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| 1. REPORT DATE (DD-MM-YYYY) 01-05-2017 | | 2. REPORT TYPE Final Report | | 3. DATES COVERED (From - To) 1-May-2016 - 31-Jan-2017 | |
| 4. TITLE AND SUBTITLE Final Report: Electrochemically Controlling the Ring Size and Molecular Topology of Cyclic Polyesters | | | 5a. CONTRACT NUMBER W911NF-16-1-0197 | | |
| | | | 5b. GRANT NUMBER | | |
| | | | 5c. PROGRAM ELEMENT NUMBER 611102 | | |
| 6. AUTHORS Kuppuswamy Arumugam | | | 5d. PROJECT NUMBER | | |
| | | | 5e. TASK NUMBER | | |
| | | | 5f. WORK UNIT NUMBER | | |
| 7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Wright State University 3640 Colonel Glenn Highway Dayton, OH 45435 -0001 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 | | | 10. SPONSOR/MONITOR'S ACRONYM(S) ARO | | |
| | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66571-CH-II.1 | | |
| 12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited | | | | | |
| 13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation. | | | | | |
| 14. ABSTRACT Five coordinated iron-bis(dithiolene) N-Heterocyclic carbene adducts [Fe(NHC)(S ₂ C ₂ R ₂) ₂] (R = phenyl or anisyl; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene or 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)] has been isolated by reaction of [[Fe(S ₂ C ₂ R ₂) ₂] with the corresponding free carbenes. The synthesized adducts (1-4) were unambiguously confirmed by NMR and single crystal X-ray crystallography. All compounds 1-4 were characterized by electrochemistry and it displayed a reversible and an irreversible reduction coupled with a reversible peak in the oxidizing direction. Spectroelectrochemistry analysis of the complexes reveals that the | | | | | |
| 15. SUBJECT TERMS N-heterocyclic carbenes, organocatalysis, cyclic polyesters | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | 17. LIMITATION OF ABSTRACT | | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT UU | b. ABSTRACT UU | c. THIS PAGE UU | UU | | Kuppuswamy Arumugam |
| | | | | 19b. TELEPHONE NUMBER 716-375-2085 | |

Report Title

Final Report: Electrochemically Controlling the Ring Size and Molecular Topology of Cyclic Polyesters

ABSTRACT

Five coordinated iron-bis(dithiolene) N-Heterocyclic carbene adducts [Fe(NHC)(S₂C₂R₂)₂] (R = phenyl or anisyl; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene or 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) has been isolated by reaction of [[Fe(S₂C₂R₂)₂] with the corresponding free carbenes. The synthesized adducts (1-4) were unambiguously confirmed by NMR and single crystal X-ray crystallography. All compounds 1-4 were characterized by electrochemistry and it displayed a reversible and an irreversible reduction coupled with a reversible peak in the oxidizing direction. Spectroelectrochemistry analysis of the complexes reveals that the irreversible reduction of compounds 1-4 readily release free N-heterocyclic carbene. Subsequently, electro-generated free NHC catalyzed organic transformation was validated with synthesis of gamma-butyrolactone from trans-cinnamaldehyde.

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Scientific Progress

Technology Transfer

STIR: Electrochemically Controlling the Ring Size and Molecular Topology of Cyclic Polyesters

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Department of Chemistry, Wright State University, Dayton, Ohio, 45435

1. **Foreword** (optional)
2. **Table of Contents** (report < 10 pages)
3. **List of Appendixes**, Illustrations and Tables (Not applicable)

4. Statement of the Problem Studied: Controlling polymer architecture is an important intrinsic material property from an application point of view. This is especially true with the case of cyclic aliphatic polyesters that are targeted for specialized applications.¹ The increasing interest for cyclic polyesters in variety of fields including medical, military, and industrial applications demands polymers with enhanced selectivity (chemo-, regio-, and stereoselectivity), molecular weight control, molecular weight distribution, and macromolecular topology (star,² graft,³ and hyperbranched⁴). Significant research has been devoted to the development of precision cyclic polyesters *via* ring-opening polymerization technique, particularly, N-heterocyclic carbenes catalyzed cyclic polyesters.⁵⁻⁶ However, specialized applications place more severe demands on cyclic polyesters with respect to molecular weight distribution, ring size control and macromolecular topology. This underscores need for a method that offers higher degree of control over ring size and macromolecular topology of cyclic polyesters.

