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Effects of Dendronization on the Linear and Third-Order Nonlinear Optical Properties of Bis(thiopyrylium) Polymethine Dyes in Solution and the Solid State

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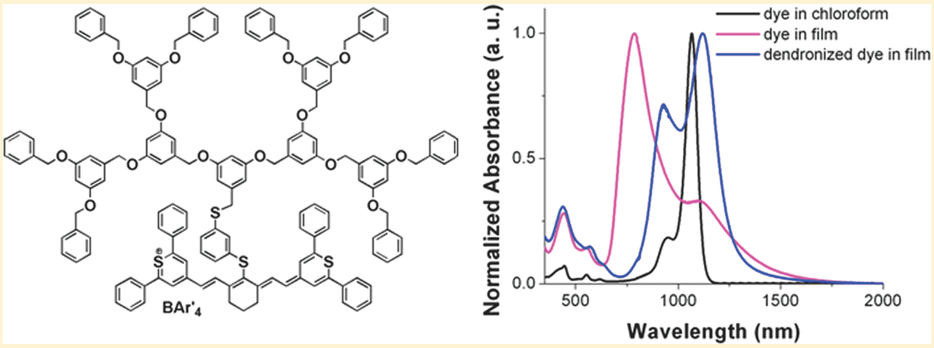
Supporting Information



ABSTRACT: Effects of the size and attachment position of benzyl aryl ether dendrons covalently attached to bis(thiopyrylium) penta- and heptamethines on the optical properties of these dyes in solution and in solid films have been investigated. In dilute solution the low-energy absorption bands of some of the dendronized species differ from those of the parent compounds in having much smaller transition dipole moments, this effect possibly due to differences in ion pairing, while at higher concentrations, dye−dye interactions lead to a decrease in the transition dipole moments of the nondendronized species, but not of the dendronized ones. Consequently, in the high concentration range, dendronized and nondendronized species exhibit similar values of the real part of the microscopic third-order polarizability at 1550 nm. Solid-state film absorption spectra suggest that the dendrons significantly disrupt the chromophore−chromophore interactions seen for the nondendronized species, reducing, but not eliminating, linear absorption losses in the near-IR, and suppressing absorption peaks that are hypsochromically shifted from the solution spectra maximum: centrally placed dendrons have a larger effect than terminal dendronization, so that the corresponding thin-film spectra more closely resemble those seen in solution with increasing generations of dendronization. Z-scan measurements at 1550 nm indicate that the third-order susceptibility of dendronized heptamethine guest−host films depend approximately linearly on doping ratio of dyes and are in reasonable agreement with values extrapolated from solution-derived third-order polarizabilities; in contrast, the susceptibilities of films highly doped with an undendronized analogue fall short of values expected from solution polarizabilities.

KEYWORDS: *polymethines, dendrons, aggregation, optical properties, third order nonlinear optical properties*

INTRODUCTION

Materials for all-optical signal processing (AOSP) applications must exhibit large ultrafast macroscopic third-order susceptibilities ($\chi^{(3)}$) and low linear and nonlinear optical loss at the wavelength(s) of interest—typically in the telecommunications wavelength range (1300−1550 nm)—as well as good processability. Cyanine-like polymethines are particularly promising organic dyes for AOSP applications due to their large (negative) nonresonant microscopic third-order polarizabilities, γ,[1−6] compared to many other conjugated materials of comparable size.[7−12] The origin of these large values can be understood using the sum-over-states expression for the static value of the real part of γ, Re(γ_0). In the case of cyanine-like polymethines, this is dominated by a term in which the transition dipole moment, M_{ge}, and transition energy, E_{ge}, between the ground- and first-excited state appear, cyanine-like species exhibiting large M_{ge} values and small E_{ge} values:

$$\mathrm{Re}(\gamma_0) \propto -{M_{ge}}^4/{E_{ge}}^3 \qquad (1)$$

Moreover, due to the similarity of the ground and excited-state geometries, the lowest energy absorption band of chromophores of this class is typically characterized by a

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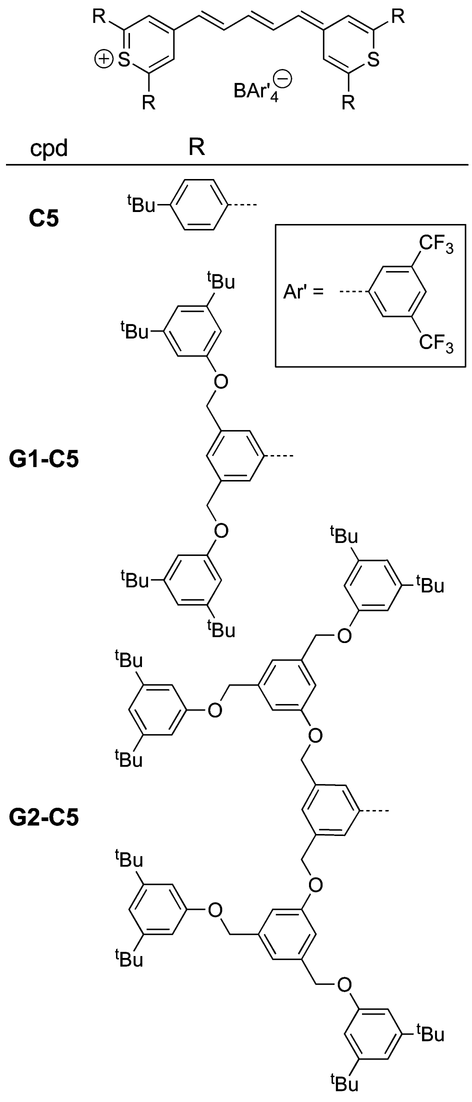
sharp low-energy onset, allowing one to use compounds with low-lying excited states and, therefore, large Re(γ_0), and to take advantage of near-resonance enhancement of γ without incurring unacceptable linear loss. We reported on a series of bis(chalcogenopyrylium)-terminated polymethines with an exceptional combination of microscopic nonlinear optical (NLO) properties at telecommunications wavelengths, that is, large real components of γ (Re(γ) is related to nonlinear refraction) and small imaginary components of γ (Im(γ) is related to nonlinear loss, specifically two-photon absorption), which could be promising for AOSP.[2]

However, while the relationship between chemical structure and the magnitude of γ is relatively well-understood,[1,2,9,13−17] an important challenge for realizing AOSP applications is to translate these promising microscopic nonlinearities into high chromophore volume-fraction materials with the correspondingly large bulk nonlinearities, $\chi^{(3)}$, needed for device operation at acceptable optical intensities while maintaining relatively short interaction lengths. It is well-known that cyanine chromophores are inherently highly polarizable and are, therefore, prone to aggregation at high concentrations, leading to the formation of dimers or other aggregates with various relative orientations of molecules, that is, H- or J-aggregates (with parallel long axes and a face-to-face arrangement or end-to-end arrangement, respectively) or oblique arrangements of chromophores. The intermolecular electronic interactions lead to a mixing of the excited state wave functions that can result in a splitting (for inclined or oblique dimers), or a hypsochromic shift (for H-aggregates) or bathochromic shift (for J-aggregates) of the electronic absorption band relative to what is seen for isolated molecules in dilute solutions.[6,18−22] Such changes in the absorption spectrum could have adverse effects on the macroscopic properties of materials derived from these dyes. In particular, a hypsochromic shift could lead to decreased $\chi^{(3)}$ relative to that expected from the solution values of γ for isolated molecules and a bathochromic shift, while potentially augmenting the macroscopic nonlinearity, could lead to increased linear losses at the operating wavelengths.

Considerable efforts have been made to control the aggregation of cyanine and cyanine-like dyes in solution[23−33] and in films.[18,34−42] For example, polymeric carbohydrates such as carboxymethylamylose have been used to promote the formation of J-aggregates of mono- and trimethine dyes in solution,[29−33] while electrostatic self-assembly of layers of trimethines alternating with layers of polymers or other dyes bearing complementary charges has been shown to lead to the formation of well-defined aggregates in films.[35,40−42] However, we are not aware of solid-state aggregation studies of polymethine dyes with sufficiently extended conjugation to exhibit promising molecular-level optical properties for AOSP. In the case of bis(chalcogenopyrylium) polymethines, an ideal situation would be retention of the dilute-solution optical properties of the dyes in the solid state, that is, prevention of aggregation phenomena. Previous studies of cyclodextrins[43] and dendrimer/cyanine host−guest systems[20] suggest routes favorable for aggregate suppression; however, the chromophore loading densities employed were orders-of-magnitude lower than the ≥10 wt % loadings required for AOSP. Covalently attached dendrons have been used to prevent aggregation of a variety of chromophores,[44−52] but this strategy has not been employed for polymethines in the context of third-order NLO materials. Here, we systematically investigate the effect of size and position of covalently attached benzyl-ether-based dendrons on the linear and NLO properties of bis(chalcogenopyrylium) polymethines (Charts 1 and 2) in both solution and solid state. As discussed above, these types of cyanine-like dyes exhibit very promising solution properties for AOSP applications; in the present study, we specifically use dyes with thiopyrylium end groups, since these have a similar NLO response to their selenium analogues,[2] but are expected to be less toxic, and a heptamethine precursor having a readily functionalizable position on the methine bridge is commercially available.

