HETEROCYCLES, Vol. 82, No. 1, 2010, pp. 791 - 802. © The Japan Institute of Heterocyclic Chemistry
Received, 25th June, 2010, Accepted, 27th July, 2010, Published online, 29th July, 2010
DOI: 10.3987/COM-10-S(E)69

PREPARATION OF HIGHLY CONJUGATED OLIGOAZA-PAHS BASED ON THE OXIDATIVE INTRAMOLECULAR COUPLING OF BICYCLO[2.2.2]OCTADIENE-FUSED PYRROLE

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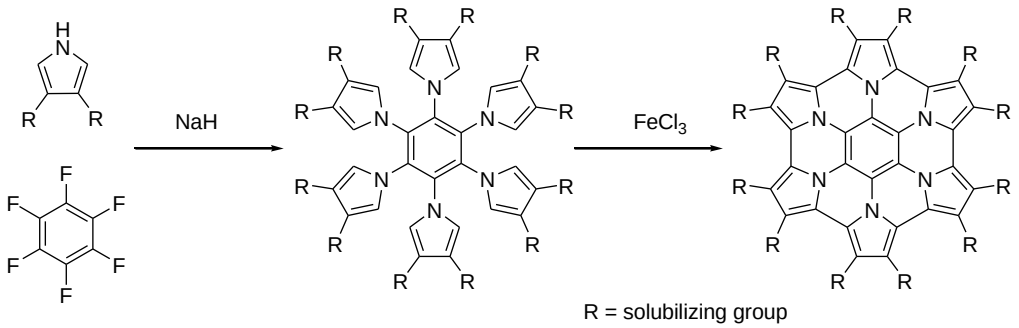
Abstract – The substitution reactions of tetrafluoro-*p*-phthalonitrile and hexafluorobenzene with 4,7-dihydro-4,7-ethano-2*H*-isoindole under basic conditions afforded tetra(4,7-dihydro-4,7-ethano-2*H*-isoindol-2-yl)-substituted *p*-phthalonitrile and 1,4-difluorobenzene in good yields, respectively. Oxidative coupling reactions of these compounds gave tetra(bicycle[2.2.2]octadiene)-fused tetrapyrrolo[1,2-*a*;1',2'-*c*;1'',2''-*h*;1''',2'''-*j*][1,4,5,8]tetraazaanthracenes, which were then converted to tetraisoindolo[1,2-*a*;1',2'-*c*;1'',2''-*h*;1''',2'''-*j*]-[1,4,5,8]tetraazaanthracenes by the retro-Diels-Alder reaction.

Dedicated to Professor Albert Eschenmoser on the occasion of his 85th birthday

INTRODUCTION

Recently compounds bearing highly conjugated π systems have attracted much attention due to their optoelectronic properties such as near-IR absorption-emmision and multiphoton-absorbing properties, which are desired for application of the dyestaffs to photodynamic therapy[1] and solar cells.[2] We have been interested in the preparation of such compounds with highly π-conjugated systems and succeeded in the preparation of acene-fused porphyrins,[3] π-expanded BODIPYs,[4] π-connected porphyrin oligomers,[5] and oligoisothianaphthenes[6] by applying the retro-diels-Alder reaction for bicyclo[2.2.2]octadiene(BCOD)-fused heterocycles in the final step. This final reaction was usually very clean, because no chemical material was required, only the activation energy was supplied by heat or

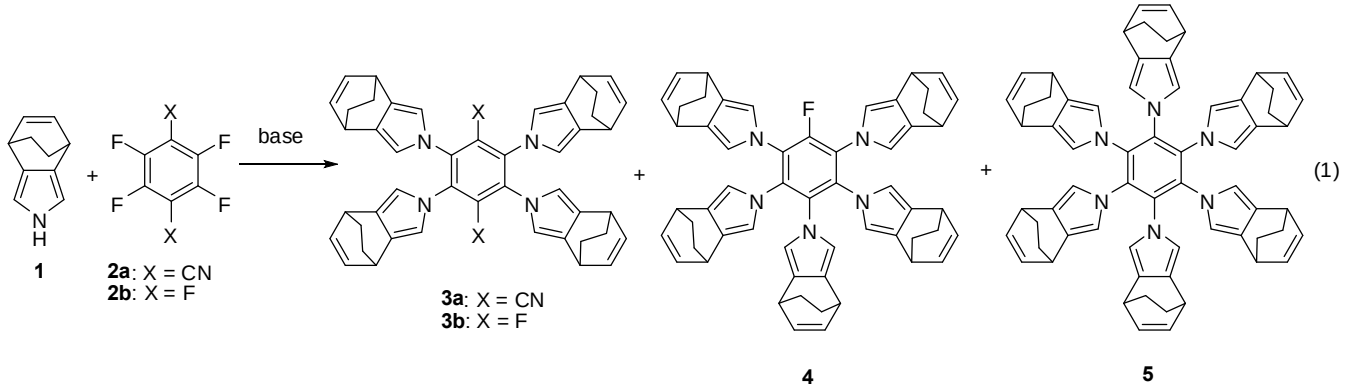
light, and the bi-product was only ethylene gas. Therefore, our strategy is very suitable for preparation of a compound with a large flat π-electron system, preparation of which seems to be very difficult due to the lack of pulification method, because such a compound has low solubility in common solvents and low vapor pressure. In our method, we do not need to pulify the targeted product if we purify the precursor, purification of which is commonly done by the usual methods such as recrystallization and chromatography. Recently, Müllen *et al.* reported the preparation of hexapyrrolohexaazacoronene derivatives with solubilizing bulky substituents (Scheme 1).[7] We thought that we could get the highly π-expanded oligoaza polyaromatic hydrocarbons (oligoaza-PAHs) with no solubilizing groups if our strategy could be applied. In this paper, we discuss our approach toward preparation of oligo-aza-PAHs by using BCOD-fused pyrrole **1** as the key compound.

