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Synthesis of Ring-Locked Tetracyclic Dithienocyclopentapyrans and Dibenzocyclopentapyran via 1,5-Hydride Shift and Copper-Catalyzed C−O Bond Formation for Nonfullerene Acceptors

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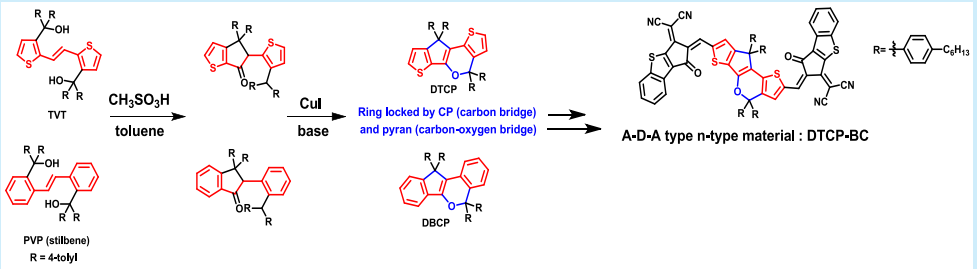

ABSTRACT: We discovered a unique synthetic route to construct 2H-pyran-containing tetracyclic dithienocyclopentapyran (DTCP) and dibenzocyclopentapyran (DBCP) architectures. The synthesis involves an acid-induced dehydration cyclization followed by a [1,5] hydride-shift isomerization to form a cyclopentanone moiety which was converted to the pyran-embedded tetracyclic products by a CuI-catalyzed intramolecular C−O bond formation in good yield. DTCP was used as a building block to prepare an acceptor−donor−acceptor (A−D−A) type n-type material DTCP-BC leading to a solar cell efficiency of 9.32%.

Planarization and rigidification of a conjugated system have been proven to extend the conjugation with red-shifted absorption and minimize the structural fluctuation to improve charge mobility.[1−8] Introduction of a bridge element to covalently ring-lock the neighboring aryl or heteroaryl groups connected by a single bond has led to a variety of fascinating multifused ladder-type structures. As such, a single-element bridge such as carbon, silicon, nitrogen ends up forming the corresponding embedded five-membered cyclopentadiene (CP),[9−11] silole,[12−19] and pyrrole[20−22] rings. The carbon-bridged ladder-type structures are particularly superior donor (D) building blocks to make n-type acceptor−donor−acceptor (A−D−A) type nonfullerene acceptors (NFA) for achieving high-performance organic photovoltaics.[23−29] More recently, utilizing a two-element carbon−oxygen bridge leading to an embedded six-membered 2H-pyran ring has also attracted much interest considering that the electron-donating enolic oxygen can further fine-tune steric and electronic properties.[28−34] Incorporation of a compact *trans*-1,2-vinylene (CH═CH) linkage in the conjugated backbone can effectively narrow the optical band gap and improve charge mobility due to the facile π-delocalization and enhanced coplanarity.[35] As a result, thiophene−vinylene−thiophene (TVT) and phenylene−vinylene−phenylene (PVP, stilbene) and their derivatives have been widely used as organic semiconducting materials for organic light-emitting diodes and organic field-effect transistors.[36−40] It is of substantial interest to implement the chemical planarization strategy in the TVT and PVP systems.

However, to our surprise, the carbon-bridge-ring-locked dithienodihydropentalene (DTDP) has never been reported and investigated presumably due to the challenging synthesis (Scheme 1). Herein, we disclosed a unique synthetic route to construct tetracyclic dithienocyclopentapyran (DTCP) and dibenzocyclopentapyran (DBCP) architectures (Scheme 1) where the TVT and PVP are covalently ring-locked by a carbon and a carbon−oxygen bridge to form an endocyclic olefin embedded between a CP and a pyran ring. The diformylated DTCP moiety was coupled with 2-(3-oxo-2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-1-ylidene)-malononitrile denoted as BC to form a low band gap n-type A−D−A type DTCP-BC material for organic photovoltaics.[41]

