## Supporting Information

Stereogenic Motif Consisting of Rigid Ring and Intraannular Chains: Isolation and Structures of Stereoisomers of 9-Alkyl-1,8-anthrylene-butadiynylene Cyclic Dimers Shinji Toyota,* Hiroyuki Onishi, Yoshihiro Kawai, Takaaki Morimoto, Hiroaki Miyahara, Tetsuya Iwanaga, Kan Wakamatsu
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## 1. Experimental Details

General. Melting points are uncorrected. NMR spectra were measured on a Varian Gemini-300 ( $\left.{ }^{1} \mathrm{H}: 300 \mathrm{MHz},{ }^{13} \mathrm{C}: 75 \mathrm{MHz}\right)$ or a JEOL GSX-400 ( ${ }^{1} \mathrm{H}: 400 \mathrm{MHz},{ }^{13} \mathrm{C}: 100 \mathrm{MHz}$ ) spectrometer. The ${ }^{13} \mathrm{C}$ NMR spectra of $\mathbf{3 a}$ and anti- $\mathbf{3 b}$ could not be measured because of the low solubility. High-resolution mass spectra were measured on a JEOL MStation-700 spectrometer by the FAB method. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. UV spectra were measure on a Hitachi U-3000 spectrometer with a 10 mm cell. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell. 1,8-Dichloro-9-anthrone $\mathbf{4}$ was prepared by the literature method [House, H . O.; Hrabie, J. A.; VanDerveer, D. J. Org. Chem., 1986, 51, 921]. Experimental procedures are described in details for the ethyl compound and the other compounds were similarly prepared unless otherwise mentioned.

1,8-Dichloro-9-ethylanthracene (5a). A solution of ethylmagnesium bromide in ether ( 150 mL ) was prepared from $\mathrm{Mg}(834 \mathrm{mg}, 34.2 \mathrm{mmol})$ and bromoethane ( $2.64 \mathrm{~mL}, 34.2$ $\mathrm{mmol})$ in an ordinary method. To the solution was added 1,8-dichloro-9-anthrone $4(3.00 \mathrm{~g}$, 11.4 mmol ), and the reaction mixture was stirred for 18 h at room temperature under Ar. This solution was quenched with aq $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{ca} .50 \mathrm{~mL})$, and the organic layer was separated. This solution was washed with aq NaCl , dried over $\mathrm{MgSO}_{4}$, and evaporated. The residual red oil, crude 1,8 -dichloro- 9 -anthrol, was dissolved in benzene ( 50 mL ), and thionyl chloride ( 8.6 mL ,
$120 \mathrm{mmol})$ and pyridine ( $15.8 \mathrm{~mL}, 216 \mathrm{mmol}$ ) were added to the solution. This reaction mixture was stirred for 90 min at room temperature, and quenched with water $(30 \mathrm{~mL})$. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic solution was washed with aq NaCl , dried over $\mathrm{MgSO}_{4}$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent. Recrystallizaiton from hexane gave the desired compound as yellow crystals. Yield 1.97 g ( $63 \%$ ); mp 197-199 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.98(3 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 4.23(2 \mathrm{H}, \mathrm{q}, J=7.1$ $\mathrm{Hz}), 7.30(2 \mathrm{H}, \mathrm{dd}, J=7.1,8.6 \mathrm{~Hz}), 7.56(2 \mathrm{H}, \mathrm{d}, J=6.4 \mathrm{~Hz}), 7.84(2 \mathrm{H}, \mathrm{d}, J=8.6 \mathrm{~Hz}), 8.21$ $(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=17.6,28.5,124.9,126.5,128.3,129.4,130.2,131.2,133.6$, 141.2; HRMS (FAB) calcd for $\mathrm{C}_{16} \mathrm{H}_{12}{ }^{35} \mathrm{Cl}_{2}: 274.0316[\mathrm{M}]^{+}$, found $\mathrm{m} / \mathrm{z}$ 274.0338; Anal. calcd for $\mathrm{C}_{16} \mathrm{H}_{12} \mathrm{Cl}_{2}$ : C, $69.84 ; \mathrm{H}, 4.40 \%$, found: $\mathrm{C}, 70.23 ; \mathrm{H}, 4.14 \%$.