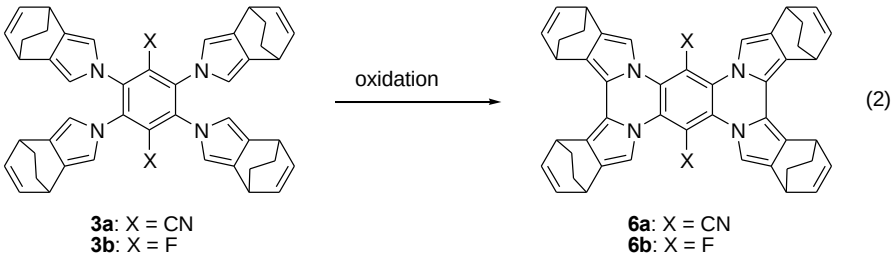


Scheme 1. Preparation of hexapyrrolohexaazacoronenes with solubilizing groups by Müllen *et al.*

RESULTS AND DISCUSSION

First, we examined the reaction of BCOD-fused pyrrole **1** with tetrafluoro-terephthalonitrile (**2a**) under the basic conditions (Eq 1). Since BCOD-fused pyrrole **1** decomposed rapidly over 170 °C and slowly over 120 °C, we conducted the reaction below 100 °C. Fozur equivalents of an anion of pyrrole **1** was generated by treatment with NaH in DMF and then reacted with tetrafluoro-terephthalonitrile (**2a**) at 60 °C for 2 h. The targeted tetrapyrrolyl terephthalonitrile **3a** was selectively obtained in 67% yield. The similar reaction of four equivalents of the anion with hexafluorobenzene (**2b**) at 60 °C for 3 h gave





3a: X = CN
3b: X = F

6a: X = CN
6b: X = F

(2)

only tetrapyrolyl *p*-difluorobenzene **3b** in 72% yield. Even when five equivalents of the anion were reacted at 70 °C for 8 h, penta-pyrolyl derivative **4** was obtained in only 14% yield and tetra-substituted derivative **3b** was still the main product (72%). Under the more severe conditions (6.1 equivalents of the anion, 80 °C, 8 h, *N*,*N*-dimethylacetamide (DMAc)), hexa-pyrolyl derivative **5** was selectively obtained in 85% yield.

Oxidation of pyrrolyl-substituted compounds **3** were carried out by using $FeCl_3$ as the oxidizing reagent.[7] Progress of the oxidation was confirmed by the TLC monitoring. However, isolation of the products was rather difficult due to formation of unknown by-products. We employed iodine as the oxidant with the aid of light. Thus, two molar equivalents of iodine and tetra-pyrrolyl derivative **3a** were dissolved in acetonitrile and the mixture was irradiated by a UV light for 3 h. Chromatographic purification followed by recrystallization gave diastereomeric tetrapyrrolotetraazaanthracene **6a** in 33% yield (Eq 2). Similarly, difluoro derivative **6b** was obtained in 27% yield. Oxidation of penta-pyrrolyl and hexa-pyrrolyl derivatives **4** and **5** was conducted under the similar conditions. However, we failed to purify the targeted products mainly due to poor solubility of the reaction products.

Before examination of the thermal behavior, crystal structural analysis of **3**–**6** was performed in order to know not only the structures but also the existence of voids between the molecules, where small solvent molecules such as water may be included. Crystals of **3a**, **3b**·$2CHCl_3$, **4**, **6a**·$2C_7H_8$, and **6b**·$2CHCl_3$ were obtained and the structures were successfully solved and the Ortep drawings are shown in Figures 1

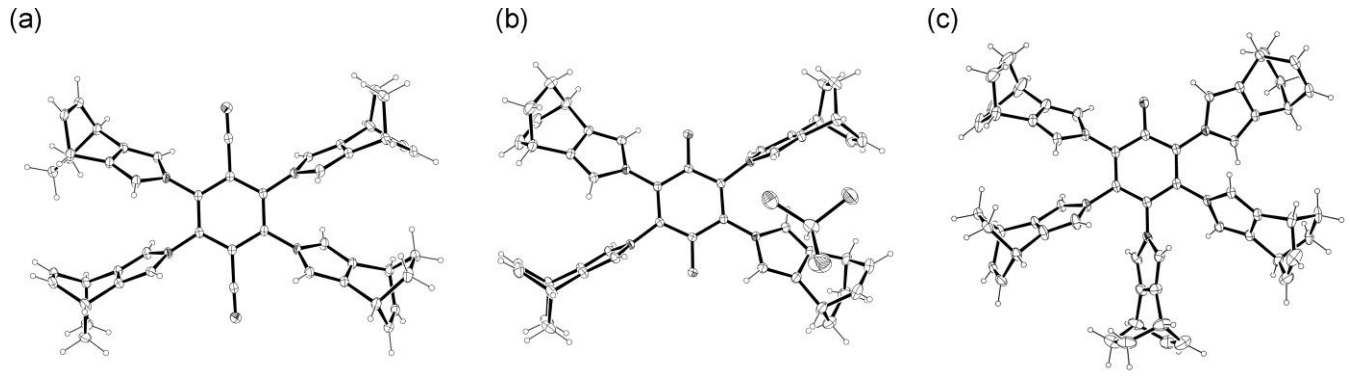


Figure 1. Ortep drawing of **3a** (a), **3b**·$2CHCl_3$ (b), and **4** (c). Disordered atoms are omitted for clarlity

