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### Synthesis, Crystal Structures, and Properties of 6,12-Diaryl-Substituted Indeno[1,2-b]fluorenes

### Jun-ichi Nishida, Shingo Tsukaguchi, and Yoshiro Yamashita<sup>\*[a]</sup>

Abstract: Fused polycyclic indeno[1,2b]fluorene derivatives with aryl substituents at the 6,12-positions have been prepared as a potential antiaromatic  $20\pi$  electronic system. They showed strong absorptions in the visible region and amphoteric redox properties. The quinoid-type molecular structures were revealed by X-ray crystal-structure analysis, which indicated that the bond lengths of the quinoid unit depend on the aryl substituents. Whereas nucleus-independent chemical

Keywords: antiaromaticity · molecular electronics · polycycles · quinodimethanes · semiconductors

shift NICS(1) calculations indicate the antiaromatic nature of the s-indacene core, they have higher stability than substituted acene derivatives. The derivatives with difluorophenyl or anthryl groups were stable in solution. Vapordeposited thin films showed ambipolar carrier transportation in the field-effect transistor devices.

#### Introduction

Polycyclic fused *n*-conjugated compounds have attracted much attention on account of their unique electronic properties.<sup>[1]</sup> They show redox-active properties that can be used for organic electronics accompanied with electron transfer<sup>[2]</sup> and nanotechnology.<sup>[3]</sup> The molecular design of new  $\pi$ -conjugated systems is important to control their physical properties. Acenes such as pentacene have been extensively studied and used as p-type semiconductors.<sup>[4]</sup> However, the introduction of cyclopentadiene rings to polycyclic systems drastically changes the physical and chemical properties as seen in pentalenes<sup>[5]</sup> and s-indacenes<sup>[6-8]</sup> that possess antiaromatic 4n electronic structures. The fused polycyclic antiaromatic systems are considered to have high HOMO levels, low LUMO levels, and narrow HOMO-LUMO gaps relative to linear acene-type aromatic compounds, which are favorable for carrier transportation and absorptions in the visible region. Although antiaromatic systems are generally unstable, the introduction of fused rings increases the stability and allows them to be handled applicatively.  $\ensuremath{^{[2a,9]}}$ 

Among the polycyclic  $4n\pi$  systems, antiaromatic s-indacene with a  $12\pi$ -electron system is an important key compound.<sup>[6]</sup> The introduction of fused benzene rings increases the stablity of the s-indacene and also promotes the quinoid-type bond alternation in indeno[1,2-b] fluorene (IF) **1**.

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Chem. Eur. J. 2012, 00, 0-0

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The quinoid structure is considered to have a biradical contribution in the form of 1\* that leads to high reactivity at

the 6,12-positions,<sup>[7a]</sup> in which positions the R substituent seems to play an important role in determining the electron-

ic structures as well as the stability. Recently derivatives

with bulky triisopropylsilylethynyl (TIPSE) groups were iso-

lated by Haley et al.<sup>[8a,b]</sup> They are stable due to the steric

protection and  $\pi$  delocalization through the ethynyl groups,

and the bond lengths and the physical properties are consid-

ered to be strongly affected by the TIPSE groups. On the

other hand, the effects of aryl substituents on the electronic

properties and the molecular structures have not been inves-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201200591.

tigated, although the diphenyl derivative **2** was reported by Scherf et al.<sup>[7b]</sup> We have now prepared IF derivatives **3–5** with 2,6-difluorophenyl, 9-anthryl, and thienyl groups, and investigated the structures by X-ray analysis to reveal the bond alternation. The electronic structures were investigated with molecular orbital (MO) calculations and their carrier transportation ability was studied by applying them to fieldeffect transistors (FET).<sup>[10]</sup>

#### **Results and Discussion**

**Synthesis**: IF derivatives **3–5** were synthesized by a similar procedure to that for 2,6-difluorophenyl or TIPSE-substituted pentacene-5,12-dione derivatives **7**, which we have re-



ported.<sup>[11]</sup> Nucleophilic addition of aryl lithium reagents to indenofluorenedione  $\mathbf{8}^{[12]}$  followed by dehydroxylation with tin(II) dichloride gave the target compounds as shown in Scheme 1. Except for thienyl derivative **5**, IF derivatives