The synthetic route is depicted in Scheme 2. In the presence of titanium tetrachloride and a reducing agent of zinc powder, 3-bromothiophene-2-carbaldehyde **1a** underwent McMurry coupling reaction to afford the dimerized alkene (*E*)-1,2-

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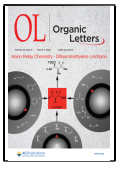

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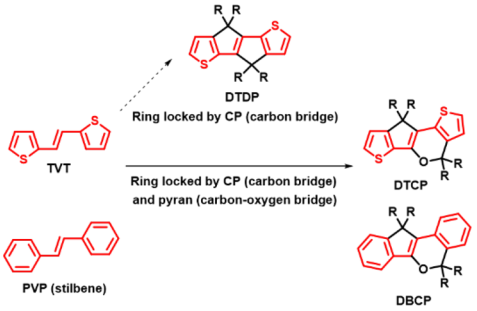
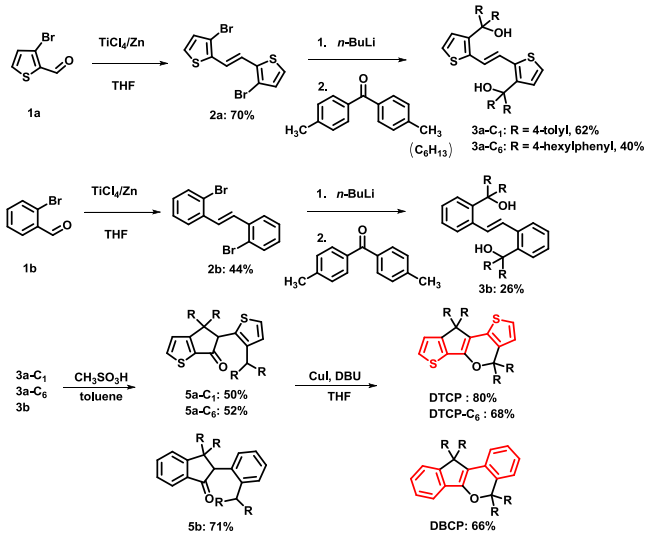
Scheme 1. Chemical Planarization of TVT and PVP Skeletons To Form Dithienocyclopentapyran (DTCP) and Dibenzocyclopentapyran (DBCP)

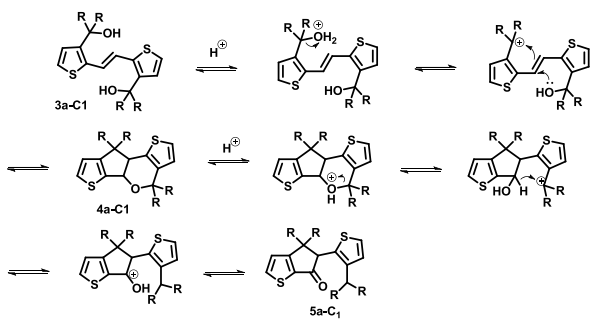


Scheme 2. Synthetic Route for DTCP, DTCP-C_6, and DBCP



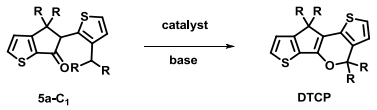
bis(3-bromothiophen-2-yl)ethene **2a**. Lithiation of **2a** by *n*-butyllithium to react with 4, 4′-dimethylbenzophenone afforded the bis(triaryl) alcohol **3a-C_1**. Initially, we envisaged that **3a-C_1** can carry out acid-induced double cyclization to yield DTDP. Nevertheless, when **3a-C_1** was treated with methanesulfonic acid, an unexpected product, monocyclic ketone **5a-C_1**, was obtained and its structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The plausible mechanism is depicted in Scheme 3. In the presence of methanesulfonic acid, **3a-C_1** first underwent a tandem cyclization to a form a bicyclic 5−6 ring intermediate **4a-C_1**

