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Rational Synthesis of Metallo-Cations Toward Redox- and Alkaline-Stable Metallo-Polyelectrolytes

Tianyu Zhu[†], Ye Sha[†], Horie Adabi Firouzjaie[‡], Xiong Peng[‡], Yujin Cha[†], D. M. M. Mevan Dissanayake[†], Mark D. Smith[†], Aaron K. Vannucci[†], William E. Mustain[‡], Chuanbing Tang^{*†}

[†] Department of Chemistry and Biochemistry, [‡] Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208 United States

ABSTRACT: Cations are crucial components in emerging functional polyelectrolytes for a myriad of applications. Rapid development in this area necessitates the exploration of new cations with advanced properties. Herein we describe a combination of computational and experimental design of cobaltocene metallo-cations that have distinct electronic and redox properties. One of direct outcomes on the first synthesis of a complete set of cation derivatives is to discover highly stable cations, which are further integrated to construct metallo-polyelectrolytes as anion-exchange membranes in solid-state alkaline fuel cells. The device performance of these polyelectrolytes under highly basic and oxidative environments is competitive with many organo-polyelectrolytes.

1. INTRODUCTION

Charged polyelectrolytes are widely used in a variety of areas, ranging from biological systems to commodity materials to membranes for energy applications.¹⁻³ At the advent of the 100th anniversary of the 'Macromolecular Hypothesis' by Hermann Staudinger, polymer science has overseen a distinct existence of metallopolymers that have a unique combination of inorganic metal centers and organic skeletons.⁴⁻⁸ Among them, cationic metallopolyelectrolytes have contributed fascinating optoelectronic and physicochemical properties and functions that could revolutionize areas such as biomedicines, energy conversion and water purification.⁹⁻¹²

The central piece of a polyelectrolyte resides on charged groups, which are the most critical in dictating properties of polymeric frameworks. Thus, there is an ingenious impetus in discovering and designing novel ionic moieties in the hope of achieving unprecedented properties in advanced materials. In conventional organo-polyelectrolytes, there are a few classes of cations such as quaternary ammonium and phosphonium, that have been well explored with a wide spectrum of derivatives to suit various needs. However, there are very few choices of metallo-polyelectrolytes, in a large extent due to the lack of tunability of metal cations. Herein we report the first complete syntheses of cobaltocene cations with 0 to 10 substituents and further evaluate their redox and chemical properties. The methodology in this work could be the first realization of rational design of metallo-cations towards metallopolyelectrolytes with similar levels of vigor to organopolyelectrolytes.

> The key dogma is to address a critical challenge how to design metallo-cations with a full spectrum of structures with tunable physiochemical properties. Recent work has

showed that metal centers can endow metallopolyelectrolytes with diverse electrochemical redox behavior, rich electrochromic properties, as well as fascinating ionic binding with macromolecular/biological substrates.¹³⁻¹⁴ These physiochemical properties rely on understanding of structures and chemical bonding of metallo-cations. In this work we demonstrate the first rational design of cobaltocene cations utilizing density functional theory (DFT) calculation, synthesize a spectrum of derivatives based on modular alkylation and chemoselective alkynylation, and evaluate their redox potentials and chemical stability. In particular, we show that this rational design allows us to design metallopolyelectrolytes as anion-exchange membranes (AEMs) for alkaline AEM fuel cells (AEMFCs).

2. RESULTS AND DISCUSSION

2.1 Bonding of cobaltocenium cations by DFT calculations.

Compared with 18-e ferrocene, the isoelectronic cobaltocene cation (commonly called cobaltocenium) is known for its chemical stability. It has been reported to behave much like a large alkali metal ion in aqueous solution.¹⁵ Although structural modifications to the cyclopentadienyl ligands in neutral metallocenes have been extensively explored,¹⁶⁻²⁰ there is a lack of a rational design of metallocene cations. In this work, we designed cobaltocenium cations by systemically installing methyl and *tert*-butyl groups and correlate electronic and steric effects on the stability of cations.

