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# Synthesis and two-photon absorption properties of novel heterocycle-based organic molecules

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Four novel heterocycle-based two-photon absorption chromophores were designed and synthesized. In these molecules, heterocyclic benzothiazole and oxadiazole derivatives are used as acceptors (A), and formyl group is another acceptor (A') applied. These dyes have the structural motif of A- $\pi$ -D- $\pi$ -A or A- $\pi$ -D- $\pi$ -A'. All the chromophores show wide linear optical transparency and strong single-photon and two-photon excited emission. The two-photon absorption cross-sections of molecules with A- $\pi$ -D- $\pi$ -A backbone with two heterocycle-based acceptors are as large as 521 GM and 461 GM at the wavelength of 788 nm in the femtosecond regime. The molecules of A- $\pi$ -D- $\pi$ -A' framework show relatively low two-photon absorbing activities due to the small  $\pi$ -conjugation systems.

## Introduction

Two-photon absorption (TPA) process corresponds to simultaneous absorption of two photons.<sup>1</sup> TPA activity scales quadratically with the intensity of the incident radiation. Many TPA molecules show up-converted emission. In recent years, two-photon technology has been utilized for a myriad of new optical applications such as three-dimensional optical data storage and microscopy,<sup>2–5</sup> two-photon optical power limiting,<sup>6,7</sup> two-photon upconverted lasing<sup>8,9</sup> and photodynamic therapy.<sup>10,11</sup> Most of these applications operate in the near-infrared region, especially at around 800 nm. So the TPA properties near 800 nm are widely studied in the research of TPA materials.

Nowadays, the TPA activities of most dyes available are not large enough for practical applications, and leads to the use of either high laser intensity and/or high fluorophore concentration. To fully exploit the greater potential of TPA process, chromophores with large TPA cross-sections  $\sigma_2$  and good solubility are required. In recent years some papers about the structure-property studies are reported. One efficient structure is to symmetrically substitute  $\pi$ -systems with donors (D) or acceptors (A), and the D- $\pi$ -D structure is more likely to show a large TPA effect.<sup>12–17</sup> Another one is to asymmetrically couple highly coplanar  $\pi$ -centers with D and A.<sup>18–21</sup> Both of these two strategies emphasize D/A strength and the efficiency of the conjugated bridge.

In the vast majority of efficient TPA molecules, simple organic functional groups with different electronic properties, such as OR, NR<sub>2</sub>, NO<sub>2</sub> and CN, serve as D or A. Recently, some heterocycle-based TPA dyes with large TPA cross-section have been reported.<sup>21–25</sup> It was found that  $\pi$ -deficient and  $\pi$ -excessive heterocycles may act as efficient electron

acceptors and donors, respectively. And molecules based on heterocycle(s) often show strong fluorescence emission, which is an important prerequisite for some TPA-based applications such as fluorescence microscopy and upconverted lasing.

Recent work confirmed that quadrupolar molecules may possess a very large TPA cross-section, seemingly correlated with a symmetrical charge transfer between the periphery and the center of the molecule.<sup>12,16,25</sup> And these efficient TPA molecules often possess nice coplanar  $\pi$ -bridges, most of which are so rigid that they reduce the solubility of the dyes.

In this paper, we have synthesized four new TPA dyes. These chromophores have a structure of A- $\pi$ -D- $\pi$ -A or A- $\pi$ -D- $\pi$ -A'. Benzothiazole and 1,3,4-oxadiazole are electron deficient heterocycles and serve as acceptors; another acceptor employed is formyl group. We chose the popular conjugated system 2,5-dialkoxyphenyl as  $\pi$ -center, the two alkoxy groups on the benzene ring would increase the electron density of the center and also promote the solubility of the molecules. The linear optical properties of these four quadrupolar dyes are measured and their TPA activities at 788 nm by a femtosecond laser are also reported in this paper.

