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# Photoactive CuI-crosslinked Polyurethane Materials

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## **Abstract.**

Using multinuclear copper iodide complexes as cross-linking agents in a polyurethane matrix, original photoluminescent stimuli-responsive materials were synthesized. The intrinsic photoluminescent properties of the covalently incorporated copper iodide complexes are thus transferred to the materials while retaining the beneficial characteristics of the polymer host. The transparent materials exhibit room temperature phosphorescence with emission switching properties by displaying luminescence thermochromism and solvatochromism. The thermochromism of luminescence is characterized by a change in the wavelength and intensity of the emission with temperature and the vapochromic effect presents a contrasted response of extinction or exaltation according to the nature of the solvent of exposure. By combining the luminescence characteristics of photoactive copper iodide complexes with the ease of polymer processing, the application of these luminescent materials as phosphors in LED (light-emitting diode) devices was also demonstrated. The present study shows that the use of copper iodide complexes as cross-linkers in polymeric materials is a relevant strategy to design materials with enhanced functionalities with in addition low cost and sustainable characteristics.

## **Keywords.**

Stimuli-responsive materials, light-emitting materials, luminescence, polyurethane, copper iodide complexes.

## Introduction.

Materials exhibiting properties responding to external stimuli meet current technological demands regarding data storage, detection and security issues.<sup>1-5</sup> Because of the readily recordable luminescence signal, the development of luminescent stimuli-responsive materials is the subject of growing interest in this research field.<sup>6</sup> Photoactive polymeric materials are particularly relevant for such applicative perspectives due to their excellent solution processability and facile coating performance.<sup>7,8</sup> The versatility of organic polymers towards chemical modifications allows tuning the chemical and physical properties of the materials and also their functionalization by photoactive guests, that leads to a wide range of stimuli-responsive luminescent polymer materials.<sup>9-11</sup> The photoactive guests can be incorporated either by direct insertion (doping)<sup>12,13</sup> or by grafting to the polymeric host matrix.<sup>14,15</sup>

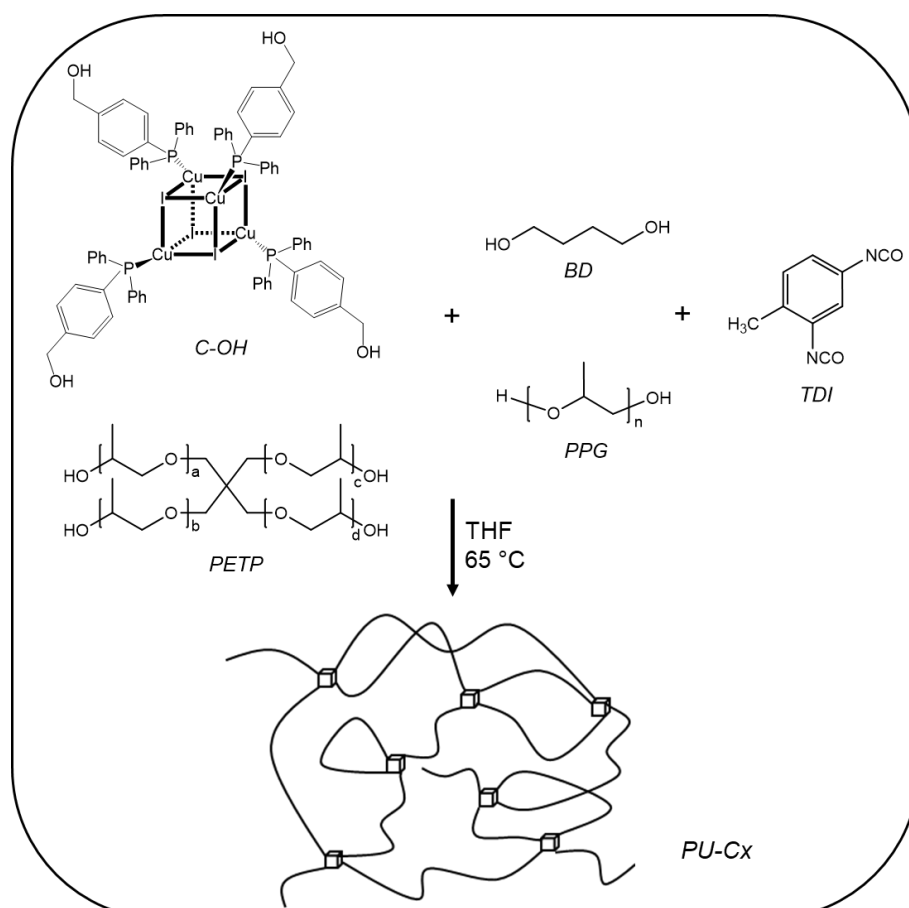
Copper(I) halide complexes constitutes an important family of luminescent compounds displaying a large panel of photophysical properties.<sup>16-22</sup> They are particularly attractive in regards to rare-earth and lead-free phosphors which are highly demanded for developing economic and sustainable solid-state lighting materials.<sup>23-27</sup> By displaying photoluminescence in the visible under UV, high PLQY (Photo-Luminescent Quantum Yield) and air stability, the copper iodide complexes are highly attractive.<sup>28,29</sup> They can additionally display stimuli-responsive properties such as luminescence thermochromism,<sup>30-34</sup> mechanochromism,<sup>35-42</sup> rigidochromism,<sup>43-45</sup> and solvatochromism.<sup>46-50</sup> The possibility of combining stimuli-responsive properties is of high interest to access original multifunctional emitting materials. All these features inspire us to use the copper iodide complexes as photoactive components in polymer materials. Several aspects have directed the choice of the polymer matrix towards polyurethanes (PU) such as the relative simplicity of synthesis and the possibility of chemical adjusting.<sup>51,52</sup> Polyurethanes actually constitute a major class of organic polymers due to their versatile properties offering a wide range of applications from insulation foam to adhesives. They can also present optical transparency in the visible and resistance to UV radiation that are relevant for developing optically active materials.<sup>53</sup> Polyurethanes incorporating photoactive guest have been reported for LED (Light Emitting Diodes) applications,<sup>54</sup> and in the design of luminescent stimuli-responsive materials.<sup>55-58</sup> For the incorporation of the photoactive guest within the polymer, covalent attachment is preferred over simple dissolution to gain in homogeneity of distribution and chemical stability, although this method is less straightforward.

