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Tetrablock Metallopolymer Electrochromes

Haibin Gu, Roberto Ciganda,* Patricia Castel, Sergio Moya, Ricardo Hernandez, Jaime Ruiz, Didier Astruc*

This article is dedicated to Prof. Dr. Michel Pouchard (ICMCB, Bordeaux) at the occasion of his 80th birthday

Abstract: Multi-block polymers are highly desirable for their addressable functions that are both unique and complementary among the blocks. With metal-containing polymers, the goal is even more challenging insofar as the metal properties may considerably extend the materials functions to sensing, catalysis, interaction with metal nanoparticles and electro- or photochrome switching. Ring-opening-metathesis polymerization (ROMP) has become available for the formation of living polymers using highly efficient initiators such as the 3^{rd} generation Grubbs catalyst [RuCl₂(NHC)(=CHPh)(3-Br-C₅H₄N)₂], **1**. Among the 24 possibilities to introduce 4 blocks of metallopolymers into a tetrablock metallocopolymer by ROMP using the catalyst **1**, we have disclosed two viable pathways. The synthesis, characterization, electrochemistry, electron-transfer chemistry and remarkable electrochromic properties of these new nanomaterials are presented herein.

Interest in metallopolymers has recently emerged due to their multiple properties as memory devices, conductive, luminescent photovoltaic and materials, catalysts. electrocatalysts and artificial metalloenzymes.^[1] Metal fragments are rarely stable in multiple redox forms, however.^[2] Yet transition-metal compounds that disclose several redox states^[2] involve color changes. These variations bring about photochrome and electrochrome properties^[3] due to changes in $d \rightarrow d$ transition that are responsible for absorption in the visible spectrum range.^[4] This concept has been pioneered with the ferrocene-ferricinium group in readily polymerizable systems by Manner's group.^[1b,5] Indeed, not only polyferrocene materials are numerous,[5,6] but also diblock metallopolymers including a ferrocene block and another organometallic block have been recently reported with a variety of materials properties.^[7] In particular, the use of very efficient ring-opening-metathesis polymerization (ROMP) catalysts such as the 3rd-generation Grubbs catalyst [RuCl₂(NHC)(=CHPh)(3-Br-C₅H₄N)₂], 1,^[8] (NHC = 1,3-dimesityl-imidazolyl-2-ylidene) has allowed the synthesis of living ferrocene-containing and di-block metallopolymers.^[7b,9]

We now wish to benefit from the excellent catalytic properties of **1** providing living polymers to combine electronreservoir late transition-metal sandwich systems spanning a broad redox scale in the construction of multi-block electrochrome metallocopolymers containing up to four blocks. The four redox-robust sandwich units (see Scheme 1) involved

Supporting information for this article is given via a link at the end of the document.

are ferrocene (FcH) and 1,2,3,4,5-pentamethylferrocene (Fc*H) that are oxidizable to 17-electron isostructual cations,^[6] and the hexafluorophosphate salts (X⁻ = PF₆⁻) of cobalticinium (CcH)^[11] and [FeCp(η^6 -C₆Me₆)]⁺,(FbH), isolobal to ferrocene, reducible to their neutral 19-electron counterparts without structural change of the sandwich unit.^[12]

These metal sandwich complexes have previously been used to synthesize monomers **7-10** that are polymerizable to living metallopolymers by ROMP using the catalyst **1**^[9a,10] (Scheme 1).



Scheme 1. The 3rd-generation Grubbs catalyst **1**, four redox-robust sandwich units and their corresponding monomers **7-10** used for ROMP reactions.

The neutral monomers 7 and 8 were polymerized in dichloromethane (DCM), and the cationic monomers 9 and 10 in dimethylformamide (DMF). The polymerization rates must be taken into account (as the polymer solubility) for the synthesis of the multi-block metallocopolymers, and the rate order is 8 > 7 > 9 > 10.^[13] The later polymerization is marred by the combination of positive charge and arene ligand bulk. Thus, among the 24 theoretical possibilities to assemble the four blocks, in practice only two routes are found feasible and are shown in Scheme 2. In all cases the monomer/ catalyst 1 feed ratio for each block is 25, and kinetics analyses are conducted at room temperature (rt, $22 \pm 1^{\circ}$ C) until the polymerization is quantitative as shown by ¹H NMR analysis (see the Supplementary Information, SI, for complete procedure, reaction times and ¹H NMR analysis). For both routes, the first block introduced is that of 8, because it provides the fastest polymerization due to its better solubility, and it renders the subsequent copolymers more soluble than when they are alone. In the first route the introduction order involves first the two neutral blocks 8, then 7, followed by 10, all

