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PAPER

Facile structure and property tuning through alteration of ring structures in conformationally locked phenyltetraene nonlinear optical chromophores†

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A series of phenyltetraene-based nonlinear optical (NLO) chromophores **1a–c** with the same donor and acceptor groups, but different tetraene bridges that are partly connected by various sizes of aliphatic rings, have been synthesized and systematically investigated. The interposed conjugated tetraene segments in three chromophores studied are based on isophorone, (1*S*)-(−)-verbenone, and 3,4,4-trimethyl-2-cyclopentenone, respectively. This kind of structural alteration has significant effect on the intrinsic electronic structures and physical properties of these highly polarizable chromophores as revealed by a variety of characterization techniques. The introduction of the verbenone- and trimethylcyclopentenone-based tetraene bridges could significantly improve the glass-forming ability of chromophores **1b** and **1c** in comparison with the highly crystalline characteristics of isophorone-based chromophores **1a**. More importantly, chromophores **1a–c** exhibited distinct optical features in absorption band shape, solvatochromic behavior, as well as energy band gap from the UV-vis-NIR absorption measurements. Quantum mechanical calculations using density functional theory (DFT) were also used to evaluate second-order NLO properties of these chromophores. The electro-optic (EO) coefficients of **1a–c** in poled polymers with the 10 wt% chromophore content showed an apparent decrease from 78 pm V^{-1} for **1a** to 42 pm V^{-1} for **1c**. This decrease is attributed to the gradual decrease of the molecular hyperpolarizability (β) of the chromophores which is associated with the progressive cyanine-like electronic structure from the isophorone-based **1a** to the cyclopentenone-based **1c** chromophore.

Introduction

Organic and polymeric EO materials have been intensively studied for the past two decades due to their potential applications for high-speed and broadband information technologies.[1] However, the dynamic development has been hampered by the fact that several critical material properties need to be simultaneously optimized. Recently, there is a resurgence of interest in organic EO materials due to the demonstration of several innovative devices using cleverly engineered processing methodologies.[2–5] To meet the stringent requirements of these devices, several series of organic EO materials have been developed through rational design of nonlinear optical (NLO) chromophores to optimize their molecular hyperpolarizability (β), and effectively translate these large β values into bulk EO activities together with improvement of other auxiliary properties through proper molecular engineering of these dipolar chromophores.[6–10] Among numerous chromophore systems studied, the combination of dialkylaminophenyl donors and strong CF_3–TCF acceptors, linked by isophorone-derived tetraene (CLD) bridges, represents one of the most effective frameworks that yield large β values and good processibility.[11] This class of D–π–A structures has served as the core π-conjugated building blocks for many of the newly developed EO materials.[12] Therefore, it has stimulated interest in further improving the properties of these materials and the synthetic methodologies of making them.

Using two-level model and bond-length-alternation (BLA) theory to calculate the optimal combination of donor and acceptor strength for a given bridge in NLO chromophores have been commonly used for achieving balanced electronic asymmetry and electron polarization.[13,14] Another structural parameter is the modification of polymethine conjugation path by incorporating part of the methine skeletons into single or fused aliphatic rings. Although this approach has been widely used to improve the thermal and photochemical stability of polyenic chromophores, its effect on tuning the ground-state polarization

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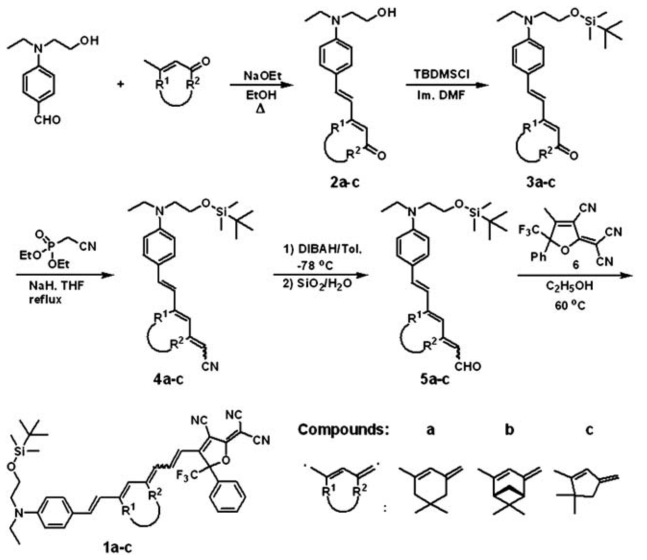
of dipolar polyene chromophores is not obvious.[15] This is partially due to the fact that some of these earlier generations of NLO chromophores only contain relatively weak electron acceptors thus possess relatively large BLA. Recent studies indicated that the intramolecular charge transfer (ICT) of highly efficient dipolar polyene chromophores can be tuned to a certain extent by different substituents along the conjugating bridge.[11a,b,16] However, it remains to be proved if the ICT of these highly polarized NLO chromophores can be modulated by structural modification of bridges.

