

# Donor–Acceptor Thiolated Polyenic Chromophores Exhibiting Large Optical Nonlinearity and Excellent Photostability

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We have successfully utilized epoxyisophorone ring-opening chemistry to efficiently incorporate the butylthio group to the phenyltetraene bridge of highly efficient nonlinear optical chromophores in high overall yield. By following the guidance of Dewar's rules, the sulfur atom functions as a moderate  $\pi$ -accepting group at a starred position of the conjugated bridge. Several of very critical material parameters of the phenyltetraenic chromophores for device applications have been intrinsically and simultaneously improved through such a simple and straightforward engineering of molecular structures. Compared with the nonsubstituted analogue **2**, thiolated chromophore **1** achieves higher molecular hyperpolarizability (34%), enhanced E-O coefficient (38%), significantly improved photochemical stability against  $^1\text{O}_2$  (by an order of magnitude), and better optical transparency (17 nm blue-shifted  $\lambda_{\text{max}}$  absorption spectrum).

## Introduction

Over the past decade, considerable progress has been made on the development of organic electro-optic (E-O) materials for photonic applications.<sup>1</sup> One of the most critical challenges in developing these materials is to design and synthesize chromophores that combine large first hyperpolarizability ( $\beta$ ), good optical transparency, and excellent photostability in the same molecular system. Among many molecular systems studied, the (4-dialkylamino)phenyl-tetraene conjugated bridges attached with terminal strong acceptors represent one of the most effective frameworks that result in large  $\beta$  values and excellent processibility.<sup>2</sup> By careful design and control of the assembly and lattice hardening in a proper polymer matrix, extraordinary E-O coefficients ( $r_{33}$ ) have been achieved from materials containing these chromophores.<sup>3</sup> However, these highly polarizable chromophores tend to be unstable under the processing and device operating conditions due to their chemical and photochemical sensitivity. In

certain cases, polyene dyes degrade rapidly when they were exposed to highly intensive near-IR laser light ( $10^5$ – $10^6$  W/cm<sup>2</sup>) under device operation. This results in an attenuated nonlinearity, increased optical loss, and shortened device lifetime. Previous studies suggest that singlet oxygen ( $^1\text{O}_2$ ) attacks the nucleophilic carbon atoms on the central polymethine chain of these chromophores, leading to material degradation.<sup>4</sup> Several material and device engineering approaches have been proposed to reduce the rate of photo-oxidation in these chromophores, such as adding singlet-oxygen quenchers in the materials or operating devices under the hermetic packaged conditions. Although these approaches work to a certain extent, it was proved that trace amounts of residual oxygen are very difficult to remove once they are trapped in the polar matrices.<sup>5</sup> Therefore, a new molecular design is urgently needed for phenyltetraene-based chromophores to overcome these obstacles. The ultimate goal is to simultaneously achieve very large optical nonlinearity,

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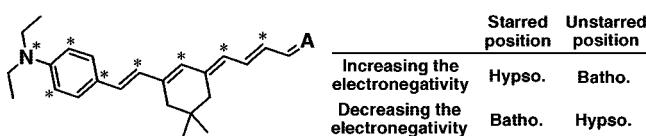
<sup>§</sup> Department of Chemistry, University of Washington.

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- (a) Dalton, L. R.; Robinson, B. H.; Nielson, R.; Jen, A. K.-Y.; Casmier, D.; Rabiei, P.; Steier, W. H. *SPIE Proc.* **2003**, *4991*, 508. (b) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845. (c) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed.* **1995**, *34*, 155. (d) *Molecular Nonlinear Optics: Materials, Phenomena and Devices*; Zyss, J., Ed.; Academic Press: Boston, 1999; p 245.
- (2) (a) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoej, J. *Science* **1994**, *263*, 511. (b) Enami, Y.; DeRose, C. T.; Mathine, D.; Loychik, C.; Greenlee, C.; Norwood, R. A.; Kim, T. D.; Luo, J.; Tian, Y.; Jen, A. K.-Y.; Peyghambarian, N. *Nature Photonics* **2007**, *1*, 180. (c) Luo, J.; Cheng, Y.-J.; Kim, T. D.; Hau, S.; Jang, S.-H.; Shi, Z.; Zhou, X.-H.; Jen, A. K.-Y. *Org. Lett.* **2006**, *8*, 1387. (d) Luo, J.; Su, H.; Cheng, Y.-J.; Kim, T. D.; Shi, Z.; Zhou, X.-H.; Jen, A. K.-Y. *Org. Lett.* **2007**, *9*, 1387–4471.

- (3) (a) Kim, T.-D.; Kang, J.-W.; Luo, J.; Jang, S.-H.; Ka, J.-W.; Tucker, N.; Benedict, J. B.; Dalton, L. R.; Gray, T.; Overney, R. M.; Park, D. H.; Herman, W. N.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2007**, *129*, 488. (b) Kim, T.-D.; Luo, J.; Ka, J.-W.; Hau, S.; Tian, Y.; Shi, Z.; Tucker, N. M.; Jang, S.-H.; Kang, J.-W.; Jen, A. K.-Y. *Adv. Mater.* **2006**, *18*, 3038.
- (4) (a) DeRosa, M. E.; He, M.; Cites, J. S.; Garner, S. M.; Tang, Y. R. *J. Phys. Chem. B* **2004**, *108*, 8725. (b) Rezzonico, D.; Jazbinsek, M.; Günter, P.; Bosshard, C.; Bale, D. H.; Liao, Y.; Dalton, L. R.; Reid, P. J. *J. Opt. Soc. Am. B* **2007**, *24*, 2199. (c) Toubchkine, A.; Kraynov, V.; Hahn, K. *J. Am. Chem. Soc.* **2003**, *125*, 4132. (d) Galvan-Gonzalez, A.; Belfield, K. D.; Stegeman, G. I.; Canva, M.; Chan, K.-P.; Park, K.; Sukhomlinova, L.; Twieg, R. J. *Appl. Phys. Lett.* **2000**, *77*, 2083. (e) Galvan-Gonzalez, A.; Belfield, K. D.; Stegeman, G. I.; Canva, M.; Marder, S. R.; Staub, K.; Levina, G.; Twieg, R. J. *J. Appl. Phys.* **2003**, *94*, 756.
- (5) Ren, Y.; Szablewski, M.; Cross, G. G. *Appl. Opt.* **2000**, *39*, 2499.

**Scheme 1. Structure of (4-Dialkylamino)phenyltetraene-Based Donor–Acceptor Chromophores, Its Starred/Unstarred Positions, and Spectral Shifts Defined by Dewar's Rules<sup>a</sup>**



<sup>a</sup> Hypso.: hypsochromic shift. Batho.: bathochromic shift.

excellent photochemical stability, and high optical transparency in the same material that contains these chromophores.

Dewar earlier reported a set of rules based on perturbational molecular orbital theory to predict qualitatively the electronic effect of structural changes on the optical properties in odd alternant hydrocarbons.<sup>6</sup> It has been widely applied to various studies conducted for understanding structure–color relationships in dye chemistry. For instance, these rules work not only remarkably well for cyanine-type systems having uniform bond order (bond length alternation is zero) but also work fairly well for donor–acceptor merocyanine systems with low degree of bond length alternation (BLA).<sup>7</sup> Because the highly dipolar push–pull phenyltetraenic chromophores also possess significantly reduced BLA, it is envisaged that Dewars' rules could be applicable to this system and provide a useful guideline for the molecular engineering of new donor–acceptor polyene chromophores.<sup>8</sup>

By following the Dewar's convention, alternate atoms in phenyltetraene-based chromophores are designated as starred or unstarred by their positions relative to the terminal donor group (Scheme 1). Through this designation, Dewar's rules predicts the spectral shifts of intramolecular charge-transfer (ICT) transition of chromophores when changing the electronegativity at certain positions.<sup>7c</sup>

For example, the substitution of an electron-withdrawing group at a starred position should cause a hypsochromic shift. This is because the increased electronegativity on that position leads to a lower HOMO energy level and weakened nucleophilicity of chromophores. As a result, the photostability of polyenic dyes could be improved by introducing an electron-withdrawing group onto a starred position. In conjunction with the hypsochromic shift of the absorption spectrum, the optical transparency at the near IR operation wavelengths is expected to be improved. However, the electron-withdrawing ability of this moiety needs to be carefully tweaked to ensure that the ICT transition of the

chromophore is maintained and gives large  $\beta$  values. To realize these criteria in the molecular design, heteroatom-like sulfur, instead of other stronger electron-withdrawing groups (i.e., cyano and nitro groups), is selected because of its unique and moderate  $\pi$ -accepting ability. Here, we report a simple and generally applicable approach to incorporate *n*-butylthio (SBu hereafter) functionality into a starred position of chromophore **1**. This compound exhibits a larger  $\beta$  value, higher E-O activity in poled polymers, remarkable photochemical stability, and better optical transparency compared to the reference chromophore **2**.

