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# Revisiting indeno[2,1-c]fluorene synthesis while exploring the fully conjugated *s*-indaceno[2,1-*c*:6,5-*c*']difluorene

Received 00th January 20xx, Accepted 00th January 20xx

Himanshu Sharma,<sup>a</sup> Priyank Kumar Sharma<sup>a</sup> and Soumyajit Das\*<sup>a</sup>

DOI: 10.1039/x0xx00000x

Described herein an alternative synthetic approach for conjugated indeno[2,1-c]fluorene, including the experimental and theoretical s-indaceno[2,1-c:6,5investigations of tetraradicaloid а c'ldifluorene that belongs to the rarely explored indacenodifluorene family containing 4n+2 monocyclic conjugated  $\pi$ -electrons. Expedient synthesis, broad absorption reaching 1150 nm, and small HOMO-LUMO energy gap make [2,1-c:6,5-c']s-IDF a promising candidate for optoelectronic applications.

Non-alternant fully conjugated indenofluorene (IF) isomers, namely indeno[1,2-b]fluorene,1 indeno[2,1-a]fluorene,2 indeno[2,1-b]fluorene,3 indeno[2,1-c]fluorene,4 and indeno[1,2-a]fluorene<sup>5</sup> have gained remarkable attention because of the amphoteric redox behaviour, open shell character, and unique optical properties.<sup>6</sup> There were efforts synthesize core-extended IFs,7 significant to heteroatom-modified IFs,8 and phenyl-fused IF derivatives too.9

Now that all the IF isomers were successfully studied, we envisaged exploring higher order fully fused π-extended IF oligomers as the non-alternant conjugated polycyclic hydrocarbon (CPH) analogues of oligoacenes. A simple approach could be the cyclopentafluorene fusion at the outer benzene ring of IF that may generate newer arrays of CPHs containing formally  $34\pi$ -electrons, called indacenodifluorene (IDF) isomers. Conjugated IDFs are made of 9 alternatingly fused 6-5-6-5-6-5-6 rings which were seldom investigated. To our knowledge, the only conjugated IDF that exists in literature was based on the cyclopenta[b]fluorene fused [1,2b]IF 1, s-indaceno[1,2-b:5,6-b']difluorene (Fig. 1a).<sup>10</sup> IDF isomers may be further categorized into s-indacenodifluorenes (s-IDFs) and as-indacenodifluorenes (as-IDFs) (Fig. S1 in ESI<sup>+</sup>). Tetraradicaloid 1 was the first isomer of the s-IDF series, and no as-IDF isomer was synthesized till date likely due to the

unavailability of proper synthetic strategies or suitable intermediates. Notably, an *as*-IDF isomer (*as*-indaceno[2,1*c*:7,8-*c*']difluorene) was mentioned in Tobe's personal account but its synthesis was undisclosed.<sup>6a</sup> Interestingly, IDF isomers may be regarded as the non-alternant isoelectronic (not isomeric) CPH analogues for the alternant oligoacenes like synthetically challenging octacene,<sup>11</sup> as well as [8]phenacene;<sup>12</sup> considering the bonding picture of the outer conjugated circuit as [34]annulene.



**Fig. 1** (a) Wu's *s*-indaceno[1,2-*b*:5,6-*b*']difluorene **1**. (b) Müllen's [2,1-*a*]IF-based polymer **2**. (c) Target scaffolds: 5,8-dimesitylindeno[2,1-*c*]fluorene **3**, and 5,8,14,17-tetramesityl-s-indaceno[2,1-*c*:6,5-*c*']difluorene **4**. (d) Plausible canonical structures for parent **4**.

The  $\pi$ -extension concept through non-benzenoid repeating units was first proposed by Müllen in the form of  $\pi$ -extended ladder polymer **2** (Fig. 1b) which may be regarded as the repeating units of cyclopenta[*a*]fluorene fused [2,1-*a*]IF.<sup>13</sup> Polymer **2**, however, suffered incomplete unsaturation in the

<sup>&</sup>lt;sup>a.</sup> Department of Chemistry, Indian Institute of Technology Ropar, Nangal Road, Rupnagar, Punjab-140001, India. E-mail: <u>chmsdas@iitrpr.ac.in</u>

<sup>\*</sup>Electronic Supplementary Information (ESI) available: Detailed syntheses and characterization data for the new compounds and **3**; X-ray crystallographic data for **4**; Details of DFT calculations; and NMR spectra. See DOI: 10.1039/x0xx0000x

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hydrocarbon backbone and slowly decomposed upon exposure to air/oxygen. Further theoretical studies by Kertesz on similar structural isomers of IF-based  $\pi$ -extended ladder polymers revealed their inherently low band gap, and more importantly the prospects of having high spin ground states.<sup>14</sup> A recent theoretical revisit by Nakano *et al.* on the IF-based  $\pi$ extended oligomers demonstrated their ability to show small multiple diradical characters that may result in potentially high second-hyperpolarizability for non-linear optical materials compared to the polyacenes.<sup>15</sup> This novel class of fully fused CPHs, realized by the condensation of 6- and 5-membered rings in alternating fashion, thus deserve to be investigated experimentally since they may become potential low band gap (perhaps open shell too) materials for optoelectronic applications.

