

Linking of amino-capped quinonediimines by divalent transition metal ions: Synthesis, characterization, and comparison to electronic structure calculations

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HIGHLIGHTS

- ▶ Synthesis of molecular wires from quinonediimine and transition metals.
- ▶ Determination of spin states by magnetic susceptibility measurement.
- ▶ Analysis of electronic state by quantum chemical calculations.

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ABSTRACT

Quantum mechanical density functional theory (DFT) calculations are reported for novel, self-assembled transition metal linked dimers of *N,N'*-bis (3'-carboxy,4'-aminophenyl)-1,4-quinonediimine, with the metals manganese, iron, cobalt, nickel, copper and zinc each in the +2 oxidation state. Infrared spectroscopy detected systematic changes in the carbon–nitrogen double bond involving the imine nitrogen atoms, from 1457 cm⁻¹ for manganese complex to 1622 cm⁻¹ for the iron complexes. The calculated electronic band gaps of the complexes compare favorably to those for the uncomplexed quinonediimines. The synthesis of the compounds demonstrates a feasible route to the design of a tunable architecture of linear molecular wires derived from properly derivatized quinonediimines.

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1. Introduction

Aniline oligomers and polymers have been investigated for their utility in catalysis [1], composites [2], corrosion inhibition [3,4], nano-junctions [5], nanoparticles and microtubules [6], non-linear optics [7], and solar cells [8]. Polyaniline (PAni) exists in at least three oxidation states: leucoemeraldine, emeraldine, and pernigraniline, several of which are readily interconvertible in the requisite physical or chemical environment. (Fig. 1) For both conducting polymer and corrosion control applications, the polymer in the “emeraldine” (intermediate) oxidation state needs to become protonated by Brønsted–Lowry acid, or reacted with a suitable Lewis acid – “doped” [9].

Studies have investigated the relationships between PAni [10] and oligoanilines structure and function [11,12]. These studies have confirmed that aniline oligomers are more effective in corrosion inhibition than the polymer. The oligomers are soluble in

a wide variety of common solvents, whereas PAni is only soluble in *N*-methyl-2-pyrrolidone (NMP). It has also been shown that the electronic states of the aniline oligomers sufficiently resemble those of the polymer for the oligomer to be an effective model of the polymer, particularly with respect to electronic states [11a].

The metals of the first transition row of the Periodic Table have enormous importance in both industry and biology. Of particular importance are the complexes of manganese [13], iron [14], cobalt [15], nickel [16], copper, and zinc [17] in their +2 oxidation states.

There is now considerable research interest in so-called “molecular wires” [18]. While oligo- and polyanilines are capable of forming completely organic molecular wires, the utilization of transition metal ions as “linkers” allows the design of novel structures with varied architectures and tuned properties.

It has been reported that the electrical conductivity of polyaniline is enhanced by the addition of transition metal complexes [19]. This follows widespread use of metals as electron deficient Lewis acids to dope PANI in a fashion analogous to the doping achieved by Brønsted–Lowry mineral acids [20]. This makes it likely that useful electronic properties will result from