We thus report herein stimuli-responsive polyurethane-based materials incorporating copper iodide complexes as emitting guests. For the materials synthesis, the complexes act as cross-linkers leading to highly cross-linked polymers with robustly grafted photoluminescent complexes. The intrinsic luminescence properties of the copper iodide complexes are thus transferred to the materials while keeping the transparency, self-standing properties and processability advantages of the thermosetting matrix. These polymer materials exhibit room temperature phosphorescence with emission switching properties by displaying luminescence thermochromism and solvatochromism. The luminescence thermochromism is characterized by a change of the emission's wavelength and intensity upon cooling and an emission quenching effect upon heating. The solvent-responsiveness presents a contrasted quenching or exaltation effect depending on the nature of the solvent. Finally, by taking advantage of the processability of these functional materials, their application as phosphors in LED devices has been successfully demonstrated.

## Results and Discussion.

### *Synthesis and characterizations.*

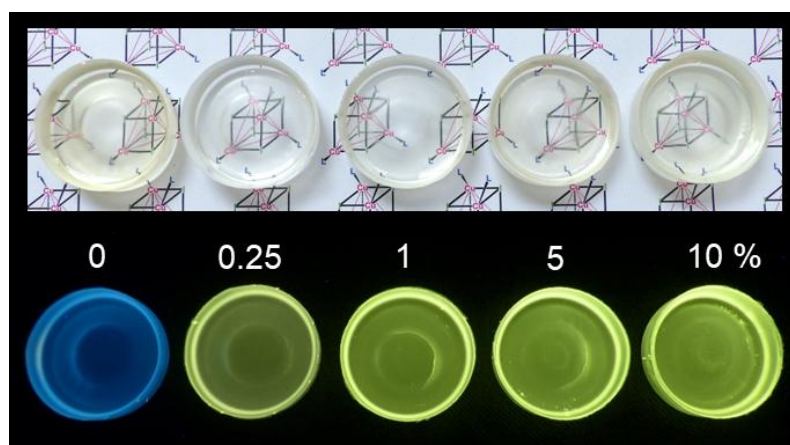
Polyurethanes are classically obtained through polycondensation reaction of diisocyanates and polyol precursors to form urethane (carbamate) linkages. For the incorporation of the copper iodide complex within the polymeric matrix through a robust covalent link, a complex having alcohol functions was targeted for acting as the polyol. A multinuclear copper iodide complex functionalized by four phosphine ligands each bearing one alcohol function was thus chosen. This molecular cluster formulated  $[\text{Cu}_4\text{I}_4\text{L}_4]$   $\text{L} = \text{PPh}_2(\text{C}_6\text{H}_4)\text{CH}_2\text{OH}$  (4-(diphenylphosphino)phenylmethanol), is of cubane geometry built on four copper atoms and four iodide atoms which alternatively occupy the vertices of a distorted cube.<sup>59</sup> The organic ligands complete the four-fold tetrahedral coordination sphere of the copper(I) atoms (Figure 1). The synthesis of this complex was previously reported by our group as well as its crystalline structure and photoluminescence properties.<sup>60</sup> As shown in Figure 1, the specific cubane geometry of this complex leads to a tetrahedral spatial distribution of the four alcohol functions which is beneficial to the formation of polymers of high dimensionality; the cluster acting as a crosslinking agent.



**Figure 1.** Schematic illustration of the synthesis of the polymer materials namely **PU-C<sub>x</sub>** ( $x = 0, 0.25, 1, 5$  and  $10$ ),  $x$  being the cluster content (wt.%).

Different experimental conditions and formulations were tested in order to get self-standing materials with optimal photoluminescence properties. As example, polymerization with tin-based catalysts were performed but the obtained polymers were opaque foams and yellow, absorbing in the visible. No catalyst was finally used and instead the reaction was conducted by heating ( $65\text{ }^\circ\text{C}$ ) for several hours (experimental details in SI). The diisocyanate used is toluene-2,4-diisocyanate (TDI) having higher

reactivity compared with aliphatic derivatives (Figure 1). Butanediol (BD) and polypropylene glycol of 400 g.mol<sup>-1</sup> average mass (PPG400), are employed as short and long diols respectively, in a  $n_{PPG}/n_{BD} = 3$  ratio. The blank polymer without complex is synthesized with pentaerythritol propoxylate (PETP: 5/4 PO/OH) as crosslinker having similar features as the [Cu<sub>4</sub>L<sub>4</sub>L<sub>4</sub>] cluster with both tetrahedral special distribution of four alcohol functions (Figure 1). For the functionalized polymers, the PETP is partly replaced by the complex (from 0.3 to 12 %) while keeping constant the  $n_{NCO}/n_{OHtotal} = 1$  and  $n_{OHCrosslinking}/n_{OHtotal} = 2/5$  ratios. Polymers with different cluster contents of 0, 0.25, 1, 5 and 10 wt% with respect to the total weight of the reactants were thus synthesized, and the corresponding materials are labelled: **PU-C<sub>x</sub>** with **x = 0, 0.25, 1, 5 and 10**. Above 10 wt%, solubility issues of the cluster in the reacting media are encountered. After mixing the reactants, the viscous mixture was heated at 65 °C for 24 h. Depending on the mold used, the polymer materials can be shaped differently, as films or bulk samples. As shown in Figure 2, the materials are colorless, transparent under visible light and crack-free. They are completely air stable; no aspect changes have been detected after several months. Under UV excitation, they all display photoluminescence. The PU polymers present a bright yellow emission while the blank polymer emits in the blue (Figure 2). Although the doping of [Cu<sub>4</sub>L<sub>4</sub>L<sub>4</sub>] clusters within acrylic polymers have been already reported,<sup>45,61</sup> **PU-C<sub>x</sub>** constitutes, to our knowledge, the first organic polymer materials which covalently incorporate the multinuclear [Cu<sub>4</sub>L<sub>4</sub>L<sub>4</sub>] photoactive complexes as cross-linkers. Note that mononuclear copper complexes covalently attached to polymers of different nature have been already studied for stress sensing applications.<sup>62</sup> However, in the case of the copper iodide complex, a two-step incorporation procedure was employed with first the grafting of the ligand and then the metalation.<sup>63</sup>

