Enhanced poling efficiency in highly thermal and photostable nonlinear optical chromophores

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A series of nonlinear optical chromophores based on the highly thermal and photostable tricyanovinylidenediphenylaminobenzene (TCVDPA) was synthesized and their thermal and optical properties were investigated. Modification of the TCVDPA chromophore with bulky groups provides reduction of dipole–dipole interactions and thus great improvement of the macroscopic electro-optic (EO) response of the polymeric materials obtained by incorporating these derivatives as a guest at high loading in polysulfone. The best result was obtained with chromophore **C5**, bearing fluorinated aromatic substituents, which shows a doubling of the EO activity at 30 wt% (25 pm V⁻¹ at 830 nm) compared with the pristine TCVDPA. The bulkier the chromophore, the lower the induced plasticization effect (as much as 50 °C difference on the T_g attenuation). Furthermore, all chromophores in this study possess good processability and exhibit high thermal decomposition temperatures (highest $T_d = 360$ °C).

Introduction

Organic materials exhibiting large electro-optic (EO) responses (r_{33}) have attracted considerable attention over the past two decades. They have great potential for use in telecommunication, information processing, phased array radar, optical storage devices, THz generation, and many other applications as active materials in photonic microdevices.¹⁻⁷ The advantages of organic materials over traditional inorganic materials such as LiNbO₃ are high and fast nonlinearities, ease of processing, device integration and the possibility of structural modification depending on the desired application.^{8,9}

However, high nonlinearity is not enough to ensure widescale commercial utilization of polymeric electro-optic devices. Other essential properties, such as good thermal, mechanical and photochemical stability, low optical loss (high transparency) and good processability, need to be simultaneously optimized in order for the active material to be successfully implemented in a practical device.

Several classes of compounds exhibiting very high thermal stability (over 300 °C) have been reported.¹⁰⁻¹² From these studies it emerges that the use of a 4-(diarylamino)phenyl

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electron donor results in a significant improvement in thermal stability compared to the 4-(dialkylamino)phenyl substituted derivatives.¹³⁻¹⁷

One of the most crucial parameters for the long term efficiency of EO devices is photostability, since they are expected to last years without significant degradation under high photon flux. The absorption of photons by molecules under illumination can lead to changes in their chemical structure and consequent loss of nonlinearity. Several research groups have done extensive work examining the photostability of EO polymers, taking into account the influence on the photodegradation of factors such as chromophore structure,^{18,19} wavelength and intensity,²⁰⁻²² and the presence of oxygen.^{19,23}

The general conclusion that can be drawn from these studies is that the most photostable compounds have a simple benzene π -bridge and a tricyanovinyl electron-acceptor group. More elongated conjugated bridges between the electron-donor and -acceptor groups lead to faster photodebleaching. Galvan-Gonzalez et al.22 identified tricyanovinylidenediphenylaminobenzene (TCVDPA; Chart 1) as the most photostable structure: it is about two orders of magnitude more stable than the DANS (4-N,N-dimethylamino-4'-nitrostilbene) chromophore and one order of magnitude more stable than the azo chromophore DR1 (4-[N-ethyl-N-2-hydroxyethyl)amino]-4'-nitroazobenzene). In fact, it shows no degradation upon irradiation at the absorption maximum (λ_{max}), nor it is acting as a sensitizer for the formation of singlet oxygen upon irradiation with UV. On the other hand, the price to pay for this higher stability is a shorter conjugation path and therefore a lower second-order nonlinearity compared to extremely large $\mu\beta$ chromophores like CLD or FTC (Table 1).18 However, it has been reported that the photostability of such chromophores is quite poor in air,²⁴ and high-cost packaging is necessary for shielding the oxygen in the air, which is responsible for the photodegradation

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Chart 1 Chemical structures of chromophores C1-C6.

Table 1	Comparison	of λ_{max}	and $\mu\beta$	values	of known	NLO	chromophores ^a
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NLO chromophore		$\lambda_{\rm max}/{\rm nm}$	$\mu\beta/10^{-48}$ esu	$\mu eta / M_{ m w}$	B^d
	DR1	475	800 ^{<i>b</i>,25}	3.0	5×10^{6}
	DANS	438	580 ²⁶	2.1	2×10^{4}
	TCVDPA	531	584 ^c	1.7	2×10^7
TBDMS-0	CLD	695	35000 ²⁷	45.7	N/A ^e
	FTC	650	18000 ²⁸	25.9	N/A ^e

^{*a*} Measured at 1907 nm unless otherwise indicated. ^{*b*} Measured at 1580 nm. ^{*c*} $\mu\beta_0$. ^{*d*} *B* is the number of absorption events needed, on average, to photodegrade a single chromophore molecule; data taken from ref. 22. ^{*e*} Data not available.

of the chromophore by the formation of singlet oxygen. Given that photostability is of key importance to the long-term reliability of devices, we strongly believe that TCVDPA holds a strong competitiveness for EO applications, particularly for the fabrication of low-cost devices (like EO-based sensors)²⁹ operating at 850 nm, where cheap laser sources are available.

