Bimetallic Liquid Crystal Blends Based on Structurally Related 3*d*-Metal Coordination Complexes

Carmen Cretu, Evelyn Popa, Giuseppe Di Maio, Angela Candreva, Ildiko Buta, Alexadru Visan, Massimo La Deda, Bertrand Donnio* and Elisabeta I. Szerb*

Table of Contents

Experimental Procedures

1,10-Phenanthroline monohydrate was purchased from Aldrich; Methyl 3,4,5-trihydroxybenzoate, $ZnCl_2$ and $CuCl_2 \cdot 2H_2O$ were acquired from Merck. The synthesis of the silver(I) salt of 3,4,5-tridodecyloxybenzoate and precursor metal complexes dichloride(1,10-phenanthroline)M(II) of general formula $(phen)MCl_2$ where phen = 1,10-phenanthroline and M = Zn(II) or Cu(II) were performed as reported previously.[1]

Sonication of the solutions were performed with an Elmasonic S 30 (H) Ultrasonic cleaning unit (37 kHz, maximum power output of 80 W) at a temperature of 28°C, for 20 minutes.

Infrared spectra (KBr) were recorded on a Cary 630 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. ^1H NMR experiments were recorded on a Bruker Avance III HD – 500 MHz spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as internal standard. Elemental analyses (CHN) were performed with a UNICUBE microanalyzer from Elementar. The percentages of M(II) were determined using a SensAA flame atomic absorption spectrometer (GBC Scientific Equipment, Australia). The flame used was an air-acetylene (oxidizing) mixture. Two determinations were made and the average absorbance value was further used. The apparatus was equipped with a copper/zinc hollow cathode lamp (for copper: detection limit: 1-5 mg/L, integration time 3s; for zinc: detection limit: 0.4-1.5 mg/L, integration time 3s).

TG/DTA curves were obtained in the temperature range of 25-800 °C with a heating rate of 10°C/min, using a TGA/SDTA 851/LF/1100 Mettler Toledo thermogravimetric analyzer. The experiments were conducted under nitrogen flow of 50 mL/min and dynamic atmosphere of air introduced at 800°C followed by a final isothermal heating for 15 min. 10-20 mg samples were placed in alumina crucible of 150 mL.

Mesophases optical textures were observed with an Olympus BX53M polarizing microscope (POM) equipped with a Linkam hot-stage. Images of the various phases were recorded using an Olympus UC90 camera. Enthalpies and transition temperatures were recorded using a Discovery DSC 25 apparatus from TA Instruments. The apparatus was calibrated with indium; three heating/cooling cycles were performed on each sample, with a heating and cooling rate of 10°C/min.

S/WAXS patterns were obtained with a transmission Guinier-like geometry. A linear focalized monochromatic Cu Kα1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. In all cases, samples were filled in home-made sealed cells of 1 mm path. The patterns were recorded with a curved Inel CPS120 counter gas-filled detector linked to a data acquisition computer (periodicities up to 90 Å) and on image plates scanned by Amersham Typhoon IP with 25 µm resolution (periodicities up to 120 Å). The sample temperature was controlled within ±0.01°C, and exposure times were varied from 2 to 6 h.

Spectrofluorimetric grade CH_2Cl_2 were used for the photophysical investigations in solution without further purification. A PerkinElmer Lambda 900 spectrophotometer was used to obtain the UV/vis absorption spectra, a Perkin-Elmer LS 50B spectrofluorimeter was used to obtain the emission spectra in solution, in both cases quartz cuvettes of a 1 cm path length were used. Solid-state emission spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The luminescence quantum yields of the samples in solution were determined using the optical dilution method[4] 2-aminopyridine in ethanol solution as a reference standard (Φ = 0.37[5]). With regard to the solid state measurements, samples were prepared by placing a given amount of powder between two quartz slides and standardizing the thickness of the sample layer by pressing and sliding to each other the quartz slides . The emission quantum yields of the solid samples were obtained by means of a 102 mm diameter integrating sphere coated with Spectralon® and mounted in the optical path of the spectrofluorimeter using, as the excitation source, a 450 W xenon lamp coupled with a double-grating monochromator for selecting wavelengths. The procedure for the measure of quantum yields with integrating sphere was based on De Mello method.[5] Measurements varying temperature were performed trough a heating sample holder connected to a heating plate (CaLCTec Instruments).

Time resolved measurements were performed using the time-correlated single-photon counting (TCSPC) on the Fluorolog-3 apparatus. NanoLEDs pulse centred at 379 nm and 265 nm (FWHM 750 ps with 1 MHz repetition rate) were used as the excitation source and fixed directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm mm^{-1} dispersion; 1200 grooves per mm). Data analysis

was performed using the commercially available DAS6 software (Horiba Jobin Yvon IBH). The quality of the fit was assessed by minimizing the reduced χ2 function and visual inspection of the weighted residuals.

Synthesis and structural characterization

All compounds were structurally characterized by FT-IR, ^{1}H NMR (for **Zn_MM**) and atomic absorption spectroscopies and elemental analysis methods.
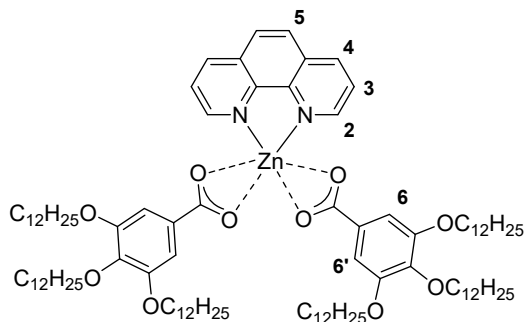
Complex Zn_MM. A solution of Ag(I) salt of 3,4,5-tridodecyloxybenzoate (0.274 g, 0.350 mmol) in 50 mL CHCl$_3$ was added dropwise to a suspension of (phen)ZnCl$_2$ (0.050 g, 0.159 mmol) in 10 mL of MeOH. The reaction mixture was stirred at room temperature for 6h. After the removal of AgCl by filtration, the mother liquor was evaporated under reduced pressure. The residue was dissolved in CHCl$_3$ and acetone was added. The precipitate formed was filtered out, and the pure product was obtained from the mother solution by repeated recrystallization from acetone and hexane/EtOH (0.188 g, 74%). FT-IR (KBr, cm^{-1}): 2921 (υ_{as},(-CH$_2$-)), 2852 (υ_s,(-CH$_2$-)), 1559 (υ_{as},(COO$^-$)), 1539 – 1422 (υC=C, υC=N) 1380 (υ_s(COO$^-$)); ^{1}H-NMR (CDCl$_3$, δ/ppm): 9.48 (d, ^3J = 4.7 Hz, 2H, H^2), 8.55 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 2H, H^4), 8.07-7.86 (overlapped peaks, 4H, H^5, H^3), 7.40 (s, 4H, H$^{6,6'}$), 3.96 (m, 12 H, -OCH_2), 1.73 (m, 12H, -OCH$_2$CH_2), 1.54 – 1.10 (overlapped peaks, 108 H), 0.87 (t, ^3J = 7.0 Hz, 18H, -CH_3). Anal. Calcd. for C$_{98}$H$_{162}$N$_2$O$_{10}$Zn (1593.73 g·mol^{-1}): C, 73.85; H, 10.25; N, 1.76. Found: C, 73.64; H, 10.12; N, 1.64%. AAS: Zn% calcd.: 4.10, found: 4.03.
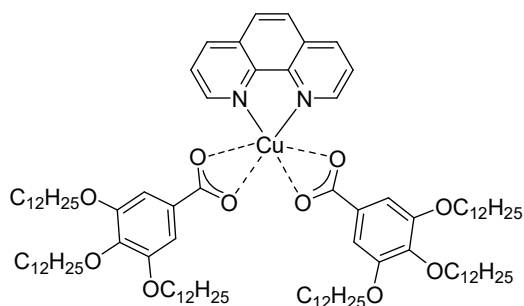
Complex Cu_MM. A solution of Ag(I) salt of 3,4,5-tridodecyloxybenzoate (0.274 g, 0.350 mmol) in 50 mL CHCl$_3$ was added dropwise to a suspension of (phen)CuCl$_2$ (0.050 g, 0.159 mmol) in 10 mL of MeOH. The reaction mixture was stirred at room temperature for 6h. After the removal of AgCl by filtration, the mother liquor was evaporated under reduced pressure. The residue was dissolved in CHCl$_3$ and acetone was added. The precipitate formed was filtered out, and the pure product was obtained from the mother solution by repeated recrystallization from acetone and hexane/EtOH (0.256 g, 58%). FT-IR (KBr, cm^{-1}): 2923 (υ_{as},(-CH$_2$-)), 2853 (υ_s,(-CH$_2$-)), 1562 (υ_{as},(COO-)), 1522 – 1425 ($\upsilon_{C=C}$, $\upsilon_{C=N}$) 1375 (υ_s(COO$^-$)). Anal. Calcd. for C$_{98}$H$_{162}$CuN$_2$O$_{10}$ (1591.89 g·mol^{-1}): C, 73.94; H, 10.26; N, 1.76. Found: C, 73.84; H, 10.10; N, 1.65%. AAS: Cu% calcd.: 3.99, found: 3.92.