Scheme 1. Preparation of IF derivatives **2–5**: a) ArLi (2 equiv) in THF, b)  $SnCl_2$  in HCl.

could be finally purified by sublimation, for which the yields after sublimation are shown. Thienyl derivative **5** was purified by silica gel column chromatography and gel-permeation chromatography (GPC; eluent: chloroform). Except for anthracene derivative **4**, which showed poor solubility in organic solvents, NMR spectra could be measured in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectra of **4** could be measured in deuterated *o*-dichlorobenzene at 90 °C.

**Optical properties**: IF derivatives 2–5 with aryl substituents exhibited intense absorptions in the visible region as depicted in Figure 1a. The absorption maxima and molar extinction coefficients in dichloromethane are summarized in Table 1. The absorption maximum of phenyl derivative 2 appears at  $\lambda = 542$  nm with a large molar extinction coefficient. The spectrum is similar to that of the substituted pentacenedione derivative **7a** with a fused quinoid system (Fig-



Figure 1. UV/Vis spectra of a) IF derivatives **2–5** and b) 2,6-difluorophenyl-substituted IF **3** and pentacenedione **7a**.

Table 1. UV-visible spectral data of 2-5 and 7a.<sup>[a]</sup>

	$\lambda_{\rm abs} [{\rm nm}] (\log \varepsilon)$	$\lambda_{edge} \ [eV]$
2	294, 323, 542 (4.60)	2.01
3	227, 316, 529 (4.53)	2.34
4	255, 315, 347, 366, 386, 522 (4.28)	2.20
5	227, 308, 397, 607 (4.57)	1.94
7a	302, 538, 578 (4.84)	1.75

[a] In CH<sub>2</sub>Cl<sub>2</sub>

ure 1b).<sup>[11]</sup> Replacement of the phenyl substituents with bulky 2,6-difluorophenyl and 9-anthryl groups brought about blueshifts of the absorption maximum to  $\lambda = 529$  and 522 nm, respectively. This result can be explained in terms of the difference in conjugation of the substituents with the indacene core since the dihedral angles between the substituents and indacene are larger in the difluorophenyl and anthracene derivatives. On the other hand, the introduction of thiophene rings afforded a redshift of the absorption maximum to 607 nm. This can be attributed to the less hindered structure as well as the electron-donating property of the thiophene ring.

**X-ray crystallographic analysis**: X-ray crystal-structure analysis of IFs **2–4** was carried out to investigate the quinoid structure (Figure 2). The single crystals were obtained by slow sublimation. In phenyl derivative **2**, the IF unit has a planar geometry with a center of symmetry, and the two phenyl rings take on a twisted conformation to the planar indacene unit with a dihedral angle of 43.3°. The C–C bond lengths of C1–C2 (1.390 Å), C9–C10 (1.360 Å), and C1–C9 (1.460 Å) show the quinoid structure of the central benzene unit. Derivatives **3** and **4** have a similar planar geometry and quinoid structure to the indacene core. Aryl substituents at the 6,12-positions are twisted, and their bond lengths and di-

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Figure 2. a-c) ORTEP drawing of 2-4, respectively, and d-f) crystal packing of 2-4, respectively (ellipsoids drawn at the 50% probability level).

hedral angles are summarized in Table 2. The dihedral angles between the aryl groups and indacene core are dependent on the aryl groups and become larger with an increase in the bulkiness of the substituents. The anthracene derivative 4 shows the largest dihedral angle of 76.5°. In addition, the bond alternation of the quinoid unit seems to relate to the dihedral angles. Thus, the bond lengths of C1–C2 and C9–C10 in 4 are shorter than those in 2, although

Table 2. Bond lengths [Å] and dihedral angles [°] of aryl-substituted IF derivatives **2–5** and TIPSE-substituted **6** in single crystals.

