Electronic Supplementary Information (ESI)

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]

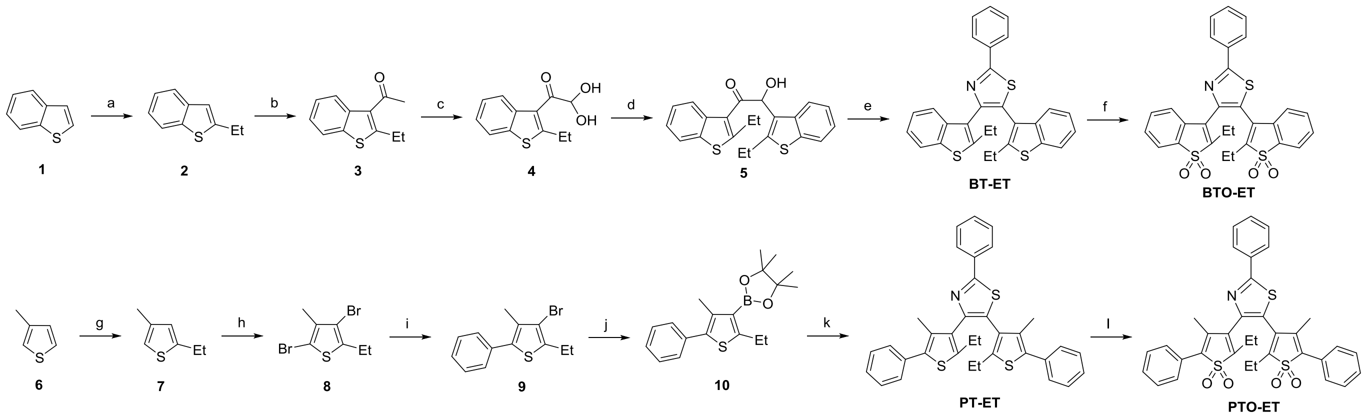
[a] *Graduate School of Materials Science, Nara Institute of Science and Technology, NAIST, Ikoma, Nara 630-0192, Japan*

[b] *NAIST-CEMES International Collaborative Laboratory for Supraphotoactive Systems, NAIST, CEMES-UPR 8011 CNRS, 29, rue Jeanne Marvig, BP 94347, 31055 Toulouse Cedex 4, France*

Table of Contents

1. Experimental detail

Synthesis



Scheme S1 Synthetic routes of **BTO-ET** and **PTO-ET**: (a) 1. *n*-BuLi, THF 2. ethyl bromide; (b) $AlCl_3$, AcCl, CH_2Cl_2; (c) SeO_2, Dioxane/H_2O; (d) 1. Benzothiophene, toluene 2. $SnCl_4$; (e) thiobenzamide, CF_3COOH; (f) *m*-CPBA, CH_2Cl_2; (g) 1. *n*-BuLi, THF 2. ethyl iodide; (h) Br_2, AcOH; (i) phenylboronic acid, $Pd(PPh_3)_4$, triphenylphosphine, 2M K_3PO_4 aq., 1,4-dioxane; (j) 1. *n*-BuLi, THF 2. Isopropoxyboronic acid pinacol ester; (k) 4,5-dibromo-2-phenylthiazole, $Pd(PPh_3)_4$, triphenylphosphine, 2M K_3PO_4 aq., 1,4-dioxane; (l) *m*-CPBA, CH_2Cl_2.

NMR spectra of BT-ET, BTO-ET, PT-ET and PTO-ET

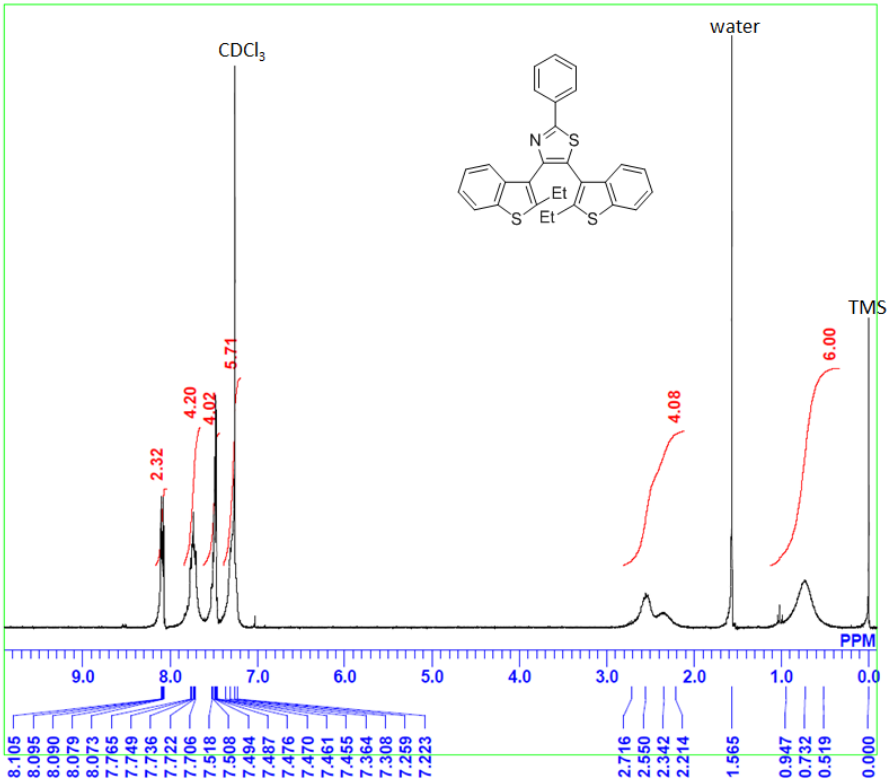


Fig. S1 ^{1}H NMR spectra of **BT-ET** (300 MHz, $CDCl_3$)