Structural characterization

The FT-IR spectra of **Zn_MM** and **Cu_MM** are superimposable, confirming the similar structure and coordination environment for both coordination complexes. Moreover, the separation of the C-O stretching vibrations: $\Delta = 179$ cm^{-1} for **Zn_MM** and 187 cm^{-1} for **Cu_MM** respectively, show a bidentate chelating nature of the carboxylate coordination mode.
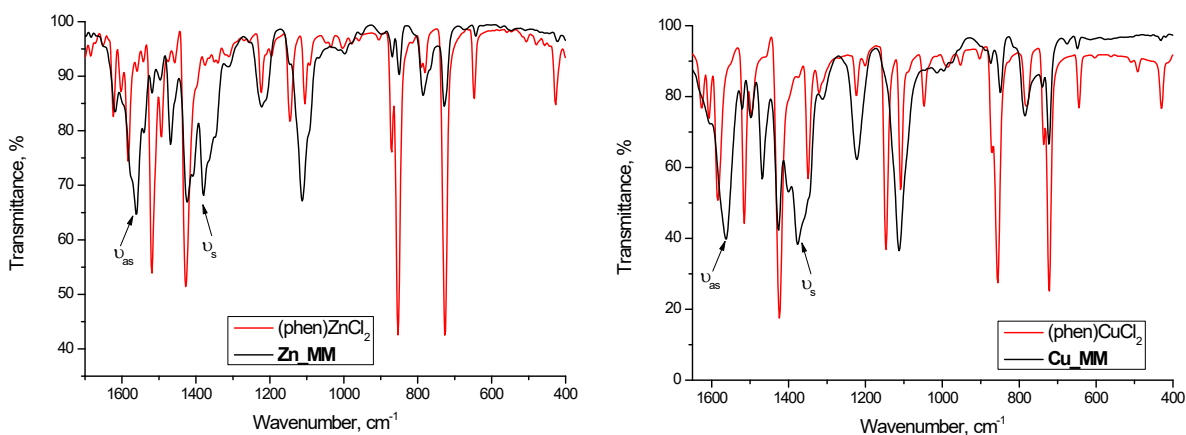
Figure S1. FT-IR spectra of complexes **Zn_MM** (left) and **Cu_MM** (right) plotted against their precursors (phen)MCl$_2$ spectra.
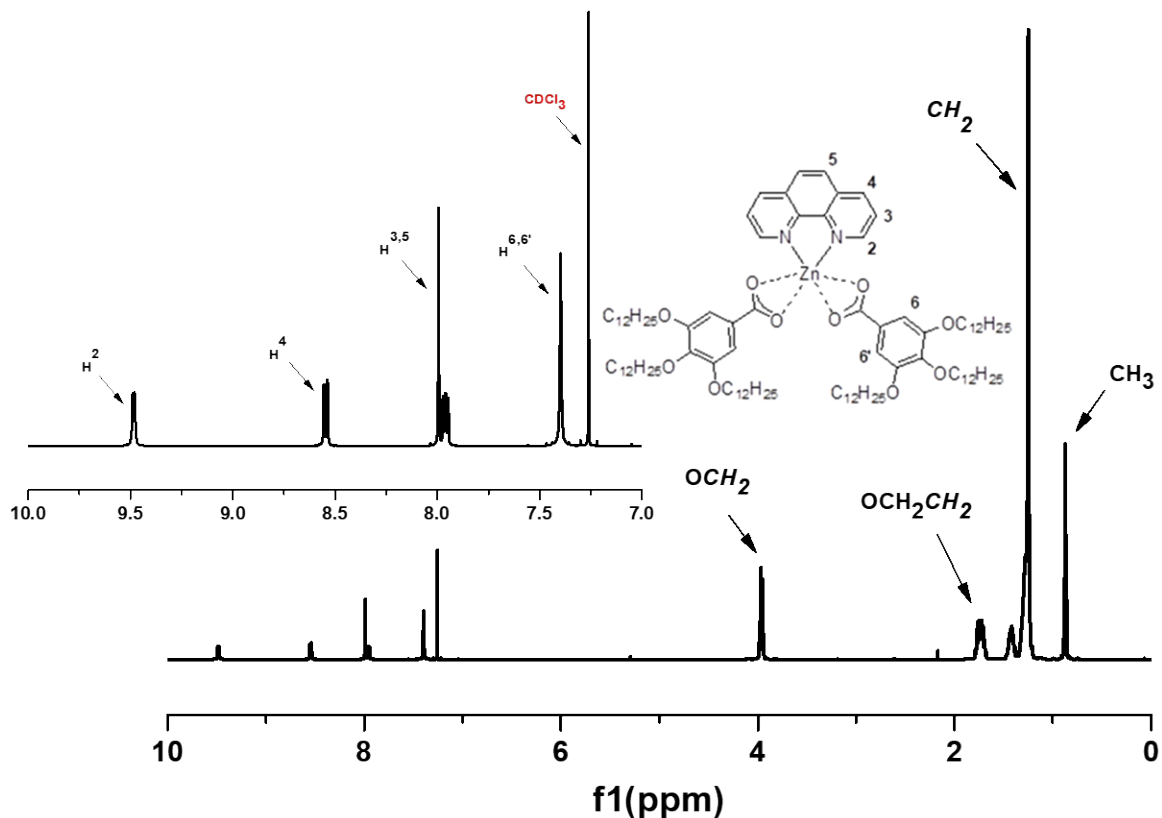
Preparation of the blends

Both complexes' blends were obtained by dissolving the proper quantities tabled bellow in 1 mL of CH_2Cl_2, followed by 20 minutes sonication (ultrasonic cleaning bath, 37 kHz, 80 W, 28°C) and evaporation at room temperature. The mixtures were then dried under vacuum.

Blend ratio (w/w)	Zn_MM	Cu_MM	Abbreviation
1:3	25 mg	75 mg	**ZnCu1:3_MM**
1:1	50 mg	50 mg	**ZnCu1:1_MM**
3:1	75 mg	25 mg	**ZnCu3:1_MM**
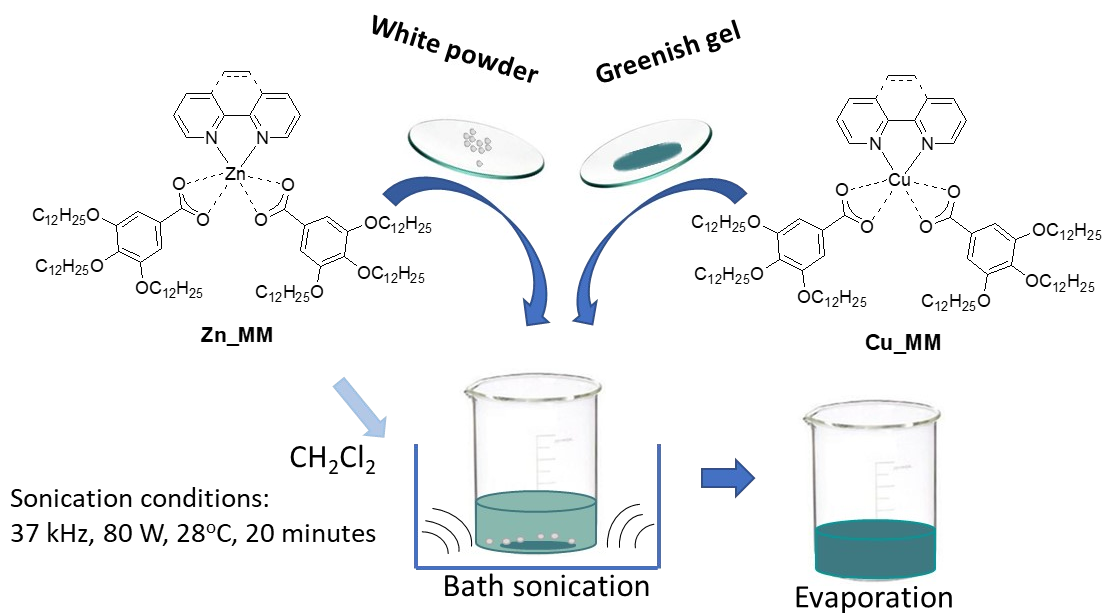
Scheme S1. Preparation of the blends.

