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for

Biphenylene-Bridged Mesostructured Organosilica as a Novel Hybrid Host Material for Ln^{III} (Ln = Eu, Gd, Tb, Er, Yb) ions in Presence of 2-Thenoyltrifluoroacetone

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Table S1. Elemental analysis data for **1-14**.[a]

Compd	C (%)		H(%)		N(%)		S(%)		O(%)	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1(OH)$_3$	42.03	42.61	2.97	3.32	2.78	3.27	5.10	4.97	19.72	19.80
2(OH)$_2$	42.21	42.16	2.98	3.04	2.80	3.32	5.12	5.00	19.17	19.69
3(OH)$_3$	41.91	42.71	2.96	3.28	2.78	3.02	5.09	5.10	19.67	19.29
4(OH)$_3$	41.78	42.35	2.95	2.99	2.77	3.19	5.07	5.09	19.60	19.94
5(OH)$_2$	41.95	42.12	2.96	3.33	2.78	3.08	5.09	5.23	19.05	19.04
6(OH)$_3$	41.99	42.81	2.97	3.45	2.78	3.16	5.10	4.99	19.70	19.02
7(OH)$_3$	41.93	42.72	2.96	3.19	2.78	3.24	5.10	5.18	19.68	19.62
8(OH)$_3$	41.97	42.55	2.97	3.36	2.78	3.24	5.10	5.10	19.70	19.23
9(OH)$_3$	41.92	42.03	2.96	3.40	2.78	3.05	5.09	5.18	19.68	19.88
10(OH)$_3$	41.92	42.23	2.96	3.46	2.78	2.99	5.09	4.81	19.67	19.63
11(OH)$_3$	41.91	42.31	2.96	3.36	2.78	3.21	5.09	5.12	19.66	19.01
12(OH)$_3$	41.86	42.12	2,96	3.29	2.77	3.11	5.08	4.83	19.64	19.50
13(OH)$_3$	41.69	42.11	2.94	3.28	2.76	2.90	5.06	5.13	19.56	19.89
14(OH)$_3$	41.92	41.88	2.96	3.29	2.78	3.13	5.09	5.08	19.67	19.69

[a] The values for C, H and N obtained for some of the compounds are larger than the calculated values and differences exceed slightly the usually accepted errors; This is probably due to the presence of trapped solvent molecules (ethanol/THF) and/or $(NO_3)^-$ ions, consistent with the 2% weight loss observed in the TG analyses in the range 25-100^0 C (see Figure 1 in main text).

Table S2. Wavenumbers observed in FT-IR spectra of compounds **1-7**, with respective vibrational assignments.

Assignment[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**
ν(N-H)(O-H)	3420	3425	3418	3425	3418	3419	3418
ν_s(NHC=O)	1694	1694	1693	1690	1688	1691	1689
δ(N-H)	1411	1410	1414	1411	1412	1411	1410
ν_S(C=O)	1603	1601	1602	1603	1605	1602	1600
	1537	1536	1538	1535	1538	1535	1536
$\nu(C_{SP}^3\text{-H})$	2974	2970	2970	2970	2970	2975	2980
	2924	2928	2927	2928	2927	2933	2927
	2888	2887	2885	2885	2885	2888	2883
ν(C=C)	1468	1471	1472	1473	1472	1477	1479
ν(C=S)	1354	1355	1354	1355	1354	1355	1353
ν(Si-C)	1291	1290	1292	1290	1290	1291	1290
ν_{as}(Si-O)	1135	1134	1133	1134	1134	1136	1134
	1075	1074	1073	1076	1075	1076	1077
ν_s(Si-O)	814	811	812	813	813	811	812
$\delta(CF_3)$	712	712	712	712	713	713	712
δ(Si-O-Si)	565	568	568	561	568	565	564

[a] *v* represents stretching, δ in plane bending, *s* symmetric, and *as* asymmetric vibrations

Table S3. Wavenumbers observed in FT-IR spectra of compounds **8-14**, with respective vibrational assignments.

