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Novel Naphthalene Based Lariat-Type Crown Ethers Using Direct Single Electron Transfer Photochemical Strategy

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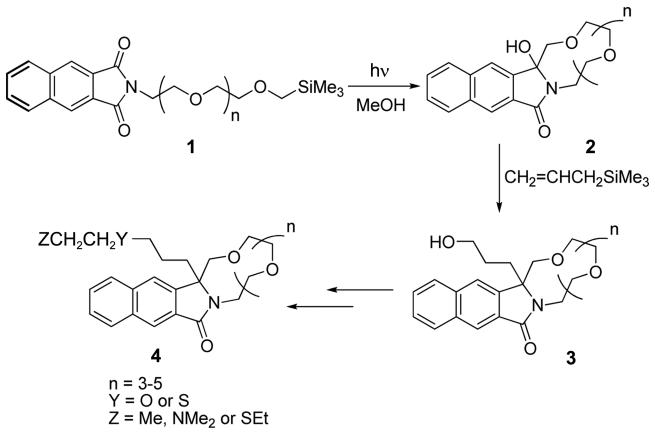
This study explored a direct SET-photochemical strategy to construct a new family of thioene conjugated-naphthalamide fluorophore based lariat-crown ethers which show strong binding properties towards heavy metal ions. Irradiations of designed nitrogen branched (trimethylsilyl)methylthio-terminated polyethylenoxy-tethered naphthalimides in acidic methanol solutions have led to highly efficient photocyclization reactions to generate naphthalamide based lariat type thiadiazacrown ethers directly in chemo- and regio-selective manners which undergo very facile secondary dehydration reactions during separation processes to produce their corresponding amidoenethio ether cyclic products tethered with electron donating diethyleneoxy- and diethyenethio-side arm chains. Fluorescence and metal cation binding properties of the lariat type enamidothio products were examined. The photocyclized amidoenethio products, thioene conjugated naphthalamide fluorophore containing lariat-thiadiazacrowns exhibited strong fluorescence emissions in region of 330-450 nm along with intramolecular exciplex emissions in region of 450-560 nm with their maxima at 508 nm. Divalent cation Hg^{2+} and Pb^{2+} showed strong binding to sulfur atom(s) in side arm chain and atoms in enethiadiazacrown ether rings which led to significant enhancement of fluorescence from its chromophore singlet excited state and concomitant quenching of exciplex emission. The dual fluorescence emission responses towards divalent cations might provide a new guide for design and development of fluorescence sensors for detecting those metals.

Key Words : Single electron transfer (SET) photocyclization, Naphthalene based lariat-type enethiadiazacrown ether, Exciplex emission, Fluorescence sensor, Heavy metal cation

Introduction

Our studies on single electron transfer (SET) photochemistry using various α-silyl electron donors uncovered that the SET photochemistry leads to highly efficient and regioselective generation of α-carbon radicals and can be used as a method for generation of α-oxygen, nitrogen, or sulfur heteroatom substituted carbon radicals.[1] Intramolecular SET-photochemical reactions of linked α-silyl electron donor-imide acceptors have proven to provide macrocyclic polyfunctionalized poly-ethers, -thioethers, -amides,[2] and -polypeptides [3] in highly efficient and regioselective manners. Further exploration to obtain information about factors governing the efficiencies and chemoselectivities of SET-promoted intramolecular photochemical reactions of linked imide acceptor-polydonor systems led to identify several key factors. The length and the nature of the chain linking the phthalimide acceptor and α-silyl electron donor sites play important roles in controlling the rates of formation of zwitterionic biradiacals that serve as penultimate intermediates in the route of macrocyclic product formations.[4]

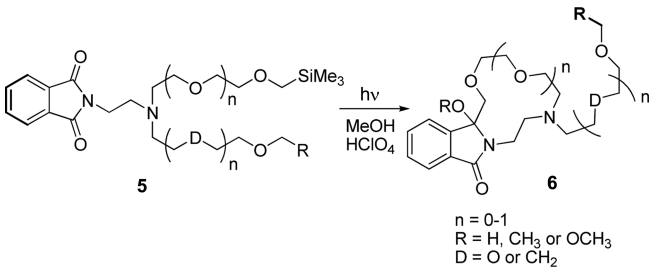
In previous reports, we described an efficient photochemical approach to the synthesis of naphthalene containing lariat-type crown ethers and their use as fluorescence sensors for metal cations.[5] The general route for preparation of these sensors takes advantage of efficient generation of naphthalene based crown ethers **2** in SET-promoted photocyclization reactions of α-silylether terminated, polyethyleneoxy-tethered 2,3-naphthalimides **1** and side chain installation to hydroxypropyl derivative **3** and functionality manipulation proce-



Scheme 1

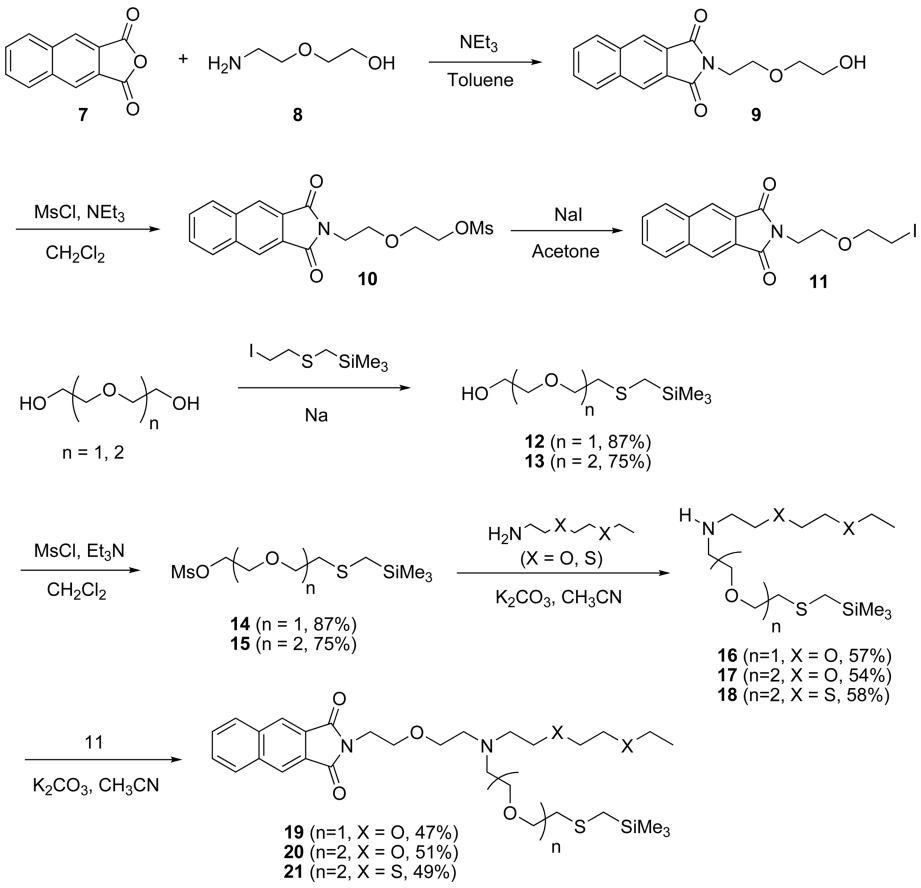
dures leading to lariat-type crown ethers **4**[5] (Scheme 1).

