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# Superelectrophilic-initiated C–H Functionalization at the β-position of Thiophenes: A One-Pot Synthesis of trans-stereospecific Saddle-shaped cyclic compounds

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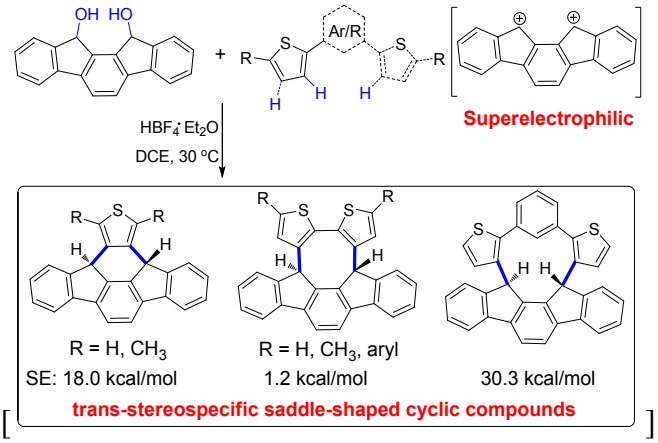
Supporting Information Placeholder




**ABSTRACT:** Superelectrophilic-initiated direct C−H functionalization of thiophenes at the β-position was developed. A series of trans-stereospecific **[2,1-a]-IF**-thiophene-fused cyclic compounds **(4)** with saddle-shaped structure was prepared in 17%-30% yields through a one-pot superelectrophilic Friedel–Crafts reaction of dihydroindenofluorene with thiophene derivatives. From the crystal packing analyses of **4a**, its skeleton shows both strong intermolecular π-π stacking and C-H···π stacking. Furthermore, the ring-dependent photophysical properties of **4** were confirmed by UV-vis absorption and photoluminescence (PL) spectroscopy as well as through the study of their fluorescence quantum yield.

## ■ INTRODUCTION

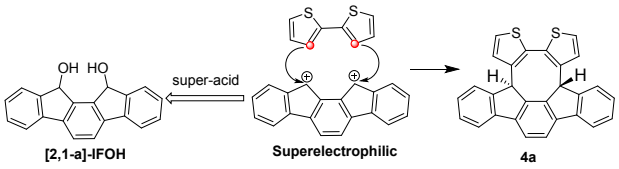
Thiophene-containing shape-persistent macrocycle architectures (Th-SPMAs) have attracted significant attention because of their potential applications in the fields of supramolecular chemistry and materials chemistry.[1] Not surprisingly, a large number of conjugate and nonconjugate Th-SPMAs with fascinating structures, such as cycloocta[1,2-b:4,3-b':5,6-b'':8,7-b''']tetrathiophene,[2] thiophene-fused cycloparaphenylenes,[3] calix[4]thiophenes[4] and crown-annulated oligothiophenes,[5] were synthesized by metal-catalyzed C-C coupling reactions, metalation reactions, Friedel-Crafts reactions and other macrocyclic reactions.1 Among Th-SPMAs, the ring closure reactions occur at the α-position of thiophene. In contrast, reactions of the β-position are rare in the field of macrocyclic chemistry and only occur when the hydrogen on the β-position is replaced by a reactive functional group (i.e. -Br, -Li, and –B(OH)2 etc.).2,6 Current approaches to β-position ring cyclization suffer from i) tedious synthetic procedures, and ii) the use of dangerous solvents. Therefore, further development of new methods that allow the facile one-pot synthesis of highly functionalized Th-SPMAs from the unactivated β-position of thiophene are still a challenge. Towards this end, we demonstrate a one-pot cyclization

strategy to afford a type of β-position linked Th-SPMAs, which contains simple operation, short reaction time and mild conditions. The β-position linked Th-SPMAs allow for different functional groups easily introducing to the α-position of thiophene for molecular modification and structural expansion compared with α-position linked Th-SPMAs. Moreover, due to the ease of functionalization, such β-position linked Th-SPMAs have been shown to exhibit superior properties in optical and electrochemical applications.[7]

Our partiular interest is superelectrophilic chemistry, which was proposed in the 1970s by Olah and coworkers[8] and has been extensively used in various organic reactions, such as the Friedel–Crafts reaction,[9] Diels−Alder reaction[10] as well as other cyclization reactions.[11] Superelectrophilic chemistry is well-known for its ability to generate di- and tri-cationic superelectrophiles in superacidic media that exhibit exceptionally high electrophilic reactivities.[12] Compared with mono-cationic electrophiles, multiple cationic superelectrophiles as highly reactive electrophilic species are capable of reacting with very weak nucleophiles (i.e., deactivated arenes and alkanes).

Inspired by superelectrophilic chemistry, we anticipated that the intramolecular electrophilic cyclization of a weak nucleophile, such as the 3,3'-position of 2,2'-bithiophene, and a 11,12-dihydroindeno[2,1-a]fluorene (**[2,1-a]-IF**)-based superelectrophilic intermediate could produce **[2,1-a]-IF**-thiophene-fused cyclic compounds. **[2,1-a]-IF**-based superelectrophilic intermediates can be afforded via 11,12-dihydroindeno[2,1-a]fluorene-11,12-diol (**[2,1-a]-IFOH**) in the presence of a superacid (Scheme 1). Herein, a C-C bond formation at the β-position of thiophene has been developed via the superacid promoted superelectrophilic Friedel–Crafts reaction of **[2,1-a]-IFOH** with 2,2'-bithiophene. This methodology provides a strategically novel access to **[2,1-a]-IF**-thiophene-fused cyclic compounds with a saddle-shaped structure (**4**). Their structures were analyzed by nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS). Furthermore, the structure of **4a** was verified by a single-crystal X-ray diffraction. The crystal packing of **4a** shows both strong intermolecular π-π stacking and C-H···π stacking. In addition, the ring-dependent properties of **[2,1-a]-IFOH**, **4** and U-shaped product **5** were confirmed by absorption and emission peaks and the fluorescence quantum yield.