Moreover, the TCVDPA chromophore possesses the unique feature of having a low absorption window in the UV region (blue window), where most of the chromophores absorb, which allows UV-crosslinking to be used for photodefinition.³⁰ Recently, we demonstrated the direct waveguide photodefinition of the negative photoresist SU8 containing TCVDPA, using a conventional (I, H, G-line) mask aligner.³¹ In addition, this system has the advantage that low temperature poling can be done in the uncrosslinked state, because the uncured SU8 is a low- T_g solid.

A major obstacle impeding the development and employment of organic electro-optic materials is the difficulty of translating a high hyperpolarizability (β) into a macroscopic EO coefficient (r_{33}) . This is because, in particular at high chromophore number density (N), dipole-dipole interactions start to become competitive with chromophore dipole-applied poling field interactions, favoring centrosymmetric arrangements of chromophores.32,33 From both theoretical and experimental analyses the Dalton group has shown that the maximum achievable EO activity of a chromophore can be greatly enhanced by modification of its shape. In fact, the derivatization of chromophores with bulky substituents will make them more spherical and hence limit intermolecular electrostatic interactions.34-39 These added side groups are only expected to contribute in minimizing the tendency of the dipoles to cluster in an anti-parallel fashion, and improving the solubility of the chromophores, positively affecting the poling efficiency and the macroscopic EO response of polymeric materials in which these chromophores are incorporated, without having any influence on the molecular hyperpolarizability.

In this contribution we describe how the EO response and the poling efficiency of a series of thermally and photochemically stable TCVDPA-based chromophores (**C2–C6**; Chart 1) considerably improve by shape modification. The chromophores are incorporated as guests in a high T_g (190 °C) polysulfone (PS) polymer host matrix. The chemical, photochemical, thermal, linear optical, and non-linear optical (NLO) characterization of these chromophores and the polymeric materials derived therefrom are described.

Results and discussion

Synthesis

The synthesis of the chromophores **C2–C6** is depicted in Scheme 1. All chromophores were synthesized using a similar approach: first the formation of the triphenylamine donor part, substituted with the desired group, followed by tricyanovinylation of the unsubstituted aryl ring (Chart 1).

The triarylamines were assembled using a copper-catalyzed amination of aryl iodides following a recently reported procedure.^{40,41} Aniline was reacted with 4-iodoanisole or 1-*tert*-butyl-4-iodobenzene, respectively, in the presence of potassium *tert*-butoxide and a catalytic amount of CuI/P(tBu)₃ complex, to afford the triarylamines 1 or 2. Demethylation of dimethoxy-triphenylamine 1 with BBr₃ gave the corresponding bisphenol 3. Subsequent functionalization of the hydroxyl groups in 3 with 1-bromo-2-ethylbutane and 2,3,4,5,6-pentafluorobenzyl bromide under Finkelstein conditions gave the dialkoxytriarylamines 4 and 5, respectively.

Derivatization of EO chromophores with highly fluorinated dendrons has been demonstrated to be an efficient way to provide the spatial isolation needed for more efficient orientation of the chromophores.⁴² Fluorinated dendron **9** was synthesized by reaction of protected dihydroxybenzoic acid 7^{43} with 2,3,4,5,6-pentafluorobenzyl bromide to give **8**, followed by deprotection of the carboxylic acid by treatment with zinc dust in glacial acetic acid (Scheme 2). Esterification of the carboxylic acid in fluorinated dendron **9** with bisphenol **3** afforded the triarylamine diester **6**. Reaction of the disubstituted triarylamines **1**, **2**, **4–6** with tetracyanoethylene (TCNE) in DMF gave the corresponding chromophores **C2–C6**, respectively.

Linear optical properties

UV spectra of chromophores C1–C6 were recorded in CH_2Cl_2 and the λ_{max} values are reported in Table 2. All chromophores



Scheme 1 Synthesis of chromophores C2–C6. *Reagents and conditions*: (a) P(tBu)₃, CuI, KOtBu, toluene, reflux; (b) TCNE, DMF, rt; (c) BBr₃, CHCl₃, rt, then CH₃OH; (d) for 4 and 5: K₂CO₃, KI, THF, reflux; for 6: DCC, DMAP, THF–CH₂Cl₂, rt; (e) TCNE, DMF, rt.



Scheme 2 Synthesis of dendron 9. *Reagents and conditions*: (a) pentafluorobenzyl bromide, K₂CO₃, KI, THF, reflux; (b) glacial acetic acid, Zn dust, THF, rt.