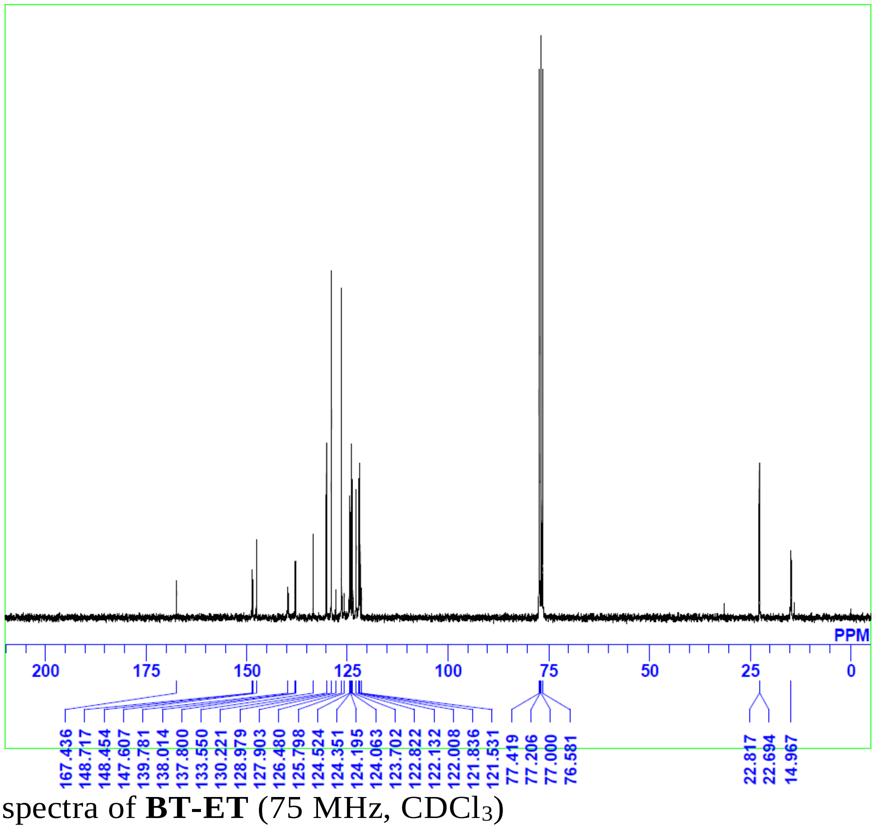


Fig. S2 ^{13}C NMR spectra of **BT-ET** (75 MHz, $CDCl_3$)

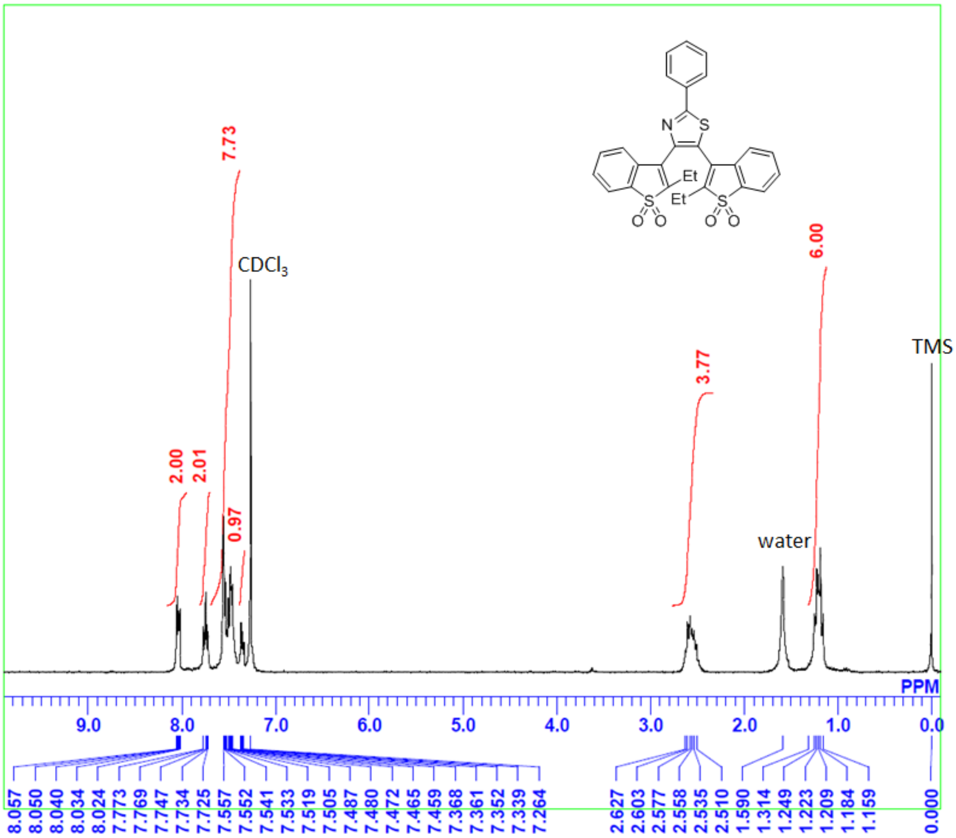


Fig. S3 ^{1}H NMR spectra of **BTO-ET** (300 MHz, $CDCl_3$)