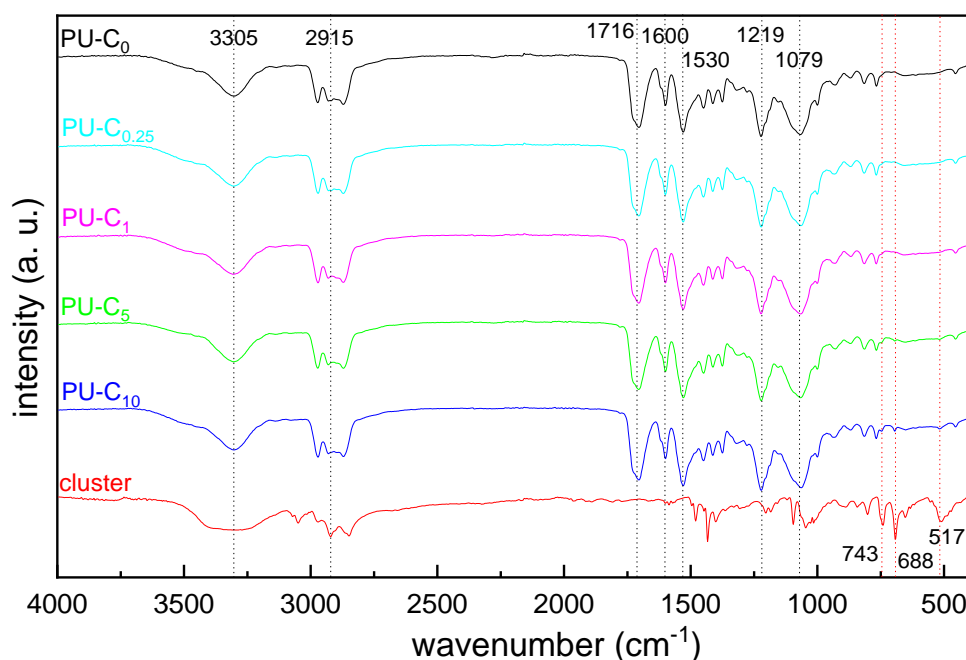


**Figure 2.** Photos of pellets of **PU-C<sub>x</sub>** ( $x = 0, 0.25, 1, 5$  and  $10$ ), under visible light and under UV excitation (365 nm UV lamp) of 25 mm in diameter.

The glass transition temperature ( $T_g$ ) of **PU-C<sub>x</sub>** was determined by DSC (Figures S1) and values of 24, 20, 21, 19, 18 °C were obtained for  $x = 0, 0.25, 1, 5$  and  $10$ , respectively. Although a slight decrease of the  $T_g$  value with the cluster content is noted, the difference is limited compared to the blank polymer which indicates that the cluster does not significantly affect the structure of the polymer network and in particular the polymer chains mobility. The crosslinking efficiency was evaluated by swelling of the materials in THF and mass loss measurement. The largest mass loss found in the **PU-C<sub>x</sub>** series was 3.5 % at  $x = 10$  (SI). These low values indicate a low amount of unreacted monomers or oligomers and therefore high degree of polymerization associated to the effective crosslinking action of the cluster within the matrix. The cluster bonding is further confirmed by the preservation of the luminescence properties of the materials after the swelling treatment (and drying). Thermogravimetric (TG) measurements indicate thermal stability up to 250 °C for **PU-C<sub>x</sub>**, that is appropriate for lighting

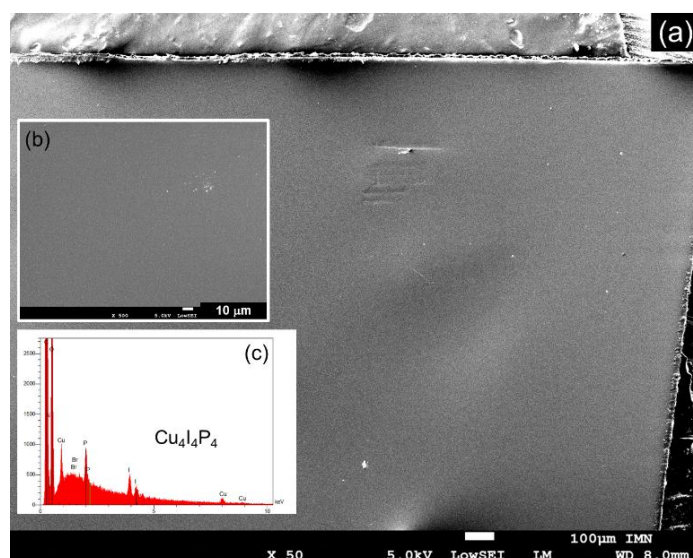
applications. The similar value for **PU-C<sub>0</sub>** agrees with the lack of perturbation of the polymeric network induced by the copper iodide complex.

The FTIR spectra of the polymers are presented in Figure 3. The spectra present the characteristic vibrational bands of the carbamate function of polyurethanes. The broad signatures of the NH and CH<sub>2</sub> vibrations are found at 3305 and 2915 cm<sup>-1</sup>, respectively. The vibrational band of the C=O carbonyl is observed at 1716 cm<sup>-1</sup> and that of C-N and C=C ones at 1600 and 1530 cm<sup>-1</sup>, respectively. At 1219 and 1079 cm<sup>-1</sup> are vibrations corresponding to C-O-C moieties. No signal of the isocyanate function (NCO) expected around 2250 cm<sup>-1</sup> is detected. This indicates that all TDI reacted and attests to the completion of the polycondensation reaction. This result is in accordance with the high degree of crosslinking of the materials. By comparing the FTIR spectra with that of the cluster powder, characteristic bands of the cluster can be detected that are more obvious for the highest cluster contents (Figure 3). According to a previous study, these bands at 743, 688 and 517 cm<sup>-1</sup> can be attributed to Cu-P, C-P and Ph vibrations of the cluster.<sup>60</sup>