$\langle$	$\begin{array}{c} C10^{*}\\ C10^{*}\\ C1\\ C2\\ C9\\ C3\\ C1^{*}\\ C10\\ C3\\ C1\\ C3\\ C3\\ C3\\ C3\\ C3\\ C3\\ C3\\ C3\\ C3\\ C3$		Ar	
	IX .	Dihe	edral angle	
	2	3	4	<b>6</b> <sup>[a]</sup>
C1-C2	1.3902(15)	1.387(3)	1.376(3)	1.390(3)
C1-C9	1.4602(15)	1.464(3)	1.467(3)	1.457(3)
C9-C10	1.3602(15)	1.360(3)	1.358(3)	1.374(3)
C1-C10*	1.4309(15)	1.435(2)	1.428(3)	1.438(3)
C2-C3	1.4682(16)	1.467(3)	1.470(3)	1.470(3)
C2-C11	1.4660(15)	1.467(3)	1.492(3)	$1.416(3)^{[b]}$
dihedral angle	43.3	56.6	76.5	-

[a] In ref. [8a]. [b] Crystallographic data in CCDC-787154.

*Chem. Eur. J.* **2012**, *00*, 0–0

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the difference is not so large compared with the experimental errors, whereas the bond lengths of C1–C9 and C2–C11 are longer than those of **2**. On the other hand, derivative  $6^{[8a]}$  with TIPSE groups shows longer bond lengths of C1– C2 (1.390 Å) and C9–C10 (1.374 Å) and shorter bond lengths of C1–C9 (1.457 Å) and C2–C11 (1.416(3) Å) relative to the aryl-substituted derivatives. The shorter bond length of C2–C11 suggests  $\pi$  conjugation through the ethynyl units. These facts indicate that the twisted aryl groups strengthen the contribution of the quinoid structure.

Molecule 2 forms a  $\pi$ -stacking columnar structure in a manner that avoids the interaction between the phenyl substituents with an interplanar distance of 3.588 Å between the central benzene and the adjacent five-membered ring as depicted in Figure 2d. The introduction of two 2,6-difluorophenyl groups in 3 afforded a well-ordered  $\pi$ -stacking structure. A half-slipped-type stacking along the molecular long axis is observed with a close interplanar distance of 3.326 Å. This structure seems favorable to carrier transportation. In anthracene derivative 4,  $\pi$  stacking of the indacene unit is not observed; instead, overlapping between the anthracene groups (3.415 Å) is observed (Figure 2f). This is attributed to the bulkiness and  $\pi$ -conjugated system of the anthracene group.



**Redox properties:** IF derivatives 2–5 showed amphoteric redox properties. The cyclic voltammograms were measured in dichloromethane, and the redox potentials are summarized in Table 3. Derivative 2 shows a reversible one-electron oxidation wave at +0.97 V and a reduction wave at -1.00 V versus SCE as shown in Figure 3a. Replacement of the phenyl groups with electron-withdrawing 2,6-difluorophenyl groups increased the electron-accepting property of inda-

Table 3. Electrochemical data of 2-5.<sup>[a]</sup>

	$E_{\rm ox}$	$E_{1\rm red}$	$E_{\rm ox} - E_{\rm red}^{[b]}$
2	+0.97	-1.00	1.97
3	+1.18	$-0.88^{[c]}$	2.06
4	+1.07	-1.05	2.12
5	+0.66	$-0.89^{[c]}$	1.55

[a]  $nBu_4NPF_6$  (0.1 M) in CH<sub>2</sub>Cl<sub>2</sub>, Pt electrode, V versus SCE. Half-wave potentials. [b]  $E_{red} = E_{pc} + 0.03$  V. [c] Quasi-reversible or irreversible peak.



Figure 3. Cyclic voltammograms of a) 2, b) 3, c) 4, and d) 5.

cene 3. On the other hand, anthracene derivative 4 showed a positive shift only in the oxidation potential. Introduction of the thienyl groups in 5 greatly lowered the oxidation potential to +0.66 V. This is attributed to the electron-donating thienyl groups. Interestingly, the reduction potential of 5 is positively shifted and the HOMO-LUMO gap is reduced. This fact indicates that the aryl groups at the 6,12-positions are important in determining the HOMO and LUMO levels. As shown in Table 3, the differences between the oxidation and reduction potentials  $(E_{ox}-E_{red})$  are related to the dihedral angles in Table 2. However, TIPSE-substituted derivative 6 shows an oxidation potential at +1.23 V and a reduction potential at -0.62 V (versus SCE),<sup>[8b]</sup> thereby resulting in a HOMO-LUMO gap of 1.85 V. The high oxidation potential can be attributed to the electron-withdrawing ethynyl group. The narrow HOMO-LUMO gap may be due to the contribution of biradical structure 1\*. The thienyl derivative 5 seems to have a similar contribution from 1\* on account of the less hindered substituent, which leads to the narrower HOMO-LUMO gap.

