

STUDIES ON CROWN ETHER CYANINE DYES

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Abstract—This review describes the syntheses and properties of crown ether cyanine dyes, in which several heterocycles (benzothiazole, benzoselenazole, benzimidazole, benzoxazole and benzotellurazole) containing different kinds of heteroatoms are annulated with benzocrown ether units.

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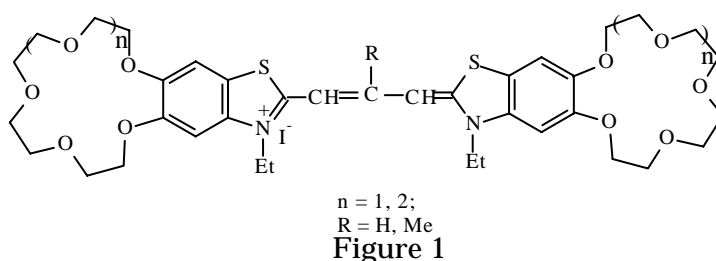
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I. Introduction

Since spectral sensitization was discovered over a century ago, thousands of sensitizing dyes have been formulated.¹ Only a few of these have found widespread use, most notably the polymethine dyes.¹ Moreover, although over 200 different heterocyclic nuclei have been incorporated into cyanine dyes, remarkably few occur in the dyes used in practice.¹ Now, the scope for the use of novel heterocycles in cyanine dyes is rather limited.¹ In recent years, there has been some interest in modifying conventional cyanines or merocyanines by linking them to some other organic species.¹

Crown ether cyanine dyes were firstly synthesized by F. Vögtle and his coworker in 1980, known as chromic crown ethers and used in analytical chemistry.² Meanwhile, our group synthesized the following crown ether benzothiazocarbocyanine dyes used as spectral sensitizers in photographic chemistry.³⁻⁵ Investigation had shown that these crown ether cyanine dyes have many important photographic properties.⁶



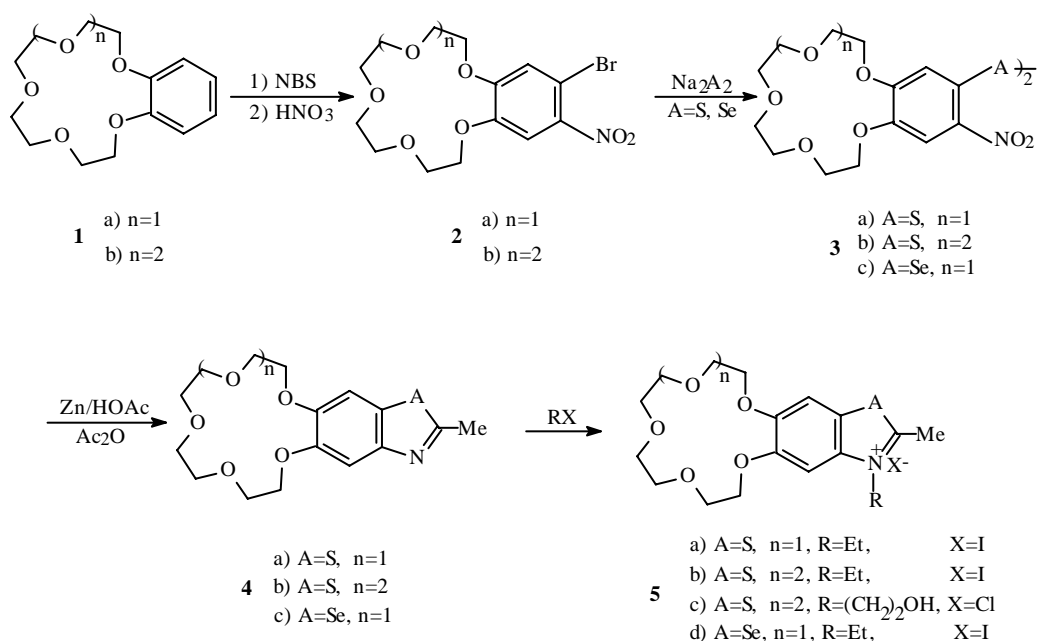
From then on, this new type of crown ether cyanine dyes was studied systematically in our laboratory. Benzimidazole,^{7,8} benzoselenazole,⁹ benzoxazole,^{10,11} and benzotellurazole¹²⁻¹⁴ cyanine dyes with an annular crown ether have been successively synthesized and studied in our laboratory. It was found that introducing the crown ether unit into cyanine dyes would enhance the stability and photosensitivity.¹⁵ This crown ether cyanine dyes were regarded as an important breakthrough in the field of sensitizing dyes by G. Fichen.¹

II. Syntheses of key heterocyclic intermediates

The most important point in obtaining crown ether cyanine dyes is how to design and synthesize heterocycles containing crown ether unit.