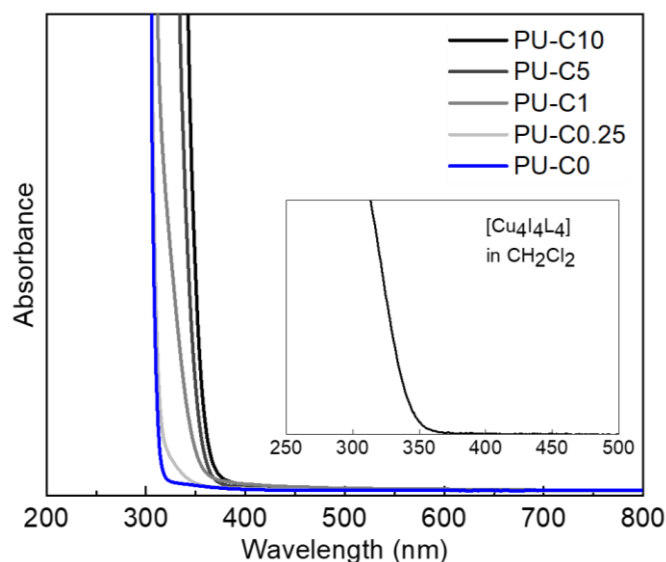
**Figure 3.** FTIR spectra of the **PU-C<sub>x</sub>** ( $x = 0, 0.25, 1, 5$  and  $10$ ) and of the crystalline cluster.

Observations under optical microscope of **PU-C<sub>10</sub>**, indicate smooth surface and homogenous distribution of the cluster within the polymeric matrix (Figure S2). The interest of the covalent grafting strategy is demonstrated upon comparison with a polymer synthesized with a cluster deprived of alcohol function ( $[\text{Cu}_4\text{I}_4(\text{PPh}_2\text{Pr})_4]$ ) but readily soluble in the reaction media. The obtained polymer was not transparent anymore presenting large clusters aggregates non-homogeneously distributed within the polymeric matrix (Figure S2). SEM (Scanning Electron Microscopy) analysis of the **PU-C<sub>x</sub>** further revealed smooth surface of the polymers (Figure 4). From EDS (Energy Dispersive Spectrometry), the expected Cu/I/P:1/1/1 stoichiometry of the  $[\text{Cu}_4\text{I}_4\text{L}_4]$  cluster was measured and the homogenous distribution of these elements in the polymers was attested by EDS elemental mapping (Figure S3), resulting from the covalent grafting.



**Figure 4.** (a) SEM image of a cut film of **PU-C<sub>10</sub>**, (b) a zoom of the surface and (c) EDS spectrum of the same sample.

The UV-visible absorption spectra of the polymers **PU-C<sub>x</sub>** are reported in Figure 5 along with that of the cluster in solution to compare. The materials present high transmittance values reaching 90 % in the visible range, in accordance to the transparent and colorless appearance of the samples (Figure S4). No scattering is observed in agreement with no cluster aggregation. The **PU-C<sub>x</sub>** materials strongly absorb in the UV region with a broad absorption band lying down to 350 nm. From 250 to 300 nm, the absorption comes from both the matrix (**PU-C<sub>0</sub>**) and the cluster whereas in the 300-350 nm range the absorption originates from the cluster solely.

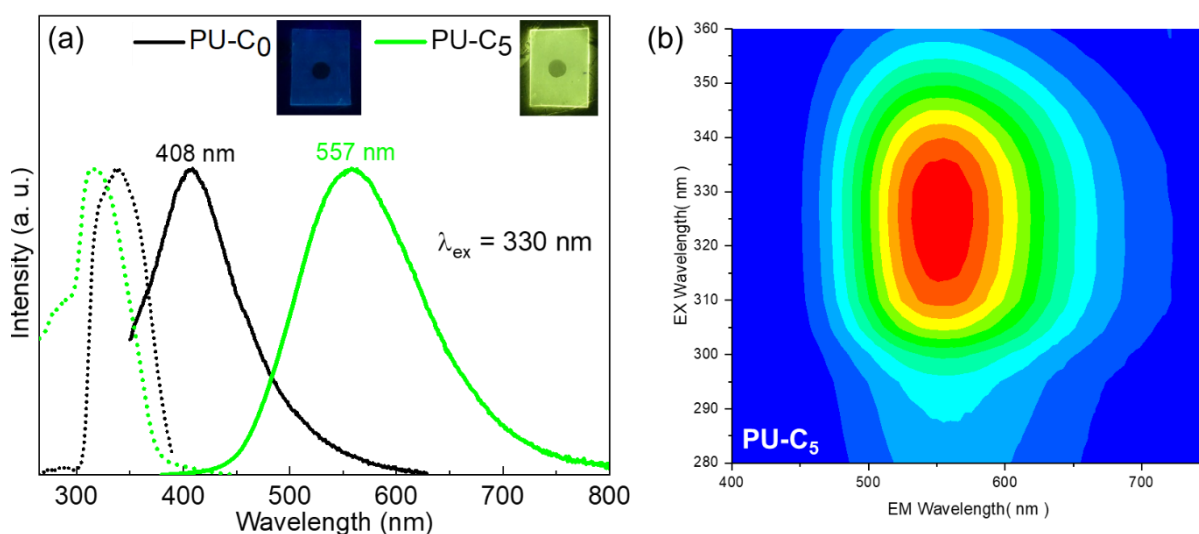


**Figure 5.** UV-visible absorption spectra of **PU-C<sub>x</sub>** ( $x = 0, 0.25, 1, 5$  and  $10$ ) deposited on quartz substrate and of the cluster dissolved in dichloromethane in insert for comparison.

### ***Photoluminescence properties.***

The yellow emission displayed by the polymers under UV excitation at room temperature (Figure 2), is characterized by one unstructured broad emission band centered around 555 nm, as presented in Figure 6a (all compositions are reported in Figure S5). At similar excitation  $\lambda_{\text{ex}} = 330$  nm, the blank polymer (**PU-C<sub>0</sub>**) presents a band centered at 408 nm corresponding to the observed blue emission.

