

Synthesis and Physical Properties of Novel 7, 12-Diaryl-*N*-phenylbenzo[*k*]fluoranthene-9, 10-dicarboximides

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To cite this article:

Yuki Nakahara, Haruki Shimosasa, Ryuta Miyatake, Naoki Kobayashi, Mitsunori Oda. Synthesis and Physical Properties of Novel 7, 12-Diaryl-*N*-phenylbenzo[*k*]fluoranthene-9, 10-dicarboximides. *Modern Chemistry*. Vol. 4, No. 6, 2016, pp. 52-58.

doi: 10.11648/j.mc.20160406.11

Received: December 14, 2016; Accepted: December 22, 2016; Published: January 16, 2017

Abstract: The title arene-dicarboximides 8a–8d, having a benzo[*k*]fluoranthene skeleton, were synthesized in two steps from *N*-phenyl-1, 3-diarylisoindole-1, 3-dione-5, 6-dicarboximides 4a–4d by the Diels-Alder reaction with acenaphthylene and subsequent dehydration with trifluoromethanesulfonic acid. Under photo-excitation these dicarboximides emit blue light, notably, with high quantum yields.

Keywords: Isoindole-1,3-dione-Dicarboximides, Diels-Alder Reaction, Dehydration, Triflic Acid, Fluorescence

1. Introduction

Arene-dicarboximides, -bis(dicarboximide)s, and poly(dicarboximide)s show interesting electrochemical, photochemical, and photophysical properties, which have attracted increased attention of a wide range of chemists and physicists due to their potential application to various electronic materials and analytical reagents. [1-10] Among them, naphthalene-dicarboximides (naphthalimides) have been most studied. In 1992, Kossanyi *et al.* found dual fluorescence of *N*-aryl-2, 3-naphthalimides [11] and, later, Saito *et al.* reported that amino acids having a 1, 8-naphthalimide chromophore show sequence-selective DNA cleavage under photo-activated conditions. [12-13] In 2010, Heagy *et al.* reported that some 2, 3-naphthalenimides can be used in white organic light-emitting devices and also are applicable to ratiometric DNA and protein detections. [9-10]

These findings have prompted organic chemists to develop various new synthetic methods access to dicarboximide compounds. [14-17] We recently developed an efficient annulation between arene-1, 2-dicarbaldehydes and maleimides [18-21] by improving the previously reported Haddadin's result. [22] As shown in Fig. 1, various

naphthalene-, anthracene-, isoindole-, and benzo[*b*]thiophene-dicarboximides 2–5 can be obtained in one-pot from maleimides 1 and the arene-1, 2-dicarbaldehydes in good to high yields. We also reported that isoindole-dicarboximides 4 served as a diene part in Diels-Alder reaction and naphthalene-

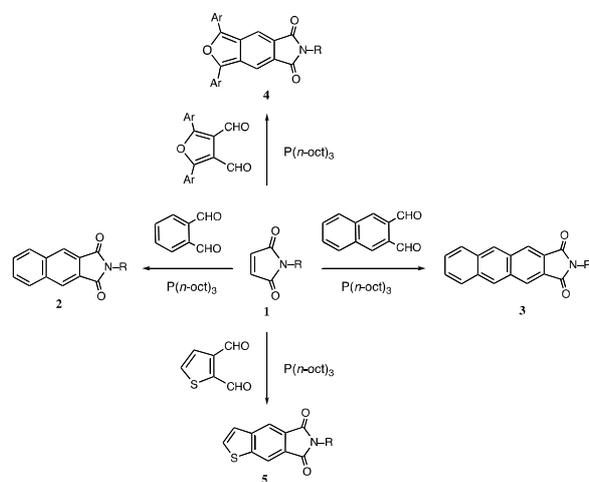


Figure 1. Various arene-dicarboximides.

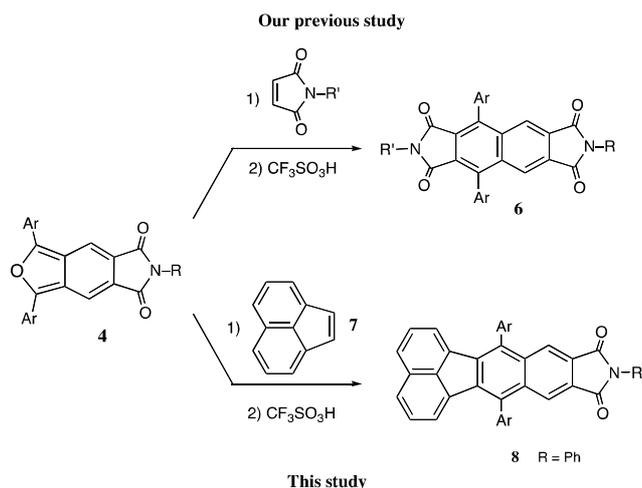


Figure 2. Diels-Alder reactions of isobenzofuran-dicarboximides 4.

