Electronic Supporting Information

Can Highly Flexible Copper(I) Cluster-containing 1D and 2D Coordination Polymers Exhibit MOF-like Properties?

Antoine Bonnot, Frank Juvenal, Antony Lapprand, Michael Knorr,* Daniel Fortin and Pierre D. Harvey*

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X-ray analyses

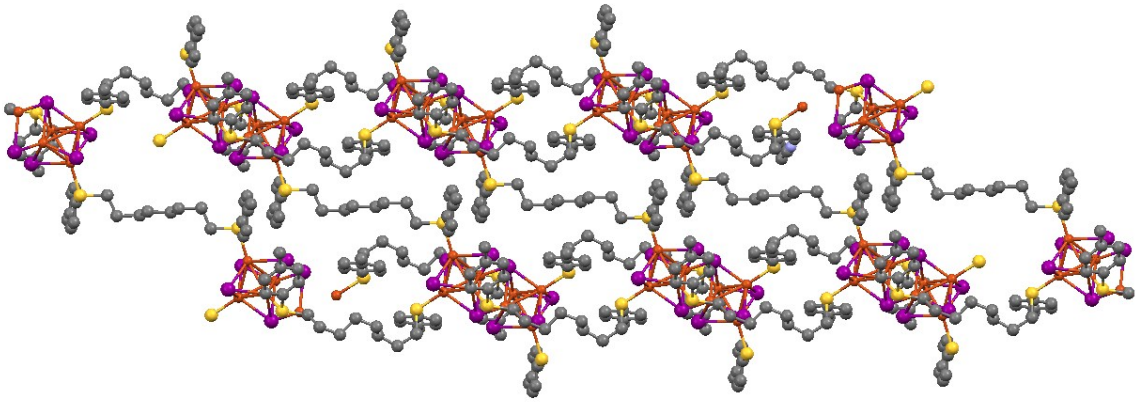

Figure S1. View of a fragment along the b axis of the 2D network of **1•EtCN** (for clarity, H atoms are omitted).

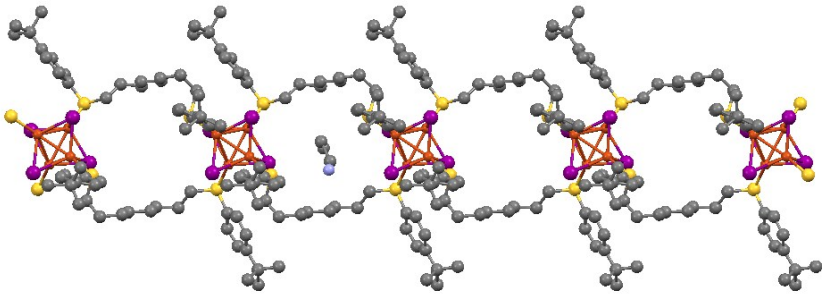

Figure S2. View of a segment of chain along the c axis of the 1D polymer $[Cu_4I_4\{\mu$-*t*BuPhS$(CH_2)_8$-*t*BuPh$\}_2]_n$, **1•EtCN** (for clarity, H atoms are omitted).

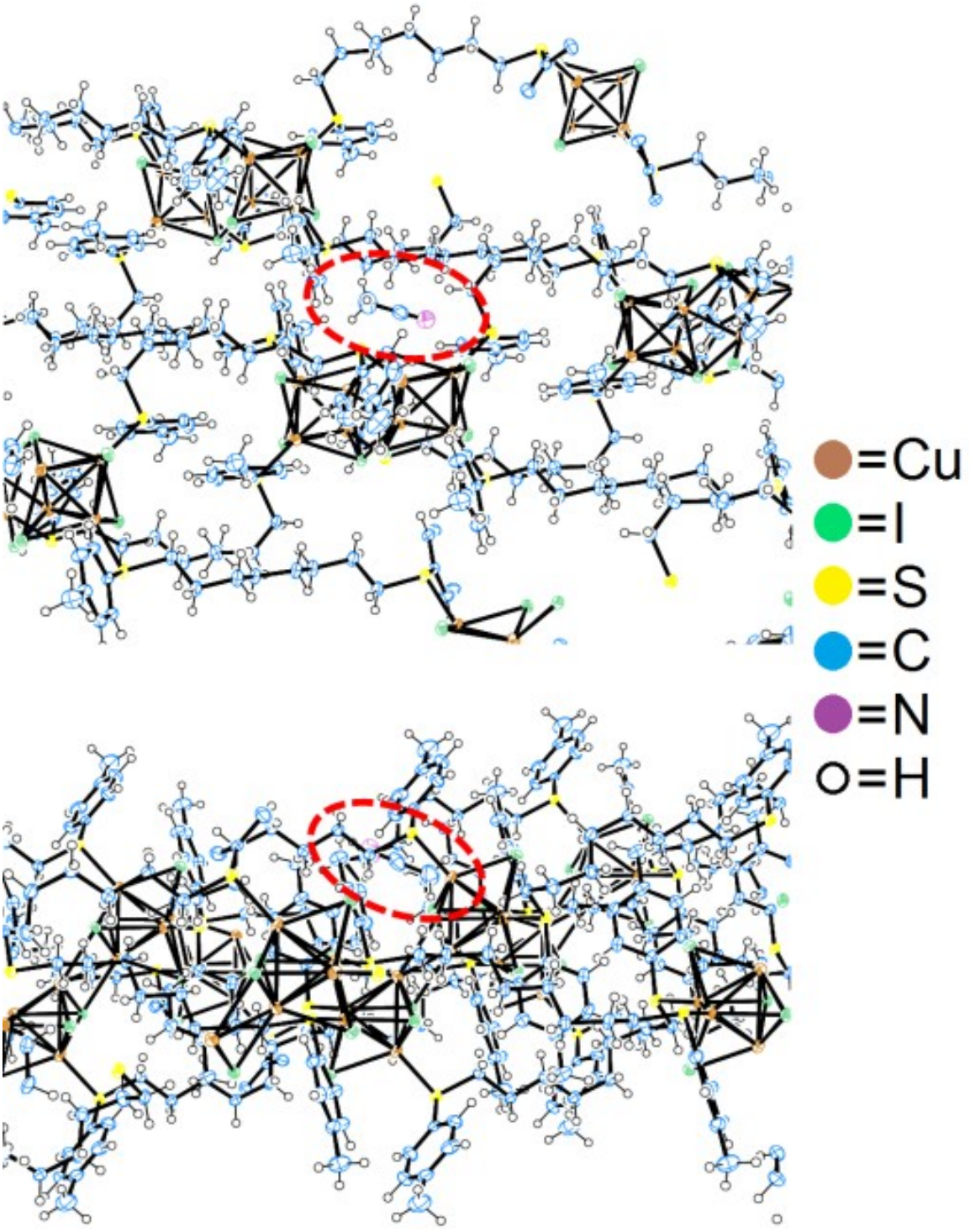

Figure S3. Top (up) and side (bottom) views of the X-ray structure of **1•MeCN**. The ellipsoids are shown at 50 % probability. The MeCN is circled in red.