The broad yellow emission band corresponds to that of the cluster itself, which is recorded at 540 nm in crystalline powder, at room temperature (Figure S6). The photoluminescence properties of the cluster are thus retained whatever its concentration in the polymers with intensity being proportional to the concentration. A moderate redshift is observed along the **PU-C<sub>x</sub>** ( $x = 0.25, 1, 5$  and  $10$ ) (Table 1) series from 564 to 554 nm that can be explained by different structural constraints induced by the polymeric matrix towards the cluster. Rigidochromism effect is actually known for copper iodide clusters,<sup>43,45</sup> which is related to different extent of the distortion of the excited state leading to a redshift of the emission wavelength when decreasing structural constraints. The matrix thus become more rigid by increasing the cluster content but as expected, the emission wavelength values still lay between that of the liquid-state (568 nm) and that of the solid-state (540 nm).<sup>64</sup> The rigidochromic effect thus observed can also be attributed to the covalent linkage of the cluster to the matrix.



**Figure 6.** (a) Normalized solid-state luminescence spectra of **PU-C<sub>5</sub>** and the blank polymer **PU-C<sub>0</sub>** with emission spectra in solid lines and excitation spectra in dotted lines at 298 K. (b) Solid-state photoluminescence map (excitation vs. emission) of **PU-C<sub>5</sub>** at 298 K.

The excitation band of the **PU-C<sub>x</sub>** presents a clear maximum around 330 nm as shown on the photoluminescence map (Figure 6b and S7). A relatively large excitation-emission Stokes shift of 1.5 eV is thus noticed for these materials. The relatively narrow excitation band is not observed for the cluster in powder having instead a very broad excitation band ranging from 250 to 400 nm (Figure S6). Comparison with the absorption spectra (Figure 5), indicates that the PU matrix actually absorbs in this 250-300 nm range and therefore it hinders that of the cluster. The cluster is consequently more efficiently excited out of the absorption band of the polymeric matrix from 300 to 350 nm. No matrix-to-cluster energy transfer seems to be at play in the studied materials. Depending on the excitation wavelength, the emission can vary. At high energy ( $\lambda_{ex} = 280$  nm), the blue emission of the PU matrix can be observed at 320 nm concomitantly with that of the cluster (Figure S5). The relative contribution of the matrix decreases by increasing the cluster content, as expected.

The internal PLQY values measured are all around 10 % for the **PU-C<sub>x</sub>** ( $x = 0.25, 1, 5$  and  $10$ ) whereas that of the matrix is low as 1 % (Table 1). This relatively high values for the functional polymers is relevant for practical applications. Because the copper iodide cluster is at the origin of the emission in all the materials, this explains the limited dependence of the internal PLQY relative to the cluster content. The lower PLQY value compared with that of the cluster in solid-state of 55 %, could originate from a less rigid environment in the polymer and also absorption competition between the matrix and the cluster. The emission lifetimes of **PU-C<sub>x</sub>** ( $x = 0.25, 1, 5$  and  $10$ ) present biexponential decays (Figure S8). The longer lifetime values in the 1-2  $\mu$ s range can be attributed to the cluster in accordance with its powder-state value of  $\tau = 3.7 \mu$ s. The shorter lifetimes contribution in the



nanosecond range is attributed to the polymeric matrix in accordance to the even shorter value measured for **PU-C<sub>0</sub>** (Table 1).

**Table 1.** Photoluminescence data of **PU-C<sub>x</sub>** ( $x = 0, 0.25, 1, 5$  and  $10$ ) recorded at  $\lambda_{\text{ex}} = 330$  nm at 293 K. Lifetimes ( $\tau$ ) and photoluminescence quantum yields (PLQY).

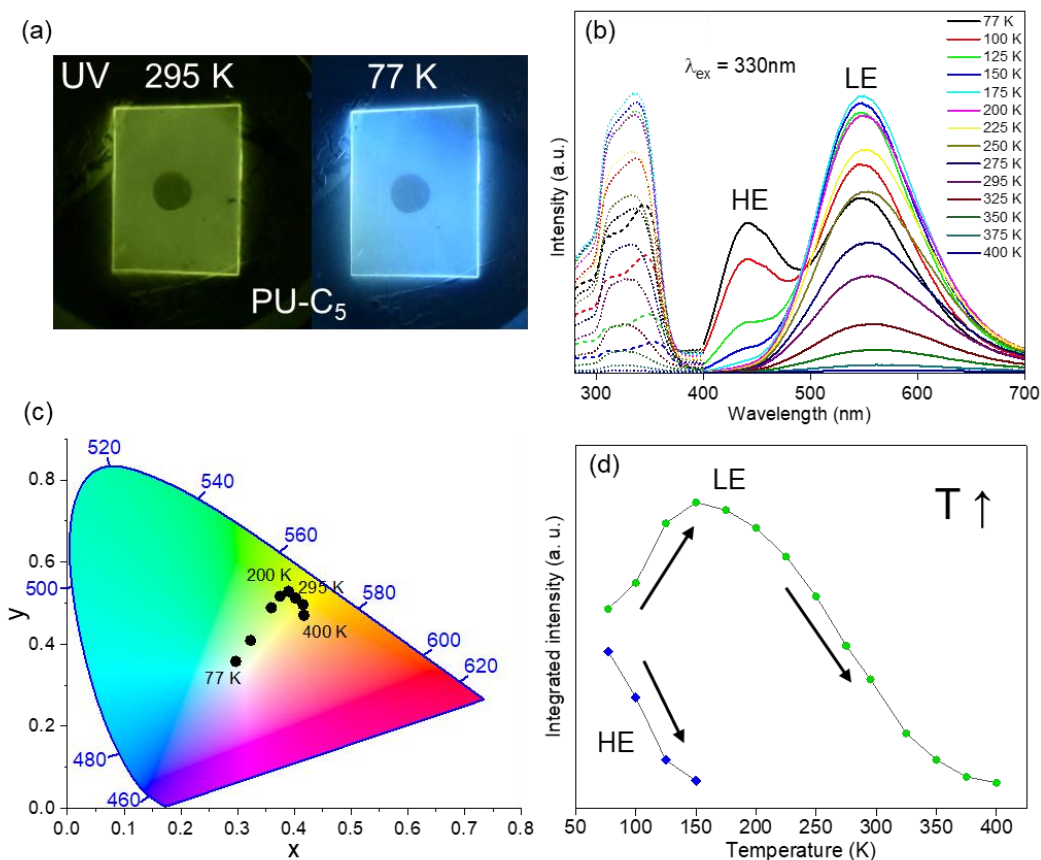
	$\lambda_{\text{em}}^{\text{max}}$ (nm) 293 K	$\tau$ ( $\mu\text{s}$ ) [ $\lambda_{\text{ex}} = 400$ nm]	PLQY (%) [ $\lambda_{\text{ex}} = 330$ nm]
<b>PU-C<sub>0</sub></b>	408	0.001	1
<b>PU-C<sub>0.25</sub></b>	564	0.04 1.09	8
<b>PU-C<sub>1</sub></b>	560	0.05 1.71	10
<b>PU-C<sub>5</sub></b>	557	0.06 1.74	11
<b>PU-C<sub>10</sub></b>	554	0.05 1.94	10