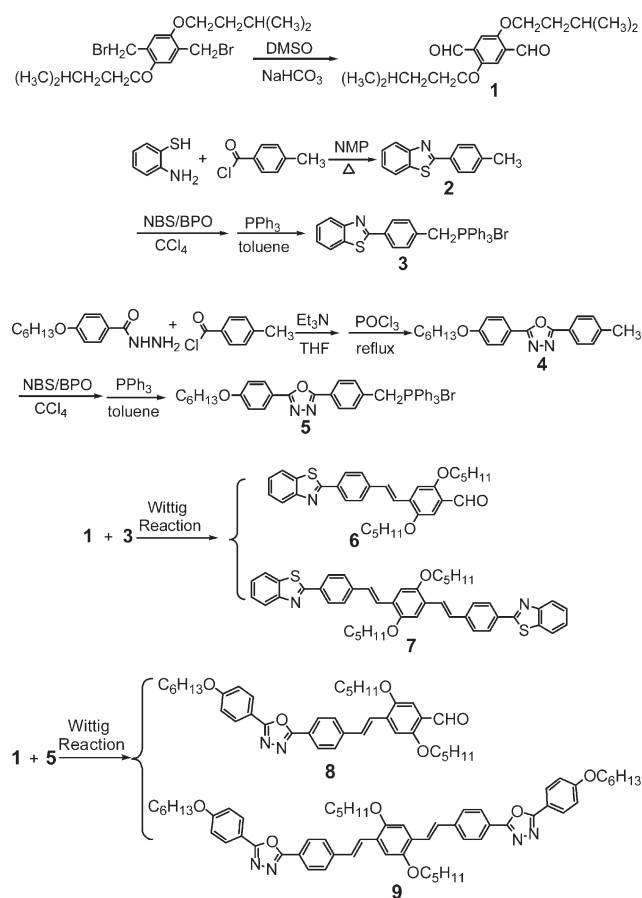
## Results and discussion

### Synthesis

The targeted compounds (**6–9**) were synthesized according to Scheme 1. These chromophores were synthesized by Wittig reaction of 2,5-bis(3'-methylbutyloxy)terephthalaldehyde (**1**) with ylide reagents (**3** or **5**) in low to moderate yields. Aldehyde **1** was prepared as we reported before, directly from 1,4-bis(3'-methylbutyloxy)-2,5-bis(bromomethyl)benzene with dimethyl sulfoxide as oxidant in a yield of 77%.<sup>26</sup> And the intermediates **3** and **5** were synthesized similar to reported in the literature.<sup>21</sup> The final compounds were purified by column chromatography and recrystallization and characterized by <sup>1</sup>H NMR and elemental analysis. The pure chromophores were

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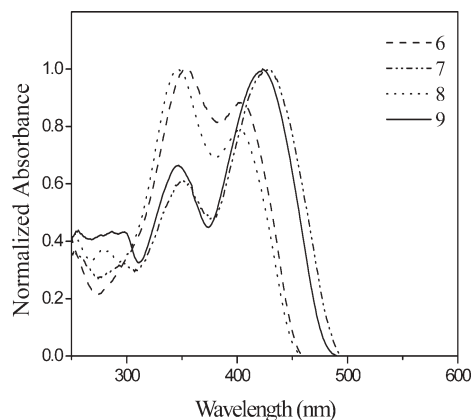


**Scheme 1** The synthetic route to the chromophores **6–9**.

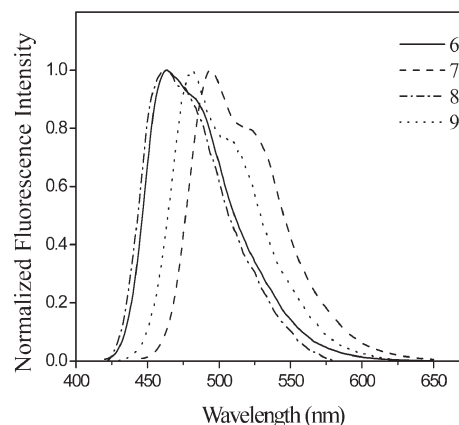
well soluble in organic solvents, such as chloroform, dichloromethane, toluene and tetrahydrofuran.

### Single-photon absorption and emission properties

The single-photon absorption of these compounds was measured in chloroform ( $\sim 10^{-6}$  M) by using a Hitachi U-3010 UV–vis recording spectrophotometer. As shown in Fig. 1, the absorption peaks of the molecules are red-shifted with the extension of the  $\pi$  systems. The absorption maximum of **6** is at 404 nm, and the peak of **7** red shifts to 429 nm. The



**Fig. 1** Normalized linear absorption spectra of compounds **6–9**.



**Fig. 2** Normalized one-photon excited fluorescence spectra for compounds **6–9**.

absorption maximum of **9** is also red-shifted (20 nm) relative to that of **8**. Comparing the single-photon absorption maximum of **7** and **9**, it was red-shifted with increasing electron-withdrawing ability of the acceptors, because a stronger electron acceptor will help to stabilize the charge-separated excited state of the molecule.