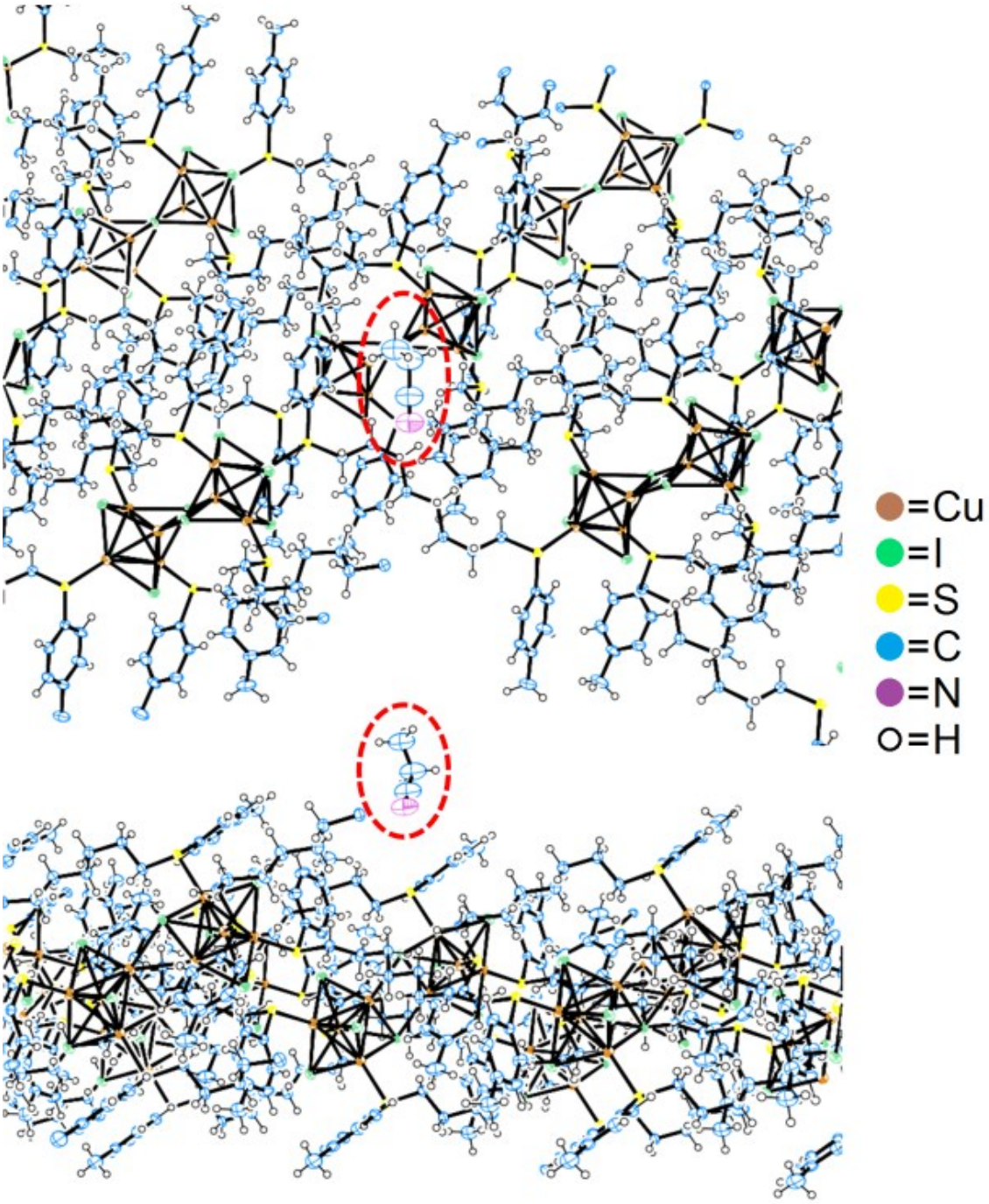

Figure S4. Top (up) and side (bottom) views of the X-ray structure of **1•EtCN**. The ellipsoids are shown at 50 % probability. The EtCN is circled in red. The octanuclear Cu_8I_8 cluster core of 2 exhibits the following Cu···Cu distances within the Cu_4I_4 cluster at 173 K: Cu1-I1 2.6217(5), Cu1-I2 2.6856(5), Cu1-I4 2.6936(6), Cu1- Cu3 2.7337(6), Cu1-Cu4 2.7193 (6), I1-I2 4.4660(5), Cu2-Cu3 2.7036(6), Cu2-Cu4 2.7218(7), Cu2-I2 2.7286(5), Cu2-I3 2.6351(5), Cu2-I4 2.6416(5), Cu3-Cu4 2.7449(7), Cu3-I1 2.6993(5), Cu3-I3 2.6884(5), Cu3-I4 2.7119(5), Cu4-I1 2.6848(5), Cu4-I2 2.7311(5), Cu4-I3 2.6863(5), Cu4-I4 4.3803(7), I2-I4 4.3538(5).

