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ORIGINAL PAPER

Fluorene oligomer with tetrathiafulvalenes as pendant groups: synthesis, electrochemical and spectroscopic properties

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Abstract An oligomeric fluorene with pendant **TTF** units (**OFT**) was synthesized by the Yamamoto coupling reaction using Ni(COD)$_2$ as catalyst. The fluorescence spectra of fluorene-**TTF** (**3a**) and **OFT** displayed weak fluorescence intensity because of the photoinduced electron transfer (PET) interaction and energy transfer between the TTF and fluorene, while the fluorescence intensity would enhance significantly after chemical oxidation. The absorption spectra and cyclic voltammetry (CV) showed that an intramolecular interaction existed between the **TTF** and fluorene moieties in **OFT**, while in **3a** such interaction could not be observed, due to the chain propagation of the fluorene backbone and an enhanced internal charge transfer interaction between the two electroactive moieties. Moreover, the conductivity showed that the doped **OFT** possessed a higher conductivity (1.4×10^{-3} S cm^{-1}) than the doped **3a** (9.8×10^{-5} S cm^{-1}). These results demonstrated that **OFT** was a good candidate of fluorescence switches and conducting materials.

Keywords Fluorene · TTF · Charge transfer · Conducting materials · Fluorescence switch

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Introduction

Fluorene derivatives, especially the fluorene oligomers or polymers, have been extensively applied as light-emitting materials [1–6], nonlinear optical materials [7, 8], fluorescence sensors [9] and electrochromic display devices [10], due to their excellent electrochemical and spectroscopic properties. Many efforts have been focused on the design and synthesis of fluorene oligomers and polymers containing pendant groups through the structural modification of the fluorene in 9-position [11, 12].

On the other hand, tetrathiafulvalene (**TTF**) and its derivatives have attracted much interesting as strong electron donors and they can be oxidized and reduced reversibly. With this unique feature, **TTF** and its derivatives have been widely employed in numerous fields [13], for example, organic metals [14], molecular sensors [15–18] and molecular logic gates [19]. Fluorescence switches consisted of **TTF** derivatives have also been investigated, such as **TTF** incorporated with porphyrin [20], perylene diimide [21] and anthracene [22]. However, most of them are single molecules and few are oligomers or polymers [23–25]. We designed a fluorene oligomer with **TTF** as pendant groups, expecting the oligomeric fluorene-**TTF** (**OFT**) would exhibit weak fluorescence and the fluorescence could be enhanced after oxidation (Fig. 1). Herein, we report the synthesis (Scheme 1), electrochemical and spectroscopic properties of **OFT** together with its chemical oxidation behaviors. The results indicated that fluorescence intensity of **OFT** could be modulated by the oxidation of **TTF** units, which makes it an attracting candidate of the fluorescence switch.

Experimental

Materials and instruments

All the reagents and solvents were of commercial quality and were distilled or dried when necessary using the standard procedures.

^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE 500 instrument operating at 500 and 100 MHz chemical shifts were quoted downfield of TMS. Elemental analyses were obtained from an Elementar vario EL III C, H, N analyzer. Mass spectra were recorded using LCQ ADVANTAGE mass spectrometer. Absorption spectra were measured with CARY 100 Conc UV-visible

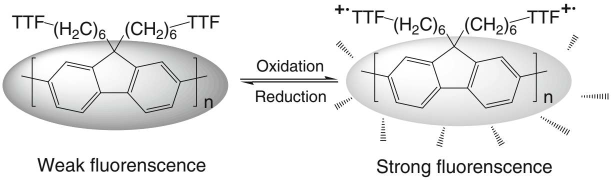
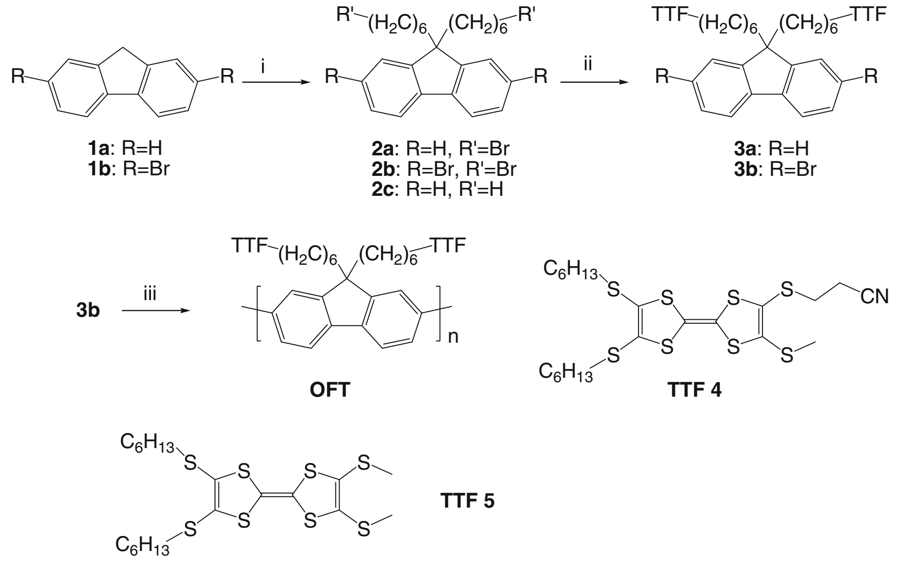


