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NONLINEAR OPTICAL MATERIALS WITH PYRIDINIUM SALT FRAGMENTS

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Self-assembly and Langmuir–Blodgett (LB) approaches to NLO materials containing pyridinium-like quaternary salt molecules are reviewed.

INTRODUCTION

Currently many works deal with nonlinear optical (NLO) materials showing large second-order hyperpolarizabilities, which are interesting in applications in molecular devices and in laser activated optical switches [1-11]. Among nonlinear optical materials, polysilanes [12], bimetallic sesquifulvalene complexes [13], and hydrogen bond directed organic complexes [14-17] should be mentioned; it was also established that the optical nonlinearity of fullerenes is enhanced by their CT complexation with amines [18]. In the search for NLO systems much attention is paid to polymers [19-21] and cyanines [22-31].

Numerous approaches to NLO materials are known [1, 2], such as the self-assembly technique [32, 33], Langmuir–Blodgett (LB) films [34, 35], and electric field poled glassy polymers [36, 37]. In these methods quaternary salts of pyridines are often used.

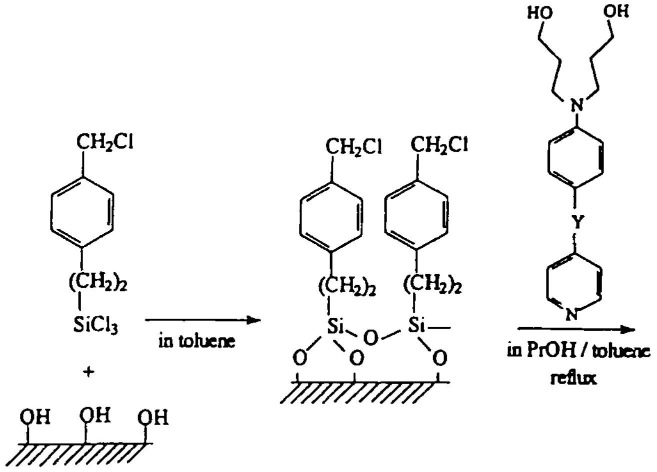
We describe in the present paper the self-assembly and LB film approaches to NLO materials.

Only methods using pyridinium quaternary salts and related compounds will be reviewed here, since our own research is on azaaromatic quaternary salts [38, 39].

SELF-ASSEMBLY APPROACH TO NLO MATERIALS

In the search for molecule-based assemblies with large second-order optical nonlinearities, the following synthetic approach to multilayer NLO materials was made [1, 32, 40-43] (Scheme 1).

Scheme 1



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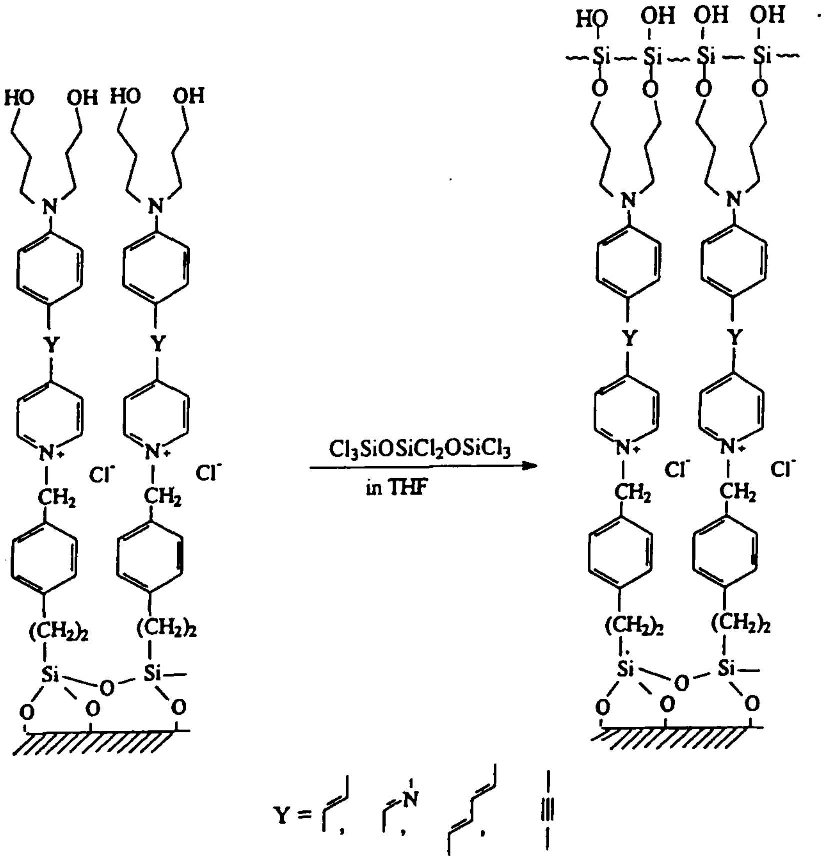
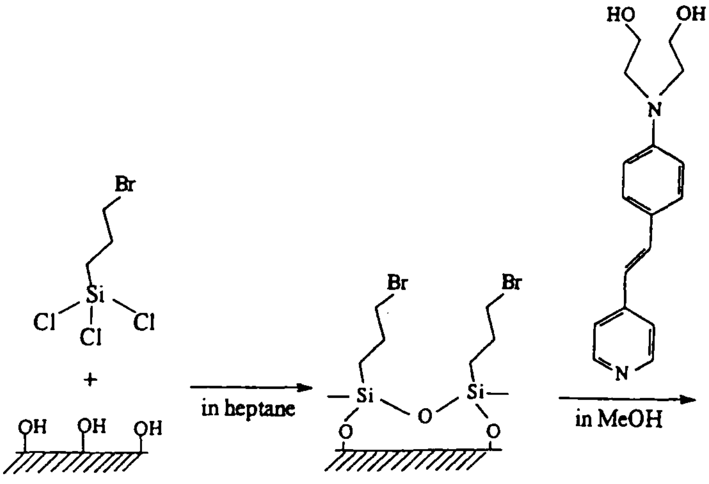


