

Weijun Ke, Xuehong Luo, Xiufang Liu, and Hansheng Xu

Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

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A series of crown ether cyanine dyes including crown ether styryl cyanine dyes, crown ether merocyanine dyes and crown ether squarylium cyanine dyes (unsymmetric and symmetric) derived from key intermediate 2-methyl-5,6(15-crown-5)benzotellurazole (**1**) were prepared.

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Since spectral sensitization was discovered over a century ago, thousands of sensitising dyes have been formulated. 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]. In view of the outstanding performance of cyanines incorporating the benzoxazole, benzothiazole, and benzoselenazole nuclei as spectral sensitizers, the synthesis of the first benzotellurazole dyes in 1983 was of major importance [2]. Although the scope for the use of novel heterocycles in cyanine dyes is now rather limited, there has in recent years been some interest in modifying conventional cyanines or merocyanines by linking them to some other organic species [1]. Crown ether cyanine dyes are novel cyanine dyes which are better spectral sensitizers than the related dyes lacking the crown-ether ring, introduction of the crown ether unit enhancing the stability and photosensitivity of the cyanine dyes [3]. In continuation of our studies of the synthesis and properties of crown ether cyanine dyes from benzothiazole, benzimidazole, benzoxazole and benzoselenazole with an annulated crown ether, we now report the syntheses of crown ether styryl cyanine dyes, crown ether merocyanine dyes and crown ether squarylium cyanine dyes derived from 2-methyl-5,6(15-crown-5)benzotellurazole (**1**) [4] which was prepared using an adaptation of the synthetic method of the important heterocycle benzotellurazole due to Gunther and his coworker [2].

To obtain the dyes, the heteroaromatic bases were usually quaternized with suitable agents in order to enhance the reactivity of the methyl group conjugated to the quaternized site. Reaction of the quaternary ammonium salt of

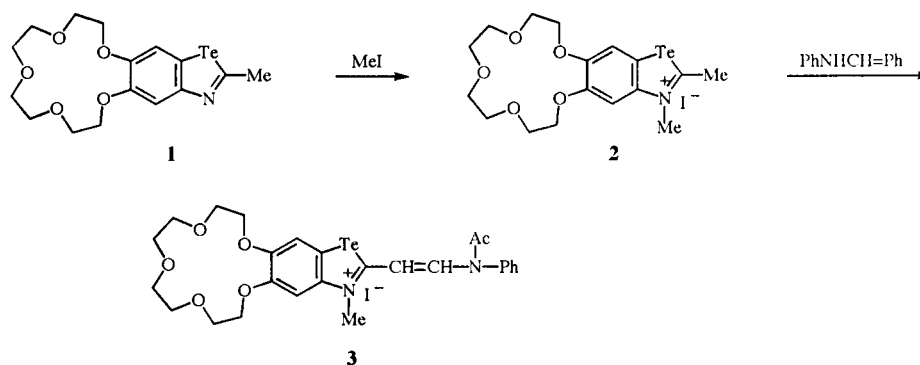
heterocycle benzotellurazolium iodide **2** with diphenyl formamide in acetic anhydride at reflux smoothly gave the active intermediate hemicyanine **3** (Scheme 1).

Merocyanines were usually obtained by condensation of active intermediates derived from heterocyclic bases with ketomethylene nuclei. Rhodanine merocyanine **4** could be obtained from hemicyanine **3** in dry pyridine by the usual method (Scheme 2). Diketone merocyanine **5** could not be produced without using the organic base triethylamine as a catalyst in pyridine medium. It will be noted that barbituric merocyanine **6** could not be obtained in pyridine, either triethylamine or piperidine was used as a catalyst. Finally, condensation between hemicyanine **3** and barbituric acid was carried out in 1-butanol using piperidine as catalyst (not triethylamine) to give **6**. These condensation reactions are closely related to the acid ketomethylene nucleus [5].