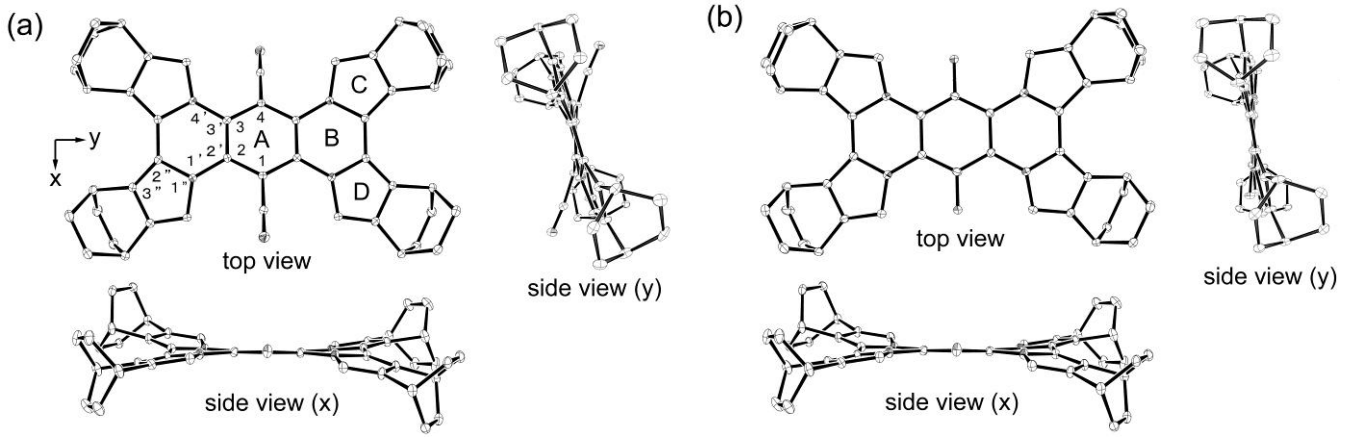


Figure 2. Ortep drawing of **6a**·$2C_7H_8$ (a) and **6b**·$2CHCl_3$ (b). Solvent, hydrogen and disordered atoms are omitted for clarlity

Table 1. Dihedral angles of aromatic rings in **6a** and **6b**[a]

Rings	**6a**			**6b**		
	B	**C**	**D**	**B**	**C**	**D**
A	9.32(6)°	19.37(8)°	24.87(8)°	4.39(15)°	9.43(17)°	16.23(18)°
B	—	12.77(8)°	16.73(8)°	—	7.00(17)°	13.37(17)°
C	—	—	21.63(9)°	—	—	18.4(2)°

[a] Ring names: refer to Figure 2

Table 2. Deviation from the mean plane (Å)

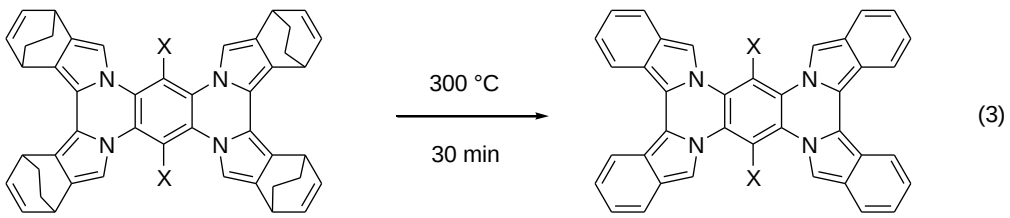
Atom No	Ring A		Ring B		Ring C		Ring D	
	6a	**6b**	**6a**	**6b**	**6a**	**6b**	**6a**	**6b**
1	0.0361(14)	0.013(3)	-0.0006(11)	0.029(2)	0.0051(10)	-0.004(2)	-0.0056(9)	-0.006(2)
2	-0.0360(14)	-0.012(3)	0.0846(15)	0.027(3)	-0.0069(14)	0.008(3)	0.0038(13)	0.007(3)
3	0.0365(14)	0.012(3)	-0.0654(15)	-0.047(5)	0.0035(14)	-0.006(3)	0.0017(13)	-0.002(3)
4	-0.0361(14)	-0.013(3)	-0.0278(11)	-0.002(2)	0.0013(13)	0.002(3)	-0.0084(15)	-0.005(3)
5	0.0360(14)	0.012(3)	0.1205(15)	0.078(4)	-0.0051(13)	0.003(3)	0.0115(16)	0.008(3)
6	-0.0365(14)	-0.012(3)	-0.1012(15)	-0.099(4)				

and 2. In the structures of **3a** (Figure 1a), the molecules occupied the special position of inversion center. One of the pyrrole moieties disordered and the occupancy ratio was calculated to be 0.64:0.36. The dihedral angles between the pyrrole and center benzene rings showed similar values of 57.54(8)°, 67.3(2)° (major), and 48.7(3)° (minor). Difluorobenzene derivative **3b** also occupied the inversion center. No pyrrole but BCOD rings disordered (ethylene vs ethynylene). Contrary to **3a**, the dihedral angles between the pyrrole and center benzene rings were quite different values (32.01(8)° and 71.55 (7)°). One of α-hydrogen atoms of the more co-planar pyrrole to benzene showed intramolecular C-H···F interaction and the distance between hydrogen and fluorine atoms were 2.29(2) Å. Accordingly, the other pyrrole ring became perpendicular to the benzene ring by the hindrance of the co-planar pyrrole.