Fig. 1 The schematic process of fluorescence switch based on **OFT**



Scheme 1 The synthetic route of **3a**, **3b**, **OFT** and the structure of compound **TTF 4** and **TTF 5**: (i) KOH (50 wt%), 1,6-dibromohexane, TBAB, 75 °C, 15 min (ii) **TTF 4**, CsOH H_2O, DMF, r.t., 12 h (iii) $Ni(COD)_2$, 2,2′-dipyridyl/cyclooctadiene, dried DMF, 60 °C, 48 h

spectrophotometer. Fluorescence spectra were carried out with CARY Eclipse Fluorescence spectrophotometer and were corrected for the spectral response of the machines. Gel permeation chromatography (GPC) was carried out with Water-Breeze GPC apparatus using THF as eluent. All the electrochemical experiments were performed in CH_2Cl_2 with n-Bu_4NPF_6 as the supporting electrolyte, platinum as the working and counter electrodes, and Ag/AgCl as the reference electrode. The scan rate was 50 mV s^{-1}. The electric conductivity was measured using a four-probe technique with a SX1934 apparatus.

Synthesis of 9,9′-bis(6″-bromohexyl)fluorene (2a)

To a mixture of potassium hydroxide (100 mL, 50 wt%), tetrabutylammonium bromide (1.55 g, 4.8 mmol) and 1,6-dibromohexane (58.06 g, 240 mmol), fluorene (4.00 g, 24 mmol) was added at 75 °C. After reacting at this temperature for 15 min, the reactant was cooled to room temperature and then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with dilute HCl (2 × 50 mL), H_2O (3 × 50 mL) and brine (2 × 50 mL) successively, and then dried over anhydrous $MgSO_4$. After removing the solvent and the excess 1,6-dibromohexane in vacuo, the residue was purified by column chromatography on silica gel (CH_2Cl_2:Petroleum ether = 1:9) to give **2a** as pale yellow oil (4.98 g, 42.1%). ^{1}HNMR ($CDCl_3$, 500 MHz):δ 7.65–7.59 (m, 2H, ph-H), 7.55–7.22 (m, 6H, ph-H), 3.22–3.19 (t, 4H, $J = 7$ Hz, Br–CH_2–), 1.87–1.84 (m, 4H, –CH_2–), 1.61–1.55

(m, 4H, –CH_2–), 1.10–1.09 (m, 4H, –CH_2–), 0.98–0.95 (m, 4H, –CH_2–), 0.55–0.50 (m, 4H, –CH_2–). MS (70 eV): $m/z = 492.1$ (M^+). Anal. Calcd for $C_{25}H_{32}Br_2$: C, 60.99; H, 6.55. Found: C, 61.21; H, 6.89.

Synthesis of 2,7-dibromo-9,9′-bis(6″-bromohexyl)fluorene (**2b**)

The procedure is similar to that of **2a**. **2b** was obtained as a colorless solid in a yield of 61.2%. Mp: 72–73 °C (lit. mp 71–72 °C [26]). ^{1}HNMR ($CDCl_3$, 500 MHz):δ 7.46 (d, 2H, $J = 8$ Hz, ph-H), 7.40–7.37 (m, 4H, ph-H), 3.24–3.21 (t, 4H, $J = 7$ Hz, Br–CH_2–), 1.87–1.84 (m, 4H, –CH_2–), 1.61–1.58 (m, 4H, –CH_2–), 1.14–1.11 (m, 4H, –CH_2–), 1.03–1.00 (m, 4H, –CH_2–), 0.53–0.51 (m, 4H, –CH_2–). MS (70 eV): $m/z = 650.01$ (M^+). Anal. Calcd for $C_{25}H_{30}Br_4$: C, 46.19; H, 4.65. Found: C, 46.25; H, 4.93.