9-Ethyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (6a). A solution of [(trimethylsilyl)ethynyl]magnesium bromide in THF ( 15 mL ) was prepared from (trimethylsilyl)ethyne ( $0.448 \mathrm{~mL}, 3.24 \mathrm{mmol}$ ) and a $1.0 \mathrm{~mol} \mathrm{~L}^{-1}$ ether solution of ethylmagnesium bromide ( $3.24 \mathrm{~mL}, 3.24 \mathrm{mmol}$ ). To the solution was added $\mathbf{5 a}(300 \mathrm{mg}, 1.08$ $\mathrm{mmol})$, $\left[\mathrm{Ni}(\mathrm{acac})_{2}\right](19.4 \mathrm{mg}, 0.076 \mathrm{mmol})$, and $\mathrm{PPh}_{3}(19.8 \mathrm{mg}, 0.076 \mathrm{mmol})$. The mixture was refluxed for 48 h under Ar , and then quenched by the slow addition of aq $\mathrm{NH}_{4} \mathrm{Cl}(20 \mathrm{~mL})$. The organic layer was separated, dried over $\mathrm{MgSO}_{4}$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent. Recrystallization from hexane afforded the desired compound as dark red crystals. A small amount of monosilylated product was obtained. Yield $475 \mathrm{mg}(87 \%) ; \mathrm{mp} 64-65^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.32(18 \mathrm{H}$, s), $1.49(3 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 5.02(2 \mathrm{H}, \mathrm{q}, J=7.1 \mathrm{~Hz}), 7.33(2 \mathrm{H}, \mathrm{dd}, J=7.8,7.1 \mathrm{~Hz}), 7.89(2 \mathrm{H}$, d, $J=7.1 \mathrm{~Hz}), 7.92(2 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 8.21(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta=0.2,19.8,23.2$,
98.7, 108.2, 119.7, 124.1, 128.1, 129.5, 131.0, 132.2, 137.2, 144.2; HRMS (FAB) calcd for $\mathrm{C}_{26} \mathrm{H}_{30} \mathrm{Si}_{2}: 398.1886[\mathrm{M}]^{+}$, found $m / z 398.1839$; Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{30} \mathrm{Si}_{2}$ : C, $78.33 ; \mathrm{H}, 7.58 \%$, found: C, $78.72 ; \mathrm{H}, 7.54 \%$.

9-Ethyl-1,8-diethynylanthracene (7a). A solution of $\mathbf{6 a}(100 \mathrm{mg}, 0.250 \mathrm{mmol})$ in THF ( 30 mL ) was treated with a $1.0 \mathrm{~mol} \mathrm{~L}^{-1}$ THF solution of TBAF ( $0.50 \mathrm{~mL}, 0.50 \mathrm{mmol}$ ). After the solution was stirred for 25 min at room temperature, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired compound as pale yellow powders. For preparative purpose, the crude product can be used without purification for the next reaction. Yield $62 \mathrm{mg}(97 \%)$; mp $104-109^{\circ} \mathrm{C}$ (dec); ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=1.51(3 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 3.53(2 \mathrm{H}, \mathrm{s}), 4.91(2 \mathrm{H}, \mathrm{q}, J=7.1 \mathrm{~Hz})$, $7.37(2 \mathrm{H}, \mathrm{t}, J=7.5 \mathrm{~Hz}), 7.91(2 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 7.95(2 \mathrm{H}, \mathrm{d}, J=7.9 \mathrm{~Hz}), 8.29(1 \mathrm{H}, \mathrm{s}),{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=19.6,23.4,81.8,86.5,118.7,124.1,128.2,129.6,131.2,132.2,137.6$, 140.8; HRMS (FAB) calcd for $\mathrm{C}_{20} \mathrm{H}_{14}: 254.1096[\mathrm{M}]^{+}$, found $m / z$ 254.1101; Anal. calcd for $\mathrm{C}_{20} \mathrm{H}_{14}: \mathrm{C}, 94.45 ; \mathrm{H}, 5.55 \%$, found: C, $94.11 ; \mathrm{H}, 5.44 \%$.

