

Supramolecular Solid-State Assemblies Exhibiting Electrooptic Effects

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In the past few decades, supramolecular chemistry has grown into a fascinating and multidisciplinary research area and numerous new concepts concerning intermolecular noncovalent interaction have been studied extensively.^{1–5} More recently, principles of supramolecular chemistry have been introduced into the area of materials science.^{5,6} These materials have the ability to undergo spontaneous assembly into solid forms such as molecular monolayers, multilayered films, liquid crystal phases, and other solid-state lattices.^{6–9} Attractive examples include the work of Jean-Marie Lehn's school and Jean Fretchet's group on supramolecular liquid crystalline materials, and more recently, the work by Meijer et al.^{8–10}

However, the potential for combining supramolecular chemistry with materials science has not been well explored. Few reports exist describing supramolecular electrooptic materials formed through noncovalent bonding.¹¹ One possible reason is that scientists are preoccupied by covalently linked polymers and their advantageous mechanical strength.¹² Supramolecular electrooptic assemblies have a great potential to compete with traditional polymers. Unlike polymers, their components are easy to purify and the assembly is easy to prepare. For example, organic second-order nonlinear optical materials have been studied for more than two decades.^{12,13} Obstacles for the practical application of these materials still exist, particularly in nonlinear optical performance.¹⁴ The key problem is the difficulty in incorporating new NLO chromophores exhibiting large $\mu\beta$ values into a suitable polymer backbone, because most of these chromophores are chemically unstable and tend to decompose during the polymerization stage.¹⁵ The supramolecular self-assembly (SSA) provides an attractive solution to this critical issue. The SSA can generate a polymer-like solid state under mild conditions so that the NLO chromophore can survive.

In this paper we report the synthesis and characterization of NLO supramolecular self-assemblies exhibiting large optical

nonlinearities (Scheme 1). These supramolecular NLO self-assemblies were built up through the spontaneous formation of three parallel hydrogen bonds between a NLO chromophore bearing two groups of 2,6-diacetamido-4-pyridone (**D1–3**) and a monomer with a diimide group or two uracil groups (**A1–3**).^{16,17} It was found that these NLO supramolecular self-assemblies can form amorphous films with good optical quality. Large optical nonlinearity, electrooptic coefficient (r_{33}) as high as 70 pm/V, and a long-term stability (4000 h) of the second harmonic generation (SHG) signal at room temperature were observed.

To prepare the SSA, monomers **A1–3** were designed as the hydrogen acceptors and monomers **D1–3** are composed with the NLO chromophore and two hydrogen-bonding moieties, with 2,6-diacetamido-4-pyridone.¹⁸ The use of the hexafluoroisopropylidene group is to enhance the solubility of monomers in common organic solvents (CHCl₃ and THF). A homogeneous solution were prepared by mixing monomer **A** (dissolved in THF by sonication and warming) with 1 equiv of monomer **D**. After THF was removed, the resultant solid dissolved in CHCl₃ and the NLO self-assemblies were prepared from that solution as glassy solid films with good optical quality. It is interesting to note that compounds **A1–3** are only slightly soluble in chloroform, but the resulting assemblies are very soluble in chloroform and form a homogeneous solution. This suggests that materials of reasonable molecular weights are formed from the self-assembly of two components **D1–3** and **A1–3**.^{19–21}