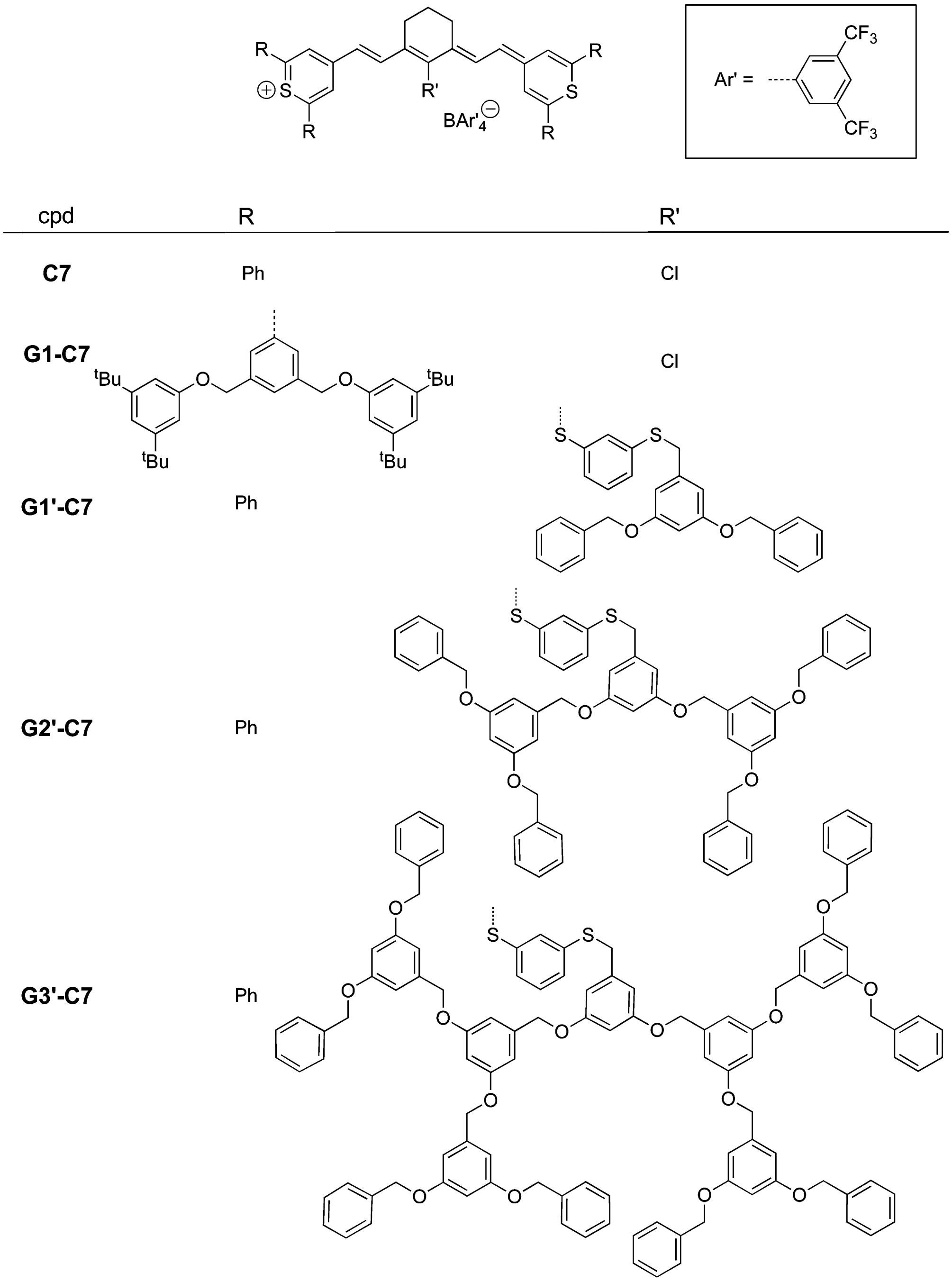
Chart 1. Structures of Pentamethines Studied in This Paper



■ EXPERIMENTAL SECTION

Starting materials were obtained from commercial sources and used without further purification. Compounds **1**,[53] **14**,[54] **15**,[55] **16a−c**,[56−58] **C7**,[2] and NaBAr'$_4$[59] were synthesized according to reported procedures. The synthesis of the new compounds is shown in Schemes 1−3 and is described in the Supporting Information, along with characterizing data. UV-visible near infrared (UV-vis-NIR) spectra were recorded in 1 cm cells using a Varian Cary 5E spectrometer. Varian 300, Bruker 400, and Bruker 500 spectrometers were used to record NMR spectra. Mass spectrometry was carried out using a Micromass Quattro LC for ESI experiments, a Micromass AutoSpec M for EI experiments and an Applied Biosystems 4700

Chart 2. Structures of Heptamethines Studied in This Paper

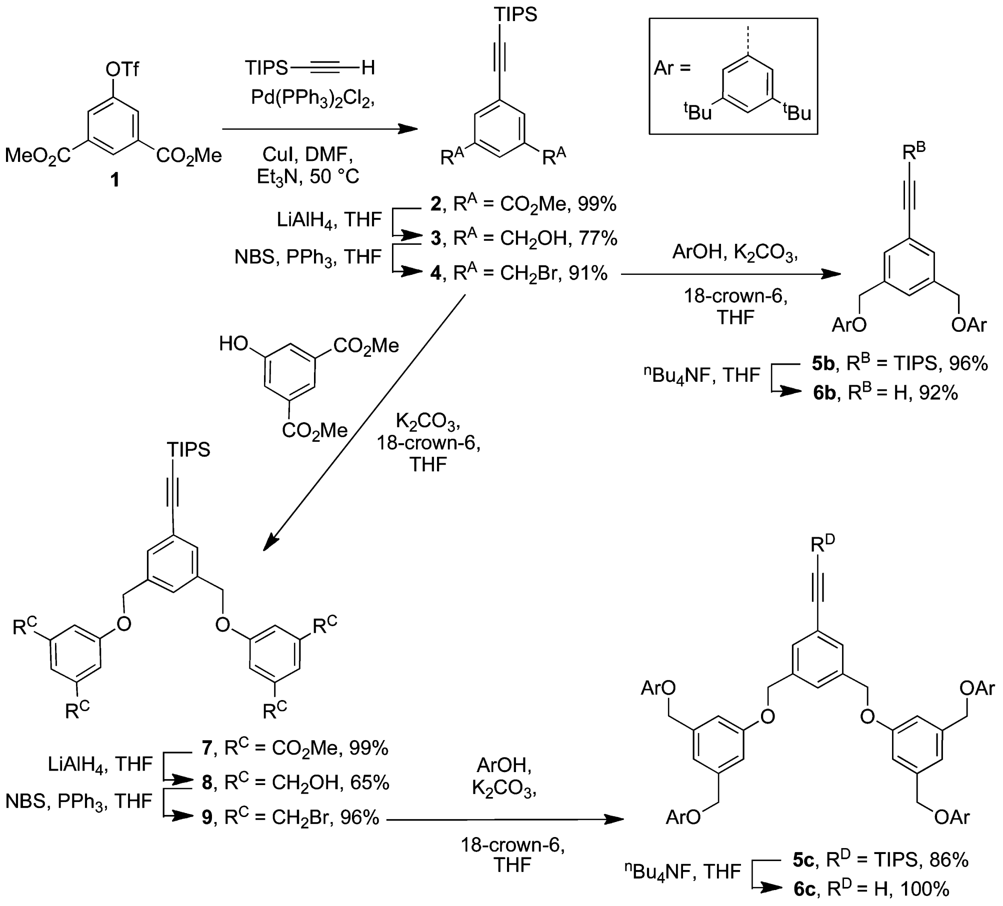


Proteomics Analyzer for MALDI-TOF experiments. Elemental analyses were performed by Atlantic Microlabs. Neat films for linear absorption measurements were prepared by dissolving each dye (10 mg) in dichloromethane (0.5 mL) in a 5 mL vial; the solution was left stirring for about 30 min and then filtered through a 0.45 μm PTFE syringe filter before it was spin coated onto a glass coverslip at 700 rpm for 1 min. Blended films for linear and nonlinear measurements were obtained by mixing a filtered dichloromethane solution of the dye (30 mg in 0.4 mL) with a 1,1,2-trichloroethane solution of APC (30 mg poly(bisphenol A carbonate), from Sigma-Aldrich, 435120, in 0.4 mL) in the desired ratio and spin-coating the mixture onto a glass coverslip at 700 rpm for 2 min (see Table S1 in Supporting Information for thicknesses of the resultant films). The real and imaginary components of the third-order polarizability, γ, and the third-order susceptibility, $\chi^{(3)}$, at 1550 nm were measured using the femtosecond-pulsed Z-scan technique,[60] in the same way as previously described in refs 2, 19, and 61.

