Linear and nonlinear luminescence properties of thiophene based materials

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Abstract: Three new thiophene based organic luminescence compounds, i.e., 2,5-bis(4'-N,N-di-methylaminostyryl)thiophene (BMST), 2,5-bis(4'-N,N-diethylaminostyryl)thiophene (BEST) and 2,5-bis(4'-N-cyclobutylaminostyryl)thiophene (BBST), were synthesized. All of their measured single-photon excited fluorescence (SPEF) are located in the range of \( \lambda \approx 530 \) nm with quantum yields of around 40 %, and the corresponding lifetime was \( \approx 1 \) ns. The examined compounds show strong solvatochromism in their SPEF spectra. Excited by a fs laser at 800 nm, a strong up-converted fluorescence of the examined compounds was detected. The profile of two-proton excited fluorescence (TPEF) was similar to that of SPEF. The two-photon absorption (TPA) cross sections of the compounds were determined by the TPEF method. All the compounds showed large TPA cross sections. Hence these thiophene derivatives may have good TPA properties.

Keywords: two-photon absorption, up-converted fluorescence, thiophene derivatives.

INTRODUCTION

The two-photon process, predicted by Goppert-Mayer in 1931 and observed by Peticolas in 1960s, received little consideration for a long time. Simultaneous to the development of laser technology, molecules with large two-photon absorption (TPA) cross sections have received more and more attention because of the variety of their applications such as two-photon excited up-converted laser, two-photon fluorescence microscopy, three-dimensional optical memory, photodynamic therapy. Thiophene has a lower resonance energy than benzene and a better coplanar conformation than polyenes, which have usually been used as electron relays in nonlinear materials in recent years. Compounds based on thiophene may have better two-photon excited fluorescence (TPEF) characteristics than those based on styrene or polyene. Hence, three new compounds derived from thiophene, i.e., 2,5-bis(4'-N,N-dimethylaminostyryl)thiophene (BMST), 2,5-bis(4'-N,N-diethylaminostyryl)thiophene (BEST) and

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2,5-bis(4'-N-cyclobutylaminostyryl)thiophene (BBST), were synthesized (the structures are shown in the Scheme 1). They all emit strong single-photon excited fluorescence (SPEF) and two-photon excited fluorescence (TPEF).

RESULTS AND DISCUSSION

Linear spectral properties

The absorption spectra were recorded on a Hitachi U-3500 spectrophotometer and the SPEF spectra on an Edinburgh FLS920 fluorescence spectrometer.

Fig. 1. Absorption spectra of BBST in toluene, tetrahydrofuran, acetone, acetonitrile and N,N-dimethylformamide.

Linear absorption spectra of the examined compounds

The structures of the compounds BMST, BEST and BBST are symmetrical, and intramolecular electron transfer in the ground state is small. Hence, there is lit-
tle bathochromic shift in the linear absorption spectra of BMST, BEST and BBST in different polar solvents (shown in Fig. 1). The profiles of the absorption spectra of BBST are almost the same in toluene and \(N,N\)-dimethylformamide. The peak absorption of the compounds are located at 436 nm (BMST), 438 nm (BEST) and 442 nm (BBST) and there is no linear absorption from 550 nm to 1000 nm. The peak shift of the different compounds may be caused by the different electron donating ability of the electron donor.

**Single-photon excited fluorescence**

The SPEF spectra of BMST, BEST and BBST measured in toluene on excitation at 400 nm with a 450 W Xe lamp are shown in Fig. 2. The shapes of the SPEF spectra of the examined compounds are similar because of their analogous structure. The peak emission is immediate and the peak at the longer wavelength is located at \(\lambda_{\text{max,em}} = 523\) (BMST), 527 (BEST) and 531 nm (BBST). In the nonpolar solvent, toluene, all the SPEF emissions are obviously split into two peaks. This may be caused by different vibrational energy levels in the excited state.

![Fluorescence spectra of BBST, BMST and BEST in toluene.](image)

**Two-photon excited fluorescence**

The TPEF of most compounds is weak, so a high concentration of the compounds is necessary, which may cause a change in their linear absorption spectra.
Before the measurement of TPEF, the absorption spectra of the compounds were measured at a high concentration (the same concentration as the one used for the TPEF measurements) (Fig. 4 and Fig. 5). The absorbance of the peak absorption is very strong at this concentration, but there was still no linear absorption at wavelengths from 580 nm to 1000 nm.

The TPEF spectra of BMST, BEST and BBST in tetrahydrofuran and toluene were recorded using a Ti:Sapphire fs laser as a pump source, and the fluorescence signal was recorded by a streak camera system (Hamamatsu model C5680). A barrier filter was put between the sample and the detector system to avoid scattered light.