In this study, we report the significant role of aliphatic rings (connected with part of the tetraene bridge), in tuning the ICT and NLO properties of chromophores **1a–c**. These chromophores contain the same dialkylaminophenyl donor and strong CF_3–TCF acceptor. Three different ring-locked tetraene bridges were derived from isophorone, verbenone, and trimethylcyclopentenone, respectively. The thermal, electrochemical, linear and nonlinear optical properties of all three chromophores were thoroughly investigated. Density functional theory (DFT), quantum mechanical calculations and electric-field poling study were also used to evaluate the changes in both microscopic and macroscopic nonlinearity to be expected with bridge modification.

Results and discussion

Scheme 1 shows the chemical structures and synthetic approach for this series of ring-locked tetraene chromophores **1a–c**.[11a] The Knoevenagel condensation between *N*-ethyl-*N*-(2-hydroxyethyl)aminobenzaldehyde and three different β-methylcycloenone derivatives, including isophorone, (1*S*)-(−)-verbenone, and 3,4,4-trimethyl-2-cyclopentenone, furnished the corresponding aminophenyldienone derivatives, of which the free hydroxyl group on the donor-end was then protected with *tert*-butyldimethylsilyl (TBDMS) group to improve the solubility and compatibility with polymer matrix. The extension of the conjugated π-bridge to yield the key aminophenyltrienal intermediates was accomplished in good overall yields by condensing the TBDMS-protected dienones with diethyl(cyanomethyl)phosphonate using the Wittig–Horner reaction, followed by reducing the resultant trienenitriles with DIBAL-H and subsequent hydrolysis. Finally, a strong CF_3–TCF-type acceptor[17] was condensed with the corresponding trienals to afford the desired phenyltetraene-based chromophores **1a–c**. As suggested by their ^{1}H-NMR spectra, chromophores **1a** and **1b** contain a mixture of inseparable *E*/*Z*-isomers with a ratio of about 82 : 18 and 70 : 30%, respectively; while **1c** has almost all-*trans* double-bond configuration.



Scheme 1 Chemical structures and synthetic scheme for the ring-locked tetraene chromophores **1a–c**.

Thermal properties of chromophores **1a–c** were evaluated by differential scanning calorimetry (DSC) and results are shown in Fig. 1. The isophorone-derived chromophore **1** exhibited a highly crystalline characteristic with a melting point at 188 °C. However, **1b** and **1c** which contain the verbenone- and trimethylcyclopentenone-based ring structures showed thermodynamically stable amorphous states and did not undergo crystallization or any other phase transition upon further heating beyond the glass transition temperature (T_g). Compared with the crystalline compound **1a**, the significantly improved glass-forming ability of **1b** and **1c** was mainly attributed to the increased steric hindrance caused by the three-dimensional ring structures around the planar tetraene chain, which can prevent close packing of molecules and hence crystallization. The T_gs of **1b** and **1c**, as measured by DSC, were at 100 °C and 75 °C, respectively. Considering few shape modifications performed in **1b** and **1c**, it is very attractive that they could act as a new class of molecular glass chromophores.[11c]

To determine the electrochemical properties of chromophores **1a–c**, cyclic voltammetry (CV) experiments were conducted in degassed anhydrous dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the supporting electrolyte. As shown in Fig. 2, chromophores **1a–c** all exhibited one reversible oxidation wave with an onset potential *versus* ferrocene/ferrocenium at about 0.20, 0.20 and 0.23 V, respectively. A slight but reliable increase of the onset oxidation potential of **1c** by around 30 mV with respect to those of **1a** and **1b** indicates the lowered electron density of the dialkylamino donor of **1c**, which probably originates from better charge transfer between the donor and acceptor groups through the conformationally locked tetraene bridge using the cyclopentene-based ring structure instead of the cyclohexene-based

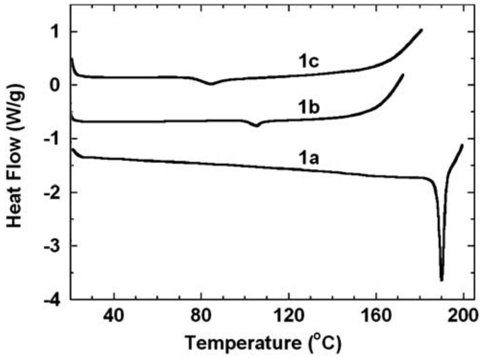


Fig. 1 DSC curves of chromophores **1a–c** with a heating rate of 10 °C min^{-1} in nitrogen.

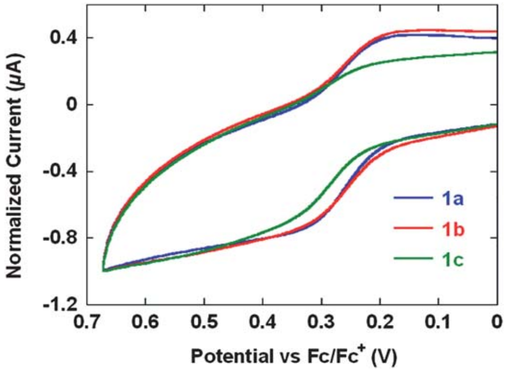


Fig. 2 Cyclic voltammograms of chromophores **1a–c** recorded in CH_2Cl_2 solutions containing 0.1 M Bu_4NPF_6 supporting electrolyte at a scan rate of 100 mV s^{-1}.

ones as in the case of **1a** and **1b**. This explanation is supported by the photophysical properties of **1a–c** using UV-vis spectroscopy.

