

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Experimental and theoretical investigation of tetra-oxidized terarylenes with high-contrast fluorescence switching

 Rui Kanazawa,^a Maki Taguchi,^a Takuya Nakashima^a and Tsuyoshi Kawai^{a,b*}

 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

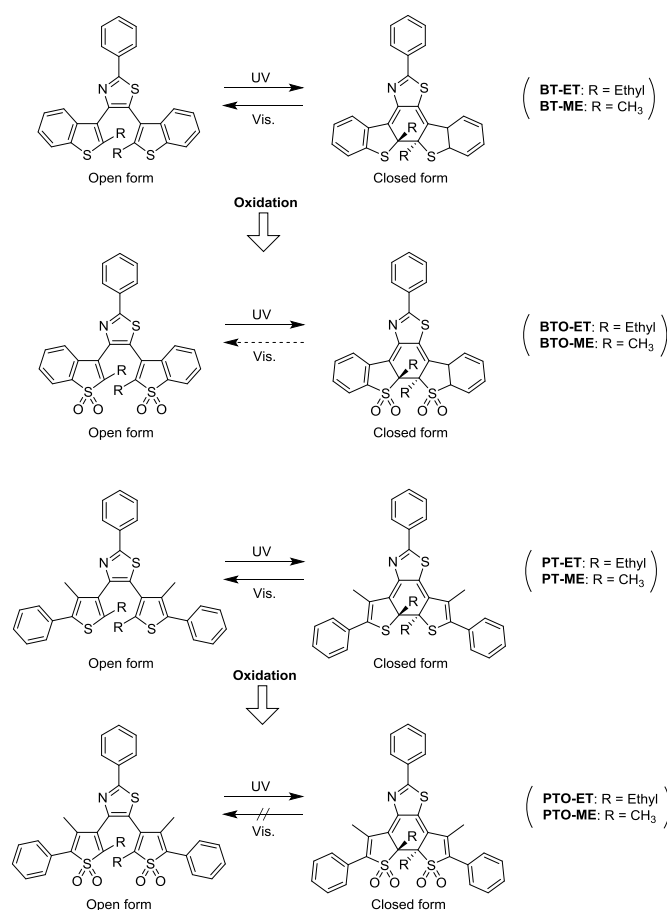
www.rsc.org/

Tetra-oxidized terarylenes having ethyl groups at the reactive carbon atoms are synthesized and their photophysical properties are studied. Their closed-ring isomers exhibit much lower cycloreversion quantum yields and relatively high fluorescence quantum yields. Introducing ethyl groups at the reactive carbon atoms provides an improvement in the fluorescence quantum yields by the intramolecular hydrogen bonding in the closed-ring isomers to reduce the non-radiative decay processes coupled with molecular motions. Quantum chemical calculations were carried out to study their geometrical and optical properties, which agree well with the experimental findings.

Introduction

Photoresponsive molecular materials have been an attractive subject of research for a long time.¹⁻³ They are even more noteworthy with the emergence of high performance optoelectronic organic devices involving photoreactive systems.^{4,5} For example, photoresponsive molecular systems were integrated with organic electronics such as photovoltaic solar cells (OPVs),^{6,7} field-effect transistors (OFETs)⁸⁻¹⁰ and light emitting diodes (OLEDs)¹¹⁻¹³ to switch their performances by means of light irradiation. Among the photoresponsive molecules, photochromic compounds based on diarylethenes show great prospects in potential applications for photonic devices due to their switchable photophysical properties.¹⁴

Meanwhile, we have proposed a triangle terarylene system which is composed of three or more heteroaryl groups to form a 6 π -hexatriene backbones, which undergo reversible photoinduced 6 π -electrocyclization in a similar manner to diarylethenes.¹⁵⁻¹⁷ This type of photochromic compounds exhibited excellent photochromic performances including very high photoreactivity¹⁸ as well as various switching capabilities.¹⁹ Recently, we reported that the substitution of aryl units with oxidized thienyl groups having *S,S*-dioxide moieties is effective to improve the fluorescence properties of closed-ring form isomers of terarylenes, in a similar manner to diarylethene based molecules^{20,21} and some of them showed quasi-irreversible photo-cyclization reaction with very small photo-cycloreversion quantum yields.²² Terarylenes with *S,S*-dioxidized aryl units were further demonstrated as an emitting material with a photo-



Scheme 1 Photochromic reaction of terarylenes

patternable property in OLED devices.¹³ Meanwhile, Irie and co-workers reported very high fluorescence quantum yields over 80% for closed-ring form of diarylethenes having *S,S*-dioxidized benzothiophenes with ethyl groups on the reactive carbon atoms at both ends of a 6 π -system.²¹ Although the effect of substituents on the photophysical properties including the fluorescence

^a Graduate School of Materials Science, Nara Institute of Science and Technology, NAIST, 8916-5 Takayama, Ikoma, Nara, 630-0192, Japan.