Synthesis of **3a**

To a solution of **TTF 4** (1.136 g, 2 mmol) in dried DMF (45 mL), CsOH H_2O (352 mg, 2.1 mmol) in dried MeOH (6 mL) was added over a period of 30 min under nitrogen. After stirring for 30 min, a solution of **2a** (492 mg, 1 mmol) in dried DMF (15 mL) was added dropwise over 1 h. The reaction mixture was stirred for another 12 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2: petroleum ether = 1:1) to give **3a** as dark-red oil (0.98 g, 72.3%). ^{1}HNMR ($CDCl_3$, 500 MHz):δ 7.69 (d, 2H, $J = 7$ Hz, ph-H), 7.34–7.29 (m, 6H, ph-H), 2.81 (m, 8H, S–CH_2–), 2.68 (t, 4H, $J = 7$ Hz, S–CH_2–), 2.36 (s, 6H, –S–CH_3), 1.97–1.94 (m, 4H, –CH_2–), 1.65–1.59 (m, 8H, –CH_2–), 1.44–1.37 (m, 12H, –CH_2–), 1.32–1.29 (m, 16H, –CH_2–), 1.18–1.13 (m, 4H, –CH_2–), 1.08–1.05 (m, 4H, –CH_2–), 0.90–0.87 (t, 12H, $J = 7$ Hz, –CH_3), 0.61–0.58 (m, 4H, –CH_2–). ^{13}HNMR ($CDCl_3$, 100 MHz):δ 150.32, 141.10, 127.09, 126.82, 122.76, 119,70, 54.91, 40.26, 36.38, 31.31, 29.75, 28.22, 23.57, 22.55, 19.21, 14.04. MS (ESI, 25 eV): $m/z = 1{,}360.3$ (M^+), 1,383.2 ($M^+ + Na$). Anal. Calcd for $C_{63}H_{90}S_{16}$: C, 55.62; H, 6.67. Found: C, 55.70; H, 6.98.

Synthesis of **3b**

The procedure was similar to that of **3a**. **3b** was obtained as dark-red oil in yield of 59.8%. ^{1}HNMR ($CDCl_3$, 500 MHz):δ 7.54 (d, 2H, $J = 10$ Hz, ph-H), 7.47–7.45 (m, 4H, ph-H), 2.83–2.72 (m, 12H, S–CH_2–), 2.41–2.35 (m, 6H, S–CH_3), 1.95–1.90 (m, 4H, –CH_2–), 1.65–1.62 (m, 8H, –CH_2–), 1.46–1.36 (m, 12H, –CH_2–), 1.30–1.26 (m, 16H, –CH_2–), 1.22–1.15 (m, 4H, –CH_2–), 1.15–1.04 (m, 4H, –CH_2–), 0.91 (t, 12H, $J = 9$ Hz, –CH_3), 0.60–0.59 (m, 4H, –CH_2–). ^{13}HNMR ($CDCl_3$, 100 MHz):δ 152.23, 139.09, 130.34, 126.13, 121.59, 121.26, 55.60, 40.11, 31.33, 29.36, 28.30, 23.60, 22.56, 14.05. MS (ESI, 25 eV): $m/z = 1{,}518.1$ (M^+), 1,541.0 ($M^+ + Na$). Anal. Calcd for $C_{63}H_{88}Br_2S_{16}$: C, 49.84; H, 5.84. Found: C, 50.01; H, 5.95.