Assignment[a]	**8**	**9**	**10**	**11**	**12**	**13**	**14**
ν(N-H)(O-H)	3415	3418	3410	3418	3421	3418	3416
ν_s(NHC=O)	1692	1689	1687	1692	1692	1689	1691
δ(N-H)	1413	1410	1411	1412	1413	1410	1411
ν_S(C=O)	1602	1601	1602	1603	1605	1600	1603
	1539	1534	1535	1537	1539	1535	1539
$\nu(C_{SP}^3\text{-H})$	2973	2974	2972	2975	2974	2973	2976
	2934	2932	2936	2935	2934	2932	2934
	2887	2886	2889	2886	2887	2886	2887
ν(C=C)	1478	1479	1480	1479	1482	1479	1482
ν(C=S)	1354	1355	1354	1355	1353	1354	1354
ν(Si-C)	1291	1290	1290	1291	1290	1288	1290
ν_{as}(Si-O)	1135	1136	1133	1135	1135	1136	1135
	1077	1075	1077	1076	1075	1076	1074
ν_s(Si-O)	810	812	809	808	812	812	809
$\delta(CF_3)$	712	712	712	712	712	712	713
δ(Si-O-Si)	564	564	567	565	564	564	564

[a] *v* represents stretching, δ in plane bending, *s* symmetric, and *as* asymmetric vibrations

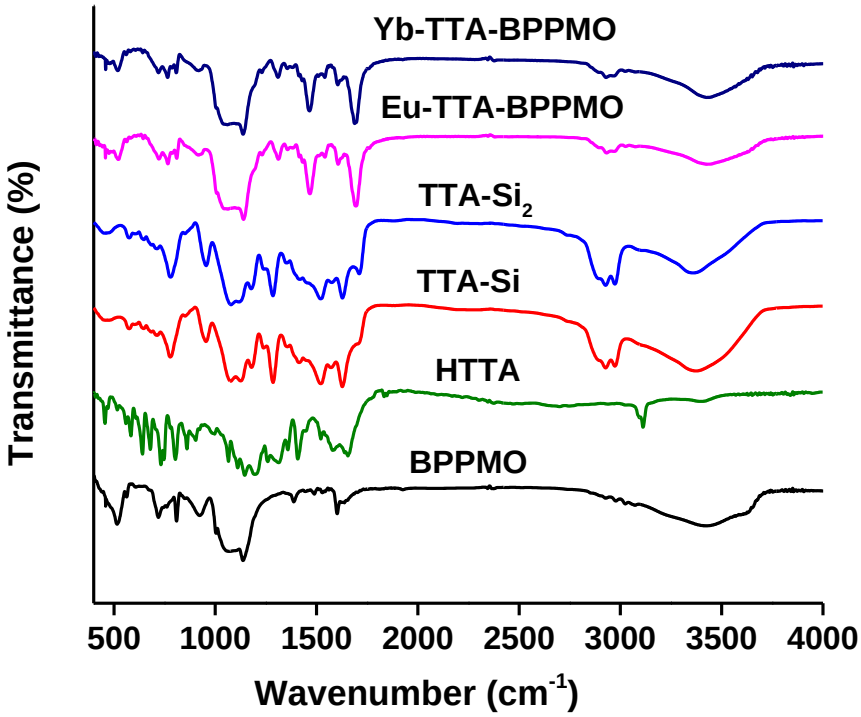

Figure S1. FTIR spectra of BPPMO, HTTA, TTA-Si, TTA-Si_2, **1** and **5**.

Table S4. ^{29}Si MAS NMR chemical shifts of compounds **1-14**.

Compnd	δ / ppm			Compnd	δ / ppm		
	T_1	T_2	T_3		T_1	T_2	T_3
1	- 61.45	- 70.05	- 79.43	**8**	- 61.83	- 69.77	-80.09
2	- 60.95	- 70.10	- 80.19	**9**	-60.91	-70.14	-81.29
3	- 61.76	- 70.58	- 78.44	**10**	-61.33	- 70.80	- 81.05
4	- 61.70	- 70.00	- 79.63	**11**	- 61.34	- 70.18	-79.23
5	- 61.76	- 70.51	- 79.43	**12**	- 60.43	- 70.51	-80.15
6	- 60.91	- 70.10	- 78.95	**13**	- 61.43	- 69.71	-80.19
7	- 61.16	- 70.51	- 79.63	**14**	-60.99	-70.14	-79.29

Table S5. ^{13}Si MAS NMR chemical shifts of compounds **1-14**.