E-mail: tkawai@ms.naist.jp

^b NAIST-CEMES International Collaborative Laboratory for Supraphotoreactive System, Centre d'Élaboration de Matériaux et d'Études Structurales, CEMES, 29, rue Jeanne Marvig, BP 94347, Toulouse 31055, France.

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

property and photochromic reactivity of tetra-oxidized diarylethenes and terarylenes have been reported, details of photophysical properties and approaches by means of quantum chemical calculations have not been fully studied.¹¹

In attempt to reveal the relationship between molecular structures and photophysical properties of these photochromic compounds, we studied terarylene derivatives which have different side aryl groups with ethyl substituents at the reactive carbon atoms. We focused on the intramolecular hydrogen bonding between the alkyl groups at the reactive carbon atoms and the oxygen atoms of SO₂ units, which is considered to contribute to the improvement of fluorescence properties in closed-ring isomers. Ethyl groups are therefore introduced at the reactive carbon atoms to enhance the CH/OS intramolecular hydrogen bonding. Terarylenes with methyl groups at the reactive carbon atoms were also prepared as reference compounds. Their photochromic and fluorescent properties are compared and quantum chemical calculations based on the density functional theory (DFT) have also been performed to investigate the effect of molecular structures on their photophysical properties.²³

Experimental

General

¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a JEOL JNM-AL300 instrument. Normal- and reverse-phase HPLC were performed with a LaChrom Elite (Hitachi). Mass spectra were measured with a JEOL AccuTOF JMS-T100LC (ESI) and JML-700 (EI) instrument. UV/Vis absorption and fluorescence spectra were obtained with a V660 spectrophotometer (JASCO) and an FP6500 fluorescence spectrophotometer (JASCO), respectively. Fluorescence lifetimes and absolute fluorescence quantum yields of compounds were measured with a FluoroCube 3000U (Horiba) and a Hamamatsu C9920-02, respectively. Quantum yields of photo-cyclization ($\Phi_{O\rightarrow C}$) and cycloreversion ($\Phi_{C\rightarrow O}$) were measured by using a photoreaction quantum yield measurement system (Shimadzu, QYM-01) with a corrected power meter, which can provide accurate irradiation photon numbers at a given wavelength.²⁴

To investigate the photochemical reactivity of terarylenes, we studied on quantum chemical calculations with Gaussian 09 program package.²⁵ Geometry optimization of compounds at the ground states was performed with density functional theory (DFT) at the ω B97XD/6-31G(d,p) level.²⁶ Calculations for the excited states were also carried out with time dependent density functional theory (TDDFT) by the ω B97XD/6-31G(d,p) level theory.

Synthesis

Methyl-substituted terarylenes (**BT-ME**, **PT-ME**, **BTO-ME** and **PTO-ME**) were prepared according to the procedures described in the previous literature.^{16a,c,22} Ethyl-substituted terarylenes were synthesized following the procedures. **BT-ET** were synthesized by the cyclization reaction of the corresponding α -hydroxyketones with

thioamides, as reported by Krayushkin and co-workers.²⁷ **PT-ET** were synthesized by conventional Suzuki cross-coupling between corresponding thiazole dibromide as the central unit and thiophene pinacol borates as the side aryl units. These precursor terarylenes are treated with 70% 3-chloro-perbenzoic acid (*m*-CPBA, containing 30 wt% water) to afford tetra-oxidized terarylenes **BTO-ET** and **PTO-ET**, respectively.

4,5-bis(2-ethylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (**BT-ET**).

2-hydroxy-1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)ethanone (1.9 g, crude) was added to a solution of thiobenzoamide (690 mg, 5.0 mmol) in CF₃CO₂H (3 mL) at room temperature for 24 h. The reaction mixture was poured into water and extracted with Et₂O. The organic layers were separated, washed with brine, dried over MgSO₄, and evaporated. Column chromatography (silica, hexae/AcOEt 10:1) and the following reverse phase HPLC (methanol) afforded 4,5-bis(2,4-diethyl-5-phenylthiophen-3-yl)-2-phenylthiazole (**BT-ET**) as a white solid (700 mg, 1.5 mmol) in 30% yield in three steps. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.11-8.06 (m, 2H), 7.83-7.60 (m, 4H), 7.52-7.46 (m, 4H), 7.36-7.22 (m, 3H), 2.72-2.21 (br m, 4H), and 0.95-0.52 (br m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 167.44, 148.72, 148.45, 147.61, 139.78, 138.01, 137.80, 133.55, 130.22, 128.98, 127.90, 126.48, 125.80, 124.52, 124.35, 124.20, 124.06, 123.70, 122.82, 122.13, 122.01, 121.84, 121.53, 22.82, 22.69, 14.97. EI HRMS: *m/z* calcd for C₂₉H₂₄NS₃⁺ [*M*]⁺: 482.11; found 482.11.