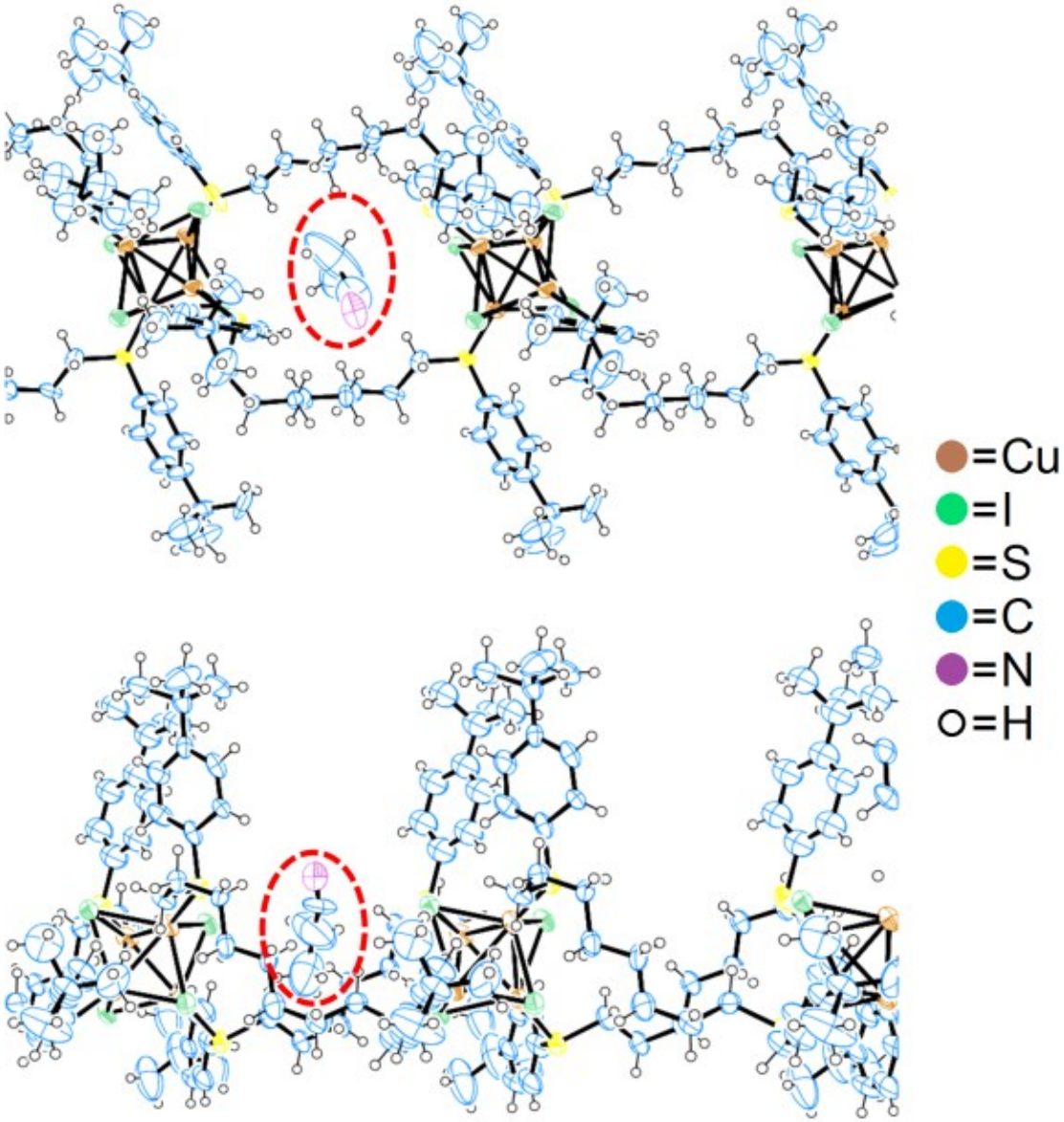

Figure S5. Top (up) and side (bottom) views of the X-ray structure of **2•EtCN**. The ellipsoids are shown at 50 % probability. The EtCN is circled in red. the tetranuclear Cu_4I_4 cluster core of **2•EtCN** exhibits the following distances at 173 K: Cu1-Cu2 2.772(4), Cu1-Cu3 2.714(4), Cu1-Cu4 2.776(4), Cu1-I1 2.727(3), Cu1-I2 2.634(3), Cu1-I4 2.705(3), Cu2-Cu4 2.685(4), Cu2-I1 2.671(3), Cu2-I2 2.758(3), Cu2-I3 2.615(3), Cu3-Cu4 2.688(3), Cu3-I2 2.677(3), Cu3-I3 2.688 (3), Cu3-I4 2.664(3), Cu4-I1 2.641(3), Cu4-I3 2.742(3), Cu4-I4 2.677(3).

IR spectra, P-XRD and Thermal stability

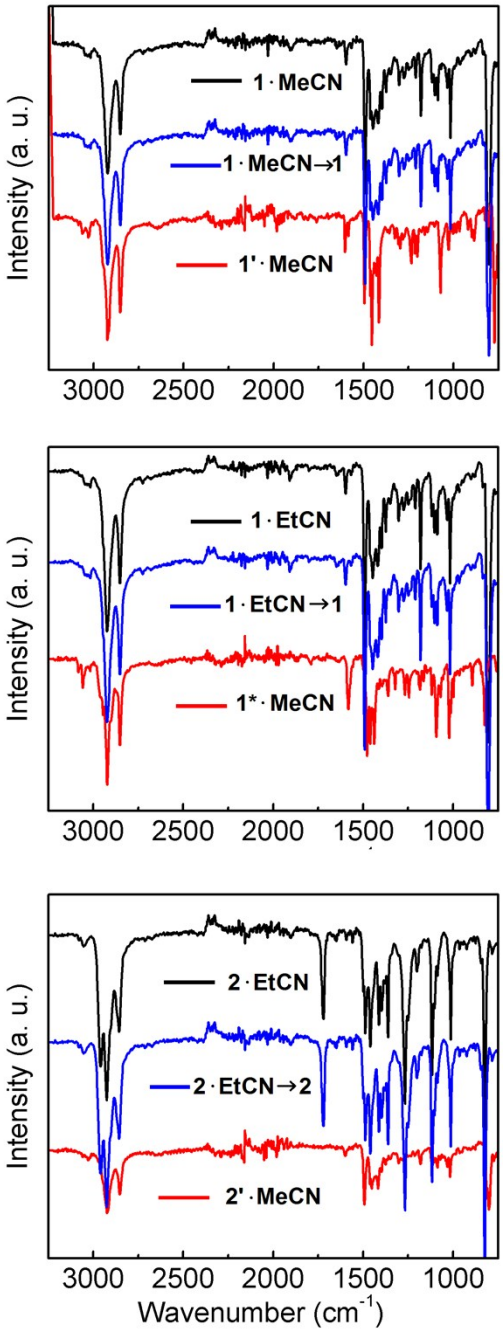

Figure S6. IR spectra before (**1•MeCN**, **1•EtCN**, **2•EtCN**; black lines) and after (**1** and **2**; blue lines) the removal of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**, red lines). No water molecules was observed.

Table S1. IR data before (**1•MeCN**, **1•EtCN**, **2•EtCN**) and after (**1** and **2**) the removal of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**)

IR (cm^{-1})	**1• MeCN**	**1**	**1'• MeCN**	**1• EtCN**	**1**	**1*• MeCN**	**2• EtCN**	**2**	**2'• MeCN**
$\nu(CH_{aro})$	3013	3113	3022	3059	3112	3088	3037	3038	3031
$\nu(CH_{ali})$	-	-	-	2964	-	2961	2952	2954	2949
$\nu(CH_{ali})$	2922	2922	2922	2921	2924	2924	2916	2926	2926
$\nu(CH_{ali})$	2852	2853	2849	2854	2854	2853	2848	2853	2851