As demonstrated in the previous efforts,[5] lariat-crown ethers of general structure **4** have metal cation binding affinities. Owing to the presence of naphthalene fluorophore and side chain, tertiary amine or thioether electron donor sites, these substances serve as selective fluorescence sensors for certain metal cations such as Mg(II), Hg(II), Pb(II), Ag(I), and Cu(II). Lariat-type crown ethers that contain a macrocyclic polyether core to which a cation complexing donor side chain is appended tend to lead more tight cation binding than do their simple crown ether analogs.[6] A number of methodologies have been employed to prepare these substances and our previous efforts for the synthesis of naphthalene fluorophore containing lariat-type crown ethers **4** takes advantage of efficient SET-promoted photocyclization reactions of α-silylether terminated, polyethyleneoxy-tethered 2,3-naphthalimides **1** to construct naphthalene based crown ethers **2** and side chain installation and functionality manipulation procedures. Our more recent studies[5,7] to delineate factors that govern the chemical selectivities and efficiencies of SET-promoted photocyclization reactions of acceptor-polydonor substrates revealed that the length and nature of the chain linking the phthalimide acceptor and α-silyl donor sites are important factors in route of the product formation. In addition the rates of methanol promoted desilylation at cation radical centers in intermediate zwitterionic biradicals also play important roles especially in cases where chain length/type is not a factor. For example, SET-promoted photocyclization reactions of nitrogen branched bis-polyethyleneoxy-tethered phthalimides **5** led to the chemoselective and efficient production of lariat-type crown ethers **6** appended with *N*-cation complexing ether donor side chains which suggest that the SET-photochemical methodology can serve as an efficient and direct route to prepare lariat-type crown ethers without further side chain installation and functionality manipulation procedure (Scheme 2).



Scheme 2

In our continuing efforts to develop new lariat-crown ether based fluorescence sensor for heavy metal ions we have designed a direct photochemical strategy for synthesis of novel naphthalene fluorophore containing lariat-type crown ethers. In order to explore the strategy nitrogen branched (trimethylsilyl)methylthio-terminated polyethylenoxy-tethered naphthalimides **19-21** were prepared (Scheme 3)



Scheme 3

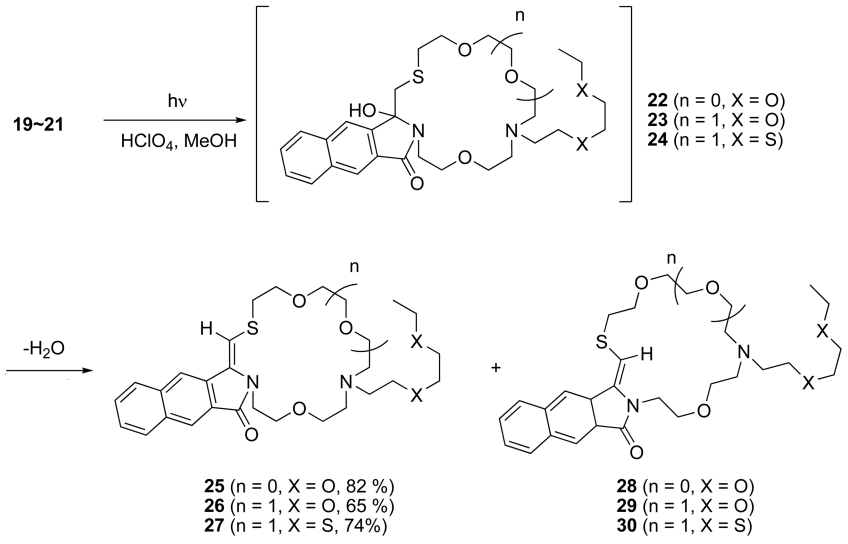
and subjected to photochemical studies. The results demonstrated that photocyclization reactions of these substances take place with high efficiencies and high degree of chemoselectivities to generate naphthalene based lariat-type thiadiazacrown ethers **22-24** directly which undergo very facile secondary reaction of dehydration to produce two isomeric amidoenethio ether cyclic products **25-27** and **28-30** (Scheme 4). Metal cation binding and fluorescence sensor properties of the amidoenethio products were explored in this study and are described below.

Results and Discussion

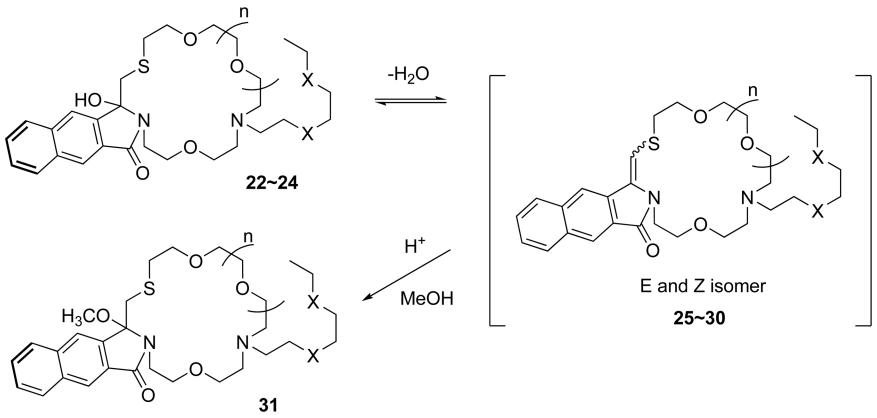
Preparation of Naphthalene Based Lariat Type Thiadiazacrown Ethers and their Enthioethers. The synthetic pathway employed to prepare (trimethylsilyl)methylthio-terminated polyethylenoxy-*N*-diethyleneoxy- or diethylenethio-branched naphthalimdes **19-21** involves amination of *N*-(2-iodoethoxy)ethyl-2,3-naphthalimide (**11**) with (trimethylsilyl)methylthio-terminated, polyethyleneoxy substituted secondary amines **16-18** which were prepared following a sequence of reaction steps shown in Scheme 3. Reactions of naphthyl iodide **11** with secondary amines **16-18** in the presence of K_2CO_3 led to generation of *N*-branched naphthalimdes **19-21** in modest yields.