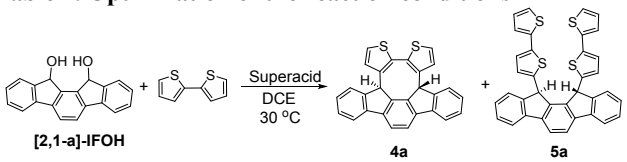
**Scheme 1. Superacid promoted superelectrophilic Friedel–Crafts reaction.**




## ■ RESULTS AND DISCUSSION

To optimize the reaction conditions and meet the requirements for the formation of a superelectrophile, such as excess superacid media and high concentration,[11d] **[2,1-a]-IFOH** (mixed stereoisomers) and, 2,2'-bithiophene were selected as model reagents(Table 1). First, several superacids (60 equiv) were investigated in 1,2-dichloroethane (DCE, 0.05 M) as the solvent at 30 °C (entries 1-4). $CF_3SO_3H$ was an effective superacid, and furnished a high trans-stereospecific **4a** (14%) with two H atoms at the 9-site in an opposite orientation as well as the U-shaped product **5a** (35%) and oligomeric byproducts. The skeletal structure of **4a** was further confirmed by a single-crystal X-ray diffraction. It is worth noting that the **5a** is a product from the reaction of **[2,1-a]-IFOH** with the α-position of 2,2'-bithiophene. When $CH_3SO_3H$ and $H_2SO_4$ were used as superacids, however, the yield of **4a** decreased to 3%-5%. To our delight, $HBF_4{\cdot}Et_2O$ afforded **4a** in 27% yield. During this process, the byproducts, including the **5a** (26%) and another undefined complex oligomer, were found. The effects of reaction time was examined under the same conditions. As a result, the yield of **4a** decreased from 27% to 18% by increasing the reaction time from 30 sec to 3 min. These results indicated that the formation of oligomers may be caused by the reaction of thiophene with the **5a** and **4a**. Thus, shortening of reaction time can protect **4a** from being attacked by another molecule of **[2,1-a]-IFOH**. Furthermore, solution concentration was explored. The results indicated that the yield of **4a** was decreased to 20% when the solvent concentration of DCE was decreased to 0.01 M. When the concentration of DCE increased to 0.1 M, the yield of **4a** subsequently decreased to 15%. Finally, the amount of $HBF_4{\cdot}Et_2O$ (20 equiv., 40 equiv., 80 equiv.) used into the reaction (entries 9-11) was explored. As a result, the yield of **4a** improved slightly until 60 equiv. of acid, after which the yield remained constant.

**Table 1. Optimization of the reaction conditions**[a]

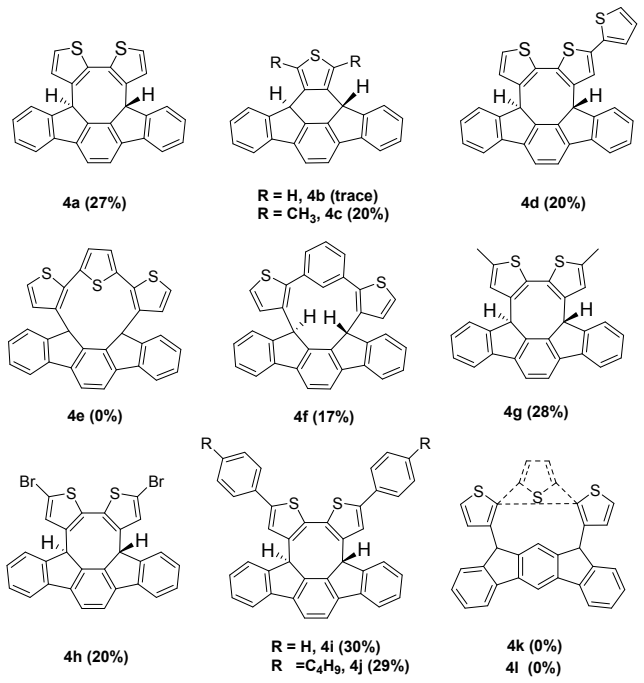



| Entry | Superacid (eq) | DCE (M) | Time | **4a**Yield[b] (%) | **5a**Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | $CF_3SO_3H$ (60) | 0.05 | 30 s | 14 | 35 |
| 2 | $CH_3SO_3H$ (60) | 0.05 | 30 s | 3 | 40 |
| 3 | $H_2SO_4$ (60) | 0.05 | 30 s | 5 | 30 |
| 4 | $HBF_4{\cdot}Et_2O$ (60) | 0.05 | 30 s | 27 | 26 |
| 5 | $HBF_4{\cdot}Et_2O$ (60) | 0.05 | 60 s | 23 | 25 |
| 6 | $HBF_4{\cdot}Et_2O$ (60) | 0.05 | 180 s | 18 | 22 |
| 7 | $HBF_4{\cdot}Et_2O$ (60) | 0.01 | 30 s | 20 | 28 |
| 8 | $HBF_4{\cdot}Et_2O$ (60) | 0.1 | 30 s | 15 | 32 |
| 9 | $HBF_4{\cdot}Et_2O$ (20) | 0.05 | 30 s | 23 | 27 |
| 10 | $HBF_4{\cdot}Et_2O$ (40) | 0.05 | 30 s | 25 | 26 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | $HBF_4 \cdot Et_2O$ (80) | 0.05 | 30 s | 27 | 26 |

[a]Reactions were carried out with **[2,1-a]-IFOH** (0.17 mmol), 2,2'-bithiophene (0.17 mmol), superacid in DCE. [b]Isolated yield.

**Scheme 2. Substrate Scope of the Reaction[a]**




[a]Reactions were carried out by using dihydroindenofluorenes (0.17 mmol) with thiophene derivatives (0.17 mmol), $HBF_4 \cdot Et_2O$ in 0.05 M DCE.