Table 2Summary of thermal and optical properties of chromophoresC1-C6

	$T_{d}{}^{5a}/{}^{\circ}C$	$T_{\rm d} \text{ onset}^{b/\circ} C$	$\lambda_{\max} c/nm$	$E^{d}/M^{-1} \text{ cm}^{-1}$	$\beta_{zzz} e/10^{-30}$ esu
C1	286	335	539	38500	425 ± 80
C2	296	331	530	24000	428 ± 16
C3	292	323	537	30000	424 ± 25
C4	350	360	545	31000	418 ± 42
C5	308	326	536	31000	409 ± 18
C6	355	365	529	33500	275 ± 17

^{*a*} The weight loss decomposition temperature, T_d^5 , is defined as the point at which 5% weight loss has occurred in the chromophore. ^{*b*} The onset temperature of degradation (T_d onset) can be calculated from the intersection of the tangent to the slope of the curve corresponding to the first weight loss event. ^{*c*} λ_{max} was measured in CH₂Cl₂. ^{*d*} Molar absorptivity in CH₂Cl₂. ^{*e*} β values were measured at 800 nm.

studied have a strong charge-transfer band (450–650 nm) in the visible region of the spectrum. In general, no significant change in the spectrum was caused by the modification, with λ_{max} lying between 529 and 545 nm. A typical spectrum is shown in Fig. 1. Moreover, all derivatives preserve the lower minimum in the absorption spectra (around 400 nm), between the charge-transfer band and the higher-energy aromatic electronic transitions. This blue window allows photo-induced crosslinking to be used for lattice hardening.

Optical loss measurements

Optical losses were measured by the prism coupling method and they are shown in Fig. 2. Slab waveguides were made on 8 μ m thick silicon oxide on silicon wafers by spincoating PS and C1 20 wt.% in PS. The resulting film thickness was about 4 μ m and it sustained three modes at 1550 nm. As the surface of the spin coated film is extremely smooth, the loss mechanism is mainly due to material absorption. White light from a broadband source was coupled into the polymer slab using a prism. After propagating a certain distance it was out-coupled using another prism and sent to a spectrum analyzer. The experiment was repeated varying the distance between the in-coupling and the out-coupling prisms. By plotting the out-coupled power as a function of the distance of propagation it was possible to obtain the absorption loss spectra.

In general, device-quality EO materials should possess good optical transparency (low optical loss), in particular at the



Fig. 1 Absorption spectrum of chromophore C6 in CH_2Cl_2 .



Fig. 2 Optical loss spectra of PS and chromophore **C1** at 20 wt.% in PS slab waveguides.

main telecom wavelengths (1310 and 1550 nm) and datacom wavelengths (840 nm). For the PS host polymer the optical loss remains relatively low (around 1 dB cm⁻¹) at 840, 1310, and 1550 nm. This retained loss could probably be attributed to light scattering from particles or roughness due to polymer processing. When 20 wt.% of chromophore **C1** is incorporated as guest into a PS host matrix, a long-wavelength tail of the main absorption peak of the chromophore appears, extending further into the near-IR and therefore causing a high loss of 7.2 dB cm⁻¹ at 840 nm. Although the high chromophore loading causes large vibrational C–H overtone absorptions to appear,

this does not have a detrimental effect on the optical transparency at telecom wavelengths, which only increase to 1.7 and 1.5 at 1310 and 1550 nm, respectively, making the material very suitable for telecom waveguide applications.

Thermal analysis

The thermal properties of the chromophores are reported in Table 2. TGA data were recorded at a heating rate of 20 $^{\circ}$ C min⁻¹. It should be noted that weight loss in these experiments may be due to sublimation and/or decomposition of the substance.

Thermal stability is a critical parameter for long term efficiency of EO devices. Since the NLO response has to be stable during processing and operation of the chromophore/polymer materials, the chromophores need to be chemically stable at all temperatures that the system encounters in electric field poling, and they should withstand all fabrication steps needed for device fabrication.

The decomposition temperatures of chromophores C1–C6 are very high, being above $320 \,^{\circ}$ C for all of them. The highest value, $365 \,^{\circ}$ C, which was recorded for C6, is among the highest ever reported for NLO chromophores.

Photobleaching test

Several research groups have done extensive work examining the photostability of EO polymers. Previous studies clearly show that the presence of oxygen can greatly increase the degradation rate of organic chromophores.^{19,44} The photodegradation of various chromophore families has been reported, including stilbenes and azobenzenes. In these studies the photobleaching measurements were made by using lasers as a light source on film samples of guest–host polymeric materials.

Here we introduce a straightforward and low-cost qualitative method for the fast screening of the photostability of new chromophores. These simple photobleaching tests are carried out by monitoring the decrease in absorbance during irradiation of oxygen-saturated solutions of chromophores in CDCl₃ with visible white light. The experiments were conducted in CDCl₃ because singlet oxygen ($^{1}O_{2}$) has a very long lifetime in this solvent, so that its effect can be established with greater sensitivity.⁴⁵ Although qualitative, thus producing relative results instead of absolute values, this technique can give a good estimation of the photostability, particularly when a direct comparison with chromophores of known photostability *B* is performed.