### **Temperature responsiveness.**

The effect of the temperature on the luminescence properties of the functional polymers was studied. Luminescence thermochromism is observed upon cooling, with the room temperature yellow emission turning light-blue at 77 K (Figure 7a). In contrast, upon heating up to 400 K, quenching of the yellow emission occurs. These two effects are relatively reversible for several cycles (Figure S11). The emission spectra recorded in the 77-400 K range are reported in Figure 7b for **PU-C<sub>5</sub>**. By lowering the temperature from 400 K, the intensity of the yellow emission band (LE for Low Energy) increases and below 175 K it starts to decrease concurrently with the appearance at higher energy of an another emission band (HE for High Energy). At 77 K, the two emission bands centered at 440 and 540 nm are of comparable intensity leading to the light-blue emission color. Emission lifetime values of the LE band are very similar to those obtained at 293 K, with a shorter component corresponding to the polymeric matrix and a longer one coming from the cluster (Figure S9). The displayed luminescence thermochromism thus presents a great variation of the emission color over the studied temperature range, as represented in the CIE chromaticity coordinates diagram in Figure 7c.

The variation of the relative intensity of two emissions bands with the temperature, is characteristic of the luminescence thermochromism displayed by the  $[\text{Cu}_4\text{I}_4\text{L}_4]$  cubane clusters.<sup>34</sup> From previous experimental and theoretical studies,<sup>60</sup> the LE band is assigned to a transition of mixed XMCT and MM character ( $X = \text{I}$  and  $M = \text{Cu}$ ). The corresponding triplet excited state is commonly labelled <sup>3</sup>CC (Cluster Centered), and involved a Cu-Cu bonding vacant orbital. A significant Cu-Cu shortening thus occurs for this triplet state compared with the fundamental one. The nature of the HE band is different and implies in this case the  $\pi^*$  orbital of the phenyl groups of the phosphine ligands and the corresponding transition is therefore of <sup>3</sup>(X+M)LCT character. The thermal equilibrium between the two corresponding excited triplet states leads to the opposite intensity variation of these two emission bands (HE and LE) and to the observed thermochromism. By comparing the luminescence thermochromism of the cluster in powder state (Figure S6), the HE band (440 nm) appears at 125 K against 150 K for the **PU-C<sub>x</sub>** polymers. This indicates that the energy necessary for populating the CC state is higher in the case of the polymers. The <sup>3</sup>CC emissive state corresponding to the LE band must be higher in energy in the case of the grafted cluster, which can be attributed to the carbamate function having a stronger withdrawing character than the alcohol function. The luminescence thermochromism of the functional polymers constitutes additionally a conclusive proof of the preservation of the cluster in the polymeric matrix. Compared with the powder state, the limited changes in the thermochromism

characteristics indicate that the covalent grafting does not significantly affect the cluster's molecular structure.

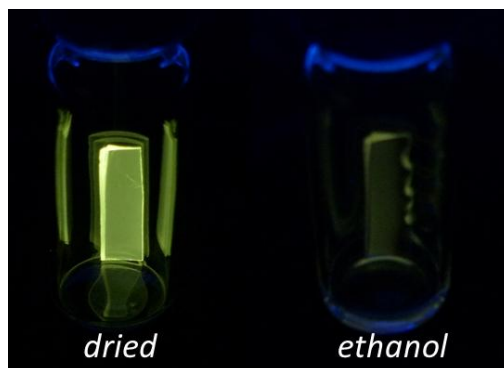


**Figure 7.** Temperature-dependent solid-state luminescence spectra of **PU-C<sub>5</sub>**. (a) Photos of polymer films at 295 and 77 K under UV excitation. (b) Emission spectra in solid lines ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ) and excitation spectra in dashed ( $\lambda_{\text{em}} = 440 \text{ nm}$ ) or dotted lines ( $\lambda_{\text{em}} = 550 \text{ nm}$ ) from 77 to 400 K. (c) CIE chromaticity coordinates diagram (1931). (d) Integrated intensity of the LE and HE emission bands as function of the temperature, the arrows indicate the emission behavior upon heating.

Upon increasing the temperature above 175 K, the emission intensity of the materials (LE band) decreases rapidly (Figure 7d). At 325 K, about 50 % of the integrated intensity of the emission band at 295 K is lost and at 400 K the emission is nearly extinguished (Figure 7d). This behavior is similar to that observed for the cluster in powder upon heating up to 400 K (Figure S6). The luminescence quenching can be attributed to the increase of non-radiative de-excitations caused by a higher thermal agitation of the cluster. The more effective quenching observed for the polymers compared with the cluster in powder state can be explained by higher mobility in the polymeric matrix. The **PU-C<sub>x</sub>** materials thus exhibit temperature-dependent emission color and intensity variation that can be exploited for luminescence thermometry applications. Regarding the LE emission band, a maximum sensitivity value as high as  $S_r = 20 \text{ \% K}^{-1}$  at 380 K was calculated (Figure S10a). By considering the two HE and LE emission bands, ratiometric temperature measurements can be even considered. Sensitivity values  $S_r$  from 3 to  $16 \text{ \% K}^{-1}$  within the 77-150 K range were obtained (Figure S10b). The **PU-C<sub>x</sub>** materials thus constitute a relevant example of ratiometric luminescence thermometers of different type compared with the more common lanthanides-based materials for which the two emissive bands are from different emitters.<sup>65</sup> Compared to powdered compounds, the **PU-C<sub>x</sub>** functional polymers can additionally be specifically designed for thermometry applications.

