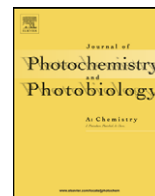




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Research paper

## 3,4-Ethylenedioxythiophene (EDOT)-based $\pi$ -conjugated oligomers: Facile synthesis and excited-state properties

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## ABSTRACT

A facile synthetic method to produce soluble 3,4-ethylenedioxythiophene (EDOT) oligomers was developed by using iron (III) nitrate nonahydrate as the oxidizing reagent. Two EDOT oligomers, i.e. octomers and octodecamers were obtained as the major products. Their UV–vis absorption, fluorescence at room temperature and 77 K, and triplet transient difference absorption have been measured in CH<sub>2</sub>Cl<sub>2</sub> solutions or glassy solutions. With increased conjugation length from EDOT octomers (A) to EDOT octodecamers (B), the UV–vis absorption, fluorescence and the triplet transient difference absorption band shift to longer wavelength. Both the oligomers also exhibit reasonably high efficiency to generate singlet oxygen.

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## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted significant attention due to its high conductivity, low oxidation potential, moderate band gap, high transparency and good environmental stability in the oxidized state [1–3]. In general, two well-established methods have been used to synthesize PEDOT. Chemical oxidative polymerization of 3,4-ethylenedioxythiophene uses oxidizing agents such as FeCl<sub>3</sub>, Fe(tosylate)<sub>3</sub> to form a black insoluble oxidized polymer [4,5]; while the electrochemical polymerization approach utilizes electrochemical oxidation of the EDOT monomer to form sky-blue thin film at the anodes [2,6–8]. Additionally, Yamamoto and Ablá [9] have synthesized undoped PEDOT based on a transition metal mediated coupling reaction of dihalogenated aromatic compounds.

On the other hand, EDOT  $\pi$ -conjugated oligomers have demonstrated potential applications in organic field effect transistors (OFET) [10], organic light emitting diodes (OLED) [11] and photovoltaic cells [12]. Extensive effort has been devoted to synthesizing EDOT oligomers with controlled molecular weight. However, compared with the synthesis of the PEDOT derivatives, producing EDOT oligomers is more difficult due to the high reactivity of

the terminal  $\alpha$ -position of the EDOT monomer [3]. Akoudad and Roncali [13] first synthesized an unstable EDOT dimer, 2,2'-bis(3,4-ethylenedioxythiophene) (*bis*-EDOT) by oxidative coupling of 2-lithio-ethylenedioxythiophene with CuCl<sub>2</sub>. Then an unstable EDOT trimer, 2,2':5'2''-*ter*(3,4-ethylenedioxy)thiophene (*ter*-EDOT) was prepared in Reynolds's group through a NiCl<sub>2</sub> catalyzed Grignard reaction [14]. Other more stable EDOT-based oligomers, EDOT oligomers end-capped with mesitylthio [15], phenyl [16], hexyl [17] chain, and trimethylsilyl [18] also have been reported. For example, Roncali and coworkers [17] prepared a series of stable and soluble EDOT oligomers end-capped with *n*-hexyl chains with four EDOT units. Janssen and coworkers [18] reported the synthesis and high resolution electronic spectra of trimethylsilyl end-capped EDOT oligomers with up to 5 repeat units. In addition, several EDOT-based hybrid co-oligomers have been successfully synthesized [19–23].

Despite the progress of current synthetic approaches, the synthesis and purification of EDOT oligomers still remain challenging. For example, the maximum chain length of EDOT-based oligomers has still been limited to 5 repeat units [18]. In this work, we developed a facile chemical oxidative polymerization route to synthesize EDOT-based oligomers under ambient condition. Instead of using traditional oxidant such as FeCl<sub>3</sub>, the reaction was carried out using iron (III) nitrate nonahydrate as the oxidizing agent in a 2:1 dichloromethane/methanol solution. In this reaction, the less reactive iron (III) nitrate resulted in a reduced reaction rate, allowing for the control of the molecular weight of the products. Additionally, the mixed solvent provided a selective solubility of the products with different molecular weight, facilitating the purification of the

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**Table 1**  
Photophysical data of EDOT oligomers **A** (octomer) and **B** (octodecamer) in CH<sub>2</sub>Cl<sub>2</sub>.