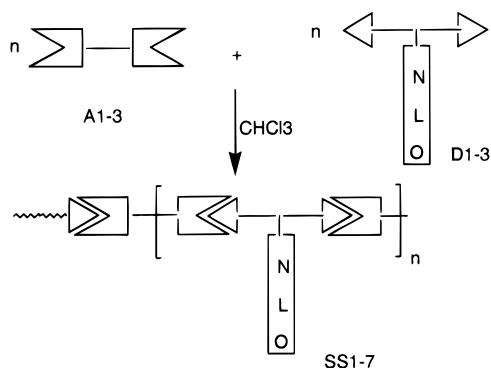
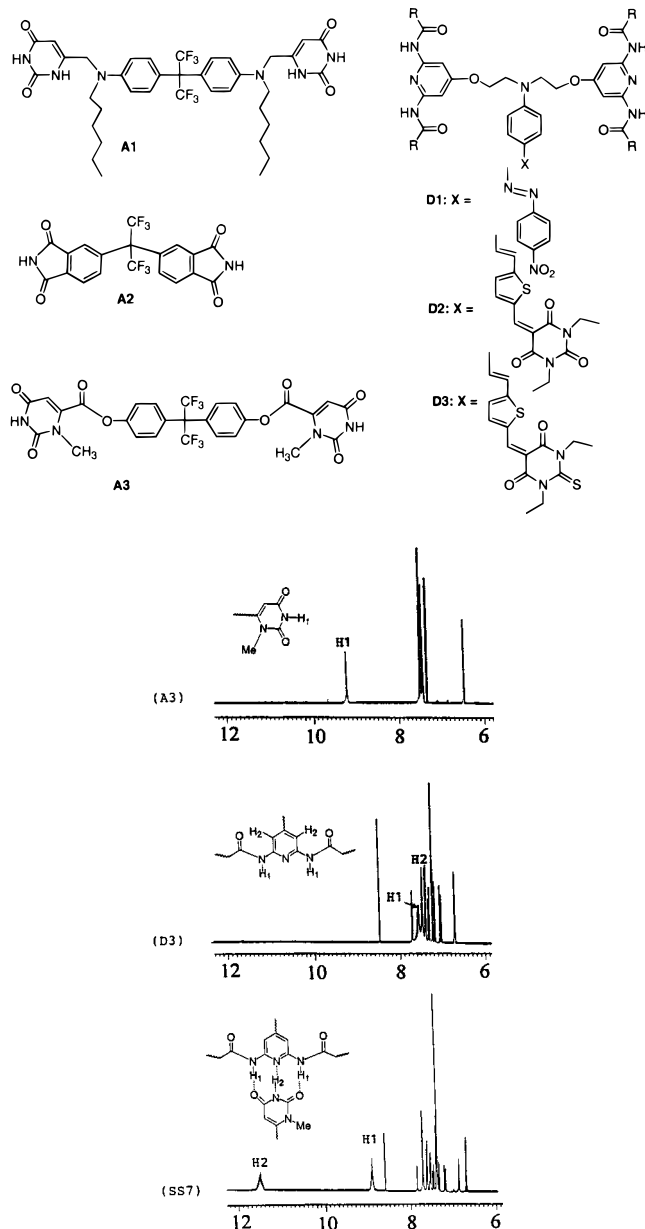
The ¹H NMR spectra for all of the NLO self-assemblies were recorded in CDCl₃ and revealed the formation of triple-hydrogen bonding. A clear downfield shift in the NH signals compared to parent monomers was observed. For example, in **SS7**, all NH protons of **A3** exhibited a downfield shift from δ 9.35 to 11.55, respectively, in **D1** from δ 7.56 to 8.98 (Figure 1). This characteristic downfield shift is due to the formation of a triple-hydrogen-bonded assemblies.^{22,23}

The molecular weight measurements of these assemblies using GPC were not successful in THF and complete dissociation was observed. The viscosity measurements of chloroform solutions of **SS1–7** with concentrations in a range of 0.04–0.065 g/dL, using an Ubbelohde capillary viscometer, indicated an intrinsic viscosity (η) around 0.06–0.09 dL/g (Table 1) for all of the **SS1–7**. These values should be viewed with caution because in diluted solutions, these systems are expected to have a small intrinsic viscosity (η) as they exist in an equilibrium with the component parts.

Thermal analysis by using DSC showed an exothermic transition above 120 °C, at which the hydrogen bonding is broken and the SSA system dissociates into its components. Indeed, films of these materials can be heated to temperatures below 120 °C for more than 1 h without changing the optical quality of these films. These systems exhibit a glass transition temperature (T_g) between 75 and 110 °C (Table 1). Like the corresponding E–O polymers,