Having established the optimal reaction conditions, we explored the substrate scope of dihydroindenofluorenes and thiophene derivatives in the presence of $HBF_4 \cdot Et_2O$ (Scheme 2). First, to explore the influence of the thiophene chain length of on the cyclization reaction, mono-, di-, tri-thiophenes were explored. The results showed that when thiophene was examined, only a trace amount of **4b** was obtained, and the U-shaped byproduct (**5b**, 30%)[13] was obtained via the reaction of the α-position of thiophene with **[2,1-a]-IFOH**. Fortunately, when the α-position of thiophene was replaced with a methyl, under the same conditions, **4c** was obtained in 20% yield. 2,2':5',2"-terthiophene was transformed into **4d** in 20% yield, whereas the expected **4e** was not observed, due to the strain energy of **4e**, 57.3 kcal·mol$^{-1}$, which was larger than that of **4d** (Table S1).[14] To verify the reduced reaction site of the tri-thiophene, it was necessary to synthesize an [**2,1-a]-IF**-thiophene-fused rings with a large strain energy. 1,3-di(thiophen-2-yl)benzene was used for this reaction, and the corresponding **4f** was obtained in 17% yield. Subsequently, by replacing both the electron-withdrawing and electron-donating groups[15] at the 5,5'-positions of the 2,2'-bithiophene with methyl, Br, phenyl, or butylphenyl, the corresponding cyclization products were produced smoothly. The 5,5'-positions of 2,2'-bithiophene containing a methyl, phenyl, or butylphenyl substituent, gave the corresponding **4g**, **4i**, and **4j** in 28%, 30% and 29% yields, respectively. However, 5,5'-dibromo-2,2'-bithiophene showed poor reactivity, as **4h** was obtained in only 20% yield. These results indicated that electron-donating groups facilitate the cyclization. Finally, to study the distance-effect between two cationic groups on the cyclizing reaction, **[2,1-b]-IFOH** as a superelectrophile precursor was subjected to the reaction sequence. However, the expected **4k** and **4l** were not observed. Instead, U-shaped byproducts **5c** and **5d** (Supporting Information) were achieved in 21% and 23% yield from the reaction between the α-positions of 2,2'-bithiophene and 2,2':5',2"-terthiophene with **[2,1-b]-IFOH**, respectively, indicating an increased distance between cationic groups in **[2,1-b]-IFOH** to avoid the generation of a superelectrophile.

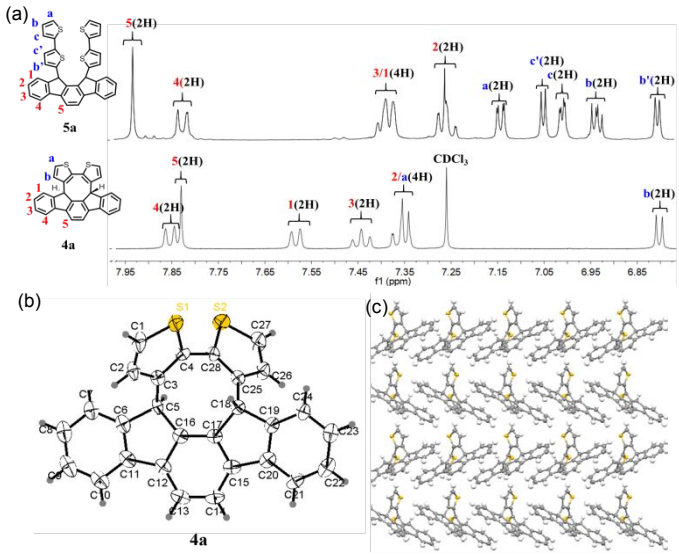


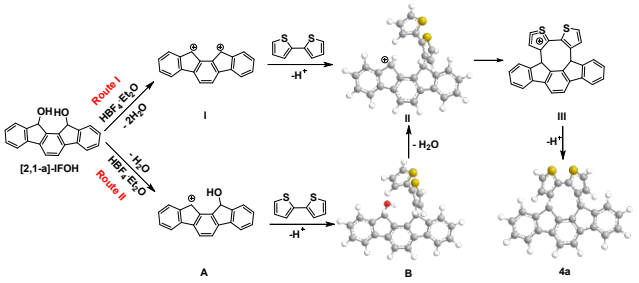

**Figure 1.** (a) $^1$H NMR spectra of the **5a** and **4a** (400 MHz, 30 °C, in $CDCl_3$). (b) ORTEP drawing of **4a** at 50% probability. (c) Packing structure of **4a**.

The conversion of **[2,1-a]-IFOH** to **[2,1-a]-IF**-thiophene-fused cyclic compounds was confirmed by $^1$H and $^{13}$C NMR spectroscopy as well as high-resolution mass spectrometry (HRMS). Figure. 1a shows the $^1$H NMR spectra of the U-shaped **5a** and **4a** in $CDCl_3$. The $^1$H NMR spectra of the U-shaped **5a**, shows four doublets at 6.80-6.81 ppm ($J$ = 3.6 Hz), 7.00-7.01 ppm ($J$ = 3.6 Hz), 7.04-7.05 ppm ($J$ = 3.6 Hz) and 7.13-7.14 ppm ($J$ = 5.2 Hz). Each doublet integrated as two hydrogens and were assigned to protons b', c, c' and a of the dithiophene group. The one triplet at 6.92-6.94 ppm ($J$ = 3.6 Hz), correspond to two hydrogens and was assigned to proton b of the dithiophene group a. In comparison, the proton c and c' of dithiophene group peak at 7.00-7.01 ppm and 7.04-7.05 ppm disappeared in the $^1$H NMR spectrum of **4a**, which demonstrated the formation of a C-C bond in the β-position of dithiophene. Additionally, in the $^1$H NMR spectrum of **4a**, due to the influence of the cyclic skeleton, proton 5 on the indenofluorene group was shielded by the induced field of the aromatic ring current and the protons a on dithiophene as well as protons 1, 2, 3 and 4 on indenofluorene group were deshielded by the induced field of the aromatic ring current. The β-proton (proton b) and α-proton (proton a) of the dithiophene group appeared as two doublets at 6.80-6.81 ppm ($J$ = 5.2 Hz)

and 7.34-7.35 ppm ($J$ = 5.2 Hz), respectively, integrating to two hydrogens each. Protons 1, 2, 3, 4 and 5 of the indenofluorene group appeared as a doublet at 7.58-7.59 ppm ($J$ = 7.6 Hz), a triplet at 7.34-7.38 ppm ($J$ = 8.0 Hz), a triplet at 7.42-7.46 ppm ($J$ = 7.6 Hz), a doublet at 7.84-7.86 ppm ($J$ = 7.6 Hz) and a singlet at 7.83 ppm. These protons integrated as a total of ten hydrogens. Proton c and c' of the dithiophene group peak disappeared in the $^1$H NMR spectrum of **4a** due to the formation of the cyclic ring.