1. Crown ether benzothiazole and benzoselenazole

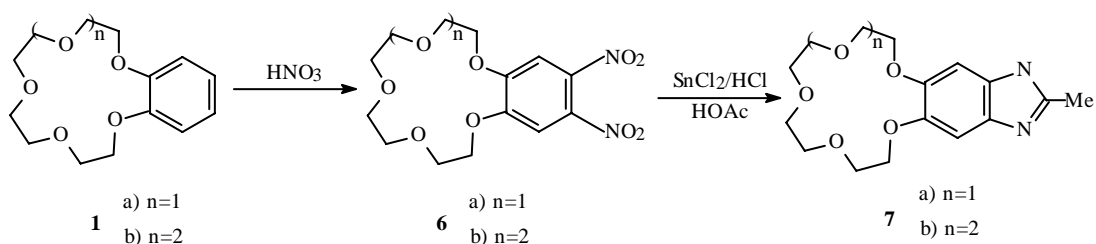
Starting from benzo-crown ether (**1**), compound (**2**) was obtained *via* bromination and nitration, then reacted with sodium disulfide (diselenide), giving intermediate (**3**). With one-pot methods, compound (**3**) was reductively cyclized by reducing agent zinc in the media of acetic acid and acetic anhydride, resulting in compound (**4**). *N*-Alkylation of **4** gave quaternary ammonium salt (**5**) (Scheme 1).^{3, 9}



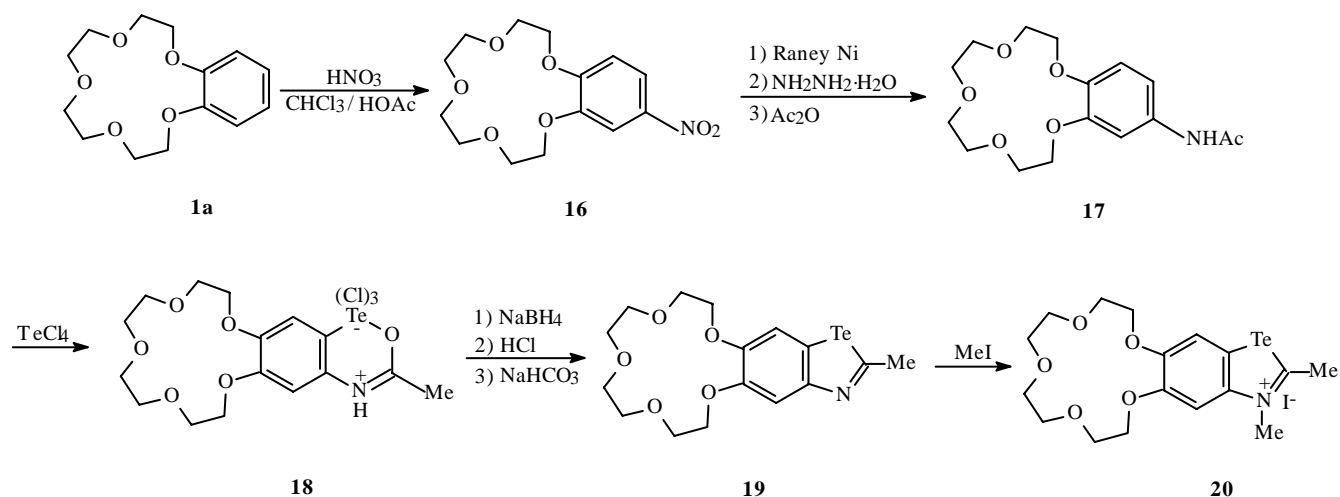
Scheme 1

2. Crown ether benzimidazole

This kind of heterocycles include two nitrogen atoms, so two nitro groups were introduced to benzene ring, which were reduced by $SnCl_2/HCl$ in acetic acid, obtaining heterocycle (**7**). *N*-Alkylation of **7** gave compounds (**8**) and (**9**).^{7, 8} (see Scheme 2)



dyes, were prepared and used rapidly in modern photographic technology.¹⁷⁻¹⁹ Benzotellurazole heterocycle containing crown ether ring (**19**) was synthesized in 1992 in our laboratory.¹² (see Scheme 4) Electrophilic substitution reaction between acetanilide derived from benzo-15-crown-5 with TeCl_4 gave inner salt (**18**), which was then reduced by NaBH_4 in a basic condition and cyclized with HCl . *N*-Alkylation of the crown ether benzotellurazole (**19**) gave quaternary ammonium salt (**20**).¹³

