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A convenient synthesis and preliminary photophysical study of novel fluoroionophores: macrocyclic polyamines containing two dansylamidoethyl side arms

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Abstract—A series of novel fluorophores, consisting of macrocyclic polyamines containing two dansylamidoethyl side arms were synthesized as potential zinc (II) fluoroionophores by the reaction of the appropriate macrocyclic polyamines with *N*-dansylaziridine in acetonitrile at reflux temperature. Preliminary photophysical studies of ligand **3a**, 1,7-dimethyl-4,10-bis(dansylamidoethyl)-1,4,7,10-tetraazacyclododecane, **3j**, 8,13-bis(dansylamidoethyl)-3-hydroxymethyl-1,3,10-trithia-8,13-diazacyclopentadecane, and their complexes with Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} are described. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The rapid and quantitative analysis of trace metal ions for environmental and biological applications is particularly demanding since it requires recognition of a particular metal ion in the presence of numerous closely related species.[1] While remarkable progress has been made for other biologically important divalent metal ions, in particular Ca^{2+} and Mg^{2+} with several selective fluorophores such as Fura-2, Quin-2, and Mag-indo-1,[2] there are few Zn^{2+} selective fluorophores.

Recently, a new type of selective and efficient Zn^{2+} fluorophore, a dansylamide-substituted macrocyclic tetraamine (dansylamidoethylcyclen), has been developed by Kimura and co-workers.[3] The success of this fluorophore is due to a high affinity of cyclen toward Zn^{2+}, a strong affinity toward aromatic sulfonamides by the Zn^{2+}-cyclen complex, and a good luminescence property of the dansyl chromophore. These properties allow this system to sense Zn^{2+} in nanomolar concentrations at physiological pH. As far as we know, this is the first example of a dansyl-containing amidoethyl-pendant macrocyclic polyamine which may be used as a Zn^{2+} fluorophore to quantify trace Zn^{2+} ion concentrations. The synthesis of dansylamidoethyl-pendant cyclen seems to be impractical because multi-step chemical reactions (5 steps) were required and the overall yield was low (only 17.3%). Very recently, we reported an efficient and convenient one-step method to introduce the dansyl chromophore onto macrocyclic polyamines.[4] Herein, we describe the full details concerning this new method, report additional new macrocyclic dansylamidoethyl-containing azacrown ethers, and report preliminary photophysical studies of ligands **3a** and **3j** and their complexes with Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}.

2. Results and discussion

Kimura and co-workers prepared dansylamidoethylcyclen **9** by a multi-step synthesis (Scheme 1).[3] Aminoethyl-pendant cyclen **6** was synthesized by treatment of dioxocyclen **4** with bromocyanomethane (to form **5**) followed by BH_3–THF reduction of the carbonyl and cyano groups. Then, **6** was converted to zinc(II) complex **7** as its diperchlorate salt. Isolated complex **7** was treated with an equimolar amount of dansyl chloride in acetonitrile at room temperature to give the desired zinc (II) complex of dansylamidoethyl-pendant cyclen **8**, which was purified as its monoperchlorate salt. Demetalation of **8** to form the dansylamidoethyl-pendant cyclen **9** was achieved by treatment with excess EDTA (5 equiv.) in H_2O. Although the yield in each step was modest (60~83%), the overall yield for the procedure was very low (17.3%), and a tedious isolation is needed for each step. Multi-step synthetic routes to dansylamidoethyl macrocyclic polyamines are available, however, the development of a convenient one-step procedure is of significance from both economical and ecological points of view. The development of one-step procedures for the