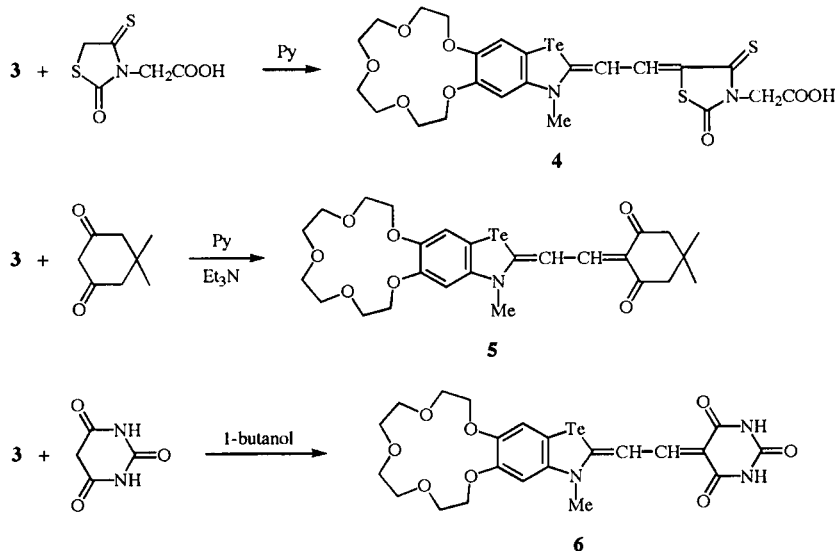
By an analogous route to that of merocyanines, we prepared styryl cyanine dyes **7a** and **7b** by reacting hemicyanine **3** with *p*-dimethylaminobenzaldehyde and *p*-dimethylaminocinnamaldehyde in 1-butanol, respectively (Scheme 3).

Bases, as the nucleophilic component, obtained by elimination of HI from 2-methyl-substituted quinolium, benzothiazolium and benzoselenazolium iodide, condense with squaric acid, giving symmetric squarylium cyanine dyes [6]. Different heterocyclic quaternary ammonium ions condense with squaric acid to give unsymmetric squarylium cyanine dyes [7]. It was surprising that the reaction between benzotellurazolium iodide with squaric acid did not give the expected symmetric cyanine dyes but only 1:1 condensation occurred as shown in Scheme 4. When crown ether benzotellurazolium iodide **2** reacted with squaric acid, 1:1 conden-

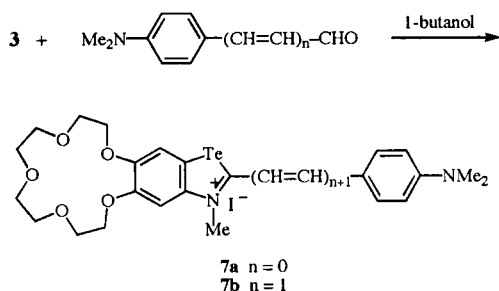
Scheme 1



Scheme 2



Scheme 3



sation compound **8** was obtained. Intermediate **8** further condensed with benzotellurazolium **9a** and benzoselenazolium **9b** iodide to give unsymmetric squarylium cyanine dyes **10a** and **10b**, respectively. This suggests a convenient way of synthesizing unsymmetric crown ether benzotellurazole squarylium cyanine dyes. Unfortunately, symmetric crown ether benzotellurazole squarylium cyanine dyes could not be obtained by the general 2:1 reaction method. Interestingly, we found that without forming the quaternary ammonium, crown ether benzotellurazole **1** could directly react with squaric acid in 1-butanol by acid catalysis, giving symmetric crown ether benzotellurazole squarylium cyanine dye **11**.

EXPERIMENTAL

The IR spectra were measured on a Nicolet-170SK infrared spectrometer. All ^1H nmr spectra were recorded on a Varian XL200 nmr spectrometer. The ms spectra were obtained with a VG7070E-HF ms spectrometer. Elemental analyses were carried out on a Perkin-Elmer 204 Elemental Analyzer. Melting points were determined on the microscope melting point apparatus and

are uncorrected. Visible spectra were measured on a Perkin-Elmer 330 spectrophotometer.

2-Methyl-5,6(15-crown-5)benzotellurazole (**1**), 2,3-dimethyl-5,6(15-crown-5)benzotellurazolium iodide (**2**) [4], diphenylformamidine [8], 3-ethyl-2-methylbenzothiazolium (**9a**) [9] and 2,3-dimethyl-benzoselenazolium iodide (**9b**) [10] were prepared as reported. Reactive hemicyanine **3** was prepared as shown in Scheme 1.

3-Carboxymethyl-5-[2-(3-methyl-5,6(15-crown-5)benzotellurazolylidene)ethylidene]rhodanine (**4**).

A mixture of compound **3** (0.36 g, 0.50 mmole) and 0.11 g (0.58 mmole) 3-carboxymethyl rhodanine in 3 ml of dry pyridine was stirred with refluxing for 20 minutes. After cooling, the solid formed was filtered and washed with ether. Recrystallization of the crude solid from ethanol gave a brownish-red powder; yield 0.12 g (37.0%); mp > 300 °C (dec.); ir: 3450, 3100, 1685, 1590, 1570, 1515, 1420, 1380, 1280, 1150, 860 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 3.5 (s, 2H, NCH₂), 3.7-4.2 (m, 19H, NCH₃, crown ether H), 5.8-6.2 (d, J = 12Hz, 2H, =CH-CH=), 7.8-8.0 (m, 2H, ArH), 8.70 (s, 1H, COOH); $\lambda_{\text{max}}^{\text{DMF}}$ (lg ϵ): 558 (4.80) nm.