Bis(dicarboximide)s 6 could be obtained by dehydration of the Diels-Alder adducts with various Brønsted acids. [19] During a course of our study on development of synthetic methods for a variety of arene-dicarboximides, we have further pursued cycloaddition reactions of 4. In this paper, we describe transformation from 4a–4d into the title compounds 8a–8d by its Diels-Alder reaction with acenaphthylene (7)

and subsequent dehydration with trifluoromethanesulfonic acid (triflic acid). (Fig. 2) Also, absorption and emission properties of these products are described.

2. Results and Discussion

In this study we employed four different 1, 3-diaryl-*N*-phenylisobenzofuran-5, 6-dicarboximides 4a–d as a diene part in the Diels-Alder reaction. We have already reported the synthesis of 4a–c. [19] The new biphenyl-substituted derivative 4d was synthesized in four steps from dimethyl 2, 5-bis (4-bromophenyl)furan-3, 4-dicarboxylate (9) according to Fig. 3. The Suzuki-Miyaura coupling of 9 with phenylboronic acid under the conditions of Pd (dppf)Cl₂/BINAP/Cs₂CO₃ [23] in refluxing toluene yielded biphenyl-substituted diester 10 in 77% yield. Then, this diester was transformed into 4d by the previously reported three-step sequence, which involves LiAlH₄ reduction, Swern oxidation [24], and phosphine-assisted annulation with *N*-phenylmaleimide. The total yield of 4d was 24% yield based on 10.

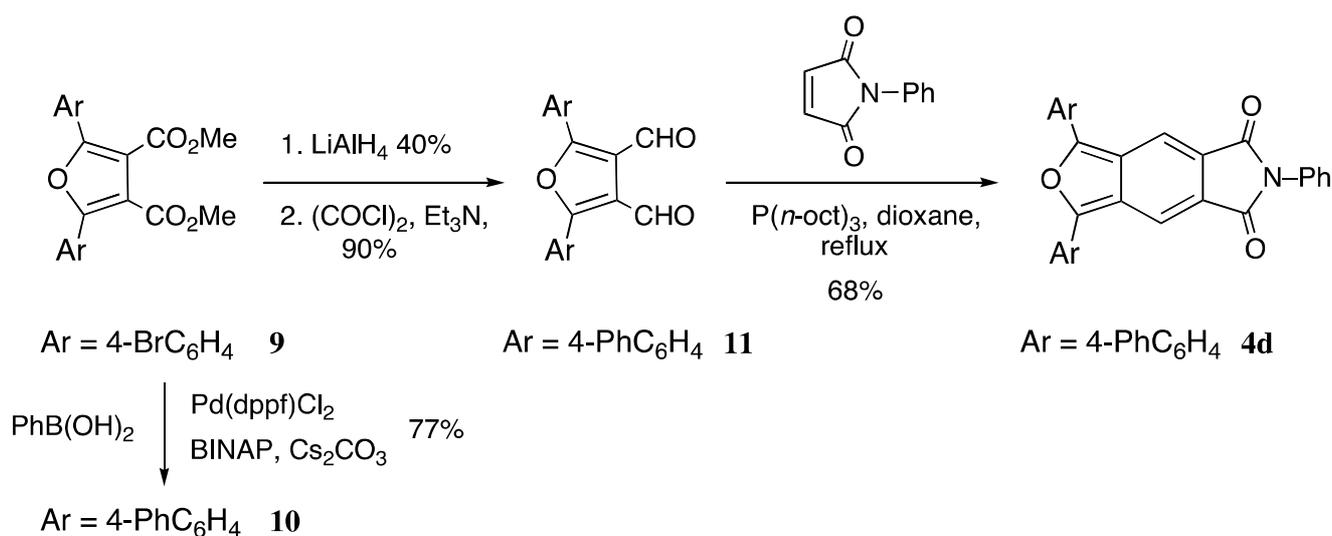


Figure 3. Synthesis of 1, 3-bis (biphenyl-4-yl)-*N*-phenylisobenzofuran-5, 6-dicarboximide (4d).