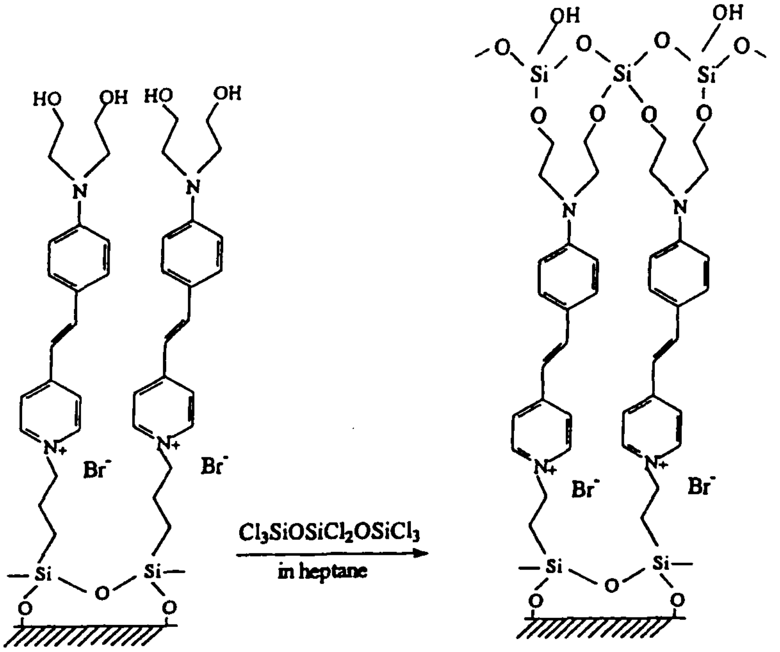
In the study of self-assembled NLO multilayer materials, the monolayer growth and microstructural evolution may be investigated *in situ* by polarized second harmonic generation (SHG) techniques [41-44].

A modification of the self-assembly approach to NLO materials is the covalent topotactic self-assembly of acentric chromophoric superlattices built up layer-by-layer via the formation of covalent bonds [40, 45]. In this method, the key assembly step is performed in either a solvent-free solid state or chemical vapor deposition mode; in this way regular structures of a large nonlinear optical response are obtained [33, 46]. As an example of the synthesis of acentric chromophoric superlattices, the sequential repetition of three layer-building steps was chosen (Scheme 2).

The process begins upon a hydroxylated surface, e.g., single-crystal silicon or SiO_2. In the first step the bromoalkyl functionality is introduced. The second step may be performed in two ways, A or B:

Scheme 2





A. A thin layer of the chromophore precursor, 4-(N,N-dihydroxyethylamino)stilbazole, is spin-coated onto the bromoalkyl-functionalized surface, followed by brief heating *in vacuo* in order to effect quaternization.

B. The precursor vapor is passed over the heated substrate in a chemical vapor deposition process.

The third step provides lateral structural stabilization via interchromophore crosslinking, in this way forming a substrate for the subsequent iterative assembly process.