Photoreactions of the *N*-branched naphthalimdes **19-21** were carried out under conditions which promote rapid desilylation of key α-silyl cation radical intermediates and block competitive SET from tertiary amine donor groups.[4a] Accordingly, irradiation of these substances in MeOH containing 0.1 M $HClO_4$ leads to chemically efficient formation of cyclized amido alcohol products **22**, **23**, and **24**, which undergo facile dehydrations to yield amidoenethioether products **25+28**, **26+29**, and **27+30** respectively in *ca.* 1:1 mixture of Z- and E-isomers. Monitoring of the progress of each reaction by TLC and NMR analysis shows initial efficient generation of amido alcohol products and their subsequent conversion to amidoenethio products (Scheme 4). The cyclized amidoenethioether products are observed to be in equilibrium with their hydrated amidol products **22-25** and methanol incorporated amido methyl ether **31** in methanol solutions[4,8] (Scheme 5). As observed in earlier studies[4,8] amido alcohol to enamido or (and) amido ether interconversion process is typical for cyclic amido alcohols formed in methanol solution containing $HClO_4$. Detailed analysis of their spectroscopic properties and comparisons with those of closely related cyclic products demonstrated that products obtained upon chromatographic separation of the crude photolysates contain amidoenethio products **25+28**, **26+29**, and **27+30** (65-82%). ^{1}H-NMR spectra of amidoenethio products show characteristic a pair of peaks for two regioisomeric alkenic protons at 6.21 and 6.67 ppm (**25+28**), 6.32 and 6.54 ppm (**26+29**), and 6.28 and 6.50 ppm (**27+30**) in *ca.* 1:1 ratios along with peaks for their corresponding protons, which support dehydrations occurred to form the amidoenethio products.

Fluorescence Properties of Naphthalamide Based Lariat Enthiacrown Ethers. Owing to the presence of the naphthalamide chromophore which is further π-conjugated with a newly formed double bond, the amidoenethiacrown ethers **25+28**, **26+29**, and **27+30** are fluorescent and display unstructured emissions in the 330-450 nm in degassed acetonitrile solution at room temperature when excited at 290 nm (Figure 1). In addition to emissions of their maxima at 376-380 nm by the conjugated naphthalamide chromophores, broad emission bands were observed in the 450-560 nm with their emission maxima at 510 nm which are aroused by exciplexes formed between the naphthalamide singlet excited state and electron donor group, *N*-diethyleneoxy and *N*-diethylenethio group in their side arm.[9] The exciplex emission becomes more vivid with lariat enthiacrown ether **27+30** which has more strongly electron donating diethylenethio group in the side arm. In order to find out intramolecular nature of the exciplex emission we measured the fluorescence spectra with varying concentration of **27+30** from 1.0×10^{-6} to 2.0×10^{-5} M all of which exhibited same shape in



Scheme 4



Scheme 5

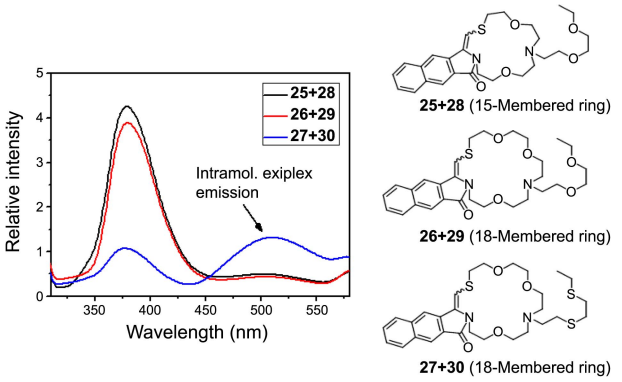
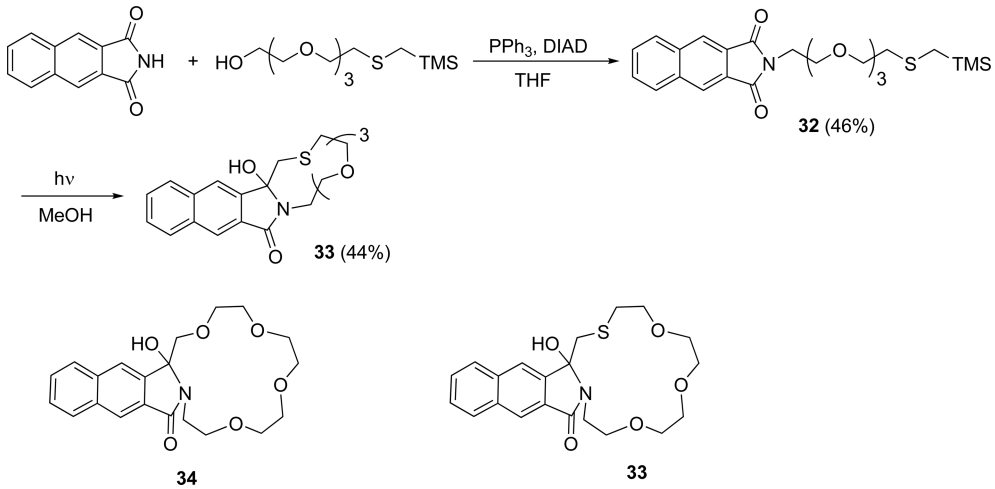


Figure 1. Fluorescence spectra in CH_3CN (1.0×10^{-5} M) solution of *N*-diethyleneoxy and *N*-diethylenethio substituted macrocyclic naphthalamide enthiacrown ethers **25+28**, **26+29**, and **27+30** (Excitation at 290 nm).

their spectra supporting intramolecular nature in their exciplex formations (Figure 1).

Comparisons of Emission Properties of Naphthalamide Enthiacrown Ethers with Naphthalamide Amidol Crown Ethers. Since thioene-conjugated naphthalaimde chromophore present in the photoproducts **25+28**, **26+29**, and **27+30** contains a thioene group which leads to further π-conjugation by a double bond and *n*-orbital of sulfur atom, the photoproducts exhibit different emission properties from those observed with naphthalamide lariat-type crown ethers which contain naphthalamide alcohol chromophores.[5] The emission spectra showed 20-30 nm of bathochromic shifts. In order to examine the sulfur atom effect present in the molecules to their emission properties, we synthesized sulfur atom containing naphthalamide alcohol **33** following synthetic steps shown in Scheme 6, and its emission was measured and compared with that of non-sulfur containing naphthalamide alcohol **34**.[5a] Both of **33** and **34** showed virtually identical structured emission spectra with their maxima at 340-341 nm and 354-356 nm regardless of the presence of sulfur atom in the ring and those spectra are also same or similar to those of naphthalamide lariat crown ethers synthesized in our earlier studies[5] (Figure 2). However the relative emission quantum efficiency differ in a large extent and sulfur containing naphthalamide **33** give only one-fourth intensity of that of non-sulfur containing **34** (Table 1) which indicates that the presence of heavy sulfur atom in the ring affects in a large extent naphthalamide singlet lifetime through possible heavy atom effect giving