Compnd	**δ / ppm**					
	$C_{aliphatic}$					**$C_{aromatic}$**
	a	**b**	**c**	**d**	**e**	
1	10.43	22.32	44.82	36.53	77.90	126.62-157.31
2	10.60	21.84	44. 22	36.23	78.31	126.49-157.67
3	10.37	21.73	45.01	36.99	78.86	126.65-158.60
4	10.43	22.32	44.82	37.73	78.02	126.77-157.31
5	10.40	22.46	44.90	37.66	77.89	126.78-157.41
6	10.31	21.33	45.01	36.99	78.86	126.65-156.99
7	10.43	22.37	44.81	37.73	78.02	126.77-157.31
8	10.00	21.54	44.64	36.99	78.86	126.49-158.60
9	11.00	24.08	43.67	36.33	77.90	126.96-157.16
10	10.35	24.15	43.10	36.99	78.86	126.55-158.56
11	10.96	24.30	43.17	36.92	77.66	127.05-158.39
12	10.43	21.65	44.93	36.71	78.54	126.92-158.01
13	10.41	22.36	44.12	36.69	77.89	126.78-157.41
14	10.31	21.33	45.01	37.19	78.86	126.65-156.99

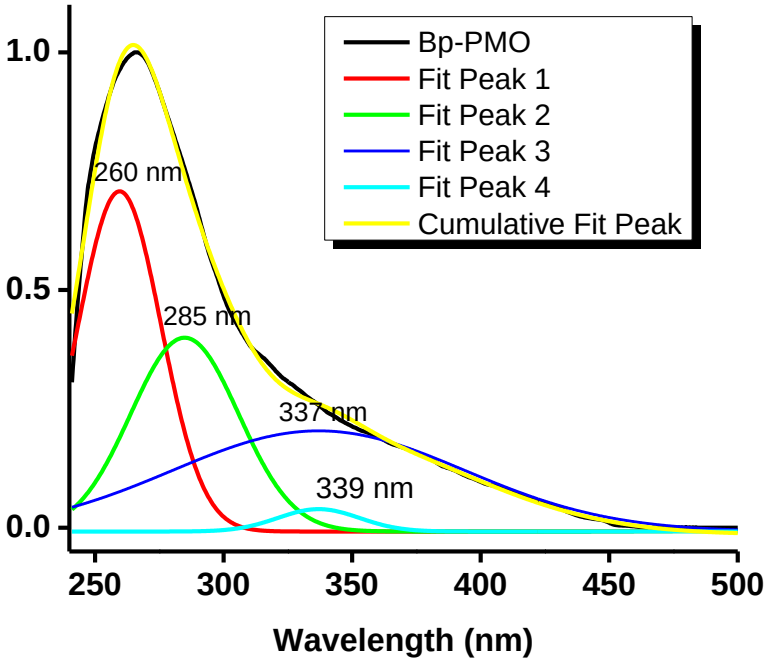

Figure S2. Decomposed absorption spectra of Bp-PMO in 2-propanol (~10^{-5} M).