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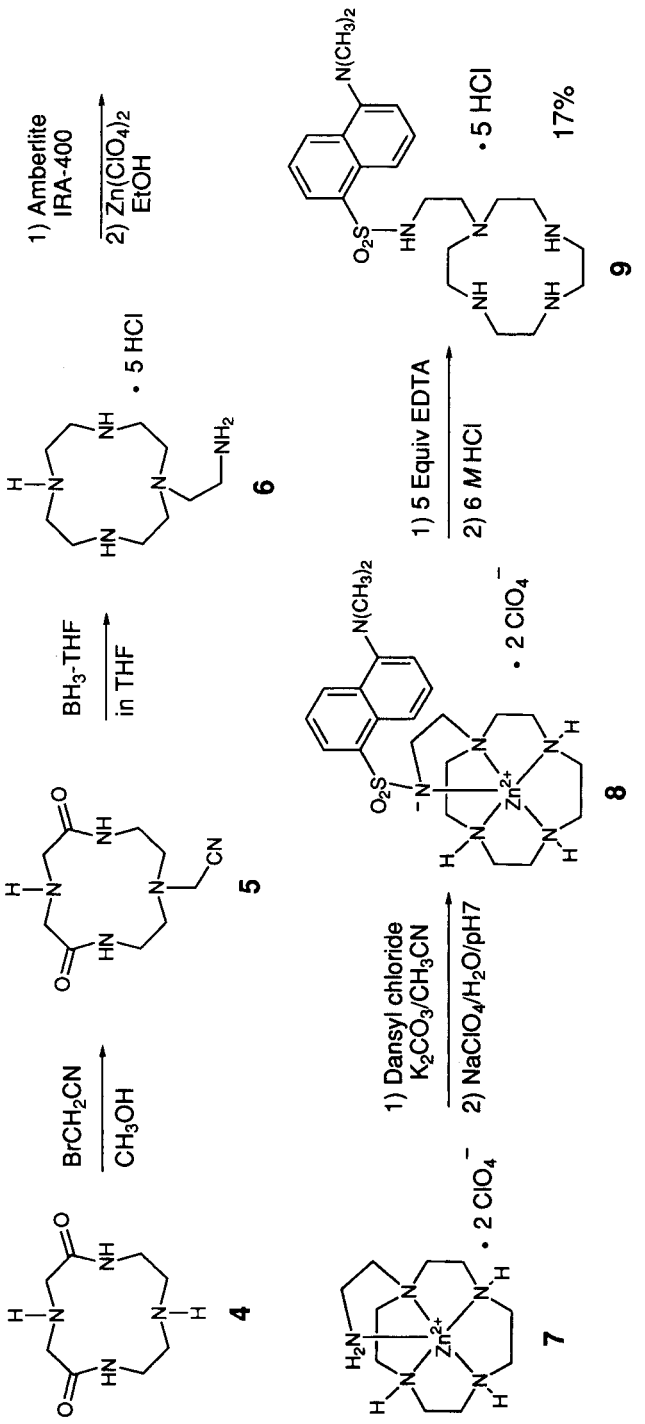


Scheme 1. Preparation of monodansylamidoethylcyclen.[3]

