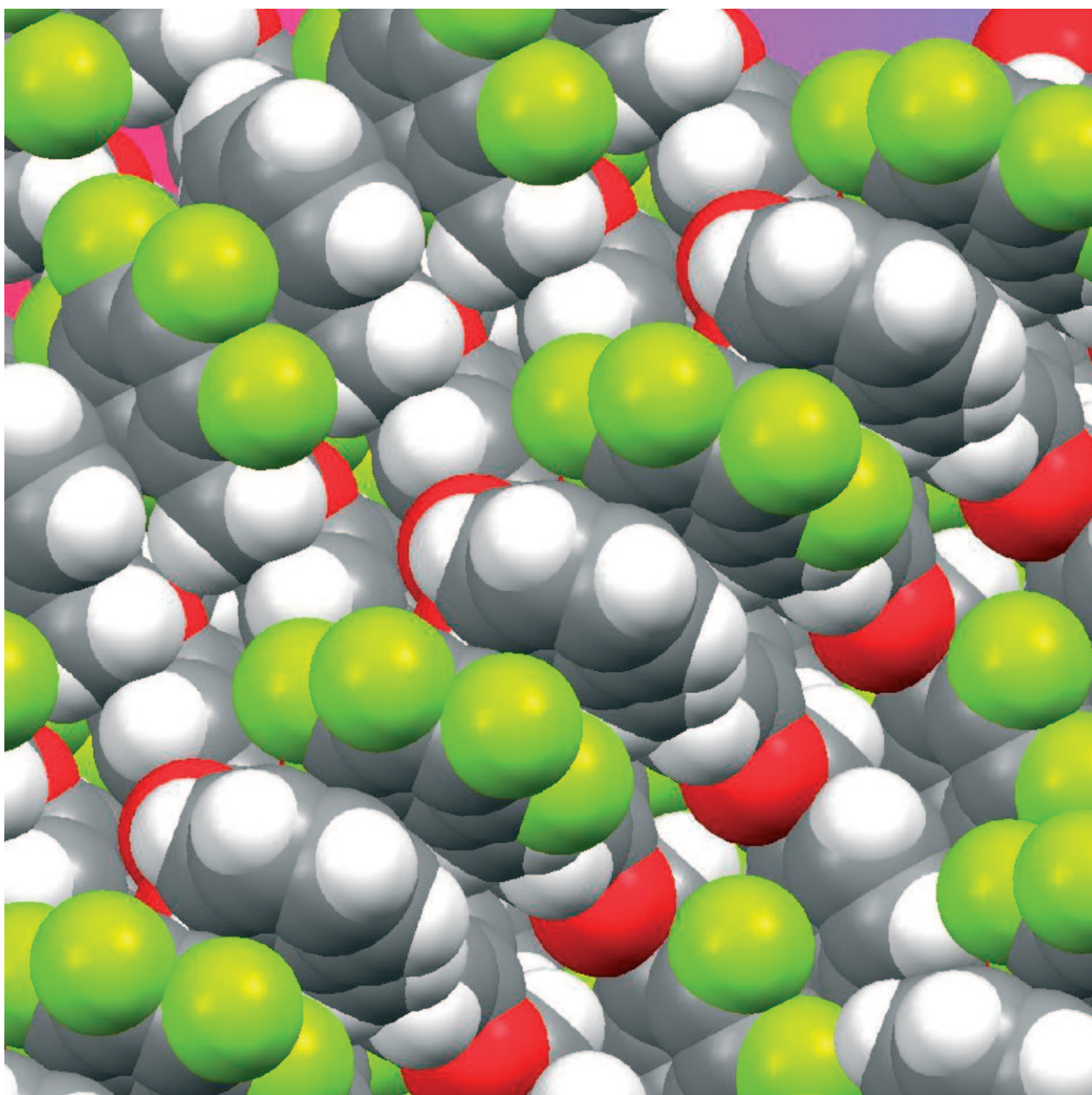


## Electro-Optic (E-O) Molecular Glasses

Sei-Hum Jang and Alex K-Y. Jen<sup>\*[a]</sup>



**Abstract:** This Focus Review describes molecular glasses as a new class of materials for nonlinear optical (NLO) applications, especially for electro-optic (E-O) devices. Examples of E-O molecular glasses are reviewed with a focus on the molecular design of NLO chromophores and solid-state engineering of molecular glasses. Molecular glasses based on dendrimers of multiple chromophores, molecular glass blends of chromophores, and molecular glasses based on reversible self-assembly of chromophores

are introduced as promising architectures to prepare morphologically stable molecular glasses with large E-O activities and improved material properties for device applications. Future directions to fully exploit the potential of molecular glasses for NLO materials are presented.

**Keywords:** amorphous materials • chromophores • molecular glasses • nonlinear optics • self-assembly

## 1. Introduction

Amorphous molecular materials represent a new class of materials for photonics and optoelectronic applications owing to their good processability, transparency, and uniform physical properties.<sup>[1]</sup> For example, they have been used extensively for organic electroluminescent (EL) devices and photoresists for semiconductor processing. However, small organic molecules with rigid molecular structures and limited conformational flexibility tend to crystallize readily below their melting temperatures. Therefore, their molecular structures should be properly designed to lower the rate of crystallization to form stable amorphous materials above room temperature.

Among the many applications that use amorphous molecular materials, small-molecule-based EL devices consisting of multilayer molecular glass thin films with charge-transporting and light-emitting properties have been extensively investigated and reviewed.<sup>[2]</sup> The amorphous molecular materials can also be used for high-resolution lithography as a result of their uniform distribution, which is free of chain entanglements. The conventional polymer-based photoresists have intrinsic limitations for sub-50 nm resolution owing to the optical scattering from structural features of polymers.

To date, most of the nonlinear optical (NLO) molecular glasses have been developed for photorefractive applications.<sup>[3]</sup> Limited E-O materials have been demonstrated since 1989 that are based on molecular glasses of NLO chro-

mophores.<sup>[4]</sup> This is due to their relatively low E-O activities and thermal properties. Recently, many highly efficient NLO chromophores with conformational flexibilities and sterically demanding hydrophobic substituents have been found by Jen and co-workers to form monolithic molecular glasses readily with good thermal properties.<sup>[5]</sup> The general material design strategy has been demonstrated to improve the E-O activities and thermal properties further through the binary chromophore molecular glass composites. Moreover, it was discovered that extended random supramolecular self-assembly of chromophores based on noncovalent interactions can be used to prepare stable amorphous E-O materials.<sup>[6]</sup>

In this article, recent progress in the amorphous molecular E-O materials (molecular E-O glasses) is reviewed with a focus on the molecular engineering of materials. The molecular architectures of chromophores and properties of molecular glasses for E-O device applications are described. Reversible self-assembly of highly efficient NLO chromophores formed by the arene-fluoroarene (Ar-Ar<sub>F</sub>) interactions are introduced as building blocks to randomly organize amorphous molecular structures in the solid state. Future research directions to fully exploit the potential of molecular glasses for E-O materials are also presented.

