



Dendritic nanodevices

Nanostructured functional dendrimers and polymers for photonics

Jingdong Luo, Hong Ma, Alex K.-Y. Jen *

Department of Materials Science & Engineering, Box 352120, University of Washington, Seattle, WA 98195–2120, USA

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Abstract

Compared to conventional molecular design for organic NLO materials, the concept of using nanoscale architectural control to tailor the size, shape, conformation, and functionality of NLO chromophores and macromolecules provides a great opportunity for simultaneous optimization of macroscopic electro-optic activity, thermal stability, and optical loss. All the results discussed in this review are extremely encouraging and this new approach may help to launch a new paradigm for the molecular engineering of next generation high-performance E–O materials. *To cite this article: A. Dirksen, L. De Cola, C. R. Chimie 6 (2003).*

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1. Introduction

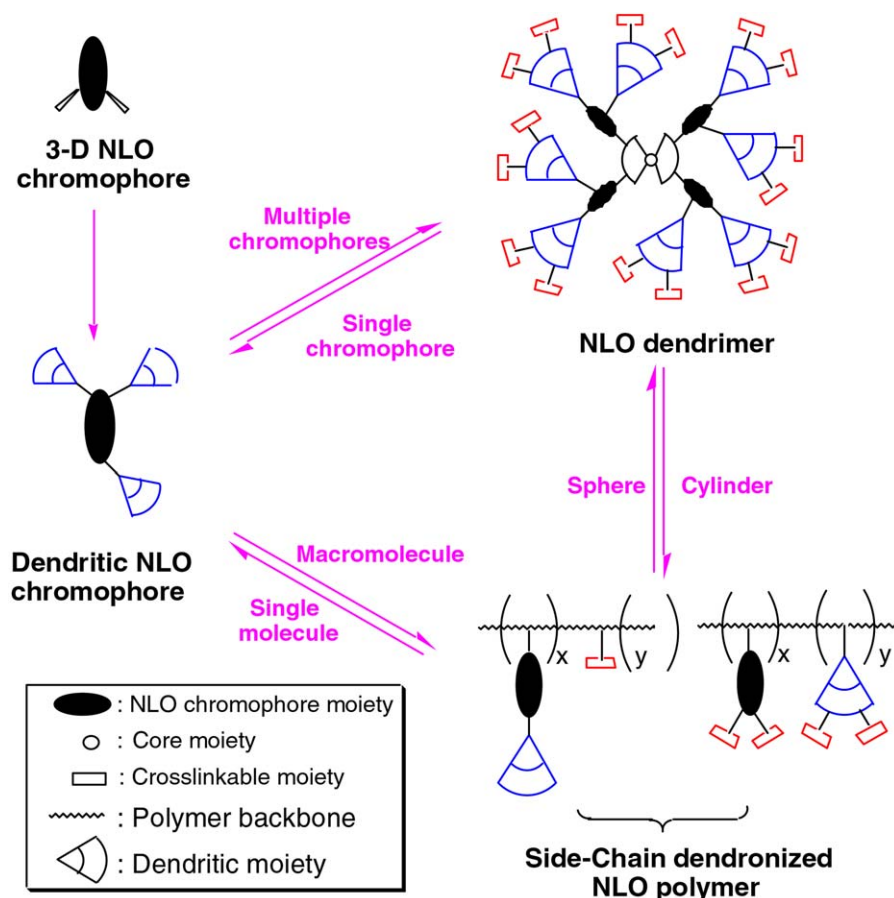
Organic polymeric second-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential for applications in photonic and opto-electronic devices, such as frequency converters and ultrahigh-speed electro-optic (E–O) switches and modulators [1]. One major obstacle that hinders the rapid development of this technology is the difficulty to translate high molecular non-linearities ($\mu\beta$) into large macroscopic E–O activities (r_{33}) in NLO poled polymers [2]. In order to achieve this goal, it is necessary to develop an effective mechanism to improve poling efficiency through minimization of the strong intermolecular electrostatic interactions between high dipole moment NLO chromophores.