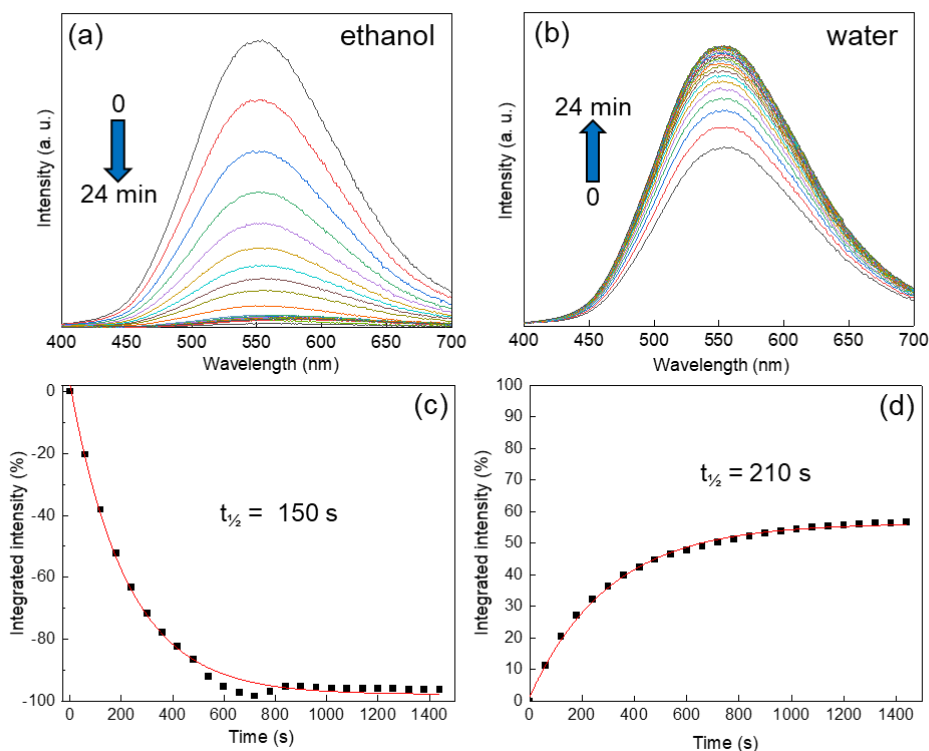
### ***Solvents responsiveness.***

Another investigated stimuli-responsive property of these functional polymers is their luminescence sensitivity to solvents exposure. Indeed, when they are exposed to solvents liquid or vapor, their emission is either quenched or exalted. As shown in Figure 8, exposure to ethanol extinguishes the emission of a self-standing film of **PU-C<sub>5</sub>**.



**Figure 8.** Photos of a self-standing film of **PU-C<sub>5</sub>** before and after exposure to ethanol, in a close container.

The observed vapochromic effect was studied quantitatively by exposing **PU-C<sub>5</sub>** polymer to solvents of different nature. Whereas ethanol, dichloromethane and diethyl ether induced a decrease of the emission intensity, water, pentane and cyclohexane have the opposite effect. The emission spectra recorded as a function of the duration of the solvent vapor exposure are presented in Figure 9 for ethanol and water and in Figure S12 for the other solvents. As shown in Figure 9a, ethanol induced a progressive decrease of the emission intensity and after 24 min a loss of 96 % of the integrated intensity is observed (Figure 9c). In the opposite, upon water vapor exposure, an increase of the emission intensity occurs and a gain of 60 % of the integrated intensity is eventually measured (Figure 9b and d). For the different solvents tested, the intensity increase is generally of less extent compared with the quenching effect. Plots of the integrated intensity as a function of exposure duration can be all fitted by a single exponential model ( $y = y_0 + A_1 e^{-(x-x_0)/t_1}$ , in Figure S12). A  $t_{1/2}$  parameter can be defined as the time at which half of the final emission intensity is lost or gained ( $t_{1/2} = \ln(2) * t_1$ ). For each tested solvent a characteristic  $t_{1/2}$  value is thus obtained with as example,  $t_{1/2} = 150$  s for ethanol and  $t_{1/2} = 600$  s for diethylether. These distinct values for each solvent, illustrate also the different kinetics of interaction between the materials and the solvents.



**Figure 9.** Emission spectra of **PU-C<sub>5</sub>** as function of solvent vapor exposure duration (a) ethanol and (b) water, recorded at  $\lambda_{\text{ex}} = 330$  nm. Corresponding time-dependent plots of % increase and decrease of the integrated intensity of the emission band of (c) ethanol and (d) water.

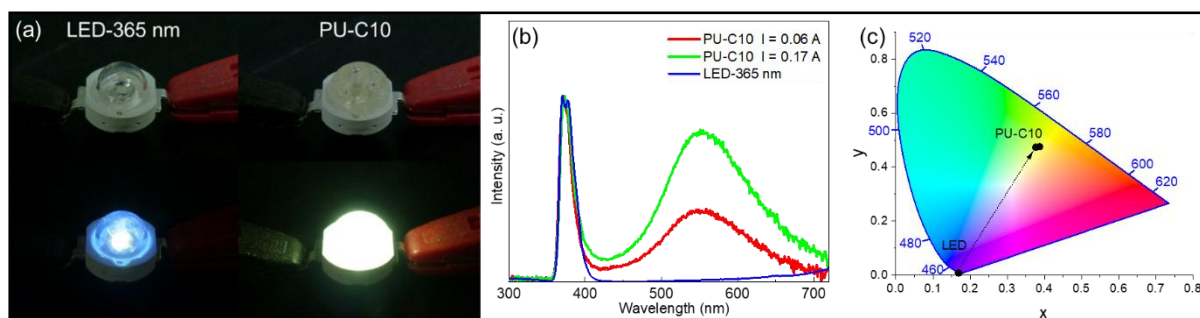
Among the different tested solvents, those inducing emission quenching are those that can swell the polymers. Indeed, swelling measurements indicate that solvents with the highest swelling rate correspond to those inducing emission quenching effect such as ethanol, dichloromethane and diethyl ether (experimental details and swelling rate values in SI). Therefore, the quenching mechanism can be attributed to non-radiative de-excitations of the cluster's emission induced by the presence of the solvent molecules within the matrix. This effect can be correlated to the weak emissivity of the cluster in solution and its demonstrated AIE (Aggregation Induced Emission) properties.<sup>64</sup> Indeed, in solution, collisions with solvent molecules and flexibility of the organic ligand is detrimental to radiative phenomena in opposite to the more rigid solid-state upon aggregation. Accordingly, a swollen polymer hosting solvent molecules gains mobility favoring non-radiative de-excitations. This effect can even be more important in the **PU-C<sub>x</sub>** polymers for which the cluster is covalently linked to the polymeric chains.

