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Design of reversible multi-electron redox systems using benzochalcogenophenes containing aryl and/or ferrocenyl fragments

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Abstract

2,3-Disubstituted benzo[*b*]thiophenes, 1,3-disubstituted benzo[*c*]thiophenes, and 1,3-disubstituted benzo[*c*]selenophene have been systematically and selectively synthesized from benzo[*b*]thiophene or phthaloyl dichloride as a starting material, respectively. Characterization of the molecules was performed by physical and spectroscopic means and X-ray crystallographic analyses. The cyclic voltammograms of the chalcogenophene derivatives containing aryl fragments showed well-defined reversible both anodic and cathodic steps derived from the unusually stable 5π chalcogenophene radical cations and 7π chalcogenophene radical anions. The cyclic voltammograms of the novel chalcogenophene derivatives containing ferrocenyl fragments showed a well-defined reversible cathodic step derived from the unusually stable 7π chalcogenophene radical anions and two distinct reversible anodic steps derived from ferrocenium cations separated from each other by a thiophene-heterocycle. The radical character of several novel 7π chalcogenophene radical anions was measured by ESR spectroscopy.

Keywords: Thiophene; Selenophene; Ferrocene; Radical cation; Radical anion; Redox reaction

1. Introduction

In recent years, the study of molecules comprising multiple reduction–oxidation (redox) centers have attracted considerable research interest in the field of material science due to the preparation of new π-conjugated materials with application in material science [1]. Moreover, this kind of molecule having more than two redox-active metal centers is a fundamentally attractive target for the study of multi-electron transfer processes via the mixed-valence state derived from these multi-metallic systems [2]. On the other hand, interest in the design of novel redox-active organic centers by the use of a 5π- and 7π-electron framework [3] containing group 16 elements has led us to explore the synthesis of new five-membered heterocycles containing sulfur and/or selenium atom(s). This time our studies are aimed at the design of reversible multi-steps redox systems using simple molecules with both organic and organometallic electron transfer fragments. Although the synthesis and characterization of substituted benzochalcogenophenes have been reported [4], there is no report concerning benzannulated thiophene and selenophene containing a ferrocene fragment on the five-membered heterocyclic unit, which are of structural and redox-characteristic interest. Recently, we reported a new type of multi-steps reversible redox systems using organic–organometallic hybrid molecules, 1-ferrocenyl- and 1,9-diferrocenyl-thianthrenes [5]. Therefore, we have designed 2,3-disubstituted benzo[*b*]thiophene and 1,3-disubstituted benzo[*c*]chalcogenophene as both cathodic and anodic multiple-redox active organic–organometallic hybrid molecules. In this paper, we provide the details on the synthesis, structural characterization, and electrochemical properties of 2,3-disubstituted benzo[*b*]thiophenes, 1,3-disubstituted benzo[*c*]thiophenes, and 1,3-disubstituted benzo[*c*]selenophenes.

