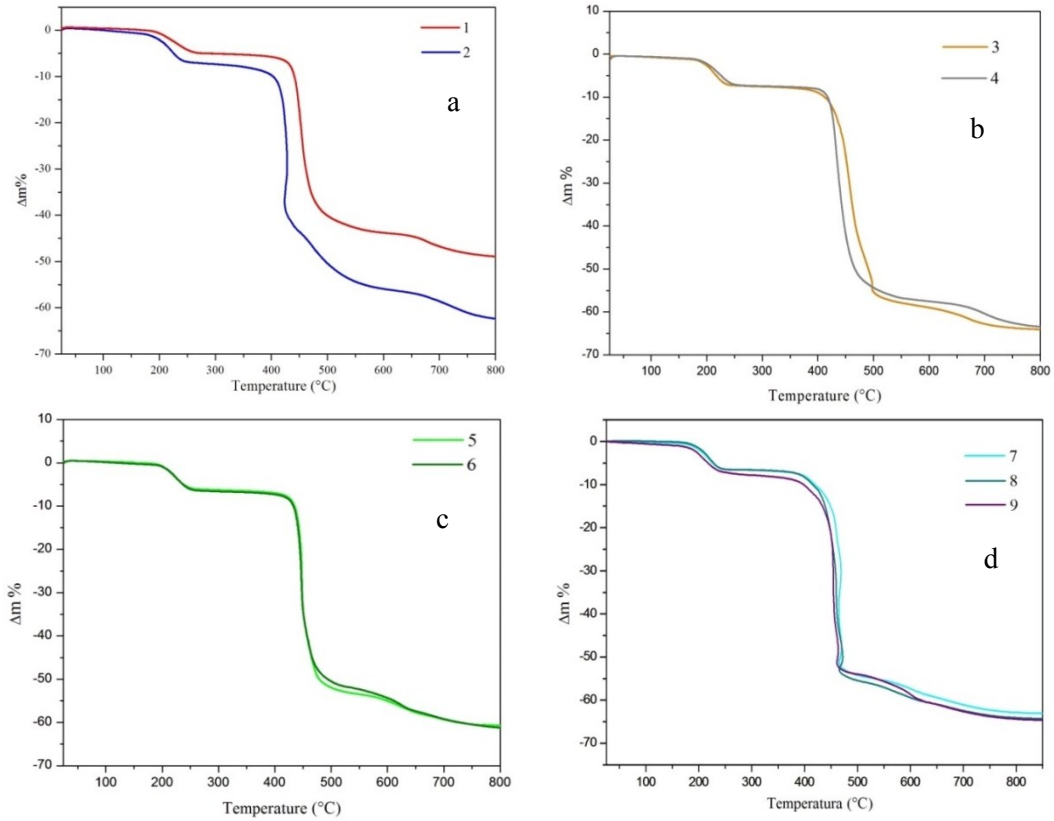

Figure S2: Thermogravimetric analysis of compounds 1, 2 (a); 3, 4 (b); 5, 6 (c) and 7-9 (d).

Table S3: Experimental mass decays of TGA curves and expected values of compounds 1-9. The associated DSC peak temperatures are also shown.

	Step 1		Step 2		
Compound	**Δm % (calc.)**	**DSC peak (°C)**	**Δm % (calc.)**	**Total Δm % (calc.)**	**Final product**
1	4.97 (4.77)	223.03	44.64 (45.12)	49.61 (49.89)	Ho_2O_3
2	6.74 (5.98)	231.78	56.11 (56.49)	62.85 (62.47)	Y_2O_3
3	6.90 (5.95)	230.56	57.20 (55.95)	64.10 (61.90)	Y_2O_3/Eu_2O_3
4	7.79 (5.87)	223.19	57.58 (55.46)	65.37 (61.33)	Y_2O_3/Eu_2O_3
5	6.15 (5.92)	222.28	54.54 (55.92)	60.69 (61.84)	Y_2O_3/Tb_2O_3
6	6.49 (5.89)	227.82	54.85 (55.66)	61.34 (61.55)	Y_2O_3/Tb_2O_3
6 100mg CTAB	6.07 (5.89)	-	53.62 (55.66)	59.69 (61.55)	Y_2O_3/Tb_2O_3
6 200mg CTAB	6.37 (5.89)	-	55.75 (55.66)	62.12 (61.55)	Y_2O_3/Tb_2O_3
6 400mg CTAB	6.22 (5.89)	-	55.73 (55.66)	61.95 (61.55)	Y_2O_3/Tb_2O_3
7	6.52 (5.915)	237.39	56.53 (55.89)	63.05 (61.81)	$Y_2O_3/Eu_2O_3/Tb_2O_3$
8	6.49 (5.83)	234.24	57.74 (55.09)	64.23 (60.92)	$Y_2O_3/Eu_2O_3/Tb_2O_3$
9	7.08 (5.80)	231.44	57.54 (54.89)	64.62 (60.69)	$Y_2O_3/Eu_2O_3/Tb_2O_3$

