Linear and Nonlinear Optical Properties of a Macrocyclic Trichromophore Bundle with Parallel-Aligned Dipole Moments

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A macrocyclic trichromophore bundle **1** with parallel-aligned dipole moments has been synthesized to study the influence of aggregation and orientation of a nonlinear optical (NLO) chromophore on its optical properties. The linear and nonlinear optical properties of **1** and a single chromophore standard **2** have been studied by UV−vis absorption, fluorescence, solvatochromic spectrometry, and hyper-Rayleigh scattering (HRS). Reduced first-order hyperpolarizability β, hypsochromic shift, enhanced solvatochromic shifts, and fluorescence quenching for individual chromophores were observed when **1** was compared with **2**. Analysis of the data showed that the transition dipole moment changes only slightly when the chromophores are parallel aligned in the bundle architecture. However, the apparent hyperpolarizability of the individual chromophores decreased significantly by about 20%. The reduction in β for the individual chromophores in **1** is largely due to the hypsochromic shift, i.e., excitation energy increase of the interband (charge-transfer) energy gap and the reduced difference between the ground-state and excited-state dipole moments. The hypsochromic shift and fluorescence quenching are consistent with exciton theory. Possible reasons for the enhanced solvatochromic shift are discussed.

Introduction

Polymeric electrooptic (EO) materials have many potential applications in telecommunications, defense, sensors, and computer industries.[1] In such materials, nonlinear optical (NLO) chromophores are doped or grafted into a polymer matrix and are poled under an external electric field to induce a noncentrosymmetric alignment, which is necessary for a nonzero electrooptical effect. Chromophores with high first-order hyperpolarizability usually have large dipole moments. Electrostatic interactions among the dipoles and between the dipoles and the external electric field play key roles in the electric field poling process.[2] Interchromophore dipolar interaction can affect the nonlinear optical properties of the chromophore due to the high chromophore concentration (normally around 25 wt %) in the polymer matrix. The absorption and fluorescence of chromophores experiencing aggregation have been extensively studied,[3] but less work on nonlinear optical properties has been reported.[4−6]

Our research focuses on the relationship between dipolar interaction and optical properties of designed and synthesized multichromophore architectures. Within the architectures, the orientation of the chromophores is defined by covalent bonds. These model compounds will lead us to a better understanding of the relationship between dipolar interaction and optical, nonlinear optical properties. Multichromophore bundles with parallel-aligned dipole moments are of particular interest. Because antiparallel dipolar interaction is more energetically favorable than parallel interaction, parallel alignment will not naturally occur unless other interactions dominate. In polymeric

EO materials, parallel alignment is induced by an external electric field. Therefore, parallel-aligned chromophore systems are important for both fundamental research of optical materials and EO applications.