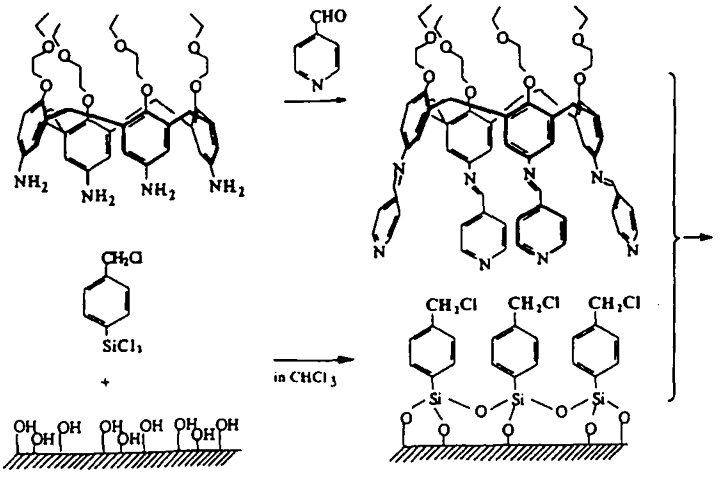
It was established that this method provides an about 30-fold increase of growth efficiency as compared with earlier work [45]; about 3-5 complete iterations of the three steps may be achieved per day.

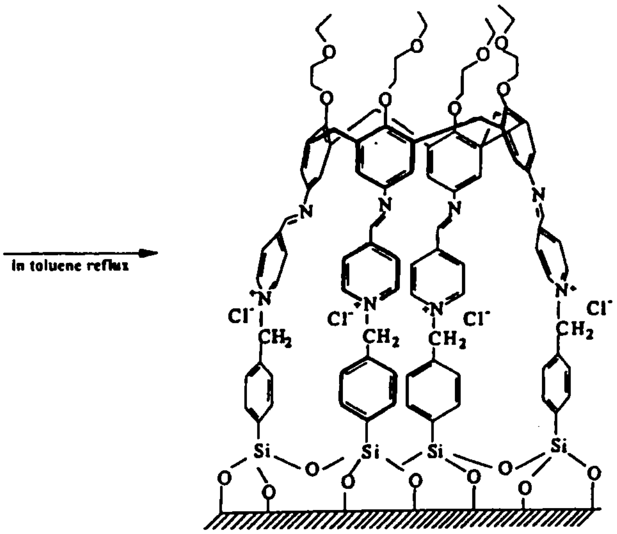
The SHG response as a function of the number of layers is a test of the superlattice regularity. The linear dependence of the square root of the SHG on the number of layers indicates the uniform arrangement of the chromophore molecules and the regularity in layer thickness. The aging investigations have shown complete thermal stability of the SHG response over many months at 25°C.

It was observed that the third, siloxane capping step of the above chromophoric superlattices can be omitted. In this case, the SHG intensity begins to decrease when the number of layers is more than three; the resulting randomization of chromophore alignment destroys the microstructural acentricity [33].

The construction of calixarene-based self-assembled monolayers with cone-shaped molecular building blocks [47] is presented in Scheme 3. In this way strong dipole alignment and large second-order nonlinearities are achieved [47].

Scheme 3





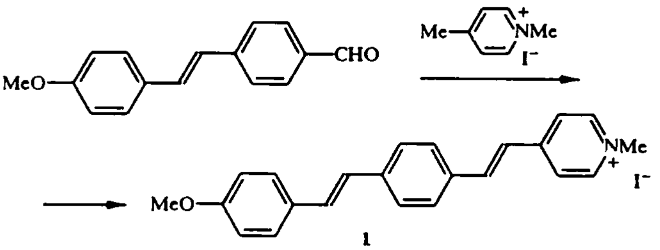
LB FILMS APPROACH TO NLO MATERIALS

Many works deal with NLD materials based on LB films [34, 48-52]. The structure of LB films for SHG must be noncentrosymmetric, i.e., of Z-type. However, most dyes form centrosymmetric Y-type structures, in which molecular layers pack head-to-head and tail-to-tail; therefore it is necessary to interleave the films with appropriate inactive spacers [53-56].

The interleaved films include bilayer structures with interlocking geometries, structures stabilized by interlayer hydrogen bonding, and polymeric LB films [54, 57].

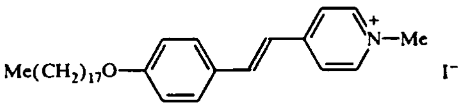
2-Docosylamino-5-nitropyridine has a Y-type structure with molecular layers arranged head-to-head and tail-to-tail. Such packings are usually centrosymmetric, but here the layers adopt a noncentrosymmetric structure [57].