DFT and nucleus-independent chemical shift (NICS) calculations: Molecular orbital calculations of 2-5 were carried out by using the Gaussian 03 program at the B3LYP/6-31G(d) level of theory to investigate the substituent effects. The optimized dihedral angles between the aryl groups and the s-indacene core are  $45.3^{\circ}$  in 2,  $51.6^{\circ}$  in 3,  $71.0^{\circ}$  in 4, and 34.1° in 5. These dihedral angles of 2-4 are consistent with those obtained from the X-ray analysis, and the dihedral angle of 34.1° in 5 suggests that the  $\pi$  conjugation through the thienyl groups is effective. The calculated bond lengths of 5 show the smallest bond alternation (see Table S2 in the Supporting Information). The calculations of the HOMO and LUMO energies are depicted in Figure 4. The HOMO-LUMO differences are dependent on the aryl substituents and the thienyl derivative 5 shows the narrowest value of 1.90 eV. Introduction of the five-membered thiophene rings weakens the quinoid character and promotes the  $\pi$  delocalization that leads to the smaller HOMO-LUMO gap.



Figure 4. HOMO and LUMO energies [eV] of 2–5 calculated by using DFT at the B3LYP/6-31G(d) level of theory.

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By extension, to investigate the aromaticity of the arylsubstituted IF derivatives,<sup>[13]</sup> we calculated the (NICS)(1) values<sup>[9,14]</sup> at the RHF/6-31+G(d) level of theory by using both the CIF files of **2–4** and the optimized molecular structures of **2–5** (Table 4). Although the calculated values are considered to be strongly influenced by the aryl groups as shown in Table S3 in the Supporting Information, the central A and B rings exhibit antiaromatic positive values in all derivatives.

Table 4. Calculated NICS(1)<sup>[a]</sup> based on CIF files of **2–4** and optimized structures of **2–5**.<sup>[b]</sup>



[a] RHF/6-31+G(d) level of theory. [b] Structures optimized using DFT at the B3LYP/6-31G(d) level of theory. Average values of B and B' rings, or C and C' rings.

**Stability in solution**: To investigate the stability in solution, the solutions of IF derivatives **2–5** in dichloromethane  $(10^{-5} \text{ M})$  were exposed to ambient light in air at 20 °C for several weeks. UV-visible spectra were recorded at regular and gradient intervals to obtain time-absorbance profiles. The results are illustrated in Figure 5. The stability increased



Figure 5. Absorbance-time profiles for IF derivatives 2-5.

relative to substituted pentacene derivatives.<sup>[4b,c]</sup> Indacenes **3** and **4** with bulky 2,6-difluorophenyl and 9-anthryl groups showed significantly longer lifetimes than the phenyl- and thienyl-substituted derivatives **2** and **5**. Plots of ln *A* (*A*: absorbance at a given  $\lambda_{max}$ ) versus time [h] afforded the rate constants (*k*) (see Figure S4 in the Supporting Information). The obtained rate constants for **2–5** were  $9.2 \times 10^{-4}$ ,  $3.5 \times 10^{-5}$ ,  $1.5 \times 10^{-4}$ , and  $9.0 \times 10^{-4}$  h<sup>-1</sup>, respectively, and their half-lives ( $t_{12}$ ) were 753, 19800, 4620, and 770 h, respective-

ly. This result indicates that introduction of bulky aryl substituents is effective in enhancing the stability of the indacene core. The higher stability of **3** compared with **4** can be ascribed to the lower HOMO level.