Mesomorphic properties

The thermal stability and the mesomorphic properties of the complexes and various blends were performed by a combination of TGA analysis, polarized optical microscopy (POM), differential scanning calorimetry (DSC) and small- and wide-angle X-ray scattering studies (S/WAXS).

6

POM characterisation

Both complexes **Zn_MM** and **Cu_MM** show fan-shaped textures suggesting columnar phases (Figure S3). Beside change of color on cooling, no sign of crystallization can be observed. All blends, and in particular **ZnCu1:3_MM** and **ZnCu1:1_MM**, also present fan-shaped textures, while that of **ZnCu3:1_MM** is less birefringent (Figure S4).
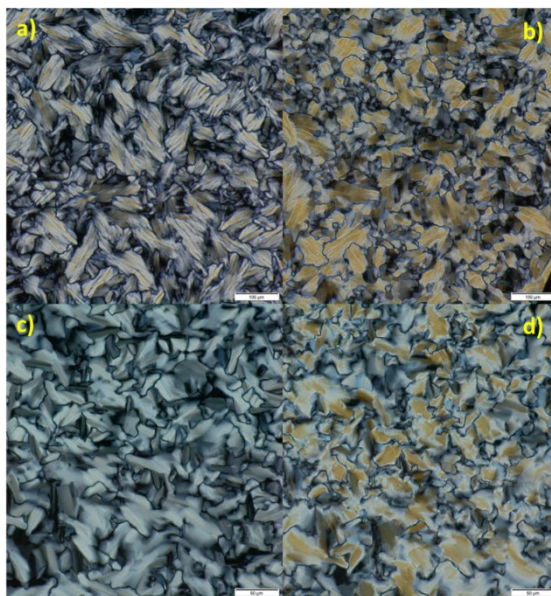
Figure S3. POM micrographs for a) **Zn_MM** on first cooling at 113°C, magnification x50; b) **Zn_MM** on first cooling at 25°C, magnification x50; c) **Cu_MM** on first cooling 100°C, magnification x20; b) **Cu_MM** on first cooling at 25°C, magnification x20.
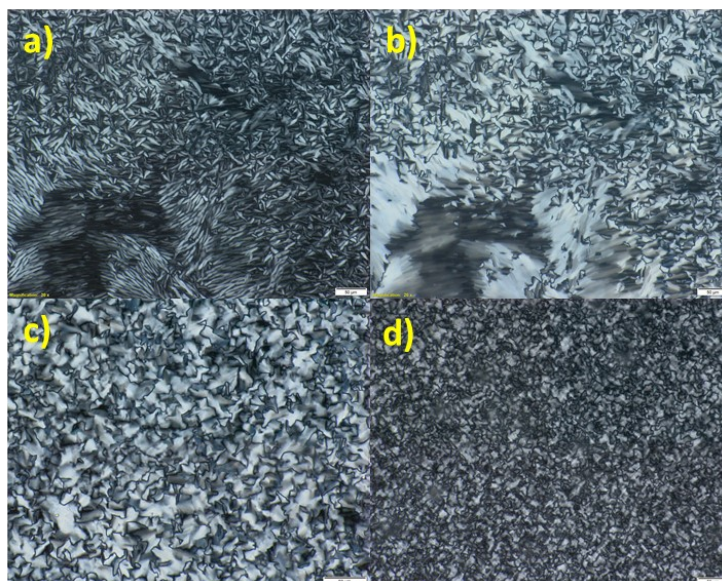
Figure S4. POM micrographs for a) **ZnCu1:3_MM** on second cooling at 88°C, magnification x20, in the binary phase: Col$_{hex}$+Iso; b) **ZnCu1:3_MM** on second cooling at 66°C, magnification x20: same position as a) in the Col$_{hex}$ phase; c) **ZnCu1:1_MM** on third cooling at 50°C, magnification x20; c) **ZnCu3:1_MM** on second cooling at 35°C, magnification x20.

TGA, DTG and DSC
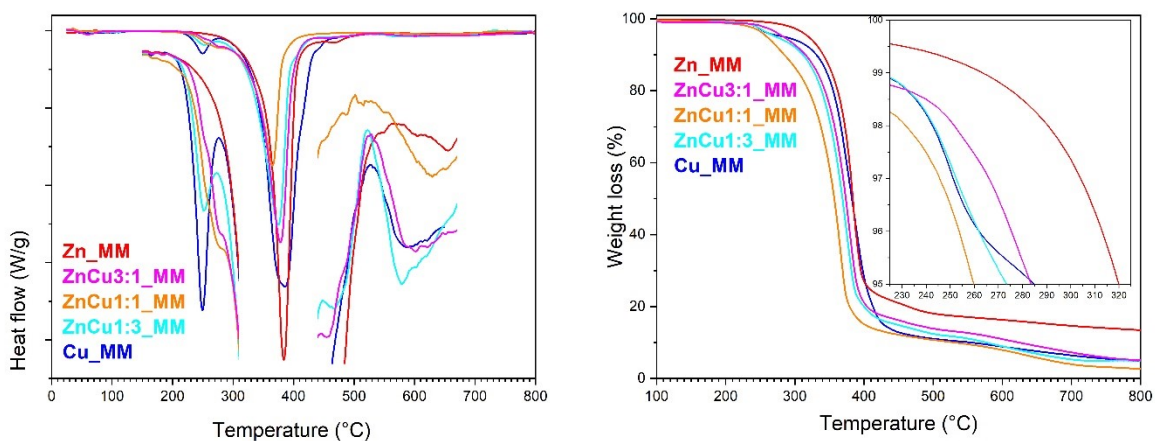
Figure S5. Superposition of DTG and TGA thermograms of metallomesogens **Zn_MM** and **Cu_MM** and corresponding blends **ZnCu1:3_MM**, **ZnCu1:1_MM**, **ZnCu3:1_MM**.

8
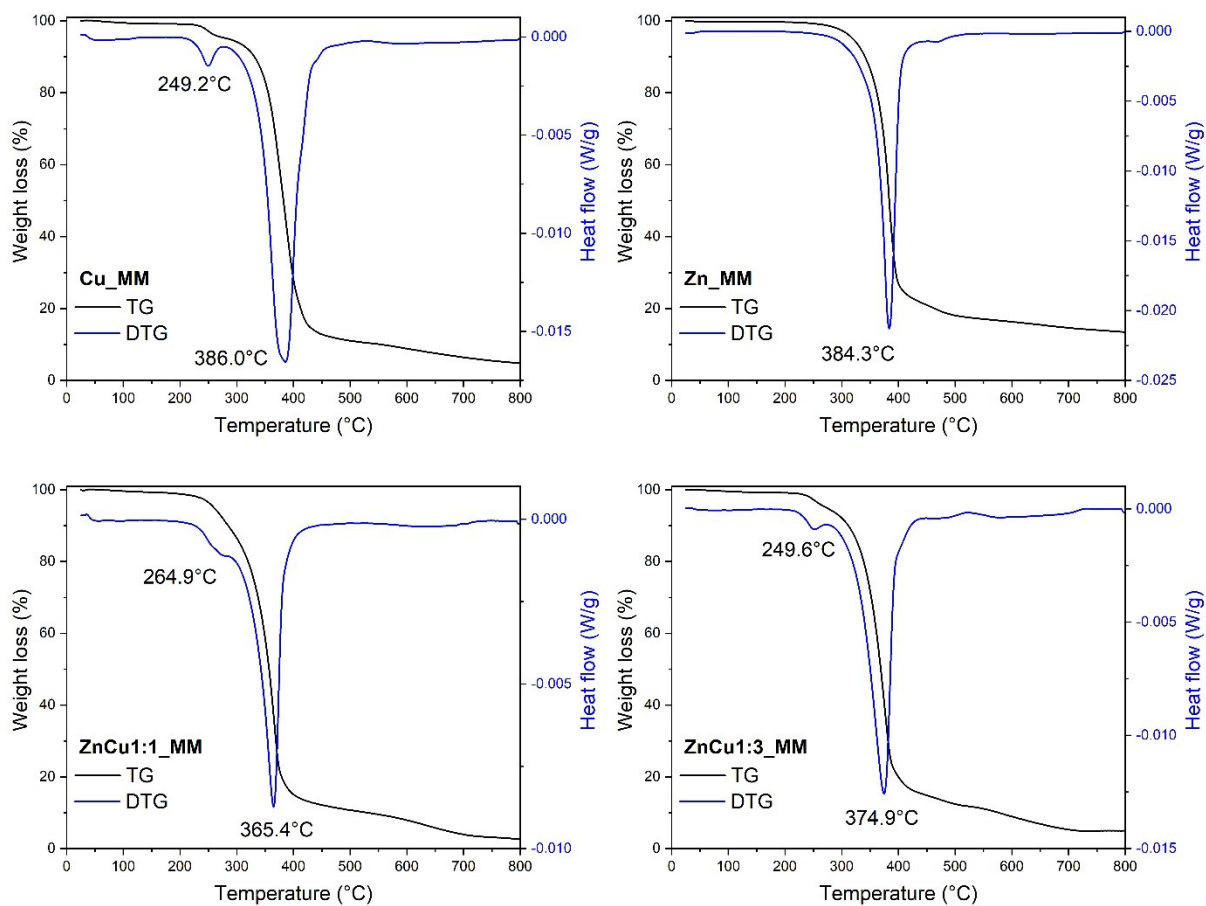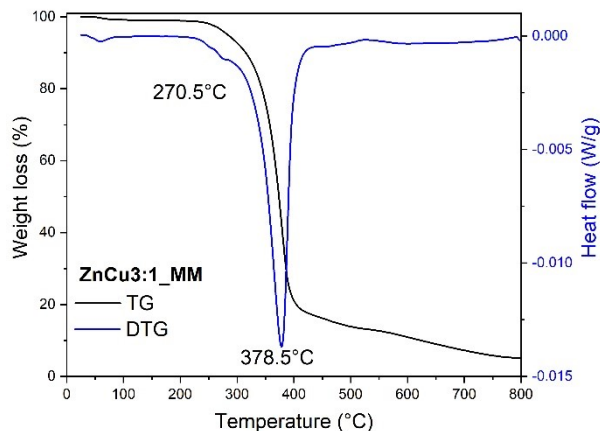
Figure S6. DTG and TGA thermograms of metallomesogens **Zn_MM** and **Cu_MM** and corresponding blends **ZnCu1:3_MM**, **ZnCu1:1_MM**, **ZnCu3:1_MM**.

