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Preparation and characterization of bis[4-dimethylamino-2-pyrimidyl] dichalcogenides (S, Se, Te): X-ray crystal structure of bis[4-dimethylamino-2-pyrimidyl] diselenide and its physicochemical behavior in microemulsion media

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ABSTRACT

Novel and synthetically important bis[4-dimethylamino-2-pyrimidyl] dichalcogenides (S, Se, Te) have been prepared and characterized with the help of elemental analysis and various spectroscopic techniques. The methodology employs hydrazine hydrate in dimethylformamide to reduce elemental chalcogen to generate the dichalcogenide anions, E_2^{2-} (E=S, Se, Te), followed by reaction with 2,4-dichloropyrimidine to afford bis[4-dimethylamino-2-pyrimidyl] dichalcogenides in good yield. It further exploits the additional compositional degree of freedom available in mixed surfactant solution to allow solubilization and stabilization of bis[4-dimethylamino-2-pyrimidyl] diselenide in microemulsion media.

1. Introduction

In the last few decades various organochalcogen (alkyl, aryl, mixed alkylaryl, pyridyl selenium, and tellurium) compounds have been extensively studied owing to their novel and unparallel properties.[1] These compounds find widespread use as convenient intermediates or reagents in organic synthesis,[2] biochemistry,[3] organic superconductors,[4] and semi-conducting materials.[5] In an effort to synthesize these compounds various procedures have been explored.[6] Tanji et al.[7] employed the reaction of 2-bromopyridine with lithium alkyl tellurolates to obtain alkyl pyridyl tellurides while Bhasin et al.[8] have developed and optimized the conditions for the preparation of stable bis(2-pyridyl) diselenide/ditelluride by lithiating pyridine using BF_3–Et_2O complex followed by insertion of elemental selenium/tellurium and subsequent oxidation. Bis(2-pyridyl) diselenide has also been shown to be a potential immuno-stimulant and inducer of interferon gamma and other cytokines in human peripheral blood leukocytes.[9]

Microemulsions are dynamic supramolecular aggregates spontaneously formed by dissolving surfactant in organic media.[10–12] These aggregates allow molecules of disparate polarities (i.e., diorganodiselenides)[13] to be brought into contact with each other. Microemulsions help in solubilization of molecules insoluble in organic and aqueous solvents and can provide useful reaction media for organic synthesis. The physiochemical properties of such systems are often very different from those of naked molecules or condensed phases and are influenced by confinement effects, inhomogeneous distribution, orientation order, and interfacial interactions.[14,15] Water-in-oil microemulsions exhibit a low electrical conductivity as the layers of surfactant separate water droplets. However, when the temperature θ increases beyond the critical value (i.e., θ_c) the conductivity increases sharply. This sudden rise in conductance has been related to increase in the attractive interactions between the droplets that facilitate migration of surfactant counter ions along connected paths through the microemulsion, leading finally to the phenomenon of electric percolation.[16–19]

In pursuance of our work[20] on pyridylchalcogen compounds, we wish to report herein, a convenient and facile method for synthesis of some newly designed pyrimidyl chalcogen compounds by employing hydrazine hydrate as a reducing agent for elemental

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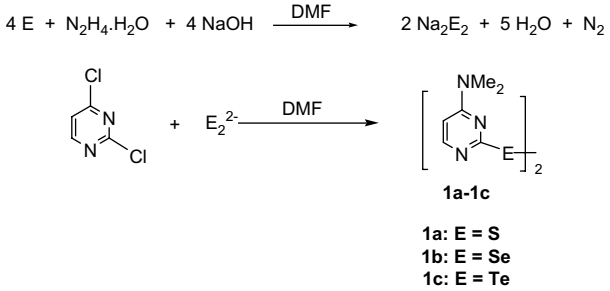
chalcogen atom in dimethylformamide. This line of approach appears to be potentially useful in view of the many known biologically important compounds,[21] which contain the pyrimidyl moiety. Amir et al.[22] have provided a broad view of antiinflamatory activity possessed by compounds having a pyrimidine nucleus. 2,4-Diaminopyrimidine derivatives, that have been well estabilished as antiviral agents, now have been modified to antitumor agents.[23] 5-Alkyl- or 5-alkylaryl-substituted pyrimidine derivatives are useful intermediates in the synthesis of antiviral nucleosides. Schinazi et al.[24] reported the synthesis and the biological activity of several 5-(phenylselenenyl)-pyrimidine nucleosides as potential antiviral agents. More recently,[25,26] a variety of newly synthesized 6-phenylselenenyl acyclic pyrimidines was found to have potent anti-humanimmunodeficiency virus type-1 (HIV-1) activity. Bardos[27] group synthesized 5-selenium-substituted derivatives (diselenides) of uracil, 2′-deoxyuridine, and 2′-deoxyuridylic acid. Amino- and dimethylamino-substituted dipyrimidyl diselenides have been reported[28] by use of UV irradiation. Curiously, these compounds have not been studied extensively compared to the corresponding aromatic and aliphatic derivatives although the pyrimidyl compounds are anticipated to exhibit interesting properties due to presence of two electron withdrawing nitrogen in their skeleton structure. To explore the behavior of studied compounds, an additional study has been carried out by assimillating bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, in water/AOT/isooctane (ME-I) and water/AOT+LC/isooctane (ME-II) microemulsion media.

