Nanostructured Molecular Materials for Device-Quality, Highly Efficient Electrooptic Poled Polymers**

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Optical telecommunications and public networking requires high-speed optical-electrical data interconversion, which in turns drives a vast need for advanced, extremely efficient device components such as waveguides, switches, emitters, and detectors.[1] Development of functional “soft materials” in the form of robust organic thin films and their integration into prototype devices offer a great challenge, which promises new device properties, enhanced performance, and eventually lower production costs.[2] Nonlinear optical (NLO) and electrooptical (EO) properties of poled polymers have improved considerably during the last two decades, and new developments have made them almost competitive to conventional inorganic materials such as lithium niobate ($LiNbO_3$).[1–7] Trends in first and second hyperpolarizabilities (β) as a result of substituent patterns, chromophore properties, and spacer lengths between donor and acceptor units have been established for various organic compounds by Marder, Blanchard-Desce, and many others.[2–7] Moreover, there is a reliable theoretical basis for understanding the mechanisms involved as well as predicting new molecular structures with even larger responses.[4]

Of the diverse synthetic approaches to acentric chromophore matrices, polymer poling,[5–7] Langmuir–Blodgett and related film-transfer techniques, and molecular self-assembly have been investigated most intensely.[2, 8] Nevertheless, innovative design of applicable noncentrosymmetric organic materials having excellent EO responses remains challenging and highly intriguing. There are still considerable fundamental gaps in the understanding of the influence of chromophore design on material structure–function relationships. One challenge is clear: For a given high-β chromophore, which parameters can be tuned to explore and establish functional device-quality materials exhibiting optimal nonlinear and electrooptical responses?

Dalton, Jen, and Steier recently reported series of new chromophores, nanostructured functional materials (i.e., phase-separating block copolymers, dendrimers) for the formation of low-loss poled polymers, and the design of prototype devices having the desirable combination of very large EO responses and excellent thermal and temporal stability.[6, 7] High chromophore density is a prerequisite for the formation of polar organic materials with exceptional EO properties. However, intermolecular electrostatic interactions in poled polymers significantly limit the value of the maximum possible macroscopic EO coefficient (r_{33}) for a given chromophore with a high dipole moment.[9] For instance, EO responses of poled polymers based on **1** (Scheme 1) are limited by the formation of dye aggregates at high chromophore densities.[6, 7]

Decreasing or preventing aggregration of thermally robust polymer matrices (i.e., polyimides, polyquinolines)[6e] and chromophore–chromophore interactions while maintaining a high chromophore density may largely increase macroscopic optical nonlinearity. Indeed, introduction of bulky substituents such as *n*-hexyl (**2**), *n*-butyl (**4**), or *tert*-butyldimethylsilyl (**3**, **5**) on chromophore precursors without affecting β resulted in poled polymers with significantly decreased electrostatic interactions among the chromophore building blocks. The noncentrosymmetric characteristics of these modified high-β chromophores are more effectively carried through into bulk properties, allowing realization of materials exhibiting better macroscopic second-order NLO effects and much higher r_{33} values. Sophisticated poled polymer modulators based on **1** and the electronically isolated compounds **2**–**5** operating at telecommunication wavelengths (1.3 and 1.55 μm) with half-wave voltages (V_π) as low as 0.8 V represent a major advance.[7] Such prototype devices are rapidly approaching or even exceeding the performance of single-crystal $LiNbO_3$-based devices in terms of bandwidth and operating voltage.

Application of poled polymers is often limited by the relatively low glass-transition temperatures (T_g) of the polymer matrices.[2, 7] Major research efforts have been devoted to increase T_g in order to prevent thermal relaxation of the chromophore dipole moment.[2, 5, 6] For instance, polyurethane (PU) matrices based on triethanolamine and toluene-2,4-diisocyanate have a dynamic stability till about 90 °C, which can be enhanced by 1) using more rigid cross-linkers and 2) chemically modifying PU polymers with urea and siloxane units (**6**, **7**; Scheme 2).[6b,c]

