

## **Development of antimicrobial strategies on plastic packaging materials for preservative-free cosmetics**

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Preservatives play a crucial role in the cosmetic industry by preventing microbial contamination and ensuring product safety and stability. However, the use of certain preservatives, such as parabens, has raised concerns due to their potential allergenic properties and associated skin reactions in consumers.

Despite being regulated and widely used in cosmetic formulations, parabens have been identified as a potential source of skin sensitization. This has led to a significant increase in demand for preservative-free cosmetic formulations, particularly among customers with sensitive skin.

In order to achieve the objective of implementing preservative-free and consumer-safe cosmetic products, it is necessary to develop packaging that can be described as a barrier against microorganisms (bacteria, fungi), preventing any retro-contamination. To accomplish this, two strategies are possible: physical/mechanical barrier and chemical/biocide barrier. These two strategies can also be combined to enhance protection, particularly in cases of imperfect contact in the closure areas of the packaging.

Regarding the chemical/biocide strategy, the project was divided into a few research axes: a literature review to identify and classify antimicrobial technologies that could be applied in the cosmetic sector from a regulatory perspective; preparation of a minimalist cream simulant (oil-in-water); incorporation of selected antimicrobial molecules into the relevant polymers through different strategies: 1) incorporation of antimicrobial molecules into the polymer matrix using solvent casting, and 2) creation of pores in the relevant polymers with the intention of incorporating antimicrobial molecules into the pores, acting as reservoirs.

A survey of antimicrobial technologies for cosmetic applications was carried out, and groups of antimicrobial molecules were chosen considering their relevance, antimicrobial effect (MIC - Minimum Inhibitory Concentration and MBC - Minimal Bactericidal Concentration), and rapidity of action (Time Killing) in commercial culture medium and cream simulant.

The cream simulant was developed with the objective of accurately replicating the properties of a cosmetic emulsion. Comparative studies were conducted using a reference commercial cosmetic product without preservatives. Microscopic examination was employed to observe the size of oil droplets, and rheological studies were performed to assess the flow behavior of the emulsions. Additionally, investigations were carried out to determine the bacterial growth in the emulsions.

The most promising technologies, as determined by MIC/MBC/Time Killing criteria, were incorporated into polymeric matrices, specifically polyamides. The antimicrobial efficacy of these polymers against bacteria and their repeatability are being investigated.

## Synthesis and reactivity of low-valent Zn<sup>I</sup>-Zn<sup>I</sup> complexes: a combined DFT and experimental study

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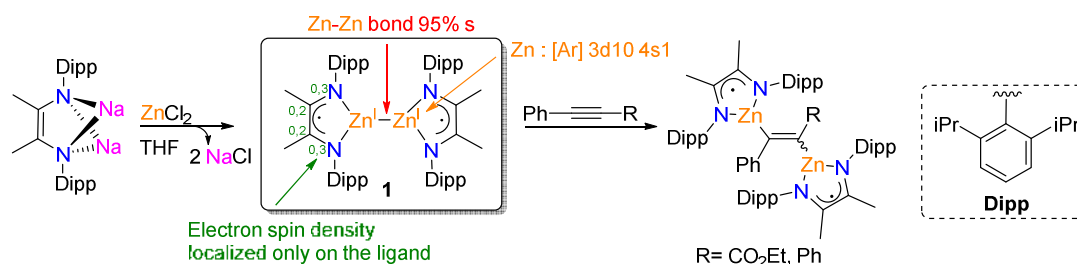
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Main-group organometallic compounds bearing a metal-metal M-M bonds are well known in the literature in the case of group 13 metals, such as boron or aluminum. More particularly di-boron compounds, which are easy to handle and relatively stable compounds, are used in a varied applications because of their ability to achieve 1,2-diboration reactions with unsaturated compounds.<sup>[1]</sup>

Since the first discovery of Cp\*<sub>2</sub>Zn<sub>2</sub>,<sup>[2]</sup> some low valent Zn<sup>I</sup>-Zn<sup>I</sup> complexes presenting an unusual formal oxidation state have been disclosed. A limited number of LZn-ZnL species have been synthesized and characterized by experimental and theoretical Zn-Zn bonding analysis.<sup>[3]</sup> Indeed, as those species are highly sensitive to moisture and oxygen, their synthesis and the study of their reactivity are challenging.