Photobleaching tests were carried out for chromophores C1, C3, and C5, and for the commercially available NLO chromophores DANS and DR1. In fact, our results are in good relative agreement with the reported data (see Table 1), showing that the stilbene chromophore DANS degrades very rapidly due to the attack on the central carbon double bond by oxygen. The most photostable compounds are characterized by benzene bridges and tricyanovinyl electron-acceptor groups. From the results reported in Fig. 3 it can be noticed that chromophores C1, C3, and C5, are photostable under our experimental conditions, showing hardly any degradation upon exposure to white light for 120 min. Moreover, comparing the decay curves of chromophores C3 and C5 with that of C1, no significant difference can



Fig. 3 Photo-bleaching curves of chromophores **C1**, **C3**, **C5**, **DR1**, and DANS in CDCl₃. *A* is the absorbance at time *t* and A_0 is the initial absorbance. Photolyses were carried out in 10 mm quartz cuvettes with light from a 75 W halogen lamp. The samples were irradiated at a distance of 10 cm from the light source and were shielded from daylight.

be noticed. More than 95% of the initial absorbance is retained after 100 min of exposure, showing that functionalization with bulky side groups does not have a detrimental influence on the photostability. From these data it can be concluded that chromophores C1–C6 possess among the highest photostabilities reported for D– π –A chromophores.

Hyper-Rayleigh scattering measurement

The hyper-Rayleigh scattering (HRS) technique was employed to measure β_{zzz} for all chromophores at 800 nm (Table 2). Crystal violet chloride (CV) was used as an external reference. In most of the cases, the hyperpolarizability is quite constant, slightly above 400×10^{-30} esu. Apparently, the functionalization at the donor site of the chromophores does not have a large influence on β_{zzz} . However, the lower value found for chromophore **C6** may be due to the ester bond directly connected to the diphenylamine moiety, reducing its electron donating ability.

Electric field poling and EO property measurements

In order to study the substituent effect on the poling efficiency, EO measurements were performed in PS doped with chromophores C1–C6 at different concentrations using cyclopentanone as a solvent. The resulting solutions were filtered through a 0.2 μ m filter and spin-coated onto indium tin oxide (ITO) coated glass wafers. The obtained films were then baked on a hot plate at 95 °C for 1 h and in a vacuum oven at 95 °C for 8 h to completely remove the solvent. A 100 nm layer of gold was then sputtered onto the films as a top electrode to perform electric-field poling. The films were contact-poled at the relevant $T_{\rm g}$ for 40 min with a DC electric field of 100 V μ m⁻¹. The r_{33} values were measured using a Teng–Man simple reflection technique at a wavelength of 830 nm.⁴⁶

The chromophore loading could be varied over a wide range without phase separation occurring and the resulting materials could easily be processed into films with high optical quality.

C1

• C3

▲ C6



F 120 -100 -80 -60 -40 -0 10 20 30 40 50 60 Chromophore wt %

Fig. 4 r_{33} at 830 nm as function of the effective concentrations of chromophores C1–C6 in PS.

As shown in Fig. 4, for unmodified chromophore C1, the EO activity increases linearly with loading up to 15 wt.%, after which the curve starts to deviate from linearity, showing evidence of chromophore-chromophore electrostatic interactions starting to take place. Similar behavior was noticed for chromophore C2, in which the methoxy groups are not large enough to significantly affect the interactions, but only providing a small improvement of about 2 pm V^{-1} with respect to C1. Moreover, C1 and C2 remain at lower r_{33} values compared with other bulky substituted chromophores, like C3, C4, and C5 (Fig. 4), suggesting a significantly higher dipole-dipole interaction already at low loadings. However, the increment in poling efficiency provided by the tert-butyl groups of C3 and the branched alkoxy moieties of C4 is clearly visible already at low chromophore loadings, whereas at larger concentrations the shape modification is even more effective showing almost doubling of r_{33} at 35 wt.% with respect to C1 (from 12.5 pm V^{-1} to 25 pm V^{-1}). The best result was obtained with chromophore C5 which provides a more significant enhancement of the EO response reaching its maximum r_{33} of 25 pm V⁻¹ at 30 wt.%. Probably, the very bulky pentafluorobenzyl groups provide the site isolation needed for free chromophore reorientation under electric field poling conditions. In the case of the dendritic chromophore C6, an EO coefficient of only 5.5 pm V^{-1} was obtained at 10 wt.%. Even though this chromophore is the bulkiest of the whole series and thus it is expected to induce the highest poling efficiency, its r_{33} value recorded at 10 wt.% does not even follow the linear slope observed for the smaller fluorinated aromatic derivative C5. The increment of r_{33} compared with C1 is only 20% at low loading. This result suggests that a good compromise has to be found for a given chromophore in order to achieve the site isolation needed for maximizing the poling efficiency.

