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DONOR-π-ACCEPTOR TYPE SYMMETRIC CYCLIC TRIINDOLES: SYNTHESIS AND PROPERTIES

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Abstract – Donor-π-acceptor type symmetric cyclic triindole derivatives, 10,15-(2-ethylhexy)-2,7,12-triaryl-10,15-dihydro-5*H*-5,10,15-triazadiindeno-[1,2-*a*;1',2'-*c*]fluorenes (**3a-c**) were prepared by the Suzuki-Miyaura cross-coupling reaction of 5,10,15-(2-ethylhexy)-2,7,12-tribromo-10,15-dihydro-5H-5,10,15-triazadiindeno[1,2-*a*;1',2'-*c*]fluorene (**2c**) which was obtained by cyclo-trimerization reaction of *N*-(2-ethylhexyl)-5-bromoindolin-2-one in phosphoryl chloride. These triindole derivatives had reversible redox oxidation potentials (E^o) in cyclic voltammetry, and furthermore, showed photoluminescence due to an intramolecular charge transfer (ICT).

INTRODUCTION

Disc-shaped π-extended molecules such as triphenylene, truxene and hexaazatriphenylene, have been of great interest for the preparation of liquid crystals,[1] fluorescent dyes,[2] organic semiconductors[3] and self-assembling supramolecules.[4] These disc-shaped molecules are cyclotrimers of benzene, indane and pyrazine, and in them properties of independent monomers are accumulated and integrated, to give rise to new functionalities. Symmetric cyclic triindoles are expected to possess strong electron-donating character due to the three electron-rich indole rings. Thus, they can be expected as a new core structure for functional materials. A few reports for the preparation of symmetric cyclic triindoles have been known hitherto[5]; for example, a six-armed symmetric cyclic triindole was prepared and applied to emission materials in organic light emitting diodes.[6]

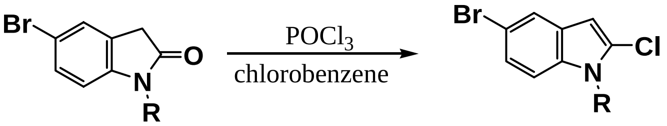
Triindole-ring unsubstituted derivative, 5,10,15-tris-(2-ethylhexyl)-10,15-dihydro- 5*H*-5,10,15-triaza-diindeno[1,2-*a*;1',2'-*c*]fluorene, was prepared and found to be unstable under light and air, due to the strong electron-donating character of the triindole ring.[7] This fact shows that acceptor groups are needed to stabilize a symmetric cyclic triindole structure.

In this paper, donor-acceptor type symmetric cyclic triindole derivatives were prepared and their electrochemical and optical characters were investigated.

RESULTS AND DISCUSSION

1. Synthesis of triindole derivatives

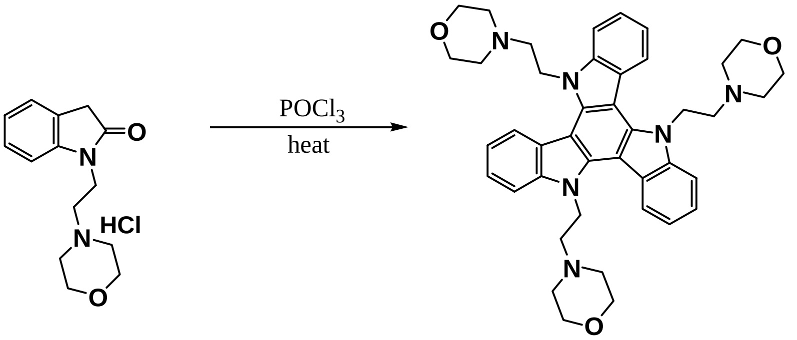
Recently, we reported that *N*-hexyl (**1a**) or *N*-(2-ethylhexyl)-5-bromoindolin-2-ones (**1b**) gave *N*-hexyl or *N*-(2-ethyhexyl)-5-bromo-2-chloroindoles in the reaction with phosphoryl chloride in chlorobenzene at 100 °C (Scheme 1).[8]