**Field-effect transistor (FET) characteristics**: Although redox-active IF derivatives were expected to show carrier transportation properties in thin films, FET devices based on them have not yet been reported. We have now succeeded in measuring the FET characteristics on the basis of aryl derivatives by using a vapor deposition method. Thin films of IFs 2–4 were thermally deposited on silica/Si wafers with interdigitated Au bottom electrodes in a high-vacuum chamber (approximately 230–350 °C:  $10^{-5}$  Pa). Silica dielectric surfaces were treated with hexamethyldisilazane (HMDS). The measurements were carried out in situ, and the results are summarized in Table 5. The film of **2** exhibited p-type

Table 5.	FET	characteristics	with	bottom	contact	geometries.	a	
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	Mobility $[cm^2V^{-1}s^{-1}]$	On/Off	Threshold [V]
2	p: $1.6 \times 10^{-5}$	60	-2
3	p: $1.9 \times 10^{-5}$	10	-48
3	n: $8.2 \times 10^{-6}$	10	+36
4	p: $1.1 \times 10^{-5}$	100	-62
4	$n: 1.6 \times 10^{-6}$	30	+65

<sup>[</sup>a] Data calculated by using transfer plots at  $V_{DS} = +/-100$  V. Silica gate dielectric: 300 nm thick. HMDS-treated surface.  $T_{sub} = 20$  °C. Interdigitated gold source and drain electrodes, L/W: 25 µm/294 mm.

semiconducting behavior with a mobility of  $1.6 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Interestingly, the introduction of 2,6-difluorophenyl groups in **3** imbued it with an electron-transporting property ( $8.2 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) as well as a hole-transporting one ( $1.9 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) as shown in Figure 6. The 9anthryl derivative **4** also showed ambipolar characteristics.



Figure 6. The a) p-type and b) n-type output characteristics of an FET based on **3**.

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These results are consistent with the amphoteric redox properties of the IF core. The relatively low mobilities obtained here may be ascribed to the less-ordered molecular arrangements in the thin films, because no sharp reflection peak was observed in the XRD diffractograms of vapor-deposited thin films. Modification of the  $\pi$ -conjugated systems by introducing substituents may improve the carrier-transporting properties.

#### Conclusion

In conclusion, we have succeeded in preparing fused polycyclic IF derivatives with aryl substituents and investigated the effect of aryl substituents. We have found here that the molecular structures, the physical properties accompanied by HOMO-LUMO energies, and the stability are significantly dependent on the aryl substituents. Twisted bulky substituents increase the contribution of the quinoid structure and enhance the stability. This fact could be supported by X-ray single-crystal analysis along with DFT calculations. Furthermore, we have demonstrated the ambipolar carrier transportation of the IFs for the first time. Although the mobilities of vapor deposition films are not so high on account of the amorphous film structures, the modification of the structures would improve the FET performances. Construction of further fused polycyclic systems is now underway in our group.

#### **Experimental Section**

**General:** Melting points were obtained using a Shimadzu DSC-60. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Jeol-ECP 300 spectrometer. An <sup>1</sup>H NMR spectrum at high temperature was recorded using a Bruker AVANCE-400 spectrometer. EI-MS and FAB-MS data were collected using a JEOL JMS-700 mass spectrometer. IR spectra were recorded using a JASCO FT/IR-4100 Fourier transform infrared spectrometer. UV/Vis spectra were recorded using a JASCO V-650 spectrophotometer. Cyclic voltammograms were recorded using a Hokuto-Denko HZ-5000. Pt disk, Pt wire, and SCE were used as working, counter, and reference electrodes. XRD measurements were carried out using a Rigaku RINT with a Cu<sub>Kα</sub> source ( $\lambda$  = 1.541 Å).