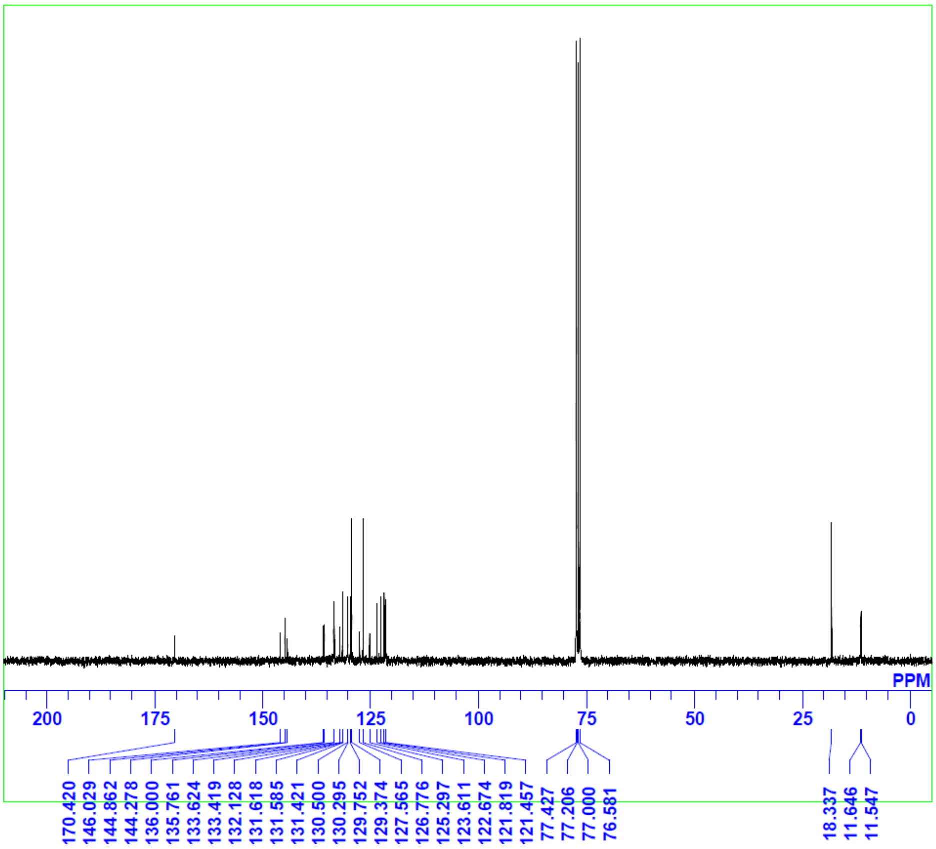


Fig. S4 ^{13}C NMR spectra of **BTO-ET** (75 MHz, $CDCl_3$)

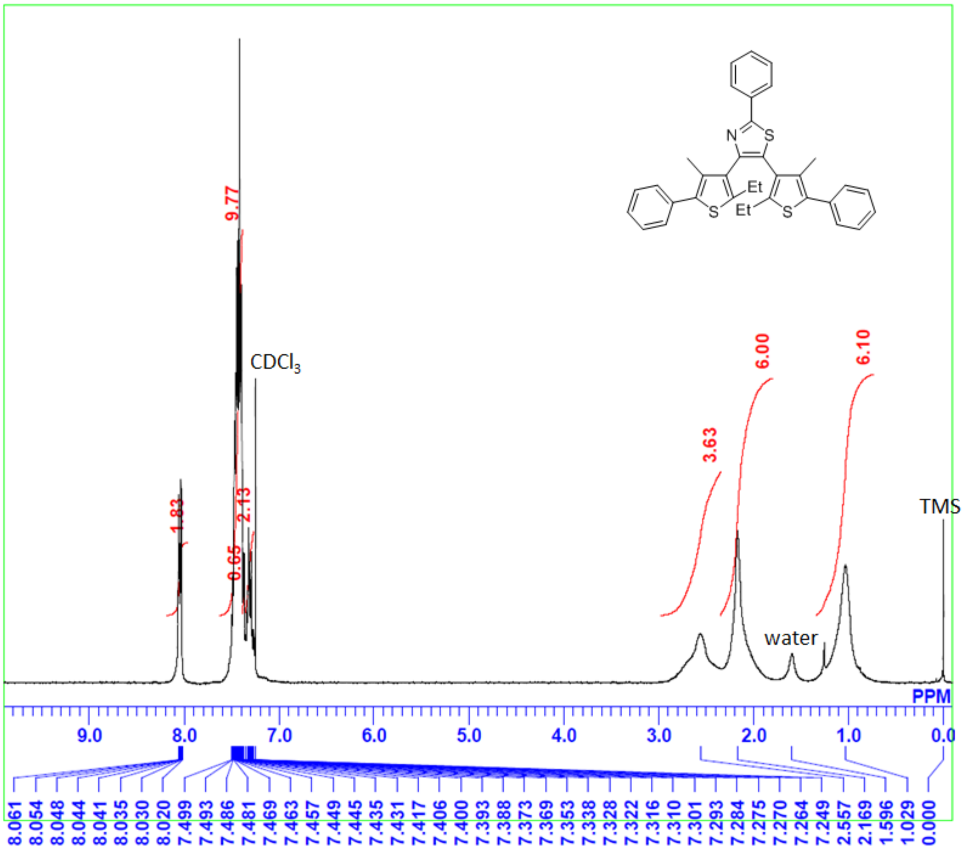


Fig. S5 ^{1}H NMR spectra of **PT-ET** (300 MHz, $CDCl_3$)