In a poled polymer, a NLO chromophore is usually surrounded by other chromophores and polymer chain

segments. During the poling process, the electric field needs to overcome not only the intermolecular electrostatic interactions between chromophores but also the restriction of chromophore reorientation imposed by polymer chain entanglements. In order to improve poling efficiency of NLO polymers, the chromophore in the polymer matrix should be structurally shielded from its neighboring chromophores to minimize the dipole-dipole interactions. Another approach is to create a well-defined macromolecular architecture that will provide a nanoscale ordering for reducing the hindrance to re-orient NLO chromophores. Previously, we have demonstrated the strategy of using shape modification of NLO chromophores to improve poling efficiency [3]; however, the initial results obtained from these studies have only shown an incremental improvement of the polymer's E–O properties. Since the globular geometry of dendrimers is well-suited for modifying chromophores to the ideal spherical shape, we have recently explored the idea of using dendritic structures to modify the shape of NLO chromophores

* Corresponding author.

E-mail address: ajen@u.washington.edu (A.K.-Y. Jen).



Scheme 1

and polymers and systematically investigate the role of the site isolation effect in determining the material properties [3–5].

In the past two decades, unprecedented control of critical dendrimer design parameters, such as size, shape, surface chemistry, flexibility and topology, has been rigorously explored to provide well-defined, dendritic architectures. Our main efforts are focused on tuning the macromolecular architecture of E–O materials ranging from the shape of flattened sphere, umbrella, to cylinder, and studying their effects on poling efficiency. Here, we highlight our latest progress in the design, synthesis, and properties of these NLO material systems. Their structures vary from the 3–D shaped dendritic chromophore to the multi-functional dendrimers with the center core connected to NLO chromophores and crosslinkable functional group at the periphery, and to the side-chain dendronized NLO

polymers (Scheme 1). All the poling results from these systems have shown dramatically enhanced E–O properties (a factor of ~2–3) compared to the conventional NLO polymers.

2. Dendritic NLO chromophore [6]

Among various NLO polymer systems, fluorinated materials are of particular interest because it has been demonstrated that fluorinated polymers exhibit a combination of high thermal stability, chemical inertness, low dielectric constants, and optical transparency due to the large electro-negativity of the fluorine atom. In order to explore the effect of fluoro-rich dendrons on the microenvironments of dipolar NLO chromophore, we have designed and synthesized a highly fluorinated dendritic NLO chromophore **2** (Fig. 1). This dendritic-

shaped chromophore was constructed by using a phenyl-tetracyanobutadienyl (Ph-TCBD) thiophene-stilbene-based NLO chromophore as the center core and it was encapsulated with three highly fluorinated aromatic dendrons.

The resulting dendritic chromophore **2** exhibits appreciably different properties, such as a large blue-shifted absorption λ_{\max} (29–42 nm), a higher thermal stability (20 °C), and a much higher E–O activity (3 ×), compared to the pristine chromophore **1**.

Since both chromophores contain the same NLO active moiety, the blue-shifted λ_{\max} is largely due to the encapsulation with fluoro-rich dendrons that have low polarizability and low dielectric constant. Moreover, the dendritic chromophore **2** also shows exactly the same UV–Vis spectra when it was dispersed in either a non-fluorinated polycarbonate or a highly fluorinated polymer, two kinds of matrices that possess significantly different dielectric constants. From these results, it indicates that the fluoro-rich dendrons dominate the microenvironments of the core chromophore in solid films.

More importantly, this comparison provides a very clear explanation about how the dendritic effect en-

hances E–O activities. Under a similar condition, the poled film of **2** exhibits an r_{33} value of 30 pm/V at 1.3 μm , which is three times higher than that derived from **1**, indicating a significant improvement in poling efficiency. The encapsulation of **2** with fluorinated dendrons makes its shape globular-like, which is very close to the ideal molecular shape for achieving the predicted optimum poling efficiency. Moreover, because the fluorinated dendrons strongly affect the microenvironments of the Ph-TCBD chromophore in solid state, the chromophores are site-isolated, thereby the intermolecular electrostatic interactions are significantly reduced. This, in turn, ameliorates the molecular orientation.

