Thermochromic 3D printed polymeric waveguides

(Article begins on next page)

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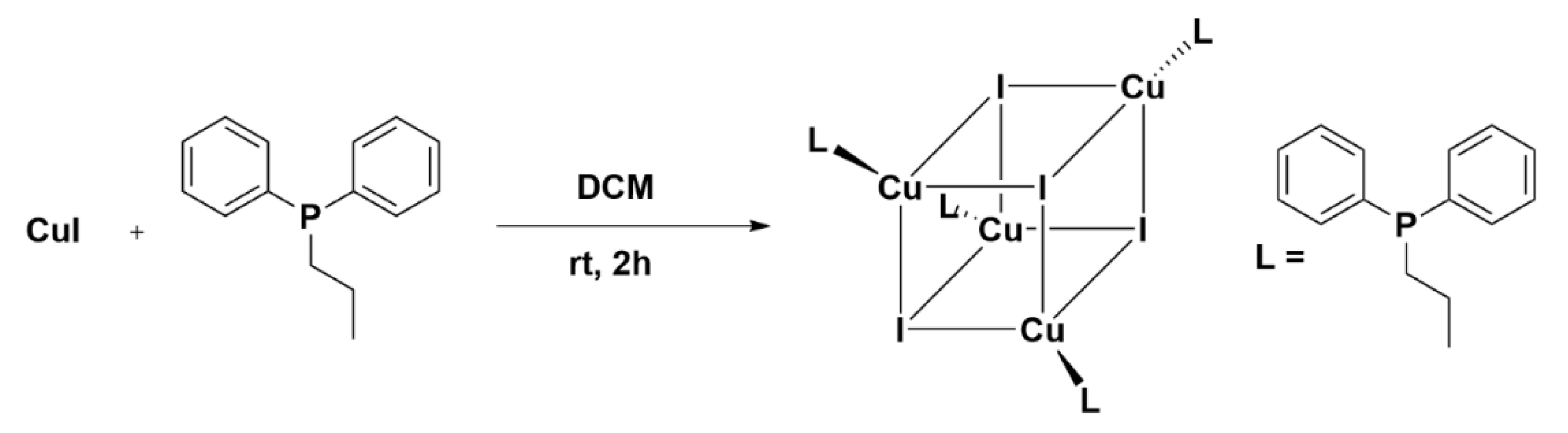
Introduction

Three-Dimensional printing (3DP) is an innovative technique, nowadays used both in industrial and academic fields. The high versatility and user-friendliness, the progressive printers' price knock off and the considerable saving of raw materials are just few advantages of these technologies. Among others, the **Digital Light Project (DLP)** printer is under investigation to widen the palette of printable formulations, producing innovative functional 3D printed devices. The exploitation of new functional materials, for example **temperature-, light- and pH-responsive polymers**, is one of the most interesting survey field.[1]

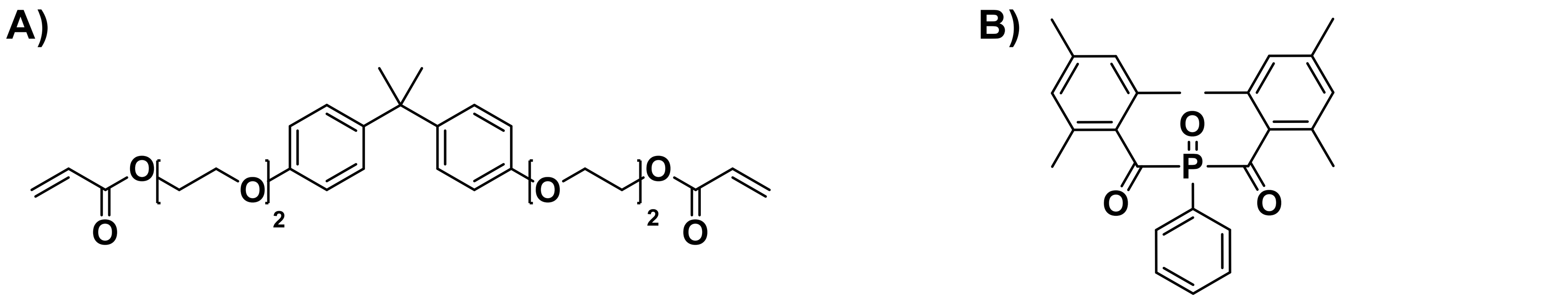
Copper iodine-based clusters were deeply investigated in the last years as easily synthesizable compounds that can act as downshifter, absorbing in UV and emit in visible range.[2] These compounds also change the emitting properties according to the temperature or to the rigidity of the system.[3] The **excellent Stokes shift** and **the high quantum yield** allow the production of polymeric **3D printed waveguides** using the DLP configuration with an almost totally transparent matrix, with promising final resolution and efficiency in guiding light from one.