Synthesis of 6,12-diphenylindeno[1,2-b]fluorene (2): n-Butyllithium (1.65 M, 2.47 mL, 4.07 mmol) was added dropwise to a solution of bromobenzene (634 mg, 4.07 mol) in dry THF (40 mL) at -78 °C under Ar. The mixture was kept for 1 h in THF (10 mL). A suspension of 8 (500 mg, 1.77 mmol) in THF (10 mL) was added to the solution, and the reaction mixture was stirred at -78°C for 2 h and warmed to RT. The reaction mixture was heated at reflux for 8 h. A solution of tin(II) chloride anhydride (0.77 g, 4.07 mmol) in concentrated HCl (10 mL) was added to the mixture, and the mixture was heated at reflux for 24 h. After the solvent was removed, the residue was neutralized with 10% aqueous NaOH (200 mL). After extraction of the mixture with toluene, the organic layer was washed with water and brine and dried over Na2SO4. After the solvent was removed, the crude product was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) followed by sublimation. Black crystals (179 mg, 0.44 mmol) of compound 2 were obtained in 25 % yield. M.p. 241-242 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 7.63$  (dd, J = 7.8, 1.8 Hz, 4 H), 7.56 (dd, J=7.8, 7.8 Hz, 4H), 7.48-7.39 (m, 4H), 7.37 (s, 2H), 7.28-7.27 (m, 2H), 7.09–7.02 ppm (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta =$ 144.28 (2C), 143.28 (2C), 139.56 (2C), 138.24 (2C), 134.21 (2C), 133.73 (2C), 129.17 (4C), 128.85 (4C), 128.50 (2C), 127.70 (2C), 127.32 (2C), 122.31 (2C), 120.41 (2C), 119.53 ppm (2C); IR (KBr):  $\tilde{\nu}$ =3054, 1563, 1557, 1488, 1367, 1346, 1332, 1170, 1028, 932, 892, 761, 697 cm<sup>-1</sup>; MS (EI) (70 eV): *m/z* (%): 404 (100) [*M*<sup>+</sup>]; elemental analysis calcd (%) for C<sub>32</sub>H<sub>20</sub>: C 95.02, H 4.98; found: C 94.89, H 4.65.

Synthesis of 6,12-bis(2,6-difluorophenyl)indeno[1,2-b]fluorene (3): n-Butyllithium (1.65 M, 2.47 mL, 4.07 mmol) was added dropwise to a solution of 1,3-difluorobenzene (464 mg, 4.07 mmol) in dry THF (40 mL) at -78°C under Ar. The mixture was kept for 1 h. A suspension of dione 8 (500 mg, 1.77 mmol) in THF (10 mL) was added to the solution, and the reaction mixture was stirred at -78 °C for 2 h and warmed to RT. The reaction mixture was heated at reflux for 8 h. A solution of tin(II) chloride anhydride (0.77 g, 4.07 mmol) in concentrated HCl (10 mL) was added to the mixture, and the mixture was heated at reflux for 24 h. After the solvent was removed, the residue was neutralized with 10% aqueous NaOH (200 mL). After extraction of the mixture with toluene, the organic layer was washed with water and brine and dried over Na2SO4. After the solvent was removed, the crude product was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) followed by sublimation. Black crystals (193 mg, 0.407 mmol) of **3** were obtained in 23 % yield. M.p. 350–351 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 21°C):  $\delta = 7.43$  (brt, 2H), 7.34 (brd, 2H), 7.15–6.98 (m, 10H), 6.94–6.89 ppm (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 162.45$  (dd, J(C,F) = 249, 7.2 Hz, 4C), 143.17 (2C), 139.89 (2C), 137.57 (2C), 136.42 (2C), 133.57 (2C), 130.39 (t, J(C,F)=10.0 Hz, 2C), 128.05 (2 C), 127.57 (2 C), 122.52 (2 C), 120.48 (2 C), 119.73 (2 C), 112.2-111.84 ppm (6 C); IR (KBr):  $\tilde{v}$  = 3060, 1622, 1573, 1568, 1456, 1359, 1264, 1232, 1153, 999, 889, 860, 770, 760, 695, 549 cm<sup>-1</sup>; EI (MS) (70 eV): m/z (%): 416 (100) [M<sup>+</sup>]; elemental analysis calcd (%) for C<sub>32</sub>H<sub>16</sub>F<sub>4</sub>: C 80.67, H 3.38; found: C 80.90, H, 3.18.