Practical polar organic materials must meet a combination of many criteria, leading often to a trade-off between EO efficiency and material stability. There are numerous organic materials available having excellent EO values,[2, 3] but high-quality films are extremely rare.[2, 5–7] The temperatures at which the devices operate and which are induced in processing require materials with long-term chemical, photochemical, mechanical, and thermal stability. Electrooptic modulation is caused by voltage-induced variations in the refractive index of a functional material requiring either relatively high voltages or long electrodes. To minimize absorption losses in large device structures, C–H moieties may be replaced by C–D and/or C–F groups, which is known to enhance polymer optical transparency at telecommunication wavelengths.[2,7c]

All the aforementioned crucial requirements placed on materials for device fabrication and performance are for the first time favorably combined in a recently developed dendrimer system based on the thienylstyrene chromophore (**8**;

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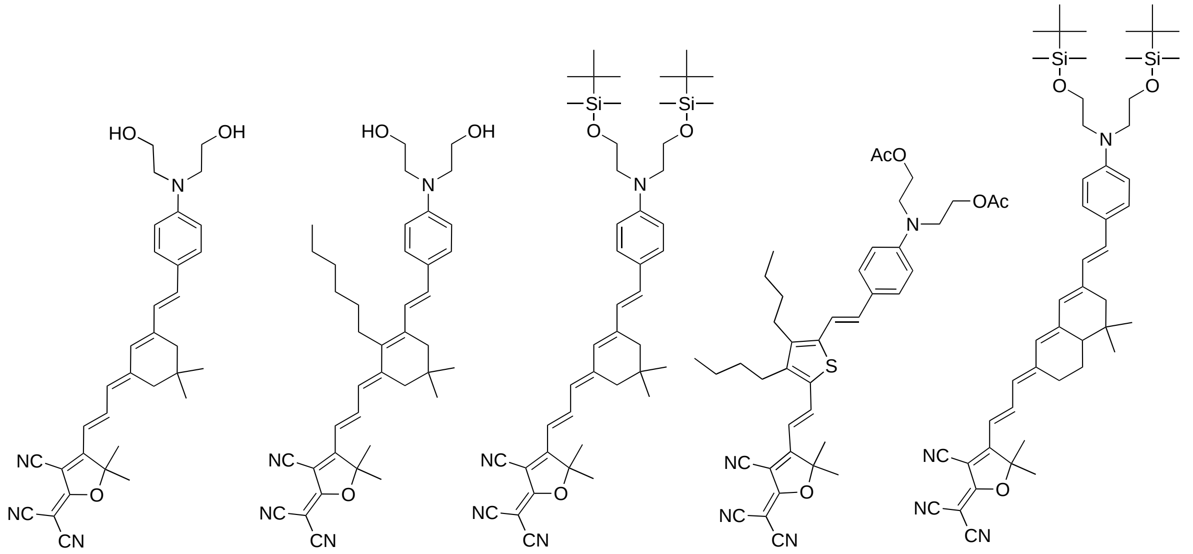
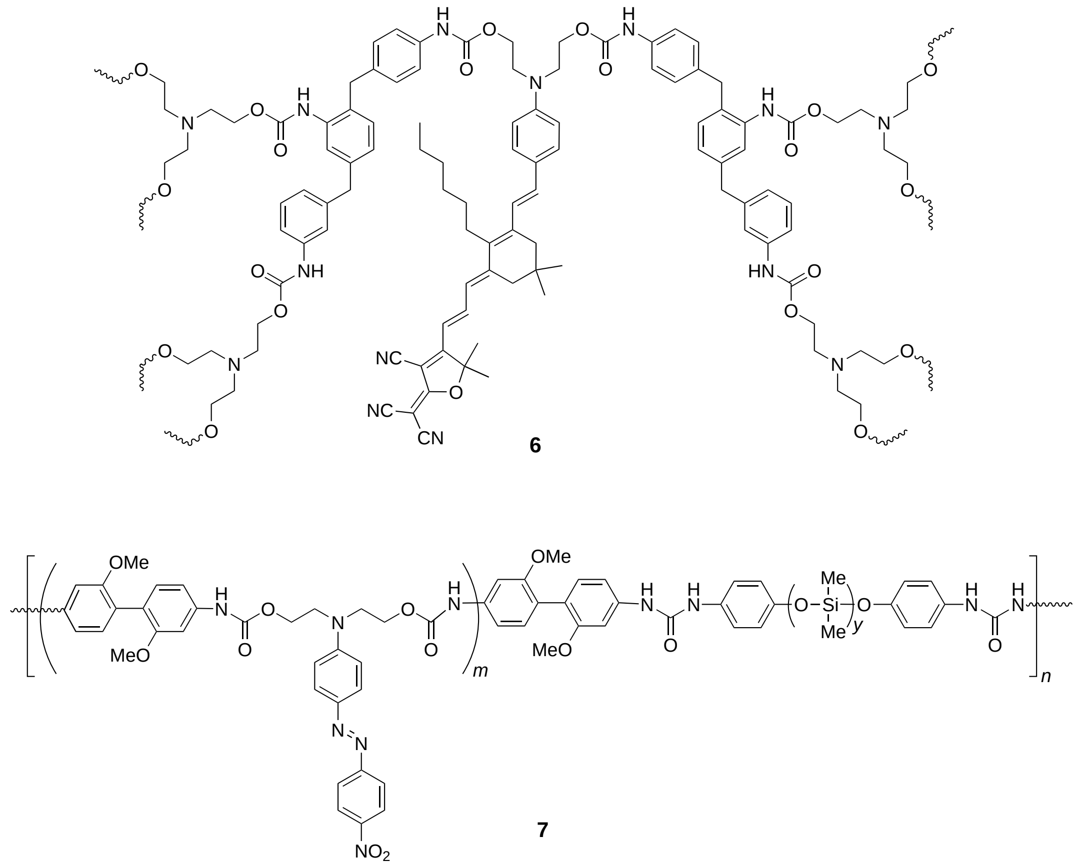