The absence of emission quenching for water and alkane solvents can be related to their non-ability to swell the polymers as testifying by their very low swelling rate values (SI). Whereas no effect on the emission intensity is expected, the exaltation is rather difficult to rationalize. The very low amount of solvent adsorbed in the polymer upon exposure to these poor solvents may be an explanation. Indeed, water can form hydrogen bonds with urethane functions thus inducing new constraints within the materials.<sup>66</sup> The lack of significant swelling and a more rigid environment would thus enhance radiative de-excitations of the cluster's emission. A more precise mechanism at the origin of the solvent effect is difficult to establish at this stage. Nonetheless, these **PU-C<sub>x</sub>** materials provide a rapid and clear visual response to solvent exposure that can be relevant for sensor applications. Detection of

air pollutants such as toxic solvents is currently a main societal issue. Studies targeting the detection of chemicals such as aliphatic aldehydes will be the subject of future work.

### Lighting applications.

The luminescence characteristics and the ease of process of the **PU-C<sub>x</sub>** functional polymers make them particularly attractive and convenient to develop new phosphor materials for LED applications. The copper iodide cluster emitting in the yellow range can indeed be envisioned as an alternative to the commercial YAG:Ce inorganic material, usually employed in phosphor-converted white LEDs.<sup>67,68</sup> In addition, considering the relative natural abundance of copper element, these complexes are more readily accessible compared to lanthanide-based compounds. The broad emission band, the relatively high PLQY and the large Stokes shift, combined with the strong absorption in the UV range of the **PU-C<sub>x</sub>** polymers, constitute actually relevant characteristics for LED devices.



**Figure 10.** (a) Photos of a 365 nm emitting LED chip without and with coating of **PU-C<sub>10</sub>**. (b) Corresponding emission spectra with LED powered by a 6 V electric source and a working current of 60 and 170 mA. (c) CIE chromaticity coordinates diagram (1931) of the 365 nm LED without and with **PU-C<sub>10</sub>** coating.

A 365 nm LED was therefore coated with **PU-C<sub>10</sub>** polymer shaped as a hemisphere. As shown in Figure 10a, the deep blue emission of the 365 nm LED is converted into a bright yellow emission with the **PU-C<sub>10</sub>** coating. In the corresponding spectra, the emission band of the polymer and that of the LED are both present (Figure 10b). By applying a higher working current, the contribution of the yellow emission can be even increased. The polymer coating greatly changes the LED characteristics with CIE chromaticity (x, y) coordinates from (0.17, 0.01) to (0.38, 0.47) and (0.39, 0.48) (Figure 10c). The resulting lighting properties are relevant for indoor lighting applications with CRI values of 66 and 68 with a color temperature of 4574 and 4375 K lying in the warm white lighting range.<sup>69,70</sup> These results are noticeable considering the absence of additional phosphors, as commonly reported. These values can additionally be easily optimized thanks to the versatility of these functional polymers for which the matrix properties and the cluster content can be neatly adjusted according to the targeted applications.

### Conclusion.

The reported functionalized polyurethane materials are synthesized by using copper iodide complexes as cross-linking agents. To our knowledge, they constitute the first organic polymer materials which covalently incorporate photoactive multinuclear copper iodide complexes as cross-linkers. The incorporation through covalent grafting of this photoactive compound brings appealing stimuli-responsive luminescence properties to these polymer materials. These densely cross-linked materials are highly transparent in the visible and present an intense yellow phosphorescence. They display luminescence thermochromism by displaying emission color and intensity change as function of the temperature. Upon cooling, the yellow emission becomes blue, in accordance with the cluster's properties. Emission quenching is also observed upon heating. The thermochromic characteristics make these materials relevant in luminescent thermometers applications. The studied photoluminescent materials are also sensitive to solvents by displaying a contrasted and easily

detected ON-OFF effect depending on the solvent nature. Indeed, some solvents quench the emission and some other, in opposite, can enhance it. These phenomena can be related to the change of the de-excitation relaxation of the copper iodide complex. The potential of these emitting polymers was additionally evaluated as phosphors in solid-state lighting. By taking advantages of the shaping potentialities of the materials, the UV emitted light of a LED was successfully converted into a warm yellow light. The present results highlight the effectiveness of using copper iodide complexes as cross-linking agents to bring enhanced functionalities to polymer materials. Based on the rich photophysical properties of the large family of copper halide complexes, this strategy can be applied even more generally for designing original polymer materials which hold promise as a new type of low cost and sustainable stimuli-responsive light-emitting materials with multiple applicative perspectives.

**Supporting Information.** Experimental details, DSC traces, optical microscope images, additional optical characterization data and solvent-dependent emission spectra. This information is available free of charge at <http://pubs.acs.org>.

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**Conflict of Interest.** The authors declare no conflict of interest.

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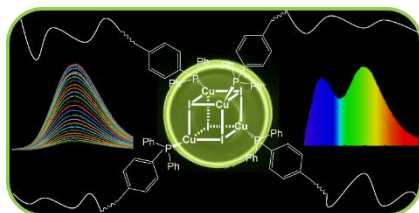
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### Photoactive CuI-crosslinked Polyurethane Materials



Polyurethane-based materials incorporating multinuclear copper iodide complexes as light-emitting crosslinkers exhibit luminescence thermochromic and solvatochromic properties and can be used as phosphors in lighting applications.