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Strong fluorescence of nano-size star-like molecules

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UV-visible absorption and fluorescence properties of 14 nano-size star-like compounds, being composed of oligothienylene units bridged by silicon atoms, have been studied in dioxane solution. The absorption and emission maximum wavelengths are found to be dependent on the oligothienylene units. High fluorescence quantum yields and longer lifetimes are observed for the star-like compounds containing bithienylene units, being related to the σ–π interaction and the star-like structure.

Introduction

Oligothiophenes contain well-defined π-conjugated systems, and their photophysical properties have been extensively studied in solution[1–3] and in the solid (film) state.[4,5] Oligothiophenes can be used to copolymerize with other monomers for development of copolymers with interesting properties. Recently, alternating copolymers of organosilicon units and oligothiophene units have attracted both scientific and technological interest.[6–16] We have systematically investigated the photophysical properties of a series of σ–π-conjugated oligothienylene–oligosilanylene copolymers in dioxane solution.[16] Some of the results are consistent with the work of Hadziioannou and coworkers.[11] It is found that the photophysical properties of these copolymers, being mainly dependent on the oligothienylene unit in the copolymer chain, are strongly influenced by the σ–π-interaction in the polymer chains. The effects of the σ–π-interaction on the photophysical properties become stronger as the oligothienylene unit becomes smaller. These effects on the fluorescent properties of the related one-dimensional molecules (polymers) prompted us to increase the fluorescence by developing two- or three-dimensional molecules. In the present work, our interest is focused on the photophysical properties of nano-size star-like molecules (compounds **1**–**14** in Fig. 1). In comparison with oligothiophenes and the oligothienylene–oligosilanylene copolymers, these compounds are expected to bring about some interesting differences in the photophysical properties. The present work will report that the σ–π-conjugation and the star-like scaffold enable the bithiophene-burst compounds to show strong fluorescence.

Experimental

Compounds **1**–**14**, with chemical structures given in Fig. 1, were chemically synthesized by the reaction of tris(chlorodimethylsilyl)methylsilane which was chosen as a core with the lithio(oligo)thienylene derivatives used for construction of the arms.[17] Once purified, these compounds were characterized by MS and NMR (^{1}H, ^{13}C, and ^{29}Si).[17] All the UV-visible absorption spectra and fluorescence properties were measured in dioxane solution, which was not degassed since the oxygen quenching of the fluorescence was not important in these samples. The solvent dioxane was of fluorescence grade, and was used as received.

Absorption spectra were obtained by use of a Shimadzu UV-3101PC scanning spectrophotometer. Emission spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer, which was corrected for the instrumental response. Fluorescence quantum yields of these compounds were measured at absorbances of *ca.* 0.08 at the excitation wavelengths by using quinine sulfate as standard.[18] Fluorescence lifetimes were determined with a Hamamatsu C4780 time-resolved spectrophotometer. The samples were excited by a N_2 laser ($\lambda_{ex} = 337$ nm, $E_{ex} = 70$ μJ, $\tau_p = 300$ ps).

Results and discussion

The UV-visible absorption and fluorescence spectra of compounds **1**–**14** in dioxane are shown in Fig. 2. Their optical absorption and fluorescence characteristics are further tabulated in Table 1, where the data for relevant oligothiophenes,[2,3] silyl- and disilanyl-end-capped oligothiophenes,[11] and oligothienylene–disilanylene copolymers[16] are also given for comparison. The disubstituted end-capped oligothiophenes may be taken as model compounds for the star-like molecules and the copolymers. The relevant copolymers are referred to as DS1T, DS2T and DS3T, respectively, for thienylene–disilanylene, bithienylene–disilanylene and terthienylene–disilanylene copolymers. It is clearly seen from Fig. 2 that the optical absorption and emission spectra of compounds **1**–**14** can be classified into different groups according to the size of the oligothienylene units, indicating that the conjugation length for the star-like molecules is mainly determined by the oligothiophene units. This is the same as observed for oligothienylene–oligosilanylene copolymers.[16] Although the conjugation is rather localized, the star-like compounds show considerably longer wavelength absorption and fluorescence maxima relative to the corresponding oligothiophenes, as reported for the oligothienylene–oligosilanylene copolymers[16] and the end-capped model compounds.[11] The absorption maximum wavelength of **1** is longer than that of thiophene, but shorter than that of DS1T. Compared to bithiophene, the absorption and fluorescence maximum wavelengths of **2**–**9** are red-shifted by *ca.* 25 nm, being close to the red shift observed for DS2T. A similar trend toward the red shift is also observed for **10**–**14** in