Multichromophore bundles based on calixarene,[7] triphenylcarbinol,[8] and cyclodextrin[9] have been studied by Reinhoudt, Jullien, and Blanchard-Desce and co-workers. The previously reported compounds showed interesting nonlinear optical and electrooptical properties. However, in all these compounds, chromophores were not tethered at both ends. Here, we report the synthesis and linear and nonlinear optical properties of a macrocyclic trichromophore bundle **1** with parallel-aligned dipole moments. In **1**, three chromophores are covalently tethered on both ends. Another important feature that differentiates **1** from all the previously reported compounds is that the flexible linkers create the possibility for the chromophores to adjust their relative positions within a certain range to reduce the energy of the dipole−dipole interaction. This makes **1** a good model for studying chromophore interactions in electric poled EO polymers. Such adjustment may be the reason behind the very high electrooptical activity observed in multichromophore-containing dendrimers.[10]
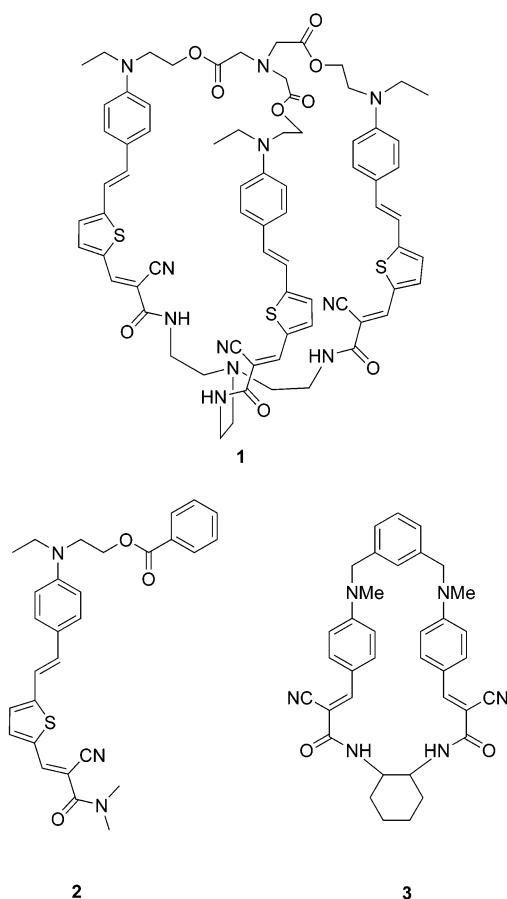
Results and Discussion

Synthesizing macrocyclic multichromophore bundles with parallel-aligned dipoles is challenging. Besides the difficulties that are common for synthesizing macrocyclic molecules, such as competing polymerization reactions, the dipole−dipole interaction also encumbers the cyclization. Chafin et al.[11] reported that α,α′-(4-formylanilino)-*m*-xylene reacted with a bis-cyanoacetamide to give a cyclic product **3**, while the *o*-xylene

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Figure 1. UV−vis spectrum of **1** and **2** in chloroform.

TABLE 2: Hyperpolarizabilities of 1, 2, and DR1

compound	λ_{max} (nm, CHCl$_3$)	$\beta/\beta_{chloroform}$	β (10^{-30} esu)
1	463	1902 ± 115	237 ± 14
2	481	775 ± 74	97 ± 9
DR1	479	783 ± 6	98

solvent as internal reference. The hyperpolarizabilities were compared to those of disperse red 1 (DR1) because it has a λ_{max} at 479 nm in chloroform which is very close to the λ_{max} of the studied chromophores. The β of DR1 has been measured by EFISH[14] and electrooptic experiment[15] to be 49 and 60 × 10^{-30} esu at 1907 nm. We therefore chose an average β of 55 × 10^{-30} esu. Using the conventional two-state model[16] to describe the wavelength dependence of β, we obtain 101 × 10^{-30} esu at 1300 nm for DR1. The β value of DR1 can be used to convert the relative β values (in terms of $\beta_{chloroform}$) into esu in the following manner. The ratios of the β for **1** and **2** to DR1 are 2.43 and 0.99. So, we obtained the β of **1** and **2** that are 237 × 10^{-30} esu and 97 × 10^{-30} esu, respectively. The results are listed in the Table 2.

According to the two-state model,[15] the first hyperpolarizability can be written as eq 1

$$\beta = \frac{3}{2\epsilon_0\hbar^2}\frac{\varpi_{eg}^2}{(\varpi_{eg}^2 - 4\varpi^2)(\varpi_{eg}^2 - \varpi^2)}\Delta\mu(\mu_{eg}^2) \qquad (1)$$

in which ω_{eg} is the maximum absorption frequency, ω is the excitation frequency, $\Delta\mu$ is the difference between the dipole moments in the ground and first excited state, and μ_{eg} is the transition dipole moment. From HRS data, we obtained that the ratio of the β of **1** and **2** is 2.5. So for an *individual* chromophore, the ratio is 0.81; thus,