Synthesis of **OFT**

Ni(COD)$_2$ (171 mg, 0.621 mmol), 2,2′-dipyridyl (97 mg, 0.621 mmol), 1,5-cyclooctadiene (1 mL) and dried DMF (15 mL) were placed in a Schlenk tube and heated at 60 °C for 30 min to obtain the purple complex. Fluorene monomer **3b** (720 mg, 0.5 mmol) was dissolved in dried DMF (10 mL), and the purple complex was added to the solution over a period of 1 h. The mixture was maintained at 60 °C for 48 h in the dark and then poured into methanol (200 mL) and filtrated. The solid was extracted with chloroform for 12 h using a Soxhlet apparatus. After removing most of the chloroform under reduced pressure, the concentration liquid was added to methanol (50 mL). The precipitate was filtrated and dried under vacuum at room temperature to give **OFT** as dark-brown solid (0.394 g, 61.6% yield). The GPC indicated the distribution of average molecular weight of the oligomer was $Mn = 6{,}399$, $Mw/Mn = 1.19$. It was reasonably soluble in common solvents such as chloroform, dichloromethane and THF. ^{1}HNMR (CDCl$_3$, 500 MHz):δ 7.45 (d, 2H, $J = 5$ Hz, ph-H), 7.36 (m, 4H, ph-H), 2.74 (m, 8H, S–CH$_2$–), 2.63 (m, 4H, S–CH$_2$–), 2.30 (m, 6H, S–CH$_3$), 1.85 (m, 4H, –CH$_2$–), 1.55–1.47 (m, 8H, –CH$_2$–), 1.33 (m, 12H, –CH$_2$–), 1.22 (m, 16H, –CH$_2$–), 1.10 (m, 4H, –CH$_2$–), 1.00 (m, 4H, –CH$_2$–), 0.82 (m, 12H, –CH$_3$), 0.51 (m, 4H, –CH$_2$–). ^{13}HNMR (CDCl$_3$, 100 MHz):δ 150.51, 139.06, 130.31, 126.09, 121.57, 121.24, 55.58, 40.11, 36.29, 31.30, 29.71, 28.20, 23.59, 22.54, 19.16, 14.05. Anal. Calcd for $(C_{63}H_{88}S_{16})_n$: C, 55.70; H, 6.54. Found: C, 55.62; H, 6.61.

Results and discussion

Design and synthesis of **OFT**

Our target is to synthesize a molecular system consisted of **TTF** and fluorene, to hope it could be polymerized so that polymeric or oligomeric TTF-fluorene could be obtained, expecting them would exhibit unique photo/electrochemical properties. However, directly linking these two molecules is impossible as there was no reactive group in them. A reasonable covalent bridge between them is needed. Based on the synthetic **TTF** chemistry, cyanoethyl groups in **TTF**s, i.e., **TTF 4** can be deprotected by cesium hydroxide monohydrate (CsOH H$_2$O) to afford **TTF** thiolates, which can be trapped by the appropriate electrophlie (usually RX, R = alkyl, CH$_2$Ph, X = I, Br, Cl) to form the expected **TTF** derivatives. According to this reaction, **TTF 4** with long alkyl chains, were designed and synthesized [27, 28]. Simultaneously, fluorene derivative **2b** was synthesized and used as an alkylation reagent. **TTF 4** reacted with **2b** in dried DMF in the presence of one equivalent of CsOH H$_2$O to form **TTF**-fluorene triad **3b** (Scheme 1). Thus, the monomer for the polymerization reaction was obtained. Then, oligomeric **OFT** was obtained by the Yamamoto coupling of **3b** using Ni (COD)$_2$ as catalyst in the yield of 61.6%. The GPC indicated the distribution of average molecular weight of the oligomer was Mn = 6,399, Mw = 7,606, Mw/Mn = 1.19. It was reasonably soluble in common solvents such as chloroform, dichloromethane and THF.

Electrochemistry

The redox properties of **3a** and **OFT** were studied by cyclic voltammetry (CV) in CH_2Cl_2 and their CV curves were presented in Fig. 2. The electrochemical behavior of **2c** [29] was also investigated under the similar conditions as references. The electrochemical data of model **TTF 5** were also listed in Table 1 [30]. CV curves of **3a** and oligomeric **OFT** both showed two-two-electron reversible redox processes, corresponding to the successively oxidation of the **TTF** units to radical cation **TTF**$^{+\cdot}$ and dication **TTF**$^{2+}$, respectively. Meanwhile a one-electron irreversible anodic wave of oxidation of the fluorene unit in **3a** and **OFT** could be observed.

For the **TTF** units in **3a**, there was about 60 mV anodic shift for the first redox potential compared with **TTF 5**, which showed that the **TTF** units of **3a** were more difficult to be oxidized than **TTF 5** due to the HOMO orbital of **3a** was located at a