We developed a new synthetic approach for [2,1-c]IF derivative 3, and designed a cyclopenta[c]fluorene fused [2,1c]IF 4, s-indaceno[2,1-c:6,5-c']difluorene, as the second unknown constitutional isomer of the barely explored s-IDF series (Fig. 1c).<sup>4,16</sup> Being fragment of fullerene-C<sub>60</sub>, [2,1-c]IF was welcomed as a new electron-accepting scaffold that showed promise in bulk-heterojunction devices.<sup>17</sup> In addition, its potential to show lower HOMO-LUMO energy gap compared to the analogous [1,2-b]IF, and kinked structure the formation favouring of tetracyclopenta[def,jkl,pqr,vwx]tetraphenylene (TCPTP) make [2,1-c]IF an unique IF isomer.<sup>4,18</sup> The usual synthetic route to [2,1-c]IF scaffold was comprised of a nucleophilic addition of aryl groups to the benzo-fused diketone precursor in pre-final step,<sup>16,4</sup> followed by SnCl<sub>2</sub>-mediated reduction of the hydroxy groups at the final step.4,7e,19,20 This approach has certain drawbacks such as the final reductive dehydroxylation with mesityl substituent failed at times,<sup>7e</sup> and the synthetic route to the benzo-fused diketone precursor required usage of harsh reaction conditions including high temperatures ranging from 220 to 280 °C.16b



Herein, a mild and convenient multistep approach to synthesize the known [2,1-c]IF **3**, 5,8-dimesitylindeno[2,1-c]fluorene, from cheap and commercially available starting materials was discussed (Scheme 1). The same approach was further extended to construct the fully conjugated *s*-IDF isomer **4**, 5,8,14,17-tetramesityl-*s*-indaceno[2,1-c:6,5-c']difluorene, which can be regarded as a potential tetraradicaloid due to the presence of two pro-aromatic *p*-quinodimethane (*p*QDM) subunits that may recover additional

(DFT) calculations at the B3LYP/6-31G(d,p) level of theory.<sup>21</sup> Selective Suzuki reaction between the 1-bromo-2iodobenzene 5 and (2-formylphenyl)boronic acid 6 afforded 7 in 72% yield (Scheme 1). Treatment of 7 with 2mesitylmagnesium bromide 8 at ambient temperature afforded 9 which was subsequently converted to 10 using BF<sub>3</sub>·Et<sub>2</sub>O mediated Friedel-Crafts alkylation approach. Pd<sup>II</sup>catalyzed Suzuki reaction of racemic 10 and 6 afforded 11 in 84% yield, which was treated with 8 to give crude alcohol 12. Treatment of crude 12 with BF<sub>3</sub>·Et<sub>2</sub>O gave the dihydro precursor 13 in 56% yield (in two steps). Under inert atmosphere, a near quantitative formation of 3 in 2 h via oxidative dehydrogenation of 13 using 1.3 equivalents of 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was attained at 90 °C in dry toluene. Compound **3** was unambiguously by nuclear magnetic resonance confirmed (NMR) spectroscopy, high resolution mass spectrometry (HRMS), and melting point analysis which were consistent with the literature report (Fig. S10 and Fig. S11 in ESI<sup>+</sup>).<sup>4</sup>

experimentally, with the support of density functional theory



Scheme 2 Synthesis of S-shaped π-conjugated system 4.

Racemic 10 was conveniently converted to the desired pinacolboronic acid ester 15 in 77% yield by the standard Pd<sup>II</sup>catalyzed Miyaura borylation reaction (Scheme 2). Pd<sup>0</sup>catalyzed Suzuki reaction between the pre-synthesized 16,22 and 2.5 equivalents of 15 afforded 17 in 76% yield. Compound 17 was subsequently treated with an excess of 8 to afford the dicarbinol 18. The addition of BF<sub>3</sub>·Et<sub>2</sub>O to the solution of crude 18 in dry dichloromethane (DCM) afforded the ring-fused product 19 as mixture of stereoisomers, and confirmed by HRMS analysis. Unsurprisingly, it was difficult to interpret the structure from its complicated <sup>1</sup>H NMR spectrum, and hence 19 was treated with 2.1 equivalents of DDQ in dry toluene at 80 °C for 45 mins to quantitatively afford a brown solid with desired mass, as analysed by HRMS after column chromatographic purification on silica gel in air. The structure of 4 was confirmed by <sup>1</sup>H NMR, 2D-COSY, and 2D-NOESY spectroscopic analysis in benzene-d<sub>6</sub> (see ESI<sup>+</sup>). <sup>1</sup>H-<sup>1</sup>H NOESY correlation was found to be useful in assigning the two different kinds of mesityl substituents attached to the exomethylene carbons of pQDM subunit. The structure of 4 was further unequivocally confirmed by the X-ray crystallographic analysis (vide infra). The region-selectivity of the BF<sub>3</sub>·Et<sub>2</sub>O mediated Friedel-Crafts ring-closure alkylation could be attributed to the more thermodynamically favourable

