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Large electro-optic activity and low optical loss derived from a highly fluorinated dendritic nonlinear optical chromophore

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A 3-D shape nonlinear optical chromophore encapsulated by highly-fluorinated dendrons exhibits significantly improved electro-optic properties and optical attenuation.

Organic polymeric second-order nonlinear optical (NLO) materials have attracted steady attention for many years due to their potential application in high-speed electro-optic (E–O) devices.[1,2] One of the most challenging problems dragging the progress of this area is to efficiently translate the large molecular hyperpolarizabilities ($\mu\beta$) of organic chromophores into large macroscopic E–O activities (r_{33}).[2] Over the past decade, the $\mu\beta$ values of chromophores based on the 'push-pull' type of compounds have been steadily improved to more than 250-fold higher.[3] However, due to strong intermolecular dipole–dipole interactions, poling-induced noncentrosymmetric alignment of these chromophores is severely limited. As a result, only several times of improvement of the r_{33} value has been achieved so far. Fortunately, controlling of the chromophore shape has been conceptually and experimentally proved to minimize this interaction to some degree, and the spherical shape has been proposed by Dalton *et al.*[4] as the ideal one for achieving efficient poling. Applying the site isolation principle[5] to E–O polymers, we have recently developed a NLO dendrimer with a crosslinkable periphery exhibiting a large r_{33} value (twice that of $LiNbO_3$) and excellent thermal stability.[6] In comparison with any conventional E–O polymers, the encapsulation effect of dendrons allows the chromophores to be spatially isolated,[5] and the large void-containing structures[7,8] can provide more space for efficient orientation of the chromophores. Furthermore, the globular geometry of dendrimers is well suited for the ideal shape modification of chromophores. Therefore, the E–O dendrimers can be considered as one of the most promising molecular topologies for the new generation of highly efficient E–O materials.[9]

Besides the large macroscopic optical nonlinearity, the device-quality E–O materials must possess high thermal stability and low optical loss,[1–4] which are totally dependent on the physical and chemical properties of the material systems. Among various NLO polymer systems, the fluorinated materials are of high interest[6,10] since it has been demonstrated that the fluorinated polymers exhibit a comprehensive combination of high thermal stability, chemical inertness, low dielectric constants and optical transparency.[11] With the view of exploring the unique nanoenvironments provided by fluoro-rich moieties, we extend our quest for high-performance E–O polymers by developing new fluorinated E–O dendrimers. Here, we report the synthesis and properties of a highly fluorinated dendritic NLO chromophore **1** (Chart 1). The core of this dendrimer is based on the phenyltetracyanobutadienyl (Ph-TCBD) thiophene-stilbene-based NLO chromophore,[12] which is three dimensionally encapsulated with several highly fluorinated dendrons. To study the microenvironment produced by the fluoro-rich dendrons on the properties of the encapsulated Ph-TCBD chromophore, a series of parallel experiments have been performed to compare the thermal stability, UV absorption and poling-orientation behaviors of **1** with those of the pristine chromophore **2**.

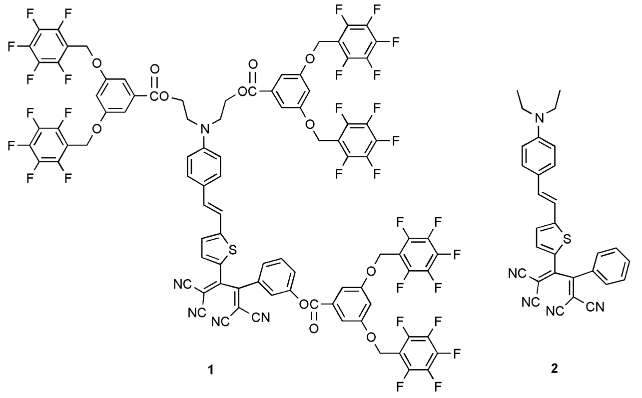
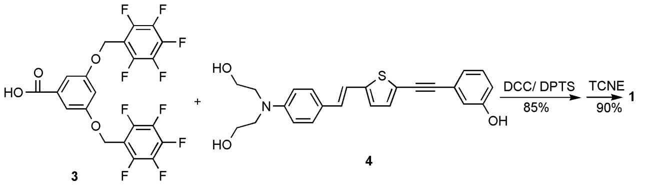


Chart 1

As shown in Scheme 1,† dendritic chromophore **1** was synthesized by the esterification between the carboxy group of the fluorinated dendron **3** and the three hydroxy groups of the chromophore precursor **4**. Then the resulting intermediate was reacted with tetracyanoethylene (TCNE) to introduce the Ph-TCBD electron-withdrawing group. Compound **1** was purified by column chromatography, and its structure was fully characterized by ^1H and ^{19}F NMR, MALDI-TOF, and UV–Vis absorption spectroscopy.‡ Like other typical dendrimers, chromophore **1** is highly soluble in common organic solvent, such as chloroform, THF, and cyclopentanone.



Scheme 1

The initial decomposition temperature of **1** is 265 °C, which is 20 °C higher than that of **2** without the dendritic encapsulation. This indicates that fluorinated dendrons can effectively improve the thermal stability of the core chromophore.