It can be concluded that, since the hyperpolarizability is similar for all chromophores, the enhancements in r_{33} for the shape modified chromophores are not due to improvements at the molecular level, but indeed to reduced electrostatic interactions between chromophores and hence to better poling efficiency.

For comparison, T_g was plotted against the loading density for films made with chromophores C1, C3, and C6. From the curves

Fig. 5 Comparison of T_g for chromophores C1, C3, and C6 incorporated in PS at different concentrations.

shown in Fig. 5, a clear decay of the T_g of the material can be seen upon increasing the chromophore concentration. This is common behavior in guest-host systems in which the NLO chromophore, being simply dissolved in a polymer matrix, can act as a plasticizer and consequently decrease the T_g of the polymeric material.³ An interesting trend can be noticed in the decay: the bulkier the chromophore (C1 < C3 < C6), the lower its plasticization effect. In fact, when C1 is incorporated in PS at 45 wt.%, the T_g of the resulting blend drops to 80 °C. Such a low T_g is detrimental for the long term efficiency of a device, causing serious relaxation of the molecular alignment. In contrast, dendritic chromophore C6 at 50 wt.% loading displays a much improved T_g of 130 °C, resulting in a better material for long term device applications.

Conclusions

200

180

160

140

Tg (°C)

A series of nonlinear optical chromophores was synthesized by applying a shape modification to the TCVDPA chromophore. These changes have led to a decrease of the chromophore induced plasticization effect and to a great reduction of intermolecular interactions. Consequently, improved poling efficiencies were observed for most of the derivatives when incorporated at high loadings in PS guest polymer. A doubling of the EO activity was even obtained for chromophore C5, compared with the pristine TCVDPA, showing an EO coefficient of 25 pm V⁻¹ at 830 nm. Moreover, all chromophores exhibit good processability and possess among the highest thermal and photochemical stabilities reported in the literature.

Experimental

General procedures

All chemicals were of reagent grade and used without further purification. THF was freshly distilled from Na/benzophenone, and CH₂Cl₂ from CaCl₂. All chromatography associated with product purification was performed by flash column techniques using Merck Kieselgel 600 (230–400 mesh). All reactions were carried out under an inert argon atmosphere. Melting points (uncorrected) of all compounds were obtained with a Reichert melting point apparatus and a Kofler stage. ¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 using tetramethylsilane (TMS) or the corresponding residual solvent signal as internal standard. FAB-MS spectra were recorded on a Finningan MAT 90 spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Thermogravimetric analyses were conducted using a Perkin-Elmer TGA-7 thermogravimetric analyzer (scanning rate: 20 °C min⁻¹). UV-Vis measurements were carried out on a Varian Cary 3E UV-spectrophotometer.

HRS measurements were performed using the 800 nm fundamental wavelength of a regenerative mode-locked Ti³⁺ sapphire laser.⁴⁷ Measurements were carried out in CH₂Cl₂, with CV as an external reference (β_{xxx}), 338 × 10⁻³⁰ esu in methanol at 800 nm, taking into account the difference in symmetry (octopolar for CV and dipolar for the chromophores). The sample was dissolved in CH₂Cl₂ and passed through 0.2 µm filters. Dilute solutions (10⁻⁵–10⁻⁶ M) were used to ensure a linear dependence of $I_{2\omega}/I_{\omega}^2$ on solute concentration, precluding the need for a Lambert–Beer correction for self-absorption of the second harmonic generation (SHG) signal. High-frequency femtosecond HRS was used to assess any multiphoton fluorescence contribution at 400 nm. No fluorescence effects were observed at 400 nm for all chromophores.

For poled films, the T_g is defined as the temperature at which a change in the reflection of the top gold electrode is first noticed, by heating the sample on a heating chuck, raising the temperature in steps of 5 °C and holding for 5 min at each step. The change of mobility in the material at the T_g causes the gold to buckle, hence losing perfect light reflectivity.

Compounds 1^{48} and 7^{43} were prepared according to procedures reported in the literature.

Compound C2

To a solution of 1 (960 mg, 3.14 mmol) in dry DMF (30 mL) was added tetracyanoethylene (805 mg, 6.28 mmol) and the resulting mixture was stirred at rt for 12 h. The solvent was removed under reduced pressure and the residue dissolved in CH₂Cl₂ (100 mL) and then washed with water (3 × 50 mL). The organic layer was dried over MgSO₄ and the resulting solid was purified by chromatography (hexane–CH₂Cl₂ 1 : 1) to give **C2** as a purple solid (1.2 g, 93%): mp 157–160 °C. ¹H NMR (CDCl₃) δ 3.84 (s, 6H, OCH₃), 6.84 (d, *J* = 9.3 Hz, 2H, ar-H), 6.95 (d, *J* = 9.0 Hz, 4H, ar-H), 7.15 (d, *J* = 9.0 Hz, 4H, ar-H), 7.95 (d, *J* = 9.6 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 55.5, 100.4, 114.2, 115.3, 116.7, 119.51, 121.9, 128.1, 132.4, 136.8, 155.0, 158.5; MS FAB⁺ *m*/z 406.1 ([M⁺], calcd for C₂₅H₁₈N₄O₂ 406.1), FAB⁻ *m*/z 405.9 ([M⁻], calcd 406.1).