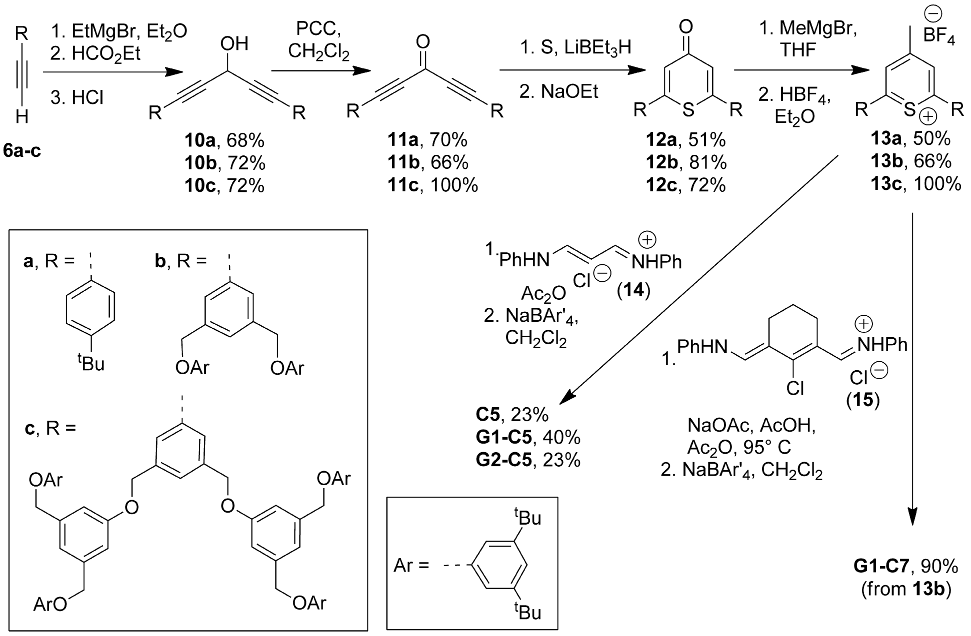
■ RESULTS AND DISCUSSION

Synthesis of Dyes with Dendronized Thiopyrylium Termini. Polymethines with dendronized thiopyrylium termini were prepared by Knoevenagel condensation of dendronized 4-methyl-thiopyrylium cations with phenylaminium-terminated tri- and pentamethines. To obtain dendronized thiopyrylium units, dendrons with a terminal alkyne at the focal point are required (**6a**–**c**). Scheme 1 shows the synthetic routes to obtain these desired dendrons. Compound **6a** is commercially available, while compounds **6b** and **6c** were prepared from dimethyl 5-(trifluoromethylsulfonyloxy)isophthalate, **1**. Sono-

Scheme 1. Synthesis of Dendrons with Alkyne Units as Focal Functionality

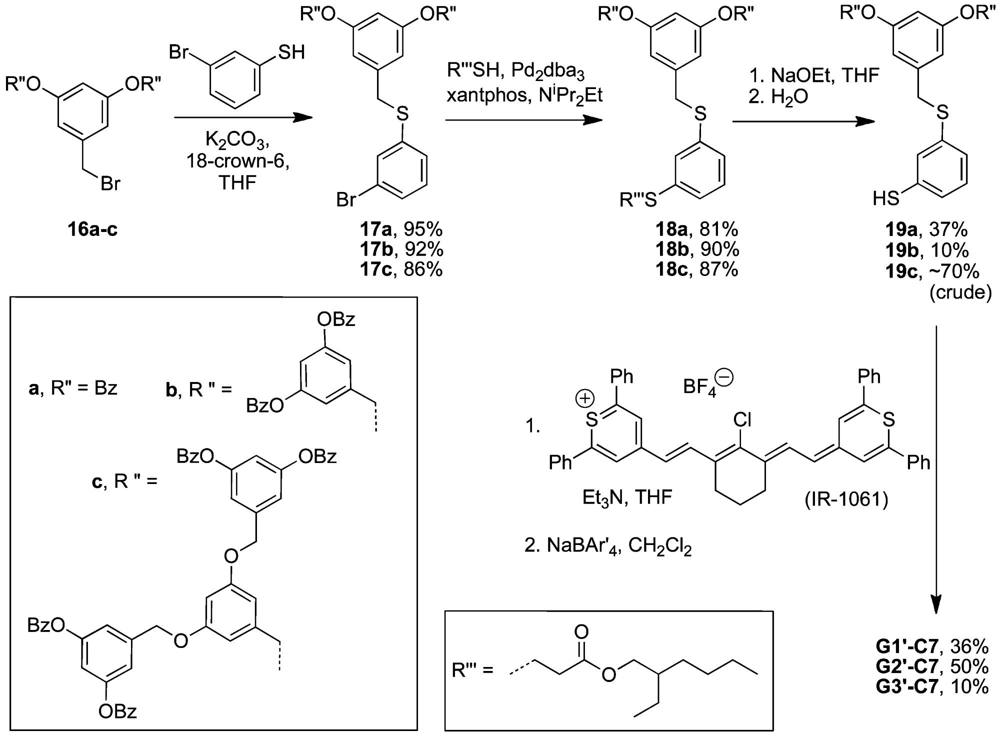


Scheme 2. Synthesis of Tetrafluoroborate Salts of Thiopyrylium Cations with Different Generations of Dendron and Their Conversion to Penta- and Heptamethines



gashira coupling between **1** and ethynyltri(isopropyl)silane led to the protected alkyne **2** in near-quantitative yield. Reduction of the methyl ester functionalities using lithium aluminum hydride gave the corresponding diol (**3**) in 77% yield; **3** was then converted to the corresponding di(bromomethyl) species (**4**) in 91% yield using *N*-bromosuccinimide (NBS) and triphenylphosphine. Compound **5b** was obtained by the nucleophilic substitution of **4** with 3,5-di-*tert*-butylphenol in

Scheme 3. Synthesis of Dendrons with a Benzene Thiol at the Focal Point and Conversion to the Corresponding Dendronized Heptamethine Cyanines



the presence of potassium carbonate and 18-crown-6. Finally, deprotection of the tri(isopropyl)silyl (TIPS) protecting group using tetra-*n*-butylammonium fluoride led to compound **6b**. To synthesize a higher generation dendron with alkyne functionality (**6c**), the di(bromomethyl) intermediate **4** was reacted with dimethyl 5-hydroxyisophthalate to obtain dendron **7**, in which the peripheral groups are methyl esters. Repetitive synthetic procedures to install 3,5-di-*tert*-butylphenyl groups at the peripheries and to deprotect the TIPS group were performed under similar conditions to those described above to afford the desired product, **6c**, in a good overall yield.

The 2,6-diaryl-4*H*-chalcogenapyran-4-ones **12a−c** were prepared according to a literature procedure[62] (Scheme 2): the reaction of ethyl formate with 2 equiv of the Grignard reagents derived from reaction of **6a−c** and ethylmagnesium bromide led to the hydroxylated dendrons **10a−c**, which were then oxidized by pyridinium chlorochromate (PCC) to give the ketone derivatives **11a−c**. These species were then reductively cyclized with sulfur to afford compounds **12a−c**. Finally, the addition of 1 equiv of methylmagnesium bromide, followed by treatment with tetrafluoroboric acid, gave the tetrafluoroborate salts of different generations of dendronized 4-methylthiopyrylium cations (**13a−c**).

The nondendronized (**C5**) and dendronized (**G1-C5** and **G2-C5**) pentamethine dyes were synthesized by reacting 2 equiv of the appropriate 4-methylthiopyrylium salt (**13a−c**) with trimethine salt **14** in acetic anhydride at 90 °C (Scheme 2). The progress of the reaction was tracked by the evolution of a characteristic absorption band of bis(thiopyrylium) pentamethines around 900 nm. When the evolution of this band had ceased, the reaction was quenched with water to give a precipitate, which was isolated by filtration. A counterion exchange was then performed using sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr'_4$). The presence of the $BAr'_4{}^-$ counterion[63] greatly increases the solubility and also facilitates purification by column chromatography, especially for the species with lower generation dendrons.

The nondendronized heptamethine dye (**C7**) was obtained from counterion metathesis with $NaBAr'_4$[59,63] of the corresponding commercially available tetrafluoroborate salt (IR-1061), as previously described,[2] to increase the solubility of the dye in common organic solvents and to allow direct comparison of the aggregation behavior of undendronized and dendronized dyes having the same counterions.

G1-C7 was prepared under conditions similar to those used for its dendronized pentamethine analogs (Scheme 2). In this case, 2 equiv of **13b** was allowed to react with the amino-terminated pentamethine salt (**15**) in acetic anhydride, and the evolution of the characteristic band associated with the heptamethine dye at ca. 1080 nm was monitored. The pure compound was obtained in 40% yield after metathesis with $NaBAr'_4$.

Synthesis of Dyes with Dendronization on the Bridge.

Bis(thiopyrylium) heptamethine dyes with dendrons attached to the middle of the polymethine bridge were obtained by nucleophilic substitution of the chloro substituent in the center of the bridge of the commercially available heptamethine dye (IR-1061) by dendrons with a nucleophile at their focal point. Benzenethiolate was chosen as the reactive group due to its high nucleophilicity, thereby allowing the use of mild reaction conditions to minimize the possibility of dye decomposition. Benzyl aryl ether dendrons containing the bromomethyl functionality at the focal point (**16a−c**) were synthesized by a convergent approach, following conditions reported in the literature (Scheme 3).[56−58] Reaction of the bromomethyl dendrons with 3-bromobenzene thiol gave the bromophenyl functionalized dendrons (**17a−c**) in excellent yields. Subsequently, the bromoaryl dendrons and 2-ethylhexyl-3-

mercaptopropionate were coupled using $Pd_2(dba)_3$ and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) as the catalyst system to obtain dendrons with the 2-ethylhexyl-3-mercaptopropionate group at their focal points in excellent yields (**18a−c**).[64] Finally, these alkylated benzene thiols were cleaved using sodium ethoxide to give the corresponding aryl thiol dendrons (**19a−c**), the formation of which could be confirmed by the presence of the thiol resonance at around 3.40 ppm in the ^{1}H NMR spectra. However, the yield in this step is quite low for **19a** and **19b** dendrons (37% and 10%, respectively). An attempt to purify G3′ benzene thiol (**19c**) failed, perhaps due to instability of the compound, and therefore, this compound was used directly in the next step of the synthetic procedure without purification.

