Canadian Journal of Chemistry
Revue canadienne de chimie

Synthesis and physical properties of [4]cyclo-3,7-dibenzo[b,d]thiophene and its S,S-dioxide

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2016-0474.R1
Manuscript Type:	Article
Date Submitted by the Author:	27-Sep-2016
Complete List of Authors:	Kayahara, Eiichi; Kyoto University, Institute for Chemical Research Xue, Zhai; Kyoto University, Institute for Chemical Research Yamago, Shigeru; Kyoto University, Institute for Chemical Research
Keyword:	n-conjugated molecule, cycloparaphenylene, dibenzothiophene, sulfur

Synthesis and physical properties of
[4]cyclo-3,7-dibenzo[*b,d*]thiophene and its
S,S-dioxide

*Eiichi Kayahara, Zhai Xue, and Shigeru Yamago**

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

(RECEIVED DATE)

*To whom correspondence should be addressed. E-mail: yamago@scl.kyoto-u.ac.jp

Abstract

Cyclic tetramers of 3,7-dibenzo[*b,d*]thiophene (DBT) and 3,7-dibenzo[*b,d*]thiophene-5,5-dioxide (DBTO), i.e., [4]cyclo-DBT ([4]CDBT) and [4]cyclo-DBTO ([4]CDBTO), respectively, are synthesized by the platinum-mediated assembly of bis-metallated DBT and DBTO and the subsequent reductive elimination of platinum. This is the first example of the synthesis of sulfur-containing cycloparaphenylene (CPP) derivatives. The structure of [4]CDBTO is unambiguously determined by the single crystal X-ray analysis. Theoretical and experimental analyses of their physical properties reveal the effect of the sulfur atom and sulfonyl group at the periphery of biphenyl units of the CPP.

Keywords: π -conjugated molecule, cycloparaphenylene, dibenzothiophene, sulfur

1 Introduction

2 There has been growing interest in hoop-shaped π -conjugated molecules because of their
3 unique molecular structures with radially oriented π systems and potential applications in
4 molecular electronics.¹⁻⁴ Cycloparaphenylenes (CPPs, Figure 1a)⁵⁻⁷, in particular, occupied a
5 central position among such molecules after their recent successful synthesis by three groups,
6 including our own.⁸⁻¹⁰ The syntheses have sparked a flurry of investigations on their physical
7 properties such as size-dependent photophysical¹¹⁻¹⁹ and redox properties²⁰⁻²⁶ and
8 size-selective host-guest chemistry.^{17,27-31} Among the synthetic methods, the
9 platinum-mediated assembly method that we reported earlier¹⁰ features milder reaction
10 conditions compared to others because aromatization reaction of the paraphenylene
11 precursors, which usually requires harsh conditions, such as strong reducing agent or high
12 temperatures under acidic and oxidative conditions, is not required in our method. This
13 characteristic feature of our method allows the synthesis of CPPs with different sizes,^{20,21,32-34}
14 CPP derivatives,³⁵⁻³⁸ and cyclic and caged new molecules.³⁹⁻⁴⁷

15 Embedding heteroatoms in π -conjugated molecules has been recognized as an important
16 strategy to tune their electronic properties in organic electronics.^{48,49} Thus, the synthesis of
17 CPP derivatives possessing heteroatoms or heteroatom substituents would be of great interest.
18 Indeed, several heteroatom-embedded CPP derivatives have been reported to date, such as
19 (bi)pyridyl-,^{50,51} carbazole-,^{37,52} chloro-,⁵³ boryl-,⁵⁴ silyl-,⁵⁴ alkoxy-,^{55,56} and
20 carbonyl^{57,58}-substituted CPP derivatives. However, sulfur-containing CPP derivatives have
21 not been reported so far besides the derivatives containing thiophene units as a part of
22 conjugated ring,^{44,45,59} despite the importance of sulfur-containing π -conjugated molecules as
23 promising materials for semiconductors.^{48,49} We report herein the platinum-mediated
24 synthesis of a cyclic tetramer of 3,7-dibenzo[*b,d*]thiophene (DBT) and
25 3,7-dibenzo[*b,d*]thiophene-5,5-dioxide (DBTO), [4]cyclo-3,7-dibenzo[*b,d*]thiophene

1 ([4]CDBT, Figure 1b), and [4]cyclo-3,7-dibenzo[*b,d*]thiophene-5,5-dioxide ([4]CDBTO,
 2 Figure 1c), as the first examples of sulfur-containing CPP derivatives. Photophysical and
 3 redox properties of [4]CDBT and [4]CDBTO are also reported.

5 **Figure 1.** Structures of a) [n]CPP, b) [4]CDBT, and c) [4]CDBTO.