$$\frac{\beta_1}{\beta_2} = \frac{\varpi_{1eg}^2(\varpi_{2eg}^2 - 4\varpi^2)(\varpi_{2eg}^2 - \varpi^2)\Delta\mu_1(\mu_{1eg}^2)}{\varpi_{2eg}^2(\varpi_{1eg}^2 - 4\varpi^2)(\varpi_{1eg}^2 - \varpi^2)\Delta\mu_2(\mu_{2eg}^2)} = 0.81$$
$$(2)$$

gave a polymeric product. Compound **1** was synthesized as in Scheme 1. The starting material **6** was synthesized following a four-step literature method.[12] We used Knoevenagel condensation in a highly diluted solution to close the three-arm precursor **4**. Therefore, **1** was synthesized by heating a diluted solution of **3** and **4** in dry THF with piperidine for 8 days (Scheme 1). The pure product was isolated by preparative TLC with a reasonable 32% yield. ^{1}H NMR showed that peaks of the protons on the linkages of both ends are clearly broader than the corresponding protons of **5** and **6**. This is consistent with the expected macrocyclic structure that has linkages with limited flexibility. Besides NMR and elemental analysis, the structure was confirmed by mass spectrometry. Both a strong M + H peak at 1334.5 and an M + 2H peak at 667.8 were observed. For comparison, **2** was also synthesized as the standard.

The optical properties of **1** and **2** were studied by UV−vis, solvatochromism, hyper-Rayleigh Scattering (HRS), and fluorescence. UV−vis spectra of **1** and **2** were taken in different solvents. A list of λ_{max} values is given in the Table 1, and the spectrum in chloroform is shown in the Figure 1. In all the tested solvents, **2** has larger λ_{max} values but smaller solvatochromic shifts than those of **1**. This is interesting because both the magnitude of bathochromic shift and solvatochromic shift are commonly used to estimate the first-order hyperpolarizability.[13] This unusual phenomenon is discussed in detail below.