The UV-vis-NIR absorption spectra of chromophores **1a–c** in dilute chloroform solution (10^{-5} M) are shown in Fig. 3. This series of dipolar tetraene chromophores exhibited quite different spectral patterns of the characteristic π–π* charge-transfer absorption. Chromophore **1a** showed a maximum absorption (λ_{max}) at 788 nm together with a broad, low-energy shoulder. In contrast, a slightly red-shifted absorption spectrum with an apparently increased long-wavelength absorption was recorded for **1b**. Two absorption peaks with comparable intensity were found at 793 and 867 nm, respectively. As for **1c**, the absorption spectrum with a slightly smaller fwhm (full width at half-maximum) showed a dominant absorption peak at 867 nm and a shoulder at 786 nm. It is noteworthy that the onset wavelength of the absorption of **1c** at the long-wavelength range was obviously blue-shifted by around 40 nm in comparison with those of **1a** and **1b**. The interesting evolution of the absorption spectra of **1a–c** showed that the low-energy absorption (at 867 nm for both **1b** and **1c**) was intensified steadily while the higher energy component (at *ca.* 790 nm for all of them) remained almost unchanged from the measurement of the extinction coefficients.

In order to understand the dependence of the electronic absorption properties of **1a–c** on their structures, the UV-vis-NIR absorption spectra were also measured quantitatively in a series of aprotic solvents with different polarity so that the solvatochromic behavior of each chromophore could be investigated in a wide range of dielectric environments (Fig. 4). With the solvents varying from the slightly polar dioxane to the moderately polar dichloromethane, a continuous shift of the absorption maxima to longer wavelength was observed for all three chromophores together with the significant alteration of the spectral shape. Such spectral behaviors were most obviously noticed from **1b** and **1c** in going from toluene to chloroform. The extinction coefficients of **1a–c** also gradually increased with increasing the solvent polarity. More dramatic effects were observed while investigating the absorption spectra of **1a–c** in highly polar solvents, such as acetone and acetonitrile. In comparison with a rather broad absorption band recorded for **1a**, chromophore **1c** showed a sharp and intense cyanine-type absorption band with a dramatically narrowed bandwidth. Chromophore **1b** fell in between the other two dyes in terms of its spectral features. Furthermore, a saturation behavior was found for **1c** in the more polar solvents, such as dichloromethane, acetone, and acetonitrile. The absorption peak of **1c** in these solvents exhibited almost no shift with increase of solvent polarity; however, the dominant low-energy peak of **1b** was still red-shifted progressively in going from dichloromethane to acetonitrile, which is consistent with the positive solvatochromic behavior observed in the less polar solvents. Additionally for all

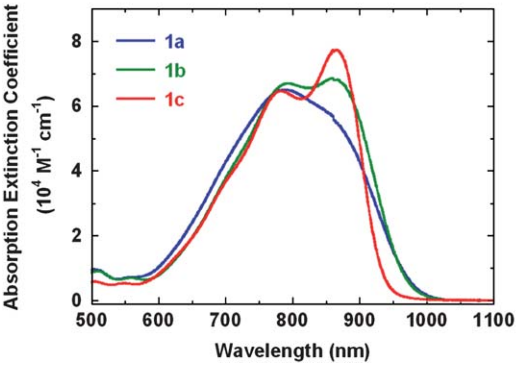


Fig. 3 UV-vis-NIR absorption spectra of chromophores **1a–c** in chloroform solutions (10^{-5} M) at room temperature.

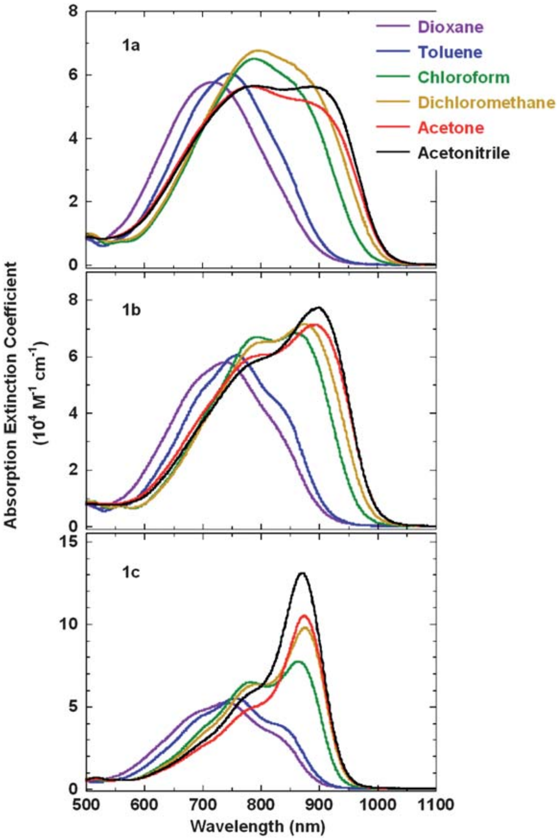


Fig. 4 Solvatochromic behaviors of chromophores **1a–c** recorded in different solvents (10^{-5} M) of varying dielectric constants (1,4-dioxane: 2.25; toluene: 2.38; chloroform: 4.81; dichloromethane: 8.93; acetone: 20.7; acetonitrile: 37.5) at room temperature.