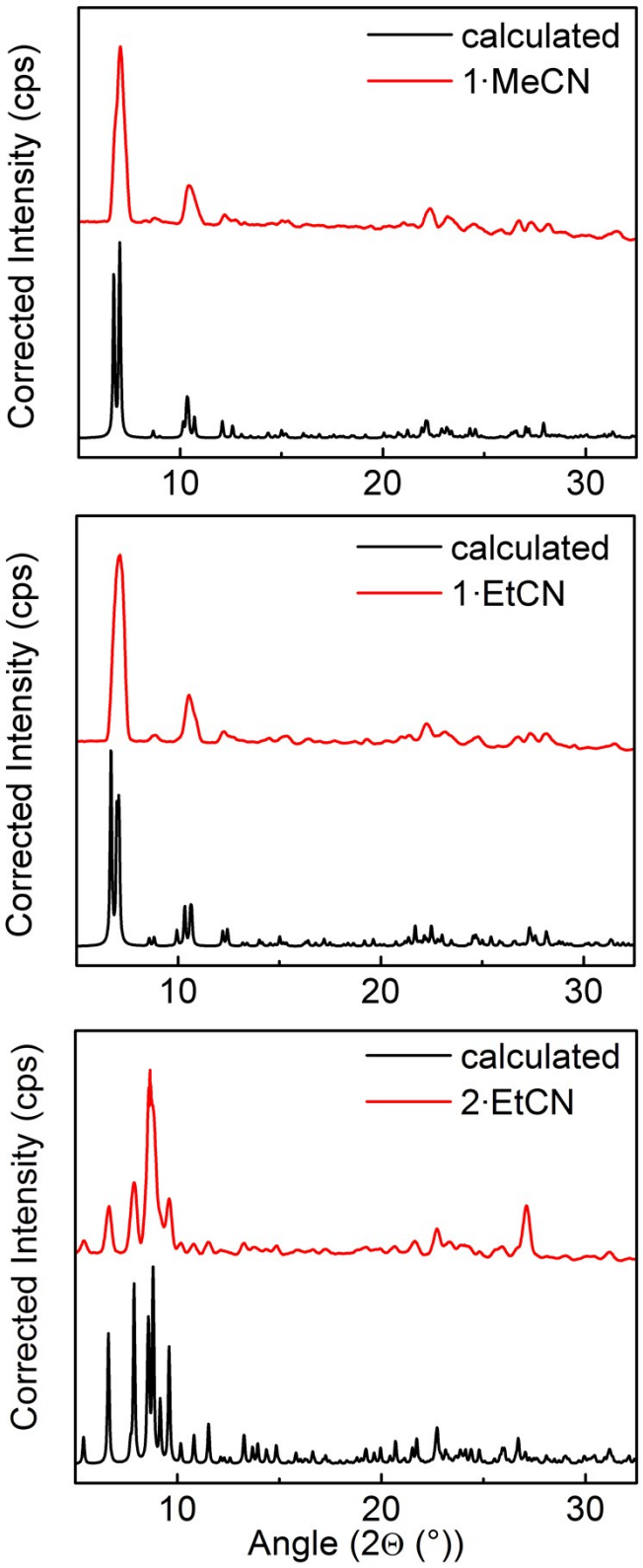

Figure S7. XRD patterns measured (red lines) and calculated (black lines) of **1•MeCN** (top), **1•EtCN** (center) and **2•EtCN** (bottom).

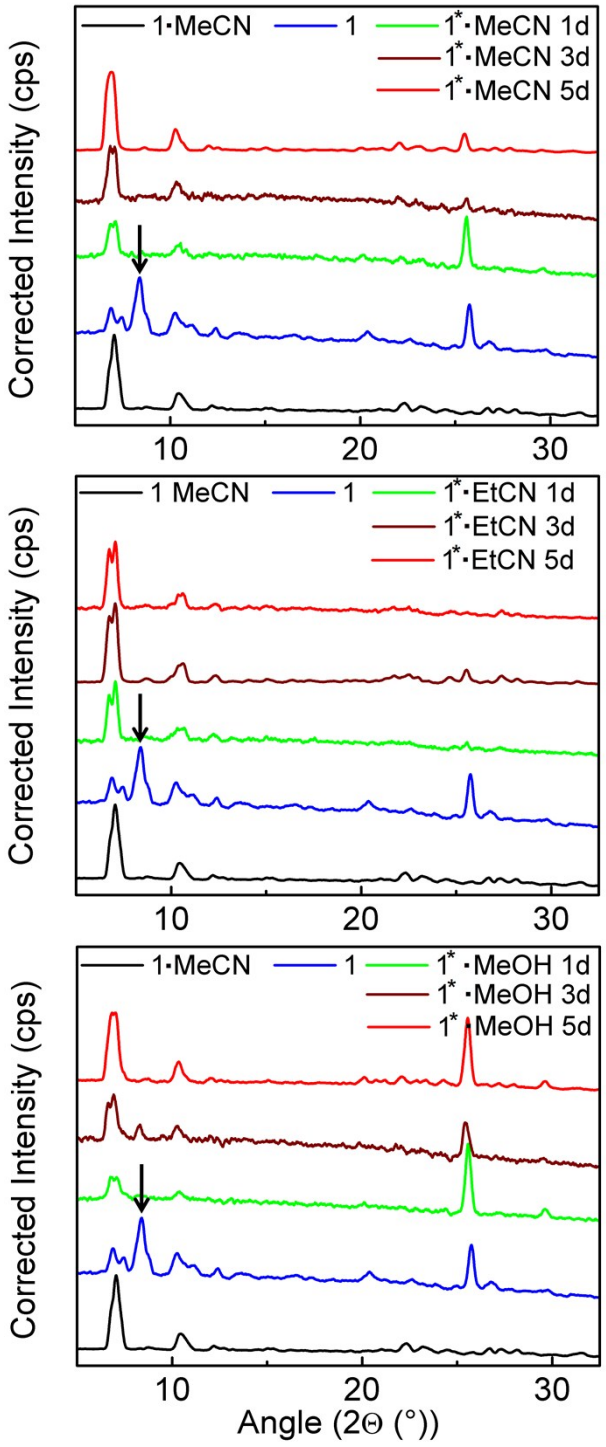

Figure S8. XRD patterns of **1•MeCN** (black) and **1** (blue), followed by the monitoring of **1** exposed to MeCN (top), EtOH (middle), and MeOH (bottom) vapour. The green, brown and red traces correspond to 1 (**1*•MeCN** (1d)), 3 (**1*•MeCN** (3d)), and 5 days of exposition (**1*•MeCN** (5d)), respectively. The black arrow points at the diagnostic signal distinguishing between phases containing solvent molecules or not.

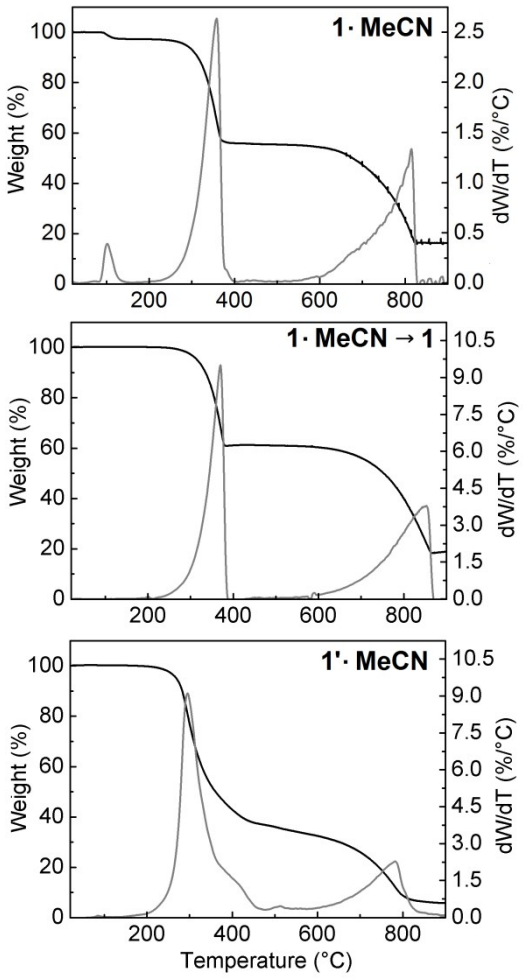

Figure S9. TGA (black) and first derivative (grey) TGA traces before (**1•MeCN**; top), after (**1**; centered) the removal of the solvent molecules, and after introduction of MeCN (**1'•MeCN**; bottom).