The first-order hyperpolarizability β was measured by hyper-Rayleigh scattering (HRS) at 1300 nm in chloroform using the
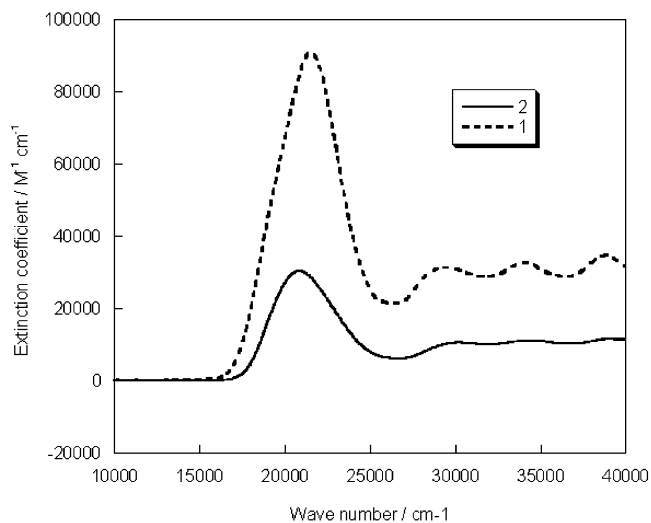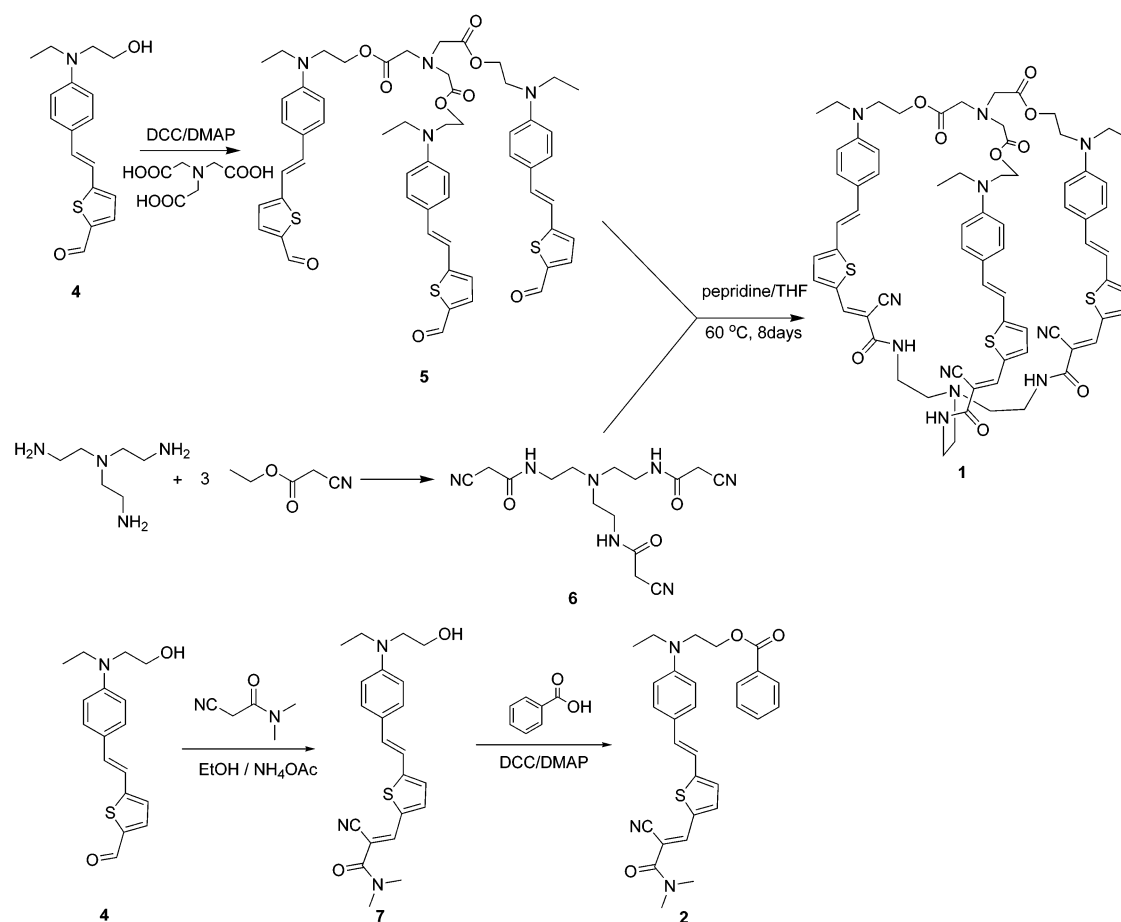
TABLE 1: Absorption of 1 and 2 in Different Solvents

λ_{max} (nm)	dioxane	chloroform	THF	dichloromethane	cyclopentanone	acetone
1	447	463	454	465	464	458
2	470	481	473	479	477	470

SCHEME 1: Synthesis of 1 and 2

This result showed that β decreased significantly in the parallel bundle structure. The decrease could be a result of reduced μ_{eg}, reduced $\Delta\mu$, increased ω_{eg}, or a combination of these factors. Therefore, these factors were analyzed individually. The ratio of μ_{eg}^2 for each individual chromophore can be obtained from integrating the absorption bands in the UV−vis spectrum[17] (Figure 1) to be $\mu_{1eg}^2/\mu_{2eg}^2 = 1.03$. (The ratio directly obtained from the spectrum is 3.10, which is divided by 3 to give the ratio for the individual chromophore.) The effect of the hypsochromic shift, i.e., excitation energy increase of the absorption band, was calculated using the λ_{max} of **1** and **2** in chloroform. We obtained that the ratio of the ω-related terms in eq 2 is 0.84; thus,

$$\frac{\varpi_{1eg}^2(\varpi_{2eg}^2 - 4\varpi^2)(\varpi_{2eg}^2 - \varpi^2)}{\varpi_{2eg}^2(\varpi_{1eg}^2 - 4\varpi^2)(\varpi_{1eg}^2 - \varpi^2)} = 0.84 \qquad (3)$$

