

# Synthesis and Properties of Tri-*tert*-butylated Trioxa and Trithia Analogues of Truxene

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Received: September 24, 2019; Accepted: November 18, 2019; Web Released: November 23, 2019

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#### Abstract

Trioxa- and trithia-truxene derivatives, 3,8,13- (para) and 2,7,12- (meta) tri-*tert*-butylated benzo[1,2-*b*:3,4-*b*':5,6-*b*'']-tri-furan and -tris[1]benzothiophenes (p-tBuTxO, m-tBuTxO, p-tBuTxS, and m-tBuTxS), have been prepared by palladium-catalyzed intramolecular triple dehydrogenative cyclization. While these compounds are soluble in common organic sol-

vents, they have high melting points, mostly more than 300 °C. m-tBuTxO shows a substantial solid state UV fluorescence with a higher quantum efficiency than p-tBuTxO. Both ptBuTxS and m-tBuTxS, however, exhibit only weak fluorescence in both solution and solid state (the  $\lambda_{max}$  of emission in solid state specifically depends on the substitution pattern), but obvious blue phosphorescence is observed in PMMA film under vacuum at r.t. as well as in MeCy at 77 K, which is attributable to the heavy atom effect of sulfur. Meanwhile, p-tBuTxS exhibits a higher hole mobility compared with that of m-tBuTxS in the evaluation of thin-film FET characteristics. These results are discussed in terms of intrinsic molecular structures and arrangements determined by X-ray crystallography.

Keywords: Trioxatruxene | Trithiatuxene | Photoluminescence

#### 1. Introduction

Heteroatom-containing polycyclic arenes are currently recognized as an important class of compounds in the field of organic electronics since they are relatively robust and often exhibit invaluable charge-transporting ability and luminescent property due to the presence of heteroatoms.<sup>1-3</sup> In order to enhance their processability upon increasing solubility, linearalkyl side chains are conventionally introduced to the mother skeletons. The alkyl groups may also promote their chargetransporting ability while furnishing smooth self-assembling nature in the thin-film state. On the other hand, introduction of bulky alkyl groups such as tert-butyl group may enhance not only their solubility, but also molecular luminescence intensity in the solid state while alleviating intermolecular  $\pi$ - $\pi$  interaction. On the contrary, certain arranged crystal packing modes that are suitable for effective charge transport are known to be realized even with the substitution of tert-butyl groups in some polycyclic heteroarenes as well as polyaromatic hydrocarbons.<sup>4</sup> For instance, Geerts and Bao reported that 2,6-di(tert-butyl)substituted BTBT ([1]benzothieno[3,2-b]benzothiophene) 1<sup>4a</sup> shows a high hole mobility (Chart 1). Takimiya demonstrated that its seleno analogue  $2^{4b}$  also has a similar charge mobility. We recently reported the synthesis and photoluminescent properties of 2,8-di-tert-butylated BBFPy (bisbenzofuro[2,3-b: 2',3'-e|pyrazine) **3a** and its 3,9-di-*tert*-butyl isomer **3b**, both of which show intense photoluminescence in solution and solid state.<sup>5</sup> The 2,8-isomer **3a** was demonstrated to specifically exhibit a unique solid state mechanochromic fluorescence in spite of its rigid central core structure, while the 3,9-isomer 3b does not at al. The difference was interpreted in terms of molecular arrangements determined by X-ray crystallography.

Besides linear heteroacenes such as BTBT and BBFPy, polycyclic heteroarenes having  $C_{3h}$  symmetry including benzo-[1,2-*b*:3,4-*b*':5,6-*b*'']trifuran<sup>1d,6</sup> and benzo[1,2-*b*:3,4-*b*':5,6-*b*'']-trithiophene<sup>7</sup> core  $\pi$ -systems have also attracted attention. We recently communicated an effective synthetic method of benzo-[1,2-*b*:3,4-*b*':5,6-*b*'']trisbenzofuran,<sup>8</sup> so-called trioxatruxene, of



Chart 1. Structure of heteroacenes 1, 2, 3a, and 3b.



Chart 2. Structure of trioxatruxenes 4a and 4b and of trithiatruxenes 5a and 5b.

which preparation in synthetically useful yield had been difficult to achieve.<sup>9</sup> Ikeda described a different effective method for constructing the trisbenzofuran.<sup>10</sup> We also successfully prepared its 3,8,13- and 2,7,12-tri-*tert*-butylated compounds, **4a** (p-tBuTxO) and **4b** (m-tBuTxO) (Chart 2). Preliminary measurement of the solid state photoluminescence for **4a** and **4b** suggested that they might have rather different crystal packing modes as anticipated. Consequently, we also have prepared the corresponding trithia analogues **5a** (p-tBuTxS) and **5b** (m-tBuTxS), i.e. 3,8,13- and 2,7,12-tri-*tert*-butylated benzo[1,2-*b*:3,4-*b*':5,6-*b*'']tris[1]benzothiophenes. Then, we have investigated the effect of defference of the heteroatoms and substitution pattern of the *tert*-butyl groups for the pairs of **4a** and **4b** and of **5a** and **5b** on the photophysical and chargetransporting properties. The results are reported herein.