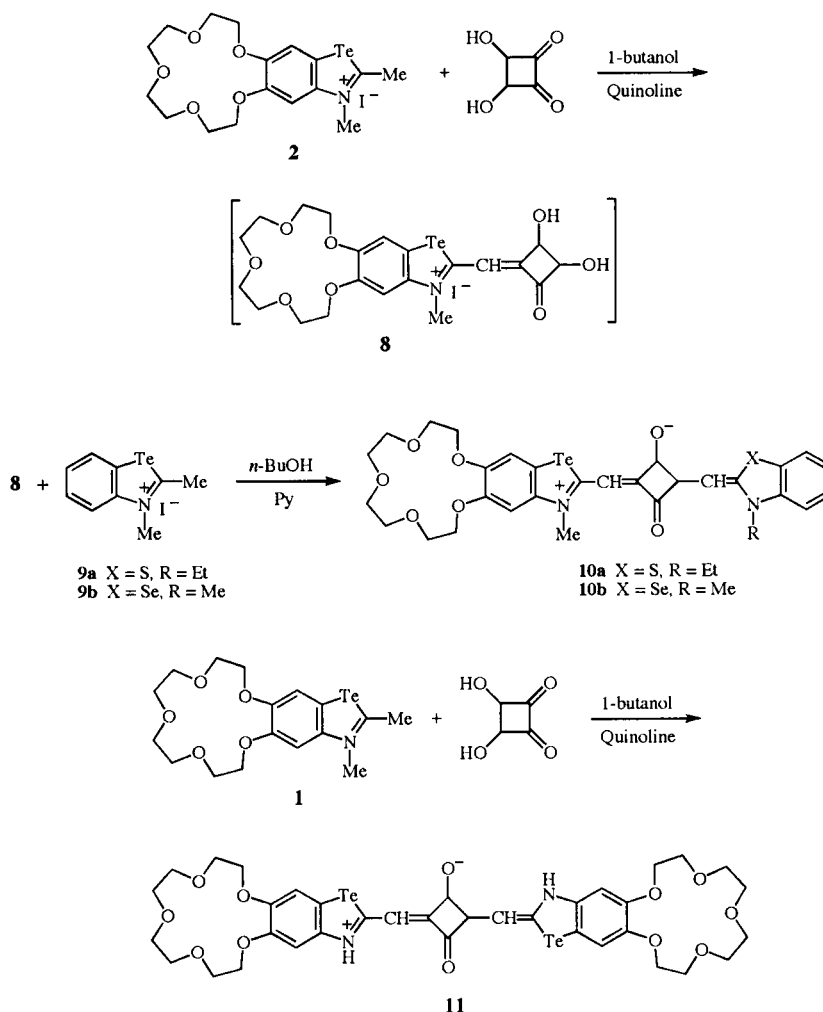
Anal. Calcd. for C₂₃H₂₆N₂O₈S₂Te: C, 42.49; H, 4.00; N, 4.31. Found: C, 42.35; H, 4.12; N, 3.36.

2-[2-(3-Methyl-5,6(15-crown-5)benzotellurazolylidene)ethylidene]-5,5-dimethyl-1,3-cyclohexanedione (**5**).

To a mixture of compound **3** (0.36 g, 0.5 mmole) and 5,5-dimethyl-1,3-cyclohexanedione (0.07 g, 0.5 mmole) in 3 ml of pyridine, several drops of triethylamine were added. The mixture was stirred and refluxed for 20 minutes. The solution turned red immediately. After cooling, beautiful scarlet flakes with a metallic luster precipitated; then were filtered and washed with ether and acetone to give 0.21 g (75%) of product; mp 274-276 °C (dec.); ir: 2890, 1640, 1570, 1520, 1260, 1220, 1140, 1060, 860 cm^{-1} . ^1H nmr (CDCl₃): δ 1.04(s, 6H, CMe₂), 2.36(s, 4H, 2 * -CH₂-), 3.6-4.3(m; 19H, NCH₃, crown ether H), 6.4-6.8 (d, J = 12Hz, 2H, =CH-CH=), 7.6-8.1 (m, 2H, ArH); (FAB) m/z (%): 601 (M⁺); $\lambda_{\text{max}}^{\text{DMF}}$ (lg ϵ): 524 (4.48) nm.