The skeletal structure of **4a** was not totally planar, but saddle-shaped (Figure 1b). The dihedral angles of the indenofluorene and the bithiophene are 56.59° and 54.86°, respectively, and the two torsional thiophenes have an angle of 60.91° (Figure S2). The packed structure of **4a** is illustrated in Figure 1c. Such saddle-shaped backbones exhibit an outstanding conjugated character and form torsional octatomic rings to facilitate intermolecular π-π stacking in the presence of indenofluorene planes. The distance between the two stacking surfaces was approximately 3.60 Å. Furthermore, the α-position of the thiophene and indenofluorene plane detected edge-to-face stacking and the distance between the adjacent interlayers was approximately 2.76 Å. Intermolecular S−S interactions were not observed. Most importantly, the style of packing mode allowed for a transverse longitudinal extension to from the 2-dimensional supramolecular framework.

**Scheme 3. Possible mechanism for the formation of [2,1-a]-IF-thiophene-fused cyclic compounds (4).**




On the basis of the results described above as well as previous studies, a possible mechanism Route I for the intramolecular electrophilic cyclization of **[2,1-a]-IFOH** and the unactivated β-position of thiophene was proposed, as depicted in Scheme 3. First, in the presence of $HBF_4{\cdot}Et_2O$, **[2,1-a]-IFOH** lost two molecules of water to form the di-cationic superelectrophile I as a highly electrophilic species.[16] Then, superelectrophile I reacts with β-position of 2,2'-bithiophene to provide complex II by removing one proton. It is worth noting that 2,2'-bithiophene would twisted from the coplanar anti and syn configuration to keep the lowest energy conformers,[17] and only syn configurations could followed by a intramolecular electrophilic cyclization to give the intermediate III. Finally, intermediate III lost one proton to generate the trans-stereospecific **4a**. Another anti 2,2'-bithiophene in complex II tend to form oligomers due to the active sites of thiophene far from sp$^3$-carbon atoms of **[2,1-a]-IFOH**. In the meanwhile, another potential mechanism Route II may also exist at the same time. Different from superelectrophile I, monocation intermediate A was generated from **[2,1-a]-IFOH** by lost one $H_2O$ when acid added in the first step. Then, intermediate A reacts with β-position of 2,2'-bithiophene to obtained intermediate B by releasing one proton, follow by intermediate B removed a molecule of water to give complex II and finally a intramolecular electrophilic cyclization to get **4a** (II→III→4a).

To study the effect of ring size on **[2,1-a]-IF**-thiophene-fused cyclic compounds, the stability and photophysical properties of **4a**, **4c** and **4f** were carried out by density functional theory (DFT) calculations, UV-vis absorption spectroscopy and photoluminescence (PL) spectroscopy. A strain energy was calculated by DFT calculations at the RB3LYP/6-31G(d) level of theory.[14] As a result, **4c** and **4f** have a high strain energy (SE: 18.0 kcal·mol$^{-1}$ and 24.0 kcal·mol$^{-1}$, respectively). In comparison, the strain energy (SE) of **4a** was 1.2 kcal·mol$^{-1}$, and it exhibited an increased stability and facile synthesis. The photophysical properties of **4a**, **4c**, **4f**, **5a** and **[2,1-a]-IFOH** were next investigated by UV-vis absorption spectroscopy and photoluminescence (PL) spectroscopy. As shown in Figure 2 and Table 2, **4a**, **4c** and **4f** exhibit almost the same UV-vis and PL spectra, and their PL spectra are significantly blue-shifted in comparison to that of **[2,1-a]-IFOH** and **5a**. In addition, band-gap energy (Eg) were gained from the onset edge of the UV-vis absorption spectra. **4a**, **4c** and **4f** were found to

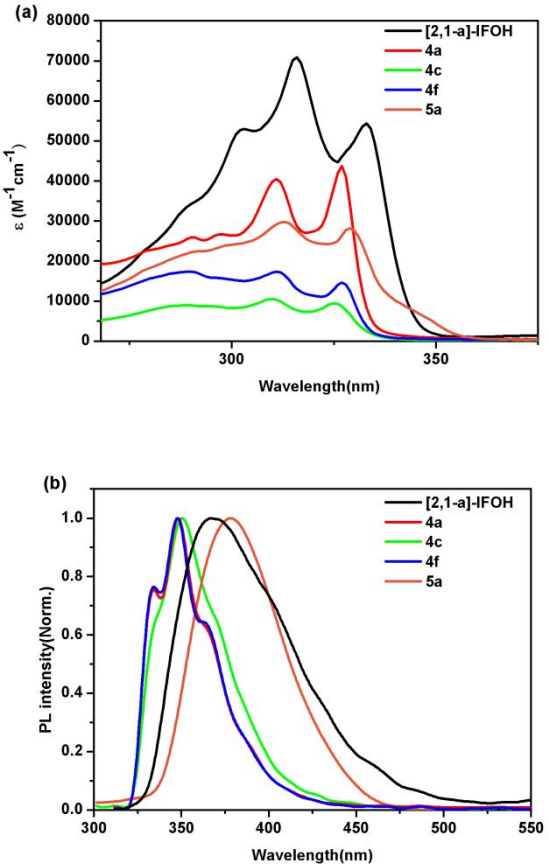



**Figure 2.** UV-vis absorption spectra (a) and PL spectra (b) of **[2,1-a]-IFOH**, **4a**, **4c**, **4f** and **5a** in $10^{-5}$ M $CH_2Cl_2$.

**Table 2. The stability and photophysical properties of [2,1-a]-IFOH, 4a, 4c, 4f and 5a.**

| Entry | λabs (nm) | λem (nm) | Eg (eV) | SE (kcal·mol$^{-1}$) | Φ (%) |
|---|---|---|---|---|---|
| **[2,1-a]-IFOH** | 303, 316,333 | 366 | 3.58 | - | 2 |
| **4a** | 290, 310, 326 | 334, 348 | 3.69 | 1.2 | 29 |
| **4c** | 288, 310, 325 | 350 | 3.67 | 18.0 | 47 |
| **4f** | 290, 311, 327 | 334, 348 | 3.68 | 24.0 | 52 |
| **5a** | 314, 330 | 379 | 3.48 | - | 5 |

be 3.69 eV, 3.67 eV and 3.68 eV, higher than that of **[2,1-a]-IFOH** (3.58 eV) and **5a** (3.48 ev), respectively. Most notably, the fluorescence quantum yield values of **[2,1-a]-IFOH** and U shaped product **5a** were quite low in $CH_2Cl_2$. However, the rings have a significant progress and the fluorescence quantum yield of **4a**, **4c** and **4f** were 29%, 47% and 52% in $CH_2Cl_2$, respectively. The results indicate that the ring skeleton has an influence on the indenofluorenol electronic structure. The ring strain of **[2,1-a]-IF**-thiophene-fused cyclic compounds, however, has almost no effect on the absorption and emission spectra.