Synthesis and photopolymerization



Synthetical pathway to synthetize propyl diphenylphospine copper iodine-based clusters

A) B)



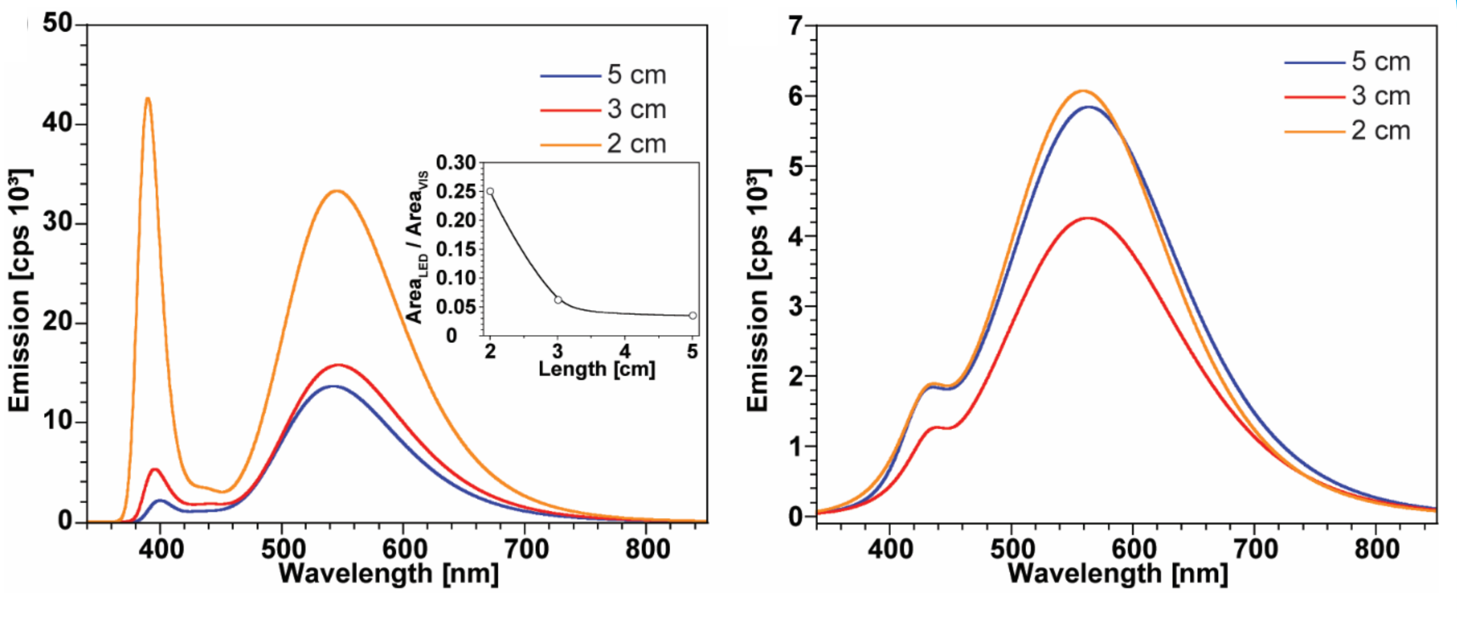
Bisphenol A ethoxylate diacrylate

Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

A) Monomer used in the formulation for the Digital Light Processing (DLP).