Anal. Calcd. for C₂₆H₃₃NO₇Te: C, 52.13; H, 5.51; N, 2.34. Found: C, 52.28; H, 5.36; N, 2.55.

Scheme 4



2-[2-(3-Methyl-5,6(15-crown-5)benzotellurazolylidene)ethylidene]barbital (**6**).

To a mixture of compound **3** (0.36 g, 0.5 mmole) and barbitalic acid (0.05 g, 0.5 mmole) in 4 ml of 1-butanol, 2-3 drops of piperidine were added. The mixture was stirred and refluxed for 20 minutes. The solution turned red immediately. After cooling, the solid was washed with dry ethanol and recrystallized from ethanol to give 0.19 g (65%) of a fresh red powder, mp 256-258 °C (dec.); ir: 3200, 1720, 1630, 1540, 1260, 1140, 1060, 860 cm^{-1} ; ^1H nmr (CDCl_3): δ 3.7-4.4(m, 19H, crown ether H, NCH_3), 6.2-6.9(m, 4H, =CH-CH=, 2 * NH), 7.7-8.2 (m, 2H, ArH); (FAB) m/z (%): 589 (M^+); $\lambda_{\text{max}}^{\text{DMF}}$ (lg ϵ): 515 (4.56) nm.

Anal. Calcd. for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_8\text{Te}$: C, 45.00; H, 4.26; N, 7.16. Found: C, 44.89; H, 4.15; N, 7.28.

3-Methyl-5,6(15-crown-5)-2-(*p*-dimethylaminostyryl)benzotellurazolium iodide (**7a**).

A mixture of compound **2** (0.29 g, 0.5 mmole) and *p*-dimethylaminobenzaldehyde (0.075 g, 0.5 mmole) in 15 ml of 1-butanol was stirred and refluxed for 1 hour. After cooling, the resulting solid was filtered and recrystallized from dry ethanol/DMF to

give 0.17 g (47%) of a bluish green solid; mp > 300°C (dec.); ir: 3100, 1610, 1580, 1560, 1450, 1270, 1150, 860 cm^{-1} ; ^1H nmr ($\text{DMSO}-d_6$): δ 3.10 (s, 6H, NMe_2), 3.7-4.3 (m, 19H, NCH_3 , crown ether H), 6.7-7.0 (m, 2H, 2 * -CH=), 7.4-8.3(m, 6H, ArH); $\lambda_{\text{max}}^{\text{DMF}}$ (lg ϵ): 539 (4.71) nm.

Anal. Calcd. for $\text{C}_{26}\text{H}_{33}\text{IN}_2\text{O}_5\text{Te}$: C, 44.09; H, 4.66; N, 3.96. Found: C, 44.24; H, 4.85; N, 4.05.

3-Methyl-5,6(15-crown-5)-2-(*p*-dimethylaminostyryl)benzotellurazolium iodide (**7b**).

Compound **7b** (45%) was prepared as described above; mp > 300°C (dec.); ir: 3020, 1620, 1575, 1545, 1460, 1380, 1275, 1160, 860 cm^{-1} ; ^1H nmr ($\text{DMSO}-d_6$): δ 3.05 (s, 6H, NMe_2), 3.6-4.2 (m, 19H, NCH_3 , crown ether H), 6.6-6.9 (m, 4H, 4 * -CH=), 7.2-8.0 (m, 6H, ArH); $\lambda_{\text{max}}^{\text{DMF}}$ (lg ϵ): 557(4.49) nm.

Anal. Calcd. for $\text{C}_{28}\text{H}_{35}\text{IN}_2\text{O}_5\text{Te}$: C, 45.80; H, 4.77; N, 3.82. Found: C, 46.13; H, 4.92; N, 3.64.

1-[3-Methyl-methine-5,6(15-crown-5-benzotellurazole)]-3-(3'-ethyl-2'-methinebenzothiazole) squarylium salt (**10a**).

2,3-Dimethyl-5,6(15-crown-5)benzotellurazolium iodide (**2**) (1.13 g, 2.0 mmole) and squaric acid (0.24 g, 2.0 mmoles) were

boiled in a mixture of 1-butanol (40 ml), benzene (10 ml) and quinoline (0.3 g) for 20 hours with simultaneous removal (azeotropic distillation) of the water formed. The solvent was evaporated under reduced pressure. The residue was washed with a little 1-butanol and mixed with 3-methyl-2-methylbenzothiazolium iodide (**9a**) (0.61 g, 2.0 mmoles) in 1-butanol (20 ml). The mixture was heated under reflux for a further 1 hour. The solution was evaporated to a small volume. Subsequent cooling yielded crystals which were filtered, washed with ether, and recrystallized from ethanol to give 0.42 g (30%) of a deeply blue solid; mp > 300 °C (dec.) ir: 2920, 2900, 1735, 1600, 1560, 1480, 1270, 1100 cm⁻¹; ¹H nmr (DMSO-d₆): δ 1.2-1.4 (t, J = 7.6Hz, 3H, -CH₃), 3.3-4.5 (m, 21H, -NCH₃, -NCH₂, crown ether H), 6.6-6.9 (d, J = 6.5Hz, 2H, 2 * =CH-), 7.3-8.2(m, 6H, ArH); λ_{max}^{DMF}(lg ε): 699 (4.69) nm.