4,5-bis(2-ethylbenzo[*b*]thiophene-*S,S*-dioxide-3-yl)-2-phenylthiazole (**BTO-ET**).

BT-ET (72 mg, 0.15 mmol) and *m*-CPBA (520 mg, 3.0 mmol) were dissolved in CH₂Cl₂ (25 mL). The mixture was stirred at room temperature for 24 h in the dark. The reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layers were separated, washed with brine, dried over MgSO₄, and evaporated. The residue was purified by short-path column chromatography (silica, chloroform), and reverse-phase HPLC (methanol). The following GPC (chloroform) afforded 4,5-bis(2,4-ethylbenzo[*b*]thiophene-*S,S*-dioxide-3-yl)-2-phenylthiazole (**BTO-ET**) as a white solid (70 mg, 0.13 mmol, 86% yields). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.06-8.02 (m, 2H), 7.77-7.73 (m, 2H), 7.56-7.46 (m, 8H), 7.37-7.34 (m, 1H), 2.63-2.51 (m, 4H), 1.25-1.16 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 170.42, 146.03, 144.86, 144.18, 136.00, 135.76, 133.42, 132.13, 131.62, 131.56, 131.42, 130.50, 130.30, 129.75, 129.37, 127.57, 126.78, 125.30, 123.61, 122.67, 121.82, 121.46, 18.34, 11.65, 11.55. EI HRMS: *m/z* calcd for C₂₉H₂₃NNaO₄S₃⁺ [*M*+Na]⁺: 568.07; found 568.07.

4,5-bis(2-ethyl-4-methyl-5-phenylthiophen-3-yl)-2-phenylthiazole (**PT-ET**).

A mixture of (2-ethyl-4-methyl-5-phenylthiophen-3-yl) boronic acid pinacol ester (2.2 g, 6.7 mmol), 4,5-dibromo-2-phenylthiazole (870 mg, 2.7 mmol) and triphenylphosphine (370 mg, 1.4 mmol), 1,4-dioxane (87 ml) and 2 M K₃PO₄ (87 ml) was treated with N₂ bubbling for 60 min. Pd(PPh₃)₄ (320 mg, 0.27 mmol) was added the mixture and was refluxed at 120 °C for 3 days. The resulting solution was poured into water, neutralized with HCl aq., extracted with AcOEt,

washed with brine, dried over MgSO_4 , and evaporated. The residue was purified by column chromatography (silica, hexane/AcOEt 19:1), and the following GPC (chloroform) afforded 4,5-bis(2-ethyl-4-methyl-5-phenylthiophen-3-yl)-2-phenylthiazole (**PT-ET**) as a yellow solid (700 mg, 45% yields). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.06-8.04 (m, 2H), 7.50-7.39 (m, 10H), 7.37-7.53 (m, 1H), 7.34-7.26 (m, 2H), 2.82-2.38 (m, 4H), 2.17 (s, 6H), 1.34-0.79 (br m, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 166.33, 149.65, 145.61, 145.02, 135.25, 134.96, 134.79, 133.62, 132.79, 132.56, 130.02, 129.17, 129.08, 128.91, 128.45, 128.37, 127.19, 126.89, 126.34, 22.37, 15.58, 14.61. EI HRMS: m/z calcd for $\text{C}_{35}\text{H}_{31}\text{NS}_3$ [M] $^+$: 561.16; found 561.16.

4,5-bis(2-ethyl-4-methyl-5-phenylthiophene-*S,S*-dioxide-3-yl)-2-phenylthiazole (PTO-ET). **PT-ET** (56 mg, 0.10 mmol) and *m*-CPBA (180 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 27 h in the dark. The reaction mixture was poured into water and extracted with CH_2Cl_2 . The organic layers were separated, washed with brine, dried over MgSO_4 , and evaporated. The residue was purified by short-path column chromatography (silica, chloroform), and the following normal-phase HPLC (hexane / AcOEt = 4 : 1) afforded 4,5-bis(2-ethyl-4-methyl-5-phenylthiophene-*S,S*-dioxide-3-yl)-2-phenylthiazole (**PTO-ET**) as a white solid (24 mg, 38% yields). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.02-7.99 (m, 2H), 7.65-7.57 (m, 4H), 7.54-7.42 (m, 9H), 2.67-2.48 (m, 4H), 2.12 (s, 3H), 1.99 (s, 3H), 1.42-1.37 (m, 3H), 1.33-1.28 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 169.52, 146.42, 143.56, 136.93, 136.25, 135.01, 133.73, 132.10, 131.50, 131.09, 129.94, 129.70, 129.35, 129.20, 129.10, 129.00, 128.28, 127.11, 126.75, 126.66, 126.07, 18.89, 18.75, 14.37, 14.00, 11.56. EI HRMS: m/z calcd for $\text{C}_{35}\text{H}_{31}\text{NNa O}_4\text{S}_3$ [$M+\text{Na}$] $^+$: 648.13; found 648.13.