8 Syntheses of [4]CDBT and [4]CDBTO were performed according to our previous
 9 synthesis of [8]CPP (Scheme 1).¹⁰ To fabricate [4]CDBT, readily available 3,7-dibromoDBT
 10 (**1ai**)⁶⁰ was treated with BuLi (2.1 equiv) followed by trimethyltin chloride (2.3 equiv) to give
 11 bisstannyl compounds **1aii** in 92% yield. Then, **1aii** was treated with Pt(cod)Cl₂ (cod =
 12 1,5-cyclooctadiene, 1.0 equiv) in 1,2-dichloroethane at 60 °C for 12 h. Because of the low
 13 solubility of the resulting mixture, the obtained crude mixture was subjected to reductive
 14 elimination of platinum without purification by triphenylphosphine (8.0 equiv) at 90 °C for 18
 15 h. Purification of the product by silica-gel column chromatography and recycling preparative
 16 gel permeation chromatography gave [4]CDBT as a yellow solid in the overall yield of 2.7%.

17 [4]CDBTO was also prepared from 3,7-dibromoDBTO (**1bi**)⁶¹ by the same synthetic
 18 procedure. When Br-Li transmetallation was carried out by BuLi, it resulted in the low yield
 19 of bisstannane **1bii**, probably due to the presence of highly electrophilic sulfone moiety. In
 20 contrast, when *i*-PrMgCl·LiCl was used instead of BuLi, **1bii** was obtained in good yield
 21 (79%). After treatment of **1bii** with Pt(cod)Cl₂, the reductive elimination of platinum by

employing triphenylphosphine at 105 °C afforded [4]CDBTO in 5.1% overall yield as a yellow solid. The reductive elimination was also carried out by treating a crude mixture, which was formed from **1bii** and PtCl₂(cod), with bis(diphenylphosphino)ferrocene (dppf) followed by the addition of bromine¹⁰, and [4]CDBTO was obtained in 3.4% overall yield. While the platinum complex could not be fully characterized because of the poor solubility in both cases, formation of the desired cyclic products supports the presence of cyclic tetranuclear platinum **2**.

and at 7.45, 7.72, and 7.90 ppm for [4]CDBTO. In the ^{13}C NMR spectra, only six peaks were observed for both compounds. These results indicate that both the compounds have a highly symmetrical structure with *anti/anti/anti* orientation with respect to the adjacent DBT and DBTO units.

The DFT calculation suggests that this *anti/anti/anti* structure with D_{2d} point group symmetry, **A**, is the thermodynamically most stable isomer among the four possible isomers **A–D** of [4]CDBT and [4]CDBTO, followed by *anti/syn/syn* (**B**), *anti/syn/anti* (**C**), and *syn/syn/syn* (**D**) isomers with C_s , C_2 , and C_{2v} point group symmetries, respectively (Figure 2). The same relative stability was already observed in the cyclic tetramers of fluorene³⁶ and carbazole.³⁷ Furthermore, the activation energy for the ring rotation from **A** to **B** was calculated as 91 and 100 kJ/mol for [4]CDBT and [4]CDBTO, respectively, suggesting the occurrence of isomerization at room temperature. Therefore, the exclusive observation of **A** would be due to the thermodynamic control instead of the kinetic control.³⁶

Figure 2. Structures and relative energies (kJ mol⁻¹) of a) [4]CDBT and b) [4]CDBTO isomers **A–D** and transition state (TS) for the rotation from **A** to **B** of c) [4]CDBT and d) [4]CDBTO. Gray, white, yellow, and red represent carbon, hydrogen, sulfur, and oxygen

atoms, respectively.

The structure of [4]CDBTO was unambiguously determined by the X-ray diffraction experiment performed on a single crystal obtained by slow vapor diffusion of *n*-hexane into a solution of [4]CDBTO in CHCl₃ at room temperature. In the solid state, [4]CDBTO exhibits the *D*_{2d} point group symmetry, which is the *anti/anti/anti* orientation with respect to the adjacent DBTO unit. The structure is identical to that of the most stable isomer **A** (Figure 3a). [4]CDBTO molecules align in a tiled form on an *ab* plane and form alternate layers along the *c* axis to form tubular channels (Figure 3b). Additionally, intermolecular hydrogen bonding (2.7–2.9 Å) is observed between S=O and the hydrogen atom of the aryl ring of the neighboring molecule.

Figure 3. a) ORTEP drawing of [4]CDBTO. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. b) Three-dimensional array of [4]CDBTO. Black, yellow, and red represent carbon, sulfur, and oxygen atoms, respectively. Blue dot lines represent intermolecular hydrogen bonding.