The blue-shifted absorption and high C–F contents in **2** also contribute to the material's low optical loss at both 1.3 μm and 1.55 μm which are the two major wavelengths used in telecommunication. From the photo-thermal deflection spectroscopy (PDS), the optical loss of the materials induced by the absolute absorption of **2** in polycarbonate are only 0.65 and 0.85 dB cm^{-1} at 1.3 and 1.55 μm , respectively. With regards to the relatively high C–H content in the polycarbonate matrix, the major contribution of these loss

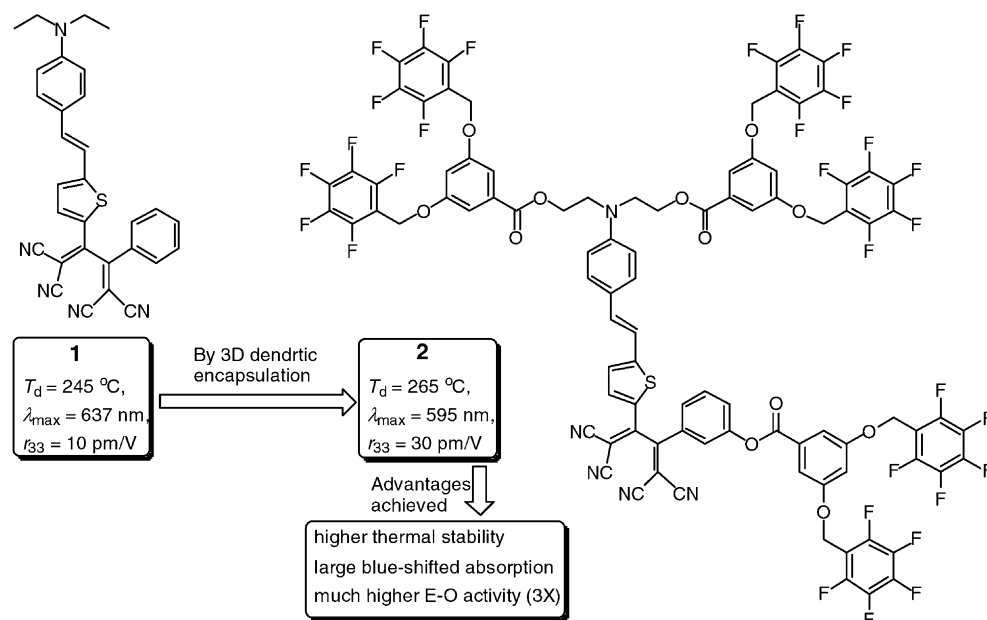


Fig. 1. Property comparison between dendritic chromophore and its pristine phenyl-tetracyanobutadienyl (Ph-TCBD) thiophene-stilbene-based NLO chromophore. T_d : initial decomposition temperature determined by seal-pan differential scanning calorimetry (DSC) at $10^\circ\text{C min}^{-1}$ under nitrogen; APC: amorphous polycarbonate (APC) {poly[Bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate]}; electro-optic coefficient (r_{33}) obtained in APC matrix with 12 wt% of core chromophore density by contact poling.

values should be originated from the matrix itself instead of from **2**. Since the intrinsic loss of **2** is lower than 1 dB cm^{-1} , this type of highly fluorinated dendritic chromophore should be very useful for photonic applications.