Scheme 6

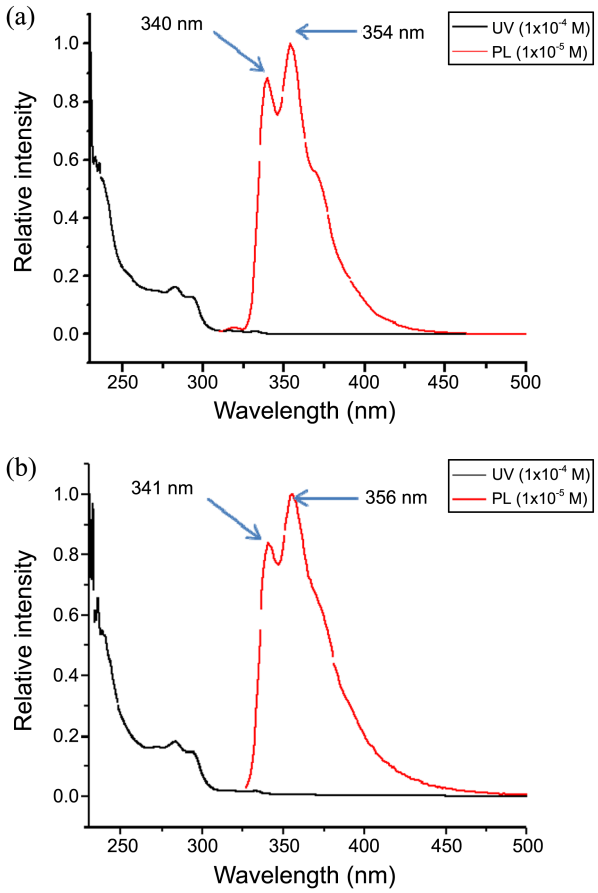


Figure 2. Fluorescence spectra in CH_3CN solution of (a) naphthalimide alcohol crown ether **34** and (b) naphthalamide alcohol thiacrown ether **33** (excitation at 290 nm).

shorter singlet lifetime and lowered fluorescence quantum efficiency.

Fluorescence Responses to Metal Cations. Thioene conjugated naphthalamide photocylized products **25+28**, **26+29**, and **27+30** contains *N*-diethyleneoxy and *N*-diethylenethio group in side arm chains which interact with the conjugated naphthalaimde chromophore singlet excited state through reversible SET. The intramolecular interactions led to observation of exciplex emissions in their emission spectra especially in the case of **27+30** with strong electron donating

Table 1. Fluorescence quantum efficiencies of the crown ether **34** and thiocrown ether **33** (Derived from fluorescence intensities at 354 nm for equally absorbing solutions (*ca.* 1×10^{-5} M) of the crown ether **34** and thiocrown ether **33** in CH_3CN solutions at 25 °C)

	34	**33**
Φ_f (rel)	1	0.23

diethylenethio group in the side arm chain. With observation of intramolecular exciplex formations and their emissions, metal cation binding to the thioene crown ether ring and side arm chain oxygen or sulfur atom is expected to lead to fluorescence enhancement by blocking intramolcular SET quenching of fluorescence. Responses of their fluorescence to metal cations were examined with some selected metal cations; alkali metal cation Li^+, Na^+, and K^+, and heavy metal cation Hg^{2+}, and Pb^{2+}. The fluorescence emission efficiencies were observed to be enhanced though not significantly by addition of alkali metal perchlorates. As can be seen from fluorescence spectra shown in Figure 3 in example, addition of $LiClO_4$ to acetonitrile solution of these substances led some fluorescence enhancement.

In contrast to monovalent cations, divalent cations such as Hg^{2+}, and Pb^{2+} led to more significant enhancements in fluorescence intensities. Fluorescence intensities at 380 nm were dramatically increased upon addition of $Hg(ClO_4)_2$ (Figure 4). Extent of the fluorescence enhancement was most dramatic with diethylenethio group containing thioene-naphthalamide **27+30** with concomitant quenching of exciplex emission at 508 nm. The quenching of long wavelength exciplex emission is a consequence of Hg^{2+} cation binding to sulfur atom(s) in the side arm chain and to thioenecrown ether ring atoms which blocks intramolcular exciplex formation between naphthalamide chromophore singlet excited state and sulfur in the side chain, and concomitantly leads to fluorescence enhancement at 380 nm coming from the naphthalamide chromophore singlet excited state.

Fluorescence response to Pb^{2+} is interestingly different from those to alkali metals and Hg^{2+} that fluorescence intensities enhanced in the initial stages and decreased in their later stages upon addition of increasing concentrations of $Pb(ClO_4)_2$ (Figure 5). However the exciplex emission observed

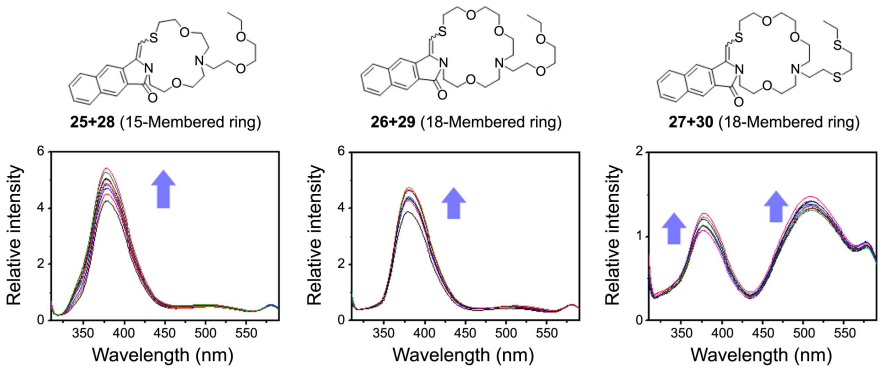


Figure 3. Fluorescence spectra of naphthalamide enethiacrown ethers **25+28**, **26+29**, and **27+30** in CH_3CN solution (2.0×10^{-5} M) at 25 °C upon increasing concentrations of $LiClO_4$ (excitation at 290 nm).