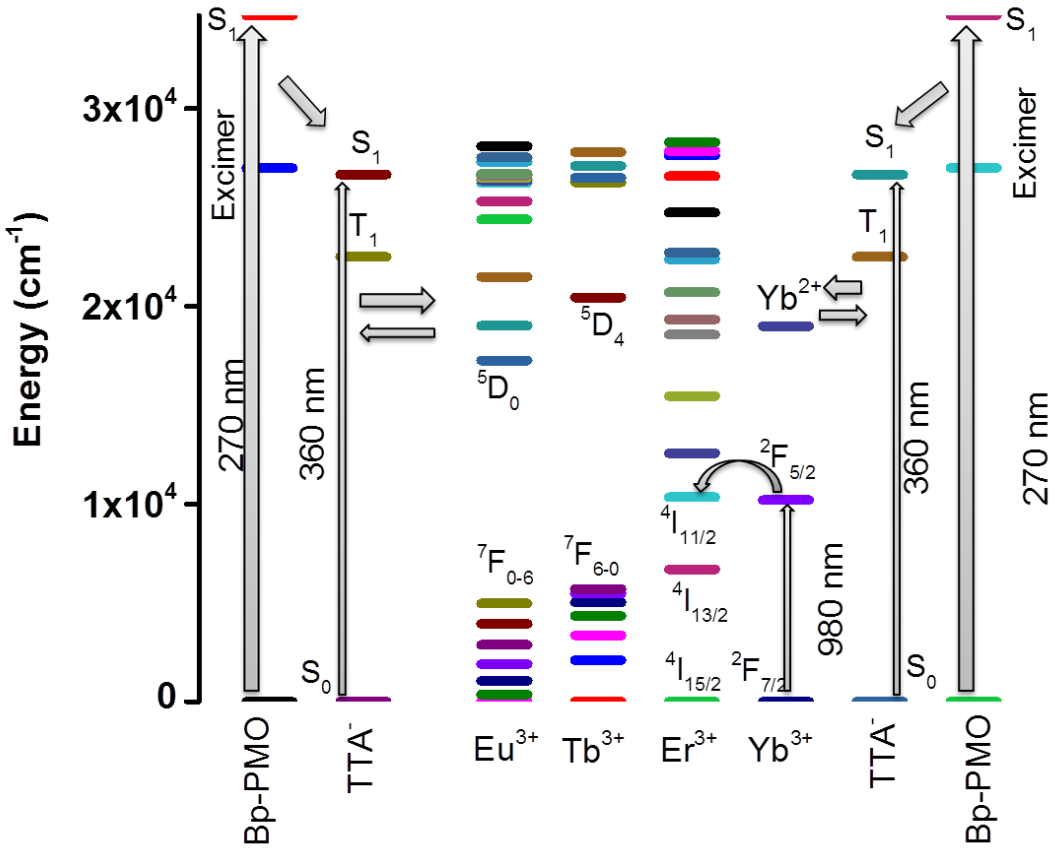

Figure S3. Energy diagram for **Bp-PMO**, **TTA** and relevant **Ln^{III}** ions.

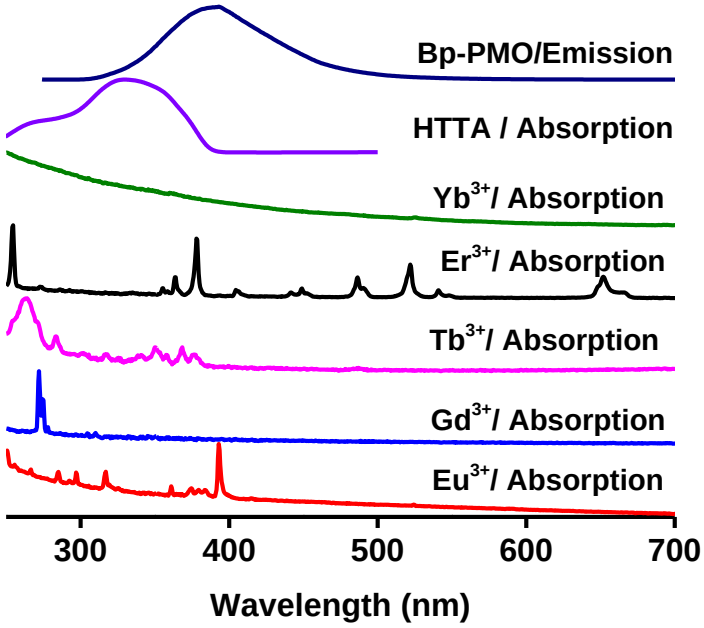

Figure S4. Absorption spectra of Ln^{III} ions (chlorides in water,10^{-4} M), HTTA (2-propanol, 10^{-5} M) and emission spectrum of Bp-PMO (solid state). Vertical scale: arbitrary units.