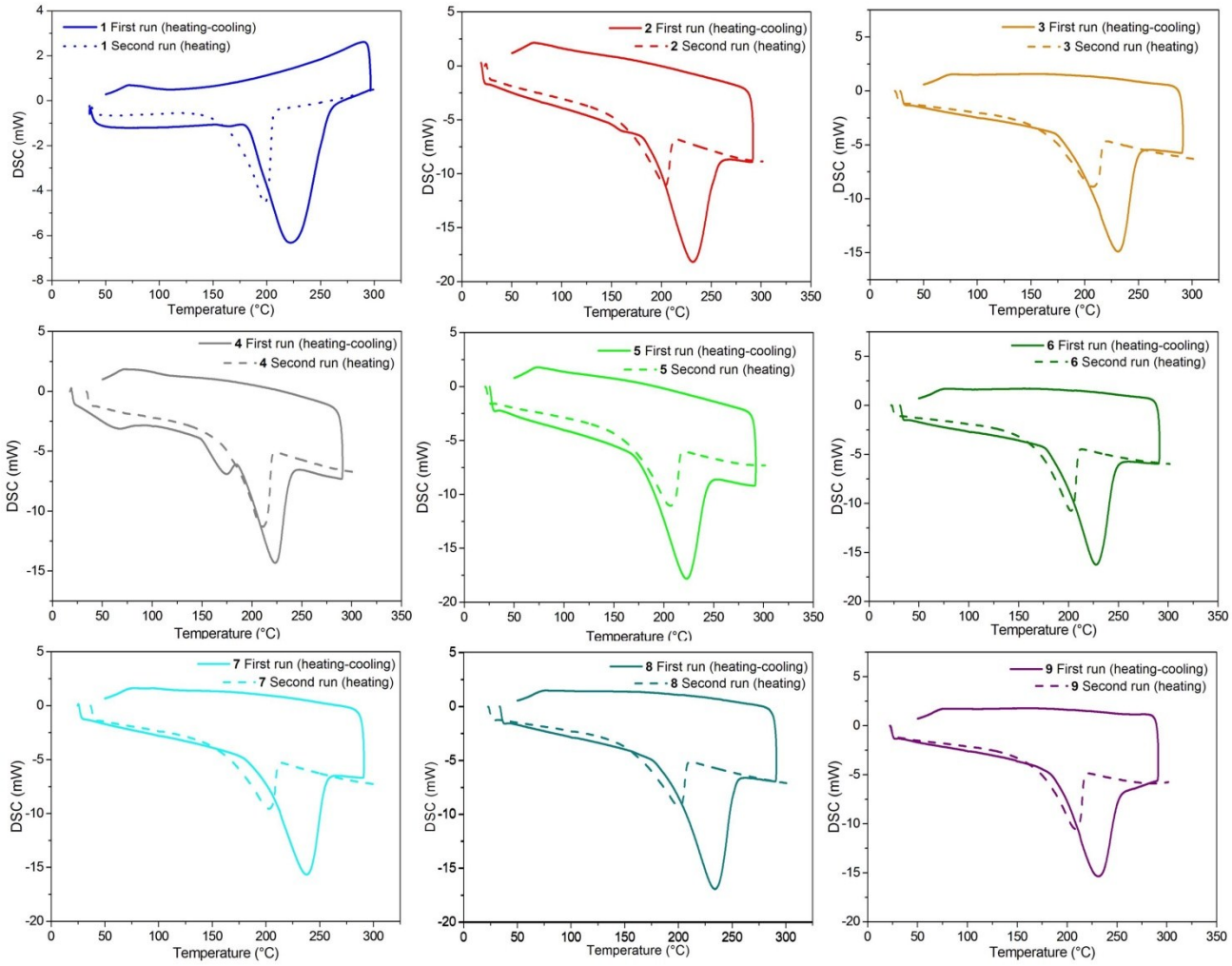

Figure S3. DSC curves of compounds 1-9 from Room Temperature to 300 °C. The solid line corresponds to the first heating run and the dashed line to the second heating run.

Section S4. FTIR spectroscopy

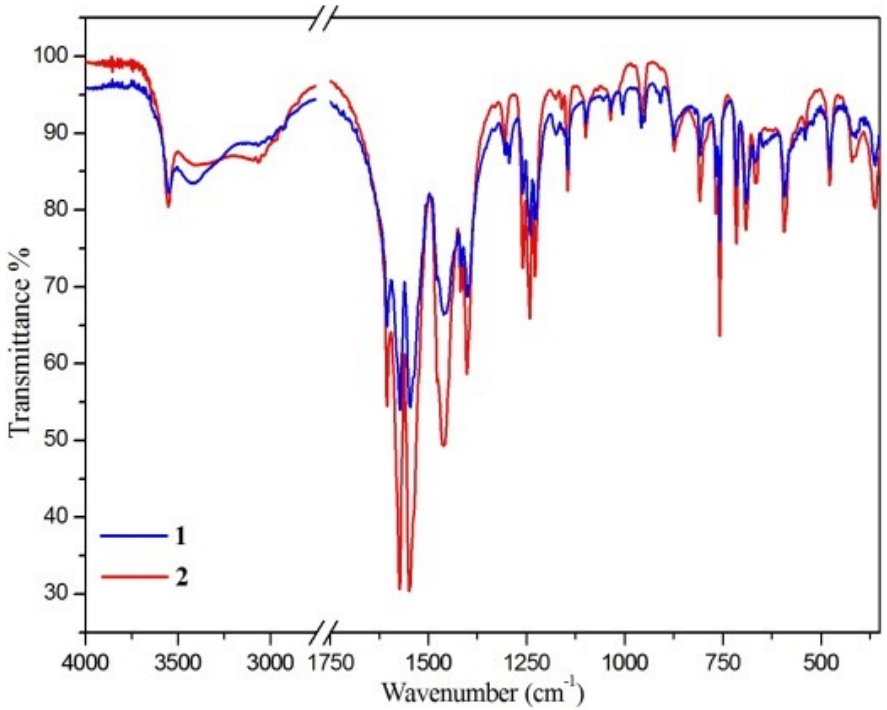

Figure S4. FTIR spectra of compounds 1 and 2.

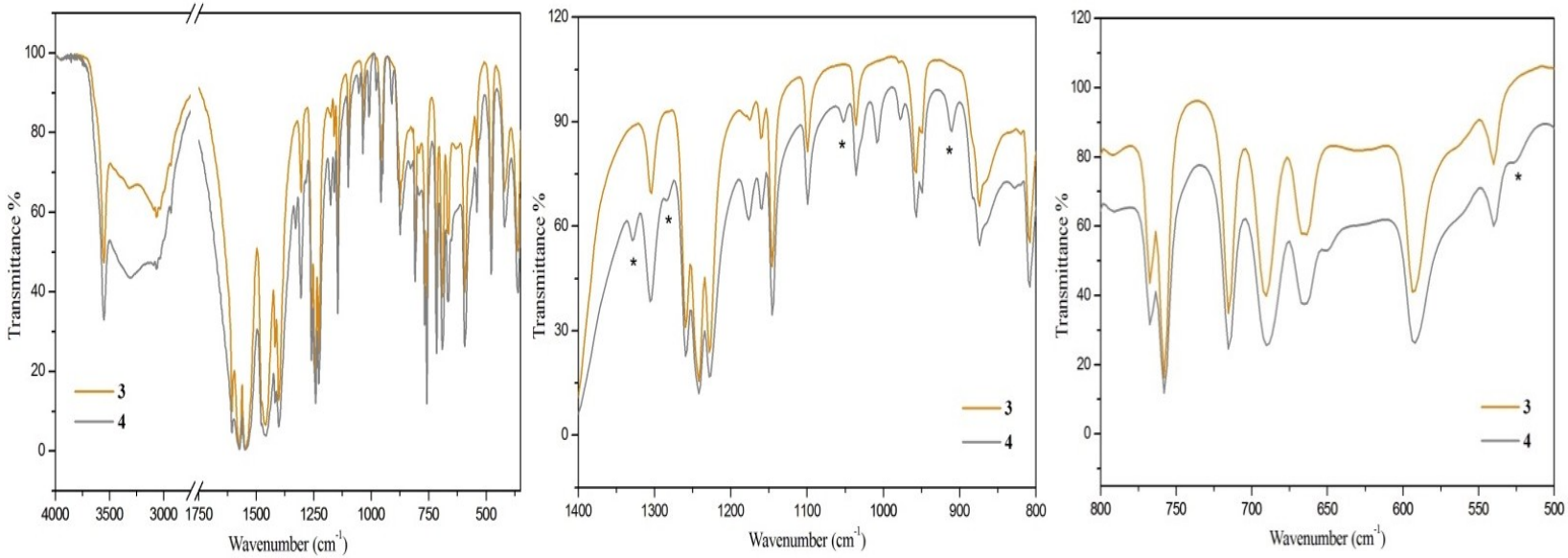

Figure S5. FTIR spectra of compounds 3 and 4.

