Supplementary Information

Improved stability of a metallic state in benzothienobenzothiophene-based molecular conductors: An effective increase of dimensionality with hydrogen bonds

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General

Commercially available materials were used as received. Anhydrous solvents (Tetrahydrofuran and dichloromethane) were purchased from Wako Pure Chemical Industries. All reactions were conducted under argon atmosphere. For thin-layer chromatography (TLC) analysis, Merck pre-coated glass plates (TLC Silica gel 60 F254) were used. Silica gel used in chromatographic separations was obtained from Kanto chemical (Silica Gel 60 N (spherical, neutral), 63–210 μ m). ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were measured with a JEOL JNM-AL300 spectrometer with CDCl₃ or acetone-*d*₆ as a solvent using Me₄Si or residual solvent as an internal standard. Melting points were measured with a hot-stage apparatus. Elemental analyses were performed at the Department of Chemistry, Graduate School of Science, the University of Tokyo.

Synthesis

1-Bromo-2-iodo-4,5-dimethoxybenzene (1)

Periodic acid (4.54 g, 20.0 mmol, 0.20 eq.), iodine (10.2 g, 40.0 mmol, 0.40 eq.), and 1-bromo-4,5-dimethoxybenzene (21.7 g, 100 mmol, 1 eq.) were dissolved in methanol (80 mL) and the mixture was refluxed for 9 h. After cooling down to room temperature, the reaction mixture was poured into an aqueous solution of sodium thiosulphate (3 g/150 mL). Then the resulting precipitate was collected and washed with cold methanol, to afford **1** (32.5 g, 94.8 mmol, yield 95%) as a white solid. This material was used for the next reaction without further purification. ¹H NMR (300 MHz, CDCl₃) δ 7.23 (s, 1H), 7.08 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H).

1-Bromo-2-[2-(trimethylsilyl)ethynyl]benzene (2)



TMS

To a mixture of bis(triphenylphosphine)palladium(II) dichloride (1.12 g, 1.60 mmol, 2 mol%), copper(I) iodide (0.609 g, 3.20 mmol, 4 mol%), 1-bromo-2-iodobenzene (22.6 g, 80.0 mmol, 1 eq.), and triethylamine (22.2 mL, 160 mmol, 2 eq.) in dry tetrahydrofuran (120 mL) was added dropwise a solution of trimethylsilylacetylene (16.6 mL, 120 mmol, 1.5 eq.) in dry tetrahydrofuran (8 mL) over a period of 10 min at room temperature, and then the resulting mixture was refluxed for 2 h. After cooling down to room temperature, the reaction mixture was filtered through Celite. The filtrate was evaporated under reduced pressure, and the residue was dissolved in diethyl ether, washed with a saturated aqueous solution of ammonium chloride, water, and brine. Then, the organic layer was dried over sodium sulphate, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (hexane, $R_{\rm f} = 0.5$), to afford **2** (19.5 g, 108 mmol, yield 96%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.58 (dd, J = 1.2 Hz, 7.8 Hz, 1H), 7.50 (dd, J = 1.8 Hz, 7.5 Hz,

1H), 7.28 (ddd, J = 1.2 Hz, 7.5 Hz, 1H), 7.17 (ddd, J = 1.8 Hz, 7.8 Hz, 1H), 0.27 (s, 9H).

1-Bromo-2-ethynylbenzene (3)



To a methanol-dichloromethane solution (30 mL, 2:1 v/v) of **2** (2.20 g, 8.69 mmol, 1 eq.) was added potassium carbonate (3.60 g, 26.1 mmol, 3 eq.), and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water, and extracted with dichloromethane (50 mL × 3). The combined organic layer was washed with brine, dried over sodium sulphate, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (hexane, $R_f = 0.4$), to afford **3** (1.44 g, 7.95 mmol, yield 92%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.60 (dd, J = 1.2 Hz, 7.8 Hz, 1H), 7.54 (dd, J = 1.8 Hz, 7.5 Hz, 1H), 7.28 (ddd, J = 1.2 Hz, 7.5 Hz, 1H), 7.21 (ddd, J = 1.8 Hz, 7.8 Hz, 1H), 3.38 (s, 1H).