Table S1: Decomposition temperatures,[a] mesophases,[b] transition temperatures (°C) and enthalpies (ΔH [J·g^{-1}])[c].

Material	$T_{dec5\%}$[a] [°C]	1st and 2nd heating	1st and 2nd cooling
Zn_MM	320	Cr 73.3 [101.8] Col$_{rec}$ 114.5 [7.0] Iso Col$_{rec}$ 114.4 [6.6] Iso	Iso 104.4 [-7.4] Col$_{rec}$ Iso 104.3 [-7.2] Col$_{rec}$
Cu_MM	285	Col$_{hex}$ 88.0 [3.8] Iso Col$_{hex}$ 86.6 [1.9] Iso	Iso 86.0 [-2.4] Col$_{hex}$ Iso 85.9 [-2.4] Col$_{hex}$
ZnCu1:3_MM	273	Col$_{hex}$ 80.8 [1.14] Col$_{hex}$+Iso 93.2 [1.54] Iso Col$_{hex}$ 80.4 [1.12] Col$_{hex}$+Iso 92.9 [1.74] Iso	Iso 89.0 [-1.99] Col$_{hex}$+Iso 70.9 [-1.14] Col$_{hex}$ Iso 88.5 [-1.92] Col$_{hex}$+I 69.9 [-1.07] Col$_{hex}$
ZnCu1:1_MM	260	Col$_{hex}$ 86.7 [1.97] Iso Col$_{hex}$ 86.6 [2.02] Iso	Iso 82.0 [-2.50] Col$_{hex}$ Iso 81.7 [-2.44] Col$_{hex}$
ZnCu3:1_MM	284	Col$_{hex}$ 81.8 [2.71] Iso Col$_{hex}$ 81.5 [2.81] Iso	Iso 75.7 [-2.46] Col$_{hex}$ Iso 75.2 [-2.29] Col$_{hex}$

[a] Decomposition temperature at 5% weight-loss (from TGA). [b] Cr: crystalline phase, Col$_{rec}$: columnar rectangular mesophase, Col$_{hex}$: columnar hexagonal mesophase. [c] DSC data on the first and second heating and cooling cycles; transition temperature is the given as the peak temperature.