One-photon excited fluorescence spectra for these compounds were recorded on a Hitachi F-4500 fluorescence spectrophotometer using dilute solutions ( $10^{-6}$  M in chloroform solutions). All the chromophores have strong one-photon fluorescence. As shown in Fig. 2, the emission peaks of the dyes were red-shifted with the increase of electron-withdrawing ability of the acceptors and the extension of the  $\pi$  systems. The quantum yields of these molecules were measured with reference to quinine sulfate ( $\Phi_f = 54.6\%$  in 1.0 M  $\text{H}_2\text{SO}_4$ ),<sup>27</sup> and listed in Table 1 (31–54%).

### Two-photon excited fluorescence

Two-photon excited fluorescence (TPEF) was collected by an ACTON spectrapro 2500I CCD-array spectrometer. All these chromophores show wide linear optical transparency in the range of 500–900 nm. However, when these dyes in dilute

**Table 1** Linear and nonlinear optical data for dyes **6–9** in chloroform solutions<sup>a</sup>

Dyes	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ( $\epsilon_{\text{max}}/10^4 \text{ M}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{spf}}/\text{nm}$	$\Phi_f^b/\%$	$\lambda_{\text{max}}^{\text{tpf}}/\text{nm}$	$\sigma_2^c/\text{GM}$
6	352 (2.5) 404 (2.2)	463	31	483	$26 \pm 2$
7	351 (3.1) 429 (5.4)	494	54	521	$521 \pm 17$
8	347 (2.3) 403 (1.5)	464	52	484	$13 \pm 1$
9	347 (3.2) 423 (5.2)	482	49	489, 514	$461 \pm 12$

<sup>a</sup>  $\lambda_{\text{max}}^{\text{abs}}$ ,  $\lambda_{\text{max}}^{\text{spf}}$ ,  $\lambda_{\text{max}}^{\text{tpf}}$ : peak wavelengths in the linear absorption, one-photon excited fluorescence and two-photon excited fluorescence spectra. <sup>b</sup> Quinine sulfate was used as reference ( $\Phi_f = 54.6\%$  in 1.0 M  $\text{H}_2\text{SO}_4$ ). <sup>c</sup> TPA cross-section values given in GM at 788 nm, Fluorescein was used as the reference ( $\sigma_2$  is assumed to be 37 GM in 0.1 M NaOH at 788 nm); 1 GM (Göppert-Mayer) =  $10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ .

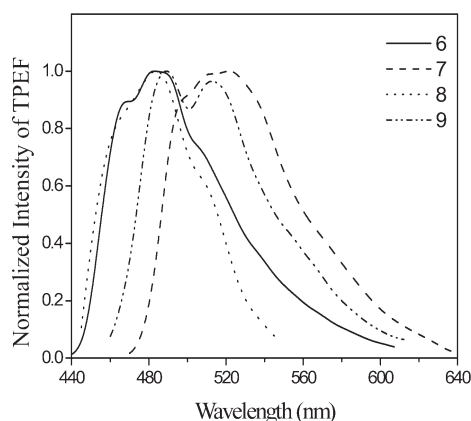


Fig. 3 Normalized TPEF spectra for compounds 6–9.

chloroform solutions ( $10^{-4}$  M) were excited by a mode-locked femtosecond laser at the wavelength of 788 nm, moderate blue upconverted fluorescence from **6** and **8** and strong green upconverted fluorescence from **7** and **9** could be seen and detected (Fig. 3).

The dependence of the TPEF intensity on the excitation intensity of these molecules was also examined. As an example, Fig. 4 shows the dependence of the intensity of up-converted emission on the incident intensity for dye **7**. The slope is nearly 2; in other words the emission intensity depends on the perfect quadratic of the laser power. This result indicates that the up-converted fluorescence observed is induced by a two-photon excitation process.

