Electrochromic Polymeric Films Derived from (Diphenylamino)phenyl-substituted Metallophthalocyanines

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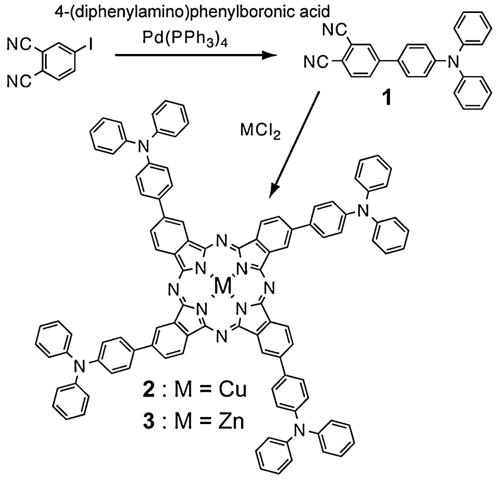
Copper and zinc phthalocyanines decorated with four triphenylamines were synthesized and a green film was formed by oxidative linkage between two peripheral triphenylamines. The film deposited onto an ITO electrode exhibited a reversible electrochromic switching among green, red-brown, and blue.

Metallophthalocyanines (MPcs) have been investigated molecular materials in many fields including non-linear optics, xerography, optical data storage, molecular electronics, catalysis, photodynamic cancer therapy, solar energy conversion, sensors, and organic light emitting diodes.[1] In order to fabricate electronic and photonic devices using MPcs, it is necessary to construct uniform thin films in which the molecular ordering can be controlled. Vacuum sublimation, the Langmuir–Blodgett film formation, spin coating, and electrodeposition have been applied to prepare uniform MPc films onto the surface of various substrates.[2] Electrochemical polymerization has great advantages for the control of resultant film thickness and the tuning of their electronic conductivity.[3] Electrochemical polymerization involves the polymerization of monomers and the deposition of insoluble one- or two-dimensional structures onto the substrates. Two-dimensional porphyrin–oligothiophene copolymers have been constructed by electrochemical polymerization reported by Segawa et al.[4] However, two-dimensional network structures of MPcs, in which MPcs were linked with conjugated oligomers, have not been as extensively explored.[5] In this study, we report syntheses of novel MPcs having triphenylamine (TPA) substituents and their electrochromic behavior of two-dimensional polymeric MPcs prepared by the electrochemical polymerization. We found the formation of two-dimensional network by the electrochemical oxidation of peripheral TPAs. Shirota et al. reported the formation of stable amorphous glasses of TPA-substituted MPcs, in which TPA units were linked with MPcs by ether linkages.[6] We also expect the formation of amorphous thin films of MPcs by the electrochemical polymerization.

Phthalocyanine precursor **1** was synthesized by the Suzuki coupling reaction between 3-iodophthalonitrile and 4-(diphenylamino)phenylboronic acid in the presence of Pd(PPh)$_3$ (Scheme 1). Copper and zinc phthalocyanines **2** and **3** were prepared from **1** by refluxing in 2-(dimethylamino)ethanol with $CuCl_2$ and $ZnCl_2$, respectively. After purification by column chromatography and preparative recycling HPLC, ca. 25% of pure products were isolated. Precursor **1**, final ZnPc **3** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry.[7] MPcs **2** and **3** are soluble in organic solvents such as CH_2Cl_2, THF, and DMF. The introduction of TPAs improved the solubility of MPcs in organic solvents.



Scheme 1.

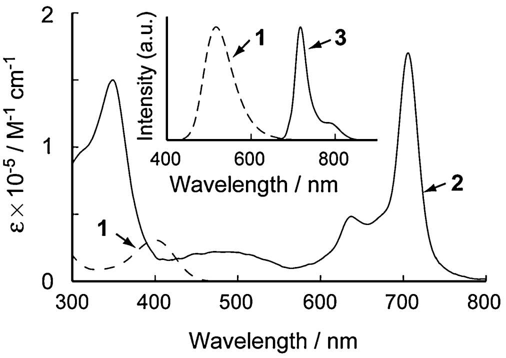


Figure 1. UV–vis spectra of **1** and **2** in dichloromethane and the inset shows the steady-state fluorescence spectra of **1** and **3** upon the excitation at the absorption maxium of **1**.