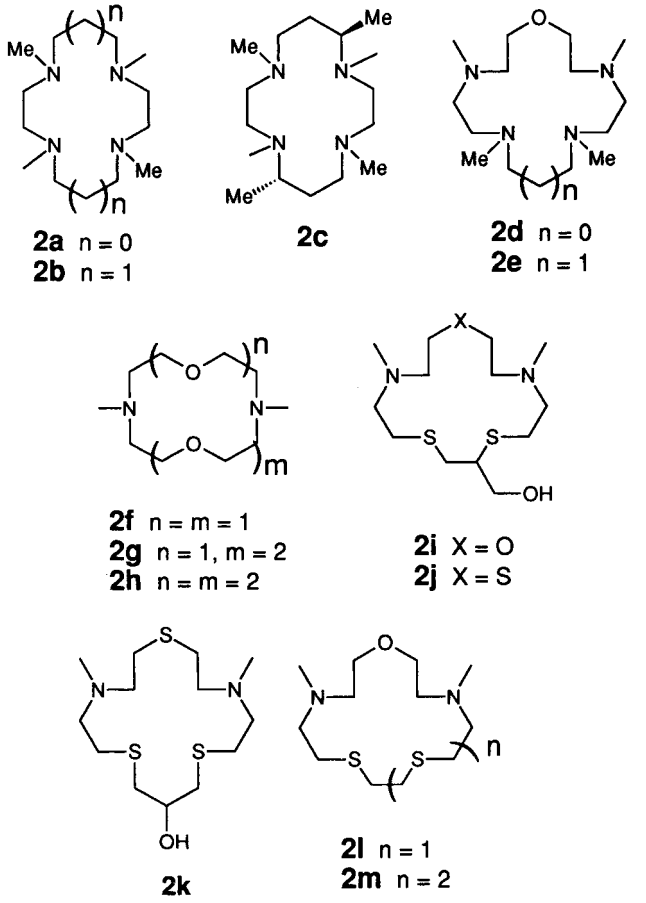
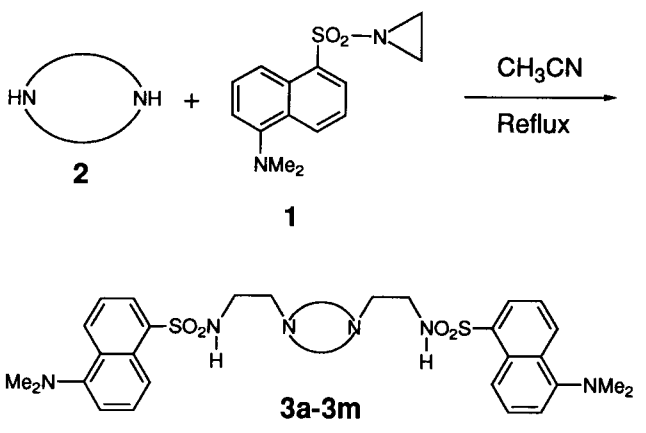


Figure 1. Structures of macrocyclic polyamines included in bis-(dansylamidoethyl)-substituted ligands in Scheme 1.

production of important organic compounds remains a challenge in organic synthesis.

Our synthetic strategy is based on ring-opening of *N*-dansylaziridine caused by the secondary amine functions of the macrocyclic polyamine. Starting *N*-dansylaziridine **1** was easily prepared by treating aziridine[5] with dansyl chloride (commercially available) as reported in our previous communication.[4] The reaction of macrocyclic polyamines **2a**–**m** (Fig. 1) with *N*-dansylaziridine in acetonitrile at reflux temperature gave the bis(dansylamidoethyl)-containing macrocyclic polyamines **3a**–**m** in high yields (Scheme 2). The crude products were purified by recrystallization from CH_2Cl_2/EtOH (1:1) or by column chromatography on silica gel using acetone/triethylamine (10:1) as eluent. Thus, a series of bis(dansylamidoethyl)-substituted macrocyclic polyamines possessing different ring sizes and different heteroatoms (O,N,S) have been prepared. We expected that these novel ligands would not only be selective for Zn^{2+} as potential zinc (II)-fluoroionophores, but would also selectively bind other transition metal ions.



Scheme 2. Preparation of macrocyclic polyamines containing two dansylamidoethyl sidearms (see Fig. 1 for structures of the macrocycles).

