

Ultralarge and Thermally Stable Electro-Optic Activities from Supramolecular Self-Assembled Molecular Glasses

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The exploration of intricate π - π interactions to create tightly packed molecular assemblies has recently led to a new class of supramolecular materials for electronic and optoelectronic applications.¹ This approach offers a very effective method to assemble chromophores and large aromatic molecules to improve their charge mobility. However, it has been seldom used for organizing dipolar molecules to improve the poling induced polar order. There are very few reports concerning the use of this method in electro-optic (EO) materials² because of the numerous difficulties encountered, for example, low EO activity, poor mechanical strength, and alignment stability.

To alleviate these problems, we have developed a new class of molecular glasses based on the reversible self-assembly of aromatic/perfluoroaromatic (Ar-Ar^F) dendron-substituted nonlinear optical (NLO) chromophores. These structures are shown in Figure 1. Both phenyl and pentafluorophenyl rings are incorporated as peripheral dendrons on the π -bridge and the donor-end of the chromophores **1**, **2**, and **3**. Using these molecular engineered dendritic chromophores and their binary chromophore composites, we have demonstrated dramatically enhanced EO activities (r_{33} as high as 327 pm/V, which is 10 times higher than the best inorganic crystal, LiNbO₃) and good alignment stability.

Structural transition properties of these molecules were studied by shear-modulation force microscopy (SM-FM)³ that was employed as a nanorheological characterization method for detecting inter- and intramolecular relaxations not obtainable by differential scanning calorimetry (DSC). SM-FM analyses of the glassy chromophores reveal in principle two thermal transitions as shown in Table 1. Only the higher-temperature transition (T_2) could be observed by DSC and corresponds to the main glass transition of the chromophore, that is, a global reorganization. The low-temperature relaxation (T_1) is due to the local reorganizations. As expected from the Ar-Ar^F interactions, chromophore **3** shows a significantly increased T_1 and T_2 compared to those obtained from **1**. These thermal transitions are also consistent with those of composite **5**, which were generated by blending chromophore **1** and **2** (1:1) to maximize the Ar-Ar^F interactions.

To prove that extended structures form as the result of the Ar-Ar^F interactions, a model compound was prepared by cocrystallizing Ar and Ar^F dendron-substituted carboxylic acids (1:1) in CHCl₃. They form cocrystals in the triclinic $\bar{P}1$ space group (No. 2). The crystal parameters are $a = 8.054$, $b = 13.011$, $c = 18.507$ Å, $\alpha = 77.022^\circ$, $\beta = 79.146^\circ$, and $\gamma = 92.596^\circ$, with two residues of each component in the asymmetric unit by alternating heterodimer stacks

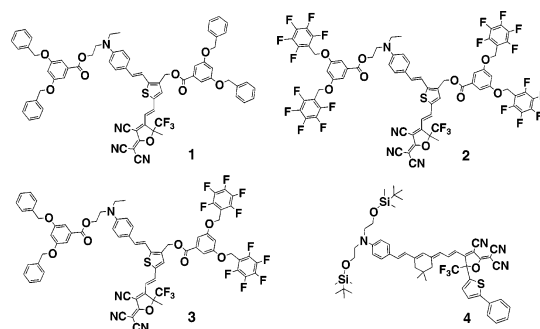


Figure 1. The structures of glass forming chromophores.

Table 1. Physical and Optical Properties of **1–3**, **4a**, **5**, and **6a,b**

materials	SM-FM ^a		number density ^b ($\times 10^{20}$ cm ⁻³)	λ_{\max}^c (nm)	applied voltage (V/ μ m)	r_{33}^d (pm/V)	temp. stab. ^e (%)
	T_1 (°C)	T_2 (°C)					
1	36	57	5.0	719	75	52	0
2	47	69	3.7	689	75	51	85
3	59	70	4.4	703	100	108	92
4a^f		101	2.5	803	100	150	86
5	50	68	4.4	704	120	130	93
6a^f	62	76	4.8	727	90	275	86
6b^f			5.3	794	80	327	83

^a Thermal transition temperature measured by SM-FM under nitrogen at the heating rate of 5 °C/min. ^b Core chromophoric moiety (formular of **1–3**: C₂₈H₂₁F₃N₄OS, molecular weight 518.6. Formular of **4**: C₃₂H₂₈F₃N₄O, molecular weight 541.6) counted by total loading weight. ^c Absorption maxima of thin films by UV-vis spectroscopy. ^d EO coefficient measured at 1310 nm by simple reflection technique. ^e Temporal alignment stability at room temperature after 3 months. ^f **4a**: 25 wt % of **4** in a PMMA. **5**: composite of 1:1 mixture of **1** and **2**. **6a**: composite of 3:1 mixture of **3** and **4**. **6b**: composite of 1:1 mixture of **3** and **4**.

with an interplanar distance of 3.5 to 3.8 Å. This structure represents a clear solid-state evidence of multiple Ar-Ar^F interactions between peripheral dendron groups to form extended structures when the chromophores are substituted with a chemo-specific combination of dendrons.