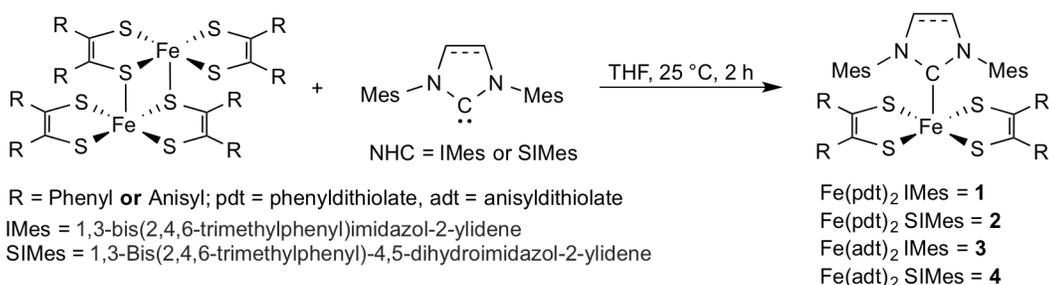
A primary objective of this project is to develop a highly regulated electrochemically controlled reversible release and recovery of N-heterocyclic carbenes to modulate the ring size of cyclic polyesters. To achieve reversible release of NHCs, metal dithiolene N-heterocyclic carbene ($[M(NHC)(S_2C_2R_2)_2]^0$ (M = Fe; R = phenyl or anisyl)) adducts were synthesized. Our rationale for synthesis of these adducts is that upon subjection to electrochemical reduction, these adducts release free NHCs. The reversible release of free NHC release coupled with zwitterionic ring-opening polymerization would help establish a route to control the ring size of cyclic polyesters. As a part of these efforts, we have synthesized several $[Fe(NHC)(S_2C_2R_2)_2]^0$ adducts and subjected them to bulk electrolysis conditions in presence of suitable organocatalytic precursors. A detailed report of these efforts is presented below.

5. Summary of the most important results: To achieve an effective strategy to electrochemically modulate the ring size of cyclic polyesters, several criteria need to be met: 1) an easy route to access $[Fe(NHC)(S_2C_2R_2)_2]^0$ (R = phenyl or anisyl) adducts has to be established 2) detailed electrochemical and spectroelectrochemical measurements has to be performed on these adducts to demonstrate reversible release and recovery of NHCs 3) as a proof of principle electrochemically controlled simple organic transformation catalyzed by free NHCs should be performed. Once these steps are in place, the use of NHCs for electrochemically controlled zwitterionic polymerization can be established. Herein, we report our efforts towards electrochemically-controlled reversible released free NHCs to control ring size of cyclic polyesters.

Over past several months, effort were directed towards synthesis of $[Fe(NHC)(S_2C_2R_2)_2]^0$ (R = phenyl or anisyl) adducts and its use in electrochemically controlled organocatalysis reactions. Reversible release of triphenylphosphine with five coordinated $[Fe(PPh_3)(S_2C_2R_2)_2]^0$ adducts were successfully demonstrated with electron rich dithiolene adducts bearing phenyldithiolate, pdt ($S_2C_2Ph_2$)²⁻ or anisyldithiolate, adt ($S_2C_2(Anisyl)_2$)²⁻ ligands.⁷ Since NHCs and phosphines share similar coordination properties, we envisioned that such release would be possible with

NHCs. Moreover, it is well documented that free NHCs such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SIMes) catalyze zwitterionic ring opening polymerization reactions to yield cyclic polyesters.⁵⁻⁶ Hence, we focused our effort towards synthesis of dithiolene-NHC adducts $[\text{Fe}(\text{IMes})(\text{S}_2\text{C}_2\text{R}_2)_2]^0$ and $[\text{Fe}(\text{SIMes})(\text{S}_2\text{C}_2\text{R}_2)_2]^0$ adducts (R = Ph or anisyl) (**1-4**) for reversible release of NHC as a means to control ring size of cyclic polyesters.

The free carbene precursors $\text{IMes}[\text{H}][\text{Cl}]^8$ and $\text{SIMes}[\text{H}][\text{Cl}]^9$ were prepared using previous literature methods. While, iron bis(dithiolene) complexes were generated using the standard procedure reported by Schrauzer and his co workers.¹⁰ The spectroscopic parameters for the prepared complexes were well in accordance with the reported values. Once, the suitable precursors were synthesized, efforts were direct towards synthesis of iron bis(dithiolene)-NHC adducts as described in **Scheme 1**.



Scheme 1: Synthesis of iron bis(dithiolene) NHC adducts.