2. Results and discussion

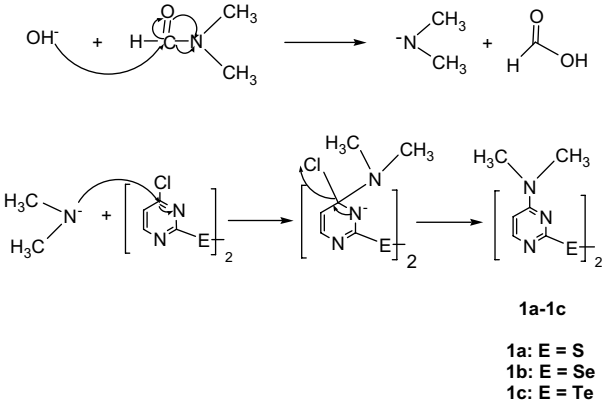
The synthetic strategy to prepare disubstituted pyrimidyl chalcogen compounds employs 100% hydrazine hydrate in DMF to reduce chalcogens to generate dichalcogenide anions E_2^{2-} (E=S, Se, Te) followed by reaction with 2,4-dichloropyrimidine to give **1a**–**1c** in good yield (Scheme 1).



Scheme 1. Synthesis of bis[4-dimethylamino-2-pyrimidyl] dichalcogenides.

The advantage of this methodology is the selective nucleophilic substitution of chlorine atom at second position of 2,4-dichloropyrimidine by dichalcogenide anion. An interesting observation in this reaction is the simultaneous substitution of chlorine atom at fourth position of 2,4-dichloropyrimidine by dimethylamino group from the solvent dimethylformamide. It is well known that DMF can act as formylating agent,[29] however, in these reactions it acts as nucleophilic reagent leading to replacement of activated chloro group by dimethylamino group, $-N(CH_3)_2$. The dimethylamino group being more bulky and less nucleophilic than the dichalcogenide anion attacks the fourth position of the pyrimidine ring. It is interesting to note that in addition to drugs like anticholinergic,[30] fungicide,[31] antipyretic,[32] antihistamine,[30] and narcotic analgesic,[33] the dimethylamino group is also present in important molecules such as 6-dimethylamino-purine (6-DMAP), a very important chemical, present in 0.78–0.08 mol % in the DNA composition of algae.[34] Recently, it has been shown that the 6-DMAP (inhibitor of cyclin dependent kinase [CDK]) is used to study the DNA endoreduplication during elongation and differentiation of primary roots.[35] 6-DMAP is also used to activate embryos and oocytes that give rise to cloned rabbits that are produced by nuclear transfer from adult somatic cells.[36]

The preparation of **1a**–**1c** involves reduction of chalcogen atom to dichalcogenide anion by hydrazine hydrate in alkaline medium followed by relatively fast nucleophilic substitution reaction on C-2 of 2,4-dichloropyrimidine (α position w.r.t. both nitrogen in the ring). Hydrazine hydrate is preferred over other reducing agents because of its low cost, easy work up, high yield, and inert reaction conditions. The chlorine atom on C-4 is also reactive and displays a slow nucleophilic substitution reaction by *N*,*N*-dimethylamino anion from DMF to give the desired products (Scheme 2).



Scheme 2. Proposed mechanism for preparation of bis[4-dimethylamino-2-pyrimidyl] dichalcogenides.

