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Vertical Step-Growth Polymerization Driven by Electrochemical Stimuli from Electrode

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Dedication ((optional))

Abstract: We presented here that vertical step-growth polymerization of monomer A-B via individual A-A or B-B coupling driven by electrochemically switching positive and negative bias on self-assembled A or B electrode. In particular, monomer is Ru(II)(bda)AB (bda = 2,2'-bipyridine-6,6'-dicarboxylate), where A and B are pyridines with pendant carbazolyl and vinyl, which can be dimerized at oxidative potential (ca. 1.0 V vs. Ag/Ag⁺) and reductive potential (ca. -1.8 V), respectively. Self-assembled monolayers on ITO glass are Ru(II)(bda)PA or Ru(II)(bda)PB (P = pyridine with pendant phosphonic acid). This well-controlled polymerization allows us to synthesize surface confined molecular wire in single molecule precision on electrode with sequence- and topology-controlled possibility. The electrocatalytic performance based on water oxidation of vertically orientated molecular wires rises up with increasing molecular length, and oversteps those of both selfassembled monolayer and randomly electropolymerized film, which were generally studied as two typical models by most of researchers. With function-tuning ability and rapid fabrication, it is highly anticipated that this polymerization and one-pot single molecule controlled assembly has highly promising potentials for practical applications with expectably superior performances.

Controlled covalent formation of organized molecular building blocks based on solution deposition is of great importance and challenge for next generation applications such as electronics,^[1] sensors,^[2] catalysis,^[3] and bio-relatives.^[4] By now, selfassembled monolayers (SAMs) and thin films are well known as two successful camps to have been considering for practical applications.^[5] Though molecules can serve in theory as an ultimate functional building block,^[6] there is lack of truly number and sequence controlled one by one single molecular assembly on substrates as well as solid phase peptide synthesis,^[7] which is key to broaden the molecular scale applications. Molecular assemblies based on non-covalent step growth polymerizations such as metal coordination,^[8] hydrogen bond^[9] and host-guest recognition^[10] have great potential in precisely single molecule controlled assembly. However, there are remaining tough challenges including that (1) how to prevent vertically molecular

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wires on substrates from self-coupling reactions, and (2) iterative dipping and rising processes are hampered by time consuming operation and the use of a large amount of solvent. Rapid and economical one-pot covalent assembly with tuning physicochemical properties becomes highly desirable for practical applications.

As a simple and low cost programmable technique, the electrochemical oxidation and reduction have long been individually used to fabricate conducting $polymers^{[11]}$ without controllable sequence and degree of polymerization because two oxidative or reductive sites^[12-14] of monomer can be simultaneously activated. Therefore, single oxidative reactive site and single reductive reactive site coexsisting in an identical molecule should enable us to one by one control the single molecular assembly via step growth polymerization by alternatively switching positive and negative bias. In this paper, we have firstly designed Ru complex with both electrooxidative (carbazolyl) and electroreductive (vinyl) reaction units for onepot single molecule controlled assembly on electrode (Scheme 1a). This vertical step growth polymerization has successfully prevented the self-coupling within SAM and between vertically molecular wires on electrode, and allows single molecule controlled assembly to be processed in one-pot without moving or changing experimental gears.



Scheme 1. Step-growth polymerization driven by electrochemically switching oxidative and reductive potentials on electrode pre-modified with CzP.

As shown in Scheme 1, monomer RuCzV possessing pendant carbazolyl and vinyl, and self-assembled monolayer CzP possessing pendant carbazolyl and phosphonic acid were designed and inspired by well-known Ru(II)(bda) (bda = 2,2'-bipyridine-6,6'-dicarboxylate) unit used for highly active water oxidation catalysts (WOCs).^[15] Electrochemically reductive coupling of vinyls^[16] and oxidative coupling of carbazolyls,^[17,18] take place at -1.8 V and 1.0 V vs. Ag/Ag⁺, respectively, and produce saturated bond (Scheme 1b) and 3,3'-bicarbazole

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formations (scheme 1c). In order to achieve the vertical molecular wire on substrate, the design of self-assembly molecule and Ru complex was considered to that how to avoid the self-coupling reactions of carbazolyls within SAM on electrode.^[19] Notably, self-assembled 9-octylcarbazole was not utilized for pre-modification of electrode due to self-coupling of carbazoles within SAM, where redox peaks of 3,3-bicarbazole was observed in cyclic voltammetry (CV) (Figure S1). In the case of CzP for SAM, Ru²⁺ and 2,2'-bipyridine units have lower oxidative and reductive potentials (Figure S2-6), and they should be preferentially oxidized or reduced as positively or negatively charged state, leading to same charge repulsion within SAM and between vertical molecular wires for probably restrained self-couplings between neighbor molecules.



