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# **Polyurethanes prepared from cyclocarbonated broccoli seed oil (PUcc): new biobased organic matrices for incorporation of phosphorescent metal nanocluster**

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## **Abstract**

New biobased polyurethanes were synthesized from cyclocarbonated broccoli seed oil and different di- or tri-amines. The isocyanate-free route to synthesize these polyurethanes was divided into three steps: the broccoli seed oil was first epoxydized, then carbonated with CO<sub>2</sub> at a pressure of 50 bar to convert oxiranes into cyclic carbonates and finally polyurethanes were prepared through the reaction of the cyclocarbonated oil with three different di- or tri-amines, i.e. butylene diamine, *m*-xylene diamine and bis(hexamethylene triamine). The chemical reactions were monitored by FTIR, NMR and MS-ESI and mechanical properties of thus-prepared polyurethanes were determined by DMA and tensile characterisation. An UV responsive material was finally prepared from butylene diamine based polyurethane integrating phosphorescent molybdenum nanoclusters.

## **Introduction**

### *Broccoli seed oil*

In recent years, there has been a growing interest in developing new polymers from renewable resources in order to find alternative feedstock to fossil fuels.[1-4] Such biobased polymers can potentially replace common polymers traditionally obtained from petrochemical derivatives. Among all the products obtained from agricultural resources that constitute interesting raw materials useful in the field of biobased polymers, vegetable oils present many advantages: they are available at moderate cost, at great quantities, renewable, harmless for the environment, non-toxic, and they are good candidates for the elaboration of innovative

green materials.[5-7] The present study is focused on the development of a new biobased polymer synthesized from broccoli seed oil (BO). Actually, this BO is a by-product generated during the manufacture of a dietary complement extracted from the broccoli bean and it is disposable in great quantities. Compared to conventional edible oils sometimes used in materials synthesis or processing, like soybean oil[7, 8], BO oil is particularly rich in long-chain fatty acids, especially erucic acid and contains an average of four insaturations available for further chemical modification[2]. Moreover, there is no competition between using broccoli oil for food and oil for material production, because, considering its high content in erucic acid (about 40%), the broccoli oil is not suitable for human consumption. Therefore, on one hand, there is no dilemma, like for most of other vegetable oils, between food and non-food uses of agricultural resources. It is thus important in these conditions to find some new added-value applications for broccoli oil that would otherwise be disposed of as waste, generating high biological oxygen demand, or simply used in animal nutrition. On the other hand, there is an increasing interest in finding new way to integrate emissive inorganic nanocomponents in easy to handle matrices to develop low cost light energy converter for uses in optoelectronic, photovoltaic, lighting or display applications.[9-13] Doping organic polymers with inorganic phosphors appears as a valuable strategy in terms of shaping ability or deposition method of usual ceramic like inorganic nanocomponents.[14-16] Thus, combining BO and inorganic phosphors obtained by high temperature solid state synthesis in a single and homogeneous hybrid matrix seems in a first attempt particularly challenging and presents undoubtedly a high interest from the ecological and economical point of views.

### *Polyurethanes from oils*

Broccoli oil, which is, like most of other vegetable oils, a triester of glycerol and fatty acids is not really considered as reactive. In order to use oils in polymer synthesis, they have to be chemically modified. Two sites are suitable for chemical modification to improve reactivity of vegetable oils: double bonds and ester bonds. Therefore, in order to prepare oil-based polymers, insaturations have to be converted to more reactive functional groups such as epoxide groups, acrylate groups, hydroxyl groups etc. Recently, broccoli oil was functionalized by the introduction of epoxide groups in order to prepare some new high temperature lubricants and stabilisers useful for polyhydroxyalkanoates transformation[2]. The epoxidation was performed in a simple way following a classical procedure involving the *in situ* formation of performic acid from formic acid and hydrogen peroxide that carried out the epoxidation of the four double bonds of the triglyceride.

The purpose of the present study was to prepare from such epoxidized broccoli oil (EBO) some new polyurethanes that could further be used as UV responsive biobased materials through incorporation of molybdenum nanoclusters. Polyurethanes, conventionally synthesized from the reaction between isocyanates and diols, are extensively used in a huge variety of different applications like paints, coatings, adhesives, elastomers, sealants etc. due to their high versatility[8]. Their mechanical, thermal and chemical properties can be tailored by the nature and length of the diols and diisocyanates chains. Nevertheless, the major drawback of polyurethanes is related to the toxicity of diisocyanates reactants derived from phosgene that might cause environment hazards and that are also known to have health effects[17] such as skin irritation and asthma. In sustainable applications, polyurethanes can effectively sometimes be prepared from renewable polyols, but isocyanates precursors are generally still prepared from petroleum products[18].

Now therefore, latest advances in vegetable oil based polymers have focused on the replacement of conventional petro-based polyurethanes, commonly formed by reacting a di- or polyisocyanate with a polyol, with fully biobased polyurethanes prepared from oil derivatives. Among these new polyurethanes, those obtained from chemical reaction between cyclic carbonate and diamine have gain major interest in the last few years[18-20]. Indeed, the isocyanate-free route to generate carbamate group is an efficient way to produce polyhydroxyurethanes (PUOH) also called non-isocyanate polyurethanes (NIPU) those are not hazardous for human and not harmful to the environment. With regard to the name, it is generally better to name things for what they are than for what they are not. For this reason we suggest the term of PUcc to describe polyurethane synthesized from cyclocarbonate.

In the present study, new vegetable oil-based polyurethanes were synthesized in three steps: the broccoli oil was first epoxidized and then carbonated with CO<sub>2</sub> at a pressure of 50 bar to convert insaturations to cyclic carbonates. Finally, PUcc were obtained through the reaction of carbonated oil with different di- or tri-amines. Thus-prepared broccoli oil PU were analysed and characterised. The different steps of the synthesis of PUcc from broccoli oil are illustrated in figure 1.