All the compounds prepared during the course of these investigations are stable to be purified by column chromatography (silica gel using hexane/ethyl acetate). The compounds are soluble in conventional organic solvents and have a shelf life of several months without any sign of decomposition even at room temperature.

2.1. Spectroscopic studies

^{1}H NMR characterization of dichalcogenide compounds shows an upfield shift of ring protons w.r.t. the protons of 2,4-dichloropyrimidine due to displacement of electronegative chlorine with chalcogen atom. The aliphatic protons of the methyl carbon of dimethylamino group resonate at higher field in selenium and tellurium compounds as compared to sulfur one. The aromatic protons in pyrimidyl ring H-3 and H-4 resonate at high δ value in case of diselenide compared to ditelluride that can be clearly explained on the basis of decreased electronegativity down the group in chalcogen family. However, the chemical shift is unusually upfield in case of disulfide (S<Te<Se) that may be attributed to interelectronic repulsions in this compound. ^{13}C NMR spectroscopic results reveal that the aromatic carbons fall in the region of 100–162 ppm. The chemical shift value of the methyl carbon of dimethylamino group appear at about 37 ppm in case of diselenide and ditelluride whereas at 36.6 ppm in disulfide. A comparison of stretching frequencies, obtained from FTIR results, ν_{E-C} (where E=S, Se, Te) in pyrimidyl dichalcogenide reveals a regular trend in the variation of absorption values.

As commonly observed in EIMS, extensive dissociation of C–E bond (E=Se, Te) occurred and consequently the base peaks did not correspond to molecular ion peaks. In case of bis[4-dimethylamino-2-pyrimidyl] diselenide, the mass spectrum is complicated due to

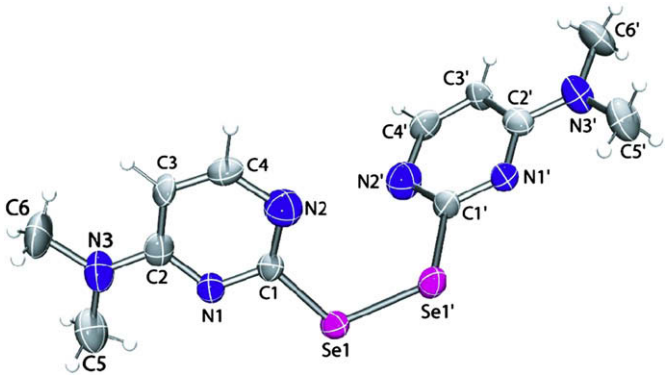


Figure 1. ORTEP diagram showing the conformation for bis[4-dimethylamino-2-pyrimidyl] diselenide (**1**).

several isotopes of selenium. The fragment corresponding to 4-*N*,*N*-dimethylamino pyrimidine radical is the most intense and appears at *m*/*e* 122 and is assigned as the base value. The fragment ions containing selenium show a highly characteristic and definite pattern of signal intensities depending on the natural abundance of various isotopes of selenium. Bis[4-dimethylamino-2-pyrimidyl] ditelluride shows prominent peak corresponding to $[C_{12}H_{16}N_6Te]^{+\bullet}$ (*m*/*e* 372) while other low intensity peaks result from $[C_{10}H_{10}N_5Te]^{+\bullet}$ (*m*/*e* 328) and $[C_{10}H_6N_5Te]^{+\bullet}$ (*m*/*e* 324).

2.2. Crystal structure determination of bis[4-dimethylamino-2-pyrimidyl] diselenide (1)

To have a better understanding of the structural details, single crystal X-ray diffraction of (**1**) was carried out. A perspective view and atom numbering scheme of (**1**) is given (Fig. 1). Crystal data for (**1**): $C_{12}H_{16}N_6Se_2$, M=402.23; monoclinic; a=9.2362(11), b=13.2178(15), c=12.7392(16) Å; V=1555.1(3) Å^3; T=200 K; ρ_{calcd}=1.718 g/cm^3; Z=4; 3601 reflections measured, R_1=0.0665, wR_2=0.1450 for 1379 [$I>2\sigma(I)$] unique reflections, which were used in all calculations. The final R indices were R_1=0.1027, wR (F^2)=0.1696 (all data).