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Scheme 2. Synthesis of the two tetrablock metallocopolymers 14 and 17. I: 1 in CH₂Cl₂, r. t. 10 min; II: 7 in CH₂Cl₂, r. t. 15 min; III: 9 in CH₂Cl₂, r. t. 10 min; IV: 10 in DMF r. t. overnight; V: 9 in CH₂Cl₂, r. t. 10 min; VI: 7 in CH₂Cl₂, r. t. 20 min; VII: 10 in DMF r. t. overnight.

three in DCM, leading to the triblock co-polymer **13**. The fourth block **9** is introduced in DMF to the DCM solution of the Ruended triblock copolymer **13**. Thus the overall order of introduction is **8-7-10-9** leading to the tetrablock copolymer **14** according to the sequence $8 \rightarrow 11 \rightarrow 12 \rightarrow 13 \rightarrow 14$. In the second route, the introduction of the neutral and cationic groups is alternated in DCM, this introduction order **8-10-7-9**, all in DCM at rt, leading to the tetrablock copolymer **17** according to the sequence $8 \rightarrow 11 \rightarrow 15 \rightarrow 16 \rightarrow 17$ (Scheme 2 and Table 1).

The electrochemical properties of the copolymers were investi-

Copolymer	Block	Conv (%) ^[a]	<i>n</i> _{p1} ^[b]	<i>n</i> _{p2} ^[c]	<i>n</i> _{p3} ^[d]
14	Fc*	>99	25	25 ± 1	30 ± 5
	Fc	>99	25	25 ± 1	20 ± 5
	FbX	>99	25	22 ± 3	28 ± 5
	Cc*	>99	25	25 ± 3	20 ± 5
17	Fc*	>99	25	25 ± 1	27 ± 5
	FbX	>99	25	22 ± 3	7
	Fc	>99	25	25 ± 2	22 ± 5
	Cc*	>99	25	26 ± 3	15

[a] Monomer conversion determined by ¹H NMR. [b] Polymerization degree obtained by ¹H NMR using monomer conversion. [c] Polymerization degree determined by ¹H NMR end-group analysis. [d] Degree of polymerization calculated using the Bard-Anson method.^[17] The values for Fb and Cc much lower than the feed ratio (25) are due to wave broadening resulting from lack of equivalence of the redox centers of same nature (see text).

gated by cyclic voltammetry (CV) using decamethylferrocene, [FeCp*₂],^[14] as the internal reference and [*n*-Bu₄N][PF₆] as the supporting electrolyte and compared with those of the corresponding homopolymers and diblock copolymers (Figure 1). DCM was used as the solvent for diblock copolymer 12 and the homopolymers of 7 and 8, whereas DMF was used as the solvent for the homopolymers of 9 and 10 and copolymers 13, 14, 15, 16 and 17. The $E_{1/2}$, ΔE and i_a/i_a data measured vs. [FeCp*2] are gathered in Tables S3, S7, S10, S13, S16 and S20 of SI. All of the waves are chemically and electrochemically reversible with slight broadening for the cathodic waves of the Cc and Fb groups due to electrostatic effects.^[15] This broadening means that all of the cationic redox centers of the same nature are not completely equivalent in these polymers due to steric constraints inside the polymer framework. Interestingly, the CV of the Fb units is considerably more flattened in the tetrablock copolymer 17 than in 14, which is best taken into account by the fact that the cationic Fb centers are more buried inside the copolymer in 17 than in 14. Since Fb is the bulkiest unit due to the C₆Me₆ ligand, the electrostatic difference among the identical Fb redox centers is more marked in 17 than in 14.^[16]

The Bard-Anson electrochemical method^[17] usually is reliable for the estimation of the number of monomer units in redoxrobust metallopolymers of relatively modest size such as those involved here.^[17] In the CV measurement, the total number (n_p) of electrons transferred in the redox wave of each redox center in the copolymer **13** should be the same as that of the corresponding monomer units in the copolymer, as only one electron is transferred from the cathode or to the anode for each redox center. This electron number n_p for each block is calculated using Bard–Anson's empirical equation **1**.^[17]

$$n_{p} = \frac{(i_{dp} / C_{p})}{(i_{dm} / C_{m})} (\frac{M_{p}}{M_{m}})^{0.275}$$
 (equation 1)

The i_d , M, and C are the CV wave intensity of the diffusion

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current, molecular weight, and concentration of the monomer (m) and polymer (p), respectively (see n_p in Tables S8 and S18 of SI). The numbers of electrons found are between 20 and 30 for theoretical numbers of 25, except in the case of the Fb units for which the values are lower due to the electrostatic-based wave broadening (*vide supra* and Table 1).