DFT calculations facilitate the understanding of thermochemistry of cobaltocenium cations, mostly bond dissociation energies (BDEs) of the metal-Cp bond (**Figure 1a**), which is closely related with redox potential and chemical stability.²¹⁻²² As shown in **Figure 1b**, the increase

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Figure 1. a. Illustration of metal-Cp bond dissociation; **b.** DFT calculation of bond dissociation energy (BDE) as a function of number of substituents; **c.** Comparison of optimized structures by DFT calculation, metal-Cp and metal-counterion distance for unsubstituted, octa-methyl and tetra-*tert*-butyl cobaltocenium. (Hydrogen atoms are omitted for clarity; **cc** represents unsubstituted cobaltocenium; **dmcc**, **tmcc**, **hmcc**, **dtcc**, and **ttcc** represent cobaltocenium with dimethyl, tetramethyl, hexamethyl, octamethyl, di-*tert*-butyl, and tetra-*tert*-butyl substituents, respectively.)

of methyl or tert-butyl groups on Cp ligands generally results in higher BDEs of multi-substituted cobaltocenium derivatives. In the case of methyl substitution, this can be rationalized by the electron-donating nature of methyl groups, which leads to more overlapped electronic wave functions of binding partners between the metal and Cp.²³ Though the electron-donating effect of *tert*-butyl increases the BDEs of di- and tetra-substituted cobaltocenium, the steric effect results in significantly tilted Cp planes when there are four *tert*-butyl groups. With further substitution of the bulky group, for example, in the case of hexa-tertbutyl cobaltocenium, the paramount steric repulsion from tert-butyl groups over the electronic effect makes BDE of metal-Cp inversely reduced (113.6 kcal/mol, not drawn in **Figure 1b**), even lower than unsubstituted cobaltocenium (123.4 kcal/mol).

40 In addition to the metal-Cp bonding, one needs to 41 consider the interaction between cobaltocenium cation and 42 counterion (e.g. PF_6 , the common anion). We calculated the 43 cobalt-counterion bonding strength and the cobaltphosphorus distance (Table S2, Figure S9). Three 44 representative structures are shown in Figure 1c. 45 Introducing methyl substituents only results in a slight 46 increase in the metal-counterion distance, e.g. only 0.13 Å 47 difference between unsubstituted and octamethyl 48 cobaltocenium. In the case of tetra-tert-butyl 49 cobaltocenium, this difference increases to 0.80 Å. In 50 general, with an increase in the number of both methyl and 51 tert-butyl substituents, ionic bonding strength weakens 52 (Figure S9b). As described in later sections, the larger 53 metal-counterion distance and weaker ionic bonding 54 strength could indicate a better protection of the cationic cobalt center from nucleophilic attack by anions, thus 55 enhancing stability of metallo-cations under caustic 56

environments such as high alkaline solution (e.g. hydroxide, alkoxide ions or hydroxide water clusters as nucleophiles).

Unsubstituted cobaltocenium (cc) and cobaltocenium derivatives with an even number of methyl (dmcc, tmcc, hmcc, omcc) or tert-butyl substituents (dtcc, ttcc) on Cp rings were prepared by the reaction of CoBr₂ and different cyclopentadienyl ligands. The complete synthetic pathways are shown in Scheme 1. No column chromatography was required during the synthesis of these compounds, and all cations can be prepared at gram scales. The chemical structures of these compounds were confirmed by nuclear magnetic resonance, UV-vis spectrometry, high-resolution mass spectrometry, and single-crystal X-ray diffraction (Figures S1-7, S14-25, Tables S3-8). Although crystal structures of **cc** and **dtcc** were previously reported and identical to our results,²⁴⁻²⁵ structures of tmcc, hmcc, omcc and ttcc have not been reported yet. From the X-ray characterization, cobaltocenium cations with different methyl substituents exhibit two parallel Cp rings, while four bulky tert-butyl substituents induce steric repulsion between Cp rings and hence lead to a tilted structure for ttcc (Scheme 1). These structures are consistent with optimized results by DFT calculations (Figure 1c). Further introducing tert-butyl substituents was unsuccessful largely due to high steric hindrance and unstable metal-Cp bonding.