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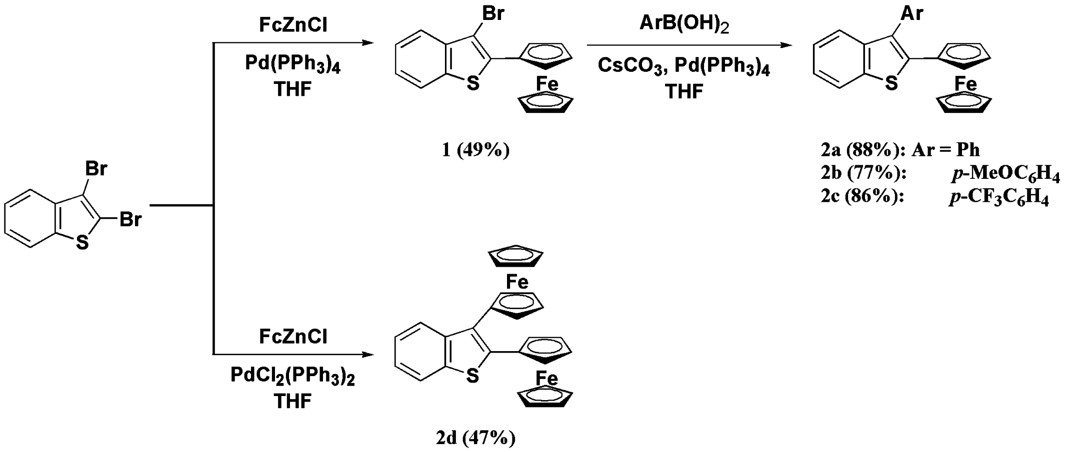
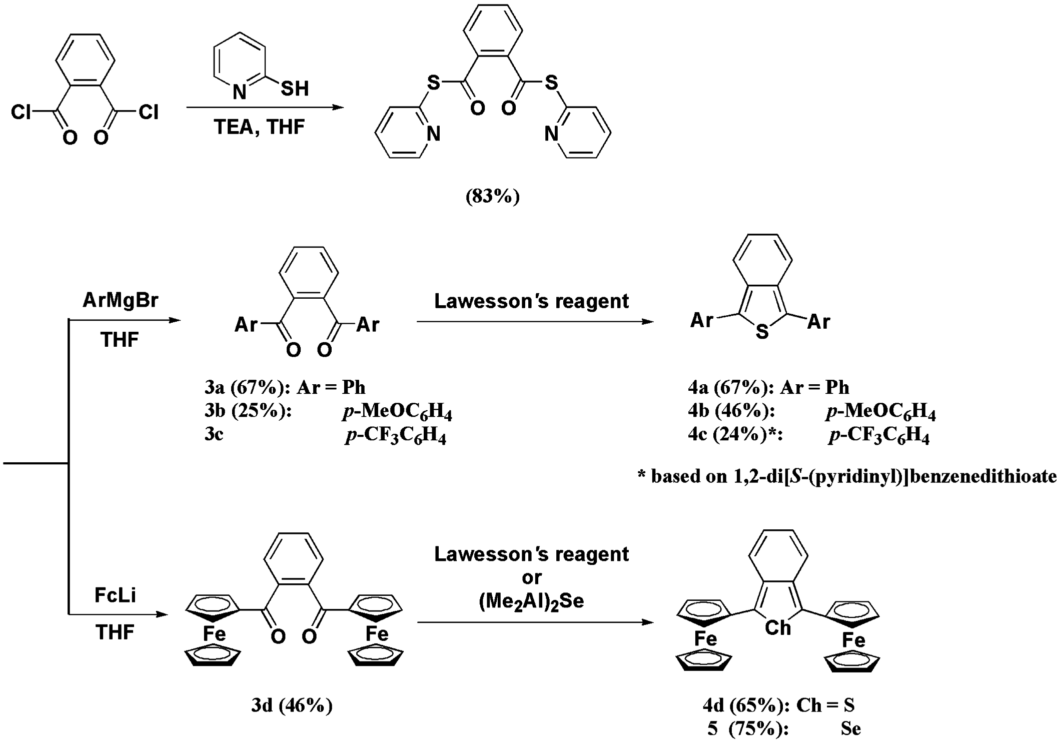
2. Results and discussion

*2.1. Synthesis of 2,3-disubstituted benzo[b]thiophenes (**2a–d**)*

Upon treatment of 2,3-dibromobenzo[*b*]thiophene, which was prepared by general bromination of benzo[*b*]thiophene with bromine [6], with ferrocenylzinc chloride in the presence of a catalytic amount of tetrakis(triphenylphophine)palladium $(PPh_3)_4Pd$, in tetrahydrofuran (THF) under reflux condition by the modified methods previously reported [7] 3-bromo-2-ferrocenylbenzo[*b*]thiophene (**1**) was obtained in moderate yield. Then, compound **1** was reacted with arylboronic acids by Suzuki-coupling [8] in the presence of a catalytic amount of $(PPh_3)_4Pd$ in dimethylformamide (DMF) at 100 °C to give 3-aryl-2-ferrocenylbenzo[*b*]thiophene (**2a–c**) in good yields. The synthesis of 2,3-diferrocenylbenzo[*b*]thiophene (**2d**) was achieved through a single step transition metal-catalyzed cross-coupling reaction of **1** with ferrocenylzinc chloride in the presence of a catalytic amount of bis(triphenylphophine)palladium(II) dichloride $(PPh_3)_2PdCl_2$, in tetrahydrofuran (THF) under reflux condition in moderate yield (Scheme 1).



Scheme 1.



Scheme 2.