1-Bromo-2-[2-(2-bromophenyl)ethynyl]-4,5-dimethoxybenzene (4)



To a mixture of bis(triphenylphosphine)palladium(II) dichloride (0.28 g, 0.40 mmol, 4 mol%), copper(I) iodide (0.15 g, 0.80 mmol, 8 mol%), **1** (3.43 g, 10.0 mmol, 1 eq.), and triethylamine (2.8 mL, 20 mmol, 2 eq.) in dry tetrahydrofuran (20 mL) was added dropwise a solution of **2** (2.0 mL, 11 mmol, 1.1 eq.) in dry tetrahydrofuran (2 mL) over a period of 5 min at room temperature, and then resulting mixture was refluxed for 9 h. After cooling down to room temperature, the reaction mixture was filtered through Celite. The filtrate was evaporated under reduced pressure, and then the residue was dissolved in ethyl acetate, washed with a saturated aqueous solution of ammonium chloride, water, and brine. Then, the organic layer was dried over sodium sulphate, filtered, and concentrated under reduced pressure. The residue was subjected to silica

gel column chromatography (dichloromethane:hexane = 1:1, $R_f = 0.3$), to afford **4** (3.3 g, 8.3 mmol, yield 83%) as a white solid. M.p. 195–196 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.63 (dd, J = 1.2 Hz, 4.5 Hz, 1H), 7.60 (dd, J = 1.8 Hz, 4.5 Hz, 1H), 7.30 (ddd, J = 1.2 Hz, 7.2 Hz, 1H), 7.19 (ddd, J = 1.8 Hz, 7.2 Hz, 1H), 7.08 (s, 1H), 7.07 (s, 1H), 3.90 (s, 6H).

1,2-Dithiin isomers (5a and 5b)



To a tetrahydrofuran solution (60 mL) of 4 (2.38 g, 6.00 mmol, 1 eq.) was added dropwise a solution of *t*-butyl lithium in *n*-pentane (1.59 M, 15.1 mL, 24.0 mmol, 4 eq.) at -78 °C. After stirred for at -78 °C 1 h, sulphur powder (0.577 g, 18.0 mmol, 3 eq.) was added. The mixture was gradually warmed up to room temperature over 3 h and then stirred at room temperature for 6 h. The mixture was quenched with a 1 M sodium hydroxide aqueous solution, followed by addition of potassium hexacyanoferrate(III) (7.90 g, 24.0 mmol, 4 eq.). The resulting mixture was extracted with dichloromethane (50 mL \times 3). The combined organic layer was washed with water and brine, dried over sodium sulphate, filtered, and concentrated under reduced The residue was subjected to silica gel column chromatography pressure. (dichloromethane:hexane = 1:1, $R_f = 0.3$). The resulting orange solid was recrystallized from ethyl acetate/methanol to afford **5a** (0.28 g, 0.85 mmol, yield 14%) as a bright yellow powder. The filtrate was concentrated under reduced pressure and then recrystallized from hexane to afford 5b (0.30 g, 9.0 mmol, yield 15%) as orange crystals.

5a: M.p. 195–196 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.46–7.51 (m, 2H), 7.23–7.35 (m, 2H), 7.28 (s, 1H), 7.15 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H); Elemental analysis Calcd for C₁₆H₁₂O₂S₃: C, 57.81; H, 3.64; N, 0.00. Found: C, 57.78; H, 3.66; N, 0.00.

5b: M.p. 129–131 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 7.2 Hz, 7.8 Hz, 1H), 7.37 (dd, *J* = 7.2 Hz, 8.1 Hz, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 3.97 (s, 3H), 3.94 (s, 3H); Elemental analysis Calcd for C₁₆H₁₂O₂S₃: C, 57.81; H, 3.64; N, 0.00. Found: C, 57.71; H, 3.67; N, 0.00.