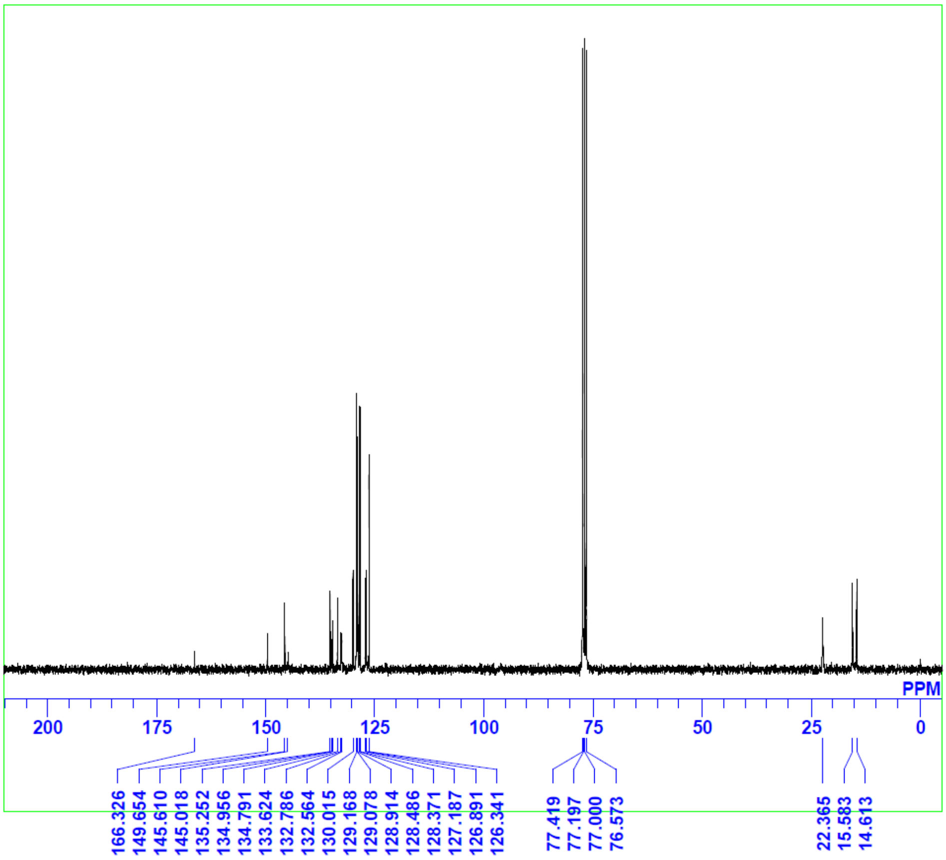


Fig. S6 ^{13}C NMR spectra of **PT-ET** (75 MHz, $CDCl_3$)

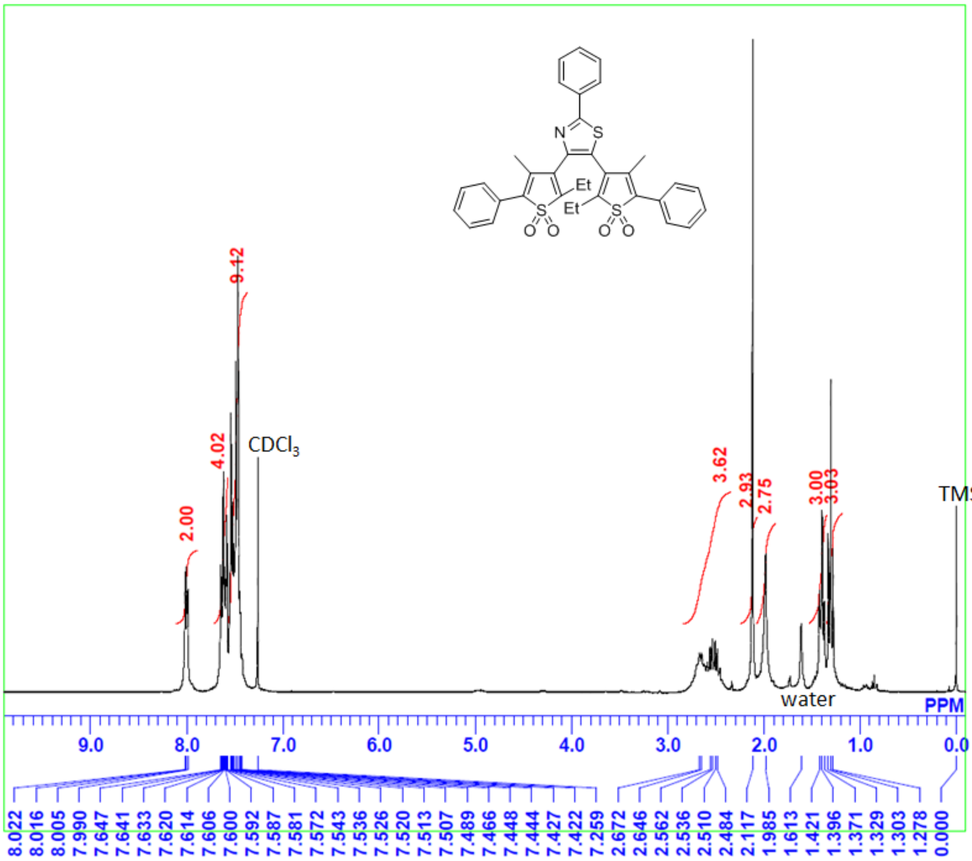


Fig. S7 ^{1}H NMR spectra of **PTO-ET** (300 MHz, $CDCl_3$)

