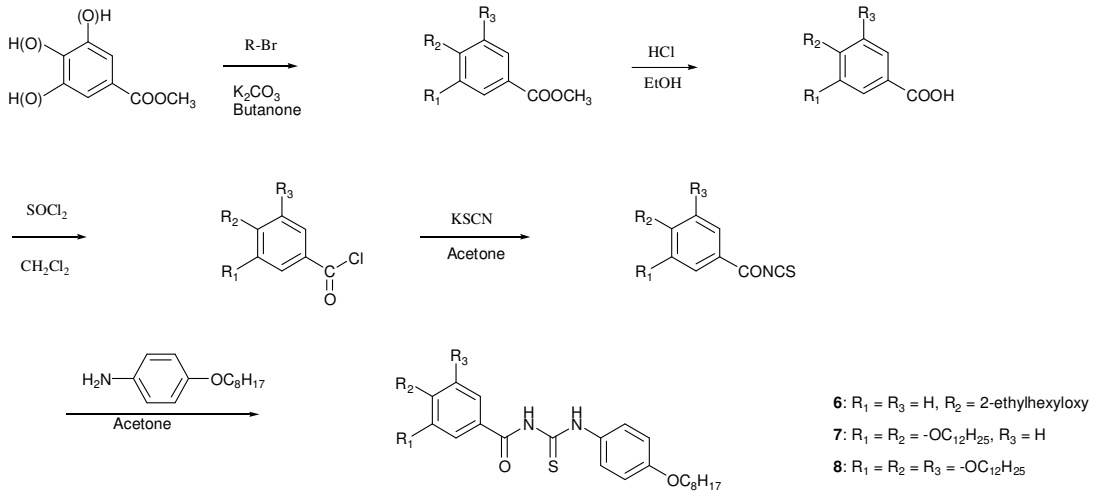
Electronic Supplementary Information for:

Room-temperature emissive liquid crystalline materials based on palladium(II) imine derivatives containing the 2-phenylpyridine core

Marin Micutz[a], Monica Iliş[a], Teodora Staicu[a], Florea Dumitraşcu[b], Iuliana Pasuk[c], Yann Molard[d], Thierry Roisnel[d], Viorel Cîrcu[a*]

[a]*Dept. of Inorganic Chemistry, University of Bucharest, 23 Dumbrava Rosie st, sector 2, Bucharest 020464, Romania, e-mail: viorel_carcu@yahoo.com, viorel.circu@g.unibuc.ro*
[b]*Centre for Organic Chemistry "C. D. Nenitzescu", Romanian Academy, Spl. Independentei 202B, Bucharest 060023, Romania*
[c]*National Institute of Materials Physics, P.O. Box MG-7, Magurele, 077125, Romania*
[d]*Sciences Chimiques de Rennes UMR 6226 CNRS Université de Rennes 1, Avenue du Général Leclerc 35042 Rennes Cedex, France*

Content:



Scheme 1. Preparation of *N*-benzoyl-*N'*-aryl thiourea derivatives (BTU)[1]

Table 1. Crystallographic data for complexes.