In this communication, we will present a combined experimental and DFT theoretical investigations on the synthesis and reactivity of the low valent Zn<sup>I</sup>-Zn<sup>I</sup> species **1**, where each zinc center is bearing a radical α-diimine ligand.<sup>[4]</sup> The formation of this Zn-Zn di-radical complex was studied by DFT calculations and the intermediates of the mechanism were characterized using Natural Bonding Orbitals.

The reduction process is exergonic but as it implies radical species as open shell system, it is necessary to use a representative model, method and chemical environment, in particular the solvent, in adequation with the electronic structure of the species. The addition onto alkynes was theoretically explored using a concerted mechanism in only one step, suggesting the feasibility of such reactivity. In parallel, experimental work is ongoing to prove such an *in silico* discovery.



**Scheme 1:** Synthesis and proposed reactivity of LZn-ZnL complex **1**.

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## Use of organometallic chemistry for the synthesis of nanocatalysts

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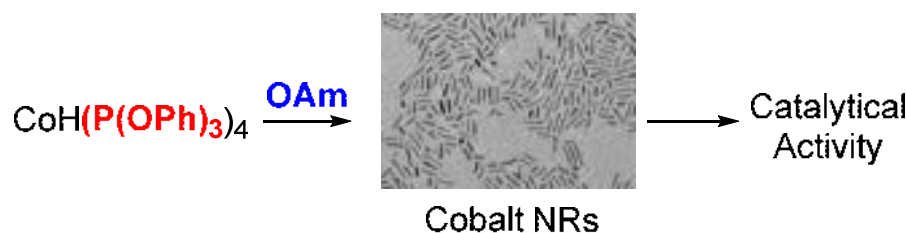
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### Summary

Enantioselective catalysis is one of the most efficient processes to access the chiral molecules needed in pharmaceutical industry. Despite being the incontestable leader in laboratory small scale synthesis, homogeneous catalysis represents only 20 to 30% of the most relevant industrial processes contrary to heterogeneous catalysis<sup>1</sup>. This is due to heterogeneous catalysis permitting an easier recycling of the catalyst and a minimization of metal leaching as well as a low cost. An ideal catalyst would gather **both** heterogeneous and homogeneous catalysts advantages.

We have recently discovered and developed a new methodology for the mild synthesis of Co<sub>2</sub>P nanorods (NRs) from [CoH(P(OPh)<sub>3</sub>)<sub>4</sub>] precursor and oleylamine as surfactant. Former synthesis of Co<sub>2</sub>P nanoparticles in the literature use red phosphorous<sup>2</sup>, NaH<sub>2</sub>PO<sub>2</sub><sup>3</sup>, or free phosphites<sup>4</sup> as phosphorous sources. Our synthesis allows us to use tunable and cheap phosphites (**P(OR)<sub>3</sub>**) as phosphorous source directly coordinated to the Co atom.

With these new promising results, we are able to develop rare unsupported Co<sub>2</sub>P nanocrystals with a whole and diverse family of cobalt hydride, with potential diverse catalytical activities.



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## Synthesis and Biological Study of Ganglioside GM<sub>3</sub> Derivatives as Anticancer Vaccine Candidates

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Glycosphingolipids (GSLs) are cell-surface antigens, and it was therefore suggested that changes in their composition would result in changes in the antigenicity (affinity to the corresponding antibody) and immunogenicity (ability to induce immune response) of the tumor cells expressing them<sup>1</sup>. As one of them, GM<sub>3</sub> is over expressed on some cancer cells, which makes it as a typical tumor-associated carbohydrate antigen (TACA) and as an important target for cancer vaccine development<sup>2</sup>.

Although natural carbohydrates can be applied as vaccine components directly, in many cases chemical modification of carbohydrates is necessary for enhanced efficacy<sup>3</sup>. As one of our research projects on cancer therapy, we have synthesized previously a series of ganglioside GM<sub>3</sub> derivatives and evaluated their anticancer activities<sup>4,5</sup>. Because the carbohydrates are extremely flexible and carry a large number of hydroxyl groups, it is worthy of study to better understand the distinctive feature of protein-carbohydrate interaction, especially the antibody-carbohydrate antigen interaction<sup>6</sup>. In this project, with building blocks of sialic acid, glucose, galactose, mannose, lactose and N-acetyl lactosamine, we have been working on developing a new type of anti-cancer vaccine by using GM<sub>3</sub> derivatives as antigens, the compounds to be synthesized are shown as follows.