## Results and Discussion

**Synthesis of Chromophores.** The synthesis of chromophores **1–3** is depicted in Scheme 2. In the presence of sodium ethoxide as the base, 1-butanethiol can be easily deprotonated to form a nucleophilic thiolate which underwent ring-opening reaction of epoxyisophorone **4** to selectively generate 2-SBu-substituted isophorone **5** in a nearly quantitative yield.<sup>9</sup> This intermediate can be reacted directly with 4-diethylaminobenzaldehyde **7** in one-pot via the Knoevenagel condensation to furnish aminophenyldienone **9a** with a high overall yield of 75%.

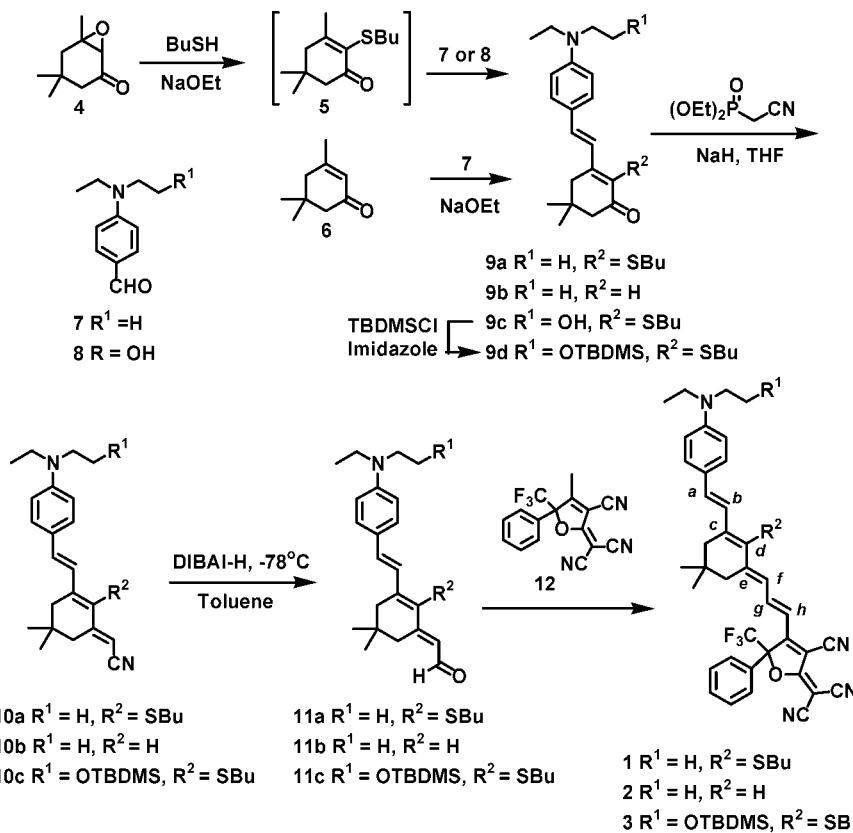
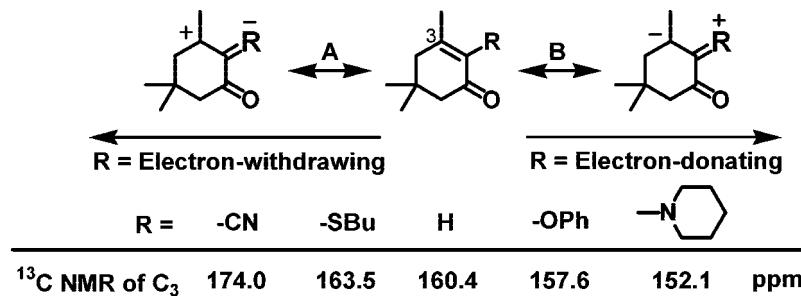
By using the Wittig–Horner reaction, **9a** was reacted with diethyl(cyanomethyl)phosphonate to result in trienenitrile **10a** with 74% yield. The reduction with DIBAL-H followed by hydrolysis converted the nitrile group on **10a** into the corresponding aminophenyltrienal **11a** in 81% yield. The aldehyde-containing donor-bridge **11a** was condensed with CF<sub>3</sub>-TCF acceptor **12** to furnish the phenyltetraenic chromophore **1** in 73% yield. The thiolated chromophore **1** can be synthesized via simple 4-step reactions in high overall yield (33%) which is higher than the overall yield (23%) for the nonsubstituted chromophore **2**, synthesized by a similar manner from isophorone **6**. It should be noted that SBu-substituted chromophore **1** has all-trans double-bond configuration while chromophore **2** contains a mixture of inseparable *E/Z*-isomers ( $C_e = C_f$ ) with a ratio of 83/17%. Chromophore **3**, which is an analogue of chromophore **1** except for the extra *tert*-butyldimethylsilyl (TBDMS) group at the donor side to improve the solubility and compatibility with polymer matrix, was also synthesized by using the same synthetic route.

**Sulfur's  $\pi$ -Accepting Ability and Dewar's Rules Applicability.** To clarify sulfur's  $\pi$ -accepting interaction with an unsaturated unit, a series of 2-substituted isophorone derivatives, the building block for the construction of ring-locked tetraene bridge, were synthesized to systematically compare their electronic effect (Scheme 3). From <sup>13</sup>C NMR, the chemical shift of C<sub>3</sub> in isophorone (R = H) is located at 160.4 ppm and serves as a reference value. Any electron-withdrawing group introduced at C<sub>2</sub> of isophorone would reduce the electron density at C<sub>3</sub> (resonance A), resulting in a downfield shift of C<sub>3</sub> relative to 160.4 ppm. If the substituent is an electron-donating group, an upfield shift of C<sub>3</sub> will be obtained (resonance B). As predicted, the C<sub>3</sub>

(6) Dewar, M. J. S. *J. Chem. Soc.* **1950**, 2329.  
 (7) (a) Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: Berlin, 1983. (b) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer-Verlag: Berlin, 1980. (c) Griffiths, J. *Color and Constitution of Organic molecules*, Academic Press: London, 1976. (d) Twieg, R. W. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, 1987; Vol. 1, p 250.  
 (8) (a) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem. Eur. J.* **1997**, 3, 1091. (b) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J.-L.; Pieroe, B. M. *Science* **1994**, 265, 632. (c) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoej, J. *Science* **1994**, 263, 511.

(9) Tobias, M. A.; Strong, J. G.; Napier, R. P. *J. Org. Chem.* **1970**, 35, 1709.

