J|A|C|S
COMMUNICATIONS

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

Tae-Dong Kim,[†] Jae-Wook Kang,[†] Jingdong Luo,[†] Sei-Hum Jang,[†] Jae-Won Ka,[†] Neil Tucker,[‡]
Jason B. Benedict,[‡] Larry R. Dalton,[‡] Tomoko Gray,[§] René M. Overney,[§] Dong Hun Park,[⊥]
Warren N. Herman,[⊥] and Alex K.-Y. Jen*,[†,‡]

*Departments of Materials Science and Engineering, Chemical Engineering, and Chemistry, University of Washington, P.O. Box 352120, Seattle, Washington 98195, and Laboratory for Physical Sciences and Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland 20742*

Received November 7, 2006; E-mail: ajen@u.washington.edu

The exploration of intricate $\pi-\pi$ 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) materials[2] 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 $\pi$-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, LiNbO$_3$) 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 CHCl$_3$. 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, $\alpha = 77.022°$, $\beta = 79.146°$, and $\gamma = 92.596°$, with two residues of each component in the asymmetric unit by alternating heterodimer stacks 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.

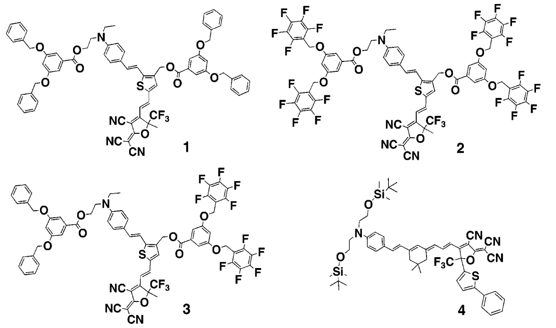

***Figure 1.*** The structures of glass forming chromophores.

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

| | SM–FM[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| materials | $T_1$ (°C) | $T_2$ (°C) | number density[b] ($\times 10^{20}$ cm$^{-3}$) | $\lambda_{max}$[c] (nm) | applied voltage (V/$\mu$m) | $r_{33}$[d] (pm/V) | temp. stab.[e] (%) |
| **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**: $C_{28}H_{21}F_3N_4OS$, molecular weight 518.6. Formular of **4**: $C_{32}H_{28}F_3N_4O$, 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.[4] [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**.

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/$\mu$m) that can be applied to pole chromophore

---

[†] Department of Materials Science and Engineering, University of Washington.
[§] Department of Chemical Engineering, University of Washington.
[‡] Department of Chemistry, University of Washington.
[⊥] University of Maryland.

10.1021/ja067970s CCC: $37.00

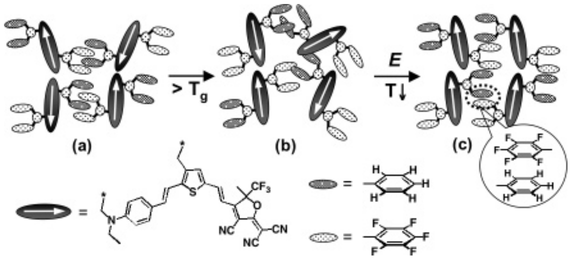

*Figure 2.* Graphical illustration of the alignment formation of self-assembled chromophore **3** by Ar−Ar$^F$ interactions: (a) locked random dipoles (shown as arrows) before poling; (b) unlocked random dipoles before poling; (c) locked acentric dipoles after poling followed by cooling.

**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 ($N \approx 5.0 \times 10^{20}$ cm$^{-3}$) in these molecular glasses are already very high (~2× 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 ($\beta$) in these glasses. In this manner, higher $\beta$ 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 ($\phi$ = 0.18) and the third ($\phi$ = 0.22) peaks were contributed from **4** as shown in Figure 3.

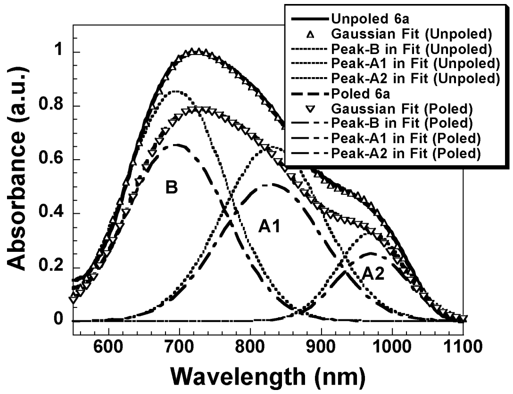

*Figure 3.* The absorption spectra with Gaussian deconvolution fitting curve for composite **6a** before and after poling.

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.

**Acknowledgment.** Financial supports from DARPA (Molecular Photonics) and National Science Foundation (S.T.C. under DMR-0120967) are acknowledged. Alex K.-Y. Jen thanks the Boeing-Johnson Foundation for its support.

**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.

### References

(1) (a) Yip, H.-L; Zou, J.; Ma, H.; Tian, Y.; Tucker, N. M.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2006**, *121*, 472. (b) Burress, C.; Elbjeirami, O.; Omary, M. A.; Gabbai, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 12166. (c) Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 16. (d) Feast, W. J.; Lovenich, P. W.; Puschmann, H.; Taliani, C. *Chem. Commun.* **2001**, 505. (e) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.

(2) (a) Kang, H.; Zhu, P.; Yang, Y.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 15974. (b) Saadeh, H.; Wang, L.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 546.

(3) (a) Gray, T.; Overney, R. M.; Haller, M. A.; Luo, J.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2005**, *86*, 211908. (b) See Supporting Information for details.

(4) Teng, C.; Man, H. *Appl. Phys. Lett.* **1990**, *56*, 1734.

(5) (a) Watt, S. W.; Dai, C.; Scott, A. J.; Burke, J. M.; Thomas, R. L.; Collings, J. C.; Viney, C.; Clegg, W.; Marder, T. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3061. (b) Kilbinger, A. F. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1563. (c) Weck, M.; Dunn, A. R.; Matsumoto, K.; Coates, G. W.; Lobkovsky, E. B.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2741.

(6) (a) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733. (b) Rodriguez, V.; Adamietz, F.; Sanguinet, L.; Buffeteau, T.; Sourisseau, C. *J. Phys. Chem. B* **2003**, *107*, 9736.

(7) Pereverzev, Y. V.; Prezhdo, O. V.; Dalton, L. R. *ChemPhysChem* **2004**, *5*, 1821.

JA067970S