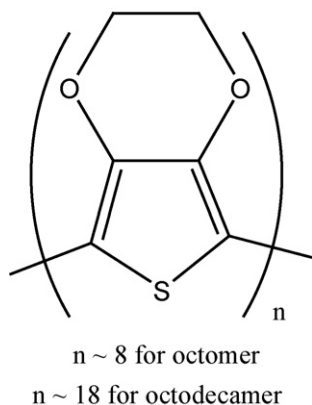
$\lambda_{\max}^{\text{abs}}/\text{nm}^{\text{a}}$ 293 K	$\lambda_{\max}^{\text{abs}}/\text{nm}^{\text{a}}$ 77 K	$\lambda_{\max}^{\text{fluo}}/\text{nm}$ ( $\tau_{\text{S1}}/\text{ps}$ ; $\Phi_{\text{T}}$ ) <sup>b</sup> 293 K	$\lambda_{\max}^{\text{fluo}}/\text{nm}^{\text{b}}$ 77 K	$\lambda_{\max}^{\text{T1-Tn}}/\text{nm}$ ( $\epsilon_{\text{T}}/\text{M}^{-1}\text{cm}^{-1}$ ; $\tau_{\text{T}}/\mu\text{s}$ ) <sup>c</sup>	$\Phi_{\Delta}^{\text{d}}$ 293 K
<b>A</b>					
443, 463	425, 453, 489	507 (255; 0.22)	507, 536	545 (5780; 15.6)	0.35
<b>B</b>					
500, 532	472, 512, 553	583 (800; 0.22)	566, 613	570 (4940; 12.8)	0.62

<sup>a</sup> UV–vis absorption band maxima.

<sup>b</sup> Fluorescence band maximum, lifetime, and quantum yield.

<sup>c</sup> Triplet transient difference absorption band maximum, triplet excited-state extinction coefficient and lifetime.

<sup>d</sup> Quantum yield of singlet oxygen generation.



**Fig. 1.** Chemical structure of EDOT-based octomer and octodecamer.

products. Two different EDOT oligomers with a repeating unit of 8 (octomer) and 18 (octodecamer) were obtained as the major products from this reaction (Fig. 1). We believe that such approach can produce a series of EDOT oligomers with controlled molecular weight. The photophysical properties, such as emission spectrum and quantum yield, triplet transient difference absorption spectrum, triplet excited-state absorption coefficients and lifetimes, and the quantum yield of singlet oxygen generation of these two oligomers have been investigated (Table 1).

## 2. Experimental

### 2.1. Synthesis

3,4-Ethylenedioxythiophene (EDOT) and iron (III) nitrate nonahydrate were purchased from Sigma–Aldrich and used without further purification. All solvents were obtained from Alfa Aesar and used as is unless otherwise noted.

Typically, 3,4-ethylenedioxythiophene (EDOT) (300  $\mu\text{L}$ , 2.82 mmol) and iron (III) nitrate nonahydrate (1.25 g, 3.15 mmol) were mixed together in 12 mL of dichloromethane and 6 mL of methanol. The color of the mixture became dark red slowly after 2 h of reaction and a small amount of precipitates appeared in the reaction mixture. The mixture was continuously stirred at room temperature for 20 h. At the end of the reaction, the mixture was centrifuged at 7000 rpm for 10 min to separate the precipitates from the solution. The precipitates were washed with methanol and acetone for 3 times with sonication followed by centrifugation. The product collected was EDOT octodecamer. For the filtrate, excess amount of ammonia was added to remove the extra iron salt. The organic phase was then collected and washed twice with water. The organic phase was dried over MgSO<sub>4</sub> and the residue obtained after solvent evaporation was separated using a short silica gel (pore size 60 Å, particle size 40–75  $\mu\text{m}$ ) column and CH<sub>2</sub>Cl<sub>2</sub> as the eluent. Although EDOT oligomers with different molecular weights can be isolated using silica gel column, octomer (the first

band eluted) was collected as the major product. The solvent was removed by N<sub>2</sub> purging. The yield of octomer and octodecamer was 8% and 11%, respectively. <sup>1</sup>H NMR was recorded on a Varian 300 MHz NMR spectrometer. Infrared spectra were obtained from a PerkinElmer 100 FT-IR spectrometer. The molecular weight of the oligomers was deduced from their *m/z* (exact mass/the charge of ionized species) data acquired from a matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF, Bruker Microflex) using 2,5-dihydroxybenzoic acid as the matrix.

