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Cyclo-oligomerization of 6,12-Diethynyl Indeno[1,2-*b*]fluorenes via Diradical Intermediates

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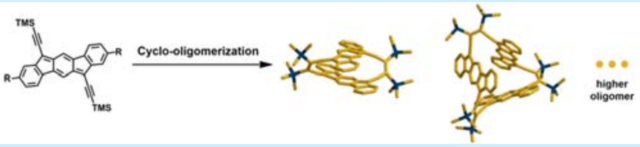
S Supporting Information

ABSTRACT: Indeno[1,2-*b*]fluorene derivatives with trimethylsilylethynyl substituents at the 6- and 12-positions were found to undergo cyclo-dimerization, cyclo-trimerization, and higher oligomerizations at room temperature. The cyclic dimer features a novel double-decker motif, composed of two face-to-face stacked bis(propadienylide)dihydroindeno[1,2-*b*]fluorenes with a short centroid-to-centroid distance of 3.50 Å. The existence of a cyclic trimer and higher oligomers was confirmed by mass spectroscopy and gel permeation chromatography. The results clearly demonstrate the diradical feature of the indeno[1,2-*b*]fluorene moiety.

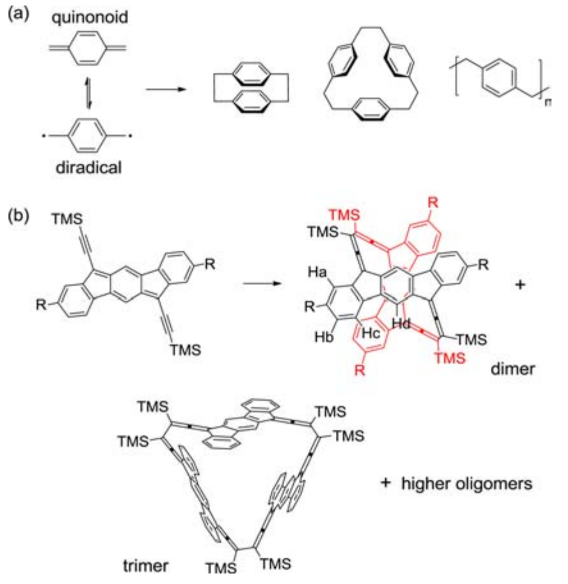


Organic molecules of diradical features are of great importance due to their unique chemical reactivity and physical properties.[1] *para*-Quinodimethane (*p*-QDM) and related structures with interconvertible quinoidal and diradical (benzenoid) forms thus attract much research interest. According to *Clar's aromatic sextet* rule,[2] the benzenoid state is stabilized by an aromatic sextet that is absent in the quinoidal form, but the diradical nature[3] renders the molecule highly reactive and it readily undergoes cyclo-oligomerization[4] and polymerization[5] (Scheme 1a). Similar reactions are also observed with thiophene-based and imidazole-functionalized *p*-QDMs.[6,7] Installing steric-hindering substituents is a classical tactic to achieve isolatable *p*-QDM derivatives, but this method typically hampers the reactivity of the molecule.[8] Designing largely extended π-conjugated systems with more recoverable sextets effectively lowers the energy of the diradical form relative to the quinoidal state. Various polycyclic molecules of this kind showing a diradical property in the ground electronic state have been developed, including Tschitschibabin's hydrocarbon,[9] biphenalenes,[10] zethrenes,[11] oligo-*p*-quinodimethane, etc.[12,13]

Indeno[1,2-*b*]fluorene (IF) is a polycyclic hydrocarbon incorporating a *p*-QDM unit. The bare structure of IF has been elusive from isolation and characterization due to the limited stability.[14] Recently, IF derivatives bearing triisopropylsilylethynyl (TIPSE) or aryl groups at the 6- and 12-positions have been prepared.[15,16] The requirement for such steric hindering substituents at specific positions implies the diradical feature of the IF framework.[17] Yet, most previous study results pointed to the major closed-shell ground-state electronic characteristics. Direct evidence for the diradical property of indeno[1,2-*b*]fluorene is hardly available.

In comparison, the diradical behaviors of a number of related indenofluorene structures, such as those of [2,1-*a*] and [2,1-*b*] configurations, are more clearly characterized.[18] Now in this contribution, we demonstrate the diradical properties of indeno[1,2-*b*]fluorene by examining the chemical reactivity of its 6,12-bis(trimethylsilylethynyl)-substituted derivatives (Figure 1), which are shown to be capable of cyclo-dimerization as well as higher oligomer formation via diradical intermediates at room temperature (Scheme 1b).