Cyclic Dimer 3a ( $\mathbf{R}=\mathbf{E t}$ ). A crude of $\mathbf{7 a}$ prepared from $\mathbf{6 a}(100 \mathrm{mg}, 0.250 \mathrm{mmol})$ by the above method was dissolved in pyridine ( 60 mL ). To the solution were added $\mathrm{Cu}(\mathrm{OAc})_{2} \cdot \mathrm{H}_{2} \mathrm{O}(1.25 \mathrm{~g}, 6.25 \mathrm{mmol})$ and $\mathrm{CuCl}(495 \mathrm{mg}, 5.00 \mathrm{mmol})$. After the mixture was stirred for 25 min , the solvent was mostly removed by evaporation. The residue was subjected to chromatography on silica gel (NH) with chloroform eluent to remove insoluble materials. The eluted compound was further purified by chromatography on silica gel (NH) with hexane-chloroform (3:1) eluent. Recrystallization from hexane-chloroform afforded the desired compound as red powders. Yield $34 \mathrm{mg}\left(54 \%\right.$ from 6a); $\mathrm{mp} 270-273{ }^{\circ} \mathrm{C}(\mathrm{dec}) ; R_{\mathrm{f}}$ 0.48 (hexane-chloroform 3:1); ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta=1.13(6 \mathrm{H}, \mathrm{br}), 4.70(4 \mathrm{H}, \mathrm{br}), 7.42(4 \mathrm{H}$, dd, $J=8.6,7.9 \mathrm{~Hz}), 7.83(4 \mathrm{H}, \mathrm{d}, J=7.9 \mathrm{~Hz}), 8.00(4 \mathrm{H}, \mathrm{d}, J=8.6 \mathrm{~Hz}), 8.28(2 \mathrm{H}, \mathrm{s}) ; \mathrm{UV}$ $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }}(\varepsilon) 257$ (38500), 283 (45700), 314 (23800), 438 ( $6400, \mathrm{sh}$ ), 463 (15800), 494 (28800); FL $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }} 506,537 \mathrm{~nm}, \lambda_{\mathrm{ex}} 393 \mathrm{~nm}\left(\Phi_{\mathrm{f}} 0.43\right)$; HRMS (FAB) calcd for $\mathrm{C}_{40} \mathrm{H}_{24}$ : $504.1878[\mathrm{M}]^{+}$, found $m / z 504.1903$; Anal. calcd for $\mathrm{C}_{40} \mathrm{H}_{24}$ : C, $95.21 ; \mathrm{H}, 4.79 \%$, found: C, 94.94; H, 4.62\%.

1,8-Dichloro-9-propylanthracene (5b). This compound was similarly prepared from 4 and propylmagnesium bromide. The crude product was purified by chromatography on silica gel to give the desired compound as yellow powders. Yield $47 \% ; \mathrm{mp} 99-102{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.63(3 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}), 1.35(2 \mathrm{H}$, sextet, $J=7.2 \mathrm{~Hz}), 4.17(2 \mathrm{H}, \mathrm{t}, J=7.2$ $\mathrm{Hz}), 7.31(2 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 7.57(2 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 7.86(2 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=14.1,26.5,37.5,124.9,126.4,128.3,129.4,130.5,131.3,133.5,139.7$; HRMS
(FAB) calcd for $\mathrm{C}_{17} \mathrm{H}_{14}{ }^{35} \mathrm{Cl}_{2}: 288.0473[\mathrm{M}]^{+}$, found $m / z 288.0444$; Anal. calcd for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{Cl}_{2}$ : C, 70.60 ; H, $4.88 \%$, found: C, 70.59 ; H, $5.16 \%$.