In the investigation of materials for nonlinear optical devices the cyanine 1 was synthesized as follows:



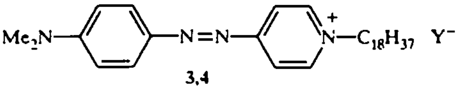
1

The LB films of 1 are noncentrosymmetric and display SHG properties [58]. Comparing cyanines 1 and 2, the longer π-conjugated structure in 1 results in higher SHG than in the case of 2 [58].

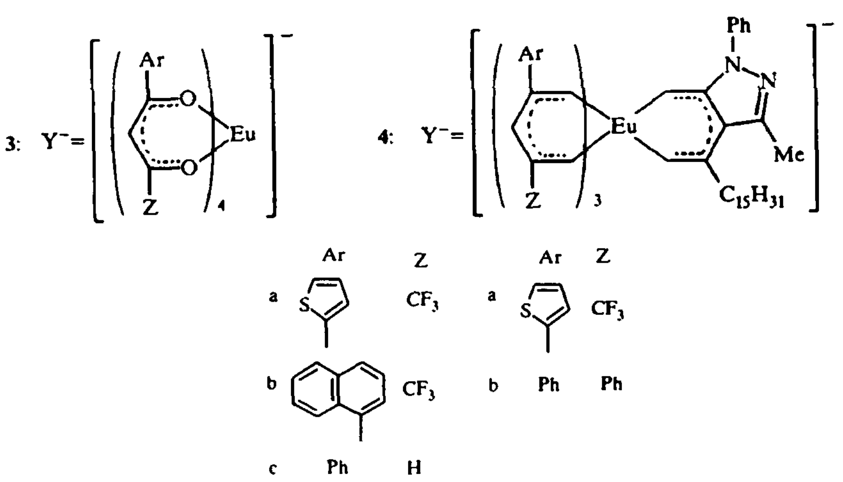


2

Nonlinear optical materials based on azo dyes 3 and 4 containing europium complex anions have been obtained and characterized [59].

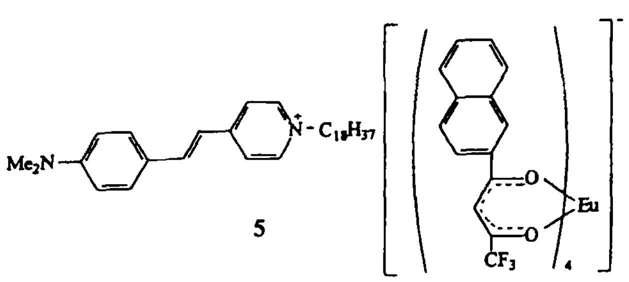


3,4



LB films of these compounds show strong SHG. The europium complex anion bearing a long alkyl group plays the role of a counterion and of a spacer, allowing the regular arrangement and the enhancement of SHG.

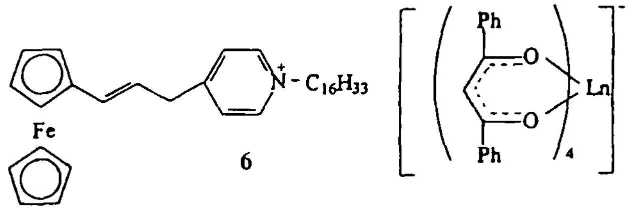
It was established that, in comparison with the europium complex **5**, the replacement of the $-CH=CH-$ group by the $-N=N-$ group increases the conjugation of the molecule, resulting in the hyperpolarizability [60, 61].



5

When a long alkyl chain is present in the anion as in the case of compounds **4a** and **4b**, the enhancement of SHG and film-forming properties takes place. It was observed that the presence of the dibenzoylmethylene group helps the chromophore to form a good monolayer, which is not the case for the thenoyltrifluoroacetone group.

In the study of LB films displaying SHG, based on metal complexes [62, 63], the ferrocenyl lanthanoid complexes **6** have been synthesized; such LB films show NLO properties [64].

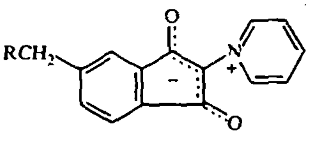


6

Ln = La, Nd, Dy, Yb

The nonlinearity observed is most probably due to the presence of the bulky lanthanoid complex anions which force charge separation [64, 65].

LB films of pyridinium zwitterions **7** of the Z-type structure have been prepared and their optical properties investigated [66].