Copper and zinc phthalocyanines **2** and **3** exhibited a sharp Q band at 706 and 707 nm, respectively (Figure 1). The positions of Q band was shifted to the longer wavelength compared to copper and zinc tetra(*t*-butyl)phthalocyanines lacking TPAs (λ_{max} at Q band = 680 nm),[8] suggesting the electronic interaction between MPc and TPAs. Broad absorptions are observed in the range of 300–600 nm for **2** and **3**, ascribed to the sum of the absorption band of TPAs and the Soret bands of MPcs.[8] While the precursor **1** emitted a strong fluorescence at 516 nm at the excitation at the absorption maximum of **1** ($\lambda_{ex} = 400$ nm), the emission from **3** was mostly from ZnPc ($\lambda_{em} = 717$ nm, and quantum yield (Φ_f) = 0.17) and the residual fluorescence from TPA was very weak. This result suggests an efficient intramolecular energy transfer from TPA to ZnPc.

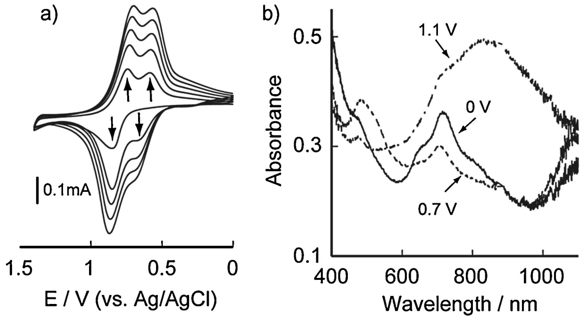


Figure 2. (a) Repeated potential scanning electro-polymerization of **2** ([**2**] = 1 mM); (b) Absorbance changes of polymerized **2** film on an ITO electrode at different potentials (vs. Ag/AgCl) in an electrolyte solution.

Electrochemical characteristics of TPAs, in which electroactive nitrogen is linked to three electron-rich phenyl groups in a propeller-like geometry, have well investigated.[9] The anodic oxidation of TPA leads to TPA cation radical and the generated cation radical TPA dimerized to form tetraphenylbenzidine (TBA).[10] Electrochemical studies of **1** and **2** were performed in CH_2Cl_2 solution containing 0.1 M Bu_4NClO_4. The cyclic voltammogram of **1** indicates an irreversible oxidation at $E_{p,a} = 1.07$ V in the first scan and a new pair of redox peaks corresponding to the formation of TBA was observed at $E_{1/2} = 0.68$ V in the second scan.[10] Repeated potential cycling between 0 and 1.4 V vs. Ag/AgCl of **2** showed both monomer oxidation and electrochemical polymerization to form an electroactive film. Figure 2a shows multiple voltamograms of **2** using an ITO glass as a working electrode. CuPc **2** also shows the appearance of new redox couple at $E_{1/2} = 0.65$ V, indicating the electrochemical dimerization of TPA segments of **2**.[10] Upon the repeated scans between 0 and 1.4 V, the peak currents of two redox couples increased and a green film was deposited onto the surface of ITO glass.[11] MALDI-TOF mass spectrum of the green material showed a dominant set of peaks corresponding to m/z of 4638 (trimer), 6184 (tetramer), 7730 (pentamer), and 9275 (hexamer).

Electropolymerized film of **2** grown on the ITO glass was discovered to be quite durable. Upon washing and equilibrating, the opto-electrochemical properties of polymer **2** in monomer-free electrolyte were probed, and the film's redox activity was found to be rather stable, exhibiting less than a 5% loss of electroactivity after 50 repeated scans between 0 and 1.4 V. The polymer exhibited at least two oxidation waves at 0.65 V and the second at 0.80 V. These potentials are almost agree with those of TBA in the solution study.[10] Upon both redox cycling and potential stepping of films grown on the ITO glass, the polymer films showed a color switching among green, red-brown, and dark blue. The absorption spectra of the film were recorded from 400 to 850 nm while incrementally stepping the potential to different redox states of the polymer film of **2** (Figure 2b). For the polymeric film of **2** at 0 V, the maximum of the Q band was found at 710 nm and the position of Q band was almost same as that of **2** in solution. This indicates that the propeller-like geometry of TBA linkages in polymerized **2** prevents the aggregation of CuPcs within the highly concentrated thin film. Upon the oxidation at 0.7 V, the absorption intensity of the Q band decreased and new peak at 480 nm having a shoulder at 530 nm appeared. The appearance of new peak at 480 nm ascribed to the generation of the one-oxidation product of TBA.[9] The decreasing of Q band intensity at 0.7 V suggests an oxidation of phthalocyanine ring.[12] At oxidation potential higher than 1.0 V, the board absorption band around 800 nm corresponding to TBA^{2+} grew up. The spectral changes as a function of the applied potential are reversible and the film color remains at each potential.

In conclusion, novel MPcs **2** and **3** directly connected with TPAs were synthesized and electrochemically polymerized to give electroactive and electrochromic films through the oxidative dimerization of TPA segments. Thin films made of TPA-substituted MPcs are expected to find applications in organic devices due to their unique optical and electronic properties.

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