Result and discussion

Photochromism in solution

As shown in Fig. 1a, the precursor terarylene **BT-ET** showed no absorption band in the visible range in solution. Upon irradiation with UV light ($\lambda_{\text{ex}} = 313$ nm), the colorless solution of **BT-ET** turned blue, and a new absorption band appeared at around 560 nm. The colored solution completely bleached upon irradiation with visible light, giving an absorption spectrum identical to that of the initial colorless solution. An isobestic point was observed at 289 nm, which supported the two-component photochromic reaction as depicted in Scheme 1. Similar reversible photochromic behaviour was also observed for **PT-ET** (Fig. 1c). The values of λ_{max} and extinction coefficient ϵ are summarized in Table 1 with the photochromic reaction quantum yields.

Colorless solutions of tetra-oxidized terarylenes **BTO-ET** and **PTO-ET** were also showed coloration behaviour upon irradiation with UV light, and turned to orange (Fig. 1b, d). **BTO-ET** slowly returned to the initial colorless solution upon irradiation with visible light, whereas **PTO-ET** showed negligible photo-breaching reaction even after irradiation with visible light for several hours.

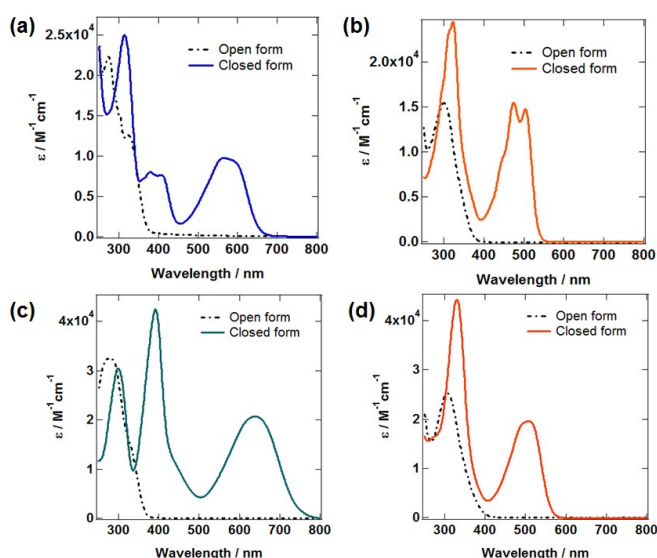


Fig. 1 Absorption spectra of (a) **BT-ET**, (b) **BTO-ET**, (c) **PT-ET** and (d) **PTO-ET** in CH_2Cl_2 : open-ring form (black dotted lines) and closed-ring form (colored solid lines).

Table 1 Optical properties of ethyl-substituted terarylenes in CH_2Cl_2

Compd.		$\lambda_{\text{max}} / \text{nm}$	$\Phi_{\text{O} \rightarrow \text{C}}$	$\Phi_{\text{C} \rightarrow \text{O}}$
		($\epsilon / 10^4 \text{M}^{-1} \text{cm}^{-1}$)		
BT-ET	Open-ring form	273 (2.28)	0.39	-
	Closed-ring form	566 (0.67)	-	0.24
BTO-ET	Open-ring form	300 (1.54)	0.40	-
	Closed-ring form	474 (1.55), 504 (1.48)	-	0.033
PT-ET	Open-ring form	281 (3.24)	0.16	-
	Closed-ring form	639 (2.07)	-	0.12
PTO-ET	Open-ring form	306 (2.52)	0.20	-
	Closed-ring form	509 (1.96)	-	$< 10^{-6}$

Cycloreversion reaction quantum yields of **BTO-ET** and **PTO-ET** were measured to be 0.033 and $< 10^{-6}$, respectively, indicating that the closed-ring isomers of tetra-oxidized terarylenes **BTO-ET** and **PTO-ET** are much less reactive than the corresponding closed-ring isomers of precursor terarylenes in a similar manner to those of the methyl-substituted counterparts.^{13,22}

The ethyl-substituted terarylenes showed lower cyclization quantum yields compared with the corresponding methyl-substituted terarylenes ($\Phi_{\text{O} \rightarrow \text{C}} = 0.58$; **BT-ME** in hexane^{16d}, 0.46; **BTO-ME** in 2-Me THF²², 0.60; **PT-ME** in hexane^{16a} and 0.23; **PTO-ME** in 2-Me THF²²). The decrease could be attributed partly to the larger steric hindrance of ethyl groups than methyl groups in the cyclization reaction. Meanwhile, alkyl groups at the reactive carbons had minor effects on the cycloreversion quantum yields ($\Phi_{\text{C} \rightarrow \text{O}} = 0.45$; **BT-ME** in hexane^{16d}, 0.024; **BTO-ME** in 2-Me THF²², 0.07; **PT-ME** in hexane^{16a} and 3×10^{-4} ; **PTO-ME** in 2-Me THF²²). The side-aryl units predominantly determined the cycloreversion reactivity.