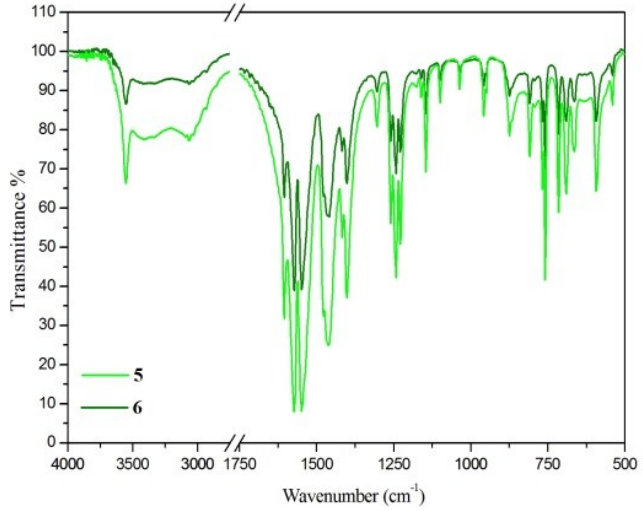

Figure S6. FTIR spectra of compounds 5 and 6.

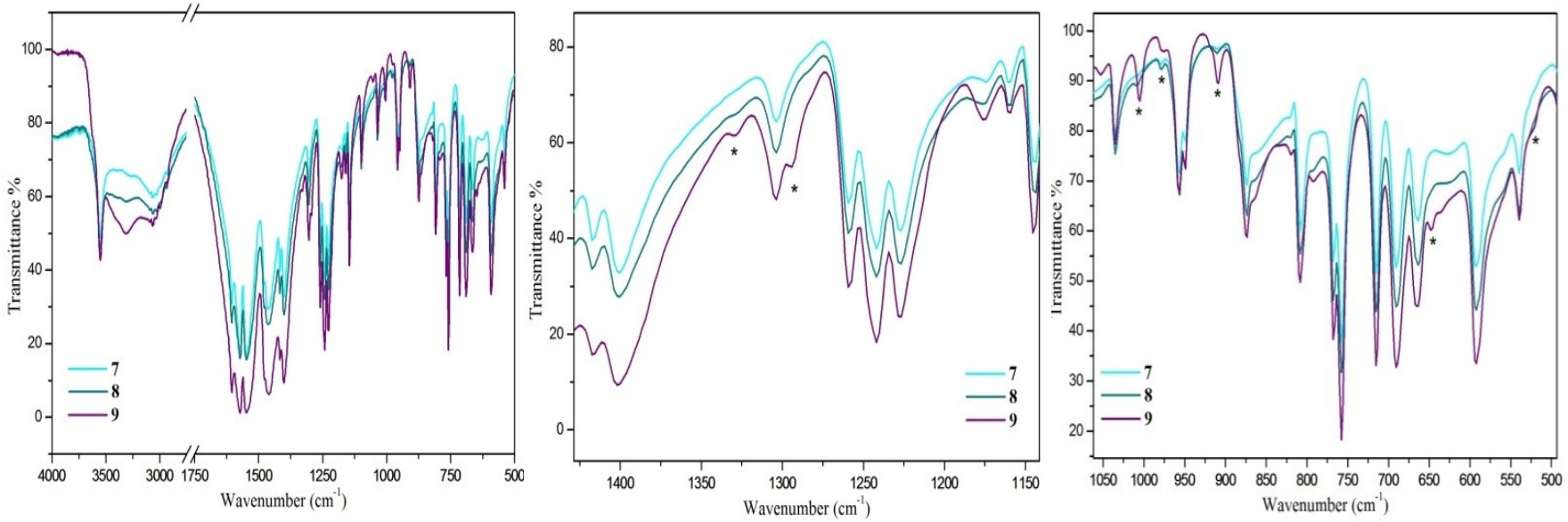

Figure S7. FTIR spectra of compounds 7-9.

Table S4: FTIR spectra assignment of compounds 1-9.

Wavenumber (cm^{-1})									Assignment
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	
3545 (m)	3549 (m)	3551 (m)	3549 (m)	3551 (m)	3548 (m)	3549 (m)	3548 (m)	3548 (m)	ν_{as}OH W
3440 (m)	3424 (m)	3408 (m)	3417 (m)	3417 (br,w)	3412 (br,vw)	3400 (vw)	3405 (vw)	3405 (vw)	
2922 (vw)	2932 (vw)	2932 (vw)	2932 (vw)	2933 (vw)	2932 (vw)	2933 (vw)	2933 (vw)	2932 (vw)	ν_{as}C-H
1605 (m)	1604 (m)	1604 (m)	1604 (m)	1605 (m)	1605 (m)	1605 (m)	1605 (m)	1605 (m)	νCC aromatic ring
1570 (s)	1573 (s)	1573 (s)	1573 (s)	1573 (s)	1572 (s)	1573 (s)	1572 (s)	1572 (s)	ν_{as}OCO bidentate bridge
1550 (s)	1548 (s)	1547 (s)	1547 (s)	1548 (s)	1547 (s)	1547 (s)	1547 (s)	1547 (s)	ν_{as}OCO quelate bridge
1480 (vw)	1477 (vw)	1478 (vw)	1478 (vw)	1477 (vw)	1477 (vw)	1478 (vw)	1478 (vw)	1477 (vw)	δCH_2
1460 (br,m)	1460 (br,m)	1458 (br,m)	1456 (br,m)	1461 (br,m)	1461 (br,m)	1461 (br,m)	1461 (br,m)	1459 (br,m)	νCC aromatic ring + δCH_2
1415 (m)	1416 (m)	1416 (m)	1416 (m)	1417 (m)	1417 (m)	1416 (m)	1416 (m)	1416 (m)	δCH_2
1400 (m)	1401 (s)	1401 (s)	1400 (m)	1401 (s)	1401 (s)	1400 (m)	1400 (m)	1400 (m)	ν_sOCO
-	-	-	1329 (w)	-	-	-	1329 (vw)	1329 (vw)	$\rho_w CH_2$
1305 (w)	1305 (m)	1305 (m)	1305 (m)	1304 (m)	1304 (m)	1304 (m)	1302 (m)	1302 (m)	$\rho_w CH_2$
-	-	-	1283 (vw)	-	-	-	-	1283 (vw)	$\rho_\tau CH_2$
1260 (m)	1258 (m)	1258 (m)	1258 (m)	1259 (m)	1259 (m)	1258 (m)	1258 (m)	1258 (m)	νC-O fenoxi
1145 (m)	1145 (m)	1145 (m)	1145 (m)	1145 (m)	1145 (m)	1144 (m)	1144 (m)	1144 (m)	δCCC aromatic
1100 (w)	1099 (w)	1099 (m)	1099 (m)	1099 (m)	1099 (m)	1098 (m)	1098 (m)	1098 (m)	νCC aromatic
1035 (vw)	1035 (vw)	1035 (vw)	1035 (vw)	1035 (w)	1035 (w)	1035 (w)	1035 (w)	1035 (w)	νCC aliphatic + δC-H aromatic
-	-	-	976 (w)	-	-	976 (vw)	976 (vw)	976 (vw)	$\rho_r CH_2$
760 (m)	757 (m)	757 (m)	757 (m)	757 (m)	757 (m)	757 (m)	757 (m)	757 (m)	ρ_rC-H o-disubstituted
-	-	-	525 (vw)	-	-	-	-	520 (vw)	$\rho_r OCO_{oop}$

Section S5. Top-Down approach

Liquid Exfoliation Procedure

As top-down approach, ultrasonication experiments were performed using 1 mg of compound **6** in 7 mL of absolute ethanol (Anedra). This mixture was placed in a glass test tube with a screw cap. The tube was placed in the ultrasound (ICSA), and tests were performed at 40 and 60 KHz; the colloidal suspension was obtained when the lowest frequency was applied. The equipment power rout put can be varied in the 10-100% range, the maximum range achievable being of 150-180 W. Three power ranges were studied: 60-72 W (40%), 90-108 W (60%) and 150-180 W (100%). Moreover, the ultrasonication time was also considered as an experimental variable, with 15, 30 and 60 min for the intermediate and highest power ranges, while 30, 60 and 120 min were applied for the lowest power range. Each sample was analysed by Scanning Electron Microscopy (SEM) by dropping the colloidal suspensions onto the sample holder. Selected samples were further characterized by Atomic Force Microscopy (AFM).