The two pyrimidine rings have an average C–C bond length of 1.319 Å and C–C–C bond angle of 115.7°. The Se–Se bond distance of 2.3162(16) Å relates well with the corresponding distances reported for other diselenides, which ranges from 2.29 to 2.39 Å (Pauling scale).[37] The Se–C bond length [Se1–C1 1.905(7) Å] is also in agreement with the value of 1.93 Å suggested by Pauling a typical value of other diselenides.[37]

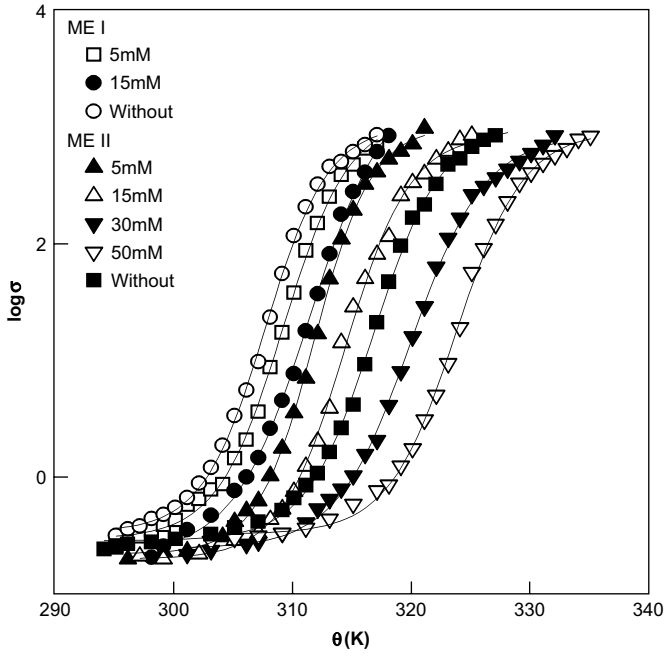


Figure 2. Variation of temperature for $C_{12}H_{16}N_6Se_2$ for ME-I and ME-II at [AOT]/[LC]=0.774:0.01.

2.3. Assimilation of bis[4-dimethylamino-2-pyrimidyl] diselenide in microemulsion media

Bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, has been assimilated in microemulsion (water/AOT/isooctane (ME-I) and water/AOT+LC/isooctane (ME-II)) and characterized with the help of conductivity and spectroscopic techniques. The conductance behavior of ME-I and ME-II has been monitored when temperature is varied under a constant composition. The solubilization increases from 2.5 to 50 mM for bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, in ME-II as compared to 15 mM in ME-I. The temperature–conductance profiles of bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, at different concentrations viz., 5 and 15 mM for ME-I and 5, 15, 30, and 50 mM for ME-II have been depicted (Fig. 2). The percolation parameters for ME-I and ME-II are tabulated in Table 1. The plots have been fitted to Sigmoidal Boltzmann equation.[38]

$$\log\sigma = \log\sigma_f\left[1+\left(\frac{\log\sigma_i-\log\sigma_f}{\log\sigma_f}\right)\{1+\exp(\theta-\theta_c)/\Delta\theta\}^{-1}\right] \quad (1)$$

where i, f, and c are the initial, final, and percolative stages.

At constant composition, bis[4-dimethylamino-2-pyrimidyl] diselenide **1b** has been found to delay the percolation process. The delay becomes more pronounced with the increase in concentration of organodiselenide.

Maitra et al.[39] have reported that in the percolative ME, the droplets retain their closed structure although infinite clusters are formed due to inter droplet interactions. The mutual contact and the bridging between the droplets are due to the presence of additives either at the interface or in the core of the droplets. The pyrimidyl derivatives have two active N-sites that anchor the droplet surface. This results in the straight bridging of the droplets and the conduit formation is favored. The pyrimidyl derivative is a rigid non-planer moiety in which one (pyrimidyl–Se–)– unit is bent leaving the central horizontal plane. It contains electronically active –(–Se–Se–)– moiety along with two N-sites. The molecule adheres to the droplet interface but the configuration results in the eclipsed bridging due to two droplets engulfing the same

Table 1
Percolation threshold temperature for and ME-I and ME-II at different organodiselenide concentrations

[Organodiselenide]	[Concn] (mM)	log σ_i	log σ_f	θ_c (K)	
				Differential	SBE
Without	—	−0.46±0.02	3.02±0.03	308.55	307.73
$C_{12}H_{16}N_6Se_2$ (ME-I)	5	−0.59±0.02	3.30±0.06	309.55	309.68
	15	−0.66±0.02	3.39±0.09	313.64	313.64
$C_{12}H_{16}N_6Se_2$ (ME-II)	2.5	−0.61±0.01	2.88±0.03	318.13	317.88
	5	−0.60±0.02	2.82±0.03	318.63	318.56
	15	−0.60±0.02	2.93±0.02	319.15	319.99
	50	−0.57±0.01	3.43±0.05	327.15	326.17

log σ_i=initial conductance, log σ_f = final conductance.