	3	**4b**	**9**
Empirical formula	$C_{26}H_{27}N_3O_2PtS$	$C_{29}H_{38}Cl_4N_2O_2PtS$	$C_{54}H_{66}N_6O_3Pd_2S_2$
M	640.66	815.56	1124.05
T/K	150(2)	150(2)	150(2)
λ/nm	0.71073 Å	0.71073Å	0.71073 Å
Crystal system	monoclinic	triclinic	triclinic
Space group	*P* $2_1/n$	*P -1*	*P -1*
a/ Å	15.5741(3)	7.4355(9)	10.2638(10)
b/ Å	8.17290(10)	8.2355(10)	14.4107(14)
c/ Å	19.7272(3)	26.969(3)	19.1385(16)
α/°	90	94.842(5)	73.808(3)
β/°	109.1100(10)	92.304(5)	89.864(4)
γ/°	90	104.881(5)	73.765(4)
V/ $Å^3$	2372.61(7)	1587.1(3)	2601.3(4)
Z,	4	2	2
Calculated density($g.cm^{-3}$)	1.794	1.707	1.435
Absorption coefficient,μ/mm^{-1}	6.031	4.852	0.820
F(000)	1256	808	1160
Crystal size/mm	0.34 x 0.21 x 0.07	0.52 x 0.13 x 0.02	0.49 x 0.16 x 0.1
Crystal color	yellow	yellow	yellow
θ range for data collection/ °	2.91 to 27.48	2.99 to 27.48	2.91 to 27.48
h_min, h_max	-20 , 20	-9 , 9	-13, 13
k_min, k_max	-10 , 9	-10 , 10	-18, 18
l_min, l_max	-25 , 23	-34 , 34	-19, 24
Reflections collected / unique	20808 / 5439 [R(int)[a] = 0.0412]	21012 / 7079 [R(int)[a] = 0.0499]	39191 / 11705 [R(int)[a] = 0.0494]
Completeness to θ_{max}	0.998	0.97	0.981
Max. and min. transmission	0.656 , 0.406	0.908 , 0.751	0.921 , 0.787
Data / restraints / parameters	5439 / 0 / 300	7079 / 0 / 355	11705 / 0 / 596
[b]Goodness-of-fit	1.033	1.04	1.051
Final *R* indices [I>2σ]	$R1^c$ = 0.0235 $wR2^d$ = 0.0471	$R1^c$ = 0.0412 $wR2^d$ = 0.0688	$R1^c$ = 0.0543 $wR2^d$ = 0.1388
R indices (all data)	$R1^c$ = 0.0306 $wR2^d$ = 0.0494	$R1^c$ = 0.055, $wR2^d$ = 0.0726	$R1^c$ = 0.0766 $wR2^d$ = 0.1609
Largest diff. peak and hole/ e.$Å^{-3}$	0.605 and -0.56	1.299 and -1.976	2.062 and -1.462

[a] $R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum [F_o^2]$
[b] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$
[c] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$
[d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$
$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] / 3$

Table 2. Bond lengths (Å) and angles (º) for complexes **3**, **4b** and **9**

Complex	3	4b	9	
M-C	1.980(3)	-	1.996(4)	2.059(4)
M-O	2.080(2)	-	2.068(3)	2.070(3)
M-N	2.037(2)	2.078(4)	2.069(3)	1.982(4)
M-S	2.2475(8)	2.2170(13)	2.2512(12)	2.2475(13)
Pt-Cl(1)		2.3016(13)		
Pt-Cl(2)		2.3037(13)		
C-M-N	80.59(11)	-	81.54(16)	81.28(16)
C-M-S	94.93(9)	-	93.97(13)	93.10(13)
N-M-O	91.21(9)	-	91.73(12)	92.58(13)
O-M-S	93.40(6)	-	92.46(9)	93.05(9)
N-Pt-Cl1		89.01(12)		
S-Pt-Cl1		87.80(5)		
N-Pt-Cl2		88.49(12)		
S-Pt-Cl2		94.70(5)		

Table 3. X-ray diffraction data for Pd(II) complexes (**11** and **12**)

Compound	T/(°C)	d_{exp}/Å	Indexation	d_{calc}/Å	Mesophase parameters
11	85	36.18	d_{10}	36.2	Col_h
		20.73	d_{11}	20.8	a=41.8 Å
		11.87	d_{30}	12.1	Z~1.5
		10.30	d_{22}	10.45	S=1513 Å^2
		9.80	d_{31}	10.0	
		8.93	d_{40}	9.04	
		8.16	d_{41}	8.09	
		7.70	-	-	
		7.10	d_{50}	7.23	
		4.6	h_{ch}		
		3.6	h_0		
		d_{exp}/ Å	Indexation	d_{calc}/Å	Mesophase parameters
12	100	32.9	d_{10}	32.9	Col_h
		19.1	d_{11}	19.0	a = 38.0 Å
		16.5	d_{20}	16.5	Z~1.1
		12.7	d_{21}	12.5	S_h = 1251Å^2
		10.9	d_{30}	11.0	
		6.5	-		
		4.7	h_{ch}		
		3.6	h_0		

The columnar lattice parameter was calculated with the following relationship $a = d_{10} \times 2/3^{1/2}$, where the cross-section area was calculated as following: $S = a^2 x 3^{1/2}/2$.