Scheme 1. Reactions of Studied 6,12-Diethynyl Indeno[1,2-*b*]fluorene Derivatives (R Groups Are Omitted in Trimer for Clarity) In Analogy to *p*-QDM



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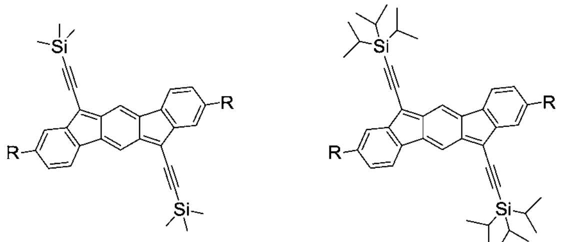


1a: R = H
1b: R = *t*-Bu
1c: R = OCH$_3$

2a: R = H (reported in ref 15b)
2b: R = *t*-Bu

Figure 1. Structures of studied indeno[1,2-*b*]fluorene derivatives.

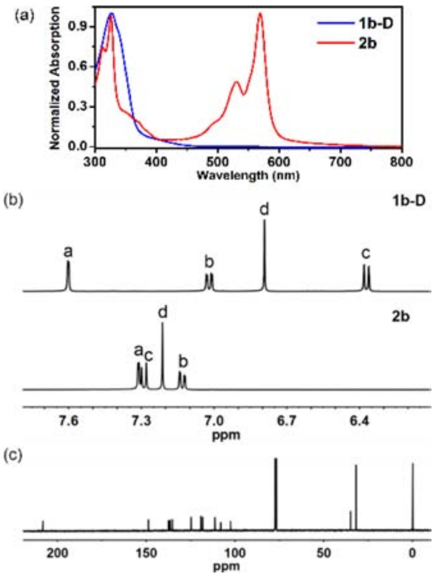


Figure 2. (a) Normalized absorption spectra of **1b-D** (blue) and **2b** (red) in CHCl$_3$ (10^{-5} M); (b) ^{1}H NMR spectra of **1b-D** and **2b** in CD$_2$Cl$_2$ (resonance assignments are shown in Scheme 1b); (c) ^{13}C NMR spectrum of **1b-D** in CDCl$_3$.

Unlike the more hindered TIPSE and aryl groups, the less bulky trimethylsilylethynyl (TMSE) substituents are found to allow the IF moieties to retain proper diradical reactivity. Cyclic dimers of such IFs are formed, with a single-crystal structure obtained for one of the dimers. The existence of cyclic trimers and cyclic tetramers is confirmed by ESI-MS, and gel-permeation chromatography reveals the appearance of even higher oligomers. For the first time, experimental evidence is acquired proving the diradical contribution to the indeno[1,2-*b*]fluorene unit. The study also shows that, in order to realize the oligomerization of such IF derivatives, the size of the side groups is crucial, for balancing the structural stability and reactivity.

First, two TIPSE-substituted analogues **2a**[15b] and **2b** were synthesized for a comparison study. Consistent with previous reports, both these TIPSE-IFs were obtained as violet crystalline substances showing adequate stability under ambient conditions. Then, similar procedures were applied to prepare TMSE-IF **1a**. A characteristic violet color indicative of IF formation appeared after the dihydroxy precursor in solution was treated with SnCl$_2$. However, when we tried to isolate the product, the violet solution turned dark during rotary evaporation, affording unidentifiable materials. Thin-layer chromatography (TLC) also confirmed the initial formation and then quick decomposition of a violet-colored product. These results indicated that **1a** was unstable under ambient conditions. Nonetheless, if we kept the original violet solution standing under a N$_2$ atmosphere at room temperature for 3 days, the violet color gradually became less intense over time. Meanwhile, a new spot with a smaller R_f was detected by TLC as the initial violet spot slowly diminished. This newly formed molecule (**1a-D**) was isolated as yellow powder upon column chromatography. Very similar phenomena were observed when the same procedures were applied to substrates that could afford **1b**, and a yellow compound (**1b-D**) was collected. Both **1a-D** and **1b-D** exhibited adequate stability under ambient conditions.

In contrast to **2a**[15b] and **2b** showing two absorption bands in the UV and visible range, **1a-D** and **1b-D** only exhibited a single absorption peak around 330 nm (Figures 2a and S1a). Furthermore, great disparity was displayed by ^{1}H NMR spectra (Figure 2b). With all four aromatic proton signals of **2b** appearing in a narrow chemical shift range of 7.04 to 7.23 ppm, the four aromatic resonances of **1b-D** were distributed over a wider range of 6.4 to 7.6 ppm. Particularly, two signals with chemical shifts of 6.77 and 6.36 ppm were quite unusual for such aromatic molecules without strongly electron-donating substituents. In spite of the different chemical shifts, similar aromatic resonance splitting patterns shown by **1b-D** and **2b** suggested that the two molecules possessed the same substitution patterns around their IF frameworks. The ^{13}C NMR spectra provided more insightful clues to the molecular structure. A particularly downfield signal at 208 ppm was detected with both **1a-D** and **1b-D** (Figure 2c). Such a large chemical shift only originates from a carbonyl carbon or the central carbon of an allene unit.