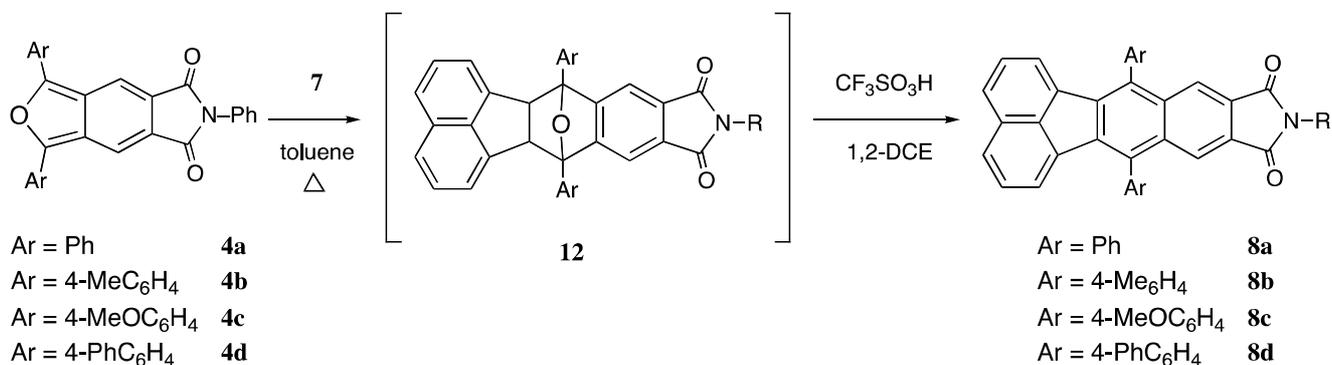


Figure 4. Synthesis of title compounds 8a-d.

Table 1. Results of the Diels-Alder reaction of 4 and dehydration reaction of 12.

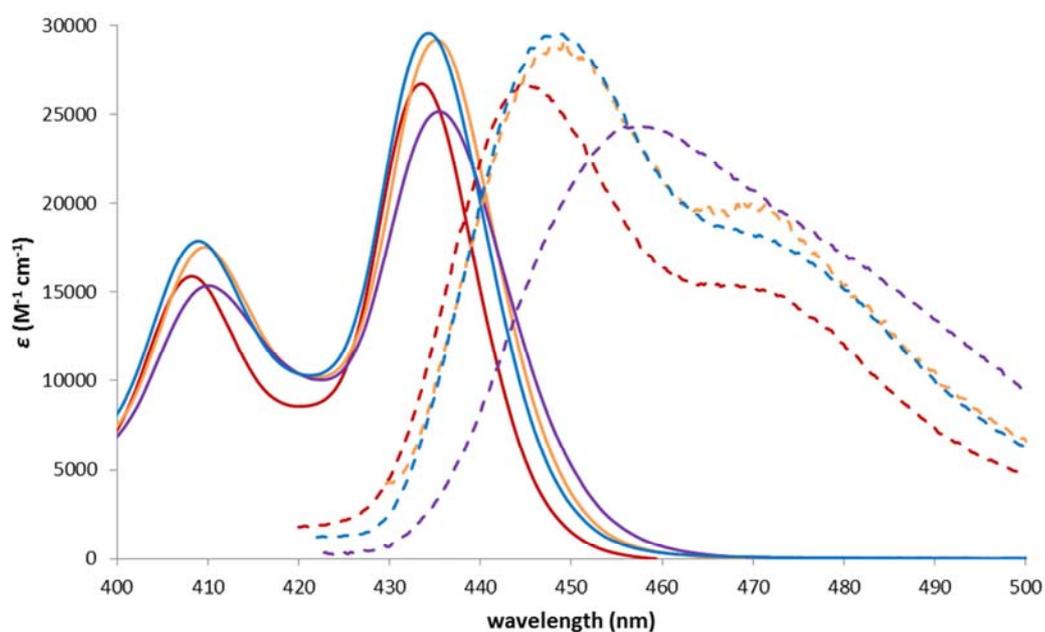
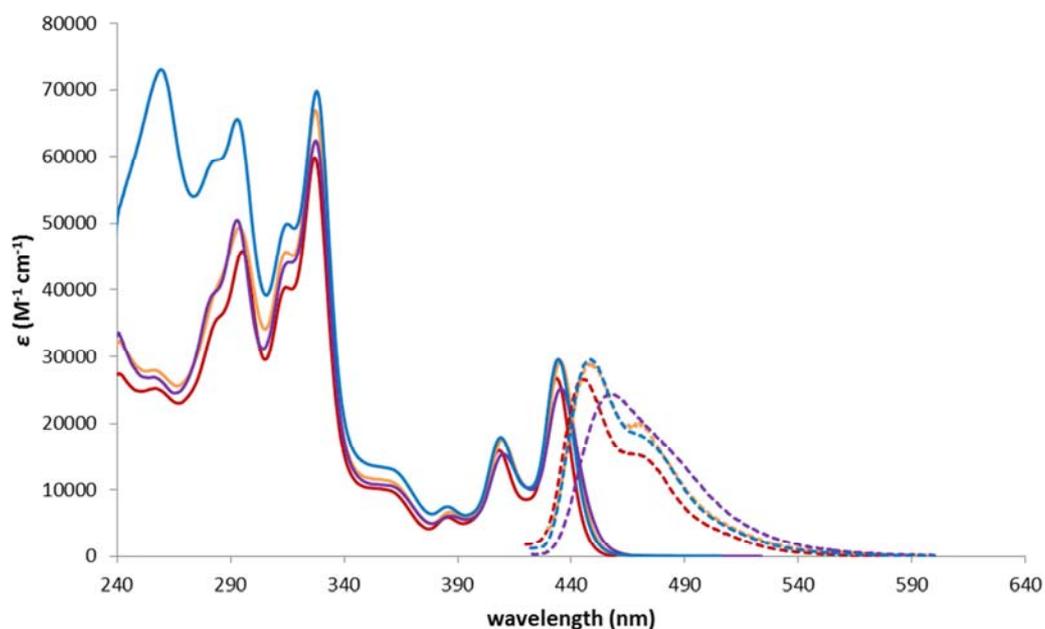
entry	Ar	reaction conditions cycloaddition//dehydration	yield/%
1	C ₆ H ₅	150°C/ 19 h // reflux/ 4 h	42 (8a)
2	4-Me-C ₆ H ₄	150°C/ 21 h // reflux/ 4 h	15 (8b)
3	4-MeO-C ₆ H ₄	150°C/ 12 h // reflux/ 4 h	34 (8c)
4	4-Ph-C ₆ H ₄	170°C/ 8 h // reflux/ 2 h	34 (8d)