B) Photoinitiator used to start the radical polymerization.

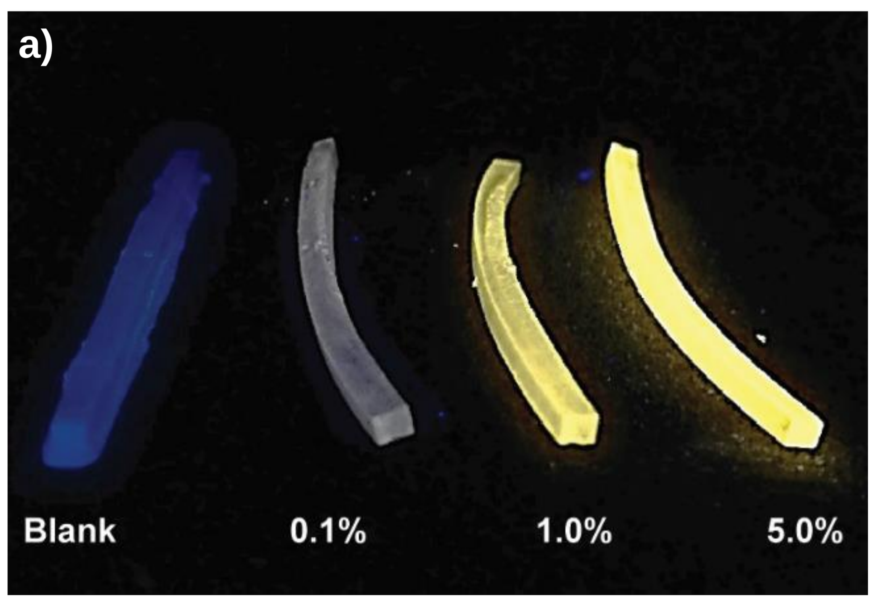
Guiding-light efficiency



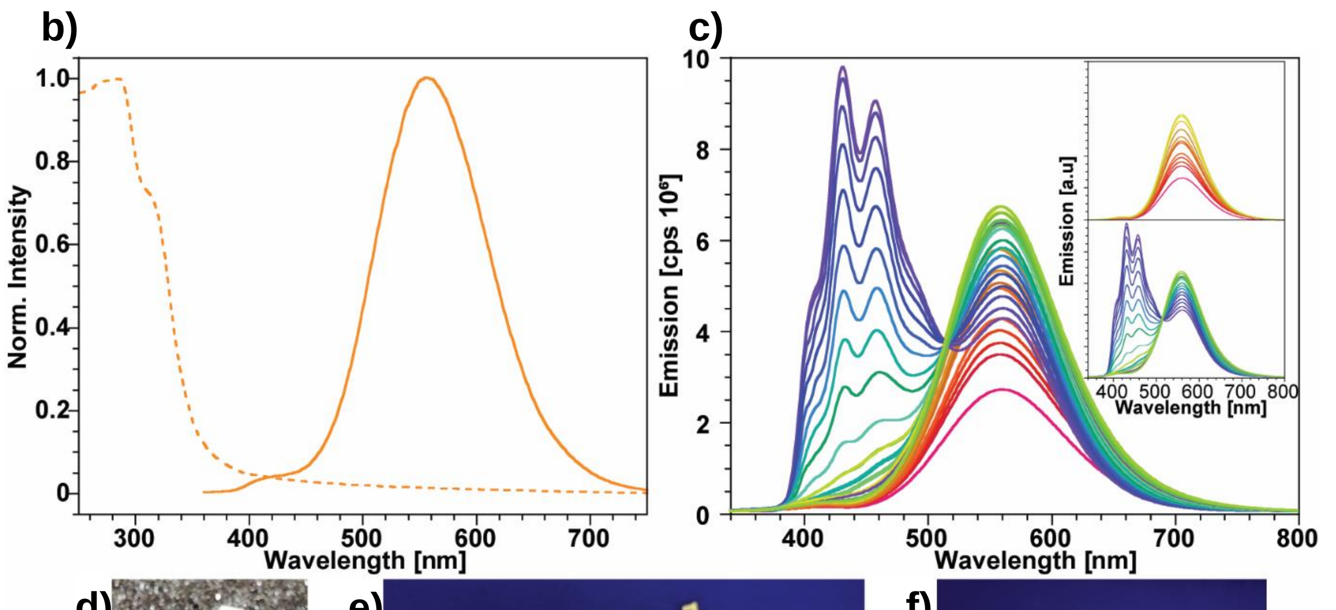
Emitting properties of 3D printed polymeric waveguides of different lenghts in (**a**) direct and (**b**) side pumping configuration. In the direct configuration excitation and detector are in the same direction of the waveguide, while in the side one the excitation in perpendicular to the waveguide.

