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Eiichi Kayahara, Xue Zhai, Shigeru Yamago

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1 # Synthesis and physical properties of

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3 # S,S-dioxide

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

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

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10 **(RECEIVED DATE)**

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

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2   **Abstract**

3   Cyclic   tetramers   of   3,7-dibenzo[*b,d*]thiophene   (DBT)   and

4   3,7-dibenzo[*b,d*]thiophene-5,5-dioxide   (DBTO),   i.e.,   [4]cyclo-DBT   ([4]CDBT)   and

5   [4]cyclo-DBTO ([4]CDBTO), respectively, are synthesized by the platinum-mediated

6   assembly of bis-metallated DBT and DBTO and the subsequent reductive elimination of

7   platinum. This is the first example of the synthesis of sulfur-containing cycloparaphenylene

8   (CPP) derivatives. The structure of [4]CDBTO is unambiguously determined by the single

9   crystal X-ray analysis. Theoretical and experimental analyses of their physical properties

10   reveal the effect of the sulfur atom and sulfonyl group at the periphery of biphenyl units of the

11   CPP.

12

[4]CDBT (R = S)
[4]CDBTO (R = SO$_2$)
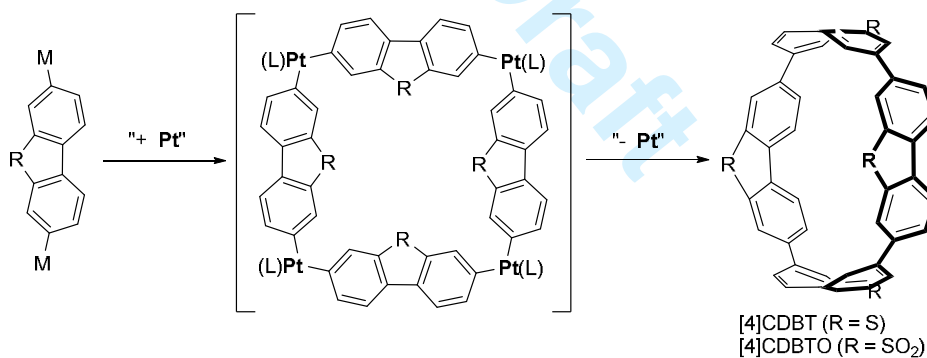
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16   **Keywords: π-conjugated molecule, cycloparaphenylene, dibenzothiophene, sulfur**

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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 photophysical[11-19] and redox properties[20-26] and

8   size-selective host–guest chemistry.[17,27-31] Among the synthetic methods, the

9   platinum-mediated assembly method that we reported earlier[10] 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.

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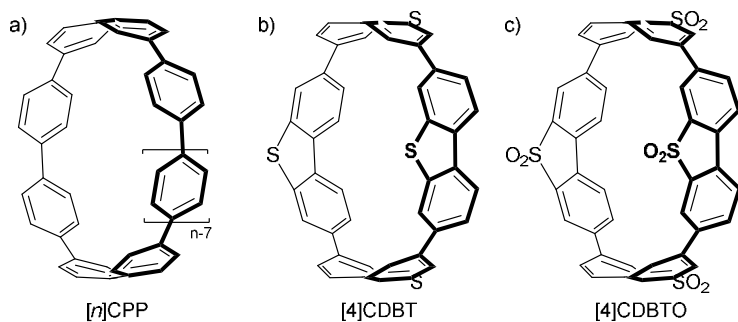
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6   **Figure 1.** Structures of a) [*n*]CPP, b) [4]CDBT, and c) [4]CDBTO.

7

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)Cl$_2$ (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)Cl$_2$, the reductive elimination of platinum by

1   employing triphenylphosphine at 105 °C afforded [4]CDBTO in 5.1% overall yield as a

2   yellow solid. The reductive elimination was also carried out by treating a crude mixture,

3   which was formed from **1bii** and PtCl$_2$(cod), with bis(diphenylphosphino)ferrocene (dppf)

4   followed by the addition of bromine[10], and [4]CDBTO was obtained in 3.4% overall yield.