The photophysical properties of [4]CDBT and [4]CDBS were next examined. In the UV-vis absorption spectrum in CHCl₃ (Figure 4), [4]CDBT shows two strong absorptions at 337 (λ_{abs1}) and 370 nm (λ_{abs2}) and a weak shoulder peak at around 400 nm, which further

1 extends to around 450 nm. In contrast, the absorption spectrum of [4]CDBTO showed a single
2 absorption band with an absorption maximum at 337 nm. Despite the difference in the shape
3 of the absorption spectra, [4]DCBT and [4]DCBTO show nearly identical absorption maxima
4 with [8]CPP.¹⁰ Time-dependent density functional theory (TD-DFT) calculations indicate that
5 the absorption bands of [4]CDBT comprise several transitions (Figure 5a); λ_{abs2} mainly
6 derives from the sum of degenerated HOMO-1 to LUMO and HOMO to the degenerated
7 LUMO+1 and λ_{abs1} from the degenerated HOMO-4 to LUMO. The complexity in the electron
8 transition of [4]CDBT is ascribed to the participation of the sulfur atoms in molecular orbitals,
9 as observed in one of the degenerated HOMO-1 and degenerated HOMO-4 orbitals. For
10 [4]CDBTO, the single absorption band can be assigned as the sum of transitions from the
11 degenerated HOMO-1 to LUMO and the HOMO to the degenerated LUMO+1 (Figure 5b).
12 Since sulfur orbitals do not participate in the HOMO-1, HOMO, LUMO, and LUMO-1 of
13 [4]CDBTO, its electron transition is identical to that observed for [n]CPP.²⁰

14 In the fluorescence spectrum, [4]CDBT and [4]CDBTO showed the band at 510 nm with
15 a quantum yield (Φ_F) of 0.21 and the bands at 429 and 529 nm with Φ_F of 0.41, respectively.
16 While their fluorescence wave lengths are similar to that of [8]CPP, their Φ_F is significantly
17 higher than that of [8]CPP (0.081).¹¹ The increase in Φ_F is probably attributed to the rigid
18 structure of DBT and DBTO units compared to that of biphenyl of [8]CPP owing to the
19 presence of sulfur atom, which reduces the loss of excited energy as vibrational energy.

Figure 4. UV-vis absorption and fluorescence spectra of [4]CDBT, [4]CDBTO, and [8]CPP.

Figure 5. Orbital energies and MO patterns of (a) [4]CDBT and (b) [4]CDBTO calculated at the B3LYP/6-31G* level of theory.

Cyclic voltammograms (CVs) were measured to examine the redox properties of [4]CDBT and [4]CDBTO for a sample dissolved in 0.1 M Bu₄NPF₆ solution in 1,1,2,2-tetrachloroethane (for oxidation) or THF (for reduction) (Figure 6). [4]CDBT showed two reversible oxidation waves with half-wave oxidation potentials, $E_{1/2}$, 0.74 and 0.96 V

versus the ferrocene/ferrocenium couple (Fc/Fc^+), which is much higher than that of [8]CPP (0.59 V). In contrast, [4]CDBTO showed no wave within the given solvent window. In the reduction region, both [4]CDBT and [4]CDBTO exhibit one quasi-reversible reduction wave at $E_{1/2} = -2.07$ and -1.57 versus Fc/Fc^+ , respectively, which are significantly lower than that of [8]CPP (-2.33 V). The results are consistent with the moderate and strong inductive effect of the sulfur and the sulfone groups, respectively.

The calculated HOMO and LUMO energies of [4]CDBT (-5.23 and -1.88 eV, respectively) and [4]CDBTO (-6.01 and -2.92 eV, respectively) are lower than those of [8]CPP (Table 1), and the results are consistent with the CV analyses. The HOMO-LUMO gap in [4]CDBT (3.35 eV) and [4]CDBTO (3.35 eV) is smaller than that of the corresponding linear analogues, [4]DBT (3.78 eV) and [4]DBTO (3.62 eV), respectively. We have already reported the effect of the cyclic structure on HOMO-LUMO gap, which is narrower than that of the corresponding linear analogue, such as 3.41 and 3.90 eV for [8]CPP and [8]paraphenylene ([8]PP), respectively.²⁰ The results reveal the generality of the cyclic effect, regardless of the presence of heteroatoms in the conjugated molecules.

Figure 6. CV of [4]CDBT (red), [4]CDBTO (blue), and [8]CPP (black) in 0.1 M

Bu₄NPF₆/1,1,2,2-tetrachloroethane (for oxidation) and THF (for reduction) at room temperature; scan rate = 0.1 (for oxidation) and 0.05 V s⁻¹ (for reduction).

