Supporting Information for

A Highly Efficient Silole-Containing Dithienylethene with Excellent Thermal Stability and Fatigue Resistance: A Promising Candidate for Optical Memory Storage Materials

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Experimental Section

Materials and Reagents

2,5-Dimethylthiophene and chlorotrimethylsilane were obtained from Apollo Scientific Company. n-Butyllithium solution (1.6 M in hexane), thianaphthene, iodic acid and tetrachloromethane were obtained from Aldrich Chemical Company. Palladium(II) chloride, allylpalladium chloride dimer and tri-t-butylphosphine were purchased from Strem Chemicals, Inc. Triphenylphosphine and lithium tert-butoxide were purchased from Acros Organics, Inc. 1,2-Dibromotetrachloroethane, iodine, bromine and acetic acid were obtained from Alfa Aesar. Ethynyltrimethylsilane was purchased from Matrix Scientific. All purchased chemicals were used without further purification. Tetrakis(triphenylphosphine)palladium(0) as catalyst for Suzuki cross-coupling was prepared according to literature procedures with slight modifications.¹ THF and toluene were purified using Innovative Technology Inc. Model PureSolv MD 5 Solvent Purification System and deaerated with prepurified argon gas before use. Tetra-n-butylammoium hexafluorophosphate was purified by at least three times of recrystallization and was dried before use. All solvents for spectroscopic studies were purchased from Sigma-Aldrich Chemical Company with spectroscopic grade and were used as received. All other solvents and reagents were of at least analytical grade and were used as received.

Physical Measurements and Instrumentation

¹H NMR spectra were recorded either on a Bruker DPX-300 (300 MHz) or a Bruker AVANCE 400 (400 MHz) fourier transform NMR spectometer with chemical shifts (δ , ppm) reported relative to tetramethylsilane (Me₄Si). All measurements were performed at 298 K unless specified otherwise. All electron impact (EI) mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. Elemental analyses of the new compound were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

UV-Vis absorption spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer. Photoirradiation was carried out using a 300 W Oriel Corporation Model 60011 Xe (ozone-free) lamp, and monochromic light was obtained by passing the light through an Applied Photophysics F 3.4 monochromator. All measurements were conducted at room temperature. The kinetics of the thermal-induced back-reaction of the closed form isomer of dithienylethene were measured at 100 °C, using a Varian Cary 50 UV-Vis spectrophotometer with a single cell peltier thermostat to control the working temperature.

Steady-state emission and excitation spectra at room temperature and 77 K were recorded on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer equipped with a R2658P PMT detertor. For solution emission and excitation spectra, samples were degassed on a high-vacuum line in a degassing cell with a 10-cm³ Pyrex round-bottomed flask connected by a side-arm to a 1-cm quartz fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles prior to the measurements. Solid-state emission and excitation spectra at room temperature were recorded with solid samples loaded in a quartz tube inside a quartz-walled Dewar flask. Solid samples at low temperature (77 K) and in butyronitrile glass at 77 K were recorded similarly, with liquid nitrogen inside the optical Dewar flask. Luminescence quantum yield was measured by the optical dilute

method developed by Demas and Crosby.² A degassed solution of quinine sulphate in 0.5 M sulfuric acid ($\phi_{lum} = 0.546$, $\lambda_{ex} = 365$ nm) at 298 K was used as the standard.³

Chemical actinometry was employed for the photochemical quantum yield determination.⁴ Incident light intensities were taken from the average values measured just before and after each photolysis experiment using ferrioxalate actinometry. In the determination of the photochemical quantum yield, the sample solutions were prepared at concentrations with absorbance slightly greater than 2.0 at the excitation wavelength.⁴ The quantum yield was determined at a small percentage of conversion by monitoring the initial rate of change of absorbance ($\Delta A/\Delta t$) in the absorption maximum of the closed form in the visible region.