Preliminary photophysical properties of ligands **3a** (1,7-dimethyl-4,10-bis(dansylamidoethyl)-1,4,7,10-tetraazacyclododecane), **3j** (8,13-bis(dansylamidoethyl)-3-hydroxymethyl-1,3,10-triathia-8,13-diazacyclopentadecane) and their complexes with Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} have been investigated. The absorption spectra of a methanol/water (1/1) solution of **3a** and **3j** present a large and unstructured band at 331 nm and a more intense one at 247 nm. These species are also highly luminescent; **3a** exhibits a large and intense band with λ_{max} at 527 nm, with a fluorescence quantum yield, Φ, of 0.09 and an excited state lifetime, τ, of 6.4 ns, while the fluorescence band of **3j** peaks at 537 nm (Φ=0.09, τ=7.0 ns). This photophysical behavior of **3a** and **3j** is in agreement with the data obtained from other dansyl derivatives.[6–12] Addition of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} ions to a methanol/water (1/1) solution of **3a** buffered at pH 9.5 leads to pronounced changes in the UV–Vis spectra of the ligand. In particular, the band at 331 nm shifts to shorter wavelengths (314, 327, 313, and 321 nm for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, respectively) and increases in intensity. The intensity increase is particularly evident upon addition of Cu^{2+}, where the absorbance almost doubles. Similar behavior was observed for **3j** under the same conditions. In this case, a blue shift was observed for Cu^{2+} (λ_{max}=328 nm, accompanied by a large absorption tail in the 400–500 nm region), Cd^{2+} (316 nm), and Hg^{2+} (328 nm), while no changes at all were observed in the case of Zn^{2+}, even after addition of up to 10 equiv. of metal ions. For **3a**, blue-shifts are also observed for the luminescence bands (502, 515, 492, and 513 nm for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, respectively). A similar behavior has been observed also for other ligands containing a dansyl chromophore,[6] for which the complexation process was concomitant to the deprotonation of the sulfonamide group. The blue shift was, in that case, explained by an increase of the electronic density on the aromatic rings caused by the deprotonation process, that moves the amine-to-naphthalene charge transfer state centered on the dansyl chromophore to higher energy. In the fluorescence spectrum of **3a**, an increase of the luminescence intensity was observed only upon addition of Zn^{2+} (I_{rel}=115%, τ=8.3 ns), while Hg^{2+} (I_{rel}=46%, τ=6.9 ns) and Cd^{2+} (I_{rel}=60%, and a double excited state lifetime, τ_1=0.7 and τ_2=7.0 ns), a modest decrease of the fluorescence quantum yield was observed. Addition of Cu^{2+} led to an almost complete quenching of the fluorescence of the ligand (I_{rel}<2%, τ<0.4 ns) as expected because complexation with such an ion makes energy- and electron-transfer processes accessible, providing a fast deactivation route to the ground state.[6]

As far as **3j** is concerned, addition of Cd^{2+} led again to a

blue-shift of the luminescence bands (497 nm), in strict analogy to that observed with **3a**, while no changes in the fluorescence maximum were observed with the other metal ions. Again, a modest decrease of the fluorescence quantum yield was observed with Hg^{2+} (I_{rel}=29%, τ=3.8 ns) and Cd^{2+} (I_{rel}=68%, and a double excited state lifetime, τ_1=0.7 and τ_2=6.2 ns), and an almost complete quenching with Cu^{2+} (I_{rel}<2%, τ<0.4 ns). In contrast to that observed with **3a**, but in agreement with that observed in the absorption spectrum, no changes were observed upon addition of up to 10 equiv. of Zn^{2+}. Furthermore, only small effects were found on the absorption and luminescence spectra upon addition of up to 10 equiv. of Zn^{2+} to a solution containing equimolar amounts of **3j** and Cu^{2+}, Cd^{2+}, or Hg^{2+}. This result, obtained both by direct and by competition experiments, indicates that Zn^{2+}, in this case, does not significantly interfere with the complexation of Cu^{2+}, Cd^{2+}, and Hg^{2+}. A different complexation behavior between **3a** and **3j** was indeed expected, since the S atoms are known to bind Hg^{2+} preferentially over Zn^{2+}. These results are important because they demonstrate, that taking advantage of their different complexation properties and their different response upon complexation, the whole set of ligands **3a**–**m** could be exploited as an efficient array for the development of a multisensory system that could allow real time determination of the concentration of several transition metal ions at once.

In conclusion, the reported synthesis procedure provides an efficient and general methodology for the introduction of the dansyl chromophore onto the macrocyclic polyamines. The procedure is simple, quick, and convenient, which should make it useful for the synthesis of new fluorophores. Photophysical properties of **3a** and **3j** and their complexes with Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} have been investigated. Further complexation and photophysical studies of compounds **3a**–**m** are in progress and detailed results will be reported in due course.