2,3-Dimethoxy-[1]benzothieno[3,2-b][1]benzothiophene (BTBT(OMe)₂)



The mixture of **5a** and **5b** (0.459 g, 1.38 mmol, 1 eq.) and copper nanopowder (0.351 mg, 5.53 mmol, 4 eq.) was stirred at 250 °C for 20 min. After the mixture was cooled down to room temperature, dichloromethane was added to the mixture, and the insoluble materials were removed by filtration through Celite. The filtrate was concentrated under reduced pressure, and the residue was subjected to a silica gel chromatography (dichloromethane:hexane = 1:1, $R_f = 0.3$) and then recrystallized from acetone/methanol to afford **BTBT(OMe)**₂ (0.35 g, 1.2 mmol, yield 84%) as a white solid. M.p. 172–174 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.5 Hz, 1H), 7.34–7.40 (m, 1H), 7.37 (s, 1H), 7.28 (s, 1H), 4.03 (s, 3H), 4.00 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 148.7, 148.5, 141.7, 134.8, 133.5, 133.3, 132.1, 126.5, 124.9, 124.5, 124.0, 121.1, 105.7, 103.2, 56.2(×2); Elemental analysis Calcd for C₁₆H₁₂O₂S₂: C, 63.98; H, 4.03; N, 0.00. Found: C, 63.98; H, 4.04; N, 0.00.

2,3-Dihydroxy-[1]benzothieno[3,2-b][1]benzothiophene (BTBT(OH)₂)



To a dichloromethane solution (12 mL) of **BTBT(OMe)**₂ (0.18 g, 0.60 mmol, 1 eq.) was added dropwise a dichloromethane solution of boron tribromide (1 M, 2.4 mL, 2.4 mmol, 4 eq.) at 0 °C. After the mixture was stirred at room temperature for 6 h, the reaction was quenched by adding water. The resulting mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine, dried over sodium sulphate, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (ethyl acetate:hexane = 1:1, R_f = 0.5) to afford **BTBT(OH)**₂ (0.15 g, 55 mmol, yield 92%) as a white to pale green powder. M.p. 250 °C (decomp.); ¹H NMR (300 MHz, acetone- d_6) δ 8.02 (d, J = 7.5 Hz, 1H), 7.48 (dd, J = 1.5 Hz, 7.5 Hz, 1H), 7.47 (s, 1H),

7.38–7.44 (m, 1H), 7.37 (s, 1H); ¹³C NMR (75 MHz, acetone- d_6) δ 146.3, 145.7, 142.3, 134.8, 134.3, 133.7, 131.9, 126.9, 125.9, 125.3, 124.9, 121.6, 110.1, 107.4.

Electrochemical crystallization of β-[BTBT(OH)₂]₂ClO₄

BTBT(**OH**)₂ (3.0 mg) was placed in one side of an H-shaped cell equipped with a glass filter. Then tetra-*n*-butylammonium perchlorate (*n*-Bu₄·ClO₄, 10 mg) was placed in the both sides and the H-shaped cell was purged with argon gas. These materials were dissolved in anhydrous dichloromethane (10 mL) by sonication. The resulting solution was kept at room temperature for 1 h, and then two Pt electrodes were inserted into the solution. A constant current of 2.0 μ A was applied for 2 days, to afford needle-like black crystals of β -[BTBT(OH)₂]₂ClO₄ suitable for X-ray diffraction analysis and physical property measurements.

Redox properties

Cyclic voltammograms were measured on ALS model 610DB electrochemical analyzer in an acetonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄·PF₆) at a scan rate of 100 mV s⁻¹ (working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: saturated calomel electrode (SCE)). **BTBT(OMe)**₂ and **BTBT(OH)**₂ show irreversible oxidation waves at the same potential of 0.88 V (Fig. S1). From the first onset oxidation potentials (E_{onset}), HOMO energies (E_{HOMO}) of **BTBT(OMe)**₂ and **BTBT(OH)**₂ were estimated to be the same value of -5.32 V, by assuming the SCE energy level of -4.44 eV below the vacuum level.^{S1}



Fig. S1 Cyclic voltammograms of BTBT derivatives.

