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APPLICATIONS OF QUATERNARY SALTS OF AZAAROMATICS

Abstract: In the paper selected examples of applications of quaternary azaaromatics such as modified polymers, dyes, catalysts and materials for optoelectronic devices are presented.

Introduction

Quaternary azaaromatics are of interest for their reactivity, physicochemical properties, biological activities and applications.

The present paper, a continuation of our former articles [1-7] and experimental work [8-11] shows selected examples of applications of quaternary azaaromatics, such as modified polymers, dyes, catalysts, photoswitchable sensors and materials for optoelectronic devices.

Quaternary azaaromatics exhibit a variety of antibacterial [12-16] and antifungal [17] activities; for a special attention deserve DNA intercalators promising as antineoplastic agents [18]. As numerous examples of biological activity of quaternary azaaromatics have been reported, this topic is not included here.

Examples of applications of quaternary azaaromatics

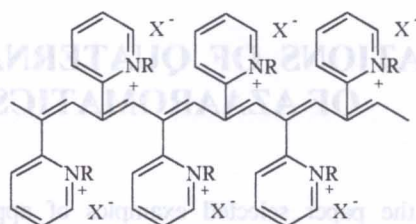
Modified polymers

Polymers modified by incorporation of quaternary azaaromatic groups are an area of a wide investigation [19-21].

Complexes of polyelectrolytes with surfactants of the opposite charge form organized solid state structures. The incorporation of quaternary

azaaromatics into polymers results in polycations; then the anionic surfactants are taken into account. This facile complexation process allows the production of a variety of new materials with properties that range from elastomers to crystalline solids. Such self-organizing structures may be applied for example as switchable permselective biological membranes or NLO materials [1,22]. (NLO= nonlinear optics).

Polymer LB (LB=Langmuir-Blodgett) films bearing quaternary azaaromatic moieties are interesting for optical and electronic applications. An example of ionic polymer based on pyridinium substituents is **1** [23].



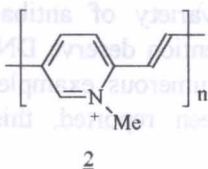
R = aryl

X = halo, TR⁻

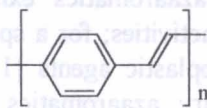
1

Such polymers offer a high tunability by changing the nature of the quaternizing agent or the counterion used.

Poly(methylpyridinium vinylene) **2**, a highly electron deficient analogue of poly(phenylene vinylene) **3** is intensively studied due to its high conductivity and electroluminescent properties allowing applications for light-emitting diode [24].



2



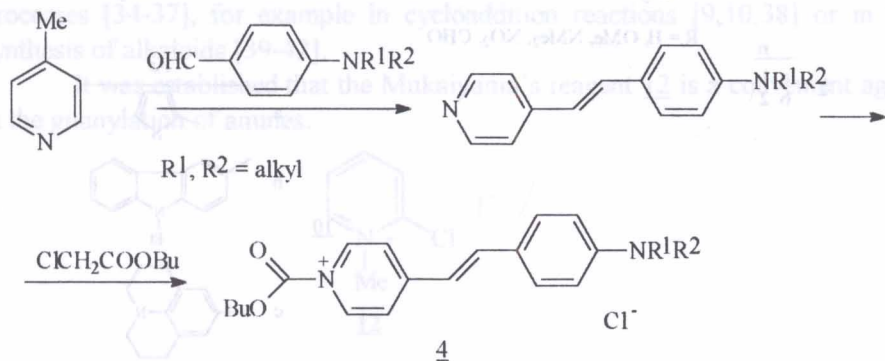
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The polymer **2** is of interest for its electroluminescence. The highly electron-deficient nature of this polymer makes possible its use in self-assembling conducting pseudopolyrotaxanes. The polyelectrolyte properties of **2** are promising in construction of self-assembling films of alternating positively and negatively charged polymers [24].