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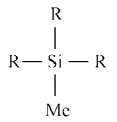

$$\mathrm{R{-}Si(R)(R){-}Me}$$

1 R – –$(Me)_2$Si–T

2 R – –$(Me)_2$Si–T–T–Br

3 R – –$(Me)_2$Si–T–T

4 R – –$(Me)_2$Si–T–T–Si$(Me)_2$–Si$(Me)_3$

5 R – –$(Me)_2$Si–T–T–$(Me)_2$Si–$(Me)_2$Si–T–T

6 R – –$(Me)_2$Si–T–T–$(Me)_2$Si–$(Me)_2$Si–T–T–$(Me)_2$Si–$(Me)_2$Si–T–T

7 R – –$(Me)_2$Si–T–T–$(Me)_2$Si–T–T–$(Me)_2$Si–T–T

8 R – –$(Me)_2$Si–T–T–$(Me)_2$Si–T–T

9 R – –T–T–$(Me)_2$Si–T–T

10 R – –T–T–T

11 R – –$(Me)_2$Si–T–T–T–Et

12 R – –$(Me)_2$Si–T–T–T–Si$(Me)_3$

13 R – –$(Me)_2$Si–T–T–T–Br

14 R – –$(Me)_2$Si–T–T–T–(i•Pr)$_2$Si–(i•Pr)$_2$Si–T–T–T–Et

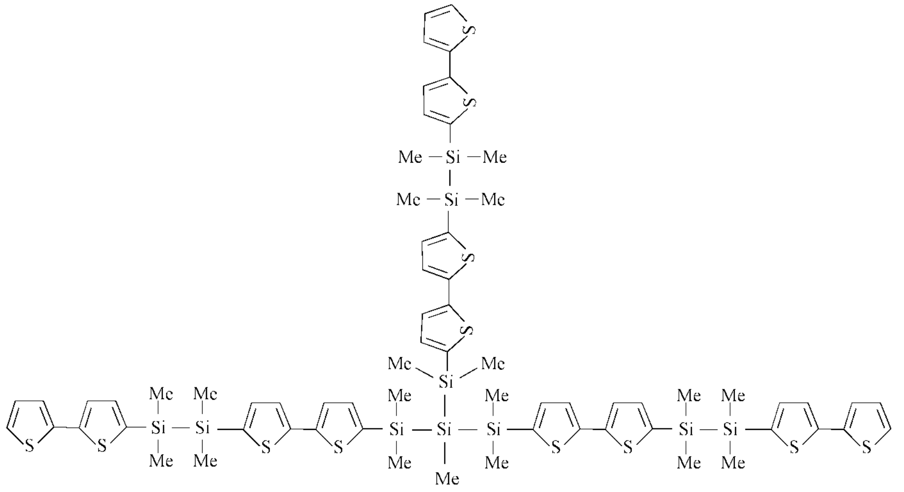

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Fig. 1 Chemical structures of compounds **1**–**14**, where T denotes a thiophene ring.

comparison with terthiophene and DS3T. This kind of considerable red-shift for compounds **1**–**14** indicates that the σ–π interaction in these compounds increases the effective conjugation length.

As the thiophene ring number (n) in the oligothienylene unit increases from 1 to 5, both fluorescence quantum yields (φ_F) and lifetimes (τ_F) of the excited state of the oligothienylene–disilanylene copolymers have been found to exhibit a minimum at $n = 3$.[16] This is different from the increasing trend observed for thiophene oligomers, where both φ_F and τ_F decrease as the molecule size (n) decreases. Such a difference is explained as a consequence of the σ–π conjugation. The σ–π conjugation in these copolymers appears to increase as n decreases.[16] This is related to the lowering of the energy of the π-system of the oligothiophene block with respect to the available electronic levels on the oligosilanylene moiety.[11,16] For compounds **1**–**14**, n ranges from 1 to 3. Therefore, these compounds are expected to show higher φ_F and longer τ_F due to the strong σ–π interaction.

The fluorescence characteristics of some model compounds and related polymers are listed in Table 1 along with those of the star-like molecules. Relative to bithiophene ($\varphi_F = 0.018$ and $\tau_F = 0.046$ ns), $Me_3SiT_2SiMe_3$ and $Me_5Si_2T_2Si_2Me_5$ give quantum yields of 0.06 and 0.23, respectively. This suggests strongly that the σ–π interaction arising from the end capping with silyl and disilanyl groups will increase the quantum yield of bithiophene. Such an effect, though weaker, is also seen when comparing terthiophene and the end-capped thiophenes.