5   While the platinum complex could not be fully characterized because of the poor solubility in

6   both cases, formation of the desired cyclic products supports the presence of cyclic

7   tetranuclear platinum **2**.

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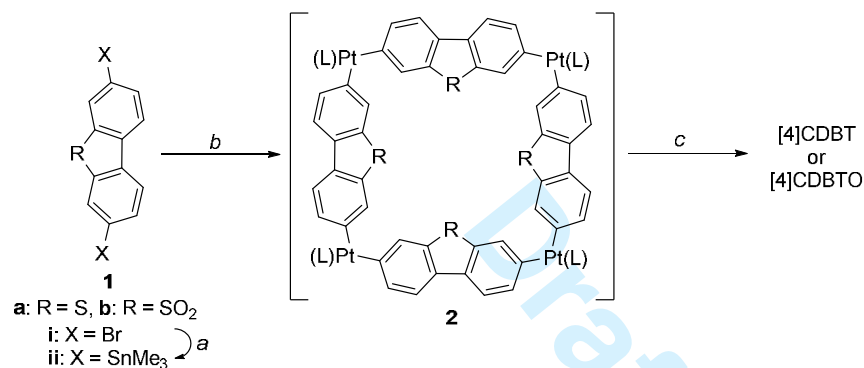
10 **Scheme 1.** Synthesis of [4]CDBT and [4]CDBTO. Reagents and conditions: a) 1) BuLi (2.1

11 equiv), THF, -70 °C, 1 h, 2) Me$_3$SnCl (2.3 equiv), THF, -70 °C to rt, 4 h, 92% (for **1ai**) or 1)

12 *i*-PrMgCl·LiCl (2.5 equiv), THF -20 to 0 °C, 2 h, Me$_3$SnCl (3.0 equiv), THF, -20 to rt, 4 h,

13 79% (for **1bi**). b) Pt(cod)Cl$_2$ (1.0 equiv), C$_2$H$_4$Cl$_2$, 60 °C, 12 h. c) PPh$_3$ (8.0 equiv), toluene,

14 90 °C, 18 h, 2.9% (2 steps from **1aii**) or 6.5% (2 steps from **1bii**). Overall yield: [4]CDBT

15 (2.7%), [4]CDBTO (5.1%).

16

17   [4]CDBT and [4]CDBS were characterized by mass and NMR spectroscopy analyses. In

18 the MALDI-TOF mass spectra, the molecular ion peak of [4]CDBT and [4]CDBTO was

19 observed at *m/z* 728.0825 and *m/z* 962.9543, respectively, as a silver ion adduct with an

20 isotopic distribution pattern identical to the theoretical values. In the ^{1}H NMR spectra at 25 °C

21 in CDCl$_3$, both compounds showed three resonances at 7.19, 7.70, and 7.95 ppm for [4]CDBT

1 and at 7.45, 7.72, and 7.90 ppm for [4]CDBTO. In the ^{13}C NMR spectra, only six peaks were

2 observed for both compounds. These results indicate that both the compounds have a highly

3 symmetrical structure with *anti/anti/anti* orientation with respect to the adjacent DBT and

4 DBTO units.

5   The DFT calculation suggests that this *anti/anti/anti* structure with D_{2d} point group

6 symmetry, **A**, is the thermodynamically most stable isomer among the four possible isomers

7 **A–D** of [4]CDBT and [4]CDBTO, followed by *anti/syn/syn* (**B**)*, anti/syn/anti* (**C**), and

8 *syn/syn/syn* (**D**) isomers with C_s, C_2, and C_{2v} point group symmetries, respectively (Figure 2).