#### TPA cross-sections at 788 nm

The TPA cross-sections  $\sigma_2$  of the compounds were determined by using the two-photon-induced fluorescence measurement technique<sup>28</sup> with the following equation,<sup>29</sup>

$$\sigma_{2s} = \sigma_{2r} (F_s/F_r)(\Phi_r/\Phi_s)(c_r/c_s)(n_r/n_s) \quad (1)$$

where the subscripts “s” and “r” stand for the sample and reference molecules respectively.  $F$  is the integrated fluorescence intensity measured at the same power of the excitation beam and  $\Phi$  is the fluorescence quantum yield. The number density of the molecules in the solution was denoted as  $c$ , the refractive index of the solution is  $n$  and  $\sigma_{2r}$  is the TPA

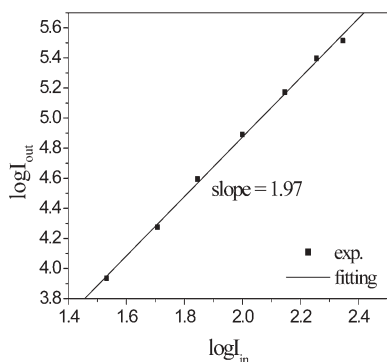


Fig. 4 The intensity of up-converted emission vs. the intensity of two-photon excitation at 788 nm for dye **7**.

cross-section of the reference molecule. In this experiment, Fluorescein was selected as reference molecule ( $10^{-5}$  M in 0.1 M NaOH) and its  $\sigma_2$  was assumed to be 37 GM at the wavelength of 788 nm, which was taken from the literature.<sup>29</sup>

The experimental set-up for the TPA cross-sections  $\sigma_2$  measurements was similar to that described by Rentzepis *et al.*<sup>28</sup> The laser system (Mira 900) emitted 150 fs, 788 nm pulses at 76 MHz repetition rate. And the intensity of the incident beam was monitored by the detector of a power meter (Coherent, FieldMaster gs). The beam was focused on the sample by a lens. And the up-converted fluorescence was collected at a direction perpendicular to the pump beam by a CCD detector (ACTON, Spectrapro 2500I). The spectrum was integrated over the entire emission range to obtain the total integrated fluorescence for the particular pump wavelength.

The molecules studied showed no linear absorption at the wavelength of two-photon excitation (788 nm). And the quadratic dependence of TPEF intensities of all the chromophores on the incident (excitation) laser power confirmed that the signal collected was indeed a result of a two-photon process. The  $\sigma_2$  values measured are listed in Table 1. The quadrupolar molecules **7** and **9** have a structure of A– $\pi$ –D– $\pi$ –A, and although the acceptors are not very strong, both dyes exhibit high TPA. Their  $\sigma_2$  values are comparable to that of some highly active TPA chromophores, which possess a comparably large  $\pi$ -system with D– $\pi$ –A– $\pi$ –D backbone.<sup>17</sup> The two alkoxyl groups substituted on the core and phenyl ring increase the electron density of the bridge, which benefits the intramolecular charge transfer between the core and the two end groups. The highly coplanar bridge of the molecules **7** and **9** is also helpful to the intramolecular charge transfer. These two modulations of the structure are important factors to the large  $\sigma_2$  values of **7** and **9**. Comparing to the  $\sigma_2$  values of **6** and **8**, the  $\sigma_2$  values of **7** and **9** are more than one order of magnitude larger, which is mainly ascribed to the expanding  $\pi$  system, this result reconfirms that, to some extent, the increase of conjugation length is an efficient way to obtain large TPA  $\sigma_2$ . As explained by Perry *et al.*,<sup>13</sup> the prolongation of conjugation length will mainly lead to an increase in the transition dipole moment ( $M_{ge}$ ) between the ground state ( $1A_g$ ) and the one-photon allowed excited state ( $1B_u$ ). The  $\sigma_2$  value is linearly dependent on the imaginary part of the second-order hyperpolarizability ( $\text{Im}\langle\gamma\rangle$ ). And  $\text{Im}\langle\gamma\rangle$  increases steadily with the square value of  $M_{ge}$ . So we can expect an increase of  $\sigma_2$  value when the  $\pi$  system is expanded.