DFT calculation

Density functional theory (DFT) calculations were performed with Gaussian03 program (revision E.01) at the B3LYP/6-31G* level of theory for a full geometry optimization.^{S2} The resulting energy levels and distribution maps of HOMO and HOMO-1 are depicted in Fig. S2.



Fig. S2 HOMO and HOMO-1 energy levels and distribution maps of the neutral BTBT derivatives, calculated at the B3LYP/6-31G* level of theory.

Crystal structures

• Data collection

The reflection data were collected on a Rigaku Mercury II CCD diffractometer with a graphite-monochromated MoK α radiation source ($\lambda = 0.71073$ Å). For indexing and integrating the diffraction peaks, the CrystalClear-SM program (Rigaku) was used. Empirical absorption correction was applied with the REQAB program.

· Analysis

The structures were solved by direct methods (SIR 2008) and refined by full-matrix least-squares by applying anisotropic temperature factors for all non-hydrogen atoms using the SHELX-97 programs.^{S3} The hydrogen atoms were placed at geometrically calculated positions. Details on crystallographic X-ray data collections and refinements are found in Table S1.

Crystals	5a	5b	BTBT(OMe) ₂	[BTBT(OH) ₂] ₂ ·H ₂ O	β -[BTBT(OH) ₂] ₂ ClO ₄
Empirical formula	$C_{16}H_{12}O_2S_3$	$C_{16}H_{12}O_2S_3$	$C_{16}H_{12}O_2S_2$	$C_{28}H_{18}O_5S_4$	C ₂₈ H ₁₆ ClO ₈ S ₄
Formula weight	332.45	332.45	300.39	562.69	644.12
Crystal shape	orange prism	orange rod	colourless plate	colorless flake	black needle
Crystal size (mm ³)	0.49×0.13×0.12	0.16×0.080×0.060	0.20×0.17×0.036	0.25×0.20×0.010	0.30×0.015×0.015
Crystal system	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	$Pna2_1$	<i>P</i> -1	C2/c	C2/c
<i>a</i> (Å)	11.122(5)	17.004(9)	10.676(4)	50.816(18)	29.418(16)
<i>b</i> (Å)	11.208(5)	7.497(4)	10.861(4)	3.9638(13)	6.652(4)
<i>c</i> (Å)	12.801(6)	23.151(11)	13.225(5)	11.696(4)	13.840(8)
α (°)	112.898(6)	90	104.975(4)	90	90
eta (°)	93.135(4)	90	102.681(4)	101.342(5)	110.708(8)
γ (°)	90.892(4)	90	99.616(4)	90	90
$V(\text{\AA}^3)$	1466.6(11)	2951(3)	1404.0(9)	2309.8(14)	2533(3)
Ζ	4	8	4	4	4
Unique refls. (R_{int})	5022 (0.0306)	5096 (0.0782)	4827 (0.0253)	2004 (0.0319)	2704 (0.0477)
$D_{\text{calc}} (\text{g/cm}^3)$	1.506	1.496	1.421	1.618	1.689
R_1	0.0508	0.0811	0.0566	0.0353	0.0784
$R_{ m w}$	0.1687	0.2058	0.1727	0.0982	0.1675
GOF	1.084	0.981	1.076	0.996	1.058
Temperature (K)	293	293	293	293	293
CCDC number	1529671	1529672	1529673	1529674	1529675

Table S1Crystallographic data.

