

Electron-deficient Anthraquinone-diimines Based Metallosupramolecular Polymers for Electrochromic Study

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ABSTRACT

The redox active anthraquinone diimines-terpyridine base metallosupramolecular polymers (MSPs) were synthesized from amine and 9,10-anthraquinone, respectively. The electrochemistry and electrochromic properties of these polymers were investigated. The spin-coating of polymer films exhibited reversible electrochemical processes and strong color changes upon electro-oxidation or electro-reduction. The remarkable electrochromic behavior of the film was clearly interpreted from spectroelectrochromic study and stability was evaluated by the electrochromic cyclic switching studies.

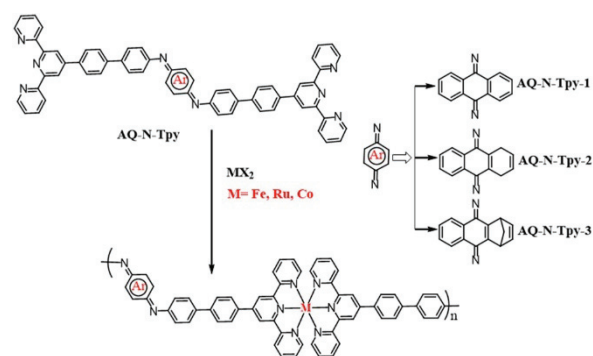
1 INTRODUCTION

Electrochromic materials are change their optical properties through a redox process by applying external voltage [1]. EC materials and device have great advancement in the last few decades for development of technological aspect such as adaptive camouflages [2], smart windows [3], antiglare mirrors [4] and displays [5] devices. Most of the EC materials are conjugated organic polymers, electro-active organic small molecules, metal oxides, transition metal-organic complexes and metallosupramolecular polymers (MSPs)[6]. Among them MSPs are one of interesting materials for electrochromism which have intense MLCT band in the visible region. These MLCT energy band tuned by the redox state of the metal and ligand structure. One of the important ditopic ligands is bisterpyridine, have been used for MSPs formation. The bridging ligand can tune the MLCT properties in metal-organic complexes. For this purpose, designing a new electro active ligand for preparation a new MSPs with some improved properties is one of the most challenging tasks in understanding the EC properties of the MSPs.

Aromatic imides exhibit many advance properties, such as excellent mechanical properties, thermal stability, excellent chemical resistance and beneficial electrical properties, e.g. low dielectric constant and high breakdown voltage. Incorporation of specific functionality into MSPs backbones leads to various advanced functional materials that exhibit certain advantageous properties, such as electrochromic, charge storage, photosensitive, proton-conducting, and memory characteristics. Anthraquinone based (AQ) derivatives and polymers have been reported to be candidates as redox-

active and near-infrared (NIR) EC materials because they exhibit intense NIR absorptions when the AQ units are electrochemically reduced to a radical anionic state or a dianionic state.[7]

Here, we now report a series substituted anthraquinone diimine containing metallo-supramolecular (**Scheme-1**) polymers which will gives reversible reduction and oxidation potentials. Furthermore, the structural modifications of the quinone diimine backbone provide the valuable possibility of large shifting of the redox properties.



Scheme-1. Ligand structure and polymer synthesis.

2 EXPERIMENT

2.1 Materials

4-bromaniline, 1,4-diaza-bicyclo[2.2.2]octane (DABCO), Titanium tetrachloride(TiCl_4), tetrakis(triphenylphosphine)palladium(0)($\text{Pd(PPh}_3)_4$) were purchased from Sigma-Aldrich and used as received. Chlorobenzene, K_2CO_3 , LiClO_4 and acetonitrile were purchased from Wako chemical. All Anthraquinone based chemicals were supplied by Air Water Performance Chemical Inc.

2.2 Preparation of polymer

PolyAQ-N-Fe

In a two-necked round-bottom flask, an equimolar mixture of prepared **AQ-N-Tpy-1** (200 mg, 0.2 mmol) and Fe(OAc)_2 (35.8 mg, 0.2 mmol) was refluxed in acetic acid solvent under a N_2 -saturated atmosphere for 24 h. The reaction mixture was cooled to room temperature, filtered, and acetic acid was evaporated to get deep violet color solid.