Together with eq 2, we can obtain that $\Delta\mu_1/\Delta\mu_2 = 0.93$. These results showed that the reduced β is mainly due to electrostatic interactions rather than orbital overlap among the chromophores in **1**. Electrostatic interactions in the parallel-dipole architecture increase the energy of the charge-transfer excited state, decrease the extent of charge transfer, thus decreases the first-order hyperpolarizability β. The increase of the energy of the charge-transfer band contributes most to the decrease of the first-order hyperpolarizability of the chromophores in **1**.

The hypsochromic shift of **1** is consistent with the exciton theory,[5a,18] which is successful in studying resonance interaction of the excited states of weakly coupled composites. Besides the hypsochromic shift, it also predicts that fluorescence quenching
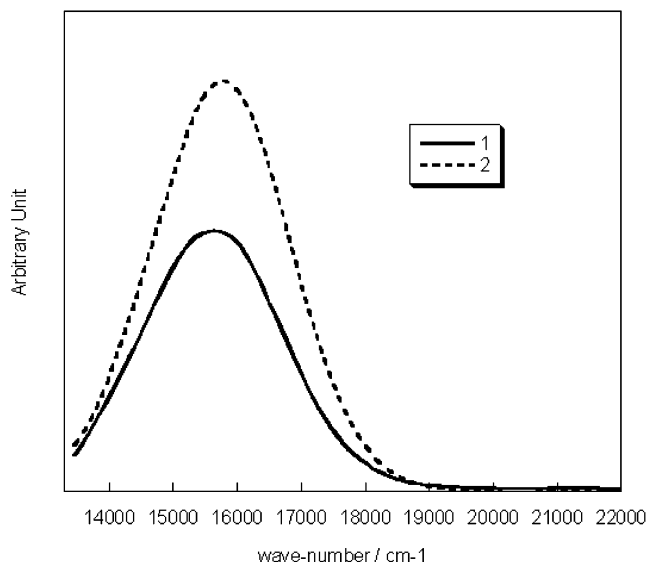

Figure 2. Fluorescence spectra of **1** and **2** in THF. (Because 1 mol of **1** contains 3 mol of the chromophores, the relative fluorescence intensity of an individual chromophore in **1** is one-third of the intensity shown in the figure.)

shall be observed. Therefore, the fluorescence spectra of **1** and **2** were taken in THF using a 400 nm excitation wavelength. Indeed, we observed that about 80% of fluorescence was quenched for **1** (Figure 2).

Compound **1** showed a larger solvatochromic effect than **2**. The solvatochromic effect depends on the dipole moment, effective solvation volume, difference between the ground-state

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and excited-state dipole moments of the solute, and the dielectric constants of the solvents.[19,20] Discussions above have shown that $\Delta\mu_1$ is actually smaller than $\Delta\mu_2$. The macrocyclic structure of **1** makes the chromophores less accessible to solvents. Both of these two factors would result in a smaller solvatochromic shift of **1** than that of **2**. However, the experimental data showed an opposite effect. This unusual phenomenon may be qualitatively explained by the solvent molecules mediating the dipolar interactions among the chromophores in the parallel bundle structure. Previous solvatochromism theories did not consider the electrostatic interaction between solute molecules. In **1**, three chromophores are close to each other; the dipolar interactions among the chromophores are strong and cause significant hypsochromic shift as shown in Table 1. Molecular modeling of **1** showed that there is enough space between chromophores to hold some solvent molecules such as chloroform. These solvent molecules sandwiched between the chromophores may mediate the dipolar interactions and lower the energy of the parallel-aligned dipoles. Such effect will be more pronounced when the polarity and polarizability of a solvent molecule increases. Therefore, the overall polarity-dependent solvation effects including the solvatochromic effect are amplified. Quantitative analysis of this unusual phenomenon requires quantum mechanical calculations that involve polarizable solvent molecules. This work is being undertaken by our group.