#### 2. Results and Discussion

**2.1 Synthesis.** The synthesis of 3,8,13-trisubstituted trioxatruxene **4a** was performed by means of the coppercatalyzed Ullmann-type reaction of 1,3,5-tribromobenzene with three equivalents of 4-*tert*-butylphenol to give 1,3,5-tris(4-*tert*butylphenoxy)benzene followed by palladium-catalyzed dehydrogenative triple cyclization using Pd(OCOCF<sub>3</sub>)<sub>2</sub> and AgOAc as catalyst and oxidant, respectively, as reported previously (Scheme 1).<sup>8,11</sup> Its 2,7,12-substituted isomer **4b** was obtained similarly.

The 3,8,13-tri-substituted thia-analogue **5a** was synthesized by the nucleophilic substitution of 1,3,5-tribromobenzene with



Scheme 1. Synthesis of trioxatruxenes 4a and 4b and of trithiatruxenes 5a and 5b. (i) ArOH, CuI, Cs<sub>2</sub>CO<sub>3</sub>, NMP, 160 °C, 24 h; *p-t*Bu 59%, *m-t*Bu 68%. (ii) Pd(OCOCF<sub>3</sub>)<sub>2</sub>, AgOAc, PivOH, 130 °C, 10 h; 4a 70%, 4b 68%. (iii) ArSH, NaH, DMF, 160 °C, 24 h; *p-t*Bu 96%. (iv) In(SAr)<sub>3</sub>, Pd(OAc)<sub>2</sub>, Xantphos, N(Et<sub>2</sub>)*i*Pr, DMF, 120 °C, 2 h; *m-t*Bu 92%. (v) Pd(OCOCF<sub>3</sub>)<sub>2</sub>, AgOAc, K<sub>2</sub>CO<sub>3</sub>, PivOH, 130 °C, 48 h; 5a 22%, 5b 19%.

4-*tert*-butylbenznenethiol followed by palladium-catalyzed dehydrogenative triple cyclization. In this cyclization, addition of K<sub>2</sub>CO<sub>3</sub> as base was essential for the reaction to proceed.<sup>12</sup> In the case of 2,7,12-substituted isomer **5b** was employed the sequence involving the palladium-catalyzed triple arylthiolation of 1,3,5-tribromobenzene with tris(3-*tert*-butylphenylthio)-indium under the reported conditions and the oxidative triple cyclization. The use of the former process is due to the ready availability of the tris(arylthio)indium species using the corresponding diaryl disulfide and indium metal (see the Supporting Information for details).<sup>13</sup>

2.2 Absorption and Fluorescence in Solution. То elucidate the effects of the substitution effect on photophysical properties, absorption and fluorescence spectra of 4a, 4b, 5a, and **5b** in chloroform were measured. In the absorption spectra, 4a and 4b have intense peaks with shoulder at 300 nm and weak peaks at the red edge of the spectra. 5a and 5b also have intense peaks around at 310 and 320 nm, and weak peaks at the red edge of spectra. The intense peaks were assignable to  $S_0$ - $S_4$ and S<sub>0</sub>-S<sub>3</sub> from TD-DFT calculation at the B3LYP/6-31G(d) level of theory in Table S2.<sup>10</sup> On the other hand the weak peaks were assignable to  $S_0$ - $S_1$  transitions. In the truxene derivatives,  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions were found to be forbidden, the oscillator strengths (f) being caluculated to be zero correspond to transitions of the HOMO $-1 \rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1, HOMO $-1 \rightarrow LUMO + 1$  and HOMO $\rightarrow LUMO$ . The transitions fobidden of 5a and 5b, also attribute to symmetry-forbidden of  $C_3$ -symmetric structures.

The fluorescence properties of chloroform solutions of **4a**, **4b** and **5a**, **5b** were measured at sufficiently dilute concentration  $(1.0 \times 10^{-5} \text{ M})$ . The solutions of **4a** and **4b** emitted fluorescence in ultraviolet region at around 350 nm (Figure 1). The solutions of **5a** and **5b** emitted deep blue fluorescence at around 390 nm. However, there is no difference depending on the posted position of the *tert*-butyl groups between the truxene derivatives having the same mother skeleton. Trioxatruxenes **4a** and **4b** gave exactly identical fluorescence spectra which have peaks at 350 nm and 363 nm. In the same way, trithiatruxenes **5a** and **5b** also gave exactly identical fluorescence spectra which have peaks at 372 nm, 388 nm, and 408 nm. The trithiatruxenes showed significantly red-shifted fluorescence spectra compared with the trioxatruxenes. Furthermore, the absorption spectra and excitation spectra in chloroform solutions were quite similar in each pair of trioxatruxenes 4a/4b and trithiatruxenes 5a/5b (Figure 1 and Figure S1). From DFT calculations at the B3LYP/6-31G(d) level of theory, trioxatruxene skeleton has a larger HOMO/LUMO energy gap  $(3.94 \text{ eV})^{10}$  than trithiatruxene skeleton (3.66 eV) (Table S2 and Figure S4). Trioxatruxene skeleton also has a deeper HOMO level compared with trithiatruxene skeleton due to the stabilization by furan ring.<sup>14</sup>