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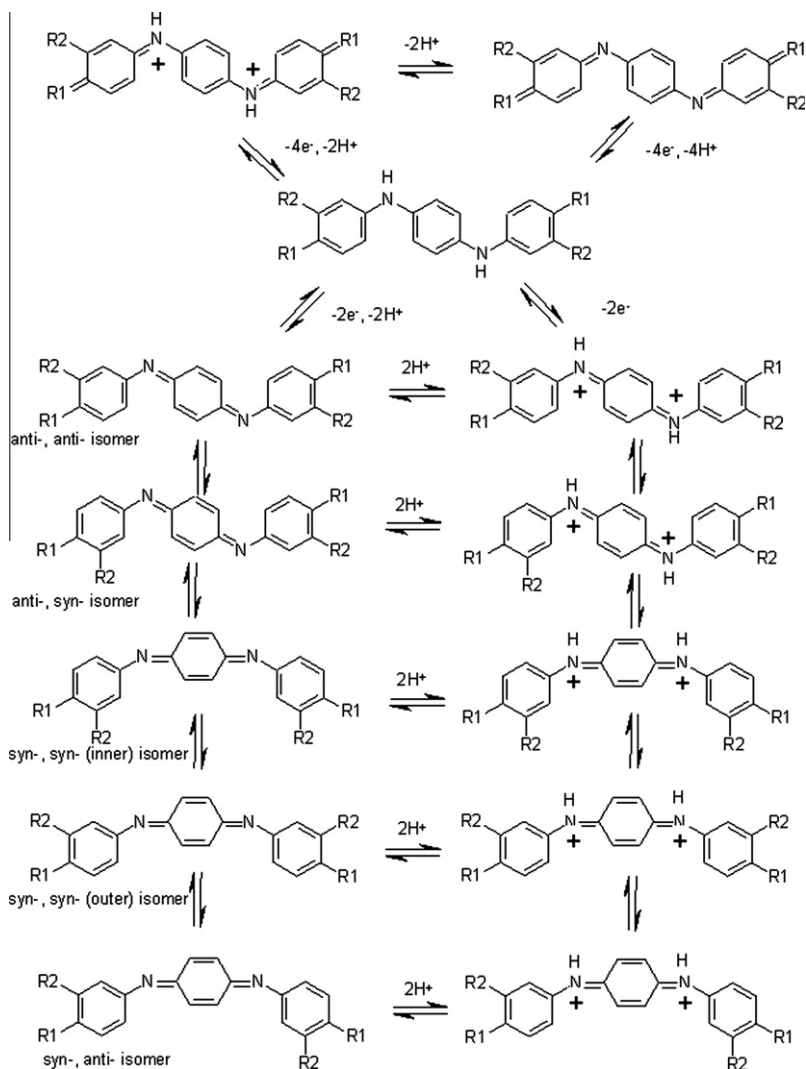


Fig. 1. Redox states of N,N' -(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine. R1 = NH_2 for leucoemeraldine and emeraldine states, and NH for pernigraniline. R2 = COOH for all redox states.

the deliberate incorporation of transition metals into the wire design.

The study of the interaction of aniline polymers and oligomers with metal ions is of considerable relevance to corrosion inhibition, since oxidation of the bulk (zero-valent) metal leads to metal cations. The interactions of metal cations with the polymer surface have not been thoroughly investigated, and it is likely that such interactions have a substantial influence on the efficacy of the polymer with regard to corrosion inhibition. For example, migration of metal cations away from the surface is one step in the degradation of the surface. If the surface coating has chemical functionalities capable of strongly binding these metal cations, migrating might be reduced, and the integrity of the surface maintained for a longer time.

Molecular wires of un-doped oligoanilines and transition metals are likely to be effective in corrosion inhibition applications in non-acidic environments where deprotonation/de-doping of the (non-complexed) oligomer is problematic.

2. Experimental methods

All reagents employed in the syntheses were purchased from Aldrich and used without further purification. AEQD was

synthesized by established methods [11b]. AEQD (~ 0.1 M) was dissolved in 0.2 M NaOH solution (Solution "A"). Separate solutions (Solution "B") of the relevant transition metal were prepared (0.5 M) from the appropriate divalent metal sulfate in de-ionized water. Even though a product of 1:1 metal to AEQD was desired, the concentration of metal ions was approximately 5:1 to drive the reaction as close to completion as possible.

Metals investigated included manganese, iron, cobalt, nickel, copper, and zinc, since sulfates salts of each with the metal in a +2 oxidation state are readily available. Solution B was added slowly to Solution A with stirring. The resulting mixture was allowed to stand, and the precipitate filtered and washed three times with cold de-ionized water. The precipitate was then allowed to air dry before characterization. The metallated products were all brittle, crystalline powders with a dull, black finish resembling ground pepper.

IR spectra were collected on a Thermo Scientific "Smart Performer" Attenuated Total Reflectance (ATR) attachment (diamond crystal) to a Nicolet 380 FT-IR. IR N,N' -bis (3'-carboxy,4'-aminophenyl)-1,4-quinonediimine (ATR, cm^{-1}): ν_{max} 1404, 748, 823, 1218, 1483, 1544, 1658, 2360, 3033, 3120.

IR poly-Mn(II)-co- N,N' -bis (3'-carboxy,4'-aminophenyl)-1,4-quinonediimine (ATR, cm^{-1}): ν_{max} 667, 1259, 1457.

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