Cyclic voltammetric measurements were performed by using a CH Instrument, Inc. model CHI620 electrochemical analyzer interfaced to a personal computer. The electrolytic cell used was a conventional two-compartment cell. The reference electrode was separated from the working electrode compartment by a vycor glass. Electrochemical measurements were performed in dichloromethane and THF solution with 0.1 mol dm⁻³ ^{*n*}Bu4NPF₆ as supporting electrolyte at room temperature. The reference electrode was a Ag/AgNO₃ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon (CH Instrument) electrode with a platinum wire as a counter electrode in a compartment separated from the working electrode by a sintered-glass frit. The ferrocenium/ferrocene couple (FeCp₂^{+/0}) was used as the internal reference.⁵ All solutions for electrochemical studies were deaerated with prepurified argon gas before measurement.

Crystal Structure Determination

Single crystals of BzThSiMe₂-DTE suitable for X-ray diffraction studies were obtained by layering of ethanol onto a concentrated dichloromethane solution of BzThSiMe₂-DTE and the solution was allowed to stand in the dark for a few days. The X-ray diffraction data were collected on a Bruker Smart CCD 1000 using graphite monochromatized Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Raw frame data were integrated with SAINT program.⁶ Semi-empirical absorption corrections with SADABS⁷ were applied. The structure was solved by direct methods employing SHELXS-97 program⁸ on PC. P, S and many non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97⁸ on PC. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices. Crystal and structure determination data and the selected bond distances and angles are summarized in Tables S3–S4, respectively. The crystal picked for structure determination showed two independent molecules in the asymmetric unit, as depicted in Figure S4 in Supporting Information. For both independent molecules of the compound, the two peripheral thiophene rings are arranged in an anti-parallel configuration and the distances between the reactive carbon atoms are 3.571 Å [C(5)–C(10)] and 3.609 Å [C(29)–C(34)], indicating that the obtained crystal is able to undergo photochemical cyclization in solid state.⁹ The dihedral angles between the benzene ring and the silole ring are 0.16 and 4.00°, which suggest that the π -conjugation is effectively extended over the backbone. However, the interplanar angles between the two peripheral thiophene rings and the fused silole core are in the range of 41.30-52.36°, indicating that the two thiophene rings are

slightly π -conjugated to the silole backbone. The X-ray crystal structures showed that the endocyclic C–Si–C bond angles of the compounds varied from 91.12–91.59°, which were much smaller than the exocyclic C–Si–C bond angles ranging from 111.10–114.80°, indicating that the central silicon atoms were significantly deviated from the ideal tetrahedral geometry. The mean value of exocyclic Si–C(sp³) bond lengths were shorter than the mean value of endocyclic Si–C(sp²) bond lengths, which was in good agreement with that observed in the previously reported siloles.¹⁰ The endocyclic C–C single bonds and C=C double bonds in the silole core were found to be in the range of 1.485–1.496 and 1.351–1.375 Å, respectively, which were within the normal C–C single bond values and double bond values in other silole systems reported by Ko and Kang.¹¹

Computational Details

Calculations were carried out using Gaussian 09 software package.¹² The ground-state geometries of the open and closed forms for **BzThSiMe₂-DTE** were fully optimized in benzene by using density functional theory (DFT) calculations at the PBE0 level^{13–15} in conjunction with the conductor-like polarizable continuum model (CPCM)^{16,17} using benzene as the solvent. For the open form, only the photochemically active antiparallel conformation was considered. Vibrational frequencies were calculated for all stationary points to verify that each was a minimum (NIMAG = 0) on the potential energy surface. Based on the ground state optimized geometries, time-dependent density functional theory (TDDFT) method^{18–20} at the same level associated with CPCM (benzene) was employed to compute the singlet–singlet transitions in the electronic absorption spectra of the two forms for **BzThSiMe₂-DTE**. For all the calculations, the 6-31G(d,p) basis set was employed to describe all the atoms.^{21–23} The DFT and TDDFT calculations were performed with a pruned (99,590) grid.