Synthesis of cobaltocenium derivatives with direct substitution of an odd number of alkyl groups was not carried out, as it requires tedious separation from derivatives with even number of substituents as a result of statistical reactions involving a mixture of two cyclopentadienyl ligands (one with odd numbers of alkyl groups, the other with even numbers of alkyl groups), often with extremely low yields (e.g. the synthesis monomethyl cobaltocenium has a yield of only 5-10%).²⁶⁻²⁷ However, recently we and others demonstrated chemoselective synthesis of mono-substituted cobaltocenium with high vields (e.g. 50-80%) via one-pot nucleophilic addition and endo-hydride abstraction.²⁸⁻²⁹ We extended this strategy to prepare cobaltocenium derivatives with odd number of substituents using the above-mentioned cobaltocenium with an even number of alkyl groups as substrates by introducing an alkyne group (alkynylation) (Scheme 1). Simply, cobaltocenium derivatives were mixed with trimethylsilylacetylene in the presence of butyl lithium, followed by the addition of trityl cation. This one-pot reaction typically involves the transitions of $\eta^5 - \eta^4 - \eta^5$ sandwich structures. The overall yields of these derivatives with odd number of substituents were over 70%. For the first time, a full spectrum of cobaltocenium derivatives from unsubstituted to complete substitution were prepared, which could serve as an ideal platform to explore their physiochemical properties and discover potential applications.

2.2 Redox properties and chemical stability.

Redox potential and chemical stability are among the most essential properties of metallo-cations; these properties ultimately dictate their utility.³⁰⁻³¹ Compared to traditional organo-cations, transition metal complexes possess unique metal-ligand bonding and usually exhibit multiple redox states due to the variable oxidation states

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Scheme 1. Synthetic routes of cobaltocenium derivatives by methyl and *tert*-butyl substitution: derivatives with even number of alkyl groups are prepared by oxidative reactions between substituted cyclopentadiene and CoBr_2 in the presence of NaPF_6 ; those with odd number of substituted groups are prepared by nucleophilic addition and endo-hydride abstraction of derivatives with even number of alkyl groups. (The center number box indicates the number of substituents). Inset: the tilted structure for **ttcc** and the angle (α) between two unparallel Cp rings.

that are available to the metals. This property can potentially empower these metal complexes for use across a wide variety of applications, ranging from catalysis to photochromic and electrochromic devices.^{13, 32-33}

We first examined the electrochemical properties of these alkylated cobaltocenium derivatives by cyclic voltammetry (CV) in acetonitrile using tetra-butyl-ammonium hexafluorophosphate as a supporting electrolyte. In all cases as shown in Figure 2b, CV scans exhibited a oneelectron reversible reduction that can be ascribed to the cobaltocenium (Co^{III})/cobaltocene (Co^{II}) redox couple.³⁴ A secondary reduction from Co^{II} to Co^I was only observed for unsubstituted cobaltocenium (1) over the investigated potential window. Due to the inductive donation of electrons from the methyl or tert-butyl groups, all multisubstituted cobaltocenium cations exhibited lower reduction potentials than 1. There is almost a linear decrease of the reduction potential of every ~110 mV for every addition of a pair of methyl groups in the Cp rings (Figure S8). In the case of the *tert*-butyl substitution, the decrease in reduction potential becomes smaller (from 95 mV to 70 mV) when more tert-butyl groups were introduced. This is probably due to steric effects, as the LUMO orbital for tilted cobaltocenium sits at a lower energy level. An earlier study by Manners and coworkers also showed the distinct shift to less negative reduction potential with increased tilting for [2]cobaltocenophane and [3]cobaltocenophane.35