The π–π^* charge-transfer absorption maxima (λ_{max}) of the push–pull compounds such as Ph-TCBD NLO chromophore can be varied by the polarisability and dielectric constant of the surrounding environments and causes solvatochromism. To provide a more explanatory insight into the microenvironment effect presented by the fluorinated dendron, the pristine Ph-TCBD chromophore was used as a probe[13] to analyze the difference between the UV–Vis absorption spectra between **1** and **2**. As shown in Table 1, 30–40 nm blue shifts of the λ_{max}s in both the solution and solid films of **1** have been observed. The

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reason for this solvatochromism is that the Ph-TCBD chromophore core in dendrimer **1** is three-dimensionally encapsulated by the attached fluoro-rich dendrons with low polarisability and low dielectric constant. Unlike other highly efficient NLO chromophores,[14] dendritic chromophore **1** shows exactly the same UV–Vis spectra when it was dispersed in either an amorphous polycarbonate (APC) or a fluorinated polymer, two kinds of matrices with significantly different dielectric constant. Therefore, in solid films of **1**, the fluoro-rich dendrons dominate the microenvironments of the core chromophore.

Blue-shifted absorption and high content of C–F bond in **1** can also contribute to the material's lower optical loss at 1.3 and 1.55 μm, the two operation wavelengths of telecommunication. To prove this, film samples with 50 wt% of **1** in APC were spin-coated onto ultra-low OH optical quality fused silica substrates, and the absolute absorption spectra was measured by photo-thermal deflection spectroscopy (PDS) (Fig. 1).[15] The optical loss of the materials is only around 0.65 and 0.85 dB cm^{-1} at 1.3 and 1.55 μm, respectively. Regarding the relatively high C–H content in the APC matrix, the major contribution of this low value is actually from the APC matrix instead of **1** itself. Hence the intrinsic loss induced by **1** may be much lower than 0.5 dB cm^{-1}, which is extremely encouraging for using this kind of highly fluorinated dendritic chromophore in potential photonic applications.

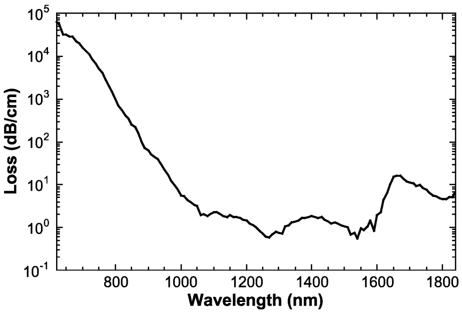

Fig. 1 Optical loss spectra of **1** in polycarbonate (APC) by photo-thermal deflection spectroscopy (PDS).

For E–O studies, **1** and **2** with the same equivalent of active component (12 wt%) were formulated into APC, respectively. Optical quality films were obtained by spin-coating 15% w/w of solutions in cyclopentanone onto the indium–tin oxide (ITO) glass slides. The films were kept in a vacuum oven at 85 °C overnight. After baking, thin layers of gold were sputtered onto the films as the top electrodes for performing parallel electrode poling. Under similar conditions, the poled films of **1** in APC exhibited an r_{33} value of 30 pm V^{-1} at 1.3 μm, which is three times higher than that of **2**, indicating a significant improvement of poling efficiency for **1**. This comparison provides a very clear explanation of how well the dendrons translate the molecular hyperpolarizabilities into large macroscopic E–O activities. The encapsulation of fluorinated dendrons makes the shape of **1** globular-like, which is very close to the ideal molecular shape for achieving the optimized poling efficiency. Moreover, because the fluorinated dendrons dominate the microenvironments of the Ph-TCBD chromophore in solid films, the chromophores are site-isolated, thereby significantly reducing the intermolecular interaction and ameliorating the molecular orientation. It should be noted that the r_{33} value of 30 pm V^{-1} for 12 wt% of **1** in APC is quite consistent with the value obtained from our first Ph-TCBD chromophore-based dendrimer.[6]

Table 1 The comparison of properties of the highly fluorinated dendritic chromophore **1** and its pristine analogue **2**

		$\lambda_{\max}$/nm		EO coefficient[c]
	T_d[a]/°C	In 1,4-dioxane	In APC[b] film	(r_{33}, pm/V at 1.3 μm)
1	265	574	595	30
2	245	603	637	10

[a] The initial decomposition temperature determined by seal-pan differential scanning calorimetry (DSC) at 10 °C min^{-1} under nitrogen; [b] Amorphous polycarbonate (APC) {poly[bisphenol A carbonate-*co*-4,4′-(3,3,5-trimethylcyclohexylidene)diphenol carbonate]}; [c] In APC matrix with 12 wt% of chromophore density by contact poling.

In summary, we have designed and synthesized a dendritic NLO molecule based on the phenyltetracyanobutadienyl (Ph-TCBD) thiophene-stilbene chromophore. It is encapsulated three dimensionally by three highly fluorinated dendrons. In comparison with its pristine analog, this dendritic chromophore displays a large ~ 30–40 nm blue shift of the charge-transfer absorption maximum, 20 °C higher decomposition temperature, and most impressively, three times higher E–O coefficient. The combination of these improvements makes this novel molecular design very promising for molecular-engineering for the next generation of E–O materials.

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Notes and references

† DCC = 1,3-dicyclohexylcarbodiimide; DPTS = 4′-(*N*,*N*-dimethylamino)pyridinium 4-tosylate.

‡ ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 6.7–7.8 (m, 21H), 5.18 (s, 4H), 5.04 (s, 8H), 4.58 (br s, 4H), 3.91 (br s, 4H); ^{19}F NMR ($\mathrm{(CD_3)_2SO}$, ppm, using 1,4-difluorobenzene as the reference (−118.8 ppm)): δ −142.4, −152.6, −161.7); MS Calcd for $\mathrm{C_{93}H_{41}F_{30}N_5O_{12}S}$: 2021, MALDI-TOF Found: 2022 [M$^+$].

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