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formation of two 5-membered rings over the 7-membered rings. Notably, the oxidative dehydrogenation of **19** to **4** took lesser time and temperature to complete, compared to that of the **13** to **3** which was formally antiaromatic.



**Fig. 2** (a) X-ray crystallographic structure of **4** with the ellipsoids drawn at 30% probability level, and the hydrogens are omitted for clarity. (b) Side view of crystal structure **4** with hydrogens shown in pink colour. (c) Experimental bond lengths (Å), calculated NICS(1)zz (purple) and HOMA (green) values for each ring in **4**. (d) Packing diagram for **4**.

Single crystals of 4, suitable for X-ray crystallographic analysis, were successfully grown by slow evaporation from chloroform/tetrahydrofuran solvent mixture for two weeks at ambient temperature (Fig. 2a).23 The molecule has a rigid and essentially planar core structure with the terminal benzene rings deviated by 11.9° due to the steric congestion at the cove-like region, as measured from the average planes between the central (E) and terminal (A) 6-membered rings (Fig. 2b). The subtle twist, and almost orthogonally deviated mesityl groups from the conjugated backbone prevent dye aggregation; and thus 4 was found to be soluble in common organic solvents like chloroform, DCM, tetrahydrofuran, toluene etc. at ambient temperature. The closest intermolecular C-C contact was found to be 3.454 Å for a symmetric herringbone arrangement in 4, formed through the intermolecular [C-H... $\pi$ ] interactions (2.831/2.785 Å) between the methyl hydrogens of one molecule and the  $\pi$ -backbone of another molecule (Fig. 2d). The bond length analysis for the pQDM at the as-indacene subunit (indicated in blue, Fig. 2c) revealed the  $C(_{sp}^2)=C(_{sp}^2)$  bond b as 1.351 Å whereas the exomethylene double bonds a and c are 1.373 Å and 1.372 Å respectively, which are similar to what was observed for closed-shell [2,1-c]IF,4 and are shorter than the pQDM structure of the s-indacene subunit in 1.10 The distribution of bond lengths for ring A (avg 1.391 Å) and ring E (avg 1.398 Å) in 4 was found to be homogeneous that additionally suggested localized aromaticity at the terminal and central 6-membered rings. The large bond length alternation indicative of quinoidal resonance in as-indacene subunit, in addition to the retention of benzene aromaticity in the central (E, Fig. 2c) and terminal (A) 6-membered rings were clearly implying a singlet ground state for **4** in the form of canonical structure **4b** (Fig. 1d).

DFT calculations, by optimizing the crystal structure, further supported a singlet ground state for **4** with the triplet

state being 6.05 kcal/mol higher in energy (Table S1 in ESIT) An NMR line broadening could consequently be observed at 363-400 K, indicating the population of the triplet state (Fig. S23 in ESI<sup>+</sup>).<sup>18</sup> The nucleus independent chemical shift [NICS(1)zz] calculations (at CAM-B3LYP/6-31G(d,p)) revealed strong to moderate quinoidal nature of the rings B (15.86), D (16.25), and C (7.85); whereas a strong to weak aromatic character of the terminal and central 6-membered rings A (-17.35) and E (-8.97) were found, respectively (Fig. 2c).<sup>10,21b</sup> The harmonic oscillator model of aromaticity (HOMA) values were also found to be in accordance with the NICS(1)zz values (Table S6 in ESI<sup>+</sup>). All the experimental and theoretical studies were eventually supporting the aromatic/quinoidal alternating resonance form 4b (among the five canonical structures) as the major contributor to the ground electronic state for 4 (Fig. 1d,  $\pi$ -sextets were shown in orange hexagon).