Scheme 2. Synthesis of Chromophores 1–3

Scheme 3. Resonance Structures and  $^{13}\text{C}$  NMR Chemical Shift (ppm) of  $\text{C}_3$  in 2-Substituted Isophorones Measured in  $\text{CDCl}_3$ 

chemical shift moves to a lower field of 174.0 ppm when a strong electron-withdrawing cyano group is introduced at  $\text{C}_2$ , whereas the shift moves to higher fields of 157.6 and 152.1 ppm when a moderate phenoxy and a strong electron-donating dialkylamino group are attached, respectively. The chemical shift of  $\text{C}_3$  in 2-SBu-isophorone (**5**) is at 163.5 ppm, suggesting that the SBu group acts as a moderate electron-withdrawing group. The  $^1\text{H}$  NMR data also further support this argument. In fact, the chemical shifts of proton on methyl and methylene groups adjacent to  $\text{C}_3$  in 2-SBu-isophorone are determined to be 2.24 and 2.37 ppm which are downfield-shifted compared to the corresponding protons in isophorone with 1.93 and 2.16 ppm.

Moreover, according to the IR spectrum,  $\text{C}_2=\text{C}_3$  absorption shifts from  $1633\text{ cm}^{-1}$  in isophorone to a lower-frequency value of  $1588\text{ cm}^{-1}$  in 2-SBu-isophorone. This indicates the electron-accepting ability of SBu group at  $\text{C}_2$  increases the single-bond character of  $\text{C}_2=\text{C}_3$  double bond and hence lowers the force constant in the vibrational stretching. Since the electronegativity of the sulfur atom (2.58) is only slightly

greater than that of carbon atom (2.55), the sulfur's inductive effect can be therefore ruled out. For many years, whenever sulfur-containing compounds exhibit unexpected physical or chemical properties, it is commonly referred to the involvement of 3d orbitals in bonding. Thus, sulfur's  $\pi$ -acceptor capability has been traditionally attributed to the formation of  $\text{p}_\pi(\text{C})-\text{d}_\pi(\text{S})$  orbital overlap where divalent sulfur accepts  $\pi$ -electron from the p-orbital of carbon–carbon double bond into its empty 3d-orbitals (resonance A).<sup>10</sup> However, since the middle of the 1980s, quantum mechanical calculations have generally suggested that the primary  $\pi$ -accepting orbital

(10) (a) Kajimoto, O.; Kobayashi, M.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2316. (b) Quinn, C. B.; Wiseman, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6120. (c) Baker, A. W.; Harris, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 1923. (d) Ojima, I.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2571. (e) Fuedo, T.; Kajimoto, O.; Izawa, K.; Masago, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1418. (f) Goodman, L.; Taft, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 4385. (g) Fraenkel, G.; Chow, A.; Gallucci, J.; Rizvi, S. Q. A.; Wong, S. C.; Finkelstein, H. *J. Am. Chem. Soc.* **1986**, *108*, 5339. (h) Beishline, R. *J. Org. Chem.* **1961**, *26*, 2533. (i) Kwart, H.; King, K. *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur*; Springer-Verlag: Berlin, 1977; and references therein.

**Table 1.** Chemical Shift (ppm) of  $^1\text{H}$  NMR Measured in  $\text{CDCl}_3$  for Olefinic Protons Attached on the Respective Carbon at the Bridge of Chromophores **1** and **2**

	H <sub>a</sub>	H <sub>b</sub>	H <sub>f</sub>	H <sub>g</sub>	H <sub>h</sub>
<b>1</b>	7.07	8.06	7.50	8.10	6.51
<b>2</b>	6.98	6.81	6.34	8.07	6.34

of sulfur is associated with a low-lying sigma antibonding orbital in character, whereas 3d orbital participation is only of secondary importance. In this case,  $p_{\pi}$  (C) orbital delocalizes into an antibonding orbital of sulfur–carbon  $\sigma$  bond  $\sigma^*_{\text{S–C}}$ , which is known as  $p_{\pi}$  (C)  $\rightarrow \sigma^*_{\text{S–C}}$  negative hyperconjugation.<sup>11</sup>

These results also reflect that the ability of sulfur to donate electrons through 3p  $\pi$ -orbital overlap is much weaker than that of oxygen, which can be further substantiated by referring to the Hammett's substitution constant ( $\sigma$ ) derived from para-substituted benzoic acids ( $\sigma = -0.83$  for *p*-N(CH<sub>3</sub>)<sub>2</sub>,  $-0.27$  for *p*-OCH<sub>3</sub>, 0.00 for *p*-SCH<sub>3</sub>).<sup>12</sup>

This electronic effect of SBu at the starred position also plays an important role in chromophore **1**. As shown in Table 1,  $^1\text{H}$  NMR spectra reveal that two olefinic protons H<sub>b</sub> and H<sub>f</sub> neighboring the sulfur atom in **1** experience significant deshielding of chemical shifts ( $>1$  ppm) compared to the corresponding protons in **2**. This result implies that the SBu group results in decreased electron density at olefinic carbons and causes the attached protons to resonate at a lower field.

Cyclic voltammetry (CV) was also employed to examine electrochemical properties of chromophores **1** and **2**. The half-wave oxidation potential versus ferrocene/ferrocenium for **1** and **2** was estimated to be +461 mV and +419 mV, respectively (Figure 1a), which suggests that the SBu substituent tends to lower the electron density of the diethylamino donor thereby increasing the oxidation potential of **1**. Furthermore, we evaluated the absorption spectra of chromophore **1** and **2** in various solvents. The  $\lambda_{\text{max}}$  of **1** and **2** are located at 712 and 729 nm in dioxane, 766 and 779 in tetrahydrofuran, and 799 and 802 nm in chloroform, respectively (Table 2). These results are in good agreement with the Dewar's rules that qualitatively predict that the electron-withdrawing perturbation at the starred position will result in a hypsochromic shift of absorption maximum. The absorption spectra of the intermediate donor bridges dienone (**9a**, **9b**), trienenitrile (**10a**, **10b**), and trienal (**11a**, **11b**) were also measured in dioxane, THF, and chloroform for comparison (Table 2).

It should be noted that the  $\lambda_{\text{max}}$  of intermediate compounds with SBu substituted at the starred position (**9a**, **10a**, **11a**) are all bathochromically shifted (ca. 25–32 nm) compared to those of the corresponding unsubstituted analogue (**9b**, **10b**, **11b**), which actually does not follow the Dewar's rules. These spectral characteristics can be rationalized by the fact that without a very strong end-capped acceptor to pull electron, the neutral form will prevail over the charge-separated form in the ground state.

(11) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434, and references therein.  
 (12) (a) Bowdell, F. G.; Cooper, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 1058.  
 (b) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. Tiemann, B. G.; Marder, S. R.; Perry, J. W.; Cheng, L. T. *Chem. Mater.* **1990**, *2*, 690.

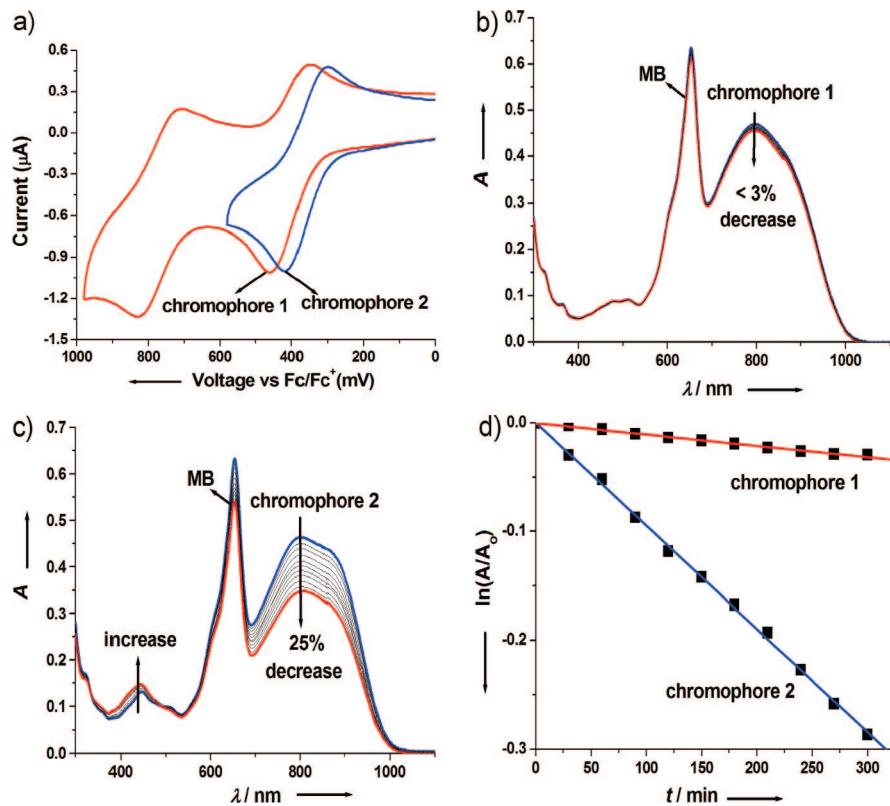
Therefore, these intermediates show a higher degree of BLA that is less justifiable by applying Dewar's rules to these systems.<sup>13</sup> As a result, the SBu substitution in these systems simply acts as a weak acceptor and results in decreased band gap. However, when coupled with a strong CF<sub>3</sub>-TCF acceptor **12**, the degree of BLA of highly polarized push–pull chromophore **1** and **2** is reduced, which provides a better molecular framework for applying Dewar's rules.