Next, dicarboximides 4a–d were subjected to the Diels-Alder reaction with 7 (Fig. 4). The reactions were conducted at 150–170°C in a sealed tube, using an excess of 7 in toluene. After removal of recovery of 7, the crude adducts were treated with triflic acid in refluxing 1, 2-dichloroethane

to give the title compounds 8a–8d. The reaction conditions and two-step yields are shown in Table 1. The compounds 8a–d were obtained as orange solid and their structures were confirmed by spectroscopic analysis. Fig. 5 shows absorption and emission spectra of 8a–d and their photophysical properties are summarized in Table 2.

Table 2. Photophysical properties of 8.

entry	compound	λ_{max}/nm	$\log \epsilon$	λ_{emi}/nm	Stokes shift/nm	Φ
1	8a	433	4.43	442	9	0.97
2	8b	433	4.12	446	13	0.85
3	8c	434	4.50	443	9	0.83
4	8d	432	4.44	444	12	0.89



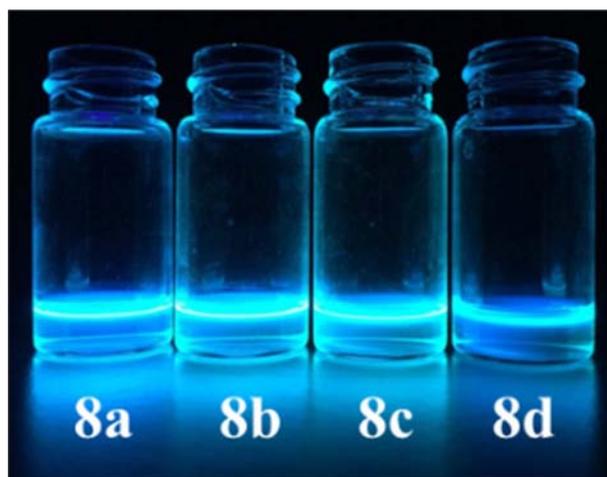


Figure 5. Top: Absorption (solid line) and normalized emission (dashed line) spectra of 8a (red), 8b (orange), 8c (violet), and 8d (sky blue). Middle: The expanded spectra at a range between 400 and 500 nm. Bottom: Luminescence color of the 10^{-4} M solutions ($\lambda_{\text{ex}} = 365$ nm) in chloroform.