3 RESULTS AND DISCUSSION

3.1 EC Performance

In three electrode system EC properties of **polyAQ-N-Fe** was investigated. During cyclic voltammetry (CV) study of polymer film exhibits reversible redox in nature between -1.2 to 1.5 V. In figure 1, polymer film shows strong oxidation peak at ~ 0.75 V vs. Ag/Ag^+ responsible for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transition and another strong reduction peak at ~ 0.45 V vs. Ag/Ag^+ assign for reduction for anthraquinone unit. The EC performance of **polyAQ-N-Fe** film was evaluated using same experimental setup. When ligand coordinated with Fe^{2+} metal ions, a strong peak was generated at 573 nm, as indicated by pink color film (Figure1b). The visible range strong peak was caused by metal-to-ligand charge transfer (MLCT) transition from the metal centers Fe^{2+} to **AQ-N-Tpy-1**. **PolyAQ-N-Fe** thin film displayed reversible color change between pink to colorless and vice versa by applying 1.0 and 0.0 V, respectively, as shown in Figure 1c. The reversible color switching associated with the redox mechanism of the metal center was responsible for the visible absorption.

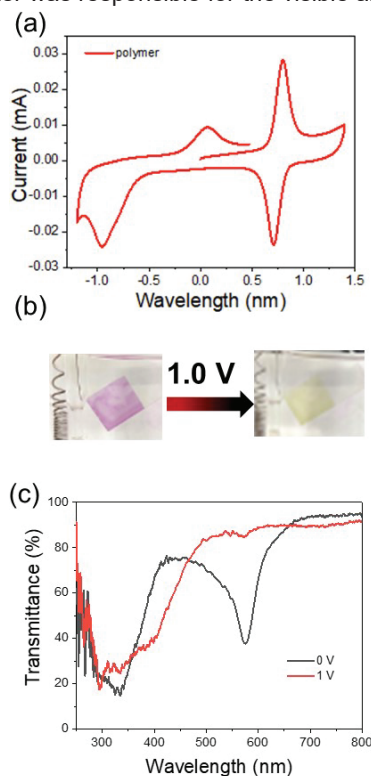


Figure-1. (a) Cyclic voltammetry of **polyAQ-N-Fe**. (b) Color change **polyAQ-N-Fe** film at 0.0 and 1.0 V. (c) Transmittance spectra at 0.0 and 1.0 V in 0.1 M LiClO_4 / acetonitrile electrolyte.

3.2 Stability test of **polyAQ-N-Fe** film

The spectroelectrochromic switching was measured by repeatedly cyclic switching of the applied potential between 0 and 1.0 V vs Ag/Ag^+ with interval time 3 s with.

Dynamic transmittance change ($T - t$) monitoring at 573 nm was recorded and continued without changing the optical contrast for several cycles. UV/vis transmittance analysis after 2000 cyclic switching, the film shows 98% retention of its EC activity (Figure 2a). Furthermore, a stable anodic/cathodic peak current over time suggested good and stable EC behavior of polymer film. The film showing optical contrast of $\sim 70\%$ at 573 nm (ΔT) upon the application of potential of 0–1.0 V and vice versa. Bleaching (t_b) and coloration time (t_c) monitoring at 573 nm were ~ 1.7 and 1.1s, respectively.

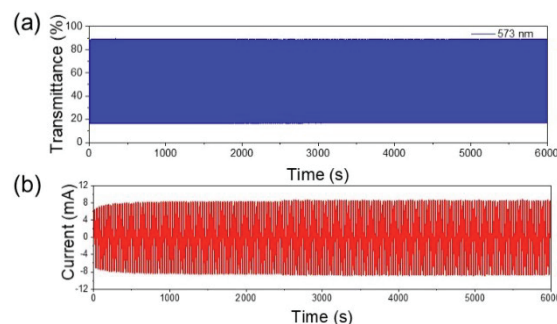


Figure-2. (a) Dynamic transmittance change (monitoring at 573 nm and (c) current flow during switching in 0.1 M LiClO_4 / acetonitrile electrolyte.

4 CONCLUSIONS

Our anthraquinone-diimide ligand-based polymer shows significant EC properties in solution state which exhibited high optical contrast, fast switching and long cycle stability. The design of dual-redox MSPs, the electrochromism at visible region, and the durable device structure will be useful for the development of next-generation energy-saving smart windows.

ACKNOWLEDGMENT

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