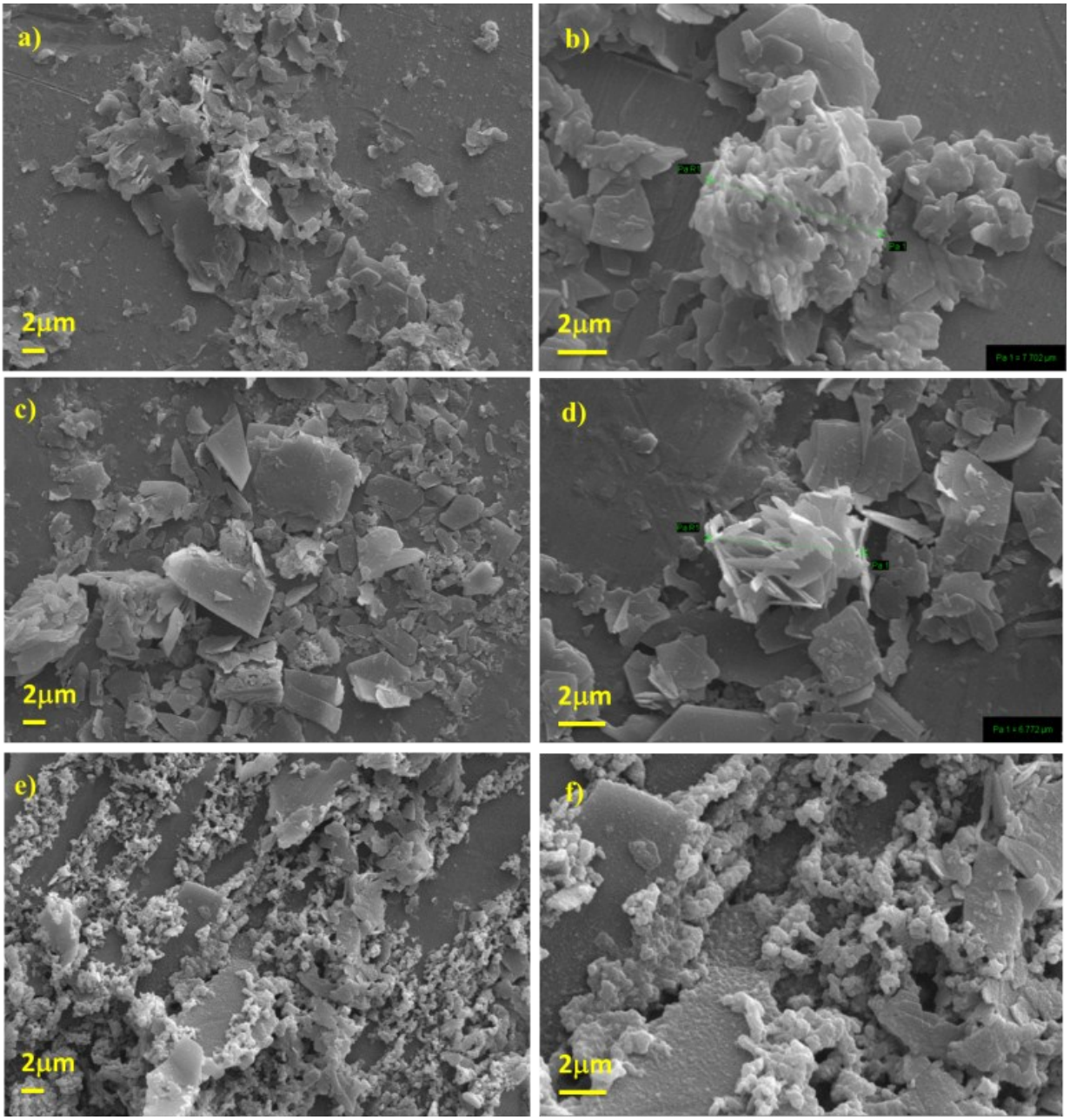

Figure S8. Figure S10: SEM micrographs of particles resulting from different LE treatment times at 66 W; 30 min (a,b), 60 min (c,d) and 120 min (e,f). A scale bar is displayed in each case.