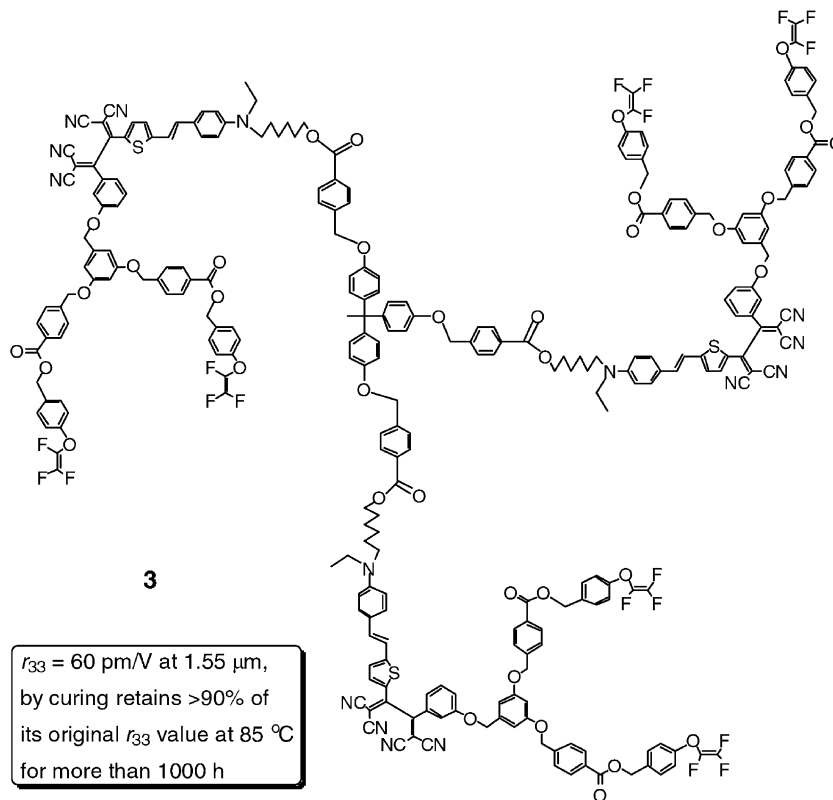
3. Crosslinkable NLO dendrimers [7]

In order to create a stand-alone NLO material that possesses the ideal spherical shape and good alignment thermal stability, we have constructed a chromophore-containing dendrimer with multiple NLO chromophore building blocks placed into a precisely designed molecular architecture with predetermined chemical compositions.

The crosslinkable NLO dendrimer **3** (Scheme 2) exhibits a very large optical non-linearity and excellent thermal stability. This NLO dendrimer was constructed through a double-end functionalization of NLO chromophore **1** as the center core and the crosslinkable trifluorovinylether-containing dendrons as the exterior

moieties. Spatial isolation from the dendrimer shell decreases chromophore-chromophore electrostatic interactions, and thus enhances macroscopic optical non-linearity. Through a sequential hardening/crosslinking process during the electric field poling, a very large E–O coefficient ($r_{33} = 60 \text{ pm/V}$ at $1.55 \mu\text{m}$), and long-term alignment stability (retaining $> 90\%$ of its original r_{33} value at $85 \text{ }^\circ\text{C}$ for more than 1000 h) were achieved for the poled dendrimer.

For comparison, E–O studies were performed on a guest/host system, in which the chromophore **1** without dendron modification (optimized loading level: 30 wt%) was formulated into a high-temperature polyquinoline (PQ-100). This guest/host system showed a much smaller E–O coefficient (less than 30 pm/V) and lower temporal stability (only retained $< 65\%$ of its original r_{33} value at $85 \text{ }^\circ\text{C}$ after 1000 h). In addition, the attempt to corona pole the non-trifluorovinyl ether functionalized dendrimer only showed a very fast decay of E–O signal ($< 10 \text{ pm/V}$) after the same sample was poled and measured at room



Scheme 2

temperature. This is due to its intrinsic low T_g ($< 50^\circ\text{C}$) and very large free volume. On the basis of this systematic study, the large r_{33} of the poled dendrimer is due to the dendritic effect that allows the NLO dendrimer to be efficiently aligned.