Phosphorescent transition metal octahedral nanoclusters of general formula  $A_nM_6X^i_8L^a_6$  (A = alkali cation, M = Mo, Re or W, X<sup>i</sup> = halogen or chalcogen, L<sup>a</sup> = halogen or organic moieties) were chosen as inorganic nanoemitters for the design of emissive hybrids. With a size at the nanometer scale, these inorganic species can be considered as intermediates between molecular transition metal complexes and nanoparticles. Their scaffold contains six Mo, Re or W atoms linked by metal-metal bonds which confers them specific intrinsic

properties and, in particular, a high phosphorescence in the red-NIR area for excitation wavelengths ranging from 350 nm up to 540 nm.[21-23] They are obtained as ternary salts ceramic-like powders by high temperature solid state synthesis.[24] Their integration in organic matrices such as liquid crystal[25, 26] or organic polymers[16, 27-31] is an emerging field in which several groups, including our, are contributing. Several strategies can be employed to reach this goal. Up to now, the most versatile is the one chosen in this study, known as the ionic approach. It relies on the replacement of the ternary salt alkali cations by tailor-made functional organic ones *via* a metathesis reaction in solution. The function beard by the organic cations can thus react with the host matrix or host matrix precursor, leading to a hybrid nanocomposite copolymer in which the metal cluster anions are homogenously integrated in the organic matrix.[29]  $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$  cluster compound was chosen as the hybrid precursor because it provides one of the most efficient red-NIR emitter in the  $\text{Mo}_6$  metal cluster family : the  $[\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6]^{2-}$  anion.[30, 32, 33].

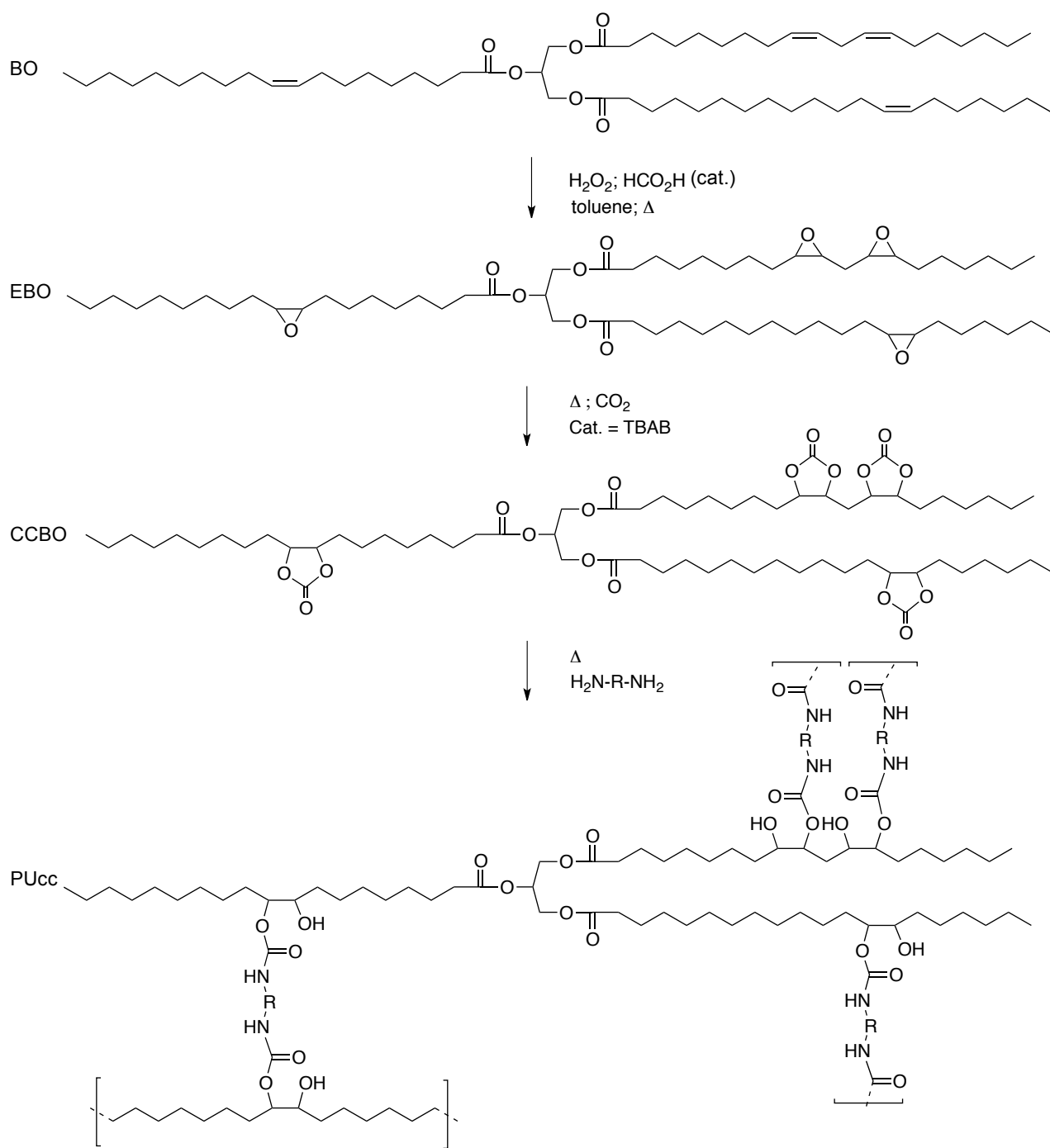


Figure 1. PUcc synthesis from broccoli oil.

## Experimental part

### Materials and reagents.

All reagents and solvents were used directly from the supplier without further purification unless noted.  $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{C}_2\text{F}_5\text{COO})_6$  precursor was synthesized as described in the literature with conform analytical data.[16]

### Synthesis.

#### *Preparation of epoxidized Broccoli seed oil (EBO).*

BO (300 g, 0.32 mol, 1 equiv.), toluene (1.4 L) and formic acid (24 mL, 0.64 mol, 2 equiv.) were mixed into a well stirred reactor. Hydrogen peroxide (35% wt in water) (143 mL, 1.91 mol, 6 equiv.) was added dropwise to the reaction mixture at 50°C. The reaction mixture was kept at the same temperature and monitored by ElectroSpray Ionisation Mass Spectrometry (MS-ESI). After 25h, the aqueous phase was extracted twice with toluene and the combined organic phases were dried ( $\text{MgSO}_4$ ). The solvent was then evaporated under reduced pressure affording the EBO (319 g, 99%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm) 0.79-1.01 (m, 9H,  $\text{CH}_3$ ), 1.18-1.77 (m, 86H,  $\text{CH}_2$ ), 2.22-2.27 (m, 6H,  $\text{CH}_2\text{-C=O}$ ), 2.82-3.15 (m, 7.8H (3.9 epoxides per molecule), epoxides), 4.07 (dd,  $J = 5.9, 11.9$  Hz, 2H,  $\text{CH}_2\text{-O}$ ), 4.22 (dd,  $J = 4.4, 11.9$  Hz,  $\text{CH}_2\text{-O}$ ), 5.17-5.22 (m, 1H,  $\text{CH-O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$  (ppm) 14.0 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 24.8 ( $\text{CH}_2$ ), 26.6 ( $\text{CH}_2$ ), 27.9 ( $\text{CH}_2$ ), 28.9-29.7 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 34.0 ( $\text{CH}_2\text{-C=O}$ ), 54.1 (epoxides), 56.7-57.2 (epoxides), 62.1 ( $\text{CH}_2\text{-O}$ ), 68.9 ( $\text{CH-O}$ ), 172.8-173.3 ( $\text{C=O}$ ); MS-ESI  $m/z$   $[\text{M}+\text{Na}]^+$  : 927.8, 941.8, 955.8, 969.8, 983.8, 997.8, 1011.8, 125.8, 1039.8, 1053.8, 1067.9, 1081.9, 1095.8.