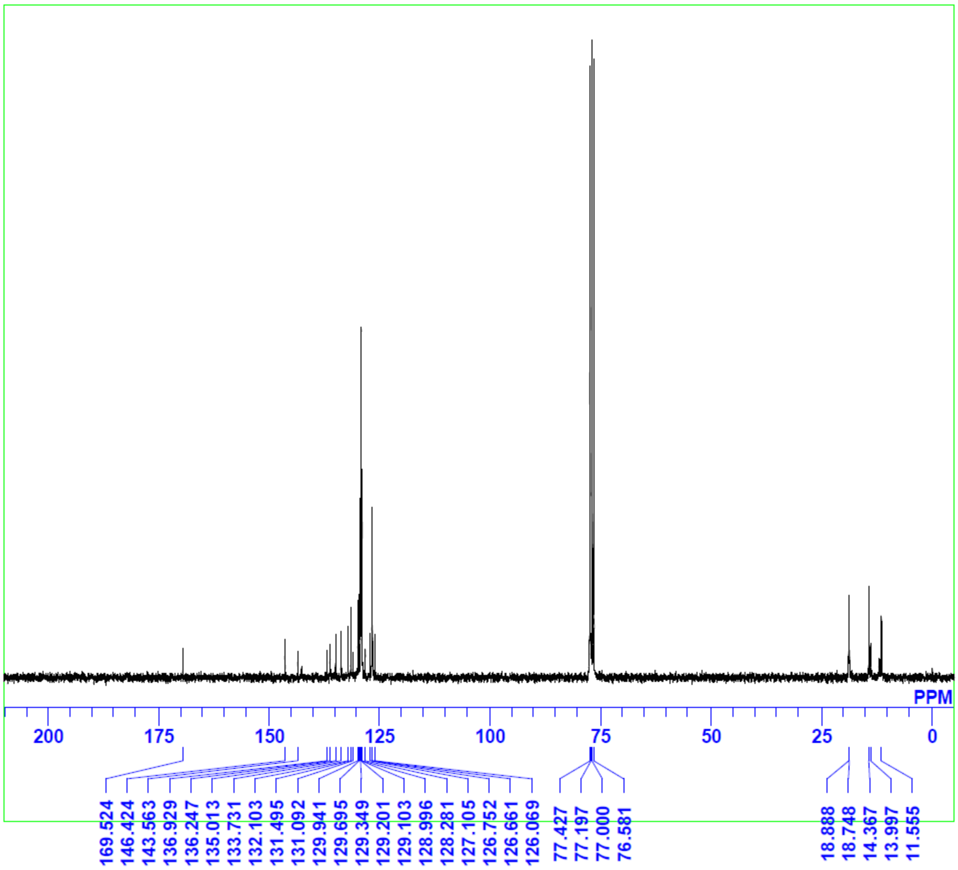


Fig. S8 ^{13}C NMR spectra of **PTO-ET** (75 MHz, $CDCl_3$)

2. Optical properties

Photochromic properties

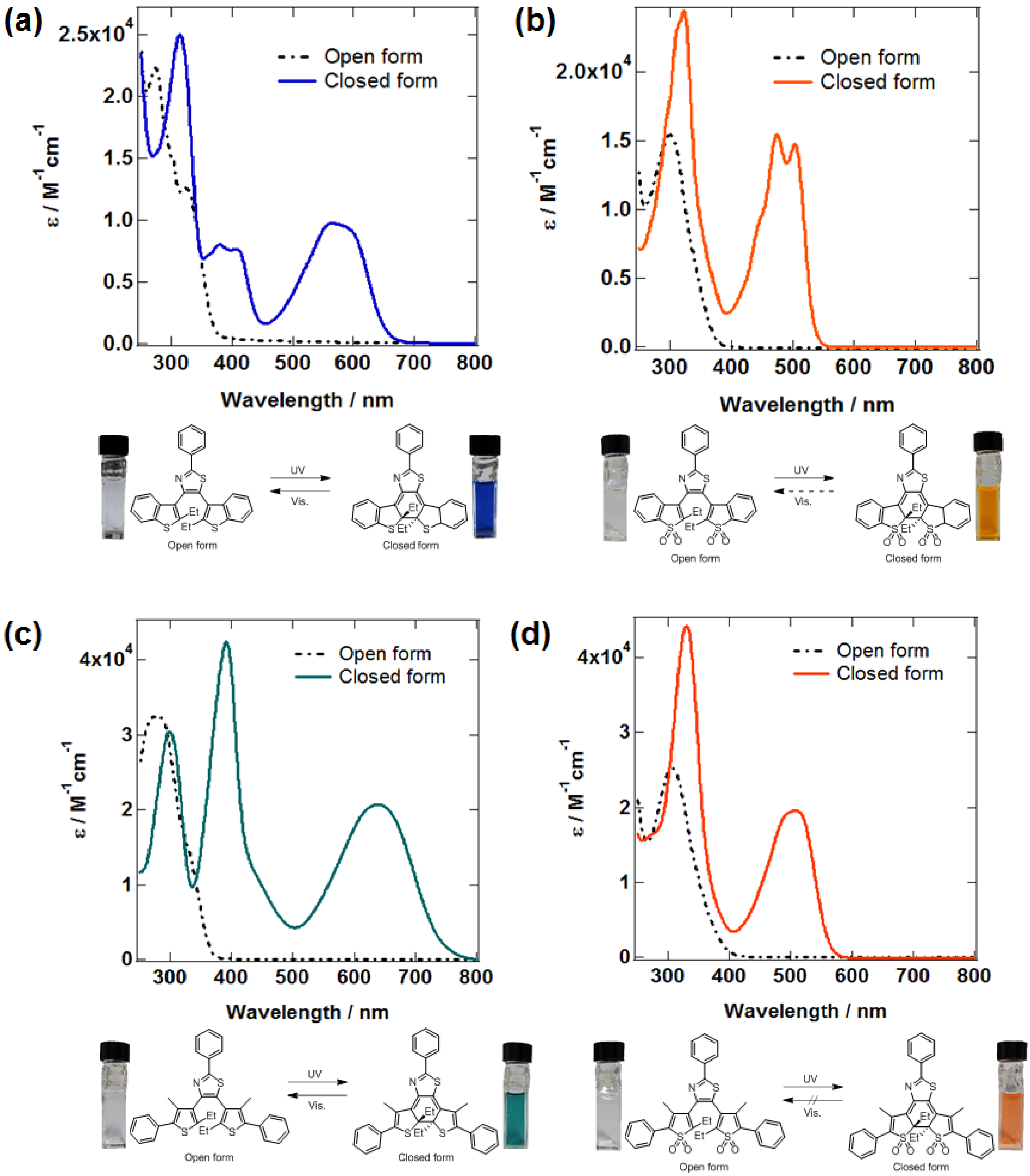


Fig. S9 Absorption spectra and photographs of solutions containing (a) **BT-ET**, (b) **BTO-ET**, (c) **PT-ET** and (d) **PTO-ET** in CH_2Cl_2 before and after UV irradiation.