In (**a**) the irradiation peak is clearly visible, due to the non complete absorbance of the waveguides, but it can be reduced increasing the length. In (**b**) the excitation is not visible, but the shoulder is due to the emission of the polymeric matrix.

Properties of the 3D printed matrix

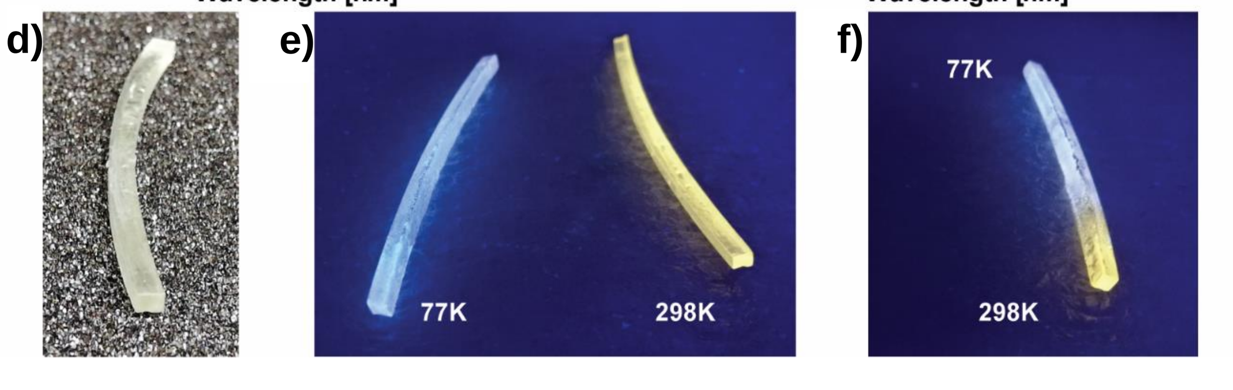


a) Emitting properties under 365 nm UV irradiation of polymeric waveguides with an increasing concentration of copper cluster (wt.%). The sample without the cluster (Blank) can emit only a weak blue light due to the polymeric matrix.



b) Absorbance (dashed) and emission (continuous) spectra of 3D printed polymeric waveguides containing 0.1 wt% of copper cluster.

c) Emission properties at different temperatures (from RT to 77K).



3DP polymeric waveguide under ambient light (**d**), under UV (365 nm) light at different temperatures (77 K and 298K) (**e**) and partially immersed in liquid nitrogen (**f**).

Conclusion

In this study we have demonstrated the possibility to use low toxic, cheap and available compounds instead of using rare earth or transition metals complexes, as usually reported in literature. These compounds can be easily solubilized in the liquid formulation for the DLP printer and 3D printed with good final resolutions achieving final complex shapes and a totally transparent polymeric matrix. The efficiency in light guiding is also demonstrated, showing the possibility to use these type of materials as polymeric waveguides in a totally innovative way. Moreover, the changes in emitting properties of these compounds open the possibility to use these devices as temperature sensors in many applications.

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