Furthermore, these four molecules had characteristic quantum efficiencies in the solutions ( $\Phi_F = 4a$ : 0.10; 4b: 0.07; 5a: 0.01; 5b: 0.02, respectively) (Table 1). The trioxatruxene derivatives moderately emitted independent from the substituent position of the *tert*-butyl groups. On the other hand, the trithiatruxene derivatives had slight fluorescence. The weak fluorescence of trithiatruxene derivatives may be attributed to the heavy atom effect of sulfur in the trithiatruxene skeleton. Such a heavy atom effect may promote intersystem crossing from S<sub>1</sub> to T<sub>1</sub>, and the T<sub>1</sub> excited state may be easily quenched by oxygen and heat that lead to the non-radiative decay.

**2.3 Crystallization.** In order to measure the luminescence properties in the solid state, each molecule was recrystallized using various methods and conditions. Each mother skeleton shows extremely low solubility in organic solvents and only sublimation at 300 °C under atmospheric pressure yielded low quality colorless plate crystals. On the contrary, the introduc-



Figure 1. Absorption and emission spectra of 4a, 4b, 5a, and 5b excited at 292 nm in chloroform solution. Dash lines and solid lines for absorption and emission spectra, respectively. The concentrations were maintained at  $1.0 \times 10^{-5}$  M.

Compd.	Abs (sol.) $\lambda_{max}$ (nm)	Fl. (sol.) <sup>a</sup> λ <sub>max</sub> (nm)	$\Phi_{\rm F}~({\rm sol.})^{\rm b}$	Excit. (cryst.) $\lambda_{max}$ (nm)	Fl. (cryst.) <sup>c</sup> $\lambda_{max}$ (nm)	$     \Phi_{\rm F} \ ({\rm cryst.})^{\rm b} $
4a	271, 298,	350	0.10	281	364	0.14
	322			333		
4b	271, 298,	351	0.07	281	363	0.36
	322			333		
5a	293, 311,	390	0.01	275	440	0.02
	322, 352			362		
5b	293, 311,	388	0.02	277	410	0.04
	322, 352			370		

Table 1. Photophysical properties of oxa- and thia-truxene derivatives in solution and crystalline state.

<sup>a</sup>Excited at 292 nm for **4a**, **4b**, **5a**, and **5b** in CHCl<sub>3</sub> solutions. <sup>b</sup>Absolute quantum efficiency determined for each sample by using an integrating sphere system. <sup>c</sup>Excited at 280 nm for **4a** and **4b** and at 293 nm for **5a** and **5b** in crystalline state, respectively.



Figure 2. Emission spectra of 4a and 4b excited at 280 nm,
5a and 5b excited at 293 nm in the crystalline state; a) at room temperature, b) at 77 K. c) Phosphorescence spectra of 4a and 4b excited at 280 nm, 5a and 5b excited at 293 nm in the crystalline state at 77 K.

tion of *tert*-butyl groups drastically improved solubility of the truxenes, which became soluble even in *n*-hexane, affording high tractability in preparing solutions and films.<sup>15</sup> Furthermore, the substituted compounds simultaneously have high melting points mostly more than 300 °C.

The trioxatruxenes **4a** and **4b** were recrystalliezed by slow evaporation from a mixed solvent of dichloromethane/*n*hexane at room temperature to give colorless needle crystals. The trithiatruxenes **5a** and **5b** were recrystallized by vapor diffusion from a mixed solvent of dichloromethane/*n*-decane at room temperature to give colorless needle crystals. The thiacompounds **5a** and **5b** were also recrystallized by sublimation at 300 °C under atmospheric pressure to give the same crystals as recrystallization from the dichloromethane/*n*-decane mixed solvent.

2.4 Fluorescence in Solid State. The luminescence properties of trioxatruxenes 4a, 4b and trithiatruxenes 5a, 5b in crystalline state were found to have behaviors different from each other.

Trioxatruxenes **4a** and **4b** showed almost the same fluorescence spectra in the ultraviolet region at around 360 nm (Figure 2) (emission maximum wavelengths ( $\lambda_{max}$ ) at 364 nm and 358 nm, respectively). These spectra were quite similar to those in diluted chloroform solutions. The excitation spectra of these trioxatruxene derivatives also overlapped exactly (Figure S1). The similarity of the fluorescence spectra and the excitation spectra in crystalline state suggested that there is also no remarkable effect of the substitution position of *tert*-butyl group on trioxatruxene skeletons even in crystalline state.<sup>5,16</sup>

To the contrary, trithiatruxenes **5a** and **5b** in crystalline state led to different results from those in solution. The fluorescence spectrum of *meta*-substituted derivative **5b** was red-shifted by 35 nm and broadened compared with that in solution. The fluorescence spectrum of *para*-substituted derivative **5a** was more largely red-shifted by 50 nm from 390 nm to 440 nm compared with that in solution. The spectral profile was further broadened. Thus, the substituent positions of *tert*-butyl groups on trithiatruxene skeleton greatly affected the fluorescence properties in crystalline state, though the substituent positions had no effect on the properties in solution.