Fluorescent properties

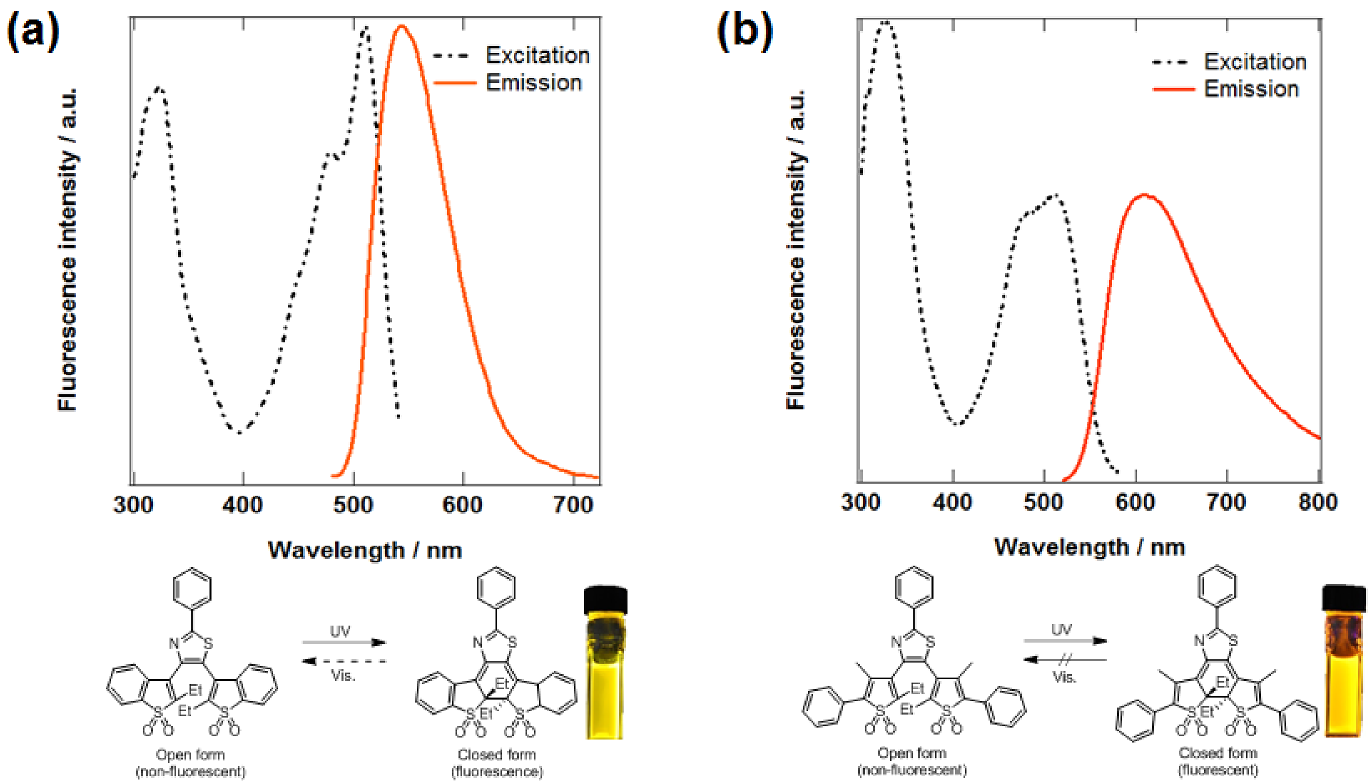


Fig. S10 Fluorescence excitation spectra and photographs of solutions containing (a) **BTO-ET** and (b) **PTO-ET** in CH_2Cl_2 after UV irradiation

Table S1 Fluorescence quantum yields of the closed-ring isomers of tetra-oxidized terarylenes in various solvents.

Compd.[a] / Solvt.	toleuene	cyclohexane	1,4-dioxane	CH_2Cl_2
BTO-ET	0.64	0.55	0.53	0.44
BTO-ME	0.45	0.40	0.33	0.29
PTO-ET	0.51	0.46	0.42	0.41
PTO-ME	0.37	0.27	0.31	0.32