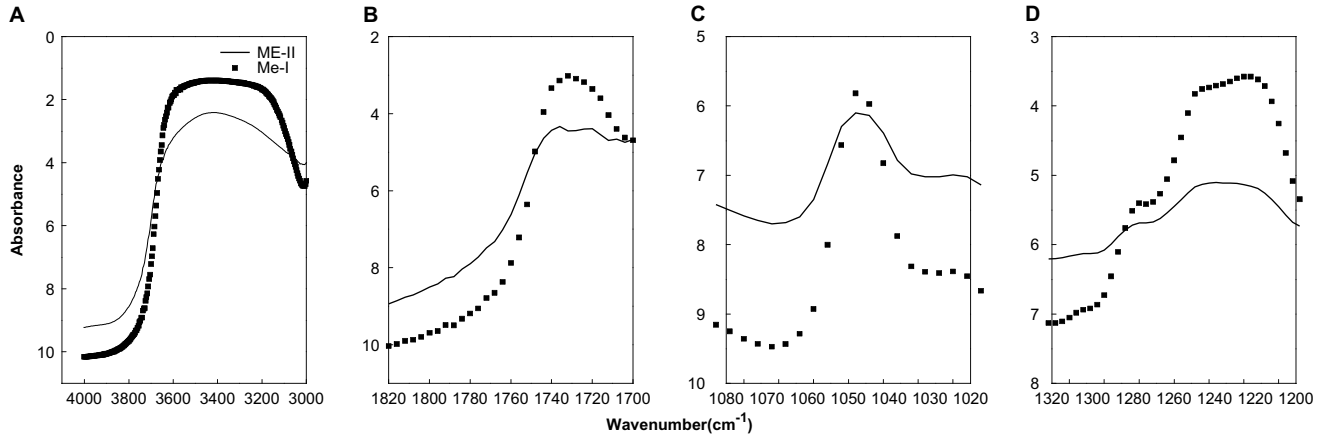


Figure 3. Comparison of infrared stretching band of ME-I and ME-II at ω=30 in the presence of organodiselenide=10 mM showing different stretching regions. (A) OH, (B) CO, (C) SO_3^-, (D) COC ester linkage.

organodiselenide moiety. However, the introduction of LC in ME-II leads to the immobilization of hydrophobic and hydrophilic regions, which allows the formation of extended structures that are organized over multiple length scale[40] and this restricts bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, only at the interface.

2.3.1. Spectroscopic characterization

^{1}H NMR spectra of ME-I and ME-II with and without the diselenide reveal a unique peak due to aromatic region in bis[4-dimethylamino-2-pyrimidyl] diselenide molecules. An inspection of data reveals that the peaks due to aromatic protons are retained in ME-I and ME-II indicating that the organodiselenide moiety is intact in ME system and is not subjected to any breakdown. Peaks due to aromatic protons and head group protons are downfield in ME-I as compared to ME-II. These findings are consistent with the fact that addition of LC in ME-I involves progressive change in the electron cloud of the protons of the head group. The organodiselenide interaction is mainly localized in the proximity of the polar head groups of the surfactant. This is revealed by the shifts of the head group protons in ME-I and ME-II.

A comparison of OH band frequencies of ME-I and ME-II assimilating bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, indicates a shift toward higher frequency of around 11.3 cm^{-1} as compared to pure ME-II than ME-I. The peak centered at 1706 cm^{-1}, assigned to CO stretching shows similar trend of shift toward the higher frequency with the incorporation of organodiselenide. The high frequency values observed in ME-II as compared to ME-I further reveal the entrapping of organodiselenide in the micellar interface and the formation of rigid interface.[41] However, a shift of around 1 cm^{-1} is observed for C–O–C and SO_3^- of AOT. A representative spectrum for different absorption regions has been presented (Fig. 3).