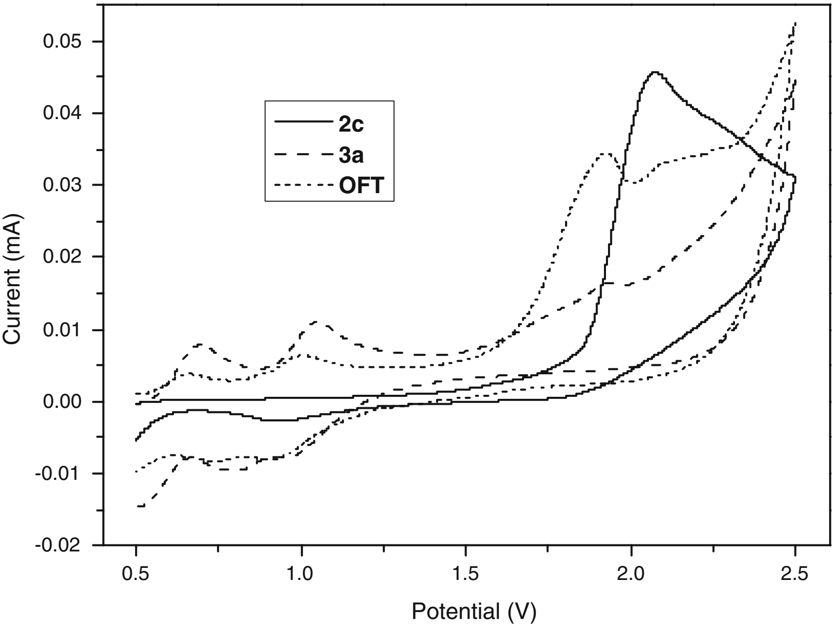


Fig. 2 The cyclic voltammograms of **2c**, **3a** and **OFT** (1×10^{-3} M) in CH_2Cl_2 (scanning rate 50 mV s^{-1}); platinum as the working and counter electrodes, AgCl/Ag as the reference electrode, *n*-Bu_4NPF_6 (0.1 M) as the supporting electrolyte

Table 1 The electrochemical data for **2c**, **3a**, **TTF 5** and **OFT** in CH_2Cl_2

Compound	$E_{ox1}^{1/2}$/V	$E_{ox2}^{1/2}$/V	E_{ox}^{flu}/V
2c			2.07
3a	0.62	0.92	1.93
5 [30]	0.56	0.91	
OFT	0.64	0.91	1.92

lower energy than that of **TTF 5** [30]. For the fluorene unit, there was about 140 mV cathodic shift in comparison with the model **2c**, which indicated the fluorene unit of **3a** was much easier to be oxidized. The phenomenon might be ascribed to the steric hindrance effect of the **TTF** unit that linked to the fluorene. As the alkyl chains with **TTF** were substituted in the same position of the fluorene and this might caused the electrostatic repulsion between the two **TTF** moieties, the fluorene framework would twist and the electron could be lost easily as the descent strength of delocalization pathway of the π-electron system.

The electrochemical behavior of **OFT** was similar to that of **3a**. More positive anodic shift (80 mV) of **TTF** units was observed, indicating that the oxidation of **OFT** was more difficult than **3a**. The chain propagation of the fluorene backbone and an enhanced internal charge transfer interaction between these two electroactive moieties made the main contribution.

UV-vis spectra

The UV-Vis absorption spectra of **3a** and **OFT** in CH_2Cl_2 are shown in Fig. 3 and the absorption curves of **TTF 5** and fluorene **2c** were also given in Fig. 3 as reference.

The absorption curve of **3a** exhibited two strong absorption peaks at 264 and 304 nm and a shoulder peak at 293 nm, respectively. Comparing with the absorption curves of **TTF 5** and fluorene **2c**, it could be found that the absorption of **3a** was just the addition of **2c** and **TTF 5**, and no new absorption band was

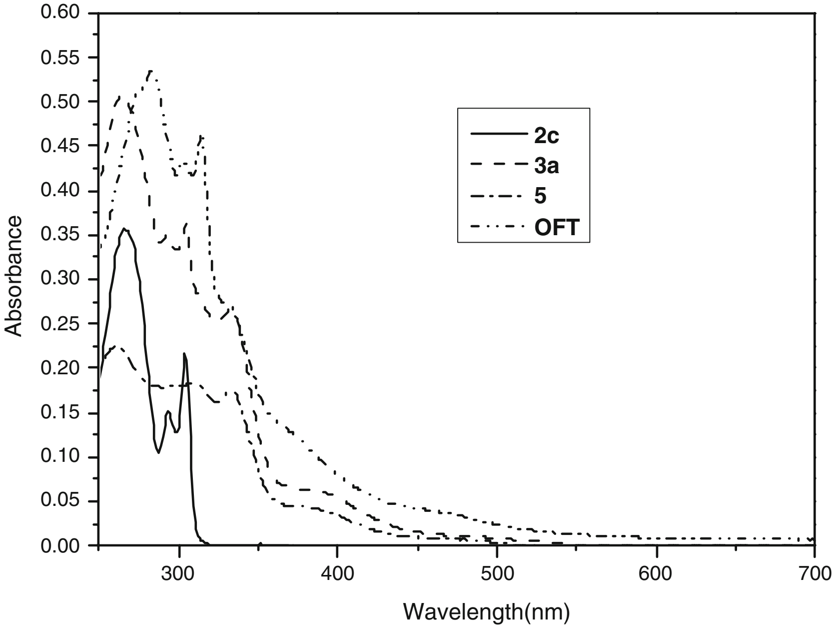


Fig. 3 The absorption spectra of **2c**, **3a**, **5** and **OFT** (1×10^{-5} M) in CH_2Cl_2