1a:R= *n*-hexyl
1b:R= 2-ethylhexyl

Scheme 1

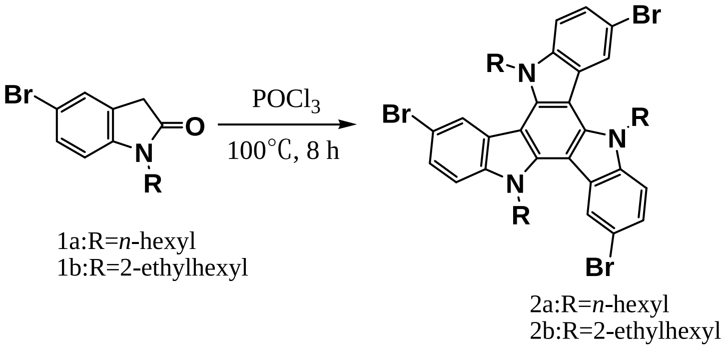
It was previously reported that 1,3-dihydro-1-[2-(4-morpholinyl)ethyl]-2*H*-indol-2-one hydrochloride cyclo-trimerized under severe reaction conditions, giving 5,10,15-[2-(4-morpholinyl)ethyl]-10,15-dihydro]-5*H*-5,10,15-triazadiindeno[1,2-*a*;1',2'-*c*]fluorene (Scheme 2).[5a]



Scheme 2

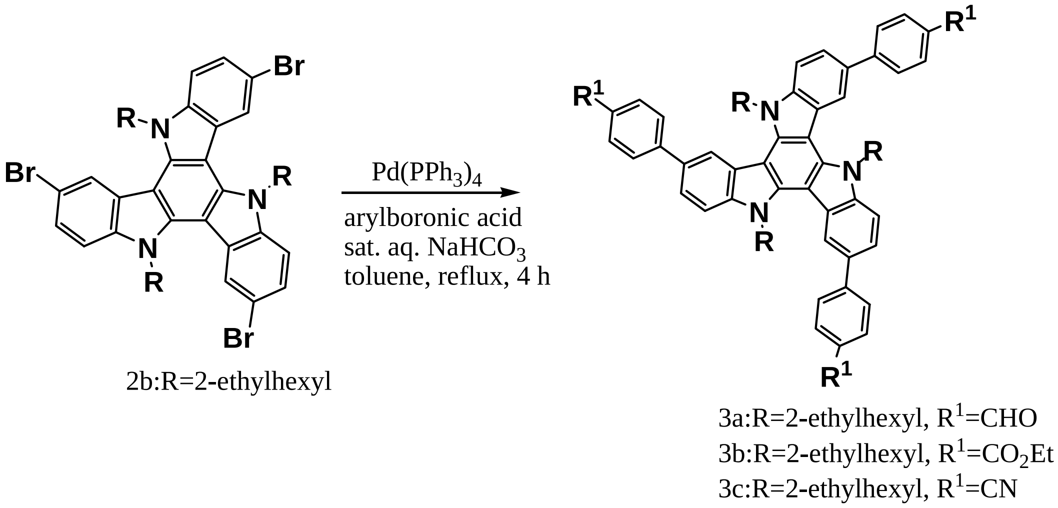
When *N*-hexyl (**1a**) or *N*-(2-ethyl)hexyl-5-bromoindolin-2-one (**1b**) was treated in phosphoryl chloride without any solvent at 100 °C, the expected symmetric cyclic triindoles (**2a**, **2b**) were produced in 29%

and 23% yields, respectively (Scheme 3). On the other hand, *N*-methyl-5-bromoindolin-2-one gave unidentified insoluble solid materials.



Scheme 3

The bromo atoms of **2b** were reactive in the Suzuki-Miyaura cross-coupling reaction[9]. Thus, triindole (**2b**) was reacted with arylboronic acids having an electron-withdrawing substituent such as formyl, cyano and ester groups in order to create a donor (D)-π-acceptor (A) system. The desired symmetric cyclic triaryl-triindoles were obtained, each, in 24% (**3a**), 39% (**3b**) and 26% (**3c**) yields (Scheme 4).



Scheme 4

2. Electrochemical and optical properties of 3a-c

The electrochemical properties of **3a-c** were studied by cyclic voltammetry measurements in benzonitrile in the presence of Bu_4NPF_6 as supporting electrolyte using a glassy-carbon working electrode and Ag/AgCl couple in electrolyte solution as a reference at room temperature (Figure 1). The cyclic voltammogram curve of **3a-c** exhibited a well-defined reversible

