Supporting Information

Synthesis and Characterization of Highly Fluorescent Indenofluorenes

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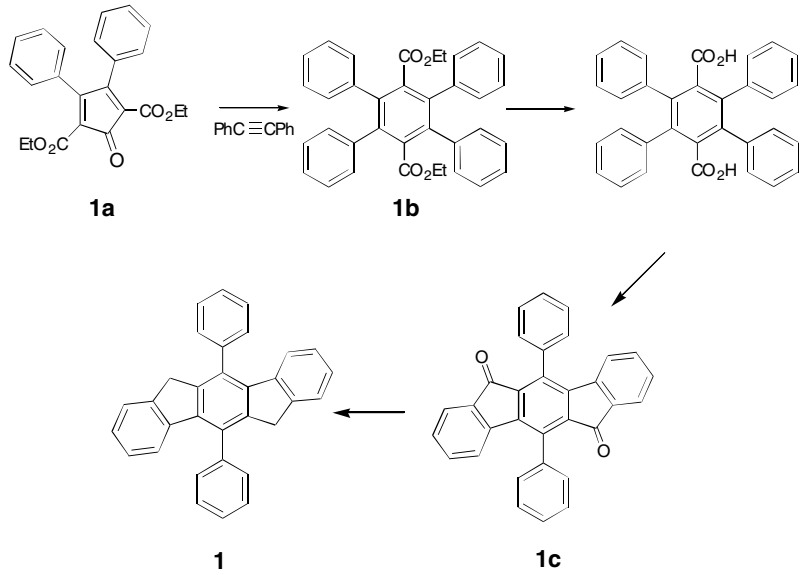
Experimental

General Methods: Unless otherwise specified, all reagents were commercially available from Aldrich Inc. All organic solvents and chemicals were used as received. NMR spectra were recorded with either a Varian Gemini 200 or a Bruker 400, using $CDCl_3$ or DMSO-d_6 as both solvent and reference. Coupling constants are given in hertz (Hz) and chemical shift (δ) in ppm. Infrared measurements were performed with a Perkin-Elmer 1600 FTIR spectrophotometer. The University of Ottawa Mass Spectroscopy Centre performed mass spectroscopic analyses. The Guelph Chemical Laboratories Ltd performed elemental analyses.

Synthesis of 5,11-diphenyl-6,12-dihydroindeno[1,2b]fluorene (1).