The single-crystal X-ray structure analysis of **5a** reveals that a crystal belongs to a triclinic system with the space group P-1 (#2). As depicted in Fig. S3, two molecules are crystallographically independent, and are twisted at the dithiin part with the dihedral angles of 18.2° and 26.6° between the phenyl group and the benzothienyl group. The unit cell contains four molecules. The molecules are dimerized along the each diagonal direction, forming a sandwich herringbone pattern so-called κ -type arrangement. In a kind of two dimers, the (blue) molecules stack with large slippage along the molecular long axis, affording the additional interaction between the adjacent dimer. Therefore, the isomer **5a** has the three-dimensional interaction.

(a) Crystallographically independent molecules.





(c) Projection along the *a* axis.



Fig. S3 Molecular structure and molecular arrangement of the dithiin isomer **5a**. The thermal ellipsoids are scaled to the 50% probability level.

The isomer **5b** belongs to an orthorhombic system with the space group $Pna2_1$ (#33). The crystallographically independent unit consists of two molecules and the unit cell contains eight molecules (Fig. S4). Two molecules are twisted with the dihedral angles of 26.2° and 25.5°. The molecules form the column structure with the π -stacked dimerization along the *b* axis without intermolecular interaction between the adjacent columns. Thus, the isomer **5b** has the simply one-dimensional interaction. The difference of the dimensionality between **5a** and **5b** results in the each crystal shape, the prism-like crystals for **5a** and the rod-like crystals of **5b**, and affects the melting point of these isomers.

- top view side view the dihedral angles between the average planes of the phenyl group and the benzothienyl group 26.2° 25.5°
- (a) Crystallographically independent molecules.



(c) Projection along the *a* axis.



Fig. S4 Molecular structure and molecular arrangement of the dithiin isomer **5b**. The thermal ellipsoids are scaled to the 50% probability level.

Plate-like colourless crystals of **BTBT**(**OMe**)₂ were obtained by a slow evaporation of an ethyl acetate solution. A crystal belongs to a triclinic system, space group P-1 (#2). Two molecules are crystallographically independent, and the unit cell contains four molecules (Fig. S5). One molecule is disordered to two positions with occupancy 86% for the major molecule and 14% for minor molecule. These molecules are assumed to be arranged in an alternate manner, but share the common methoxy parts. Both crystallographically independent molecules are almost planar, and are arranged in a herringbone motif within a head-to-tail type dimerization.



(a) Crystallographically independent molecules.

Fig. S5 Molecular structure and molecular arrangement of $BTBT(OMe)_2$. The thermal ellipsoids are scaled to the 50% probability level.

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Plate-like colourless crystals of the hemihydrate, $[BTBT(OH)_2]_2 \cdot H_2O$, were obtained by a diffusion method of a dichloromethane/acetone solution. $[BTBT(OH)_2]_2 \cdot H_2O$ crystallizes in a monoclinic system, space group C2/c (#15), with the $BTBT(OH)_2$ molecule in a general position and the H₂O molecule on a two-fold rotary axis (Fig. S6). Accordingly, one of $BTBT(OH)_2$ and half of H₂O are crystallographically independent, and the stoichiometry ratio is 2:1. The $BTBT(OH)_2$ molecule is almost planar, and is arranged in a herringbone motif within a head-to-head-type bilayered structure governed by three kinds of O–H···O intermolecular H-bonding formation between the hydroxy group and H₂O molecule with that of 2.816(3) Å. Note that this result originates from the concerted molecular cohesive nature between the herringbone packing of the unsubstituted BTBT and the H-bonding interaction of the catechol moiety.^{S4,S5}





(c) Projection along the stacking (crystallographic *b*) axis.



Fig. S6 Molecular structure and molecular arrangement of $[BTBT(OH)_2]_2 \cdot H_2O$. The thermal ellipsoids are scaled to the 50% probability level. Transfer integrals: b = 21.2, p = -21.8, q = -23.5 meV.