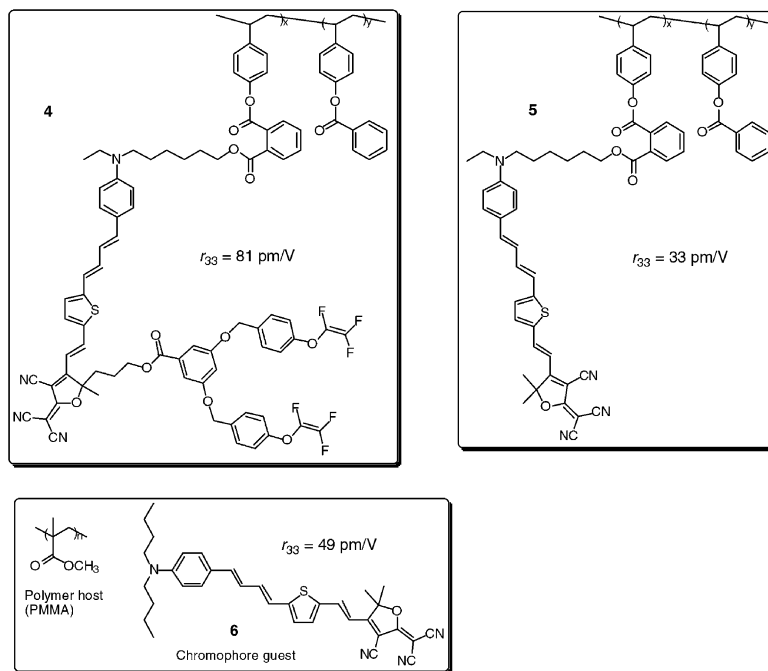
4. Side-chain dendronized NLO polymers [8]

To further optimize E–O material properties, a series of hybrid crosslinkable dendritic NLO polymers have also been developed to combine the synthetic simplicity and good processability offered by linear polymers and the excellent site-isolation effect provided by dendrimers. The first side-chain dendronized polymer **4** synthesized for this study is illustrated in Scheme 3. The poled film of **4** (contact poling) showed a very large E–O coefficient ($r_{33} = 81 \text{ pm/V}$) at $1.3 \mu\text{m}$. In order to provide a systematic comparison, E–O properties derived from the conventional side-chain and guest/host polymers bearing a similar chromophore with the same loading level were also studied.

The E–O activity of side-chain dendronized polymer **4** is significantly higher than those obtained from the side-chain polymer **5** and the guest–host polymer

system (**6**/PMMA). The low E–O coefficients of the poled films **5** and **6**/PMMA indicate that strong chromophore–chromophore electrostatic interactions significantly limit the attainable E–O activities in ordinary NLO polymeric systems that do not have effective site isolation moieties. Although several other factors, such as conductivity of the samples and different polymer matrix may also affect the E–O activities of the materials, the contribution of these factors can be limited to a minor factor. For example, in both side-chain polymers **4** and **5**, the same polystyrene-based backbone and poling electric fields were utilized; however, the r_{33} value of the side-chain dendronized NLO polymer **4** is ~ 2.5 times higher than that of the pristine side-chain NLO polymer **5**. Therefore, high poling efficiency obtained in the poled film of **4** is mainly due to better site isolation that allows the chromophores to be spatially well distributed and efficiently oriented. This result is also quite consistent with the poling behaviors obtained from both the E–O dendrimer and the dendritic NLO chromophore doped polymer previously described.

More interestingly, the poled polymer **4** with such a large free volume and without even crosslinking can still retain more than 90% of its original r_{33} value after



Scheme 3

several hundred hours at room temperature. This may be because the bulky dendrons provide quite a large steric hindrance and inhibit the free rotation of the polymer chains.

When this new molecular engineering concept was applied to a more efficient NLO molecule (a CLD-type chromophore), extremely large E–O coefficients ($r_{33} = 97$ and 111 pm/V at $1.3 \mu\text{m}$) were achieved from the poled side-chain dendronized NLO polymer **7** and **8**, respectively. To our knowledge, these values are among the highest one ever reported for side-chain NLO polymers (Fig. 2). These values are also superior to those reported from the CLD-based guest-host E–O polymer systems, resuming the high poling efficiency of all the dendron-containing NLO materials mentioned above.

Polymer **8** also displays a very interesting macromolecular structure. The densely packed bulky side groups may self assemble to cause the flexible polymer main chain to form a cylindrical rod shape (Fig. 3) [9–11]. The NLO chromophores are expected to be well spatially isolated in the channels of such formed cylindrical structures. Moreover, due to the high rigidity of this type of polymers, the commonly observed chain entanglement in linear polymers should also be suppressed. This may provide a new paradigm to mo-

lecular engineer the morphology and properties of NLO materials to the next level.