Computational studies and photochemical reactivity

To gain the insight into the photochemical reaction mechanisms, we have performed the potential energy surface (PES) scan along the reaction coordinate with varied bond length between the reactive carbon atoms. The geometries of compounds at the

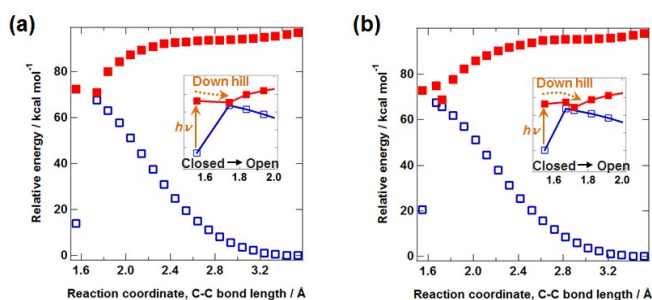


Fig. 2 Potential energy surfaces as a function of the C-C bond length of the S_0 (blue open square) and S_1 (red filled squares) state of (a) **BT-ET** and (b) **PT-ET** obtained at an ω B97XD/6-31G(d,p) level. The insets are enlarged view for cycloreversion reaction.

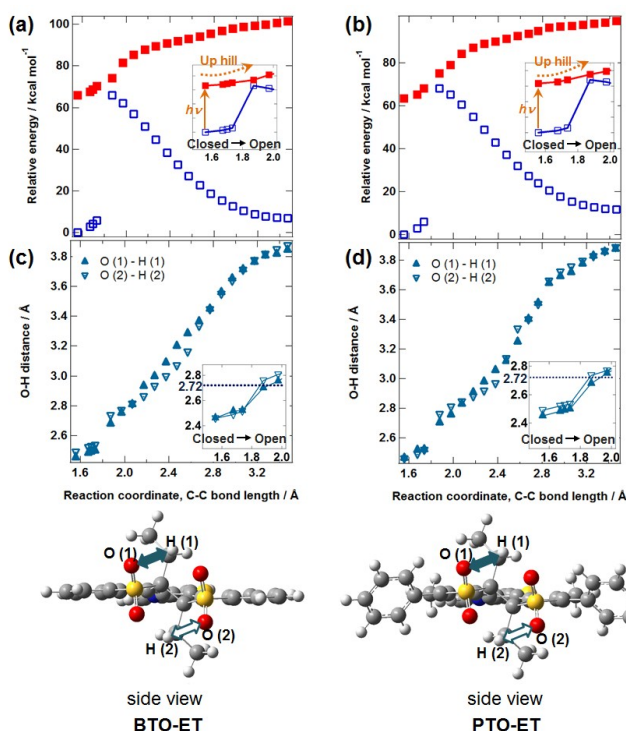


Fig. 3 Potential energy surfaces of the S_0 (blue open square) and S_1 (red filled squares) state (a, b) and CH/OS distance (c, d) as a function of C-C bond length for **BTO-ET** (a, c) and **PTO-ET** (b, d) obtained at an ω B97XD/6-31G(d,p) level. The insets are enlarged views for cycloreversion reaction

ground states were optimized for every step of the surface scans and only the reaction coordinate (the C-C bond length) was kept frozen. For the scans on the excited state, we performed single-point energy calculations for the excited states of corresponding geometries optimized at the ground state.

The results of the PES scans for the ground state (S_0) and for the first excited state (S_1) are summarized in Fig. 2 and 3. For **BT-ET** and **PT-ET**, there is no barrier on the S_1 surface for the reaction coordinates toward both the photo-cyclization and cycloreversion reactions (Fig. 2). These simple downhill profiles of the S_1 surface supported the experimental results that **BT-ET** and **PT-ET** showed reversible photochromic reactions with relatively high quantum yields (Table 1). On the other hand, for **BTO-ET** and **PTO-ET**, the potential energy surfaces of the S_1 states from closed- to open-ring cycloreversion shows an uphill profile (Fig. 3a, b). Therefore, the bond-cleavage for the

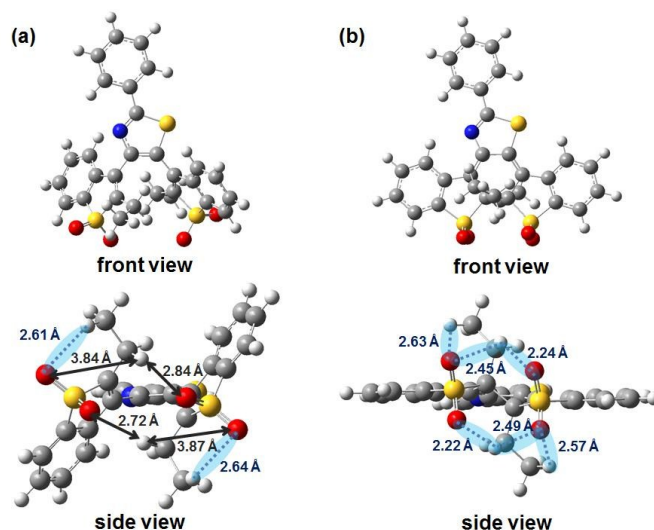


Fig. 4 Optimized structures for **BTO-ET**; (a) open- and (b) closed-ring form obtained at an ω B97XD/6-31G(d,p) level.