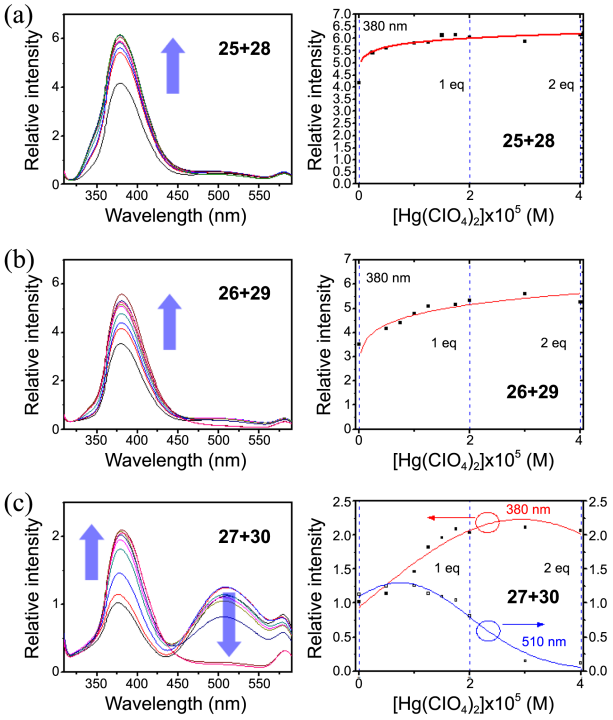


Figure 4. Fluorescence spectra of *N*-diether- and dithioether-tethered naphthalimide enthiacrown ethers **25+28**, **26+29**, and **27+30** with increasing concentrations of divalent Hg^{2+}.

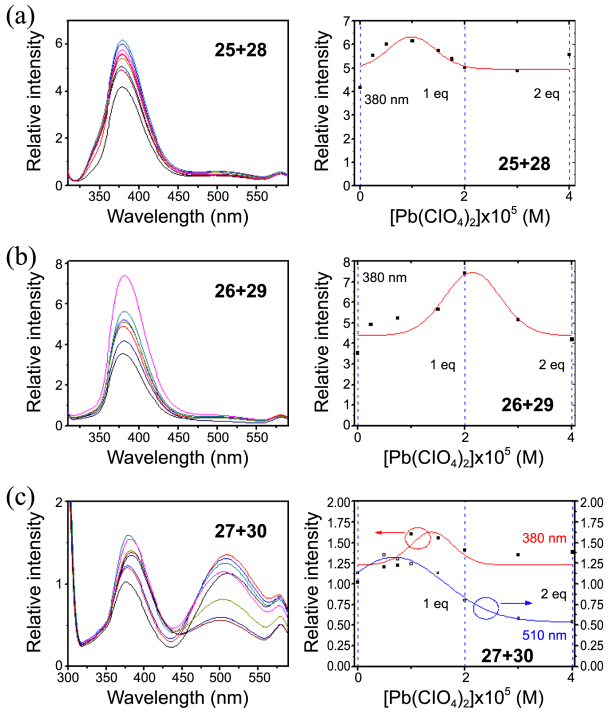


Figure 5. Fluorescence spectra of *N*-diether- and dithioether-tethered naphthalimide enthiacrown ethers **25+28**, **26+29**, and **27+30** with increasing concentration of divalent Pb^{2+}.

with **27+30** at longer wavelength 508 nm continuously decreased which indicates that Pb^{2+} strongly binds to sulfur atom(s) in side chain and thioencrown ether ring atoms. While strong binding with increasing concentrations of Pb^{2+} lead to block intamolecular excipex formation and thus lead to fluorescence enhancement from conjugated naphthalamide chromophore singlet excited state in the early stage of increasing concentrations, greater extent of Pb^{2+} binding in the latter stage results in more increased intersystem crossing from singlet to triplet excited state and make fluorescence be quenched.

A dual type of fluorescence responses observed with *N*-diethylenethio group containing naphthalamide **27+30** towards Hg^{2+} and Pb^{2+} provides a good guide in designing a new fluorescence detector for heavy atom Hg^{2+} and Pb^{2+}.

In summary, this study explored our direct SET-photochemical strategy to construct a new family of thioene conjugated-naphthalamide fluorophore based lariat-diazacrown ethers which show strong binding properties towards heavy metal ions. Irradiations of designed nitrogen branched (trimethylsilyl)methylthio-terminated polyethylenoxy-tethered naphthalimides in acidic methanol solutions have led to highly efficient photocyclization reactions to generate naphthalamide based lariat type thiadiazacrown ethers directly which undergo very facile secondary dehydration reactions during separation processes to produce their corresponding amidoenethio ether cyclic products which contain electron donating diethyleneoxy and diethyenethio side arm chains. Fluorescence and metal cation binding properties of the amidoenethio products were explored. The photocyclized products, thioene conjugated naphthalamide fluorophore containing lariat-thiadiazacrowns exhibit strong fluorescence emissions in region of 330-450 nm along with intramolecular exciplex emissions in region of 450-560 nm with their maxima at 508 nm. Divalent cation Hg^{2+} and Pb^{2+} showed strong binding to sulfur atom(s) in side arm chain and atoms in thiadiazacrown ether rings which led to significant enhancement of fluorescence from its chromophore singlet excited state and concomitant quenching of exciplex emission. The dual fluorescence emission responses towards divalent cations provide a potential guide for new design and development of fluorescence sensors for detecting those metals.

Experimental

General. All reagents were obtained from commercial sources and used without further purification and solvent were used dried using standard procedures. Chemical shifts of ^1H NMR and ^{13}C NMR spectra are reported in parts per million relative $CHCl_3$ (7.24 ppm for ^1H and 77.0 ppm for ^{13}C) which were used as a chemical shift internal standard for samples in $CDCl_3$. HRMS data were obtained by using fast bombardment. All compounds isolated as oils unless otherwise specified and the purity of each was determined to be over 90% by ^1H NMR and ^{13}C NMR analysis.

Preparation of 2-(2-Hydroxyethoxy)ethylnaphthalimide (9). 2-(2-Aminoethoxy)ethanol (2.5 mL, 25.2 mmol) was added to a solution of 2,3-naphthalenedicarboxylic anhydride (**7**, 5 g, 25.2 mmol) and triethylamine (7.2 mL, 50.4 mmol) in toluene (100 mL) and the solution was stirred and

refluxed for 24 h. After reflux the solution was diluted with dichloromethane and extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford **9** (6.6 g, 91%).

9: ^{1}H NMR ($CDCl_3$) δ 3.58-3.61 (m, 2H), 3.66-3.68 (m, 2H), 3.76 (t, 2H, *J* = 5.7 Hz), 3.93 (t, 2H, *J* = 5.7 Hz), 7.62-7.65 (m, 2H), 7.95-7.98 (m, 2H), 8.23 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 37.7, 61.6, 68.2, 72.2, 124.6, 127.5, 129.1, 130.1, 168.0; HRMS (FAB) *m/z* 286.1083 (M+H, $C_{16}H_{16}NO_4$ requires 286.1079).