*Preparation of cyclocarbonated Broccoli seed oil (CCBO).* EBO (30.0 g) and tetrabutylammonium bromide (TBAB, 4% w/w) were blended in a glass tube inserted in a pressure reactor connected to a  $\text{CO}_2$  bottle and equipped with a manometer and a magnetic stirrer. The reactor was pressurized with  $\text{CO}_2$  up to 50 bar (5 MPa) and placed in an oil bath at 120°C for determined time. The progress of the carbonatation reaction was followed by NMR and Fourier Transform InfraRed Spectroscopy (FTIR). At the end of the reaction, the catalyst was removed by water extraction (x2).

*Preparation of PUcc : general procedure.* CCBO (2.0g, 1.70 mmol) was placed in a small glass tube heated at 70°C in a water bath. The diamine or triamine (2 equiv., 3.39 mmol) was then added and the homogenous blend was vigorously stirred. Three different kind of amine were used: an aliphatic diamine, the butylene diamine (BDA), an aromatic diamine, the *m*-xylene diamine (*m*-XDA) and an aliphatic triamine, the bis(hexamethylene triamine)

(HMTA). The obtained viscous solution was then poured into a 15 mm x 40 mm silicon mould. The mould was disposed in an oven at 70°C for 12 h and then at 110°C for 3 h. The flexible materials obtained in these conditions were slightly yellow and transparent. They were thus characterised by ATR-FTIR, DMA and stress-strain testing. Samples names and compositions are summarized in table 1. As regards HMTA based samples, the carbonate to amine ratio was calculated assuming that both primary and secondary amine participates to the reaction with cyclocarbonate. In these conditions, the 1:1.33 carbonate to amine ratio finally correspond to a 1:1 carbonate to primary amine ratio, assuming that secondary amine may not react with the cyclocarbonate functions under mild condition[19].

**Synthesis of 4-amino, N-ethylpyridinium Iodide salt.** Ethyl iodide (10.6 mL, 0.13 mol, 2.5 eq) was added dropwise to a suspension of 4-aminopyridine (5 g, 0.053 mol) in dry acetone (55 mL) in an ice-water bath to keep the temperature below 30°C. The reaction was kept at room temperature overnight. The white precipitate formed during the reaction was filtered and washed with acetone (30 mL). The solid was dried under vacuum overnight to afford the salt as a white powder (12.6 g, 95%).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz), δ (ppm) 1.35 (t, J = 8 Hz, 3H, CH<sub>3</sub>), 4.16 (q, J= 8 Hz, 2H, CH<sub>2</sub>), 6.83 (d, J = 8 Hz, 2H, H<sup>Ar</sup>), 8.01 (bs, 2H), 8.21 (d, J = 8 Hz, 2H, H<sup>Ar</sup>). Elemental analysis: calculated for C<sub>7</sub>H<sub>11</sub>N<sub>2</sub>I: C, 33.62; H, 4.43; N, 11.20; found C, 33.54; H, 4.46; N, 10.98

**Synthesis of (4-aminoN-ethylpyridinium)<sub>2</sub>Mo<sub>6</sub>I<sub>8</sub>(C<sub>2</sub>F<sub>5</sub>COO)<sub>6</sub>.** A solution of the pyridinium salt (1 g, 0.35 mmol) in methanol (30 mL) was slowly added to a solution of Cs<sub>2</sub>Mo<sub>6</sub>I<sub>8</sub>(C<sub>2</sub>F<sub>5</sub>COO)<sub>6</sub> (0.76 g, 0.70 mmol) in acetone (30 mL). The mixture was stirred for 1h. The solvent was evaporated and the crude dispersed in acetone. A white precipitate was obtained which was filtered through Celite<sup>®</sup>. The dark orange solution was evaporated to afford a dark orange solid in quantitative yield.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>): δ (ppm) 1.36 (t, J = 8, 3H, CH<sub>3</sub>), 4.14 (q, J = 8, 2H, CH<sub>2</sub>), 6.81 (d, J = 8, 2H, H<sup>Ar</sup>), 8.02 (bs, 2H), 8.19 (d, J = 8, 2H, H<sup>Ar</sup>). <sup>19</sup>F-NMR (376 MHz, DMSO-d<sub>6</sub>): δ (ppm) -81.6 (3F), -119.5 (2F). EDS: No Cs, Mo, 11.24, I, 14.78, F, 73.98; Elemental analysis: calculated for C<sub>32</sub>H<sub>22</sub>F<sub>30</sub>I<sub>8</sub>Mo<sub>6</sub>N<sub>4</sub>O<sub>12</sub>: C, 13.65; H, 0.79; N, 1.99; found C, 13.48; H, 0.87; N, 2.11.

**Integration of inorganic nanocluster in PU<sub>CC</sub>.** The nanocluster was incorporated in m-XDA based PU<sub>CC</sub> samples. The cluster (100 mg, 4% w/w) was dissolved in the diamine (462 mg, 3.39 mmol., 2 equiv.). The resulting mixture was added to the CCBO (2g, 1.70

mmol., 1equiv.) and poured into a silicon mold (15 mm x 40 mm). The mold was disposed in an oven at 70°C for 12 h and then at 110°C for 3 h.

### **Characterization**

**NMR.** Nuclear magnetic resonance spectra were recorded at 400 MHz ( $^1\text{H}$ ), 100 MHz ( $^{13}\text{C}$ ) and 376 MHz ( $^{19}\text{F}$ ). For  $\text{CDCl}_3$  solutions, the chemical shifts ( $\delta$ ) are reported as parts per million (ppm) referenced to the appropriate residual solvent peak. Coupling constants are reported in Hertz (Hz). Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogen atoms, attribution). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), bs (broad singlet). The NMR peak assignments were determined from 2D NMR experiments such as COSY, HSQC, HMBC.

**Mass spectra.** Mass spectra were performed on a MS-ESI spectrometer and are reported as m/z. Masses are reported for the molecular ion  $[\text{M}+\text{Na}]^+$ .