UV–vis spectra of the prepared MEs are depicted (Fig. 4) with peak values at 326.61 nm in ME-I and 321.30 nm in ME-II. The observed values are due to Se-$C_4H_2N_2$ chromophore, which involves 4p electrons of Se in conjugation with 6π electrons of the pyrimidyl ring. This is supported by the interpretation of UV–vis spectra of related compounds cited in the literature.[42] The slight red shift observed in ME-I as compared to ME-II suggests that the organodiselenide is more tightly held at the micellar interface in ME-II and, therefore, indicate that ME-II serves as a better host for the assimilation of organodiselenide.

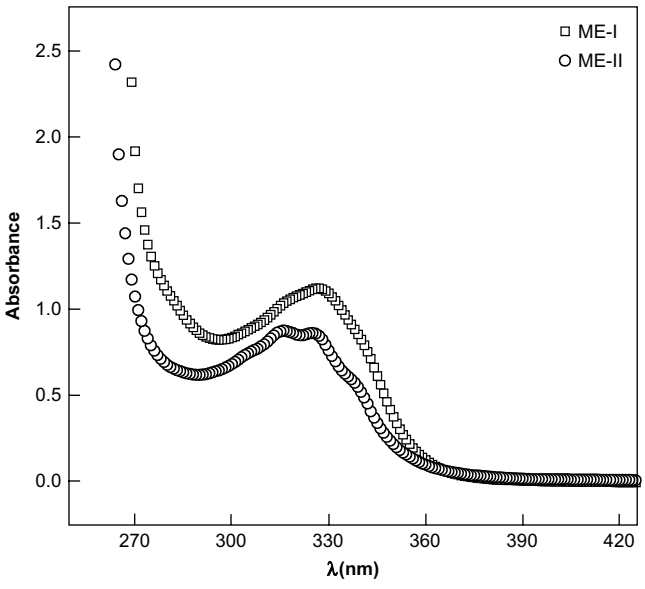


Figure 4. Variation of absorbance versus wavelength for $C_{12}H_{16}N_6Se_2$.

3. Conclusion

The present report constitutes the first successful attempt to synthesize novel bis[4-dimethylamino-2-pyrimidyl] dichalcogenides (S, Se, Te) by simple synthetic methodology. The synthesis involve nucleophilic substitution by dimethylamino group from the solvent dimethylformamide, which otherwise act as a formylating agent. These compounds are anticipated to have potential applications in medicinal field. In addition, the interactions of bis[4-dimethylamino-2-pyrimidyl] diselenide with core water, AOT, and Lecithin head groups in microemulsion media reveal significant enhancement of its solubilization capacity.

4. Experimental section

4.1. Materials and instrumentation

All experiments were carried out in dry oxygen-free nitrogen atmosphere. Hydrazine hydrate (Qualigens India, purity >99%), selenium (Hi-media, purity >99%), elemental sulfur (Hi-media, purity >99%), tellurium (Hi-media, purity >96%), uracil (Hi-media, purity >95%), sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) (Fluka, purity >99%), phosphatidylcholine (Lecithin) (LC) (Fluka, purity ~98%), isooctane (E-Merck, purity >99%) were newly purchased and stored in dessicator prior to use.

IR spectra were recorded between KBr plates on a Perkin–Elmer Model 1430 ratio recording spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard for ^{1}H NMR and ^{13}C NMR spectra whereas ^{77}Se NMR with dimethylselenide as an external reference in $CCl_4/CDCl_3$ on a Jeol 300 MHz. The mass spectra were obtained on Q-TOF micro mass spectrometer. Carbon, hydrogen, and nitrogen were estimated microanalytically on a Perkin–Elmer 2400 CHN Elemental Analyzer.

4.2. Synthesis of 2,4-dichloropyrimidine

In a 500 ml, two-necked, round-bottom flask equipped with a condenser, uracil (100 g, 0.82 mol) was dissolved in phosphorous oxychloride (400 ml). The solution was refluxed with stirring for 3.5 h at 110 °C. The residual phosphorous oxychloride was removed in vacuo at 50 °C and the remaining oil was poured into 50 g of ice followed by extraction with chloroform (3×50 ml). The combined organic extract was washed with dilute sodium carbonate solution and dried over anhydrous sodium sulfate. 2,4-Dichloropyrimidine was obtained by evaporation of solvent.