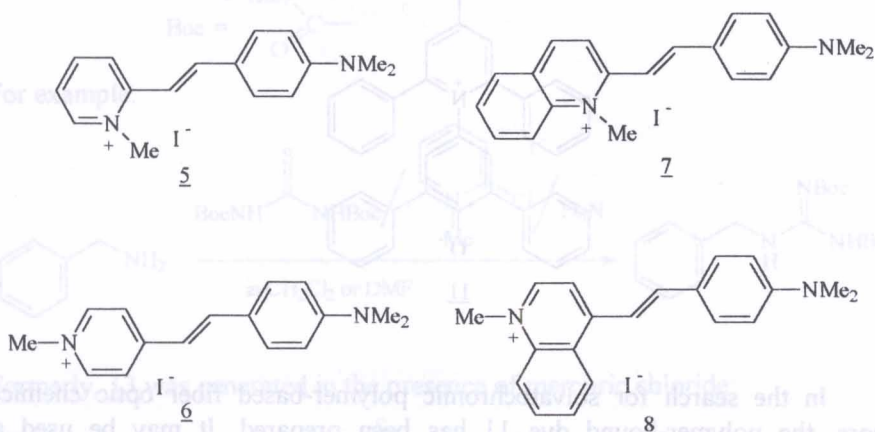
Dyes

Numerous cyanine dyes have been reported [6]. Cyanine dyes **4** may be used as fluorescent viscosity probes for measurement of viscosity in liquids, in a very small volume, e.g. in living cells [25].

The synthesis of **4** proceeds as follows:



Cyanines of electron donor-acceptor type **5** - **8** may find analytical application as luminescent probes. Dynamic changes upon light excitation are sensitive to local environment, so they provide information on the polarity and viscosity of the surrounding medium; they are solvent polarity indicators and fluorescence probes for viscosity [26].



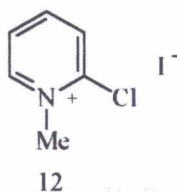
Charge-transfer dyes of the type **9a,b** and **10a-c** have been obtained by reaction of methyl group of zwitterionic pyridiniums with appropriate aldehydes. Their absorption range depends on the kind of substituents [27].

It should be pointed out that solvatochromic dyes of this type may be covalently immobilized on silica substrates with retention of solvatochromic properties, thus allowing construction of optical chemical sensors [33].

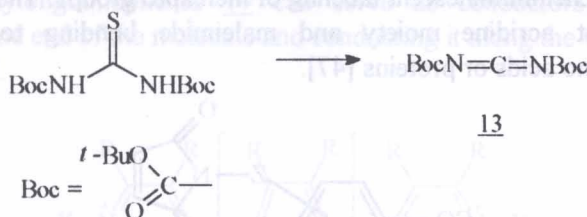
Reagents

Quaternary azaaromatics are used as reagents in a variety of chemical processes [34-37], for example in cycloaddition reactions [9,10,38] or in the synthesis of alkaloids [39-42].

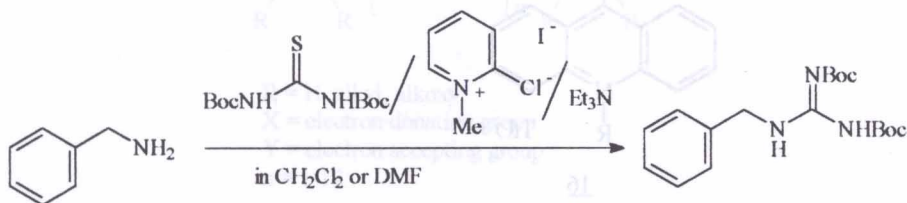
It was established that the Mukaiyama's reagent 12 is a convenient agent in the guanylation of amines.



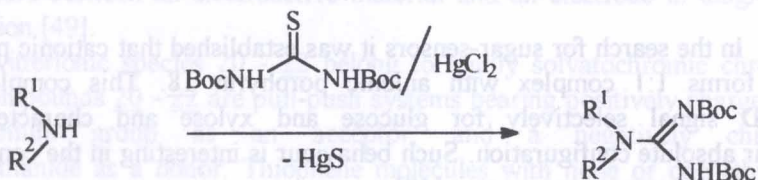
The process involves the formation of *N,N'*-bis(*tert*-butoxycarbonyl)-carbodiimide 13 from *N,N'*-bis(*tert*-butoxycarbonyl)thiourea [43].



For example:



Formerly, 13 was generated in the presence of mercuric chloride:

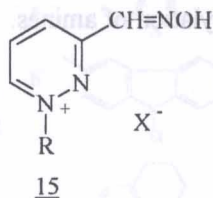
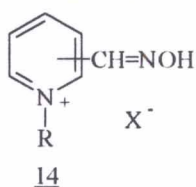


$\text{R}^1, \text{R}^2 = \text{alkyl, aryl}$

The use of 12 avoids the environmental hazard of mercuric sulfide waste, the reaction proceeds at room temperature and the yields are high. The method may be used for guanylation of resin-bound amines and may be applied in the synthesis of protected guanidines [43].