## 2. Molecular Glasses

Amorphous molecular materials are of interest because of their unique macroscopic structures and properties. An ideal molecular amorphous solid is defined as a geometrical structure with perfectly random packing of molecules.<sup>[7]</sup> Since the structure of each molecule affects the packing of molecules in the solid state, the formation and stability of molecular glasses is strongly dependent on the conformational flexibili-

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ty of molecules and intermolecular interactions between them.

Since an amorphous solid is not in a state of thermodynamic equilibrium, molecular glasses can undergo macroscopic relaxation depending on their molecular structures and intermolecular interactions, and exhibit glass-transition behavior that is commonly observed for amorphous polymers. Several characterization techniques like differential scanning calorimetry (DSC), polarizing microscopy, X-ray diffraction (XRD), and Raman spectroscopy are commonly used to study the phase transition of molecular glasses. However, the elucidation of the phase-transition behavior of amorphous molecular materials can be rather complex.

The glass-transition temperature ( $T_g$ ) is the most important parameter to understand the thermal stability of amorphous molecular materials. The  $T_g$  value of molecular glasses can be considered as the temperature at which molecular motions of a group of molecules begin to take place, resulting in a change in the distributions of distances between molecules and the relative orientation of individual molecules. It can be increased proportionally to the increase of the molecular weight, and by the introduction of structurally rigid or sterically demanding molecular components such as polycyclic aromatic groups.

Detailed studies of the relationship between molecular structures and glass-forming properties and stability of the amorphous state have provided several important guidelines

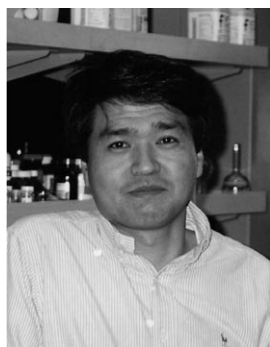
for the design of molecular glasses.<sup>[1]</sup> In addition to the conformational complexities, the introduction of asymmetric (or chiral), bulky, or heavy substituents has been shown to increase the number of conformers and change the mode of packing of the molecules. As a result, crystallization of these molecules is hindered and the formation of glass becomes more favorable and stable.<sup>[8]</sup> Moreover, the incorporation of heavy substituents tends to hinder translational, rotational, and vibrational motions of the molecule, leading to an increase in  $T_g$ . Nonplanar molecular structure has also been proposed as a supplemental approach for the formation of stable amorphous glasses.

Like amorphous polymers, homogeneous and isotropic molecular glasses can be prepared without noticeable phase separations. However, contrary to amorphous polymers having chain entanglement in high-molecular-weight polymers, the local free volumes of amorphous molecular glasses are dependent on the distances between molecules and their relative orientations. The positron annihilation lifetime (PAL) technique can be used to measure the free volume of amorphous materials.<sup>[9]</sup> The PAL technique probes the free volume of amorphous materials in that the positronium atom (a positron–electron bound state) is trapped in unoccupied regions of materials.

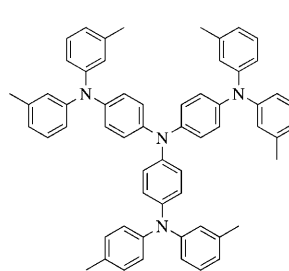
The average size of the free volume in molecular glasses of a series of polyaromatic amines such as *m*-MTDATA (**1**) and *m*-MTDAPB (**2**) have been estimated by Kusumoto and



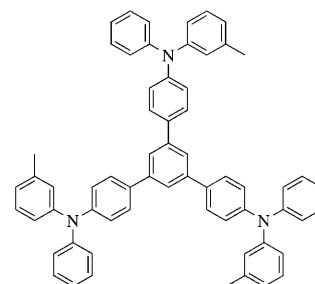
**Alex K.-Y. Jen** is currently the Boeing–Johnson Chair Professor in the Department of Materials Science & Engineering and Professor of Chemistry at the University of Washington. For his contributions in molecular engineering of organic photonics and electronics, Jen was selected as a Fellow by the American Association of the Advancement of Science (AAAS) in 2005, the International Society of Optical Engineering (SPIE) in 2006, and by the Optical Society America (OSA) in 2007. His interests include the interdisciplinary areas of organic functional materials and devices for opto-electronics and photonics, and molecularly or biologically inspired self-assemblies for sensing and electronics.



**Sei-Hum Jang** received his PhD in physical organic chemistry from Michigan State University in 1993 working with Professor Jame E. Jackson. He was a principal research scientist at the Institute for Advanced Engineering in Korea from 1997 to 2000, and has been a research scientist in the group of Professor Jen since 2003. His main research fields are in materials chemistry, focusing on the molecular engineering of materials for device applications.



*m*-MTDATA (**1**)  
Molecular Weight: 831.10



*m*-MTDAPB (**2**)  
Molecular Weight: 850.10

co-workers, and compared with that of polystyrene using the PAL technique.<sup>[10]</sup> They found that the average size of the free volume of the molecular glasses was about 70% that of a polystyrene glass at 30 °C, (**1**: 80 Å<sup>3</sup>, **2**: 87 Å<sup>3</sup>, polystyrene: 120 Å<sup>3</sup>) and the average size of the free volume of molecular glasses increases with increasing molecular size. It has been suggested that the local free volume of molecular glasses made of compounds **1** and **2** are not large enough for the whole molecules to isomerize or reorient at 30 °C.

One of the major advantages of using molecular glasses for device applications is their good processability. Uniform thin films of molecular glasses can be prepared by various fabrication techniques, for example, spin coating from solution, vacuum vapor deposition, electrochemical deposition, and layer-by-layer self-assembly methods. Both ordered and



disordered films can be prepared, depending on the fabrication methods. Furthermore, since molecular glasses are made of discrete molecular structures with finite molecular weights, general preparative organic chemistry can be used not only for purifying these materials, such as by sublimation, chromatography, or recrystallization, but also for producing materials with uniform physical properties.

To use molecular glasses for device applications, both thermal and morphological stability of the materials is required. Thus, it is necessary to design molecular glasses with high  $T_g$  values. Even though structural modifications of molecules with rigid substituents can increase the  $T_g$  value of the resulting molecular glasses, such modifications may also significantly lower the conformational flexibility of the molecules required to form stable molecular glasses. Therefore, structural modification of molecules to increase the  $T_g$  values of molecular glasses can be a trade-off for morphological stability of molecular glasses. Self-assembly of molecules through noncovalent intermolecular interactions such as hydrogen bonding or electrostatic interactions can provide balanced material design approaches to increase  $T_g$  while maintaining the random packing of molecules to form morphologically stable molecular glasses.

### 3. Organic E-O Materials

The electric and magnetic field components of light can interact with electrons in organic molecules to induce polarization of the electrons. The induced polarization of electrons is linearly proportional to the strength of the electric field with a weak intensity of light. However, with increasing intensity of light having a stronger electric field component, the polarization of  $\pi$  electrons in organic molecules can be nonlinearly proportional to the applied electric field of light. The magnitude and direction of the nonlinear responses of materials are dependent on the electronic structure of the molecules used and their macroscopic arrangements in the solid state. Thus, the nonlinear response of organic molecules and materials can be optimized through careful engineering of their chemical structures.