In summary, we have successfully achieved the synthesis of [4]CDBT and [4]CDBTO for the first time through a platinum-mediated assembly of linear bis-metallated DBT and DBTO, followed by the elimination of platinum. Photophysical and electrochemical analyses revealed that the introduction of bridging by a sulfur atom and a sulfonyl group on the biphenyl units of CPP affect the optical and electronic properties of CPPs. This work provides a new insight into the effect of functional groups on the optoelectronic properties of CPPs.

Acknowledgement

This work was partly supported by the Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Grant 26410043 for E.K. and 16H06352 for S.Y.). Single-crystal X-ray analysis was performed at BL02B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; 2015B1311).

Experimental section

General. All reactions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen atmosphere. Recycling preparative gel permeation chromatography was performed on JAIGEL 1H and 2H polystyrene columns (Japan Analytical Industry Co., Ltd.) with CHCl₃ as the eluent. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were measured for a CDCl₃ solution of a sample and are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak. MALDI-TOF MS spectrum was obtained on a spectrometer in the positive reflection mode and at 20 kV acceleration voltage. Samples were prepared from a THF solution by mixing a sample (1

1 mg/mL) and dithranol (10 mg/mL) in a 1:1 ratio. UV-vis and fluorescence spectra were
2 measured in CHCl_3 at room temperature. CV was measured with a Pt electrode for
3 1,1,2,2-tetrachloroethane or THF solution of a sample (1 mmol L^{-1}) in the presence of an
4 supporting electrolyte (Bu_4NPF_6 , 0.1 mol L^{-1}) at room temperature under nitrogen
5 atmosphere. The scan rates of 100 mV s^{-1} was employed for CV. The potentials were
6 calibrated with respect to Fc/Fc^+ .

7 **Materials.** Unless otherwise noted, commercially available materials were used without
8 purification. CH_2Cl_2 , $(\text{CH}_2\text{Cl})_2$, and $(\text{CHCl}_2)_2$ were distilled successively from P_2O_5 and
9 K_2CO_3 and stored over molecular sieves. Toluene was distilled from CaH_2 and stored over
10 molecular sieves. Water content in solvents were determined by Karl-Fisher water titrater.
11 Compounds **1ai**,⁶⁰ **1bi**,⁶¹ $\text{Pt}(\text{cod})\text{Cl}_2$,⁶² and dppf ⁶³ were synthesized according to literature
12 procedures. $i\text{-PrMgCl}\cdot\text{LiCl}$ ⁶⁴ was immediately prepared before use as described in literature.

13 **Synthesis of 1aii.** To a solution of **1ai** (1.00 g, 2.92 mmol) in THF (15 mL) was slowly added
14 BuLi (3.72 mL, 1.65 M in hexane, 6.13 mmol) at -70°C . After stirring for 1 h at this
15 temperature, a solution of trimethylstannyl chloride (1.34 g, 6.72 mmol) in THF (5 mL) was
16 slowly added, and the resulting mixture was slowly warmed to room temperature. After
17 stirred for 4 h at this temperature, the reaction mixture was quenched with saturated aqueous
18 NH_4Cl solution, and was extracted with ether. The combined organic layer was washed with
19 brine, dried over MgSO_4 , filtered and concentrated under reduced pressure to give a crude
20 mixture. The residue was purified by recrystallization from hexane to give **1aii** (1.37 g, 92%)
21 as colorless solids. ^1H NMR (CDCl_3 , 400 MHz) δ = 0.36 (s, $J_{119\text{Sn}-\text{C}}$ = 55.21 Hz, $J_{117\text{Sn}-\text{C}}$ =
22 52.80 Hz, 18 H, $-\text{SnMe}_3$), 7.54 (dd, J = 8.0, 0.8 Hz, 8H, $-\text{ArH}$), 7.97 (s, 2H, $-\text{ArH}$), 8.13 (dd, J
23 = 7.8, 0.4 Hz, 8H, $-\text{ArH}$) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = -9.31 ($J_{\text{Sn}-\text{C}}$ = 350.70 Hz),
24 121.00, 129.97, 131.09, 135.61, 139.37, 141.05 ppm; HRMS (FAB) m/z : Calcd for
25 $\text{C}_{18}\text{H}_{24}\text{SSn}_2 (\text{M})^+$, 509.8700; Found 509.8742.