9 The same relative stability was already observed in the cyclic tetramers of fluorene[36] and

10 carbazole.[37] Furthermore, the activation energy for the ring rotation from **A** to **B** was

11 calculated as 91 and 100 kJ/mol for [4]CDBT and [4]CDBTO, respectively, suggesting the

12 occurrence of isomerization at room temperature. Therefore, the exclusive observation of **A**

13 would be due to the thermodynamic control instead of the kinetic control.[36]

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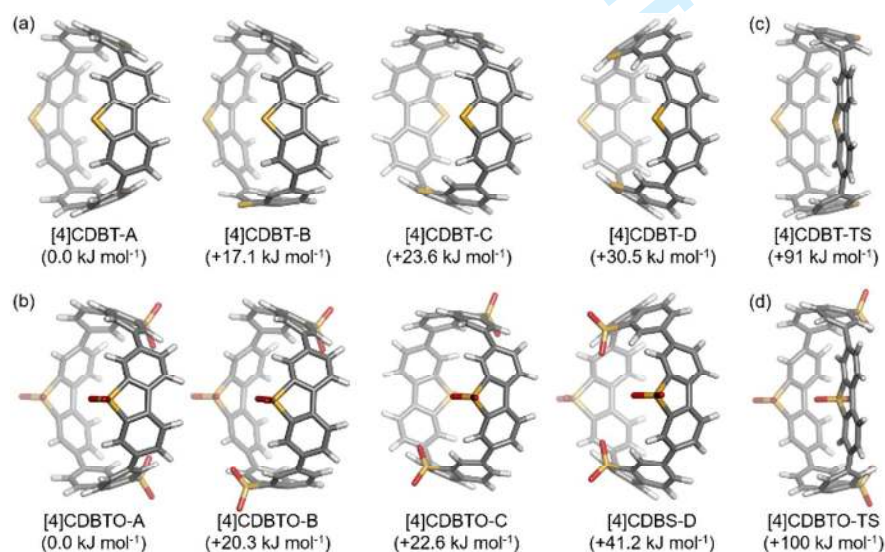
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16 **Figure 2.** Structures and relative energies (kJ mol^{-1}) of a) [4]CDBT and b) [4]CDBTO

17 isomers **A–D** and transition state (TS) for the rotation from **A** to **B** of c) [4]CDBT and d)

18 [4]CDBTO. Gray, white, yellow, and red represent carbon, hydrogen, sulfur, and oxygen

1   atoms, respectively.

2

3   The structure of [4]CDBTO was unambiguously determined by the X-ray diffraction

4   experiment performed on a single crystal obtained by slow vapor diffusion of *n*-hexane into a

5   solution of [4]CDBTO in CHCl$_3$ at room temperature. In the solid state, [4]CDBTO exhibits

6   the D_{2d} point group symmetry, which is the *anti/anti/anti* orientation with respect to the

7   adjacent DBTO unit. The structure is identical to that of the most stable isomer **A** (Figure 3a).

8   [4]CDBTO molecules align in a tiled form on an *ab* plane and form alternate layers along the

9   *c* axis to form tubular channels (Figure 3b). Additionally, intermolecular hydrogen bonding

10   (2.7–2.9 Å) is observed between S=O and the hydrogen atom of the aryl ring of the

11   neighboring molecule.

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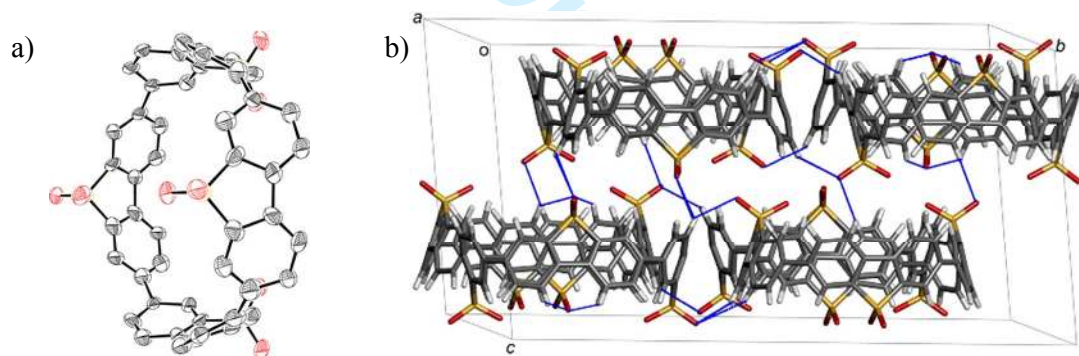
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14   **Figure 3.** a) ORTEP drawing of [4]CDBTO. Thermal ellipsolids are drawn at the 50%

15   probability level. Hydrogen atoms are omitted for clarity. b) Three-dimensional array of

16   [4]CDBTO. Black, yellow, and red represent carbon, sulfur, and oxygen atoms, respectively.