**Photochemical Stability against Singlet Oxygen.** In order to investigate the photochemical stability of chromophores **1** and **2**, an accelerated testing protocol was conducted using Methylene Blue (MB) as an efficient photosensitizer to generate  $^1\text{O}_2$ .<sup>14</sup> The chloroform solutions containing chromophores (5  $\mu\text{M}$ ) and MB (5  $\mu\text{M}$ ) were saturated with oxygen prior to the irradiation of 650 nm light to excite MB. After 5 h of irradiation, the absorption intensity at  $\lambda_{\text{max}}$  of **2** dropped by 25%, whereas **1** decreased by only less than 3% (Figure 1b,c). Similar experiments were also carried out without adding MB into the solutions. Almost no bleaching for **1** or **2** was found after 5 h of irradiation, which suggests that the reduction of absorbance is mainly due to the reaction of chromophores with  $^1\text{O}_2$ .

The slope of these plots yields the first-order rate constants for **1** and **2** to be  $1.05 \times 10^{-4} \text{ min}^{-1}$  and  $9.49 \times 10^{-4} \text{ min}^{-1}$ , respectively (Figure 1d). This result indicated that the thiolated chromophore **1** shows much improved resistance to  $^1\text{O}_2$  and lower photobleaching rate by an order of magnitude compared to **2**. The SBu group in **1** exerts a mild electron-withdrawing effect, allowing a certain amount of electron drift from the  $\pi$ -system into its  $\pi$ -accepting orbitals, thus weakening the  $\pi$ -conjugated bridge's reactivity toward the highly electrophilic  $^1\text{O}_2$ .<sup>15</sup> Consequently, chromophore **1** is more resistant to oxidation, which is also consistent with its increased oxidation potential.<sup>16</sup>

**HRS Measurements.** The first molecular hyperpolarizabilities ( $\beta$ ) of **1** and **2** were characterized by using the Hyper-Rayleigh scattering (HRS) technique at 1.907  $\mu\text{M}$ . A chromophore, EZ-FTC, was used as the external reference.<sup>17</sup> Chromophore **1** exhibited a remarkably larger  $\beta$  value of  $10\ 200 \times 10^{-30}$  esu compared to that of  $7600 \times 10^{-30}$  esu for **2**. This shows that the perturbation of SBu substituent does not affect the efficient one-dimensional charge-transfer excitation which determines the principal  $\beta$  tensor within a two-level model.<sup>18</sup> Instead, an auxiliary  $\pi$ -accepting SBu

(13) Tiemann, B. G.; Marder, S. R.; Perry, J. W.; Cheng, L. T. *Chem. Mater.* **1990**, *2*, 690.  
 (14) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.  
 (15) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258.  
 (16) (a) Toutchkine, A.; Nguyen, D.-V.; Hahn, K. M. *Org. Lett.* **2007**, *9*, 2775. (b) Scurlock, R. D.; Wang, B.; Ogilby, P. R.; Sheats, J. R.; Clough, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 10194. (c) Yogo, T.; Urano, Y.; Ishitsuka, Y.; Maniwa, F.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 12162. (d) Dam, N.; Scurlock, R. D.; Wang, B.; Ma, L.; Sundahl, M.; Ogilby, P. R. *Chem. Mater.* **1999**, *11*, 1302. (e) Renikuntla, B. R.; Rose, H. C.; Eldo, J.; Waggoner, A. S.; Armitage, B. A. *Org. Lett.* **2004**, *6*, 909. (f) Lux, A.; Holmes, A. B.; Cervini, R.; Davies, J. E.; Moratti, S. C.; Gruner, J.; Cacialli, F.; Friend, R. H. *Synth. Met.* **1997**, *84*, 293.  
 (17) Firestone, K. A.; Lao, D. B.; Casmier, D. M.; Clot, O.; Dalton, L. R.; Reid, P. J. *Proc. SPIE-Int. Soc. Opt. Eng.* **2005**, *5935* (Linear and Nonlinear Optics of Organic Materials V), 49–59350P.  
 (18) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Marder, S. R.; Beratan, D. N.; Cheng, L. T. *Science* **1991**, *252*, 103.



**Figure 1.** (a) Cyclic voltammetry of oxidative scan for **1** (red) and **2** (blue) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) of CHCl<sub>3</sub> at a scan rate of 100 mV s<sup>-1</sup>. The CV curves were calibrated using ferrocene as the standard. Methylene Blue-sensitized photobleaching of **1** (b) and **2** (c) in CHCl<sub>3</sub>. The solutions were irradiated with a 650 nm light. Changes in absorbances at  $\lambda_{\text{max}}$  were monitored every 30 min for 5 h. (d) Plot of  $\ln(A_t/A_0)$  as a function of the irradiation time for **1** and **2**, where  $A_0$  and  $A_t$  are the chromophores'  $\lambda_{\text{max}}$  absorbances at time = 0 and time =  $t$ , respectively. The photodegradation rate was quantified by plotting  $\ln(A_t/A_0)$  vs irradiation time.

**Table 2. Absorption Maxima (nm) of Chromophores 1 and 2 and Their Corresponding Bridge Intermediates (dienoies 9a and 9b, trienenitrile 10a and 10b, and trienals 11a and 11b) in dioxane, THF, and chloroform<sup>a</sup>**

	dioxane ( $\lambda_{\text{max}}$ )	THF ( $\lambda_{\text{max}}$ )	chloroform ( $\lambda_{\text{max}}$ )
<b>9a</b>	435 (32)	435 (30)	451 (31)
<b>9b</b>	403	405	420
<b>10a</b>	445 (26)	445 (25)	453 (26)
<b>10b</b>	419	420	427
<b>11a</b>	455 (25)	457 (26)	471 (31)
<b>11b</b>	430	431	440
<b>1</b>	712 (-17)	766 (-13)	799 (-3)
<b>2</b>	729	779	802

<sup>a</sup> The values in parentheses are the  $\lambda_{\text{max}}$  shifted values of SBu<sub>2</sub>-substituted compounds relative to those of their unsubstituted analogues in the same solvent; a positive value denotes a red shift, and a negative value denotes a blue shift.

conjugated with the amino donor and located in the middle of the bridge may potentially generate a small off-diagonal component of the two-dimensional  $\beta$  tensor.<sup>19</sup> From another perspective, the enhanced  $\beta$  value of **1** might be also ascribed to the fact that by adding a SBu group perpendicular to the conjugated backbone at the center of the bridge, not only can it make the all-trans double bond have better conjugation, but also serve as an efficient spacer to reduce the formation

of dipole couples.<sup>20</sup> To the best of our knowledge, this value represents the highest known hyperpolarizability for a phenyltetraene-based dipolar NLO material. The thin film absorption spectra (25 wt % in PMMA) showed that the  $\lambda_{\text{max}}$  of **1** and **2** locates at 793 and 810 nm, respectively. The increased  $\beta$  value of chromophore **1**, with a 17 nm hypsochromic shift of absorption maximum, offers a pleasant surprise to the nonlinearity—transparency tradeoff that almost inevitably occurs in the dipolar donor- $\pi$ -acceptor systems.