9
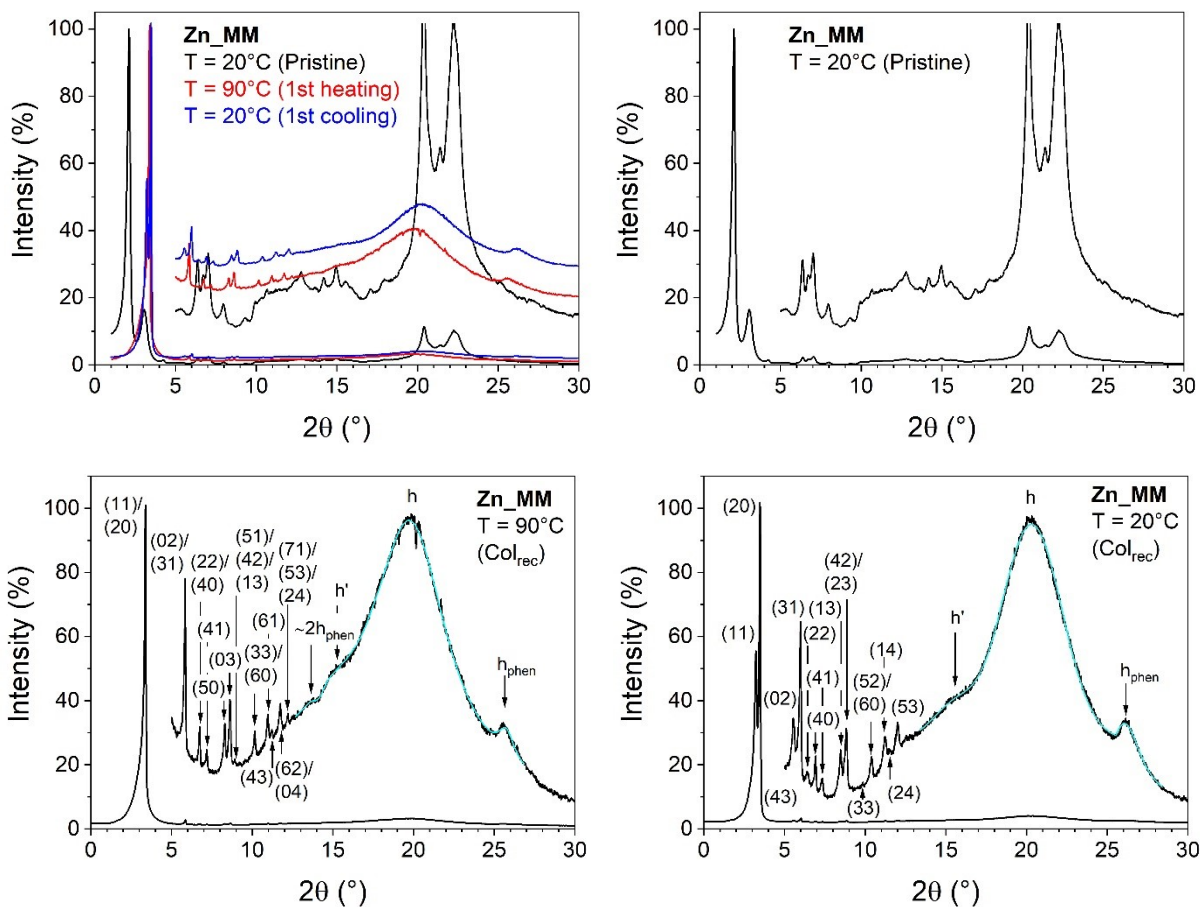
S/WAXS

Figure S7. S/WAXS patterns of **Zn_MM** at various temperatures.
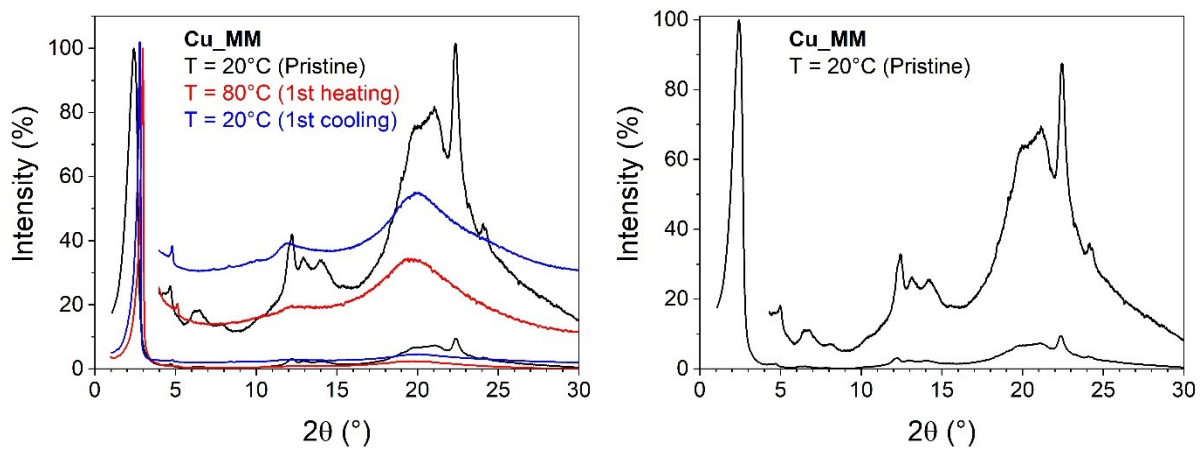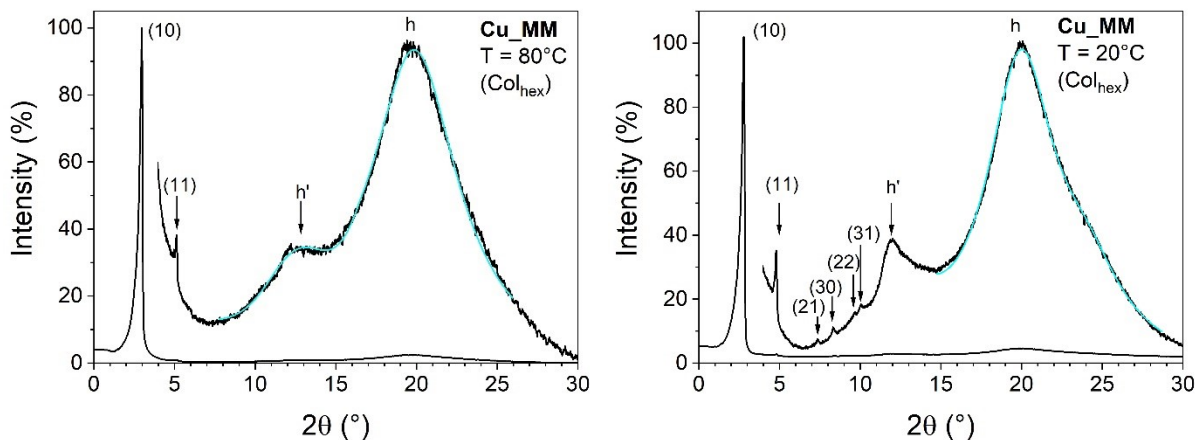
Figure S8. S/WAXS patterns of **Cu_MM** at various temperatures.
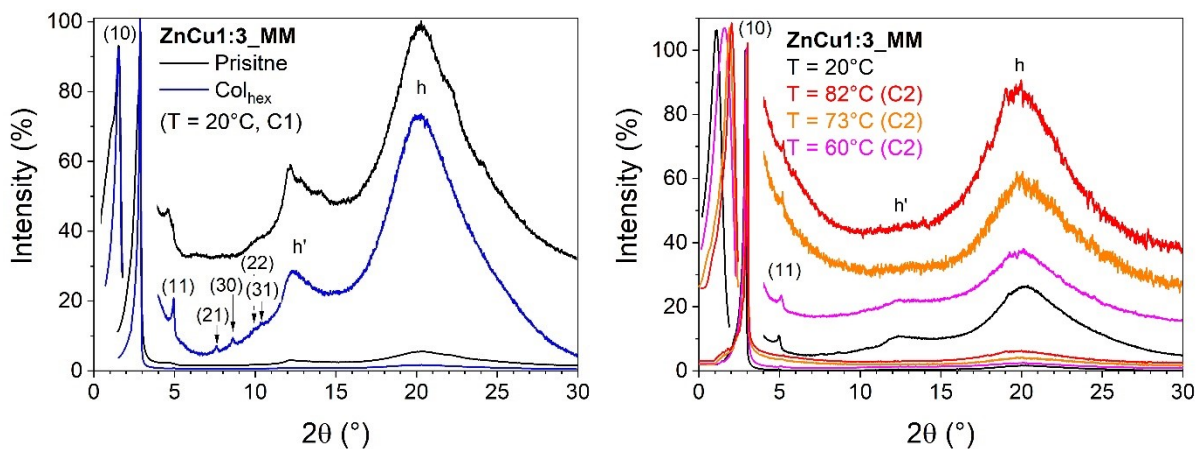
Figure S9. S/WAXS patterns of **ZnCu1:3_MM** at various temperatures. Left: heated to 70°C then cooled to 20°C, without crossing the isotropic temperature. Right: Second heating after thermal treatment.

Figure S10. S/WAXS patterns of **ZnCu1:1_MM** at various temperatures after thermal treatment.
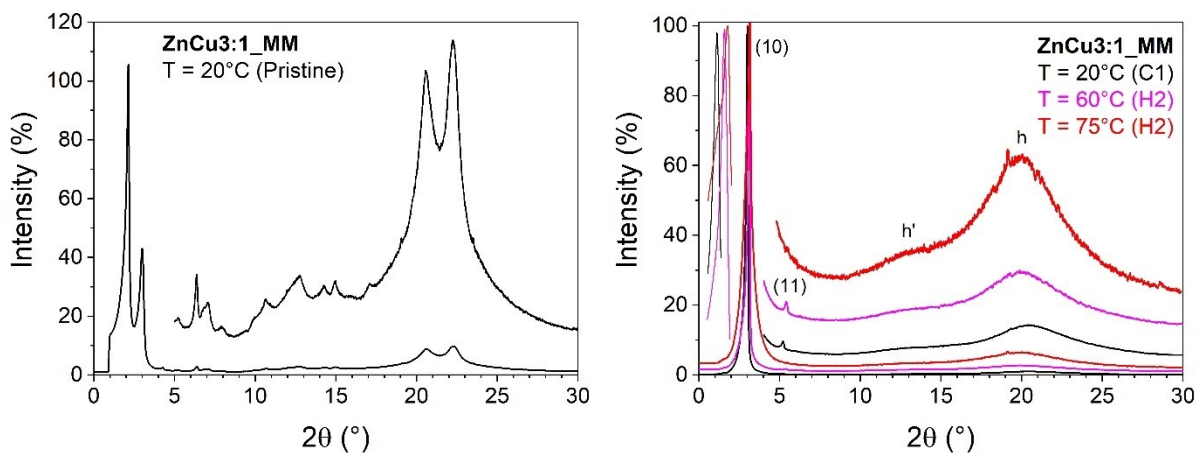
Figure S11. S/WAXS patterns of **ZnCu3:1_MM** at various temperatures and after thermal treatment.