Dendrons were attached to the heptamethine bridge by the reaction of dendron-functionalized benzene thiols **19a−c** with IR-1061 using triethylamine as a base in THF (Scheme 3). The formation of the desired products was again monitored by UV-vis-NIR spectrometry and was indicated by a 5−10 nm bathochromic shift in the position of the absorption maximum relative to that of the starting material and differences in the vibronic structure of this absorption feature. Finally, the G1′-G3′ dendronized dyes were subjected to metathesis with $NaBAr'_4$ to afford the desired products, **G1′-C7**, **G2′-C7**, and **G3′-C7**.

Table 1. Linear Optical Properties of Bis(Thiopyrylium) Polymethines in Dilute (< 10 μM) Chloroform Solutions

cmpd	λ_{max} (nm)	$\varepsilon_{max}{}^{a}$ (M^{-1} cm^{-1})	M_{ge} (D)^{b}
C5	904	3.11×10^5	15.9
G1-C5	904	3.55×10^5	17.0
G2-C5	899	2.72×10^5	15.5
C7	1067	4.01×10^5	19.3
G1-C7	1079	3.66×10^5	18.5
G1′-C7	1081	3.34×10^5	18.8
G2′-C7	1081	2.67×10^5	17.0
G3′-C7	1085	2.48×10^5	16.3

[a] Experimental uncertainty in ε_{max} estimated to be ±2%. [b] Obtained from $M_{ge} = 0.09584(\int \varepsilon d\nu/\nu_{max})^{0.5}$, where M_{ge} is in debye, D, ε is in M^{-1} cm^{-1}, and ν_{max}, the wavenumber corresponding to the absorption maximum, is in cm^{-1}, and the integral is over the lowest energy absorption band.

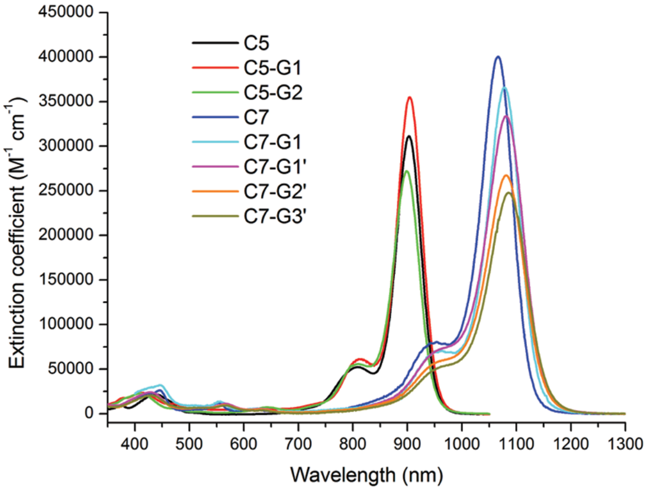


Figure 1. Absorption spectra of polymethine dyes in chloroform.

Linear Absorption Spectra in Dilute Solution. Figure 1 shows the UV-vis-NIR absorption spectra of bis(thiopyrylium) pentamethine and heptamethine dyes in chloroform at low concentrations (<10 μM); absorption maxima (λ_{max}), molar absorptivities (ε_{max}), and transition dipole moments (M_{ge}) for the low-energy transitions are summarized in Table 1.[65] Dendronization only has a minor effect on the position of the absorption maxima for either the penta- or heptamethines (±155 cm^{-1}), but for many of the dendronized species, ε_{max} and M_{ge} are significantly decreased: in the pentamethine series, the G2 species possesses a weaker transition than its G1 and undendronized analogues, while in the heptamethines the transitions are weaker for all the dendronized species than for the undendronized reference compound and decrease in strength with increasing generation of bridge-based dendronization. No deviation from Beer's law was observed at the concentrations used (<10 μM), suggesting that aggregate formation is not responsible for the observed reduction in ε_{max} values. However, differences in ion pairing between the dendronized species and the nondendronized model compounds may play a role: for example, similar spectral modifications for an indolinium-based heptamethine have been attributed to counterion- and solvent-dependent ion-pairing effects,[66] and similar changes are found for the spectra of **C7** (IR1061) analogues possessing various counterions in solvents with different polarity (see Supporting Information, Figure S2, Table S2).

Linear Absorption Spectra in Concentrated Solutions. To investigate the efficacy of dendron units in the prevention of aggregate formation, UV-vis-NIR spectra of dyes **C7**, **G1-C7**, and **G3′-C7** were recorded at concentrations up to three orders-of-magnitude larger than those discussed in the previous section (up to 3.9×10^{-3} M, 8.6×10^{-4} M, and 8.0×10^{-4} M, respectively, see Figure 2). In the absence of the dendron unit, an increase in dye concentration causes the normalized absorption spectra of **C7** to show increases in intensity of the higher lying vibronic (E_{0-1}) band relative to the lowest energy band (E_{0-0}). Furthermore, concomitant decreases in ε_{max} and M_{ge} are observed. This deviation from Beer's law is suggestive of aggregate formation at these elevated concentrations, although changes in the extent of ion-pairing may also contribute. However, when dendron units are introduced at the periphery (**G1-C7**) or at the center of the dye (**G3′-C7**), the shape and ε_{max} values of the spectra do not change significantly when dye concentration is increased; that is, dendronization is effective at suppressing concentration dependence, perhaps by reducing chromophore−chromophore interactions. An important consequence in the context of the solution NLO measurements described below is that the high-concentration solution values of M_{ge} for **C7** and for the dendronized heptamethines are similar (see Supporting Information, Table S3), apparently due to the similarity of the effects of chromophore−chromophore interactions on the spectrum of the former to those of dendronization on the spectra of the latter.

Linear Absorption Spectra in Films. The absorption spectrum of the bis(thiopyrylium) pentamethine dye without the dendron (**C5**) as a neat film exhibits two prominent low-energy maxima (Figure 3). The higher-energy of these maxima is at 721 nm, hypsochromically shifted by ca. 2800 cm^{-1} from the solution absorption maximum of **C5**, while a weaker feature has a maximum at 917 nm, slightly bathochromically shifted

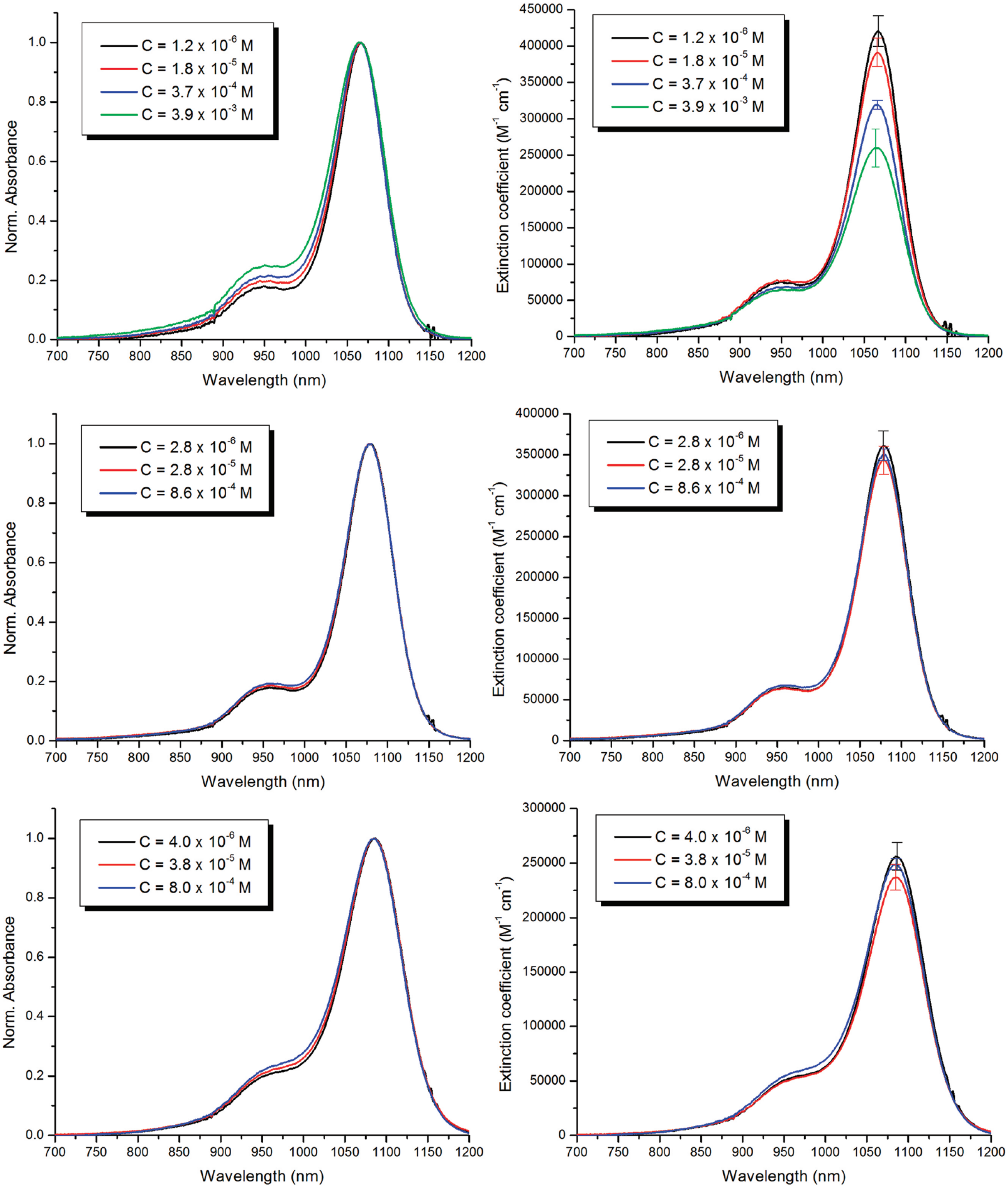


Figure 2. Absorption spectra of **C7** (top), **G1-C7** (middle), and **G3′-C7** (bottom) in chloroform at different concentrations. Left: Spectra graphed on a normalized absorbance scale. Right: Spectra graphed on an ε scale.

relative to the solution peak. According to the two-level model for γ of eq 1, the overall hyspochromic shift of the majority of the transition oscillator strength is expected to lead to a decreased magnitude of the third-order polarizability and susceptibility. Moreover, the film spectrum also shows a tail extending to much longer wavelengths than for the solution spectrum, which may be due to either absorption or scattering, and is potentially problematic from the point of view of obtaining good linear transparency in the near-IR for AOSP applications.