Preparation of 2-(2-Mesyloxyethoxy)ethylnaphthalimide (10). Mesyl chloride (1.2 mL, 15.7 mmol) was added to a solution of **9** (3 g, 10.5 mmol) and triethylamine (2.3 mL, 15.7 mmol) in dichloromethane (50 mL) and the resulting solution was stirred for 24 h. The solution was diluted with dichloromethane and extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford **10** (3.3 g, 87%).

10: ^{1}H NMR ($CDCl_3$) δ 3.73-3.76 (m, 2H), 3.80 (t, 2H, *J* = 5.7 Hz), 3.96 (t, 2H, *J* = 5.7 Hz), 4.30-4.33 (m, 2H), 7.68-7.72 (m, 2H), 8.03-8.06 (m, 2H), 8.32 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 37.4, 37.5, 68.1, 68.4, 68.9, 124.7, 127.6, 129.2, 130.2, 135.4, 167.8; HRMS (FAB) *m/z* 364.0857 (M+H, $C_{17}H_{18}NO_6S$ requires 364.0855).

Preparation of 2-(2-Iodoethoxy)ethylnaphthalimide (11). A solution of **10** (3.0 g, 8.3 mmol) in acetone (100 mL) containing sodium iodide (2.5 g, 16.6 mmol) was refluxed at 80 °C for 18 h. The solvent was removed and the resulting mixture was extracted with dichloromethane and *sat*. $Na_2S_2O_3$ (aq). The organic layer was combined, dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford **11** (2.3 g, 71%).

11: ^{1}H NMR ($CDCl_3$) δ 3.18 (t, 2H, *J* = 6.6 Hz), 3.73 (t, 2H, *J* = 6.6 Hz), 3.78 (t, 2H, *J* = 5.7 Hz), 3.96 (t, 2H, *J* = 5.7 Hz), 7.65-7.68 (m, 2H), 8.00-8.03 (m, 2H), 8.03-8.06 (m, 2H), 8.30 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.6, 37.5, 67.4, 71.2, 124.6, 127.8, 129.1, 130.2, 135.4, 167.8; HRMS (FAB) *m/z* 396.0099 (M+H, $C_{16}H_{15}INO_3$ requires 396.0097).

Preparation of ω-(Trimethylsilylmethylthio)polyethylene glycol 12 and 13. A solution of triethylene glycol (20 g, 256 mmol) containing Na metal (1.1 g, 37 mmol) was stirred at 50 °C for 24 h. Ttrimethylsilylmethylthioethyl iodide[5] (10 g, 36 mmol) was added dropwise and the resulting solution was stirred for 7 h at 60 °C. This solution was diluted with ethyl acetate and extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford a residue which was subjected to silica gel column chromatography (EtOAc:*n*-hexane = 1:4) to afford ω-(trimethylsilylmethylthio)-triethylene glycol **13** (8.2 g, 89%). ω-(Trimethylsilylmethylthio)diethylene glycol **12** was prepared through known procedure.[2a]

13: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.83 (s, 2H), 2.38 (t, 1H , *J* = 6.1 Hz), 2.72 (t, 2H, *J* = 7.2 Hz), 3.60-3.76 (m, 10H); ^{13}C NMR ($CHCl_3$) δ 1.8, 18.9, 35.3, 61.8, 70.3, 70.4, 72.4; HRMS (FAB) *m/z* 253.1298 (M+H, $C_{10}H_{25}O_3SSi$ requires 253.1294).

Preparation of ω-(Trimethylsilylmethylthio)polyethylene Glycol Mesylate 14 and 15. A solution of ω-(trimethylsilylmethylthio)triethylene glycol **13** (8.0 g, 32 mmol) in anhydrous methylene chloride (50 mL) containing triethylamine (3.9 g, 38 mmol) was stirred at 0 °C for 30 min. Methanesulfonyl chloride (4.4 g, 38 mmol) was added dropwise and the resulting solution was stirred for 8 h at room temperature. The resulting solution was extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated in vacuo to afford a residue which was subjected to silica gel column chromatography (EtOAc:*n*-hexane = 1:5) to afford ω-(Trimethylsilylmethylthio)triethylene glycol mesylate **15** (9.0 g, 86%). ω-(Trimethylsilylmethylthio)diethylene glycol mesylate **14** was prepared through known procedure.[2]

15: ^{1}H NMR ($CDCl_3$) δ 0.089 (s, 9H), 1.824 (s, 2H), 2.706 (t, 2H, *J* = 7.2 Hz), 3.080 (s, 3H), 3.624-3.671 (m, 6H), 3.760-3.791 (m, 2H); ^{13}C NMR ($CHCl_3$) δ 1.8, 18.9, 35.3, 61.8, 70.3, 70.4, 72.4; HRMS (FAB) *m/z* 353.0886 (M+Na, $C_{11}H_{27}O_5S_2SiNa^+$ requires 353.0889).

Preparation of *N*-(Diethyleneoxyether)-*N′*-(silylthioether terminated polyethyleneoxy)amines 16 and 17. The solution of known 3,6-dioxaoctylamine[10] (2.5 g, 18.7 mmol) in CH_3CN (50 mL) containing K_2CO_3 (5 g, 36 mmol) was stirred at 70 °C for 1 h. The mesylate compound (**14**; 4 g, 14 mmol, **15**; 4g, 12 mmol) was added dropwise and the resulting solution was stirred for 12 h at 70 °C. Concentration of solution *in vacuo* gave a residue which was diluted with EtOAc and extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (MeOH:CH_2Cl_2 = 1:20) to afford **16** (2.6 g, 57%) and **17** (2.4 g, 54%) respectively.

16: ^{1}H NMR ($CDCl_3$) δ 0.087 (s, 9H), 1.215 (t, 3H, *J* = 6.9 Hz), 1.823 (s, 2H), 2.173 (s, 1H), 2.700 (t, 2H, *J* = 7.2 Hz), 2.805-2.858 (m, 4H), 3.491-3.649 (m, 12H); ^{13}C NMR ($CHCl_3$) δ 1.8, 15.1, 18.9, 35.3, 49.2, 49.2, 66.627, 69.712, 69.627, 69.712, 70.0, 70.1, 70.4; HRMS (FAB) *m/z* 324.2023 (M+H, $C_{14}H_{34}NO_3Si$ requires 324.2029).