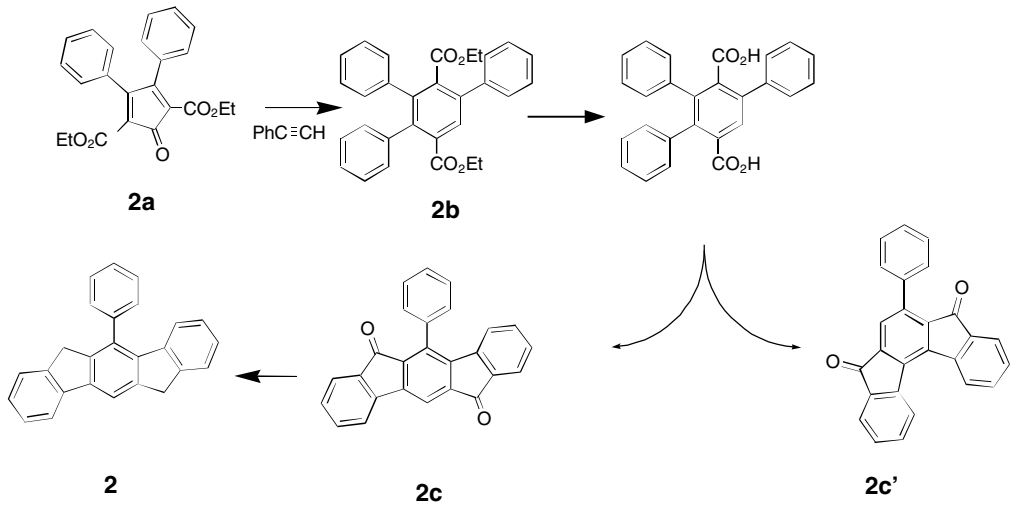
1a 1b 1c 1

The cyclone **1a** (15.020 g, 39.89 mmol) was dissolved in 50 ml of 1,2-dichlorobenzene. Diphenylacetylene (17.77 g, 99.73 mmol) was added and the mixture was heated at reflux for 12 hrs. the reaction was monitored by TLC (2:1 % hexane in ether). The flask was allowed to cool down in ice and the Diels-Alder product recrystalized from the solvent. The white precipitate was filtered under suction, washed with hexane and dried in a vacuum oven at 100 ^{0}C overnight. Compound **1b** was recrystalized from glacial acetic acid : 19.0 g, 90% yield. Mp : 240-242 ^{O}C. IR (KBr) 3058, 2974, 1731, 1601, 1579, 1497, 1464, 1441, 1416, 1366, 1326, 1190, 1057, 761, 702 cm^{-1}. MS (EI, m/e, relative intensity %) 526 ($M^{\bullet+}$, 100).

The diester **1b** (19.020 g, 36.12 mmol) was hydrolyzed in 100 ml of glacial acetic acid in the presence of 20 ml of HBr (48%). The mixture was heated at reflux for 48 hrs and monitored by TLC (2:1 % hexane in ether). The diacid precipitated from the solvent, was filtered, was dissolved in potassium carbonate solution and filtered again. The diacid was recovered from the filtrate with addition of conc. HCl : 11.9 g, 70% yield. IR (KBr) 3434, 3000, 2632, 1707, 1601, 1497, 1431, 1322, 1223, 1075, 753, 698 cm^{-1}. The diacid (2.033 g, 4.32 mmol) was then dissolved by portions in 50 ml of conc. H_2SO_4. The red mixture was stirred for 3 hrs at room temperature (25 ^{O}C). It was then poured into ice. The red precipitate was filtered, washed with water and stirred in potassium carbonate solution for a few hours. The precipitate was filtered again, washed with water until neutral pH and dried in a vacuum oven at 100 ^{O}C. Recrystalisation from AcOH gave **1c** as a red solid: 1.7 g, 90% yield. Mp : 340 ^{O}C (DSC). IR (KBr) : 1712, 1602, 1465, 1441, 1183, 1096, 928, 722, 699 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 10H) ; 7.45-7.42 (md, J=6.4, 2H) ; 7.37 (dd, J=3.2,5.4, 2H) ; 7.09 (dq, J=1.8,6.7, 2H) ; 6.22-6.19 (md, J=6.7, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.2, 143.7, 142.1, 135.4, 135.1, 135.0, 134.9, 133.7, 129.5, 128.8, 128.5, 128.3, 123.8, 122.8. MS (EI, m/e, relative intensity %) 434 ($M^{\bullet+}$, 27). HRMS Calcd for $C_{32}H_{18}O_2$: 434.1307. Found: 434.1305.

The diketone **1c** (200 mg, 0.460 mmol) was suspended in diethylene glycol (13 ml) containing KOH (650 mg, 11.42 mmol). Hydrazine monohydrate (98%, 0.7 ml) was added. The mixture was heated at 180-190 ^{O}C for 24 hrs. The hot solution was poured into ice containing HCl. The white precipitate was filtered, washed and dried. Recrystallisation from AcOH gave compound **1**: 168 mg, 95%. Mp : 296 ^{O}C (DSC). IR (KBr) 3062, 2891, 1602, 1438, 1292, 1219, 763, 724, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.47 (m, 10H) ; 7.39 (d, J=7.15, 2H) ; 7.15 (dt, J= 1.1, 7.4, 2H) ; 7.01 (dt, J=1.1, 7.8, 2H) ; 6.65 (d, J=7.8, 2H) ; 3.70 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.4, 141.8, 139.6, 137.4, 133.6, 129.1, 129.0, 127.7, 126.3, 126.0, 124.7, 122.7, 36.2. MS (EI, m/e, relative intensity %) 406 ($M^{\bullet+}$, 100). HRMS Calcd for $C_{32}H_{22}$: 406,1722. Found: 406.1722. Anal. Calcd for $C_{32}H_{22}$: C, 94.55 ; H, 5.45. Found C, 94.29 ; H, 5.47.