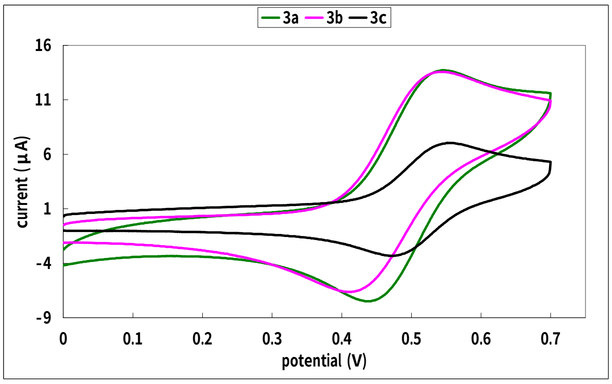


Figure 1 Cyclic voltammogram of **3a-c**

redox wave. Oxidation potentials ($\mathbf{E^o}$) associated with generation of the cation radical were evaluated at 0.50 (**3a**), 0.48 (**3b**) and 0.51 V (**3c**), each.[11] These reversible oxidation potentials ($\mathbf{E^o}$) were not seen in the corresponding indole derivatives. It was supposed that in the radical cations of **3**, the reactive sites (3 and 5 positions of the indole ring) were occupied; thus, the triindole ring is resistant to electrochemical degradation.[10] These low oxidation potentials ($\mathbf{E^o}$) suggest a better electron-donating ability of **3** than those of indole or carbazole derivatives. Triindoles (**3a-c**) have three electron-withdrawing groups; nevertheless, in the cathodic wave, no peak potentials ($\mathbf{E_{pc}}$) are observed.[12]

UV-vis and fluorescence emission data of **3** are shown in Figure 2 and Table 1. Disc-shaped molecules tend to aggregate due to their large planar structures; however, **3** did not form any aggregates under UV-vis and ^{1}H-NMR measurement conditions. The UV-vis spectra exhibited an absorption band around 365 nm for **3a** and around 350 nm for **3b** and **3c**. The spectra were solvent-independent in dichloromethane and toluene. On the other hand, the fluorescent spectra of **3a-c** were solvatochromic; especially that of **3a** were strongly solvent-dependent. Compound (**3a**) showed strong fluorescence at 462 nm in toluene with quantum yield of 0.52. In dichloromethane, the fluorescence was observed at 582 nm, exhibiting a large red-shift of 120 nm. The quantum yield drastically decreased to 0.016. Fluorescence spectra of **3b** and **3c** were observed around 425 nm in toluene. Similar to **3a**, **3b** and **3c** showed fluorescent-solvatochromism in dichloromethane, but to less extent; they emitted fluorescence at 509 and 480 nm, respectively. Their quantum yields in toluene (0.47 and 0.49) were similar to those (0.39 and 0.47) in dichloromethane.

The fluorescent solvatochromism and unresolved vibronic structure of UV-vis and fluorescent spectra mentioned above indicated the presence of intramolecular charge transfer (ICT) between the central donor triindole ring part and the acceptor end part in **3**. A large solvatochromism of formyl derivative (**3a**) with the poor quantum yield suggested a contribution of a quinoid structure in the excited state, like mero-cyanine dyes[13], leading to increased ICT character and quenching by a polar solvent. In **3b,** such a delocalized planar structure may contribute to less extent, because of the bulky ester group. The effect of the cyano substituent was not explained clearly.[14] Compounds (**3**) are fluorescent in the solid state, as well.

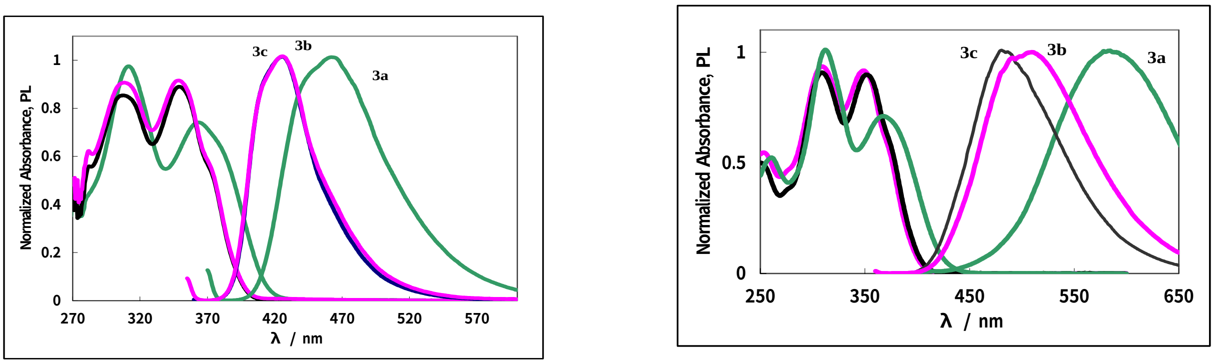


Figure 2 UV-vis and fluorescence spectra of **3a-c** in toluene (left) or dichloromethane (right)

Table 1 UV-vis and PL spectra of **3a-c**[a]