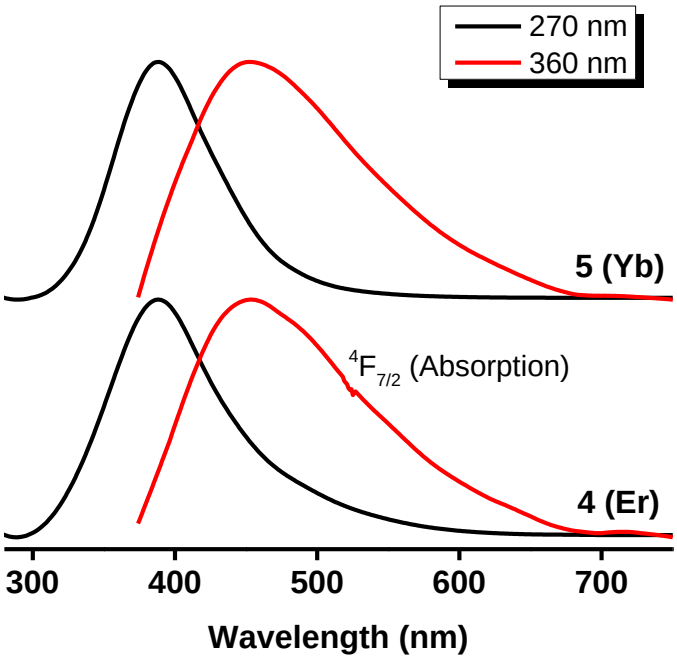

Figure S5. Corrected and normalized room-temperature emission spectra of solid-state hybrid materials **4-5** in the visible range; λ_{ex} = 270 (black line) and 360 (red line) nm. Vertical scale: arbitrary units.

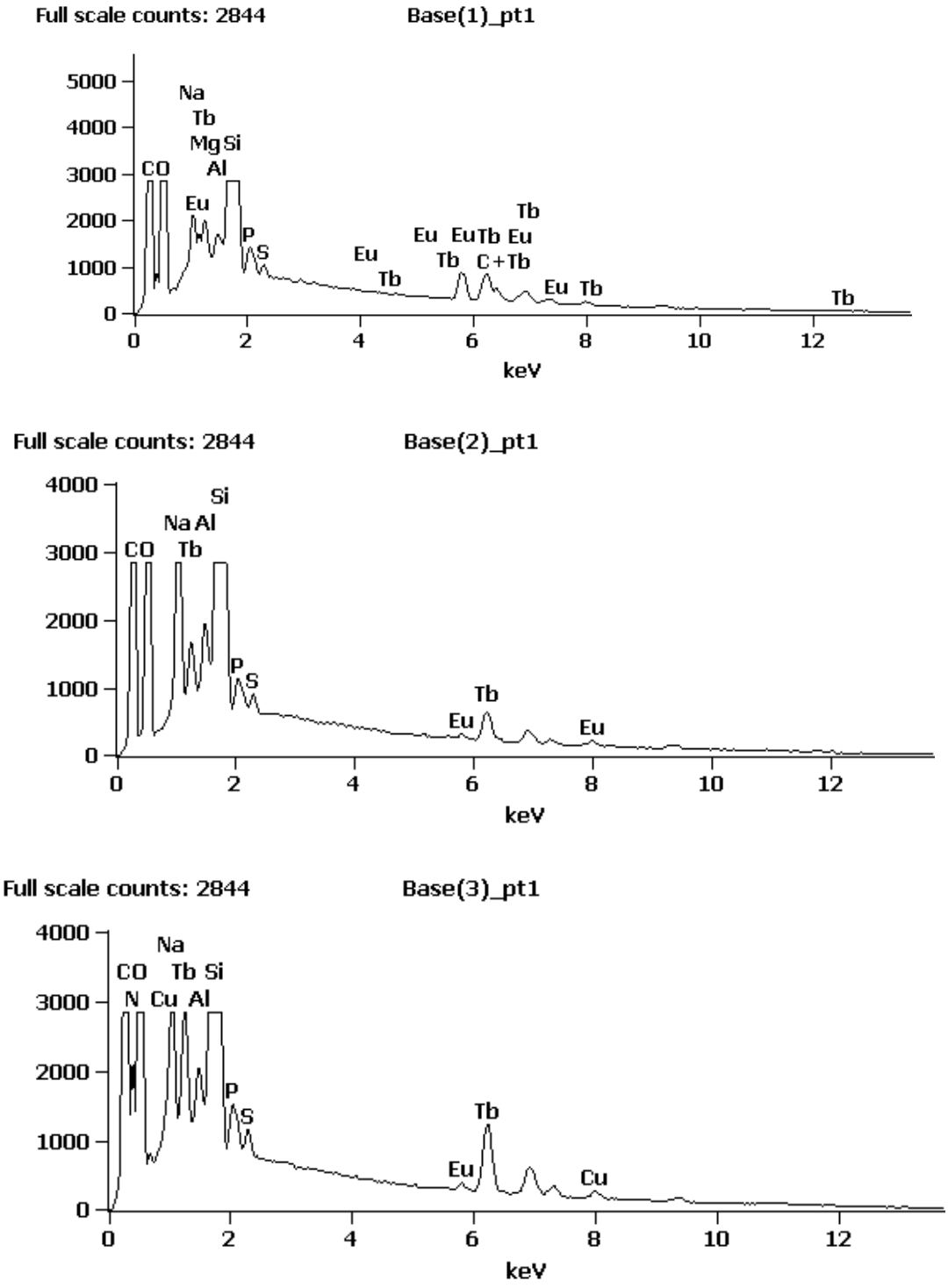

Figure S6. EDS spectra of compounds **8-10**.