17   Blue dot lines represent intermolecular hydrogen bonding.

18

19   The photophysical properties of [4]CDBT and [4]CDBS were next examined. In the

20   UV-vis absorption spectrum in CHCl$_3$ (Figure 4), [4]CDBT shows two strong absorptions at

21   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.
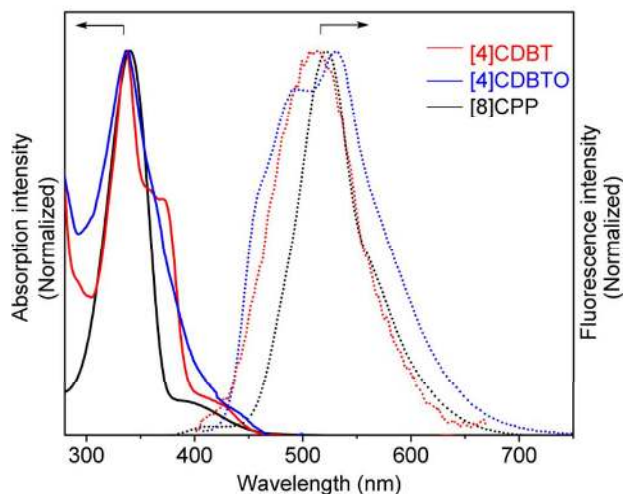
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2   **Figure 4.** UV-vis absorption and fluorescence spectra of [4]CDBT, [4]CDBTO, and [8]CPP.
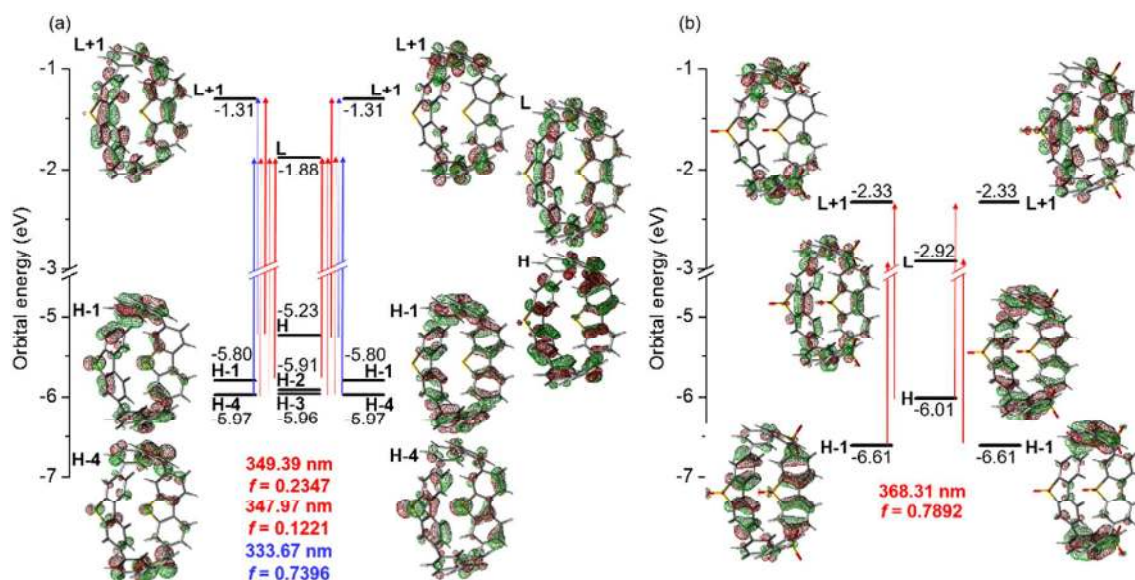
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4   **Figure 5.** Orbital energies and MO patterns of (a) [4]CDBT and (b) [4]CDBTO calculated at

5   the B3LYP/6-31G* level of theory.