When the **G1** dendron (**G1-C5**) is incorporated at the thiopyrylium termini, the resulting low-energy absorption of the neat film exhibits three distinct maxima, the strongest of which appears at about 805 nm, that is, hypsochromically

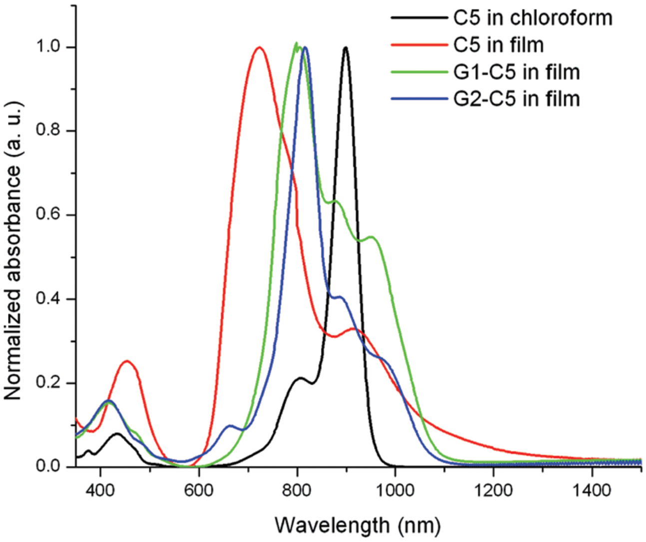


Figure 3. UV-vis-NIR absorption spectra of **C5** in chloroform and **C5** and its dendronized analogs as neat films.

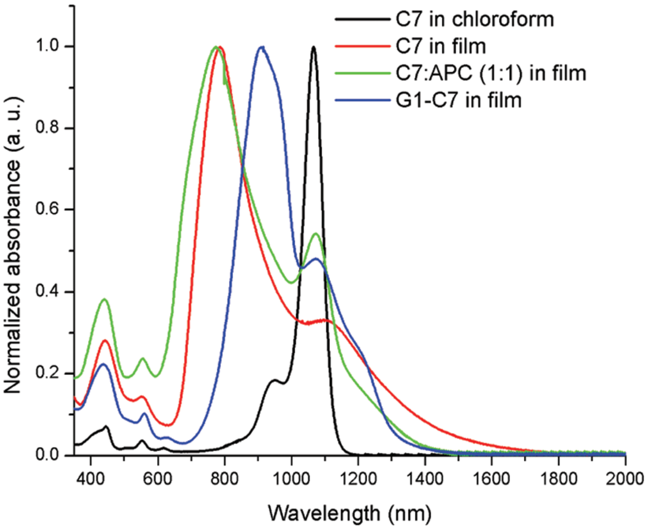


Figure 4. UV-vis-NIR absorption spectra of **C7** in chloroform and films of neat **C7**, 1:1 w/w **C7** in APC, and neat **G1-C7**.

shifted from that seen in solution, but less so than that of its nondendronized analog (**C5**), with additional maxima at 879 and 954 nm. A qualitatively similar spectrum is seen for a neat film of **G2-C5**, differing mainly in the relative absorbance at the three maxima. The spectra of these dendronized pentamethine systems also exhibit a sharper low-energy band edge than their nondendronized counterparts: whereas the absorption/scattering tail of the **C5** film extends to ca. 1500 nm, the onset of extinction is ca. 1150 nm in the **G1-C5** film. Thus, **G1** or **G2** dendronization at the termini evidently leads to modification of the type of aggregation with respect to that found in neat films of nondendronized chromophores; however, the spectra are still very different from those observed in solution, suggesting that the NLO properties may also deviate significantly from those seen in solution. Nonetheless, the decrease in linear optical loss throughout the telecommunications wavelength range (1300−1550 nm) suggests that this approach may be advantageous for AOSP applications.

The neat film of the parent bis(thiopyrylium) heptamethine **C7** shows an absorption peak at 785 nm (Figure 4), substantially blue-shifted relative to the main absorption maximum in solution, and a broad band ($\lambda_{\max}$ = 1103 nm), slightly red-shifted from the monomeric absorption peak; that is, the spectrum is reminiscent of that of the neat **C5** film discussed above. The effect of terminal dendronization on the spectrum is similar to that in the case of the pentamethine dyes: the strongest absorption in the spectrum of a neat **G1-C7** film ($\lambda_{\max}$ = 896 nm, Figure 4) is less blue-shifted than that of a **C7** film and the extent of the absorption/scattering tail is reduced. It should be noted here that dendronization dilutes the density of the active chromophore in the films. To investigate whether the observed spectral differences between films of nondendronized and dendronized systems are caused purely by this dilution of dye content or by the architectural difference between these two molecules, a film containing **C7** and amorphous polycarbonate (APC) in a 1:1 weight ratio was prepared. This film contains 50% by weight of "chromophore" (henceforth defined as the thiopyrylium polymethine molecule and counterion excluding the dendron), similar to that of neat **G1-C7** (45%). The two absorption bands of the blended film appear at nearly the same positions as those of the **C7** neat film but with a slight difference in their relative absorbances (Figure 4); thus, the effect of dendronization on the neat film spectrum of **G1-C7** cannot be fully attributed to a dilution effect, suggesting that this type of dendronization does modify the chromophore−chromophore interactions in the films.

Attaching dendrons to the middle of the heptamethine bridge also leads to two maxima in the lower-energy part of the neat-film spectra (Figure 5a). The higher energy of the two maxima in each case ($\lambda_{\max}$ = 918, 919, and 923 nm in **G1′-C7**, **G2′-C7**, and **G3′-C7**, respectively) is blue-shifted compared to the respective solution maximum, while a lower energy maximum appears at around 1120 nm in all cases, the relative absorbance (compared to the respective higher energy peak) of which increases with increasing size of the dendron (Figure 5a). Since the neat films of **Gi′-C7** have different concentrations of chromophores (77, 63, and 46 wt % for **G1′-C7**, **G2′-C7**, and **G3′-C7**, respectively) APC-blended films of **C7** and the **Gi′-C7** series containing similar concentrations of the chromophore (Figure 5b, 1:1 **G3′-C7**/APC, 3:7 **G2′-C7**/APC, 3:7 **G1′-C7**/APC, and 3:7 **C7**/APC, containing 23, 19, 23, and 30% chromophore by weight, respectively) were prepared to compare once again the effect of dendrons on intermolecular interactions. The trend in the relative absorbance of the two main features can be mainly attributed to the specific effects of the dendron, as opposed to a simple chromophore dilution effect. In all cases, the thin-film spectra show absorption and/or scattering tails that extend into the telecommunications region, potentially adversely affecting the utility of these species for AOSP.

Figure 6 compares the absorption spectra of **G1-C7** and **G3′-C7** dyes having dendrons attached at the different positions in the neat films but with similar chromophore content (45% and 46%, respectively). The prominent absorption peaks appear at similar wavelengths for these two compounds, suggesting chromophore−chromophore interactions in the two films to be similar. However, the low-energy absorption of **G1-C7** is weaker than the higher energy feature, while the converse is true for **G3′-C7**. This suggests that, for a similar chromophore concentration, placing a bulkier dendron in the middle of the bridge is more efficient at reducing the prominence of the aggregate-induced higher-energy band than when multiple