Synthetic Procedures

((2,5-Dimethylthiophen-3-yl)ethynyl)trimethylsilane

To a solution mixture of 3-iodo-2,5-dimethylthiophene²⁴ (1.6 g, 6.72 mmol), copper(I) iodide (64 mg, 0.34 mmol), dichorobis(triphenylphosphine)palladium(II) (0.24 g, 0.34 6.86 mmol) triphenylphosphine (0.18)mmol) degassed and g, in *N*,*N*-diisopropylamine (60 mL) was added ethynyltrimethylsilane (1.4 mL, 10.1 mmol) under an inert atmosphere of argon. The reaction mixture was maintained at 60 °C overnight. After cooling to room temperature, diethyl ether was added to precipitate out the salt. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane as the eluent to afford the product as a colorless oil. Yield: 1.2 g, 5.76 mmol, 84 %. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.23 (s, 9H, -SiMe₃), 2.36 (s, 3H, -CH₃), 2.44 (s, 3H, -CH₃), 6.60 (s, 1H, thienyl). Positive EI-MS, m/z: 208. HRMS (Positive EI) calcd for $C_{11}H_{16}^{32}S^{28}Si: m/z = 208.0737$; found: 208.0736 [M]⁺.

3-Ethynyl-2,5-dimethylthiophene

To a solution of ((2,5-dimethylthiophen-3-yl)ethynyl)trimethylsilane (1.7 g, 8.16 mmol) in THF-methanol (40 mL, 3:1 v/v) was added an excess of anhydrous potassium carbonate (4.5 g, 32.6 mmol). The mixture was stirred overnight, after which the reaction mixture was quenched with deionized water. This was then extracted with diethyl ether. The combined extracts were washed with brine and deionized water, and finally dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane as the eluent to afford the product as a colorless oil. Yield: 970 mg, 7.12 mmol, 87 %. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 2.37 (s, 3H, –CH₃), 2.46 (s, 3H, –CH₃),

3.12 (s, 1H, $-C \equiv CH$), 6.62 (s, 1H, thienyl). Positive EI-MS, m/z: 136. HRMS (Positive EI) calcd for C₈H₈³²S: m/z = 136.0341; found: 136.0340 [M]⁺.

1,2-Bis(2,5-dimethylthiophen-3-yl)ethyne

To a solution mixture of 3-ethynyl-2,5-dimethylthiophene (1.4 g, 10.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.59 g, 0.51 mmol) and copper(I) iodide (98 mg, 0.51 mmol) in degassed *N*,*N*-diisopropylamine (60 mL) was added 3-iodo-2,5-dimethylthiophene²⁴ (2.5 g, 10.5 mmol) under an inert atmosphere of argon. The reaction mixture was maintained at 60 °C overnight. After cooling to room temperature, diethyl ether was added to precipitate out the salt. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane as the eluent. Further purification was achieved by recrystallization from a minimal amount of methanol to afford the product as white crystals. Yield: 2.14 g, 8.70 mmol; 84 %. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 2.39 (s, 6H, –CH₃), 2.49 (s, 6H, –CH₃), 6.65 (s, 2H, thienyl). Positive EI-MS, *m/z*: 246. HRMS (Positive EI) calcd for C₁₄H₁₄³²S₂: *m/z* = 246.0531; found: 246.0530 [M]⁺.