Table 1 Summary of experimental and theoretical data of chromophores **1a–c**

		Absorption in $CHCl_3$			DFT calculation in CH_2Cl_2			
Compd	T_g/°C	λ_{max}/nm	E/M^{-1} cm^{-1}	λ_{onset}/nm	BLA/Å	μ/D	$\beta_{zzz}(0)/10^{-30}$ esu	r_{33}/pm V^{-1} @ 100 V μm^{-1}
1a	188 (mp)	788	65 100	978	0.0170	41.1	1849	78
1b	100	867 (793)	68 100 (66 900)	966	0.0171	41.4	1732	63
1c	75	867 (796)	77 300 (64 600)	931	0.0155	42.7	1664	42

of the more polar solvents, a significant blue shift of the long-wavelength absorption tail of **1c** was found with respect to those of **1a** and **1b**.

For a given donor–acceptor-substituted polymethine molecule, such as chromophores **1a–c**, the ground-state structure could be viewed as a combination of neutral and charge-separated canonical resonance forms. The relative contribution of these two resonance forms to the ground state can be controlled by the polarity of the solvent in which the chromophore is dissolved. The positive solvatochromism observed for chromophores **1a–c** in most of the solvents used for the study indicated their neutral polyene-like electronic structures; however, in the most polar solvents of acetone and acetonitrile, an electron distribution near the so-called cyanine limit (with equal contributions from neutral and charge-separated resonance forms) was realized for **1c**, as dictated by a very sharp cyanine-type absorption band and vanished solvatochromism in the highly polar solvents. The more pronounced polarization effect exerted on **1c** by polar solvents suggests that the cyclopentene-based tetraene bridge employed in **1c** might provide the most effective pathway to achieve charge redistribution between the donor and acceptor groups due to its more straight and coplanar molecular structure in comparison with the cyclohexene-based ones utilized in **1a** and **1b**.[18] Such structural difference is also responsible for the apparent narrowing of the spectral band and the significant blue shift of the low-energy absorption tail observed for **1c**. Notably, similar solvent-dependent changes of UV/vis spectra were also found for some merocyanine dyes[19] or even the tetraene chromophores containing the much stronger heteroaryl-amino donors.[20]

In order to obtain further understanding of the bridge dependent ground-state polarization of this intriguing series of EO chromophores, DFT[21,22] calculations using Gaussian 09[23] were carried out on chromophores **1a–c** at the hybrid B3LYP[24,25] level employing the split valence 6-31G*[26] basis set (detailed in the ESI†). When used carefully and consistently, this method of DFT has been shown to give relatively consistent descriptions of first-order hyperpolarizabilities for a number of similar chromophores.[8a,27] All molecules were assumed to be in *trans*-configurations and their geometries were optimized in dichloromethane using default PCM parameters. The relevant theoretically calculated parameters of **1a–c**, including bond-length alternation (BLA), dipole moment (μ), and zero-frequency molecular first hyperpolarizability [$\beta_{zzz}(0)$], are displayed in Table 1. It was found that there was a decrease of BLA in going from cyclohexene (**1a** and **1b**) to cyclopentene (**1c**) containing chromophores. This result corroborates the hypothesis that the chromophores show a trend in increasing ground-state polarization going from chromophores **1a** to **1c**. The calculation of the critical figure-of-merit, [$\beta_{zzz}(0)$], for all three chromophores, showed a progressive decrease from chromophores **1a** to **1c**, owing to their gradually increased cyanine-like electronic structure as suggested by the experimental UV-vis spectral results presented in the previous section.

To evaluate their EO activity, 10 wt% of the chromophores **1a–c** were doped into a commonly used polymer matrix, poly(methyl methacrylate) (PMMA), as guest−host polymers. By avoiding severe intermolecular electrostatic interactions at such low chromophore loading level, the performance of the materials was more related to the intrinsic molecular properties. Therefore, this could help shed some light for deeper understanding of the structure–property relationships within this series of chromophores. The EO activities (r_{33} values) of poled films were measured by the Teng–Man method at a wavelength of 1.31 μm using carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections.[28] For this series of tetraene chromophores, the obtained r_{33} values showed a gradual decrease from 78 pm V^{-1} for **1a** to 63 pm V^{-1} for **1b**, and further to 42 pm V^{-1} for **1c**. In order to elucidate the origins of the significant variation of the EO activities of **1a–c**, we also measured the order parameters of the poled films of EO polymers based on linear optical dichroism of intramolecular charge transfer bands.[29] The axial orientation of the poled samples was described as the order parameter $\Phi = 1 - A/A_0$, where A_0 and A are the integral absorbance for the unpoled and poled samples at normal incidence, instead of the absorbance maximum, due to the change of the spectral shape after poling (particularly for **1b** and **1c**). The decreased absorbance and changed band shape of the poled films could nearly recover after being annealed at poling temperatures for 10 min, indicating that very litter chemical degradation occurred during poling. The order parameters of **1a–c** in the formulated polymer composites were 0.11, 0.13, and 0.16, respectively, showing a progressive enhancement. Since the chromophore number density was also pretty similar for all the EO polymers, the considerable decrease in the EO activity from **1a** to **1c** should be mainly attributed to the decrease in the first hyperpolarizability (β) of the chromophores doped in the polar polymer matrix. This corresponded well with the results of solvatochromism study and DFT calculations on these molecules. The relevant physical properties of chromophores **1a–c** are summarized in Table 1.