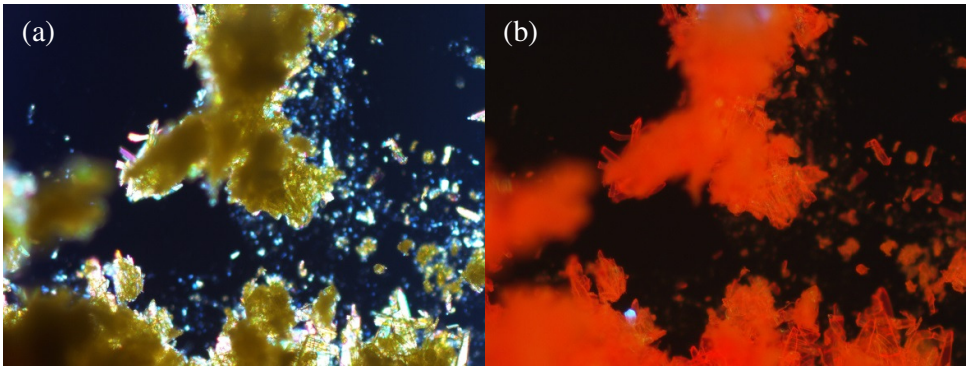


Figure S1. Pictures of **10** taken at room temperature, without irradiation (a) and of the same area irradiated within the 380 - 420 nm range (b)

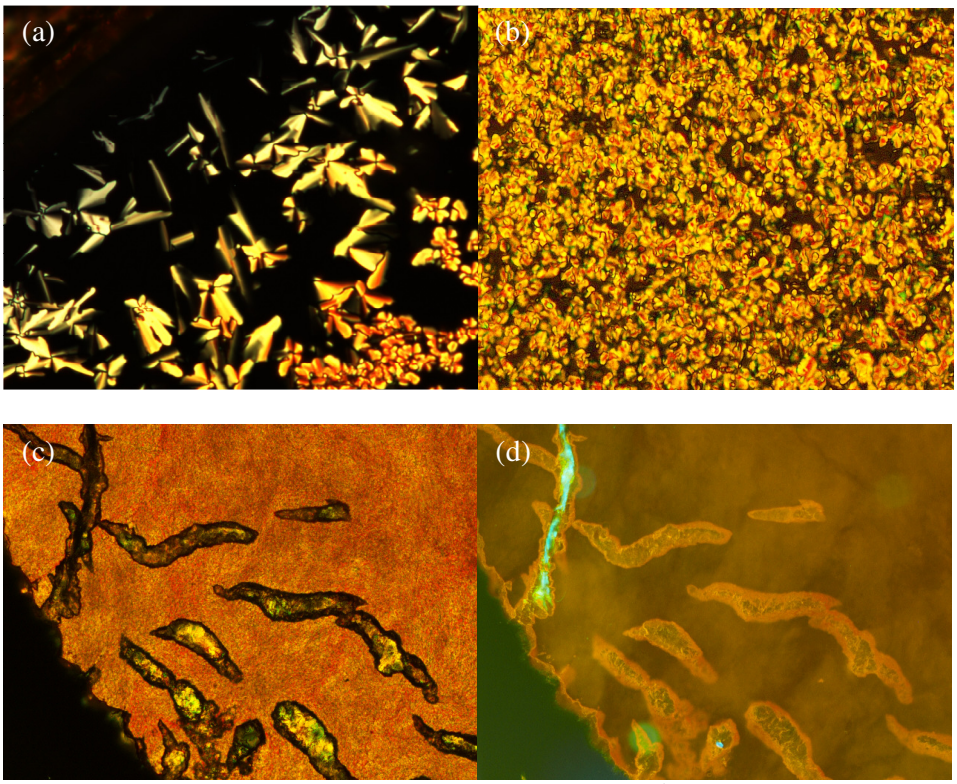


Figure S2. POM textures shown by complex **11** at 140°C (a) and complex **12** at 110°C (b). Pictures of complex **12** taken at 30°C with no irradiation (c) and irradiated within the 380 - 420 nm range (d)