9-Propyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (6b). This compound was similarly prepared from $\mathbf{5 b}$. The crude product was purified by chromatography on silica gel to give the desired compound as brown solid. Yield $56 \%$; mp $77-80{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta$ $=0.33(18 \mathrm{H}, \mathrm{s}), 1.02(3 \mathrm{H}, \mathrm{t}, J=7.5 \mathrm{~Hz}), 1.69(2 \mathrm{H}$, septet, $J=6.9 \mathrm{~Hz}), 5.00(2 \mathrm{H}, \mathrm{t}, J=8.3 \mathrm{~Hz})$, $7.33(2 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}), 7.84(2 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz}), 7.89(2 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz}), 8.22(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.0,13.5,26.9,31.9,99.4,108.1,119.9,124.1,127.6,129.9,130.8,132.1$, 137.2, 140.2; HRMS (FAB) calcd for $\mathrm{C}_{27} \mathrm{H}_{32} \mathrm{Si}_{2}: 412.2043$ [M] ${ }^{+}$, found $m / z$ 412.2006; Anal. calcd for $\mathrm{C}_{27} \mathrm{H}_{32} \mathrm{Si}_{2}$ : C, $78.57 ; \mathrm{H}, 7.82 \%$, found: C, $78.81 ; \mathrm{H}, 8.03 \%$.

1,8-Diethynyl-9-propylanthracene (7b). This compound was similarly prepared from $\mathbf{6 b}$. The crude product was purified by chromatography on silica gel to give the desired compound as brown solid. Yield $84 \%$; mp $102-104{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta=1.08(3 \mathrm{H}, \mathrm{t}, J=$ $7.2 \mathrm{~Hz}), 1.97(2 \mathrm{H}$, sextet, $J=7.3 \mathrm{~Hz}), 3.53(2 \mathrm{H}, \mathrm{s}), 4.76(2 \mathrm{H}, \mathrm{t}, J=8.6 \mathrm{~Hz}), 7.37(2 \mathrm{H}, \mathrm{dd}, J=$ $7.2,6.8 \mathrm{~Hz}), 7.90(2 \mathrm{H}, \mathrm{d}, J=6.8 \mathrm{~Hz}), 7.96(2 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz}), 8.30(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=12.6,27.4,31.7,81.4,86.6,118.7,124.0,128.2,129.9,131.2,132.0,137.7$, 139.3; HRMS (FAB) calcd for $\mathrm{C}_{21} \mathrm{H}_{16}: 268.1252[\mathrm{M}]^{+}$, found $m / z$ 268.1234; Anal. calcd for $\mathrm{C}_{21} \mathrm{H}_{16}$ : C, 93.99 ; H, $6.01 \%$, found: C, $94.27 ; \mathrm{H}, 6.06 \%$.