Synthesis of 1bii. To a solution of **1bi** (10.0 g, 26.7 mmol) in THF (183 mL) was added a solution of *i*-PrMgCl·LiCl (69.6 mL, 0.96 M in THF, 66.8 mmol) at -20 °C. After stirring for 1 h at this temperature and 1 h at 0 °C, a solution of trimethylstannyl chloride (16.0 g, 80.2 mmol) in THF (183 mL) was added at -20 °C, and the resulting mixture was slowly warmed to room temperature. After stirred for 4 h at this temperature, the reaction mixture was quenched with saturated aqueous NH₄Cl solution, and was extracted with ether. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude mixture. Purification by silica gel chromatography using hexane as an eluent afforded **1bii** (11.4 g, 79%) as colorless solids. ¹H NMR (CDCl₃, 400 MHz) δ = 0.37 (s, $J_{119\text{Sn-C}} = 54.83$ Hz, $J_{117\text{Sn-C}} = 54.78$ Hz, 18 H, -SnMe₃), 7.54 (m, 4H, -ArH), 7.94 (s, 2H, -ArH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = -9.27 ($J_{119\text{Sn-C}} = 350.15$ Hz, $J_{117\text{Sn-C}} = 348.98$ Hz), 120.67, 128.57, 131.70, 136.60, 141.01, 147.04 ppm; HRMS (FAB) *m/z*: Calcd for C₁₈H₂₄O₂SSn₂ (M)⁺, 541.9529; Found 541.9576.

Synthesis of [4]CDBT. Pt(cod)Cl₂ (374.2 mg, 1.0 mmol) and **1aii** (510 mg, 1.0 mmol) were dissolved in (CH₂Cl)₂ (340 mL), and the mixture was heated to 60 °C for 20 h under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was washed with hexane and ether to give an off-white solid.

The suspension of above obtained solid and PPh₃ (0.52 g, 2.0 mmol) in toluene (200 mL) was stirred at room temperature under a nitrogen atmosphere. After 3 h, the resulting mixture was heated at 105 °C for 18 h. The resulting suspension was filtered, and the filtrate was concentrated under reduced pressure to give a crude mixture. The residue was purified by silica gel chromatography and preparative gel permeation chromatography to give [4]CDBT (4.9 mg, 2.9%, 2 steps) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ = 7.19 (s, 8H, -ArH), 7.70 (dd, $J = 8.6, 1.4$ Hz, 8H, -ArH), 7.95 (d, $J = 8.4$ Hz, 8H, -ArH) ppm; ¹³C NMR

1 (CDCl₃, 100 MHz) δ =118.90, 124.10, 126.75, 134.21, 137.25, 139.69 ppm; HRMS
2 (MALDI-TOF) m/z : Calcd for C₄₈H₂₄S₄ (M)⁺, 728.0761; Found 728.0805.

3 **Synthesis of [4]CDBTO.** Pt(cod)Cl₂ (748 mg, 2.0 mmol) and **1bii** (1.08 g, 2.0 mmol) were
4 dissolved in (CH₂Cl)₂ (500 mL), and the mixture was heated to 60 °C for 12 h under a
5 nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was
6 washed with hexane and ether to give an off-white solid.

7 The suspension of above obtained solid and PPh₃ (1.04 g, 4.0 mmol) in toluene (400 mL) was
8 stirred at room temperature under a nitrogen atmosphere. After 3 h, the resulting mixture was
9 heated at 105 °C for 18 h. The resulting suspension was filtered, and the filtrate was
10 concentrated under reduced pressure to give a crude mixture. The residue was purified by
11 silica gel chromatography and preparative gel permeation chromatography to give [4]CDBTO
12 (27.9 mg, 6.5%, 2 steps) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ = 7.45 (d, J = 1.6
13 Hz, 8H, -ArH), 7.72 (d, J = 8.0 Hz, 8H, -ArH), 7.90 (dd, J = 8.4, 1.6 Hz, 8H, -ArH) ppm; ¹³C
14 NMR (CDCl₃, 100 MHz) δ = 123.82, 127.22, 128.95, 130.03, 133.46, 150.01 ppm; MS
15 (MALDI-TOF) m/z : Calcd for C₄₈H₂₄AgO₈S₄ [M+Ag]⁺ 962.9405, Found 962.9543.

16

17

Table 1. Redox properties and orbital energies of [4]CDBT, [4]CDBTO, [8]CPP, [4]DBT, [4]DBTO, and [8]Paraphenylene ([8]PP).

Compound	$E_{1/2}^{\text{ox}}$ (V) ^a	$E_{1/2}^{\text{red}}$ (V) ^a	HOMO (eV) ^b	LUMO (eV) ^b
[4]CDBT	0.74, 0.96	-2.07	-5.23	-1.88
[4]CDBTO	n.o. ^c	-1.57	-6.01	-2.92
[8]CPP	0.59 ^d	-2.33	-5.11 ^d	-1.70 ^d
[4]DBT	--	--	-5.51	-1.73
[4]DBTO	--	--	-6.29	-2.67
[8]PP	--	--	-5.43	-1.53

^aV vs. ferrocene/ferrocenium couple; Bu₄NPF₆ (0.1 mol L⁻¹) in 1,1,2,2-tetrachloroethane (oxidation) or THF (reduction). ^bData obtained from DFT calculations at the B3LYP/6-31G* level of theory. ^cn.o.: not observed. ^dTaken from Ref 20.