Conclusions

Supramolecule **1** with three parallel-aligned chromophores has been synthesized. Reduced first-order hyperpolarizability, hypsochromic shift, enhanced solvatochromic shifts, and fluorescence quenching for individual chromophores were observed when **1** was compared with **2**. Analysis of data showed that the transition dipole moment changes only slightly when the chromophores are parallel aligned in the bundle architecture. However, the apparent hyperpolarizability of the individual chromophores decreased significantly by about 20%. The reduced β for the individual chromophores in **1** is related to the hypsochromic shift, i.e., excitation energy increase of the absorption band, and the reduced difference between the ground-state and excited-state dipole moments. The increase of the energy of the charge-transfer band contributes most to the decrease of the first-order hyperpolarizability. The hypsochromic shift and fluorescence quenching are consistent with the exciton theory. The enhanced solvatochromic shift may be due to solvent mediation of electrostatic interactions among the chromophores in **1**.

Experimental Section

General Procedures. All commercially available compounds were used as supplied unless mentioned in the procedures. Tetrahydrofuran, dichloromethane, and diethyl ether were distilled over drying agents under nitrogen before used. UV–vis spectra were recorded on a SHIMADZU 1601 UV spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM 300. Prevalere Life Sciences, Inc. performed all elemental analyses.

Synthesis of 5. To a mixture of 1 g (3.3 mmol) of **4**,[12] 0.2 g (1.0 mmol) of nitrilotriacetic acid, 0.7 g (3.5 mmol) of 1,3-dicyclohexylcarbodiimide (DCC), and 41 mg (0.34 mmol) of 4-(dimethylamino)pyridine (DMAP) were added in 25 mL of dry dichloromethane. The mixture was stirred under N_2 at room temperature for 24 h. The resultant mixture was concentrated and pass through a silica gel column using 10% ethyl acetate in dichloromethane as the eluant to yield 680 mg (62%) of **5**. ^{1}H NMR (CDCl_3): 1.19, (9H, t, $J = 7.1$ Hz), 3.42 (6H, q, $J =$

7.1 Hz), 3.54–3.62 (12 H, m), 4.28 (6H, t, $J = 6.3$ Hz), 6.70 (6H, d, $J = 8.9$ Hz), 6.97 (3H, d, $J = 16.1$ Hz), 7.05 (3H, d, $J = 3.9$ Hz), 7.06 (3H, d, $J = 16.1$ Hz), 7.37 (6H, d, $J = 8.9$ Hz), 7.63 (3H, d, $J = 3.9$ Hz), 9.83 (3H, s). HRMS (ESP) m/e: 1041.3582 (M + H).

Synthesis of 6. To 4.26 g (37.7 mmol) of ethyl cyanoacetate was added 1.6 g (10.9 mmol) of tris(2-aminoethyl)amine. The resultant mixture was added to 10 mL of absolute ethanol. The reaction was stirred at room temperature for 3 days. The white precipitates were collected and washed with ethanol and ether to yield 3.2 g (84.5%) of the product. ^{1}H NMR (acetonitrile-d_3): 2.54, (6H, t, $J = 5.7$ Hz), 3.23 (6H, q, $J = 5.52$ Hz), 3.51 (6H, s), 6.97 (3H, s, br). HRMS (ESP) m/e: 348.1789 (M + H); 370.1610 (M + Na).

