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Novel H-Shaped Persistent Architecture Based on a Dispiro Building Block System

**Ling-Hai Xie, Xiao-Ya Hou, Chao Tang, Yu-Ran Hua, Rui-Jie Wang,
Run-Feng Chen, Qu-Li Fan, Lian-Hui Wang, Wei Wei, Bo Peng, and
Wei Huang*,[†],[‡]**

Institute of Advanced Materials (IAM), Fudan University, Shanghai 200433, China

wei-huang@fudan.edu.cn; chehw@nus.edu.sg

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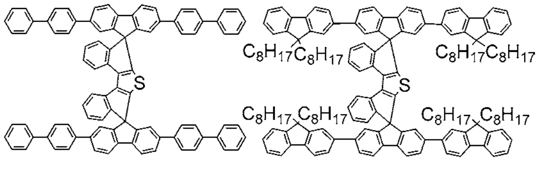
ABSTRACT



TBP-DSFDITF   **TDOF-DSFDITF**

A novel dispiro building block, dispiro[fluorene-9,5′(7′*H*)-diindeno[2,1-*b*:1′,2′-*d*]thiophene-7′,9′′-fluorene], and its two derivatives, TBP-DSFDITF and TDOF-DSFDITF, were designed and synthesized. Because of the rigidity and orthogonality of the spiro structure, TBP-DSFDITF exhibits a well-defined H-shaped architecture, which consists of two ter(biphenyls) as the arms of the H-shape and 3,4-diphenylthiophene as the rung, connecting via completely rigid dispiro linkages with two sp^3 carbon atoms.

Shape-persistent molecular architectures on the nanometer scale,[1] e.g., macromolecular disks,[2] helical macromolecules,[3] π-conjugated macrocycle molecules,[4] and ladder macromolecules,[5] have currently attracted a great deal of attention because of their many applications in the fields of supramolecular chemistry and organic electronics. For example, π-conjugated macrocycles have assembled into discotic liquid crystals or nanotubes,[4b] and helicenes with a precisely ordered stereostructure have been applied to chiral separation and molecular recognition.[6] The common feature of these molecules is a typical π-conjugated or helical conjugated backbone. One strategy for devising new shape-persistent molecular architectures with special self-assembly behavior is to incorporate the stiff semiconjugated or π-interrupted backbones into the above architectures.[7] By doing this, new supramolecular phenomena can occur, e.g., calix[4]arenes for molecular recognition[8] and bicyclic ring-bridged iptycene for molecular motor devices,[9] although strong $\pi-\pi$ stacking supramolecular interaction is not found.

[†] Institute of Advanced Materials (IAM), Nanjing University, Nanjing 210093, China.

[‡] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 119260, Republic of Singapore.

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It is fascinating that dispiro building blocks are used to create new shape-persistent architectures via synthesis, e.g., orthogonal squares, tubes, and ladder structures. The orthogonally cross-shaped dispiro building blocks exhibit unique geometric profiles. In terms of the geometric features, the dispiro compounds can be categorized into five conformational structures, as shown in Figure 1, including linear antarafacial **I**, linear suprafacial **II**, bent suprafacials **III** and **V**, and bent antarafacial **IV**. Thus, di- or polyspirans allow construction of novel well-defined unique scaffolds with many potential applications on the nanometer scale. Moreover, when polyspiro-type structures are end-capped with a trialkylsilyl or/and thio group, they are likely to develop the "stand-up" molecules anchoring on the silicon or Au surface, as reported in the literature.[10] However, as far as we know, there are few reports on the design and synthesis of the above conformational structures. Our objective is to construct a novel kind of shape-persistent molecular architecture based on rigid cross-shaped di- or/and polyspiro building blocks. In the present work, a fundamental dispiro building block dispiro[fluorene-9,5′(7′*H*)-diindeno[2,1-*b*:1′,2′−d]thiophene-7′,9″-fluorene] (**10a**) with conformational structure **III** was successfully designed and synthesized. In addition, its two derivatives, TBP-DSFDITF and TDOF-DSFDITF, were fully characterized and confirmed by ^{1}H and ^{13}C NMR, MALDI-TOF-MS, and elemental analysis. Their optical and thermal properties were also investigated.