3. Experimental

The ^1H and ^{13}C NMR spectra were recorded at 200 or 300 MHz and 50 or 75 MHz in $CDCl_3$ unless otherwise indicated. Melting points are uncorrected. HRMS spectra were determined using the fast atom bombardent (FAB) method. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. For spectrophotometric measurements, methanol (Uvasol, Merck) and Millipore grade water were used as solvents. Solutions of the ligands were 1.0×10^{-5} M unless otherwise noted. Absorption spectra were recorded with a Perkin–Elmer lambda 40 spectrophotometer. Uncorrected emission, and corrected excitation spectra were obtained with a Perkin–Elmer LS 50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ±5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D_2. In order to allow comparison among emission intensities, we performed corrections for instrumental response, inner filter effects, and phototube sensitivity.[13] A correction for differences in the refraction index was introduced when necessary. Solvents and starting materials were purchased from commercial sources where available. Compounds **1**,[4] **2a**,[14] **2b**,[15] **2c**,[16] **2d**, **e**[17], **2j**, **k**,[18] and **2i**, **l**, **m**,[19] were prepared as reported.

3.1. General procedure for the syntheses of compounds 3a–m

N-Dansylaziridine **1** (2.4 mmol) in dry CH_3CN (20 mL) was added dropwise over 30 to 40 min to a refluxing solution of the appropriate macrocyclic polyamine (1.0 mmol) in dry CH_3CN (30 mL) under nitrogen. The mixture was stirred at reflux for 4–5 h. After evaporation of the solvent, the crude products were purified by recrystallization from CH_2Cl_2/EtOH (1:1) (**3a**–**c** and **3f**) or by column chromatography on silica gel using acetone/triethylamine (10:1) as eluent (**3d**, **e** and **3g**–**m**). The physical and spectroscopic data of **3a**–**e** have been described.[4]

3.1.1. 4,10-Bis(dansylamidoethyl)-1,7-dioxa-4,10-diazacyclododecane (3f). This compound was prepared in 90% yield as a pale yellow solid; mp 171–173°C; ^1H NMR δ 8.51 (d, J=8.4 Hz, 2H), 8.39 (d, J=8.4 Hz, 2H), 8.23 (d, J=7.4 Hz, 2H), 7.50 (m, 4H), 7.16 (d, J=7.2 Hz, 2H), 6.91 (br, 2H), 3.64 (t, J=4.8 Hz, 8H), 3.05 (s, 4H), 2.88 (s, 12H), 2.60 (m, 12H); ^{13}C NMR (DMSO-D6) δ 151.4, 136.0, 129.4, 129.1,129.1, 128.2, 127.8, 123.6, 119.1, 115.1, 68.3, 54.4, 45.1, 40.8, 40.4; HRMS: *m/z* calcd for $C_{36}H_{50}N_6O_6S_2Na$ $(M+Na)^+$: 749.3135, Found: 749.3124. Anal. Calcd for $C_{36}H_{50}N_6O_6S_2$: C, 59.48; H, 6.93. Found: C, 59.60; H, 6.73.

3.1.2. 4,13-Bis(dansylamidoethyl)-1,7,10-trioxa-4,13-diazacyclopentadecane (3g). This compound was prepared in 88% yield as a pale yellow solid; mp 59–60°C; ^1H NMR δ 8.52 (d, J=8.4 Hz, 2H), 8.41 (d, J=8.6 Hz, 2H), 8.25 (d, J=7.6 Hz, 2H), 7.51 (m, 4H), 7.18 (d, J=7.4 Hz, 2H), 6.33 (br, 2H), 3.64 (s, 4H), 3.46 (t, J=4.8 Hz, 8H), 2.99 (s, 4H), 2.90 (s, 12H), 2.67 (m, 12H), ^{13}C NMR δ 151.9, 135.8, 130.2, 130.1, 130.0, 129.2, 128.2, 123.4, 119.7, 115.3, 70.4, 69.7, 69.2, 54.9, 54.5, 45.6, 41.5; HRMS: *m/z* calcd for $C_{38}H_{54}N_6O_7S_2Na$ $(M+Na)^+$: 793.3397. Found: 793.3386. Anal. Calcd for $C_{38}H_{54}N_6O_7S_2$: C, 59.19; H, 7.06. Found: C, 59.30; H, 6.86.