#### Electric Field Poling and E-O Property Measurements.

To study their E-O activity, 25 wt % of the chromophores **1** and **2** were doped into a commonly used polymer matrix, poly(methyl methacrylate) (PMMA), as guest–host polymers. The E-O activities of poled films were measured by the Teng-Man method<sup>21</sup> using carefully selected thin ITO electrode (from thin film devices) with low reflectivity and good transparency in order to minimize the contribution from multiple reflections.<sup>22</sup> The 34% enhancement of the microscopic  $\beta$  value in **1** relative to **2** can be fully translated into the performance of the macroscopic E-O coefficient. Chromophore **1** achieved an exceptional  $r_{33}$  value of 219 pm/V which represents a 38% improvement over **2** with an  $r_{33}$  value of 158 pm/V at 1.31  $\mu$ M under a poling field of 120 V/ $\mu$ m.

(19) (a) Kang, H.; Evmenenko, G.; Dutta, P.; Clays, K.; Song, K.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 6194. (b) Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Lenug, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 12950. (c) Oudar, J. L.; Zyss, J. *Phys. Rev. A* **1982**, *26*, 2016.

(20) Liakatas, I.; Cai, C.; Bösch, M.; Jäger, M.; Bosshard, Ch.; Günter, P.; Zhang, C.; Dalton, L. R. *Appl. Phys. Lett.* **2000**, *76*, 1368.

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

(22) Park, D. H.; Lee, C. H.; Herman, W. N. *Opt. Exp.* **2006**, *14*, 8866.

## Optical Power Handling Capability of Waveguides.

Chromophore **3**, which contains a solubilizing TBDMS group at the donor end, was formulated into an amorphous polycarbonate (**APC**) with a high loading of 30 wt %. The optical power handling (OPH) capability of waveguides made from this guest–host polymer was then tested at the 1550-nm wavelength. The loss of optical confinement due to photobleaching of chromophores is monitored by the change of waveguide output transmittance relative to initial transmittance. Under a relatively high optical density of  $\sim 5 \times 10^5$  W/cm<sup>2</sup>, the waveguides of **3/APC** were quite stable and showed nearly unchanged optical transmission after 12 h of continuous irradiation, indicating excellent photostability of the **3/APC** films in a continuously operating device. Under the similar testing condition, this result exceeds the performance of **CLD1/APC**<sup>23</sup> by a factor of 3 and is comparable to that of **P2ANS/MMA**,<sup>24</sup> a side-chain polymer with the 4-dimethylamino-4'-nitrostilbene-based chromophore (**DANS**). This result is extremely encouraging, given the fact that among them **3/APC** films showed the most red-shifted ICT transition ( $\lambda_{\text{max}}$  of 793 nm, vs 667 nm for **CLD1/APC**, 430 nm for **PMMA-DANS**) and highest E-O activities (164 pm/V @ 1310 nm, vs 47 pm/V for **CLD1/APC**,  $\sim 10$  pm/V for **PMMA-DANS**).

## Conclusions

As considerable efforts have been spent previously to improve the intrinsic properties of phenyltetraene-based chromophores by optimizing donor<sup>25</sup> and acceptor<sup>26</sup> strength, the electronic modification of the polyene bridging unit is much more synthetically challenging and has not been well explored. The utilization of epoxyisophorone ring-opening chemistry allows efficient introduction of the SBu group at a starred position of the ring-locked bridge to function as a moderate  $\pi$ -accepting group. Compared with the nonsubstituted analogue **2**, chromophore **1** achieves higher molecular hyperpolarizability (34%), enhanced E-O coefficient (38%), significantly improved photochemical stability against  $^1\text{O}_2$  (by an order of magnitude), and a further blue-shifted absorption spectrum. Such improvement in photostability has been observed under both resonant (i.e., 650 nm) and nonresonant excitation (i.e., telecommunication wavelengths of 1310 and 1550 nm). This can potentially provide means to tackle more sophisticated photostability issues in nonlinear optical processes, such as second harmonic generation and two-photon fluorescence. We envision that Dewar's rules could be utilized as a general tool to guide the future molecular design for second-order as well as third-order nonlinear optical materials through fine-tuned ICT, optical transparency, and photochemical stability.

## Experimental Section

**HRS Measurement.** Details of the HRS spectrometer have been provided elsewhere.<sup>17</sup> The sample concentrations from 1 to 80  $\mu\text{M}$  in chloroform (Fisher ACS Spectranalyzed) were investigated. The sample was circulated through a low-volume flow cell and filtered using an in-line 0.1  $\mu\text{M}$  PTFE filter to minimize chromophore photodecomposition and scattering from particulate matter. UV-vis absorption measurements (Shimadzu UV-1601) were obtained for each sample before and after each experiment check for chromophore photodegradation. No evidence of photodegradation was observed. Data analysis entailed fitting the HRS intensity to a Gaussian function after subtraction of the multiphoton-excited fluorescence background. The internal reference method was used to determine  $\beta$  for EZ-FTC relative to chloroform, and the external reference method was used to determine  $\beta$  for the chromophores of interest relative to EZ-FTC. The proximity of the second-harmonic wavelength (953.5 nm) to the wavelength of maximal absorption (799 and 802 nm for **1** and **2**, respectively) will result in resonance enhancement. Because of the similarity of the latter wavelengths, this enhancement will also be very similar.

**Poling Conditions and  $r_{33}$  Measurement.** For studying the E-O property derived from the chromophores, guest–host polymers were generated by formulating chromophores **1** or **2** (25 wt %) into poly(methyl methacrylate) (PMMA) using 1,1,2-trichloroethane (TCE) as the solvent. The resulting solutions (with the solid content of 10 wt %) were filtered through a 0.2- $\mu\text{M}$  PTFE filter and spin-coated onto thin-film device (TFD) indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 80 °C overnight to ensure the removal of the residual solvent. Then, a thin layer of gold was sputtered onto the films as a top electrode for contact poling. The  $r_{33}$  values were measured using the Teng-Man simple reflection technique at the wavelength of 1.31  $\mu\text{m}$ .<sup>21</sup>

**Photobleaching of Chromophores **1** and **2** in the Presence of Methylene Blue Photosensitizer.** Four milliliters of a chloroform solution containing NLO chromophore (5  $\mu\text{M}$ ) and methylene blue (5  $\mu\text{M}$ ) was bubbled with oxygen for 5 min then placed in a quartz cuvette with a path length of 1 cm. The cuvette was irradiated by a light of 650 nm obtained from a 150 W xenon arc lamp (oriel model 6263) with a monochromotor. The absorbance spectra of the samples were measured every 30 min of irradiation using a Perkin-Elmer Lambda 9 UV-vis/NIR spectrophotometer. The rate constants of photobleaching were obtained from a plot of  $\ln(A_0/A)$  vs time.  $A_0$  is the absorbance of **1** at 799 nm or **2** at 802 nm before irradiation.  $A$ , is the absorbance after every 30 min irradiation.

**Cyclic Voltammetry Measurement.** Cyclic voltammetric data were performed on a BAS CV-50W voltammetric analyzer using a conventional three-electrode cell with a Pt metal as the working electrode, a Pt gauze as the counter-electrode, and an Ag/AgNO<sub>3</sub> as the reference electrode at a scan rate of 100 mV s<sup>-1</sup>. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CHCl<sub>3</sub> is the electrolyte. The CV curves were calibrated using ferrocene as the standard.

**Characterization of Molecules.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker 300 or 500 instrument spectrometer. High-resolution mass spectrometry (HRMS) was performed by UW Bio-Mass Spectrometry. Infrared spectra were measured by a Bruker Vector 33 FT-IR spectrophotometer. Absorption spectra were recorded by a Perkin-Elmer Lambda 9 UV-vis/NIR spectrophotometer.