## ■ CONCLUSIONS

In summary, we have developed a novel superelectrophilic Friedel–Crafts reaction between dihydroindenofluorene and thiophene derivatives for the one-pot construction of **[2,1-a]-IF**-thiophene-fused cyclic compounds with a saddle-shaped structure in 17%-30% yields under mild conditions. The structure of **4a** was linked by the β-position of 2,2'-bithiophene and sp$^3$-carbon atoms of **[2,1-a]-IFOH** to form a saddle-shaped compound which was verified by a single-crystal X-ray diffraction, and its crystal packing show both strong intermolecular π-π stacking and edge-to-face stacking. In addition, due to the existence of active sites on 2,2'-bithiophene and dihydroindenofluorene, respectively, further molecular modification and structural expansion can be performed on **4a**. To study the effect of ring skeleton on **[2,1-a]-IF**-thiophene-fused cyclic compounds, the photophysical properties of **4a**, **4c**, **4f**, **5a** and **[2,1-a]-IFOH** were investigated. The results show that **4a**, **4c** and **4f** exhibit almost the similar UV-vis and PL spectra with λabs at near 310, 325 nm and λem at near 350 nm. Moreover, compared to **5a** and **[2,1-a]-IFOH, [2,1-a]-IF**-thiophene-fused cyclic compounds **4a**, **4c** and **4f** have a significant progress in the fluorescence quantum yield which indicating the ring skeleton has an influence on the indenofluorenol electronic structure. Further work on applications of **[2,1-a]-IF**-thiophene-fused cyclic compounds type compounds is ongoing in our laboratory.

## ■ EXPERIMENTAL SECTION

**General information.** Unless otherwise information noted, all the solvents and reagents were purchased from commercial suppliers and used without further purification. Some products were purified via column chromatography over silica gel (200-300 mesh) (from Nanjing Wanqing Chemical Instruments Company), some were isolated by using recycling GPC (Japan Analytical Industry Co., Ltd.) and a little of them were purified by recrystallization. $^1$H NMR and $^{13}$C{$^1$H} NMR spectra were recorded at 20 $^o$C on a Varian 400 MHz and 100 MHz, respectively. Chemical shifts are exhibited as δ in units of parts per million (ppm) relative to internal standard ($^1$H NMR: TMS = 0.00 ppm) or relative residual peaks ($^1$H NMR: 7.26 for $CDCl_3$, 2.50 for d6–DMSO; $^{13}$C NMR: 77.0 triplet for $CDCl_3$, 39.25 for d6–DMSO). Multiplicities in briefly were shown as: s (singlet); d (doublet); t (triplet); dd (doublet of doublets); m (multiplet). High resolution (HR) mass spectrometry (MS) experiments were performed on Thermo Fisher Scientific LTQ FTICR-MS and Waters Micromass GCT. Coupling constants are reported as a *J* value in Hz.

**Preparation of indeno[2,1-a]fluorene-11,12-dione.** The synthesis of the **indeno[2,1-a]fluorene-11,12-dione**,[18] including intermediates Dimethyl 1',4'-dihydro-[1,1':4',1''-terphenyl]-2',3'-dicarboxylate (**1**),[19] Dimethyl [1,1':4',1''-terphenyl]-2',3'-dicarboxylate (**2**),[20] have been previously reported.

*Dimethyl 1',4'-dihydro-[1,1':4',1''-terphenyl]-2',3'-dicarboxylate (**1**).* White solid. 88% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.34 (m, 4H), 7.31-7.28 (m, 6H), 5.81 (s, 2H), 4.50 (s, 2H), 3.58 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 167.9, 141.2, 135.7, 128.8, 128.3, 127.2, 126.1, 52.1, 44.0.

*Dimethyl [1,1':4',1''-terphenyl]-2',3'-dicarboxylate (**2**).* White solid. 91% yield.. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.52 (s, 2H), 7.45-7.41 (m, 4H), 7.40-7.38 (m, 4H), 7.37-7.36 (t, *J* = 3.2 Hz, 2H), 3.61 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 168.9, 139.9, 139.7, 132.1, 131.7, 128.4, 128.3, 127.8, 52.4.

*Indeno[2,1-a]fluorene-11,12-dione.* Yellow solid. Yield: 95%. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.69 (d, *J* = 7.2 Hz, 2H), 7.60 (s, 2H), 7.50-7.49 (d, *J* = 4 Hz, 4H), 7.33-7.30 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 145.2, 143.6, 134.7, 133.7, 132.4, 129.5, 124.8, 120.1.

**Synthesis of [2,1-a]-IFOH.** Indeno[2,1-a]fluorene-11,12-dione (1 g, 3.54 mmol) was dissolved in methyl alcohol (100 mL). The reaction mixture was stirred at room tempreture, and small portions (ca 20 mg) of sodium borohydride (total: 200 mg, 5.3 mmol) were added to the solution every two minutes. The excess of sodium borohydride was reduced by addition of water (100 mL) and then left standing the solution until the precipitate completely precipitated. The yellow precipitate formed was further collected by filtration, washed with water and dried in an oven at 50°C to give **[2,1-a]-IFOH** as a colourless solid (0.91 g, 3.2 mmol).

Yellow solid (0.91 g, 90% yield); $^1$H NMR (400 MHz, DMSO-d6) δ: 7.83-7.81 (d, *J* = 9.6 Hz, 4H), 7.63-7.61 (d, *J* = 6.8 Hz, 2H), 7.44-7.40 (t, *J* = 7.2 Hz, 2H), 7.36-7.32 (t, *J* = 7.2 Hz, 2H), 6.14 (s, 2H), 5.92 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-d6) δ: 145.9, 143.7, 140.3, 139.7, 129.2, 128.1, 125.7, 121.1, 120.7, 73.6. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{14}O_2^+$, 286.0994; found, 286.1001.

**Preparation of Indeno[2,1-b]fluorene-10,12-dione.** The synthesis of the **Indeno[2,1-b]fluorene-10,12-dione**,[18] including intermediates 4,6-Dibromoisophthalic acid (**3a**), Diethyl 4,6-dibromoisophthalate (**3b**), Diethyl [1,1':3',1''-

terphenyl]-4',6'-dicarboxylate (**3c**) have been previously reported.