To be active for E-O applications, the macroscopic arrangement of dipoles of NLO chromophores should be non-centrosymmetric (polar). In organic NLO materials, the macroscopic polar order of NLO chromophores can be generated by various techniques to orient their dipoles, such as electric field poling, photon-assisted electric poling, and photochemical (all-optical) poling. In electric field poling, a strong DC electric field (typically about  $100 \text{ V } \mu\text{m}^{-1}$ ) is applied to induce the reorientation of dipolar NLO chromophores in solid solutions when the materials are heated near or above the  $T_g$ . By cooling the materials below the  $T_g$  while the poling field is applied, the noncentrosymmetric arrangement of the dipolar NLO chromophores can be “frozen in” to form poled polymers.<sup>[11]</sup>

The macroscopic E-O coefficient ( $r_{33}$ ) of molecular NLO materials to an external field is proportional to the scalar

product of the ground-state dipole moment  $\mu$  and the molecular hyperpolarizability  $\beta$  of dipolar NLO chromophores with acentric order. Efficient translation of large hyperpolarizability of chromophores into thermally and chemically stable polymeric E-O materials can be achieved by careful modification of molecular structures of chromophores and host polymers. Recently, polymeric E-O materials have shown commercial potential as active media in high-speed broadband waveguides for optical switches, optical sensors, and information processors.<sup>[12]</sup>

In principle, the guest–host system (the dispersion of guest NLO chromophores in a supporting host polymer) is the most straightforward way to produce polymeric E-O materials. There are many commercially available optical polymers such as amorphous polyacrylates and polycarbonates that can be used as host polymers. Usually, the perfectly aligned dipolar NLO chromophores with large hyperpolarizability in a polymer composite is the ideal configuration in maximizing the macroscopic E-O activity of materials. However, such arrangements of NLO chromophores with very large ground-state dipole moments are not thermodynamically stable even at low concentrations. Therefore, one of the major challenges in the development of organic E-O materials based on dipolar NLO chromophores is to optimize the size and shape of the molecules to minimize the formation of strong electrostatic dipole–dipole interactions that produce centrosymmetric aggregates of chromophores in the solid state. In some cases, controlled molecular-scale preorganization of acentric aggregates can enhance the poling efficiency, and therefore, the macroscopic E-O activities of the materials.

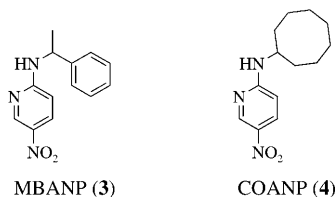
The electric-field-induced polar order of chromophores in poled polymers tends to decrease slowly with time. Generally, the long-term alignment stability (or temporal alignment stability) of guest–host polymers can be improved by increasing the poling temperature (or  $T_g$  of the host polymer) relative to the device operation temperature. Since chromophores in a guest–host polymer can act as plasticizers and lower the  $T_g$  value of the polymer composite, the use of high- $T_g$  host polymers is advantageous to improve the temporal alignment stability. However, many highly efficient dipolar NLO chromophores can thermally decompose during the high-temperature poling process, and the choice of high- $T_g$  host polymers is limited by the thermal stability of the chromophores.

### 4. Molecular E-O Glasses

As described, molecular engineering of chromophores and polymers can be used to modulate the strong electrostatic interactions between chromophores and improve the poling efficiency of polymeric E-O materials. However, such modification of molecular structures can add significant passive weight to the materials and effectively lower the E-O activities of polymeric E-O materials.

The most important advantage of a monolithic molecular E-O glass is that the volume fraction of active chromophores can be maximized without phase separation. The chromophores can often separate from host matrices as aggregates or crystallites in polymeric E-O materials, especially with a very high loading concentration of chromophores (number density,  $N > 2.5 \times 10^{20} \text{ cm}^{-3}$ ). Since the molecular E-O glasses are made of molecular components with discrete molecular structures and weights, reproducible physical and optical properties of the materials are expected also.

In 1989, Eich and co-workers introduced the first examples of monolithic molecular E-O glasses based on small organic molecules, (*S*)-2-*N*- $\alpha$ -(methylbenzylamino)-5-nitropyridine (MBANP, **3**) and 2-*N*-(cyclooctylamino)-5-nitropyridine (COANP, **4**), as a new class of NLO materials.<sup>[4]</sup> They



found that some NLO-active molecules can be supercooled into amorphous states, at relatively slow cooling rates of about  $10^\circ\text{C min}^{-1}$  during the studies of crystalline organic NLO materials. MBANP and COANP showed extremely slow rates of crystallization near the glass-transition temperatures,  $0^\circ\text{C}$  and  $-10^\circ\text{C}$ , respectively. These glasses could be poled by applying an electric field to produce a polar arrangement of dipoles above  $T_g$ , and cooled to temperatures below  $T_g$  to generate the polar order. However, amorphous phases of monolithic molecular glasses based on small molecules are not thermodynamically stable at high temperatures in general, and do not have physical properties suited for device applications.

Recently, Ishow and co-workers reported monolithic molecular E-O glasses of small NLO chromophores with acentric order. Optical-quality films of the molecular E-O glasses with improved thermal properties were directly prepared by physical vapor deposition using small NLO chromophores with aromatic electron donor groups connected through short conjugation bridges to groups with varying acceptor strength. These are the first genuine examples of amorphous organic E-O materials formed by spontaneous self-assembly of small NLO chromophores.<sup>[13]</sup> However, the molecular glasses are not thermodynamically stable and lose the acentric order when heated above glass-transition temperatures ( $74\text{--}96^\circ\text{C}$ ) as evidenced by the disappearance of NLO activities ( $d_{33} = 0.1\text{--}17 \text{ pm V}^{-1}$ ).

Recently, many highly efficient NLO chromophores with conformational flexibilities and sterically demanding hydrophobic substituents have been found by Jen and co-workers that can form molecular glasses readily with good thermal properties.<sup>[5]</sup> Nevertheless, the physical properties of molec-

ular glasses based on relatively small NLO chromophores may not be robust enough for certain device applications. To be useful for device applications, the molecular E-O glasses should have thermal and morphological stability, process compatibility with device fabrications, and good solubility in common organic solvents. Several material design approaches to overcome such challenges while maintaining the advantages of molecular E-O glasses will be described in the following sections.