4-4'-Di-tert-butyltriarylamine (2)

4-4'-Di-*tert*-butyltriarylamine was prepared analogously to compound **1**, starting from aniline (0.48 mL, 5.24 mmol), 1-*tert*-butyl-4-iodobenzene (2.0 mL, 11.53 mmol), CuI (40 mg, 0.21 mmol), tributyl phosphine (0.10 mL, 0.42 mmol), and KOtBu (1.9 g, 15.72 mmol). Compound **2** was obtained as a white solid (1.16 g, 62%): mp 100–102 °C. ¹H NMR (CDCl₃) δ 1.39 (s, 18H, C(CH₃)₃), 7.01 (t, J = 6.9 Hz, 1H, ar-H), 7.09

(d, J = 8.4 Hz, 4H, ar-H), 7.14 (d, J = 7.8 Hz, 2H, ar-H), 7.29 (t, J = 7.8 Hz, 2H, ar-H), 7.32 (d, J = 8.4 Hz, 4H, ar-H); ¹³C NMR (CDCl₃) δ 31.4, 34.2, 121.8, 123.3, 123.7, 125.9, 129.0, 145.1, 145.3, 148.1; MS MALDI-TOF *m*/*z* 357.5 ([M⁺], calcd for C₂₆H₃₁N 357.5).

Compound C3

Triarylamine **2** (550 mg, 1.54 mmol) was reacted with tetracyanoethylene (790 mg, 6.16 mmol) following a procedure similar to that used for **C2**, giving **C3** as a purple solid (0.57 g, 80%): mp > 230 °C; ¹H NMR (CDCl₃) δ 1.36 (s, 18H, C(CH₃)₃), 6.91 (d, J = 9.0 Hz, 2H, ar-H), 7.16 (d, J = 8.4 Hz, 4H, ar-H), 7.44 (d, J = 8.4 Hz, 4H, ar-H), 7.97 (d, J = 9.0 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 31.2, 34.4, 113.2, 113.4, 114.2, 117.4, 126.4, 127.0, 132.3, 139.2, 141.3, 150.3, 154.8; MS MALDI-TOF m/z 458.1([M⁺], calcd for C₃₁H₃₀N₄ 458.2), FAB⁻ m/z 458.2 ([M⁻], 458.1).

Bisphenol 3

A solution of 1 (7.5 g, 24.6 mmol) in dry chloroform (100 mL) was cooled to 0 °C, and BBr3 (98.4 mL 1 M solution in CH₂Cl₂, 94.8 mmol) was added dropwise. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm to rt and stirred for 5 h. The reaction was carefully quenched with methanol using an ice bath. The solvent was removed under reduced pressure and the residue dissolved in ethyl acetate (200 mL). The resulting solution was washed with a saturated solution of NaHCO₃ (2 \times 100 mL) and water (2 \times 100 mL), dried over MgSO₄, and evaporated to give 3 as a grey solid (6.8 g, 100%): mp 220–222 °C; ¹H NMR (DMSO- d_6) δ 6.64 (d, J = 8.4 Hz, 2H, ar-H), 6.70 (d, J = 8.3 Hz, 4H, ar-H), 6.50–6.75 (m, 1H, ar-H), 6.88 (d, J = 8.3 Hz, 4H, ar-H), 7.09 (t, J = 7.2 Hz, 2H, ar-H), 9.22 (s, 2H, OH); ¹³C NMR (DMSO-d₆) δ 116.8, 119.0, 119.8, 127.7, 129.5, 139.4, 149.6, 154.61; MS FAB⁺ m/z 277.1 ([M⁺], calcd for C₁₈H₁₅NO₂ 277.1), FAB⁻ m/z 276.0 ([M - H⁻], calcd 276.0).

Dialkoxytriarylamine 4

To a solution of 3 (1.5 g, 5.4 mmol) in dry DMF (15 mL) was added K₂CO₃ (5.9 g, 43.3 mmol) and the mixture was stirred at rt for 30 min. After the addition of 1-bromo-2-ethylbutane (6.6 mL, 32.5 mmol) and KI (5.4 g, 32.4 mmol), the reaction mixture was allowed to warm to 70 °C and stirred for 24 h. After evaporating the solvent, the residue was dissolved in CH₂Cl₂ (100 mL) and then washed with a 10% HCl solution until neutral pH and water (3 \times 50 mL). The organic phase was dried over MgSO₄, concentrated under reduced pressure and the residue further purified by chromatography (hexane- $CH_2Cl_2 4 : 1$) to afford 4 as a colorless oil (1.9 g, 85%): ¹H NMR (CDCl₃) δ 0.94 (t, J = 7.2 Hz, 12H, CH₃), 1.42–1.53 (m, 8H, CH₂), 1.68–1.62 (m, 2H, CH), 3.82 (d, J = 5.4 Hz, 4H, OCH₂), 6.75– 6.86 (m, 5H, ar-H), 6.40 (d, J = 7.8 Hz, 2H, ar-H), 7.03 (d, J = 7.5 Hz, 4H, ar-H), 7.13 (t, J = 7.0 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 11.4, 23.6, 41.2, 70.6, 115.4, 120.6, 120.9, 126.6, 129.1, 141.1, 149.1, 155.8; MS FAB⁺ m/z 445.3 ([M⁺], calcd for C₃₀H₃₉NO₂ 445.3).