**ATR-FTIR.** For infrared spectroscopy a Perkin-Elmer Spectrum 100 system infrared spectrometer was used in attenuated total reflectance (ATR) mode using a DTGS detector (4  $\text{cm}^{-1}$  resolution) with the spectral range of 650–4000  $\text{cm}^{-1}$ . In these measurements 15 scans were applied and the data were collected and analysed using the Spectrum ES 5.0 software. The sample is placed onto the surface of a diamond prism and the infrared radiation is collected after total reflection from the diamond–sample interface.

**Stress-strain testing.** Tensile strength, elongation at break and Young's modulus were inferred from tensile tests carried out using Shimadzu Autograph AGS-X series Universal Testing Machine equipped with a load cell of 1 kN. Uniaxial stress-strain and ultimate properties were performed onto normalized samples (dumbbell specimens according to the standard iso 527-2 type 1BA) employing rubber jaws and a crosshead speed of 10  $\text{mm}\cdot\text{min}^{-1}$  or 50  $\text{mm}\cdot\text{min}^{-1}$ . Data were the average of five samples. Stress-strain curves plotted on figure 5 were obtained from experimental data as close as possible to the mean mechanical properties.

**DMA.** *Dynamic Mechanical Analysis.* The viscoelastic properties of the PUcc were measured with a DMA instrument (Q800, TA Instruments). Rectangular specimens, 18 mm in

length, 13 mm in width, and 2 mm in thickness, were prepared. The measurements were taken in single cantilever mode at a frequency of 1Hz and deformation amplitude of 20  $\mu\text{m}$ . The temperature ranged from -100 to 100°C at scanning rate of 3°C.min<sup>-1</sup>. The storage modulus (E'), loss modulus (E''), and loss factor (tan  $\delta$ ) were measured as a function of the temperature.

**Elemental Analysis.** Elemental analyses were performed in the CRMPO with a Microanalyser Flash EA1112 CHNS/O Thermo Electron.

**EDS.** Energy dispersive spectroscopy. EDS analysis were performed on a JEOL JSM 7100F scanning electron microscope equipped with a XEDS Oxford field spectrometer.

**Emission measurements.** Luminescence spectra were recorded with an ocean optic QE6500 photodetector mounted via an optical fiber on an optical microscope Nikon 80i equipped with a Nikon Intensilight irradiation source and a Linkam LTS420 hot stage. In order to take into account the nonlinear sensitivity of the set up, it was calibrated with an Ocean Optics HL-2000-CAL Calibrated Tungsten Halogen Light Source. Optical filters were used to select the excitation wavelength with a bandwidth of 330-380 nm.

## Results and discussion

**Epoxidized broccoli seed oil (EBO).** The epoxidation of the broccoli seed oil (BO) has been described by our research group in a previous paper.[34] It follows a classical procedure involving the *in situ* formation of performic acid from formic acid and hydrogen peroxide that carried out the epoxidation of the 3.9 double bonds of the triglyceride in toluene (figure 1). The recycling of formic acid permits to use it in a catalytic amount. This epoxidation process based on an *in situ* generated performic acid is the cheapest method used at the industrial scale and it is actually the major route of preparation of the epoxidized soybean oil. We further optimised the oxidation process reducing the equivalencies of hydrogen peroxide (6 equiv./BO) and catalytic formic acid (2 equiv./BO). The reaction mixture is kept at 50°C for 24h to reach a complete epoxidation as demonstrated by MS and NMR monitoring.

**Cyclocarbonated broccoli oil (CCBO).** The reaction of CO<sub>2</sub> with EBO was performed in a pressure reactor at 100°C and 50 bar using tetrabutylammonium bromide (TBAB) as organocatalyst (2 wt%). Under these conditions, the best conversion rates were obtained after 48h hours of reaction. The progress of the carbonatation reaction was monitored by <sup>1</sup>H and <sup>13</sup>C NMR.

Figure 2 represents the FTIR spectra of carbonated broccoli oil compared to the initial epoxidized broccoli oil. The conversion was confirmed by the disappearance of the band at  $841\text{ cm}^{-1}$  characteristic of the epoxide function and the appearance of new bands at  $1802$  and  $1045\text{ cm}^{-1}$  corresponding to C=O carbonyl stretching and C-O stretching of carbonate function respectively.

The conversion of EBO to CCBO was also confirmed by  $^1\text{H}$  NMR analyses.