Figure 1. UV-vis spectra (a), absorbance at 500 nm (b), CVs (c) and current intensity of redox peaks of $Ru^{2+/3+}$ (d) of $CzP(Ru)_n$ or/and $VP(Ru)_n$.

During alternatively switching positive and negative potentials of self-assembled ITO/CzP electrode in 0.5 mM RuCzV acetonitrile solution, the couplings of carbazolyl and vinyl of RuCzV in solution with carbazolyl and vinyl of ITO/CzP electrode were performed under nitrogen environment at dynamic potentials (E = -0.3 V~1.0 V, 20 mV/s, 1 cycle, Figure S7a) and constant potential (E = -1.8 V, 100 s, Figure S7b), respectively, considered based on dynamic controllability and low reactivity of vinyl in Ru complex.^[14b,d] The polymerization of molecular wire CzP(Ru)_n continues in single molecular precision (Scheme 1d) and it can be demonstrated by single molecular dependent absorbance (the metal to ligand charge transfer band at ~510 nm, Figure S8) and electrochemical redox peaks ($Ru^{2+/3+}$, $E_{1/2}$ = 0.43 V vs. Aq/AqCI). As the number of Ru units increases referred to SAM ($CzP(Ru)_n$, n = 0), the absorbance and current intensity of CzP(Ru)_n regularly grow and exhibit good linear relationship with switching times of alternative potentials (Figure 1.2a). Additionally, the intermittent growth of peak at 700 nm can be ascribed to emergence of more Ru³⁺ species through electrochemical oxidation (Figure S9) according to previous reports.^[20] Mass spectrometries were utilized for analyzing the molecular wire after treatment of HF, but no evidence was obtained probably due to detection limit for trace molecules. CVs were measured in aqueous solution instead of acetonitrile because of better observation of redox peaks. After n rises up to 9, the further polymerization is going to be difficult (Figure 1a) probably due to that the length of CzP(Ru)₉ has reached the width of electric double layer, which is generally considered to be 20 nm as maximum. As auxiliary evidences, CzP(Ru)9 in solid state has a thickness of ~23 nm (Figure 2b,c), which is in good agreement with theoretical value of 25.8 nm in extended state (Figure 2d). In contrast to linear molecular wire (Figure 2a), the molecular wire $VP(Ru)_n$ (VP = Ru complex possessing pyridines with pendant vinyl and phosphonic acid) with different sequence can be obtained on self-assembled VP on ITO electrode (Figure 1b,1d, 2e, S10). The cross-point in Figure 1b is considered to be due to the random measurement points of UV-vis spectra, while good linear relationships in Figure 1d is obtained from statistical measurement of entire electrode. Furthermore, topologically controlled non-linear molecular wires could be possible if both C(3)-C(3') and C(6)-C(6') couplings of carbazole were simultaneously activated at high oxidative potential of ≥1.2 V.^[18]



Figure 2. (a) $CzP(Ru)_n$ synthesized by step polymerization. (b) Thicknesses obtained from AFM image (b), SEM image (c), and theoretical value (d). (e) $VP(Ru)_n$ with alternative sequence by step polymerization.



Figure 3. Illustrations and AFM images of surface confined $CzP(Ru)_n$ (a) and random poly $(RuCz_2)_m$ film (b) with similar molecular surface coverage of Ru units controlled by CV cycles.

CzP(Ru) _n	in	solid	state	show	surface	confined
nanostructures	with	tiny	change	of RMS	(Figure	3a, Figure

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S13a), in contrast to non-specific random and uniform $poly(RuCz_2)_m$ (RuCz_2 = Ru(II)(bda) complex possessing two pyridines with pendant carbazolyls) film (Figure 3b, Figure S13b) with similar surface coverage of Ru units (Figure S11, S12). Furthermore, $CzP(Ru)_n$ (n = 0 and 9) with this specially nanostructural orientation was estimated by electrochemically active surface area (ECSA)^[21] and electrochemical kinetics at electrode-media interfaces. According to typical scan rate dependent CV traces (Figure 4a, S14), the capacitive current at 0.05 V is plotted as a function of scan rate to extract double layer capacitance (C_{DL}) from the slopes of fitting lines (Figure 4b). C_{DL} of $CzP(Ru)_9$ is calculated to be 0.19 mF, which is significantly ~5 times higher than those of CzP and poly(RuCz₂)_m film with a value of 0.039 mF. In equation ECSA = C_{DL}/C_s , C_s are similar if CzP(Ru)₉ and poly(RuCz₂)_m films were considered to possess same Ru units, which can be confirmed by redox charges of Ru units (Figure S15). Thus, CzP(Ru)₉ should have superior large ECSA to poly(RuCz₂)_m film. Additionally, the electrode kinetics was evaluated by electrochemical impedance spectroscopy (EIS) that CzP(Ru)₉ and CzP have almost identical diffusion impedance, which is much higher than those of poly(RuCz₂)_m film with mostly resistive behavior (Figure 4c), indicating that the surface-confined assemblies without altering interfacial electronic property of their original SAM template. CzP(Ru)₉ and CzP have the charge transfer dominating region as semicircles at high frequency with resistances of 52.9 Ω and 58.9 Ω, respectively, while poly(RuCz₂)_m film has a relatively high resistance of 67.1 Ω, probably owing to the facilitating funneling or hopping process of electron transfer between oriented molecular wires^[22] compared to compact and uniform poly(RuCz₂)_m film (Figure 4d).