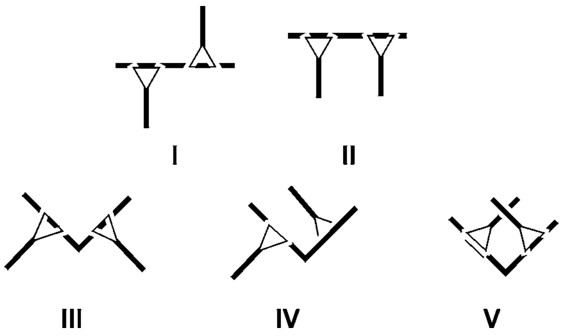
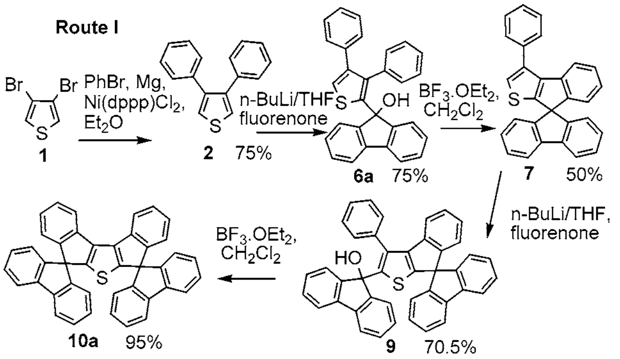


Figure 1. Geometric profiles of dispiro building blocks.

First of all, synthesis of unsubstituted **10a** as a model compound mainly involved the preparation of tertiary alcohol and Friedel−Crafts dehydration cyclization. Dispiro **10a** can be obtained from the cyclization reaction of either tertiary alcohol **9** or thiophene diol **4a**. The former is depicted in Scheme 1, labeled as route **I**; the latter is depicted in Schemes 2 and 3, labeled as route **II**, including routes **II** (**a**) and **II** (**b**), respectively.

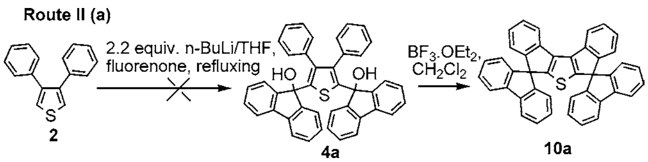
Scheme 1. Synthetic Route **I** to **10a**



In route **I**, the starting material 3,4-dibromothiophene, which is commercially available, was converted into 3,4-diphenylthiophene (**2**) via Kumada-type coupling reactions (i.e., a nickel-catalyzed Grignard−Wurtz cross-coupling reaction involving an arylbromide and a Grignard reagent). Compound **2** was treated with 1.2 equiv of *n*-BuLi in THF at −78 °C, followed by quenching with fluorenone to give the tertiary alcohol **6a** in 75% yield. Friedel−Crafts dehydration cyclization of **6a** with BF$_3$·OEt$_2$/CH$_2$Cl$_2$ gave the monospiro product **7** in nearly 50% yield. The above steps were replicated to obtain the tertiary alcohol **9** in 70.5% yield and **10a** in 95% yield. It was noteworthy that route **I** would be effective to prepare a variety of derivatives, especially odd substituent **10a**, which were useful building blocks for the construction of unique architectures. For example, a useful monobromide **10a** can be obtained by reacting 2-bromofluorenone with monospiro **7**.

Route **I** is a multistep synthetic pathway. To simplify the complicated procedures, we attempted to prepare the thiophene diol **4a** by treating **2** with 2.2 equiv of *n*-BuLi in THF at −78 °C, followed by quenching with 2.5 equiv of fluorenone via one step (as shown in Scheme 2). However, no diol **4a** was obtained, although similar diols have been reported in the literature.[11]

Scheme 2. Synthetic Route **II** (**a**) to **10a**



Fortunately, an efficient synthetic route **II** (**b**) to **10a** was developed, as depicted in Scheme 3. Treatment of **2** with 2 equiv of NBS led to **3** in 88% yield, which was transformed into a double Grignard reagent by reacting with 2.1 equiv of Mg in anhydrous THF. The Grignard reagent was then quenched with fluorenone to provide the diol **4a** in 49% yield, together with the monosubstituted **5a** (36%) and **6a** (13%). Diol **4a** proceeded smoothly in BF$_3$·OEt$_2$/CH$_2$Cl$_2$ to obtain the desirable product **10a** in overall yields of more than 40% starting from **3**. The byproducts **7** and **8** were also