Benzo[b]thiophen-3-yltrimethylsilane

To a well-stirred solution of 3-bromobenzo[*b*]thiophene¹⁴ (2.0 g, 9.39 mmol) in anhydrous diethyl ether at -78 °C was added *n*-butyllithium (1.6 M in hexane, 6.5 mL, 10.4 mmol) in a dropwise manner. The solution mixture was stirred and maintained at this temperature for 1 hour. To this reaction mixture was added chlorotrimethylsilane (1.4 mL, 11.0 mmol) in a dropwise manner. After the addition was complete, the mixture was stirred at -78 °C for 1 hour and then allowed to stir at room temperature for 24 hours. The reaction mixture was quenched with deionized water and then extracted with diethyl ether. The combined extracts were washed with brine and deionized water, and finally dried over anhydrous magnesium sulfate. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane as the eluent to afford the product as a colorless oil. Yield: 1.36 g, 6.57 mmol; 70 %. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.41 (s, 9H, -SiMe₃), 7.33–7.41 (m, 2H, phenyl), 7.54 (s, 1H, phenyl), 7.94 (t, *J* = 8.5 Hz, 2H, phenyl). Positive EI-MS, *m/z*: 206. HRMS (Positive EI) calcd for C₁₁H₁₄³²S²⁸Si: *m/z* = 206.0580; found: 206.0579 [M]⁺.

(2-Bromobenzo[b]thiophen-3-yl)trimethylsilane

To a well-stirred solution of benzo[b]thiophen-3-yltrimethylsilane (2.0 g, 9.69 mmol) in anhydrous THF at -78 °C was added *n*-butyllithium (1.6 M in hexane, 6.6 mL, 10.6 mmol) in a dropwise manner. The solution mixture was stirred and maintained at this temperature for 1 hour. To this reaction mixture was added dropwise a solution 1,2-dibromotetrachloroethane (3.45 g, 10.6 mmol) in THF over 5 min. After the addition was complete, the mixture was stirred at -78 °C for 1 hour and then allowed to stir at room temperature for 24 hours. The reaction mixture was quenched with deionized water and then extracted with diethyl ether. The combined extracts were washed with brine and deionized water, and finally dried over anhydrous magnesium sulfate. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane as the eluent. Further purification was achieved by recrystallization from a minimal amount of ethanol to afford the product as white crystals. Yield: 2.27 g, 7.95 mmol; 75 %. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.53 (s, 9H, -SiMe₃), 7.28-7.32 (m, 2H, phenyl), 7.73–7.76 (m, 1H, phenyl), 7.88–7.92 (m, 1H, phenyl). Positive EI-MS, m/z: 284. HRMS (Positive EI) calcd for $C_{11}H_{13}^{79}Br^{32}S^{28}Si: m/z = 283.9685$; found: 283.9678 $[M]^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)-1,1-dimethyl-1H-benzo[*b*]silolo[2,3-*d*]thiophene (*trans*-BzThSiMe₂-DTE) (BzThSiMe₂-DTE).

The target compound was prepared according to a literature procedure for C(sp³)–Si bond cleavage²⁵ with slight modifications and the reaction was performed under nitrogen. To a well-stirred solution of [PdCl(*π*-allyl)]₂ (18.6 mg, 0.0507 mmol) in anhydrous toluene was added P'Bu₃ (0.61 mL, 0.33 M, 0.203 mmol). The solution mixture was stirred at room temperature for 20 min. To this reaction mixture were added (2-bromobenzo[b]thiophen-3-yl)trimethylsilane (695 mg, 2.44 mmol), 1,2-bis(2,5-dimethylthiophen-3-yl)ethyne (500 mg, 2.03 mmol), LiO'Bu (487 mg, 6.09 mmol) and 4-nirtobenzaldehyde (307 mg, 2.03 mmol). The reaction mixture was stirred at 120 °C for 24 hr. The reaction mixture was guenched with water and then extracted with diethyl ether. The combined extracts were washed with brine and water, and finally dried over anhydrous magnesium sulfate. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70-230 mesh) using hexane-dichloromethane (4:1 v/v) as the eluent. Further purification was achieved by recrystallization from a minimal amount of ethanol to afford the product as pale yellow crystals. Yield: 757 mg, 1.73 mmol; 71 %. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 0.38 (s, 3H, Si-CH₃), 0.58 (s, 3H, Si-CH₃), 1.84 (s, 3H, -CH₃), 1.93 (s, 3H, -CH₃), 2.38 (s, 3H, -CH₃), 2.43 (s, 3H, -CH₃), 6.39 (s, 1H, thienyl), 6.72 (s, 1H, thienyl), 7.21–7.28 (m, 1H, phenyl), 7.32–7.37 (m, 1H, phenyl), 7.72 (d, J = 7.7 Hz, 1H, phenyl), 7.82 (d, J = 8.0 Hz, 1H, phenyl). Positive EI-MS, m/z: 436. HRMS (Positive EI) calcd for C₂₄H₂₄³²S₃²⁸Si: m/z = 436.0804; found: 436.0806 [M]⁺. Elemental analyses, Found (%): C 65.5, H 5.65; Calcd (%) for C₂₄H₂₄S₃Si•0.5(CH₃CH₂OH): C 65.31, H 5.92.