The similar effect was observed in the structure of **4**. The dihedral angles in **4** were 49.18(9)°, 58.24(9)°, 62.26(8)°, 58.35(8)°, and 36.19(8)°. The pyrrole rings neighboring to the fluorine atom were more co-planar than other pyrrole rings.

As the molecules of **6a** and **6b** occupied the special positions of inversion center, there are four independent rings. Ortep drawing views from three molecular axes with ring and atom names are shown in Figure 2. Dihedral angles between the rings and deviations (Å) from the mean planes are listed in Tables 1 and 2, respectively. From Table 1, dicyano derivative **6a** showed greater out-of-plane distortion than **6b**. In the case of **6a**, large repulsive interaction between the pyrrolic hydrogen atoms and positively charged carbons of cyano groups was expected in addition to the repulsion of BCOD bridge-head hydrogen atoms. In fact, carbon and nitrogen atoms of the cyano group greatly deviated from the mean plane of the center benzene ring (0.433(3) Å and 0.866(4) Å, respectively). Therefore, the center benzene rings of **6a** showed large 1,3,5-alternate out-of-plane distortion. On the other hand, attractive interaction of the hydrogen with fluorine observed in the structures **3b** and **4** would occur to flatten the benzene ring. Thus, the fluorine atoms were almost in plane of the benzene ring and the deviation from the mean plane was 0.064(6) Å. The distances between the hydrogen and fluorine atoms were 2.03(2) and 2.15(2) Å.

The thermal behavior of **6a** and **6b** was examined by thermogravimetric (TG) analysis (Figure 3). There were two steep weight losses at the temperature ranges of 180–210 and 230–280 °C in **6a**, and the values were 5.6 and 13.7%. On the other hand, one large steep loss was observed at the temperature range of 210–300 °C in **6b** as well as the small loss at 140–160 °C. These weight losses were 17.1 and 1%, respectively. The samples of **6a** and **6b** were proved to contain a quarter molecule of chloroform and a half molecule of water, respectively, by the combustion analysis. Theoretical values for the losses are 4.1 (a quarter chloroform molecule in **6a**·1/4$CHCl_3$), 15.4 (four ethylene molecules in **6a**·1/4$CHCl_3$), 1.3 (a half water molecule in **6b**·1/2H_2O), and 16.2% (four ethylene molecules in **6b**·1/2H_2O). These values were well in accord with the observed weight losses. Therefore, we concluded that co-solvents included in the samples were first lost, then four ethylene molecules were simultaneously extruded, and unknown decomposition occurred above ca. 330 °C. The bulk thermal conversion of **6** was carried out at 300 °C for 30 min. The targeted tetrabenzo derivatives were obtained quantitatively.



6a: X = CN
6b: X = F

7a: X = CN
7b: X = F

(3)

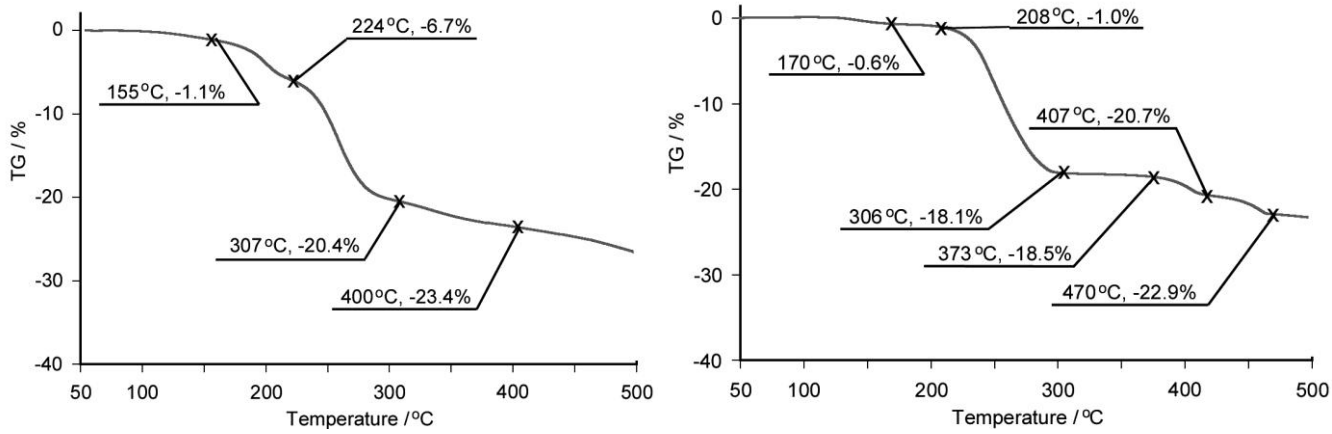


Figure 3. TG curves of **6a** (left) and **6b** (right).