Compd	λmax(nm)	logε	λem(nm)	λem(nm) solid	φ[b]
3a	363 (367)	4.87 (4.85)	462 (582)	540	0.52 (0.016[c])
3b	349 (349)	4.96 (4.96)	426 (509)	453	0.47 (0.39)
3c	351 (349)	4.95 (4.95)	425 (480)	461	0.49 (0.47)

[a] UV-vis and fluorescence spectra were measured in toluene (dichloromethane) in 10^{-5} M (UV-vis) or 10^{-6} M (fluorescence). [b] Quinine sulfate (φ = 0.55) as a standard [c] Rhodamine B (φ = 0.65) as a standard

CONCLUSION

Symmetric cyclic triaryl-triindoles (**3a-c**) of donor-acceptor type were prepared using the Suzuki-Miyaura cross-coupling reaction of **2b**. These triindoles were stable towards light and air. They exhibited reversible oxidation potentials (E^0) around 0.5 V (vs Ag/AgCl). Compounds (**3a-c**) emitted, in solution as well as in solid state, relatively strong fluorescence of ICT character between the donor triindole part and the acceptor end aryl groups.

EXPERIMENTAL

General

All melting points are uncorrected. ^{1}H-NMR spectra were determined in $CDCl_3$ with a VARIAN Mercury 300 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (*J*) are reported in hertz (Hz). Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Electron impact mass spectrometry (EI-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer at 70 eV using a direct inlet system. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. UV-vis spectra were measured on a JASCO V-570 spectrophotometer in a 1.0 cm width quartz cell (0.01 mM). Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer. Cyclic voltammetry measurements were performed on BAS model 600 electrochemical analyzer in deaerated benzonitrile solution (0.5 mM) containing tetrabutyl ammonium hexafluorophosphate (0.1 M) as a supporting electrolyte at 298 K (100 mV s^{-1}). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode. Analytical TLC was carried out on silica gel coated on glass plate (Merck 60 F_{254}).

Column chromatography was carried out on silica gel (KANTO 60N). Reagents were purchased from commercial suppliers and used without further purification.

General Procedure for the Preparation of 5,10,15-alkyl-2,7,12-tribromo-10,15-dihydro-5*H*-5,10,15-triazadiindeno[1,2-*a*;1',2'-*c*]fluorenes (2a) and (2b)

To a mixture of *N*-hexyl-5-bromoindolin-2-one (**1a**) (40 g, 135 mmol) and phosphoryl chloride (240 mL) were heated at 100 ℃ for 8 h. The reaction mixture was evaporated in vacuo to remove phosphoryl chloride. The residue was added water and neutralized with aqueous NaOH. The resulting solid was filtered, washed with water and dissolved in boiling toluene (300 mL). The solution was filtered and evaporated in vacuo to dryness. The residue (brown solid) was recrystallized from toluene/AcOEt (1:9, v/v) to give **2a** in 29% yield (10.9 g, 13.1 mmol).

white solid: mp 207 ℃: FAB-MS (NBA, positive); m/z 831(M^+), 833, 835: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J*=6.9 Hz, 9H), 1.19-1.41 m, 18H), 1.88-2.10 (m, 6H), 4.59 (t, *J*=8.3 Hz, 6H), 7.41 (d, *J*=8.7 Hz, 3H), 7.52 (dd, J=1.5, 8.7 Hz, 3H), 8.21(d, *J*=1.5 Hz, 3H): ^{13}C-NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 26.3, 30.2, 31.6, 47.1, 102.0, 111.6, 113.1, 123.8, 124.5, 125.6, 139.0, 139.3: Anal. Calcd for $C_{48}H_{60}N_3Br_3$: C, 62.75; H, 6.58; N, 4.57. Found: C, 62.75; H, 6.61; N, 4.56.

5,10,15-Tris(2-ethylhexyl)-2,7,12-tribromo-10,15-dihydro-5*H*-5,10,15-triazadiindeno[1,2-*a*;1',2'-*c*]-fluorene (2b)

According to a method similar to the preparation of **2a**, **2b** was obtained in 23% yield from *N*-(2-ethylhexyl)-5-bromoindolin-2-one (**1b**). The crude product was purified by recrystallization from hexane.

white solid: mp 170 ℃: FAB-MS (NBA, positive); m/z : m/z 915(M^+), 917, 919: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.30-0.39 (m, 9H), 0.50-0.67 (m, 9H), 0.69-1.00 (m,15H), 1.57-1.80 (m, 3H), 4.22 (bs, 6H), 7.43 (d, *J*=8.4 Hz, 3H), 7.57 (d, *J*=8.4 Hz, 3H), 7.85 (s, 3H): Anal. Calcd for $C_{42}H_{48}N_3Br_3$: C, 60.44; H, 5.80; N, 5.03. Found: C, 60.49; H, 5.79; N, 4.99.