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## Upgrading Phosphinoferrocene Structures through Catalytic C–H Bond Functionlizations

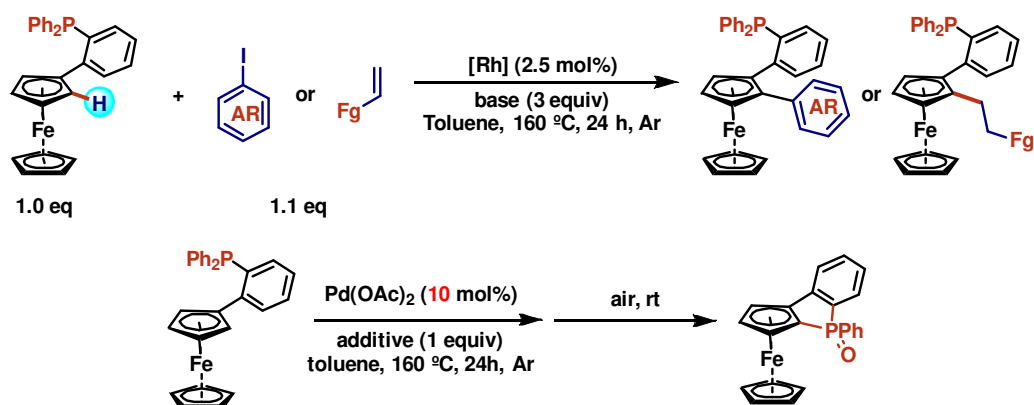
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Phosphorus-containing molecules represent a powerful and prominent platform for forming active motifs pervasive in bioactive drug molecules and materials.<sup>1</sup> Moreover, phosphines widely serve as ligands in catalytic transformations, allowing to discover of novel reactivities and/or alternative regio- or chemoselectivity.<sup>2</sup> Combined with ferrocene scaffolds, such hybrid structures have also proven to be privileged ligands in asymmetric catalysis.<sup>3</sup> However, phosphino-ferrocene is found little application in materials sciences due to challenging access to molecular diversity.<sup>4</sup>

Following the pioneering work of Hartwig and co-workers on Pd-catalyzed direct polyarylation of 1-(di-*tert*-butylphosphino)ferrocene,<sup>5</sup> and our recent work on P(III)-chelation-assisted C–H bond functionalization of biarylphosphines,<sup>6</sup> we turned our attention to C–H bond functionalization of 2-[2-(diphenylphosphino)phenyl]ferrocene. We discovered that C–H bond arylation occurred regioselectively on the same Cp ring at the *ortho*-position of 2-phosphinophenyl unit. The system employs a rhodium(I) center, and the P(III) atom acts as the directing group. Moreover, catalytic conditions to transform these modified phosphinoferrocenes to phosphole derivatives for material applications will be also presented.



**Acknowledgments:** We thank ANR for the financial support.

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## Regioselective C(sp<sup>3</sup>)-H Bond Arylation of Allylamines by Dual Photoredox and Nickel Catalysis

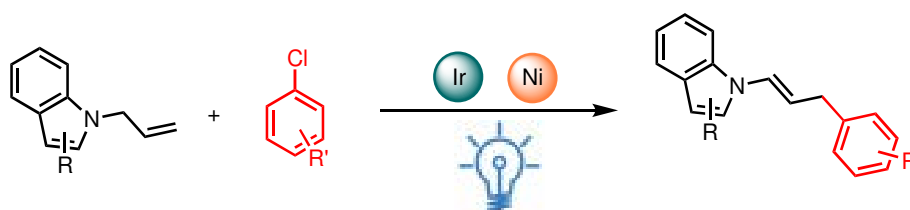
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Allylation reaction is a textbook organic reaction widely employed in synthesis because the resulting products are valuable and versatile building blocks. Moreover, their omnipresence in bioactive species makes them valuable in the medicinal science and pharmaceutical industries. Among the various methods to access allylarenes, the noble metal-catalyzed allylic substitution of pre-activated allylation agents (e.g., allylic carboxylates, carbonates, and halides) with aryl nucleophiles have been extensively studied.<sup>1</sup> Recent efforts have focused on converting C(sp<sup>3</sup>)-H bonds directly to C(sp<sup>3</sup>)-C bonds to minimize pre-functionalization and streamline the synthesis of complex molecules.<sup>2-4</sup> This strategy has been widely applied for the allylation of C(sp<sup>2</sup>)-H bonds using pre-activated allylation agents and transition metal catalysis.