Scheme 3. Proposed Mechanism of the Acid-Induced Cyclization of 3a-C_1



which was then swiftly isomerized to **5a-C_1**. The isomerization involves the generation of a triaryl carbocation upon cleavage of the O−C bond in **4a-C_1** followed by an intramolecular [1,5]-hydride shift from the hydroxyl carbon to the adjacent triaryl carbocation to simultaneously form the ketone group in **5a-C_1**.[42−44] The key intermediate **4a-C_1** can be observed and isolated when **3a-C_1** was treated with HCl in acetic acid. **4a-C_1** can be indeed converted to **5a-C_1** under the identical conditions, i.e. methanesulfonic acid in toluene, which verified the proposed mechanism. Despite the fact that the acid-induced cyclization of **3a-C_1** resulted in the unexpected cyclic ketone in **5a-C_1**, we proposed that **5a-C_1** could further conduct an intramolecular dehydrogenative cyclization to form a new C−O single bond via a metal-catalyzed methodology, leading to the tetracyclic DTCP (Table 1).

Table 1. Optimization of Metal-Catalyzed Cyclization Reaction[a]



entry	catalyst[b]	base[c]	solvent	yield (%)[d]
1	$Pd(PPh_3)_2Cl_2$	DBU	THF	30
2	$Pd(PPh_3)_2Cl_2$	NaOEt	THF	none
3	$Pd(PPh_3)_2Cl_2$	NaOAc	THF	none
4	$Pd(OAc)_2$	DBU	THF	25
5	CuI	DBU	THF	80
6	CuI with TEMPO[e]	DBU	THF	66
7	CuCl	DBU	THF	75
8	CuO	DBU	THF	none

[a]Reactions were completed within 15 min. [b]Catalytic amount (10 mol %). [c]Stoichiometric amount. [d]Isolated yield after silica gel chromatography. [e]1 equiv of TEMPO was added.

The screening of optimal reaction conditions is shown in Table 1. At first, we found that palladium catalyst Pd-$(PPh_3)_2Cl_2$ or $Pd(OAc)_2$ combined with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as the base successfully carried out the reaction to form DTCP in 30% and 25% yield (entry 1 and 4), respectively. The structure of DTCP was unambiguously confirmed by the single crystal X-ray diffraction shown in Figure 1. Using bases such as NaOEt and NaOAc resulted in failure of the reaction (entry 2 and 3), indicating that DBU is a key component. Most importantly, we found that copper(I) iodide and copper(I) chloride with DBU were able to catalyze the reaction at room temperature in a higher yield of 80% and 75%, respectively, in just 15 min (entry 5 and 7). However, copper(II) oxide failed to yield the product (entry 8). This

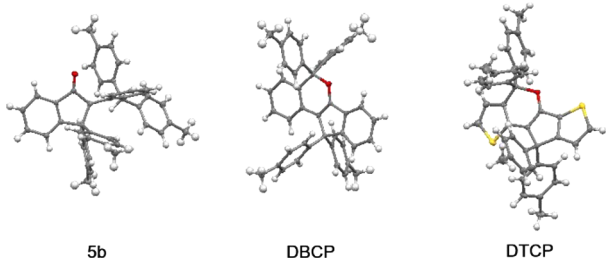


Figure 1. X-ray single crystal structure of DBCP, DTCP, and compound **5b** (50% probability for thermal ellipsoids).

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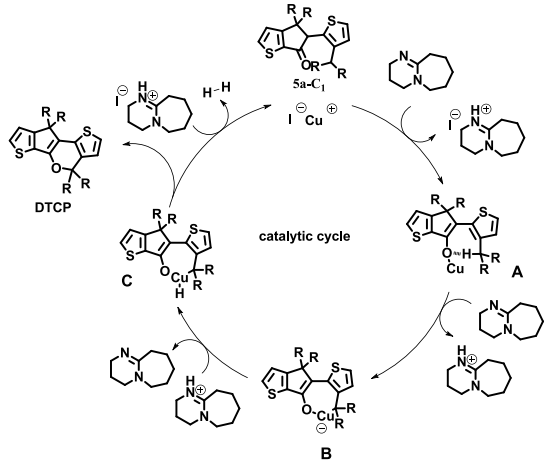
reaction is still valid in the presence of a radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), suggesting that this reaction does not proceed via radical mechanism (entry 6). The proposed mechanism of catalytic cycle for the Cu(I)-catalyzed ring closure is thus depicted in Scheme 4.