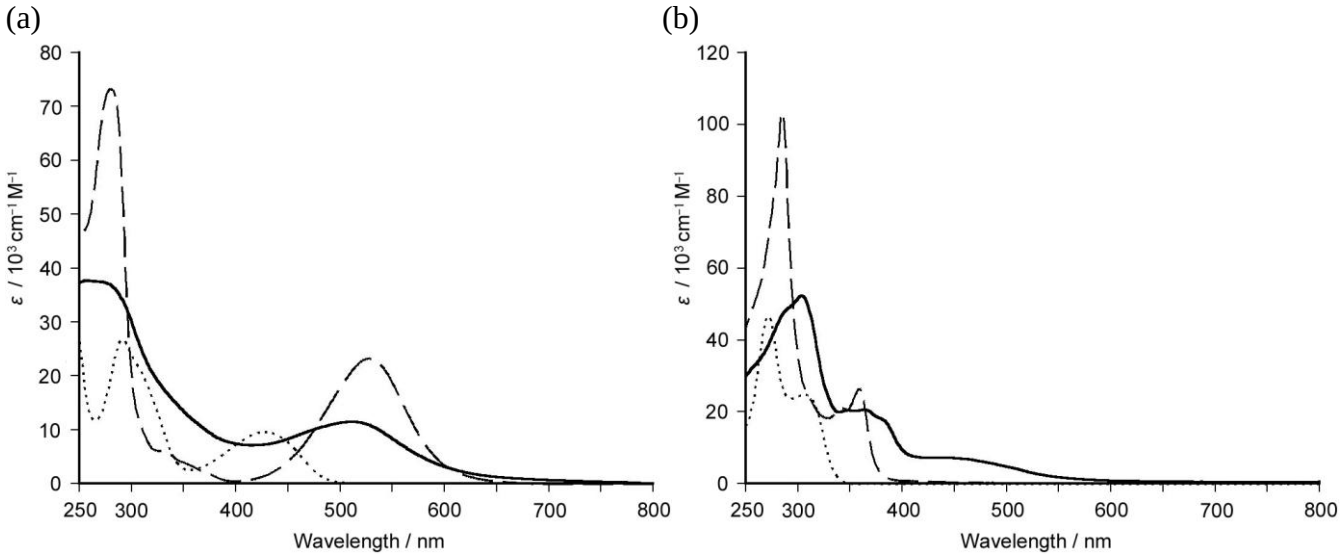


Figure 4. UV-vis spectra of dicyano derivative (left) and difluoro derivative (right). **3**: dotted line; **6**: broken line; and **7**: solid line.

UV-vis spectra of **3**, **6**, and **7** were measured in CH_2Cl_2 and shown in Figure 4. In the series of difluoro derivatives (Figure 4b), the absorption edges reached to longer wavelengths of 350, 400, and 600 nm, as the π systems were enlarged from **3b** to **7b**. The absorption spectra of the dicyano derivatives were a little confusing. The absorption peaks with the lowest energies in **3a** and **6a** was at 427 and 529 nm, respectively, while the peak in **7a** was at 511 nm.

In conclusion, we succeeded in preparation of highly conjugated aza-PAH by oxidative coupling of the BCOD-fused pyrrole moieties followed by the thermal extrusion of ethylene molecules from the BCOD rings. In the preparation of more highly conjugated aza-PAH, solubility of oxidatively coupled derivative must be increased. Our approach for the increase of solubility[8] would be helpful.

EXPERIMENTAL

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. Otherwise noted, NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using $CDCl_3$ as a solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, $CFCl_3$ as a standard for ^{19}F. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. Mass spectra (MALDI-TOF and FAB) were measured with a Voyger DE Pro (Applied Bio) and/or JEOL JMS-700 spectrometer, respectively. Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. UV-vis spectra were measured in dichloromethane with a HITACHI U-2810 spectrophotometer. Dehydrated tetrahydrofuran and dichloromethane were purchased from Kanto Chemical Co. and used without further purification. Acetonitrile was distilled from CaH_2 under a nitrogen atmosphere and stored over molecular sieves 4A. DMF and DMAc were distilled under a reduced pressure and stored over molecular sieves 13X. Other commercially available materials were used without further purification. X-Ray measurements of the single crystals were done with Rigaku AFC8S Mercury CCD (1.5 kW Mo sealed tube), Rigaku Rapid (15 kW Cu rotating anode), or Rigaku Rapid-HR (1.2 kW super bright rotating anode). Single crystals for X-ray analysis were obtained by the difusion method. A sample was placed in a small sample tube and dissolved with chloroform (**3a**, **3b**, **4**, **5**, and **6b**) or toluene (**6a**). The sample tube was placed in a jar containing heptane. A cap of the jar was tightly closed and left in the dark for an appropriate time. X-Ray diffraction data were processed by CrystalClear 1.6.3 or Rapid followed by CrystalStructure Ver. 3.8.2.[9] Structures were solved by using the processed data by CrystalStructure or WinGX[10] installed with SIR (2004 and 97),[11] and then refined by SHELXL-97.[12] Final structures were validated by Platon CIF check.[13]

2,3,5,6-Tetra(4,7-dihydro-4,7-ethano-2*H*-isoindol-2-yl)benzene-1,4-dicarbonitrile (3a)

BCOD-fused pyrrole **1** (0.581 g, 4.00 mmol) in 20 mL of dry DMF was added 60% NaH (0.213 g, 5.33 mmol) under nitrogen at room temperature in the dark. The mixture was stirred for 30 min at room temperature and tetrafluoroterephthalonitrile (**2a**; 0.200 g, 1.00 mmol) was added. The mixture was stirred at 60 °C for 2 h and then cooled to room temperature. The reaction was quenched by water and the mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) to give 0.468 g (0.668 mmol, 67%) of the title compound as yellow crystals: mp 220–230 °C (decomp.); R_f 0.5 (50% $CHCl_3$/hexane); ^1H NMR δ 1.47–1.53 (m, 16H), 3.68 (s, 8H), 6.02 (s, 8H), 6.41-6.43 (m, 8H); ^{13}C NMR δ 27.21, 32.86, 111.20, 112.88, 113.17, 132.75, 135.31, 139.09; UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 427 (3.99), 291 (4.43), 229 (4.55); IR (KBr) ν_{max}/cm^{-1} 3045, 2954, 2933, 2860, 2233, 1481; MS (MALDI-TOF) *m/z* 701.09, 672.10, 644.10, 617.54, 588.12; MS (FAB$^+$) *m/z* 701.4, 672.5. Anal. Calcd for $C_{48}H_{40}N_6 \cdot 1/4CHCl_3$: C, 79.31; H, 5.55; N, 11.50. Found: C,

79.48; H, 5.67; N, 11.48%.