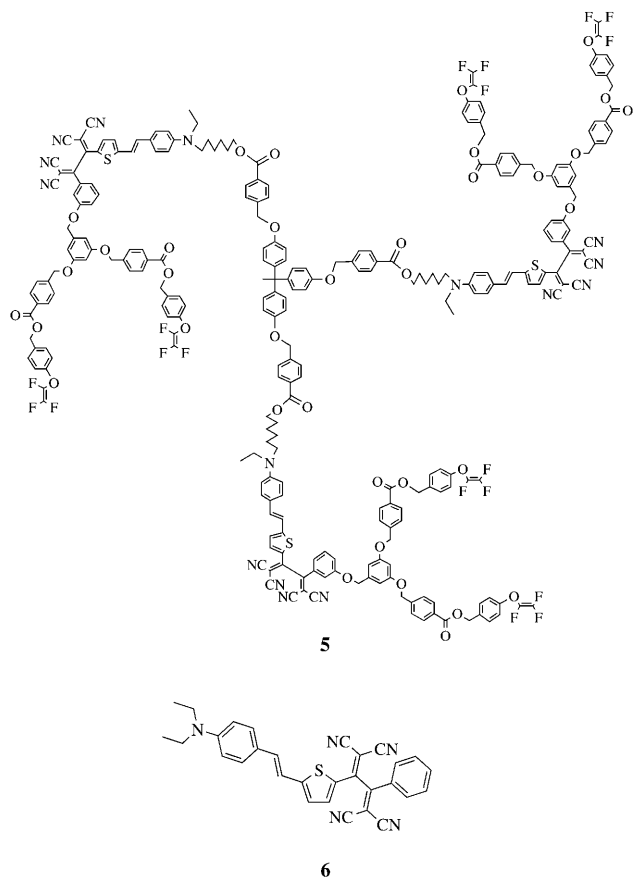
#### 4.1. Dendrimer Glasses

One of the molecular architectures with improved thermal and physical properties of E-O glasses for device application is a dendrimer of chromophores, an assembly of multiple chromophores connected by a simple dissymmetric core structure. The improved thermal and glass-forming properties of molecular glasses based on the dendrimer are mainly due to the random distribution of various conformers of flexible chromophores<sup>[14]</sup> and the relatively large molecular weight of such structures. Dendrimers are a relatively new class of macromolecules different from the conventional linear, cross-linked, or branched polymers. Dendrimers are especially interesting because of their nanoscale dimensions and their regular, well-defined and highly branched three-dimensional architectures. Contrary to linear polymers, these new types of macromolecules can be viewed as an assembly of chromophore building blocks.

Among many dendrimer architectures dendrons, or dendritic modification of bulky substituents, are especially useful for organic E-O materials. For example, the first and second generations of “Frechét-type” dendrons with peripheral perfluoro groups have been shown to be useful to minimize absorption optical loss from the vibrational overtone of C–H groups by substitution with C–F groups. Careful selection and location of the fluorinated dendron in chromophore structures have led to a lowering of the electrostatic dipole–dipole interactions and improvement of poling efficiency, even for highly efficient NLO chromophores with very large ground-state dipole moments.<sup>[15]</sup> Moreover, an envelope of fluorinated dendrons around chromophores can improve the solubility and compatibility of chromophores with host matrices while maintaining excellent dielectric properties of the materials.

A dendrimer of multiple NLO chromophores that branch out from a passive but dissymmetric core can be constructed with predetermined chemical composition. The globular geometry of dendrimers is ideal for efficient poling, and the large void within the dendrimer structure can provide free volume for efficient reorientation of the chromophores. In such structures, the terminal functional groups can be anchor points to build up the next generation (layer) of multiple NLO chromophore blocks, or functionalized with peripheral groups. The terminal groups can be used to screen chromophores from each other, to control their solubility and processability, to improve the chemical and photochemical stability of the materials, and to improve the temporal

stability of poled materials by incorporating various cross-linkers for postpoling lattice-hardening processes. Furthermore, the controlled intra- and intermolecular interactions between chromophores and dendrimers may provide spontaneous local polar order to further enhance the poling efficiency. For example, a molecular E-O glass based on cross-linkable dendrimer **5** exhibits a large optical nonlinearity



and excellent thermal stability. The NLO dendrimer was constructed through a double-end functionalization of the three-dimensional Ph-TCBD chromophores as the center core and the cross-linkable trifluorovinylether-containing dendrons as terminal cross-linkers.<sup>[16]</sup> In dendrimer **5**, the chromophore core is spatially isolated by the fluorinated dendrons that decrease electrostatic interactions between the chromophores and enhances the macroscopic optical nonlinearity. In addition, the NLO dendrimer can be directly spin-coated to form a monolithic molecular glass with a large molecular weight (4664 Da) after evaporation of the solvents without any prepolymerization process to build up viscosity. The chromophore loading density of 33 wt % of dendrimer **5** is rather high, and no indication of phase separation between the chromophore and the peripheral dendrons was observed.

Several additional advantages exist in the case of molecular glass **5**, such as excellent alignment stability and mechan-

ical properties, which are obtained through the sequential cross-linking reactions (140–190 °C) during the high-temperature (165–190 °C) electric field poling process. A large E-O coefficient ( $r_{33}$  value of 60 pm V<sup>-1</sup> at 1.55  $\mu$ m) and temporal alignment stability (retaining greater than 90 % of its initial  $r_{33}$  value for more than 1000 h at 85 °C) were achieved for the poled and cross-linked molecular E-O glass. In comparison, E-O studies performed on the guest–host polymer film of similar chromophore **6** (30 wt %) in a polyquinoline (PQ-100) showed a much smaller  $r_{33}$  value of less than 30 pm V<sup>-1</sup> and lower temporal stability.

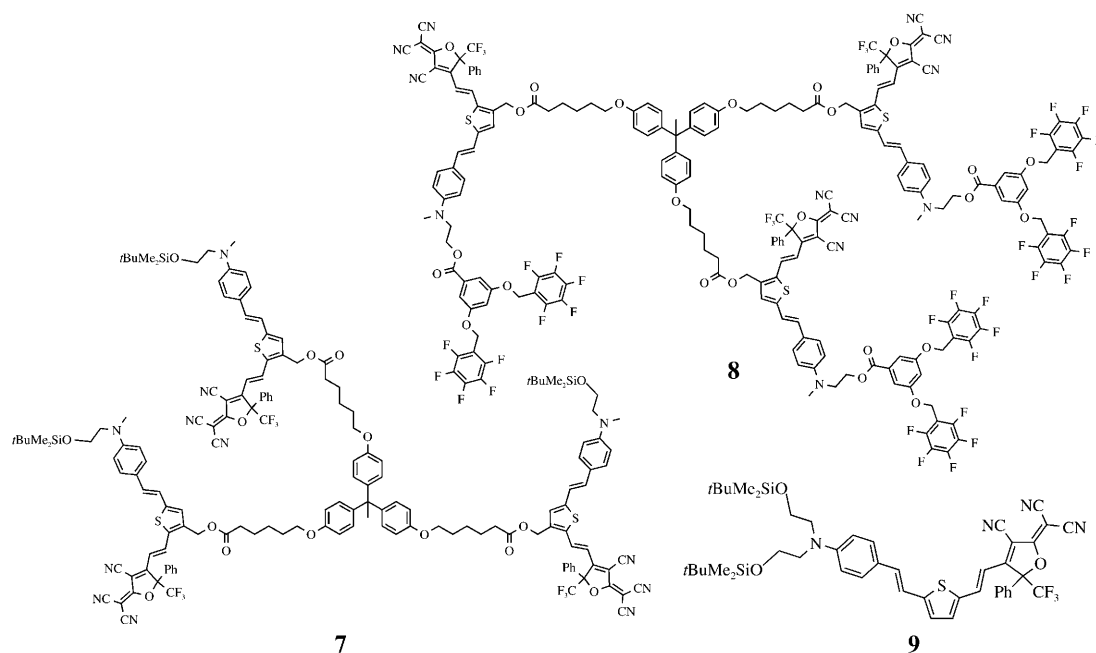
Recently, additional molecular E-O glasses based on dendrimers of multiple chromophores have been reported.<sup>[17]</sup> The design parameters for the dendrimers **7** and **8** were rationalized by statistical and quantum mechanical modeling. The E-O activities of monolithic molecular glasses of dendrimers **7** and **8** were measured to be 140 and 90 pm V<sup>-1</sup>, respectively, while the value for comparable guest–host polymers based on chromophore **9** in amorphous polycarbonate (APC;  $N = 1.78 \times 10^{20}$  cm<sup>-3</sup>) was previously reported as 52 pm V<sup>-1</sup>.<sup>[18]</sup>