cycloreversion reaction needs further activation energy in the excited state, which might be attributed to the multiple CH/OS intramolecular weak hydrogen bonding interactions between the ethyl groups and SO_2 units in their closed-ring forms. Fig. 3c, d showed increases of (S)O-(C)H distances between SO_2 moieties and ethylene units in the ethyl groups along with cycloreversion reaction with increasing the photoreactive C-C distance. The C-C bond length of 1.9 Å could correspond to the point at which this bond cleavage. Across this point, the S(O)-(C)H distances jump from 2.5 to more than 2.7 Å, corresponding to the sum of *van der Waals* radii of O and H (2.72 Å). Optimized geometries of open- and closed-ring forms for **BTO-ET** are also shown in Fig. 4. In the closed-ring form all protons of the ethyl groups are possible to interact with SO_2 groups in the range smaller than 2.72 Å, while these distances thoroughly increase in the opening form (Fig. 4a). Therefore, the cycloreversion reaction requires the cleavage of multiple CH/OS interactions at the moment of C-C bond cleavage. These results of calculations could partly explain the dramatically suppressed values of $\Phi_{\text{C} \rightarrow \text{O}}$ for tetra-oxidized terarylenes.

The open-ring form is more stable than the closed-ring form for **BT-ET** and **PT-ET** at the ground state by 14 kcal mol⁻¹ and 20 kcal mol⁻¹, respectively, suggesting the higher aromatic stabilization energy of open-ring form structure of **BT-ET** and **PT-ET**. However, in the case of **BTO-ET** and **PTO-ET**, the side aryl groups were oxidized to sulfones, which may lower the effect of aromatic stabilization in the open form and reverse the relative energy between the open- and closed-ring forms. As the result, the closed-ring forms with the expanded π -conjugation system are more stable than the open-ring forms by 6.9 kcal mol⁻¹ (**BTO-ET**) and 12 kcal mol⁻¹ (**PTO-ET**).

Fluorescent property of tetra-oxidized terarylenes in closed-ring form isomer

Upon irradiation with UV light, the open-ring isomer of **BTO-ET** turned to the closed-ring isomer, which emits clear yellow fluorescence. Similar intense emission was also observed in the

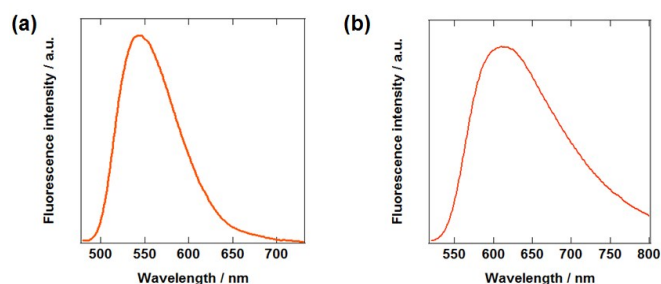


Fig. 5 Fluorescence spectra of (a) BTO-ET and (b) PTO-ET in CH₂Cl₂.

Table 2 Fluorescence properties of the closed-ring isomer of tetra-oxidized terarylenes in CH₂Cl₂

Compd. ^a	Φ_{em}	τ_{em} / ns	$k_f / 10^9 \text{ s}^{-1}$	$k_{nr} / 10^9 \text{ s}^{-1}$
BTO-ET	0.44	5.4	6.1×10^{-2}	0.12
BTO-ME	0.29	3.4	7.8×10^{-2}	0.21
PTO-ET	0.41	5.6	7.3×10^{-2}	0.11
PTO-ME	0.32	4.1	7.8×10^{-2}	0.17

^a Closed-ring forms

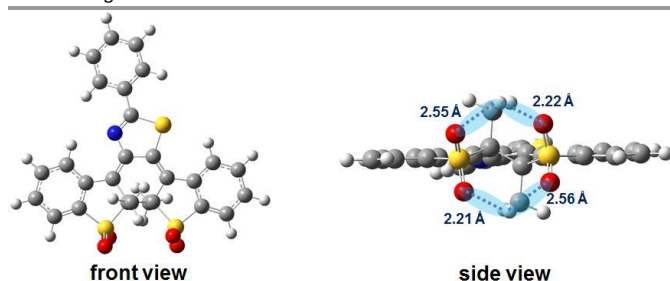


Fig. 6 Optimized structures for the closed-ring form of BTO-ME obtained at an ω B97XD/6-31G(d,p) level.

closed-ring isomer of PTO-ET. Fluorescence spectra of closed-ring isomers of BTO-ET and PTO-ET in CH₂Cl₂ are shown in Fig. 5a and b, respectively. As shown in Table 2, the ethyl-substituted terarylenes BTO-ET and PTO-ET showed higher fluorescence quantum yields (Φ_{em}) than the corresponding methyl-substituted terarylenes in all solvents (see the ESI †, Table S1).