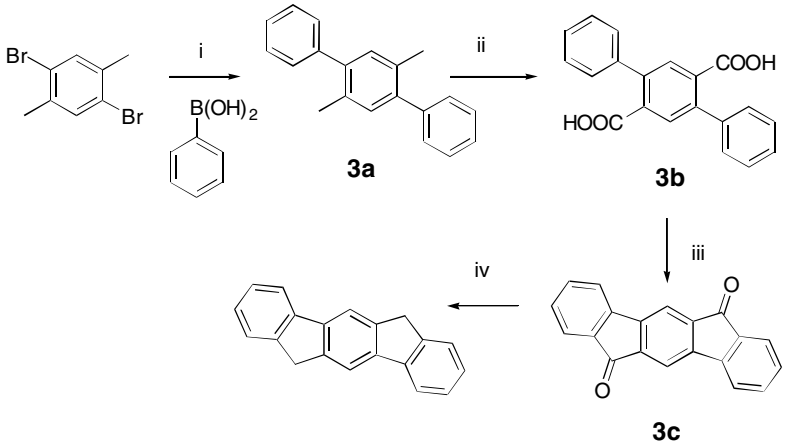
Synthesis of 5-phenyl-6,12-dihydroindeno[1,2b]fluorene (2).



The synthesis of the corresponding diketone (**2c** and **2c'**) followed the same procedure with similar yield described above from **1c**. However, the product obtained was a mixture of the two isomers in about 70/30 proportions (determined by integration of ^{1}H NMR distinct signals at 6.3 ppm and 8.2 ppm for **2c** and **2c'** respectively). **2c** (red) and **2c'** (yellow) were separated by fractional recrystalisation in toluene. IR (KBr) 1713, 1603, 1466, 1060, 926, 760, 712, 699 cm^{-1}. **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H); 7.66-7.64 (md, J=6.9, 1H) ; 7.61-7.52 (m, 6H) ; 7.39-7.37 (md, J=4.6, 2H) ; 7.31 (dt, J=7.3, 1.0, 1H) ; 7.20 (dt, J=7.5, 1.1, 1H) ; 7.16 (dt, J=7.5, 1.3, 1H) ; 6.32-6.29 (md, J=7.1, 1H). MS (EI, m/e, relative intensity %) 358 ($M^{\bullet+}$, 100). HRMS calcd for $C_{26}H_{14}O_2$: 358.0994. Found: 358.0991. **2c'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J=7.7, 4.9, 2H); 7.85 (qd, J=7.4, 0.6, 1H); 7.74 (qd, J=7.4, 0.6, 1H); 7.67 (qd, J=7.5, 1.3, 2H) ; 7.61 (s, 1H) ; 7.51-7.41 (m, 6H). MS (EI, m/e, relative intensity %) 358 ($M^{\bullet+}$, 73). HRMS calcd for $C_{26}H_{14}O_2$: 358.0994. Found: 358.1009.

Compound **2c** (0.267 g) was reduced to give **2,** following the same procedure described for **1**: 0.246 g, yield 98%. Mp: 150 ^{O}C. IR (KBr) 3049, 2901, 1602, 1500, 1435, 1400, 1301, 1216, 761, 723, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H); 7.83 (d, J=7.5, 1H); 7.58-7.49 (m, 5H); 7.45-7.42 (md. J=7.7, 2H); 7.37 (t, J=7.4, 2H); 7.26 (dt, J=7.4, 1.1, 2H); 7.17 (dt, J=7.4, 1.0, 1H) ; 7.01 (t, J=7.4, 1H) ; 6.63 (d, J=7.8, 1H) ; 4.01 (s, 1H) : 3.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.9, 143.2, 141.8, 141.6, 140.2, 139.6, 137.9, 134.3, 129.0, 128.8, 127.6, 126.7, 126.5, 126.3, 125.9, 124.9, 124.7, 122.5, 119.8, 115.5, 36.7, 36.2. MS (EI, m/e, relative intensity %) 330 ($M^{\bullet+}$, 100). HRMS Calcd for $C_{26}H_{18}$: 330.1409. Found: 330.1414. Anal Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 93.49; H, 5.51.