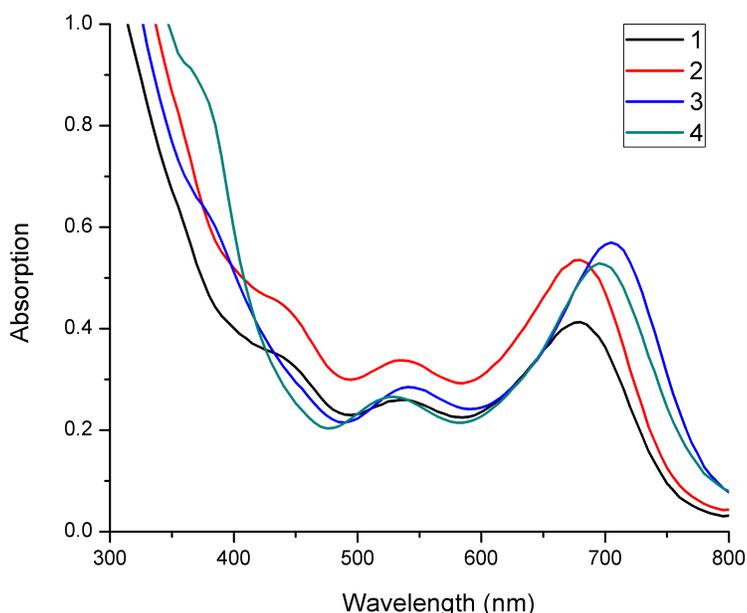
All four adducts (**1-4**) were prepared by reacting free carbene that is generated in situ by treating the corresponding imidazolium salts with NaHMDS (sodium bis(trimethylsilyl)amide) with the corresponding iron dithiolene dimers (**Scheme 1**). Compounds **1-4** were confirmed by a variety of spectroscopy techniques including, NMR spectroscopy and UV-Vis absorption spectroscopy. In ¹H NMR, peaks corresponding to mesityl groups for compounds **1-4** were observed in between ~2.0 – 2.4 ppm (CDCl₃), indicative of presence of mesityl group with integrations adding to 6 and 12 hydrogens, respectively. As expected, peaks for pdt and adt (pdt = phenyldithiolate, adt = anisyldithiolate) were observed in between 6.8 – 7.3 ppm (CDCl₃). In ¹³C NMR, Fe-C_{carbene} carbon for **1-4** resonates at ~182 ppm (CDCl₃), indicative of presence of metal-carbene bond. This value was in the range reported for other reported iron-NHC complexes (189 ppm in C₂D₆O).¹¹ To get further insights in to solid-state structure of **1-4**, X-ray quality single crystals were grown by vial in a vial diffusion method. Solid-state structure of complexes **1-4** were probed using single crystal X-ray crystallography.

To assign the formal reduction and oxidation potential of the synthesized adducts cyclic voltammetry (CV) experiments and differential pulse voltammetry (DPV) has been carried out for compounds **1-4** in THF solvent with $[\text{N}(\text{tBu})_4]\text{PF}_6$ as the supporting electrolyte at 25 °C. All peaks were internally referenced to decamethylferrocene ($\text{Fc}^{*+}/\text{Fc}^*$). Compounds **1-4** displayed two reduction peaks and one oxidation peak. The oxidation wave for compound at 0.50 corresponds to the **1**⁺, the first redox wave at -0.68 V corresponds to the one electron reduced **1**¹⁻ species, and the second irreversible reduction wave is assigned to **1**²⁻ (**Figure 1**). The irreversibility of the second reduction peak is indicative of cleavage of iron-C_{carbene} bond.¹² Electrochemical potential displayed by other **1-4** are displayed in Table 1.

Table 1. Redox potentials of Fe-bis(dithiolene) NHC adducts determined by CV at -20 °C.

| Adduct | $E_{1/2}$ (V) (1 ⁺ /0) | $E_{1/2}$ (V) (0/1 ⁻) | $E_{1/2}$ (V) (1 ⁻ /2 ⁻) |
|----------|--------------------------------------|--------------------------------------|--|
| 1 | 0.50 | -0.68 | -1.9 |
| 2 | 0.53 | -0.74 | -1.9 |
| 3 | 0.35 | -0.77 | -2.0 |
| 4 | 0.44 | -0.78 | -1.95 |

To understand the electronic excitations of the iron-bis(dithiolene) *N*-heterocyclic adducts, compounds **1-4** were subjected to UV-Vis spectroscopy in THF. All four compounds (**1-4**) displayed distinctive absorption around 681 nm, 672 nm, 704 nm and 697 nm, respectively, attributed to intervalence ligand to ligand charge-transfer (**Figure 1**). It is important to note that the corresponding charge-transfer band is absent in dimer $[\text{FeS}_2\text{C}_2\text{R}_2]_2^0$.