Conclusions

A series of highly polarizable phenyltetraene-based chromophores **1a–c** has been synthesized by fusing different aliphatic rings into the tetraene chain. In addition to the widely used isophorone-based tetraene (CLD) bridge, two new tetraene structures, derived from verbenone and trimethylcyclopentenone, were introduced as efficient π-bridges to construct the new phenyltetraene chromophores. The effects of the different ring-locked tetraene bridges on the comprehensive properties of the resultant chromophores were systematically investigated.

Our results demonstrated that apart from the variation of the donor and acceptor groups, the intrinsic electronic structure and the ultimate optical properties for these phenyltetraene-based NLO chromophores could also be effectively tuned through conformationally locked aliphatic ring structures. By varying the ring structures from cyclohexene to cyclopentene, the molecular polarization of the tetraene chromophores could be significantly enhanced. Therefore, the ground-state electronic character of chromophore **1c** could be readily tuned from polyene to cyanine type by increasing the solvent polarity as suggested from the band shape and solvatochromism of its UV-vis spectra. This provides a deeper understanding of the structure–property relationships of polyene chromophores, which is beneficial for further optimization of their molecular properties for improving bulk EO material performance.

Experimental

Materials and measurements

All chemicals were purchased from Aldrich and used as received. 3,4,4-Trimethyl-2-cyclopentenone and chromophore **1a** were prepared according to the literature procedures, respectively.[11a,30] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV300 and AV500 spectrometer using $CDCl_3$ as solvent in all cases. High-resolution mass spectrometry (HRMS) was performed on a Bruker APEX III 47e Fourier transform mass spectrometer. Thermal transitions were analyzed with a TA Instruments differential scanning calorimeter (DSC) Q20 under nitrogen at a heating rate of 10 °C min^{-1}. Cyclic voltammetric data were measured 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/$AgNO_3$ as the reference electrode at a scan rate of 100 mV s^{-1}. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) in CH_2Cl_2 is the electrolyte. UV-vis-NIR spectra were recorded on a Perkin-Elmer spectrophotometer (Lambda 9 UV/vis/NIR).

Poling and r_{33} measurements

For studying the EO property derived from the chromophores, guest–host polymers were generated by formulating chromophores **1a–c** (10 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 μM PTFE filter and spincoated onto thin-film device (TFD) indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 60 °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 μm.

Compound 2b. To a solution of 4-[*N*-(2-hydroxyethyl)-*N*-ethylamino]benzaldehyde (1.06 g, 5.49 mmol) and (1*S*)-(−)-verbenone (1.00 g, 6.65 mmol) in anhydrous ethanol was added a freshly prepared solution of sodium ethoxide (7.00 mmol) by syringe. The reaction mixture was stirred at 70 °C for 24 h and then was poured into a saturated solution of ammonium chloride and extracted with ethyl acetate; the combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography using hexane/ethyl acetate as eluent to give the product as orange-red solids (1.36 g, yield: 76%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.38 (2H, d, $J = 9.0$ Hz, Ar-H), 6.86 (1H, d, $J = 16.2$ Hz, CH), 6.75 (1H, d, $J = 16.2$ Hz, CH), 6.72 (2H, d, $J = 9.0$ Hz, Ar-H), 5.84 (1H, s, CH), 3.83 (2H, t, $J = 6.0$ Hz, CH_2OH), 3.54–3.44 (4H, m, NCH_2), 3.12 (1H, td, $J = 6.0$ and 1.5 Hz, CH), 2.89 (1H, dt, $J = 9.0$ and 5.7 Hz, CH_2), 2.70 (1H, td, $J = 6.0$ and 1.8 Hz, CH), 2.11 (1H, d, $J = 9.0$ Hz, CH_2), 1.57 (3H, s, CH_3), 1.21 (3H, t, $J = 6.3$ Hz, CH_3), 1.01 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 204.91, 165.94, 149.16, 135.90, 129.31, 123.99, 122.59, 120.18, 112.18, 60.17, 58.22, 52.95, 52.43, 45.66, 43.94, 40.20, 26.94, 22.30, 12.16. HRMS (ESI) (M^+, $C_{21}H_{27}NO_2$): calcd: 325.2042; found: 325.2035%.