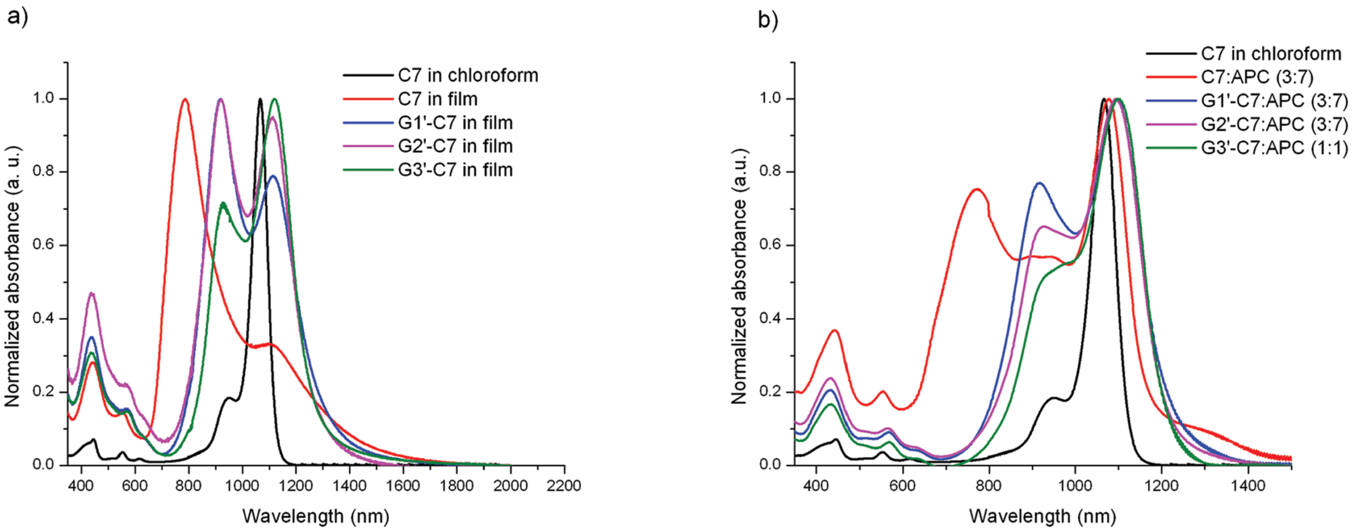


Figure 5. UV-vis-NIR absorption spectra of nondendronized and dendronized heptamethine dyes in (a) neat films and (b) blended films having similar chromophore densities. The solution spectrum of **C7** is included for comparison.

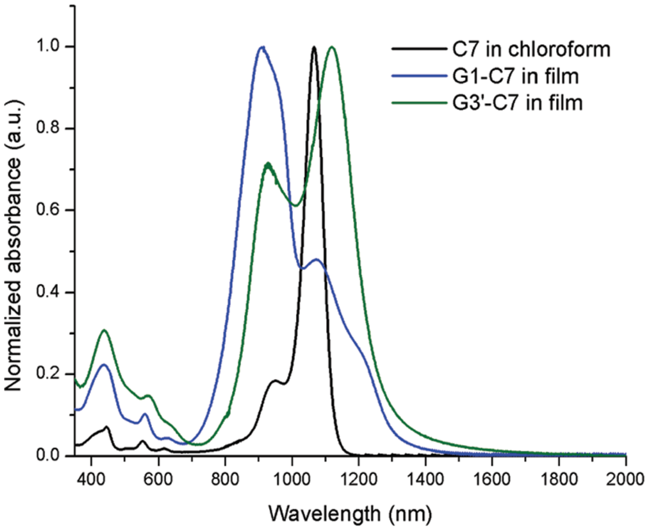


Figure 6. Neat film absorption spectra of heptamethine dyes having dendrons at the periphery (**G1-C7**) and at the center (**G3′-C7**) of the polymethine bridge with ca. 45% of chromophore. The solution spectrum of **C7** is included for comparison.

smaller dendrons are placed at the termini of the chromophores.

Microscopic Third-Order Nonlinear Optical Properties in Solution. The real and imaginary components of the third-order polarizability, γ, at 1550 nm were measured for the dyes dissolved in chloroform and the results are summarized in Table 2. The values of Re(γ) (Table 2) are negative in sign and large in magnitude, as expected for third-order nonlinearities of cyanine-like polymethines in the NIR spectral region.[2,4,5,19,61] The heptamethines exhibit the expected marked increase in Re(γ) compared to the pentamethines[2] and are quite similar in magnitude to those of selenopyrylium heptamethines reported at the same excitation wavelength.[2] Experimentally determined values of |Re(γ)/Im(γ)| are also shown in Table 2; this parameter defines the molecular two-photon figure-of-merit for all-optical switching,[2] and the values are quite large, particularly for the heptamethines, owing to favorably spaced two-photon absorption (2PA) resonances, consistent with results reported previously for a vinylogous series of bis(selenopyrylium) polymethines.[2]

Table 2. Microscopic Third-Order Nonlinear Optical Properties of Bis(Thiopyrylium) Polymethines in Chloroform Solution[a]

cmpd	Re(γ) (esu)	|Re(γ)/Im(γ)|
C5	-1.7×10^{-32}	3.2
G1-C5	-2.2×10^{-32}	4.7
G2-C5	-1.7×10^{-32}	3.2
C7	-3.6×10^{-32}	52
G1-C7	-5.1×10^{-32}	27
G1′-C7	-3.9×10^{-32}	22
G2′-C7	-3.9×10^{-32}	16
G3′-C7	-4.4×10^{-32}	20

[a] Measurements performed using the femtosecond-pulsed Z-scan technique at λ_{exc} = 1550 nm. Experimental uncertainties were estimated to be ±10% in Re(γ) and ±14% in |Re(γ)/Im(γ)|.

The values for Re(γ) of the dendronized polymethines are quite similar to those of their parent molecules. For the heptamethine series, this similarity is the result of the aforementioned effects of intermolecular interactions on the concentrated-solution spectra. For the elevated concentrations (0.8−4.0 mM) at which Z-scan measurements were performed, the values of M_{ge} were found to be comparable between dendronized and nondendronized species (see Supporting Information, Table S3). As such, the simplified two-level model for γ given by eq 1 was adequate in describing the third-order NLO response of these compounds (see Supporting Information, Table S3). It is worth noting that |Re(γ)/Im(γ)| values (Table 2) for the dendronized heptamethines are all lower than that of **C7**; given the similarity of the Re(γ) values for all these systems, the changes are attributed to a larger magnitude of Im(γ) in the dendronized compounds, which is indicative of stronger 2PA at this wavelength. This may be due to differences in the shape and/or strength of the low-lying 2PA bands, either the vibronically assisted excitation into the main one-photon state[67,68] or a higher lying 2PA-allowed state; however, a more detailed understanding would require broadband 2PA spectroscopy, which is beyond the scope of this study.

Table 3. Macroscopic Third-Order Nonlinear Optical Properties of Bis(thiopyrylium) Heptamethines in Neat and Blended Films

APC/dye (wt %)	chromophore (wt %)[a]	Re$\chi^{(3)}$ measured[b] (esu)	Re$\chi^{(3)}$ neat[c] (esu)	Re$\chi^{(3)}$ extrapol.[d] (esu)
10:90 (**C7**)	90	-4.3×10^{-11}	-4.8×10^{-11}	-7.5×10^{-11}
50:50 (**C7**)	50	-2.7×10^{-11}	-5.4×10^{-11}	
90:10 (**C7**)	10	-0.8×10^{-11}	-8.0×10^{-11}	
0:100 (**G1-C7**)	45	*e*	*e*	-4.9×10^{-11}
10:90 (**G1-C7**)	41	-3.6×10^{-11}	-4.0×10^{-11}	
50:50 (**G1-C7**)	22	-2.9×10^{-11}	-5.8×10^{-11}	
90:10 (**G1-C7**)	4	*e*	*e*	
50:50 (**G1′-C7**)	38	-8.3×10^{-11}	-17×10^{-11}	-6.4×10^{-11}
70:30 (**G1′-C7**)	23	-2.6×10^{-11}	-8.7×10^{-11}	
10:90 (**G2′-C7**)	57	-5.1×10^{-11}	-5.7×10^{-11}	-5.2×10^{-11}
50:50 (**G2′-C7**)	32	-2.7×10^{-11}	-5.4×10^{-11}	
70:30 (**G2′-C7**)	19	-1.6×10^{-11}	-5.3×10^{-11}	
10:90 (**G3′-C7**)	42	-5.7×10^{-11}	-6.3×10^{-11}	-4.3×10^{-11}
50:50 (**G3′-C7**)	23	-2.1×10^{-11}	-4.2×10^{-11}	

[a] Chromophore wt % is determined by the amount of thiopyrylium polymethine molecule excluding the dendron, but including the counterion. [b] Measurements performed using the femtosecond-pulsed Z-scan technique at λ_{exc} = 1550 nm. Experimental uncertainties were estimated to be ±15%. Unfortunately reliable values of Im$\chi^{(3)}$ could not be obtained due to saturable absorption (see text). [c] Nonlinearity for an effective neat film determined by dividing the measured Re$\chi^{(3)}$ value by the doping wt % of dye. [d] Extrapolated neat values of Re$\chi^{(3)}$ were determined using the following equation, $\chi^{(3)} = \gamma \cdot N \cdot L^4$, where the values of γ were taken from Table 2, N is the density of dyes in the film (assuming a film density of 1 g/cm^3) and L is the Lorentz field factor assuming a film refractive index of 1.6. [e] Certain films did not give a measurable closed-aperture Z-scan signal, likely due to insufficiently thick films and/or too low dye doping levels, and therefore, a Re$\chi^{(3)}$ value is not reported.

Macroscopic Third-Order Nonlinear Optical Properties of Dyes in Films. We also investigated the third-order NLO properties of the heptamethine dyes in the solid state using the femtosecond-pulsed Z-scan technique at 1550 nm. The measured macroscopic nonlinearities (Re$\chi^{(3)}$) are summarized in Table 3 (third column) for the films with varying doping ratios of dye with respect to the host polymer. It is instructive to examine at the values of Re$\chi^{(3)}$ for the films of the **C7** parent molecule: first, the macroscopic nonlinearities are negative in sign and large in magnitude, in accordance with the microscopic nonlinearities discussed above, and similar to other polymethine-based films measured in the NIR spectral region;[19] second, the magnitude of Re$\chi^{(3)}$ increases with the dye wt %, although this increase is sublinear. In the absence of intermolecular interactions, the nonlinearity should scale linearly with the concentration of the cyanine dye. By dividing the measured Re$\chi^{(3)}$ values of the various films by their respective doping wt % to give neat-film effective values of Re$\chi^{(3)}$ (see fourth column in Table 3), the impact of dye−dye interactions can clearly be seen: the effective neat nonlinearities exhibit a monotonic decrease of |Re$\chi^{(3)}$| with increasing dye wt %.