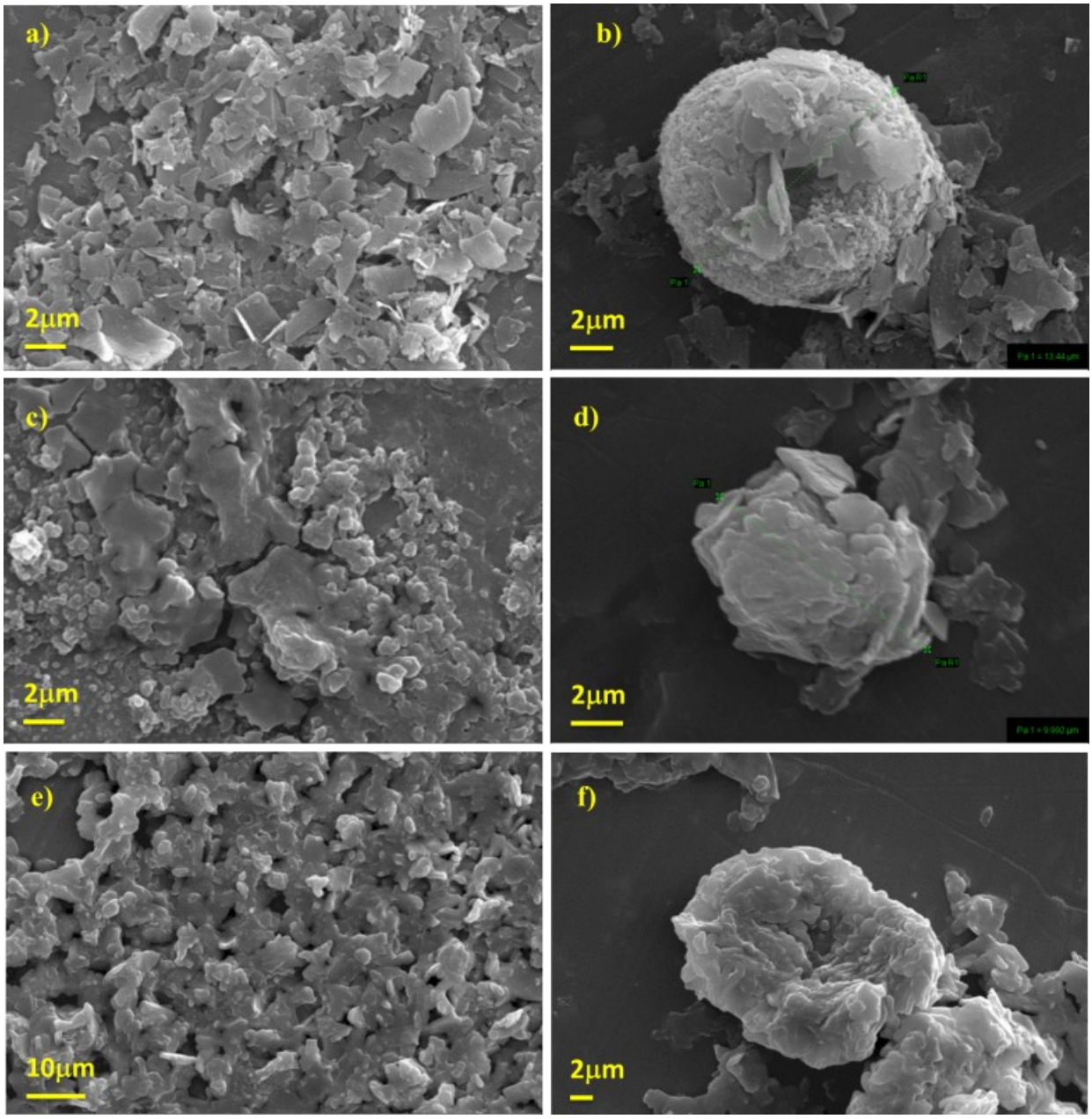

Figure S9: SEM micrographs of particles resulting from different LE treatment times at 99 W; 15 min (a,b), 30 min (c,d) and 60 min (e,f). A scale bar is displayed in each case.

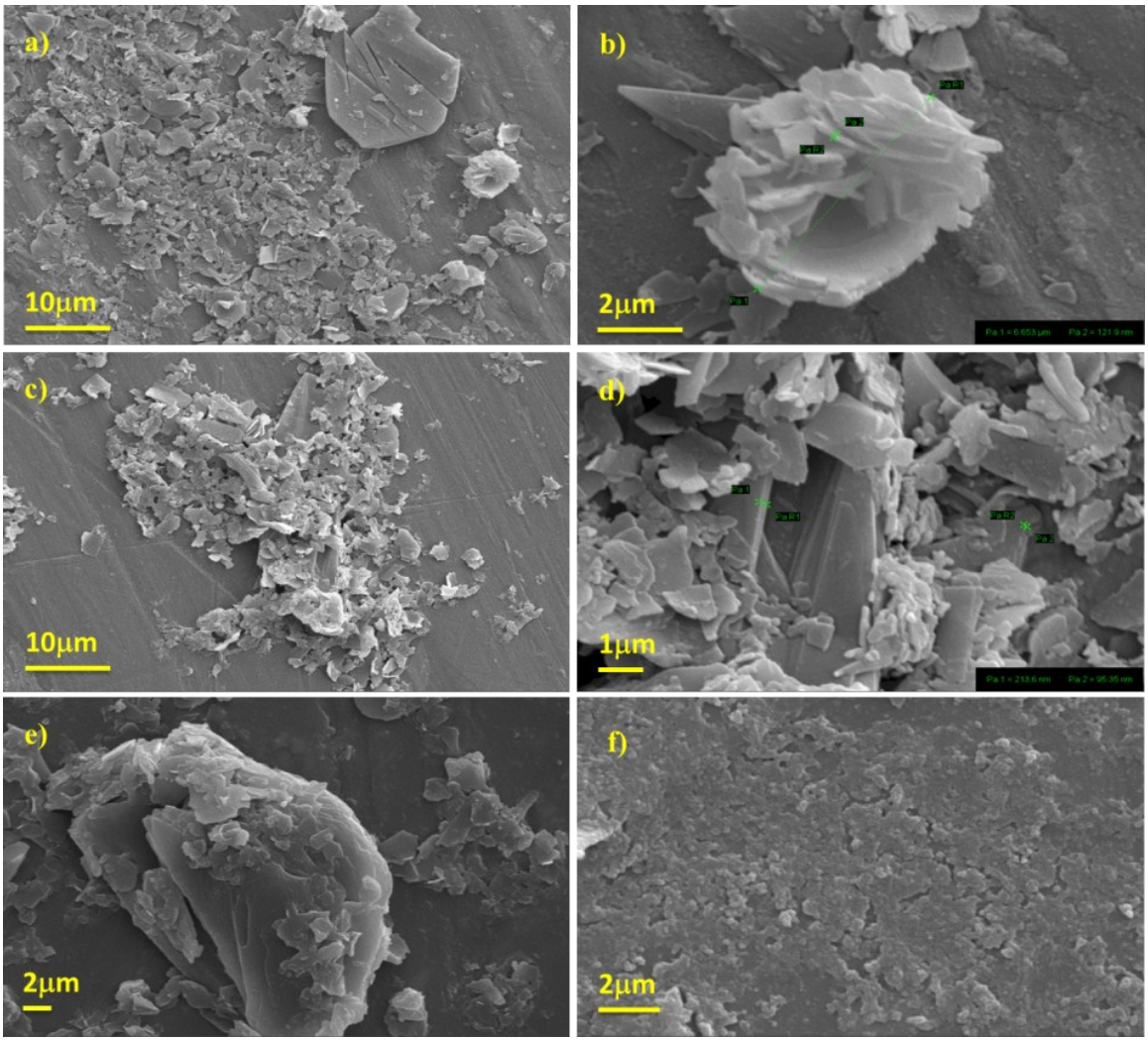

Figure S10: SEM micrographs of particles resulting from different LE treatment times at 165 W; 15 min (a,b), 30 min (c,d) and 60 min (e,f). A scale bar is displayed in each case.

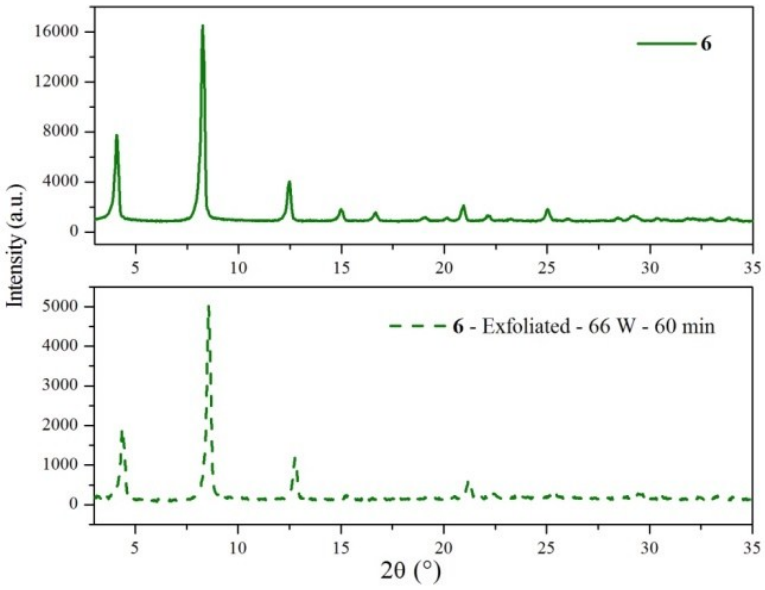

Figure S11. Comparison between PXRD patterns of compound 6 before and after exfoliation treatment.