Compounds 8a–8c show very similar absorption spectra, but the absorption coefficient increases slightly depending on electron-donating nature of the aryl substituents. The spectrum of 8d was slightly different from the others, having strong absorption maxima at a range between 240–280 nm, which are assignable to a band due to the biphenyl groups at the 7, 12 positions. The other absorption bands of 8d are shown in the same way to those of 8a–8c. Thus, the main absorptions based on the benzofluoranthene-dicarboximide skeleton show no difference between 8a–8d, suggesting discreteness of π -conjugation between the core skeleton and the aryl groups at the 7, 12 positions. This can be grasped in a perpendicular conformation between them in the optimized structure (Fig. 6). [25] Upon photo-excitation, 8a–8d emit blue light. The emission spectra of 8a–8d are seen nearly as mirror image to their absorption spectra, respectively, with small Stokes shifts (9–13 nm). The broadening band observed in that of 8c may be accounted by existence of vibrational sublevels due to rotation of the methoxy groups on the aryl groups. The emission quantum yields of 8a–8d were found high up to 0.97 (Table 2), while the emission quantum yield of 7, 12-diphenylbenzo [*k*]fluoranthene, which does not have a dicarboximide moiety, is 0.48. [26] It is worthy to note that introduction of the dicarboximide moiety on this π -system has brought about a great advance in their emission efficiency. Further studies on cycloaddition of 4 for synthesis of π -extended arene-dicarboximides and their application to electronic devices are in progress.

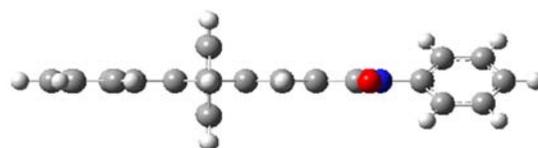
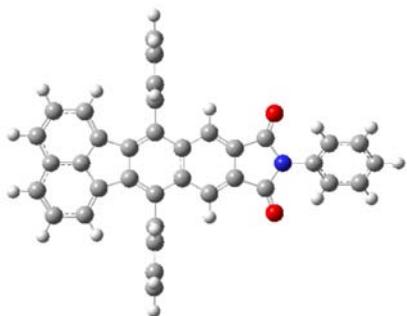


Figure 6. An optimized structure of 8a. Carbon and hydrogen atoms are shown in gray, oxygen atoms in red, and nitrogen atoms in blue. Top view (left) and side view (right).

3. Experimental

3.1. General Remarks

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Emission spectra were recorded on a Shimadzu RF5300-PC spectrometer. Emission quantum yields were obtained by calculations based on the absolute value of anthracene ($\Phi = 0.27$ in ethanol). [27–28] ^1H - and ^{13}C -NMR spectra were recorded on JEOL $\lambda 400$ and ECA500 spectrometers. Chemical shift values of tetramethylsilane ($\delta = 0$ ppm) for ^1H -NMR spectra and CDCl_3 ($\delta = 77.0$ ppm) for ^{13}C -NMR spectra were used as internal standard. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60N from Kanto Chem. Dioxane, dimethylsulfoxide (DMSO), and tetrahydrofuran (THF) were purchased from Kanto Chem. and were distilled over CaH_2 . Chloroform, dichloromethane (DCM), 1, 2-dichloroethane (DCE), and toluene were purchased also from Kanto Chem. and were distilled over P_2O_5 . *N*-Phenylmaleimide, bis-(diphenylphosphino)-1, 1'-binaphthyl (BINAP), triethylamine, tri-*n*-butylphosphine, and tri-*n*-octylphosphine, and triflic acid were purchased from Tokyo Chemical Industry, Inc. Oxalyl chloride and LiAlH_4 were purchased from Wako Chem. $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ and cesium carbonate were purchased from Aldrich-Sigma Co. Diester 9 was prepared according to a procedure reported by Wang *et al.* [29]

3.2. Synthesis of Dimethyl 2, 5-bis-(4-Bromophenyl)Furan-3, 4-Dicarboxylate (9)

To a solution of 4-bromobenzoylchloride (11.0 g, 50.0 mmol) in 50 mL of THF was added 4.32 g (3.00 mmol) of dimethyl maleate, followed by 11.7 g (58.0 mmol) of tri-*n*-butylphosphine and 10.5 mL (75.0 mmol) of triethylamine. This mixture was stirred at room temperature under nitrogen atmosphere for 20 h. The resulted dark brown reaction mixture was poured into water and was extracted with chloroform (50 ml x 3). The combined organic layer was washed with 1M HCl solution, a saturated NaHCO₃ aqueous solution, and brine. After drying over Na₂SO₄, the solvent was evaporated. The residual solids were recrystallized from chloroform to give 6.28 g (54% yield) of 9 as colorless microcrystals. M.p. = 163–164°C. ¹H NMR (400 MHz, CDCl₃) δ = 3.81 (s, 6H), 7.52 (dt, *J* = 9.0, 2.2 Hz, 4H), 7.66 (dt, *J* = 9.0, 2.2 Hz, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 163.8, 152.6, 131.9, 128.9, 127.5, 124.2, 115.8, 52.6 ppm; IR (KBr) ν = 1719vs, 1487s, 1101s, 992s, 825vs cm⁻¹; UV-Vis (CHCl₃) λ_{max} (logε) = 310 (logε = 4.40) nm; MS (EI) *m/z* (%) = 496 (M⁺, 51), 494 (M⁺, 100), 492 (M⁺, 51), 465 (12), 463 (24), 461 (12), 185 (10), 183 (10). HRMS calcd for C₂₀H₁₄⁷⁹Br₂O₅ (M⁺) 491.9208, found 491.9217.