A graphical illustration of the electric field poling of the self-assembled chromophores is shown in Figure 2. Owing to the possible extended structure induced by Ar-Ar^F interactions, chromophore **3** gave the highest r_{33} (108 pm/V) among all monolithic molecular glasses. This value is more than two times higher than those obtained from chromophores **1** or **2** that do not have such interactions. Moreover, the composite **5** (1:1 blend of **1** and **2**) showed an r_{33} of 130 pm/V. Again, the enhanced r_{33} in this composite verifies that it is possible to form supramolecular self-assembly between different chromophores. High electric fields (greater than 100 V/ μ m) that can be applied to pole chromophore

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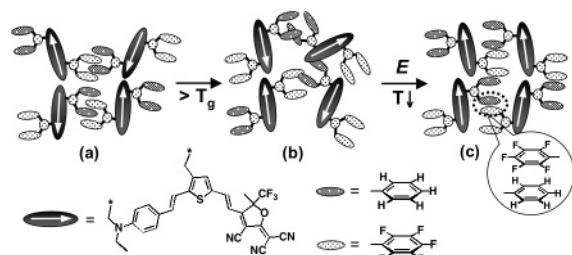


Figure 2. Graphical illustration of the alignment formation of self-assembled chromophore **3** by Ar–Ar^F interactions: (a) locked random dipoles (shown as arrows) before poling; (b) unlocked random dipoles before poling; (c) locked acentric dipoles after poling followed by cooling.

3 and composite **5**, and their resultant high r_{33} values, also suggest that they possess improved dielectric strength. These poled thin films could retain over 90% of their original r_{33} values at room temperature for more than 2 years. On the contrary, the temporal stability of the glasses without the Ar–Ar^F interactions deteriorated dramatically within 1 month. The initial decay of the r_{33} values of chromophore **4** in polymethylmethacrylate (PMMA) (**4a**) and composites **5** and **6a** are compared at 50 °C (see Supporting Information). The doped polymer **4a** showed the lowest temporal stability compared to those obtained from molecular glass composites **5** and **6a**. This reveals that the temporal stability of these materials is dictated mainly by the low-temperature structural relaxation, T_1 , as seen from the SM–FM analysis.

Although the chromophore number density ($N \approx 5.0 \times 10^{20} \text{ cm}^{-3}$) in these molecular glasses are already very high ($\sim 2 \times$ of the typical guest–host polymers), it is still possible to further enhance the r_{33} values of these materials by doping a second chromophore with higher hyperpolarizability (β) in these glasses. In this manner, higher β and loading level could be achieved simultaneously in the same materials. The resulting binary glass composites **6a** (3/4 = 3:1) and **6b** (3/4 = 1:1) exhibited ultralarge r_{33} values, 275 pm/V for **6a** and 327 pm/V for **6b**. This is quite amazing considering that severe intermolecular static interactions may exist in such high-loading level of chromophores.

To verify that improved dipole alignment also plays a role in the enhanced r_{33} values, we have studied order parameter change of the poled molecular glasses by measuring the change of their absorption spectra after poling.⁶ The axial orientation of the poled chromophores was described as the order parameter $\phi = 1 - A/A_0$, where A_0 and A are the absorbance maxima for the unpoled and poled samples at normal incidence. The shapes of the absorption spectra of all films before and after poling were similar, indicating that no chemical degradation occurred during poling. The decreased absorbance of the poled film of **3** could recover >95% of its original value after being annealed at a temperature close to its T_2 for 20 min. Furthermore, the r_{33} values could be reproduced through poling and depoling cycles. On the basis of these experiments, the order parameter for **3** with an r_{33} of 80 pm/V is 0.17. There are bathochromic absorption shoulders that appear in the films of **4a**, composites **6a**, and **6b** suggesting the possibility of forming acentric J -aggregates of chromophore **4**. The absorption spectra of the films of **4a** could be deconvoluted into a simple sum of two Gaussian components to separate the main energy transition from its absorption shoulder. We can obtain two order parameters, 0.13 (from the main peak) and 0.09 (from the shoulder peak) for **4a**, which has an r_{33} of 120 pm/V. We have also done a similar deconvolution of the spectra for composite **6a**. The first peak ($\phi = 0.25$) located at the higher energy side of the spectrum was assigned to be the charge-transfer peak of chromophore **3** while the second

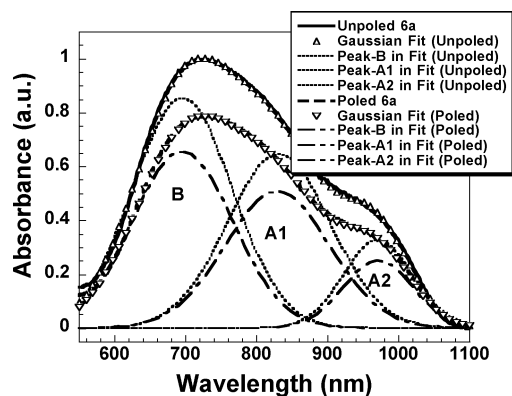


Figure 3. The absorption spectra with Gaussian deconvolution fitting curve for composite **6a** before and after poling.

($\phi = 0.18$) and the third ($\phi = 0.22$) peaks were contributed from **4** as shown in Figure 3.

It is noteworthy that the order parameter and r_{33} (up to 230 pm/V) for chromophore **4** blended in the dendritic glass **3** have increased significantly after poling. The improved poling efficiency observed in the composites suggests that self-assembled chromophore matrices may act as pseudo-Ising lattices to help organize doped chromophores and improve their polar order.⁷

In conclusion, a series of molecular engineered organic glasses were prepared to exploit the use of complementary Ar–Ar^F interactions to improve poling efficiency. These self-organized molecular glasses were used as host in the binary chromophore system to further improve the number density of chromophores and r_{33} values. Ultrahigh r_{33} (up to 327 pm/V at the wavelength of 1310 nm) values have been achieved in these materials. To our knowledge this is the highest value ever reported for organic EO materials.

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Supporting Information Available: Experimental details and additional characterization not included in the manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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