The TPEF spectra of BMST in tetrahydrofuran are shown in Fig. 4. The peak emission wavelength in the TPEF spectrum is at 527 nm,
which is the same position as that in the SPEF spectrum. This may be explained by
the assumption that the emission energy level corresponding to the TPEF is the
same as the one corresponding to the SPEF, even though the excitation energy is
different (the summation energy of the two photons in the TPEF experiments was
higher than that of the single photon in SPEF experiments).

The spectra of linear absorption, SPEF and TPEF of BBST in toluene are
shown in Fig. 5. The maximum of the absorption is at 438 nm and there is no linear
absorption from 590 nm to 1000 nm even with a concentration of 5.0×10^{-4} mol/L.
In the low polar solvent, toluene, the SPEF emission obviously splits into two
peaks, one at 501 nm and the other at 531 nm. However, the spectral profile of the
TPEF is a single peak at 537 nm. This may be explained by re-absorption. The ab-
sorption at 501 nm with a concentration 5.0×10^{-4} mol/L in toluene cannot be ne-
glected, so the supposed emission peak of TPEF at this wavelength may be ab-
sorbed. The remaining emission peak is located at 537 nm, the analogous wave-
length as one or the SPEF.

*TPA cross section measurement*

The two-photo absorption cross section, σ, is one of the most important parame-
ter of TPA materials. In our experiments, the TPA cross section of the studied com-
ounds BMST, BEST and BBST were obtained by the TPEF method.\textsuperscript{10} Using
strictly the same experimental condition, the TPEF spectra of BMST, BEST and
BBST in toluene (or in tetrahydrofuran) and that of fluorescein in 0.1 mol/L NaOH
solution (all the concentration of the solution in the measurements were fixed at
5.0×10^{-4} mol/L) were recorded. The σ values of the compounds were determined by
comparing their TPEF integral intensities with that of fluorescein according to\textsuperscript{10}

\[
σφ = σ_\text{flu} φ_\text{flu} \left( \frac{C_\text{flu}}{C} \right) \left( \frac{n_\text{flu} F}{n F_\text{flu}} \right)
\]
where $\phi$, $C$, $n$ and $F$ are the fluorescence quantum yield, concentration, refractive index and the TPEF intensity, respectively. The subscript flu refers to the standard fluorescein. At the wavelength of the incident laser, i.e., 800 nm, the TPA cross section $\sigma_{\text{flu}}$ is $36 \times 10^{-50}$ (cm$^4$ s) photon$^{-1}$ and its fluorescence quantum yield $\phi_{\text{flu}}$ is 0.9.$^{10}$ The calculated values of the TPA cross sections $\sigma$ of the studied compounds are shown in Table I:

<table>
<thead>
<tr>
<th>Target compounds</th>
<th>BMST</th>
<th>BEST</th>
<th>BBST</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA cross section $(10^{-50}$ cm$^4$ s/photon$)$</td>
<td>tetrahydrofuran</td>
<td>85</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>84</td>
<td>106</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Three new compounds derived from thiophene, i.e., BMST, BEST and BBST, were synthesized. All the compounds showed good linear fluorescence properties. The peak emissions are located at $\approx 530$ nm and the corresponding lifetimes are $\approx 1$ ns. The fluorescence spectra exhibit solvatochromism. This may be explained by intramolecular charge transfer in the excited states.

All the compounds emit strong up-converted fluorescence with 800 nm laser excitation. The two-photon absorption (TPA) cross sections of the compounds were determined by the TPEF method. All the studied compounds showed a large TPA cross section. Hence the thiophene derivatives may have good TPA properties.

**EXPERIMENTAL**

*General methods*

The studied compounds were synthesized by the Witting reaction which was conducted under a dry $N_2$ atmosphere. The reagents were used as received from commercial supplier. THF was distilled over sodium and the other solvents were redistilled before use.

*Synthesis of 2,5-diformacylthiophene*

To 8 mL (0.1 mol) thiophene and THF in a flask under a $N_2$ atmosphere were added dropwise under stirring 125 mL 1.6 $n$-butyllithium in hexane. The stirring was continued for 1 h at room temperature. Then, 23 mL (0.3 mol) DMF was dropped into the flask at $-78$ °C, after 2 h, the solution was poured into 500 mL water, the pH was adjusted to 7, and the product was extracted with CHCl$_3$. On further purification by column chromatography, a yellow powder was obtained (yield 53 %). $^1$H-NMR(CDCl$_3$) $\delta$ 9.97 ppm ($s$, 2H), 7.80 ppm ($d$, $J$ = 4.5, 2H).

*Synthesis of dialkylaminobenzaldehyde*

The dialkylaminobenzaldehydes were synthesized according to Ref. 12. Diethylaminobenzaldehyde is a pale yellow solid (yield 67 %). $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 6.96 ppm ($s$, 1H), 7.68 ppm ($d$, $J$ = 8.8, 2H), 6.65 ppm ($d$, $J$ = 8.8, 2H), 3.41 ppm ($q$, $J$ = 7.0, 4H), 1.19 ppm ($t$, $J$ = 7.1, 6H).