3.3. Synthesis of Dimethyl 2, 5-bis (Biphenyl-4-yl) Furan-3, 4-Dicarboxylate (10)

A mixture of 2.53 g (5.14 mmol) of 9, 1.63 g (13.4 mmol) of phenylboronic acid, 178 mg (0.28 mmol) of BINAP, and 203 mg (0.249 mmol) of Pd (dppf)Cl₂·CH₂Cl₂ in 75 mL of toluene was refluxed on an oil bath under argon atmosphere for 3 h. The resulted reaction mixture was poured into water and was extracted with chloroform (50 mL x 3). The combined organic layer was washed with a saturated NaHCO₃ solution and brine, and was dried over Na₂SO₄. The solvent was removed and the residue was purified by SiO₂ chromatography (AcOEt/Hexane = 3/7) to give 1.93 g (77% yield) of 10 as colorless solids. M.p. = 132–133°C. ¹H NMR (400 MHz, CDCl₃) δ = 3.92 (s, 6H), 7.39 (tt, *J* = 7.4, 1.5 Hz, 2H), 7.47 (tm, *J* = 7.4 Hz, 4H), 7.65 (dm, *J* = 8.1 Hz, 4H), 7.70 (dt, *J* = 8.1, 2.0 Hz, 4H), 7.97 (dt, *J* = 8.1, 2.0 Hz, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 164.3, 153.3, 142.3, 140.2, 128.9, 127.81, 127.76, 127.6, 127.2, 127.1, 115.4, 52.5 ppm; IR (KBr) ν = 1728vs, 1486s, 1100s, 767s, 727s, 694s, 666s cm⁻¹; UV-Vis (CHCl₃) λ_{max} = 248 (logε = 4.23), 293sh (4.40), 330 (4.54) nm; MS (EI) *m/z* (%) = 488 (M⁺, 100), 457 (6), 245 (4), 244 (10), 181 (11), 153 (4), 152 (5). HRMS calcd for C₃₂H₂₄O₅ (M⁺) 488.1624, found 488.1621.

3.4. Synthesis of 2, 5-bis (Biphenyl-4-yl) Furan-3, 4-Dicarbaldehyde (11)

A solution of 850 mg (1.74 mmol) of 10 in 10 mL of THF was added slowly to a suspension of 160 mg of LiAlH₄ (4.21 mmol) in 30 mL of THF at 0°C. After being stirred at room temperature for 3 h, the reaction mixture was carefully quenched by ethanol/water. The resulted mixture was passed

through a Celite pad and was washed well with ether. The filtrate was dried over MgSO₄ and the solvent was evaporated to give the crude solids. Recrystallization from ethanol/diethyl ether provided 291 mg (40% yield) of 2, 5-bis (biphenyl-4-yl)-3, 4-bis (hydroxymethyl)furan as colorless microcrystals. M.p. > 200°C (dec.). ¹H NMR (400 MHz, DMSO-d₆) δ = 4.62 (s, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 4H), 7.75 (d, *J* = 8.1 Hz, 4H), 7.83 (d, *J* = 8.1 Hz, 4H), 7.94 (d, *J* = 8.1 Hz, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 149.0, 139.5, 139.3, 129.3, 129.0, 127.6, 127.1, 126.6, 126.4, 123.8, 53.0 ppm; IR (KBr) ν = 3384m, 3330m, 1485vs, 1446s, 1432s, 1013vs, 996s, 984s, 848s, 768vs, 755s, 692s cm⁻¹; MS (EI) *m/z* (%) = 432 (M⁺, 100), 430 (18), 416 (13), 414 (25), 181 (14), 152 (10). HRMS calcd for C₃₂H₂₄O₅ (M⁺) 432.1725, found 432.1726.