**Figure 2.** UV-Vis absorption spectroscopy of the **1-4** in THF.

From CV measurements of **1**, it was observed that second electron reduction is irreversible, indicative of iron-carbene bond dissociation and concurrent formation of free NHC and dianion dimer $[\text{FeS}_2\text{C}_2\text{R}_2]_2^{2-}$ in the solution. This phenomenon was further confirmed by spectroelectrochemical analysis. This experiment was carried out in a special electrochemical quartz cell fitted with Pt mesh working electrode, Pt counter electrode and silver wire quasi-reference electrode. Bulk reduction of **1** at -2.0 V (vs. AgCl) and concomitant UV measurement was carried out and UV-Vis absorption measurement was recorded for every 30 sec. The intervalence interligand-charge transfer absorption peak slowly reduced up on reduction and after several seconds the complex was completely reduced which is inferred by the complete suppression of the charge transfer peak (**Figure 2**).

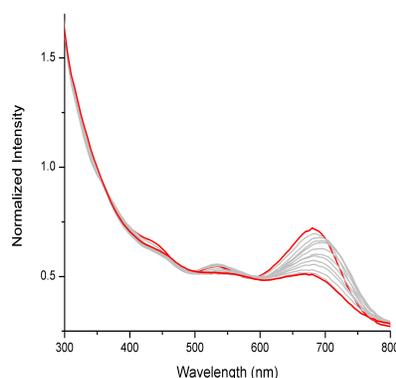
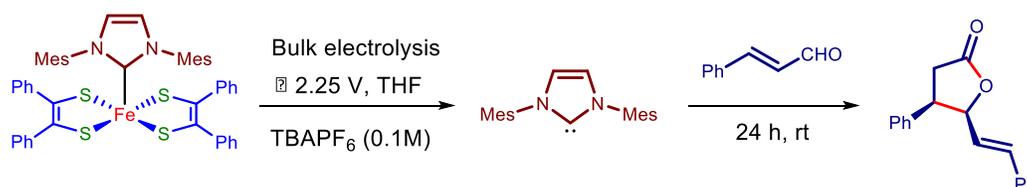


Figure 3. Spectroelectrochemistry of **1** in THF solvent at 25°C with $[N(n\text{-Bu})_4][\text{PF}_6]$ as the supporting electrolyte.

Cyclic voltammetry and spectroelectrochemical measurements strongly suggest that the release of free NHC upon bulk reduction of compound **1**. As proof of principle we choose free NHC catalyzed conjugate umpolung reactivity of unsaturated aldehyde as recently disclosed by Glorius and his co-workers.¹³ For this, IMes catalyzed γ -butyrolactone synthesis starting from cinnamaldehyde was chosen as the substrate.¹³ Bulk electrolysis of **1** was conducted in a two compartment cell separated by glass frit at 25 °C in 20 ml of 0.1M $[N(n\text{-Bu})_4][\text{PF}_6]$ as the supporting electrolyte in THF. Platinum mesh working electrode, Pt mesh counter electrode and Ag/Ag⁺ non-aqueous reference electrode were used as the required electrodes. Compound **1** was taken in the working electrode compartment and bulk electrolysis was carried out holding at -2.25 V. After complete reduction ($1^0/1^{2-}$), the reduced electrolysis solution was pipetted in to a 20 ml vial containing *trans*-cinnamaldehyde and left for stirring at room temperature. After 24 h a drop of solution drawn from the reaction mixture was spotted against the starting reagents on the TLC plate. γ -butyrolactone was isolated in 33% yield as presented in **Scheme 2**. Our current efforts are directed towards using this methodology to generate cyclic polyesters. Once this is successful, in situ generation, followed by electrochemical reversible release will be performed to control ring size of cyclic polyesters.



Scheme 2. Electrochemically generated carbene catalyzed synthesis of γ -butyrolactone.

Conclusion

In sum, we have isolated several $[\text{Fe}(\text{NHC})(\text{S}_2\text{C}_2\text{R}_2)_2]^0$ adducts in good yields by treating free carbene with corresponding dithiolene dimers. The adducts were fully characterized by NMR, X-ray crystallography, electronic and spectroelectro chemistry. Upon bulk reduction of compound **1**, free carbene is released and the electro generated free carbene was used for synthesis of γ -butyrolactone. Further expanding this concept to cyclic polyester synthesis would allow to precisely control the ring size of cyclic polyesters. The time lag behind every successive reduction and oxidation cyclic would determine the exact ring size of the polymer.