In view of the above studies and the emergence of the merge of nickel(0) with photoredox catalysis,<sup>5</sup> we decided to investigate a reverse strategy, namely the direct arylation of C(sp<sup>3</sup>)-H allylic bond. With the optimal conditions in hand, we investigated the allylic C-H alkylation of N-allyl heterocycles with various aryl chlorides. The reaction is regioselective and gives only linear products. The reaction may involve the formation of a radical cation of N-allyl heterocycle followed by H-atom transfer to deliver a C-center radical, which can react with Ni<sup>II</sup>-Ar complexes.



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## Dual magnetic and redox molecular switches for molecular electronics

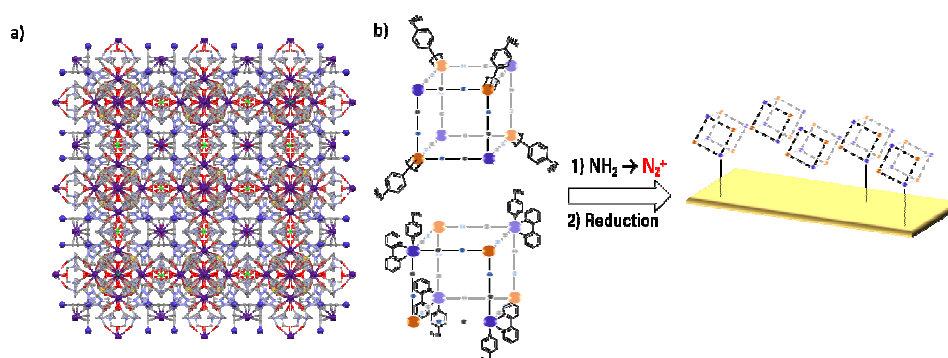
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Molecular Switches, whose physical properties can be changed by chemical or physical stimuli, are a field of interest both in fundamental and applied research, as their bistability can give rise to application in sensors, actuator, memories, etc. In this context, the ERMMEs team has developed discrete Prussian Blue Analogues (PBAs), in the form of cubic octametallic complexes of general formula:  $A\llbracket[(M)(L)(CN)_3]_4[(M')(L')]_4\rrbracket$ , where the metals (M and M') are linked by cyanides and usually capped by scorpionate ligands (L and L'), and in which a cation  $A^+$  (an alkali metal or Tl<sup>I</sup>) can be inserted. These cubes display interesting electronic properties, from multiple accessible redox states and electrochromism to photo- or thermally-induced spin-transition and/or electron transfer, making them redox-, thermo- and photo-magnetic switches.<sup>1,2</sup> Substantial fundamental work has been done in our team on those systems. Here, our efforts are focused on the integration of these switches into materials and onto surfaces, to make a step forward in the design of memristors or electrochemical sensors. Both approaches require the design of functionalized cubes that bear adequate peripheral coordination or anchoring sites.

In the first approach, the M' metals are capped by scorpionates bearing an  $SO_3^-$  moiety. The use of an excess of cation leads to the formation of weak  $SO_3^- - A^+ - OSO_2^-$  coordination bonds, yielding 3D networks (fig. 1.a). Our work is focused on understanding the formation and properties of those networks, to be able to rationalize their synthesis and to exacerbate their switching properties. The second approach consists in grafting cubes on conductive surfaces through diazonium salts ( $N_2^+$ ) reduction, while trying to preserve their electronic properties (fig. 1.b) To this end, we have developed new scorpionate ligands, bearing an aniline group that can be easily transformed into a  $N_2^+$ . We also developed an alternative approach by choosing a pair of easily available bidentate and monodentate ligands, instead of one tridentate, to cap the M' metallic ion. The  $Cs\llbracket[Fe(Tp)(CN)_3]_4[Co(2,2-bipy)(py-NH_2)]_4\rrbracket$  cube was successfully obtained, and the first tries of  $N_2^+$  formation and grafting were performed.