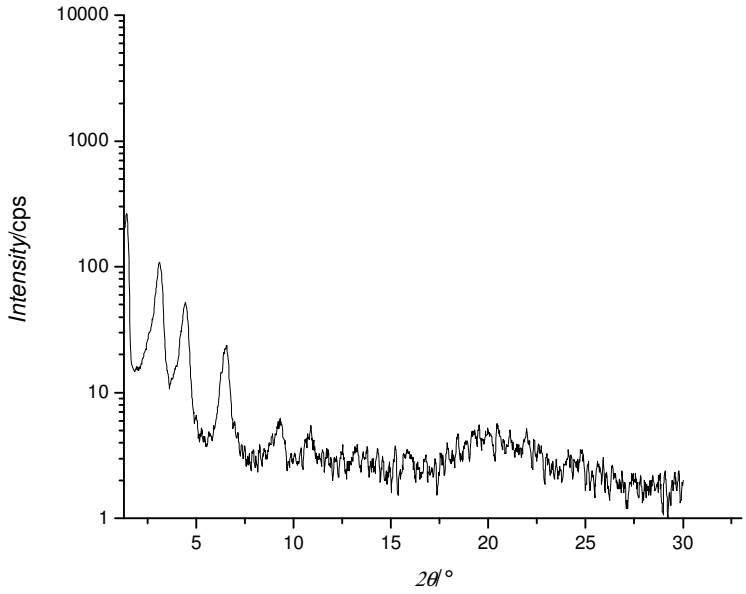


Figure S3. Powder X-ray diffractogram of complex **11** recorded at 30ºC before melting

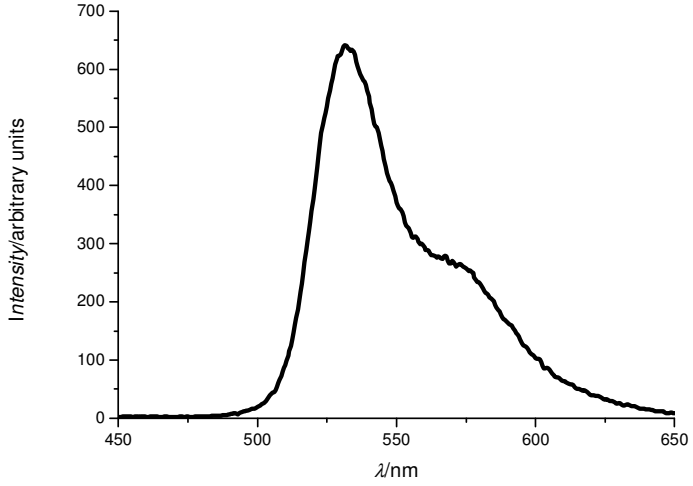


Figure S4. The emission spectrum of complex **3**, (λ_{exc} = 380 nm, Φ = 0.08, 1x10^{-4}M in CH_2Cl_2 solution)

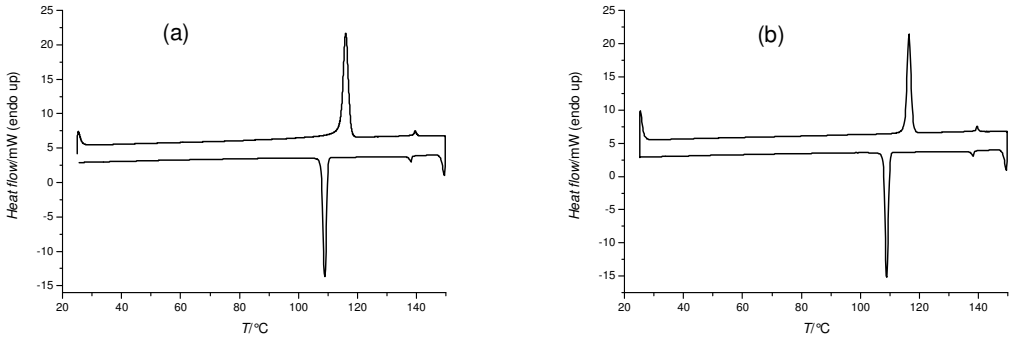


Figure S5. DSC curve for **1b** (first heating-cooling cycle (a) and second heating - cooling cycle (b))