Comparing the excitation spectra of two trithiatruxene derivatives, there were peaks at the similar regions and no significant difference in their profiles overall. From these results, it was considered that the fluorescence emissions of **5a** and **5b** were derived from the same excitation species even though fluorescence spectra were different.<sup>16</sup>

Furthermore, trioxatruxene and trithiatruxene derivatives showed interesting results of the fluorescence quantum efficiencies  $\Phi_{\rm F}$  in crystalline state. The quantum efficiencies of *para-* and *meta-*substituted trithiatruxenes **5a** and **5b** were 0.02 and 0.04, respectively (Table 1). These values were very slightly improved compared with those in solution. Similarly, the quantum efficiency of *para-*substituted trioxatruxene **4a** was also slightly improved to 0.14. In contrast, surprisingly, the quantum efficiency of *meta-*substituted trioxatruxene **4b** was drastically improved to 0.36. These results indicate that each mother skeleton and each substituent position show aggregation-induced enhanced emission (AIEE)<sup>17</sup> in crystalline state. In particular, the *meta-*substituted trioxatruxene **4b** had the largest AIEE and its quantum efficiency was increased fivefold (Table 1).

**2.5 Relationship between Fluorescence in Solid State and Crystal Structure.** In order to elucidate these intriguing luminescence phenomena, we performed single crystal X-ray analysis for these four crystals (Figure 3). Each molecule originally has a  $C_{3h}$  symmetric structure but gives intrinsically different crystal structure.

Unfortunately, para-substituted trioxatruxene 4a did not give a suitable guest-free crystal for single X-ray diffraction analysis by any methods or conditions. The recrystallization from the mixed solvent of dichloromethane/n-hexane gave a characteristic porous structure with a honeycomb arrangement (Figure 3a). *n*-Hexane used as a poor solvent was incorporated in this pore. Two molecules on the junction of the honeycomb arrangement did not directly overlap and the arms of other three molecules were inserted between the two molecules (Figure S5). The stacking distance between the center molecule and the inserted molecule was 3.41 Å, but the tert-butyl group interfered and the molecular cores were largely slipped; therefore, there is almost no  $\pi$ - $\pi$  overlap. Additionally, apolar *n*-hexane in the pore had no effect on the fluorescence; para-substituted trioxatruxene 4a crystal showed the monomeric emission on the ultraviolet region even in crystalline state (Figure 2a).



Figure 3. Crystal structures of a) 4a, b) 4b, c) 5a, and d) 5b. The white arrows denote the interplanar distance between truxene skeletons between adjacent molecules. Grey: carbon; red: oxygen; yellow: sulfur; white: hydrogen.

In the crystal structure of *meta*-substituted trioxatruxene **4b**, two triangle mother skeletons were overlapped upside down to form a dimer as a partial structure (Figure 3b). The dimers were aggregated alternately to form layer structure, and then the layers were stacked to hierarchically form the whole crystal structure (Figure S6). Even though the degree of the overlap in the dimer was large the stacking distance between two molecules was 3.80 Å. This distance indicates that there is no effective  $\pi$ - $\pi$  interaction in the dimer.<sup>16</sup> In addition, the *tert*-butyl groups were inserted between the dimers in the layer structure. Therefore, there is also no significant interaction between the dimers. Consequently, the crystal of the *meta*-substituted trioxatruxene derivative showed the same monomeric emission in the ultraviolet region as that of the *para*-substituted derivative.

In the crystal structure of *para*-substituted trithiatruxene **5a**, the molecules were stacked straight along the *c* axis to form a columnar structure while reversing to avoid steric hindrance of the *tert*-butyl groups (Figure 3c). Subsequently, the columnar structures were bundled in hexagonal to lead to the whole crystal structure. Adjacent columnar structures were in the same phase, and trithiatruxene **5a** assembled into a layer structure in the *ab* plane (Figure S7). The distance between trithiatruxene skeletons was 3.54 Å and there was a large degree of overlap between them to give a strong  $\pi$ - $\pi$  interaction infinitely along the *c* axis. This strong infinite  $\pi$ - $\pi$  interaction caused the larger red-shift and the greater broadening in the fluorescence of trithiatruxene **5a** in crystalline state (Figure 2a).<sup>18</sup>

Moreover, two triangle mother skeletons of *meta*-substituted trithiatruxene **5b** were also overlapped upside down in crystalline state to lead to a dimer as a partial structure in the same way as those of *meta*-substituted trioxatruxene **4b** (Figure 3b, d). These dimer structures seen in **4b** and **5b** should be considered to be a common structure for alleviating the steric hindrance of the *tert*-butyl group at the *meta* position. In the case of **5b**, however, the dimers were aggregated in parallel to form a layer structure, and then the layers were stacked to form the whole crystal structure (Figure S8). In this crystal, the degree of the overlap in the dimer was large and the stacking distance between two molecules was significantly close, 3.43 Å. These two factors caused an effective  $\pi$ - $\pi$  interaction in the dimer but there is no significant interaction between the dimers due to the steric hindrance of the *tert*-butyl groups. The large red-shift and the broadening in the fluorescence of trithiatruxene **5b** in crystalline state were only due to the effective  $\pi$ - $\pi$  interaction in the dimer.