		Absorption ^a	Emission			
Compound	Configuration -	$\lambda_{\rm abs}$ / nm	Medium	$\lambda_{\rm em}/~{\rm nm}^{\rm b}$		
		$(\epsilon / dm^3 mol^{-1} cm^{-1})$	(T/K)	(τ_0 / ns)	<i>P</i> /umĭ	
BzThSiMe ₂ -	open	332 (6450), 371 (8820)	Benzene (298)	491 (2.37)	0.14	
DTE			Solid (298)	_		
			Solid (77)	491		
			Glass ^d (77)	473		
	closed	343(25800), 359 (38790), 474 (4470)	Benzene (298)	-	-	

Table S1Photophysical data of **BzThSiMe₂-DTE**

^a Data obtained in benzene at 298 K

^b Emission maxima are corrected values

^c Luminescence quantum yields are reported using a degassed solution of quinine sulphate in 0.5 M sulfuric acid ($\phi_{lum} = 0.546$, $\lambda_{ex} = 365$ nm) as standard at 298 K ^d Butyronitrile

Table S2First singlet-singlet transition of the open and closed forms in
BzThSiMe2-DTE computed by TDDFT/CPCM using benzene as the
solvent

Compound	Transition	Excitation ^a	Coefficient ^b	$f^{\mathfrak{c}}$	Vertical excitation wavelength (nm)
BzThSiMe ₂ -DTE (open)	$S_0 \to S_1$	$\mathrm{H} \to \mathrm{L}$	0.70	0.341	387
BzThSiMe ₂ -DTE (closed)	$S_0 \to S_1$	$\mathrm{H} \rightarrow \mathrm{L}$	0.70	0.209	497

^a Orbitals involved in the major excitation (H = HOMO and L = LUMO).

^b The coefficients in the configuration interaction (CI) expansion.

^cOscillator strengths.

Empirical formula	C24H24S3Si
Formula weight	436.70
Temperature, K	301 (2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> na 2 ₁ (No.3)
<i>a</i> , Å	18.3041 (19)
b, Å	17.6314 (18)
<i>c</i> , Å	14.4784 (15)
a, deg	90.00
β , deg	90.00
γ, deg	90.00
Volume, Å ³	4672.6 (8)
Ζ	8
Density (calculated), g/cm ³	1.242
<i>F</i> (000)	1840.0
Crystal size	$0.5 \text{ mm} \times 0.35 \text{ mm} \times 0.32 \text{ mm}$
Theta range for data collection	5.12 to 50.06°
Index ranges	$-21 \leq h \leq 21, -18 \leq k \leq 20, -17 \leq l \leq 16$
Reflections collected	25164
Independent reflections	8143 [<i>R</i> (int) = 0.0287]
Goodness-of-fit on F^2	1.027
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0496, wR_2 = 0.1204$
Final <i>R</i> indexes [all data]	$R_1 = 0.0630, wR_2 = 0.1296$
Largest diff. peak and hole	0.75 and -0.15 eÅ ⁻³