Compound 2c. The procedure for compound **2b** was followed to prepare **2c** from 4-[*N*-(2-hydroxyethyl)-*N*-ethylamino]benzaldehyde and 3,4,4-trimethyl-2-cyclopentenone as orange-red solids (yield: 54%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.41 (2H, d, $J = 9.0$ Hz, Ar-H), 7.20 (2H, d, $J = 16.2$ Hz, CH), 6.74 (2H, d, $J = 9.0$ Hz, Ar-H), 6.59 (1H, d, $J = 16.2$ Hz, CH), 6.15 (1H, s, CH), 3.87–3.81 (2H, m, CH_2OH), 3.54 (2H, t, $J = 5.7$ Hz, NCH_2), 3.49 (2H, t, $J = 6.9$ Hz, NCH_2), 2.38 (2H, s, CH_2), 1.33 (6H, s, CH_3), 1.20 (3H, t, $J = 6.9$ Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 207.54, 181.79, 149.24, 139.51, 129.26, 123.60, 122.66, 114.68, 112.01, 60.13, 52.25, 52.22, 45.51, 42.03, 27.59, 11.94. HRMS (ESI) (M^+, $C_{19}H_{25}NO_2$): calcd: 299.1885; found: 299.1880%.

Compound 3b. *tert*-Butyldimethylsilyl chloride (0.483 g, 3.20 mmol) was added in portions to the mixture of compound **2b** (0.862 g, 2.65 mmol) and imidazole (0.236 g, 3.47 mmol) in anhydrous dimethylformamide. After stirring at room temperature for 4 h, the reaction mixture was poured into water and extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography using hexane/ethyl acetate as eluent to give the product as orange-red oil (0.920 g, yield: 79%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.36 (2H, d, $J = 9.0$ Hz, Ar-H), 6.86 (1H, d, $J = 15.9$ Hz, CH), 6.74 (1H, d, $J = 15.9$ Hz, CH), 6.65 (2H, d, $J = 9.0$ Hz, Ar-H), 5.83 (1H, s, CH), 3.77 (2H, t, $J = 6.3$ Hz, OCH_2), 3.49–3.41 (4H, m, NCH_2), 3.12 (1H, td, $J = 6.0$ and 1.2 Hz, CH), 2.89 (1H, dt, $J = 9.0$ and 5.7 Hz, CH_2), 2.69 (1H, td, $J = 6.0$ and 1.8 Hz, CH), 2.11 (1H, d, $J = 9.3$ Hz, CH_2), 1.57 (3H, s, CH_3), 1.17 (3H, t, $J = 6.9$ Hz, CH_3), 1.01 (3H, s, CH_3), 0.89 (9H, s, CH_3), 0.03 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 204.66, 165.76, 148.96, 135.88, 129.33, 123.59, 122.42, 120.23, 111.75, 60.77, 58.31, 52.84, 52.58, 45.76, 43.98, 40.17, 27.00, 26.09, 25.89, 22.36, 18.50, 12.36, −5.18. HRMS (ESI) (M^+, $C_{27}H_{41}NO_2Si$): calcd: 439.2907; found: 439.2901%.

Compound 3c. The procedure for compound **3b** was followed to prepare **3c** from compound **2c** as orange-red oil (yield: 76%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.39 (2H, d, $J = 9.0$ Hz, Ar-H), 7.20 (2H, d, $J = 16.2$ Hz, CH), 6.67 (2H, d, $J = 9.0$ Hz, Ar-H), 6.58 (1H, d, $J = 16.2$ Hz, CH), 6.15 (1H, s, CH), 3.78 (2H, t, $J = 6.3$ Hz, OCH_2), 3.50–3.42 (4H, m, NCH_2), 2.38 (2H, s, CH_2), 1.33 (6H, s, CH_3), 1.18 (3H, t, $J = 6.9$ Hz, CH_3), 0.89 (9H, s, CH_3), 0.04 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 207.35, 181.71, 149.02, 139.59, 129.26, 123.05, 122.57, 114.33, 111.50, 60.52, 52.37, 52.27, 45.57, 42.02, 27.64, 25.86, 18.25, 12.12, −5.40. HRMS (ESI) (M^+, $C_{25}H_{39}NO_2Si$): calcd: 413.2750; found: 413.2745%.

Compound 4b. Under N_2 atmosphere to the mixture of NaH (0.093 g, 3.87 mmol) in dry THF was added diethyl cyanophosphonate (0.685 g, 3.87 mmol) dropwise by syringe at 0 °C with an ice bath. After the solution became clear, compound **3b** (0.848 g, 1.93 mmol) in dry THF was added. The mixture was refluxed for 3 h and then poured into a saturated solution of ammonium chloride and extracted with ethyl acetate; the combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography using hexane/ethyl acetate as eluent to give the product orange-red oil (0.758 g, yield: 85%). The ratio of the $Z : E$ isomers is 50 : 50% calculated by the integration of respective protons. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.34–7.29 (2H, m, Ar-H), 6.72–6.62 (4H, m, Ar-H and CH), 6.47 (0.5H, s, CH), 6.05 (0.5H, s, CH), 4.92 (0.5H, s, CH), 4.79 (0.5H, s, CH), 3.79–3.74 (2H, m, OCH_2), 3.48–3.40 (4H, m, NCH_2), 3.27 (0.5H, td, $J = 5.7$ and 1.5 Hz, CH), 3.02–2.96 (1H, m, CH_2), 2.79–2.68 (1.5H, m, CH), 1.69–1.63 (1H, m, CH_2), 1.54 (1.5H, s, CH_3), 1.49 (1.5H, s, CH_3), 1.20–1.14 (3H, m, CH_3), 0.89 (9H, s, CH_3), 0.84 (3H, s, CH_3), 0.03 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 165.30, 165.06, 156.54, 156.24, 148.45, 132.86, 132.70, 128.78, 124.19, 123.37, 123.10, 121.07, 119.17, 118.35, 111.80, 87.26, 86.00, 60.82, 52.60, 52.29, 49.58, 47.72, 47.56, 45.74, 43.22, 43.07, 37.41, 37.27, 26.60, 26.10, 25.90, 21.92, 18.48, 12.40, −5.16. HRMS (ESI) (M^+, $C_{29}H_{42}N_2OSi$): calcd: 462.3066; found: 462.3061%.