Synthesis of 6,12-bis(anthracen-9-yl)indeno[1,2-b]fluorene (4): n-Butyllithium (1.65 M, 2.47 mL, 4.07 mmol) was added dropwise to a solution of 9-bromoanthracene (1.04 g, 4.07 mmol) in dry THF (40 mL) at -78°C under Ar. The suspension was kept for 1 h in THF (10 mL). A suspension of dione 8 (500 mg, 1.77 mmol) in THF (10 mL) was added to the solution, and the reaction mixture was stirred at -78°C for 2 h and warmed to RT. The reaction mixture was heated at reflux for 8 h. A solution of tin(II) chloride anhydride (0.77 g, 4.07 mmol) in concentrated HCl (10 mL) was added to the mixture, and the mixture was heated at reflux for 24 h. The crude product was filtered by suction, washed with water, methanol, and hexane, and dried under vacuum. Purification by sublimation gave black crystals (0.150 mg, 0.248 mmol) of 4 in 14 % yield. M.p. >350 °C; <sup>1</sup>H NMR (400 MHz,  $[D_4]o$ -dichlorobenzene, 90 °C):  $\delta =$ 8.53 (s, 2H), 8.11 (d, J=8.5 Hz, 4H), 8.06 (d, J=8.5 Hz, 4H), 7.45 (t, J= 8.5 Hz, 4H), 7.31 (t, J=8.5 Hz, 4H), 6.91 (d, J=1.1 Hz, 2H), 6.88 (d, J= 7.5 Hz, 2H), 6.81 (t, J=7.5 Hz, 2H), 6.73 (t, J=7.5 Hz, 2H), 6.42 ppm (d, J = 7.5 Hz, 2 H; IR(KBr):  $\tilde{\nu} = 3046, 2357, 1713, 1567, 1557, 1443, 1410,$ 1344, 1266, 890, 759, 737, 703, 514 cm<sup>-1</sup>; MS (EI) (70 eV): m/z (%): 604 (100) [M<sup>+</sup>]; elemental analysis calcd (%) for C<sub>48</sub>H<sub>28</sub>: C 95.33, H 4.67; found: C 95.46, H 4.48.

Synthesis of 6,12-bis(5-hexylthiophen-2-yl)indeno[1,2-b]fluorene (5): n-Butyllithium (1.65 M, 2.46 mL, 4.07 mmol) was added dropwise to a solution of 2-hexylthiophene (690 mg, 4.07 mmol) in dry THF (30 mL) at -78°C under Ar. The mixture was kept for 1 h. A suspension of dione 8 (500 mg, 1.77 mmol) in THF (20 mL) was added to the solution, and the reaction mixture was stirred at -78°C for 2 h and warmed to RT. The reaction mixture was heated at reflux for 12 h. A solution of tin(II) chloride dihydrate (SnCl\_2/2H\_2O) (0.77 g, 4.07 mmol) in concentrated HCl (10 mL) was added to the mixture, and the mixture was heated at reflux for 2 h. After the solvent was removed, the residue was neutralized with 10% aqueous NaOH (200 mL). After extraction of the mixture with toluene, the organic layer was washed with water and brine, and dried over Na2SO4. After solvent was removed, the crude product was purified by silica column chromatography (CH2Cl2) and by GPC (CHCl3) to give a blue solid (37 mg, 0.0633 mmol) of 5 in 4% yield. M.p. 120-121 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 7.74$  (s, 2H), 7.61 (brt, 2H), 7.51 (brt, 2H), 7.41 (d, J=3.3 Hz, 2H), 7.11 (brt, 4H), 6.94 (d, J=3.3 Hz, 2H), 2.96 (t, J=7.5 Hz, 4H), 1.81-1.70 (m, 4H), 1.51-1.26 (m, 12H), 1.00–0.92 ppm (m, 6H);  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>, 23 °C):  $\delta = 148.84$ 