We next examined the chemical stability of these metallocations. Coates, Noonan and coworkers have investigated the long-term stability of various organic cations in the presence of nucleophilic hydroxide or alkoxide.³⁶⁻³⁹ In comparison, comprehensive evaluation of the stability of metallo-cations has not been done, largely due to the lack of a set of derivatives with tunable electronic properties.^{7, 40-45} Herein we evaluated methylated and *tert*-butylated cobaltocenium cations under highly alkaline conditions (5M KOH/CD₃OH at 80 °C) and attempted to compare them with organo-cations. It is worthwhile to note that the tests were done in an oxidative atmosphere (with constant charging of air), while most reported alkaline stability has been done in sealed or inert environments, which are far from the reality of many applications that operate under oxidative conditions.

CD₃OH was used as a reaction medium for KOH instead of deuterated water to preclude the undesirable hydrogen/deuterium exchange process involving the Cp rings (a hurdle for NMR analysis), and it also provides more aggressive reaction conditions to accelerate potential degradation of the cations.^{36-37, 42-43} We monitored the cation stability by NMR spectroscopy. Initially, we explored the methyl substituent effect on the stability of cobaltocenium cations (Figure 2c, Figures S30-32). Di, tetra, octamethyl cobaltocenium cations with chloride as the counterion were prepared due to their good solubility in methanol. Previous studies have reported good alkaline stability of unsubstituted cobaltocenium in inert atmosphere (e.g. under nitrogen protection).^{7, 15} However, under air purging, it lost over 40% within 232 hours. Dimethyl cobaltocenium was observed to behave similarly to the unsubstituted cobaltocenium. The degradation was unable to be monitored by NMR after 232 hours, due to the formation of paramagnetic cobalt salts. The introduction of four methyl groups resulted in considerable improvement in stability, with 37.4% cation loss after 392 hours. Further increasing the number of substituents to eight methyl groups (2c) produced a much more inert cation, and the octamethyl cobaltocenium only degraded by 10.9% and 18.5% after 553 hours and 1025 hours, respectively. We then investigated steric effects on the stability of tert-butyl



Figure 2. a. Chemical structures of cobaltocenium derivatives, and two organo-cations used in this study for comparison; **b.** Cyclic voltammetry curves for cobaltocenium cations and organo-cations at a scan of 100 mV/s in acetonitrile with 0.1 M tetra-butyl-ammonium hexafluorophosphate as the supporting electrolyte, shadows represent HOR and ORR potentials; **c.** Stability of cobaltocenium cations and organo-cations (0.025 M) in 5M KOH/CD₃OH at 80 °C under air.

cobaltocenium (**Figure 2c, Figures S33-34**). We hypothesized that the presence of *tert*-butyl groups makes cobaltocenium more resistant to nucleophilic attack from alkoxide and hydroxide ion clusters by keeping them away from the cationic metal center. Di-*tert*-butyl cobaltocenium cation (**3a**) exhibited substantial alkaline stability with a 26.6% loss after 1025 hours. The cation with the best alkaline stability is tetra-*tert*-butyl cobaltocenium (**3b**), which showed a minimal degradation over 1025 hours under harsh oxidative and high alkaline conditions (only ~ 8.2% cation loss).

Furthermore, we compared the stability of these cobaltocenium cations with conventional organo-cations, benzyl trimethylammonium (**4**) and multi-substituted imidazole (**5**) (**Figure 2c**, **Figures S35-36**, **Table S9**).^{36, 46-47} Cation **4** degrades rapidly under oxidative alkaline conditions, with more than 50% of the cations degraded within the first week. Cation **5** is considered to be a signature organo-cation because of its excellent alkaline stability under inert conditions.^{36, 38-39} However, it lost about 60.6% under oxidative conditions after 1025 hours, much less stable than cobaltocenium cations **2c**, **3a**, and **3b**.