17: ^{1}H NMR ($CDCl_3$) δ 0.086 (s, 9H), 1.215 (t, 3H, *J* = 6.9 Hz), 1.786 (br, 1H), 1.829 (s, 2H), 2.715 (t, 2H, *J* = 7.5 Hz), 2.801-2.841 (m, 4H), 3.491-3.675 (m, 16H); ^{13}C NMR ($CHCl_3$) δ 1.9, 15.0, 18.7, 35.0, 49.0, 66.4, 69.6, 70.0, 70.1, 70.2, 70.2, 70.4, 70.4.; HRMS (FAB) *m/z* 368.2294 (M+H, $C_{16}H_{38}NO_4SSi$ requires 368.6277).

Preparation of *N*-(Diethylenedithioether)-*N′*-(silylthioether terminated polyethyleneoxy)amine 18. A solution of known 3,6-dithaoctylamine[5b] (4 g, 24 mmol) in CH_3CN 50 mL containing K_2CO_3 (5 g, 36 mmol) was stirred at 70 °C for 1 h. the mesylate compound **15** (4 g, 12 mmol) was added dropwise and the resulting solution was stirred for 12 h at 70 °C. Concentration of solutions *in vacuo* gave a residue which was diluted with EtOAc and extracted with water. The extracts were dried with Na_2SO_4 filtered and concentrated *in vacuo* to afford residue which were subjected to silica gel column chromatography (1:30 MeOH:CH_2Cl_2) to afford **18** (2.8 g, 58%).

18: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.26 (t, 3H, *J* = 7.2 Hz), 1.83 (s, 2H), 2.60 (q, 2H, *J* = 7.5 Hz), 2.70-2.84 (m, 4H), 3.44-3.62 (m, 16H); ^{13}C NMR ($CHCl_3$) δ 1.91, 15.0,

18.7, 35.0, 49.0, 66.4, 69.6, 70.0, 70.1, 70.17, 70.23, 70.4, 70.4; HRMS (FAB) *m/z* 400.1836 (M+H, $C_{16}H_{38}NO_2S_3Si$ requires 400.1834).

Preparation of *N*-(Diethyleneoxyether or -(diethylenedithioether)-*N′*-(silylthioether terminated polyethyleneoxy) Tethered Naphthalimides 19-21. Solutions of *N*-bis chain amine compounds **19** (2.0 g, 6.2 mmol), **20** (2.0 g, 5.4 mmol) and **21** (2.0g, 5.0 mmol) in CH_3CN 50 mL containing K_2CO_3 (2.0 g, 15 mmol) were stirred at 70 °C for 1 h. Iodoethylnaphthalimide **11** (2.8 g, 7.0 mmol) in 20 mL DMF solution, was added dropwise and the resulting solutions were stirred for 12 h. at 70 °C. Concentration of solution *in vacuo* gave residues which were diluted with methylene chloride and extracted with water. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (MeOH:CH_2Cl_2 = 1:20 for **19** and **20**, 1:40 for **21**) to afford **14** (1.7 g, 47%), **15** (1.7 g, 51%) and **16** (1.6 g, 49%) respectively.

19: ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H), 1.18 (t, 3H, *J* = 6.9 Hz), 1.79 (s, 2H), 2.62 (t, 2H, *J* = 6.9 Hz), 2.71-2.73 (b, 6H), 3.43-3.57 (m, 14H), 3.70 (t, 2H, *J* = 6.0 Hz), 3.93 (t, 2H, *J* = 5.4 Hz), 7.66-7.70 (m, 2H), 8.02-8.05 (m, 2H), 8.32 (s, 2H); ^{13}C NMR ($CHCl_3$) δ 1.8, 15.1, 18.8, 35.2, 37.5, 54.3, 54.36, 54.42, 66.5, 67.6, 69.2, 69.3, 69.6, 69.7, 70.0, 70.3, 124.6, 127.7, 129.1, 130.2, 135.3, 167.9; HRMS (FAB) *m/z* 591.2927 (M+H, $C_{30}H_{47}N_2O_6SSi$ requires 591.2924).

20: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.19 (t, 3H, *J* = 7.2 Hz), 1.81 (s, 2H), 2.67-2.73 (m, 8H), 3.45-3.64 (m, 16H), 3.72 (t, 2H, *J* = 6.0 Hz), 3.95 (t, 2H, *J* = 5.7 Hz), 7.68-7.71 (m, 2H), 8.04-8.07 (m, 2H), 8.34 (s, 2H) ; ^{13}C NMR ($CHCl_3$) δ 1.8, 15.1, 18.8, 35.2, 37.6, 54.4, 66.5, 67.7, 69.1, 69.5, 69.7, 70.1, 70.25, 70.278, 70.33, 124.6, 127.8, 129.1, 130.2, 135.4, 167.9; HRMS (FAB) *m/z* 635.3188 (M+H, $C_{30}H_{47}N_2O_6SSi$ requires 635.3186).

21: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H), 1.24 (t, 3H, *J* = 7.5 Hz), 1.82 (s, 2H), 2.51-2.59 (m, 4H), 2.66-2.72 (m, 12H), 3.46-3.65 (m, 10H), 3.72 (t, 2H, *J* = 5.7 Hz), 3.96 (t, 2H, *J* = 5.7 Hz), 7.69-7.72 (m, 2H), 8.05-8.08 (m, 2H), 8.35 (s, 2H); ^{13}C NMR ($CHCl_3$) δ 1.8, 14.8, 18.8, 25.9, 29.7, 31.7, 32.2, 35.2, 37.5, 53.8, 53.84, 55.3, 67.8, 69.1, 69.7, 70.1, 70.3, 124.7, 127.8, 129.1, 130.3, 135.4, 167.9; HRMS (FAB) *m/z* 667.2731 (M+H, $C_{32}H_{51}N_2O_5S_3Si$ requires 667.2729).

Photoreactions of Naphthalimides 19-21 and Formations of Cyclized *N*-(Diethylenedioxy)-and *N*-(Diethylenedithio)-naphthalene Amidoenethiodiazacrown Ether Products, 25-30. The nitrogen purged solution of naphthalimide (0.3 g, 0.51 mmol of **19**, 0.3 g, 0.51 mmol of **20**, 0.3 g, 0.51 mmol of **21**) in 150 mL of MeOH containing 100 mM $HClO_4$ (1 mmol) was irradiated by using Pyrex glass filtered light for 0.5 h to give almost 100% conversion respectively. Concentration of the photolysates *in vacuo* gave residues which were diluted with CH_2Cl_2 and extracted with 5% $NaHCO_3$. The extracts were dried with Na_2SO_4, filtered and concentrated *in vacuo* to afford residues which were subjected to silica gel column chromatography (MeOH:CH_2Cl_2 = 1:20) to yield **25**+**28** (210 mg, 82%), **26**+**29** (190 mg, 65%), **27**+**30** (193 mg, 74%). ^{1}H-NMR data indicate that E- and Z-isomer **25**+**28**, **26**+**29**, and **27**+**30** were in equilibrium states giving about equal ratio between the isomers respectively.