1 **Reference**

- 2 (1) Scott, L. T. *Angew. Chem. Int. Ed.* **2003**, 42, 4133.
- 3 (2) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, 106, 5274.
- 4 (3) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, 106, 5250.
- 5 (4) Evans, P. J.; Jasti, R. *Top. Curr. Chem.* **2013**, 4, 1.
- 6 (5) Golder, M. R.; Jasti, R. *Acc. Chem. Res.* **2015**, 48, 557.
- 7 (6) Omachi, H.; Segawa, Y.; Itami, K. *Acc. Chem. Res.* **2012**, 45, 1378.
- 8 (7) Yamago, S.; Kayahara, E.; Iwamoto, T. *Chem. Rec.* **2014**, 14, 84.
- 9 (8) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.*
10 **2008**, 130, 17646.
- 11 (9) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew.*
12 *Chem. Int. Ed.* **2009**, 48, 6112.
- 13 (10) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem. Int. Ed.* **2010**, 49,
14 757.
- 15 (11) Fujitsuka, M.; Cho, D. W.; Iwamoto, T.; Yamago, S.; Majima, T. *Phys.*
16 *Chem. Chem. Phys.* **2012**, 14, 14585.
- 17 (12) Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle,
18 S.; Itami, K. *Org. Biomol. Chem.* **2012**, 10, 5979.
- 19 (13) Nishihara, T.; Segawa, Y.; Itami, K.; Kanemitsu, Y. *J. Phys. Chem. Lett.*
20 **2012**, 3, 3125.
- 21 (14) Fujitsuka, M.; Iwamoto, T.; Kayahara, E.; Yamago, S.; Majima, T.
22 *ChemPhysChem* **2013**, 14, 1570.
- 23 (15) Alvarez, M. P.; Burrezo, P. M.; Kertesz, M.; Iwamoto, T.; Yamago, S.; Xia,
24 J.; Jasti, R.; Navarrete, J. T. L.; Taravillo, M.; Baonza, V. G.; Casado, J. *Angew. Chem. Int.*
25 *Ed.* **2014**, 53, 7033.

- 1 (16) Fujitsuka, M.; Lu, C.; Iwamoto, T.; Kayahara, E.; Yamago, S.; Majima, T. *J.*
2 *Phys. Chem. A* **2014**, *118*, 4527.
- 3 (17) Pena Alvarez, M.; Mayorga Burrezo, P.; Iwamoto, T.; Qiu, L.; Kertesz, M.;
4 Taravillo, M.; Baonza, V. G.; Lopez Navarrete, J. T.; Yamago, S.; Casado, J. *Faraday*
5 *Discuss.* **2014**, *173*, 157.
- 6 (18) Chen, H.; Golder, M. R.; Wang, F.; Jasti, R.; Swan, A. K. *Carbon* **2014**, *67*,
7 203.
- 8 (19) Hines, D. A.; Darzi, E. R.; Jasti, R.; Kamat, P. V. *J. Phys. Chem. A* **2014**,
9 *118*, 1595.
- 10 (20) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am.*
11 *Chem. Soc.* **2011**, *133*, 8354.
- 12 (21) Kayahara, E.; Iwamoto, T.; Suzuki, T.; Yamago, S. *Chem. Lett.* **2013**, *42*,
13 621.
- 14 (22) Zabula, A. V.; Filatov, A. S.; Xia, J.; Jasti, R.; Petrukhina, M. A. *Angew.*
15 *Chem. Int. Ed.* **2013**, *52*, 5033.
- 16 (23) Fujitsuka, M.; Tojo, S.; Iwamoto, T.; Kayahara, E.; Yamago, S.; Majima, T.
17 *J. Phys. Chem. Lett.* **2014**, *5*, 2302.
- 18 (24) Toriumi, N.; Muranaka, A.; Kayahara, E.; Yamago, S.; Uchiyama, M. *J. Am.*
19 *Chem. Soc.* **2015**, *137*, 82.
- 20 (25) Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S. *J. Am. Chem. Soc.* **2016**,
21 *138*, 338.
- 22 (26) Alvarez, M. P.; Ruiz Delgado, M. C.; Taravillo, M.; Baonza, V. G.; Lopez
23 Navarrete, J. T.; Evans, P.; Jasti, R.; Yamago, S.; Kertesz, M.; Casado, J. *Chem. Sci.* **2016**.
- 24 (27) Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. *Angew.*
25 *Chem. Int. Ed.* **2011**, *50*, 8342.