Like thiophene, compound **1** yields no fluorescence, whereas all of the other star-like molecules show fluorescence (Table 1). The quantum yields and lifetimes for compounds **2**–**14** are significantly dependent on both n and g (the number of the oligothienylene units in the arm group R). In addition to the effect of the σ–π interaction, introducing a star-like structure into the molecules possibly enhances their fluorescence. The φ_F and τ_F values for compounds **11** and **12** are greater than those for their analogue terthiophene, and the φ_F values are slightly larger than those of the model compounds with silyl or disilanyl groups as end-capping substituents. The φ_F and τ_F values for compound **14** increase further as g increases to 2, where the arm group R looks like a dimer of that in compound **12**. A stronger enhancing effect of the star-like structure on the fluorescence is observable for the compounds of $n = 2$. The φ_F and τ_F values for compound **3** ($g = 1$) increase drastically to 0.49 and 0.51 ns, respectively. When the bithiophene units in the molecule are end-capped with Me_3Si–Me_2Si- groups, these values increase further to 0.68 and 0.92 ns for compound **4**, respectively. As the arm group R increases in length with increasing g to 2 (compound **5**) and then to 3 (compound **6**), φ_F and τ_F further increase. Similar strong fluorescence is also observed for compounds **7**–**9**.

It should be noted that φ_F for compound **2** is close to that of bithiophene, but much lower than that of its other star-like analogues (compounds **3**–**9**), and similarly that φ_F of com-

Table 1 Absorption and fluorescence characteristics of compounds **1**–**14** in dioxane

Compound	$\lambda_{\text{max, Abs}}$/nm	$\lambda_{\text{max, F}}$/nm	φ_F	τ_F/ns	k_R/ns^{-1}	k_{NR}/ns^{-1}
1	249					
2	330	377	0.012	0.21	0.06	4.71
3	324	378	0.49	0.51	0.96	1.00
4	339.5	381	0.68	0.92	0.74	0.35
5	330	384	0.71	1.08	0.66	0.27
6	329	384	0.75	1.12	0.67	0.22
7	328	380	0.78	1.00	0.78	0.22
8	327	378	0.60	0.99	0.61	0.40
9	325	374	0.67	0.68	0.98	0.48
10	370	423	0.15	0.51	0.29	1.67
11	372	430	0.14	0.50	0.28	1.72
12	372	430	0.15	0.50	0.30	1.70
13	370	431	0.068	0.50	0.14	1.86
14	380	437	0.23	0.79	0.29	0.97
Thiophene	232					
Bithiophene	303	362	0.018	0.046	0.39	21.34
Terthiophene	354	407	0.066	0.21	0.31	4.45
$Me_3SiTSiMe_3$[a,b]	243					
$Me_5Si_2TSi_2Me_5$[a,b]	260					
$Me_3SiT_2SiMe_3$[a,b]	316	374	0.06			
$Me_5Si_2T_2Si_2Me_5$[a,b]	325	390	0.23			
$Me_3SiT_3SiMe_3$[a,b]	362	418	0.10			
$Me_5Si_2T_3Si_2Me_5$[a,b]	368	424	0.12			
DS1T[c]	281	354	0.14	1.08	0.13	0.80
DS2T[c]	332	383	0.33	0.81	0.41	0.83
DS3T[c]	385	434	0.20	0.40	0.50	1.99

[a] Reference 11, where *n*-hexane was used as solvent. [b] T, T_2 and T_3 represent thienylene, bithienylene, and terthienylene, respectively. [c] Reference 16; DS1T, DS2T and DS3T represent thienylene–disilanylene, bithienylene–disilanylene and terthienylene–disilanylene copolymers, respectively.

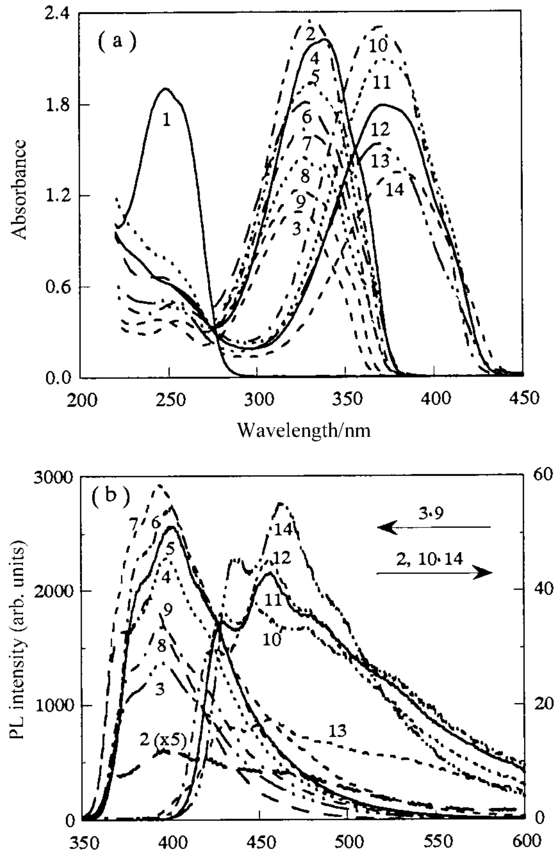

Fig. 2 (a) Absorption and (b) emission spectra of compounds **1**–**14** in dioxane, where the numerals denote the compounds. The emission spectra were obtained with the excitation wavelength of 366 nm, where the sample solution showed an absorbance of *ca.* 0.08. For clarity in (a), however, the compound concentrations were adjusted in the range of 0.2 to 1 mM.