5. Crosslinkable low optical loss dendrimers

For fabricating integrated optical waveguide devices based on the above active dendrimers, the development of low optical loss crosslinkable passive dendrimers is quite important because they can provide a more compatible and better index-matched cladding material. Crosslinkable fluorinated dendrimers can also provide good processability (high solubility and low viscosity to allow high solid content in solution formulation) and low optical loss compared to linear polymers. In the literature, there are many examples describing the incorporation of fluorocarbons into the periphery of dendrimers that leads to the formation of amphiphilic fluorinated dendrimers with surfactant-like properties [12]. However, there is hardly any report discussing the use of crosslinkable fluorinated dendrimers in optical waveguide devices.

Recently, we have developed a series of highly fluorinated crosslinkable dendrimers such as macromolecule **9** that possesses most of the desirable properties needed for the fabrication of optical waveguides [13] (Scheme 4). The trifluorovinyl ether-containing den-

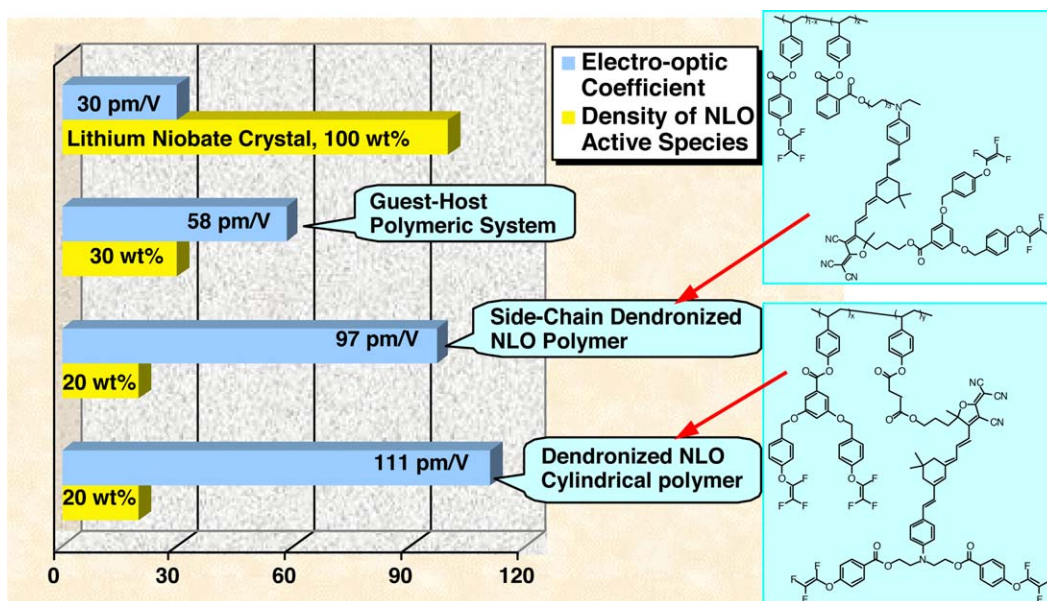


Fig. 2. Property comparison between side-chain dendronized NLO polymers and guest-host system containing the similar CLD-type chromophore.