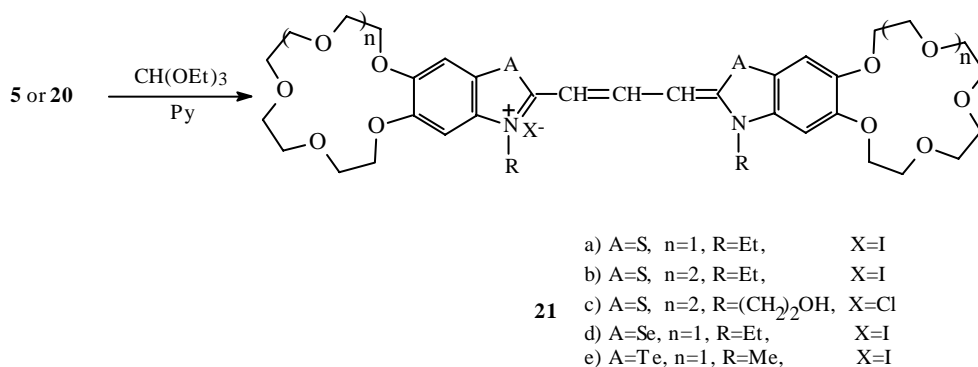


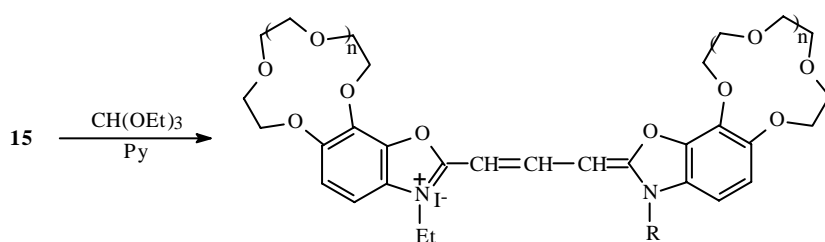
Scheme 4

III. Preparation of crown ether cyanine dyes

1. Symmetric bis-crown ether cyanine dyes

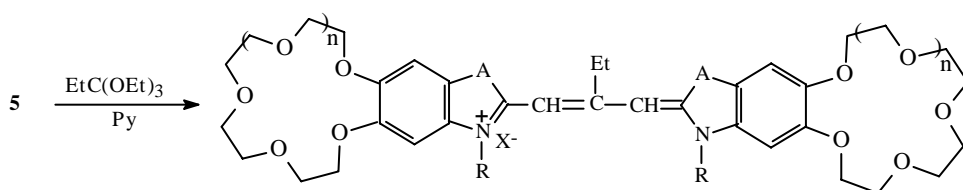
Dyes of this type can be synthesized by condensation of different crown ether heterocycle ammonium salts with ethyl orthoformate in pyridine or acetic anhydride (see Scheme 5).^{4,9,11-12} However, the symmetric dye of crown ether benzimidazole was not obtained in the similar condition, which can be explained by the strong basic capacity of this heterocycle.⁷





Scheme 5 22 a) $n=0$
b) $n=1$

Introducing an alkyl group in the middle of polymethine chain will be beneficial for increasing the sensitization of dyes. Using ethyl orthopropanoate as condensation agent, we obtained cyanine dyes with ethyl group in polymethine chain, as shown in Scheme 6.²⁰

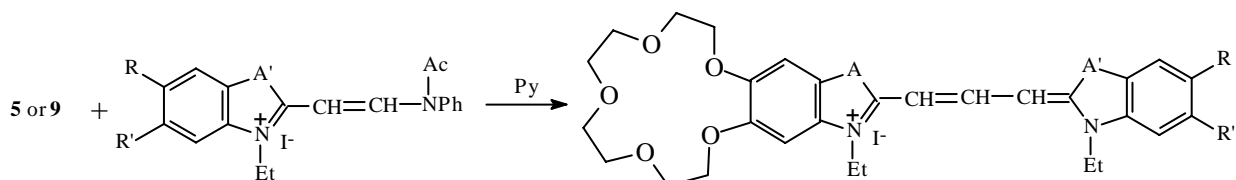


23 a) $A=S, n=1, R=Et, X=I$
b) $A=S, n=2, R=Et, X=I$
c) $A=S, n=2, R=(CH_2)_2OH, X=Cl$
d) $A=Se, n=1, R=Et, X=I$

Scheme 6

2. Unsymmetric crown ether cyanine dyes

Condensation of crown ether heterocycle ammonium salts with non-crown ether hemicyanines (**24**) in pyridine gave unsymmetric dye (**25**), as shown in Scheme 7.^{8, 9, 13, 20}