pound **13** is close to that of terthiophene, but only about half of that of its star-like analogues (compounds **11** and **12**). The weaker fluorescence of compounds **2** and **13** is possibly related to the terminal Br atom in the molecule, possibly due to the heavy atom effect. For other terminal groups, capping with a disilanyl group seems to be favourable to stronger fluorescence for the compounds of $n = 2$, while no difference is clearly seen between the compounds of $n = 3$.

As mentioned above, comparisons of the fluorescence characteristics between oligothiophenes, end-capped oligothiophenes with silyl and silanyl groups, and the oligothienylene–oligosilanylene copolymers lead to a conclusion that the fluorescence properties are improved by the σ–π interaction. The nano-size star-like molecules, except for compound **1** ($n = 1$) and the compounds with a terminal Br atom, give higher φ_F and longer τ_F, indicating that in addition to the effect of the σ–π interaction, the fluorescence is further promoted by the star-like structure, which increases with increasing arm length.

A simple kinetic analysis was carried out for the decay process of the first singlet excited state. The first singlet excited state decays through both radiative and nonradiative pathways, and the rate constants of these pathways can be calculated as the radiative (or fluorescence) rate constant $k_R = \varphi_F/\tau_F$, and the nonradiative rate constant $k_{NR} = (1 - \varphi_F)/\tau_F$. The nonradiative pathway includes the internal conversion and intersystem crossing. Therefore, $k_{NR} = k_{ISC} + k_{IC}$, where the intersystem crossing rate constant $k_{ISC} = \varphi_T/\tau_F$, the internal conversion rate constant $k_{IC} = (1 - \varphi_F - \varphi_T)/\tau_F$, and φ_T is the quantum yield of the triplet formation. The radiative rate constant k_R and the nonradiative rate constant k_{NR} are calculated as shown in Table 1, although the experimental determination of φ_T and the calculation of k_{ISC} and k_{IC} were not attempted. It has been reported for thiophene oligomers that as the molecule size (n) decreases from 5 to 1, k_R does not undergo significant variation, whereas k_{ISC} and in turn k_{NR} show progressive and notable increases.[1–3] The triplet formation is an important deactivation pathway for the singlet excited state of the thiophene oligomers. In a direct observation of the intersystem crossing in poly(3-alkylthiophenes) and α-oligothiophene with 12 repeat units,[19] Heeger and coworkers have recently found that the intersystem crossing rate for derived thiophenes is determined primarily by the relatively large spin–orbit interactions due to the sulfur heteroatom, but not by chain defects, chain ends, or effects due to the side groups. The σ–π interaction may reduce somewhat the triplet yields by suppressing the torsional motions between the thienyl rings or by suppressing the singlet–triplet coupling. Thus, it was found for the oligothienylene–oligosilanylene copolymers that as n becomes smaller from 5 to 1, the change in k_{NR} is rather small, along with a very small alternation of k_R.[16] This accounts for the observed higher φ_F and longer τ_F for the oligothienylene–oligosilanylene copolymers with smaller oligothienylene blocks ($n = 1$–3) than their corresponding oligothiophenes.[16] In the present work, the σ–π interaction in compounds **3**–**12** and **14** reduces the k_{NR} (or k_{ISC}) to small values as shown in Table 1, increasing φ_F and τ_F for these compounds. As mentioned above, the σ–π conjugation in related compounds appears to increase as n decreases.[11,16] Related to bithiophene-containing star-like compounds **3**–**9**, the enhancement in fluorescence is weaker for terthiophene-containing compounds **10**–**14**. This demonstrates that a strong σ–π conjugation is a primarily important factor for a great enhancement in the fluorescence for the star-like molecules. In addition to the effect of the σ–π interaction, the star-like structure is also an important factor for enhancing the fluorescence. This is easily seen from the high quantum yield for compounds **3** and **4**. The effect of the rigid structure becomes somewhat stronger as the side group R increases in length. The substituent at the bridging Si atoms and the terminal one in the arm group R may take an important role in the strong fluorescence of these star-like molecules. A comparison between the quantum yields for compounds **3** and **4** indicates that the end-capping of the bithiophene units with disilanyl groups is favourable to enhancement of fluorescence. Moreover, any steric hindrance limiting the rotation of the C–C bond between two adjacent thiophene rings, may decrease the rate of the nonradiative decay of the excited state, and in turn increase the quantum yield. A more detailed explanation needs a theoretical study.

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