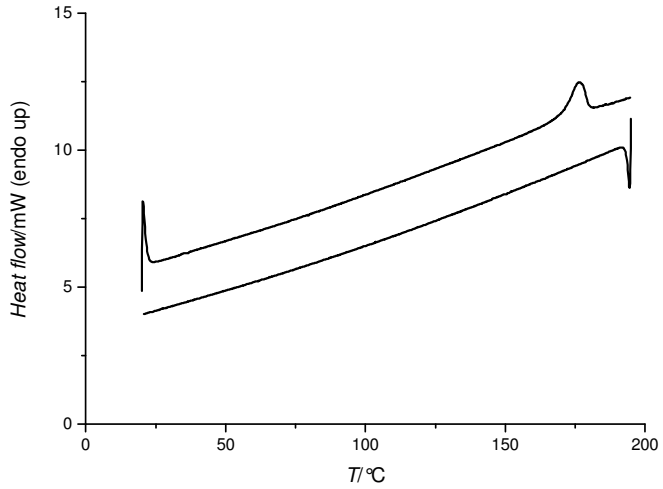


Figure S6. DSC trace for complex **10**

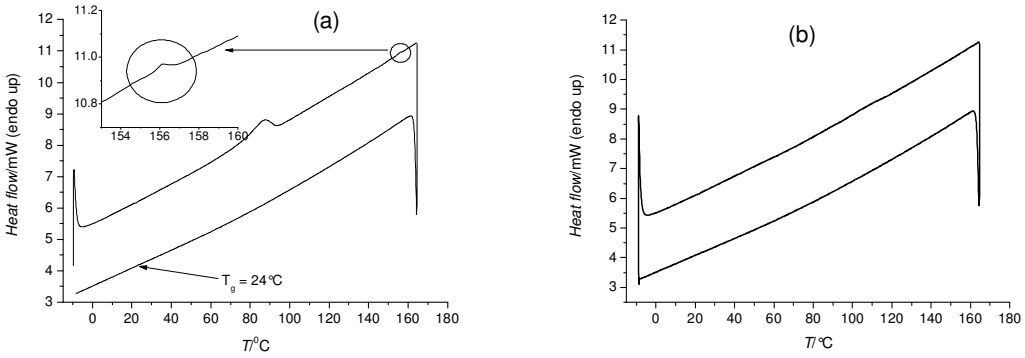


Figure S7. DSC trace for complex **11**, first heating-cooling cycle (a) and second heating-cooling cycle (b)

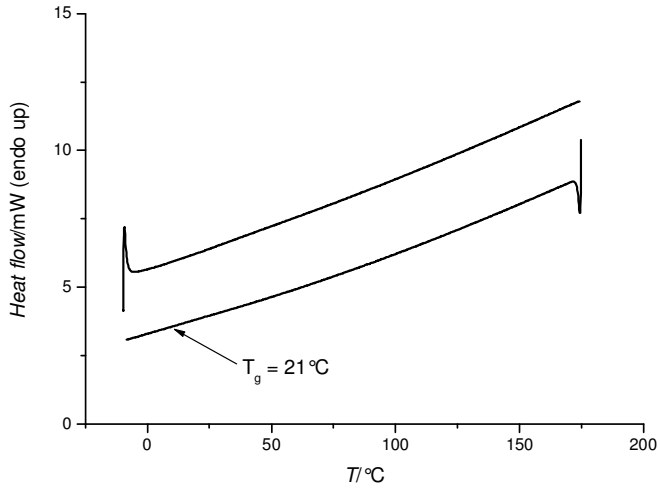


Figure S8. DSC trace for complex **12**

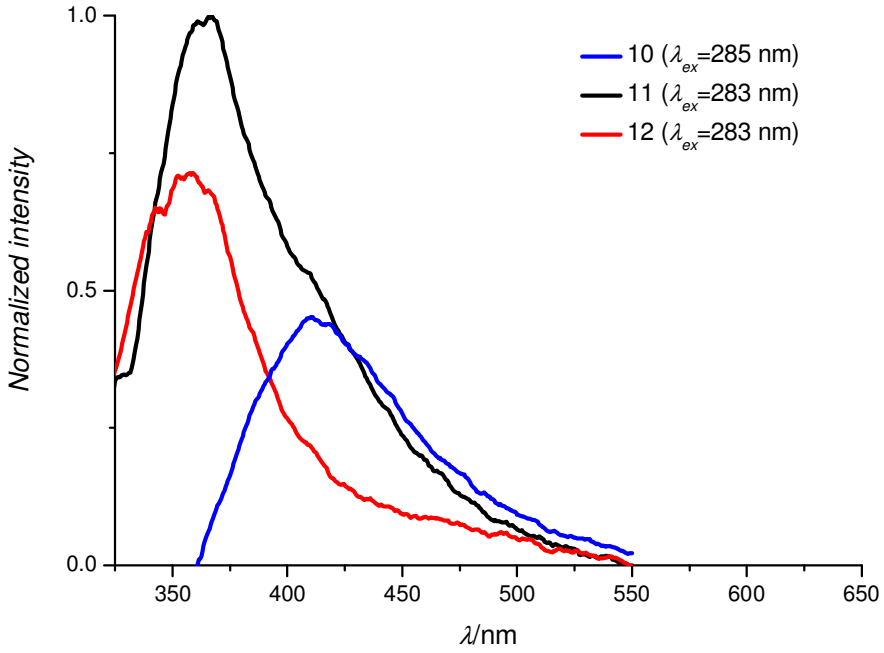


Figure S9. The emission spectra of palladium(II) complexes recorded in dichloromethane solution