Table S2. Indexation and mesophases' parameters

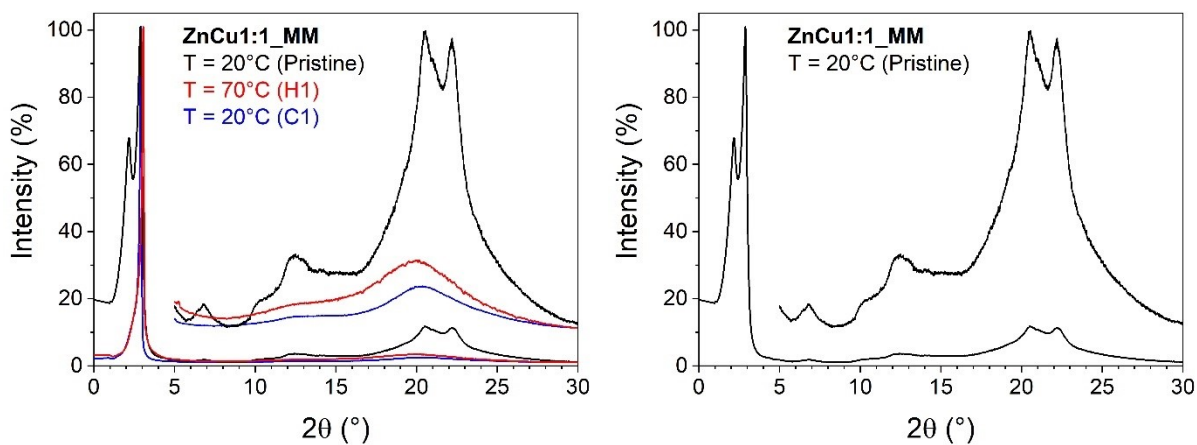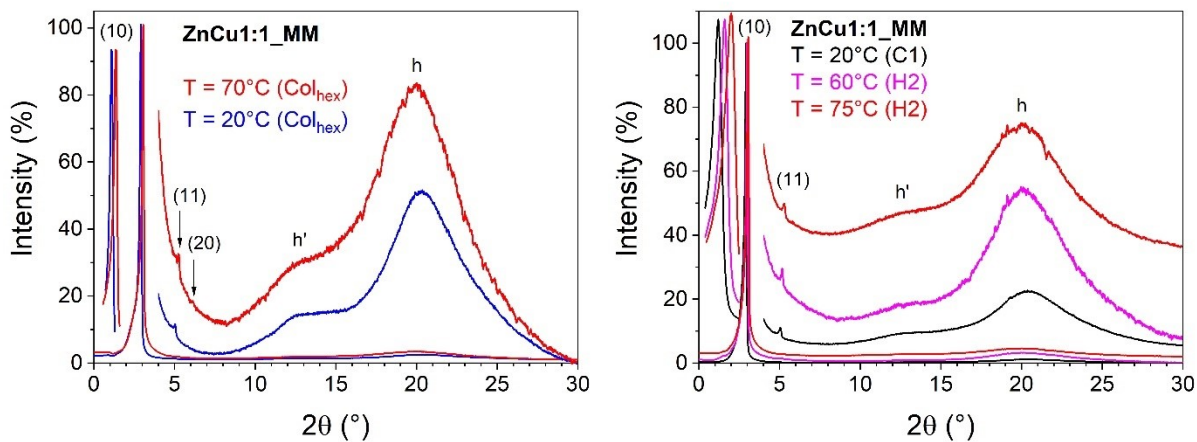| Complex/ blend	T	2θ	$d_{meas.}$	*hk*	I	$d_{calc.}$	Δ	Parameters
Zn_MM Col_{rec}-*p2gg*	90	3.395	26.00	11/20	VW (sh)	26.00	0.00	a = 52.00 Å
		5.882	15.01	31/02	VS (sh)	15.01	0.00	b = 32.02 Å
		6.793	13.01	40/22	W (sh)	13.00	0.01	A = 1665.04 Å
		7.235	12.21	41	VW (sh)	11.93	0.28	Z_{col} = 2
		8.351	10.58	50	VW (sh)	10.40	0.18	
		8.728	10.12	03	VW (sh)	10.01	0.11	V_{mol} = 2720 Å³
		8.992	9.82	51/42/13	VW (sh)	9.83	0.01	h_{mol} =3.27 Å
		10.196	8.67	60/33	VW (sh)	8.67	0.00	N_{mol} = 1
		10.970	8.05	61	VW (sh)	8.33	0.28	
		11.262	7.85	43	VW (sh)	7.93	0.08	
		11.779	7.51	04/62	VW (sh)	7.50	0.01	
		12.242	7.22	71/53/24	VW (sh)	7.21	0.01	
		13.61	6.50	-	W (br)	~$2h_{phen}$		
		15.35	5.77	-	W (br)	h'		
		19.84	4.47	-	VS (br)	h		
		26.32	3.38	-	W (br)	h_{phen}		
Zn_MM Col_{rec}-*p2gg*	20	3.247	27.19	11	VS (sh)	27.19	0.00	a = 50.24 Å
		3.506	25.12	20	VS (sh)	25.12	0.00	b = 32.33 Å
		5.472	16.14	02	W (sh)	16.16	0.02	A = 1624.26 Å
		6.008	14.70	31	VW (sh)	14.87	0.17	Z_{col} = 2
		6.437	13.72	22	VW (sh)	13.59	0.13	
		6.950	12.71	40	VW (sh)	12.56	0.15	V_{mol} = 2600 Å³
		7.372	11.98	41	VW (sh)	11.77	0.21	h_{mol} =3.20 Å
		8.456	10.44	13	VW (sh)	10.54	0.10	N_{mol} = 1
		8.934	9.88	42/23	VW (sh)	9.92/9.90	0.04/0.02	
		9.861	8.96	33	VW (sh)	9.06	0.10	
		10.432	8.47	60/52	VW (sh)	8.37/8.53	0.10/0.08	
		11.285	7.83	14	VW (sh)	7.98	0.15	
		11.568	7.64	24	VW (sh)	7.70	0.06	
		12.046	7.34	53	VW (sh)	7.35	0.01	
		15.56	5.69	-	W (br)	h'		
		20.33	4.36	-	VS (br)	h		
		26.09	3.41	-	W (br)	h_{phen}		
ZnCu3:1_MM	20	2.993	29.43	10	VS (sh)	29.40	0.03	a = 33.95 Å
		5.206	16.96	11	VW (sh)	16.97	0.01	A = 998.08 Å
		12.84	6.89	-	S (br)	h'		Z_{col} = 1
		20.48	4.33	-	VS (br)	h		
								V_{mol} = 2591 Å³
								h_{mol} = 3.90 Å
								N_{mol} = 1.5
ZnCu3:1_MM	60 *	3.136	28.15	10	VS (sh)	28.13	0.02	a = 32.48 Å
		5.440	16.23	11	VW (sh)	16.24	0.01	A = 913.75 Å
		12.67	6.98	-	S (br)	-		Z_{col} = 1
		19.98	4.44	-	VS (br)	-		
								V_{mol} = 2656 Å³
								h_{mol} = 4.36 Å
								N_{mol} = 1.5
ZnCu3:1_MM	75	3.200	27.57	10	VS (sh)	27.57	-	a = 31.83 Å

*		12.94	6.83	-	S (br)	-		A = 877.69 Å
		19.83	4.47	-	VS (br)	-		Z_{col} = 1
								V_{mol} = 2683 Å³
								h_{mol} = 4.58 Å
								N_{mol} = 1.5
ZnCu1:1_MM	70	3.044	29.00	10	VS (sh)	28.98	0.02	a = 33.46 Å
		5.275	16.74	11	W (sh)	16.73	0.01	A = 969.76 Å
Col_{hex}-*p6mm*		6.100	14.48	20	VW (sh)	14.49	0.01	Z_{col} = 1
		12.57	7.03	-	S (br)	h'		
		19.90	4.46	-	VS (br)	h		V_{mol} = 2665 Å³
								h_{mol} = 4.12 Å
								N_{mol} = 1.5
ZnCu1:1_MM	20	2.916	30.28	10	VS (sh)	30.28	0.00	a = 34.96 Å
		5.052	17.48	11	W (sh)	17.48	0.00	A = 1058.72 Å
Col_{hex}-*p6mm*		12.47	7.09	-	S (br)	h'		Z_{col} = 1
		20.39	4.35	-	VS (br)	h		
								V_{mol} = 2582 Å³
								h_{mol} = 3.66 Å
								N_{mol} = 1.5
ZnCu1:1_MM	20 *	2.946	29.96	10	VS (sh)	29.96	0.00	a = 34.59Å
		5.103	17.30	11	W (sh)	17.30	0.00	A = 1036.46 Å
		12.48	7.09	-	S (br)	h'		Z_{col} = 1
		20.35	4.36	-	VS (br)	h		
								V_{mol} = 2582 Å³
								h_{mol} = 3.74 Å
								N_{mol} = 1.5
ZnCu1:1_MM	60 *	2.987	29.55	10	VS (sh)	29.53	0.02	a = 34.10 Å
		5.179	17.04	11	W (sh)	17.05	0.01	A = 1007.04 Å
		12.62	7.01	-	S (br)	h'		Z_{col} = 1
		20.16	4.40	-	VS (br)	h		
								V_{mol} = 2647 Å³
								h_{mol} = 3.94 Å
								N_{mol} = 1.5
ZnCu1:1_MM	75 *	3.071	28.74	10	VS (sh)	28.74	0.00	a = 33.19 Å
		5.321	16.59	11	W (sh)	16.59	0.00	A = 953.77 Å
		12.40	7.13	-	S (br)	h'		Z_{col} = 1
		20.11	4.41	-	VS (br)	h		
								V_{mol} = 2674 Å³
								h_{mol} = 4.20Å
								N_{mol} = 1.5
ZnCu1:3_MM	20	2.883	30.61	10	VS (sh)	30.61	0.00	a = 35.34 Å
		4.997	17.67	11	W (sh)	17.67	0.00	A = 1081.92 Å
Col_{hex}-*p6mm*		7.631	11.57	21	VW (sh)	11.57	0.00	Z_{col} = 1
		8.648	10.22	30	VW (sh)	10.20	0.02	
		10.02	8.82	22	VW (sh)	8.84	0.02	V_{mol} = 2573 Å³
		10.40	8.50	31	VW (sh)	8.49	0.01	h_{mol} = 3.57 Å
		12.30	7.19	-	S (br)	h'		N_{mol} = 1.5
		20.09	4.41	-	VS (br)	h		
ZnCu1:3_MM	20	2.887	30.58	10	VS (sh)	30.57	0.01	a = 35.30 Å