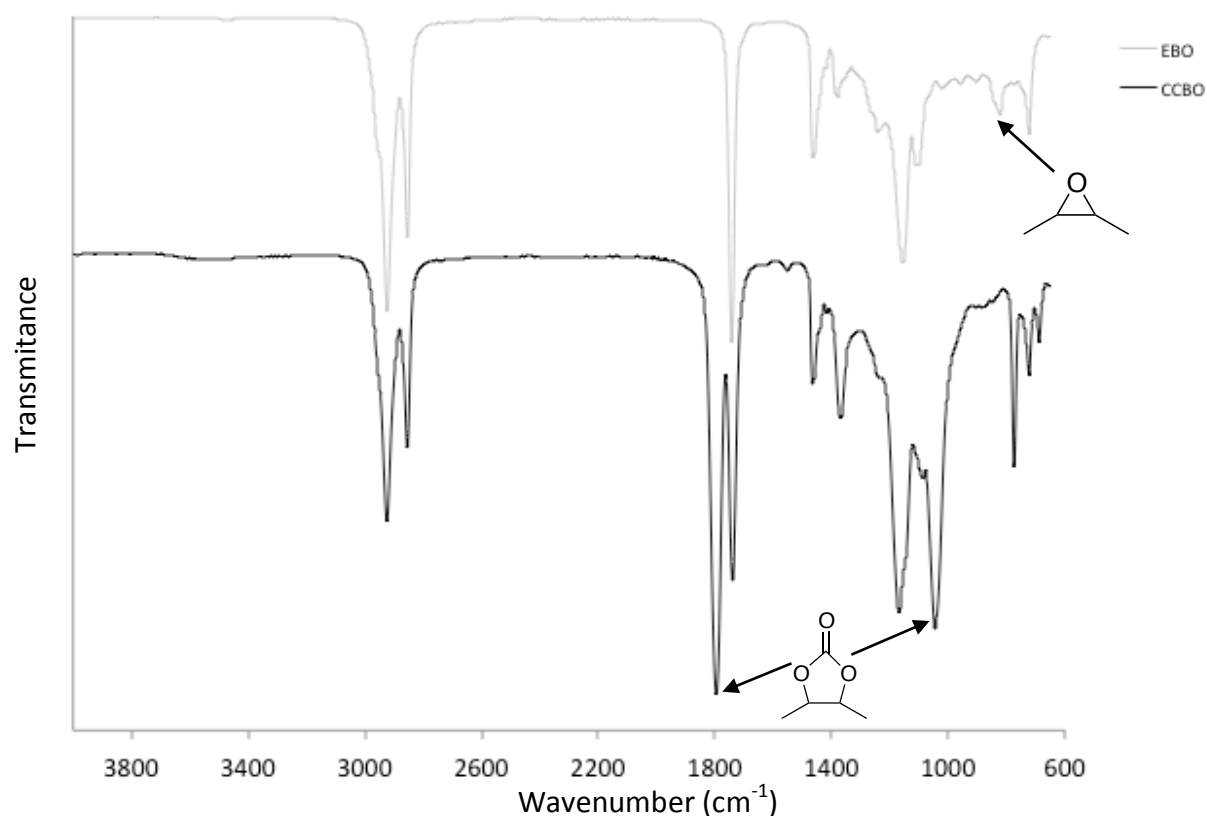


Figure 2: FTIR spectra of epoxidized broccoli oil (EBO, grey line) and cyclocarbonated broccoli oil (CCBO, black line)

### PUcc synthesis

**FTIR.** PUcc were prepared by mixing cyclocarbonated broccoli oil (CCBO) with different di- or tri-amines. The reaction was monitored using infrared spectroscopy. The FTIR spectra of synthesized PUcc reported on figure 3 are showing the same functional groups. As previously mentioned, the absorption band at  $1802\text{ cm}^{-1}$  can be assigned to the remaining cyclic carbonate. The peak at  $1742\text{ cm}^{-1}$  was correlated to the ester carbonyl of the triglyceride. The major peak appearing at around  $1694\text{ cm}^{-1}$  was attributed to the formation of urethane bonds. The amide group resulting from the aminolysis of the triglyceride ester

group[19] was noticeable as a shoulder around  $1650\text{ cm}^{-1}$  on the urethane absorption band. The broad peak between  $3400$  and  $3300\text{ cm}^{-1}$  was assigned to the OH and NH absorption band from hydroxyl and urethane groups.

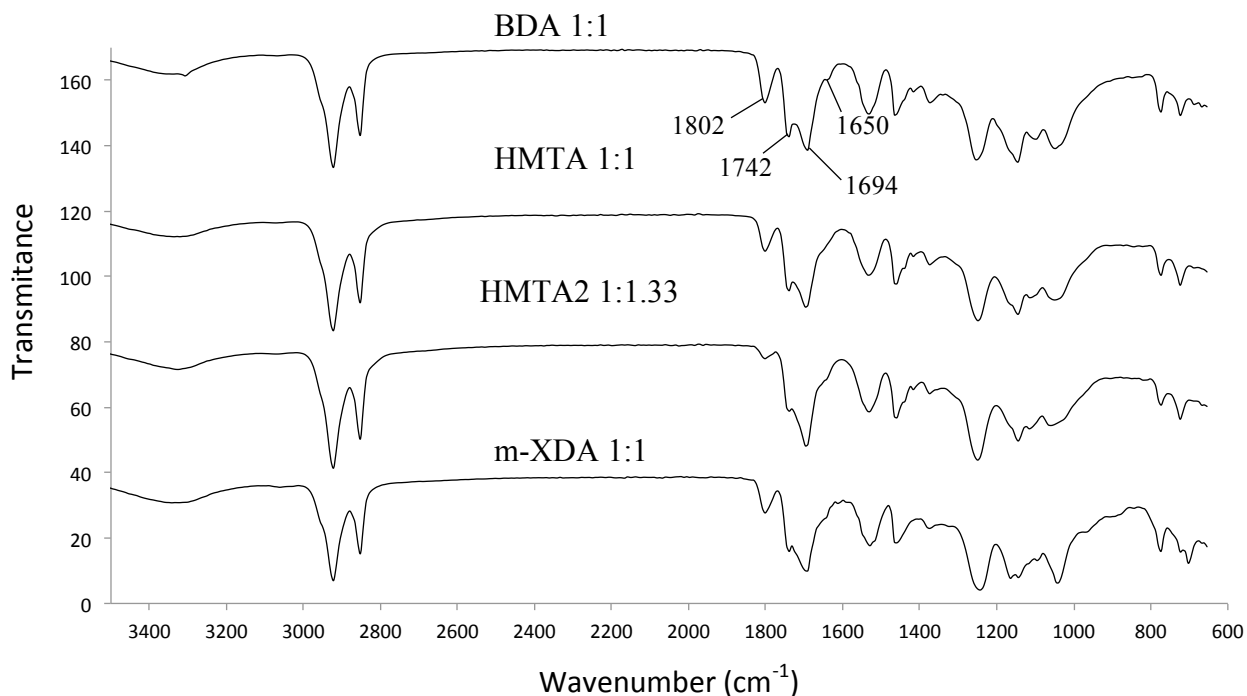


Figure 3: FTIR spectra of synthesized PUcc. (BDA=butylene diamine, HMTA=bis(hexamethylene triamine), m-XDA=m-xylene diamine)

For all samples, the residual peak at  $1802\text{ cm}^{-1}$  confirmed that all the carbonates did not react with the amines. Nevertheless, in the HMTA2 sample prepared with an excess of amine (carbonate to amine ratio 1:1.33) this carbonate absorption band was significantly lower than for other samples prepared with stoichiometric ratios of amine to carbonate. Considering this HMTA2 sample, the urethane absorption peak at  $1694\text{ cm}^{-1}$  corresponding to the urethane bond formation was also the strongest compared to the peak at  $1742\text{ cm}^{-1}$  assigned to the ester groups. The amide peak at  $1650\text{ cm}^{-1}$ , resulting from the glyceric ester aminolysis was observed for each sample, but its intensity was difficult to estimate considering that this small amide band only appeared as a shoulder to the strong urethane peak at  $1694\text{ cm}^{-1}$ .

## Mechanical properties

**DMA.** All the polyurethane (PUcc) obtained from different di-or tri-amines were characterized by DMA at a frequency of 1 Hz. Figure 4 shows representative temperature dependence of the storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ ) obtained for the PUcc prepared from m-XDA diamine with a 1:1 cyclocarbonate to amine ratio. The recorded DMA curves exhibited similar shape for all synthesized PUcc: the  $\tan \delta$  curve showed one major peak located around 20°C and the loss modulus curve showed for each PUcc two peaks located around 0°C and -70°C.