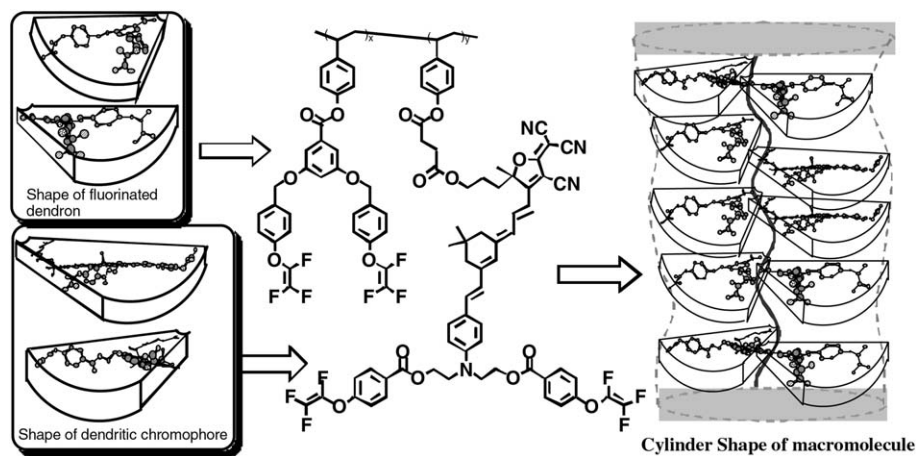
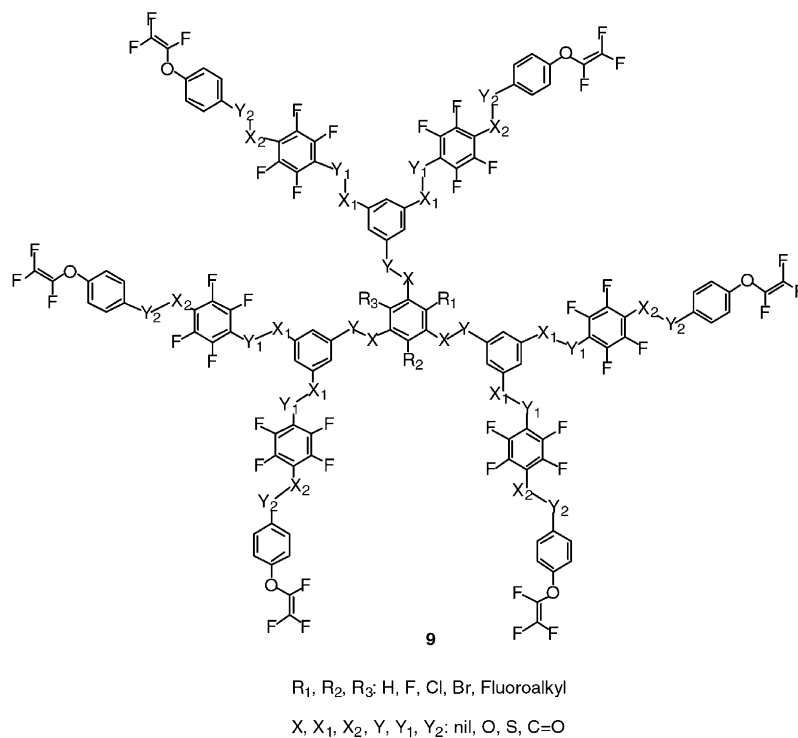


Fig. 3. Site-isolation effect in cylinder-like dendronized NLO polymer.



Scheme 4

dendrimer **9**, with a M_w of 18 000 can still be formulated into non-polar solvent like mesitylene to afford a very high solid content (50 wt%). Preliminary data from the PDS optical loss measurements have shown that the optical loss for the crosslinked dendrimer **9** (cured at 225 °C for 20 min) are as low as 0.36 and 0.52 dB cm⁻¹

at 1300 and 1550 nm, respectively. Since this sample contains ~1 wt% DCM dye as dopant for proper PDS calibration, the intrinsic optical loss of the dendrimer should be even lower. This dendrimer also possesses very good solvent resistance after curing that makes it suitable for multilayer integration.

6. Summary and outlook

Compared to conventional molecular design for organic NLO materials, the concept of using nanoscale architectural control to tailor the size, shape, conformation, and functionality of NLO chromophores and macromolecules provides a great opportunity for simultaneous optimization of macroscopic electro-optic activity, thermal stability, and optical loss. All the results discussed in this review are extremely encouraging and this new approach may help to launch a new paradigm for the molecular engineering of next generation high-performance E–O materials.

For the dendron-modified NLO chromophore/polymer systems, the interaction between chromophore and high T_g aromatic polymer should be further investigated in addition to the chromophore-chromophore electrostatic interactions. For the crosslinkable NLO dendrimers and side-chain dendronized NLO polymers, the environment such as dendron shape, size, dielectrics, hydrophilicity/hydrophobicity, rigidity and chirality, and the distribution of chromophores inside the macromolecular environments will play a very critical role for achieving the maximum realizable macroscopic NLO properties. With all these integrated efforts, the realization of the full potential of organic NLO materials will be unprecedented.

Acknowledgements

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