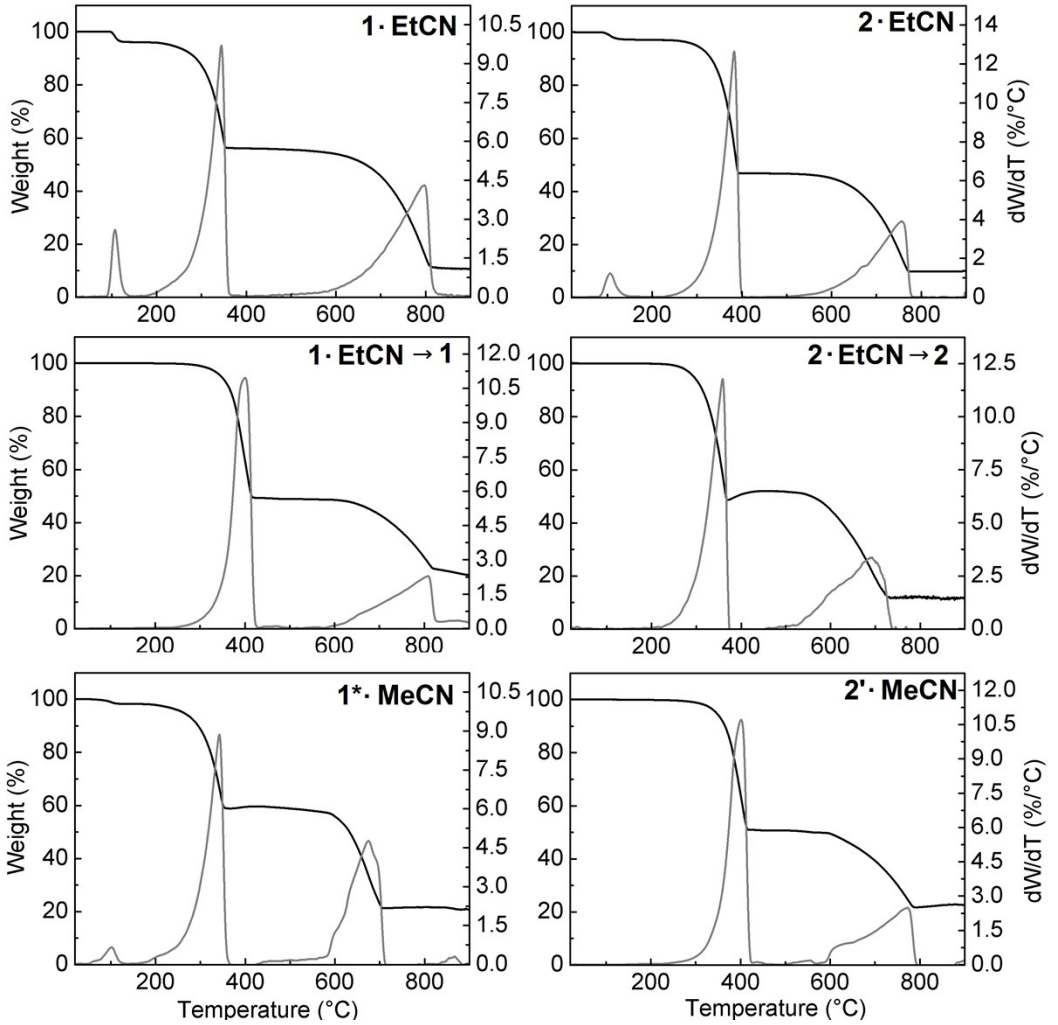

Figure S10. TGA (black) and first derivative (grey) TGA traces before (**1•EtCN**, **2•EtCN**; top), after (**1** and **2**; centered) removals of the solvent molecules, and after introduction of MeCN (**1*•MeCN**, **2'•MeCN**; bottom).

Table S2. TGA data for compounds before (**1•MeCN**, **1•EtCN**, **2•EtCN**) and after (**1** and **2**) removals of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**).[a]

CP	**1• MeCN**	**1**	**1'• MeCN**	**1• EtCN**	**1**	**1*• MeCN**	**2• EtCN**	**2**	**2'• MeCN**
T (°C)	~71	-	~84	~97	-	~70	~89	-	-
$^{Exp}\Delta_m$(%) **($^{Th}\Delta_{m1}$(%))**	3 (3)	0 (0)	<1 (3)	4 (3)	0 (0)	2 (3)	3 (3)	0 (0)	<1 (3)
T (°C)	~305	~315	~272	~281	~347	~278	~322	~295	~346
$^{Exp}\Delta_m$(%) **($^{Th}\Delta_{m2}$(%))**	40 (40)	39 (41)	48 (40)	34 (40)	49 (41)	41 (40)	50 (52)	52 (54)	49 (52)
T (°C)	~654	~701	~697	~640	~665	~613	~641	~579	~641
$^{Exp}\Delta_m$(%) **($^{Th}\Delta_{m3}$(%))**	40 (38)	42 (39)	34 (38)	49 (38)	29 (39)	35 (38)	36 (30)	36 (31)	28 (30)
T (°C)	>820	>861	>820	>805	>816	>702	>767	>730	>780
$^{Exp}\Delta_m$(%) **($^{Th}\Delta_{m4}$(%))**	17 (19)	19 (20)	17 (19)	13 (19)	22 (20)	22 (19)	11 (15)	12 (15)	23 (15)

[a] The first reported temperature corresponds to a weight loss of 5% of the total mass, except for solvent's weight loss which correspond of 0.2% of the total mass. The percentages of the relative mass losses over the total mass are indicated in the column Δ_m(%) ($^{Exp}\Delta_m$(%) = experimental weight loss. For comparison purposes, the theoretical relative mass losses of the ligands are provided as $^{Th}\Delta_{m1}$(%)=relative contribution of the solvant over the total weight; $^{Th}\Delta_{m1}$(%) = relative contribution of the ligand over the total weight; $^{Th}\Delta_{m2}$(%) = relative contribution of iodine atom over the total weight; $^{Th}\Delta_{m3}$(%) = relative contribution of the copper atom over the total weight. The data for CPs **1•MeCN**, **1•EtCN**, and **2•EtCN** are reported in the text too, they are kept here for comparison reasons.