[a] Closed-ring forms

3. Quantum chemical calculations

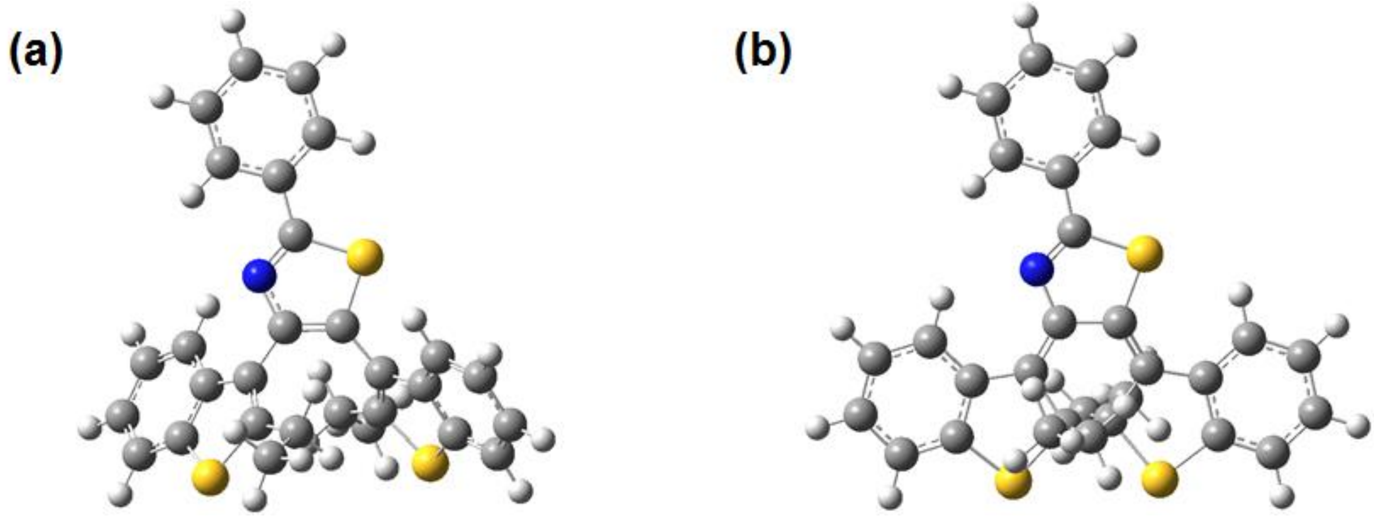


Fig. S11 Optimized structures for **BT-ET**; (a) open- and (b) closed-ring form obtained at an ωB97XD/6-31G(d,p) level.

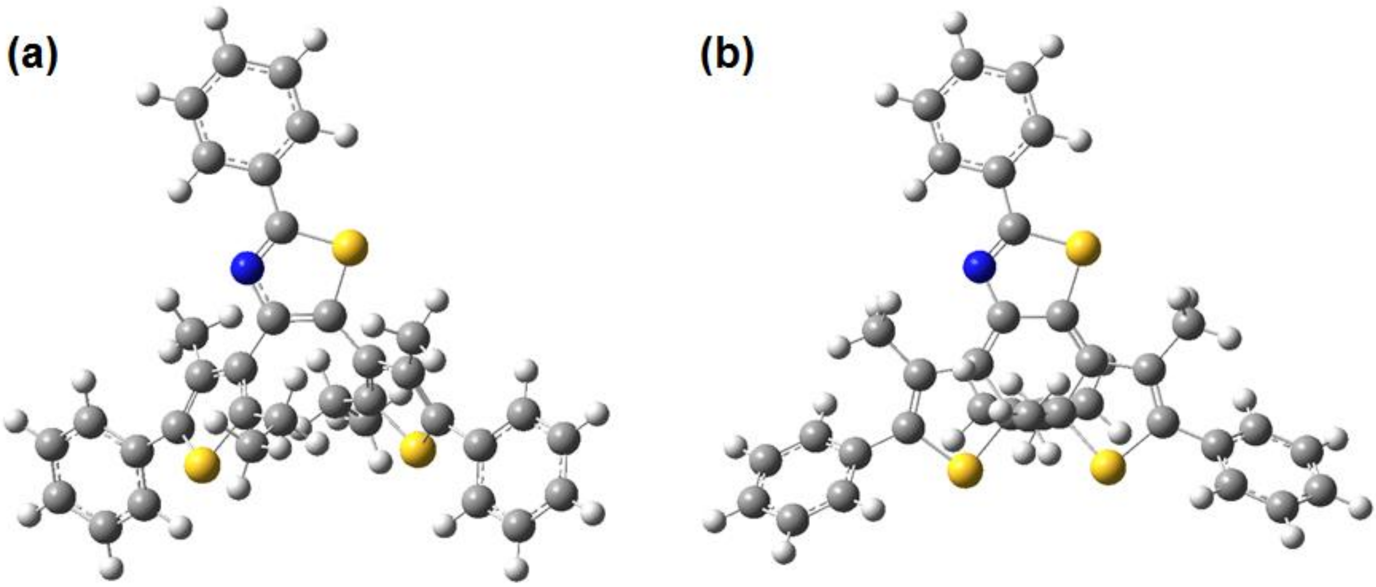


Fig. S12 Optimized structures for **PT-ET**; (a) open- and (b) closed-ring form obtained at an ωB97XD/6-31G(d,p) level.