Phase	T	2θ	$d_{meas.}$	hk		$d_{calc.}$	Δ	
Col$_{hex}$-*p6mm*	*	5.004 12.48 20.19	17.64 7.09 4.39	11 - -	W (sh) S (br) VS (br)	17.65 h' h	0.01	A = 1079.12 Å Z$_{col}$ = 1 V$_{mol}$ = 2573 Å^3 h$_{mol}$ = 3.58 Å N$_{mol}$ = 1.5
ZnCu1:3_MM Col$_{hex}$-*p6mm*	60 *	2.963 5.132 12.39 19.90	29.81 17.20 7.14 4.46	10 11 - -	VS (sh) W (sh) S (br) VS (br)	29.80 17.20 h' h	0.01 0.00	a = 34.41 Å A = 1025.42 Å Z$_{col}$ = 1 V$_{mol}$ = 2638 Å^3 h$_{mol}$ = 3.86 Å N$_{mol}$ = 1.5
ZnCu1:3_MM Col$_{hex}$-*p6mm*	73 *	3.005 5.215 20.00	29.37 16.93 4.44	10 11 -	VS (sh) W (sh) VS (br)	29.35 16.94 h	0.02 0.01	a = 33.89 Å A = 994.47 Å Z$_{col}$ = 1 V$_{mol}$ = 2661 Å^3 h$_{mol}$ = 4.01 Å N$_{mol}$ = 1.5
ZnCu1:3_MM Col$_{hex}$-*p6mm*	82 *	3.044 5.278 19.90	29.00 16.73 4.46	10 11 -	VS (sh) W (sh) VS (br)	28.99 16.74 h	0.01 0.01	a = 33.47 Å A = 970.34 Å Z$_{col}$ = 1 V$_{mol}$ = 2678 Å^3 h$_{mol}$ = 4.14 Å N$_{mol}$ = 1.5
Cu_MM Col$_{hex}$-*p6mm*	80	2.974 5.152 12.70 19.88	29.68 17.14 6.96 4.46	10 11 - -	VS (sh) W (sh) M (br) VS (br)	29.68 17.14 h' h	0.00 0.00 - -	a = 34.27 Å A = 1017.18 Å Z$_{col}$ = 1 V$_{mol}$ = 2682 Å^3 h$_{mol}$ =3.95 Å N$_{mol}$ = 1.5
Cu_MM Col$_{hex}$-*p6mm*	20	2.781 4.817 7.377 8.338 9.674 10.034 11.97 19.99	31.74 18.33 11.97 10.59 9.13 8.81 7.39 4.44	10 11 21 30 22 31 - -	VS (sh) M (sh) W (sh) W (sh) W (sh) W (sh) M (br) VS (br)	31.72 18.31 11.99 10.57 9.16 8.80 h' h	0.02 0.02 0.02 0.02 0.03 0.01 - -	a = 36.63 Å A = 1161.81 Å Z$_{col}$ = 1 V$_{mol}$ = 2581 Å^3 h$_{mol}$ =3.33 Å N$_{mol}$ = 1.5

Annotation. T: temperature of the experiment; 2θ: measured diffraction angles; $d_{meas.}$ and $d_{calc.}$: measured and calculated distances; VS, S, M, W, VW stand for very strong, strong, medium, weak, very weak; sh and br stand for sharp and broad; *hk*: Miller indices of columnar lattice reflection; h: average distance between alkyl chains and gallate fragments, h = h_{ch}+h_{gal} (+h_{phen}); h' ≈ $2h_{phen.}$; h_{phen}: average stacking distance between the phen frgaments; a: columnar lattice parameters; Δ = |$d_{meas.}$ − $d_{calc.}$|; a,b: lattice parameters; S: columnar cross-section (A = S = $a^2/\sqrt{3}$ for Col$_{hex}$, and A = 2S = a×b for Col$_{rec}$); Zc$_{ol}$: number of columns per lattice; V_{mol}: molecular volume; h_{mol}: columnar slice thickness; N_{mol}: number of molecules per slice of column h_{mol}-thick: h_{mol}×A/Z_{col} = N_{mol}×V_{mol}. * After thermal treatment (i.e. heating above the isotropic temperature and cooled down).
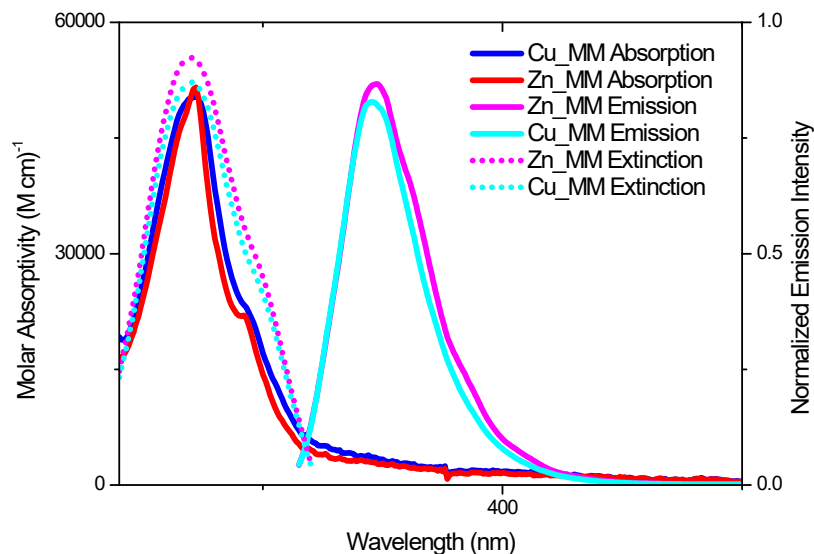
Optical properties

Figure S12. Absorption, Emission (λ_{ex} = 292 nm) and Excitation (λ_{em} = 345 nm) spectra of **Cu_MM** and **Zn_MM** in CH_2Cl_2 dilute solutions (2.7 10^{-6} M).

Table S3. Main photophysical data of complexes in CH_2Cl_2 dilute solution.