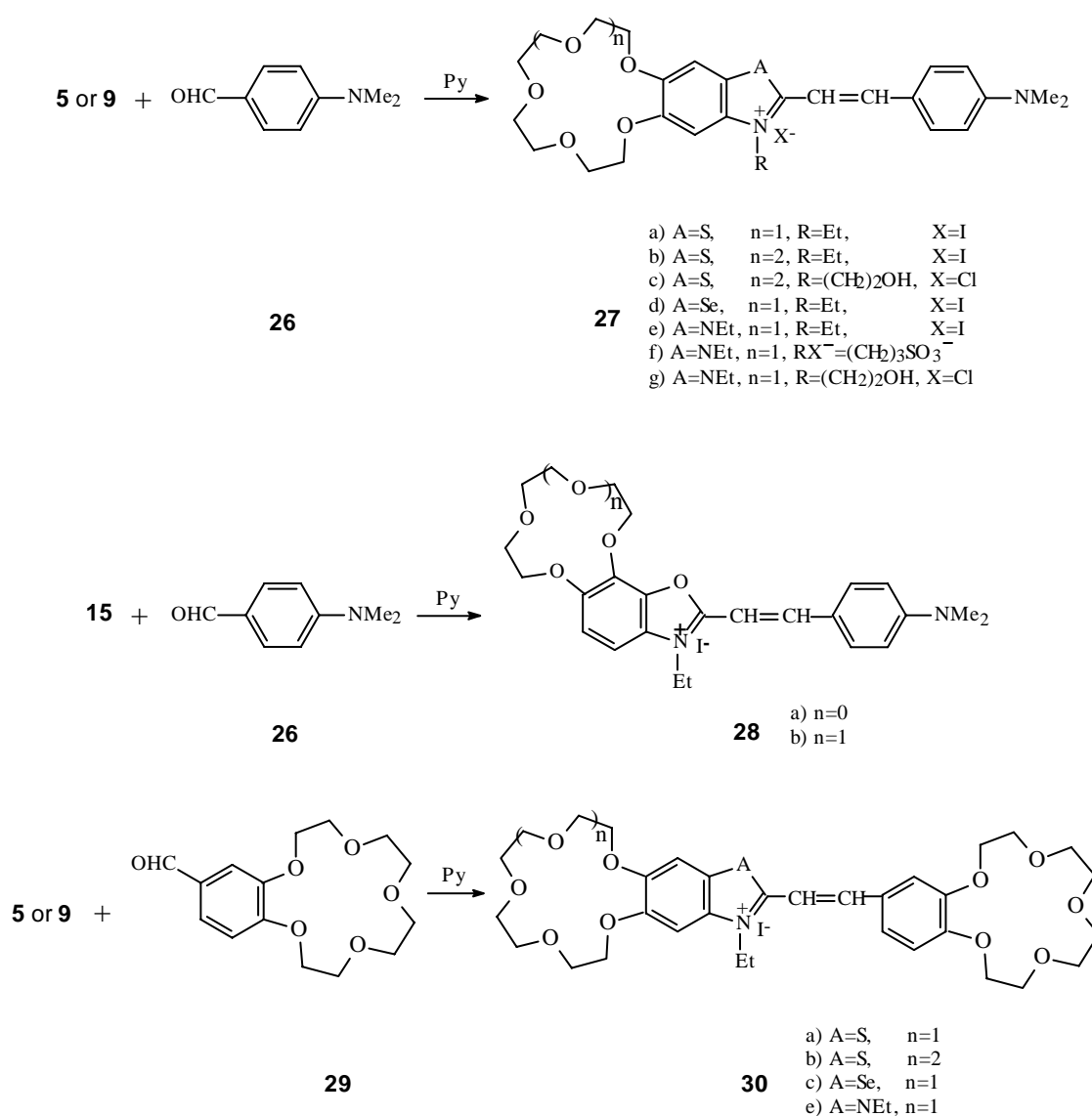


25 a) $A=S, A'=S, R=H, R'=H$
b) $A=Se, A'=Se, R=H, R'=H$
c) $A=NEt, A'=O, R=H, R'=OH$
d) $A=NEt, A'=NEt, R=Cl, R'=Cl$
e) $A=Te, A'=S, R=H, R'=H$

Scheme 7

3. Crown ether polymethine styrylcyanine dyes

Starting from the quaternary ammonium salts and *p*-(dimethylamino) benzaldehyde (**26**) or 4-formylbenzo-crown ether (**29**) in pyridine, we got a series of dimethine styryl cyanine dyes as shown in Scheme 8.^{8, 11} Nevertheless, *n*-butanol was used as reactive medium when we synthesized crown ether benzotellurazole styryl cyanine dye.¹⁴ In this case of the syntheses of styryl cyanine dye (**30**), aldehyde can act as both reactant and catalyst.