Section S6. Photoluminescent properties

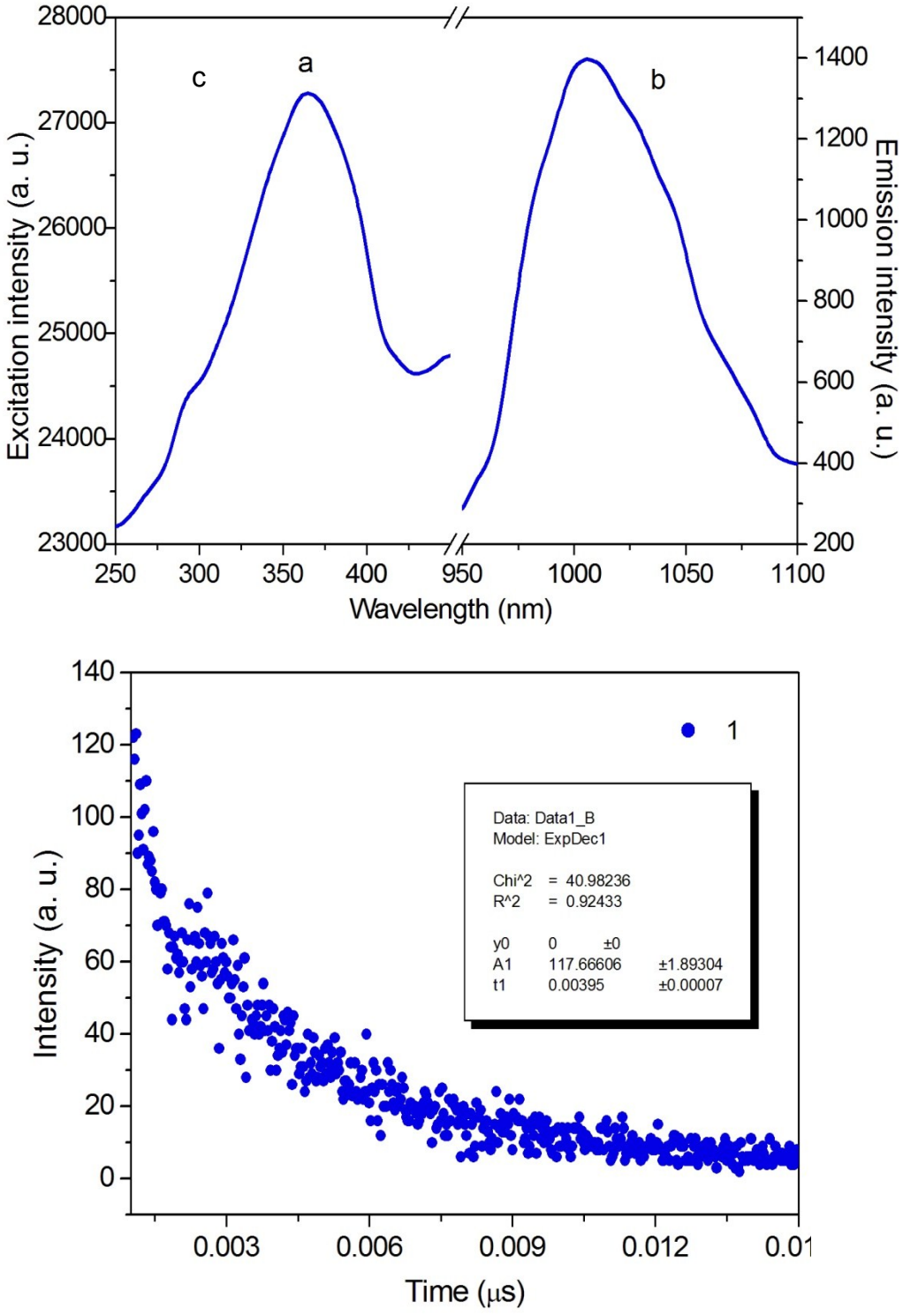

Figure S12. Excitation (a) and emission (b) spectra and luminescence time decay (c) of compound 1.

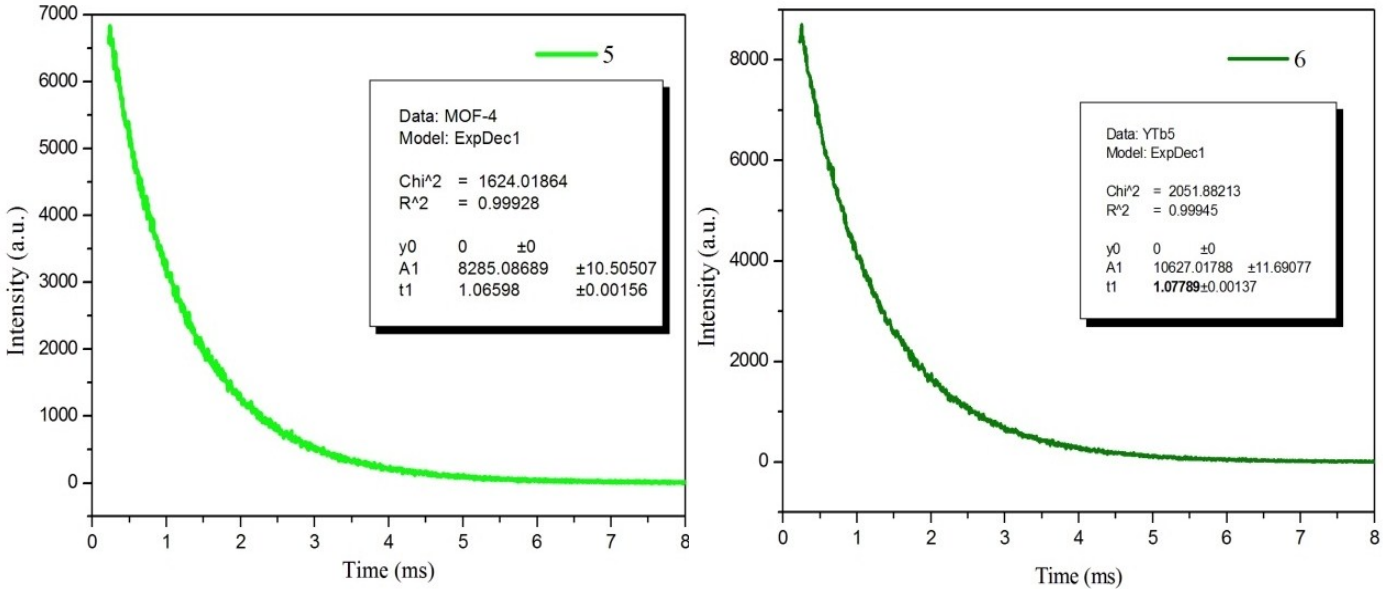

Figure S12. Lifetime decays of compounds 5 and 6. The inset shows the corresponding parameters obtained from the profile fittings

Table S5: Excitation and emission spectra assignment of compounds 1-9.

Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **1** RT							
a	364	27282.9	$S_0 \rightarrow {}^1S^*$	b	1006.1	1396.6	${}^5F_5 \rightarrow {}^5I_7$
Compound **2** RT							
a	317	31545.7	$S_0 \rightarrow {}^1S^*$	b	390	25641.0	${}^1S^* \rightarrow S_0$
				c	461	21692.0	${}^1S^* \rightarrow S_0$
Compound **2** 70 K							
				b	377	26525.2	${}^1S^* \rightarrow S_0$
				b*	425	23529.4	${}^3T^* \rightarrow S_0$
				c	464	21551.7	${}^1S^* \rightarrow S_0$
Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	Transition
Compound **3** RT							
c	356	28089.9	${}^5D_4 \rightarrow {}^7F_0$	h	470	21276.6	${}^1S^* \rightarrow S_0$
d	373	26809.7	${}^5D_4 \rightarrow {}^7F_1$				
e	393	25445.3	${}^5L_6 \rightarrow {}^7F_0$				
g	465	21505.4	${}^5D_2 \rightarrow {}^7F_0$				
Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **4** RT							
a	297	33670.0	${}^5I_4 \rightarrow {}^7F_1$	h	470	21276.6	${}^1S^* \rightarrow S_0$
b	320	31250.0	$S_0 \rightarrow {}^1S^*$	i	620	18484.3	${}^5D_0 \rightarrow {}^7F_2$
c	356	28089.9	${}^5D_4 \rightarrow {}^7F_0$				
d	373	26809.7	${}^5D_4 \rightarrow {}^7F_1$				
e	393	25445.3	${}^5L_6 \rightarrow {}^7F_0$				
f	416	24038.5	${}^5D_3 \rightarrow {}^7F_1$				
g	465	21505.4	${}^5D_2 \rightarrow {}^7F_0$				
Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **5** RT							
a	323	30959.8	$S_0 \rightarrow {}^1S^*$	b	488	20491.8	${}^5D_4 \rightarrow {}^7F_6$
				c	541	18484.3	${}^5D_4 \rightarrow {}^7F_5$
				d	583	17152.7	${}^5D_4 \rightarrow {}^7F_4$

				e	621	16103.1	$^5D_4 \rightarrow {}^7F_3$

Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **6** RT (10 K)*							
a	323	30959.8	$S_0 \rightarrow {}^1S^*$	b (b)	488	20491.8	$^5D_4 \rightarrow {}^7F_6$
				c (c)	541	18484.3	$^5D_4 \rightarrow {}^7F_5$
				d (d)	583	17152.7	$^5D_4 \rightarrow {}^7F_4$
				e (e)	621	16103.1	$^5D_4 \rightarrow {}^7F_3$
				(f)	653	15313.9	$^5D_4 \rightarrow {}^7F_2$
				(g)	669	14947.7	$^5D_4 \rightarrow {}^7F_1$
				(h)	692	14450.9	$^5D_4 \rightarrow {}^7F_0$

Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **7** RT (10 K) *							
a	323	30959.8	$S_0 \rightarrow {}^1S^*$	b (b)	488	20491.8	$^5D_4 \rightarrow {}^7F_{6\ (Tb3+)}$
				c (c)	541	18484.3	$^5D_4 \rightarrow {}^7F_{5\ (Tb3+)}$
				d (d)	583	17152.7	$^5D_4 \rightarrow {}^7F_{4\ (Tb3+)}$
				(e)	612	16339.9	$^5D_0 \rightarrow {}^7F_{2\ (Eu3+)}$
				f (f)	621	16103.1	$^5D_4 \rightarrow {}^7F_{3\ (Tb3+)}$
				g (g)	648	15432.1	$^5D_4 \rightarrow {}^7F_{2\ (Tb3+)}$
				h (h)	668	14970.1	$^5D_4 \rightarrow {}^7F_{1\ (Tb3+)}$
				i (i)	685	14598.5	$^5D_4 \rightarrow {}^7F_{0\ (Tb3+)}$

Excitation				Emission			
label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **8** RT							
a	323	30959.8	$S_0 \rightarrow {}^1S^*$	b	488	20491.8	$^5D_4 \rightarrow {}^7F_6$
				c	541	18484.3	$^5D_4 \rightarrow {}^7F_5$
				d	583	17152.7	$^5D_4 \rightarrow {}^7F_4$
				e	621	16103.1	$^5D_4 \rightarrow {}^7F_3$
				f	648	15432.1	$^5D_4 \rightarrow {}^7F_2$
				g	668	14970.1	$^5D_4 \rightarrow {}^7F_1$
				h	685	14598.5	$^5D_4 \rightarrow {}^7F_0$

Excitation				Emission			

label	wavelength (nm)	energy (cm^{-1})	transition	label	wavelength (nm)	energy (cm^{-1})	transition
Compound **9** RT							
a	323	30959.8	$S_0 \rightarrow {}^1S^*$	b	488	20491.8	$^5D_4 \rightarrow {}^7F_6$
				c	541	18484.3	$^5D_4 \rightarrow {}^7F_5$
				d	583	17152.7	$^5D_4 \rightarrow {}^7F_4$
				e	621	16103.1	$^5D_4 \rightarrow {}^7F_3$
				f	648	15432.1	$^5D_4 \rightarrow {}^7F_2$
				g	668	14970.1	$^5D_4 \rightarrow {}^7F_1$
				h	685	14598.5	$^5D_4 \rightarrow {}^7F_0$