To gain further insight into the fluorescence properties, the fluorescence lifetimes (τ_{em}) were measured in CH₂Cl₂. The fluorescence (k_f) and non-radiative decay rate constants were also derived from the values of Φ_{em} and τ_{em} which was well-characterised single component decay profile (Table 2). There are little changes in the values of k_f for terarylenes irrespective of the substituents on the reactive carbon atoms. By contrast, k_{nr} values for BTO-ET and PTO-ET are obviously smaller than those for BTO-ME and PTO-ME, respectively (Table 2). This decrease in k_{nr} for ethyl-substituted terarylenes suggests that the ethyl substituents suppress non-radiative decay processes more effectively than methyl substituents. The optimized geometries of the closed-ring isomer for BTO-ET (Fig. 4b) were compared with that of BTO-ME (Fig. 6). As already discussed in the previous section, all the protons in the ethyl groups could be in the range wherein the CH/OS interactions operate for the closed-ring isomer of BTO-ET (Fig. 4b). Although the methyl groups are also possible to interact with SO₂ moieties in the closed-ring form of BTO-ME (Fig. 6), the number of CH/OS interactions is apparently larger for BTO-ET. One may consider that the extension of alkyl chain length increases the probability of molecular motions, which

adversely affects the emission property. However, the reversal results strongly supports the impact of CH/OS interactions on the emission property of the ethyl-substituted terarylenes to make the molecular geometry rigid and decrease the non-radiative decay constants.

Conclusions

In summary, photochromic terarylenes having ethyl groups at the reactive carbon atoms were synthesized and their photophysical properties were studied. The closed-ring isomers of tetra-oxidized terarylenes showed strong emission and the much suppressed reactivity in cycloreversion reaction. The quantum chemical calculations well reproduced the small reactivity of cycloreversion reaction, which might be attributed to the stronger CH/OS intramolecular interactions in the closed-ring forms partly. The ethyl substituents were also considered to be responsible for the improved fluorescence quantum yields in the closed-ring forms by the multiple CH/OS intramolecular hydrogen bonding interactions to reduce the non-radiative decay constants. The present study would provide a promising approach for the design of high-contrast fluorescence switching materials which might be used for various optoelectronics devices.

Acknowledgements

The authors thanks Y. Nishikawa for their assistance in HRMS spectroscopic measurements. This research was partly supported by the Green Photonics Project at NAIST and the Grant-in-Aid for Scientific Research on a Priority Area, "Photosynergetics", sponsored by the Ministry of Education, Culture, Sports, Science and Technology, MEXT (Japan).

Notes and references

- (a) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; (b) V. Balzani, M. Venturi and A. Cred, *Molecular Devices and Machines: Journey into the Nanoworld*, Wiley-VCH, Weinheim, 2003.
- S. Shinkai, *Pure Appl. Chem.*, 1987, **59**, 425-430.
- I. Willner, *Acc. Chem. Res.*, 1997, **30**, 347-356.
- T. Tsujioka and M. Irie *J. Photochem. Photobiol. C; Photochem. Rev.* 2010, **11**, 1-14.
- R. C. Shallcross, P. Zacharias, A. Köhnen, P. O. Körner, E. Maibach and K. Meerholz, *Adv. Mater.*, 2013, **25**, 469-476.
- M. Suzuki, T. Aotake, Y. Yamaguchi, N. Noguchi, H. Nakano, K. Nakayama and H. Yamada, *J. Photochem. Photobiol. C; Photochem. Rev.* 2014, **18**, 50-70.
- C. Fan, P. Yang, X. Wang, G. Liu, X. Jiang, H. Chen, X. Tao, M. Wang and M. Jiang, *Sol. Energy Mater. Sol. Cells.*, 2011, **95**, 992-1000.
- R. Hayakawa, K. Higashiguchi, K. Matsuda, T. Chikyow and Y. Wakayama, *Appl. Mater. Interfaces* 2013, **5**, 3625-3630.
- M. El Gemayel, J. Börjesson, M. Herder, D. T. Duong, J. A. Hutchison, C. Rusi , G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu and P. Samor  *Nature Commun.*, 2015, **6**, 6330.
- Q. Shen, L. Wang, S. Liu, Y. Cao, L. Gan, X. Guo, M. L. Steigerwald, Z. Shuai, Z. Liu and C. Nuckolls, *Adv. Mater.*, 2010, **22**, 3282-3287.