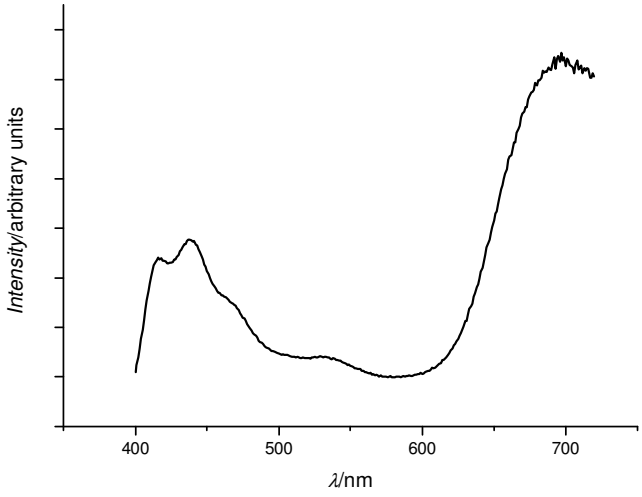


Figure S10. The solid-state emission spectra of **12** (λ_{exc}=380 nm)

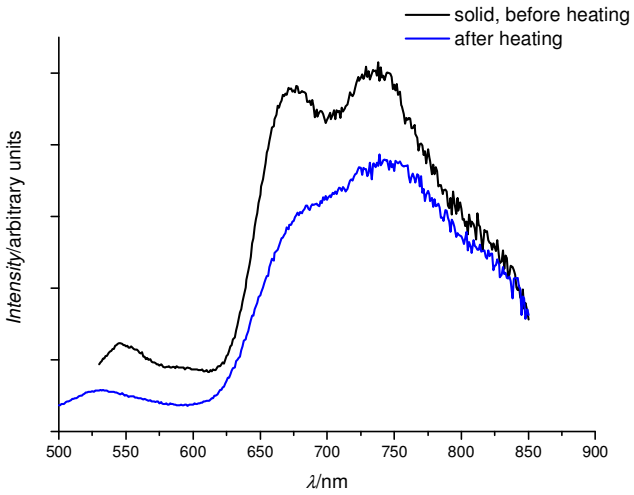


Figure S11. The solid-state emission of **11** before and after heating (λ_{exc}=480 nm)

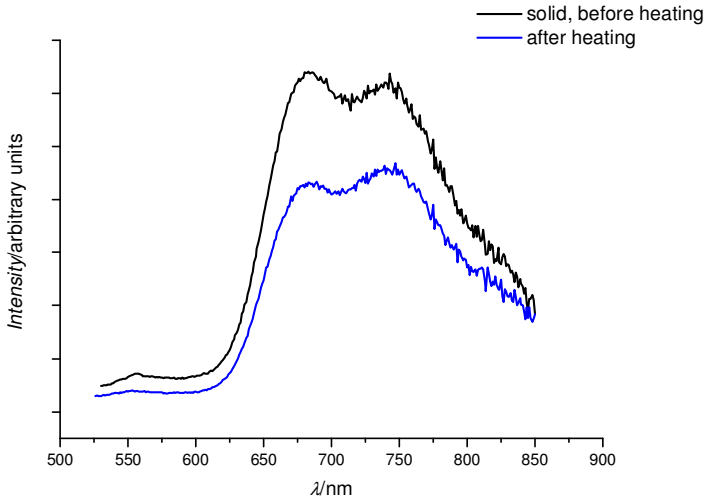


Figure S12. The solid-state emission of **12** before and after heating (λ_{exc}=480 nm)

References:

1. M. Ilis, M. Bucos, F. Dumitrascu and V. Circu, *J. Mol. Struct.*, 2011, **987**, 1.