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 (18) (a) Detailed descriptions are described in the Supporting Information. (b) The second harmonic generation (SHG) signals of the poled NLO polymeric self-assembly films were measured by using a model-locked Nd:YAG laser (Continuum-PY61C-10 with a pulse width of 25 ps and a repetition rate of 10 Hz) as a fundamental source (1.064 μ m). A quartz crystal was used as the reference sample.
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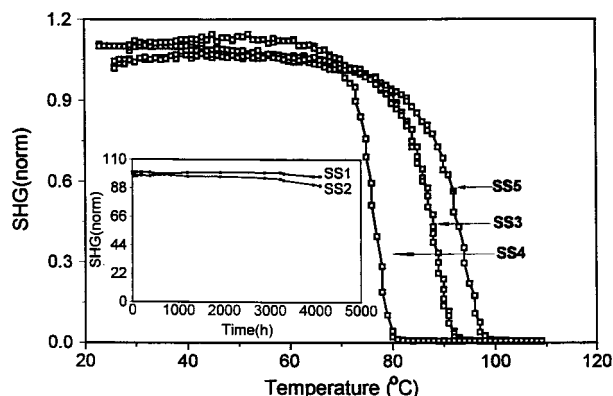
Scheme 1. Synthesis of Supramolecular Self-Assemblies SS1–7**Scheme 2.** Structures of SSA monomers A1–3 and D1–3**Figure 1.** ^1H NMR of A3 and D3 and their supramolecular self-assembly SS7.

the molecular dipoles in these SSA can be efficiently aligned along the direction of the high electric field. Order parameters of 0.15–0.20 ($\Phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the SSA film before and after corona poling, respectively) were observed.

Table 1. The Optical Properties of Self-Assembled Polymers

	H-dono (D)	H-acc (A)	viscosity (η_{int})	T_g ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)	λ_{max}	Φ	r_{33}^b (pm/V)
SS1	D1	A1	0.075	<i>a</i>	150	467	0.18	16
SS2	D1	A2	0.06	<i>a</i>	125	466	0.15	10
SS3	D2	A1	NA	93	166	543	0.19	40
SS4	D2	A2	0.066	72	140	541	0.20	36
SS5	D2	A3	0.083	<i>a</i>	166	540	0.19	38
SS6	D3	A2	0.065	<i>a</i>	123	579	0.2	NA
SS7	D3	A3	0.09	100	166	577	0.22	70

^a The T_g was not observed. ^b Reproducible within experimental error of 20%.

**Figure 2.** The SHG signal of SS3, SS4, and SS5 as a function of temperature (heating rate = 3 deg C/min). The inset shows the temporal stability of SHG signals of SS1 and SS2 at room temperature in the air.

It was found that the poled sample showed a stable SHG signal until the temperature gets closer to T_g of the material, wherein the SHG signals disappear completely at T_g . Figure 2 shows the SHG signal as a function of temperature for selected self-assemblies (SS3, SS4, SS5). Self-assemblies made of either A1 or A3 showed better stability of the SHG signal than the ones made of A2. At room temperature in air, all of the SS series were stable and showed no decay in the intensity of SHG signal after 4000 h, as shown in Figure 2 (inset). These behaviors are quite similar to corresponding polymeric materials.

The electrooptic coefficients (r_{33}) were measured using a simple reflection technique at 1300 nm,²⁴ which is beyond the absorption band of the NLO chromophore. The r_{33} measurements of SSA films²⁵ revealed a large E–O coefficient for SSA systems made from D3 (r_{33} values of 50–70 pm/V). Systems prepared from D1 showed the lowest r_{33} values (10–16 pm/V). Systems made from D2 showed r_{33} values around 40 pm/V (Table 1). The trend in r_{33} values is consistent with the $\mu\beta$ values of corresponding chromophores. The highest r_{33} values are twice as large as LiNbO₃ and are promising for future exploration for application.

In conclusion, molecular recognition between complementary hydrogen-bonding units could be utilized to synthesize supramolecular self-assembly for electrooptic applications. The mild preparatory conditions allow the chemically sensitive NLO chromophores to survive. The resulting SSAs exhibit large r_{33} values (10–70 pm/V at 1.3 μm) and a good temporal stability at room temperature. Various structural parameters can be changed to fine-tune the physical properties of the SSA materials. Thus, this approach to electrooptical materials is promising.

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Supporting Information Available: General experimental procedures and ^1H NMR and elemental analyses of all new compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) A spin-coated film (0.4–0.60 μm) on an Indium-Tin-Oxide (ITO) substrate was poled under a corona discharge at a temperature range from 70 to 110 $^{\circ}\text{C}$. The poled film was coated with silver electrodes 0.1 μm thick.