Cyclic Dimer 3b $(\mathbf{R}=\mathbf{P r})$. This compound was similarly prepared from $\mathbf{6 b}$. The reaction mixture was stirred for 1 h . The crude product was purified by chromatography on silica gel (NH) with hexane-chloroform (8:1) eluent to give a mixture of isomers in $49 \%$ yield from $\mathbf{6 b}$. Further chromatographic separation afforded the anti isomer ( $16 \%$ ) and the syn isomer ( $10 \%$ ). anti-3b: red solid; mp 280-290 ${ }^{\circ} \mathrm{C}(\mathrm{dec}) ; R_{\mathrm{f}} 0.61$ (hexane-chloroform 3:1); ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta=0.54(6 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 1.48(4 \mathrm{H}, \mathrm{m}), 4.60(4 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz})$, $7.43(4 \mathrm{H}, \mathrm{dd}, J=7.1,8.2 \mathrm{~Hz}), 7.82(4 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 8.00(4 \mathrm{H}, \mathrm{d}, J=8.2 \mathrm{~Hz}), 8.28(2 \mathrm{H}, \mathrm{s})$; $\mathrm{UV}\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }}(\varepsilon) 256$ (45900), 280 (50600), 314 (26200), 435 ( 7400 , sh), 460 (19300), 491 (37200) nm; FL $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }} 501,533 \mathrm{~nm}, \lambda_{\mathrm{ex}} 393 \mathrm{~nm}\left(\Phi_{\mathrm{f}} 0.35\right)$; HRMS (FAB) calcd for $\mathrm{C}_{42} \mathrm{H}_{28}$ : $532.2191[\mathrm{M}]^{+}$, found $m / z 532.2219$. syn-3b: orange solid; mp $182-195{ }^{\circ} \mathrm{C}(\mathrm{dec}) ; R_{\mathrm{f}}$ 0.48 (hexane-chloroform 3:1); ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.59(6 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 1.59(4 \mathrm{H}, \mathrm{m})$, $4.68(4 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 7.41(4 \mathrm{H}, \mathrm{dd}, J=7.0,8.2 \mathrm{~Hz}), 7.81(4 \mathrm{H}, \mathrm{d}, J=7.0 \mathrm{~Hz}), 7.98(4 \mathrm{H}, \mathrm{d}, J$ $=8.2 \mathrm{~Hz}), 8.25(2 \mathrm{H}, \mathrm{s}){ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right) \delta=14.2,26.1,37.6,80.7,86.0,119.0,124.3,126.6$, $130.8,132.0,132.6,134.0,140.3 ; \mathrm{UV}\left(\mathrm{CHCl}_{3}\right) \lambda_{\max }(\varepsilon) 257$ (45900), 281 (57700), 313 (27500), 437 (9900, sh), 463 (19100), 493 (29300) nm; FL $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }} 504,537 \mathrm{~nm}, \lambda_{\text {ex }} 393$ $\mathrm{nm}\left(\Phi_{\mathrm{f}} 0.32\right)$; HRMS (FAB) calcd for $\mathrm{C}_{42} \mathrm{H}_{28}: 532.2191[\mathrm{M}]^{+}$, found $m / z 532.2172$.

9-Butyl-1,8-dichloro-9-anthracene (5c). This compound was similarly prepared from 4 and butylmagnesium bromide. The crude product was purified by chromatography on silica gel to give the desired compound as a yellow oil. Yield $25 \%$; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=$ $0.71(3 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 1.04(2 \mathrm{H}, \mathrm{q}, J=7.1 \mathrm{~Hz}), 1.26(2 \mathrm{H}$, sextet, $J=7.9 \mathrm{~Hz}), 4.20(2 \mathrm{H}, \mathrm{t}, J$ $=7.9 \mathrm{~Hz}), 7.28(2 \mathrm{H}, \mathrm{dd}, J=7.1,7.9 \mathrm{~Hz}), 7.54(2 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 7.80(2 \mathrm{H}, \mathrm{d}, J=7.9 \mathrm{~Hz})$, $8.16(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=13.8,22.9,35.3,124.9,126.3,128.2,129.3,130.4,131.2$, 133.4, 139.8; HRMS (FAB) calcd for $\mathrm{C}_{18} \mathrm{H}_{16}{ }^{35} \mathrm{Cl}_{2}: 426.2199$ [M] ${ }^{+}$, found $m / z 426.2152$.

9-Butyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (6c). This compound was similarly prepared from $\mathbf{5 c}$. The crude product was purified by chromatography on silica gel to give the desired compound as yellow crystals. Yield $80 \%$; mp $64-66{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ $\delta=0.35(18 \mathrm{H}, \mathrm{s}), 0.90(4 \mathrm{H}, \mathrm{t}, J=7.3 \mathrm{~Hz}), 1.46(2 \mathrm{H}, \mathrm{m}), 1.62(2 \mathrm{H}, \mathrm{m}), 4.81(2 \mathrm{H}, \mathrm{t}, J=8.6$ $\mathrm{Hz}), 7.35(2 \mathrm{H}, \mathrm{dd}, J=8.3,7.1 \mathrm{~Hz}), 7.86(2 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 7.91(2 \mathrm{H}, \mathrm{d}, J=8.3 \mathrm{~Hz}), 8.23$ $(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=14.4,22.0,30.3,36.2,99.4,108.0,119.8,124.1,127.1,129.8$, 130.8, 132.1, 137.1, 140.3; HRMS (FAB) calcd for $\mathrm{C}_{28} \mathrm{H}_{34} \mathrm{Si}_{2}: 426.2199$ [M] ${ }^{+}$, found $\mathrm{m} / \mathrm{z}$ 426.2152; Anal. calcd for $\mathrm{C}_{28} \mathrm{H}_{34} \mathrm{Si}_{2}$ : C, $78.81 ; \mathrm{H}, 8.03 \%$, found: C, $78.53 ; \mathrm{H}, 8.00 \%$.