Compound C4

Reaction of **4** (780 mg, 1.75 mmol) with tetracyanoethylene (1.3 g, 10.5 mmol) following a procedure similar to that for **C2**, yielded **C4** as a purple solid (717 mg, 75%): mp 130 °C; ¹H NMR (CDCl₃) δ 0.96 (t, J = 7.5 Hz, 12H, CH₃), 1.42–1.50 (m, 8H, CH₂), 1.61–1.71 (m, 2H, CH), 3.85 (d, J = 6.0 Hz, 4H, OCH₂), 6.84 (d, J = 9.0 Hz, 2H, ar-H), 6.92 (d, J = 8.7 Hz, 4H, ar-H), 7.12 (d, J = 8.7 Hz, 4H, ar-H), 7.93 (d, J = 9.6 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 11.4, 23.6, 41.1, 70.6, 79.9, 113.6, 113.8, 114.5, 116.1, 116.9, 119.7, 128.3, 132.6, 137.7, 155.4, 158.6; MS FAB⁺ m/z 546.0 ([M⁺], calcd for C₃₅H₃₈F₁₀N₄O₂ 546.3).

Dialkoxytriarylamine 5

To a solution of 3 (700 mg, 2.52 mmol) in dry DMF (15 mL) was added K₂CO₃ (3.5 g, 25.2 mmol) and the mixture was stirred at rt for 30 min. After the addition of 2,3,4,5,6-pentafluorobenzyl bromide (1.53 mL, 10.1 mmol) and KI (1.68 g, 10.1 mmol), the reaction mixture was allowed to warm to 70 °C and stirred for 24 h. After evaporating the solvent, the residue was dissolved in CH₂Cl₂ (100 mL) and then washed with a 10% HCl solution until neutral pH and water (3 \times 50 mL). The organic phase was dried over MgSO₄, concentrated under reduced pressure and the residue further purified by chromatography (hexane- CH_2Cl_2 6 : 4) to afford 5 as an off-white solid (1.40 g, 88%): mp 103–105 °C; ¹H NMR (CDCl₃) δ 5.02 (s, 4H, 0CH₂), 6.80 (d, J = 9.3 Hz, 4H, ar-H), 6.70–6.98 (m, 1H, ar-H), 6.90 (d, J = 8.4 Hz, 2H, ar-H), 6.97 (d, J = 9.3 Hz, 4H, ar-H), 7.12 (t, J = 8.4 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 57.8, 110.2, 115.8, 121.4, 121.9, 126.0, 129.0, 138.8, 140.4, 142.3, 142.9, 144.5, 146.9, 148.3, 153.8; MS FAB⁺ m/z 637.2 ([M⁺], calcd for $C_{32}H_{17}F_{10}NO_2$ 637.1).

Compound C5

Reaction of **5** (1.36 g, 2.14 mmol) with tetracyanoethylene (823 mg, 6.42 mmol) following a procedure similar to that for **C2**, gave **C5** as a purple solid (1.10 g, 68%): mp 207–209 °C; ¹H NMR (CDCl₃) δ 5.14 (s, 4H, OCH₂), 6.86 (d, J = 9.0 Hz, 2H, ar-H), 7.01 (d, J = 9.3 Hz, 4H, ar-H), 7.18 (d, J = 9.3 Hz, 4H, ar-H), 7.18 (d, J = 9.3 Hz, 4H, ar-H), 7.95 (d, J = 9.0 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 57.6, 81.0, 113.0, 113.3, 114.2, 116.3, 117.0, 119.80, 128.3, 132.3, 137.9, 147.0, 154.7, 156.7; MS FAB⁺ *m*/*z* 738.8 ([M⁺], calcd for C₃₇H₁₆F₁₀N₄O₂ 738.1, FAB⁻ *m*/*z* 738.5 ([M⁻], calcd 738.1).