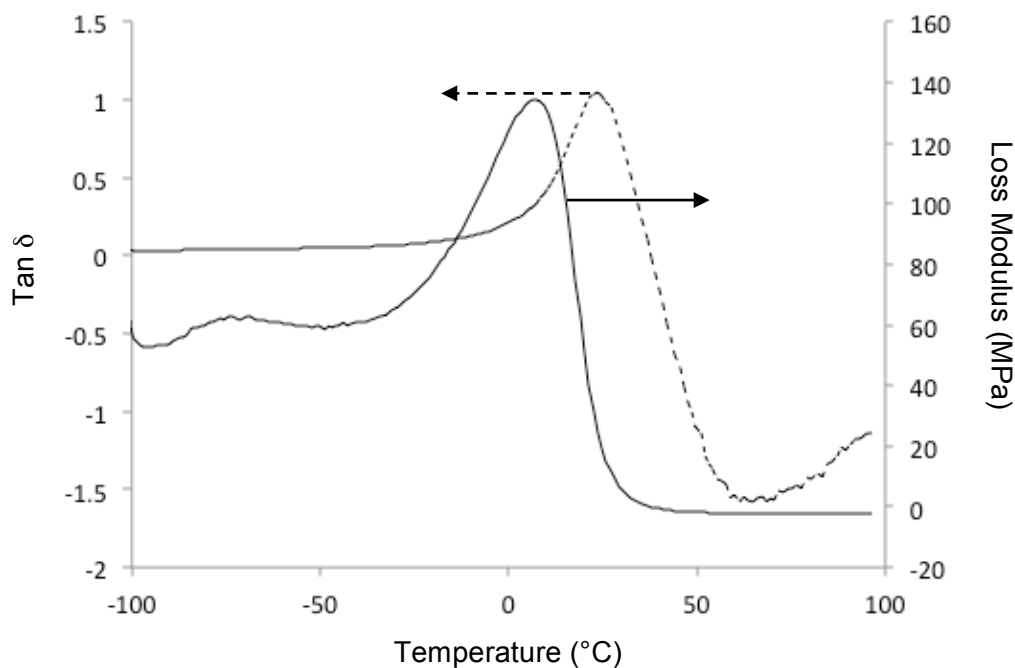


Figure 4 : Temperature dependence of the loss factor  $\tan \delta$  (dashed line) and the storage modulus (full line) at 1 Hz for m-XDA based PUcc sample.

The  $\tan \delta$  peak at around 20°C can be assigned to the  $\alpha$  relaxation and associated to the glass transition temperature ( $T_g$ ) of the synthesized polyurethanes. Glass transition temperatures ( $T_g$ ) determined from  $\tan \delta$  peak for each PUcc sample are summarized in Table 1. On the curve representing the temperature dependence of the loss modulus, the major peak around

0°C can be correlated to the primary  $\alpha$  relaxation also visible on the  $\tan \delta$  curve. The minor peak at about -70°C can be assigned to the secondary  $\beta$  relaxation. This  $\beta$  relaxation was already described in other crosslinked systems[5, 35, 36], like polyesters or other polyurethanes. This secondary relaxation can be associated to the motion of the urethane segments involved in crosslinks.

**Stress-strain properties.** Stress-strain curves of synthesized PUcc are plotted on figure 5. For all samples, the stress raised continuously with the increase of the elongation until the sample breaks. The general shape of PUcc curves derived from aliphatic amines are quite similar, but for PUcc prepared from the m-XDA aromatic diamine, the stress increased less for a net increase of the maximum elongation.

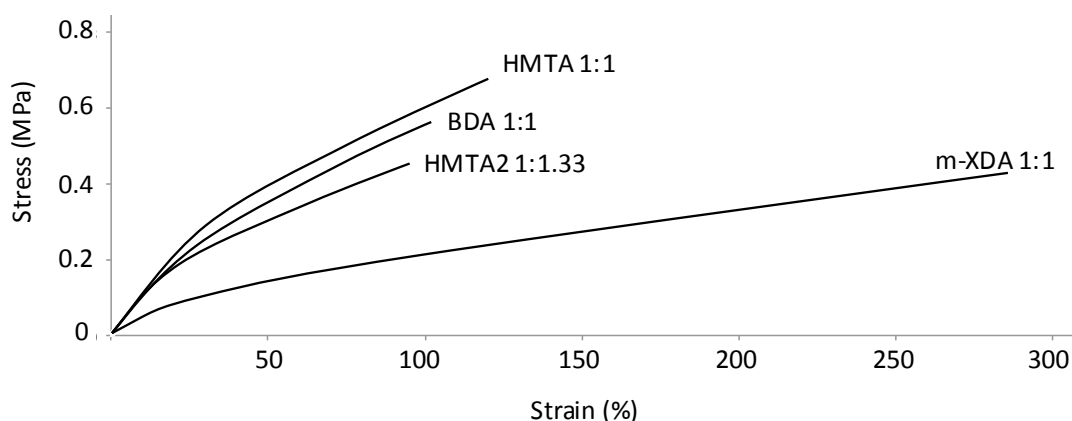


Figure 5: Stress-strain curves of synthesized PUcc

For each synthesized PUcc, mechanical data obtained from stress-strain curves and glass transition temperatures determined from DMA analysis are gathered in table 1.

Sample	Carbonate to amine ratio	Tensile Strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	T <sub>g</sub> DMA (°C)
BDA	1 : 1	0.46 ± 0.06	0.99 ± 0.08	85 ± 15	20.8
HMTA	1 : 1	0.42 ± 0.04	0.90 ± 0.18	89 ± 16	15.0
HMTA2	1 : 1.33	0.71 ± 0.02	1.15 ± 0.13	124 ± 5	19.8
m-XDA	1 : 1	0.41 ± 0.04	0.50 ± 0.09	272 ± 32	23.0

Table 1: mechanical properties of synthesized PUcc.