Single crystals were obtained by the slow difusion of heptane into a solution of **3a** in chloroform. *Crystal data:* $C_{48}H_{40}N_6$; *FW* = 700.88, yellow prism, 0.35 x 0.25 x 0.15 mm, *monoclinic*, *P2₁/c* (#14), *Z* = 2 in a cell of dimensions *a* = 13.0325(11) Å, *b* = 11.1577(9) Å, *c* = 13.3627(14) Å, β = 112.159(4)°, *V* = 1799.6(3) Å^3, D_{calc} = 1.293 g·cm^{-3}, *Mo Kα*, *F(000)* = 740, *T* = 150, 4118 unique reflections, 3098 with $F^2 > 2\sigma(F^2)$. The final R_1 = 0.0602, wR_2 (all) = 0.1768, goodness-of-fit = 1.085 for 317 parameters refined on F^2, CCDC No. 780943.

1,4-Difluoro-2,3,5,6-Tetra(4,7-dihydro-4,7-ethano-2*H*-isoindol-2-yl)benzene (3b)

BCOD-fused pyrrole **1** (1.16 g, 8.00 mmol) in 20 mL of dry DMF was added 60% NaH (0.512 g, 12.8 mmol) under nitrogen at room temperature in the dark. The mixture was stirred for 15 min at room temperature and hexafluorobenzene (**2b**; 0.23 mL, 2.0 mmol) was added. The mixture was stirred at 60 °C for 3 h and then cooled to room temperature. The reaction was quenched by water and the mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) to give 0.995 g (1.45 mmol, 73%) of the title compound as white crystals; mp 220–230 °C (decomp.); R_f 0.5 (30% $CHCl_3$/hexane); ^{1}H NMR δ 1.49–1.55 (m, 16H), 3.69 (s, 8H), 6.00 (s, 8H), 6.43–6.45 (m, 8H); ^{13}C NMR δ 27.49, 32.96, 111.62, 124.81, 131.27, 135.60, 146.55; ^{19}F NMR δ -134.66; UV-vis (CH_2Cl_2) λ_{max}/ nm (logε) 307(4.40), 272 (4.67); IR (KBr) ν_{max}/cm^{-1} 3045, 2960, 2864, 1670, 1533, 1498, 1113; MS (MALDI-TOF) *m/z* 687.22, 658.23, 632.64, 602.73, 573.25; MS (FAB) *m/z* : 687 (M^++1), 686, 658 (M^+−CH_2=CH_2). Anal. Calcd for $C_{46}H_{40}F_2N_4$·1/2H_2O: C, 79.63; H, 5.67; N, 8.08. Found: C, 79.20; H, 5.86; N, 8.08%.

Single crystals were obtained by the slow difusion of heptane into a solution of **3b** in chloroform. *Crystal data:* $C_{46}H_{40}F_2N_4$,·2$CHCl_3$; *FW* = 925.60, colorless platelet, 0.50 x 0.25 x 0.10 mm, *triclinic*, *P-1* (#2), *Z* = 1 in a cell of dimensions *a* = 8.036(2) Å, *b* = 9.233(2) Å, *c* = 15.877(4) Å, α = 106.350(9)°, β = 92.514(10)°, γ = 105.608(12)°, *V* = 1079.6(5) Å^3, D_{calc} = 1.424 g·cm^{-3}, *Mo Kα*, *F(000)* = 478, *T* = 298, 4926 unique reflections, 3213 with $F^2 > 2\sigma(F^2)$. The final R_1 = 0.0506, wR_2 (all) = 0.1523, goodness-of-fit = 1.036 for 272 parameters refined on F^2, CCDC No. 780942.

1-Fluoro-2,3,4,5,6-penta(4,7-dihydro-4,7-ethano-2*H*-isoindol-2-yl)benzene (4)

BCOD-fused pyrrole **1** (377 mg, 2.60 mmol) in 20 mL of dry DMF was added 60% NaH (120 mg, 3.0 mmol) under nitrogen at room temperature in the dark. The mixture was stirred for 15 min at room temperature and hexafluorobenzene (**2b**; 0.06 mL, 0.52 mmol) was added. The mixture was stirred at 70 °C for 8 h and then cooled to room temperature. The reaction was quenched by water and the mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$,

and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) to give 52 mg (0.064 mmol, 12%) of the title compound as well as 257 mg of **3b**. **4**: white crystals; mp >220 °C (decomp.); ^{1}H NMR δ 1.32–1.51 (m, 20H), 3.51 (m, 6H), 3.67 (s, 6H), 6.02 (s, 4H), 6.31–6.34 (m, 6H), 6.41-6.43 (m, 4H); ^{19}F NMR δ -134.25; MS (FAB) *m/z* 812 (M^++1).