Photophysical properties

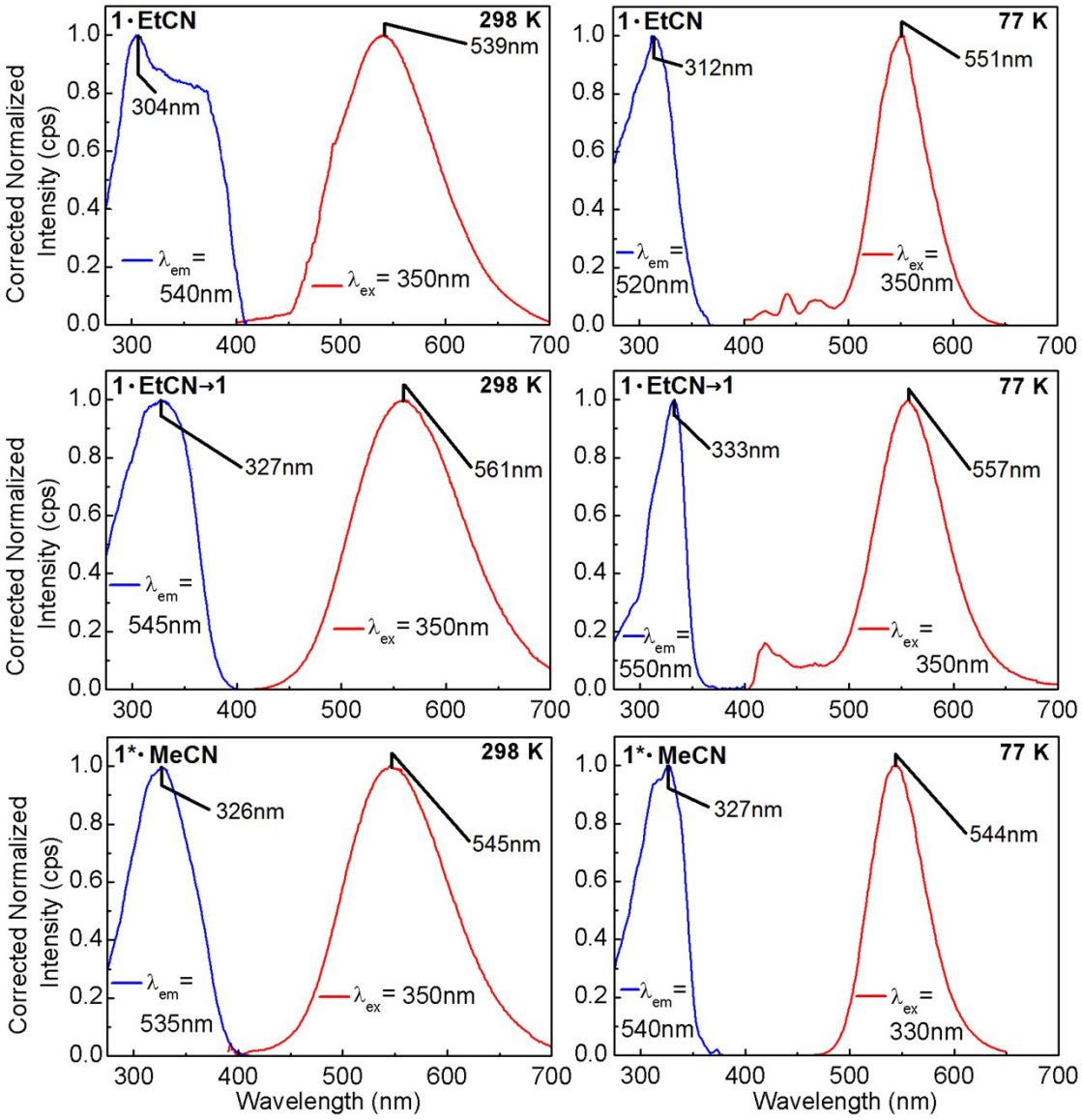

Figure S11. Solid-state excitation (blue) and emission spectra (red) at 298 and 77 K before (**1•EtCN**; top) and after (**1**; centered) removals of the solvent molecules, and after introduction of MeCN (**1*•MeCN**; bottom).

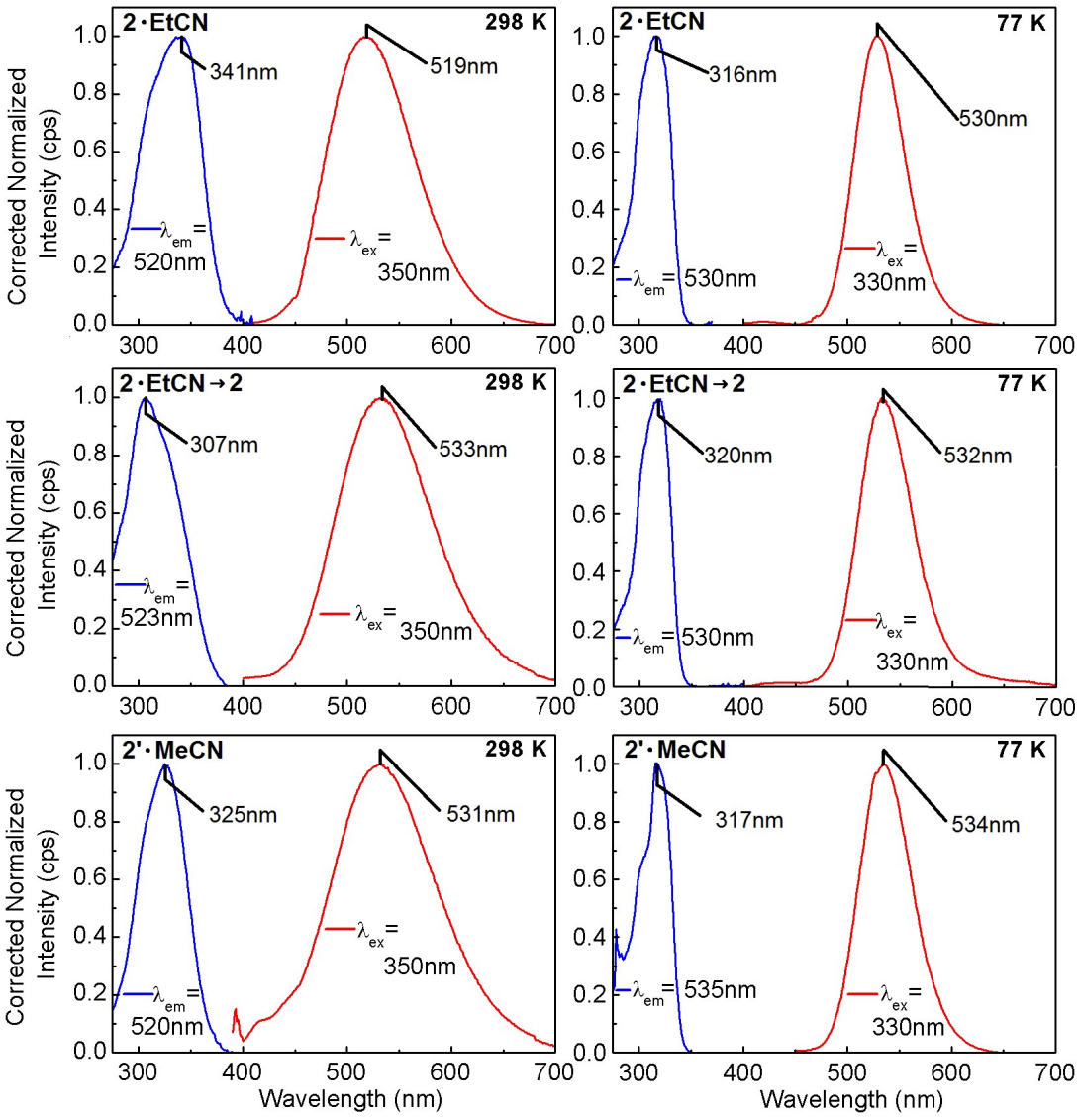

Figure S12. Solid-state excitation (blue) and emission spectra (red) at 298 and 77 K before (**2•EtCN**; top) and after (**2**; centered) removals of the solvent molecules, and after introduction of MeCN (**2'•MeCN**; bottom).