6

7   Cyclic voltammograms (CVs) were measured to examine the redox properties of

8   [4]CDBT and [4]CDBTO for a sample dissolved in 0.1 M Bu_4NPF_6 solution in

9   1,1,2,2-tetrachloroethane (for oxidation) or THF (for reduction) (Figure 6). [4]CDBT showed

10   two reversible oxidation waves with half-wave oxidation potentials, $E_{1/2}$, 0.74 and 0.96 V

1   versus the ferrocene/ferrocenium couple (Fc/Fc$^+$), which is much higher than that of [8]CPP

2   (0.59 V). In contrast, [4]CDBTO showed no wave within the given solvent window. In the

3   reduction region, both [4]CDBT and [4]CDBTO exhibit one quasi-reversible reduction wave

4   at $E_{1/2}$ = -2.07 and -1.57 versus Fc/Fc$^+$, respectively, which are significantly lower than that of

5   [8]CPP (-2.33 V). The results are consistent with the moderate and strong inductive effect of

6   the sulfur and the sulfone groups, respectively.

7   The calculated HOMO and LUMO energies of [4]CDBT (-5.23 and -1.88 eV,

8   respectively) and [4]CDBTO (-6.01 and -2.92 eV, respectively) are lower than those of

9   [8]CPP (Table 1), and the results are consistent with the CV analyses. The HOMO-LUMO

10   gap in [4]CDBT (3.35 eV) and [4]CDBTO (3.35 eV) is smaller than that of the corresponding

11   linear analogues, [4]DBT (3.78 eV) and [4]DBTO (3.62 eV), respectively. We have already

12   reported the effect of the cyclic structure on HOMO-LUMO gap, which is narrower than that

13   of the corresponding linear analogue, such as 3.41 and 3.90 eV for [8]CPP and

14   [8]paraphenylene ([8]PP), respectively.[20] The results reveal the generality of the cyclic effect,

15   regardless of the presence of heteroatoms in the conjugated molecules.

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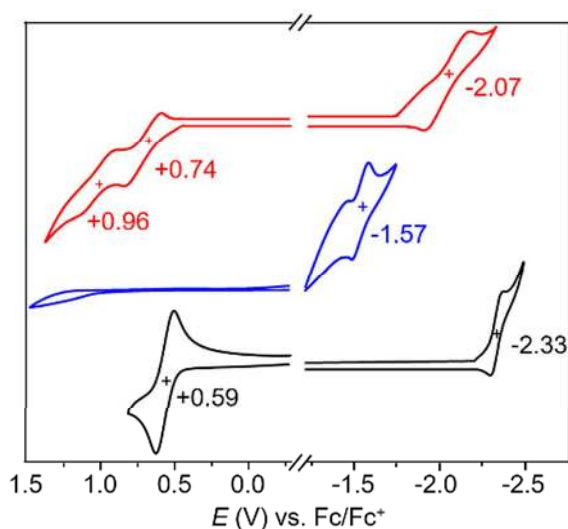
18   **Figure 6.** CV of [4]CDBT (red), [4]CDBTO (blue), and [8]CPP (black) in 0.1 M

1   Bu_4NPF_6/1,1,2,2-tetrachloroethane (for oxidation) and THF (for reduction) at room

2   temperature; scan rate = 0.1 (for oxidation) and 0.05 V s^{-1} (for reduction).

3

4   In summary, we have successfully achieved the synthesis of [4]CDBT and [4]CDBTO for

5   the first time through a platinum-mediated assembly of linear bis-metallated DBT and DBTO,

6   followed by the elimination of platinum. Photophysical and electrochemical analyses revealed

7   that the introduction of bridging by a sulfur atom and a sulfonyl group on the biphenyl units

8   of CPP affect the optical and electronic properties of CPPs. This work provides a new insight

9   into the effect of functional groups on the optoelectronic properties of CPPs.