The dendrimers showed a linear relationship between the chromophore number density  $N$  and E-O activities up to an extremely high net chromophore loading density of  $N = 6.45 \times 10^{20}$  cm<sup>-3</sup> for dendrimer **7** and  $N = 4.6 \times 10^{20}$  cm<sup>-3</sup> for dendrimer **8**. The linear relationship is a significant deviation from the usual saturation behavior of E-O activities based on the conventional guest–host polymers as described earlier. These results provide new insight into the ordering behavior of E-O materials based on dendrimers to overcome the dependence of E-O activity on the chromophore number density through rational design of molecular structures of chromophores.

To understand the linear relationship between E-O activity and chromophore number density further, the poling efficiency has been defined as the slope,  $r_{33}/E_p$ , of a linear plot of E-O activity,  $r_{33}$ , with respect to electric field,  $E_p$  (V  $\mu$ m<sup>-1</sup>), applied at optimum poling temperature for a given material. Compared to the poling efficiency ( $r_{33}/E_p$ ) of chromophore **9** in an APC host polymer of 0.45 (nm V<sup>-1</sup>)<sup>2</sup>, dendrimers **7** and **8** showed  $r_{33}/E_p$  values of 1.42 and 1.04 (nm V<sup>-1</sup>)<sup>2</sup>, respectively. That is, the molecular glass based on dendrimer **7** showed a rather significant improvement of poling efficiency over a guest–host polymer based on chromophore **9** by a factor of 3.

#### 4.2. Self-Assembled Molecular Glasses

Another class of molecular architectures with improved thermal and physical properties of molecular E-O glasses is a random reversible self-assembly of multiple chromophores by noncovalent intermolecular interactions. Even if the smaller free volume in molecular glasses relative to E-O polymers can lower the poling efficiency, the temporal alignment stability of poled molecular glasses can be improved significantly, especially if the polar order can be stabilized by supramolecular self-assembly.



There are various noncovalent intermolecular interactions that can be used for the construction of the supramolecular self-assembly of chromophores in molecular glasses based on a large database acquired from crystal engineering of NLO crystals. These include electrostatic interactions between charges, multiple hydrogen bonds, metal–organic ligand coordination,  $\pi$ – $\pi$  aromatic interactions, and van der Waals interactions between functional groups of chromophores and the chromophores themselves. Some or all of the interactions can be simultaneously used in the design of self-assembly of chromophores to control structures and properties of molecular glasses. We will focus on the supramolecular self-assembly of NLO chromophore glasses based on the  $\pi$ – $\pi$  aromatic interactions and van der Waals interactions here to demonstrate the potential of such approaches.

One of the most attractive  $\pi$ – $\pi$  aromatic interactions for the self-assembly of chromophores is the arene–fluoroarene ( $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$ ) interaction. Since organic materials based on  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  interactions are not widely known yet, we shall explain the interaction in more detail here. Benzene and hexafluorobenzene are known to cocrystallize with a melting point more than 18°C higher than either component in nearly parallel alternating molecular stacks with an interplanar distance of 3.4 to 3.7 Å.<sup>[19]</sup> The stabilization energy of the benzene–hexafluorobenzene dimer from both computational and experimental studies was estimated to be between 4 and 5 kcal mol<sup>−1</sup>. The interaction can be rationalized mostly on the basis of the complementary quadrupole moments of benzene ( $-29.0 \times 10^{-4} \text{ C m}^{-2}$ ) and hexafluorobenzene ( $+31.7 \times 10^{-4} \text{ C m}^{-2}$ ), which are similar in magnitude but opposite in sign.<sup>[20]</sup> The formation of parallel alternating infinite molecular stacks is a common structural feature of all molecular  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  complexes reported (Figure 1).

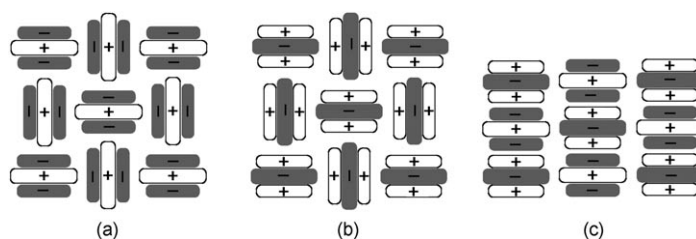


Figure 1.  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$ ,  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$ , and  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  in the crystal of a) benzene, b) hexafluorobenzene, and c) alternating stacks of benzene–hexafluorobenzene cocrystal.

The  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  interaction has attracted growing interest in diverse fields of molecular design<sup>[21]</sup> and is now being accepted as a reliable synthon in crystal engineering.<sup>[22]</sup> Moreover, the  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  interaction has been used in recent years to control supramolecular organization in reversible media such as liquid-crystalline phases and the hydrogel formation of polymers and oligomers.<sup>[23]</sup>

For some time, it has been asked whether the  $\text{Ar}^{\text{F}}\text{--Ar}^{\text{F}}$  interaction can be explored for the construction of a reversible supramolecular self-assembly of NLO chromophores to form morphologically stable molecular glasses that can be poled by an electric field and cross-linked into a robust extended network of NLO chromophores with acentric order, and improved material properties. To be useful for E-O materials, the self-assembly unit should be designed to be sufficiently strong to form a reliable and reproducible extended structure using mild solution processing. In addition, it should be flexible enough to be randomly reorganized with control, using minimal external energies (electric field). Furthermore, it would be very intriguing to design a molecular

glass based on spontaneous supramolecular self-assemblies of NLO chromophores with acentric order by modulating the balance between competing dipolar and quadrupolar electrostatic interactions between chromophores.