In each crystal, the improvement of the quantum efficiency was caused by the suppression of the vibrational deactivation by the molecular immobilization in crystalline state.<sup>19</sup> Additionally, the bulky *tert*-butyl group effectively suppressed the interaction between fluorophores even in crystalline state. Furthermore, in the crystal of *meta*-substituted trioxatruxene **4b** which showed the largest AIEE, the trioxatruxene skeleton was distorted by the steric hindrance of the *tert*-butyl groups (Figure S6d). Consequently, centrosymmetry breaking should be induced to lead to the prominent AIEE.<sup>20</sup> These results indicate that in the trioxatruxene and trithiatruxene crystals, the posted position of the *tert*-butyl groups plays an important role in the profiles and the strengths of the crystalline state emission.

2.6 Phosphorescence in Solid State. The steady-state luminescence measurement of each crystal was also performed at 77 K. Both trioxatruxenes 4a and 4b only showed fluorescence at the original peak position which was not different from the room temperature measurement. On the other hand, both trithiatruxenes 5a and 5b came to show phosphorescence in addition to fluorescence even in the steady-state luminescence measurement (Figure 2b). The crystal of meta-substituted trithiatruxene 5b emitted fluorescence at the original peak position (430 nm) and larger broad phosphorescence at around 540 nm. Similarly, the crystal of para-substituted trithiatruxene 5a also exhibited a little sharpened fluorescence at the original peak position (450 nm) and broad phosphorescence at around 570 nm. As comparing these two crystals, the phosphorescence of 5a was shifted to longer wavelength than that of 5b as in the case of the fluorescence. This result indicates that the phosphorescence in crystalline state is also influenced by the interaction between molecules.

Furthermore, the phosphorescence measurement at 77 K revealed that both **4a** and **4b** also had weak phosphorescence at a longer wavelength region (Figure 2c). The crystals of **4a** and **4b** exhibited almost the same phosphorescence at around 430 nm. As mentioned before, the crystals of **4a** and **4b** emitted fluorescence at almost the same wavelength. This result implied that the structural factors of **4a** and **4b** also had no effect on the phosphorescence in crystalline state. In contrast, the phosphorescence measurement showed that the profile of **5a** was broad and the profile of **5b** had a vibrational structure.<sup>21</sup>

From TD-DFT calculation (Table S2 and Figure S4), the oscillator strengths (f) of the S<sub>0</sub>-T<sub>1</sub>, S<sub>0</sub>-T<sub>2</sub>, and S<sub>0</sub>-T<sub>3</sub> transitions of trithiatruxene skeleton are also zero, therefore these transitions are found to be forbidden. The prominent phosphorescence of trithiatruxenes **5a** and **5b** may be attributed to the heavy atom effect of sulfur on the trithiatruxene skeleton. The heavy atom effect may promote the efficient intersystem crossing from S<sub>1</sub> to T<sub>n</sub>, and subsequent phosphorescence from T<sub>1</sub> excited state is not quenched by the suppression of the molecular vibration at 77 K. From the orbital distribution and the oscillator strengths (f), n- $\pi^*$  transition is forbidden, therefore the phosphorescence of trithiatruxene seems to be derived from  $\pi$ - $\pi^*$  transition.

**2.7 Luminescence in Polymer Films.** Next, we performed the luminescence measurement of the trioxatruxene and trithiatruxene derivatives in polymer films under various conditions. Each PMMA film in which each derivative was only doped at 1 wt% was prepared by spin coating. Steady-state luminescence measurement at room temperature in the air revealed that each PMMA film emitted in the same manner

with each chloroform solution (Figure 1 and 4a). Because molecules are not closely packed in the film, there is no effective interaction between the luminophores. PMMA films containing the *meta*- and *para*-substituted derivatives exhibited the same fluorescence profiles.

On the other hand, the quantum efficiencies of PMMA films of meta- and para-trioxatruxene derivatives 4a and 4b were effectively enhanced compared with those of chloroform solution from 0.10 and 0.07 to 0.20 and 0.24, respectively (Table 1 and 2). These enhancements for the trioxatruxene derivatives are attributable to the suppression of the molecular vibration in polymer matrix.<sup>22a</sup> However, the quantum efficiencies of doped PMMA films of the trithiatruxene derivatives were still low due to the heavy atom effect. This characteristic fluorescence profile of each derivative was observed in apolar Zeonex film in the same manner (Figure S3).<sup>22</sup> Therefore, it seems likely that there is no difference in the type of polymer matrix in the emission profile of these derivatives. However, the quantum efficiencies in Zeonex films of 4a and 4b were more enhanced than those in PMMA films (Table S1). Zeonex is a cycloolefin polymer and is less polar and somewhat superior in the oxygen barrier property compared with PMMA.<sup>22a</sup> These properties might affect the quantum efficiencies.