9-Butyl-1,8-diethynylanthracene (7c). This compound was similarly prepared from 6c. The crude product was purified by chromatography on silica gel to give the desired compound as yellow crystals. Yield $80 \% ; \mathrm{mp} 128-129^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.95(4 \mathrm{H}, \mathrm{t}$, $J=7.3 \mathrm{~Hz}), 1.53(2 \mathrm{H}, \mathrm{m}), 1.85(2 \mathrm{H}, \mathrm{m}), 3.53(1 \mathrm{H}, \mathrm{s}), 4.81(2 \mathrm{H}, \mathrm{t}, J=8.6 \mathrm{~Hz}), 7.35(2 \mathrm{H}, \mathrm{dd}, J$ $=8.4,7.0 \mathrm{~Hz}), 7.89(2 \mathrm{H}, \mathrm{d}, J=7.0 \mathrm{~Hz}), 7.93(2 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz}), 8.27(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=14.6,21.8,30.2,36.5,81.6,86.6,118.7,124.1,128.1,129.9,131.2,132.1,137.2$, 139.6; HRMS (FAB) calcd for $\mathrm{C}_{22} \mathrm{H}_{18}: 282.1409[\mathrm{M}]^{+}$, found $m / z$ 282.1437; Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18}$ : C, 93.57 ; H, $6.43 \%$, found: C, $93.32 ; \mathrm{H}, 6.63 \%$.

Cyclic Dimer 3c $(\mathbf{R}=\mathbf{B u})$. This compound was similarly prepared from $\mathbf{6 c}$. The reaction mixture was stirred for 1 h . The crude product was purified by chromatography on silica gel (NH) with hexane-chloroform (3:1) eluent to give a mixture of the isomers in $52 \%$ yield from 6c. Further chromatographic separation afforded the anti and syn isomers as the first and second fractions, respectively. anti-3c: red crystals; yield $30 \%$; mp $243-245{ }^{\circ} \mathrm{C}$ (dec); $R_{\mathrm{f}} 0.60$ (hexane-chloroform 3:1); ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.59(6 \mathrm{H}, \mathrm{t}, J=7.8 \mathrm{~Hz}), 0.94$ $(4 \mathrm{H}, \mathrm{m}), 1.41(4 \mathrm{H}, \mathrm{m}), 4.64(4 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}), 7.42(4 \mathrm{H}, \mathrm{dd}, J=7.2,8.7 \mathrm{~Hz}), 7.82(4 \mathrm{H}, \mathrm{d}, J$ $=7.2 \mathrm{~Hz}), 7.99(4 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz}), 8.28(2 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=13.7,22.7,34.6,34.9$, 80.7, 86.3, 119.1, 124.4, 126.8, 130.8, 132.2, 132.5, 134.5, 140.4; UV $\left(\mathrm{CHCl}_{3}\right) \lambda_{\max }(\varepsilon) 256$ (76700), 280 (83200), 314 (43000), 435 (12600, sh), 461 (32100), 492 (61000) nm; FL $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }} 501,534 \mathrm{~nm}, \lambda_{\text {ex }} 393 \mathrm{~nm}\left(\Phi_{\mathrm{f}} 0.36\right)$; HRMS (FAB) calcd for $\mathrm{C}_{44} \mathrm{H}_{32}: 560.2504$ $[\mathrm{M}]^{+}$, found $\mathrm{m} / \mathrm{z} 560.2516$. syn-3c: orange crystals; yield $10 \%$; mp $178-180^{\circ} \mathrm{C}(\mathrm{dec}) ; R_{\mathrm{f}} 0.48$
(hexane-chloroform 3:1); ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=0.67(6 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 0.96(4 \mathrm{H}, \mathrm{m}), 1.55$ $(4 \mathrm{H}, \mathrm{m}), 4.73(4 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 7.41(4 \mathrm{H}, \mathrm{dd}, J=8.6,7.1 \mathrm{~Hz}), 7.82(4 \mathrm{H}, \mathrm{d}, J=7.1 \mathrm{~Hz}), 7.98$ $(4 \mathrm{H}, \mathrm{d}, J=8.6 \mathrm{~Hz}), 8.25(2 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta=14.0,22.7,35.1,35.2,80.7,86.0$, 119.0, 124.4, 126.6, 130.8, 132.1, 132.6, 134.1, 140.6; UV $\left(\mathrm{CHCl}_{3}\right) \lambda_{\text {max }}(\varepsilon) 256$ (57900), 280 (63900), 314 ( 31500 ), 434 ( 10200 , sh), 460 (23000), 491 (40300) nm; FL ( $\left.\mathrm{CHCl}_{3}\right) \lambda_{\text {max }} 504$, $537 \mathrm{~nm}, \lambda_{\text {ex }} 393 \mathrm{~nm}\left(\Phi_{\mathrm{f}} 0.40\right)$; HRMS (FAB) calcd for $\mathrm{C}_{44} \mathrm{H}_{32}: 560.2504[\mathrm{M}]^{+}$, found $\mathrm{m} / \mathrm{z}$ 560.2540 .