*4,6-Dibromoisophthalic acid (**3a**)*. White solid. Yield: 65%. $^1$H NMR (400 MHz, DMSO-d6) δ: 8.15 (s, 1H), 8.12 (s, 1H), 2.27 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-d6) δ: 166.4, 138.9, 134.6, 133.6, 133.1, 132.8, 124.2, 100.0.

*Diethyl 4,6-dibromoisophthalate (**3b**)*. White solid. Yield: 40%. $^1$H NMR (400 MHz, DMSO-d6) δ: 8.18 (s, 1H), 8.10 (s, 1H), 4.37-4.31 (m, 4H), 1.34-1.31 (t, *J* = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-d6) δ: 164.7, 139.1, 132.8, 132.2, 124.7, 62.5, 14.4.

*Diethyl [1,1':3',1''-terphenyl]-4',6'-dicarboxylate (**3c**)*. Colorless oil. Yield: 90%. $^1$H NMR (400 MHz, DMSO-d6) δ: 8.10 (s, 1H), 7.42-7.35 (m, 11H), 4.10-4.04 (m, 4H), 0.98-0.95 (t, *J* = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-d6) δ: 167.5, 144.5, 139.9, 133.1, 131.0, 130.4, 129.4, 128.7, 128.3, 127.9, 127.1, 61.5, 13.9.

*Indeno[2,1-b]fluorene-10,12-dione*. Brown solid. Yield: 90%. $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, 1H), 7.69-7.67 (d, *J* = 7.2 Hz, 2H), 7.65 (s, 1H), 7.61-7.59 (d, *J* = 7.2 Hz, 2H), 7.56-7.52 (t, *J* = 7.2 Hz, 2H), 7.40-7.36 (t, *J* = 7.2 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 151.5, 142.8, 134.9, 134.8, 134.6, 130.5, 124.5, 121.1, 120.1.

**Synthesis of [2,1-b]-IFOH.** The title compound was synthesized as the same way of **[2,1-a]-IFOH**. The NMR spectrum data could not be measured due to the extremely poor solubility of the product. Brown solid (0.90 g, 89% yield); HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{14}O_2^+$, 286.0094; found, 286.1000.

**Synthesis of 5,5'-Dibromo-2,2'-bithiophene.** To a solution of 2,2'-bithiophene (3 g, 18.0 mmol) in acetone (30 ml) were added *N*-bromosuccinimide (9.7 g, 54.1 mmol) by dropping in a solution of acetone (30 ml). Then the mixture was stirred at the room temperature until the dripped off. After that, increasing the reaction temperature to 60 °C in an oil bath overnight. The mixed organic phase was washed with water, extracted with $CH_2Cl_2$, dried over anhydrous $MgSO_4$ before organic phase was filtered and concentrated under low pressure. The crude product was purified by column chromatography (silica gel, pure petroleum ether) to give 5,5'-dibromo-2,2'-bithiophene (5.8 g, 16.2 mmol).
Yellow solid (5.8 g, 90% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ: 6.96-6.95 (d, *J* = 3.6 Hz, 2H), 7.85-7.84 (d, *J* = 4 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 137.8, 130.7, 124.2, 111.6. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_8H_4Br_2S_2^+$, 321.8116; found, 321.8113.

**Synthesis of 5,5'-Diphenyl-2,2'-bithiophene.** 5,5'-dibromo-2,2'-bithiophene (4 g, 12.4 mmol), phenylboronic acid (3.8 g, 31.1 mmol), tetrakis-(triphenylphosphine) palladium0 (1.4 g, 1.2 mmol) and potassium carbonate (5 g, 36.2 mmol) were dissolved in a mixture THF/water (2.5:1, 150 mL) under an nitrogen atmosphere. The resulting mixture was stirred overnight at 70°C in an oil bath. The mixed organic phase was washed with water, extracted with $CH_2Cl_2$, dried over anhydrous $MgSO_4$ before organic phase was filtered and concentrated under low pressure. The crude product was purified by column chromatography (silica gel, pure petroleum ether) to give 5,5'-diphenyl-2,2'-bithiophene (3.2 g, 10.0 mmol). Yellow solid (3.2 g, 81% yield) $^1$H NMR (400 MHz, $CDCl_3$) 7.62-7.61 (d, *J* = 6.4 Hz, 4H), 7.41-7.37 (t, *J* = 7.6 Hz, 4H), 7.31-7.25 (m, 6H), 7.18 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 129.0, 127.6, 125.6, 124.5, 123.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}S_2^+$: 319.0610; found, 319.0607.

**Synthesis of 5,5'-Bis(4-butylphenyl)-2,2'-bithiophene.** The 5,5'-bis(4-butylphenyl)-2,2'-bithiophene was synthesized as the same way of 5,5'-diphenyl-2,2'-bithiophene and purified by column chromatography (silica gel, pure petroleum ether) to give 5,5'-bis(4-butylphenyl)-2,2'-bithiophene (1.7 g, 4.0 mmol). Yellow solid (1.7 g, 85% yield) $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.51 (d, *J* = 8.0 Hz, 4H), 7.21-7.19 (m, 6H), 7.15-7.14 (d, *J* = 3.6 Hz, 2H), 2.65-2.61 (t, *J* = 7.6 Hz, 4H), 1.64-1.60 (t, *J* = 8.0 Hz, 4H), 0.96-0.93 (t, *J* = 7.2 Hz, 4H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 143.2, 142.6, 136.3, 131.5, 129.0, 125.5, 124.3, 123.3, 35.4, 33.6, 22.4, 14.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{31}S_2^+$ , 431.1862; found, 431.1859.