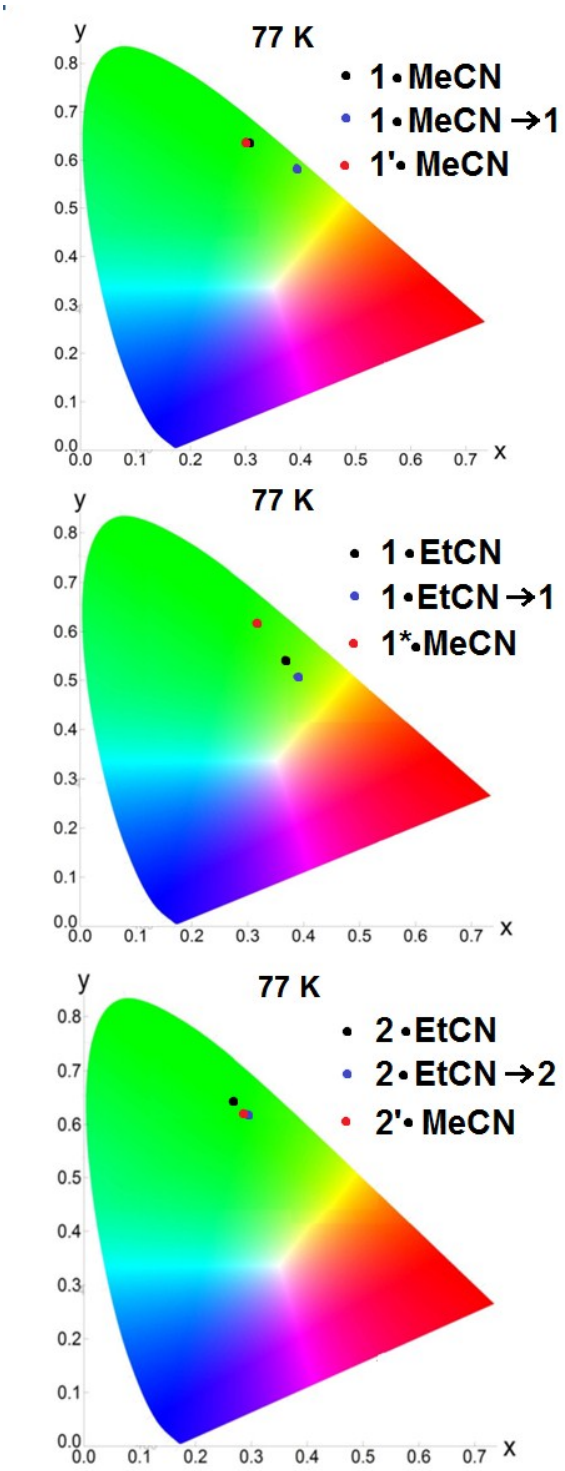

Figure S13. Chromaticity diagrams at 77 K before (**1•MeCN**, **1•EtCN**, **2•EtCN**; black spots) and after (**1** and **2**; blue spots) removals of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**; red spots).

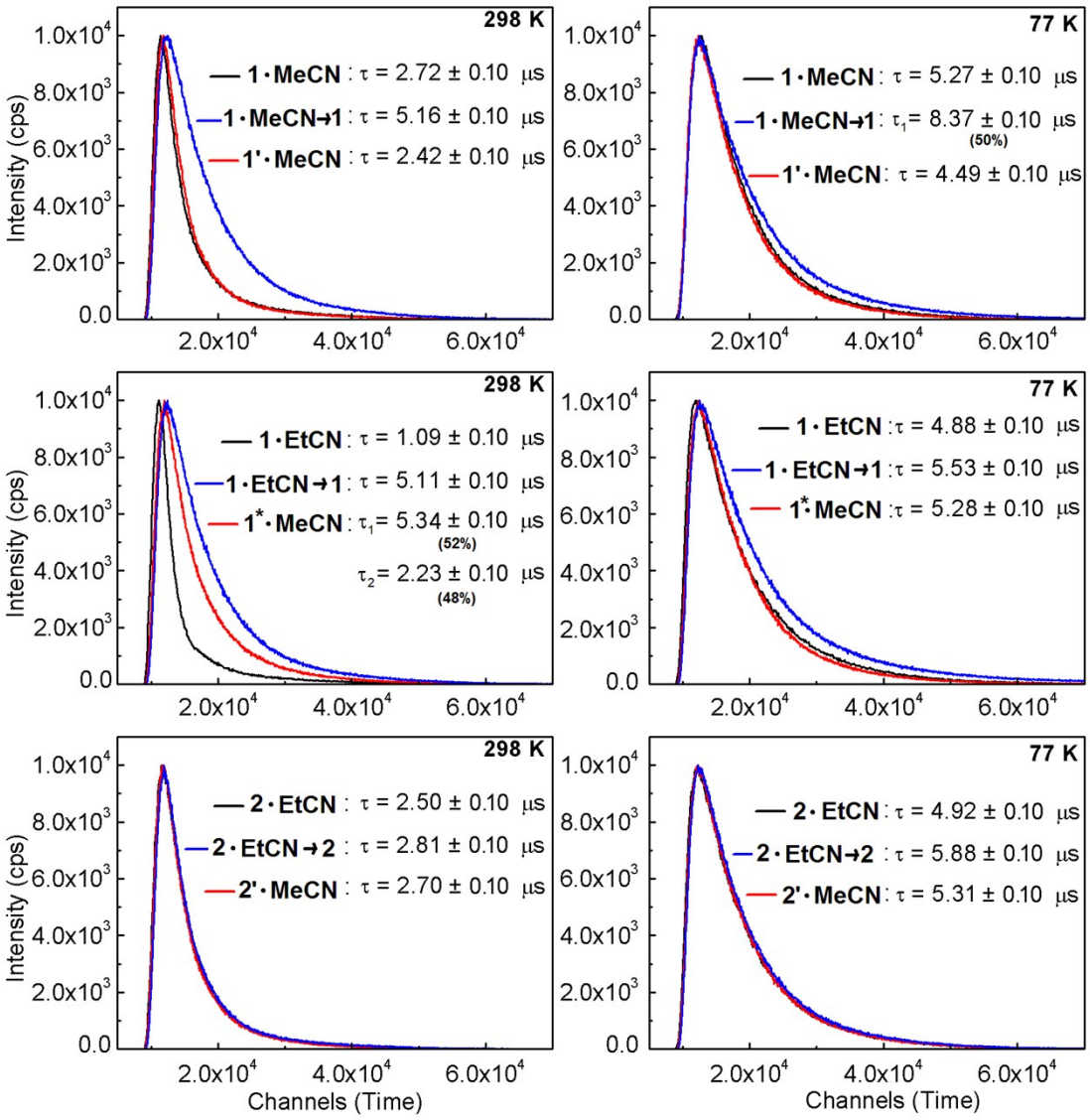

Figure S14. Solid-state emission lifetime decay measurements at 298 and 77 K before (**1•MeCN**, **1•EtCN**, **2•EtCN**; black lines) and after (**1** and **2**; blue lines) removals of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**; red lines).

Table S3. Solid-state emission, excitation maxima, FWHM, chromaticity coordinates and emission lifetimes at 298 K before (**1•MeCN**, **1•EtCN**, **2•EtCN**) and after (**1** and **2**) the removal of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**). (λ_{em}: emission maxima; λ_{ex}: excitation maxima; τ_p: emission lifetime; Φ_p: quantum yield; k_r; radiative constant; k_{nr}; non-radiative constant).