### 2.2. Photophysical measurement

The UV–vis absorption spectra were measured using an Agilent 8453 spectrophotometer in a 1-cm quartz cuvette in CH<sub>2</sub>Cl<sub>2</sub> solutions. The steady state fluorescence spectra and the quantum yields of fluorescence were measured on a SPEX fluorolog-3 fluorimeter/phosphorimeter in CH<sub>2</sub>Cl<sub>2</sub> solutions. The triplet transient difference absorption spectra and the triplet excited-state lifetimes were obtained in CH<sub>2</sub>Cl<sub>2</sub> solutions on an Edinburgh LP920 laser flash photolysis spectrometer. The third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulse width ~4.1 ns, repetition rate 1 Hz) was used as the excitation source. Each sample was purged with argon for 30 min before measurement.

The fluorescence quantum yields were measured by the comparative method [24], in which rhodamine 6G in ethanol ( $\Phi_{\text{T}}=0.94$ ) [25] was used as the reference. The excitation wavelength was 472 nm for both oligomers.

The triplet excited-state molar extinction coefficients were determined by the singlet depletion method [26]. The following equation was used to calculate the  $\epsilon_{\text{T}}$  [26].

$$\epsilon_{\text{T}} = \frac{\epsilon_{\text{S}} \times \Delta OD_{\text{T}}}{\Delta OD_{\text{S}}} \quad (1)$$

where  $\Delta OD_{\text{S}}$  and  $\Delta OD_{\text{T}}$  are the optical density changes of the ground state and the triplet excited state after excitation, which correspond to the optical density of the bleaching band maximum and the positive band maximum at the triplet difference transient absorption spectra, respectively.  $\epsilon_{\text{S}}$  is the ground-state extinction coefficient.

The quantum yield of singlet oxygen generation ( $\Phi_{\Delta}$ ) was determined by measuring the emission of <sup>1</sup>O<sub>2</sub> in air-saturated dichloromethane solution using an EI-P ultrafast and ultrasensitive germanium detector. A silicon cut-off filter (>1100 nm) was used to reduce the scattered light from the YAG laser. The  $\Phi_{\Delta}$  value was calculated by comparing the singlet oxygen quantum yield of a reference sample (1H-phenalen-1-one, *i.e.* perinaphthenone,  $\Phi_{\Delta}=0.93$  in benzene) [27] and that of the EDOT oligomers according to

$$\Phi_{\Delta}^{\text{S}} = \Phi_{\Delta}^{\text{REF}} \times \frac{G_{\Delta}^{\text{S}}}{G_{\Delta}^{\text{REF}}} \times \frac{A_{\text{REF}}}{A_{\text{S}}} \times \left( \frac{n_{\text{S}}}{n_{\text{REF}}} \right)^2 \quad (2)$$

where  $G_{\Delta}$  is the integrated emission intensity,  $\Phi_{\Delta}^{\text{REF}}$  and  $\Phi_{\Delta}^{\text{S}}$  are the singlet oxygen quantum yields of the reference and the sample,

respectively.  $A_{REF}$  and  $A_S$  are the absorbances of the reference and the sample at 355 nm, respectively.  $n$  is the refractive index of the solvent.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of EDOT oligomers