3.1.3. 7,16-Bis(dansylamidoethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (3h). This compound was prepared in 87% yield as a green solid; mp 106–108°C; ^1H NMR δ 8.51 (d, J=8.4 Hz, 2H), 8.38 (d, J=8.4 Hz, 2H), 8.24 (d, J=7.4 Hz, 2H), 7.51 (m, 4H), 7.16 (d, J=7.4 Hz, 2H), 6.16 (br, 2H), 3.60 (s, 8H), 3.41 (t, J=5.4 Hz, 8H), 2.91 (m, 4H), 2.87 (s, 12H), 2.58 (m, 12H); ^{13}C NMR δ 151.9, 135.3, 130.1, 130.0, 129.8, 129.3, 128.2, 123.3, 119.4, 115.2; HRMS: *m/z* calcd for $C_{40}H_{58}N_6O_8S_2Na$ $(M+Na)^+$: 837.3659, Found: 837.3637. Anal. Calcd for $C_{40}H_{58}N_6O_8S_2$: C, 58.94; H, 7.17. Found: C, 58.91; H, 7.32.

3.1.4. 4,13-Bis(dansylamidoethyl)-8-hydroxymethyl-1-oxa-7,10-dithia-4,13-diazacyclopentadecane (3i). This compound was prepared in 86% yield as a yellow solid; mp. 57–59°C; ^1H NMR δ 8.52 (d, J=8.6 Hz, 2H), 8.37 (d, J=8.6 Hz, 2H), 8.24 (d, J=7.2 Hz, 2H), 7.52 (m, 4H), 7.18 (d, J=7.6 Hz, 2H), 5.93 (br, 2H), 3.80 (dd, J=5.0 and 12 Hz, 1H), 3.60 (dd, J=6.6, 11.2 Hz, 1H), 3.37 (m, 4H), 2.88 (s, 12H), 2.97–2.46 (m, 24H); ^{13}C NMR δ 152.2,

135.2, 130.6, 130.2, 130.0, 129.7, 128.5, 123.4, 119.5, 115.4, 70.0, 69.7, 64.3, 55.1, 54.9, 53.5, 53.4, 53.1, 49.4, 45.6, 41.1, 35.0, 31.0, 29.6; HRMS: *m/z* calcd for $C_{39}H_{56}N_6O_6S_4Na$ $(M+Na)^+$: 855.3046; Found: 855.3043. Anal. Calcd for $C_{39}H_{56}N_6O_6S_4$: C, 56.22; H, 6.78. Found: C, 56.16; H, 6.61.

3.1.5. 8,13-Bis(dansylamidoethyl)-3-hydroxymethyl-1,3,10-triathia-8,13-diazacyclopentadecane (3j). This compound was prepared in 83% yield as a yellow solid; mp 68–70°; ^{1}H NMR δ 8.53 (d, J=8.6 Hz, 2H), 8.31 (d, J=8.6 Hz, 2H), 8.25 (d, J=7.4 Hz, 2H), 7.52 (m, 4H), 7.18 (d, J=7.8 Hz, 2H), 5.94 (br, 2H), 3.78 (m, 1H), 3.67 (m, 1H), 2.88 (s, 12H), 2.95–2.43 (m, 28H); ^{13}C NMR δ 152.1, 135.1, 134.9, 130.6, 130.1, 129.7, 128.5, 123.4, 119.2, 115.4, 64.2, 54.2, 53.9, 53.5, 53.3, 49.9, 45.7, 40.9, 35.1, 31.1, 30.7, 30.2; HRMS: *m/z* calcd for $C_{39}H_{56}N_6O_5S_5Na$ $(M+Na)^+$: 871.2819, Found: 871.2811. Anal. Calcd for $C_{39}H_{56}N_6O_5S_5$: C, 55.19; H, 6.65. Found: C, 55.32; H, 6.80.