Other applications

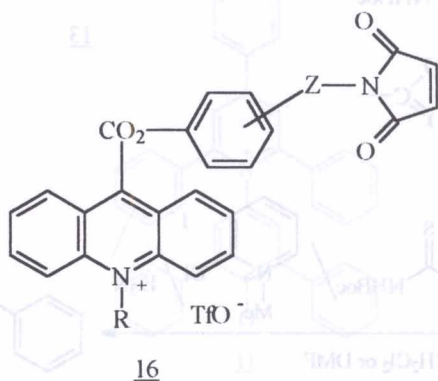
Among quaternary azaaromatics showing catalytic properties [44] should be mentioned 14 and 15 serving as catalysts for cleavage of phosphate esters [45].



R = Me, C₁₂H₂₅

X = Br, I

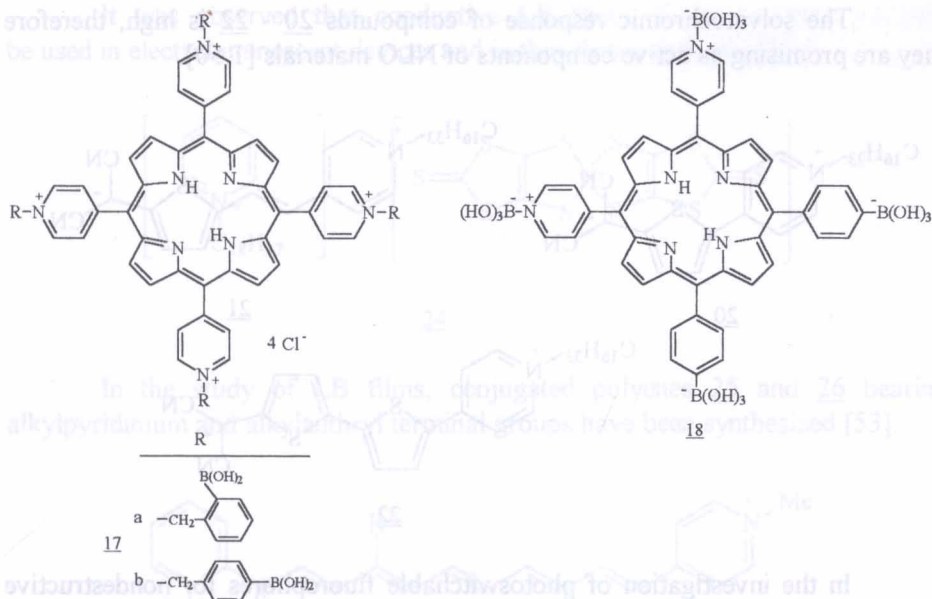
Quaternary azaaromatics may be used as labels [46], for example 16 are reagents for chemiluminescent labeling of mercapto groups. The salts 16 bear chemiluminescent acridine moiety and maleimide bonding to SH groups contained in amino acids or proteins [47].



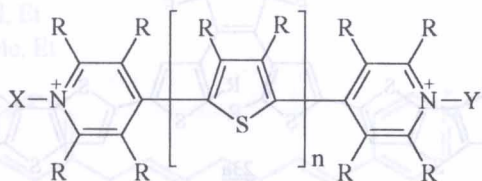
R = C₁₋₆ alkyl, aryl

Z = (CH₂)_n, n = 1-6; O(CH₂CH₂O)_m, m = 1-3

In the search for sugar-sensors it was established that cationic porphyrin 17a,b forms 1:1 complex with anionic porphyrin 18. This complex gives the CD signal selectively for glucose and xylose and characteristically for their absolute configuration. Such behaviour is interesting in the construction of reading-out-type sugar sensors [48].



Bipyridyloligothiophenes 19 can serve as conductors by accepting an electron at one end of the molecule and conducting it along the whole structure to the other end.

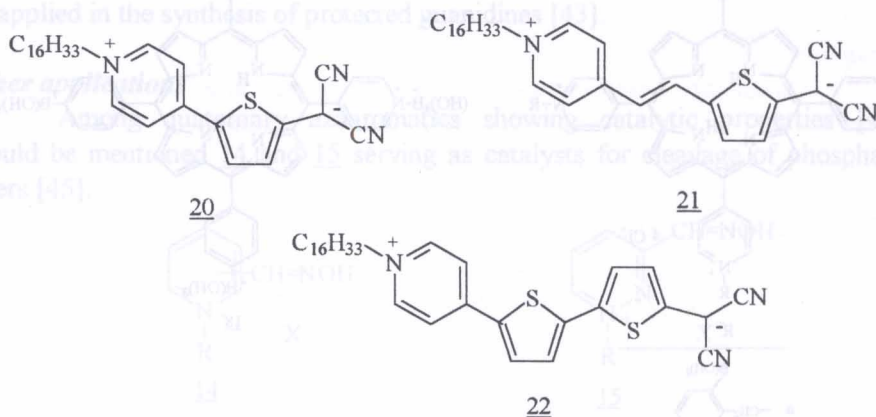


R = H, alkyl, alkoxy
 X = electron donating group
 Y = electron accepting group
 n = 1-12