Table S3Crystal and structure determination data of BzThSiMe2-DTE

Bond Distances / Å							
Si(1)–C(23)	1.853 (5)	Si(2)–C(48)	1.854 (5)				
Si(1)–C(24)	1.866 (4)	Si(2)–C(47)	1.854 (4)				
Si(1)–C(7)	1.904 (4)	Si(2)-C(40)	1.848 (4)				
Si(1)–C(16)	1.872 (4)	Si(2)–C(31)	1.910 (4)				
C(7)–C(8)	1.367 (5)	C(40)-C(39)	1.372 (5)				
C(8)–C(15)	1.485 (5)	C(32)–C(39)	1.496 (5)				
C(15)-C(16)	1.375 (5)	C(31)–C(32)	1.351 (5)				
C(22)–C(17)	1.424 (5)	C(41)–C(46)	1.396 (5)				

 Table S4
 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for BzThSiMe₂-DTE

Bond	Angle	es / °
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C(23)-Si(1)-C(24)	111.1 (2)	C(40)-Si(2)-C(48)	114.7 (2)
C(23)-Si(1)-C(16)	114.8 (2)	C(40)-Si(2)-C(47)	111.69 (19)
C(24)-Si(1)-C(16)	112.49 (19)	C(48)-Si(2)-C(47)	112.2 (2)
C(23)-Si(1)-C(7)	111.7 (2)	C(48)-Si(2)-C(31)	112.1 (2)
C(24)-Si(1)-C(7)	113.99 (19)	C(47)-Si(2)-C(31)	113.4 (2)
C(16)-Si(1)-C(7)	91.59 (16)	C(40)-Si(2)-C(31)	91.12 (17)
C(8)–C(7)–Si(1)	108.9 (3)	C(32)–C(31)–Si(2)	109.9 (3)
C(7)-C(8)-C(15)	113.5 (3)	C(31)-C(32)-C(39)	112.3 (3)
C(16)-C(15)-C(8)	119.3 (3)	C(40)-C(39)-C(32)	119.4 (3)
C(15)-C(16)-Si(1)	106.4 (3)	C(39)-C(40)-Si(2)	107.1 (3)



 Figure S1
 Electronic absorption spectrum of open form of BzThSiMe₂-DTE in benzene at 298 K



 Figure S2
 Electronic absorption spectrum of closed form of BzThSiMe₂-DTE in benzene at 298 K



Figure S3 UV-Vis absorbance changes of BzThSiMe₂-DTE at 474 nm on alternate excitation at the isosbestic wavelength of 370 nm and at the absorption maximum of the closed form at 474 nm over five cycles in non-degassed benzene solution at 298 K



Figure S4 Perspective view of BzThSiMe₂-DTE showing two independent molecules with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 30% probability level.