Subsequently, we performed the luminescence measurement in polymer films at room temperature under vacuum condition in order to eliminate the effect of oxygen. There was no change in the emission spectra of PMMA films of trioxatruxene derivatives **4a** and **4b** in the steady-state luminescence measurement (Figure 4a, b). Each film showed only fluorescence at around 350 nm which is also the same as that in chloroform solution.



**Figure 4.** Emission spectra of PMMA polymer films containing **4a** and **4b** (1 wt%) excited at 270 nm, **5a** and **5b** (1 wt%) excited at 293 nm at room temperature a) in the air and b) under vacuum. c) Photographs of PMMA films of *para*-substituted trithiatruxene **5a** (prepared in an NMR tube) in the air (left) and under vacuum (right) under UV irradiation ( $\lambda = 254$  nm).

Table 2. Photophysical properties of truxene derivatives in PMMA films in the air or under vacuum.

Compd. –	Steady-state photoluminescence in the air			Steady-state photoluminescence under vacuum					Phosphorescence under vacuum	
	Fl <sup>a</sup> ) (nm)	Ph λ (nm)	${\varPhi_{\mathrm{F}}}^{\mathrm{b}}$	Fl <sup>a</sup> λ (nm)	Ph <sup>a</sup> λ (nm)	${{ { { { \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! $	${\varPhi_{\mathrm{P}}}^{\mathrm{b}}$	$ au_{\mathrm{Ph}}~(\mathrm{sec})^{\mathrm{c}}$	Ph <sup>a</sup> λ (nm)	$ au_{\mathrm{Ph}}~(\mathrm{sec})^{\mathrm{d}}$
	max (IIII)	Max (IIII)		Mmax (IIII)	Max (IIII)				max (IIII)	
4a	351, 364	n.d.	0.20	351, 364	faint (447)			—	451	2.51
4b	351, 365	n.d.	0.24	351, 365			_	_	448	1.72
5a	375, 390, 410	n.d.	0.01	374, 390, 410	456, 483	0.01	0.15	0.13	_	_
5b	372, 389, 409	n.d.	0.02	372, 389, 409	457, 485	0.02	0.18	0.14	—	—

<sup>a</sup>Excited at 270 nm for **4a** and **4b**, and at 293 nm for **5a** and **5b** in film, respectively. <sup>b</sup>Absolute quantum efficiency determined for each sample by using an integrating sphere system. <sup>c</sup>Detected at 456 nm for **5a** and **5b**. <sup>d</sup>Detected at 450 nm for **4a** and **4b**.



Figure 5. Steady-state luminescence of methylcyclohexane solution at room temperature and 77 K. Dash lines for the room temperature measurement and solid line for the measurement of frozen solution at 77 K. a) 4a and 4b excited at 271 nm, b) 5a and 5b excited at 287 nm. c) Photograph of 4a and 5a upon irradiation with 254 nm UV light in the frozen methylcyclohexane at 77 K and afterglow light changes over time.

Phosphorescence measurement revealed the PMMA films of **4a** and **4b** have extremely weak phosphorescence at around 450 nm (Figure S2). On the other hand, PMMA films of 5a and 5b came to emit prominent phosphorescence, which had peaks at 460 nm and 485 nm even in the steady-state luminescence measurement under vacuum (Figure 4b and 4c). Each PMMA film of trithiatruxene derivatives 5a and 5b exhibited almost identical phosphorescence unlike the crystalline state. These phosphorescence emissions of the films were observed at shorter wavelength region relative to those of the crystals. In addition, much weaker fluorescence at around 380 nm, which was the same as that in air was simultaneously observed compared with phosphorescence. These results also strongly supported the efficient intersystem crossing in the polymer film of trithiatruxene derivatives. The fluorescence quantum efficiencies of the para- and meta-substituted trithiatruxenes 5a and 5b were  $\Phi_{\rm F} = 0.01$  and 0.02 under vacuum condition, respectively. These values are the same as those in chloroform solution and PMMA film in air. However, the phosphorescence quantum efficiencies of **5a** and **5b** were sufficiently large as  $\Phi_{\rm P} =$ 0.15 and 0.18, respectively. And their phosphorescence life times were  $\tau_{\rm P} = 0.13$  sec and 0.14 sec, respectively.

In the phosphorescence measurement under vacuum, the PMMA films of *para-* and *meta-*substituted trioxatruxenes **4a** and **4b** yielded the same phosphorescence profiles (Figure S2) as that of trioxatruxene without *tert-*butyl group substitution at 77 K reported by Ikeda.<sup>10</sup>

In the dispersed state such as solution and polymer matrix, it does not matter whether *tert*-butyl groups are present or not, because molecular conformation is not restricted. The phosphorescence quantum efficiencies and life times of PMMA films of **4a** and **4b** under vacuum were  $\Phi_P = 0.02$  and 0.01,  $\tau_{Ph} = 2.51$  sec and 1.72 sec, respectively (Table 2). Namely, the phosphorescence intensity was low but the phosphorescence life time in a trade-off relationship was long in trioxatruxene derivatives. On the other hand, the PMMA films of **5a** and **5b** exhibited strong phosphorescence but the life times of them were one order of magnitude shorter compared with those of the PMMA films of **4a** and **4b**.