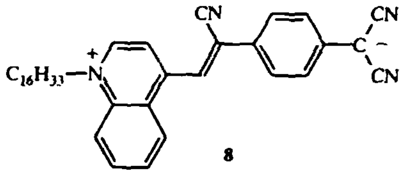


7

R = Me(CH$_2$)$_9$, Me(CH$_2$)$_{15}$

Few materials give Z-type structures required for SHG properties; however, this packing is observed in some unconventional film-forming materials with an optically nonlinear chromophore bearing hydrophobic end groups [35]. Conventional dyes often invert during deposition, achieving a head-to-head and tail-to-tail structure, but when both ends of the molecule are hydrophobic this inversion may be avoided [67].

The zwitterion **8** forming Z-type films has been synthesized [67]. The zwitterion **8** has nonlinear optical properties; the films deposited onto glass surfaces show a quadratic increase in the SHG with the number of LB layers.



8

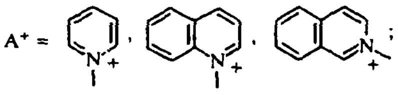
The film properties of zwitterions of the type **8** are dependent on the hydrophobic chain length. For n ≥ 16 of the nitrogen substituent C_nH_{2n+1} the films are purple and the SHG is similar to that of corresponding films of hemicyanine halides [35, 48]; the molecular arrangement within the L layer is parallel, and quadratic SHG enhancement is maintained to 200 LB layers. For lower homologs of n ≤ 14 the films are turquoise; in this case the SHG is very weak due to the antiparallel packing of chromophores [67].

LB films of chromophores **9** may adopt Z-type structure and are promising in NLO applications [35, 56, 68, 69].

C_nH_{2n+1}–A^+–(π–bridge)–Y–Alk

9

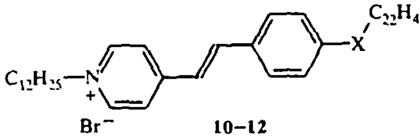
$8 \leq n \leq 20$



; Y = O,S,Se,N(H),OC(O)

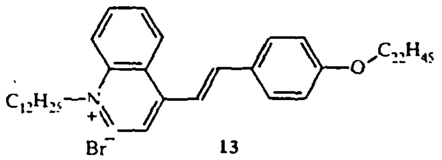
The dyes **10-13** have been synthesized from N-alkyl-4-picolinium bromide and appropriate para-substituted benzaldehyde in the presence of piperidine [56], and they show nonlinear optical properties.

LB multilayers of **10** are centrosymmetric (Y-type) for n ≤ 6 and noncentrosymmetric (Z-type) for 8 ≤ n ≤ 20. It was found that long-chain homologs do not invert during deposition; the molecules adopt a stretched rather than a U-shaped configuration at the air–water interface. The SHG from films of the higher homologs (n ≥ 10) increases quadratically with the number of LB layers. For dyes **11-13** NLO properties have been observed for suitable combinations of alkyl chain lengths [56].



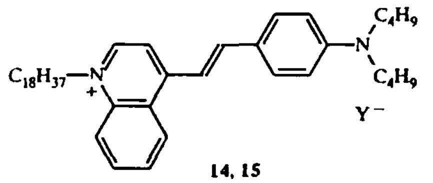
10–12

10 X = O; **11** X = S; **12** X = Se



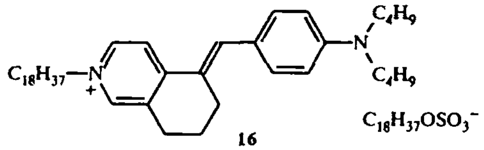
13

It was established that the nonlinear optical properties of some cationic dyes may be increased by the addition of a third alkyl chain, and the presence of an amphiphilic anion; examples are dyes **14-16** [57].



14, 15

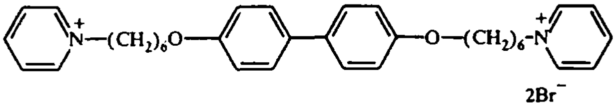
14 Y = I, **15** Y = $C_{18}H_{37}OSO_3^-$



16

The LB films of **14-16** have Z-type structure, and their SHG values are high. These dyes may find application in wave-guiding overlays, evanescently coupled to optical fibers [57].

One should also mention here organic – inorganic alternating films, which are promising in nonlinear optics. The molecular deposition (MD) method has been used for constructing MD matrices adopted for the assembly of PbI_2 nanoparticles into a multilayer structure; PbI_2 particles are here a semiconductor quantum dot material. The bipolar salt **17** serves as a cationic species [70].



17

The electrostatic attraction between anionic and cationic parts guarantees a well-defined layer structure of the organic – inorganic alternating film.

CONCLUSION

Numerous works concerning NLO materials reflect the great interest in this rapidly developing area of chemistry and physics, providing new systems with various possibilities of application.

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