All PUcc presented tensile strength between 0.46 and 0.71 MPa, elongation at break between 85 and 272 % and young's modulus in the range 0.50-1.15 MPa. As noticed for curves plotted on figure 5, the mechanical properties of PUcc based on aliphatics amines (BDA and HMTA) are rather similar, with young's modulus comprised between 0.9 and 1.15 and elongations at break in the range 85-124 %. However, it can just be noted that the HMTA2 sample containing a slight excess of amine with regard to the carbonate function (1:1.33 carbonate to amine ratio) showed higher tensile strength (0.71 MPa), and less markedly higher Young's modulus (1.15 MPa) and elongation at break (124 %). This could be correlated to an increase in crosslinking density. Thus, in HMTA2 sample, the slight excess of amine function compared to carbonate causes an increase of the number of urethane segments, leading to more crosslinked samples, which exhibited enhanced tensile properties compared to other PUcc samples prepared from aliphatic amines. For the same reason, HMTA2 sample also exhibited higher glass transition temperature (19.8°C) compared to HMTA sample (15.0°C). Interestingly, the m-XDA PUcc sample based on aromatic diamine showed significantly different mechanical properties (curve m-XDA, figure 5). The young's modulus of m-XDA sample was about half the value of PUcc based on aliphatic amine and in the same time the elongation at break was about three times higher (272 %) than PUcc based on aliphatic amines. The higher glass transition temperature ( $T_g = 23^\circ\text{C}$ ) determined for the m-XDA PUcc sample can be assigned to the presence of rigid aromatic segments (ref). Thus, we could expect to obtain higher tensile strength and elastic modulus for PUcc based on the aromatic amine compared to other samples based on aliphatic amines. This was clearly not the case: m-XDA sample had lower hardness, probably due to the non-symmetric geometry of m-XDA, making hydrogen bonding between urethane groups more difficult as already mentioned by Javni *et al.* [19] From FTIR spectra (figure 3, m-XDA curve), it was also noticed that all cyclocarbonate functions were not involved in the network formation, which is correlated to the remaining absorption band at  $1802\text{ cm}^{-1}$ . It can then be considered that, in the same way, an excess of aromatic diamine was still present in the sample. The aromatic diamine in excess could then act as a plasticizer by increasing the network free volume and decreasing low energy interactions between polymer chains, leading to a more deformable material. These results clearly show that using different amines and/or different carbonate to amine ratios, it is possible to synthesize PUcc having different mechanical properties.

**Integration of inorganic nanocluster.** Figure 6 illustrates the pathway used to integrate the nanoclusters in PUcc by the ionic approach which is the most versatile one. We

chose to integrate the red-NIR phosphor in the last synthetic step of PUcc, when primary amine derivatives are used to crosslink the cyclocarbonated broccoli seed oil. Thus, we first synthesized an organic cation bearing a primary amine by reacting the 4-aminopyridine with ethyliodide in acetone. The metathesis reaction with  $\text{Cs}_2\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6$  was realized in acetone and provided the hybridized cluster in a quantitative yield. This compound was mixed with m-XDA and the same procedure as the one used to obtain m-XDA containing PUcc was followed to obtain nanocluster doped-PUcc. The homogeneity of the hybrid was assessed by EDS mapping, looking at Mo, I and F distribution within the material at the micron scale. Figure 7 presents one of the analysis realized on the doped-PUcc and shows that these three elements that constitute the central core of the nanocluster units are homogeneously distributed within the polymer matrix.

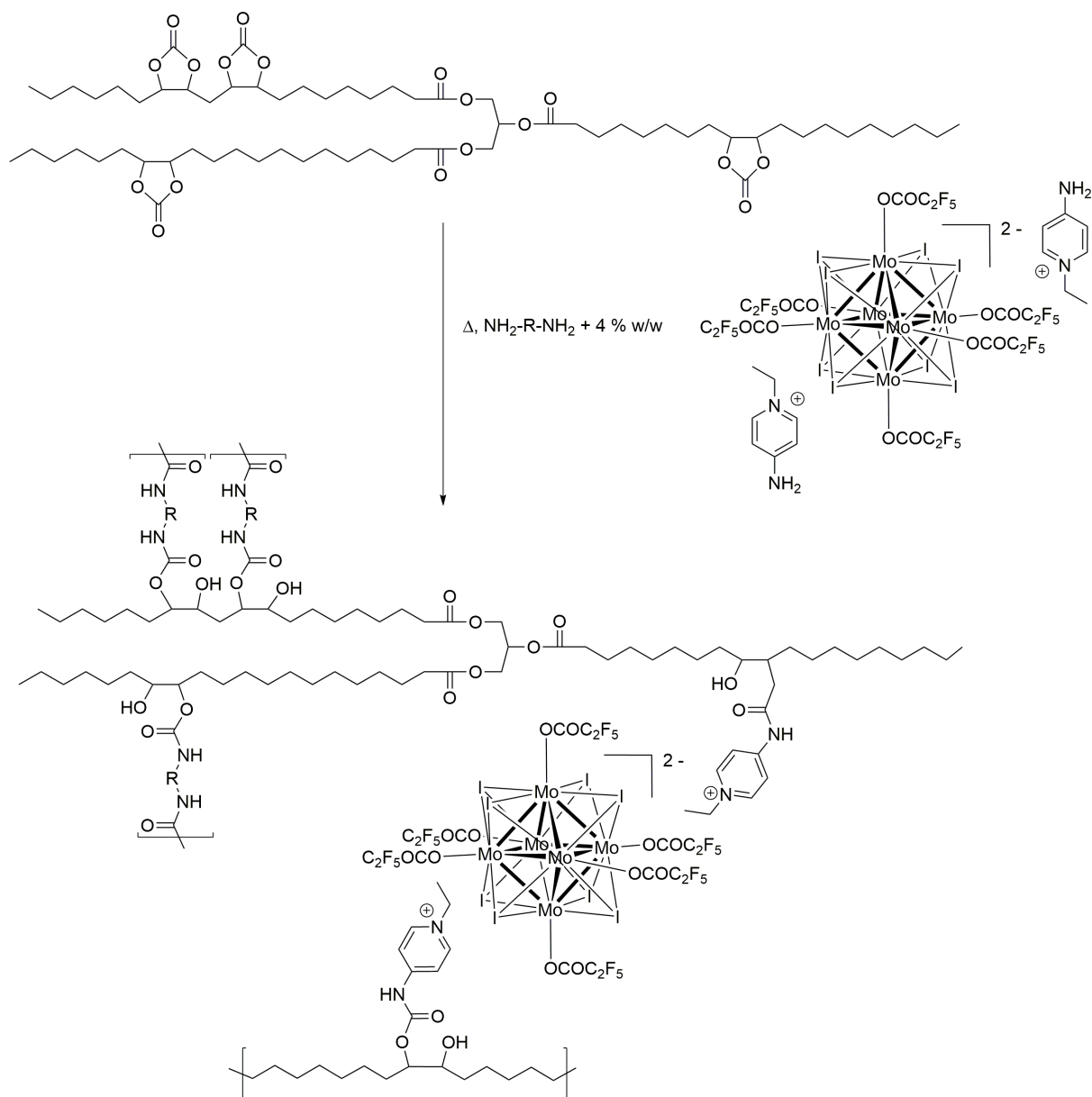


Figure 6. Nanocluster doped PUcc synthesis scheme

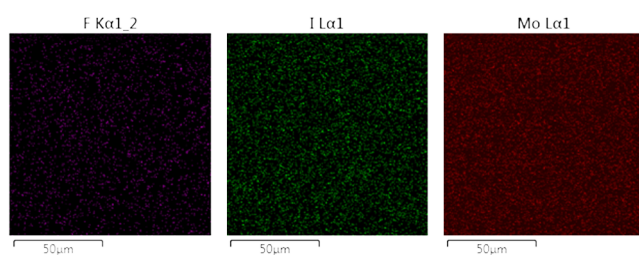


Figure 7. EDS mapping analysis showing the distribution of F, I and Mo in the doped-PUcc