A solution of dimethylsulfoxide (0.5 mL) in 10 mL of DCM was added dropwise to a solution of oxalyl chloride (0.25 mL, 53.1 mmol) in 5 mL of DCM at -80°C, followed by addition of a solution of 363 mg (0.840 mmol) of 2, 5-bis (biphenyl-4-yl)-3, 4-bis (hydroxymethyl)furan in 2 mL of DMSO and 5 mL of DCM, and then triethylamine (2.0 mL). After being stirred at the same temperature for 2 h, the resulted reaction mixture was poured into water (30 mL) and was extracted with DCM (20 mL x 3). The combined organic layer was washed with brine and dried over NaSO₄. The solvent was removed and the residual solids were purified by recrystallization from hexane/chloroform to give 334 mg (90% yield) of 11 as colorless needles. M.p. = 180–182°C. ¹H NMR (400 MHz, CDCl₃) δ = 7.42 (tt, *J* = 7.6, 1.5 Hz, 2H), 7.50 (tm, *J* = 7.6 Hz, 4H), 7.67 (dm, *J* = 7.6 Hz, 4H), 7.78 (dm, *J* = 7.6 Hz, 4H), 8.09 (dm, *J* = 7.6 Hz, 4H), 10.51 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 186.9, 159.2, 143.8, 139.8, 129.02, 129.00, 128.2, 127.5, 127.2, 126.7, 121.5 ppm; IR (KBr) ν = 1687vs, 1660vs, 871s, 847s, 768vs, 733s, 695s cm⁻¹; UV-Vis (CHCl₃) λ_{max} = 261 (logε = 4.53), 343 (4.60) nm; MS (EI) *m/z* (%) = 428 (M⁺, 100), 401 (11), 400 (36), 181 (23), 153 (10), 152 (15). HRMS calcd for C₃₀H₂₀O₃ (M⁺) 428.1412, found 428.1417.

3.5. Synthesis of 1, 3-bis (Biphenyl-4-yl)-*N*-Phenylisobenzofuran-5, 6-Dicarboximide (4d)

A solution of 11 (98.0 mg, 0.23 mmol), *N*-phenylmaleimide (78.0 mg, 1.10 mmol), and tri-*n*-octylphosphine (4.0 mL) in 3 mL of dioxane was refluxed on an oil bath under argon atmosphere for 3 h. The orange solids formed were collected and washed well with hexane to give 89 mg (68% yield) of 4d. M.p. > 300°C. ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.41–7.56 (m, 11H), 7.73 (d, *J* = 7.1 Hz, 4H), 7.85 (d, *J* = 8.6 Hz, 4H), 8.16 (d, *J* = 8.6 Hz, 4H), 8.59 (s, 2H) ppm; IR (KBr) ν = 1758vs, 1707vs, 1482vs, 1366s, 1341vs, 1210s, 1143s, 1116s, 1104s, 848s, 768vs, 752s, 728s, 698s, 612s cm⁻¹; UV (CHCl₃) λ_{max} = 253 (logε = 4.69), 300 (4.33), 339 (4.18), 438sh (3.89), 475 (3.91) nm; MS (FAB) *m/z* (%) = 568 (M⁺, 100). HRMS (FAB) calcd for C₄₀H₂₅NO₃ (M⁺) 568.1907, found 568.1908. [30]

3.6. General Procedure for Synthesis of 7, 12-Diaryl-*N*-Phenylbenzo[*k*]Fluoranthene-9, 10-Dicarboximides 8

A solution of 4 (1.00 mmol) and 7 (6.00 mmol) in 10 mL of toluene was placed in a sealed tube under argon atmosphere and was heated on an oil bath until the isobenzofuran was consumed completely (8–21 h). Then, the solvent was removed and the residue was chromatographed through SiO₂ to remove acenaphthylene. This crude adduct was dissolved in a solution of 10 equiv. of triflic acid in 5 mL of DCE. After being heated at 65°C for 1–4 h, the resulted reaction mixture was poured into water and was extracted with chloroform (20 mL x 3). The combined organic layer was washed with a saturated NaHCO₃ solution and brine, and was dried over Na₂SO₄. The solvent was removed and the residue was purified by SiO₂ chromatography to give the title compound. Yields are shown in Table 1.

8a: Orange powder, m.p. > 300°C. ¹H NMR (500 MHz, CDCl₃) δ = 6.66 (d, *J* = 7.1 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.40–7.44 (m, 3H), 7.50 (tm, *J* = 7.7 Hz, 2H), 7.57 (dm, *J* = 7.5, 1.8 Hz, 4H), 7.71 (m, 6H), 7.80 (d, *J* = 8.1 Hz, 2H), 8.28 (s, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 167.2, 138.1, 137.5, 136.9, 135.6, 135.45, 135.44, 132.0, 130.0, 129.8, 129.7, 129.1, 128.8, 128.13, 128.12, 127.2, 126.8, 126.7, 124.1, 123.6 ppm; IR (KBr) ν = 1769s, 1719vs cm⁻¹; UV (CHCl₃) λ_{max} = 257 (log ε = 4.45), 284 (4.60), 295 (4.71), 314 (4.66), 327 (4.84), 360 (4.06), 385 (3.84), 408 (4.27), 434 (4.49) nm; MS *m/z* (%) = 549 (M⁺, 100), 505 (6), 429 (11), 400 (11), 275 (8), 199 (5). HRMS calcd for C₄₀H₂₃NO₂ (M⁺) 549.1729, found 549.1721.