The effects of intermolecular interactions in these **C7** guest−host films can be further studied by comparing the effective neat Re$\chi^{(3)}$ values with extrapolated values of Re$\chi^{(3)}$ based on the solution Re(γ) values given in Table 2 (see last column in Table 3).[69] It is interesting to note that the extrapolated Re$\chi^{(3)}$ value (from Re(γ)) is very similar to the neat value of Re$\chi^{(3)}$ for a film containing 10 wt % of **C7**, consistent with the similarity of the main absorption band of **C7** in this low wt % film (Figure 7, 10 wt % dye) to that seen in solution. Nonetheless, there are clear differences between this film spectrum and that of even the most concentrated solutions (Figures 2 and S2, Supporting Information): in addition to increased relative absorbance in the vicinity of the vibronic shoulder of the main absorption band, there is a higher energy feature similar to the aggregation-induced band seen in neat films (Figure 4). The higher wt % films exhibit spectra in which this blue-shifted absorption is increasingly prominent (see Figure 7). With an appreciable amount of oscillator strength present in these hypsochromically shifted bands, a corresponding reduction in the magnitude of the effective neat Re$\chi^{(3)}$ should be expected according to eq 1; this is indeed observed in the values in Table 3.

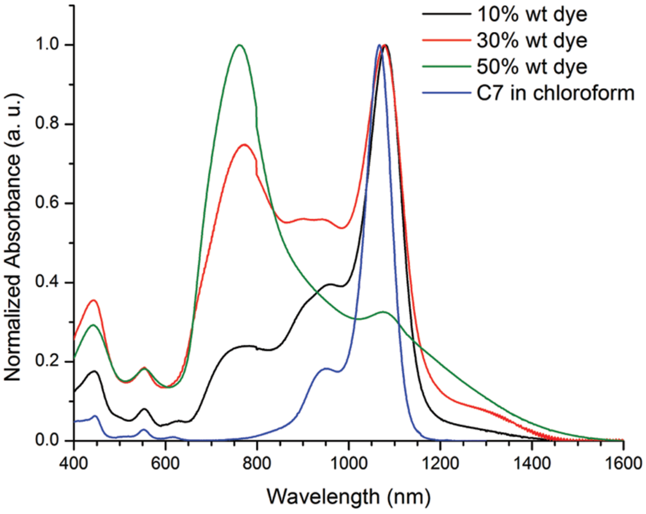


Figure 7. Absorption spectra of **C7**:APC blends at different dye content.

It should be noted that there are few reliable studies involving nonresonant third-order nonlinearities of cyanine-like dyes in the solid-state. One previous study investigated quinoline-based heptamethines in guest−host films *via* third-harmonic generation in the 1.85−2.15 μm spectral range.[70] A 50 wt % film was found to give a |$\chi^{(3)}$| value of 2×10^{-11} esu at the peak of what was likely a three-photon resonance. The deviation from a linear relationship between |$\chi^{(3)}$| and the wt % of dye in the film at higher dye concentrations was attributed to aggregation effects, the existence of which was inferred from the linear absorption spectra. A dioxaborine-based nonamethine dye has also been shown to exhibit significant excitonic splitting in spectra of neat films.[19] However, in this case, the observed Re$\chi^{(3)}$ values agreed well with the values extrapolated from the solution Re(γ), likely due to a distribution of the oscillator strength between the hypsochromically shifted and bathochromically shifted bands in the solid film spectrum such that the decreased and increased contributions to Re$\chi^{(3)}$ for those two bands roughly balanced one another. Consequently, while the Re(γ) values at 1550 nm for the dioxaborine nonamethine dye of ref 19 and the thiopyrylium heptamethine dye **C7** discussed here are comparable, the nonamethine dye possesses a neat Re$\chi^{(3)}$ value nearly four times that of the heptamethine (using the results for the 50 or 90 wt % films).

In light of the impacts of aggregation on the NLO response of cyanine-like dyes in the solid-state, and of the efficacy of dendronization in changing their aggregation behavior, as gauged from the absorption spectra of films of the compounds, it is now critical to assess if the third order susceptibility is also affected by the presence of dendrons. The Re$\chi^{(3)}$ values of the films containing the dendronized heptamethines (see Table 3) show similar behavior to that of the nondendronized analogue **C7**: large magnitude, negative sign, and increased magnitude with increased cyanine wt %. However, in most cases, the calculated neat values of Re$\chi^{(3)}$ seem to show a smaller variability with doping wt % and closer agreement with the solution-extrapolated values of Re$\chi^{(3)}$. This can be rationalized by noting that in the linear absorption spectra the relative contributions from the higher energy bands compared to the lower energy bands are reduced and the hypsochromic shifts are smaller than those seen in the nondendronized films (Figures 4 and 5). Thus, the presence of dendrons serves to reduce the type of aggregation observed in the **C7** films thereby suppressing some of the deleterious impacts on Re$\chi^{(3)}$ observed in the latter films. This impact is further emphasized if one compares the nonlinearities of the films with similar chromophore wt % (second column, Table 3): the dendronized films consistently exhibit larger values of Re$\chi^{(3)}$ compared to their nondendronized counterparts. While results from linear absorption studies suggested the centrally placed dendrons may be more effective at preventing aggregation than terminal dendron susbtitution, the NLO results are inconclusive.

Finally, we should mention that values of $|\mathrm{Re}\chi^{(3)}/\mathrm{Im}\chi^{(3)}|$ could not be determined for films. The presence of non-negligible linear absorption at 1550 nm led to open-aperture Z-scan signals that gave signatures typically associated with saturable absorption. Since these signals are opposite in sign compared to those associated with 2PA, which provides the relevant value of Im$\chi^{(3)}$ for AOSP, the two effects partially cancel one another and a meaningful value of Im$\chi^{(3)}$ could not be obtained from the experimental results.