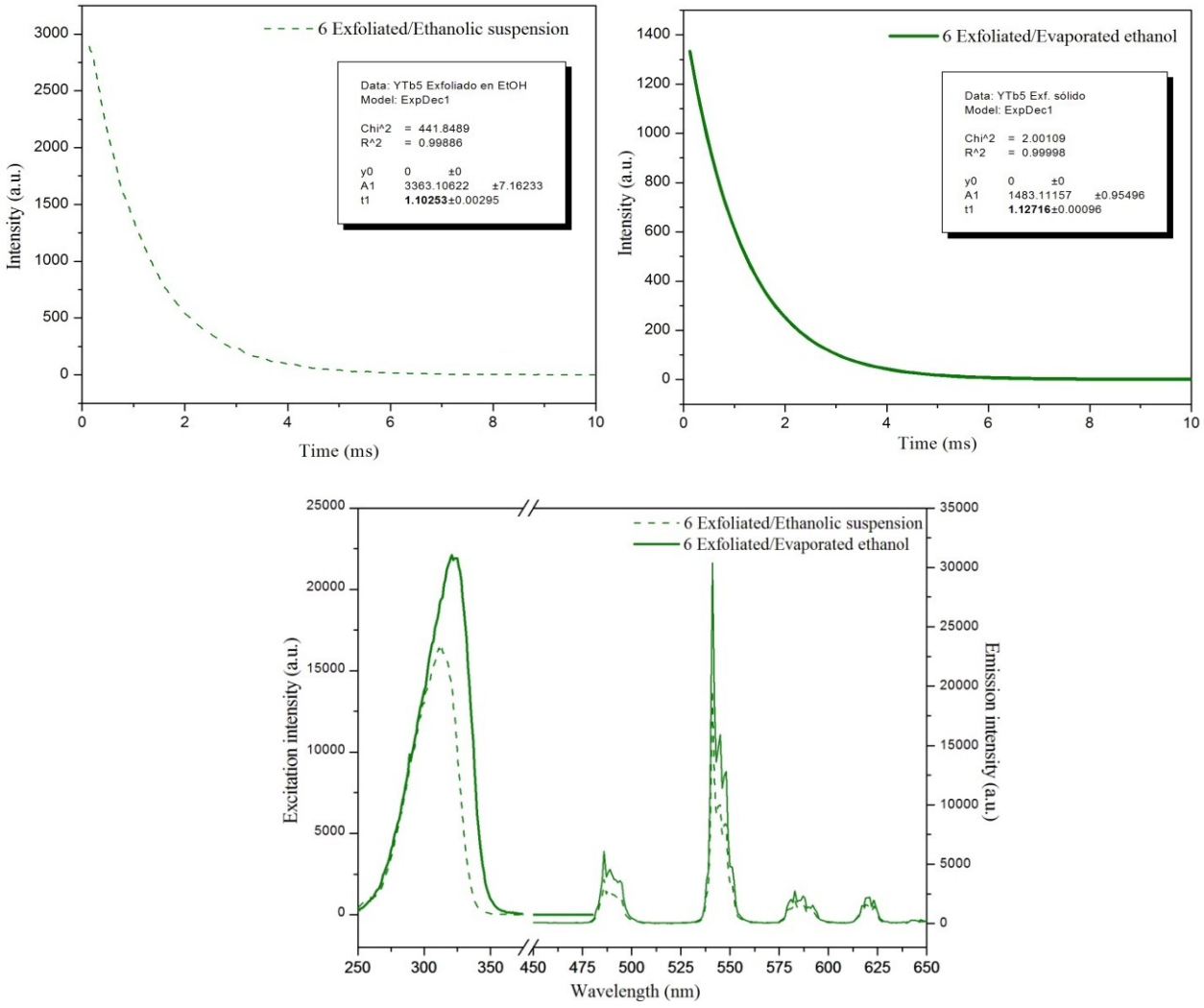

Figure S14. Top-left: lifetime decay of compound 6´ in ethanolic suspension; top-right: lifetime decay of compound 6´ after ethanol evaporation. Bottom: Excitation and emission spectra of compound 6´ in ethanolic suspension and after solvent evaporation.

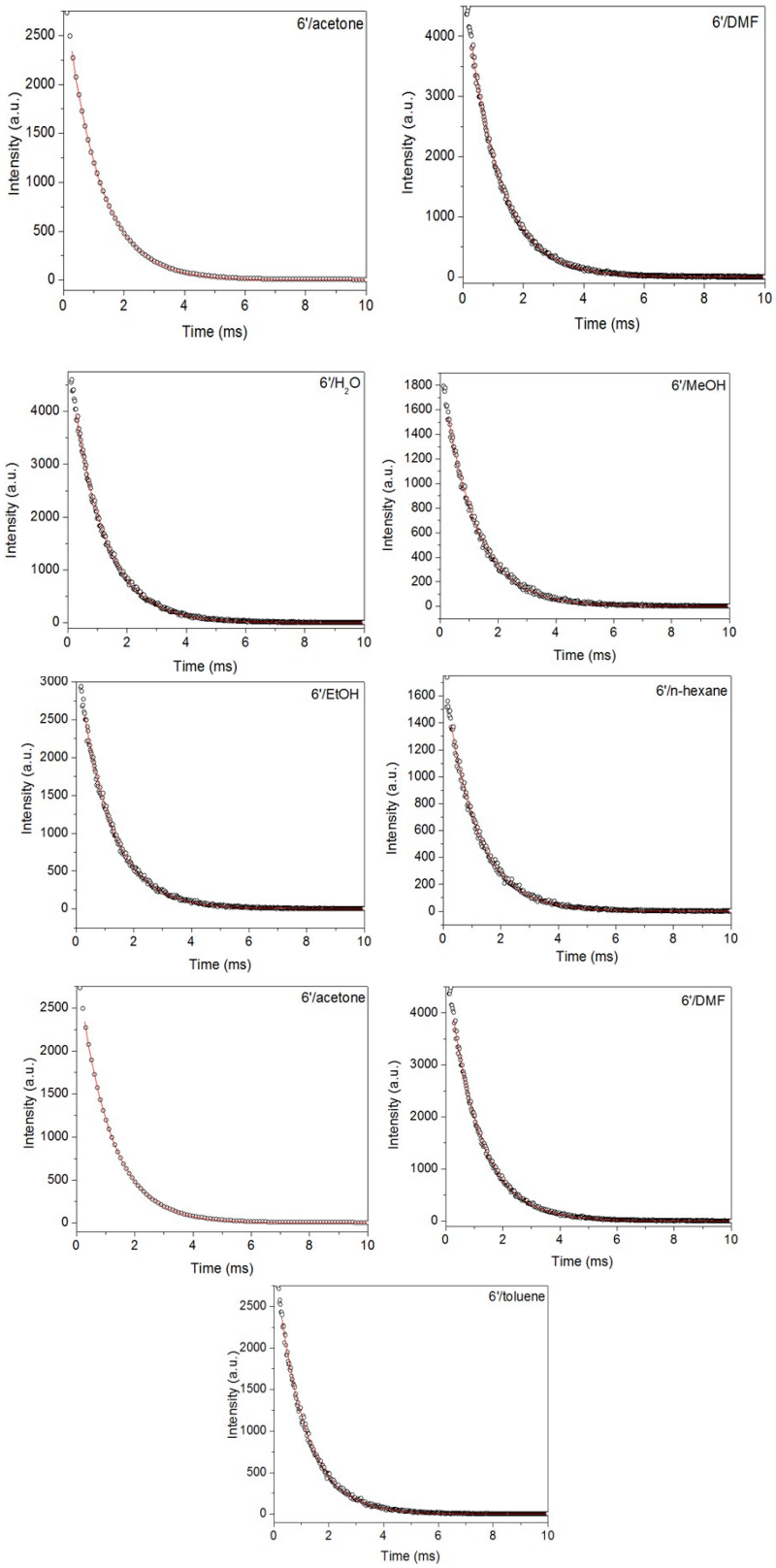

Figure S15. Lifetime decays of compound 6´ in suspensions of different solvents.

Table S6: Lifetime calculated from the corresponding decay fittings of the data in Figure S15.

6'/solvent	τ_{obs} (ms)
6'	1.127
6'/H_2O	1.092
6'/MeOH	1.13
6'/EtOH	1.102
6'/n-hexane	1.093
6'/acetone	1.087
6'/DMF	1.079
6'/toluene	1.040