**Synthesis of 1,3-Di(thiophen-2-yl)benzene.** 1,3-dibromobenzene (3 g, 12.8 mmol), thiophen-2-ylboronic acid (5 g, 38.5 mmol), tetrakis(triphenylphosphine) palladium0 (1.3 g, 1.1 mmol) and potassium carbonate (5 g, 63.7 mmol) were dissolved in a mixture THF/water (2.5:1, 150 mL) under an nitrogen atmosphere. The resulting mixture was stirred overnight at 70°C in an oil bath. The mixed organic phase was washed with water, extracted with $CH_2Cl_2$, dried over anhydrous $MgSO_4$ before organic phase was filtered and concentrated under low pressure. The crude product was purified by column chromatography (silica gel, pure petroleum ether) to give 1,3-di(thiophen-2-yl)benzene (2.6 g, 10.6 mmol). White solid (2.6 g, 83% yield) $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.55-7.53 (dd, *J* = 7.6 , 1.2 Hz, 2H), 7.42-7.40 (d, *J* = 7.6 Hz, 1H), 7.38-7.37 (dd, J = 3.6 , 1.2 Hz, 2H), 7.33-7.31 (dd, *J* = 5.0, 1.0 Hz, 2H), 7.13-7.11 (dd, *J* = 5.2, 3.6 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 144.0, 135.1, 129.5, 128.1, 125.1, 123.6, 123.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}S_2^+$ , 243.0297; found, 243.0296.

**General procedure for synthesis of compounds 4 and 5 (4a is an example).** In a round-bottom flask charged with **[2,1-a]-IFOH** (50.0 mg, 0.17mmol) and 2,2'-bithiophene(29.0 mg, 0.17mmol) in 3.4 mL (0.05 M) 1, 2-dichloroethane (DCE), then 60 equiv $HBF_4$•$Et_2O$ was added into the mixture and stirred for 30s at 30 °C in an oil bath. Subsequently, $H_2O$ was added，and the mixture was extracted with $CH_2Cl_2$. The mixed organic phase was washed with potassium carbonate solution, dried over anhydrous $MgSO_4$ before organic phase was filtered and concentrated under low pressure. The crude product was purified by recycling GPC to give **4a** in 27% yield.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4a**)*. White solid (19.6 mg, 27% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.83 (m, 4H), 7.59-7.57 (d, *J* = 8 Hz, 2H), 7.46-7.42 (t, *J* = 7.2 Hz, 2H), 7.37-7.34 (m, 4H), 6.81-6.80 (d, *J* = 5.2 Hz, 2H), 4.95 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 145.3, 141.7, 140.3, 139.3, 131.5, 127.5, 126.9, 126.8, 125.6, 120.2, 119.3, 47.0. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{16}S_2^+$, 416.0693; found, 416.0695.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4c**)*. Brown solid (12.7 mg, 20% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.07-8.05 (d, *J* = 7.6 Hz, 2H), 7.84-7.82 (d, *J* = 7.6 Hz, 2H), 7.69 (s, 2H), 7.44-7.40 (t, *J* = 7.6 Hz, 2H), 7.35-7.32 (t, *J* = 6.4 Hz, 2H), 5.05 (s, 2H), 2.48 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ: 144.3, 143.8, 143.7, 138.4, 136.7, 130.1, 127.6, 127.4, 125.7, 121.0, 119.4, 47.6, 29.7, 16.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{19}S^+$, 363.1202; found, 363.1200.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4d**)*. Brown solid (17.4 mg, 20% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ : 7.88-7.84 (m, 4H), 7.63-7.58 (m, 2H), 7.48-7.43 (m, 2H), 7.40-7.35 (m, 2H), 7.19-7.18 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.15-7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.00-6.97 (m, 2H), 6.87 (s, 1H), 6.82-6.81

(d, $J$ = 5.2 Hz, 1H), 5.05 (s, 1H), 4.93 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3) δ: 145.2, 145.0, 141.7, 140.3, 140.0, 139.6, 139.3, 138.5, 137.1, 131.1, 130.2, 127.8, 127.6, 127.1, 127.0, 126.8, 125.6, 124.8, 123.9, 123.4, 120.2, 119.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{32}H_{19}S_3^+$, 499.0643; found, 499.0639.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4f**)*. White solid (14.6 mg, 17% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.88-7.83 (m, 2H), 7.82 (s, 2H), 7.61-7.59 (d, $J$ = 7.2 Hz, 1H), 7.56-7.53 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.51-7.49 (d, $J$ = 7.6 Hz, 2H), 7.47-7.42 (m, 2H), 7.37-7.34 (m, 3H), 7.31-7.29 (m, 2H), 7.10-7.08 (m, 2H), 6.74-6.73 (d, $J$ = 5.2 Hz, 1H), 5.05 (s, 1H), 4.90 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 145.4, 145.2, 143.6, 142.3, 141.9, 141.5, 14.9, 139.3, 139.0, 138.5, 138.2, 137.0, 135.6, 132.8, 128.1, 127.6, 127.5, 127.0, 126.9, 126.8, 126.2, 126.1, 125.5, 125.2, 125.0, 123.5, 120.2, 119.3, 119.2, 50.0, 46.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{34}H_{21}S_2^+$, 493.1079; found, 493.1076.

***[2,1-a]-IF**-thiophene-fusedcyclic compound (**4g**)*. Red solid (21.7 mg, 28% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.85-7.81 (m, 4H), 7.60-7.58 (d, $J$ = 7.6 Hz, 2H), 7.45-7.42 (t, $J$ = 7.2 Hz, 2H), 7.37-7.34 (t, $J$ = 7.6 Hz, 2H), 6.44 (s, 2H), 4.94 (s, 2H), 2.42 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 145.5, 141.7, 140.9, 140.5, 139.2, 138.8, 129.3, 127.4, 126.8, 125.6, 125.0, 120.1, 119.2, 47.2, 15.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{21}S_2^+$, 445.1079; found, 445.1074.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4h**)*. Brown solid (20.0 mg, 20% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.86-7.83 (m, 4H), 7.58-7.56 (d, $J$ = 7.6 Hz, 2H), 7.48-7.44 (t, $J$ = 7.6 Hz, 2H), 7.40-7.37 (t, $J$ = 6.8 Hz, 2H), 6.76 (s, 2H), 4.93 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 144.7, 142.1, 140.6, 139.9, 139.4, 132.4, 131.2, 127.9, 127.2, 124.5, 120.5, 119.6, 112.6. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{14}Br_2S_2^+$, 571.8904; found, 571.8912.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4i**)*. Yellow solid (29.8 mg, 30% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.90-7.86 (m, 4H), 7.65-7.64 (d, $J$ = 7.6 Hz, 2H), 7.54-7.53 (d, $J$ = 7.2 Hz, 4H), 7.49-7.45 (t, $J$ = 7.2 Hz, 2H), 7.40-7.38 (d, $J$ = 6.4 Hz, 2H), 7.36-7.32 (t, $J$ = 7.2 Hz, 4H), 7.28-7.25 (t, $J$ = 7.6 Hz, 2H), 7.03 (s, 2H), 5.06 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 145.5, 145.2, 141.7, 140.2, 139.3, 134.1, 130.7, 128.9, 127.8, 127.6, 127.1, 125.8, 125.7, 123.0, 120.2, 119.5, 47.3. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{40}H_{24}S_2^+$, 568.1319; found, 568.1329.