Synthesis of 6,12-dihydroindeno[1,2b]fluorene (3).



To a 20 ml flask flushed with argon and equipped with a rubber septum, a stirring-bar, 2,5-dibromo-*p*-xylene (1.000 g, 3.79 mmol), phenylboronic acid (1.015 g, 8.33 mmol), $Pd(OAc)_2$ (1.7 mg, $7.56.10^{-6}$ mol = 0.2 mol%), K_2CO_3 (2.618 g, 18.95 mmol) and n-Bu_4NBr (2.443 g, 7.58 mmol) were added. Water (8.3 ml) was added via a syringe and the resulting suspension was vigorously stirred. The mixture was stirred and heated for 2 hrs at 70 ^{O}C under argon. It was then cooled, diluted with water and extracted with toluene. The organic phase was dried over $MgSO_4$ and evaporated to yield **3a** as white solid: 959 mg, 98% yield. Mp: 180 ^{O}C (lit[1]: 182-184 ^{O}C). IR (KBr) : 3033, 1455, 1426, 1049, 991, 860, 759, 720, 672 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46-7.32 (m, 10H), 7.15 (s, 2H), 2.35 (s, 6H). MS (EI, m/e, relative intensity %) 258 ($M^{\bullet+}$, 100).

Compound **3a** (800 mg, 3.09 mmol) in 19 ml of pyridine and 1.8 ml of water containing 2.3 g of $KMnO_4$ was heated at reflux for 2 hrs. At every ½ hour 3 ml of water and 1.0 g of $KMnO_4$ were added four times. After 5-6 hours, 20 ml of water was added and kept refluxing overnight. The MnO_2 precipitate was filtered hot and washed with boiling water. The filtrate was decolored (if necessary) with active carbon and filtered through Celite. The filtrate was concentrated and the acid was recovered by addition of conc. HCl. The acid product was dried overnight at 80 ^{0}C in a vacuum oven: 945 mg, 96% yield. Mp = 282 ^{O}C (lit[1]: 280-287 ^{O}C). IR (KBr) 340, 1706, 1473, 1403, 1293, 1247, 1139, 1061, 915, 783 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.73 (s, 2H) ; 7.40-7.52 (m, 10H).

The diacid **3b** (2.000 g, 6.29 mmol) was dissolved by small portions in 100 ml of H_2SO_4. The green mixture was stirred for 2 hrs at room temperature (25 ^{O}C). It was then poured into ice. The purple precipitate was filtered and washed with water. The solid was then stirred in a potassium carbonate solution for a few hours, filtrated under suction and dried at 100 ^{O}C in a vacuum oven: 1.596 g, 90% yield. Mp > 300 ^{O}C (lit[1]: 341-342 ^{O}C). IR (KBr) 1714, 1603, 1470, 1429, 1180, 1123, 1086, 919, 755, 723 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H); 7.63 (d, J=7.3, 2H); 7.51-7.48 (m, 4H); 7.31-7.26 (m, 2H). MS (EI, m/e, relative intensity %) 282 ($M^{\bullet+}$, 100). HRMS Calcd for $C_{20}H_{10}O_2$: 282.0681. Found: 282.0686.

The diketone **3c** was reduced following the same procedure described for **1c**, increasing the reaction time to 48 hrs: 1.09 g, 76% yield. Mp: 300-302 ^{O}C. IR (KBr) 3055, 3013, 2922, 1602, 1491, 1445, 1432, 1399, 1304, 1190, 950, 863, 763, 725. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (s, 2H) ; 7.93 (d, J=7.5, 2H) ; 7.59 (d, J=7.5, 2H) ; 7.39 (t, J=7.4, 2H) ; 7.30 (dt, J=7.4, 1.0, 2H) ; 3.98 (s, 4H). MS (EI, m/e, relative intensity %) 254 ($M^{\bullet+}$, 100). HRMS Calcd for $C_{20}H_{14}$: 254.1096. Found 254.1101. Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found C, 93.55; H, 5.67.

