Enhanced Chromophore Polymeric NLO Materials

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See Attached
13. Nonlinear optical (NLO) materials are an important component of many prospective Air Force applications including optical signal processing (switches, modulators, and guided-wave devices), and new laser sources (optical parametric oscillators and harmonic generators). Considerable progress has been made in the synthesis of frequency doubling (second harmonic generation - SHG) NLO chromophores and of polymeric materials containing such chromophores. A number of these SHG-NLO materials show noteworthy promise in small-scale characterizations. Commercialization of any of them requires that significant quantities of the materials, of demonstrable purity and stability, be readily available on a routine basis to these researchers who determine processing conditions as well as device manufactures. The results of the Phase I study have established the feasibility of synthesizing known SHG-NLO chromophores in reasonable quantities and of demonstrable purity for advanced processing and device studies. The process involved five steps: a) confirming the existing synthetic scheme (25g scale), b) investigating changes in the scheme to enhance yields, c) developing or improve purification procedures, d) evaluating scale-up potential (100g scale), e) using the chromophores as a basis for the synthesis of derivatives with enhanced SHG-NLO properties. Several known chromophores as well as two new derivative were synthesized.
SBIR Final Report

entitled

"ENHANCED CHROMOPHORE POLYMERIC NLO MATERIALS"

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Nonlinear optical (NLO) materials are an important component of many prospective Air Force applications including optical signal processing (switches, modulators, and guided-wave devices), and new laser sources (optical parametric oscillators and harmonic generators). Considerable progress has been made in the synthesis of frequency doubling (second harmonic generation - SHG) NLO chromophores and of polymeric materials containing such chromophores. A number of these SHG-NLO materials show noteworthy promise in small-scale characterizations. Commercialization of any of them requires that significant quantities of the materials, of demonstrable purity and stability, be readily available on a routine basis to those researchers who determine processing conditions as well as device manufacturers.

The synthesis of several reported SHG-NLO chromophores has been carried out. Significant quantities of demonstrable purity have been made available. Experimental procedures for the synthesis of these SHG chromophores was provided by Prof. T. Marks, Northwestern University.

1) The chromophore NPPOH (3) has been synthesized. Thus, prolinol (1) was reacted with p-fluoronitrobenzene (2) to produce NPPOH (3) (15g of purified material is available).

![Chemical Reaction](image-url)
The chromophore NPPOH (3) can be converted to the corresponding tosyl derivative NPPOTs (4) by reaction with tosyl chloride in pyridine (50g of purified material is available).

![Chemical structure](image)

2) The chromophore "Tosylated Benzylated HNPP" (9) has been synthesized. The reaction of 2-nitro-5-fluorophenol (5) with benzyl bromide (6) yields 1-nitro-2-benzyloxy-4-fluorobenzene (7) (50g of purified material is available).

![Chemical structure](image)

The reaction of 7 with prolinol (1) yields the product 8 (65g of purified material is available).

![Chemical structure](image)
Conversion of 8 to the corresponding tosyl derivative 9 has also been completed (40 g recrystallized material is available).

3) The synthesis of a polymer 11 having pendent SHG chromophore functions (i.e. 9) has been accomplished on a scale comparable with that reported (1.5 g purified material is available).

4) The transformations reported in 1), 2), and 3) above, confirm the validity of the syntheses with minor changes, have led to enhanced purification methods for these materials, and scale-up to the 100 g level was either demonstrated or is considered feasible. To illustrate the potential that existing SHG chromophores present for the preparation of advanced materials, two new syntheses are
reported in this section. The SHG chromophores 3 and 12 served as the starting point for the preparation of new advanced materials.

The synthesis of the SHG chromophore 13 was accomplished by 1) the protection of the primary alcohol function of 3 (to prevent interference in the second step) and 2) the reduction of the protected nitro compound 12 followed by an immediate reaction with 2,5-dimethylxyfuran. The acetate protective function, while effective for model studies, does not offer the reactivity needed for many applications and will be replaced by the tosyl function in future work. The pyrrole function is a known acceptor function and 13 is being evaluated for SHG potential.

\[
\begin{align*}
\text{Ac}_2\text{O} & \quad \text{Ac}_2\text{O} \\
\text{H}_2, \text{Pd/C} & \quad \text{MeO} - \text{O} - \text{OMe} \\
\text{3} & \quad 12 & \quad 13
\end{align*}
\]

The synthesis of the crosslinkable chromophore 17 has been initiated. The diol 14 was prepared by the reaction of prolinol (1) and 2-nitro-5-fluorophenol (5). The reaction of 14 with 4-maleimidobenzoyl chloride 16 has been carried out and purification of the bismaleimido-chromophore is in progress.

\[
\begin{align*}
\text{K}_2\text{CO}_3 & \quad \text{THF} \\
\text{1} & \quad 5 & \quad 14
\end{align*}
\]
Conclusions

The results of the Phase I study have established the feasibility of synthesizing known SHG-NLO chromophores in reasonable quantities and of demonstrable purity for advanced processing and device studies. The process involved five steps:

a) Confirm the existing synthetic scheme (25g scale)

b) Investigate changes in the scheme to enhance yields

c) Develop or improve purification procedures

d) Evaluate scale-up potential (100g scale)

e) Use the chromophores as a basis for the synthesis of derivatives with enhanced SHG-NLO properties