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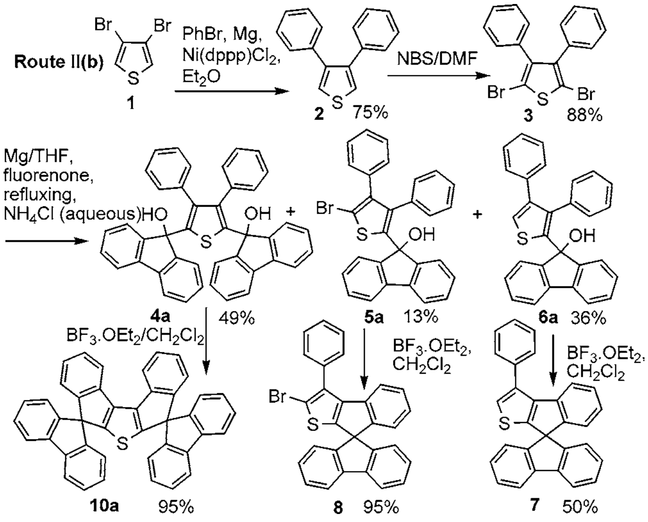
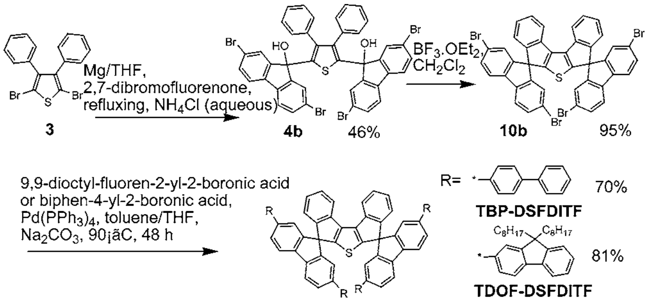
Scheme 3. Synthetic Route **II** (**b**) to **10a**



obtained from the following cyclization of **6a** and **5a**, respectively. It was found that the double Grignard reagent is more effective than dilithium in the addition reaction with fluorenone.

TBP-DSFDITF and TDOF-DSFDITF were prepared via a Suzuki coupling reaction, as shown in Scheme 4. Tetrabrominated **10b**, as a key building block for H-shaped architectures, has been smoothly synthesized via route **II** (**b**) in overall yields of about 45%. Despite the low solubility of **10b** in toluene, the Suzuki coupling reaction of **10b** with 4.4 equiv of biphenyl boronic acid proceeded smoothly in a solvent mixture of toluene and THF at 90 °C, providing the crude product TBP-DSFDITF in 70% yield. After the byproducts were eluted by CH_2Cl_2, the main product was effectively purified by flash column chromatography using chloroform as eluent. Unfortunately, TBP-DSFDITF did not show high solubility as expected; thus, no ^{1}H NMR signals can be observed using $CDCl_3$ as solvent. MALDI-TOF-MS and elemental analysis were utilized to confirm the structure. To fully characterize the novel structure and the electronic properties, TDOF-DSFDITF was also designed and synthesized. TDOF-DSFDITF possesses sufficient solubility due to the introduction of flexible alkyl side chains at the C-9 position of fluorene. Finally, the product was confirmed by ^{1}H and ^{13}C NMR, MALDI-TOF-MS, and elemental analysis.

Scheme 4. Synthesis of TBP-DSFDITF and TDOF-DSFDITF



The comparison of ^{1}H NMR spectra of **10a**, **10b**, and TDOF-DSFDITF is illustrated in Figure 2. The ^{1}H NMR spectrum of **10a** exhibits two kinds of peaks with an expected 4:2 integral intensity ratio, which are readily assigned to the protons on fluorene rings and the protons on benzene rings at the vertical plane, respectively. Using d_6-acetone as solvent, the ^{1}H NMR spectrum of **10b** is unambiguously assigned in the absence of an overlap of two peaks observed in $CDCl_3$. The spectrum of TBP-DSFDITF was not gathered because of unfavorable solubility in $CDCl_3$, whereas TDOF-DSFDITF can be fully confirmed by ^{1}H and ^{13}C NMR. It is noteworthy that the C signals of alkyl chains at the C-9 position of fluorene exhibit a double split, which was probably ascribed to the different chemical circumstances between the interior and exterior of the rigid H-shaped architecture; i.e., while one alkyl stretches inside, the other alkyl on the same carbon atom has to stretch outside. The optimized conformations of TBP-DSFDITF with energy minimization have been calculated by the Gaussian 03 program at the B3LYP /3-21G* level, as shown in Figure 3. The architecture consists of two ter(biphenyls) as the arms of the H-shape of about 2.37 nm length and one 3,4-diphenylthiophene as the rung, connecting via completely rigid dispiro linkages with two sp^3 carbon atoms.