Cyclobutanylaminobenzaldehyde is a yellow solid (yield 54 %), m.p. 78–80 °C. $^1$H-NMR (CDCl$_3$, 300 MHz), $\delta$ 9.71 ppm ($s$, 1H), 7.71 ($d$, $J$ = 8.7, 2H), 6.59 ($d$, $J$ = 8.8, 2H), 3.38 ($t$, $J$ = 6.6, 4H), 2.05 ($t$, $J$ = 6.6, 4H).
Synthesis of dialkylaminotoluenyltriphenylphosphonium bromide

15.0 g (0.1 mol) dimethylaminobenzaldehyde, 2.0 g (0.04 mol) KBH₄, 300 mL ethanol were refluxed for 4 h in a 500 mL flask. The solution was neutralized with dilute hydrochloric acid and extracted with CHCl₃. The CHCl₃ solution, 41 g (0.1 mol) HP⁺Ph₃Br⁻ and 300 mL CHCl₃, were refluxed for 3 h, distilled and treated with ether. Dimethylaminotoluenyltriphenylphosphonium bromide was obtained as a white solid. Yield 97 %. ¹H-NMR (CDCl₃, 300 MHz) δ 7.71 ppm (m, 19H), 5.34 ppm (d, J = 13.5, 2H), 3.06 ppm (s, 6H).

Diethylaminotoluenyltriphenylphosphonium bromide was synthesized by the same method. Yield 98 %.

Cyclobutanylaminotoluenyltriphenylphosphonium bromide was obtained by the same method. Yield 97 %.

Synthesis of 2,5-bis(4’-N,N-dimethylaminostyryl)thiophene (BMST)

Under N₂ and at 0 °C, a solution of 0.03 mol t-BuOK in 50 mL THF was added dropwise to a flask containing 0.02 mol dimethylaminotolueneethyltriphenylphosphonium bromide, 2,5-diformacylthiophene and 200 mL THF. The reaction mixture was kept for 15 h at room temperature. The mixture was poured into 500 mL water, and the product extracted with CHCl₃. After further purified by column chromatography, a dark-red powder was obtained (yield 42 %). ¹H-NMR (CDCl₃, 300 MHz) δ 7.19 (m, 3H), 2.98 (s, 3H). MS (70 eV) m/z (%) 374 (M⁺ 32).

Synthesis of 2,5-bis(4’-N,N-diethylaminostyryl)thiophene (BEST)
The same method was used to synthesize BEST. Yield 38 %. ¹H-NMR (CDCl₃, 300 MHz) δ 7.25 (d, J = 8.8, 1H), 6.75 (m, 6H), 3.30 (q, J = 8.0, 4H), 1.10 (d, J = 8.0, 6H). MS (70 eV) m/z (%) 430 (M⁺ 100).

Synthesis of 2,5-bis(4’-N-cyclobutylaminostyryl)thiophene (BBST)
The same method was used to synthesize BBST. Yield 29 %. ¹H-NMR (CDCl₃, 300 MHz) δ 7.68 (m, 1H), 7.26 (m, 3H), 3.41 (m, 2H), 2.31 (m, 2H). MS (70 eV) m/z (%) 426 (M⁺ 100).

ИЗВОД

ЛИНЕАРНЕ И НЕЛИНЕАРНЕ ЛУМИНИСЦЕНТНЕ ОСОБИНЕ МАТЕРИЈАЛА БАЗИРАНОГ НА ТИОФЕНУ

ПИНГ ЛУ и ГУАНГ МИНГ ХИА
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Синтетизована су три нова органска луминисцентне јединиње заснована на тиофену, и то: 2,5-бис(4’-N,N-диметиламиностирил)тиофен (BMST), 2,5-бис(4’-N,N-дигетиламиностирил)тиофен (BEST) и 2,5-бис(4’-N-циклобутиламиностирил)тиофен (BBST). Све њихове једно-фотонске побуђене флоресценције (SPEF) налазе се у области око 530 nm са квантним приносом од 40 % уз одговарајуће време живота од око 1 ns. Проучена јединиња показују јак солватохромизам у својим SPEF спектрима. Побуђивањем са fS лазером испитивана јединиња показују флоресценцију ка повећаним таласним дужинама. Профил дво-фотонског побуђења флоресценције (TPEF) је сличан као код SPEF. Попречни пресек дво-фотонске асорпције (TPA) одређен је TPEF методом. Сва испитана јединиња имају велики TPA попречни пресек. Стога, ови деривати тиофена имају добре TPA особине.

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REFERENCES