25: ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, 3H, *J* = 6.9 Hz), 2.59 (m, 2H), 2.89 (m, 2H), 3.13 (m, 2H), 3.37-3.81 (m, 16H), 3.88 (m, 2H), 3.94 (m, 2H), 4.03 (m, 2H), 4.39 (m, 2H), 6.67 (s, 1H), 7.49-7.54 (m, 2H), 7.93-8.03 (m, 2H), 8.36 (s, 1H), 8.58 (s, 1H), HRMS (FAB) *m/z* 533.2688 (M-H, $C_{28}H_{41}N_2O_6S$ requires 533.2680).

28: ^{1}H-NMR ($CDCl_3$) δ 1.14 (t, 3H, *J* = 6.9 Hz), 2.62 (m, 2H), 2.86 (m, 2H), 3.13 (m, 2H), 3.37-3.81 (m, 16H), 3.88 (m, 2H), 3.94 (m, 2H), 4.03 (m, 2H), 4.39 (m, 2H), 6.21 (s, 1H), 7.55-7.62 (m, 2H), 7.97-8.00 (m, 2H), 7.98 (s, 1H), 8.31 (s, 1H), HRMS (FAB) *m/z* 533.2688 (M-H, $C_{28}H_{41}N_2O_6S$ requires 533.2680).

26: ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, 3H, *J* = 7.2 Hz), 2.84-3.15 (m, 6H), 3.41-3.78 (m, 16H), 3.88-3.92 (m, 4H), 4.01-4.06 (m, 2H), 4.34-4.41 (m, 2H), 6.54 (s, 1H), 7.61-7.49 (m, 2H), 7.89-8.04 (m, 2H), 8.35 (s, 1H), 8.62 (s, 1H), HRMS (FAB) *m/z* 545.2684 (M+H, $C_{29}H_{41}N_2O_6S$ requires 545.2685).

29: ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, 3H, *J* = 7.2 Hz), 2.84-3.15 (m, 6H), 3.41-3.78 (m, 16H), 3.88-3.92 (m, 4H), 4.01-4.06 (m, 2H), 4.34-4.41 (m, 2H), 6.32 (s, 1H), 7.61-7.49 (m, 2H), 7.89-8.04 (m, 2H), 8.01 (s, 1H), 8.33 (s, 1H), HRMS (FAB) *m/z* 545.2684 (M+H, $C_{29}H_{41}N_2O_6S$ requires 545.2685).

27: ^{1}H-NMR ($CDCl_3$) δ 1.42 (t, 3H, *J* = 7.5 Hz), 2.49-2.80 (m, 12H), 3.06-3.14 (m, 2H), 3.42-3.71 (m, 8H), 3.73-3.88 (m, 4H), 4.01 (m, 2H), 4.34 (m, 2H), 6.50 (s, 1H), 7.46-7.61 (m, 2H), 7.84-7.99 (m, 2H), 8.32 (s, 1H), 8.58 (s, 1H), HRMS (FAB) *m/z* 577.2225 (M+H, $C_{29}H_{41}N_2O_4S_3$ requires 577.2228).

30: ^{1}H-NMR ($CDCl_3$) δ 1.42 (t, 3H, *J* = 7.5 Hz), 2.49-2.80 (m, 12H), 3.06-3.14 (m, 2H), 3.42-3.71 (m, 8H), 3.73-3.88 (m, 4H), 4.01 (m, 2H), 4.34 (m, 2H), 6.28 (s, 1H), 7.46-7.61 (m, 2H), 7.84-7.99 (m, 2H), 7.98 (s, 1H), 8.29 (s, 1H), HRMS (FAB) *m/z* 577.2225 (M+H, $C_{29}H_{41}N_2O_4S_3$ requires 577.2228).

Preparation of *N*-[(ω-Trimethylsilylmethylthio)polyoxathioalkyl]-2,3-naphthalimide (32). The nitrogen purged solution of 2,2-dimethyl-7,10,13-trioxa-4-thia-2-silapentadecane-15-ol[13] (1.9 g, 6.36 mmol), 2,3-naphthalenedicarboximide (1.51 g, 7.69 mmol) and triphenylphosphine (2 g, 7.69 mmol) in THF (40 mL) was stirred at room temperature for 1 h. Diisopropyl azodicarboxylate (1.52 mL, 7.69 mmol) was added dropwise and then solution was stirred for 12 h at room temperature. Concentration of solution *in vacuo* gave residues which were subjected to silica gel column chromatography (Ethyl acetate:*n*-Hexane = 1:3) to afford **32** (1.4 g, 46%).

32: ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.79 (s, 2H), 2.65 (t, 2H, *J* = 7.5 Hz), 3.52-3.65 (m, 10H), 3.78 (t, 2H, *J* = 5.7 Hz), 3.96 (t, 2H, *J* = 6.0 Hz), 7.67-7.70 (m, 2H), 8.03-8.06 (m, 2H), 8.32 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ −1.9, 18.7, 35.0, 37.3, 67.7, 69.96, 70.01, 70.2, 70.4, 124.3(2C), 127.6(2C), 128.9(2C), 130.0(2C), 135.2(2C), 167.6(2C); HRMS (FAB) *m/z* 498.1746 (M+Na^+, calcd for $C_{21}H_{33}NO_5SSiNa$, 498.1849).

Photocyclization Reaction of 32 to Naphthalamide

Containing Thiacrown Ether 33. The nitrogen purged solution of naphthalimide, **32** (0.3 g, 0.63 mmol) in 200 mL of MeOH was irradiated by using Pyrex glass filtered light for 0.5 h to give almost 100% conversion. Concentration of the photolysate *in vacuo* gave residues which were subjected to silica gel column chromatography ($CHCl_3$:Acetone = 3:1) to yield **33** (0.1 g, 44%).

33: ^{1}H-NMR ($CDCl_3$) δ 2.63-2.71 (m, 2H), 2.93-3.02 (m, 2H), 3.48, 3.63 (2d, 2H, J = 13.8 Hz), 3.69-4.00 (m, 12H), 4.25-4.30 (m, 1H), 4.33-4.35 (m, 1H), 5.69 (s, 1H), 7.51-7.60 (m, 2H), 7.94-7.98 (m, 2H), 8.24 (s, 1H), 8.28 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 33.3, 40.0, 41.5, 70.3, 70.57, 71.4, 71.5, 71.6, 73.2, 89.4, 122.6, 124.0, 127.0, 127.9, 128.9, 129.1, 129.7, 133.9, 135.7, 141.3, 167.4; HRMS (FAB) *m/z* 402.1375 (M-H$^+$, calcd for $C_{21}H_{24}NO_5S$, 402.1453).

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