Kirchmeyer and Reuter [28] studied the polymerization mechanism of EDOT using iron (III) tosylate. The overall reaction of EDOT is the oxidative polymerization that starts with the slowest, rate determining step, e.g. the oxidation of EDOT to radical cations, followed by a fast dimerization of the free radicals. The resultant dimers combine two radical cationic end groups, and generate higher oligomers with a high rate constant. Such reaction can be catalyzed by protic acid and a variety of Lewis acids (i.e.  $\text{FeCl}_3$ ). The high rate constant of dimerization and polymerization leads to products with uncontrolled molecular weight. Therefore, low molecular weight EDOT oligomers with different end-capped group are usually obtained by a time-consuming stepwise synthetic method with low yields [13–23]. In order to control the oxidative polymerization of EDOT, we rationalized that chloride should be replaced by another anion since the anion can affect the hydrolysis equilibrium of Fe (III) compounds, which determines their reactivity. Iron (III) nitrate has been investigated in the polymerization of pyrrole, and been demonstrated to have lower reactivity [29]. Nitrate has lower complexation ability than chloride, making iron (III) nitrate a weaker Lewis acid. We anticipated that the polymerization rate of EDOT would be decreased if iron (III) nitrate is used as an oxidant. Indeed, when we used iron (III) nitrates nonahydrate as an oxidant, the oxidative reaction took place at a much lower rate. The color of the mixture became dark red slowly after 2 h of reaction, and a small amount of precipitates appeared in the reaction mixture. In contrast, when iron (III) chloride was used as the oxidant, black precipitates were observed within an hour. In our studies, when the molecular weight of EDOT oligomer increased, its solubility decreased and finally precipitated out from the solution to prevent further oxidative polymerization. Two major EDOT oligomers were obtained from the solution and the precipitate, respectively. Both oligomers exhibited good solubility in organic solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , THF, and DMF. A MALDI-TOF mass spectrometer was used to obtain the molecular weight of two oligomers. The measured  $m/z$  (exact mass/the charge of ionized species) data indicated that the oligomer from the solution had a molecular weight around 1000 with about 8 repeat units (octomer), while the oligomer from the precipitate had a molecular weight around 2500 with about 18 repeat units (octodecamer).  $^1\text{H}$  NMR spectra of EDOT octomer was obtained using deuterated  $N,N$ -dimethylformamide ( $\text{DMF-}d_7$ ) as the solvent. A peak at  $\delta 3.5$  ppm is attributed to the  $\text{O-CH}_2$  protons in EDOT unit, and the small peak at about  $\delta 5.8$  ppm can be assigned to the protons on the terminal thiophene group.

The FT-IR spectra of the synthesized EDOT oligomers are shown in Fig. 2. The vibration peaks at 1530 and  $1481\text{ cm}^{-1}$  for EDOT octomer, and 1567 and  $1489\text{ cm}^{-1}$  for octodecamer originate from the  $\text{C=C}$  asymmetric and symmetric stretching vibration in the thiophene ring, respectively [30,31]. The vibration peaks at 1306 and  $1376\text{ cm}^{-1}$  for octomer, and 1310 and  $1370\text{ cm}^{-1}$  for octodecamer are assigned to  $\text{C-C}$  stretching in the thiophene ring. The  $\text{C-S}$  stretching vibration can be observed at 947 and  $977\text{ cm}^{-1}$  for octomer, and  $954\text{ cm}^{-1}$  for octodecamer [30]. The peaks at  $1102\text{ cm}^{-1}$  (octomer) and  $1047\text{ cm}^{-1}$  (octodecamer) arise from the  $\text{C-O}$  stretching in the  $-\text{OCH}_2\text{CH}_2-$  group [32]. In addition, the elemental analysis results revealed that the ratio of  $\text{C:S:O}$  is 6:1:2. All the aforementioned characterizations confirm the structures of the oligomers.

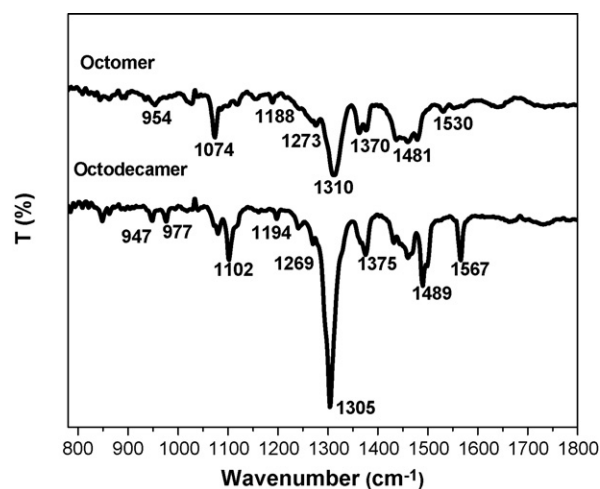


Fig. 2. FT-IR spectra of EDOT octomer and octodecamer.