- 1 (28) Iwamoto, T.; Watanabe, Y.; Takaya, H.; Haino, T.; Yasuda, N.; Yamago, S.
2 *Chem. Eur. J.* **2013**, *19*, 14061.
- 3 (29) Iwamoto, T.; Slanina, Z.; Mizorogi, N.; Guo, J.; Akasaka, T.; Nagase, S.;
4 Takaya, H.; Yasuda, N.; Kato, T.; Yamago, S. *Chem. Eur. J.* **2014**, *20*, 14403.
- 5 (30) Nakanishi, Y.; Omachi, H.; Matsuura, S.; Miyata, Y.; Kitauro, R.; Segawa,
6 Y.; Itami, K.; Shinohara, H. *Angew. Chem. Int. Ed.* **2014**, *53*, 3102.
- 7 (31) Ueno, H.; Nishihara, T.; Segawa, Y.; Itami, K. *Angew. Chem. Int. Ed.* **2015**,
8 *54*, 3707.
- 9 (32) Kayahara, E.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *Org. Lett.* **2012**, *14*,
10 3284.
- 11 (33) Kayahara, E.; Patel, V. K.; Yamago, S. *J. Am. Chem. Soc.* **2014**, *136*, 2284.
- 12 (34) Kayahara, E.; Patel, V. K.; Xia, J.; Jasti, R.; Yamago, S. *Synlett* **2015**, *26*,
13 1615.
- 14 (35) Iwamoto, T.; Kayahara, E.; Yasuda, N.; Suzuki, T.; Yamago, S. *Angew.*
15 *Chem. Int. Ed.* **2014**, *53*, 6430.
- 16 (36) Kayahara, E.; Qu, R.; Kojima, M.; Iwamoto, T.; Suzuki, T.; Yamago, S.
17 *Chem. Eur. J.* **2015**, *21*, 18939.
- 18 (37) Kuroda, Y.; Sakamoto, Y.; Suzuki, T.; Kayahara, E.; Yamago, S. *J. Org.*
19 *Chem.* **2016**, *81*, 3356.
- 20 (38) Liu, Y.-Y.; Lin, J.-Y.; Bo, Y.-F.; Xie, L.-H.; Yi, M.-D.; Zhang, X.-W.;
21 Zhang, H.-M.; Loh, T.-P.; Huang, W. *Org. Lett.* **2016**, *18*, 172.
- 22 (39) Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat Commun* **2011**, *2*,
23 492.
- 24 (40) Hitosugi, S.; Yamasaki, T.; Isobe, H. *J. Am. Chem. Soc.* **2012**, *134*, 12442.
- 25 (41) Matsuno, T.; Kamata, S.; Hitosugi, S.; Isobe, H. *Chem. Sci.* **2013**, *4*, 3179.

- 1 (42) Kayahara, E.; Iwamoto, T.; Takaya, H.; Suzuki, T.; Fujitsuka, M.; Majima,
2 T.; Yasuda, N.; Matsuyama, N.; Seki, S.; Yamago, S. *Nat. Commun.* **2013**, *4*, 2694.
- 3 (43) Jiang, H.-W.; Tanaka, T.; Mori, H.; Park, K. H.; Kim, D.; Osuka, A. *J. Am.*
4 *Chem. Soc.* **2015**, *137*, 2219.
- 5 (44) Ball, M.; Fowler, B.; Li, P.; Joyce, L. A.; Li, F.; Liu, T.; Paley, D.; Zhong,
6 Y.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2015**, *137*,
7 9982.
- 8 (45) Asai, K.; Fukazawa, A.; Yamaguchi, S. *Chem. Comm.* **2015**, *51*, 6096.
- 9 (46) Chen, Q.; Trinh, M. T.; Paley, D. W.; Preefer, M. B.; Zhu, H.; Fowler, B. S.;
10 Zhu, X. Y.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2015**, *137*, 12282.
- 11 (47) Jiang, H.-W.; Tanaka, T.; Kim, T.; Sung, Y. M.; Mori, H.; Kim, D.; Osuka,
12 A. *Angew. Chem. Int. Ed.* **2015**, *54*, 15197.
- 13 (48) Wang, X.; Sun, G.; Routh, P.; Kim, D.-H.; Huang, W.; Chen, P. *Chem. Soc.*
14 *Rev.* **2014**, *43*, 7067.
- 15 (49) Stępień, M.; Gońka, E.; Żyła, M.; Sprutta, N. *Chem. Rev.* **2016**.
- 16 (50) Matsui, K.; Segawa, Y.; Itami, K. *Org. Lett.* **2012**, *14*, 1888.
- 17 (51) Darzi, E. R.; Hirst, E. S.; Weber, C. D.; Zakharov, L. N.; Lonergan, M. C.;
18 Jasti, R. *ACS Cent. Sci.* **2015**, *1*, 335.
- 19 (52) Myśliwiec, D.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Stępień, M. *J.*
20 *Am. Chem. Soc.* **2015**, *137*, 1643.
- 21 (53) Ishii, Y.; Matsuura, S.; Segawa, Y.; Itami, K. *Org. Lett.* **2014**, *16*, 2174.
- 22 (54) Kubota, N.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 1356.
- 23 (55) Tran-Van, A.-F.; Huxol, E.; Basler, J. M.; Neuburger, M.; Adjizian, J.-J.;
24 Ewels, C. P.; Wegner, H. A. *Org. Lett.* **2014**, *16*, 1594.