Scheme 4. Proposed Mechanism of the Copper-Catalyzed Cyclization Reaction



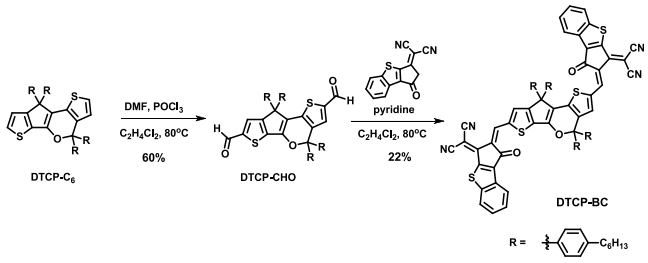
Deprotonation of **5a-C$_1$** by DBU forms the enolate ion to yield the copper-coordinated species A. The sp^3-CH bond is activated and deprotonated to form complex B which abstracts a proton to yield complex C. This is the putative active species that undergoes reductive elimination to afford the pyran-ring in DTCP. The resulting copper(I) hydride reacts with the protonated base to produce hydrogen and regenerate the active copper(I) species.[45,46]

In a similar pathway through dimerization and nucleophilic addition, 1-bromo-2-benzaldehyde **1b** can lead to **3b** which underwent the acid-induced cyclization followed by the [1,5] hydride shift to form **5b** (Scheme 2). The structure of **5b** was confirmed by single crystal X-ray diffraction unambiguously (Figure 1). Finally, the copper-catalyzed intramolecular C−O bond formation in **5b** yielded the corresponding DBCP in 66% yield. On the other hand, DTCP-C$_6$ using the 4-hexylphenyl group as the side chain can be also synthesized by using **3a-C$_6$** as the starting material.

The absorption spectra of DTCP and DBCP are shown in Figure S1. DTCP showed a significant bathochromic shift of the absorption onset (λ_{onset} = 446 nm) compared to DBCP (λ_{onset} = 387 nm). The larger E_g^{opt} of DBCP is caused by the higher aromaticity of the benzene rings. Similar results are observed in our previous works.[47,48] The ring-locked molecules exhibited greater red-shifted absorption than the nonfused TVT and stilbene counterparts due to the enhanced rigidity and the oxygen atom incorporation.

DTCP-C$_6$ was further formylated by POCl$_3$/DMF Vilsmeier−Haack reaction to afford DTCP-CHO (Scheme 5). Aldol condensation of DTCP-CHO with BC[41] formed a new A−D−A type NFA DTCP-BC. DTCP-BC with four 4-hexylphenyl side chains exhibited adequate solubility in common organic solvents. DTCP-BC showed a high thermal decomposition temperature (T_d) of 346 °C determined by thermogravimetric analysis (TGA). The absorption spectrum of DTCP-BC in solution state and thin film are shown in Figure 2a. The optical properties are listed in Table 2. DTCP-BC exhibited a

Scheme 5. Synthesis of n-Type Material DTCP-BC



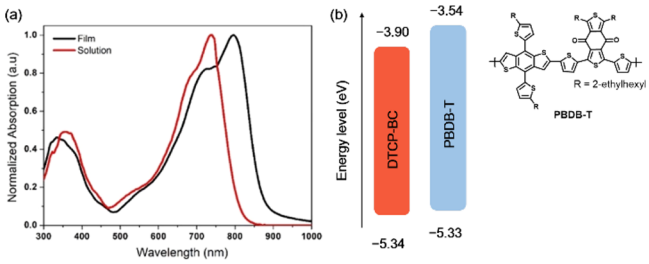


Figure 2. (a) Normalized absorption spectra of DTCP-BC in dichloromethane and thin film state, (b) energy levels of PBDB-T polymer and DTCP-BC.