BzThSiMe ₂ -DTE (open form)				BzThSiMe ₂ -DTE (closed form)					
1	С	1.537871	1.943988	-1.117793	1	С	-2.218330	1.037523	0.408706
2	С	0.598445	1.643509	-0.157485	2	С	-2.581148	-0.178913	-0.451140
3	С	0.301287	2.767406	0.686693	3	С	-1.595498	-1.303846	-0.127214
4	С	1.010779	3.893327	0.389125	4	С	-0.281212	-1.013086	0.043274
5	S	2.055610	3.590681	-0.962891	5	С	0.158250	0.396795	0.052872
6	С	-0.066791	0.334706	-0.023366	6	С	-0.754463	1.409267	0.153781
7	С	-1.541529	0.268297	-0.003043	7	С	-2.254370	-2.582288	-0.099443
8	С	-2.176394	-0.945374	0.099900	8	С	-3.606000	-2.527759	-0.069478
9	Si	-0.818468	-2.227540	0.159958	9	S	-4.252918	-0.888641	-0.088857
10	С	-0.707886	-3.177098	1.778398	10	S	-3.179049	2.561550	-0.022359
11	С	0.969971	5.224549	1.062940	11	С	-1.726110	3.550575	0.040107
12	С	2.096417	1.078530	-2.196321	12	С	-0.579571	2.833148	0.131294
13	С	0.531383	-0.894206	0.048903	13	С	-4.555241	-3.673412	-0.009395
14	С	1.966521	-1.169091	0.150075	14	С	-2.507865	0.090175	-1.963161
15	С	2.843082	-0.580681	1.038537	15	Si	1.222236	-2.142611	0.164102
16	S	4.433073	-1.252966	0.866589	16	С	1.372355	-3.356521	-1.266280
17	С	3.940345	-2.340087	-0.393307	17	С	1.611531	0.488157	-0.010169
18	С	2.610174	-2.181234	-0.644502	18	С	2.365405	-0.667253	0.029908
19	С	4.908180	-3.269735	-1.046809	19	С	-1.856691	5.032318	-0.020411
20	С	2.581934	0.457509	2.077053	20	С	-2.389646	0.797673	1.918622
21	С	-0.870937	-3.410769	-1.303237	21	С	1.367388	-3.060250	1.801590
22	Н	0.675729	6.022059	0.372202	22	Н	-2.431044	5.412094	0.832164
23	н	1.942306	5.498916	1.486145	23	Н	-2.384522	5.345483	-0.928389
24	Н	0.242435	5.200622	1.878206	24	Н	-0.871222	5.503753	-0.013606
25	Н	-0.405379	2.723723	1.509284	25	Н	0.386862	3.324753	0.154747
26	Н	2.283408	1.647956	-3.111449	26	Н	-3.433625	0.603885	2.173268
27	Н	1.393866	0.273300	-2.426627	27	Н	-2.051582	1.684061	2.460811
28	Н	3.037913	0.609045	-1.888781	28	Н	-1.784406	-0.057156	2.233863
29	Н	3.187924	0.290080	2.972594	29	Н	-3.245605	0.834344	-2.269866
30	Н	1.527670	0.435533	2.365918	30	Н	-2.700220	-0.840893	-2.501909
31	Н	2.794877	1.467403	1.707745	31	Н	-1.510462	0.450643	-2.231513
32	Н	2.089711	-2.752931	-1.406695	32	Н	-1.715402	-3.524124	-0.057122
33	Н	5.715993	-2.729809	-1.552697	33	Н	-5.202848	-3.603341	0.871801
34	Н	4.388961	-3.874808	-1.794556	34	Н	-4.011311	-4.619812	0.035260
35	Н	5.371666	-3.950713	-0.324766	35	Н	-5.209271	-3.688091	-0.888472
36	Н	0.219692	-3.757910	1.817557	36	Н	0.588713	-4.120427	-1.222086
37	Н	-1.547486	-3.872024	1.882961	37	Н	2.338377	-3.872061	-1.238458
38	Н	-0.719424	-2.495536	2.633828	38	Н	1.289966	-2.840856	-2.227392
39	Н	-0.855890	-2.867571	-2.252599	39	Н	1.284039	-2.370306	2.646333
40	Н	-1.788078	-4.008800	-1.270441	40	Н	2.331317	-3.575077	1.876049
41	Н	-0.022199	-4.101910	-1.285327	41	Н	0.577823	-3.813296	1.897978
42	S	-2.639346	1.613493	-0.184491	42	S	2.590876	1.933036	-0.121176
43	С	-3.601787	-0.818239	0.035450	43	C	3.773912	-0.401137	-0.022901
44	С	-4.010312	0.532688	-0.114414	44	C	4.057976	0.984228	-0.108816
45	C	-5.356667	0.891446	-0.188603	45	C	5.363707	1.468939	-0.173982
46	С	-6.311992	-0.112992	-0.118996	46	С	6.407427	0.553298	-0.150971
47	С	-5.931184	-1.456364	0.025198	47	С	6.151759	-0.823595	-0.064935
48	С	-4.594956	-1.811355	0.102848	48	С	4.853165	-1.301539	-0.001623
49	Η	-5.651356	1.930497	-0.301094	49	Н	5.561388	2.534575	-0.239936
50	Н	-7.365171	0.145357	-0.177097	50	Н	7.432163	0.909354	-0.199963
51	Н	-6.696245	-2.225597	0.077666	51	Н	6.983705	-1.521597	-0.048274
52	Н	-4.307508	-2.853016	0.217836	52	Н	4.662944	-2.369461	0.064142