8b: Orange powder, m.p. > 300°C. ¹H NMR (500 MHz, CDCl₃) δ = 2.62 (s, 6H), 7.39 (t, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 7.2 Hz, 2H), 7.43 (m, 7H), 7.50 (m, 6H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.29 (s, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 167.3, 138.5, 138.2, 137.0, 135.69, 135.66, 135.60, 134.4, 132.1, 130.37, 130.36, 130.0, 129.7, 129.1, 128.1, 127.1, 126.74, 126.71, 124.2, 123.6, 21.6 ppm; IR (KBr) ν = 1766s, 1718vs cm⁻¹; UV (CHCl₃) λ_{max} = 256 (log ε = 4.41), 284sh (4.57), 294 (4.66), 314 (4.62), 327 (4.79), 356sh (4.03), 387 (3.79), 409 (4.21), 435 (4.43) nm; MS *m/z* (%) = 577 (M⁺, 100), 457 (5), 430 (5), 289 (7). HRMS calcd for C₄₂H₂₇NO₂ (M⁺) 577.2042, found 577.2032.

8c: Orange powder, m.p. > 300°C. ¹H NMR (500 MHz, CDCl₃) δ = 4.03 (s, 6H), 6.79 (d, *J* = 6.6 Hz, 2H), 7.24 (dm, *J* = 8.7 Hz, 4H), 7.38–7.44 (m, 5H), 7.47 (dm, *J* = 8.7 Hz, 4H), 7.50 (tm, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 8.31 (s, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ = 167.3, 159.9, 138.4, 136.6, 135.9, 135.66, 135.64, 132.0, 131.0, 130.0, 129.5, 129.0, 128.13, 128.10, 127.1, 126.77, 126.73, 124.1, 123.6, 115.1, 55.5 ppm; IR (KBr) ν = 1765s, 1717vs cm⁻¹; UV (CHCl₃) λ_{max} = 256 (log ε = 4.43), 282 (4.59), 293 (4.70), 316 (4.64), 327 (4.79), 360 (4.03), 386 (3.79), 409 (4.18), 435 (4.40) nm; MS *m/z* (%) = 609 (M⁺, 100). HRMS calcd for C₄₂H₂₇NO₄ (M⁺) 609.1940, found 609.1944.

8d: Orange powder, m.p. > 300°C. ¹H NMR (400 MHz, CDCl₃ at 80°C) δ = 6.86 (d, *J* = 7.7 Hz, 2H), 7.34–7.48 (m,

9H), 7.54 (t, *J* = 7.7 Hz, 4H), 7.65 (d, *J* = 7.7 Hz, 4H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 4H), 7.95 (d, *J* = 7.7 Hz, 4H), 8.35 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 167.1, 142.0, 140.8, 138.4, 136.8, 136.7, 136.0, 135.8, 135.7, 132.6, 130.54, 130.45, 129.1, 129.0, 128.4, 128.2, 128.0, 127.8, 127.4, 127.3, 126.7, 124.0, 123.8 ppm; IR (KBr) ν = 1765vs, 1720vs cm⁻¹; UV (CHCl₃) λ_{max} = 263 (log ε = 4.84), 282sh (4.77), 291 (4.81), 315sh (4.70), 329 (4.84), 363sh (4.10), 385 (3.87), 410 (4.25), 436 (4.45) nm; MS *m/z* (%) = 702 (M⁺, 100). HRMS calcd for C₅₂H₃₁NO₂ (M⁺) 702.2428, found 702.2440.

4. Conclusion

We have demonstrated that the novel title compounds, 7, 12-diaryl-*N*-phenylbenzo[*k*]fluoranthene-9, 10-dicarboximides (8a-d), could be synthesized from 1, 3-diaryl-*N*-phenylisobenzofuran-5, 6-dicarboximides 4a-d in two steps by the Diels-Alder reaction with acenaphthylene (7) and subsequent dehydration with triflic acid. The long wavelength absorptions of 8a-d were observed similarly, suggesting that the aryl groups at the 7 and 12 positions do not make any contribution for extension of π-conjugation with the benzo[*k*]fluoranthene moiety. The fact can be rationalized by their perpendicular conformation between the aryl groups and the arene moiety. These dicarboximides 8a-d showed emission under photo-excitation and their emission quantum yields were found very high.

Acknowledgements

A financial support (H26 Kenkyu-Keihi) from the Faculty of Science in Shinshu University (for M. O.) is greatly acknowledged.

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