We then endeavored to acquire single crystals. Although all efforts failed with **1b-D**, a suitable single crystal was obtained with **1a-D**, which upon X-ray diffraction analyses revealed a cyclic dimer structure (Figure 3). Two benzenoid IF units were joined via the outer carbons of allene substituents, and an arched double-decker motif with a $\pi-\pi$ distance of 3.50 Å was presented. Pronounced bond length differences were displayed by **1a-D** and **2a**. The C−C triple bonds (1.206(6) Å[19]) in **2a** were extended to 1.301(4) Å in **1a-D**, whereas the bonds connecting the acetylene carbon to the IF skeleton were

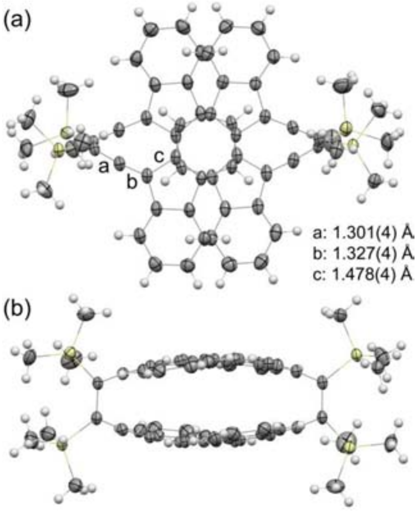


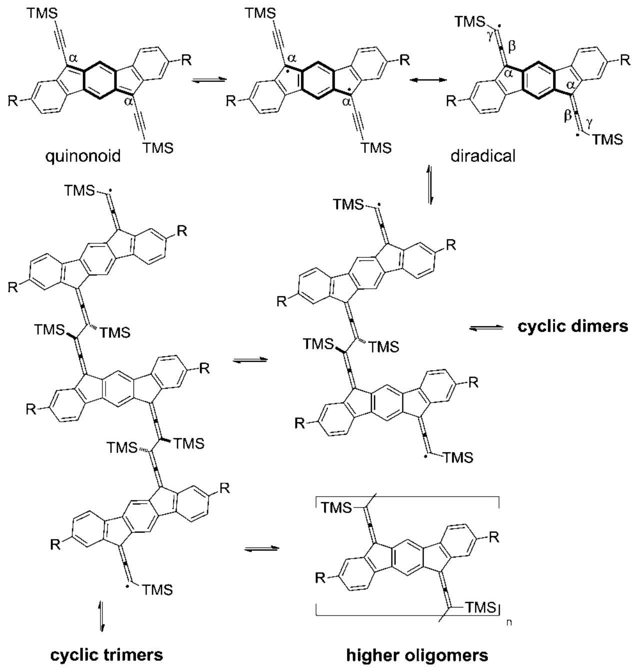
Figure 3. ORTEP drawings of top (a) and side views (b) of **1a-D** at 50% probability.

shortened from 1.411(6) Å in **2a** to 1.327(4) Å in **1a-D**. These bond length changes all supported the presence of allene groups in **1a-D**. Corresponding bond length changes were also observed with the IF moiety, in agreement to a quinoidal structure in **2a** switched to a benzenoid form in **1a-D** (Table S1). The crystallography data also confirmed that **1a-D** possessed a chiral structure, which appeared as enantiomer pairs in the crystal lattice (Figure S2).

The clearly correlated ^{1}H and ^{13}C NMR data of **1b-D** and **1a-D** (Figure S1, b–c) confirmed that a similar cyclic dimer structure was also adopted by **1b-D**. In the dimer scaffold, H_c and H_d (Scheme 1) were positioned right above the π-framework of the other IF unit in the same molecule. The significant ring-current shielding effect reasonably explained the particularly upfield chemical shifts (Figure 2b).

Two different reaction mechanisms were considered for the cyclo-dimerization of **1a** and **1b**, i.e., the concerted pericyclic cyclo-addition vs radical-mediated stepwise cyclization. For cyclo-addition involving 2n π-electron pairs, dimerization of **1a**/**1b** via the pericyclic process should only be allowed under photochemical conditions. We however observed that **1b-D** was generated in very similar yield when the reaction was carried out in the dark, which strongly supported the radical mechanism (Scheme 2). Conducting reactions in the presence of TEMPO demonstrated the involvement of radical intermediates as described in the Supporting Information (S15–S16, Figure S6).