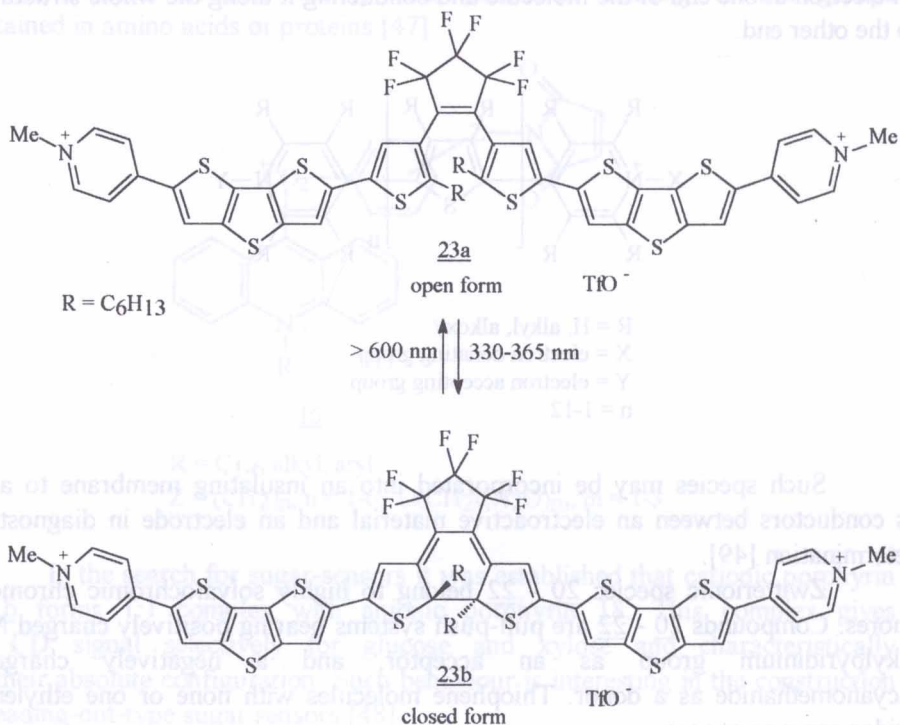
Such species may be incorporated into an insulating membrane to act as conductors between an electroactive material and an electrode in diagnostic determination [49].

Zwitterionic species 20 - 22 belong to highly solvatochromic chromophores. Compounds 20 - 22 are pull-push systems bearing positively charged N-alkylpyridinium group as an acceptor, and a negatively charged dicyanomethanide as a donor. Thiophene molecules with none or one ethylene bridge serve as spacer.

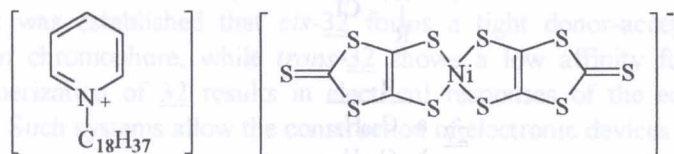
The solvatochromic response of compounds 20 - 22 is high, therefore they are promising as active components of NLO materials [1,50].



In the investigation of photoswitchable fluorophores for nondestructive readout for optical memory, the photoswitching unit 23a,b has been prepared. This system is thermally stable, fatigue resistant and sensitive to diode laser wavelength [51].

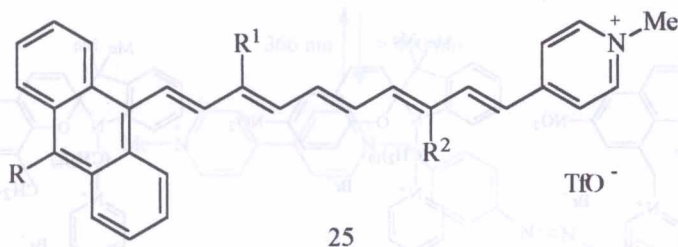


It was observed that conductive LB films of the complex 24 may be used in electroluminescent devices and in thin-film transistors [52].