observed. It indicated that there was no distinctive internal interaction between the fluorene and **TTF** moieties in the ground state of **3a**. Furthermore, the absorption curve of **OFT** was nearly identical with **3a** in shape, but the two strong absorption peaks were at 282 and 314 nm and a shoulder peak was at 303 nm, i.e., there was a red shift of 10–18 nm compared to **3a**. This red shift indicated a significant electronic interaction between fluorene and **TTF** units existed. Obviously, the chain propagation of **OFT** could be the main contribution to this red shift. In other words, the propagation of the fluorene backbone in **OFT** might enhance the electronic interaction between the pendant **TTF** units and the conjugated backbone in the ground state.

Fluorescence spectra

The fluorescence spectra of **2c**, **3a** and **OFT** were excited at $\lambda_{ex} = 282$ nm, as shown in Fig. 4.

As shown in Fig. 4, compound **2c** indicated a strong fluorescence emission with the maximum emission peak at 310 nm, however, a strong fluorescence quench (ca 99%) was observed for **3a** or **OFT**. As there was a big overlap between the absorption spectra of **TTF** and the emission curve of fluorene, according to the Förster mechanism, the energy transfer from fluorene moiety to the **TTF** moiety would happen easily. Hence, such energy transfer interaction between the **TTF** and fluorene units should be main reason for this strong quench and the photoinduced electron transfer interaction from **TTF** to the fluorene unit in the excited state might be another reason for the fluorescence quench [31].

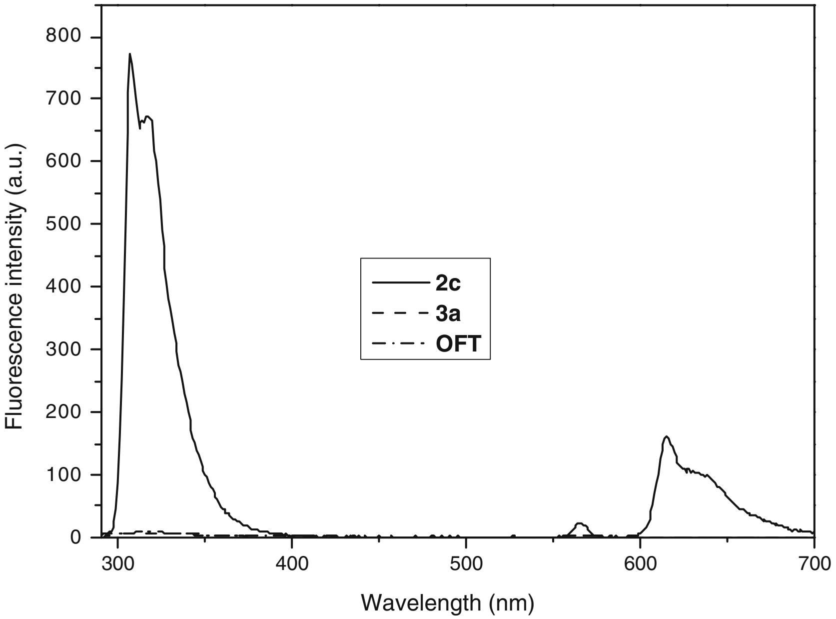


Fig. 4 The fluorescent spectra of **2c**, **3a**, and **OFT** (1×10^{-5} M) in CH_2Cl_2. $\lambda_{ex} = 282$ nm

Chemical oxidation

The chemical oxidations were carried out in the solutions of **3a** and **OFT** in THF by adding increasing amount of $Fe(ClO_4)_3$ in it, respectively, in order to examine the potential of **3a** and **OFT** as fluorescence switches. The absorption spectra were measured and recorded in Fig. 5.

Two new broad absorption bands centered at 450 and 639 nm appeared on the new absorption spectra after adding the oxidant. This could be ascribed to the absorption bands of the **TTF** radical cation, which was matched with previous reports [32]. Meanwhile, all the absorbance at 282, 303, and 314 nm decreased with the increasing amount of $Fe(ClO_4)_3$ and this could also be explained by the same mechanism.