Single crystals were obtained by the slow difusion of heptane into a solution of **4** in chloroform. *Crystal data:* $C_{56}H_{50}FN_5$; *FW* = 812.04, colorless platelet, 0.20 x 0.20 x 0.05 mm, *triclinic*, *P-1* (#2), Z = 2 in a cell of dimensions a = 10.597(2) Å, b = 14.953(3) Å, c = 15.871(4) Å, α = 115.323(8)°, β = 90.049(9)°, γ = 107.949(8)°, V = 2136.8(7) Å^3, D_{calc} = 1.262 g·cm^{-3}, *Mo K*α, *F(000)* = 860, T = 133, 9729 unique reflections, 6967 with $F^2 > 2\sigma(F^2)$. The final R_1 = 0.0588, wR_2 (all) = 0.1778, goodness-of-fit = 1.098 for 660 parameters refined on F^2, CCDC No. 780940.

1,2,3,4,5,6-Hexa(4,7-dihydro-4,7-ethano-2*H*-isoindol-2-yl)benzene (5)

BCOD-fused pyrrole **1** (874 mg, 6.02 mmol) in 25 mL of dry DMAc was added 60% NaH (380 mg, 9.5 mmol) under nitrogen at room temperature in the dark. The mixture was stirred for 15 min at room temperature and hexafluorobenzene (**2b**; 0.11 mL, 1.0 mmol) was added. The mixture was stirred at 85 °C for 8 h and then cooled to room temperature. The reaction was quenched by water and the mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was washed with chloroform and hexane to give 820 mg (0.88 mmol, 88%) of the title compound as white crystals; mp 241–244 °C (decomp.); ^{1}H NMR δ 1.30–1.32 (m, 12H), 1.42–1.56 (m, 12H), 3.51 (s, 12H), 5.61 (s, 12H), 6.32–6.348 (m, 12H); ^{13}C NMR δ 27.71, 32.87, 110.72, 130.80, 133.42, 135.52; UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 284 (4.70); IR (KBr) ν_{max}/cm^{-1} 3045, 2954, 2862, 1496, 1113; MS (MALDI-TOF) *m/z* 935 (M^+−1). Anal. Calcd for $C_{66}H_{60}N_6 \cdot H_2O$: C, 82.99; H, 6.54; N, 8.80; O, 1.67. Found: C, 83.08; H, 6.26; N, 9. 01%.

1,4,10,13,14,17,23,26-Octahydro-1,4;10,13;14,17;23,26-tetraethanotetraisoindolo[1,2-*a*;1',2'-*c*;1",2"-*h*;1'",2'"-*j*][1,4,5,8]tetraazaanthracene-7,19-dicarbonitrile (6a)

Phthalonitrile **3a** (352 mg, 0.502 mmol) was dissolved in a mixture of CH_2Cl_2 (20 mL) and MeCN (30 mL) and iodine (280 mg, 1.1 mmol) was added. The mixture was stirred and irradiated with light for 3 h. After consumption of **3a** was monitored by TLC, the mixture was quenched with *aq*-$NaHSO_3$. The mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) and fractions containing a spot of R_f = 0.7 were collected. The combined fractions were concentrated to reave a red solid, which was recrystallized from toluene to give 115 mg (0.165 mmol, 33%) of the title compound as a mixture of diastereomers: red crystals; mp 220–230 °C (decomp.); ^{1}H NMR δ 1.67–1.74 (m, 16H), 3.95 (s, 4H), 4.29 (m, 4H), 6.54–6.60 (m, 8H), 7.97 (s, 4H); ^{13}C NMR δ

26.48, 26.51, 26.72, 26.82, 33.13, 33.92, 34.06, 89.24, 107.61, 115.95, 115.95, 116.00, 118.59, 123.73, 123.82, 126.28, 126.33, 135.07, 135.08, 135.25, 135.37, 135.47, 135.55, 135.56; UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 527, (4.37), 279 (4.87); IR(KBr) ν_{max}/cm^{-1} 3045, 2935, 2864, 2210, 1468, 1236; MS (MALDI-TOF) *m/z* 697.18, 670.46, 641.46, 615.17, 585.16. Anal. Calcd for $C_{48}H_{36}N_6 \cdot 1/2H_2O$: C, 81.68; H, 5.28; N, 11.91. Found: C, 81.95; H, 5.53; N, 11.54%.

Single crystals were obtained by the slow difusion of heptane into a solution of **6a** in toluene. *Crystal data:* $C_{48}H_{36}N_6 \cdot 2C_7H_8$; *FW* = 881.13, red block, 0.20 x 0.13 x 0.10 mm, *triclinic*, *P-1* (#2), *Z* = 1 in a cell of dimensions *a* = 9.583(3) Å, *b* = 11.113(4) Å, *c* = 11.338(4) Å, α = 81.921(12)˚, β = 76.291(12)˚, γ = 71.774(11)˚, *V* = 1111.4(7) Å^3, D_{calc} = 1.316 g·cm^{-3}, *Mo K*α, *F(000)* = 466, *T* = 150, 5080 unique reflections, 3649 with $F^2 > 2\sigma(F^2)$. The final R_1 = 0.0622, wR_2 (all) = 0.1506, goodness-of-fit = 1.065 for 335 parameters refined on F^2, CCDC No. 780944.