**Synthesis of Compound **9a**.** To a solution of ethanol (30 mL) was carefully added sodium metal (0.31 g, 12.96 mmol) under N<sub>2</sub> atmosphere. The solution was vigorously stirred at room temperature until the sodium was completely dissolved. 1-Butanethiol (1.52 mL,

(23) Zhang, C.; Dalton, L. R.; Oh, M.-C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043.  
 (24) Mortazavi, M. A.; Yoon, H. N.; Teng, C. C. *J. Appl. Phys.* **1993**, *74*, 4871.  
 (25) Cheng, Y.-J.; Luo, J.; Hau, S.; Bale, D. H.; Kim, T.-D.; Shi, Z.; Lao, D. B.; Tucker, N. M.; Tian, Y.; Ried, P. J.; Dalton, L. R.; Jen, A. K.-Y. *Chem. Mater.* **2007**, *19*, 1154.  
 (26) Liu, S.; Haller, M. A.; Ma, H.; Dalton, L. R.; Jang, S. H.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 603.

12.96 mmol) was added to the above solution by syringe, and the mixture was stirred for 10 min followed by addition of isophorone oxide **4**<sup>27</sup> (2 g, 12.96 mmol). The mixture became dark shortly and was stirred at room temperature for another 1 h to form intermediate compound **5**. 4-(Diethylamino)benzaldehyde **7** (2.3 g, 12.96 mmol) was added to the mixture which was then heated to 65 °C for 18 h. After the removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to give a red solid **9a** (3.7 g, 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.89 (t, *J* = 7 Hz, 3 H), 0.94 (s, 3 H), 1.02 (s, 3 H), 1.25 (t, *J* = 7 Hz, 6 H), 1.40–1.49 (m, 2 H), 1.49–1.60 (m, 2 H), 2.30 (d, *J* = 15.5 Hz, 1 H), 2.40 (d, *J* = 15.5 Hz, 1 H), 2.53–2.68 (m, 4 H), 3.47 (q, *J* = 7 Hz, 4 H), 6.51 (d, *J* = 14.5 Hz, 1 H), 6.70 (d, *J* = 8.5 Hz, 2 H), 7.07 (d, *J* = 16 Hz, 2 H), 7.47–7.70 (m, 8 H), 8.06 (d, *J* = 16 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 12.6, 13.6, 21.9, 27.8, 28.5, 30.4, 31.6, 35.9, 41.1, 41.6, 44.6, 57.0, 94.6, 95.7 (q, <sup>13</sup>C–<sup>19</sup>F *J* = 31 Hz), 111.0, 111.5, 111.6, 111.8, 116.5, 122.1 (q, <sup>13</sup>C–<sup>19</sup>F *J* = 285 Hz), 124.1, 124.5, 126.7, 128.4, 129.6, 130.2, 130.8, 131.2, 138.5, 147.5, 149.2, 155.0, 158.8, 162.3, 175.7. HRMS (ESI) (M<sup>+</sup>, C<sub>42</sub>H<sub>43</sub>F<sub>3</sub>N<sub>4</sub>OS): calcd, 708.3110; found, 708.3111.

**Synthesis of Compound 10a.** A 50 mL three-necked flask was charged with NaH (0.37 g, 16.2 mmol) in dry THF (20 mL) under N<sub>2</sub> atmosphere. Diethyl (cyanomethyl)phosphonate (2.55 mL, 16.2 mmol) was slowly introduced to the mixture dropwise by syringe. After the solution became clear, compound **9a** (2.5 g, 6.48 mmol) in THF (10 mL) was added to the mixture which was then refluxed for 18 h. After removal of THF in *vacuo*, the residue was directly purified by the column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to give an orange solid **10a** (1.97 g, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.92 (t, *J* = 7.5 Hz, 3 H), 1.06 (s, 6 H), 1.23 (t, *J* = 7 Hz, 6 H), 1.40–1.49 (m, 2 H), 1.49–1.58 (m, 2 H), 2.51 (s, 2 H), 2.59 (t, *J* = 7 Hz, 2 H), 2.61 (s, 2 H), 3.43 (q, *J* = 7 Hz, 4 H), 6.27 (s, 1 H), 6.69 (d, *J* = 9 Hz, 2 H), 6.88 (d, *J* = 16.5 Hz, 1 H), 7.45 (d, *J* = 9 Hz, 2 H), 7.90 (d, *J* = 16.5 Hz, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 12.6, 13.6, 21.8, 29.0, 30.1, 31.7, 35.2, 41.5, 43.4, 44.4, 94.1, 111.4, 119.4, 123.8, 124.0, 126.2, 128.9, 134.6, 148.2, 148.9, 158.6. HRMS (ESI) (M<sup>+</sup> + Na, C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>NSNa): calcd, 431.2497; found, 431.2501.

**Synthesis of compound 11a.** To a solution of compound **10a** (1.5 g, 3.6 mmol) in toluene (20 mL) was added a 1 M solution of diisobutyl aluminum hydride in hexanes (7.2 mL, 7.2 mmol) by syringe at –78 °C. The reaction was stirred at this temperature for 2 h. Ethyl acetate (20 mL) was added to quench the reaction which was then allowed to warm up to room temperature. The solution was added by saturated aqueous ammonium chloride (50 mL) and stirred vigorously for hydrolysis until the color of organic layer became red. Organic solvent was removed in *vacuo* and the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to give a red solid **11a** (0.61 g, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.90 (t, *J* = 7 Hz, 3 H), 1.07 (s, 6 H), 1.22 (t, *J* = 7 Hz, 6 H), 1.39–1.49 (m, 2 H), 1.49–1.59 (m, 2 H), 2.54 (s, 2 H), 2.59 (t, *J* = 7 Hz, 2 H), 2.77 (s, 2 H), 3.43 (q, *J* = 7 Hz, 4 H), 6.69 (d, *J* = 9 Hz, 2 H), 6.89 (d, *J* = 16.5 Hz, 1 H), 7.05 (d, *J* = 8 Hz, 2 H), 7.46 (d, *J* = 9 Hz, 2 H), 8.00 (d, *J* = 16.5 Hz, 1 H), 10.18 (d, *J* = 8 Hz, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 12.6, 13.6, 21.8, 28.2, 29.9, 31.7, 35.1, 39.8, 41.5, 44.3, 111.4, 124.1, 124.5, 126.6, 128.5, 128.9, 134.6, 148.2, 150.0, 156.8, 191.6. HRMS (ESI) (M<sup>+</sup> + H, C<sub>26</sub>H<sub>38</sub>NOS): calcd, 412.2674; found, 412.2683.

**Synthesis of Compound 1.** A mixture of compound **11a** (0.3 g, 0.73 mmol) and acceptor **12** (0.25 g, 0.8 mmol) in ethanol (2 mL) and chloroform (2 mL) was stirred at 50 °C for 2 h. After removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1). The product was further purified by redissolving it in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) then adding

into methanol to precipitate and get a dark solid **1** (0.38 g, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.89 (t, *J* = 7 Hz, 3 H), 0.94 (s, 3 H), 1.02 (s, 3 H), 1.25 (t, *J* = 7 Hz, 6 H), 1.40–1.49 (m, 2 H), 1.49–1.60 (m, 2 H), 2.30 (d, *J* = 15.5 Hz, 1 H), 2.40 (d, *J* = 15.5 Hz, 1 H), 2.53–2.68 (m, 4 H), 3.47 (q, *J* = 7 Hz, 4 H), 6.51 (d, *J* = 14.5 Hz, 1 H), 6.70 (d, *J* = 8.5 Hz, 2 H), 7.07 (d, *J* = 16 Hz, 2 H), 7.47–7.70 (m, 8 H), 8.06 (d, *J* = 16 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 12.6, 13.6, 21.9, 27.8, 28.5, 30.4, 31.6, 35.9, 41.1, 41.6, 44.6, 57.0, 94.6, 95.7 (q, <sup>13</sup>C–<sup>19</sup>F *J* = 31 Hz), 111.0, 111.5, 111.6, 111.8, 116.5, 122.1 (q, <sup>13</sup>C–<sup>19</sup>F *J* = 285 Hz), 124.1, 124.5, 126.7, 128.4, 129.6, 130.2, 130.8, 131.2, 138.5, 147.5, 149.2, 155.0, 158.8, 162.3, 175.7. HRMS (ESI) (M<sup>+</sup>, C<sub>42</sub>H<sub>43</sub>F<sub>3</sub>N<sub>4</sub>OS): calcd, 708.3110; found, 708.3111.