Taken together, it was concluded that the chemical stability and redox properties of these new metallo-cations can be modulated by the substituent effect. For cobaltocenium with the same type of substituents, both alkaline and redox stability has the same trend with the BDEs, i.e., **2c>2b>2a>1** and **3b>3a>1**. However, the most alkaline stable cobaltocenium is not the one with eight

methyl groups (2c), but the one with four steric *tert*-butyl groups (3b), indicating that the steric effect plays an important role in determining stability, while electronic effects have a more dominant role in determining their redox behavior.

2.3 Constructing metallo-cation-based polyelectrolytes as anion-exchange membranes.

Given the successful synthesis and understanding of physiochemical properties of cobaltocenium derivatives, we intended to design a class of polyelectrolytes with cobaltocenium as cations and further correlate macromolecular properties with redox and chemical stability of cations. Cobaltocenium-containing polyelectrolytes have been utilized as AEMs that show a good alkaline stability under inert atmosphere and reasonable ionic conductivity,^{7,42,43} which could be useful for fabricating electrochemical devices, such as AEMFCs.⁴⁸⁻ ⁴⁹ Because of the good stability of the substituted cobaltocenium cations in alkaline and oxidative atmosphere, we believe that they could be used to construct polyelectrolytes that would be more stable than traditional organic polyelectrolytes.49-54

However, it is important that the redox potential of the cation is outside the operating voltage window of fuel cell devices. In AEMFCs, the hydrogen oxidation reaction (HOR) potential at the anode is -828 mV (vs. SHE for all potentials mentioned here), and oxygen reduction reaction

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Figure 3. a. Synthesis of octamethyl cobaltocenium polyelectrolytes as AEMs; **b.** Stress-strain curves of omccAEM membrane in a dry state and a hydrated condition; **c.** Chloride and hydroxide conductivity of omccAEM as a function of temperature under fully hydrated conditions; **d.** Polarization curves and power densities for omccAEM in a H₂/O₂ fuel cell (Anode: 0.8 mg PtRu/C cm⁻², Cathode: 0.49 mg Pt/C cm⁻² on 5% PTFE GDL). (synthesis details. **i:** HBr/HAc; **ii:** NaN₃, DMF, 70 °C; iii: ethynyltrimethylsilane, *n*-BuLi, THF; **iv:** triphenylcarbenium hexafluorophosphate, DCM; **v:** CuSO₄, Na ascorbate, THF/H₂O; **vi:** Grubbs III catalyst, DMAc/xylenes, *p*-toluenesulfonyl hydrazide, Bu₃N; vii: aqueous NH₄Cl, ion-exchange resin, 60 °C.)

(ORR) potentials, which would preclude many redox-active cations (Figure S13c).49 For example, unsubstituted cobaltocenium can be reduced to neutral cobaltocene complex at HOR relevant potentials (Figure 2b). Despite the fact that it is thermodynamically more stable, tetra-tertbutyl cobaltocenium was not chosen due to its redox potential overlapping with the HOR. On the other hand, alkyl substituents were chosen rather than other functional groups because heteroatoms are more vulnerable for side reactions under oxidative and alkaline conditions. Based on the redox properties observed in our CV studies, octamethyl cobaltocenium is redox stable over the entire potential range for operating AEMFCs and provides a larger operating window compared to other cations. Besides, octamethyl cobaltocenium also exhibits high alkaline stability. Thus, it was chosen to construct polyelectrolytes as AEMs (labeled as omccAEM). As shown in Figure 3a, octamethyl cobaltocenium cyclooctene monomer (2c-2) was firstly prepared by a copper-catalyzed click reaction between 5-azidocyclooct-1-ene and ethynyl octamethyl cobaltocenium hexafluorophosphate (2c-1). Then, metallopolyelectrolytes were prepared by ring-opening metathesis polymerization (ROMP) of monomer (2c-2) with ciscyclooctene as a co-monomer, followed by backbone hydrogenation and ion exchange. The monomer and copolymers with hexafluorophosphate counterion were characterized by ¹H NMR spectroscopy (Figures S26-28).