Syntheses of Iron(bis-dithiolene) NHC adducts: A 10 mL scintillation vial with stir bar was charged with IMes.HCl (100 mg, 0.29 mmol), $\text{NaN}(\text{SiMe}_3)_2$ (58 mg, 0.31 mmol) and 4 mL of dry THF. The resulting mixture was stirred at 25 °C for 45 mins, which resulted a yellow solution with white suspension. The heterogeneous mixture was filtered in to a clean 20 mL scintillation vial containing $[\text{Fe}(\text{Ardt})_2]_2$ (0.145 mmol) in 2 mL THF. An immediate color change was noticed from blue-green solution to black solution. The resulting mixture was stirred at rt for 12 h. The black colored solution was filtered through pad of celite and dried. To dried black residue was dissolved in minimum amount of dichloromethane solvent and precipitate out the compound using hexane 15 mL. the resulting black precipitate further washed with ether and dried under vacuum for 24 h.

Compound 1: 110 mg, 90% yield; $^1\text{H-NMR}$ (300 MHz, CDCl_3): d 7.31-7.28 (m, 8H), 7.22-7.18 (m, 12H), 6.96 (s, 4H), 6.84 (s, 2H), 2.36 (s, 6H), 2.00 (s, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): d 182.18, 143.19, 139.13, 136.82, 135.80, 129.65, 129.31, 127.69, 127.00, 126.77, 21.41, 18.60.

Compound 2: 103 mg, 84% yield; $^1\text{H-NMR}$ (300 MHz, CDCl_3): d 7.28-7.26 (m, 8H), 7.23-7.18 (m, 12H), 6.95 (s, 4H), 3.72 (s, 4H), 2.34 (s, 6H), 2.26 (s, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): d 181.3, 143.06, 138.20, 137.26, 136.39, 129.62, 127.65, 127.02, 51.97, 21.35, 18.75.

Compound 3: 129 mg, 92% yield; $^1\text{H-NMR}$ (300 MHz, CDCl_3): d 7.27-7.24 (m, 8H), 6.94 (s, 4H), 6.82 (s, 2H), 6.76-6.73 (m, 8H), 3.82 (s, 12 H), 2.36 (s, 6H), 2.00 (s, 12H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): d 181.05, 158.68, 138.94, 136.80, 136.51, 135.87, 130.73, 129.17, 126.63, 113.09, 55.33, 21.49, 18.62.

Compound 4: 122 mg, 87% yield; $^1\text{H-NMR}$ (300 MHz, CDCl_3): d 7.21-7.28 (m, 8H), 6.90 (s, 4H), 6.73-6.70 (m, 8H), 3.79 (s, 12H), 3.64 (s, 4 H), 2.33 (s, 6H), 2.22 (s, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): d 180.32, 158.70, 138.03, 137.29, 136.48, 136.39, 130.72, 129.53, 113.06, 55.33, 51.94, 21.42, 18.77.

Organocatalysis of *in situ* electrochemical generated carbene: Synthesis of g-Butyrolactone

10 ml of the electrolyte solution TBAPF6 (0.1M in degassed THF) was transferred to the both compartment of the electrochemical cell. (0.02 mmol) of the catalyst 3aa was dissolved on working electrode compartment. Working electrode (Pt mesh) and reference electrode (Ag/Ag^+ in MeCN) were immersed to one side compartment and Pt mesh counter electrode is immersed on the other compartment. Electrolysis was conducted at -2.25 V potential. After completing the electrolysis, the solution inside the working electrode compartment was transferred in to a 20 ml vial containing *trans*-cinnamaldehyde (0.4 mmol, 53 mg) and the solution was stirred for 24 h. After evaporating the THF solvent, 3 x 10 ml (90:10 Ether:DCM) mixture was used to extract the product from residue. The extract was dried and followed by silica gel column purification using hexane: EtOAc (10%) elution solvent offered the g-butyrolactone in 33% yield (18 mg), 89:11 *dr*. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.21-7.28 (m, 8H), 6.90 (s, 4H), 6.73-6.70 (m, 8H), 3.79 (s, 12H), 3.64 (s, 4 H), 2.33 (s, 6H), 2.22 (s, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 180.32, 158.70, 138.03, 137.29, 136.48, 136.39, 130.72, 129.53, 113.06, 55.33, 51.94, 21.42, 18.77.

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7. Appendixes

Not Applicable