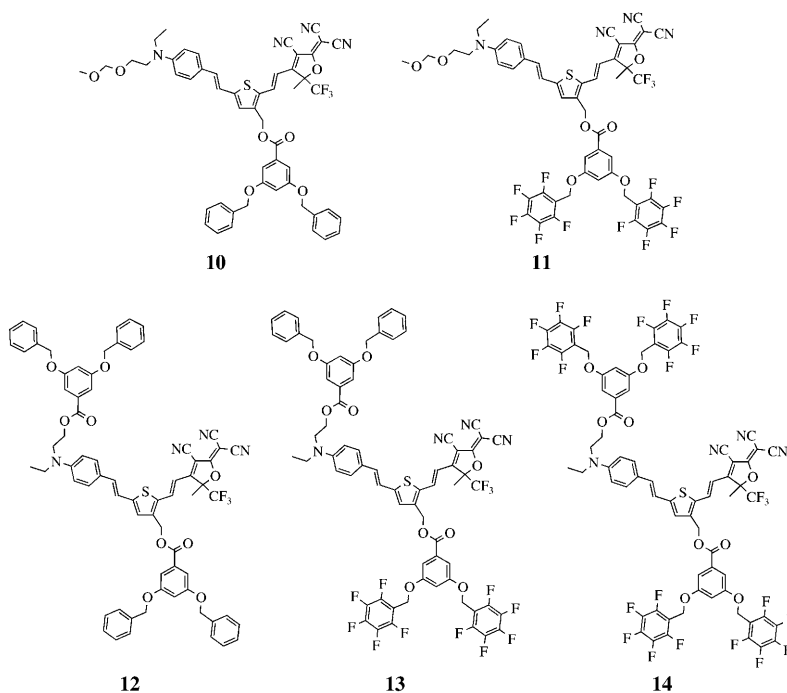
As described above, systematic studies have shown that the structural modification of chromophores and polymers with fluorinated dendrons can lead to polymeric E-O materials with excellent materials properties. Much of the improvement in material performance is due to the use of fluorinated dendrons that have low optical loss, good solubility and processability, and excellent thermal stability with dielectric strength. The initial research interest in the field was to understand the effect of fluorinated dendrons as substituents on improving material properties through the shape modification of chromophores. Later on, it was extended to understanding intermolecular interactions between chromophores having different numbers of fluorinated dendrons with different molecular structures and locations within chromophores.

Particularly, understanding the effect of inter- and intramolecular interactions between electron-deficient fluorinated dendrons and electron-rich donors on the electronic structure of chromophores (intramolecular charge transfer band) and their aggregation behavior in the solid state were two of the main concerns. If the electron-deficient fluorinated dendrons can interact with electron-rich donor groups in neighboring chromophores by intermolecular interactions, then the interactions can be used not only to prevent the electrostatic dipole–dipole interactions between chromophores, but to preorganize or self-assemble chromophores into extended aggregate structures (J-aggregate) that can efficiently respond to an applied electric field by the conventional poling process.

Moreover, the approach to the self-assembly of chromophores based on the  $\pi$ – $\pi$  electron interactions between the fluorinated dendron and electron-rich donor of the chromophore has been extended to self-assembly of chromophores functionalized with electron-rich dendrons and electron-deficient dendrons both at the diagonal ends of the same chromophore. Reversible self-assembly of monolithic molecular glasses of chromophores based on intermolecular Ar–Ar<sup>F</sup> interactions can be generated from bifunctional chromophores, depending on the substitution patterns of functional dendrons. Such a molecular material design approach is general enough not only to apply to multiple chromophore sys-

tems (multiple chromophore solution) with the same set of dendrons, but also to extend to a reversible and physical postfunctionalization method of conventional polymers, and can be used to physically cross-link side-chain NLO polymers reversibly. An example of E-O materials based on self-assembly of monolithic chromophore glass is described in more detail here.

A series of systematically designed NLO chromophore glasses with rational substitution patterns for self-assembly has been developed recently by Kim and co-workers.<sup>[6]</sup> The molecular structures of the chromophores in the study are shown below. Both phenyl and pentafluorophenyl rings are incorporated diagonally as peripheral dendrons on the  $\pi$  bridge and the donor of the chromophores **12**, **13**, and **14**. Chromophores **10** and **11** are partially modified with den-



tems and cannot form an extended supramolecular assembly by Ar–Ar<sup>F</sup> interactions. No melting point was detected for the series, indicating that they represent a noncrystalline phase. The  $T_g$  value increased with molecular weight. Glass-transition temperatures of the chromophore glasses were determined by DSC to be 56, 63, 57, 75, and 76 °C for **10**, **11**, **12**, **13**, and **14**, respectively. Especially, as expected from the Ar–Ar<sup>F</sup> interactions, chromophore **13** shows a significantly increased  $T_g$  value (18 °C) compared to those obtained from **12**. The thermal transitions are also consistent with the  $T_g$  value of composite **15**, which is a 1:1 mixture of chromophore **12** and **14**.

The molecular glasses based on the supramolecular self-assembly of engineered chromophore showed very large E-O activities, with good temporal alignment stability. Owing to the possible extended structure formed by Ar–Ar<sup>F</sup> inter-



actions, chromophore **13** gave the highest  $r_{33}$  value of  $108 \text{ pm V}^{-1}$  at  $1.3 \mu\text{m}$  among monolithic molecular glasses. This value is more than two times higher than those obtained from chromophores **12** or **14**, which do not have such interactions. Moreover, the composite **15** (1:1 blend of **12** and **14**) showed an  $r_{33}$  value of  $130 \text{ pm V}^{-1}$ . Again, the enhanced  $r_{33}$  value in this composite shows that it is also possible to form a supramolecular self-assembly between complementary but different chromophores. The fact that high electric fields of greater than  $100 \text{ V } \mu\text{m}^{-1}$  can be applied to pole chromophore **13** and composite **15** suggests improved dielectric properties of chromophore glasses of **13** and composite **15**. On the contrary, the  $r_{33}$  values measured for a guest–host polymer doped with 20 wt% of chromophore **11** in APC, and in a postfunctionalized side-chain NLO polymer, showed only 55 and  $52 \text{ pm V}^{-1}$ , respectively, using a higher poling field of  $130 \text{ V } \mu\text{m}^{-1}$ .

These poled molecular glasses could retain over 90% of their original  $r_{33}$  values at room temperature for more than two years. On the contrary, the temporal stability of the glasses without the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions deteriorated dramatically within one month. The decreased absorbance of the poled film (a direct optical evidence for dipole alignment) of the host **13** could recover more than 95% of its original value after being annealed for 20 min at a temperature close to its  $T_g$ . Moreover, the  $r_{33}$  values could be reproduced through poling and depoling cycles, thus demonstrating the stability of molecular glasses and reversibility of the supramolecular self-assembly of chromophores. A graphical illustration of the poling process of the supramolecular self-assembly of chromophore glasses of **13** is shown in Figure 2.

However, the relatively poor glass-transition properties of these chromophore glasses are not adequate for device application yet, and further studies are ongoing to improve the thermal properties by increasing the strength of the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions and molecular weights of the chromophores with more rigid structures, and by cross-linking the aligned chromophore glasses after poling. Physical and optical properties of **12**, **13**, **14**, and composite **15** are summarized in Table 1.

Table 1. Physical and optical properties of monolithic glasses of chromophores **12**, **13**, **14**, and **15**.

Material	$T_g^{[a]}$ [°C]	$N^{[b]}$ [ $\times 10^{20} \text{ cm}^{-3}$ ]	$\lambda_{\text{max}}^{[c]}$ [nm]	Applied voltage [ $\text{V } \mu\text{m}^{-1}$ ]	$r_{33}^{[d]}$ [ $\text{pm V}^{-1}$ ]	Temp. stab. <sup>[e]</sup> [%]
<b>12</b>	57	5.0	719	75	52	0
<b>13</b>	70	4.4	703	100	108	92
<b>14</b>	69	3.7	689	75	51	85
<b>15</b>	68	4.4	704	120	130	93

[a] Thermal transition temperature measured under nitrogen at a heating rate of  $5^\circ\text{C min}^{-1}$ . [b] Number density of core chromophoric moiety. [c] Absorption maxima of thin films by UV/Vis spectroscopy. [d] E-O coefficient measured at 1310 nm by simple reflection technique. [e] Temporal alignment stability at room temperature after 3 months.