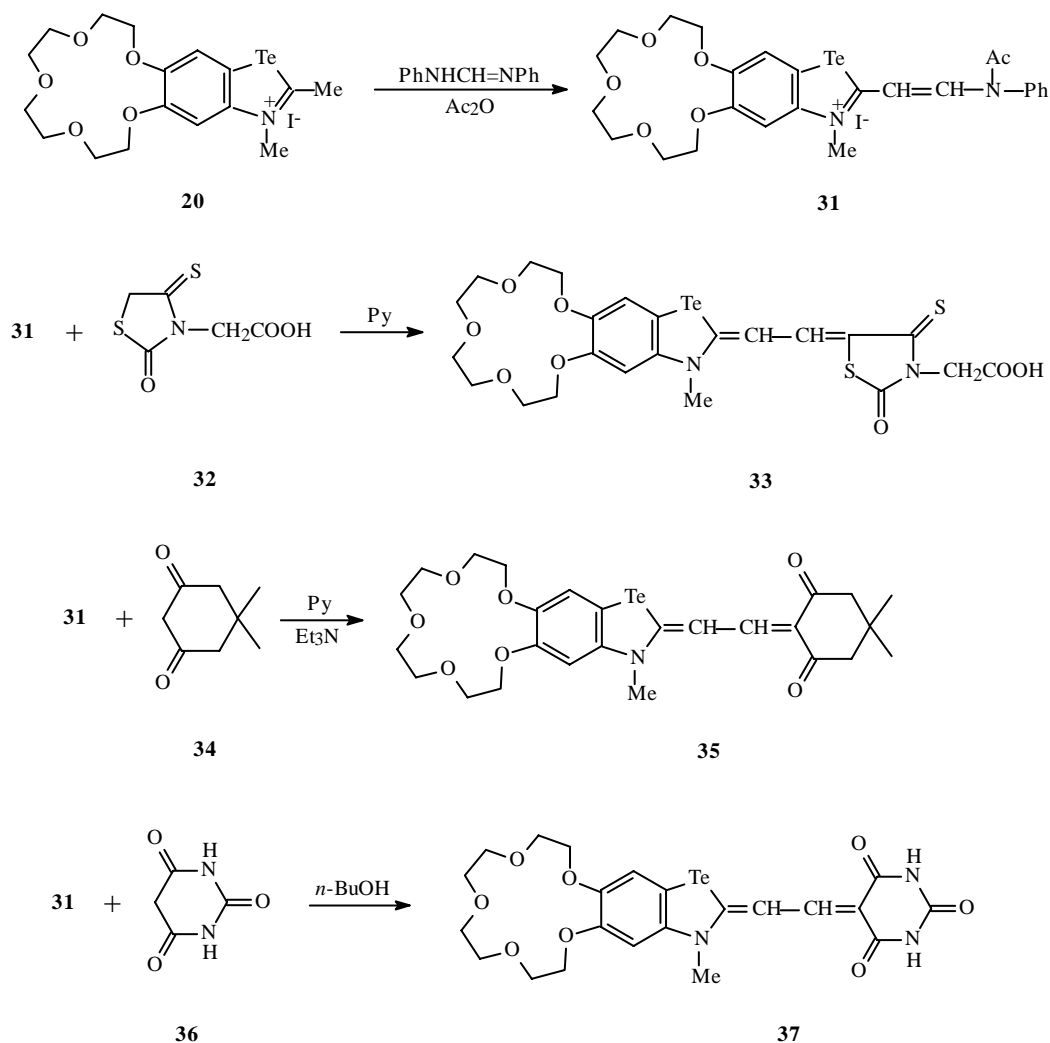


Scheme 8

4. Crown ether merocyanine dyes

Active intermediate (**31**), obtained by condensation of heterocycle ammonium salts with

diphenylformamidine, can react with *N*-carboxymethylrhodanine (**32**), 5,5-dimethyl-1,3-cyclohexanedione (**34**) and barbituric acid (**36**) to give different crown ether merocyanines in basic condition, as shown in Scheme 9.¹⁴ Dyes of this type can be used as photoelectric materials.