**2.8 Phosphorescence in Frozen Solution at 77 K.** Finally, we performed the luminescence measurements of trioxatruxene and trithiatruxene derivatives in frozen solution.

Trioxatruxenes **4a** and **4b** had only very sharp vibrational fluorescence in methylcyclohexane at room temperature. But these derivatives came to simultaneously exhibit significant phosphorescence comparable to the original fluorescence when the solution was cooled to 77 K and frozen (Figure 5a). These phosphorescence emissions had the maximum peaks at around 450 nm and some side peaks around the maximum peak ( $\tau_{ph} =$ **4a**: 5.01 sec and **4b**: 4.67 sec, respectively), which were almost identical to those of unsubstituted trioxatruxene.<sup>10</sup> As mentioned before, in contrast, the polymer films of **4a** and **4b** did not show phosphorescence under vacuum (Figure 4b). These results indicate that non-radiative deactivation of T<sub>1</sub> excited state of trioxatruxene is more efficiently reduced by the suppression of the molecular vibration than by the suppression of the energy transition to oxygen.

Trithiatruxenes **5a** and **5b** also had only very sharp vibrational fluorescence in methylcyclohexane at room temperature. On the other hand, these trithiatruxene derivatives in the frozen

evaporated thin film of each compound.aCompd.HOMOLUMO $E_{\rm g}$  (Opt.)

the

of

vacuum-

 Table 3.
 Electrochemical
 properties

Compd.	HOMO	LUMO	$E_{g}$ (Opt.)
<b>4</b> a	5.69	1.81	3.88
4b	5.74	1.94	3.80
5a	5.29	1.65	3.64
5b	5.52	1.98	3.54

<sup>a</sup>HOMO was measured by photoelectron yield spectroscopy. LUMO was measured by subtracting optical energy gap from the measured HOMO level.

solution at 77 K came to overwhelmingly exhibit phosphorescence from the original fluorescence in the same manner in PMMA films under vacuum (Figure 5b).

The phosphorescence profiles of the methylcyclohexane frozen solutions of the trithiatruxene derivatives were sharpened but similar to those of the PMMA films under vacuum (Figure 4b).

The trithiatruxene derivatives had comparatively short phosphorescence lifetime ( $\tau_{ph} = 5a$ : 0.45 sec and 5b: 0.46 sec, respectively) in exchange for strong phosphorescence. Figure 5c shows the photographs of 4a and 5a upon irradiation with 254 nm UV light and the changes over time of the afterglow light. Truxenes 4a and 5a emitted moderate deep blue light and strong greenish-blue light upon irradiation 254 nm, respectively. When the UV light was turned off, the phosphorescence of 5a, which has a short life-time was rapidly reduced at 0.5 sec and completely quenched at 3 sec. On the other hand, the phosphorescence of 4a which has the longer life time was still observed even after 5 sec.

**2.9 Thin-Film Properties.** These truxene compounds are thermally stable and soluble due to the *tert*-butyl units. Thus, stable and uniform thin films can be prepared by both vacuum evaporation and spin-coating.

Thin-film of each compound was prepared by a vacuum evaporation technique. The HOMO and LUMO levels of the thin-films are summarized in Table 3. The photoelectron yield spectra and UV/vis absorption spectra are shown in Figure S9. The trithiatruxenes indicated higher HOMO levels compared to the trioxatruxenes. This trend is attributable to the extended orbital of the sulfur atom and agrees with the DFT calculation results. The photoabsorption edge was around 350 nm for the trithiatuxenes, and around 320 nm for the trioxatruxenes, resulting in a lower energy gap for the trithiatruxenes. In comparison of the substituent positions, *para*-substituted compounds (**4a** and **5a**) indicated higher HOMO levels in comparison with the corresponding *meta*-substituted compounds (**4b** and **5b**).

Thin-film X-ray diffraction patterns of each compound are shown in Figure S10. All the compounds indicated diffraction peaks for vacuum-evaporated films on the room-temperature substrates, suggesting they have measureable crystalline characters in the film state, although they have bulky substituents of *tert*-butyl groups and high solubility. Particularly, **5a** indicating a sharp diffraction peak appeared to have more crystalline character. The higher HOMO level of **5a** is attributable to the stronger electronic (HOMO-HOMO) interaction with the neighboring molecules. The peak at 6.2 degrees corresponds to (2-10)



Figure 6. a) Output characteristics at  $V_{\rm G} = -100$  V and b) transfer characteristics at  $V_{\rm DS} = -100$  V for 5a films prepared by the gap-cast method. The open and filled symbols indicate a forward and reverse scan, respectively.

plane of the single crystal structure, indicating the molecules tend to align with edge-on orientation on the substrate.