Structural insight of the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions in the monolithic glasses has been provided by a single-crystal X-ray structure of a dimeric cocrystal of model compounds, a phenyl group terminated dendron and pentafluorophenyl group terminated dendron carboxylic acid (1:1). A space-filling structure of alternating cocrystal stacks is shown in Figure 3. The structure represents a clear solid-state evidence of the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions between peripheral dendron groups to form extended structures when the chromophores are substituted with a chemospecific combination of dendrons.

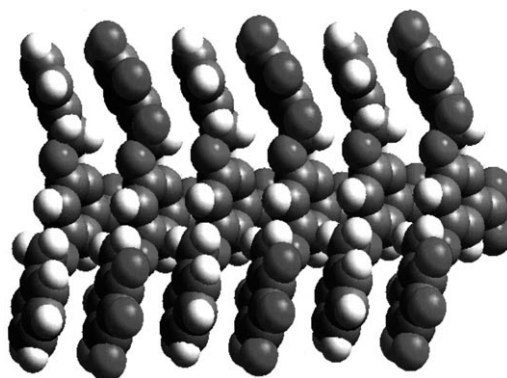


Figure 3. A space-filling single-crystal X-ray structure of alternating cocrystal stacks of self-assembling heterodimeric dendrons.

### 4.3. Molecular Glass Composites

As described above, reversible supramolecular self-assembly of chromophores based on the intermolecular  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions can be rationally designed to tune the aggregate structures of chromophores in the solid state. Such a molecular material design approach is proven to be general enough for multiple-chromophore systems (multiple-chromophore solutions) with a complementary combination of dendron structures. The supramolecular chromophore composite **15** was formed from a 1:1 solid solution of **12** and **14**, and the molecular glass composite illustrates an example of molecular glasses based on multiple chromophores.

In the composite **15**, the core structure of chromophores used was the same as in **12** and **14**. One could use different

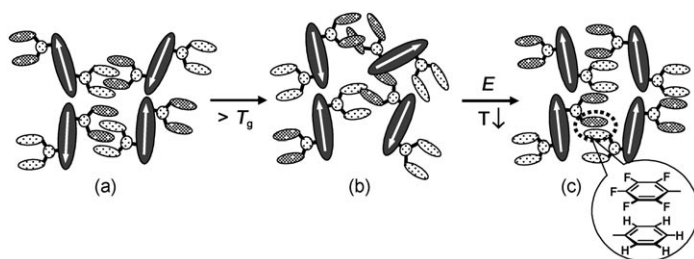


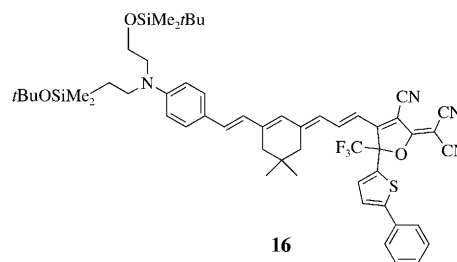
Figure 2. Graphical illustration of material processing sequences to generate the macroscopic polar order of supramolecular self-assembly of chromophore glasses by  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions and electric field poling. a) Amorphous supramolecular self-assembly of chromophores with random dipoles (shown as arrows) before poling. b) Mobile rubbery state with random dipoles before poling. c) Polar amorphous supramolecular self-assembly of chromophores after poling with subsequent cooling.

pairs of core structures as far as they have complementary dendron structures for the intermolecular  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions if the differences in core structures are not significant enough to phase separate each other or interfere with the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions between functional dendrons in the solid solution. One can also take combinatorial material approaches to make a series of solid solutions (composites) of two different chromophores with varying fractions. For example, molecular E-O glasses based on binary supramolecular chromophores with  $x:(1-x)$  mixtures of chromophores of different type  $\text{Ar}-\text{B}-\text{Ar}^{\text{F}}$  and  $\text{Ar}-\text{C}-\text{Ar}^{\text{F}}$  (chromophores B and C having dendrons Ar and  $\text{Ar}^{\text{F}}$ ) can be systematically designed and prepared. An example of such a material design approach to a series of composites made of a molecular glass and poly methyl methacrylate (PMMA) with varying volume fractions has been reported recently.<sup>[24]</sup>

Blends of multiple chromophores can form a completely new class of supramolecular molecular glasses as far as chromophores have complementary dendron structures for the intermolecular  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions, do not form strong centrosymmetric aggregates between multiple chromophores, do not phase separate each other, or interfere with the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions between dendrons in the solid solution. Moreover, the monolithic supramolecular chromophore glasses can be used as a host matrix for structurally compatible guest chromophores as long as the guest chromophores do not disrupt the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions of the host chromophore glasses and the host matrix maintains the local random extended supramolecular self-assembly. However, it should be noted that the macroscopic E-O activities of such solid solutions will still be limited by the electrostatic dipole-dipole interactions between chromophores and may show a saturation of  $r_{33}$  values with an extremely high loading density of chromophores.

Nevertheless, the molecular design approach described above can be a powerful guiding principle for the development of molecular E-O glasses based on supramolecular self-assembly of chromophores as long as the  $r_{33}$  value continues to increase linearly with an increasing net concentration of chromophores, and as long as the materials do not electrochemically break down during the electric field poling process. This very general material design strategy will be extended in the future to other supramolecular glasses based on noncovalent interactions other than the  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions between dendrons and fluorinated dendrons. It is expected that such materials may show significant cooperative improvement in poling efficiencies since the host matrices and guest can both respond to the poling field. The cooperative improvement in poling efficiencies of materials with field-responsive host matrices can be described as “matrix-assisted poling”.<sup>[25]</sup>

A highly efficient dipolar NLO chromophore **16** has been used as a guest chromophore in various host polyacrylates and polycarbonates. The chromophore forms a stable monolithic glass by itself and shows a very large  $r_{33}$  value of  $150 \text{ pm V}^{-1}$  when poled with relatively low poling fields of  $25\text{--}40 \text{ V }\mu\text{m}^{-1}$ . As stated, the optimum poling field strength



was limited to less than  $50 \text{ V }\mu\text{m}^{-1}$  owing to the high conductivity and low dielectric strength of the molecular glass film at temperatures around  $T_g$ .

Based on the concept of “matrix-assisted poling”, the chromophore **16** (not modified with a functional group for self-assembly) was doped into the supramolecular self-assembly of chromophore glass **13** as a host matrix to form a binary composite of chromophore glasses. A series of binary composites of chromophore glasses can be prepared with varying amounts of chromophore **16** in the host glass matrix. The composite **17** was made of 25 wt % of chromophore **16** in the glass matrix of **13**. A very large  $r_{33}$  value of  $275 \text{ pm V}^{-1}$  was measured for the binary composite **17** after the usual electric field poling. More importantly, the E-O activities of these poled composites do not show saturation maxima even with extremely high chromophore loading densities ( $N \approx 5.0 \times 10^{20} \text{ cm}^{-3}$ , more than twice the maximized loading density in a guest-host polymer) and can retain about 90 % of their initial value for more than 500 h at room temperature.