Spectral Analysis

The UV-Vis absorption spectra were recorded with a UV/Vis/NIR Perkin Elmer Lambda 900 spectrometer. Fluorescence emission spectra were recorded with a RF-1501 Shimadzu spectrofluorophotometer. All spectra were recorded at 25 ^{O}C. Quinine sulfate in 1N H_2SO_4 was used as reference in determining the fluorescence quantum yield of compounds **1**, **2**, and **3**. Fluorescence emission spectra of reference and sample compounds ($0.6.10^{-6}$M) were collected at 90^{O} to the angle of excitation.

The procedure for determining the fluorescence quantum yield follows established techniques[2,3]. The quantum yield is determinated according to Equation (1),

$$\phi_s = \phi_r \frac{\Im_s}{\Im_r} \cdot \frac{q_s}{q_r} \cdot \frac{A_r}{A_s} \qquad (1)$$

where subscripts s and r refer to the sample and reference, respectively. The integrated area of the emission peak in arbitrary units is given as $\Im$, q is relative to the source intensity and A is the absorbance. We considered that the ratio q_s/q_r is close to 1 since all spectra are recorded with close $\lambda_{excitation}$. The samples were prepared at a concentration of $0.6.10^{-6}$M in cyclohexane for **1** and **2** and in decalin for **3**.

Table 1. Physical constants and quantum yield data.

compound	$\lambda_{excitation}$ (nm)	$\lambda_{emission}$ (nm)	$\Im$	A	Φ_{litt}	Φ_{exp}
Quinine sulfate	239	456	35021	0.010590	0.55	
1	329	375	35175	0.041059		0.74
2	331	364	20768	0.034580		0.78
3	333	340,346	35000	0.056182		0.73

Cyclic Voltammetry

The cyclic voltammetry was performed on a BAS 100W electrochemical workstation. Nitrogen was used to purge the solution. Carbon electrode was used as the working electrode, Pt electrode was the counter electrode and a silver electrode was used as the reference electrode. Ferrocene/ferrocenium ion couple was added as an internal standard. n-Bu_4NPF_6 (0.1 M) in DMF as electrolyte for reduction and $LiClO_4$ (0.1 M) in acetonitrile for oxidation were used.

Table 2. Electrochemical data and band gap values of **1**, **2**, and **3**.

compounds	$E_{red\ 1}^{0}$ (V)	$E_{red\ 2}^{0}$ (V)	E_{ox}^{0} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta_{electrochemical}$ (V)	$\Delta_{optical}$ (eV)
1	-2.2	-2.4 (E_{pc})	-	-	-2.42	-	3.77
2	-1.8	-2.2 (E_{pc})	-	-	-2.28	-	3.75
3	-2.6	-2.9	1.25	-5.65	-2.16	3.85	3.71

HOMO and LUMO energy levels were estimated from the equations : $E_{HOMO} = E_{ox}^{0} + 4.4$ eV and $E_{LUMO} = E_{red}^{0} + 4.40$ eV, where E_{ox}^{0} and E_{red}^{0} are oxidation and reduction potentials with respect to the standard hydrogen electrode, and the value of 4.4 is the ionization potential for hydrogen in eV[4]. In the case of several reduction potentials, the lowest one, which leads to the lowest electrochemical edge, was taken. Unfortunately, it was unable to determinate the oxidation potential values of **1** and **2.** The band gap ($\Delta_{electrochemical}$) of 3.85 eV is in good agreement with the value ($\Delta_{optical}$) of 3.71 eV as assessed by spectroscopic means.

[1] Ebel, F.; Deutschel, W. *Ber.* **1956**, *89*, 2794.
[2] "Standards in Fluorescence Spectrometry", UV Spectrometry Group, edited by J.N. Miller, London.
[3] Parker, C.A.; Rees, W.T. *Analyst*, **1960**, *85*, 587.
[4] Wang, L.; Ng, M.K.; Yu, L. *Physical Review B* **2000**, *62,* 4973.