Bond length comparison

The donor molecule **BTBT**(**OH**)₂ shows a clear bond length changes upon oxidation, especially at the central thienothiophene moiety (C6–C7, C7–C8, and C8–C9) as listed in Table S2. The neutral donor in [**BTBT**(**OH**)₂]₂•**H**₂**O** displays a bond alternation based on the stilbene backbone, whereas the oxidized donor in β -[**BTBT**(**OH**)₂]₂**ClO**₄ does not clearly show such bond alternation, which is reminiscent of the quinoid contribution in the cationic state.¹⁴ On the other hand, the bond lengths in the fused benzene rings are practically unchanged between the neutral and oxidized states. These results are overwhelmingly supported by the calculated results, and suggest that the +0.5e charge in the oxidized state is primarily delocalized at the thienothiophene part in the BTBT backbone. In addition to such a charge distribution, a 5.5 π -electron system of BTBT salts is essentially distinct from that of TTF conductors.

Table S2 Experimentally observed bond lengths of **BTBT(OH)**₂, [**BTBT(OH)**₂]₂•**H**₂**O** for the neutral (0) state and β -[**BTBT(OH)**₂]₂**ClO**₄ for the 0.5+ charged state and the difference (Δ), and theoretically obtained bond lengths of **BTBT(OH)**₂ for the neutral (0) and cation (1+) states and the difference (Δ).



	Experimental			Theoretical		
	0	0.5+	Δ	0	1+	Δ
C1–C2	1.386(3)	1.385(7)	-0.001(8)	1.398	1.380	-0.018
C2–C3	1.371(4)	1.385(7)	0.014(8)	1.390	1.408	0.018
C3–C4	1.402(3)	1.424(9)	0.022(9)	1.420	1.444	0.024
C4–C5	1.377(3)	1.373(7)	-0.004(8)	1.386	1.377	-0.009
C5-C6	1.401(4)	1.404(7)	0.003(8)	1.408	1.417	0.009
C1-C6	1.416(3)	1.425(9)	0.009(9)	1.414	1.436	0.022
C6-C7	1.436(3)	1.408(7)	-0.028(8)	1.434	1.405	-0.029
С7-С8	1.369(3)	1.395(7)	0.026(8)	1.377	1.419	0.042
C8–C9	1.434(3)	1.427(7)	-0.007(8)	1.435	1.414	-0.021
C9-C10	1.395(4)	1.390(7)	-0.005(8)	1.405	1.415	0.010
C10-C11	1.378(3)	1.382(7)	0.004(8)	1.389	1.384	-0.005
C11-C12	1.399(4)	1.395(10)	-0.004(11)	1.405	1.408	0.003
C12-C13	1.374(4)	1.372(8)	-0.002(9)	1.393	1.402	0.009
C13-C14	1.387(3)	1.402(8)	0.015(9)	1.396	1.386	-0.010
C9-C14	1.418(3)	1.416(9)	-0.002(9)	1.421	1.429	0.008
S1-C1	1.746(3)	1.751(5)	0.005(6)	1.770	1.779	0.009
S1-C8	1.739(2)	1.732(6)	-0.007(6)	1.757	1.743	-0.014
S2-C7	1.737(2)	1.733(6)	-0.004(6)	1.757	1.740	-0.017
S2-C14	1.751(3)	1.742(5)	-0.009(6)	1.771	1.780	0.009
O1–C3	1.380(3)	1.338(6)	-0.042(7)	1.364	1.330	-0.034
O2–C4	1.384(3)	1.354(6)	-0.030(7)	1.365	1.344	-0.021

Conducting properties

The electrical resistivity was measured by the conventional four-probe method by using low-frequency alternating current (AC). The measurements were done along the crystal long axis, corresponding to the molecular stacking direction for β -[BTBT(OH)₂]₂ClO₄ (crystallographic *b* axis), in the temperature range of 7–293 K under He atmosphere. The temperature dependence of the electrical resistivity for β -[BTBT(OH)₂]₂ClO₄ and (BTBT)₂PF₆⁵ is shown in Fig. S7.



Fig. S7 Temperature dependence of the electrical resistivity for β -[BTBT(OH)₂]₂ClO₄ (black) and (BTBT)₂PF₆ (gray).⁵

References

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