CP	1• MeCN	1	1'• MeCN	1• EtCN	1	1*• MeCN	2• EtCN	2	2'• MeCN
λ_{ex} (nm)	328	312	355	304	327	365	341	307	325
λ_{em} (nm)	530	560	547	539	561	545	519	533	531
τ_p (μs)	2.72 ± 0.10	5.16 ± 0.10	2.42 ± 0.10	1.09 ± 0.10	5.11 ± 0.10	5.34 ± 0.10 (52%) 2.23 (48%) 0.10	2.50 ± 0.10	2.81 ± 0.10	2.70 ± 0.10
Φ_p (%)	56	35	50	10	40	33	19	21	26
k_r ($10^5 s^{-1}$)	2.1	0.7	2.1	0.9	0.8	1.0	0.8	0.7	1.0
k_{nr} ($10^5 s^{-1}$)	1.6	1.3	2.1	8.2	1.2	2.0	3.2	2.8	2.7
FWHM (cm^{-1})	4230	3895	3510	3853	3881	3782	3554	3726	4057
Chrom. Coord.	0.3718, 0.5433	0.3903, 0.5169	0.3526, 0.5413	0.3308, 0.5126	0.3906, 0.5174	0.3555, 0.5183	0.2505, 0.5073	0.3016, 0.5070	0.2951, 0.4683

* The values of emission, excitation maxima and emission lifetimes at 298 K for CPs **1•MeCN**, **1•EtCN**, and **2•EtCN** are reported in the text too, they are kept here for comparison with the data measured at 77 K (table S5)

Table S4. Solid-state emission, excitation maxima, FWHM, chromaticity coordinates and lifetimes at 77 K before (**1•MeCN**, **1•EtCN**, **2•EtCN**) and after (**1** and **2**) the removal of the solvent molecules, and after introduction of MeCN (**1'•MeCN**, **1*•MeCN**, **2'•MeCN**). (λ_{em}: emission maxima; λ_{ex}: excitation maxima; τ_p: emission lifetime).

CP	1• MeCN	1	1'• MeCN	1• EtCN	1	1*• MeCN	2• EtCN	2	2'• MeCN
λ_{ex} (nm)	336	313	329	312	333	327	316	320	317
λ_{em} (nm)	538	555	543	551	557	544	530	532	534
τ_p (μs)	5.27 ± 0.10	5.23 ± 0.10 (50%) 8.37 ± 0.10 (50%)	4.93 ± 0.10	4.88 ± 0.10	5.53 ± 0.10	5.28 ± 0.10	4.93 ± 0.10	5.88 ± 0.10	5.31 ± 0.10
FWHM (cm^{-1})	1820	2470	1750	1953	2443	2056	1992	2087	2017
Chrom. Coord.	0.3083, 0.6460	0.3846, 0.5801	0.2905, 0.6454	0.3206, 0.53745	0.3665, 0.5124	0.3290, 0.6350	0.2432, 0.6492	0.2816, 0.6277	0.2770, 0.6492

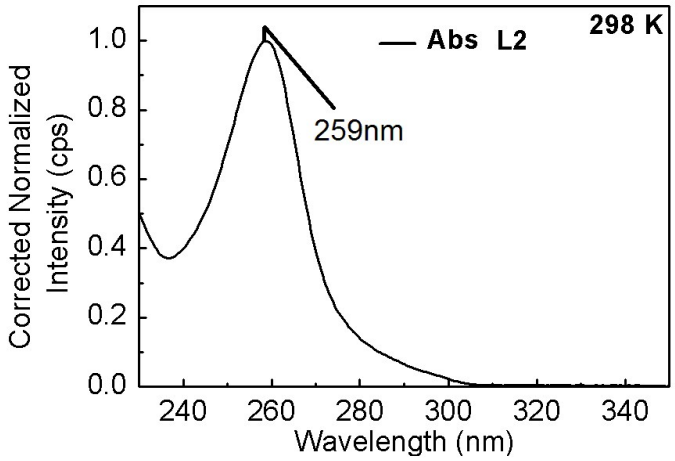

Figure S15. Absorbance spectra at 298 K for **L2** in solution (dichloromethane).

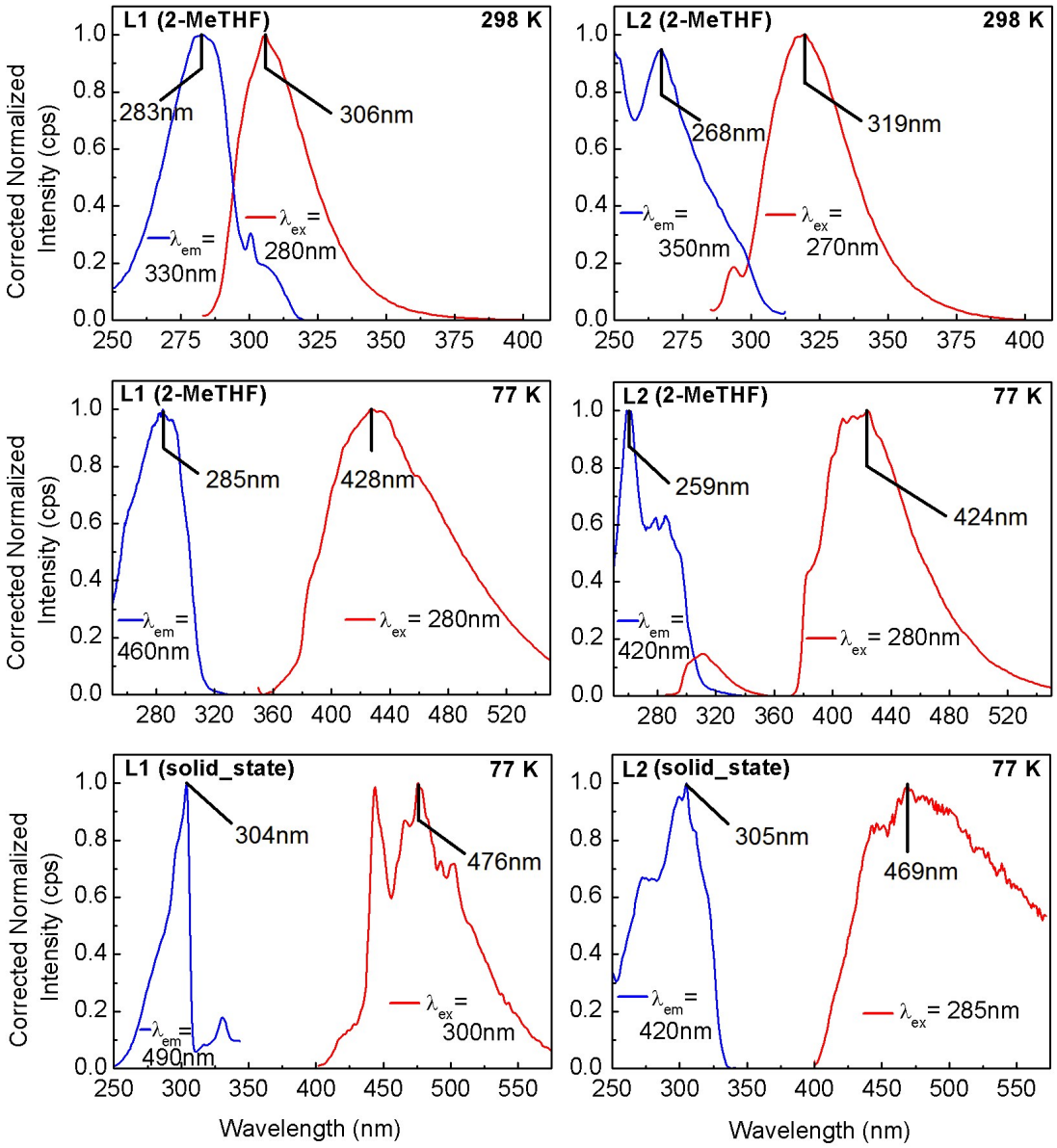

Figure S16. Excitation (blue) and emission spectra (red) for **L1** (left) **L2** (right) (top: in 2-MeTHF at 298 K; centered: in 2-MeTHF at 77 K; bottom: in solid-state at 77 K).