5,10,15-Tris(2-ethylhexyl)-2,7,12-tris(4-formylphenyl)-10,15-dihydro-5*H*-5,10,15-triazadiindeno-[1,2-*a*;1',2'-*c*]fluorene (3a)

To a mixture of **2b** (459 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium(0) (5 mol%) in toluene (80 mL), and saturated aqueous $NaHCO_3$ (40 mL) was added 4-formylphenylboronic acid (680 mg, 4.5 mmol) in ethanol (5 mL) under a nitrogen atmosphere. The resulting mixture was heated at refluxing temperature for 4 h. The reaction mixture was poured into water and extracted with AcOEt (100 mL). The organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo to dryness. The residue was separated by silica gel column chromatography (KANTO 60N) eluting with $CHCl_3$ to give **3a** in 24.0% yield (119 mg, 0.120 mmol).

yellow powder: mp 246 °C: FAB-MS (NBA, positive); m/z 994 [(M+H)$^+$]: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.40-0.45 (m, 9H), 0.58-0.63 (m, 9H), 0.64-0.79 (m, 6H), 0.81-1.05 (m, 18H), 2.00-2.15 (m, 3H), 4.99 (d, *J*=7.2 Hz, 6H), 7.69 (d, *J*=8.4 Hz, 3H), 7.76 (dd, *J*=1.2, 8.4 Hz, 3H), 7.96 d, *J*=8.3 Hz, 6H), 8.05 (d, *J*=8.3 Hz, 6H), 8.53 (s, 3H): Anal. Calcd for $C_{69}H_{75}N_3O_3$: C, 83.34; H, 7.60; N, 4.23. Found: 83.24; H, 7.52; N, 4.08.

5,10,15-Tris(2-ethylhexyl)-2,7,12-tris(4-ethoxycarbonylphenyl)-10,15-dihydro-5*H*-5,10,15-triazadiindeno [1,2-*a*;1',2'-*c*]fluorene (3b)

According to a method similar to the preparation of **3a**, **3b** was obtained in 39% yield from **2b**.

light yellow-green powder: mp 205 °C: FAB-MS (NBA, positive); m/z 1126 [(M+H)$^+$]: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.32-0.46 (m, 9H), 0.54-0.77 (m, 15H), 0.81-1.40 (m, 18H), 1.47 (t, *J*=7.1 Hz, 6H), 1.93-2.40 (m, 3H), 4.47 (quartet, *J*=7.1 Hz, 6H), 4.80-4.90 (m, 6H), 7.57 (d, *J*=8.3 Hz, 3H), 7.70 (d, *J*=8.3 Hz, 3H), 7.88 (d, *J*=8.6 Hz, 6H), 8.24 (d, J=8.6 Hz, 6H), 8.38 (s, 3H): HR-MS (FAB): Calcd for 1126.6673; Found: 1126.6676: Anal. Calcd for $C_{75}H_{87}N_3O_6$: C, 79.96; H, 7.78; N, 3.73. Found: C, 79.85; H, 7.77; N, 3.80.

5,10,15-Tris(2-ethylhexyl)-2,7,12-tris(4-cyanophenyl)-10,15-dihydro-5*H*-5,10,15-triazadiindeno [1,2-*a*;1',2'-*c*]fluorene (3c)

According to a method similar to the preparation of **3a**, **3c** was obtained in 26% yield from **2b**.

light yellow-green powder: mp 333 °C: FAB-MS (NBA, positive); m/z 985 [(M+H)$^+$]: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.40-0.48 (m, 9H), 0.58-0.63 (m, 9H), 0.72-0.80 (m, 6H), 0.81-1.10 (m, 18H), 2.00-2.17 (m, 3H), 5.00 (d, *J*=7.8 Hz, 6H), 7.70 (dd, *J*=1.5, 8.6 Hz, 3H), 7.74 (d, *J*=8.6 Hz, 3H), 7.80 (d, *J*=8.7 Hz, 6H), 7.88 (d, *J*=8.7 Hz, 6H), 8.51 (s, 4H): HR-MS (FAB): Calcd for 985.5897; Found: 985.5903: Calcd for $C_{69}H_{72}N_6$: C, 84.11; H, 7.37; N, 8.53. Found: C, 83.89; H, 7.36; N, 8.34.

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