■ CONCLUSION

A series of thiopyrylium-terminated polymethines functionalized with flexible benzyl aryl ether dendrons have been synthesized to examine whether the dendrons can disrupt interchromophore interactions that lead to undesirable effects on the linear and nonlinear optical properties of high number-density films at telecommunication wavelengths. In dilute solution, the low-energy linear absorption bands of the dendronized polymethines differ from those of their nondendronized analogues, showing significantly lower transition dipole moments, perhaps due to ion-pairing effects. However, the linear absorption properties (band position, spectral shape, extinction coefficient) of the dendronized heptamethine were found to be independent of concentration into the mM range, a regime where concentration effects are evident in the parent compound, suggesting that dendronization affects interchromophore interactions. The dendronization significantly affects the spectra of high-number density films with centrally substituted dendrons seemingly reducing aggregation to a greater degree than terminally substituted dendrons. The third-order polarizabilities of the dendronized dyes in solution at mM concentrations were found to be similar to those of their nondendronized analogues. Conversely, the real part of the third-order susceptibility (Re$\chi^{(3)}$) in the solid state was significantly affected by the presence of the dendrons: macroscopic nonlinearities in high-chromophore density films approached values extrapolated from microscopic nonlinearities, which was not the case for films of the parent polymethines at comparable dye loading, suggesting that dendronization is successful in reducing the negative effects of aggregation on Re$\chi^{(3)}$. However, the dendronization is insufficient to give completely solution-like optical properties in the solid-state, with linear absorption at telecommunication wavelengths still present in films of the dendronized compounds, although reduced relative to that seen for films of the nondendronized compounds; presumably this is due to the intrinsic flexibility of the dendrons, which may still allow the conjugated cyanine cores of neighboring molecules to interact with one another to some extent. Moreover, the use of the higher generation dendrons, which are the most effective at minimizing the adverse effects of aggregation, is inevitably accompanied by dilution effects. Consequently, the covalent attachment of other more rigid bulky moieties might prove a more effective approach at disrupting aggregation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of new compounds, tables showing film thicknesses, effects of solvent on linear spectra, and values of Re(γ) estimated using the two-level model and Figures showing solvent-dependent spectra and spectra of **C7** in solution and APC at the same concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(2) Hales, J. M.; Matichak, J.; Barlow, S.; Ohira, S.; Yesudas, K.; Brédas, J.-L.; Perry, J. W.; Marder, S. R. *Science* **2010**, *327*, 1485.
(3) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243.
(4) Hermann, J. P. *Opt. Commun.* **1974**, *12*, 102.
(5) Johr, T.; Werncke, W.; Pfeiffer, M.; Lau, A.; Dähne, L. *Chem. Phys. Lett.* **1995**, *246*, 521.
(6) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973.
(7) Hales, J. M.; Perry, J. W. In *Introduction to Organic Electronic and Optoelectronic Materials and Devices*; Sun, S.-S., Dalton, L., Eds.; CRC Press: Orlando, FL, 2008; p 521.
(8) May, J. C.; Lim, J. H.; Biaggio, I.; Moonen, N. N. P.; Michinobu, T.; Diederich, F. *Opt. Lett.* **2005**, *30*, 3057.
(9) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Guenter, P. *J. Phys. Chem. B* **1998**, *102*, 4451.
(10) Wong, M. S.; Samoc, M.; Samoc, A.; Luther-Davies, B.; Humphrey, M. G. *J. Mater. Chem.* **1998**, *8*, 2005.
(11) Kato, S.-i.; Beels, M. T. R.; La Porta, P.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J.-P.; Biaggio, I.; Diederich, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6207.
(12) Marder, S. R.; Torruellas, W. E.; Blanchard-Desce, M.; Ricci, V.; Stegeman, G. I.; Gilmour, S.; Brédas, J. L.; Li, J.; Bublitz, G. U.; Boxer, S. G. *Science* **1997**, *276*, 1233.
(13) Gorman, C. B.; Marder, S. R. *Chem. Mater.* **1995**, *7*, 215.
(14) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.
(15) Pierce, B. M. In *Molecular and Biomolecular Electronics (Advances in Chemistry Series, No. 240)*; Birge, R. R., Ed.; ACS: Washington DC, 1994; p 243.
(16) Senge, M. O.; Fazekas, M.; Notaras, E. G. A.; Blau, W. J.; Zawadzka, M.; Locos, O. B.; Mhuircheartaigh, E. M. N. *Adv. Mater.* **2007**, *19*, 2737.
(17) Zhang, Y.; Xiang, J.; Tang, Y.; Xu, G.; Yan, W. *Chem. Lett.* **2006**, *35*, 1316.
(18) Gulen, D.; Atasoylu, O.; Ozcelik, S. *Chem. Phys.* **2009**, *355*, 73.
(19) Hales, J. M.; Zheng, S. J.; Barlow, S.; Marder, S. R.; Perry, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 11362.
(20) Kohn, F.; Hofkens, J.; Wiesler, U. M.; Cotlet, M.; van der Auweraer, M.; Müllen, K.; De Schryver, F. C. *Chem.—Eur. J.* **2001**, *7*, 4126.
(21) Li, Z. Y.; Jin, Z. H.; Kasatani, K.; Okamoto, H.; Takenaka, S. *Phys. Status Solidi B* **2005**, *242*, 2107.
(22) von Berlepsch, H.; Bottcher, C.; Dähne, L. *J. Phys. Chem. B* **2000**, *104*, 8792.
(23) Gadonas, R.; Feller, K.; Pugzlys, A.; Jonusauskas, G.; Oberle, J.; Rulliere, C. *J. Chem. Phys.* **1997**, *106*, 8374.
(24) Yao, H.; Kitamura, S.; Kimura, K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4560.
(25) Vaidyanathan, S.; Patterson, L.; Mobius, D.; Gruniger, H. *J. Phys. Chem.* **1985**, *89*, 491.
(26) Gorner, H.; Chibisov, A.; Slavnova, T. *J. Phys. Chem. B* **2006**, *110*, 3917.
(27) Tiddy, G.; Mateer, D.; Ormerod, A.; Harrison, W.; Edwards, D. *Langmuir* **1995**, *11*, 390.
(28) von Berlepsch, H.; Bottcher, C.; Ouart, A.; Burger, C.; Dähne, S.; Kirstein, S. *J. Phys. Chem. B* **2000**, *104*, 5255.
(29) Kim, O.-K.; Je, J.; Jernigan, G.; Buckley, L.; Whitten, D. *J. Am. Chem. Soc.* **2006**, *128*, 510.
(30) Whitten, D. G.; Achyutan, K. E.; Lopez, G. P.; Kim, O.-K. *Pure Appl. Chem.* **2006**, *78* (12), 2313.
(31) Panova, I. G.; Takikolov, A. S. *Dokl. Biol. Sci.* **2005**, *402*, 183.
(32) Achyutan, K. E.; Lu, L.; Lopez, G. P.; Whitten, D. G. *Photochem. Photobiol. Sci.* **2006**, *5*, 931.
(33) Kim, O.-K.; Melinger, J.; Chung, S.-J.; Pepitonet, M. *Org. Lett.* **2008**, *10*, 1625.
(34) Kawasaki, M.; Aoyama, S.; Kozawa, E. *J. Phys. Chem. B* **2006**, *110*, 24480.
(35) Lodi, A.; Ponterini, G. *Thin Solid Films* **2006**, *496*, 585.
(36) Owens, R.; Smith, D. *Langmuir* **2000**, *16*, 562.
(37) Hada, H.; Hanawa, R.; Haraguchi, A.; Yonezawa, Y. *J. Phys. Chem.* **1985**, *89*, 560.
(38) Ishimoto, C.; Tomimuro, H.; Seto, J. *Appl. Phys. Lett.* **1986**, *49*, 1677.
(39) Lehmann, U. *Thin Solid Films* **1988**, *160*, 257.
(40) Nakajima, H.; Asami, K.; Yonezawa, Y.; Kajimoto, O. *Chem. Phys. Lett.* **1998**, *294*, 619.
(41) Bourbon, S.; Gao, M.; Kirstein, S. *Synth. Met.* **1999**, *101*, 152.
(42) Rousseau, E.; Van der Auweraer, M.; De Schryver, F. C. *Langmuir* **2000**, *16*, 8865.
(43) Rao, T.; Huff, J.; Bieniarz, C. *Tetrahedron* **1998**, *54*, 10627.
(44) Vogtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987.
(45) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.
(46) Pollak, K. W.; Leon, J. W.; Frechet, J. M. J.; Maskus, M.; Abruna, H. D. *Chem. Mater.* **1998**, *10*, 30.
(47) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1.
(48) Jakubiak, R.; Bao, Z.; Rothberg, L. *Synth. Met.* **2000**, *114*, 61.
(49) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.
(50) Yang, S. H.; Chen, S. Y.; Wu, Y. C.; Hsu, C. S. *J. Polym. Sci. A Polym. Chem.* **2007**, *45*, 3440.
(51) Ma, H.; Liu, S.; Luo, J. D.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K. Y. *Adv. Funct. Mater.* **2002**, *12*, 565.
(52) Ma, H.; Jen, A. K. Y. *Adv. Mater.* **2001**, *13*, 1201.
(53) Sutton, A. E.; Clardy, J. *Tetrahedron Lett.* **2001**, *42*, 547.
(54) Jung, M. E.; Kim, W.-J. *Biorg. Med. Chem.* **2006**, *14*, 92.
(55) Flanagan, J. H., Jr.; Khan, S. H.; Menchen, S.; Soper, S. A.; Hammer, R. P. *Bioconjugate Chem.* **1997**, *8*, 751.
(56) Wooley, K. L.; Hawker, C. J.; Frechet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1059.
(57) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(58) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.
(59) Smith, C. R.; Zhang, A.; Mans, D. J.; RajanBabu, T. V. *Org. Synth.* **2008**, *85*, 248.
(60) Sheik-Bahae, M.; Said, A. A.; Van Stryland, E. W. *Opt. Lett.* **1989**, *14*, 955.
(61) Matichak, J. D.; Hales, J. M.; Ohira, S.; Barlow, S.; Jang, S. H.; Jen, A. K. Y.; Brédas, J.-L.; Perry, J. W.; Marder, S. R. *ChemPhysChem* **2010**, *11*, 130.
(62) Detty, M. R.; Murray, B. J.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1968.
(63) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(64) Itoh, T.; Mase, T. *J. Org. Chem.* **2006**, *71*, 2203.
(65) The values of $\varepsilon_{\max}$ and M_{ge} for **C7** have been previously reported in the Supporting Information of reference 2; however, these values were incorrectly reported and should have read $\varepsilon_{\max} = 3.67 \times 10^5$ M^{-1} cm^{-1} and M_{ge} = 18.2 D. It is clear that these values exhibit a statistically significant deviation from the values reported in Table 1. The reason for this discrepancy is unknown. The current and previously reported values were measured using different batches of the dye; however, both were pure according to ^{1}H NMR spectroscopy and elemental analysis.
(66) Bouit, P. A.; Aronica, C.; Toupet, L.; Le Guennic, B.; Andraud, C.; Maury, O. *J. Am. Chem. Soc.* **2010**, *132*, 4328.
(67) Fu, J.; Padilha, L. A.; Hagan, D. J.; Van Stryland, E. W.; Przhonska, O. V.; Bondar, M. V.; Slominsky, Y. L.; Kachkovski, A. D. *J. Opt. Soc. Am. B* **2007**, *24*, 56.
(68) Scherer, D.; Dorfler, R.; Feldner, A.; Vogtmann, T.; Schwoerer, M.; Lawrentz, U.; Grahn, W.; Lambert, C. *Chem. Phys.* **2002**, *279*, 179.
(69) Given the environmental effects on the linear and NLO properties in solution, it was important to determine whether, in the

current polymer host environment, extrapolation of solution-determined γ values to $\chi^{(3)}$ values in films is appropriate. To estimate the impact of the host environment, APC/**C7** blends with the same wt % of dye as the solution concentrations used in the femtosecond Z-scan measurements were fabricated (i.e., 3.9 mM corresponds to 0.4 wt % dye). The absorption spectra of this solution and film are remarkably similar (see Supporting Information, Figure S3), supporting the validity of the aforementioned extrapolation. We note that this does not address possible reduction in the extinction coefficient or transition dipole moment in the APC host environment.

(70) Matsumoto, S.; Kubodera, K.; Kurihara, T.; Kaino, T. *Opt. Commum.* **1990**, *76*, 147.