- 11 Z. Zhang, X. Liu, Z. Li, Z. Chen, F. Zhao, F. Zhang and C.-H. Tung, *Adv. Func. Mater.*, 2008, **18**, 302-307.
- 12 P. Zacharias, M. C. Gather, A. Kohnen, N. Rehmman and K. Meerholz, *Angew. Chem. Int. Ed.*, 2009, **48**, 4038-4041.
- 13 M. Taguchi, T. Nakagawa, T. Nakashima, C. Adachi and T. Kawai, *Chem. Commun.*, 2013, **49**, 6373-6375.
- 14 (a) M. Irie, *Chem. Rev.*, 2000, **100**, 1685-1716.; (b) M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174-12277.
- 15 T. Kawai, T. Iseda and M. Irie, *Chem. Commun.*, 2004, 72-73.
- 16 (a) T. Nakashima, K. Atsumi, S. Kawai, T. Nakagawa, Y. Hasegawa and T. Kawai, *Eur. J. Org. Chem.*, 2007, 3212-3218.; (b) S. Kawai, T. Nakashima, K. Atsumi, T. Sakai, M. Harigai, Y. Imamoto, H. Kamikubo, M. Kataoka and T. Kawai, *Chem. Mater.*, 2007, **19**, 3479-3483; (c) S. Kawai, T. Nakashima, Y. Kutsunugi, H. Nakagawa, H. Nakano and T. Kawai, *J. Mater. Chem.*, 2009, **19**, 3606-3611; (d) Y. Kutsunugi, S. Kawai, T. Nakashima and T. Kawai, *New J. Chem.*, 2009, **33**, 1368-1373.
- 17 (a) G. Gavrel, P. Yu, A. Leautic, R. Guillot, R. Metivier and K. Nakatani, *Chem. Commun.*, 2012, **48**, 10111-10113; (b) T. Nakashima, K. Yamamoto, Y. Kimura and T. Kawai, *Chem. Eur. J.*, 2013, **19**, 16972-16980; (c) T. Nakashima, K. Imamura, K. Yamamoto, Y. Kimura, S. Katao, Y. Hashimoto and T. Kawai, *Chem. Eur. J.*, 2014, **20**, 13722-13729.
- 18 (a) S. Fukumoto, T. Nakashima and T. Kawai, *Angew. Chem. Int. Ed.*, 2011, **50**, 1565-1568; (b) H. Ogawa, K. Takagi, T. Ubukata, A. Okamoto, N. Yonezawa, S. Delbaere and Y. Yokoyama, *Chem. Commun.*, 2012, **48**, 11838-11840; (c) Y. Wu, Y. Xie, Q. Zhang, H. Tian, W. Zhu and A. D. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 2090-2094.
- 19 (a) T. Nakashima, M. Goto, S. Kawai and T. Kawai, *J. Am. Chem. Soc.*, 2008, **130**, 14570-14575; (b) B. M. Neilson, V. M. Lynch and C. W. Bielawski, *Angew. Chem. Int. Ed.*, 2011, **50**, 10322-10326; (c) V. W. Yam, J. K. Lee, C. C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2009, **131**, 912-913; (d) K. Suzuki, T. Ubukata and Y. Yokoyama, *Chem. Commun.*, 2012, **48**, 765-767; (e) C. Coudret, T. Nakagawa, T. Kawai and J.-C. Micheau, *New J. Chem.*, 2009, **33**, 1386-1392.
- 20 Y.-C. Jeong, S. I. Yang, K.-H. Ahn and E. Kim, *Chem. Commun.*, 2005, 2503-2505.
- 21 K. Uno, H. Niihara, M. Morimoto, Y. Ishibashi, H. Miyasaka and M. Irie, *J. Am. Chem. Soc.*, 2011, **133**, 13558-13564.
- 22 M. Taguchi, T. Nakagawa, T. Nakashima and T. Kawai, *J. Mater. Chem.*, 2011, **21**, 17425-17432.
- 23 (a) G. Sivaraman and D. Chellappa, *J. Mater. Chem. B*, 2013, **1**, 5768-5772; (b) T. Anand, G. Sivaraman, M. Iniya, A. Siva and D. Chellappa, *Analytica Chimica Acta*, 2015, **876**, 1-8.
- 24 T. Sumi, Y. Takagi, A. Yagi, M. Morimoto and M. Irie, *Chem. Commun.*, 2014, **50**, 3928-3930.
- 25 Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.
- 26 J. D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620.
- 27 (a) M. M. Krayushkin, S. N. Ivanov, A. Yu. Martynkin, B. V. Lichitsky, A. A. Dudinov and B. M. Uzhinov, *Russ. Chem. Bull.*, 2001, **50**, 116-121; (b) M. M. Krayushkin, S. N. Ivanov, A. Yu. Martynkin, B. V. Lichitsky, A. A. Dudinov and B. M. Uzhinov, *Russ. Chem. Bull.*, 2001, **50**, 2424-2427.