Kinetics Measurement. About 3 mg of pure anti-3b was dissolved in toluene- $d_{8}$ in an NMR sample tube. This tube was heated in refluxing water, and the isomeric ratios were monitored by signal intensities of NMR signals at appropriate intervals. The ratios of the anti isomer are as follows: ratio (time/s) 1.00 ( 0 ), 0.917 (1800), 0.824 (3600), 0.738 (5400), 0.685 (7200), 0.636 ( 9000 ), 0.590 (10800), 0.542 (14400), 0.528 (18000), 0.515 (21600), 0.474 (43200). The data were analyzed by assuming reversible first-order equilibrium, where the equilibrium constant was 1.11 . The first seven points were applied for least-square fitting to give the following kinetic and thermodynamic parameters: $k=(6.27 \pm 0.15) \times 10^{-5} \mathrm{~s}^{-1}, \Delta G_{373}^{\neq}$ $=122 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta G_{373}^{\circ}=-0.33 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for anti to syn isomer. No isomerization was observed for anti-3c or syn-3c at $110^{\circ} \mathrm{C}$ for 18 h , and the heating for longer time or at higher temperature resulted in significant decomposition. The rate constant of isomerization should be less than $1 \times 10^{-7} \mathrm{~s}^{-1}$ at the temperature corresponding to the barrier of $>146 \mathrm{~kJ} \mathrm{~mol}^{-1}$. For 3a, two sets of ethyl proton signals were measured at $-40^{\circ} \mathrm{C}$ in $\mathrm{CDCl}_{3}: \delta 1.20(6 \mathrm{H}, \mathrm{t}, J=7.1$ $\mathrm{Hz}), 4.74(4 \mathrm{H}, \mathrm{q}, J=7.1 \mathrm{~Hz})$ for the major isomer, and $\delta 1.04(6 \mathrm{H}, \mathrm{t}, J=7.1 \mathrm{~Hz}), 4.55(4 \mathrm{H}, \mathrm{q}$, $J=7.1 \mathrm{~Hz}$ ) for the major isomer in the ratio of $55: 45$. The chemical shift difference and the coalescence temperature of the methylene proton signals were 75 Hz and $5^{\circ} \mathrm{C}$, respectively.