7,19-Difluoro-1,4,10,13,14,17,23,26-Octahydro-1,4;10,13;14,17;23,26-tetraethanotetraisoindolo[1,2-*a*;1',2'-*c*;1",2"-*h*;1'",2'"-*j*][1,4,5,8]tetraazaanthracene (6b)

Difluorobenzene **3b** (995 mg, 1.45 mmol) was dissolved in a mixture of CH_2Cl_2 (140 mL) and MeCN (100 mL) and iodine (761 mg, 3.00 mmol) was added. The mixture was stirred and irradiated with light for 5 h. After consumption of **3b** (TLC), the mixture was quenched with an aqueous $NaHSO_3$ solution. The mixture was extracted with chloroform. The organic extract was washed with water, sat. *aq*-$NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) and fractions containing a spot of R_f = 0.75 were collected. The combined fractions were concentrated to reave a red solid, which was recrystallized from toluene to give 115 mg (0.168 mmol, 12%) of the title compound as a mixture of diastereomers: White crystals; mp 226–229 °C (decomp.); ^{1}H NMR δ 1.68–1.76 (m, 16H), 3.98 (s,4H), 4.45–4.50 (m, 4H), 6.60 (m, 8H), 7.62 (s, 8H); ^{13}C NMR δ 26.80, 26.93, 27.03, 33.21, 34.24, 34.39, 115.83, 121.57, 135.79, 135.89, 136.01, 155.59; ^{19}F NMR δ -136.06 (s); UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 359 (4.42), 285 (5.02); IR (KBr) ν_{max}/cm^{-1} 3041, 2931, 2862, 1508; MS (MALDI-TOF) *m/z* 684.2, 683.19, 657.64, 629.73, 601.81, 573.32. Anal. Calcd for $C_{46}H_{36}F_2N_4 \cdot 1/4CHCl_3$: C, 77.95; H, 5.13; N, 7.86. Found: C, 77.57; H, 5.23; N, 7.87%.

Single crystals were obtained by the slow difusion of heptane into a solution of **6b** in chloroform. *Crystal data:* $C_{46}H_{36}F_2N_4 \cdot CHCl_3$; *FW* = 802.19, yellow block, 0.20 x 0.15 x 0.15 mm, *triclinic*, *P-1* (#2), *Z* = 1 in a cell of dimensions *a* = 6.1030(7) Å, *b* = 10.6968(10) Å, *c* = 14.0894(14) Å, α = 86.755(7)˚, β = 78.584(7)˚, γ = 86.081(7)˚, *V* = 898.61(16) Å^3, D_{calc} = 1.482 g·cm^{-3}, *Mo K*α, *F(000)* = 416, *T* = 133, 3164 unique reflections, 2811 with $F^2 > 2\sigma(F^2)$. The final R_1 = 0.0981, wR_2 (all) = 0.1983, goodness-of-fit = 1.115 for 260 parameters refined on F^2, CCDC No. 780941.

Tetraisoindolo[1,2-*a*;1',2'-*c*;1",2"-*h*;1'",2'"-*j*][1,4,5,8]tetraazaanthracene-7,19-dicarbonitrile (7a)

Tetrapyrrolotetraazaanthracenedicarbonitrile **6a** (13.9 mg, 0.020 mmol) was weighed in a small sample tube, which was placed in a small flask. The flask was evacuated by an oil rotary pump and placed in a glass tube oven pre-heated at 300 °C. After 30 min, the flask was cooled to room temperature and the material in the sample tube was the title compound (11.4 mg, 0.0195 mmol, 98%) as a brown solid: UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 258 (4.58), 511 (4.06); IR (KBr) ν_{max}/cm^{-1} 3057, 2202, 1471, 1419, 1348, 1306, 737; MS (MALDI-TOF) *m/z* 585.51 (M^++1). No NMR spectrum was recorded due to solubility problem.

7,19-Difluoro-tetraisoindolo[1,2-*a*;1',2'-*c*;1",2"-*h*;1'",2'"-*j*][1,4,5,8]tetraazaanthracene (7b)

Difluorotetrapyrrolotetraazaanthracene **6b** (18.5 mg, 0.027 mmol) was weighed in a small sample tube, which was placed in a small flask. The flask was evacuated by an oil rotary pump and placed in a glass tube oven pre-heated at 300 °C. After 30 min, the flask was cooled to room temperature and the material in the sample tube was the title compound (14.8 mg, 0.026 mmol, 96%) as a drown solid: UV-vis (CH_2Cl_2) λ_{max}/nm (logε) 283 (sh; 4.66), 302 (4.72), 348 (4.31), 363 (4.31), 381 (sh ; 4.25), 441 (3.68); IR (KBr) ν_{max}/cm^{-1} 3032, 1508, 1468, 1367, 1159, 735; MS (MALDI-TOF) *m/z* 570 (M^+). No NMR spectrum was recorded due to the solubility problem. Anal. Calcd for $C_{38}H_{36}F_2N_4$: C, 79.99; H, 3.53; N, 9.82. Found: C, 79.69; H, 3.60; N, 9.63%.

ACKNOWLEDGEMENTS

This work was also partially supported by Grant-in-Aids for the Scientific Research (20550047 and 21108517) from the Japanese Ministry of Education, Culture, Sports, Science and Technology. The X-ray diffraction data were taken either by using a Rigaku Rapid-HR FR-E Super-Bright (Mo irradiation) or Rigaku Rapid (Cu irradiation) instrument at Institute for Materials Chemistry and Engineering, Kyushu University (Nanotechnology Network), or by using Rigaku Mercury-CCD (Mo irradiation) at Integrated Center for Sciences, Ehime University. Preparative work by Miss Kaoru Yamagami is acknowledged.

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