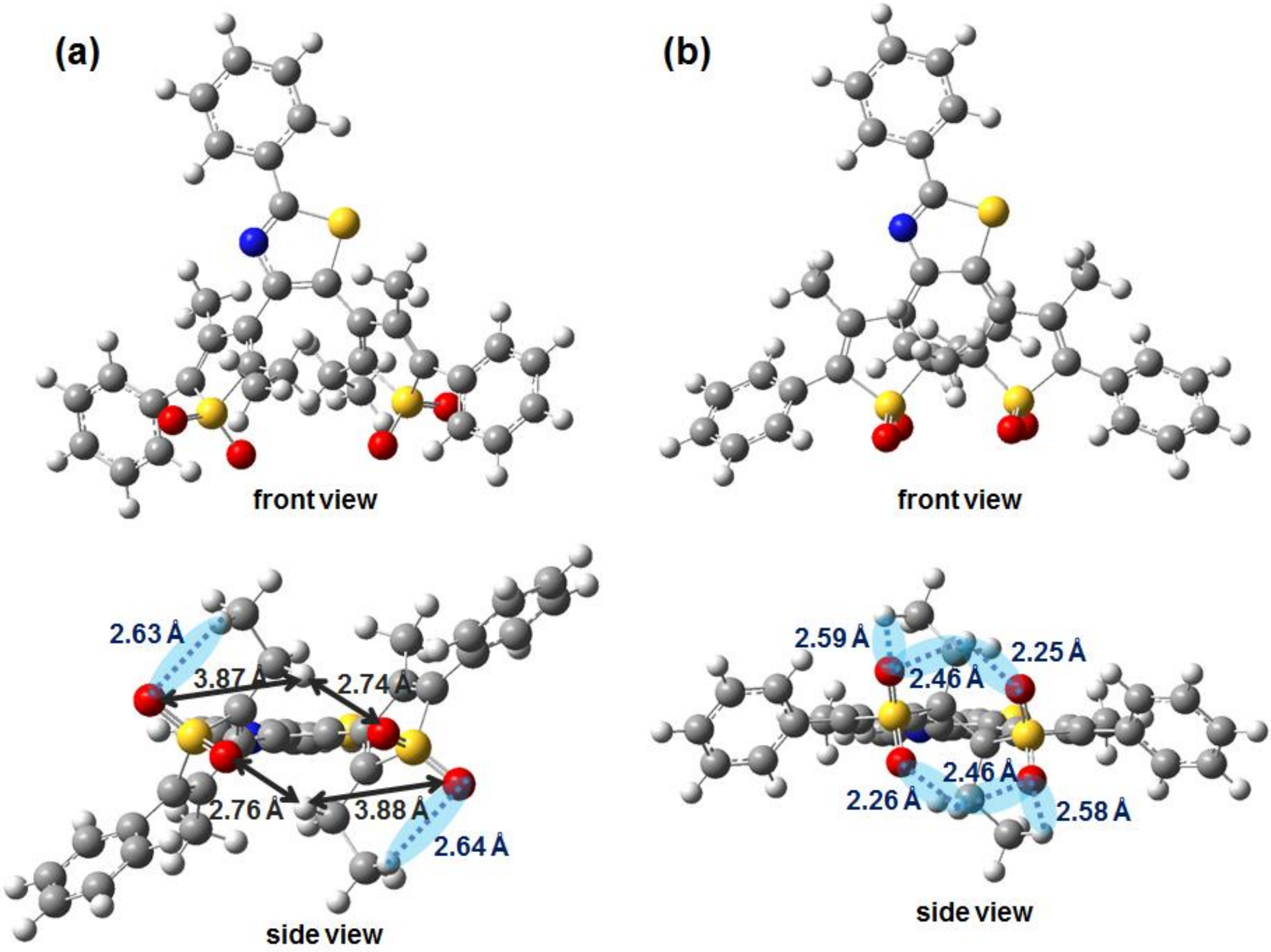


Fig. S13 Optimized structures for **PTO-ET**; (a) open- and (b) closed-ring form obtained at an ωB97XD/6-31G(d,p) level.

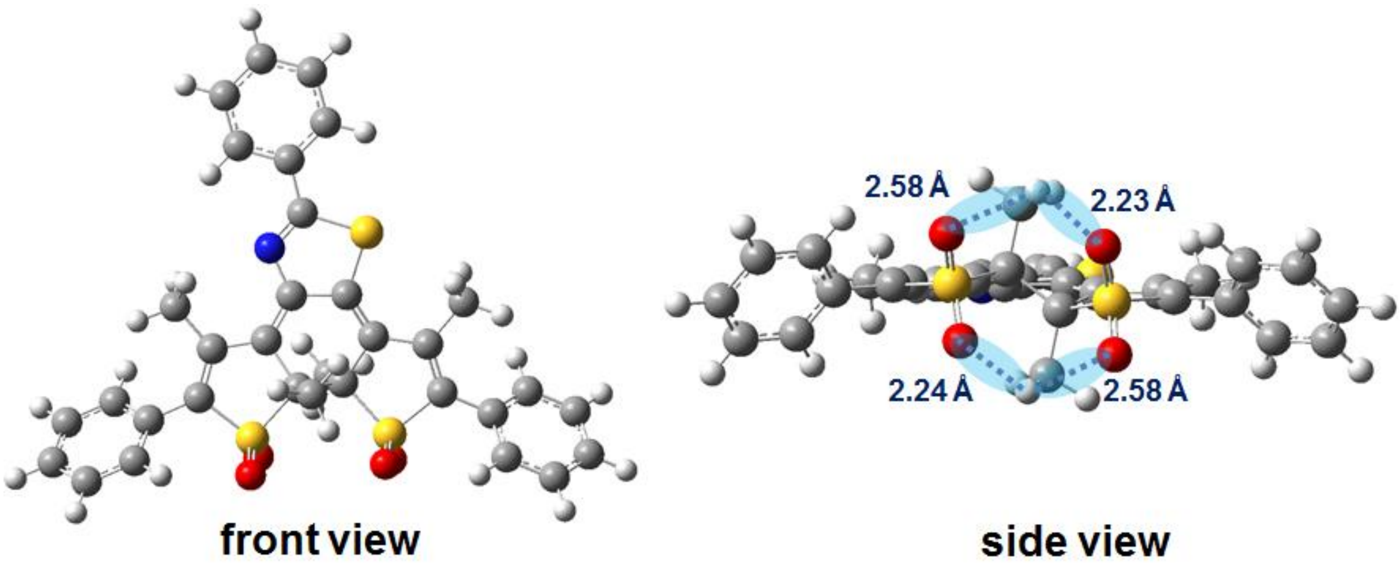


Fig. S14 Optimized structures for the closed-ring form of **PTO-ME** obtained at an ωB97XD/6-31G(d,p) level.