As shown in **Figure 3b**, these metallo-polyelectrolyte membranes exhibit robust mechanical properties, probably due to the presence of a flexible polyethylene-like backbone with a tunable side chain composition. For example,

omccAEM has a tensile strain of 390 % and a tensile stress of 21 MPa at 100% RH under ambient temperature. With such excellent mechanical properties, it would allow to make membranes very thin, e.g. ~40 μ m thick, which is desirable for facilitating the water back-diffusion and supporting a high current density in a fuel cell.^{50, 55-57}

The temperature-dependent ionic conductivity of omccAEM with hydroxide and chloride counterions is shown in Figure 3c. Membranes with chloride and hydroxide counterions showed increased conductivity at elevated temperature, which can be rationalized by faster ion migration and higher water uptake. The hydroxide conductivity is 33.3 and 83.7 mS/cm at room temperature and 80 °C, respectively. It should be noted that the omccAEM with inert polyethylene backbone and a highly stable cobaltocenium cation also preserved the hydroxide conductivity (91% retention) after testing in a 3 M KOH solution at 60 °C for 30 days under open air (Figure S13b). Moreover, distinct microphase separation between hydrophilic and hydrophobic domains was observed by both atomic force microscopy (AFM) and small-angle X-ray scattering (SAXS) (Figure S11b). Such phase-separated morphology is critical to facilitate ion-transport by forming connected ion-transport channels in polyelectrolyte membranes.3,7,9

The electrochemical performance of the omccAEM was investigated in an AEMFC operating with H_2 and O_2 reacting gases. **Figure S10** and **Figure 3d** show the high frequency resistance (HFR) and device performance, respectively, at several temperature. To the best of our knowledge, this is the first test of metallo-polyelectrolytes at a device level. In

Figure 3d, the polarization curves and power density curves show that the performance of the cell improved as the temperature increased. A maximum peak power density of 350 mW cm⁻² was achieved with the metallopolyelectrolyte membrane fuel cell, which is comparable to a variety of AEMs with organic cations reported recently.^{51-52, 55, 58-61} This is very promising and it is likely that refinement in the structure of metallo-polyelectrolyte membranes will allow further increases in ionic conductivity and water transport properties and even better fuel cell performance.

3. CONCLUSIONS

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In summary, we have combined computational and experimental studies, for the first time, toward a complete set of substituted cobaltocenium cations with tunable electronic and redox properties. The synthesis enabled the substitution of even numbers of methyl and *tert*-butyl groups followed by chemoselective nucleophilic addition and hydride abstraction. The selection of electron-donating alkyl groups allowed the design of highly stable metallocations under harsh conditions. Metallo-polyelectrolytes with octamethyl cobaltocenium as the cation were evaluated as anion-exchange membranes. Our results demonstrated the first tests of such membranes that can perform well under highly alkaline, oxidative and humid environments of a fuel cell device.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Materials and characterization methods, experimental and calculation details, crystal structures and compound characterization (PDF)

AUTHOR INFORMATION

Corresponding Author

* Chuanbing Tang: tang4@mailbox.sc.edu (C.T.)

ORCID

- 41Tianyu Zhu: 0000-0001-9115-646242Ye Sha: 0000-0003-3338-122843Xiong Peng: 0000-0001-8737-583044Yujin Cha: 0000-0001-6624-6626
- 45 Mark D. Smith: 0000-0001-6977-7131
- Aaron K. Vannucci: 0000-0003-0401-7208
- William E. Mustain: 0000-0001-7804-6410 47 Chuaphing Tang, 0000, 0002, 0242, 8241
- Chuanbing Tang: 0000-0002-0242-8241

Notes

The authors declare no competing financial interest.

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