The electronic absorption spectrum of 4 in chloroform showed two major higher energy absorption bands in the UVvis region ( $\lambda_{max}$  = 401 nm,  $\varepsilon$  = 49600 M<sup>-1</sup> cm<sup>-1</sup>;  $\lambda_{max}$  = 524 nm,  $\varepsilon$ = 22850 M<sup>-1</sup> cm<sup>-1</sup>), and one broad lower energy absorption band ( $\lambda_{max}$  = 836 nm,  $\varepsilon$  = 8400 M<sup>-1</sup> cm<sup>-1</sup>) reaching 1150 nm in the near-IR region (Fig. 3a). The time dependent DFT calculations in the gas phase predicted a highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) transition at 1043.9 nm for 4 with moderate oscillator strength (f = 0.2171) which was attributable to the lower energy transition at 836 nm (Fig. S24, Fig. S26 and Table S3 in ESI<sup>+</sup>). No noticeable change in absorption profile was observed by changing solvent polarity, suggesting negligible intramolecular charge transfer character. The lower energy absorption maximum for the 4 was remarkably red shifted (~114 nm) compared to that of isomer 1 with electronwithdrawing group.<sup>10</sup> Notably, the low energy HOMO  $\rightarrow$  LUMO transition for [2,1-c]IF was allowed, whereas it was forbidden for [1,2-b]IF motif.<sup>24</sup> The  $\pi\text{-extension}$  in  $\boldsymbol{4}$  clearly shifted the lower energy absorption maximum to the longer wavelength compared to that of 603 nm for **3**,<sup>4</sup> however, it was 73 nm less than the antiaromatic cyclic congener TCPTP.<sup>18</sup> In comparison to **1**, a lower optical HOMO-LUMO energy gap  $E_g^{opt} = 1.15 \text{ eV}$ was obtained for 4 from the UV-vis-NIR absorption onset, however, the electrochemical energy gap  $E_{g}^{ec}$  = 1.37 eV was found to be the same. This observation is in line with earlier reports that [2,1-c]IF-based  $\pi$ -systems may show lower HOMO-LUMO energy gap compared to the analogous [1,2-b]IF  $\pi$ -systems.<sup>4,7e,10</sup> Unlike the [2,1-c]IF,<sup>4,7e</sup> two reversible oxidation waves were found for 4 with the half-wave potentials at  $E_{1/2}^{ox}$ = 0.17 V and 0.56 V (vs

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ferrocene/ferrocenium (Fc/Fc<sup>+</sup>)), while the electron acceptability was greatly reduced as quasi-reversible reduction waves appeared at  $E_{1/2}^{red} = -1.41$  V and -1.69 V (*vs* Fc/Fc<sup>+</sup>) (Fig. 3b) in cyclic voltammogram. The HOMO and LUMO levels were estimated as -4.89 eV and -3.52 eV from the CV, respectively, which were in line with the theoretical values (Table S5 in ESI<sup>+</sup>). The  $\pi$ -extension in **4** resulted in a reduced HOMO-LUMO energy gap, however, the LUMO level was found to be still higher than that of **3**, reflecting the strong electron-accepting nature of the formally antiaromatic **3** compared to **4** with  $34\pi$ -electrons.<sup>4</sup>

In conclusion, an expedient synthetic approach for mesitylsubstituted [2,1-c]IF 3 was reported along with the synthesis and characterization of [2,1-c:6,5-c']s-IDF 4 as the second isomer of the conjugated s-IDF series containing  $34\pi$ -electrons. All experimental and theoretical studies corroborate to an aromatic/quinoidal alternating form for 4 with the maximum number of localized Clar's  $\pi$ -sextets determining the singlet ground state with a thermally accessible triplet state owing to the narrow singlet-triplet energy gap. Compound 4 showed low oxidation potential, small HOMO-LUMO energy gap, and a low energy  $\pi \rightarrow \pi^*$  transition with the absorption spectrum reaching the NIR region. Unlike the previous synthetic route,<sup>16,4</sup> our approach to **3** does not suffer from harsh reaction conditions including potentially high temperatures, and mav allow the introduction of separate aryl/heteroaryl/ethynyl groups at the exo-methylene carbons on pQDM subunits in order to make new derivatives of 4 with improved solid state packing, and optoelectronic properties which are currently underway. Our work will also shed light on the syntheses of higher order fully fused  $\pi$ -extended IF oligomers as the non-alternant alternatives of alternant acenes with tuneable properties and ground state.

We gratefully acknowledge the financial support received from the SERB-DST India (SRG/2019/000401), and IIT Ropar (ISIRD). We thank Mr. Kamlesh Satpute for crystallographic analysis, Mr. Sarasija Das for the UV-vis-NIR measurement, and Dr. Tullimilli Y. Gopalakrishna for fruitful discussions. H.S and P.K.S thank IIT Ropar and CSIR, respectively, for research fellowships.

#### **Conflicts of interest**

There are no conflicts to declare.

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**Table of Contents Entry** 

#### View Article Online DOI: 10.1039/D0CC04418K



Ground state of tetraradicaloid *s*-indaceno[2,1-*c*:6,5-*c'*] difluorene with small HOMO-LUMO energy gap was studied alongside an alternative synthetic approach for indeno[2,1-*c*] fluorene.