#### 3.2. UV-vis absorption and fluorescence

As shown in Fig. 3, the UV-vis absorption spectra of the EDOT oligomers have one prominent band in the visible region that can be attributed to the  $^1\pi,\pi^*$  transition. The absorption band maximum red-shifts from 460 nm for octomer to 530 nm for octodecamer, which is a result of the decreased HOMO-LUMO band gap when the conjugation length of the oligomer increases. However, the extinction coefficient does not change significantly when the conjugation length of the oligomer increases. In contrast to the thiophene oligomers with 1–7 repeat units that devoid of vibronic structures [33], the  $^1\pi,\pi^*$  transition band of oligomers exhibit somewhat vibronic structures with a progression space of  $1073\text{ cm}^{-1}$  for octomer and  $1283\text{ cm}^{-1}$  for octodecamer, which are characteristics of the aromatic vibrational mode of thiophene ring. This feature is consistent with the results reported by Janssen and coworkers [18] for trimethylsilyl end-capped EDOT oligomers with 1–5 repeat units, in which it is assumed that the attractive interactions between S and O can stabilize the *trans*-conformation between the adjacent thiophene rings, resulting in a more planar and rigid structure. This structural feature consequently reduces the inhomogeneous broadening due to the inter-ring rotation that is commonly observed in oligothiophene without the ethylenedioxy bridge. As a result, the vibronic structure is observed in the EDOT oligomers.

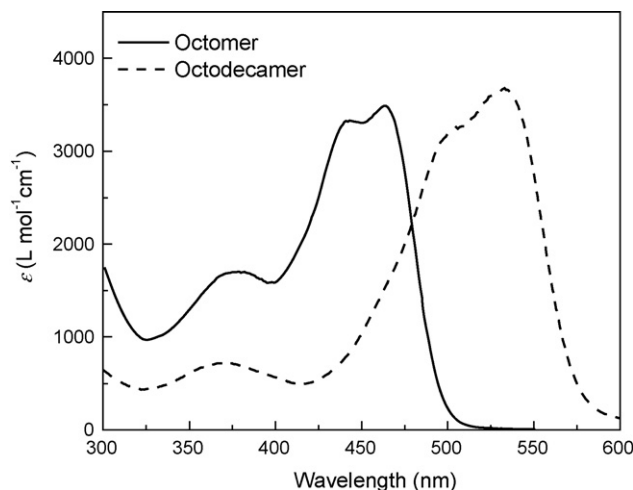
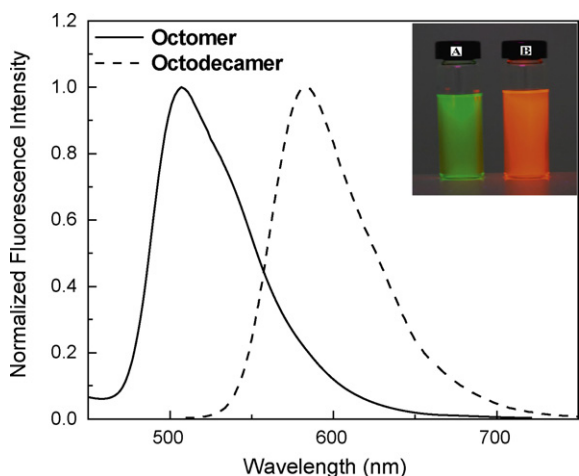


Fig. 3. UV-vis absorption spectra for EDOT octomer and octodecamer in dichloromethane.



**Fig. 4.** Normalized fluorescence spectra of EDOT octamer (A) and octodecamer (B) in  $\text{CH}_2\text{Cl}_2$  at room temperature.