**Synthesis of Compound 9b.** To a solution of ethanol (30 mL) was carefully added sodium metal (0.33 g, 14.5 mmol) under N<sub>2</sub> atmosphere. The solution was vigorously stirred at room temperature until the sodium was completely dissolved. 4-(Diethylamino)benzaldehyde **7** (2.56 g, 14.5 mmol) and isophorone **6** (2 g, 14.5 mmol) were added to the mixture which was then heated to 65 °C for 24 h. After the removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to give a yellow solid **9b** (3.4 g, 79%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.13 (s, 6 H), 1.22 (t, *J* = 7 Hz, 6 H), 2.32 (s, 2 H), 2.49 (s, 3 H), 3.42 (q, *J* = 7 Hz, 4 H), 6.03 (s, 1 H), 6.67 (d, *J* = 9 Hz, 2 H), 6.74 (d, *J* = 16.5 Hz, 1 H), 6.96 (d, *J* = 16.5 Hz, 1 H), 7.40 (d, *J* = 9 Hz, 2 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 12.6, 28.5, 33.3, 39.1, 44.4, 51.4, 111.4, 123.1, 124.1, 124.8, 129.0, 135.7, 148.5, 156.1, 200.1. HRMS (ESI) (M<sup>+</sup> + Na, C<sub>20</sub>H<sub>27</sub>NONa): calcd, 320.1990; found, 320.1997

**Synthesis of Compound 10b.** A 50 mL three-necked flask was charged with NaH (0.4 g, 16.75 mmol) in dry THF (20 mL) under N<sub>2</sub> atmosphere. Diethyl (cyanomethyl)phosphonate (2.63 mL, 16.75 mmol) was slowly introduced to the mixture dropwise by syringe. After the solution became clear, compound **9b** (2 g, 6.7 mmol) was added to the mixture which was then refluxed for 18 h. After removal of THF in *vacuo*, the residue was directly purified by the column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to give an brown solid **10b** (1.8 g, 85%). The ratio of the Z:E isomers is 45:55% calculated by the integration of respective protons. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.03 (s, 3.3 H, *E*), 1.07 (s, 2.7 H, *Z*), 1.21 (t, *J* = 7 Hz, 6 H), 2.25 (s, 1.1 H, *E*), 2.34 (s, 2 H), 2.49 (s, 0.9 H, *Z*), 3.42 (q, *J* = 7 Hz, 4 H), 4.92 (s, 0.55 H, *E*), 5.09 (s, 0.45 H, *Z*), 6.24 (s, 0.55 H, *E*), 6.6–6.7 (m, 3 H), 6.75 (s, 0.45 H, *Z*), 6.78 (s, 1 H), 7.3–7.4 (m, 2 H). HRMS (ESI) (M<sup>+</sup> + H, C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>): calcd, 321.2331; found, 321.2333.

**Synthesis of Compound 11b.** To a solution of compound **10b** (2 g, 6.24 mmol) in toluene (20 mL) was added a 1 M solution of diisobutyl aluminum hydride in hexanes (12.48 mL, 12.48 mmol) by syringe at –78 °C. The reaction was stirred at this temperature for 2 h. Ethyl acetate (20 mL) was added to quench the reaction which was then allowed to warm up to room temperature. The solution was added by saturated aqueous ammonium chloride (50 mL) and stirred vigorously for hydrolysis until the color of organic layer became red. Organic solvent was removed in *vacuo* and the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 6/1) to give a red solid **11b** (1.05 g, 52%). The relatively low yield is due to the poor solubility of compound **10b** in toluene at –78 °C. The ratio of the Z:E isomers is 30:70% calculated by the integration of respective protons. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.05 (s, 4.2 H, *E*), 1.09 (s, 1.8 H, *Z*), 1.21 (t, *J* = 7 Hz, 6 H), 2.32 (s, 0.6 H, *Z*), 2.38 (s, 0.6 H, *Z*), 2.39 (s, 1.4 H, *E*), 2.49 (s, 1.4 H, *E*), 3.42 (q, *J* = 7 Hz, 4 H), 5.73 (d, *J* = 8 Hz, 0.3 H, *Z*), 5.94 (d, *J* = 8.5 Hz, 0.7 H, *E*), 6.29 (s, 0.7 H, *E*), 6.67 (d, *J* = 8.5 Hz, 2 H), 6.7–6.85 (m, 2 H), 7.21 (s, 0.3 H,

(27) Rissafi, B.; Rachiqi, N.; Louzi, A. E.; Loupy, A.; Petit, A.; Ekih-Tétouani, S. *Tetrahedron* **2001**, 57, 2761.

Z), 7.35–7.43 (m, 2 H), 10.08 (d,  $J$  = 8.5 Hz, 0.7 H, E), 10.24 (d,  $J$  = 8 Hz, 0.7 H, Z). HRMS (ESI) ( $M^+$  + H,  $C_{22}H_{30}NO$ ): calcd, 324.2327; found, 324.2326.

**Synthesis of Compound 2.** A mixture of compound **11b** (0.2 g, 0.62 mmol) and acceptor **12** (0.25 g, 0.68 mmol) in ethanol (2 mL) was stirred at 50 °C for 2 h. After removal of solvent, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1). The product was further purified by redissolving it in  $CH_2Cl_2$  (1 mL) and then adding into methanol to precipitate and to get a dark solid **2** (0.26 g, 67%). The ratio of the Z:E isomers is 17:83% calculated by the integration of respective protons.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  1.05 (s, 4.2 H, E), 1.09 (s, 1.8 H, Z), 1.21 (t,  $J$  = 7 Hz, 6 H), 2.32 (s, 0.6 H, Z), 2.38 (s, 0.6 H, Z), 2.39 (s, 1.4 H, E), 2.49 (s, 1.4 H, E), 3.42 (q,  $J$  = 7 Hz, 4 H), 5.73 (d,  $J$  = 8 Hz, 0.3 H, Z), 5.94 (d,  $J$  = 8.5 Hz, 0.7 H, E), 6.29 (s, 0.7 H, E), 6.67 (d,  $J$  = 8.5 Hz, 2 H), 6.7–6.85 (m, 2 H), 7.21 (s, 0.3 H, Z), 7.35–7.43 (m, 2 H), 10.08 (d,  $J$  = 8.5 Hz, 0.7 H, E), 10.24 (d,  $J$  = 8 Hz, 0.7 H, Z). HRMS (ESI) ( $M^+$  + H,  $C_{38}H_{35}F_3N_4O$ ): calcd, 620.2763; found, 620.2754.