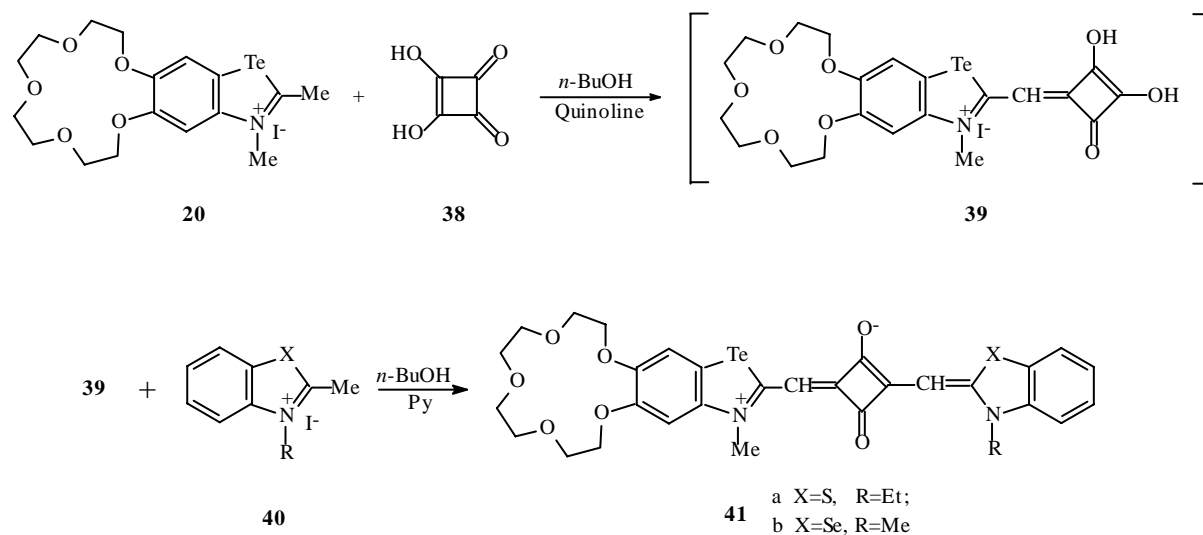


Scheme 9

5. Crown ether squaric cyanine dyes

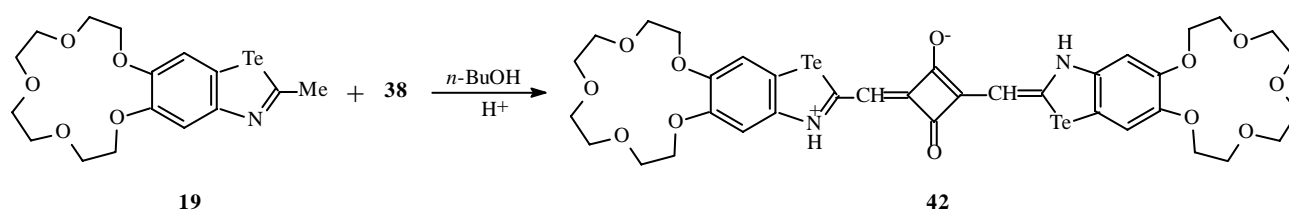
Bases, as nucleophilic component, obtained by elimination of HI from 2-methyl-substituted quinolinium, benzothiazolium and benzoselenazolium iodide, condense with squaric acid, giving intensely colored, betaine-like symmetric dyes that contain the structural element of cyclobutenolate. This kind of dyes were first synthesized in 1967.²¹ When crown ether benzotellurazolium iodide reacted with squaric acid, it was surprisingly found that only 1:1 condensation compound (**39**) was obtained instead of symmetric dyes.

The intermediate (**39**) can continuously react with different quaternary ammonium salts of other heterocycles (**40**) in the presence of organic base of pyridine, giving unsymmetric squaric cyanine dyes (**41**).²² (see Scheme 10)



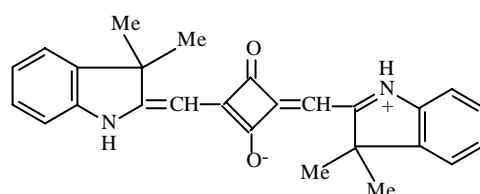
Scheme 10

On the other hand, it should be noted that, without forming quaternary ammonium salts, crown ether benzotellurazole (**19**) could directly react with squaric acid in *n*-butanol by catalysis of acid to give 2:1 condensation product – symmetric squarylium cyanine dye (**42**).²³ (shown in Scheme 11)



Scheme 11

Some Chinese chemists also synthesized the following squaric cyanine dyes, which were derived from 3,3-dimethyl-2-methyldeneindole²³ and crown ether benzothiazole.²⁴ (See Figure 2)



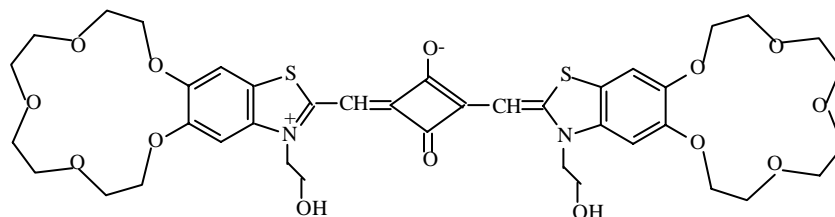


Figure 2

IV. The properties of crown ether cyanine dyes

1. Complexation of crown ether unit with metal ions and its effect on absorption spectra of the dyes

As expected, crown ether dyes form complexes with Group IA and IIA metal ions; the complexes all show a hypsochromic shift of light absorption, some as large as 60 nm.⁶ In addition, the hypsochromic shift of light absorption for bis-crown ether dyes is usually larger than mono-crown ether dyes.¹⁴

2. Thermal stability and light stability of crown ether cyanine dyes

It was shown that the thermal stability of bis-crown ether benzothiazole cyanine dye was ten times higher than non-crown ether benzothiazole cyanine dye.²⁵ It was also found that the light stability of crown ether benzoselenocarbocyanine dye was higher than non-crown ether dye, especially for bis-crown ether dye.²⁵