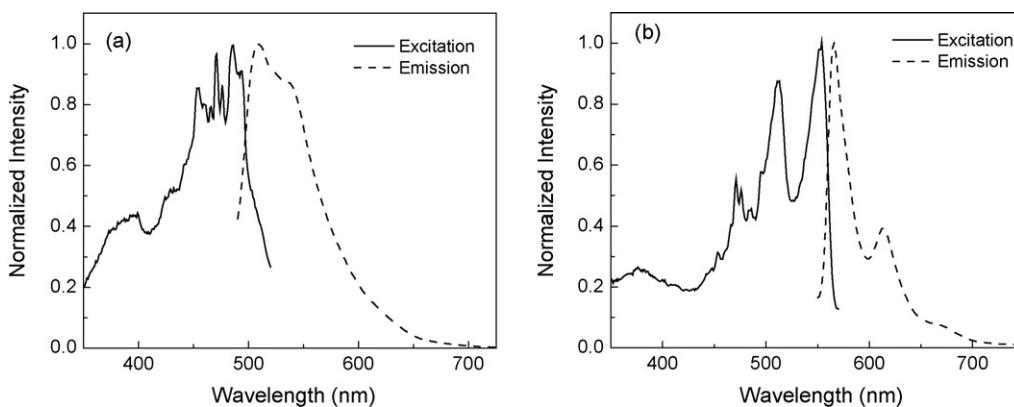
When excited at their absorption band maxima, both EDOT oligomers exhibit fluorescence at room temperature (Fig. 4) and 77 K (Fig. 5). At room temperature, octamer shows an emission peak at 510 nm with a green color and octodecamer shows an emission peak at 580 nm corresponding to an orange color. In contrast to the absorption spectra, the room temperature fluorescence spectra are structureless. The fluorescence spectra are independent of the excitation wavelength, indicating a single emitting state. The fluorescence quantum yields of both octamer and octodecamer are similar ( $\Phi_f=0.22$ ) when excited at 472 nm, but the singlet

excited-state lifetime increases from 255 ps for octamer to 800 ps for octodecamer. The latter is consistent with the trend reported by Janssen and coworkers [18] for trimethylsilyl end-capped EDOT oligomers with 1–5 repeat units.

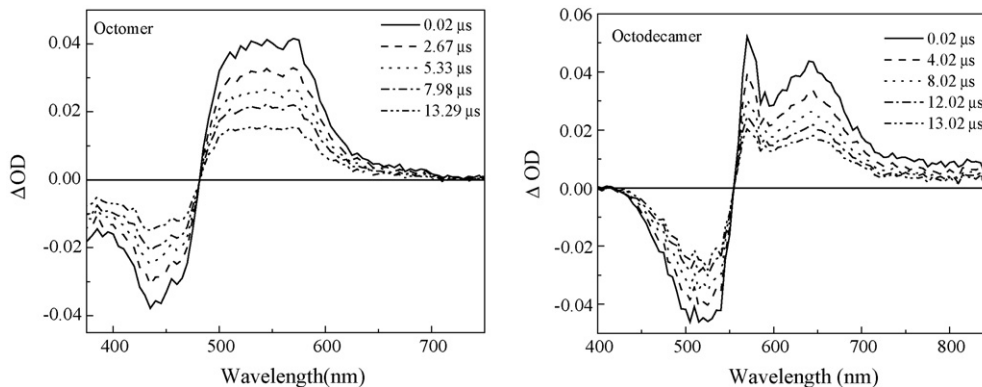
Fig. 5 displays the fluorescence spectra and excitation spectra of EDOT octamer and octodecamer at 77 K. In comparison to the absorption spectra at room temperature as shown in Fig. 3, the excitation spectra at 77 K shift to a longer wavelength with a well resolved vibronic structure. The vibronic progression spacing of octamer is approximately  $1625$  and  $1450\text{ cm}^{-1}$  between (0,0) and (0,1), and (0,1) and (0,2) vibronic states, respectively, while for octodecamer is  $1655$  and  $1450\text{ cm}^{-1}$ . The fluorescence spectra at 77 K also exhibit a clear vibronic structure compared to those at room temperature, with a vibronic progression spacing of  $1070\text{ cm}^{-1}$  for octamer and  $1355\text{ cm}^{-1}$  for octodecamer. These values correspond well to those observed from the absorption spectra at room temperature. The observation of the vibronic structure of the emission at 77 K is in line with what was observed from trimethylsilyl end-capped EDOT oligomers with 1–5 repeat units [18] and the vibronic spacing corresponds to the C–C or C–O bond stretch vibrations.