Figure 4. (a) CVs of CzP(Ru)₉ in non-Faradaic region at scan rates of 5, 10, 25, 50, 100, 200, 400, 600 and 800 mV/s, and (b) current intensity of redox peaks at 0.05 V as a function of scan rates. (c) Nyquist plots of CzP, CzP(Ru)₉, poly(RuCz₂)_m, and (d) their magnifications of high-frequency region with illustration of equivalent circuit.

With superiorities of high ECSA, abundant active sites and fast electron transfer kinetics of $CzP(Ru)_n$ at interface of electrode, one attractive potential application lies in

electrocatalytic water oxidation inspired by well-known Ru complex.^[15] With length increase from n = 0 to n = 9 of $CzP(Ru)_n$, the catalytic currents density of water oxidation, progressively rises up to 66.2 µA cm⁻² in Figure 5a (surface coverage is 13.2×10⁻¹⁰ mol cm⁻²), while poly(RuCz₂)_m film with similar surface coverage (13.8×10⁻¹⁰ mol cm⁻²) shows a current density of 35.5 µA cm⁻², indicating CzP(Ru)₉ is superior to SAM and poly(RuCz₂)_m film for electrocatalytic water oxidation. The oxidation peaks of Ru^{2+}/Ru^{3+} and Ru^{3+}/Ru^{4+} of $CzP(Ru)_n$ appear at 0.77 V and 1.40 V (vs. NHE) respectively,^[23] and gradually increase as build-up of CzP(Ru)n. The oxidation peak of 3,3bicarbazole should be at 1.20 V (vs. NHE). As for poly(RuCz₂)_m film, the oxidative potential of Ru2+ slightly increases to 0.84 V and has a broader peak width, indicating sluggish electron transfer, which is in good agreements with Figure 4c-d. In controlled potential electrolysis (Figure 5b), CzP(Ru)₉ and $poly(RuCz_2)_m$ show negligible current decline during 1 h electrolysis, indicating the robust catalysts loading without desorption or inactivation occurs. The catalytic current density of 41.4 µA cm⁻² for molecular wire CzP(Ru)₉ also significantly surpass over that of poly(RuCz₂)_m film with a value of 26.1 µA cm⁻². Molecular wire CzP(Ru)_n not only offers tunable electrocatalytic properties based molecular scale, also exhibits superior electrocatalytic performance to general SAM and electropolymerized film, making it promising candidate for single molecule controlled catalysts loading.



Figure 5. (a) Linear sweep voltammetry of bare ITO, CzP(Ru)_n, poly(RuCz₂)_m, and CzP(Ru)_x on ITO at a scan rate of 20 mV/s. (b) controlled potential electrolysis at 1.7 V (vs. NHE) in 0.1 M HClO₄ aqueous solution, and (c) Absorption spectra of CzP, CzP(Ru)₉ and CzP(Ru)_x prepared by switching constant potentials between 1.0 V and -1.8 V (d).

To further elucidate the advantage of electrochemical route in high speed assembly, in 10 min, the molecular wire CzP(Ru)_x with a surface coverage of 7.85×10^{-10} mol cm⁻², which is ~70% of CzP(Ru)₉, was fabricated by programmable switching constant potentials between 1.0 V and -1.8 V (Figure 5c-d). Though this rapid mode does not provide theoretically values in absorbance, linear sweep voltammetry and controlled potential electrolysis (Figure 5a-c) probably due to sluggish molecular immigrations at interface of electrode, it does also show

excellent electrocatalytic performance with further optimizing possibility by varying electrochemical conditions.

In conclusion, vertical step growth polymerization driven by electrochemical stimuli with tunable interface function of electrode was successfully developed via alternation of reductive and oxidative reactions. Thanks to the controlled electrochemical couplings and template effect of SAM, this polymerization has not only fabricated vertical molecular wire on electrode, also showed the sequence and topology controllable possibility. The resulting surface confined molecular wire presented fast electron transfer as well as SAM, and superior electrocatalytic performance to general SAM and random electropolymerized film widely used before. With rapid and programmable electrochemical features, in principle for practical applications, various types of metal complexes could be introduced into molecular wire with sequence controllability in one-pot or in alternative solutions. It is highly anticipated that this simple polymerization can be generalized for practical molecular interface relative applications with expectably superior performances.

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