1, r_{33} = 45 pmV^{-1} **2**, r_{33} = 55 pmV^{-1} **3**, r_{33} = 90 pmV^{-1} **4**, r_{33} = 55 pmV^{-1} **5**, r_{33} = 105 pmV^{-1}

Scheme 1. Chemical structures of phenyltetraene chromophore **1** and related compounds **2**–**5** with high dipole moments.[6b,d, 7c]



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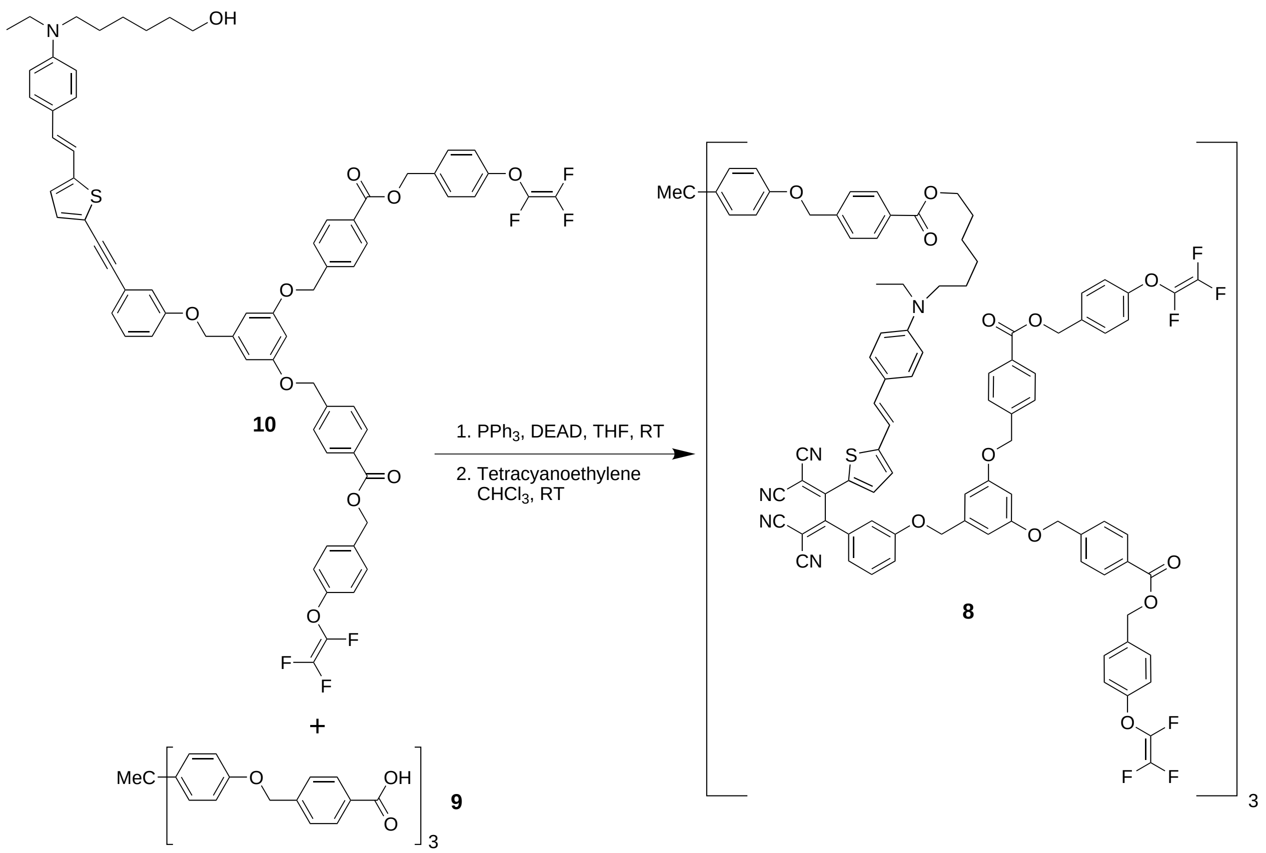
Scheme 2. Examples of polyurethane-based films (**6** and **7**) with enhanced thermal stability.[6b,c]