With the addition of $Fe(ClO_4)_3$ to the solution of **3a** or **OFT**, the fluorescence intensity was recovered (Figs. 6, 7). The oxidation of neutral **TTF** to the radical cation **TTF**$^{+\cdot}$ could prevent the **TTF**$^{+\cdot}$ from acting as an electron donor to quench the fluorescence of the fluorene units and could recover the fluorescence intensities [20]. Notably, the fluorescence intensity of **OFT** after oxidation was increased 20 times while **3a** was increased 6 times under the same conditions, which revealed **OFT** was more sensitive than **3a**. Considering the result of CV, it could be deduced that **OFT** could be treated as a potential fluorescence switch, and was more sensitive than **3a**.

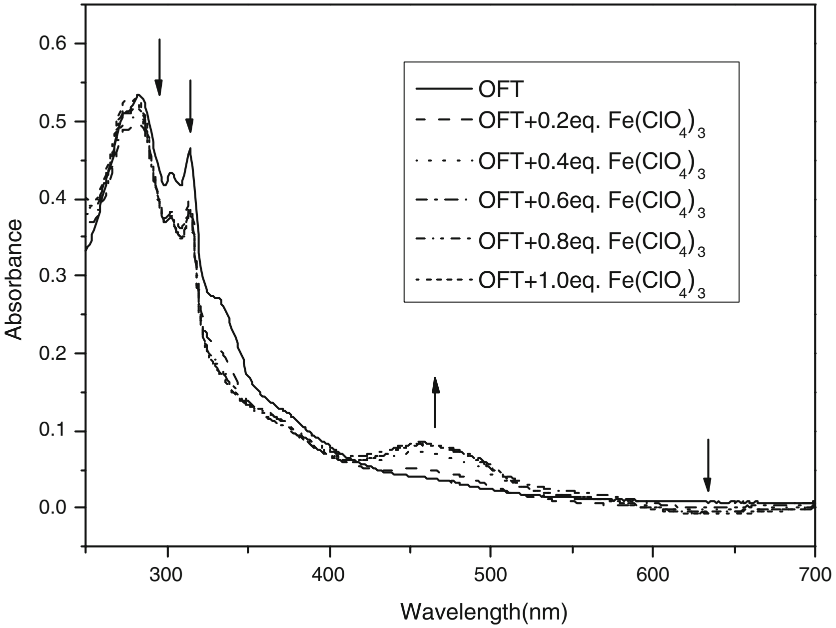


Fig. 5 The absorption spectra of **OFT** (1×10^{-5} M) in THF upon addition of increasing amount of the oxidant Fe $(ClO_4)_3$

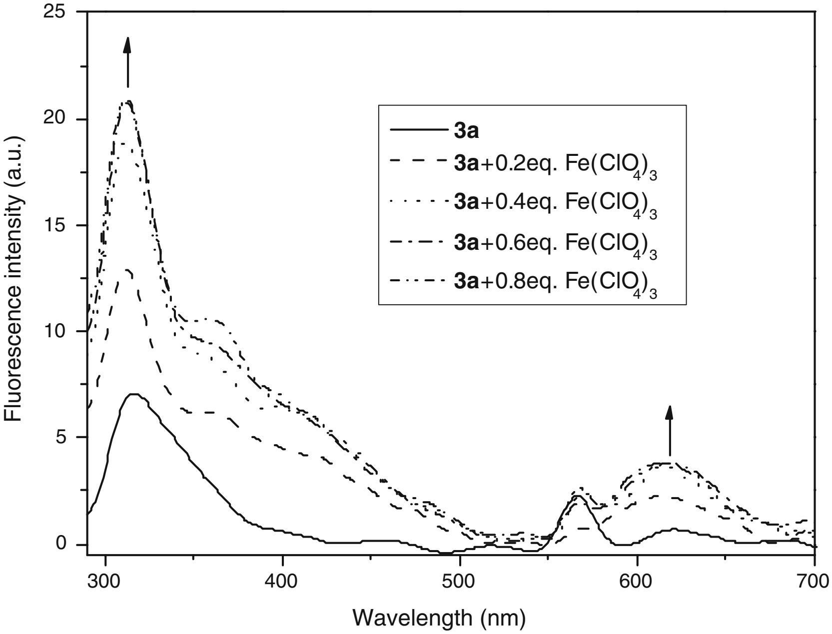


Fig. 6 The fluorescence spectra of **3a** (1×10^{-5} M) in THF upon addition of increasing amount of the oxidant $Fe(ClO_4)_3$. $\lambda_{ex} = 282$ nm