Scheme 2. Quinoidal and Diradical Structures of TMSE-IF and the Cyclic Dimer, Trimer, and Higher Oligomer Formation Pathways



In benzenoid **1a**/**b**, the diradical can be delocalized to both the α- and γ-positions (Scheme 2). With the latter, allene functionality emerges. The cyclo-dimerization actually took place by joining the γ-positions rather than α-positions likely for two reasons. One is that the ring strain of a cyclic dimer formed by coupling the α positions would be much greater than that of **1a**/**b-D**. Additionally, joining the γ-positions produces larger π-conjugated systems with two additional C═C double bonds connected to each benzenoid IF.

These cyclic dimers were found to be photoresponsive molecules. When **1b-D** in $CHCl_3$ was exposed to UV irradiation ($\lambda_{max} \approx 365$ nm), the yellow solution quickly turned violet in a few minutes. The absorption spectra collected at different time intervals displayed a steady increase of a peak around 570 nm, with the stationary state reached in ca. 20 min. The resultant spectrum was nearly identical to that of **2b** (Figure S3), proving that **1b** was generated from dissociation of **1b-D**. A similar phenomenon of photoinduced dissociation was also observed with **1a-D** (Figure S4). Such experimental phenomena also confirmed that the (retro-) cyclo-addition of pertinent IF derivatives was a photochemically allowed process. Therefore, the above cyclo-dimerization of **1a** and **1b** in the absence of photoirradiation should be radical-mediated reactions.

The influence of side group structures on the cyclo-dimerization was then investigated. When the same reaction conditions used for preparing **1b-D** were applied to **2b**, no cyclic dimer or higher oligomeric product was observed, with **2b** recovered. We also attempted the cyclo-dimerization with desilylated **2b**. Upon adding TBAF to a solution of **2b** under a nitrogen atmosphere, the violet color quickly disappeared and some unidentifiable dark materials were generated. These results indicated that careful tuning of the steric hindrance was crucial for accomplishing the cyclo-dimerization. The medium size of the TMS group conferred a suitable steric effect for attaining a proper balance between the chemo-stability and reactivity of diradical IFs. The larger TIPS unit completely prohibited the intermolecular reaction, while the desilylated **2b** lacking any bulky side group was unstable even under a N_2 atmosphere.

If the dimers were formed following the diradical pathway, it should also be possible for higher oligomers to occur by joining additional monomer units to the open-chain dimer before the ring was closed (Scheme 2). Hence, we went back and checked whether higher oligomers were present in the reaction mixtures. Gel-permeation chromatography (GPC) analysis of the reaction mixtures producing **1b-D** indeed revealed the presence of higher molecular-weight (MW) species than dimers (Figure S5). Following the major peak corresponding to the size of dimers, two additional peaks emerged in the GPC trace, with average MWs of ca. 3000 and >9000, respectively. Unfortunately, these polydispersed higher oligomers could not be separated into monodisperse components.

In order to elucidate whether the higher oligomers were also of cyclic structures, we employed the high-resolution (HR) ESI MS. Unfortunately, both product mixtures from **1a** and **1b** gave insufficient signal intensity of the oligomers, presumably due to the low ionization percentage. Subsequently, we further prepared another TMSE-IF derivative, **1c**, which incorporated methoxy groups, making the molecule more susceptible to ionization through the ESI process. HR MS was then successfully obtained, clearly revealing the molecular ions of the cyclic dimer, cyclic trimer, and cyclic tetramer of **1c** (Figure S7).

In summary, we observed the cyclo-dimerization, cyclo-trimerization, and higher oligomerization processes of a series of TMSE-substituted indeno[1,2-*b*]fluorene molecules at room temperature. Structure characterizations including single crystal analysis unambiguously revealed that the cyclic dimer featured a double-decker macrocycle formed by two benzenoid IF units substituted by allene groups at the 6- and 12-positions. The appearance of higher-oligomer products in the reaction mixture further proved that the oligomerization proceeded via diradical intermediates. These results provide clear evidence supporting the diradical contribution to the indeno[1,2-*b*]fluorene structure, despite the major close-shell feature of the ground electronic state.

Furthermore, the cyclic dimers are found to readily dissociate into IF monomeric units upon photoirradiation. This property offers a unique opportunity for developing relevant indeno[1,2-*b*]fluorene derivatives into functional materials and feasible synthons. Basically, the stable dimers may serve as latent and storable precursors, which can in situ generate the reactive/functional IF monomers upon UV irradiation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03000.

Synthetic procedures, absorption spectra, NMR spectra, single crystal results of **1a-D**, mass spectra, gel-permeation chromatography trace (PDF)

Crystallographic data for **1a-D** (CIF)

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Notes

The authors declare no competing financial interest.

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