10

16

17   **Experimental section**

18   **General.** All reactions dealing with air- and moisture sensitive compounds were carried out in

19   a dry reaction vessel under nitrogen atmosphere. Recycling preparative gel permeation

20   chromatography was performed on JAIGEL 1H and 2H polystyrene columns (Japan

21   Analytical Industry Co., Ltd.) with $CHCl_3$ as the eluent. ^1H (400 MHz) and ^{13}C NMR (100

22   MHz) spectra were measured for a $CDCl_3$ solution of a sample and are reported in parts per

23   million (δ) from internal tetramethylsilane or residual solvent peak. MALDI-TOF MS

24   spectrum was obtained on a spectrometer in the positive reflection mode and at 20 kV

25   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, $(CH_2Cl)_2$, and $(CHCl_2)_2$ 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] $Pt(cod)Cl_2$,[62] and dppf[63] were synthesized according to literature

12   procedures. i-PrMgCl·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 ºC. 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) $\delta = 0.36$ (s, $J_{119Sn\text{-}C} = 55.21$ Hz, $J_{117Sn\text{-}C} =$

22   52.80 Hz, 18 H, -$SnMe_3$), 7.54 (dd, $J = 8.0, 0.8$ Hz, 8H, -ArH), 7.97 (s, 2H, -ArH), 8.13 (dd, J

23    $= 7.8, 0.4$ Hz, 8H, -ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = -9.31$ ($J_{Sn\text{-}C} = 350.70$ Hz),

24   121.00, 129.97, 131.09, 135.61, 139.37, 141.05 ppm; HRMS (FAB) m/z: Calcd for

25    $C_{18}H_{24}SSn_2$ $(M)^+$, 509.8700; Found 509.8742.

1   **Synthesis of 1bii.** To a solution of **1bi** (10.0 g, 26.7 mmol) in THF (183 mL) was added a

2   solution of i-PrMgCl·LiCl (69.6 mL, 0.96 M in THF, 66.8 mmol) at -20 ℃. After stirring for

3   1 h at this temperature and 1 h at 0 ℃, a solution of trimethylstannyl chloride (16.0 g, 80.2

4   mmol) in THF (183 ml) was added at -20 ℃, and the resulting mixture was slowly warmed to

5   room temperature. After stirred for 4 h at this temperature, the reaction mixture was quenched

6   with saturated aqueous NH_4Cl solution, and was extracted with ether. The combined organic

7   layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced

8   pressure to give a crude mixture. Purification by silica gel chromatography using hexane as an

9   eluent afforded **1bii** (11.4 g, 79%) as colorless solids. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 0.37$

10   (s, $J_{119Sn-C} = 54.83$ Hz, $J_{117Sn-C} = 54.78$ Hz, 18 H, $-SnMe_3$), 7.54 (m, 4H, -ArH), 7.94 (s, 2H,

11   -ArH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = -9.27$ ($J_{119Sn-C} = 350.15$ Hz, $J_{117Sn-C} = 348.98$

12   Hz), 120.67, 128.57, 131.70, 136.60, 141.01, 147.04 ppm; HRMS (FAB) m/z: Calcd for

13   $C_{18}H_{24}O_2SSn_2$ (M)$^+$, 541.9529; Found 541.9576.

14   **Synthesis of [4]CDBT**. $Pt(cod)Cl_2$ (374.2 mg, 1.0 mmol) and **1aii** (510 mg, 1.0 mmol) were

15   dissolved in $(CH_2Cl)_2$ (340 mL), and the mixture was heated to 60 ℃ for 20 h under a

16   nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was

17   washed with hexane and ether to give an off-white solid.