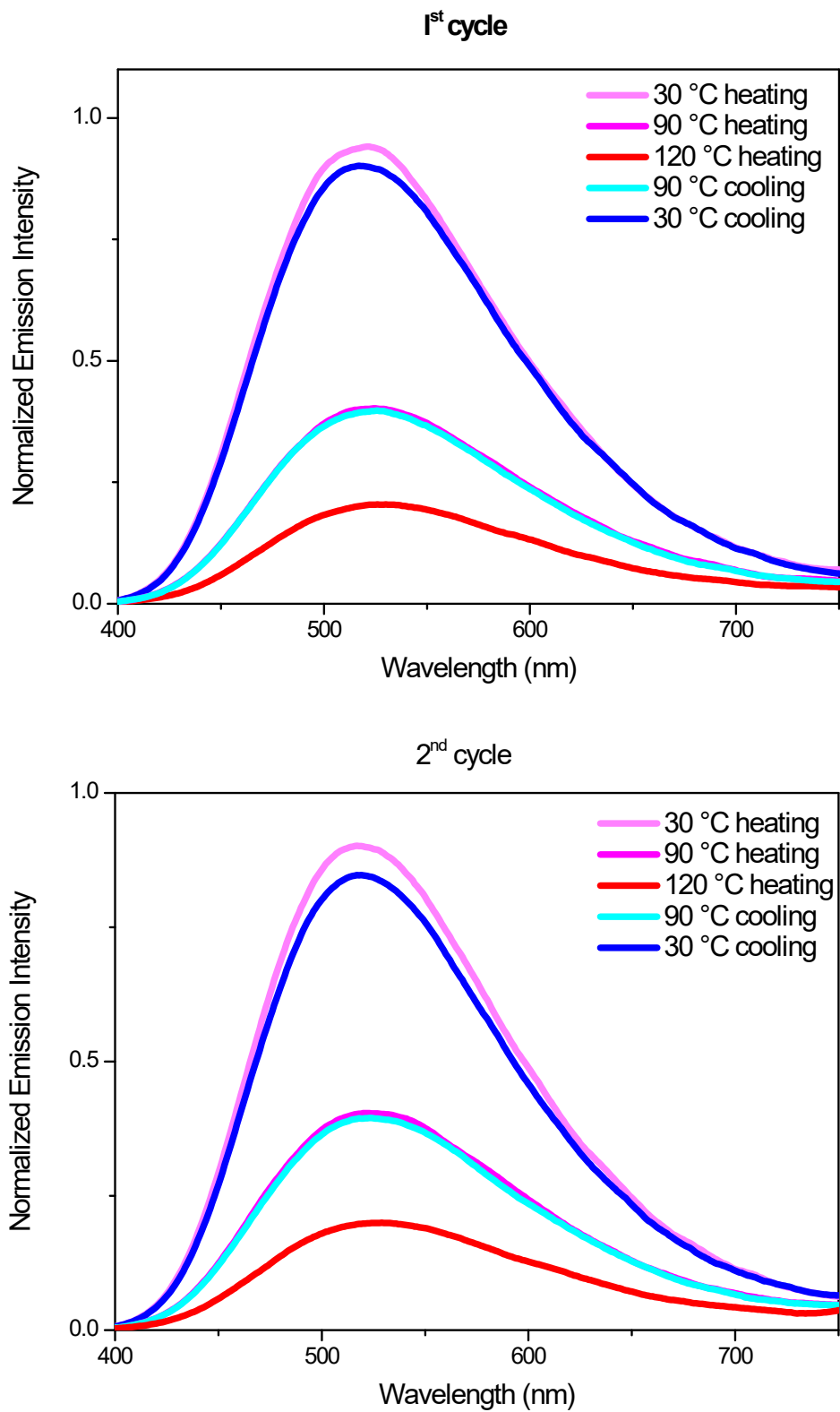| Sample	Absorption, λ_{max}/nm (ϵ/M^{-1} cm^{-1})	Emission, λ_{max}/nm [λ_{ex}/nm]	Lifetime, τ/ns	Quantum yields, ϕ /% [Concentration, mol/L]
Cu_MM	266(46700), 272(50400), 292(23400)	345 [293]	2.6	7.5 [2.7 10^{-6} M]
				5.6 [5.4 10^{-6} M]
				4.4 [8.1 10^{-6} M]
Zn_MM	266(46700), 272(51600), 292(22000)	345 [293]	2.6	7.9 [2.7 10^{-6} M]
				4.5 [5.4 10^{-6} M]
				3.3 [8.1 10^{-6} M]

Figure S13. Emission spectra of **Zn_MM** varying temperature during the 1st (top) and the 2nd (bottom) heating/cooling cycles.
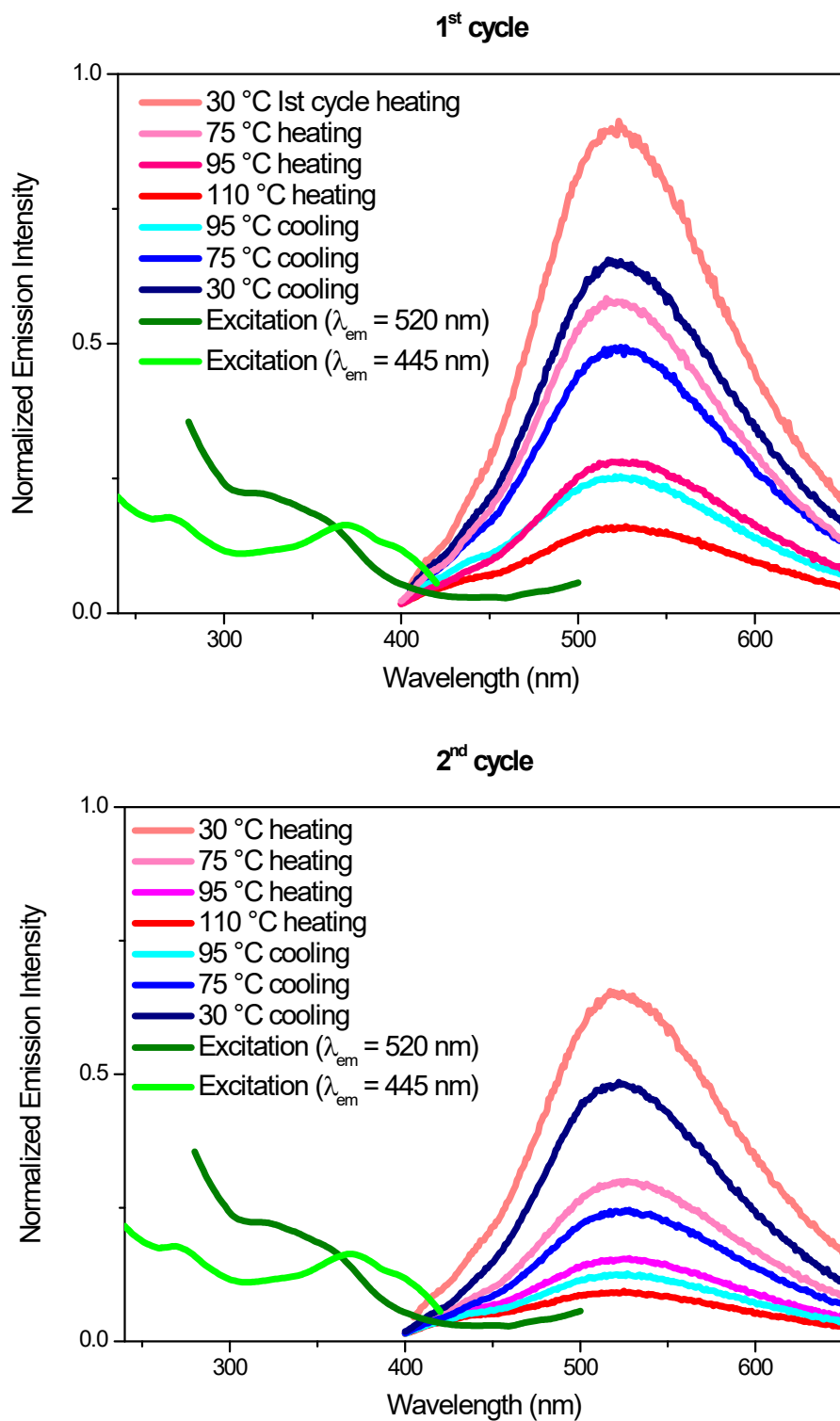
Figure S14. Emission spectra of **ZnCu3:1_MM** varying temperature during the 1st (top) and the 2nd (bottom) heating/cooling cycles.

Table S4. Photophysical data of **Zn_MM** by varying temperature.

T (°C)	Emission, λ_{max}/nm[a]	Quantum yield, ϕ /%
Ist cycle		
30	520	**3.8**
90	520	**1.7**
120	530	**0.9**
90	520	**1.7**
30	520	**3.7**
IInd cycle		
90	520	**1.7**
120	530	**0.9**
90	520	**1.7**
30	520	**3.5**

[a]λ_{ex} = 345 nm

Table S5. Photophysical data of sample **ZnCu3:1_MM** by varying temperature.

T (°C)	Emission, λ_{max}/nm[a]	Integral of emission spectra[b]
Ist cycle		
30	445, 523	**1**
75	445, 524	**0.58**
95	445, 524	**0.32**
110	445, 526	**0.15**
95	445, 527	**0.19**
75	445, 525	**0.31**
30	445, 522	**0.61**
IInd cycle		
75	445, 527	**0.33**
95	445, 528	**0.18**
110	445, 525	**0.11**
95	445, 527	**0.15**
75	445, 528	**0.27**
30	445, 522	**0.50**

[a]λ_{ex} = 345 nm; [b]Because an instrumental issue hindered the registration of the emission quantum yield of **ZnCu3:1_MM** at room temperature, its variation was expressed respect to a reference value, assumed equal to 1

References

[1] a) E. I. Szerb, D. Pucci, A. Crispini, M. La Deda, *Mol. Cryst. Liq. Cryst.* **2013**, *573*, 34-45; b) A. E. Ozel, S. Kecel, S. Akyuz, *J. Mol. Struct.* **2007**, *834–836*, 548–554.

[2] G. A. Crosby, and J. N. Demas, *Review J. Phys. Chem.* **1971**, 75, 991–1024.

[3] R. Rusakowicz, and A. C. Testa, *The Journal of Physical Chemistry*, **1951**, 41, 2680-81.

[4] J. C. de Mello, H. F. Wittmann, and R. H. Friend, *Advanced Materials*, **1997**, 9, 230–2.