**2.10 Charge Carrier Mobilities.** The charge carrier mobility was measured by organic field-effect transistor devices. The active layer was thermally evaporated on an Si/SiO<sub>2</sub> substrate with a top contact configuration. Both the thia- and oxatruxenes showed p-type modulation. The device performance parameters are summarized in Table S3. For the thermally evaporated films, the estimated hole mobilities were on the order of  $10^{-6}$  cm<sup>2</sup>/Vs. *para*-Thiatruxene **5a** showed the highest mobility among these compounds and the *para*-substituted compounds (**4a** and **5a**) indicated somewhat higher mobilities compared to the corresponding *meta*-substituted compounds (**4b** and **5b**):  $\mu$  (×10<sup>-6</sup> cm<sup>2</sup>/Vs) **5a** 8.63 > **4a** 8.25 > **4b** 4.84 > **5b** 4.44.

To obtain highly crystalline films, we also prepared the FET devices with a gap-cast technique for the thiatruxene **5a**. In the gap-cast technique, a film is prepared by injecting a solution into a gap between a substrate and a glass lid on it with a spacer.<sup>23</sup> This technique allows slow drying to form the crystalline films. The output characteristics and transfer curves for **5a** are shown in Figure 6. The FET mobility was improved with about two orders of magnitude and estimated to be  $4.94 \times 10^{-4} \text{ cm}^2/\text{Vs}$ .

Here, we discuss relationship between the crystal structure of each compound and potential for carrier transport through the crystal. The FET mobilities can be partially interpreted from the electronic coupling between neighboring molecules.<sup>24</sup> Figure 7 shows electronic couplings for each crystal structure calculated by using Amsterdam Density Functional (ADF) software. Compound **5a** (p-tBuTxS) with one-dimensional stacking structure indicated electronic couplings as large as 138.5 meV



Figure 7. Electronic coupling with the neighboring molecules in the single crystal calculated by ADF.

due to the strong  $\pi$ - $\pi$  interaction, while the intercolumnar interaction is nearly zero. Compound 5b (m-tBuTxS) forms dimer structure in the crystal. The electronic coupling within the dimer is very high (175.9 meV), but that between the dimer is very small. This means there is no efficient pathway for carrier transport through the crystal. Compound 4a (p-tBuTxO) has honeycomb structure, where  $\pi$ - $\pi$  interaction in c-axis is not so high, but lateral interaction in ab plane exists. Compound 4b (m-tBuTxO) also indicated dimer structure. From the viewpoint of crystal structure, meta-substituted compounds tend to form dimer in the crystal, which is not suitable for effective charge transport. The para-substituted compounds having successive  $\pi$ - $\pi$  stacking may show relatively higher charge mobilities. The thiatruxene 5a has the stronger electronic coupling and higher crystallinity in the thin films, but such an isolated onedimensional column is disadvantageous because carrier transport is easily disturbed by unavoidable defects. In contrast, 4a has the weaker electronic coupling and lower crystallinity, but the honeycomb structure brings about two-dimensional carrier transport, which is more robust for defects. Consequently, 5a and 4a is considered to indicate the comparable mobilities in the FET devices.

#### 3. Conclusion

Tri-*tert*-butylated trioxatruxene and trithiatruxene derivatives were successfully synthesized by a palladium-catalyzed dehydrogenative triple cyclization. Introduction of the *tert*butyl groups formed the sparingly soluble trioxatruxene and

trithiatruxene skeletons which have large triangle  $\pi$ -planes, making them highly soluble in various organic solvents, even in *n*-hexane, with keeping high melting points over 300 °C. The trioxatruxene derivatives exhibited significant fluorescence in crystalline state: especially the *meta*-substituted derivative had a prominent AIEE in crystalline state due to distortion of the molecular skeleton. On the other hand, fluorescence of the trithiatruxene derivatives was effectively quenched by the heavy atom effect of sulfur in the truxene skeleton. However, when inactivation factors of  $T_1$  excited state such as oxygen and molecular vibration were suppressed, the trithiatruxene derivatives came to emit prominent phosphorescence in various states. Furthermore, the posted position of tert-butyl groups was found to be a crucial factor determining the crystal packing patterns that affect charge-transporting properties as well as solid state photoluminescence. Thus, the para-substituted compounds were found to show better charge mobilities with the favorable molecular packings. These results may provide useful information for designing new polycyclic heteroaromatic compounds as  $\pi$ -conjugated organic materials. We are currently preparing related polycyclic heteroarenes and will report the results in due course.

#### 4. Experimental Section

Details of experimental procedures and characterization data of compounds are provided in the Supporting Information.

CCDC 1920623 (4a), 1920624 (4b), 1920625 (5a), and 1920626 (5b) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

This work was supported by JSPS KAKENHI Grant Numbers JP17H06092 (Grant-in-Aid for Specially Promoted Research) to M.M., JP17H05371 and JP 19H04580 (in Coordination Asymmetry) to N.T., and JP 17H03134 (Grant-in-Aid for Scientific Research (B)) to K.N. The authors wish to acknowledge Mr. H. Kaida (Osaka University) for the initial synthetic work and Prof. A. Saeki (Osaka University) for the PYS measurements.

#### **Supporting Information**

Experimental procedures, characterization data of compounds, and descriptions for theoretical caluculations. This material is available on https://doi.org/10.1246/bcsj.20190269.

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