Table 2. Summary of the Intrinsic Properties of DTCP-BC

	λ_{max} (nm)						
NFA	CH_2Cl_2	Film	λ_{onset} (nm)[a]	E_g^{opt} (eV)[b]	HOMO (eV)[c]	LUMO (eV)[c]	E_g^{ele} (eV)[c]
DTCP-BC	738	796	861	1.44	−5.34	−3.90	1.44

[a]Calculated in the solid state. [b]E_g^{opt} = 1240/λ_{onset}. [c]Determined by cyclic voltammetry.

maximum absorption peak at 738 nm in CH_2Cl_2 solution and a broad absorption band extending to near-infrared region from 500 to 900 nm in thin film which is beneficial to obtaining high short circuit current (J_{sc}) in photovoltaic devices.

The oxidation and reduction potential of DTCP-BC were measured by cyclic voltammetry (CV). The HOMO and LUMO level were determined to be −5.34/−3.90 eV. The energy level diagram of DTCP-BC and polymer donor PBDB-T is depicted in Figure 2b. It should be emphasized that DTCP-BC with a relatively short tetracyclic DTCP unit can readily possess a very small band gap of 1.44 eV. The endocyclic double bond promotes π-delocalization to facilitate intramolecular charge transfer (ICT), while the enolic oxygen enhances the electron-donating strength of the central DTCP to upshift the HOMO energy level. Both factors dramatically narrow the optical band gap of DTCP-BC.

The inverted solar cell devices using the ITO/ZnO/active layer/MoO_3/Ag configuration were fabricated. PBDB-T was chosen as the p-type polymer in the active layer.[49] The J−V curve and the corresponding external quantum efficiency (EQE) spectrum are depicted in Figure 3. The PBDB-T:DTCP-BC (1:1 in wt %) device delivered a moderate efficiency of 9.32% with an open circuit voltage (V_{oc}) of 0.78 V, a high J_{sc} of 20.96 mA/cm^2, and an FF (fill factor) of 56.99%. The J_{sc} is ascribed to the wide absorption spectrum of DTCP-BC with two strong absorption bands in the longer (796 nm) and shorter (325 nm) wavelength regions.

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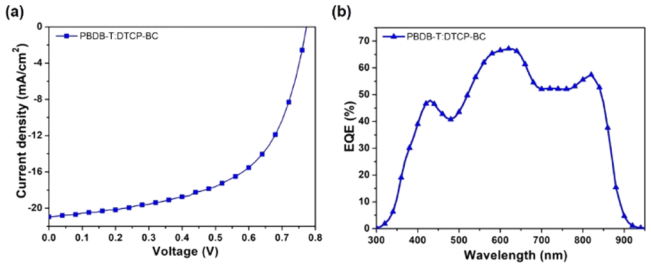

Figure 3. (a) *J*−*V* curve and (b) EQE spectrum of the PBDB-T:DTCP-BC (1:1 in wt %) device.

In summary, new multifused tetracyclic dithienocyclopentapyran (DTCP) and dibenzocyclopentapyran (DBCP) architectures were developed. The symmetrical TVT- or stilbene-based skeleton **3** substituted with bis-triaryl alcohols underwent an acid-catalyzed ring closure followed by a [1,5] hydride shift to form a cyclopentanone moiety in **5**. CuI/DBU-catalyzed intramolecular C−O bond formation in **5** efficiently furnished the central bicyclic CP-pyran ring in the tetracyclic products in good yield. The ring-locked molecules showed significant red-shifted absorption spectra as a result of the enhanced rigidity and oxygen incorporation. DTCP was used as a donor to prepare a A−D−A type nonfullerene acceptor DTCP-BC showing a low optical band gap of 1.44 eV. The DTCP-BC-based solar cell device exhibited an efficiency of 9.32%. This research disclosed a facile and general protocol to access a class of unprecedented CP-pyran ring-locked 1,2-diarylvinylene derivatives. These new π-conjugated frameworks can serve as promising building blocks for making high-performance organic semiconducting materials. Further material derivatization and device optimization are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00110.

Detailed synthetic and device fabrication procedures, single-crystal X-ray crystallographic data, photophysical properties, and NMR spectra (PDF)

Accession Codes

CCDC 2009366−2009368 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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