4.2.1. 2,4-Dichloropyrimidine[43]

Yield=72.3%, white crystalline solid, mp=60–61 °C. [Found: C, 31.82; H, 1.02; N, 18.80. $C_4H_2N_2Cl_2$ requires: C, 32.21; H, 1.34; N, 18.79]. R_f (10% Et_2O/hexane) 0.57; IR (KBr, cm^{-1}): 1532.3, 1410.4, 1380.4, 1202.2, 1180.2, 810.6, 690.9; ^{1}H NMR (300 MHz, $CCl_4/CDCl_3$) δ 8.45–8.42 (1H, d, *J* 6.6 Hz, H-6), 7.38–7.35 (1H, d, *J* 6.6 Hz, H-5); ^{13}C NMR (75 MHz, $CCl_4/CDCl_3$) δ 162.6, 161.4, 159.8, 120.0.

4.3. Synthesis of bis[4-dimethylamino-2-pyrimidyl] dichalcogenide

To a vigorously stirred mixture of powdered sodium hydroxide (3.0 g, 75 mmol), elemental chalcogen (S=1.6 g, Se=4.0 g, Te=6.4 g, 50 mmol), and dimethylformamide (30 ml), 100% hydrazine hydrate was added slowly. After stirring for nearly 6 h at room temperature, a solution of 2,4-dichloropyrimidine (100 mmol) dissolved in 15 ml DMF was added dropwise. The reaction was monitored by TLC. After completion of reaction, it was diluted with about 250 ml of distilled water and extracted in dichloromethane (3×50 ml). The organic layer was decanted and solvent evaporated to get the crude product in solid form. The product was subjected to purification on a silica column using hexane as eluant (5:1).

4.3.1. Bis[4-dimethylamino-2-pyrimidyl] disulfide

Yield=65%, yellow crystalline solid, mp=152–154 °C. [Found: C, 68.83; H, 3.52; N, 40.73. $C_{12}H_{16}N_6S_2$ requires: C, 69.23; H, 3.84; N, 40.38%]. R_f (10% Et_2O/hexane) 0.48; IR (KBr, cm^{-1}): 2925.4, 1568.3, 1405.4, 1340.6, 1208.3, 790.4, 550.7; ^{1}H NMR (300 MHz, $CCl_4/CDCl_3$) δ 7.76–7.74 (1H, d, *J* 6.3 Hz, H-6), 5.70–5.68 (1H, d, *J* 6.3 Hz, H-5), 3.50 (6H, s, NMe_2); ^{13}C NMR (75 MHz, $CCl_4/CDCl_3$) δ 158.2, 154.0, 150.4, 101.8, 36.6.

4.3.2. Bis[4-dimethylamino-2-pyrimidyl] diselenide

Yield=70%, yellow crystalline solid, mp=79–81 °C. [Found: C, 33.96; H, 3.60; N, 20.43. $C_{12}H_{16}N_6Se_2$ requires: C, 33.60; H, 3.96; N, 20.79%]. R_f (10% Et_2O/hexane) 0.35; IR (KBr, cm^{-1}): 2924.4, 2853.3, 1566.0, 1521.4, 1458.0, 1405.3, 1340.4, 786.8, 534.3; ^{1}H NMR (300 MHz, $CCl_4/CDCl_3$) δ 8.13–8.11 (1H, d, *J* 6.3 Hz, H-6), 7.44–7.41 (1H, d, *J* 6.3 Hz, H-5), 3.14 (6H, s, NMe_2); ^{13}C NMR (75 MHz, $CCl_4/CDCl_3$) δ 161.2, 157.1, 154.7, 107.3, 37.0; ^{77}Se NMR (57 MHz, $CCl_4/CDCl_3$) δ 431; MS-EI, *m*/*e* (assignment, R.I. %): 404 ($[C_{12}H_{16}N_6Se_2]^{+\bullet}$, 25), 201 ($[C_6H_{18}N_3Se]^{+\bullet}$, 68), 122 ($[C_6H_8N_3]^{+\bullet}$, 100), 79 ($[C_6H_2N_2]^{+\bullet}$, 18).