Table S6. EDS elemental analysis data for heterometallic compounds. L and M indicate the X-ray band used.

$Ln_xLn'_{1-x}$	Element	Wt (%)	At (%)	Ln/Ln'
$Eu_{0.5}Gd_{0.5}$	Eu-L	2.35	0.26	1.04
	Gd-L	2.26	0.25	
$Eu_{0.5}Yb_{0.5}$	Eu-L	2.98	0.35	0.97
	Yb-L	3.51	0.36	
$Eu_{0.5}Er_{0.5}$	Eu-L	2.15	0.24	1.04
	Er-L	2.06	0.23	
$Tb_{0.5}Gd_{0.5}$	Tb-L	0.52	0.05	1.25
	Gd-L	0.38	0.04	
$Tb_{0.5}Eu_{0.5}$	Tb-L	4.15	0.45	1.09
	Eu-L	3.56	0.41	
$Tb_{0.9}Eu_{0.1}$	Tb-L	4.31	0.47	11.75
	Eu-L	0.33	0.04	
$Tb_{0.95}Eu_{0.05}$	Tb-L	5.54	0.59	19.66
	Eu-L	0.28	0.03	
$Yb_{0.9}Er_{0.1}$	Yb-L	8.79	0.87	9.66
	Er-L	0.91	0.09	
$Yb_{0.9}Tm_{0.1}$	Yb-M	21.3	2.59	9.59
	Tm-M	2.22	0.27	
$Yb_{0.9}Gd_{0.1}$	Yb-L	4.04	0.40	10.00
	Gd-L	0.40	0.04	
$Gd_{0.9}Er_{0.1}$	Gd-L	3.55	0.38	9.50
	Er-M	0.37	0.04	
$Gd_{0.9}Tm_{0.1}$	Gd-L	7.45	0.87	9.66
	Tm-L	0.77	0.09	

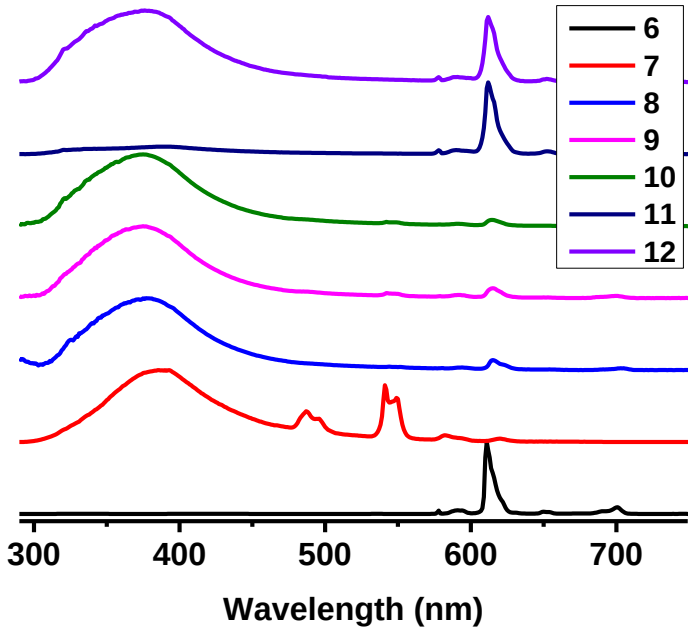

Figure S7. Emission spectra of hybrid materials **6-12** (λ_{ex} = 270 nm).