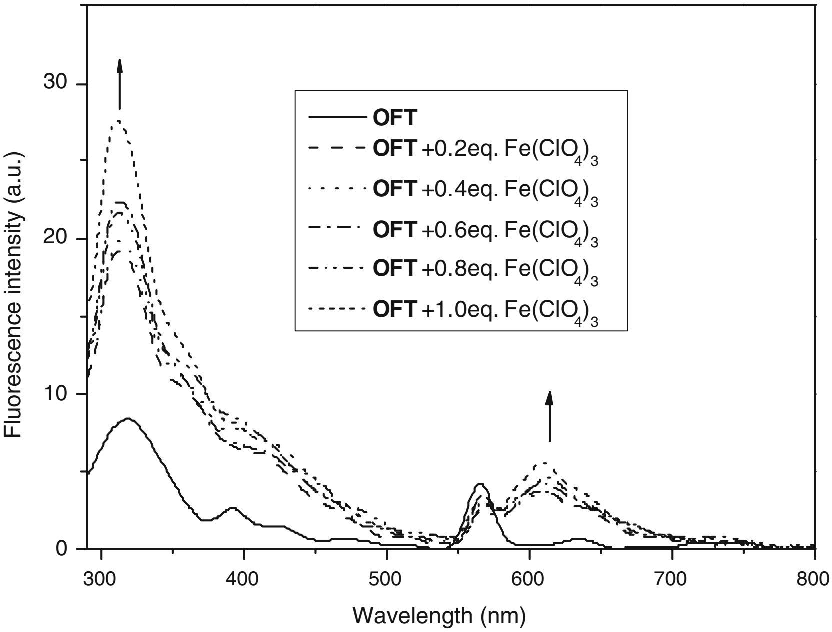


Fig. 7 The fluorescence spectra of **OFT** (1×10^{-5} M) in THF upon addition of increasing amount of the oxidant $Fe(ClO_4)_3$. $\lambda_{ex} = 282$ nm

Table 2 The conductivity of neutral and doped **3a** and **OFT**

Compound	Neutral conductivity/S cm^{-1}	Doped conductivity/S cm^{-1}
3a	2×10^{-7}	9.8×10^{-5}
OFT	1.2×10^{-6}	1.4×10^{-3}

Conductivity

The solution of **OFT** in THF was treated with electron acceptor tetracyanoquinodimethane (TCNQ), thus a doped oligomer film was obtained from a drop of cast solution of **OFT**/TCNQ (1:4 molar ratio) onto ITO glass plates [24], followed by drying in vacuum at 35 °C for 10 h. The electric conductivity of neutral and doped **3a** or **OFT** were measured using a four-probe technique with a SX1934 apparatus and the values were listed in Table 2.

As shown in Table 2, in the neutral state, the conductivity of **OFT** was at the lower potential and was increased about 10^3 times after chemical doping with TCNQ which was caused by the oxidation of neutral **TTF** to $\mathbf{TTF}^{+\cdot}$. In the doped state, the delocalized charges between the $\mathbf{TTF}^{+\cdot}$ moiety and the conjugated fluorene oligomer backbone facilitated the π–π interactions between neighboring $\mathbf{TTF}^{+\cdot}$ units [33, 34] and aroused the higher conductivity. Compared to **3a**, the much higher conductivity of **OFT** could be related to the intermolecular interaction between **TTF** units and higher conjugated fluorene oligomer backbone. The results demonstrated that doped **OFT** was a good candidate of conducting materials. Moreover, the doped **OFT** were stable in air and its conductivity was almost changeless just like other **TTF**-based polymers [34].

Conclusions

Two kinds of new molecules **3a** and oligomeric **OFT** based on fluorene or oligomeric fluorene with pendant **TTF** units were synthesized and characterized. The redox data and UV-vis absorption spectra showed there was no intramolecular charge-transfer process between the **TTF** and fluorene moieties in the ground state of **3a**, while **OFT** exhibited its intramolecular interaction between these two electroactive moieties. The fluorescence intensity of both **3a** and **OFT** was strongly quenched, which might be caused by the energy transfer and PET interaction between the **TTF** and fluorene units in the excited state. After chemical oxidation, the fluorescence intensities of both **3a** and **OFT** were recovered. Their conductivities showed that doped **OFT** showed a higher conductivity than that of **3a**. The results indicated that **OFT** was a good candidate of fluorescence switches and conducting materials.

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