Anal. Calcd. for C₃₁H₃₂N₂O₇STe: C, 52.89; H, 4.55; N, 3.98. Found: C, 52.75; H, 4.58; N, 3.93.

1-[3-Methyl-2-methine-5,6(15-crown-5)benzotellurazole]-3-(methyl-2'-methinebenzoselenazo-le)squarylium salt (**10b**).

Compound **10b** (32%) was prepared as described above; mp > 300 °C (dec.); ir: 2920, 2900, 1740, 1640, 1500, 1255, 1140, 1060 cm⁻¹; ¹H nmr (DMSO-d₆): δ 3.3-4.4 (m, 22H, crown ether H, NCH₃), 6.5-6.8 (d, J = 6.5Hz, 2H, 2 * =CH-), 7.4-8.2 (m, 6H, ArH); λ_{max}^{DMF}(lg ε): 686 (4.25) nm.

Anal. Calcd. for C₃₀H₃₀N₂O₇SeTe: C, 48.87; H, 4.07; N, 3.80. Found: C, 48.50; H, 4.12; N, 3.76.

1,3-Bis-[2-methine-5,6(15-crown-5)benzotellurazole]squarylium salt (**11**).

3-Methyl-5,6(15-crown-5)benzotellurazole **1** (0.23 g, 0.53 mmole) and squaric acid 0.03 g (0.26 mmole) were dissolved in 1-butanol (5 ml) under a nitrogen atmosphere and refluxed for 18-20 hours. The solution was evaporated to a small volume. Subsequent cooling yielded crystals which were filtered, washed with water and recrystallized from ethyl acetate to give 0.14 g

(57%) of a blue-green solid; mp >300 °C (dec.); ir: 2920, 2900, 1640, 1620, 1590, 1530, 1440, 1280, 1250, 1140, 1060 cm⁻¹; ¹H nmr (CDCl₃): δ 3.2-3.4 (m, 32H, crown ether H), 6.7 (s, 2H, 2 * NH), 6.8 (s, 2H, 2 * -CH=), 7.6-8.0 (m, 4H, ArH); λ_{max}^{DMF}(lg ε): 414 (4.67) nm.

Anal. Calcd. for C₃₈H₄₀N₂O₁₆Te₂: C, 46.95; H, 4.12; N, 2.87. Found: C, 46.73; H, 4.14; N, 2.87.

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REFERENCES AND NOTES

- [1] G. Ficken, *Chem. & Ind.* (London), **10**, 672 (1989).
- [2] W. H. H. Gunther, R. E. Leone, and R. Przyklek, *USP* 4,576,905, 1983.
- [3] P. F. Chu, J. Y. Zhang, F. J. Zeng, L. Jiang, Q. X. Lin, and H. S. Xu, *Kexue Tongbao (foreign lang. ed.)*, **28**, 762 (1983).
- [4] X. F. Liu, X. H. Luo and H. S. Xu, *Chin. Chem. Lett.*, **4**, 1043 (1993).
- [5] C. E. K. Mees and T. H. James, *The Theory of Photographic Process*, Vol. **1**, H. Tao, L. Jiang, X. M. Ren, C. Wang, H. J. Xu, C. S. Yang, F. J. Zeng, Y. E. Xu, B. M. Zhou, X. M. Ding, and T. Shen, ed, Science Press, Beijing, 1979, p277.
- [6] H. E. Sprenger and W. Ziegenbein, *Angew. Chem. Int. Ed. Engl.*, **6**, 553 (1967).
- [7] S. C. Jiang, R. L. Fan, and Z. H. Zhu, *Acta Chim. Sinica*, **44**, 1182 (1986).
- [8] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, Jr., *J. Am. Chem. Soc.*, **73**, 5332 (1951).
- [9] P. Glafkides, *Photograph Chemistry*, Vol **4** (Photosensitive Chemistry), D. Liu, ed, China Film Press, Beijing, 1984, p 69.
- [10] L. M. Clark, *J. Chem. Soc.*, 2317 (1928).