Cartesian coordinates for the optimized geometries

References

- (1) Coulson, D. R. Inorg. Synth. 1990, 28, 107; Angelici R. J., Ed.
- (2) Demas, J. N.; Crosby, G. A. J. Phys. Chem. 1971, 75, 991.
- (3) (a) Melhuish, W. H. J. Phys. Chem. 1961, 65, 229. (b) Meech, S. R.; Phillips, D. J. Photochem. 1983, 23, 193.
- (4) (a) Hatchard, C. G.; Parker, C. A. Proc. R. Soc. London, Ser. A 1956, 235, 518.
 (b) Murov, S. L. Handbook of Photochemistry; Marcel Dekker: New York, 1973. (c) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Pure Appl. Chem. 2004, 76, 2105. (d) Wegner, E. E.; Adamson, A.W. J. Am. Chem. Soc. 1966, 88, 394.
- (5) (a) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* 1980, 19, 2854. (b)
 Connelly, N. G.; Geiger, W. E. *Chem. Rev.* 1996, 96, 877.
- (6) SAINT+. *SAX area detector integration program*, Version 7.34A; Bruker AXS, Inc.: Madison, WI, 2006.
- (7) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, 2004.
- (8) Sheldrick, G. M. *SHELXS97. Programs for Crystal Structure Analysis*, (Release 97–2); University of Goetingen: Germany, 1997.
- (9) Yamaguchi, T.; Irie, M. J. Org. Chem. 2005, 25, 10323.
- (10) (a) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Eur. J.* 2000, *6*, 1683. (b) Yamaguchi, S.; Itami, Y.; Tamao, K. *Organometallics* 1998, *17*, 4910.
- (11) (a) Son, H.-J.; Han, W,-S.; Chun, J.-Y.; Lee, C.-J.; Han, J.-I.; Ko, J.; Kang, S. O. *Organometallics* 2007, *26*, 519. (b) Son, H.-J.; Han, W.-S.; Chun, J.-Y.; Kwon, S.-N.; Ko, J.; Kang, S. O. *Organometallics* 2008, *27*, 2464.
- (12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J.

J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision C.01, Gaussian, Inc.: Wallingford, CT, 2010.

- (13) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865.
- (14) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1997, 78, 1396.
- (15) Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158.
- (16) Barone, V.; Cossi, M. J. Phys. Chem. A 1998, 102, 1995.
- (17) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. Comput. Chem. 2003, 24, 669.
- (18) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. J. Chem. Phys. 1998, 109, 8218.
- (19) Bauernschmitt, R.; Ahlrichs, R. Chem. Phys. Lett. 1996, 256, 454.
- (20) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. J. Chem. Phys. 1998, 108, 4439.
- (21) Hehre, W. J.; Ditchfield, R.; Pople, J. A. J. Chem. Phys. 1972, 56, 2257.
- (22) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. J. Chem. Phys. **1982**, 77, 3654.
- (23) Hariharan, P. C.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213.
- (24) Sevez, G.; Pozzo, J.-L. Dyes Pigments 2011, 89, 246.
- (25) Liang, Y.; Geng, W.; Wei, J.; Xi, Z.; Angew. Chem. Int. Ed. 2012, 51, 1934.