Compounds **7** and **9**, **6** and **8** have nearly the same  $\pi$ -conjugation length but differ in the terminal groups. As shown in Table 1, the linear absorption maximum is red-shifted with the enhancement of the electron-withdrawing ability of the acceptors. Their  $\sigma_2$  values are also promoted in the same order. The  $\sigma_2$  value of chromophore **7** is 521 GM, which is larger than that of **9** (461 GM). And the  $\sigma_2$  value of **6** is 26 GM, which is the twice the magnitude of that of the dye **8** (13 GM). These were similar to the order in the literature.<sup>12</sup>

Finally, one of the promising applications of TPA materials is two-photon induced fluorescent microscopy. For this kind of application, large  $\sigma_2$  and proper fluorescent properties, such as high fluorescence quantum yield and the emissive wavelength, are desirable. Molecules **6–9** are highly emissive upon

excitation. And molecule **6** and **8** give off blue emission which is attractive because blue emission is relatively lacking. Molecule **7** and **9** give off green emission and exhibit large  $\sigma_2$ . Therefore, they may have potential application in two-photon induced fluorescent microscopy.

## Conclusions

We have reported the design and synthesis of four novel heterocycle-based TPA chromophores. These molecules have a structure of A- $\pi$ -D- $\pi$ -A or A- $\pi$ -D- $\pi$ -A'. In these molecules, heterocycles benzothiazole and oxadiazole derivatives and formyl groups are used as acceptors. By having symmetrically terminated two heterocycle groups on the coplanar  $\pi$  system, large TPA  $\sigma_2$  values can be obtained. The large TPA  $\sigma_2$  values measured by a femtosecond laser indicate that these two heterocycles are efficient acceptors for A- $\pi$ -D- $\pi$ -A structure. Molecules **6** and **7**, with strong acceptors, show larger TPA  $\sigma_2$  values than their analogues **8** and **9**, with weak acceptors. And increasing the  $\pi$ -conjugation length can promote the TPA  $\sigma_2$  values greatly. All the chromophores show wide linear optical transparency and strong single-photon emission. And their intense up-converted fluorescence induced by two-photon excitation can be seen and detected.

## Experimental

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Varian Mercury VX300 FT-NMR spectrometer (Varian, USA) operating at 298 K. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane (TMS). Elemental analysis was performed by a Calo-Erba elemental analyser (Model 1106). Column chromatography was carried out on silica gel zcx-II(200–300 mesh). All chemicals are commercially available and were used as received unless stated otherwise. The intermediates **1–5** were synthesized as reported.<sup>21,26,30</sup> The four chromophores were prepared by Wittig reaction and the procedures were presented as the following:

### General synthetic procedure for Wittig reaction

2,5-Bis(3'-methylbutyloxy)terephthalaldehyde (1 equivalent), the triphenylphosphonium salt (1.2 to 2.5 equivalent) and catalyst 18-crown-6 were dissolved in anhydrous dichloromethane (40 mL), and then *t*-BuOK power (1.8 to 3.8 equivalent) was added in portions under nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight. Then the mixture was poured into water (20 mL), extracted with chloroform (30 mL  $\times$  3), dried with sodium sulfate, and concentrated. Purification was performed by column chromatography (eluent:  $\text{CH}_2\text{Cl}_2$ -petroleum ether 5 : 1 in volume for **6** and **7**, chloroform for **8** and **9**). Further purification by recrystallization in ethanol-chloroform gave pure products in moderate yields.

### 4-(2-(4-(Benzothiazol-2-yl)-phenyl)-vinyl)-2,5-bis(3'-methylbutyloxy)benzaldehyde (**6**)

Pale yellow plate, 58% yield.  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.01 (d, 12H,  $\text{CH}_3$ ), 1.76–1.94 (m, 6H, CH &  $\text{CH}_2$ ), 4.08 (t, 2H,

$\text{OCH}_2$ ), 4.15 (t, 2H,  $\text{OCH}_2$ ), 7.20 (s, 1H, ArH), 7.26–7.42 (m, 3H, ArH), 7.49 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.58 (d,  $J$  = 16.5 Hz, 1H, CH=CH), 7.66 (d,  $J$  = 8.1 Hz, 2H, ArH), 7.92 (d,  $J$  = 7.8 Hz, 1H, ArH), 8.06–8.13 (t, 3H, ArH), 10.45 (s, 1H, CHO). Calcd. for  $\text{C}_{32}\text{H}_{35}\text{NO}_3\text{S}$ : C 74.82, H 6.87, N 2.73; Found: C 74.56, H 6.77, N 2.28.