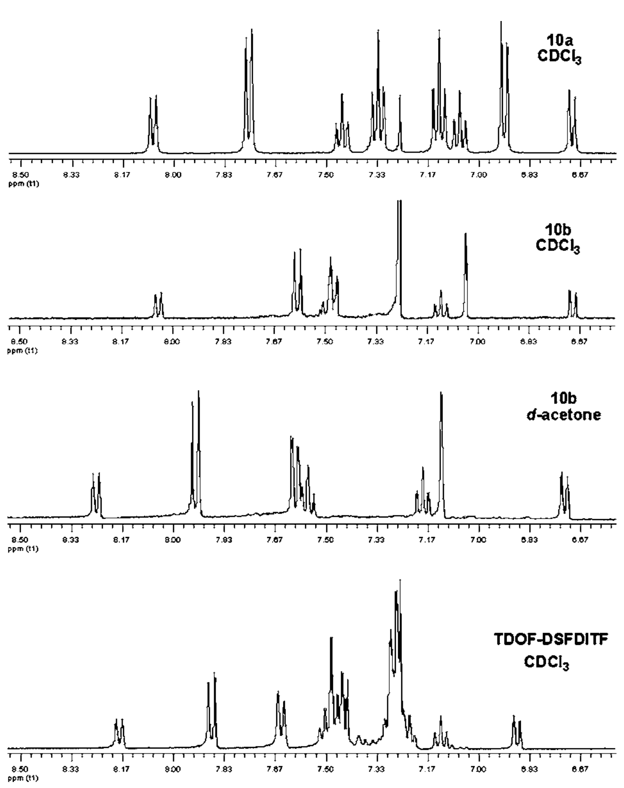


Figure 2. Comparison of ^{1}H NMR spectra of **10a**, **10b**, and TDOF-DSFDITF.

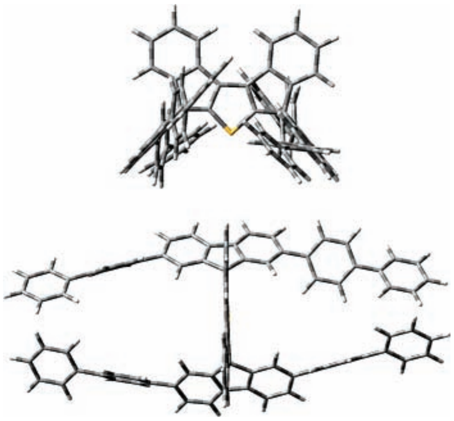


Figure 3. Optimized conformations of TBP-DSFDITF with energy minimization calculated by the Gaussian 03 program at the B3LYP/3-21G* level; (top) view perpendicular to the thiophene, (bottom) view parallel to the thiophene.

The UV−vis absorption and emission spectra of dispiro compounds **10a**, TBP-DSFDITF, and TDOF-DSFDITF were measured in dilute chloroform solutions (1 μM), as shown in Figure 4. TBP-DSFDITF shows the $\pi-\pi^*$ absorption at 345 nm and a blue-colored emission at 386 and 405 nm, which is very similar to the absorption (344 nm) and emission (386 and 404 nm) of the single spiro analogue.[12] The results indicate that there exists little intramolecular interaction between the chromophores on the parallel arms of the H-shaped architecture, which can be an ideal model for intermolecular interaction. Compared with TBP-DSFDITF, the electronic absorption and emission spectra of TDOF-DSFDITF undergo a bathochromic shift of about 7 and 3 nm, respectively. The reason is that there are longer conjugation lengths in fluorene than in biphenyl due to the coplanar linkage via C-9 of fluorene. Although the thiophene ring exists in the architecture, TDOF-DSFDITF has shown high luminescent quantum efficiency (80%) in chloroform, which is probably attributed to the fixation of two spiro linkages to the thiophene ring. Dispiro compounds have also shown high thermal stability, up to about 450 °C for TBP-DSFDITF and high glass transition temperatures, T_g (320 °C for TBP-DSFDITF).

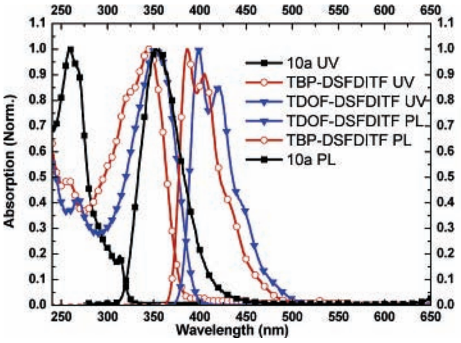


Figure 4. UV−vis and PL spectra of **10a**, TBP-DSFDITF, and TDOF-DSFDITF in chloroform solution (1 μM).

In conclusion, we have designed and synthesized dispiro **10a** as a nonplanar building block to construct H-shaped persistent architectures on the nanometer scale. The interior and exterior parts of the rigid H-shaped architectures exhibit different chemical circumstances identified by ^{13}C NMR. High thermal stability and quantum yield indicate that dispiro **10a** is a potential building block for constructing organic semiconducting materials with unique three-dimensional structures.

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Supporting Information Available: The experimental procedures for the new compounds and ^{1}H and ^{13}C NMR, MS spectra, TG, and DSC thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The single spiro analogue is 2′,7′-bis([1,1′-biphenyl]-4-yl)-spiro-[indeno[2,1-*b*]thiophene-8,9′-fluorene], which shows absorption (343 nm) and emission (385 and 403 nm).