2,2,2-Trichloroethyl 3,5-bis(perfluorobenzyloxy)benzoate (8)

2,2,2-Trichloroethyl 3,5-bis(perfluorobenzyloxy)benzoate was prepared analogously to **5** starting from **7** (1.6 g, 5.60 mmol), pentafluorobenzyl bromide (2.03 mL, 13.4 mmol), K₂CO₃ (7.7 g, 56.0 mmol) and KI (3.7 g, 22.4 mmol) in dry THF (30 mL) instead of dry DMF. Compound **8** was obtained as a colorless oil (1.18 g, 33%). ¹H NMR (CDCl₃) δ 4.97 (s, 2H, COOCH₂), 5.17 (s, 4H, OCH₂), 6.82 (t, J = 2.1 Hz, 1H, ar-H), 7.41 (d, J = 2.1 Hz, 2H, ar-H); MS FAB⁺ m/z 645.4, calcd for C₂₃H₉Cl₃F₁₀O₄ 645.6.

3,5-Bis(perfluorobenzyloxy)benzoic acid (9)

To a solution of **8** (1.18 g, 1.82 mmol) in dry THF (6 mL) was added glacial acetic acid (6 mL), and the mixture was stirred at rt for 10 min. Zn dust (0.74 g, 11.5 mmol) was then added and the resulting mixture was stirred vigorously for 1.5 h. The reaction mixture was filtered and the filtrate was poured into water (100 mL). After extracting with diethyl ether (2 × 50 mL) the combined extracts were dried over MgSO₄ and the solvent removed under reduced pressure to afford **9** as a white solid (0.94 g, 100%): mp 158–159 °C; ¹H NMR (CDCl₃) δ 5.16 (s, 4H, CH₂), 6.79 (t, J = 3.0 Hz, 1H, ar-H), 7.40 (d, J = 3.0 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 58.0, 108.5, 109.6, 131.7, 136.1, 144.3, 147.6, 159.3, 170.7; MS FAB⁺ m/z 514.1 ([M⁺], calcd for C₂₁H₈F₁₀O₄ 514.0), FAB⁻ m/z 512.8 ([M – H⁻], calcd 513.0).

Fluorinated dendron (6)

To a solution of 9 (600 mg, 1.17 mmol) in a mixture of dry CH₂Cl₂ (4 mL) and dry THF (8 mL) was added 3 (147 mg, 0.53 mmol) followed by 4-dimethylaminopyridine (DMAP) (65 mg, 0.53 mmol), and the mixture was stirred at rt for 15 min. N,N'-Dicyclohexylcarbodiimide (DCC) (264 mg, 1.28 mmol) was then added, and the mixture was stirred for 48 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by silica gel column chromatography (hexane-CH₂Cl₂ 1 : 1) to afford 6 as a yellow solid (347 mg, 52%): mp 69–71 °C; ¹H NMR (CDCl₃) δ 5.18 (s, 8H, OCH2), 6.81-6.83 (m, 2H, ar-H), 7.02-7.07 (m, 1H, ar-H), 7.07-7.12 (m, 4H, ar-H), 7.12-7.15 (m, 2H, ar-H), 7.16-7.18 (m, 4H, ar-H), 7.28–7.30 (m, 2H, ar-H), 7.48–7.49 (m, 4H, ar-H); ¹³C NMR (CDCl₃) δ 58.0, 108.2, 109.6, 122.5, 123.4, 124.5, 125.1, 129.6, 132.2, 136.1, 139.5, 144.3, 145.8, 146.2, 147.8, 159.4, 164.7; MS MALDI-TOF m/z 1269.1 ([M⁺], calcd for C₆₀H₂₇F₂₀NO₈ 1269.0).

Compound C6

To a solution of 6 (300 mg, 0.24 mmol) in DMF (10 mL) was added tetracyanoethylene (605 mg, 4.72 mmol), followed by heating at 90 °C for 48 h. The solvent was removed under reduced pressure and the residue dissolved in CH₂Cl₂ (50 mL). The solution was washed with a saturated brine solution (4 \times 100 mL). The organic layer was dried over MgSO₄ and the resulting solid was purified by chromatography (hexane- CH_2Cl_2 3 : 7) to give C6 as a purple solid (279 mg, 86%): mp 103-105 °C; ¹H NMR (CDCl₃) δ 5.20 (s, 8H, OCH₂), 6.86 (t, J = 2.1 Hz, 2H, ar-H), 7.04 (d, J = 9.3 Hz, 2H, ar-H), 7.26 (d, J = 9.0 Hz, 4H, ar-H), 7.33 (d, J = 9.0 Hz, 4H, ar-H), 7.49 (d, J = 2.1 Hz, 4H, ar-H), 8.00 (d, J = 9.3 Hz, 2H, ar-H); ¹³C NMR (CDCl₃) δ 58.0, 108.3, 109.6, 113.1, 114.2, 118.5, 120.8, 123.7, 128.1, 131.6, 132.5, 138.6, 142.1, 149.4, 154.3, 159.4, 164.3; MS MALDI-TOF *m/z* 1369.4 ([M⁻], calcd for C₆₅H₂₆F₂₀N₄O₈ 1370.0).

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