**Fig. 1 :** (a) XRD structure of the  $Cs\llbracket[Fe(Ttp)(CN)_3]_4[Co(Tpms)]_4\rrbracket\cdot Cs_4$  network; and (b) Schemes illustrating the two types of  $NH_2$ -bearing cubes developed for covalent-grafting on surfaces

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## Selective CO<sub>2</sub> Reduction to Formic Acid using Bismuth-based electrocatalysts

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Electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>R) into fuels and valuable chemical feedstocks using low-carbon electricity sources is a promising route to recycle CO<sub>2</sub> emissions. Formic acid has some of the highest market values among CO<sub>2</sub>R products<sup>1</sup>, due its wide range of applications in industrial processes, and particularly its excellent properties as a safe and convenient H<sub>2</sub> carrier<sup>2</sup>. In our study, we synthesized a bismuth catalyst for the selective electroreduction of CO<sub>2</sub> to formic acid. The catalyst activity was investigated using different type of electrochemical cells, from a standard H-type cell to more advanced systems enabling the production of formic acid at high rates with industrially-relevant current densities ( $j \geq 100 \text{ mA cm}^{-2}$ ). We also studied the influence of pH which is a key parameter for the catalytic performance of the system. While most studies only use neutral or alkaline electrolytes to inhibit the competitive hydrogen evolution reaction (HER), our catalytic system could maintain a high selectivity for CO<sub>2</sub> reduction in acidic conditions (pH 1). Indeed, acidic CO<sub>2</sub>R has recently gathered a lot of interest as a way to improve the carbon efficiency of CO<sub>2</sub>R processes by suppressing the formation of (bi)carbonate salts in the electrolyte and thus eliminating excessive costs related to electrolyte regeneration<sup>3,4</sup>.

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## ELECTRONICALLY ACTIVE ULTRA-THIN FILMS BASED ON Fe<sub>4</sub>Co<sub>4</sub> CYANIDE CAGES

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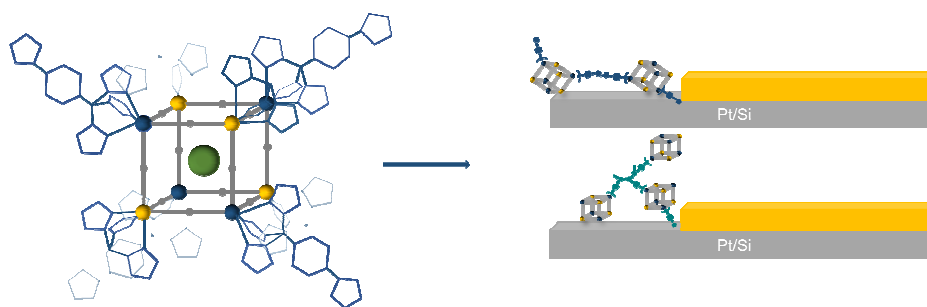
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Prussian blue analogues (PBAs) are well-known 3D inorganic polymers which have been extensively investigated because of their tuneable electronic properties and nanoporosity. However, as they are usually insoluble in organic solvents, it can be difficult to integrate them into microelectronic devices.

In this framework, our group developed PBAs on a molecular scale based on FeCo cages which are robust in solution and can be integrated into nanomaterials through simple solution approaches. These compounds are cyanide-bridged  $\{[\text{Fe}(\text{Tp})(\mu^2\text{-CN})_3]_4[\text{Co}(\text{RTp})]_4\}$  cubic cages where the metal ions are blocked by tris-pyrazolylborate ligands. As the FeCo PBA parent compound, the system shows switchable properties and the occurrence of a photo-induced metal-to-metal Electron Transfer Coupled to a Spin Transition (ETCST). Moreover, they also show interesting redox behaviour with up to nine accessible oxidation states.<sup>i</sup>

In this work, with the aim of integrating these switchable molecules into nanodevices, we developed a simple synthetic strategy to obtain electronically active thin film directly onto a conductive substrate. For that, cubes were functionalized by an RTp ligand showing a thiophene moiety, which was used as the electropolymerizable group. Such approach is simple, as electropolymerization is not a costly deposition method and ensures the formation of a film of controlled thickness on different electrodes, with different configurations depending on the thiophene derivative used.<sup>ii</sup>