18   The suspension of above obtained solid and PPh_3 (0.52 g, 2.0 mmol) in toluene (200 mL) was

19   stirred at room temperature under a nitrogen atmosphere. After 3 h, the resulting mixture was

20   heated at 105 ℃ for 18 h. The resulting suspension was filtered, and the filtrate was

21   concentrated under reduced pressure to give a crude mixture. The residue was purified by

22   silica gel chromatography and preparative gel permeation chromatography to give [4]CDBT

23   (4.9 mg, 2.9%, 2 steps) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.19$ (s, 8H,

24   -ArH), 7.70 (dd, $J = 8.6, 1.4$ Hz, 8H, -ArH), 7.95 (d, $J = 8.4$ Hz, 8H, -ArH) ppm; ^{13}C NMR

1   (CDCl$_3$, 100 MHz) δ=118.90, 124.10, 126.75, 134.21, 137.25, 139.69 ppm; HRMS

2   (MALDI-TOF) m/z: Calcd for C$_{48}$H$_{24}$S$_4$ (M)$^+$, 728.0761; Found 728.0805.

3   **Synthesis of [4]CDBTO**. Pt(cod)Cl$_2$ (748 mg, 2.0 mmol) and **1bii** (1.08 g, 2.0 mmol) were

4   dissolved in (CH$_2$Cl)$_2$ (500 mL), and the mixture was heated to 60 ºC 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 PPh$_3$ (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 micture was

9   heated at 105 ºC 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. ^{1}H NMR (CDCl$_3$, 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; ^{13}C

14 NMR (CDCl$_3$, 100 MHz) δ= 123.82, 127.22, 128.95, 130.03, 133.46, 150.01 ppm; MS

15 (MALDI-TOF) m/z: Calcd for C$_{48}$H$_{24}$AgO$_8$S$_4$ [M+Ag]$^+$ 962.9405, Found 962.9543.

16

17

1   **Table 1.** Redox properties and orbital energies of [4]CDBT, [4]CDBTO, [8]CPP, [4]DBT,

2   [4]DBTO, and [8]Paraphenylene ([8]PP).

Compound	$E_{1/2}^{ox}$ (V)^a	$E_{1/2}^{red}$ (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

3   ^{a}V vs. ferrocene/ferrocenium couple; Bu_4NPF_6 (0.1 mol L^{-1}) in 1,1,2,2-tetrachloroethane

4   (oxidation) or THF (reduction). ^{b}Data obtained from DFT calculations at the

5   B3LYP/6-31G* level of theory. ^{c}n.o.: not observed. ^{d}Taken from Ref 20.

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1   **Legends of Figures and Schemes.**

2

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

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5   **Figure 2.** Structures and relative energies (kJ mol^{-1}) of a) [4]CDBT and b) [4]CDBTO

6   isomers **A–D** and transition state (TS) for the rotation from **A** to **B** of c) [4]CDBT and d)

7   [4]CDBTO. Gray, white, yellow, and red represent carbon, hydrogen, sulfur, and oxygen

8   atoms, respectively.

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10   **Figure 3.** a) ORTEP drawing of [4]CDBTO. Thermal ellipsolids are drawn at the 50%

11   probability level. Hydrogen atoms are omitted for clarity. b) Three-dimensional array of

12   [4]CDBTO. Black, yellow, and red represent carbon, sulfur, and oxygen atoms, respectively.

13   Blue dot lines represent intermolecular hydrogen bonding.

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

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17   **Figure 5.** Orbital energies and MO patterns of (a) [4]CDBT and (b) [4]CDBTO calculated at

18   the B3LYP/6-31G* level of theory.

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

21   Bu$_4$NPF$_6$/1,1,2,2-tetrachloroethane (for oxidation) and THF (for reduction) at room

22   temperature; scan rate = 0.1 (for oxidation) and 0.05 V s^{-1} (for reduction).

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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) Me$_3$SnCl (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, Me$_3$SnCl (3.0 equiv), THF, -20 to rt, 4 h,

5   79% (for **1bi**). b) Pt(cod)Cl$_2$ (1.0 equiv), C$_2$H$_4$Cl$_2$, 60 °C, 12 h. c) PPh$_3$ (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%).

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