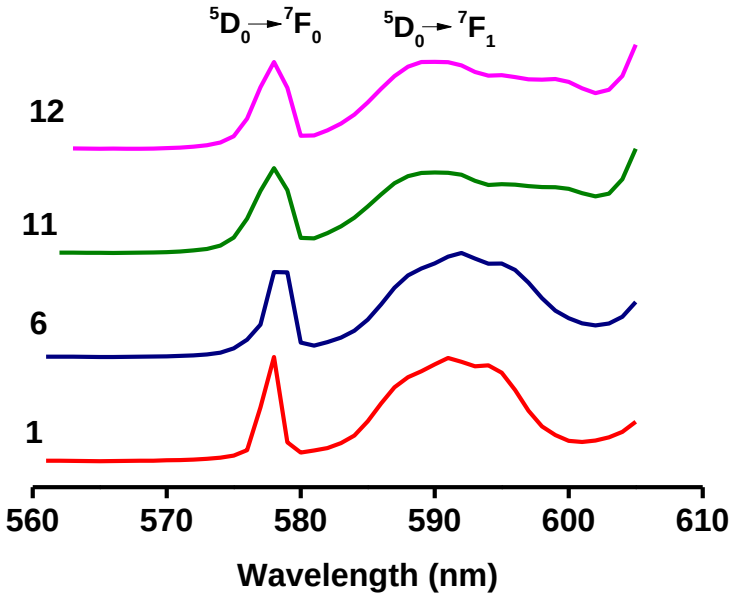

Figure S8. $^5D_0 \rightarrow {}^7F_{0\text{-}1}$ transitions in **1, 6, 11** and **12** (λ_{ex} = 360 nm).

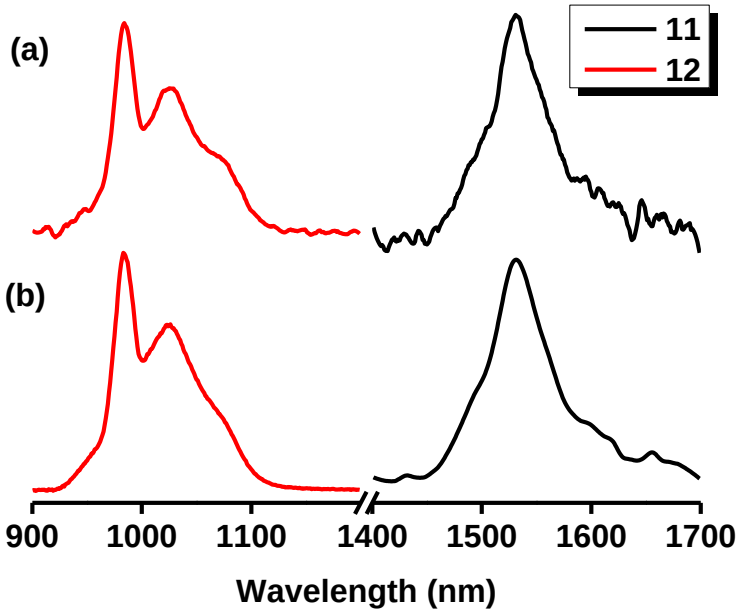

Figure S9. Emission spectra of hybrid materials **11** and **12**; λ_{ex} = (a) 270 nm, (b), 360 nm.

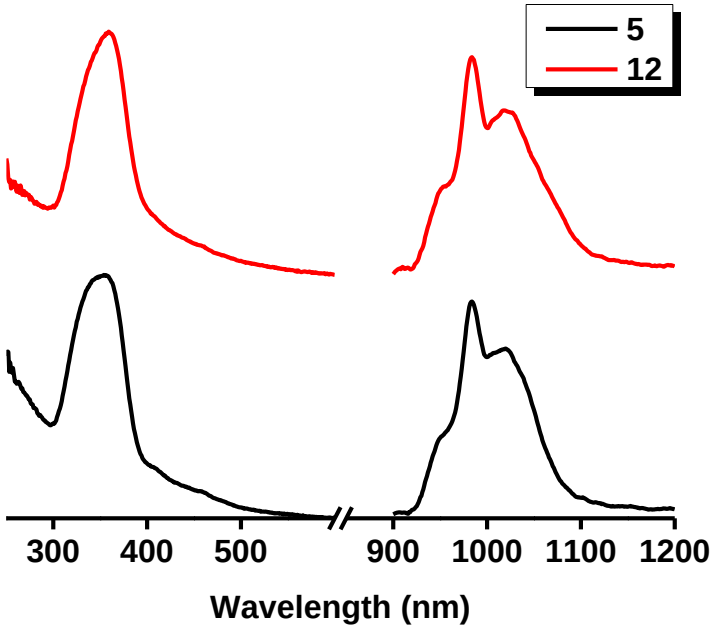

Figure S10. Excitation (left, λ_{em} = 984 nm) and emission (right, λ_{ex} = 500 nm) spectra of hybrid materials **5** and **12**.