3.1.6. 8,14-Bis(dansylamidoethyl)-3-hydroxy-1,5,11-trithia-8,14-diazacyclohexadecane (3k). This compound was prepared in 85% yield as a yellow solid; mp 68–69°C; ^{1}H NMR δ 8.53 (d, J=8.1 Hz, 2H), 8.37 (d, J=8.7 Hz, 2H), 8.25 (d, J=7.2 Hz, 2H), 7.52 (m, 4H), 7.18 (d, J=7.8 Hz, 2H), 5.99 (br, 2H), 3.85 (m, 1H), 2.97 (m, 4H), 2.89 (s, 12H), 2.77–2.48 (m, 24H); ^{13}C NMR δ 152.2, 135.1, 130.6, 130.1, 129.9, 129.7, 128.5, 123.4, 119.3, 115.4, 70.9, 54.4, 54.2, 53.5, 45.7, 41.0, 38.6, 31.3, 30.5; HRMS: *m/z* calcd for $C_{39}H_{57}N_6O_5S_5$ (M^+): 849.2999, Found: 849.3003. Anal. Calcd for $C_{39}H_{56}N_6O_5S_5$: C, 55.19; H, 6.65, Found: C, 55.32; H, 6.43.

3.1.7. 4,13-Bis(dansylamidoethyl)-1-oxa-7,10-dithia-4,13-diazacyclopentadecane (3l). This compound was prepared in 81% yield as a yellow solid; mp 70–72°C; ^{1}H NMR δ 8.53 (d, J=8.4 Hz, 2H), 8.37 (d, J=9.9 Hz, 2H), 8.25 (d, J=7.2 Hz, 2H), 7.52 (m, 4H), 7.18 (d, J=7.8 Hz, 2H), 5.88 (br, 2H), 3.34 (m, 4H), 2.89 (s, 12H), 2.90–2.49 (m, 24H); ^{13}C NMR δ 152.1, 135.1, 130.6, 130.1, 129.9, 129.7, 128.4, 123.4, 119.3, 115.3, 55.4, 53.5, 53.2, 45.7, 41.2, 32.8, 32.6, 30.3; HRMS: *m/z* calcd for $C_{38}H_{55}N_6O_5S_4$ $(M+1)^+$: 803.3121, Found: 803.3112. Anal. Calcd for $C_{38}H_{54}N_6O_5S_4$: C, 56.83; H, 6.78. Found: C, 57.12; H, 6.88.

3.1.8. 4,16-Bis(dansylamidoethyl)-1-oxa-7,10,13-trithia-4,16-diazacyclooctadecane (3m). This compound was prepared in 80% yield as a yellow solid; mp 60°C; ^{1}H NMR δ 8.53 (d, J=8.4 Hz, 2H), 8.36 (d, J=8.6 Hz, 2H), 8.24 (d, J=7.0 Hz, 2H), 7.54 (m, 4H), 7.18 (d, J=7.8 Hz, 2H), 5.93 (br, 2H), 3.30 (m, 4H), 2.88 (s, 12H), 2.80–2.54 (m, 28H); ^{13}C NMR δ 151.9, 134.7, 130.2, 129.8, 129.6, 129.4, 128.1, 123.1, 119.0, 115.1, 69.2, 54.3, 53.4, 53.0, 45.4, 40.9, 32.6, 32.3, 30.5; HRMS: *m/z* calcd for $C_{40}H_{58}N_6O_5S_5Na$ $(M+Na)^+$: 885.2975, Found: 885.2966. Anal. Calcd for $C_{40}H_{58}N_6O_5S_5$: C, 55.65; H, 6.77, Found: C, 55.71; H, 6.50.

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