***[2,1-a]-IF**-thiophene-fused cyclic compound (**4j**)*. Yellow solid (34.5 mg, 29% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.89-7.86 (m, 4H), 7.65-7.63 (d, $J$ = 7.6 Hz, 2H), 7.50-7.46 (m, 2H), 7.45-7.42 (d, $J$ = 8 Hz, 4H), 7.39-7.35 (t, $J$ = 8.4 Hz, 2H), 7.16-7.14 (d, $J$ = 8.4 Hz, 4H), 6.98 (s, 2H), 5.05 (s, 2H), 2.61-2.57 (t, $J$ = 7.6 Hz, 4H), 1.63-1.59 (t, $J$ = 7.6 Hz, 4H), 1.38-1.32(m, 4H), 0.94-0.90 (t, $J$ = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 145.6, 145.3, 142.8, 141.7, 140.3, 139.3, 131.6, 130.3, 129.0, 127.6, 127.0, 125.7, 122.5, 120.2, 119.4, 47.3, 35.4, 33.5, 22.4, 14.0. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{48}H_{40}S_2^+$, 680.2571; found, 680.2565.

*11,12-Di([2,2'-bithiophen]-5-yl)-11,12-dihydroindeno[2,1-a]fluorene (**5a**)*. Brown solid (18.9 mg, 26% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 2H), 7.83-7.81 (d, $J$ = 8.4 Hz, 2H), 7.40-7.37 (t, $J$ = 6.4 Hz, 4H), 7.27-7.24 (t, $J$ = 7.2 Hz, 2H), 7.15-7.13 (d, $J$ = 5.2 Hz, 2H), 7.05-7.04 (d, $J$ = 3.6 Hz, 2H), 7.01-7.00 (d, $J$ = 3.6 Hz, 2H), 6.94-6.92 (dd, $J$ = 5.2, 3.6 Hz, 2H), 6.81-6.80 (d, $J$ = 3.6 Hz, 2H), 5.13 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 147.2, 142.7, 142.1, 140.8, 140.0, 137.6, 136.5, 127.7, 127.5, 126.9, 125.1, 124.0, 123.3, 123.0, 120.1, 48.0. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{36}H_{22}S_4^+$, 582.0609; found, 582.0604.

*11,12-Di(thiophen-2-yl)-11,12-dihydroindeno[2,1-a]fluorene (**5b**)*. Yellow solid (17.5 mg, 30% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 2H), 7.82-7.80 (d, $J$ = 7.2 Hz, 2H), 7.38-7.34 (t, $J$ = 7.2 Hz, 2H), 7.33-7.32 (d, $J$ = 7.6 Hz, 2H), 7.25-7.21 (t, $J$ = 7.2 Hz, 2H), 7.15-7.14 (d, $J$ = 5.2 Hz, 2H), 6.95-6.93 (dd, $J$ = 5.2, 3.6 Hz, 2H), 6.78-6.77 (d, $J$ = 3.2 Hz, 2H), 5.06 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.6, 165.5, 147.5, 143.0, 142.8, 140.8, 140.0, 129.8, 129.7, 129.6, 127.5, 127.3, 126.5, 125.9, 125.0, 124.4, 120.0, 119.9, 63.0, 47.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{19}S_2^+$, 419.0923; found, 419.0919.

*10,12-di([2,2'-bithiophen]-5-yl)-10,12-dihydroindeno[2,1-b]fluorene(**5c**)*. Yellow solid (15.3 mg, 21% yield); Due to the presence of isomers and difficulty in separation, there is a bias in the NMR spectrum. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 8.19-8.17 (m, 1H), 7.91-7.89 (d, $J$ = 7.6 Hz, 3H), 7.58 (s, 1H), 7.50-7.48 (m, 3H), 7.46-7.44 (m, 3H), 7.35-7.31 (d, $J$ = 7.2 Hz, 3H), 7.15-7.14 (d, $J$ = 4.8 Hz, 2H), 7.05-7.04 (d, $J$ = 3.6 Hz, 2H), 7.03-7.02 (d, $J$ = 3.6 Hz, 2H), 6.97-6.96 (d, $J$ = 3.6 Hz, 2H), 6.95-6.93 (m, 2H), 5.31 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 146.9, 146.5, 143.5, 140.6, 140.4, 137.5, 136.4, 127.9, 127.7, 127.5, 126.4, 126.2, 125.4, 124.1, 123.4, 123.3, 122.3, 120.1, 111.4, 49.2.

*10,12-di([2,2':5',2''-terthiophen]-5-yl)-10,12-dihydroindeno-[2,1-b]fluorene(**5d**)*. Yellow solid (20.0 mg, 23% yield); Due to the presence of isomers and difficulty in separation, there is a bias in the NMR spectrum. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.91-7.89 (d, $J$ = 7.6 Hz, 3H), 7.58 (s, 1H), 7.50-7.48 (m, 3H), 7.46-7.44 (m, 3H), 7.36-7.32 (d, $J$ = 7.2 Hz, 4H), 7.20-7.18 (d, $J$ = 4.8 Hz, 2H), 7.13-7.12 (d, $J$ = 3.6 Hz, 2H), 7.04-7.03 (d, $J$ = 3.6 Hz, 2H), 7.01-7.00 (d, $J$ = 4.0 Hz, 2H), 6.98-6.97 (m, 2H), 6.92-6.91 (d, $J$ = 3.6 Hz, 2H), 5.31 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 146.9, 146.5, 143.7, 140.7, 140.4, 137.2, 136.3, 136.1, 135.9, 128.0, 127.9, 127.6, 127.5, 126.5, 125.4, 124.4, 124.3, 123.9, 123.6, 123.3, 122.3, 120.1, 49.2. HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{44}H_{26}S_6^+$, 746.0359; found,746.0365.

## ■ ASSOCIATED CONTENT

### Supporting Information

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CCDC 1887120 and 1887122 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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