Compound 4c. The procedure for compound **4b** was followed to prepare **4c** from compound **3c** as orange-red oil (yield: 83%). The ratio of the $Z : E$ isomers is 45 : 55% calculated by the integration of respective protons. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.37–7.32 (2H, m, Ar-H), 7.12 (0.45H, d, $J = 16.2$ Hz, CH), 7.04 (0.55H, d, $J = 16.2$ Hz, CH), 6.67–6.63 (2.45H, m, Ar-H and CH), 6.47 (1H, d, $J = 16.2$ Hz, CH), 6.31 (0.55H, s, CH), 5.00 (0.55H, t, $J = 2.1$ Hz, CH), 4.79 (0.45H, t, $J = 2.1$ Hz, CH), 3.79–3.75 (2H, m, OCH_2), 3.49–3.41 (4H, m, NCH_2), 2.77 (1.1H, d, $J = 2.1$ Hz, CH_2), 2.60 (0.9H, d, $J = 2.1$ Hz, CH_2), 1.28 (3.3H, s, CH_3), 1.26 (2.7H, s, CH_3), 1.20–1.15 (3H, m, CH_3), 0.89 (9H, s, CH_3), 0.04 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 168.33, 148.48, 136.34, 135.86, 128.67, 128.58, 123.71, 123.64, 122.42, 119.59, 119.04, 115.63, 115.37, 111.53, 83.04, 81.91, 60.55, 52.40, 48.19, 47.70, 45.97, 45.80, 45.55, 27.93, 27.84, 25.88, 18.27, 12.15, −5.38. HRMS (ESI) (M^+, $C_{27}H_{40}N_2OSi$): calcd: 436.2910; found: 436.2905%.

Compound 5b. The solution of compound **4b** (0.694 g, 1.50 mmol) in dry toluene was cooled to −78 °C and the solution of DIBAL in hexane (1.0 M, 2.6 mL, 2.6 mmol) was added dropwise by syringe. After being kept at −78 °C for 2 h, wet silica gel was added to quench the reaction and the mixture was stirred at 0 °C for 2 h. The product mixture was filtered off, and the resulting precipitates were washed with ethyl acetate. Evaporation of the solvent and purification by column chromatography using hexane/ethyl acetate as eluent gave the product as dark red oil (0.580 g, yield: 83%). The ratio of the $Z : E$ isomers is 25 : 75% calculated by the integration of respective protons. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 10.14 (0.25H, d, $J = 8.1$ Hz, CHO), 9.89 (0.75H, d, $J = 8.1$ Hz, CHO), 7.35–7.31 (2H, m, Ar-H), 6.93 (0.25H, s, CH), 6.74–6.70 (2H, m, CH), 6.64 (2H, d, $J = 9.0$ Hz, Ar-H), 6.10 (0.75H, s, CH), 5.84 (0.75H, d, $J = 8.4$ Hz, CH), 5.63 (0.25H, d, $J = 8.4$ Hz, CH), 3.76 (2H, t, $J = 6.0$ Hz, OCH_2), 3.70 (1H, t, $J = 5.4$ Hz, CH), 3.48–3.40 (4H, m, NCH_2), 3.04 (1H, t, $J = 5.4$ Hz, CH), 2.81–2.70 (1H, m, CH_2), 1.76 (1H, d, $J = 9.0$ Hz, CH_2), 1.56 (2.2H, s, CH_3), 1.51 (0.8H, s, CH_3), 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 0.89 (12H, s, CH_3), 0.03 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 190.02, 189.84, 164.83, 164.36, 157.87, 157.63, 148.48, 133.02, 132.92, 128.79, 124.17, 123.87, 123.57, 123.33, 123.00, 120.18, 117.01, 111.78, 60.78, 53.67, 52.57, 47.81, 45.71, 45.51, 43.62, 43.49, 37.56, 37.51, 26.91, 26.71, 26.07, 22.04, 21.92, 18.44, 12.36, −5.20. HRMS (ESI) (M^+, $C_{29}H_{43}NO_2Si$): calcd: 465.3062; found: 465.3055%.