On the contrary, the  $r_{33}$  values of a guest-host polymer **18** based on 25 wt % chromophore **16** in PMMA (much higher  $T_g$  of  $101^\circ\text{C}$ ) showed dramatically decreased temporal alignment stability (ca. 60 % of the initial  $r_{33}$  value) at  $50^\circ\text{C}$  in 25 h compared to the binary composites **17** (ca. 80 % of the initial  $r_{33}$  value). Such behavior is totally different from the commonly observed fast relaxation of poling-induced polar order in a low- $T_g$  guest-host polymer. The physical and optical properties of the binary glass composite **17** and a guest-host polymer **18** based on chromophore **16** are compared in Table 2.

The large E-O activities of the binary molecular glass composites suggest several critical structural factors about the approach: The supramolecular self-assembly of **13** based on  $\text{Ar}-\text{Ar}^{\text{F}}$  interactions is robust enough and were not disturbed by the addition of up to 50 wt % of completely foreign guest chromophore. The poling efficiency of guest chromophores in the glass composites are significantly improved by the “matrix-assisted poling” and the measured  $r_{33}$  values are at least the sum of the  $r_{33}$  values from the guest and host chromophores. The dielectric properties of the binary glass composites were mainly dictated by the self-assembly of the hosting glass matrix so that a poling field as high as  $90 \text{ V }\mu\text{m}^{-1}$  could be applied to the composites.

The improved poling efficiencies in the glass composites were supported further by the measured order parameters

Table 2. Physical and optical properties of the binary glass composite **17** and a guest–host polymer **18**.

Material	$T_g^{[a]}$ [°C]	$N^{[b]}$ [ $\times 10^{20} \text{ cm}^{-3}$ ]	$\lambda_{\text{max}}^{[c]}$ [nm]	Applied volt- age [V $\mu\text{m}^{-1}$ ]	$r_{33}^{[d]}$ [pm V $^{-1}$ ]	Temp. stab. <sup>[e]</sup> [%]
<b>17</b> <sup>[f]</sup>	76	4.8	727	90	275	86
<b>18</b> <sup>[f]</sup>	101	2.5	803	100	150	86

[a] Thermal transition temperature measured by under nitrogen at the heating rate of 5 °C min $^{-1}$ . [b] Number density of core chromophoric moiety of **16** (C $_{32}$ H $_{28}$ F $_3$ N $_4$ O, molecular weight 541.6) counted by total loading weight. [c] Absorption maxima of thin films by UV/Vis spectroscopy. [d] E-O coefficient measured at 1310 nm by simple reflection technique. [e] Temporal alignment stability at room temperature after 3 months. [f] **17**: 25 wt % of **16** in a host matrix glass **13**; **18**: 25 wt % of **16** in PMMA.

based on linear optical dichroism of intramolecular charge-transfer bands. The shapes of the absorption spectra of all films before and after poling were similar, indicating that no chemical degradation occurred during poling. The order parameters were 0.13 for the guest chromophore glass of **16** and 0.17 for the host glass of **13** individually. The order parameters were increased to 0.18 for guest chromophore **16** and 0.25 for host chromophore **13** in the binary chromophore glass composites **17**.

Molecular glasses based on dendrimers of multiple chromophores can also be used as a host matrix for structurally compatible guest chromophores. It should be noted that the dendrimers or hyperbranched oligomers of multiple chromophores can be used as guests or hosts with conventional polymers to improve material properties for device applications. Examples of molecular glass composites based on binary chromophores, composites of chromophores with amorphous dendrimers of multiple chromophores, composites of cross-linkable dendrimers of multiple chromophores, and guest–host polymers based on dendrimers of multiple chromophores in inert host polymers have been reported recently.<sup>[26]</sup>

## 5. Conclusions and Perspectives

The long-term temporal stability of dipolar alignment is a major concern in poled molecular E-O glasses mainly owing to relatively low glass-transition temperatures of these materials. Various molecular conformational relaxations can take place and decrease the polar order over time. Efforts to increase the  $T_g$  value of molecular glasses based on chromophore core structures should be continued while improving the E-O activity of molecular glasses further. Careful structure–property correlation of chromophores can be applied based on the molecular design factors described above.

For the molecular glasses based on supramolecular self-assembly of chromophores, the balance between the strength of the noncovalent interactions and poling efficiency should be considered to increase the  $T_g$  value of the materials. The combination of different noncovalent interactions can be

used to introduce complementary control over local assembly of chromophores to improve material properties further without adding significant absorption or scattering losses. For example, the  $T_g$  value of the supramolecular glass of chromophore **13** based on Ar–Ar<sup>F</sup> interactions can be significantly increased by replacing the phenyl groups in the self-assembly unit with more rigid anthracenyl groups, which have been shown to have stronger Ar–Ar<sup>F</sup> interactions with hexafluorobenzene. The development of supramolecular glasses using stronger Ar–Ar<sup>F</sup> interactions between more efficient polyene chromophores, for example, chromophore **16** modified with dendrons of anthracenyl groups, will be reported elsewhere.

The most effective method to prevent the relaxation of aligned dipoles in molecular E-O glasses is to cross-link the poled materials as demonstrated for dendrimer **5**. The cross-linkers can be incorporated as part of chromophores and/or dendrimers of chromophores, or added as passive components during the formulation of the materials. Many studies of polymeric E-O materials have shown that such approaches can improve long-term alignment stabilities significantly. However, a reduction of 20–40 % in E-O activity is usually accompanied with such an approach, since typical poling of conventional thermoset E-O polymers is achieved through a sequential lattice hardening and poling process. As a result, the cross-linking significantly reduces the orientational flexibility of chromophores owing to the continuous increase of the  $T_g$  value of the polymers. The lowered flexibility of polymers severely limits chromophore reorientation under the poling field, resulting in decreased poling efficiency. To overcome such problems, the cross-linking reactions should be ideally separated from the poling process under mild conditions. The cross-linking reactions can be induced by thermal or photochemical activations. The development of supramolecular E-O glasses of highly efficient polyene chromophores with photochemically active cross-linkers based on Ar–Ar<sup>F</sup> interactions is in progress.

Recent progress of molecular E-O glasses was described in this Focus Review. Recent developments in the monolithic molecular E-O glasses, molecular E-O glass composites, and reversible random assembly of chromophores in molecular E-O glasses were introduced with a focus on the molecular design of dipolar NLO chromophores and solid-state engineering of molecular E-O glasses.

Particular attention was given to present the rationale and potential of molecular glasses of dendrimers of multiple chromophores, molecular glass composites of multiple chromophores, and self-assembled supramolecular glasses to improve material properties. Dendrimers of multiple chromophores and self-assembled supramolecular glasses have been demonstrated as cross-linkable and field-responsive host matrices for organic E-O materials. More examples of molecular amorphous materials for other NLO applications demonstrating the full potential of molecular NLO glasses are expected in the near future.

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