3. Spectral sensitization of crown ether dyes

It has been shown that crown ether cyanine dyes as well as their complexes with metal ions have better spectral sensitivity than the related dyes lacking the crown ether ring.^{6,14} Furthermore, the films sensitized by crown ether cyanine dyes or their complexes show better storage stability and fog resistance.⁶

Although the complexes of the dyes with Group IA and IIA metal ions show a hypsochromic shift of light absorption, they have no effect on the sensitization maximum of AgX emulsions,⁶ because the crown ether ring will chelate with Ag²⁺ ultimately.²⁶

4. Crown ether cyanine dyes used for other purposes

Crown ether cyanine dyes were first investigated as ion selective dyes as a type of chromogenic crown ether. The color of these dyes changes when complexed with different alkali and alkaline earth metals, resulting in the difference of their absorption spectra, which suggested a method of ion analysis.²⁷

In recent two decades, crown ether styryl dyes have been the subject of intense investigation. They were

synthesized *via* the condensation of corresponding quaternary ammonium salts of heterocyclic bases with derivatives of benzaldehyde containing crown ether units. The properties of this type of crown ether dyes were very interesting. S. P. Gromov and co-workers had done many works in this field. They first synthesized the following benzothiazolium styryl dye containing 15-crown-5 (see Figure 3).²⁸ X-Ray crystal structure analysis shows that the macrocycle is in the *trans*-gauche conformations.

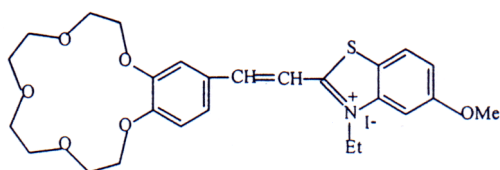


Figure 3

Benzothiazolium crown ether styryl dyes bearing sulfoalkyl *N*-substituents were prepared (Figure 4).²⁹ Photo-isomerization and complexation with alkali and alkaline earth metal cations of crown ether styryl dyes containing 15-crown-5 ether group and *N*-(sulfoalkyl)benzothiazolium group represent interesting properties. The stability of the complexes with alkali and alkaline earth metal cations drastically changed by photoisomerization with enhanced stability of the *cis* ligand complex, which was attributed to the intramolecular complexation of cation with a tethered sulfonate anion. The uncapped *trans* complexes may be partially aggregated, as a result of the association of the sulfonate anion of one dye with the crown-complexed cation of a second molecule.³⁰ The self-aggregation ability of the crown ether styryl dyes is strongly geared to the length of the sulfoalkyl *N*-substituent.³¹

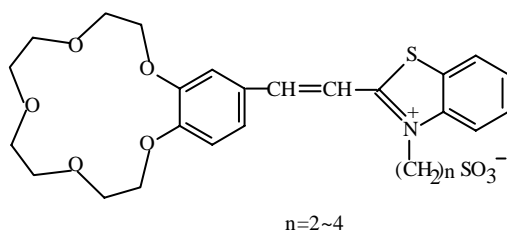


Figure 4

Syntheses and complexation-induced photoisomerization of styryl dyes containing monoaza crown ether were also studied (Figure 5).³² Interestingly, small cations can complex with the oxygen atoms of crown ether ring, but not with the aza crown nitrogen atom.³³ This kind of dyes exhibits special fluorescence

effect and its fluorescence quenching time increased with increasing viscosity. This change is attributed to the barrier of *trans-cis* isomerization occurring in the singlet state.³⁴

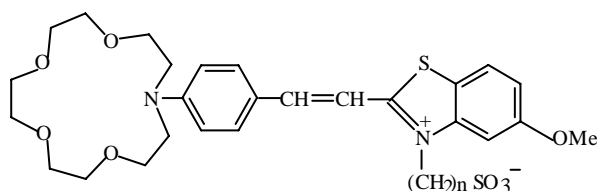


Figure 5

Another interesting type of styryl dye is amphiphilic crown ether dyes, which exhibited reversible photochemistry in the *cis-trans* isomerism and high selectivity for various metal cations in monolayer.³⁵⁻³⁶ In multilayer Langmuir-Blodgett films, the amphiphilic styryl dye incorporated with indole heterocycle (Figure 6) was mainly in the *trans* form and formed a complex with Ca^{2+} . The Ca^{2+} was eliminated on photoexcitation of the dye.³⁷

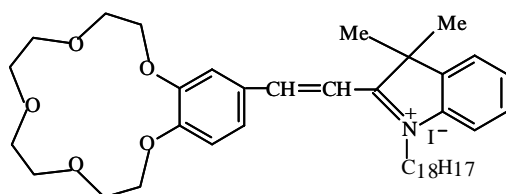


Figure 6

The amphiphilic benzothiazolium styryl dye containing 1,10-dithia-18-crown-6 ether group (Figure 7) was claimed to form aggregates both in floating monolayers on an acidic subphase and in LB films immersed in acidic water. The aggregates exhibit red-shifted absorption peaks and may be broken down by complex formation with Ag^+ cation in water.³⁸