Scheme 3).[6a] The multifunctional dendrimer **8** has trifluorovinyl ether dendrons that can be cross-linked to enhance thermal and temporal stability of the poled polymer and prevent thermal relaxation of the chromophore dipole alignment.

The high-β chromophore functionalized **8** was prepared stepwise by the Mitsunobu condensation between the carboxy groups of the core **9** and the hydroxy groups of **10**, followed by treatment with tetracyanoethylene. Dendrimer **8** was well-characterized by a combination of gel permeation chromatography, mass spectrometry, and ^{1}H and ^{19}F NMR spectroscopy. Chromophore dipole alignment was achieved by applying corona poling at elevated temperatures on vac-



Scheme 3. Chemical structure and synthesis of dendrimer **8** for the formation of high-quality poled polymers by applying corona poling.[6a] DEAD = diethyl azodicarboxylate.

uum-dried films spin-coated onto an indium tin oxide (ITO) glass electrode. An additional advantage in terms of processing is the relatively high molecular weight (4664 Da), which makes a prepolymerization step to increase viscosity prior to spin-coating unnecessary. Conventional reflection techniques were used to determine r_{33} values at 1.55 μm. The cross-linked, poled dendrimer system has a high chromophore density (33 %, w/w), excellent EO responses ($r_{33} = 60\,\mathrm{pm\,V^{-1}}$), and a good temporal stability; the poled, defect-free material retained more than 90 % of its initial high r_{33} value at 85 °C in nitrogen for more than 40 days. No aggregration was observed. The importance of this dendritic method was unambiguously demonstrated by control experiments. Related materials lacking moieties that could be cross-linked and nondendron guest–host polymers showed significantly lower thermal and temporal stability as well as reduced r_{33} values.

The state-of-the-art in "organic" electrooptics has advanced considerably during the past five years in terms of improved electrooptic activity, low optical loss, and enhanced thermal and photochemical stability.[1–7] Further optimization and fine-tuning of these parameters by applying the recent findings to other high-β chromophores that can be processed and macromolecules that can be cross-linked is a distinct possibility for generating series of device-quality poled polymers. Applicable organic EO modulators and other devices may soon become a reality,[7,10] whereas the dendritic approach highlighted here is a valuable strategy for the formation of a variety of covalently interlinked, functional organic materials.[11]

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