24

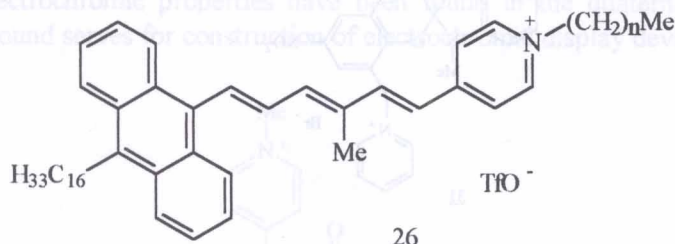
In the study of LB films, conjugated polyenes 25 and 26 bearing alkylpyridinium and alkylanthryl terminal groups have been synthesized [53].



$R = C_6H_{13}, C_{10}H_{21}, C_{16}H_{33}$

$R^1 = H, Et$

$R^2 = Me, Et$



26

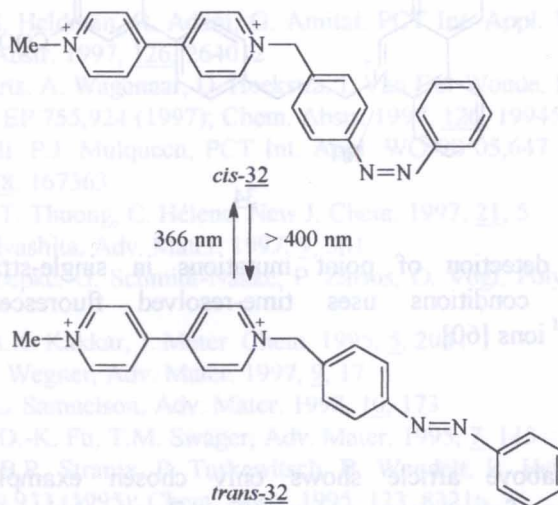
$n = 7, 11$

The introduction of long alkyl chains decreases the solubility in water, thus improving the ability to form LB films [53].

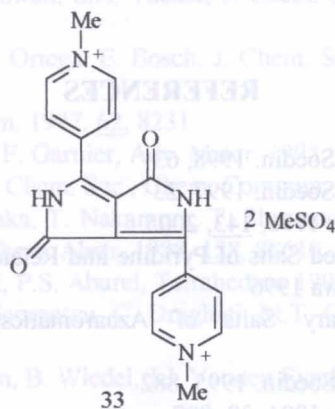
Among works concerning cationic surfactants [54] the adsorption of decyl- and tetradecylpyridinium chlorides 27a,b onto porous silicas from aqueous solutions has been investigated [55].

Quaternary azaaromatics find application in designing of molecular optoelectronic systems, where the light stimulated formation and dissociation of supramolecular donor-acceptor complexes may be utilized.

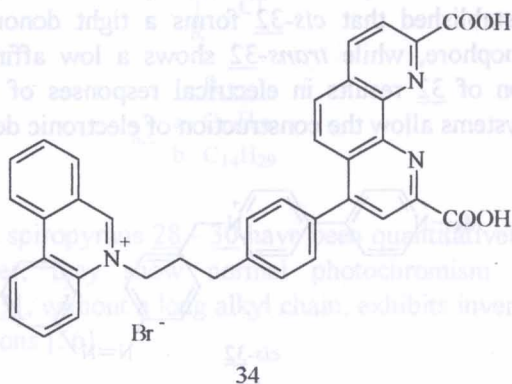
It was established that *cis*-32 forms a tight donor-acceptor complex with eosin chromophore, while *trans*-32 shows a low affinity for eosin. The photoisomerization of 32 results in electrical responses of the eosin modified electrode. Such systems allow the construction of electronic devices [57,58].



Electrochromic properties have been found in the quaternary salt 33. This compound serves for construction of electrochromic display devices [59].



It was observed that the salt **34** can serve as an intercalator-sensitizer in a simple method for the direct *in situ* identifications of mutations in a target strand of DNA [60].



This detection of point mutations in single-strand DNA, under homogeneous conditions uses time-resolved fluorescence spectroscopy involving Eu^{III} ions [60].

Conclusion

The above article shows only chosen examples of a variety of applications of quaternary azaaromatics. Due to their interesting properties these compounds are useful in many areas and are promising in nanotechnological applications.

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Zastosowanie czwartorzędowych soli związków azaaromatycznych

Streszczenie: W artykule przedstawiono przykłady zastosowań czwartorzędowych soli związków azaaromatycznych, jak modyfikowane polimery, barwniki, katalizatory oraz materiały do konstrukcji urządzeń elektro-
nicznych.