**Emission properties** were investigated in the solid state for the m-XDA based PUcc samples (doped and non-doped) and the cluster precursors. Figure 8a presents the emission spectra observed by irradiating samples at 350 nm. Pure m-XDA PUcc emits broadly in the blue region with a maximum centred around 450 nm that is typical of urea moieties emission embedded in polymer.[37]  $\text{Cs}_2[\text{Mo}_6\text{I}_8(\text{OCOC}_2\text{F}_5)_6]$  and  $(4\text{-amino},\text{N-ethylpyridinium})_2\text{Mo}_6\text{I}_8(\text{C}_2\text{F}_5\text{COO})_6$  present the same emission maximum centred around 650 nm while once integrated in PUcc, this maximum is slightly red-shifted to 680 nm. This phenomenon was already observed when the same cluster anion was used as  $\text{O}_2$  sensor in a polyurethane matrix and indicates that the nanocluster ability to emit is poorly influenced by the polymeric matrix. The inset of Fig7a shows the red emission of the doped-PUcc sample taken under a 365 nm irradiation and gives another evidence of the homogeneous integration of nanoclusters in PUcc. Recently, we showed that the nanocluster anion emission behaviour toward a temperature modulation could be used to sense the molecular nanostructuration changes within a liquid crystalline hybrid material.[38, 39] Here, we decided to investigate if such ability could also be observed within a polymer matrix. To do so, we recorded the doped polymer emission spectra upon heating from  $-160^\circ\text{C}$  up to  $100^\circ\text{C}$  every  $10^\circ\text{C}$  (Fig 8b). Increasing the temperature induces a decrease of the emission intensity due to higher non radiative deactivation of the nanocluster excited state without any shift of the emission maximum. Therefore, the emission intensity is expected to decrease following an exponential law of the type  $I(T) = I_0\exp(-A/T)$  where  $I_0$  the emission intensity at a given temperature (in our case: 113 K) and  $A$  is a constant.[40, 41] Hence, reporting  $\ln(I/I_{113})$  versus  $1/T$  (insets figure 8b) should give a straight line if the emission is only temperature dependent. This is clearly not the case with our doped-PUcc. From the obtained curve, two tangents can be drawn with their intersection corresponding merely to the glass transition temperature of PUcc. At this point, we wish to emphasize that, to the best of our knowledge, this is the first time that such phenomenon is reported with a dye containing polymer and further studies are needed to understand it in depth.

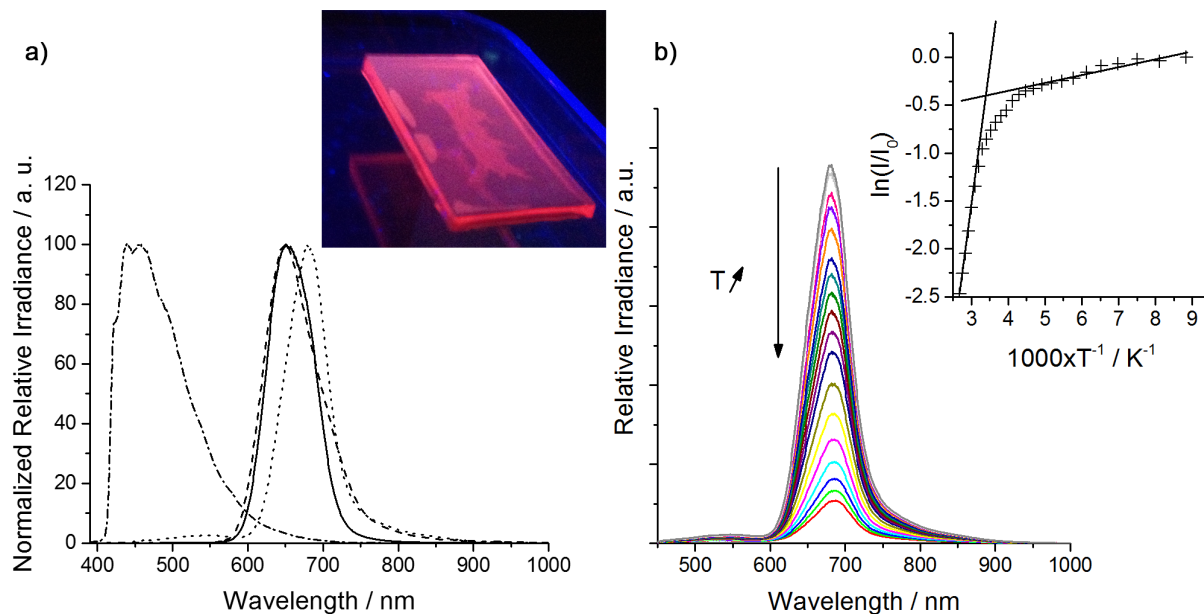


Figure 8. a) Emission spectra of doped PUcc sample ( $\lambda_{exc} = 360$  nm). Inset: picture of sample taken under UV irradiation at 365 nm; b). temperature dependent emission spectra of doped PUcc sample from  $-160^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  by  $10^{\circ}\text{C}$  steps, inset: evolution of signal intensity at 680 nm with the temperature.

## Conclusion

New polyurethanes – PUcc - were prepared from cyclocarbonated broccoli oil and three different di- or tri-amines. With different amines and/or different carbonate to amine ratios, it is possible to synthesize PUcc with adjustable mechanical properties. The synthesized PUcc presented tensile strength between 0.46 and 0.71 MPa, elongation at break between 85 and 272 % and Young's modulus in the range 0.50-1.15 MPa. The glass transition temperatures ( $T_g$ ) of the different PUcc samples, depending on the amine type and amine to carbonate ratios, were relatively close to each other and comprised between  $15$  and  $23^{\circ}\text{C}$ . Finally, a soft UV responsive material was prepared through the homogeneous integration, via copolymerization, of a molybdenum nanocluster in a polyurethane material prepared from cyclocarbonated broccoli oil and m-xylene diamine (m-XDA PUcc). The emission properties of the native cluster are retained within the PUcc matrix and their trends with temperature is likely to be dependent on the material plasticity. This new and surprising feature will be further investigated with other polymer families and will be reported in due time.

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