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(2C), 142.22 (2C), 139.12 (2C), 138.52 (2C), 135.78 (2C), 134.51 (2C), 132.62 (2C), 128.22 (2C), 127.47 (2C), 127.11 (2C), 125.39 (2C), 122.68 (2C), 120.13 (2C), 119.07 (2C), 31.57–31.58 (4C), 30.42 (2C), 28.89 (2C), 22.60 (2C), 14.10 ppm (2C); IR (KBr):  $\tilde{\nu}$ =1727, 1549, 1509, 1451, 1342, 1134, 929, 889, 809, 760, 700 cm<sup>-1</sup>; MS (FAB): *m*/*z* 584 [*M*<sup>+</sup>]; HRMS (FAB): *m*/*z* calcd for C<sub>40</sub>H<sub>40</sub>S<sub>2</sub>: 584.2571 [*M*<sup>+</sup>]; found: 584.2568; elemental analysis calcd (%) for C<sub>40</sub>H<sub>40</sub>S<sub>2</sub>: C 82.14, H 6.89, S 10.96; found: C 80.19, H 7.86, S 8.88.

X-ray crystal-structure analysis: The X-ray measurements of 2, 3, and 4 were carried out using a Rigaku R-AXIS RAPID imaging plate diffractometer with  $Mo_{K\alpha}$  radiation ( $\lambda$ =0.71075 Å) at -180 °C. The structures were solved by direct methods (SIR2004) and refined by full-matrix least-squares methods on  $F^2$  with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were refined using the riding model. Absorption correction was applied using an empirical procedure.

**Crystal data for 2:**  $C_{32}H_{20}$ ;  $M_r$ =404.51; crystal dimensions  $0.78 \times 0.78 \times 0.75$  mm; orthorhombic; space group *Pbcn*; *a*=26.8450(13), *b*=10.3708(5), *c*=7.3818(3) Å; *V*=2055.13(16) Å<sup>3</sup>; *Z*=4;  $\rho_{calcd}$ =1.307 gcm<sup>-3</sup>; 18425 reflections collected, 2365 independent ( $R_{int}$ =0.045); GoF=1.09,  $R_1$ =0.048,  $wR_2$ =0.140 for all reflections.

**Crystal data for 3**:  $C_{32}H_{16}F_4$ ;  $M_r$ =476.47; crystal dimensions  $0.30 \times 0.30 \times 0.25$  mm; monoclinic; space group  $P2_1/c$ ; a=8.4169(8), b=11.2467(10), c=11.3554(11) Å;  $\beta$ =90.082(3)°; V=1074.93(17) Å<sup>3</sup>; Z=2;  $\rho_{calcd}$ = 1.472 gcm<sup>-3</sup>; 10065 reflections collected, 2470 independent ( $R_{int}$ =0.063); GoF=1.087,  $R_1$ =0.061,  $wR_2$ =0.182 for all reflections.

**Crystal data for 4**:  $C_{48}H_{28}$ ;  $M_r = 604.75$ ; crystal dimensions  $0.40 \times 0.30 \times 0.30 \text{ mm}$ ; monoclinic; space group C2/c; a = 20.6738(20), b = 8.3161(8), c = 17.5904(19) Å;  $\beta = 91.287(3)^\circ$ ; V = 3023.5(5) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.328 \text{ g cm}^{-3}$ ; 14150 reflections collected, 3456 independent ( $R_{int} = 0.084$ ); GoF = 1.073,  $R_1 = 0.061$ ,  $wR_2 = 0.196$  for all reflections.

CCDC-866841 (2), -866842 (3), and -866843 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (nos. 19350092 and 22550162) from the Ministry of Education and Culture, Sports, Science and Technology, Japan, and by the Global COE program "Education and Research Center for Emergence of New Molecular Chemistry". We thank Material Analysis Suzukake-dai Center, Technical Department, Tokyo Institute of Technology, for elemental analysis, MS measurements, and high-temperature NMR spectroscopic measurements.

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Received: February 23, 2012 Published online: ■ ■ 10, 0000

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#### **Quinoid Compounds -**

J.-i. Nishida, S. Tsukaguchi, Y. Yamashita\*.....

Synthesis, Crystal Structures, and Properties of 6,12-Diaryl-Substituted Indeno[1,2-b]fluorenes



Substituent dependency: Fused polycyclic indeno[1,2-*b*]fluorene derivatives with aryl substituents have been prepared as a potential example of antiaromatic  $20\pi$  electronic systems (see scheme). X-ray analysis revealed quinoid-type molecular structures, which indicated that the bond lengths of the quinoid unit depend on the aryl substituents.