X-ray analysis. Single crystals of anti-3c and syn-3c were obtained by crystallization from chlorobenzene and hexane solutions, respectively. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer or on a Rigaku RAXIS-RAPID imaging plate diffractometer with Mo $K \alpha$ radiation $\left(\lambda=0.71070 \AA\right.$ ) to a maximum $2 \theta$ value of $55.0^{\circ}$. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method (SHELXS-97) and refined by the full-matrix least-squares method on $F^{2}$ (SHELEXL-97). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions.
anti-3c: Formula $\mathrm{C}_{44} \mathrm{H}_{32}, M=560.70$, triclinic, space group $P \overline{1}(\# 2), a=9.0642(7), b=$ 10.2306(7), $c=10.1873(7) \AA, \alpha=113.734(5), \beta=100.374(3), \gamma=111.086(2)^{\circ}, V=$ $746.24(9) \AA^{3}, Z=1, D_{\mathrm{c}}=1.248 \mathrm{~g} / \mathrm{cm}^{3}, \mu(\mathrm{Mo} \mathrm{K} \alpha)=0.070 \mathrm{~mm}^{-1}, T=173 \mathrm{~K}, F(000)=296$,

2819 independent reflections, $R 1=0.0617, \mathrm{w} R 2=0.1673[I>2 \sigma(I)], \mathrm{GOF}=1.07 . \mathrm{CCDC}$ 705746.
syn-3c: Formula $\mathrm{C}_{44} \mathrm{H}_{32}, M=560.70$, triclinic, space group $P \overline{1}$ (\#2), $a=11.1772(7), b$ $=11.9076(14), c=13.265(3) \AA$ 道 $\alpha=72.870(12), \beta=72.915(14), \gamma=68.027(9)^{\circ}, V=$ $1530.6(4) \AA^{3}, Z=2, D_{\mathrm{c}}=1.217 \mathrm{~g} / \mathrm{cm}^{3}, \mu(\mathrm{Mo} \mathrm{K} \alpha)=0.069 \mathrm{~mm}^{-1}, T=113 \mathrm{~K}, F(000)=592$, 6933 independent reflections, $R 1=0.0586, \mathrm{w} R 2=0.1035[I>2 \sigma(I)] \mathrm{GOF}=0.95 . \mathrm{CCDC}$ 705747.

Single crystal of syn-3b was obtained by crystallization from ethanol. The diffraction data was collected on a Rigaku HR-RAXIS imaging plate diffractometer with Mo $\mathrm{K} \alpha$ radiation ( $\lambda=0.71070 \AA$ ) to a maximum $2 \theta$ value of $55.0^{\circ}$. Crystal data for syn-3b: $\mathrm{C}_{42} \mathrm{H}_{28}$, $M=532.64$, orthorhombic, $P \mathrm{bca}(\# 61), a=16.753(4), b=17.878(5), c=18.941(7) \AA, V=$ $5673(3) \AA^{3}, Z=8, D_{\mathrm{c}}=1.247 \mathrm{~g} / \mathrm{cm}^{3}, \mu(\mathrm{Mo} \mathrm{K} \alpha)=0.071 \mathrm{~mm}^{-1}, T=123 \mathrm{~K}, F(000)=2240$, 6419 independent reflections, $R_{1}=0.0651, w R_{2}=0.1264$ for $[I>2 \sigma(I)], G O F=0.98$. CCDC 705748. The X-ray structure is shown in Figure S3.

DFT Calculation. The calculations were carried out with Gaussian 03W program on a Windows computer. The structures were optimized by the hybrid DFT method at the B3LYP/6-31G(d) level. The frequency analysis gave no imaginary frequency for each optimized structure. The optimized structures of the anti and syn isomers of 3a-c are shown in Figure S4.


Figure S1. UV-vis spectra of compounds $\mathbf{3 a}-\mathbf{c}$ in $\mathrm{CHCl}_{3}$.


Figure S2. Fluorescence spectra of $3 \mathbf{a}-\mathbf{c}$ in $\mathrm{CHCl}_{3}$.



Figure S3. ORTEP drawings of syn-3b.
As for disordered carbon atoms marked with *, ellipsoids are placed at one of the positions for clarity.
$\mathbf{3 a}$ (Et)




Figure S4. Optimized structures of anti-3 and syn-3 at the B3LYP/6-31G(d) level. Relative energies are indicated above the arrows.
(zHW 00ع) \&



-(ZHW GL) ${ }^{\text {® }}$ )



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