4.3.3. Bis[4-dimethylamino-2-pyrimidyl] ditelluride

Yield=50%, red crystalline solid, mp=112–114 °C. [Found: C, 28.93; H, 3.32; N, 16.52. $C_{12}H_{16}N_6Te_2$ requires: C, 28.80; H, 3.20; N, 16.80%]. R_f (10% Et_2O/hexane) 0.26; IR (KBr, cm^{-1}): 3370.1, 2925.0, 1538.0, 1458.0, 1409.0, 1168.6, 793.6, 688.2, 460.4; ^{1}H NMR (300 MHz, $CCl_4/CDCl_3$) δ 7.81–7.79 (1H, d, *J* 5.1 Hz, H-6), 7.08–7.07 (1H, d, *J* 5.1 Hz, H-5), 3.15 (6H, s, NMe_2); ^{13}C NMR (75 MHz, $CCl_4/CDCl_3$) δ 163.4, 159.2, 156.57, 115.34, 37.02; MS-EI, *m*/*e* (assignment, R.I. %): 500 ($[C_{12}H_{16}N_6Te_2]^{+\bullet}$, 5), 372 ($[C_{12}H_{16}N_6Te]^{+\bullet}$, 85), 328 ($[C_{10}H_{10}N_5Te]^{+\bullet}$, 8), 324 ($[C_{10}H_6N_5Te]^{+\bullet}$, 7), 156 ($[C_8H_4N_4]^{+\bullet}-1$, 24).

4.4. Preparation of microemulsion

A series of experiments were assembled and [AOT]=0.784 M and [AOT]/[LC]=0.774 M:0.01 M at ω=([H_2O]/[surfactant])=30.0 were found to be most acceptable concentrations to enhance assimilation of bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$. All the samples were transparent and optically clear. The assimilation of bis[4-dimethylamino-2-pyrimidyl] diselenide, $C_{12}H_{16}N_6Se_2$, in ME-II enhanced the solubilization from 2.5 to 50 mM in ME-II as compared to 15 mM in ME-I.

4.5. Physical measurements

IR spectra were recorded between AgCl plates on a Perkin–Elmer Model 1430 ratio recording spectrometer. ^{1}H NMR spectra were recorded in D_2O using tetramethylsilane as an internal standard using Bruker 400 MHz spectrometer. UV–vis absorption spectra were obtained in the spectral range of 250–500 cm^{-1} using HITACHI 330 model spectrophotometer with precision of ±0.2 nm using quartz cells with a path length of 1 cm^{-1}. The electrical conductivity measurements of the samples were carried out with Pico digital conductivity meter operating at 50 Hz using Labindia instruments with an absolute accuracy of ±3% and precision of ±0.1%. The cell constant used was 1.0 cm^{-1}. The temperature was kept constant with the help of RE320 Ecoline thermostat with an accuracy of ±0.01 K. Triple distilled water with conductance less than 3 $\mu S\,cm^{-1}$ was used for the preparation of microemulsions.

4.5.1. Bis[4-dimethylamino-2-pyrimidyl] diselenide

Clear yellow solution in ME-I and ME-II. ^{1}H NMR (400 MHz, $CCl_4/CDCl_3$) δ 8.21–8.20 (1H, d, *J* 6.4 Hz, H-6), 7.10–7.09 (1H, d, *J* 6.4 Hz, H-5), 4.43, 3.40, 1.92, 1.56, 1.39, 1.15 (ME-I), 8.07–8.06 (1H, d, *J* 5.2 Hz, H-6), 6.91–6.90 (1H, d, *J* 5.2 Hz, H-5), 5.43, 4.15, 3.22, 1.74, 1.42, 1.13, 0.98 (ME-II); UV–vis absorption spectroscopy: λ_{max}/nm 326.61 (ME-I), 321.30 (ME-II); IR (AgCl, cm^{-1}) 3325.0, 1702.8, 1045.5, 1230.9 (ME-I), 3336.3, 1707.3, 1045.8, 1225.3 (ME-II), 3323.0, 1706.4, 1045.2, 1225.5 (pure ME-I), 3343.1, 1704.5, 1046.1, 1225.1 (pure ME-II) for OH, CO, SO_3^-, C–O–C.

4.6. X-ray crystallographic studies

Diffraction quality yellow colored single crystals of (**1**) were obtained by the slow evaporation of dichloromethane/hexane solution of the compound. Suitable crystals were chosen from a crop of crystals, mounted on glass fibers and data collected on VG 7070H diffractometer for the cell determination and intensity data collection. The diffraction data were collected using monochromatic Mo Kα radiation at 200 K. Crystal structure was solved by direct methods (SHELX-97)[44] and refined by full matrix least squares method.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC 697324. Copy of data can be obtained, free of charge, on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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