- 1 (56) Huang, C.; Huang, Y.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang,
2 K. K. *Org. Lett.* **2014**, *16*, 2672.
- 3 (57) Miyauchi, Y.; Johmoto, K.; Yasuda, N.; Uekusa, H.; Fujii, S.; Kiguchi, M.;
4 Ito, H.; Itami, K.; Tanaka, K. *Chem. Eur. J.* **2015**, *21*, 18900.
- 5 (58) Li, S.; Huang, C.; Thakellapalli, H.; Farajidizaji, B.; Popp, B. V.; Petersen, J.
6 L.; Wang, K. K. *Org. Lett.* **2016**, *18*, 2268.
- 7 (59) Zhang, F.; Götz, G.; Winkler, H. D. F.; Schalley, C. A.; Bäuerle, P. *Angew.*
8 *Chem. Int. Ed.* **2009**, *48*, 6632.
- 9 (60) Dias, F. B.; King, S.; Monkman, A. P.; Perepichka, I. I.; Kryuchkov, M. A.;
10 Perepichka, I. F.; Bryce, M. R. *J. Phys. Chem. B* **2008**, *112*, 6557.
- 11 (61) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Palsson, L.-O. *Chem.*
12 *Commun.* **2005**, 3397.
- 13 (62) DesEnfants Ii, R. E.; Gavney Jr, J. A.; Hayashi, R. K.; Rae, A. D.; Dahl, L.
14 F.; Bjarnason, A. *J. Organomet. Chem.* **1990**, *383*, 543.
- 15 (63) Cullen, W. R.; Kim, T. J.; Einstein, F. W. B.; Jones, T. *Organometallics*
16 **1983**, *2*, 714.
- 17 (64) Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 3333.

18

19

20

Legends of Figures and Schemes.

Figure 1. Structures of a) [*n*]CPP, b) [4]CDBT, and c) [4]CDBTO.

Figure 2. Structures and relative energies (kJ mol⁻¹) of a) [4]CDBT and b) [4]CDBTO isomers **A–D** and transition state (TS) for the rotation from **A** to **B** of c) [4]CDBT and d) [4]CDBTO. Gray, white, yellow, and red represent carbon, hydrogen, sulfur, and oxygen atoms, respectively.

Figure 3. a) ORTEP drawing of [4]CDBTO. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. b) Three-dimensional array of [4]CDBTO. Black, yellow, and red represent carbon, sulfur, and oxygen atoms, respectively. Blue dot lines represent intermolecular hydrogen bonding.

Figure 4. UV-vis absorption and fluorescence spectra of [4]CDBT, [4]CDBTO, and [8]CPP.

Figure 5. Orbital energies and MO patterns of (a) [4]CDBT and (b) [4]CDBTO calculated at the B3LYP/6-31G* level of theory.

Figure 6. CV of [4]CDBT (red), [4]CDBTO (blue), and [8]CPP (black) in 0.1 M Bu₄NPF₆/1,1,2,2-tetrachloroethane (for oxidation) and THF (for reduction) at room temperature; scan rate = 0.1 (for oxidation) and 0.05 V s⁻¹ (for reduction).

1

2 **Scheme 1.** Synthesis of [4]CDBT and [4]CDBTO. Reagents and conditions: a) 1) BuLi (2.1
3 equiv), THF, -70 °C, 1 h, 2) Me₃SnCl (2.3 equiv), THF, -70 °C to rt, 4 h, 92% (for **1ai**) or 1)
4 *i*-PrMgCl·LiCl (2.5 equiv), THF -20 to 0 °C, 2 h, Me₃SnCl (3.0 equiv), THF, -20 to rt, 4 h,
5 79% (for **1bi**). b) Pt(cod)Cl₂ (1.0 equiv), C₂H₄Cl₂, 60 °C, 12 h. c) PPh₃ (8.0 equiv), toluene,
6 90 °C, 18 h, 2.9% (2 steps from **1aii**) or 6.5% (2 steps from **1bii**). Overall yield: [4]CDBT
7 (2.7%), [4]CDBTO (5.1%).

8

Draft