**Synthesis of Compound 9c.** In a similar manner as described above, **9c** was synthesized from **4** and **8** (68%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  0.89 (t,  $J$  = 7.5 Hz, 3 H), 1.10 (s, 6 H), 1.22 (t,  $J$  = 7 Hz, 3 H), 1.38–1.47 (m, 2 H), 1.47–1.55 (m, 2 H), 2.00 (s, 1 H), 2.44 (s, 2 H), 2.64 (s, 2 H), 2.76 (t,  $J$  = 7.5 Hz, 2 H), 3.50 (q,  $J$  = 7 Hz, 2 H), 3.56 (t,  $J$  = 6 Hz, 2 H), 3.86 (t,  $J$  = 6 Hz, 2 H), 6.77 (d,  $J$  = 9 Hz, 2 H), 7.01 (d,  $J$  = 16.5 Hz, 1 H), 7.48 (d,  $J$  = 9 Hz, 2 H), 7.94 (d,  $J$  = 16.5 Hz, 1 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  12.0, 13.7, 21.8, 28.3, 32.0, 32.2, 34.0, 41.2, 45.5, 51.9, 52.3, 60.2, 112.1, 123.8, 124.5, 128.7, 129.3, 136.8, 149.0, 157.7. HRMS (ESI) ( $M^+$  + H,  $C_{24}H_{36}NO_2S$ ): calcd, 402.2467; found, 402.2461.

**Synthesis of Compound 9d.** To a solution of compound **9c** (1.3 g, 3.2 mmol) in dry DMF (15 mL) was added *tert*-butyldimethylsilyl chloride (0.54 g, 3.6 mmol) and imidazole (0.24 g, 3.6 mmol). The mixture was stirred at room temperature for 4 h. The mixture was extracted with ethyl acetate (50 mL) and water (100 mL × 3). After the removal of the organic layer, the residue was directly purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 4/1) to give an orange compound **9d** (1.4 g, 85%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  0.06 (s, 6 H), 0.90 (t,  $J$  = 7.5 Hz, 3 H), 0.92 (s, 9 H), 1.11 (s, 6 H), 1.22 (t,  $J$  = 7 Hz, 3 H), 1.38–1.48 (m, 2 H), 1.48–1.57 (m, 2 H), 2.45 (s, 2 H), 2.65 (s, 2 H), 2.76 (t,  $J$  = 7.5 Hz, 2 H), 3.49 (q,  $J$  = 7.5 Hz, 2 H), 3.51 (t,  $J$  = 6 Hz, 2 H), 3.81 (t,  $J$  = 6 Hz, 2 H), 6.70 (d,  $J$  = 9 Hz, 2 H), 7.02 (d,  $J$  = 16.5 Hz, 1 H), 7.47 (d,  $J$  = 9 Hz, 2 H), 7.94 (d,  $J$  = 16.5 Hz, 1 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  –5.2, 12.4, 13.9, 18.5, 22.1, 26.1, 28.6, 32.2, 32.5, 34.3, 41.5, 45.8, 52.2, 52.6, 60.8, 111.8, 123.7, 124.1, 128.7, 129.6, 137.2, 149.1, 158.0, 196.1. HRMS (ESI) ( $M^+$ ,  $C_{30}H_{49}NO_2SSi$ ): calcd, 515.3253; found, 515.3248.

**Synthesis of Compound 10c.** In a similar manner as described above, **10c** was synthesized from **9d** (69%).  $^1H$  NMR (300 MHz,

$CDCl_3$ ):  $\delta$  0.64 (s, 6 H), 0.89 (t,  $J$  = 7.2 Hz, 3 H), 0.91 (s, 9 H), 1.04 (s, 6 H), 1.20 (t,  $J$  = 7.2 Hz, 3 H), 1.35–1.58 (m, 4 H), 2.49 (s, 2 H), 2.57 (t,  $J$  = 7.2 Hz, 2 H), 2.60 (s, 2 H), 3.47 (q,  $J$  = 7.2 Hz, 2 H), 3.50 (t,  $J$  = 6.3 Hz, 2 H), 3.80 (t,  $J$  = 6.3 Hz, 2 H), 6.25 (s, 1 H), 6.69 (d,  $J$  = 9 Hz, 2 H), 6.86 (d,  $J$  = 16.2 Hz, 1 H), 7.43 (d,  $J$  = 9 Hz, 2 H), 7.88 (d,  $J$  = 16.5 Hz, 1 H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  –5.4, 12.2, 13.6, 18.2, 21.9, 25.9, 28.0, 30.1, 35.2, 41.5, 43.4, 45.5, 52.4, 60.5, 94.2, 111.5, 119.4, 124.0, 124.3, 126.4. HRMS (ESI) ( $M^+$ ,  $C_{32}H_{50}N_2OSSi$ ): calcd, 538.3413; found, 538.3408.

**Synthesis of Compound 11c.** In a similar manner as described above, **11c** was synthesized from **10c** (80%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  0.06 (s, 6 H), 0.88 (t,  $J$  = 7.5 Hz, 3 H), 0.91 (s, 9 H), 1.06 (s, 6 H), 1.20 (t,  $J$  = 7 Hz, 3 H), 1.37–1.48 (m, 2 H), 1.48–1.57 (m, 2 H), 2.53 (s, 2 H), 2.57 (t,  $J$  = 7.5 Hz, 2 H), 2.76 (s, 2 H), 3.47 (q,  $J$  = 7 Hz, 2 H), 3.49 (t,  $J$  = 6.5 Hz, 2 H), 3.80 (t,  $J$  = 6.5 Hz, 2 H), 6.69 (d,  $J$  = 9 Hz, 2 H), 6.87 (d,  $J$  = 16 Hz, 1 H), 7.04 (d,  $J$  = 8 Hz, 1 H), 7.43 (d,  $J$  = 9 Hz, 2 H), 7.99 (d,  $J$  = 16 Hz, 1 H), 10.17 (d,  $J$  = 8 Hz, 1 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  –5.4, 12.2, 13.7, 18.3, 21.9, 25.9, 28.3, 30.0, 31.7, 35.1, 39.9, 41.6, 45.5, 52.4, 60.6, 111.6, 124.4, 124.8, 126.8, 128.8, 128.9, 134.5, 148.4, 150.0, 156.9, 191.7. HRMS (ESI) ( $M^+$  + H,  $C_{32}H_{52}NO_2SSi$ ): calcd, 542.3488; found, 542.3483.

**Synthesis of Chromophore 3.** In a similar manner described above, **3** was synthesized from **11c** (70%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  0.07 (s, 6 H), 0.88 (t,  $J$  = 7 Hz, 3 H), 0.92 (s, 9 H), 0.94 (s, 3 H), 1.02 (s, 3 H), 1.24 (t,  $J$  = 7 Hz, 3 H), 1.40–1.49 (m, 2 H), 1.49–1.58 (m, 2 H), 2.30 (d,  $J$  = 15.5 Hz, 1 H), 2.39 (d,  $J$  = 15.5 Hz, 1 H), 2.58 (s, 2 H), 2.59 (t,  $J$  = 7 Hz, 2 H), 3.52 (q,  $J$  = 7.5 Hz, 2 H), 3.54 (t,  $J$  = 6 Hz, 2 H), 3.83 (t,  $J$  = 6 Hz, 2 H), 6.52 (d,  $J$  = 14.5 Hz, 1 H), 6.73 (d,  $J$  = 8.5 Hz, 2 H), 7.06 (d,  $J$  = 16 Hz, 1 H), 7.48 (d,  $J$  = 8.5 Hz, 2 H), 7.50–7.65 (m, 5 H), 8.06 (d,  $J$  = 16 Hz, overlap 2 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  –5.4, 12.1, 13.6, 18.2, 21.8, 25.8, 27.7, 28.4, 30.4, 31.6, 35.8, 41.1, 41.6, 45.6, 52.3, 57.0, 60.5, 94.6, 95.7 (q,  $^{13}C$ – $^{19}F$   $J$  = 31 Hz), 111.0, 111.4, 111.7, 111.8, 116.6, 122.0 (q,  $^{13}C$ – $^{19}F$   $J$  = 286 Hz), 124.3, 124.5, 126.7, 128.4, 129.5, 130.0, 130.1, 130.8, 131.2, 138.4, 147.5, 149.5, 154.9, 158.8, 162.3, 175.7. HRMS (ESI) ( $M^+$ ,  $C_{48}H_{57}F_3N_4O_2SSi$ ): calcd, 838.3924; found, 838.3918.

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**Supporting Information Available:**  $^1H$ ,  $^{13}C$  NMR and IR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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