### 2-(4-(4-(Benzothiazol-2-yl)-styryl)-2,5-bis(3'-methylbutyloxy)-styryl)-phenyl)benzothiazole (**7**)

Bright yellow solid, 31% yield.  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.05 (d, 12H,  $\text{CH}_3$ ), 1.79–1.85 (m, 4H,  $\text{CH}_2$ ), 1.95–2.00 (m, 2H, CH), 4.13 (t, 4H,  $\text{OCH}_2$ ), 7.17 (s, 2H, ArH), 7.21 (d,  $J$  = 16.5 Hz, 2H, CH=CH), 7.40 (t,  $J$  = 7.8 Hz, 2H, ArH), 7.51 (t,  $J$  = 7.8 Hz, 2H, ArH), 7.61 (d,  $J$  = 16.5 Hz, 2H, CH=CH), 7.65 (d,  $J$  = 8.4 Hz, 4H, ArH), 7.92 (d,  $J$  = 7.8 Hz, 2H, ArH), 8.07–8.12 (t, 6H, ArH). Calcd. for  $\text{C}_{46}\text{H}_{44}\text{N}_2\text{O}_2\text{S}_2$ : C 76.63, H 6.15, N 3.89; Found: C 76.90, H 5.78, N 4.01.

### 4-(4-(5-(4-(Hexyloxy)-phenyl)-1,3,4-oxadiazol-2-yl)-styryl)-2,5-bis(3'-methylbutyloxy)-benzaldehyde (**8**)

Pale yellow plate, 46% yield.  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.92 (t, 3H,  $\text{CH}_3$ ), 1.01 (d, 12H,  $\text{CH}_3$ ), 1.36–1.49 (m, 6H,  $\text{CH}_2$ ), 1.78–1.90 (m, 8H, CH &  $\text{CH}_2$ ), 4.07 (quintet, 4H,  $\text{OCH}_2$ ), 4.16 (t, 2H,  $\text{OCH}_2$ ), 7.03 (d,  $J$  = 9 Hz, 2H, ArH), 7.21 (s, 1H, ArH), 7.29 (d,  $J$  = 15.9 Hz, 1H, CH=CH), 7.35 (s, 1H, ArH), 7.59 (d,  $J$  = 15.9 Hz, 1H, CH=CH), 7.69 (d,  $J$  = 8.1 Hz, 2H, ArH), 8.08 (d,  $J$  = 9 Hz, 2H, ArH), 8.14 (d,  $J$  = 8.1 Hz, 2H, ArH), 10.45 (s, 1H, CHO). Calcd. for  $\text{C}_{39}\text{H}_{48}\text{N}_2\text{O}_5$ : C 74.97, H 7.74, N 4.48; Found: C 74.85, H 7.27, N 4.81.

### 2-(4-(4-(5-(4-(Hexyloxy)phenyl)-1,3,4-oxadiazol-2-yl)styryl)-2,5-bis(3'-methylbutyloxy)styryl)phenyl)-5-(4-(hexyloxy)-phenyl)-1,3,4-oxadiazole (**9**)

Bright yellow solid, 28% yield.  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.92 (t, 6H,  $\text{CH}_3$ ), 1.05 (d, 12H,  $\text{CH}_3$ ), 1.36–1.50 (m, 12H,  $\text{CH}_2$ ), 1.81–2.02 (m, 10H, CH &  $\text{CH}_2$ ), 4.05 (t, 4H,  $\text{OCH}_2$ ), 4.13 (t, 4H,  $\text{OCH}_2$ ), 7.03 (d,  $J$  = 9 Hz, 4H, ArH), 7.17 (s, 2H, ArH), 7.21 (d,  $J$  = 15.5 Hz, 2H, CH=CH), 7.61 (d,  $J$  = 15.5 Hz, 2H, CH=CH), 7.68 (d,  $J$  = 8.4 Hz, 4H, ArH), 8.08 (d,  $J$  = 9 Hz, 4H, ArH), 8.13 (d,  $J$  = 8.4 Hz, 4H, ArH). Calcd. for  $\text{C}_{60}\text{H}_{70}\text{N}_4\text{O}_6$ : C 76.40, H 7.48, N 5.94; Found: C 76.11, H 7.03, N 5.74.

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