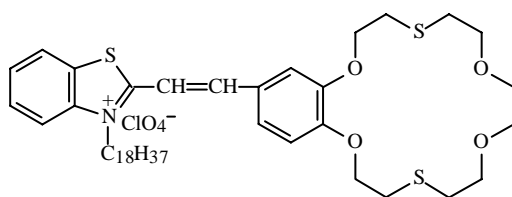


Figure 7

The complexation-induced photochromic properties of crown ether cyanine dyes containing the structure

of spirobenzopyran are topics of some current interest. K. Kimura synthesized the spirobenzopyran derivatives incorporating a monoazacrown moiety at the 8-position in 1992 (Figure 8).³⁹ Binding of alkali metal ions by the crown moieties led to isomerization of the crowned spirobenzopyrans even under dark conditions. The crown-complexed metal ion interacts intramolecularly with the phenolate anion, thus being bound more strongly than that in the corresponding spiropyran isomer, owing to an additional binding-site. UV-light irradiation in tetrahydrofuran promotes the isomerization to the merocyanine form. Under visible light irradiation, the cation-bound merocyanine form readily reverts to the spiropyran form, releasing the metal ions to some extent.

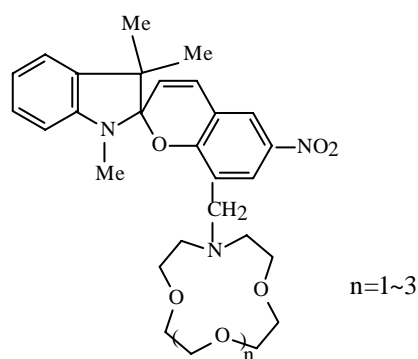


Figure 8

M. Inouye and his coworkers also prepared spiropyrans containing monoaza crown ether moiety on *N*-atom of heterocycle in 1992 (Figure 9).⁴⁰ The selectivity of the coloration was governed by several factors: (1) the size of the crown ether ring; (2) the position of recognition; (3) electric properties of both the complexed cations and the merocyanine dipoles, and (4) the length of the alkyl chains connecting the spirobenzopyran units and the crown units. The spirobenzopyrans represent rationally designed multifunctional artificial receptors for alkali-metal cations.

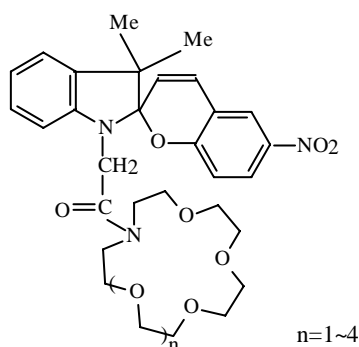
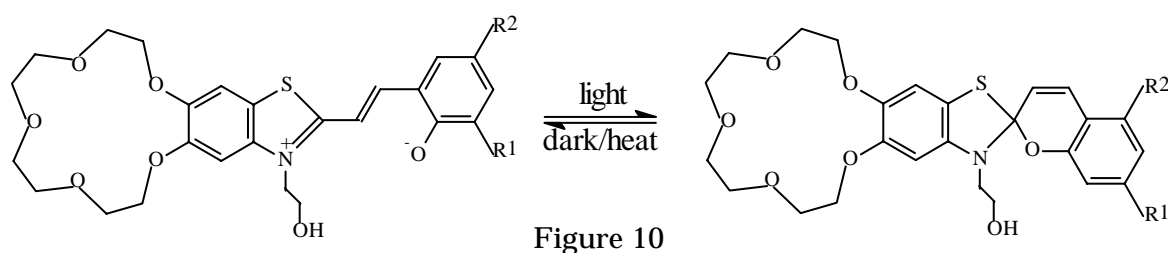


Figure 9

D. X. Wu has prepared a type of photochromic crown ether merocyanine dyes incorporated with the crown ether component on the heterocycle of benzothiazole (Figure 10).⁴¹ It was found that these crown ether merocyanine dyes and the corresponding spiropyran isomer were in reverse photochromic and thermochromic equilibrium where the merocyanine form is more stable than the spiropyran form.



V. Conclusion and prospect

Modification of conventional cyanine dyes by introducing crown ether units into the molecule leads to a kind of novel crown ether cyanine dye, which exhibit important photosensitizing properties in photographic chemistry. Moreover, the property of the crown ether cyanine dyes can also be used as photoelectric material.^{42,43} Besides, the photo-induced isomerization and the complexation-induced photochromic properties of crown ether styryl cyanine and merocyanine dyes have been investigated in recent two decades. Studies in all these fields are interesting and important, which would lead to the improvement of material science.

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