The determination of these numbers of units in each block are fine by ¹HNMR, including end-group analysis. The electrochemistry results are less precise (n = 25 ± 5). They become erratic for the numbers of cationic redox centers in **17** in which neutral and cationic blocks are alternating, in particular for the bulky Fb centers presumably for steric packing reasons.



Based on the redox potentials observed by CV (Figure 1), suitable redox reagents with known redox potentials^[6,11b] (Figure 2) are added stoichiometrically vs. a given block to the tetrablock copolymer **14** in order to provide exergonic electron-transfer reactions. A difference of 0.12 V between the redox potentials of the reagent and the given redox centers of the copolymer provides a 99% yield at 22°C for such reversible redox reactions.^[6a] Selective color changes upon addition of the redox reagents are shown in Figures 2 and 3.



Figure 2. Electrochromic activity of the tetrablock copolymer 14: selective color changes upon selective oxidation and reduction reactions of the tetrablock copolymer 14 (framed in yellow on the right side) by stoichiometric amounts of redox reagents with precise redox potentials insuring exergonic redox reactions (see UV-vis. in SI). On the right side, the blocks are represented by the metal, and FE for the $[FeCp(\eta^6-C_6Me_6)]$ -based block.





Figure 1 Compared CVs of the homopolymers of 7 (a, in CH_2CI_2), 8 (b, in CH_2CI_2), 9 (c, in DMF) and 10 (d, in DMF), triblock copolymers 13 (e, in DMF) and 16 (f, in DMF), and tetrablock 14 (g, in DMF) and 17 (h, in DMF). Internal reference: [FeCp₂]; reference electrode (0.0V): Ag; working and counter electrodes: Pt; scan rate: 0.4 V/s; supporting electrolyte: 0.1 M [*n*-Bu₄N][PF₆].

Figure 3. Electrochromic activity of the tetrablock copolymer 14: reaction of HAuCl₄ with 14 selectively oxidizes its 25 Fc* centers to green 14[Cl]₂₅ and ligand-stabilized AuCl that disproportionates overnight at rt, finally producing very large globular purple Au nanoparticles with 130 ± 5 nm size (see SI).

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Figure 2 shows that addition of colorless $NO^+PF_6^-$ ($E^\circ = 1.54 V$ vs. FeCp^{*}₂) to 14 in DCM oxidizes the 25 Fc^{*} centers ($E_{1/2}$ = 0.36V vs. FeCp*2) of 14 with an exergonic driving force of 1.18 V yielding the olive-green polymer 14[PF₆]₂₅. Oxidation of 14 with HAuCl₄ in THF (Figure 3) also gives an olive-green color that slowly turns light-purple, however, the color of Au nanoparticles (AuNPs with 130-nm core, Figures S82 and S83) due to slow disproportionation of the Au(I) intermediate. $^{\left[10a,18\right] }$ Addition in DCM of additional $NO^+PF_6^-$ to olive-green **14**[PF₆]₂₅ oxidizes its 25 Fc centers (E° = 0.62 V vs. FeCp^{*}₂) with an exergonic driving force of 0.92 V yielding the green polymer 14[PF₆]₅₀ (Figure 2). Selective reductions with color change proceed similarly in DMF/THF. Addition of light brown 1,2,3,4,5-Me₅-CcH (E° = -1.10 V vs. FeCp^{*}₂) to **14** specifically reduces its 25 CcX centers (E° = -0.71 V vs. FeCp*2) with an exergonic driving force of 0.39 V yielding the orange reduced polymer. Subsequent addition of 1% Na/Hg (E° = - 1.61 V vs. FeCp*₂) reduces the 25 Fb centers $(E^{\circ} = 0.56 \text{ V vs. FeCp}_{2}^{*})$ with an exergonic driving force of 0.12 V yielding a neutral deep-green form of polymer 14 (Figure 2).

In conclusion, the first tetrablock metallocopolymers have been synthesized with 25 metallo-units in each bock using the very efficient Ru ROMP catalyst **1**. The design of the robustness of the four distinct redox-robust centers allows electrochemical redox cascades and various color changes upon addition of exergonic redox reagents of suitable redox potentials, which forms rich multi-color electrochromes. A forthcoming challenge will involve film technology.

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Keywords: electrochrome • copolymer • redox activity • electron transfer • metallocene

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Two tetrablock metallocopolymers composed of polymers of norbornene derivatives with four distinct redoxrobust metallocenic redox centers in the side chains were assembled by ROMP; they showed extended redox cascades and multi-electrochromic behavior using adequate redox reagents.



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