Compound 5c. The procedure for compound **5b** was followed to prepare **5c** from compound **4c** as orange-red oil (yield: 77%). The ratio of the $Z : E$ isomers is 28 : 72% calculated by the integration of respective protons. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 9.98 (0.28H, d, $J = 8.1$ Hz, CHO), 9.77 (0.72H, d, $J = 8.1$ Hz, CHO), 7.38–7.33 (2H, m, Ar-H), 7.17–7.09 (1.28H, m, CH), 6.66 (2H, d, $J = 9.0$ Hz, Ar-H), 6.58–5.50 (1H, m, CH), 6.41 (0.72H, s, CH), 5.94 (0.72H, td, $J = 1.8$, 8.1 Hz, CH), 5.76–5.73 (0.28H, td, $J = 1.8$, 8.1 Hz, CH), 3.77 (2H, t, $J = 6.3$ Hz, CH_2), 3.49–3.42 (4H, m, CH_2), 2.98 (1.44H, d, $J = 1.8$ Hz, CH_2), 2.71 (0.56H, d, $J = 1.8$ Hz, CH_2), 1.31 (4.32H, s, CH_3), 1.29 (1.68H, s, CH_3), 1.18 (3H, t, $J = 6.9$ Hz, CH_3), 0.89 (9H, s, CH_3), 0.04 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 190.79, 189.85, 168.96, 168.64, 168.51, 167.54, 148.57, 148.54, 136.64, 136.34, 128.71, 128.70, 125.91, 123.70, 123.69, 120.11, 118.03, 117.33, 115.90, 115.67, 111.53, 60.53, 52.38, 49.89, 46.09, 45.54, 45.50, 44.11, 28.02, 27.83, 25.86, 18.24, 12.13, −5.40. HRMS (ESI) (M^+, $C_{27}H_{41}NO_2Si$): calcd: 439.2907; found: 439.2902%.

Compound 1b. Compound **5b** (0.158 g, 0.34 mmol) and acceptor **6** (0.097 g, 0.38 mmol) were dissolved in the mixture solvent of anhydrous ethanol and CH_2Cl_2. The reaction mixture was allowed to stir at 60 °C for 1–3 h and monitored by TLC. After removal of the solvents, the residue was purified by column chromatography eluting with hexane/ethyl acetate. Further purification of the product by reprecipitation from methanol/dichloromethane afforded the desired chromophore as dark solids (0.150 g, yield: 58%). The ratio of the $Z : E$ isomers is 30 : 70% calculated by the integration of respective protons. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 8.54 (0.30H, t, $J = 12.6$ Hz, CH), 8.16 (0.40H, t, $J = 12.6$ Hz, CH), 7.91 (0.30H, b, CH), 7.51–7.49 (5H, m, Ar-H), 7.42–7.36 (2H, m, Ar-H), 6.95–6.88 (1H, m, CH), 6.82–6.73 (1H, m, CH), 6.67 (2H, d, $J = 9.0$ Hz, Ar-H), 6.56 (0.30H, s, CH), 6.32–6.13 (2.40H, m, CH), 6.02 (0.30H, d,

J = 12.6 Hz, CH), 3.78 (2H, m, CH_2), 3.52–3.44 (4H, m, CH_2), 3.16–3.04 (2H, m, CH), 2.83–2.73 (1H, m, CH_2), 1.76 (1H, d, J = 9.0 Hz, CH_2), 1.59–1.52 (4H, m, CH_3), 1.19 (3H, t, J = 6.9 Hz, CH_3), 0.88 (9H, s, CH_3), 0.82 (1H, s, CH_3), 0.74 (1H, s, CH_3), 0.03 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 176.41, 168.60, 164.51, 161.73, 149.90, 146.65, 146.46, 145.89, 138.06, 137.94, 137.59, 131.22, 130.36, 130.33, 129.65, 126.96, 126.73, 126.04 125.49, 125.39, 124.05, 123.04, 119.10, 114.85, 112.09, 111.67, 60.79, 52.60, 51.12, 47.00, 45.92, 44.89, 39.28, 27.15, 26.96, 26.04, 21.96, 21.88, 21.79, 18.42, 12.38, −5.23. HRMS (ESI) (M^+, $C_{45}H_{49}F_3N_4O_2Si$): calcd: 762.3577; found: 762.3571%.

Compound 1c. The procedure for chromophore **1b** was followed to prepare **1c** from compound **5c** and acceptor **6** as dark solids (yield: 45%). Almost only *E*-isomer was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 8.01 (1H, b, CH), 7.50 (5H, s, Ar-H), 7.42 (2H, d, J = 9.0 Hz, Ar-H), 7.33 (1H, d, J = 16.2 Hz, CH), 6.69 (2H, d, J = 9.0 Hz, Ar-H), 6.62 (1H, d, J = 16.2 Hz, CH), 6.57 (1H, s, CH), 6.37 (1H, d, J = 12.9 Hz, CH), 6.16 (1H, d, J = 14.4 Hz, CH), 3.79 (2H, t, J = 6.0 Hz, CH_2), 3.54–3.46 (4H, m, CH_2), 2.80–2.75 (2H, m, CH_2), 1.30 (6H, s, CH_3), 1.21 (3H, t, J = 6.9 Hz, CH_3), 0.89 (9H, s, CH_3), 0.03 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 176.62, 173.15, 150.75, 148.74, 145.3, 142.94, 131.10, 130.95, 129.57, 127.73, 126.79, 123.53, 121.54, 121.30, 115.92, 113.12, 112.67, 112.20, 112.13, 60.77, 52.65, 46.04, 28.27, 26.03, 25.82, 18.41, 12.36, −5.23. HRMS (ESI) (M^+, $C_{43}H_{47}F_3N_4O_2Si$): calcd: 736.3420; found: 736.3415%.

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