### 3.3. Triplet excited-state absorption

The triplet transient difference absorption spectra of both octamer and octodecamer were measured in degassed  $\text{CH}_2\text{Cl}_2$  solutions and are presented in Fig. 6. Following laser excitation at 355 nm, a bleaching band at ca. 440 nm for octamer and 530 nm for octodecamer and the formation of a new band at ca. 545 nm for octamer and two bands at ca. 572 nm and 643 nm for octodecamer were observed. The wavelength of the bleaching band is



**Fig. 5.** Normalized fluorescence and excitation spectra of EDOT octamer (a) and octodecamer (b) in glassy  $\text{CH}_2\text{Cl}_2$  solutions at 77 K.



**Fig. 6.** Time-resolved triplet–triplet transient difference absorption spectra of octamer and octodecamer in a 1-cm cell. The concentration used is  $3.1 \times 10^{-5}$  mol/L for octamer and  $3.0 \times 10^{-5}$  mol/L for octodecamer.

consistent with the  $\pi, \pi^*$  transition band at the UV–vis absorption spectra, indicating that the transient absorption could possibly arise from the triplet  $\pi, \pi^*$  excited state. Similar to the UV–vis absorption spectra and emission spectra shown before, the increase of the conjugation length in octodecamer causes a significant red-shift of the transient absorption band.

According to the singlet depletion method [26], the triplet difference extinction coefficients ( $\Delta\epsilon_T$ ) were measured to be 5780 L mol<sup>-1</sup> cm<sup>-1</sup> for octomer at the absorption band of 545 nm, and 4940 L mol<sup>-1</sup> cm<sup>-1</sup> for octodecamer at the absorption band of 570 nm. The lifetimes of the triplet excited-state were measured to be 15.6  $\mu$ s at 545 nm for octomer and 12.8  $\mu$ s at 570 nm for octodecamer. These values are on the order of the lifetimes for oligothiophenes with 1–6 repeat units [34,35].

#### 3.4. Singlet oxygen quantum yields

It has been reported that oligothiophenes and derivatives can generate singlet oxygen effectively [34–36]. Because of the similar photophysical properties of the EDOT octomer and octodecamer to those of oligothiophenes reported in the literature, it is expected that octomer and octodecamer can also generate singlet oxygen. Using 1H-phenalen-1-one, *i.e.* perinaphthenone ( $\Phi_\Delta = 0.93$  in benzene) [27] as a reference, the singlet oxygen emission was monitored in aerated CH<sub>2</sub>Cl<sub>2</sub> solutions. The singlet oxygen formation quantum yields were obtained to be 0.35 for octomer and 0.62 for octodecamer. Because the fluorescence quantum yield for octomer and octodecamer were measured to be 0.22, this sets up the limit for the triplet excited-state quantum yield to be 0.78. The much higher singlet oxygen generation efficiency for octodecamer implies that energy transfer from the triplet excited-state of octodecamer to ground-state oxygen is more efficient. This trend disaccords to what has been reported for oligothiophenes with 1–6 repeat units, in which it has been found that energy transfer efficiency is independent of the conjugation length of the oligothiophenes and is almost unity [33]. Although the cause that accounts for this inconsistency is not clear at this time, this study provides valuable information on the ability of these oligomers to generate singlet oxygen and has important implications in explaining the instability of these oligomers upon exposure to air and light.

#### 4. Conclusion

We have developed a facile method to synthesize EDOT-based oligomers with 8 and 18 repeating units. The photophysics of these two oligomers have been studied. It has been demonstrated that the UV–vis absorption band maxima, the emission band maxima, and the triplet–triplet transient absorption band maxima all shift to longer wavelengths when repeating EDOT units of the oligomer increase from octomer to octodecamer. Both oligomers are emissive in solutions and they can generate singlet oxygen in a reasonably good yield. The bright emission of these oligomers suggests

that they could have potential application in organic light emitting devices (OLED).

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