Synthesis of 1. Compound **5** (200 mg, 0.19 mmol) and **6** (67.5 mg, 0.19 mmol) was dissolved in 250 mL of dry THF. To the solution was added 1.5 mL of piperidine. The solution was heated at 65–70 °C (oil bath temperature) under N_2 for 8 days. The red precipitates were filtered off. The filtrate was concentrated. The pure product was isolated by preparative TLC using 5% methanol in dichloromethane as the eluant. The yield is 83 mg (32%). ^{1}H NMR (CDCl_3): 1.19 (9H, t, $J = 6.9$ Hz), 2.75 (6H, br), 3.42 (6H, q, $J = 7.0$ Hz), 3.55 (6H, br), 3.62 (6H, t, $J = 6.1$ Hz), 3.69 (6H, s), 4.31 (6H, t, $J = 6.4$ Hz), 6.73 (6H, d, $J = 8.8$ Hz), 6.80 (3H, d, $J = 18.1$ Hz), 6.82(3H, d, $J = 15.8$ Hz), 6.94 (3H, t, $J = 4.3$ Hz), 7.23 (6H, d, 8.8 Hz), 7.49 (3H, d, 4.0 Hz), 8.30 (3 H, s). HRMS (ESP): m/e 1334.5036 (M + H). Anal. Calcd. for $C_{72}H_{75}N_{11}O_9S_3 \cdot CH_2Cl_2$: C, 61.76; H, 5.47; N, 10.85. Found: C, 61.41; H, 5.22; N, 10.71.

Synthesis of 7. To a solution of 0.25 g (0.83 mmol) of **4** and 0.186 g (1.66 mmol) of *N,N*-dimethylcyanoacetamide in 2 mL of dichloromethane was added 7 mL of ethanol and 64 mg (0.83 mmol)of ammonium acetate. The mixture was stirred overnight. A couple of drops of water were added to the mixture, and the solution was concentrated. The residue was purified by silica gel column using a gradient of 10–30% of ethyl acetate in dichloromethane as the eluant. The pure product was obtained as a red crystalline solid. The yield is 230 mg (71%).^{1}H NMR (CDCl_3): 1.22 (3H, t, $J = 7.0$ Hz), 3.17 (6H, br), 3.50 (2H, q, $J = 7.0$ Hz), 3.55 (2H, t, $J = 5.8$ Hz), 3.85 (2H, t, $J = 5.8$ Hz), 6.76 (2H, d, $J = 8.9$ Hz), 7.01 (1H, d, $J = 16.0$ Hz), 7.03 (1H, d, $J = 4.1$ Hz), 7.10 (1H, d, $J = 16.1$ Hz), 7.40 (2H, d, $J = 8.9$ Hz), 7.52 (1H, dd, $J_1 = 4.0$ Hz, $J_2 = 0.55$ Hz), 7.97 (1H, s). HRMS (ESP): m/e 396.1783 (M + H).

Synthesis of 2. Benzoic acid (47 mg, 0.38 mmol) and 100 mg (0.25 mmol) of **7** were dissolved in 1.5 mL of dichloromethane. To the solution was added 78 mg (0.39 mmol) of DCC and 5 mg (0.04 mmol) of DMAP. The solution was stirred at room temperature overnight. The pure product was isolated by silica gel column using 10% ethyl acetate in dichloromethane as the eluant. The yield is 100 mg (65%).^{1}H NMR (CDCl_3): 1.25 (3H, t, $J = 7.0$ Hz), 3.16 (3H, s, br), 3.18 (3H, s, br), 3.53 (2H, q, $J = 7.0$ Hz), 3.76 (2H, t, $J = 6.3$ Hz), 4.52 (2H, t, $J = 6.3$ Hz), 7.02 (1H, d, $J = 15.9$ Hz), 7.03 (1H, d, $J = 4.0$ Hz), 7.11 (1H, d, $J = 16.0$ Hz), 7.42 (2H, d, 8.7 Hz), 7.47 (2H, d, 7.0 Hz), 7.52 (1H, d, 4.0 Hz), 7.59 (1H, tt, $J_1 = 7.4$ Hz, $J_2 = 2.1$ Hz), 7.98 (1H, s), 8.03 (2H, dd, $J_1 = 8.7$ Hz, $J_2 = 1.2$ Hz). HRMS (ESP): m/e 500.2003 (M + H).

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