**Figure 1.** {Fe<sub>4</sub>Co<sub>4</sub>} cages deposited on Pt/Si through electropolymerization.

### Acknowledgments:

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## **Synthesis of main group metal based tandem catalysts for polyesters & Polymerization from acceptorless dehydrogenative coupling**

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### Summary

The first part of this project is to fabricate highly active catalysts for controlling the structure selectivity of polymerization with rac-lactide and other monomers. Our work mainly includes two parts. (i) synthesis of metal (Ge/Fe/Ca/Mg) based amines from hexamethyl disilylamine (HMDS). (ii) fabrication of silamide grafted silica catalysts. Our approach is based on some recent research work. Heterogeneous catalysts are proved to be more effective in stereostructure control for polymerization with their well-defined active sites on surface.<sup>[1-2]</sup> One way to form heterogeneous catalysts is to graft amide onto silica surface to generate M(M=Ge/Fe/Ca/Mg)-N bonds which attributes to polymerization.<sup>[3]</sup> Our recent efforts are taken into synthesizing metal based amides and then graft them onto silica. Characterization including NMR, IR and XRD have been used to check the properties of our product.

The second part of this project is polymerization of diols/diamine with the help of acceptorless dehydrogenative coupling by Milstein catalysts.<sup>[4]</sup> This kind of pincer complex PNN-Ru(II) helps to generate polyester and polyurethane from diols/diamines with the release of hydrogen as the only by-product, which is atom-economical and environmentally friendly. We start from some simple aliphatic diols including 1,3 propane diols, 1,5 pentane diols and 1,3 butane diols. Characterization including NMR, IR and GPC are used for checking the properties of the polymers.

### **Acknowledgments:**

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## One-pot synthesis of biobased triblock copoly(meth)acrylates as thermoplastic elastomers (TPEs) towards tunable thermal performance

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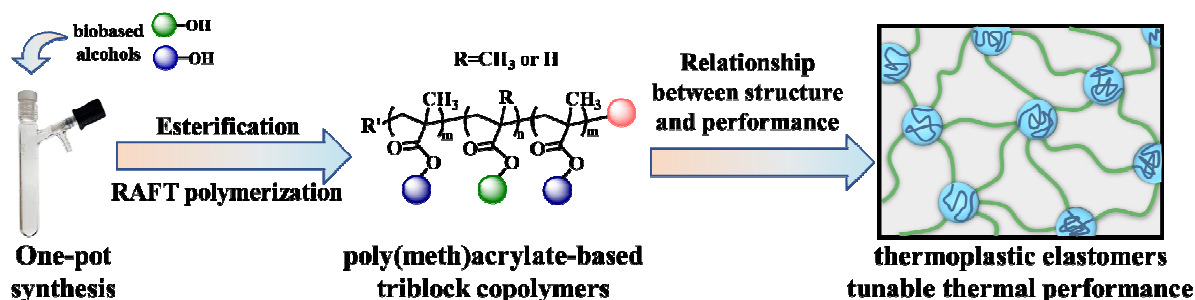
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### Summary

Herein, a library of poly(meth)acrylate-based triblock copolymers (triBCPs) as biobased thermoplastic elastomers (TPEs) was designed and synthesized via “one-pot” strategy including sequential multistep esterification and reversible addition-fragmentation chain transfer (RAFT) polymerization. Facing the key technical issues of achieving full conversion for each step in one-pot, the biobased (meth)acrylates were firstly produced by esterification with full conversion between (meth)acrylic acid and alcohol using ditert-butyl dicarbonate as coupling agent and (TMP)MgCl·LiCl (TMP=2,2,6,6-tetramethylpiperidide) as high-efficiency catalyst, and then RAFT polymerization of (meth)acrylates were performed under optimized conditions to reach polymerization conversion of each segment as close as possible to 100%. In these prepared triBCPs, three kinds of lignin-based polymethacrylates with different rigid degree were used as hard segment (HS), and linear alkyl, alkyl lactate ester as well as branched alkyl poly(meth)acrylates were used as soft segment (SS), which can endow triBCPs with sufficiently-wide tunable range of thermal performance, including glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and thermal degradation temperature ( $T_d$ ), and thus can meet the potential application requirements with different service temperature and processing temperature. The relationship between chemical structures and thermal performances in poly(meth)acrylate-based triBCPs is revealed.

ChemDraw schemes: ACS Document 1996 settings



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