

# A novel photochemical approach to the synthesis of naphthalene-containing lariat-type crown ethers and an evaluation of their metal cation binding and fluorescence sensing properties

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## Abstract

A novel method has been developed for the synthesis of naphthalene chromophore containing, lariat-type crown ethers. The route employs SET-promoted photocyclization reactions of polyether-tethered 2,3-naphthalimides to generate the variously ring-sized crown ether cores and an allylsilane *N*-acyliminium ion addition process to install amino ether side chains. The metal cation binding properties of the lariat-crown ethers, prepared in this manner, were evaluated. In addition, the ability of the lariat-crown ethers to serve as SET-based, fluorescence sensors of metal cations was probed. The results show that although the novel lariat-crown ethers strongly complex alkali metal cations (Na, K, Rb, Cs), this complexation is not associated with enhanced fluorescence from the naphthalene chromophores as would be expected if cation binding impeded SET quenching by the tertiary amine donor in the side chains. In contrast, the novel lariat-crown ethers serve as sensitive sensors for the divalent metal cations of Mg and Cu and the monovalent cation of Ag.

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## 1. Introduction

Previous studies in our laboratories have led to the discovery, mechanistic delineation and synthetic application of a variety of photochemical processes that are promoted by excited state single electron transfer (SET) [1]. In linked electron donor–acceptor substrates **1** (Scheme 1), these processes take place through the intermediacy of zwitterionic biradicals **2**, which by design possess  $\alpha$ -electrofugal groups (SiR<sub>3</sub> or SnR<sub>3</sub>). As a result, rapid heterolytic fragmentation reactions ( $\sim$ R<sub>3</sub>Si<sup>+</sup> or  $\sim$ R<sub>3</sub>Sn<sup>+</sup>) ensue leading to formation of biradi-

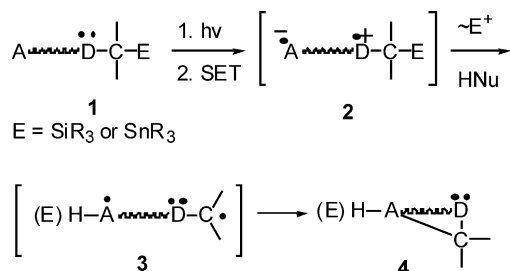
cals **3** that undergo C–C bond formation to generate cyclic products **4**. The earlier investigations have demonstrated that photochemical reactions following this general pathway can be used to produce a wide variety of functionally and structurally complex targets [2]. In addition, the processes have served as platforms for studies aimed at gaining information about the chemistry of cation radicals and the factors governing their reactivity [3].

More recent efforts in this area have provided information about the factors that control the chemical and quantum efficiencies of SET-promoted photoreactions of linked acceptor–polydonor systems [4]. In this work, we uncovered photocyclization reactions of trimethylsilyl-terminated polydonor-linked phthalimides that serve as highly efficient methods to construct macrocyclic poly-ethers, -thioethers

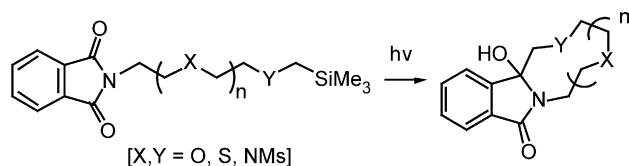
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Scheme 1.



Scheme 2.

and -sulfonamides (Scheme 2) [5]. The processes serve as the foundation of new strategies for the preparation of functionally interesting macrocyclic substances in the crown ether families. From the time of the early studies by Pedersen, Cram and Lehn [6], a large number of crown ethers, calixarenes and cryptands have been prepared and their metal and ammonium ion complexation properties have been probed. In this light, the SET-promoted photochemical method for crown ether synthesis uncovered in our recent efforts comes at a rather advanced stage of this area of science. However, the simplicity and high efficiencies of these processes make studies of their applications to the synthesis of functional crown ether worthwhile.

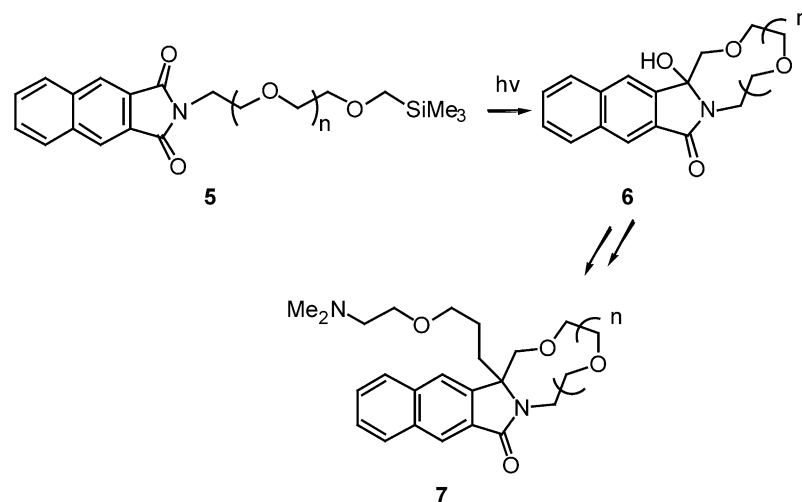
One goal of our continuing investigations of SET-promoted photocyclization reactions of acceptor–polydonor substrates is to develop concise methods of preparing new types of metal ion, fluorescence sensors. As shown earlier by de Silva and others [7], SET based fluorescence sensors are useful materials that signal guest binding by blocking

SET-quenching of excited states of fluorophores that are appended to the host. Following this principle, we have prepared prototypical naphthalene-containing fluorescence sensors of general structure **7** by employing photocyclization reactions of 2,3-naphthalimido-polyethers **5** (Scheme 3). The macrocyclic photoproducts **6** are then transformed to tertiary amine side chain containing, lariat-type [8] crown ether sensors **7**. The amine grouping in **7** is designed to serve as an electron donor to SET-quench the fluorescence of the naphthalene chromophore when a metal cation guest is absent. We anticipated that metal cation binding to **7** would be assisted by the pendant side chain oxygen (and perhaps nitrogen) and, as a result, it would be accompanied by a dislocation of the side chain tertiary amine moiety with a concomitant reduction in intramolecular quenching of the naphthalene fluorescence. Fluorescence and metal cation binding studies have been performed with these substances in order to determine if they serve as useful SET-based metal cation sensors. The results of this effort are reported below.

## 2. Results

### 2.1. Synthesis of the lariat-type crown ethers

The preparative routes used to construct a representative series of lariat-type crown ethers that have metal cation sensing potential begin with synthesis of the trimethylsilyl-terminated 2,3-naphthalimide polyethers **8a–c** (Scheme 4). Reactions of potassium 2,3-naphthalimide with the known polyethylene glycol derived iodides [9] produce the naphthalimides **8a–c**, which undergo photomacrocyclization processes when irradiated in methanol solutions to efficiently form the macrocyclic-amidols **9a–c** (71–76%). Incorporation of functionalized sided chains into these substances takes advantage of allylation reactions of *N*-acyliminium ions formed by treatment of **9a–c** with a Lewis acid. Accord-



Scheme 3.

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